# Supporting Infomation

# One-Pot Synthesis of Ferrocenyl-Substituted Allylamine Derivatives by Three-Component Reaction of *α*-(hydroxy) Alkyl Ferrocenes, Aldehydes and Secondary Amines

Hao Yang[a,‡], Jia-An Zheng [a,b,‡], Hui Yuan[a], Meimei Zhang[c], Wei-Wei Zhang[d], Zi-Qiang Wang[a], Jia-Xin He[a], Yifan Ouyang[e], Yan-Ru Fan [a,*], Yu Huang [a,*], Qi-Peng Zhao [a,*]

[a] School of Pharmacy, Ningxia Medical University, 750004 Yinchuan, China.

[b] NingCheng Central Hospital of ChiFeng, ChiFeng 024200, China.

[c] School of Basic Medicine, Ningxia Medical University, Yinchuan 750004, China

[d] School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China.

[e] School of Medicine, Ningde Normal University, Ningde, Fujian 352100, China.

Corresponding Author: risefyr@163.com (Y.-R. Fan), huangyunxmu@163.com (Y. Huang), zhqp623@nxmu.edu.cn (Q. Zhao).

‡ These authors contributed equally to the work.

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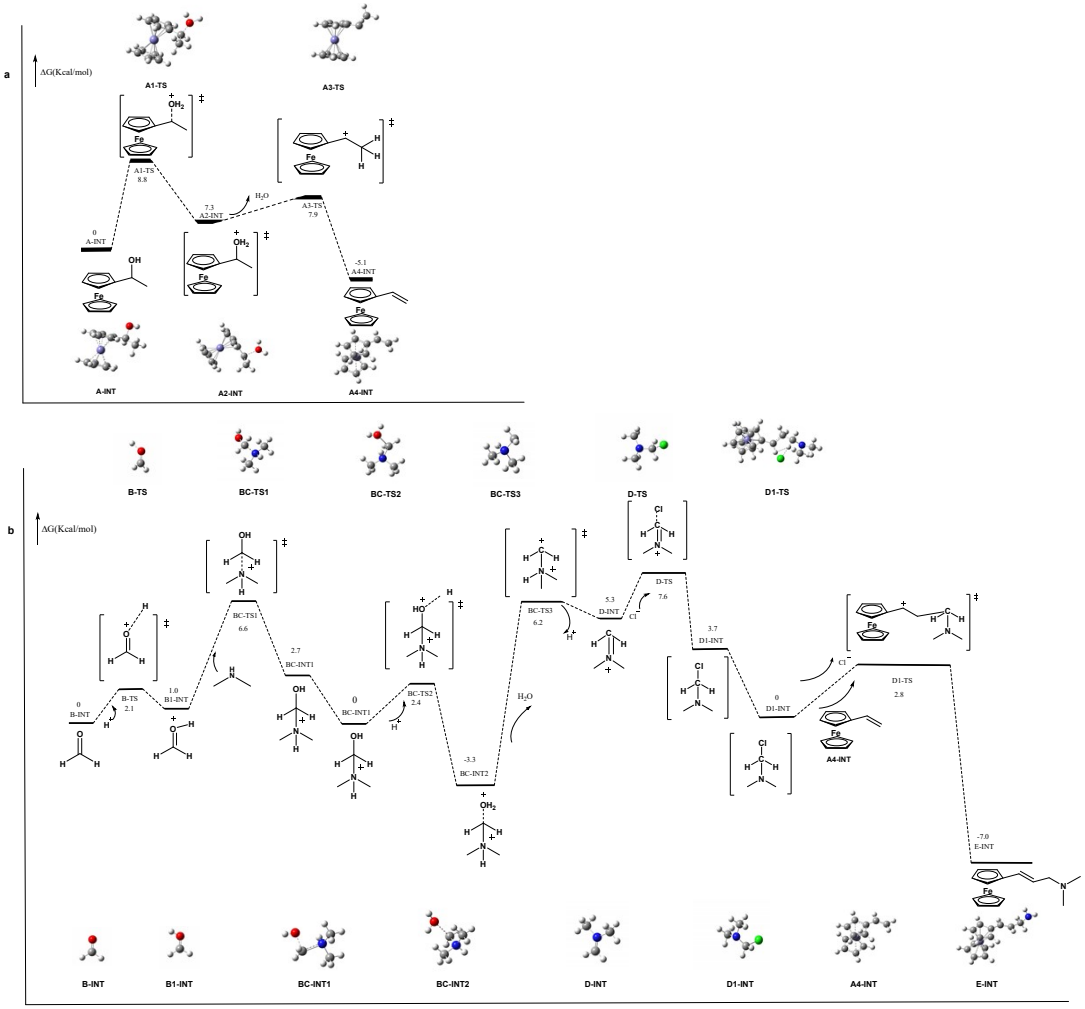



Figure S1. DFT-calculated transition states and energies. The unit of energy is kcal/mol. (a) Several transition states of α-(hydroxy) alkyl ferrocenes to ferrocene ethylene catalyzed by HCl; (b) Several transition states in the reaction of formaldehyde, dimethylamine, and ferrocenylamine to form ferrocenyl-substituted allylamine derivatives.

| Thermodynamic properties of the individual components involved in the reaction[a] | | | |
|---|---|---|---|
| Entry[b] | G[c] | U[d] | E[e] |
| **A-INT** | 0.190338 | -1804.321509 | -1804.320565 |
| **B-INT** | 0.004952 | -114.474480 | -114.473536 |
| **Dimethylamine** | 0.067354 | -135.064841 | -135.063896 |
| **E-INT** | 0.204927 | -1822.785475 | -1822.784530 |
| **$H_2O$** | 0.003433 | -76.381529 | -76.380585 |

Table S1. The change in the Gibbs free energy of the reaction system.

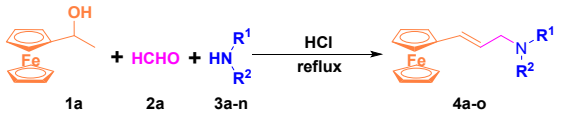
[a] 1 Hartree per particle is equivalent to 627.51 kcal/mol; [b] **A-INT**, **B-INT**, and dimethylamine correspond to the reactants α-(hydroxy) alkyl ferrocenes (**1a**), formaldehyde (**2a**), and dimethylamine (**3a**), respectively, while the products are **E-INT** (ferrocenyl-substituted allylamine) and $H_2O$; [c] Thermal correction to the Gibbs free energy; [d] Sum of the electronic and thermal energies; [e] Sum of the electronic and thermal enthalpies.

# 1. General information

All of the chemical reagent and solvents were obtained from commercial sources and used directly without further purification. 1-(ferrocenyl)-1-propanol, 1-(ferrocenyl)-1-butanol and 1-(ferrocenyl)-1-pentanol were synthesized according to literature with some modification. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVIII 400 spectrometer and mass spectra were recorded on a Shimadzu LCMS-IT-TOF.

# 2. Experimental Details and Characterization Data

## 2.1 General procedure for the one-pot reaction of ferrocenyl-substituted allylamine derivatives




To a solution of *α*-(hydroxy) alkyl ferrocenes **1** (2.0 mmol, 1 equiv） in 5 mL isopropanol, aldehyde **2** (8.0 mmol, 4 equiv) and amine **3** (4.0 mmol, 2 equiv) were added. After stirring for 5 min, hydrochloric acid (20 μL) was added into the reaction mixture. Then the reaction mixture was then refluxed in an oil bath for 4 h at 85 °C. After completion of the reaction, the resulting mixture was treated with 20 mL of saturated sodium bicarbonate at room temperature and extracted with 20 mL DCM for 3 times. The organic layer was washed saturated saline, dried over anhydrous sodium sulfate. After removed the solvent in a vacuum, the resulting residue was then purified by column chromatography on silica gel to give the desired products **4**.

*N-[(2-Ferrocenylvinyl)methyl]dimethylamine (**4a**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (65.7 mg, 71% yield). IR (KBr, cm$^{-1}$): 2971, 2939, 2854 (C-H), 1657 (C=C), 1242 (C-N). $^{1}$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.23 (dt, $J$ = 15.8, 1.5 Hz, 1H, =CH), 5.80 (dt, $J$ = 15.7, 6.7 Hz, 1H, =CH), 4.41 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.21 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.16 - 4.00 (m, 5H, -ferrocene), 2.86 (dd, $J$ = 6.7, 1.4 Hz, 2H, -$CH_2$), 2.15 (s, 6H, -$CH_3$). $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 131.1 (s, 1C, =CH), 123.7 (s, 1C, =CH), 83.03 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.9 (s, 2C, -ferrocene), 67.1 (s, 2C, -ferrocene), 61.5 (s, 1C, -$CH_2$), 44.8 (s, 2C, -$CH_3$). HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{20}FeN^+$ 270.0940; Found 270.0932.

*N-[(2-Ferrocenylvinyl)methyl]diethylamine (**4b**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (100.2 mg, 58% yield). IR (KBr, cm$^{-1}$): 3091, 2972, 2799 (C-H), 1662 (C=C), 1241 (C-N). $^{1}$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.25 (d, $J$ = 15.7 Hz, 1H, =CH), 5.81 (dt, $J$ = 15.7, 6.8 Hz, 1H, =CH), 4.41 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.20 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.18-4.03 (m, 5H, -ferrocene), 3.06 (d, $J$ = 6.8 Hz, 2H, -$CH_2$), 0.98 (t, $J$ = 7.1 Hz, 6H, -$CH_3$). $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.6 (s, 1C, =CH), 125.1 (s, 1C, =CH), 83.5 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (s, 2C, -ferrocene), 66.9 (s, 2C, -ferrocene), 55.3 (s, 1C, -$CH_2$), 46.5 (s, 2C, -$CH_3$), 12.3 (s, 2C, -$CH_2$). HR-MS[M+H]$^+$ 298.1260 (calcd for $C_{17}H_{24}FeN^+$: 298.1246). HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{17}H_{24}FeN^+$ 298.1253; Found 298.1246.

*N-[(2-Ferrocenylvinyl)methyl]di-n-propylamine (**4c**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (78.1 mg, 56% yield). IR (KBr, cm$^{-1}$): 2926, 2873, 2796 (C-H), 1616 (C=C), 1268 (C-N). $^{1}$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.22 (dt, $J$ = 15.7, 1.5 Hz, 1H, =CH), 5.81 (dt, $J$ = 15.7, 6.7 Hz, 1H, =CH), 4.40 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.20 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.12 (d, $J$ = 9.4 Hz, 5H, -ferrocene), 3.03 (dd, $J$ = 6.7,

1.4 Hz, 2H, -$CH_2$), 2.42-2.29 (m, 4H , -$CH_2$), 1.43 (h, $J$ = 7.4 Hz, 4H, -$CH_2$), 0.85 (t, $J$ = 7.4 Hz, 6H, -$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.5 (s, 1C, =CH), 125.3 (s, 1C, =CH), 83.5 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (s, 2C, -ferrocene), 66.9 (s, 2C, -ferrocene), 56.5 (s, 1C, -$CH_2$), 55.7 (s, 2C, -$CH_3$), 20.4 (s, 2C, -$CH_2$), 12.3 (s, 2C, -$CH_2$). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{28}FeN^+$ 326.1566; Found 326.1558.

*N-[(2-Ferrocenylvinyl)methyl]di-n-butylamine (**4d**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (56.9 mg, 49% yield). IR (KBr, $cm^{-1}$): 2964, 2932, 2868 (C-H), 1630 (C=C), 1277 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.28-6.18 (m, 1H, =CH), 5.80 (dt, $J$ = 15.7, 6.7 Hz, 1H, =CH), 4.40 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.23-4.17 (m, 2H, -ferrocene), 4.13-4.05 (m, 5H, -ferrocene), 3.02 (dd, $J$ = 6.8, 1.3 Hz, 2H, -$CH_2$), 2.44-2.33 (m, 4H, -$CH_2$), 1.45-1.35 (m, 4H, -$CH_2$), 1.33-1.24 (m, 4H, -$CH_2$), 0.89 (t, $J$ = 7.3 Hz, 6H, -$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.0 (s, 1C, =CH), 124.8 (s, 1C, =CH), 83.0 (s, 1C, -ferrocene ), 68.8 (s, 5C, -ferrocene ), 68.2 (s, 2C, -ferrocene), 66.4 (s, 2C, -ferrocene), 56.0 (s, 1C, -$CH_2$), 52.8 (s, 2C, -$CH_3$), 28. 9 (s, 2C, -$CH_2$), 20.1 (s, 2C, -$CH_2$), 13.9 (s, 2C, -$CH_2$). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{32}FeN^+$ 354.1879; Found 354.1853.

*N-[(2-Ferrocenylvinyl)methyl]di-iso-propylamine (**4e**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (72.7 mg, 33% yield). IR (KBr, $cm^{-1}$): 3095, 2966, 2922 (C-H), 1667 (C=C), 1261 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.22 (d, $J$ = 15.7 Hz, 1H, =CH), 5.82-5.71 (m, 1H, =CH), 4.38 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.18 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.13-4.06 (m, 5H, -ferrocene), 3.13-3.06 (m, 2H, -$CH_2$), 3.04 (q, $J$ = 6.5 Hz, 2H, -CH), 0.99 (d, $J$ = 6.7 Hz, 12H, -$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.0 (s, 1C, =CH), 127.4 (s, 1C, =CH), 83.9 (s, 1C, -ferrocene), 69.2 (s, 5C, -ferrocene), 68.7 (s, 2C, -ferrocene), 66.8 (s, 2C, -ferrocene), 48.0 (s, 2C, -CH), 47.5 (s, 1C, -$CH_2$), 21.1 (s, 4C, -$CH_3$). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{28}FeN^+$ 326.1566; Found 326.1531.

*N-[(2-Ferrocenylvinyl)methyl]di-tert-butyl amine (**4f**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (60.0 mg, 19% yield). IR (KBr, $cm^{-1}$): 2984, 2880, 2812 (C-H), 1682 (C=C), 1234 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.21 (d, $J$ = 15.8 Hz, 1H, =CH), 5.79 (dt, $J$ = 15.7, 6.7 Hz, 1H, =CH), 4.39 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.20 (dd, $J$ = 4.0, 2.2 Hz, 2H, -ferrocene), 4.13-4.09 (m, 5H, -ferrocene), 2.99 (dd, $J$ = 6.8, 1.4 Hz, 2H, -$CH_2$), 2.13 (d, $J$ = 7.2 Hz, 4H, -$CH_2$), 1.73 (dp, $J$ = 13.6, 6.7 Hz, 2H, -CH), 0.87 (d, $J$ = 6.6 Hz, 12H, -$CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.12(s, 1C, =CH), 124.7 (s, 1C, =CH), 83.0 (s, 1C, -ferrocene), 68.7 (s, 5C, -ferrocene), 68.3 (s, 2C, -ferrocene), 66.4 (s, 2C, -ferrocene), 62.8 (s, 2C, -CH), 57.0 (s, 1C, -$CH_2$), 26.0 (s, 2C, -$CH_2$), 20.8 (s, 4C, -$CH_3$). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{32}FeN^+$ 354.1879; Found 354.1858.

*N-[(2-Ferrocenylvinyl)methyl]di-hydroxyethylamine (**4g**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (64.4 mg, 39% yield). IR (KBr, $cm^{-1}$): 3411(-OH), 2928, 2875 (C-H), 1630 (C=C), 1244 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.23 (d, $J$ = 15.7 Hz, 1H, =CH), 5.82 (dt, $J$ = 15.7, 6.7 Hz, 1H, =CH), 4.40 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.20 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.14-4.07 (m, 5H, -ferrocene), 3.45 (q, $J$ = 5.9, 4.7 Hz, 4H, -$CH_2$), 3.17-3.08 (m, 2H, -$CH_2$), 2.55 (t, $J$ = 6.4 Hz, 4H, -$CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.62 (s, 1C, =CH),124.2 (s, 1C, =CH), 82.9 (s, 1C, -ferrocene), 68.9 (s, 5C, -ferrocene), 68.3 (s, 2C, -

ferrocene), 66.5 (s, 2C, -ferrocene), 59.2 (s, 2C, -$CH_2$), 57.1 (s, 1C, -$CH_2$), 56.1 (s, 2C, -$CH_2$). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{24}FeNO_2^+$ 330.1151; Found 330.1125.

*N-[(2-Ferrocenylvinyl)methyl] pyrrolidine (**4h**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (93.3 mg, 52% yield). IR (KBr, $cm^{-1}$): 3067, 2890, 2789 (C-H), 1662 (C=C), 1201 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.31 (d, $J$ = 15.7 Hz, 1H, =CH), 5.86 (dt, $J$ = 15.7, 6.8 Hz, 1H, =CH), 4.41 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.22 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.18-4.07 (m, 5H, -ferrocene), 3.19 (d, $J$ = 6.7 Hz, 2H, -$CH_2$), 2.60 (d, $J$ = 6.5 Hz, 4H, -pyrrolidine), 1.74 (p, $J$ = 3.2 Hz, 4H, -pyrrolidine). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.0 (s, 1C, =CH), 125.6 (s, 1C, =CH), 83.5 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.7 (s, 2C, -ferrocene), 66.9 (s, 2C, -ferrocene), 58.3 (s, 1C, -$CH_2$), 53.8 (s, 2C, -pyrrolidine), 23.6 (s, 2C, -pyrrolidine). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{22}FeN^+$ 296.1096; Found 296.1072.

*N-[(2-Ferrocenylvinyl)methyl] proline (**4i**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (39.8 mg, 16% yield). IR (KBr, $cm^{-1}$): 2955, 2923 (C-H), 1620 (C=C), 1650 (C=O), 1269 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.48 (d, $J$ = 15.8 Hz, 1H, =CH), 5.85 (d, $J$ = 16.0 Hz, 1H, =CH), 4.43 (d, $J$ = 8.5 Hz, 2H, -ferrocene), 4.26 (s, 2H, -ferrocene), 4.16 (d, $J$ = 19.0 Hz, 5H, -ferrocene), 3.62-3.41 (m, 4H), 2.88 -2.81(t, $J$ = 2.1 Hz, 1H, -proline), 1.94- 1.68 (m, 4H, -proline). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 134.8 (s, 1C, =CH), 117.9 (s, 1C, =CH), 81.5 (s, 1C, -ferrocene), 69.0 (s, 5C, -ferrocene), 68.9 (s, 2C, -ferrocene), 66.9 (s, 2C, -ferrocene), 55.7 (s, 1C, -proline), 55.0 (s, 1C, -$CH_2$), 53.0 (s, 1C, -proline), 28.8 (s, 1C, -proline), 23.3 (s, 1C, -proline). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{21}FeNO_2Na^+$ 362.0814; Found 362.0801.

*N-[(2-Ferrocenylvinyl)methyl] proline methyl ester (**4j**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (58.2 mg, 43% yield). IR (KBr, $cm^{-1}$): 2986, 2874 (C-H), 1730 (C=O), 1202(C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.22 (d, $J$ = 15.7 Hz, 1H, =CH), 5.88-5.79 (m, 1H, =CH), 4.39 (ddt, $J$ = 21.2, 2.5, 1.4 Hz, 2H, -ferrocene), 4.20 (t, $J$ = 2.5, 1.4 Hz, 2H, -ferrocene), 4.10 (s, 5H, -ferrocene), 3.61 (s, 1H, -proline methyl ester), 3.30-3.24 (m, 1H, -proline methyl ester), 3.21 (dt, $J$ = 9.0, 4.6 Hz, 1H, -proline methyl ester), 3.12-3.01 (m, 1H, -proline methyl ester), 3.01-2.94 (m, 1H, -proline methyl ester), 2.47-2.41 (m, 1H, -proline methyl ester), 2.10 -1.98 (m, 1H, -proline methyl ester), 1.85-1.71 (m, 3H, -$CH_3$), 1.18 (t, $J$ = 7.1 Hz, 2H, -$CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.7 (s, 1C,=CH), 124.6 (s, 1C, =CH), 83.3 (s, 1C,-ferrocene), 69.3 (s, 5C, -ferrocene), 68.7 (s, 1C, -ferrocene), 67.2 (s, 1C, -ferrocene), 66.6 (s, 1C, -ferrocene), 64.4 (s, 1C, -ferrocene), 60.3 (s, 1C, -proline methyl ester), 56.1 (s, 1C, -$CH_2$), 52.91(s, 1C, -proline methyl ester), 29.33(s, 1C, -proline methyl ester), 23.3 (s, 1C, -proline methyl ester), 14.6 (s, 1C, -$CH_3$). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{23}FeNO_2Na^+$ 376.0970; Found 376.0972.

*N-[(2-Ferrocenylvinyl)methyl] piperidine (**4k**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (73.6 mg, 58% yield). IR (KBr, $cm^{-1}$): 2992, 2872, 2865 (C-H), 1635 (C=C), 1205(C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.21 (d, $J$ = 15.8 Hz, 1H, =CH), 5.81 (dt, $J$ = 15.8, 6.8 Hz, 1H, =CH), 4.41 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.20 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.09 (s, 5H, -ferrocene), 2.90 (d, $J$ = 6.7 Hz, 2H, -$CH_2$), 2.36 (p, $J$ = 5.4 Hz, 4H, -piperidine), 1.50 (p, $J$ = 5.4 Hz, 4H, -piperidine), 1.38 (d, $J$ = 7.3 Hz, 2H, -piperidine). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.9 (s, 1C, =CH), 124.9 (s, 1C, =CH), 83.4 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (s, 2C, -ferrocene), 67.0 (s, 2C, -ferrocene), 61.6 (s, 1C, -$CH_2$), 54.3 (s, 2C, -

piperidine), 26.1 (s, 2C, -piperidine), 24.6 (s, 1C, -piperidine). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{24}FeN^+$ 310.1253; Found 310.1217.

*N-[(2-Ferrocenylvinyl)methyl] morpholine (**4l**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (58.1 mg, 37% yield). IR (KBr, $cm^{-1}$): 2968, 2892, 2815 (C-H), 1636 (C=C), 1206(C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.28-6.21 (m, 1H, =CH), 5.80 (dt, $J$ = 15.8, 6.8 Hz, 1H, =CH), 4.41 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.21 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.12 - 4.05 (m, 5H, -ferrocene), 3.58 (t, $J$ = 4.6 Hz, 4H, -morpholine), 2.94 (dd, $J$ = 6.8, 1.3 Hz, 2H, -morpholine), 2.37 (d, $J$ = 4.8 Hz, 4H, -morpholine). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 130.7 (s, 1C, =CH), 123.9 (s, 1C, =CH), 83.2 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (s, 2C, -ferrocene), 67.0 (s, 2C, -ferrocene), 66.7 (s, 2C, -morpholine), 61.2 (s, 1C, $-CH_2$), 53.6 (s, 2C, -morpholine). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{22}FeNO^+$ 312.1045; Found 312.1003.

*N-[(2-Ferrocenylvinyl)methyl] piperazine (**4m**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (68.2 mg, 35% yield). IR (KBr, $cm^{-1}$): 2961, 2813, 2789 (C-H), 1667 (C=C), 1286 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.25-6.18 (m, 1H, =CH), 5.80 (dt, $J$ = 15.7, 6.8 Hz, 1H, =CH), 4.41 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.20 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.08 (s, 5H, -ferrocene), 2.89 (dd, $J$ = 6.7, 1.3 Hz, 2H, $-CH_2$), 2.68 (d, $J$ = 9.7 Hz, 4H, -piperazine), 2.29 (s, 4H, -piperazine). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 130.2 (s, 1C, =CH), 124.5 (s, 1C, =CH), 83.3 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (s, 2C, -ferrocene), 67.0 (s, 2C, -ferrocene), 61.6 (s, 1C, $-CH_2$), 54.5 (s, 2C, -piperazine), 46.1 (s, 2C, -piperazine). HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{23}FeN_2^+$ 311.1205; Found 311.1182.

*N, N'-di-[(2-Ferrocenylvinyl)methyl] piperazine (**4n**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (96.2 mg, 20% yield). IR (KBr, $cm^{-1}$): 2947, 2898, 2884 (C-H), 1657 (C=C), 1258 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.24 (d, $J$ = 15.8 Hz, 2H, =CH), 5.82 (dt, $J$ = 15.7, 6.6 Hz, 2H, =CH), 4.40 (t, $J$ = 1.9 Hz, 4H, -ferrocene), 4.20 (t, $J$ = 1.9 Hz, 4H, -ferrocene), 4.15-4.03 (m, 10H, -ferrocene), 2.95 (d, $J$ = 6.8 Hz, 4H, $-CH_2$), 2.44 (s, 8H, -piperazine). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.5 (s, 2C, =CH),124.1 (s, 2C, =CH),82.7 (s, 2C, -ferrocene), 68.7 (s, 10C, -ferrocene), 68.2 (s, 4C, -ferrocene), 66.4 (s, 4C, -ferrocene), 60.2 (s, 2C, $-CH_2$), 52.5 (s, 4C, -piperazine). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{30}H_{34}Fe_2N_2Na^+$ 557.1313; Found 557.1324.

*N-Methyl-N-[(2-Ferrocenylvinyl)methyl] 1-naphthalenemethylamine (**4o**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (85.2 mg, 59% yield). IR (KBr, $cm^{-1}$): 3098 (Ar-H), 2839, 2789 (C-H), 1638 (C=C), 1265 (C-N). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.31 (dd, $J$ = 8.4, 1.3 Hz, 1H, -naphthalene), 7.92 (dd, $J$ = 7.9, 1.6 Hz, 1H, -naphthalene), 7.85 (dd, $J$ = 6.8, 2.7 Hz, 1H, -naphthalene), 7.54 (dddd, $J$ = 19.2, 8.1, 6.8, 1.4 Hz, 2H, -naphthalene), 7.49 - 7.43 (m, 2H, -naphthalene), 6.32 (d, $J$ = 15.7 Hz, 1H, =CH), 5.94 (dt, $J$ = 15.7, 6.8 Hz, 1H, =CH), 4.45 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.21 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.13-3.98 (m, 5H, -ferrocene), 3.90 (s, 2H, $-CH_2$), 3.09 (dd, $J$ = 6.8, 1.3 Hz, 2H, $-CH_2$), 2.16 (s, 3H, $-CH_3$). $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta$ $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 135.4 (s, 1C, -naphthalene), 134.0 (s, 1C, -naphthalene), 132.5 (s, 1C, -naphthalene), 130.7 (s, 1C, -naphthalene), 128.7 (s, 1C, -naphthalene), 128.2 (s, 1C, -naphthalene), 127.8 (s, 1C, -naphthalene), 126.1 (s, 1C, -naphthalene), 125.7 (s, 1C, -naphthalene), 125.4 (s, 1C,=CH), 124.6 (s, 1C, =CH), 83.3 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (s, 2C, -ferrocene), 67.0

(s, 2C, -ferrocene), 60.3 (s, 1C, -$CH_2$), 59.68 (s, 1C, -$CH_2$), 42.35 (s, 1C, -$CH_3$). HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{25}H_{25}FeNNa^+$ 418.1229; Found 418.1221.

*N-[1-(2-Ferrocenylvinyl)ethyl]dimethylamine (**4p**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (77.2 mg, 12% yield). IR (KBr, cm$^{-1}$): 2938, 2867, 2818 (C-H), 1577 (C=C), 1260 (C-N). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.16 (d, $J$ = 15.8 Hz, 1H, =CH), 5.76 (dd, $J$ = 15.8, 7.7 Hz, 1H, =CH), 4.40 (dq, $J$ = 16.9, 1.8 Hz, 2H, -ferrocene), 4.20 (s, 2H, -ferrocene), 4.17-3.99 (m, 5H, -ferrocene), 2.87 (p, $J$ = 6.8 Hz, 1H, -CH), 2.23-2.10 (m, 6H, -$CH_3$), 1.09 (d, $J$ = 6.6 Hz, 3H, -$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 129.3 (s, 1C, =CH), 128.1 (s, 1C, =CH), 83.4 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 68.8 (d, $J$ = 5.5 Hz，2C, -ferrocene), 67.2 (s, 1C, -ferrocene), 66.7 (s, 1C, -ferrocene), 62.3 (s, 1C, -$CH_3$), 42.1 (s, 2C, -$CH_3$), 18.2 (s, 1C, -CH). HRMS (ESI) m/z [M - $C_2NH_7$]$^+$ calcd for $C_{14}H_{15}Fe^+$ 239.0518; Found 239.0498.

*N-[1-(2-Ferrocenylvinyl)-n-propyl]dimethylamine (**4q**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (68.8 mg, 9% yield). IR (KBr, cm$^{-1}$): 2964, 2936, 2857 (C-H), 1634 (C=C), 1279 (C-N). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.15 (d, $J$ = 15.8 Hz, 1H, =CH), 5.68 (dd, $J$ = 15.8, 8.9 Hz, 1H, =CH), 4.42 (dq, $J$ = 8.1, 1.7 Hz, 2H, -ferrocene), 4.21 (t, $J$ = 1.9 Hz, 2H, -ferrocene), 4.09 (s, 5H, -ferrocene), 2.59 (td, $J$ = 8.6, 5.2 Hz, 1H, -CH), 2.16 (s, 6H , -$CH_3$), 1.63-1.53 (m, 1H, -$CH_2$), 1.40 (ddd, $J$ = 15.4, 14.1, 7.5 Hz, 1H, -$CH_2$), 0.84 (t, $J$ = 7.4 Hz, 3H, -$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 130.2 (s, 1C, =CH), 126.2 (s, 1C, =CH), 83.4 (s, 1C, -ferrocene), 69.3 (s, 5C, -ferrocene), 69.3 (s, 1C, -$CH_3$), 68.8 (d, $J$ = 3.3 Hz, 2C, -ferrocene), 67.0 (s, 1C, -ferrocene), 66.9 (s, 1C, -ferrocene), 41.9 (s, 2C, -$CH_3$), 25.6(s, 1C, -$CH_2$), 11.4 (s, 1C, -CH). HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{17}H_{24}FeN^+$ 298.1253; Found 298.1235.

*N-(3-Ferrocenyl-2-methyl-allyl)dimethylamine (**4r**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (39.7 mg, 47% yield). IR (KBr, cm$^{-1}$): 2939, 2916, 2864 (C-H), 1621 (C=C), 1260 (C-N). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.04 (q, $J$ = 1.3 Hz, 1H, =CH), 4.37 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.21 (t, $J$ = 1.8 Hz, 2H, -ferrocene), 4.13 (d, $J$ = 16.0 Hz, 5H, -ferrocene), 2.81-2.73 (m, 2H, -$CH_2$), 2.13 (s, 6H, -2$CH_3$), 1.78 (d, $J$ = 1.3 Hz, 3H, -$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 132.9 (s, 1C, C), 123.8 (s, 1C, =CH), 82.3 (s, 1C, -ferrocene), 68.9 (s, 1C, -$CH_2$), 68.7 (s, 2C, -ferrocene), 68.7 (s, 5C, -ferrocene), 68.1 (s, 2C, -ferrocene), 45.0 (s, 2C, -$CH_3$), 16.7 (s, 1C, -$CH_3$). HRMS (ESI) m/z [M - $C_2NH_7$]$^+$ calcd for $C_{14}H_{15}Fe^+$ 239.0518; Found 239.0503.

*N-(3-Ferrocenyl-2-ethyl-allyl)dimethylamine (**4s**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (66.8 mg, 43% yield). IR (KBr, cm$^{-1}$): 3058, 2942, 2854 (C-H), 1647 (C=C), 1274 (C-N). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.00 (s, 1H, =CH), 4.39-4.32 (m, 2H, -ferrocene), 4.28-4.20 (m, 2H, -ferrocene), 4.12 (d, $J$ = 10.7 Hz, 5H, -ferrocene), 2.79 (s, 2H, -$CH_2$), 2.23 (q, $J$ = 7.5 Hz, 2H, -$CH_2$), 2.14 (s, 6H, -2$CH_3$), 1.05 (t, 7.5 Hz, 3H, -$CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 138.39 (s, 1C, C), 123.4 (s, 1C, =CH), 81.8 (s, 1C, -ferrocene), 68.8 (d, $J$ = 2.0 H, 5C, -ferrocene), 68.6 (d, $J$ = 3.5 Hz, 2C, -ferrocene), 68.2 (s, 2C, -ferrocene), 66.4 (s, 1C, -$CH_2$), 45.1 (s, 2C, -$CH_3$), 22.8(s, 1C, -$CH_2$), 12.5 (s, 1C, -$CH_3$). HRMS (ESI) m/z [M - $C_2NH_7$]$^+$ calcd for $C_{15}H_{17}Fe^+$ 253.0674; Found 253.0658.

*N-(3-Ferrocenyl-2-n-propyl-allyl)dimethylamine (**4t**)*

The title compound was isolated by silica gel flash column chromatography (PE/EA = 2:1-1:1) as a yellow solid (45.3 mg, 42% yield). IR (KBr, $cm^{-1}$): 3095, 2854, 2811 (C-H), 1677 (C=C), 1257 (C-N). $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.05 (d, $J$ = 18.3 Hz, 1H, =CH), 4.34 (dt, J = 9.0, 1.9 Hz, 2H, -ferrocene), 4.22 (dt, $J$ = 11.6, 1.8 Hz, 2H, -ferrocene), 4.12 (d, $J$ = 14.1 Hz, 5H, -ferrocene), 2.78 (d, $J$ = 1.2 Hz, 2H, $-CH_2$), 2.27-2.15 (m, 2H, $-CH_2$), 2.13 (d, $J$ = 2.5 Hz, 6H, $-2CH_3$), 1.59-1.41 (m, 2H, $-CH_2$), 0.95 (t, $J$ = 7.3 Hz, 3H, $-CH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 137.0 (s, 1C, C), 124.0 (s, 1C, =CH), 81.9 (s, 1C, -ferrocene), 68.7 (s, 5C, -ferrocene), 68.6 (s, 2C, -ferrocene), 68.2 (s, 2C, -ferrocene), 66.8 (s, 1C, $-CH_2$), 45.1 (s, 2C, $-CH_3$), 31.9 (s, 1C, $-CH_2$), 20.8 (s, 1C, $-CH_2$), 14.3 (s, 1C, $-CH_3$). HRMS (ESI) m/z [M - $C_2NH_7$ ]$^+$ calcd for $C_{16}H_{19}Fe^+$ 267.0831; Found 267.0814.

## 3. DFT studies

### 3.1 Computational Methods

All DFT calculations were conducted utilizing Gaussian 16 software[1]. All molecular structures in this study were thoroughly optimized, frequency calculations were carried out, and transition-state searches were performed at the non-localized B3LYP[2] functional level, employing hybrid basis sets. The 6-31G(d)[3] basis set was applied to all non-metal atoms (C, H, O, and N), whereas the tzvp basis set was employed for all metal atoms (Fe). The DFT-D3[4] method was employed to apply dispersion corrections, ensuring the accuracy and reliability of the calculations. To mitigate potential errors arising from basis set overlap, all structural optimizations were carried out without imposing geometric constraints. The thermodynamic energies of all structures along the reaction pathway at 298 K were corrected using the Shermo method, maintaining the same computational level throughout the process. All transition-state structures along the reaction pathway underwent Hessian analysis, and each transition state exhibited a single negative frequency. Additionally, all transition states were further validated through Intrinsic Reaction Coordinate (IRC)[5] calculations.

### 3.2 Absolute values and cartesian coordinates (Å) for optimised structures

**A-INT**

| | |
|---|---|
| Zero-point correction= | 0.230397 (Hartree/Particle) |
| Thermal correction to Energy= | 0.243137 |
| Thermal correction to Enthalpy= | 0.244081 |
| Thermal correction to Gibbs Free Energy= | 0.190338 |
| Sum of electronic and zero-point Energies= | -1804.334249 |
| Sum of electronic and thermal Energies= | -1804.321509 |
| Sum of electronic and thermal Enthalpies= | -1804.320565 |
| Sum of electronic and thermal Free Energies= | -1804.374308 |

| | | | |
|---|---|---|---|
| C | -1.15829619 | -1.73807502 | -0.56541322 |
| C | -1.87225603 | -0.80427256 | -1.37752604 |
| C | -2.70429720 | -0.02059195 | -0.52057134 |
| C | -2.50483317 | -0.46980771 | 0.82088567 |
| C | -1.54943465 | -1.53162889 | 0.79377379 |
| H | -0.44196353 | -2.47000426 | -0.91843291 |
| H | -1.78864007 | -0.70117584 | -2.45246799 |
| H | -3.36144693 | 0.78206808 | -0.83213394 |
| H | -2.98488725 | -0.06798285 | 1.70474141 |
| H | -1.18116540 | -2.07769804 | 1.65371436 |

| | | | |
|---|---|---|---|
| Fe | -0.73264486 | 0.18579161 | 0.01608000 |
| C | -0.15479986 | 1.83527418 | 1.09338316 |
| C | -0.23226682 | 2.15371319 | -0.29708106 |
| C | 0.79454622 | 0.78147115 | 1.25161213 |
| H | -0.72757468 | 2.29926491 | 1.88717081 |
| C | 0.66631289 | 1.29282239 | -0.99322370 |
| H | -0.87451228 | 2.90237435 | -0.74477983 |
| C | 1.30270920 | 0.43226883 | -0.04135648 |
| H | 1.06650382 | 0.31461025 | 2.18989474 |
| H | 0.83995791 | 1.28017573 | -2.06259542 |
| C | 2.39071380 | -0.55470112 | -0.37583865 |
| H | 2.12928895 | -1.03189126 | -1.33654653 |
| C | 2.59026857 | -1.64781219 | 0.67622238 |
| H | 1.67394273 | -2.22787741 | 0.82874029 |
| H | 3.37952394 | -2.34197757 | 0.36021793 |
| H | 2.89358249 | -1.20822012 | 1.63260042 |
| O | 3.59042737 | 0.21760480 | -0.54071127 |
| H | 4.29253694 | -0.39504801 | -0.79171300 |

**Dimethylamine**

| | | | |
|---|---|---|---|
| N | -0.00000001 | 0.56634126 | -0.15000218 |
| H | 0.00000069 | 1.32709316 | 0.52482224 |
| C | 1.21323485 | -0.22283961 | 0.02051162 |
| H | 1.27617498 | -0.96893477 | -0.78335190 |
| H | 2.09184700 | 0.42871678 | -0.06121228 |
| H | 1.27379490 | -0.76848527 | 0.98409101 |
| C | -1.21323516 | -0.22283956 | 0.02051174 |
| H | -2.09184761 | 0.42871437 | -0.06122844 |
| H | -1.27616613 | -0.96894482 | -0.78334289 |
| H | -1.27380184 | -0.76847325 | 0.98409732 |

| | |
|---|---|
| Zero-point correction= | 0.092786 (Hartree/Particle) |
| Thermal correction to Energy= | 0.097152 |
| Thermal correction to Enthalpy= | 0.098097 |
| Thermal correction to Gibbs Free Energy= | 0.067354 |
| Sum of electronic and zero-point Energies= | -135.069207 |
| Sum of electronic and thermal Energies= | -135.064841 |
| Sum of electronic and thermal Enthalpies= | -135.063896 |
| Sum of electronic and thermal Free Energies= | -135.094639 |

**A1-TS**

| | |
|---|---|
| Zero-point correction= | 0.235918 (Hartree/Particle) |
| Thermal correction to Energy= | 0.249683 |
| Thermal correction to Enthalpy= | 0.250627 |
| Thermal correction to Gibbs Free Energy= | 0.194348 |
| Sum of electronic and zero-point Energies= | -216.442398 |
| Sum of electronic and thermal Energies= | -216.428633 |
| Sum of electronic and thermal Enthalpies= | -216.427689 |
| Sum of electronic and thermal Free Energies= | -216.483968 |

| | | | |
|---|---|---|---|
| C | -2.15929836 | -0.68914692 | -1.33888310 |
| C | -2.87944798 | 0.10059747 | -0.39675447 |
| C | -2.61720566 | -0.41748991 | 0.90554955 |
| C | -1.73420968 | -1.52709940 | 0.76847028 |
| C | -1.44870593 | -1.69385245 | -0.61888330 |
| H | -2.14738372 | -0.54739080 | -2.40831530 |
| H | -3.50824808 | 0.94632977 | -0.62756531 |

| | | | |
|---|---|---|---|
| H | -3.01294564 | -0.03267405 | 1.83246175 |
| H | -1.34488265 | -2.13057128 | 1.57396570 |
| H | -0.80846751 | -2.44874310 | -1.04956749 |
| Fe | -0.77375936 | 0.24167480 | 0.01447618 |
| C | 0.06803352 | 1.92517254 | 1.05378684 |
| C | -0.01547037 | 2.22387867 | -0.33843557 |
| C | 0.91590308 | 0.79449549 | 1.21595331 |
| H | -0.43407308 | 2.45838380 | 1.84600166 |
| C | 0.77918699 | 1.27702915 | -1.04046820 |
| H | -0.59370475 | 3.02007029 | -0.78087624 |
| C | 1.36573327 | 0.38247591 | -0.08256495 |
| H | 1.17143566 | 0.32385218 | 2.15298049 |
| H | 0.91851165 | 1.22413649 | -2.11026594 |
| C | 2.28191748 | -0.72480711 | -0.39385141 |
| H | 2.19071448 | -1.05302702 | -1.42857991 |
| C | 2.33674297 | -1.87005309 | 0.58552378 |
| H | 1.37359556 | -2.39006206 | 0.62471445 |
| H | 3.10807176 | -2.58359797 | 0.29358517 |
| H | 2.57669483 | -1.50737930 | 1.58669139 |
| O | 3.80408962 | -0.10683259 | -0.37325545 |
| H | 3.74733347 | 0.87137612 | -0.32845378 |
| H | 5.08929873 | -0.26678911 | -0.48377020 |

**A2-INT**

| | |
|---|---|
| Zero-point correction= | 0.244405 (Hartree/Particle) |
| Thermal correction to Energy= | 0.258045 |
| Thermal correction to Enthalpy= | 0.258990 |
| Thermal correction to Gibbs Free Energy= | 0.203769 |
| Sum of electronic and zero-point Energies= | -216.299133 |
| Sum of electronic and thermal Energies= | -216.285493 |
| Sum of electronic and thermal Enthalpies= | -216.284549 |
| Sum of electronic and thermal Free Energies= | -216.339770 |

| | | | |
|---|---|---|---|
| C | -2.17022693 | -0.65320693 | -1.34612509 |
| C | -2.84640787 | 0.18495566 | -0.40993512 |
| C | -2.61811153 | -0.33732523 | 0.89487273 |
| C | -1.79570426 | -1.49522125 | 0.77140607 |
| C | -1.52467064 | -1.69205475 | -0.61660853 |
| H | -2.15828081 | -0.52667340 | -2.41751676 |
| H | -3.42909164 | 1.06102735 | -0.64874478 |
| H | -2.99435978 | 0.07713155 | 1.81740141 |
| H | -1.46087605 | -2.12269198 | 1.58311533 |
| H | -0.94460581 | -2.49667217 | -1.04358550 |
| Fe | -0.76220962 | 0.19731290 | 0.00550529 |
| C | 0.08615243 | 1.90794009 | 1.07136665 |
| C | 0.01935046 | 2.21257017 | -0.33351747 |
| C | 0.89877700 | 0.77703628 | 1.25117633 |
| H | -0.41606184 | 2.45594166 | 1.85339527 |
| C | 0.78992753 | 1.27051289 | -1.03183547 |
| H | -0.54160119 | 3.02370276 | -0.77098888 |
| C | 1.35288837 | 0.35017092 | -0.05884617 |
| H | 1.13711426 | 0.30928985 | 2.19448517 |
| H | 0.93894493 | 1.22284824 | -2.10089593 |
| C | 2.14210283 | -0.78371627 | -0.37091668 |
| H | 2.18901259 | -1.05154216 | -1.42316219 |
| C | 2.38352995 | -1.88241672 | 0.60590213 |
| H | 1.48264176 | -2.50547400 | 0.64804054 |
| H | 3.20542137 | -2.52711276 | 0.29568591 |

| | | | |
|---|---|---|---|
| H | 2.57980882 | -1.50275352 | 1.60803842 |
| O | 3.90341387 | -0.02201818 | -0.42804542 |
| H | 3.94111355 | 0.94062167 | -0.32182106 |
| H | 4.75531492 | -0.46710226 | -0.55385750 |

**A3-TS**

| | |
|---|---|
| Zero-point correction= | 0.196424 (Hartree/Particle) |
| Thermal correction to Energy= | 0.207981 |
| Thermal correction to Enthalpy= | 0.208925 |
| Thermal correction to Gibbs Free Energy= | 0.156930 |
| Sum of electronic and zero-point Energies= | -1727.819705 |
| Sum of electronic and thermal Energies= | -1727.808148 |
| Sum of electronic and thermal Enthalpies= | -1727.807204 |
| Sum of electronic and thermal Free Energies= | -1727.859200 |

| | | | |
|---|---|---|---|
| C | -2.47312567 | 0.10586384 | -0.72644071 |
| C | -2.48172976 | 0.10718587 | 0.70008871 |
| C | -1.81144740 | -1.07389044 | 1.14175619 |
| C | -1.40139934 | -1.80239279 | -0.00446166 |
| C | -1.79683247 | -1.07515793 | -1.15709295 |
| H | -2.90530959 | 0.85916831 | -1.36747902 |
| H | -2.92215418 | 0.86150266 | 1.33434391 |
| H | -1.63869142 | -1.35886204 | 2.16877223 |
| H | -0.82679543 | -2.71712346 | -0.00038084 |
| H | -1.60926739 | -1.36114037 | -2.18126385 |
| Fe | -0.49653760 | 0.17154434 | 0.00103376 |
| C | 1.74409484 | 0.11279175 | 0.02573542 |
| C | 1.16439565 | 0.77542014 | 1.16406973 |
| C | 1.20102144 | 0.75560085 | -1.13943851 |
| C | 0.41235270 | 1.89788849 | 0.70285147 |
| H | 1.32397748 | 0.49815421 | 2.19538108 |
| C | 0.42660176 | 1.87980887 | -0.71949042 |
| H | 1.38835565 | 0.45739822 | -2.15997803 |
| H | -0.08359962 | 2.62248237 | 1.33069220 |
| H | -0.05780125 | 2.58681206 | -1.37594747 |
| C | 2.48403761 | -1.10870667 | 0.00824563 |
| C | 3.86706490 | -1.12923910 | -0.09723479 |
| H | 4.38485697 | -2.08565205 | -0.14812714 |
| H | 4.48510186 | -0.24063653 | -0.26406659 |
| H | 3.36109902 | -1.25329356 | 1.04964706 |

**A4-INT**

| | |
|---|---|
| Zero-point correction= | 0.202830 (Hartree/Particle) |
| Thermal correction to Energy= | 0.213000 |
| Thermal correction to Enthalpy= | 0.213945 |
| Thermal correction to Gibbs Free Energy= | 0.167196 |
| Sum of electronic and zero-point Energies= | -587.769528 |
| Sum of electronic and thermal Energies= | -587.759358 |
| Sum of electronic and thermal Enthalpies= | -587.758414 |
| Sum of electronic and thermal Free Energies= | -587.805162 |

| | | | |
|---|---|---|---|
| C | -2.48109241 | -0.06440091 | 0.25159224 |
| C | -1.75770207 | -0.84640763 | 1.21947162 |
| C | -0.90317174 | -1.75866122 | 0.50600285 |
| C | -1.10094525 | -1.54220029 | -0.90292552 |
| C | -2.07570533 | -0.49471997 | -1.06036667 |
| H | -3.18857938 | 0.72271538 | 0.47155384 |

| | | | |
|---|---|---|---|
| H | -1.82404593 | -0.74658353 | 2.29381448 |
| H | -0.20292791 | -2.45553562 | 0.94651154 |
| H | -0.58348844 | -2.05722375 | -1.70094176 |
| H | -2.42466685 | -0.08688214 | -1.99861599 |
| Fe | -0.44385334 | 0.18485019 | 0.00836922 |
| C | 1.59709518 | 0.37906228 | -0.21858021 |
| C | 1.18220663 | 0.83018503 | 1.08882666 |
| C | 0.89449382 | 1.18166222 | -1.19247049 |
| C | 0.24532579 | 1.90676600 | 0.91819040 |
| H | 1.50040316 | 0.40938045 | 2.03334580 |
| C | 0.06604767 | 2.12383859 | -0.49363333 |
| H | 0.97604754 | 1.06856515 | -2.26594249 |
| H | -0.25642833 | 2.44210645 | 1.71194049 |
| H | -0.59080674 | 2.85247244 | -0.94702383 |
| C | 2.48859577 | -0.73199973 | -0.54515950 |
| H | 2.51723387 | -1.00837830 | -1.60124114 |
| C | 3.25422236 | -1.40958341 | 0.33376438 |
| H | 3.89076559 | -2.23023867 | 0.01825543 |
| H | 3.27045777 | -1.15774861 | 1.39246936 |

**B-INT**

| | |
|---|---|
| Zero-point correction= | 0.026613 (Hartree/Particle) |
| Thermal correction to Energy= | 0.029481 |
| Thermal correction to Enthalpy= | 0.030425 |
| Thermal correction to Gibbs Free Energy= | 0.004952 |
| Sum of electronic and zero-point Energies= | -114.477348 |
| Sum of electronic and thermal Energies= | -114.474480 |
| Sum of electronic and thermal Enthalpies= | -114.473536 |
| Sum of electronic and thermal Free Energies= | -114.499009 |

| | | | |
|---|---|---|---|
| C | -0.00000533 | 0.52683613 | 0.00000000 |
| H | 0.93918978 | 1.12431070 | 0.00000000 |
| H | -0.93911521 | 1.12445570 | 0.00000000 |
| O | -0.00000533 | -0.67622290 | 0.00000000 |

**B-TS**

| | |
|---|---|
| Zero-point correction= | 0.028711 (Hartree/Particle) |
| Thermal correction to Energy= | 0.032315 |
| Thermal correction to Enthalpy= | 0.033259 |
| Thermal correction to Gibbs Free Energy= | 0.005353 |
| Sum of electronic and zero-point Energies= | -23.290177 |
| Sum of electronic and thermal Energies= | -23.286573 |
| Sum of electronic and thermal Enthalpies= | -23.285629 |
| Sum of electronic and thermal Free Energies= | -23.313535 |

| | | | |
|---|---|---|---|
| C | 0.64828202 | 0.00005738 | 0.05404883 |
| H | 1.19469707 | 0.93707253 | 0.18242859 |
| H | 1.19475427 | -0.93676040 | 0.18360202 |
| O | -0.57071573 | -0.00018238 | -0.20022195 |
| H | -1.71341765 | 0.00080261 | 0.91145205 |

**B1-INT**

| | |
|---|---|
| Zero-point correction= | 0.040633 (Hartree/Particle) |
| Thermal correction to Energy= | 0.043553 |
| Thermal correction to Enthalpy= | 0.044497 |
| Thermal correction to Gibbs Free Energy= | 0.018612 |
| Sum of electronic and zero-point Energies= | -114.750553 |

| | |
|---|---|
| Sum of electronic and thermal Energies= | -114.747633 |
| Sum of electronic and thermal Enthalpies= | -114.746689 |
| Sum of electronic and thermal Free Energies= | -114.772573 |

| | | | |
|---|---|---|---|
| C | 0.04874331 | 0.62410321 | -0.00000000 |
| C | 0.04874331 | 0.62410321 | -0.00000000 |
| H | -0.87999024 | 1.20627340 | -0.00000000 |
| H | 1.03422188 | 1.09903690 | 0.00000000 |
| O | 0.04874331 | -0.62457596 | 0.00000000 |
| H | -0.83663804 | -1.05332190 | 0.00000000 |

**Formaldehyde**

| | |
|---|---|
| Zero-point correction= | 0.112555 (Hartree/Particle) |
| Thermal correction to Energy= | 0.119076 |
| Thermal correction to Enthalpy= | 0.120021 |
| Thermal correction to Gibbs Free Energy= | 0.082291 |
| Sum of electronic and zero-point Energies= | -633.969392 |
| Sum of electronic and thermal Energies= | -633.962870 |
| Sum of electronic and thermal Enthalpies= | -633.961926 |
| Sum of electronic and thermal Free Energies= | -633.999656 |

| | | | |
|---|---|---|---|
| N | 0.00000000 | 0.56634100 | -0.15000200 |
| H | 0.00000000 | 1.32709400 | 0.52482200 |
| C | 1.21323500 | -0.22283900 | 0.02051200 |
| H | 1.27616700 | -0.96894400 | -0.78334400 |
| H | 2.09184700 | 0.42871500 | -0.06122700 |
| H | 1.27380200 | -0.76847500 | 0.98409600 |
| C | -1.21323500 | -0.22283900 | 0.02051200 |
| H | -2.09184700 | 0.42871400 | -0.06122800 |
| H | -1.27616600 | -0.96894400 | -0.78334300 |
| H | -1.27380200 | -0.76847400 | 0.98409700 |

**BC-TS1**

| | |
|---|---|
| Zero-point correction= | 0.126027 (Hartree/Particle) |
| Thermal correction to Energy= | 0.133367 |
| Thermal correction to Enthalpy= | 0.134311 |
| Thermal correction to Gibbs Free Energy= | 0.095416 |
| Sum of electronic and zero-point Energies= | -249.917196 |
| Sum of electronic and thermal Energies= | -249.909856 |
| Sum of electronic and thermal Enthalpies= | -249.908912 |
| Sum of electronic and thermal Free Energies= | -249.947808 |

| | | | |
|---|---|---|---|
| C | -0.77064812 | -0.30877759 | 1.07853059 |
| H | -0.98219677 | 0.67170677 | 1.57343438 |
| H | -2.26739646 | -0.80214738 | -0.38578089 |
| O | -1.69235630 | -0.00401313 | -0.41815327 |
| H | -2.17391162 | 0.63955535 | -1.50330337 |
| N | 0.67974726 | -0.01268617 | 0.45773269 |
| H | 1.28877769 | -0.02909005 | 1.28486177 |
| C | 0.85127752 | 1.31511009 | -0.25391608 |
| H | 0.10396488 | 1.35667365 | -1.04903253 |
| H | 0.65952594 | 2.11884871 | 0.46238610 |
| H | 1.86341401 | 1.41196710 | -0.66825820 |
| C | 1.06579054 | -1.16386913 | -0.43351003 |
| H | 0.94334681 | -2.08499833 | 0.13868715 |
| H | 0.36863166 | -1.16794503 | -1.27260824 |
| H | 2.09794379 | -1.04844280 | -0.78591571 |

**BC-INT1**

| | |
|---|---|
| Zero-point correction= | 0.142506 (Hartree/Particle) |
| Thermal correction to Energy= | 0.151107 |
| Thermal correction to Enthalpy= | 0.152052 |
| Thermal correction to Gibbs Free Energy= | 0.109238 |
| Sum of electronic and zero-point Energies= | -250.449814 |
| Sum of electronic and thermal Energies= | -250.441213 |
| Sum of electronic and thermal Enthalpies= | -250.440268 |
| Sum of electronic and thermal Free Energies= | -250.483082 |

| | | | |
|---|---|---|---|
| N | 0.62366353 | 0.05915312 | -0.30398410 |
| H | 0.28664351 | 0.15068705 | -1.25805064 |
| C | 1.68026824 | -0.95540112 | -0.19562440 |
| H | 1.86445934 | -1.16510715 | 0.85880015 |
| H | 1.36255472 | -1.87229071 | -0.69062272 |
| H | 2.60626315 | -0.59938826 | -0.65645268 |
| C | 0.97003512 | 1.36564859 | 0.27330375 |
| H | 0.16598038 | 2.08002013 | 0.09443266 |
| H | 1.12524588 | 1.25335858 | 1.34710132 |
| H | 1.88807794 | 1.75780371 | -0.17490956 |
| C | -0.97442861 | -0.79672613 | 0.73311704 |
| H | -1.31943468 | -1.75101660 | 0.35064228 |
| H | -1.41781756 | -0.37554525 | 1.62977239 |
| O | -1.98803657 | 0.20928117 | -0.44092581 |
| H | -2.28877277 | 1.03556817 | -0.03124761 |
| H | -2.78980061 | -0.28353886 | -0.67894870 |

**BC-TS2**

| | |
|---|---|
| Zero-point correction= | 0.143652 (Hartree/Particle) |
| Thermal correction to Energy= | 0.152080 |
| Thermal correction to Enthalpy= | 0.153024 |
| Thermal correction to Gibbs Free Energy= | 0.111630 |
| Sum of electronic and zero-point Energies= | -250.617959 |
| Sum of electronic and thermal Energies= | -250.609531 |
| Sum of electronic and thermal Enthalpies= | -250.608587 |
| Sum of electronic and thermal Free Energies= | -250.649981 |

| | | | |
|---|---|---|---|
| N | 1.00812722 | 0.07142081 | -0.51103437 |
| H | 1.61211296 | 0.17849591 | -1.32391946 |
| C | 1.24416348 | -1.25026892 | 0.10002945 |
| H | 0.51874261 | -1.36635925 | 0.91186293 |
| H | 1.07194603 | -2.03278883 | -0.64776818 |
| H | 2.26848769 | -1.35007083 | 0.49466205 |
| C | 1.26269595 | 1.16791197 | 0.44330678 |
| H | 1.15296964 | 2.13089493 | -0.07052056 |
| H | 0.50235227 | 1.09000339 | 1.22944566 |
| H | 2.27284632 | 1.11515411 | 0.88087521 |
| C | -1.87513218 | -0.18357164 | 0.87385886 |
| H | -2.19553107 | -1.23493811 | 0.72064597 |
| H | -2.85848904 | 0.33322160 | 0.92938020 |
| O | -1.59759792 | 0.13221614 | -0.79244742 |
| H | -0.55206501 | 0.11795737 | -0.79810179 |
| H | -1.85984303 | 1.05632647 | -0.91291262 |

**BC-INT2**

| | |
|---|---|
| Zero-point correction= | 0.145118 (Hartree/Particle) |
| Thermal correction to Energy= | 0.153043 |

| | |
|---|---|
| Thermal correction to Enthalpy= | 0.153987 |
| Thermal correction to Gibbs Free Energy= | 0.113930 |
| Sum of electronic and zero-point Energies= | -250.659988 |
| Sum of electronic and thermal Energies= | -250.652063 |
| Sum of electronic and thermal Enthalpies= | -250.651119 |
| Sum of electronic and thermal Free Energies= | -250.691177 |

| | | | |
|---|---|---|---|
| C | -0.00570658 | 0.00009918 | 1.41575733 |
| H | 0.30301226 | 0.88359509 | 1.99738989 |
| H | -1.49755104 | 0.00020740 | 0.48739961 |
| O | -2.12366276 | 0.00009515 | -0.34551136 |
| H | -3.03499140 | -0.00005749 | -0.02487304 |
| N | 0.94338272 | -0.00004926 | 0.20751603 |
| H | 1.94036537 | -0.00010856 | 0.46118933 |
| C | 0.70924469 | 1.22807220 | -0.61267438 |
| H | -0.34905561 | 1.22917993 | -0.89046414 |
| H | 0.93595454 | 2.09913114 | 0.00836735 |
| H | 1.36192996 | 1.21483008 | -1.49332885 |
| C | 0.70900578 | -1.22820897 | -0.61254294 |
| H | 0.93544888 | -2.09925515 | 0.00861546 |
| H | -0.34929294 | -1.22905556 | -0.89036044 |
| H | 1.36174927 | -1.21523190 | -1.49315234 |
| H | 0.30279036 | -0.88342583 | 1.99745567 |

**BC-TS3**

| | |
|---|---|
| Zero-point correction= | 0.107518 (Hartree/Particle) |
| Thermal correction to Energy= | 0.113297 |
| Thermal correction to Enthalpy= | 0.114241 |
| Thermal correction to Gibbs Free Energy= | 0.079120 |
| Sum of electronic and zero-point Energies= | -174.244585 |
| Sum of electronic and thermal Energies= | -174.238805 |
| Sum of electronic and thermal Enthalpies= | -174.237861 |
| Sum of electronic and thermal Free Energies= | -174.272982 |

| | | | |
|---|---|---|---|
| N | -0.03627316 | -0.06351894 | 0.27613121 |
| H | 0.02229143 | 0.03258746 | 1.51342978 |
| C | -0.29871439 | 1.33680797 | -0.11213058 |
| H | -0.24475276 | 1.44690169 | -1.20016573 |
| H | -1.30252070 | 1.58971713 | 0.24173638 |
| H | 0.42728420 | 2.00333864 | 0.39653470 |
| C | 1.32424110 | -0.45307547 | -0.10027474 |
| H | 1.41695841 | -1.51758474 | 0.11450779 |
| H | 1.50609939 | -0.27680524 | -1.16607260 |
| H | 2.04019812 | 0.13074625 | 0.51534901 |
| C | -1.07283931 | -1.10052454 | -0.08499590 |
| H | -1.38987258 | -0.83862125 | -1.11927207 |
| H | -1.93789779 | -0.82489513 | 0.55544162 |

**D-INT**

| | |
|---|---|
| Zero-point correction= | 0.111060 (Hartree/Particle) |
| Thermal correction to Energy= | 0.116305 |
| Thermal correction to Enthalpy= | 0.117249 |
| Thermal correction to Gibbs Free Energy= | 0.083657 |
| Sum of electronic and zero-point Energies= | -173.510835 |
| Sum of electronic and thermal Energies= | -173.505590 |
| Sum of electronic and thermal Enthalpies= | -173.504646 |
| Sum of electronic and thermal Free Energies= | -173.538238 |

| | | | |
|---|---|---|---|
| C | -0.00000002 | 1.40217652 | -0.00005565 |
| H | -0.94251399 | 1.94564922 | -0.00006181 |
| H | 0.94251395 | 1.94564923 | -0.00006181 |
| N | -0.00000000 | 0.12245424 | 0.00021570 |
| C | -1.25279042 | -0.66514664 | -0.00002356 |
| H | -2.11374823 | 0.00551542 | 0.00035702 |
| H | -1.26385290 | -1.29725619 | -0.89369412 |
| H | -1.26381939 | -1.29814815 | 0.89295227 |
| C | 1.25279044 | -0.66514661 | -0.00002356 |
| H | 1.26385311 | -1.29725590 | -0.89369431 |
| H | 2.11374823 | 0.00551547 | 0.00035739 |
| H | 1.26381924 | -1.29814839 | 0.89295209 |

**D-TS**

| | |
|---|---|
| Zero-point correction= | 0.112555 (Hartree/Particle) |
| Thermal correction to Energy= | 0.119076 |
| Thermal correction to Enthalpy= | 0.120021 |
| Thermal correction to Gibbs Free Energy= | 0.082291 |
| Sum of electronic and zero-point Energies= | -633.969392 |
| Sum of electronic and thermal Energies= | -633.962870 |
| Sum of electronic and thermal Enthalpies= | -633.961926 |
| Sum of electronic and thermal Free Energies= | -633.999656 |

| | | | |
|---|---|---|---|
| N | 0.98779925 | -0.00000000 | 0.39130765 |
| C | 1.38171907 | -1.22327193 | -0.29894837 |
| H | 2.46430608 | -1.20864792 | -0.47053894 |
| H | 1.14153640 | -2.09088578 | 0.32585160 |
| H | 0.86935155 | -1.33823869 | -1.26815833 |
| C | 1.38171905 | 1.22327195 | -0.29894835 |
| H | 1.14153635 | 2.09088578 | 0.32585163 |
| H | 2.46430606 | 1.20864796 | -0.47053892 |
| H | 0.86935152 | 1.33823872 | -1.26815831 |
| C | -0.27590638 | -0.00000002 | 0.96127542 |
| H | -0.47145783 | -0.90490183 | 1.53646394 |
| H | -0.47145784 | 0.90490177 | 1.53646397 |
| Cl | -1.75572103 | 0.00000000 | -0.30392132 |

**D1-INT**

| | |
|---|---|
| Zero-point correction= | 0.113751 (Hartree/Particle) |
| Thermal correction to Energy= | 0.123078 |
| Thermal correction to Enthalpy= | 0.120021 |
| Thermal correction to Gibbs Free Energy= | 0.080251 |
| Sum of electronic and zero-point Energies= | -633.969392 |
| Sum of electronic and thermal Energies= | -633.957843 |
| Sum of electronic and thermal Enthalpies= | -633.954723 |
| Sum of electronic and thermal Free Energies= | -633.998736 |

| | | | |
|---|---|---|---|
| N | 1.09025052 | -0.00032846 | 0.53161394 |
| C | 1.36814422 | -1.20036568 | -0.27062403 |
| H | 2.39608819 | -1.20065427 | -0.56766126 |
| H | 1.16517383 | -2.07417161 | 0.31261368 |
| H | 0.74544700 | -1.19976766 | -1.14076645 |
| C | 1.36909769 | 1.20013388 | -0.26965657 |
| H | 1.16682133 | 2.07363036 | 0.31428536 |
| H | 2.39704166 | 1.19984530 | -0.56669379 |
| H | 0.74640048 | 1.20073191 | -1.13979898 |

| | | | |
|---|---|---|---|
| C | -0.32197157 | 0.00006800 | 0.93969311 |
| H | -0.52494196 | -0.87373792 | 1.52293082 |
| H | -0.52424793 | 0.87356448 | 1.52363503 |
| Cl | -1.34622119 | 0.00105167 | -0.49156918 |

**D1-TS**

| | |
|---|---|
| Zero-point correction= | 0.311890 (Hartree/Particle) |
| Thermal correction to Energy= | 0.331611 |
| Thermal correction to Enthalpy= | 0.332555 |
| Thermal correction to Gibbs Free Energy= | 0.259638 |
| Sum of electronic and zero-point Energies= | -2361.932228 |
| Sum of electronic and thermal Energies= | -2361.912506 |
| Sum of electronic and thermal Enthalpies= | -2361.911562 |
| Sum of electronic and thermal Free Energies= | -2361.984480 |

| | | | |
|---|---|---|---|
| C | 3.84513894 | 1.17600441 | -0.16224563 |
| C | 3.47663272 | 0.98740796 | 1.19055190 |
| C | 2.13228519 | 1.47129577 | 1.35340310 |
| C | 1.68125002 | 1.95336548 | 0.09471619 |
| C | 2.72955739 | 1.73766966 | -0.84426587 |
| H | 4.78612673 | 0.89365361 | -0.61110566 |
| H | 4.09915985 | 0.56913330 | 1.96738904 |
| H | 1.57903558 | 1.49532236 | 2.28010664 |
| H | 0.70208402 | 2.35520156 | -0.12681555 |
| H | 2.68464248 | 1.96537330 | -1.89939009 |
| Fe | 2.09423009 | -0.14948531 | 0.01438039 |
| C | 0.20671280 | -1.45400532 | -0.24863609 |
| C | 1.06096128 | -1.80128882 | 0.87810972 |
| C | 1.06398346 | -1.51247553 | -1.41726436 |
| C | 2.32463320 | -2.19514321 | 0.38315526 |
| H | 0.75440447 | -1.85165449 | 1.91167604 |
| C | 2.31984959 | -2.00807689 | -1.04551920 |
| H | 0.75675592 | -1.24256905 | -2.41755084 |
| H | 3.14228682 | -2.59102506 | 0.96655017 |
| H | 3.14707082 | -2.20336664 | -1.71203549 |
| C | -1.13864040 | -1.10535930 | -0.26401218 |
| H | -1.56324969 | -0.84334719 | -1.22545662 |
| C | -2.04043262 | -1.09144353 | 0.93075169 |
| H | -1.45081840 | -0.96517554 | 1.84159005 |
| H | -2.52846168 | -2.07181352 | 1.03551573 |
| N | -4.37423461 | -0.28887446 | 0.36842194 |
| C | -5.45393055 | 0.65213151 | 0.64318661 |
| H | -6.41404017 | 0.16449052 | 0.47132016 |
| H | -5.39986245 | 0.98680837 | 1.67843025 |
| H | -5.37690679 | 1.52676263 | -0.01681731 |
| C | -4.46709773 | -1.00103158 | -0.89639305 |
| H | -3.81401718 | -1.87303859 | -0.89873459 |
| H | -5.49342866 | -1.33448306 | -1.04734098 |
| H | -4.18549247 | -0.33960279 | -1.72826113 |
| C | -3.11542702 | 0.01260452 | 0.92306399 |
| H | -3.25477346 | 0.43386401 | 1.91977871 |
| H | -2.65848907 | 0.91398442 | 0.29217644 |
| Cl | -1.82913085 | 2.05825237 | -0.86738124 |

**$CI^-$**

| | |
|---|---|
| Zero-point correction= | 0.000000 (Hartree/Particle) |
| Thermal correction to Energy= | 0.001416 |

| | |
|---|---|
| Thermal correction to Enthalpy= | 0.002360 |
| Thermal correction to Gibbs Free Energy= | -0.015677 |
| Sum of electronic and zero-point Energies= | -460.136242 |
| Sum of electronic and thermal Energies= | -460.134826 |
| Sum of electronic and thermal Enthalpies= | -460.133882 |
| Sum of electronic and thermal Free Energies= | -460.151919 |

**E-INT**

| | |
|---|---|
| Zero-point correction= | 0.247197 (Hartree/Particle) |
| Thermal correction to Energy= | 0.261129 |
| Thermal correction to Enthalpy= | 0.262073 |
| Thermal correction to Gibbs Free Energy= | 0.204927 |
| Sum of electronic and zero-point Energies= | -1822.799407 |
| Sum of electronic and thermal Energies= | -1822.785475 |
| Sum of electronic and thermal Enthalpies= | -1822.784530 |
| Sum of electronic and thermal Free Energies= | -1822.841676 |

| | | | |
|---|---|---|---|
| C | -3.04818064 | -0.71174070 | -0.47182236 |
| C | -2.79744641 | -0.85720913 | 0.92442131 |
| C | -1.60512893 | -1.62461903 | 1.08046835 |
| C | -1.11936541 | -1.95293013 | -0.21876015 |
| C | -2.01048294 | -1.38818007 | -1.17857659 |
| H | -3.86702560 | -0.16613807 | -0.91577936 |
| H | -3.39368381 | -0.44170628 | 1.72261036 |
| H | -1.13945481 | -1.89086749 | 2.01712488 |
| H | -0.21638050 | -2.50312486 | -0.43603344 |
| H | -1.90699916 | -1.44529231 | -2.25156009 |
| Fe | -1.20038422 | 0.11036046 | 0.01163159 |
| C | 0.72939272 | 0.88070522 | -0.23415249 |
| C | 0.21166121 | 1.20817956 | 1.06262950 |
| C | -0.17393271 | 1.44271187 | -1.19742096 |
| C | -0.97553016 | 1.97637801 | 0.89465574 |
| H | 0.63881920 | 0.90609734 | 2.00654120 |
| C | -1.21521540 | 2.12118099 | -0.50344563 |
| H | -0.07376151 | 1.35860100 | -2.26960003 |
| H | -1.60026773 | 2.35742116 | 1.68835246 |
| H | -2.04991085 | 2.63522965 | -0.95542536 |
| C | 1.93904568 | 0.12789157 | -0.56122864 |
| H | 2.01472896 | -0.20285113 | -1.59619901 |
| C | 2.94199984 | -0.15967243 | 0.27548444 |
| H | 2.91827596 | 0.18939067 | 1.30499615 |
| C | 4.16844764 | -0.93480723 | -0.10582486 |
| H | 4.10380842 | -1.21873231 | -1.16893285 |
| H | 4.19611633 | -1.87009300 | 0.46823590 |
| N | 5.37953744 | -0.17950086 | 0.24938223 |
| H | 6.20839311 | -0.73809161 | 0.07158282 |
| H | 5.44898280 | 0.64996027 | -0.33257669 |
| H | -0.37794300 | 0.46464424 | 0.00608250 |

**$H_2O$**

| | |
|---|---|
| Zero-point correction= | 0.021088 (Hartree/Particle) |
| Thermal correction to Energy= | 0.023922 |
| Thermal correction to Enthalpy= | 0.024866 |
| Thermal correction to Gibbs Free Energy= | 0.003433 |
| Sum of electronic and zero-point Energies= | -76.384364 |
| Sum of electronic and thermal Energies= | -76.381529 |
| Sum of electronic and thermal Enthalpies= | -76.380585 |

| | | | |
|---|---|---|---|
| Sum of electronic and thermal Free Energies= | -76.402018 | | |
| O | 0.00000000 | 0.00000000 | 0.11751800 |
| H | 0.00000000 | 0.76688000 | -0.47007200 |
| H | 0.00000000 | -0.76688000 | -0.47007200 |

**$H^+$**

| | |
|---|---|
| Zero-point correction= | 0.000000 (Hartree/Particle) |
| Thermal correction to Energy= | 0.001416 |
| Thermal correction to Enthalpy= | 0.002360 |
| Thermal correction to Gibbs Free Energy= | -0.010000 |
| Sum of electronic and zero-point Energies= | 0.000000 |
| Sum of electronic and thermal Energies= | 0.001416 |
| Sum of electronic and thermal Enthalpies= | 0.002360 |

## 4. The change in the Gibbs free energy of the reaction system.

Table S1. Thermodynamic properties of the individual components involved in the reaction[a]

| Entry[b] | G[c] | U[d] | E[e] |
|---|---|---|---|
| **A-INT** | 0.190338 | -1804.321509 | -1804.320565 |
| **B-INT** | 0.004952 | -114.474480 | -114.473536 |
| **Dimethylamine** | 0.067354 | -135.064841 | -135.063896 |
| **E-INT** | 0.204927 | -1822.785475 | -1822.784530 |
| **$H_2O$** | 0.003433 | -76.381529 | -76.380585 |

[a] 1 Hartree per particle is equivalent to 627.51 kcal/mol; [b] **A-INT**, **B-INT**, and dimethylamine correspond to the reactants α-(hydroxy) alkyl ferrocenes (**1a**), formaldehyde (**2a**), and dimethylamine (**3a**), respectively, while the products are **E-INT** (ferrocenyl-substituted allylamine) and $H_2O$; [c] Thermal correction to the Gibbs free energy; [d] Sum of the electronic and thermal energies; [e] Sum of the electronic and thermal enthalpies.

△G = [G (**E-INT**) + 2*G (**$H_2O$**)] - [G (Dimethylamine) + G (**B-INT**) + G (**A-INT**)] * 627.51 kcal/mol = 31.9 kcal/mol

## 5. Refences

(1) Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene,

C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

(2) (a) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A **1988**, *38*, 3098-3100; (b) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. **1993**, *98*, 5648-5652; (c) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B, **1988**, *37*, 785-789; (d) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. **1980**, *58*, 1200-1211.

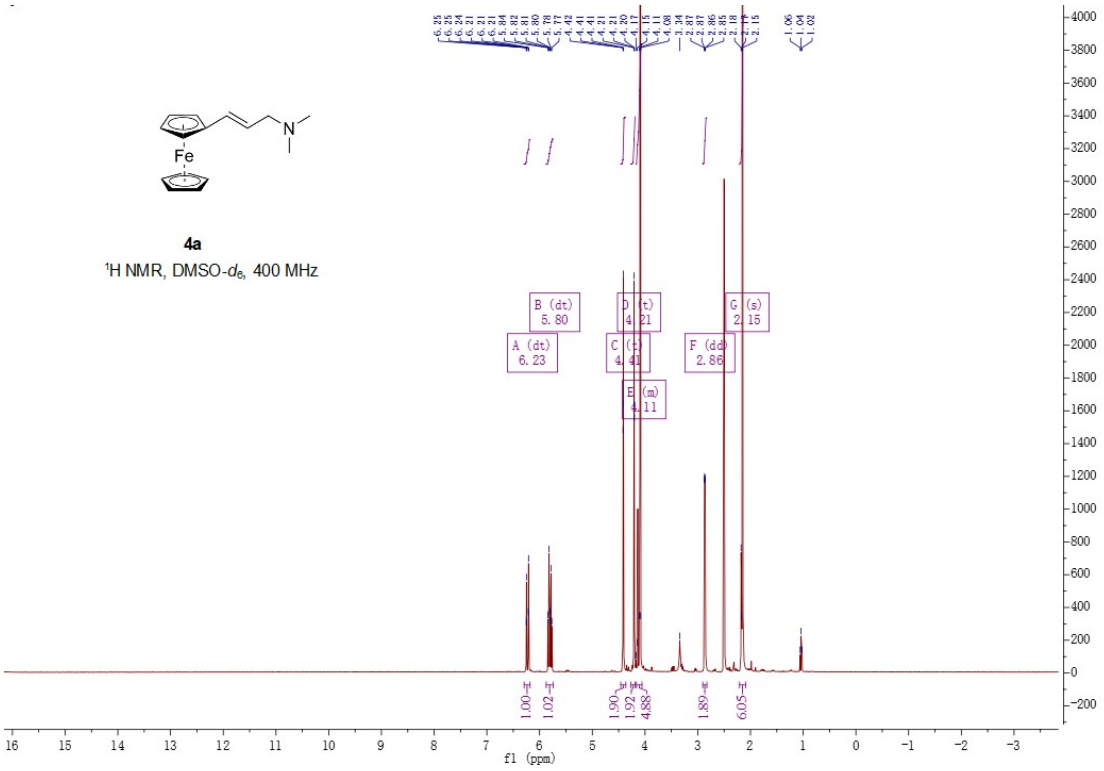
(3) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A., Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. J. Chem. Phys. **1971**, *54*, 724-728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A., Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J. Chem. Phys. **1972**, *56*, 2257-2261. (c) Hariharan, P. C.; Pople, J. A., The influence of polarization functions on molecular orbital hydrogenation energies. Theoret. Chim. Acta. **1973**, *28*, 213-222.

(4) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. **2010**, *132*, 154104-154119. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. **2011**, *32*, 1456-1465.

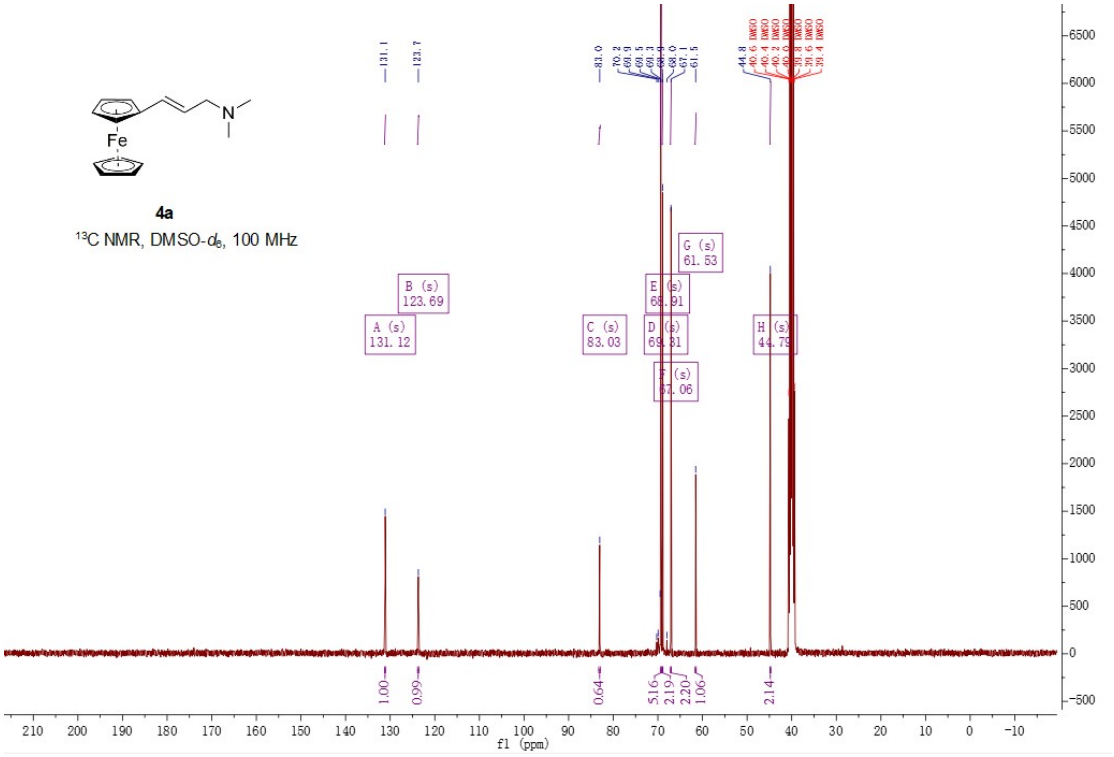
(5) (a) For the IRC method: Gonzalez, C.; Schlegel, H. B., An improved algorithm for reaction path following. J. Chem. Phys. **1989**, *90*, 2154-2161. (b) Gonzalez, C.; Schlegel, H. B., Improved algorithms for reaction path following: Higher-order implicit algorithms. J. Chem. Phys. **1991**, *95*, 5853-5860. For the IRC-implemented Hessian predictor-corrector and update algorithms: (c) Hratchian, H. P.; Schlegel, H. B., Accurate reaction paths using a Hessian based predictor– corrector integrator. J. Chem. Phys. **2004**, *120*, 9918-9924. (d) Hratchian, H. P.; Schlegel, H. B., Using Hessian Updating to Increase the Efficiency of a Hessian Based Predictor-Corrector Reaction Path Following Method. J. Chem. Theory Comput. **2005**, *1*, 61-69.

## 6. NMR Spectra

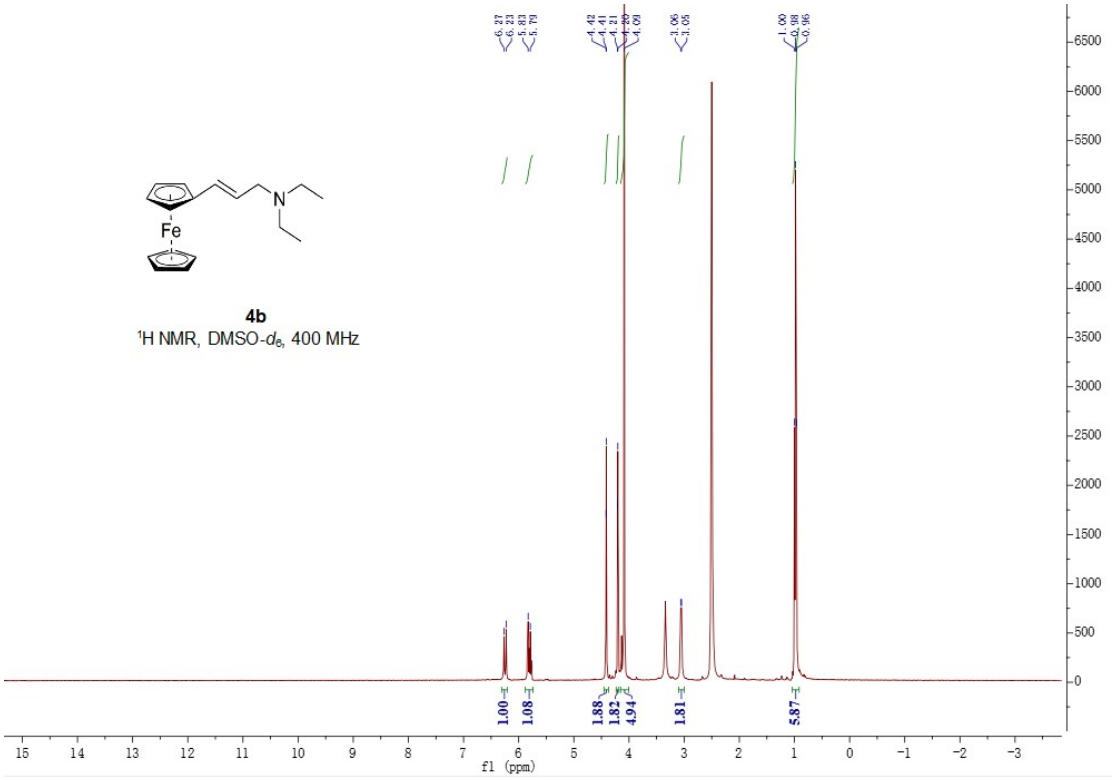
$^{1}$H NMR Spectrum of **4a**



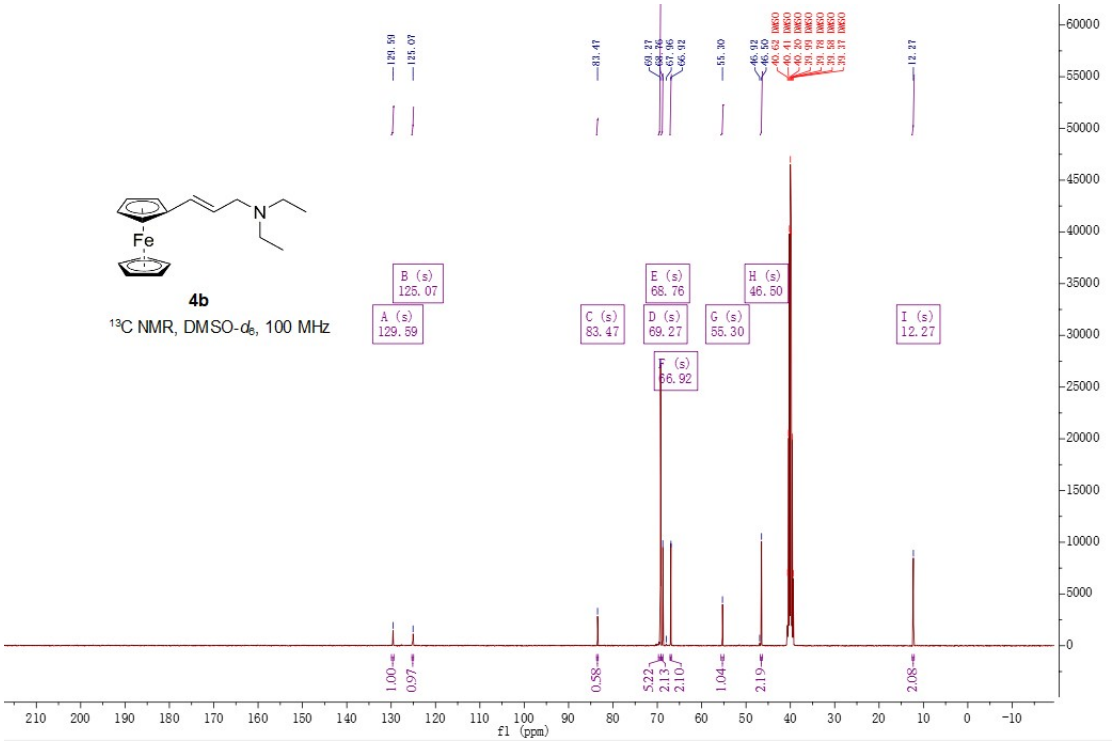

$^{13}$C NMR Spectrum of **4a**



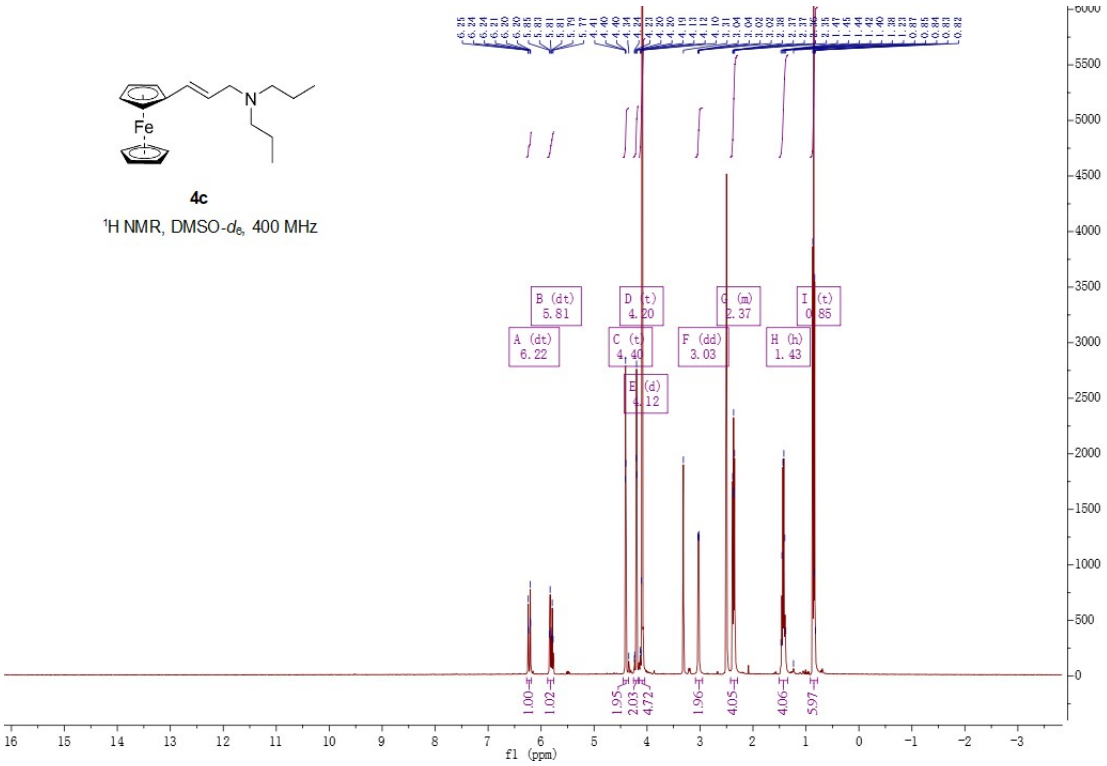
$^{1}$H NMR Spectrum of **4b**



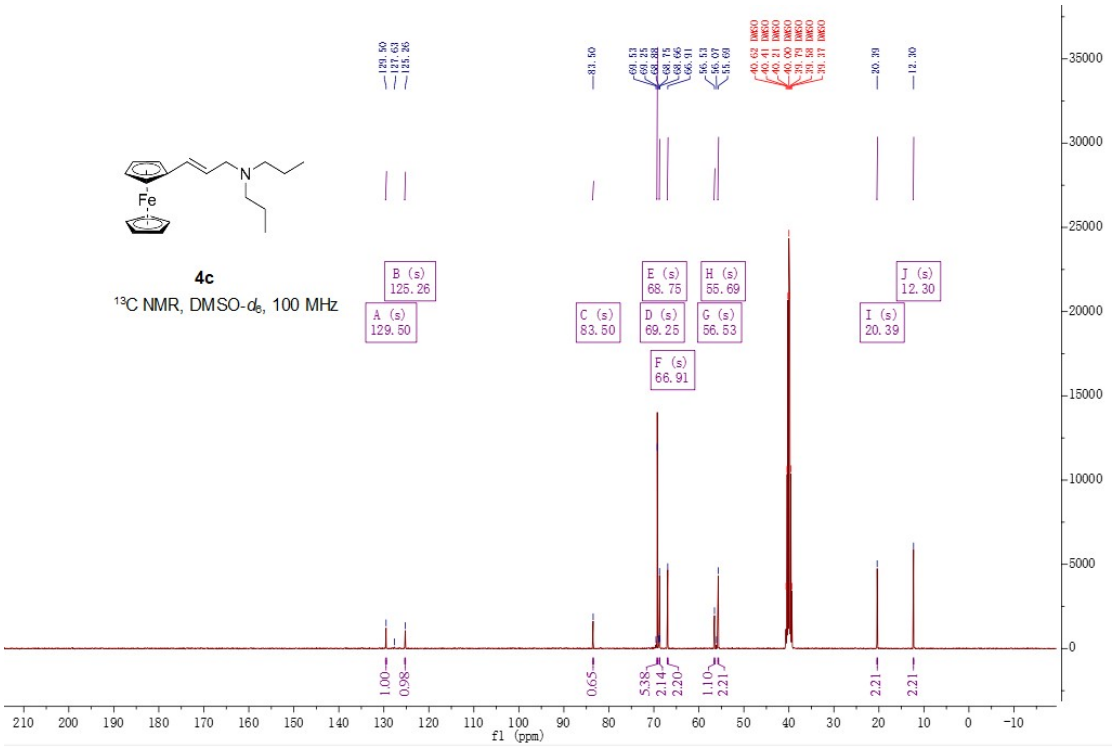

$^{13}$C NMR Spectrum of **4b**



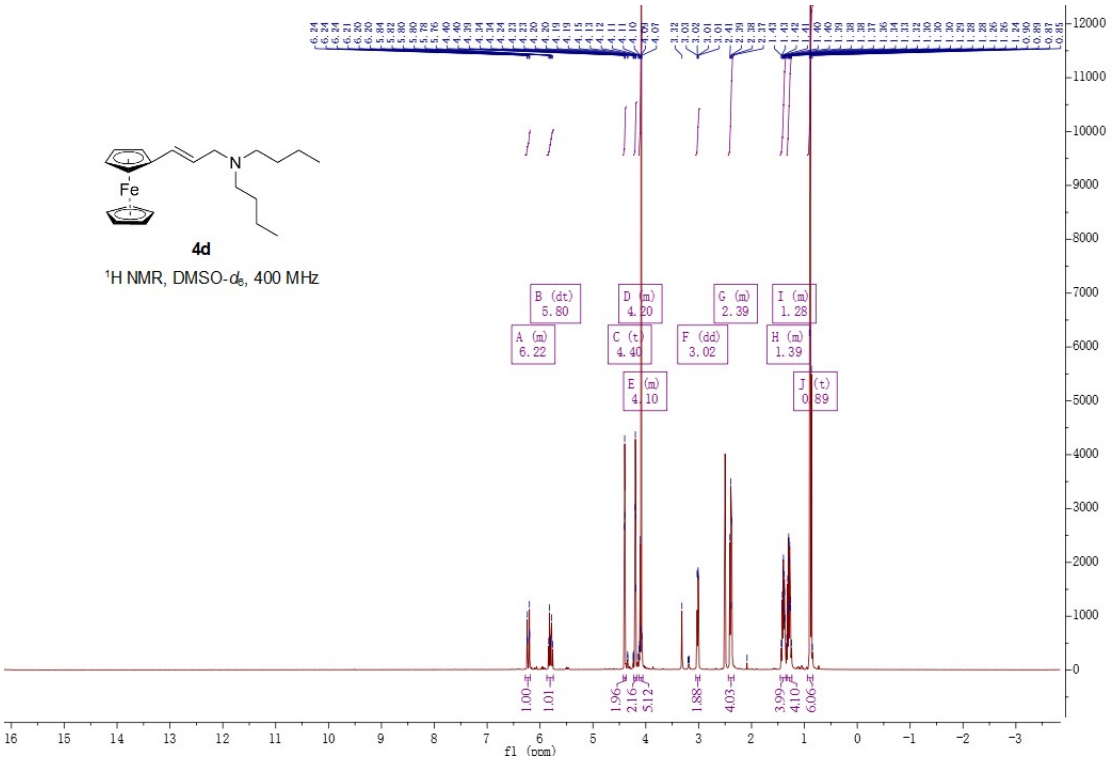
$^{1}$H NMR Spectrum of **4c**



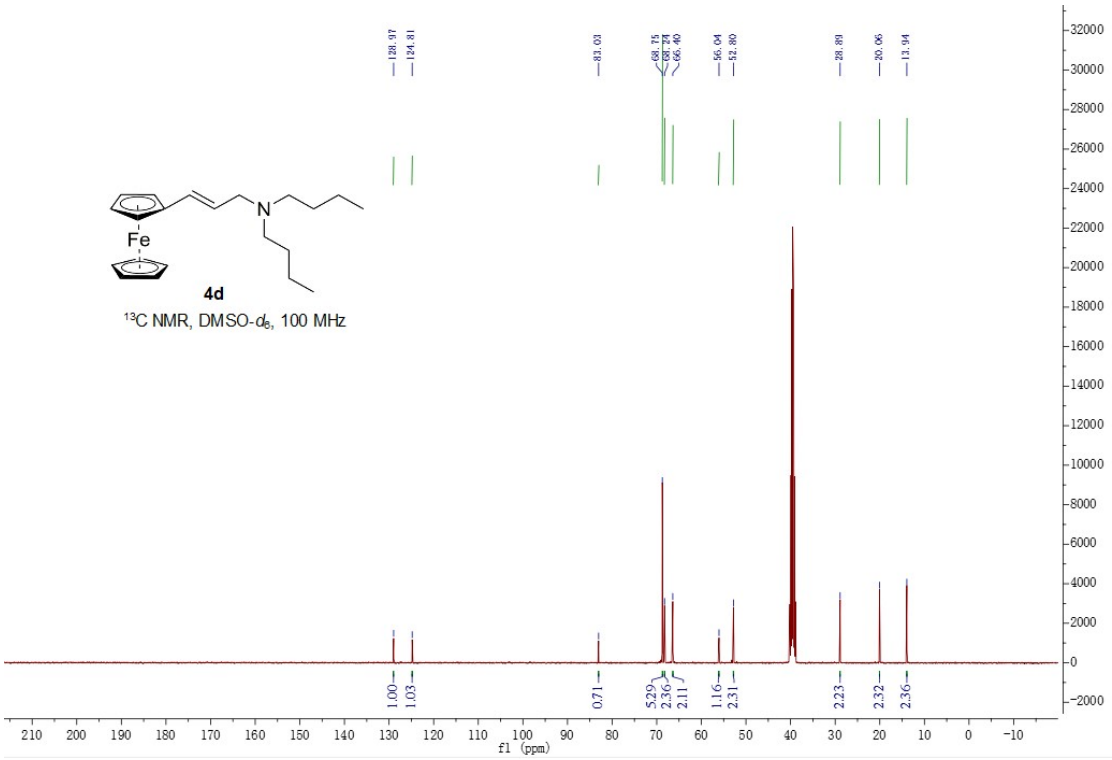

$^{13}$C NMR Spectrum of **4c**



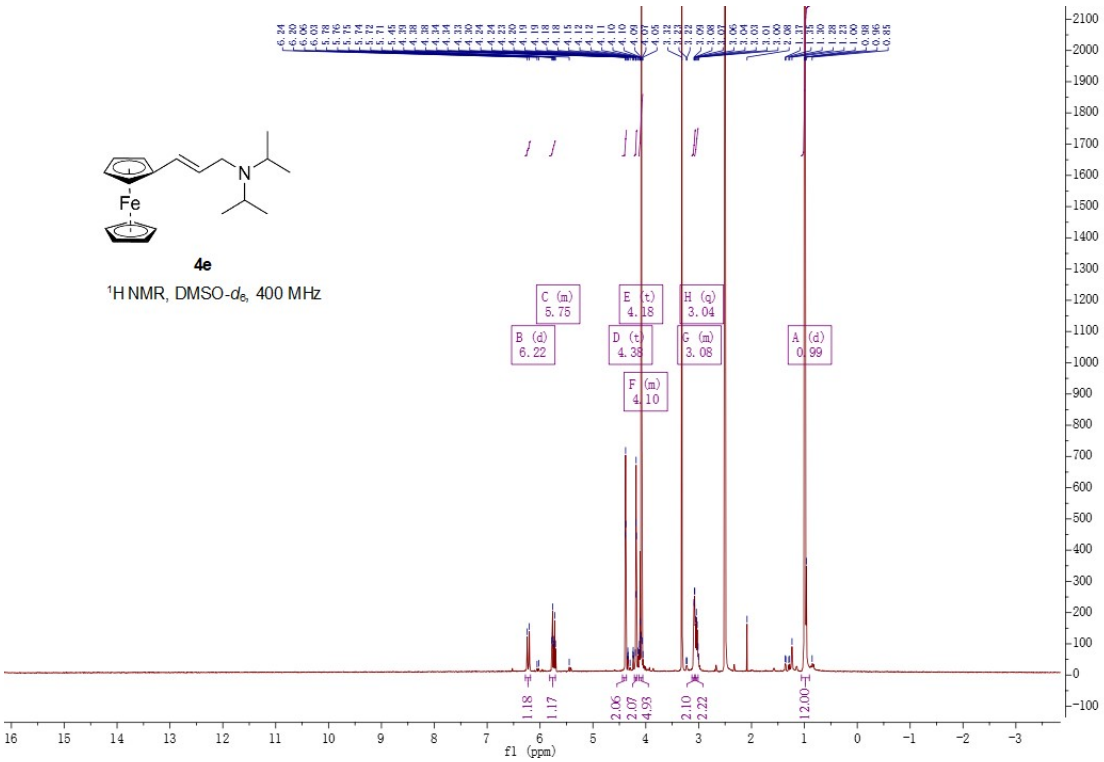
$^{1}$H NMR Spectrum of **4d**



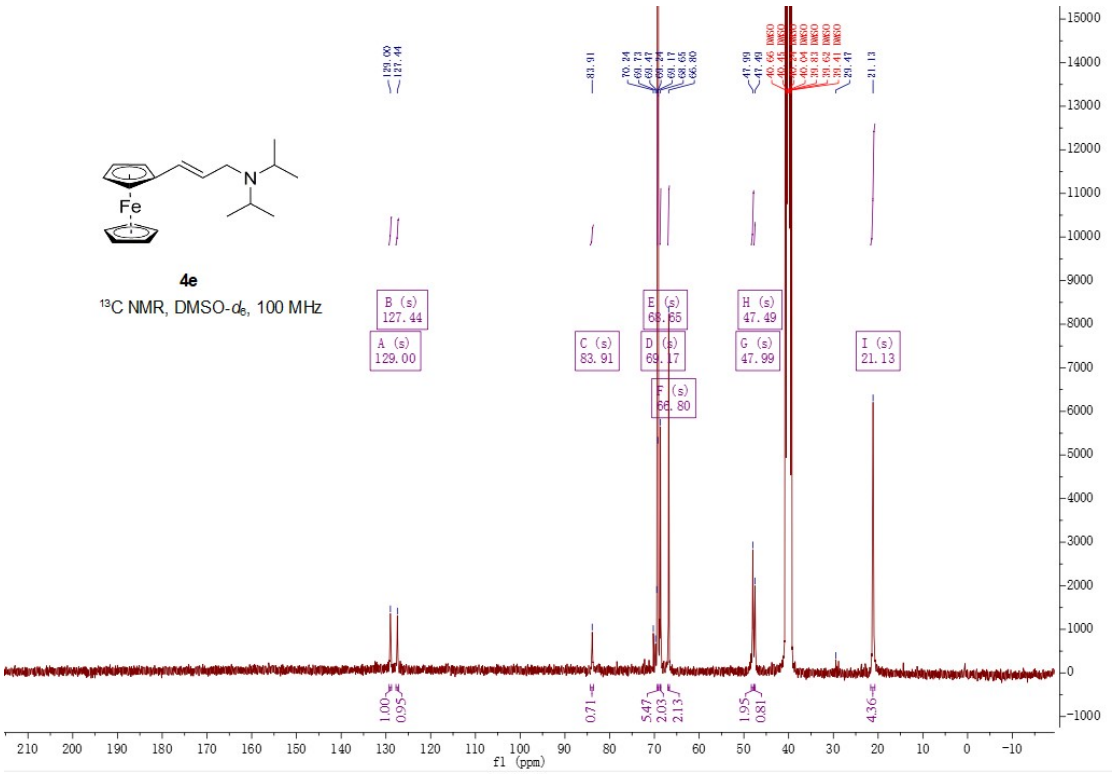

$^{13}$C NMR Spectrum of **4d**



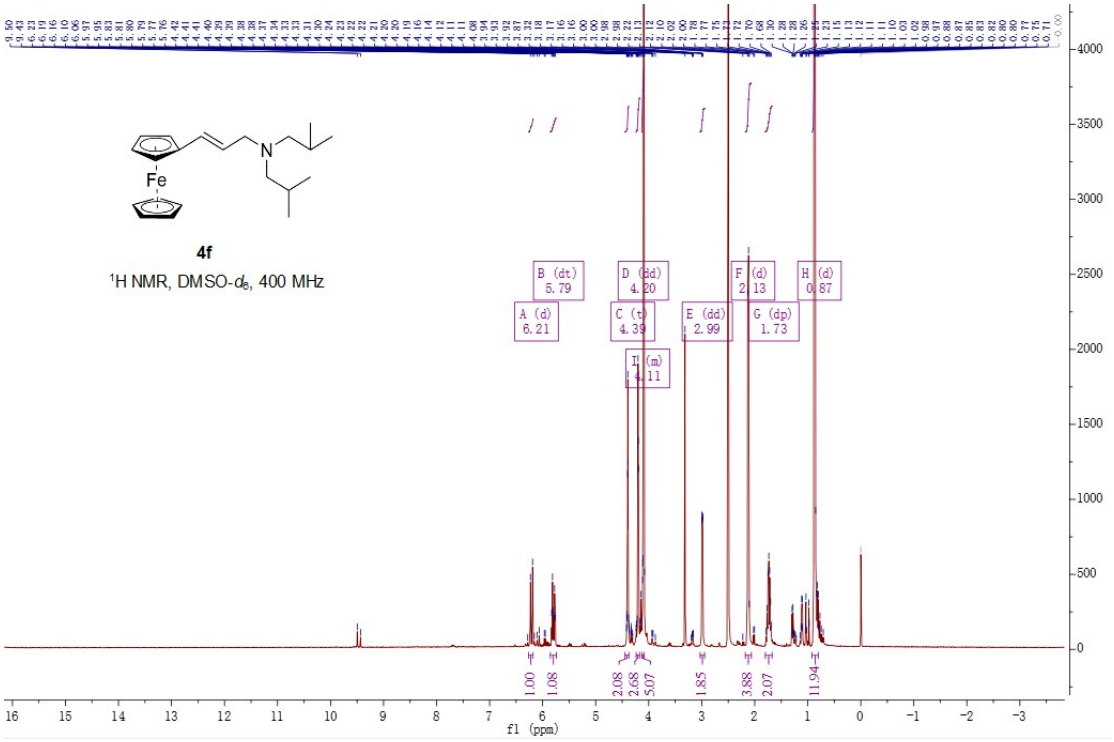
$^{1}$H NMR Spectrum of **4e**



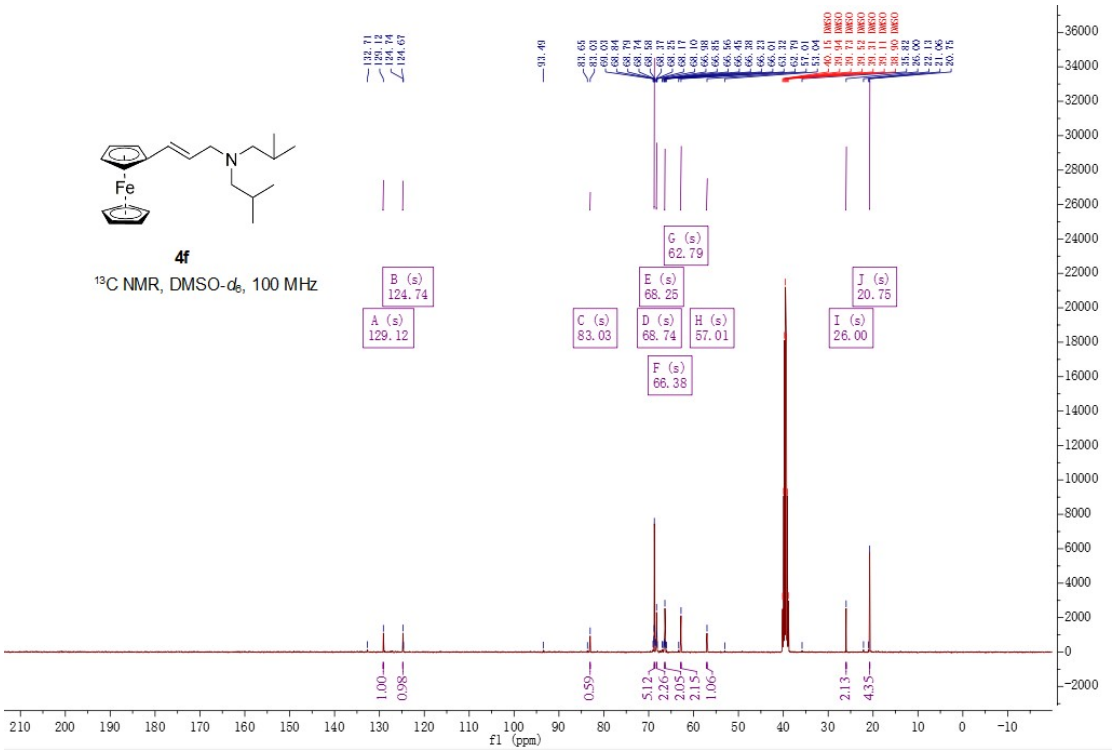

$^{13}$C NMR Spectrum of **4e**



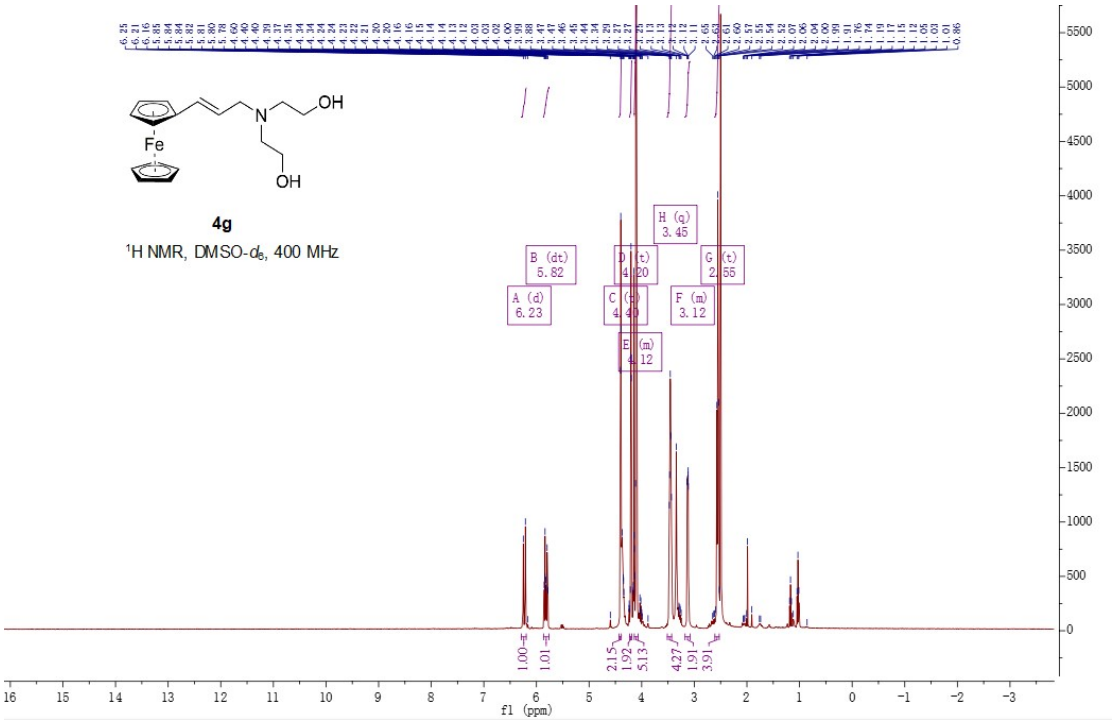
$^{1}$H NMR Spectrum of **4f**



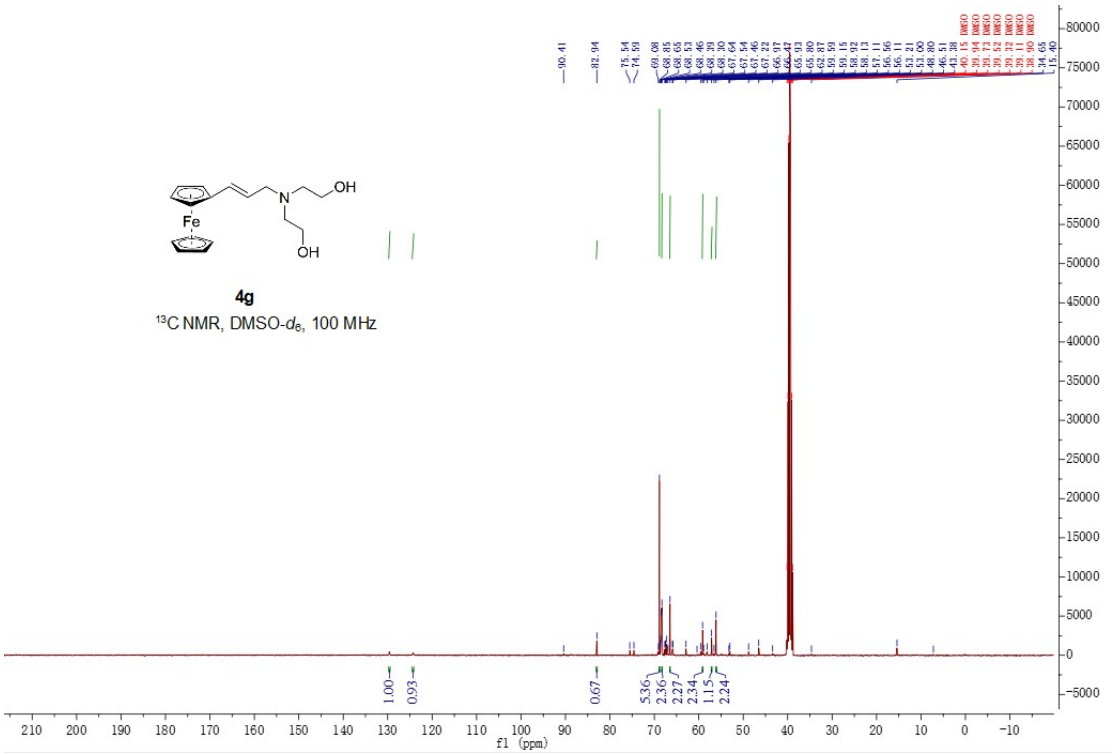

$^{13}$C NMR Spectrum of **4f**



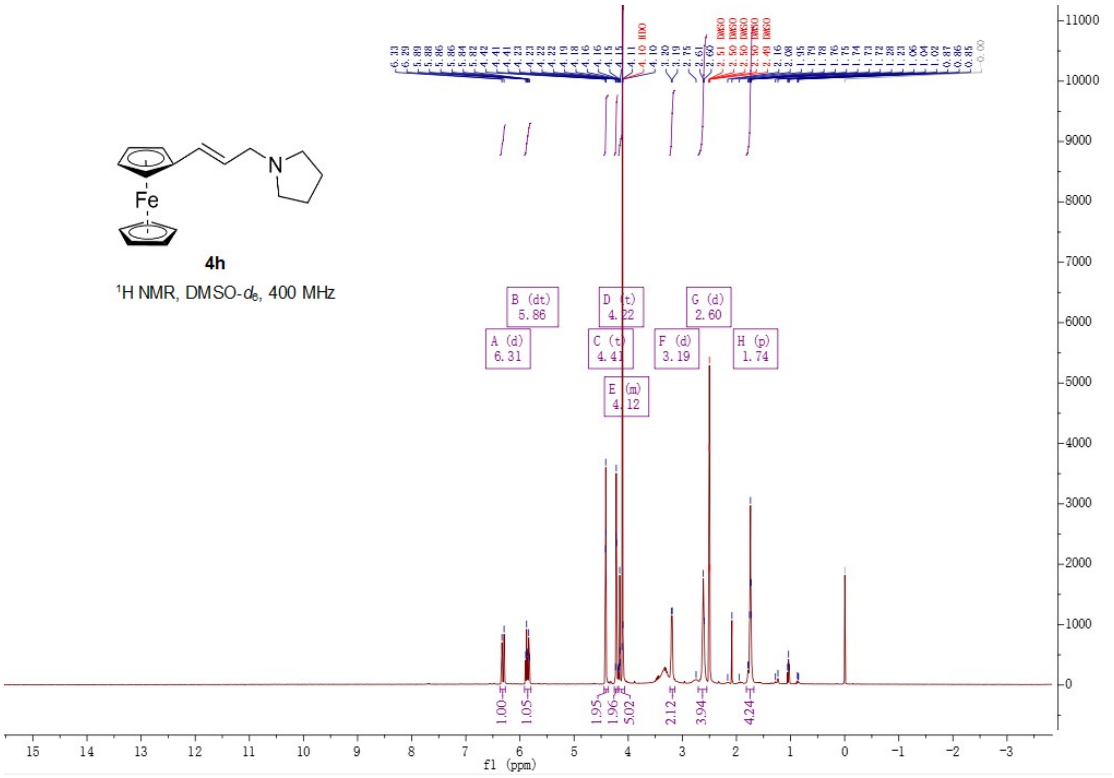
$^{1}$H NMR Spectrum of **4g**



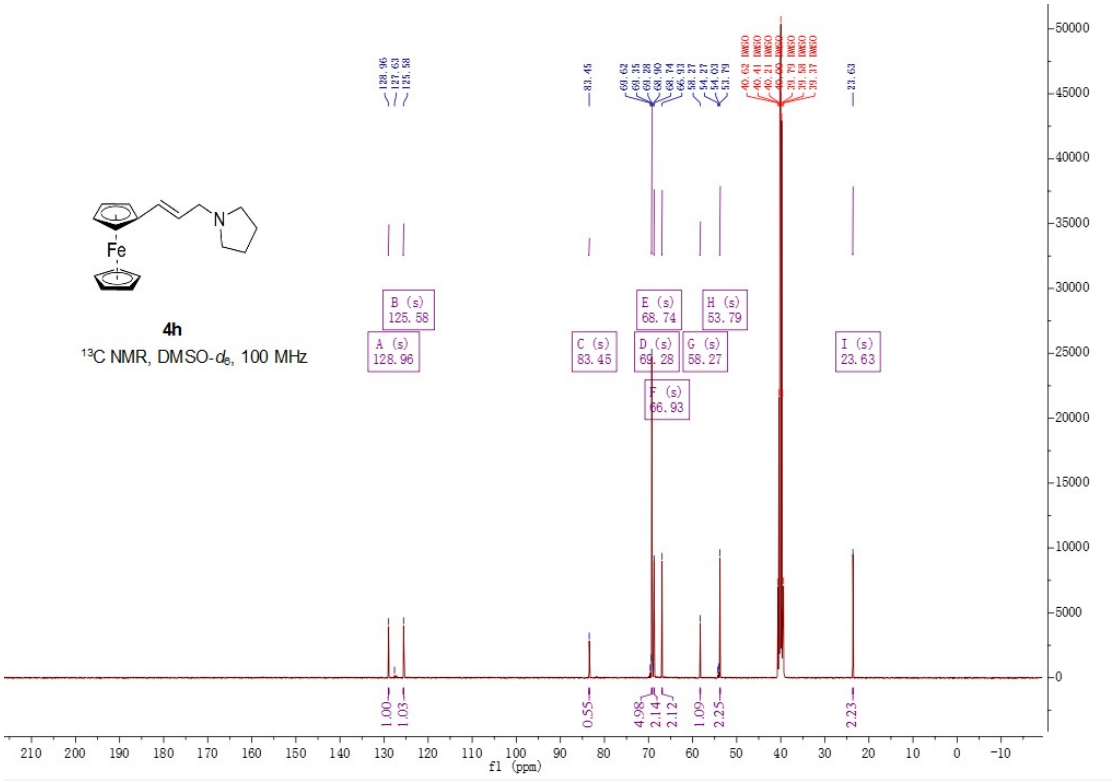

$^{13}$C NMR Spectrum of **4g**



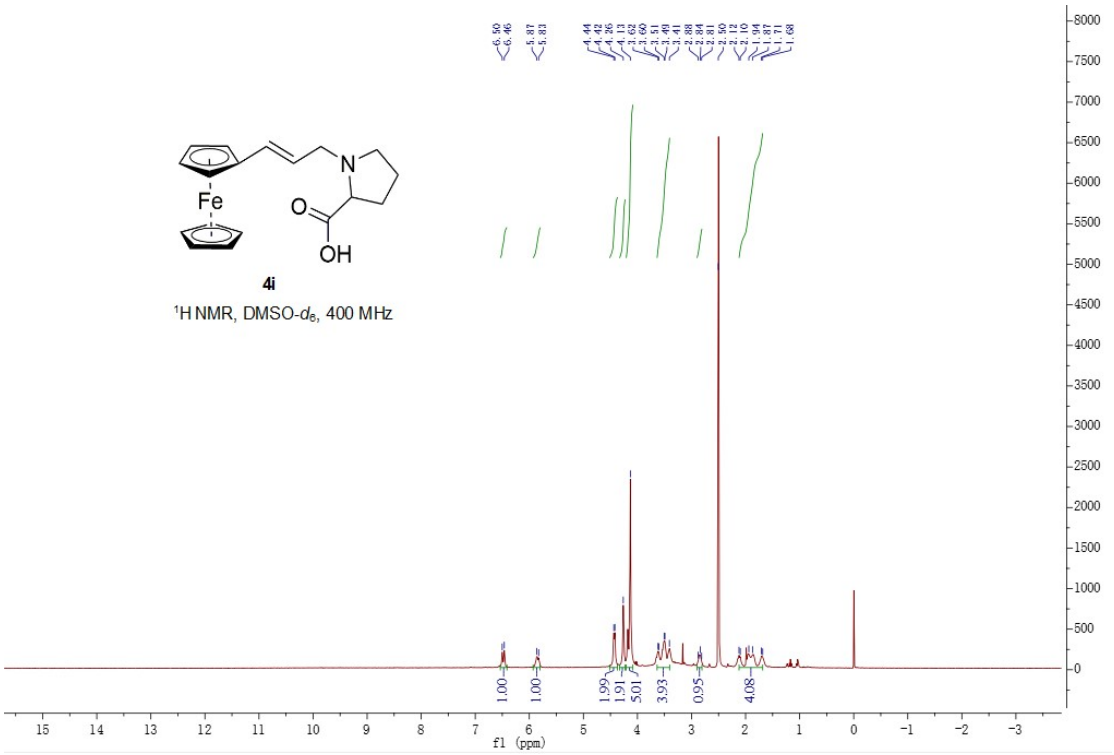
$^{1}$H NMR Spectrum of **4h**



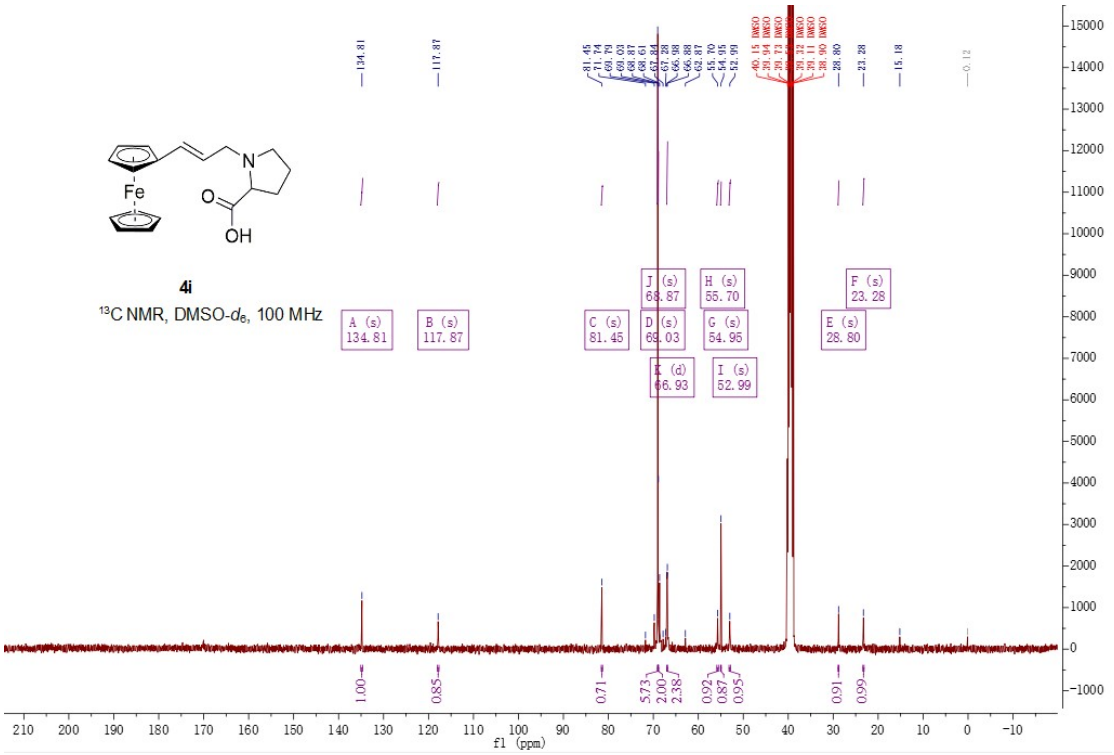

$^{13}$C NMR Spectrum of **4h**



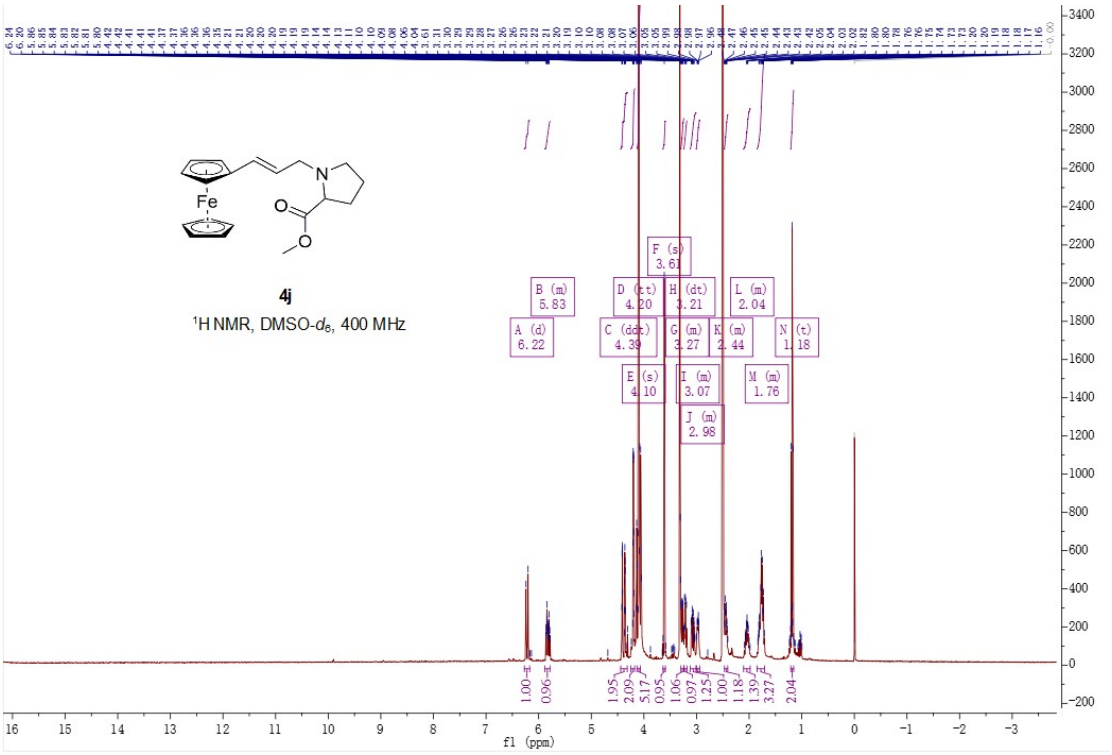
$^{1}$H NMR Spectrum of **4i**



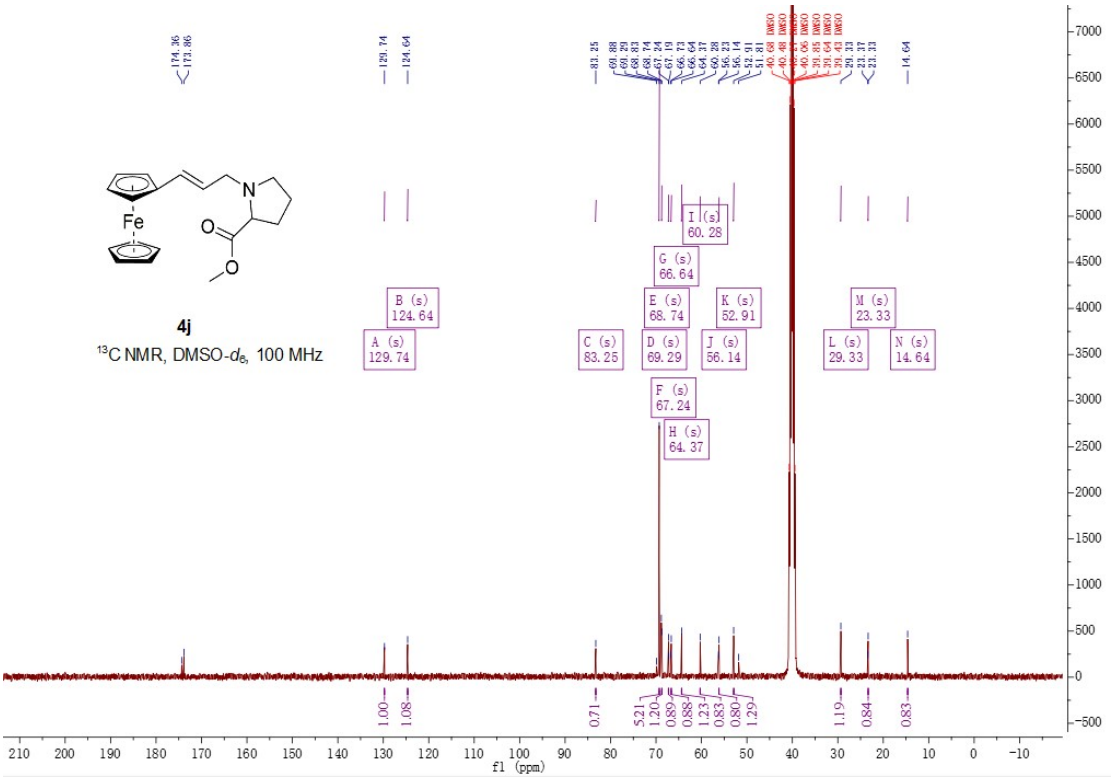

$^{13}$C NMR Spectrum of **4i**



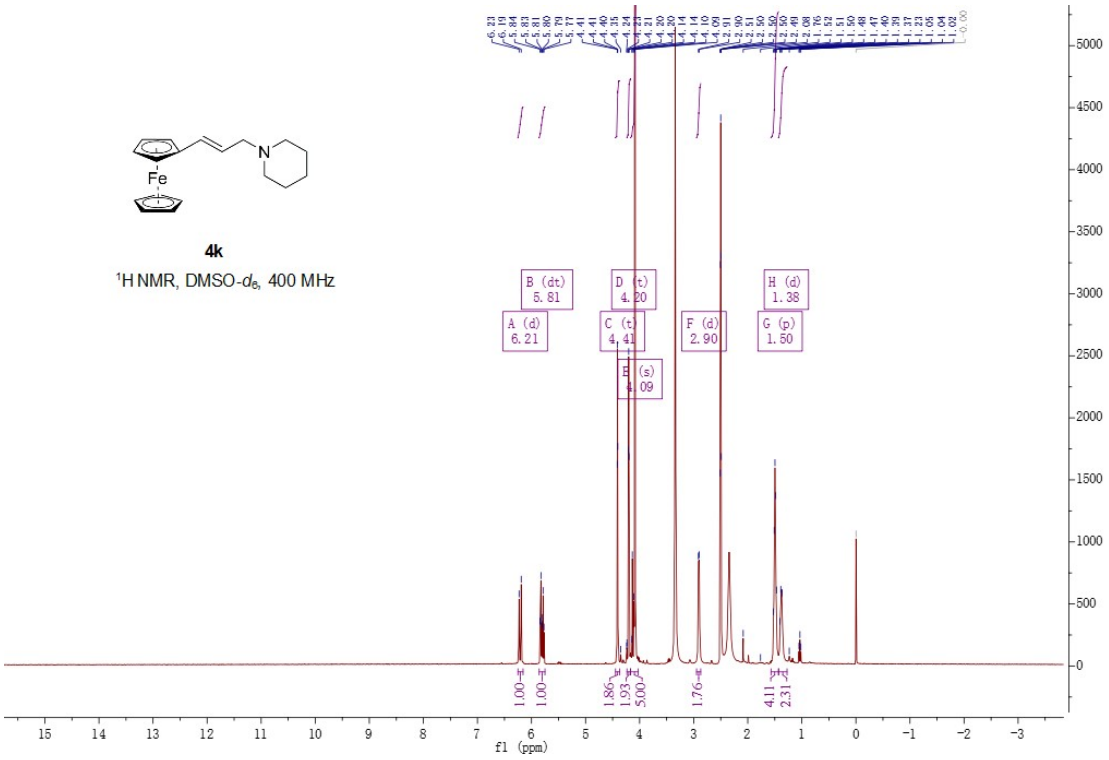
$^{1}$H NMR Spectrum of **4j**



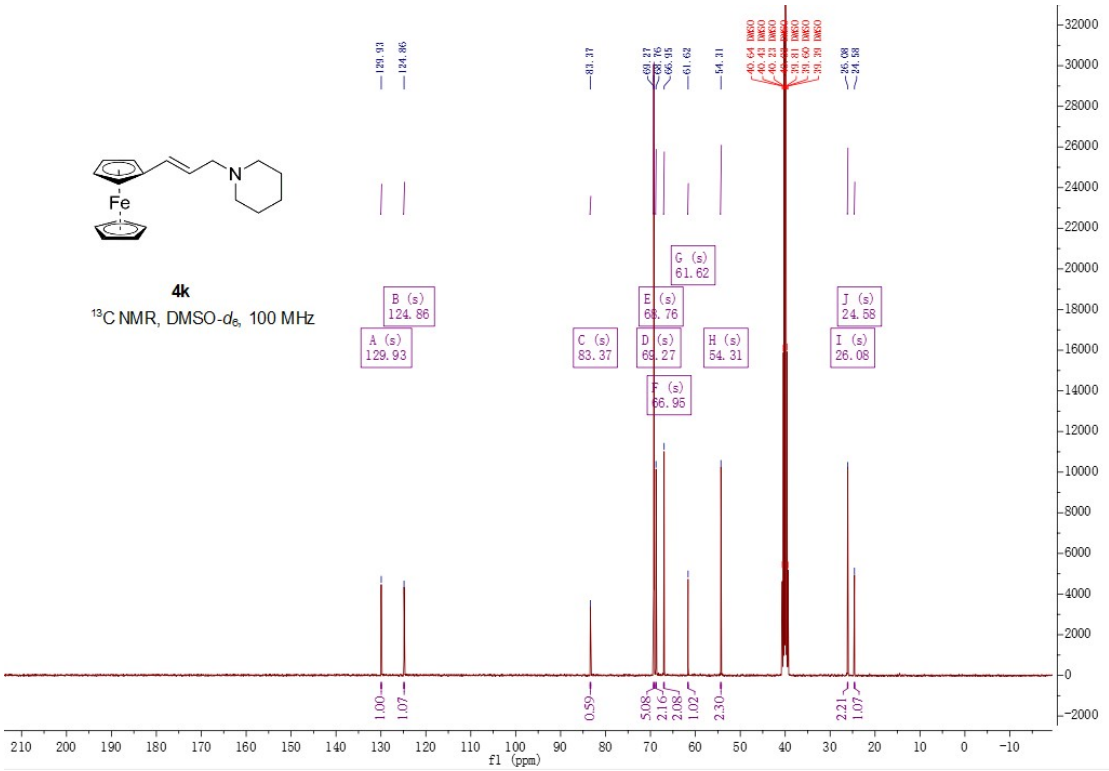

$^{13}$C NMR Spectrum of **4j**



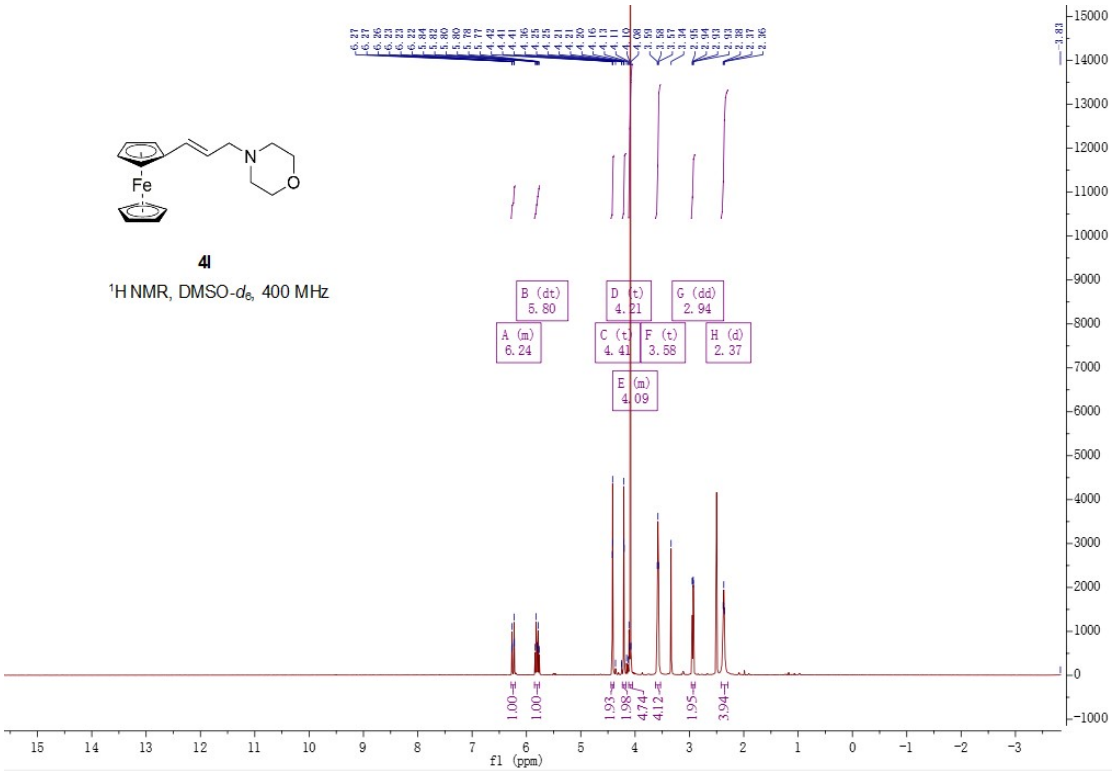
$^{1}$H NMR Spectrum of **4k**



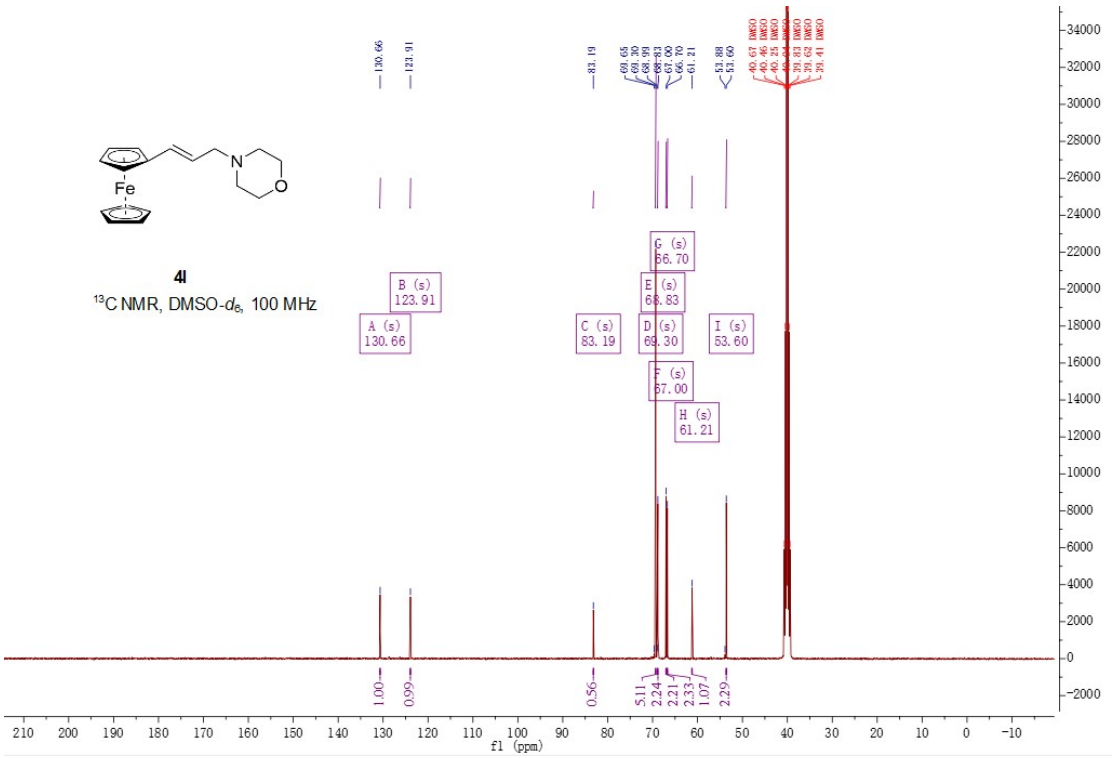

$^{13}$C NMR Spectrum of **4k**



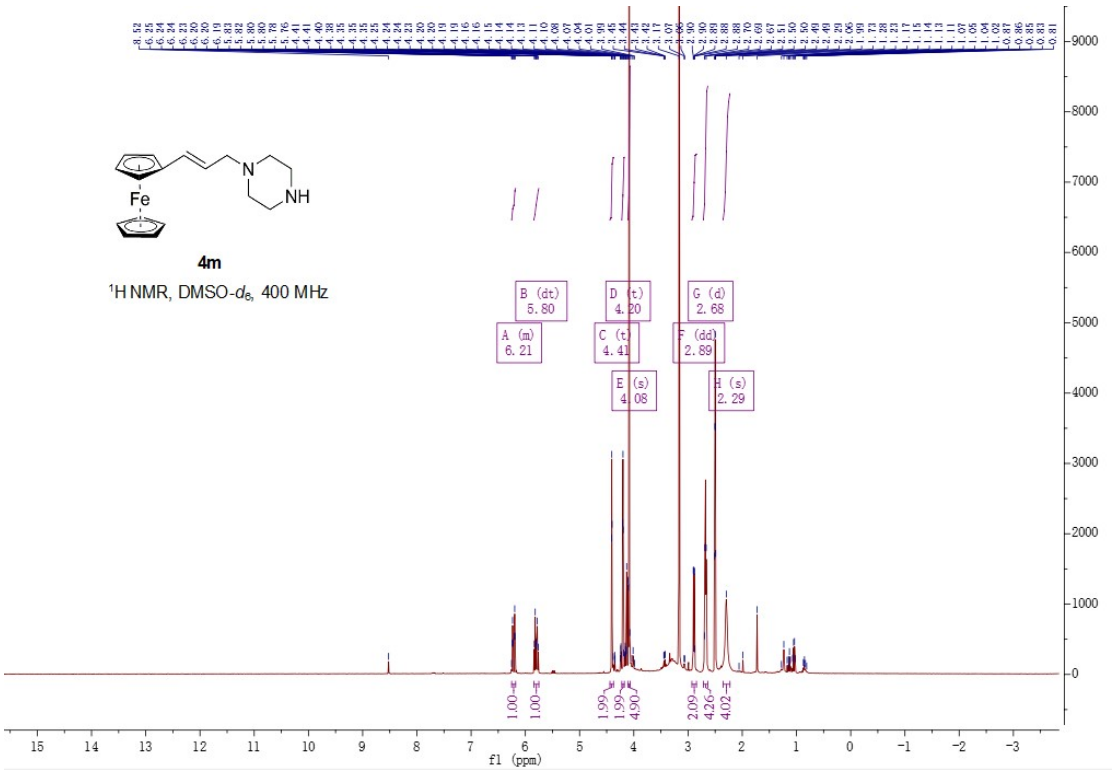
$^{1}$H NMR Spectrum of **4l**



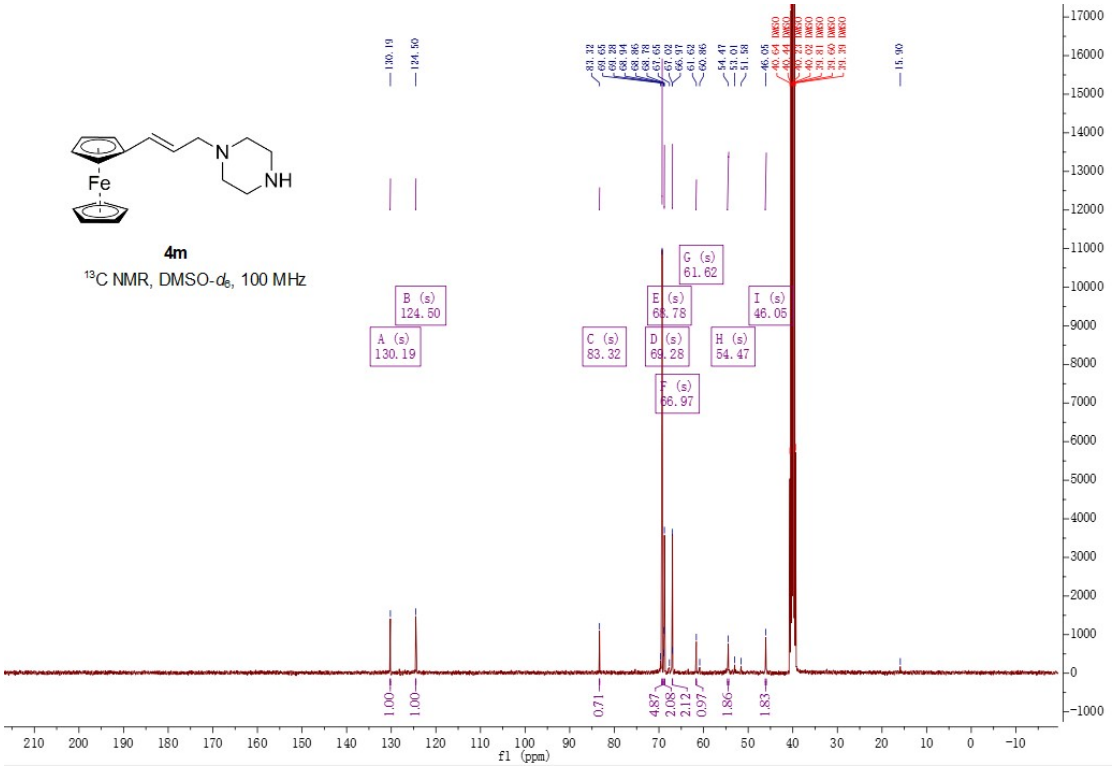

$^{13}$C NMR Spectrum of **4l**



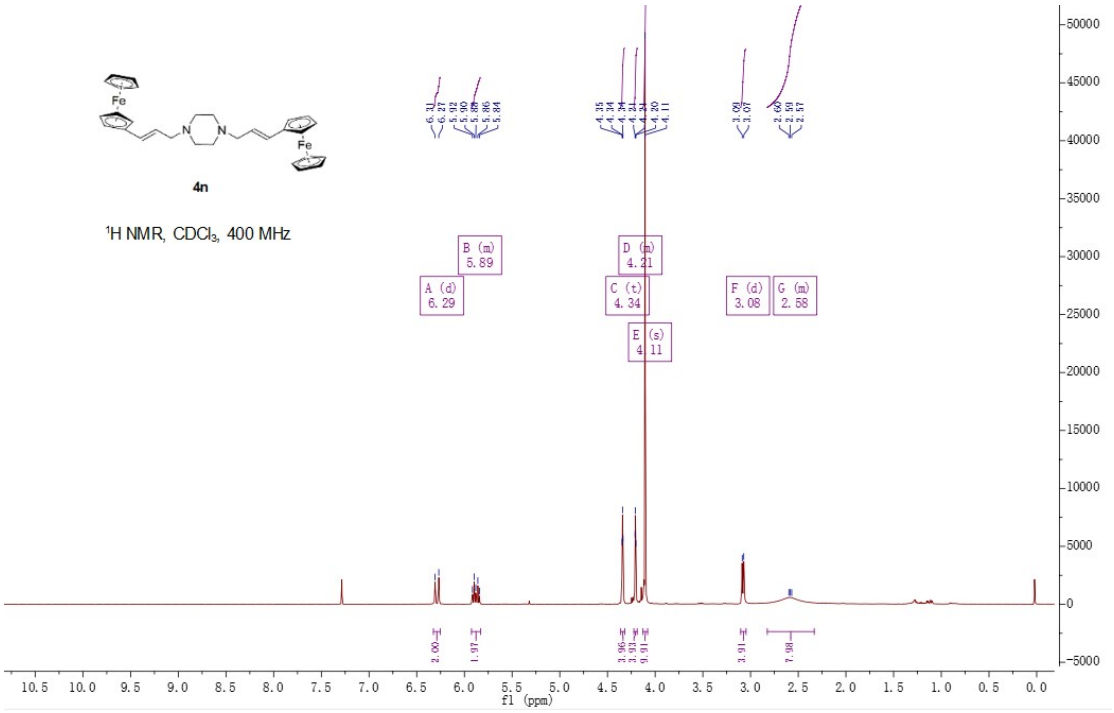

$^{1}$H NMR Spectrum of **4m**



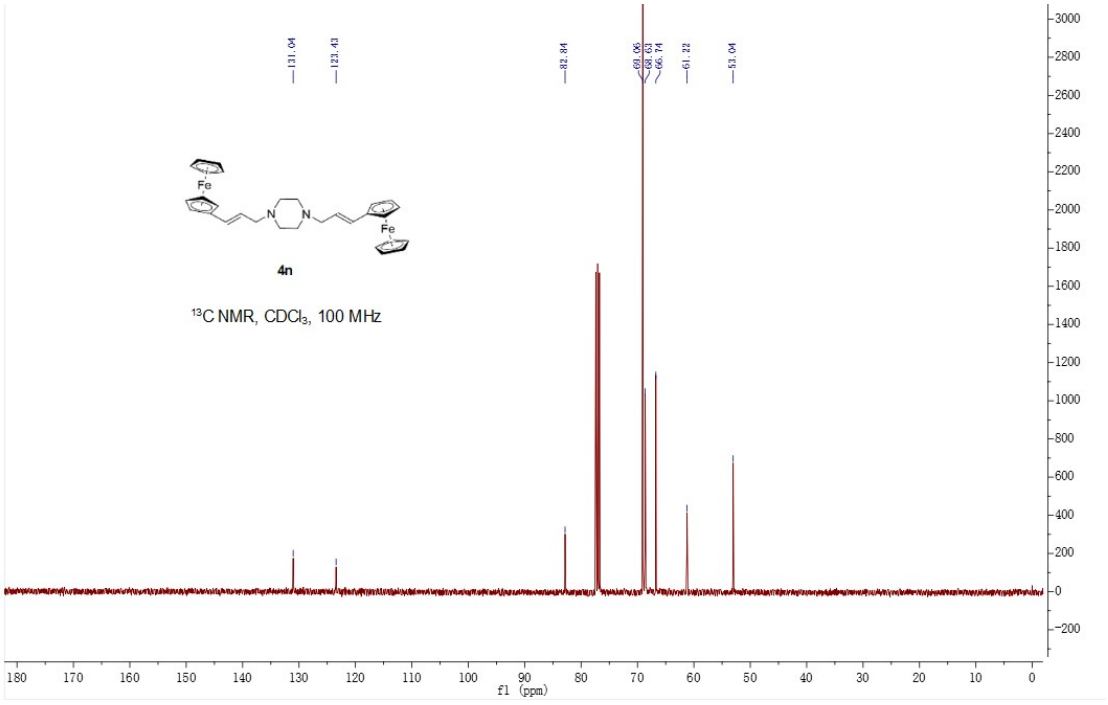

$^{13}$C NMR Spectrum of **4m**



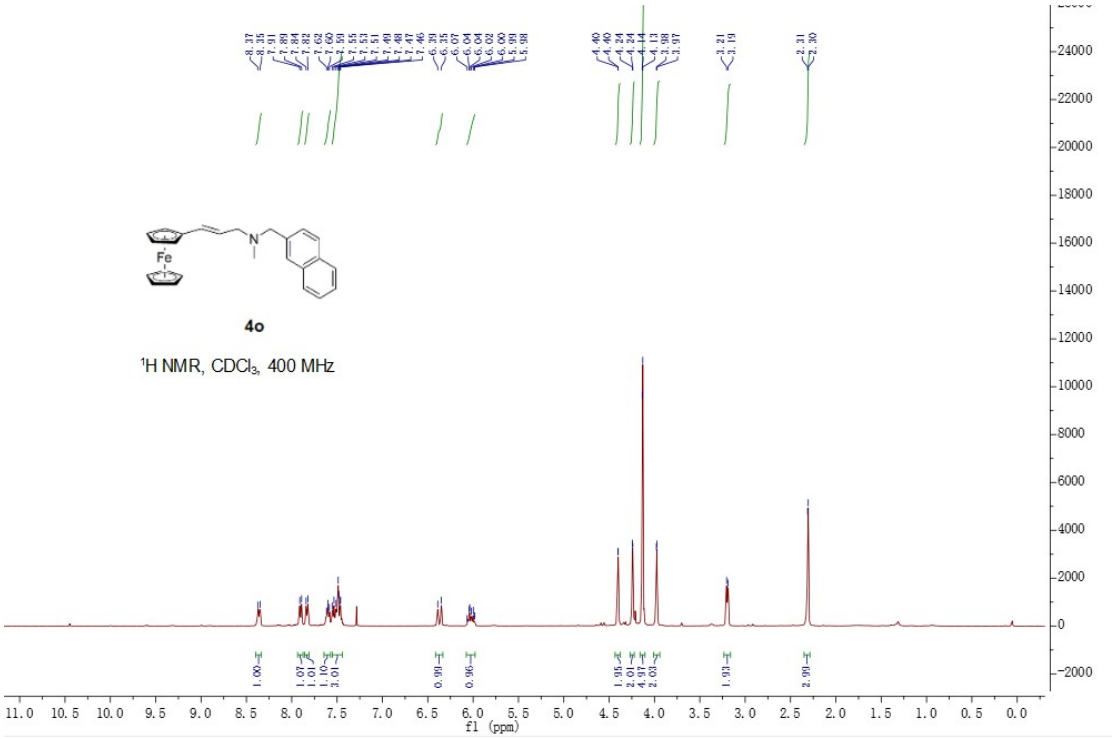

$^{1}$H NMR Spectrum of **4n**



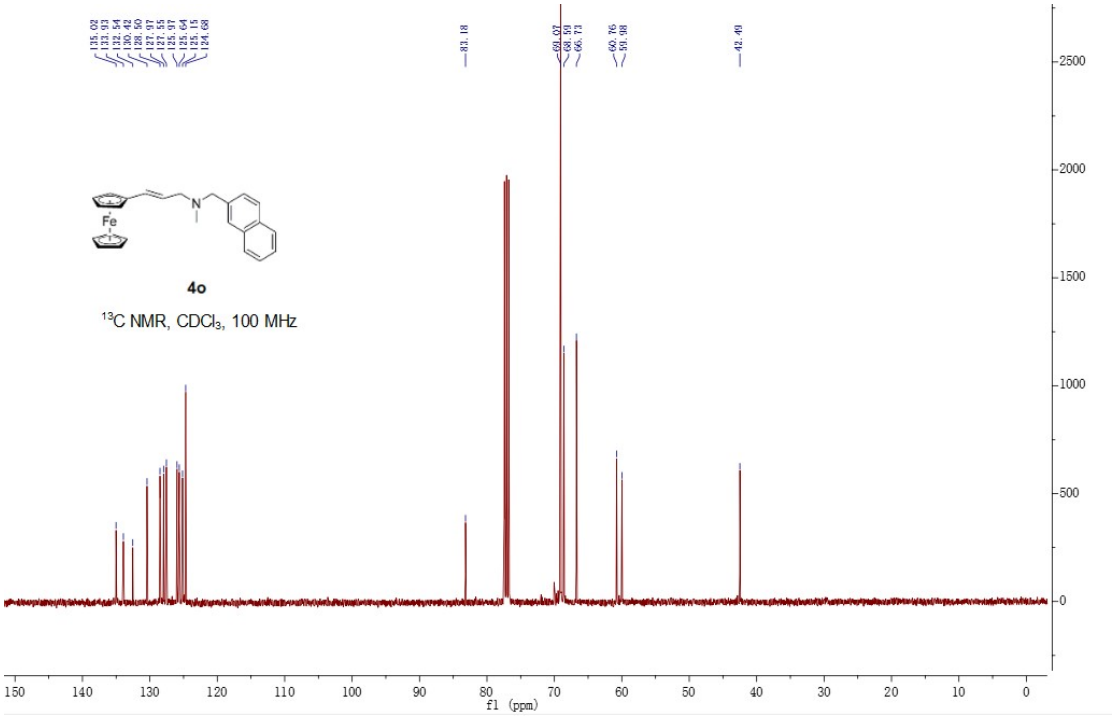

$^{13}$C NMR Spectrum of **4n**



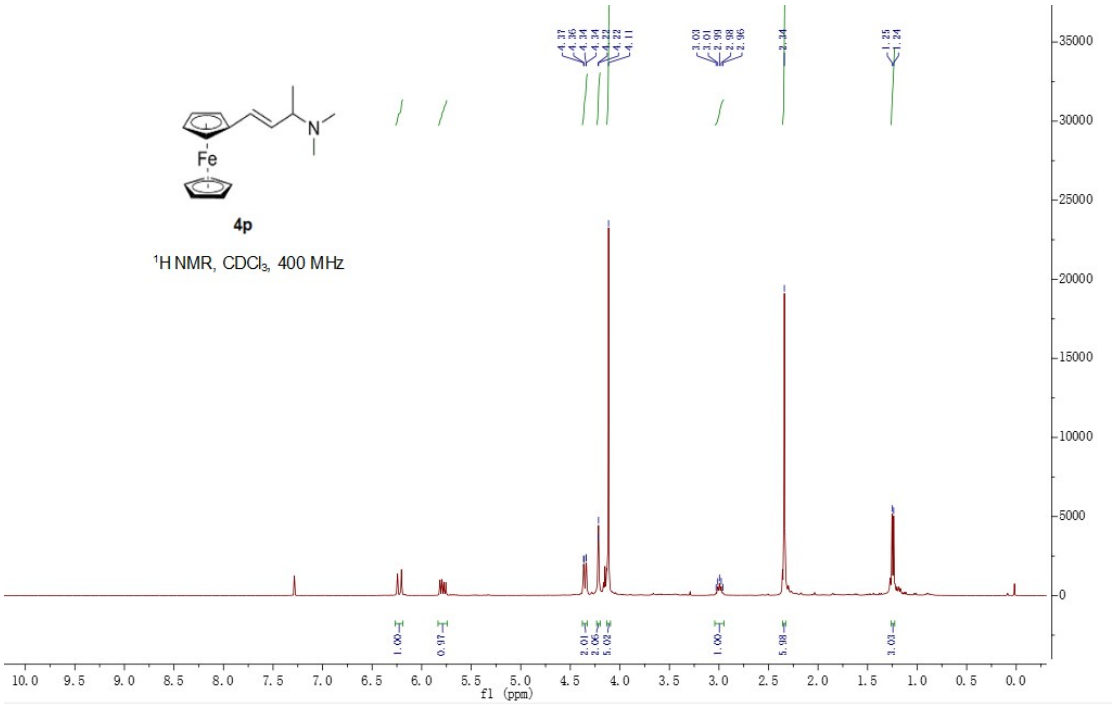

$^1$H NMR Spectrum of **4o**



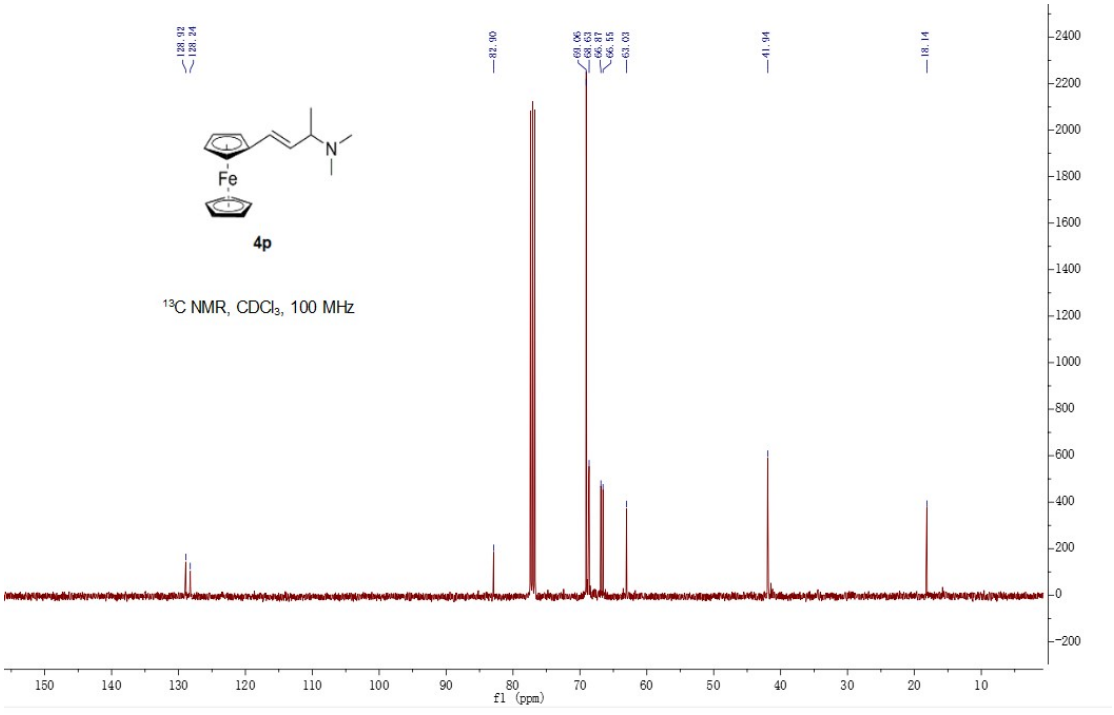

$^{13}$C NMR Spectrum of **4o**



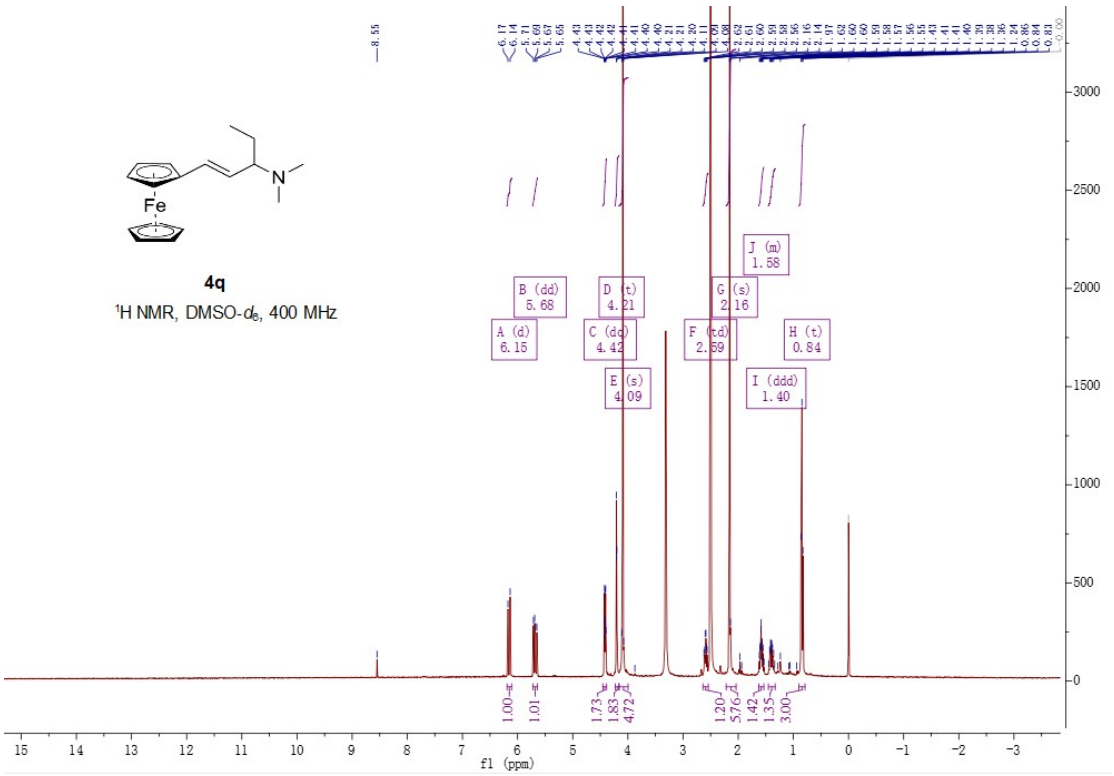

$^1$H NMR Spectrum of **4p**



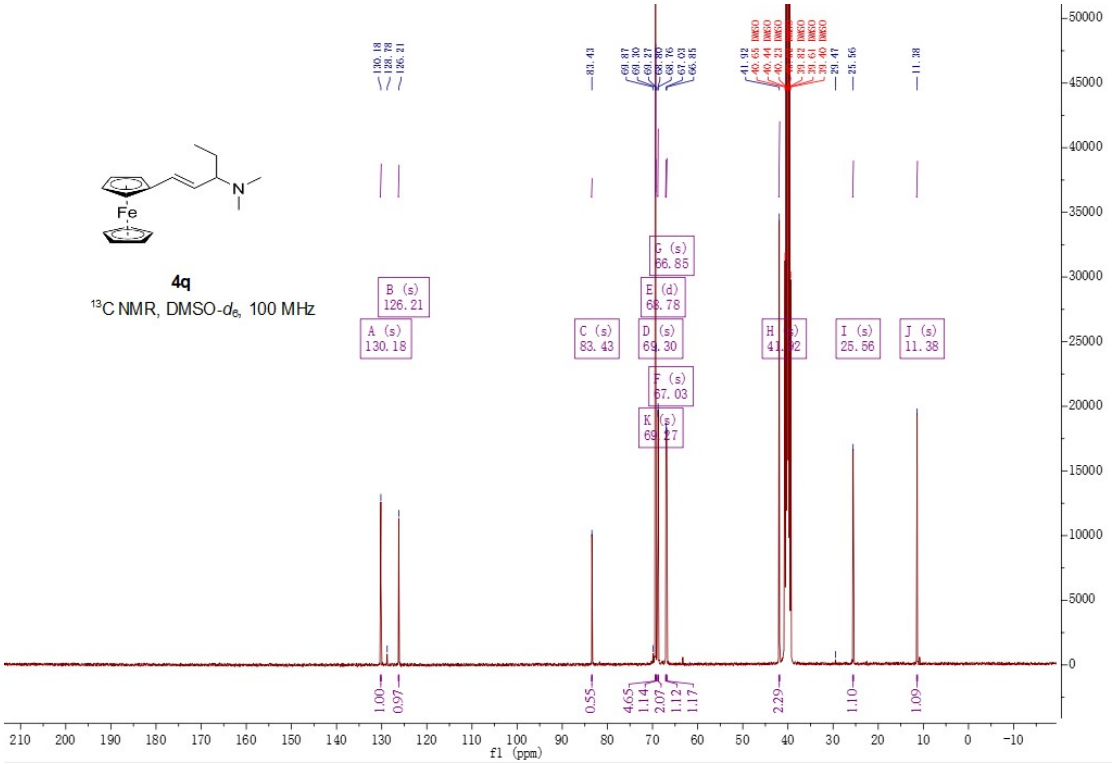

$^{13}$C NMR Spectrum of **4p**



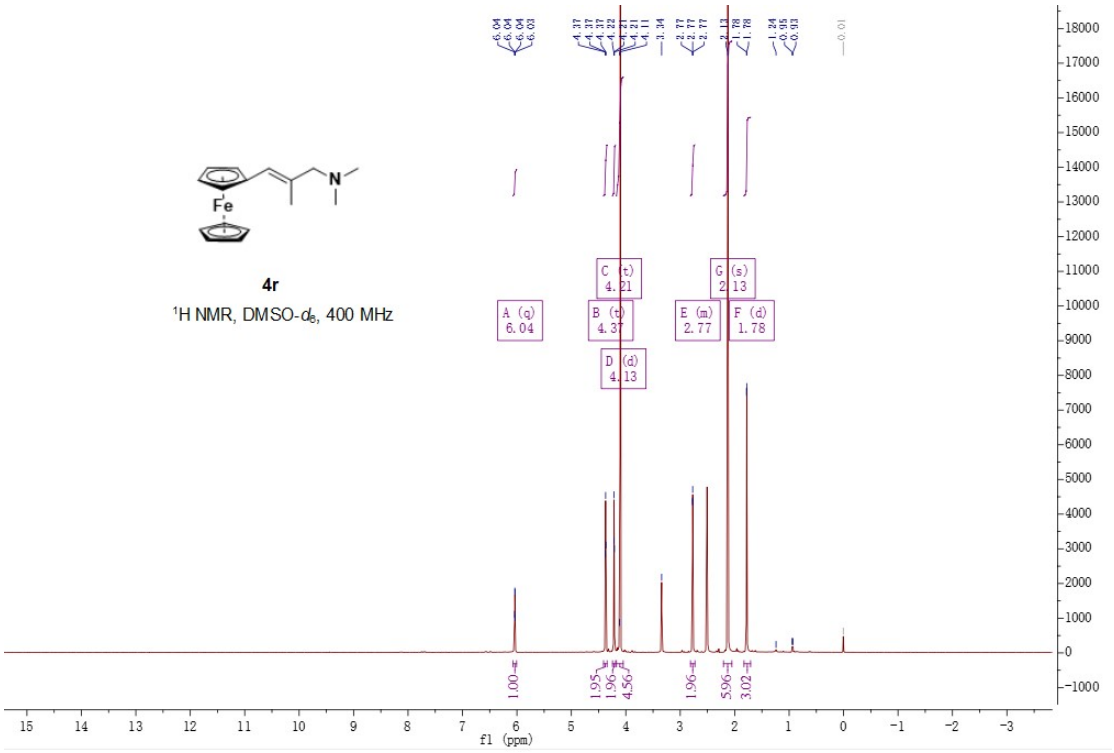

$^1$H NMR Spectrum of **4q**



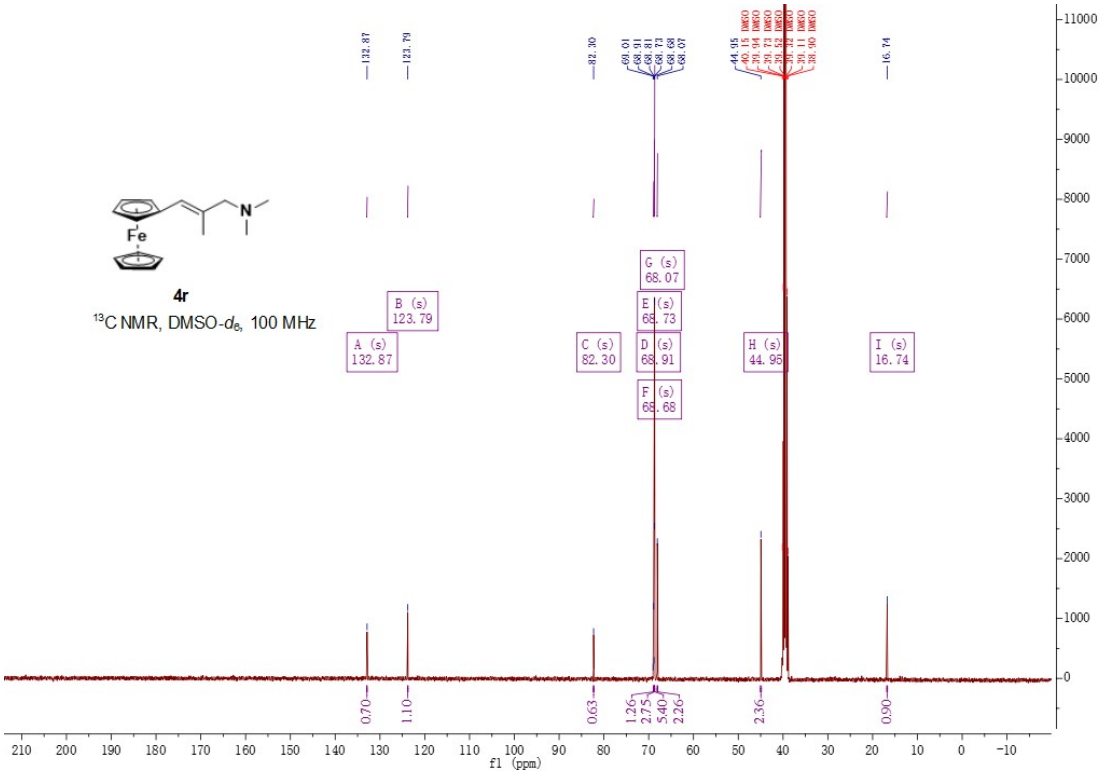

$^{13}$C NMR Spectrum of **4q**



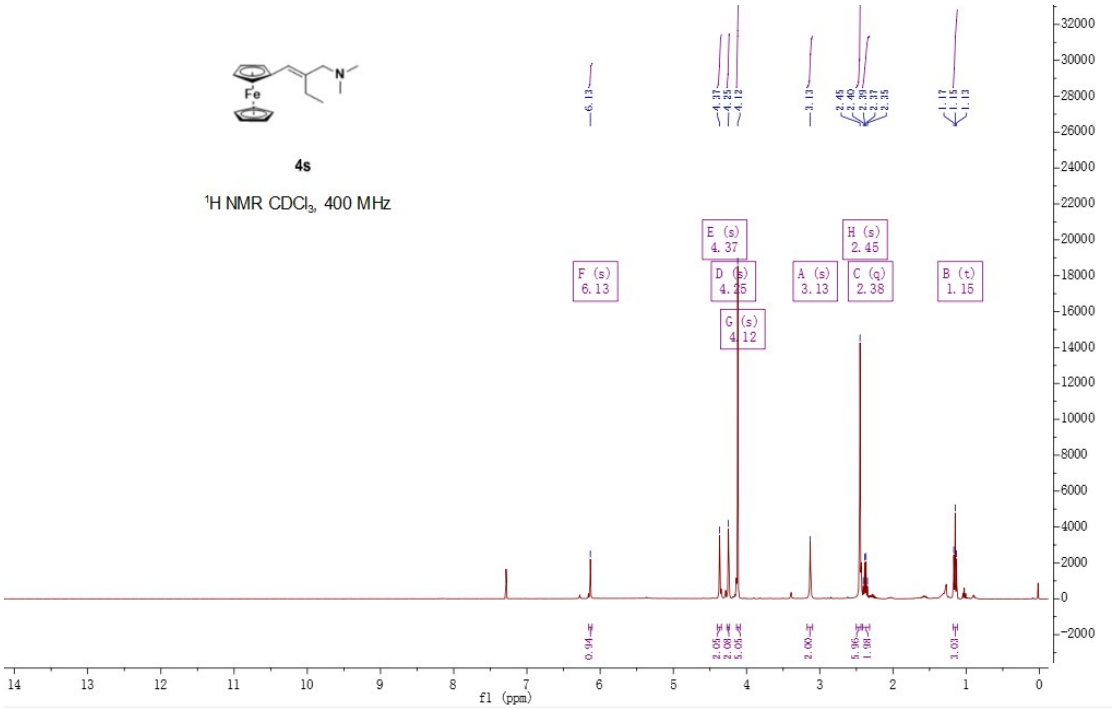

$^{1}$H NMR Spectrum of **4r**



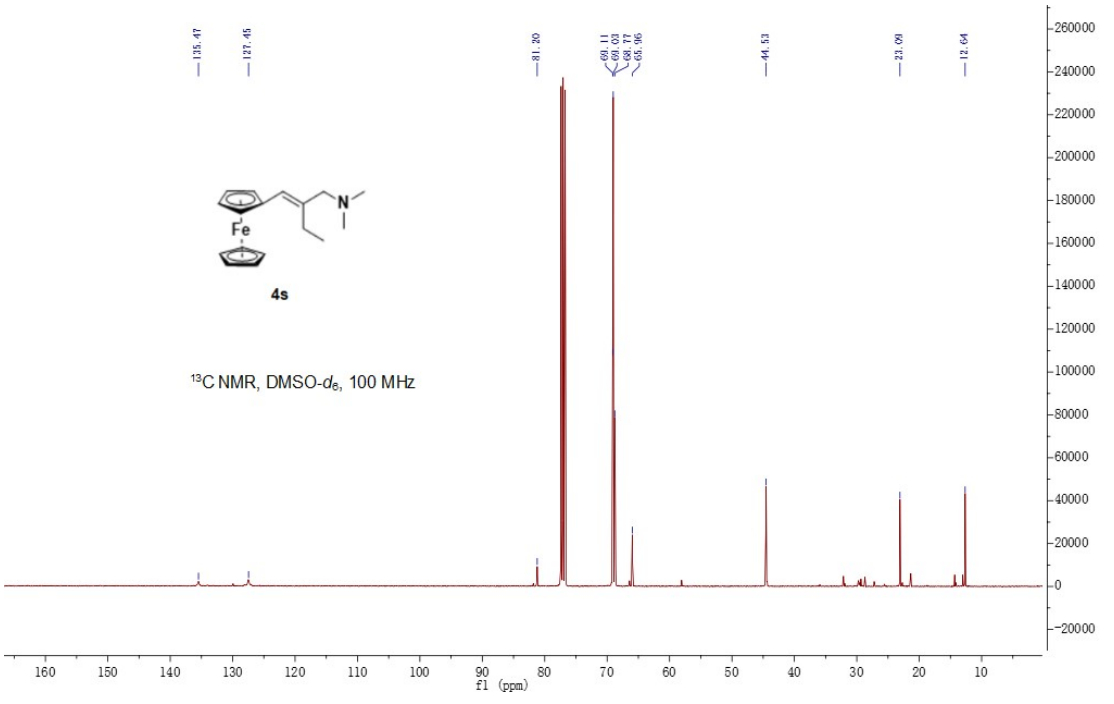

$^{13}$C NMR Spectrum of **4r**



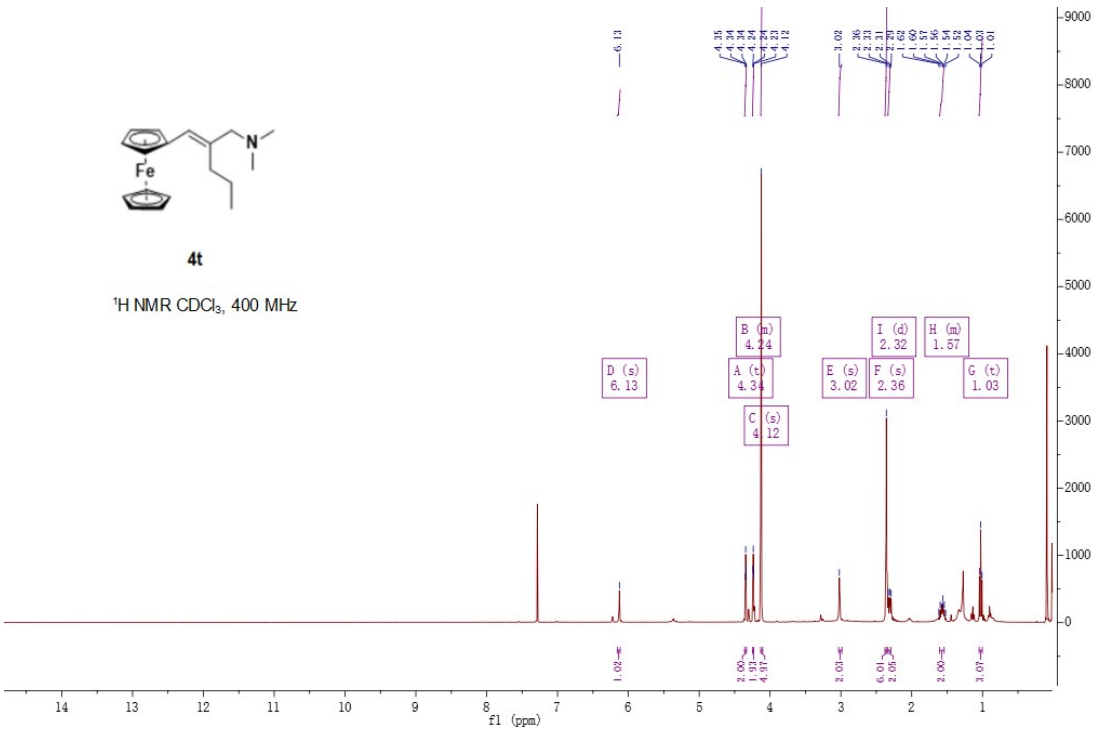

$^{1}$H NMR Spectrum of **4s**




$^{13}$C NMR Spectrum of **4s**




$^{1}$H NMR Spectrum of **4t**




$^{13}$C NMR Spectrum of **4t**