Supporting Information

In-situ Oxidizable Directing Group-Enabled Enantioselective Synthesis of Chiral Platform Ferrocene Formaldehydes

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General Experimental Details

Starting materials were prepared under an inert atmosphere (N_2, Ar), and Pd-Catalyzed 1,2 substituted ferrocene formaldehyde was prepared under dry air. Primary analyses were carried out using thin-layer chromatography (TLC) with silica-coated plates. Reagents were procured from commercial sources, including Sigma Aldrich, Alfa Aesar, BLD Pharma, and Spectrochem. The Solvents were meticulously dried by following standard procedures. Nuclear Magnetic Resonance (NMR) spectral data were collected using Bruker 400, 500, and 700 MHz spectrometers, with chemical shift values reported in parts per million (ppm) relative to $CDCl_3$ as an internal standard (7.26 ppm for ^1H, 77.16 ppm for ^{13}C). ^{19}F NMR data are reported in δ units (ppm) and were measured relative to the signals for residual $CFCl_3$ (0.00 ppm) in the deuterated chloroform solvent unless otherwise stated. Multiplicity was denoted using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet), and m (multiplet). High-resolution mass spectrometric (HRMS) analyses were performed using a quadrupole time-of-flight mass spectrometry (Q-TOF-MS) instrument with an electrospray ionization (ESI) technique. Chiral analysis was carried out using high-performance liquid chromatography (HPLC) equipment from Agilent Technologies, employing CHIRALCELL OZ-3, AD-H, IC-3, and AD-3 chiral HPLC columns. The weighing balance utilized was from Sartorius (model BSA224S-CW). Single crystal X-ray data were collected using a Bruker APEX-II CCD diffractometer equipped with a CMOS Photon 100 detector. Crystal structures were refined using the Olex2 and WinGX Program System package with the SHELXL-2019/2 program. The starting material and amines were freshly prepared by following a reported procedure with slight modifications, while ferrocene carboxaldehyde was directly purchased from BLD Pharm India and used without further purification. Amino acids and *R*-BINOL were directly purchased from commercial sources and further modified using the reported procedure.

Synthesis of ferrocenyl amines precursors 1a-1h

Ferrocenyl amines **1a-1f**, and **1h** were synthesized according to the previously reported literature procedure[1] and ferrocenyl amine **1g** was purchased commercially.

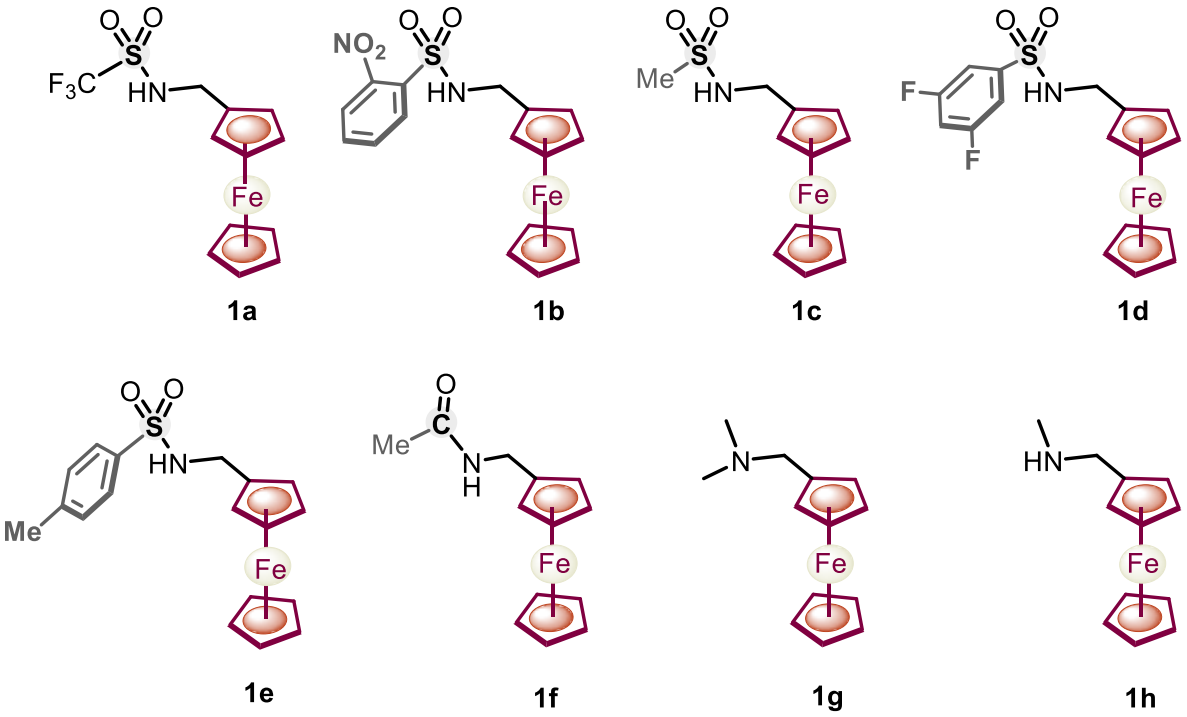


Figure S1. Synthesis of ferrocenyl amines **1a-1h**

Synthesis of olefins precursors 2a-2aa

Olefins **2a-2t**, **2z**, and **2aa** were synthesized according to the previously reported literature procedure[2], and olefins **2u-2y** were purchased commercially.

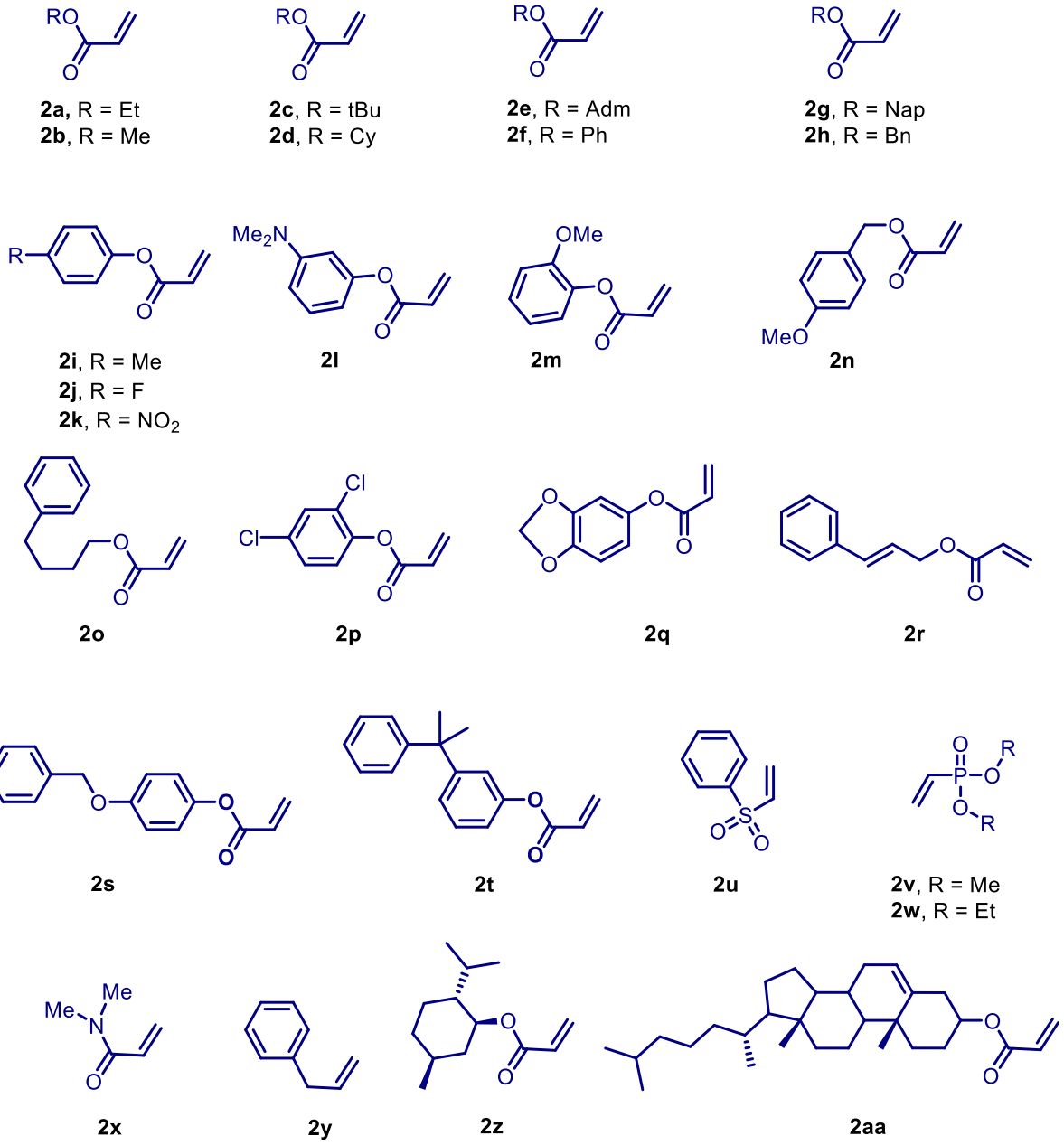


Figure S2. Synthesis of olefins **2a-2aa**

Synthesis of monoprotected amino acid ligand L1-L9

Monoprotected amino acid-derived ligand **L1-L9** was synthesized according to the reported literature procedure.[3]

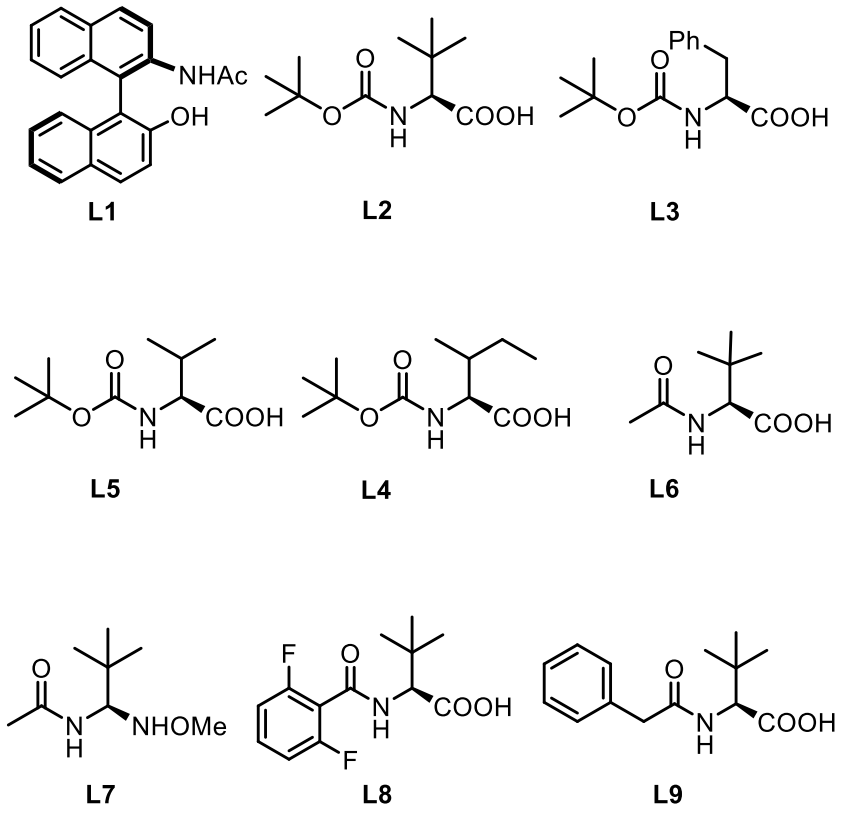
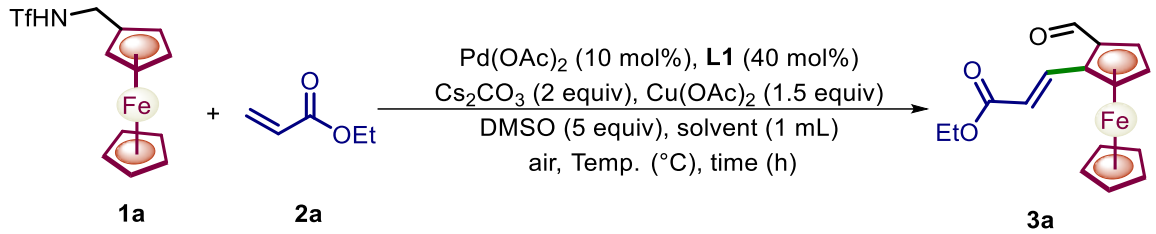


Figure S3. Synthesis of monoprotected amino acid ligand **L1-L9**

Reaction Optimization

Reaction optimization for enantioselective synthesis of Chiral 1,2-alkenylated ferrocene formaldehydes.

Table S1. Reaction optimization by varying the solvents, time, and temperature [a]

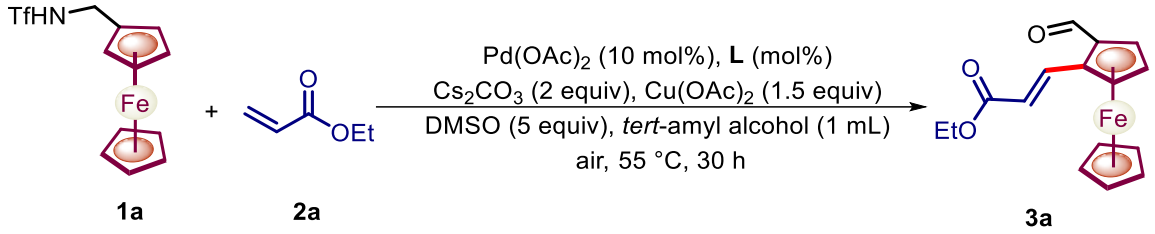


1a **2a** **3a**

Entry	Solvent	Time (h)	Temp. (°C)	Yield (%)[b]	*er* (%)[c]
1	THF	24	60	20	90:10
2	Toluene	24	60	18	85:15
3	DMF	24	60	15	70:30
4	DMSO	24	60	10	78:22
5	*tert*-amyl alcohol	24	60	32	70:30
6	*tert*-amyl alcohol	30	60	38	70:30
7	***tert*-amyl alcohol**	**30**	**55**	**42**	**78:22**

Reaction conditions: (a) **1a** (35 mg, 0.1 mmol, 1 equiv), **2a** (2 equiv), $Pd(OAc)_2$ (10 mol%), L1 (40 mol%), Cs_2CO_3 (2 equiv), $Cu(OAc)_2$ (1.5 equiv), DMSO (5 equiv), dry solvent (1 mL), air, 60 °C, 24h. (b) Crude yield of **3a** is determined by ^1H NMR with CH_2Br_2 as an internal standard. (c) *er* of **3a** was determined by HPLC analysis. (d) The reaction was stirred for 30 h at 55 °C.

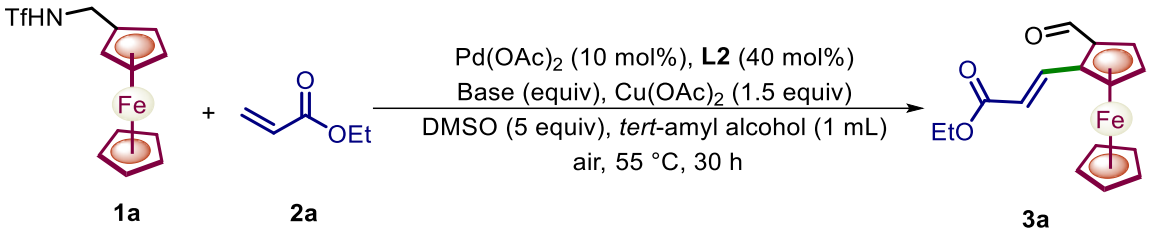
Table S2. Ligand Screening [a]



Entry	Ligand (mol%)	Yield (%)[b]	*er* (%)[c]
1	L1 (40 mol%)	42	78:22
2	**L2 (40 mol%)**	**75**	**98:2**
3	L3 (40 mol%)	65	96:4
4	L4 (40 mol%)	68	94:6
5	L5 (40 mol%)	64	95:5
6	L6 (40 mol%)	50	94:6
7	L7 (40 mol%)	32	87:13
8	L8 (40 mol%)	61	96:4
9	L9 (40 mol%)	42	92:8
10	L2 (20 mol%)	45	92:8
11	L2 (30 mol%)	51	94:6
12	L2 (50 mol%)	73	98:2
13[d]	L2 (40 mol%)	60	96:4

Reaction conditions: (a) **1a** (35 mg, 0.1 mmol, 1 equiv), **2a** (2 equiv), $Pd(OAc)_2$ (10 mol%), ligand (mol%), Cs_2CO_3 (2 equiv), $Cu(OAc)_2$ (1.5 equiv), DMSO (5 equiv), dry *tert*-amyl alcohol (1 mL), air, 55 °C, 24h. (b) Crude yield of **3a** is determined by ^1H NMR with CH_2Br_2 as an internal standard. (c) *er* of **3a** was determined by HPLC analysis. (d) THF solvent was used instead of *tert*-amyl alcohol.

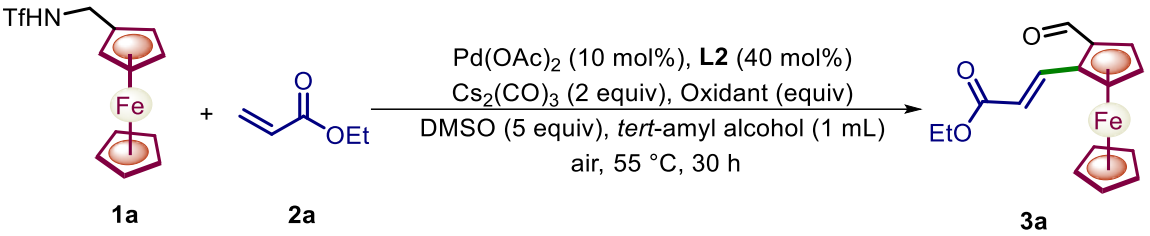
Table S3. Base Optimization [a]



Entry	Base	Equiv	Yield (%)[b]	*er* (%)[c]
1	**Cs_2CO_3**	**2**	**75**	**98:2**
2	K_2CO_3	2	65	94:6
3	Na_2CO_3	2	57	88:12
4	Li_2CO_3	2	22	65:35
5	$CsHCO_3$	2	62	95:5
6	K_2HPO_4	2	62	94:6
7	KOAc	2	28	84:16
8	CsOAc	2	30	87:13
9	NaOAc	2	18	80:20
10	KF	2	15	87:13
11	CsF	2	20	89:11
12	NEt_3	2	3	N.R.
13	Cs_2CO_3	1.5	68	97:3
14	Cs_2CO_3	1	60	94:6
15	Cs_2CO_3	2.5	71	98:2

Reaction conditions: (a) **1a** (35 mg, 0.1 mmol, 1 equiv), **2a** (2 equiv), $Pd(OAc)_2$ (10 mol%), **L2** (40 mol%), Base, $Cu(OAc)_2$ (1.5 equiv), DMSO (5 equiv), *tert*-amyl alcohol (1 mL), air, 55 °C, 30h. (b) Crude yield of **3a** is determined by ^1H NMR with CH_2Br_2 as an internal standard. (c) *er* of **3a** was determined by HPLC analysis.

Table S4. Oxidant Screening [a]

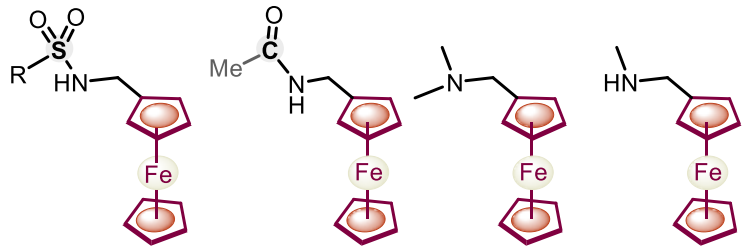


1a **2a** **3a**

Entry	Oxidant	Equiv	Yield (%)[b]	*er* (%)[c]
1	Air	1.5	5	96:4
2	O_2	1.5	7	95:5
3	Ag_2CO_3	1.5	16	95:5
4	AgOAc	1.5	30	95:5
5	$Cu(OTf)_2$	1.5	35	96:4
6	CuOTf	1.5	20	95:5
7	**$Cu(OAc)_2$**	**1.5**	**75**	**98:2**
8	CuO	1.5	32	99:1
9	$Cu(OAc)_2$	1.0	58	98:2
10	$Cu(OAc)_2$	2.0	76	98:2

Reaction conditions: (a) **1a** (35 mg, 0.1 mmol, 1 equiv), **2a** (2 equiv), $Pd(OAc)_2$ (10 mol%), **L2** (40 mol%), Cs_2CO_3 (2.0 equiv), oxidant, DMSO (5 equiv), *tert*-amyl alcohol (1 mL), air, 55 °C, 30h. (b) Crude yield of **3a** is determined by ^1H NMR with CH_2Br_2 as an internal standard. (c) *er* of **3a** was determined by HPLC analysis.

Table S5. Amine Screening [a]

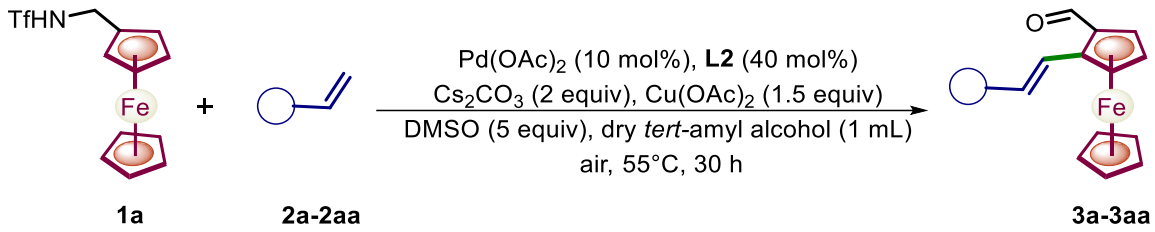


1a, R; CF_3 (75%);[b] 98:2 *er*[c]
1b, R; Nosyl (55%); 98:2 *er*
1c, R; Me (5%); 88:12 *er*
1d, R; 3,5-di-F-Ph (36%); 94:6 *er*
1e, R; Tosyl (25%); 97:3 *er*

1f, NR **1g**, NR **1h**, NR

Reaction conditions: (a) **1** (1 equiv), **2a** (2 equiv), $Pd(OAc)_2$ (10 mol%), **L2** (40 mol%), Cs_2CO_3, (2 equiv), $Cu(OAc)_2$ (1.5 equiv), DMSO (5 equiv), *tert*-amyl alcohol (1 mL), air, 55 °C, 30h. (b) Crude yield of **3a** is determined by ^1H NMR with CH_2Br_2 as an internal standard. (c) *er* of **3a** was determined by HPLC analysis.

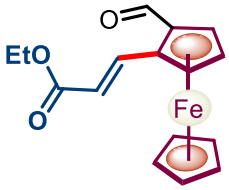
General procedure for the Pd-catalyzed C-H activation, oxidative deamination of ferrocenylamine 1a with olefins 2a-2aa



1a **2a-2aa** **3a-3aa**

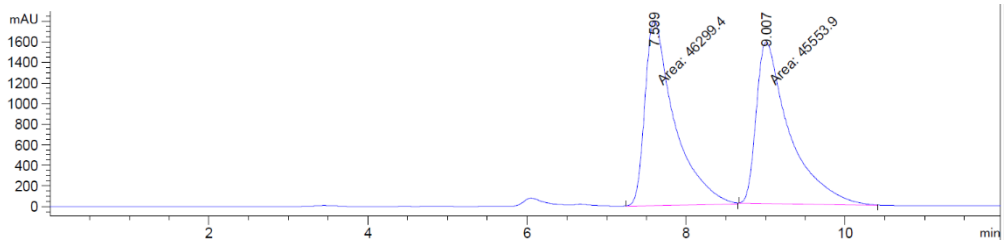
Scheme S1. Pd-catalyzed C-H activation oxidative deamination of ferrocenylamine **1a** with olefins **2a-2aa**

In a Schlenk tube, $Pd(OAc)_2$ (2.3 mg, 0.011 mmol, 10 mol%), **L2** (10 mg, 0.044 mmol, 40 mol %), $Cu(OAc)_2$ (30.0 mg, 0.16 mmol, 1.5 equiv), Cs_2CO_3 (71.2 mg, 0.22 mmol, 2 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv), and ferrocenyl amine **1a** (38 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl alcohol (1.5 mL) under an inert atmosphere and the resulting green-colored solution was stirred for 10 min. After pre-stirring, olefin **2a** (24 µL, 0.22 mmol, 2 equiv) was added to the resulting reaction mixture. The tube was sealed with a rubber septum, and a dry air atmosphere was maintained in the flask with a balloon. The reaction was heated at 55 °C, stirred for 30 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, evaporation, and column chromatography on silica gel (mesh 230-400) using a hexane: ethyl acetate solvent system to afford Chiral 1,2 alkenylated ferrocene formaldehydes (**3a-3aa)**.



Chiral 1,2-formyl ferrocenyl acrylate 3a was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 85:15), obtained as an orange solid, mp: 114-116 ºC. Yield: 24 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.04 (d, J = 15.9 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 5.04 – 4.96 (m, 2H), 4.81 (t, J = 2.7 Hz, 1H), 4.31 (s, 5H), 4.30 – 4.24 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (CH), 166.7 (C), 141.8 (CH), 118.3 (CH), 80.9 (C), 78.3 (C), 73.9 (CH), 73.3 (CH), 71.7 (CH), 71.4 (CH), 60.5 (CH_2), 14.3 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{17}FeO_3$ 313.0522, found 313.0501. Enantioselectivity of **3a** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

Racemic sample (**3a**)

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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----|-------|----|-------|----------|----------|--------|
   1   7.599 MM    0.4303 4.62994e4  1793.44482  50.4058
   2   9.007 MM    0.4844 4.55539e4  1567.42871  49.5942
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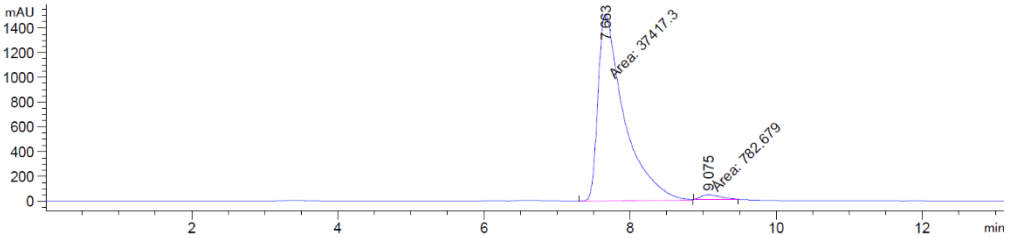
Asymmetric sample (**3a**)

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.663 MM    0.4128 3.74173e4  1510.84119  97.9511
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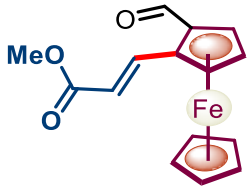
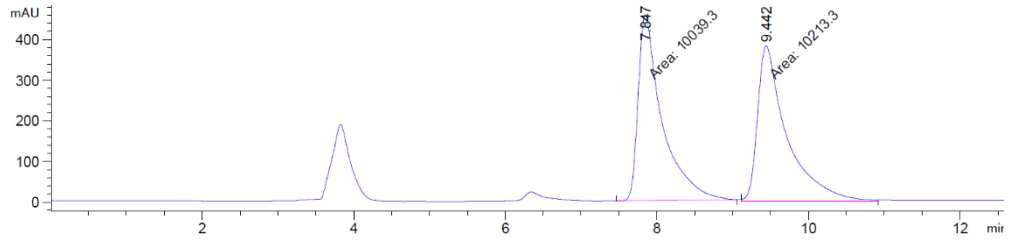


Chiral 1,2-formyl ferrocenyl acrylate 3b was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 90:10), obtained as an orange solid, mp:110-112 ºC. Yield: 22 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.07 (d, J = 15.9 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 5.00 (t, J = 2.9 Hz, 2H), 4.81 (t, J = 2.7 Hz, 1H), 4.31 (s, 5H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (CH), 167.1 (C), 142.1 (CH), 117.8 (CH), 80.7 (C), 78.4 (C), 74.0 (CH), 73.5 (CH), 71.7 (CH), 71.4 (CH), 51.6 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{15}FeO_3$ 299.0365, found 299.0357. Enantioselectivity of **3b** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

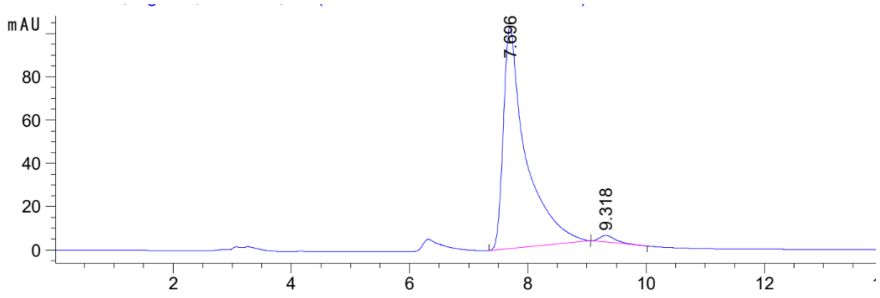
Racemic sample (**3b**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

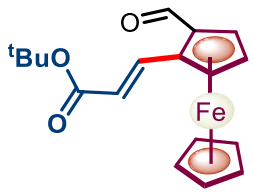
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.847	MM	0.3650	1.00393e4	458.37061	49.5705
2	9.442	MM	0.4453	1.02133e4	382.25613	50.4295

Asymmetric sample (**3b**)



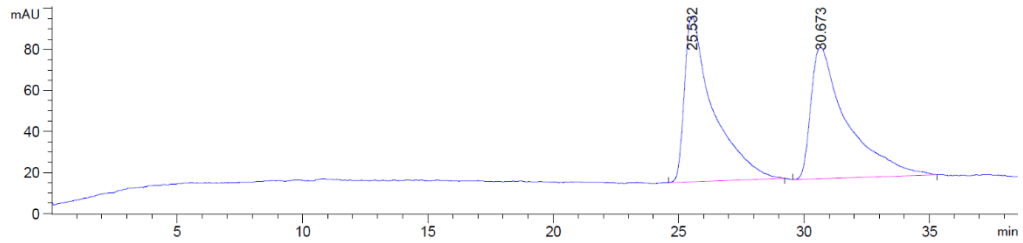
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.696	BB	0.3677	2721.39502	102.52766	97.8594
2	9.318	BB	0.2865	59.52804	3.12124	2.1406



Chiral 1,2-formyl ferrocenyl acrylate 3c was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 85:15), obtained as an orange solid, mp:118-120 ºC. Yield: 27 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.92 (d, J = 15.8 Hz, 1H), 6.19 (d, J = 15.8 Hz, 1H), 4.99 (dd, J = 7.7, 6.4 Hz, 2H), 4.79 (t, J = 2.6 Hz, 1H), 4.31 (s, 5H), 1.56 (s, 9H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (C), 166.1 (C), 140.5 (CH), 120.3 (CH), 81.4 (C), 80.5 (C), 78.2 (C), 73.8 (CH), 72.9 (CH), 71.7 (CH), 71.3 (CH), 28.2 (CH_3). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{20}FeO_3Na$ 363.0654, found 363.0641. Enantioselectivity of **3c** was determined by chiral HPLC analysis on AD-3 (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

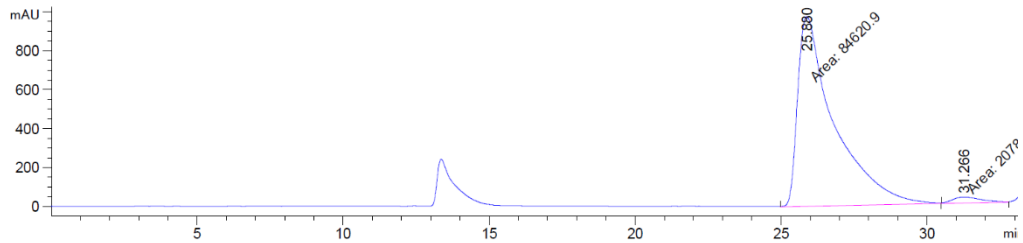
Racemic sample (**3c**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.532	BB	1.0860	6411.56201	80.77689	50.0516
2	30.673	BB	1.3307	6398.34717	63.98307	49.9484

Asymmetric sample (**3c**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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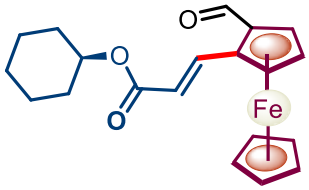
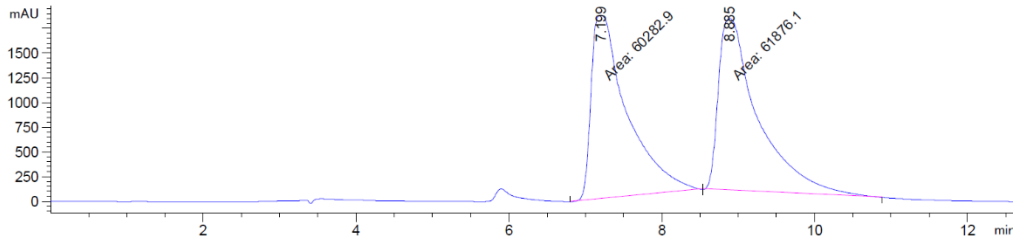
1	25.880	MM	1.4469	8.46209e4	974.71625	97.6027
2	31.266	MM	1.1246	2078.46118	30.80349	2.3973



Chiral 1,2-formyl ferrocenyl acrylate 3d was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:129-131 ºC. Yield: 27 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.01 (d, J = 15.9 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 5.00 (s, 2H), 4.86 – 4.91 (m, 1H), 4.81 (d, J = 1.7 Hz, 1H), 4.31 (s, 5H), 1.96 (dd, J = 9.5, 5.3 Hz, 2H), 1.81 (dd, J = 9.8, 6.5 Hz, 2H), 1.58 – 1.35 (m, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.9 (C), 166.3 (C), 141.5 (CH), 118.9 (CH), 81.0 (C), 78.2 (C), 74.0 (CH), 73.2 (CH), 72.9 (CH), 71.8 (CH), 71.4 (CH), 31.7 (CH_2), 25.4 (CH_2), 23.8 (CH_2). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{23}FeO_3$ 367.0991, found 367.0977. Enantioselectivity of **3d** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 75:25, 1 mL/min, λ=254 nm).

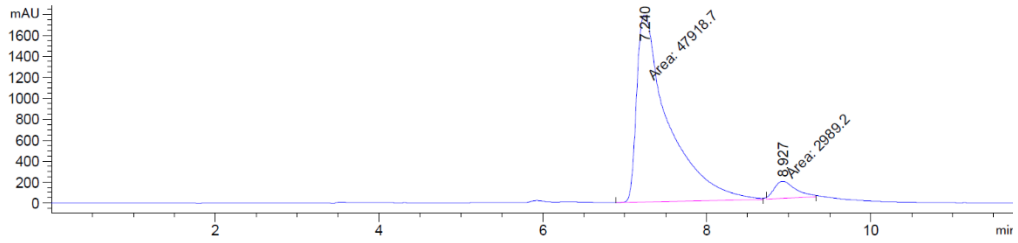
Racemic sample (**3d**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

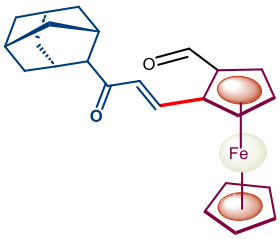
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.199	MM	0.5425	6.02829e4	1851.91248	49.3479
2	8.885	MM	0.5958	6.18761e4	1730.98865	50.6521

Asymmetric sample (**3d**)



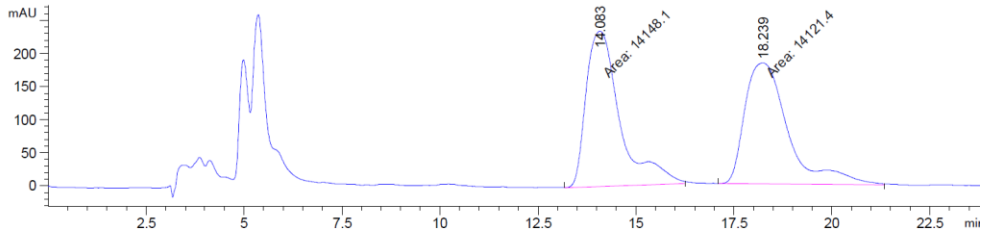
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.240	MM	0.4478	4.79187e4	1783.62268	94.1282
2	8.927	MM	0.3045	2989.20142	163.63492	5.8718



Chiral 1,2-formyl ferrocenyl acrylate 3e was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:139-141 ºC. Yield: 30 mg (65%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.90 (d, J = 15.8 Hz, 1H), 6.18 (d, J = 15.8 Hz, 1H), 4.98 (d, J = 24.6 Hz, 2H), 4.78 (s, 1H), 4.30 (s, 5H), 4.24 – 4.07 (m, 1H), 2.22 (s, 8H), 1.80 – 1.66 (m, 7H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (CH), 165.7 (C), 140.4 (CH), 120.4 (CH), 81.4 (C), 80.6 (C), 78.2 (CH), 73.8 (CH), 72.7 (CH), 71.7 (CH), 71.3 (CH), 41.4 (CH), 36.2 (CH), 30.8 (CH_2), 29.7 (CH_2), 28.6 (CH_2). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{27}FeO_3$ 419.1304, found 419.1270. Enantioselectivity of **3e** was determined by chiral HPLC analysis on IC-3 (hexane: isopropanol = 60:40, 1 mL/min, λ=254 nm).

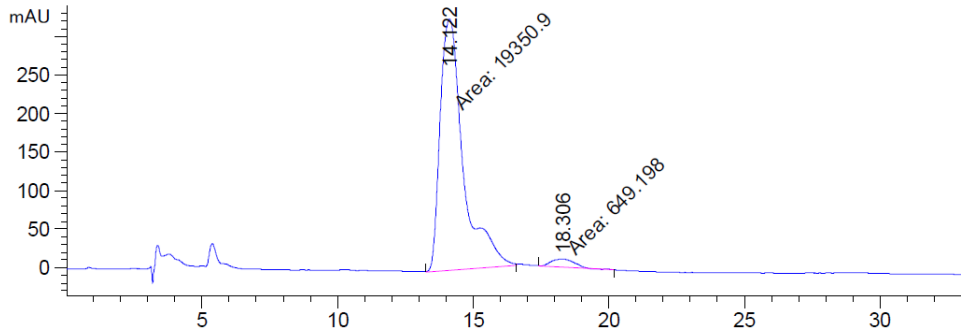
Racemic sample (**3e**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

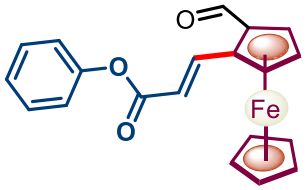
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.083	MM	1.0045	1.41481e4	234.73433	50.0472
2	18.239	MM	1.2854	1.41214e4	183.09344	49.9528

Asymmetric sample (**3e**)



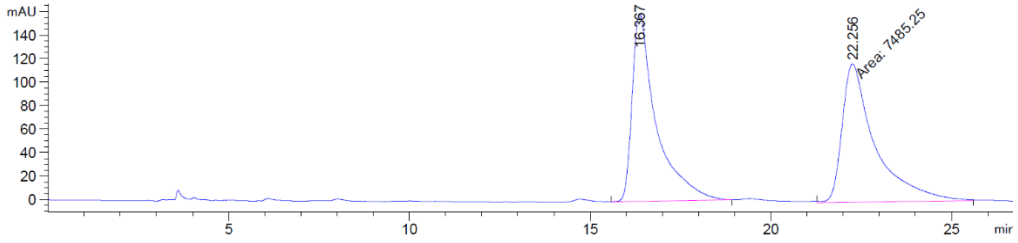
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.122	MM	0.9893	1.93509e4	326.01703	96.7540
2	18.306	MM	0.9955	649.19849	10.86883	3.2460



Chiral 1,2-formyl ferrocenyl acrylate 3f was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:136-139 ºC. Yield: 26 mg (67%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.27 (d, J = 15.8 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.26 (s, 1H), 7.20 (d, J = 7.8 Hz, 2H), 6.46 (d, J = 15.8 Hz, 1H), 5.06 (d, J = 10.2 Hz, 2H), 4.87 (s, 1H), 4.36 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (CH), 165.1 (C), 150.8 (C), 144.3 (CH), 129.4 (CH), 125.7 (CH), 121.6 (CH), 117.2 (CH), 80.3 (C), 78.6 (C), 74.3 (CH), 74.0 (CH), 72.0 (CH), 71.5 (CH). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{17}FeO_3$ 361.0522, found 361.0529. Enantioselectivity of the product **3f** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 85:15, 1 mL/min, λ=254 nm).

Racemic sample (**3f**)

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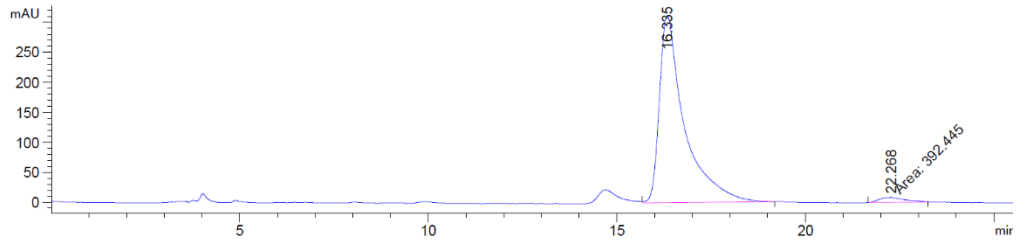
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

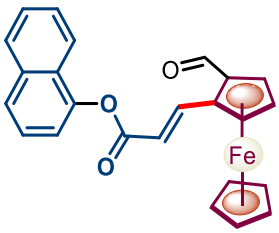
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.367 BB    0.6549 7383.10400  159.85188  49.6565
   2  22.256 MM    1.0612 7485.24707  117.56206  50.3435
```

Asymmetric sample (**3f**)



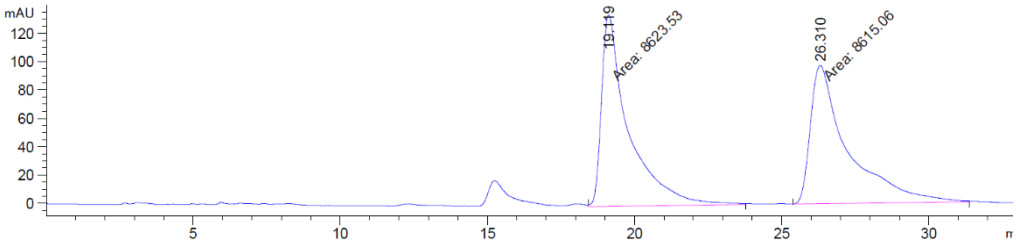

```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.335 VB    0.6536 1.43848e4   312.18893  97.3443
   2  22.268 MM    0.7854  392.44504    8.32751   2.6557
```



Chiral 1,2-formyl ferrocenyl acrylate 3g was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 75:25), obtained as an orange solid, mp:144-146 ºC. Yield: 29 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.32 (d, J = 15.8 Hz, 1H), 7.95 – 7.83 (m, 3H), 7.69 (d, J = 1.9 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.35 (dd, J = 8.8, 2.3 Hz, 1H), 6.52 (d, J = 15.8 Hz, 1H), 5.12 – 5.05 (m, 2H), 4.88 (t, J = 2.7 Hz, 1H), 4.38 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (C), 165.3 (C), 148.5 (C), 144.5 (C), 133.4 (CH), 131.5 (CH), 129.4 (CH), 127.8 (CH), 127.7 (CH), 126.5 (C), 125.6 (CH), 121.3 (CH), 118.6 (CH), 117.1 (CH), 80.3 (C), 78.6 (C), 74.4 (CH), 74.2 (CH), 72.0 (CH), 71.5 (CH). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{19}FeO_3$ 411.0678, found 411.0678. Enantioselectivity of **3g** was determined by chiral HPLC analysis on AD-3 (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

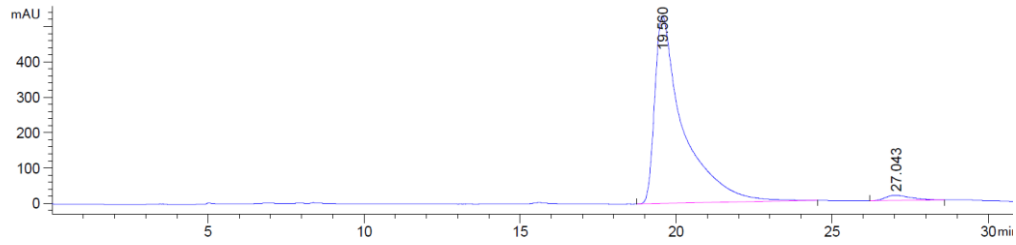
Racemic sample (**3g**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

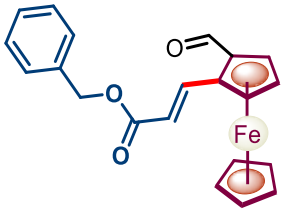
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.119	MM	1.0639	8623.52930	135.09583	50.0246
2	26.310	MM	1.4707	8615.05957	97.62795	49.9754

Asymmetric sample (**3g**)



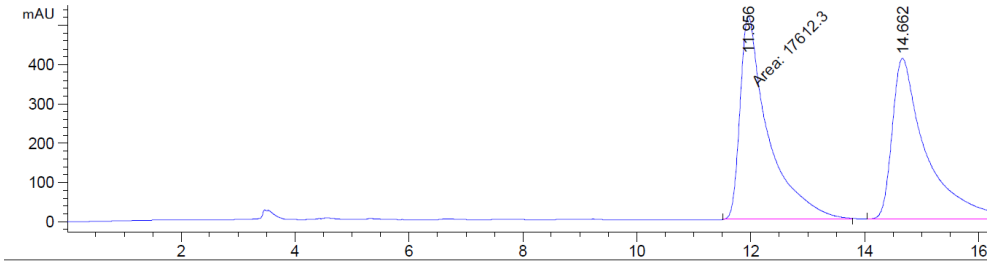
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.560	BB	0.8873	3.37088e4	530.49377	97.4867
2	27.043	BB	0.7720	869.02753	14.99706	2.5133



Chiral 1,2-formyl ferrocenyl acrylate 3h was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 75:25), obtained as an orange solid, mp:140-141 ºC. Yield: 26 mg (64%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.09 (s, 1H), 7.45 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 7.2 Hz, 1H), 6.31 (d, J = 15.8 Hz, 1H), 5.26 (d, J = 4.6 Hz, 2H), 5.02 – 5.00 (m, 1H), 4.98 (s, 1H), 4.81 (t, J = 2.6 Hz, 1H), 4.31 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (CH), 166.5 (C), 142.6 (CH), 136.1 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 117.8 (CH), 80.7 (C), 78.5 (C), 74.1 (CH), 73.4 (CH), 71.8 (CH), 71.4 (CH), 66.3 (CH_2). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{19}FeO_3$ 375.0678, found 375.0689. Enantioselectivity of **3h** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

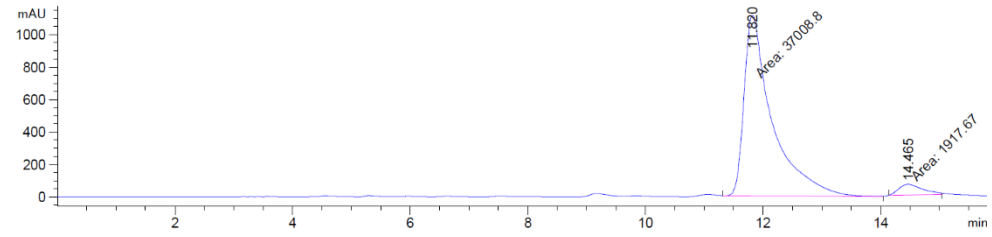
Racemic sample (**3h**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

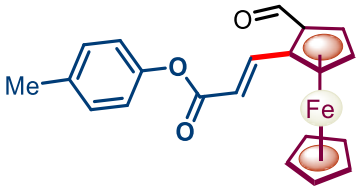
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.956	MM	0.5671	1.76123e4	517.65149	50.8017
2	14.662	BB	0.5826	1.70564e4	408.96808	49.1983

Asymmetric sample (**3h**)



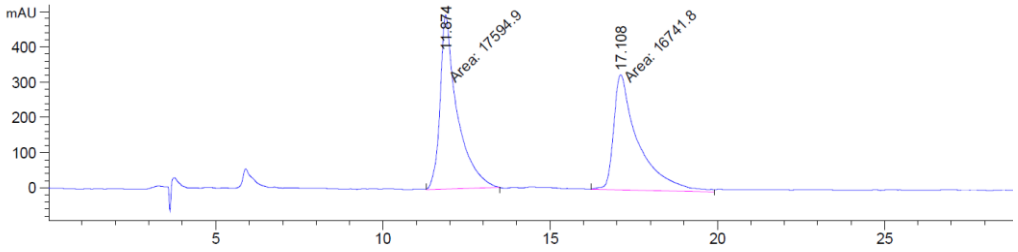
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.820	MM	0.5541	3.70088e4	1113.15479	95.0736
2	14.465	MM	0.4799	1917.67139	66.59586	4.9264



Chiral 1,2-formyl ferrocenyl acrylate 3i was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:140-142 ºC. Yield: 27 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.25 (d, J = 16.6 Hz, 1H), 7.23 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.46 (d, J = 16.1 Hz, 1H), 5.06 (s, 2H), 4.87 (s, 1H), 4.36 (s, 5H), 2.39 (s, 3H).^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (CH), 165.3 (C), 148.6 (C), 144.1 (C), 135.4 (CH), 129.9 (CH), 121.3 (CH), 117.3 (CH), 80.4 (C), 78.5 (C), 74.3 (CH), 73.9 (CH), 72.0 (CH), 71.5 (CH), 20.9 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{19}FeO_3$ 375.0678, found 375.0644. Enantioselectivity of **3i** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

Racemic sample (**3i**)

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.874 MM    0.5929 1.75949e4   494.60864  51.2423
   2  17.108 MM    0.8545 1.67418e4   326.54636  48.7577
```
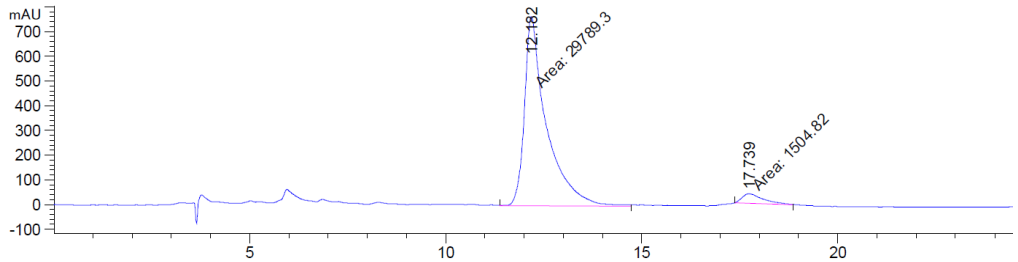

Asymmetric sample (**3i**)

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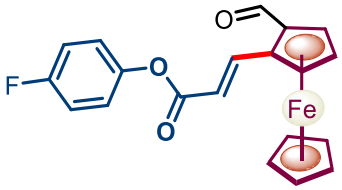
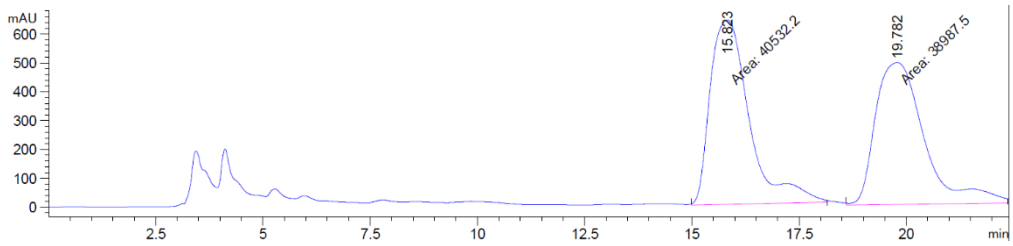
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.182 MM    0.6487 2.97893e4   765.38721  95.1914
   2  17.739 MM    0.6395 1504.81995   39.21744   4.8086
```



Chiral 1,2-formyl ferrocenyl acrylate 3j was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:142-144 ºC. Yield: 25 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.28 (d, J = 15.9 Hz, 1H), 7.24 – 7.04 (m, 4H), 6.45 (d, J = 15.2 Hz, 1H), 5.06 (brs, 2H), 4.87 (s, 1H), 4.36 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (C), 165.1 (C), 160.1 (d, $J_{C\text{-}F}$ = 244.1 Hz; CF).144.7 (C), 123.0 (CH), 116.8 (CH), 115.9 (CH), 80.1 (C), 78.6 (C), 74.4 (CH), 74.3 (CH), 72.0 (CH), 71.5 (CH). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{16}FFeO_3$ 379.0428, found 379.0399. Enantioselectivity of **3j** was determined by chiral HPLC analysis on IC-3 (hexane: isopropanol = 60:40, 1 mL/min, λ=254 nm).

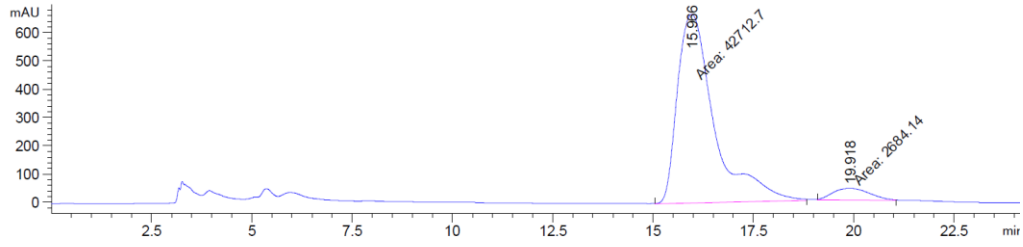
Racemic sample (**3j**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

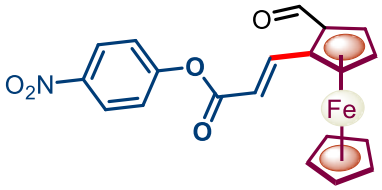
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.823	MM	1.0576	4.05322e4	638.74640	50.9713
2	19.782	MM	1.3212	3.89875e4	491.80896	49.0287

Asymmetric sample (**3j**)



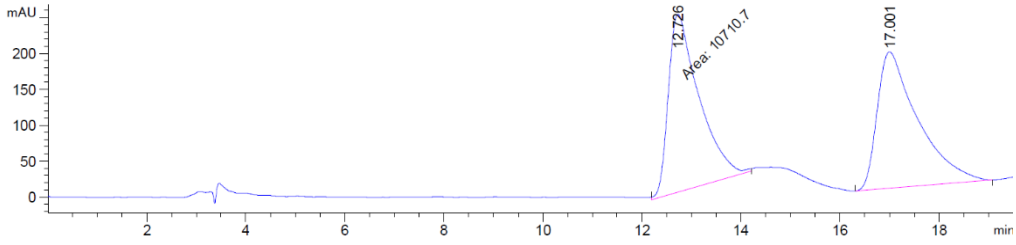
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.966	MM	1.0664	4.27127e4	667.55646	94.0874
2	19.918	MM	1.0715	2684.13940	41.74949	5.9126



Chiral 1,2-formyl ferrocenyl acrylate 3k was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:147-149 ºC. Yield: 22 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.28 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 15.8 Hz, 1H), 7.61 (d, J = 8.7 Hz, 2H), 6.34 (d, J = 16.3 Hz, 1H), 5.02 (s, 2H), 4.86 – 4.82 (m, 1H), 4.32 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (C), 166.2 (C), 147.7 (C), 143.9 (C), 143.5 (C), 128.4 (C), 123.8 (C), 116.9 (C), 80.2 (C), 78.6 (C), 74.2 (C), 71.9 (C), 71.5 (C), 64.7 (CH). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{14}FeNO_5$ 380.0202, found 380.0187. Enantioselectivity of **3k** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm)

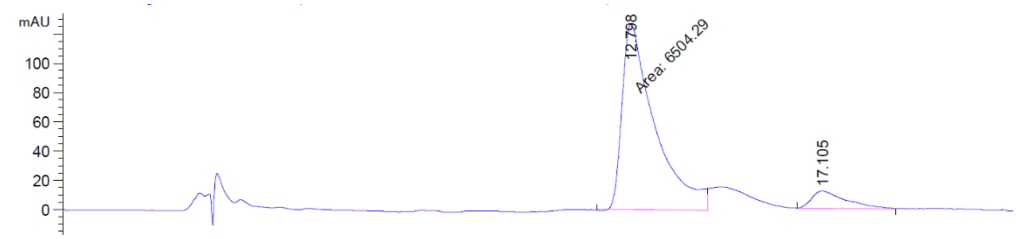
Racemic sample (**3k**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

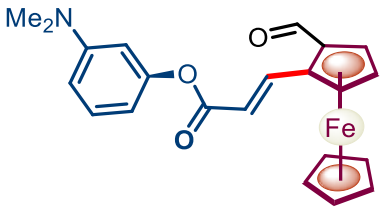
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.726	MM	0.7194	1.07107e4	248.14980	49.7156
2	17.001	BB	0.8010	1.08332e4	190.04221	50.2844

Asymmetric sample (**3k**)



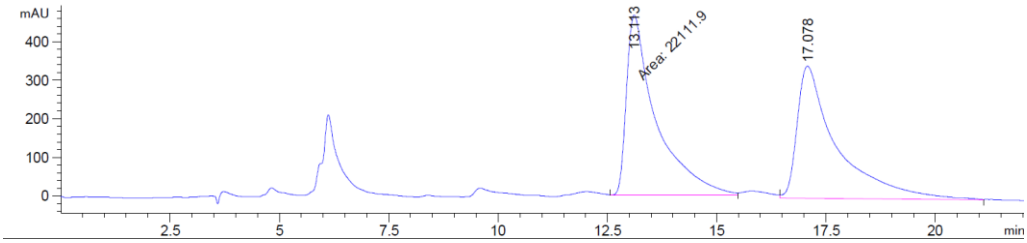
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.798	MM	0.8526	6504.28711	127.15352	91.3087
2	17.105	BB	0.7084	619.11993	11.79384	8.6913



Chiral 1,2-formyl ferrocenyl acrylate 3l was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:144-146 ºC. Yield: 24 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.24 (d, J = 15.7 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.63 (d, J = 8.7 Hz, 1H), 6.53 (dd, J = 7.2, 5.3 Hz, 2H), 6.46 (d, J = 16.0 Hz, 1H), 5.06 (s, 2H), 4.86 (s, 1H), 4.36 (s, 5H), 2.99 (s, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (C), 165.3 (C), 151.9 (C), 151.7 (C), 143.8 (C), 129.6 (C), 117.6 (C), 109.9 (C), 109.3 (C), 105.6 (C), 80.5 (C), 78.6 (C), 74.2 (C), 73.8 (C), 71.9 (C), 71.5 (C), 40.5 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{23}FeNO_3$ 404.0944, found 404.0964. Enantioselectivity of **3l** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm).

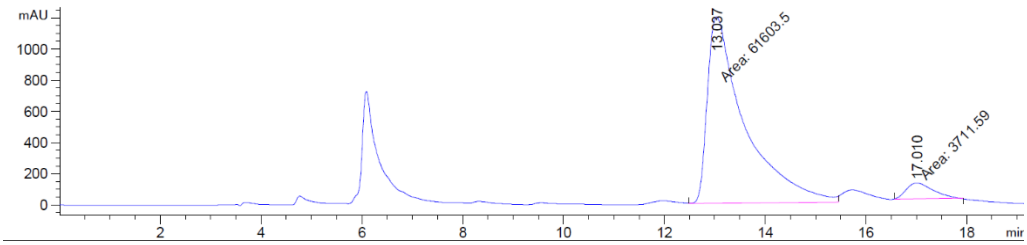
Racemic sample (**3l**)




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

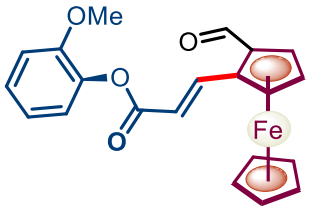
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.113 MM    0.7904 2.21119e4   466.23764  50.5221
   2  17.078 VB    0.8694 2.16549e4   342.61578  49.4779
```

Asymmetric sample (**3l**)



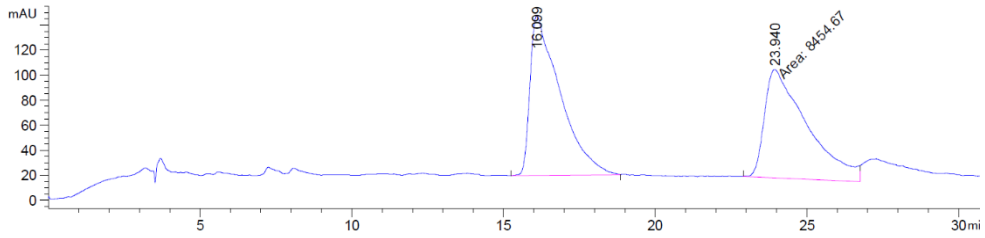

```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.037 MM    0.8582 6.16035e4  1196.37036  94.3174
   2  17.010 MM    0.6100 3711.58936  101.40859   5.6826
```



Chiral 1,2 formyl ferrocenyl acrylate 3m was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:140-141 ºC. Yield: 22 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.27 (d, J = 15.8 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 6.80 (dd, J = 18.2, 9.5 Hz, 3H), 6.45 (d, J = 15.7 Hz, 1H), 5.06 (s, 2H), 4.87 (s, 1H), 4.36 (s, 5H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6 (CH), 164.9 (C), 160.5 (C), 151.8 (C), 144.3 (CH), 129.8 (CH), 117.2 (CH), 113.8 (CH), 111.7 (CH), 107.6 (CH), 80.3 (C), 78.6 (C), 74.0 (CH), 72.0 (CH), 71.5 (CH), 68.6 (CH), 55.4 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{19}FeO_4$ 391.0627, found 391.0638. Enantioselectivity of **3m** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm).

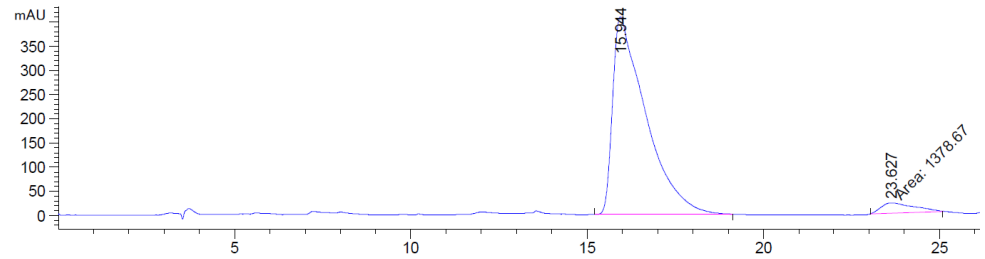
Racemic sample (**3m**)




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

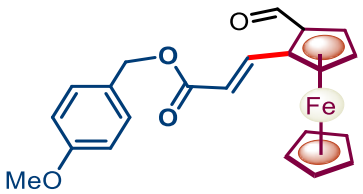
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.099 BB    0.9151 8782.60352  127.90868  50.9512
   2  23.940 MM    1.6299 8454.66797   86.45444  49.0488
```

Asymmetric sample (**3m**)



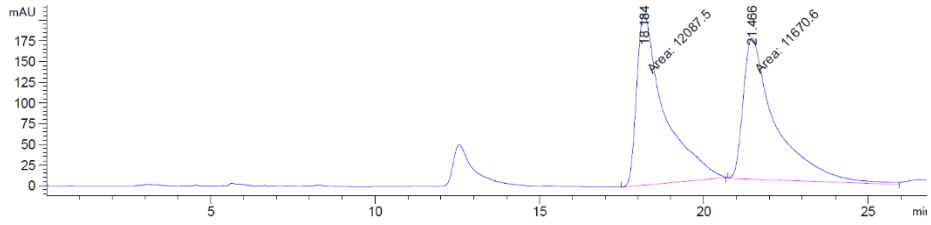

```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.944 BB    0.8717 2.66559e4   408.26297  95.0822
   2  23.627 MM    1.0800 1378.67236   21.27544   4.9178
```



Chiral 1,2 formyl ferrocenyl acrylate 3n was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:134-136 ºC. Yield: 28 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.07 (d, J = 15.9 Hz, 1H), 7.39 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.29 (d, J = 15.8 Hz, 1H), 5.19 (d, J = 2.8 Hz, 2H), 4.99 (d, J = 16.9 Hz, 2H), 4.81 (t, J = 2.6 Hz, 1H), 4.30 (s, 5H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (C), 166.6 (C), 159.7 (C), 142.3 (CH), 130.2 (CH), 128.2 (C), 118.0 (CH), 114.0 (CH), 80.8 (C), 78.4 (C), 74.0 (CH), 73.3 (CH), 71.8 (CH), 71.4 (CH), 66.1 (CH_2), 55.3 (CH_3). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{20}FeO_4Na$ 427.0603, found 427.0597. Enantioselectivity of **3n** was determined by chiral HPLC analysis on AD-3 (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

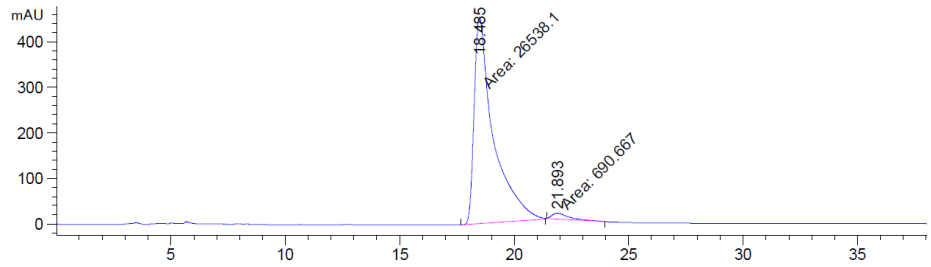
Racemic sample (**3n**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

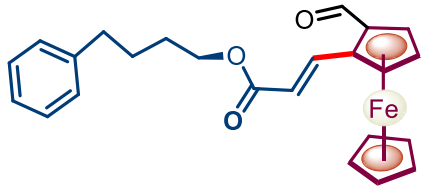
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.184	MM	0.9716	1.20875e4	207.33798	50.8775
2	21.466	MM	1.1415	1.16706e4	170.40532	49.1225

Asymmetric sample (**3n**)



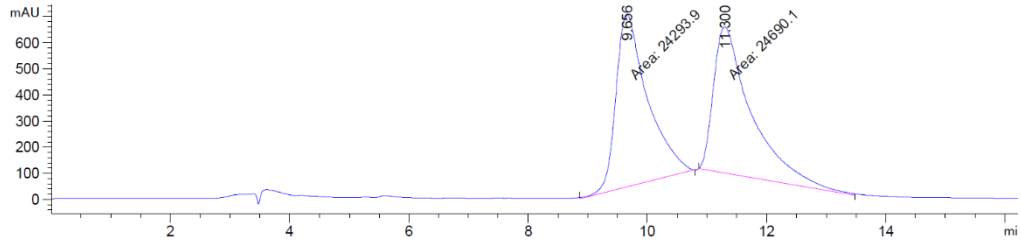
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.485	MM	0.9732	2.65381e4	454.48755	97.4635
2	21.893	MM	0.8803	690.66656	13.07585	2.5365



Chiral 1,2-formyl ferrocenyl acrylate 3o was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 75:25), obtained as an orange solid, mp:139 ºC. Yield: 29 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.04 (d, J = 16.0 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.23 (d, J = 7.4 Hz, 3H), 6.26 (d, J = 15.6 Hz, 1H), 5.00 (d, J = 9.5 Hz, 2H), 4.81 (s, 1H), 4.31 (s, 5H), 4.24 (t, J = 5.1 Hz, 2H), 2.71 (t, J = 6.3 Hz, 2H), 1.77 (t, J = 9.7 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6 (CH), 166.7 (C), 142.1 (C), 141.9 (CH), 128.4 (CH), 128.3 (CH), 125.8 (CH), 118.2 (CH), 80.9 (C), 78.4 (C), 74.0 (CH), 73.3 (CH), 71.7 (CH), 71.3 (CH), 68.6 (CH_2), 64.4 (CH_2), 35.5 (CH_2), 27.8 (CH_2). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{25}FeO_3$ 417.1148, found 417.1124. Enantioselectivity of **3o** was determined by chiral HPLC analysis on AD-3 (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

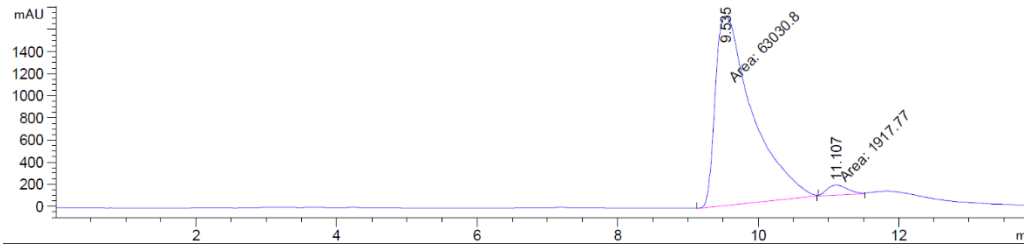
Racemic sample (**3o**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

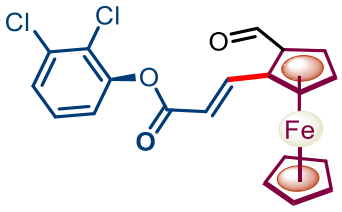
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.656	MM	0.6123	2.42939e4	661.30304	49.5956
2	11.300	MM	0.7360	2.46901e4	559.08557	50.4044

Asymmetric sample (**3o**)



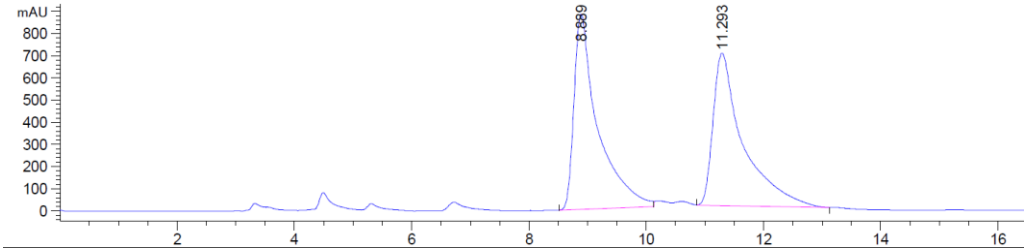
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.535	MM	0.6131	6.30308e4	1713.43518	97.0472
2	11.107	MM	0.3462	1917.77332	92.33771	2.9528



Chiral 1,2 formyl ferrocenyl acrylate 3p was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:142 ºC. Yield: 26 mg (55%). ^{1}H NMR (700 MHz, CDCl3) δ 10.20 (s, 1H), 8.36 (d, J = 15.9 Hz, 1H), 7.51 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 8.6, 2.5 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 6.46 (d, J = 15.8 Hz, 1H), 5.09 (d, J = 1.2 Hz, 1H), 5.07 (d, J = 2.8 Hz, 1H), 4.89 (t, J = 2.7 Hz, 1H), 4.36 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.7 (CH), 163.8 (C), 145.9 (C), 131.8 (C), 130.1 (CH), 128.0 (CH), 127.9 (CH), 124.7 (CH), 115.6 (CH), 79.5 (C), 78.8 (C), 74.6 (CH), 74.5 (CH), 72.0 (CH), 71.6 (CH). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{14}FeCl_2O_3Na$ 450.9562, found 450.9577. Enantioselectivity of **3p** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm).

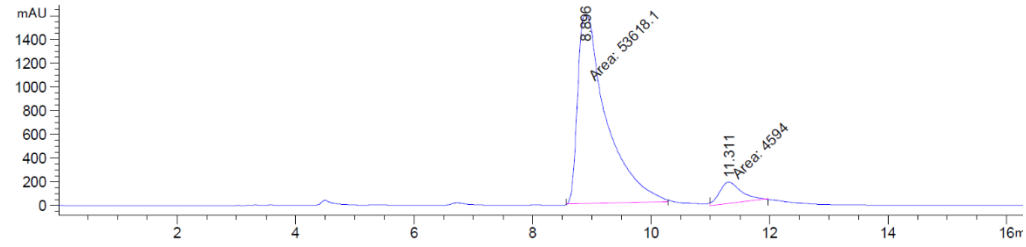
Racemic sample (**3p**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

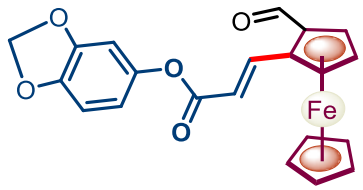
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.889	BV	0.3953	2.48767e4	881.30548	50.5071
2	11.293	BB	0.4978	2.43771e4	687.31519	49.4929

Asymmetric sample (**3p**)



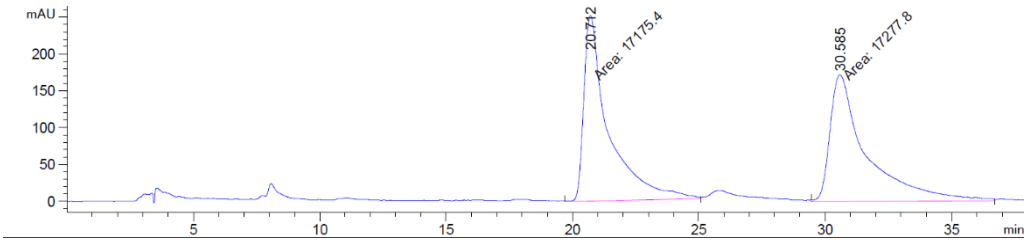
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.896	MM	0.5621	5.36181e4	1589.67603	92.1082
2	11.311	MM	0.4235	4594.00195	180.79378	7.8918



Chiral 1,2-formyl ferrocenyl acrylate 3q was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:140-141 ºC. Yield: 26 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.25 (d, J = 15.3 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.73 (s, 1H), 6.64 (d, J = 8.3 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.02 (s, 2H), 5.05 (s, 2H), 4.87 (s, 1H), 4.36 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (CH), 165.3 (C), 148.0 (C), 145.3 (C), 145.1 (C), 144.3 (CH), 117.0 (CH), 114.0 (CH), 108.0 (CH), 103.8 (CH), 101.7 (CH_2), 80.2 (C), 78.6 (C), 74.3 (CH), 74.0 (CH), 71.9 (CH), 71.5 (CH). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{17}FeO_5$ 405.0420, found 405.0428. Enantioselectivity of **3q** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

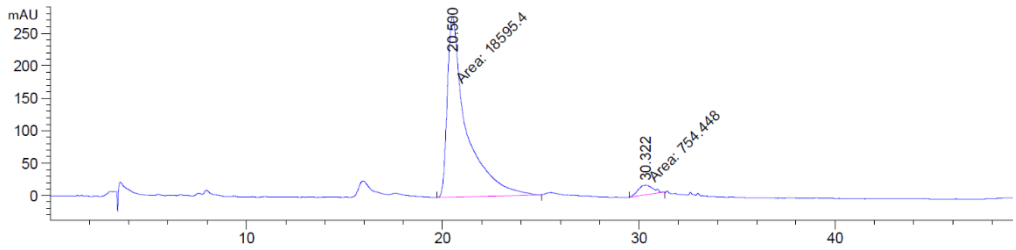
Racemic sample (**3q**)




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.712 MM    1.1358 1.71754e4   252.02060  49.8513
   2  30.585 MM    1.6706 1.72778e4   172.37042  50.1487
```

Asymmetric sample (**3q**)

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.500 MM    1.1164 1.85954e4   277.61673  96.1010
   2  30.322 MM    0.8682  754.44818   14.48236   3.8990
```
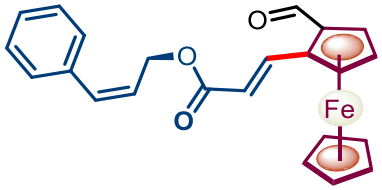
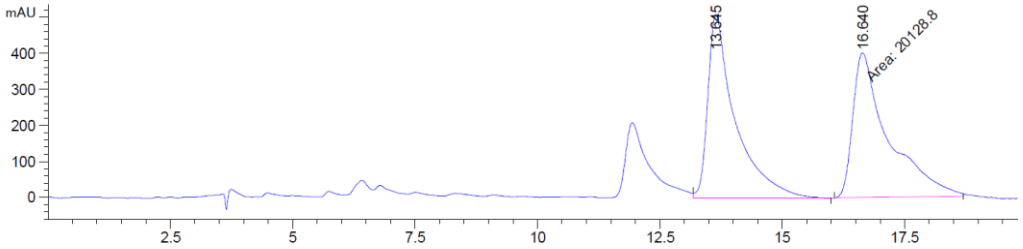



Chiral 1,2-formyl ferrocenyl acrylate 3r was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:132-135 ºC. Yield: 26 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.11 (d, J = 16.0 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.39 – 7.30 (m, 3H), 6.74 (d, J = 16.0 Hz, 1H), 6.47 – 6.35 (m, 1H), 6.31 (d, J = 15.8 Hz, 1H), 5.05 – 4.97 (m, 2H), 4.88 (d, J = 6.2 Hz, 2H), 4.82 (s, 1H), 4.32 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (CH), 166.4 (C), 142.4 (C), 136.2 (CH), 134.2 (CH), 128.6 (CH), 128.0 (CH), 126.6 (CH), 123.3 (CH), 117.9 (CH), 80.7 (CH), 78.4 (CH), 74.0 (CH), 73.0 (CH), 71.7 (CH), 71.4 (CH), 65.1 (CH_2). HRLCMS (ESI) *m/z*: [M+H]+ calcd for $C_{23}H_{21}FeO_3$ 401.0835, found 401.0851. Enantioselectivity of **3r** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

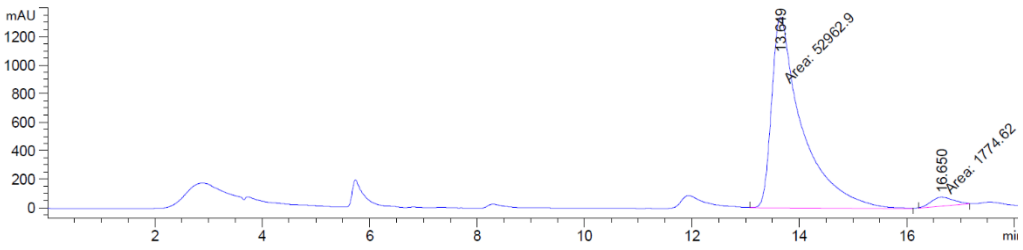
Racemic sample (**3r**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

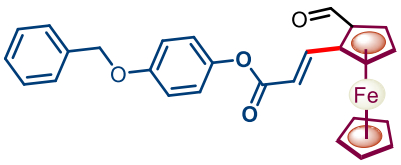
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.645	VB	0.5438	1.99172e4	509.78543	49.7357
2	16.640	MM	0.8363	2.01288e4	401.14093	50.2643

Asymmetric sample (**3r**)



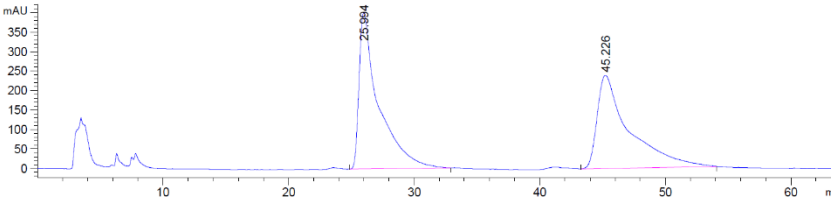
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.649	MM	0.6593	5.29629e4	1338.79089	96.7579
2	16.650	MM	0.4740	1774.62085	62.39433	3.2421



Chiral 1,2 formyl ferrocenyl acrylate 3s was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as an orange solid, mp:135-137 ºC. Yield: 27 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.25 (d, J = 14.9 Hz, 1H), 7.52 – 7.35 (m, 7H), 7.12 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 6.45 (d, J = 14.5 Hz, 1H), 5.09 (s, 2H), 5.06 (s, 2H), 4.86 (s, 1H), 4.36 (s, 5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 192.6 (CH), 165.4 (C), 156.44 (C), 144.5 (C), 144.0 (C), 128.6 (CH), 128.0 (CH), 127.5 (CH), 122.4 (CH), 117.3 (CH), 116.0 (CH), 115.4 (CH), 80.4 (C), 78.6 (C), 74.2 (CH), 73.9 (CH), 71.9 (CH), 71.5 (CH), 70.4 (CH_2). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{23}FeO_4$ 467.0941, found 467.0964. Enantiopurity of **3s** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

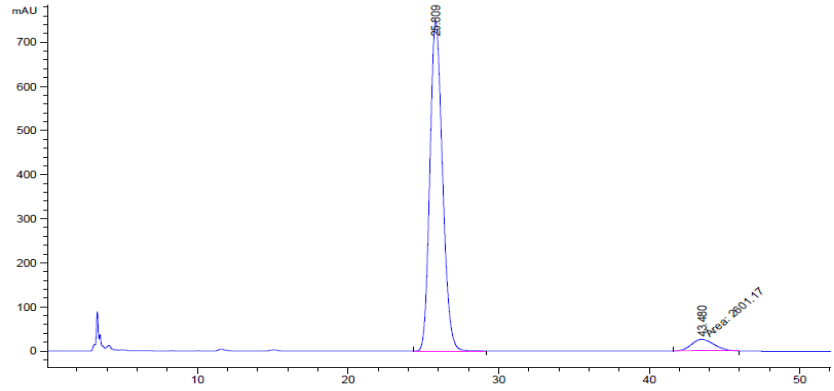
Racemic sample (**3s**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

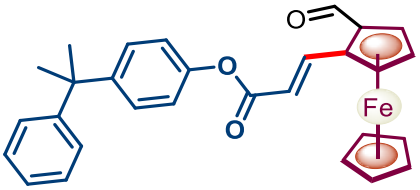
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.994	BB	1.4783	4.35806e4	402.78561	50.7998
2	45.226	BB	2.3625	4.22083e4	239.21284	49.2002

Asymmetric sample (**3s**)



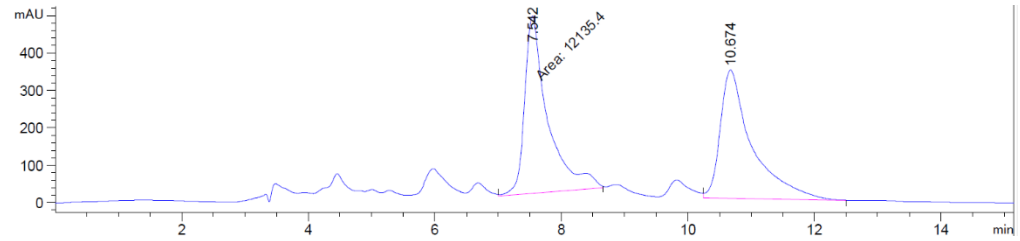
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.809	BB	0.9061	4.35442e4	747.00928	94.3631
2	43.480	MM	1.6794	2601.16553	25.81367	5.6369



Chiral 1,2-formyl ferrocenyl acrylate 3t was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 75:25), obtained as an orange solid, mp:137-139 ºC. Yield: 33 mg (62%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.24 (d, J = 15.8 Hz, 1H), 7.30 (d, J = 7.1 Hz, 2H), 7.28 – 7.25 (m, 4H), 7.23 – 7.19 (m, 1H), 7.09 (d, J = 8.7 Hz, 2H), 6.44 (d, J = 15.8 Hz, 1H), 5.13 – 4.99 (m, 2H), 4.87 (t, J = 2.7 Hz, 1H), 4.35 (s, 5H), 1.72 (s, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.8 (CH), 165.2 (C), 150.4 (C), 148.6 (C), 148.1 (CH), 144.2 (CH), 128.0 (CH), 127.8 (CH), 126.8 (CH), 125.7 (CH), 120.9 (CH), 117.2 (CH), 80.3 (C), 78.5 (C), 74.3 (CH), 74.0 (CH), 72.0 (CH), 71.5 (CH), 42.7 (C), 30.8 (CH_3). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{29}H_{26}FeO_3Na$ 501.1124, found 501.1149. Enantiopurity of **3t** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm).

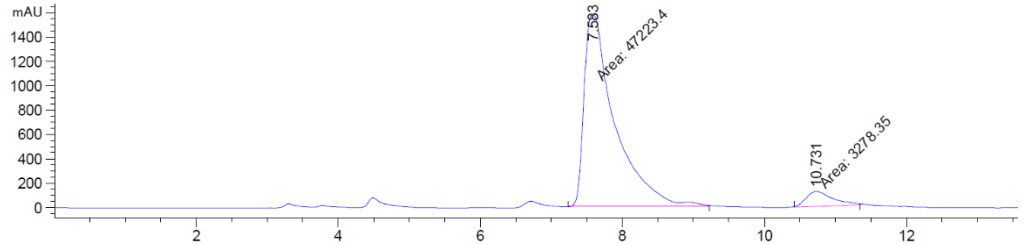
Racemic sample (**3t**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

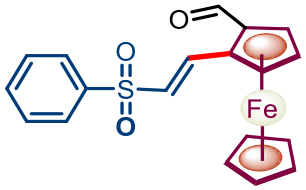
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.542	MM	0.4264	1.21354e4	474.28387	50.4304
2	10.674	VB	0.4900	1.19283e4	342.76691	49.5696

Asymmetric sample (**3t**)



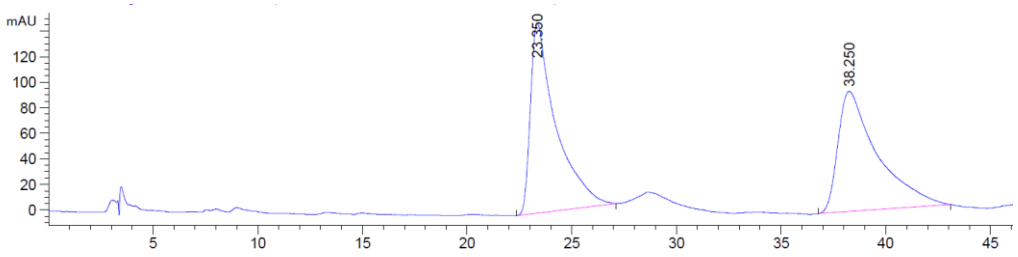
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.583	MM	0.4978	4.72234e4	1581.15308	93.5084
2	10.731	MM	0.4393	3278.35181	124.37627	6.4916



Chiral 1,2-formyl ferrocenyl acrylate (3u) was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:124-126 ºC. Yield: 25 mg (61%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.08 (d, J = 15.2 Hz, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.63 (t, J = 9.5 Hz, 1H), 7.57 (t, J = 9.2 Hz, 2H), 6.82 (d, J = 15.3 Hz, 1H), 5.02 (s, 1H), 4.92 (s, 1H), 4.82 (s, 1H), 4.31 (s, 5H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.4 (CH), 141.0 (C), 140.8 (CH), 133.2 (CH), 129.3 (CH), 127.5 (CH), 126.5 (CH), 78.8 (C), 78.0 (C), 75.0 (CH), 74.4 (CH), 72.7 (CH), 71.5 (CH). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{17}FeO_3S$ 381.0242, found 381.0247. Enantiopurity of **3u** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm).

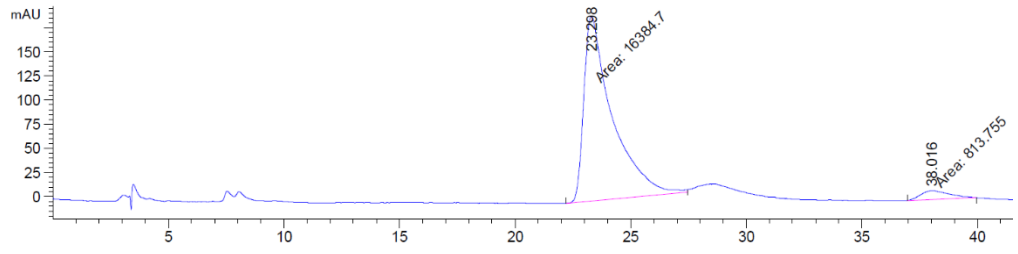
Racemic sample (**3u**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

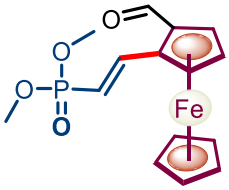
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.350	BB	1.1577	1.25977e4	148.80722	50.6608
2	38.250	BB	1.8061	1.22691e4	94.03867	49.3392

Asymmetric sample (**3u**)



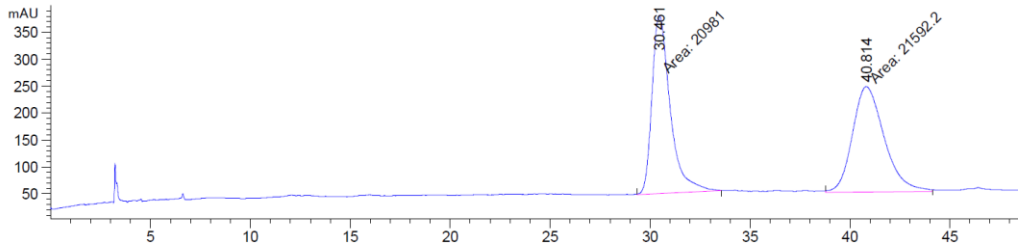
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.298	MM	1.4254	1.63847e4	191.58116	95.2685
2	38.016	MM	1.4444	813.75458	9.38964	4.7315



Chiral 1,2-formyl ferrocenyl acrylate 3v was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:128 ºC. Yield: 25 mg (65%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.84 (dd, J = 22.0, 17.4 Hz, 1H), 6.09 (t, J = 18.1 Hz, 1H), 5.17 – 4.90 (m, 2H), 4.80 (t, J = 2.7 Hz, 1H), 4.30 (s, 5H), 3.81 (dd, J = 11.1, 4.6 Hz, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (d, $J_{C\text{-}P}$ = 3.6 Hz; CH), 146.4 (d, $J_{C\text{-}P}$ = 7.5 Hz; CH), 112.4 (d, $J_{C\text{-}P}$ = 192.6 Hz; CH), 81.4 (d, $J_{C\text{-}P}$ = 27.2 Hz; C), 78.1 (CH), 73.9 (CH), 73.7 (CH), 71.8 (CH), 71.4 (CH), 52.5 (CH_3). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{17}FeO_4PNa$ 371.0106, found 371.0087. Enantiopurity of **3v** was determined by chiral HPLC analysis on OJ-3 (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm).

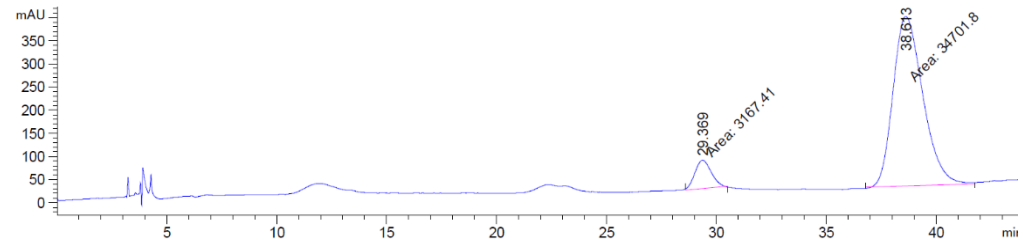
Racemic sample (**3v**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

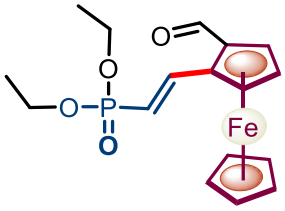
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.461	MP	1.0571	2.09810e4	330.78006	49.2821
2	40.814	MM	1.8387	2.15922e4	195.71974	50.7179

Asymmetric sample (**3v**)



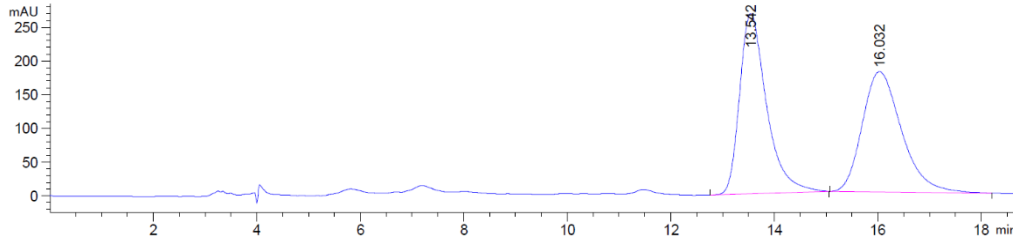
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.369	MM	0.8577	3167.40869	61.55090	8.3641
2	38.613	MM	1.5779	3.47018e4	366.54413	91.6359



Chiral 1,2-formyl ferrocenyl acrylate 3w was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:135-136 ºC. Yield: 27mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.81 (dd, J = 21.8, 17.6 Hz, 1H), 6.12 (dd, J = 18.0, 17.4 Hz, 1H), 4.98 (s, 2H), 4.79 (s, 1H), 4.30 (s, 5H), 4.24 – 4.06 (m, 4H), 1.40 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.6 (d, $J_{C\text{-}P}$ = 4.2 Hz; CH), 145.3 (d, $J_{C\text{-}P}$ = 7.5 Hz; CH), 114.1 (d, $J_{C\text{-}P}$ = 191.9 Hz; CH), 81.7 (d, $J_{C\text{-}P}$ = 27.2 Hz; C), 78.0 (C), 73.8 (CH), 73.4 (CH), 71.7 (CH), 71.3 (CH), 61.9 (dd, $J_{C\text{-}P}$ = 12.0, 5.5 Hz; CH_2), 16.4 (d, $J_{C\text{-}P}$ = 6.3 Hz; CH_3). Enantiopurity of **3w** was determined by chiral HPLC analysis on OJ-3 (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm).

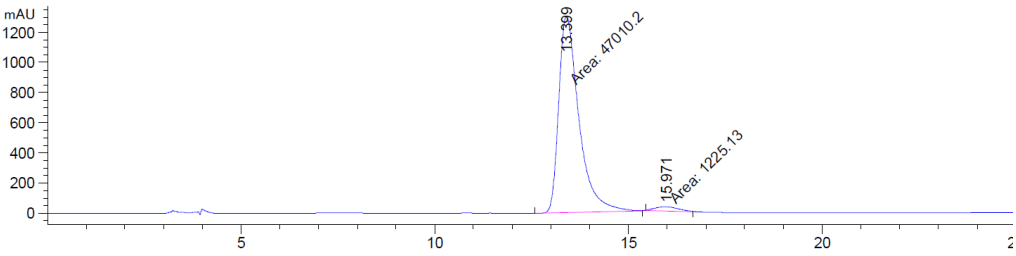
Racemic sample (**3w**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

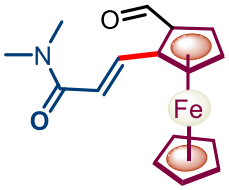
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.542	BB	0.5477	9667.14551	267.46536	50.6685
2	16.032	BB	0.8056	9412.03809	178.38710	49.3315

Asymmetric sample (**3w**)



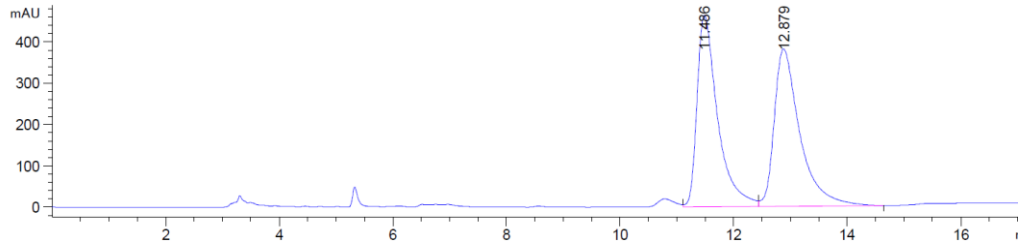
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.399	MM	0.6020	4.70102e4	1301.45166	97.4601
2	15.971	MM	0.7151	1225.13220	28.55343	2.5399



Chiral 1,2-formyl ferrocenyl acrylate 3x was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as an orange solid, mp:130-132 ºC. Yield: 19 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.83 (d, J = 15.2 Hz, 1H), 6.83 (d, J = 14.5 Hz, 1H), 5.01 (s, 1H), 4.93 (s, 1H), 4.77 (s, 1H), 4.30 (s, 5H), 3.17 (s, 3H), 3.08 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.5 (CH), 166.5 (C), 138.5 (CH), 118.1 (CH), 82.9 (C), 78.0 (C), 73.5 (CH), 72.7 (CH), 72.4 (CH), 71.2 (CH), 42.6 (CH_3). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{16}H_{17}FeNO_2Na$ 334.0501, found 334.0509. Enantiopurity of **3x** was determined by chiral HPLC analysis on OJ-3 (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

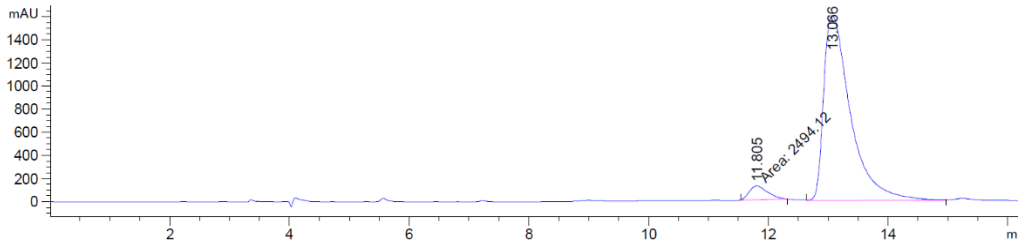
Racemic sample (**3x**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

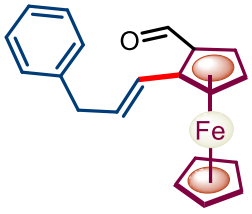
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.486	VV	0.3759	1.16881e4	464.00394	49.3571
2	12.879	VB	0.4674	1.19926e4	380.86612	50.6429

Asymmetric sample (**3x**)

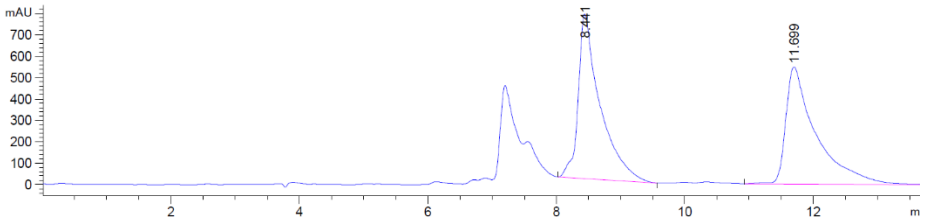


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.805	MM	0.3494	2494.11694	118.98089	4.7613
2	13.066	VV	0.4673	4.98895e4	1601.95691	95.2387



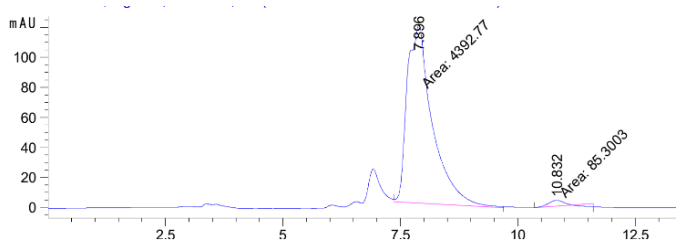
Chiral 1,2-formyl ferrocenyl acrylate 3y was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 70:30), obtained as a yellow-orange solid, mp:113-115 ºC. Yield: 17 mg (48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.43 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 6.55 – 6.28 (m, 2H), 4.78 (s, 1H), 4.56 (d, J = 14.4 Hz, 2H), 4.28 (s, 5H), 3.70 – 3.45 (m, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 193.7 (CH), 137.3 (C), 130.9 (CH), 128.6 (CH), 128.5 (CH), 127.2 (CH), 126.1 (CH), 90.0 (C), 74.0 (C), 73.2 (CH), 71.43 (CH), 70.3 (CH), 70.1 (CH), 31.4 (CH_2). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{18}FeONa$ 353.0599, found 353.0621. Enantiopurity of **3y** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm). Racemic sample (**3y**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

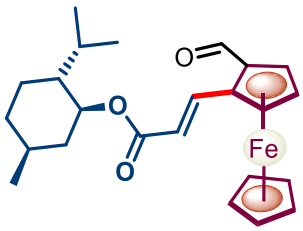
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.441	BB	0.3223	1.82336e4	769.84558	50.4824
2	11.699	BBA	0.4470	1.78851e4	547.68359	49.5176

Asymmetric sample (**3y**)

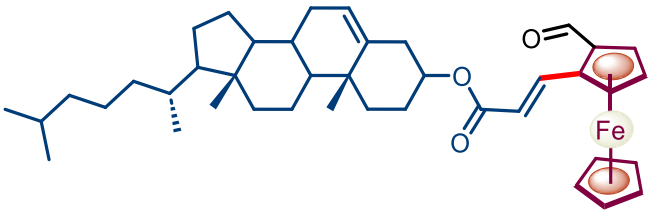


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.896	MM	0.6170	4392.77344	118.65778	98.0952
2	10.832	MM	0.3680	85.30027	3.86302	1.9048



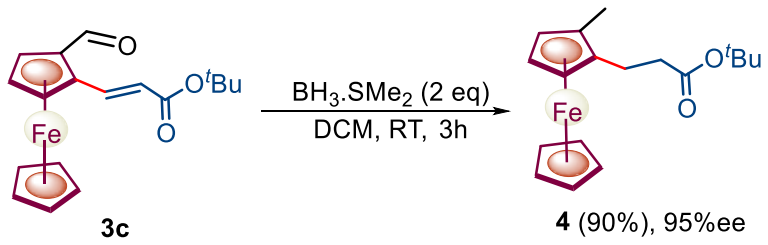
Chiral 1,2-formyl ferrocenyl acrylate 3z was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 85:15), obtained as a yellow-orange solid, mp:123-126 ºC. Yield: 24 mg (51%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.98 (d, J = 15.8 Hz, 1H), 6.25 (d, J = 15.8 Hz, 1H), 5.01 (dd, J = 2.6, 1.3 Hz, 1H), 4.99 (d, J = 2.3 Hz, 1H), 4.84 – 4.79 (m, 2H), 4.31 (s, 5H), 2.09 (t, J = 7.9 Hz, 1H), 1.95 (ddd, J = 13.9, 9.1, 4.2 Hz, 1H), 1.73 (dd, J = 14.1, 2.6 Hz, 3H), 1.51 – 1.46 (m, 1H), 1.10 – 1.03 (m, 2H), 0.94 (dd, J = 6.8, 1.0 Hz, 6H), 0.83 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 192.9 (CH), 166.5 (C), 141.6 (CH), 118.8 (CH), 81.1 (C), 78.1 (C), 74.4 (CH), 74.0 (CH), 73.2 (CH), 72.0 (CH), 71.4 (CH), 47.1 (CH), 40.9 (CH), 34.2 (CH), 31.4 (CH_2), 26.42 (CH_2), 23.62 (CH_2), 22.0 (CH_3), 20.7 (CH_3), 16.5 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{31}FeO_3$ 423.1617, found 423.1631.



Chiral 1,2-formyl ferrocenyl acrylate 3aa was purified on silica gel (mesh 230-400) in (hexanes: ethylacetate; 80:20), obtained as a yellow-orange solid, mp:133-135 ºC. Yield: 36 mg (49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (d, J = 1.9 Hz, 1H), 8.00 (d, J = 15.8 Hz, 1H), 6.25 (d, J = 15.8 Hz, 1H), 5.42 (d, J = 5.0 Hz, 1H), 5.00 (t, J = 3.1 Hz, 2H), 4.81 (t, J = 2.8 Hz, 1H), 4.79 – 4.69 (m, 1H), 4.31 (s, 5H), 2.42 (d, J = 7.9 Hz, 2H), 2.00 – 1.83 (m, 5H), 1.70 (m, 1H), 1.57 – 1.44 (m, 5H), 1.36 (dd, J = 7.8, 3.5 Hz, 3H), 1.21 – 1.11 (m, 4H), 1.07 (s, 3H), 0.94 (d, J = 6.5 Hz, 4H), 0.89 (dd, J = 6.6, 2.3 Hz, 9H), 0.71 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 193.0 (CH), 166.3 (C), 141.8 (CH), 139.6 (CH), 122.7 (CH), 118.7 (CH), 80.9 (C), 78.2 (C), 74.2 (CH), 74.1 (CH), 73.4 (CH), 71.9 (CH), 71.4 (CH), 56.7 (CH_2), 56.1 (CH_2), 50.0 (C), 42.3 (C), 39.7 (CH), 39.5 (CH), 38.2 (CH), 37.0 (CH), 36.6 (CH), 36.1 (CH), 35.8 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 28.2 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 24.3 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 22.5 (CH_2), 21.0 (CH_3), 19.3 (CH_3), 18.7 (CH_3), 11.8 (CH_3). HRLCMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{42}H_{58}FeO_3$ 666.3731, found 666.3711.

Post-synthetic Transformation of Chiral 1,2-Ferrocene Formaldehydes

Reduction of *tert*-butyl-(*E*)-3-(2-formylferrocenyl)acrylate 3c with $BH_3 \cdot SMe_2$

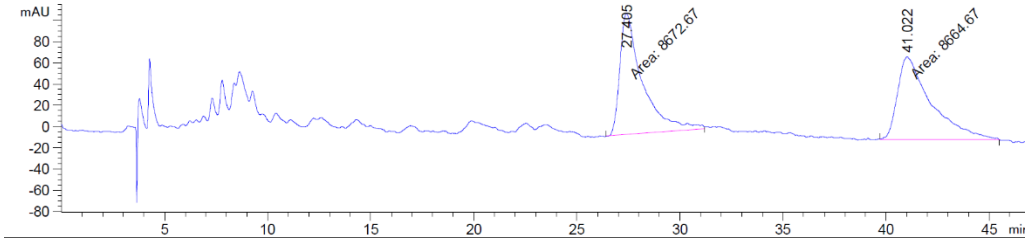


3c **4** (90%), 95%ee

Scheme S2. Reduction with $BH_3 \cdot SMe_2$

In a Schlenk tube, *tert*-butyl-(*E*)-3-(2-formylferrocenyl)acrylate **3c** (17 mg, 0.05 mmol, 1 equiv), $BH_3.SMe_2$ (20 µL, 0.1mmol, 2 equiv) was mixed in DCM at room temperature and stirred for 3h under an inert atmosphere. The crude reaction mixture passed through a celite pad, quenched with 1N HCl, evaporation, and column chromatography on silica gel (mesh 230-400) using hexane: ethyl acetate solvent system to afford *tert*-butyl 3-(*o*-methylferrocenyl)propanoate (**4)** as a yellow solid (mp:129-131 ºC). Yield: 15 mg (90%).^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (s, 6H), 3.99 (dd, J = 2.5, 1.5 Hz, 1H), 3.93 (t, J = 2.4 Hz, 1H), 2.72 – 2.61 (m, 2H), 2.49 – 2.36 (m, 2H), 1.98 (s, 3H), 1.48 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6 (C), 86.2 (C), 82.6 (C), 80.3 (CH), 77.2 (CH), 69.1 (CH), 67.2 (CH), 64.9 (C), 36.5 (CH_2), 28.1 (CH_2), 23.5 (CH_3), 13.1 (CH_3). HRLCMS (ESI) *m/z*: [M] calcd for $C_{18}H_{24}FeO_2$ 328.1120, found 328.1118. Enantiopurity of **4** was determined by chiral HPLC analysis on OJ-3 (hexane: isopropanol = 100:00, 0.5 mL/min, λ=254 nm).

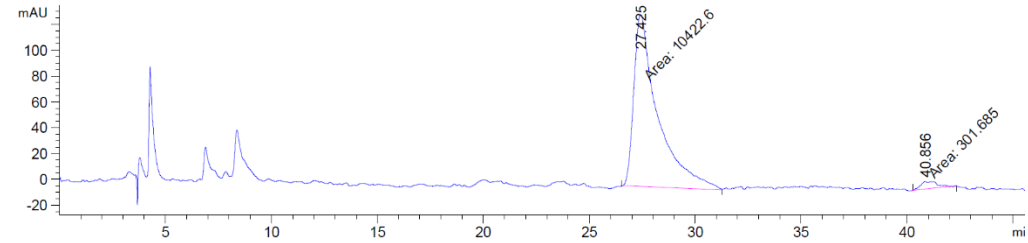
Racemic sample (**4**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.405	MM	1.2700	8672.67090	113.81454	50.0231
2	41.022	MM	1.8593	8664.66699	77.67159	49.9769

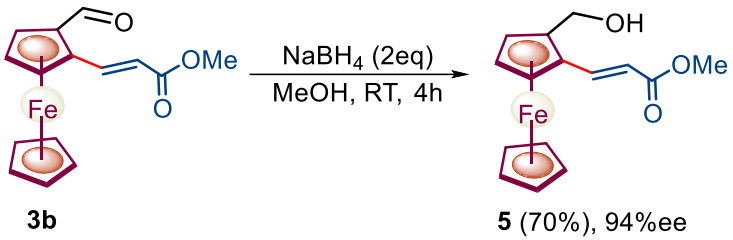
Asymmetric sample (**4**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.425	MM	1.3058	1.04226e4	133.02591	97.1869
2	40.856	MM	0.8524	301.68549	5.89861	2.8131

Reduction of methyl-(*E*)-3-(2-formylferrocenyl)acrylate 3b with sodium borohydride

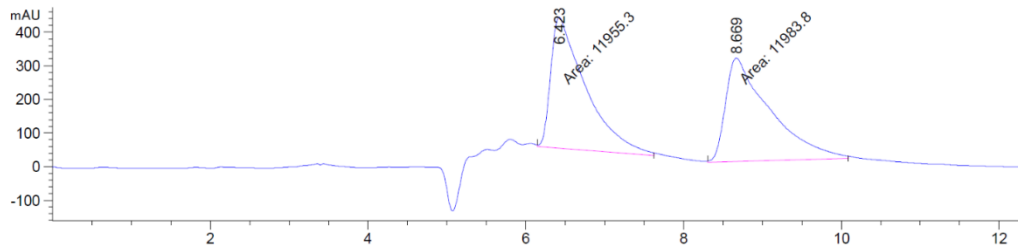


3b **5** (70%), 94%ee

Scheme S3. Reduction with $NaBH_4$

In a Schlenk tube, methyl-(*E*)-3-(2-formylferrocenyl)acrylate **3b** (17 mg, 0.05 mmol, 1 equiv), $NaBH_4$ (4 mg, 0.11mmol, 2.1 equiv) was mixed in MeOH at room temperature and stirred for 4h under an inert atmosphere. The crude reaction mixture passed through a celite pad, quenched with 1N HCl, evaporation, and column chromatography on silica gel (mesh 230-400) using hexane: ethyl acetate solvent system to afford methyl-(*E*)-3-(2-(hydroxymethyl)ferrocenyl)acrylate (**5)** as a yellow solid (mp: 131-134 ºC). Yield: 11 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 15.7 Hz, 1H), 6.16 (d, J = 15.8 Hz, 1H), 4.68 – 4.56 (m, 2H), 4.53 (s, 2H), 4.45 (s, 1H), 4.19 (s, 5H), 3.80 (s, 3H), 2.07 (s, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 167.5 (C), 143.5 (CH), 115.7 (CH), 88.2 (C), 78.0 (C), 71.9 (CH), 70.0 (CH), 67.7 (CH), 60.4 (CH), 59.1 (CH_3), 51.5 (CH_2). HRLCMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{16}FeO_3Na$ 323.0341, found 323.0319. Enantiopurity of **5** was determined by chiral HPLC analysis on AD-H (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

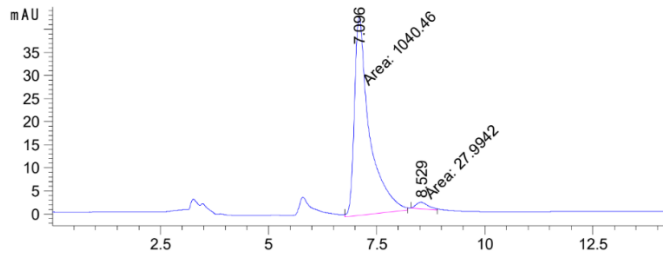
Racemic sample (**5**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.423	MM	0.5109	1.19553e4	390.03912	49.9404
2	8.669	MM	0.6492	1.19838e4	307.66867	50.0596

Asymmetric sample (**5**)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

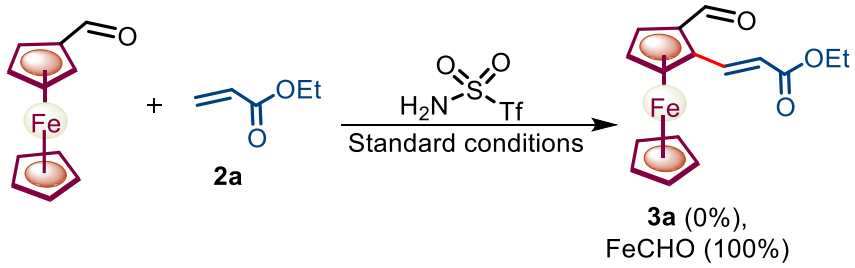
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.096	MM	0.4031	1040.45667	43.01512	97.3799
2	8.529	MM	0.3294	27.99417	1.41633	2.6201

Mechanistic Investigation

Control experiment 1: Understanding of C-H activation versus oxidation pathways

(a) Possibility of transient directed C-H activation

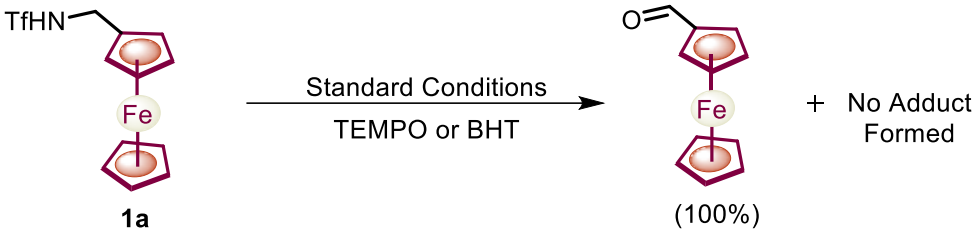
In a Schlenk tube, $Pd(OAc)_2$ (2.3 mg, 0.011 mmol, 10 mol%), **L2** (10 mg, 0.044 mmol, 40 mol %), $Cu(OAc)_2$ (30.0 mg, 0.16 mmol, 1.5 equiv), Cs_2CO_3 (71.2 mg, 0.22 mmol, 2 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv), ferrocene carboxaldehyde (24 mg, 0.11 mmol, 1 equiv), and trifluoromethanesulfonamide (16 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl alcohol (1.5 mL) under an argon atmosphere and the resulted green colored solution was stirred for 10 min. After pre-stirring, olefin **2a** (24 µL, 0.22 mmol, 2 equiv) was added. The tube was sealed with a rubber septum, and a dry air atmosphere was maintained in the flask with a balloon. The reaction was heated at 55 °C, stirred for 30 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, evaporation, and subjected to crude NMR.



Scheme S4. Controlled experiment for determining the possibility of transient directed C-H activation

(b) Possibility of free radical-driven amine oxidation.

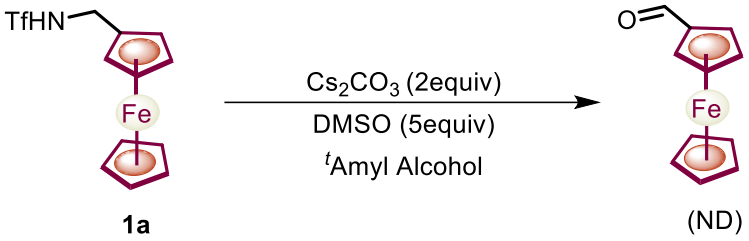
In a Schlenk tube, $Pd(OAc)_2$ (2.3 mg, 0.011 mmol, 10 mol%), **L2** (10 mg, 0.044 mmol, 40 mol %), $Cu(OAc)_2$ (30.0 mg, 0.16 mmol, 1.5 equiv), Cs_2CO_3 (71 mg, 0.22 mmol, 2 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv) TEMPO (17 mg, 0.11 mmol, 1 equiv) or BHT (24 mg, 0.11 mmol, 1 equiv) and ferrocenyl amine **1a** (38 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl Alcohol (1.5 mL) under a dry AIR atmosphere. The reaction was heated at 55 °C, stirred for 30 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, evaporation, and subjected to crude NMR and mass analysis.



Scheme S5. Controlled experiment for free radical-driven amine oxidation

(c) Possibility of base driven amine deamination

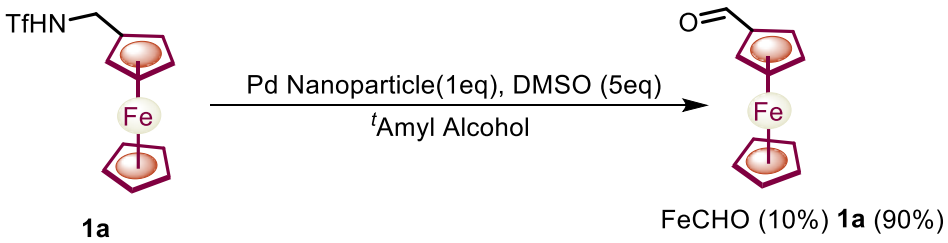
In a Schlenk tube, Cs_2CO_3 (71 mg, 0.22 mmol, 2 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv) and ferrocenyl amine **1a** (38 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl Alcohol (1.5 mL) under a dry air atmosphere. The reaction was heated at 55 °C, stirred for 30 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, evaporation, and subjected to crude NMR.



Scheme S6. Controlled experiment with base Cs_2CO_3

(d). Possibility of heterogeneous palladium nanoparticle-driven amine oxidation

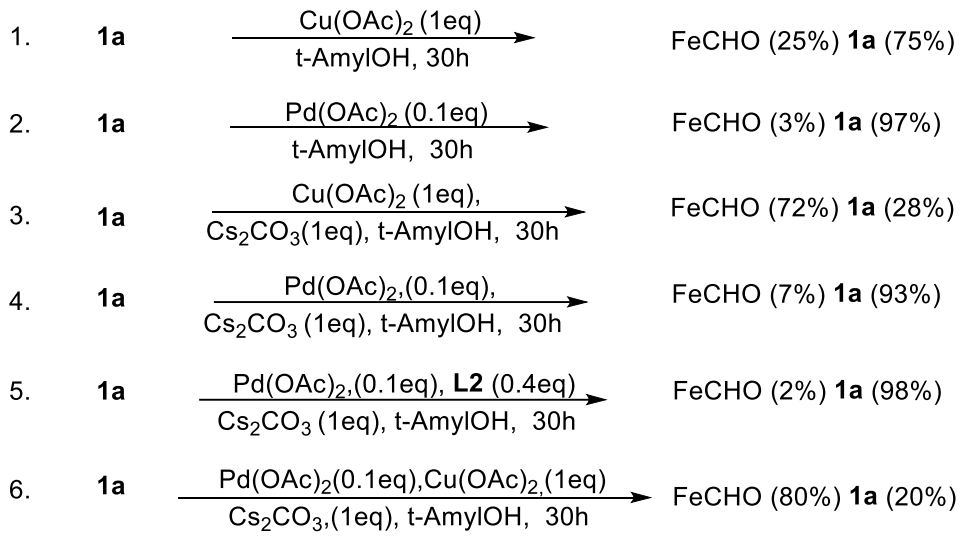
In a Schlenk tube, Pd(NPs) (12 mg, 0.11 mmol, 1 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv) and ferrocenyl amine **1a** (38 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl Alcohol (1.5 mL) under a dry air atmosphere. The reaction was heated at 55 °C, stirred for 30 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, dried under vacuo, and subjected to crude NMR.



Scheme S7. Controlled experiment with Pd nanoparticles

(e) Possibility of transition metal-driven amine oxidation

In a Schlenk tube, the stoichiometry of the reagents was varied as shown in Scheme S12 below. The reaction was heated at 55 °C, stirred for 30 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, evaporation, and subjected to crude NMR.



Scheme S8. Controlled experiments with variation in stoichiometry of the reagents

Control experiment 2: Relative rate of C-H activation versus amine oxidation with ligand (L2)

In a Schlenk tube, $Pd(OAc)_2$ (2.3 mg, 0.011 mmol, 10 mol%), **L2** (10 mg, 0.044 mmol, 40 mol %), $Cu(OAc)_2$ (30 mg, 0.16 mmol, 1.5 equiv), Cs_2CO_3 (71 mg, 0.22 mmol, 2 equiv), DMSO (40 μL, 0.55 mmol, 5 equiv), and ferrocenyl amine **1b** (44 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl alcohol (1.5 mL) under an inert atmosphere and the result in green colored solution was stirred for 10 min. Next, olefin **2d** (34 μL, 0.22 mmol, 2 equiv) was added to the reaction mixture. The tube was sealed with a rubber septum, and a dry air atmosphere was maintained in the flask with a balloon. The reaction was heated at 55 °C, and after every 10 min time interval 250μL aliquot was taken and passed through a celite pad, evaporation and submitted for crude ^{1}H NMR. Fractional conversion of C-H activated product with oxidized aldehyde has been monitored with time.

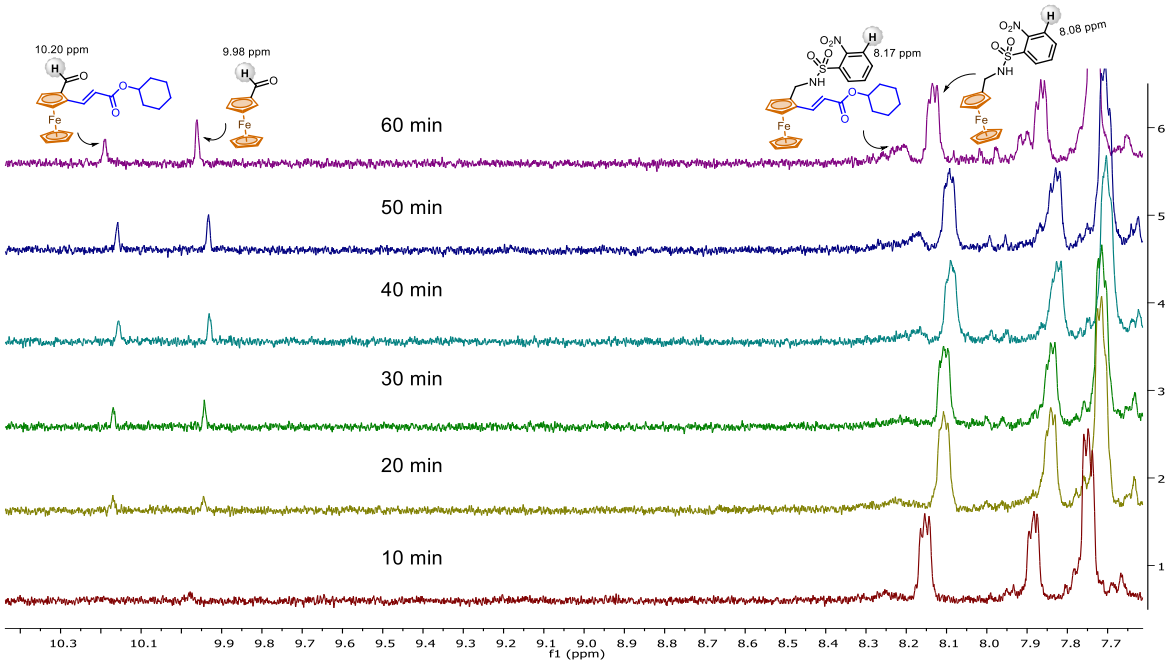


Figure S4. ^{1}H NMR plot for fractional conversion of C-H activated product along with FeCHO with time

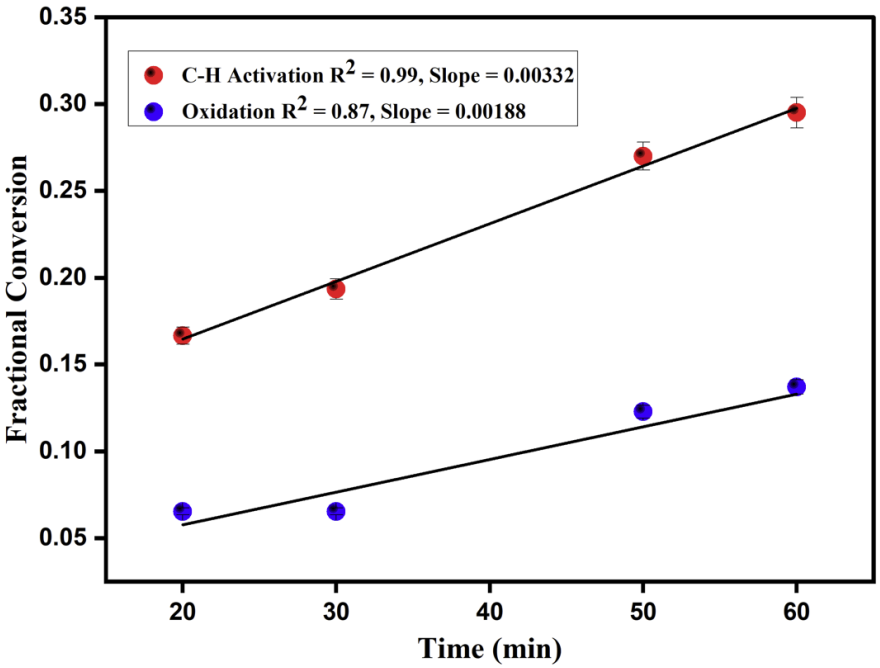


Figure S5. Plot for a relative rate of C-H activation and amine oxidation *versus* time with **L2**

Control experiment 3: Relative rate of C-H activation *versus* amine oxidation without ligand (L2)

In a Schlenk tube, $Pd(OAc)_2$ (2.3 mg, 0.011 mmol, 10 mol%), $Cu(OAc)_2$ (30 mg, 0.16 mmol, 1.5 equiv), Cs_2CO_3 (71 mg, 0.22 mmol, 2 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv), and ferrocenyl amine **1b** (44 mg, 0.11 mmol, 1 equiv) were added in dry *tert*-amyl alcohol (1.5 mL) under an inert atmosphere and the resulted in green colored solution was stirred for 10 min. Next, olefin **2d** (34 µL, 0.22 mmol, 2 equiv) was added to the reaction mixture. The tube was sealed with a rubber septum, and a dry air atmosphere was maintained in the flask with a balloon. The reaction was heated at 55 °C, and after every 10 min time interval 250 µL aliquot was taken and passed through a celite pad, evaporation and submitted for crude ^{1}H NMR. Fractional conversion of C-H activated product with oxidized aldehyde has been monitored with time.

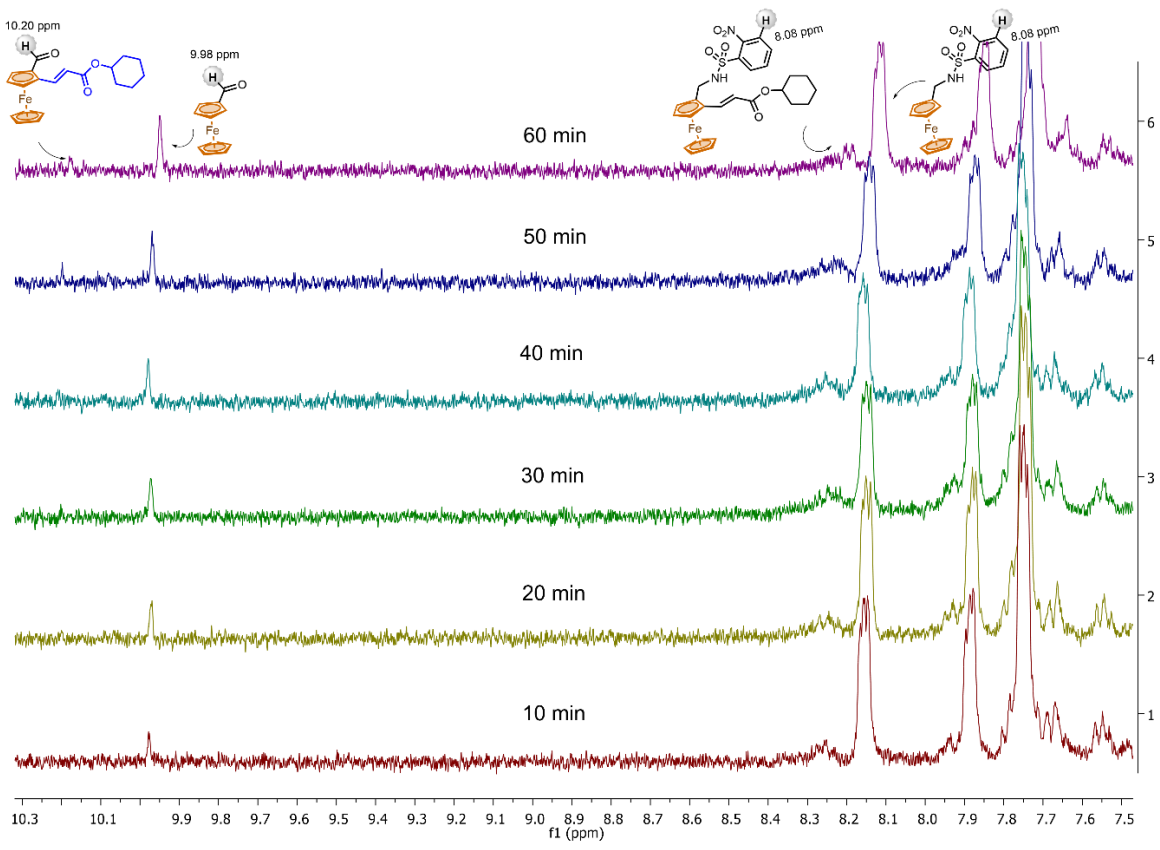


Figure S6. NMR plot for fractional conversion of C-H activated product along with oxidized FeCHO with time

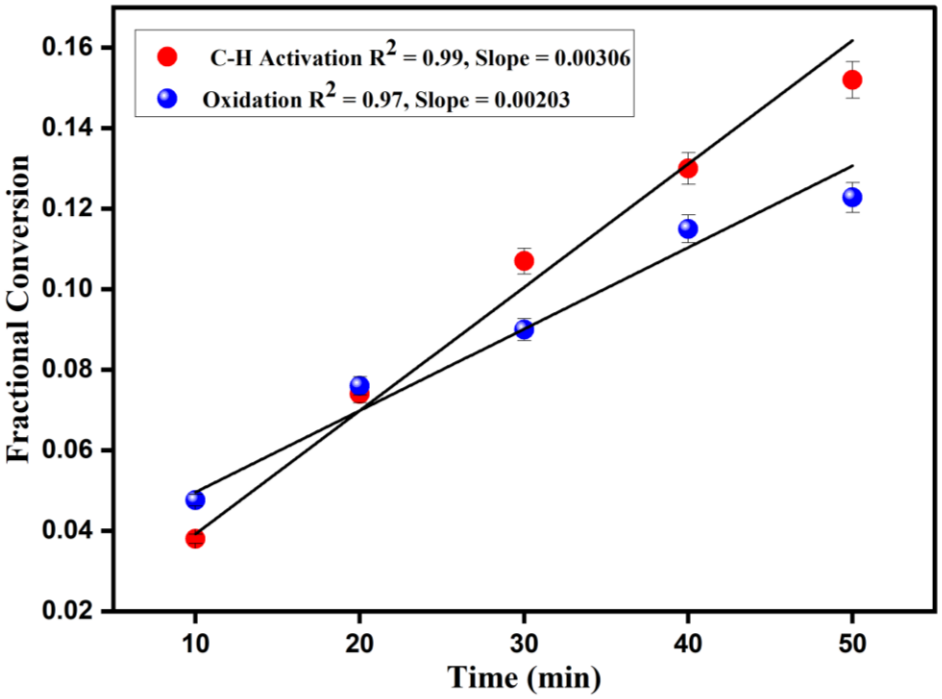


Figure S7. Plot for a relative rate of C-H activation *versus* amine oxidation without **L2**

Control experiment 4: Ligand acceleration experiment

Two parallel reactions were performed in two different Schlenk tubes. In one Schlenk tube, $Pd(OAc)_2$ (2.3 mg, 0.011 mmol, 10 mol%), $Cu(OAc)_2$ (30 mg, 0.16 mmol, 1.5 equiv), Cs_2CO_3 (71 mg, 0.22 mmol, 2 equiv), DMSO (40 µL, 0.55 mmol, 5 equiv), Ferrocenyl amine **1b** (44 mg, 0.11 mmol, 1 equiv), and ligand **L2** (10 mg, 0.044 mmol, 40 mol %) were added to the dry *tert*-amyl alcohol (1.5 mL) under an inert atmosphere and the resulted in green colored solution was pre-stirred for 10 min. In another Schlenk tube, all reagents were added to the dry *tert*-amyl alcohol (1.5 mL) except ligand **L2** under an inert atmosphere at pre-stirred for 10 min. Next, Olefin **2d** (34 µL, 0.22 mmol, 2 equiv) was added to the resulting reaction mixture. The tube was sealed with a rubber septum, and a dry air atmosphere was maintained in the flask with a balloon. The reaction was heated at 50 °C, and after every 10 min time interval 250µL aliquot was taken and passed through a celite pad, evaporation and submitted for crude ^1H NMR. The fractional conversion of C-H-activated products has been monitored with time.

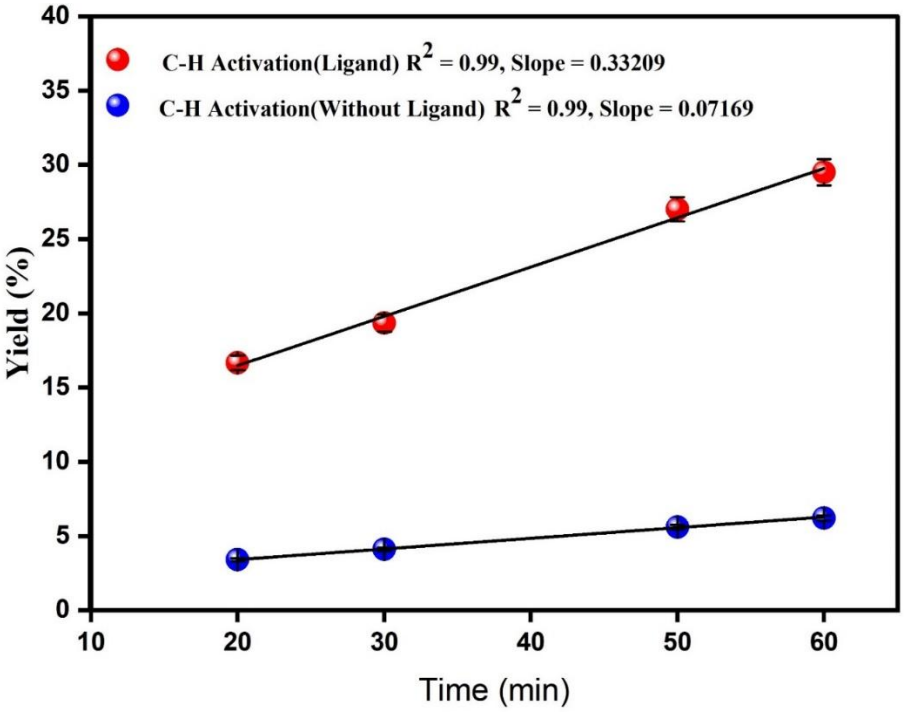


Figure S8. Ligand acceleration experiment plot

Control experiment 5: ^{19}F NMR experiment for determining triflamide co-ordination with Cs^+

In an NMR tube, ferrocenyl amine **1a** (10 mg, 0.03 mmol, 1 equiv), Cs_2CO_3 (20 mg, 0.06 mmol, 2 equiv), DMSO (10 µL, 0.55 mmol, 5 equiv) were added in CD_3OD solvent (0.5 mL). In another NMR tube CsOAc (12 mg, 0.06 mmol, 2 equiv) was added in the place of Cs_2CO_3 in CD_3OD solvent (0.5 mL). ^{19}F NMR were recorded after 30 minutes of mixing on both of the NMR tubes and we have compared the ^{19}F NMR chemical shifts of triflamide in the presence of cesium acetate and cesium carbonate with respect to the triflamide. A downfield chemical shift difference of 1.24 ppm was observed in case of triflamide and Cs_2CO_3 and 0.22 ppm was observed in triflamide and CsOAc with respect to only triflimide in the ^{19}FNMR. This chemical shift difference suggestive of an interaction occurs even in the presence of acetate and carbonate anion between cesium and triflamide

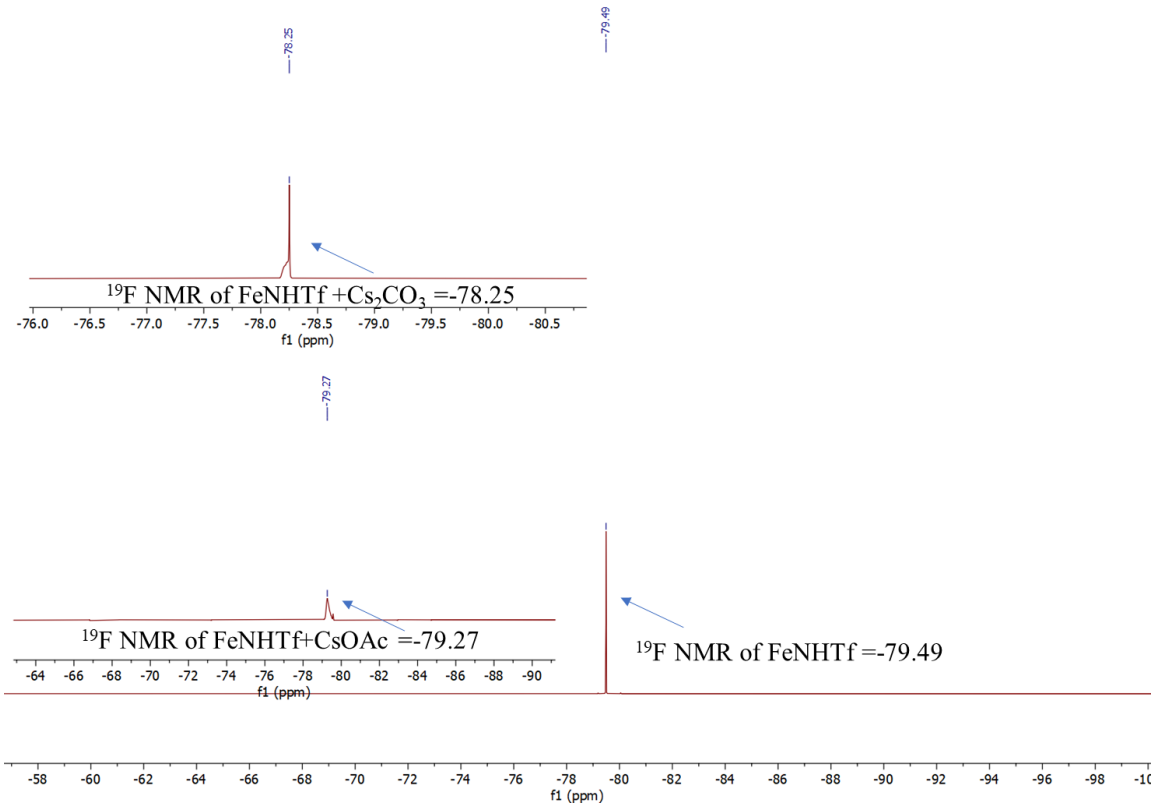


Figure S9. ^{19}F NMR experiment using protic solvent, CD_3OD, combined with 5 eq of DMSO, of cesium acetate and cesium carbonate with respect to the triflamide.

Computational Studies

Computational studies were performed with the Gaussian 09 Revision A.02 program suite with the DFT method of Becke's three-parameter hybrid Hartree-Fock procedure with the Lee Yang-Parr correlation function (B3LYP). The geometry optimization and energy calculations of the reactants, intermediates, and transition state were fully optimized by the DFT/B3LYP method with LANL2DZ basis set in the solution phase using the CPCM (conductor-like Polarizable Continuum Model) model in tetrahydrofuran (THF) solvent. Energy obtained from computation is listed in Hartree and converted to kcal/mol. The difference between the favorable and unfavorable transition states is 2.48 kcal/mol.

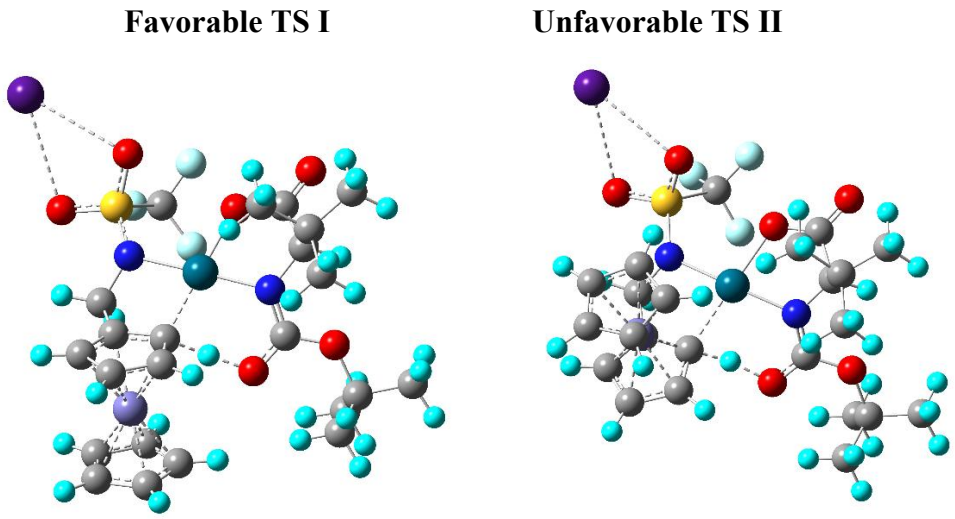


Figure S10. Optimized structure of favorable and unfavorable transition states

Energy Data

Structure	Electronic and Thermal Correction to G_{solv}	ΔG_{solv}
TS I	-2034.381945	0.00 kcal/mol
TS II	-2034.377985	+2.48 kcal/mol

Relative energies were calculated at the level of B3LYP/LANL2DZ/CPCM(THF) at 298K

Co-ordinates of Optimized Structures

Favourable TS I

Electronic + Thermal Free Energies: -2034.381945

Correction to Gibbs' free energy: 0.422242

Zero-point correction: 0.502647

Imaginary vibration frequency: 1 (associated imaginary frequency i1277.14 cm^{-1})

Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
Fe	0.000726564	-0.000035682	-0.001004340
C	-0.001454155	-0.001851942	-0.000481310
C	-0.000744977	0.000164172	0.001643055
C	-0.003341090	0.001315388	-0.003654564
C	0.001443667	-0.003294859	-0.000717470
C	0.003050478	0.000166106	0.002601633
C	0.000080818	0.002580173	0.002524857
H	-0.000243959	0.000537294	-0.000214023
H	0.000138087	0.000260520	0.000160404
H	0.000204188	0.000460223	0.000218217
H	-0.000117785	0.000116618	-0.000073666
H	-0.000020471	-0.000248107	0.000077476
H	0.000073468	-0.000005200	0.000195202
S	-0.000329268	-0.000261712	-0.000251436
O	0.000045398	-0.000320812	0.000110026
O	-0.000077743	0.000114062	0.000147438
C	0.002566861	-0.001391706	0.002514457
H	-0.000347328	-0.000104308	-0.000133825
C	-0.002861000	0.004060085	-0.002851233
C	0.000779685	-0.000349235	-0.000055059
C	-0.000517333	-0.000171772	-0.000882900

H	0.000027533	-0.000146675	0.000072857
H	-0.000075310	0.000153315	-0.000155719
F	0.000097625	0.000004073	-0.000051113
F	-0.000236034	0.000153687	-0.000134025
F	-0.000295496	0.000257105	0.000236074
N	0.000027443	0.000001296	-0.000138806
C	-0.001008938	0.000178168	0.000922373
H	0.000123992	-0.000655180	-0.000538553
C	-0.000083353	-0.000088353	0.000059931
C	0.001141231	-0.000203875	-0.000894764
Pd	-0.000955333	0.000623300	-0.000387234
O	-0.000235914	-0.000428463	-0.000068055
O	0.000159931	0.000139531	0.000249015
Cs	-0.000096668	0.000268067	0.000059241
C	0.002951089	-0.002494076	0.000104109
H	0.000030940	0.000149053	0.000028257
O	-0.000048840	0.000012040	-0.000021202
O	0.000045654	-0.000001451	0.000074850
C	0.000011211	0.000001122	0.000028782
C	-0.000024236	0.000018677	-0.000016617
H	-0.000011687	0.000006427	-0.000015360
H	-0.000017362	0.000003152	0.000030993
H	0.000023267	-0.000013428	0.000000873
C	0.000017747	0.000013544	-0.000012545
H	-0.000009043	0.000033842	0.000018621
H	0.000036376	0.000037523	-0.000046288
H	-0.000011612	-0.000036200	0.000004686
C	-0.000004255	-0.000007782	0.000007850
H	-0.000045891	0.000002747	0.000002655
H	-0.000000709	-0.000032872	-0.000021939

1	0.000027962	0.000021439	0.000013317
6	-0.000007446	0.000048067	0.000015065
6	0.000016512	0.000022982	-0.000017928
1	-0.000002517	-0.000012468	-0.000011735
1	-0.000014226	0.000007004	-0.000001313
1	0.000004295	-0.000011859	-0.000013611
6	0.000016133	0.000006587	-0.000004024
1	-0.000002018	0.000004378	-0.000000591
1	-0.000007081	-0.000003222	-0.000000072
1	0.000000205	0.000000520	-0.000016468
6	0.000002968	0.000005806	-0.000012170
1	-0.000002939	0.000005692	0.000000528
1	0.000000546	-0.000003061	0.000006947
1	0.000004016	0.000004629	-0.000003176
6	0.000062556	-0.000017434	-0.000029374
1	0.000067203	-0.000030653	-0.000001447
7	-0.000753633	0.000263974	0.000804168

Unfavorable TS II

Electronic + Thermal Free Energies: -2034.377985

Correction to Gibbs' free energy: 0.423065

Zero-point correction: 0.502632

Imaginary vibration frequency: 1 (associated imaginary frequency *i*1100.96 cm^{-1})

Atomic	Forces (Hartrees/Bohr)		
Number	X	Y	Z
Fe	0.000214113	0.001143114	-0.000067044
C	0.000075349	-0.000221431	0.000005507
C	-0.000038673	-0.000018047	-0.000008942
C	-0.000016415	-0.000192574	0.000157195
C	-0.000125925	-0.000186952	-0.000107353

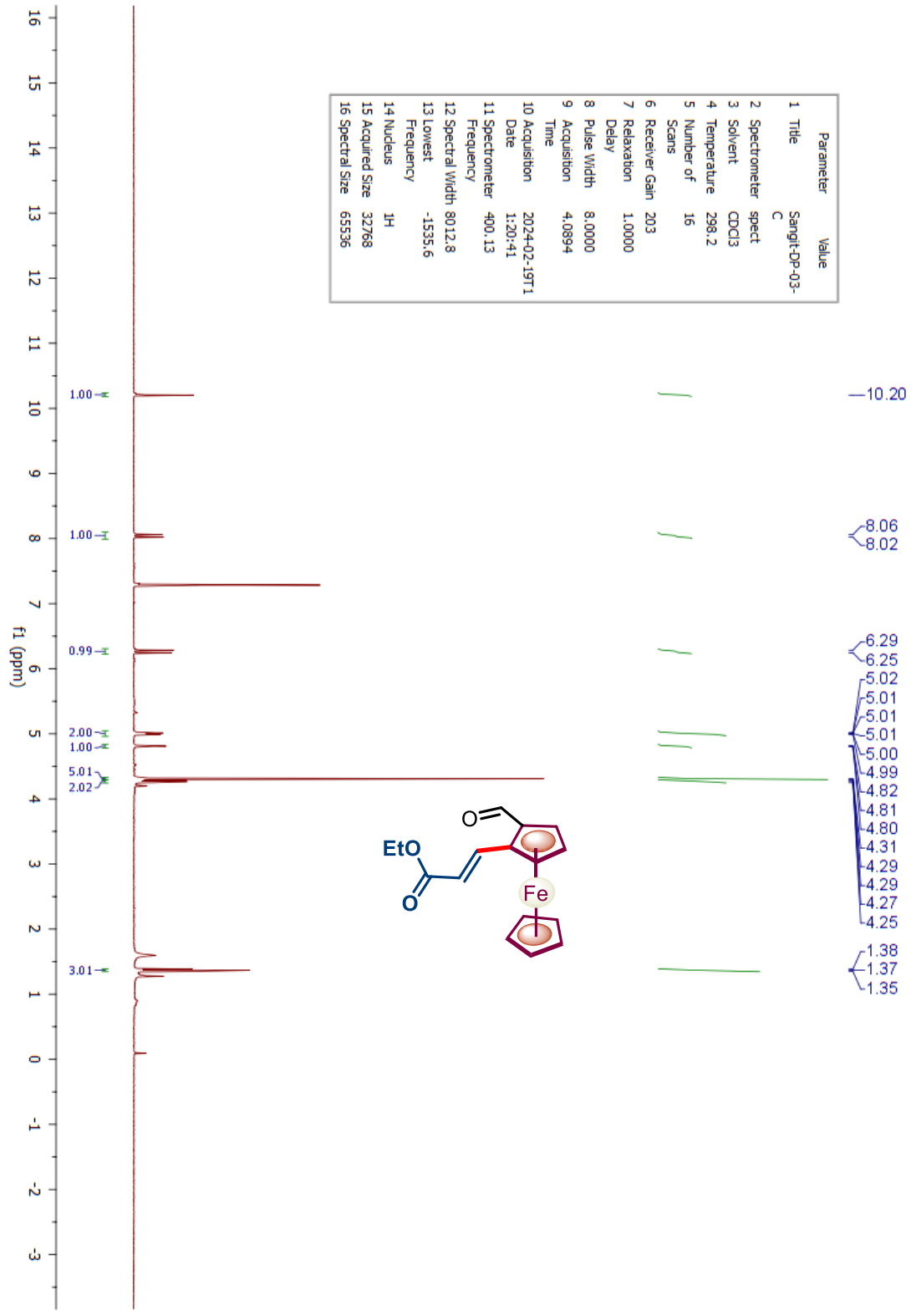
C	-0.000022683	-0.000027720	0.000016479
C	0.000009334	-0.000043021	0.000018703
H	0.000004815	0.000013752	-0.000001527
H	0.000032756	0.000034248	0.000009322
H	0.000007632	-0.000005982	0.000008707
H	-0.000033977	-0.000006825	-0.000023859
H	0.000024756	0.000023762	0.000005976
H	-0.000016296	0.000054623	-0.000017909
S	0.000038002	-0.000036901	-0.000080416
O	-0.000107399	0.000058795	0.000008788
O	-0.000076785	-0.000001327	-0.000000736
C	0.000066313	-0.000184949	0.000183997
H	-0.000025281	0.000012761	-0.000012067
C	0.000021159	-0.000203876	0.000034134
C	-0.000005779	-0.000003000	0.000004955
C	0.000017322	0.000010133	-0.000028336
H	0.000008454	0.000003258	-0.000008277
H	-0.000002083	0.000007146	0.000004625
F	0.000030562	-0.000005184	-0.000025848
F	-0.000012152	0.000014036	-0.000009150
F	0.000058190	-0.000035649	0.000001846
N	0.000025480	-0.000017500	0.000049945
C	-0.000199896	-0.000175348	-0.000156346
H	0.000008119	0.000002149	0.000008483
C	-0.000001852	-0.000015383	-0.000006850
C	-0.000045787	0.000045490	-0.000023211
Pd	-0.000003302	-0.000025887	-0.000020113
O	0.000056773	-0.000002882	-0.000024291
O	0.000006026	0.000014375	0.000047915
Cs	0.000046013	0.000031840	0.000053665

C	-0.000017660	-0.000043420	-0.000012273
H	-0.000005450	0.000016898	-0.000010908
O	0.000003471	-0.000004700	-0.000021735
O	0.000032098	-0.000020531	0.000018281
C	-0.000012424	-0.000005362	-0.000012968
C	-0.000002204	-0.000000706	-0.000001468
H	-0.000000241	-0.000000235	-0.000001199
H	-0.000000615	0.000000013	-0.000000936
H	0.000000204	-0.000000309	-0.000001681
C	0.000000219	-0.000002142	0.000002613
H	0.000002021	-0.000002742	-0.000001463
H	-0.000001731	0.000000638	0.000002565
H	-0.000000631	0.000002878	-0.000003014
C	0.000001908	0.000001174	-0.000000272
H	0.000000784	0.000000802	-0.000001079
H	-0.000000575	0.000001141	-0.000000921
H	-0.000000679	0.000000461	-0.000001076
C	-0.000001649	0.000015411	-0.000001814
C	-0.000000724	-0.000018066	0.000001749
H	0.000000183	-0.000009652	-0.000002593
H	-0.000001473	0.000002257	0.000008856
H	0.000000794	0.000008531	-0.000007530
C	0.000008120	0.000004919	0.000000677
H	0.000009117	0.000005661	-0.000001470
H	-0.000000428	-0.000008299	0.000009331
H	-0.000011037	0.000006191	-0.000003259
C	-0.000010806	0.000004183	0.000000930
H	-0.000006945	0.000002340	0.000000514
H	0.000003049	-0.000000636	0.000004470
H	0.000000762	-0.000001425	-0.000005384

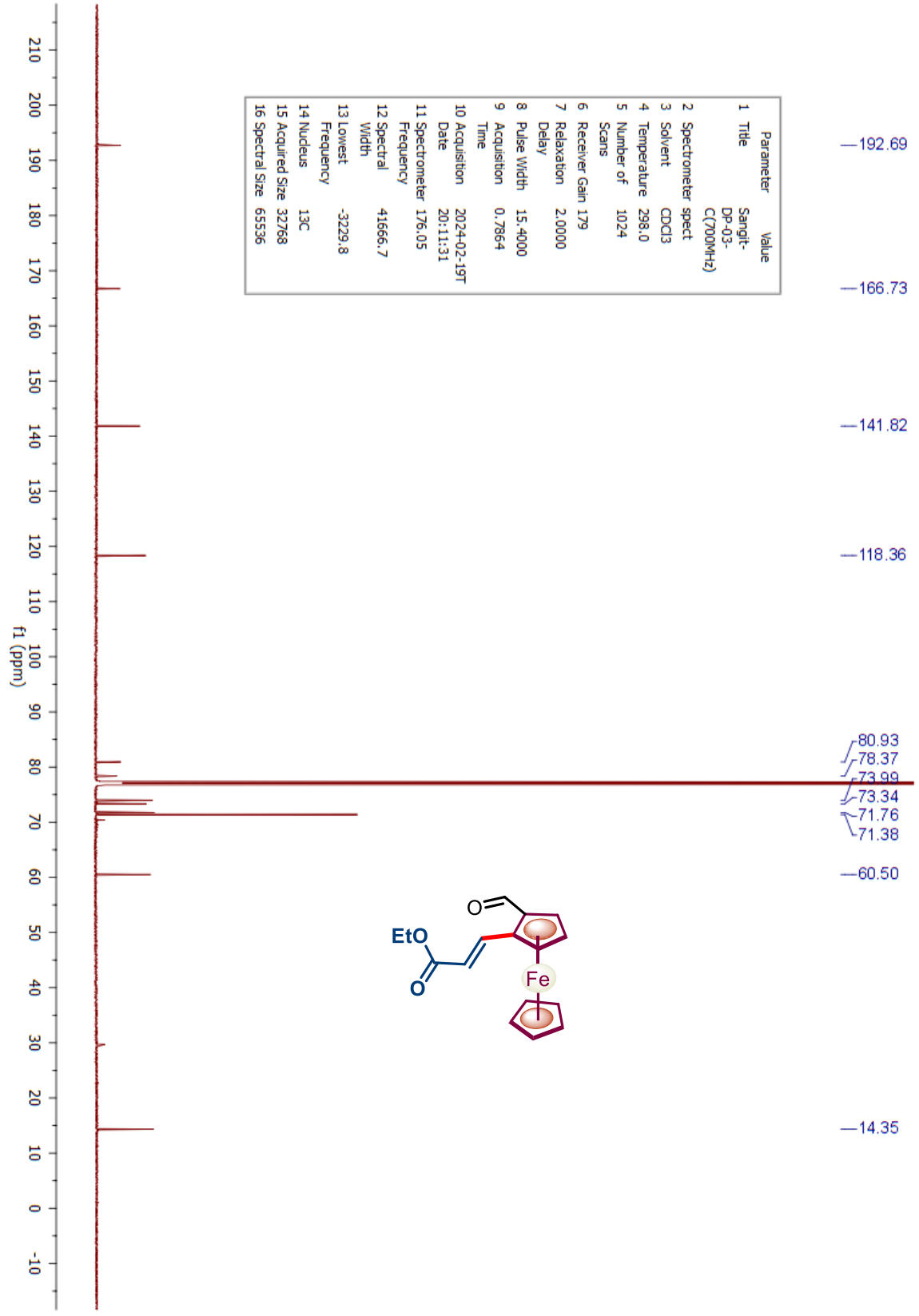
C	-0.000007621	0.000003723	-0.000008831
H	0.000008975	-0.000002307	0.000009067
N	-0.000005698	-0.000015731	0.000044855

NMR Spectra of Chiral 1,2-Ferrocene Formaldehyde Derivatives and Post-derivatized Compounds

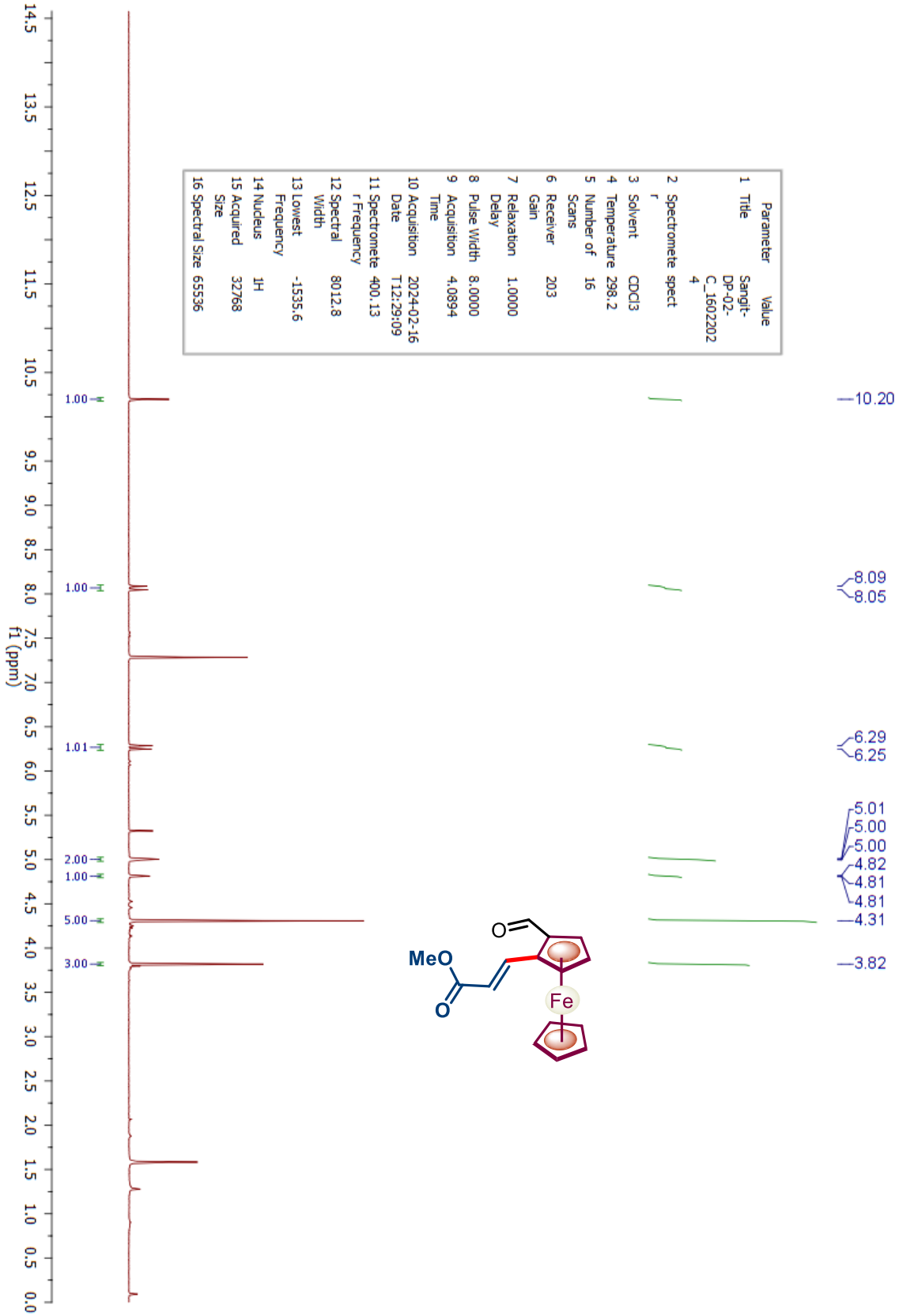
^{1}H NMR Spectrum of 3a



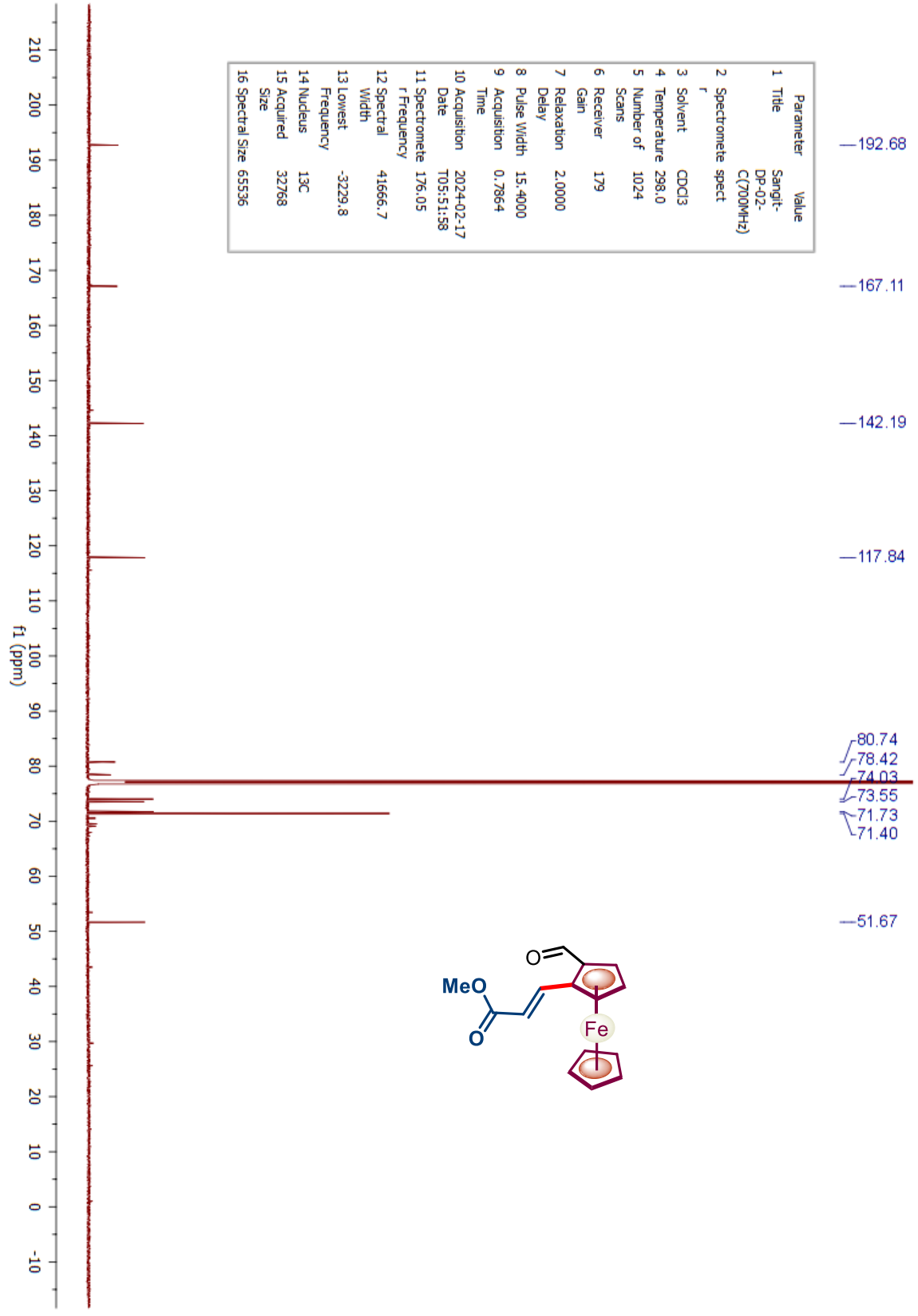
$^{13}C\{^{1}H\}$ NMR Spectrum of 3a



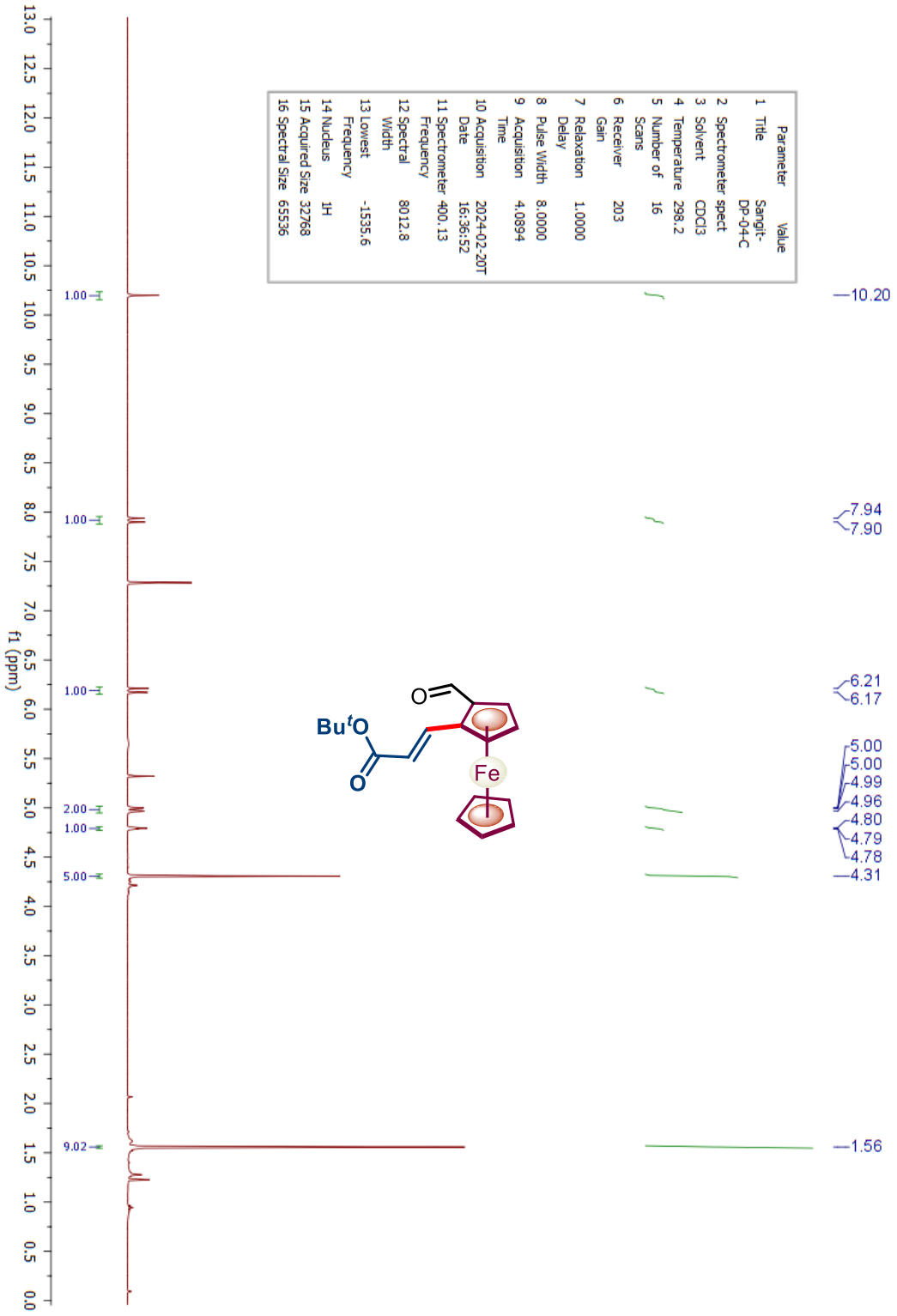
^{1}H NMR Spectrum of 3b



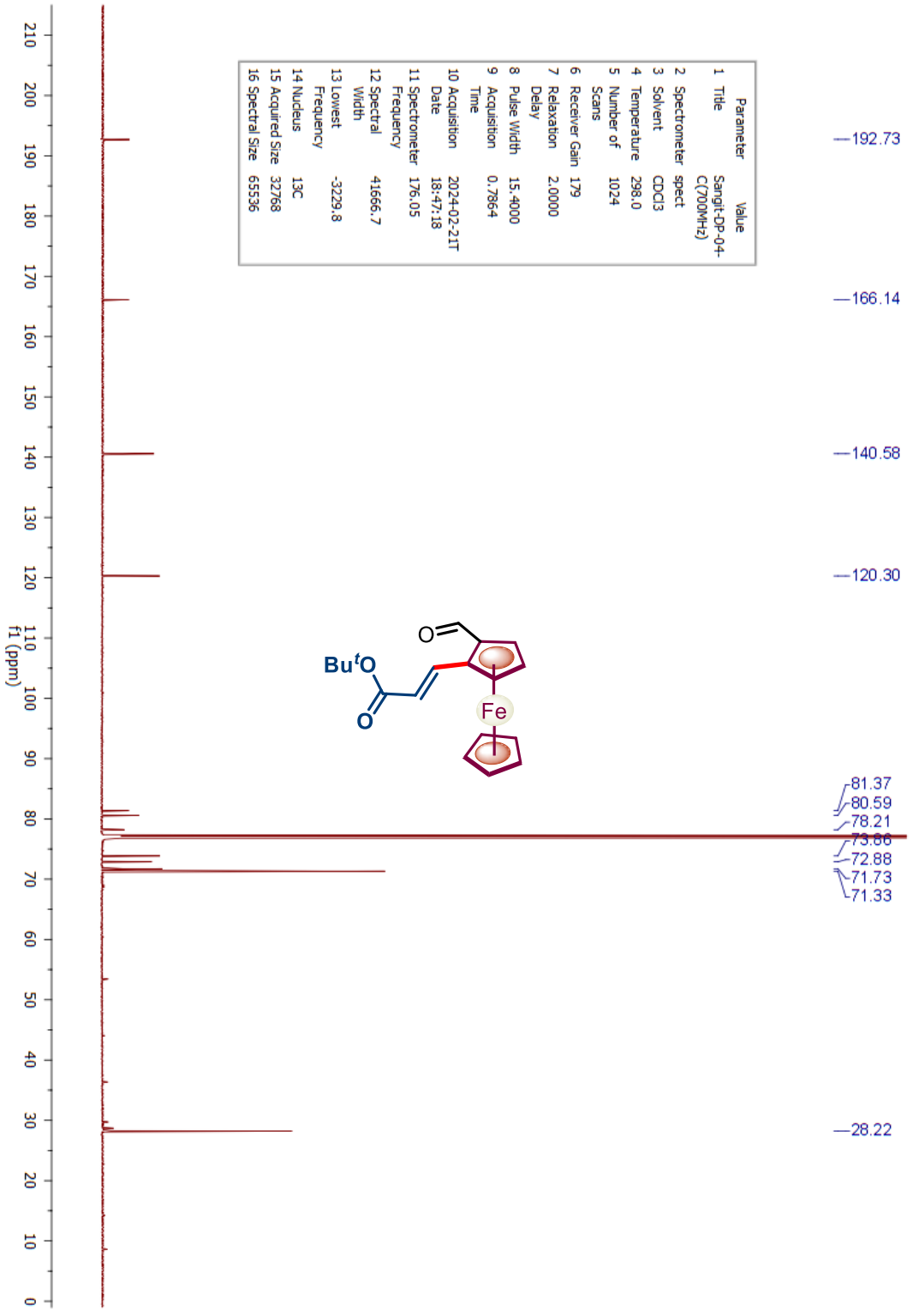
$^{13}C\{^{1}H\}$ NMR Spectrum of 3b



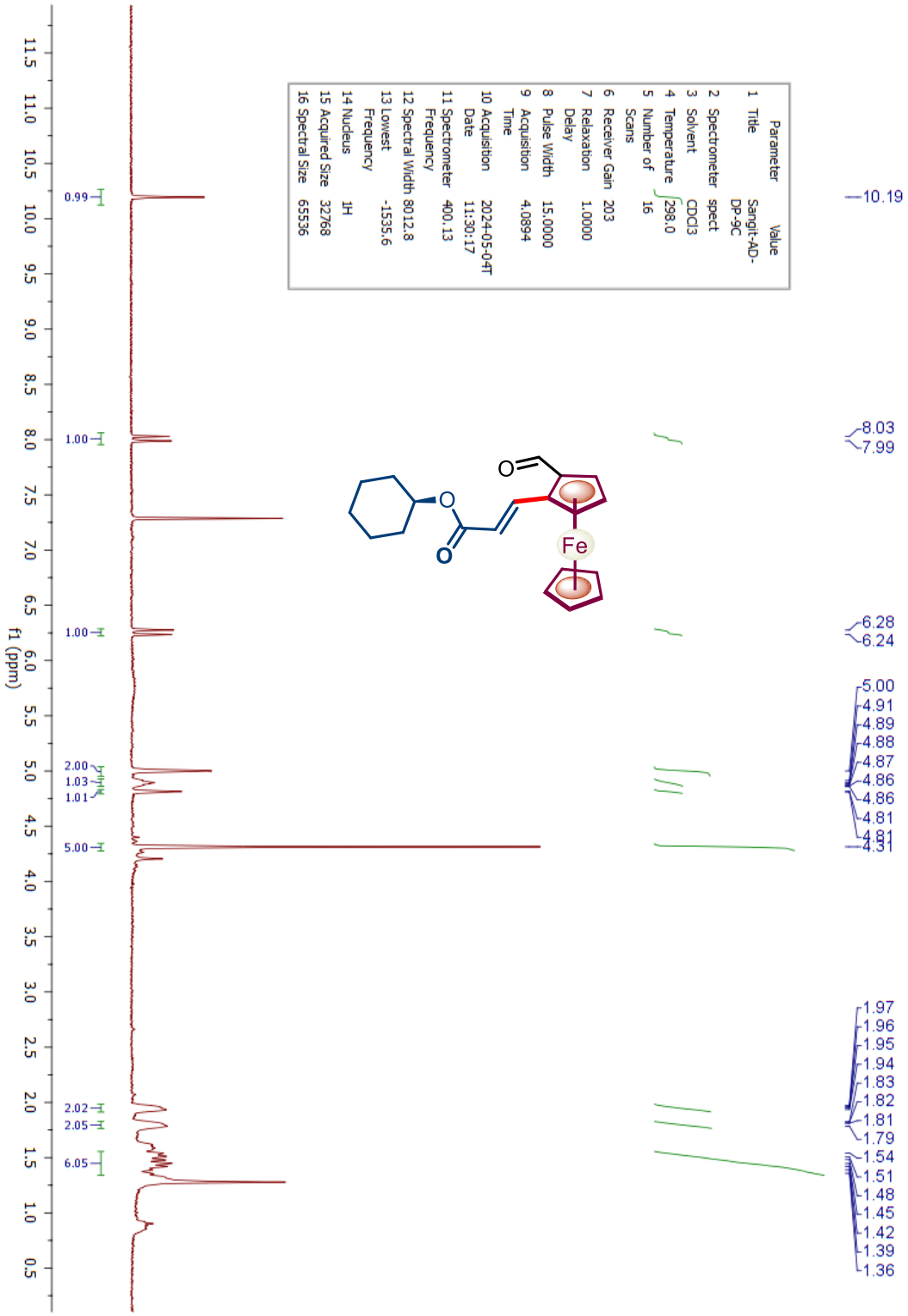
^{1}H NMR Spectrum of 3c



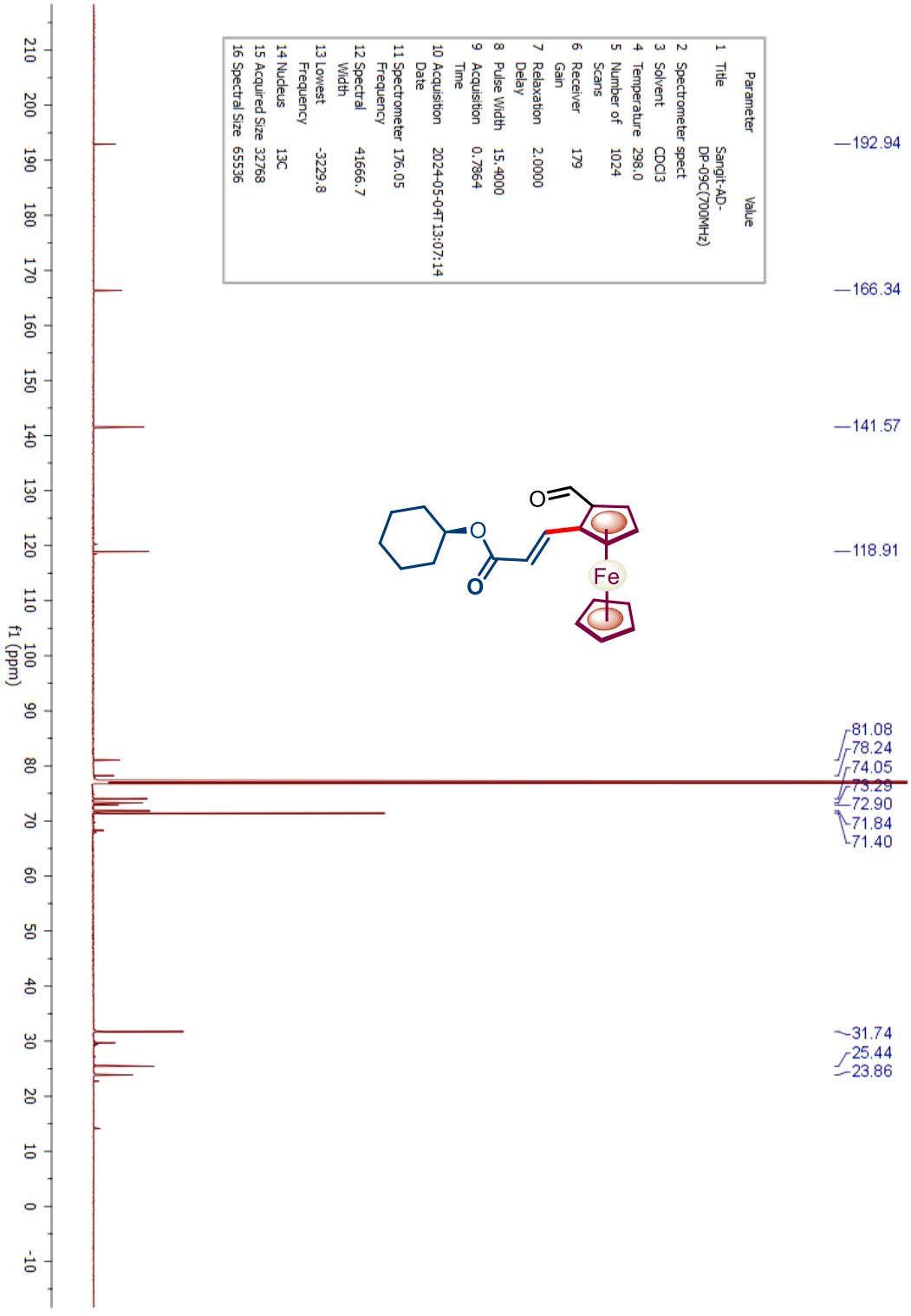
$^{13}C\{^{1}H\}$ NMR Spectrum of 3c



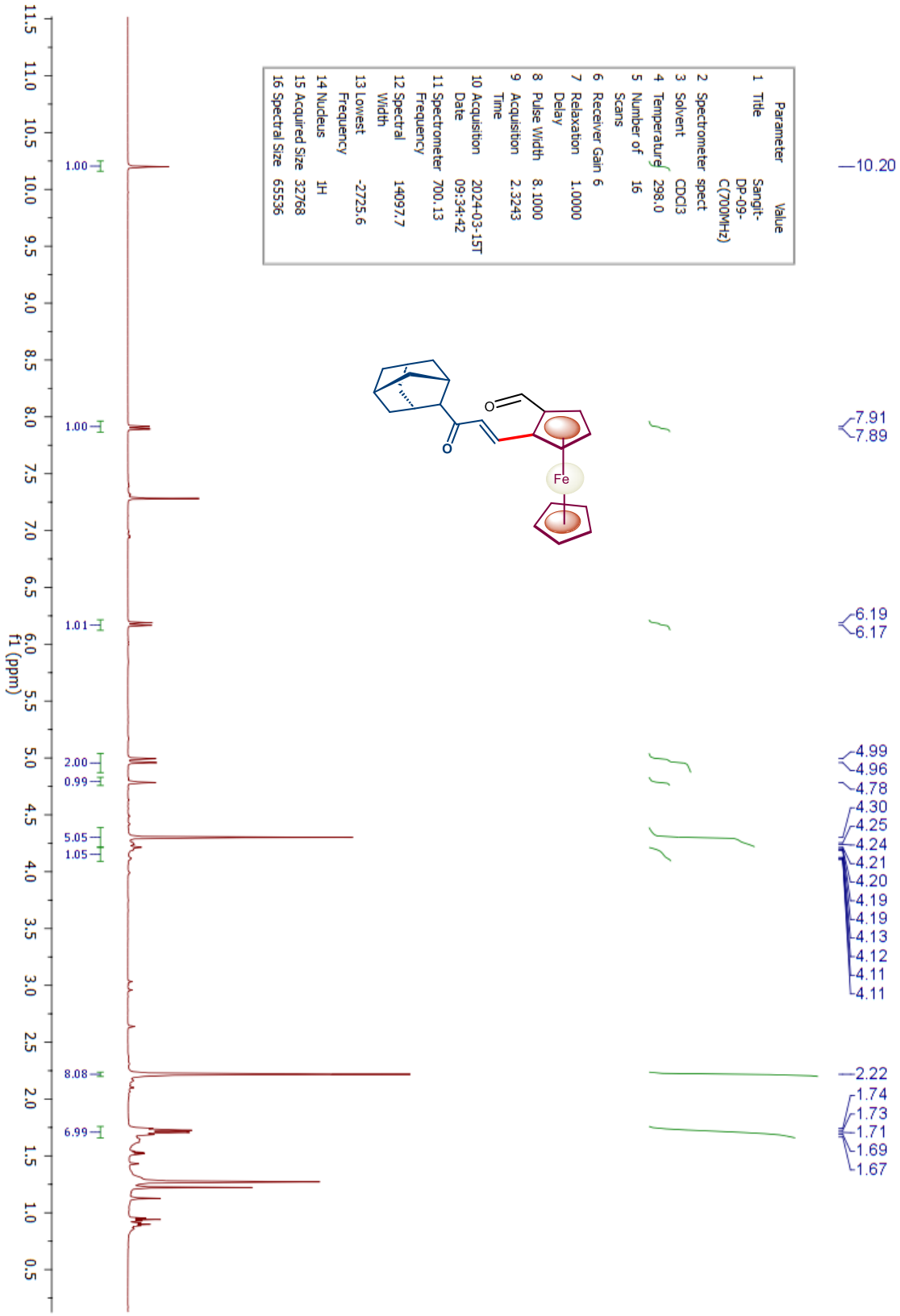
^{1}H NMR Spectrum of 3d



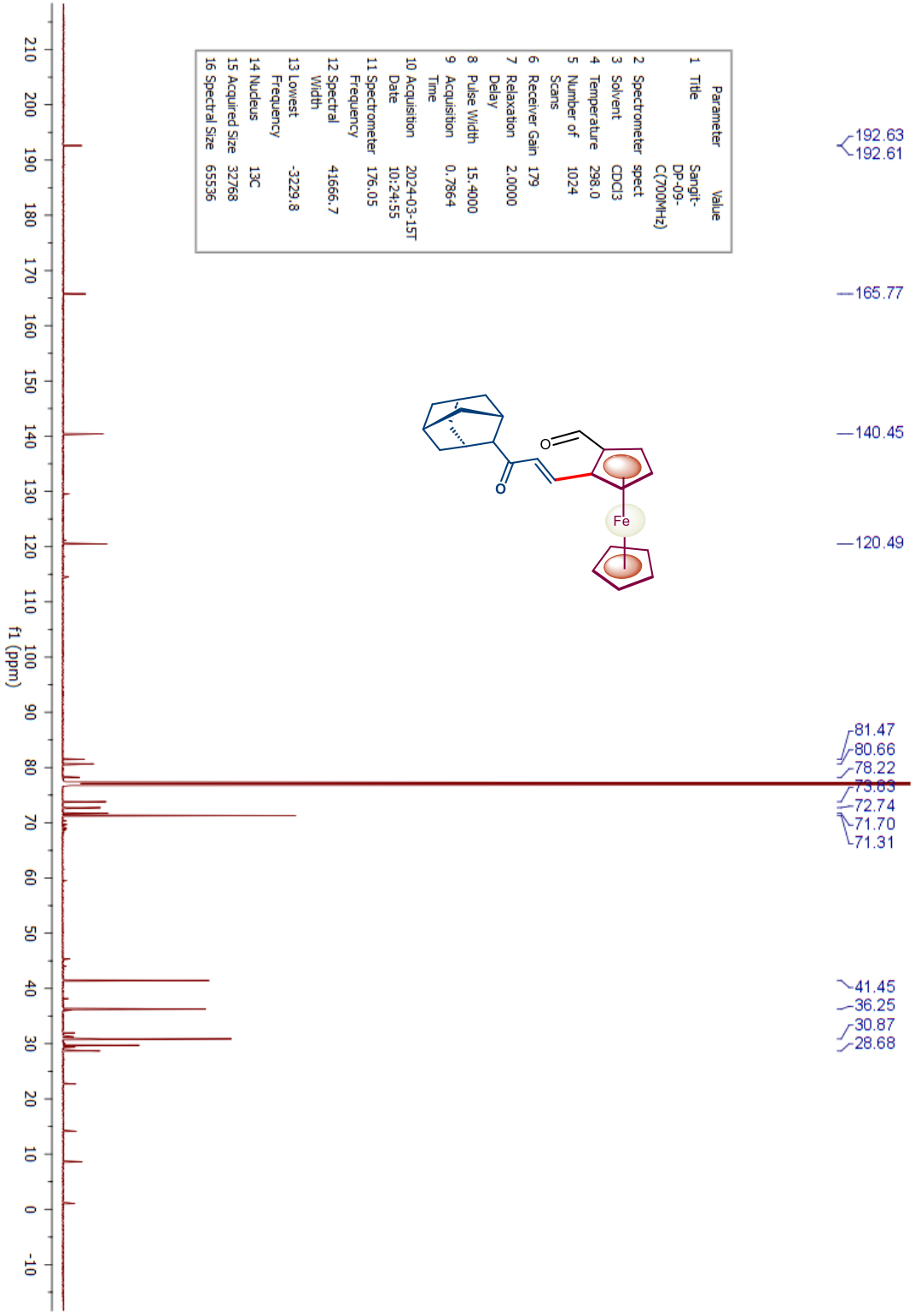
$^{13}C\{^{1}H\}$ NMR Spectrum of 3d



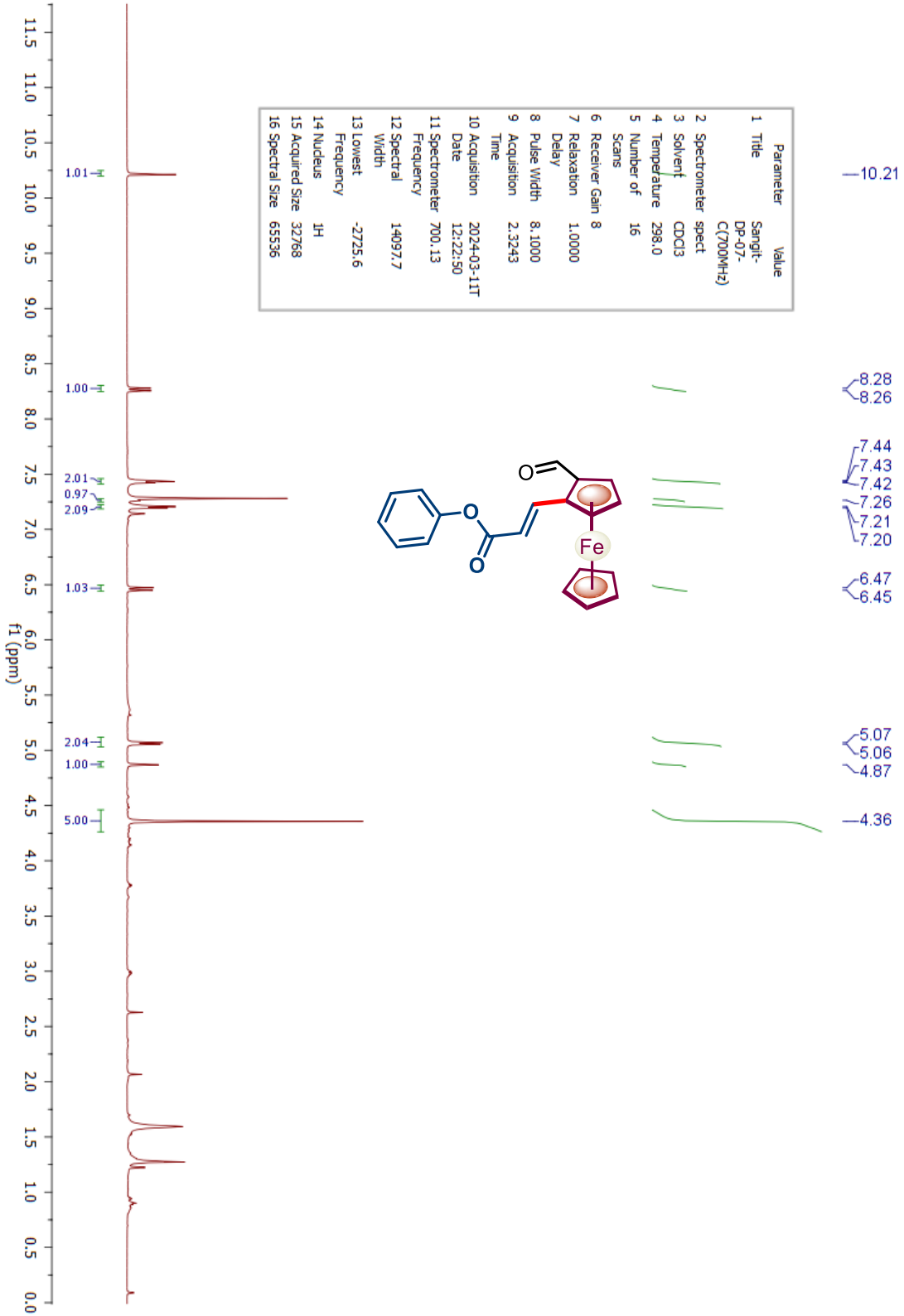
^{1}H NMR Spectrum of 3e



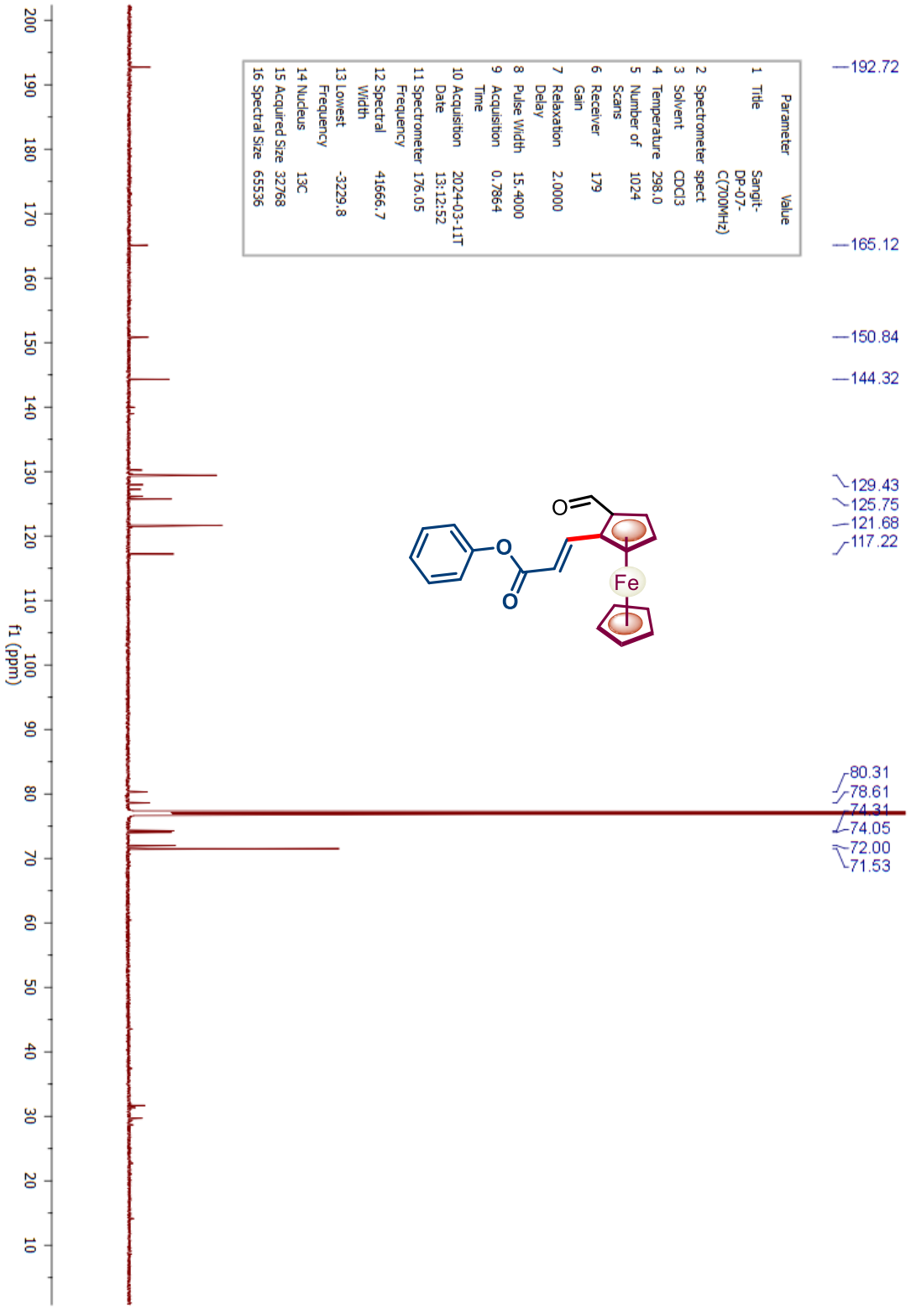
$^{13}C\{^{1}H\}$ NMR Spectrum of 3e



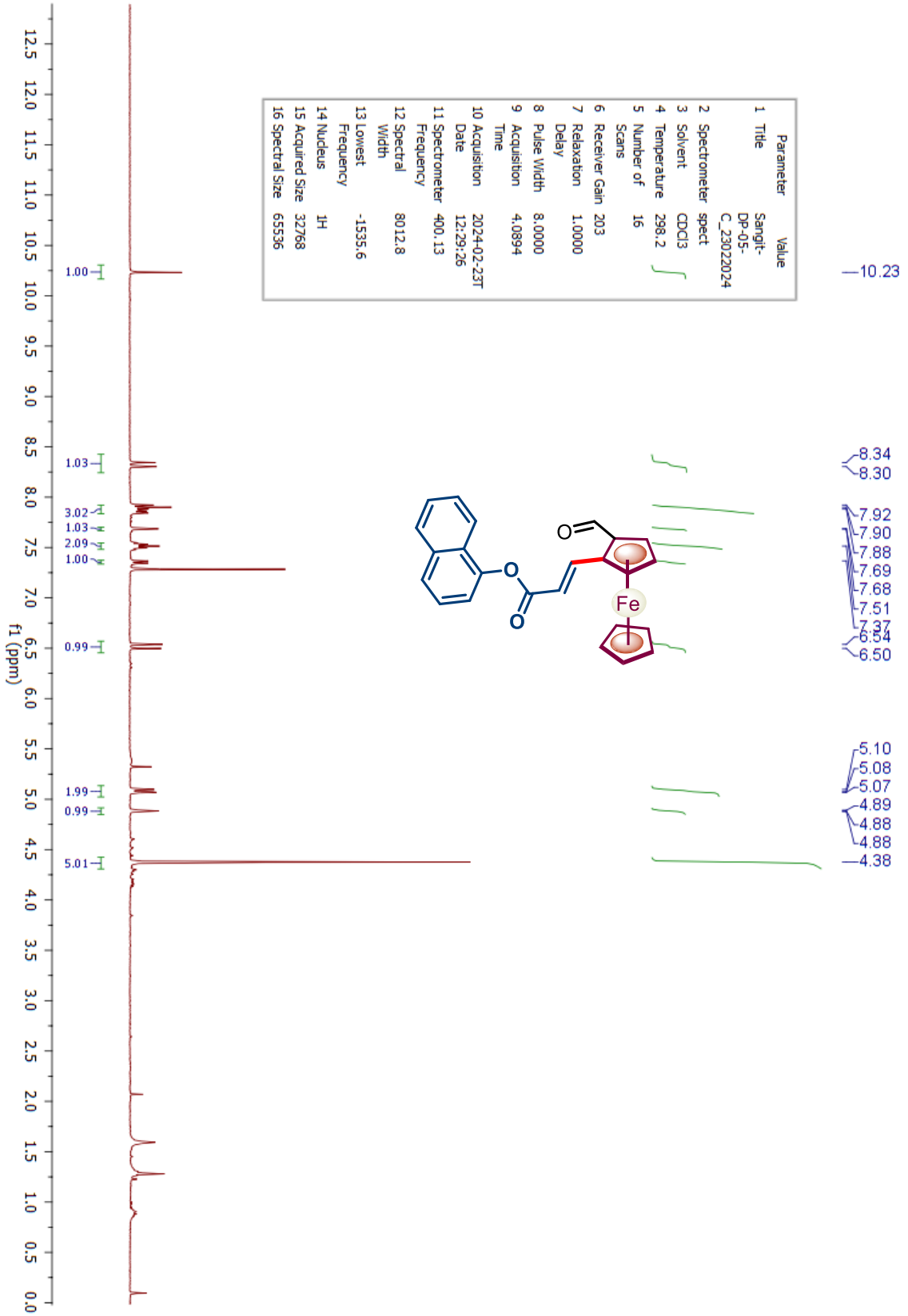
^{1}H NMR Spectrum of 3f



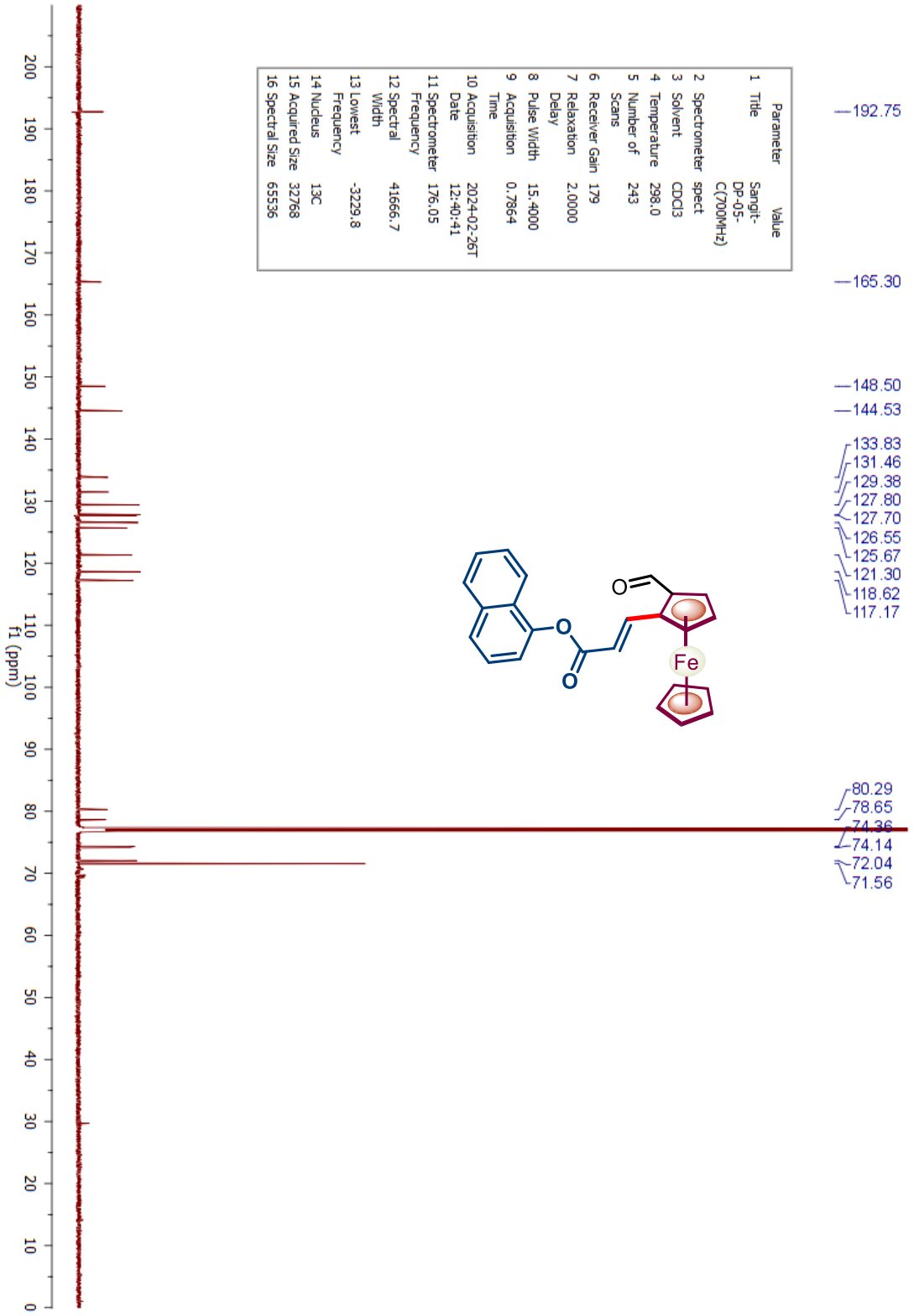
$^{13}C\{^{1}H\}$ NMR Spectrum of 3f



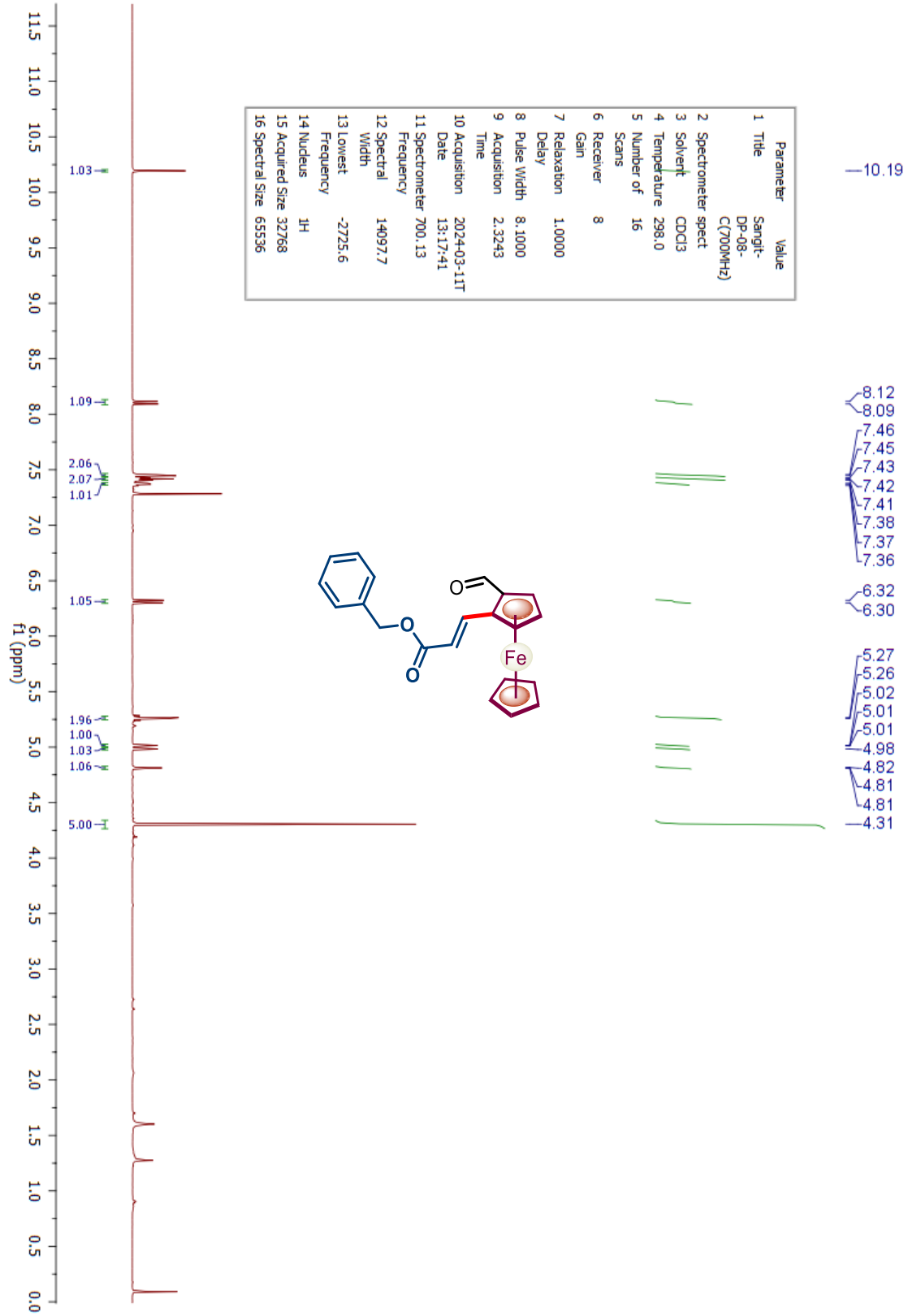
^{1}H NMR Spectrum of 3g



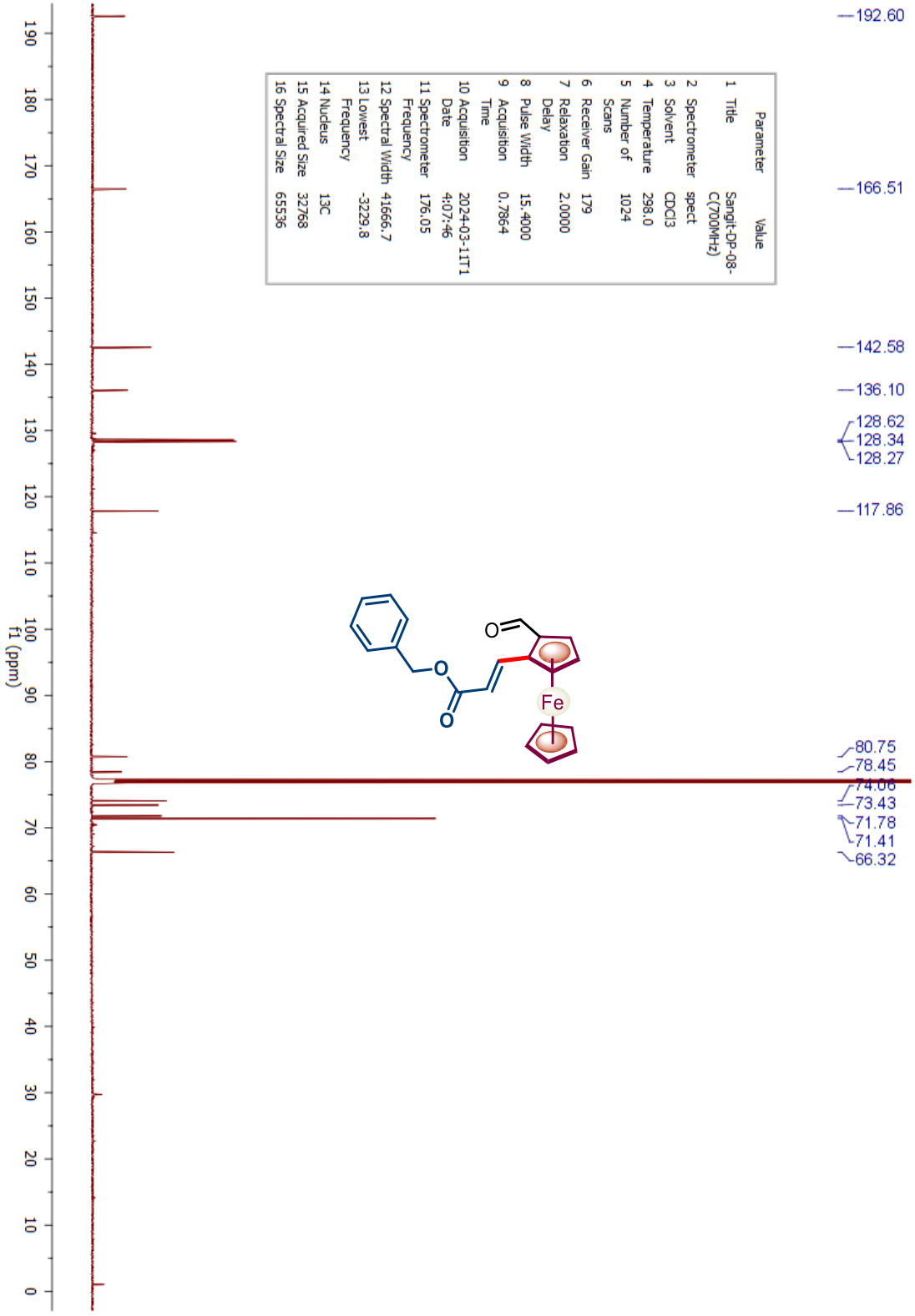
$^{13}C\{^{1}H\}$ NMR Spectrum of 3g



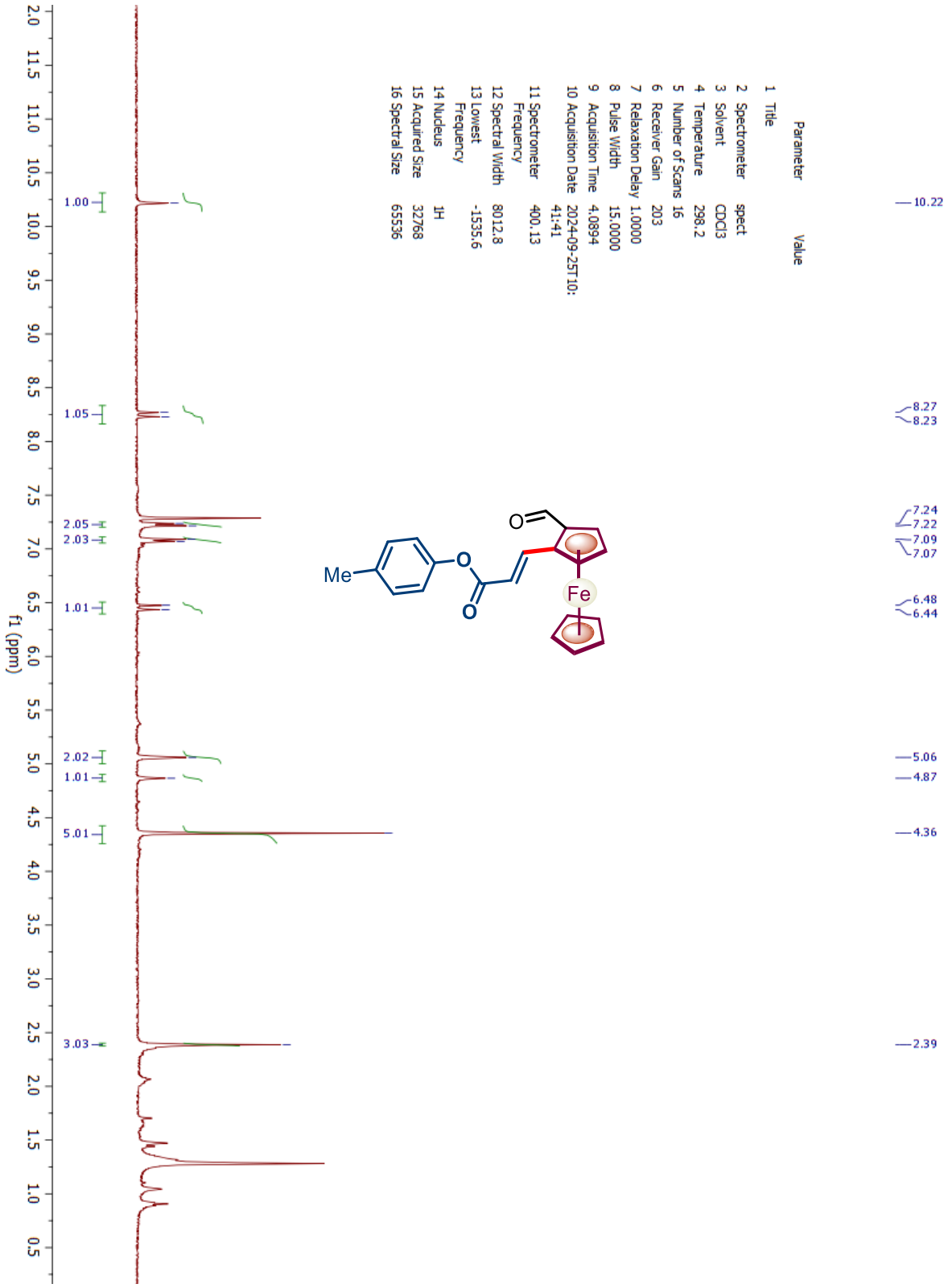
^{1}H NMR Spectrum of 3h



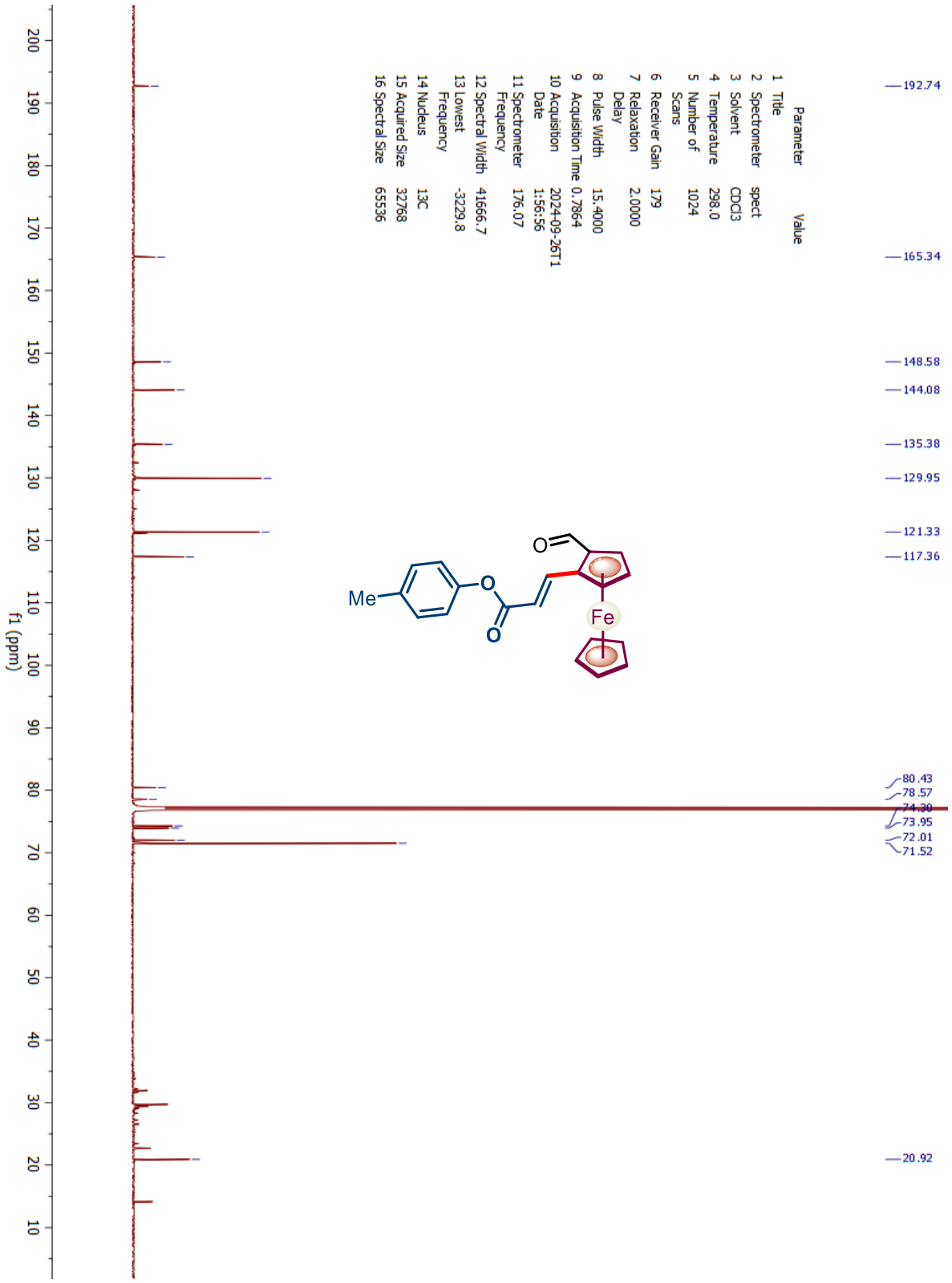
$^{13}C\{^{1}H\}$ NMR Spectrum of 3h



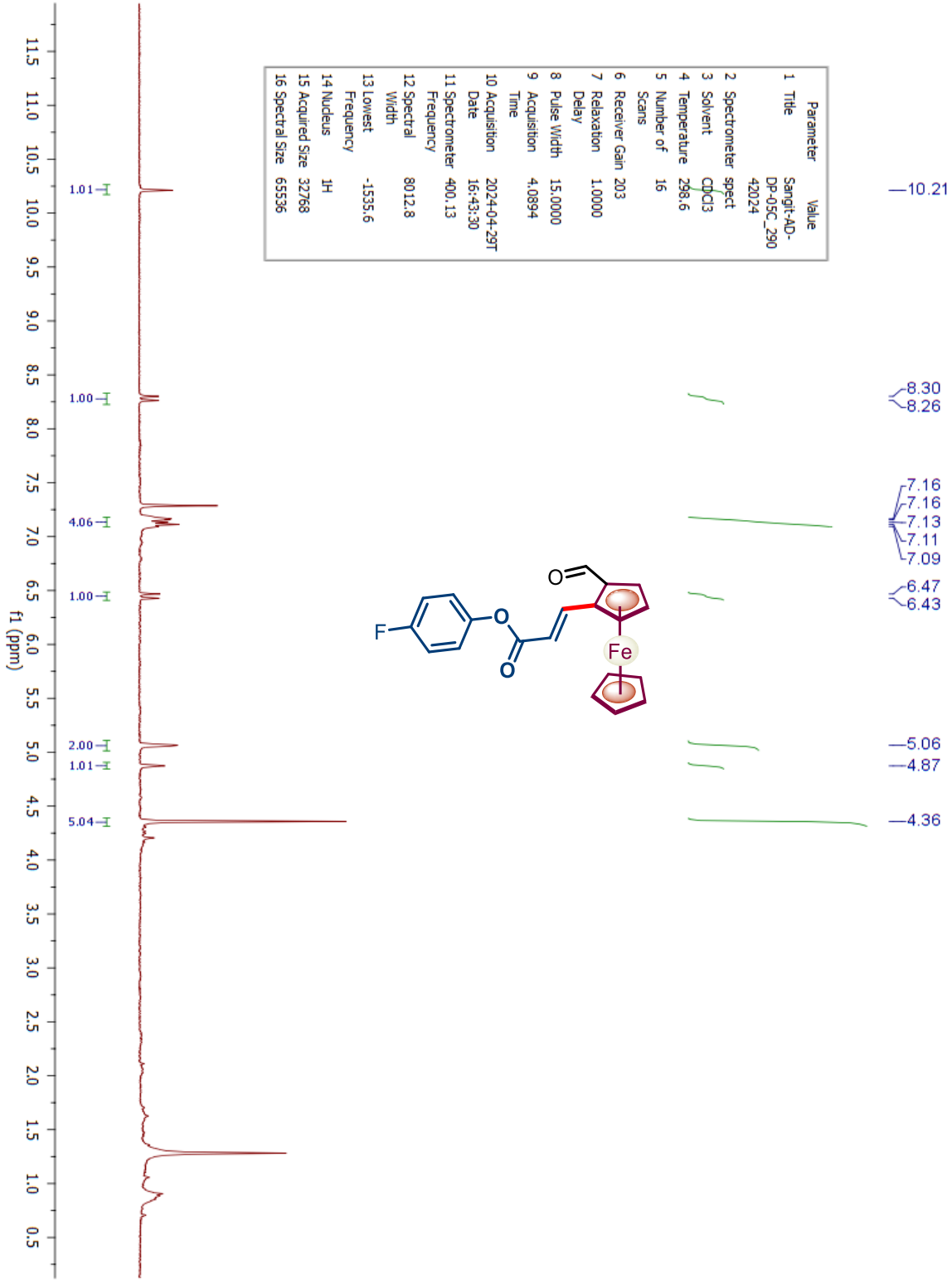
^{1}H NMR Spectrum of 3i



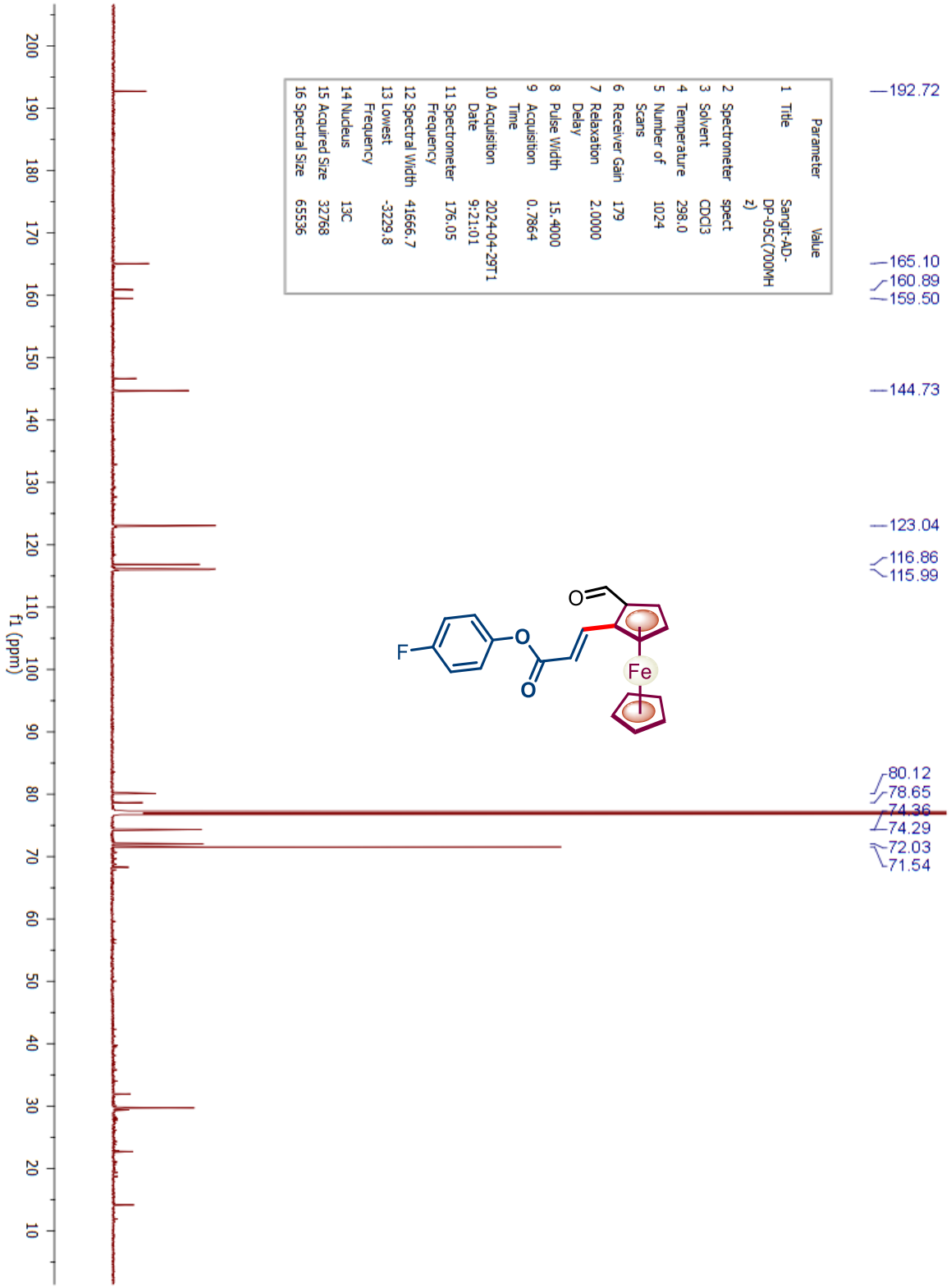
$^{13}C\{^{1}H\}$ NMR Spectrum of 3i



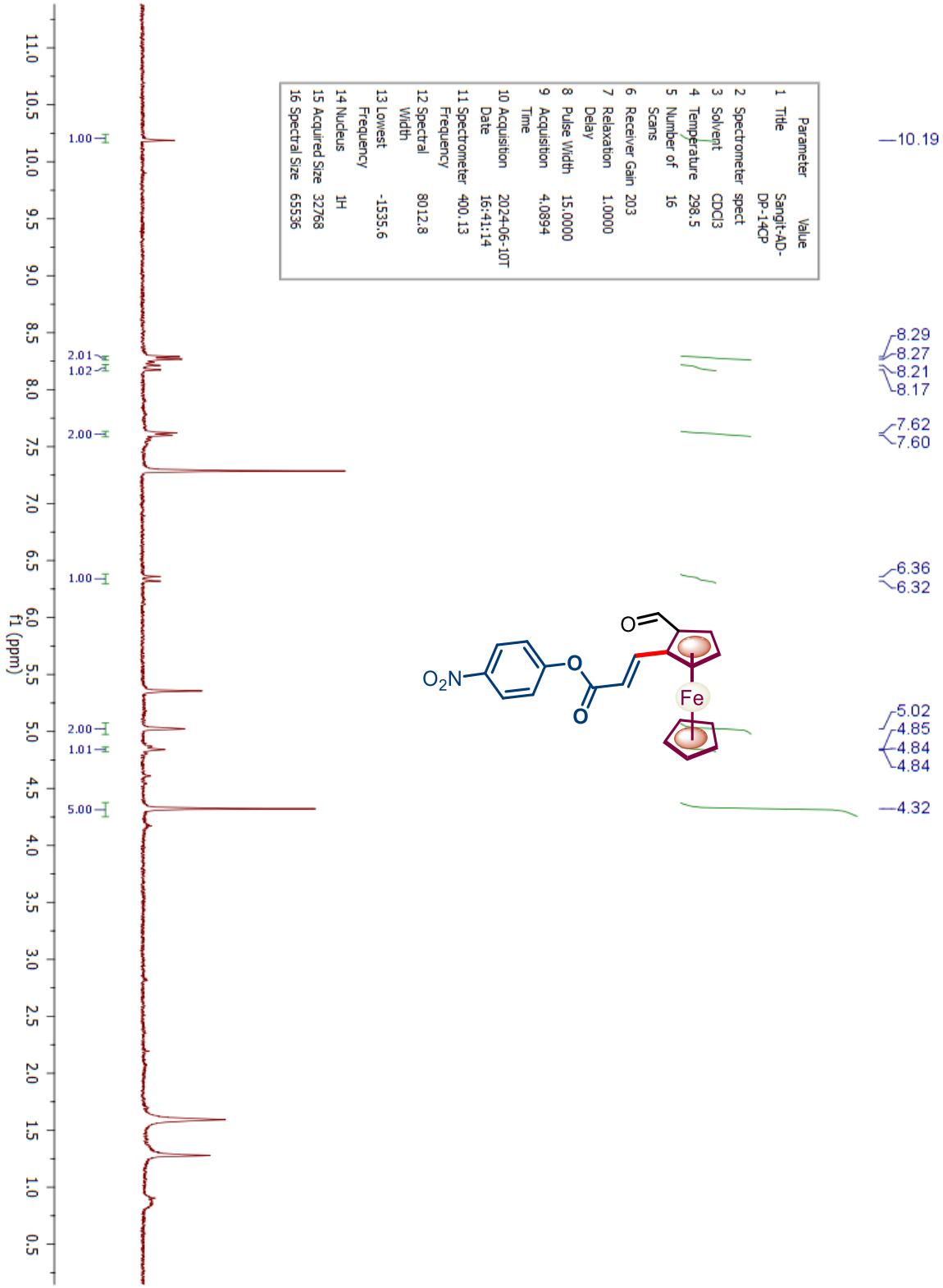
^{1}H NMR Spectrum of 3j



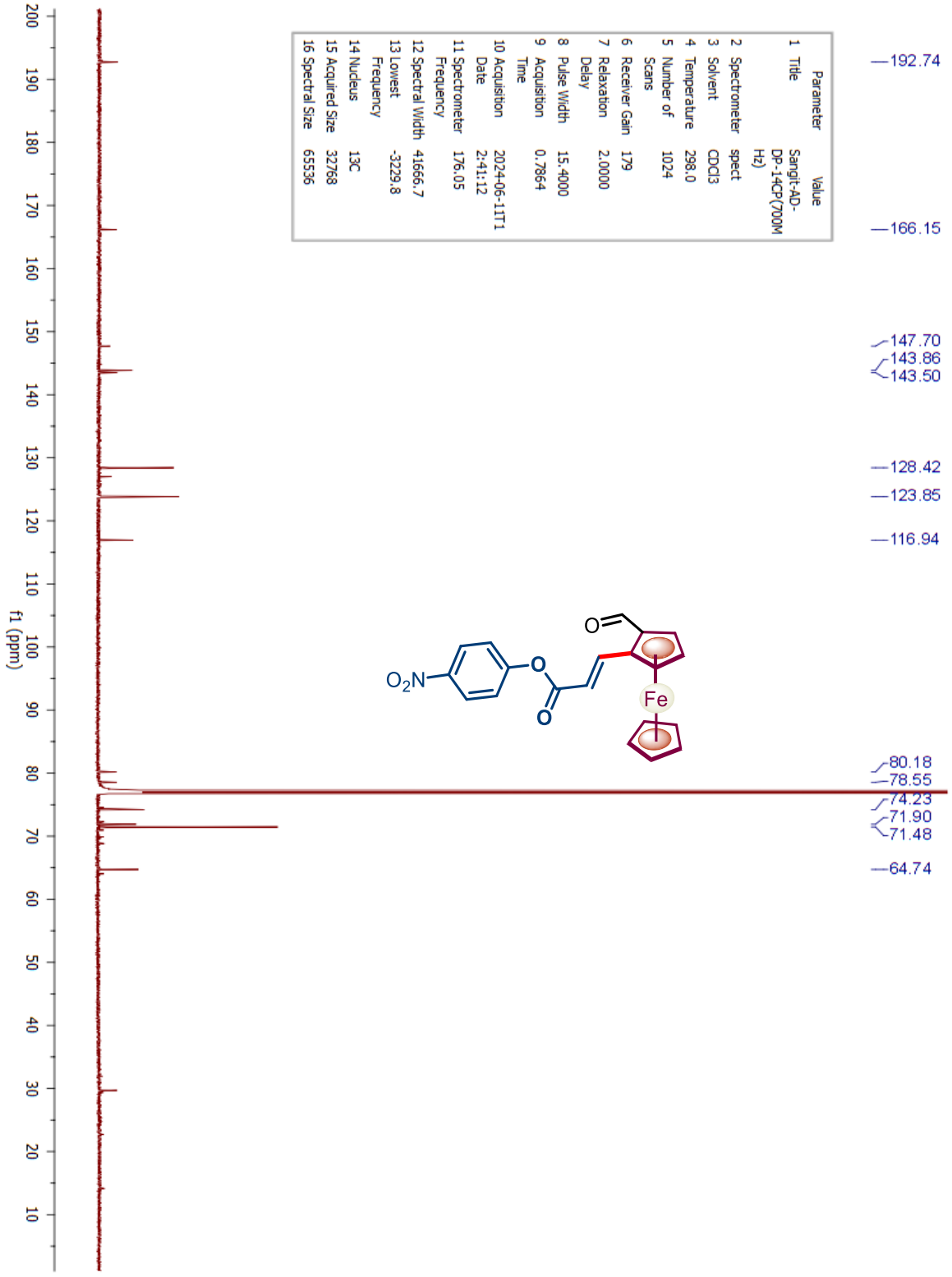
$^{13}C\{^{1}H\}$ NMR Spectrum of 3j



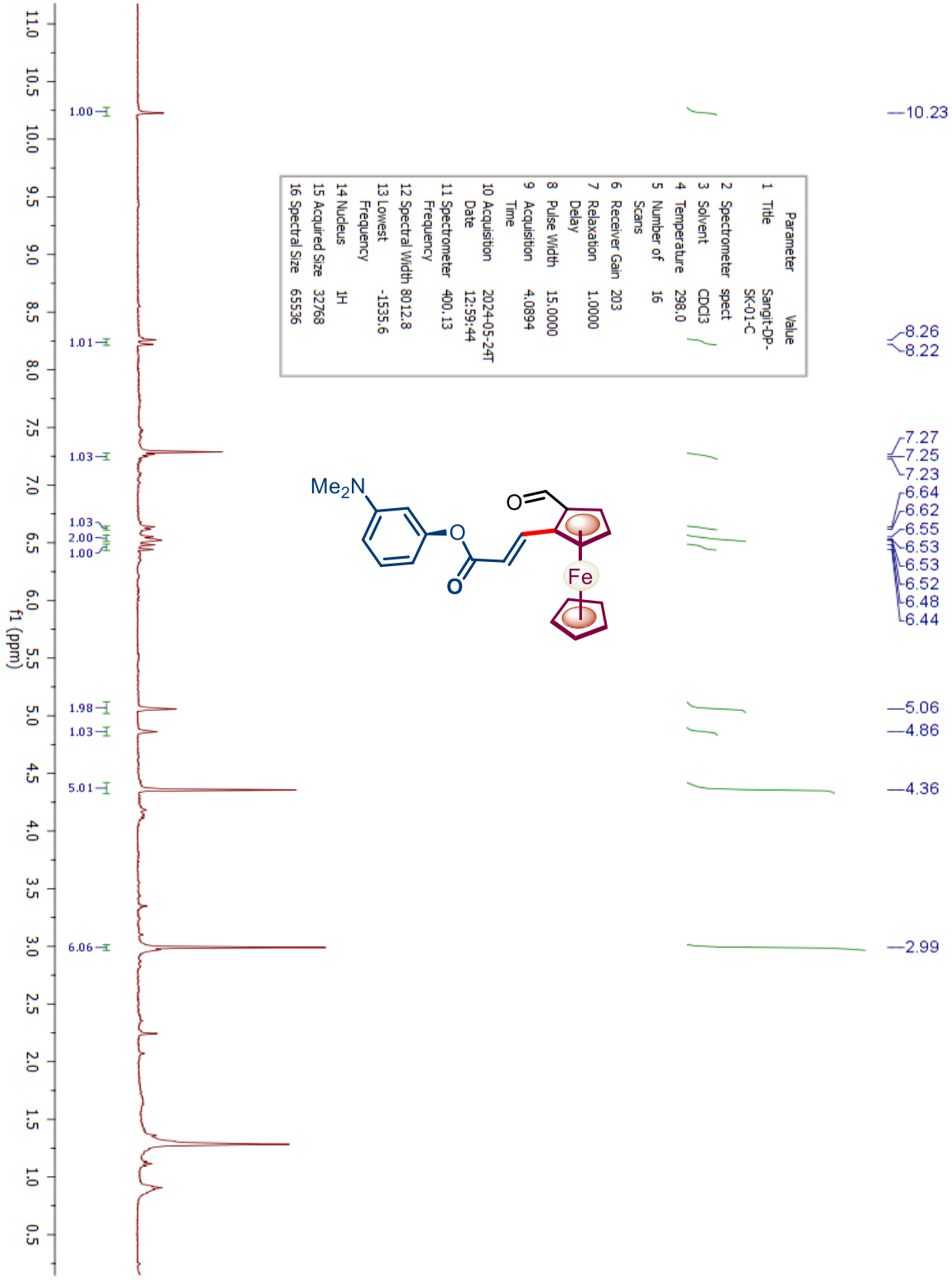
^{1}H NMR Spectrum of 3k



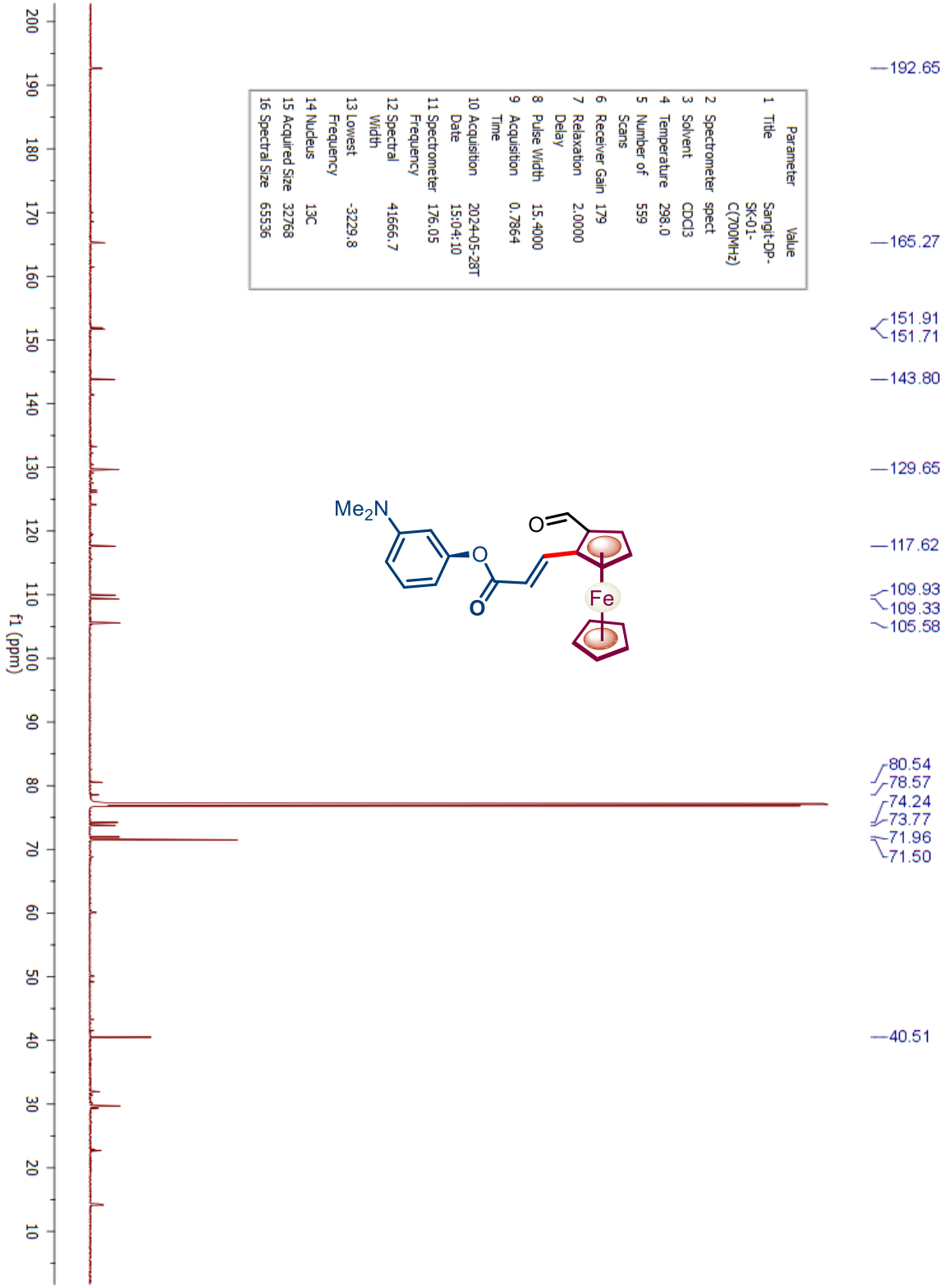
$^{13}C\{^{1}H\}$ NMR Spectrum of 3k



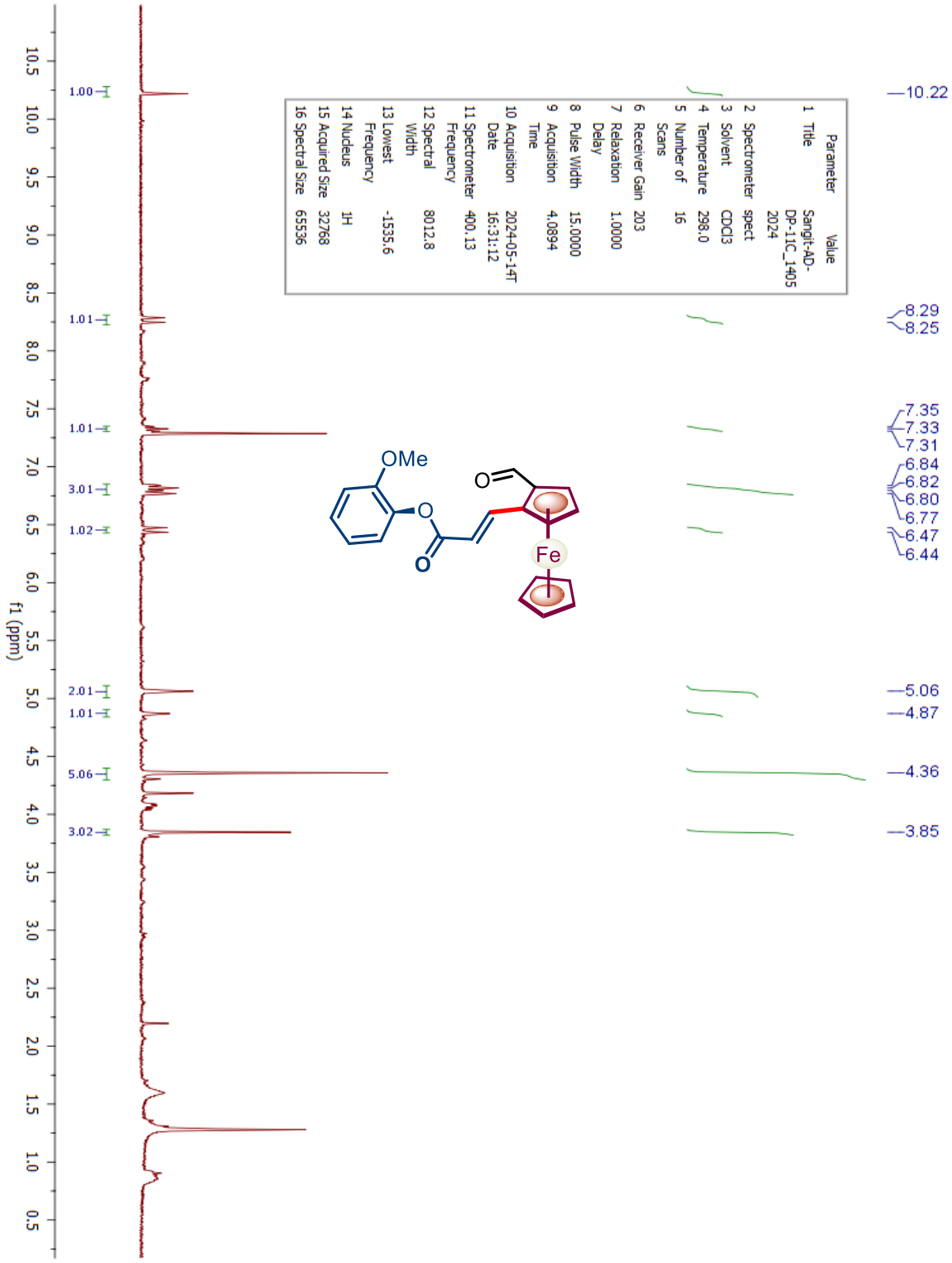
^{1}H NMR Spectrum of 3l



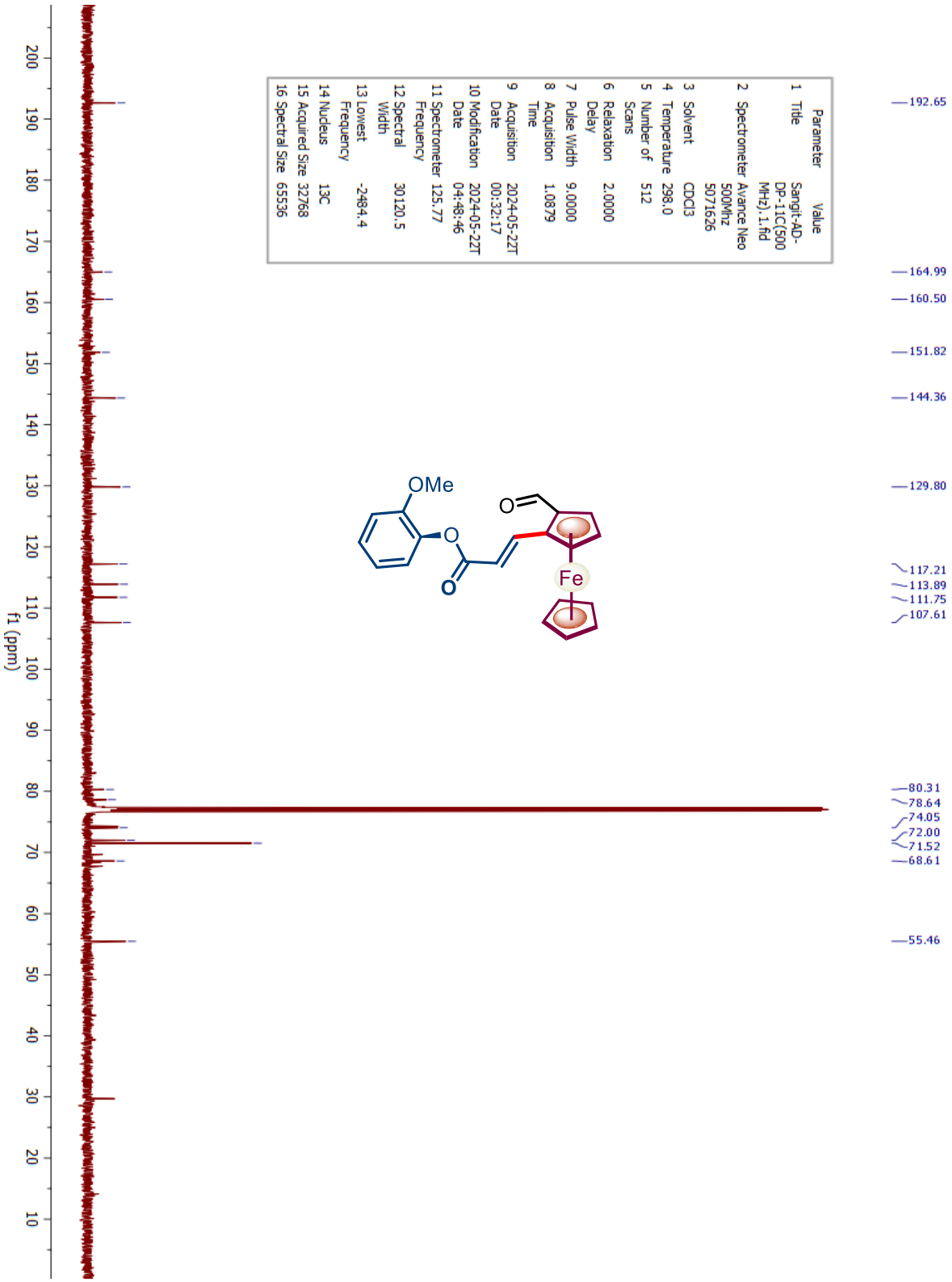
$^{13}C\{^{1}H\}$ NMR Spectrum of 3l



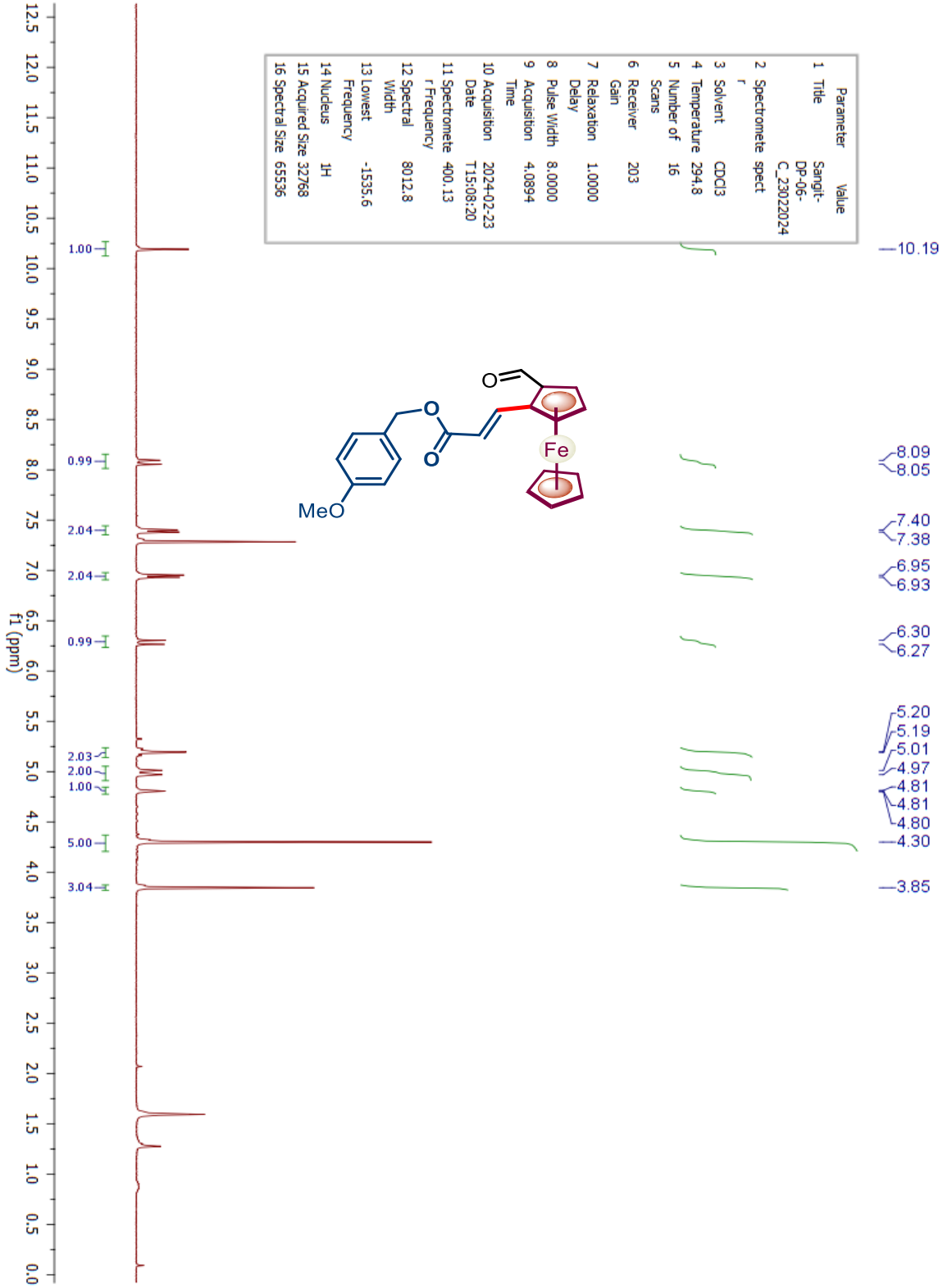
^{1}H NMR Spectrum of 3m



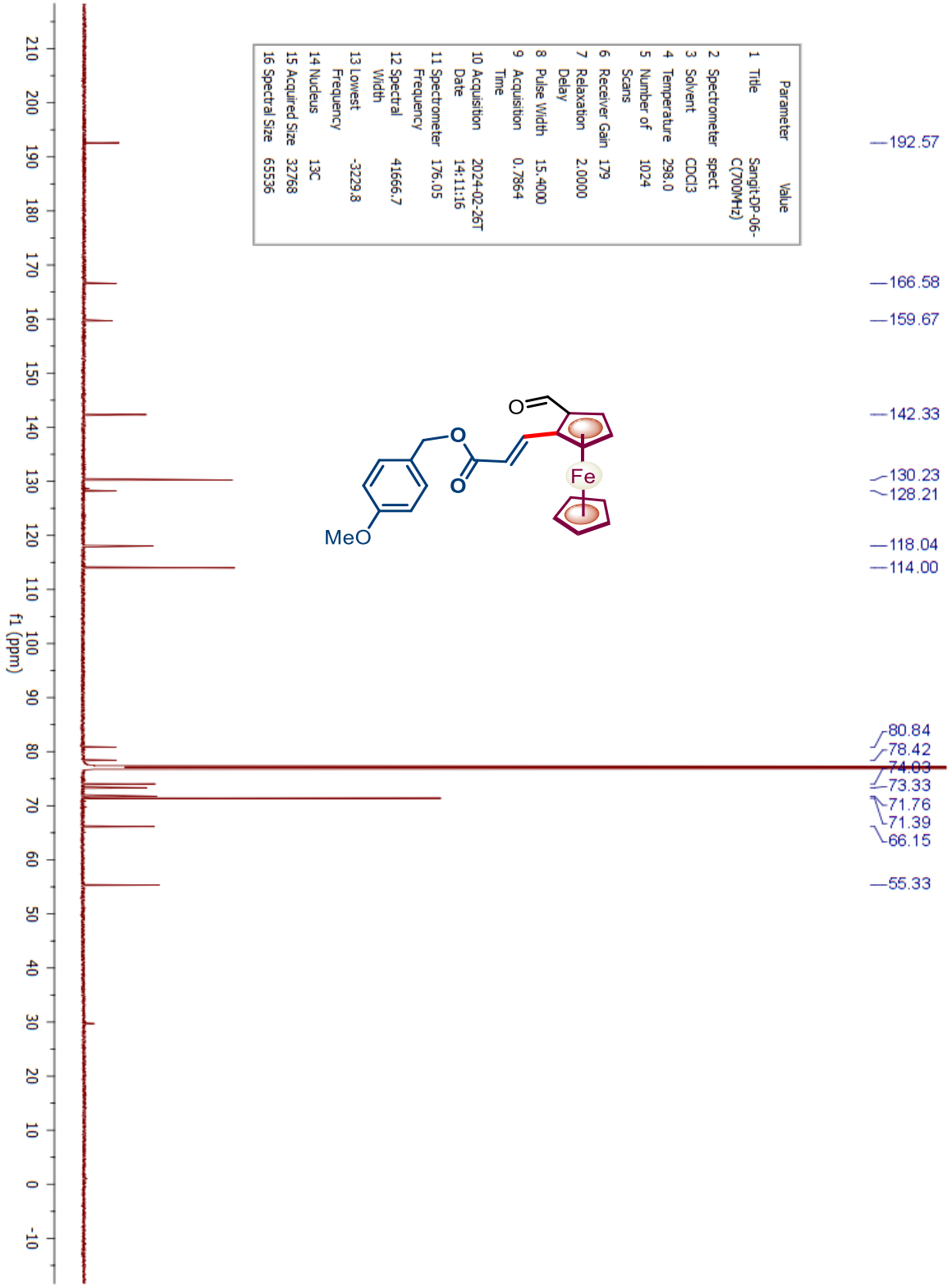
$^{13}C\{^{1}H\}$ NMR Spectrum of 3m



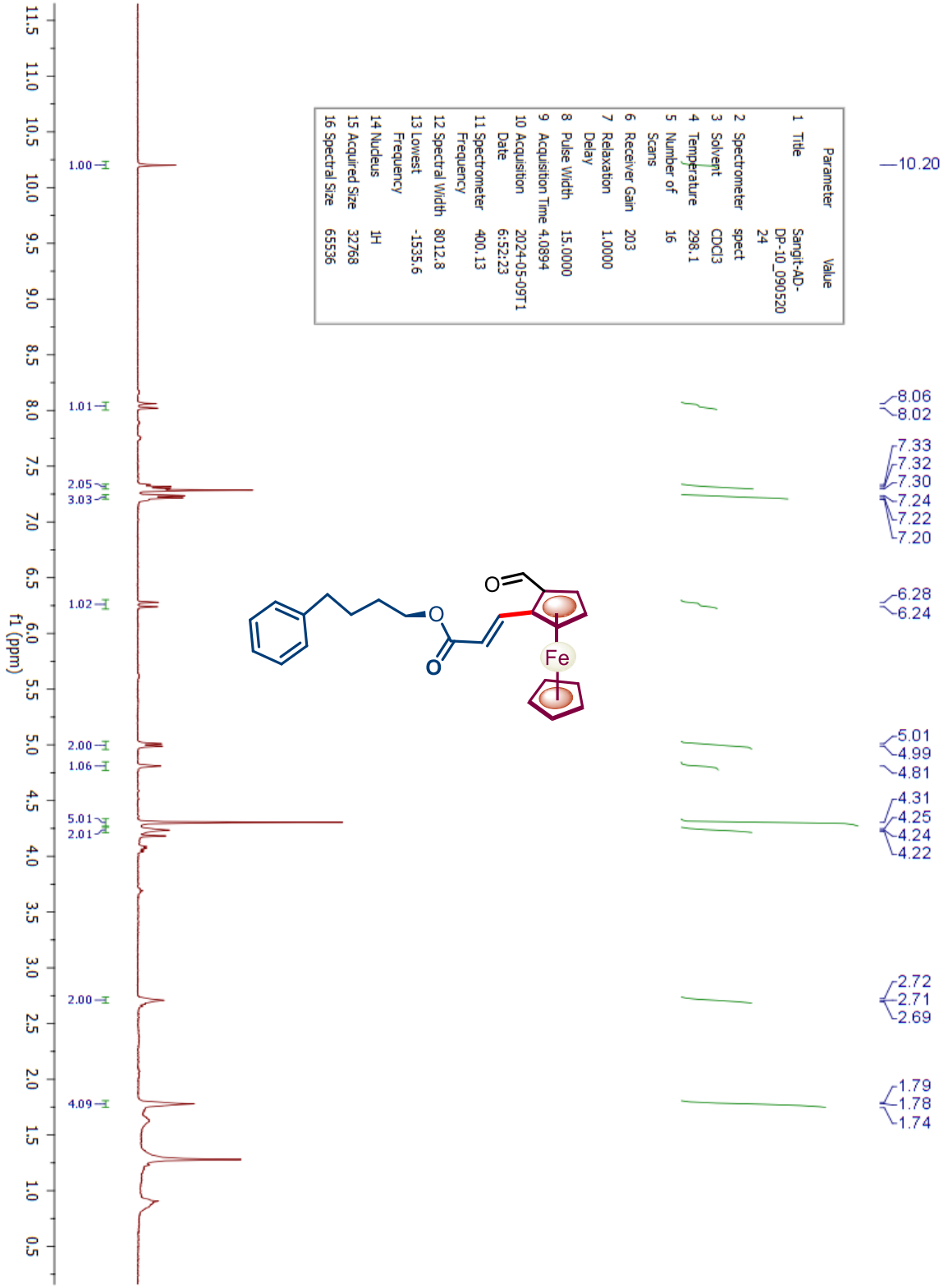
^{1}H NMR Spectrum of 3n



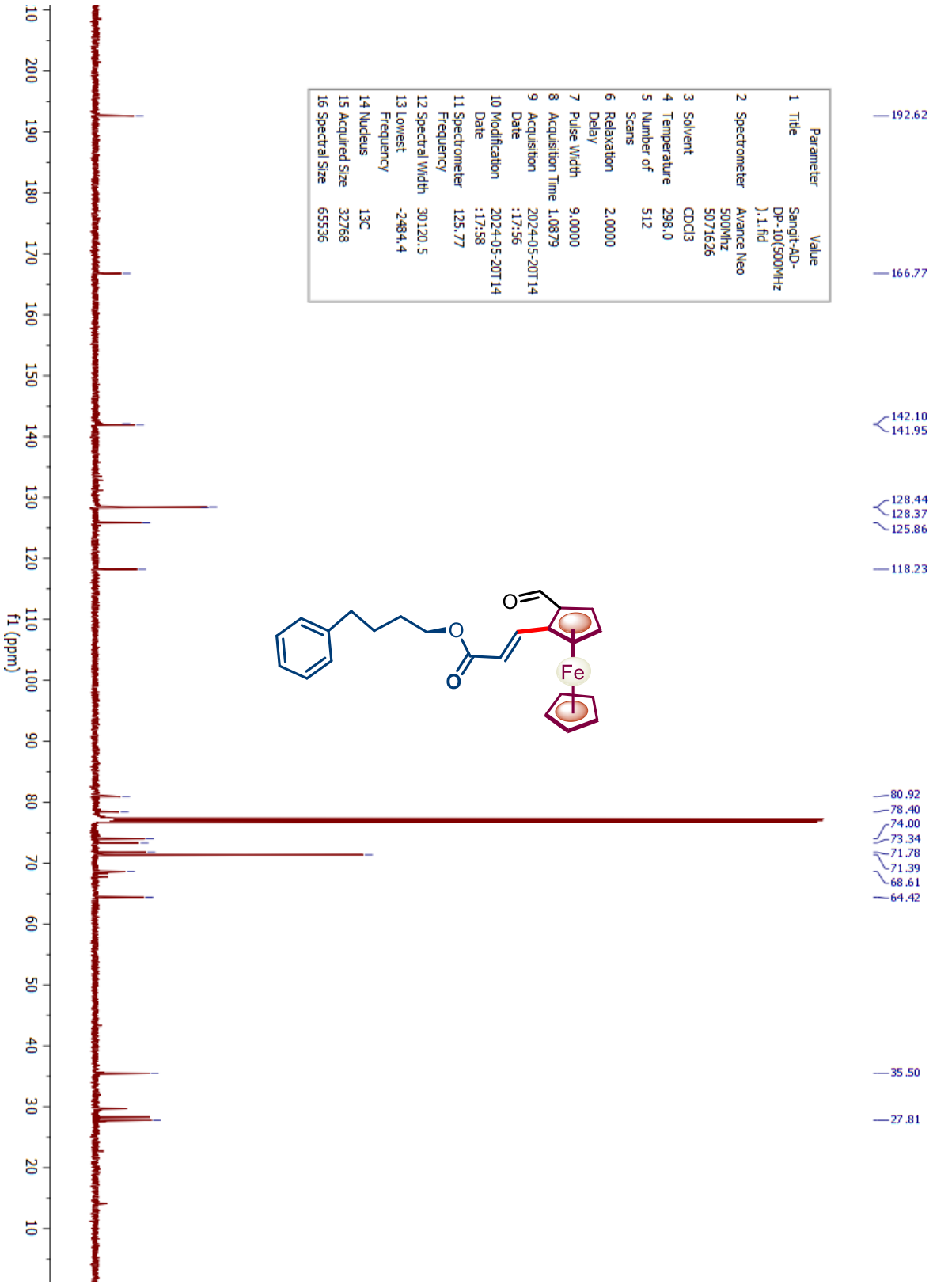
$^{13}C\{^{1}H\}$ NMR Spectrum of 3n



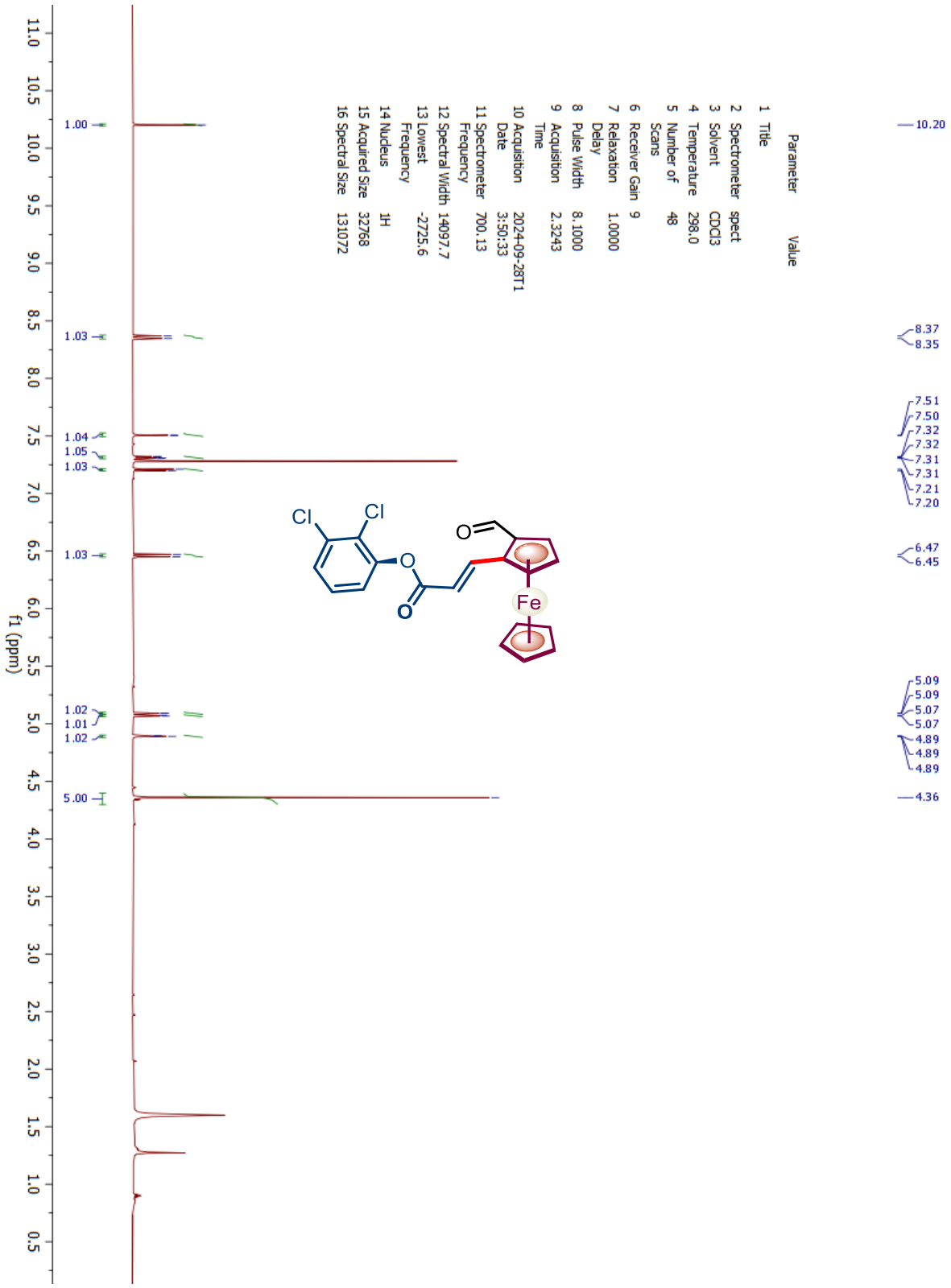
^{1}H NMR Spectrum of 3o



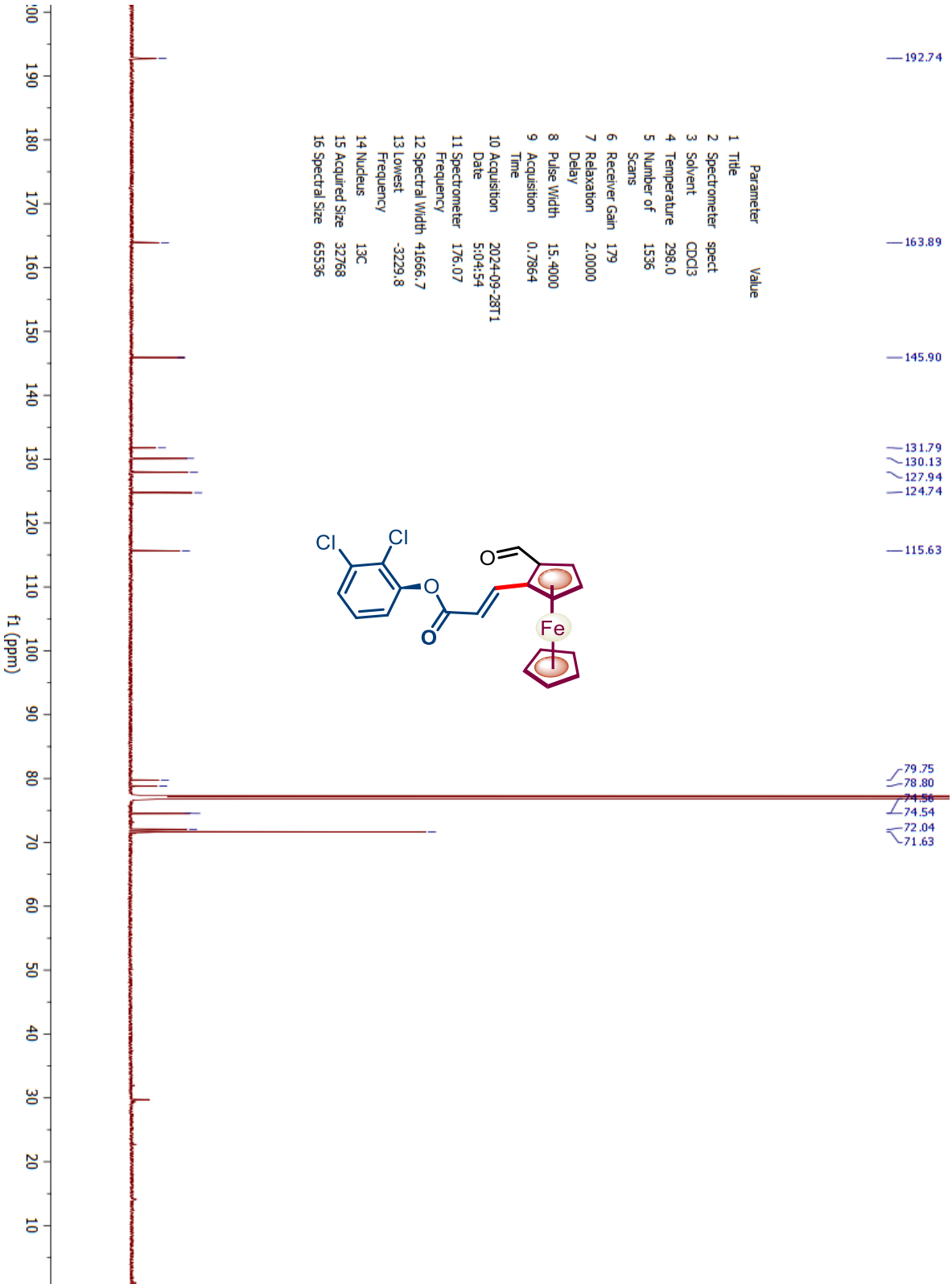
$^{13}C\{^{1}H\}$ NMR Spectrum of 3o



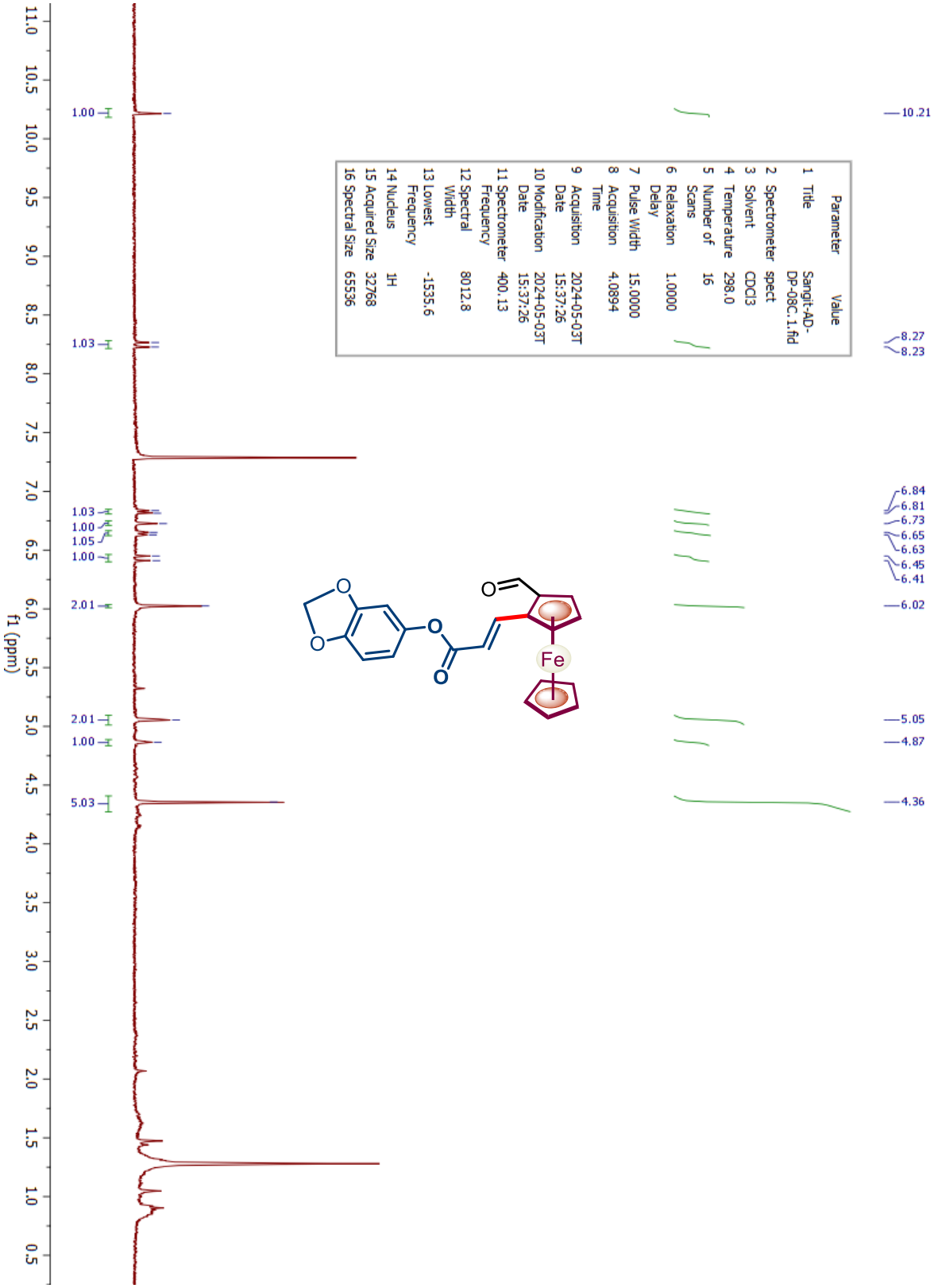
^{1}H NMR Spectrum of 3p



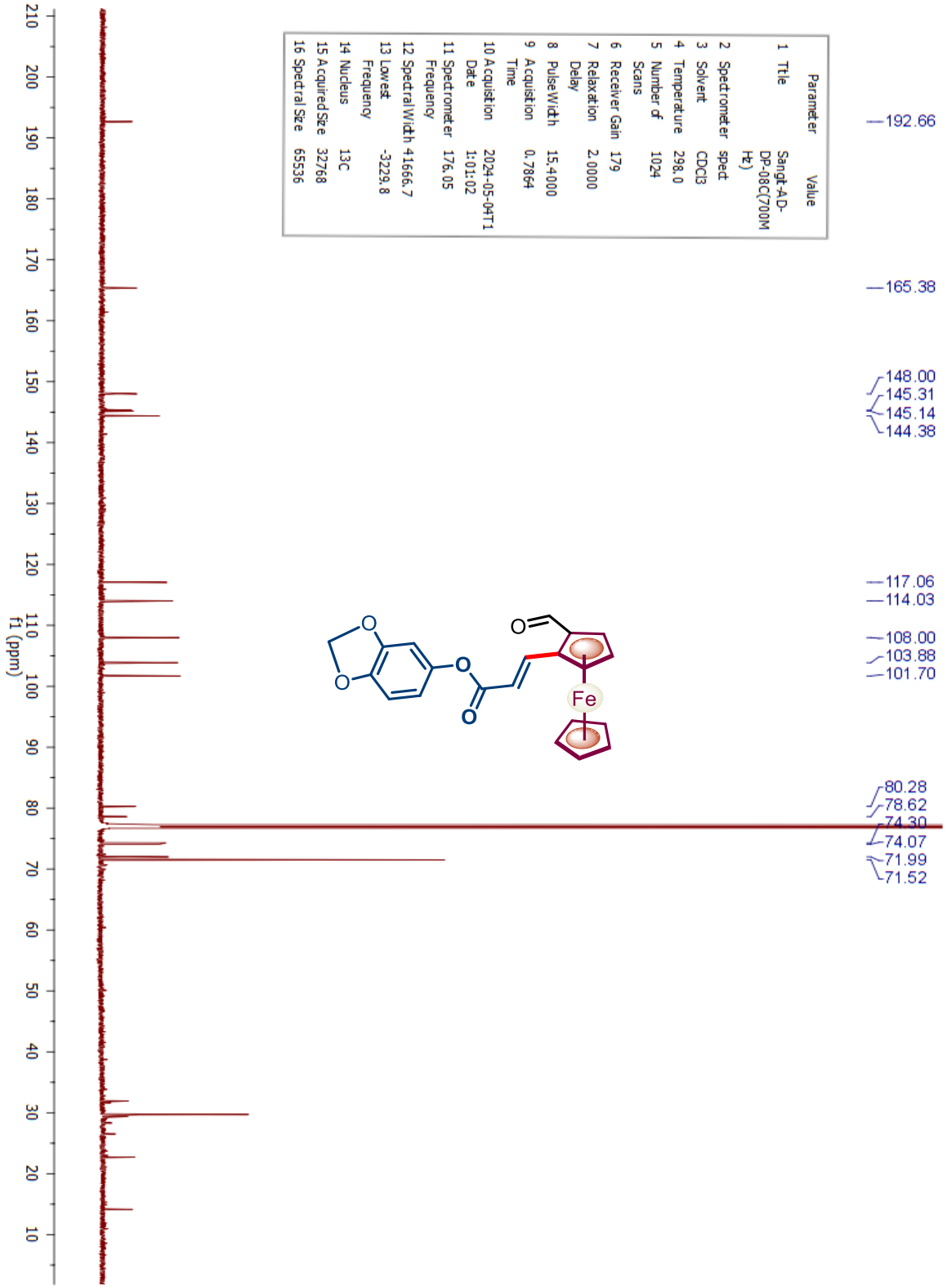
$^{13}C\{^{1}H\}$ NMR Spectrum of 3p



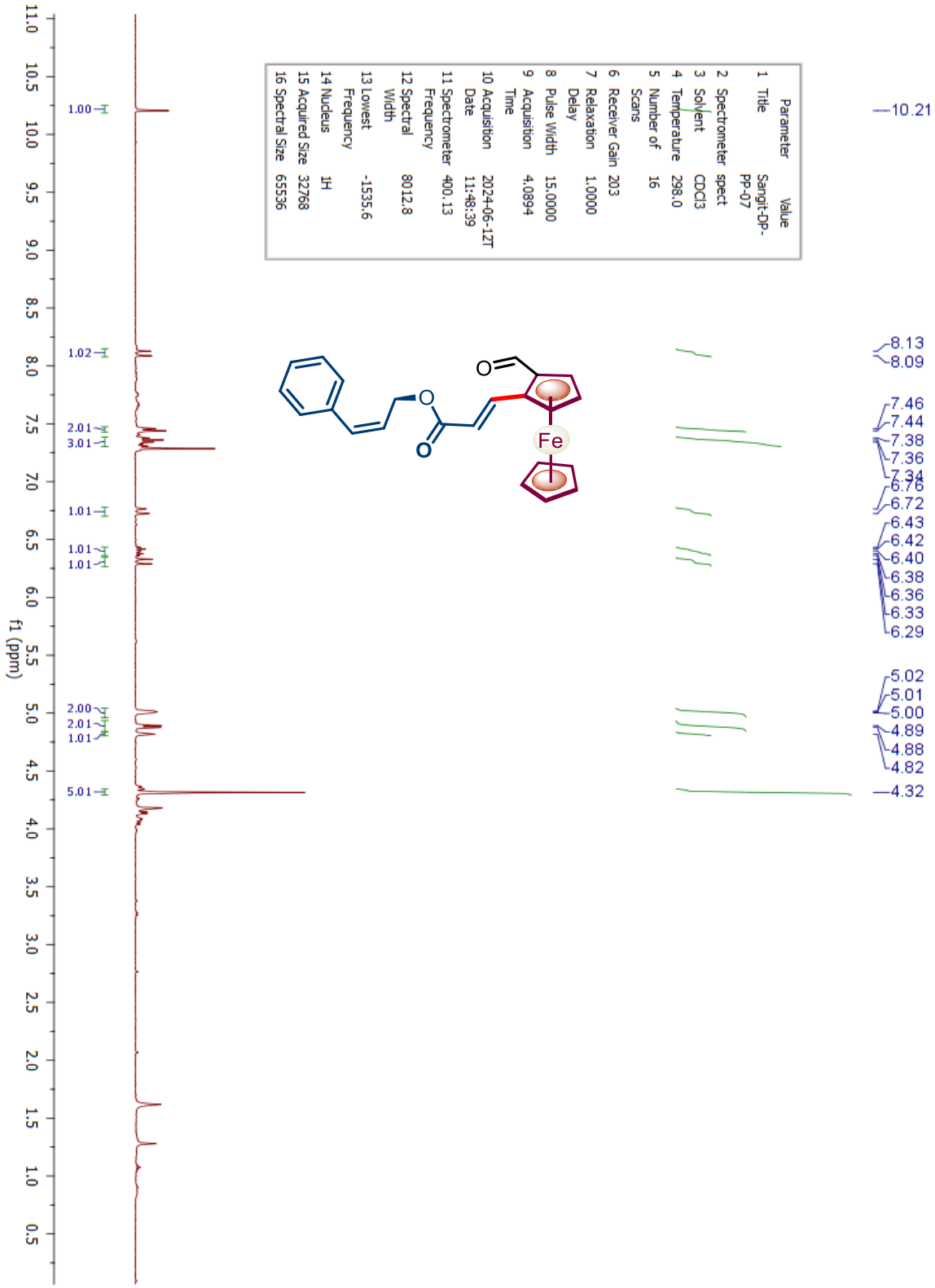
^{1}H NMR Spectrum of 3q



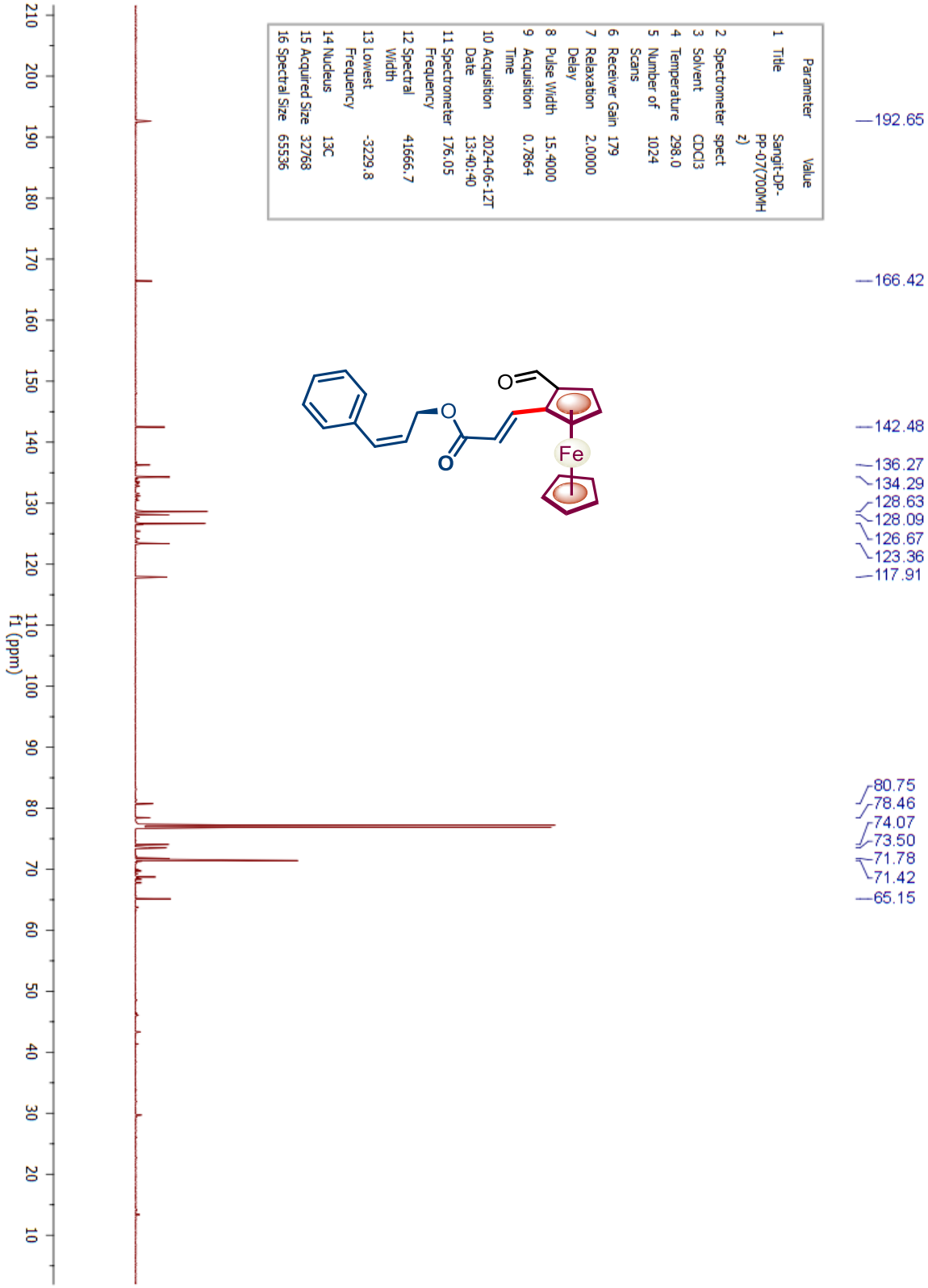
$^{13}C\{^{1}H\}$ NMR Spectrum of 3q



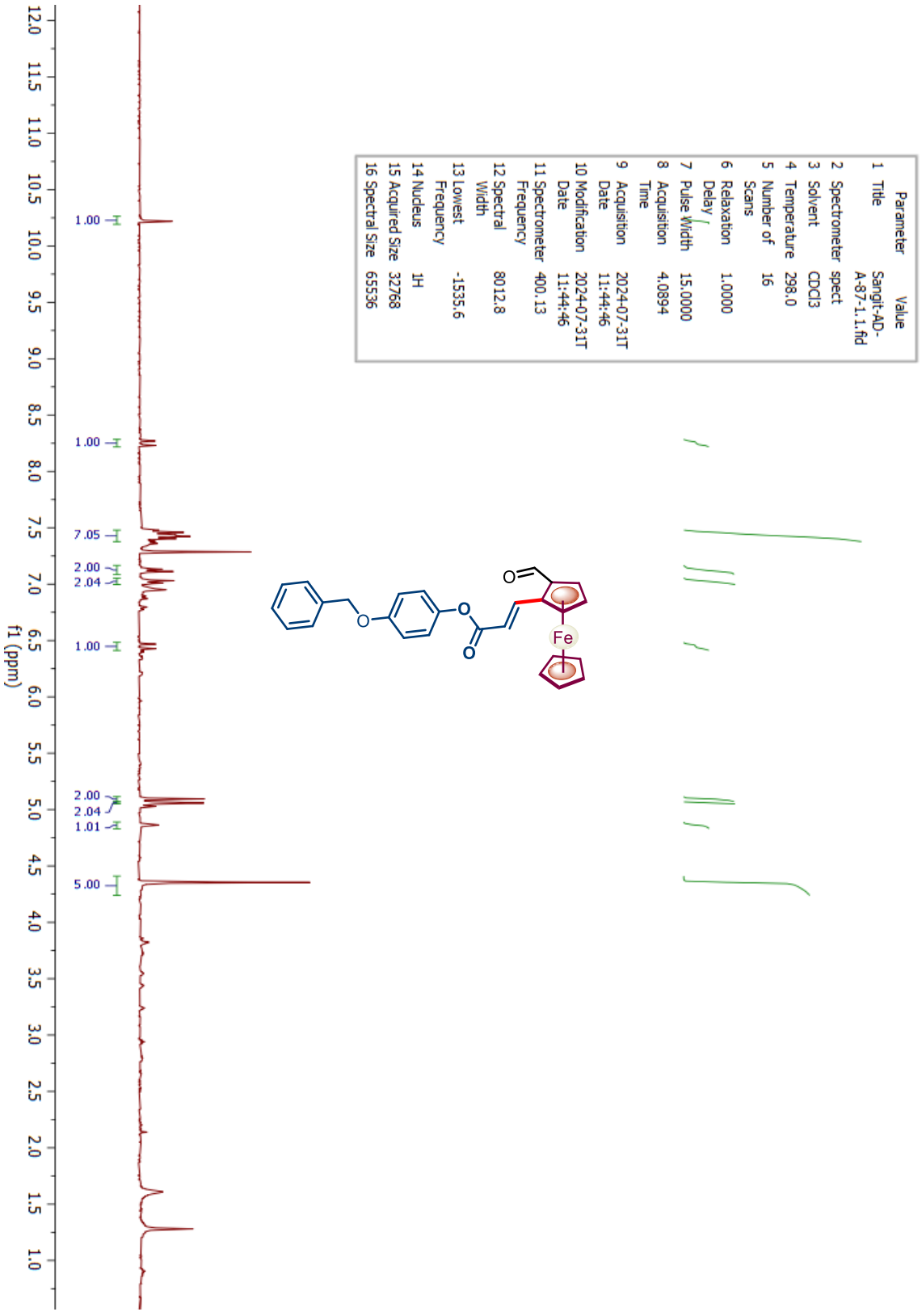
^{1}H NMR Spectrum of 3r



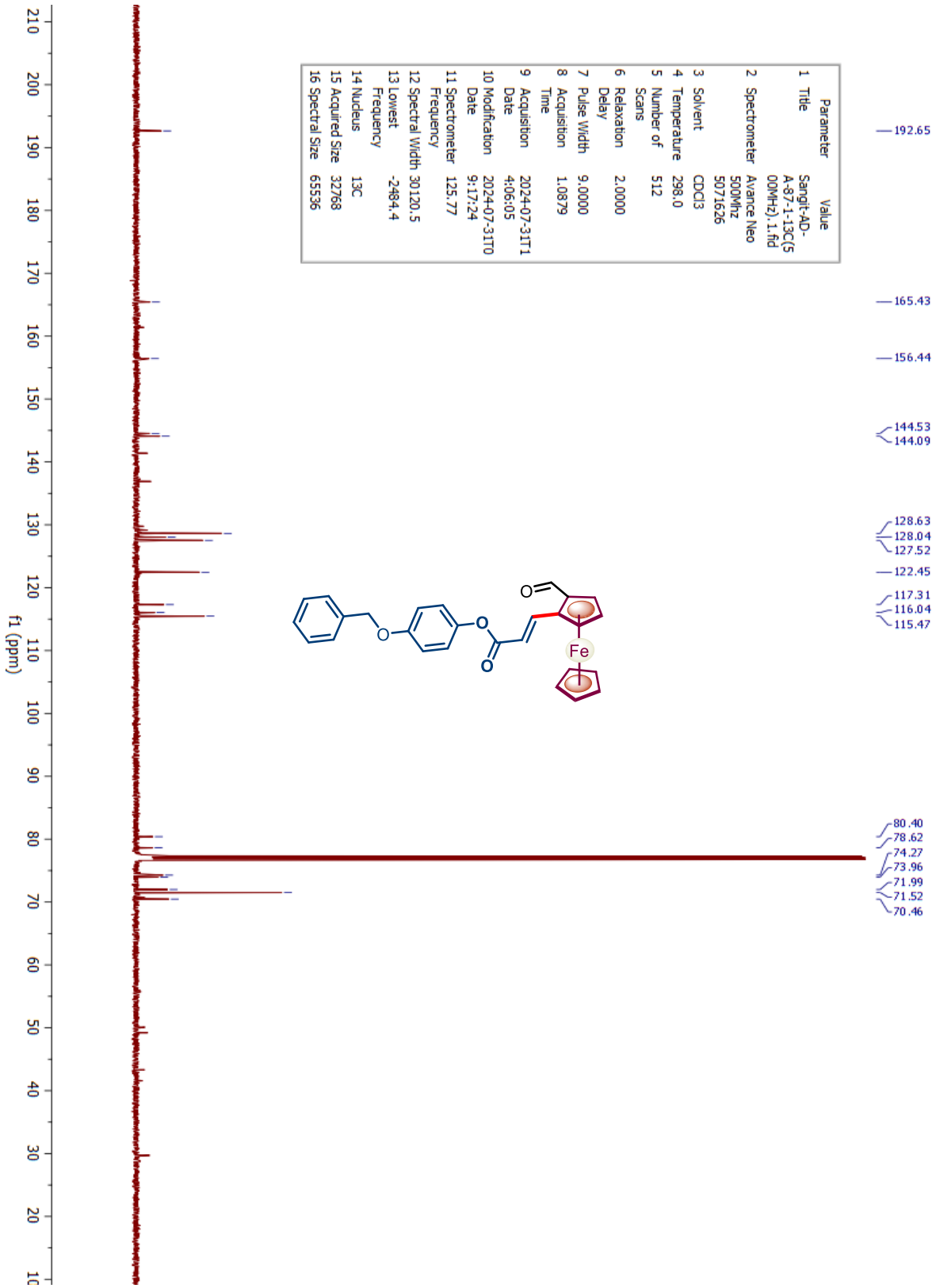
$^{13}C\{^{1}H\}$ NMR Spectrum of 3r



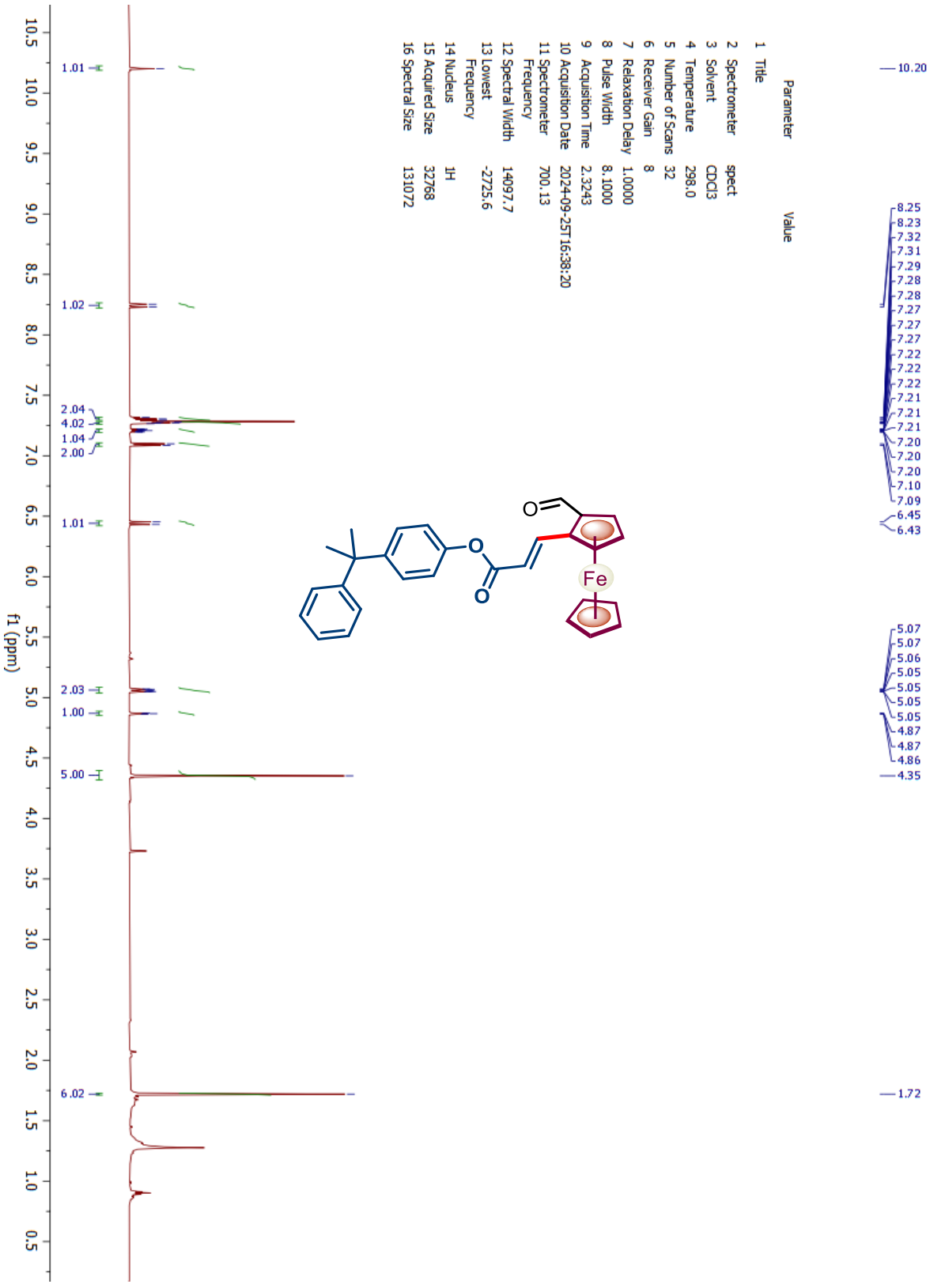
^{1}H NMR Spectrum of 3s



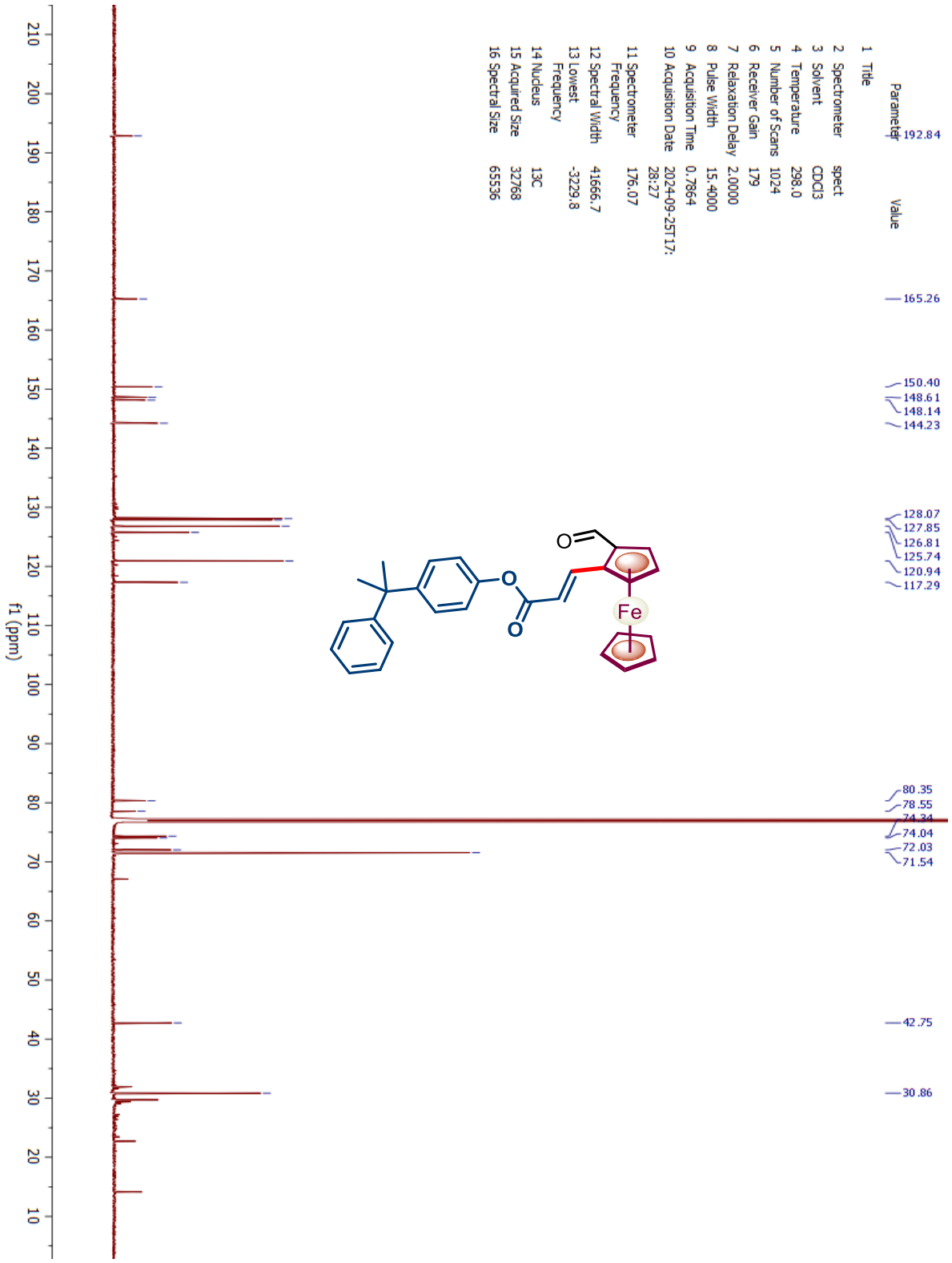
$^{13}C\{^{1}H\}$ NMR Spectrum of 3s



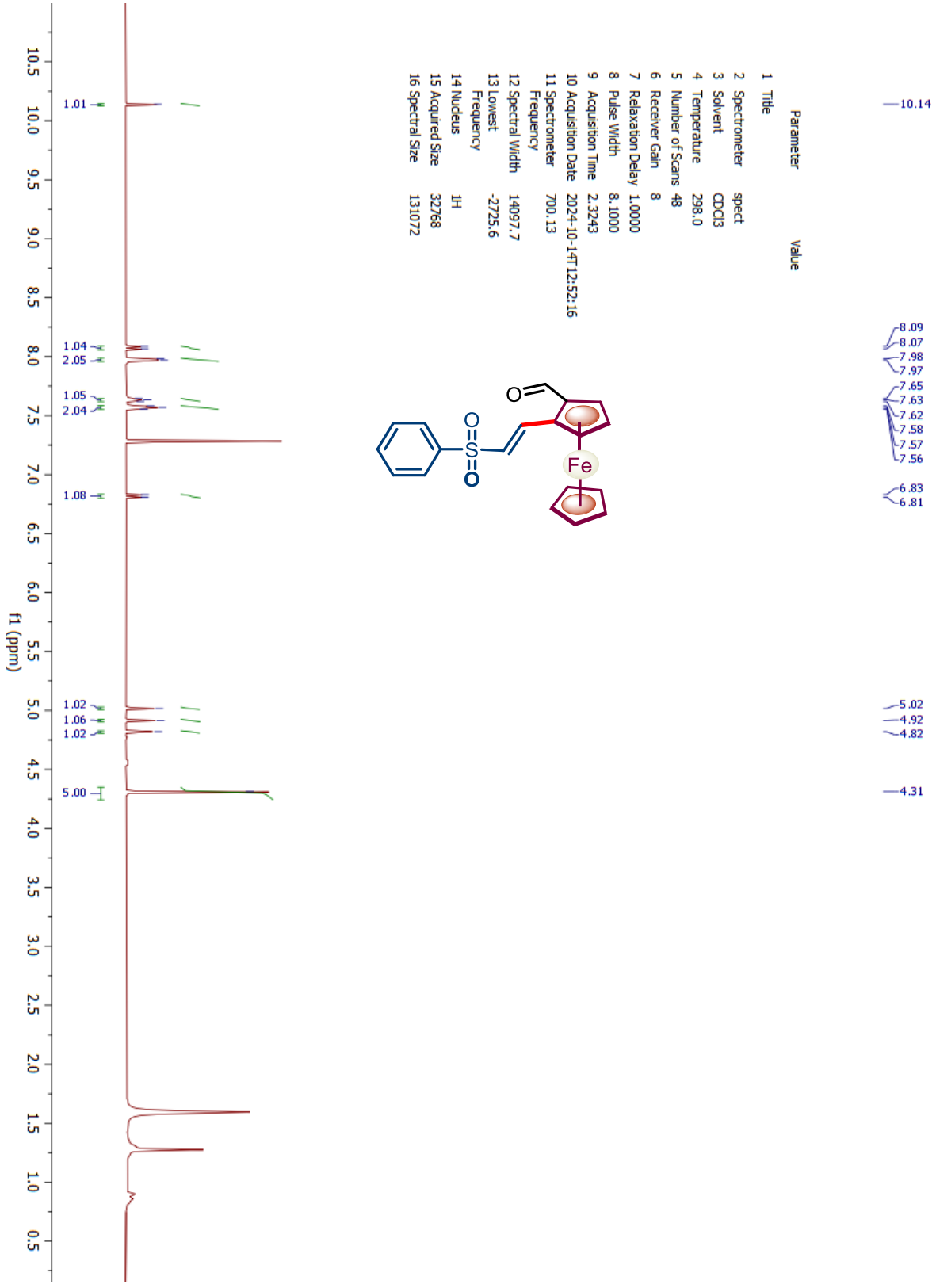
^{1}H NMR Spectrum of 3t



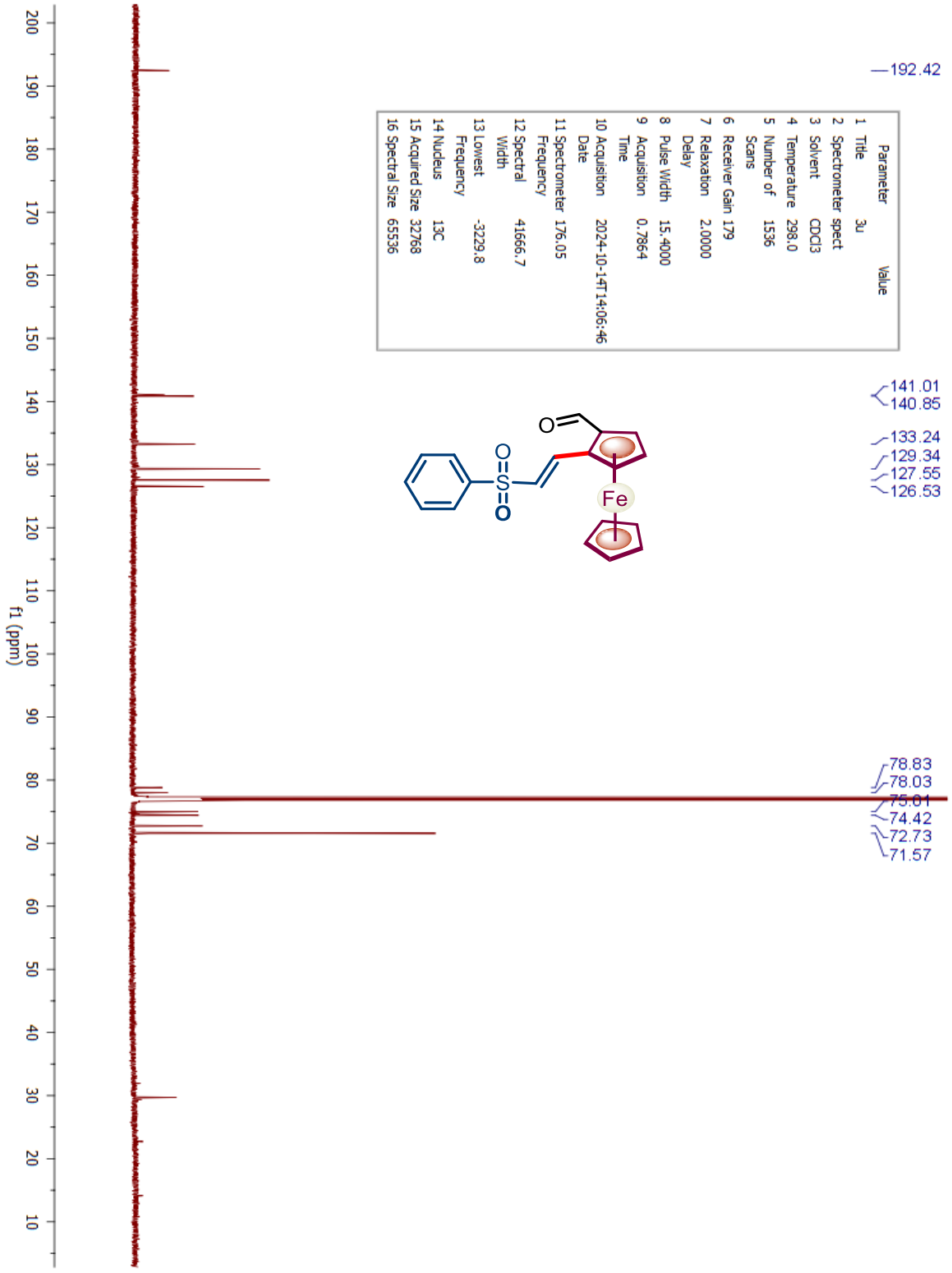
$^{13}C\{^{1}H\}$ NMR Spectrum of 3t



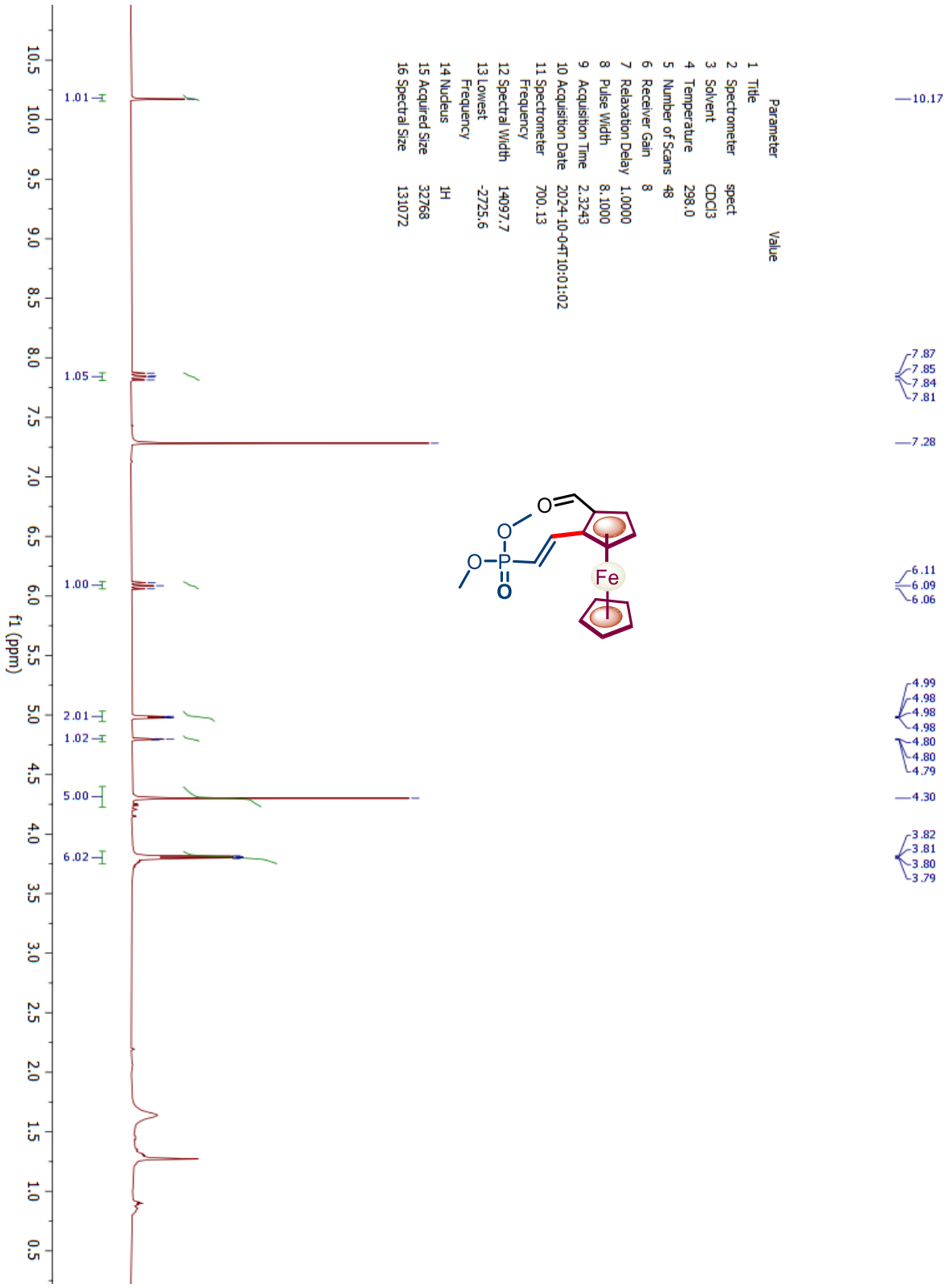
^{1}H NMR Spectrum of 3u



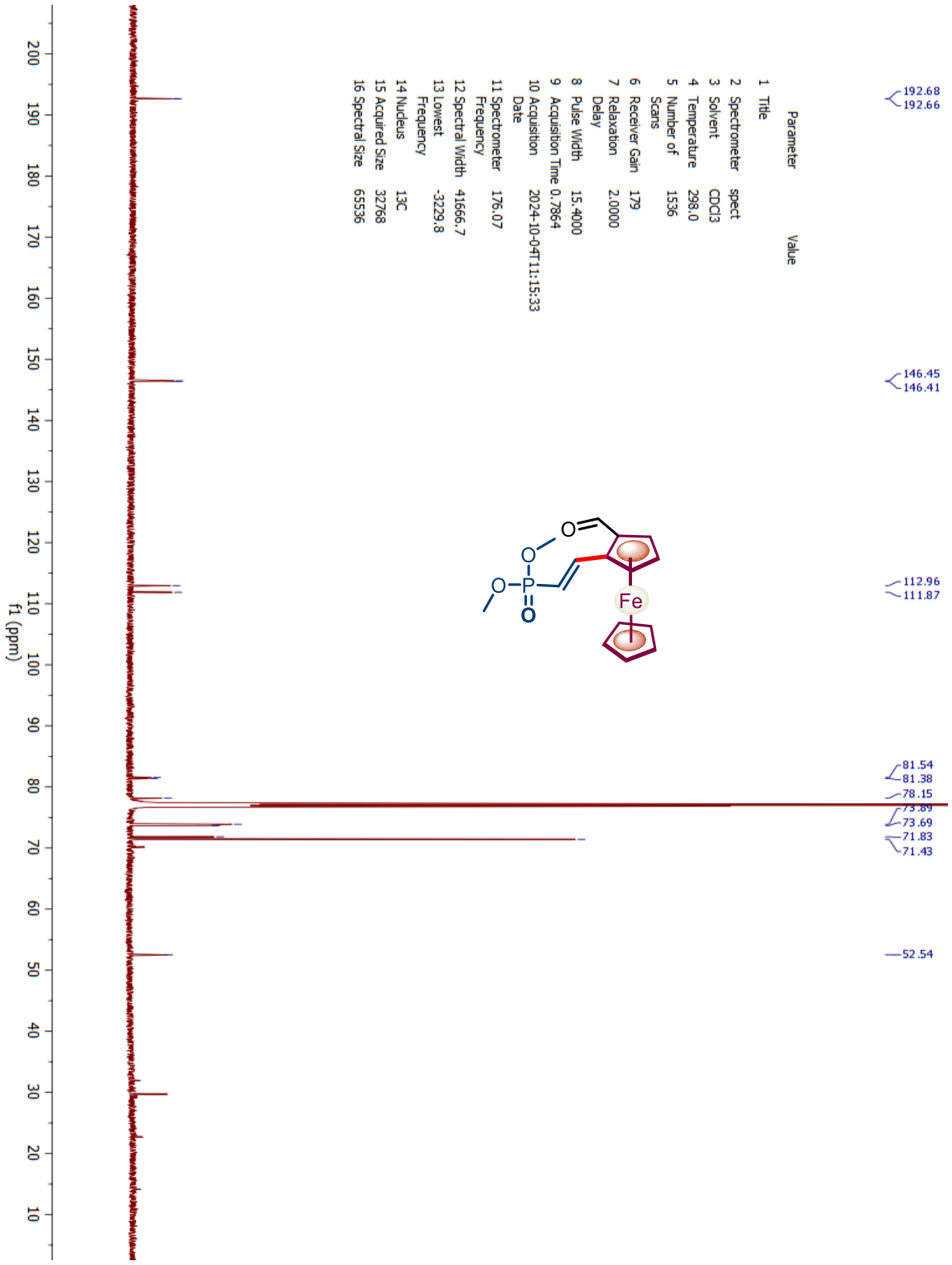
$^{13}C\{^{1}H\}$ NMR Spectrum of 3u



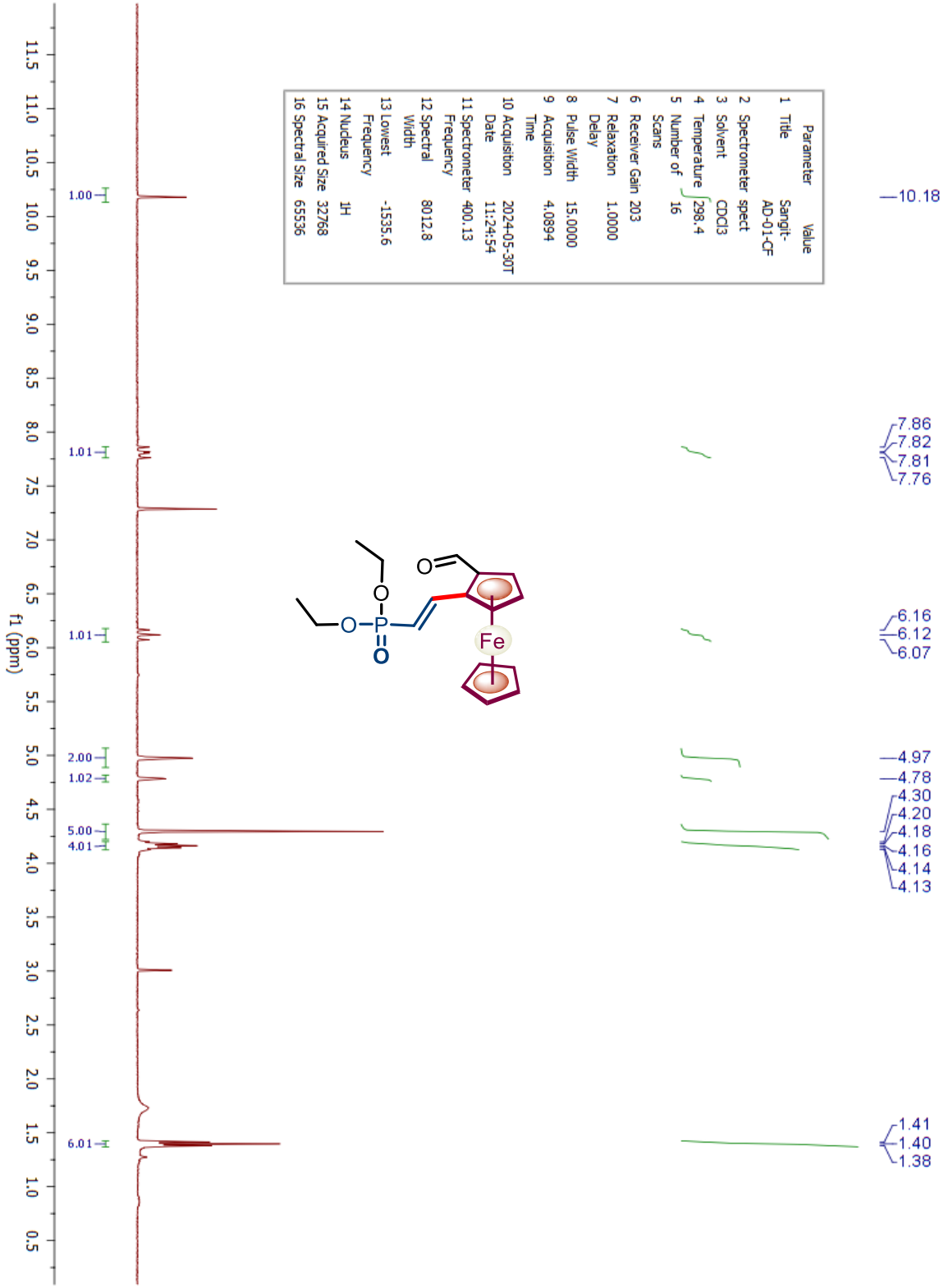
^{1}H NMR Spectrum of 3v



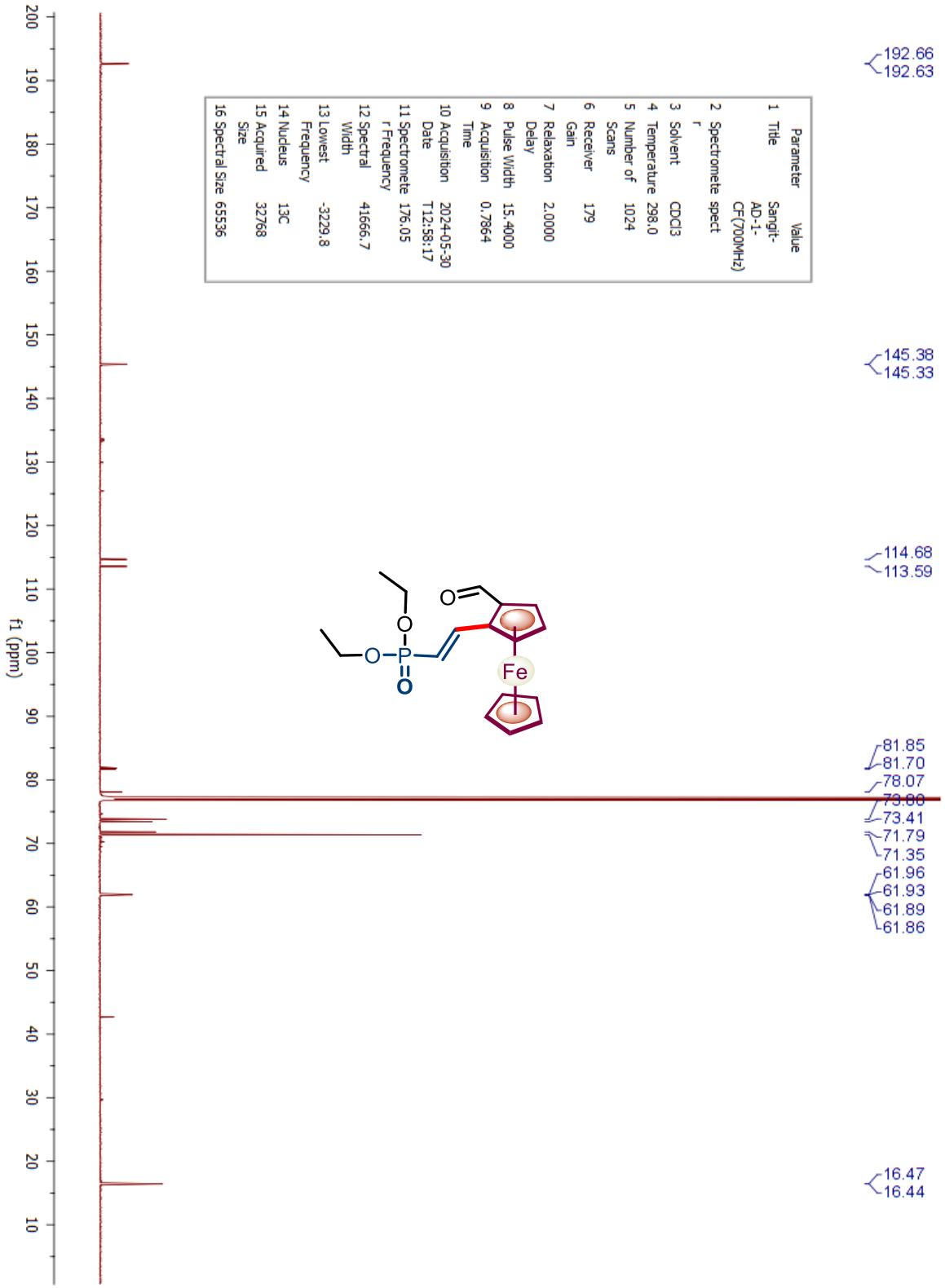
$^{13}C\{^{1}H\}$ NMR Spectrum of 3v



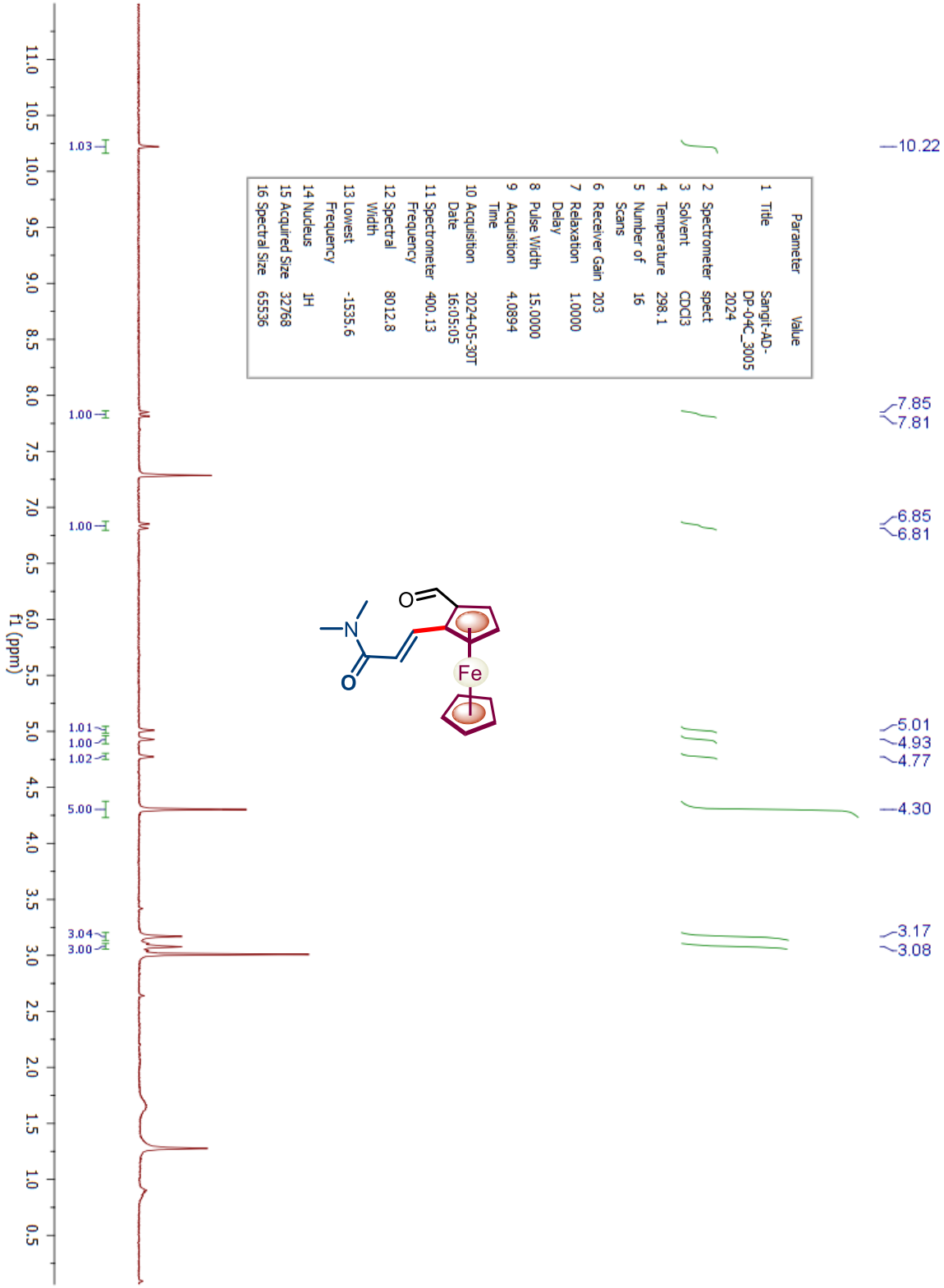
^{1}H NMR Spectrum of 3w



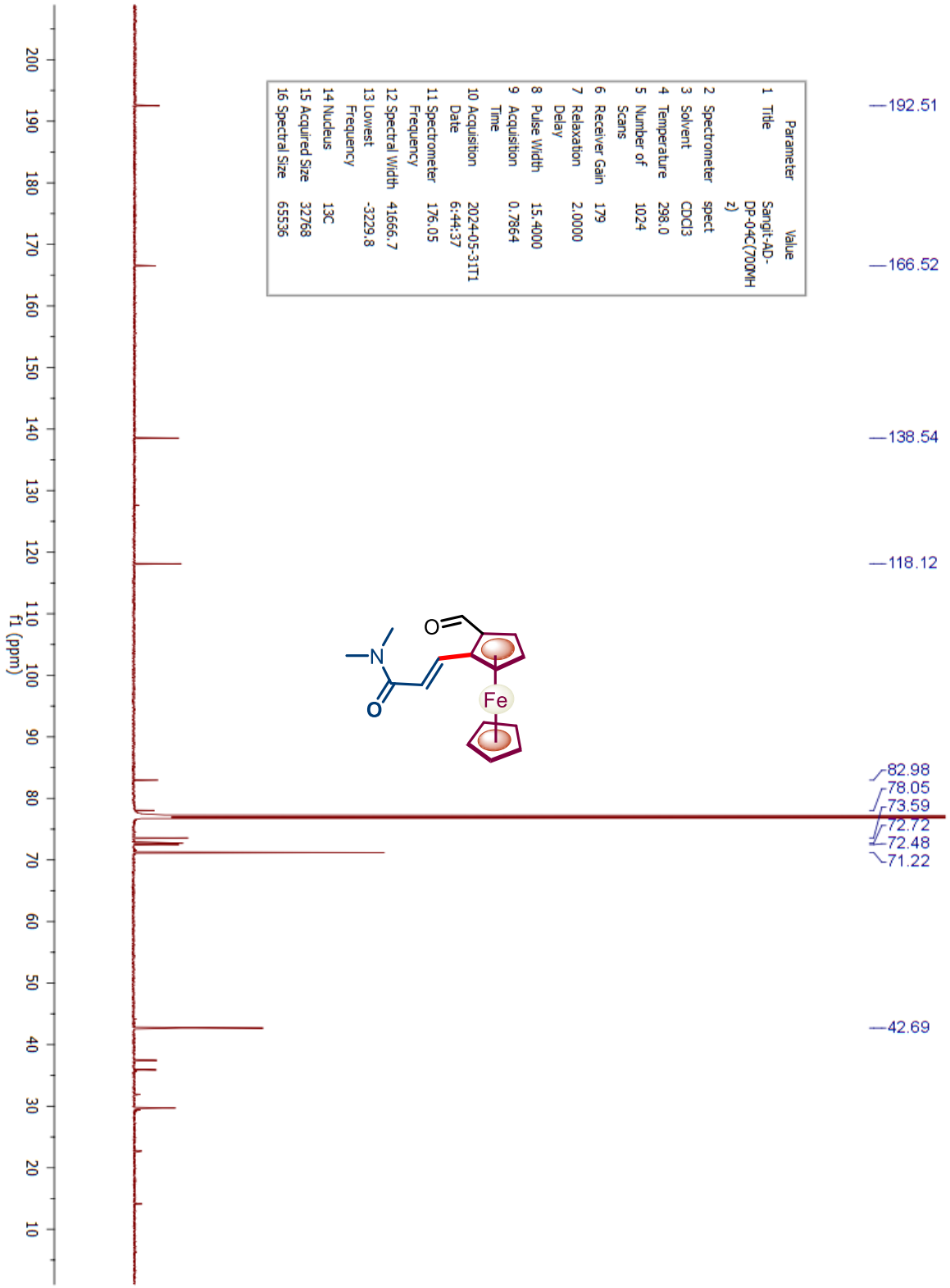
$^{13}C\{^{1}H\}$ NMR Spectrum of 3w



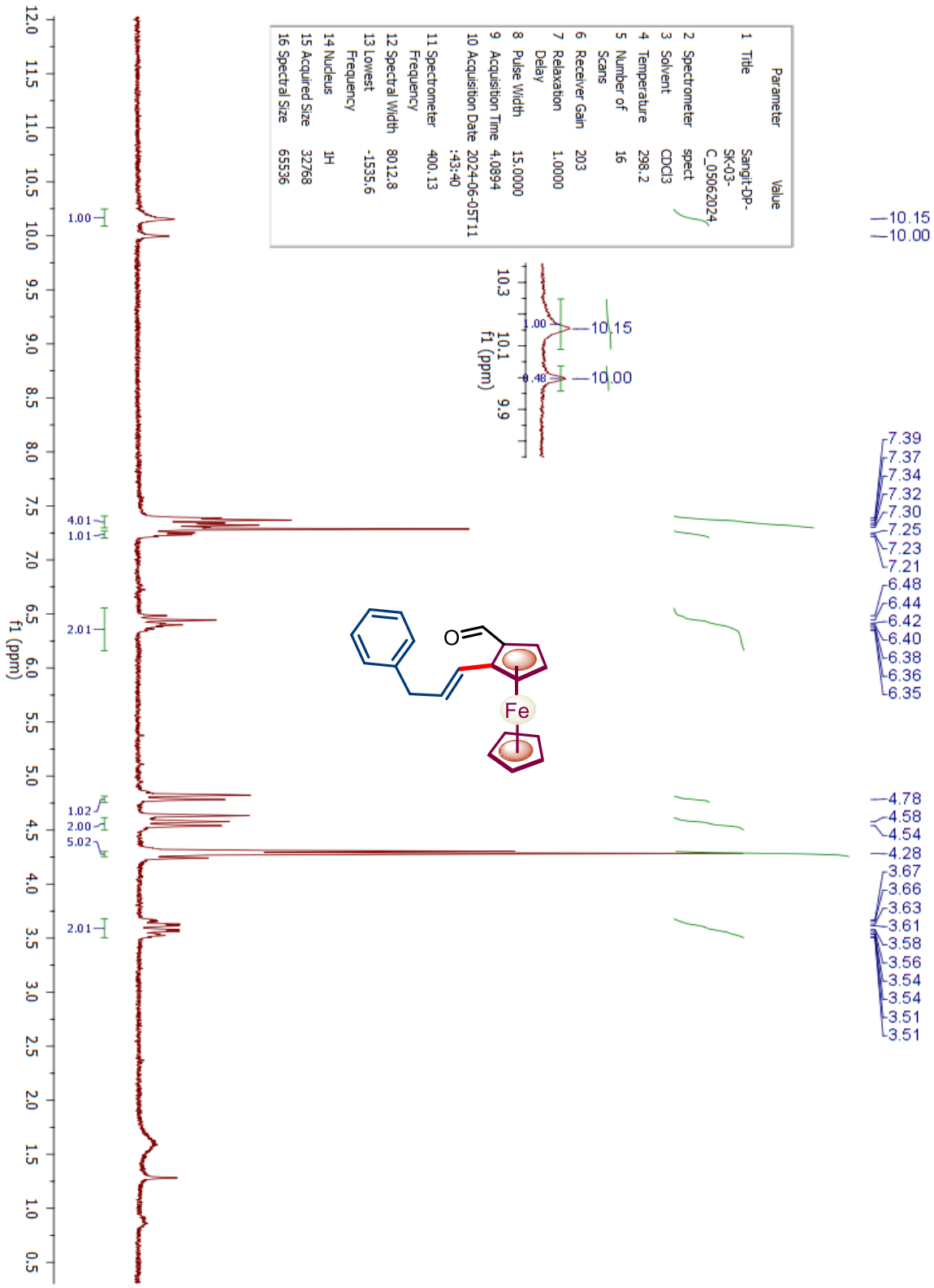
^{1}H NMR Spectrum of 3x



$^{13}C\{^{1}H\}$ NMR Spectrum of 3x

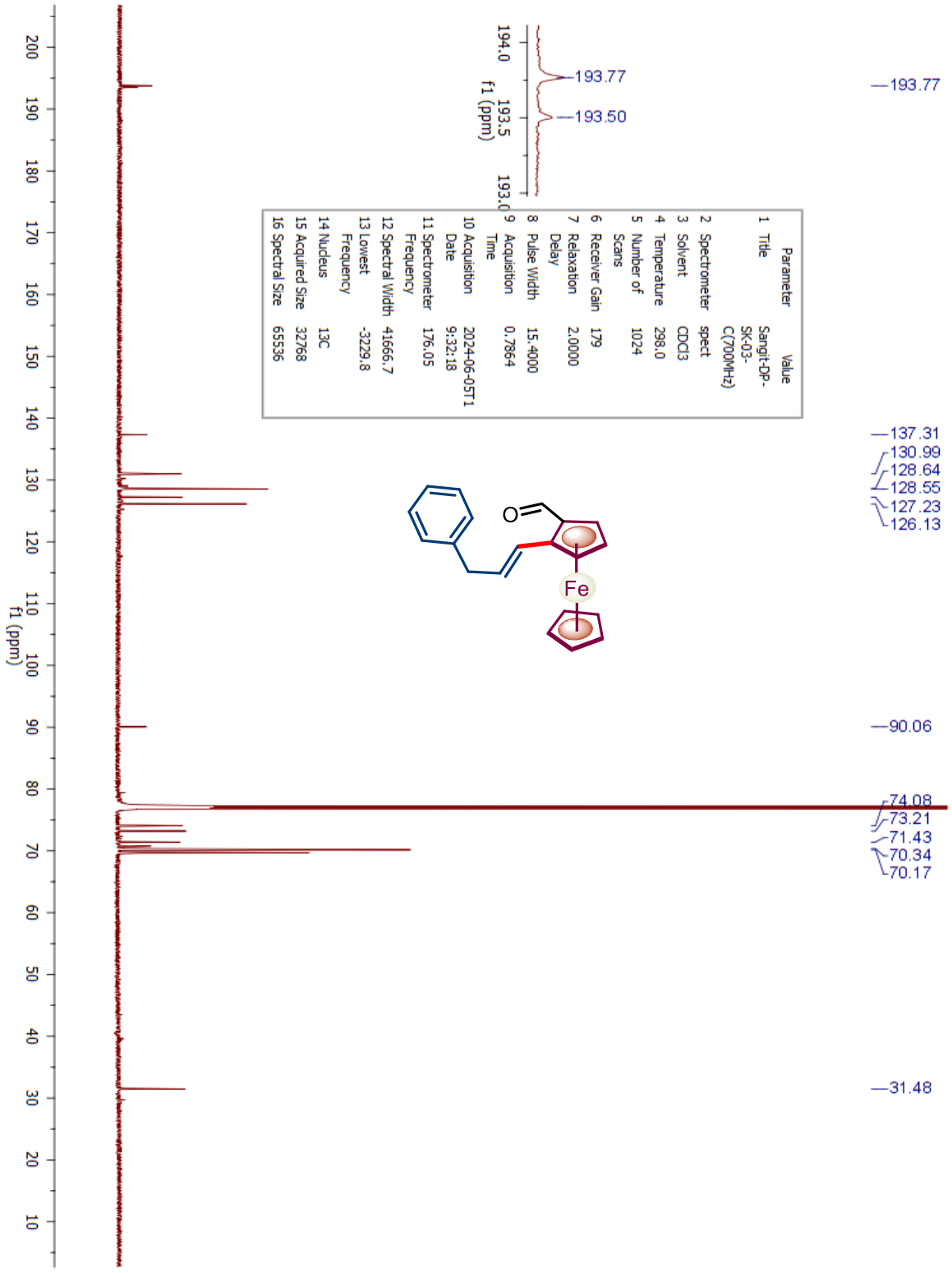


^{1}H NMR Spectrum of 3y



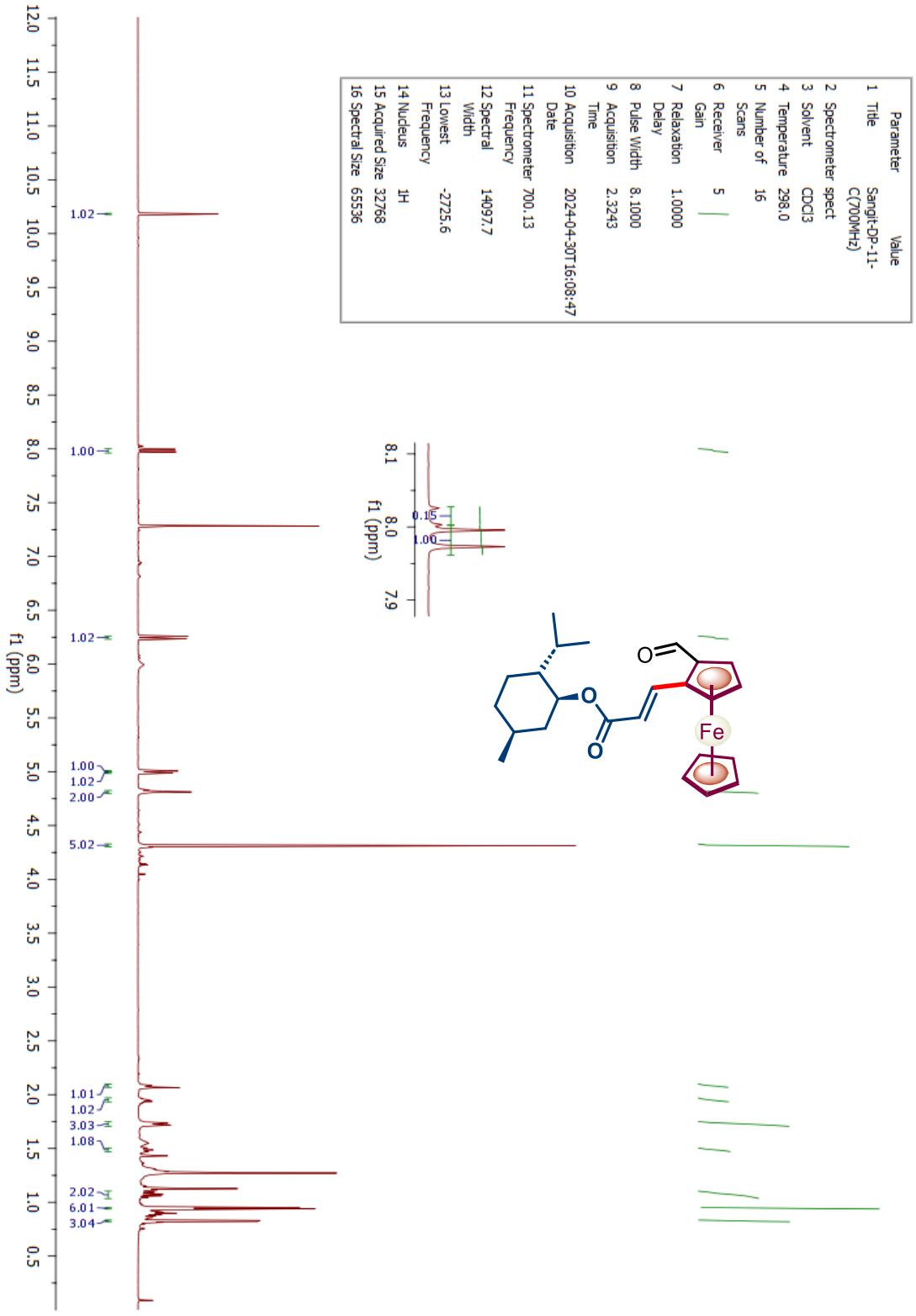
During purification, of **3y,** slight inseparable impurities of aldehyde is observed after several repeated attempts.

$^{13}C\{^{1}H\}$ NMR Spectrum of 3y

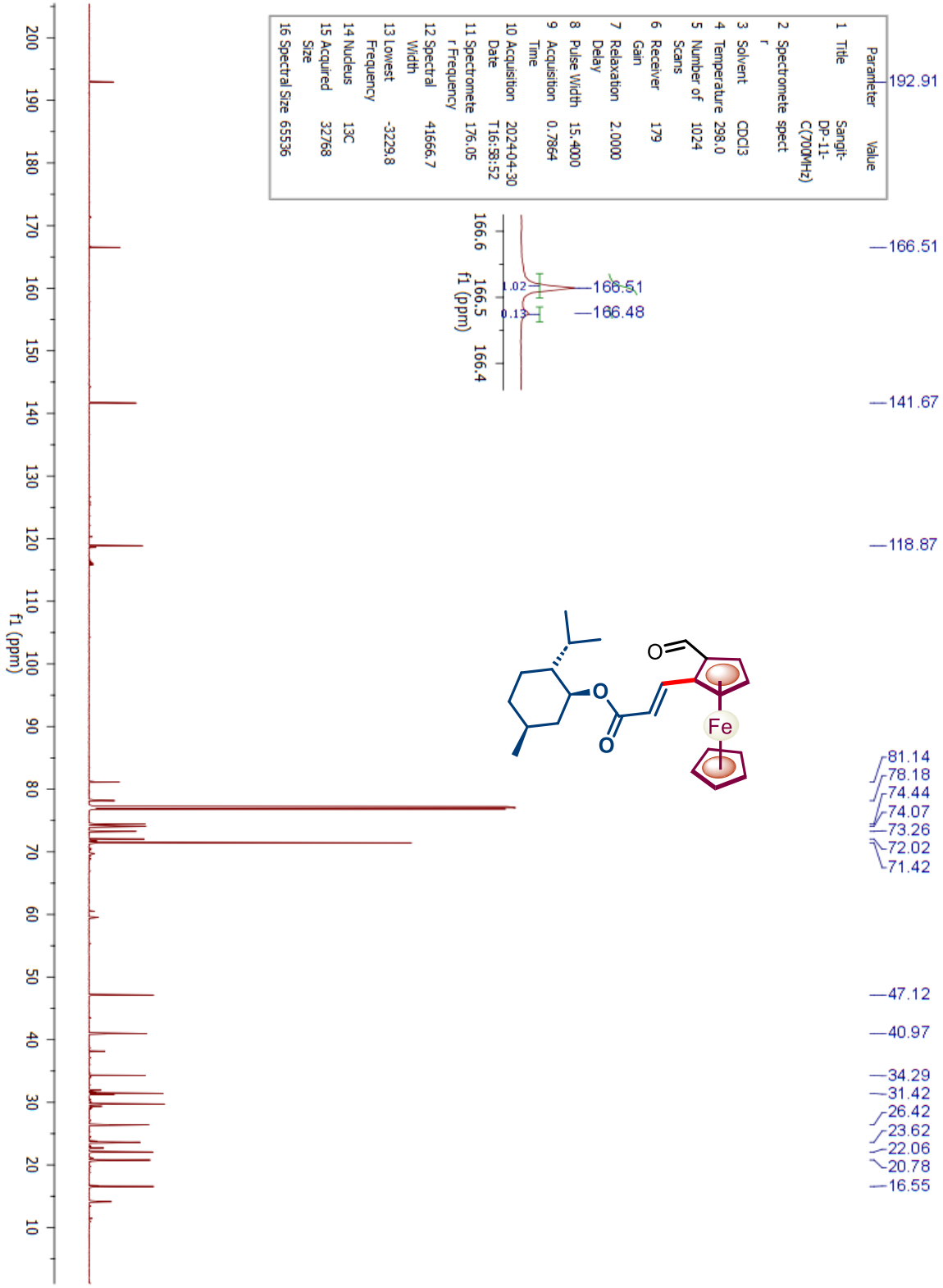


During purification, of **3y** slight inseparable impurities of aldehyde is observed after several attempts.

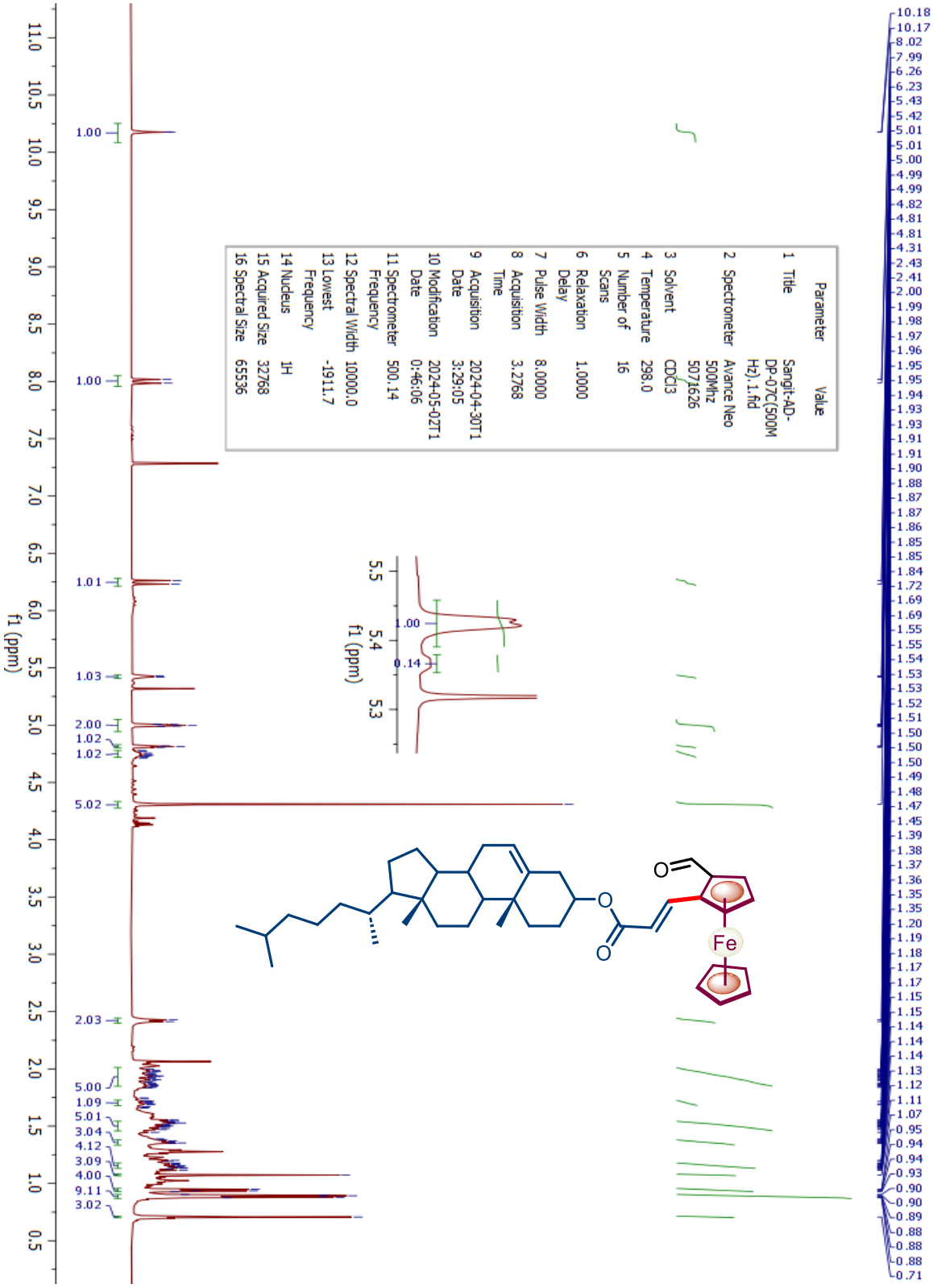
^{1}H NMR Spectrum of 3z



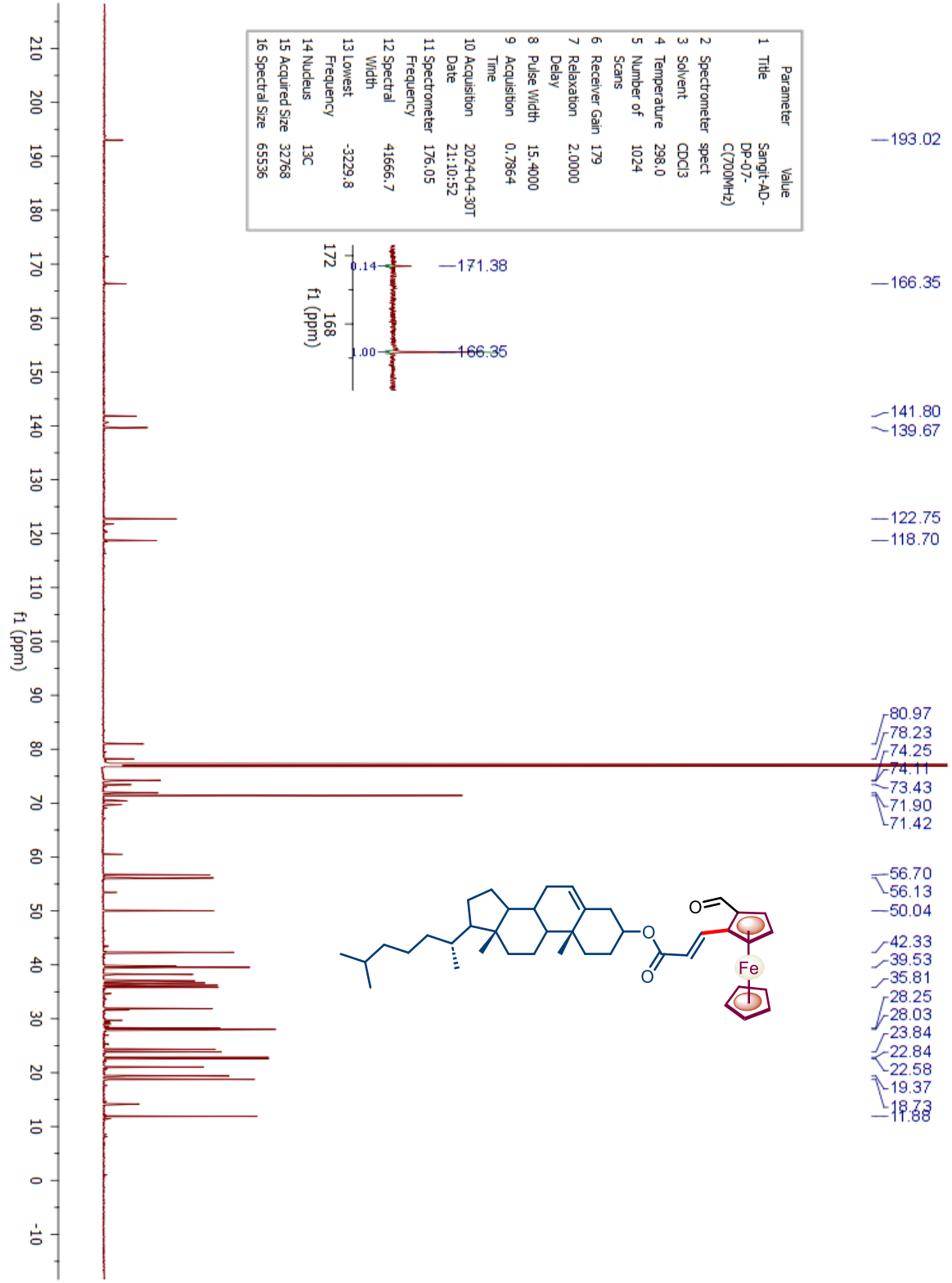
$^{13}C\{^{1}H\}$ NMR Spectrum of 3z



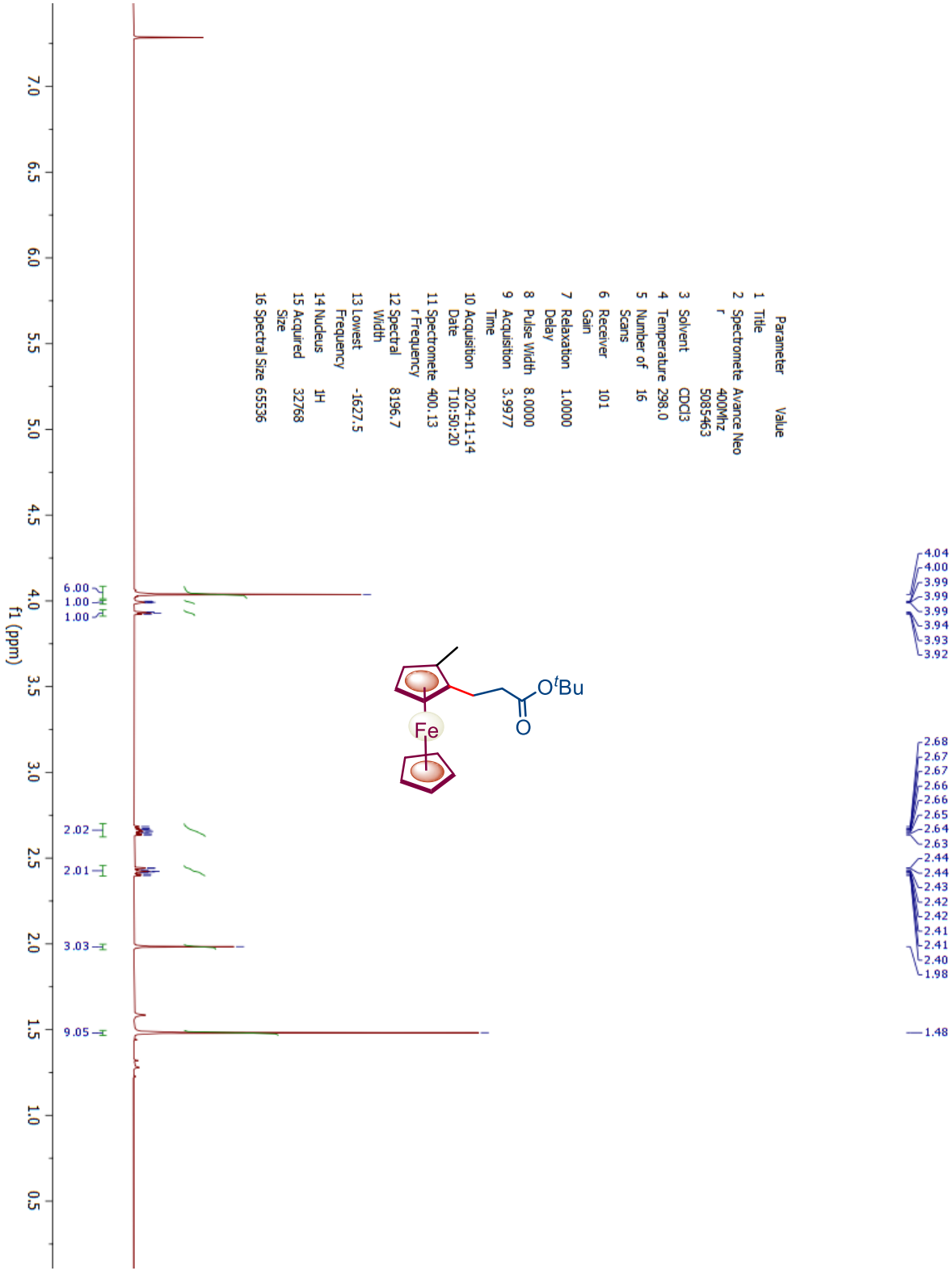
^{1}H NMR Spectrum of 3aa



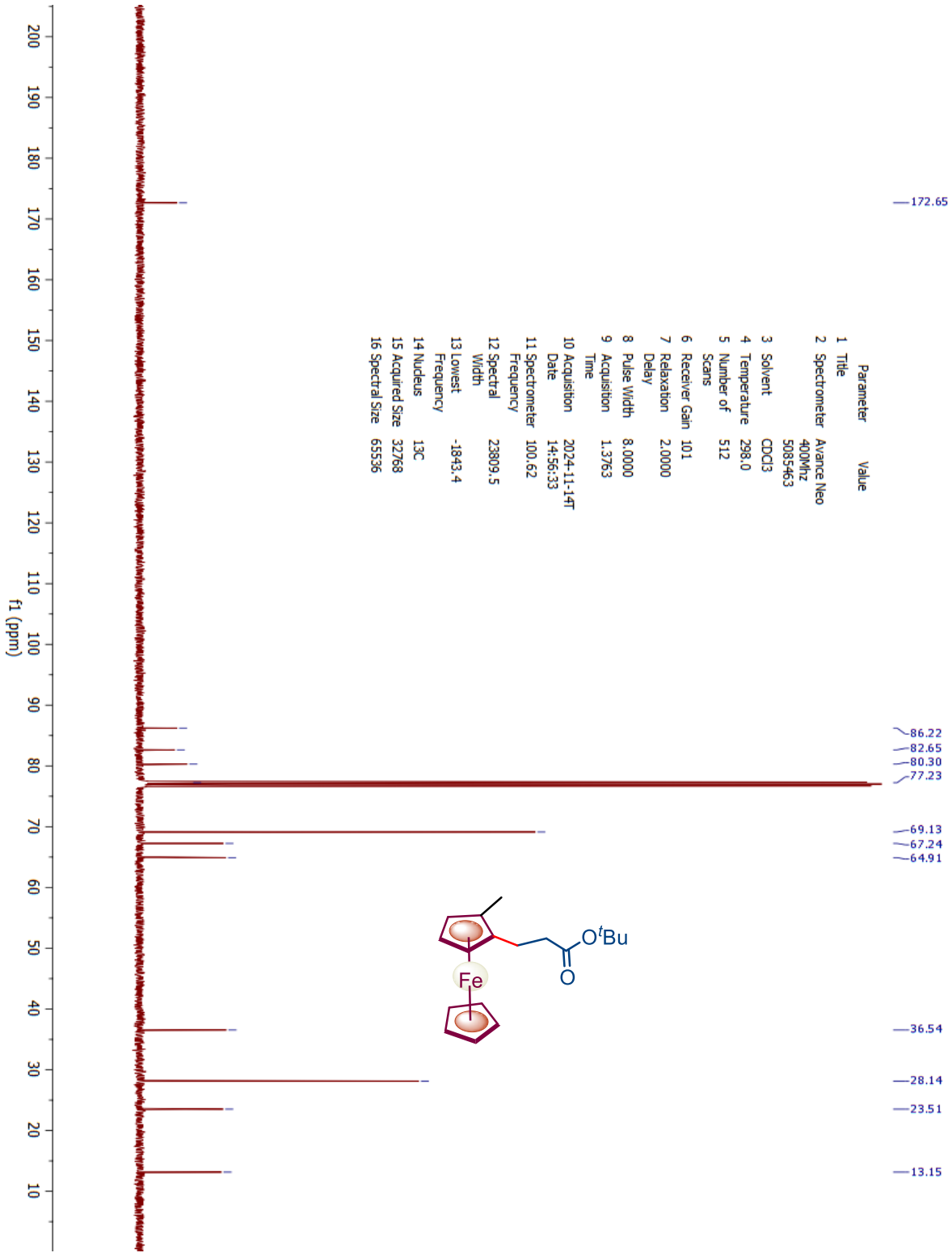
$^{13}C\{^{1}H\}$ NMR Spectrum of 3aa



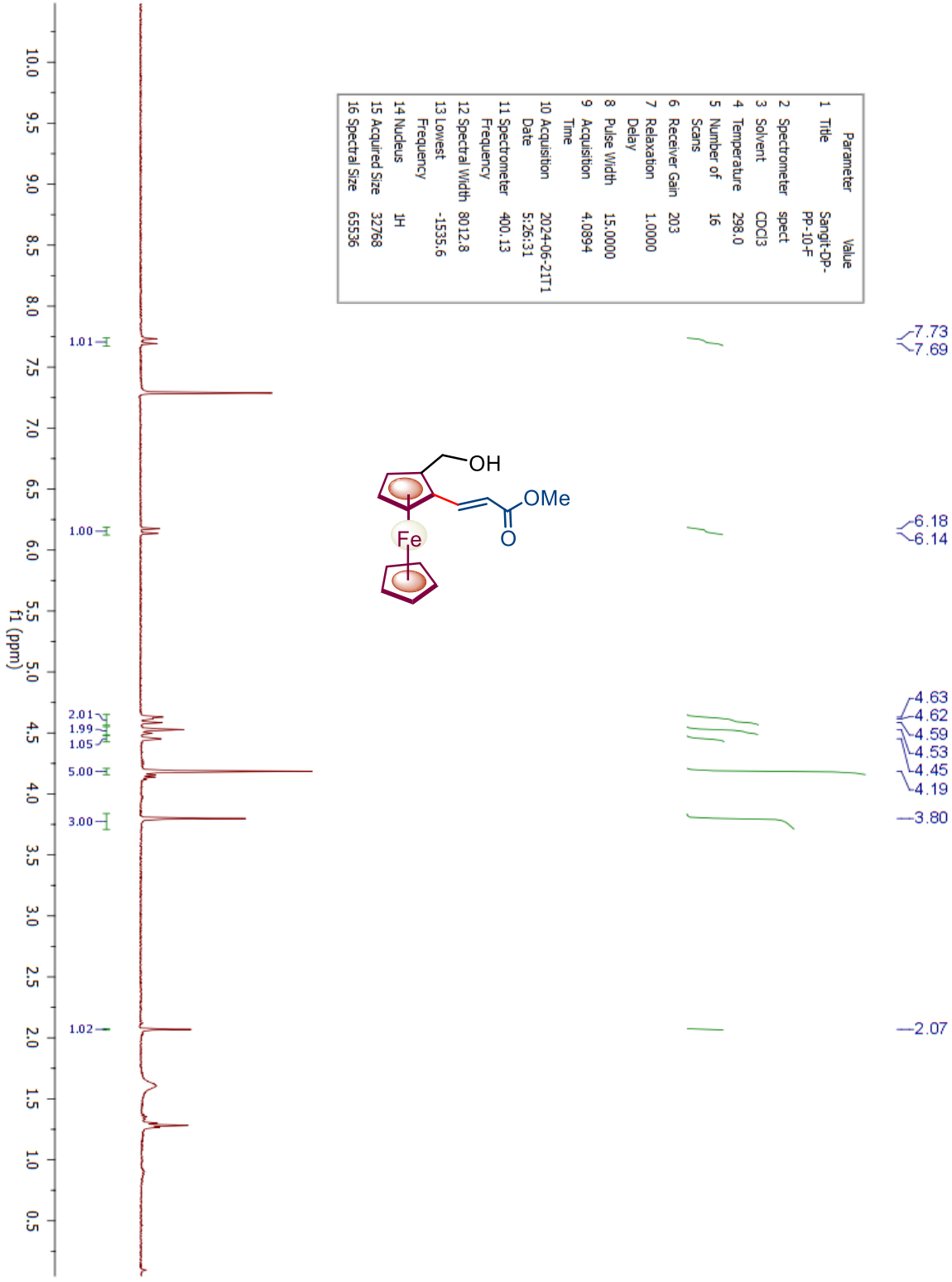
^{1}H NMR Spectrum of 4



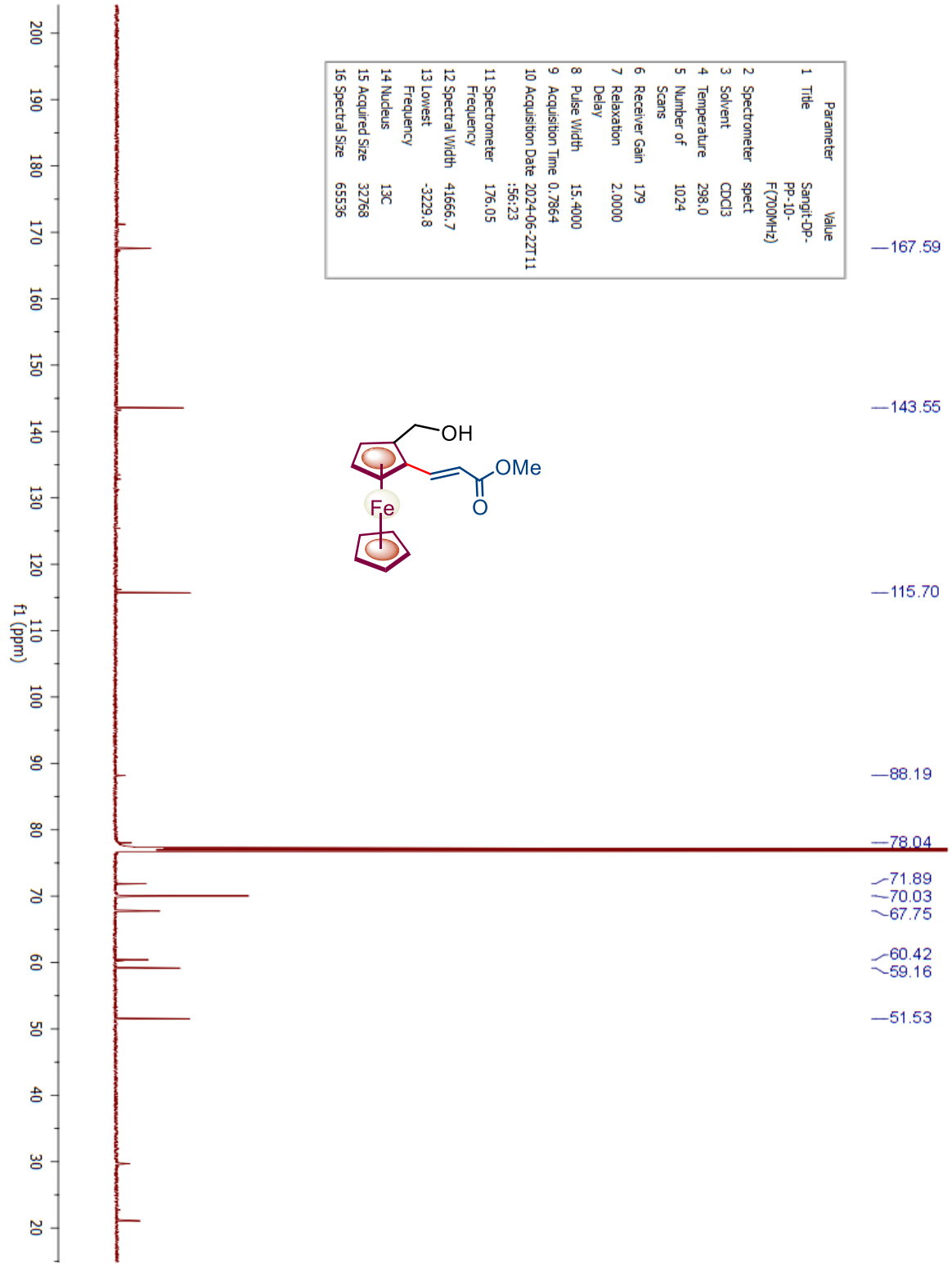
$^{13}C\{^{1}H\}$ NMR Spectrum of 4



^{1}H NMR Spectrum of 5



$^{13}C\{^{1}H\}$ NMR Spectrum of 5



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2. Q. J. Yao, P. P. Xie, Y. J. Wu, Y. L. Feng, M. Y. Teng, X. Hong, and B. F. Shi, *J. Am. Chem. Soc.,* 2020, **142,** 18266−18276.
3. (a) B.-F. Shi, N. Maugel, Y. H. Zhang, and J.-Q. Yu, *Angew. Chem. Int. Ed.,* 2008, **47,** 4882–4886. (b) J. M. González, X. Vidal, M. A. Ortuño, J. L. Mascareñas, and M. Gulías, *J. Am. Chem. Soc.*, 2022, **144,** 21437−21442.