

## Supporting Information

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### **Synthesis and Reactivity of Mononuclear Iron Models of [Fe]-Hydrogenase That Contain an Acylmethylpyridinol Ligand**

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## Experimental Section

### A. Chemicals and Reagents

All manipulations were carried out under an inert N<sub>2</sub>(g) atmosphere using a Schlenk line. Solvents were distilled from appropriate drying agents under N<sub>2</sub> before use. All reagents were purchased from commercial sources. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use. 2-*tert*-butoxy-6-chloropyridine was prepared as described previously.<sup>[S1]</sup>

### B. Physical methods

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced to residual solvent as determined relative to Me<sub>4</sub>Si (δ = 0 ppm). The <sup>13</sup>C{<sup>1</sup>H} chemical shifts were reported in ppm relative to the carbon resonance of CDCl<sub>3</sub> (77.0 ppm). IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Mass spectra were performed on an Agilent 6530 Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) mass spectrometer, equipped with an ESI source. X-ray diffraction studies were carried out in a Xcalibur E X-ray single crystal diffractometer. Data collections were performed using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption.<sup>S2</sup> Solution, refinement and geometrical calculations for all crystal structures were performed by SHELXTL.<sup>S3</sup>

### C. Synthetic methods

#### Synthesis of 2-*tert*-butoxy-6-methylpyridine

2-*tert*-butoxy-6-methylpyridine was prepared using a similar method as described previously.<sup>[S1]</sup> A solution of CH<sub>3</sub>MgBr/ether (3 M, 10.8 mL, 32.4 mmol) was added drop-wise to a mixture of 2-*tert*-butoxy-6-chloropyridine (4.0 g, 21.6 mmol) and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride (34.2 mg, 0.0648 mmol) in THF (40 mL). The mixture was stirred at room temperature for 4 h. The reaction was diluted with ether (20 mL) and quenched by addition of H<sub>2</sub>O to dissolve inorganics. The organic phase was washed with H<sub>2</sub>O. After drying the organic phase over Na<sub>2</sub>SO<sub>4</sub> and evaporation of the solvent, the crude products were purified by silica gel column chromatography, giving 2-*tert*-butoxy-6-methylpyridine as a colorless oil (2.79 g, 16.9 mmol; yield 78 %).

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 7.41 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 2.43 (s, 3H), 1.57 (s, 9H) ppm. <sup>13</sup>C NMR (400.13 MHz, CDCl<sub>3</sub>): 163.2, 155.7, 138.3, 115.2, 109.7, 79.1, 28.7, 24.2. MS (ESI, positive mode): Calcd for C<sub>10</sub>H<sub>15</sub>NO + H: 166.1232. Found: 166.1223. Anal. Calcd for C<sub>10</sub>H<sub>15</sub>NO: C, 72.7; H, 9.2; N, 8.5. Found: C, 73.0; H, 9.1, N, 8.2.

#### Synthesis of [(2-CH<sub>2</sub>CO-6-*t*-BuOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>3</sub>I] (**1**)

*n*-BuLi (5 mL, 1.6 M, 8.0 mmol) was added into a solution of 2-*tert*-butoxy-6-methylpyridine (1.32 g, 8.0 mmol) in THF (50 mL) under stirring at 0 °C. After stirring for 0.5 h at this temperature, the solution was added into a solution of Fe(CO)<sub>5</sub> (1.57 g, 8.0 mmol) in THF (50 mL) at -50 °C, and the resulting solution was warmed slowly to -20 °C (about 2 h). The solution was then cooled to -60 °C, followed by adding solid I<sub>2</sub> (2.03 g, 8.0 mmol) at the same temperature. The resulting solution was kept at -60 °C for 2 hours. The solvent was then evaporated in vacuum. The residue was placed in an Al<sub>2</sub>O<sub>3</sub> column. Elution with CH<sub>2</sub>Cl<sub>2</sub> developed a red band, which afforded **1** (1.87 g, 4.1 mmol; yield: 51 %) as red crystals after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ether.

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 7.73 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.42 (d, *J* = 20.0 Hz, 1H), 4.29 (d, *J* = 20.0 Hz, 1H), 1.70 (s, 9H) ppm. IR (ν<sub>CO</sub>, KBr, cm<sup>-1</sup>): 2089 (s), 2045 (s), 2034 (s), 2011 (s), 2000 (s). IR (ν<sub>CO</sub>, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2088 (s), 2040 (s), 2008 (s). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>FeINO<sub>5</sub>: C, 36.6; H, 3.1; N, 3.1. Found: C, 36.7; H, 3.1, N, 2.9.

### Synthesis of [(2-CH<sub>2</sub>CO-6-*t*-BuOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>{S-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}] (2)

A newly synthesized sample of (2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)SNa (228.0 mg, 1.38 mmol), which was prepared by NaH (33.2 mg, 1.38 mmol) and (2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)SH (190.6 mg, 1.38 mmol) in THF, was mixed with complex **1** (634.0 mg, 1.38 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). After stirring for 0.5 h at room temperature in the dark, the solvent was evaporated in vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 mL). After removing the solvent of the filtrate, the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane at -30 °C in the dark to afford **2** (430.0 mg, 0.975 mmol; yield: 71 %) as red crystals.

<sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN): 7.97 (t, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.44 (d, *J* = 20.0 Hz, 1H), 4.04 (d, *J* = 20.0 Hz, 1H), 2.30 (s, 6H), 1.58 (s, 9H) ppm. IR (ν<sub>CO</sub>, KBr, cm<sup>-1</sup>): 2013 (s), 1948 (s). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>FeNO<sub>4</sub>S: C, 57.2; H, 5.3; N, 3.2. Found: C, 57.5; H, 5.4; N, 3.4.

### Reaction of **2** with CO: Formation of [(2-CH<sub>2</sub>CO-6-*t*-BuOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>3</sub>{S-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}] (3)

A solution of **2** (20 mg, 0.045 mmol) in 0.5 mL CDCl<sub>3</sub> was added to a J Young NMR tube. The solution was frozen and the tube was evacuated under vacuum. 1 atm of CO was added and the tube was sealed. The color changed from red to yellow as soon as the solution was thawed. The NMR and IR showed [(6-*t*-BuO-C<sub>5</sub>H<sub>3</sub>N-2-CH<sub>2</sub>CO)Fe(CO)<sub>3</sub>{S-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}] (**3**) formed. If the tube was opened and flushed with N<sub>2</sub>, **3** would transform back to **2**.

<sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 7.72 (br s, 1H), 7.12-6.90 (m, 5H), 5.18 (d, *J* = 20.0 Hz, 1H), 4.05 (d, *J* = 20.0 Hz, 1H), 2.19 (s, 6H), 1.63 (s, 9H) ppm. <sup>13</sup>C NMR (400.13 MHz, CDCl<sub>3</sub>): 260.9 (CH<sub>2</sub>CO), 210.3 (terminal CO), 208.3 (terminal CO), 205.8 (terminal CO), 163.6, 161.5, 144.3, 141.7, 139.6, 127.2, 125.0, 114.9, 108.6, 84.4, 66.0, 28.7, 22.4. ppm. IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2078 (s), 2027 (s), 2001 (s).

### Synthesis of [(2-CH<sub>2</sub>CO-6-*t*-BuOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup>(CF<sub>3</sub>COO)<sup>-</sup> (4)

CF<sub>3</sub>COOH (25.9 mg, 0.227 mmol) was added into a solution of **2** (100.0 mg, 0.227 mmol) in CH<sub>3</sub>CN (2 mL) under stirring at room temperature. The color changed from red to yellow immediately. After 1 min, the solvent was evaporated. The solid residue was washed with Et<sub>2</sub>O (10 mL) and dried in vacuum. Compound **4** was isolated as a yellow solid in a quantitative yield (113.2 mg, 0.227 mmol). Attempts to remove the *t*-Bu group with excess of CF<sub>3</sub>COOH were failed.

<sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN): 7.84 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.62 (d, *J* = 20.0 Hz, 1H), 3.66 (d, *J* = 20.0 Hz, 1H), 1.94 (s, 6H), 1.62 (s, 9H) ppm. IR (ν<sub>CO</sub>, KBr, cm<sup>-1</sup>): 2047 (s), 1988 (s). Anal. Calcd for C<sub>19</sub>H<sub>20</sub>F<sub>3</sub>FeN<sub>3</sub>O<sub>6</sub>: C, 45.7; H, 4.0; N, 8.4. Found: C, 45.9; H, 4.1; N, 8.7.

### Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>3</sub>I] (5)

Me<sub>3</sub>SiI (610.0 mg, 3.05 mmol) was added into a solution of **1** (400.0 mg, 0.871 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) under stirring at room temperature. After 12 h, H<sub>2</sub>O (20 mL) was added into the mixture. The water phase was washed with CH<sub>2</sub>Cl<sub>2</sub> (20 mL × 3) and ether (10 mL), respectively. The combined organic phase was washed with H<sub>2</sub>O (20 mL). After drying over Na<sub>2</sub>SO<sub>4</sub> and evaporation of the solvent, the residue was extracted with ether (10 mL), and the filtrate was dried in vacuum. The residue was washed with hexane (40 mL) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL), respectively. The solid residue was then extracted with ether (10 mL) again, and the filtrate was dried in vacuum. The residue was washed with hexane (20 mL) and recrystallized from ether/hexane to afford **5** (110.0 mg, 0.273 mmol; yield: 31 %) as a red solid.

<sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN): 10.17 (s, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.46 (d, *J* = 20.0 Hz, 1H), 4.08 (d, *J* = 20.0 Hz, 1H) ppm. IR (ν<sub>CO</sub>, KBr, cm<sup>-1</sup>): 2102 (s), 2048 (s), 2023 (s), 2014 (s). IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2068 (s), 2050 (s), 1996 (s). Anal. Calcd for C<sub>10</sub>H<sub>6</sub>FeNO<sub>5</sub>I: C, 29.8; H, 1.5; N, 3.5. Found: C, 30.1; H, 1.5; N, 3.8.

### Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup>(BF<sub>4</sub>)<sup>-</sup> (6)

AgBF<sub>4</sub> (48.1 mg, 0.248 mmol) was added into a solution of **5** (100.0 mg, 0.248 mmol) in CH<sub>3</sub>CN (5 mL) under stirring. Gas (CO) was formed immediately. After 1 min, the mixture was filtered and the filtrate was dried in vacuum. The residue was washed with ether (10 mL) and dried in vacuum to afford **6** (101.0 mg, 0.242 mmol; 98 %) as a light yellow oily solid.

<sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN): 9.33 (s, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 20.0 Hz, 1H), 3.89 (d, *J* = 20.0 Hz, 1H), 1.96 (s, 6H) ppm. IR (ν<sub>CO</sub>, KBr, cm<sup>-1</sup>): 2057 (s), 1999 (s). IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2065 (s), 2010 (s). Anal. Calcd for C<sub>13</sub>H<sub>12</sub>BF<sub>4</sub>FeN<sub>3</sub>O<sub>4</sub>: C, 37.5; H, 2.9; N, 10.1. Found: C, 37.7; H, 3.0, N, 9.9.

Reaction of **6** with HS-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) and NEt<sub>3</sub>: Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>{S-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}] (**7**)

HS-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (6.62~13.2 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in CH<sub>3</sub>CN (5 mL) under stirring. NEt<sub>3</sub> (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2011 and 1944 cm<sup>-1</sup>. The intensity of the two bands decreased quickly, with the emergence of two new bands at 2063 and 1983 cm<sup>-1</sup>. After about 10 mins, almost all the bands between 2100-1900 cm<sup>-1</sup> disappeared, and the color changed to black.

If HBF<sub>4</sub>·Et<sub>2</sub>O (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of **7**, **6** was regenerated.

IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2011 (s), 1944 (s).

Reaction of **7** with CO: Formation [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>3</sub>{S-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}] (**7a**)

HS-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (6.62~13.2 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in CH<sub>3</sub>CN (5 mL) under CO atmosphere. NEt<sub>3</sub> (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing four ν(CO) absorption bands at 2063, 2011, 1983 and 1944 cm<sup>-1</sup>. The intensity of the peak at 2063 cm<sup>-1</sup> is about 50 % of that of the peak at 1944 cm<sup>-1</sup>, indicating that about 33 % of **7** transformed to **7a**.

**7a**: IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2063 (s), 2011 (s), 1983 (s).

Reaction of **6** with HS-(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>) and NEt<sub>3</sub>: Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>{S-(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)}] (**8**)

HS-(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>) (7.43~14.9 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in CH<sub>3</sub>CN (5 mL) under stirring. NEt<sub>3</sub> (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2013 and 1953 cm<sup>-1</sup>. The intensity of the two bands decreased quickly, with the emergence of two new bands at 2071 and 1992 cm<sup>-1</sup>. After about 10 mins, almost all the bands between 2100-1900 cm<sup>-1</sup> disappeared, and the color changed to black.

If HBF<sub>4</sub>·Et<sub>2</sub>O (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of **8**, **6** was regenerated.

IR (ν<sub>CO</sub>, solid, cm<sup>-1</sup>): 2014 (s), 1953 (s). IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2013 (s), 1953 (s).

Reaction of **6** with HS-(C<sub>6</sub>F<sub>5</sub>) and NEt<sub>3</sub>: Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>{S-(C<sub>6</sub>F<sub>5</sub>)}] (**9**)

HS-(C<sub>6</sub>F<sub>5</sub>) (9.59~19.2 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in CH<sub>3</sub>CN (5 mL) under stirring. NEt<sub>3</sub> (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to deep yellow immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2020 and 1956 cm<sup>-1</sup>. The intensity of the two bands decreased with the time, and two new bands at 2074 and 1989 cm<sup>-1</sup> appeared.

After about 1 h, almost all the bands between 2100-1900  $\text{cm}^{-1}$  disappeared, and the color changed to black.

If  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of **9**, **6** was regenerated.

IR ( $\nu_{\text{CO}}$ , solid,  $\text{cm}^{-1}$ ): 2024 (s), 1960 (s). IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 2020 (s), 1956 (s).

Reaction of **6** with  $\text{NaS}(\text{C}_6\text{F}_5)$ : An alternative route to synthesize **9**

$\text{NaS}(\text{C}_6\text{F}_5)$  (2.66 mg, 0.012 mmol) was added into a solution of **6** (5.00 mg, 0.012 mmol) in  $\text{CD}_3\text{CN}$  (0.6 mL) in a J Young NMR tube at  $-30^\circ\text{C}$ . The  $^1\text{H}$  NMR was measured immediately, which showed **9** formed. Some precipitate can be found in the tube after the  $^1\text{H}$  NMR measurement.

$^1\text{H}$  NMR (400.13 MHz,  $\text{CD}_3\text{CN}$ ): 7.73 (br s, 1H), 6.98-6.71 (m, 2H), 4.37 (d,  $J = 20.0$  Hz, 1H), 3.91 (d,  $J = 20.0$  Hz, 1H) ppm.

Reaction of **9** with CO: Formation of  $[(2\text{-CH}_2\text{CO-6-HOC}_5\text{H}_3\text{N})\text{Fe}(\text{CO})_3\{\text{S}(\text{C}_6\text{F}_5)\}]$  (**9a**)

$\text{HS}(\text{C}_6\text{F}_5)$  (9.59~19.2 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) under a CO atmosphere.  $\text{NEt}_3$  (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at  $-30^\circ\text{C}$ . The IR spectrum was recorded immediately, showing four  $\nu(\text{CO})$  absorption bands at 2074, 2020, 1989 and 1956  $\text{cm}^{-1}$ . The intensity of the peak at 2074  $\text{cm}^{-1}$  is about 60 % of that of the peak at 1956  $\text{cm}^{-1}$ , showing that about 38 % of **9** transformed to **9a**.

**9a**: IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 2074 (s), 2020 (s), 1989 (s).

Reaction of **9** with *p*-toluenesulfonylmethylisocyanide

$\text{HS}(\text{C}_6\text{F}_5)$  (9.59~19.2 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in  $\text{CH}_3\text{CN}$  (5 mL).  $\text{NEt}_3$  (4.85~9.79 mg, 0.048~0.096 mmol) and *p*-toluenesulfonylmethylisocyanide (9.36~18.7 mg, 0.048~0.096 mmol) were added into the mixture at  $-30^\circ\text{C}$ , respectively. The IR spectrum was recorded immediately, showing two  $\nu(\text{CO})$  absorption bands at 2027 and 1974  $\text{cm}^{-1}$ . The product decomposed completely in 15 mins at room temperature in the dark.

Reaction of **6** with *t*-BuSH and  $\text{NEt}_3$ : Synthesis of  $[(2\text{-CH}_2\text{CO-6-HOC}_5\text{H}_3\text{N})\text{Fe}(\text{CO})_2(\text{S-}t\text{-Bu})]$  (**10**)

*t*-BuSH (4.32~8.64 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) under stirring.  $\text{NEt}_3$  (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at  $-30^\circ\text{C}$ . The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense  $\nu(\text{CO})$  absorption bands at 2017 and 1956  $\text{cm}^{-1}$ . The intensity of the two bands decreased quickly, with the emergence of two new bands at 2061 and 1978  $\text{cm}^{-1}$ . After about 3 mins, almost all the bands between 2100-1900  $\text{cm}^{-1}$  disappeared, and the color changed to black.

If  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of **10**, **6** was regenerated.

IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 2017 (s), 1956 (s).

Reaction of **6** with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$  and  $\text{NEt}_3$ : Synthesis of  $[(2\text{-CH}_2\text{CO-6-HOC}_5\text{H}_3\text{N})\text{Fe}(\text{CO})_2(\text{SCH}_2\text{CH}_2\text{CH}_3)]$  (**11**)

$\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$  (3.65~7.30 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) under stirring.  $\text{NEt}_3$  (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at  $-30^\circ\text{C}$ . The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense  $\nu(\text{CO})$  absorption bands at 2008 and 1947  $\text{cm}^{-1}$ . After about 3 mins, almost all the bands between 2100-1900  $\text{cm}^{-1}$  disappeared, and the color changed to black.

If  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (7.77 mg~23.3 mg, 0.048~0.14 mmol) was added quickly after the formation of **11**, **6** was regenerated.

IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 2008 (s), 1947 (s).

Reaction of **6** with HOCH<sub>2</sub>CH<sub>2</sub>SH and NEt<sub>3</sub>: Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>OH)] (**12**)

HOCH<sub>2</sub>CH<sub>2</sub>SH (3.74~7.48 mg, 0.048~0.096 mmol) was added into a solution of **6** (20.0 mg, 0.048 mmol) in CH<sub>3</sub>CN (5 mL) under stirring. NEt<sub>3</sub> (4.85~9.79 mg, 0.048~0.096 mmol) was added into the mixture at -30 °C. The color changed from light yellow to red immediately. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2006 and 1937 cm<sup>-1</sup>. After about 10 mins, almost all the bands between 2100-1900 cm<sup>-1</sup> disappeared, and the color changed to black.

IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2006 (s), 1937 (s).

Reaction of **5** with CH<sub>3</sub>COOAg: Synthesis of [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>(CH<sub>3</sub>COO)] (**13**) and/or [(2-CH<sub>2</sub>CO-6-HOC<sub>5</sub>H<sub>3</sub>N)Fe(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup>(CH<sub>3</sub>COO)<sup>-</sup> (**13a**)

CH<sub>3</sub>COOAg (41.2 mg, 0.248 mmol) was added into a solution of **5** (50.0 mg, 0.124 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) under stirring. Gas (CO) was formed immediately. After 5 mins, the mixture was filtered and the filtrate was dried in vacuum. The residue was washed with ether (10 mL) and dried in vacuum to afford **13** (35.0 mg, 0.114 mmol, 92 %) as yellow oily solid. When dissolved in CH<sub>3</sub>CN, parts of **13** transformed to **13a**.

**13**: <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 7.67 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.01 (d, *J* = 20.0 Hz, 1H), 3.92 (d, *J* = 20.0 Hz, 1H), 2.41 (s, 3H) ppm. IR (ν<sub>CO</sub>, solid, cm<sup>-1</sup>): 2042 (s), 1972 (s). IR (ν<sub>CO</sub>, CH<sub>2</sub>, cm<sup>-1</sup>): 2051 (s), 1986 (s). MS (ESI, negative mode): Calcd for C<sub>11</sub>H<sub>9</sub>FeNO<sub>6</sub> - H: 305.9701. Found: 305.9706. Anal. Calcd for C<sub>11</sub>H<sub>9</sub>NFeO<sub>6</sub>: C, 43.0; H, 3.0; N, 4.6. Found: C, 42.7; H, 3.2, N, 4.3.

Mixture of **13** and **13a**: <sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN): 7.73 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), [4.20 (d, *J* = 20.0 Hz), 4.05 (d, *J* = 20.0 Hz) (1H in total)], [3.85 (d, *J* = 20.0 Hz), 3.82 (d, *J* = 20.0 Hz) (1H in total)], 1.96 (m) ppm. IR (ν<sub>CO</sub>, CH<sub>3</sub>CN, cm<sup>-1</sup>): 2054 (s), 2044 (sh), 1994 (s), 1979 (sh).

Reaction of **13** with HS-(C<sub>6</sub>F<sub>5</sub>) and NEt<sub>3</sub>: An alternative route to synthesize **9**

HS-(C<sub>6</sub>F<sub>5</sub>) (13.0~26.0 mg, 0.065~0.130 mmol) was added into a solution of **13** (20.0 mg, 0.065 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) under stirring. NEt<sub>3</sub> (6.57~13.1 mg, 0.065~0.130 mmol) was added into the mixture at -30 °C. The IR spectrum was recorded immediately, showing two intense ν(CO) absorption bands at 2022 and 1958 cm<sup>-1</sup>. CH<sub>3</sub>CN (53.3 mg, 0.65 mmol) was then added to the solution, and there was no change of the ν(CO) absorptions, which meant that CH<sub>3</sub>CN did not coordinate with Fe center.

#### D. Crystallographic Details for **2**

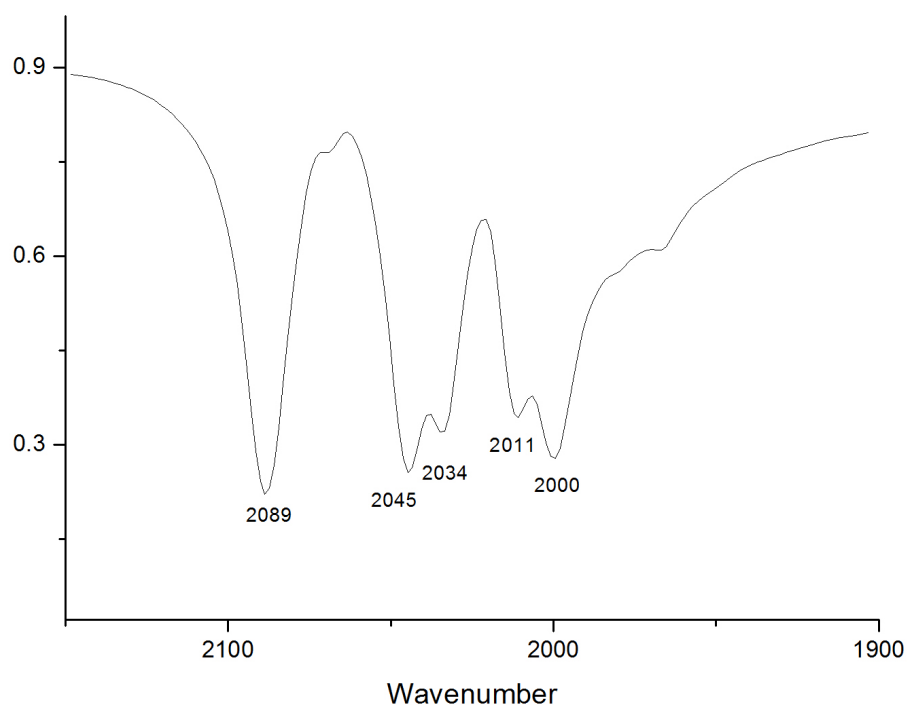
A total of 4644 reflections ( $-12 \leq h \leq 12$ ,  $-13 \leq k \leq 8$ ,  $-12 \leq l \leq 11$ ) were collected at *T* = 293(2) K in the range of 2.94 to 25° of which 2898 were unique (*R*<sub>int</sub> = 0.0395); MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 1.520 and -0.542 eÅ<sup>-3</sup>, respectively. The least squares refinement converged normally with residuals of *R*(*F*) = 0.0898, *wR*(*F*<sup>2</sup>) = 0.2337 and a GOF = 1.098 (*I* > 2σ(*I*)). C<sub>21</sub>H<sub>23</sub>FeNO<sub>4</sub>S, Mw = 441.31, space group *P*2(1), Monoclinic, *a* = 10.2510(18), *b* = 11.4645(10), *c* = 10.414(2) Å, β = 114.51(2)°, *V* = 1113.6(3) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.316 Mg/m<sup>3</sup>. CCDC 963961 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### References

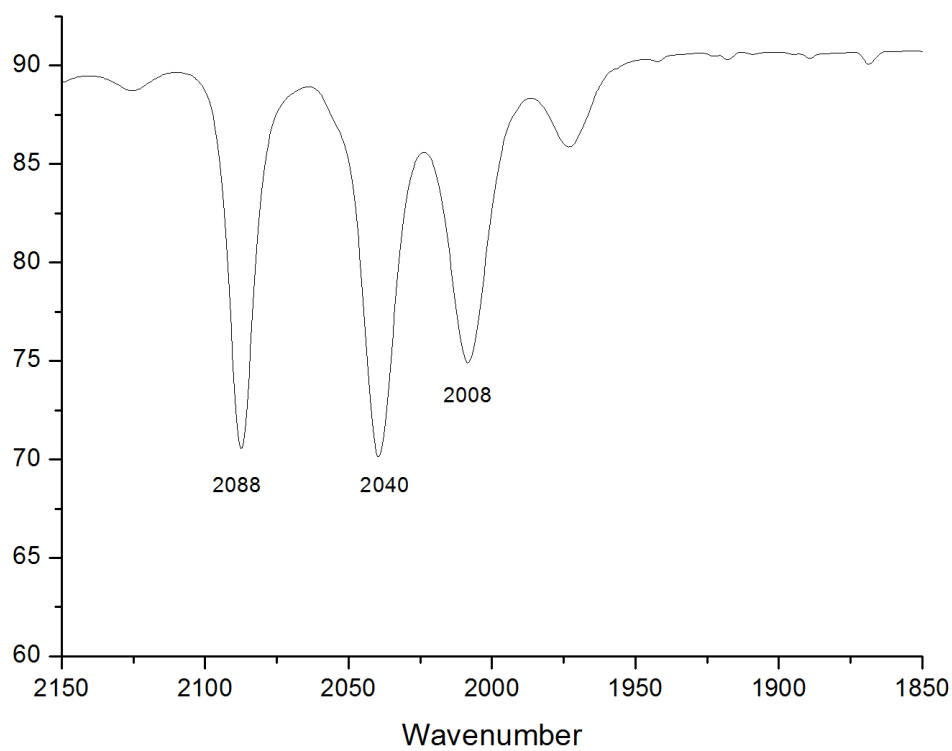
- (S1) Hintermann, L.; Dang, T. T.; Labonne, A.; Kribber, T.; Xiao, L.; Naumov, P. *Chem. Eur. J.* **2009**, *15*, 7167-7179.  
(S2) Blessing, R. H. *Acta Crystallogr. A* **1995**, *51*, 33-38.

(S3) Sheldrick, G. M. *SHELXTL* release 6.1.4 ed.; Bruker AXS Inc.: Madison, Wisconsin, 53719, USA, 2003.

## IR spectra

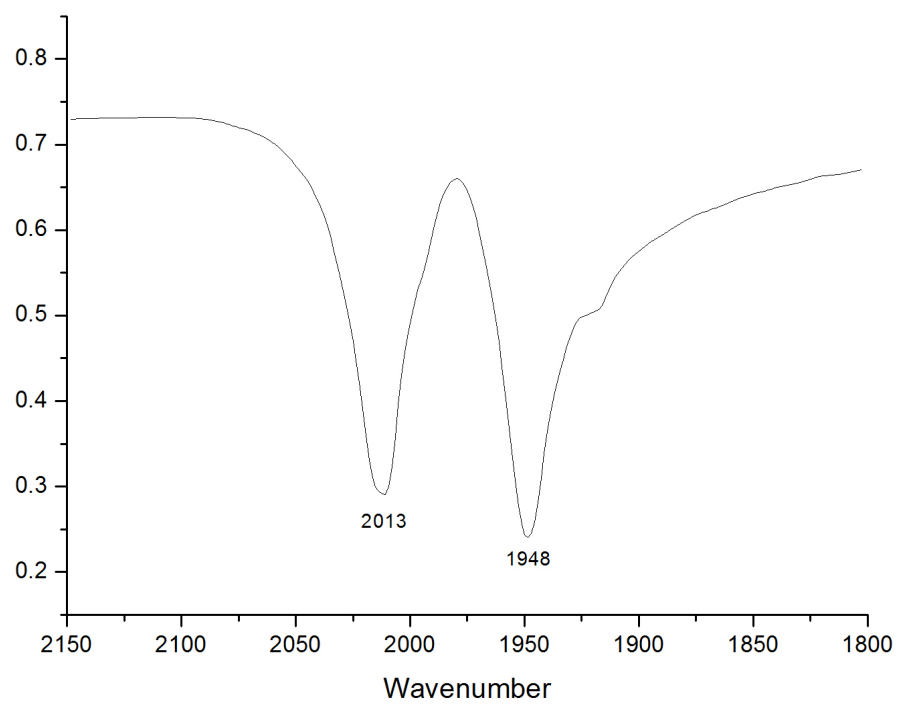


**Figure S1.** IR spectrum of **1** in the solid state.

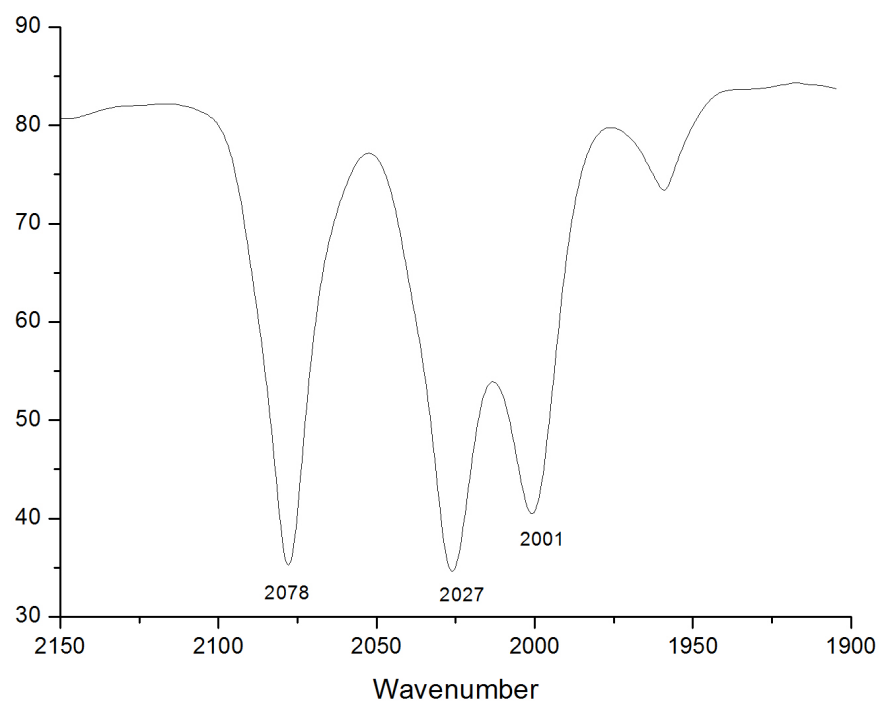


**Figure S2.** IR spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub>.

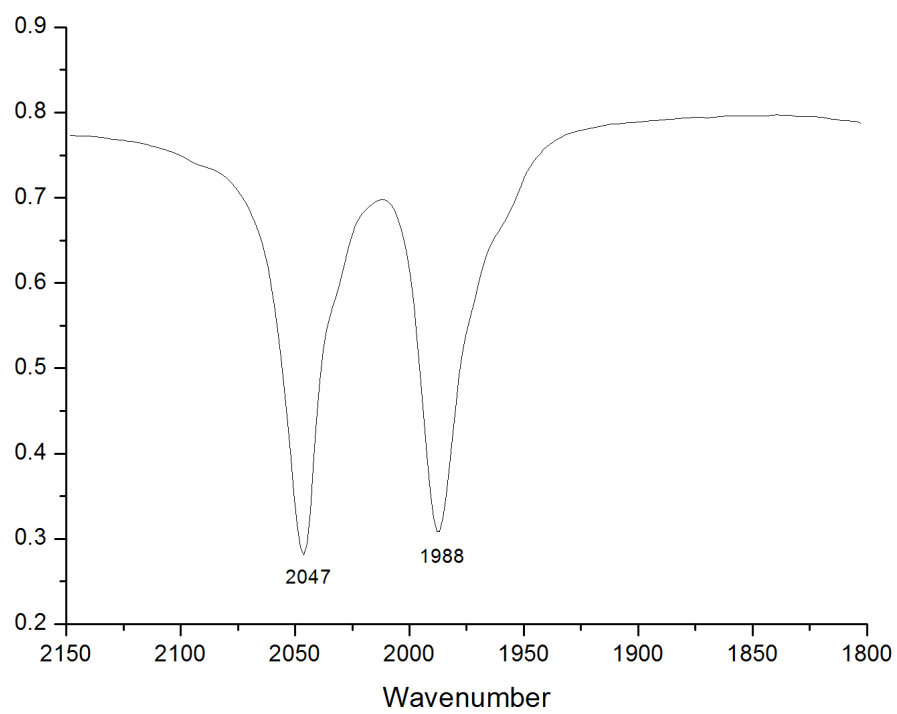




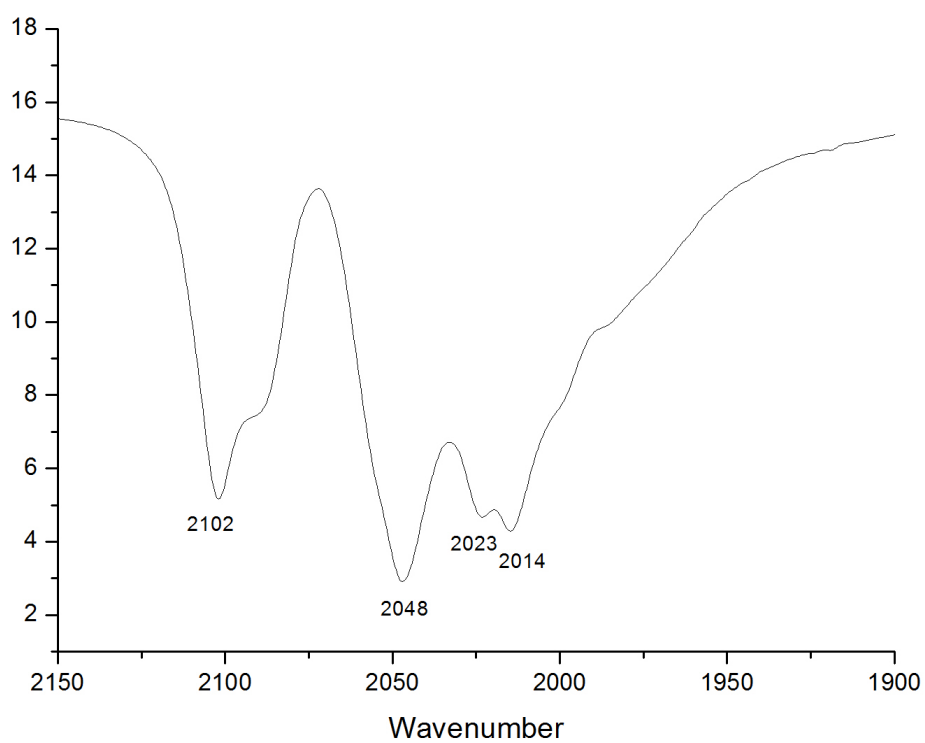
**Figure S3.** IR spectrum of **2** in the solid state.



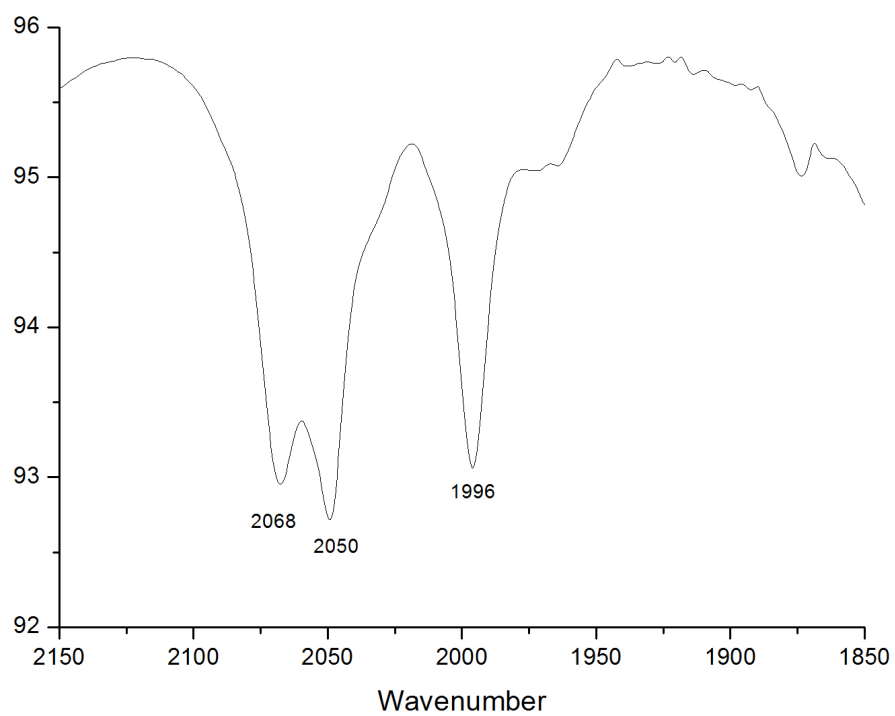
**Figure S4.** IR spectrum of **3** in CH<sub>3</sub>CN.



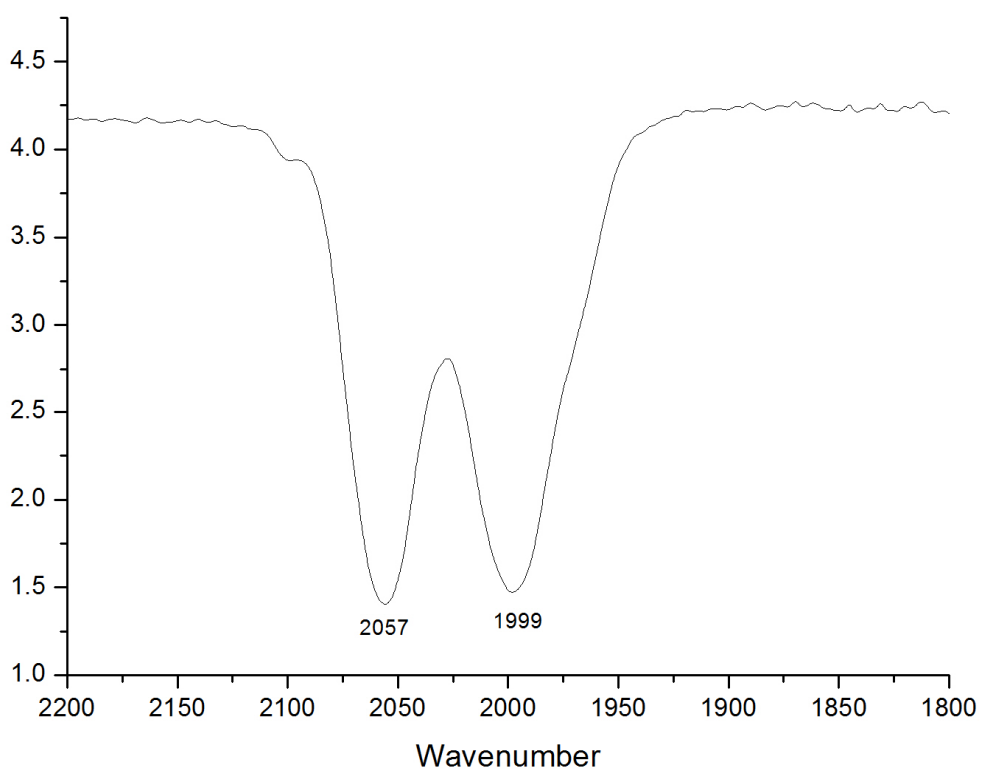
**Figure S5.** IR spectrum of **4** in the solid state.



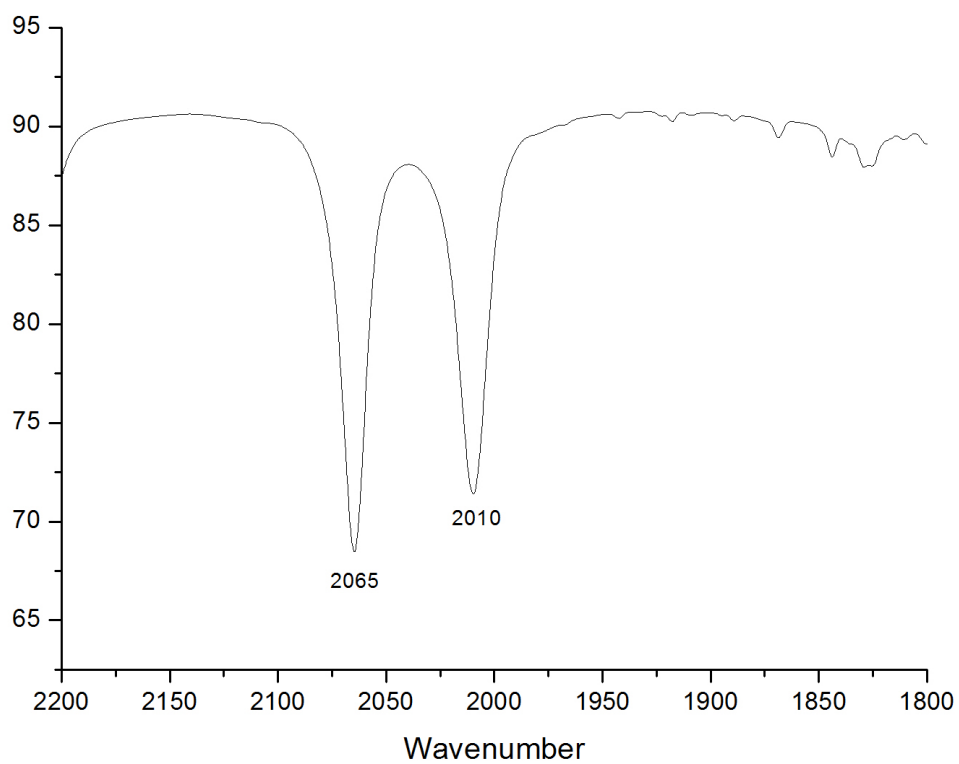
**Figure S6.** IR spectrum of **5** in the solid state.



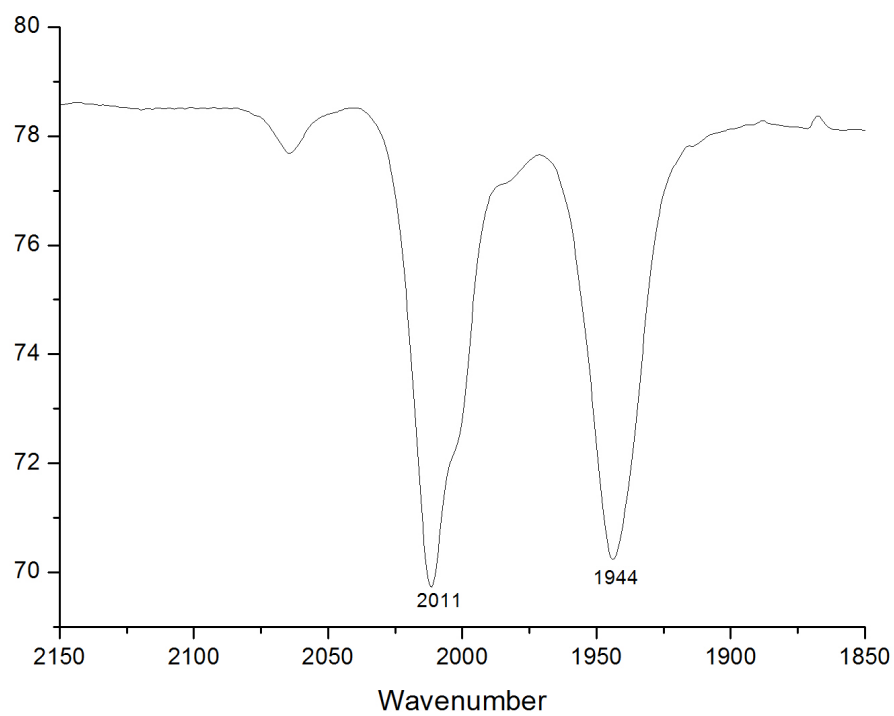
**Figure S7.** IR spectrum of **5** in  $\text{CH}_3\text{CN}$ .



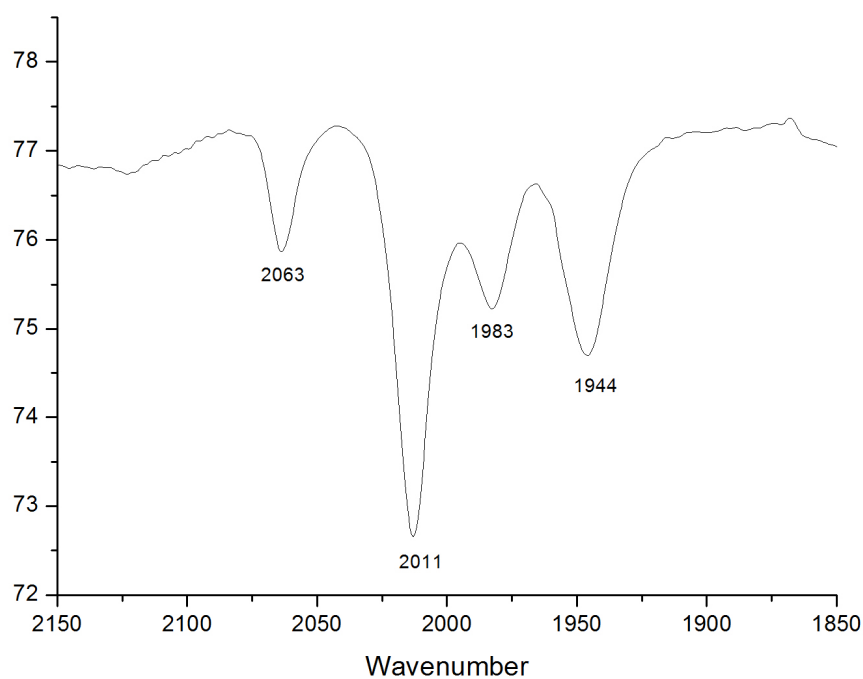
**Figure S8.** IR spectrum of **6** in the solid state.



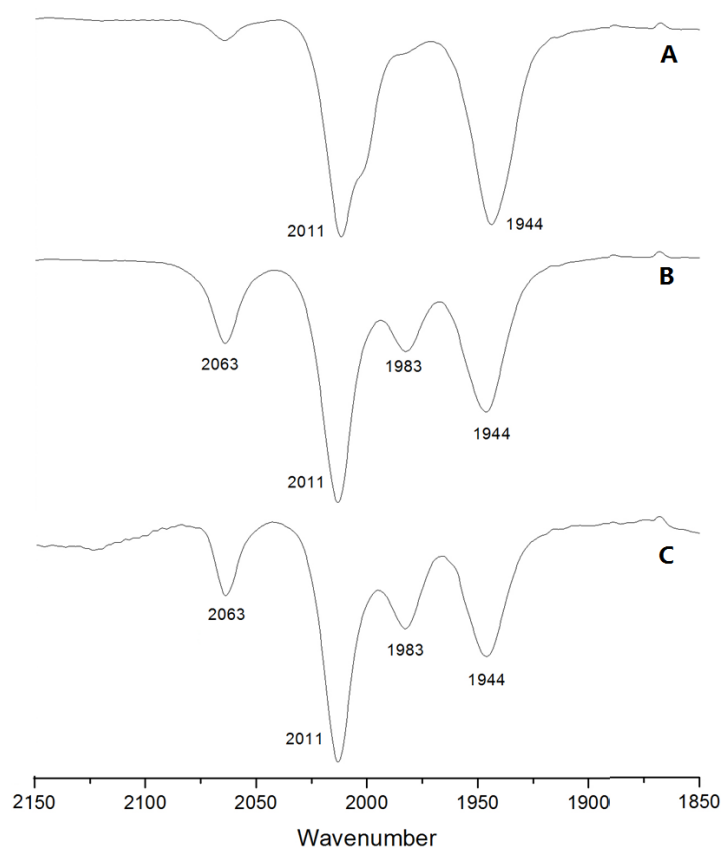
**Figure S9.** IR spectrum of **6** in CH<sub>3</sub>CN.



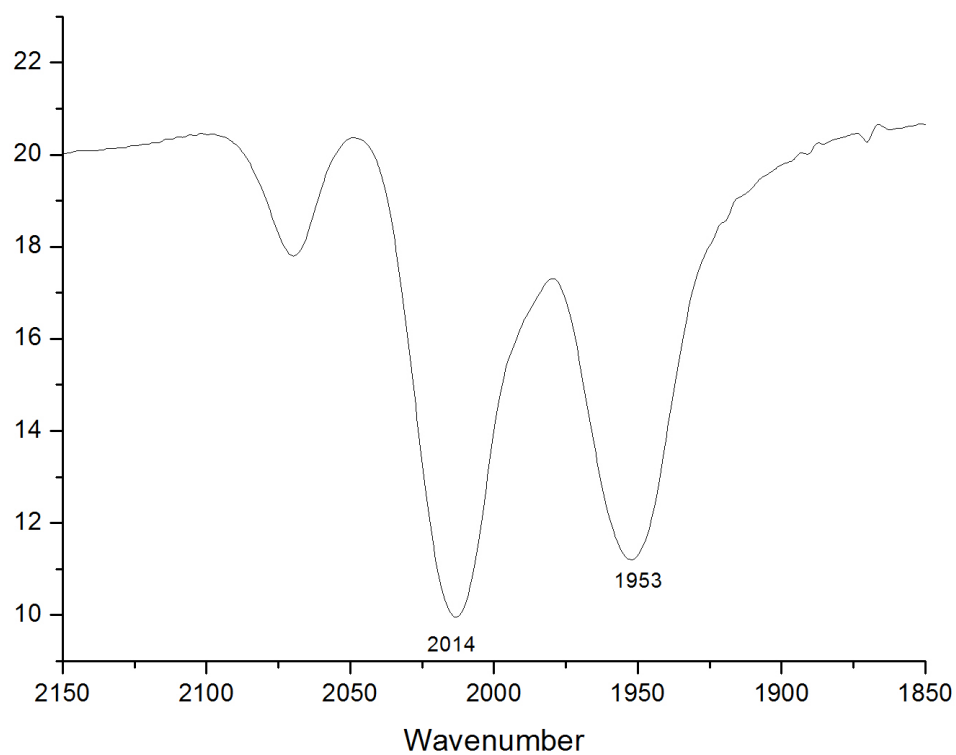
**Figure S10** IR spectrum of **7** in CH<sub>3</sub>CN.



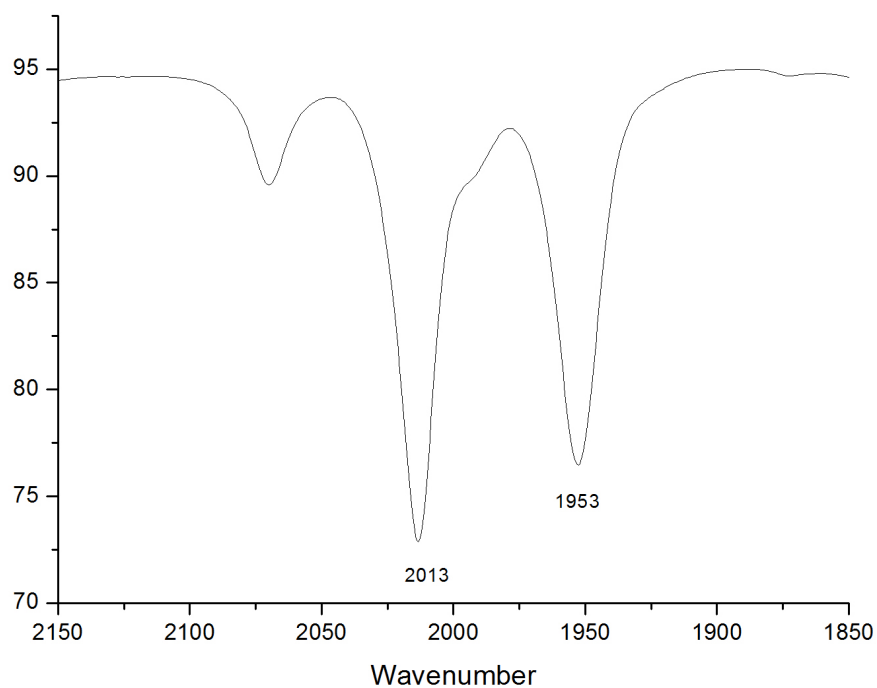
**Figure S11.** Reaction of **7** with CO



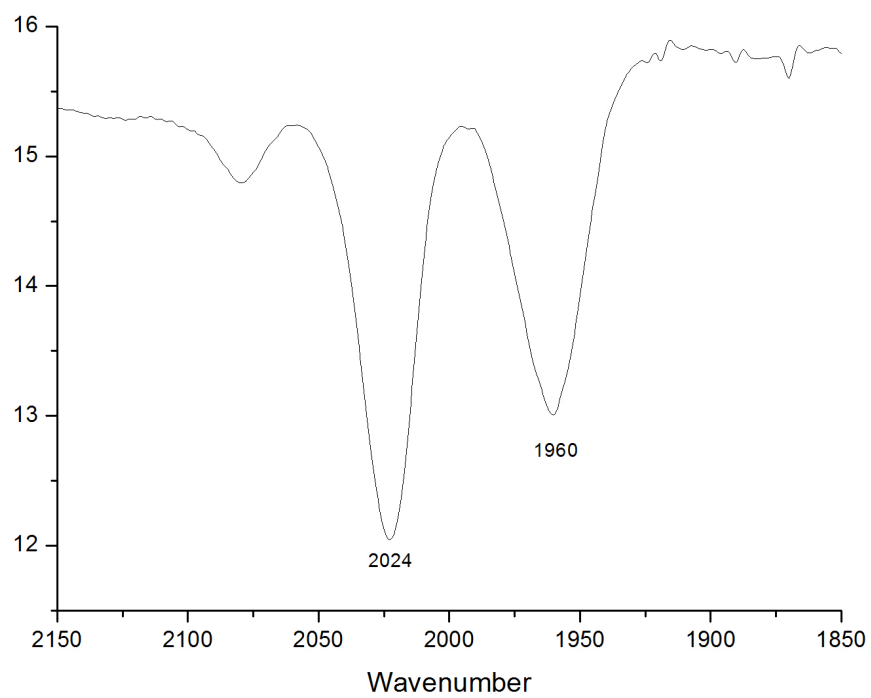
**Figure S12.** IR spectra of **7** or a mixture with **7a**: (A) **7** in CH<sub>3</sub>CN; (B) 2 mins later of **7** in CH<sub>3</sub>CN at -30 °C; (C) **7** in the presence of CO (a mixture of **7** and **7a**).



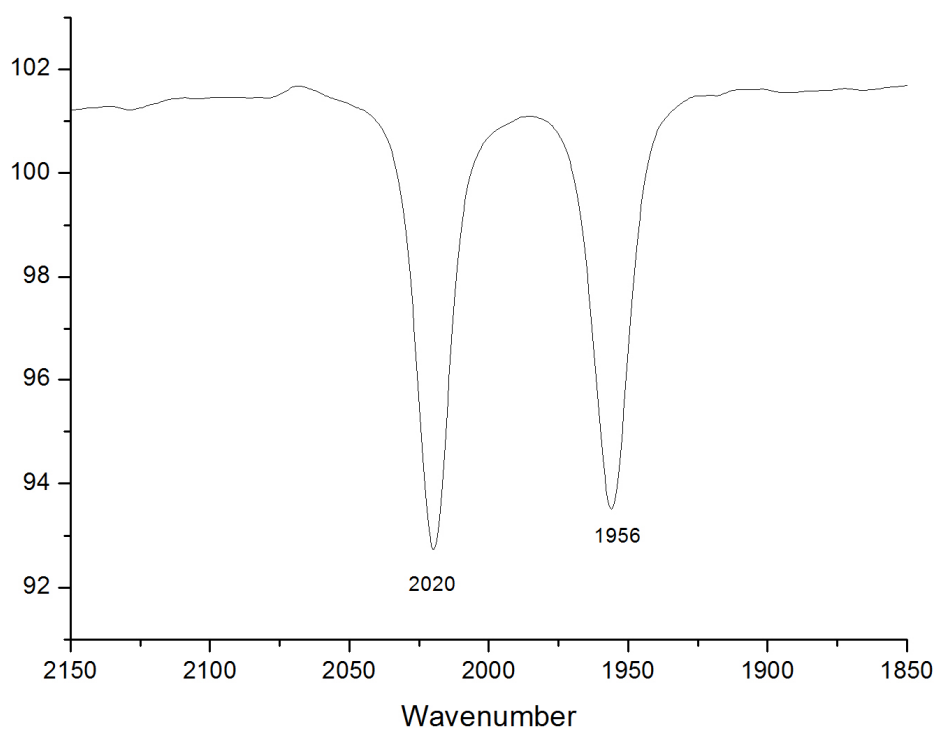
**Figure S13.** IR spectrum of **8** in the solid state.



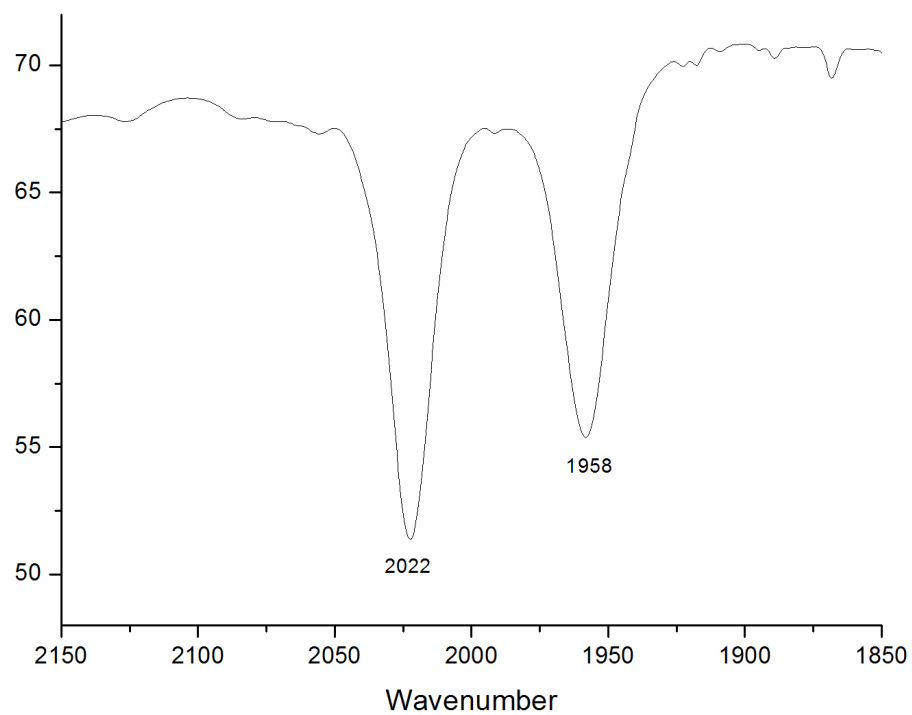
**Figure S14.** IR spectrum of **8** in CH<sub>3</sub>CN.



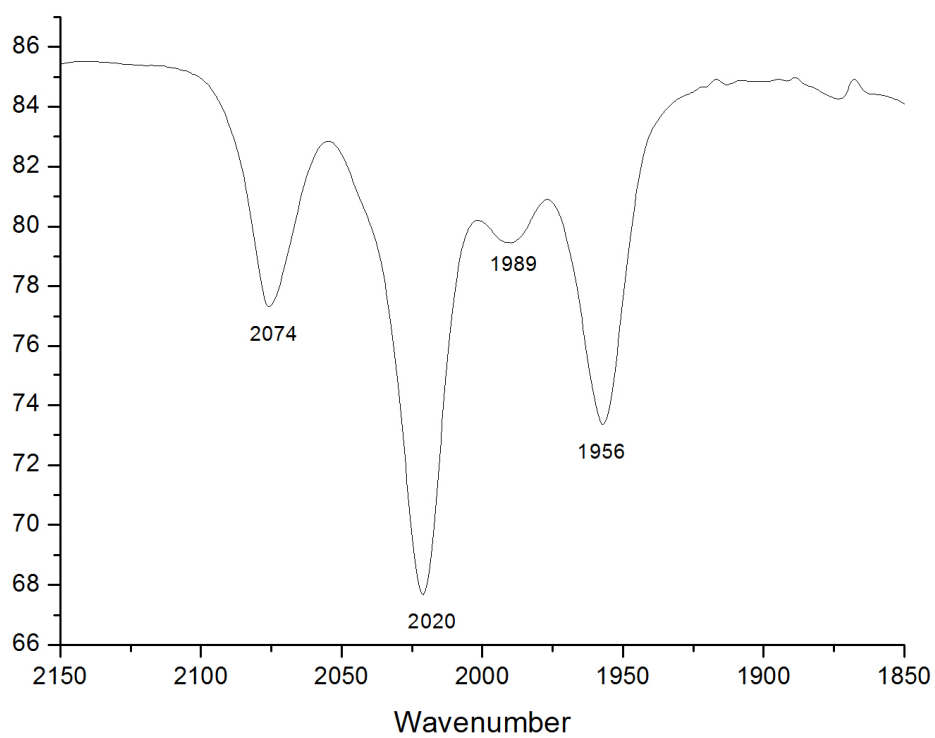
**Figure S15.** IR spectrum of **9** in the solid state.



**Figure S16.** IR spectrum of **9** in CH<sub>3</sub>CN.

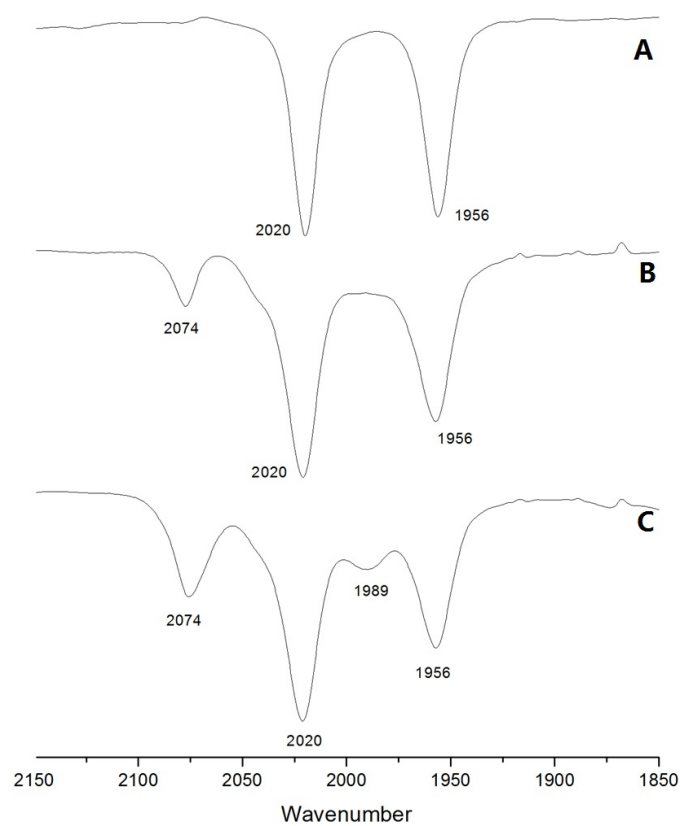


**Figure S17.** IR spectrum of **9** in  $\text{CH}_2\text{Cl}_2$ .

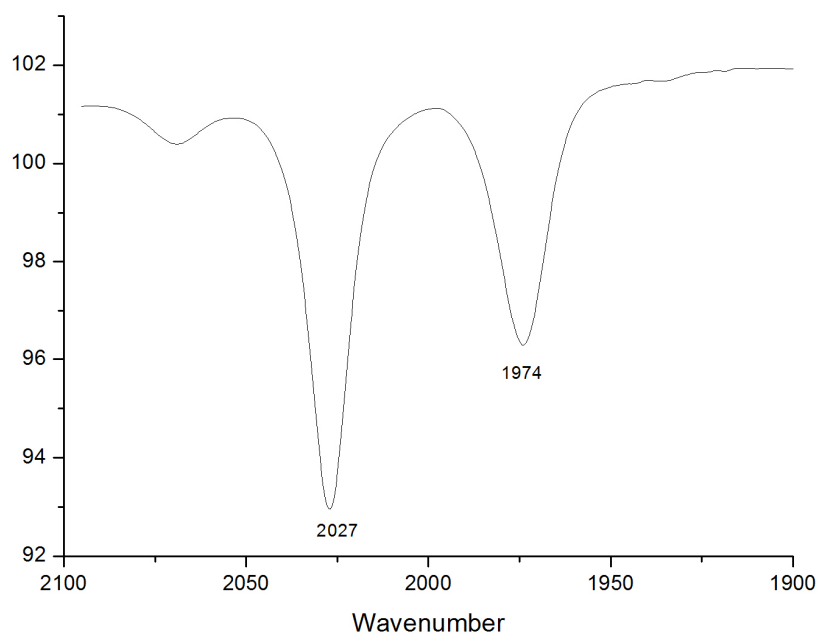


**Figure S18.** Reaction of **9** with CO.

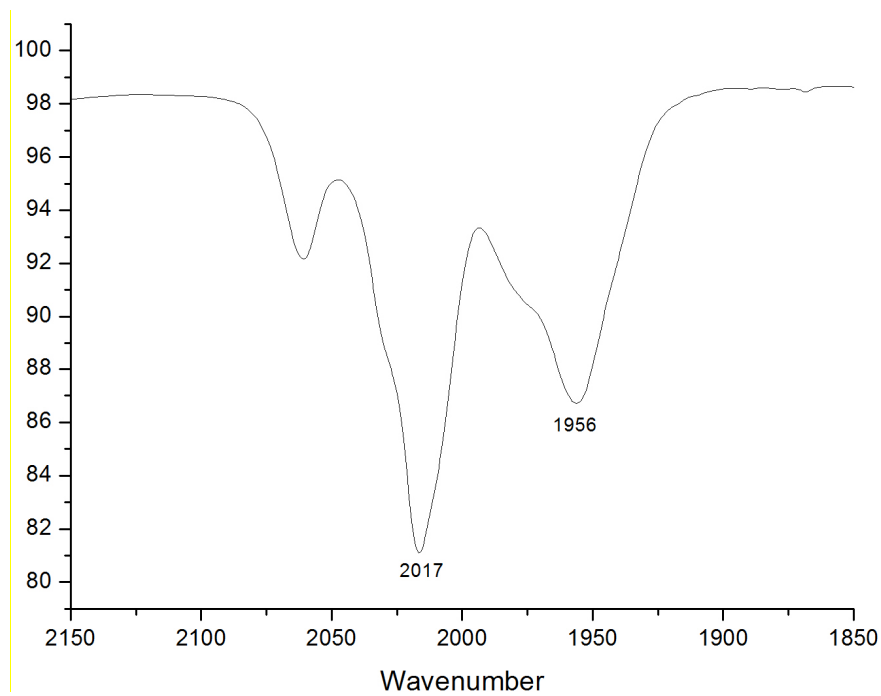




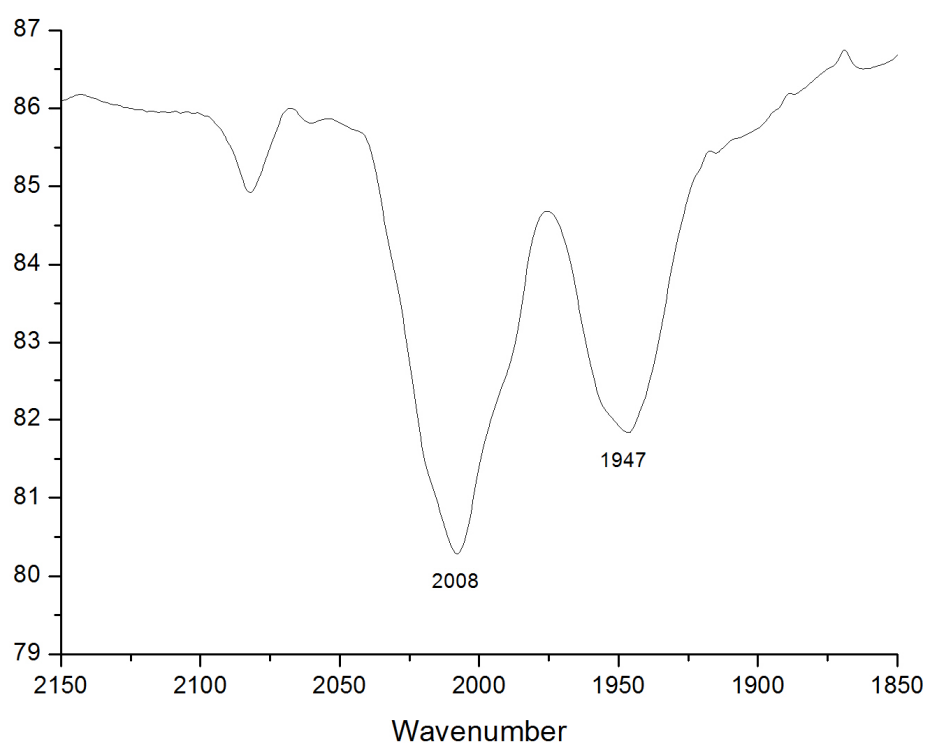
**Figure S19.** IR spectra of **9** or a mixture with **9a**: (A) **9** in  $\text{CH}_3\text{CN}$ ; (B) 20 mins later of **9** in  $\text{CH}_3\text{CN}$  at room temperature; (C) **9** in the presence of CO (a mixture of **9** and **9a**).



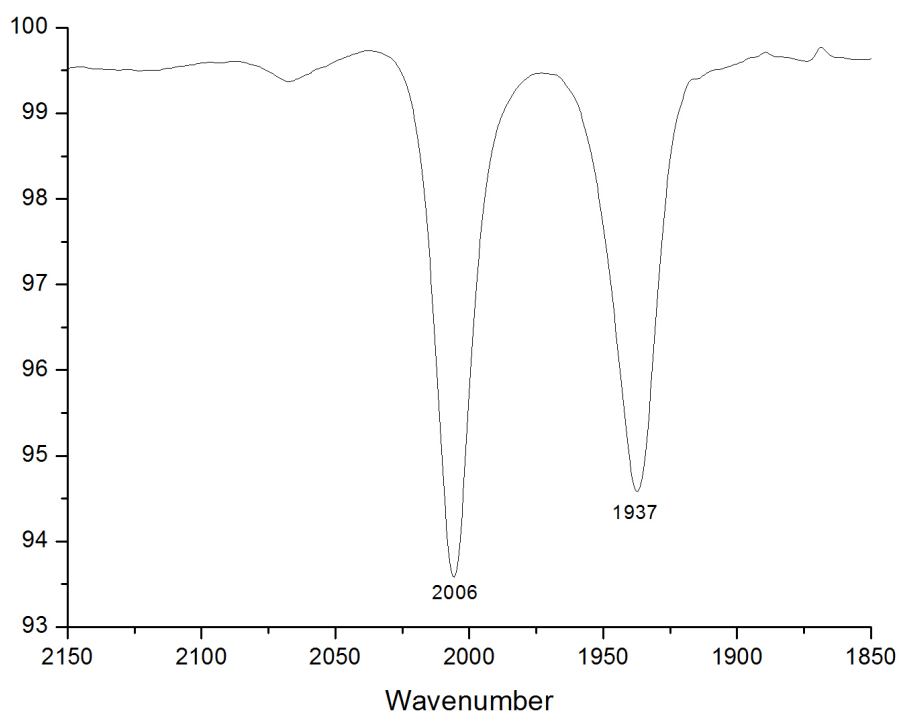
**Figure S20.** Reaction of **9** with *p*-toluenesulfonylmethylisocyanide in  $\text{CH}_3\text{CN}$ .



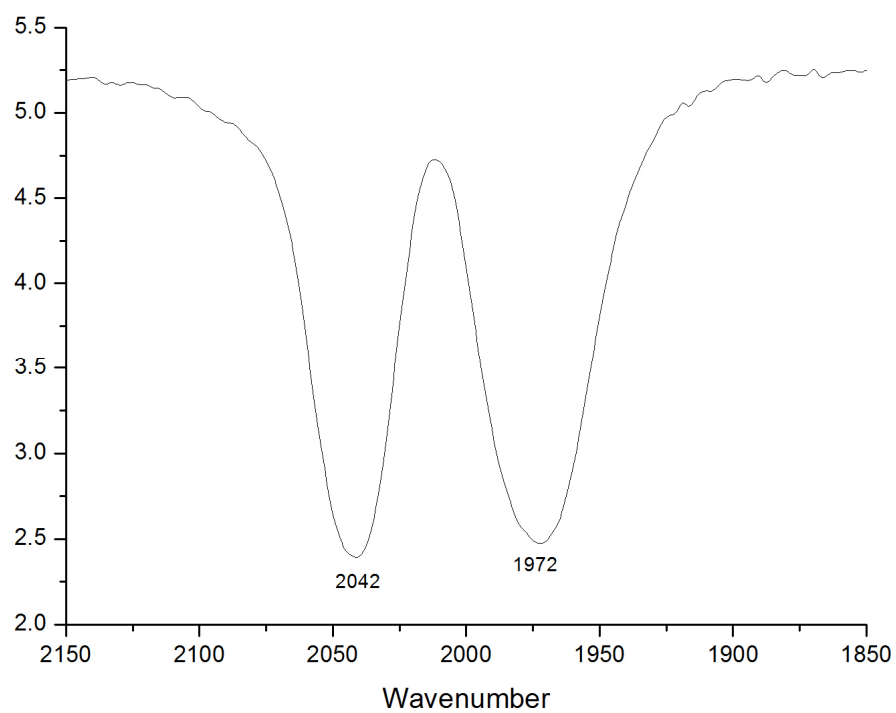
**Figure S21.** IR spectrum of **10** in  $\text{CH}_3\text{CN}$ .



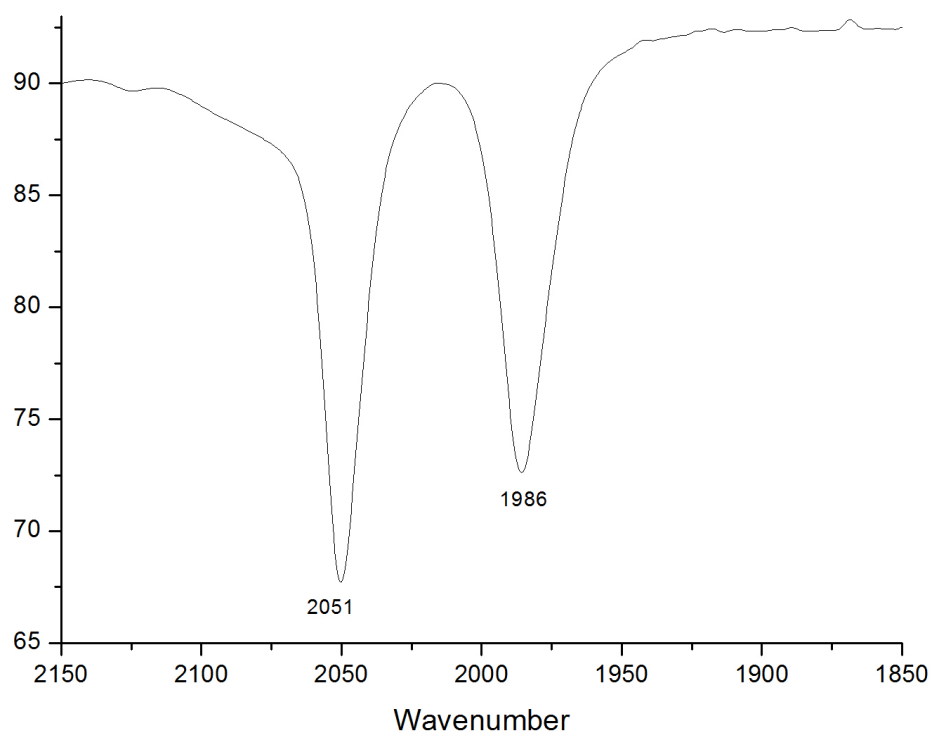
**Figure S22.** IR spectrum of **11** in  $\text{CH}_3\text{CN}$ .



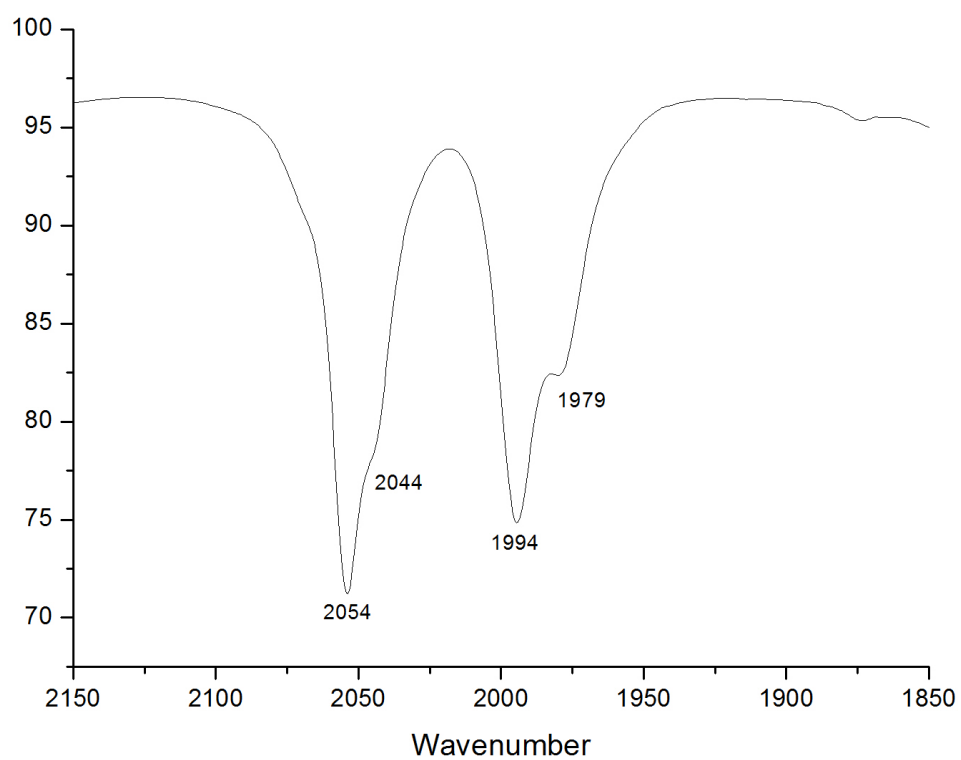
**Figure S23.** IR spectrum of **12** in  $\text{CH}_3\text{CN}$ .



**Figure S24.** IR spectrum of **13** in the solid state.

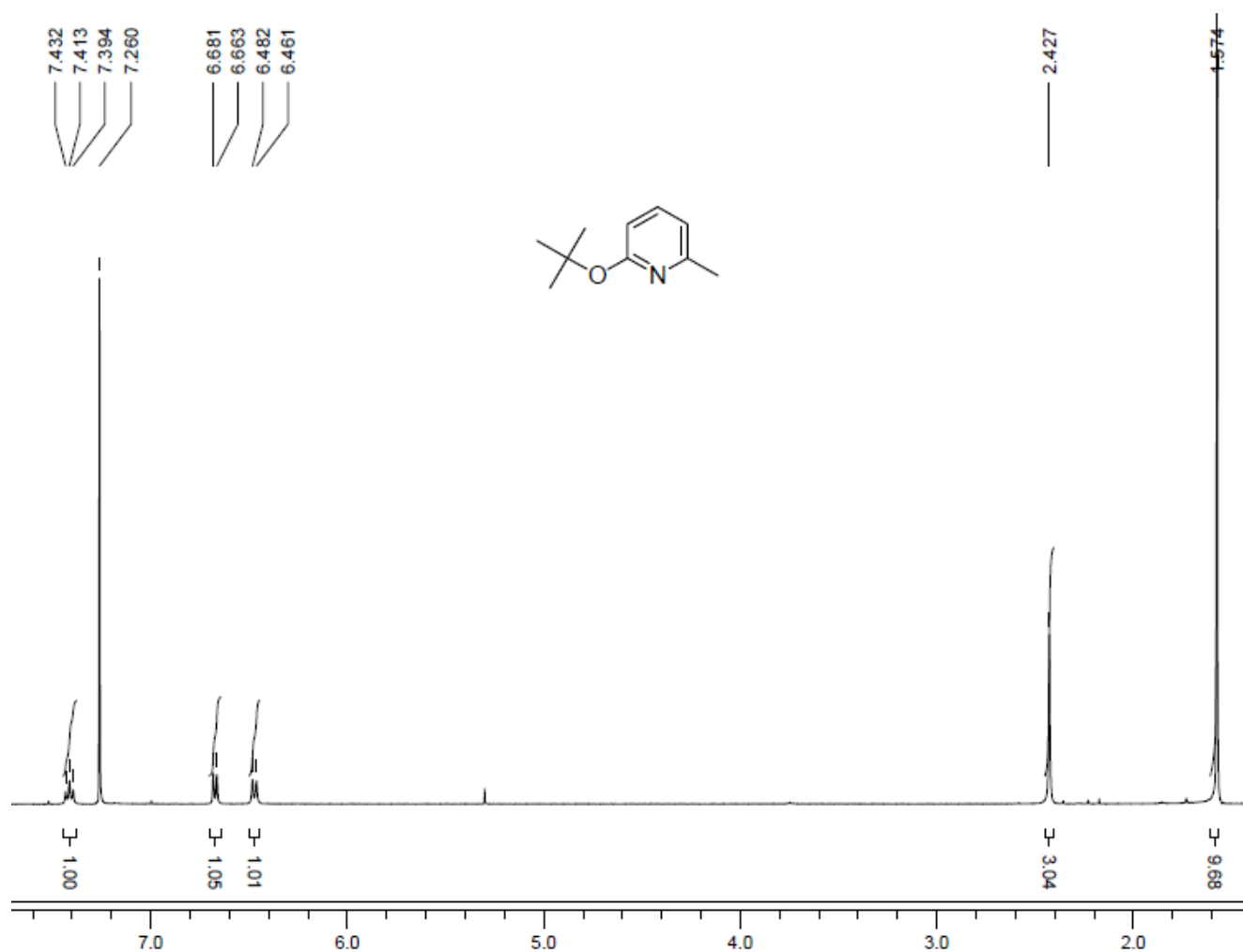


**Figure S25.** IR spectrum of **13** in  $\text{CH}_2\text{Cl}_2$ .

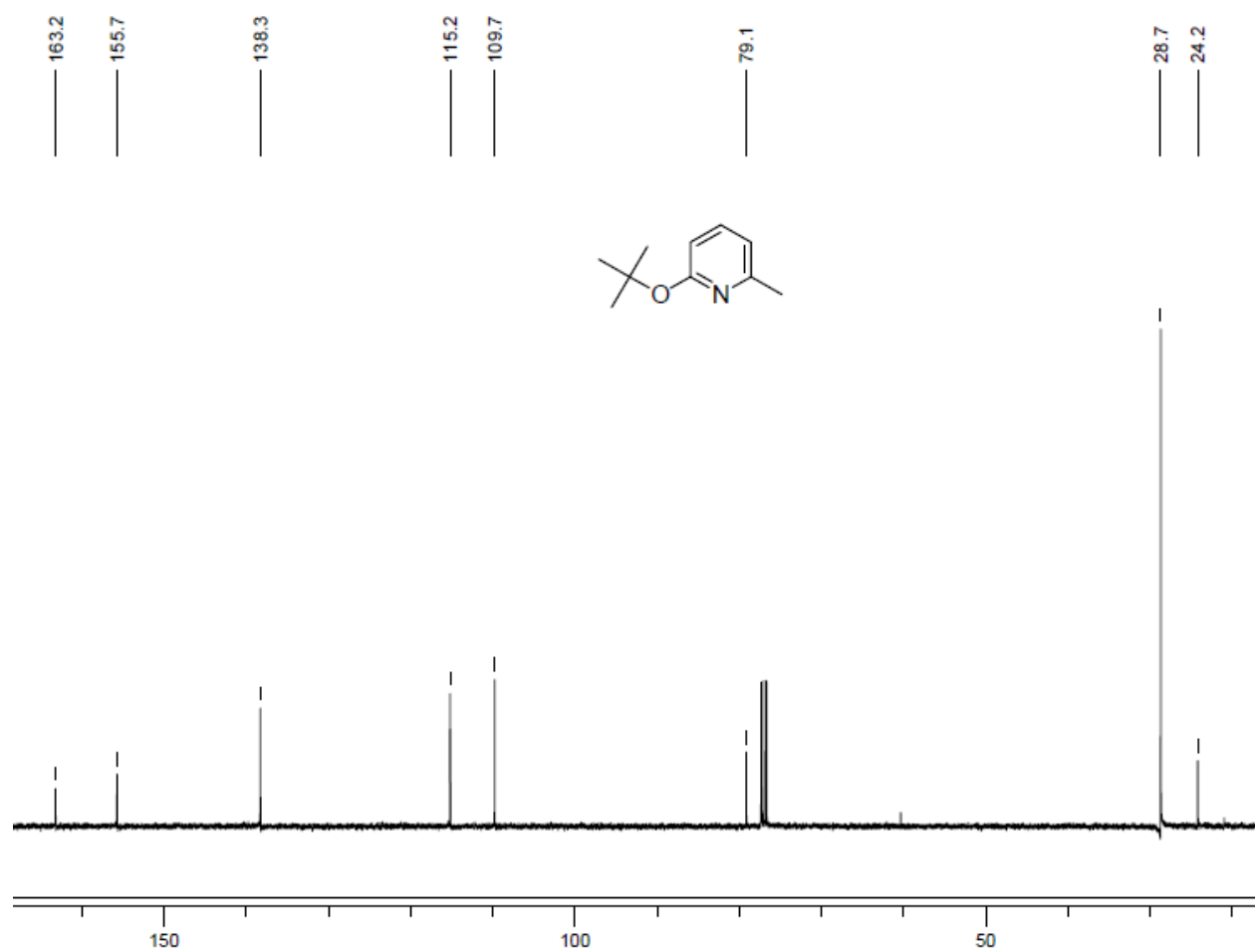


**Figure S26.** IR spectrum of **13** and **13a** in  $\text{CH}_3\text{CN}$ .

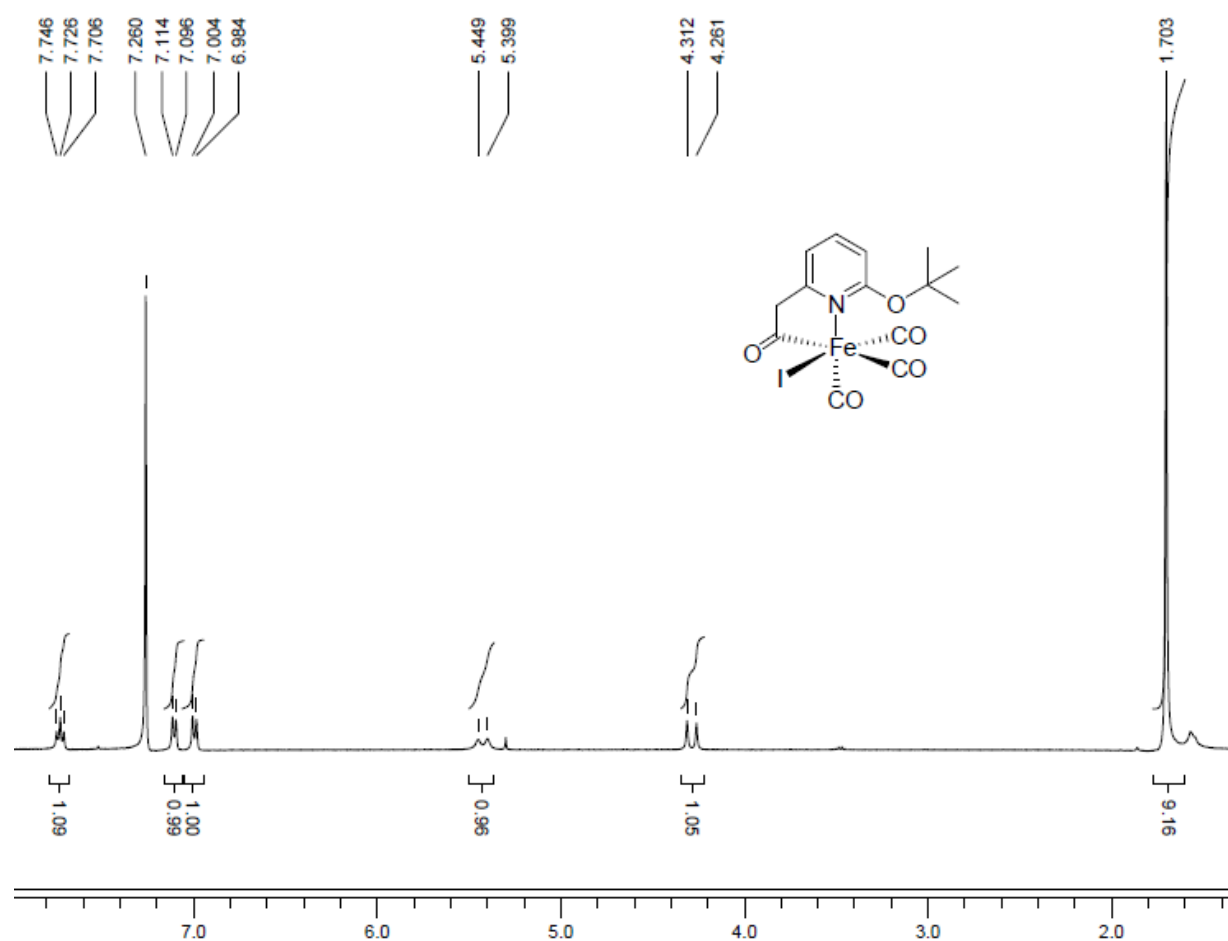
## NMR spectra



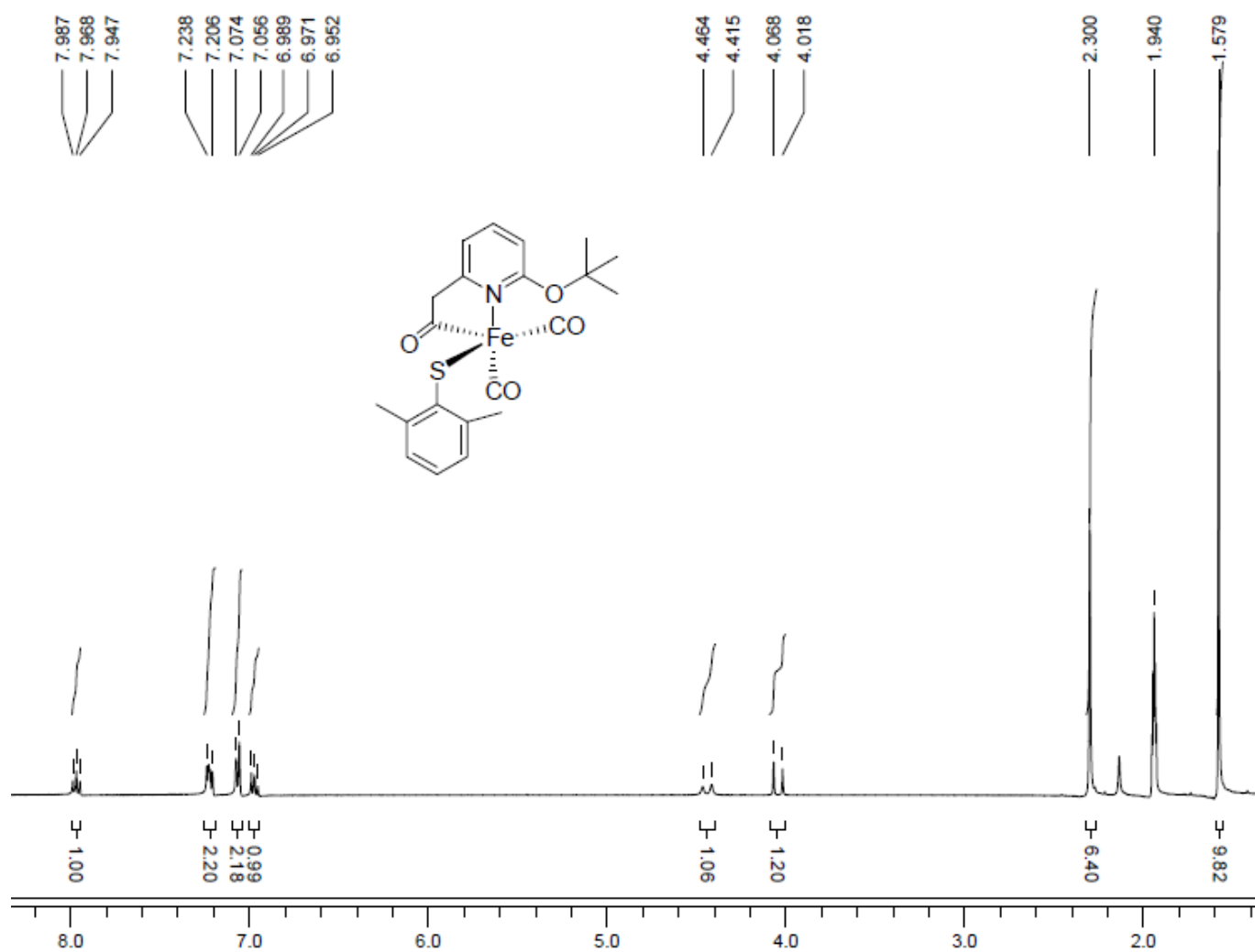
**Figure S27.**  $^1\text{H}$  NMR spectrum of 2-*tert*-butoxy-6-methylpyridine in  $\text{CDCl}_3$ .



**Figure S28.**  $^{13}\text{C}$  NMR spectrum of 2-*tert*-butoxy-6-methylpyridine in  $\text{CDCl}_3$ .

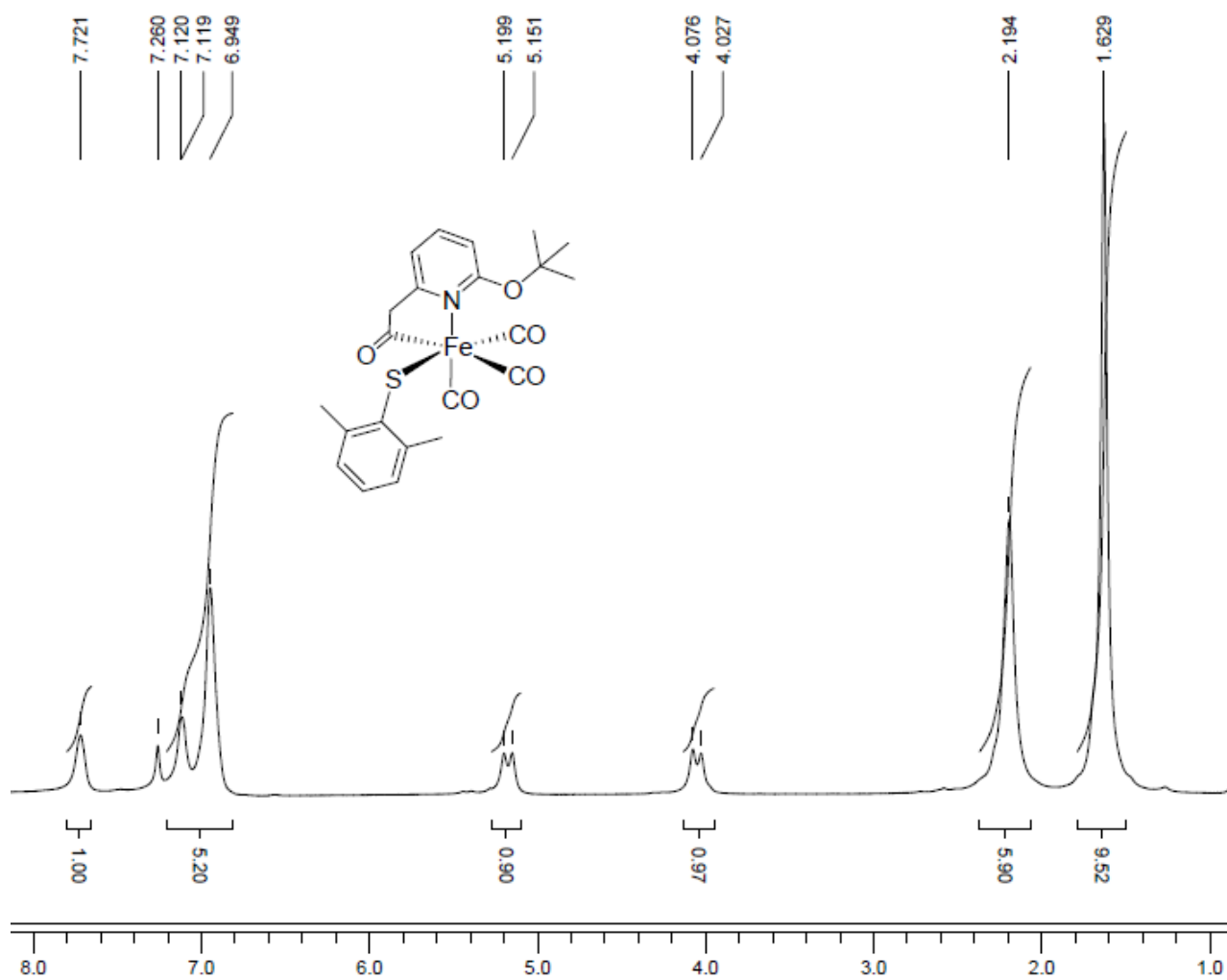


**Figure S29.** <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub>.

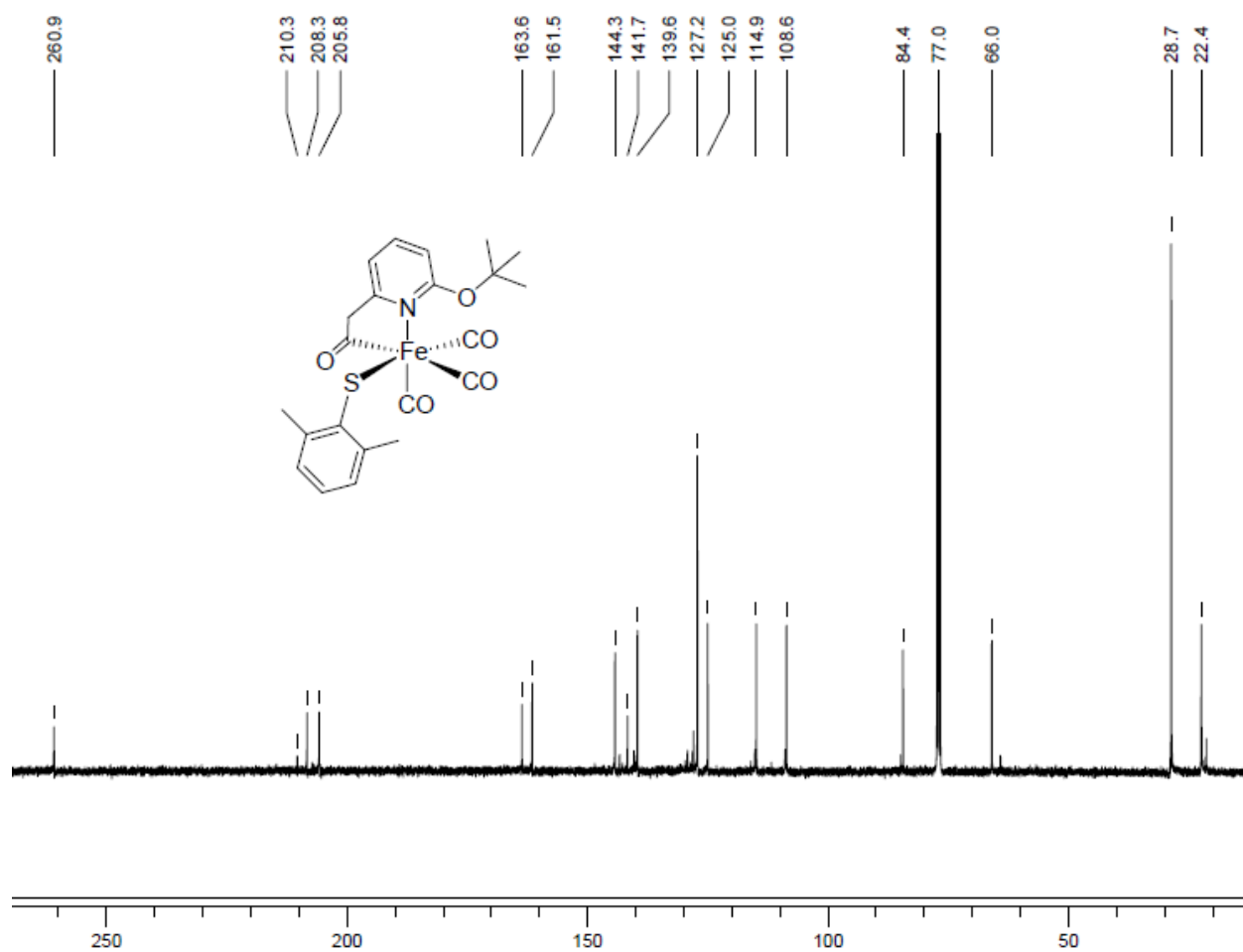


**Figure S30.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$ .

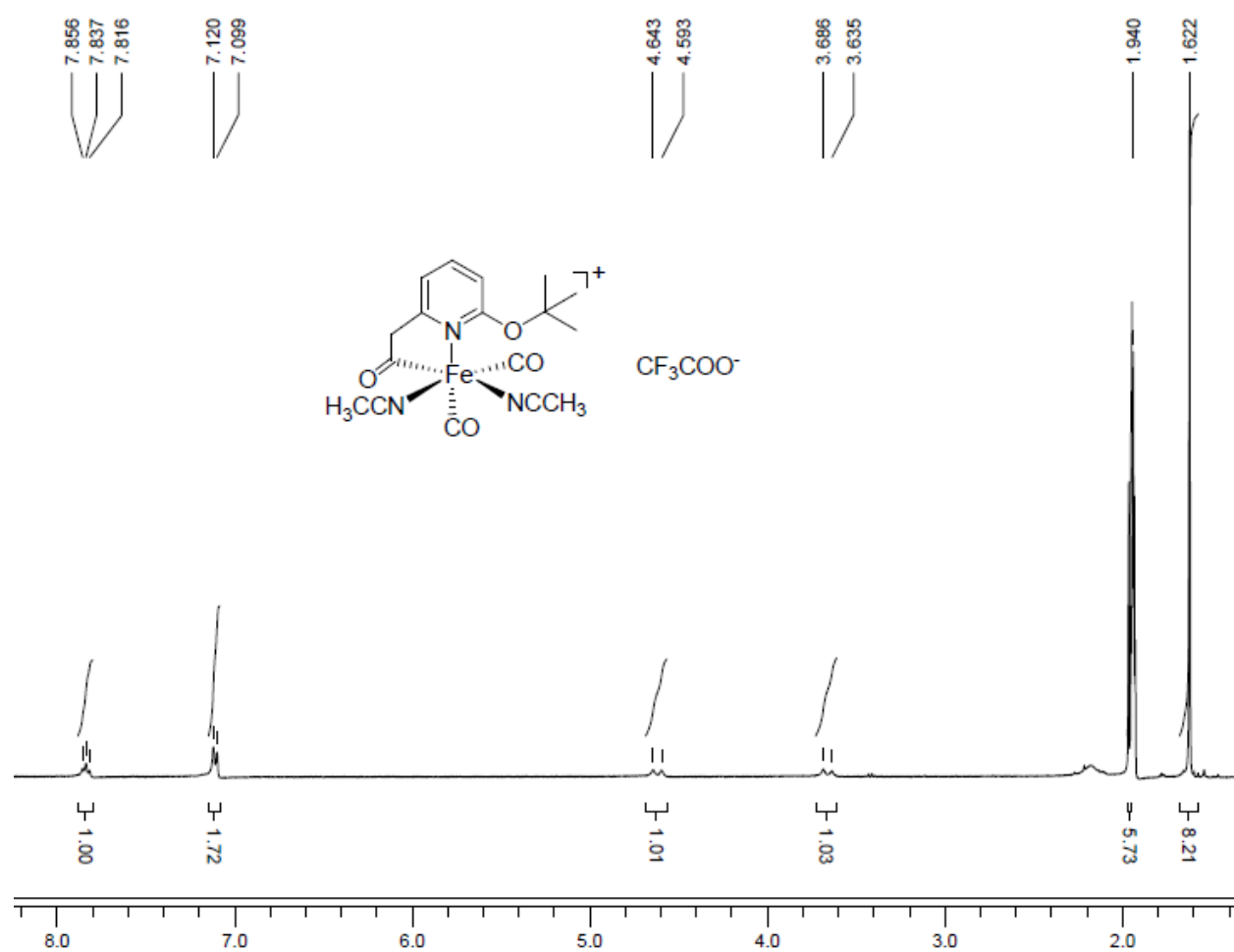




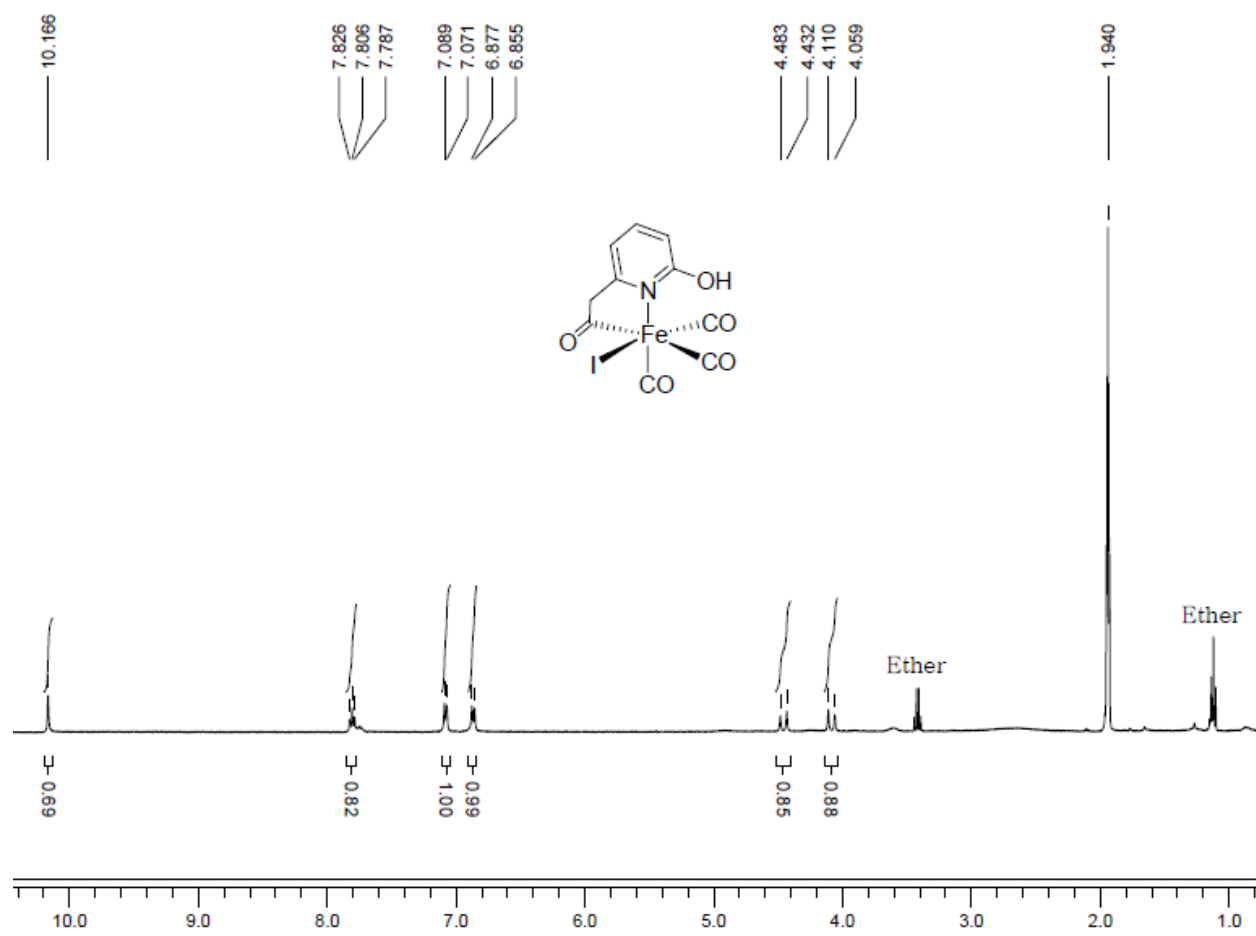
**Figure S31.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



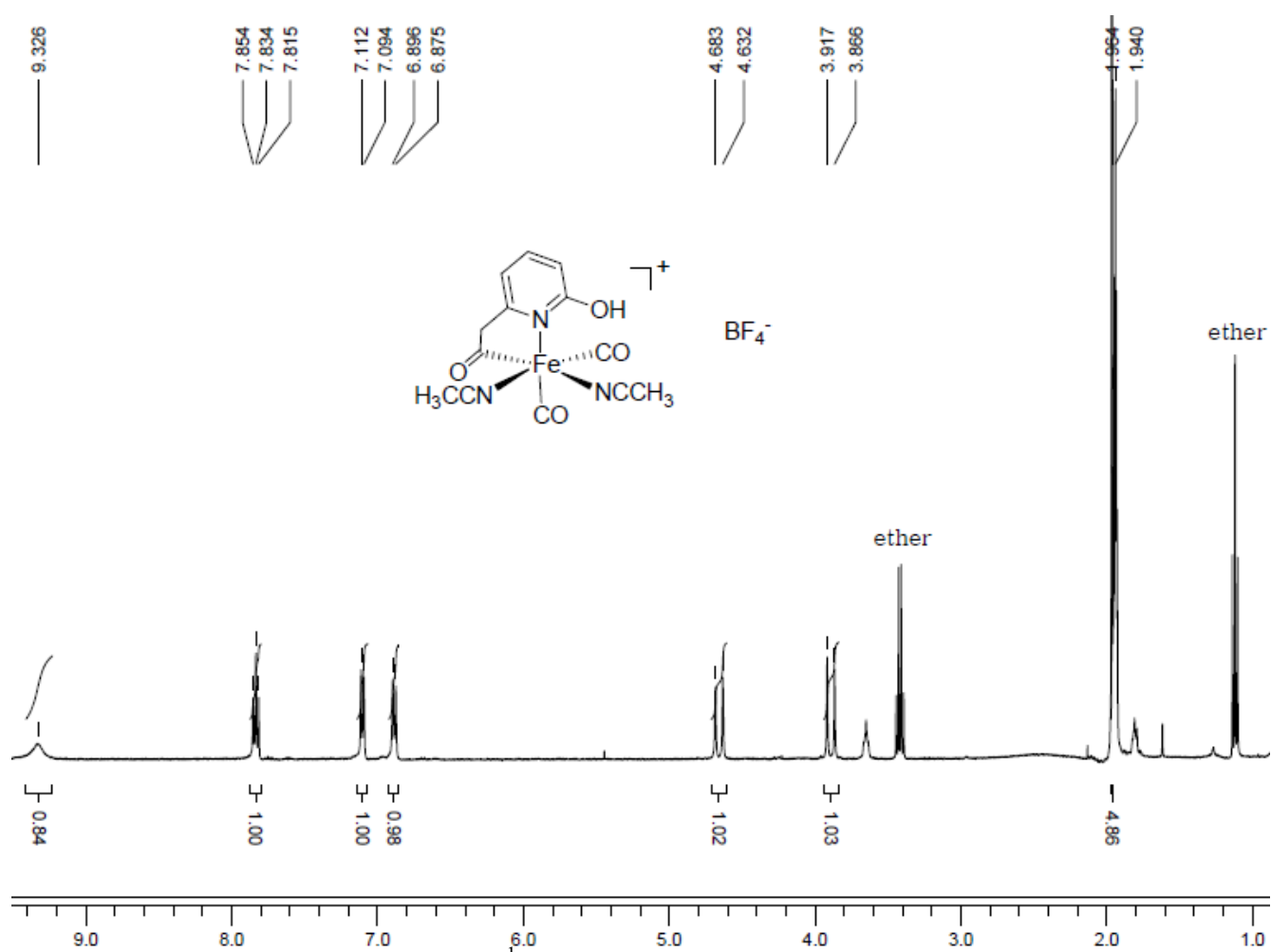
**Figure S32.**  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



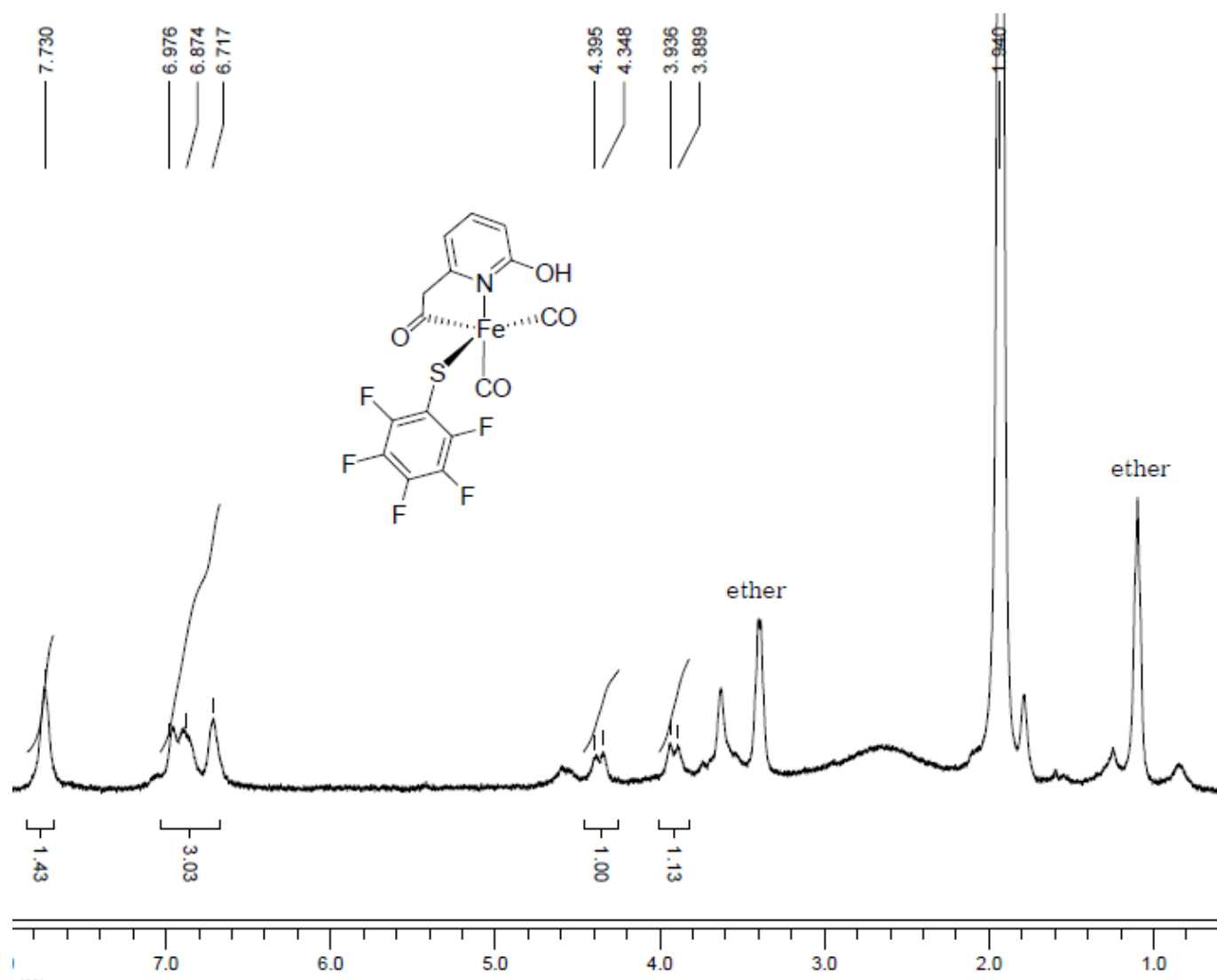
**Figure S33.**  $^1\text{H}$  NMR spectrum of **4** in  $\text{CD}_3\text{CN}$ .



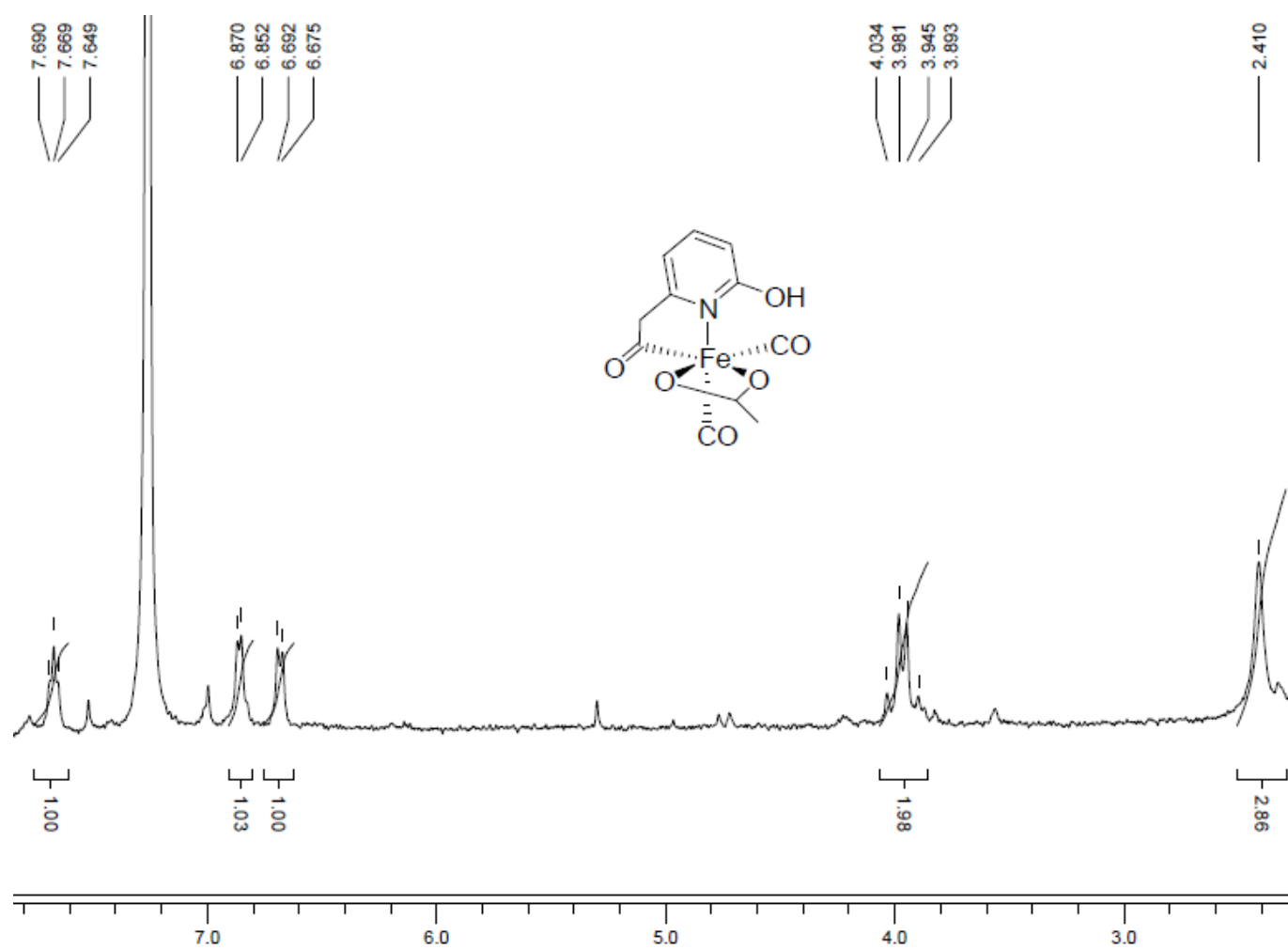
**Figure S34.**  $^1\text{H}$  NMR spectrum of **5** in  $\text{CD}_3\text{CN}$ .



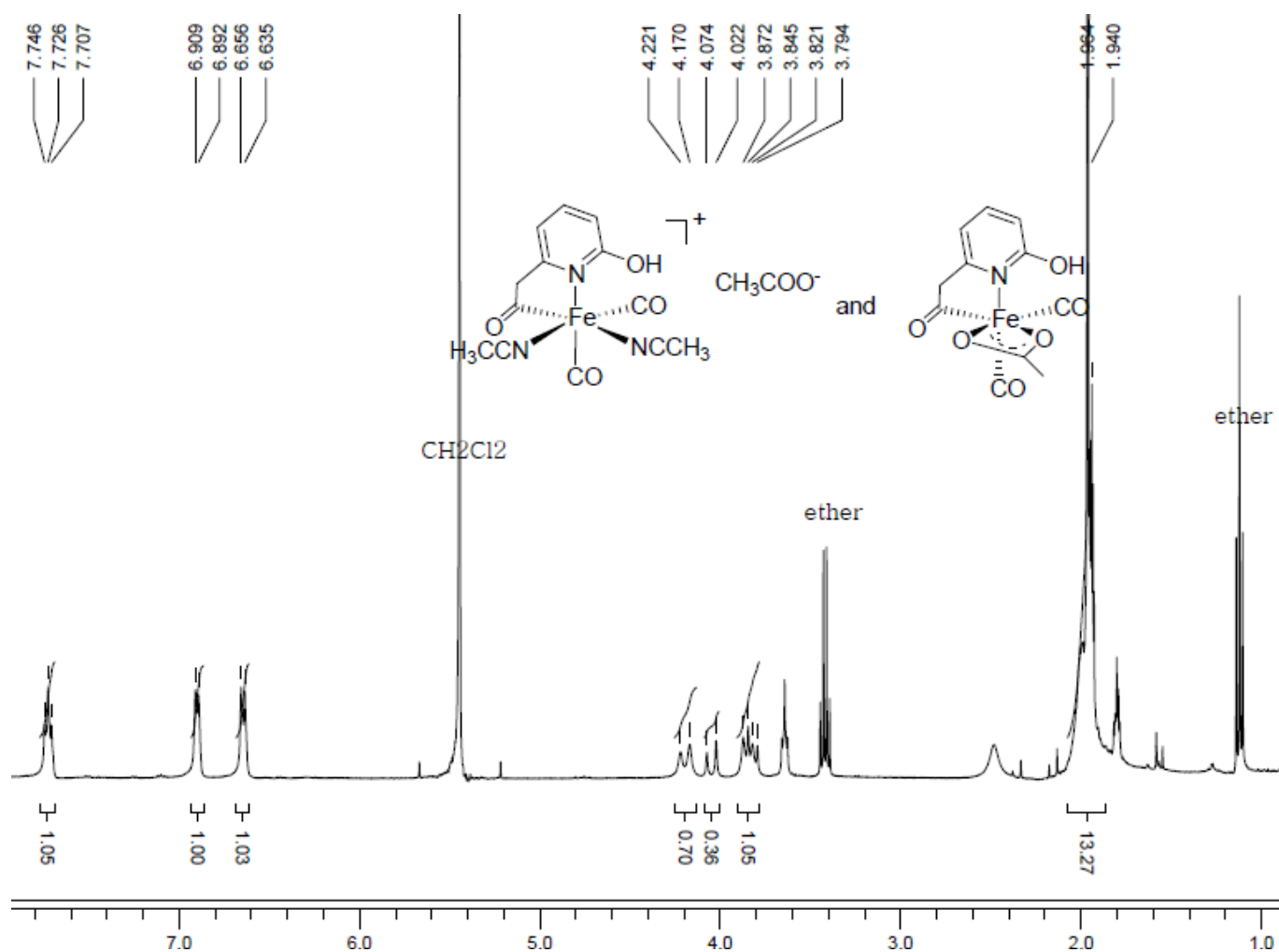
**Figure S35.** <sup>1</sup>H NMR spectrum of **6** in CD<sub>3</sub>CN.



**Figure S36.**  $^1\text{H}$  NMR spectrum of **9** in  $\text{CD}_3\text{CN}$ .



**Figure S37.**  $^1\text{H}$  NMR spectrum of **13** in  $\text{CDCl}_3$ .



**Figure S38.**  $^1\text{H}$  NMR spectrum of **13** and **13a** in  $\text{CD}_3\text{CN}$ .