Electronic Supplementary Material (ESI) for ChemComm.


# Electronic Supplementary Information for

## Palladium-catalyzed enantioselective C($sp^2$)–H arylation of ferrocenyl ketones enabled by a chiral transient directing group

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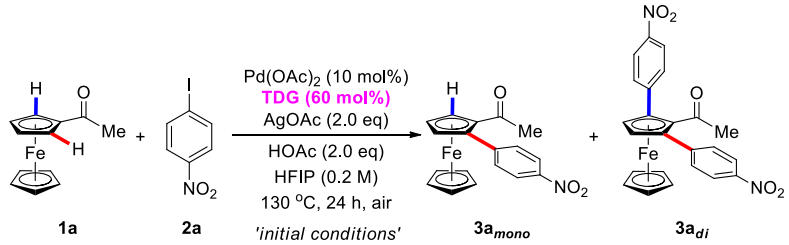
## 1. General Information

All solvents and chemicals were from Sigma-Aldrich, Acros and Alfa Aesar and used directly without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. Preparative TLC was performed on 1.0 mm silica gel (Analtech). Columns for flash chromatography (FC) contained silica gel (32–63μ, Dynamic Adsorbents, Inc.). The melting points were measured with Tektronix X4 microscopic melting point apparatus and thermometer are uncorrected. $^{1}$H NMR spectra were recorded on Bruker AV-400 instrument (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). $^{13}$C NMR spectra were recorded on Bruker AV-400 instrument (100 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet peak at 77.0 ppm of chloroform-*d* and the center line of a septet peak at 40.0 ppm of $d_6$-DMSO. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Enantiomeric excesses (ee) of asymmetric arylation products were determined by chiral High Performance Liquid Chromatography (HPLC). HPLC analysis was performed with Shimadzu CTO-10 AS and Agilent 1260DAD instruments. Acetylferrocene and 1,1′-diacetylferrocene are commercially available, and other ferrocenyl ketones were prepared from the substituted ferrocenes via a Friedel-Crafts reaction according to the previous procedure.[1]

## 2. Optimization for *ortho*-C–H Arylation of Ferrocenyl Ketones

### 2.1. Screening of Transient Directing Group

**Table S1. Screening of Transient Directing Group**[a]

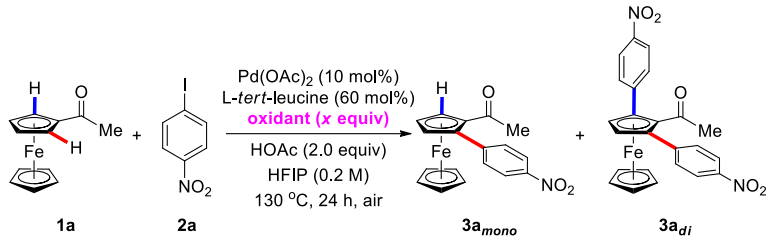



| entry | transient directing group | mono:di[b] | yield (%)[c] | ee (%)[b] |
|---|---|---|---|---|
| 1 | L-alanine | 79:21 | 26 | 38 |
| 2 | L-valine | 94:6 | 12 | 69 |
| 3 | L-phenylalanine | 91:9 | 21 | 36 |
| 4 | L-leucine | 90:10 | 25 | 30 |
| 5 | L-*iso*-leucine | 93:7 | 14 | 65 |
| **6** | **L-*tert*-leucine** | **98:2** | **8** | **78** |
| 7 | L-tryptophan | 89:11 | 10 | 59 |
| 8 | L-serine | 65:35 | 18 | 29 |
| 9 | L-threonine | 71:29 | 15 | 65 |
| 10 | L-aspartic acid | n.d. | n.r. | n.d. |
| 11 | L-glutamic acid | n.d. | n.r. | n.d. |
| 12 | L-phenylglycine | n.d. | n.r. | n.d. |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), TDG (60 mol %), AgOAc (0.4 mmol), HOAc (0.4 mmol), HFIP (1.0 mL), 130 °C, 24 h, air. [b]Determined by HPLC analysis. [c]Determined by $^1H$ NMR analysis with $CH_2Br_2$ as an internal standard. n.r.: no reaction. n.d.: not detected.

## 2.2. Screening of Oxidant

**Table S2. Screening of oxidant**[a]

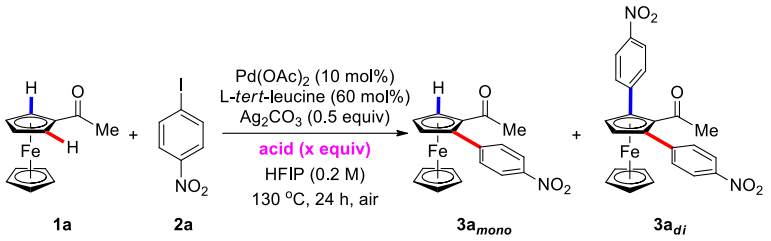



| entry | oxidant (*x* equiv) | mono:di[b] | yield (%)[c] | ee (%)[b] |
|---|---|---|---|---|
| 1 | AgOAc (2.0 eq) | 98:2 | 8 | 78 |
| 2 | AgOPiv (2.0 eq) | 97:3 | 9 | 71 |
| 3 | AgOBz (2.0 eq) | 97:3 | 12 | 65 |
| 4 | $Ag_2CO_3$ (2.0 eq) | 97:3 | 17 | 75 |
| 5 | AgOTFA (2.0 eq) | n.d. | n.r. | n.d. |
| 6 | AgOTf (2.0 eq) | n.d. | n.r. | n.d. |
| 7 | $Ag_2O$ (2.0 eq) | n.d. | n.r. | n.d. |
| 8 | AgO (2.0 eq) | n.d. | n.r. | n.d. |
| 9 | $AgNO_3$ (2.0 eq) | n.d. | n.r. | n.d. |
| 10 | $AgF_2$ (2.0 eq) | n.d. | n.r. | n.d. |
| 11 | $Cu(OAc)_2$ (2.0 eq) | n.d. | n.r. | n.d. |
| 12 | $Ag_2CO_3$ (1.5 eq) | 94:6 | 22 | 72 |
| 13 | $Ag_2CO_3$ (1.0 eq) | 97:3 | 23 | 70 |
| 14 | $Ag_2CO_3$ (0.75 eq) | 97:3 | 27 | 73 |
| **15** | **$Ag_2CO_3$ (0.5 eq)** | **98:2** | **35** | **75** |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), L-*tert*-leucine (60 mol %), oxidant (*x* mmol), HOAc (0.4 mmol), HFIP (1.0 mL), 130 °C, 24 h, air. [b]Determined by HPLC analysis. [c]Determined by $^1H$ NMR analysis with $CH_2Br_2$ as an internal standard. n.r.: no reaction. n.d.: not detected.

## 2.3. Screening of Carboxylic Acid

**Table S3. Screening of Carboxylic Acid**[a]

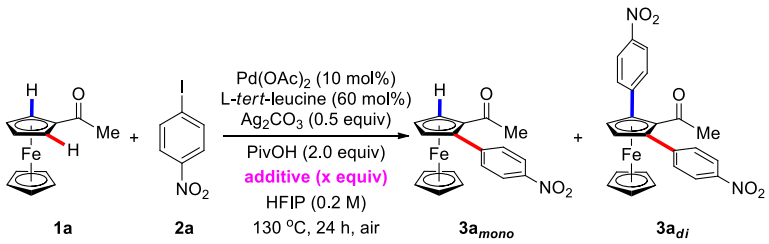



| entry | acid (*x* equiv) | mono:di[b] | yield (%)[c] | ee (%)[b] |
|---|---|---|---|---|
| 1 | HOAc (2.0 eq) | 98:2 | 35 | 75 |
| 2 | *i*PrCO$_2$H (2.0 eq) | 98:2 | 28 | 82 |
| **3** | **PivOH (2.0 eq)** | **98:2** | **45** | **93** |
| 4 | PhCO$_2$H (2.0 eq) | 97:3 | 32 | 75 |
| 5 | HOCH$_2$CO$_2$H (2.0 eq) | 97:3 | 28 | 84 |
| 6 | TfOH (2.0 eq) | 97:3 | 15 | 89 |
| 7 | ClCH$_2$CO$_2$H (2.0 eq) | n.d. | trace | n.d. |
| 8 | CF$_3$CO$_2$H (2.0 eq) | n.d. | trace | n.d. |
| 9 | TsOH (2.0 eq) | n.d. | trace | n.d. |
| 10 | PivOH (1.0 eq) | 99:1 | 28 | 93 |
| 11 | PivOH (4.0 eq) | 99:1 | 32 | 91 |
| 12 | PivOH (6.0 eq) | 99:1 | 25 | 92 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Pd(OAc)$_2$ (10 mol %), L-*tert*-leucine (60 mol %), Ag$_2$CO$_3$ (0.1 mmol), acid (*x* equiv), HFIP (1.0 mL), 130 °C, 24 h, air. [b]Determined by HPLC analysis. [c]Determined by $^1$H NMR analysis with CH$_2$Br$_2$ as an internal standard. n.r.: no reaction. n.d.: not detected.

## 2.4. Screening of Additive

**Table S4. Screening of Additive**[a]

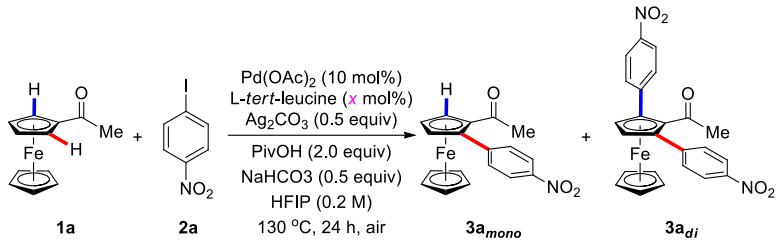



| entry | additive (*x* equiv) | mono:di[b] | yield (%)[c] | ee (%)[b] |
|---|---|---|---|---|
| 1 | none | 98:2 | 45 | 93 |
| 2 | NaOAc (1.0 eq) | 98:2 | 30 | 93 |
| 3 | KOAc (1.0 eq) | 97:3 | 39 | 90 |
| 4 | CsOAc (1.0 eq) | 88:12 | 42 | 89 |
| 5 | $NaHCO_3$ (1.0 eq) | 98:2 | 68 | 95 |
| 6 | $KHCO_3$ (1.0 eq) | 98:2 | 57 | 94 |
| 7 | $Li_2CO_3$ (1.0 eq) | 95:5 | 38 | 93 |
| 8 | $Na_2CO_3$ (1.0 eq) | n.d. | trace | n.d. |
| 9 | $K_2CO_3$ (1.0 eq) | n.d. | trace | n.d. |
| 10 | $Cs_2CO_3$ (1.0 eq) | 90:10 | 29 | 92 |
| 11 | KF (1.0 eq) | 87:13 | 19 | 87 |
| 12 | $K_3PO_4$ (1.0 eq) | n.d. | trace | n.d. |
| 13 | $KH_2PO_4$ (1.0 eq) | 86:14 | 28 | 92 |
| 14 | $PhCO_2K$ (1.0 eq) | 95:5 | 35 | 94 |
| 15 | KOPiv | 99:1 | 32 | 95 |
| 16 | $NaHCO_3$ (2.0 eq) | 97:3 | 30 | 92 |
| 17 | $NaHCO_3$ (1.5 eq) | 98:2 | 49 | 94 |
| 18 | $NaHCO_3$ (0.8 eq) | 98:2 | 72 | 94 |
| 19 | $NaHCO_3$ (0.5 eq) | 98:2 | 75 | 95 |
| 20 | $NaHCO_3$ (0.3 eq) | 99:1 | 52 | 95 |
| **21**[d] | **$NaHCO_3$ (0.5 eq)** | **98:2** | **81(72)**[e] | **95** |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), L-*tert*-leucine (60 mol %), $Ag_2CO_3$ (0.1 mmol), PivOH (2.0 equiv), additive (*x* equiv), HFIP (1.0 mL), 130 °C, 24 h, air. [b]Determined by HPLC analysis. [c]Determined by $^1H$ NMR analysis with $CH_2Br_2$ as an internal standard. [d]36 h. [e]Isolated yield. n.r.: no reaction. n.d.: not detected.

## 2.5 Loading of Transient Directing Group

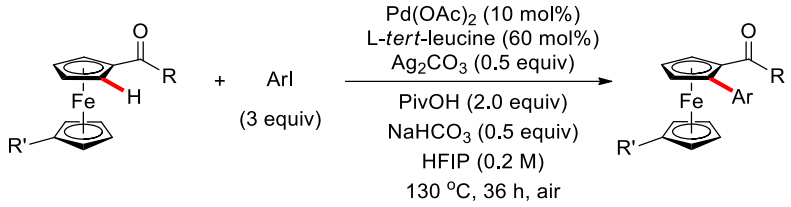
**Table S5. Loading of Transient Directing Group**[a]




| entry | equiv. of TDG (mol%) | mono:di[b] | yield (%)[c] | ee (%)[b] |
|---|---|---|---|---|
| 1 | 10 | 98:2 | 15 | 94 |
| 2 | 20 | 98:2 | 23 | 93 |
| 3 | 30 | 98:2 | 41 | 95 |
| 4 | 40 | 98:2 | 62 | 95 |
| **5** | **60** | **98:2** | **81** | **95** |
| 6 | 80 | 98:2 | 75 | 94 |
| 7 | 100 | 98:2 | 80 | 95 |

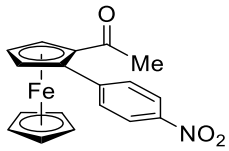
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), L-*tert*-leucine (x mol %), $Ag_2CO_3$ (0.1 mmol), PivOH (2.0 equiv), $NaHCO_3$ (0.5 equiv), HFIP (1.0 mL), 130 °C, 36 h, air. [b]Determined by HPLC analysis. [c]Determined by $^1H$ NMR analysis with $CH_2Br_2$ as an internal standard.

## 3. General Procedure for Enantioselective *ortho*-C–H Arylation of Ferrocenyl Ketones with Aryl Iodides




**Typical procedure for Pd-catalyzed C–H arylation of ferrocenyl ketones:** To a 20 mL reaction tube was added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), L-*tert*-Leucine (15.75 mg, 0.12 mmol), $Ag_2CO_3$ (27.6 mg, 0.1 mmol), $NaHCO_3$ (8.4 mg, 0.1 mmol), trimethylacetic acid (40.8 mg, 0.4 mmol), ferrocenyl ketone (0.2 mmol), aryl iodide (0.6 mmol), and hexafluoroisopropanol (1.0 mL). The tube was then sealed and the mixture was stirred at room temperature for 5 min before being heated to 130 °C for 36 h. The reaction mixture was cooled to room temperature, filtrated via celite, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate) to provide the desired arylation products.

Isolated yields were reported in the text and characterization data for new compounds listed as following:



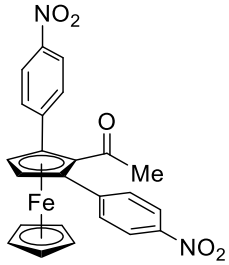

**1-Acetyl-2-(4-nitrophenyl)ferrocene (3a)**

Red oil. $R_f$ = 0.22, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –122.8 (c 1.0 in chloroform)

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.16–8.14 (m, 2H), 7.73–7.71 (m, 2H), 4.90–4.88 (m, 1H), 4.78–4.75 (m, 1H), 4.68–4.66 (m, 1H), 4.24 (s, 5H), 2.45 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.7, 146.4, 145.6, 130.7, 122.6, 87.6, 76.5, 76.1, 73.1, 71.7, 71.5, 29.0.

HR-MS (ESI) m/z calcd for $C_{18}H_{16}FeNO_3^+$ [M+H$^+$] 350.0474, found 350.0477.

95% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 36 bar, $t_R$= 13.91 min for minor isomer and $t_R$= 15.54 min for major isomer.

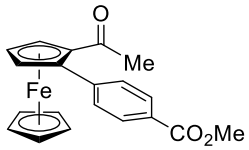



**1-Acetyl-2,5-di-(4-nitrophenyl)ferrocene** (**3a**$_{di}$)

Red oil. $R_f$ = 0.20, (6:1, hexane: ethyl acetate).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.20 (d, $J$ = 8.8 Hz, 4H), 7.64 (d, $J$ = 8.4 Hz, 4H), 4.86 (s, 2H), 4.26 (s, 5H), 2.24 (s, 5H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 203.7, 146.8, 144.9, 129.8, 123.4, 87.4, 86.5, 73.3, 71.0, 33.1.

HR-MS (ESI) m/z calcd for $C_{24}H_{19}FeN_2O_5^+$ [M+H$^+$] 471.0638, found 471.0640.



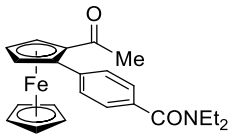

**1-Acetyl-2-(4-methoxylcarbonylphenyl)ferrocene (3b)**

Red oil. $R_f$ = 0.23, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –140.7 (c 1.0 in chloroform)

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.98 (d, $J$ = 8.4 Hz, 2H), 7.62 (d, $J$ = 8.0 Hz, 2H), 4.86 (s, 1H), 4.71 (s, 1H), 4.60 (s, 1H), 4.23 (s, 5H), 3.92 (s, 3H), 2.38 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.7, 167.0, 142.8, 130.1, 128.8, 128.5, 89.6, 75.9, 72.0, 71.5, 71.0, 52.0, 29.3.

HR-MS (ESI) m/z calcd for $C_{20}H_{19}FeO_3^+$ [M+H$^+$] 363.0678, found 363.0682.

97% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 14.05 min for minor isomer and $t_R$= 17.69 min for major isomer.



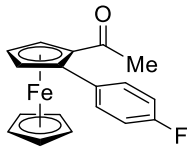

**1-Acetyl-2-(4-*N*,*N*-diethylcarboxamidephenyl)ferrocene (3c)**

Red oil. $R_f$ = 0.39, (1:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –97.5 (c 1.0 in chloroform).

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.57 (d, $J$ = 8.4 Hz, 2H), 7.32 (d, $J$ = 8.0 Hz, 2H), 4.86–4.84 (m, 1H) , 4.67–4.65 (m, 1H) , 4.59–4.56 (m, 1H), 4.23 (s, 5H), 3.56 (s, 2H), 3.34 (s, 2H), 2.37 (s, 3H), 1.25 (s, 3H), 1.16 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.1, 171.2, 138.4, 135.7, 130.1, 125.7, 90.2, 75.7, 71.7, 71.3, 70.7, 43.3, 39.2, 29.3, 14.2, 12.9.

HR-MS (ESI) m/z calcd for $C_{23}H_{26}FeNO_2^+$ [M+H$^+$] 404.1307, found 404.1305.

95% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 50:50, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 36 bar, $t_R$= 5.48 min for minor isomer and $t_R$= 8.12 min for major isomer.



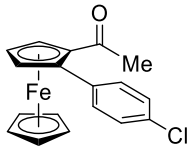

**1-Acetyl-2-(4-fluorophenyl)ferrocene (3d)**

Red oil. $R_f$ = 0.42, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –120.7 (c 1.0 in chloroform).

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.53 (s, 2H), 7.00 (s, 2H), 4.82 (s, 1H), 4.62 (s, 1H), 4.56 (s, 1H), 4.23 (s, 5H), 2.35 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.1, 161.9 (d, $J_{C-F}$ = 245 Hz), 132.9, 131.8 (d, $J_{C-F}$ = 7 Hz), 114.4 (d, $J_{C-F}$ = 21 Hz), 90.3, 75.5, 71.4, 71.2, 70.5, 29.3.

HR-MS (ESI) m/z calcd for $C_{18}H_{16}FFeO^+$ [M+H$^+$] 323.0529, found 323.0533.

92% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 88:12, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 7.79 min for minor isomer and $t_R$= 9.10 min for major isomer.



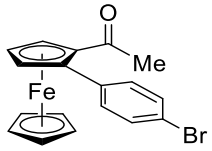

**1-Acetyl-2-(4-chlorophenyl)ferrocene (3e)**

Red oil. $R_f$ = 0.45, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –340.8 (c 1.0 in chloroform).

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.47 (d, $J$ = 8.0 Hz, 2H), 7.25 (d, $J$ = 8.4 Hz, 2H), 4.80 (s, 1H), 4.61 (s, 1H) , 4.54 (s, 1H), 4.19 (s, 5H), 2.34 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.9, 135.7, 132.7, 131.4, 127.6, 89.8, 76.8, 75.5, 71.7, 71.3, 70.7, 29.3.

HR-MS (ESI) m/z calcd for $C_{18}H_{16}ClFeO^+$ [M+H$^+$] 339.0234, found 339.0234.

96% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 88:12, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 8.13 min for minor isomer and $t_R$= 9.26 min for major isomer.



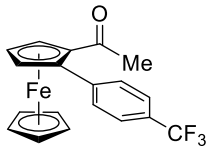

**1-Acetyl-2-(4-bromophenyl)ferrocene (3f)**

Red oil. $R_f$ = 0.46, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –285.4 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.43 (s, 4H), 4.84–4.82 (m, 1H), 4.66–4.63 (m, 1H), 4.59–4.55 (m, 1H), 4.22 (s, 5H), 2.37 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.9, 136.2, 131.8, 130.6, 120.8, 89.8, 75.5, 71.8, 71.3, 70.7, 29.3.

HR-MS (ESI) m/z calcd for $C_{18}H_{16}BrFeO^+$ [M+H$^+$] 382.9728, found 382.9730.

96% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 88:12, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 8.56 min for minor isomer and $t_R$= 9.80 min for major isomer.




**1-Acetyl-2-(4-trifluoromethylphenyl)ferrocene (3g)**

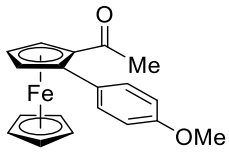
Red oil. $R_f$ = 0.43, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –193.2 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.68 (d, $J$ = 7.6 Hz, 2H), 7.56 (d, $J$ = 8.0 Hz, 2H), 4.86 (s, 1H), 4.70 (s, 1H), 4.61 (s, 1H), 4.24 (s, 5H), 2.40 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.7, 141.4, 130.4, 128.8 (q, $J_{C\text{-}F}$ = 32 Hz), 127.0 (q, $J_{C\text{-}F}$ = 270 Hz), 124.3 (q, $J_{C\text{-}F}$ = 1.5 Hz), 89.1, 75.8, 72.2, 71.4, 71.0, 29.2.

HR-MS (ESI) m/z calcd for $C_{19}H_{16}F_3FeO^+$ [M+H$^+$] 373.0497, found 373.0498.

95% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 32:1, flow rate = 0.495 mL/min, wavelength = 254 nm UV detector, pressure = 35 bar, $t_R$= 22.50

min for minor isomer and $t_R$= 23.52 min for major isomer.



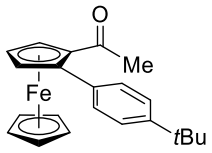

**1-Acetyl-2-(4-methoxyphenyl)ferrocene (3h)**

Red oil. $R_f$ = 0.32, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –60.8 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.48 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.0 Hz, 2H), 4.81 (s, 1H), 4.60 (s, 1H), 4.53 (sm, 1H), 4.22 (s, 5H), 3.84 (s, 3H), 2.33 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.2, 158.7, 131.3, 129.0, 113.1, 91.5, 75.3, 71.1, 70.8, 70.3, 55.3, 29.4.

HR-MS (ESI) m/z calcd for $C_{19}H_{19}FeO_2^+$ [M+H$^+$] 335.0729, found 335.0733.

94% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 35 bar, $t_R$= 9.30 min for minor isomer and $t_R$= 11.59 min for major isomer.



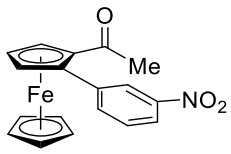

**1-Acetyl-2-(4-tert-butylphenyl)ferrocene (3i)**

Red oil. $R_f$ = 0.56, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –130.8 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.47 (d, $J$ = 8.0 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 4.84–4.81 (m, 1H), 4.65–4.62 (m, 1H), 4.55–4.52 (m, 1H), 4.23 (s, 5H), 2.33 (s, 3H), 1.35 (s, 9H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.3, 149.9, 133.8, 129.9, 124.6, 91.6, 75.7, 71.1, 70.9, 70.4, 34.5, 31.3, 29.5.

HR-MS (ESI) m/z calcd for $C_{22}H_{25}FeO^+$ [M+H$^+$] 361.1249, found 361.1253.

94% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 98:2, flow rate = 0.5 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 27.18 min for minor isomer and $t_R$= 22.01 min for major isomer.



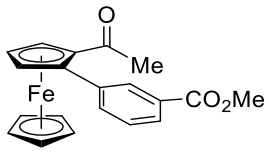

**1-Acetyl-2-(3-nitrophenyl)ferrocene (3j)**

Red oil. $R_f$ = 0.25, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –189.8 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.46–8.44 (m, 1H), 8.12 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 7.90 (d, $J$ = 7.6 Hz, 1H), 7.45 (t, $J$ = 8.0 Hz, 1H), 4.88–4.85 (m, 1H), 4.77–4.74 (m, 1H), 4.66–4.63 (m, 1H), 4.26 (s, 5H), 2.44 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.8, 147.5, 139.6, 136.3, 128.1, 124.8. 121.7, 88.1, 76.3, 75.8, 72.7, 71.6, 71.2, 29.0.

HR-MS (ESI) m/z calcd for $C_{18}H_{16}FeNO_3^+$ [M+H$^+$] 350.0474, found 350.0479.

94% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 33 bar, $t_R$= 11.11 min for minor isomer and $t_R$= 13.13 min for major isomer.



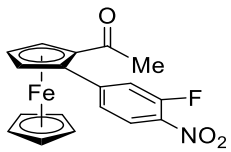

**1-Acetyl-2-(3-methoxycabonylphenyl)ferrocene (3k)**

Red oil. $R_f$ = 0.25, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –85.4 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.24 (s, 1H), 7.95 (d, $J$ = 7.6 Hz, 1H), 7.76 (d, $J$ = 7.6 Hz, 1H), 7.39 (t, $J$ = 7.6 Hz, 1H), 4.85 (s, 1H), 4.70 (s, 1H), 4.59 (s, 1H), 4.25 (s, 5H), 3.93 (s, 3H), 2.36 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.9, 167.1, 137.7, 134.8, 131.2, 129.5, 128.1, 127.6, 90.2, 76.8, 75.8, 71.7, 71.4, 70.8, 52.2, 29.2.

HR-MS (ESI) m/z calcd for $C_{20}H_{19}FeO_3^+$ [M+H$^+$] 363.0678, found 363.0680.

98% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 10.09 min for minor isomer and $t_R$= 12.89 min for major isomer.



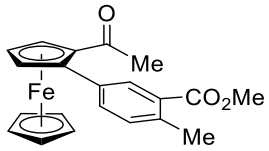

**1-Acetyl-2-(3-fluoro-4-nitrophenyl)ferrocene (3l)**

Red oil. $R_f$ = 0.15, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –235.6 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.99 (t, $J$ = 8.0 Hz, 1H), 7.55–7.45 (m, 2H), 4.92–4.89 (m, 1H), 4.79–4.75 (m, 1H), 4.71–4.67 (m, 1H), 4.25 (s, 5H), 2.47 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.6, 154.8 (d, $J_{C\text{-}F}$ = 262 Hz), 147.7 (d, $J_{C\text{-}F}$ = 9 Hz), 126.0 (d, $J_{C\text{-}F}$ = 4 Hz), 125.0 (d, $J_{C\text{-}F}$ = 2 Hz), 119.6, 119.4, 86.2, 76.4, 76.1, 73.6, 71.8, 71.8, 29.0.

HR-MS (ESI) m/z calcd for $C_{18}H_{15}FFeNNO_3^+$ [M+H$^+$] 368.0380, found 368.0381.

95% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 82:18, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 33 bar, $t_R$= 11.39 min for minor isomer and $t_R$= 13.25 min for major isomer.



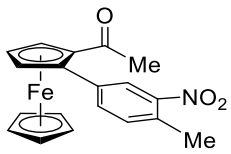

**1-Acetyl-2-(4-methyl-3-methoxycarbonylphenyl)ferrocene (3m)**

Red oil. $R_f$ = 0.31, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –146.0 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.11 (d, $J$ = 1.6 Hz, 1H), 7.61 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1H), 7.20 (d, $J$ = 8.0 Hz, 1H), 4.85–4.81 (m, 1H), 4.68–4.65 (m, 1H) , 4.58–4.55 (m, 1H), 4.24 (s, 5H), 3.90 (s, 3H), 2.60 (s, 3H), 2.35 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.0, 167.9, 139.0, 134.7, 133.8, 132.2, 131.0, 128.7, 90.2, 75.6, 71.4, 71.3, 71.2, 70.6, 51.9, 29.3, 21.5.

HR-MS (ESI) m/z calcd for $C_{21}H_{21}FeO_3^+$ [M+H$^+$] 377.0835, found 377.0836.

96% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 33 bar, $t_R$= 9.39 min for minor isomer and $t_R$= 11.33 min for major isomer.



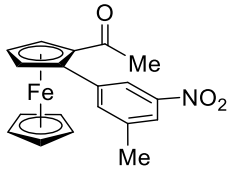

**1-Acetyl-2-(4-methyl-3-nitrophenyl)ferrocene (3n)**

Red oil. $R_f$ = 0.25, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –76.6 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.21 (d, $J$ = 1.6 Hz, 1H), 7.70 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1H), 7.28–7.24 (m, 1H), 4.85–4.81 (m, 1H), 4.73–4.70 (m, 1H), 4.63–4.60 (m, 1H), 4.24 (s, 5H), 2.60 (s, 3H), 2.43 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.8, 148.4, 136.8, 134.8, 132.0, 131.7, 125.9, 88.0, 76.4, 75.5, 72.5, 71.5, 71.1, 29.0, 20.3.

HR-MS (ESI) m/z calcd for $C_{19}H_{18}FeNO_3^+$ [M+H$^+$] 364.0631, found 364.0635.

96% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 35 bar, $t_R$= 9.69 min for minor isomer and $t_R$= 11.69 min for major isomer.



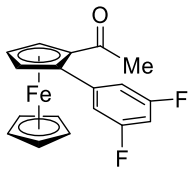

**1-Acetyl-2-(5-methyl-3-nitrophenyl)ferrocene (3o)**

Red oil. $R_f$ = 0.36, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –181.4 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.26 (s, 1H), 7.94 (s, 1H), 7.67 (s, 1H), 4.86–4.84 (m, 1H), 4.73–4.71 (m, 1H), 4.64–4.61 (m, 1H), 4.26 (s, 5H), 2.47 (s, 3H), 2.43 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.8, 147.6, 139.2, 138.5, 137.0, 122.3, 122.2, 88.4, 76.3, 75.8, 72.5, 71.5, 71.1, 29.0, 21.3.

HR-MS (ESI) m/z calcd for $C_{19}H_{18}FeNO_3^+$ [M+H$^+$] 364.0631, found 364.0634.

98% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 30 bar, $t_R$= 8.42 min for minor isomer and $t_R$= 11.11 min for major isomer.



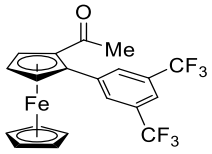

**1-Acetyl-2-(3,5-difluorophenyl)ferrocene (3p)**

Red oil. $R_f$ = 0.48, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –213.4 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.10 (d, $J$ = 6.8 Hz, 2H), 6.73 (t, $J$ = 8.0 Hz, 1H), 4.84 (s, 1H), 4.67 (s, 1H), 4.59 (s, 1H), 4.24 (s, 5H), 2.41 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.6, 162.2 (d, $J_{C\text{-}F}$ = 245 Hz), 162.0 (d, $J_{C\text{-}F}$ = 245 Hz), 141.2 (t, $J_{C\text{-}F}$ = 10 Hz), 113.1 (d, $J_{C\text{-}F}$ = 26 Hz), 113.1 (d, $J_{C\text{-}F}$ = 12 Hz), 102.3 (t, $J_{C\text{-}F}$ = 25 Hz), 88.6, 75.7, 72.2, 71.5, 70.9, 29.2.

HR-MS (ESI) m/z calcd for $C_{18}H_{15}F_2FeO^+$ [M+H$^+$] 341.0435, found 341.0439.

97% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 91:9, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 6.45 min for minor isomer and $t_R$= 7.00 min for major isomer.



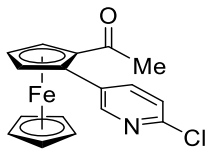

**1-Acetyl-2-(3,5-(ditrifluoromethyl)phenyl)ferrocene (3q)**

Red oil. $R_f$ = 0.53, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –187.6 (c 1.0 in chloroform).

H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.03 (s, 2H), 7.76 (s, 1H), 4.89–4.86 (m, 1H), 4.77–4.74 (m, 1H), 4.68–4.64 (m, 1H), 4.25 (s, 5H), 2.45 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.7, 140.1, 130.5 (q, $J_{C\text{-}F}$ = 33 Hz), 130.3 (q, $J_{C\text{-}F}$ = 4 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271 Hz), 120.4 (quint, $J_{C\text{-}F}$ = 4 Hz), 87.4, 76.1, 75.9, 73.0, 71.6, 71.4, 28.8.

HR-MS (ESI) m/z calcd for $C_{20}H_{15}F_6FeO^+$ [M+H$^+$] 441.0371, found 441.0375.

96% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 96:4, flow rate = 0.5 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 9.15 min for minor isomer and $t_R$= 10.16 min for major isomer.



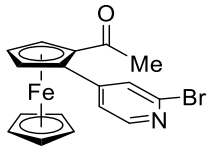

**1-Acetyl-2-(2-chloro-5-pyridinyl)ferrocene (3r)**

Red oil. $R_f$ = 0.15, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –105.2 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.57 (s, 1H), 7.91–7.86 (m, 1H), 7.26–7.23 (m, 1H), 4.86–4.84 (m, 1H), 4.72–4.68 (m, 1H), 4.65–4.62 (m, 1H), 4.23 (s, 5H), 2.43 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.9, 150.0, 149.5, 140.5, 132.5, 122.7, 85.1, 76.2, 75.4, 72.8, 71.5, 71.3, 28.9.

HR-MS (ESI) m/z calcd for $C_{17}H_{15}ClFeNO^+$ [M+H$^+$] 340.0186, found 340.0189.

97% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 82:18, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 37 bar, $t_R$= 13.22 min for minor isomer and $t_R$= 11.12 min for major isomer.



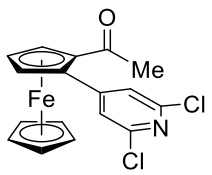

**1-Acetyl-2-(2-bromo-4-pyridinyl)ferrocene (3s)**

Red oil. $R_f$ = 0.12, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –112.4 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.26 (d, $J$ = 5.2 Hz, 1H), 7.67 (s, 1H), 7.45 (d, $J$ = 5.2 Hz, 1H), 4.88 (s, 1H), 4.76 (s, 1H), 4.66 (s, 1H), 4.24 (s, 5H), 2.46 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.5, 149.9, 148.8, 141.6, 128.6, 124.2, 85.1, 75.8, 73.5, 71.8, 71.7, 29.0.

HR-MS (ESI) m/z calcd for $C_{17}H_{15}BrFeNO^+$ [M+H$^+$] 383.9681, found 383.9685.

93% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 82:18, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 10.99 min for minor isomer and $t_R$= 14.14 min for major isomer.



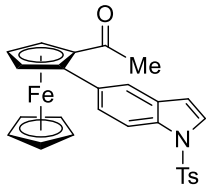

**1-Acetyl-2-(2,6-dichloro-4-pyridinyl)ferrocene (3t)**

Red oil. $R_f$ = 0.34, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –238.4 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.46 (s, 2H), 4.92–4.88 (m, 1H), 4.79–4.76 (m, 1H), 4.71–4.67 (m, 1H), 4.26 (s, 5H), 2.47 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.5, 152.9, 149.5, 123.7, 83.9, 76.3, 76.0, 73.9, 72.0, 71.9, 28.9.

HR-MS (ESI) m/z calcd for $C_{17}H_{14}Cl_2FeNO^+$ [M+H$^+$] 373.9796, found 373.9800.

97% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 7.82 min for minor isomer and $t_R$= 9.06 min for major isomer.



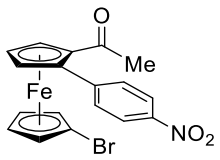

**1-Acetyl-2-(1-tosyl-1*H*-indole-5-yl)ferrocene (3u)**

Red oil. $R_f$ = 0.41, (2:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –88.7 (c 1.0 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.90 (d, $J$ = 8.8 Hz, 1H), 7.81 (d, $J$ = 8.0 Hz, 2H), 7.70 (d, $J$ = 1.2 Hz, 1H), 7.57 (d, $J$ = 3.6 Hz, 1H), 7.51 (d, $J_1$ = 8.8 Hz, $J_2$ = 1.6 Hz, 1H), 7.25 (d, $J$ = 8.4 Hz, 2H), 6.65 (d, $J$ = 3.6 Hz, 1H), 4.84–4.81 (m, 1H) , 4.65–4.62 (m, 1H) , 4.56–4.54 (m, 1H), 4.23 (s, 5H), 2.36 (s, 3H), 2.32 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.3, 145.0, 135.3, 133.8, 132.0, 130.2, 129.9, 127.2, 126.9, 126.6, 122.7, 112.4, 108.9, 91.6, 77.1, 75.8, 71.2, 71.2, 70.5, 29.4, 21.6.

HR-MS (ESI) m/z calcd for $C_{27}H_{24}FeNO_3S^+$ [M+H$^+$] 498.0821, found 498.0821.

95% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 75:25, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 30 bar, $t_R$= 20.38 min for minor isomer and $t_R$= 26.55 min for major isomer.




**1′-Bromo-1-acetyl-2-(4-nitrophenyl)ferrocene (4a)**

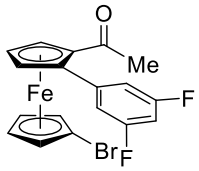
Red oil. $R_f$ = 0.35, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –213.6 (c 0.5 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.18–8.13 (m, 2H), 7.77–7.71 (m, 2H), 4.88 (s, 1H), 4.75–4.72

(m, 1H), 4.44 (s, 2H), 4.14 (s, 2H), 2.48 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.1, 146.6, 144.5, 130.9, 127.7, 88.7, 78.3, 78.1, 76.1, 74.0, 73.7, 73.1, 71.3, 71.1, 29.4.

HR-MS (ESI) m/z calcd for $C_{18}H_{15}BrFeNO_3^+$ [M+H$^+$] 427.9579, found 427.9580.

92% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 31 bar, $t_R$= 17.64 min for minor isomer and $t_R$= 19.84 min for major isomer.



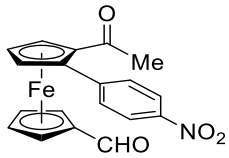

**1′-bromo-1-acetyl-2-(3,5-difluorophenyl)ferrocene (4b)**

Red oil. $R_f$ = 0.43, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –178.4 (c 0.5 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.16–7.09 (m, 2H), 6.77–6.71 (m, 1H), 4.85–4.82 (m, 1H), 4.68–4.63 (m, 2H), 4.48–4.43 (m, 2H), 4.17–4.13 (m, 2H), 2.44 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.1, 162.3 (d, $J_{C\text{-}F}$ = 245 Hz), 162.1 (d, $J_{C\text{-}F}$ = 246 Hz), 140.2 (t, $J_{C\text{-}F}$ = 10 Hz), 113.3 (d, $J_{C\text{-}F}$ = 25 Hz), 113.3 (d, $J_{C\text{-}F}$ = 11 Hz), 102.6 (t, $J_{C\text{-}F}$ = 25 Hz), 89.6, 78.2, 78.2, 77.9, 75.3, 73.6, 73.4, 72.9, 71.2, 71.1, 29.5.

HR-MS (ESI) m/z calcd for $C_{18}H_{14}BrF_2FeO^+$ [M+H$^+$] 418.9540, found 418.9544.

92% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 33 bar, $t_R$= 7.54 min for minor isomer and $t_R$= 8.38 min for major isomer.




**1′-Formyl-1-acetyl-2-(4-nitrophenyl)ferrocene (4c)**

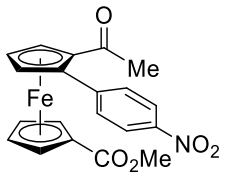
Red oil. $R_f$ = 0.55, (2:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –140.4 (c 0.5 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 10.13 (s, 1H), 8.24 (d, $J$ = 8.8 Hz, 2H), 7.70 (d, $J$ = 8.8 Hz, 2H), 5.10–5.06 (m, 1H), 4.94–4.90 (m, 1H), 4.86–4.80 (m, 3H), 4.58–4.50 (m, 2H), 2.25 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 200.6, 191.8, 147.1, 142.6, 130.2, 123.6, 89.5, 81.6, 75.2, 75.1, 74.0,

72.8, 72.7, 72.3, 27.7.

HR-MS (ESI) m/z calcd for $C_{19}H_{16}FeNO_4^+$ [M+H$^+$] 378.0423, found 378.0428.

97.5% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), *n*-hexane/2-propanol = 60:40, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 9.61 min for minor isomer and $t_R$= 10.57 min for major isomer.



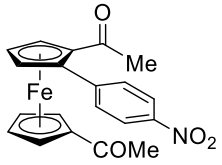

**1′-Methoxycarbonyl-1-acetyl-2-(4-nitrophenyl)ferrocene (4d)**

Red oil. $R_f$ = 0.48, (2:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –252.8 (c 0.5 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.18–8.14 (m, 2H), 7.75–7.71 (m, 2H), 4.90–4.80 (m, 3H), 4.74–4.71 (m, 1H), 4.70–4.68 (m, 1H), 4.44–4.38 (m, 2H), 3.79 (s, 3H), 2.42 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 201.0, 170.0, 146.7, 144.0, 130.9, 122.7, 88.8, 77.5, 76.7, 74.8, 74.5, 74.4, 74.0, 73.5, 72.8, 72.5, 51.9, 29.2.

HR-MS (ESI) m/z calcd for $C_{20}H_{18}FeNO_5^+$ [M+H$^+$] 408.0529, found 408.0531.

92% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 60:40, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 7.24 min for minor isomer and $t_R$= 9.10 min for major isomer.



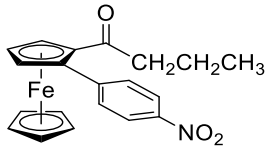

**1,1′-Diacetyl-2-(4-nitrophenyl)ferrocene (4e)**

Red oil. $R_f$ = 0.34, (2:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –160.5 (c 0.5 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.17 (d, $J$ = 8.4 Hz, 2H), 7.69 (d, $J$ = 8.4 Hz, 2H), 4.88 (s, 1H), 4.83 (s, 1H), 4.79 (s, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 4.50 (s, 2H), 2.41 (s, 3H), 2.25 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 200.9, 200.7, 146.8, 143.6, 130.7, 122.8, 89.0, 81.3, 77.5, 75.7, 74.4, 72.7, 72.5, 72.3, 29.3, 27.7.

HR-MS (ESI) m/z calcd for $C_{20}H_{18}FeNO_4^+$ [M+H$^+$] 392.0580, found 392.0580.

92% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 38 bar, $t_R$= 9.87 min for minor isomer and $t_R$= 10.98 min for major isomer.




**1-Butyryl-2-(4-nitrophenyl)ferrocene (4f)**

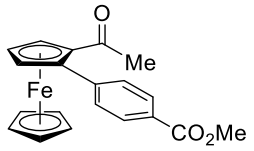
Red oil. $R_f$ = 0.52, (6:1, hexane: ethyl acetate). $[\alpha]_D^{28}$ = –133.2 (c 0.5 in chloroform).

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.15 (d, $J$ = 8.8 Hz, 2H), 7.72 (d, $J$ = 8.8 Hz, 2H), 4.91–4.88 (m, 1H), 4.76–4.73 (m, 1H), 4.67–4.64 (m, 1H), 4.24 (s, 5H), 2.85–2.65 (m, 2H), 1.80–1.70 (m, 2H), 1.01 (t, $J$ = 7.2 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 204.2, 146.4, 145.7, 130.8, 122.5, 87.7, 76.5, 75.7, 72.5, 71.6, 71.4, 42.7, 17.7, 14.0.

HR-MS (ESI) m/z calcd for $C_{20}H_{20}FeNO_3^+$ [M+H$^+$] 378.0787, found 378.0792.

92% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm UV detector, pressure = 42 bar, $t_R$= 17.03 min for minor isomer and $t_R$= 20.19 min for major isomer.

## 4. X-ray Diffraction Analysis of Compound ($R_p$)-3b



(Compound ($R_p$)-**3b**)

The single crystals of this compound suitable for X-ray diffraction analysis was obtained by slow diffusion of hexane into a dichloromethane solution of compound ($R_p$)-**3b**. According to crystallographic data, the absolute configuration of compound **3b** was assigned to be *R*. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1573176 contains the crystallographic data for compound ($R_p$)-**3b** and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

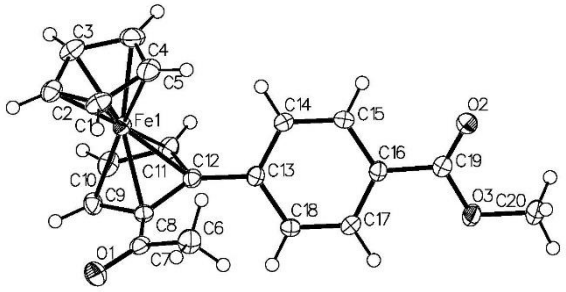


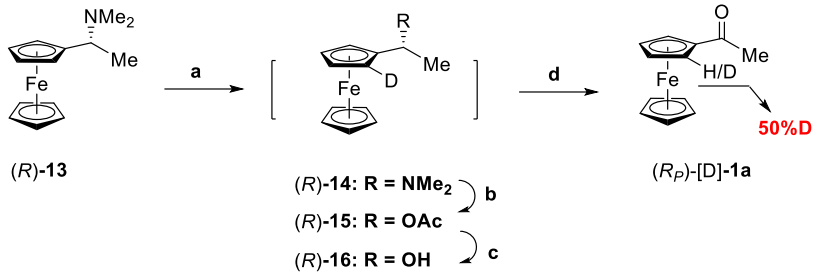

Fig. 1S The crystal structure of compound ($R_p$)-**3b**.

Crystal data for compound ($R_p$)-**3b**: $C_{20}H_{18}FeO_3$, orthorhombic $P2_12_12_1$, Hall symbol: P 2ac 2ab, Mo *K*α radiation: λ = 0.71073 Å, a = 10.0132 (a) Å, b = 10.02044 Å, c = 16.0394 Å; α = β = γ = 90 °, $\theta$ = 2.1–31.1°, $\mu$ = 0.95 $mm^{-1}$, *V* = 1609.34 (6) Å, *T* = 133 K, *Z* = 4, *F*(000) = 752.

## 5. Mechanistic Studies

### 5.1 Deuteration Experiments

### Synthesis of ($R_p$)-[D]-1a




Reaction conditions: (**a**) 1. *tert*-BuLi, THF; 2. $CH_3OD$, 95% yield; (**b**) $Ac_2O$, 90 °C, 2h, 87% yield; (**c**) LiOH, THF/$H_2O$, rt, 78% yield; (d) $MnO_2$, $CH_2Cl_2$, rt, 94% yield.

To a stirred solution of (*R*)-**13** (1.4 g, 5.45 mmol) in THF (30 mL) under nitrogen atmosphere at –78 °C, *tert*-BuLi (4.6 mL, 1.3 M, 6.0 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After that, the $CH_3OD$ (360 mg, 10.9 mmol) was added. The reaction mixture was further stirred for 30 min and then diluted with meanthol (5 mL). The solution was concentrated on rotary evaporator. The residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate/$Et_3N$ = 12/7/0.1) to give (*R*)-**14** as a red oil (1.34 g, 95%), $R_f$ = 0.35, (12 : 7 : 0.1, hexane : ethyl acetate : $Et_3N$). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 4.15–4.08 (m, 8H), 3.62–3.55 (m, 1H), 2.07 (s, 6H), 1.44 (d, $J$ = 6.8 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 87.2, 87.1, 69.3, 68.5, 67.3, 67.2, 67.2, 67.1, 66.8, 58.6, 58.6, 40.7, 16.1.

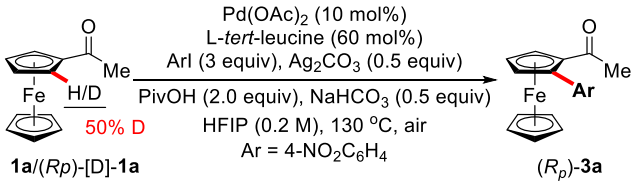
A solution of (*R*)-**14** (645 mg, 2.5 mmol) in acetic anhydride (5.0 mL) was heated to 90 °C for 2 h under nitrogen atmosphere (monitored by TLC). After the starting material disappeared, the reaction was diluted with toluene (30 mL) and concentrated under reduced pressure. The operation was repeated 3 times. The remaining red oil [(*R*)-**15**, 594 mg, 87%], was directly used in the next step without further purification.

To a solution of (*R*)-**15** (200 mg, 0.73 mmol) in THF (15 mL), LiOH [175 mg, 7.3 mmol, dissolved in water (5 mL)] were added. The reaciton mixture was stirred at room temperature for 24 h. The resulting mixture was diluted with $CH_2Cl_2$ (20 mL) and washed with water (20 mL). The organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The

resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 8/1) to provide (*R*)-**16** (132 mg, 78%) as a yellow solid, $R_f$ = 0.25, (10 : 1, hexane : ethyl acetate). m.p. 74–76 °C. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 4.60–4.50 (m, 1H), 4.23–4.15 (m, 8H), 1.88 (d, *J* = 4.4 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 94.8, 94.7, 68.2, 67.9, 67.8, 67.8, 66.1, 66.0, 65.5, 23.7.

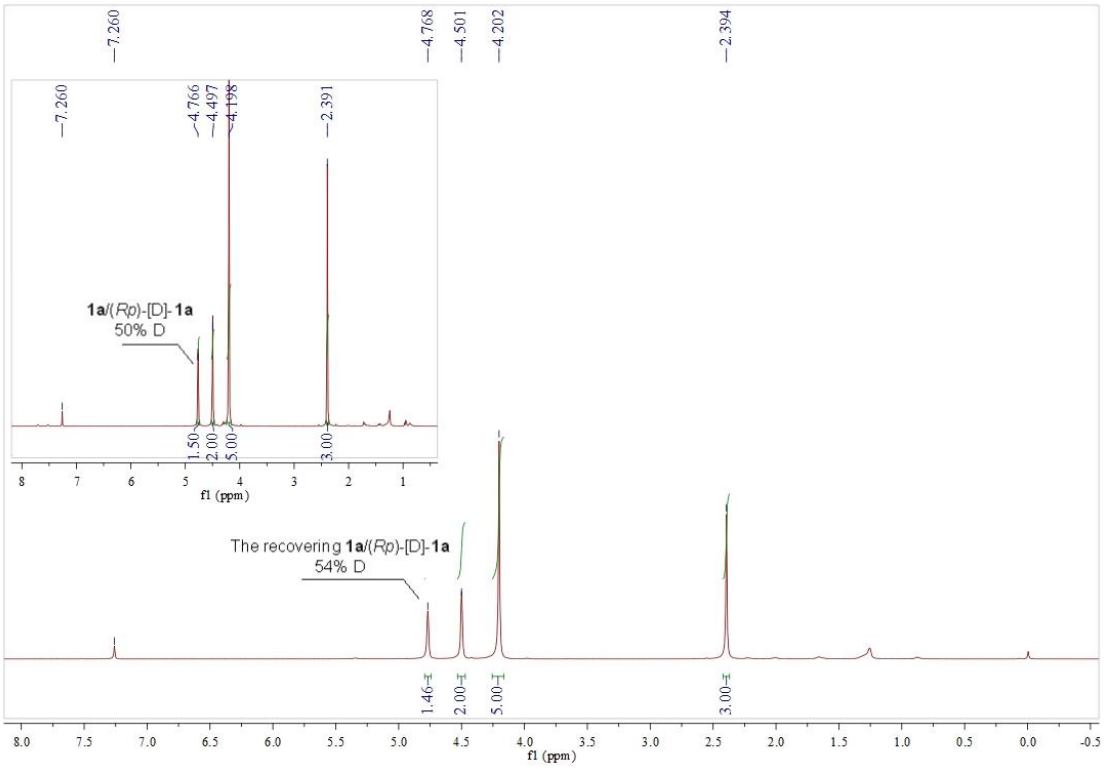
To a solution of (*R*)-**16** (300 mg, 1.3 mmol) in $CH_2Cl_2$ (20 mL), active $MnO_2$ (1.13g, 13 mmol) was added. The reaciton mixture was stirred at room temperature for 1 h. The solution was diluted with $CH_2Cl_2$ (20 mL) and filtered via a plug of celite and concentrated under reduced pressure. The remaining orange oil was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 8/1) to give **($R_p$)-[D]-1a** as orange solid (253 mg, 85%) as an orange solid, $R_f$ = 0.28, (10 : 1, hexane : ethyl acetate). m.p. 78–79 °C. $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 4.77 (s, 1.5H), 4.50 (s, 2H), 4.20 (s, 5H), 2.39 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 202.1, 79.3, 79.2, 72.3, 72.2, 69.8, 69.6, 27.4.

## KIE Experiment



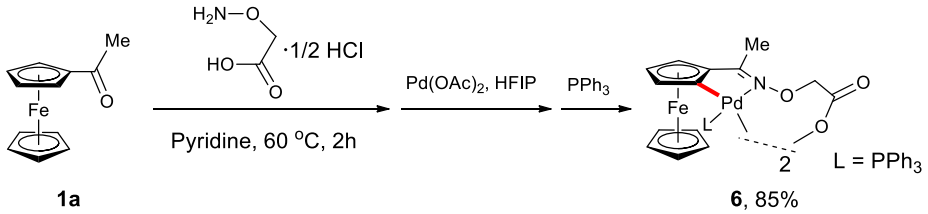

To a 20 mL reaction tube was added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), L-*tert*-Leucine (15.75 mg, 0.12 mmol), $Ag_2CO_3$ (27.6 mg, 0.1 mmol), $NaHCO_3$ (8.4 mg, 0.1 mmol), trimethylacetic acid (40.8 mg, 0.4 mmol), **($R_p$)-[D]-1a** (50% D, 45.6 mg, 0.2 mmol), 4-nitro-1-iodobenzene(149.4 mg, 0.6 mmol) and hexafluoroisopropanol (1.0 mL). The tube was then sealed and the mixture was stirred at room temperature for 5 min before being heated to 130 °C for 12 h. The reaction mixture was cooled to room temperature, filtrated via celite, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: 8/1, hexane/ethyl acetate) to recovery deuterated substrate (30.6 mg, 0.1336 mmol) and then its isotopic distribution was analyzed by $^1$H NMR spectra. After calculation, the conversion of the reaction was 33% and the isotopic distribution of the recovering **($R_p$)-[D]-1a** was 54% D. The kinetic isotope effect of this

reaction was determined to be $k_H/k_D \approx 1.37$.




## 5.2 Preparation of the Intermediate Cyclopalladated Complex

### Synthesis of Palladacycle Dimer 6




Acetylferrocene **1a** (456 mg, 2.0 mmol) and aminooxyacetic acid hemihydrochloride (437 mg, 4.0 mmol) were weighed into an oven dried 100 mL round bottom flask. Then, pyridine(5 mL) was added and the mixture was stirred at 60 °C for 2 h. Upon completion, most pyridine was evaporated under reduced pressure. The resulting mixture was diluted with EtOAc (60 mL) and washed with water (100 mL) and diluted HCl aqueous solution (100 mL, ca. 0.01 M). The organic phase was dried with anhydrous $Na_2SO_4$ and the solvent was removed under vacuum. The remaining red oil

(542 mg, 90%) was directly used in the next step without further purification.

The abovementioned red oil (270 mg, 0.9 mmol), $Pd(OAc)_2$ (243 mg, 1.08 mmol) and HFIP (10.0 mL) were weighed into a reaction vial (50 mL). The reaction mixture was stirred at 80 °C for 12 h. After that, the reaction mixture was cooled to room temperature and $PPh_3$ (283 mg, 1.08 mmol) was added. The reaction was stirred for another 1 h at 80 °C. Upon completion, the reaction mixture was cooled to room temperature and diluted with EtOAc (30 mL). Then the solution was filtered via a plug of celite and concentrated under reduced pressure. The remaining red oil was purified by silica gel column chromatography (eluent: EtOAc/MeOH = 35/1) to give **6** as red solid (510 mg, 85%). $R_f$ = 0.21, (35 : 1, EtOAc : MeOH). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.73–7.66 (m, 6H), 7.50–7.40 (m, 9H), 4.58–4.45 (m, 2H), 4.36 (d, $J$ = 2.4 Hz, 1H), 4.09 (t, $J$ = 2.4 Hz, 1H), 3.96 (s, 5H), 3.18 (d, $J$ = 2.0 Hz, 1H), 2.24 (s, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 171.6, 170.4, 134.7, 134.6, 130.9, 130.9, 130.3, 129.8, 128.8, 128.5, 128.4, 95.4, 95.3, 84.9, 75.9, 75.8, 75.7, 70.5, 68.4, 65.9, 65.5, 30.5, 19.1, 13.7, 12.0. $^{31}$P-NMR $\delta$ = 31.78.

## The Crystal Structure of Palladacycle Dimer 6

The single crystals of this compound suitable for X-ray diffraction analysis was obtained by slow diffusion of hexane into a chloroform solution of compound **6**. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1586952 contains the crystallographic data for compound **6** and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

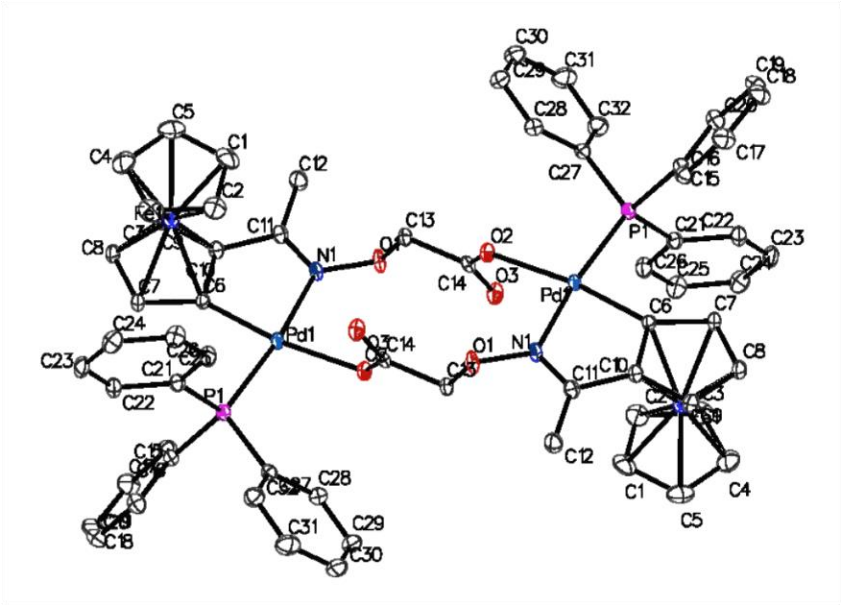
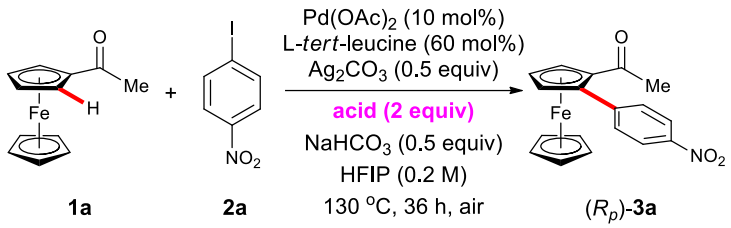



Fig. 2S The crystal structure of palladacycle dimer **6**. All hydrogen atoms were omitted for clarity. Crystal data for compound **6**: $C_{32}H_{28}FeNO_3PPd \cdot 3(CHCl_3)$, red block, triclinic *P*-1, Mo *K*α radiation: λ = 0.71073 Å, a = 11.649 (2) Å, b = 12.431 (3) Å, c = 15.066 (3) Å; α = 98.08 (3)º, β = 104.26 (3)º, γ = 105.36 (3)º, $\theta$ = 1.9–27.9º, $\mu$ = 1.50 $mm^{-1}$, $V$ = 1988.8 (8) $Å^3$, $T$ = 113 K, $Z$ = 2, $F$(000) = 1024.

## 5.3 Effect of Carboxylic Acid on Enantioselectivity in the C–H Arylation

**Table S6 Effect of Carboxylic Acid on Enantioselectivity in the C–H Arylation.**

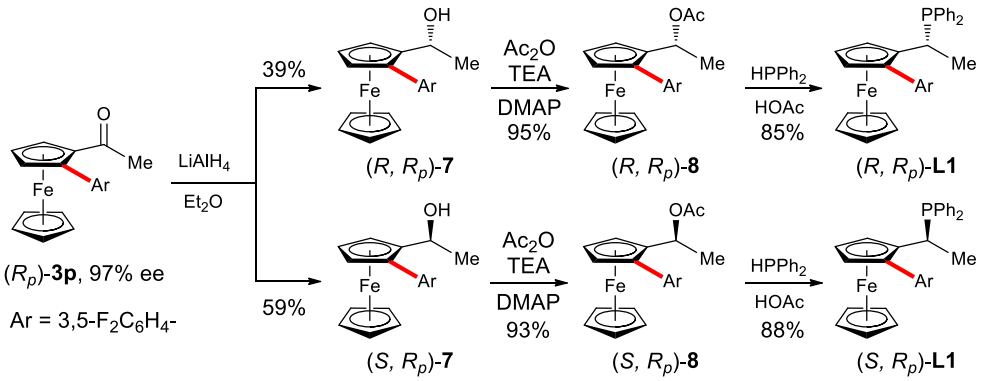



| Entry | Carboxylic acid | pKa | ee (%)[b] |
|---|---|---|---|
| 1 | acetic acid | 4.76 | 86 |
| 2 | propanoic acid | 4.78 | 91 |
| 3 | *iso*-butyric acid | 4.90 | 92 |
| 4 | 2,2,2-trimethylacetic acid | 5.03 | 95 |
| 5 | cyclohexanecarboxylic acid | 4.88 | 90 |
| 6 | 1-adamantanecarboxylic aicd | 4.90 | 94 |
| 7 | 2,4,6-trimethylbenzoic acid | 3.45 | 72 |
| 8 | benzoic acid | 4.19 | 76 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), L-*tert*-leucine (60 mol %), $Ag_2CO_3$ (0.1 mmol), acid (2.0 equiv), HFIP (1.0 mL), 130 °C, 36 h, air. [b]Determined by HPLC analysis.

## 6. Synthesis of Novel Chiral Ferrocene Ligands

### 6.1. Synthesis of new chiral mono-phosphine ferrocene ligands



To a solution of ($R_p$)-**3p** (97 % ee, 600 mg, 1.76 mmol) in ether (30 mL) under nitrogen atmosphere at 0 °C, $LiAlH_4$ (134 mg, 3.53 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. After that, the solution was quenched with water (30 mL) at 0 °C and diluted with ether (20 mL). The organic layer was separated and the aqueous layer extracted with ether (2 x 20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 12/1) to provide the two diastereoisomers (*R*, $R_P$)-**7** (235 mg, 39%) and (*S*, $R_P$)-**7** (355 mg, 59%), respectively**.**

**(*R*, $R_P$)-7**: orange oil, $R_f$ = 0.42, (6:1, hexane: ethyl acetate). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.02 (d, *J* = 6.8 Hz, 2H), 6.70 (t, *J* = 9.2 Hz, 1H), 4.82–4.75 (m, 1H), 4.48–4.43 (m, 2H), 4.34–4.30 (m, 1H), 4.21 (s, 5H), 2.12 (s, 1H), 1.37 (t, *J* = 6.0 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 162.7 (d, $J_{C-F}$ = 246 Hz), 162.6 (d, $J_{C-F}$ = 246 Hz), 142.2 (t, $J_{C-F}$ = 10 Hz), 111.9 (d, $J_{C-F}$ = 26 Hz), 111.9 (d, $J_{C-F}$ = 12 Hz), 101.9 (t, $J_{C-F}$ = 25 Hz), 94.5, 84.7, 69.8, 69.6, 67.5, 66.2, 63.6, 24.5. HR-MS (ESI) m/z calcd for $C_{18}H_{17}F_2FeO^+$ [M+H$^+$] 343.0591, found 343.0595.

**(*S*, $R_P$)-7**: orange oil, $R_f$ = 0.38, (6:1, hexane: ethyl acetate). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.34–7.26 (m, 2H), 6.73–6.65 (m, 1H), 5.00–4.93 (m, 1H), 4.53–4.50 (m, 1H), 4.45–4.41 (m, 1H), 4.35–4.31 (m, 1H), 4.10 (s, 5H), 1.71 (d, *J* = 6.8 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 162.8 (d, $J_{C-F}$ = 246 Hz), 162.6 (d, $J_{C-F}$ = 246 Hz), 142.5 (t, $J_{C-F}$ = 10 Hz), 111.8 (d, $J_{C-F}$ = 26 Hz), 111.8 (d, $J_{C-F}$ = 12 Hz), 101.7 (t, $J_{C-F}$ = 26 Hz), 88.8, 84.8, 70.9, 70.4, 67.8, 66.8, 64.7, 22.9. HR-MS (ESI) m/z calcd for $C_{18}H_{17}F_2FeO^+$ [M+H$^+$] 343.0591, found 343.0596.

To a solution of (*R*, $R_P$)-**7** (235 mg, 0.69 mmol) in triethylamine (15 mL), acetic anhydride (352 mg, 3.45 mmol) and DMAP (8.43 mg, 0.069 mmol) were added. The reaciton mixture was stirred at room temperature for 12 h. The solution was quenched with water (20 mL) and then diluted with ethyl acetate (35 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The remaining orange oil, [(*R*, $R_P$)-**8**, 252 mg, 95%], was directly used in the next step without further purification. In a similar manner, (*S*, $R_P$)-**8** (371mg, 93%) was prepared

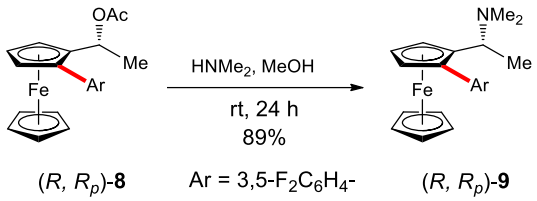
from (*S*, $R_P$)-**7**.

**(*R*, $R_P$)-L1**: (*R*, $R_P$)-**8** (252 mg, 0.65 mmol) was suspended in 10 mL of anhydrous and degassed acetic acid under an argon atmosphere. After addition of diphenylphosphine (145 mg, 0.78 mmol), the reaction mixture was stirred at 125 °C for 2 h. After that, aqueous sodium bicarbonate was added into the reaction solution at 0 °C and diluted with $CH_2Cl_2$. The organic layer was separated and the aqueous layer extracted with $CH_2Cl_2$ (2 x 20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The remaining red oil was chromatographed on neutral alumina (eluent: hexane/ethyl acetate = 100/1) to give (*R*, $R_P$)**-L1** as orange oil (282 mg, 85%). Similarly, **(*S*, $R_P$)-L1** (434 mg, 88%) was also prepared from (*S*, $R_P$)-**8**.

**(*R*, $R_P$)-L1**: orange oil, $R_f$ = 0.25, (100 : 1, hexane : ethyl acetate). $[\alpha]_D^{28}$ = +22.6 (c 1.0 in chloroform). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.51–7.45 (m, 2H), 7.40–7.35 (m, 3H), 7.12–7.06 (m, 1H), 6.91–6.86 (m, 2H), 6.71–6.66 (m, 2H), 6.63–6.50 (m, 3H), 4.37–4.34 (m, 1H), 4.33–4.31 (m, 1H), 4.18–4.15 (m, 1H), 4.13 (s, 5H), 3.56–3.50 (m, 1H), 1.70–1.63 (m, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 162.0 (dd, $J_{C\text{-}F}$ = 245, 14 Hz), 142.4 (t, $J_{C\text{-}F}$ = 9.9 Hz), 136.2 (t, $J_{C\text{-}F}$ = 16.8 Hz), 133.8 (d, $J_{C\text{-}P}$ = 19.8 Hz), 133.7 (d, $J_{C\text{-}P}$ = 19.6 Hz), 133.2 (d, $J_{C\text{-}P}$ = 19 Hz), 133.1 (d, $J_{C\text{-}P}$ = 18.3 Hz), 129.1, 129.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.4, 127.3, 116.3 (d, $J_{C\text{-}P}$ = 21.7 Hz), 112.5 (d, $J_{C\text{-}P}$ = 21.2 Hz), 112.2 (d, $J_{C\text{-}P}$ = 11.9 Hz), 112.1 (d, $J_{C\text{-}F}$ = 24.9 Hz), 101.0 (t, $J_{C\text{-}F}$ = 25.7 Hz), 92.3 (d, $J_{C\text{-}P}$ = 16 Hz), 85.7, 77.2, 69.8, 69.7, 67.5, 67.4, 67.3, 67.1, 66.4, 28.5 (d, $J_{C\text{-}P}$ = 13 Hz), 20.1 (d, $J_{C\text{-}P}$ = 22.4 Hz). $^{31}$P-NMR $\delta$ = 7.68. HR-MS (ESI) m/z calcd for $C_{30}H_{26}F_2FeP^+$ [M+H$^+$] 511.1084, found 511.1085.

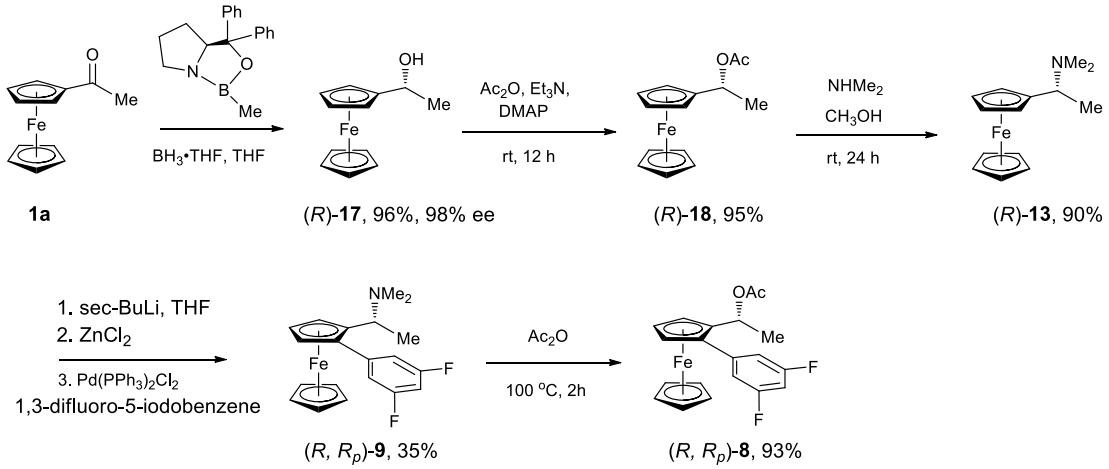
**(*S*, $R_P$)-L1**: orange oil, $R_f$ = 0.23, (100 : 1, hexane : ethyl acetate). $[\alpha]_D^{28}$ = –13.8 (c 1.0 in chloroform). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.66–7.60 (m, 2H), 7.44–7.37 (m, 5H), 7.33–7.28 (m, 5H), 6.72 (t, *J* = 8.4 Hz, 1H), 4.26–4.23 (m, 1H), 4.07 (s, 6H), 3.79–3.76 (m, 1H), 3.54–3.47 (m, 1H), 1.15–1.11 (m, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 162.2 (dd, $J_{C\text{-}F}$ = 246, 14 Hz), 143.2 (t, $J_{C\text{-}F}$ = 10 Hz), 138.2 (d, $J_{C\text{-}P}$ = 15 Hz), 136.7 (d, $J_{C\text{-}P}$ = 17 Hz), 134.3 (d, $J_{C\text{-}P}$ = 20 Hz), 133.6 (d, $J_{C\text{-}P}$ = 19 Hz), 129.1, 128.7, 128.4, 128.3, 128.2, 128.1, 113.3 (d, $J_{C\text{-}P}$ = 5 Hz), 113.2 (d, $J_{C\text{-}F}$ = 6 Hz), 113.1 (d, $J_{C\text{-}P}$ = 5 Hz), 101.7 (t, $J_{C\text{-}F}$ = 25 Hz), 90.9 (d, $J_{C\text{-}P}$ = 17 Hz), 85.8, 77.2, 70.5, 70.4, 70.3,

70.2, 70.0, 69.9, 69.8, 66.5, 31.5 (d, $J_{C\text{-}P}$ = 14 Hz), 20.2 (d, $J_{C\text{-}P}$ = 13 Hz). $^{31}$P-NMR $\delta$ = -1.58. HR-MS (ESI) m/z calcd for $C_{30}H_{26}F_2FeP^+$ [M+H$^+$] 511.1084, found 511.1082.




(*R*, *R*$_P$)-**8** (500 mg, 1.30 mmol) was dissolved in 10 mL of MeOH. After addition of dimethylamine (1.5 mL, 40% in water), the reaction mixture was stirred at room temperature for 24 h. Then, the water (15 mL) and ethyl acetate (40 mL) were added to the solution. The organic layer was separated, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate/$Et_3N$ = 7/12/0.1) to give (*R*, *R*$_P$)-**9** (427 mg, 89%) as a red oil, $R_f$ = 0.23, (7:12:0.1, Hexane: Ethyl Acetate: $Et_3N$). $[\alpha]_D^{28}$ = –27.0 (c 1.0 in chloroform). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 7.38–7.31 (m, 2H), 6.71–6.64 (m, 1H), 4.48–4.45 (m, 1H), 4.32–4.28 (m, 2H), 4.07 (s, 5H), 3.88–3.82 (m, 1H), 2.05 (s, 6H), 1.50 (d, *J* = 6.8 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 162.6 (d, $J_{C\text{-}F}$ = 244 Hz), 162.5 (d, $J_{C\text{-}F}$ = 244 Hz), 143.7 (t, $J_{C\text{-}F}$ = 10 Hz), 112.2 (d, $J_{C\text{-}F}$ = 25 Hz), 112.2 (d, $J_{C\text{-}F}$ = 11 Hz), 101.2 (t, $J_{C\text{-}F}$ = 26 Hz), 88.2, 85.0, 70.3, 69.6, 68.3, 67.1, 55.5, 39.9, 12.9. HR-MS (ESI) m/z calcd for $C_{20}H_{22}F_2FeN^+$ [M+H$^+$] 370.1064, found 370.1061.

## 6.2. Absolute Configuration Assignment on Carbon Stereogenic Center



To a solution of (*S*)-1-methyl-3,3-diphenyltetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*][1,3,2]oxazaborole[2] (729 mg, 2.63 mmol) in THF (10 mL) was added 1 M $BH_3$-THF solution (2.63 mL, 2.63 mmol) and the mixture was stirred at room temperature for 30 min under an argon atmosphere. Then, 1 M $BH_3$-THF solution (11.9 mL, 11.9 mmol) and **1a** (3 g, 13.2 mmol, dissolved in THF (20 mL)) were added dropwise. The reaction mixture was stirred until **1a** was disappeared on a TLC. The reaction was quenched with MeOH and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 10/1) to give (*R*)-**17** (2.92 g, 96% yield, 98 % ee).[3]

To a solution of (*R*)-**17** (2.92 g, 12.7 mmol) in triethylamine (60 mL), acetic anhydride (6.48 g, 63.5 mmol) and DMAP (155 mg, 1.27 mmol) were added. The reaction mixture was stirred at room temperature for 12 h. The solution was quenched with water (40 mL) and diluted with ethyl acetate (80 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 x 40 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The remaining orange oil (*R*)-**18** (3.28 g, 95%), was directly used in the next step without further purification.

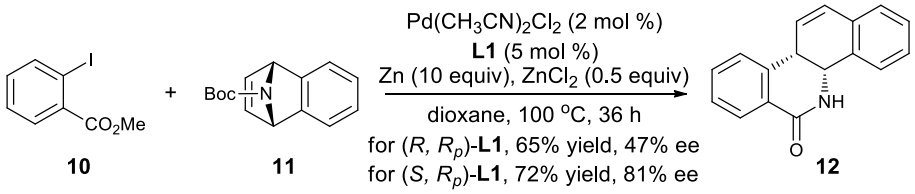
The crude ester (*R*)-**18** (3.28 g, 12.0 mmol) was dissolved in 30 mL of MeOH. After addition of dimethylamine (15 mL, 40 % in water), the reaction mixture was stirred at room temperature for 24 h. Then, the water (50 mL) and ethyl acetate (80 mL) were added to the solution. The organic layer was separated, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate/$Et_3N$ = 12/7/0.1) to give (*R*)-**13** as red oil (2.79 g, 90%). The physical data for this compound are identical with the previous literature.[4]

To a solution of (*R*)-**13** (2.79 g, 10.85 mmol ) in dry THF (40 mL) was added dropwise *sec*-BuLi (10 mL, 1.3 M, 13.0 mmol) at 0 $^oC$ under an argon atmosphere. After stirring the reaction mixture for 1 h, a solution of zinc chloride (13.6 mL, 13.6 mmol, 1M in THF) was added and the solution was stirred for an additional hour. After addition of $Pd(PPh_3)_2Cl_2$ (381 mg, 0.54 mmol) and a solution of 1,3-difluoro-5-idobenzene (5.21 g, 21.7 mmol) in THF (10 mL) the reaction mixture was refluxed for three days. The solvent was removed under reduced pressure and the residue redissolved in $CH_2Cl_2$. Water (30 mL) and a sodium hydroxide solution (5 M) were added and the organic layer separated. The aqueous layer was extracted with $CH_2Cl_2$ (2 x 30 mL), and the

combined organic layers were washed with water (2 x 20 mL) and dried over $Na_2SO_4$. After removal of the solvent the residue was purified by silica gel column chromatography (eluent: Hexane/Ethyl Acetate/$Et_3N$ = 12/7/0.1) to give (*R, R*$_P$)-**9** as red oil (1.4 g, 35%). The physical data for this compound are identical with compound derived from C–H arylation product **3p**.

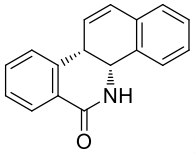
A solution of (*R, R*$_P$)-**9** (500 mg, 1.35 mmol) in acetic anhydride (5.0 mL) was heated to 100 °C for 2 h (monitored by TLC). After the starting material disappeared, the solution was quenched with water (20 mL) and diluted with ethyl acetate (20 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 x 15 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: Hexane/Ethyl Acetate = 50:1) to give (*R, R*$_P$)-**8** (482 mg, 93%). The physical data for this compound are identical with compound derived from C–H arylation product **3p**.

## 7. Asymmetric Catalysis Using Chiral Ferrocene Mono-Phosphine Ligand




**10** **11** **12**

To a flame-dried round-bottom flask, $Pd(CH_3CN)_2Cl_2$ (2.6 mg, 0.01 mmol, 5 mol%), (*R, R*$_p$)-**L1** or (*S, R*$_p$)-**L1** (10.2 mg, 0.02 mmol, 10 mol%) and 2 mL 1,4-dioxane were introduced under an argon atmosphere and stirred for 1 hour at room temperature. Azabenzonorbornadiene **11** (63.2 mg, 0.22 mmol), methyl 2-iodobenzoate **10** (64.4 mg, 0.2 mmol), Zn (131.0 mg, 2 mmol) and $ZnCl_2$ (13.6 mg, 0.1 mmol) were then introduced and the resultant mixture heated at 100 °C for 20 h. The reaction mixture was then diluted with $CH_2Cl_2$, filtered through celite, and washed with $CH_2Cl_2$ several times. The combined organic solution was condensed in a rotary evaporator. The residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to afford the desired product **12**[5] as a white solid in 65 % yield (47% ee) and 72% yield (81% ee), respectively.




**12**

White solid. $R_f$ = 0.33, (2:1, hexane: ethyl acetate), m.p. 177–178 °C. $[\alpha]_D^{25}$ = -2.4 (c 0.5 in chloroform) (81% ee).[5]

H-NMR (400 MHz, $CDCl_3$) $\delta$ = 8.08 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.52 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.39 (td, $J_1$ = 7.6 Hz, $J_2$ = 0.8 Hz, 1H), 7.35–7.26 (m, 4H), 7.16 (d, $J$ = 7.2 Hz, 1H), 6.58 (dd, $J_1$ = 9.6 Hz, $J_2$ = 2.4 Hz, 1H), 5.82–5.70 (m, 2H), 4.87 (d, $J$ = 5.6 Hz, 1H), 3.90–3.88 (m, 1H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ =165.0, 139.6, 133.0, 132.6, 131.9, 129.3, 128.6, 128.3, 128.0, 127.6, 127.6, 127.3, 127.1, 127.1, 52.2, 38.6.

HR-MS (ESI) m/z calcd for $C_{17}H_{14}NO^+$ [M+H$^+$] 248.1070, found 248.1074.

47% or 81% ee. [HPLC condition: Chiralcel AD-H column, (25 cm × 0.46 cm ID), n-hexane/2-propanol = 70:30, flow rate = 1.0 mL/min, wavelength = 230 nm UV detector, pressure = 48 bar, $t_R$= 8.69 min for minor isomer and $t_R$= 10.52 min for major isomer.

## 8. Reference

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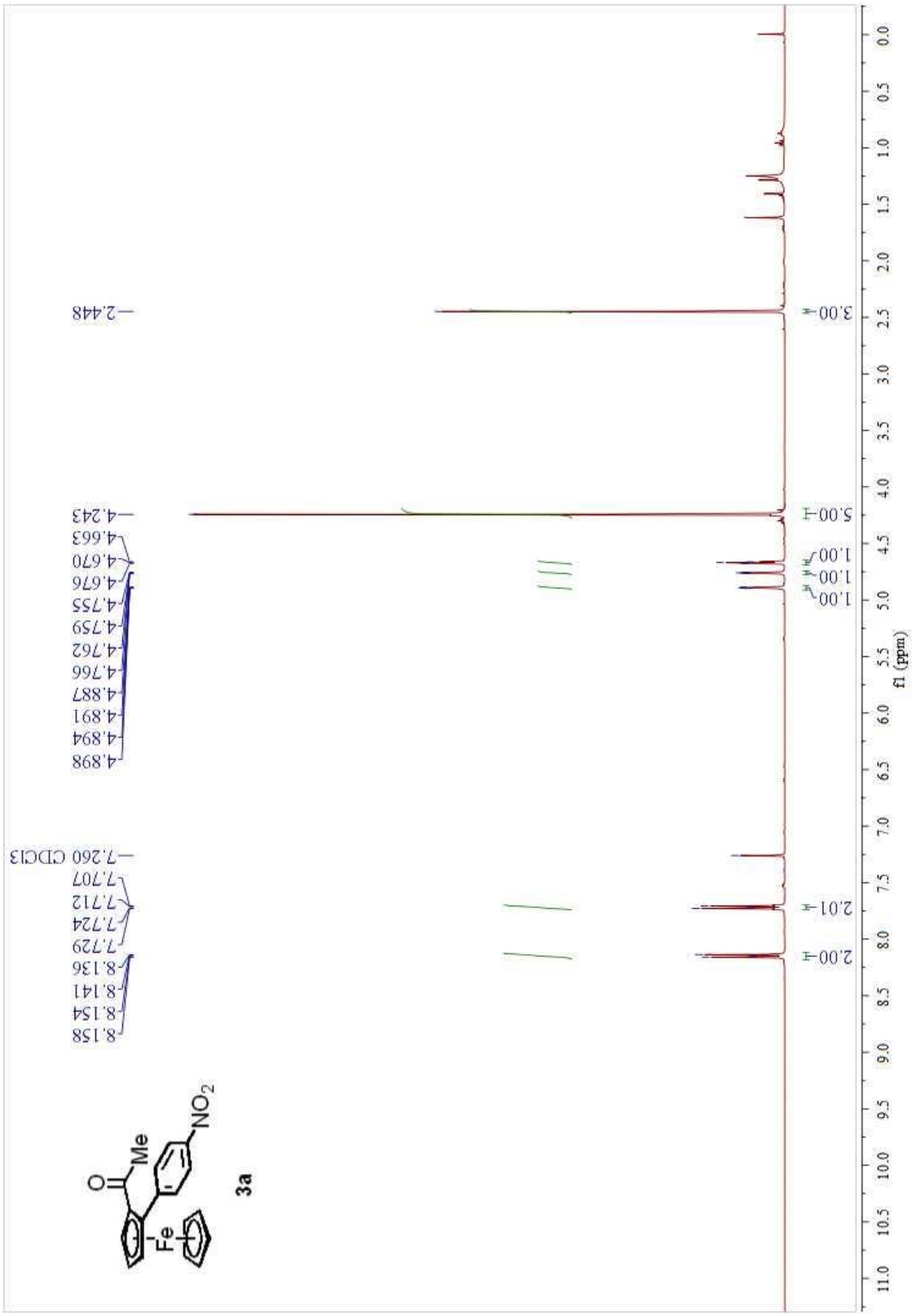
(2) E. J. Corey, R. K. Bakshi, S. Shibata, C.-P. Chen, V. K. Singh, *J. Am. Chem. Soc.*, 1987, **109**, 7925.

(3) B. Lu, Q. Wang, M. Zhao, X. Xie, Z. Zhang, *J. Org. Chem.*, 2015, **80**, 9563.

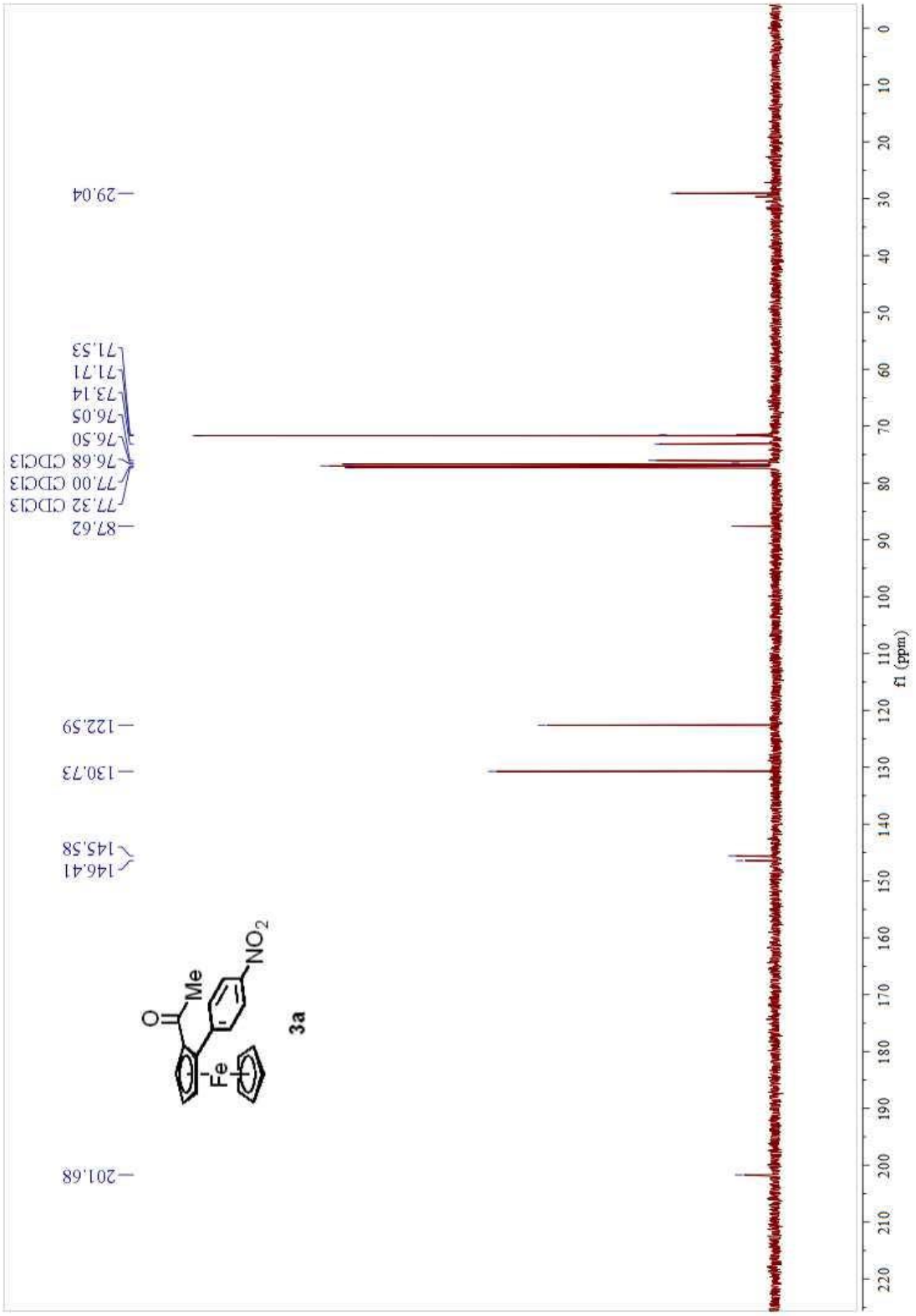
(4) (a) L. F. Battelle, R. Bau, G. W. Gokel, R. T. Oyakawa, I. K. Ugi, *J. Am. Chem. Soc.*, 1973, **95**, 482; (b) G. W. Gokel, D. Marquarding, I. K. Ugi, *J. Org. Chem.*, 1972, **37**, 3052.

(5) K.-L. Huang, C. Guo, L.-J. Cheng, L.-G. Xie, Q.-L. Zhou, X.-H. Xu, S.-F. Zhu, *Adv. Synth. Catal.*, 2013, **355**, 2833.

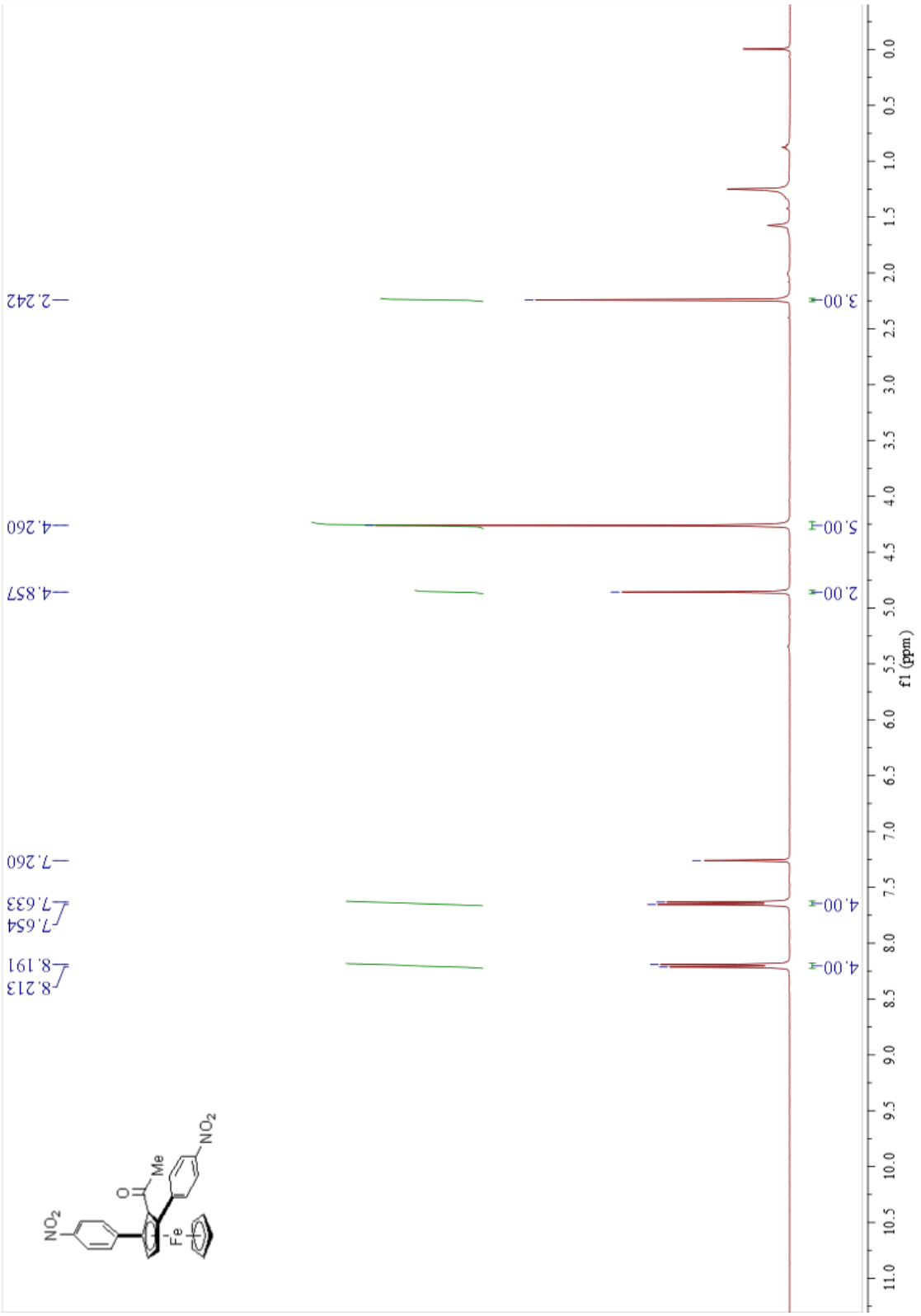
## 9. NMR Spectra Data for New Compounds



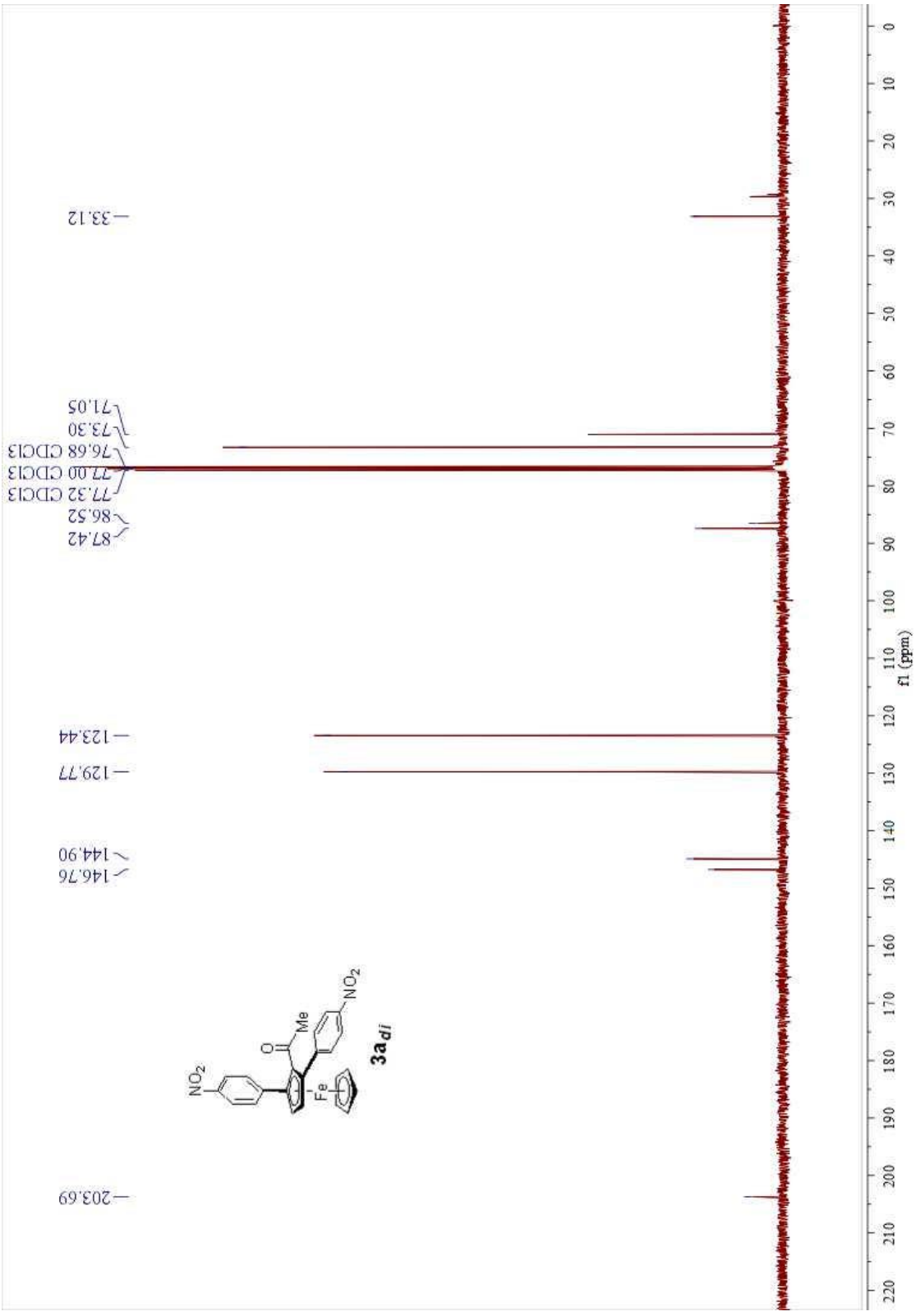

$^{1}$H NMR Spectra of Compound **3a**



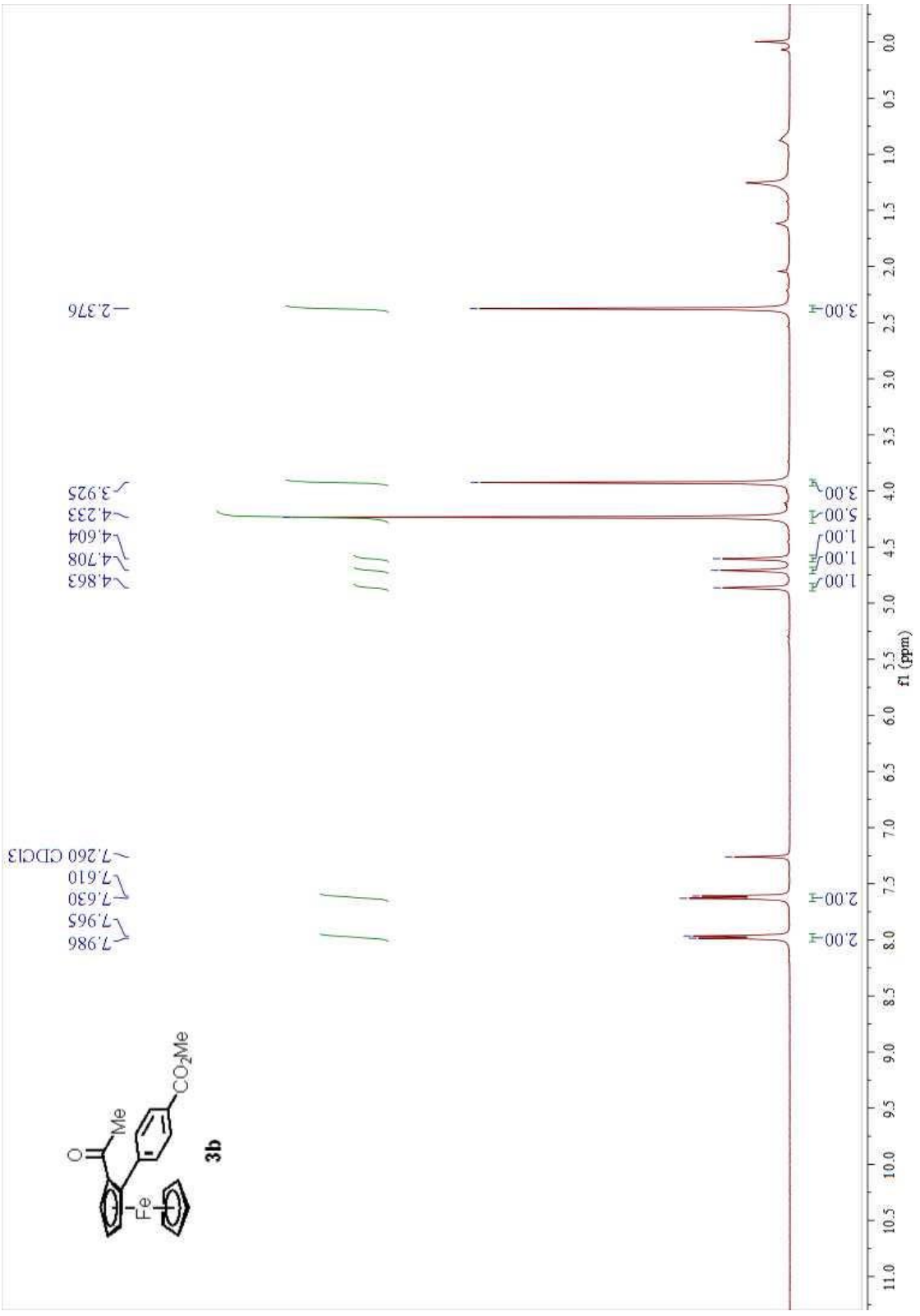

$^{13}$C NMR Spectra of Compound **3a**



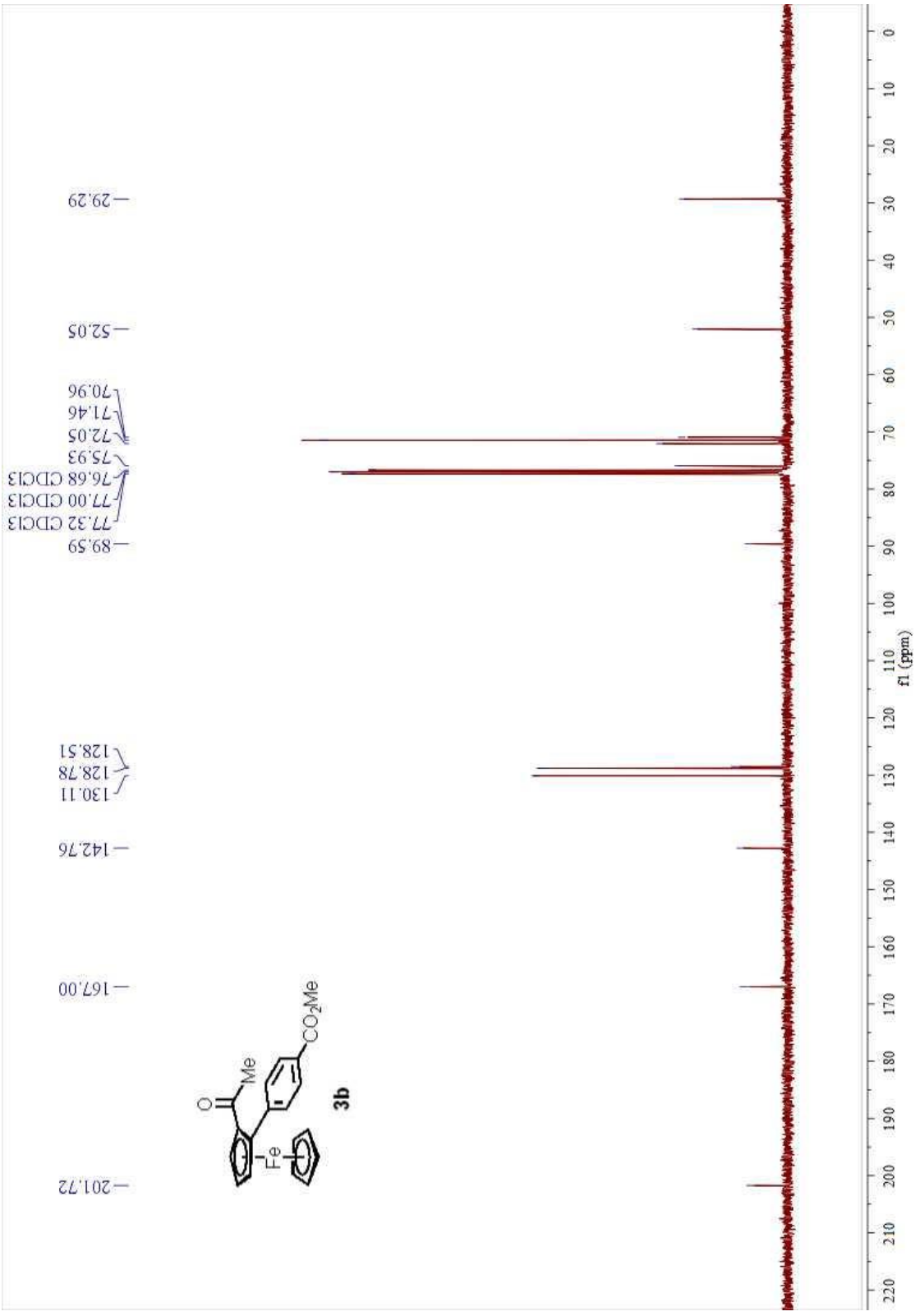

$^{1}$H NMR Spectra of Compound **3a**$_{di}$



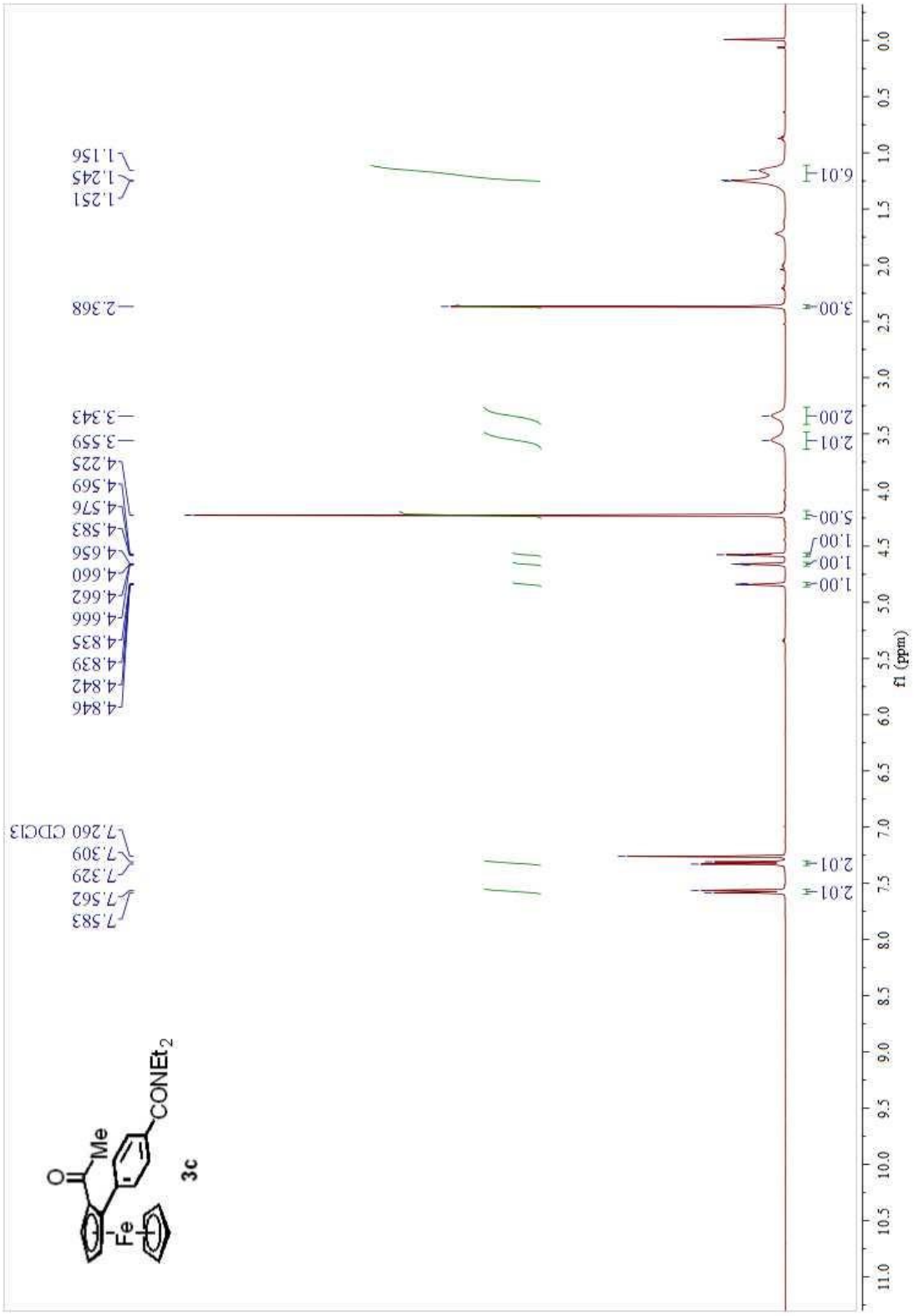

$^{13}$C NMR Spectra of Compound **3a*di***



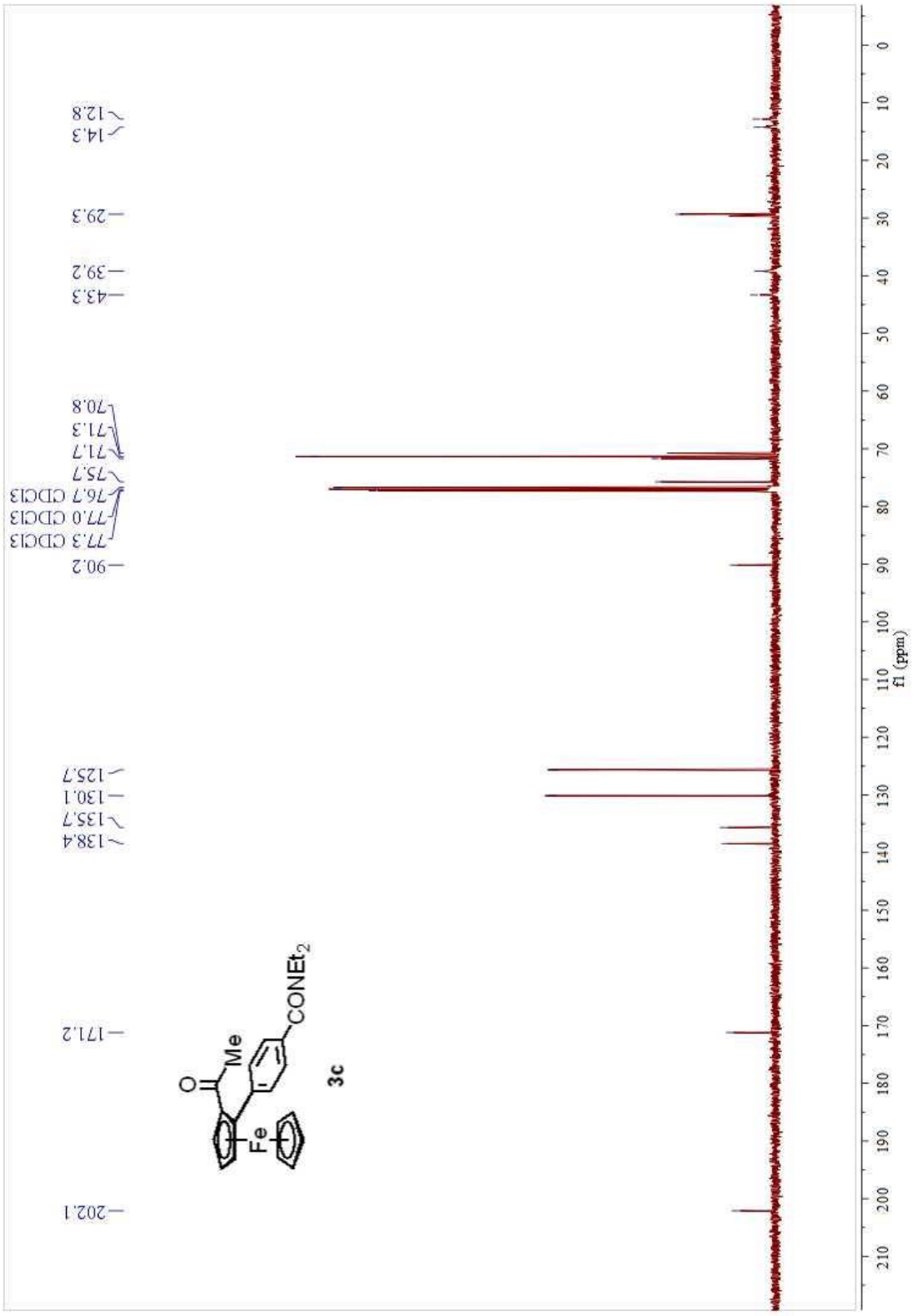

$^{1}$H NMR Spectra of Compound **3b**



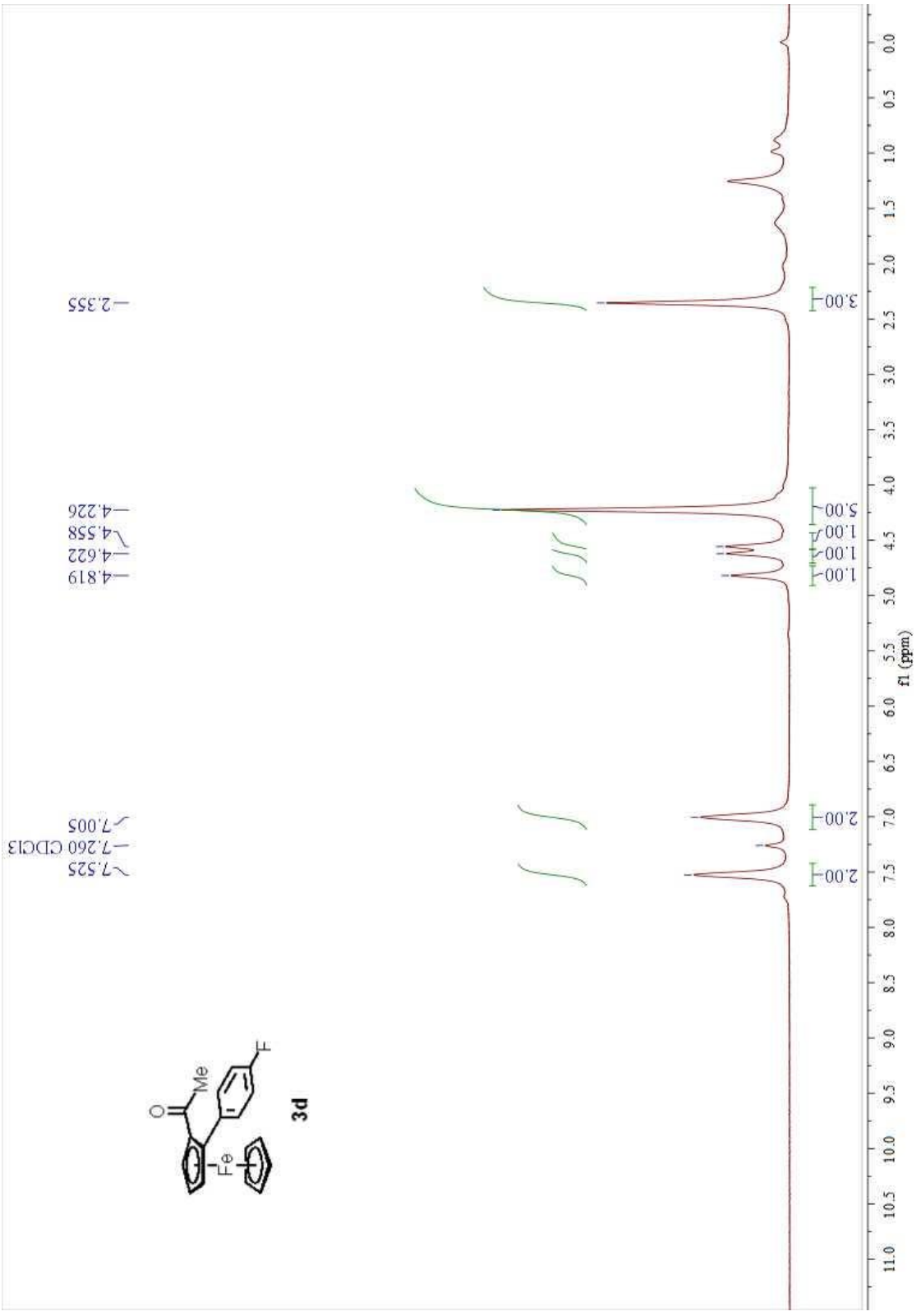

$^{13}$C NMR Spectra of Compound **3b**



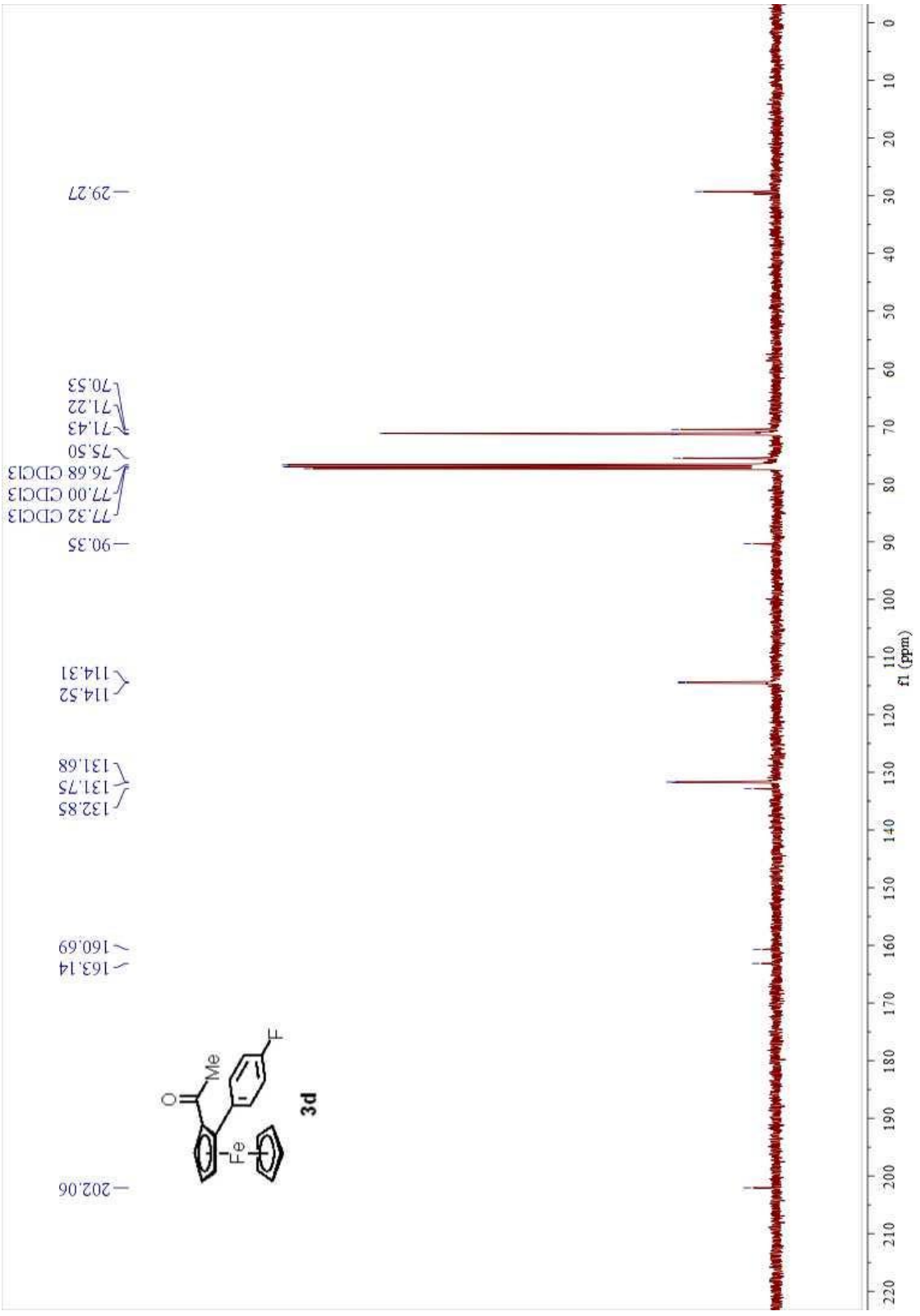

$^{1}$H NMR Spectra of Compound **3c**



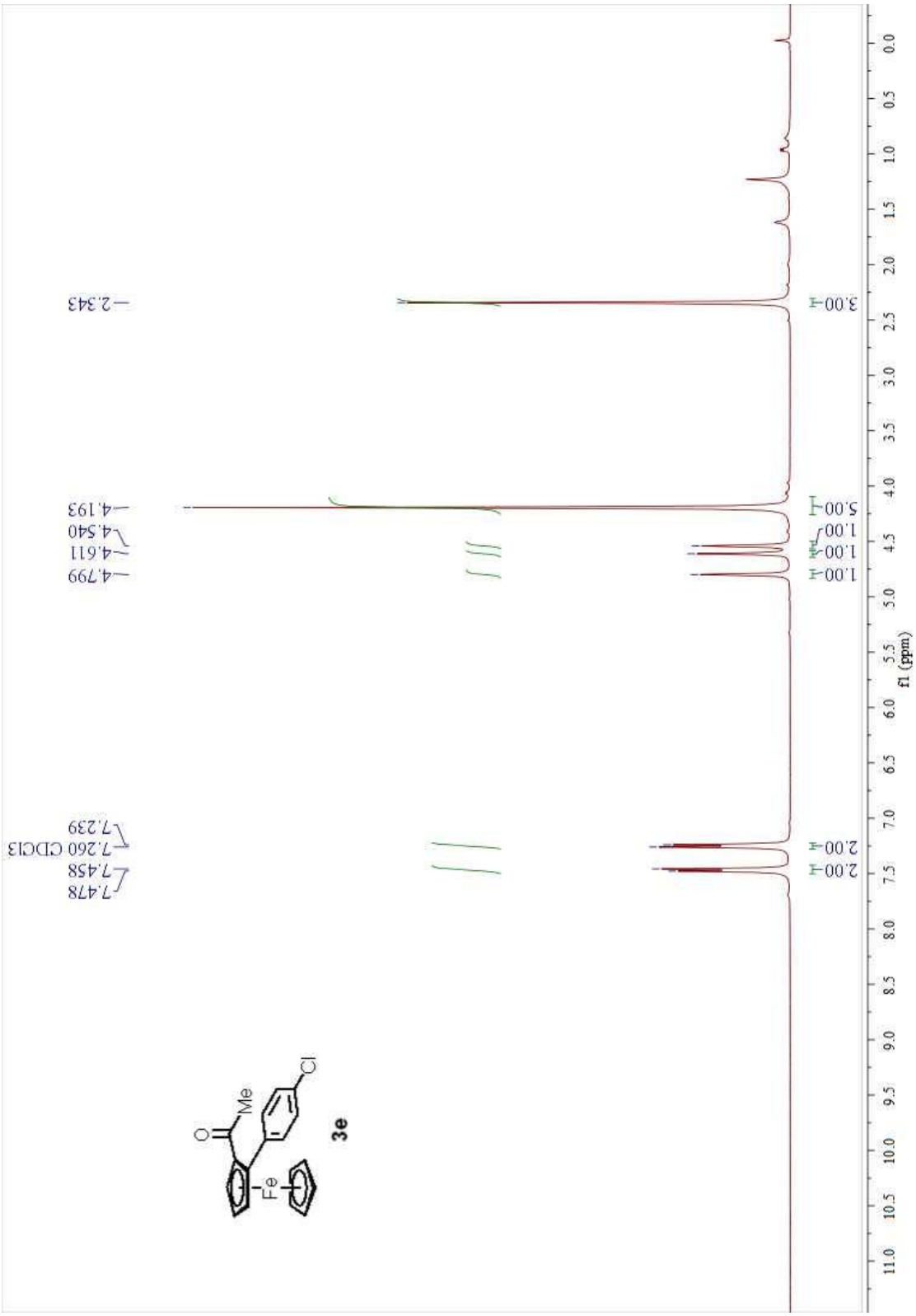

$^{13}$C NMR Spectra of Compound **3c**



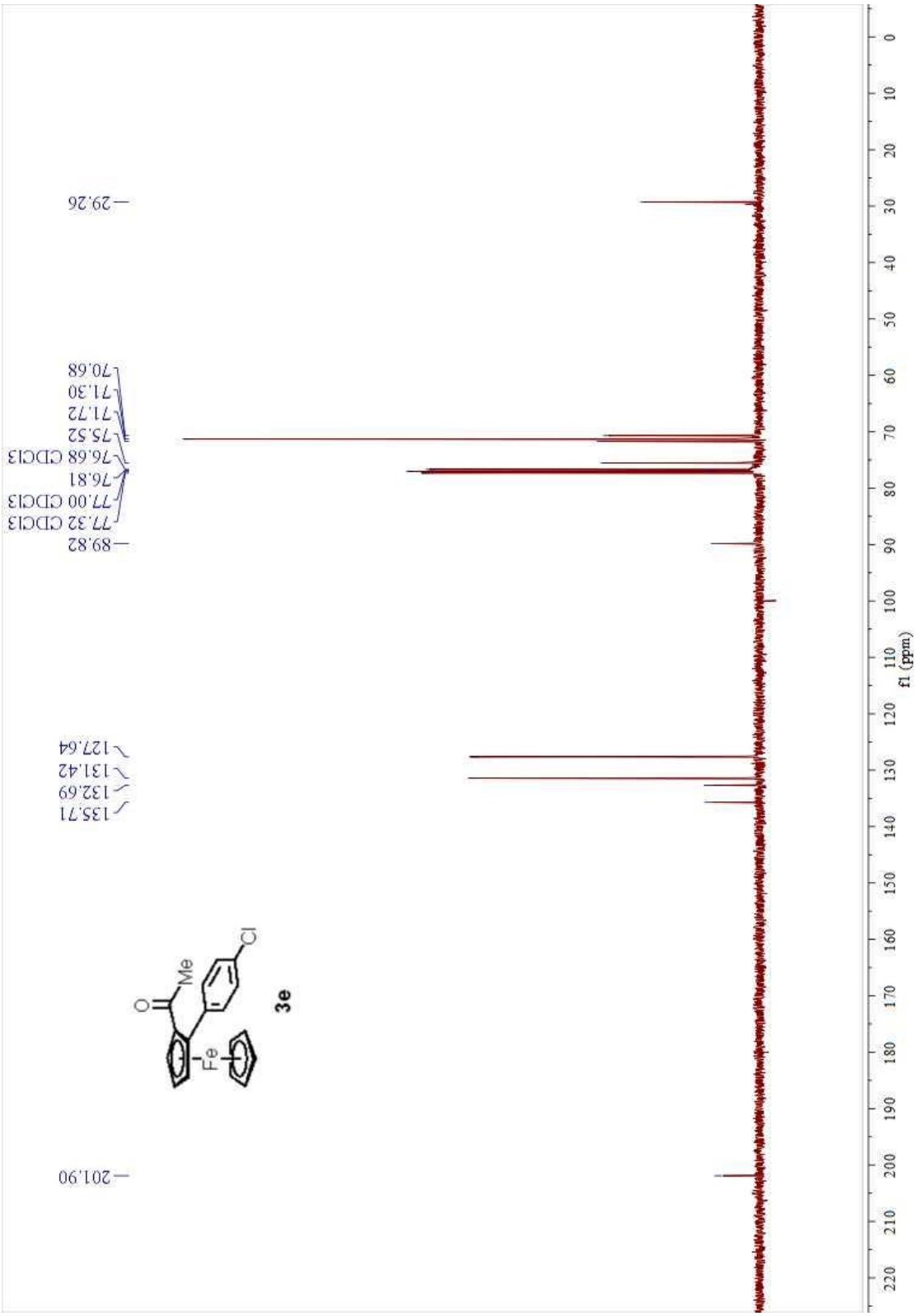

$^{1}$H NMR Spectra of Compound **3d**



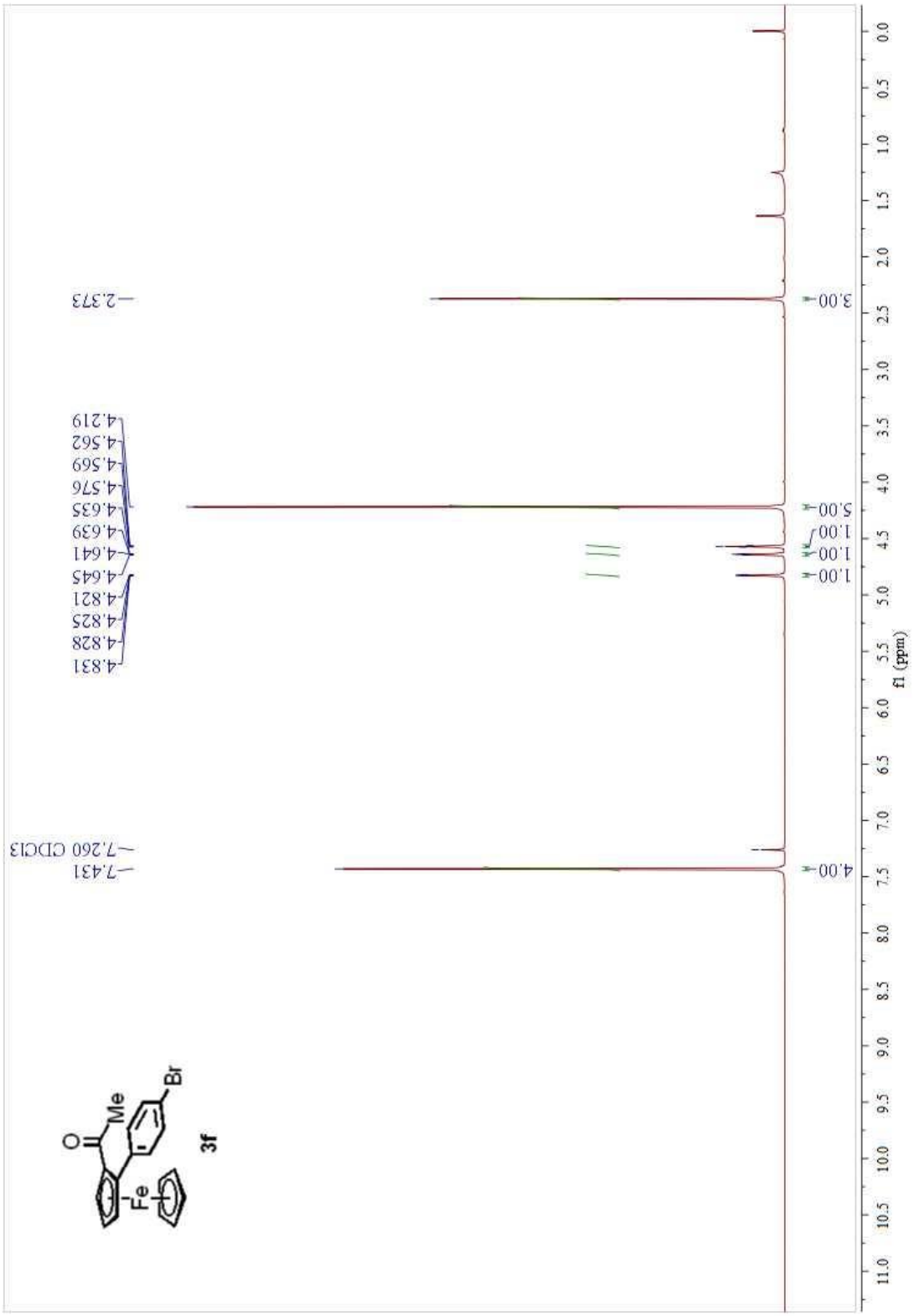

$^{13}$C NMR Spectra of Compound **3d**



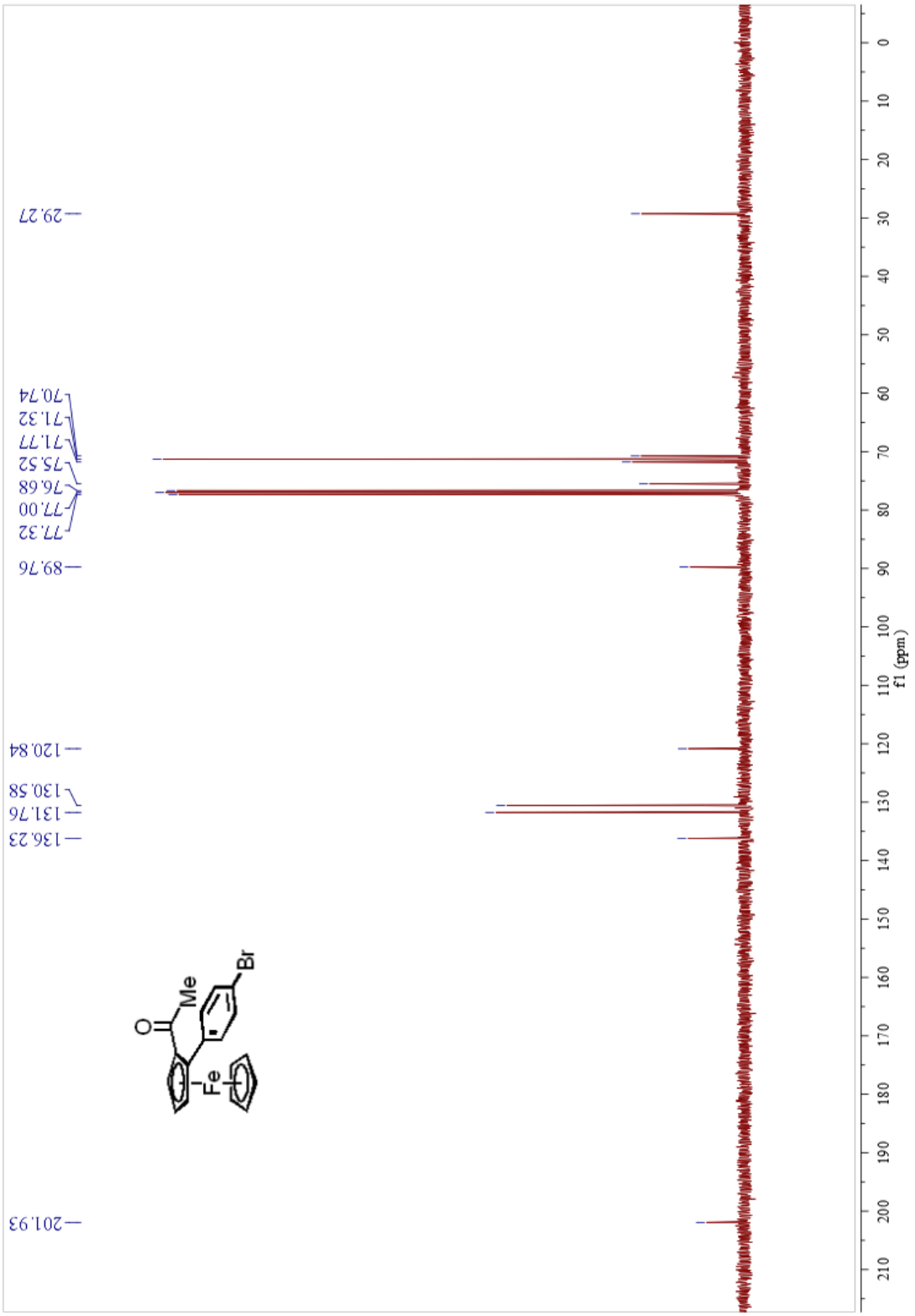

$^{1}$H NMR Spectra of Compound **3e**



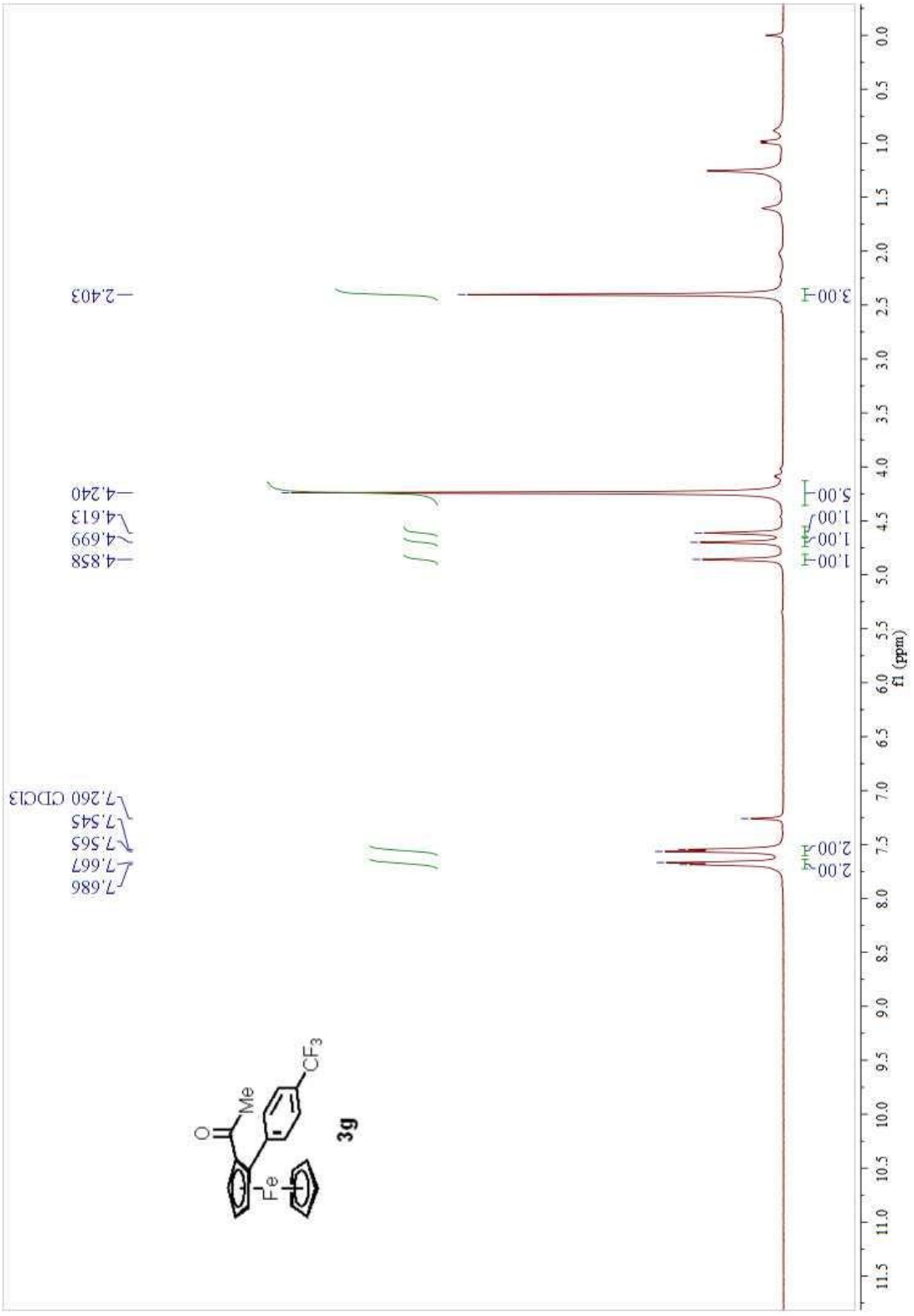

$^{13}$C NMR Spectra of Compound **3e**



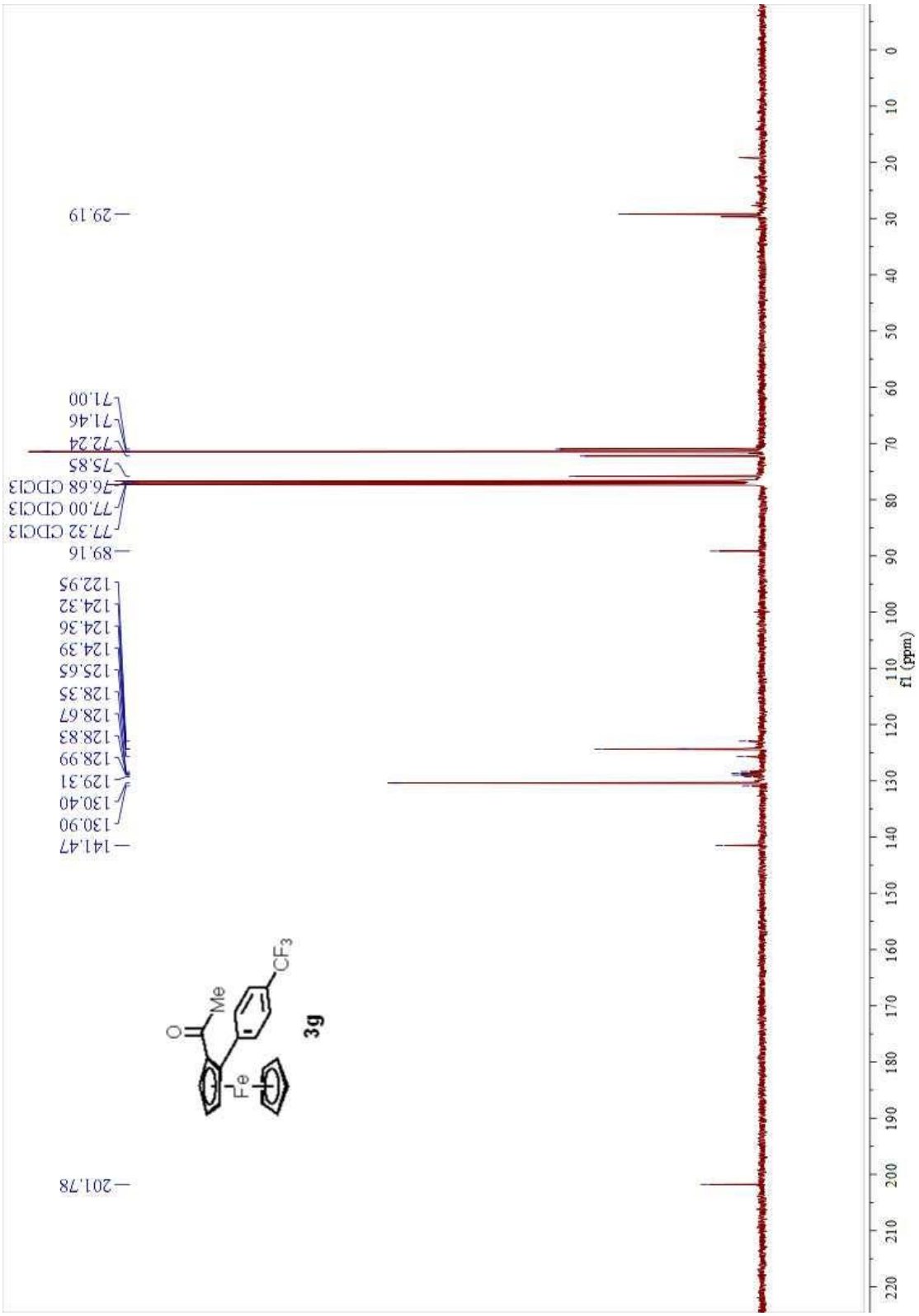

$^{1}$H NMR Spectra of Compound **3f**



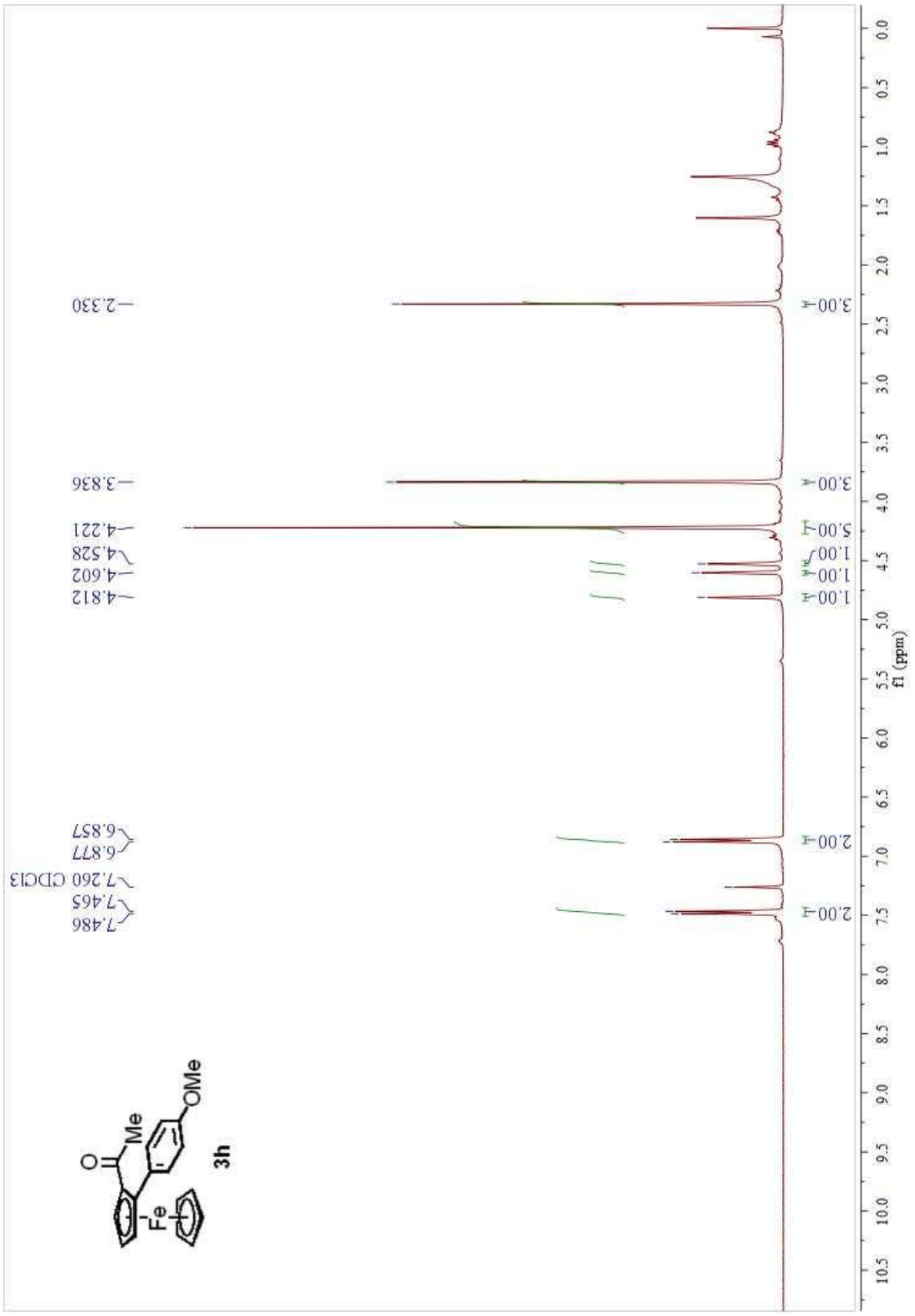

$^{13}$C NMR Spectra of Compound **3f**



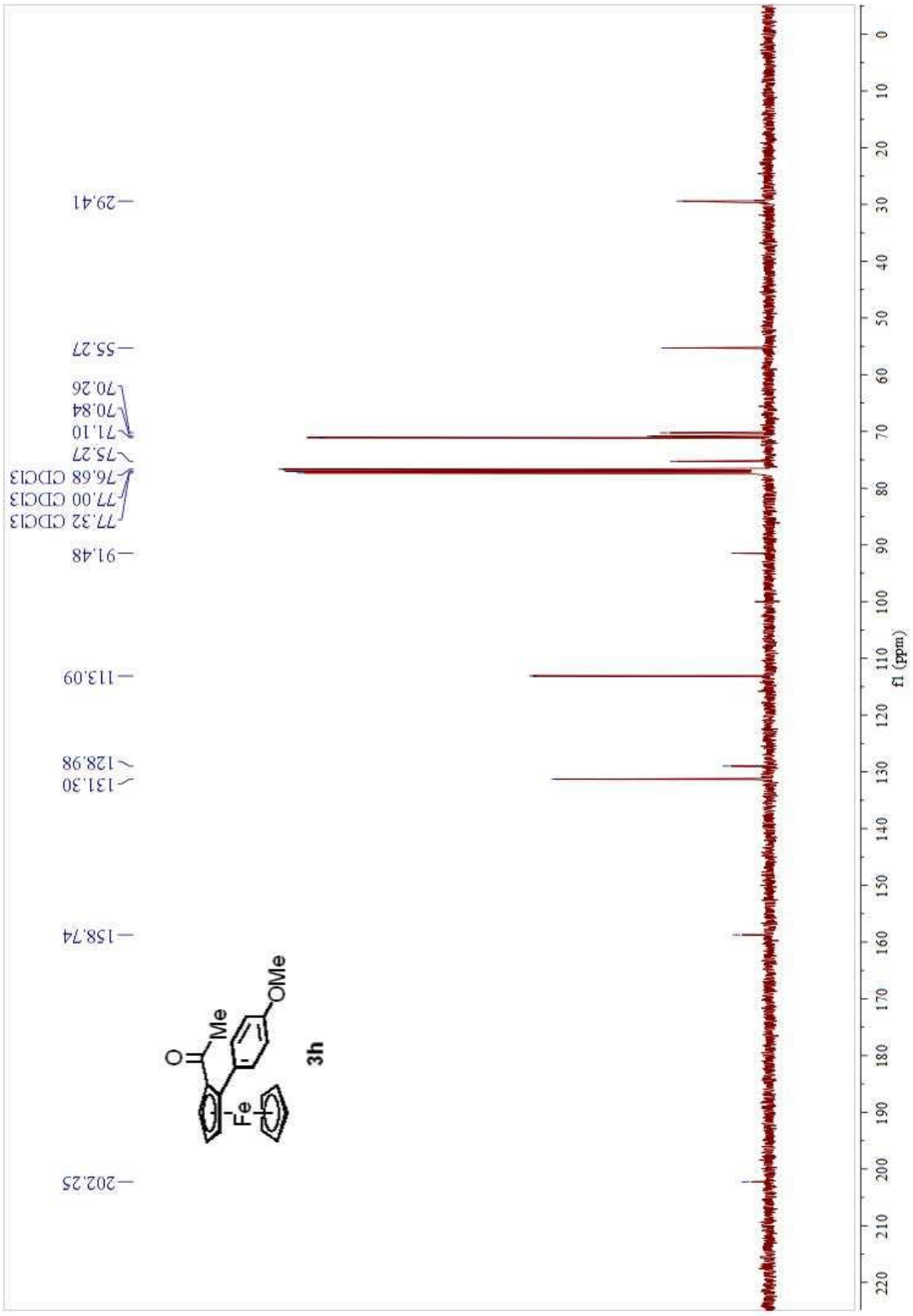

$^{1}$H NMR Spectra of Compound **3g**



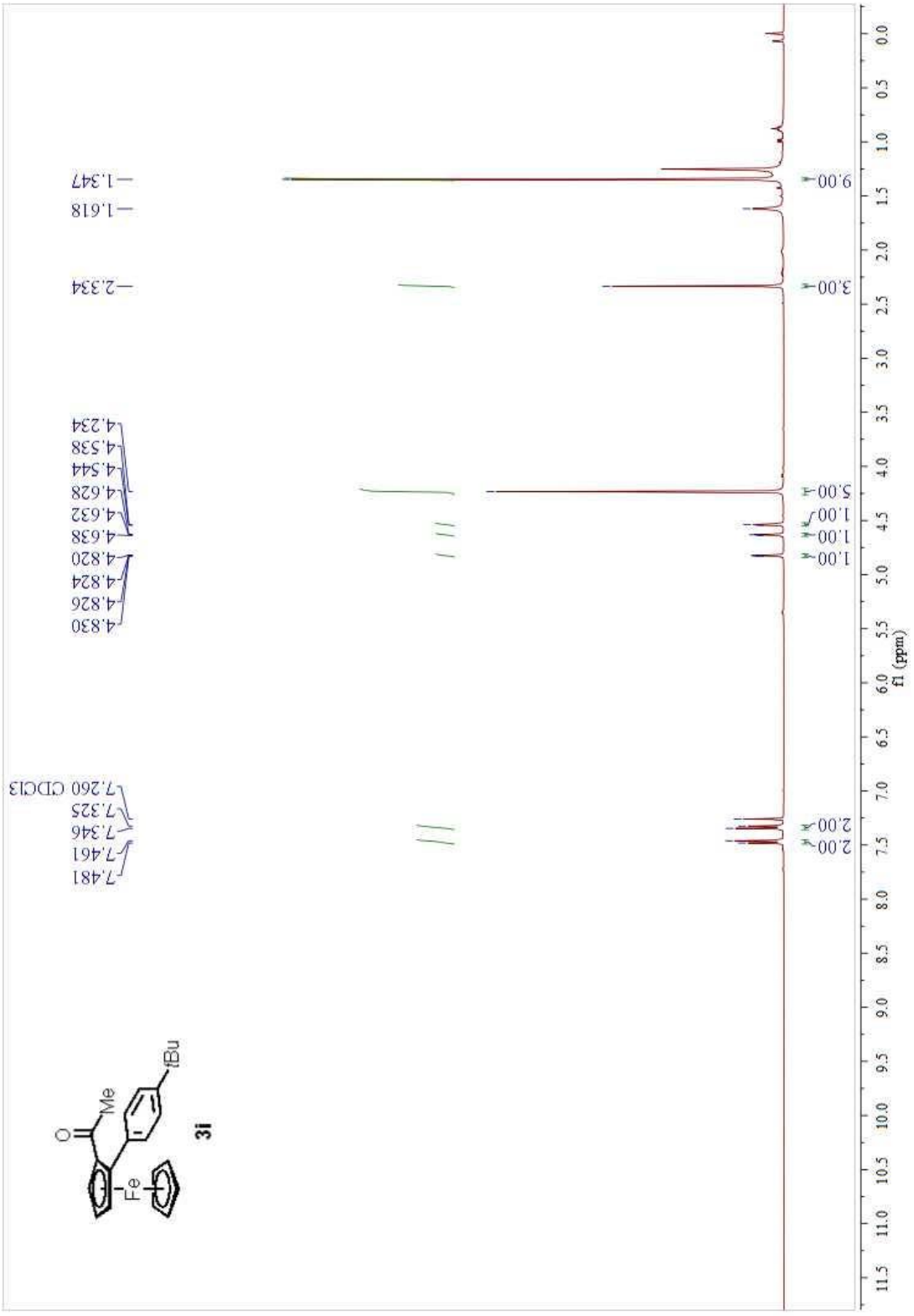

$^{13}$C NMR Spectra of Compound **3g**



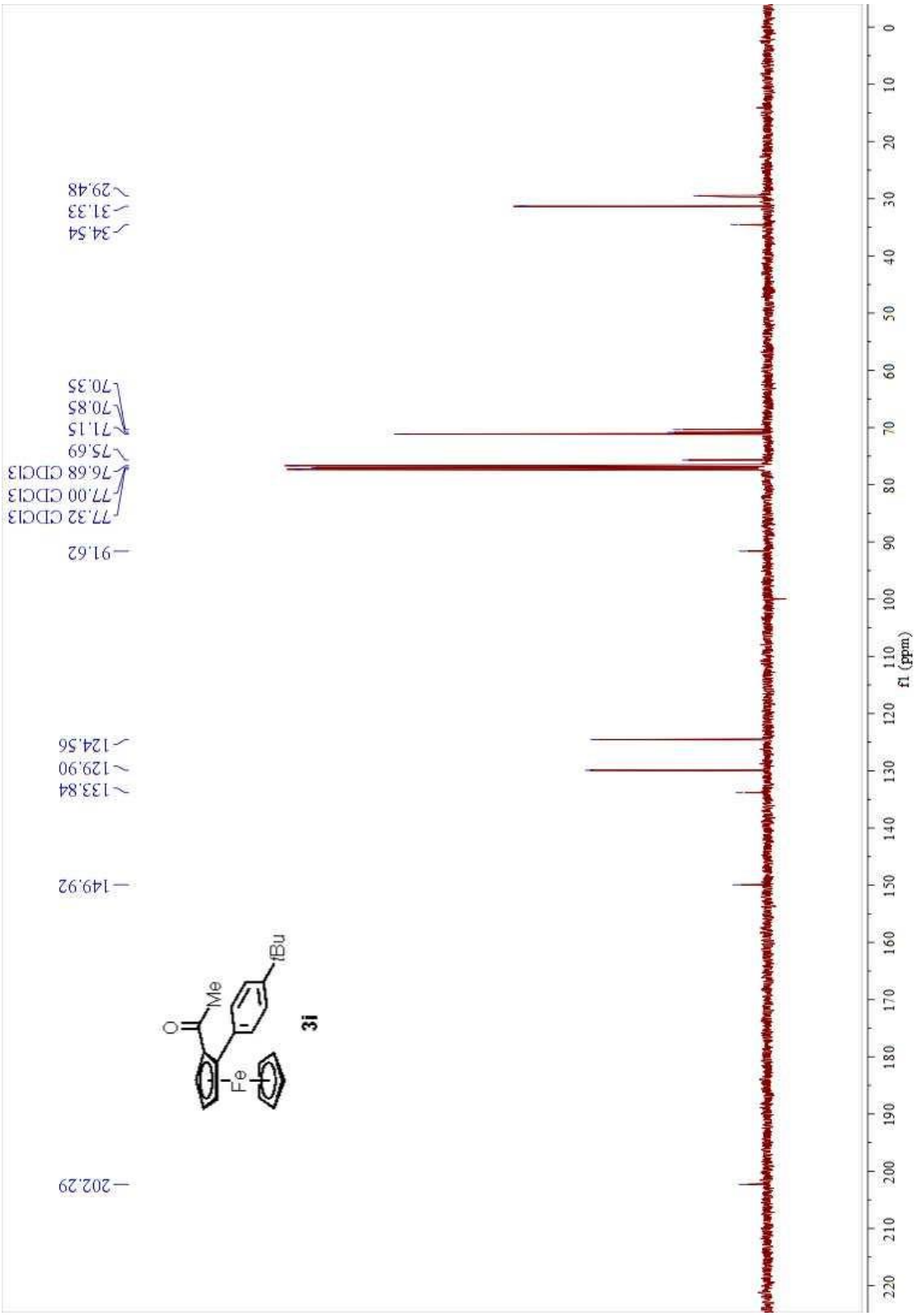

$^{1}$H NMR Spectra of Compound **3h**



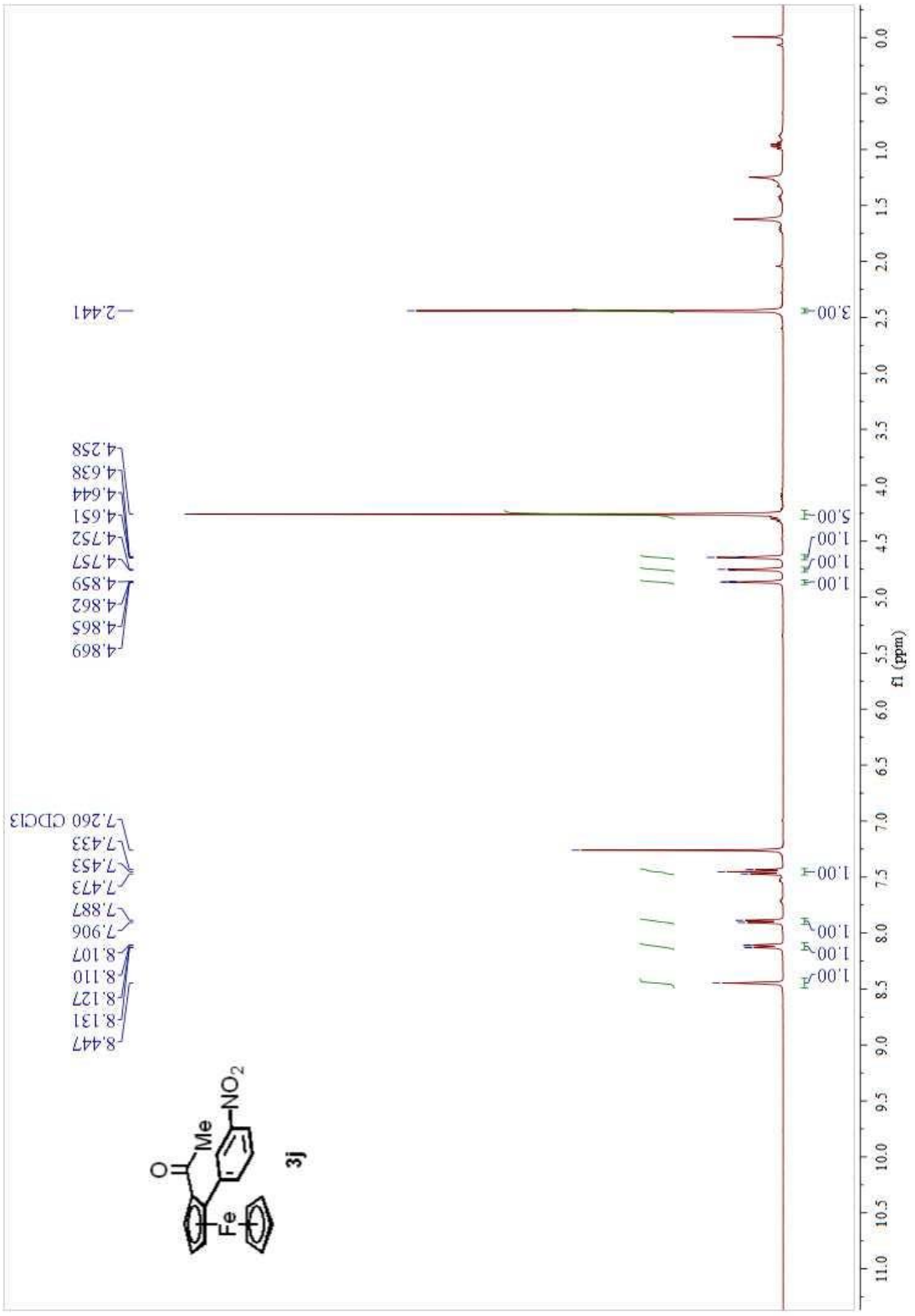

$^{13}$C NMR Spectra of Compound **3h**



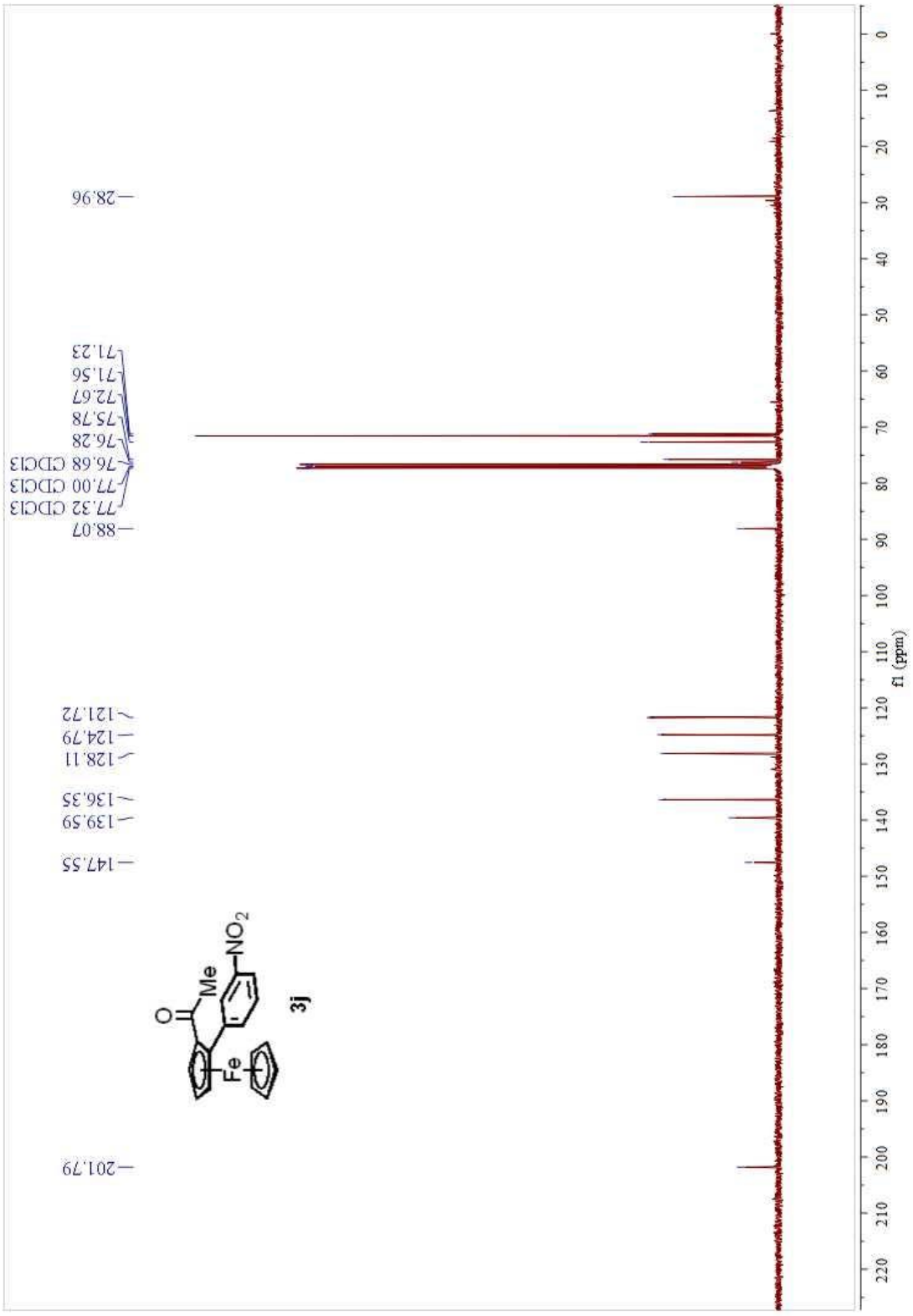

$^{1}$H NMR Spectra of Compound **3i**



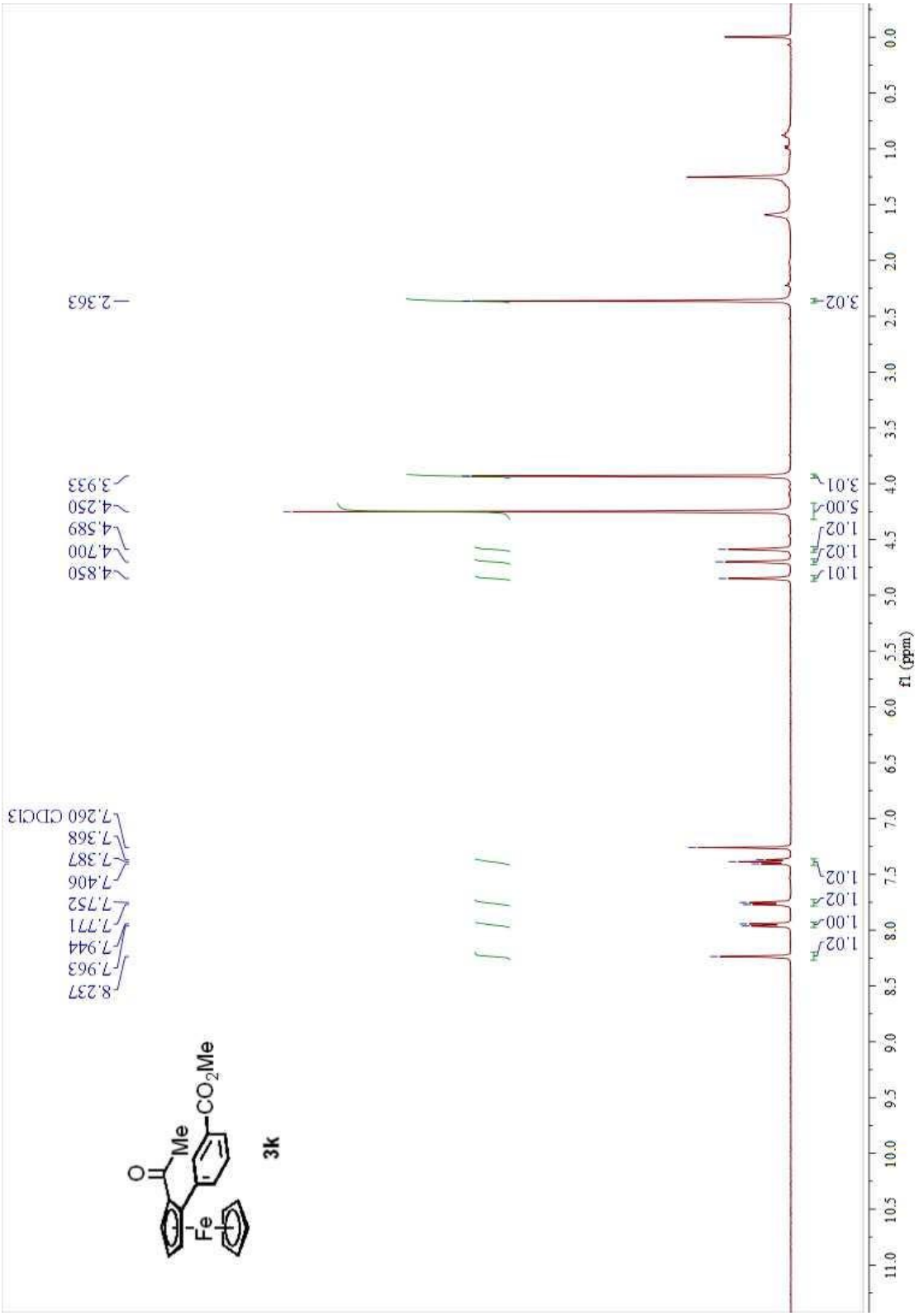

$^{13}$C NMR Spectra of Compound **3i**



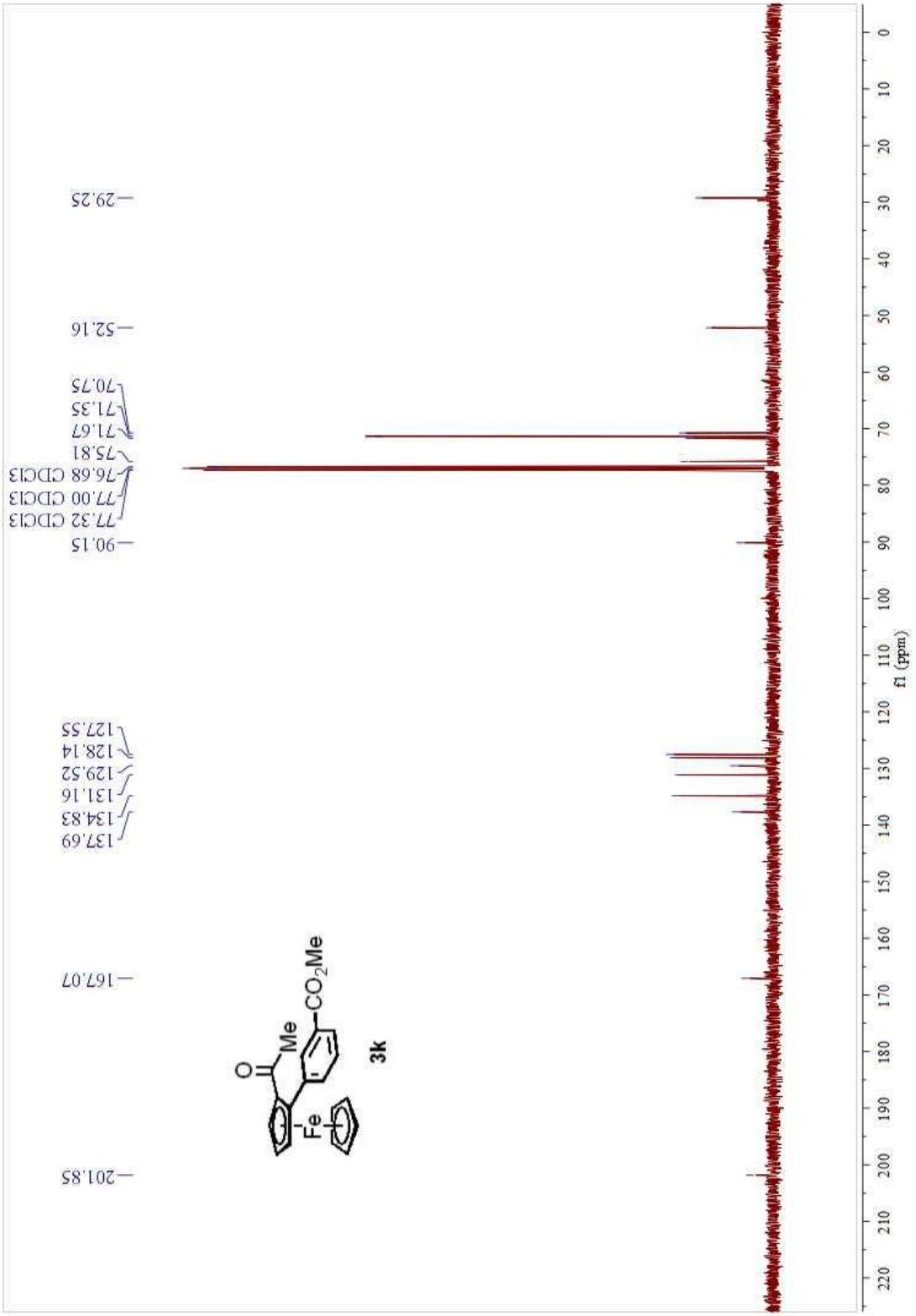

$^{1}$H NMR Spectra of Compound **3j**



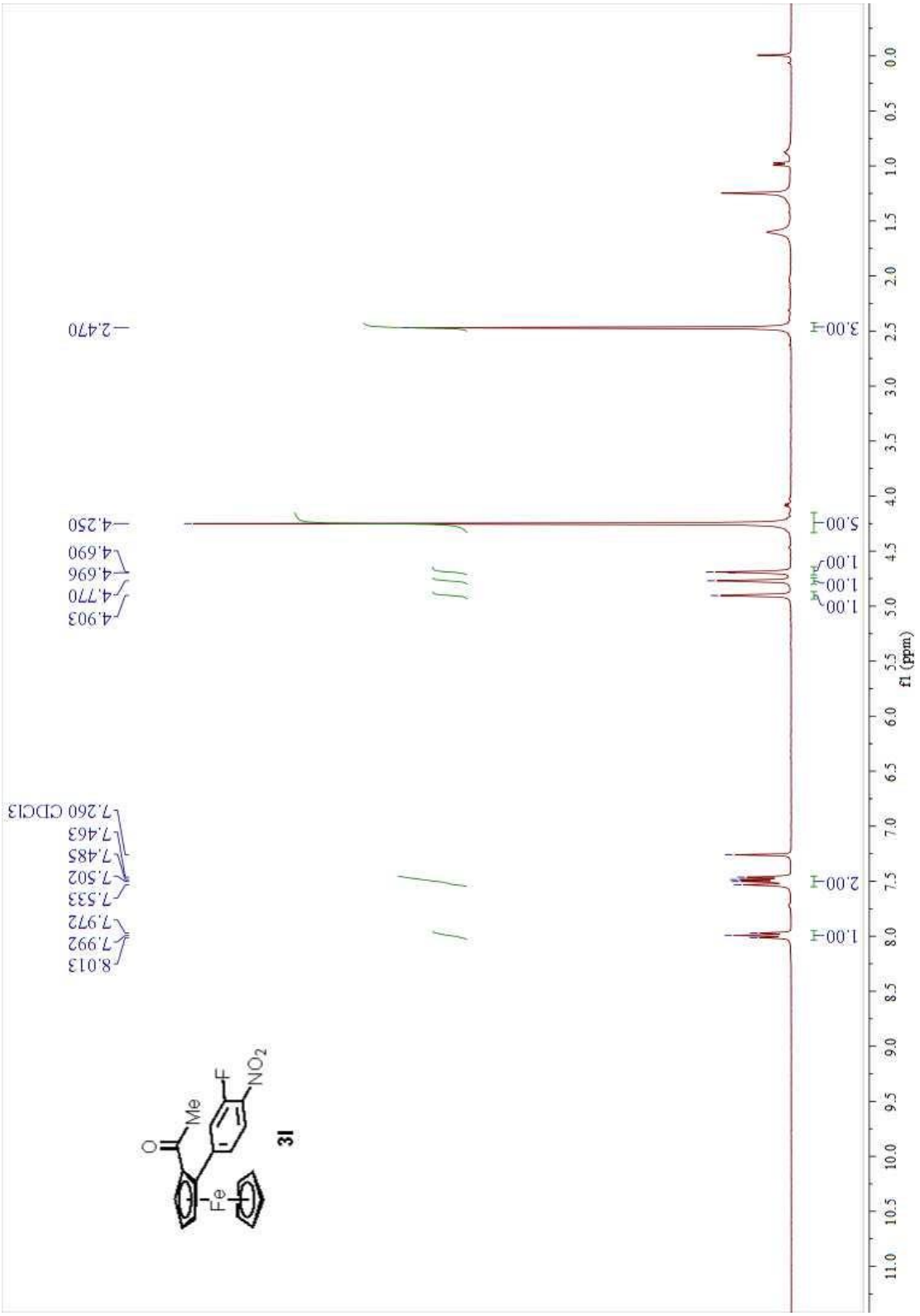

$^{13}$C NMR Spectra of Compound **3j**



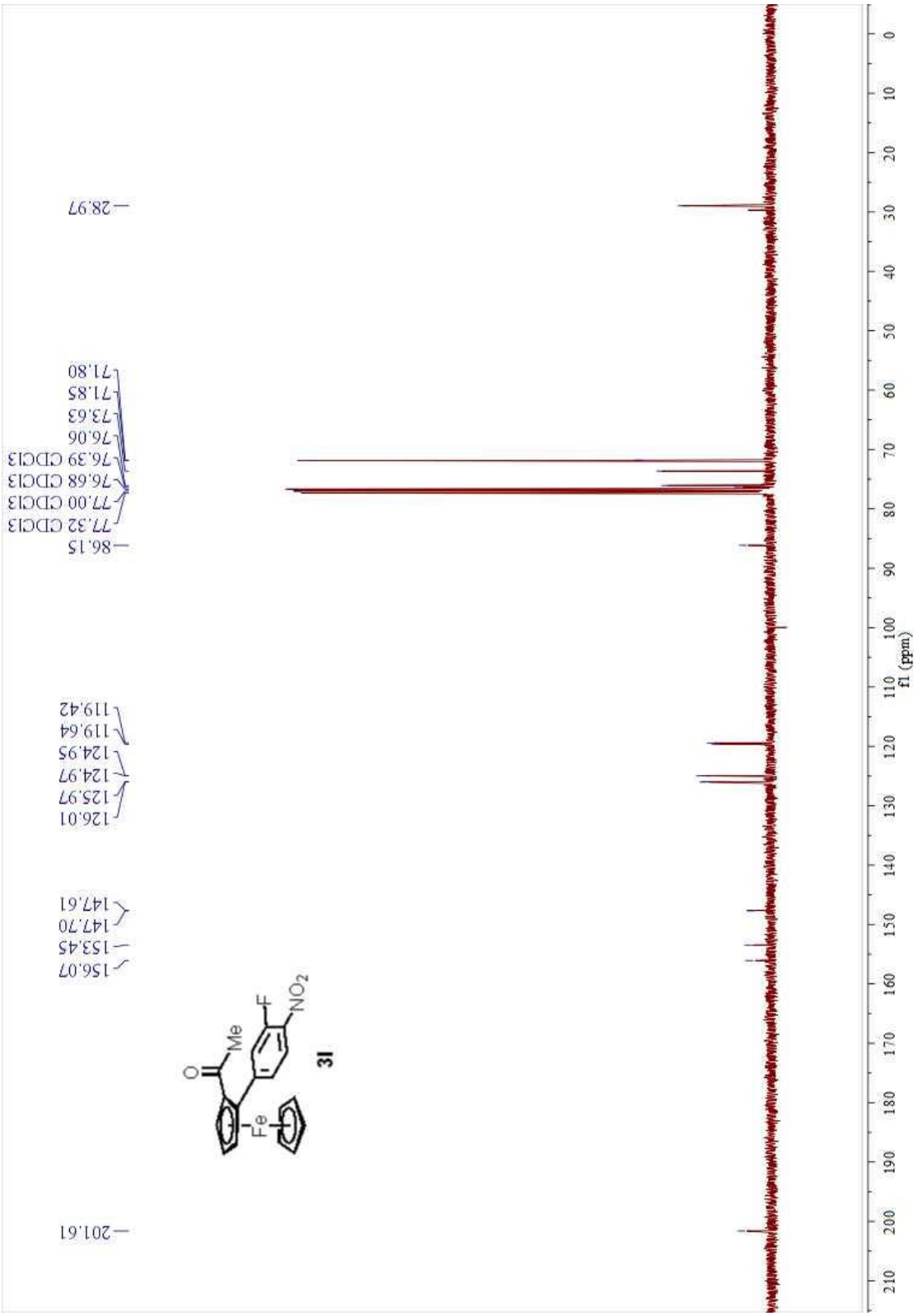

$^{1}$H NMR Spectra of Compound **3k**



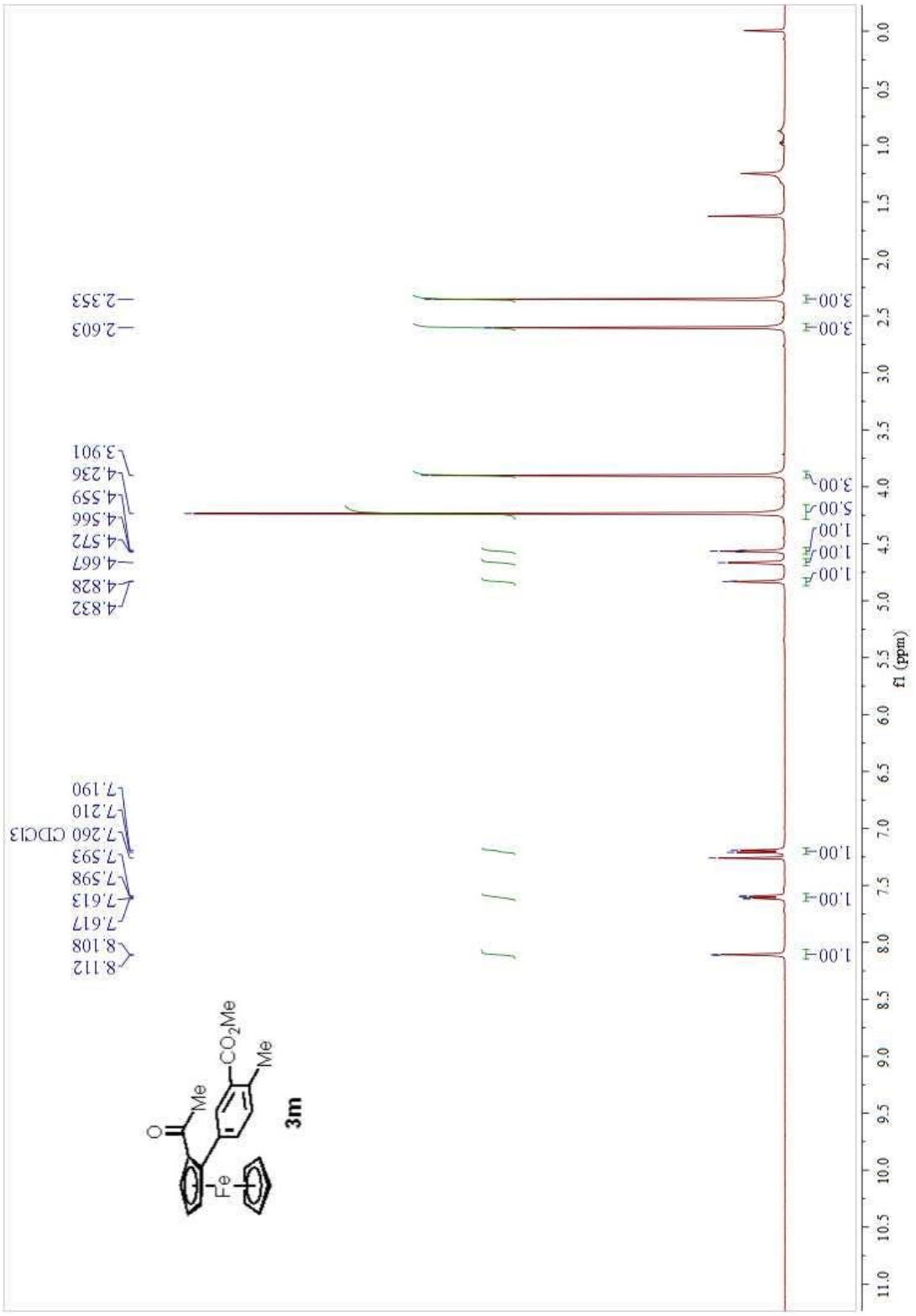

$^{13}$C NMR Spectra of Compound **3k**



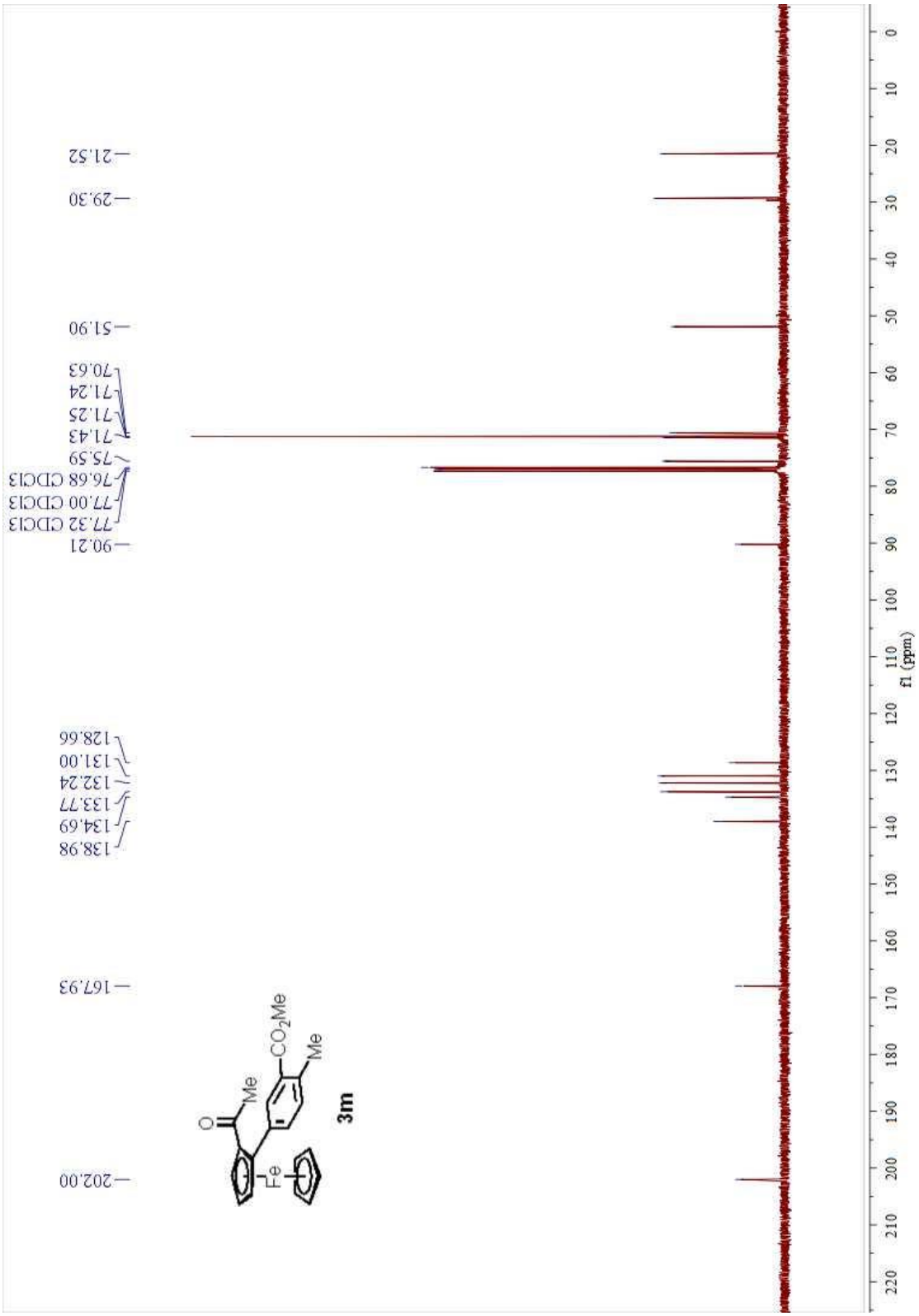

$^{1}$H NMR Spectra of Compound **3l**



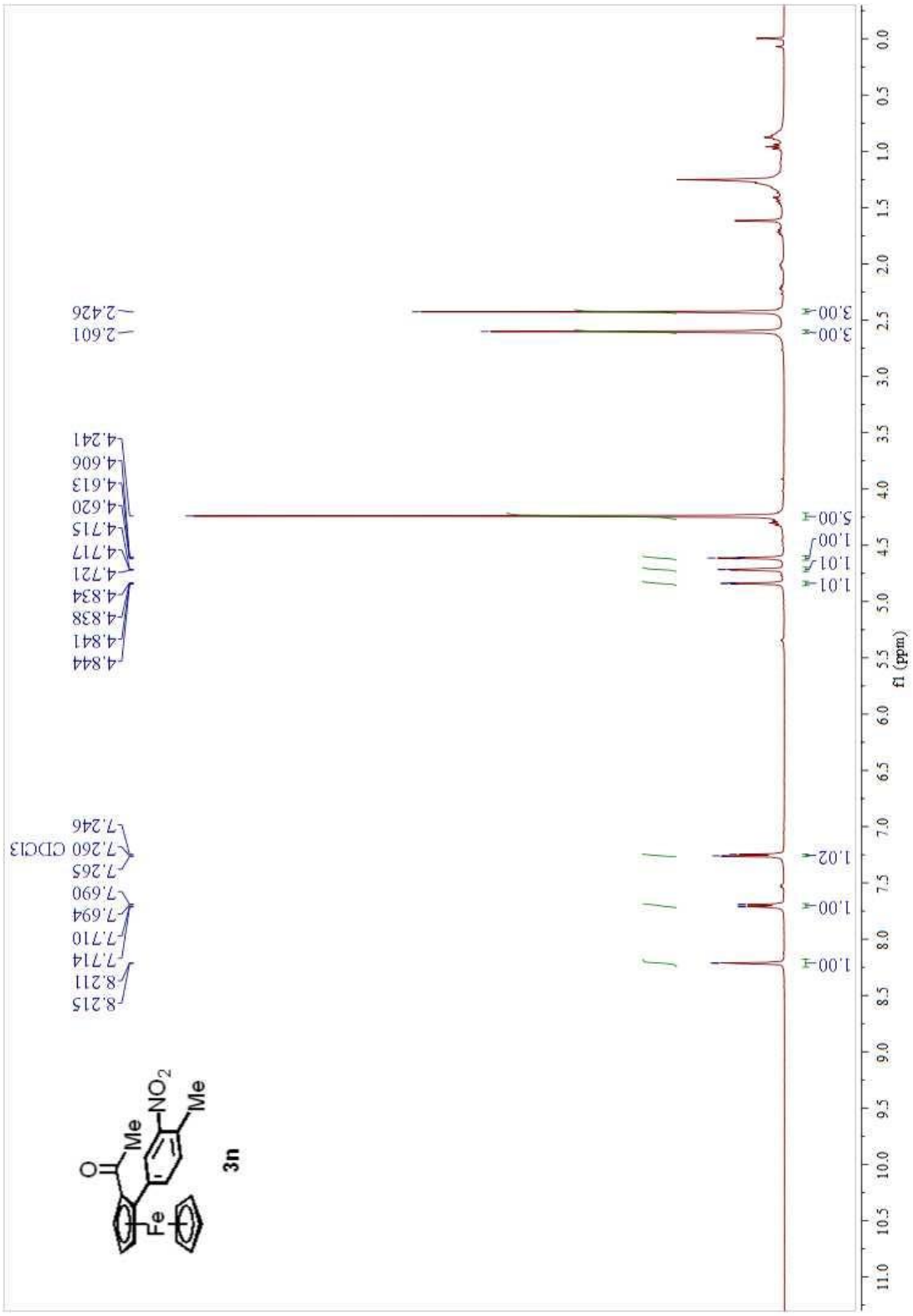

$^{13}$C NMR Spectra of Compound **3l**



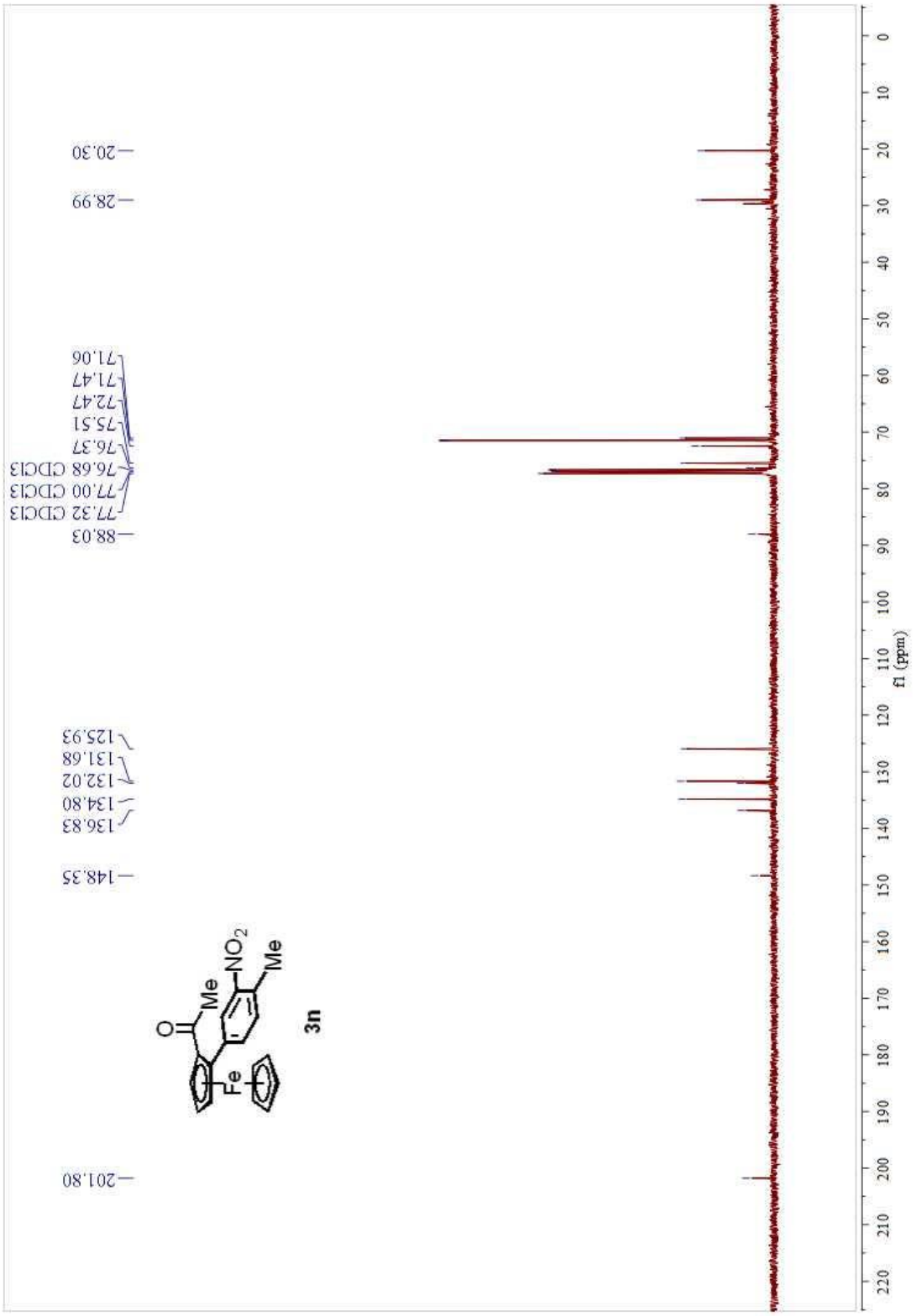

$^{1}$H NMR Spectra of Compound **3m**



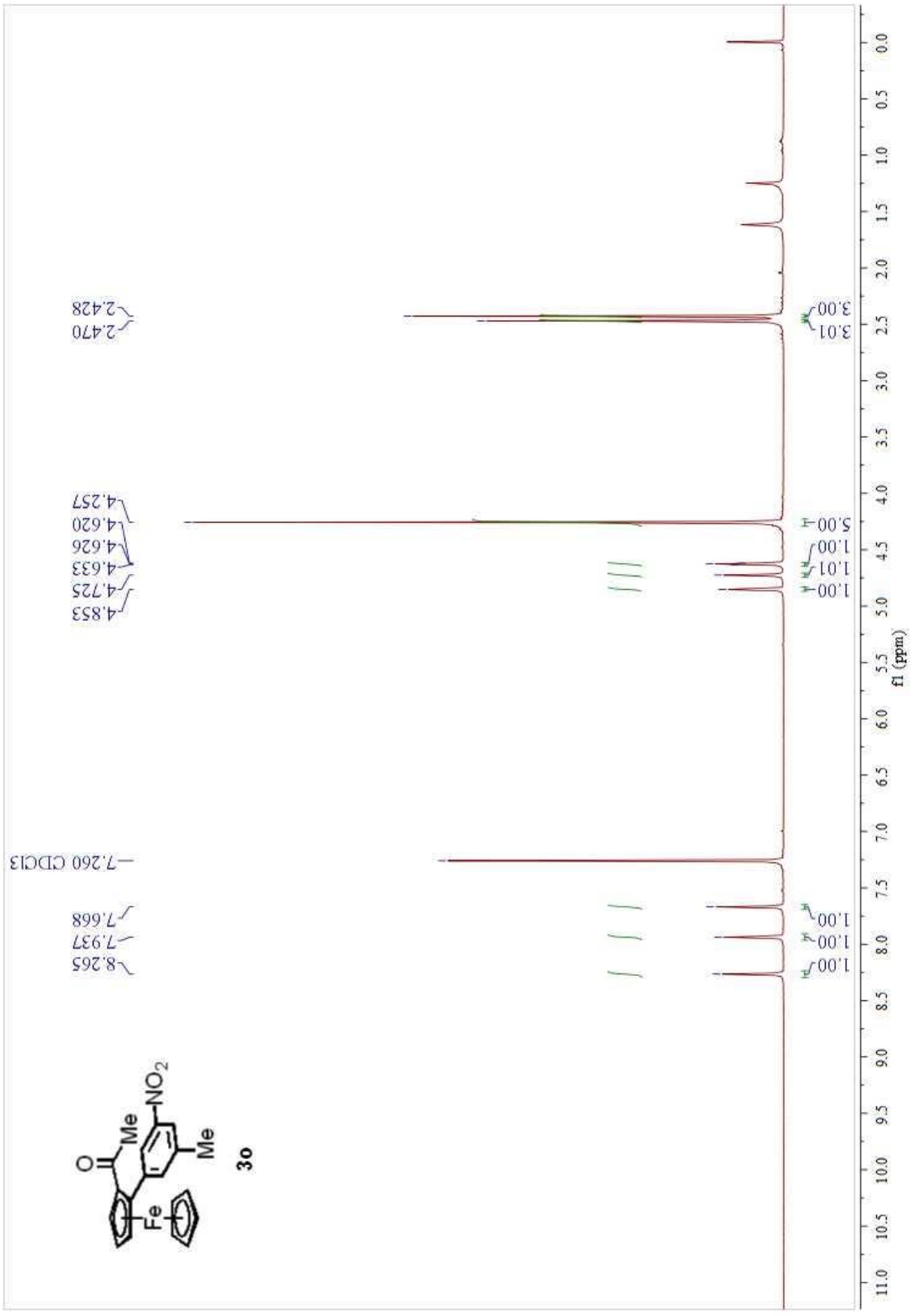

$^{13}$C NMR Spectra of Compound **3m**



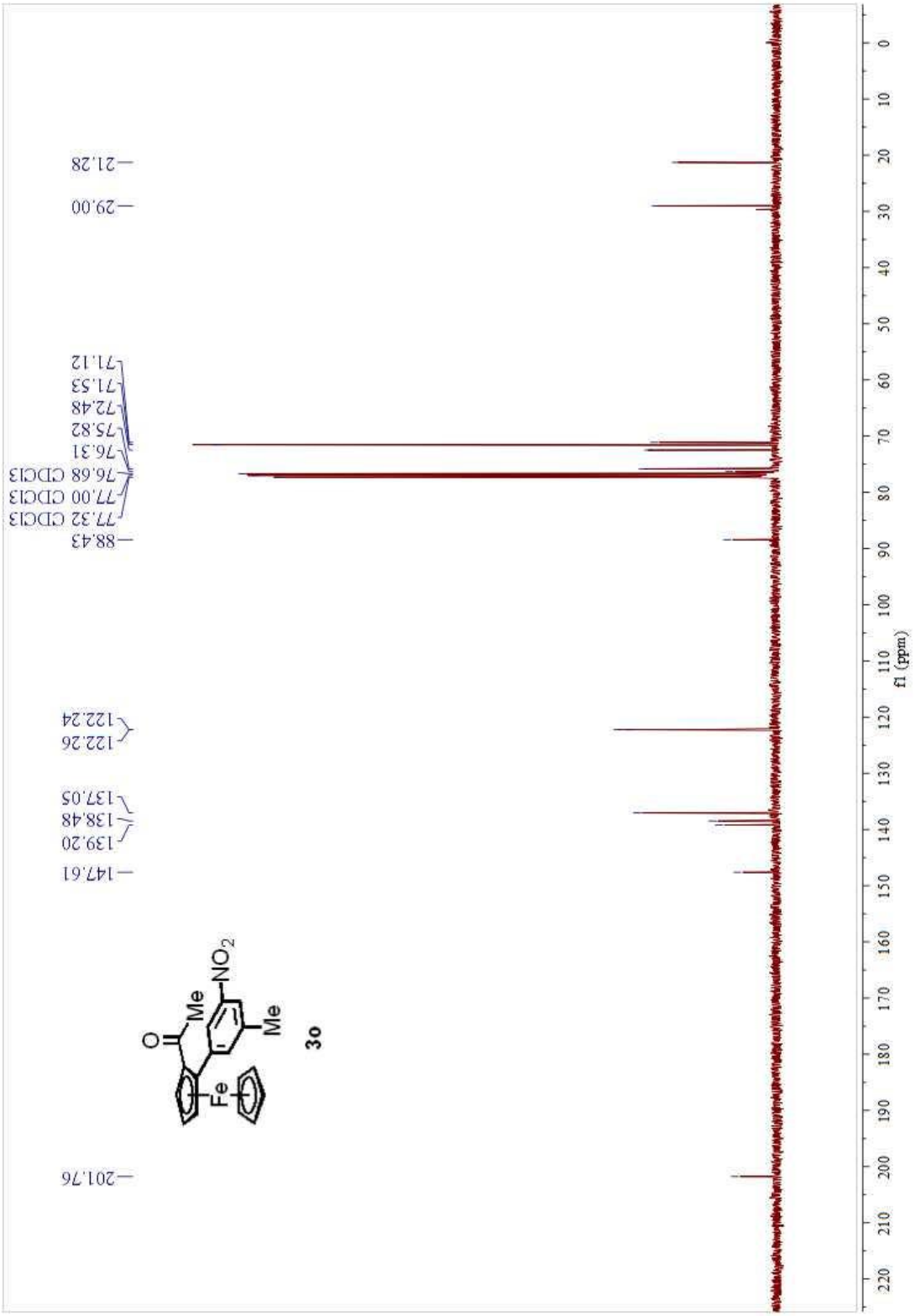

$^{1}$H NMR Spectra of Compound **3n**



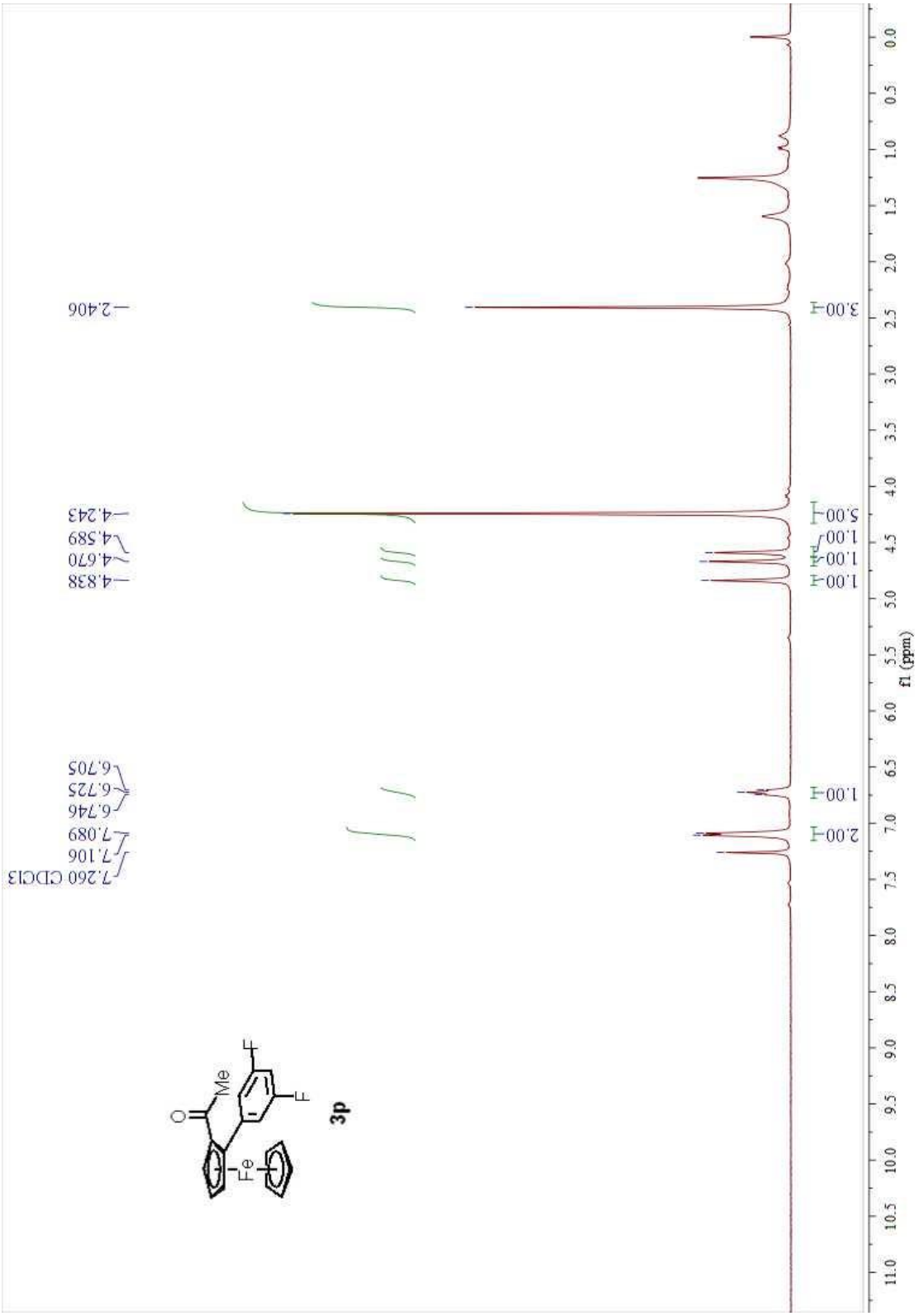

$^{13}$C NMR Spectra of Compound **3n**



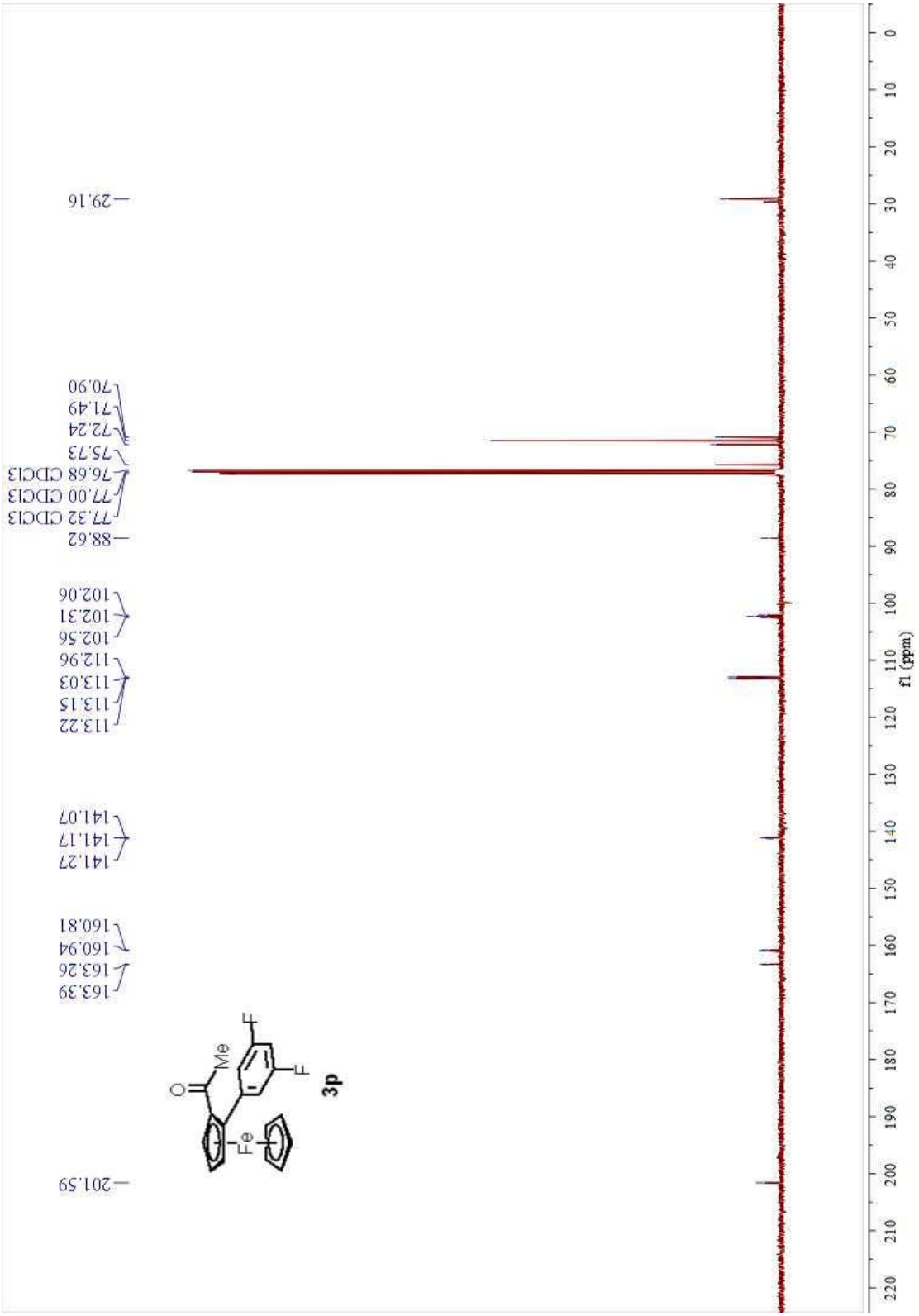

$^{1}$H NMR Spectra of Compound **3o**



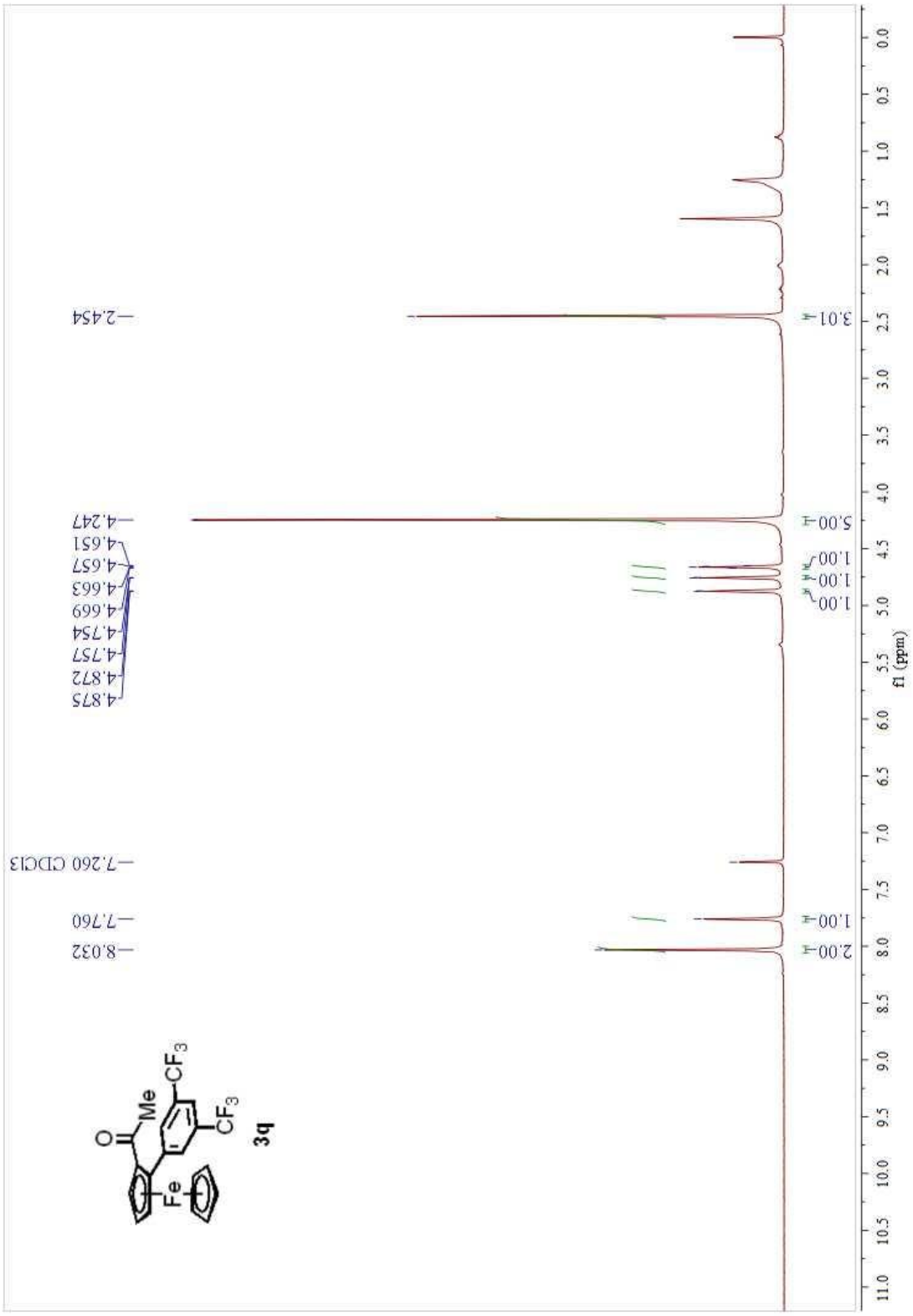

$^{13}$C NMR Spectra of Compound **3o**



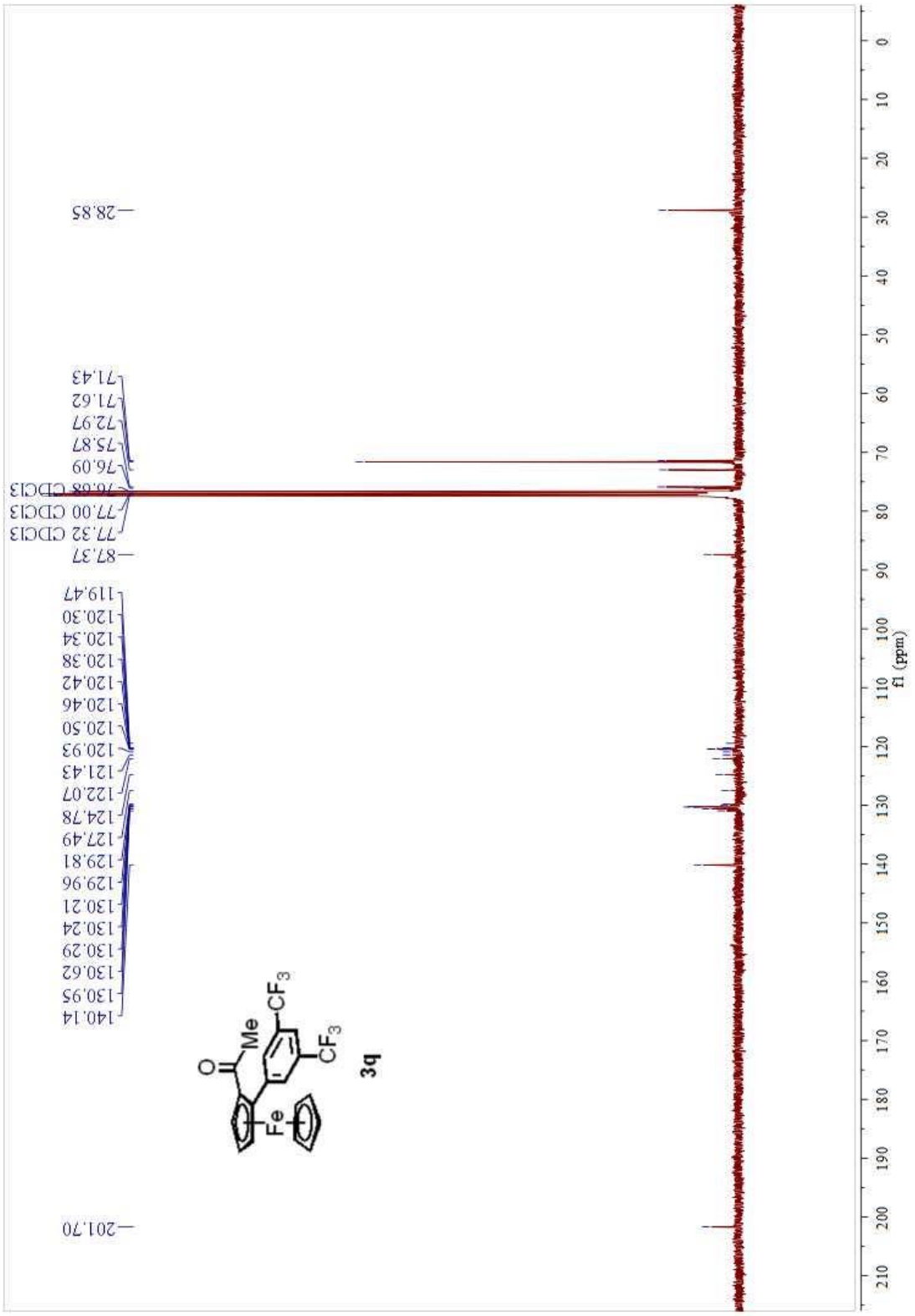

$^{1}$H NMR Spectra of Compound **3p**



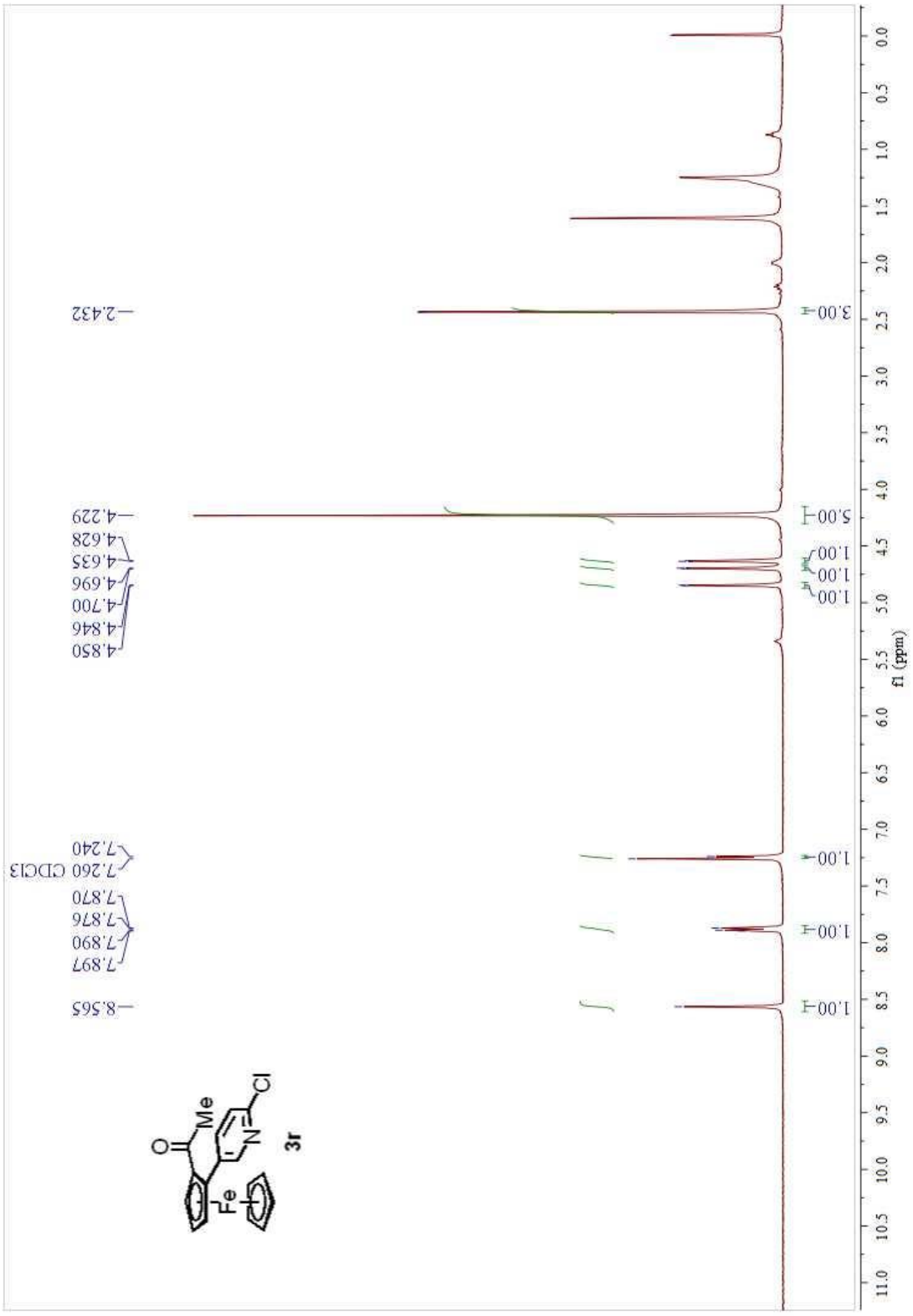

$^{13}$C NMR Spectra of Compound **3p**



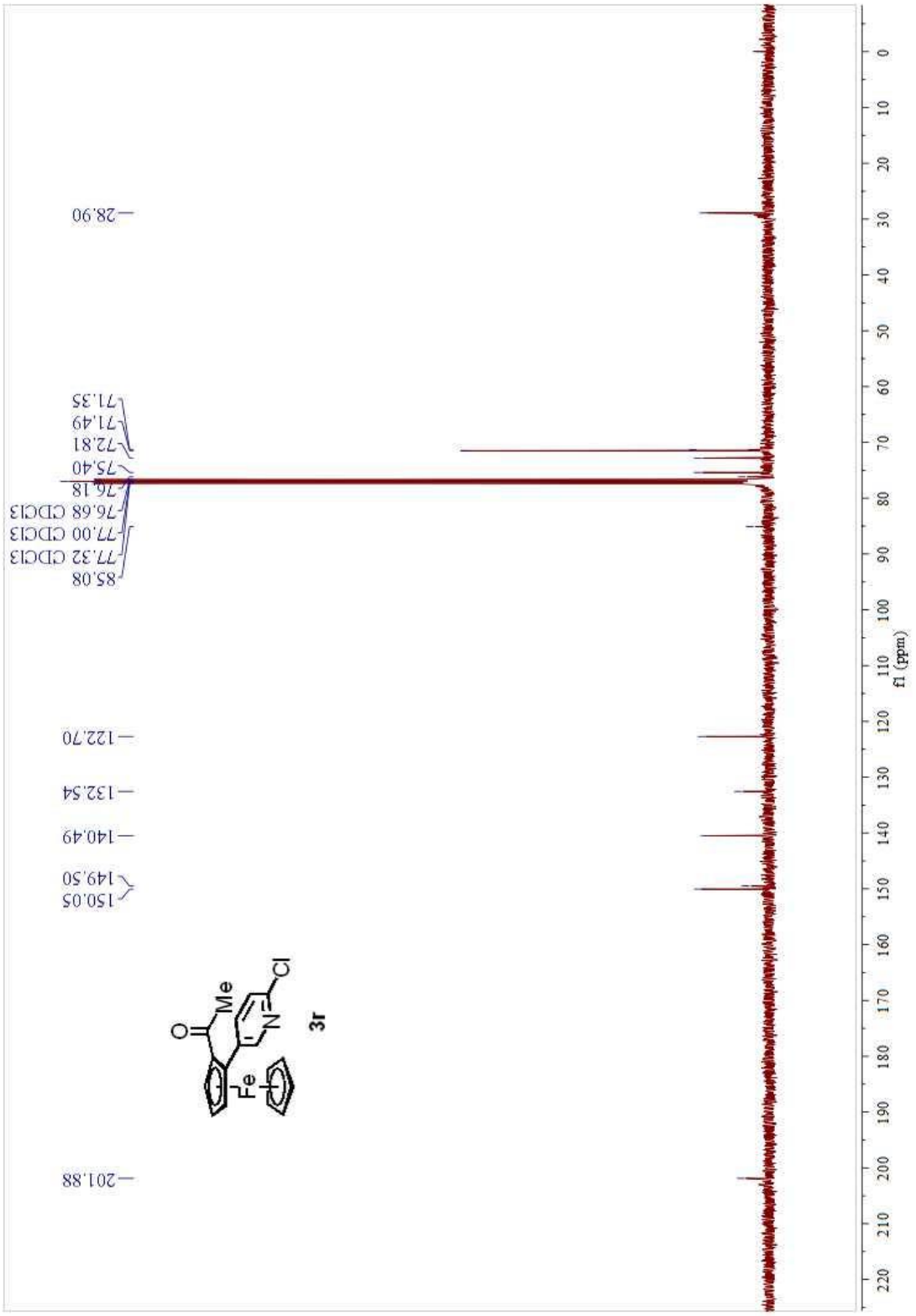

$^{1}$H NMR Spectra of Compound **3q**



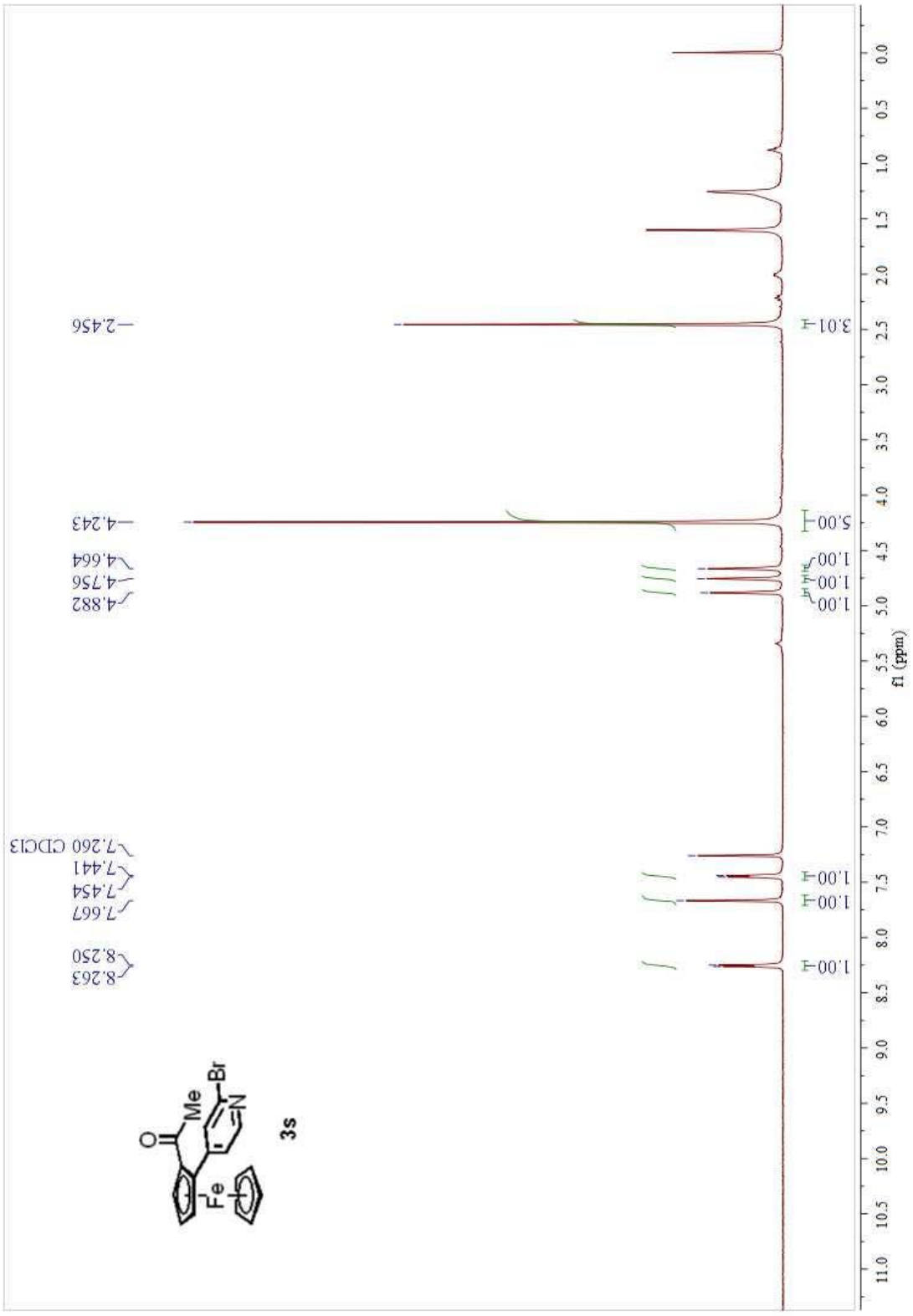

$^{13}$C NMR Spectra of Compound **3q**



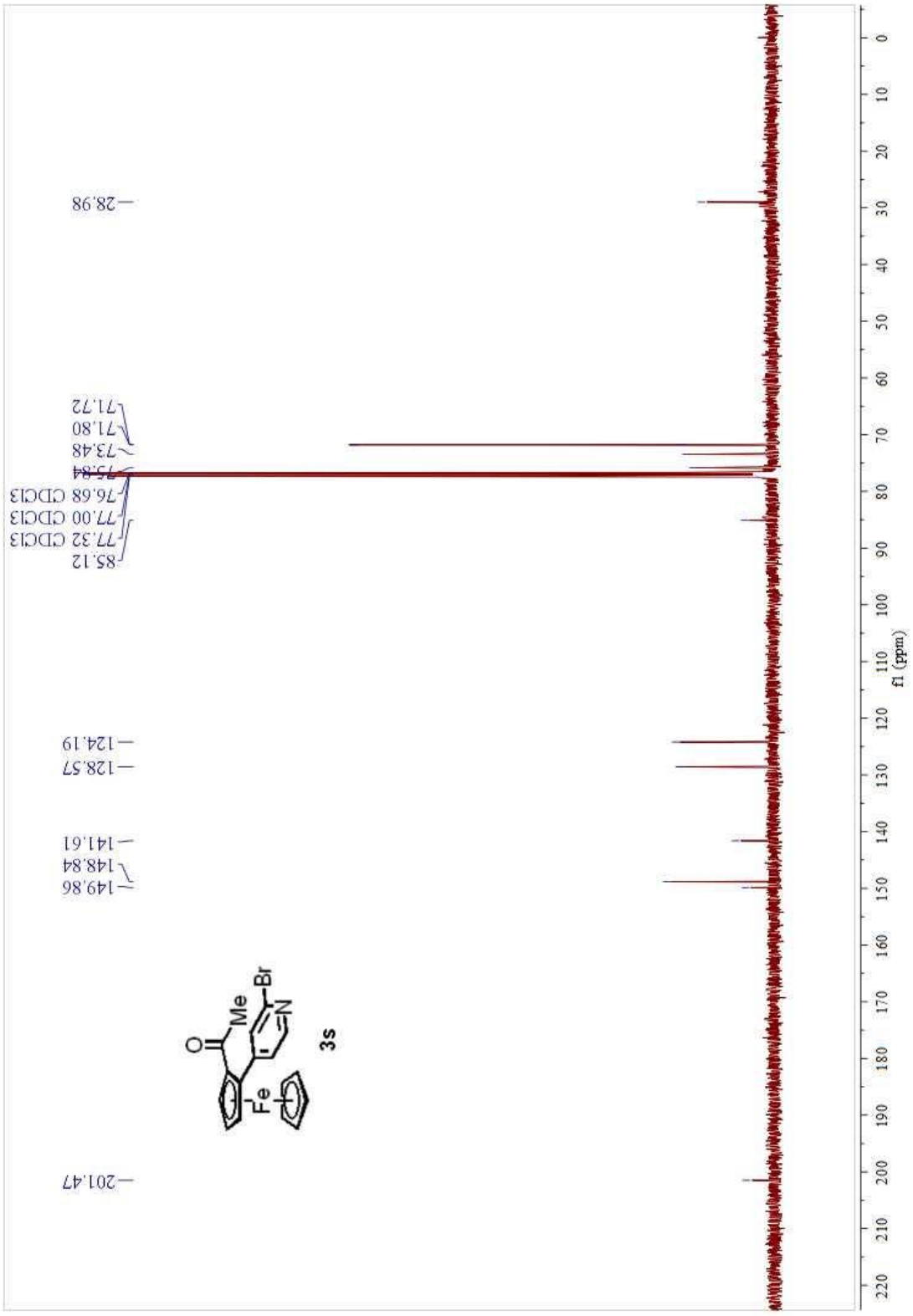

$^{1}$H NMR Spectra of Compound **3r**



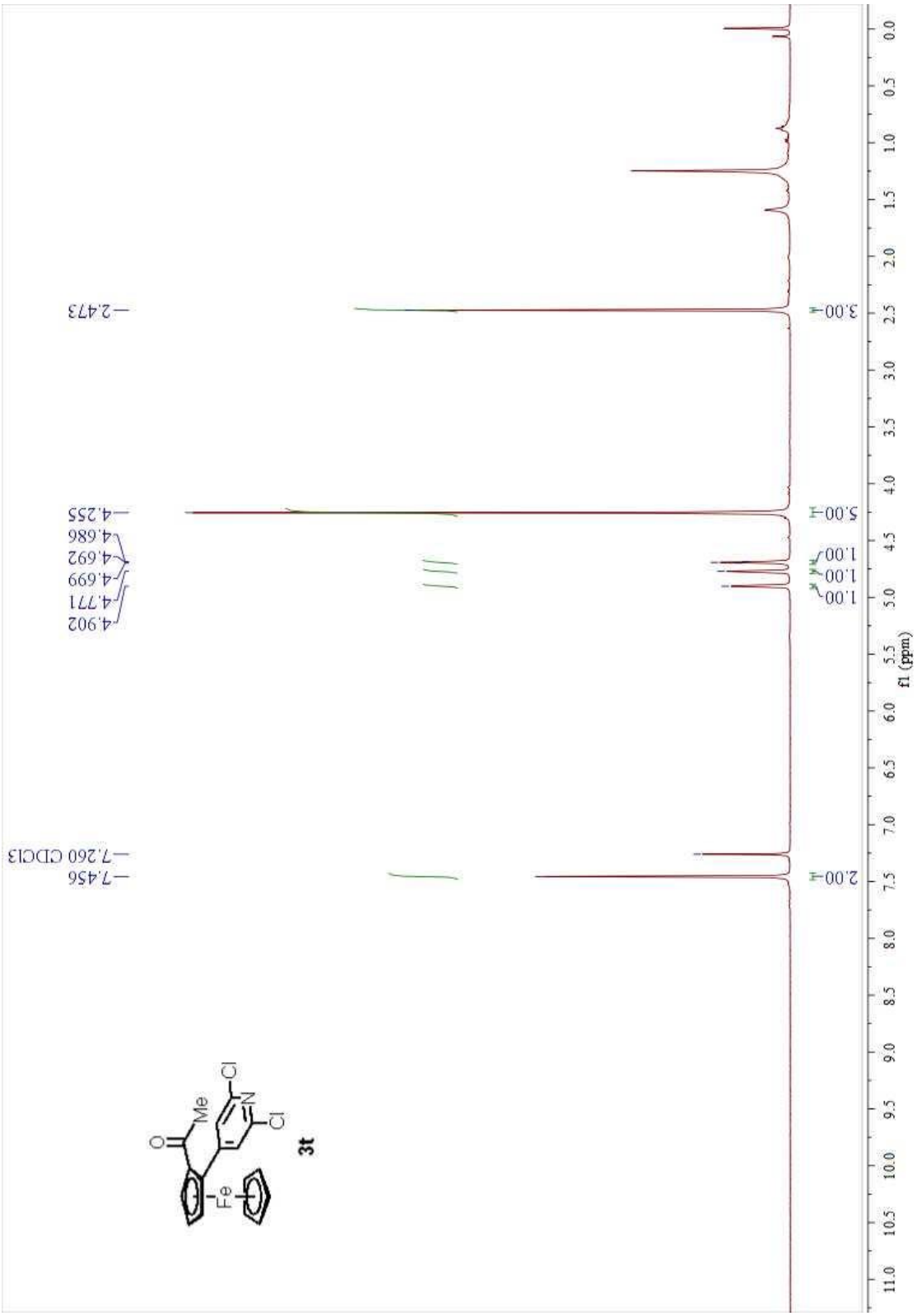

$^{13}$C NMR Spectra of Compound **3r**



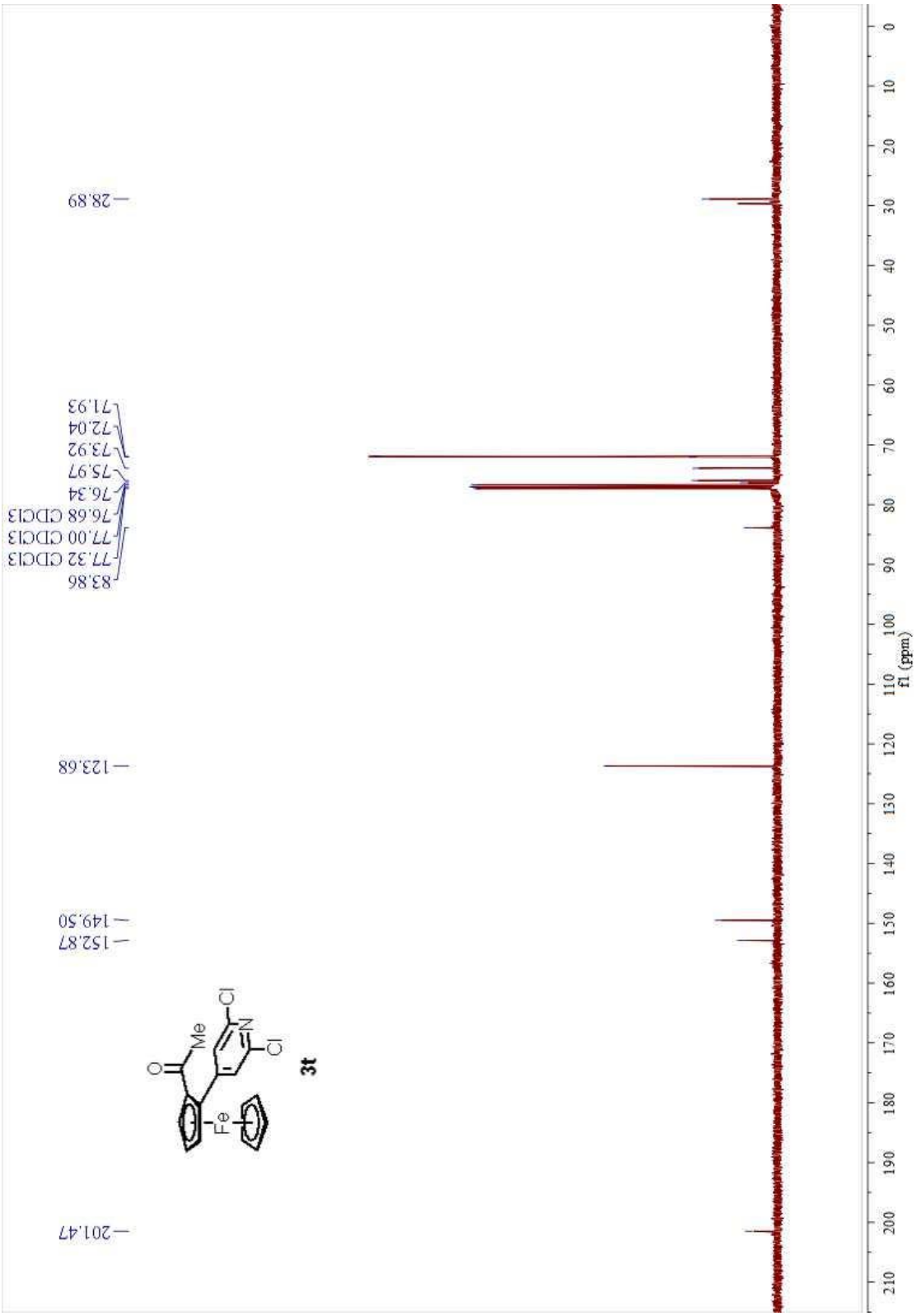

$^{1}$H NMR Spectra of Compound **3s**



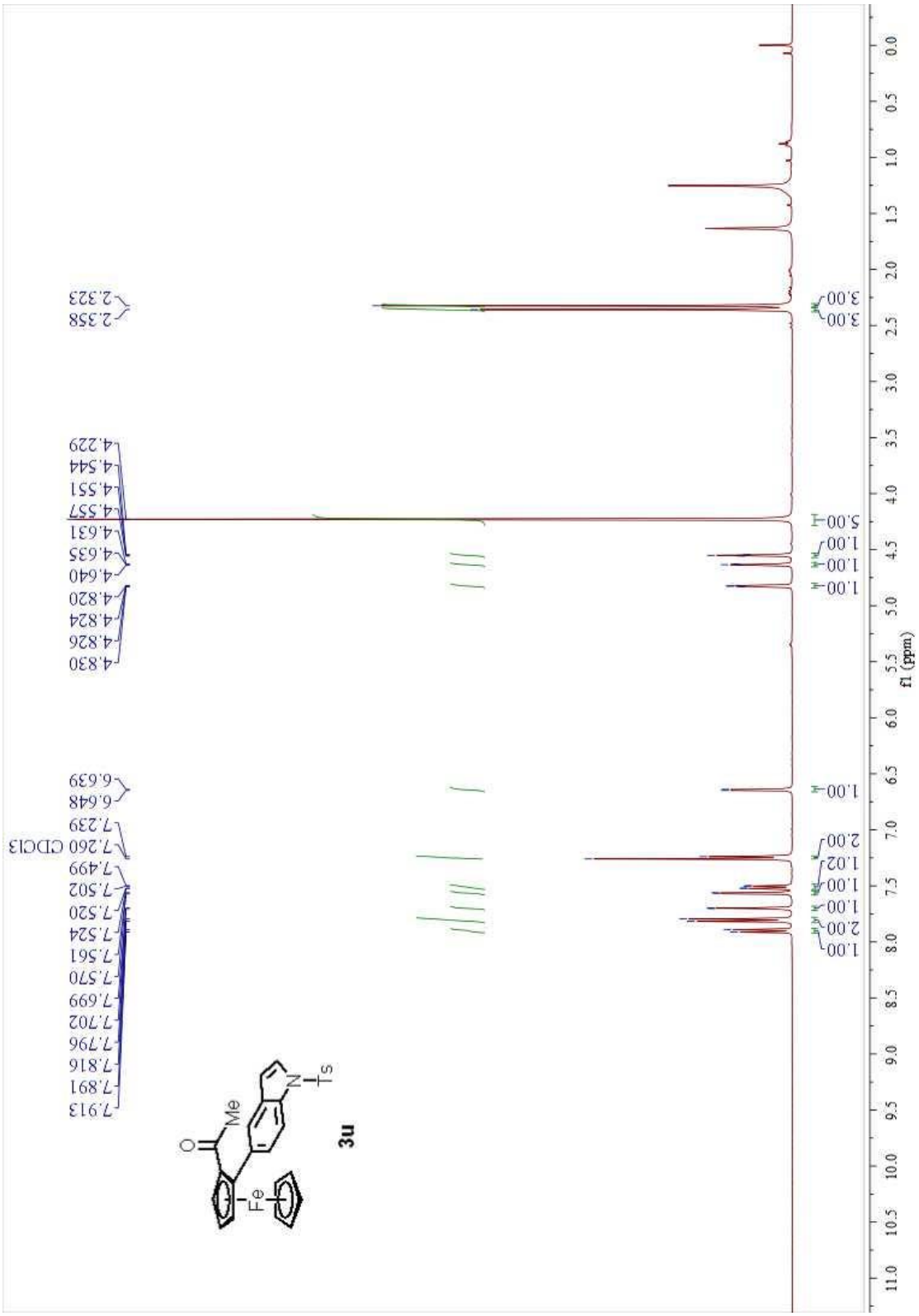

$^{13}$C NMR Spectra of Compound **3s**



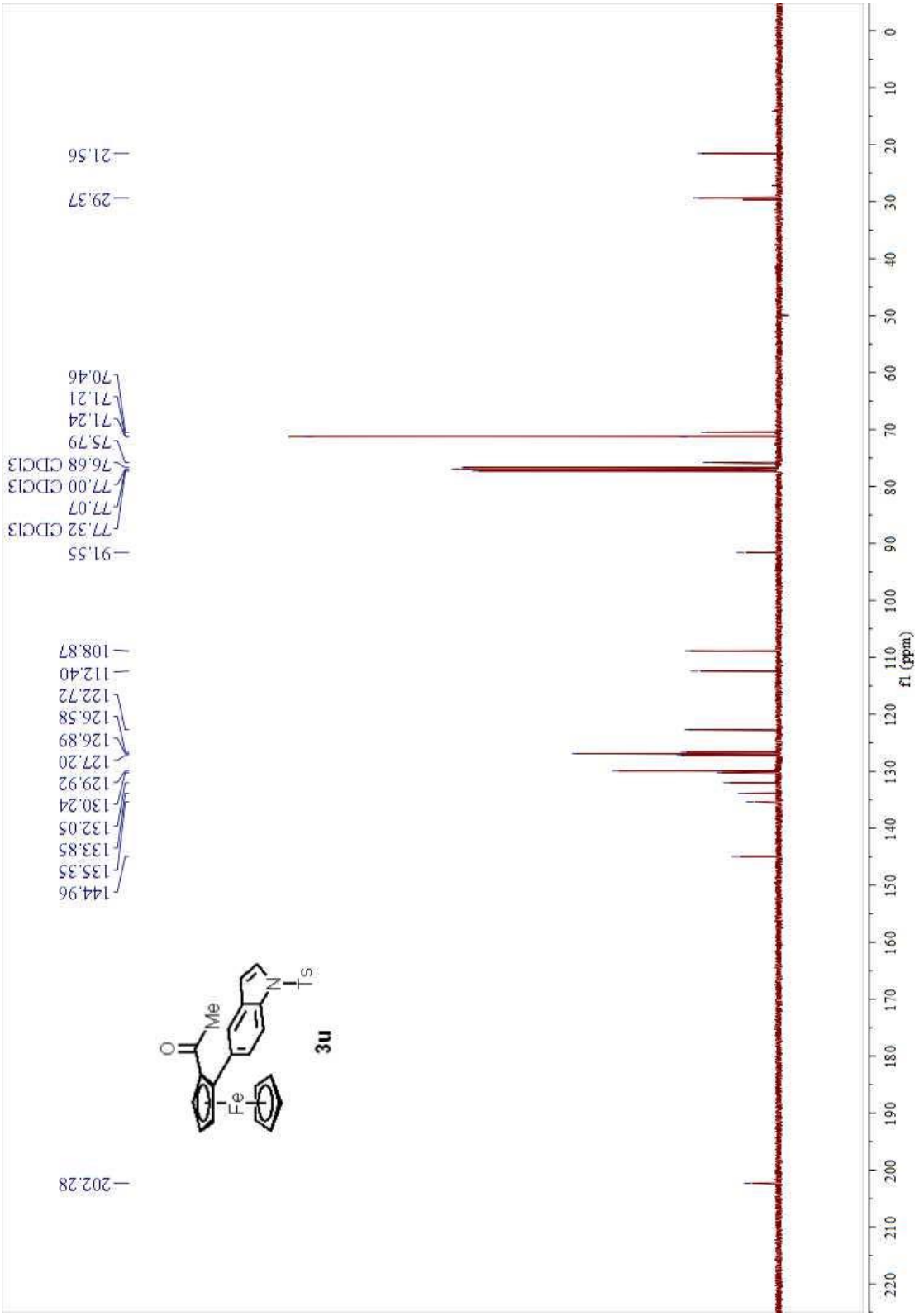

$^{1}$H NMR Spectra of Compound **3t**



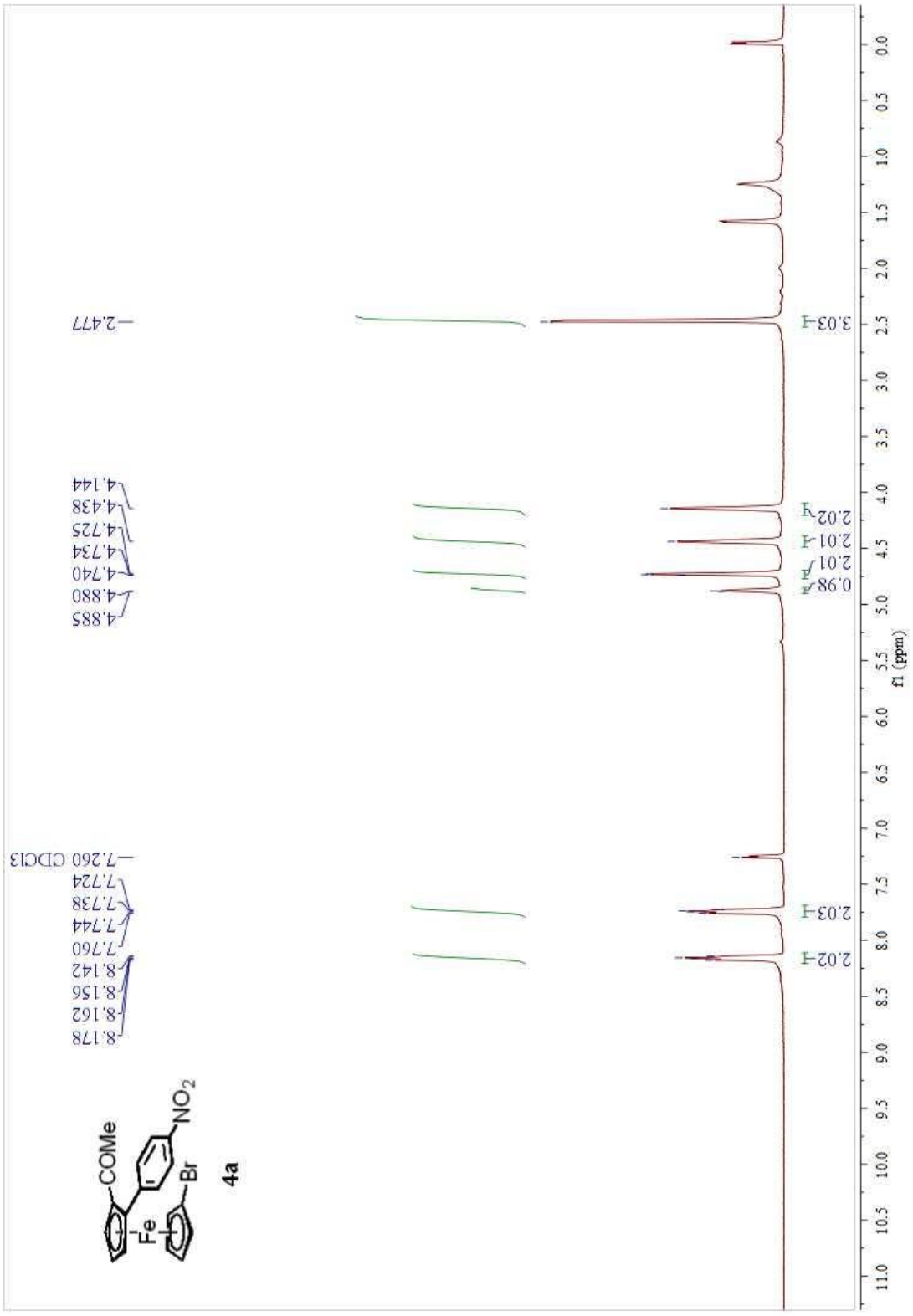

$^{13}$C NMR Spectra of Compound **3t**



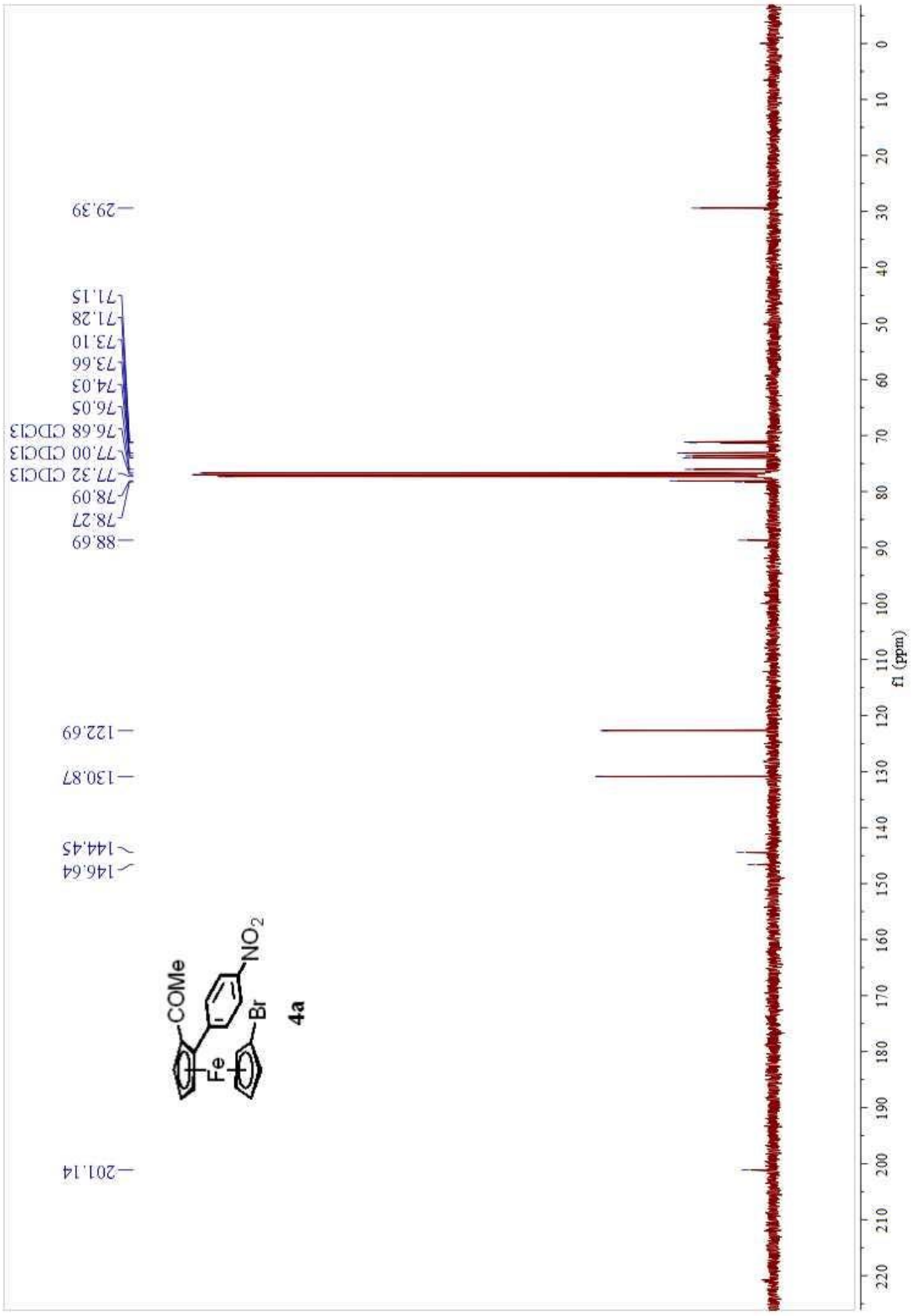

$^{1}$H NMR Spectra of Compound **3u**



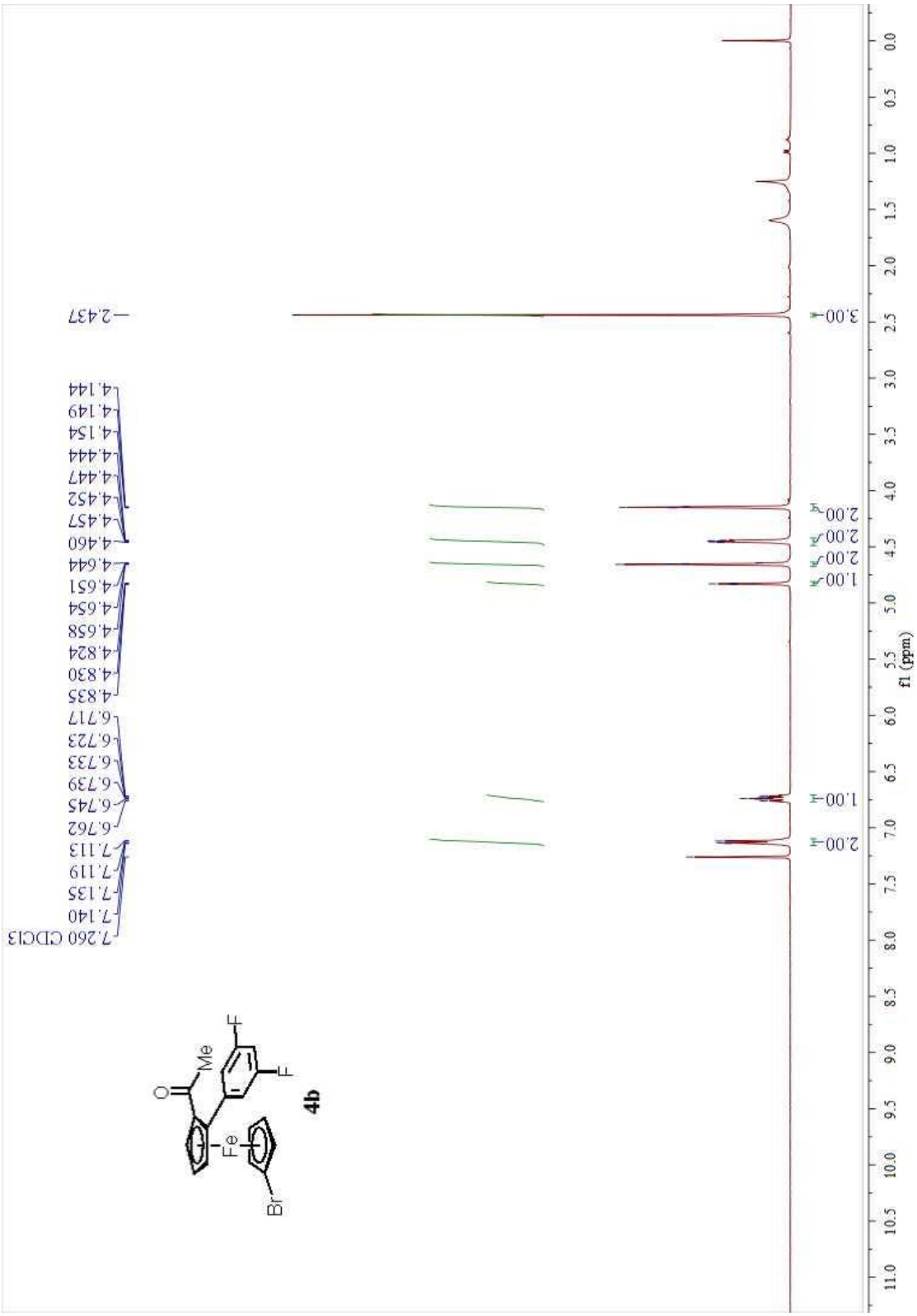

$^{13}$C NMR Spectra of Compound **3u**



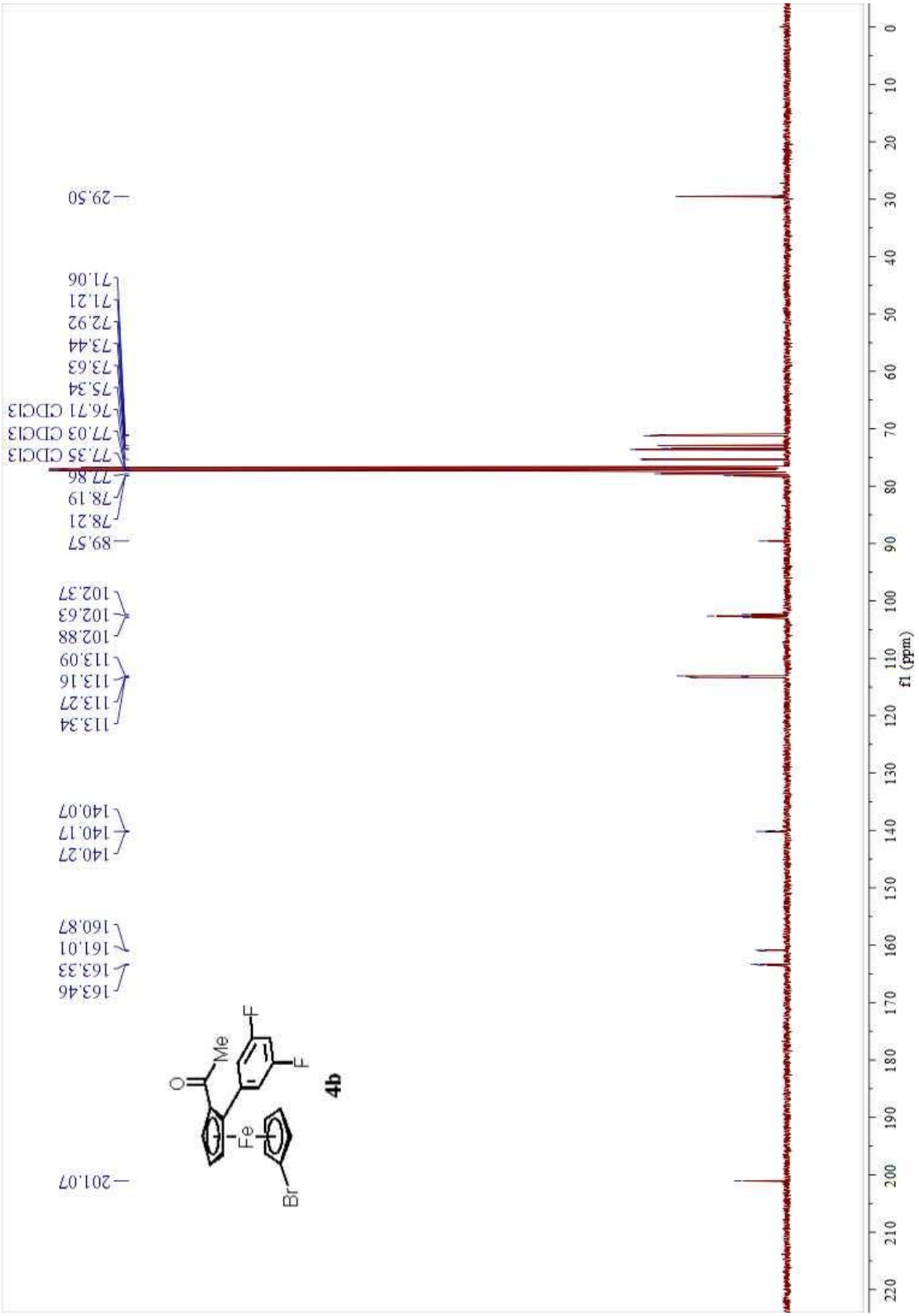

$^{1}$H NMR Spectra of Compound **4a**



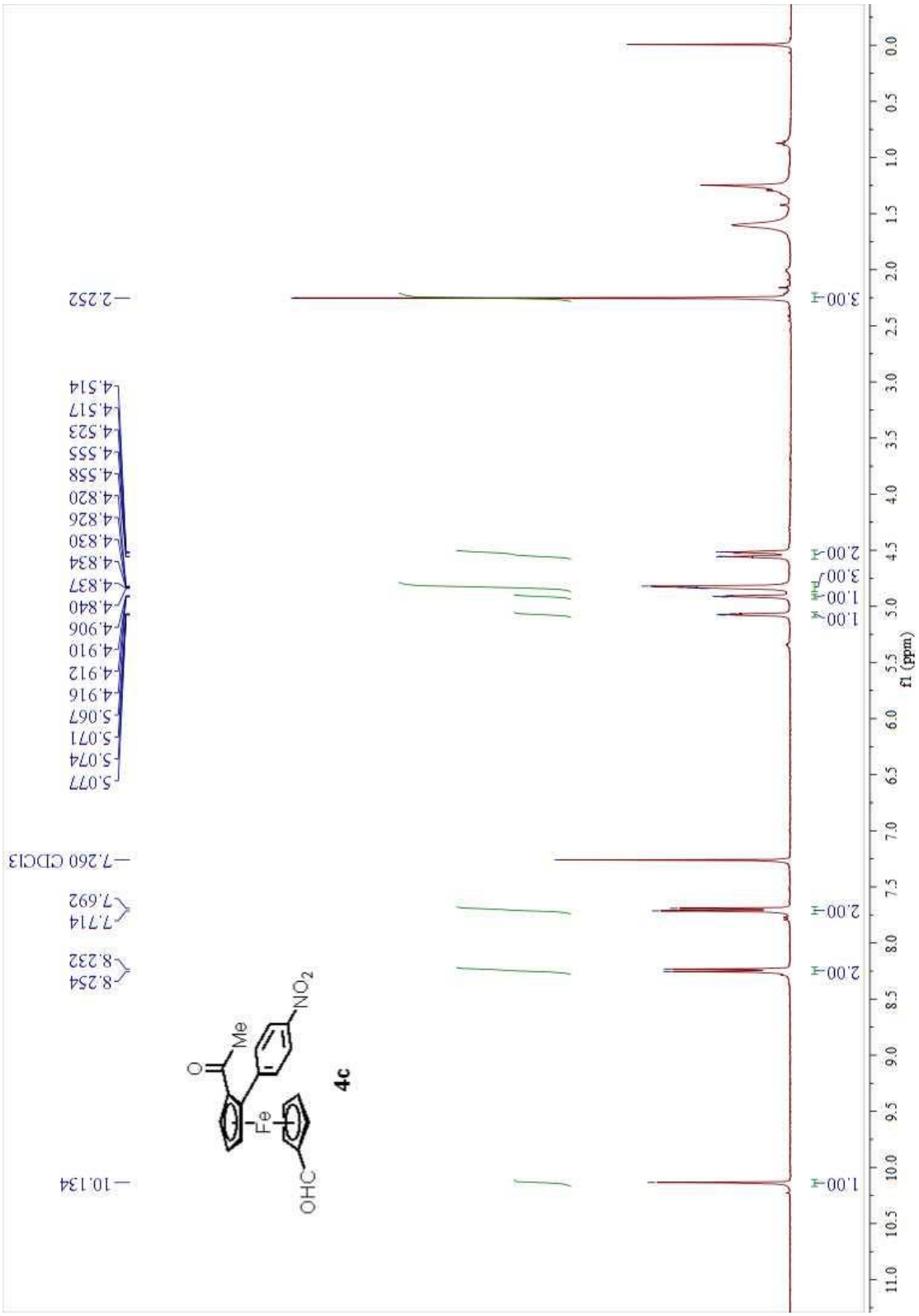

$^{13}$C NMR Spectra of Compound **4a**



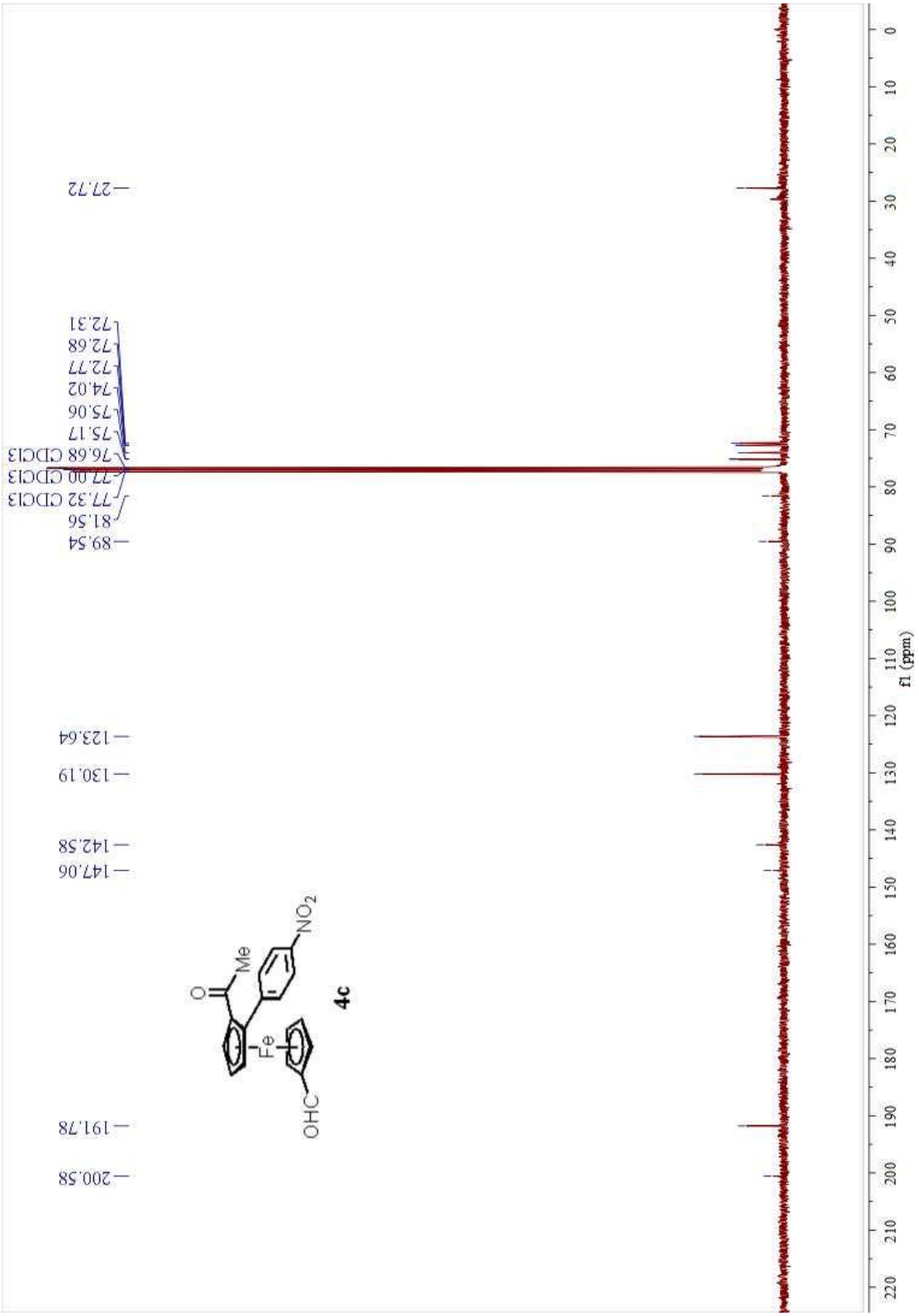

$^{1}$H NMR Spectra of Compound **4b**



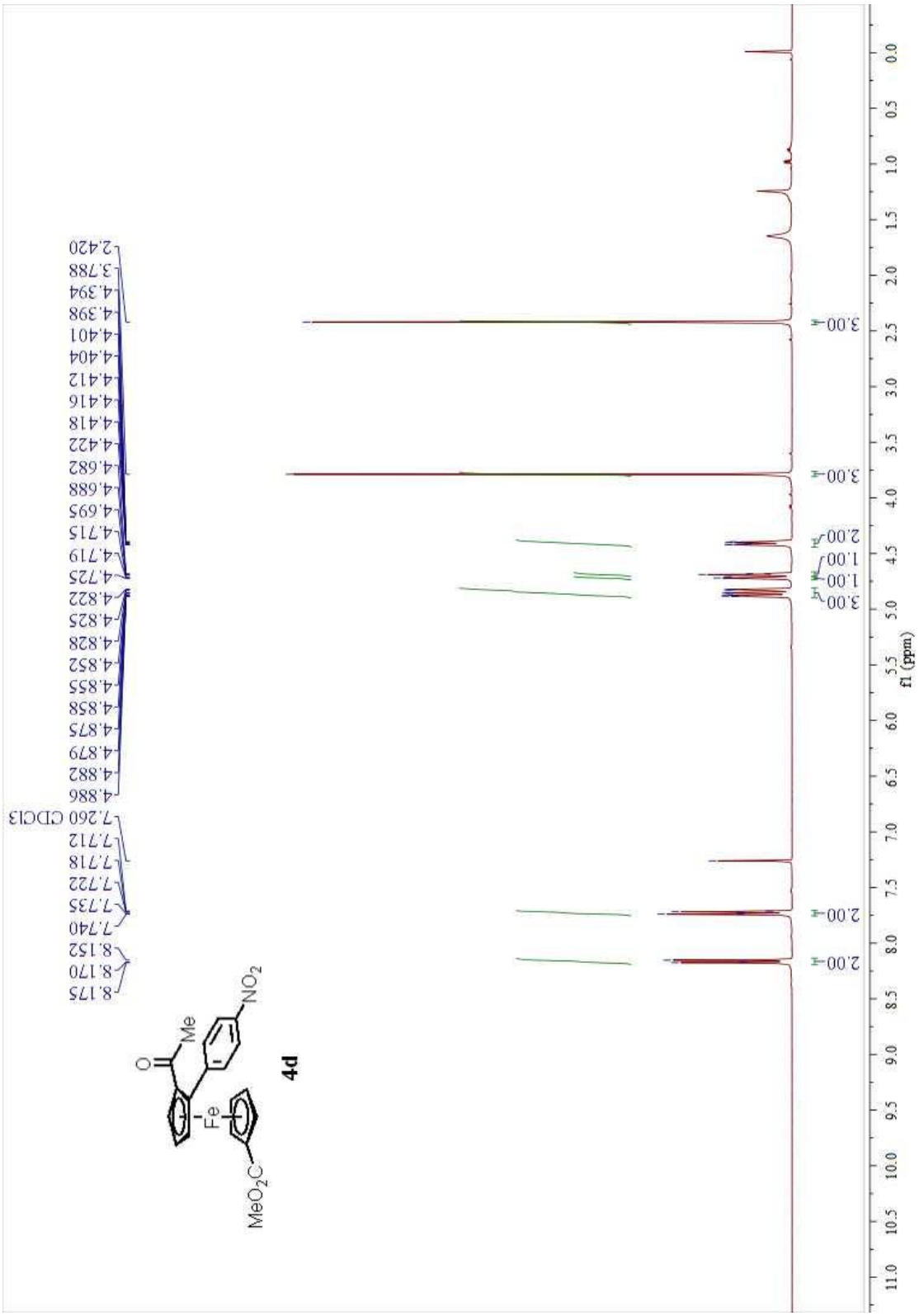

$^{13}$C NMR Spectra of Compound **4b**



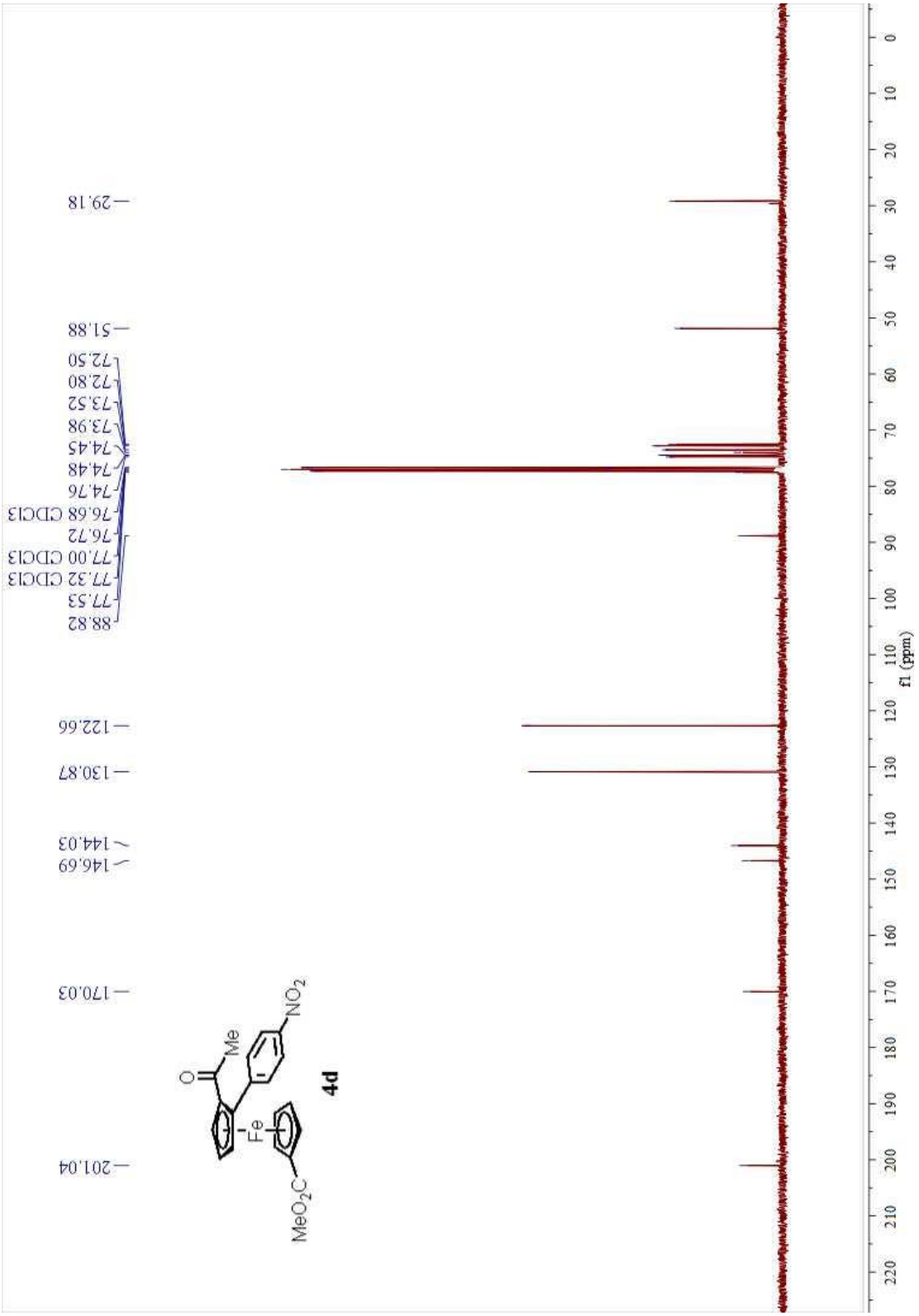

$^{1}$H NMR Spectra of Compound **4c**



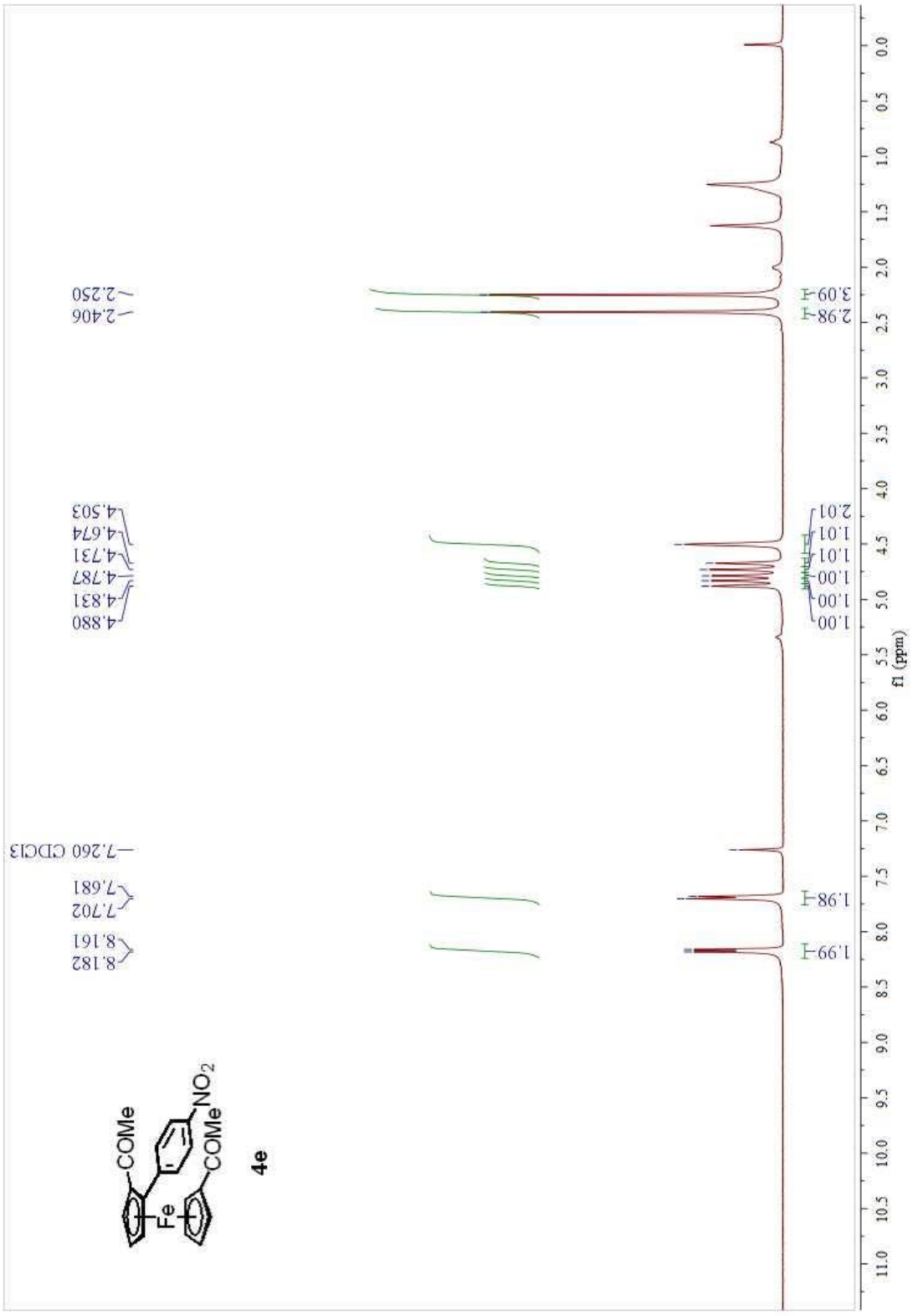

$^{13}$C NMR Spectra of Compound **4c**



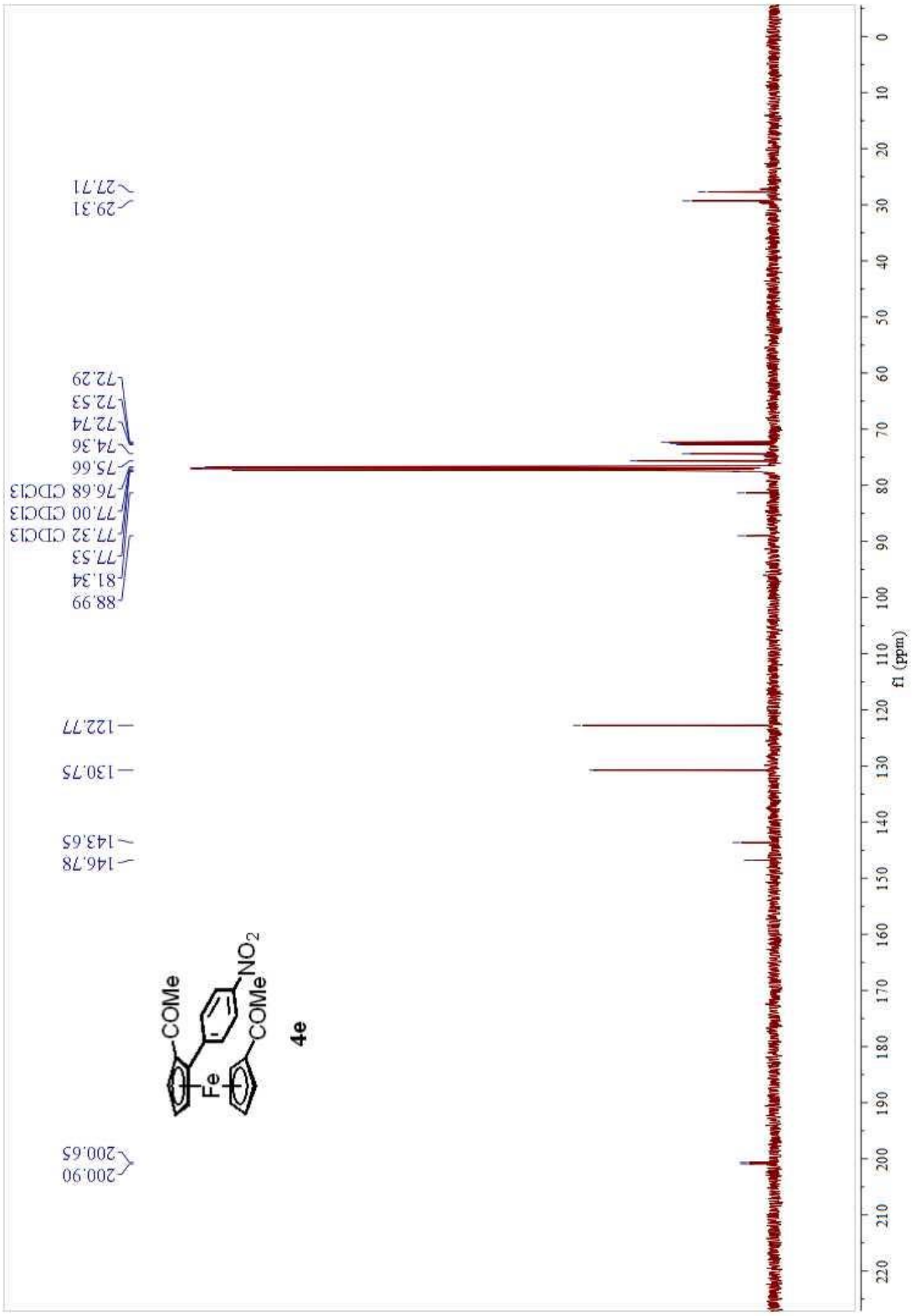

$^{1}$H NMR Spectra of Compound **4d**



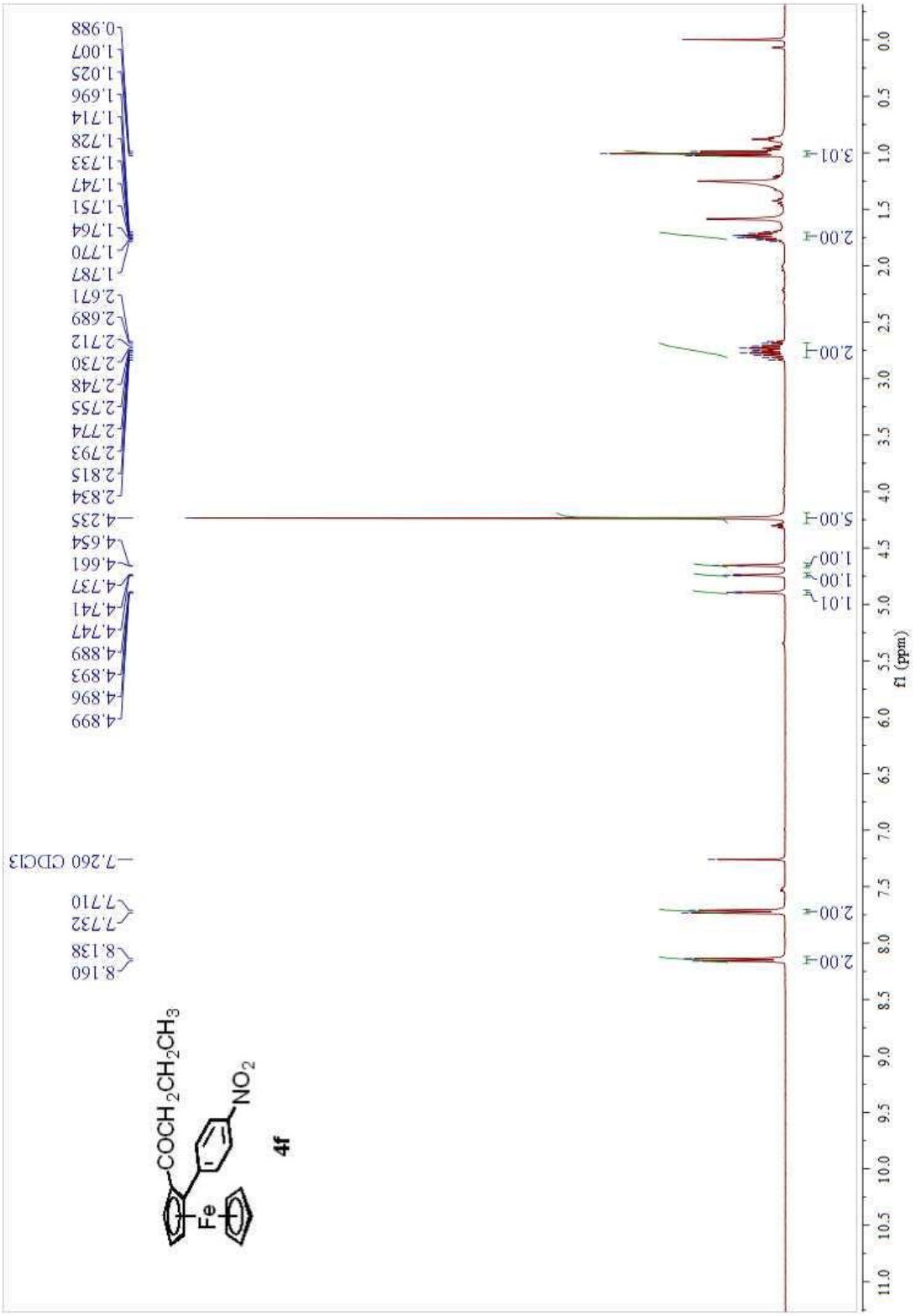

$^{13}$C NMR Spectra of Compound **4d**



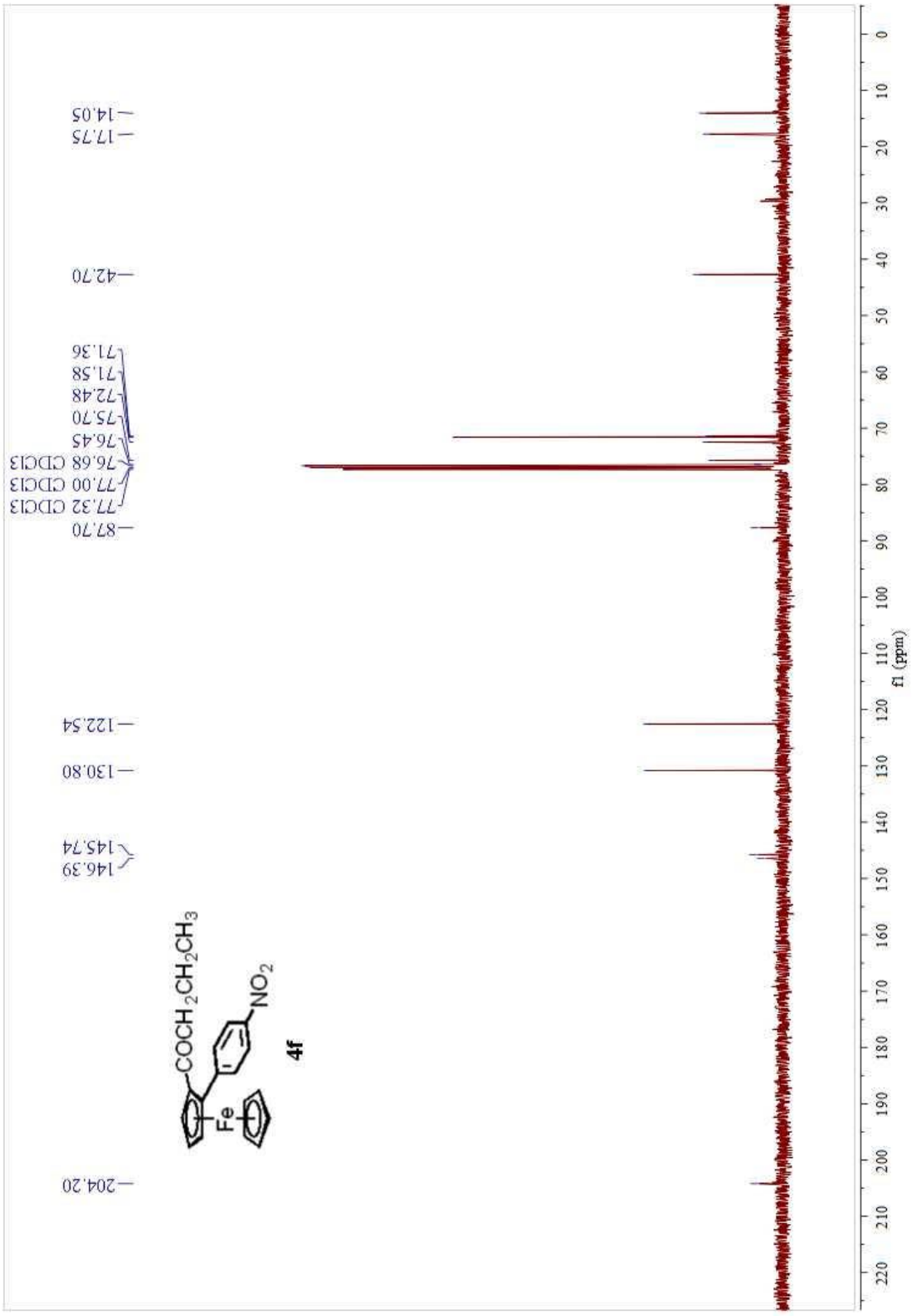

$^{1}$H NMR Spectra of Compound **4e**



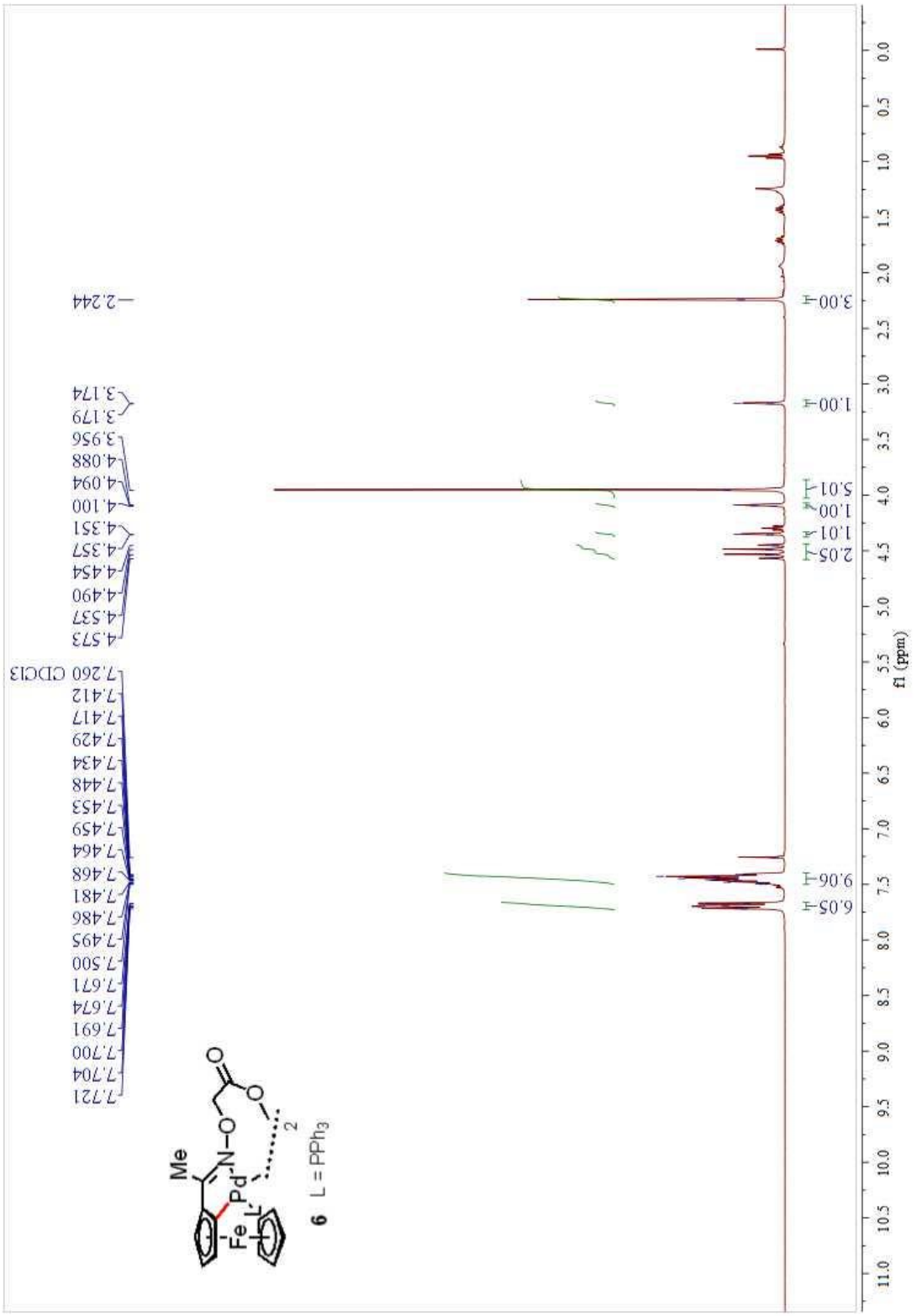

$^{13}$C NMR Spectra of Compound **4e**



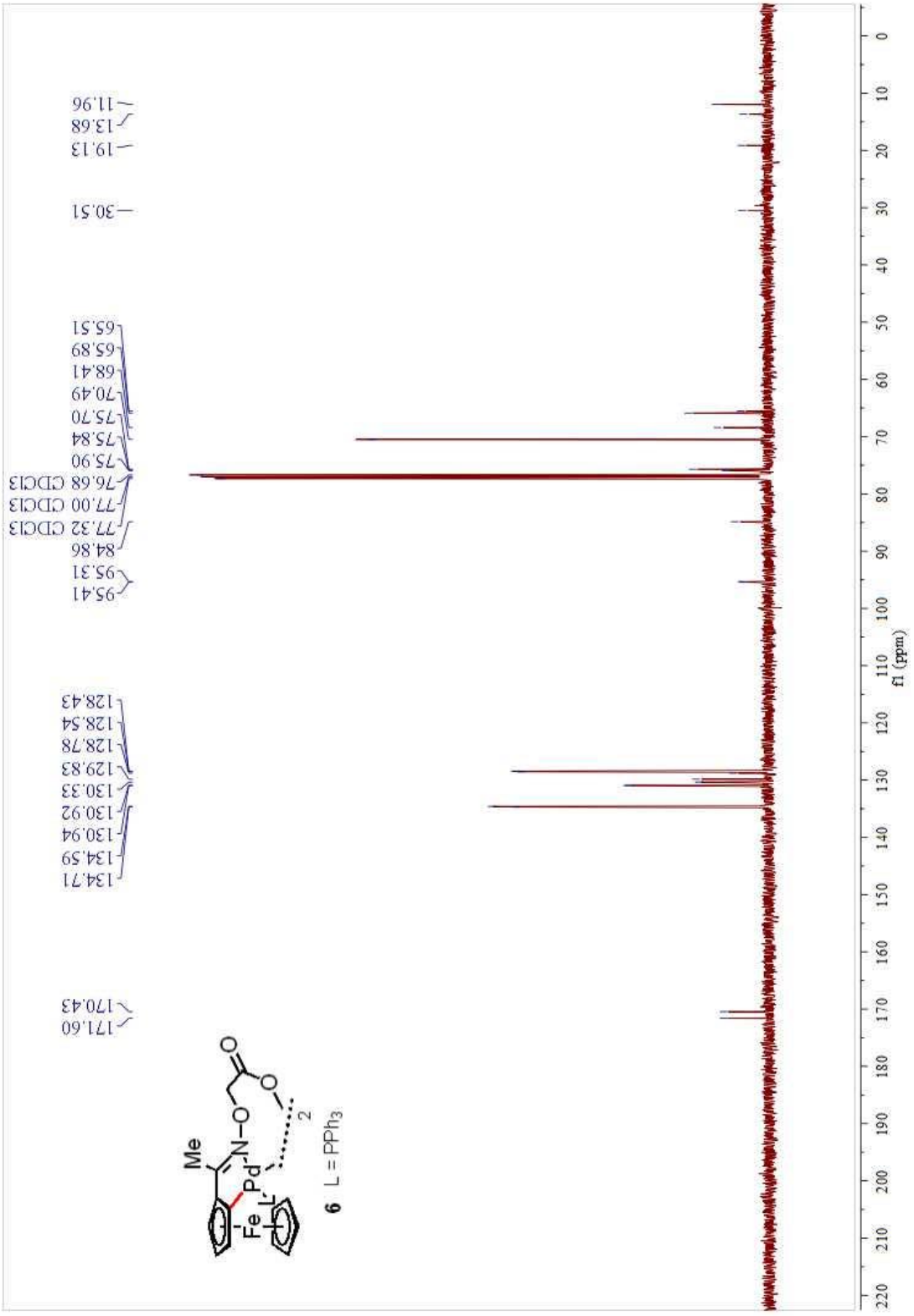

$^{1}$H NMR Spectra of Compound **4f**



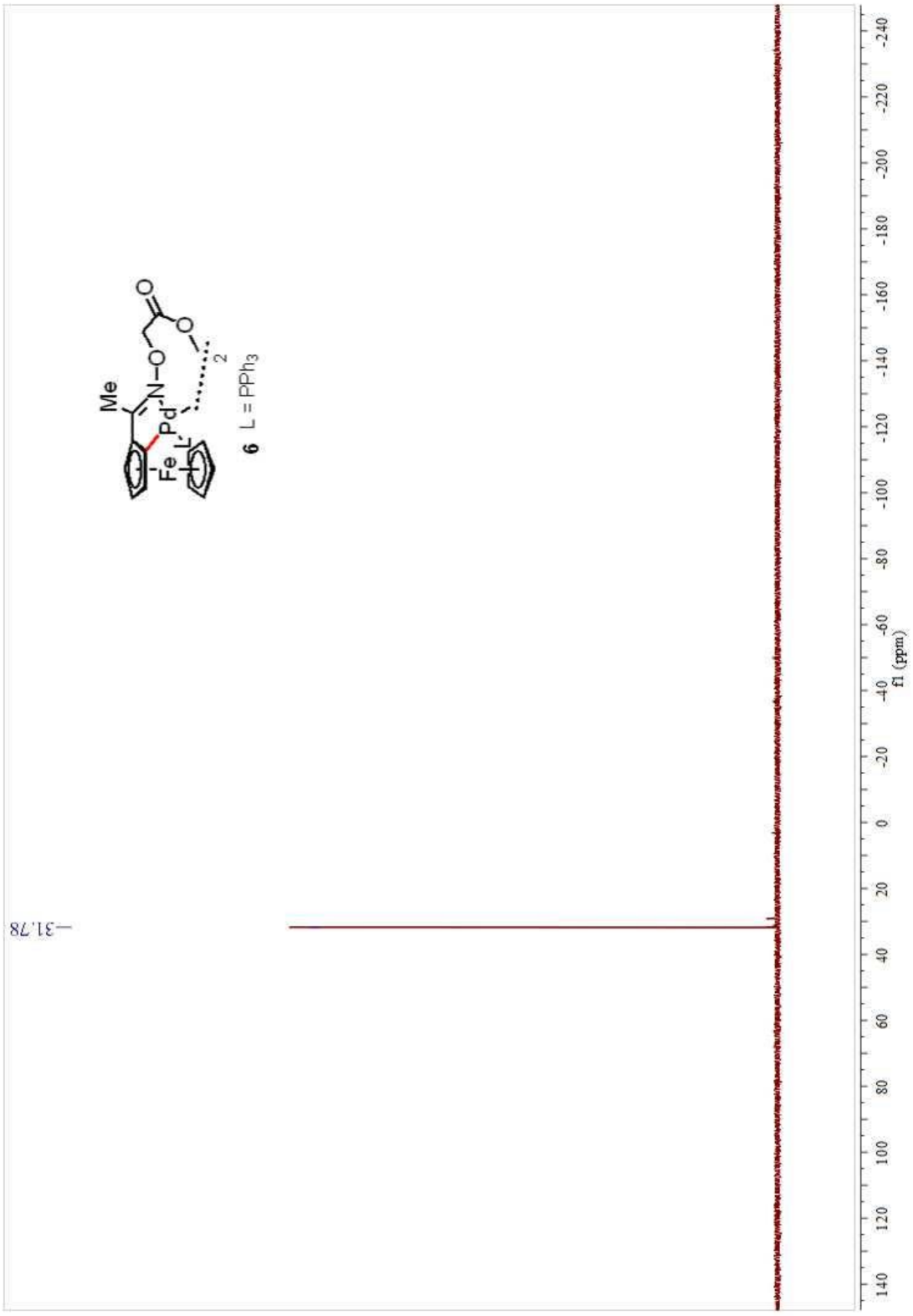

$^{13}$C NMR Spectra of Compound **4f**



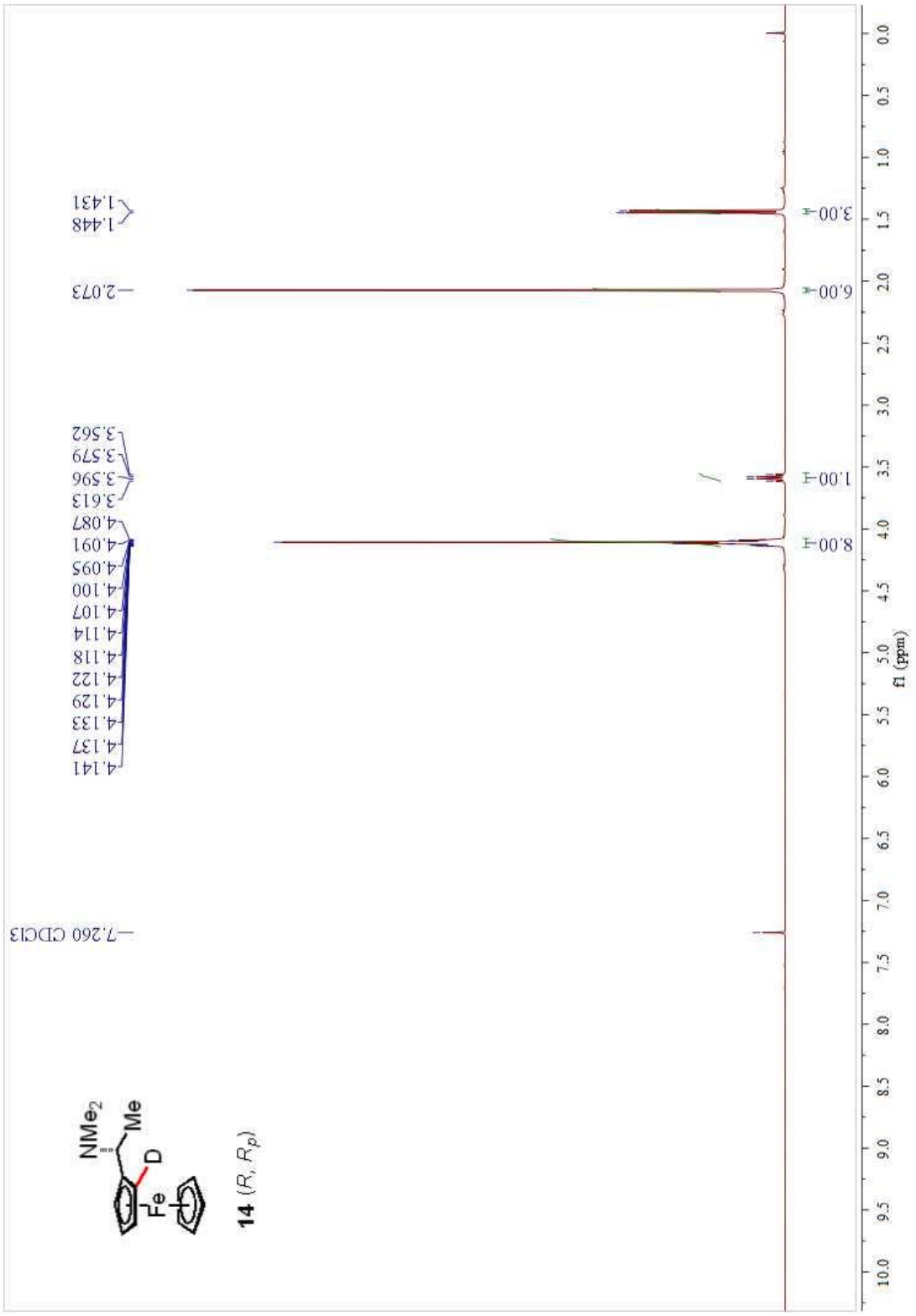

$^{1}$H NMR Spectra of Compound **6**



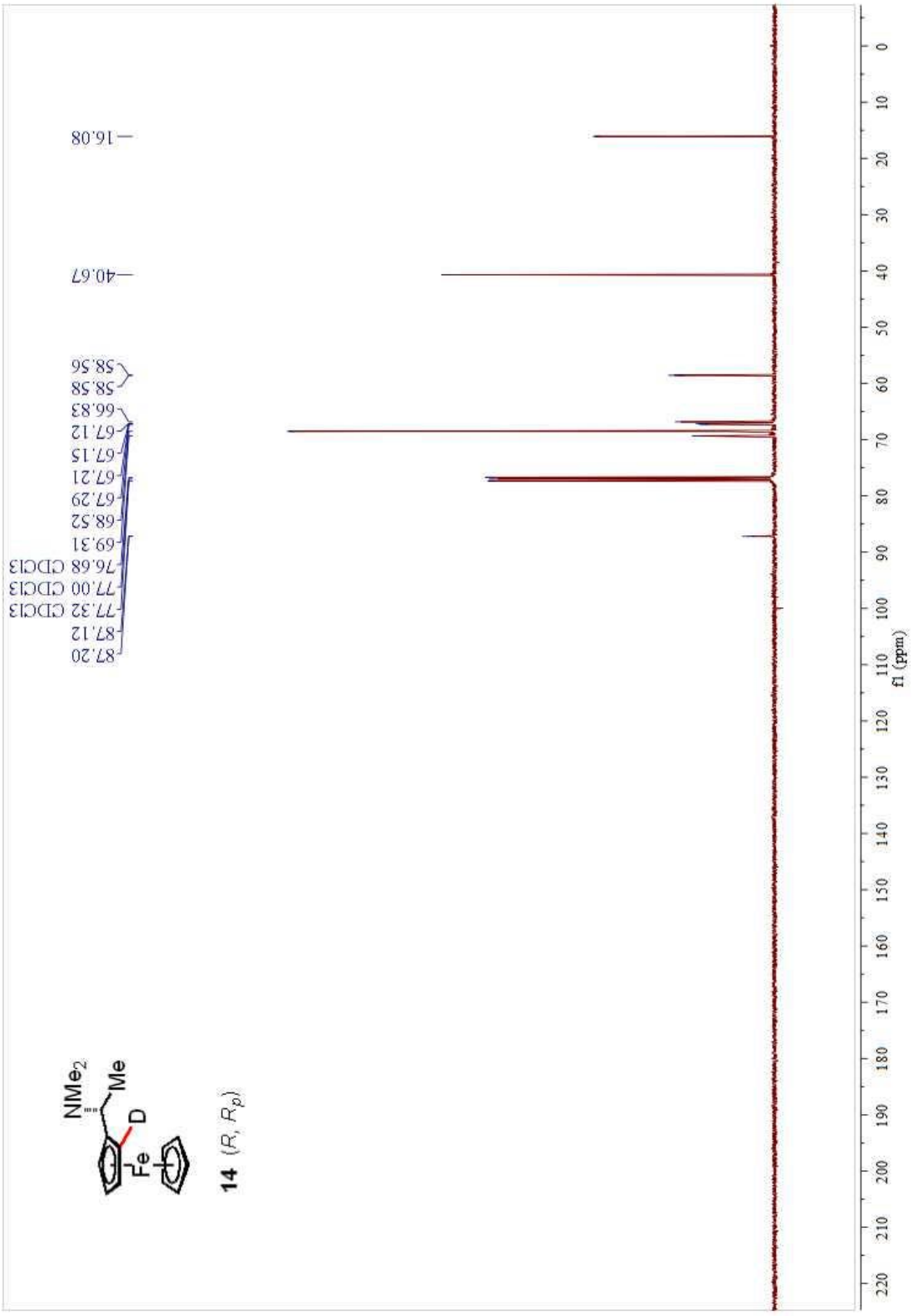

$^{13}$C NMR Spectra of Compound **6**



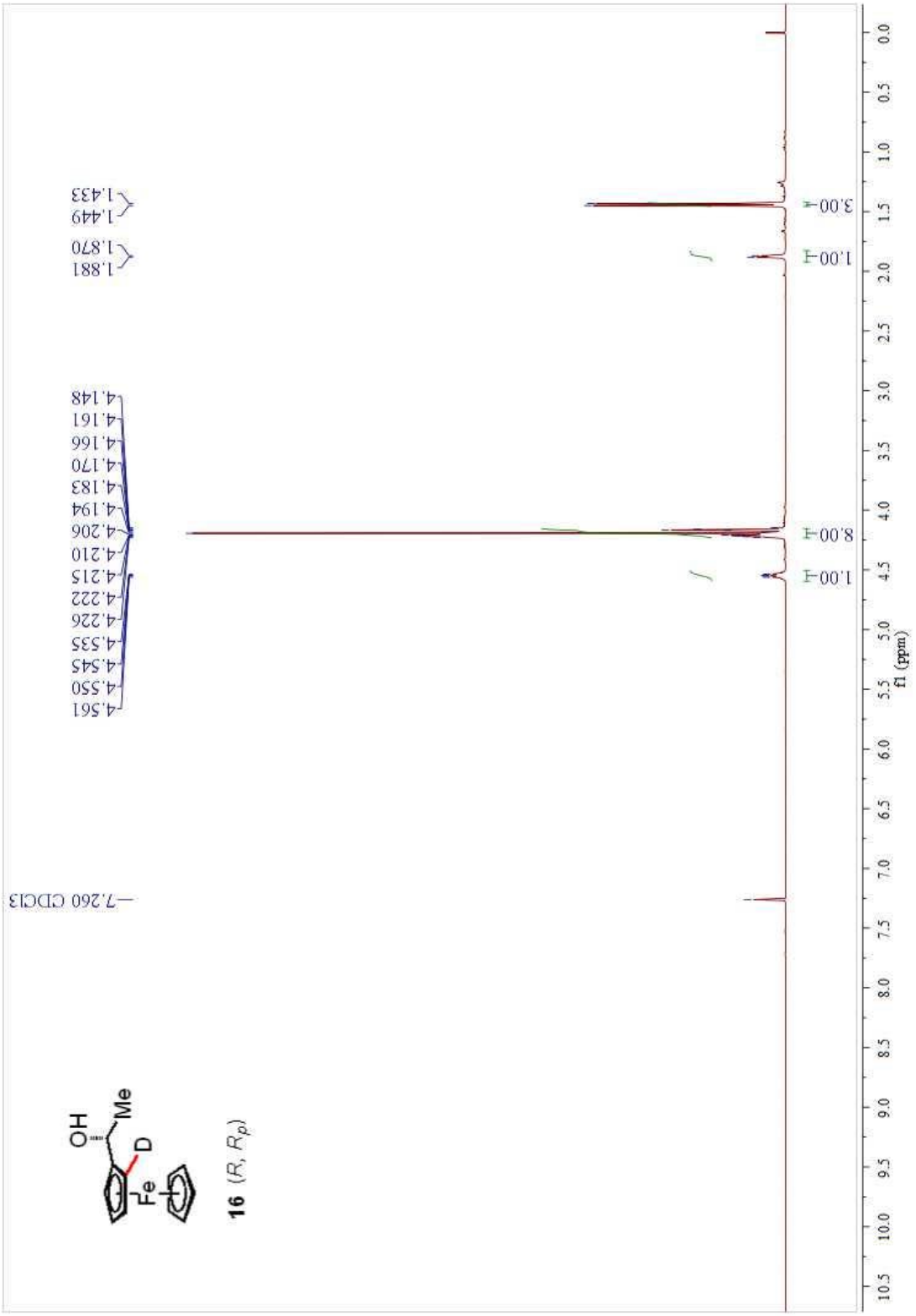

$^{31}$P NMR Spectra of Compound **6**



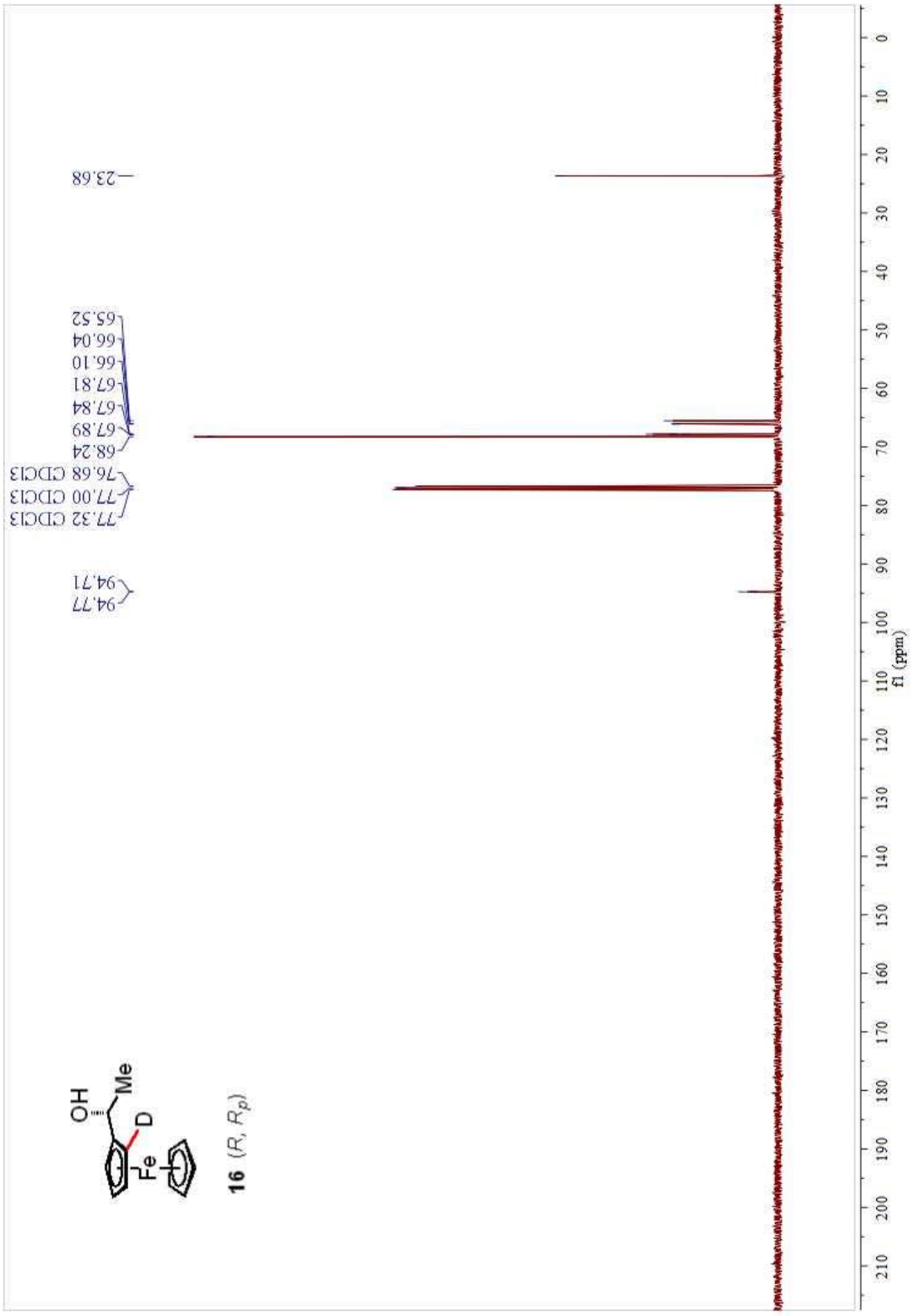

$^{1}$H NMR Spectra of Compound **14**



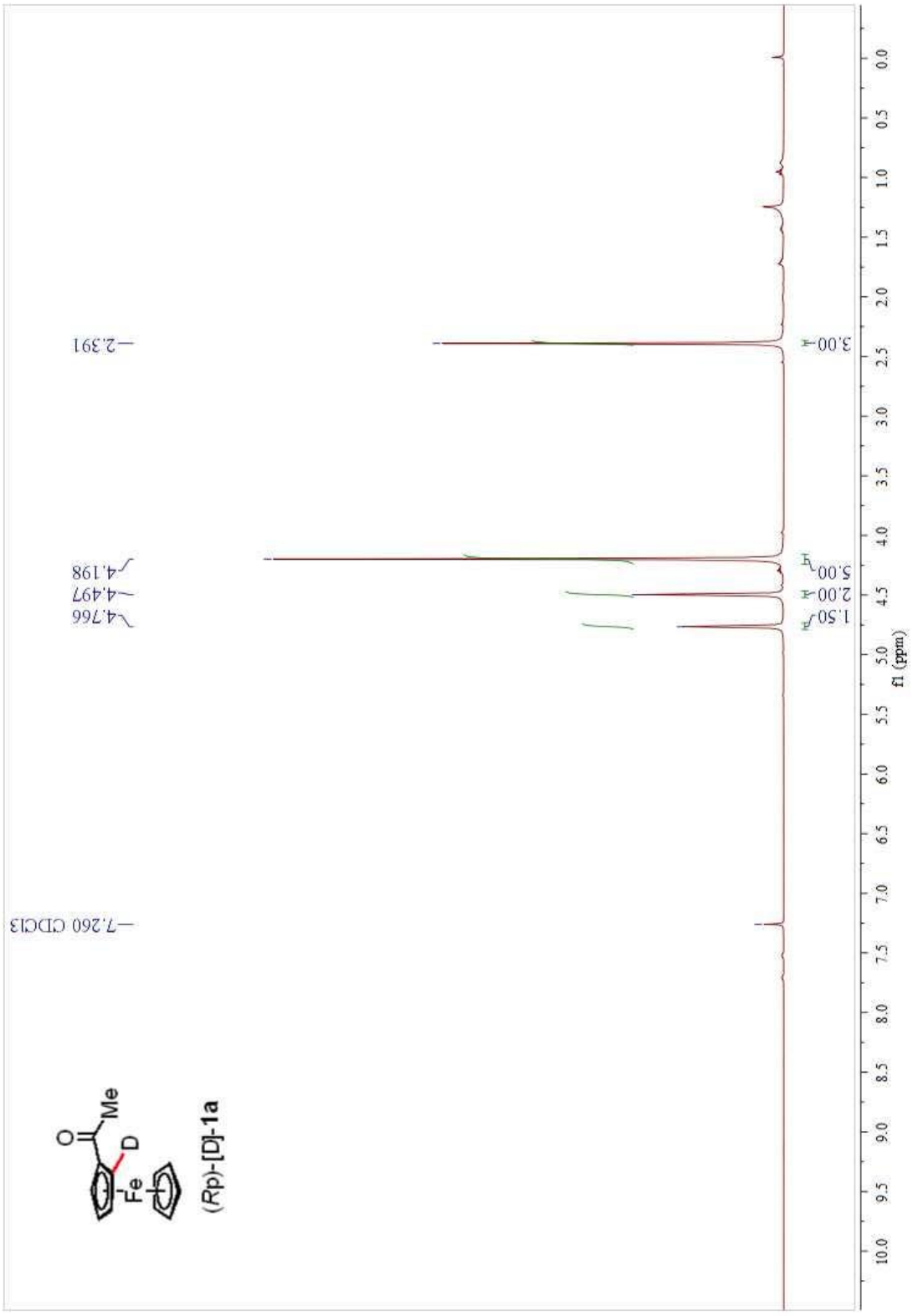

$^{13}$C NMR Spectra of Compound **14**



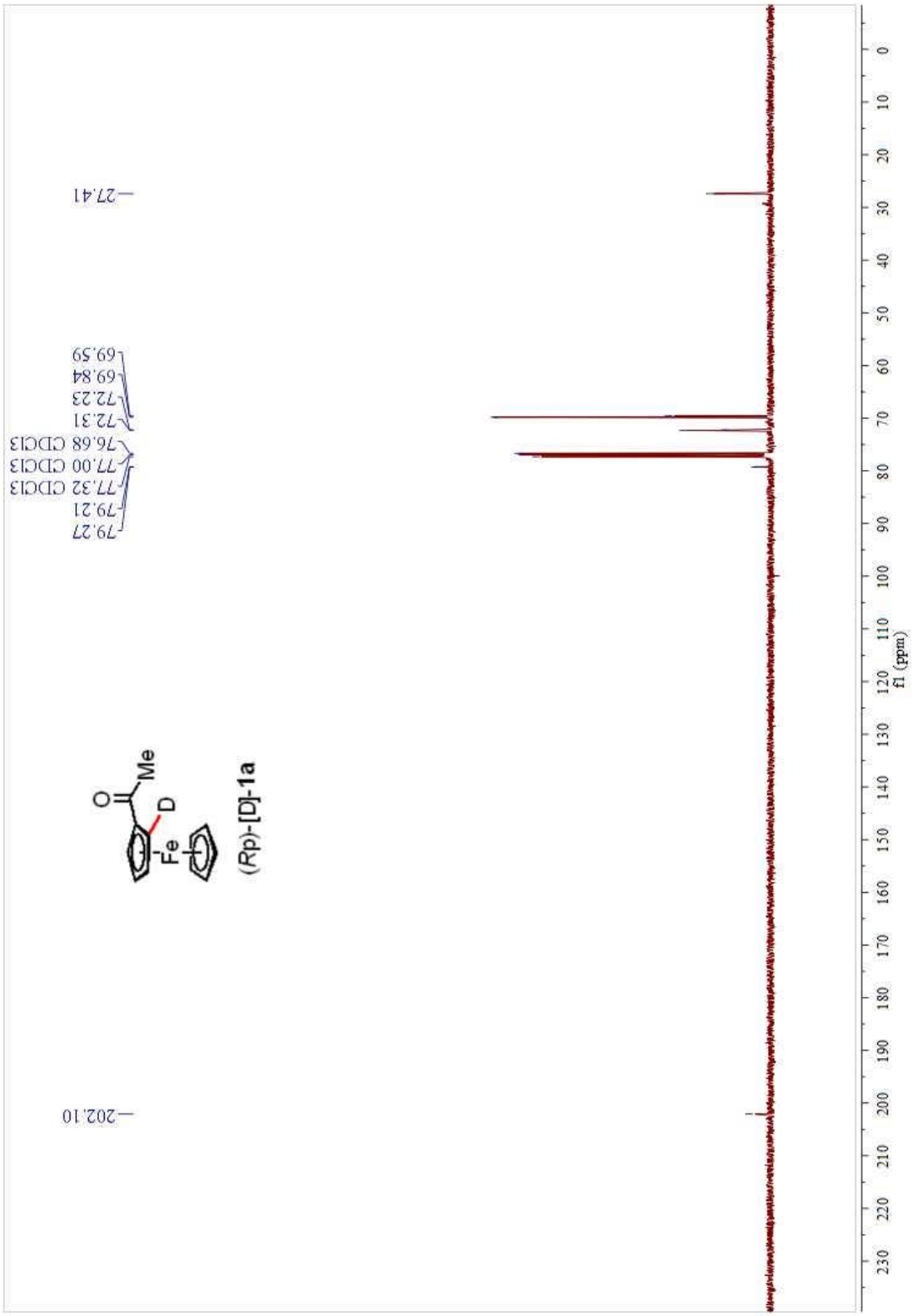

$^{1}$H NMR Spectra of Compound **16**



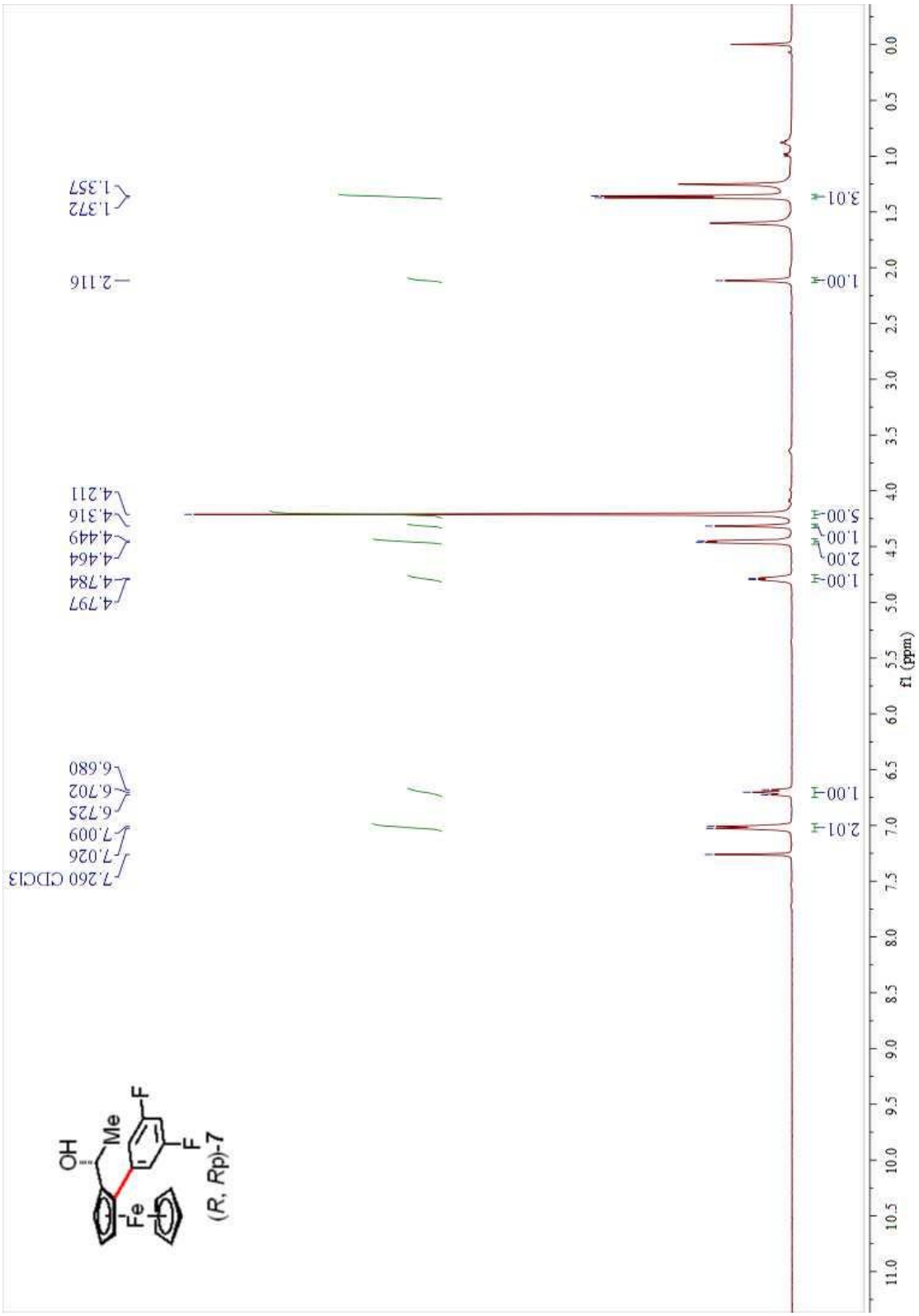

$^{13}$C NMR Spectra of Compound **16**



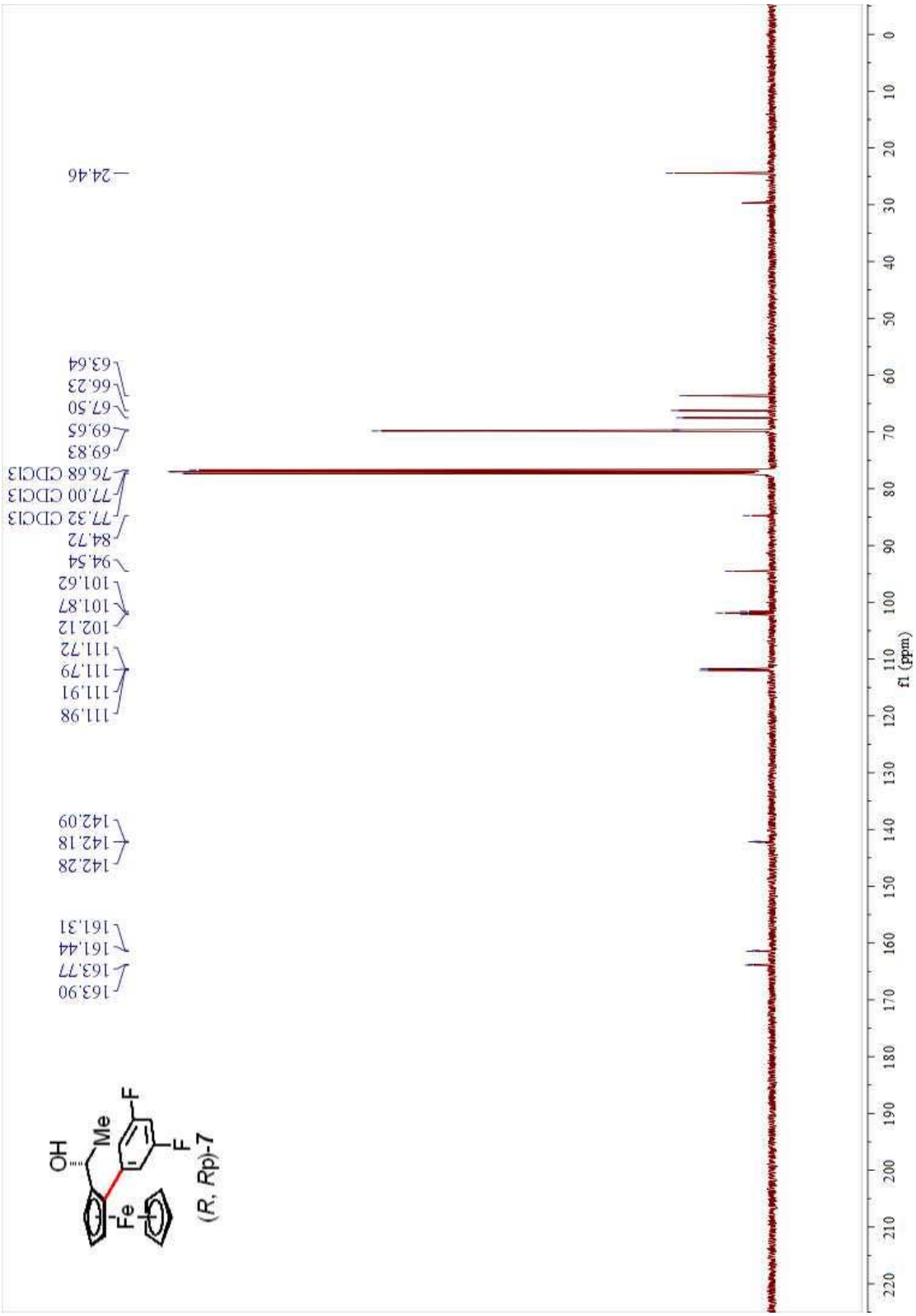

$^1$H NMR Spectra of Compound ($R_p$)-[D]-**1a**



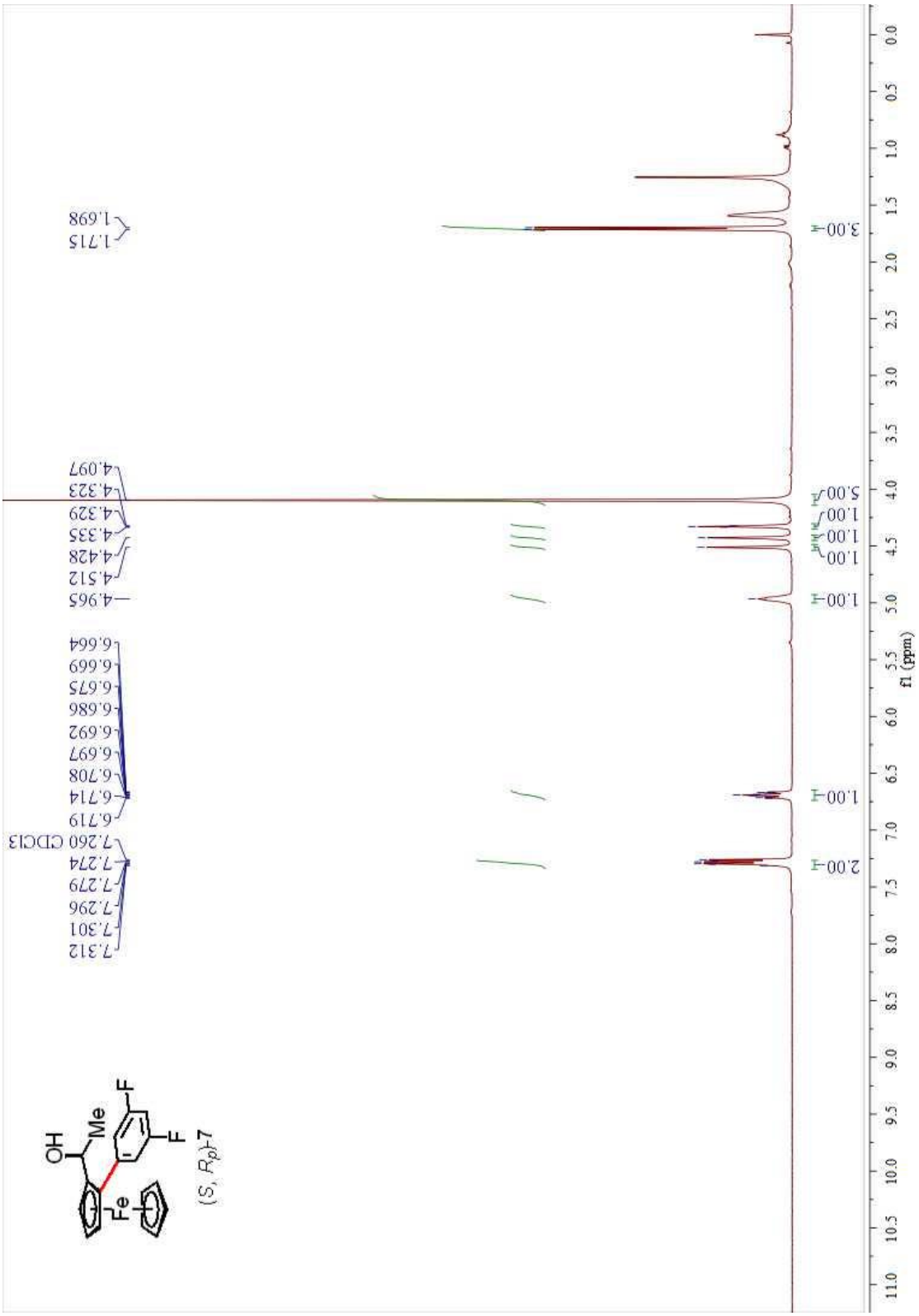

$^{13}$C NMR Spectra of Compound ($R_p$)-[D]-**1a**



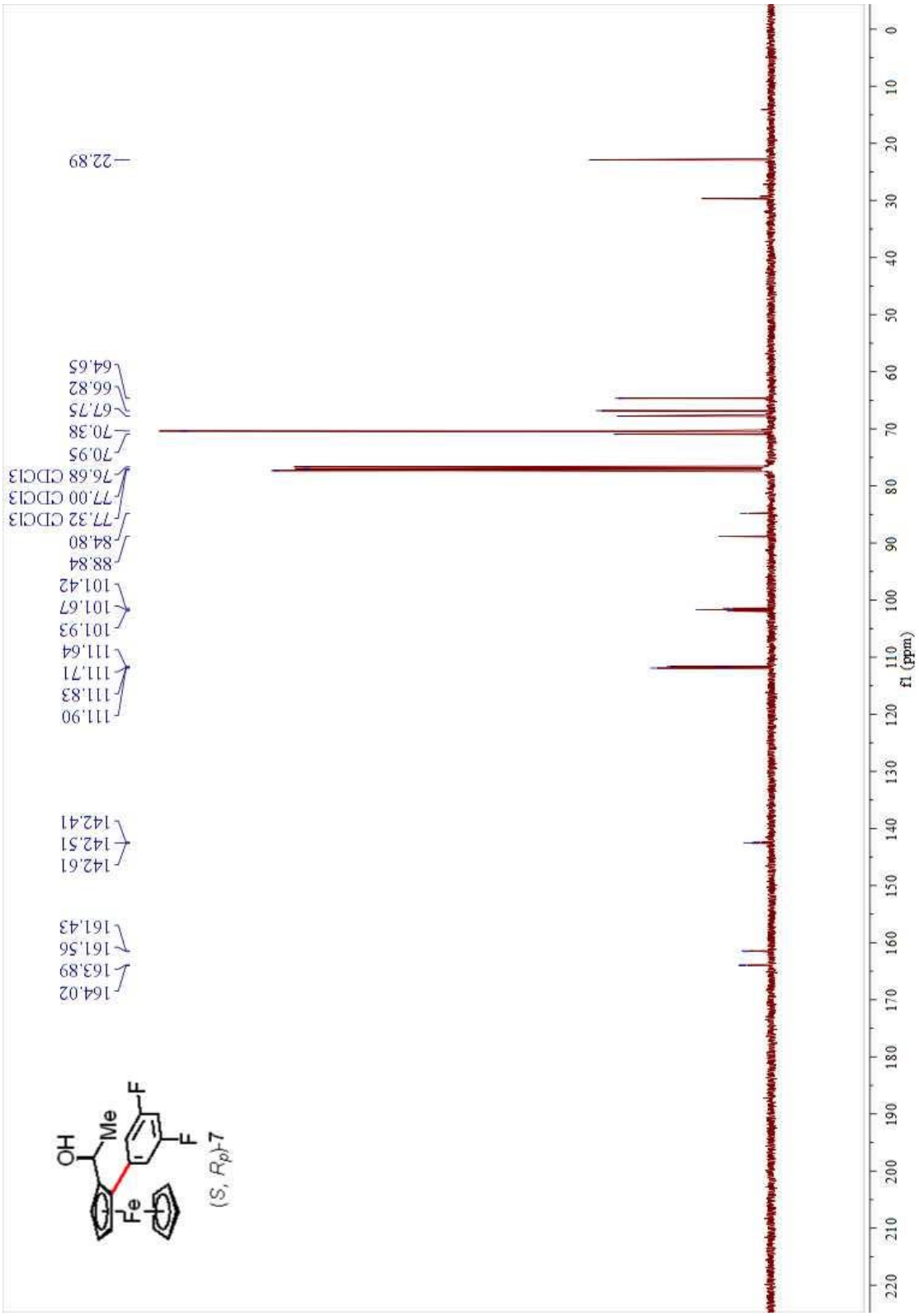

$^1$H NMR Spectra of Compound (*R*, $R_p$)-**7**



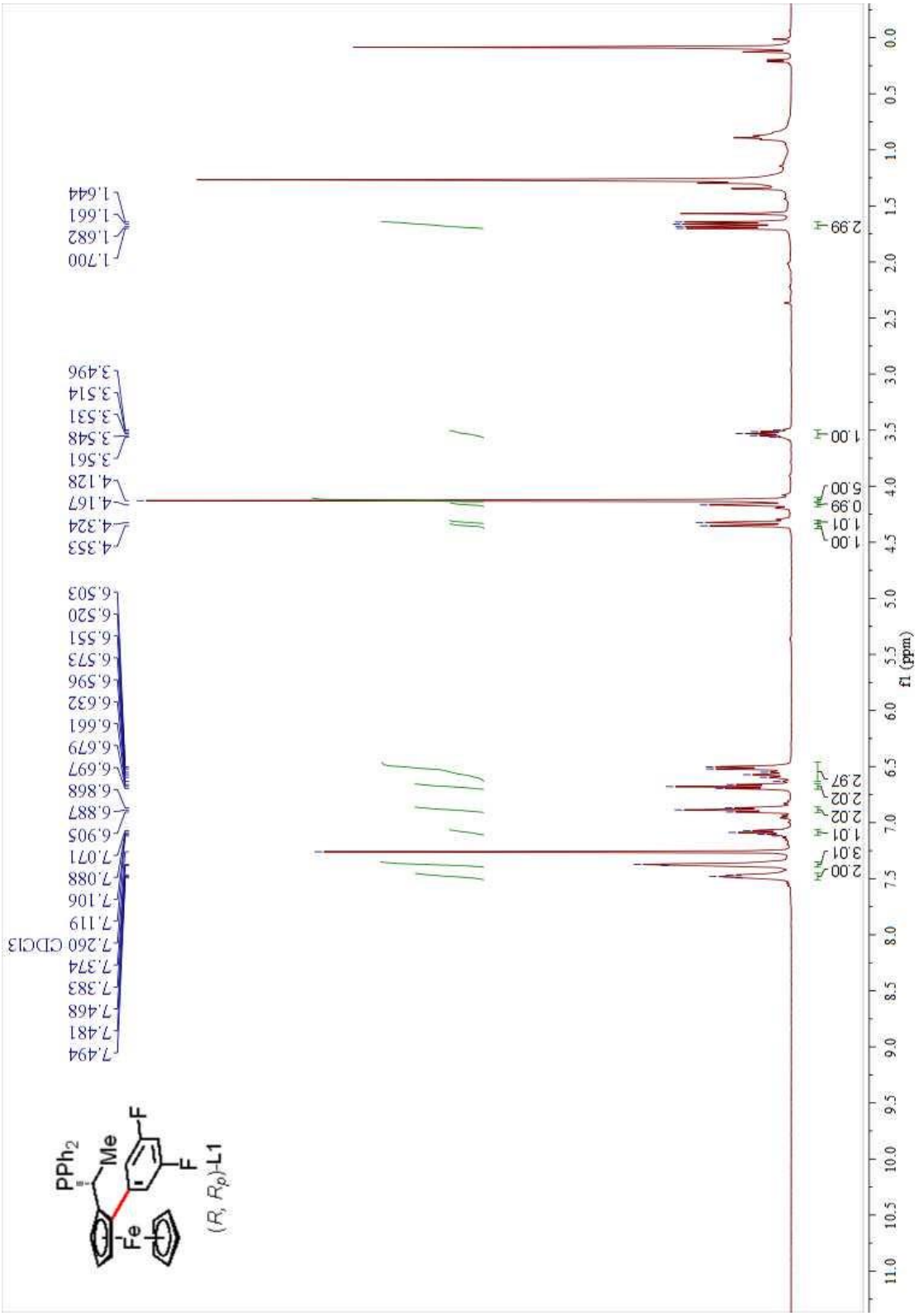

$^{13}$C NMR Spectra of Compound (*R*, $R_p$)-**7**



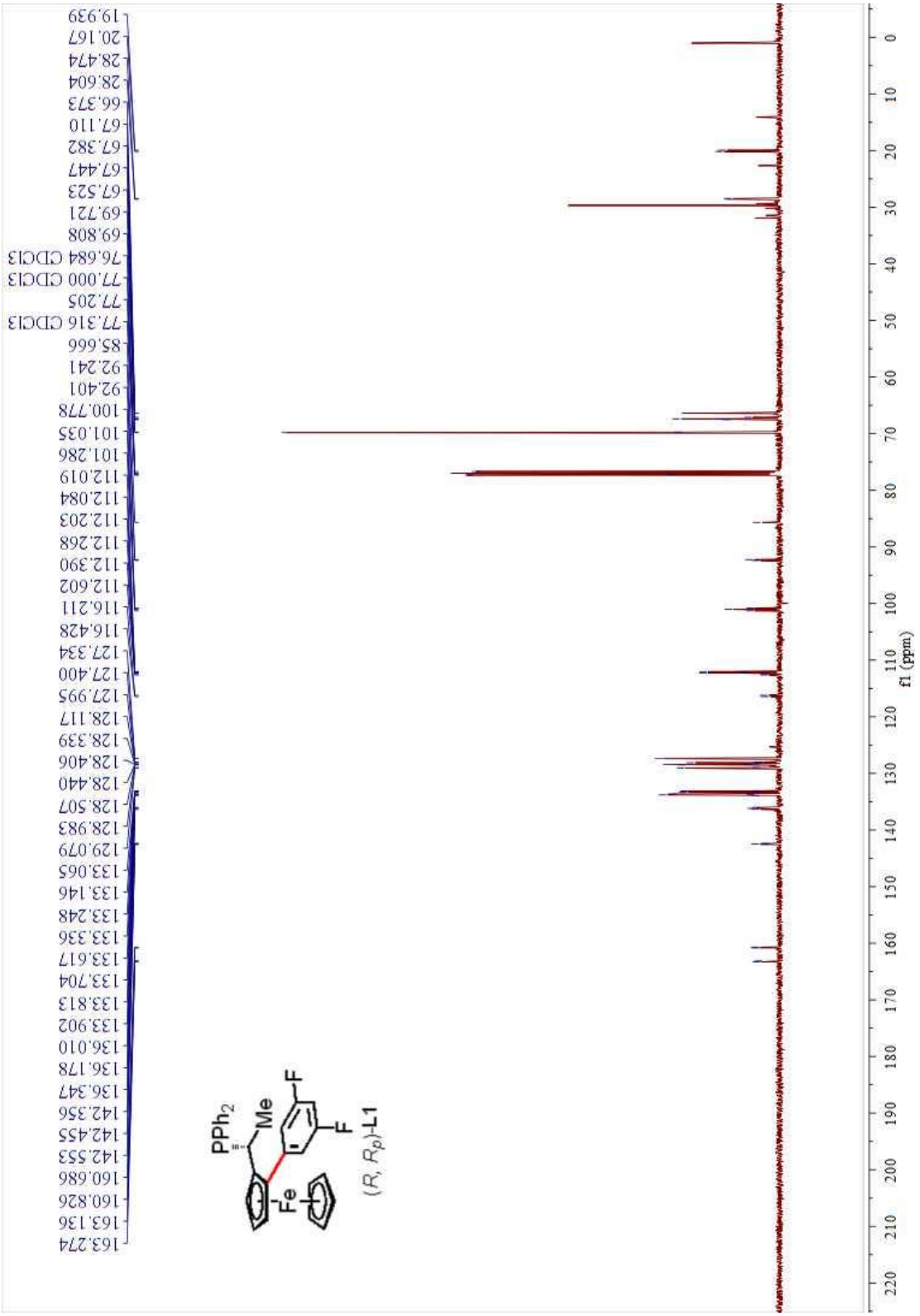

$^1$H NMR Spectra of Compound (*S*, $R_p$)-**7**



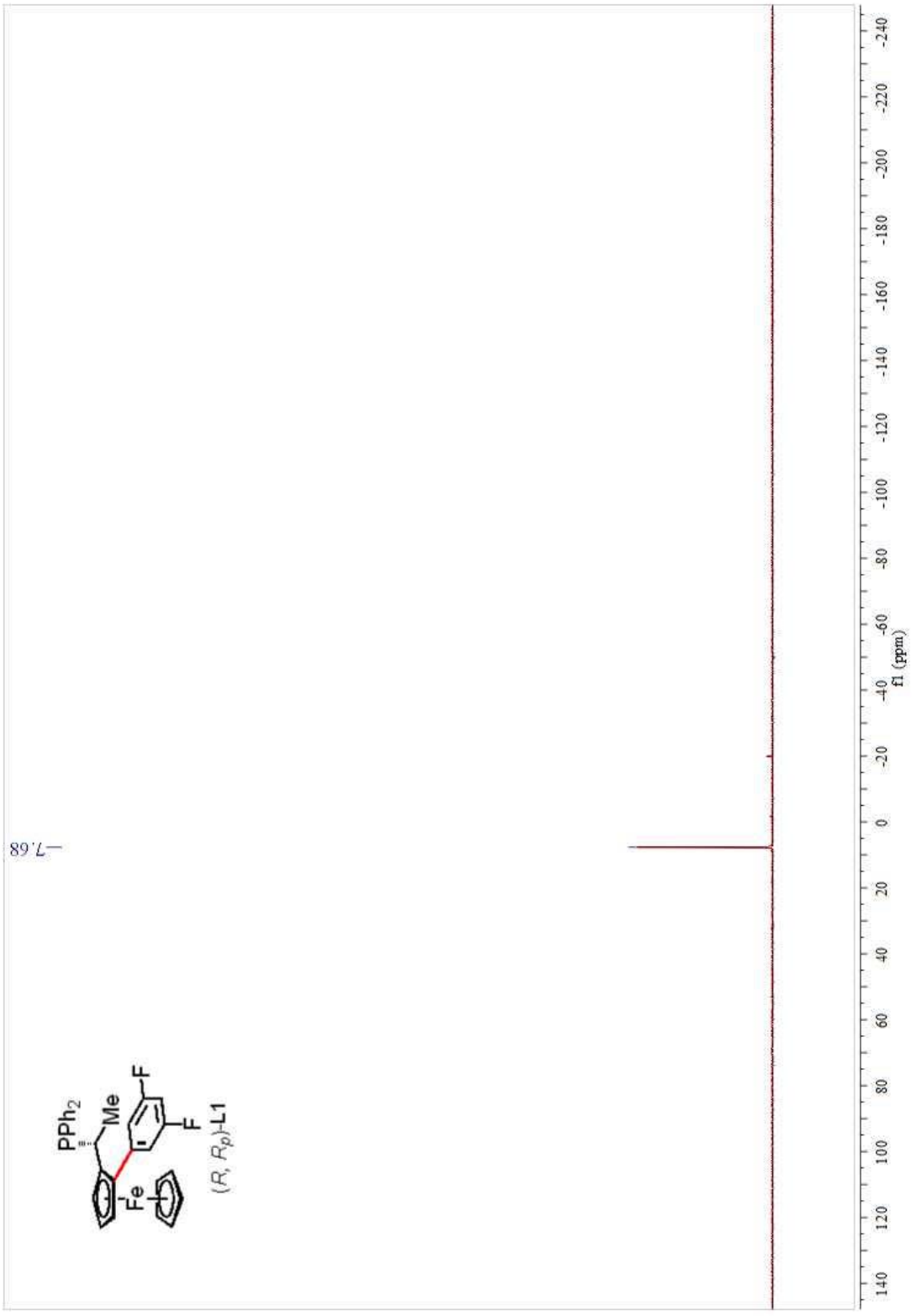

$^{13}$C NMR Spectra of Compound (*S*, $R_p$)-**7**



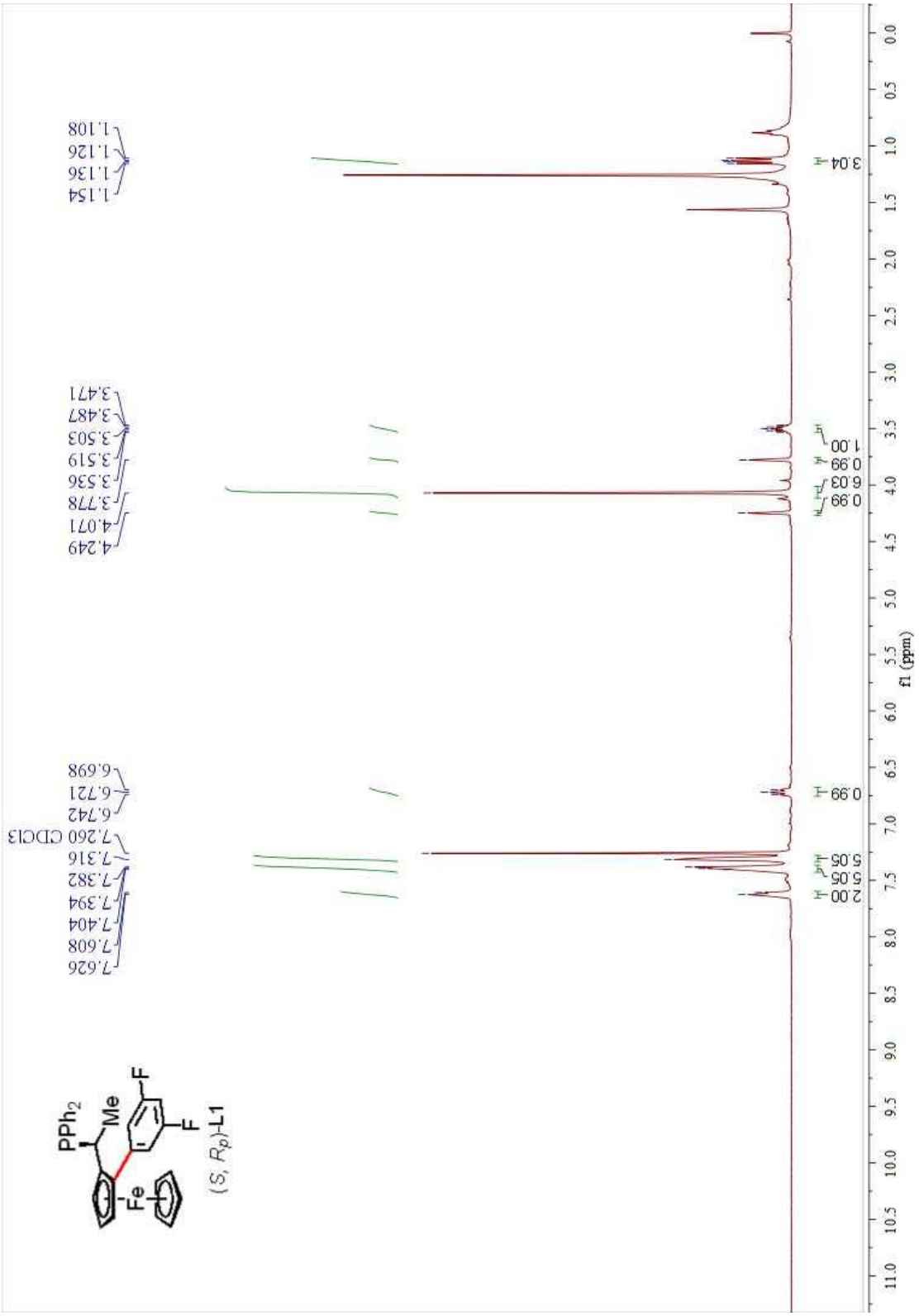

$^1$H NMR Spectra of Compound ($R$, $R_p$)-**L1**



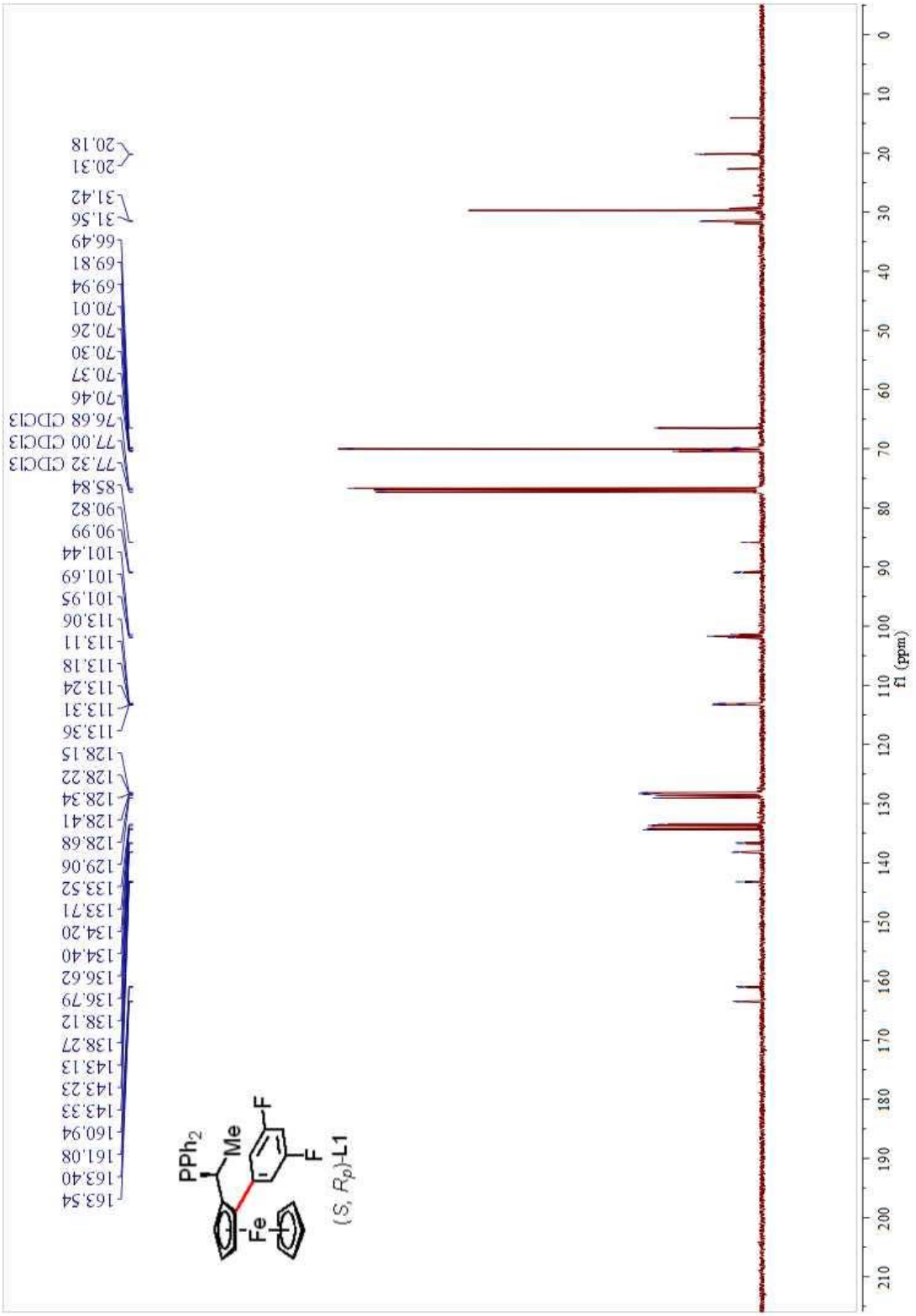

$^{13}$C NMR Spectra of Compound (*R*, $R_p$)-**L1**



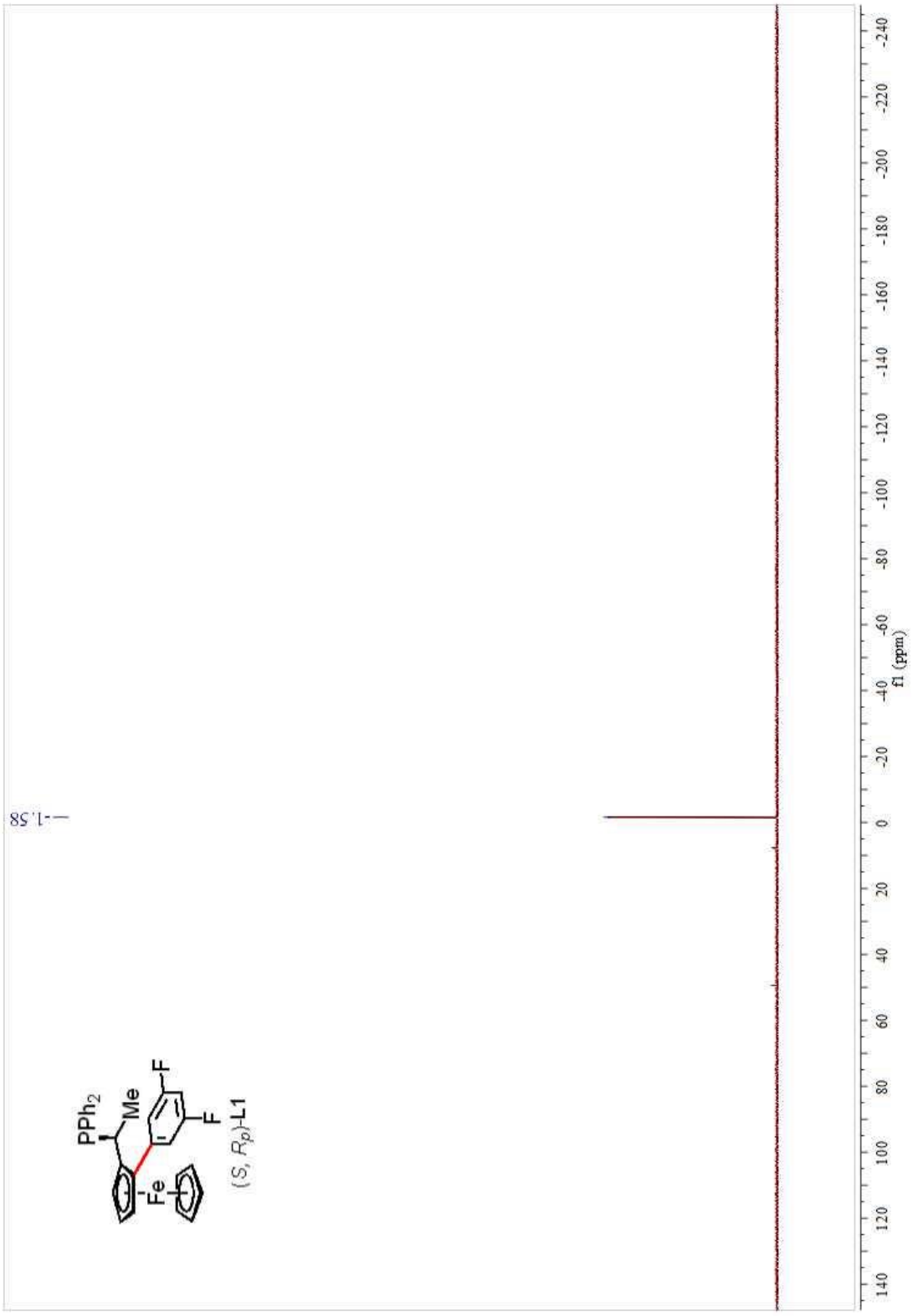

$^{31}$P NMR Spectra of Compound (*R*, $R_p$)-**L1**



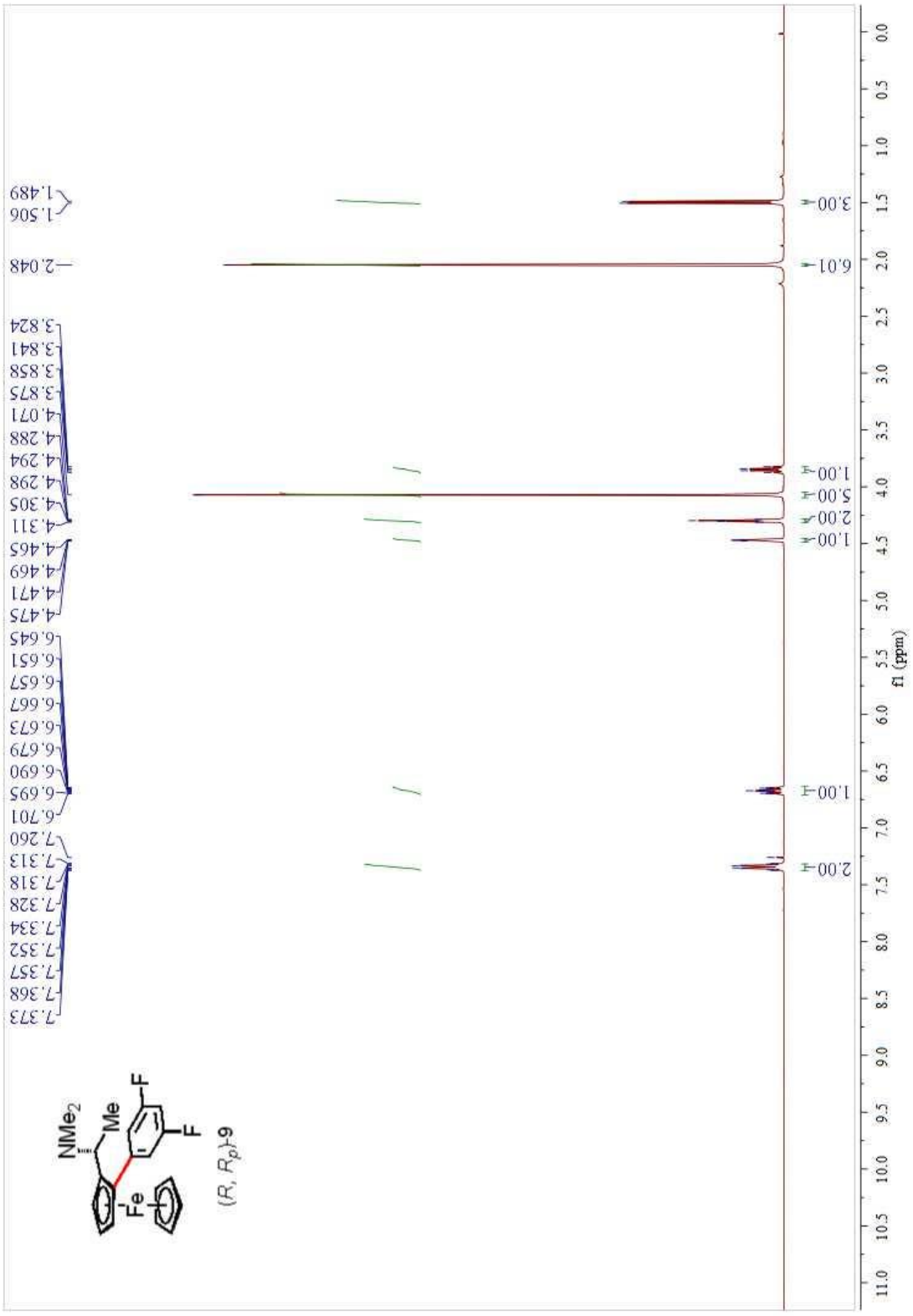

$^1$H NMR Spectra of Compound (*S*, $R_p$)-**L1**



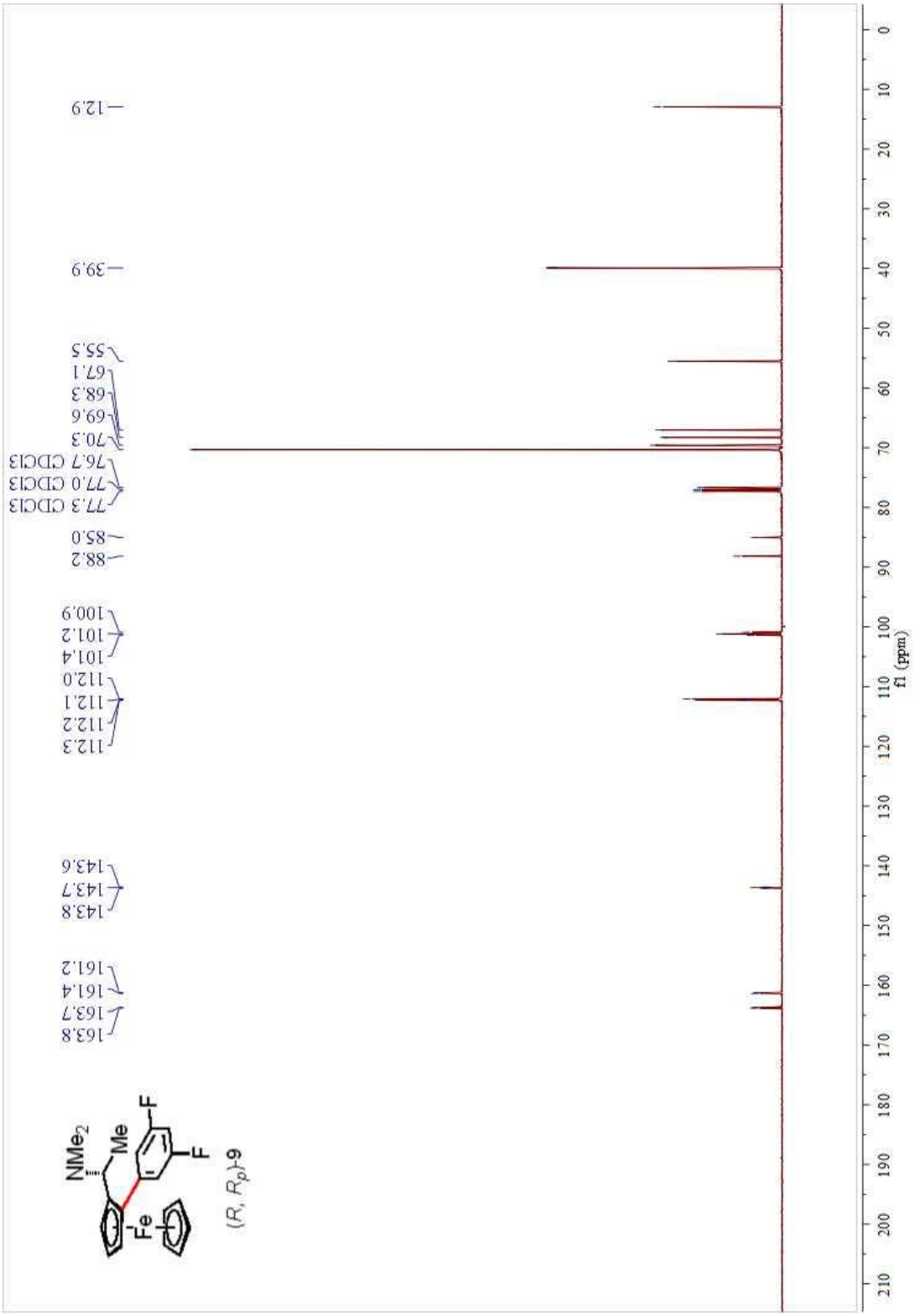

$^{13}$C NMR Spectra of Compound (*S*, $R_p$)-**L1**



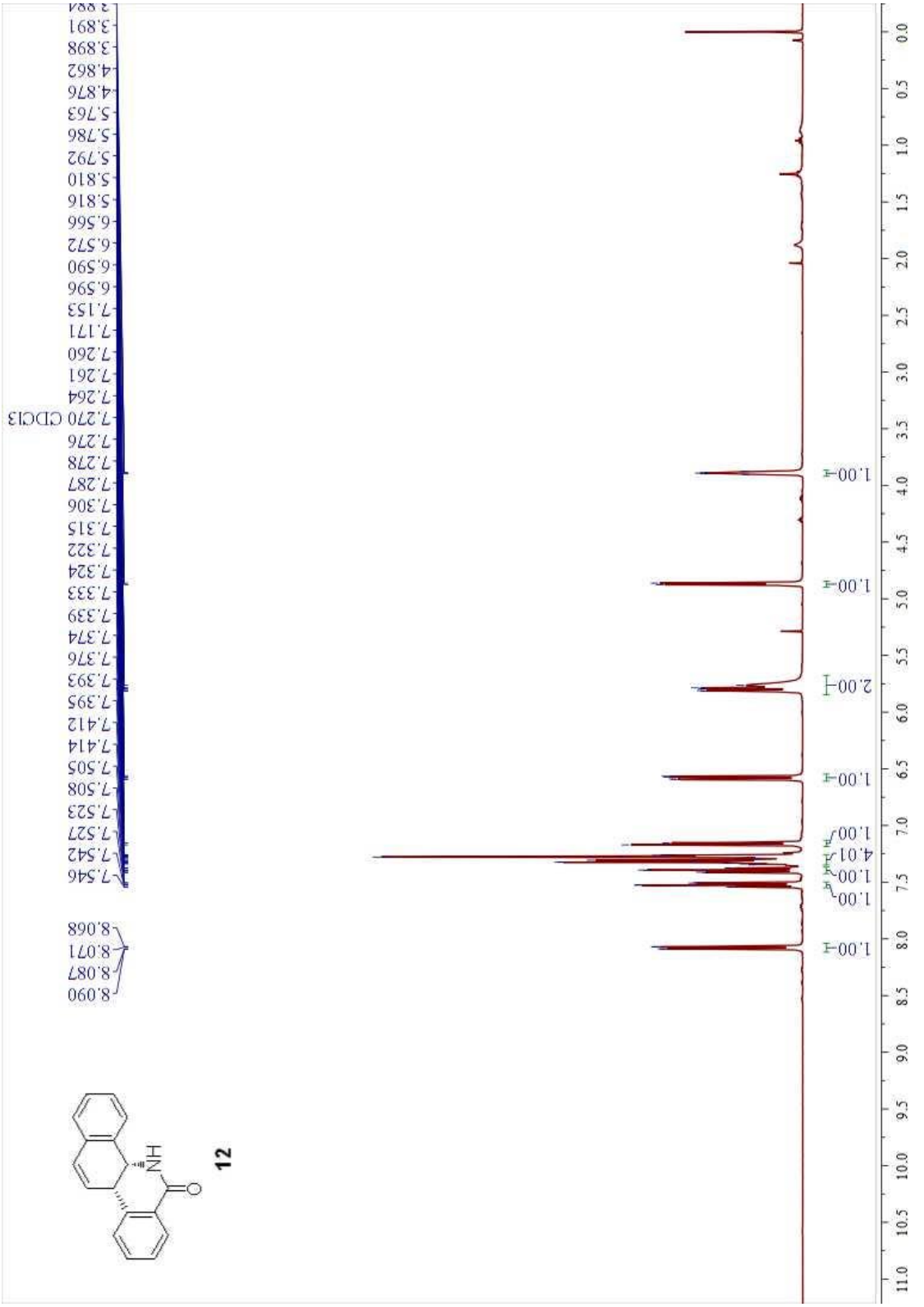

$^{31}$P NMR Spectra of Compound (*S*, $R_p$)-**L1**



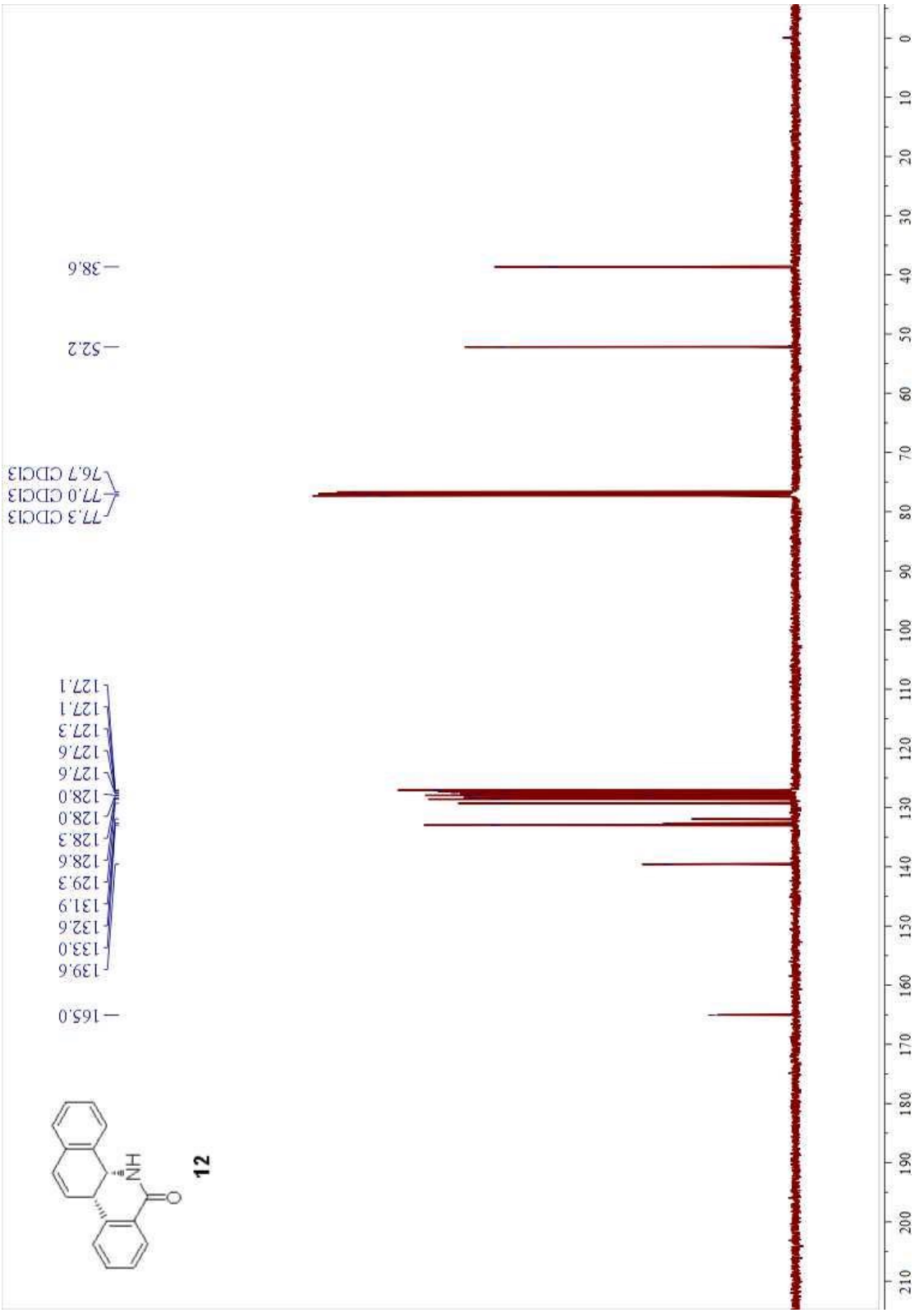

$^1$H NMR Spectra of Compound ($R$, $R_p$)-**9**




$^{13}$C NMR Spectra of Compound (*R*, $R_p$)-**9**

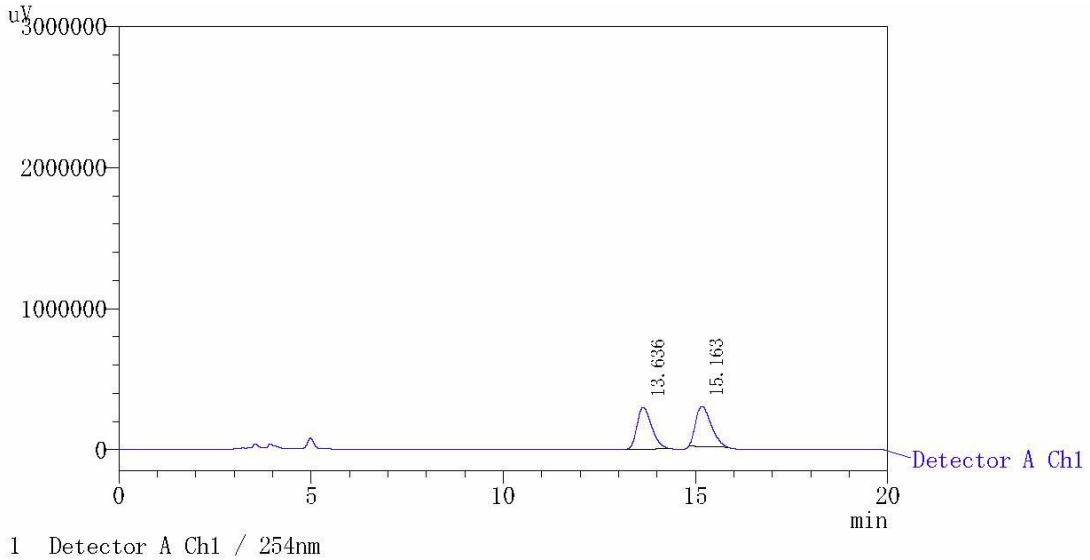



$^{1}$H NMR Spectra of Compound **12**




$^{13}$C NMR Spectra of Compound **12**

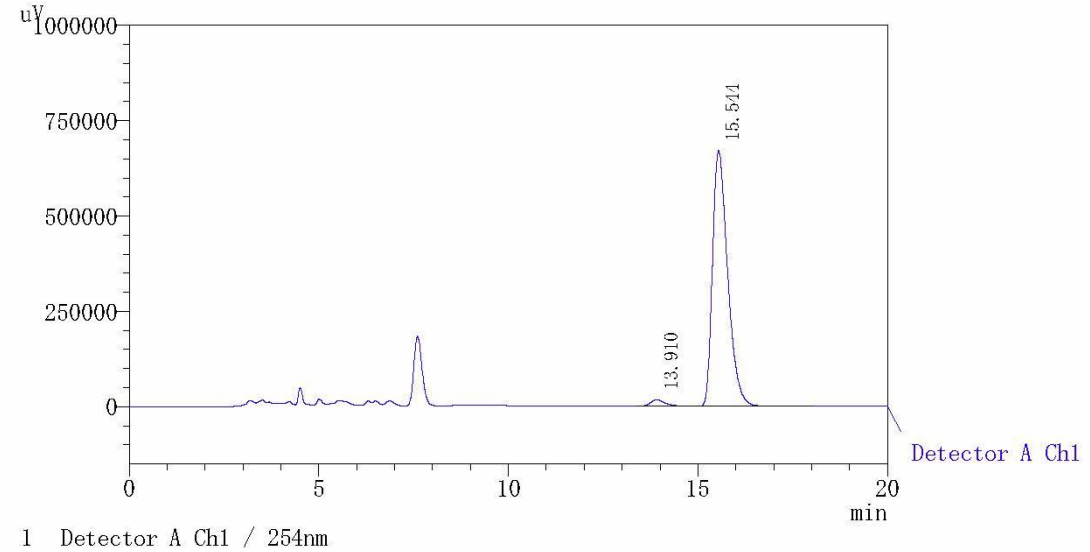
## 10. HPLC Charts of C–H Arylation Products




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

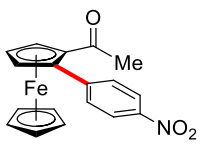
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 13.636 | 7837295 | 296849 | 49.352 |
| 2 | 15.163 | 8043043 | 286053 | 50.648 |



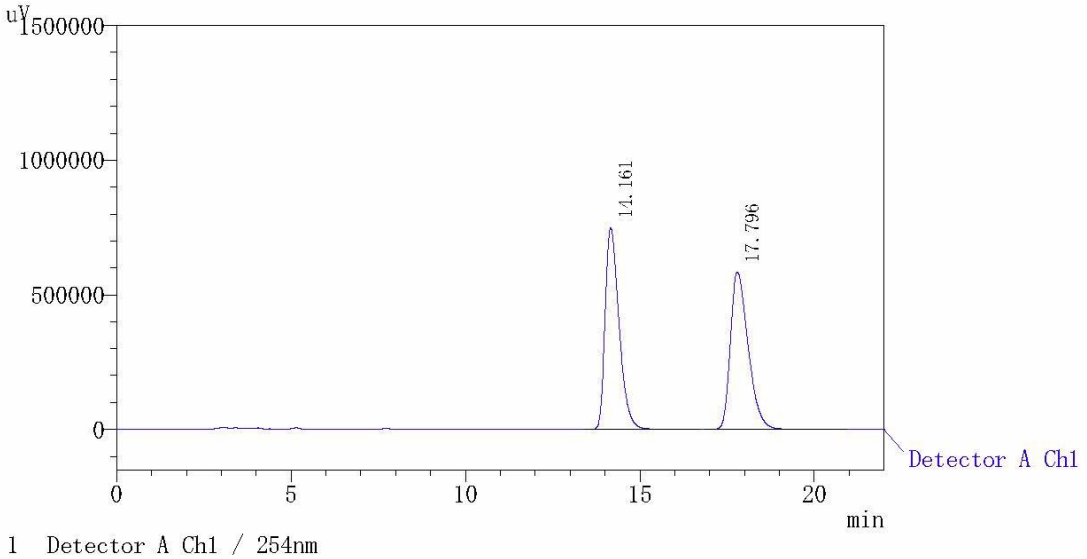

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 13.910 | 450003 | 17090 | 2.355 |
| 2 | 15.544 | 18660146 | 670875 | 97.645 |



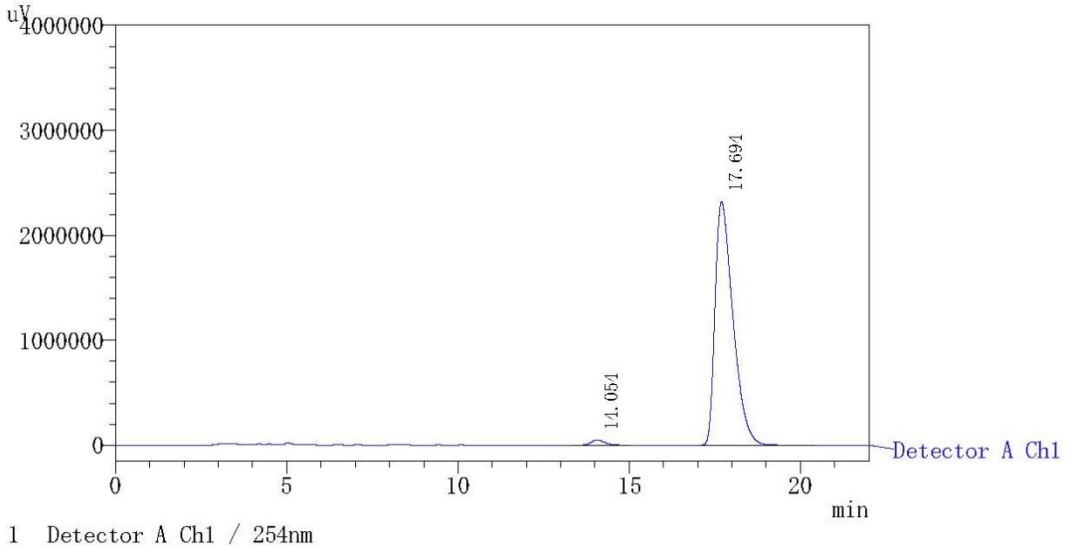

(**3a**), 95% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

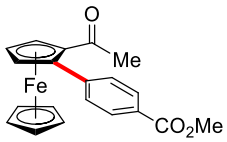
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 14.161 | 20660835 | 749150 | 50.049 |
| 2 | 17.796 | 20620711 | 584921 | 49.951 |



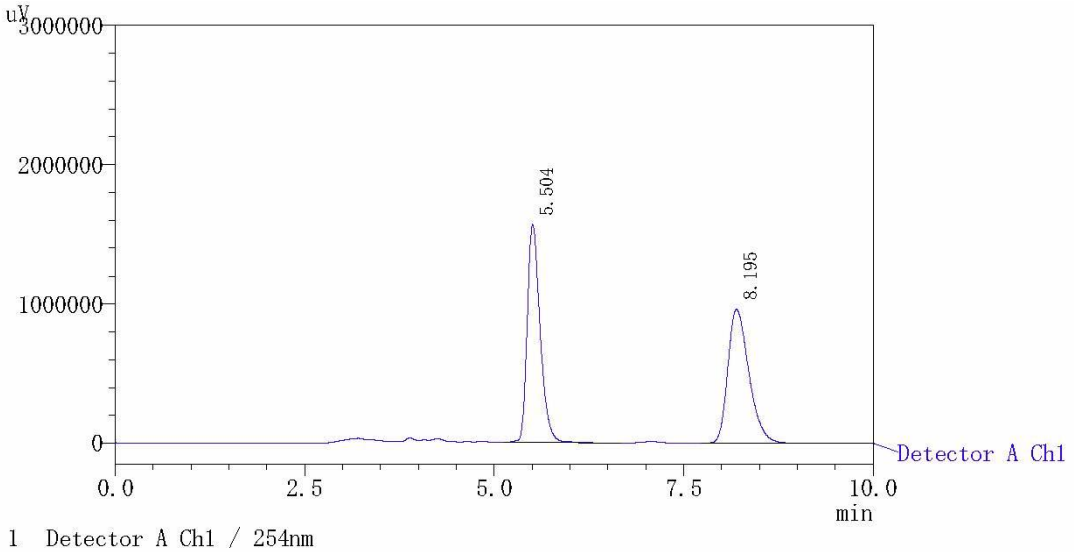

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 14.054 | 1374057 | 50008 | 1.602 |
| 2 | 17.694 | 84418807 | 2322108 | 98.398 |



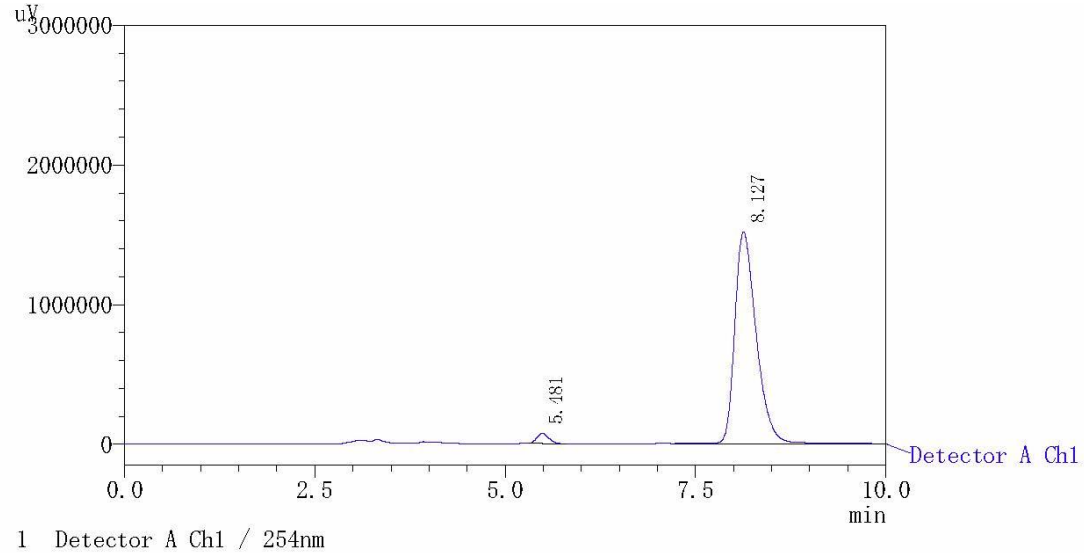

(**3b**), 97% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

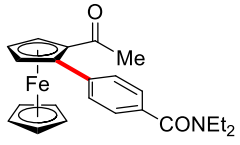
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 5.504 | 18679375 | 1570559 | 50.134 |
| 2 | 8.195 | 18579831 | 962949 | 49.866 |



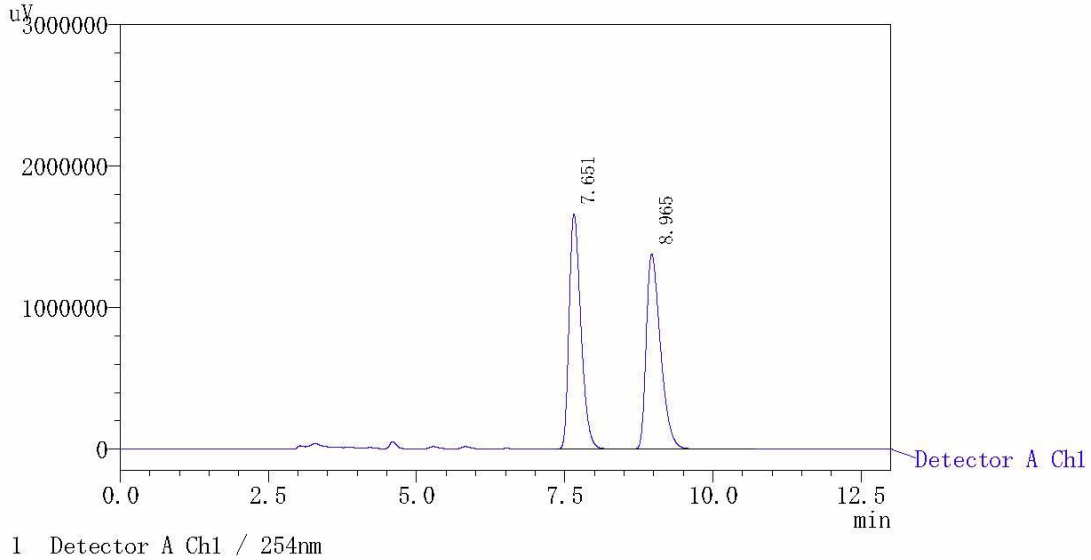

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 5.481 | 789492 | 71878 | 2.569 |
| 2 | 8.127 | 29947349 | 1515978 | 97.431 |



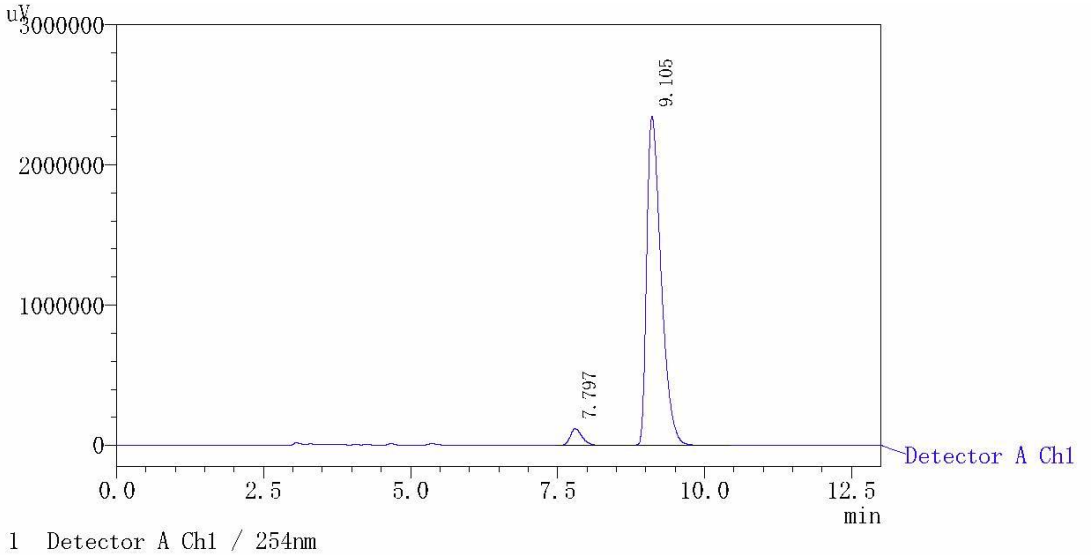

(**3c**), 95% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

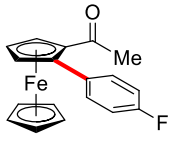
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.651 | 22921583 | 1661592 | 49.965 |
| 2 | 8.965 | 22954114 | 1377683 | 50.035 |



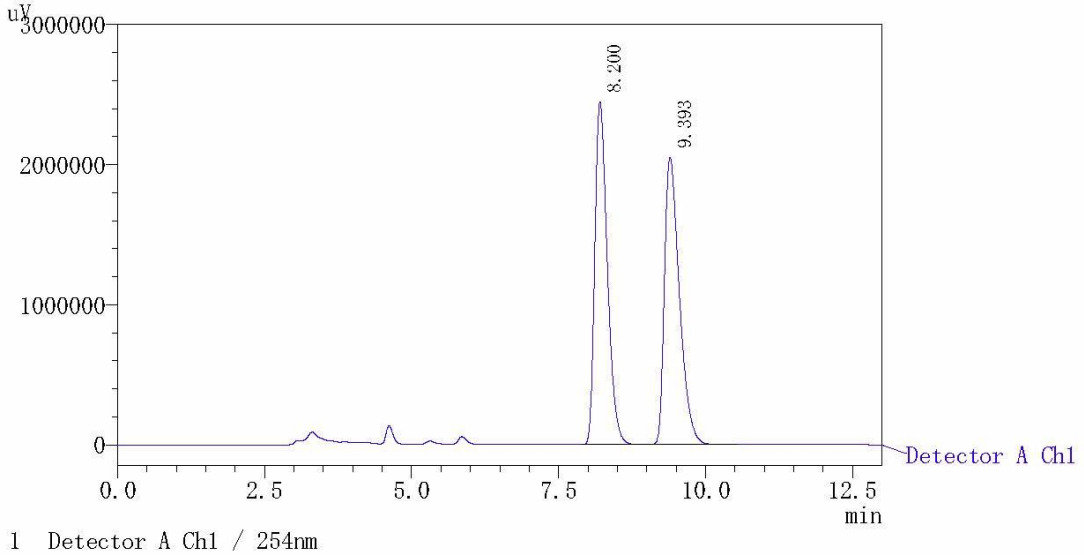

1 Detector A Ch1 / 254nm

Dctcctor A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.797 | 1624387 | 117479 | 3.934 |
| 2 | 9.105 | 39666406 | 2347118 | 96.066 |



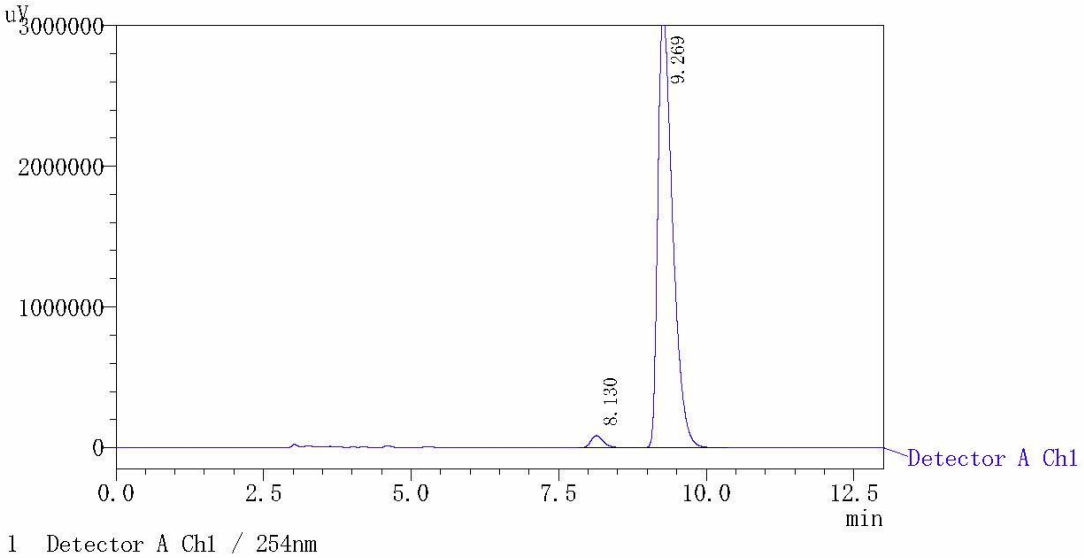

(**3d**), 92% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

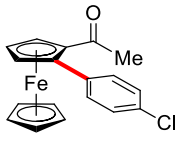
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.200 | 36135816 | 2444965 | 49.953 |
| 2 | 9.393 | 36203774 | 2050245 | 50.047 |



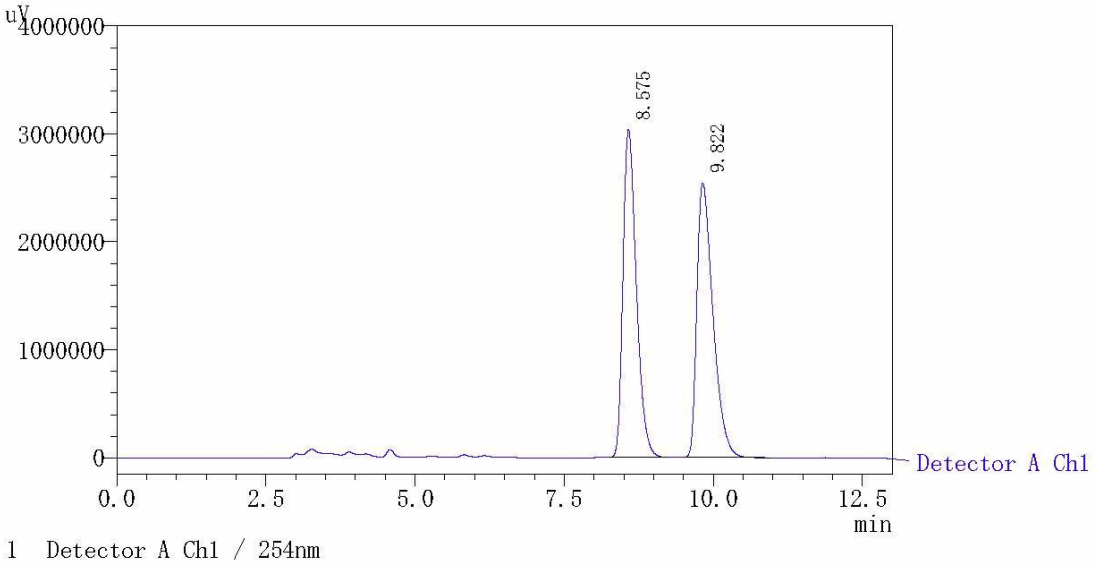

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.130 | 1219763 | 85558 | 2.220 |
| 2 | 9.269 | 53712296 | 3082561 | 97.780 |



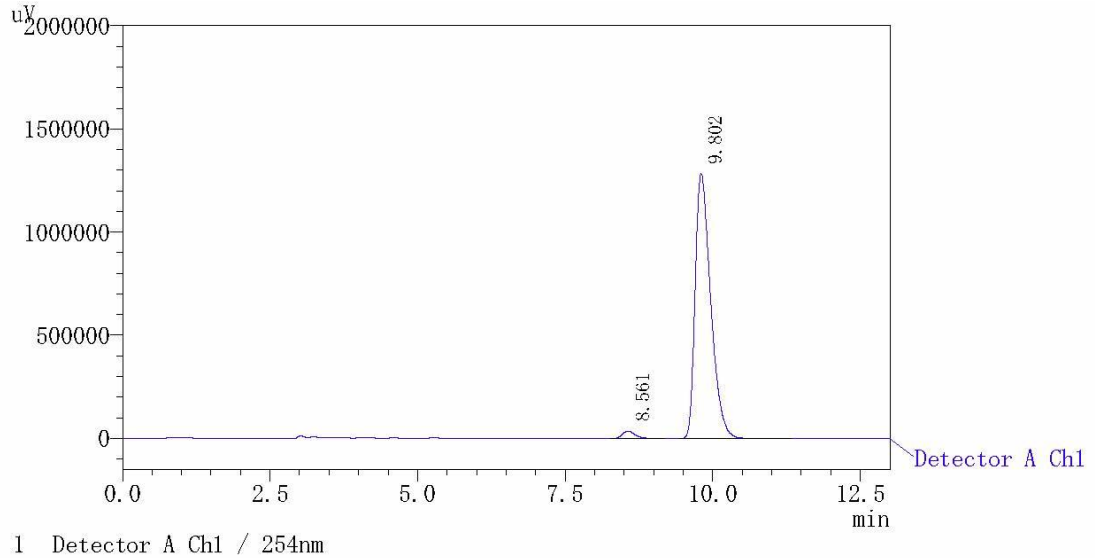

(**3e**), 96% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

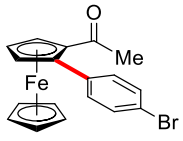
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.575 | 47366426 | 3036567 | 49.942 |
| 2 | 9.822 | 47476343 | 2541644 | 50.058 |



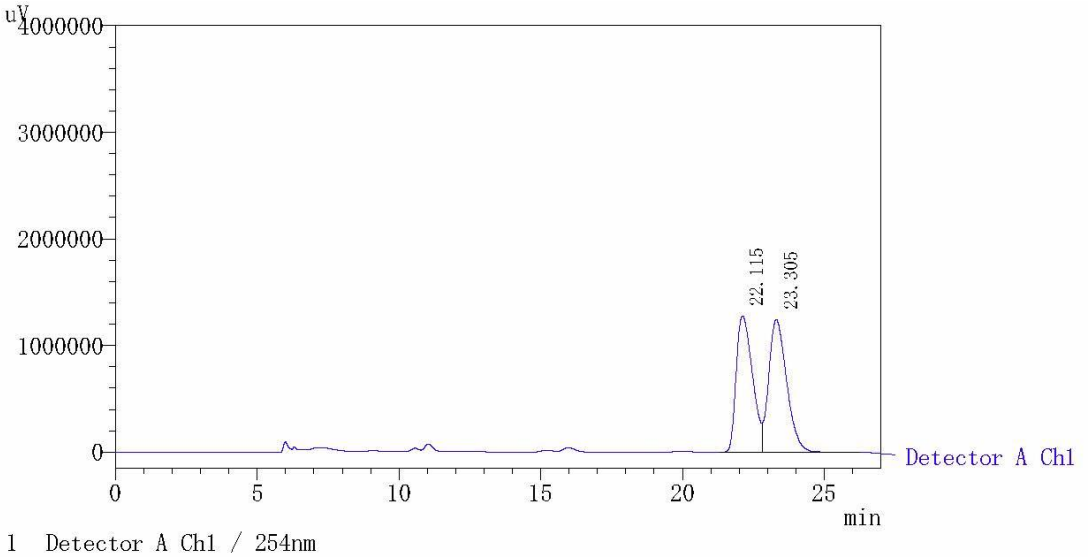

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.561 | 524258 | 34543 | 2.194 |
| 2 | 9.802 | 23365468 | 1282200 | 97.806 |



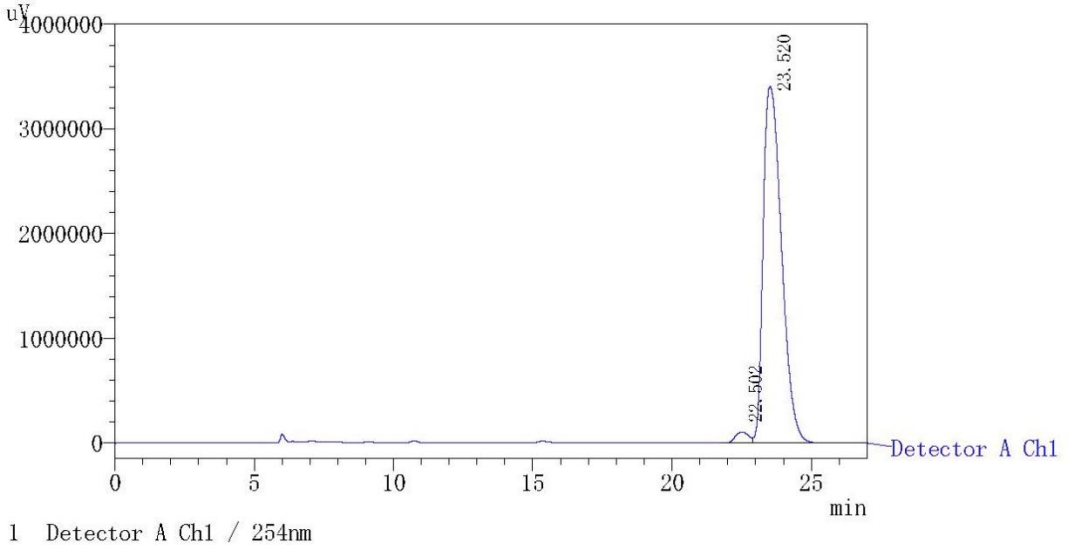

(**3f**), 96% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

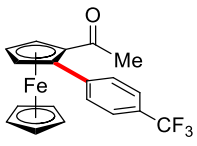
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 22.115 | 50856941 | 1279168 | 48.044 |
| 2 | 23.305 | 54997449 | 1243339 | 51.956 |



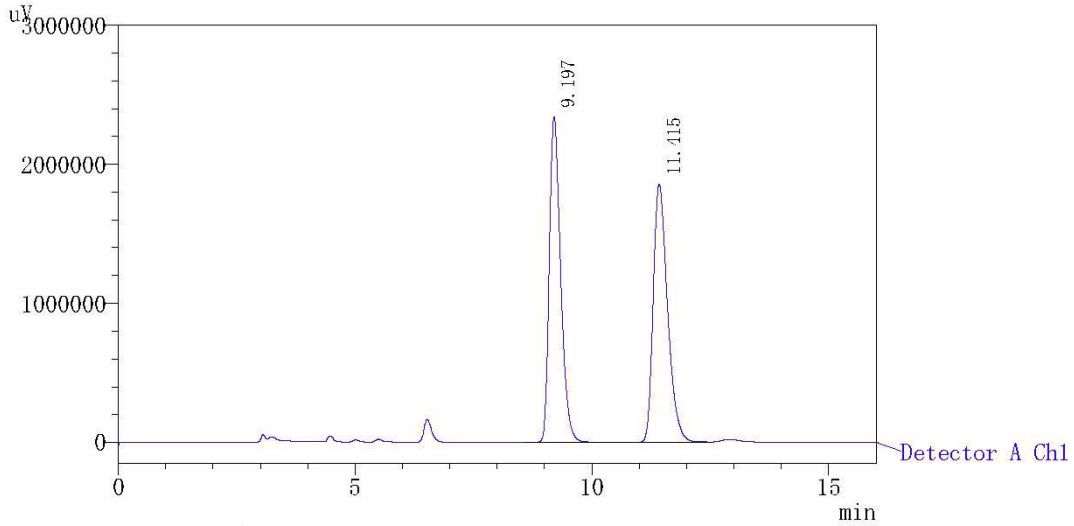

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 22.502 | 3619859 | 107658 | 2.257 |
| 2 | 23.520 | 156760557 | 3407257 | 97.743 |

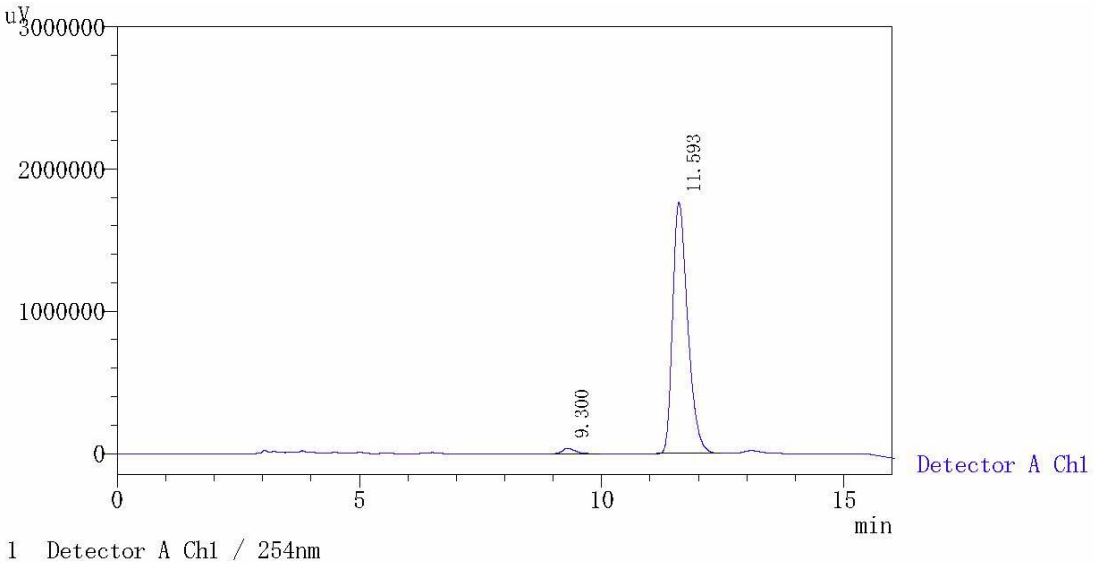



(**3g**), 96% ee



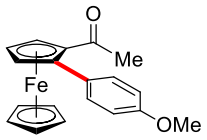

1 Detector A Ch1 / 254nm

| Dctcctor A Ch1 254nm | | | | |
|---|---|---|---|---|
| Peak# | RetTime | Area | Height | Area % |
| 1 | 9.197 | 39049646 | 2339641 | 50.002 |
| 2 | 11.415 | 39046617 | 1853225 | 49.998 |

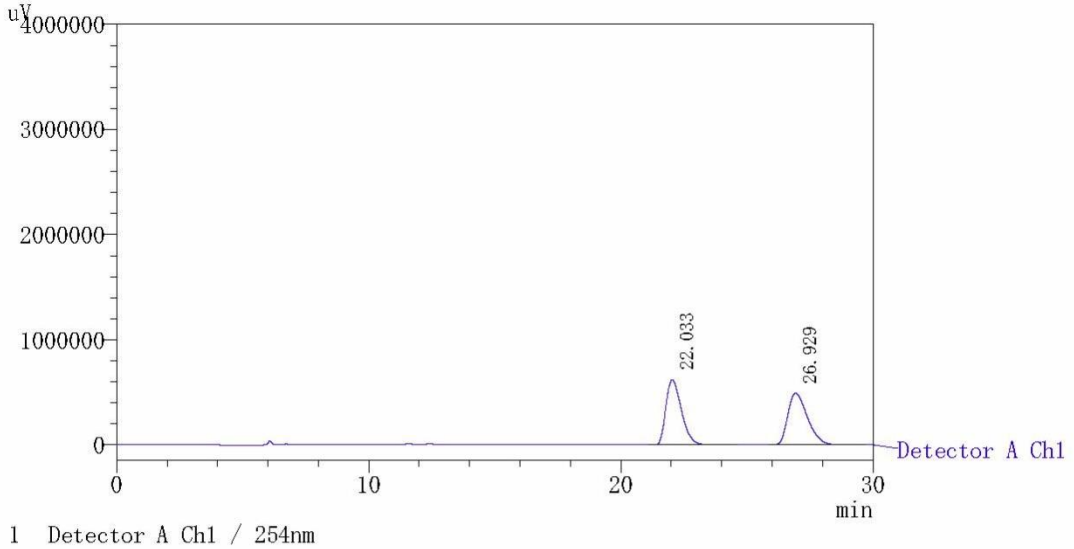



1 Detector A Ch1 / 254nm

| Detector A Ch1 254nm | | | | |
|---|---|---|---|---|
| Peak# | RetTime | Area | Height | Area % |
| 1 | 9.300 | 628093 | 37158 | 1.630 |
| 2 | 11.593 | 37903375 | 1765761 | 98.370 |



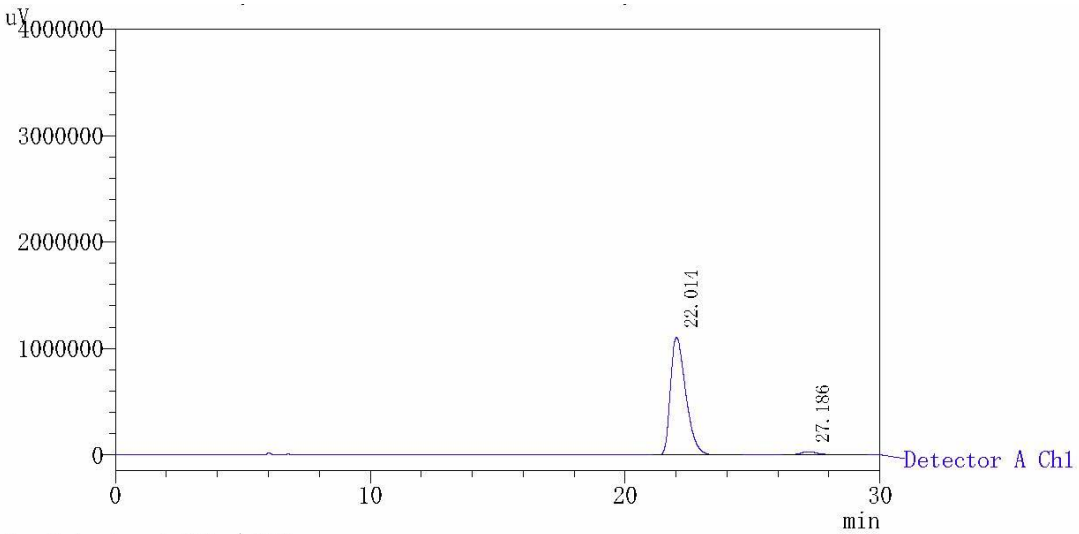

(**3h**), 96.7% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

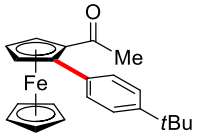
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 22.033 | 26589045 | 620273 | 49.909 |
| 2 | 26.929 | 26685702 | 491542 | 50.091 |



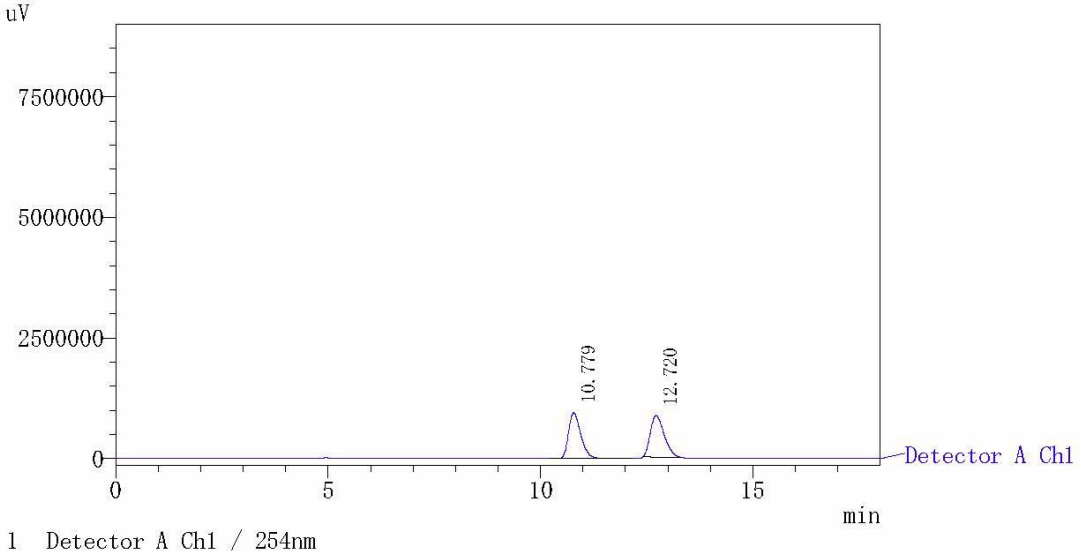

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 22.014 | 46064047 | 1103266 | 97.073 |
| 2 | 27.186 | 1388826 | 25737 | 2.927 |



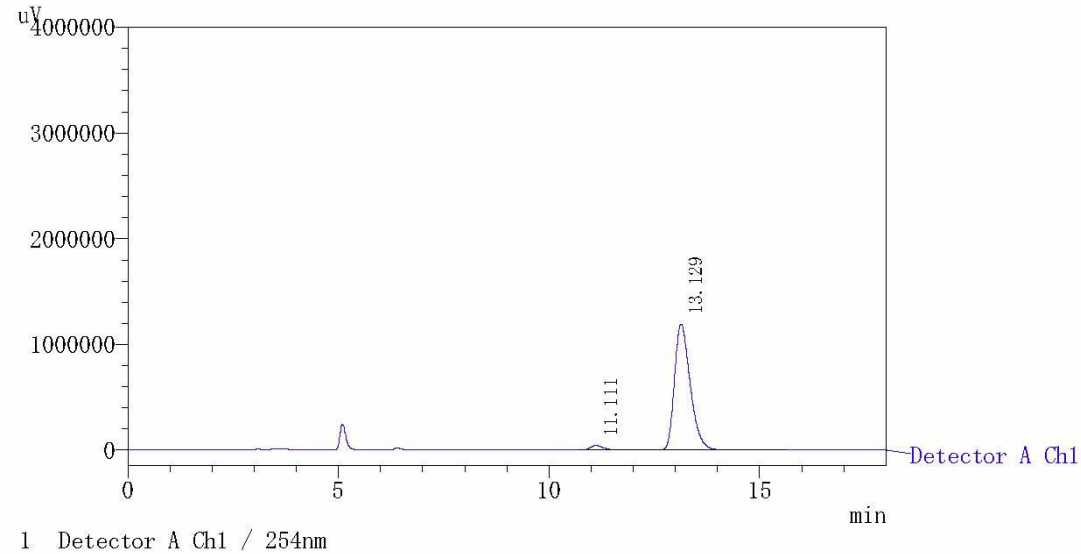

(**3i**), 94% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

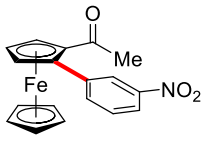
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.779 | 18967462 | 951729 | 49.584 |
| 2 | 12.720 | 19286057 | 858663 | 50.416 |



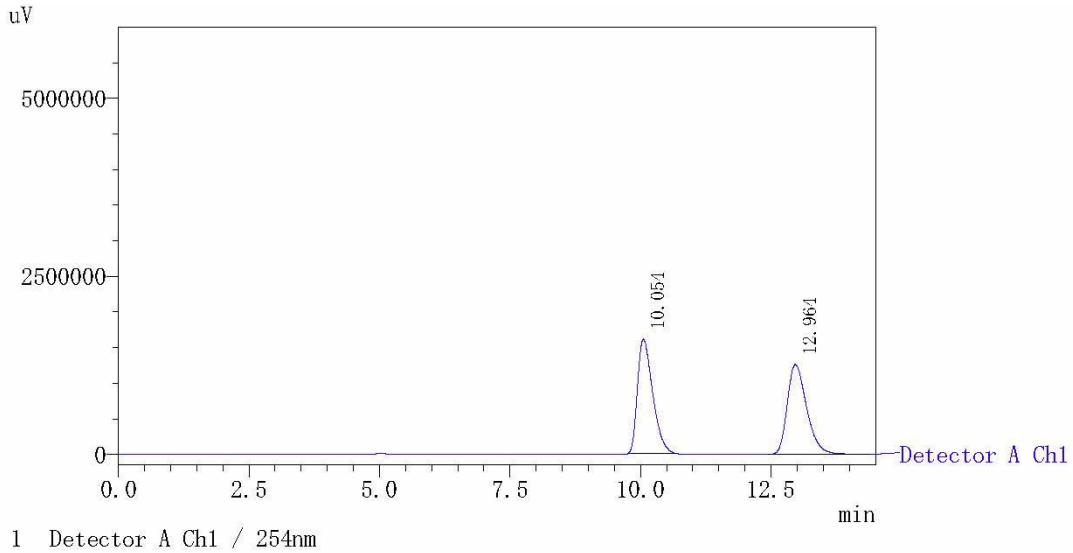

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.111 | 946636 | 43463 | 2.967 |
| 2 | 13.129 | 30954913 | 1192881 | 97.033 |



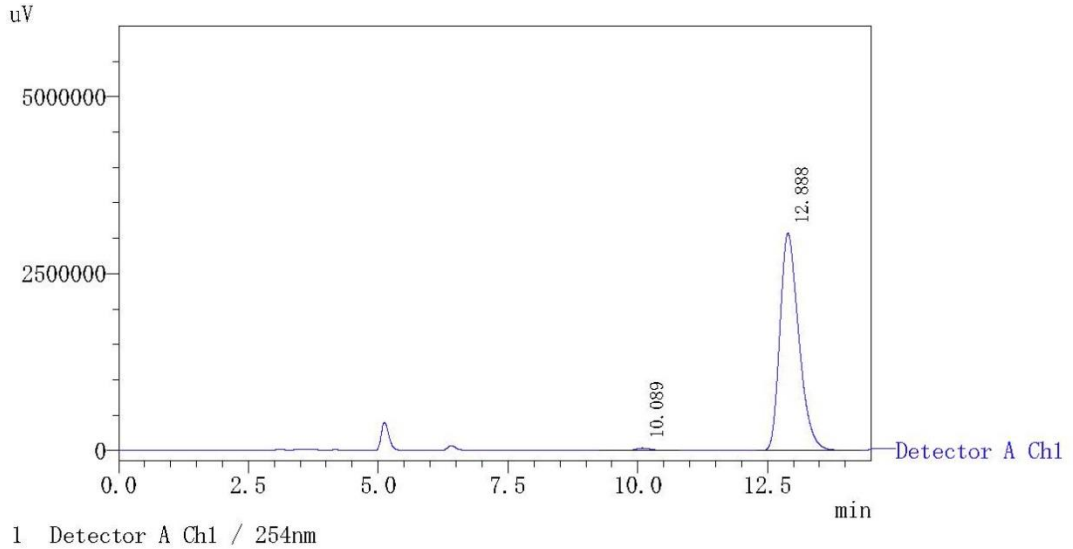

(**3j**), 94% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

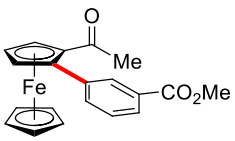
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.054 | 32297082 | 1608213 | 50.071 |
| 2 | 12.964 | 32205610 | 1259086 | 49.929 |



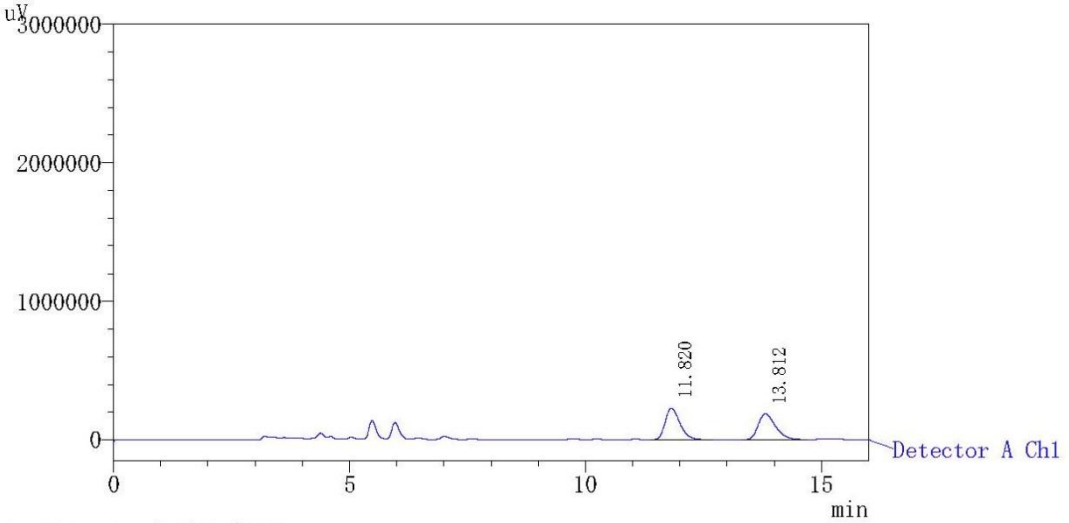

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.089 | 684573 | 34248 | 0.877 |
| 2 | 12.888 | 77331912 | 3072453 | 99.123 |



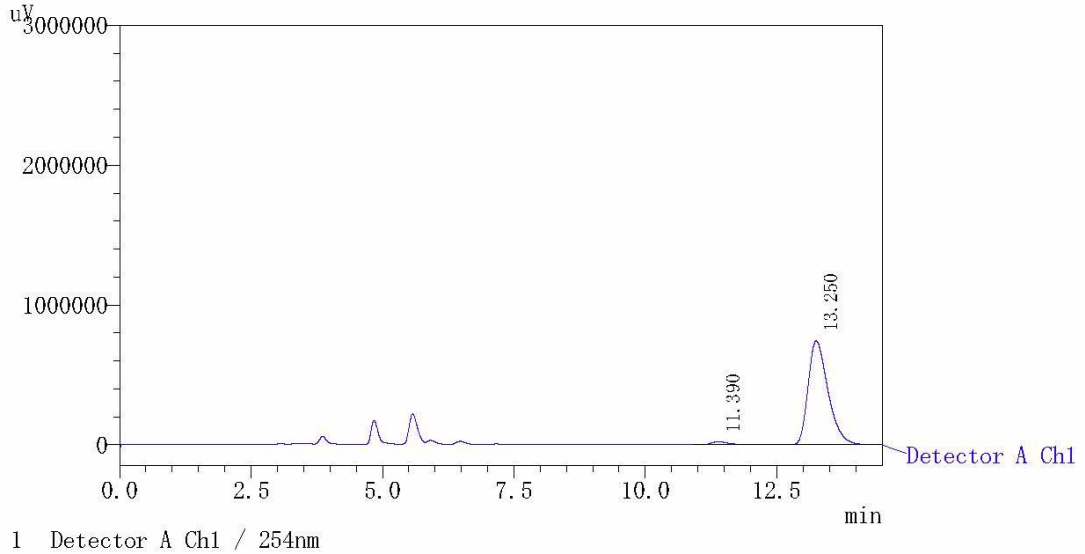

(**3k**), 98% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

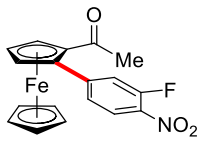
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.820 | 4888655 | 226494 | 50.817 |
| 2 | 13.812 | 4731520 | 185867 | 49.183 |



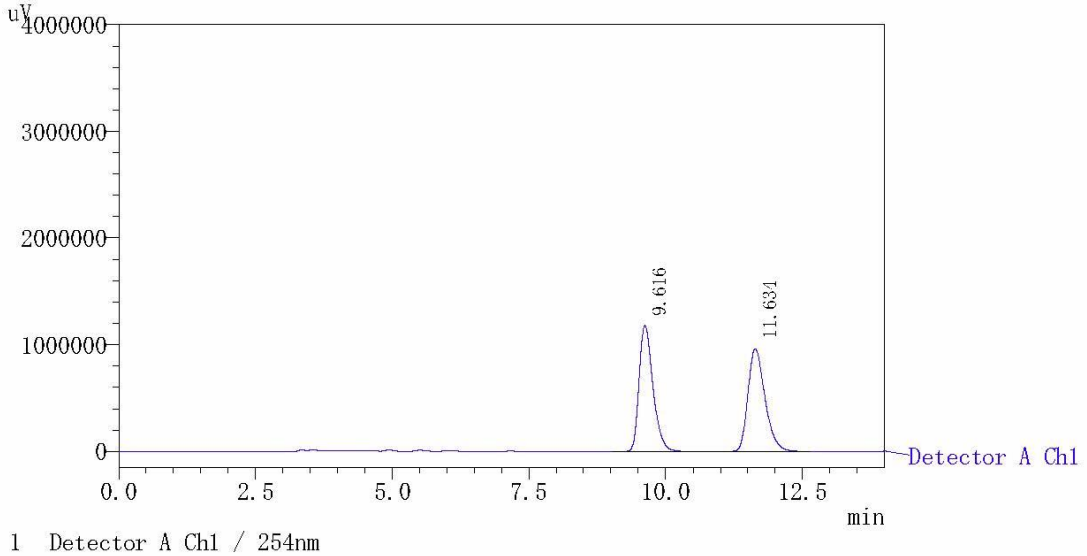

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.390 | 484433 | 21125 | 2.404 |
| 2 | 13.250 | 19668820 | 743134 | 97.596 |



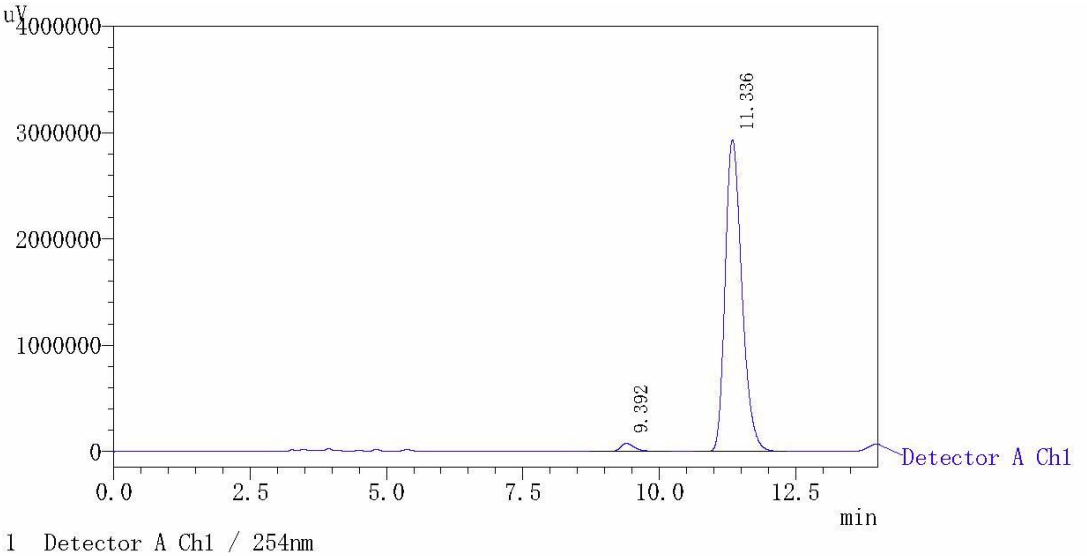

(**3l**), 95% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

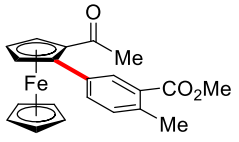
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.616 | 20755289 | 1181910 | 49.966 |
| 2 | 11.634 | 20783898 | 962254 | 50.034 |



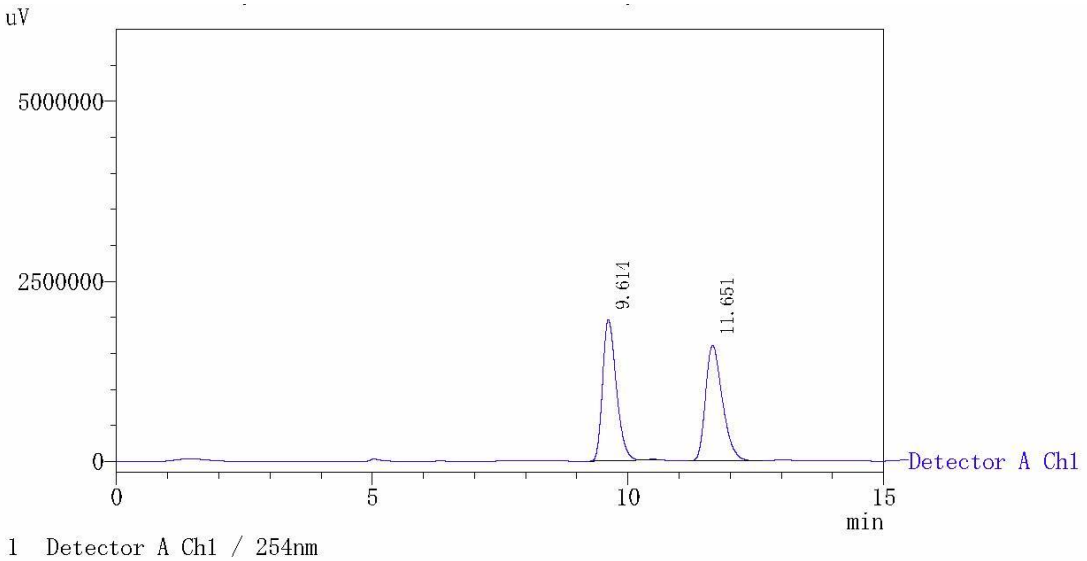

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.392 | 1370217 | 77401 | 2.151 |
| 2 | 11.336 | 62334730 | 2927466 | 97.849 |



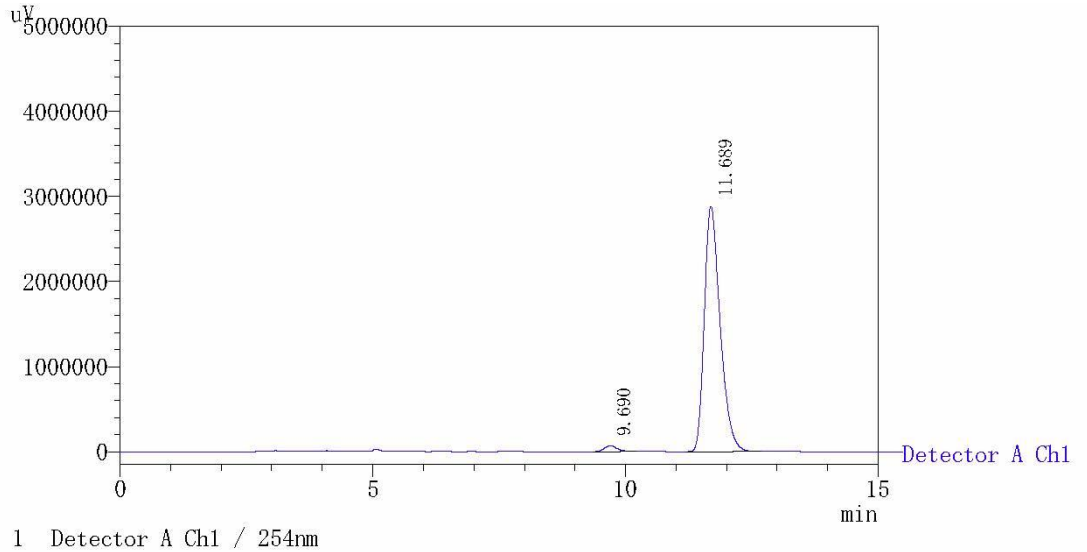

(**3m**), 96% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

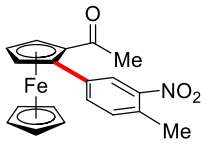
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.614 | 36593620 | 1961192 | 49.886 |
| 2 | 11.651 | 36761108 | 1602352 | 50.114 |



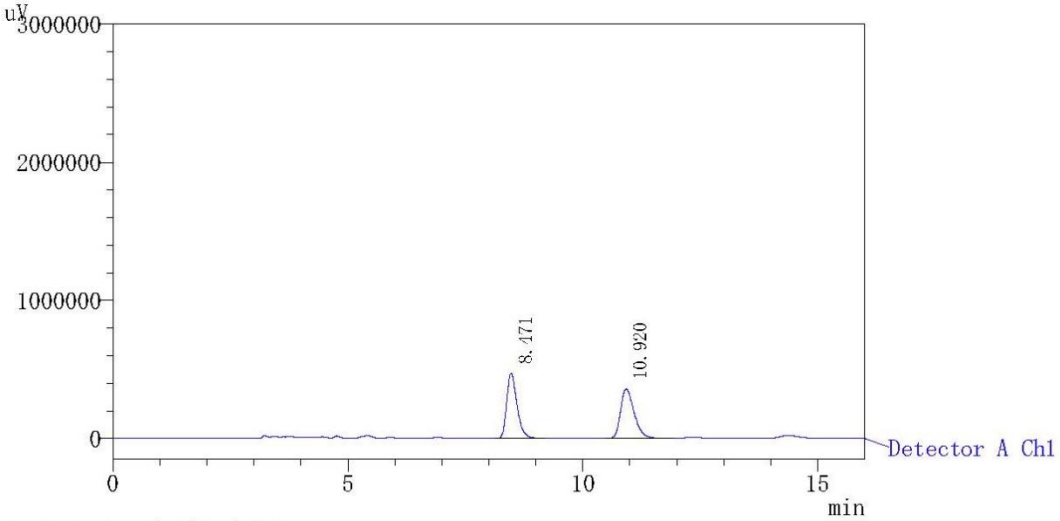

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.690 | 1214668 | 69412 | 1.899 |
| 2 | 11.689 | 62752613 | 2880946 | 98.101 |



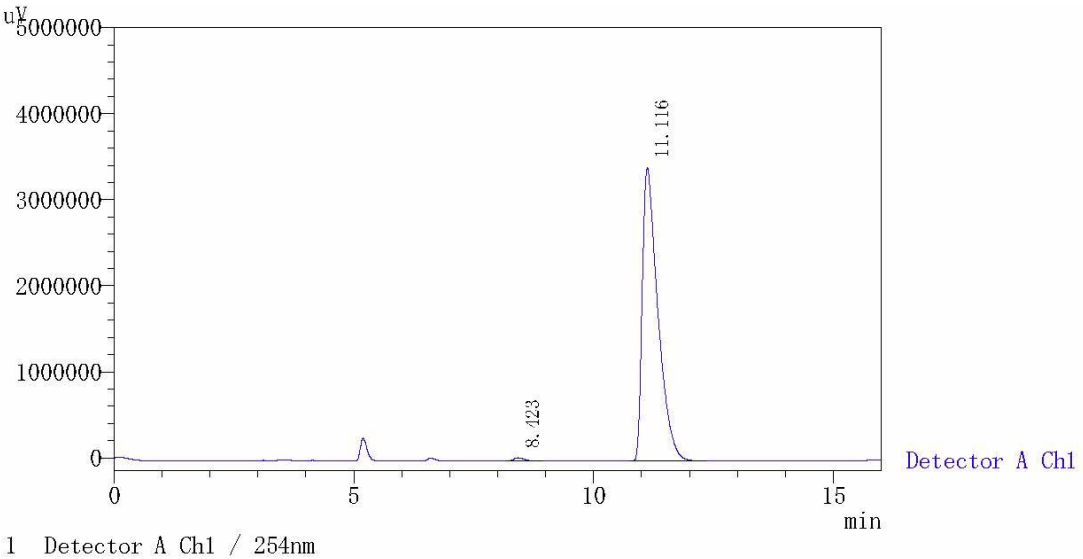

(**3n**), 96% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

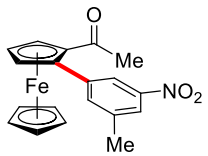
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.471 | 7111882 | 469481 | 49.968 |
| 2 | 10.920 | 7120926 | 357335 | 50.032 |



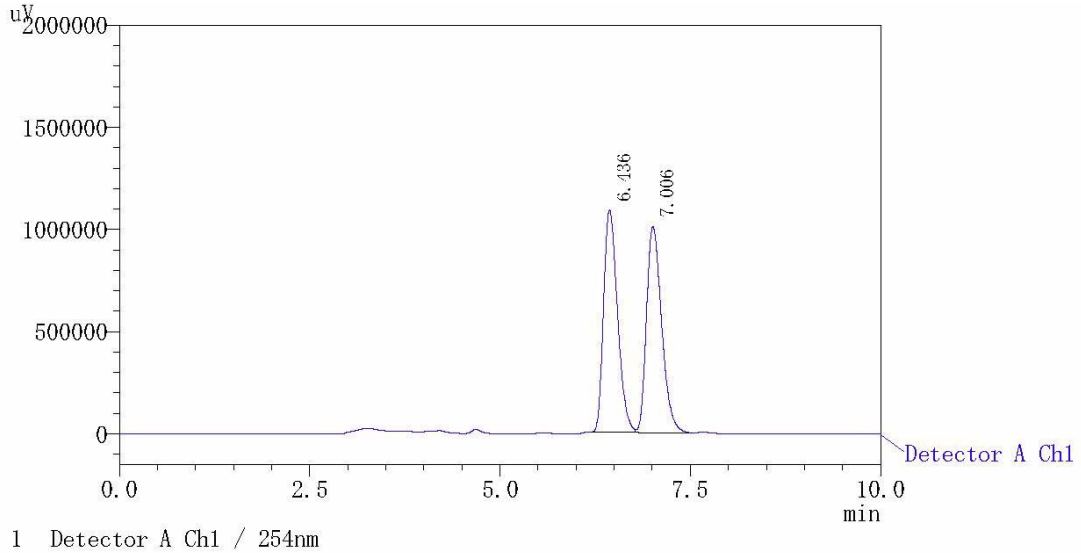

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.423 | 612340 | 38932 | 0.791 |
| 2 | 11.116 | 76831904 | 3406154 | 99.209 |



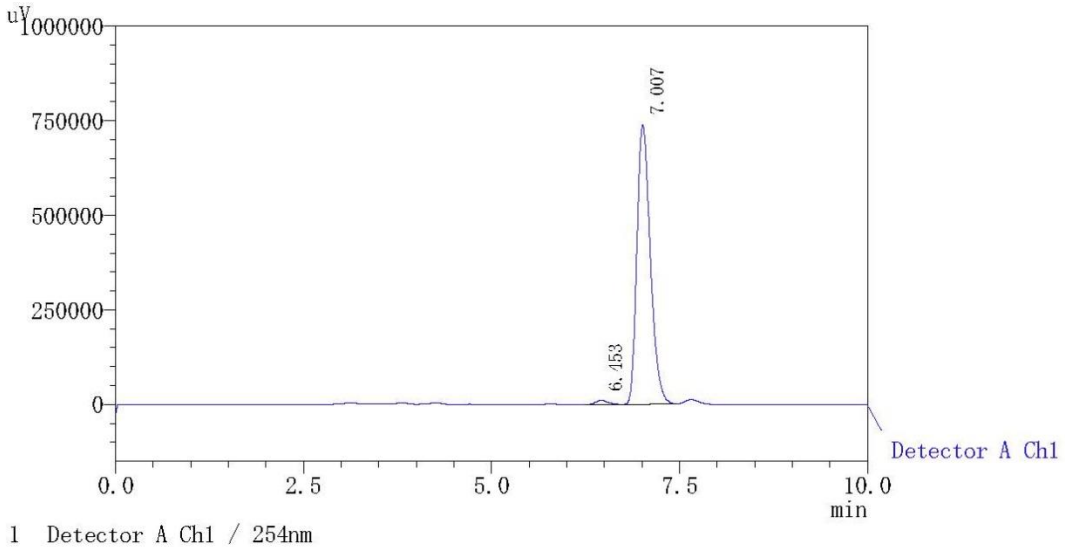

(**3o**), 98.4% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

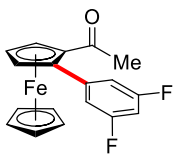
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 6.436 | 13824550 | 1086754 | 49.764 |
| 2 | 7.006 | 13955567 | 1008745 | 50.236 |



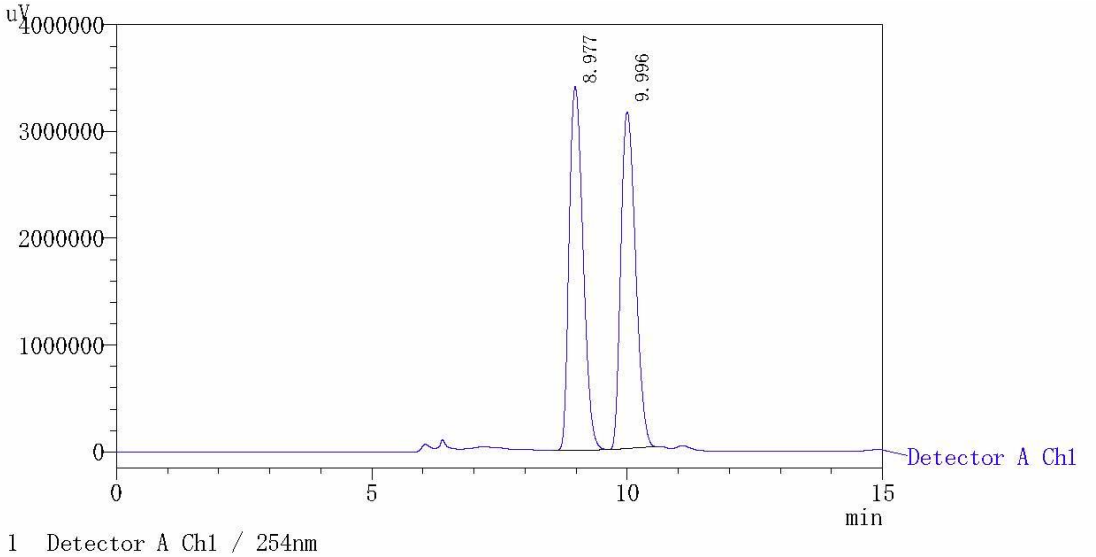

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 6.453 | 126194 | 11277 | 1.358 |
| 2 | 7.007 | 9168595 | 739553 | 98.642 |



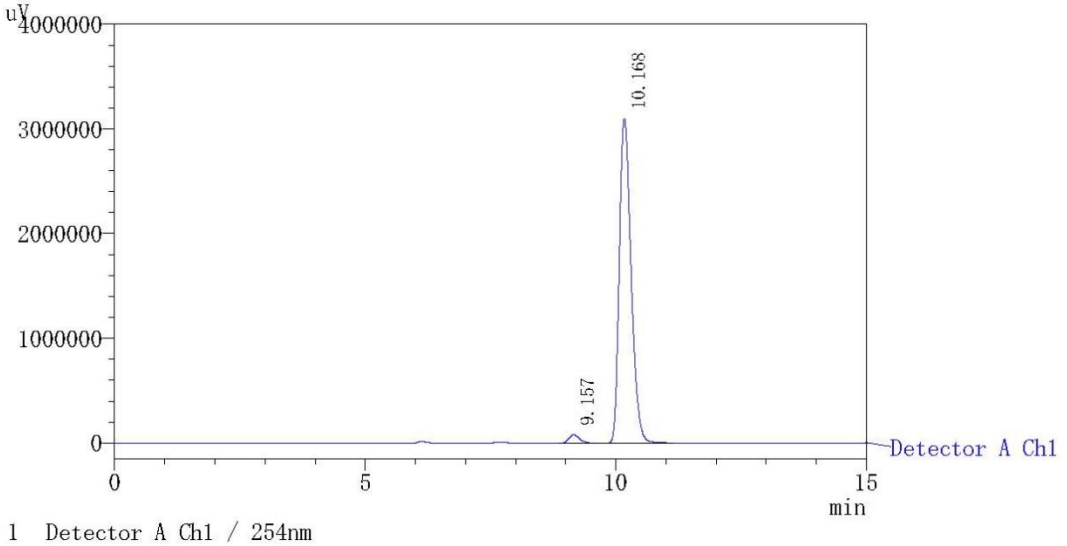

(**3p**), 97% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

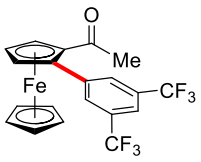
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.977 | 64159225 | 3402563 | 50.409 |
| 2 | 9.996 | 63117959 | 3154739 | 49.591 |



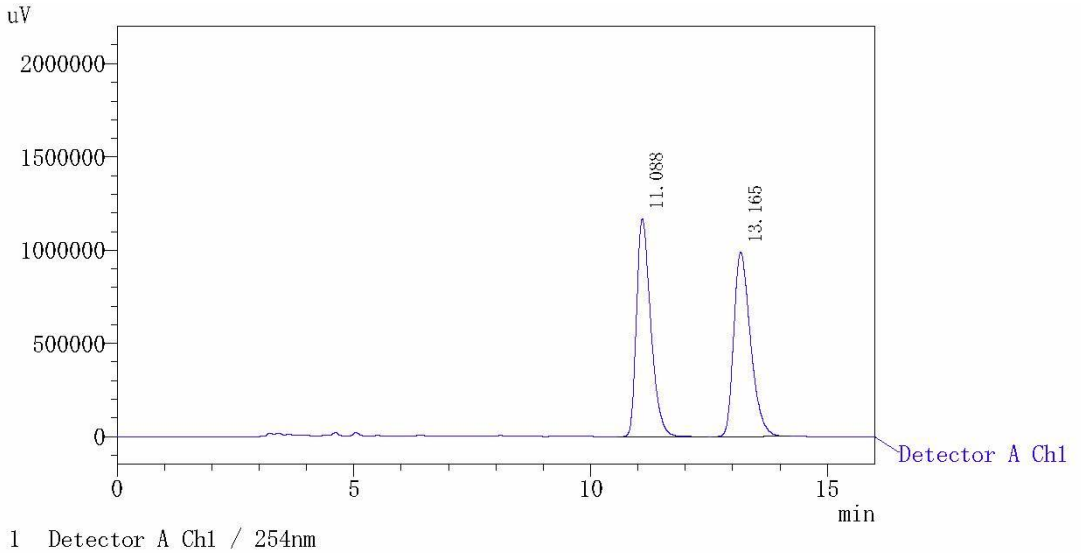

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.157 | 1141911 | 78592 | 2.214 |
| 2 | 10.168 | 50437941 | 3100975 | 97.786 |



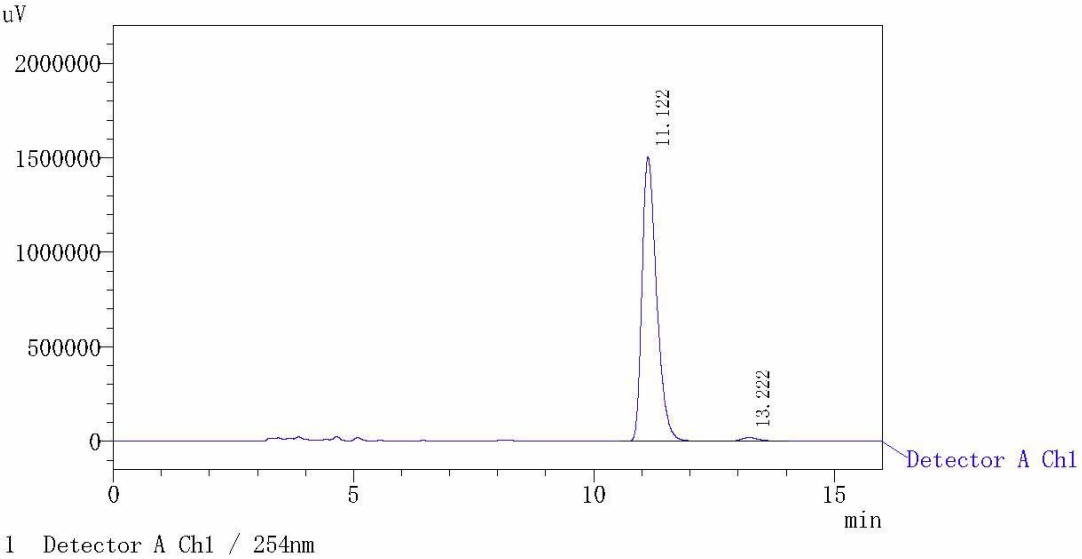

(**3q**), 96% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

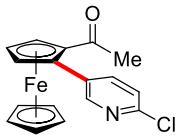
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.088 | 24489691 | 1167646 | 50.090 |
| 2 | 13.165 | 24401669 | 987298 | 49.910 |



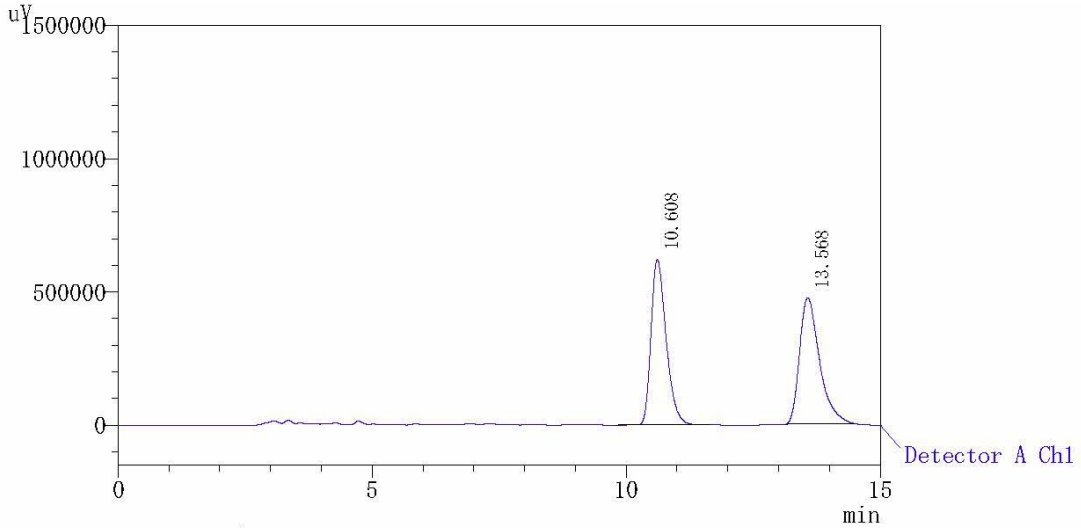

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.122 | 31587520 | 1504716 | 98.503 |
| 2 | 13.222 | 479902 | 19166 | 1.497 |



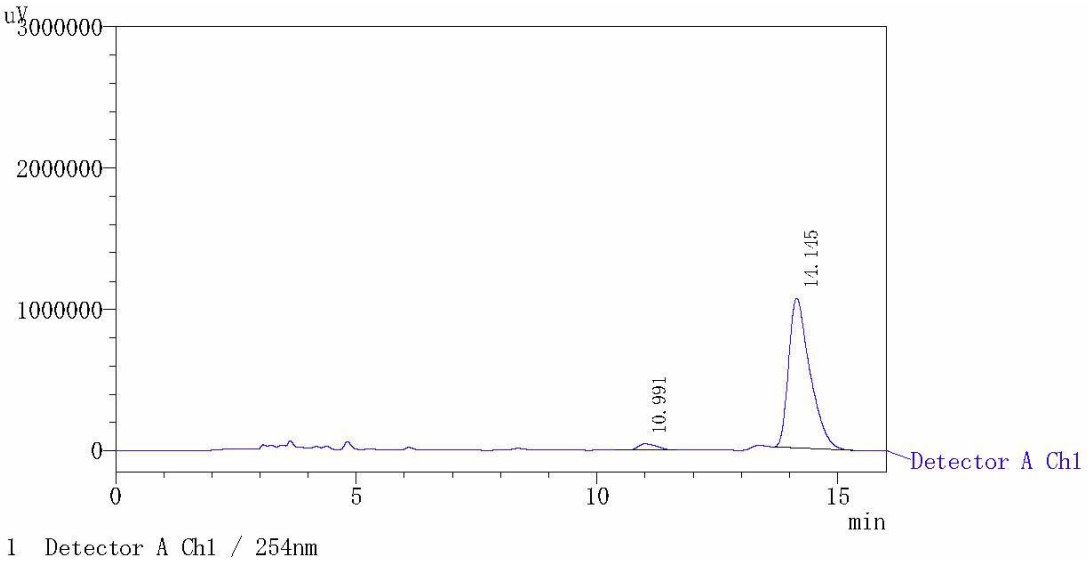

(**3r**), 97% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

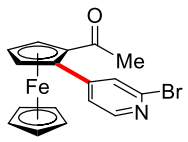
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.608 | 12913127 | 620420 | 49.812 |
| 2 | 13.568 | 13010750 | 473310 | 50.188 |



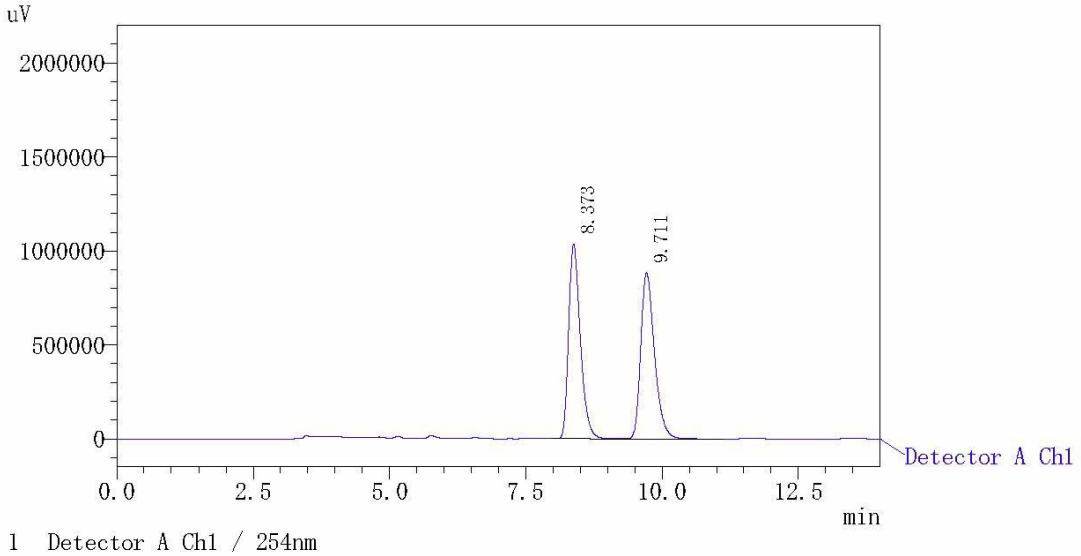

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 10.991 | 1192931 | 44642 | 3.534 |
| 2 | 14.145 | 32559316 | 1059408 | 96.466 |



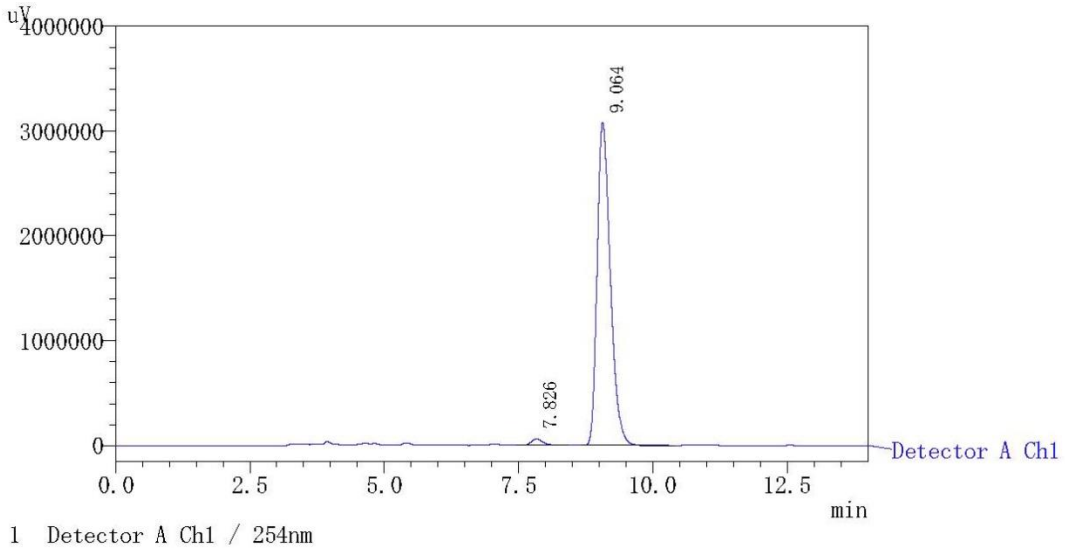

(**3s**), 93% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

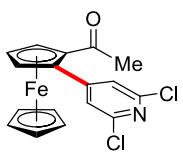
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.373 | 15580370 | 1037645 | 50.022 |
| 2 | 9.711 | 15566666 | 884579 | 49.978 |



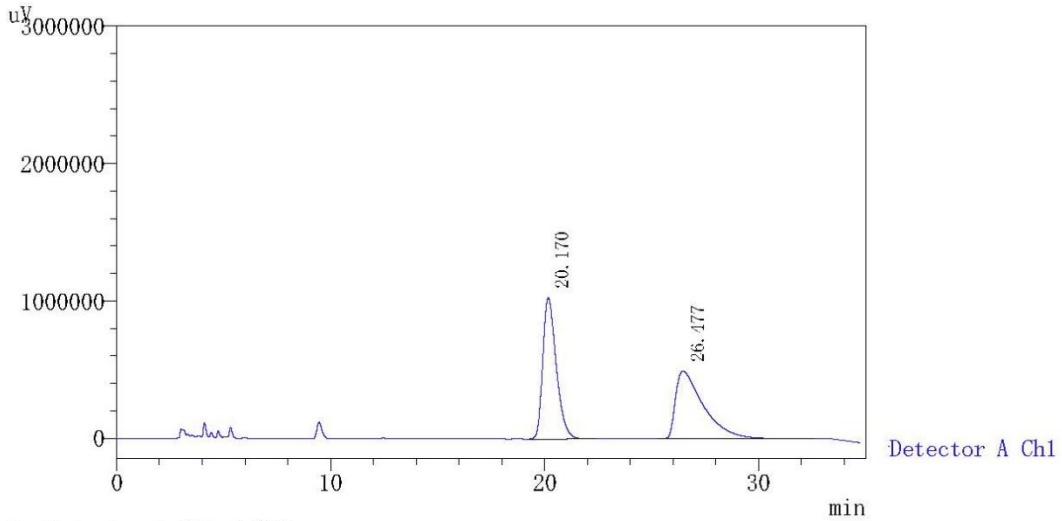

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.826 | 915997 | 59705 | 1.717 |
| 2 | 9.064 | 52435244 | 3081030 | 98.283 |



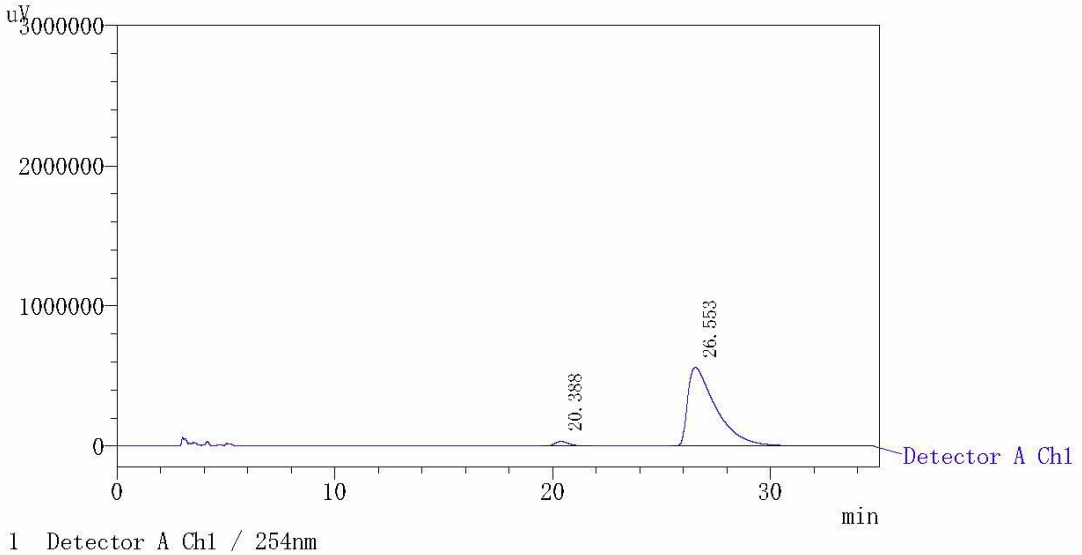

(**3t**), 97% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

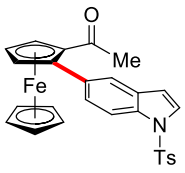
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 20.170 | 45115059 | 1027309 | 49.959 |
| 2 | 26.477 | 45189397 | 493939 | 50.041 |



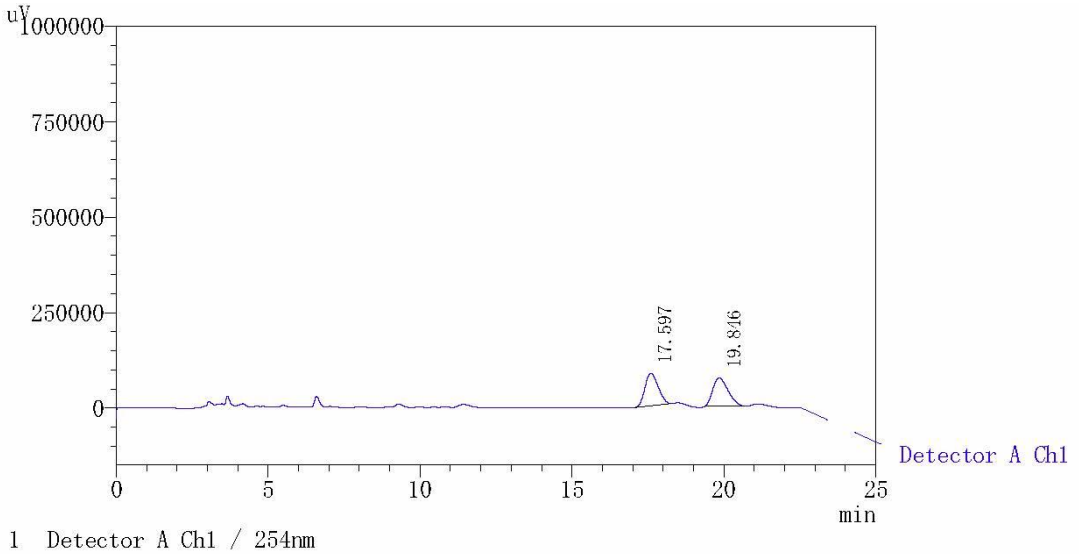

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 20.388 | 1425633 | 33009 | 2.718 |
| 2 | 26.553 | 51016779 | 562202 | 97.282 |



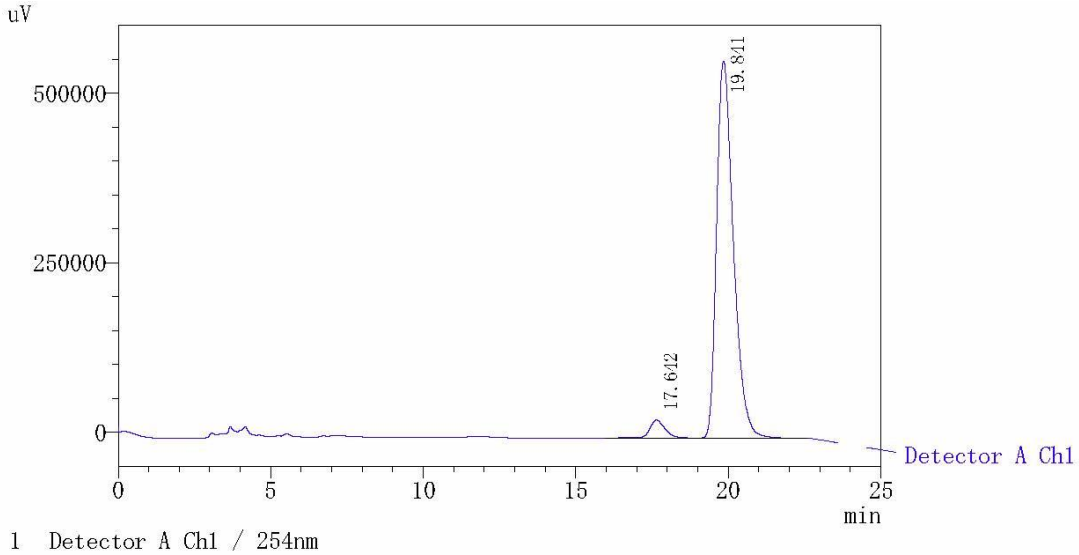

(**3u**), 95% ee




1 Detector A Ch1 / 254nm

Dctcctor A Ch1 254nm

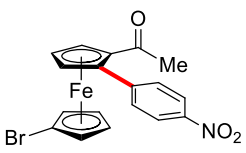
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 17.597 | 2560675 | 85479 | 49.657 |
| 2 | 19.846 | 2596018 | 74013 | 50.343 |



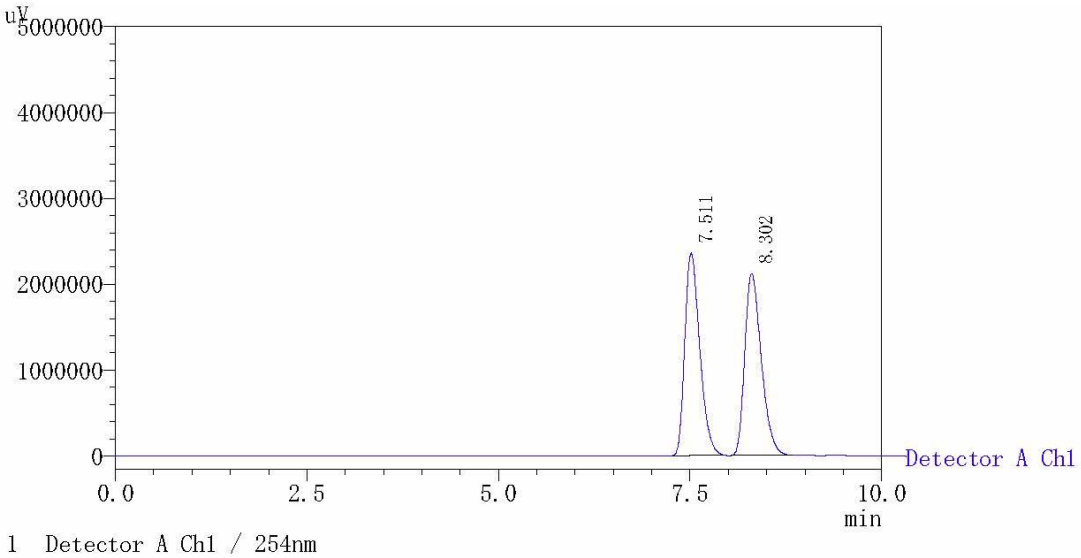

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 17.642 | 920271 | 26395 | 4.135 |
| 2 | 19.841 | 21332881 | 556183 | 95.865 |



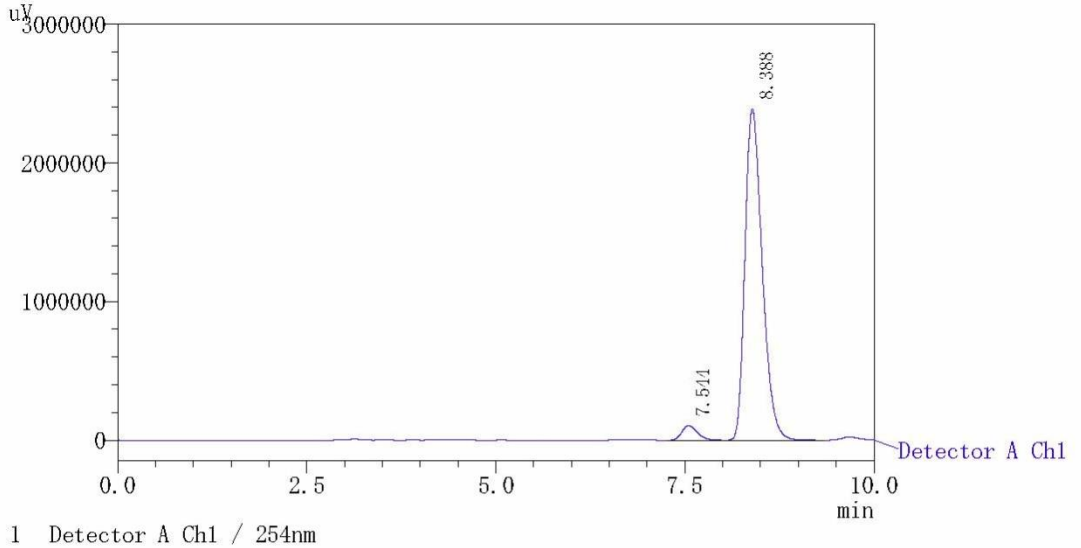

(**4a**), 92% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

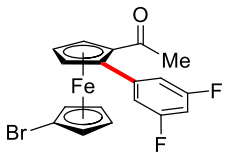
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.511 | 31826198 | 2356944 | 50.038 |
| 2 | 8.302 | 31777974 | 2115833 | 49.962 |



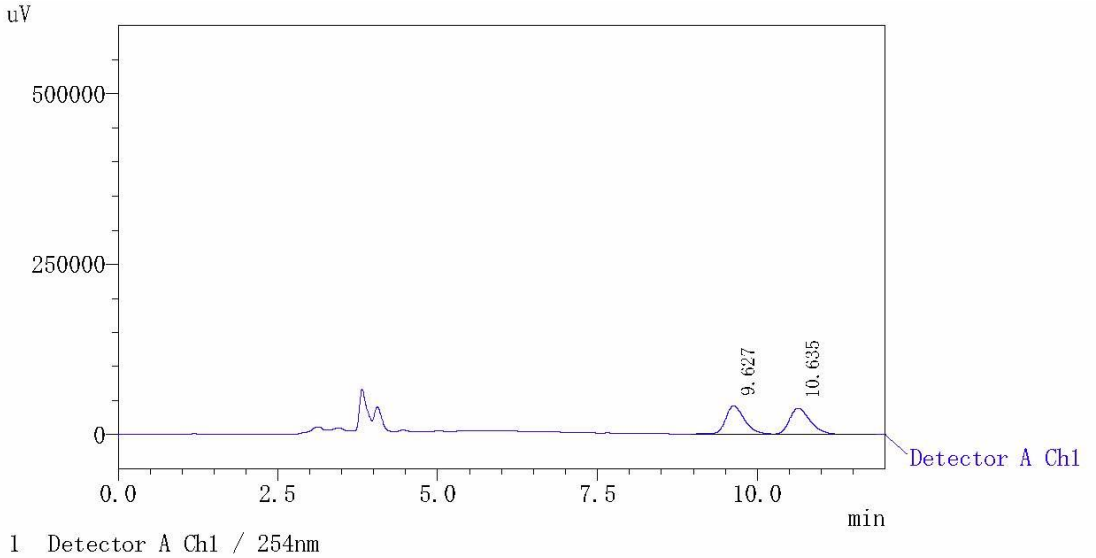

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.544 | 1490092 | 103756 | 3.779 |
| 2 | 8.388 | 37936025 | 2386356 | 96.221 |



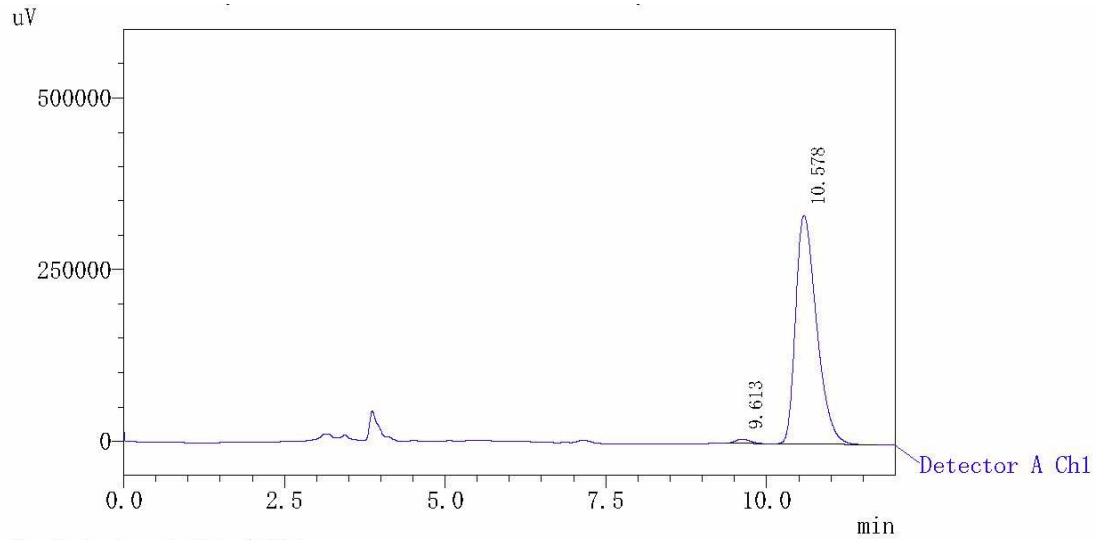

(**4b**), 93% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

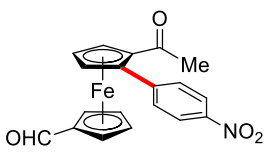
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.627 | 855573 | 41440 | 49.789 |
| 2 | 10.635 | 862837 | 38241 | 50.211 |



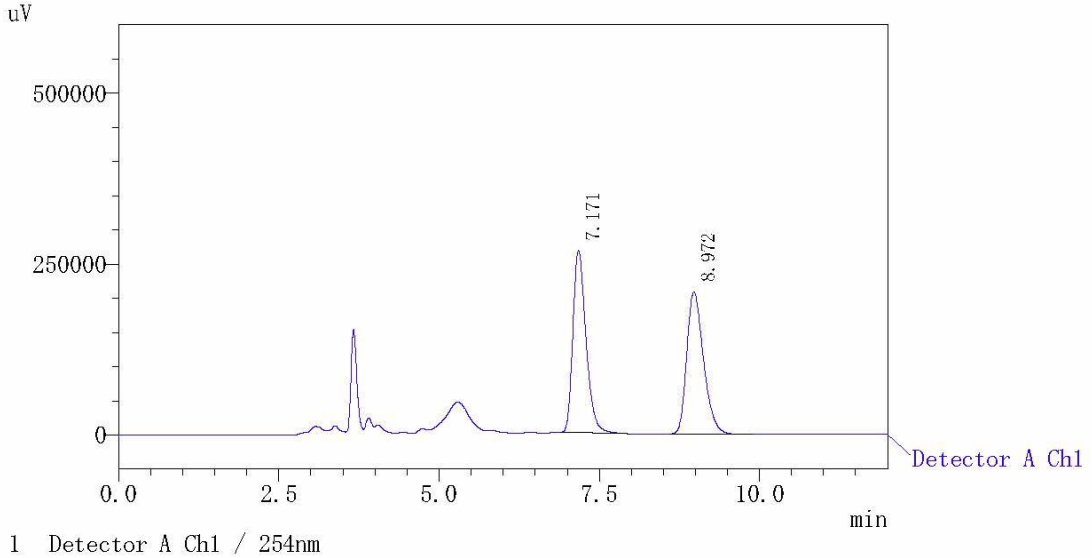

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.613 | 96848 | 6034 | 1.267 |
| 2 | 10.578 | 7545744 | 332782 | 98.733 |



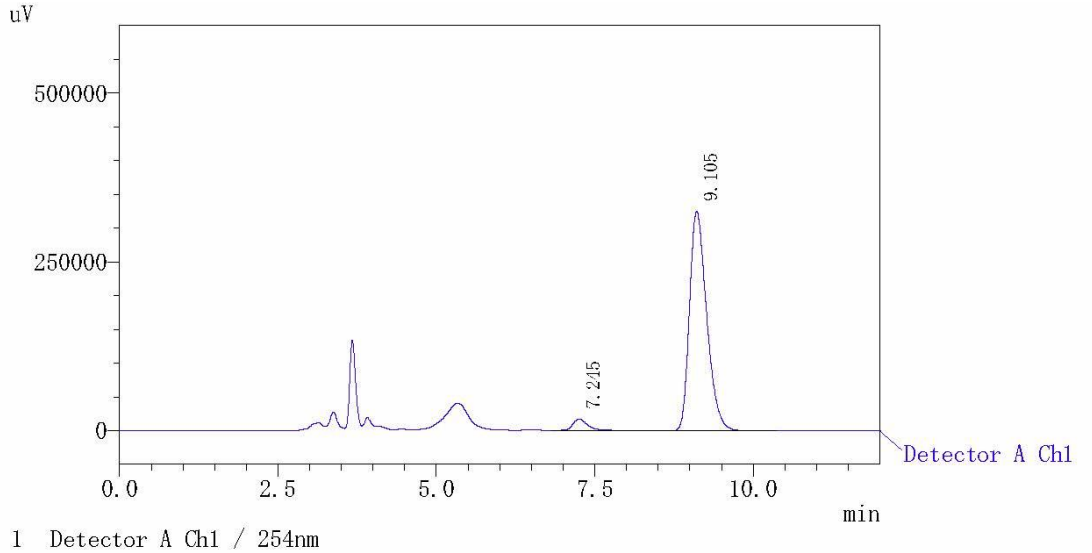

(**4c**), 97.5% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

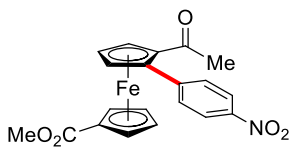
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.171 | 3774188 | 266385 | 50.186 |
| 2 | 8.972 | 3746152 | 207790 | 49.814 |



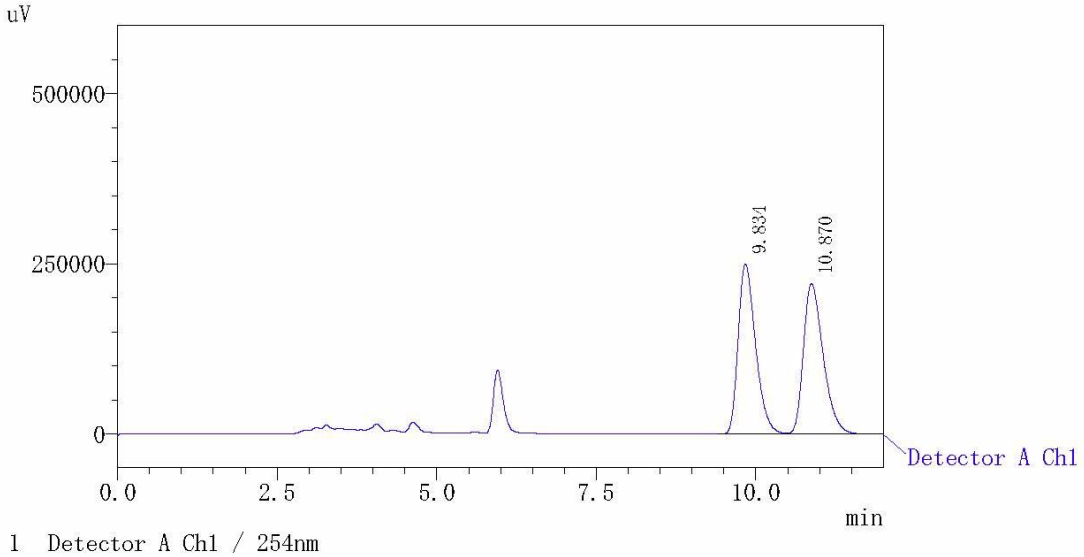

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 7.245 | 264164 | 17026 | 4.135 |
| 2 | 9.105 | 6124326 | 325196 | 95.865 |



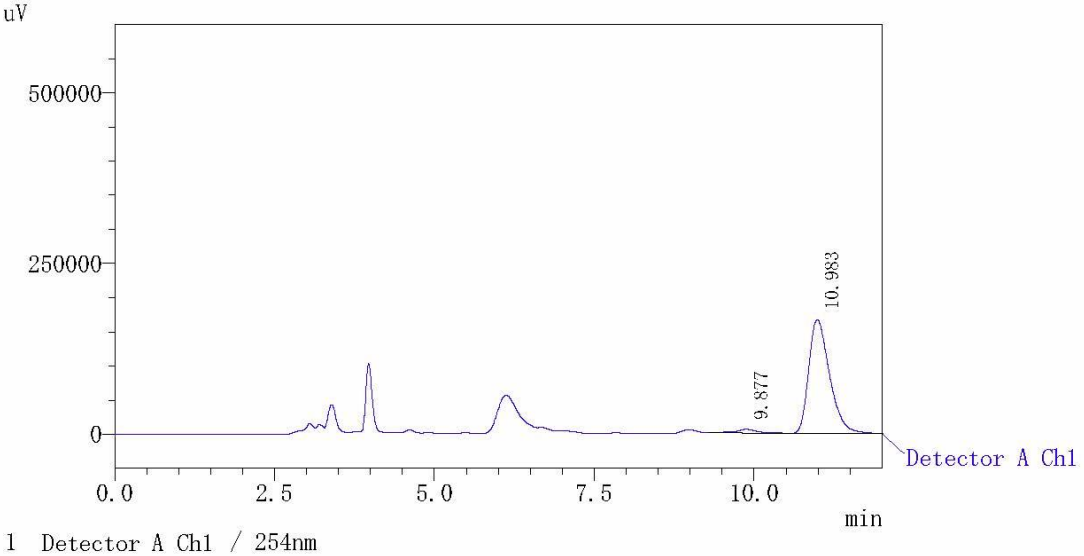

(**4d**), 92% ee




1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

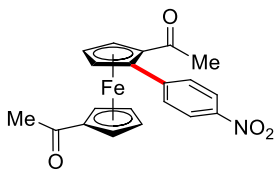
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.834 | 4736865 | 250145 | 49.905 |
| 2 | 10.870 | 4754974 | 221301 | 50.095 |



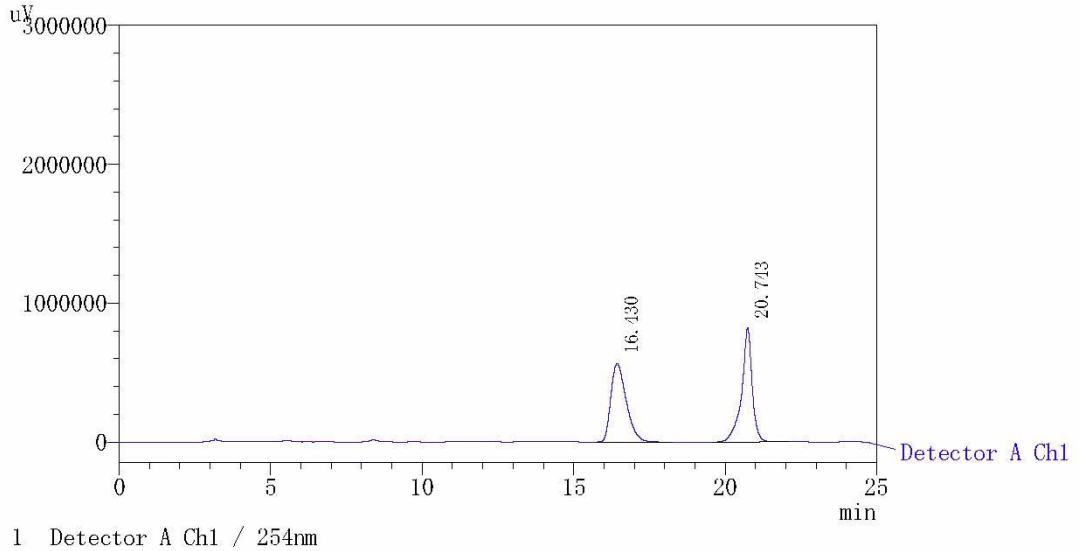

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.877 | 147460 | 5649 | 3.774 |
| 2 | 10.983 | 3759411 | 166591 | 96.226 |



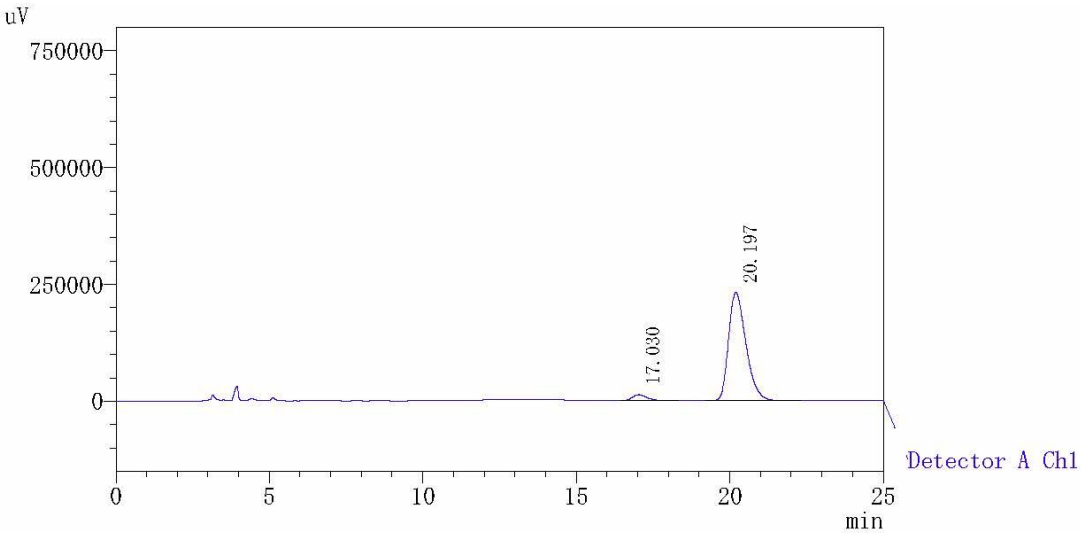

(**4e**), 92.5% ee




1 Detector A Ch1 / 254nm

Dctcctor A Ch1 254nm

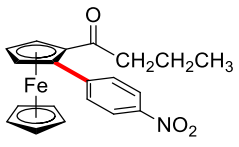
| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 16.430 | 19856486 | 564125 | 50.034 |
| 2 | 20.743 | 19829301 | 820577 | 49.966 |



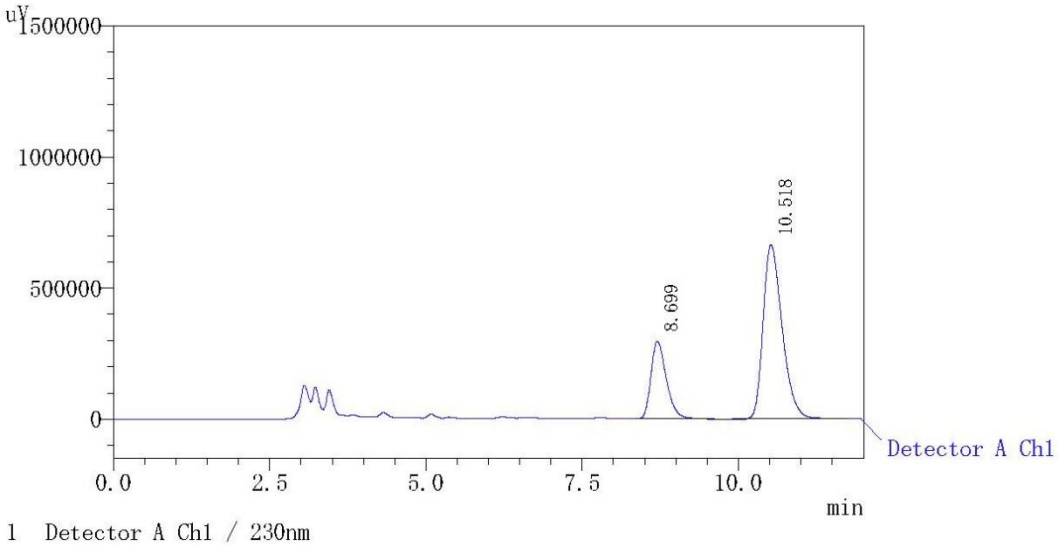

1 Detector A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 17.030 | 399464 | 12611 | 4.210 |
| 2 | 20.197 | 9089361 | 231579 | 95.790 |



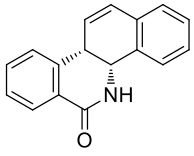

(**4f**), 92% ee



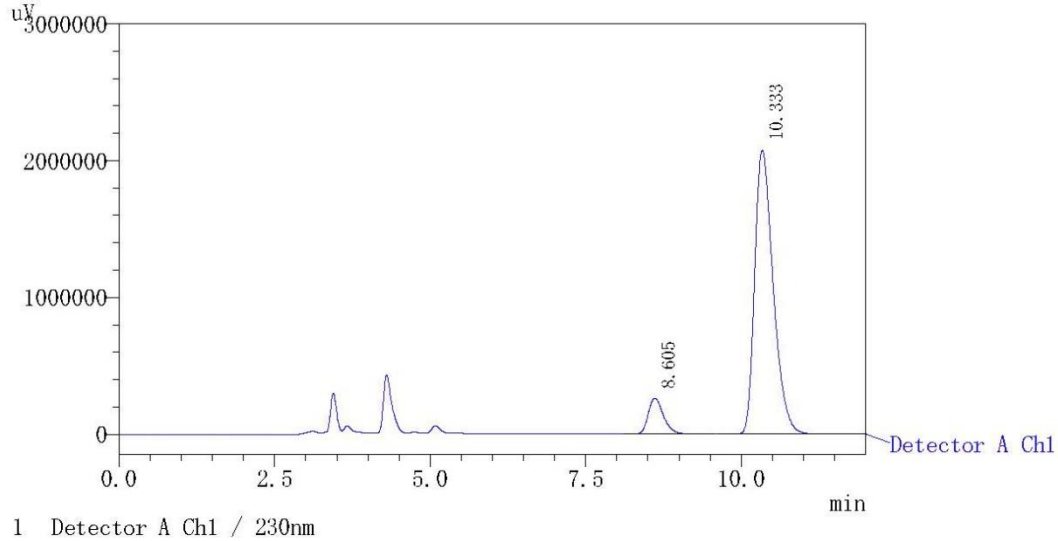

1 Detector A Ch1 / 230nm

Dctcctor A Ch1 230nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.699 | 5041721 | 294974 | 26.375 |
| 2 | 10.518 | 14074008 | 663991 | 73.625 |



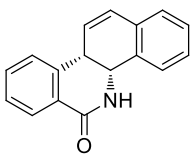

(**10**), 47% ee (cat. (*R*, $R_p$)-**L1**)



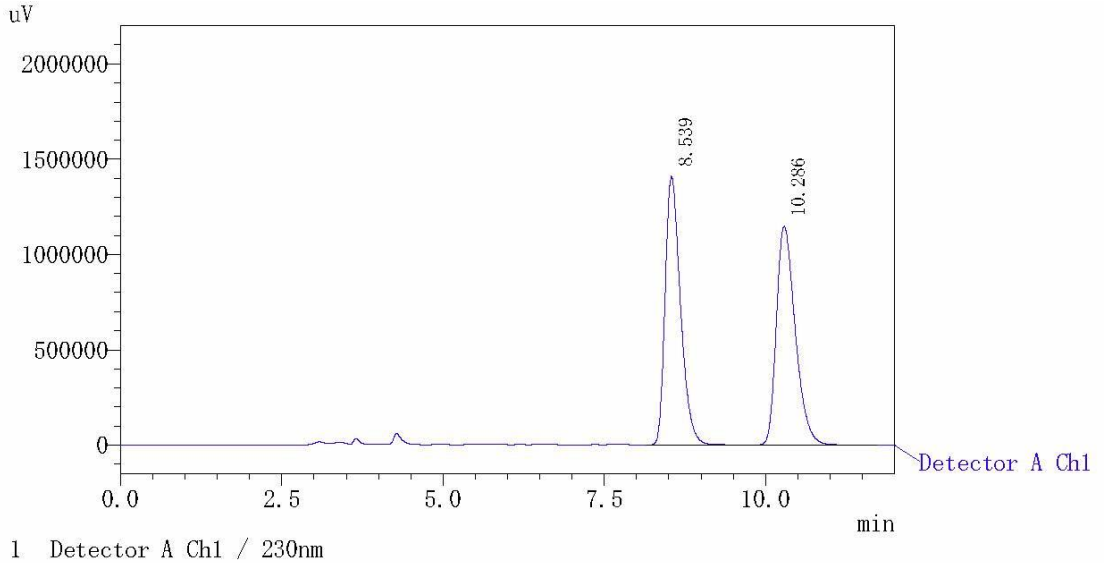

1 Detector A Ch1 / 230nm

Dctcctor A Ch1 230nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.605 | 4396943 | 262920 | 9.316 |
| 2 | 10.333 | 42800199 | 2075366 | 90.684 |



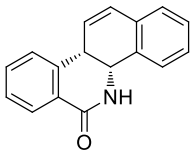

(**10**), 81% ee (cat. (*S*, $R_p$)-**L1**)




1 Detector A Ch1 / 230nm

Detector A Ch1 230nm

| Peak# | RetTime | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.539 | 23343592 | 1410381 | 50.023 |
| 2 | 10.286 | 23322587 | 1148042 | 49.977 |




(*rac*-**10**)