# Supporting Information

# Synthesis, Structures and Chemical Reactivity of Dithiolato-Bridged Ni–Fe Complexes as Biomimetics for the Active Site of [NiFe]-Hydrogenases

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**Contents:**

## 1. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of $[A](BF_4)_2$

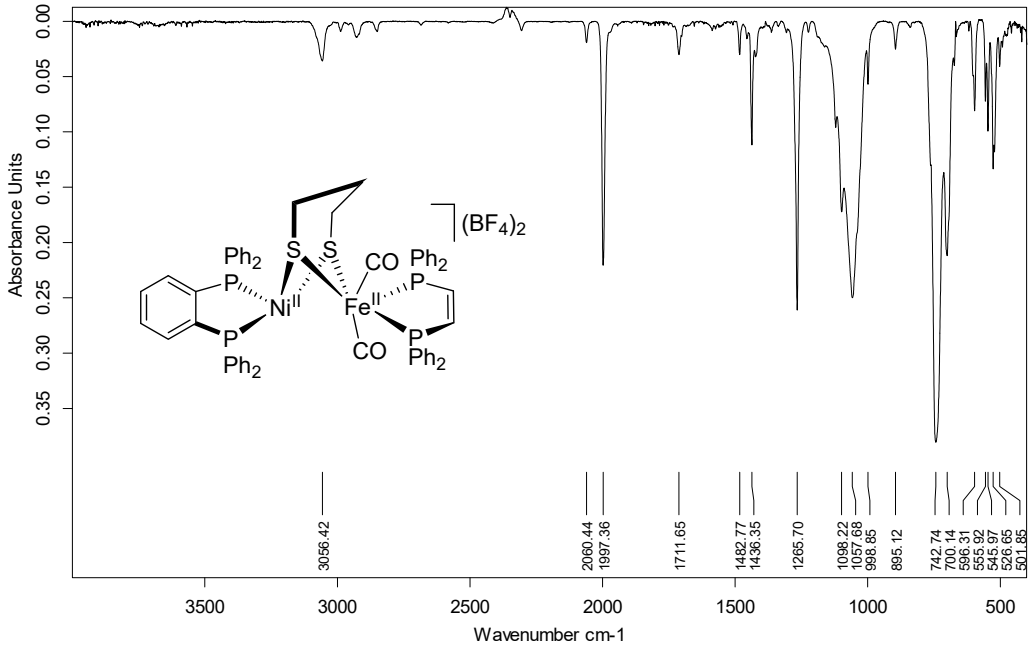


**Figure S1.** IR spectrum of $[A](BF_4)_2$

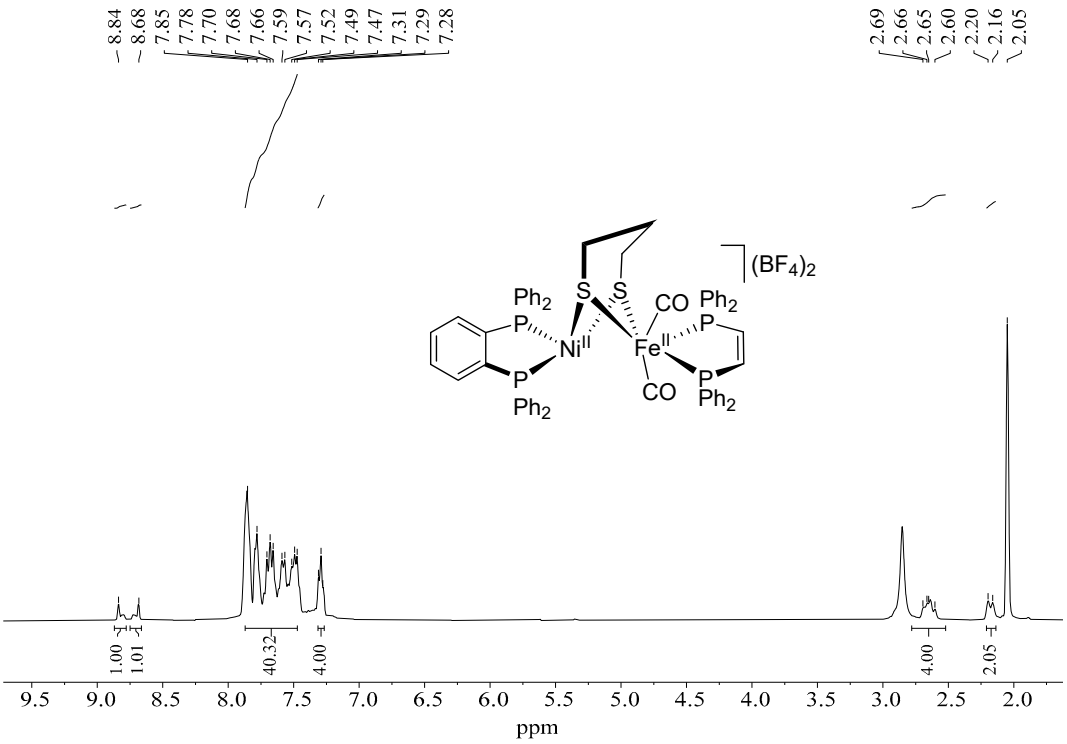


**Figure S2.** $^{1}H$ NMR spectrum of $[A](BF_4)_2$ in acetone-$d_6$

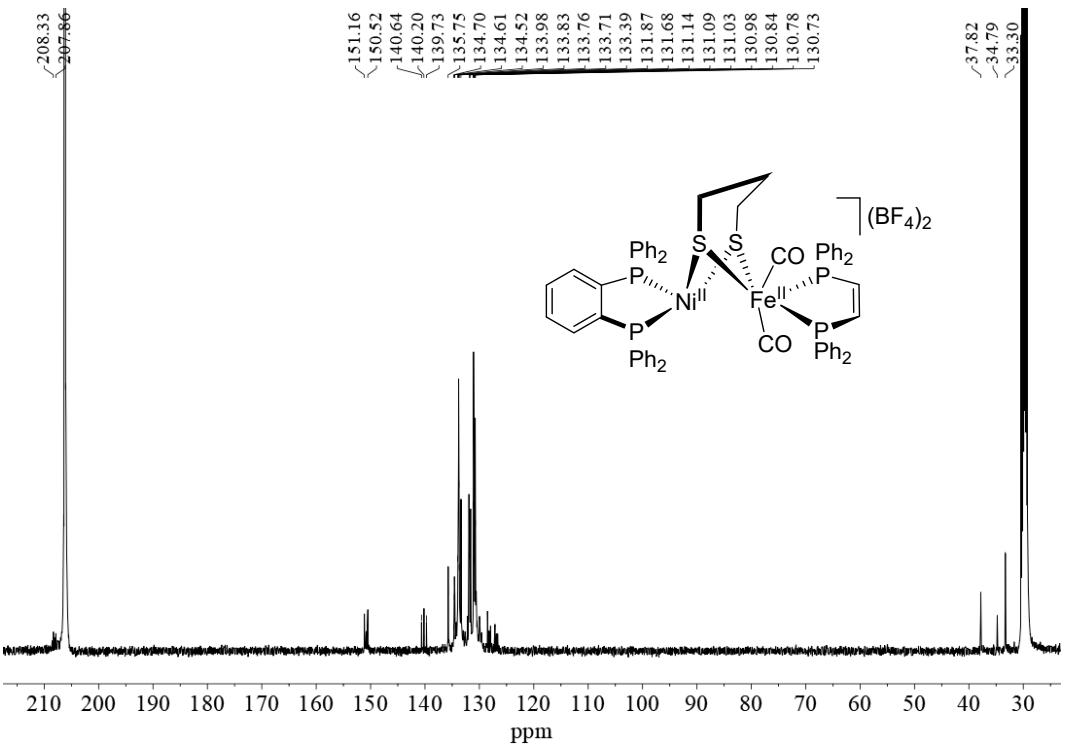


**Figure S3.** $^{13}$C NMR spectrum of **[A](BF$_4$)$_2$** in acetone-$d_6$

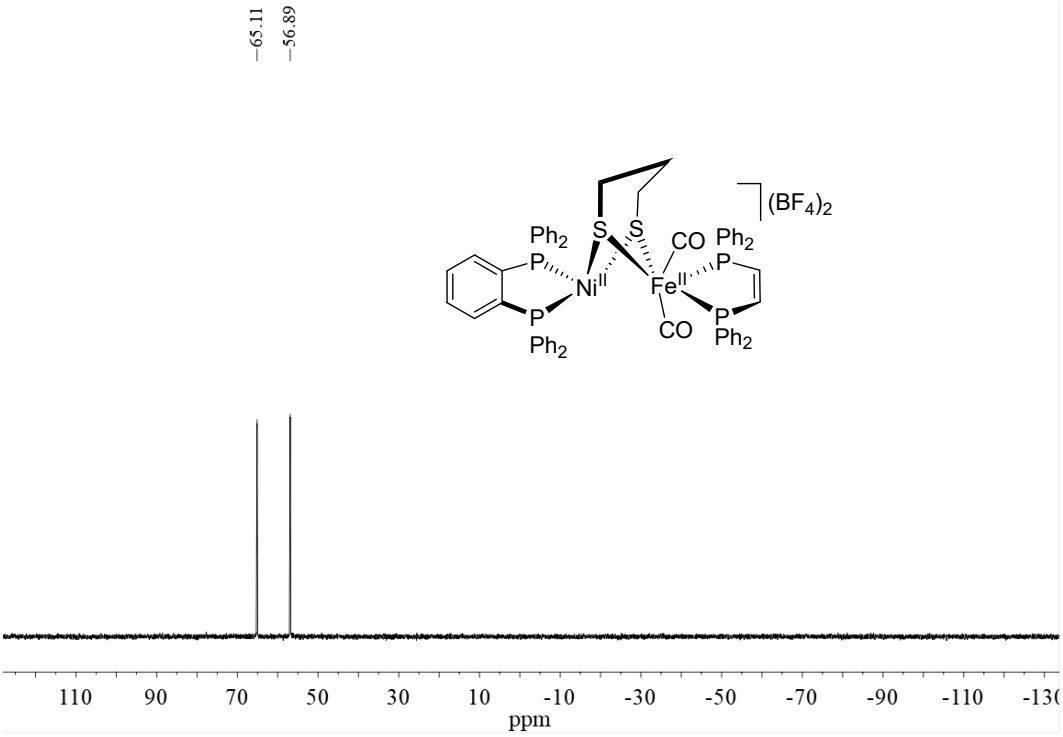


**Figure S4.** $^{31}$P NMR spectrum of **[A](BF$_4$)$_2$** in acetone-$d_6$

## 2. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of [1]$BF_4$

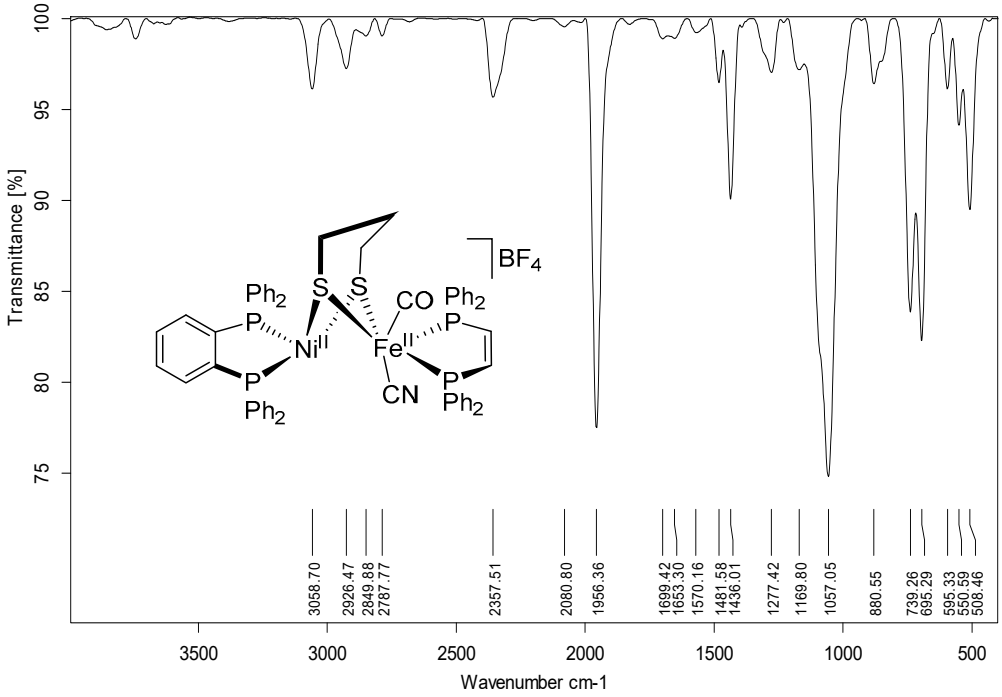


**Figure S5.** IR spectrum of **[1]$BF_4$**

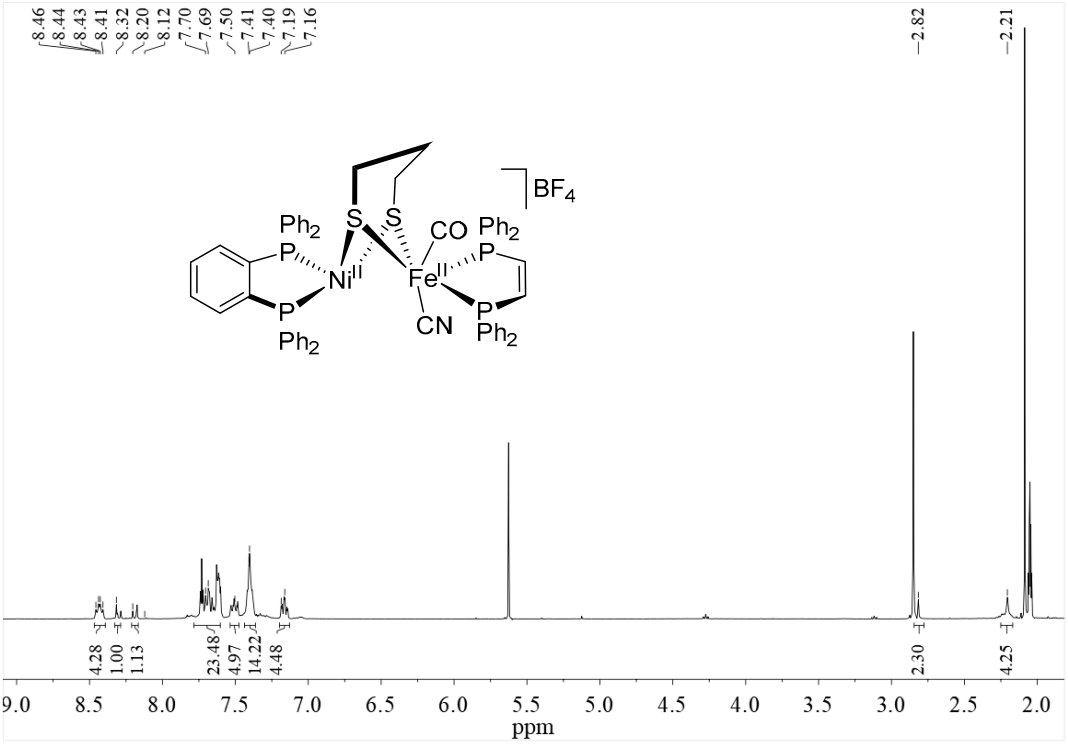


**Figure S6.** $^{1}H$ NMR spectrum of **[1]$BF_4$** in acetone-$d_6$

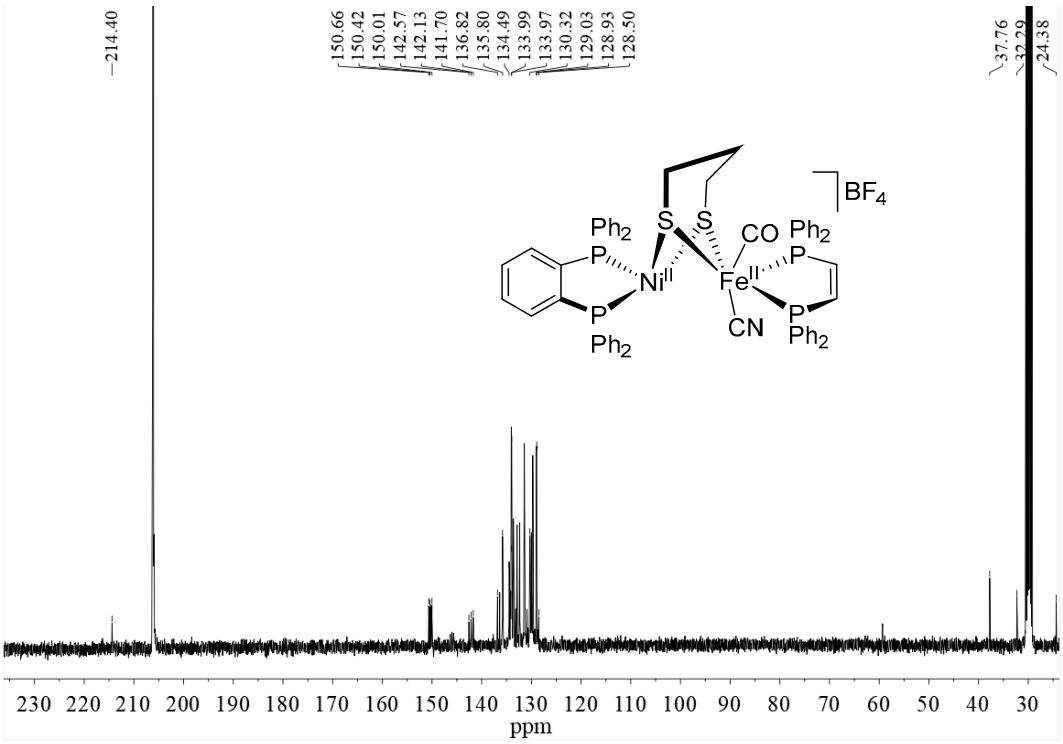


**Figure S7.** $^{13}$C NMR spectrum of **[1]BF$_4$** in acetone-$d_6$

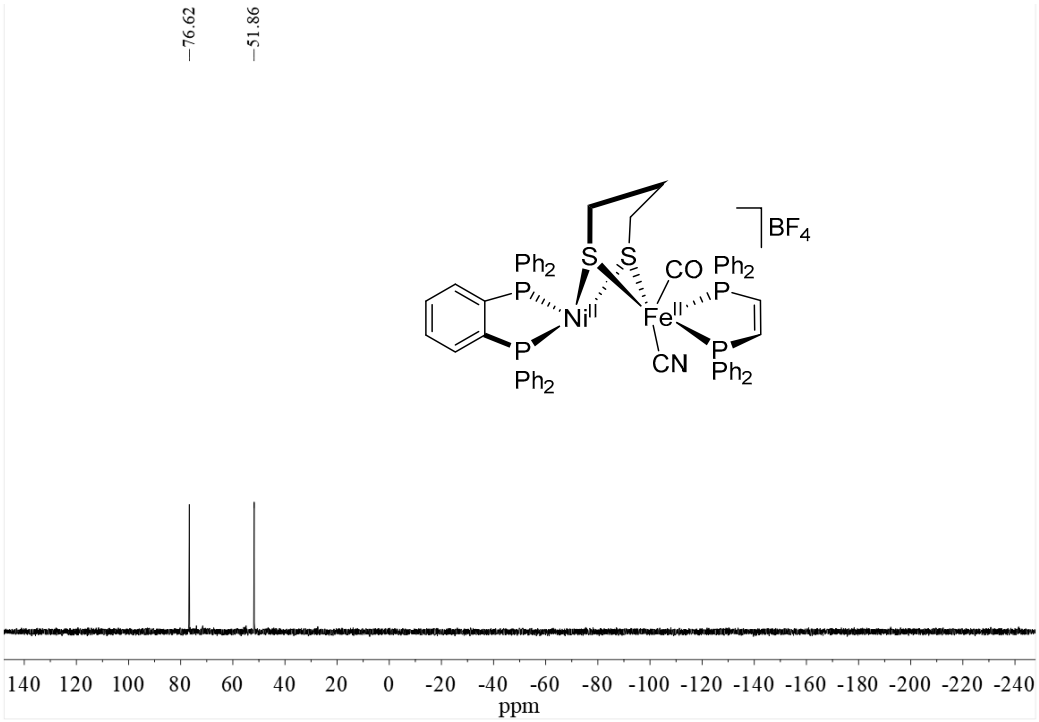


**Figure S8.** $^{31}$P NMR spectrum of **[1]BF$_4$** in acetone-$d_6$

## 3. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of [2]$BF_4$

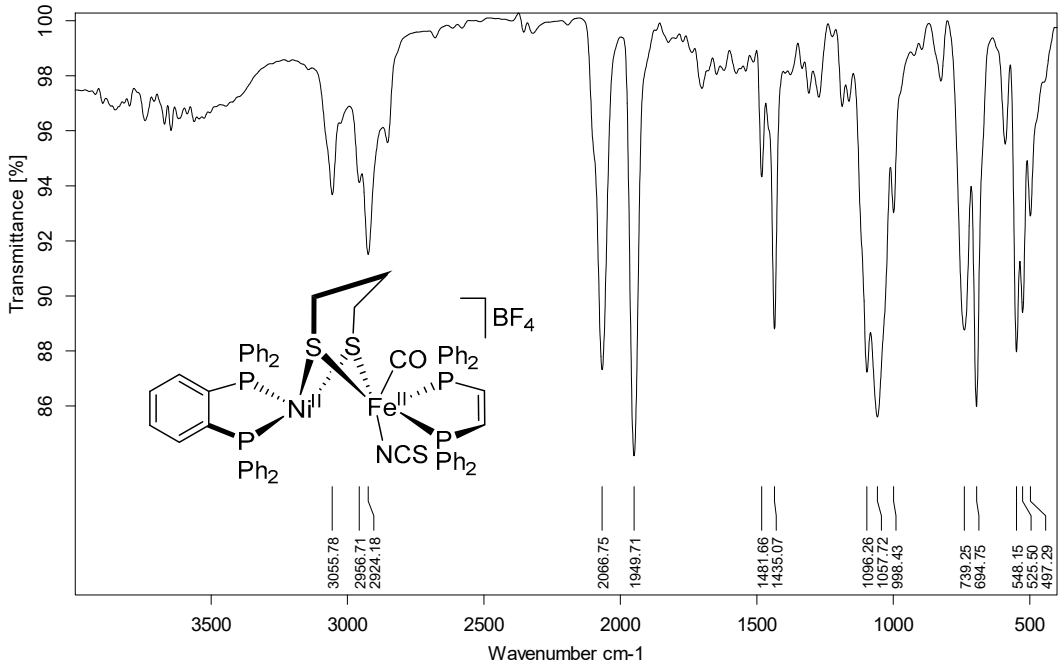


**Figure S9.** IR spectrum of **[2]$BF_4$**

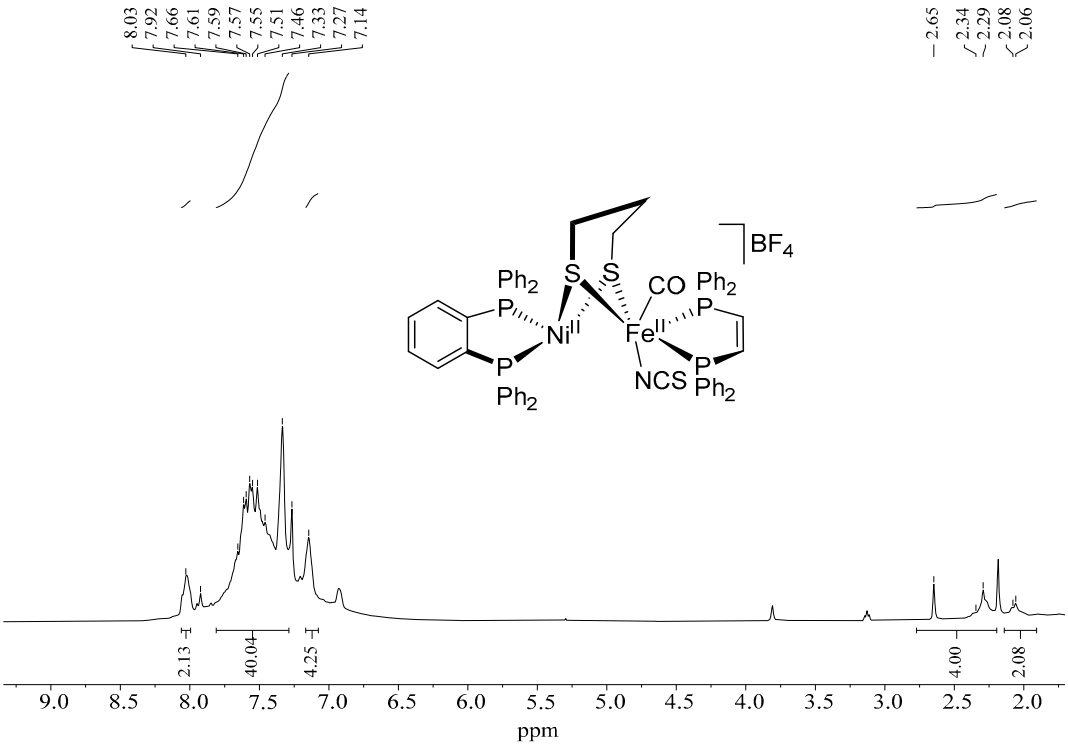


**Figure S10.** $^{1}H$ NMR spectrum of **[2]$BF_4$** in $CDCl_3$

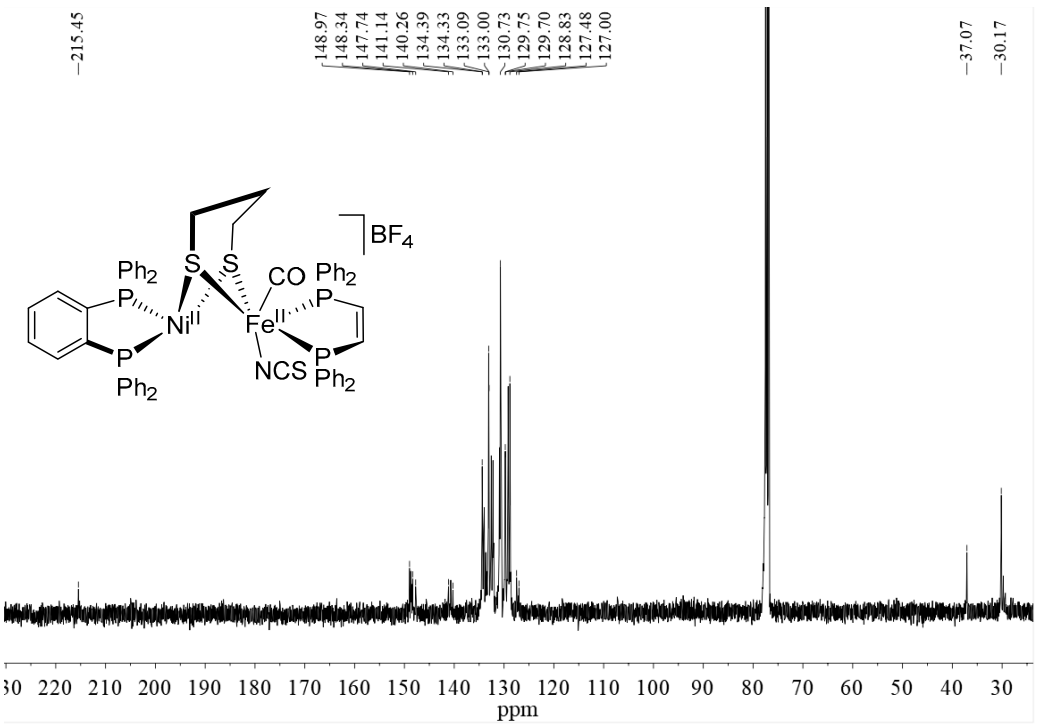


**Figure S11.** $^{13}$C NMR spectrum of **[2]BF$_4$** in $CDCl_3$

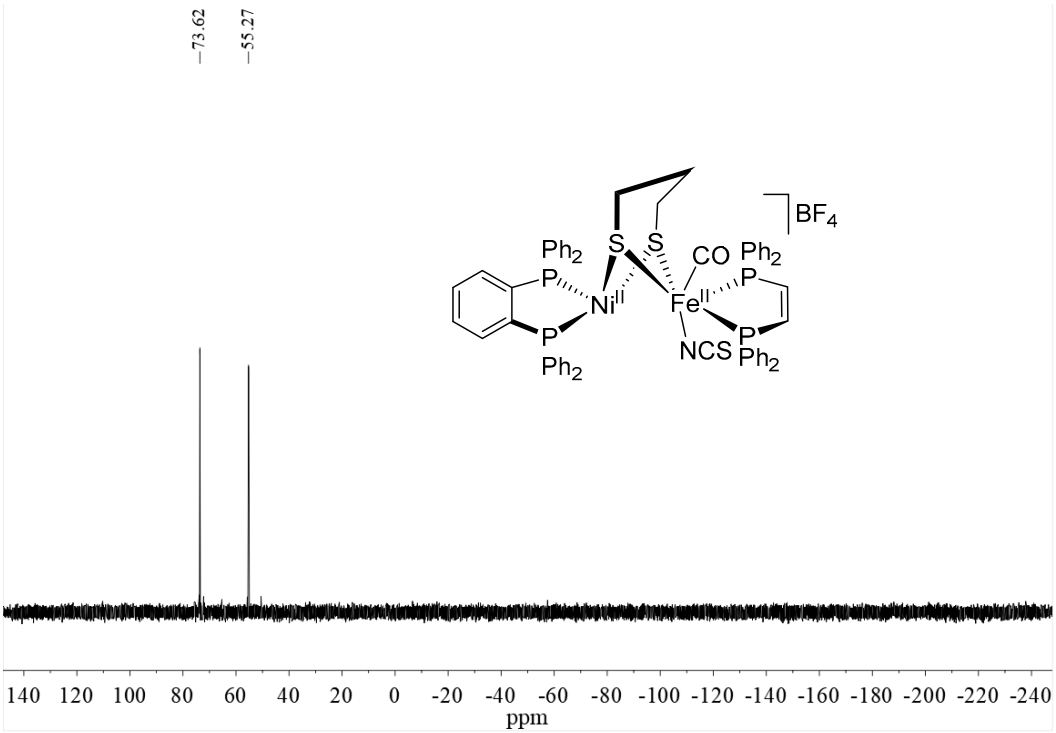


**Figure S12.** $^{31}$P NMR spectrum of **[2]BF$_4$** in acetone-$d_6$

## 4. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of [3]$BF_4$

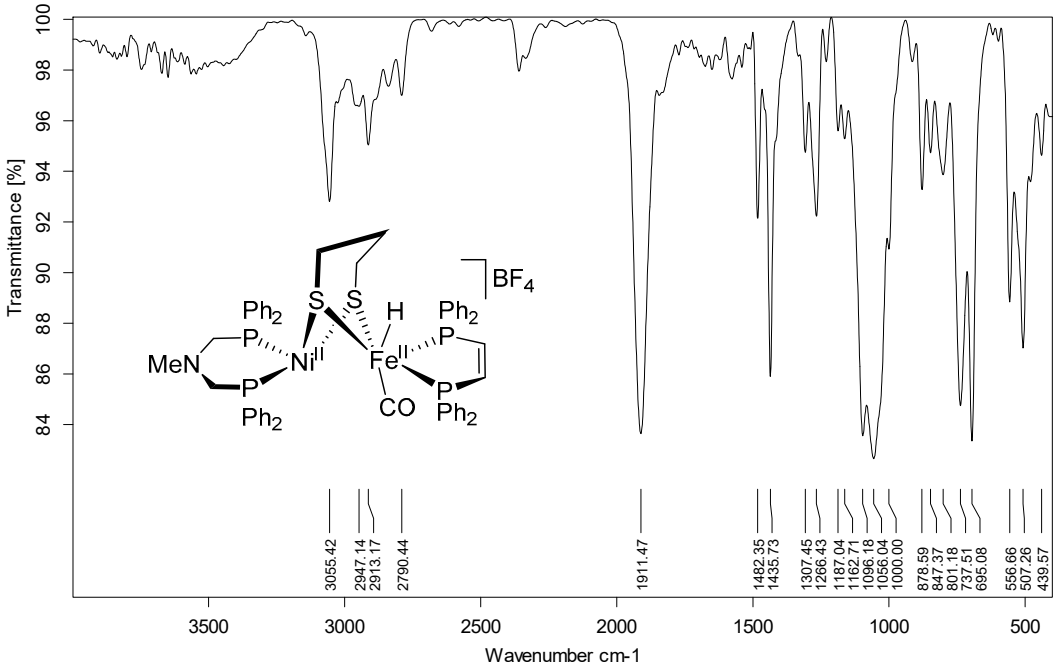


**Figure S13.** IR spectrum of **[3]$BF_4$**

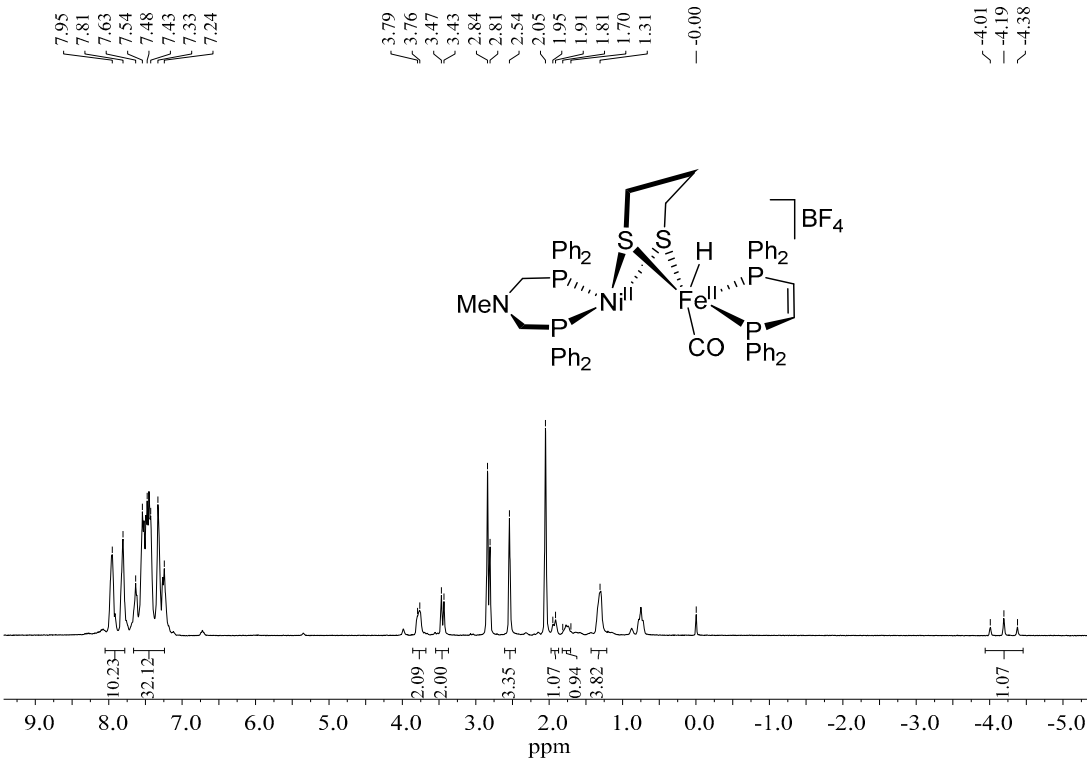


**Figure S14.** $^{1}H$ NMR spectrum of **[3]$BF_4$** in acetone-$d_6$

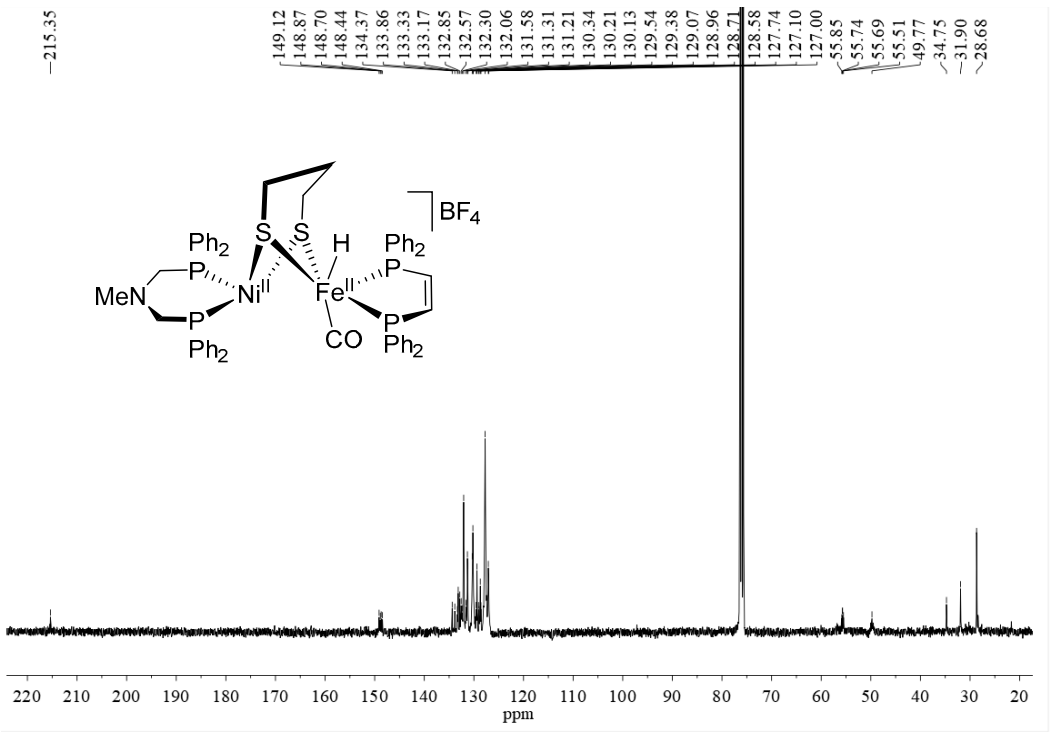


**Figure S15.** $^{13}$C NMR spectrum of **[3]BF$_4$** in $CDCl_3$

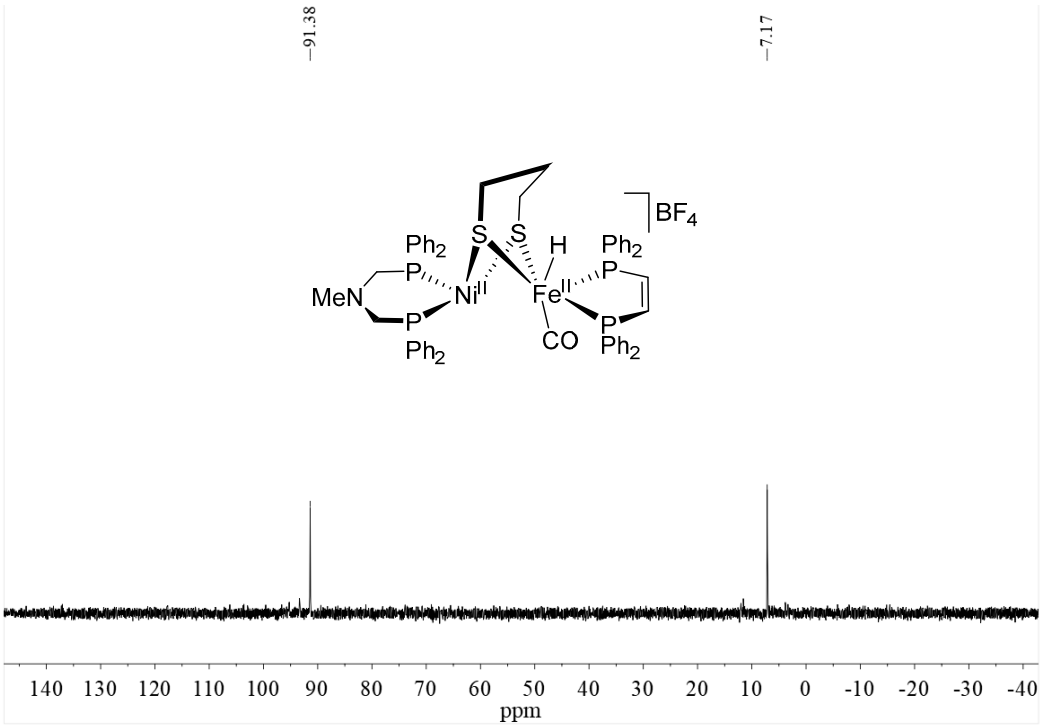


**Figure S16.** $^{31}$P NMR spectrum of **[3]BF$_4$** in $CDCl_3$

## 5. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of [4]$BF_4$

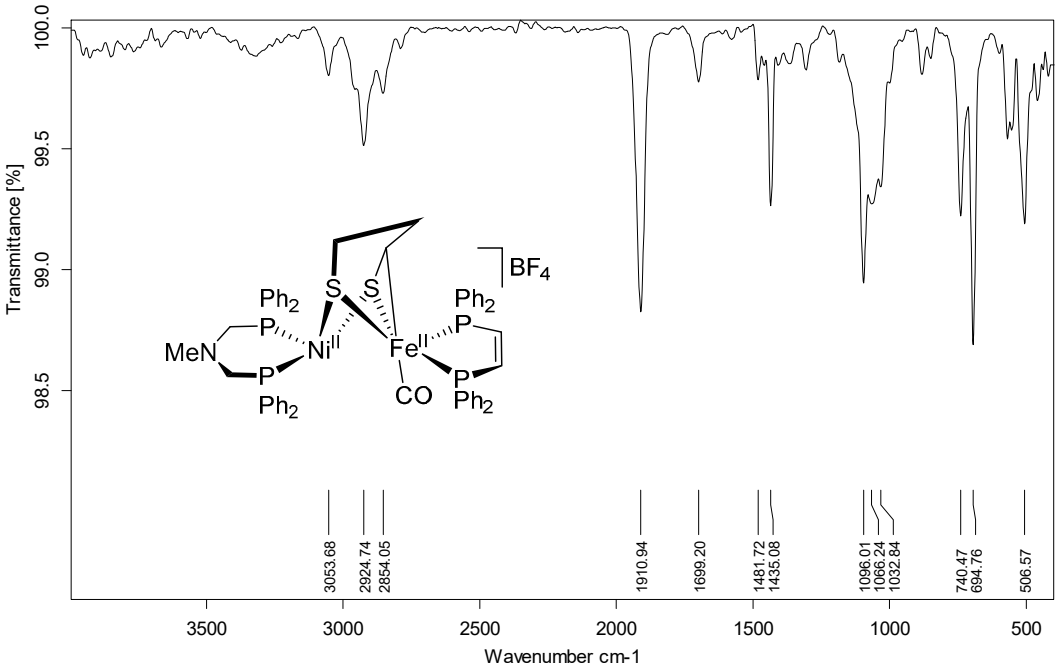


**Figure S17.** IR spectrum of **[4]$BF_4$**

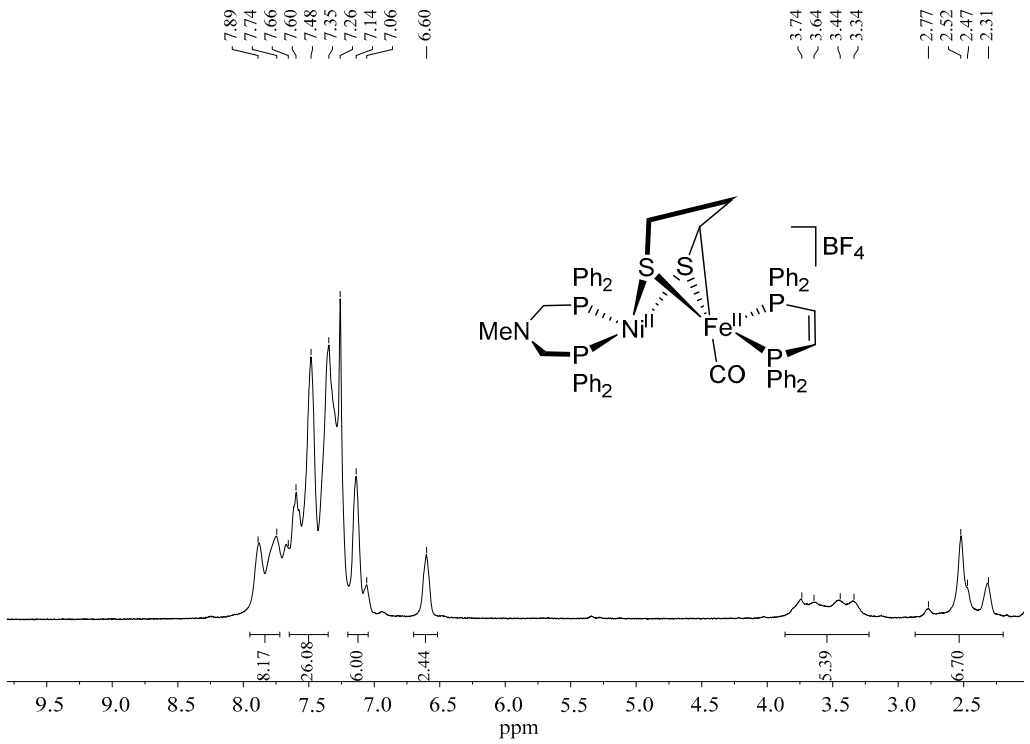


**Figure S18.** $^{1}H$ NMR spectrum of **[4]$BF_4$** in $CDCl_3$

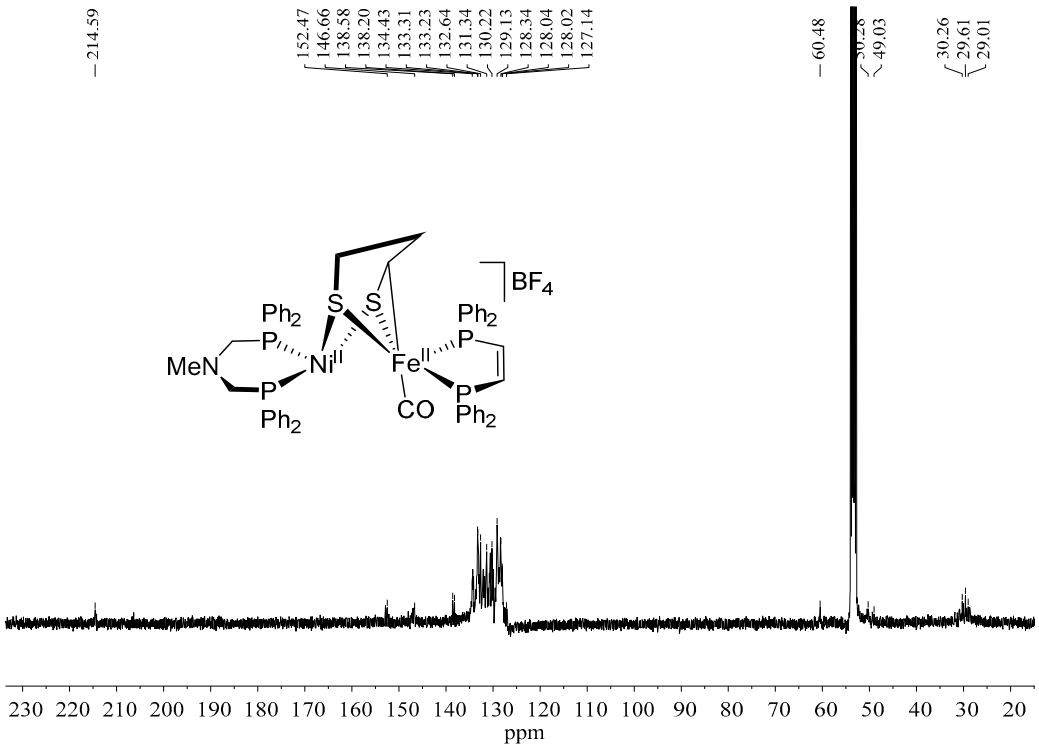


**Figure S19.** $^{13}$C NMR spectrum of **[4]BF$_4$** in $CD_2Cl_2$

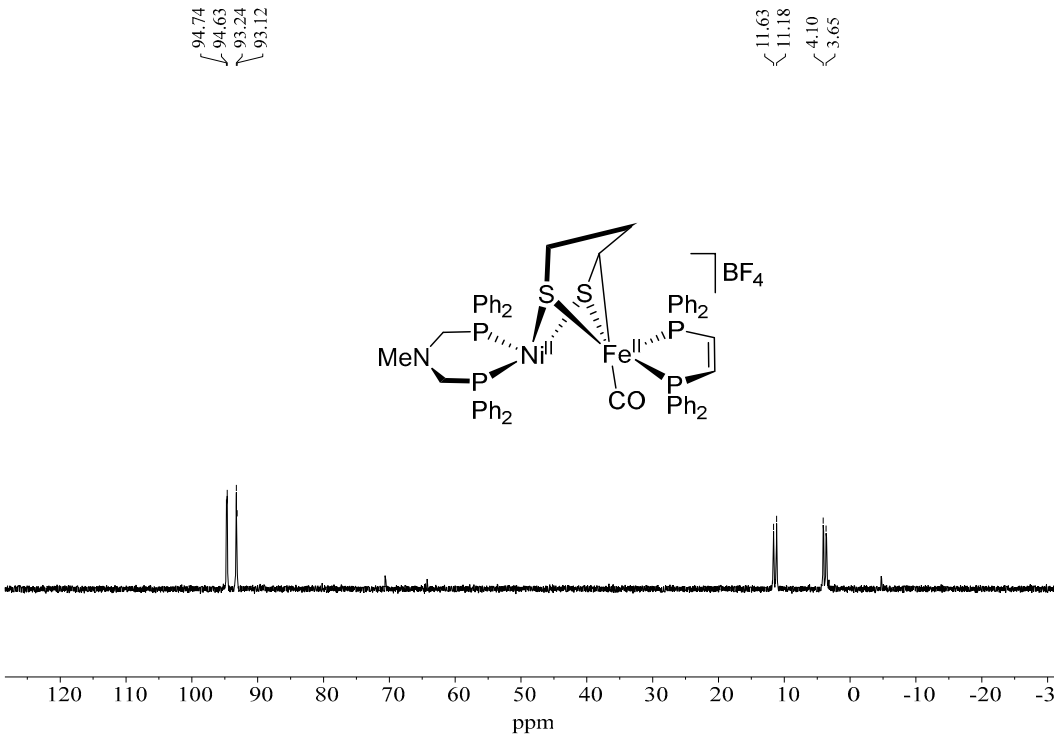


**Figure S20.** $^{31}$P NMR spectrum of **[4]BF$_4$** in acetone-$d_6$

## 6. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of [5]$BF_4$

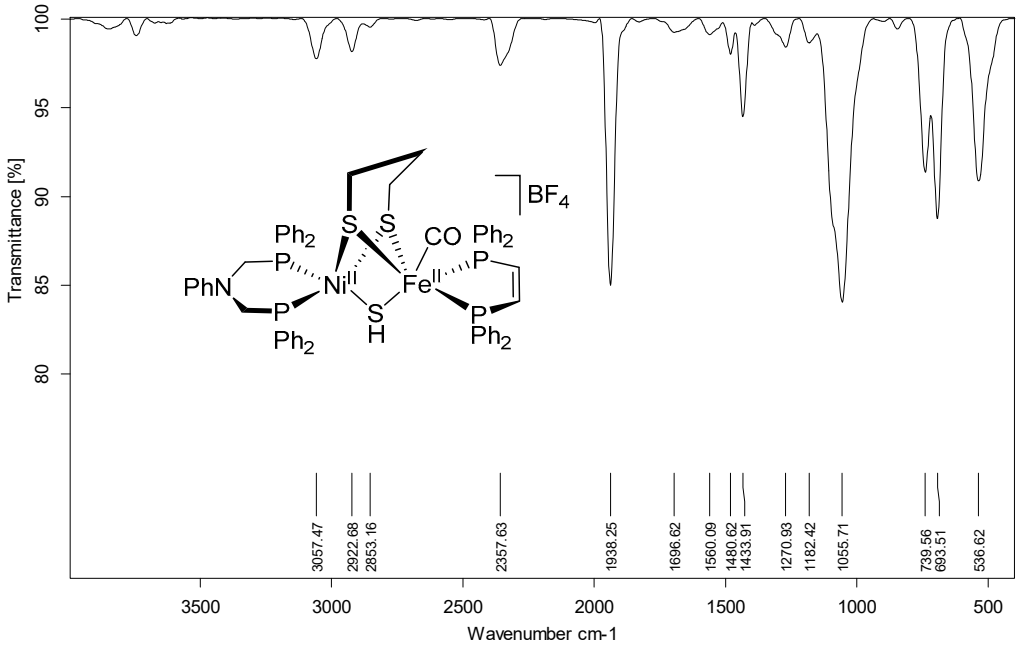


**Figure S21.** IR spectrum of **[5]$BF_4$**

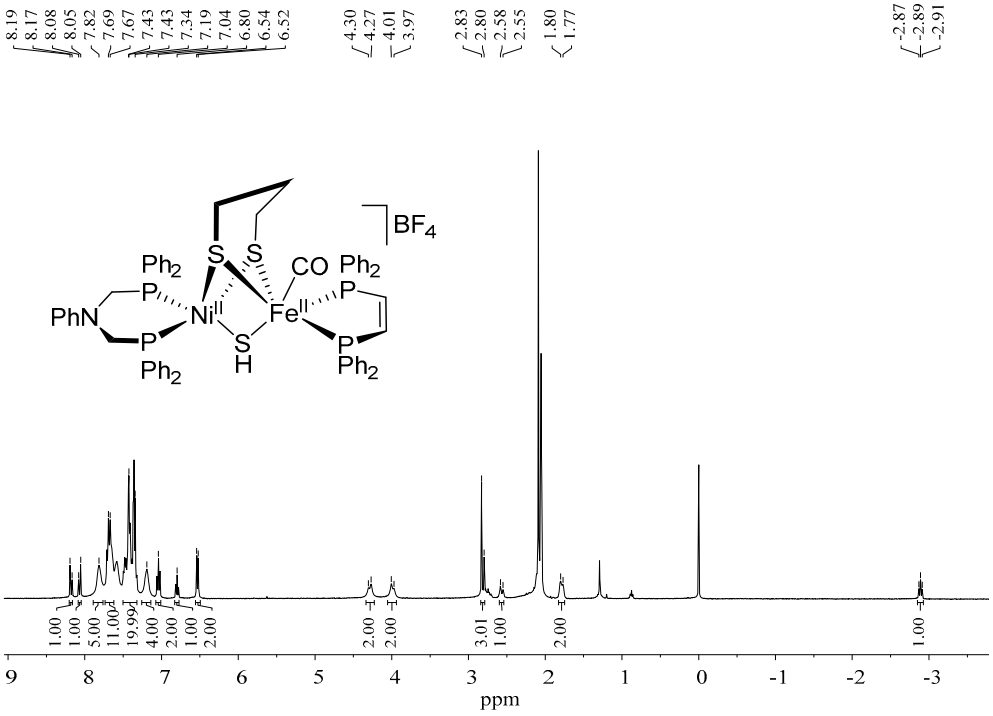


**Figure S22.** $^{1}H$ NMR spectrum of **[5]$BF_4$** in acetone-$d_6$

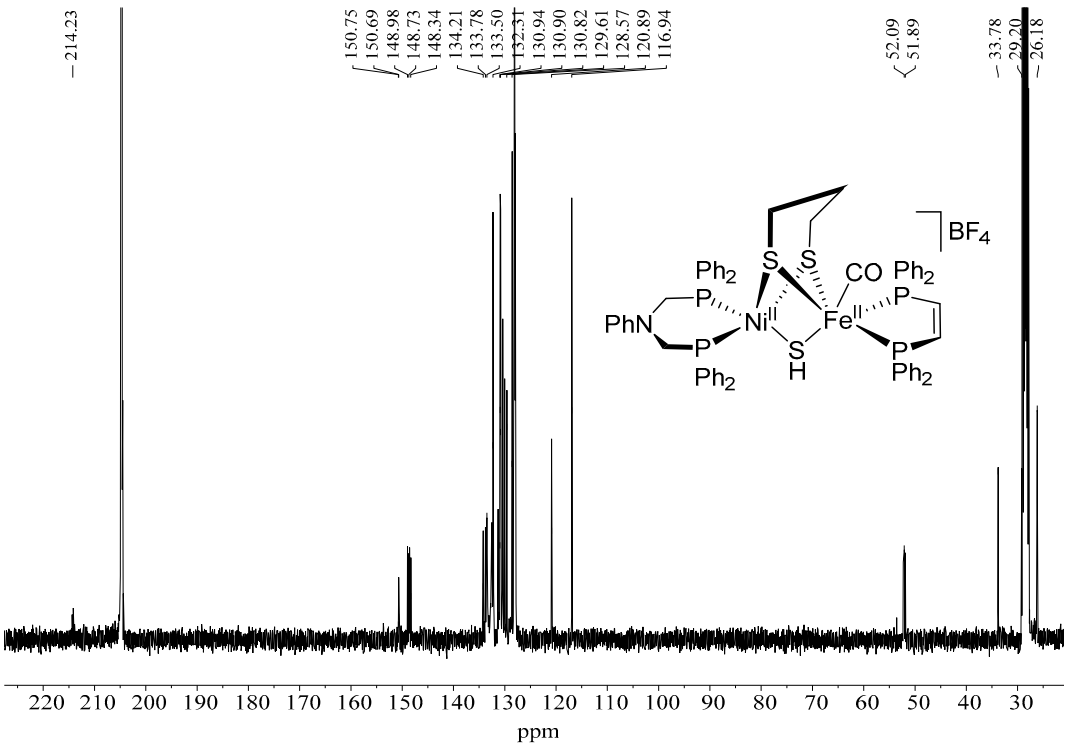


**Figure S23.** $^{13}$C NMR spectrum of **[5]BF$_4$** in acetone-$d_6$

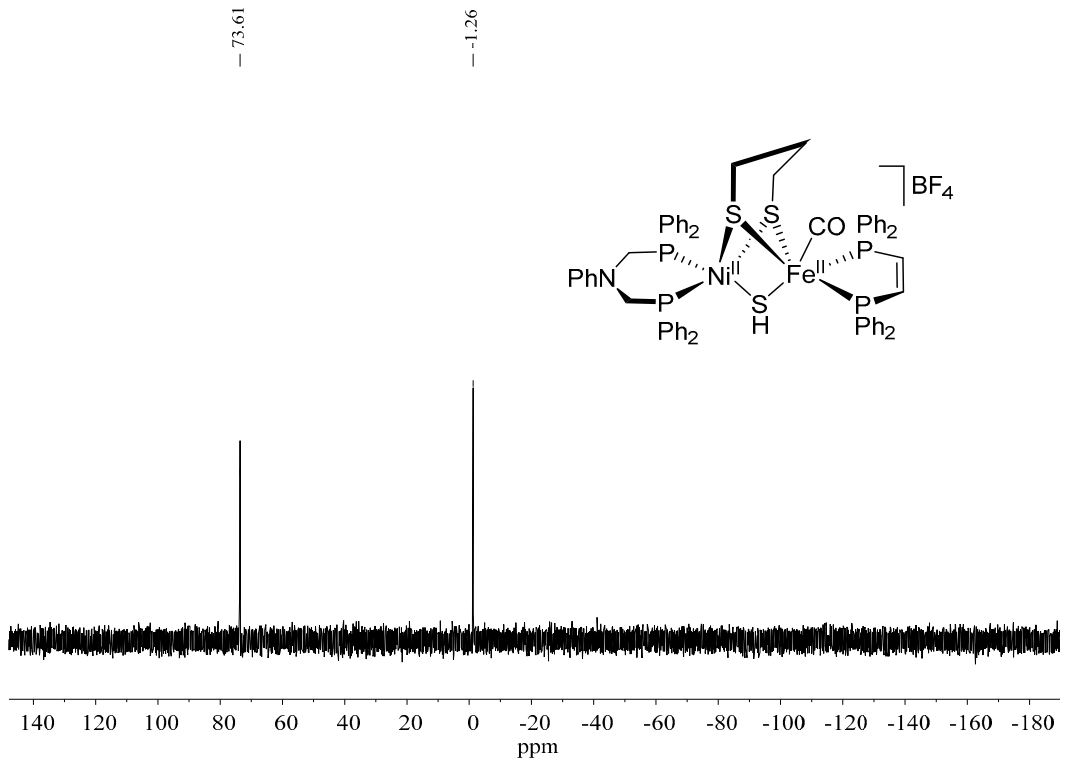


**Figure S24.** $^{31}$P NMR spectrum of **[5]BF$_4$** in acetone-$d_6$

## 7. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of $[D](BF_4)_2$

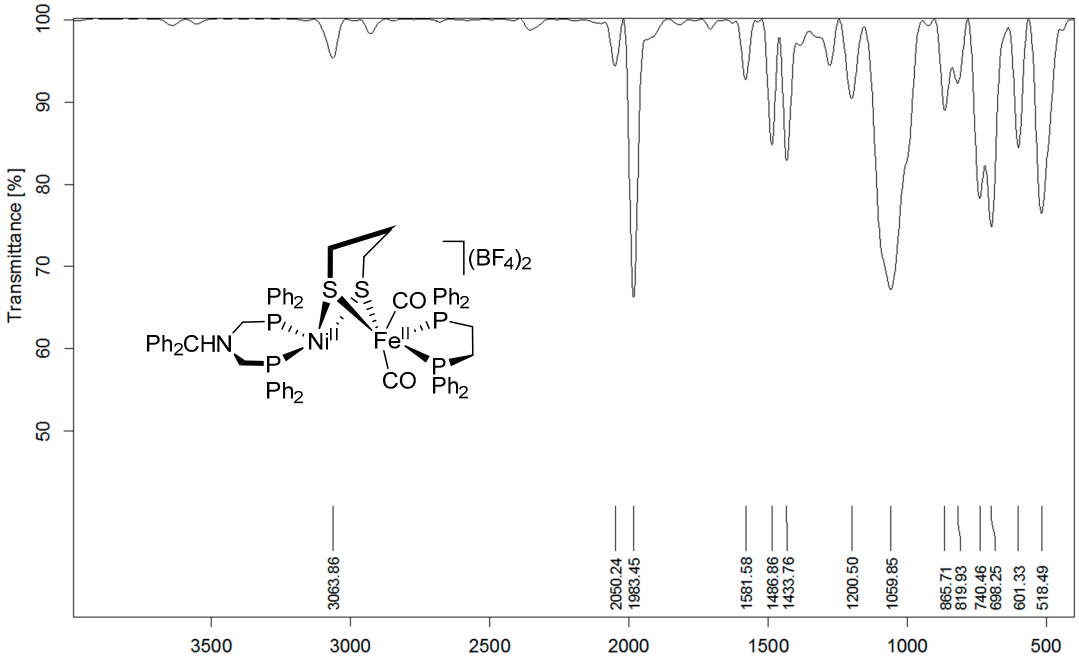


**Figure S25.** IR spectrum of $[D](BF_4)_2$

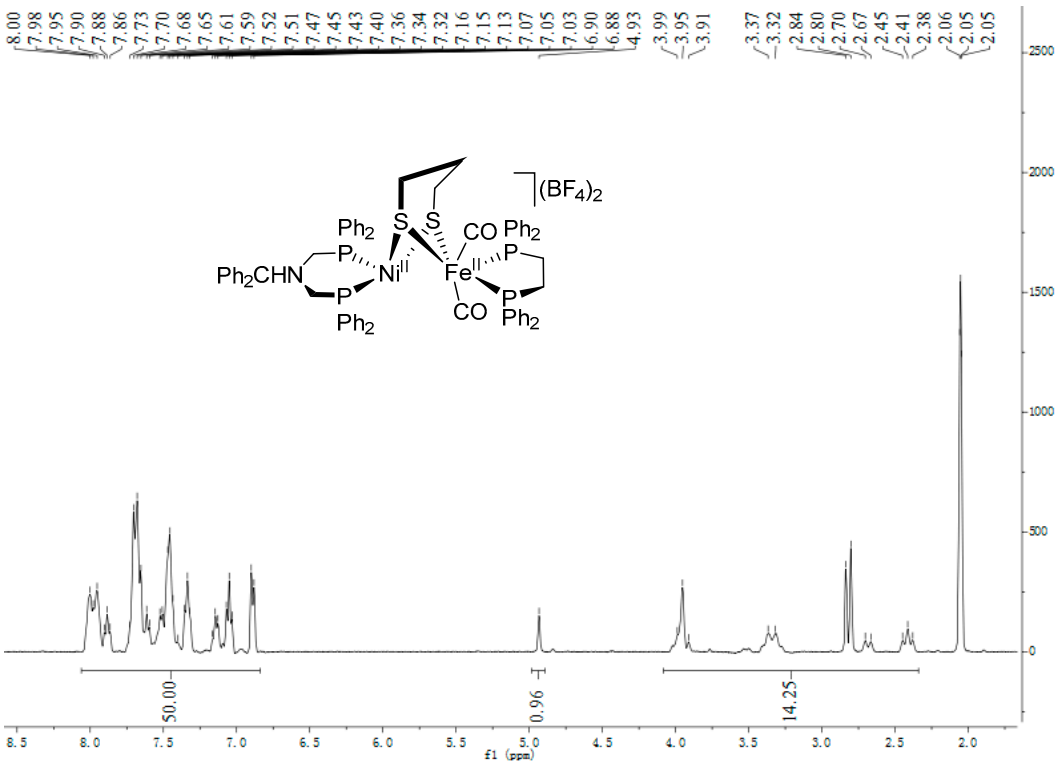


**Figure S26.** $^{1}H$ NMR spectrum of $[D](BF_4)_2$ in acetone-$d_6$

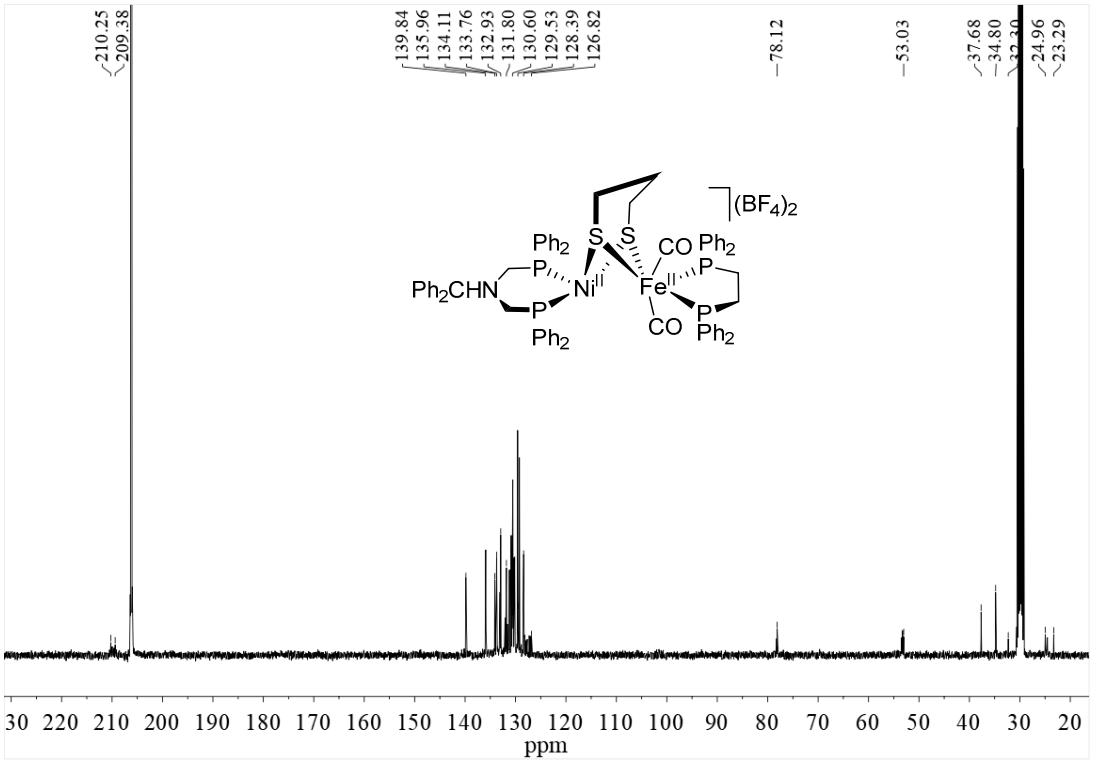


**Figure S27.** $^{13}$C NMR spectrum of **[D](BF$_4$)$_2$** in acetone-$d_6$

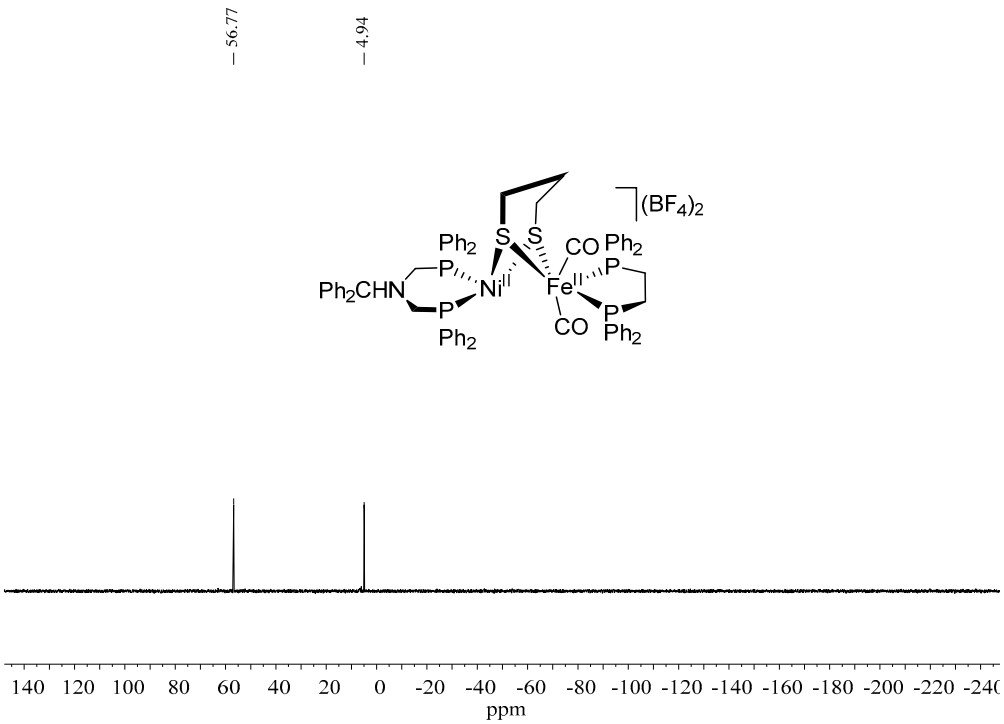


**Figure S28.** $^{31}$P NMR spectrum of **[D](BF$_4$)$_2$** in acetone-$d_6$

## 8. IR and $^{1}H$ ($^{13}C$, $^{31}P$) NMR spectra of [6]$BF_4$

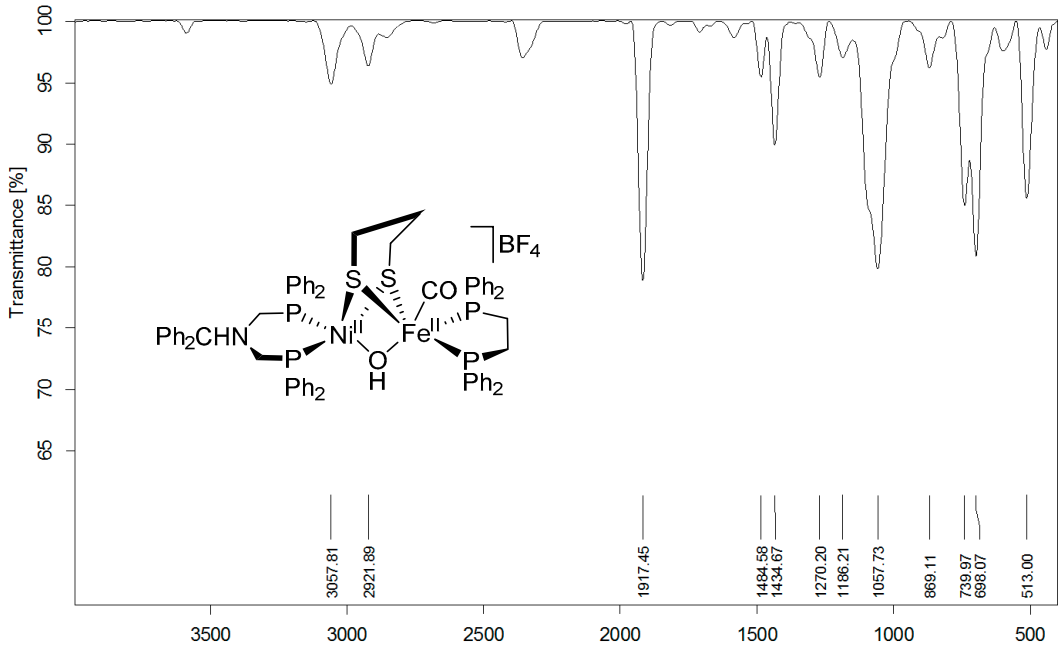


**Figure S29.** IR spectrum of **[6]$BF_4$**

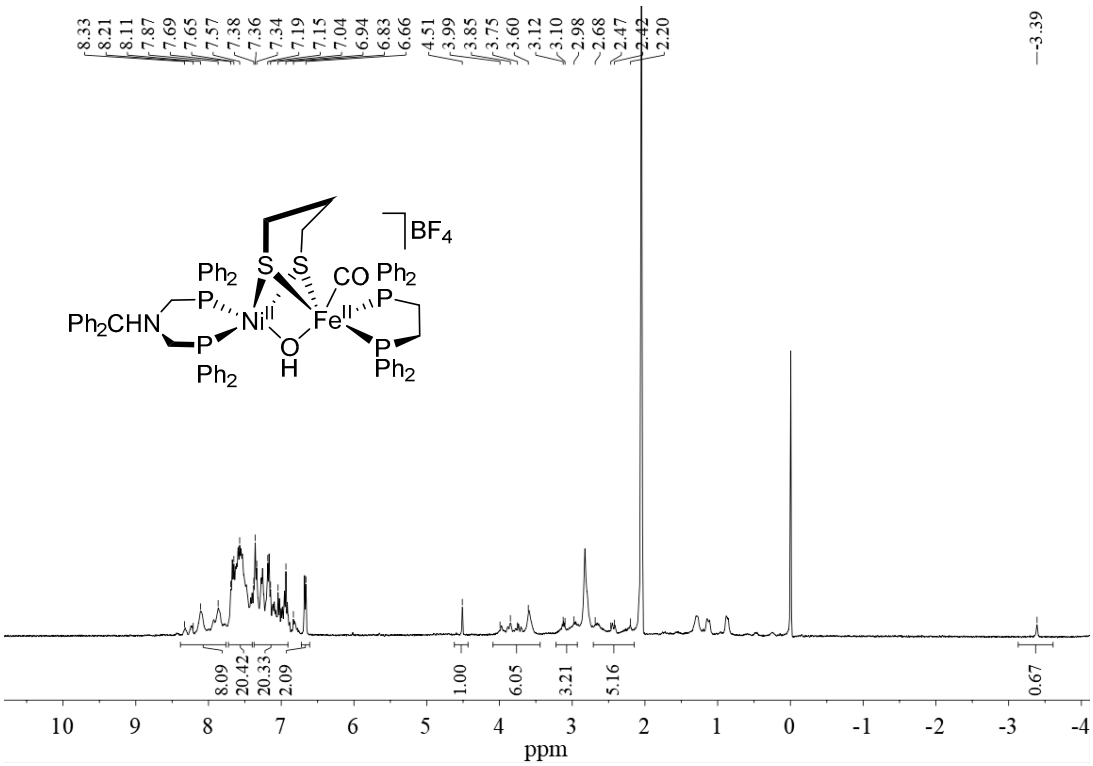


**Figure S30.** $^{1}H$ NMR spectrum of in **[6]$BF_4$** in acetone-$d_6$

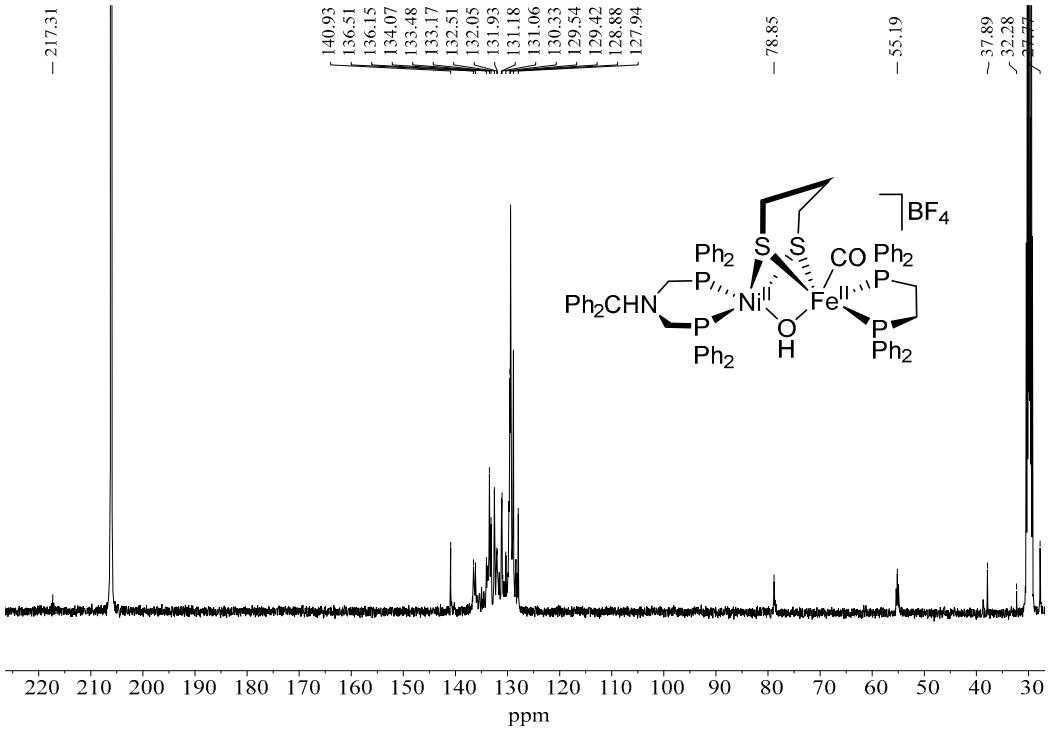


**Figure S31.** $^{13}$C NMR spectrum of **[6]BF$_4$** in acetone-$d_6$

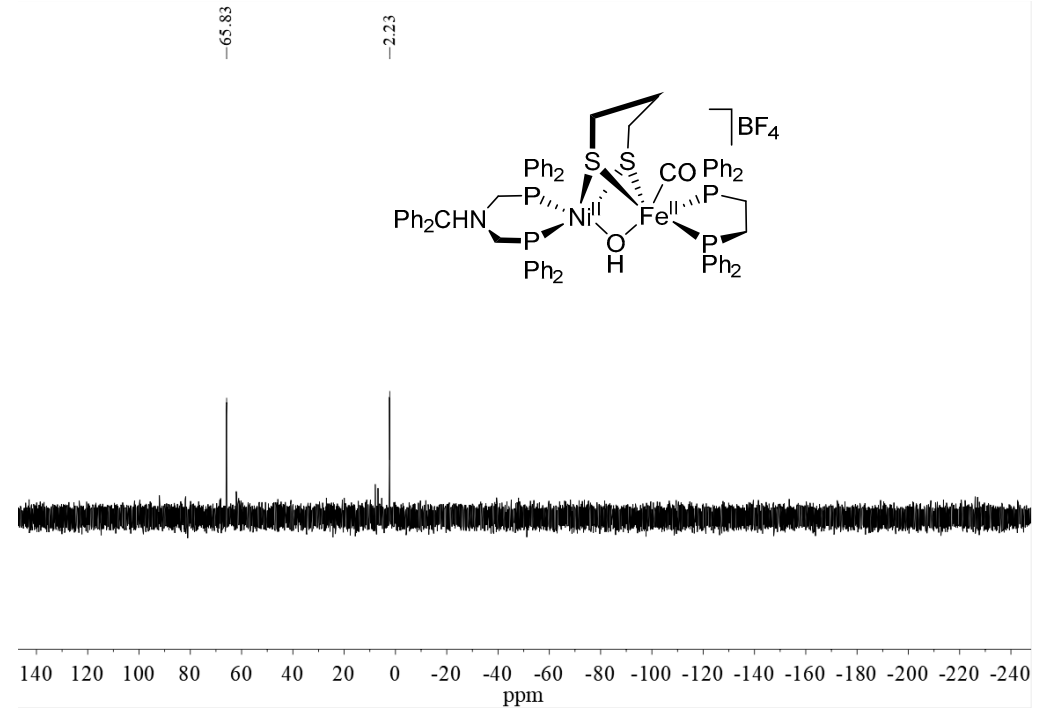


**Figure S32.** $^{31}$P NMR spectrum of **[6]BF$_4$** in acetone-$d_6$

## 9. Crystal data and structure refinement for $[A](BF_4)_2$, $[1]BF_4$, $[2]BF_4$, $[4]BF_4$, $[5]BF_4$ and $[D](BF_4)_2$ (Tables S1–S3)

**Table S1.** Crystal data and structure refinement for $[A](BF_4)_2$ and $[1]BF_4$.

| Complex | $[A](BF_4)_2$ | $[1]BF_4$ |
|---|---|---|
| Empirical formula | $C_{61}H_{52}B_2F_8FeNiO_2P_4S_2 \cdot 2CH_2Cl_2$ | $C_{61}H_{52}BF_4FeNNiOP_4S_2 \cdot CH_2Cl_2 \cdot H_2O$ |
| Formula weight | 1463.05 | 1307.34 |
| Temperature/K | 137.2(3) | 151.6(6) |
| Crystal system | triclinic | Monoclinic |
| Space group | P-1 | $P2_1/n$ |
| a/Å | 13.5359(5) | 12.16469(13) |
| b/Å | 13.9046(4) | 23.5596(3) |
| c/Å | 19.5358(7) | 20.6266(2) |
| α/° | 101.369(3) | 90 |
| β/° | 92.861(3) | 90.0624(9) |
| γ/° | 114.983(3) | 90 |
| Volume/Å$^3$ | 3230.6(2) | 5911.48(11) |
| Z | 2 | 4 |
| $\rho_{calc}$/g·cm$^{-3}$ | 1.504 | 1.469 |
| μ/mm$^{-1}$ | 5.792 | 5.354 |
| F(000) | 1492.0 | 2688.0 |
| Crystal size/mm$^3$ | 0.150 × 0.140 × 0.120 | 0.160 × 0.140 × 0.120 |
| Radiation | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 7.2268 to 148.1318 | 7.504 to 134.152 |
| Index ranges | $-16 \le h \le 15$, $-16 \le k \le 16$, $-23 \le l \le 22$ | $-14 \le h \le 14$, $-28 \le k \le 23$, $-22 \le l \le 24$ |
| Reflections collected | 23359 | 40305 |
| Independent reflections | 11539 [$R_{int}$ = 0.0419, $R_{sigma}$ = 0.0575] | 10570 [$R_{int}$ = 0.0563, $R_{sigma}$ = 0.0465] |
| Data/restraints/parameters | 11539/134/807 | 10570/9/729 |
| Goodness-of-fit on $F^2$ | 1.028 | 1.019 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0622, $wR_2$ = 0.1600 | $R_1$ = 0.0425, $wR_2$ = 0.1032 |
| Final R indexes [all data] | $R_1$ = 0.0735, $wR_2$ = 0.1706 | $R_1$ = 0.0524, $wR_2$ = 0.1099 |
| Largest diff. peak and hole/e Å$^{-3}$ | 2.15 and -1.39 | 1.66 and -1.07 |

**Table S2.** Crystal data and structure refinement for **[2]$BF_4$** and **[4]$BF_4$**.

| Complex | **[2]$BF_4$** | **[4]$BF_4$** |
|---|---|---|
| Empirical formula | $C_{61}H_{52}BF_4FeNNiOP_4S_3$ | $C_{57}H_{54}BF_4FeNNiOP_4S_2 \cdot 2(C_3H_6O)$ |
| Formula weight | 1236.46 | 1274.53 |
| Temperature/K | 152(2) | 100.00(10) |
| Crystal system | triclinic | Triclinic |
| Space group | P-1 | P-1 |
| a/Å | 13.6077(9) | 10.4504(3) |
| b/Å | 13.8784(10) | 17.3852(6) |
| c/Å | 20.6526(15) | 17.3954(6) |
| α/° | 70.414(7) | 85.080(3) |
| β/° | 87.819(6) | 81.056(3) |
| γ/° | 74.103(6) | 75.973(3) |
| Volume/Å$^3$ | 3527.9(5) | 3025.10(18) |
| Z | 2 | 2 |
| $\rho_{calc}$/g·cm$^{-3}$ | 1.164 | 1.399 |
| μ/mm$^{-1}$ | 4.037 | 4.433 |
| F(000) | 1272.0 | 1324.0 |
| Crystal size/mm$^3$ | 0.150 × 0.140 × 0.130 | 0.160 × 0.140 × 0.120 |
| Radiation | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 7.036 to 134.144 | 7.166 to 134.154 |
| Index ranges | -16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -20 ≤ l ≤ 24 | -12 ≤ h ≤ 12, -19 ≤ k ≤ 20, -20 ≤ l ≤ 16 |
| Reflections collected | 22648 | 20587 |
| Independent reflections | 12095 [$R_{int}$ = 0.0948, $R_{sigma}$ = 0.1438] | 10804 [$R_{int}$ = 0.0696, $R_{sigma}$ = 0.0895] |
| Data/restraints/parameters | 12095/64/695 | 10804/12/726 |
| Goodness-of-fit on $F^2$ | 0.880 | 1.039 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0790, $wR_2$ = 0.1944 | $R_1$ = 0.0705, $wR_2$ = 0.1765 |
| Final R indexes [all data] | $R_1$ = 0.1375, $wR_2$ = 0.2390 | $R_1$ = 0.0897, $wR_2$ = 0.1968 |
| Largest diff. peak and hole/e Å$^{-3}$ | 1.16 and -0.67 | 1.42 and -0.76 |

**Table S3.** Crystal data and structure refinement for **[5]$BF_4$** and **[D]$(BF_4)_2$**.

| Complex | **[5]$BF_4$** | **[D]$(BF_4)_2$** |
|---|---|---|
| Empirical formula | $C_{62}H_{58}BF_4FeNNiOP_4S_3 \cdot 0.5(C_6H_{14})$ | $C_{70}H_{65}B_2F_8FeNNiO_2P_4S_2 \cdot 4(CH_2Cl_2)$ |
| Formula weight | 1297.61 | 1768.10 |
| Temperature/K | 293(2) | 113 |
| Crystal system | trigonal | monoclinic |
| Space group | P-3 | $P2_1/c$ |
| a/Å | 26.3215(7) | 16.1180(9) |
| b/Å | 26.3215(7) | 24.5373(12) |
| c/Å | 19.6548(5) | 22.9864(14) |
| α/° | 90 | 90 |
| β/° | 90 | 108.562(2) |
| γ/° | 120 | 90 |
| Volume/$Å^3$ | 11792.9(7) | 8618.0(8) |
| Z | 6 | 4 |
| $\rho_{calc}/g \cdot cm^{-3}$ | 1.096 | 1.412 |
| $\mu/mm^{-1}$ | 3.642 | 0.820 |
| F(000) | 4038.0 | 3728.0 |
| Crystal size/$mm^3$ | 0.210 × 0.200 × 0.190 | 0.150 × 0.130 × 0.110 |
| Radiation | CuKα (λ = 1.54184) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 7.756 to 148.056 | 6.05 to 50.04 |
| Index ranges | $-31 \le h \le 23$, $-31 \le k \le 30$, $-24 \le l \le 18$ | $-19 \le h \le 18$, $-27 \le k \le 29$, $-27 \le l \le 27$ |
| Reflections collected | 29801 | 73887 |
| Independent reflections | 15472 [$R_{int}$ = 0.0740, $R_{sigma}$ = 0.1049] | 15107 [$R_{int}$ = 0.0348, $R_{sigma}$ = 0.0244] |
| Data/restraints/parameters | 15472/122/787 | 15107/0/928 |
| Goodness-of-fit on $F^2$ | 0.903 | 0.896 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0689, $wR_2$ = 0.1841 | $R_1$ = 0.0539, $wR_2$ = 0.1480 |
| Final R indexes [all data] | $R_1$ = 0.0834, $wR_2$ = 0.1981 | $R_1$ = 0.0624, $wR_2$ = 0.1563 |
| Largest diff. peak and hole/e $Å^{-3}$ | 1.28 and -0.59 | 1.61 and -1.37 |