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# Cyanide-Alkene Competition at a Diiron Complex and Isolation of a Multisite (Cyano)Alkylidene–Alkene Species

Giulio Bresciani, Silvia Schoch, Lorenzo Biancalana, Stefano Zacchini, Marco Bortoluzzi, Guido Pampaloni, Fabio Marchetti

# Supporting Information

**Table of contents** *Pages*

**Figure S1.** DFT-optimized structures of the isomers of **2** and relative Gibbs energy values (kcal $mol^{-1}$). Colour map: Fe, green; N, blue; O, red; C, grey; H, white.

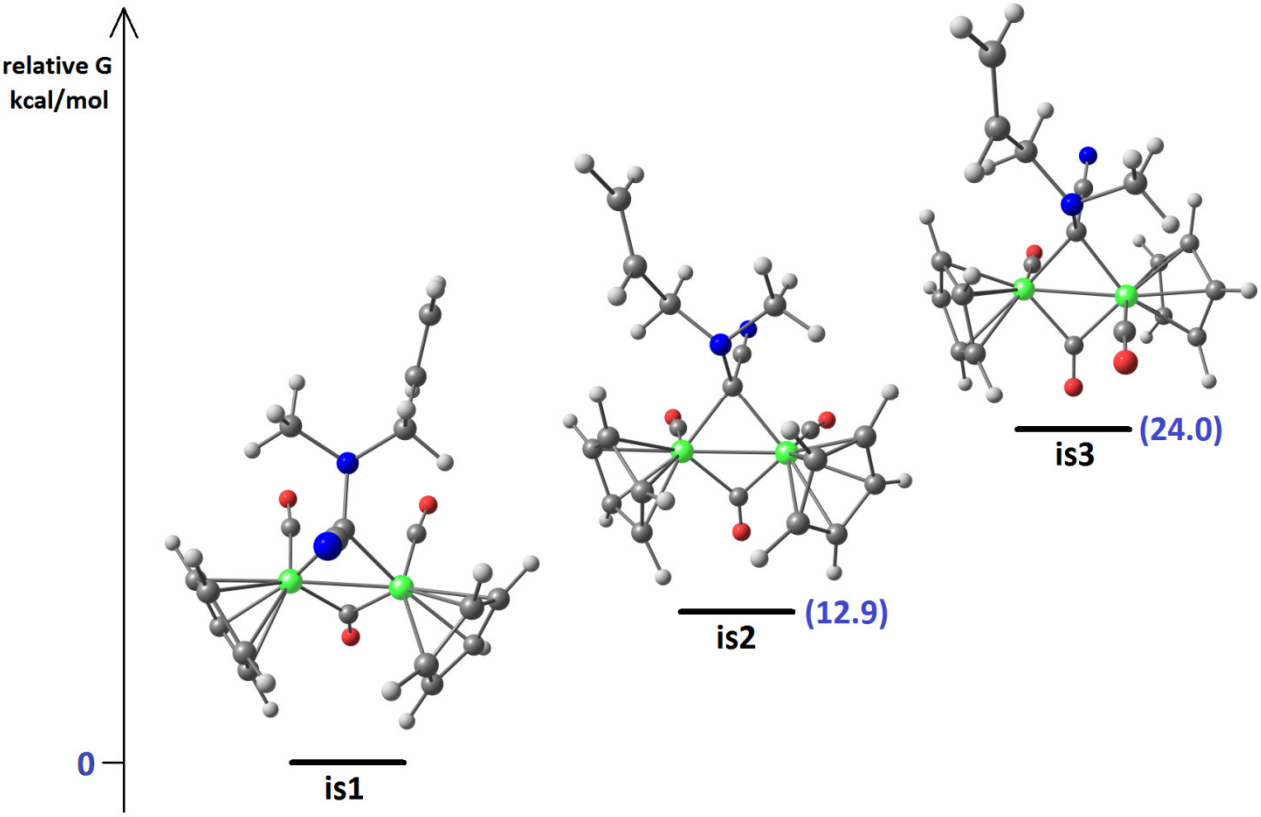


**Figure S2.** DFT-optimized structures of the isomers of **4** and relative Gibbs energy values (kcal $mol^{-1}$). Colour map: Fe, green; N, blue; O, red; C, grey; H, white. Selected bond lengths for **4-is1** (Å): Fe-Fe, 2.491; Fe-C (alkylidyne) 1.853 (average); Fe-C (CO) 1.747; Fe-C (CN) 1.887; Fe-C (μ-CO) 1.914 (average); Fe-C (Cp) 2.119 (average).

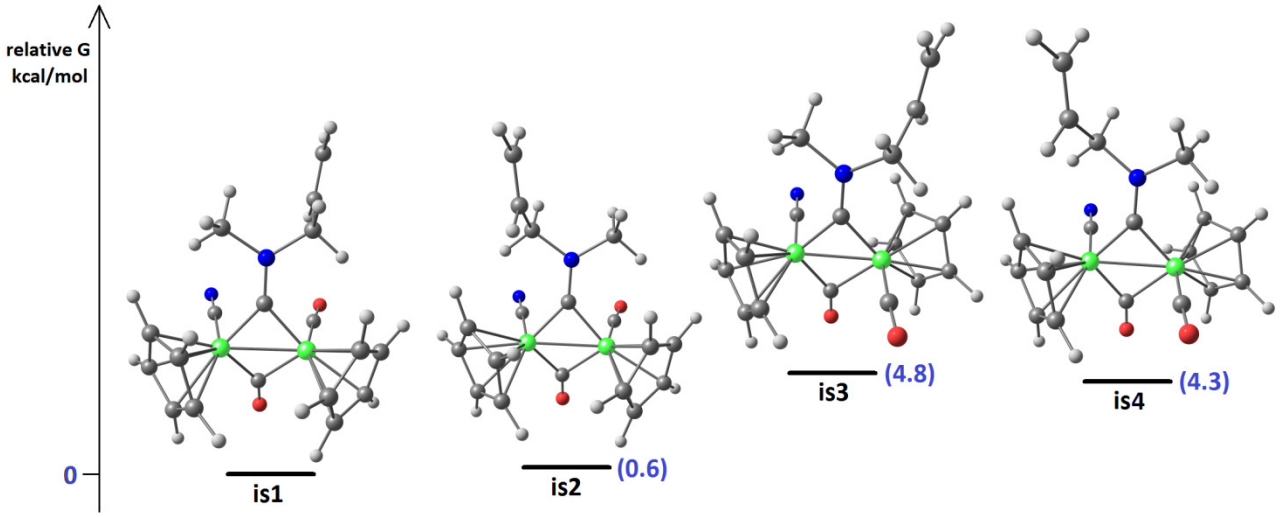
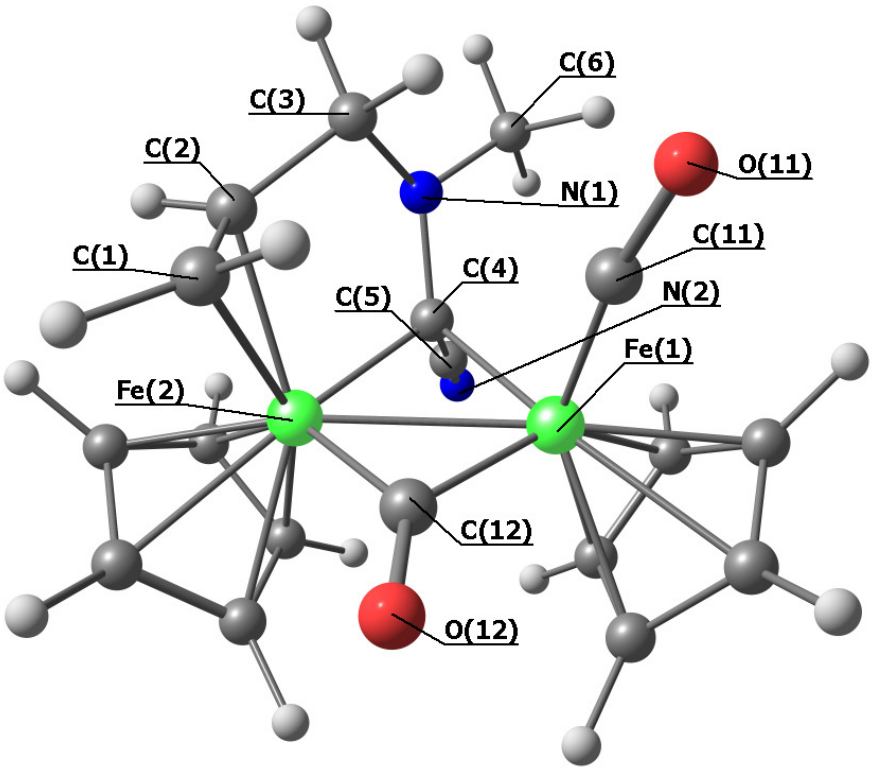


**Figure S3.** DFT-optimized structure of the most stable isomer of **3**. Colour map: Fe, green; N, blue; O, red; C, grey; H, white. Selected computed and experimental bond lengths (Å) and angles (°) are compared in the table below.




| Bond | X-ray | DFT |
|---|---|---|
| Fe(1)-Fe(2) | 2.535(3) | 2.545 |
| Fe(1)-C(11) | 1.79(2) | 1.744 |
| Fe(1)-C(12) | 1.91(3) | 1.887 |
| Fe(2)-C(12) | 1.90(3) | 1.910 |
| Fe(1)-C(4) | 2.02(2) | 2.036 |
| Fe(2)-C(4) | 1.99(2) | 1.985 |
| Fe(2)-C(1) | 2.14(2) | 2.125 |
| Fe(2)-C(2) | 2.13(3) | 2.101 |
| C(1)-C(2) | 1.37(4) | 1.390 |
| C(2)-C(3) | 1.45(3) | 1.506 |
| C(3)-N(1) | 1.42(3) | 1.437 |
| N(1)-C(4) | 1.42(3) | 1.417 |
| N(1)-C(6) | 1.42(3) | 1.444 |
| C(4)-C(5) | 1.43(3) | 1.444 |
| C(5)-N(2) | 1.14(3) | 1.167 |
| C(11)-O(11) | 1.12(3) | 1.155 |
| C(12)-O(12) | 1.17(2) | 1.180 |
| **Angle** | **X-ray** | **DFT** |
| Fe(1)-C(11)-O(11) | 165(2) | 170.0 |
| Fe(1)-C(12)-Fe(2) | 83.4(8) | 84.2 |
| Fe(1)-C(4)-Fe(2) | 78.3(7) | 78.5 |
| C(1)-C(2)-C(3) | 123(2) | 122.4 |
| C(2)-C(3)-N(1) | 109.4(19) | 107.4 |
| C(3)-N(1)-C(4) | 110.3(18) | 112.8 |
| C(3)-N(1)-C(6) | 117.0(19) | 117.0 |
| C(6)-N(1)-C(4) | 116.7(19) | 120.5 |
| N(1)-C(4)-C(5) | 107.8(19) | 107.7 |
| C(4)-C(5)-N(2) | 177(2) | 178.4 |

**Figure S4.** Relative stability (Gibbs energy values, kcal mol$^{-1}$) of complex **3** (**is1**), its trans isomer (**is2**) and the isomers with terminal alkylidene moiety (**is3** and **is4**). Colour map: Fe, green; N, blue; O, red; C, grey; H, white.

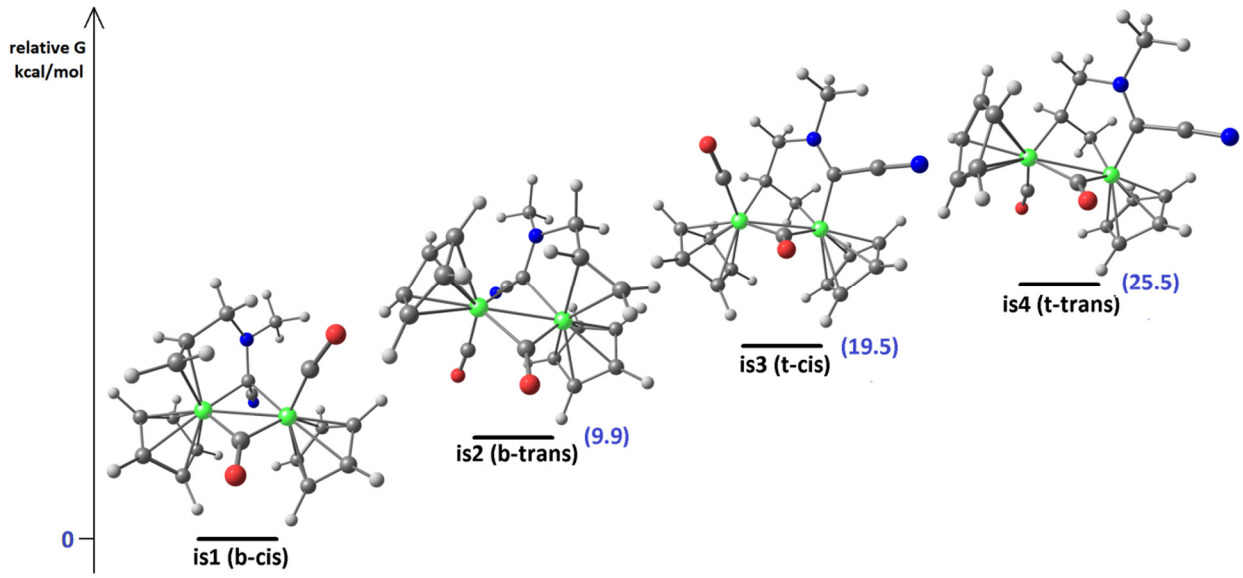


**Figure S5.** DFT-optimized structures of the most stable isomers of **3**, **4** and **5** and relative Gibbs energy values. Colour map: Fe, green; N, blue; O, red; C, grey; H, white.

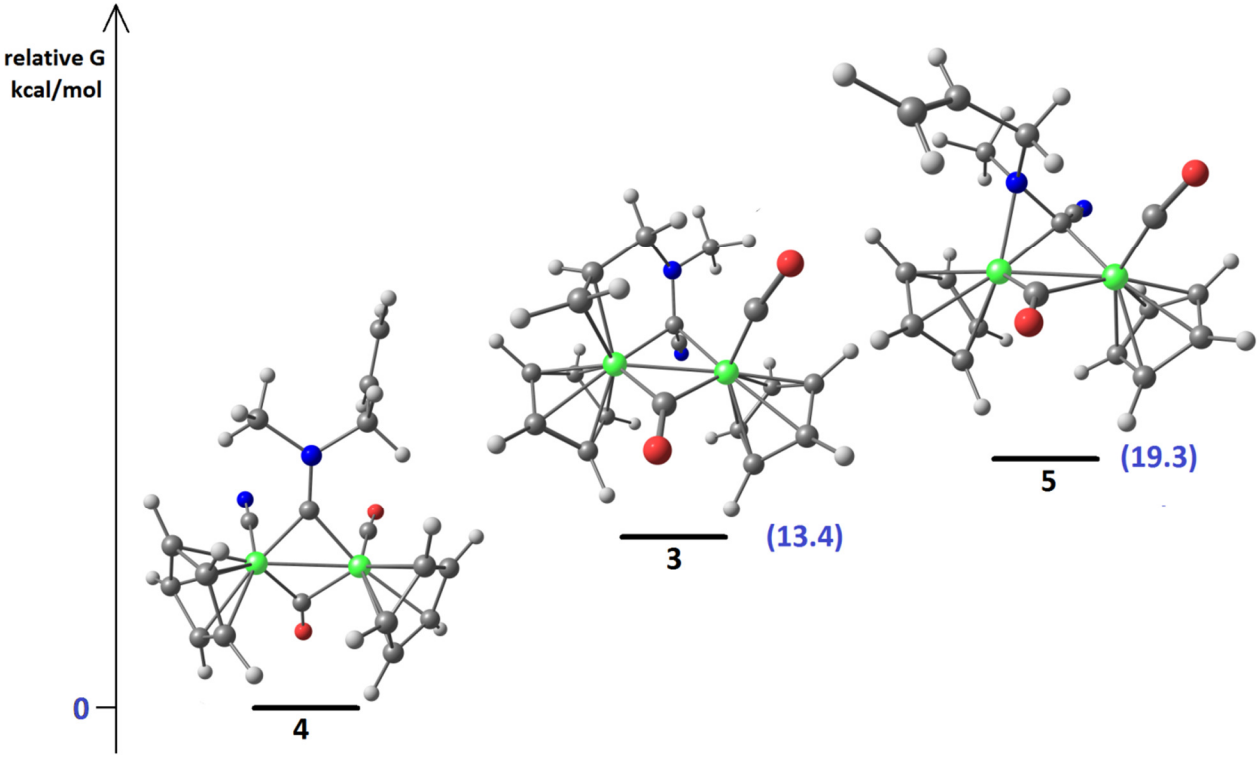



**Figure S6.** Chemdraw structure of [$Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\kappa C,N\text{-}C(CN)NMe(CH_2CH{=}CH_2)\}$], **5**.

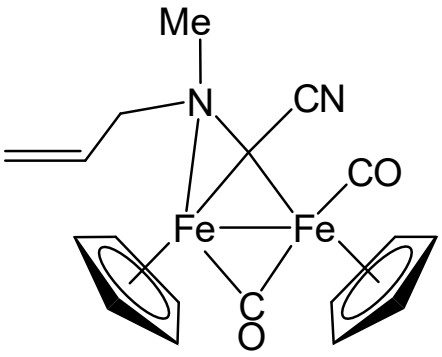


**Figure 7.** DFT-optimized structures of possible intermediates involved in the conversion from **3** to **4** and relative Gibbs energy values (kcal $mol^{-1}$). Colour map: Fe, green; N, blue; O, red; C, grey; H, white. Selected bond lengths for **int1** (Å): Fe-Fe, 2.494; Fe-C (alkylidene) 1.977 (average); Fe-C (CO) 1.739; Fe---H 1.827; Fe-C (μ-CO) 1.893 (average); Fe-C (Cp) 2.106 (average). Selected bond lengths for **int2** (Å): Fe-Fe, 2.540; Fe-C (alkylidene) 2.007 (average); Fe-C (CO) 1.750; Fe---C(CN) 2.010; Fe---N(CN) 2.192; Fe-C (μ-CO) 1.909 (average); Fe-C (Cp) 2.111 (average).

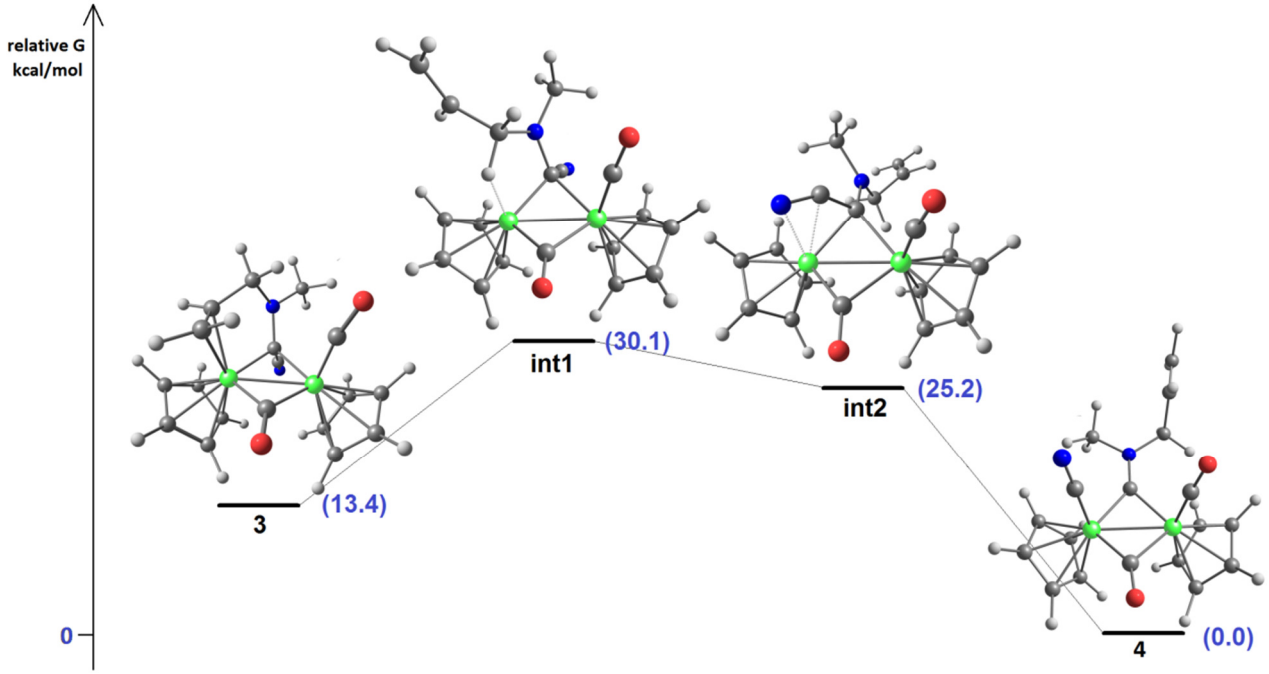


**Figure S8.** $^{1}H$ NMR spectrum (401 MHz, $CDCl_3$) of **2**.

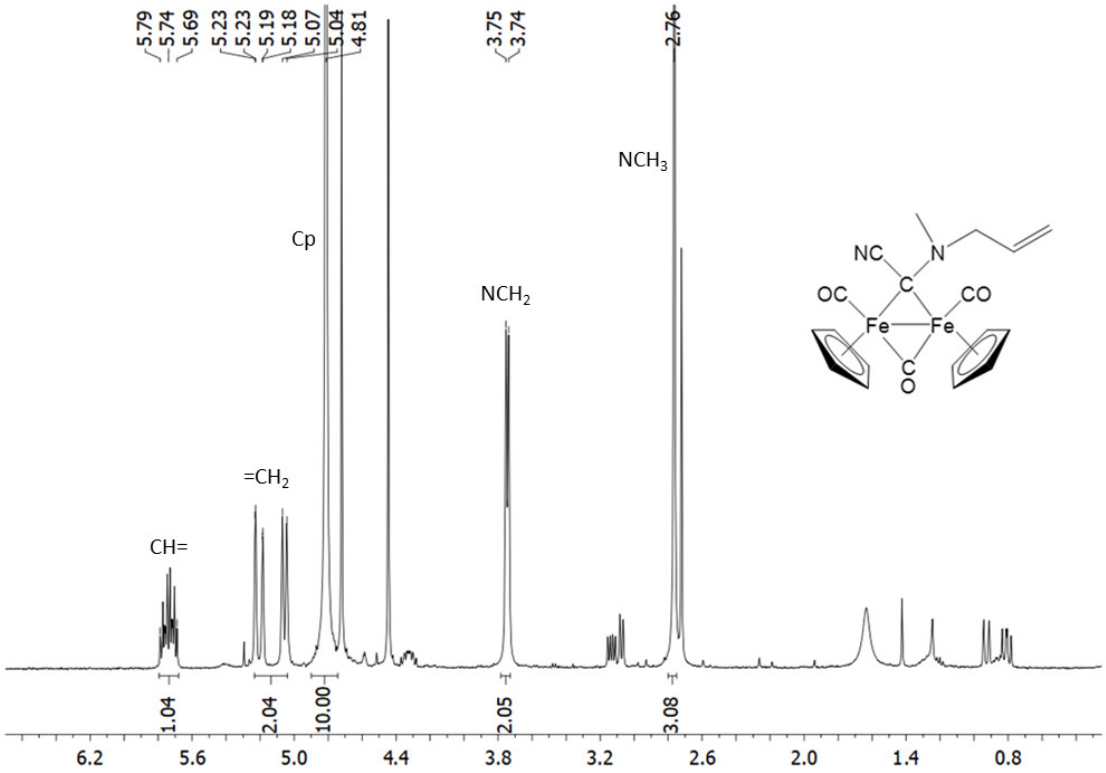



**Figure S9.** $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2**.

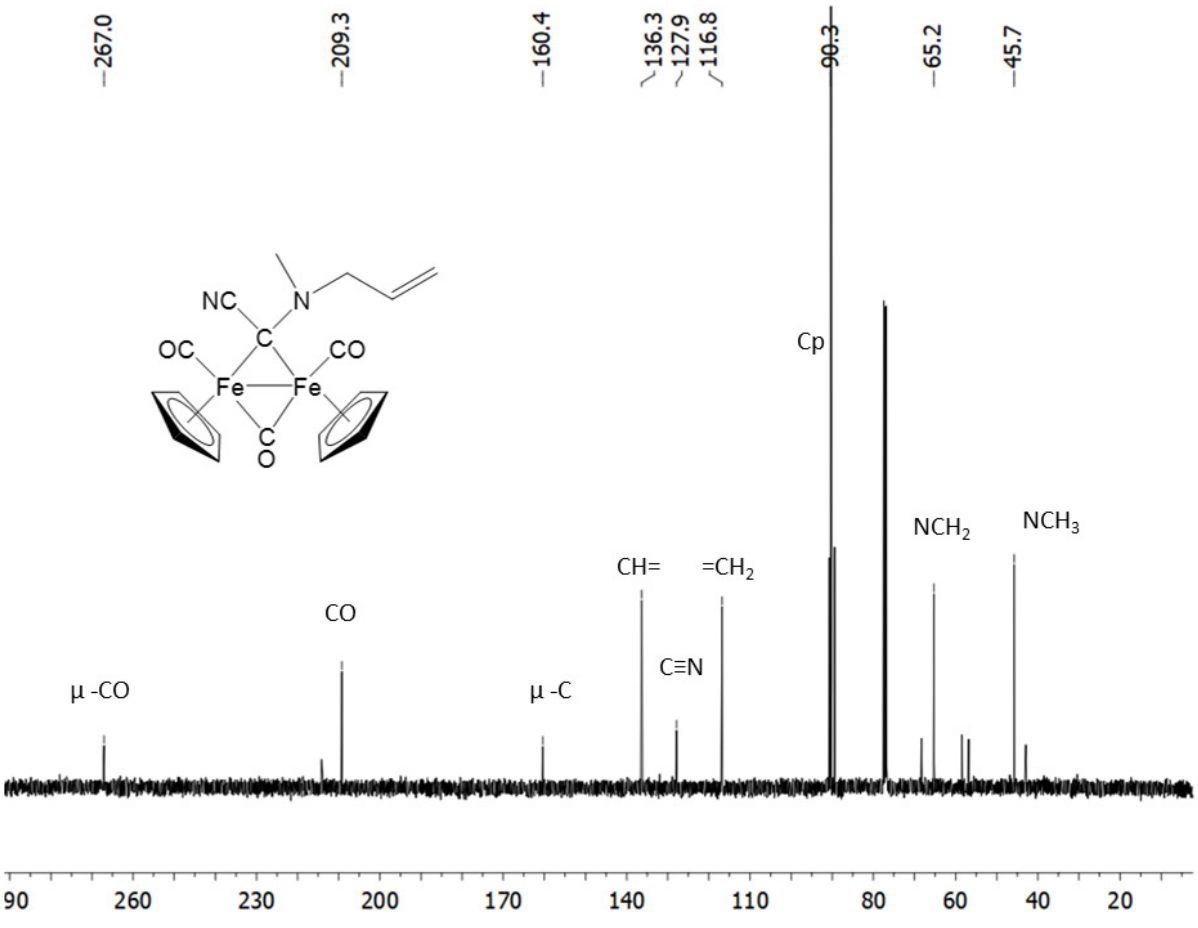


**Figure S10.** $^{1}H$ NMR spectrum (401 MHz, $CDCl_3$) of **3**.

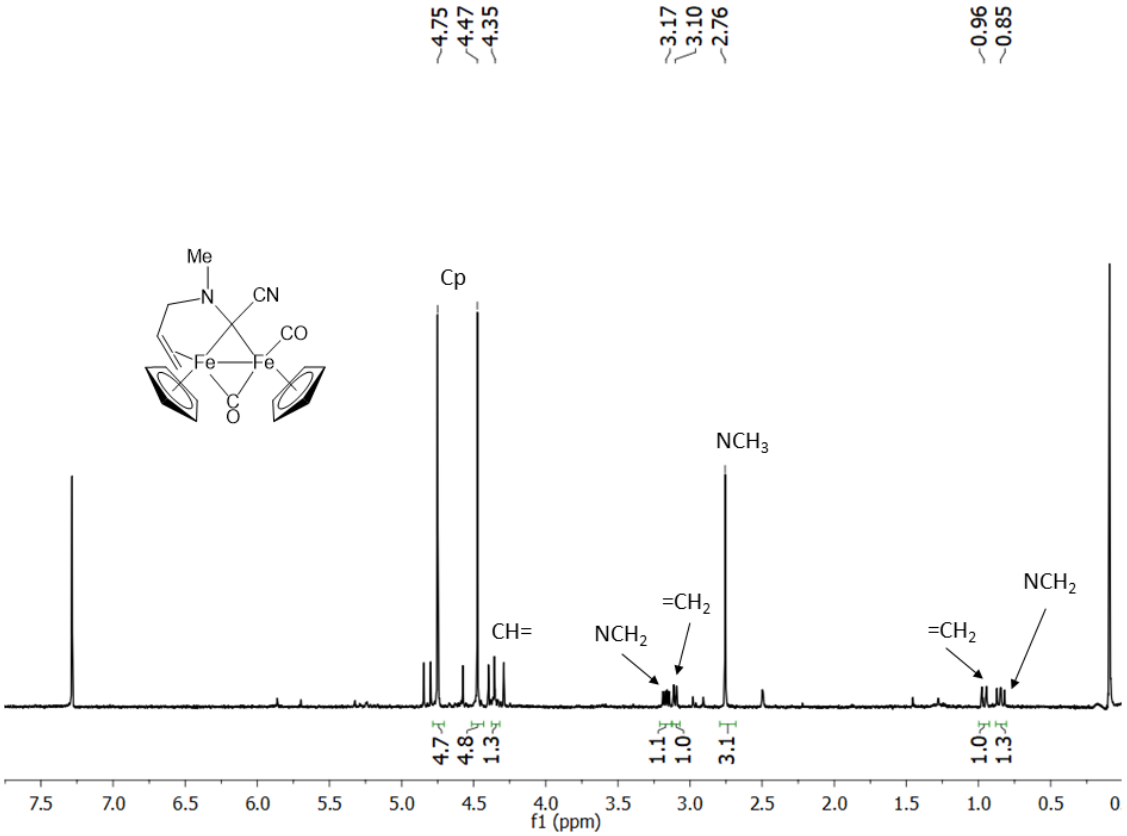



**Figure S11.** $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3**.

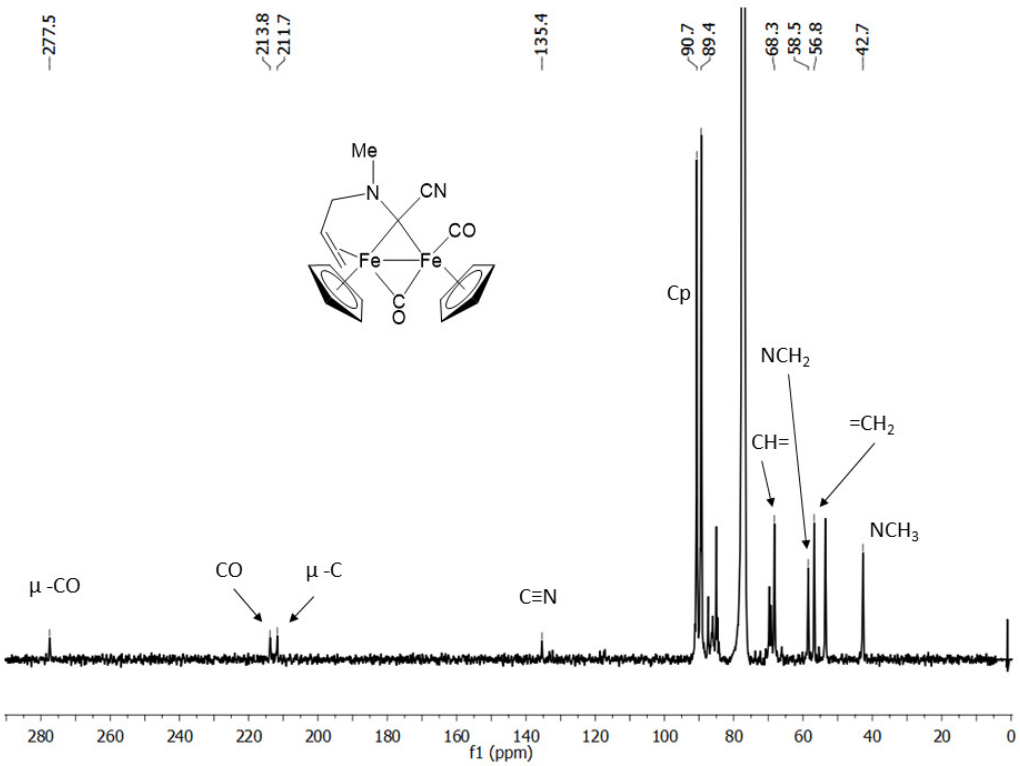


**Figure S12.** $^{1}H$ NMR spectrum (401 MHz, $CDCl_3$) of **4**.

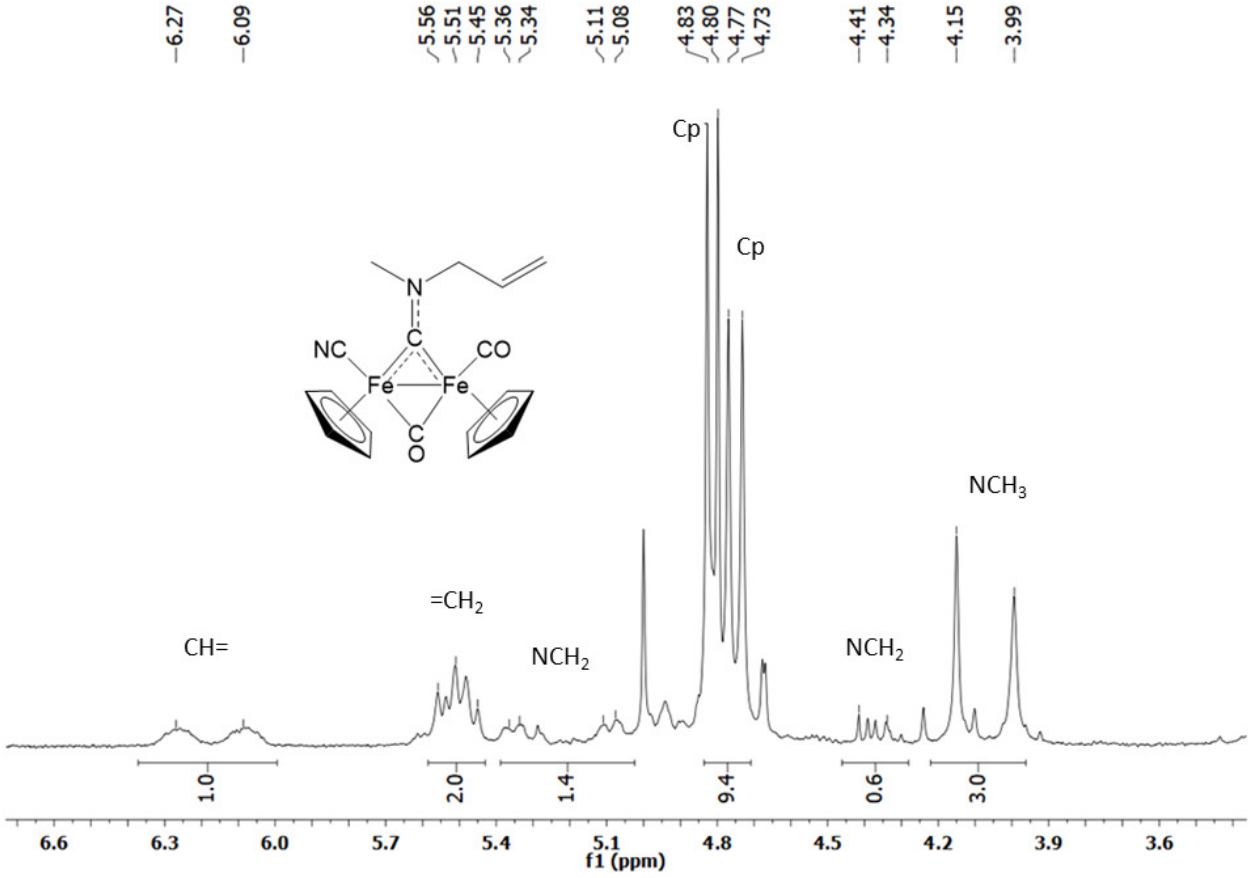



**Figure S13.** $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4**.

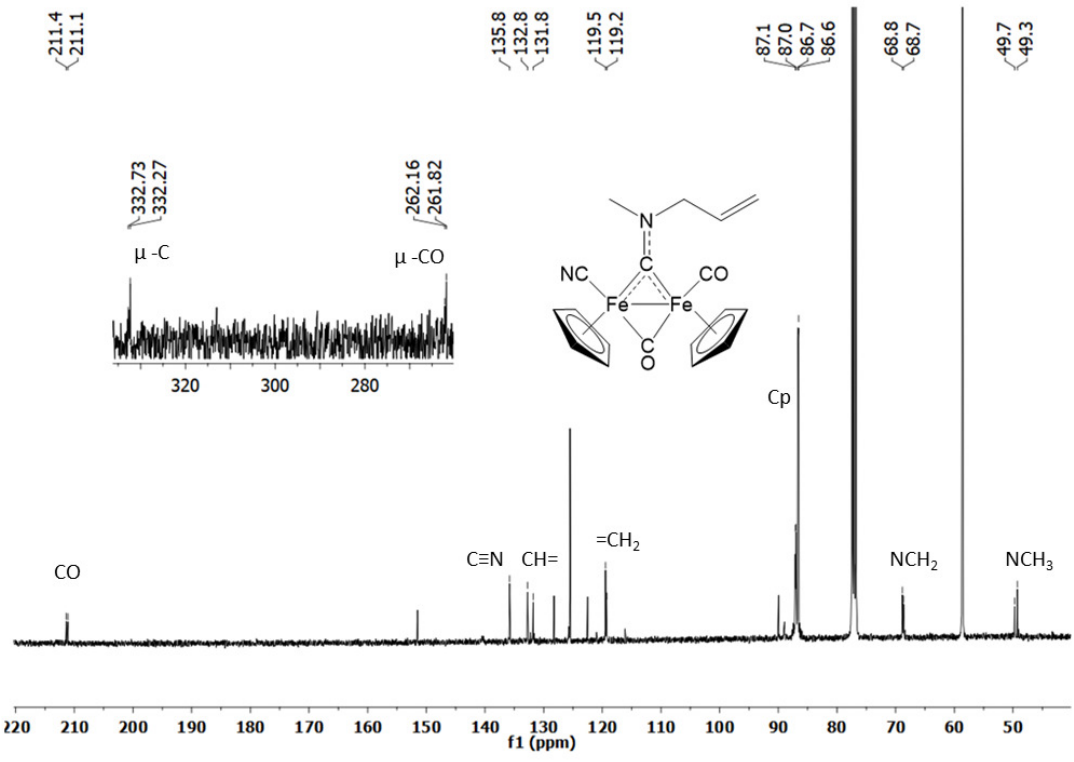


**Figure S14.** $^{1}H$ NMR spectrum (401 MHz, $CDCl_3$) of [**6**]$CF_3SO_3$.

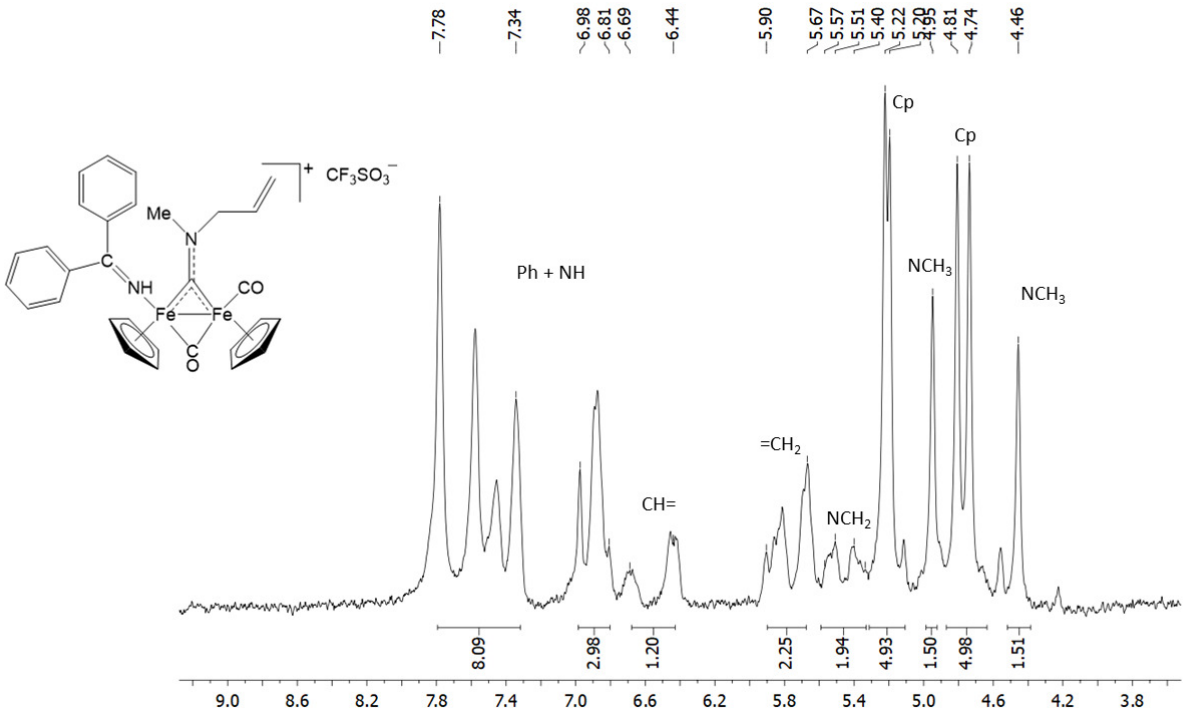



**Figure S15.** $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of [**6**]$CF_3SO_3$

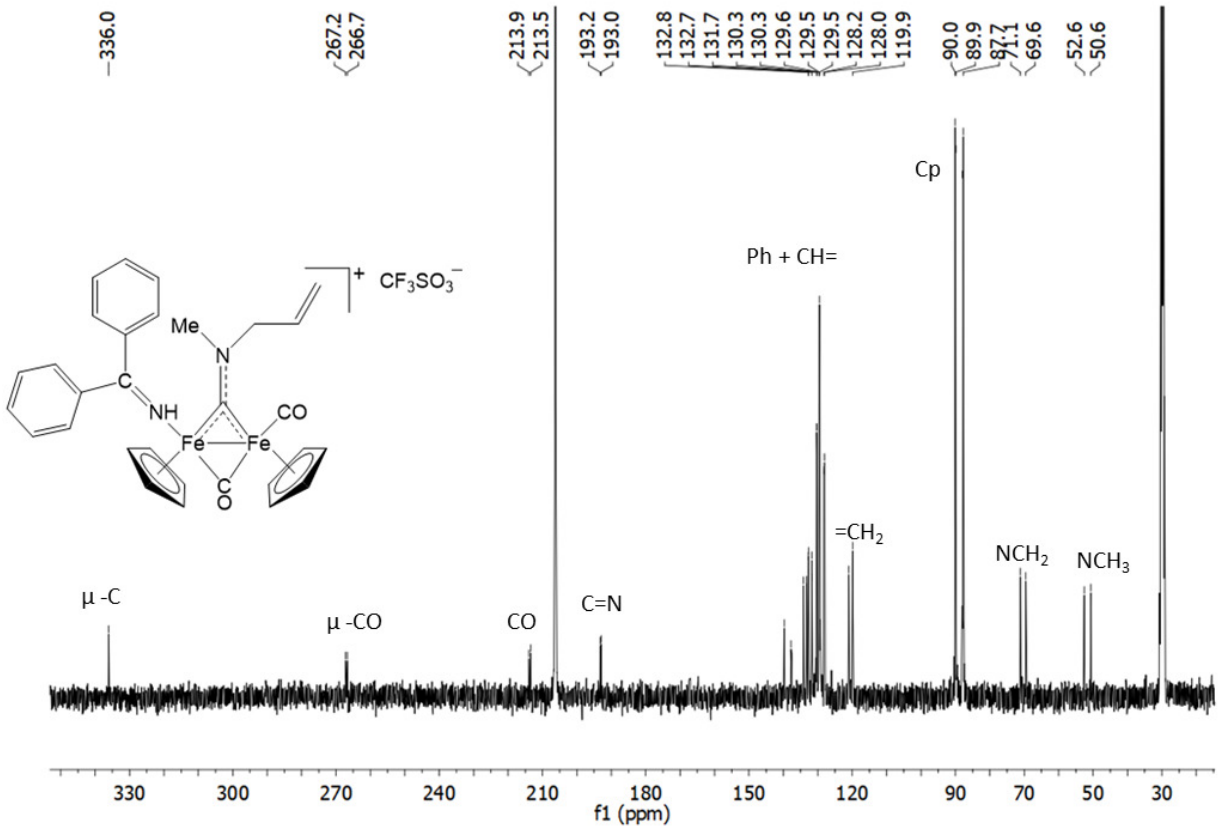


**Figure S16.** Solution ($CH_2Cl_2$) IR spectrum of **2**.

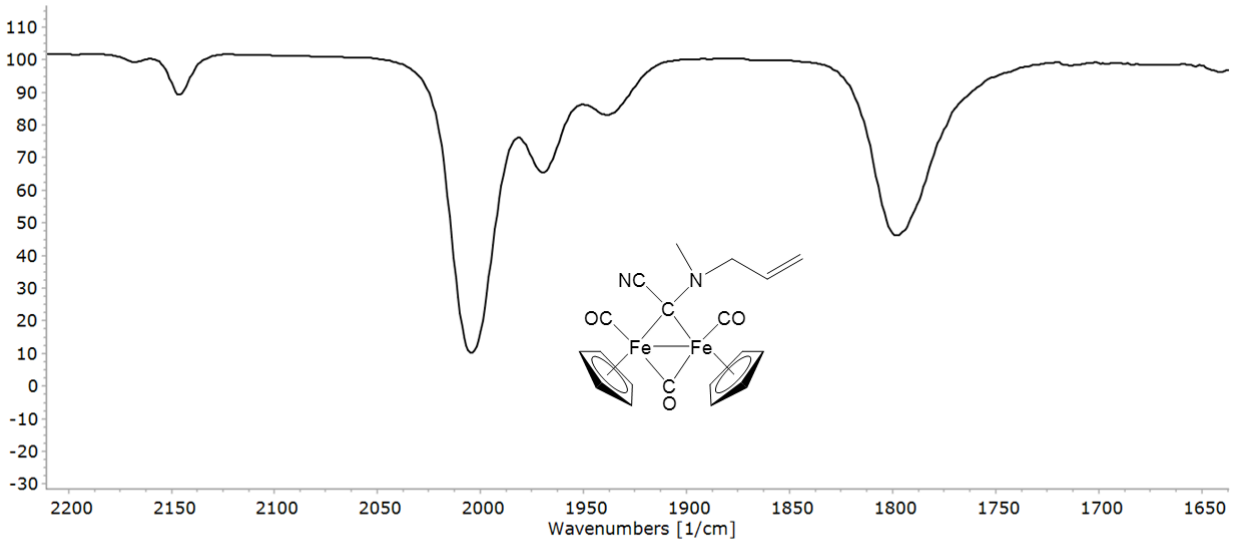



**Figure S17.** Solution ($CH_2Cl_2$) IR spectrum of **3**.

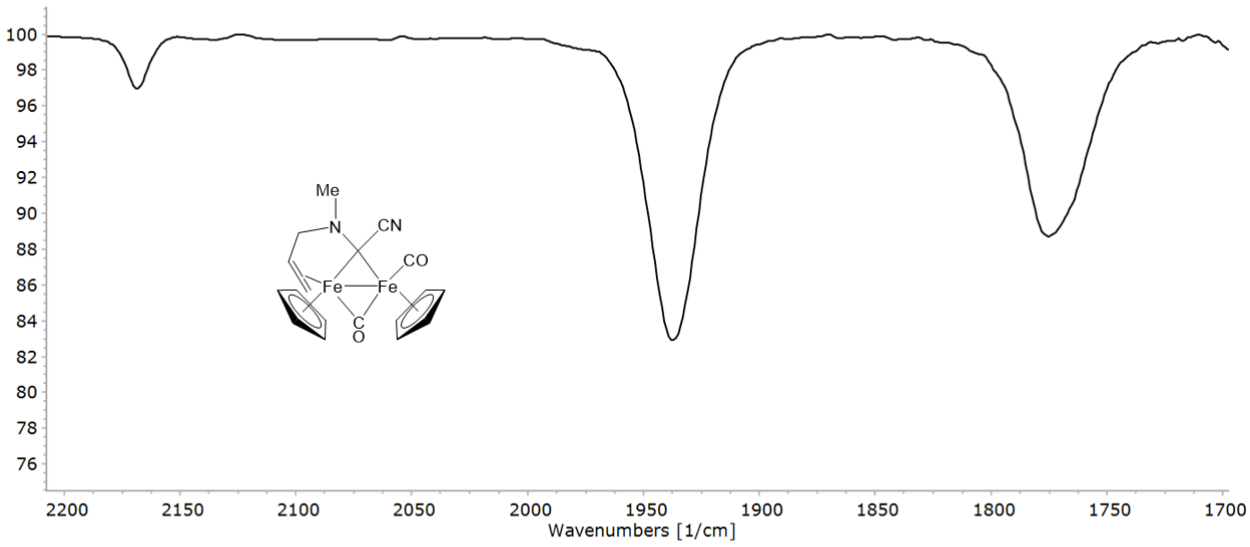


**Figure S18.** Solution ($CH_2Cl_2$) IR spectrum of **4**.

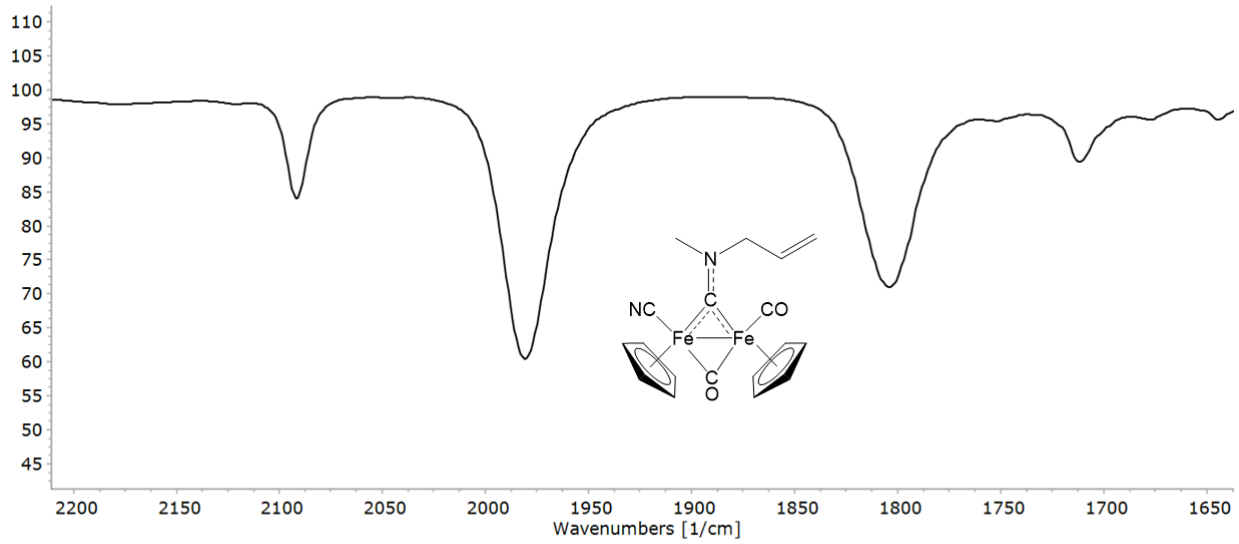



**Figure S19.** Solution ($CH_2Cl_2$) IR spectrum of **[6]**$CF_3SO_3$.

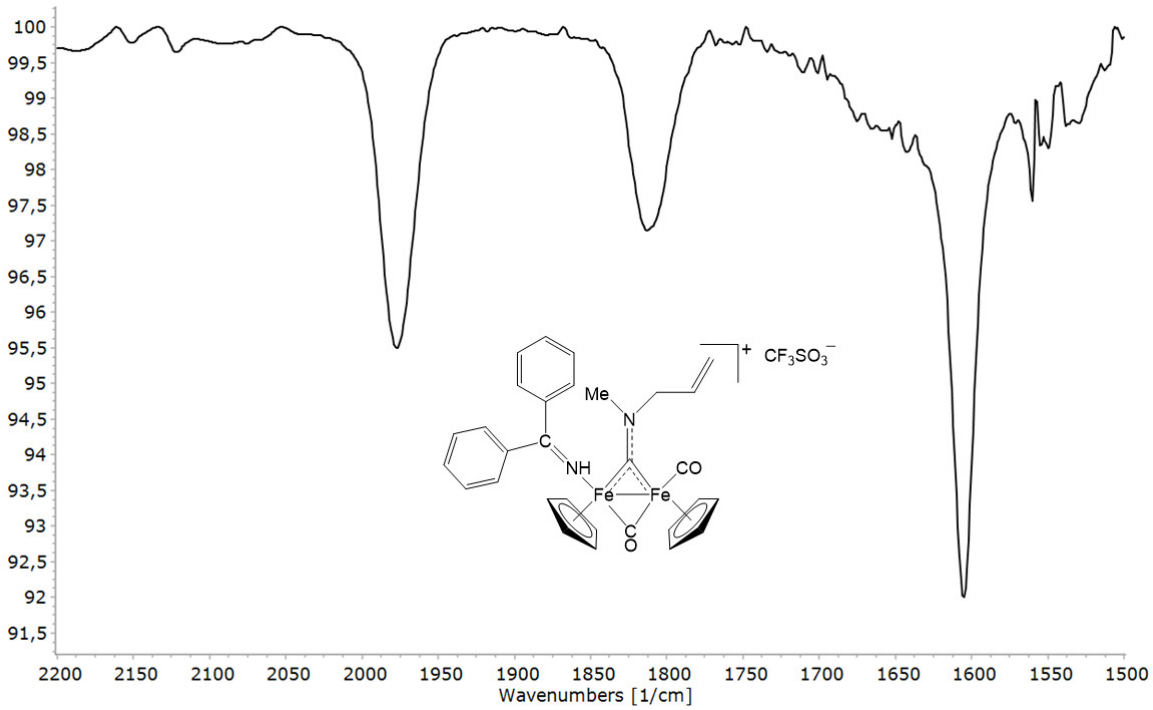


**Figure S20.** ESI-MS spectrum of **3**.