Supporting Information

Substrate NOBINAc Ligand Affinity for Pd^{II}-Catalyzed Enantioselective C-H Activation over Reactive β-C-H Bond in Ferrocenyl Amines

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General Experimental Details

Strating materials were prepared under an inert atmosphere (N_2, Ar) and Pd-Catalyzed ferrocene fused tetrahydropyridines were 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 ^{1}H, 77.16 ppm for ^{13}C). 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. Starting material allenes 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. Aminoacids, *S*-BINOL, and *R*-BINOL were directly purchased from commercial sources and further modified using the reported procedure. DFT calculations were performed using the Gaussian 16 package to identify suitable intermediates and transition states along the reaction pathway.

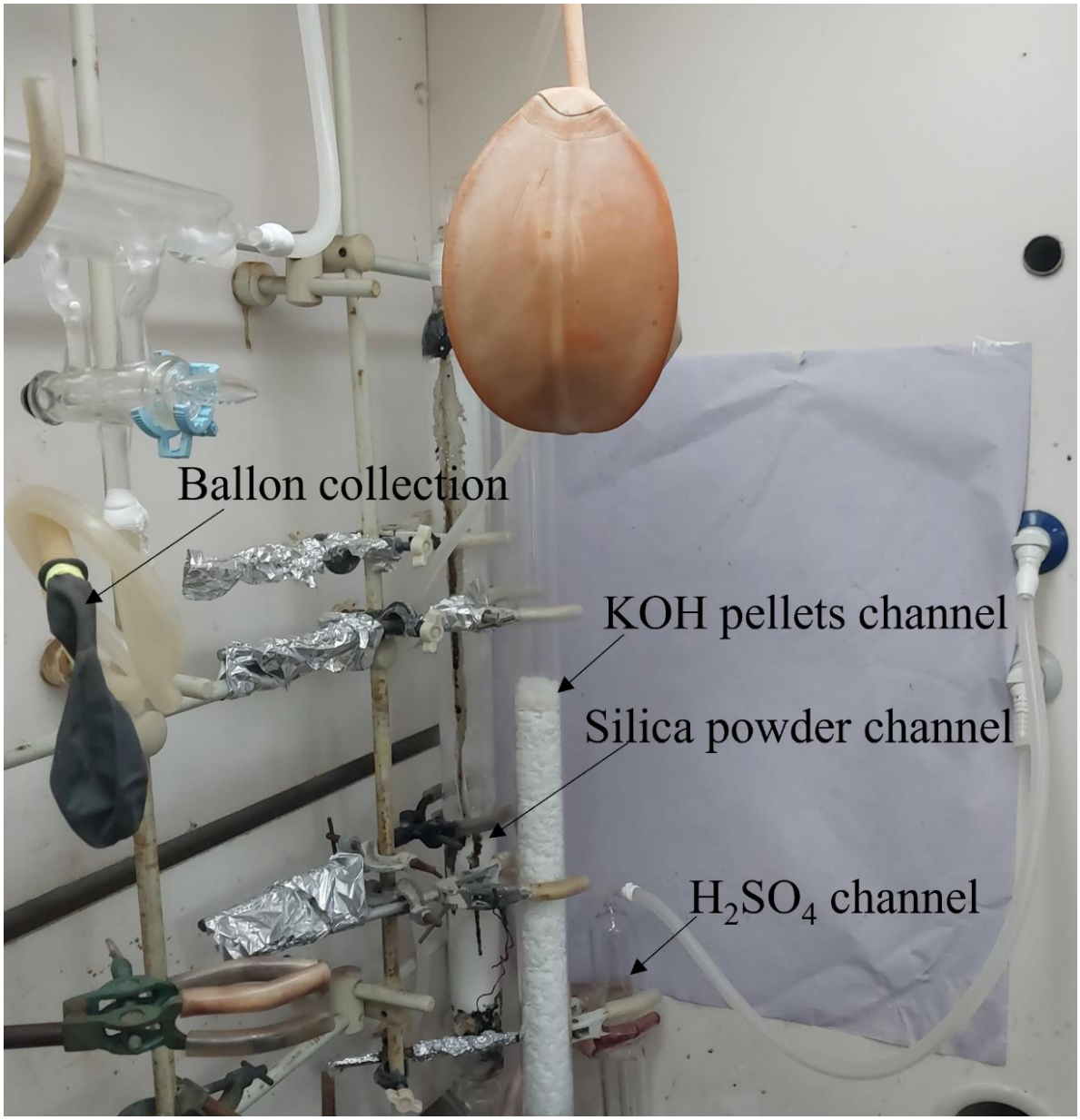


Figure S1. Setup for Dry Air used for Enantioselective CH Activation of Ferrocenyl Amines

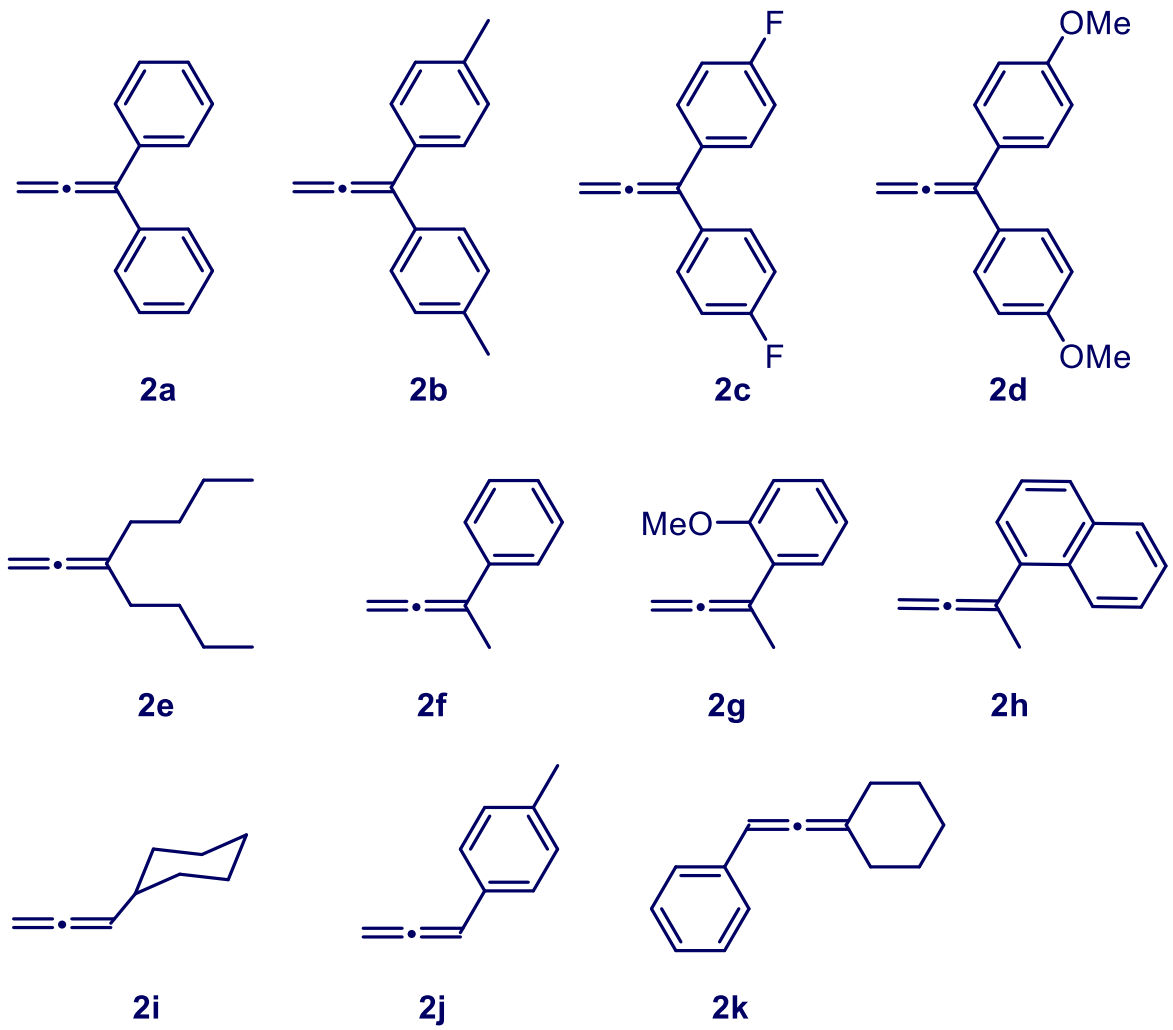


Figure S2. Allenes **2a-2k** was used for the enantioselective annulation reaction. Allenes **2a-2k** were synthesized according to the previously reported literature procedure,[1] and **2i** were purchased from a commercially available source.

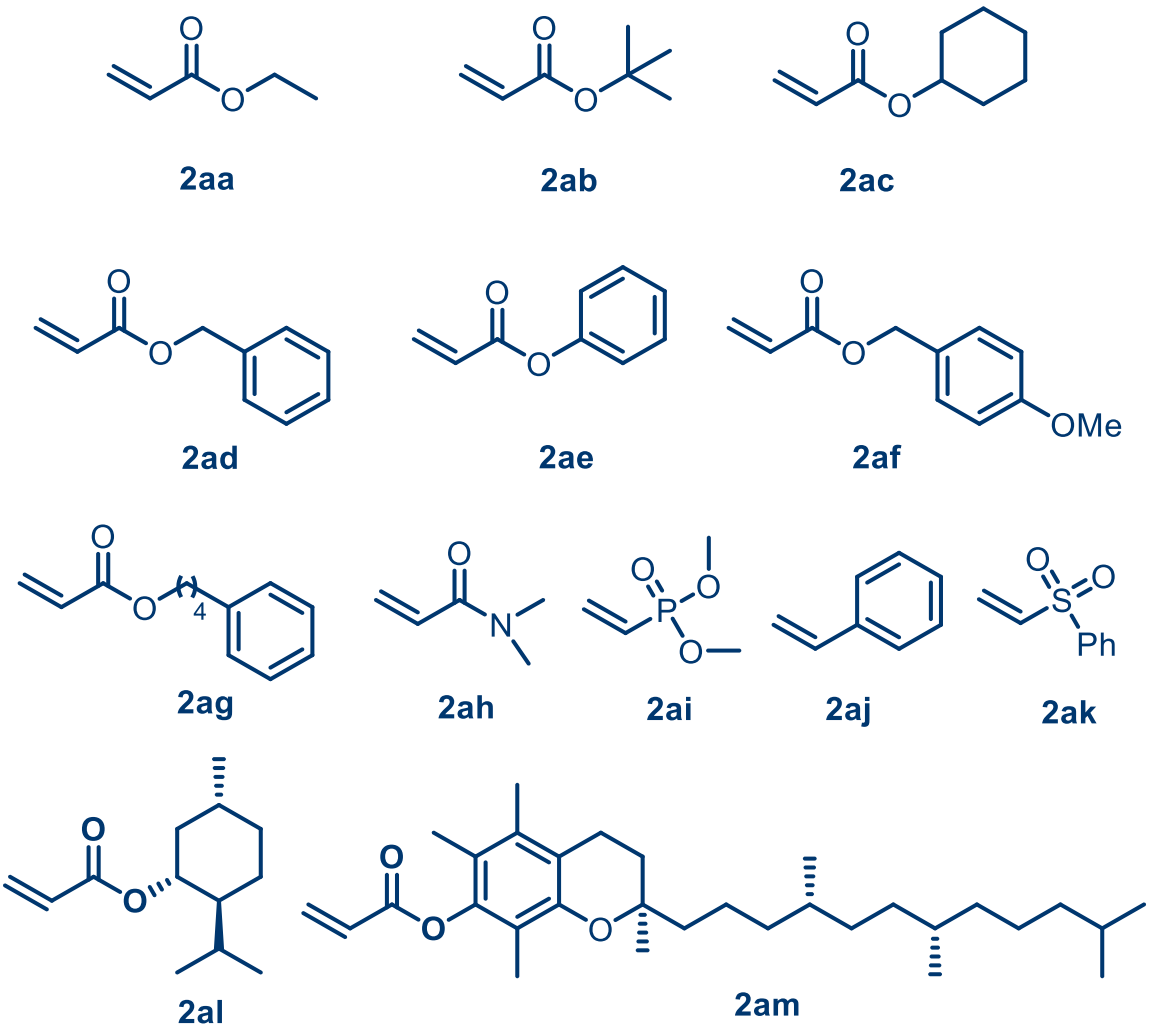
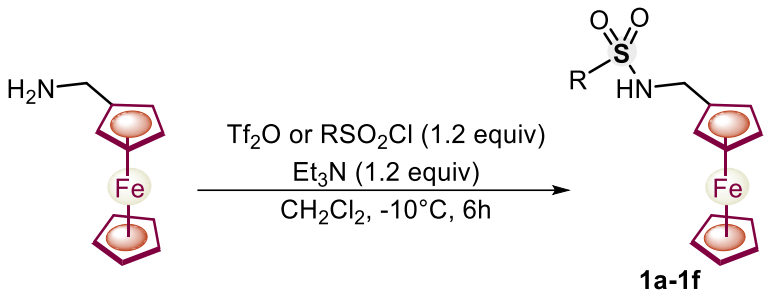
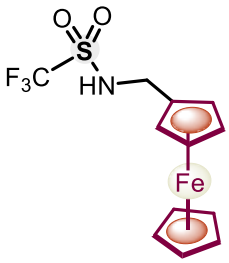


Figure S3. Alkenes **2aa-2al** are used for the enantioselective alkenylation reaction. Alkenes **2aa-2am** were synthesized according to the previously reported literature procedure,[2] and **2ah-2ak** were purchased from a commercially available source.

Scheme S1. General procedure for synthesizing *N*-ferrocenyl sulfonamides **1a-1f**

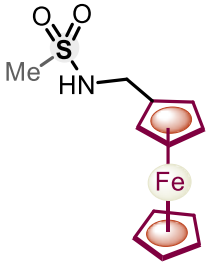


Ferrocenyl methyl amine was synthesized according to the reported literature procedure,[3] and used further without any purification for the synthesis of *N*-ferrocenyl sulfonamides **1a-1f**. To a solution of ferrocenyl methyl amine (2.0 mL, 9.3 mmol, 1 equiv) in dichloromethane (31 mL, 0.3 M) under argon atmosphere, triethylamine (1.4 mL, 11.2 mmol, 1.2 equiv) was added at -10 ºC. After that, the solution was stirred for 5 minutes at -10 ºC, and trifluoromethanesulfonic anhydride (1.8 mL, 11.2 mmol, 1.2 equiv) was added dropwise to the solution. The reaction was allowed to be stirred for 6 h before being quenched with water. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (25 mL x 3). The combined organic phase was washed with brine and then dried over Na_2SO_4. Evaporation of the solvent on a rotary evaporator under vacuum and column chromatography on silica gel (100-200 mesh) using hexanes: ethyl acetate 80:20 eluent afforded *N*-methyl ferrocenyl 1,1,1-trifluoromethanesulfonamide **1a**.

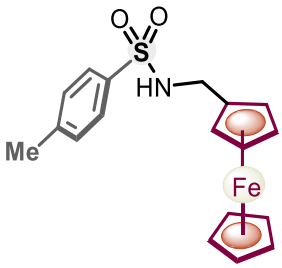


***N*-Methylferrocenyl 1,1,1-trifluoromethanesulfonamide 1a**. Orange-yellow solid, mp: 67-69 °C. Yield: 1.60 g (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (s, 1H), 4.25 (brs, 4H), 4.22 (s, 5H), 4.19 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 119.7 (d, J = 321.2 Hz, C), 82.4 (C),

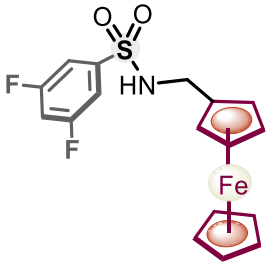
69.0 (CH), 68.9 (CH), 68.4 (CH), 44.0 (CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.38. HRLCMS [APCI] *m/z*: $[M-H]^+$ Calcd for $C_{12}H_{11}F_3FeNO_2S$ 345.9799; Found 345.9807



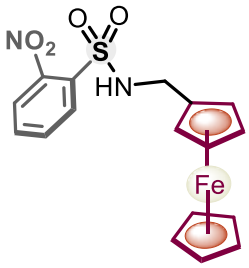
***N*-Methylferrocenyl methanesulfonamide 1b.** Yellow solid, mp: 82-84 °C. Yield: 1.96 g (72%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.48 (s, 1H), 4.32 (brs, 2H), 4.26 (brs, 7H), 4.03 (brs, 2H), 2.89 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 84.3 (C), 69.3 (CH), 69.0, (CH), 68.9, (CH), 42.9 (CH_2), 41.1 (CH_3). HRLCMS [ESI] *m/z*: [M] Calcd for $C_{12}H_{15}FeNO_2S$ 293.0167; Found 293.0149.



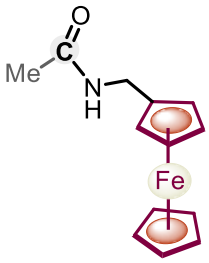
***N*-Methylferrocenyl 4-methylbenzenesulfonamide 1c**. Yellow solid, mp: 89-90 °C. Yield: 2.20 g (65%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.56 (brs, 1H), 4.16 (brs, 7H), 4.10 (brs, 2H), 3.83 (d, J = 5.2 Hz, 2H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 143.5 (C), 136.9 (C), 129.8 (CH), 127.2 (CH), 84.2 (C), 69.2 (CH), 68.8 (CH), 68.5 (CH), 42.6 (CH_2), 21.6 (CH_3). HRLCMS [ESI] *m/z*: [M] Calcd for $C_{18}H_{19}FeNO_2S$ 369.0481; Found 369.0480.



***N*-Methylferrocenyl 3,5-difluorobenzenesulfonamide 1d.** Orange solid, mp: 97-98 °C. Yield: 2.10 g (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.02 – 7.08 (m, J = 8.5, 2.3 Hz, 1H), 4.70 (s, 1H), 4.18 (s, 5H), 4.16 (s, 2H), 4.10 (s, 2H), 3.94 (d, J = 5.6 Hz, 2H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 162.83 (dd, J = 254.7 Hz, C), 143.5 (t, J = 8.2 Hz, C), 110.6 (dd, J = 22.4, Hz, CH), 108.2 (t, J = 25.1 Hz, CH), 82.9 (C), 68.8 (CH), 68.6 (CH), 68.2 (CH), 42.9 (CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.57. HRLCMS [ESI] *m/z*: [M] Calcd for $C_{17}H_{15}FeF_2NO_2S$ 391.0141; Found 391.0138.



***N*-Methylferrocenyl 2-nitrobenzenesulfonamide 1e**. Yellow solid, mp: 102 °C-103°C. Yield: 2.40 g (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 1H), 7.92 – 7.84 (m, 1H), 7.79 – 7.71 (m, 2H), 5.62 (t, J = 5.5 Hz, 1H), 4.18 (s, 5H), 4.08 (d, J = 2.6 Hz, 4H), 4.04 (d, J = 5.8 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.9 (C), 133.9 (C), 133.6 (CH), 132.9 (CH), 131.1 (CH), 125.4 (CH), 83.0 (C), 68.6 (CH), 68.3 (CH), 67.8 (CH), 43.4 (CH_2). HRLCMS [ESI] *m/z*: [M] Calcd for $C_{17}H_{16}FeN_2O_4S$ 400.0175; Found 400.0174.



***N*-Methylferrocenyl acetamide 1f.** Yellow solid, mp: 85 °C-86 °C. Yield: 1.7 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (brs, 1H), 4.20 (d, J = 1.6 Hz, 2H), 4.18 (s, 5H), 4.15 (d, J = 4.8 Hz, 4H), 1.99 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4 (C), 84.6 (C), 68.7 (CH), 68.5 (CH), 68.3 (CH), 68.2 (CH), 39.0 (CH_2), 23.2 (CH_3). HRLCMS [ESI] *m/z*: [M] Calcd for $C_{13}H_{15}FeNO$ 257.0503; Found 257.0497.

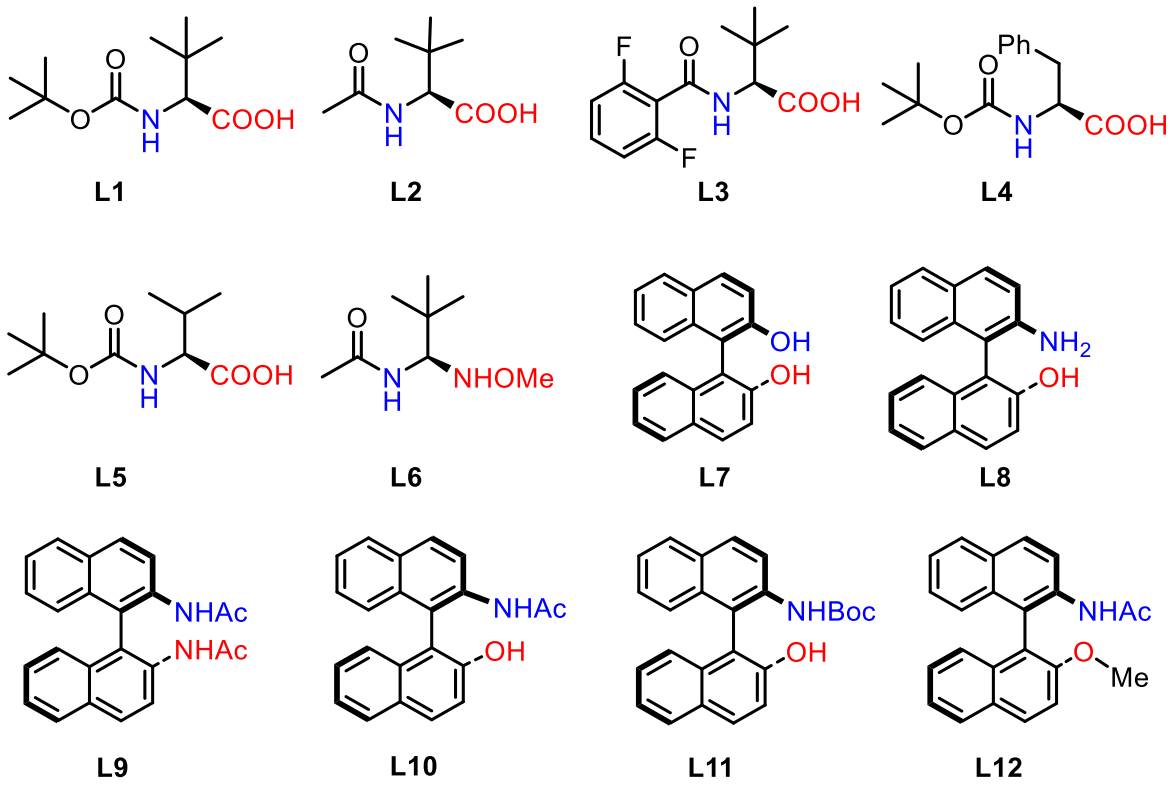
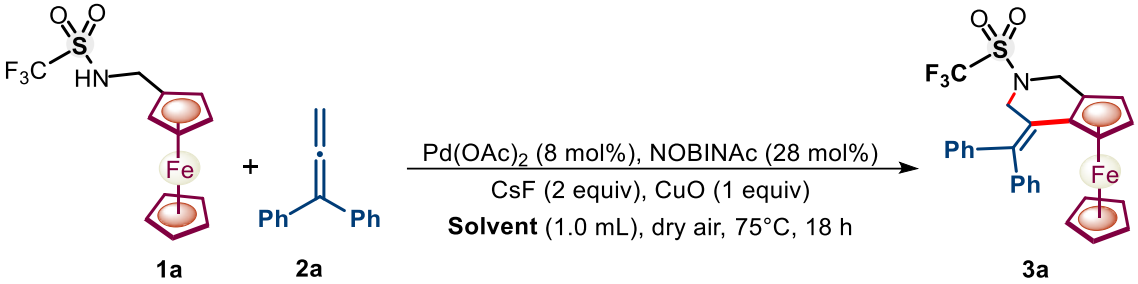


Figure S4. Ligands **L1**, **L2**, and **L7** are commercially available and ligands **L3**-**L6** and **L8**-**L12** were synthesized according to the reported literature procedure.[4]

Reaction Optimization

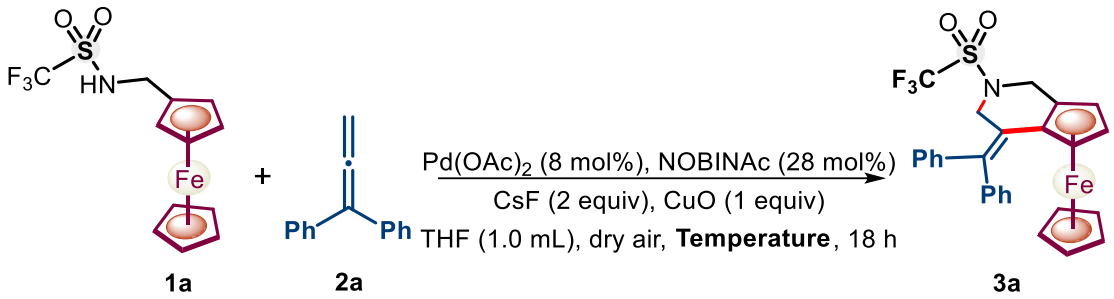
Table S1. Solvent Screening[a]



S. No.	Solvent	Yield of 3a[b]	*ee* of 3a[c]
1	*t*-amyl alcohol	6%	17%
2	toluene	25%	60%
3	DMSO	18%	41%
4	DMAc	42%	32%
5	Toluene + *t*-amyl alcohol (5:1)	21%	35%
6	Toluene + DMSO (5:1)	28%	62%
7	Toluene + DMAc (5:1)	53%	40%
8	Toluene + DMAc (15:1)	37%	76%
9	Toluene (1ml) + DMAc (15 equiv)	39%	85%
10	THF	70%	98%

[a] Reaction conditions: **1a** (0.11 mmol, 1 equiv), **2a** (0.22 mmol, 2 equiv), $Pd(OAc)_2$ (8 mol %), NOBINAc (28 mol %), CsF (0.22 mmol, 2 equiv), CuO (0.11 mmol, 1 equiv) in 1.0 mL solvent under dry air 18h at 75 °C. [b] Yield of **3a** determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] enantioselectivity of **3a** was determined by HPLC analysis.

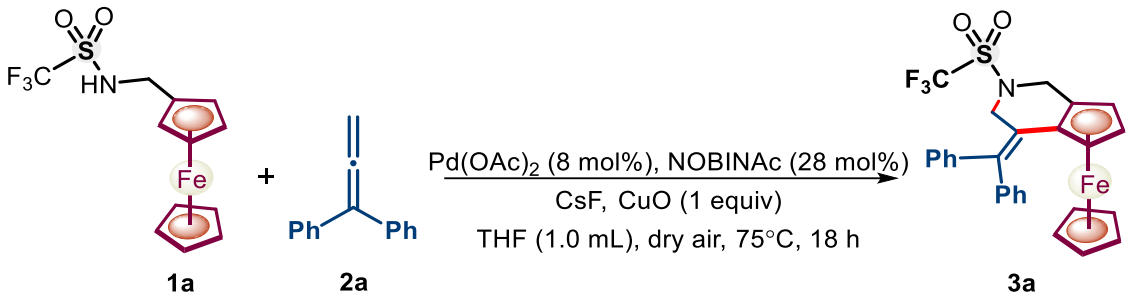
Table S2. Temperature Optimization [a]



S. No.	Temperature	Yield of 3a [b]	*ee* of 3a[c]
1	65ºC	62%	98%
2	80ºC	71%	97%
3	100ºC	65%	86%
4	40ºC	32%	98%

[a] Reaction conditions: **1a** (0.11 mmol, 1 equiv), **2a** (0.22 mmol, 2 equiv), $Pd(OAc)_2$ (8 mol %), NOBINAc (28 mol %), CsF (0.22 mmol, 2 equiv), CuO (0.11 mmol, 1 equiv) in 1.0 mL THF under dry air atmosphere 18h at T °C. [b] Crude yield of **3a** determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] enantioselectivity of **3a** was determined by HPLC analysis.

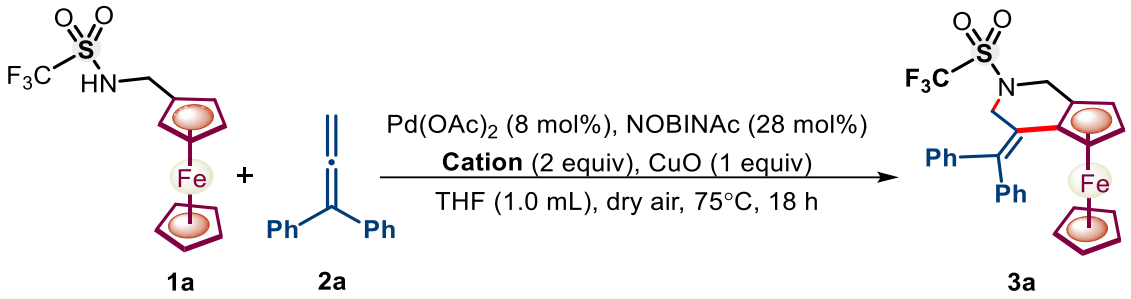
Table S3. Variation in the Stoichiometry of Cs^+ Cation



S. No.	Cation (equiv)	Yield of 3a [b]	*ee* of 3a [c]
1	0.5 equiv	34%	70%
2	1 equiv	48%	85%
3	1.5 equiv	57%	93%
4	2 equiv	70%	98%

[a] Reaction conditions: **1a** (0.11 mmol, 1 equiv), **2a** (0.22 mmol, 2 equiv), $Pd(OAc)_2$ (8 mol %), NOBINAc (28 mol %), CsF (xx equiv), CuO (0.11 mmol, 1 equiv) in 1.0 mL THF at 75 °C under dry air 18h. [b] Crude yield of **3a** determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] enantioselectivity of **3a** was determined by HPLC analysis.

Table S4. Optimization for Source of Cation

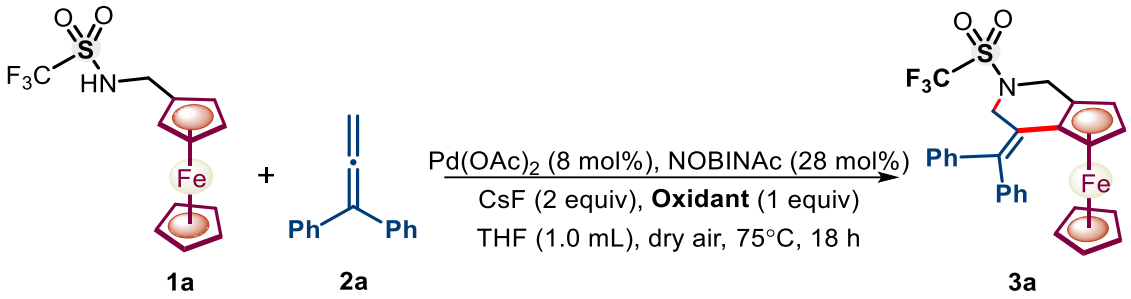


1a **2a** **3a**

S. No.	Cation source	Yield of 3a [b]	*ee* of 3a [c]
1	Cs_2CO_3	40%	93%
2	K_2CO_3	35%	87%
3	Na_2CO_3	23%	55%
4	Li_2CO_3	12%	10%
5	KOAc	28%	45%
6	CsOAc	30%	52%
7	NaOAc	18%	20%
8	KF	48%	89%
9	CsF	70%	98%
10	NEt_3	5%	0%

[a] Reaction conditions: **1a** (0.11 mmol, 1 equiv), **2a** (0.22 mmol, 2 equiv), $Pd(OAc)_2$ (8 mol %), NOBINAc (28 mol %), Cation source (0.22 mmol, 2 equiv), CuO (0.11 mmol, 1 equiv) in 1.0 mL THF at 75 °C under dry air 18h. [b] Crude yield of **3a** determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] Enantioselectivity of **3a** was determined by HPLC analysis.

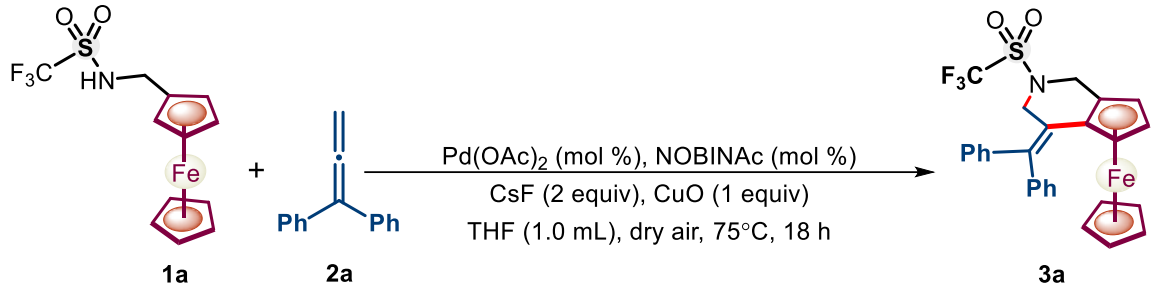
Table S5. Oxidant Screening



S. No.	Oxidant	Yield of 3a [b]	*ee* of 3a [c]
1	Air	52%	80%
2	O_2	32%	86%
3	Ag_2CO_3	26%	75%
4	AgOAc	42%	52%
5	$Cu(OAc)_2$	50%	82%
6	CuO (1 equiv)	70%	98%

[a] Reaction conditions: **1a** (0.11 mmol, 1 equiv), **2a** (0.22 mmol, 2 equiv), $Pd(OAc)_2$ (8 mol %), NOBINAc (28 mol %), CsF (0.22 mmol, 2 equiv), Oxidant (0.11 mmol, 1 equiv) in 1.0 mL THF at 75 °C 18h in dry air. [b] Crude yield of **3a** determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] Enantioselectivity of **3a** was determined by HPLC analysis.

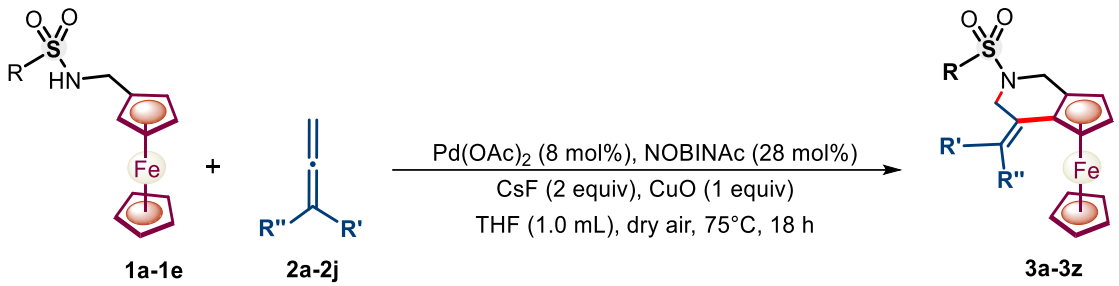
Table S6. Ligand to Pd(II) Ratio Screening



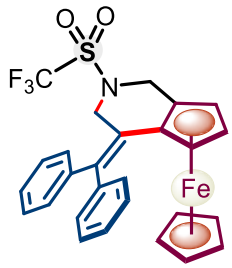
S. No.	$Pd(OAc)_2$ (mol %)	NOBINAc (mol %)	Yield 3a (%) [b]	*ee* 3a (%)[c]
1	5	5	32	85
2	5	10	36	89
3	8	8	45	84
4	8	16	56	90
5	10	20	58	90
6	8	24	64	93
7	**8**	**28**	**70**	**98**
8	8	32	71	98

[a] Reaction conditions: **1a** (0.11 mmol, 1 equiv), **2a** (0.22 mmol, 2 equiv), CsF (0.22 mmol, 2 equiv), CuO (0.11 mmol, 1 equiv) in 1.0 mL THF at 75 °C 18 h in dry air by varying $Pd(OAc)_2$ (mol %), and NOBINAc (mol %) loading. [b] Crude yield of **3a** determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] Enantioselectivity of **3a** was determined by HPLC analysis.

Scheme S2. General procedure for the Pd-catalyzed annulation of ferrocenyl secondary amines with allenes

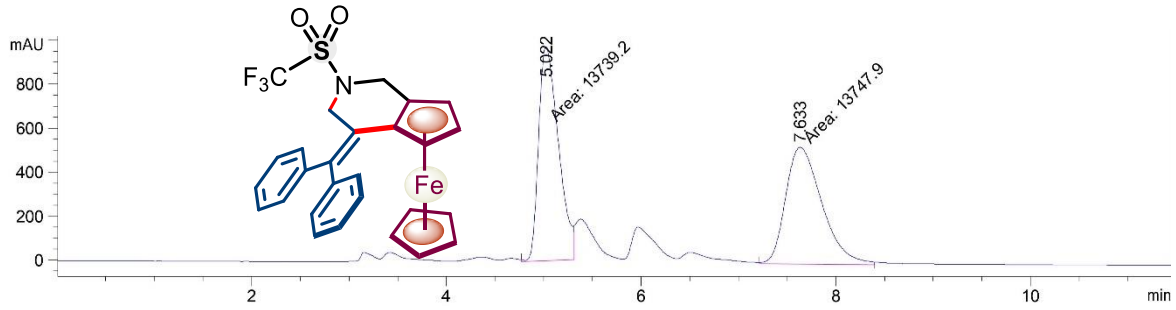


In a Schlenk tube, $Pd(OAc)_2$ (2.5 mg, 0.012 mmol, 8 mol%), NOBINAc (14 mg, 0.04 mmol, 28 mol %), CuO (11.5 mg, 0.14 mmol, 1 equiv.), CsF (44 mg, 0.28 mmol, 2 equiv.) and ferrocenyl secondary amine **1a** (50 mg, 0.14 mmol, 1 equiv.) were added in dry THF (1.5 mL) under an inert atmosphere and the resulted orange colored solution was stirred for 10 min. After pre-stirring, allene **2a** (55 μL, 0.29 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 75 °C, stirred for 18 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 hexane: ethyl acetate solvent system to afford ferrocene fused tetrahydropyridines (**3a-4a**).



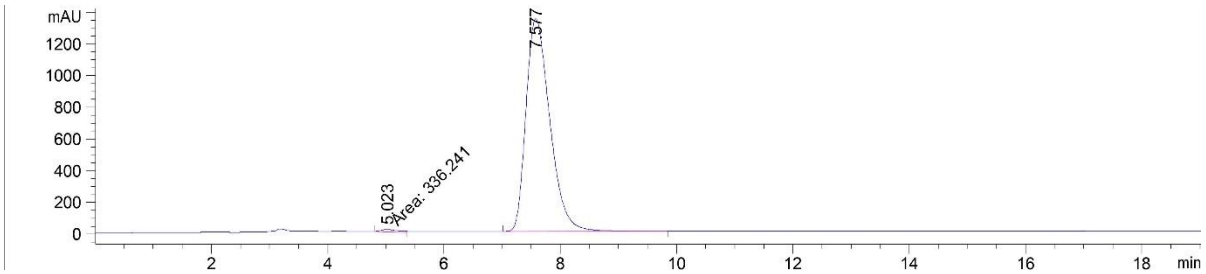
Ferrocene fused tetrahydropyridine 3a was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange-red solid, mp: 122-124 ºC. Yield: 52 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.33 (m, 5H), 7.31 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 7.4 Hz, 2H), 7.21 (d, J = 7.4 Hz, 2H), 4.69 (d, J = 13.4 Hz, 2H), 4.37 (s, 2H), 4.20 (brs, 6H), 4.06 (s, 1H), 3.27 (s, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 142.5 (C), 141.3 (C), 138.2 (C), 129.2 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 127.5 (CH), 127.4 (CH), 126.9 (C), 120.03 (d, J = 323.7 Hz CF_3), 81.5 (C), 70.6 (CH), 68.1 (CH), 66.4 (CH), 65.2 (CH), 48.9 (CH_2), 47.1 (CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.38. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{27}H_{22}F_3FeNO_2S$ 537.0660; Found 537.0668. The enantioselectivity of product **3a** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 95:5, 1 mL/min, λ=254 nm).

Racemic sample of **3a**



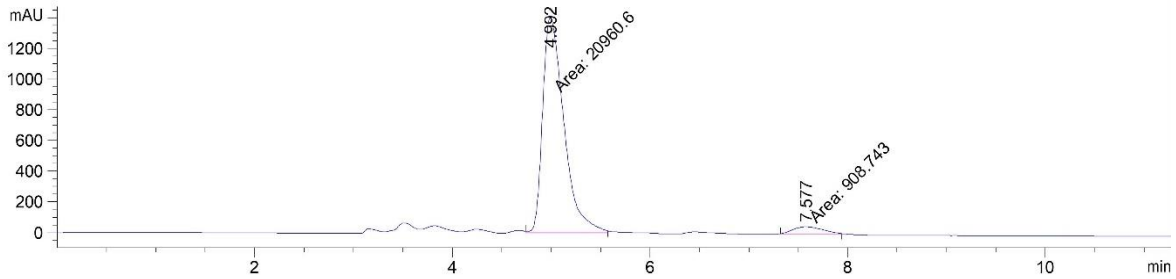
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.022	MM	0.2354	1.37392e4	972.89185	49.9843
2	7.633	MM	0.4318	1.37479e4	530.64594	50.0157

Asymmetric sample of (*Rp*)-**3a** obtained using *R*-NOBINAc

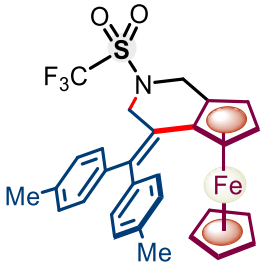


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.023	MM	0.3563	336.24100	15.73049	0.8749
2	7.577	BB	0.4395	3.80976e4	1340.87231	99.1251

Asymmetric sample of (*Sp*)-**3a** obtained using *S*-NOBINAc

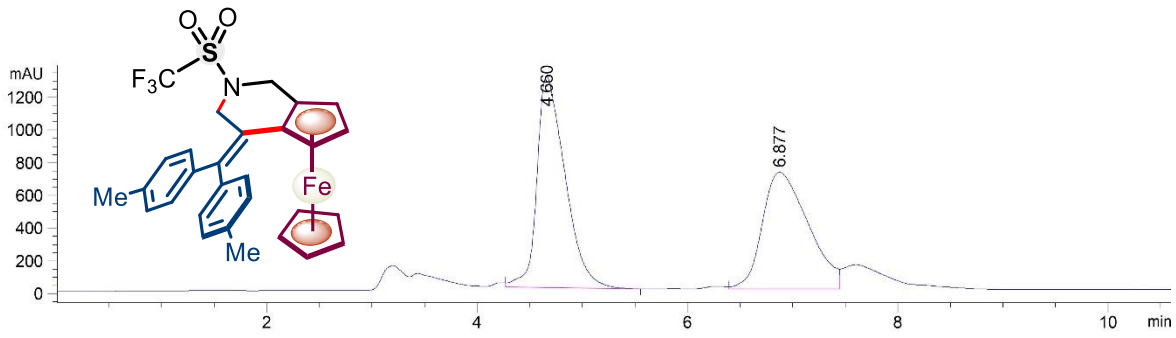


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.992	MM	0.2487	2.09606e4	1404.80542	95.8447
2	7.577	MM	0.3394	908.74316	44.63121	4.1553



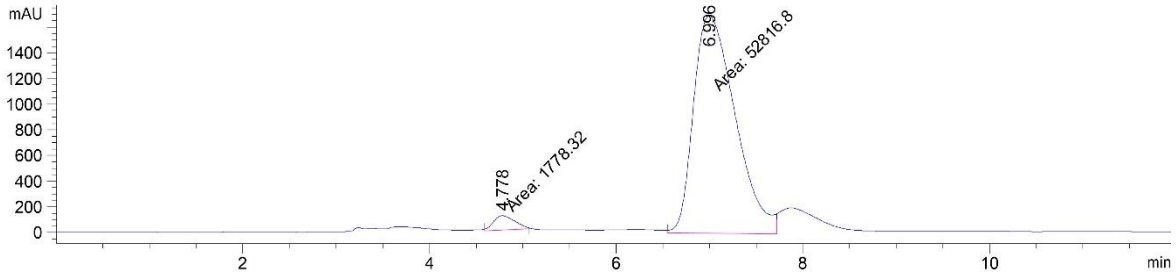
Ferrocene fused tetrahydropyridine 3b was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 98:2), obtained as an orange solid, mp: 117-118 ºC. Yield: 51 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.5 Hz, 2H), 7.15 (dd, J = 12.5, 7.9 Hz, 4H), 7.07 (d, J = 7.9 Hz, 2H), 4.75 (d, J = 14.7 Hz, 1H), 4.68 (d, J = 12.8 Hz, 1H), 4.39 (d, J = 11.8 Hz, 1H), 4.31 (s, 1H), 4.16 (s, 6H), 4.03 (t, J = 2.4 Hz, 1H), 3.31 (d, J = 1.2 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 139.7 (C), 138.6 (C), 138.3 (C), 137.2 (CH), 137.0 (CH), 129.4 (CH), 129.2 (CH), 129.0 (CH), 128.8 (CH), 126.1 (C), δ 120.0 (q, J = 324.0 Hz, CF_3), 81.3 (C), 70.6 (CH), 68.8 (C), 67.9 (CH), 66.5 (CH), 65.0 (CH), 49.1 (CH_2), 47.1 (CH_2), 21.4 (CH_3), 21.2 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.33. HRLCMS (APCI) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{27}F_3FeNO_2S$ 566.1063; Found 566.1107. The enantioselectivity of product **3b** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample **(3b)**



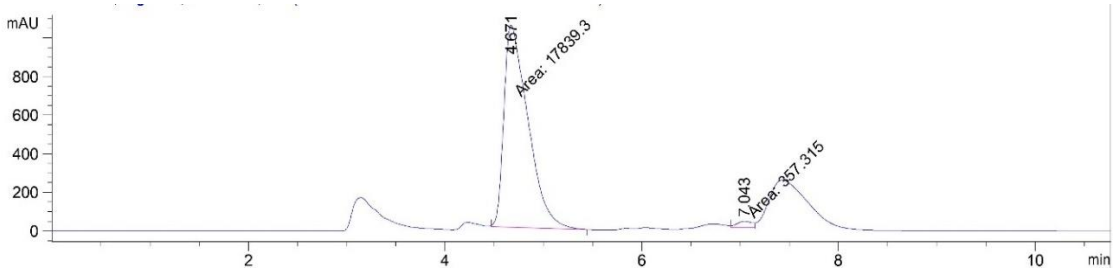
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.660	MM	0.3027	3.51966e4	1937.99377	50.0635
2	6.880	MM	0.4917	3.51073e4	1189.95642	49.9365

Asymmetric sample of (*Rp*)-**3b** obtained using *R*-NOBINAc

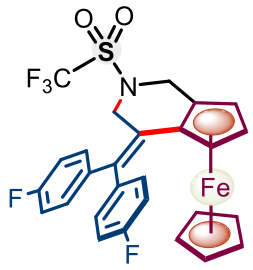


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.778	MM	0.2653	1778.32129	111.71938	3.2573
2	6.996	MM	0.5192	5.28168e4	1695.42053	96.7427

Asymmetric sample of (*Sp*)-**3b** obtained using *S*-NOBINAc

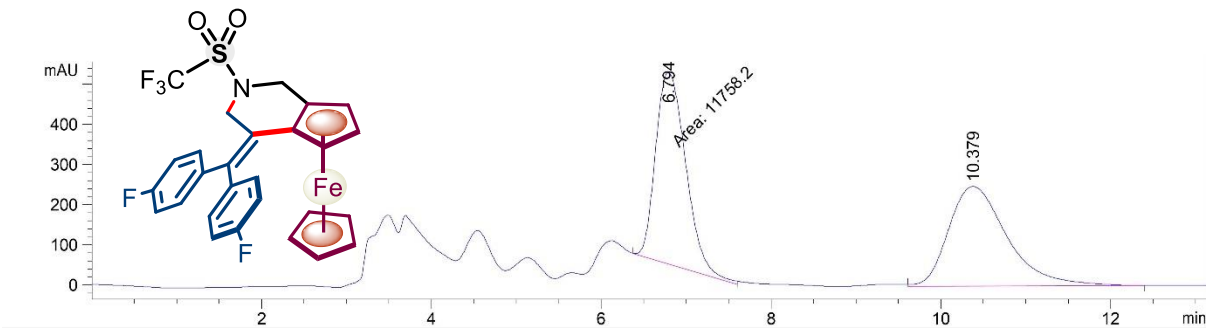


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.671	MM	0.2837	1.78393e4	1048.19385	98.0364
2	7.043	MM	0.1843	357.31464	32.30664	1.9636



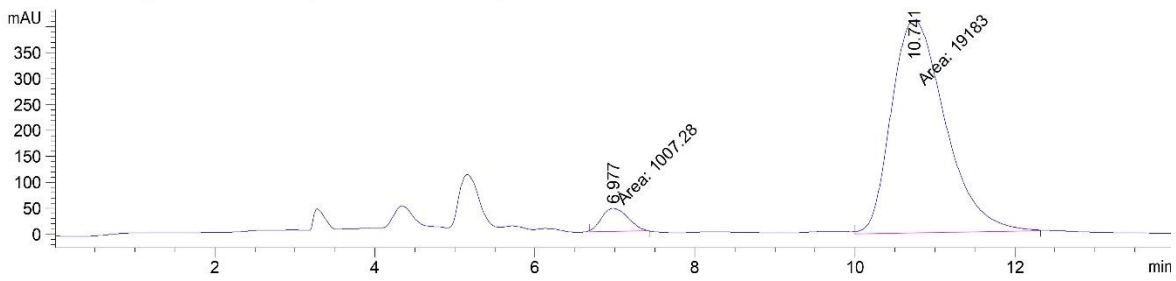
Ferrocene fused tetrahydropyridine 3c was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 98:2), obtained as an orange solid, mp: 112 ºC -113ºC. Yield: 56 mg (68%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.21 (brs, 2H), 7.17 – 7.06 (m, 6H), 4.74 (brs, 1H), 4.64 (brs, 1H), 4.38 (d, J = 32.7 Hz, 2H), 4.16 (s, 6H), 4.08 (s, 1H), 3.27 (s, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 162.8 (d, J = 25.8 Hz CF), 161.4 (d, J = 26.1 Hz CF), 138.2 (C), 137.1 (C), 135.8 (C), 131.0 (d, J = 7.2 Hz CH), 130.7 (d, J = 7.7 Hz CH), 127.9 (CH), δ 119.9 (d, J = 323.4 Hz CF_3), 115.8 (d, J = 21.6 Hz CH), 115.7 (d, J = 21.7 Hz CH), 81.6 (C), 70.6 (CH), 68.2 (CH), 66.3 (CH), 65.4 (CH), 49.0 (CH_2), 47.0 (CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.46, -114.0. HRLCMS (APCI) *m/z*: [M] Calcd for $C_{27}H_{20}F_5FeNO_2S$ 573.0479; Found 573.0483. The enantioselectivity of product **3c** was determined by chiral HPLC analysis on the OZ-3 column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**3c)**

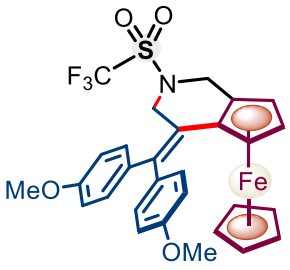


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.794	MM	0.4105	1.17582e4	477.45154	49.7680
2	10.379	VB	0.7380	1.18678e4	248.14557	50.2320

Asymmetric sample (**3c**)

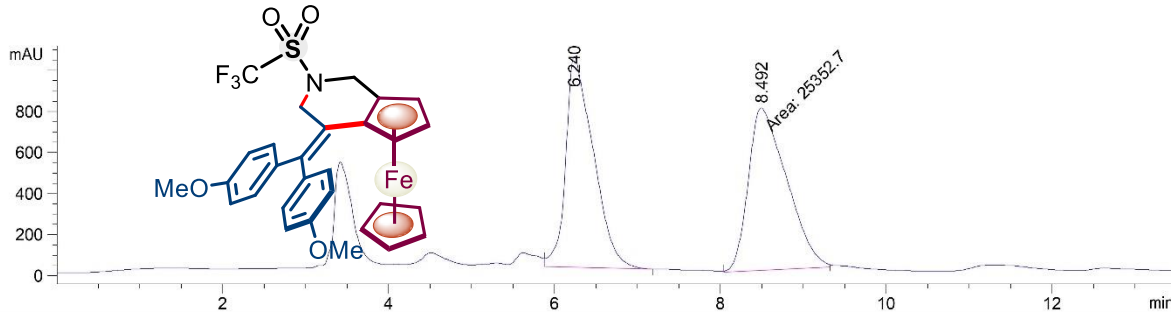


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.977	MM	0.3799	1007.28290	44.18793	4.9889
2	10.741	MM	0.7787	1.91830e4	410.56448	95.0111



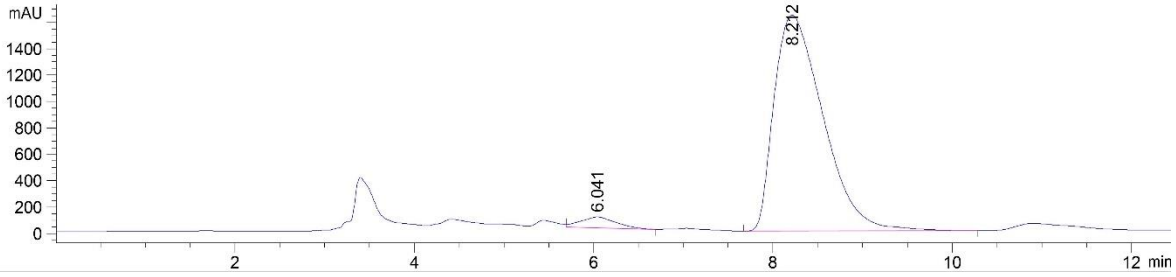
Ferrocene fused tetrahydropyridine 3d was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange solid, mp:107 ºC-108 ºC. Yield: 53 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.91 (dd, J = 14.8, 8.5 Hz, 4H), 4.72 (t, J = 20.3 Hz, 2H), 4.47 – 4.35 (m, 1H), 4.31 (s, 1H), 4.15 (s, 5H), 4.09 (d, J = 14.0 Hz, 1H), 4.05 – 4.02 (m, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.35 (s, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 159.5 (C), 159.4 (C), 145.3 (C), 134.2 (C), 131.2 (CH), 130.7 (C), 128.9 (CH), δ 120.9 (d, J = 337.0 Hz, CF_3), 120.4 (C), 113.9 (CH), 113.6 (CH), 80.4 (C), 69.8 (CH), 69.0 (CH), 68.9 (CH), 68.6 (CH), 68.4 (C), 55.4 (CH_3), 55.3 (CH_3), 47.8 (CH_2), 46.4 (CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.36. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{29}H_{26}F_3FeNO_4S$ 597.0879; Found 597.0895. The enantioselectivity of the product **3d** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 96:4, 1 mL/min, λ=254 nm).

Racemic sample **3d**

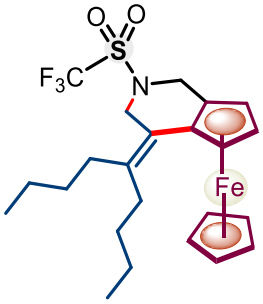


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.240	VB	0.3194	2.39082e4	1027.80359	48.5339
2	8.492	MM	0.5346	2.53527e4	790.43469	51.4661

Asymmetric sample (**3d**)

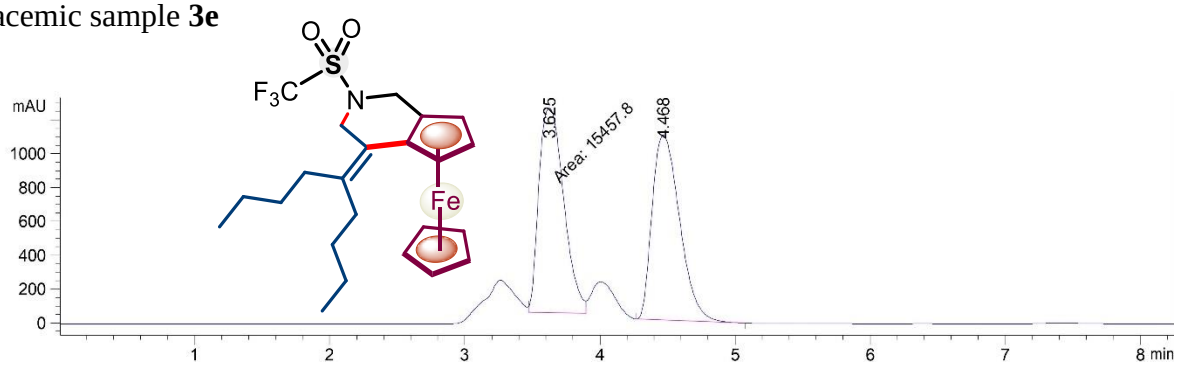


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.041	VB	0.3820	2290.65186	83.50723	3.5567
2	8.212	BB	0.6108	6.21138e4	1636.51929	96.4433



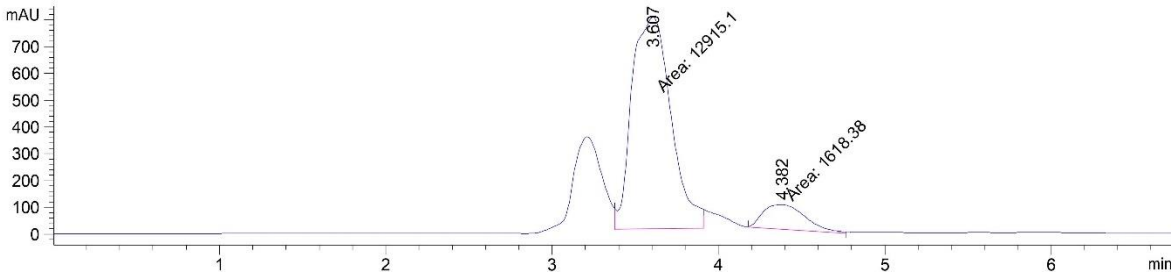
Ferrocene fused tetrahydropyridine 3e was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 99:1), obtained as a yellow viscous liquid. Yield: 42 mg (59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, J = 14.1 Hz, 2H), 4.43 (s, 1H), 4.32 (s, 1H), 4.26 (s, 1H), 4.15 (s, 5H), 4.06 (s, 1H), 2.57 (s, 1H), 2.10 – 2.16 (m, 4H), 1.63 – 1.38 (m, 8H), 1.08 – 0.98 (m, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 139.4 (C), 121.5 (C), 120.3 (q, J = 324.0 Hz CF_3).80.5 (C), 70.7 (CH), 70.2 (CH), 68.0 (CH), 66.9 (CH), 64.9 (C), 47.5 (CH_2), 46.9 (CH_2), 33.9 (CH_2), 33.4 (CH_2), 31.0 (CH_2), 30.6 (CH_2), 23.3 (CH_2), 23.0 (CH_2), 14.2 (CH_3), 13.9 (CH_3).^{19}F NMR (471 MHz, $CDCl_3$) δ -75.1. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{26}H_{22}F_3FeNO_2S$ 497.1294; Found 497.1260. The enantioselectivity of the product **3e** was determined by chiral HPLC analysis on OZ3 column (hexane: isopropanol = 99:1, 1 mL/min, λ=254 nm).

Racemic sample **3e**

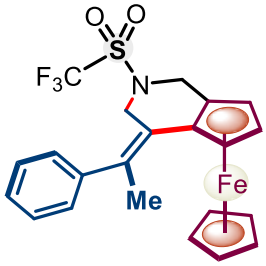


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.625	MM	0.2131	1.54578e4	1208.95850	49.9239
2	4.468	BB	0.2254	1.55050e4	1093.59460	50.0761

Asymmetric sample **3e**

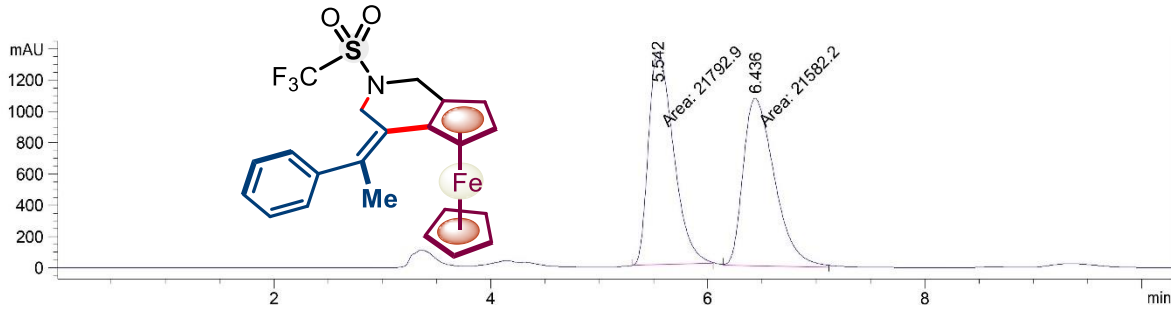


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.607	MM	0.2723	1.29151e4	790.48096	88.8645
2	4.382	MM	0.2948	1618.37610	91.50945	11.1355



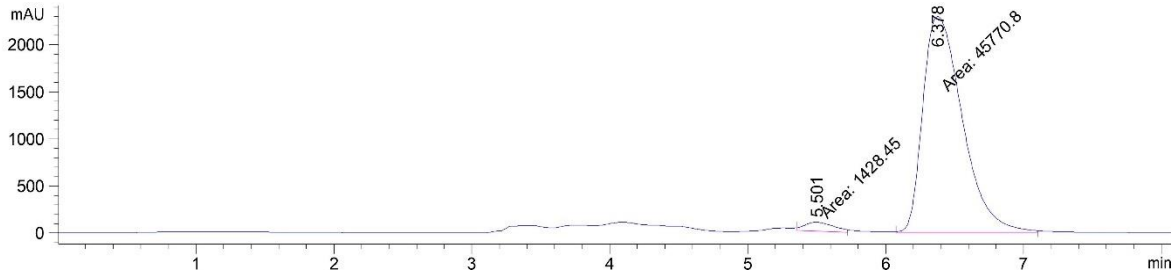
Ferrocene fused tetrahydropyridine 3f was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 98:2), obtained as an orange solid, mp:103 ºC -104ºC. Yield: 43 mg (63%, *E:Z* 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 7.4 Hz, 2H), 7.34 (d, J = 7.4 Hz, 1H), 7.19 (d, J = 7.1 Hz, 2H), 4.80 (d, J = 14.5 Hz, 1H), 4.67 (d, J = 1.5 Hz, 1H), 4.45 (d, J = 14.4 Hz, 1H), 4.38 (s, 1H), 4.33 (t, J = 2.5 Hz, 1H), 4.24 (s, 6H), 3.78 – 3.57 (m, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.5 (C), 134.8 (CH), 128.5 (CH), 127.9 (CH), 127.1 (CH), 124.7 (C), δ 121.3 (d, J = 337.0 Hz CF_3), 80.8 (C), 70.5 (CH), 68.8 (C), 68.0 (CH), 67.2 (CH), 65.0 (CH), 48.9 (CH_2), 47.0 (CH_2), 23.0 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.50. HRLCMS (APCI) *m/z*: [M] Calcd for $C_{22}H_{20}F_3FeNO_2S$ 476.0589; Found 476.0585. The enantioselectivity of product **3f** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**3f**)

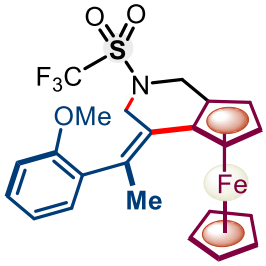


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.542	MM	0.2670	2.17929e4	1360.58948	50.2428
2	6.436	MM	0.3360	2.15822e4	1070.59888	49.7572

Asymmetric sample (**3f**)

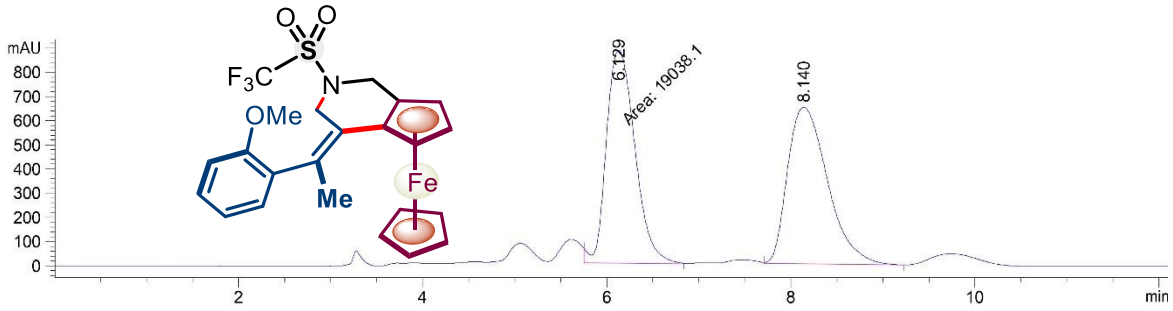


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.501	MM	0.2484	1428.44519	95.83167	3.0264
2	6.378	MM	0.3324	4.57708e4	2294.73291	96.9736



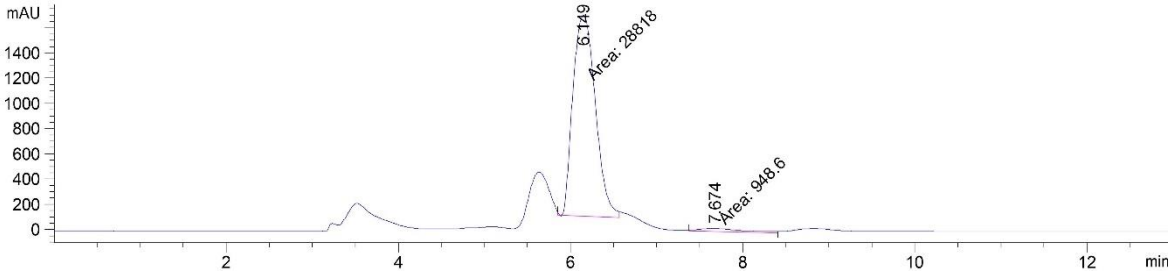
Ferrocene fused tetrahydropyridine 3g was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange solid, mp:105 ºC-106 ºC. Yield: 40 mg (55%, *E:Z* 1:1.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 6.95 (d, J = 6.1 Hz, 2H), 4.74 (s, 1H), 4.37 (s, 2H), 4.31 (s, 2H), 4.28 (s, 5H), 3.89 (s, 3H), 3.59 (s, 1H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 155.7 (C), 132.2 (C), 129.5 (CH), 128.9 (CH), 124.7 (CH), δ 120.3 (d, J = 334.0 Hz CF_3), 111.0 (C), 80.7 (C), 70.5 (CH), 68.8 (C), 67.9 (CH), 67.4 (CH), 66.4 (CH), 55.3 (CH_3), 48.8 (CH_2), 46.9 (CH_2), 22.0 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.41. HRLCMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}F_3FeNO_3S$ 505.0617; Found 505.0617. The enantioselectivity of the product **3g** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 92:8, 1 mL/min, λ=254 nm).

Racemic sample (**3g)**

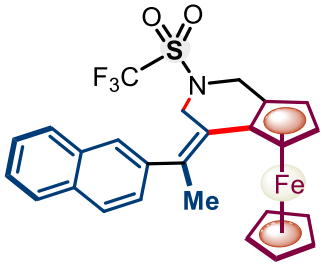


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.129	MM	0.3599	1.90381e4	881.56976	49.2972
2	8.140	VB	0.4823	1.95810e4	648.35516	50.7028

Asymmetric sample (**3g**)

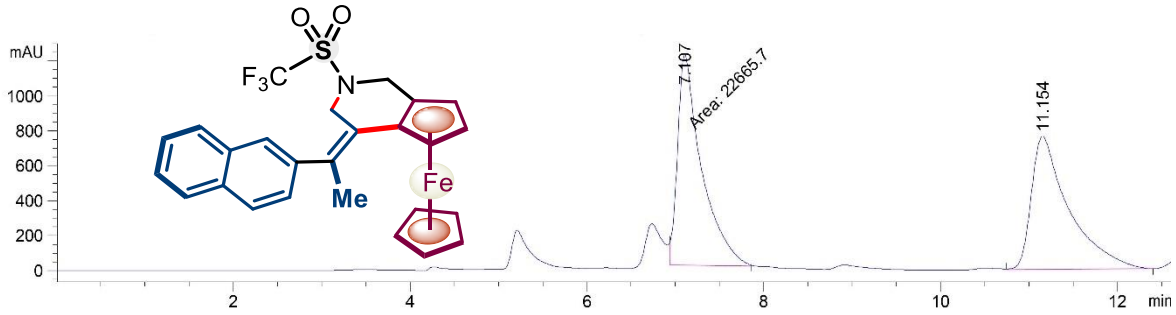


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.149	MM	0.3011	2.88180e4	1595.08899	96.8132
2	7.674	MM	0.6414	948.59967	24.64769	3.1868



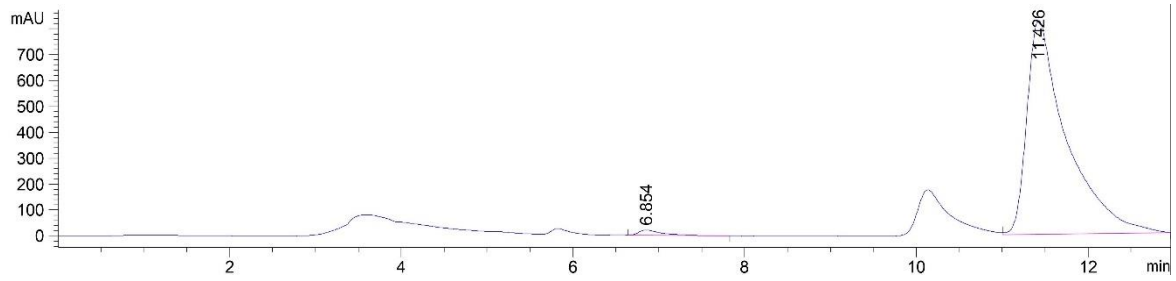
Ferrocene fused tetrahydropyridine 3h was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 98:2), obtained as an orange solid, mp: 110 ºC-111 ºC. Yield: 47 mg (60%, *E:Z* 1:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 3H), 7.64 (s, 1H), 7.52 (dd, *J* = 6.7, 2.6 Hz, 2H), 7.36 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.82 (d, *J* = 14.4 Hz, 1H), 4.71 (d, *J* = 1.5 Hz, 1H), 4.55 (d, *J* = 15.7 Hz, 1H), 4.40 (d, *J* = 1.5 Hz, 1H), 4.35 (t, *J* = 2.5 Hz, 1H), 4.27 (s, 5H), 4.23 (d, *J* = 6.7 Hz, 1H), 3.72 (brs, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 140.9 (C), 134.7 (C), 133.3 (C), 132.4 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 126.6 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 125.2 (C), 119.9 (d, *J* = 323.5 Hz CF_3), 80.8 (C), 70.5 (CH), 68.8 (CH), 68.1 (CH), 67.3 (CH), 65.0 (C), 49.0 (CH_2), 47.1 (CH_2), 23.1 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.50. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{26}H_{22}F_3FeNO_2S$ 548.0565; Found 548.0568. The enantioselectivity of the product **3h** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**3h)**

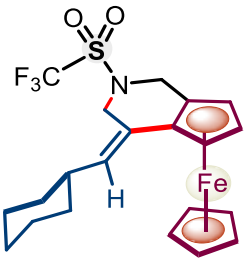


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.107	MM	0.3127	2.26657e4	1208.19507	50.2169
2	11.154	VB	0.4117	2.24699e4	762.66101	49.7831

Asymmetric sample (**3h**)

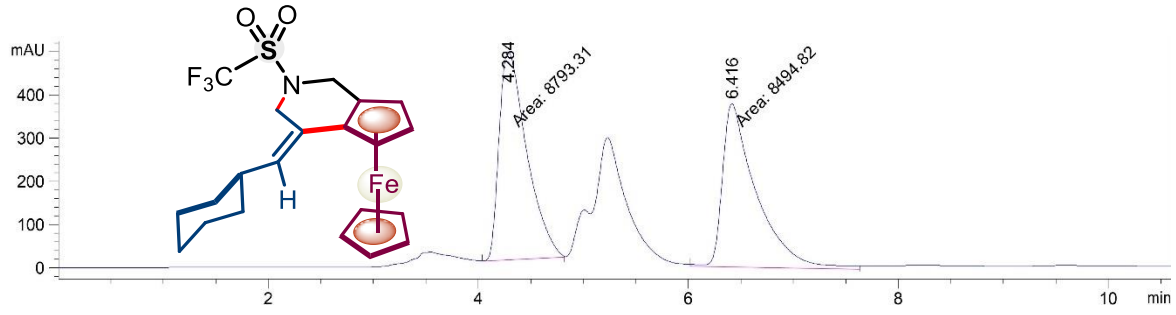


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.854	VB	0.2800	429.72818	21.60877	1.5896
2	11.426	VBA	0.4493	2.66034e4	827.02936	98.4104



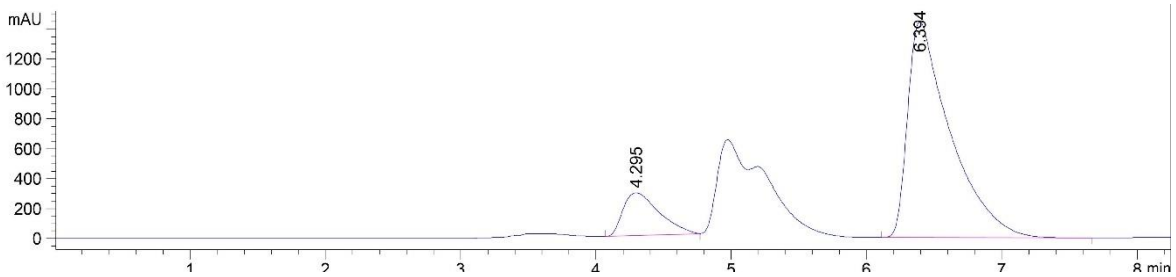
Ferrocene fused tetrahydropyridine 3i was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 99:1), obtained as a yellow viscous liquid. Yield: 38 mg (56%, *E:Z* 1:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, J = 9.4 Hz, 1H), 4.77 (d, J = 14.3 Hz, 1H), 4.49 (d, J = 0.9 Hz, 1H), 4.37 (s, 1H), 4.33 (brs, 2H), 4.14 (s, 6H), 3.87 (d, J = 14.0 Hz, 1H), 2.71 – 2.55 (m, 1H), 1.88 (t, J = 10.1 Hz, 2H), 1.83 – 1.66 (m, 5H), 1.44 – 1.38 (m, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 133.5 (C), 126.0 (CH), 120.15 (d, J = 323.1 Hz CF_3). 80.6(C), 70.7 (CH), 68.1 (CH), 67.1 (CH), 64.9 (C), 61.4 (CH), 52.7 (CH_2), 47.0 (CH_2), 37.7 (CH), 33.0 (CH_2), 32.6 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.8 (CH_2).^{19}F NMR (471 MHz, $CDCl_3$) δ -75.52. HRLCMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{25}F_3FeNO_2S$ 468.0902; Found 468.0886. The enantioselectivity of product **3i** was determined by chiral HPLC analysis on the AD-H column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**3i)**

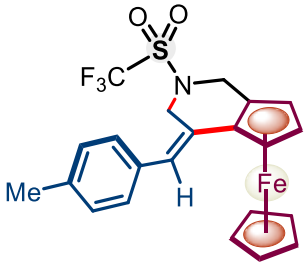


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.284	MM	0.3048	8793.30664	480.84598	50.8633
2	6.416	MM	0.3742	8494.82324	378.32681	49.1367

Asymmetric sample (**3i**)

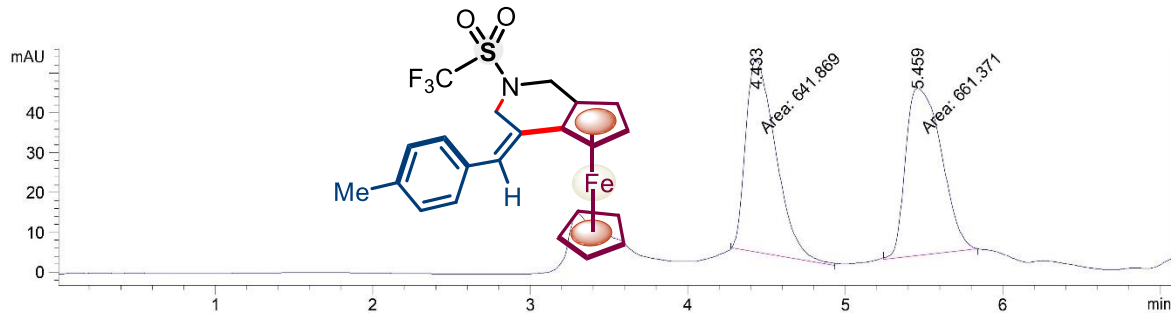


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.295	BB	0.2822	5289.54541	285.38135	14.3162
2	6.394	BB	0.3053	3.16584e4	1446.78540	85.6838



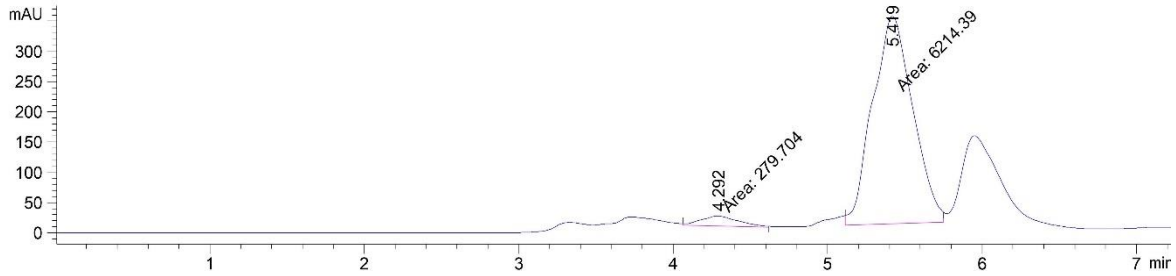
Ferrocene fused tetrahydropyridine 3j was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 99:1), obtained as a yellow orange solid, mp: 89 ºC-90 ºC. Yield: 34 mg (50%, *E:Z* 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 3.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.78 (s, 1H), 4.78 (d, J = 14.3 Hz, 1H), 4.69 (s, 1H), 4.60 (d, J = 14.8 Hz, 1H), 4.42 (s, 1H), 4.33 (brs, 2H), 4.22 (s, 6H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 137.0 (C), 129.4 (CH), 129.0 (CH), 128.5 (CH), 128.4 (C), 122.6 (C), 120.2 (d, J = 324.0 Hz CF_3). 80.7 (C), 71.3 (CH), 70.7 (CH), 68.2 (CH), 67.7 (CH), 61.9 (C), 46.6 (CH_2), 46.4 (CH_2), 21.3 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.11, -75.16. HRLCMS (ESI) *m/z*: $[M-H]^+$ Calcd for $C_{22}H_{20}F_3FeNO_2S$ 475.0511; Found 475.0509. The enantioselectivity of the product **3j** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**3j)**

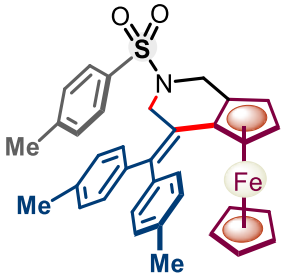


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.433	MM	0.2203	641.86871	48.56398	49.2518
2	5.459	MM	0.2626	661.37146	41.97504	50.7482
Totals :				1303.24017	90.53902	

Asymmetric sample (**3j**)

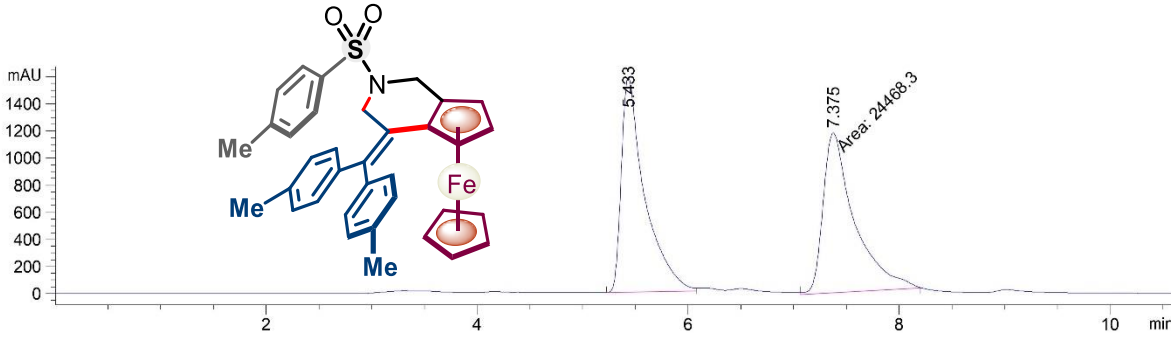


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.292	MM	0.2787	279.70404	16.72396	4.3071
2	5.419	MM	0.3019	6214.38916	343.07669	95.6929
Totals :				6494.09320	359.80065	



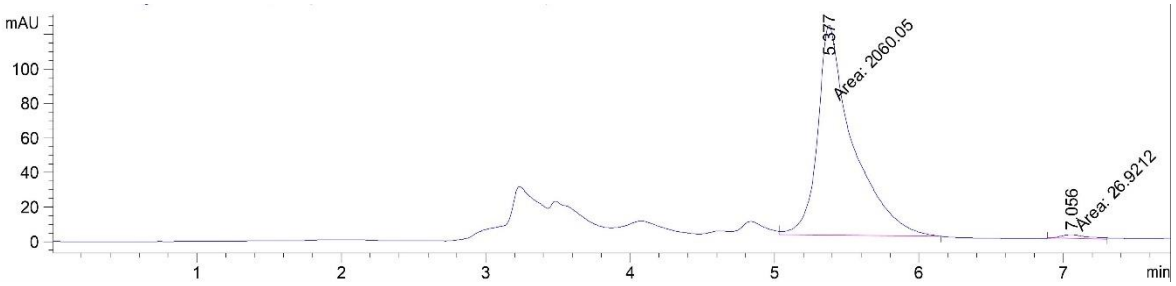
Ferrocene fused tetrahydropyridine 3k was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange red solid, mp: 141 ºC-142 ºC. Yield: 47 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.27 (s, 2H), 7.20 – 7.09 (m, 4H), 7.03 (d, J = 7.4 Hz, 2H), 6.89 (d, J = 2.7 Hz, 2H), 4.50 (dd, J = 25.1, 14.4 Hz, 2H), 4.25 (s, 1H), 4.08 (s, 5H), 3.93 (d, J = 13.4 Hz, 2H), 3.73 (s, 1H), 3.13 (s, 1H), 2.45 (s, 3H), 2.38 (s, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.3 (C), 140.0 (C), 139.0 (C), 137.1 (CH), 136.9 (CH), 136.7 (CH), 135.0 (CH), 129.6 (CH), 129.4 (C), 129.2 (C), 129.1 (CH), 129.0 (C), 127.5 (C), 127.1 (C), 82.3 (C), 70.6 (CH), 67.6 (CH), 67.1 (CH), 66.0 (CH), 65.1 (C), 48.6 (CH_2), 46.4 (CH_2), 21.6 (CH_3), 21.3 (CH_3), 21.2 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{35}H_{33}FeNO_2S$ 587.1576; Found 587.1566. The enantioselectivity of the product **3k** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 75:25, 1 mL/min, λ=254 nm).

Racemic sample (**3k)**



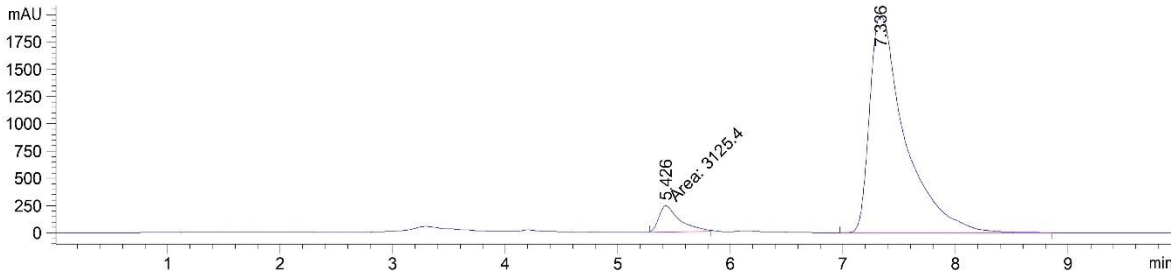
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.433	BV	0.2170	2.43483e4	1586.51257	49.8771
2	7.375	MM	0.3453	2.44683e4	1180.87219	50.1229

Asymmetric sample of (*Sp)*-**3k** obtained using *S*-NOBINAc

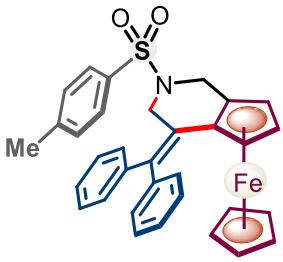


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.377	MM	0.2820	2060.04565	121.74028	98.7100
2	7.056	MM	0.2194	26.92121	2.04496	1.2900

Asymmetric sample of (*Rp)*-**3k** obtained using *R*-NOBINAc

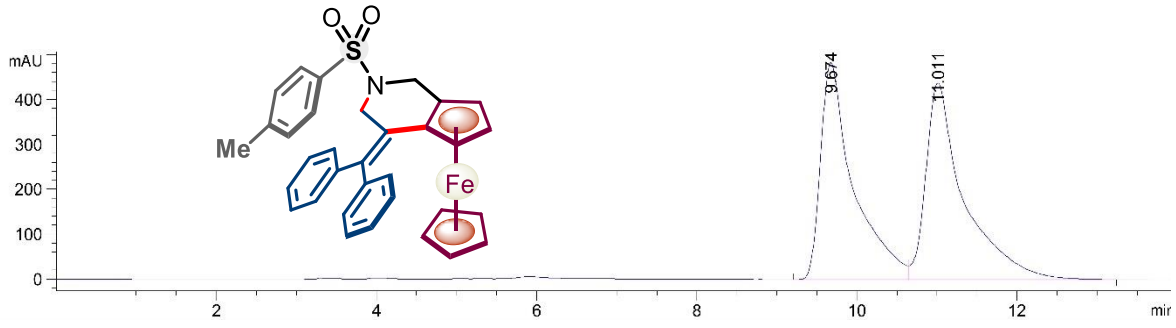


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.426	MM	0.2133	3125.39771	244.15727	6.7069
2	7.336	BB	0.3153	4.34742e4	1986.34509	93.2931



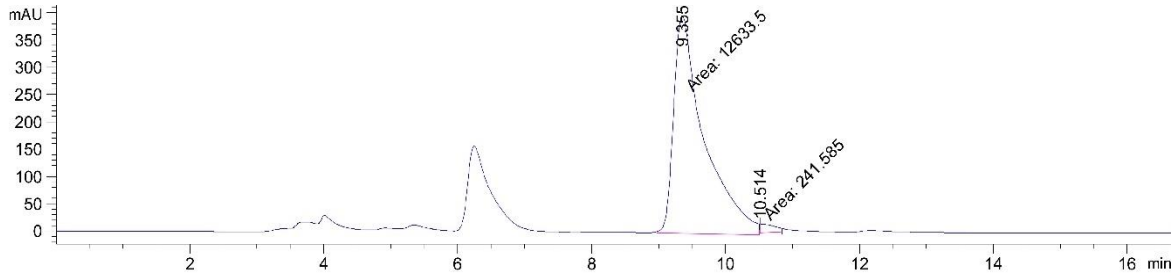
Ferrocene fused tetrahydropyridine 3l was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as an orange red solid, mp: 132 ºC-132 ºC. Yield: 47 mg (58%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.41 – 7.29 (m, 6H), 7.28 (s, 2H), 7.16 (d, J = 7.6 Hz, 2H), 7.11 – 6.98 (m, 2H), 4.54 (d, J = 14.2 Hz, 1H), 4.47 (d, J = 14.3 Hz, 1H), 4.27 (s, 1H), 4.10 (s, 5H), 4.03 (d, J = 14.2 Hz, 1H), 3.92 (s, 1H), 3.85 (d, J = 14.4 Hz, 1H), 3.06 (s, 1H), 2.45 (s, 3H).^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.3 (C), 142.7 (C), 141.7 (CH), 137.1 (CH), 134.8 (CH), 129.6 (CH), 129.5 (CH), 129.2 (CH), 128.5 (CH), 128.4 (CH), 127.9 (C), 127.5 (C), 127.2 (C), 127.1 (C), 82.5 (C), 78.8 (CH), 70.6 (CH), 67.7 (CH), 66.0 (CH), 65.3 (C), 48.6 (CH_2), 46.3 (CH_2), 21.5 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{33}H_{29}FeNO_2S$ 559.1263; Found 559.1253. The enantioselectivity of the product **3l** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 85:15, 0.9 mL/min, λ=254 nm).

Racemic sample (**3l)**



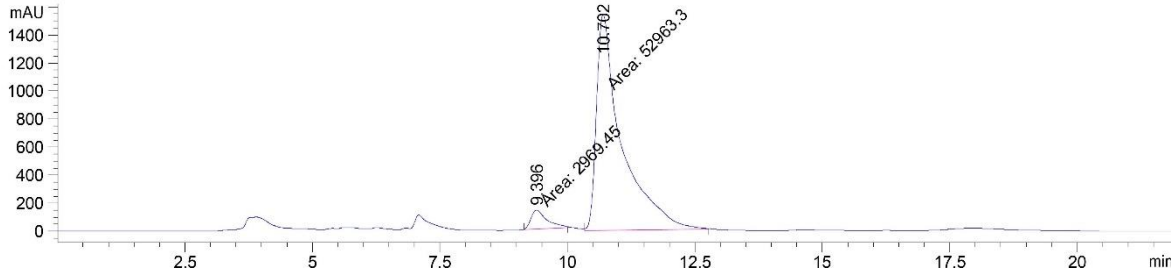
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.674	BV	0.4024	1.37642e4	483.13043	48.8097
2	11.011	VB	0.4613	1.44355e4	437.08127	51.1903

Asymmetric sample of (*Sp)*-**3l** obtained using *S*-NOBINAc

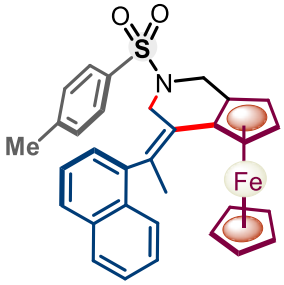


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.355	MM	0.5285	1.26335e4	398.38388	98.1236
2	10.514	MM	0.1814	241.58542	16.67377	1.8764

Asymmetric sample of (*Rp)*-**3l** obtained using *R*-NOBINAc

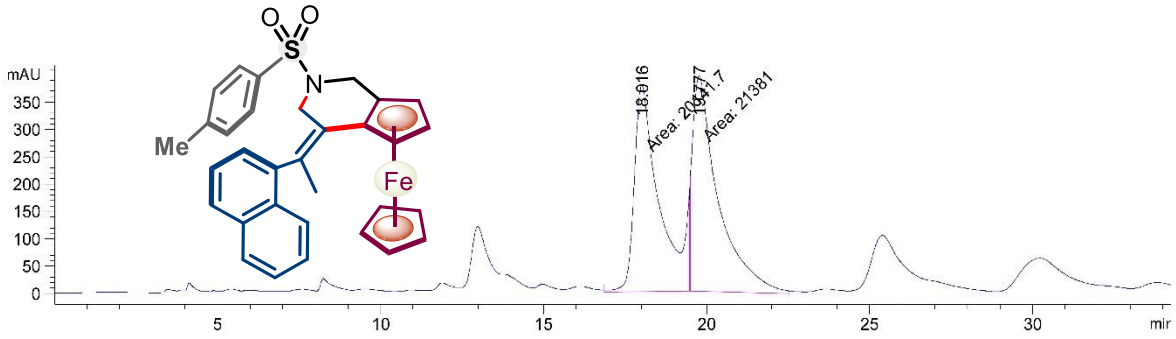


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.396	MM	0.3638	2969.44556	136.03685	5.3090
2	10.702	MM	0.5736	5.29633e4	1538.93127	94.6910



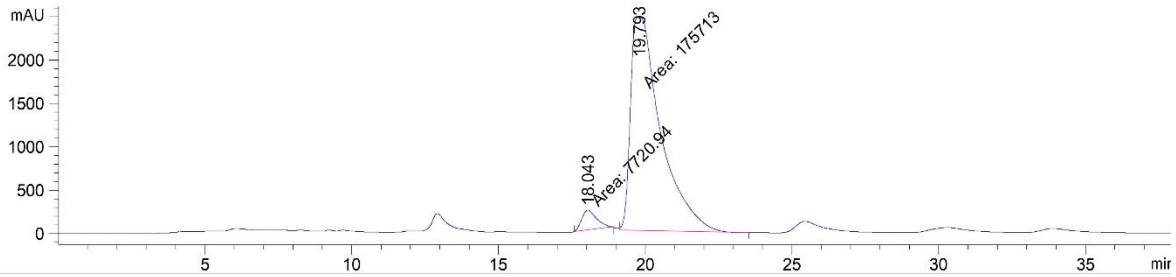
Ferrocene fused tetrahydropyridine 3m was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 90:10), obtained as an orange red solid, mp: 129 ºC-130 ºC. Yield: 42 mg (53%, *E:Z* 1:10). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 3H), 7.63 (s, 1H), 7.57 – 7.51 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.60 (d, *J* = 13.9 Hz, 2H), 4.37 (d, *J* = 13.5 Hz, 1H), 4.35 (d, *J* = 1.8 Hz, 1H), 4.25 (t, *J* = 2.5 Hz, 1H), 4.19 (s, 5H), 3.72 (d, *J* = 13.6 Hz, 1H), 3.23 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.3 (C), 141.4 (C), 134.0 (CH), 133.3 (CH), 133.0 (CH), 132.3 (CH), 129.4 (CH), 128.1 (CH), 128.0 (CH), 127.7 (C), 127.5 (CH), 126.7 (C), 126.6 (C), 126.4 (CH), 126.2 (C), 125.8 (C), 82.0 (C), 79.2 (CH), 70.5 (CH), 67.8 (CH), 66.9 (CH), 65.3 (C), 48.7 (CH_2), 46.4 (CH_2), 22.9 (CH_3), 21.5(CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{32}H_{29}FeNO_2S$ 547.1263; Found 547.1232. The enantioselectivity of the product **3m** was determined by chiral HPLC analysis on the AD-H column (hexane: isopropanol = 90:10, 0.9 mL/min, λ=254 nm).

Racemic sample (**3m)**

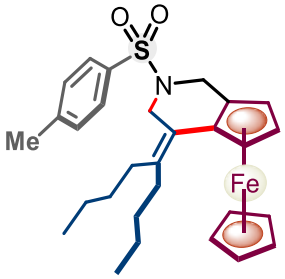


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.016	MM	0.8877	2.01417e4	378.15561	48.5077
2	19.777	MM	0.9049	2.13810e4	393.81238	51.4923

Asymmetric sample (**3m**)

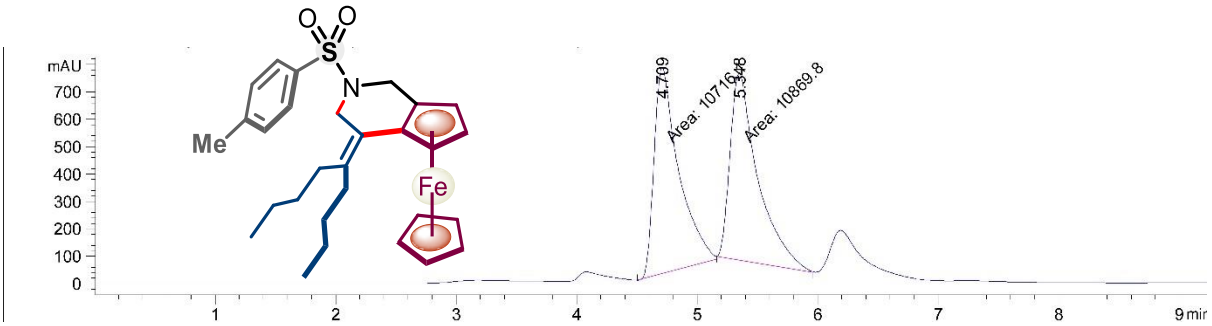


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.043	MM	0.5727	7720.93701	224.69550	4.2091
2	19.793	MM	1.1893	1.75713e5	2462.41479	95.7909



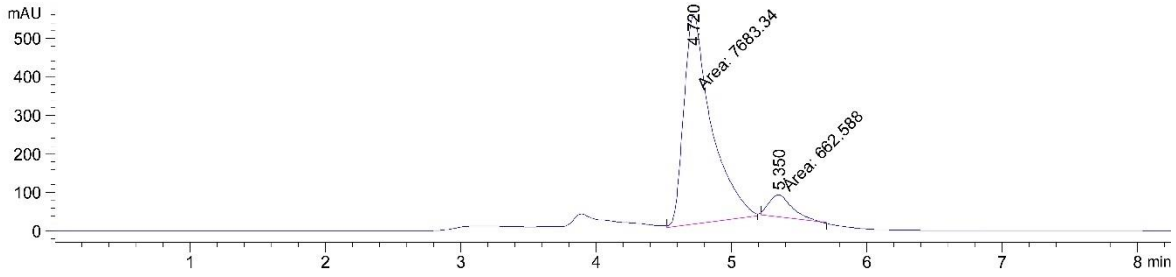
Ferrocene fused tetrahydropyridine 3n was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 90:10), obtained as an orange red solid, m.p: 117 ºC-118 ºC. Yield: 42 mg (56%, *E*:*Z* 3:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.47 (d, *J* = 13.8 Hz, 1H), 4.43 (d, *J* = 13.5 Hz, 1H), 4.31 (s, 1H), 4.23 (s, 1H), 4.14 (d, *J* = 2.4 Hz, 1H), 4.05 (s, 5H), 3.66 (d, *J* = 13.4 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.44 (s, 3H), 2.14 – 2.08 (4H), 1.52 – 1.40 (m, 8H), 1.1 –0.9 (m, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.4 (C), 137.9 (C), 133.9 (C), 129.6 (CH), 127.6 (CH), 122.5 (C), 81.5 (C), 79.3 (C), 70.4 (CH), 67.3 (CH), 66.2 (CH), 64.9 (CH), 47.0 (CH_2), 46.3 (CH_2), 34.0 (CH_2) 33.6 (CH_2), 31.0 (CH_2), 30.6 (CH_2), 23.3 (CH_2), 23.0 (CH_2), 21.5 (CH_3), 14.2 (CH_3), 14.0 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{29}H_{37}FeNO_2S$ 519.1889; Found 519.1868. The enantioselectivity of the product **3n** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 95:5, 1 mL/min, λ=254 nm).

Racemic sample (**3n)**

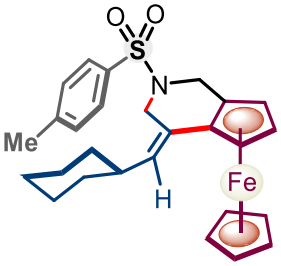


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.709	MM	0.2373	1.07161e4	752.56592	49.6440
2	5.348	MM	0.2653	1.08698e4	682.87201	50.3560

Asymmetric sample (**3n**)

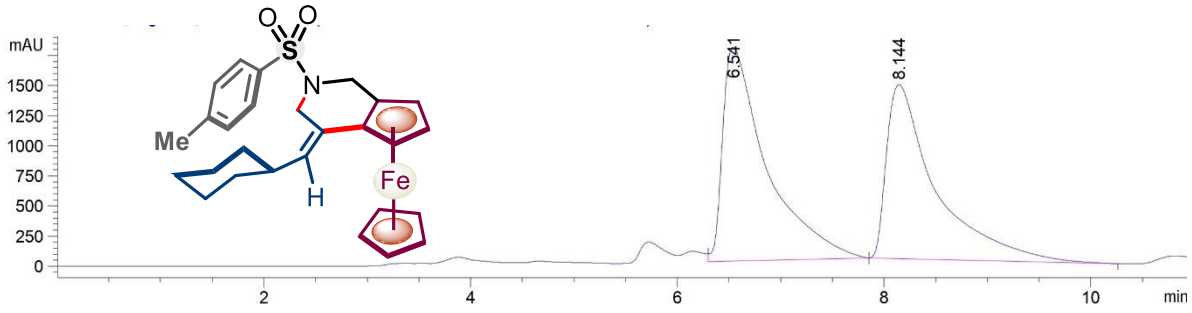


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.720	MM	0.2354	7683.34131	543.95502	92.0609
2	5.350	MM	0.1938	662.58795	56.98755	7.9391



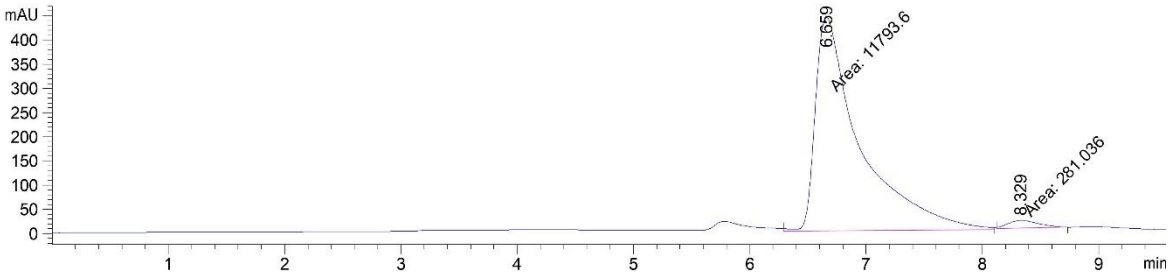
Ferrocene fused tetrahydropyridine 3o was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange yellow solid, m.p: 114 ºC-115 ºC. Yield: 37 mg, (53%, *E:Z* 1:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.34 (d, J = 9.7 Hz, 1H), 4.49 (d, J = 13.5 Hz, 1H), 4.39 (s, 1H), 4.26 (s, 1H), 4.16 (d, J = 4.9 Hz, 2H), 4.07 (s, 5H), 3.63 (d, J = 13.6 Hz, 1H), 3.34 (d, J = 12.9 Hz, 2H), 2.63 – 2.47 (m, 1H), 1.80 – 1.74 (m, 7H), 1.47 – 1.30 (m, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.5 (C), 133.6 (C), 132.6 (C), 129.6 (CH), 127.7 (CH), 126.9 (C), 81.7 (C), 70.8 (CH), 68.7 (CH), 67.8 (CH), 66.0 (CH), 65.1 (C), 52.4 (CH_2), 46.5 (CH_2), 37.7 (CH), 33.0 (CH_2), 32.8 (CH_2), 27.0 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 21.5 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{27}H_{31}FeNO_2S$ 489.1420; Found 489.1420. The enantioselectivity of the product **3o** was determined by chiral HPLC analysis on OD-3 column (hexane: isopropanol = 93:7, 1 mL/min, λ=254 nm).

Racemic sample (**3o)**

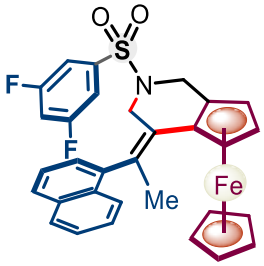


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.541	VB	0.4279	5.23946e4	1777.49768	52.2900
2	8.144	BB	0.4737	4.78054e4	1445.93958	47.7100
Totals :				1.00200e5	3223.43726	

Asymmetric sample (**3o**)

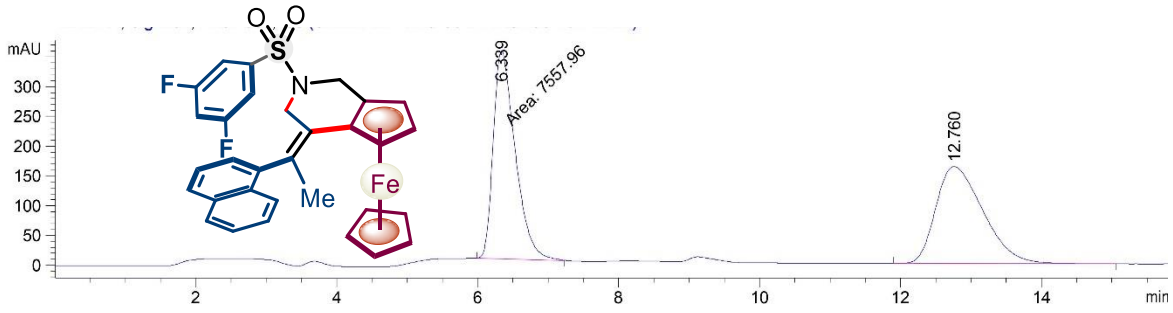


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.659	MM	0.4441	1.17936e4	442.61905	97.6725
2	8.329	MM	0.3033	281.03629	15.44449	2.3275



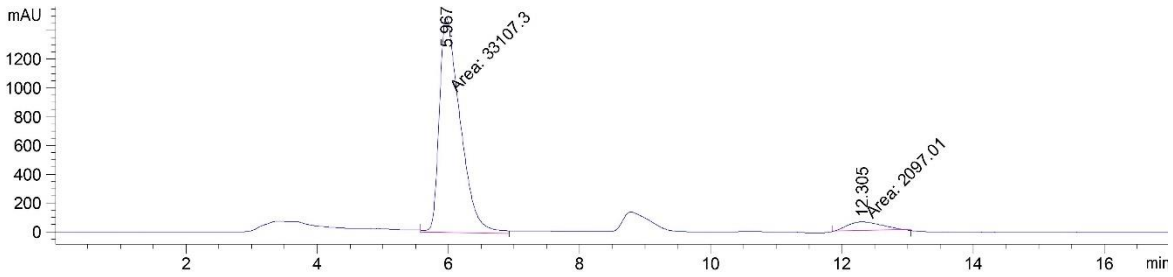
Ferrocene fused tetrahydropyridine 3p was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange yellow solid, m.p: 125 ºC-126 ºC. Yield: 39 mg (47%, *E:Z* 1:10). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.95 (s, 1H), 7.90 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.2 Hz, 1H), 7.56 (dd, J = 13.5, 10.2 Hz, 3H), 7.27 (s, 1H), 4.73 (d, J = 14.7 Hz, 1H), 4.52 (s, 1H), 4.33 (d, J = 15.3 Hz, 2H), 4.25 (s, 1H), 4.22 (s, 1H), 4.20 (s, 5H), 3.83 (d, J = 14.6 Hz, 1H), 2.22 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 141.4 (CH), 140.8 (CH), 133.8 (CH), 133.3 (CH), 132.5 (C), 132.4 (C), 132.2 (CH), 128.4 (CH), 127.9 (CF), 127.8 (CF), 127.5 (C), 126.6 (C), 126.5 (C), 126.1 (CH), 125.9 (CH), 125.0 (CH), 123.2 (C), 121.6 (C), 80.9 (C), 78.9 (CH), 70.4 (CH), 68.1 (CH), 66.8 (CH), 65.4 (C), 49.0 (CH_2), 46.8 (CH_2), 22.7 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.90. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{31}H_{25}F_2FeNO_2S$ 569.0923; Found 569.0930. The enantioselectivity of the product **3p** was determined by chiral HPLC analysis on IC-3 column (hexane: isopropanol = 85:15, 1 mL/min, λ=254 nm).

Racemic sample (**3p)**

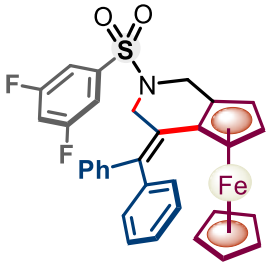


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.339	MM	0.3605	7557.95801	349.42419	49.9387
2	12.760	BB	0.7388	7576.52490	162.85172	50.0613

Asymmetric sample (**3p**)

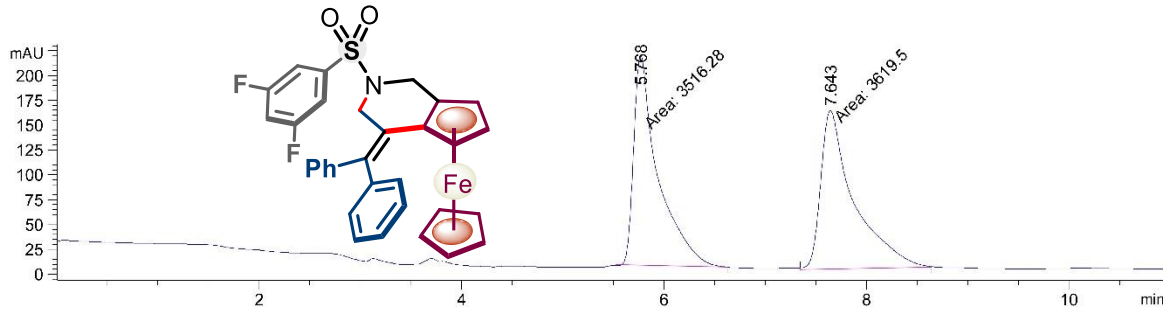


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.967	MM	0.3683	3.31073e4	1498.35449	94.0433
2	12.305	MM	0.5925	2097.00830	58.98545	5.9567



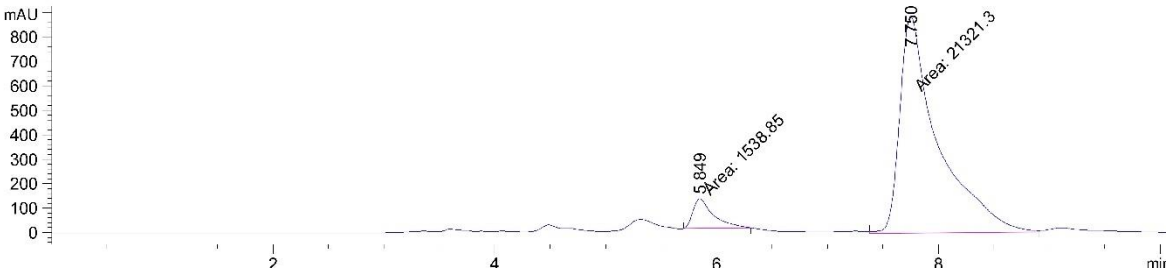
Ferrocene fused tetrahydropyridine 3q was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange yellow solid, mp: 131 ºC-132 ºC. Yield: 38 mg (45%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 (d, J = 6.9 Hz, 1H), 7.39 (dd, J = 9.2, 5.8 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.20 (d, J = 3.9 Hz, 2H), 7.17 (d, J = 7.1 Hz, 2H), 7.02 – 7.31 (m, 2H), 4.61 (d, J = 14.6 Hz, 1H), 4.51 (d, J = 14.6 Hz, 1H), 4.29 (d, J = 1.1 Hz, 1H), 4.17 (s, 1H), 4.11 (s, 5H), 4.03 (d, J = 15.0 Hz, 1H), 3.95 (t, J = 2.5 Hz, 1H), 3.10 (d, J = 1.4 Hz, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 162.7 (dd, J = 254.7, 11.7 Hz CF), 142.5 (C), 141.4 (CH_2), 137.5 (CH_2), 129.3 (CH_2), 129.1 (CH_2), 128.5 (CH_2), 128.3 (CH_2), 128.0 (C), 127.5 (CH_2), 127.3 (C), 127.2 (C), 110.8 (dd, J = 22.2, 5.6 Hz C), 108.1 (t, J = 25.0 Hz CH), 81.90 (C), 78.76 (CH), 70.65 (CH), 67.94 (CH), 66.19 (CH), 65.29 (C), 48.53 (CH_2), 46.4 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.64. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{32}H_{25}FeF_2NO_2S$ 581.0918; Found 581.0933. The enantioselectivity of the product **3q** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm).

Racemic sample (**3q)**

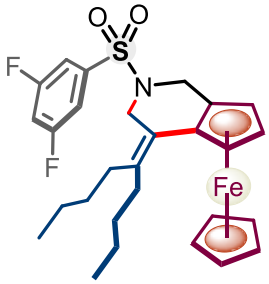


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.768	MM	0.2770	3516.28027	211.53900	49.2767
2	7.643	MM	0.3784	3619.50415	159.42012	50.7233

Asymmetric sample (**3q**)

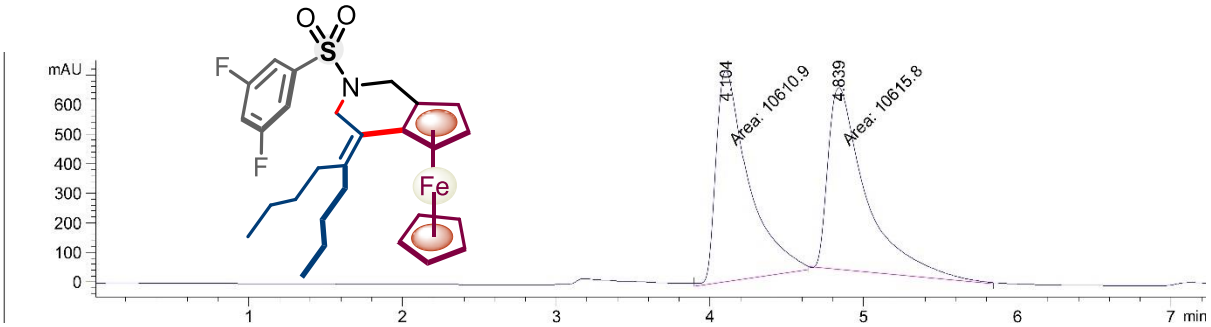


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.849	MM	0.2129	1538.84717	120.47400	6.7316
2	7.750	MM	0.4002	2.13213e4	887.90741	93.2684



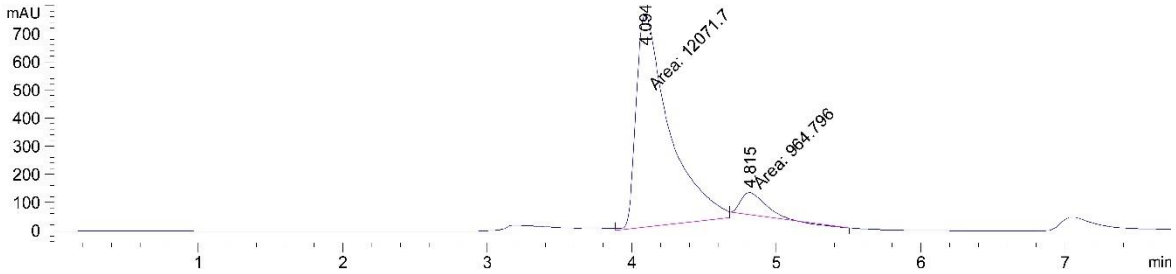
Ferrocene fused tetrahydropyridine 3r was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 95:5), obtained as an orange yellow solid, mp: 120 ºC-120 ºC. Yield: 35 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 4.3 Hz, 2H), 7.01 (tt, J = 8.4, 2.2 Hz, 1H), 4.55 (d, J = 13.9 Hz, 1H), 4.44 (d, J = 13.7 Hz, 1H), 4.31 (s, 1H), 4.24 (s, 1H), 4.16 (t, J = 2.4 Hz, 1H), 4.06 (s, 5H), 3.85 (d, J = 13.9 Hz, 1H), 3.64 (d, J = 13.7 Hz, 1H), 2.33 – 1.98 (m, 4H), 1.55 – 1.37 (m, 8H), 1.02 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 162.7 (dd, J = 254.6, 11.6 Hz, CF), 140.9 (t, J = 8.0 Hz , C), 138.4 (CH), 121.9 (CH), 110.9 (dd, J = 22.3, 5.7 Hz, C), 108.1 (t, J = 25.1 Hz, C), 80.8 (C), 79.2 (CH), 70.5 (CH), 67.5 (CH), 66.3 (CH), 64.9 (C), 47.2 (CH_2), 46.5 (CH_2), 34.0 (CH_2), 33.7 (CH_2), 31.0 (CH_2), 30.4 (CH_2), 23.3 (CH_2), 23.0 (CH_2),14.2 (CH_3), 14.0 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.86. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{28}H_{33}FeF_2NO_2S$ 541.1544; Found 541.1588. The enantioselectivity of the product **3r** was determined by chiral HPLC analysis on OD-3 column (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm).

Racemic sample (**3r)**

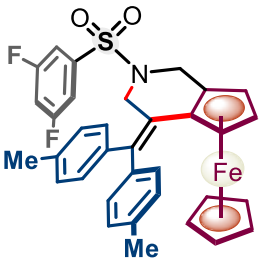


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.104	MM	0.2477	1.06109e4	713.99713	49.9886
2	4.839	MM	0.2870	1.06158e4	616.41479	50.0114

Asymmetric sample (**3r**)

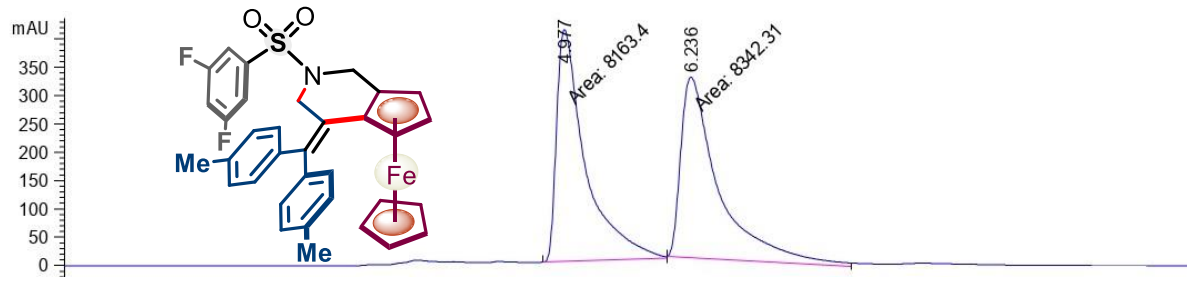


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.094	MM	0.2659	1.20717e4	756.68420	92.5993
2	4.815	MM	0.2027	964.79559	79.30970	7.4007



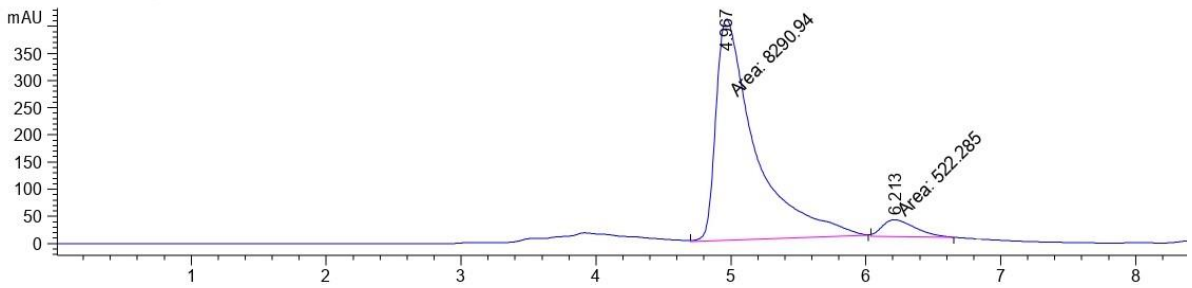
Ferrocene fused tetrahydropyridine 3s was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 90:10), obtained as an orange red solid, mp: 135 ºC; $[\alpha]_D^{25}$= +41 ($CHCl_3$, c= 0.12). Yield: 43 mg (50%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.18 (d, J = 7.8 Hz, 4H), 7.13 (d, J = 6.4 Hz, 2H), 7.01 (d, J = 7.6 Hz, 3H), 6.87 (s, 2H), 4.47 (d, J = 14.4 Hz, 2H), 4.37 (s, 1H), 4.17 (s, 5H), 4.14 (d, J = 14.7 Hz, 2H), 4.01 (s, 1H), 3.26 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 162.7 (dd, J = 254.6, 11.5 Hz CF), 141.9 (t, J = 8.0 Hz C), 139.5 (C), 138.6 (C), 137.9 (C), 137.2 (C), 136.9 (C), 129.3 (CH), 129.2 (CH), 126.4 (C), 110.9 (dd, J = 22.2, 5.6 Hz CH), 108.1 (t, J = 25.0 Hz, CH), 82.1 (C), 80.1 (C), 71.2 (CH), 68.4 (CH), 66.4 (CH), 65.5 (CH), 48.6 (CH_2), 46.5 (CH_2), 21.3 (CH_3), 21.2 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.73. HRLCMS (ESI) *m/z*: [M] Calcd for $C_{34}H_{29}FeF_2NO_2S$ 609.1231; Found 609.1234. The enantioselectivity of the product **3s** was determined by chiral HPLC analysis on OD-3 column (hexane: isopropanol = 85:15, 1 mL/min, λ=254 nm).

Racemic sample (**3s)**

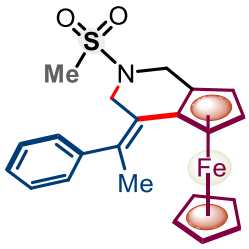


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.977	MM	0.3325	8163.40039	409.25189	49.4581
2	6.236	MM	0.4361	8342.30566	318.83063	50.5419

Asymmetric sample (**3s**)

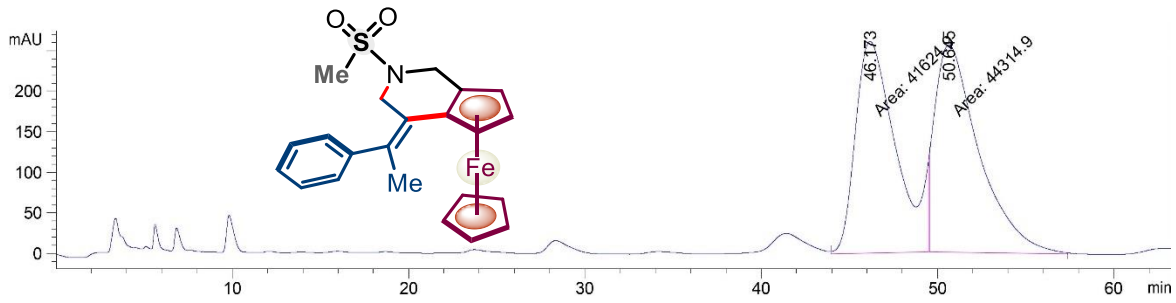


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.967	MM	0.3391	8290.93750	407.44418	94.0738
2	6.213	MM	0.2845	522.28479	30.59200	5.9262



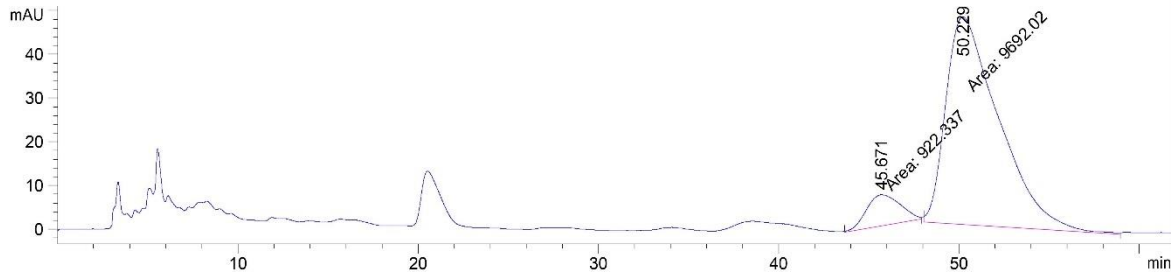
Ferrocene fused tetrahydropyridine 3t was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 113 ºC-114 ºC. Yield: 25 mg (42%, *E*:*Z* 1:10). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.41 (t, J = 7.1 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.21 (d, J = 7.0 Hz, 2H), 4.67 (brs, 2H), 4.65 (d, J = 14.7 Hz, 1H), 4.31 – 4.27 (m, 2H), 4.19 (s, 5H), 4.09 (d, J = 14.5 Hz, 1H), 3.68 (d, J = 14.0 Hz, 1H), 2.69 (s, 3H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.8 (C), 133.5 (CH), 128.6 (CH), 128.0 (CH), 127.0 (C), 125.6 (C), 81.9 (C), 70.5 (CH), 67.9 (CH), 67.8 (CH), 66.8 (CH), 65.3 (C), 48.4 (CH_2), 46.2 (CH_2), 36.6 (CH_3), 22.9 (CH_3). HRLCMS (ESI) *m/z*: $[M-H]^+$ Calcd for $C_{22}H_{22}FeNO_2S$ 420.0715; Found 420.0693. The enantioselectivity of the product **3t** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 85:15, 1 mL/min, λ=254 nm).

Racemic sample (**3t)**

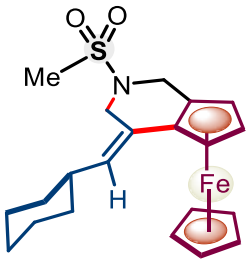


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.173	MM	2.6581	4.16249e4	260.99533	48.4350
2	50.645	MM	2.8888	4.43149e4	255.67107	51.5650

Asymmetric sample (**3t**)

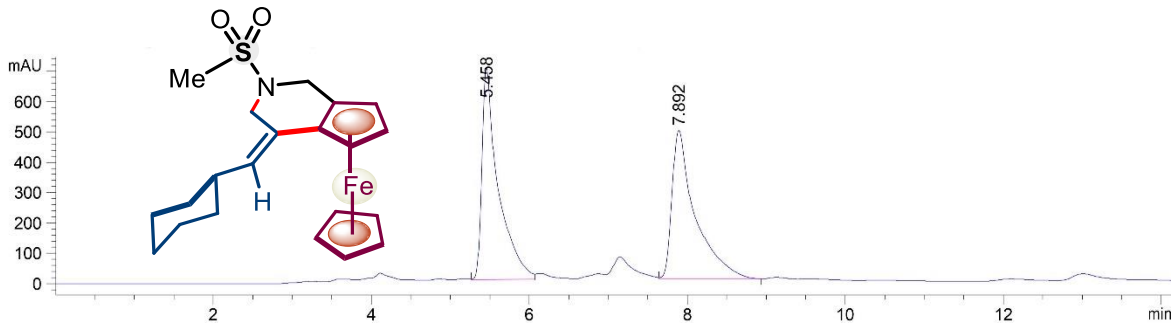


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.671	MM	2.1561	922.33679	7.12954	8.6895
2	50.229	MM	3.4045	9692.01660	47.44727	91.3105



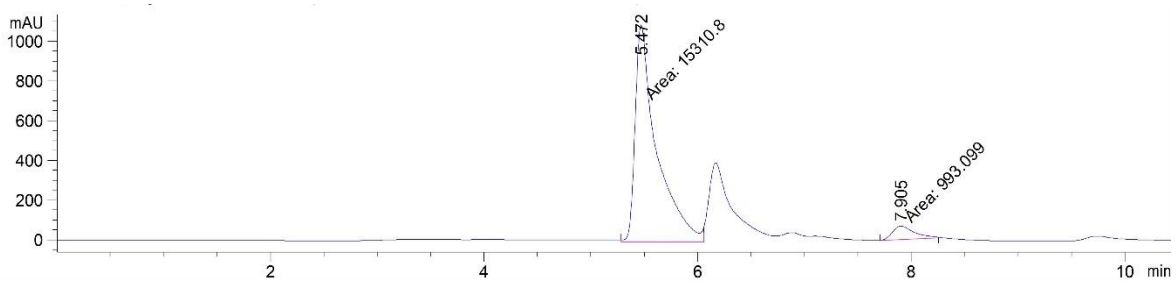
Ferrocene fused tetrahydropyridine 3u was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 109 ºC-110 ºC. Yield: 23 mg (38%, *E:Z* 1:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (d, J = 9.2 Hz, 1H), 4.60 (d, J = 15.3 Hz, 1H), 4.50 (s, 1H), 4.33 (s, 1H), 4.28 (d, J = 4.0 Hz, 1H), 4.24 (d, J = 9.6 Hz, 1H), 4.11 (s, 5H), 4.08 – 4.03 (m, 1H), 3.93 (d, J = 14.2 Hz, 1H), 2.72 (s, 3H), 2.53 (dd, J = 19.4, 10.1 Hz, 1H), 1.87 (t, J = 12.2 Hz, 2H), 1.23 (d, J = 5.8 Hz, 8H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 132.8 (C), 126.7 (C), 81.8 (C), 77.9 (CH), 70.7 (CH), 67.9 (CH), 65.6 (CH), 65.2 (C), 52.2 (CH_2), 46.2 (CH_2), 37.5 (CH), 37.1 (CH_2), 32.9 (CH_2), 32.8 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.7 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{21}H_{27}FeNO_2S$ 413.1107; Found 413.1096. The enantioselectivity of the product **3u** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

Racemic sample (**3u)**

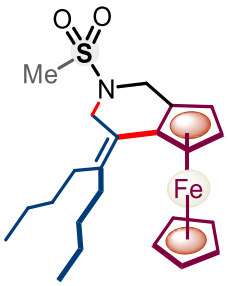


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.458	VV	0.2002	1.00683e4	698.32629	50.1783
2	7.892	VB	0.2843	9996.71289	489.47974	49.8217

Asymmetric sample (**3u**)

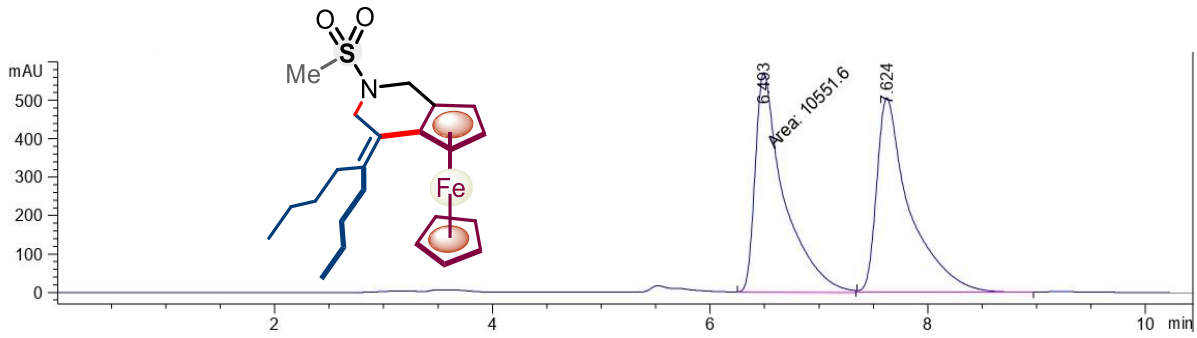


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.472	MM	0.2332	1.53108e4	1094.21545	93.9088
2	7.905	MM	0.2415	993.09906	68.53255	6.0912



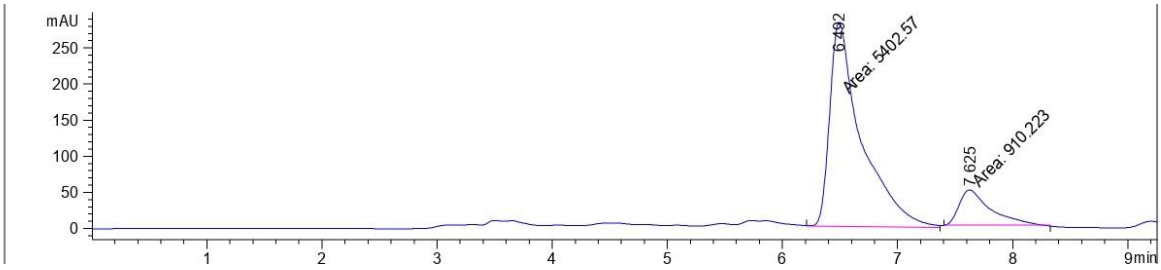
Ferrocene fused tetrahydropyridine 3v was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 112 ºC-113 ºC. Yield: 22 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (brs, 2H), 4.34 (d, J = 14.1 Hz, 2H), 4.28 (s, 1H), 4.17 (s, 1H), 4.13 (brs, 6H), 2.70 (s, 3H), 2.2 – 1.6 (m, 4H), 1.53 – 1.38 (m, 8H), 1.06 – 0.95 (m, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 138.2 (C), 122.3 (C), 81.4 (C), 70.5 (CH), 68.7 (CH), 67.5 (CH), 66.1 (CH), 65.0 (C), 46.9 (CH_2), 46.3 (CH_2), 36.7 (CH_3), 34.0 (CH_2), 33.8 (CH_2), 31.2 (CH_2), 30.5 (CH_2), 23.3 (CH_2), 23.0 (CH_2), 14.2 (CH_3), 14.0 (CH_3). HRLCMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{33}FeNO_2SNa$ 466.1474; Found 466.1462. The enantioselectivity of the product **3v** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 85: 15, 1 mL/min, λ=254 nm).

Racemic sample (**3v)**

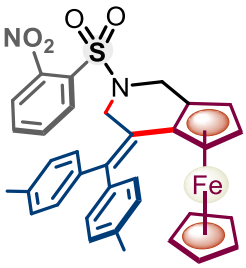


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.493	MM	0.3074	1.05516e4	572.00067	49.8391
2	7.624	VB	0.2949	1.06197e4	505.84946	50.1609

Asymmetric sample (**3v**)

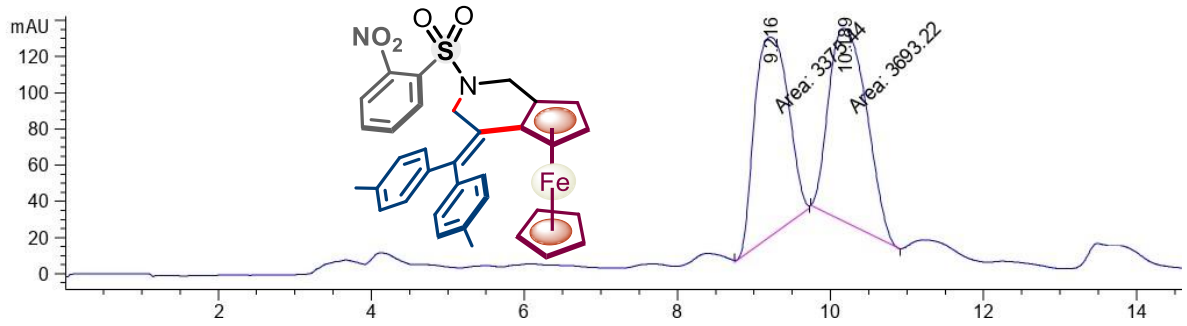


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.492	MM	0.3185	5402.57031	282.68707	85.5813
2	7.625	MM	0.3141	910.22327	48.29060	14.4187



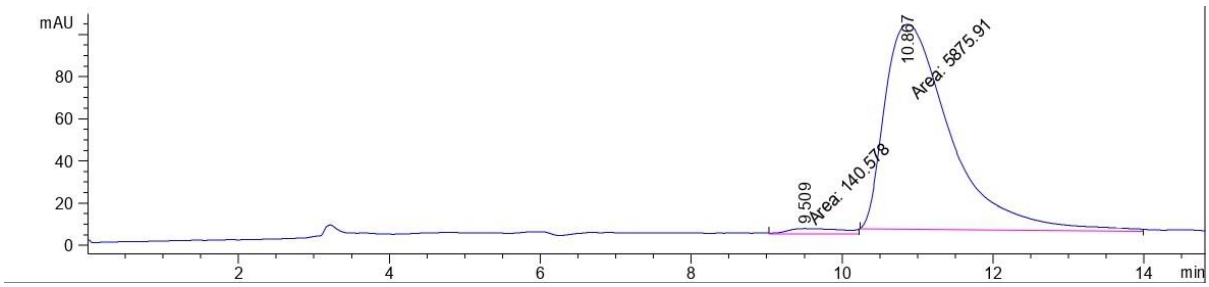
Ferrocene fused tetrahydropyridine 3w was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as an orange yellow solid, mp: 140 ºC-141 ºC. Yield: 25 mg (28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.9, 1.1 Hz, 1H), 7.68 – 7.53 (m, 3H), 7.15 (dd, J = 15.2, 7.7 Hz, 4H), 7.03 (d, J = 8.0 Hz, 2H), 6.96 – 6.87 (m, 2H), 4.70 (d, J = 15.1 Hz, 1H), 4.59 (d, J = 14.7 Hz, 1H), 4.42 (d, J = 15.1 Hz, 1H), 4.32 (d, J = 1.1 Hz, 1H), 4.19 (d, J = 6.2 Hz, 1H), 4.13 (s, 5H), 3.97 (t, J = 2.5 Hz, 1H), 3.21 (dd, J = 2.4, 1.0 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 148.1 (C), 139.8 (C), 138.9 (C), 137.3 (CH), 137.0 (CH), 136.9 (C), 133.2 (C), 132.9 (CH), 131.6 (CH), 131.1 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 129.0 (CH), 126.9 (C), 124.0 (C), 82.9 (C), 79.4 (C), 70.5 (CH), 67.7 (CH), 66.2 (CH), 65.0 (CH), 48.4 (CH_2), 46.5 (CH_2), 21.3 (CH_3), 21.2 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{34}H_{30}FeN_2O_4S$ 618.1271; Found 618.1245. The enantioselectivity of the product **3w** was determined by chiral HPLC analysis on IC-3 column (hexane: isopropanol = 93:7, 1 mL/min, λ=254 nm).

Racemic sample (**3w)**

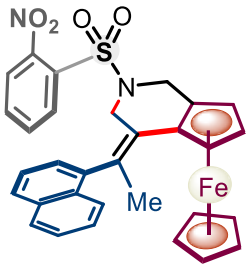


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.216	MM	0.5105	3375.43848	110.19186	47.7522
2	10.189	MM	0.5771	3693.21875	106.66720	52.2478

Asymmetric sample (**3w**)

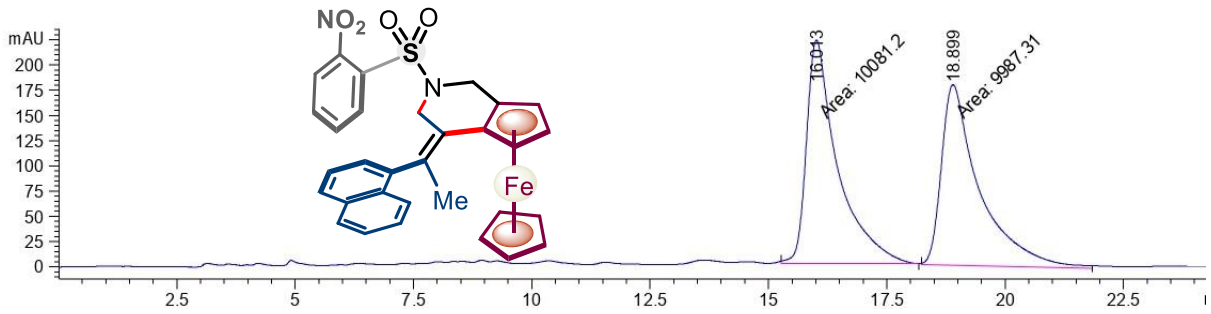


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.509	MM	0.8835	140.57751	2.65192	2.3365
2	10.867	MM	1.0066	5875.90918	97.29389	97.6635



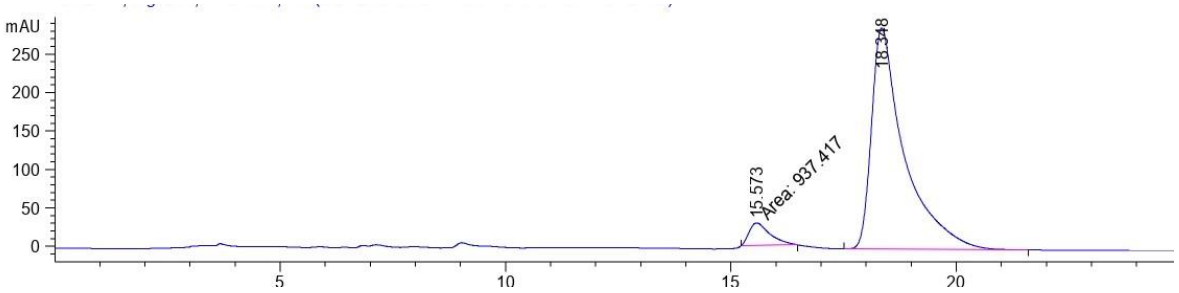
Ferrocene fused tetrahydropyridine 3x was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 135 ºC-135 ºC. Yield: 26 mg (31%, *E:Z* 1:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 3H), 7.68 (s, 1H), 7.53 (q, *J* = 5.5 Hz, 5H), 7.39 (d, *J* = 8.3 Hz, 1H), 4.84 (d, *J* = 14.8 Hz, 1H), 4.66 (d, *J* = 1.5 Hz, 1H), 4.41 – 4.35 (m, 1H), 4.31 (t, *J* = 2.5 Hz, 1H), 4.28 (s, 5H), 4.21 – 4.18 (m, 1H), 4.12 (s, 1H), 3.44 (dd, *J* = 14.4, 1.3 Hz, 1H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 147.8 (C), 141.4 (C), 133.5 (C), 133.3 (C), 133.2 (CH), 132.3 (CH), 132.2 (CH), 131.4 (CH), 130.8 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 126.7 (CH), 126.2 (CH), 126.0 (CH), 125.9 (CH), 125.7 (CH), 125.6 (CH), 124.0 (CH), 123.6 (C), 82.1 (C), 78.9 (C), 70.6 (CH), 67.9 (CH), 67.0 (CH), 65.1 (CH), 47.9 (CH_2), 46.4 (CH_2), 22.9 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{31}H_{26}FeN_2O_4S$ 578.0958; Found 578.0936. The enantioselectivity of the product **3x** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 85:15, 1 mL/min, λ=254 nm).

Racemic sample (**3x)**

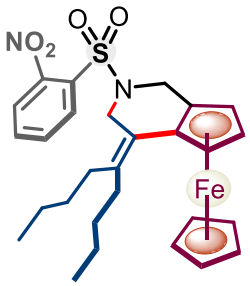


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.977	MM	0.3325	8163.40039	409.25189	49.4581
2	6.236	MM	0.4361	8342.30566	318.83063	50.5419

Asymmetric sample (**3x**)

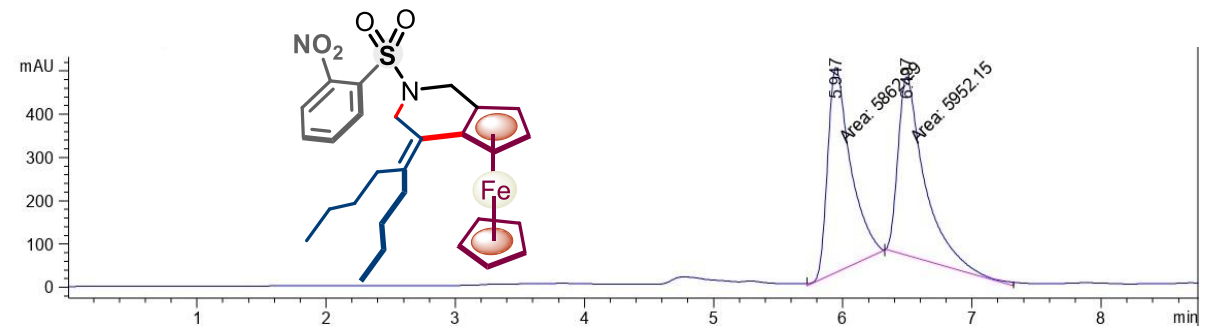


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.573	MM	0.5321	937.41718	29.36063	6.0381
2	18.348	BB	0.7153	1.45876e4	287.84317	93.9619



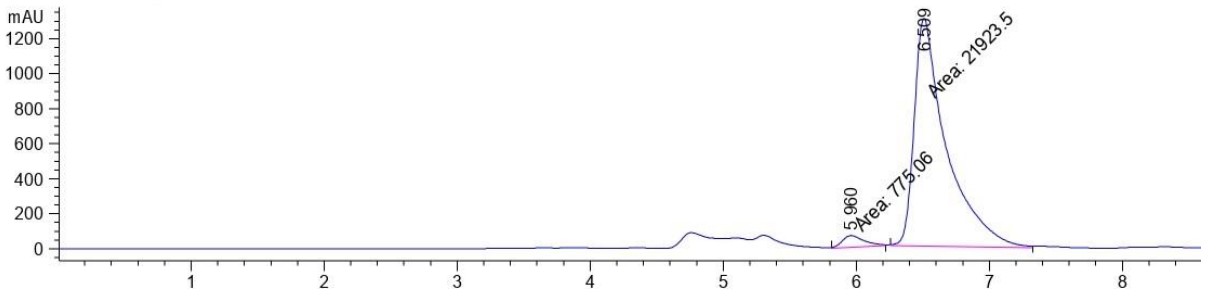
Ferrocene fused tetrahydropyridine 3y was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 90:10), obtained as an orange yellow solid, mp: 122 ºC-123 ºC. Yield: 27 mg (34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 1H), 7.73 – 7.68 (m, 2H), 7.68 – 7.61 (m, 1H), 4.68 (d, *J* = 14.1 Hz, 1H), 4.59 (d, *J* = 14.1 Hz, 1H), 4.37 (s, 1H), 4.29 (s, 1H), 4.19 (s, 1H), 4.11 (s, 5H), 4.02 (d, *J* = 14.1 Hz, 1H), 3.66 (d, *J* = 14.0 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.09 – 2.16 (m, 3H), 1.56 – 1.40 (m, 8H), 1.03 – 0.9 (m, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 148.5 (C), 138.5 (C), 133.5 (CH), 131.9 (C), 131.5 (CH), 130.6 (CH_3), 124.1 (CH), 122.1 (C), 81.3 (C), 79.2 (C), 70.5 (CH), 67.5 (CH), 66.4 (CH), 64.9 (CH), 46.8 (CH_2), 46.4 (CH_2), 34.0 (CH_2), 33.8 (CH_2), 31.0 (CH_2), 30.6 (CH_2), 23.4 (CH_2), 23.1 (CH_2), 14.3 (CH_3), 14.1 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{28}H_{34}FeN_2O_4S$ 550.1584; Found 550.1580. The enantioselectivity of the product **3y** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm).

Racemic sample (**3y)**

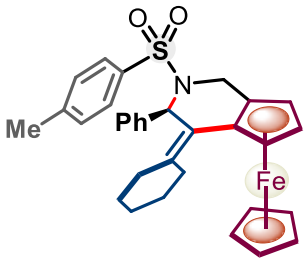


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.947	MM	0.2057	5862.28711	474.99173	49.6197
2	6.497	MM	0.2411	5952.14551	411.41379	50.3803

Asymmetric sample (**3y**)

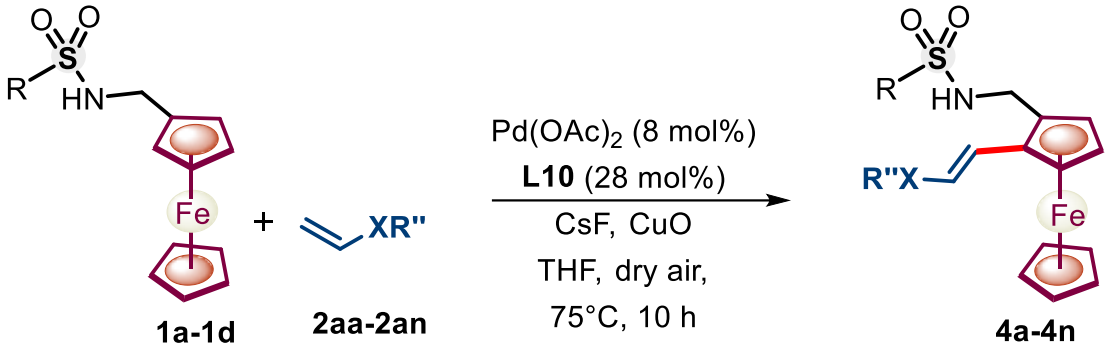


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.960	MM	0.1901	775.06006	67.94447	3.4146
2	6.509	MM	0.2807	2.19235e4	1301.77283	96.5854

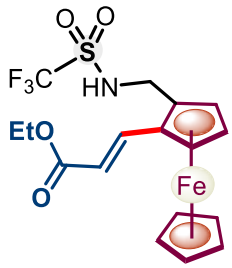


Ferrocene fused tetrahydropyridine 3z was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 145 ºC-146 ºC. Yield: 46 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.11 – 7.05 (m, 2H), 6.27 (s, 1H), 4.62 (d, J = 15.6 Hz, 1H), 4.24 (s, 1H), 4.08 (t, J = 2.4 Hz, 1H), 4.01 (s, 1H), 3.84 (s, 5H), 3.78 (d, J = 15.6 Hz, 1H), 2.97 – 2.77 (m, 2H), 2.44 (s, 3H), 2.40 (dd, J = 7.6, 3.7 Hz, 1H), 2.28 (dd, J = 8.8, 4.5 Hz, 1H), 1.82 – 1.68 (m, 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.3 (C), 138.7 (C), 138.6 (C), 137.7 (C), 129.6 (CH), 128.4 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 121.8 (C), 80.5 (C), 79.8 (C), 70.6 (CH), 69.9 (CH), 67.5 (CH), 63.2 (CH), 56.4 (CH_2), 41.5 (C), 31.8 (CH_2), 31.3 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 26.7 (CH_2), 21.5 (CH_3). HRLCMS (ESI) *m/z*: [M] Calcd for $C_{32}H_{33}FeNO_2S$ 551.1576; Found 551.1587.

Scheme S3. General procedure for the Pd-catalyzed alkenylation of ferrocenyl secondary amines with olefins

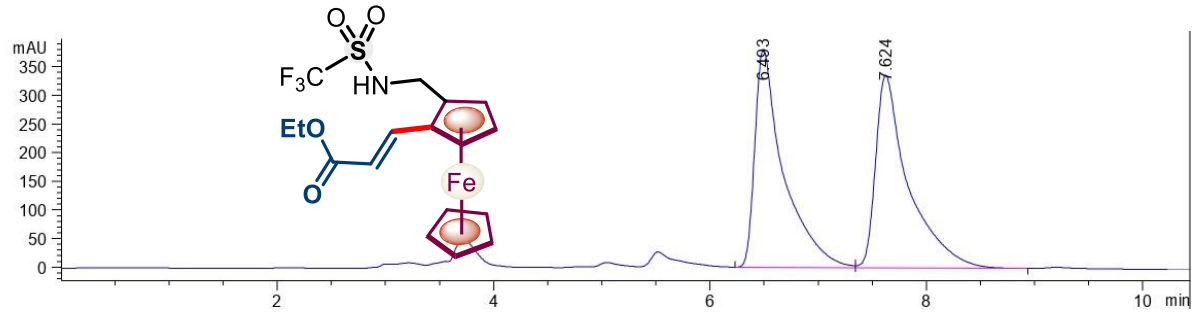


In a Schlenk tube, $Pd(OAc)_2$ (2.5 mg, 0.012 mmol, 8 mol%), NOBINAc (14 mg, 0.04 mmol, 28 mol%), CuO (11.5 mg, 0.14 mmol, 1 equiv.), CsF (44 mg, 0.28 mmol, 2 equiv.) and ferrocenyl secondary amine **1a** (50 mg, 0.14 mmol, 1 equiv.) were added in dry THF (1.5 mL) under an inert atmosphere and the resulted orange colored solution was stirred for 10 min. After pre-stirring, olifin **2aa** (55 μL, 0.29 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 75 °C, stirred for 10 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 hexane: ethyl acetate (85:15) eluent to afford chiral 1,2 alkenylated ferrocenyl amines (**4a-4n**).



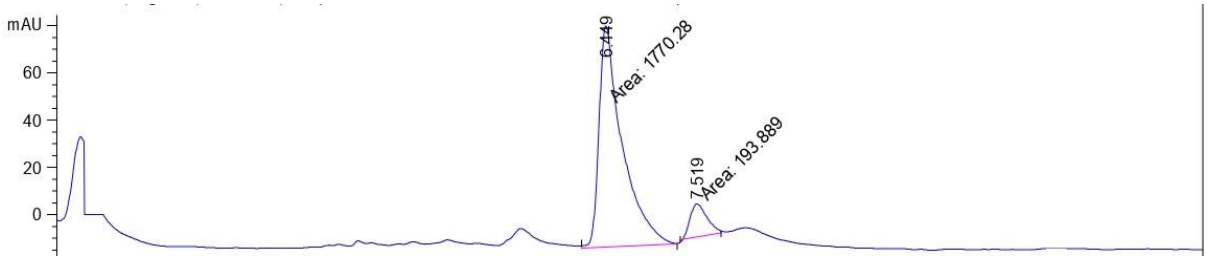
Chiral 1,2 alkenylated ferrocenyl amine 4a was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 104 ºC-105 ºC. Yield: 32 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 15.6 Hz, 1H), 6.11 (d, J = 15.6 Hz, 1H), 5.46 (s, 1H), 4.66 (s, 1H), 4.52 (d, J = 17.2 Hz, 2H), 4.38 (t, J = 5.8 Hz, 2H), 4.24 (d, J = 7.1 Hz, 2H), 4.20 (s, 5H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 167.1 (C), 141.9 (CH), δ 119.7 (d, J = 321.2 Hz CF_3), 116. (CH), 83.2 (C), 78.0 (C), 71.9 (CH), 70.6 (CH), 70.4 (CH), 67.2 (CH), 60.5 (CH_2), 42.2 (CH_2), 14.2 (CH_3). HRLCMS (ESI) *m/z:* $[M+Na]^+$ Calcd for $C_{17}H_{18}F_3FeNO_4SNa$ 468.0150; Found 468.0144. The enantioselectivity of the product **4a** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm).

Racemic sample (**4a)**

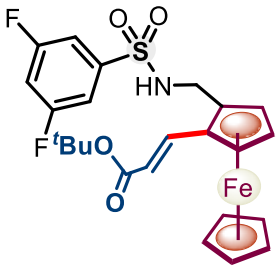


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.493	BV	0.2591	7016.11914	380.49390	49.7528
2	7.624	VB	0.2958	7085.84619	336.38715	50.2472

Asymmetric sample (**4a**)

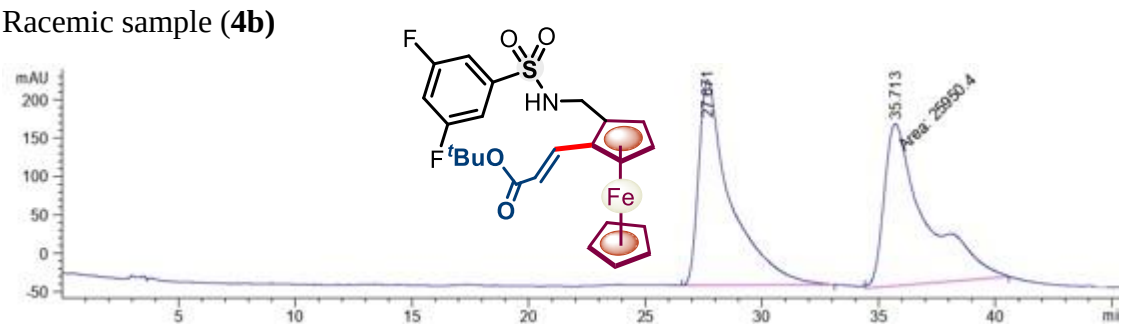


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.449	MM	0.3153	1770.28333	93.59005	90.1287
2	7.519	MM	0.2305	193.88928	14.01961	9.8713



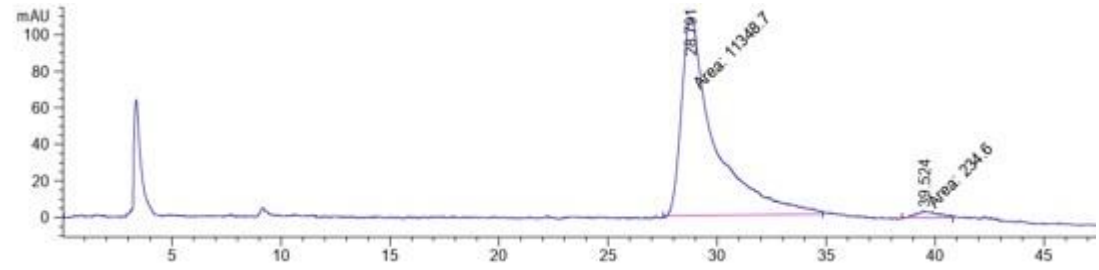
Chiral 1,2 alkenylated ferrocenyl amine 4b was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as an orange red solid, mp: 112-113 ºC. Yield: 40 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.02 (t, J = 8.9 Hz, 1H), 5.96 (d, J = 15.3 Hz, 1H), 4.89 (t, J = 7.2 Hz, 1H), 4.52 (s, 1H), 4.35 (d, J = 6.6 Hz, 2H), 4.14 (s, 7H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 166.4 (C), 162.7 (dd, J = 254.6, 11.7 Hz C-F), 143.6 (t, J = 8.3 Hz C), 140.7 (CH), 118.3 (CH), 110.6 (dd, J = 22.4, 5.7 Hz CH), 108.2 (t, J = 25.0 Hz CH), 83.5 (C), 80.5 (C), 78.0 (CH), 71.6 (CH), 70.2 (CH), 69.8 (CH), 66.8 (C), 41.2 (CH_2), 28.2 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M]^+$ Calcd for $C_{24}H_{25}F_2FeNO_4S$ 517.0817; Found 517.0814. The enantioselectivity of the product **4b** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 95:5, 1 mL/min, λ=254 nm)

Racemic sample (**4b)**

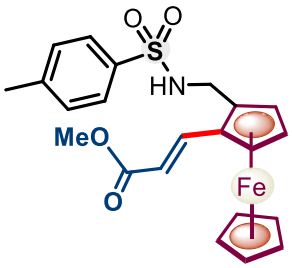


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.671	BB	1.3173	2.54164e4	267.79654	49.4803
2	35.713	MM	2.0496	2.59504e4	211.02377	50.5197

Asymmetric sample (**4b**)

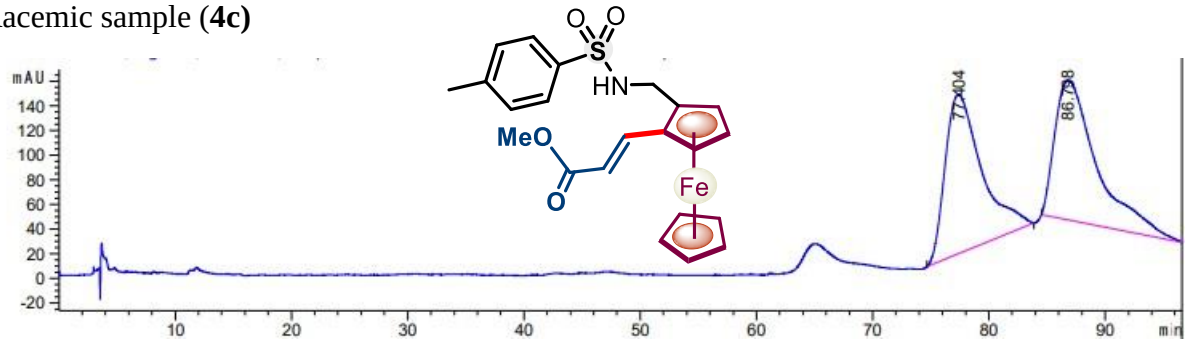


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.791	MM	1.7484	1.13487e4	108.18298	97.9747
2	39.524	MM	1.1072	234.59998	3.53142	2.0253



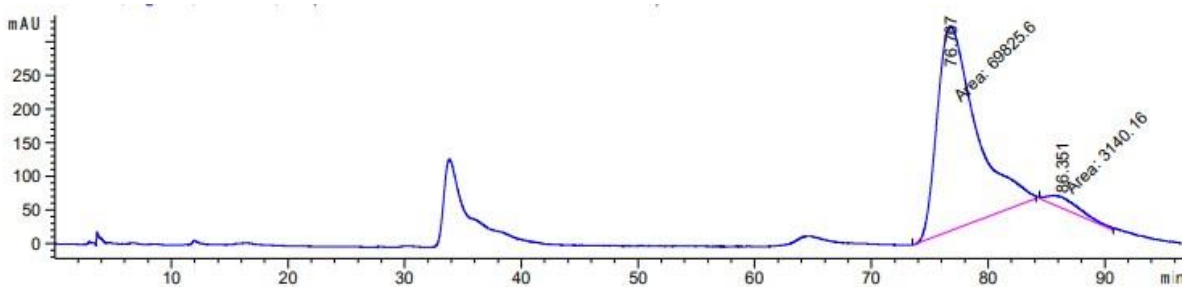
Chiral 1,2 alkenylated ferrocenyl amine 4c was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as an orange red solid, mp: 104-105 ºC. Yield: 30 mg (47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 15.5 Hz, 1H), 7.35 (d, J = 7.4 Hz, 2H), 6.03 (d, J = 15.3 Hz, 1H), 4.58 (s, 1H), 4.54 (s, 1H), 4.39 (s, 2H), 4.14 (s, 5H), 4.02 (s, 2H), 3.79 (s, 3H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 167.3 (C), 143.7 (C), 142.7 (C), 136.7 (CH), 129.9 (CH), 127.2 (CH), 115.8 (CH), 85.1 (C), 78.6 (C), 72.5 (CH), 71.3 (CH), 71.0 (CH), 67.8 (CH), 51.6 (CH_3), 41.0 (CH_2), 21.6 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{24}FeNO_4S$ 454.0770; Found 454.0778. The enantioselectivity of the product **4c** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 90:10, 1 mL/min, λ=254 nm)

Racemic sample (**4c)**

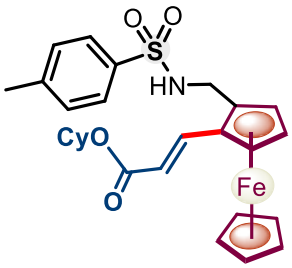


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	77.404	BB	2.5803	2.80602e4	128.97166	49.6750
2	86.798	BBA	2.9365	2.84274e4	113.24978	50.3250
Totals :				5.64876e4	242.22144	

Asymmetric sample (**4c**)

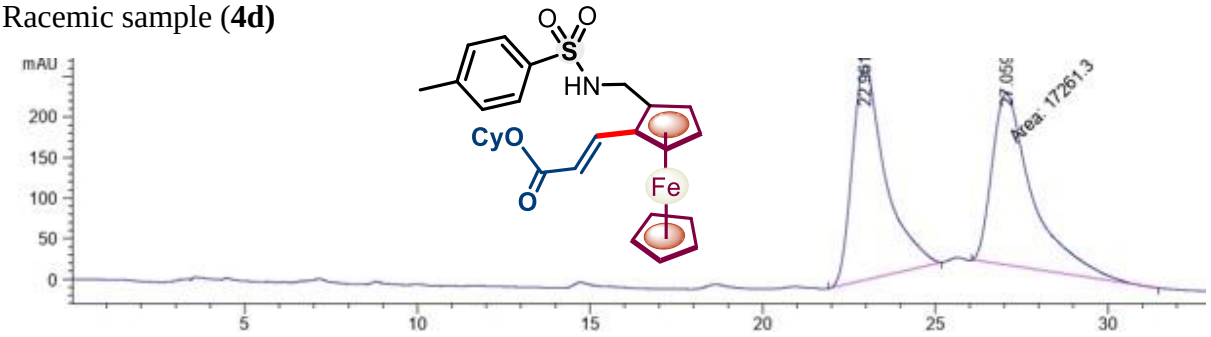


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	76.767	MM	3.8306	6.98256e4	303.80820	95.6964
2	86.351	MM	3.2767	3140.16357	15.97230	4.3036
Totals :				7.29658e4	319.78050	



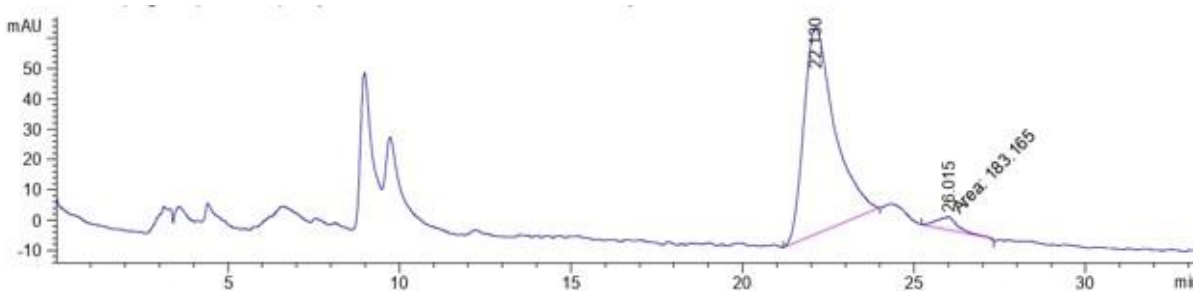
Chiral 1,2 alkenylated ferrocenyl amine 4d was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 75:25), obtained as an orange red solid, mp: 120-121 ºC. Yield: 41 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.7 Hz, 2H), 7.46 (d, J = 15.7 Hz, 1H), 7.35 (d, J = 7.4 Hz, 2H), 6.03 (d, J = 15.5 Hz, 1H), 4.87 (s, 1H), 4.55 (s, 2H), 4.35 (s, 2H), 4.13 (s, 5H), 4.04 (d, J = 5.7 Hz, 2H), 2.47 (s, 3H), 1.99 – 1.90 (m, 2H), 1.85 – 1.76 (m, 2H), 1.52-1.37 (m, , 6H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 166.4 (C), 143.6 (C), 141.9 (C), 136.7 (CH), 129.9 (CH), 127.1 (CH), 116.9 (CH), 84.2 (C), 77.9 (C), 72.7 (CH), 71.3 (CH), 70.2 (CH), 69.9 (CH), 67.0 (CH), 40.9 (CH_2), 31.8 (CH_2), 25.4 (CH_2), 23.9 (CH_2), 21.5 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M]^+$ Calcd for $C_{27}H_{31}FeNO_4S$ 521.1318; Found 521.1311. The enantioselectivity of the product **4d** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 75:25, 1 mL/min, λ=254 nm)

Racemic sample (**4d)**

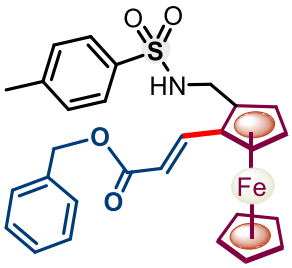


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.961	BB	0.9803	1.76863e4	265.10019	50.6080
2	27.059	MM	1.3587	1.72613e4	211.73032	49.3920

Asymmetric sample (**4d**)

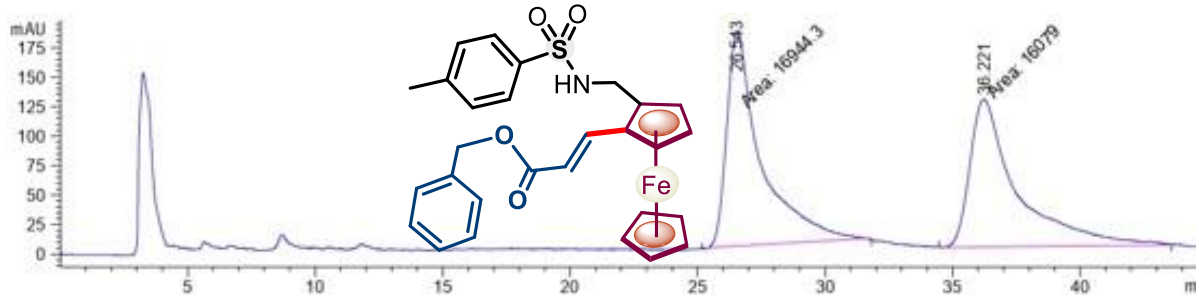


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.130	BB	0.9009	4247.79834	68.17578	95.8662
2	26.015	MM	0.6978	183.16504	4.37457	4.1338



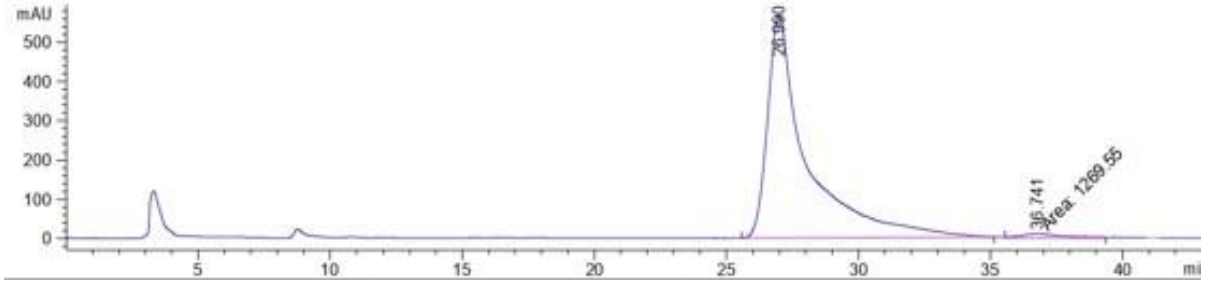
Chiral 1,2 alkenylated ferrocenyl amine 4e was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate;80:20), obtained as an orange yellow solid, mp: 114-115 ºC. Yield: 44 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.53 (d, J = 15.4 Hz, 1H), 7.48 – 7.35 (m, 5H), 7.31 (d, J = 8.0 Hz, 2H), 6.08 (d, J = 15.8 Hz, 1H), 5.24 (s, 2H), 4.62 (t, J = 6.4 Hz, 1H), 4.55 (s, 1H), 4.37 (s, 2H), 4.12 (s, 5H), 4.03 (d, J = 5.6 Hz, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 166.7 (C), 143.7 (C), 143.0 (CH), 136.7 (CH), 136.1 (CH), 129.9 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 127.1 (CH), 115.8 (CH), 84.3 (C), 77.6 (C), 71.5 (CH), 70.3 (CH), 70.0 (CH), 67.1 (CH), 66.2 (CH_2), 40.9 (CH_2), 21.5 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{27}FeNO_4SNa$ 552.0903; Found 552.0886. The enantioselectivity of the product **4e** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm)

Racemic sample (**4e)**

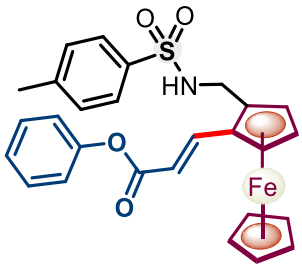


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.543	MM	1.5495	1.69443e4	182.25853	51.3102
2	36.221	MM	2.1393	1.60790e4	125.26550	48.6898

Asymmetric sample (**4e**)

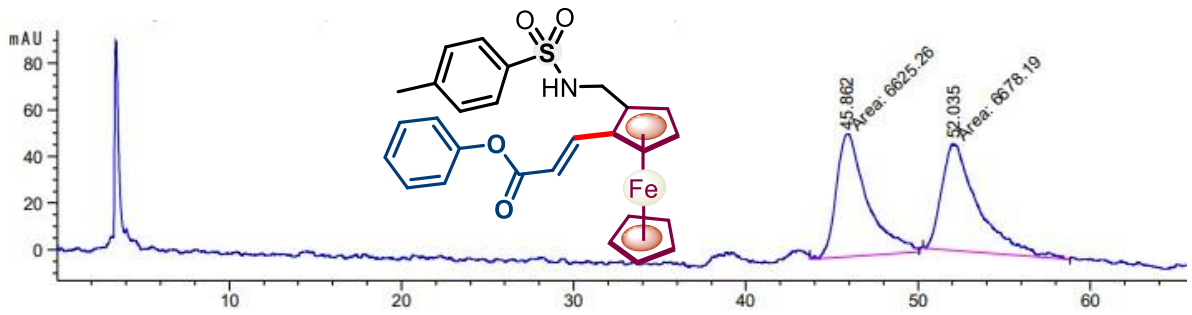


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.990	BB	1.4092	5.84010e4	567.23132	97.8724
2	36.741	MM	1.9674	1269.54712	10.75491	2.1276



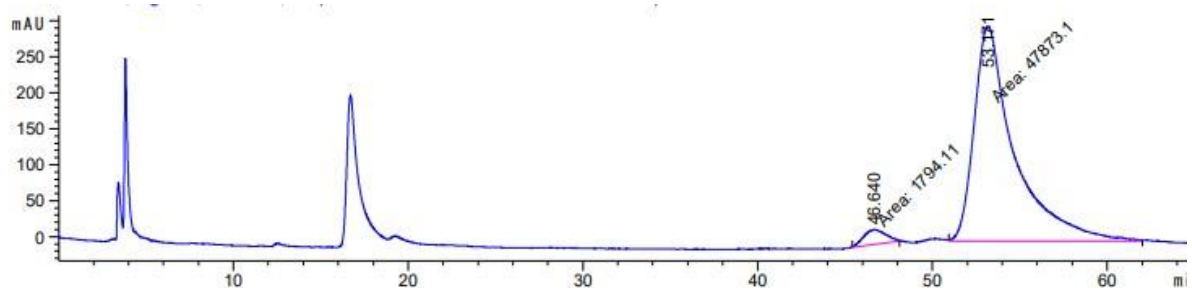
Chiral 1,2 alkenylated ferrocenyl amine 4f was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 111-112 ºC. Yield. 25 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 15.3 Hz, 1H), 7.41 (dt, *J* = 14.9, 8.1 Hz, 5H), 7.34 (d, *J* = 6.3 Hz, 2H), 6.21 (d, *J* = 15.2 Hz, 1H), 4.66 (s, 1H), 4.58 (s, 2H), 4.22 (s, 5H), 4.12 – 3.99 (m, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 171.2 (C), 165.1 (C), 150.9 (C), 144.8 (C), 136.7 (CH), 129.9 (CH), 129.3 (CH), 127.2 (CH), 125.7 (CH), 121.5 (CH), 115.3 (CH), 84.1 (C), 78.3 (C), 73.6 (CH), 72.5 (CH), 70.8 (CH), 67.8 (CH), 46.5 (CH_2), 21.5 (CH_3). HRLCMS (QTOF-ESI) *m/z*: $[M+ Na]^+$ Calcd for $C_{27}H_{25}FeNO_4SNa$ 538.0746 Found 538.0730. The enantioselectivity of the product **4f** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm)

Racemic sample (**4f)**

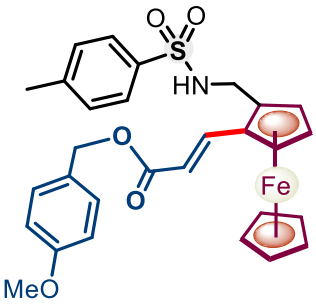


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.862	MM	2.0921	6625.26123	52.78083	49.8011
2	52.035	MM	2.4361	6678.18604	45.68973	50.1989
Totals :				1.33034e4	98.47056	

Asymmetric sample (**4f**)

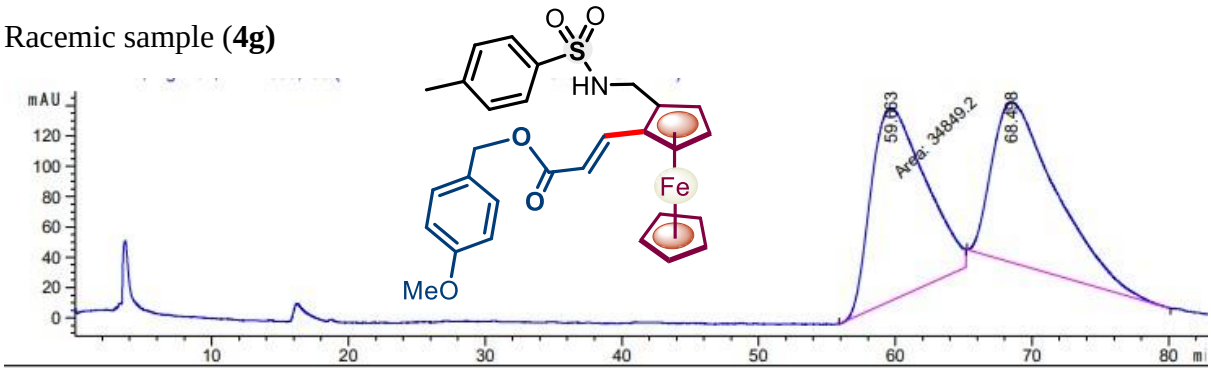


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.640	MM	1.4555	1794.10571	20.54396	3.6123
2	53.171	MM	2.6712	4.78731e4	298.69876	96.3877
Totals :				4.96672e4	319.24272	



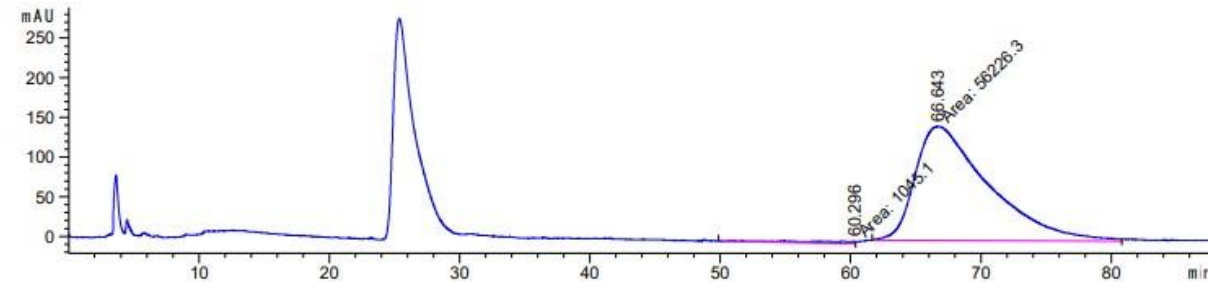
Chiral 1,2 alkenylated ferrocenyl amine 4g was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 85:15), obtained as an orange yellow solid, mp: 110-111 ºC. Yield: 45 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 15.6 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.05 (d, J = 15.9 Hz, 1H), 5.16 (s, 2H), 4.64 (t, J = 6.0 Hz, 1H), 4.53 (s, 1H), 4.36 (s, 2H), 4.11 (s, 5H), 4.02 (d, J = 5.9 Hz, 2H), 3.84 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 166.8 (C), 159.6 (C), 143.6 (C), 142.8 (C), 136.7 (C), 130.2 (CH), 129.8 (CH), 127.1 (CH), 126.4 (CH), 115.9 (CH), 114.0 (CH), 84.3 (C), 77.6 (C), 71.4 (CH), 70.2 (CH), 70.0 (CH), 67.0 (CH), 66.0 (CH_2), 55.3 (CH_3), 40.96 (CH_2), 21.58 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M]^+$ Calcd for $C_{29}H_{29}FeNO_5S$ 559.1116; Found 559.1111. The enantioselectivity of the product **4g** was determined by chiral HPLC analysis on OZ-3 column (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm)

Racemic sample (**4g)**

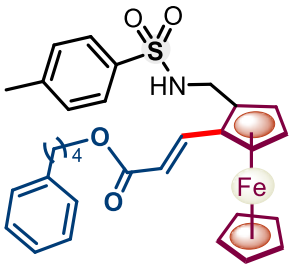


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.663	MM	4.5552	3.48492e4	127.50578	49.9982
2	68.498	BB	3.8528	3.48517e4	105.91933	50.0018
Totals :				6.97010e4	233.42511	

Asymmetric sample (**4g**)

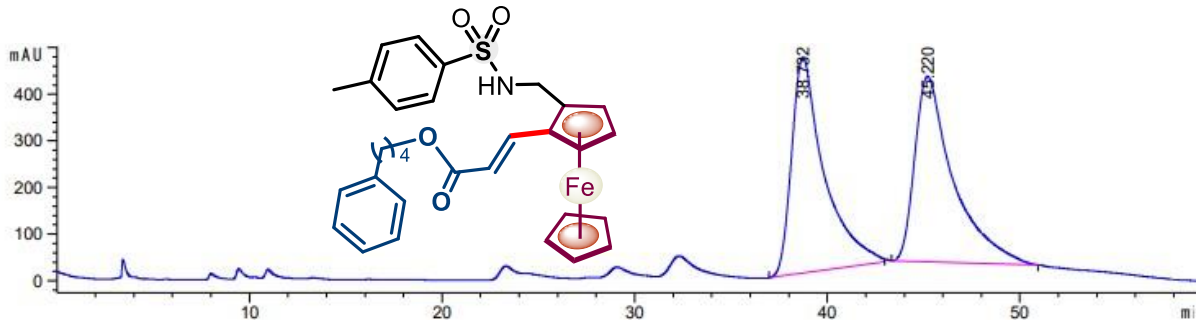


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.296	MM	5.3448	1045.10059	3.25892	1.8248
2	66.643	MM	6.5269	5.62263e4	143.57619	98.1752
Totals :				5.72714e4	146.83510	



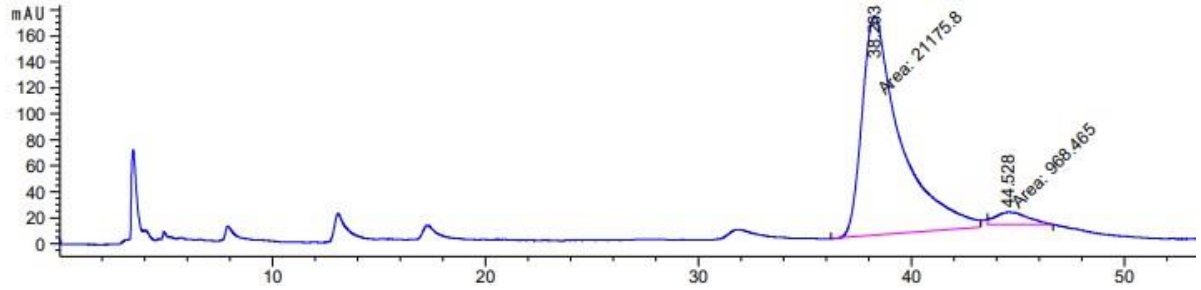
Chiral 1,2 alkenylated ferrocenyl amine 4h was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as an orange yellow solid, mp: 113-114 ºC. Yield: 53 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 15.6 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 4H), 7.22 (d, *J* = 7.5 Hz, 3H), 6.03 (d, *J* = 15.7 Hz, 1H), 4.97 – 4.80 (m, 1H), 4.54 (s, 1H), 4.36 (s, 2H), 4.20 (d, *J* = 5.9 Hz, 2H), 4.09 (d, *J* = 13.0 Hz, 5H), 4.03 (d, *J* = 5.7 Hz, 2H), 2.70 (brs, 2H), 2.45 (s, 3H), 1.76 (brs, 4H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) *δ* 167.0 (C), 143.6 (C), 142.6 (C), 142.1 (C), 136.8 (CH), 129.8 (CH), 128.4 (CH), 128.3 (CH), 127.1 (CH), 125.8 (CH), 116.0 (CH), 84.3 (C), 77.6 (C), 71.4 (CH), 70.2 (CH), 69.9 (CH), 66.9 (CH), 64.3 (CH_2), 40.9 (CH_2), 35.5 (CH_2), 28.3 (CH_2), 27.8 (CH_2), 21.6 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M]^+$ Calcd for $C_{31}H_{33}FeNO_4S$ 571.1475; Found 571.1478. The enantioselectivity of the product **4h** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm)

Racemic sample (**4h)**

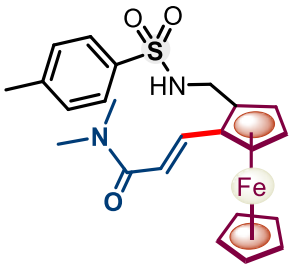


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.732	BV	1.6878	5.43959e4	462.60364	49.6174
2	45.220	BB	1.9643	5.52349e4	397.71985	50.3826
Totals :				1.09631e5	860.32349	

Asymmetric sample (**4h**)

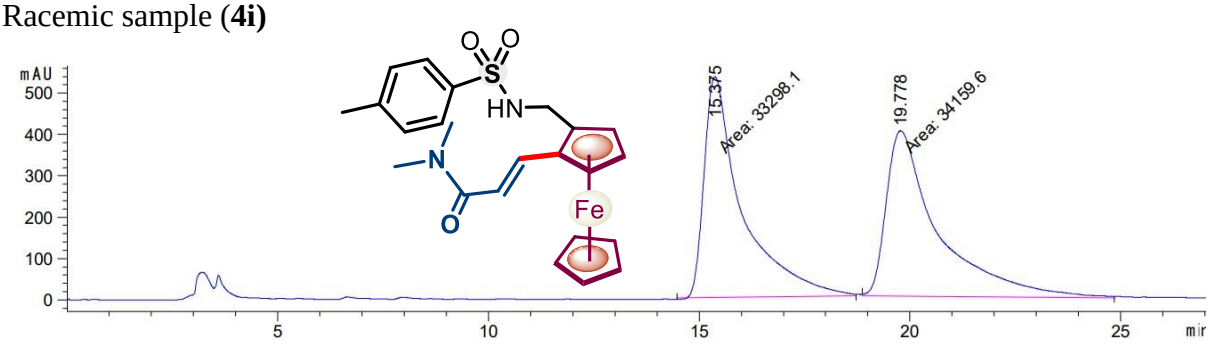


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.263	MM	2.0960	2.11758e4	168.38132	95.6266
2	44.528	MM	1.7507	968.46454	9.21972	4.3734
Totals :				2.21443e4	177.60103	



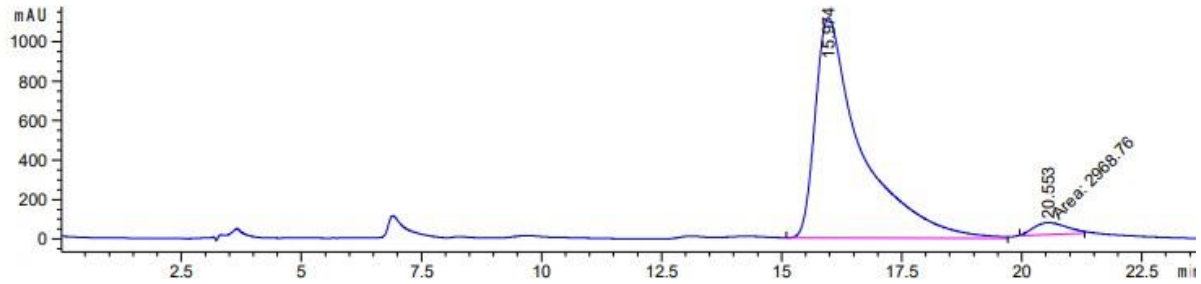
Chiral 1,2 alkenylated ferrocenyl amine 4i was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 60:40), obtained as an orange yellow solid, mp: 120-121 ºC. Yield: 38 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 15.0 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 15.0 Hz, 1H), 4.88 (t, *J* = 6.4 Hz, 1H), 4.54 (s, 1H), 4.35 – 4.27 (m, 2H), 4.10 (s, 5H), 4.08 (d, *J* = 7.0 Hz, 1H), 3.96 (dd, *J* = 13.9, 5.6 Hz, 1H), 3.14 (s, 3H), 3.05 (s, 3H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.7 (C), 143.5 (C), 139.7 (C), 136.8 (CH), 129.8 (CH), 127.1 (CH), 115.6 (CH), 83.3 (C), 79.3 (C), 71.3 (CH), 70.0 (CH), 69.3 (CH), 67.7 (CH), 41.4 (CH_2), 37.4 (CH_3), 35.9 (CH_3), 21.59 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M]^+$ Calcd for $C_{23}H_{26}FeN_2O_3S$ 466.1008; Found 466.0994. The enantioselectivity of the product **4i** was determined by chiral HPLC analysis on AD-3 column (hexane: isopropanol = 65:35, 1 mL/min, λ=254 nm)

Racemic sample (**4i)**

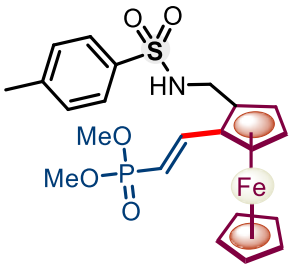


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.375	MM	1.0397	3.32981e4	533.80139	49.3615
2	19.778	MM	1.4253	3.41596e4	399.44928	50.6385

Asymmetric sample (**4i**)

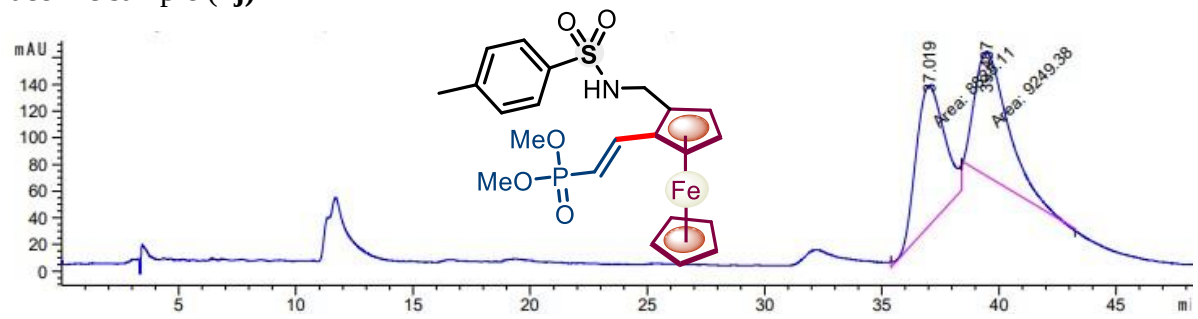


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.974	BV	0.9238	7.40190e4	1116.06067	96.1439
2	20.553	MM	0.8061	2968.76221	61.38442	3.8561
Totals :				7.69878e4	1177.44509	



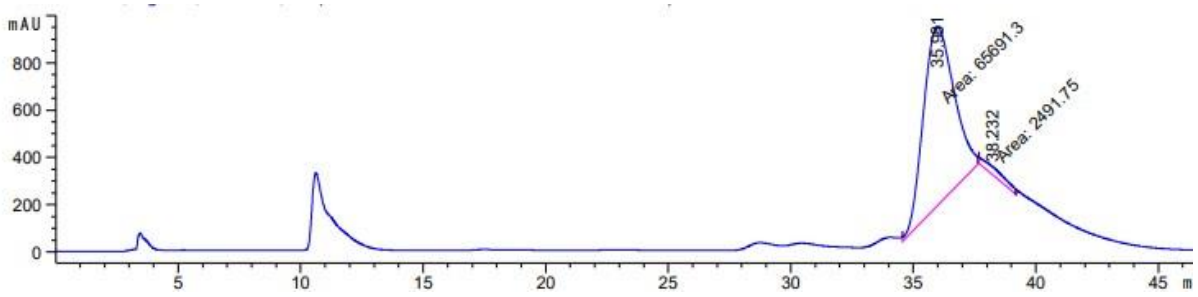
Chiral 1,2 alkenylated ferrocenyl amine 4j was purified on silica gel mesh (230-400) in (hexanes: ethylacetate; 50:50), obtained as an orange yellow solid, mp: 120-121 ºC. Yield: 28 mg (40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 6.1 Hz, 2H), 7.33 (d, J = 7.0 Hz, 2H), 6.46 – 6.09 (m, 1H), 5.80 (brs, 1H), 4.91 (s, 1H), 4.76 (d, J = 36.9 Hz, 1H), 4.52 (d, J = 30.1 Hz, 2H), 4.30 (s, 5H), 4.14 (d, J = 7.2 Hz, 1H), 4.02 – 3.95 (brs, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.6 (C), 143.53 (CH), 136.98 (C), 129.8 (CH), 127.11 (CH), 109.7 (d, J = 194.0 Hz CH), 84.2 (C), 78.2 (C), 71.7 (CH), 70.3 (CH), 69.9 (CH), 67.1 (CH), 60.4 (CH_3), 52.4 (CH_3), 40.9 (CH_2), 21.5 (CH_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.9. HRLCMS (ESI-QTOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{27}FeNO_5PS$ 504.0692; Found 504.0712. The enantioselectivity of the product **4j** was determined by chiral HPLC analysis on AD-H column (hexane: isopropanol = 80:20, 1 mL/min, λ=254 nm)

Racemic sample (**4j)**

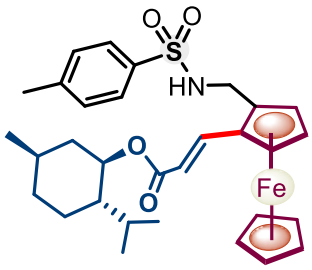


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.019	MM	1.4009	8828.11230	105.03038	48.8348
2	39.487	MM	1.6557	9249.37793	93.10825	51.1652
Totals :				1.80775e4	198.13863	

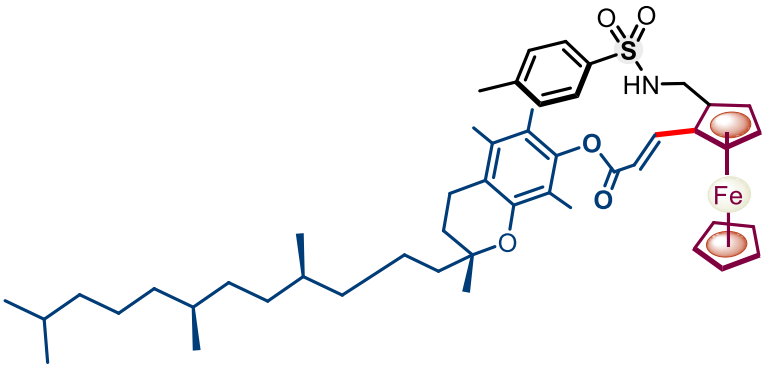
Asymmetric sample (**4j**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.981	MM	1.4442	6.56913e4	758.10669	96.3455
2	38.232	MM	1.2459	2491.74805	33.33333	3.6545
Totals :				6.81830e4	791.44002	

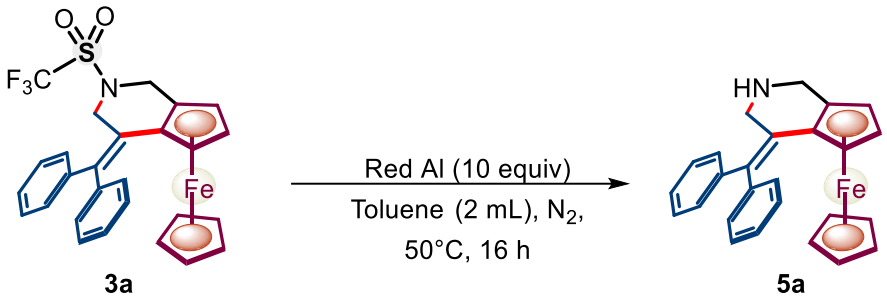


Chiral 1,2 alkenylated ferrocenyl amine 4m was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as inseprable mixture with **1d** an orange yellow solid, mp: 110-111 ºC. Yield: 47 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 12.0 Hz, 2H), 7.47 (d, J = 15.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 6.01 (d, J = 15.9 Hz, 1H), 4.80 (td, J = 10.5, 3.5 Hz, 1H), 4.71 (t, J = 5.5 Hz, 1H), 4.54 (s, 1H), 4.35 (s, 2H), 4.12 (s, 5H), 4.03 (d, J = 5.8 Hz, 2H), 2.46 (s, 3H), 2.06 (t, J = 6.3 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.73 (d, J = 11.8 Hz, 2H), 1.60 – 1.42 (m, 2H), 0.95 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 166.6 (C), 143.6 (C), 142.3 (C), 136.8 (CH), 129.8 (CH), 127.1 (CH), 116.7 (CH), 84.2 (C), 77.9 (C), 74.11 (CH), 71.30 (CH), 70.25 (CH), 69.88 (CH), 67.13 (CH), 47.15 (CH_2), 41.2 (CH_3), 41.0 (CH), 34.3 (CH), 31.4 (CH_2), 26.4 (CH_2), 23.6 (CH), 22.1 (CH_2), 21.6 (CH_3), 20.8 (CH_3), 16.5 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M]^+$ Calcd for $C_{31}H_{39}FeNO_4S$ 577.1944; Found 577.1946.



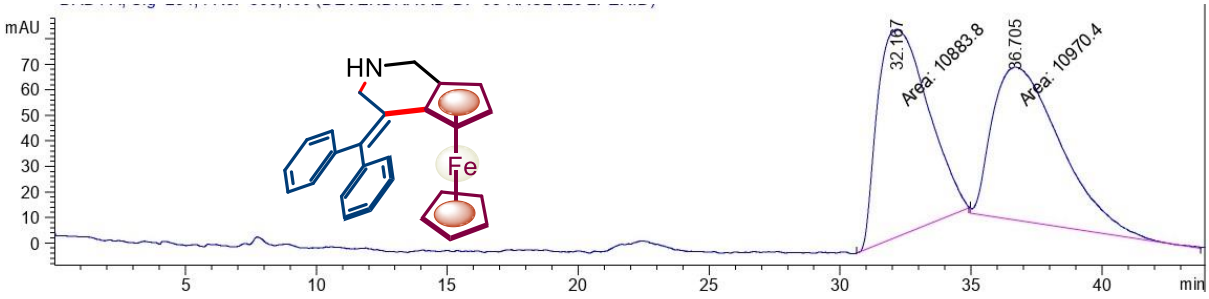
Ferrocene fused tetrahydropyridine 4n was purified on silica gel (mesh 230-400) in (hexanes: ethyl acetate; 80:20), obtained as inseprable mixture with **1d** as an orange yellow solid, mp: 125-126 ºC. Yield: 57 mg (48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 2H), 7.68 (d, J = 15.0 Hz, 1H), 7.35 (d, J = 7.9 Hz, 2H), 6.27 (d, J = 15.6 Hz, 1H), 4.65 (s, 1H), 4.51 (s, 1H), 4.44 (s, 2H), 4.16 (s, 5H), 4.05 (d, J = 5.2 Hz, 2H), 2.64 (t, J = 6.5 Hz, 2H), 2.47 (s, 1H), 2.39 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.94 – 1.74 (m, 3H), 1.58 – 1.49 (m, 4H), 1.49 – 1.36 (m, 5H), 1.34 – 1.29 (m, 2H), 1.22 – 1.13 (m, 4H), 1.08 (dd, J = 11.0, 5.5 Hz, 3H), 0.93 – 0.83 (m, 14H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 165.4 (C), 149.4 (C), 144.1 (C), 143.7 (C), 143.5 (C), 140.4 (C), 136.8 (C), 136.6 (C), 129.7 (CH), 127.1 (CH), 123.0 (CH), 117.4 (CH), 115.1 (CH), 84.4 (C), 77.4 (C), 75.0 (CH), 71.8 (CH), 70.4 (CH), 70.3 (CH), 67.2 (C), 60.4 (CH_2), 42.5 (CH_2), 40.9 (CH_2), 39.4 (CH_2), 37.5 (CH_2), 37.4 (CH_2), 37.3 (CH), 32.8 (CH), 28.0 (CH), 24.8 (CH_2), 24.4 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 21.6 (CH_2), 21.4 (CH_2), 21.0 (CH_2), 20.6 (CH_3), 19.8 (CH_3), 19.7 (CH_3), 19.6 (CH_3), 14.2 (CH_3), 13.0 (CH_3), 12.2 (CH_3), 11.9 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{50}H_{69}FeNO_5SNa$ 874.4140; Found 874.4139.

Scheme S4. Removal of protecting group



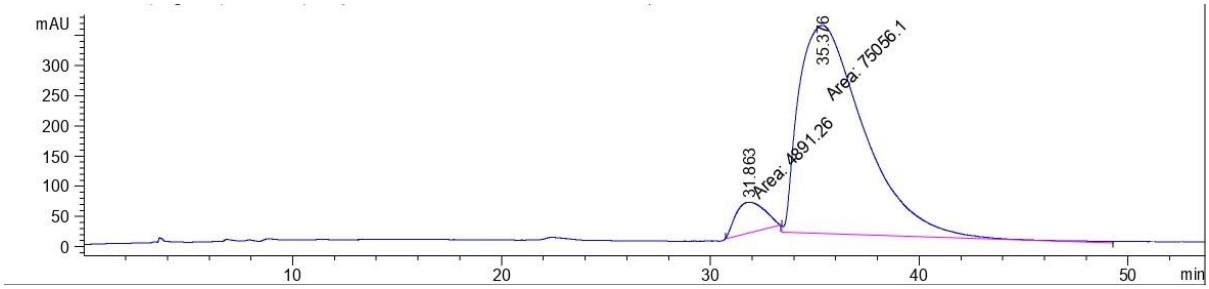
To a solution of **3a** (0.12 mmol, 1 equiv) in Toluene (2 mL, 0.06 M) under a nitrogen atmosphere, Red Al (1.2 mmol, 10 equiv) was slowly added at 0 ºC. After the completion of the addition, the reaction was allowed to be stirred for 16 h before being quenched with NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic phase was washed with brine and then dried over Na_2SO_4. Evaporation and column chromatography on basic silica gel (mesh 100-200) with the solvent mixture of hexanes: ethyl acetate (20: 80) afforded **5a**. Orange yellow solid, mp: 110 ºC-111 ºC. Yield: 45mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 7H), 7.28 – 7.23 (m, 1H), 7.19 (d, J = 7.6 Hz, 2H), 4.25 (s, 1H), 4.11 (s, 5H), 4.04 (d, J = 16.4 Hz, 1H), 3.98 (d, J = 6.4 Hz, 1H), 3.74 (d, J = 15.5 Hz, 1H), 3.65 (d, J = 14.9 Hz, 2H), 3.11 (s, 1H), 2.04 (s, 1H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 143.4 (C), 142.0 (C), 135.9 (CH), 130.8 (CH), 129.6 (C), 129.3 (C), 128.6 (CH), 128.2 (CH), 127.0 (CH), 126.8 (CH), 85.2 (C), 79.1 (C), 70.2 (CH), 67.5 (CH), 65.9 (CH), 65.3 (CH), 48.5 (CH_2), 45.3 (CH_2). HRLCMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{24}FeN$ 406.1253; Found 406.1237. The enantioselectivity of product **5a** was determined by chiral HPLC analysis on IE-3 column (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**5a)**



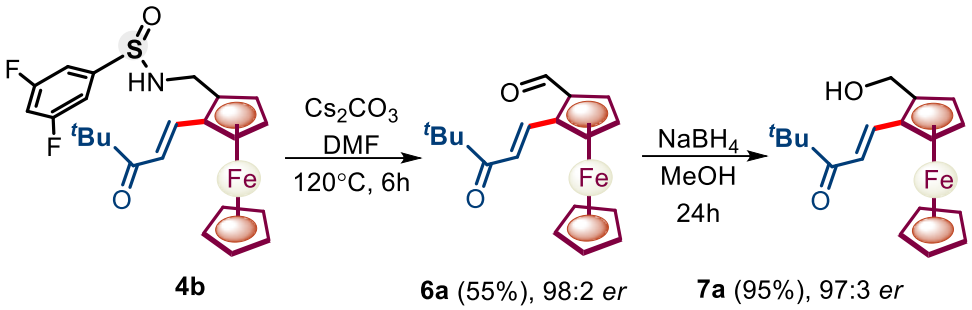
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.167	MM	2.2289	1.08838e4	81.38326	49.8019
2	36.705	MM	3.0459	1.09704e4	60.02793	50.1981

Asymmetric sample (**5a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.863	MM	1.6110	4891.25830	50.60256	6.1181
2	35.376	MM	3.6289	7.50561e4	344.71545	93.8819

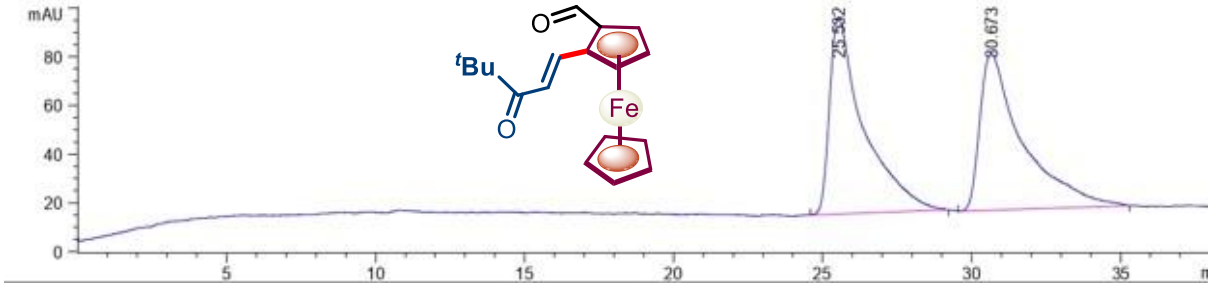
Scheme S5. Oxidation of Amine and Aldehyde Reduction



4b **6a** (55%), 98:2 *er* **7a** (95%), 97:3 *er*

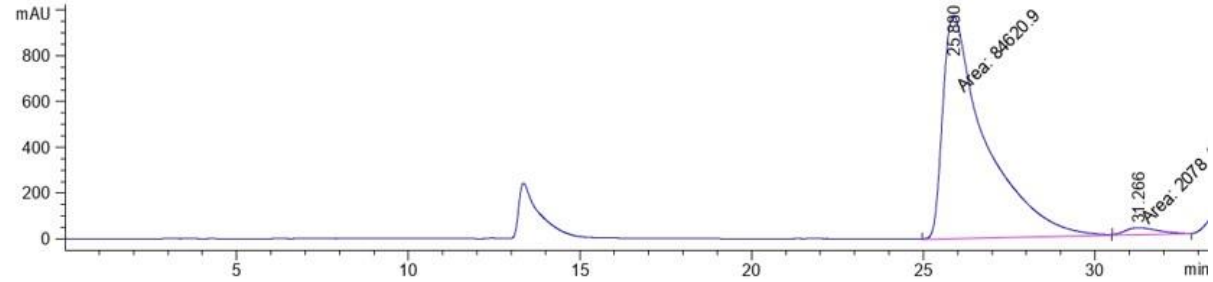
2-Alkenylated ferrocenyl amine **4b** (0.12 mmol, 1 equiv) and Cs_2CO_3 (0.24 mmol, 2 equiv) were dissolved in DMF (2 mL, 0.06 M) solvent under open air atmosphere. The reaction was stirred at 110ºC for 6 h. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with brine and then dried over Na_2SO_4. Evaporation and column chromatography on basic silica gel (mesh 100-200) with the solvent mixture of hexanes: ethyl acetate (20: 80) afforded **6a**. Orange red solid, mp: 109 ºC-110 ºC. Yield: 24mg (55%). ^{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 the product **6a** was determined by chiral HPLC analysis on AD-3 (hexane: isopropanol = 98:2, 1 mL/min, λ=254 nm).

Racemic sample (**6a)**



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

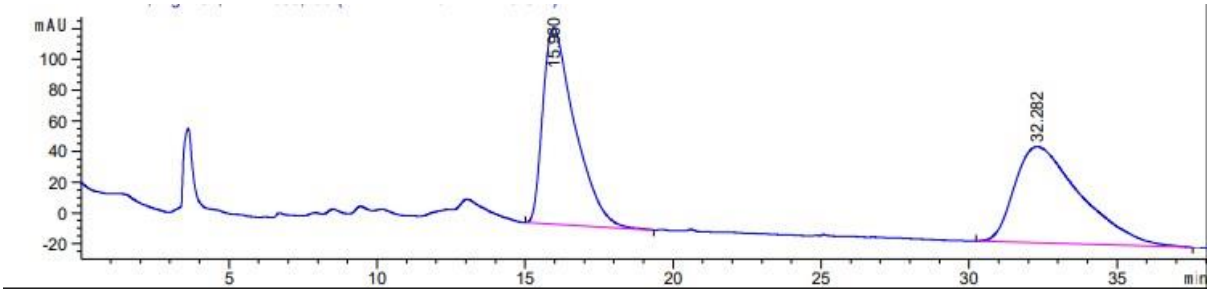
Asymmetric sample (**6a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.880	MM	1.4469	8.46209e4	974.71625	97.6027
2	31.266	MM	1.1246	2078.46118	30.80349	2.3973

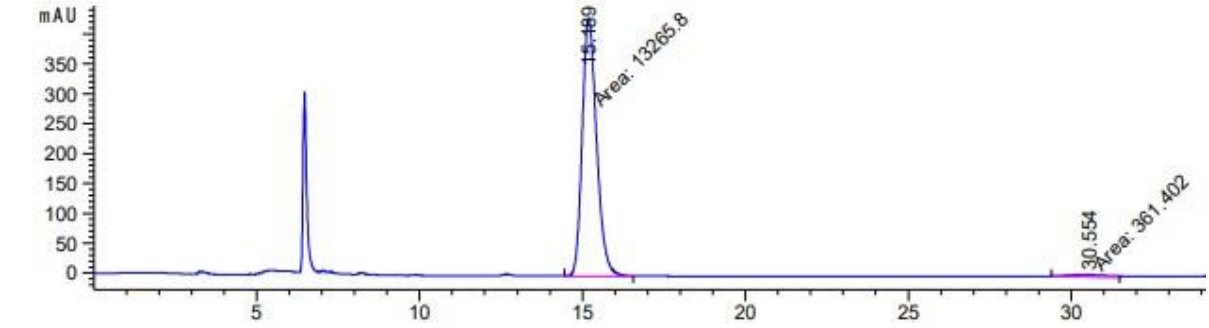
Further compound **6a** was reduced with $NaBH_4$ in MeOH solvent for 24 h to isolated compound **7a** before being quenched with 1M NaOH solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with brine and then dried over Na_2SO_4. Evaporation and column chromatography on basic silica gel (mesh 100-200) with the solvent mixture of hexanes: ethyl acetate (30: 70) afforded an orange yellow solid **7a**, mp: 119 ºC-120 ºC. Yield: 32mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 12.7 Hz, 1H), 6.08 (d, J = 15.4 Hz, 1H), 4.60 (d, J = 4.0 Hz, 2H), 4.50 (brs, 2H), 4.42 (s, 1H), 4.18 (s, 5H), 2.05 (brs, 1H), 1.55 (s, 9H). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 166.6 (C), 141.9 (CH), 118.1 (CH), 88.0 (C), 80.2 (C), 78.4 (C), 71.6 (CH), 70.0 (CH), 69.7 (CH), 67.6 (CH), 59.1 (CH_2), 28.2 (CH_3). HRLCMS (ESI-QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{22}FeO_3Na$ 365.0811; Found 365.0825. Enantioselectivity of the product **7a** was determined by chiral HPLC analysis on OZ-3 (hexane: isopropanol = 70:30, 1 mL/min, λ=254 nm).

Racemic sample (**7a)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.960	BB	1.0956	9627.60547	127.98519	49.8837
2	32.282	BB	1.8876	9672.49707	62.42896	50.1163
Totals :				1.93001e4	190.41415	

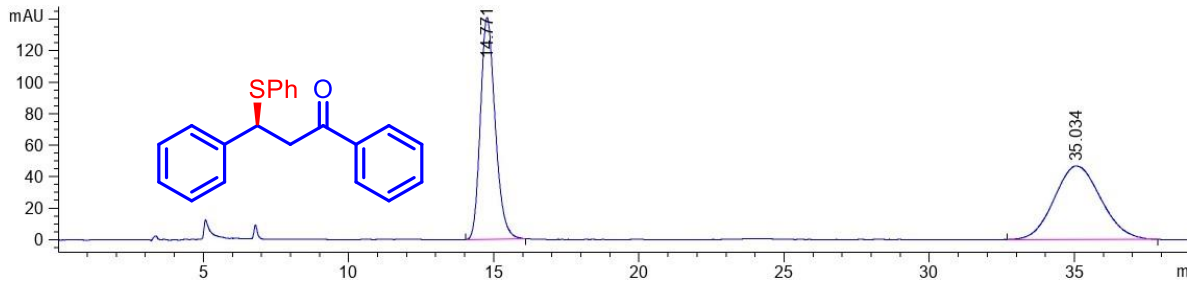
Asymmetric sample (**7a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.189	MM	0.5123	1.32658e4	431.53833	97.3479
2	30.554	MM	1.5251	361.40231	3.94949	2.6521
Totals :				1.36272e4	435.48782	

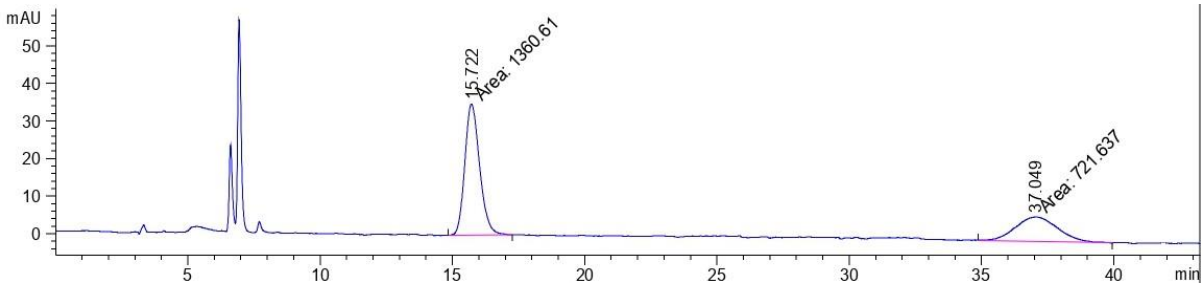
Scheme S6. Asymmetric thia-Michael reaction using post-derivatized ferrocene fused tetrahydropyridine **5a**.[5]

Racemic sample (**5a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.771	BB	0.5434	4992.38965	140.87692	48.9066
2	35.034	BB	1.4294	5215.62061	46.68568	51.0934

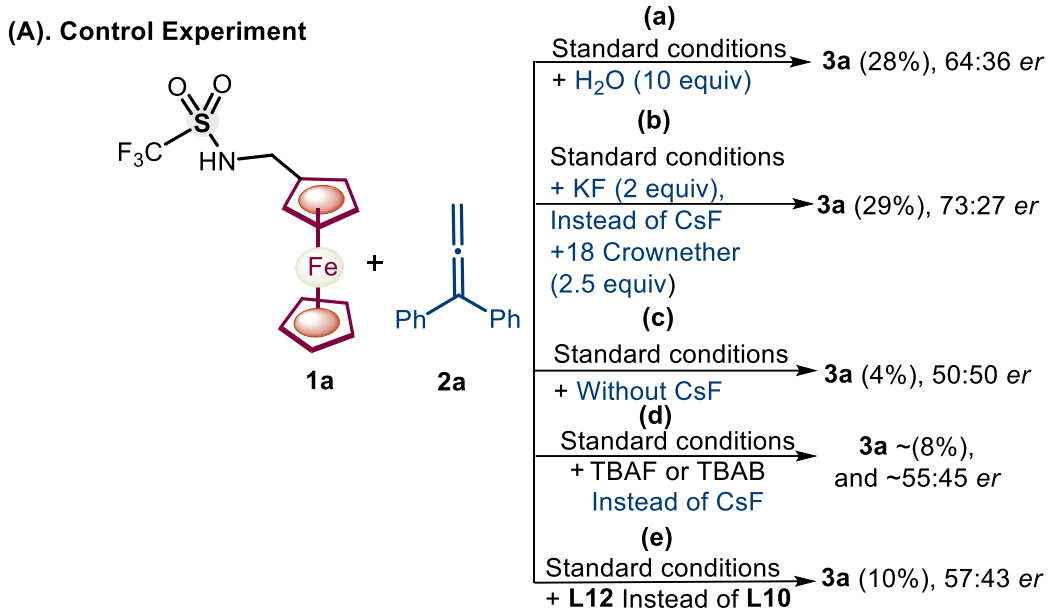
Asymmetric sample (**5a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.722	MM	0.6497	1360.60925	34.90311	65.3433
2	37.049	MM	1.8342	721.63727	6.55738	34.6567

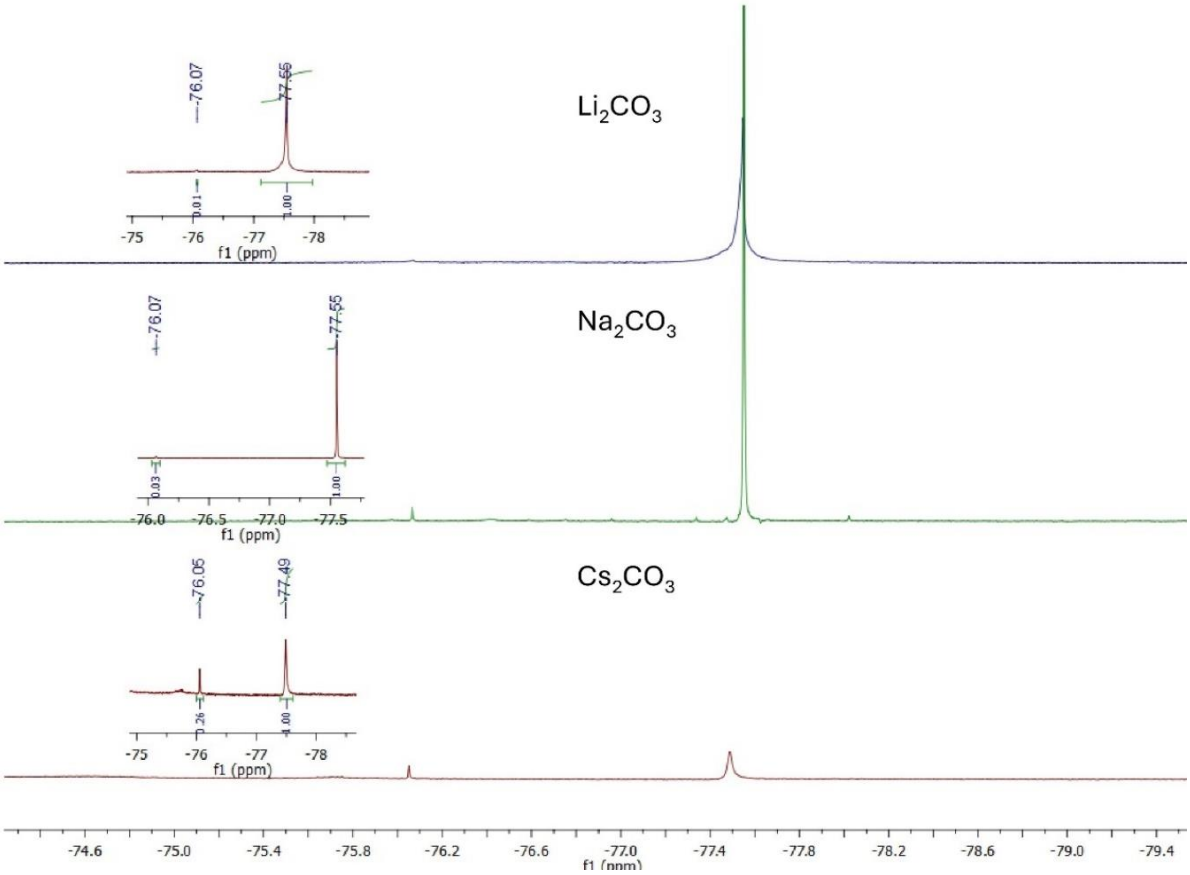
Mechanistic Investigation

Control Experiment 1: Removal of cation from the catalytic cycle



In a Schlenk tube, $Pd(OAc)_2$ (2.5 mg, 0.012 mmol, 8 mol%), NOBINAc (14 mg, 0.04 mmol, 28 mol%), CuO (12 mg, 0.14 mmol, 1 equiv.), CsF (44 mg, 0.29 mmol, 2 equiv.), and *N*-Methylferrocenyl 1,1,1-trifluoromethanesulfonamide **1a** (50 mg, 0.14 mmol, 1 equiv.) were dissolved in dry THF (1.5 mL) under inert atmosphere and was stirred for 10 min. After pre-stirring, 10 equiv of H_2O or 2.5 equiv of 18 crown ether and allene **2a** (55 µL, 0.29 mmol, 2 equiv.) was added to it. The tube was sealed with a rubber septum, maintaining a dry air atmosphere in the flask with a balloon. The reaction was heated at 75° C, stirred for 18 h, and then cooled to room temperature. The crude reaction mixture was passed through a celite pad, then evaporation and column chromatography on silica gel (mesh 230-400) in (hexane: ethyl acetate; 95:5) afforded **3a**.

Control Experiment 2: Stoichiometric ^{19}F NMR experiment with different cation sources. In NMR tube $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 1 equiv.), NOBINAc (9.8 mg, 0.03 mmol, 1 equiv.), M_2CO_3 (0.045 mmol, 1.5 equiv.), and *N*-Methylferrocenyl 1,1,1-trifluoromethanesulfonamide **1a** (10 mg, 0.03 mmol, 1 equiv.) was added in (0.8 mL) $CDCl_3$. Further heated for 60 min, then submitted for ^{19}F NMR. A new peak at -76.07 ppm corresponding to CF_3 of **1a** emerges and increases to a maximum with the increase of the size of the cations (Li, Na, and Cs), which could be attributed to initial C-H activated species.

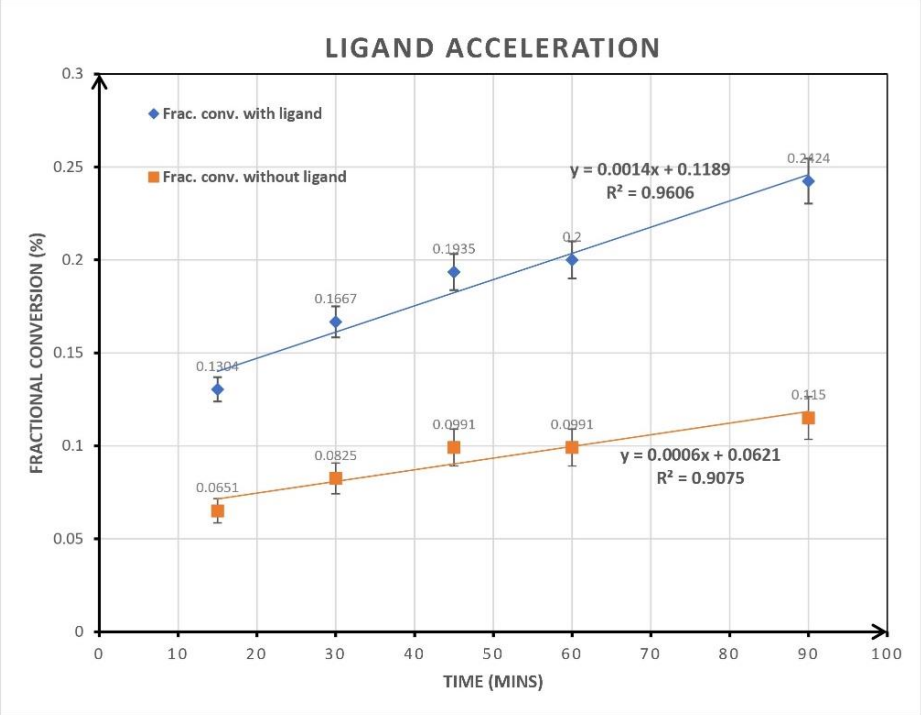


Control Experiment 3: Ligand acceleration experiment.

In a Schlenk tube, $Pd(OAc)_2$ (2.5 mg, 0.012 mmol, 8 mol%), NOBINAc (14 mg, 0.04 mmol, 28 mol%), CuO (11.5 mg, 0.14 mmol, 1 equiv.), CsF (44 mg, 0.29 mmol, 2 equiv.), and *N*-Methylferrocenyl 1,1,1-trifluoromethanesulfonamide **1a** (50 mg, 0.14 mmol, 1 equiv.) were mixed in dry THF (1.5 mL) and without ligand stirred for 10 min under dry air atmosphere. After pre-stirring of 10 min, allene **2a** (55 μL, 0.29 mmol, 2 equiv.) was added to it. The tube was sealed with a rubber septum, maintaining the dry air atmosphere in the flask with a balloon, and further reaction mixture was heated at 75 ºC. Next, after a regular interval of 15 min, a 250 μL reaction aliquot was pumped out, and then the crude reaction mixture was passed through a celite pad. After the evaporation of the solvent, the crude sample was submitted for ^{19}F NMR.

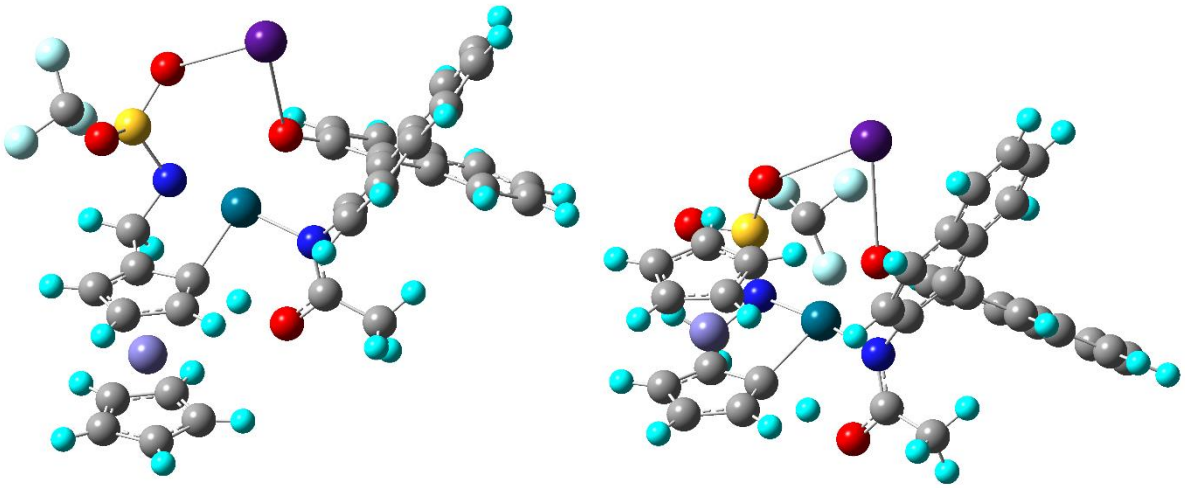
Ligand Acceleration experiment

S. NO>	Time (Mins)	Fractional Conversion (19F-NMR) with NOBINAc Ligand	Fractional Conversion (19F-NMR) without NOBINAc ligand
1	15	0.1304	0.0651
2	30	0.1667	0.0825
3	45	0.1935	0.0991
4	60	0.2000	0.0991
5	90	0.2424	0.115



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 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 10.45 kcal/mol.



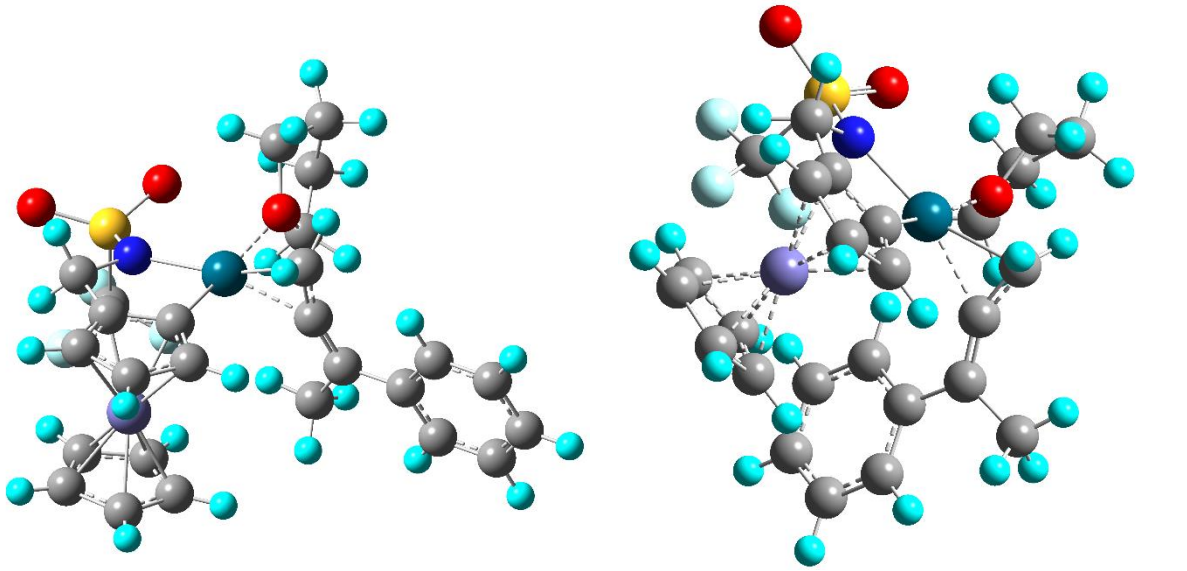
Favorable TS I **Unfavorable TS II**

Figure S5. Optimized structure of favorable and unfavorable transition states

Energy Data

Structure	Electronic and Thermal Correction to G_{solv}	ΔG_{solv}
TS I	-2300.642230	0.00 kcal/mol
TS II	-2300.625582	+10.45 kcal/mol

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



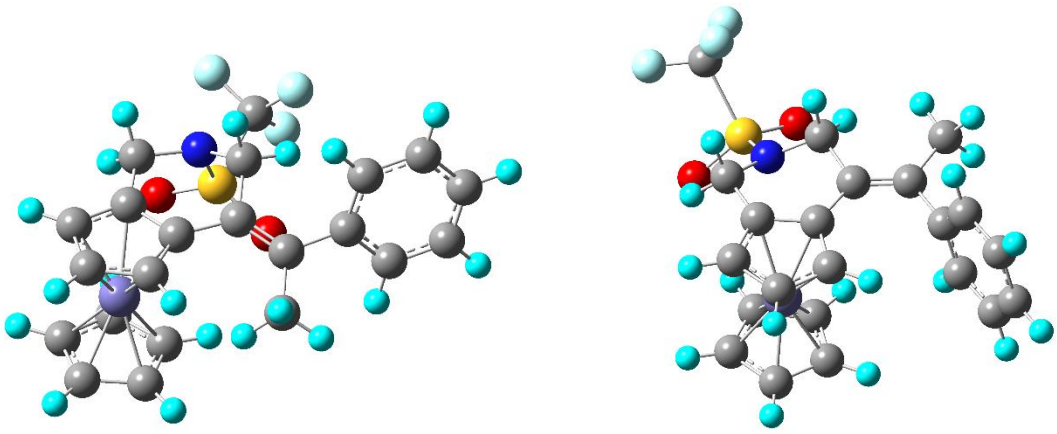
Intermediate **IIIA** (having *Z*-configuration) Intermediate **IIIB** (having *E*-configuration)

Figure S6. Optimized structure of Intermediate **III** having *Z*- and *E*-configurations

Energy Data

Structure	Electronic and Thermal Correction to G_{solv}	ΔG_{solv}
Intermediate IIIA	-1847.021831	0.00 kcal/mol
Intermediate IIIB	-1847.016332	+3.45 kcal/mol

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



3f (having *Z*-configuration) **3f** (having *E*-configuration)

Figure S7. Optimized structure of **3f** having *Z*- and *E*-configurations

Energy Data

Structure	Electronic and Thermal Correction to G_{solv}	ΔG_{solv}
***Z*-3f**	-1487.952045	0.00 kcal/mol
***E*-3f**	-1487.949645	+1.51 kcal/mol

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

Molecular Orbital Picture:

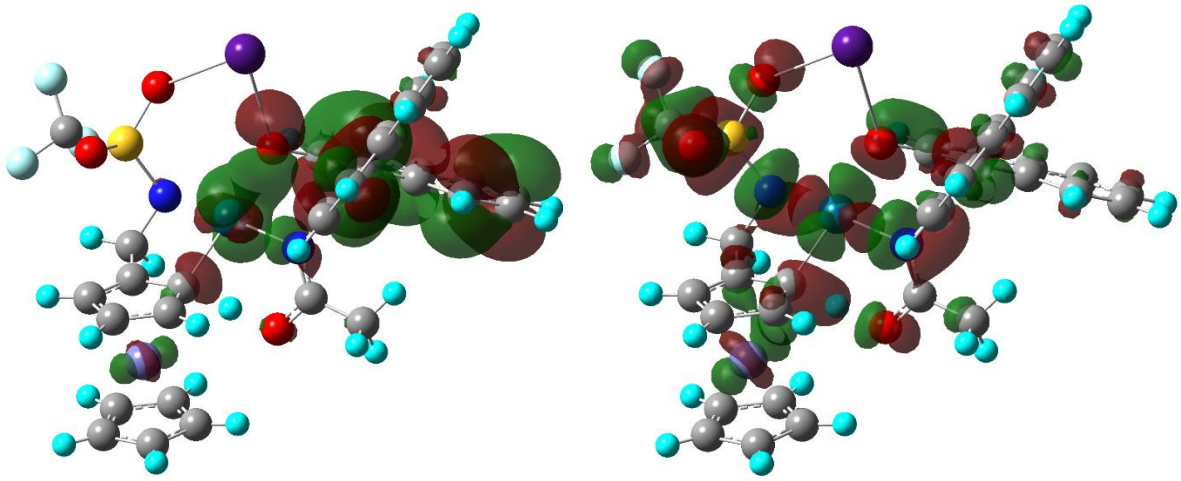


Figure S8. Pictorial view of HOMO (left) and LUMO (right) of favorable **TS I**

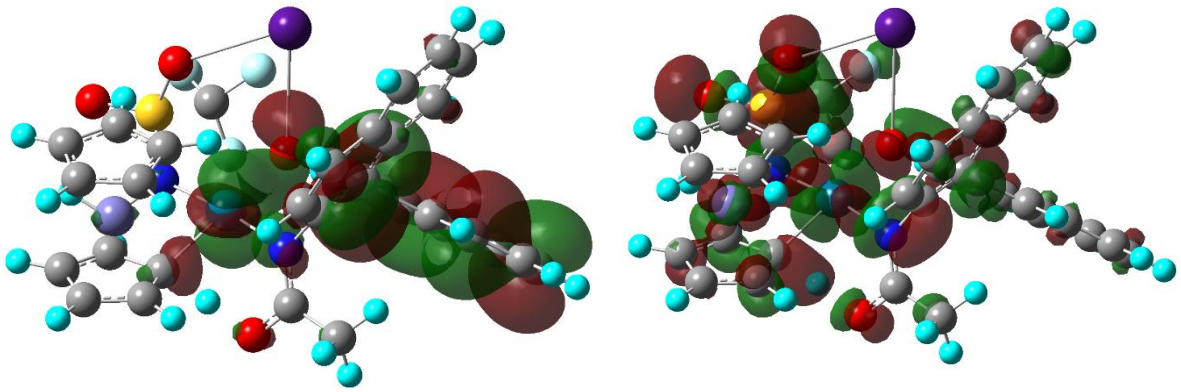


Figure S9. Pictorial view of HOMO (left) and LUMO (right) of unfavorable **TS II**

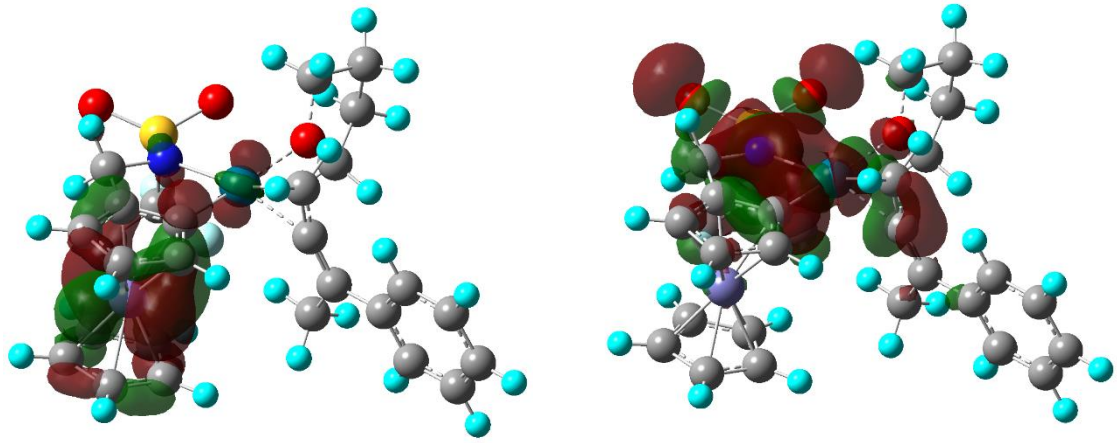


Figure S10. Pictorial view of HOMO (left) and LUMO (right) of intermediate **IIIA**

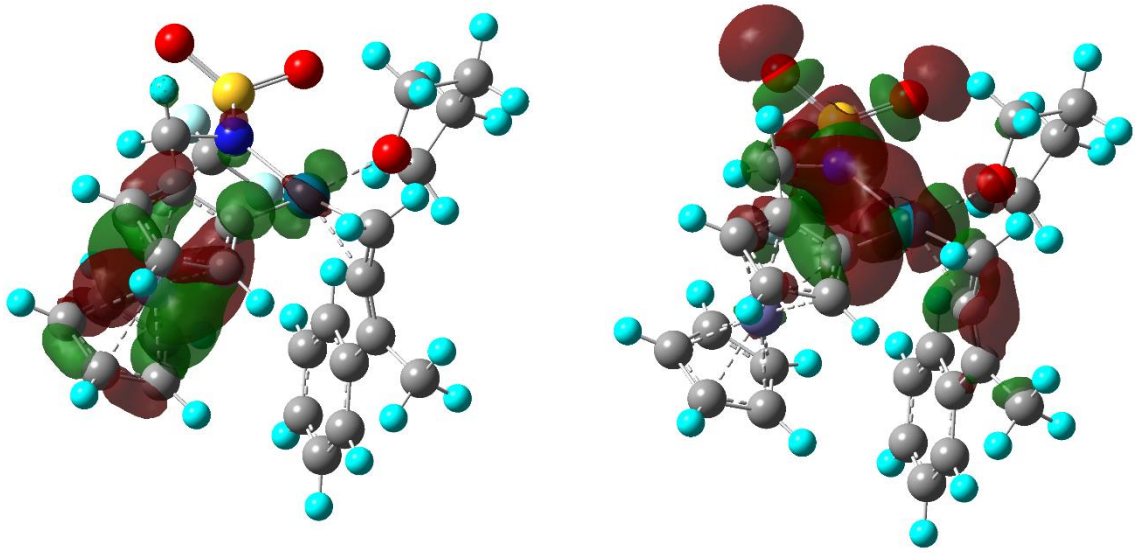


Figure S11. Pictorial view of HOMO (left) and LUMO (right) of intermediate **IIIB**

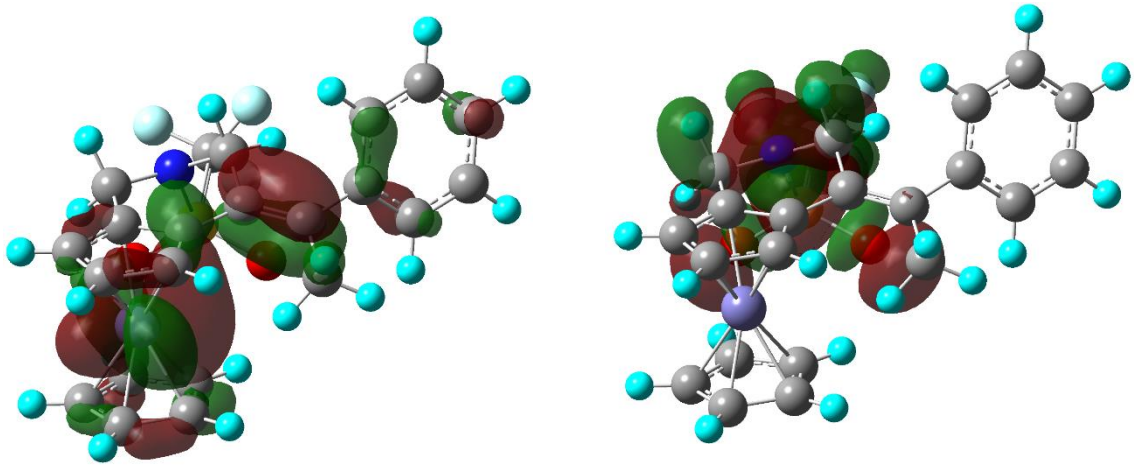


Figure S12. Pictorial view of HOMO (left) and LUMO (right) of ***Z*-3f**

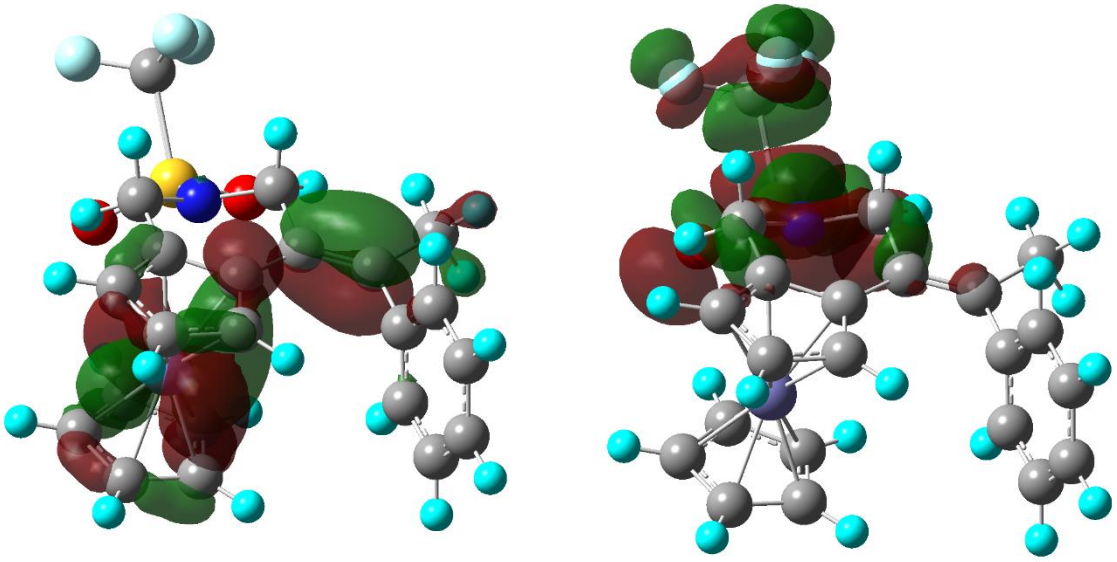


Figure S13. Pictorial view of HOMO (left) and LUMO (right) of ***E*-3f**

Co-ordinates of Optimized Structures

Favourable TS I

Electronic + Thermal Free Energies: -2300.642230

Correction to Gibb's free energy: 0.442038

Zero-point correction: 0.524528

Imaginary vibration frequency: 1 (associated imaginary frequency *i*1194.80 cm^{-1})

Symbol	Coordinates (Å)		
	X	Y	Z
Fe	-4.265047	2.028064	-0.686603
C	-5.079536	3.932474	-1.188275
C	-4.083269	0.716786	-2.376747
C	-4.045281	4.077343	-0.195105
C	-6.112616	3.084834	-0.641393
C	-4.440711	3.321308	0.974158
C	-5.721769	2.715947	0.698221
H	-5.070950	4.363153	-2.180155
H	-4.644861	0.817096	-3.296013
H	-3.112254	4.607561	-0.312518

H	-7.017910	2.781889	-1.148952
H	-3.872687	3.223380	1.888660
H	-6.282309	2.080567	1.370129
S	-1.946794	-2.866145	0.364482
O	-0.548318	-3.648235	0.687695
O	-2.554965	-3.137380	-1.134845
C	-4.502381	-0.028314	-1.213017
H	-5.410791	-0.608412	-1.121309
C	-3.498452	0.137025	-0.204466
C	-3.277906	-3.875807	1.551552
C	-3.297133	-0.572934	1.098476
H	-4.097648	-1.283273	1.330144
H	-3.226270	0.125825	1.941137
F	-4.572052	-3.781340	1.049750
F	-3.270907	-3.392710	2.853665
F	-2.923225	-5.214130	1.581281
N	-1.909260	-1.216676	1.100749
C	-2.409989	0.966889	-0.731947
H	-1.763469	2.036446	-0.168241
C	1.932707	-0.020601	1.593877
C	2.862113	0.851869	0.987643
C	1.854731	-0.090099	3.027647
C	3.662534	1.726273	1.803748
C	2.652605	0.709529	3.826764
H	1.146289	-0.792754	3.459660
C	4.556121	2.703688	1.248038
C	3.563453	1.648072	3.244001
H	2.585362	0.644556	4.911020
C	5.311770	3.537894	2.064130
H	4.636524	2.794496	0.168848

C	4.360924	2.511792	4.057377
C	5.222875	3.441129	3.485942
H	5.977332	4.273244	1.618003
H	4.275609	2.434208	5.139598
H	5.823040	4.096385	4.111953
C	2.947686	0.862983	-0.509614
C	4.130278	0.410274	-1.207170
C	1.845622	1.285105	-1.266157
C	5.267196	-0.118672	-0.510214
C	4.183623	0.467057	-2.652096
C	1.900319	1.330151	-2.695305
C	6.394035	-0.553070	-1.196953
H	5.236365	-0.183037	0.572529
C	5.363954	0.022664	-3.329877
C	3.047003	0.946568	-3.373869
H	1.020564	1.667409	-3.236843
C	6.449930	-0.476065	-2.621974
H	7.242724	-0.953992	-0.648508
H	5.393310	0.076841	-4.416083
H	3.086742	0.992609	-4.459725
H	7.340931	-0.812440	-3.145642
N	0.601216	1.619939	-0.633552
C	0.182571	2.870501	-0.458663
Pd	-0.607700	0.103074	0.098977
O	-1.038406	3.096083	-0.005303
C	1.032803	4.082527	-0.771352
H	0.779504	4.464738	-1.768751
H	0.808717	4.869805	-0.045751
H	2.100243	3.852428	-0.748415
O	1.115778	-0.831468	0.846224

Cs	2.052272	-3.235204	-0.870806
C	-2.809848	1.315606	-2.094773
H	-2.251471	1.949158	-2.771904

Unfavorable TS II

Electronic + Thermal Free Energies: -2300.625582

Correction to Gibb's free energy: 0.439285

Zero-point correction: 0.519781

Imaginary vibration frequency: 1 (associated imaginary frequency *i*1154.52 cm^{-1})

Symbol	Coordinates (Å)		
	X	Y	Z
Fe	-3.547423	-1.747050	0.278059
C	-2.914930	-2.722843	2.041762
C	-2.981479	-2.923705	-1.325416
C	-4.344991	-2.510580	2.064704
C	-2.278409	-1.432166	1.966789
C	-4.583748	-1.087082	1.997317
C	-3.306437	-0.421211	1.932263
H	-2.413998	-3.680339	2.065112
H	-2.350872	-3.800141	-1.279492
H	-5.101761	-3.281830	2.099170
H	-1.214339	-1.261013	1.908274
H	-5.552554	-0.607796	1.975548
H	-3.130960	0.641252	1.864643
S	-2.404613	2.616511	-0.187767
O	-1.827037	2.504162	1.337111
O	-3.820826	3.418932	-0.358613
H	-1.484233	-1.777325	-2.464042
C	-3.700326	-0.723218	-1.619486

C	-1.026567	3.912381	-1.016331
C	-3.622965	0.769870	-1.771547
H	-4.499452	1.264640	-1.341718
H	-3.559257	1.048688	-2.832850
F	-0.690136	3.497600	-2.296984
F	0.123427	4.016143	-0.248716
F	-1.591266	5.181131	-1.111301
N	-2.352266	1.174945	-1.073655
C	-4.857205	-1.534946	-1.380884
H	-5.877580	-1.183998	-1.313375
C	1.818370	0.896550	-1.100497
C	2.715355	-0.148697	-0.794120
C	2.167079	1.843010	-2.124398
C	3.926669	-0.306183	-1.550982
C	3.349677	1.729418	-2.834241
H	1.465025	2.644551	-2.323881
C	4.833008	-1.398347	-1.333631
C	4.255434	0.650263	-2.581861
H	3.597371	2.455518	-3.606282
C	5.995875	-1.528333	-2.083941
H	4.599975	-2.135522	-0.570802
C	5.462272	0.495502	-3.331987
C	6.322294	-0.570978	-3.092575
H	6.665395	-2.366307	-1.904487
H	5.695177	1.227328	-4.103235
H	7.236725	-0.683371	-3.669407
C	2.359426	-1.112560	0.294397
C	3.075969	-1.145783	1.543284
C	1.271979	-1.972049	0.121021
C	4.157915	-0.245710	1.821438

C	2.681923	-2.082280	2.570010
C	0.893222	-2.911054	1.127475
C	4.806635	-0.265327	3.050014
H	4.459559	0.463475	1.056969
C	3.378166	-2.087866	3.820264
C	1.589846	-2.972552	2.322992
H	0.041275	-3.557807	0.937763
C	4.417405	-1.197552	4.061058
H	5.619471	0.429276	3.246363
H	3.074400	-2.798884	4.585498
H	1.299705	-3.683217	3.093172
H	4.937530	-1.204957	5.015353
N	0.427896	-1.826516	-1.024440
C	0.458350	-2.580810	-2.115563
Pd	-0.895393	-0.283434	-0.957651
O	-0.474462	-2.420576	-3.040846
C	1.511729	-3.638503	-2.347054
H	1.108492	-4.623929	-2.081908
H	1.774084	-3.655504	-3.408566
H	2.407683	-3.452337	-1.749408
O	0.630793	1.058168	-0.431717
Cs	0.900670	1.998363	2.552558
C	-4.416096	-2.906601	-1.237767
H	-5.054815	-3.762103	-1.068716
C	-2.508680	-1.561649	-1.616085

Intermediate IIIA (having *Z*-configuration**)**

Electronic + Thermal Free Energies: -1847.021831

Correction to Gibb's free energy: 0.415488

Zero-point correction: 0.489278

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
C	-0.631474	2.572058	1.831908
C	-1.877480	3.194105	1.454663
C	-1.577963	4.496181	0.909154
C	-0.145861	4.678076	0.946397
C	0.439552	3.487119	1.514884
H	-0.524522	1.594325	2.277702
H	-2.861014	2.759551	1.562849
H	-2.299051	5.206697	0.528787
H	0.393504	5.548238	0.598250
H	1.495058	3.314268	1.672503
C	-0.115458	3.470510	-2.239938
C	-1.503431	3.067806	-2.176742
C	0.701004	2.369270	-1.775209
H	0.248543	4.435698	-2.564640
C	-1.540811	1.714771	-1.679455
H	-2.355638	3.674819	-2.450264
C	-0.183114	1.273689	-1.451878
H	1.779276	2.374470	-1.702262
Fe	-0.631607	3.000188	-0.256345
C	-2.693248	0.783609	-1.457868
H	-3.447989	1.212727	-0.788428
H	-3.194970	0.537610	-2.403977

Cs	0.038966	-0.632702	-0.953935
N	-2.066115	-0.467862	-0.883833
S	-3.183927	-1.496671	-0.100958
C	-3.192459	-0.964546	1.883409
F	-3.672628	0.335040	2.032322
F	-1.899009	-1.007951	2.404533
F	-3.991396	-1.815151	2.632520
O	-4.738505	-1.212350	-0.520654
O	-2.675564	-3.039979	-0.007394
C	-0.065802	-3.831248	-1.574188
C	0.402332	-3.409213	0.788049
C	0.301460	-5.158811	-0.898548
H	0.492699	-3.624875	-2.491322
H	-1.142100	-3.740577	-1.744915
C	-0.009192	-4.880527	0.595246
H	-0.275745	-2.856626	1.441361
H	1.436922	-3.298359	1.130146
H	1.365335	-5.384392	-1.040236
H	-0.286869	-5.991838	-1.296123
H	-1.080999	-4.997045	0.783207
H	0.542812	-5.546615	1.265692
O	0.330251	-2.797786	-0.574378
C	2.190737	-0.422746	-0.594768
C	2.822727	-0.231388	0.567989
C	2.016326	-0.704415	-1.930675
H	2.016193	0.078608	-2.686166
H	2.104289	-1.728045	-2.293103
C	2.056858	-0.075161	1.872409
H	2.284937	0.884419	2.353287
H	0.980832	-0.127031	1.697804

H	2.326828	-0.871333	2.578505
C	4.324044	-0.176088	0.609043
C	4.996447	-0.034385	1.848645
C	5.111847	-0.260485	-0.568798
C	6.401905	0.017168	1.909464
H	4.432625	0.035843	2.772886
C	6.513336	-0.209880	-0.508051
H	4.630385	-0.362214	-1.536878
C	7.169337	-0.070951	0.733257
H	6.893361	0.125781	2.873144
H	7.093928	-0.276022	-1.424870
H	8.254517	-0.030543	0.779815

Intermediate IIIB (having *E*-configuration**)**

Electronic + Thermal Free Energies: -1847.016332

Correction to Gibb's free energy: 0.416874

Zero-point correction: 0.489341

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
C	-2.911143	-1.799234	1.405372
C	-4.123512	-2.139802	0.700115
C	-4.754013	-0.911212	0.276206
C	-3.930545	0.188089	0.721196
C	-2.793990	-0.360942	1.421409
H	-2.211773	-2.497465	1.842876
H	-4.489860	-3.139664	0.511134
H	-5.674021	-0.830665	-0.286470

H	-4.128141	1.238196	0.556602
H	-1.995833	0.207149	1.874457
C	-3.093159	-1.156139	-2.668842
C	-2.398427	-2.341198	-2.216236
C	-2.290808	-0.000134	-2.330017
H	-4.055770	-1.137071	-3.161300
C	-1.163341	-1.915720	-1.605841
H	-2.745533	-3.360559	-2.316648
C	-1.083340	-0.474942	-1.693659
H	-2.550855	1.027744	-2.538584
Fe	-2.825097	-1.069308	-0.586879
C	-0.035486	-2.717735	-1.031528
H	-0.356954	-3.330123	-0.180616
H	0.392473	-3.395641	-1.782439
Cs	0.663794	0.324494	-1.191269
N	0.998184	-1.689144	-0.630859
S	2.231824	-2.322746	0.372184
C	1.643808	-2.003828	2.320705
F	0.283274	-2.277628	2.455527
F	1.853650	-0.676526	2.690406
F	2.342212	-2.816440	3.200088
O	2.331080	-3.954108	0.325119
O	3.613995	-1.466785	0.306766
C	3.355921	1.678255	0.309827
C	3.771052	0.768436	-1.917209
C	4.873823	1.583102	0.062397
H	3.025724	1.045858	1.135761
H	3.010435	2.707894	0.449610
C	5.001472	1.573461	-1.482944
H	3.403181	1.013189	-2.917143

H	3.927655	-0.309062	-1.814384
H	5.262068	0.647327	0.476475
H	5.410916	2.420604	0.518310
H	4.959015	2.592816	-1.885193
H	5.931755	1.104655	-1.819095
O	2.714173	1.176560	-0.945709
C	-0.124563	2.368552	-1.382814
C	-0.686058	3.249386	-0.545732
C	0.358128	1.968079	-2.612307
H	-0.298836	1.577868	-3.386644
H	1.361461	2.250865	-2.927387
C	-1.138398	4.578125	-1.165983
H	-2.233565	4.657508	-1.160896
H	-0.738422	5.426025	-0.596056
H	-0.801668	4.661248	-2.202641
C	-0.897441	3.067051	0.919257
C	-0.090717	2.190543	1.686616
C	-1.887368	3.821371	1.597312
C	-0.270290	2.062751	3.073545
H	0.688722	1.618241	1.197271
C	-2.074227	3.690361	2.985616
H	-2.522109	4.509031	1.046984
C	-1.265902	2.811770	3.732892
H	0.366911	1.386364	3.636791
H	-2.845503	4.274574	3.481252
H	-1.405007	2.715659	4.806567

Product 3f (having *Z*-configuration**)**

Electronic + Thermal Free Energies: -1487.952045

Correction to Gibb's free energy: 0.314873

Zero-point correction: 0.374271

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
Fe	2.826668	-0.465017	0.003584
S	-0.683898	2.063371	0.447755
F	-3.267072	2.382216	-0.597049
N	-0.512370	1.323578	-1.223650
O	-1.165415	1.076739	1.647810
C	-0.292071	-1.190017	-0.826235
O	0.499178	3.148988	0.703814
F	-1.948013	4.196353	-0.829446
F	-2.831042	3.691283	1.181603
C	-1.141128	-0.034659	-1.360371
H	-1.288207	-0.118035	-2.447090
H	-2.128495	-0.009578	-0.898235
C	1.135836	-1.048645	-1.184616
C	-0.851746	-2.216473	-0.115415
C	1.679137	0.216819	-1.648164
C	2.207558	-2.024190	-1.285675
H	2.145121	-3.071666	-1.038383
C	0.856557	1.465119	-1.810397
H	1.339065	2.352943	-1.390199
H	0.676090	1.669399	-2.875641
C	-2.335972	-2.354440	0.055331
C	3.370372	-1.369740	-1.825103

H	4.324601	-1.838355	-2.020550
C	3.047557	0.019279	-2.042429
H	3.709986	0.776977	-2.437353
C	4.431463	-0.745285	1.361586
H	5.324603	-1.316770	1.149466
C	-2.907814	-2.471403	1.346900
H	-2.269592	-2.416107	2.225620
C	-4.295368	-2.628829	1.511645
H	-4.714431	-2.700714	2.512280
C	-4.587141	-2.591984	-0.904493
H	-5.228527	-2.649816	-1.780502
C	4.244064	0.663384	1.105659
H	4.973749	1.331613	0.669234
C	2.268561	-0.169737	2.031420
H	1.255266	-0.231376	2.403491
C	-2.310492	3.169803	0.015913
C	-3.198620	-2.422431	-1.066402
H	-2.778660	-2.369054	-2.068215
C	2.908351	1.019843	1.519594
H	2.454396	1.997529	1.443533
C	-5.142625	-2.692448	0.385805
H	-6.214462	-2.821647	0.513394
C	3.209818	-1.260046	1.933886
H	3.032959	-2.283864	2.233024
C	-0.025156	-3.315667	0.534608
H	0.133765	-4.155769	-0.158113
H	0.954669	-2.954925	0.859413
H	-0.548116	-3.723350	1.405862

Product 3f (having *E*-configuration**)**

Electronic + Thermal Free Energies: -1487.949645

Correction to Gibb's free energy: 0.312754

Zero-point correction: 0.374236

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
Fe	-1.100818	1.918225	0.226015
S	3.171273	-0.218879	-0.782756
F	4.267591	-1.597059	1.428323
N	1.762250	-0.324889	0.230040
O	2.988244	-1.223731	-2.043267
C	-0.513295	-1.311820	0.316890
O	3.542659	1.347281	-0.991413
F	5.633815	0.017900	0.644304
F	5.438023	-1.930419	-0.470679
C	0.998893	-1.596293	0.290910
H	1.296476	-2.150368	1.194790
H	1.270700	-2.188410	-0.583069
C	-0.869240	-0.059037	1.025422
C	-1.385610	-2.232168	-0.188082
C	0.148112	0.845221	1.535601
C	-2.879426	-2.059134	-0.170740
C	-2.150901	0.508460	1.408278
H	-3.121913	0.100405	1.184954
C	1.624077	0.618987	1.364140
H	2.147212	1.550750	1.132526
H	2.065453	0.182983	2.274530
C	-1.912191	1.707412	2.168355

H	-2.673639	2.343869	2.596663
C	-0.488187	1.921335	2.244646
H	0.014385	2.739949	2.740369
C	-3.535110	-1.374033	-1.218857
H	-2.947128	-0.925937	-2.016259
C	-1.998717	3.594415	-0.713892
H	-2.755729	4.222759	-0.265103
C	-3.660829	-2.653176	0.846883
H	-3.169787	-3.190804	1.655139
C	-4.939410	-1.266851	-1.239210
H	-5.428567	-0.734057	-2.051206
C	-0.570371	3.788231	-0.621345
H	-0.071648	4.587229	-0.089960
C	-5.709499	-1.847246	-0.211118
H	-6.793348	-1.763177	-0.224674
C	-0.956264	1.867613	-1.891069
H	-0.794829	0.972432	-2.475796
C	4.769608	-0.992269	0.283069
C	0.074749	2.719766	-1.347342
H	1.141403	2.574688	-1.453992
C	-5.064760	-2.542921	0.832080
H	-5.650990	-2.997140	1.627319
C	-2.237016	2.406480	-1.499552
H	-3.204237	1.989169	-1.742585
C	-0.976056	-3.555539	-0.821152
H	-1.329873	-3.603210	-1.860974
H	0.099075	-3.748892	-0.818759
H	-1.461282	-4.386591	-0.290079

Crystallographic Details

The structures of ferrocene fused tetrahydropyridine (*Sp*)-**3a** (CCDC: 2347472), (*Rp*)-**3a** (CCDC: 2347473), and **3f** (CCDC: 2402043) were confirmed by X-ray structure analysis. We isolated the suitable single crystal by slow evaporation method in the 1:3 ratio solvents of Hexane in Dichloromethane

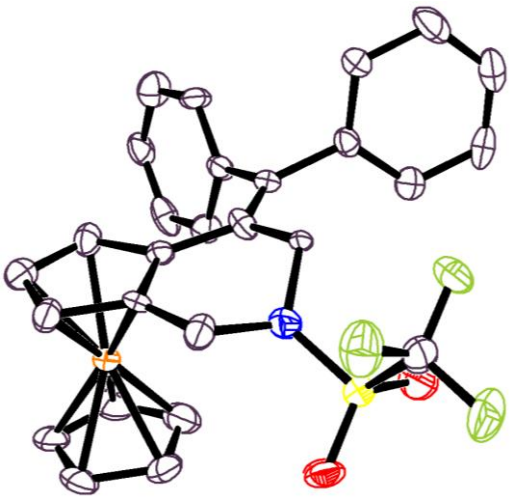


Table S7. Crystal data and structure refinement for (*Sp*)-**3a**.

Identification code	(*Sp*)-**3a**
CCDC Number	**2347572**
Empirical formula	$C_{27}H_{22}F_3FeNO_2S$
Formula weight	537.36
Temperature/K	140(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5134(15)
b/Å	9.8740(15)
c/Å	24.656(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2316.1(7)
Z	4
ρ_{calc}g/cm^3	1.541

μ/mm^{-1}	6.509
F(000)	1104.0
Crystal size/mm^3	0.122 × 0.021 × 0.015
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.648 to 127.37
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -28 ≤ l ≤ 28
Reflections collected	41812
Independent reflections	3728 [R_{int} = 0.1272, R_{sigma} = 0.0602]
Data/restraints/parameters	3728/20/321
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0940, wR_2 = 0.2625
Final R indexes [all data]	R_1 = 0.1008, wR_2 = 0.2680
Largest diff. peak/hole / e Å^{-3}	1.73/-1.00
Flack parameter	0.12(2)

Table S8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for (*Sp*)-**3a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{IJ} tensor**.**

Atom	***X***	***y***	***z***	**U(eq)**
Fe1	7428(2)	5161.7(18)	6168.1(8)	22.5(6)
S1	2875(3)	4310(3)	5484.0(14)	27.0(8)
F1	1234(9)	5880(9)	4925(4)	37(2)
F2	823(10)	3734(11)	4817(5)	52(3)
F3	2633(9)	4686(10)	4443(3)	45(2)
O1	1939(11)	4552(10)	5924(4)	37(2)
O2A	3450(20)	3009(16)	5361(19)	30(5)
O2B	3530(100)	3080(80)	5560(70)	30(5)
N1	4057(11)	5430(11)	5474(5)	27(2)
C1	6537(13)	5882(12)	5485(6)	22(3)
C2	8026(14)	5697(14)	5400(6)	26(3)
C3	8712(16)	6540(15)	5788(6)	29(3)

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (*Sp*)-**3a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{IJ} tensor**.**

Atom	***X***	***y***	***z***	**U(eq)**
C4	7703(13)	7209(13)	6107(5)	25(3)
C5	6318(14)	6838(13)	5906(5)	20(3)
C6	6365(18)	4247(16)	6772(7)	39(4)
C7	6504(16)	3319(16)	6326(7)	39(3)
C8	7980(16)	3148(15)	6235(7)	37(2)
C9	8709(17)	3942(15)	6634(7)	36(2)
C10	7718(18)	4574(15)	6959(6)	40(3)
C11	5360(13)	5251(15)	5154(6)	28(3)
C12	3795(13)	6819(12)	5644(6)	20(3)
C13	4899(14)	7322(14)	6042(5)	24(3)
C14	4560(13)	8224(13)	6419(6)	22(3)
C15	3099(13)	8854(13)	6445(5)	22(3)
C16	2027(15)	8220(15)	6744(6)	29(3)
C17	671(15)	8815(18)	6770(6)	36(4)
C18	446(14)	10039(18)	6526(6)	35(3)
C19	1482(16)	10710(17)	6229(7)	41(4)
C20	2831(14)	10092(14)	6191(6)	30(3)
C21	5557(13)	8735(13)	6844(5)	21(3)
C22	6005(15)	7818(15)	7250(5)	26(3)
C23	6964(15)	8276(17)	7652(6)	34(4)
C24	7424(15)	9600(14)	7642(6)	31(3)
C25	6973(16)	10507(16)	7253(6)	34(3)
C26	6011(13)	10042(13)	6859(5)	24(3)
C27	1809(14)	4684(15)	4879(6)	30(3)

Table S9. Anisotropic Displacement Parameters ($Å^2×10^3$) for (*Sp*)-**3a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Fe1	19.1(10)	16.4(9)	32.1(10)	2.5(8)	0.9(8)	0.7(8)
S1	22.2(16)	20.8(15)	38.0(18)	0.4(13)	0.1(13)	-1.2(12)
F1	31(4)	27(4)	55(5)	-1(4)	-7(4)	10(4)
F2	28(5)	54(6)	73(7)	-10(5)	-7(5)	-13(4)
F3	37(4)	59(6)	40(5)	-10(4)	4(4)	-3(5)
O1	38(5)	37(5)	37(5)	4(4)	7(3)	2(4)
O2A	35(6)	14(3)	41(13)	-2(5)	-7(9)	-5(3)
O2B	35(6)	14(3)	41(13)	-2(5)	-7(9)	-5(3)
N1	24(6)	20(6)	38(6)	-5(5)	-2(5)	1(5)
C1	20(6)	11(6)	35(7)	3(5)	1(5)	5(5)
C2	21(6)	26(6)	31(3)	-3(4)	4(4)	-4(5)
C3	29(7)	25(8)	34(8)	0(6)	5(6)	-2(6)
C4	19(6)	31(7)	26(6)	4(5)	-2(6)	-2(5)
C5	20(6)	13(6)	26(7)	-2(5)	-2(5)	-1(5)
C6	44(9)	27(8)	44(9)	3(7)	6(7)	9(7)
C7	32(5)	23(5)	62(8)	15(5)	-1(6)	-6(4)
C8	34(5)	20(3)	58(6)	5(3)	-8(6)	10(5)
C9	33(5)	18(7)	56(6)	12(4)	-7(4)	2(4)
C10	49(8)	31(7)	38(3)	14(4)	-4(4)	8(6)
C11	22(6)	28(7)	33(7)	-1(6)	3(5)	-4(6)
C12	13(6)	8(6)	40(8)	-2(5)	-3(5)	0(5)
C13	21(6)	26(7)	25(7)	2(5)	-1(5)	8(5)
C14	20(6)	13(6)	34(7)	2(5)	2(5)	2(5)
C15	18(6)	21(6)	28(7)	-6(5)	-4(5)	2(5)
C16	26(7)	30(7)	32(7)	1(6)	3(6)	0(6)
C17	17(7)	53(10)	39(8)	-3(7)	2(6)	-9(7)
C18	19(6)	47(9)	41(8)	-11(7)	-1(6)	3(7)
C19	35(8)	35(8)	52(10)	-3(7)	-20(7)	12(7)

Table S9. Anisotropic Displacement Parameters ($Å^2×10^3$) for (*Sp*)**-3a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20	23(6)	26(7)	41(7)	9(6)	-2(6)	3(6)
C21	20(6)	17(6)	28(7)	-2(5)	-3(5)	4(5)
C22	29(7)	25(7)	25(7)	-3(5)	-2(6)	-1(6)
C23	26(7)	54(10)	22(7)	0(6)	-5(6)	16(7)
C24	20(6)	35(8)	39(7)	-3(6)	-10(6)	4(6)
C25	33(7)	36(8)	35(8)	-9(6)	-6(6)	-7(7)
C26	28(6)	13(6)	32(7)	3(6)	-7(5)	-2(5)
C27	26(6)	26(7)	38(8)	-9(6)	-2(6)	-3(6)

Table S10. Bond Lengths for (*Sp*)**-3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	C1	2.014(14)	C3	C4	1.41(2)
Fe1	C2	2.048(14)	C4	C5	1.455(18)
Fe1	C3	2.056(15)	C5	C13	1.470(18)
Fe1	C4	2.044(13)	C6	C7	1.44(2)
Fe1	C5	2.067(13)	C6	C10	1.41(2)
Fe1	C6	2.014(17)	C7	C8	1.43(2)
Fe1	C7	2.058(16)	C8	C9	1.44(2)
Fe1	C8	2.063(14)	C9	C10	1.39(2)
Fe1	C9	2.062(15)	C12	C13	1.521(18)
Fe1	C10	2.054(14)	C13	C14	1.328(19)
S1	O1	1.424(11)	C14	C15	1.524(17)
S1	O2A	1.430(18)	C14	C21	1.500(19)
S1	O2B	1.38(7)	C15	C16	1.41(2)
S1	N1	1.577(11)	C15	C20	1.397(19)
S1	C27	1.842(15)	C16	C17	1.42(2)
F1	C27	1.307(17)	C17	C18	1.37(2)
F2	C27	1.335(17)	C18	C19	1.39(2)

Table S10. Bond Lengths for (*Sp*)-**3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F3	C27	1.331(17)	C19	C20	1.424(19)
N1	C11	1.481(17)	C21	C22	1.416(19)
N1	C12	1.455(16)	C21	C26	1.361(18)
C1	C2	1.444(18)	C22	C23	1.42(2)
C1	C5	1.418(19)	C23	C24	1.38(2)
C1	C11	1.520(18)	C24	C25	1.38(2)
C2	C3	1.43(2)	C25	C26	1.412(19)

Table S11. Bond Angles for (*Sp*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Fe1	C2	41.6(5)	C11	C1	Fe1	128.0(9)
C1	Fe1	C3	68.6(6)	C1	C2	Fe1	67.9(8)
C1	Fe1	C4	69.1(5)	C3	C2	Fe1	69.9(8)
C1	Fe1	C5	40.6(5)	C3	C2	C1	106.1(13)
C1	Fe1	C7	106.9(6)	C2	C3	Fe1	69.4(8)
C1	Fe1	C8	120.9(6)	C4	C3	Fe1	69.5(8)
C1	Fe1	C9	156.9(6)	C4	C3	C2	109.7(13)
C1	Fe1	C10	161.8(6)	C3	C4	Fe1	70.4(8)
C2	Fe1	C3	40.7(6)	C3	C4	C5	108.0(12)
C2	Fe1	C5	69.3(5)	C5	C4	Fe1	70.1(7)
C2	Fe1	C7	121.5(6)	C1	C5	Fe1	67.7(7)
C2	Fe1	C8	104.6(6)	C1	C5	C4	106.4(11)
C2	Fe1	C9	120.1(6)	C1	C5	C13	121.2(12)
C2	Fe1	C10	156.1(6)	C4	C5	Fe1	68.4(7)
C3	Fe1	C5	68.3(5)	C4	C5	C13	132.2(12)
C3	Fe1	C7	157.8(7)	C13	C5	Fe1	131.1(10)
C3	Fe1	C8	121.5(6)	C7	C6	Fe1	70.9(9)
C3	Fe1	C9	106.8(6)	C10	C6	Fe1	71.3(10)
C4	Fe1	C2	69.0(5)	C10	C6	C7	108.3(15)

Table S11. Bond Angles for (*Sp*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	Fe1	C3	40.1(6)	C6	C7	Fe1	67.7(10)
C4	Fe1	C5	41.5(5)	C8	C7	Fe1	69.9(9)
C4	Fe1	C7	160.6(6)	C8	C7	C6	106.6(15)
C4	Fe1	C8	157.9(6)	C7	C8	Fe1	69.5(9)
C4	Fe1	C9	122.9(6)	C7	C8	C9	107.5(15)
C4	Fe1	C10	109.4(6)	C9	C8	Fe1	69.6(8)
C6	Fe1	C1	124.4(6)	C8	C9	Fe1	69.7(8)
C6	Fe1	C2	160.0(6)	C10	C9	Fe1	70.0(9)
C6	Fe1	C3	158.9(7)	C10	C9	C8	108.3(14)
C6	Fe1	C4	124.2(6)	C6	C10	Fe1	68.3(9)
C6	Fe1	C5	109.5(6)	C9	C10	Fe1	70.6(9)
C6	Fe1	C7	41.3(7)	C9	C10	C6	109.2(15)
C6	Fe1	C8	68.7(7)	N1	C11	C1	106.3(11)
C6	Fe1	C9	67.9(6)	N1	C12	C13	112.0(11)
C6	Fe1	C10	40.4(7)	C5	C13	C12	112.4(11)
C7	Fe1	C5	123.3(6)	C14	C13	C5	126.9(13)
C7	Fe1	C8	40.7(6)	C14	C13	C12	120.3(11)
C7	Fe1	C9	68.3(6)	C13	C14	C15	121.7(12)
C8	Fe1	C5	157.9(6)	C13	C14	C21	124.1(12)
C9	Fe1	C5	160.7(6)	C21	C14	C15	114.2(11)
C9	Fe1	C8	40.7(6)	C16	C15	C14	120.1(12)
C10	Fe1	C3	122.7(7)	C20	C15	C14	120.3(12)
C10	Fe1	C5	126.3(6)	C20	C15	C16	119.6(12)
C10	Fe1	C7	68.2(7)	C15	C16	C17	119.9(13)
C10	Fe1	C8	67.5(7)	C18	C17	C16	119.3(14)
C10	Fe1	C9	39.4(7)	C17	C18	C19	122.6(14)
O1	S1	O2A	123.5(14)	C18	C19	C20	118.0(14)
O1	S1	N1	109.9(6)	C15	C20	C19	120.6(13)
O1	S1	C27	103.8(6)	C22	C21	C14	117.9(12)

Table S11. Bond Angles for (*Sp*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2A	S1	N1	110.6(9)	C26	C21	C14	122.7(12)
O2A	S1	C27	103(2)	C26	C21	C22	119.4(12)
O2B	S1	O1	109(7)	C21	C22	C23	118.9(13)
O2B	S1	N1	108(4)	C24	C23	C22	119.5(13)
O2B	S1	C27	122(6)	C23	C24	C25	122.0(13)
N1	S1	C27	103.9(6)	C24	C25	C26	117.9(14)
C11	N1	S1	121.4(9)	C21	C26	C25	122.3(13)
C12	N1	S1	122.3(9)	F1	C27	S1	109.9(10)
C12	N1	C11	114.1(11)	F1	C27	F2	110.6(11)
C2	C1	Fe1	70.4(8)	F1	C27	F3	108.4(12)
C2	C1	C11	126.3(12)	F2	C27	S1	109.8(11)
C5	C1	Fe1	71.7(8)	F3	C27	S1	109.3(9)
C5	C1	C2	109.6(12)	F3	C27	F2	108.8(11)
C5	C1	C11	123.9(11)				

Table S12. Torsion Angles for (*Sp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	C1	C2	C3	-59.9(10)	C4	C5	C13	C14	-3(2)
Fe1	C1	C5	C4	57.6(9)	C5	C1	C2	Fe1	61.3(10)
Fe1	C1	C5	C13	-125.6(12)	C5	C1	C2	C3	1.4(17)
Fe1	C1	C11	N1	72.7(14)	C5	C1	C11	N1	-19.8(18)
Fe1	C2	C3	C4	-57.8(10)	C5	C13	C14	C15	167.3(13)
Fe1	C3	C4	C5	-60.3(9)	C5	C13	C14	C21	-11(2)
Fe1	C4	C5	C1	-57.1(9)	C6	C7	C8	Fe1	-58.0(11)
Fe1	C4	C5	C13	126.6(15)	C6	C7	C8	C9	1.5(19)
Fe1	C5	C13	C12	-93.5(14)	C7	C6	C10	Fe1	61.7(11)
Fe1	C5	C13	C14	94.5(17)	C7	C6	C10	C9	2.8(17)
Fe1	C6	C7	C8	59.3(11)	C7	C8	C9	Fe1	-59.3(11)
Fe1	C6	C10	C9	-58.9(10)	C7	C8	C9	C10	0.2(18)

Table S12. Torsion Angles for (*Sp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	C7	C8	C9	59.4(11)	C8	C9	C10	Fe1	-59.3(11)
Fe1	C8	C9	C10	59.5(10)	C8	C9	C10	C6	-1.9(17)
Fe1	C9	C10	C6	57.5(10)	C10	C6	C7	Fe1	-61.9(11)
S1	N1	C11	C1	-143.4(10)	C10	C6	C7	C8	-2.6(19)
S1	N1	C12	C13	130.7(11)	C11	N1	C12	C13	-65.8(15)
O1	S1	N1	C11	164.5(10)	C11	C1	C2	Fe1	-123.3(14)
O1	S1	N1	C12	-33.2(13)	C11	C1	C2	C3	176.8(12)
O1	S1	C27	F1	52.0(11)	C11	C1	C5	Fe1	123.9(13)
O1	S1	C27	F2	-69.8(11)	C11	C1	C5	C4	-178.5(12)
O1	S1	C27	F3	170.9(9)	C11	C1	C5	C13	-2(2)
O2A	S1	N1	C11	25(2)	C12	N1	C11	C1	52.8(15)
O2A	S1	N1	C12	-173(2)	C12	C13	C14	C15	-4(2)
O2A	S1	C27	F1	-178.3(12)	C12	C13	C14	C21	177.3(12)
O2A	S1	C27	F2	59.9(13)	C13	C14	C15	C16	88.5(17)
O2A	S1	C27	F3	-59.4(13)	C13	C14	C15	C20	-94.0(16)
O2B	S1	N1	C11	46(7)	C13	C14	C21	C22	-68.4(18)
O2B	S1	N1	C12	-152(7)	C13	C14	C21	C26	113.3(16)
O2B	S1	C27	F1	176(6)	C14	C15	C16	C17	179.6(13)
O2B	S1	C27	F2	54(6)	C14	C15	C20	C19	-177.8(13)
O2B	S1	C27	F3	-65(6)	C14	C21	C22	C23	179.2(12)
N1	S1	C27	F1	-62.9(10)	C14	C21	C26	C25	-178.6(13)
N1	S1	C27	F2	175.2(9)	C15	C14	C21	C22	112.9(13)
N1	S1	C27	F3	56.0(11)	C15	C14	C21	C26	-65.4(17)
N1	C12	C13	C5	38.5(15)	C15	C16	C17	C18	-3(2)
N1	C12	C13	C14	-149.0(13)	C16	C15	C20	C19	0(2)
C1	C2	C3	Fe1	58.6(10)	C16	C17	C18	C19	3(2)
C1	C2	C3	C4	0.8(16)	C17	C18	C19	C20	-1(2)
C1	C5	C13	C12	-7.0(18)	C18	C19	C20	C15	0(2)
C1	C5	C13	C14	-179.0(14)	C20	C15	C16	C17	2(2)

Table S12. Torsion Angles for (*Sp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C1	C5	Fe1	-60.5(10)	C21	C14	C15	C16	-92.8(15)
C2	C1	C5	C4	-2.9(16)	C21	C14	C15	C20	84.7(16)
C2	C1	C5	C13	173.9(12)	C21	C22	C23	C24	1(2)
C2	C1	C11	N1	165.4(13)	C22	C21	C26	C25	3(2)
C2	C3	C4	Fe1	57.7(10)	C22	C23	C24	C25	0(2)
C2	C3	C4	C5	-2.6(15)	C23	C24	C25	C26	0(2)
C3	C4	C5	Fe1	60.5(9)	C24	C25	C26	C21	-2(2)
C3	C4	C5	C1	3.4(14)	C26	C21	C22	C23	-2(2)
C3	C4	C5	C13	-173.0(15)	C27	S1	N1	C11	-85.0(11)
C4	C5	C13	C12	168.9(13)	C27	S1	N1	C12	77.4(12)

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*Sp*)-**3a**.

Atom	*x*	*Y*	*z*	U(eq)
H2	8460.99	5128.54	5137.72	31
H3	9701.34	6636.04	5824.95	35
H4	7893.08	7798.9	6402.43	30
H6	5506.08	4580.93	6915.99	46
H7	5761.96	2901.29	6130.07	47
H8	8400.49	2607.91	5960.37	45
H9	9700.01	4020.99	6668.16	43
H10	7922.39	5139.04	7261.35	47
H11A	5274.99	5709.31	4797.92	33
H11B	5547.3	4277.3	5090.64	33
H12A	2856.47	6874.24	5815.37	24
H12B	3790.83	7414.13	5320.55	24
H16	2254.14	7393.07	6928.06	35
H17	-71.24	8368.82	6955.38	44
H18	-453.34	10449.72	6559.29	43

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*Sp*)-**3a**.

Atom	***x***	***Y***	***z***	**U(eq)**
H19	1294.16	11552.38	6057.72	49
H20	3555.93	10525.26	5990	36
H22	5669.42	6911.76	7253.67	31
H23	7286.51	7673.77	7925.75	41
H24	8069.6	9896.77	7910.98	38
H25	7300.14	11416.56	7251.19	41
H26	5669.5	10661.83	6595.89	29

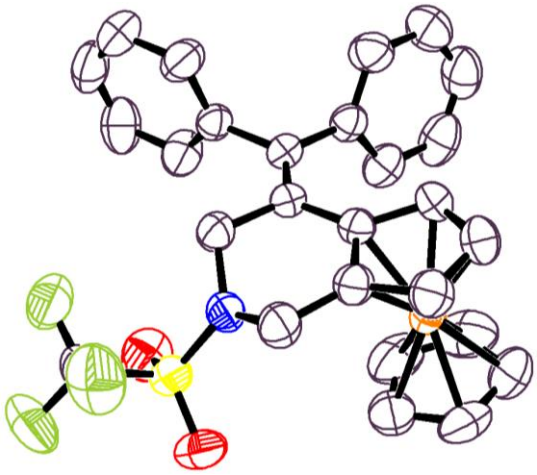


Table S14. Crystal data and structure refinement for (*Rp*)-**3a**.

Identification code	(*Rp*)-**3a**
CCDC Number	2347573
Empirical formula	$C_{27}H_{22}F_3FeNO_2S$
Formula weight	537.37
Temperature/K	303.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5665(14)
b/Å	9.8290(17)
c/Å	25.415(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2389.7(7)
Z	4
ρ_{calc}g/cm^3	1.494
μ/mm^{-1}	0.768
F(000)	1104.0
Crystal size/mm^3	0.02 × 0.012 × 0.01

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.44 to 59.16
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -35 ≤ l ≤ 35
Reflections collected	61813
Independent reflections	6676 [R_{int} = 0.0621, R_{sigma} = 0.0350]
Data/restraints/parameters	6676/0/316
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.0897
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.0964
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.19
Flack parameter	0.005(15)

Table S15. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for (*Rp*)-**3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor**.**

Atom	***x***	***y***	***z***	**U(eq)**
Fe1	2496.4(3)	5171.7(3)	6166.82(13)	47.87(9)
S1	6982.8(6)	4351.0(6)	5500.9(3)	55.59(15)
F1	8651.6(17)	5875.2(19)	4951.2(8)	81.2(5)
N1	5813.4(17)	5489.1(19)	5479.3(8)	50.1(4)
O2	7908(2)	4595(2)	5924.8(8)	76.9(5)
C11	5004(2)	7365(2)	6045.7(8)	40.7(4)
O1	6373(2)	3057.1(18)	5403.7(11)	87.1(7)
F2	7271(2)	4666(2)	4488.2(7)	99.2(6)
F3	9044(2)	3749(2)	4869.8(11)	113.7(8)
C12	6094(2)	6893(2)	5652.9(9)	49.2(5)
C1	3593(2)	6860(2)	5925.2(9)	42.7(5)
C15	5362(2)	8237(2)	6426.0(9)	42.9(4)

Table S15. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (*Rp*)-**3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor**.**

Atom	***x***	***y***	***z***	**U(eq)**
C5	3363(2)	5917(2)	5498.4(10)	47.3(5)
C22	4388(2)	8699(2)	6846.4(9)	45.8(5)
C2	2235(2)	7226(2)	6117.8(10)	48.4(5)
C13	4512(2)	5320(3)	5177.1(10)	54.0(5)
C16	6803(2)	8846(2)	6451.5(9)	44.3(4)
C3	1217(2)	6557(3)	5817.2(11)	58.1(6)
C4	1897(2)	5740(3)	5432.9(11)	56.7(6)
C23	4016(3)	7823(3)	7246.9(10)	61.9(6)
C8	1255(4)	3938(4)	6615.9(16)	87.4(11)
C27	3851(3)	10008(3)	6847.1(10)	62.2(6)
C17	7832(3)	8283(3)	6753.5(11)	65.1(7)
C18	9154(3)	8882(4)	6779.5(12)	76.7(9)
C24	3106(3)	8265(4)	7641.8(11)	76.0(8)
C20	8422(3)	10614(3)	6203.9(15)	78.4(8)
C9	1939(4)	3181(3)	6238.0(17)	83.8(9)
C25	2567(3)	9556(4)	7630.3(12)	78.2(8)
C6	3583(4)	4195(4)	6737.8(16)	89.1(11)
C14	8051(3)	4676(3)	4915.9(12)	67.2(7)
C21	7107(3)	10031(3)	6176.6(12)	64.7(6)
C10	3393(3)	3333(3)	6306.3(17)	84.4(11)
C19	9435(3)	10045(3)	6510.3(13)	76.3(9)
C26	2939(3)	10428(3)	7238.5(12)	75.6(8)
C7	2266(5)	4581(3)	6927.0(13)	91.9(11)

Table S16. Anisotropic Displacement Parameters ($Å^2×10^3$) for (*Rp*)-**3a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	39.40(13)	44.41(15)	59.79(18)	2.37(13)	-0.20(15)	-5.85(13)
S1	48.5(3)	45.1(3)	73.1(4)	-0.5(3)	-0.3(3)	-2.7(2)
F1	70.6(9)	84.7(12)	88.2(12)	-0.3(10)	17.1(9)	-19.2(9)
N1	39.9(8)	49.2(10)	61.1(11)	-14.7(9)	1.3(8)	-2.4(7)
O2	67.9(10)	85.8(13)	77.1(12)	10.7(11)	-16.0(10)	3.7(10)
C11	41.7(9)	35.0(9)	45.4(12)	0.6(8)	3.5(8)	-1.2(8)
O1	72.6(12)	41.4(10)	147(2)	-4.5(12)	3.5(14)	-6.0(9)
F2	93.9(12)	137.0(16)	66.6(10)	-29.0(11)	2.6(9)	-5.1(13)
F3	75.9(11)	104.4(16)	161(2)	-34.6(15)	28.3(13)	28.6(11)
C12	46.5(11)	47.1(12)	54.1(13)	-8.2(10)	7.6(9)	-6.8(9)
C1	40.2(10)	37.4(10)	50.5(12)	2.0(9)	-1.6(9)	0.8(8)
C15	43.1(10)	38.3(10)	47.2(11)	2.1(9)	3.1(9)	-3.0(8)
C5	44.0(10)	47.0(12)	50.8(12)	-1.0(10)	-4.1(9)	-0.8(8)
C22	47.9(11)	46.6(12)	42.8(11)	-5.8(9)	1.1(9)	-6.4(9)
C2	41.2(11)	46.2(10)	57.8(13)	0.8(10)	2.9(9)	6.4(8)
C13	46.7(10)	59.0(14)	56.2(13)	-10.7(11)	-4.0(9)	-3.0(10)
C16	45.4(10)	42.9(10)	44.6(11)	-6.8(9)	3.9(9)	-6.5(9)
C3	39.2(10)	65.7(16)	69.3(16)	1.1(13)	-5.8(11)	5.5(10)
C4	46.7(11)	61.3(14)	62.1(15)	-4.1(12)	-13.0(11)	0.2(11)
C23	64.6(14)	64.2(16)	56.8(14)	6.9(12)	3.6(12)	-10.1(12)
C8	73.1(18)	76(2)	113(3)	18(2)	33(2)	-17.6(17)
C27	74.8(15)	51.7(15)	60.2(14)	-6.0(12)	11.8(12)	-1.6(12)
C17	56.0(14)	73.3(17)	65.9(15)	13.3(13)	-1.6(11)	-5.7(12)
C18	48.9(13)	113(3)	68.6(17)	-0.1(18)	-5.1(13)	-2.9(15)
C24	74.3(17)	101(2)	52.5(15)	2.5(16)	12.0(14)	-24.0(18)
C20	69.0(16)	63.1(16)	103(2)	5.5(18)	16.2(17)	-20.3(13)

Table S16. Anisotropic Displacement Parameters ($Å^2×10^3$) for (*Rp*)-**3a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C9	92(2)	49.5(14)	110(3)	0.7(17)	11(2)	-24.5(15)
C25	65.1(15)	98(2)	71.3(17)	-30.2(16)	16.4(15)	-9.7(19)
C6	89(2)	71(2)	108(3)	40(2)	-29(2)	-12.5(17)
C14	51.3(12)	75.8(18)	74.3(17)	-22.6(15)	5.7(13)	4.1(13)
C21	57.8(12)	55.6(14)	80.8(17)	11.5(14)	-1.4(12)	-11.4(10)
C10	76.3(19)	51.6(15)	125(3)	30.5(19)	24(2)	7.6(14)
C19	53.0(13)	90(2)	85.4(19)	-19.6(18)	13.7(13)	-24.7(15)
C26	79.2(17)	70.4(18)	77.3(19)	-19.9(15)	15.6(15)	7.9(15)
C7	140(3)	68.3(19)	67.8(18)	17.0(14)	18(2)	-3(2)

Table S17. Bond Lengths for (*Rp*)-**3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	C1	2.057(2)	C15	C22	1.489(3)
Fe1	C5	2.027(2)	C15	C16	1.504(3)
Fe1	C2	2.039(2)	C5	C13	1.490(3)
Fe1	C3	2.035(3)	C5	C4	1.423(3)
Fe1	C4	2.030(3)	C22	C23	1.380(3)
Fe1	C8	2.045(3)	C22	C27	1.385(3)
Fe1	C9	2.036(3)	C2	C3	1.402(3)
Fe1	C6	2.027(3)	C16	C17	1.366(3)
Fe1	C10	2.032(3)	C16	C21	1.389(3)
Fe1	C7	2.029(3)	C3	C4	1.422(4)
S1	N1	1.5830(19)	C23	C24	1.397(4)
S1	O2	1.415(2)	C8	C9	1.380(5)
S1	O1	1.4211(19)	C8	C7	1.400(5)
S1	C14	1.832(3)	C27	C26	1.386(4)

Table S17. Bond Lengths for (*Rp*)-**3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C14	1.314(3)	C17	C18	1.396(4)
N1	C12	1.473(3)	C18	C19	1.360(5)
N1	C13	1.473(3)	C24	C25	1.371(5)
C11	C12	1.516(3)	C20	C21	1.384(4)
C11	C1	1.471(3)	C20	C19	1.363(5)
C11	C15	1.336(3)	C9	C10	1.409(5)
F2	C14	1.318(3)	C25	C26	1.361(5)
F3	C14	1.321(3)	C6	C10	1.398(5)
C1	C5	1.444(3)	C6	C7	1.401(5)
C1	C2	1.434(3)			

Table S18. Bond Angles for (*Rp*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	Fe1	C1	41.40(9)	C5	C1	C11	120.91(19)
C5	Fe1	C2	68.96(9)	C2	C1	Fe1	68.81(12)
C5	Fe1	C3	68.79(10)	C2	C1	C11	132.5(2)
C5	Fe1	C4	41.06(9)	C2	C1	C5	106.20(18)
C5	Fe1	C8	156.81(14)	C11	C15	C22	123.70(19)
C5	Fe1	C9	121.92(14)	C11	C15	C16	121.41(19)
C5	Fe1	C10	107.17(12)	C22	C15	C16	114.89(18)
C5	Fe1	C7	161.02(14)	C1	C5	Fe1	70.42(13)
C2	Fe1	C1	41.00(8)	C1	C5	C13	123.49(18)
C2	Fe1	C8	123.38(12)	C13	C5	Fe1	128.22(17)
C3	Fe1	C1	68.70(9)	C4	C5	Fe1	69.57(16)
C3	Fe1	C2	40.25(10)	C4	C5	C1	108.5(2)
C3	Fe1	C8	106.93(13)	C4	C5	C13	127.9(2)

Table S18. Bond Angles for (*Rp*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	Fe1	C9	121.63(13)	C23	C22	C15	120.0(2)
C4	Fe1	C1	69.39(9)	C23	C22	C27	118.9(2)
C4	Fe1	C2	68.70(10)	C27	C22	C15	121.1(2)
C4	Fe1	C3	40.96(10)	C1	C2	Fe1	70.19(12)
C4	Fe1	C8	120.78(14)	C3	C2	Fe1	69.75(14)
C4	Fe1	C9	105.78(14)	C3	C2	C1	109.0(2)
C4	Fe1	C10	121.62(15)	N1	C13	C5	107.07(18)
C8	Fe1	C1	160.22(13)	C17	C16	C15	121.6(2)
C9	Fe1	C1	159.28(13)	C17	C16	C21	118.1(2)
C9	Fe1	C2	157.71(12)	C21	C16	C15	120.3(2)
C9	Fe1	C8	39.52(14)	C2	C3	Fe1	70.00(13)
C6	Fe1	C1	109.52(12)	C2	C3	C4	108.8(2)
C6	Fe1	C5	124.16(13)	C4	C3	Fe1	69.31(15)
C6	Fe1	C2	125.15(14)	C5	C4	Fe1	69.37(15)
C6	Fe1	C3	159.70(16)	C3	C4	Fe1	69.73(15)
C6	Fe1	C4	158.94(16)	C3	C4	C5	107.5(2)
C6	Fe1	C8	67.51(15)	C22	C23	C24	119.7(3)
C6	Fe1	C9	67.39(15)	C9	C8	Fe1	69.88(17)
C6	Fe1	C10	40.30(16)	C9	C8	C7	108.0(3)
C6	Fe1	C7	40.41(16)	C7	C8	Fe1	69.31(17)
C10	Fe1	C1	123.67(11)	C22	C27	C26	120.7(3)
C10	Fe1	C2	160.67(12)	C16	C17	C18	120.6(3)
C10	Fe1	C3	157.71(15)	C19	C18	C17	120.6(3)
C10	Fe1	C8	67.68(14)	C25	C24	C23	120.5(3)
C10	Fe1	C9	40.54(14)	C19	C20	C21	120.3(3)
C7	Fe1	C1	124.78(13)	C8	C9	Fe1	70.59(18)

Table S18. Bond Angles for (*Rp*)-**3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	Fe1	C2	109.16(12)	C8	C9	C10	109.0(4)
C7	Fe1	C3	122.79(14)	C10	C9	Fe1	69.57(17)
C7	Fe1	C4	157.34(15)	C26	C25	C24	120.0(3)
C7	Fe1	C8	40.18(15)	C10	C6	Fe1	70.04(19)
C7	Fe1	C9	67.17(16)	C10	C6	C7	108.4(3)
C7	Fe1	C10	67.99(15)	C7	C6	Fe1	69.89(19)
N1	S1	C14	104.07(12)	F1	C14	S1	110.15(19)
O2	S1	N1	110.43(12)	F1	C14	F2	108.0(3)
O2	S1	O1	122.75(15)	F1	C14	F3	108.1(2)
O2	S1	C14	103.84(12)	F2	C14	S1	110.61(18)
O1	S1	N1	109.64(12)	F2	C14	F3	109.2(2)
O1	S1	C14	104.12(15)	F3	C14	S1	110.7(2)
C12	N1	S1	121.51(15)	C20	C21	C16	120.8(3)
C13	N1	S1	122.40(16)	C9	C10	Fe1	69.89(19)
C13	N1	C12	114.59(19)	C6	C10	Fe1	69.66(19)
C1	C11	C12	112.99(18)	C6	C10	C9	106.8(4)
C15	C11	C12	119.77(18)	C18	C19	C20	119.5(2)
C15	C11	C1	127.03(19)	C25	C26	C27	120.1(3)
N1	C12	C11	111.01(17)	C8	C7	Fe1	70.5(2)
C11	C1	Fe1	132.73(15)	C8	C7	C6	107.8(3)
C5	C1	Fe1	68.19(13)	C6	C7	Fe1	69.70(19)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	C1	C5	C13	-123.5(2)	C3	Fe1	C9	C10	162.1(2)
Fe1	C1	C5	C4	59.36(19)	C3	Fe1	C6	C10	159.3(3)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	C1	C2	C3	-59.12(17)	C3	Fe1	C6	C7	39.9(5)
Fe1	C5	C13	N1	-72.0(3)	C3	Fe1	C10	C9	-43.5(5)
Fe1	C5	C4	C3	59.53(19)	C3	Fe1	C10	C6	-161.2(3)
Fe1	C2	C3	C4	-58.62(19)	C3	Fe1	C7	C8	76.9(2)
Fe1	C3	C4	C5	-59.30(19)	C3	Fe1	C7	C6	-164.6(2)
Fe1	C8	C9	C10	59.2(2)	C4	Fe1	C1	C11	-150.2(2)
Fe1	C8	C7	C6	-60.0(2)	C4	Fe1	C1	C5	-37.67(13)
Fe1	C9	C10	C6	60.2(2)	C4	Fe1	C1	C2	80.86(15)
Fe1	C6	C10	C9	-60.3(2)	C4	Fe1	C5	C1	119.5(2)
Fe1	C6	C7	C8	60.5(2)	C4	Fe1	C5	C13	-122.8(3)
S1	N1	C12	C11	-128.19(18)	C4	Fe1	C2	C1	-82.69(14)
S1	N1	C13	C5	140.58(18)	C4	Fe1	C2	C3	37.45(15)
N1	S1	C14	F1	63.5(2)	C4	Fe1	C3	C2	-120.2(2)
N1	S1	C14	F2	-55.9(2)	C4	Fe1	C8	C9	77.0(2)
N1	S1	C14	F3	-177.07(19)	C4	Fe1	C8	C7	-163.6(2)
O2	S1	N1	C12	31.3(2)	C4	Fe1	C9	C8	-119.6(2)
O2	S1	N1	C13	-163.5(2)	C4	Fe1	C9	C10	120.5(3)
O2	S1	C14	F1	-52.1(2)	C4	Fe1	C6	C10	-36.2(4)
O2	S1	C14	F2	-171.5(2)	C4	Fe1	C6	C7	-155.7(3)
O2	S1	C14	F3	67.3(2)	C4	Fe1	C10	C9	-76.8(3)
C11	C1	C5	Fe1	127.8(2)	C4	Fe1	C10	C6	165.6(2)
C11	C1	C5	C13	4.2(4)	C4	Fe1	C7	C8	39.0(4)
C11	C1	C5	C4	-172.9(2)	C4	Fe1	C7	C6	157.4(3)
C11	C1	C2	Fe1	-129.2(3)	C4	C5	C13	N1	-164.9(3)
C11	C1	C2	C3	171.7(3)	C23	C22	C27	C26	-0.9(4)
C11	C15	C22	C23	73.0(3)	C23	C24	C25	C26	-1.3(5)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C11	C15	C22	C27	-107.5(3)	C8	Fe1	C1	C11	85.0(4)
C11	C15	C16	C17	-94.6(3)	C8	Fe1	C1	C5	-162.4(4)
C11	C15	C16	C21	87.2(3)	C8	Fe1	C1	C2	-43.9(4)
O1	S1	N1	C12	169.5(2)	C8	Fe1	C5	C1	165.0(3)
O1	S1	N1	C13	-25.2(2)	C8	Fe1	C5	C13	-77.3(4)
O1	S1	C14	F1	178.34(19)	C8	Fe1	C5	C4	45.5(4)
O1	S1	C14	F2	59.0(2)	C8	Fe1	C2	C1	163.67(18)
O1	S1	C14	F3	-62.2(2)	C8	Fe1	C2	C3	-76.2(2)
C12	N1	C13	C5	-53.2(3)	C8	Fe1	C3	C2	122.05(18)
C12	C11	C1	Fe1	93.0(2)	C8	Fe1	C3	C4	-117.74(18)
C12	C11	C1	C5	5.1(3)	C8	Fe1	C4	C5	-160.92(18)
C12	C11	C1	C2	-166.7(2)	C8	Fe1	C4	C3	80.3(2)
C12	C11	C15	C22	-176.5(2)	C8	Fe1	C9	C10	-119.9(4)
C12	C11	C15	C16	4.6(3)	C8	Fe1	C6	C10	81.5(2)
C1	Fe1	C5	C13	117.7(2)	C8	Fe1	C6	C7	-37.9(2)
C1	Fe1	C5	C4	-119.5(2)	C8	Fe1	C10	C9	36.6(3)
C1	Fe1	C2	C3	120.1(2)	C8	Fe1	C10	C6	-81.1(2)
C1	Fe1	C3	C2	-37.51(13)	C8	Fe1	C7	C6	118.4(3)
C1	Fe1	C3	C4	82.70(16)	C8	C9	C10	Fe1	-59.8(3)
C1	Fe1	C4	C5	37.96(14)	C8	C9	C10	C6	0.4(4)
C1	Fe1	C4	C3	-80.86(16)	C27	C22	C23	C24	0.3(4)
C1	Fe1	C8	C9	-166.5(3)	C17	C16	C21	C20	0.7(4)
C1	Fe1	C8	C7	-47.1(5)	C17	C18	C19	C20	-1.4(5)
C1	Fe1	C9	C8	167.1(3)	C24	C25	C26	C27	0.7(5)
C1	Fe1	C9	C10	47.2(5)	C9	Fe1	C1	C11	-70.2(4)
C1	Fe1	C6	C10	-119.4(2)	C9	Fe1	C1	C5	42.4(4)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	Fe1	C6	C7	121.1(2)	C9	Fe1	C1	C2	160.9(3)
C1	Fe1	C10	C9	-161.8(2)	C9	Fe1	C5	C1	-163.68(16)
C1	Fe1	C10	C6	80.5(2)	C9	Fe1	C5	C13	-45.9(2)
C1	Fe1	C7	C8	162.42(18)	C9	Fe1	C5	C4	76.9(2)
C1	Fe1	C7	C6	-79.2(2)	C9	Fe1	C2	C1	-162.2(3)
C1	C11	C12	N1	-37.0(3)	C9	Fe1	C2	C3	-42.1(4)
C1	C11	C15	C22	9.0(4)	C9	Fe1	C3	C2	162.63(17)
C1	C11	C15	C16	-169.9(2)	C9	Fe1	C3	C4	-77.2(2)
C1	C5	C13	N1	18.6(3)	C9	Fe1	C4	C5	-120.80(17)
C1	C5	C4	Fe1	-59.88(18)	C9	Fe1	C4	C3	120.38(17)
C1	C5	C4	C3	-0.4(3)	C9	Fe1	C8	C7	119.4(3)
C1	C2	C3	Fe1	59.39(15)	C9	Fe1	C6	C10	38.6(2)
C1	C2	C3	C4	0.8(3)	C9	Fe1	C6	C7	-80.8(2)
C15	C11	C12	N1	147.8(2)	C9	Fe1	C10	C6	-117.7(4)
C15	C11	C1	Fe1	-92.3(3)	C9	Fe1	C7	C8	-37.0(2)
C15	C11	C1	C5	179.8(2)	C9	Fe1	C7	C6	81.4(2)
C15	C11	C1	C2	8.1(4)	C9	C8	C7	Fe1	59.4(2)
C15	C22	C23	C24	179.7(2)	C9	C8	C7	C6	-0.6(4)
C15	C22	C27	C26	179.7(2)	C6	Fe1	C1	C11	7.4(3)
C15	C16	C17	C18	-178.7(3)	C6	Fe1	C1	C5	119.92(18)
C15	C16	C21	C20	178.9(3)	C6	Fe1	C1	C2	-121.55(19)
C5	Fe1	C1	C11	-112.5(3)	C6	Fe1	C5	C1	-80.84(19)
C5	Fe1	C1	C2	118.52(18)	C6	Fe1	C5	C13	36.9(3)
C5	Fe1	C2	C1	-38.50(13)	C6	Fe1	C5	C4	159.7(2)
C5	Fe1	C2	C3	81.63(16)	C6	Fe1	C2	C1	79.2(2)
C5	Fe1	C3	C2	-82.09(15)	C6	Fe1	C2	C3	-160.66(19)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5	Fe1	C3	C4	38.12(15)	C6	Fe1	C3	C2	51.3(4)
C5	Fe1	C4	C3	-118.8(2)	C6	Fe1	C3	C4	171.5(3)
C5	Fe1	C8	C9	44.0(4)	C6	Fe1	C4	C5	-53.0(4)
C5	Fe1	C8	C7	163.3(3)	C6	Fe1	C4	C3	-171.8(3)
C5	Fe1	C9	C8	-161.2(2)	C6	Fe1	C8	C9	-81.3(3)
C5	Fe1	C9	C10	78.9(3)	C6	Fe1	C8	C7	38.1(2)
C5	Fe1	C6	C10	-75.6(2)	C6	Fe1	C9	C8	81.6(3)
C5	Fe1	C6	C7	164.98(19)	C6	Fe1	C9	C10	-38.4(3)
C5	Fe1	C10	C9	-119.4(3)	C6	Fe1	C10	C9	117.7(4)
C5	Fe1	C10	C6	123.0(2)	C6	Fe1	C7	C8	-118.4(3)
C5	Fe1	C7	C8	-159.7(3)	C14	S1	N1	C12	-79.6(2)
C5	Fe1	C7	C6	-41.2(5)	C14	S1	N1	C13	85.6(2)
C5	C1	C2	Fe1	58.15(16)	C21	C16	C17	C18	-0.5(4)
C5	C1	C2	C3	-1.0(3)	C21	C20	C19	C18	1.5(5)
C22	C15	C16	C17	86.4(3)	C10	Fe1	C1	C11	-35.2(3)
C22	C15	C16	C21	-91.7(3)	C10	Fe1	C1	C5	77.3(2)
C22	C23	C24	C25	0.8(4)	C10	Fe1	C1	C2	-164.15(19)
C22	C27	C26	C25	0.4(4)	C10	Fe1	C5	C1	-121.80(16)
C2	Fe1	C1	C11	128.9(3)	C10	Fe1	C5	C13	-4.1(2)
C2	Fe1	C1	C5	-118.52(18)	C10	Fe1	C5	C4	118.74(18)
C2	Fe1	C5	C1	38.14(12)	C10	Fe1	C2	C1	43.4(4)
C2	Fe1	C5	C13	155.9(2)	C10	Fe1	C2	C3	163.5(4)
C2	Fe1	C5	C4	-81.32(16)	C10	Fe1	C3	C2	-165.7(3)
C2	Fe1	C3	C4	120.2(2)	C10	Fe1	C3	C4	-45.4(4)
C2	Fe1	C4	C5	82.00(15)	C10	Fe1	C4	C5	-79.68(19)
C2	Fe1	C4	C3	-36.82(14)	C10	Fe1	C4	C3	161.49(16)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	Fe1	C8	C9	160.5(2)	C10	Fe1	C8	C9	-37.5(3)
C2	Fe1	C8	C7	-80.2(2)	C10	Fe1	C8	C7	81.8(2)
C2	Fe1	C9	C8	-47.3(5)	C10	Fe1	C9	C8	119.9(4)
C2	Fe1	C9	C10	-167.3(3)	C10	Fe1	C6	C7	-119.4(3)
C2	Fe1	C6	C10	-162.57(17)	C10	Fe1	C7	C8	-81.0(2)
C2	Fe1	C6	C7	78.0(2)	C10	Fe1	C7	C6	37.4(2)
C2	Fe1	C10	C9	165.4(3)	C10	C6	C7	Fe1	-59.7(2)
C2	Fe1	C10	C6	47.7(5)	C10	C6	C7	C8	0.9(4)
C2	Fe1	C7	C8	119.4(2)	C19	C20	C21	C16	-1.2(5)
C2	Fe1	C7	C6	-122.1(2)	C7	Fe1	C1	C11	49.9(3)
C2	C1	C5	Fe1	-58.55(15)	C7	Fe1	C1	C5	162.42(17)
C2	C1	C5	C13	177.9(2)	C7	Fe1	C1	C2	-79.1(2)
C2	C1	C5	C4	0.8(3)	C7	Fe1	C5	C1	-49.7(4)
C2	C3	C4	Fe1	59.05(18)	C7	Fe1	C5	C13	68.0(4)
C2	C3	C4	C5	-0.3(3)	C7	Fe1	C5	C4	-169.2(3)
C13	N1	C12	C11	65.5(3)	C7	Fe1	C2	C1	121.38(18)
C13	C5	C4	Fe1	123.1(3)	C7	Fe1	C2	C3	-118.5(2)
C13	C5	C4	C3	-177.3(2)	C7	Fe1	C3	C2	81.0(2)
C16	C15	C22	C23	-108.0(2)	C7	Fe1	C3	C4	-158.81(18)
C16	C15	C22	C27	71.4(3)	C7	Fe1	C4	C5	170.9(3)
C16	C17	C18	C19	0.9(5)	C7	Fe1	C4	C3	52.1(4)
C3	Fe1	C1	C11	165.8(2)	C7	Fe1	C8	C9	-119.4(3)
C3	Fe1	C1	C5	-81.67(14)	C7	Fe1	C9	C8	37.6(2)
C3	Fe1	C1	C2	36.85(14)	C7	Fe1	C9	C10	-82.3(3)
C3	Fe1	C5	C1	81.43(14)	C7	Fe1	C6	C10	119.4(3)
C3	Fe1	C5	C13	-160.8(2)	C7	Fe1	C10	C9	80.1(3)

Table S19. Torsion Angles for (*Rp*)-**3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	Fe1	C5	C4	-38.03(16)	C7	Fe1	C10	C6	-37.5(2)
C3	Fe1	C2	C1	-120.1(2)	C7	C8	C9	Fe1	-59.0(2)
C3	Fe1	C4	C5	118.8(2)	C7	C8	C9	C10	0.2(4)
C3	Fe1	C8	C9	119.5(2)	C7	C6	C10	Fe1	59.6(2)
C3	Fe1	C8	C7	-121.1(2)	C7	C6	C10	C9	-0.8(4)
C3	Fe1	C9	C8	-77.9(3)					

Table S20. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*Rp*)-**3a**.

Atom	*x*	*y*	*z*	U(eq)
H12A	6090	7494	5350	59
H12B	7013	6937	5813	59
H2	2059	7813	6397	58
H13A	4334	4363	5111	65
H13B	4581	5785	4842	65
H3	255	6635	5862	70
H4	1462	5189	5184	68
H23	4369	6941	7254	74
H8	292	4009	6657	105
H27	4105	10612	6582	75
H17	7651	7494	6944	78
H18	9849	8480	6983	92
H24	2865	7678	7914	91
H20	8616	11398	6012	94
H9	1510	2656	5980	101
H25	1947	9837	7890	94
H6	4439	4467	6876	107

Table S20. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*Rp*)-**3a**.

Atom	*x*	*y*	*z*	U(eq)
H21	6419	10438	5972	78
H10	4091	2936	6103	101
H19	10311	10450	6535	92
H26	2581	11308	7233	91
H7	2094	5161	7209	110

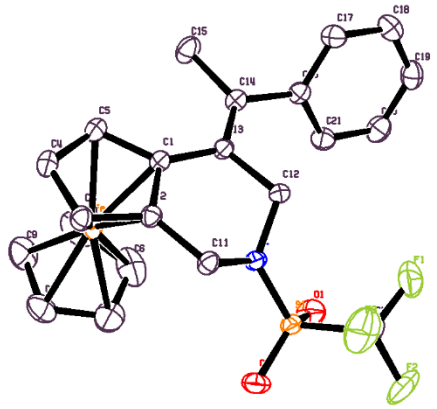


Table 21. Crystal data and structure refinement for 3f.

Identification code	**3f**
CCDC Number	2402043
Empirical formula	$C_{44}H_{40}F_6Fe_2N_2O_4S_2$
Formula weight	950.60
Temperature/K	103(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6500(6)
b/Å	10.5668(6)
c/Å	11.6109(8)
α/°	89.893(2)
β/°	69.144(2)

γ/°	67.203(2)
Volume/Å^3	1007.15(11)
Z	1
ρ_{calc}g/cm^3	1.567
μ/mm^{-1}	0.899
F(000)	488.0
Crystal size/mm^3	0.051 × 0.035 × 0.024
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.962 to 60.078
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	64227
Independent reflections	5806 [R_{int} = 0.0466, R_{sigma} = 0.0215]
Data/restraints/parameters	5806/0/351
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0749
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0788
Largest diff. peak/hole / e Å^{-3}	0.84/-0.40

Table 22. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3f. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Fe1	8064.7(2)	2551.0(2)	1753.7(2)	17.93(6)
S1	4684.9(3)	7020.2(3)	1924.0(3)	16.97(7)
F1	5179.8(15)	9279.9(10)	1619.0(12)	43.5(3)
F2	2983.7(14)	9416.7(11)	1448.0(13)	50.6(3)
F3	5306.9(16)	8239.6(12)	-32.8(10)	46.9(3)
O1	4086.1(12)	7502.2(11)	3224.7(9)	26.7(2)
O2	3888.8(12)	6418.7(11)	1420.2(11)	26.9(2)

Table 22. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3f. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	6570.0(12)	6052.6(10)	1409.3(10)	15.15(18)
C1	9300.8(14)	3800.2(12)	1364.5(11)	15.4(2)
C2	8592.2(14)	3774.1(12)	468.7(11)	15.0(2)
C3	9231.1(15)	2383.2(13)	-135.9(12)	17.8(2)
C4	10340.7(16)	1525.3(13)	381.5(13)	20.8(2)
C5	10378.7(16)	2381.6(13)	1310.4(13)	20.6(2)
C6	6111(2)	3497.4(19)	3398.9(15)	38.2(4)
C7	5589.7(19)	3186.6(17)	2483.7(17)	33.1(3)
C8	6387(2)	1724.7(17)	2083.3(15)	29.5(3)
C9	7397(2)	1130.9(17)	2745.2(16)	32.5(3)
C10	7227(3)	2230(2)	3566.6(15)	38.4(4)
C11	7390.7(15)	5050.2(12)	244.9(11)	16.2(2)
C12	7670.2(15)	6379.7(12)	1852.1(12)	16.5(2)
C13	8839.8(14)	5104.1(12)	2151.5(11)	15.0(2)
C14	9473.8(15)	5259.9(12)	2979.5(11)	16.4(2)
C15	10818.7(18)	4080.9(14)	3206.0(14)	24.3(3)
C16	8927.7(15)	6636.5(12)	3723.7(11)	16.4(2)
C17	10057.3(16)	7196.2(14)	3605.7(13)	21.3(2)
C18	9602.6(18)	8455.3(15)	4316.2(14)	25.5(3)
C19	8010.0(19)	9170.4(14)	5161.6(13)	25.3(3)
C20	6876.7(17)	8624.7(15)	5295.8(13)	24.3(3)
C21	7329.9(16)	7361.8(14)	4585.7(12)	20.2(2)
C22	4523(2)	8587.8(15)	1200.8(16)	30.6(3)

Table 23. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	21.42(10)	16.36(9)	17.77(10)	4.85(6)	-7.41(7)	-9.73(7)
S1	12.48(13)	15.56(13)	20.52(14)	-0.55(10)	-6.69(11)	-3.13(10)
F1	58.9(7)	23.5(4)	67.4(7)	17.6(5)	-39.9(6)	-22.1(5)
F2	42.8(6)	25.6(5)	78.3(8)	5.4(5)	-40.4(6)	6.5(4)
F3	64.2(7)	40.1(6)	36.2(5)	20.6(5)	-26.2(5)	-15.2(5)
O1	20.5(5)	28.3(5)	21.5(5)	-4.5(4)	-2.8(4)	-5.0(4)
O2	16.4(4)	26.4(5)	37.8(6)	-4.6(4)	-12.1(4)	-7.1(4)
N1	12.5(4)	14.9(4)	16.8(4)	-0.3(3)	-6.8(4)	-3.4(3)
C1	14.0(5)	14.1(5)	17.2(5)	2.6(4)	-6.3(4)	-4.7(4)
C2	14.2(5)	14.3(5)	14.7(5)	2.2(4)	-4.3(4)	-5.2(4)
C3	17.5(5)	16.0(5)	17.5(5)	0.2(4)	-5.0(4)	-6.1(4)
C4	21.0(6)	13.7(5)	25.4(6)	1.3(4)	-9.5(5)	-4.3(4)
C5	19.4(6)	15.0(5)	26.8(6)	3.1(4)	-11.9(5)	-3.9(4)
C6	43.2(9)	36.8(8)	25.2(7)	-0.8(6)	6.6(7)	-25.1(7)
C7	22.7(7)	31.7(7)	39.5(8)	11.6(6)	-2.3(6)	-14.5(6)
C8	32.8(7)	32.4(7)	32.1(7)	11.3(6)	-11.6(6)	-23.0(6)
C9	43.2(9)	30.0(7)	32.9(8)	17.6(6)	-15.3(7)	-23.4(7)
C10	55.0(11)	54.0(10)	21.8(7)	16.0(7)	-14.8(7)	-38.1(9)
C11	16.2(5)	15.3(5)	14.9(5)	0.4(4)	-6.8(4)	-3.7(4)
C12	15.3(5)	14.7(5)	22.0(6)	2.9(4)	-10.6(4)	-5.5(4)
C13	13.5(5)	13.7(5)	16.3(5)	2.4(4)	-5.5(4)	-4.5(4)
C14	15.6(5)	16.1(5)	16.5(5)	2.5(4)	-6.3(4)	-5.2(4)
C15	26.9(7)	20.2(6)	25.1(6)	2.6(5)	-16.5(6)	-3.2(5)
C16	17.6(5)	17.5(5)	14.3(5)	2.7(4)	-7.6(4)	-6.2(4)
C17	18.6(6)	24.1(6)	21.1(6)	1.9(5)	-7.2(5)	-9.2(5)
C18	29.5(7)	25.3(6)	27.4(7)	3.2(5)	-12.2(6)	-15.8(6)

Table 23. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	32.4(7)	18.8(6)	23.3(6)	-0.3(5)	-10.8(5)	-9.0(5)
C20	22.7(6)	22.7(6)	20.0(6)	-0.3(5)	-5.2(5)	-4.6(5)
C21	18.8(6)	22.8(6)	18.4(5)	2.7(4)	-6.1(5)	-9.2(5)
C22	34.5(8)	19.2(6)	40.8(8)	7.8(6)	-24.5(7)	-4.6(5)

Table 24. Bond Lengths for 3f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	C1	2.0502(12)	C1	C13	1.4737(16)
Fe1	C2	2.0291(12)	C2	C3	1.4235(16)
Fe1	C3	2.0495(13)	C2	C11	1.4938(16)
Fe1	C4	2.0511(13)	C3	C4	1.4258(18)
Fe1	C5	2.0385(13)	C4	C5	1.4286(18)
Fe1	C6	2.0458(16)	C6	C7	1.414(3)
Fe1	C7	2.0473(16)	C6	C10	1.422(3)
Fe1	C8	2.0455(15)	C7	C8	1.422(2)
Fe1	C9	2.0511(14)	C8	C9	1.411(2)
Fe1	C10	2.0488(15)	C9	C10	1.425(2)
S1	O1	1.4239(10)	C12	C13	1.5199(16)
S1	O2	1.4269(10)	C13	C14	1.3501(17)
S1	N1	1.5807(10)	C14	C15	1.5148(17)
S1	C22	1.8334(15)	C14	C16	1.4922(17)
F1	C22	1.3234(19)	C16	C17	1.3963(18)
F2	C22	1.3212(18)	C16	C21	1.3982(17)
F3	C22	1.332(2)	C17	C18	1.3918(19)
N1	C11	1.4731(15)	C18	C19	1.387(2)
N1	C12	1.4781(15)	C19	C20	1.386(2)

Table 24. Bond Lengths for 3f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.4393(16)	C20	C21	1.3953(19)
C1	C5	1.4417(16)			

Table 25. Bond Angles for 3f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Fe1	C4	69.12(5)	C2	C1	C13	121.40(10)
C1	Fe1	C9	151.51(6)	C5	C1	Fe1	68.92(7)
C2	Fe1	C1	41.32(5)	C5	C1	C13	132.17(11)
C2	Fe1	C3	40.85(5)	C13	C1	Fe1	125.28(8)
C2	Fe1	C4	68.52(5)	C1	C2	Fe1	70.13(7)
C2	Fe1	C5	69.10(5)	C1	C2	C11	123.00(10)
C2	Fe1	C6	117.47(6)	C3	C2	Fe1	70.34(7)
C2	Fe1	C7	107.56(6)	C3	C2	C1	109.30(10)
C2	Fe1	C8	128.33(6)	C3	C2	C11	127.69(11)
C2	Fe1	C9	166.43(6)	C11	C2	Fe1	126.19(8)
C2	Fe1	C10	151.26(6)	C2	C3	Fe1	68.81(7)
C3	Fe1	C1	69.44(5)	C2	C3	C4	107.44(11)
C3	Fe1	C4	40.69(5)	C4	C3	Fe1	69.71(8)
C3	Fe1	C9	128.64(6)	C3	C4	Fe1	69.59(7)
C4	Fe1	C9	108.88(6)	C3	C4	C5	108.54(11)
C5	Fe1	C1	41.29(5)	C5	C4	Fe1	69.08(8)
C5	Fe1	C3	69.06(5)	C1	C5	Fe1	69.79(7)
C5	Fe1	C4	40.89(5)	C4	C5	Fe1	70.03(8)
C5	Fe1	C6	127.07(7)	C4	C5	C1	108.31(11)
C5	Fe1	C7	165.07(6)	C7	C6	Fe1	69.85(9)
C5	Fe1	C8	152.48(6)	C7	C6	C10	108.10(15)

Table 25. Bond Angles for 3f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	Fe1	C9	118.30(6)	C10	C6	Fe1	69.79(9)
C5	Fe1	C10	107.33(7)	C6	C7	Fe1	69.73(10)
C6	Fe1	C1	106.28(6)	C6	C7	C8	107.76(16)
C6	Fe1	C3	151.69(7)	C8	C7	Fe1	69.60(9)
C6	Fe1	C4	165.87(7)	C7	C8	Fe1	69.74(9)
C6	Fe1	C7	40.42(8)	C9	C8	Fe1	70.06(9)
C6	Fe1	C9	68.39(7)	C9	C8	C7	108.56(15)
C6	Fe1	C10	40.65(8)	C8	C9	Fe1	69.63(8)
C7	Fe1	C1	126.74(6)	C8	C9	C10	107.65(15)
C7	Fe1	C3	118.59(6)	C10	C9	Fe1	69.57(9)
C7	Fe1	C4	152.82(7)	C6	C10	Fe1	69.56(9)
C7	Fe1	C9	68.28(7)	C6	C10	C9	107.93(16)
C7	Fe1	C10	68.19(8)	C9	C10	Fe1	69.75(9)
C8	Fe1	C1	165.71(6)	N1	C11	C2	106.47(9)
C8	Fe1	C3	108.86(6)	N1	C12	C13	112.09(10)
C8	Fe1	C4	119.46(6)	C1	C13	C12	113.58(10)
C8	Fe1	C6	68.10(7)	C14	C13	C1	126.41(11)
C8	Fe1	C7	40.65(7)	C14	C13	C12	119.65(10)
C8	Fe1	C9	40.31(7)	C13	C14	C15	123.49(11)
C8	Fe1	C10	68.00(7)	C13	C14	C16	122.07(11)
C10	Fe1	C1	116.95(6)	C16	C14	C15	114.41(10)
C10	Fe1	C3	166.60(7)	C17	C16	C14	119.40(11)
C10	Fe1	C4	128.38(7)	C17	C16	C21	118.44(12)
C10	Fe1	C9	40.68(7)	C21	C16	C14	122.10(11)
O1	S1	O2	121.70(7)	C18	C17	C16	120.93(12)
O1	S1	N1	110.52(6)	C19	C18	C17	120.07(13)

Table 25. Bond Angles for 3f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	C22	104.26(7)	C20	C19	C18	119.71(13)
O2	S1	N1	109.57(6)	C19	C20	C21	120.33(13)
O2	S1	C22	104.05(7)	C20	C21	C16	120.51(12)
N1	S1	C22	105.14(7)	F1	C22	S1	110.53(10)
C11	N1	S1	121.92(8)	F1	C22	F3	108.39(15)
C11	N1	C12	114.94(9)	F2	C22	S1	110.87(12)
C12	N1	S1	120.89(8)	F2	C22	F1	108.62(13)
C2	C1	Fe1	68.56(7)	F2	C22	F3	108.43(13)
C2	C1	C5	106.39(10)	F3	C22	S1	109.93(10)

Table 26. Hydrogen Bonds for 3f.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C11	H11B	O2	0.913(19)	2.421(18)	2.8828(15)	111.4(13)
C11	H11B	O2[1]	0.913(19)	2.496(19)	3.2966(16)	146.6(15)
C12	H12A	O1	0.916(18)	2.513(18)	2.9685(16)	111.2(13)

[1]1-X,1-Y,-Z

Table 27. Torsion Angles for 3f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	C1	C2	C3	-59.63(8)	C3	C4	C5	Fe1	58.54(9)
Fe1	C1	C2	C11	120.93(11)	C3	C4	C5	C1	-0.97(15)
Fe1	C1	C5	C4	59.66(9)	C5	C1	C2	Fe1	58.78(8)
Fe1	C1	C13	C12	-88.71(12)	C5	C1	C2	C3	-0.85(14)
Fe1	C1	C13	C14	98.37(14)	C5	C1	C2	C11	179.71(11)
Fe1	C2	C3	C4	-59.23(9)	C5	C1	C13	C12	178.64(13)
Fe1	C2	C11	N1	62.36(13)	C5	C1	C13	C14	5.7(2)

Table 27. Torsion Angles for 3f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	C3	C4	C5	-58.22(10)	C6	C7	C8	Fe1	-59.52(10)
Fe1	C4	C5	C1	-59.51(9)	C6	C7	C8	C9	-0.01(17)
Fe1	C6	C7	C8	59.44(10)	C7	C6	C10	Fe1	59.57(11)
Fe1	C6	C10	C9	-59.41(11)	C7	C6	C10	C9	0.16(18)
Fe1	C7	C8	C9	59.51(11)	C7	C8	C9	Fe1	-59.32(10)
Fe1	C8	C9	C10	59.42(11)	C7	C8	C9	C10	0.10(17)
Fe1	C9	C10	C6	59.29(11)	C8	C9	C10	Fe1	-59.45(11)
S1	N1	C11	C2	-140.89(9)	C8	C9	C10	C6	-0.16(18)
S1	N1	C12	C13	134.89(9)	C10	C6	C7	Fe1	-59.53(11)
O1	S1	N1	C11	159.04(10)	C10	C6	C7	C8	-0.09(17)
O1	S1	N1	C12	-38.89(11)	C11	N1	C12	C13	-61.86(13)
O1	S1	C22	F1	49.65(13)	C11	C2	C3	Fe1	-121.09(12)
O1	S1	C22	F2	-70.86(12)	C11	C2	C3	C4	179.68(12)
O1	S1	C22	F3	169.27(11)	C12	N1	C11	C2	56.05(13)
O2	S1	N1	C11	22.28(12)	C12	C13	C14	C15	-171.24(12)
O2	S1	N1	C12	-175.65(10)	C12	C13	C14	C16	6.87(18)
O2	S1	C22	F1	178.15(11)	C13	C1	C2	Fe1	-119.16(11)
O2	S1	C22	F2	57.64(13)	C13	C1	C2	C3	-178.79(11)
O2	S1	C22	F3	-62.23(12)	C13	C1	C2	C11	1.77(18)
N1	S1	C22	F1	-66.67(13)	C13	C1	C5	Fe1	119.08(14)
N1	S1	C22	F2	172.82(11)	C13	C1	C5	C4	178.74(13)
N1	S1	C22	F3	52.95(12)	C13	C14	C16	C17	-119.96(14)
N1	C12	C13	C1	31.66(14)	C13	C14	C16	C21	63.14(17)
N1	C12	C13	C14	-154.89(11)	C14	C16	C17	C18	-177.84(12)
C1	C2	C3	Fe1	59.50(8)	C14	C16	C21	C20	177.82(12)
C1	C2	C3	C4	0.27(14)	C15	C14	C16	C17	58.31(16)

Table 27. Torsion Angles for 3f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C11	N1	-26.10(15)	C15	C14	C16	C21	-118.59(14)
C1	C13	C14	C15	1.3(2)	C16	C17	C18	C19	0.3(2)
C1	C13	C14	C16	179.40(11)	C17	C16	C21	C20	0.90(19)
C2	C1	C5	Fe1	-58.55(8)	C17	C18	C19	C20	0.1(2)
C2	C1	C5	C4	1.11(14)	C18	C19	C20	C21	0.0(2)
C2	C1	C13	C12	-4.03(16)	C19	C20	C21	C16	-0.5(2)
C2	C1	C13	C14	-176.96(12)	C21	C16	C17	C18	-0.83(19)
C2	C3	C4	Fe1	58.66(8)	C22	S1	N1	C11	-89.01(11)
C2	C3	C4	C5	0.44(15)	C22	S1	N1	C12	73.06(11)
C3	C2	C11	N1	154.57(12)					

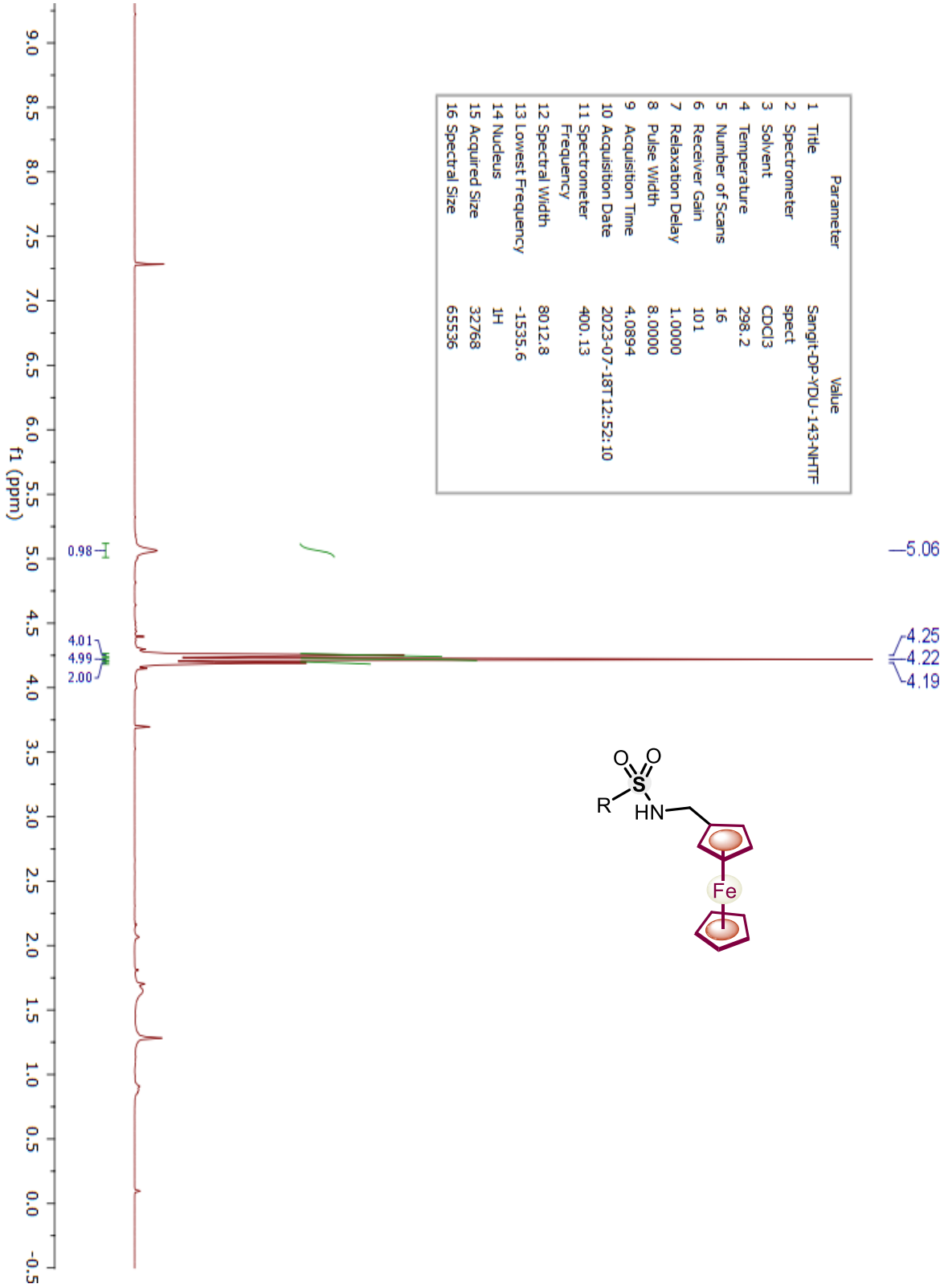
Table 28. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3f.

Atom	*x*	*y*	*z*	U(eq)
H3	8960(20)	2051(18)	-760(17)	22(4)
H4	10920(20)	553(19)	173(16)	21(4)
H5	10980(20)	2020(18)	1841(17)	23(4)
H6	5870(30)	4380(20)	3790(20)	42(6)
H7	4880(30)	3840(20)	2180(20)	46(6)
H8	6260(20)	1230(20)	1447(19)	32(5)
H9	8100(30)	170(20)	2640(20)	37(5)
H10	7850(30)	2080(30)	4040(20)	55(7)
H11A	7911(19)	5443(17)	-449(15)	15(4)
H11B	6630(20)	4865(18)	65(17)	23(4)
H12A	7030(20)	7072(19)	2527(17)	21(4)
H12B	8280(20)	6718(19)	1216(17)	24(4)
H15A	10350(20)	3470(20)	3654(18)	30(5)

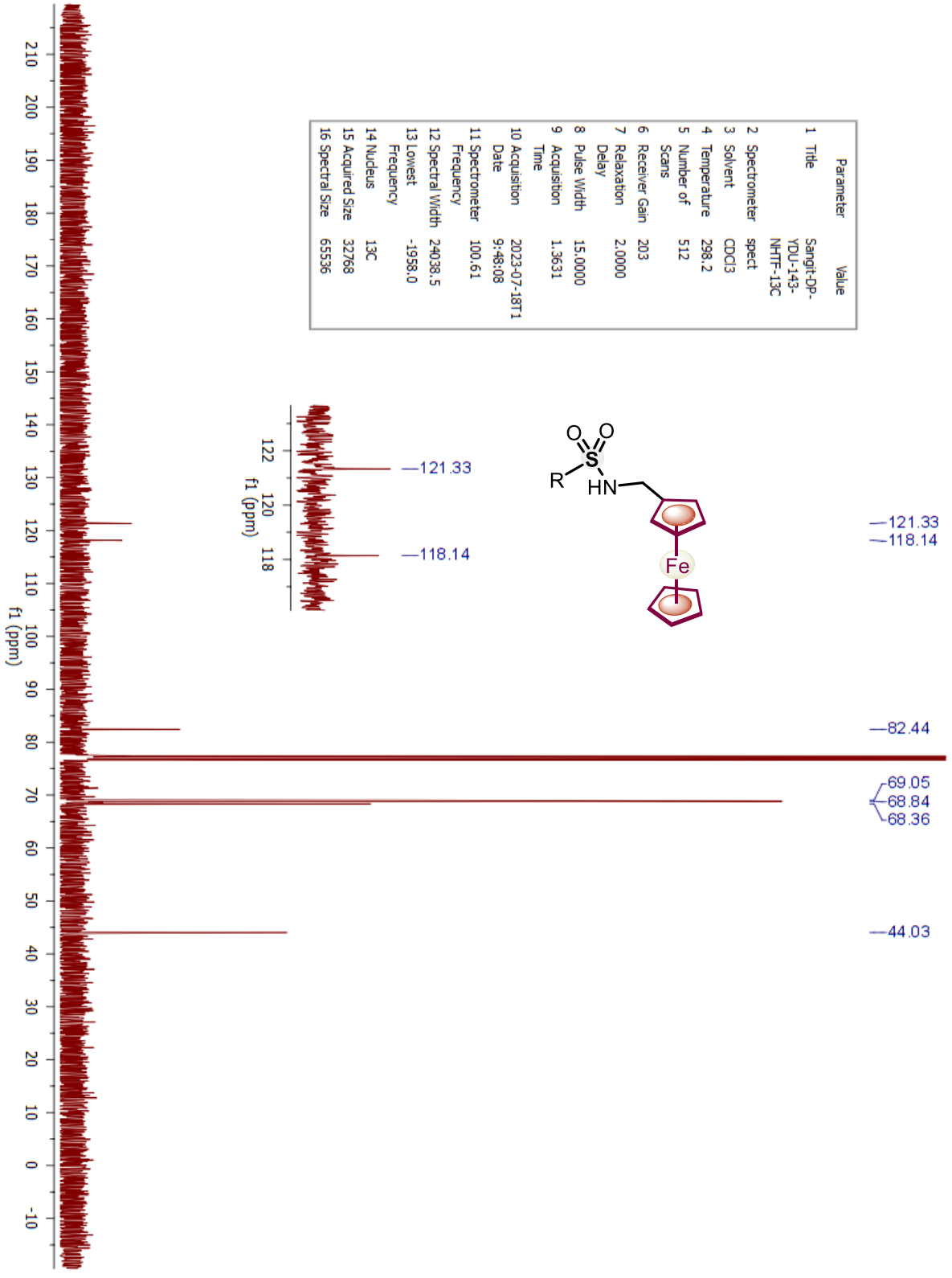
Table 28. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3f.

Atom	*x*	*y*	*z*	U(eq)
H15B	11780(20)	3530(20)	2429(19)	30(5)
H15C	11240(30)	4470(30)	3720(20)	56(7)
H17	11180(20)	6688(19)	3004(17)	23(4)
H18	10390(20)	8820(20)	4193(18)	30(5)
H19	7700(20)	10020(20)	5621(18)	30(5)
H20	5800(20)	9080(20)	5884(19)	32(5)
H21	6610(20)	6930(20)	4700(18)	31(5)

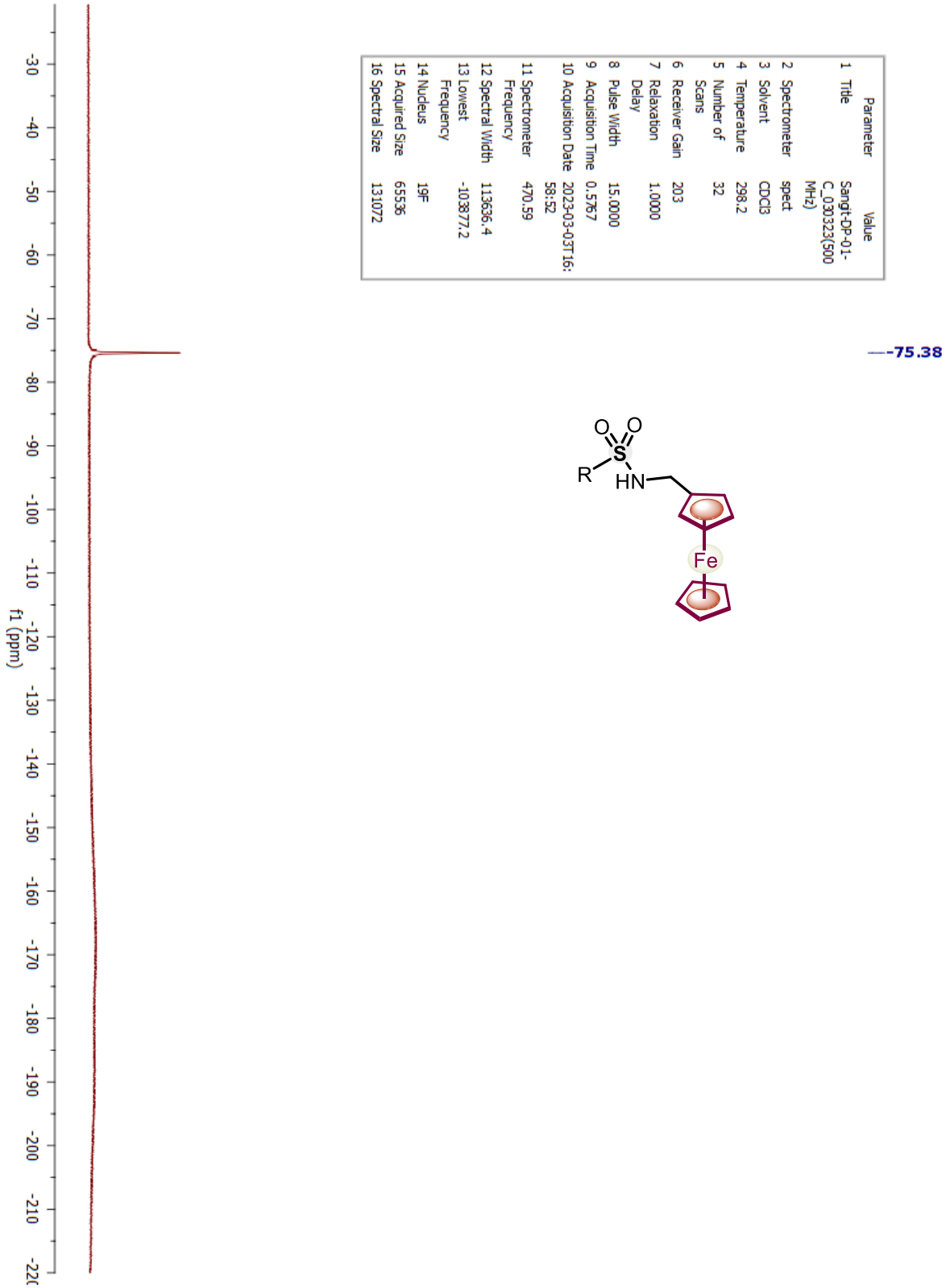
^{1}H NMR Spectrum of **1a**



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

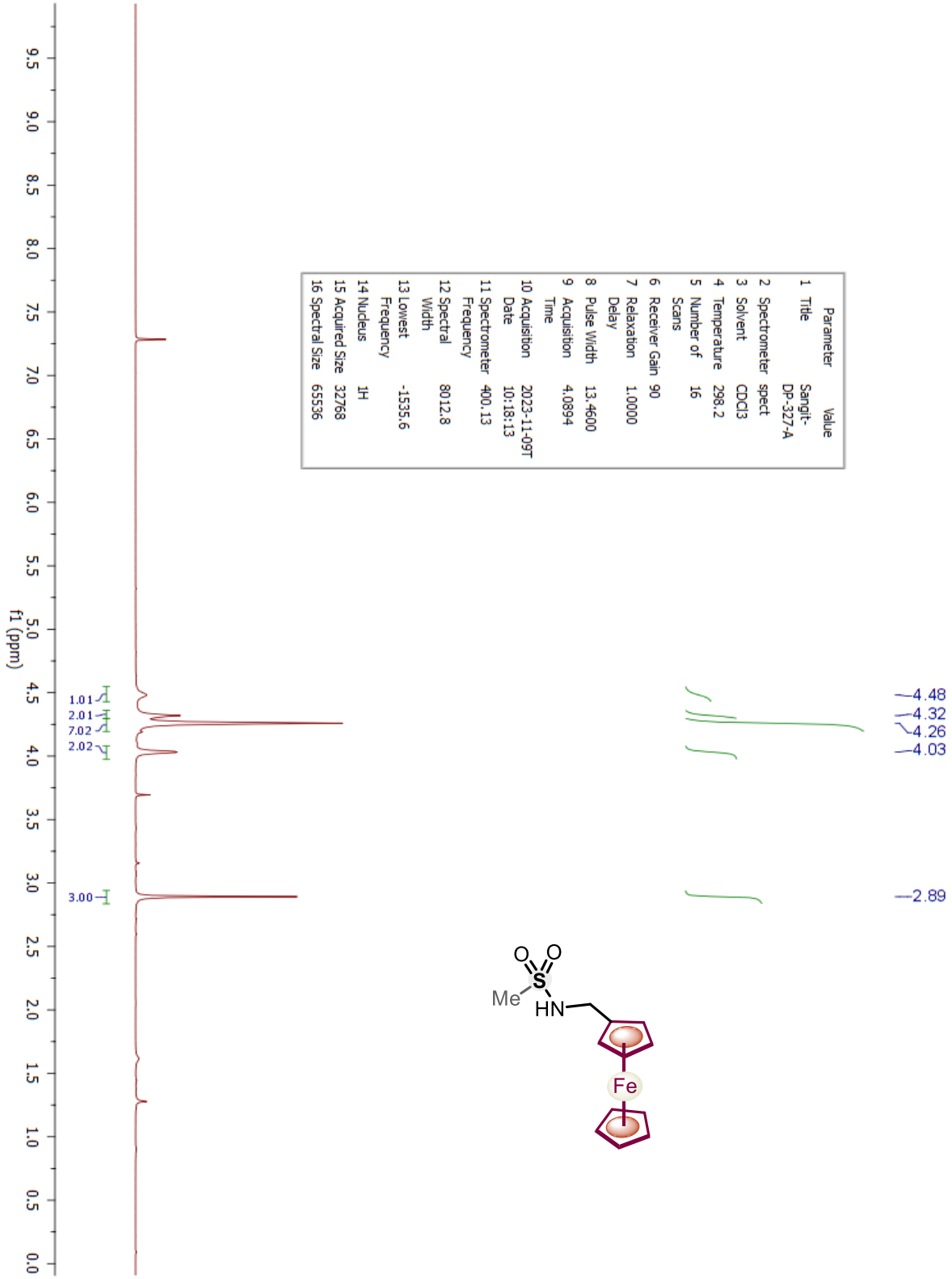


^{19}F NMR spectrum of **1a**

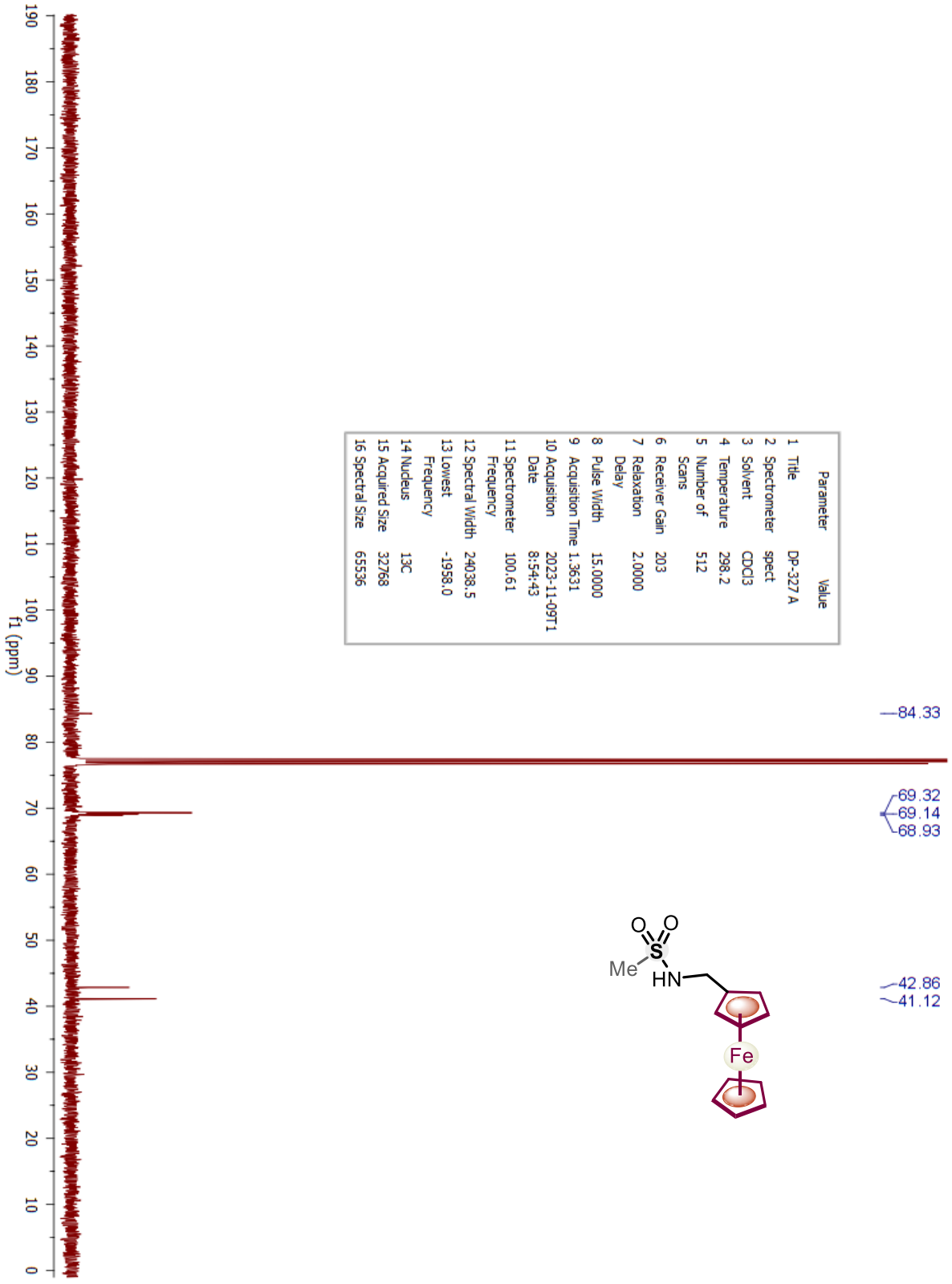


	Parameter	Value
1	Title	Sangit-DP-01-C_030323(500 MHz)
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Number of Scans	32
6	Receiver Gain	203
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Acquisition Time	0.5767
10	Acquisition Date	2023-03-03T16:58:52
11	Spectrometer Frequency	470.59
12	Spectral Width	113636.4
13	Lowest Frequency	-103877.2
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

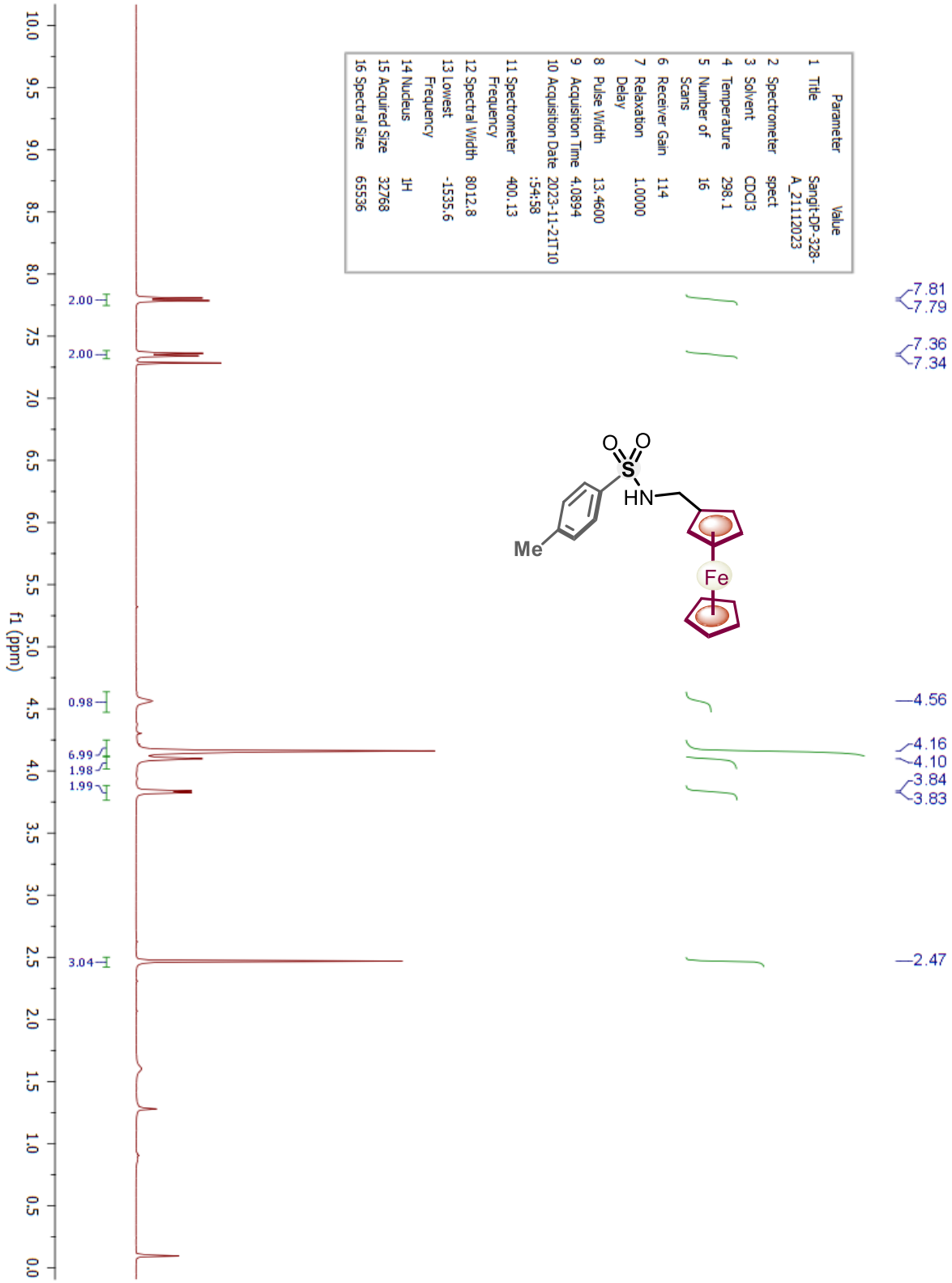
^{1}H NMR Spectrum of **1b**



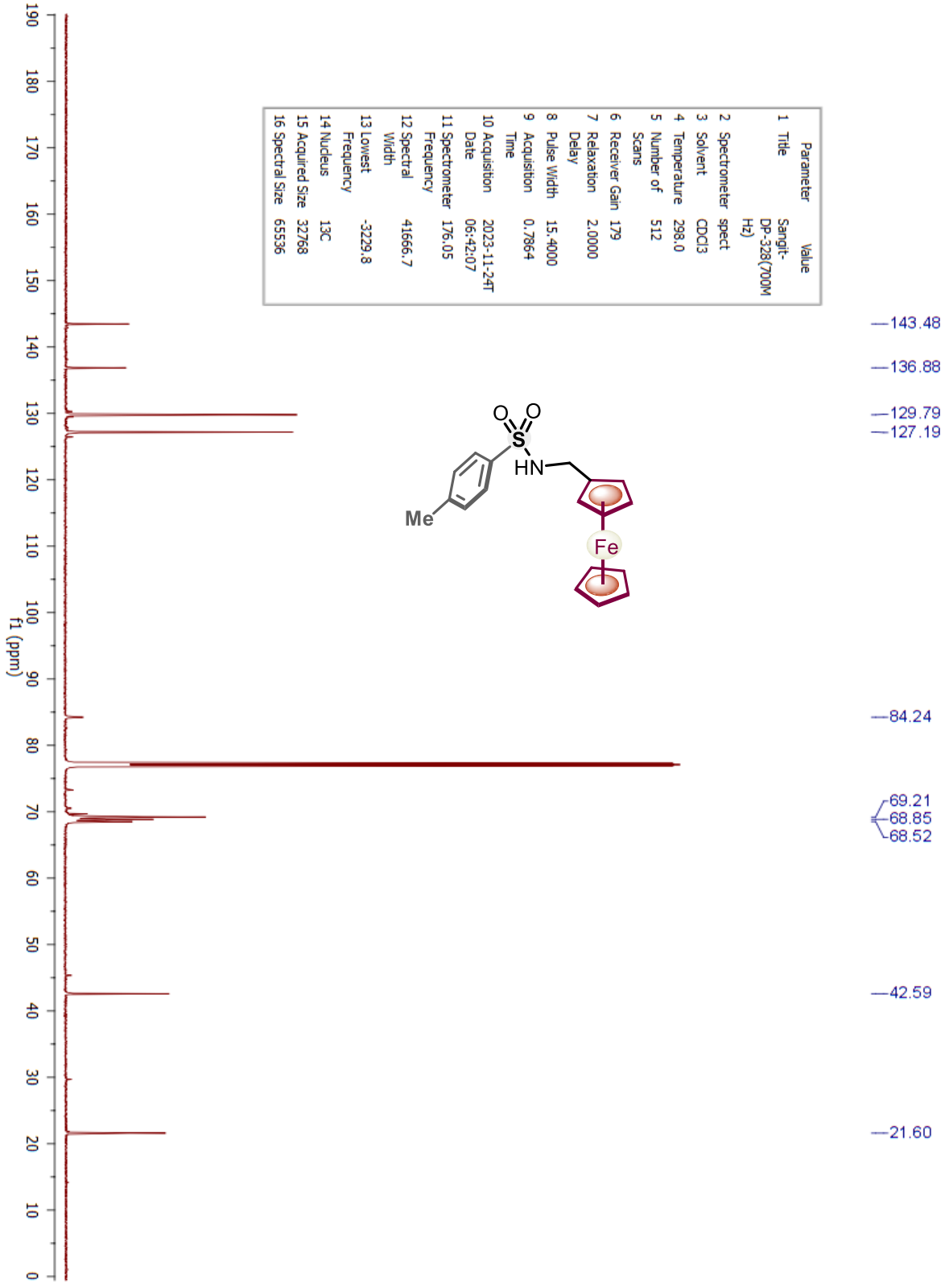
$^{13}C\{^{1}H\}$ NMR Spectrum of **1b**



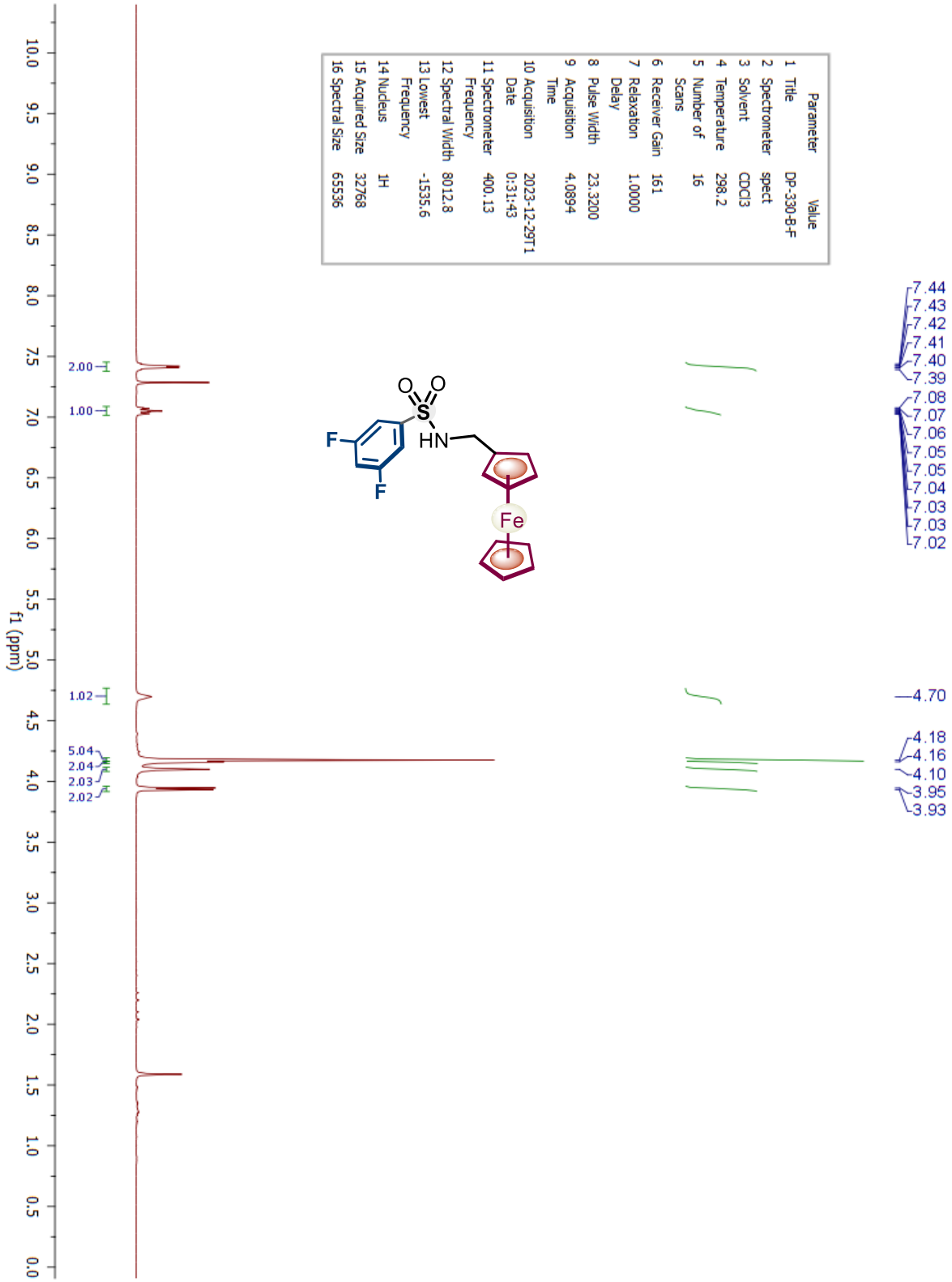
^{1}H NMR Spectrum of **1c**



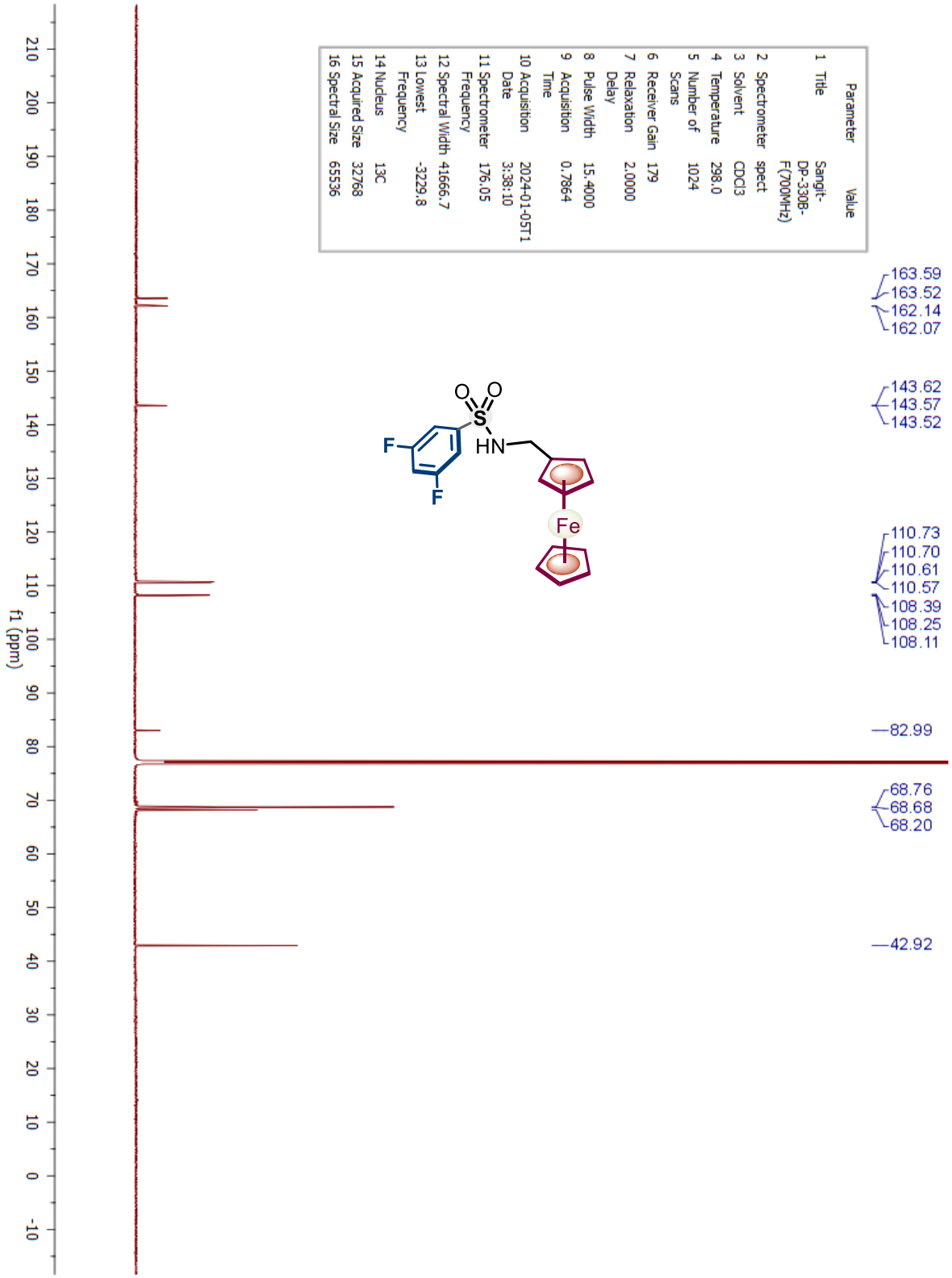
$^{13}C\{^{1}H\}$ NMR Spectrum of **1c**



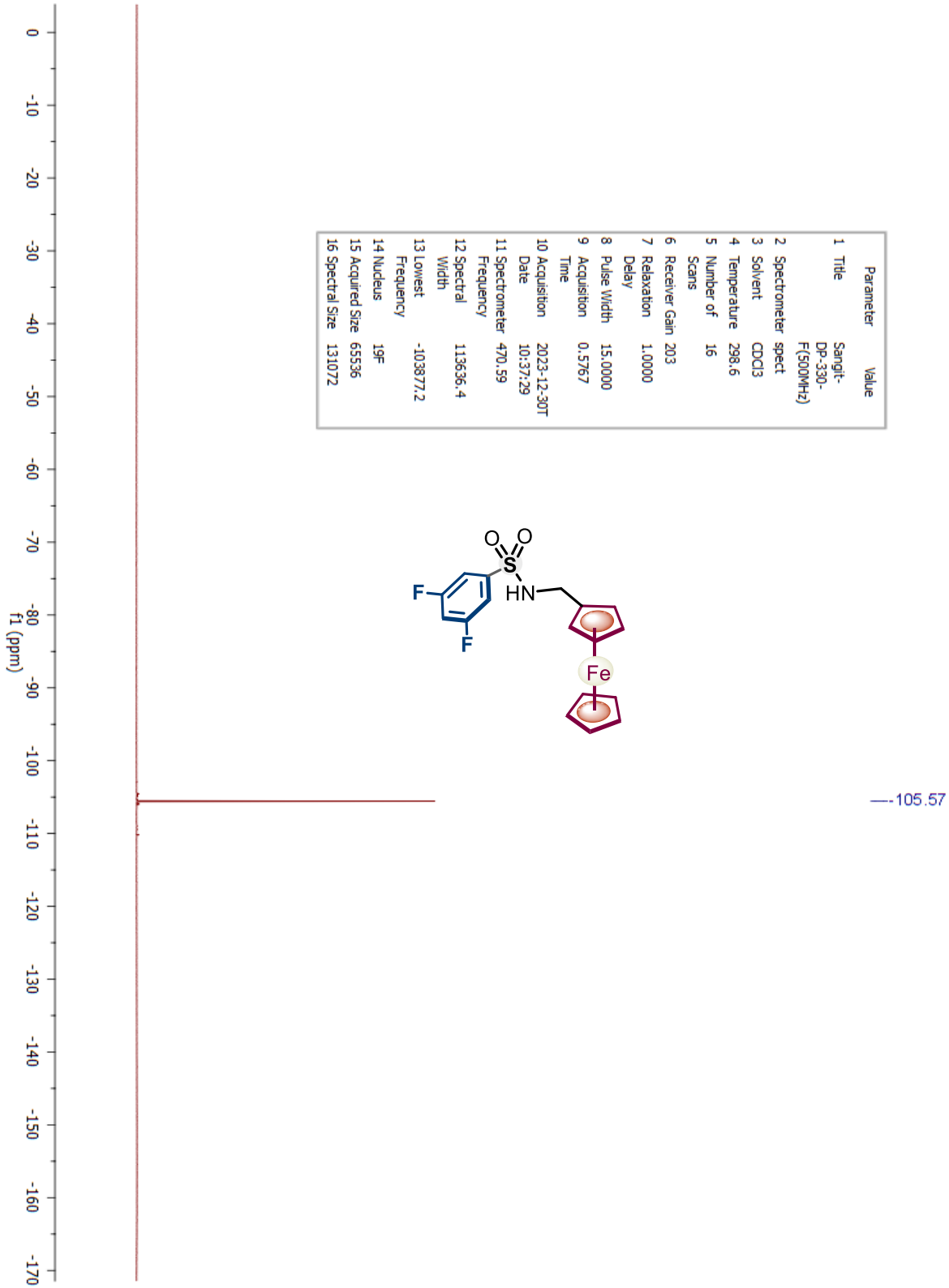
^{1}H NMR Spectrum of **1d**



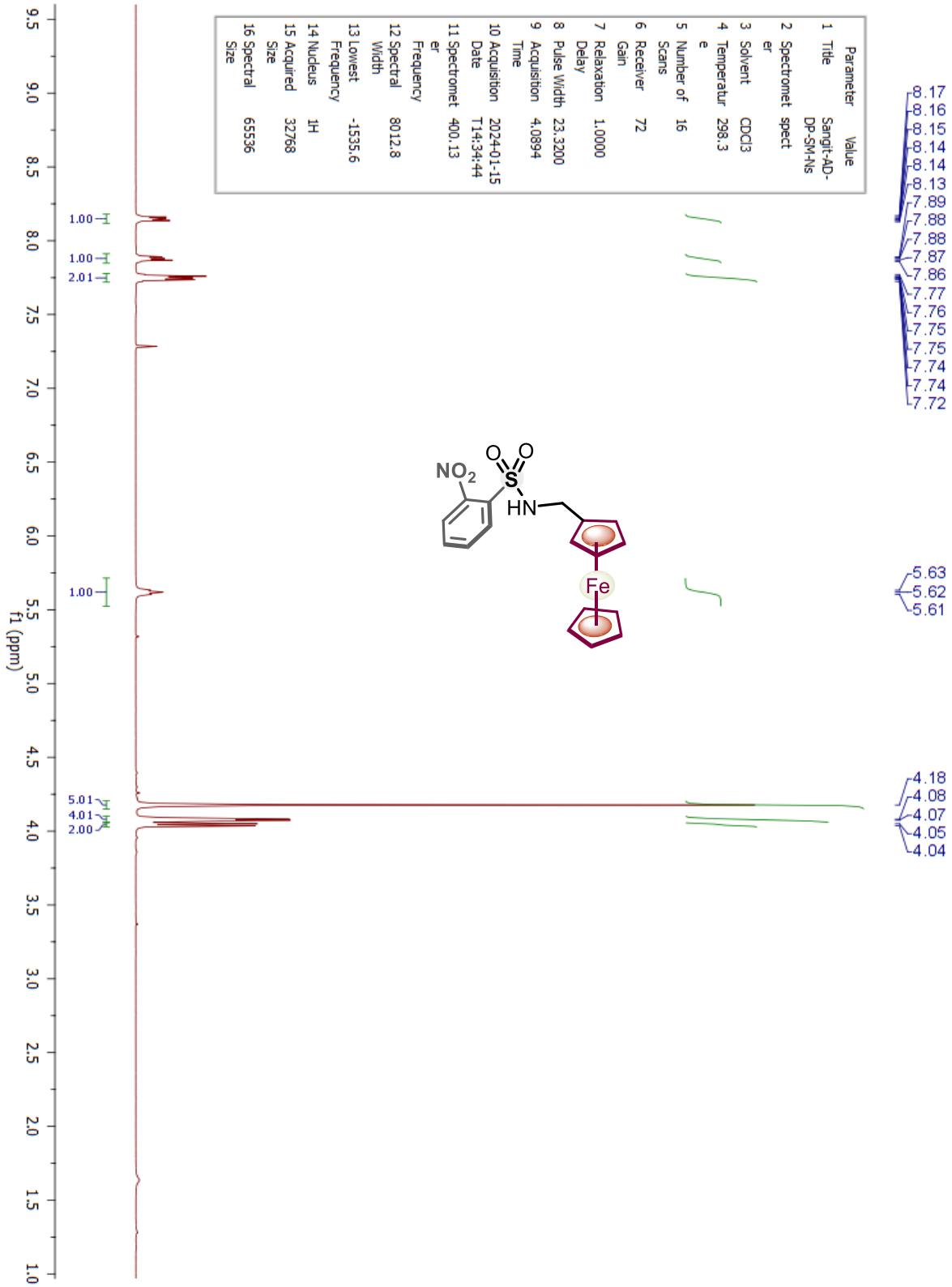
$^{13}C\{^{1}H\}$ NMR Spectrum of **1d**



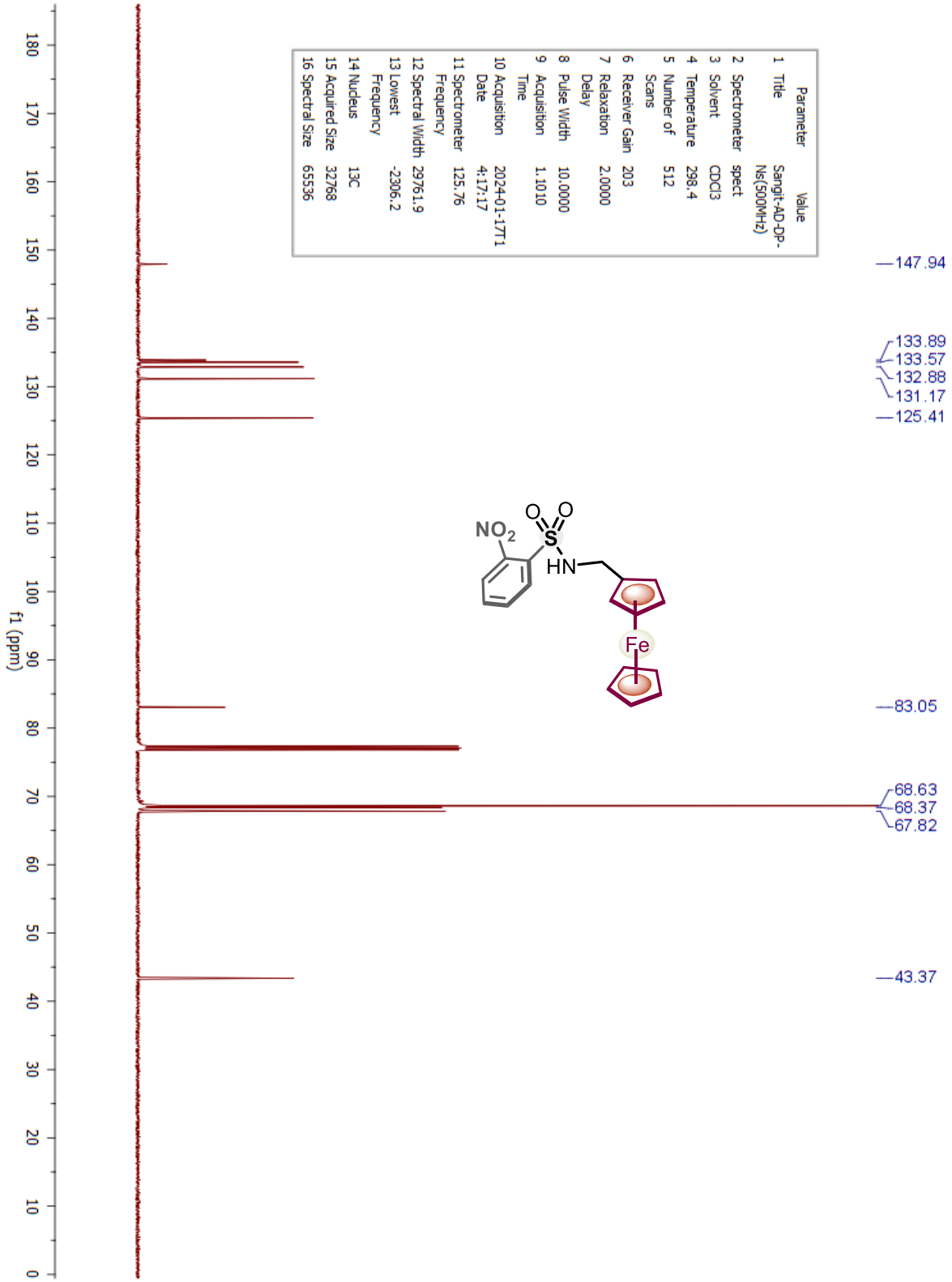
^{19}F NMR Spectrum of **1d**



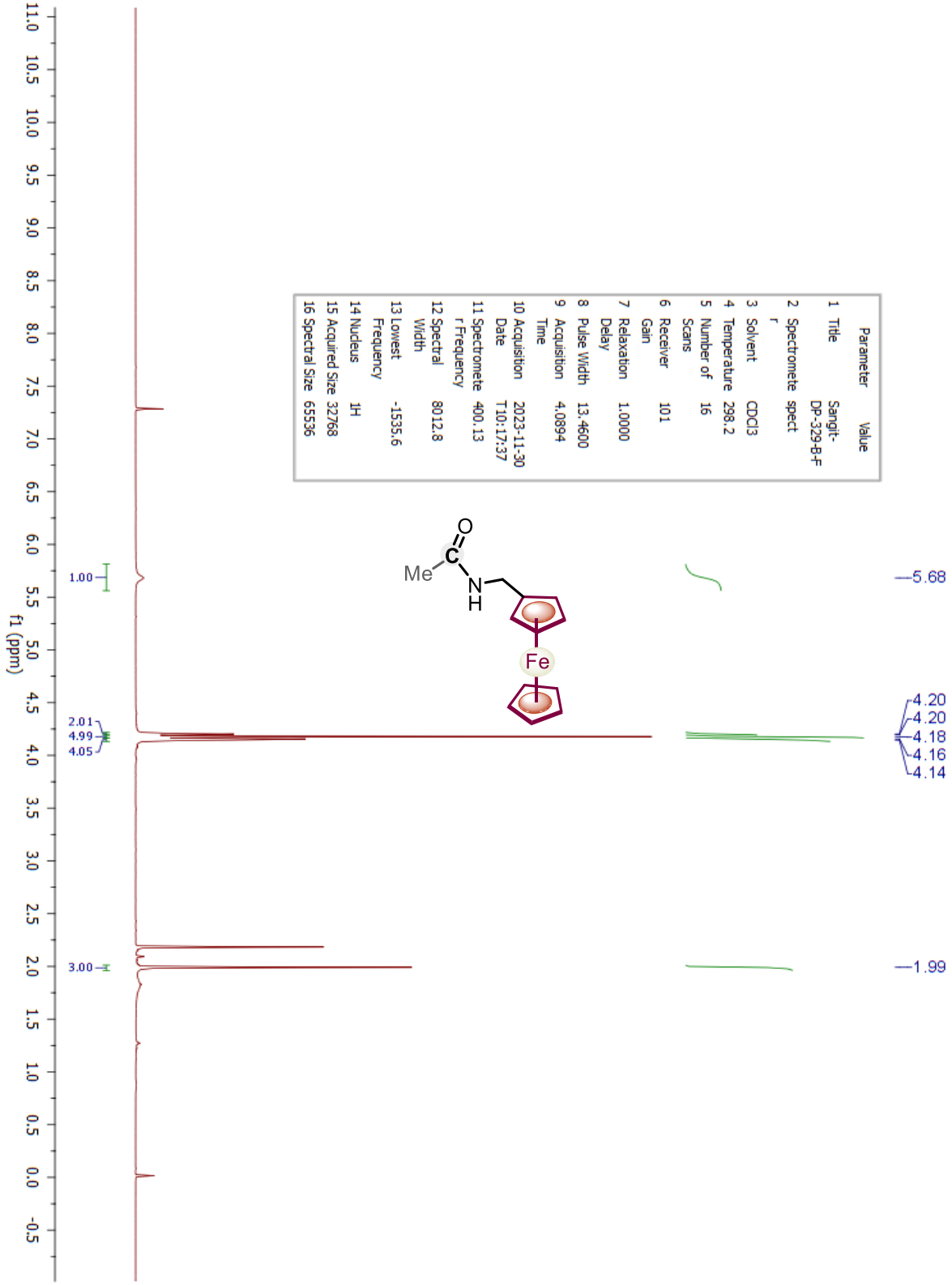
^{1}H NMR Spectrum of **1e**



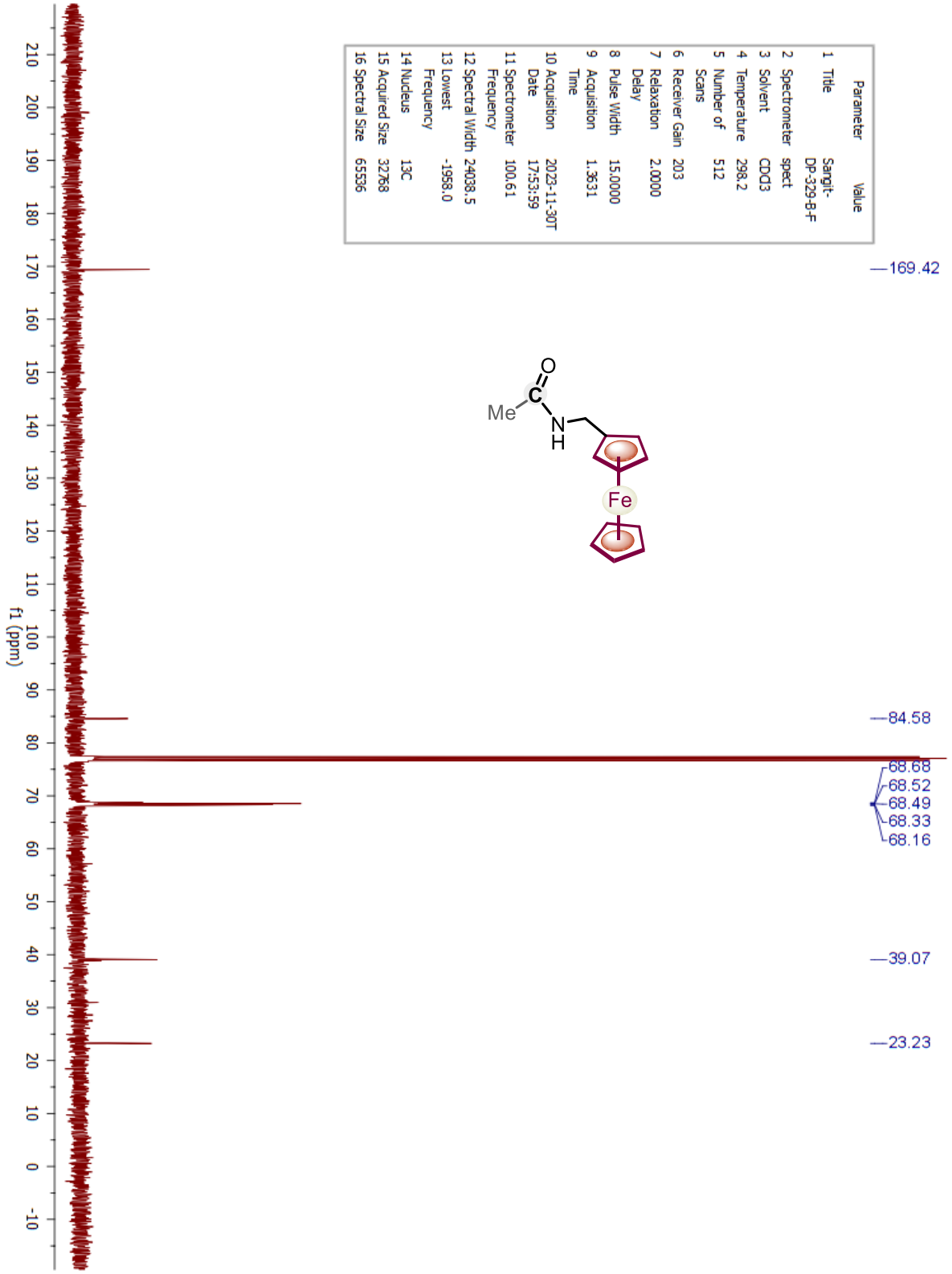
$^{13}C\{^{1}H\}$ NMR Spectrum of **1e**



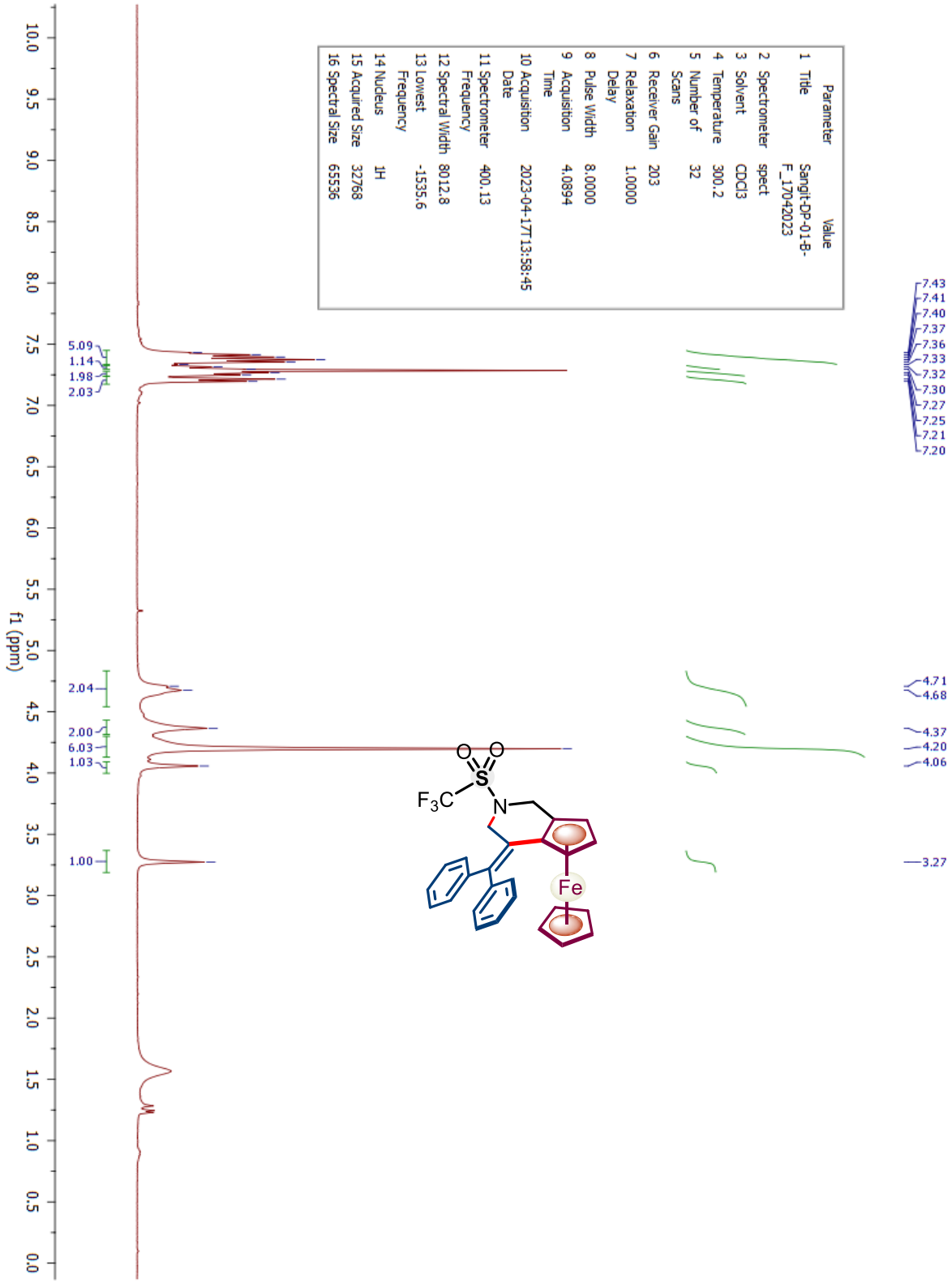
^{1}H NMR Spectrum of **1f**



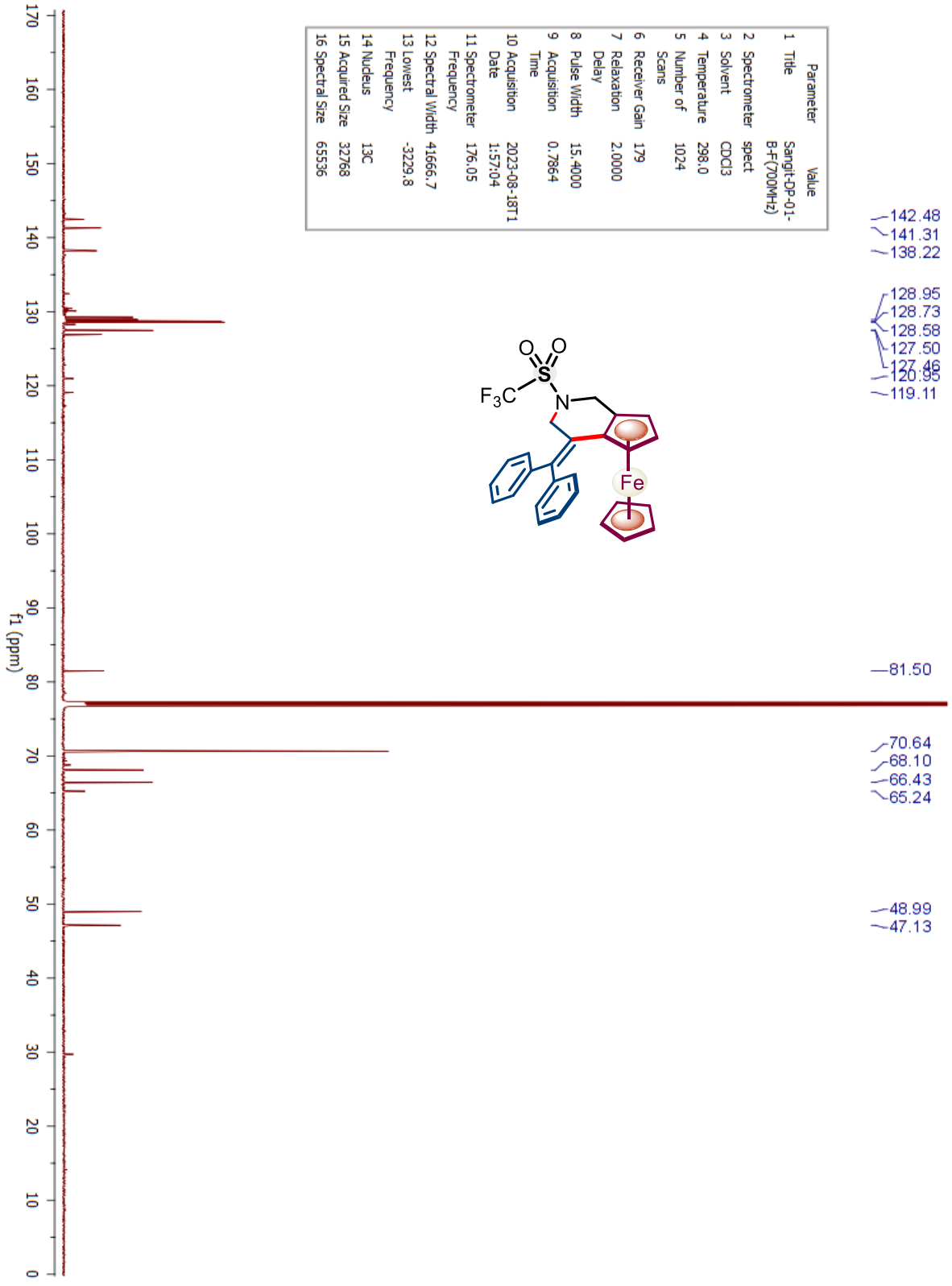
$^{13}C\{^{1}H\}$ NMR Spectrum of **1f**



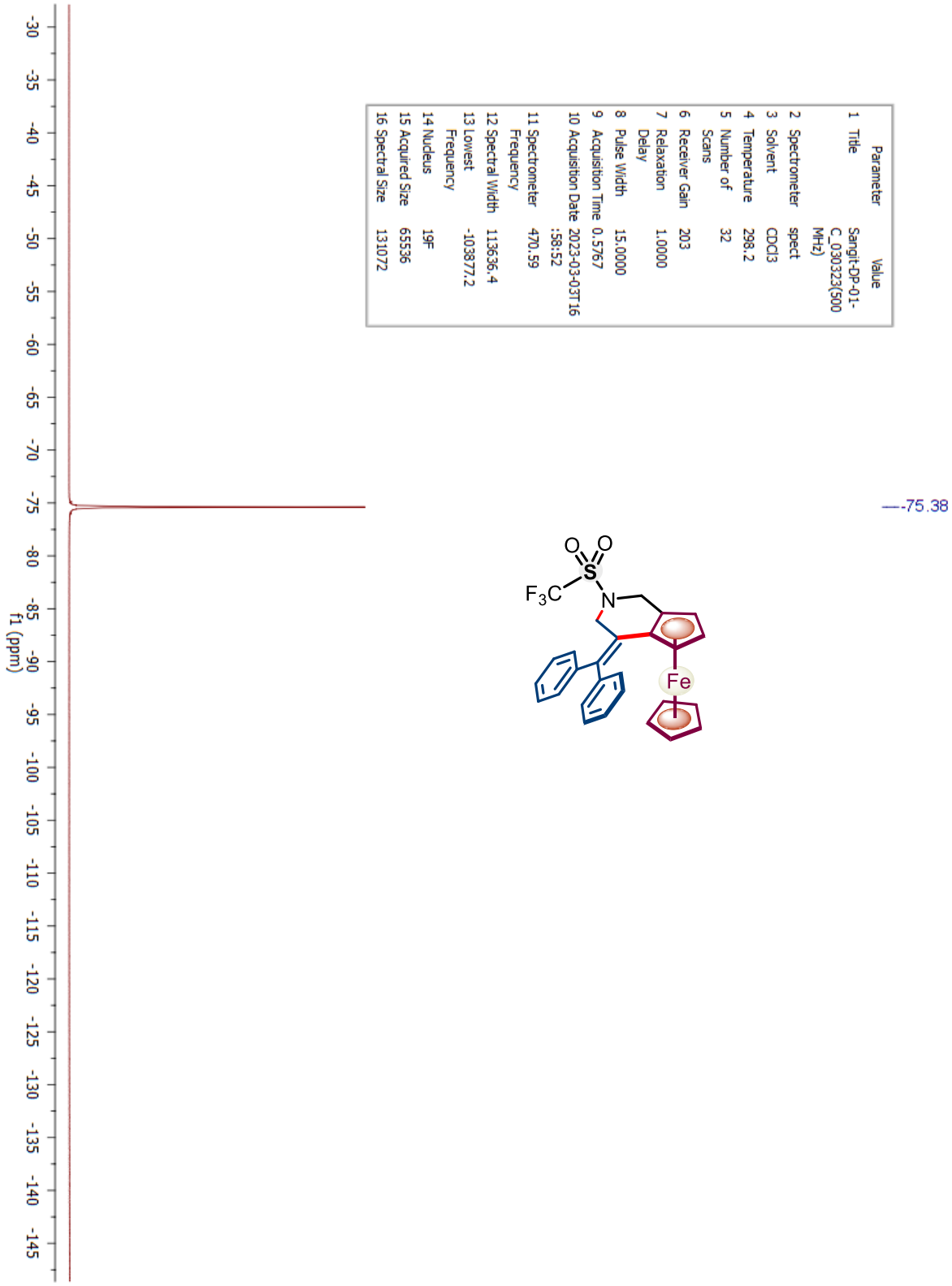
^{1}H NMR Spectrum of **3a**



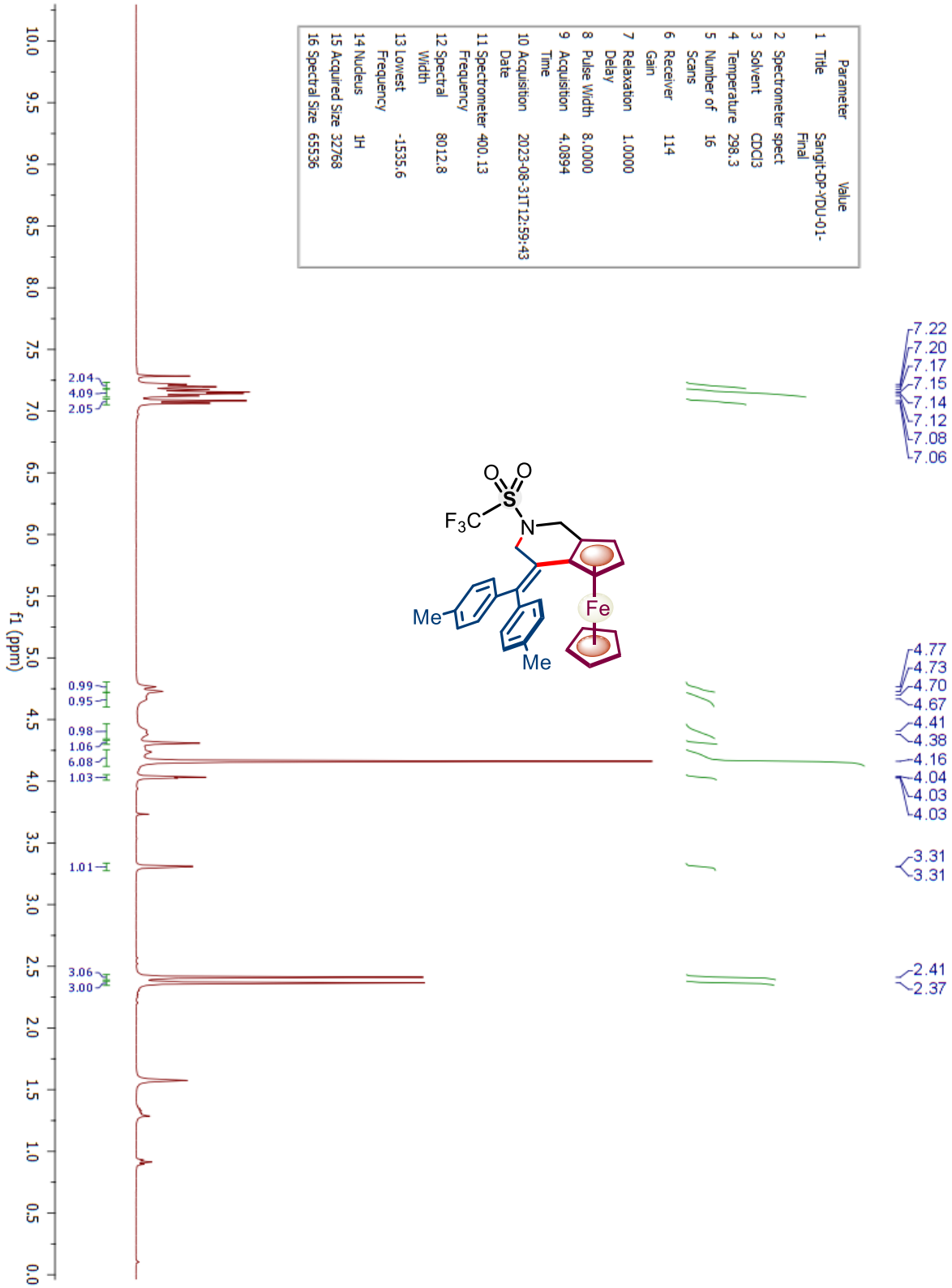
$^{13}C\{^{1}H\}$ NMR Spectrum of **3a**



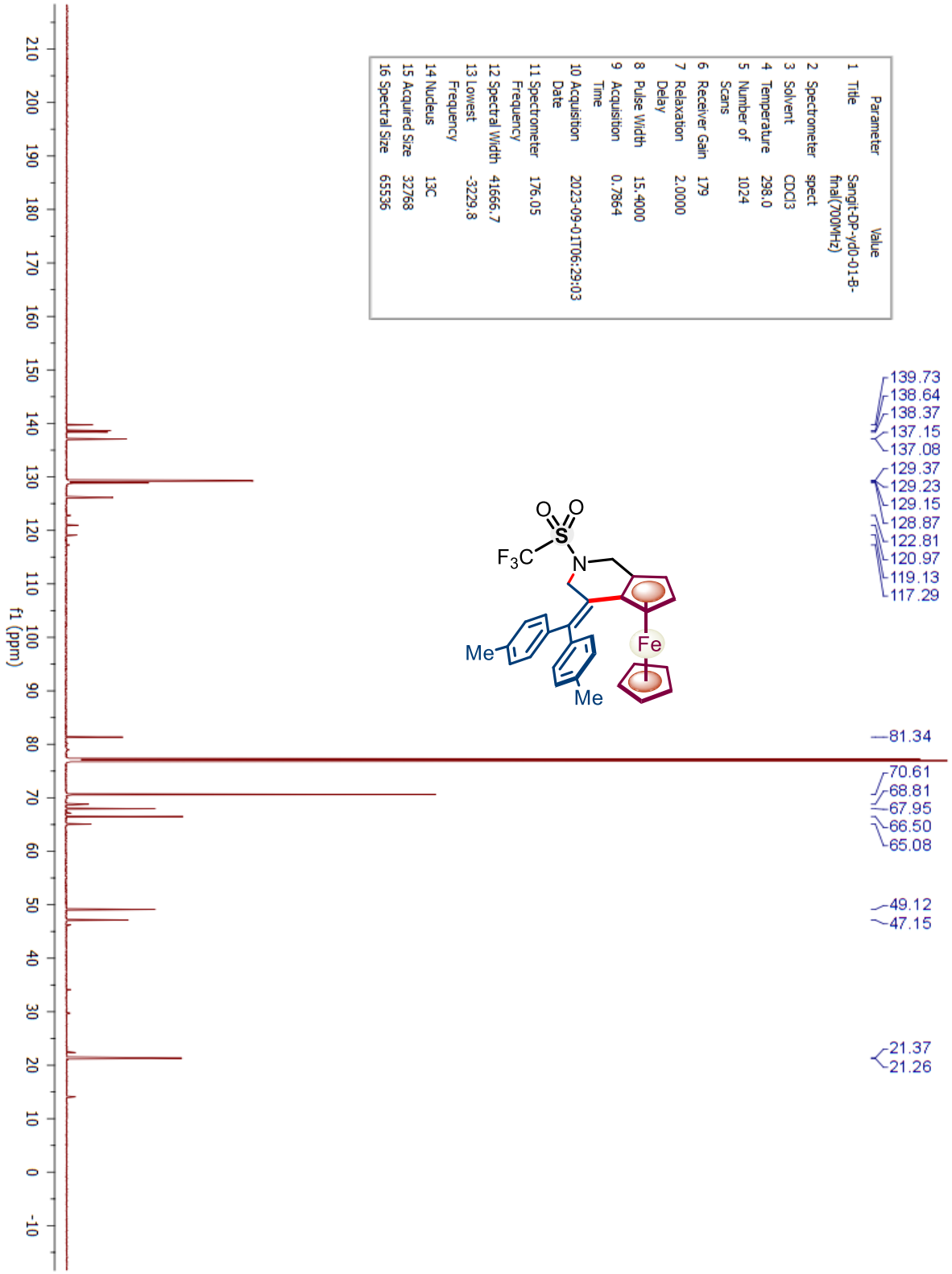
^{19}F NMR Spectrum of **3a**



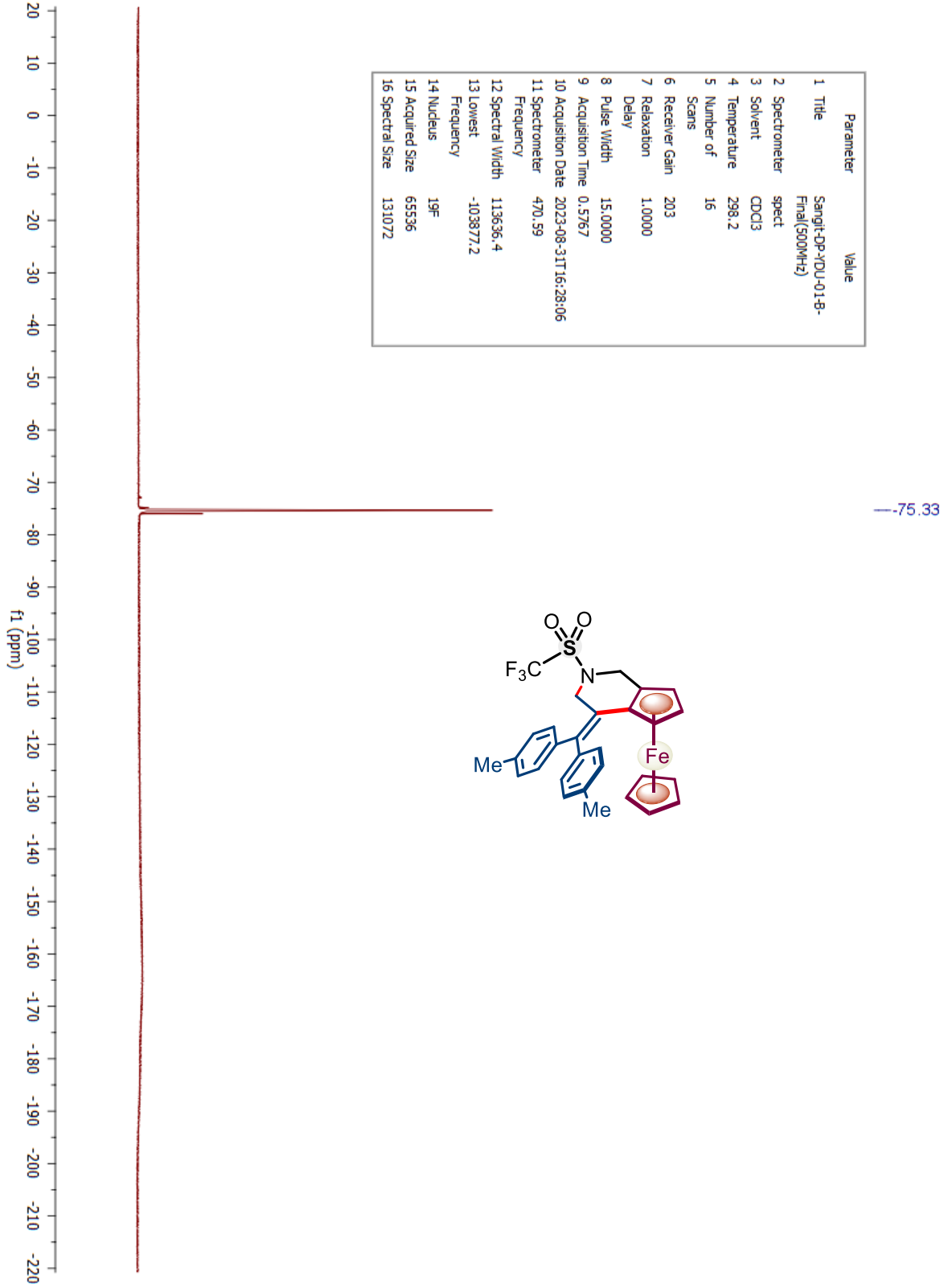
^{1}H NMR Spectrum of **3b**



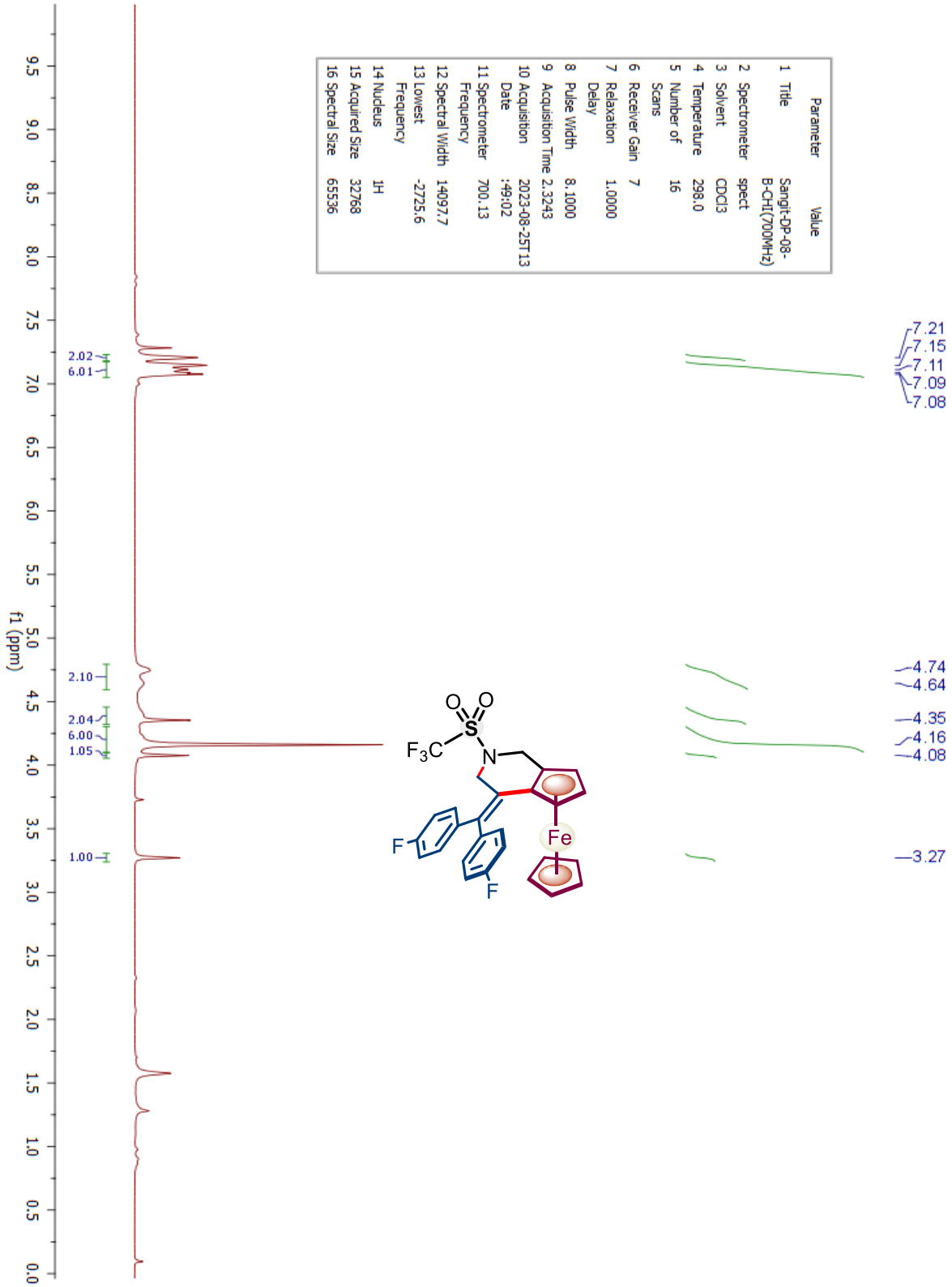
$^{13}C\{^{1}H\}$ NMR Spectrum of **3b**



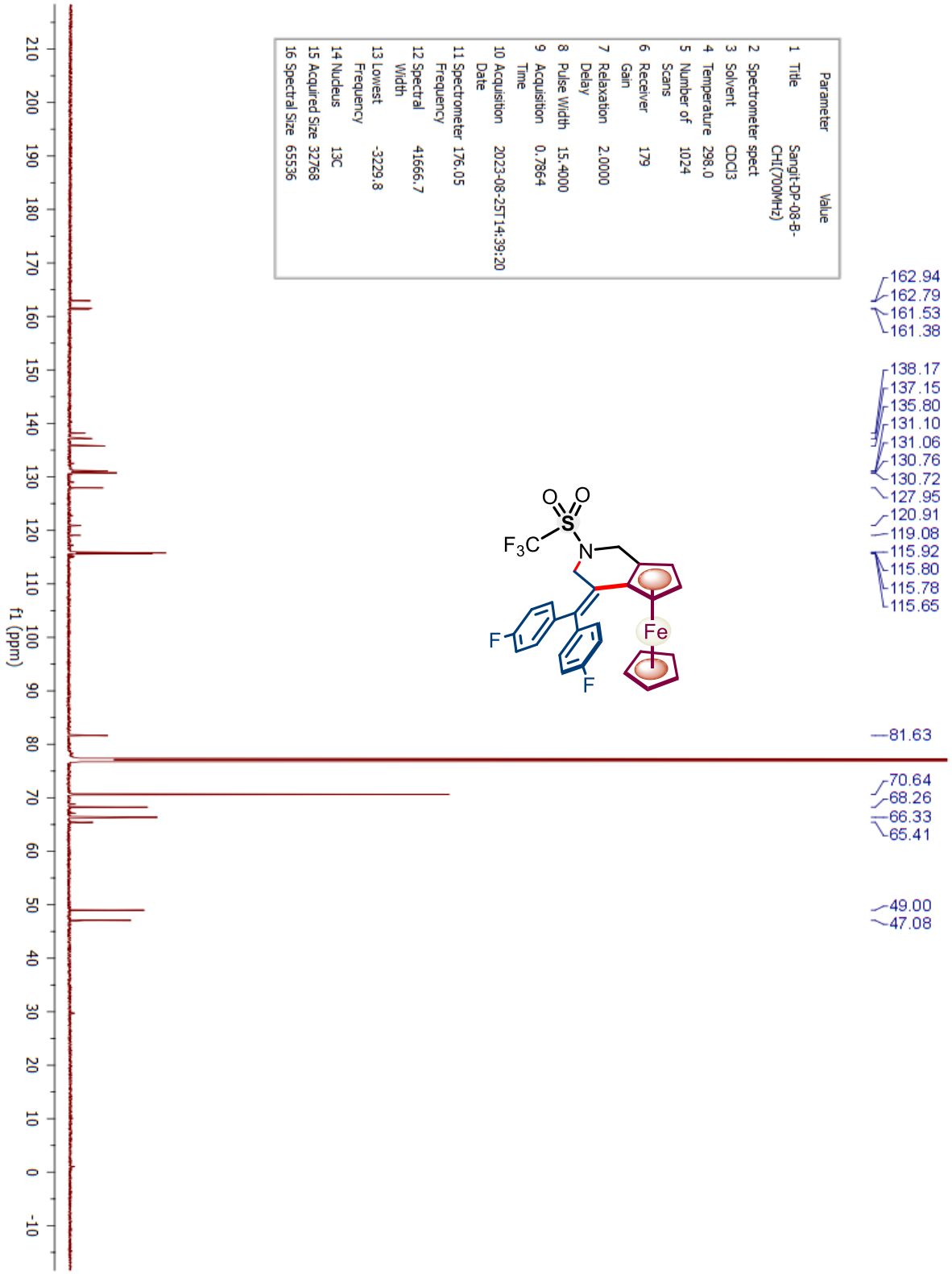
^{19}F NMR Spectrum of **3b**



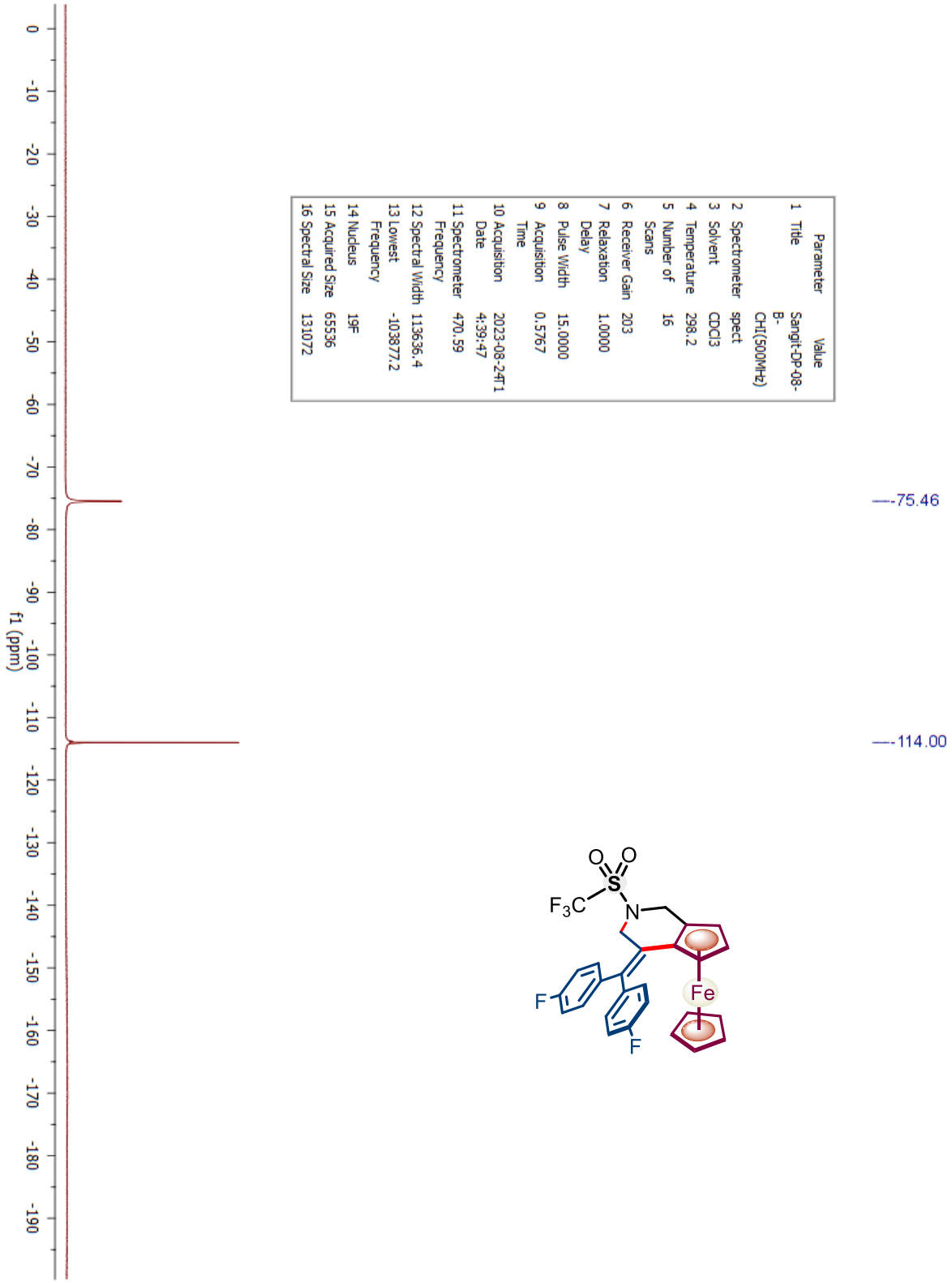
^{1}H NMR Spectrum of **3c**



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

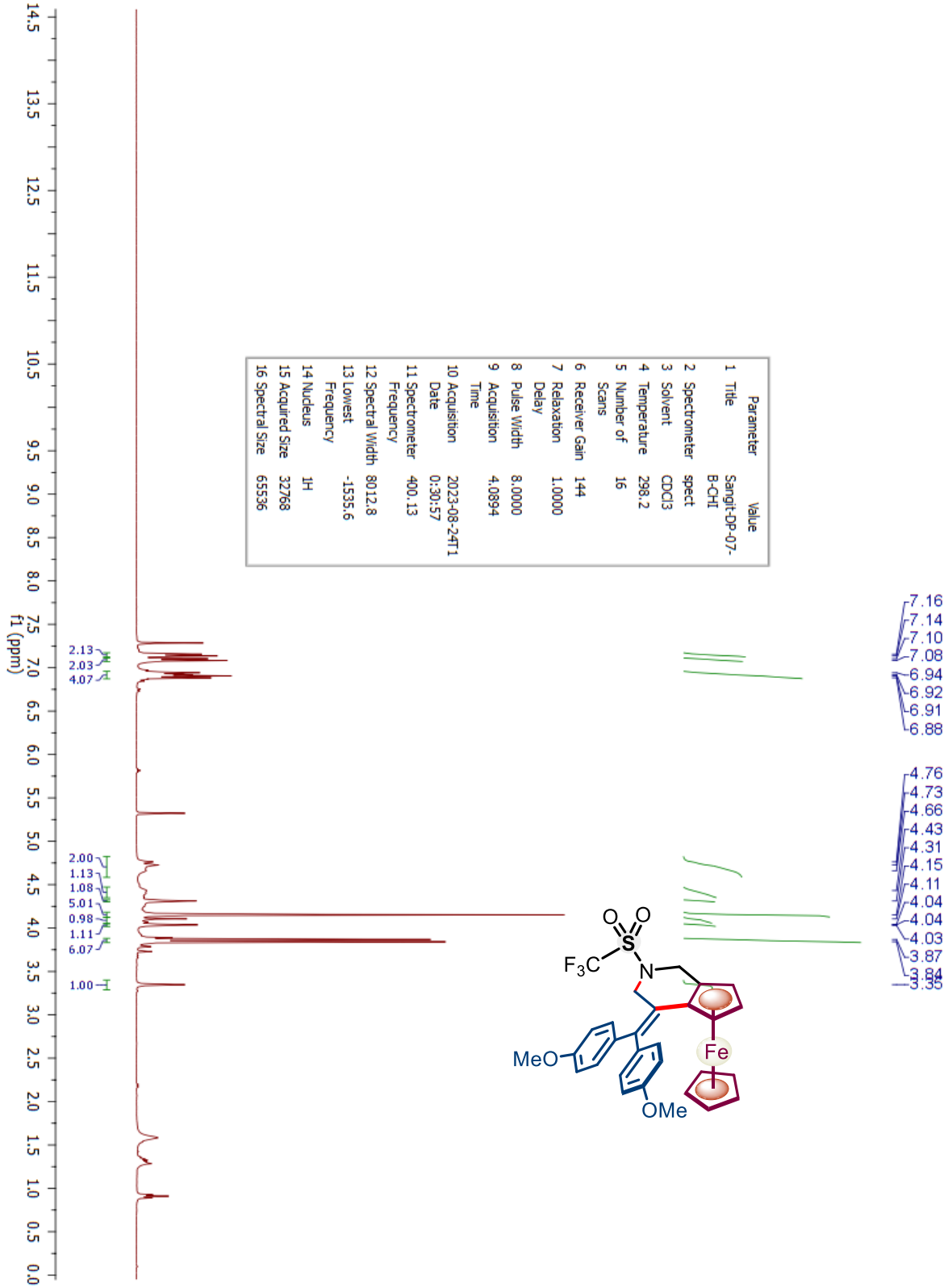


^{19}F NMR Spectrum of **3c**

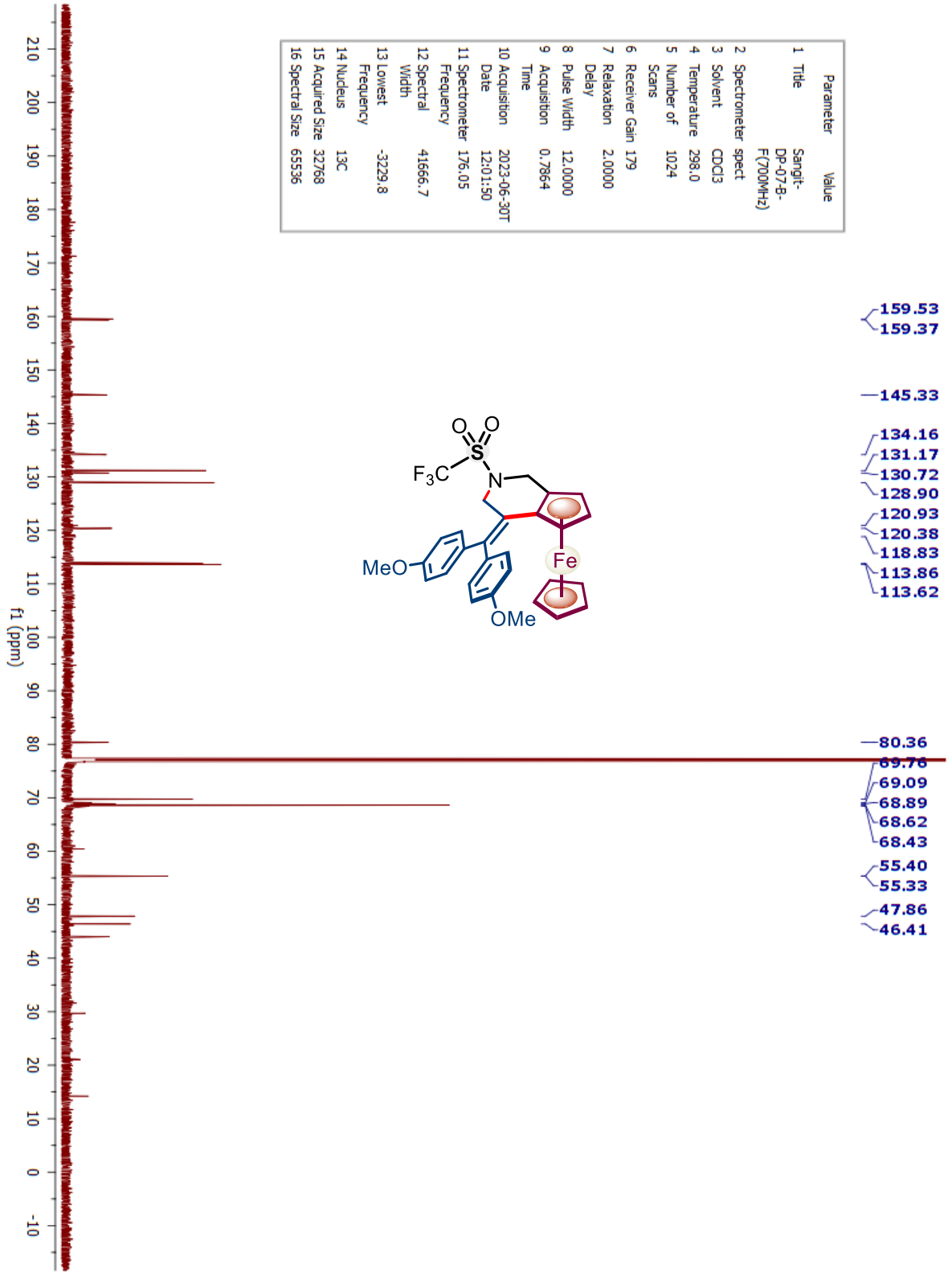


	Parameter	Value
1	Title	Sangit-DP-08-B-CHI(500MHz)
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Number of Scans	16
6	Receiver Gain	203
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Acquisition Time	0.5767
10	Acquisition Date	2023-08-24T14:39:47
11	Spectrometer Frequency	470.59
12	Spectral Width	113636.4
13	Lowest Frequency	-103877.2
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

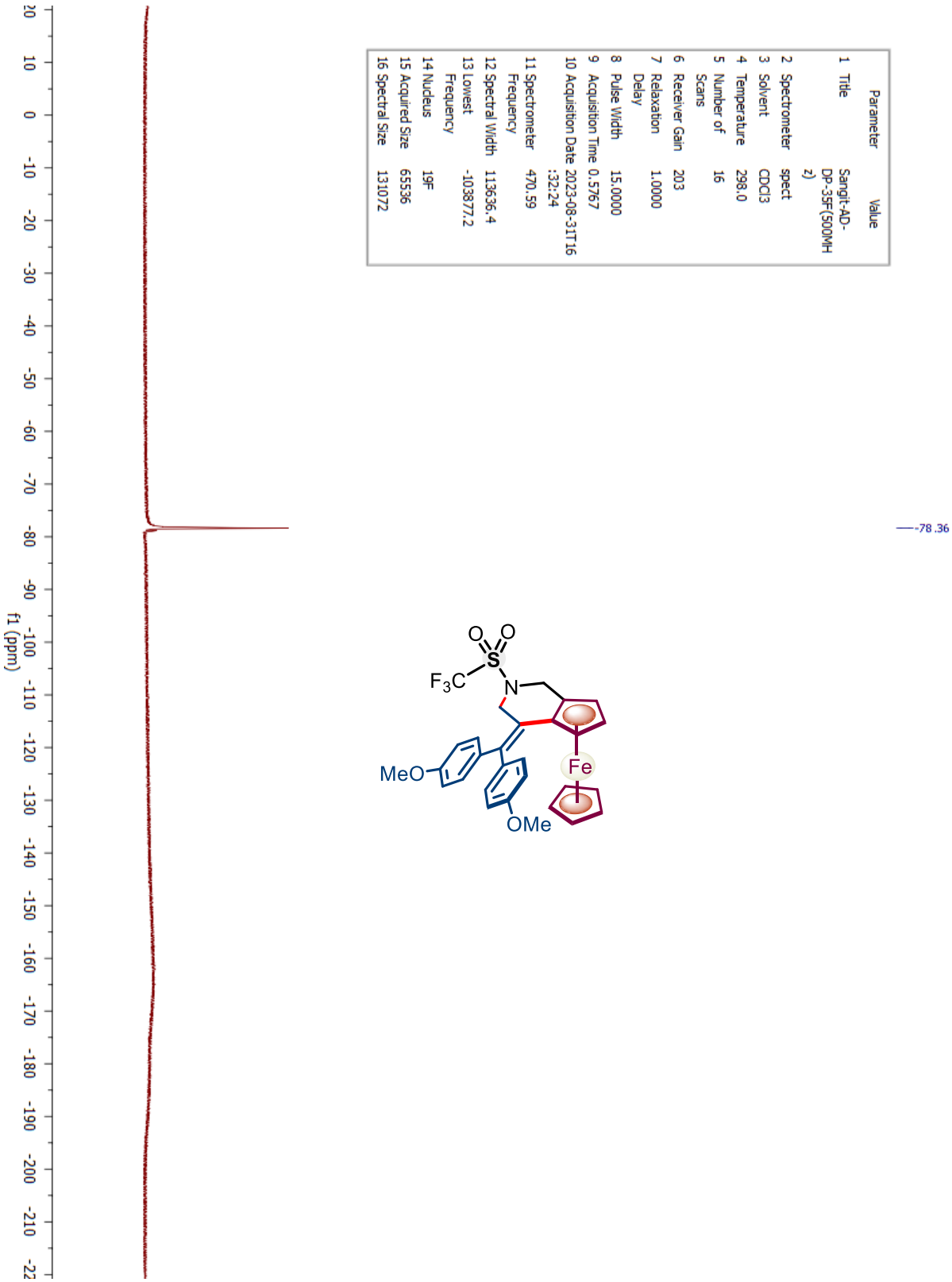
^{1}H NMR Spectrum of **3d**



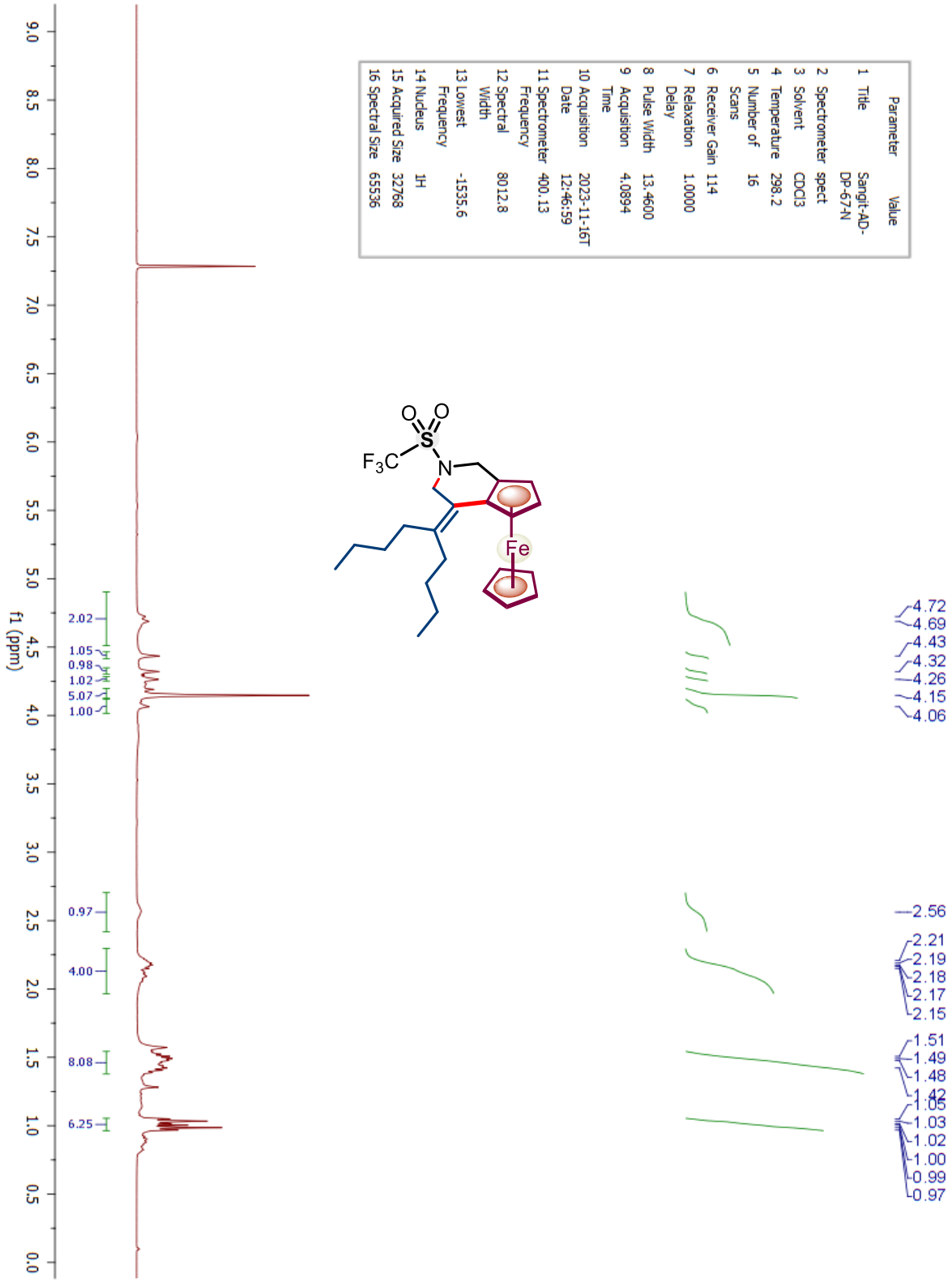
$^{13}C\{^{1}H\}$ NMR Spectrum of **3d**



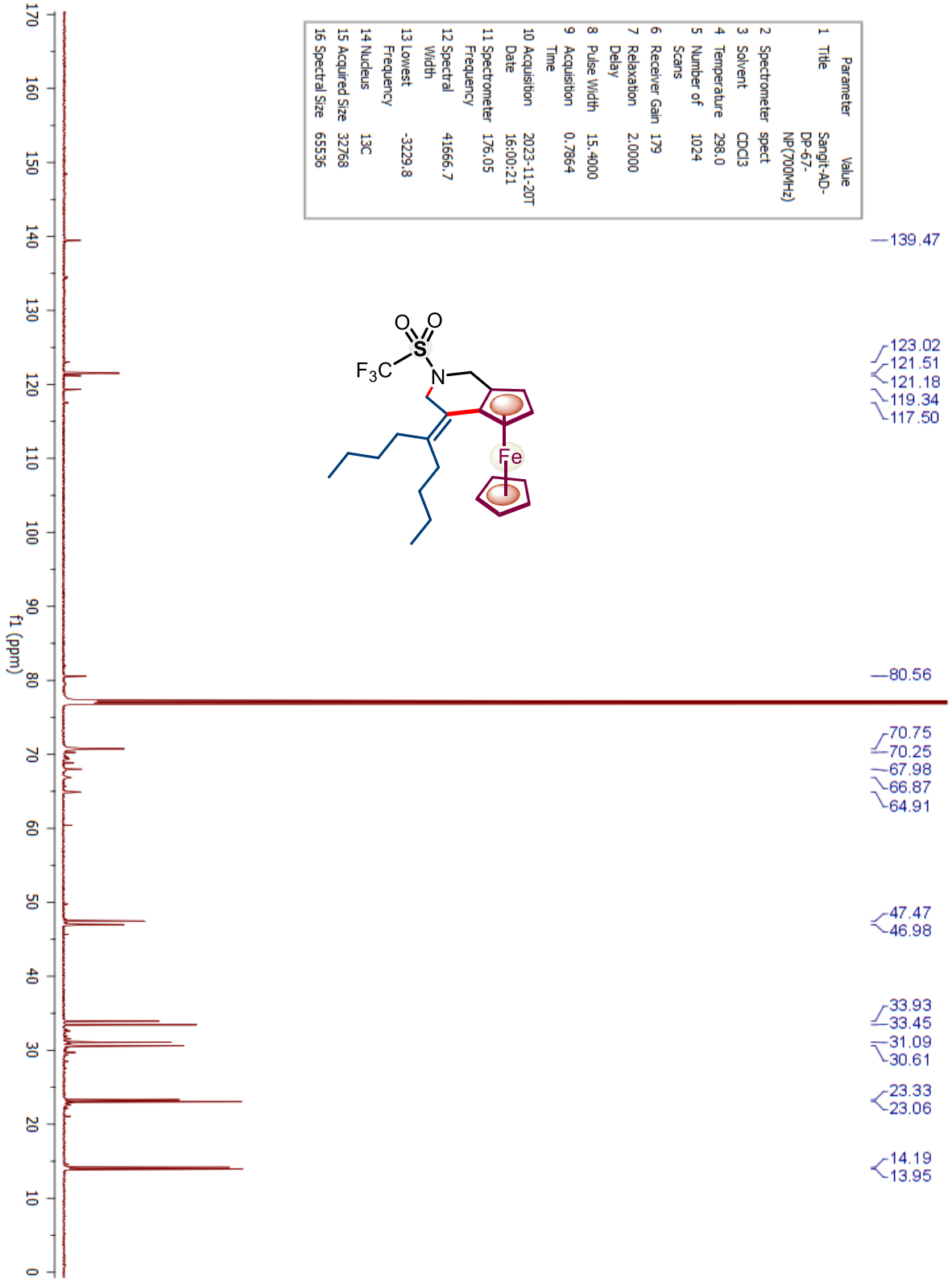
^{19}F NMR Spectrum of **3d**



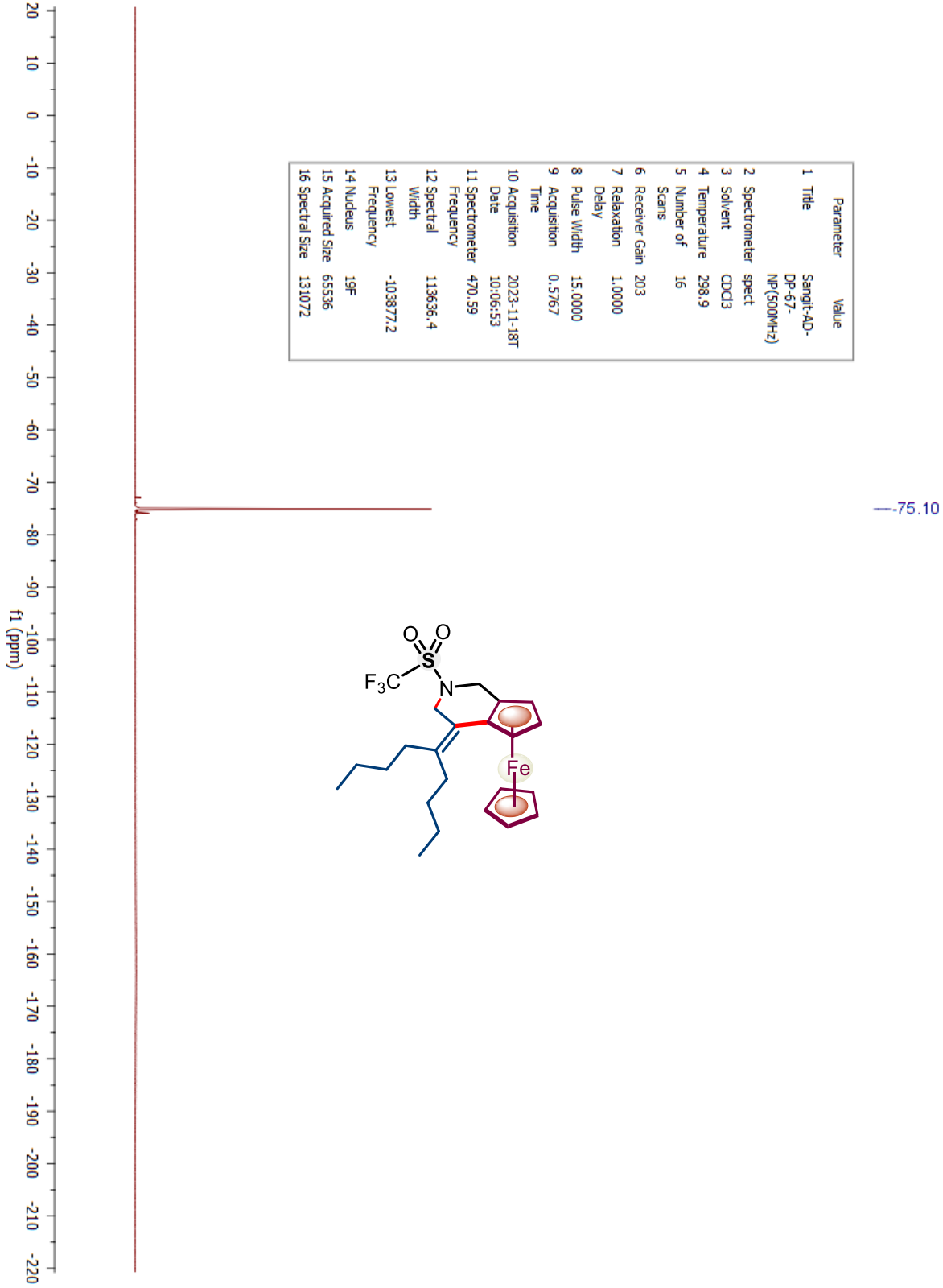
^{1}H NMR Spectrum of **3e**



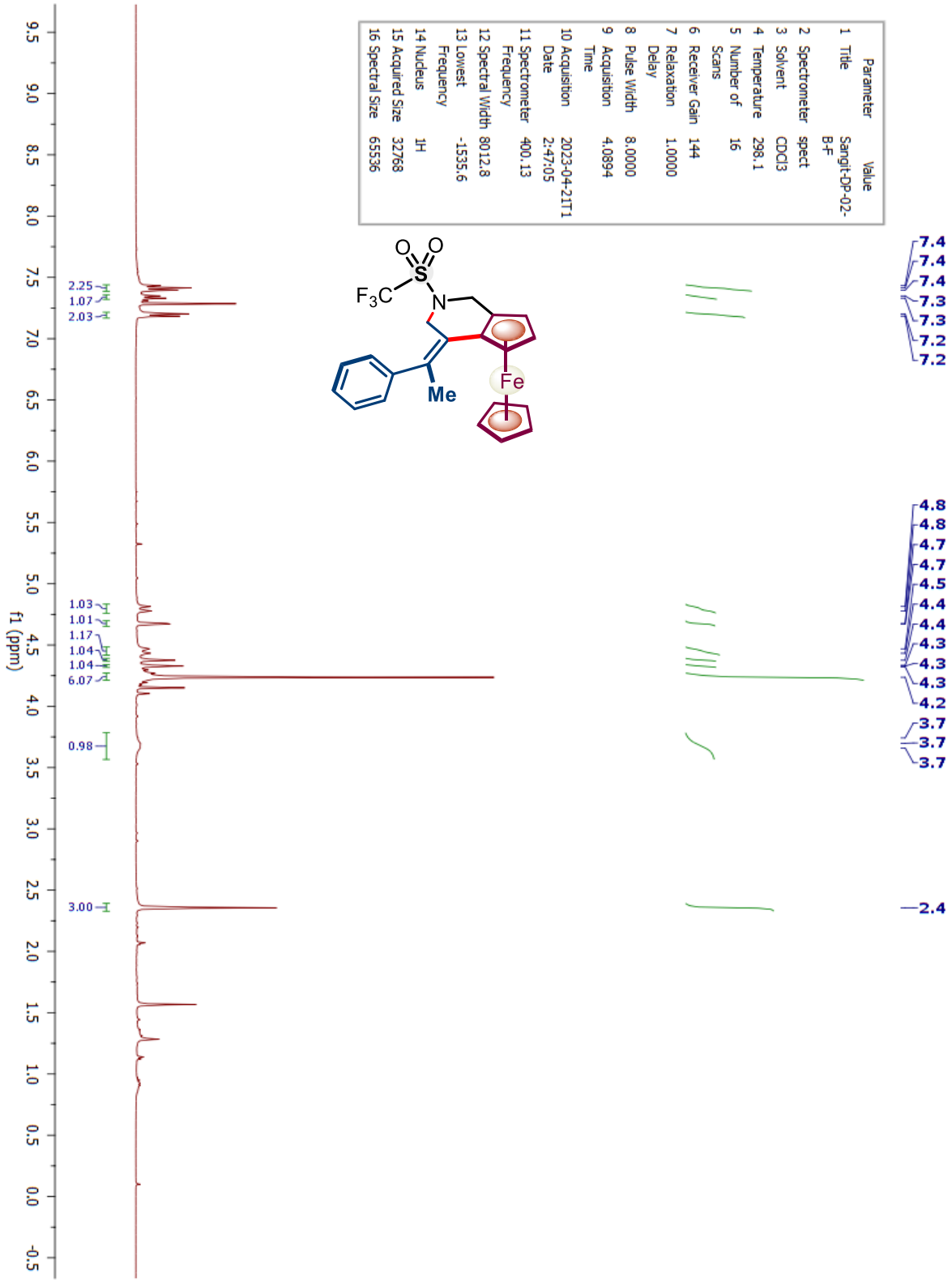
$^{13}C\{^{1}H\}$ NMR Spectrum of **3e**



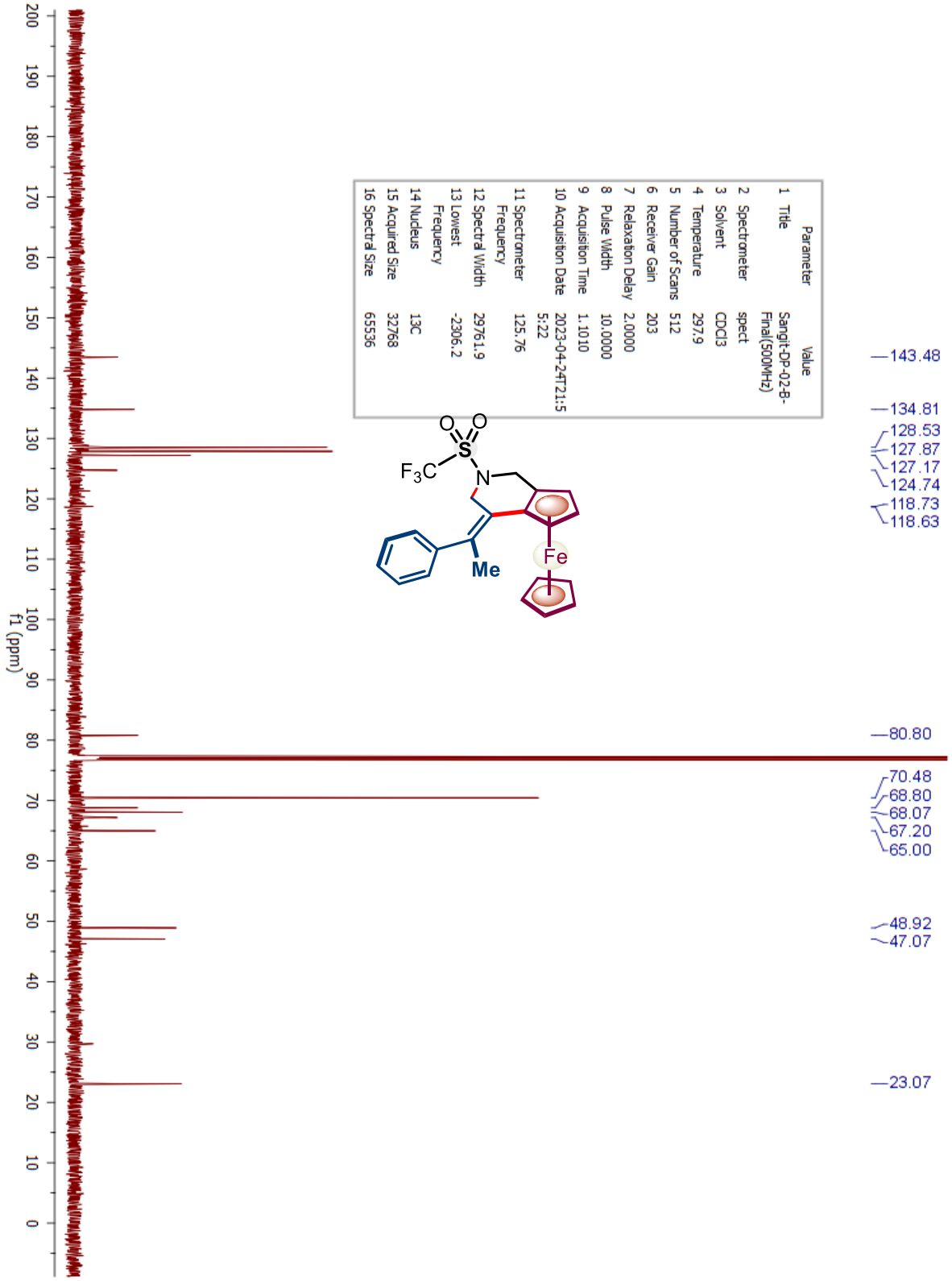
^{19}F NMR Spectrum of **3e**



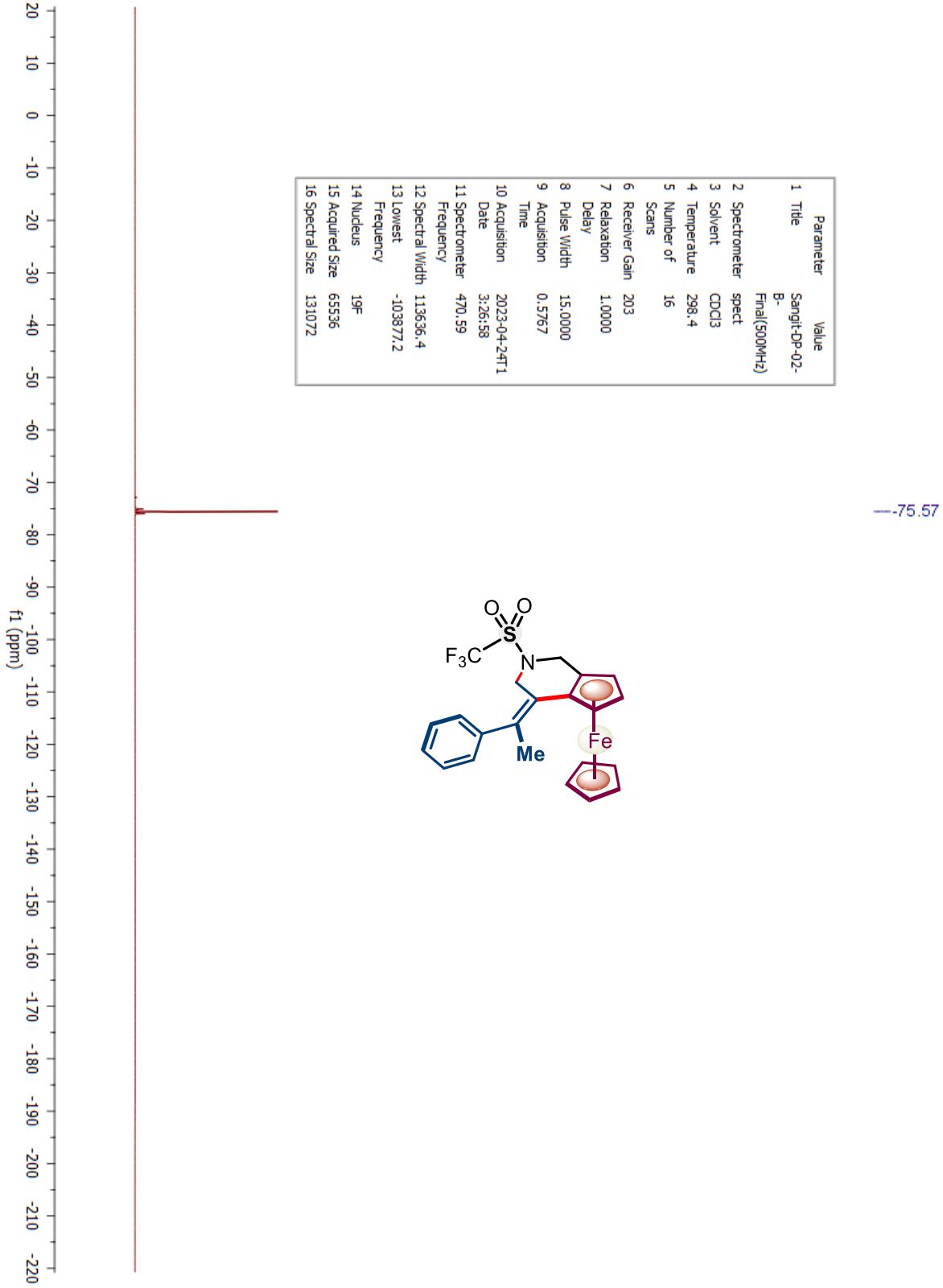
^{1}H NMR Spectrum of **3f**



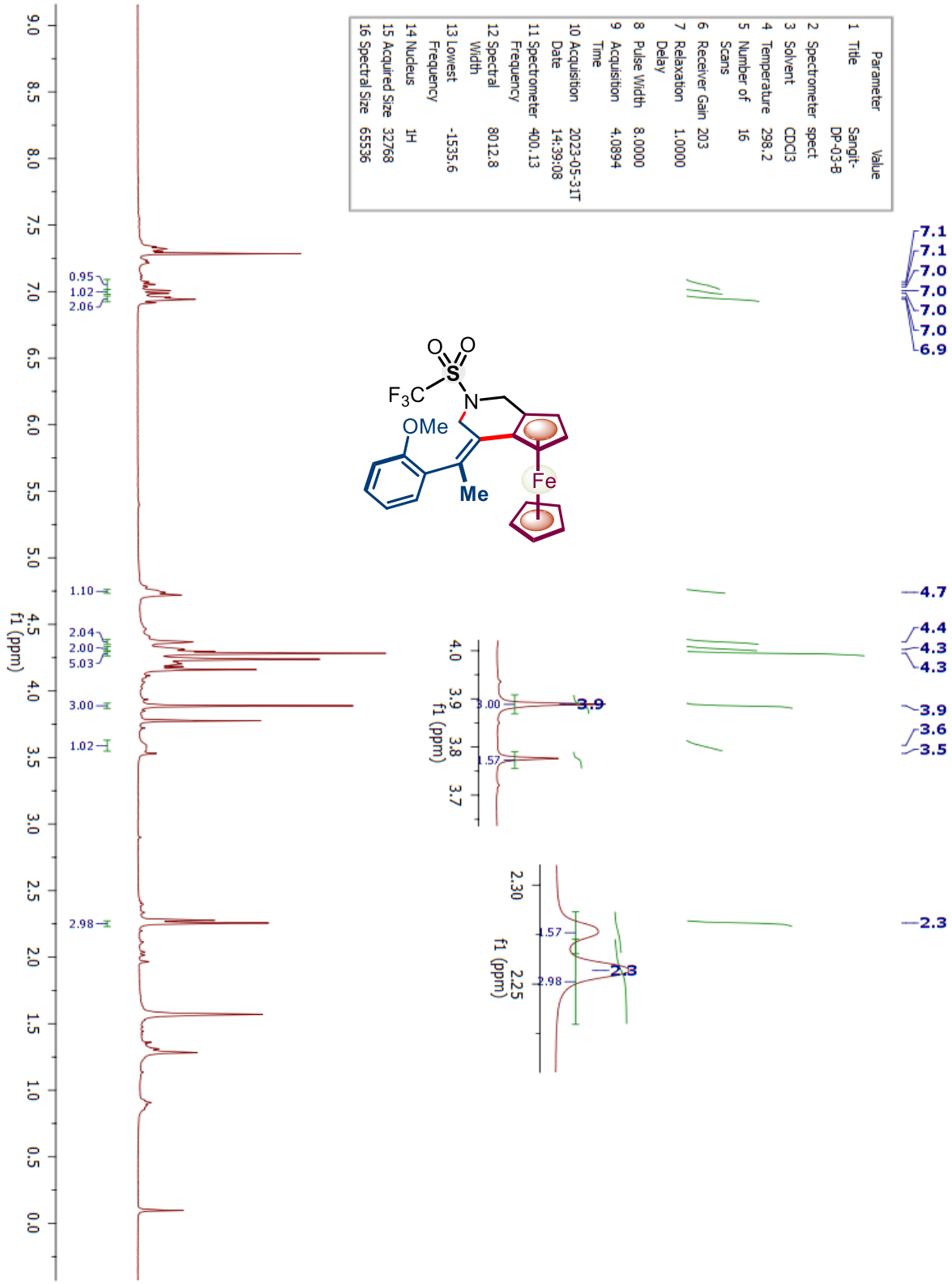
$^{13}C\{^{1}H\}$ NMR Spectrum of **3f**



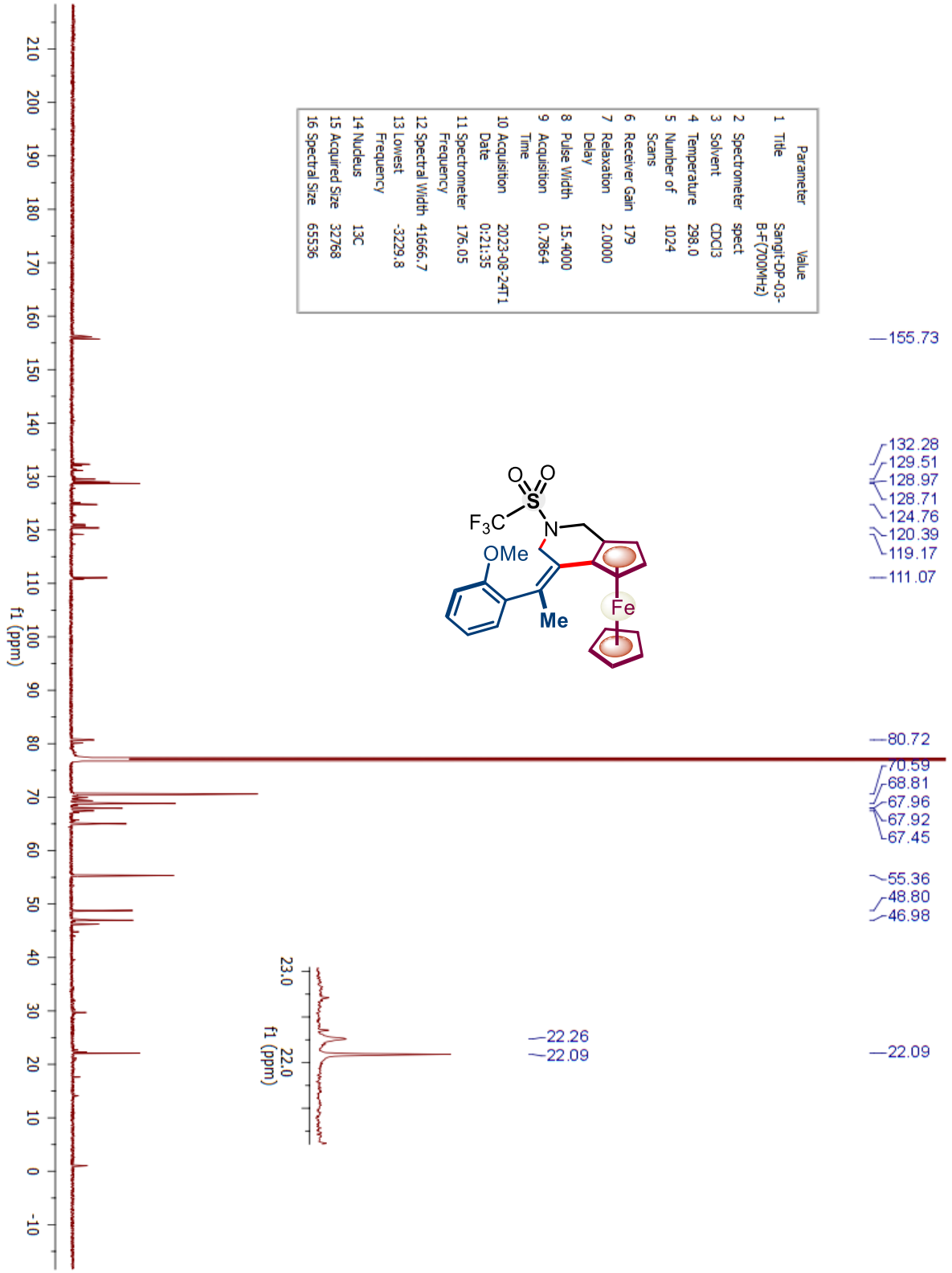
^{19}F NMR Spectrum of **3f**



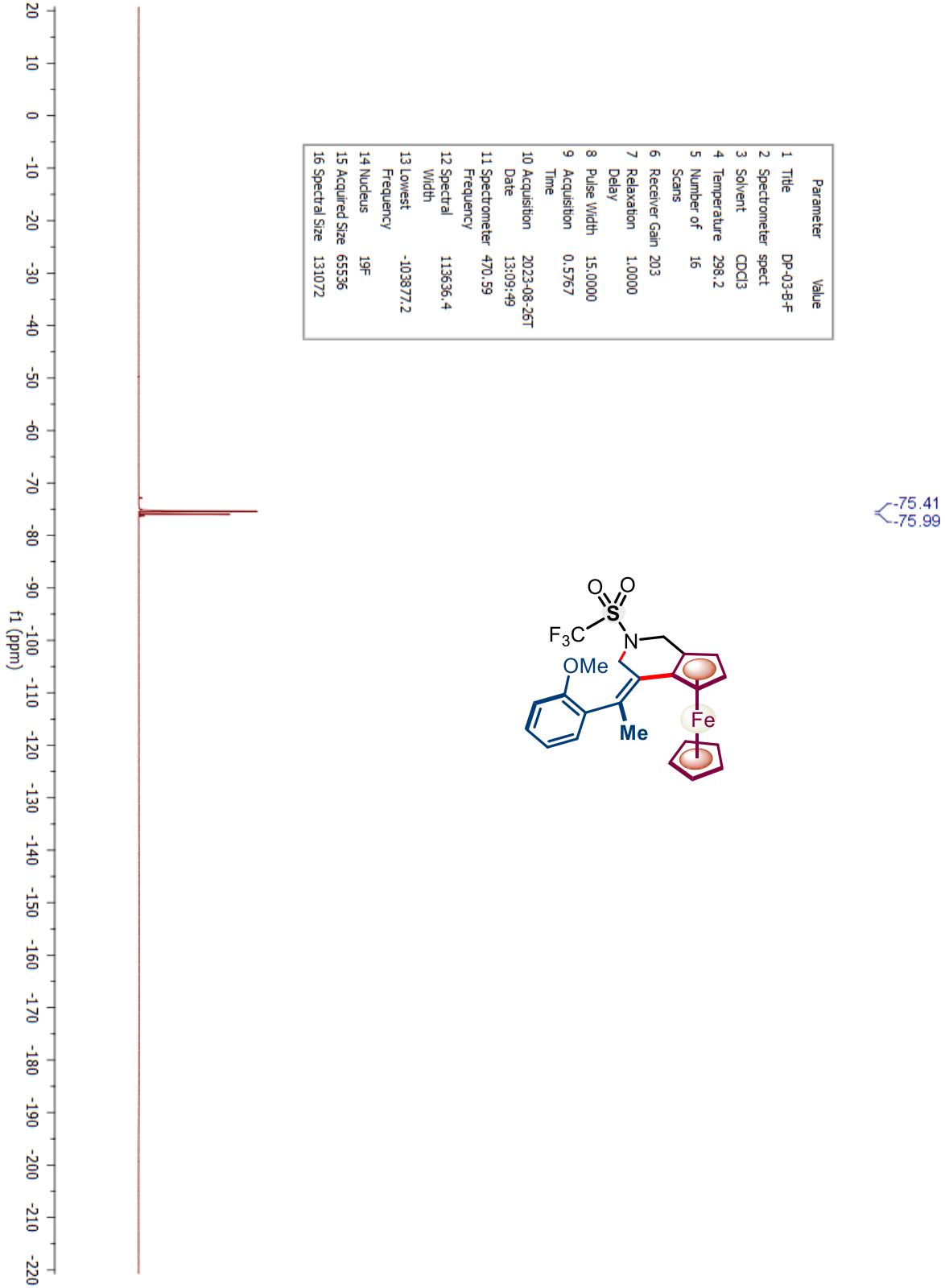
^{1}H NMR Spectrum of **3g**



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

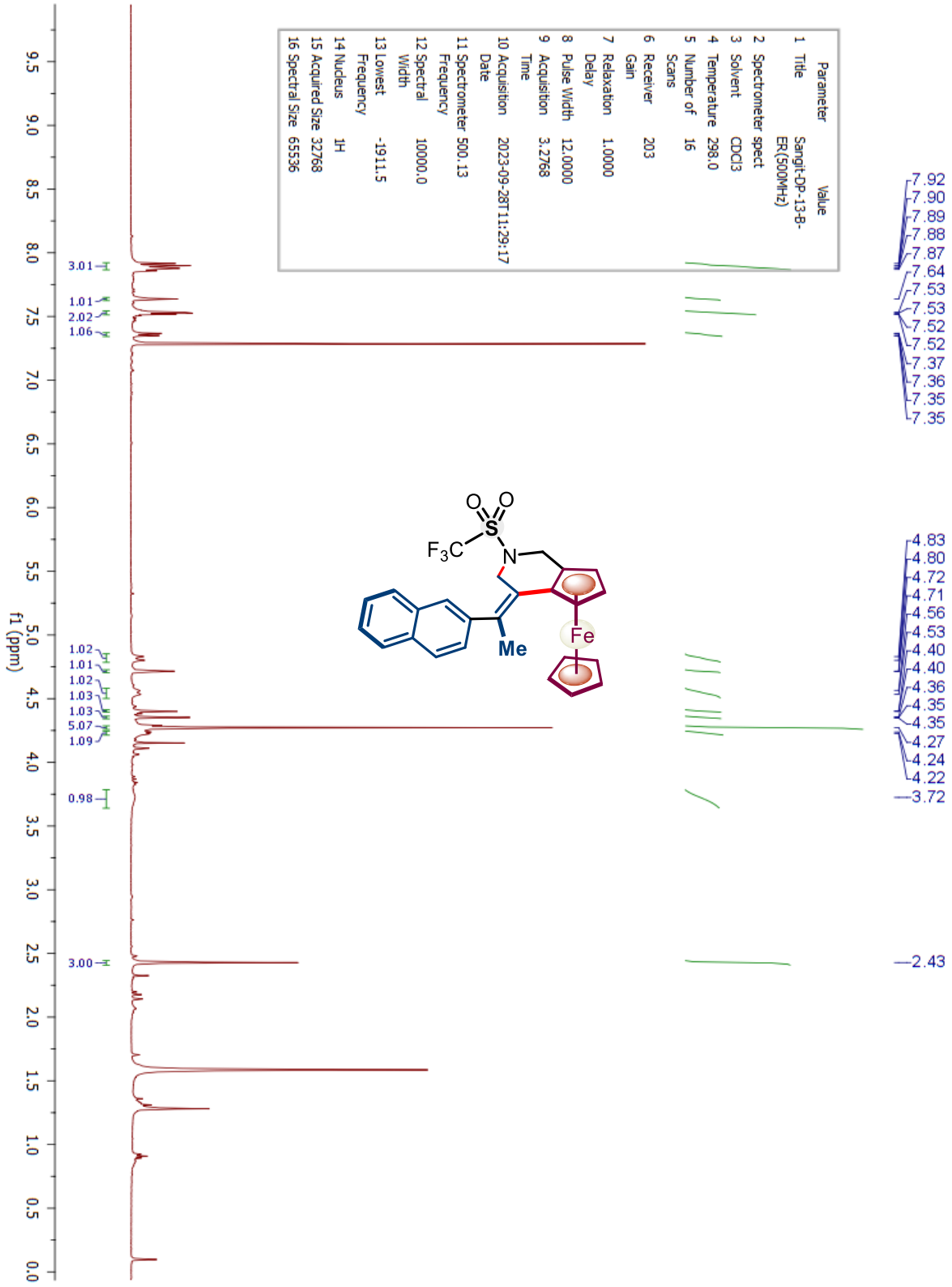


^{19}F NMR Spectrum of **3g**

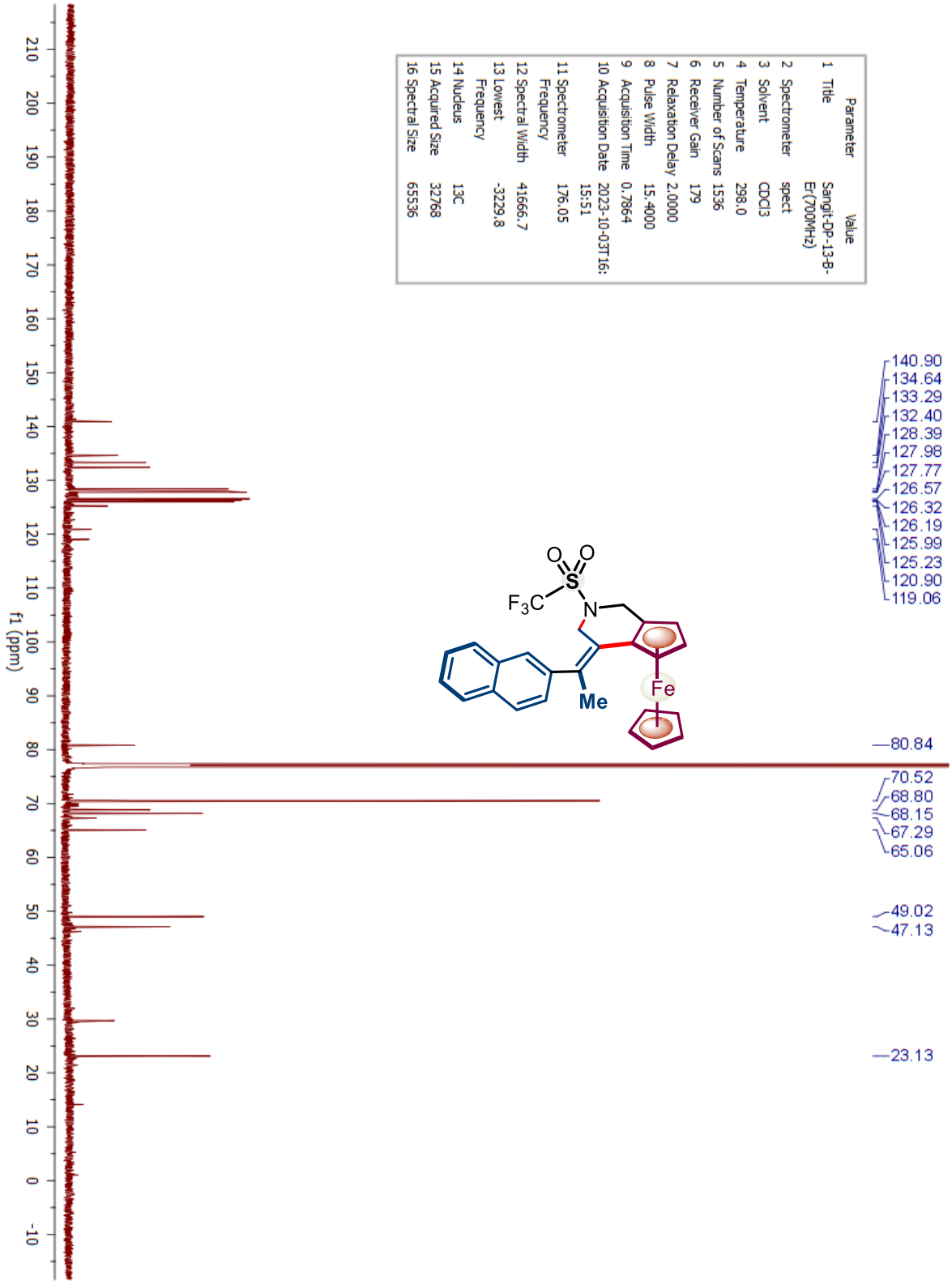


	Parameter	Value
1	Title	DP-03-B-F
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Number of Scans	16
6	Receiver Gain	203
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Acquisition Time	0.5767
10	Acquisition Date	2023-08-26T 13:09:49
11	Spectrometer Frequency	470.59
12	Spectral Width	113636.4
13	Lowest Frequency	-103877.2
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

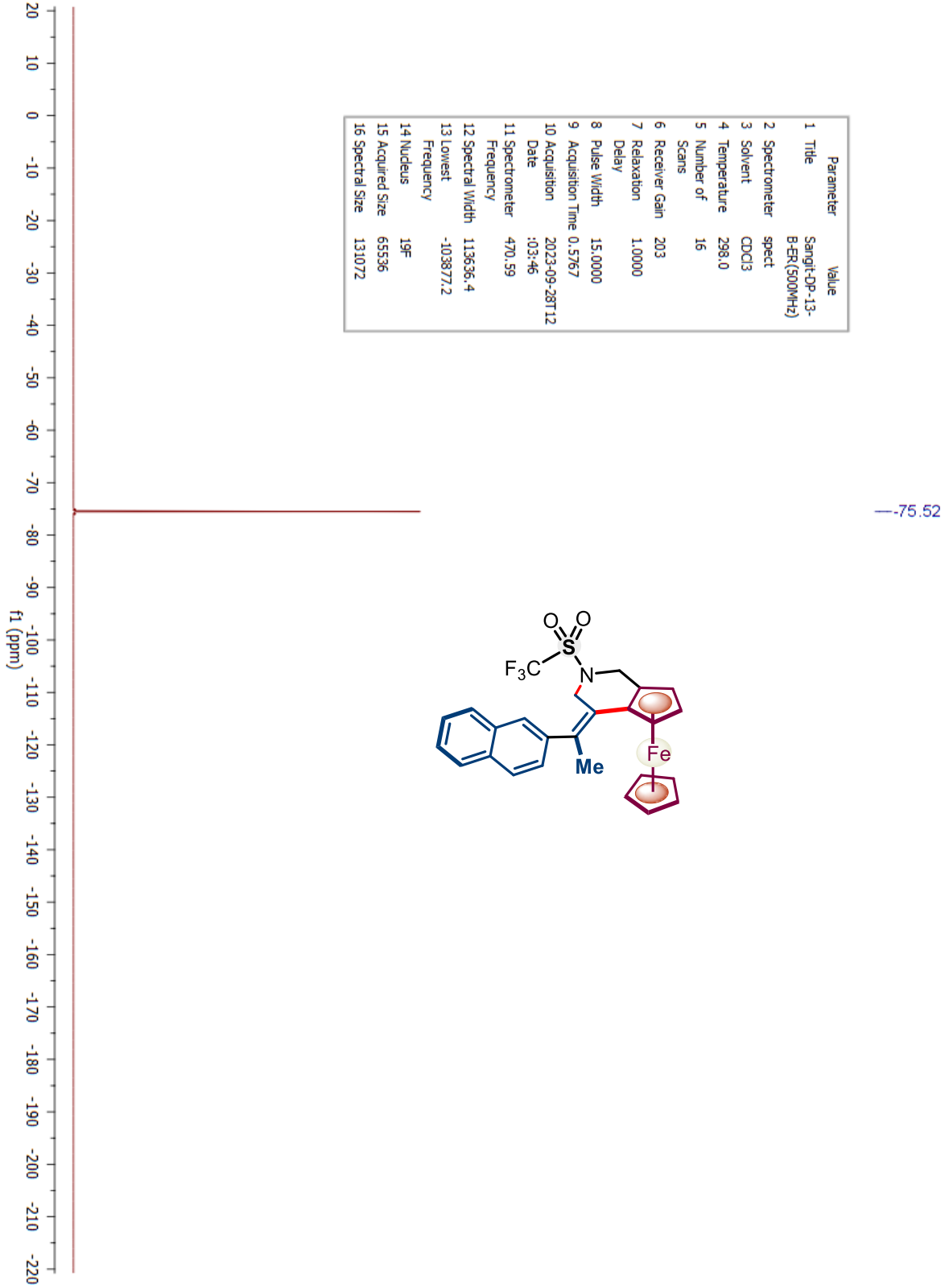
^{1}H NMR Spectrum of **3h**



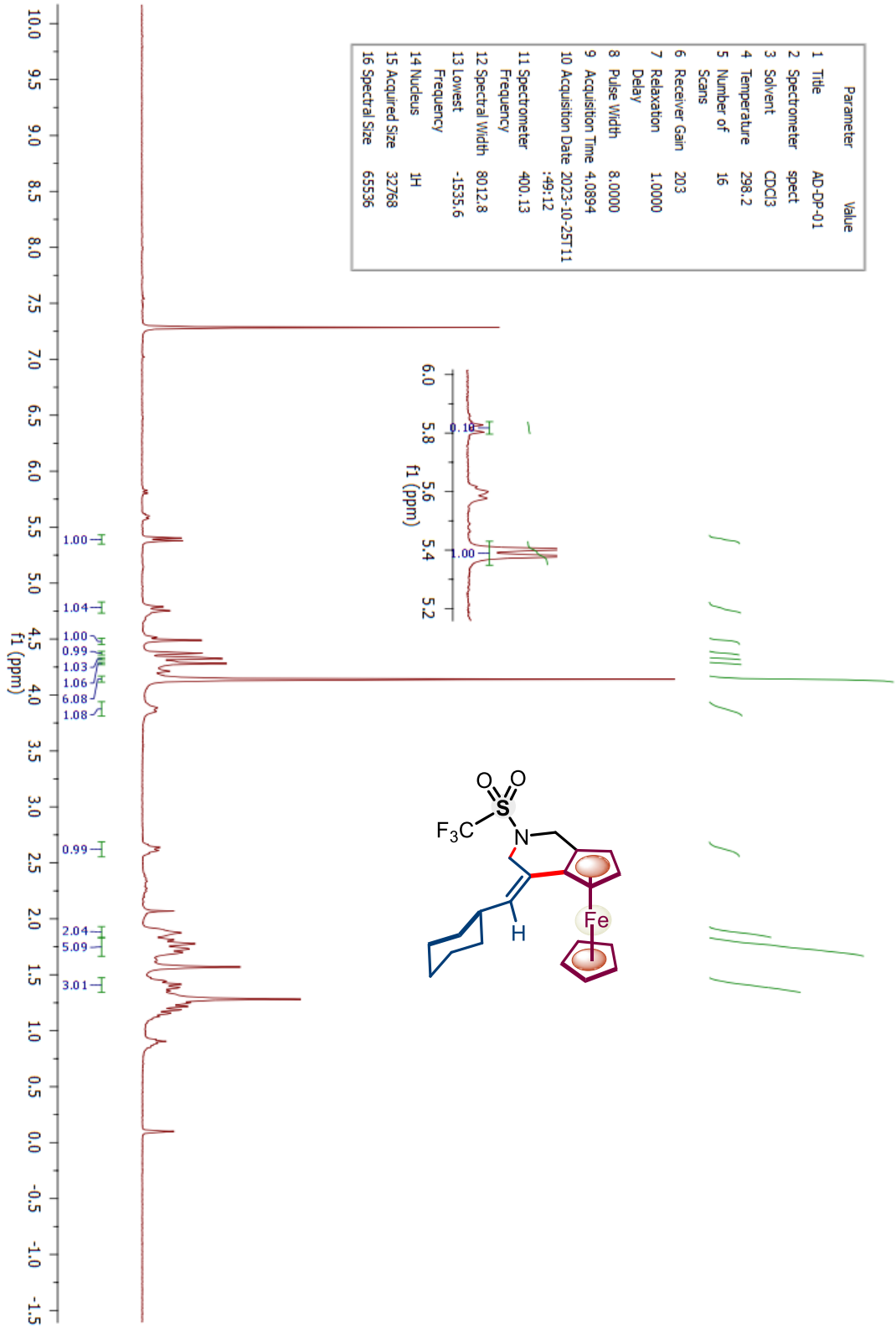
$^{13}C\{^{1}H\}$ NMR Spectrum of **3h**



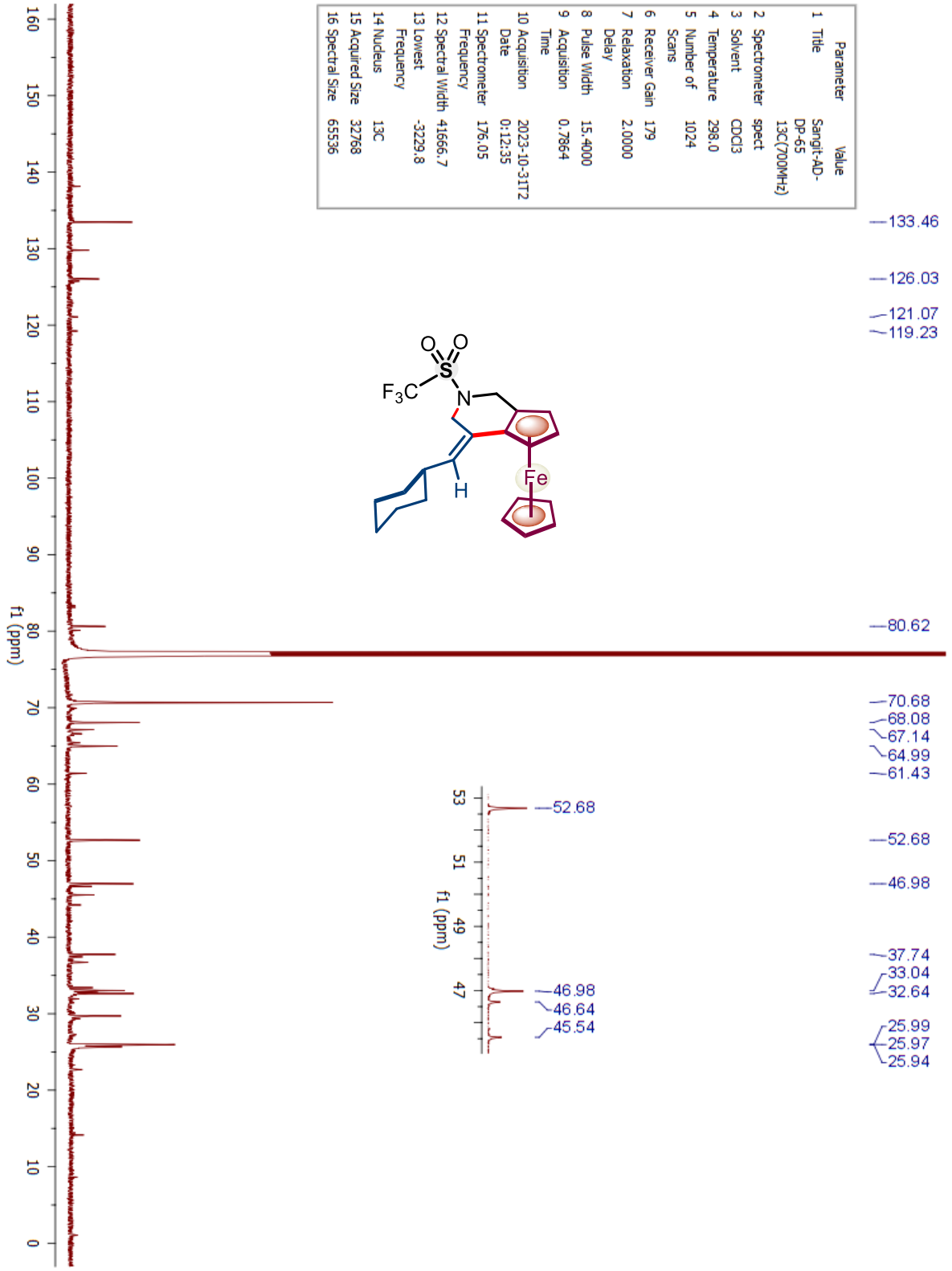
^{19}F NMR Spectrum of **3h**



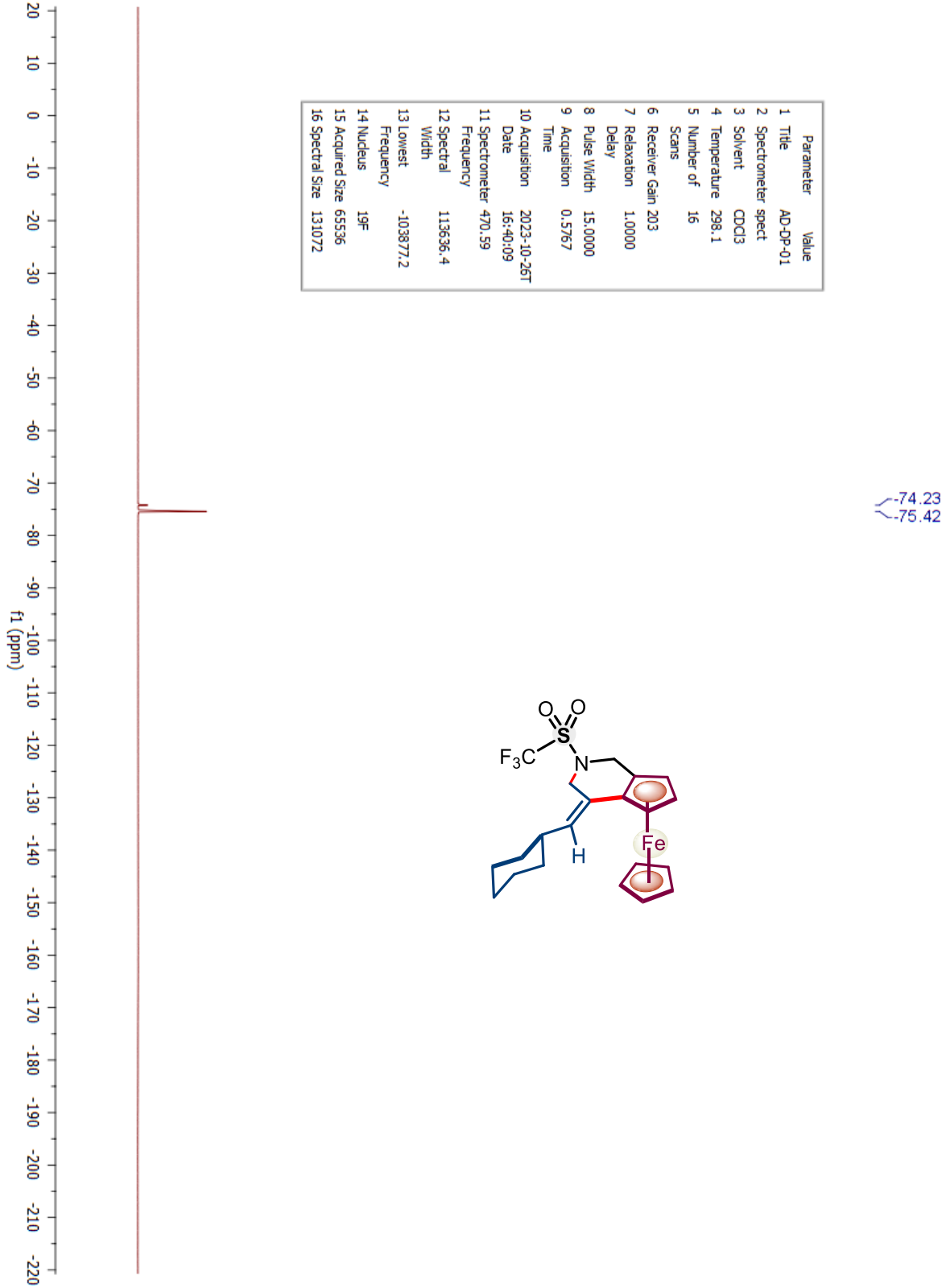
^{1}H NMR Spectrum of **3i**



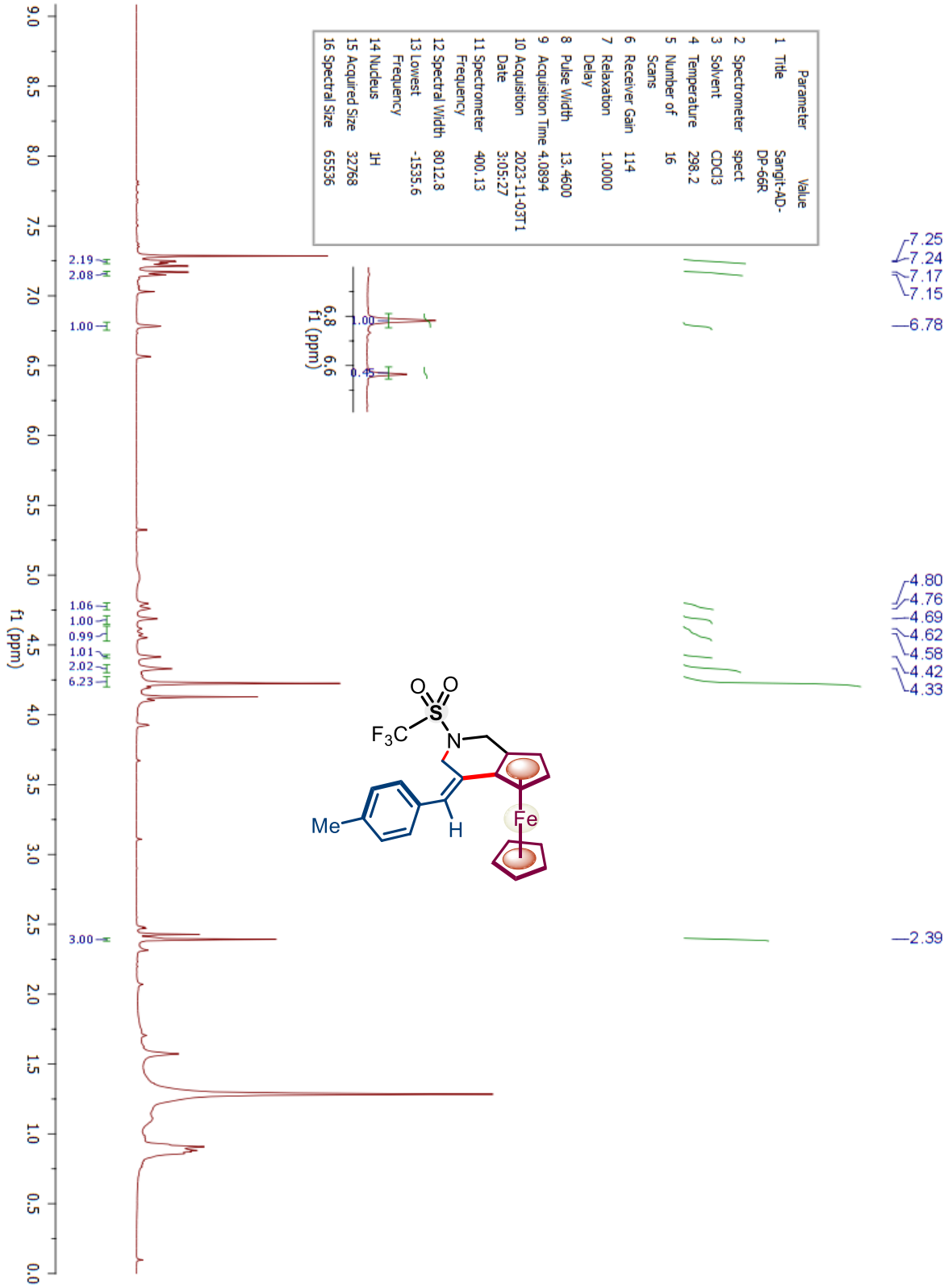
$^{13}C\{^{1}H\}$ NMR Spectrum of **3i**



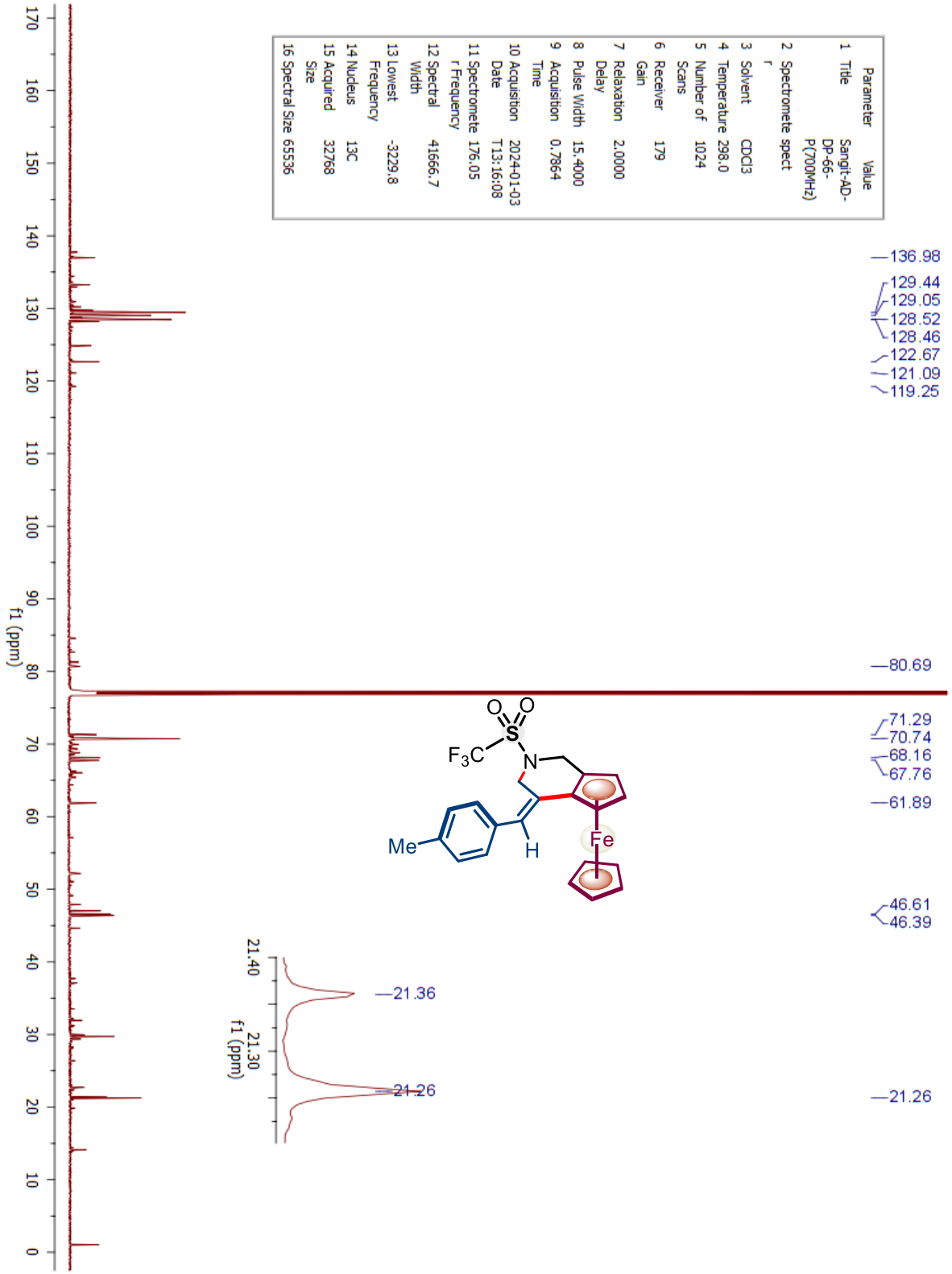
^{19}F NMR Spectrum of **3i**



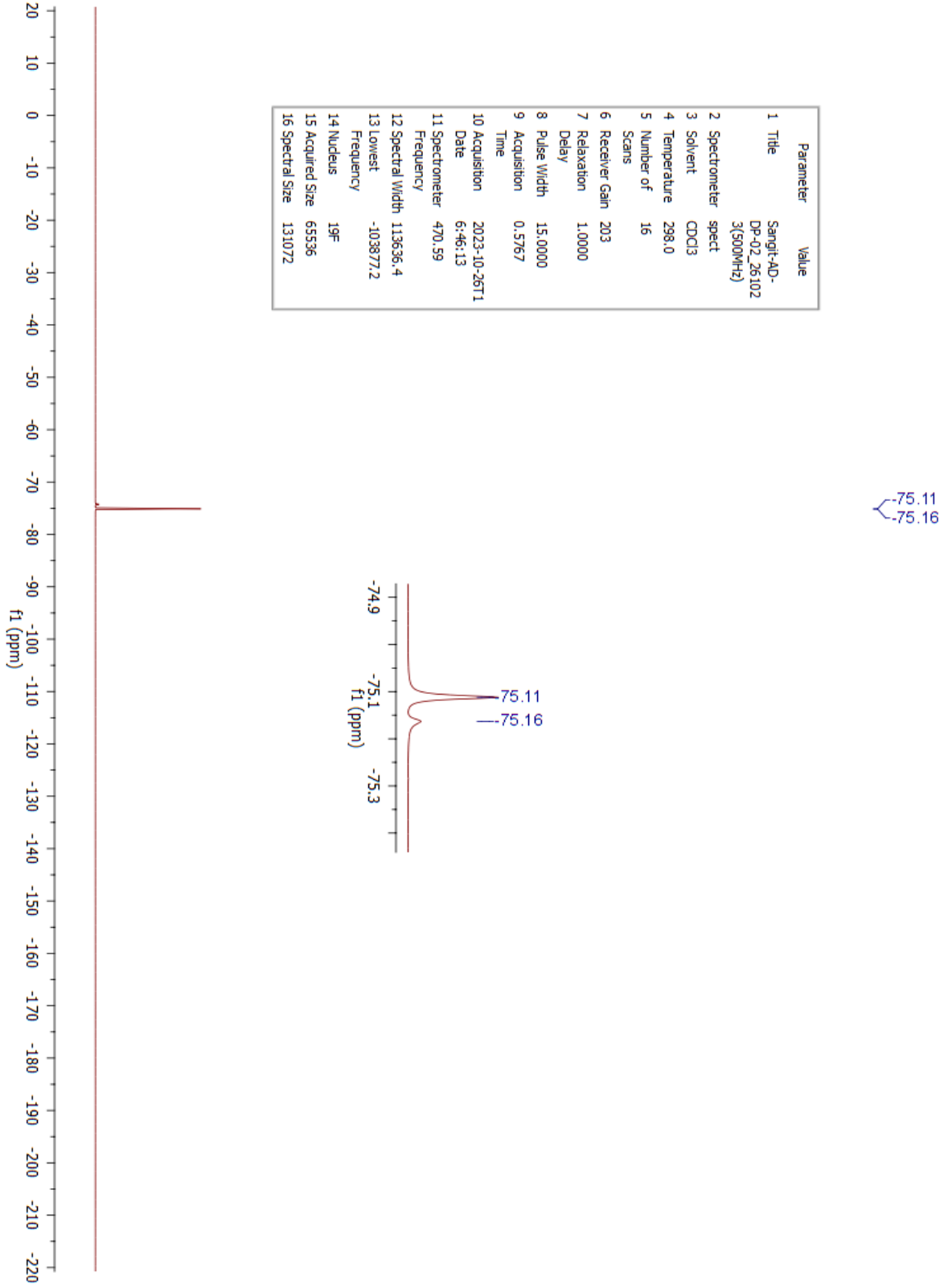
^{1}H NMR Spectrum of **3j**



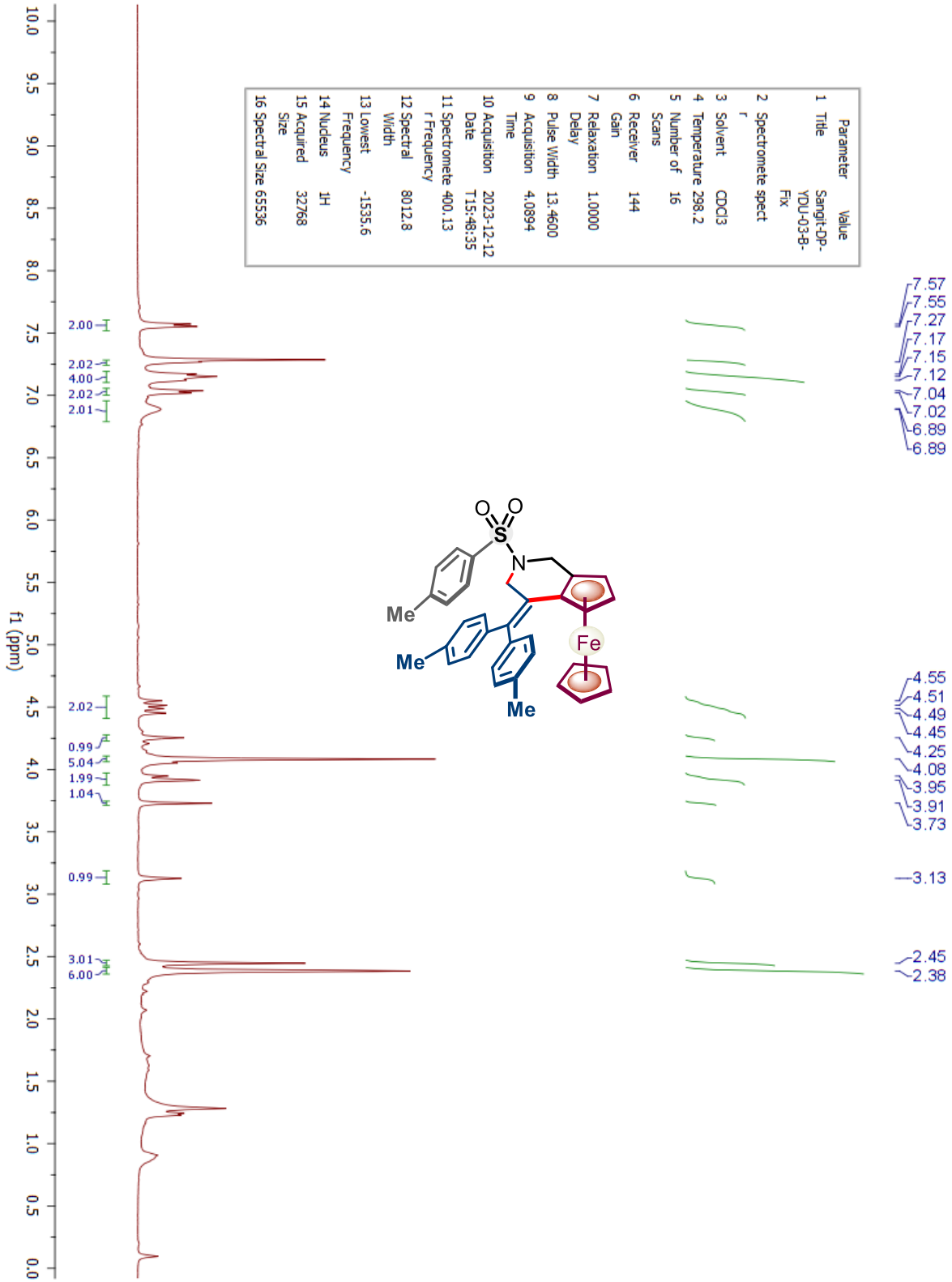
$^{13}C\{^{1}H\}$ NMR Spectrum of **3j**



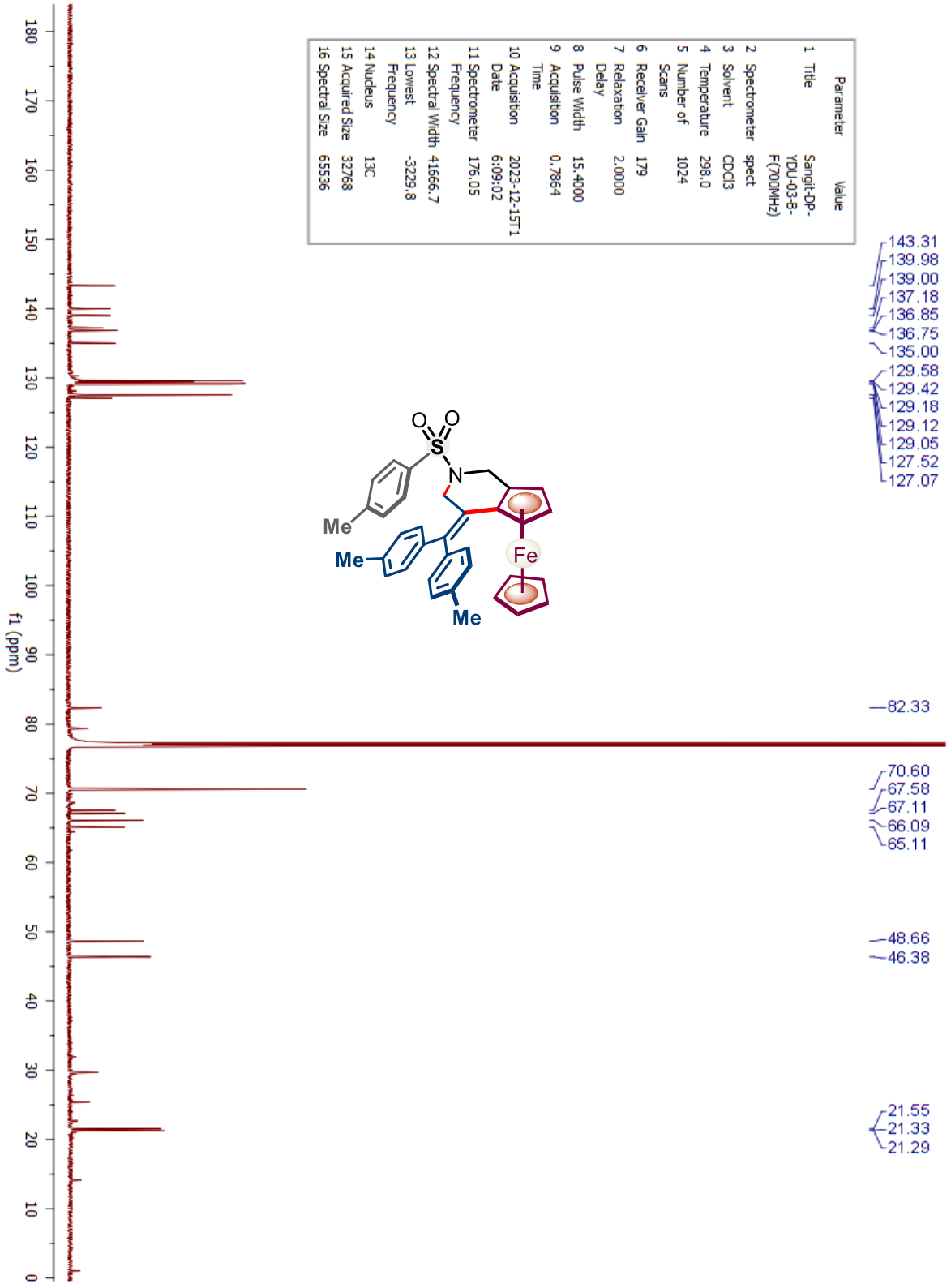
^{19}F NMR Spectrum of **3j**



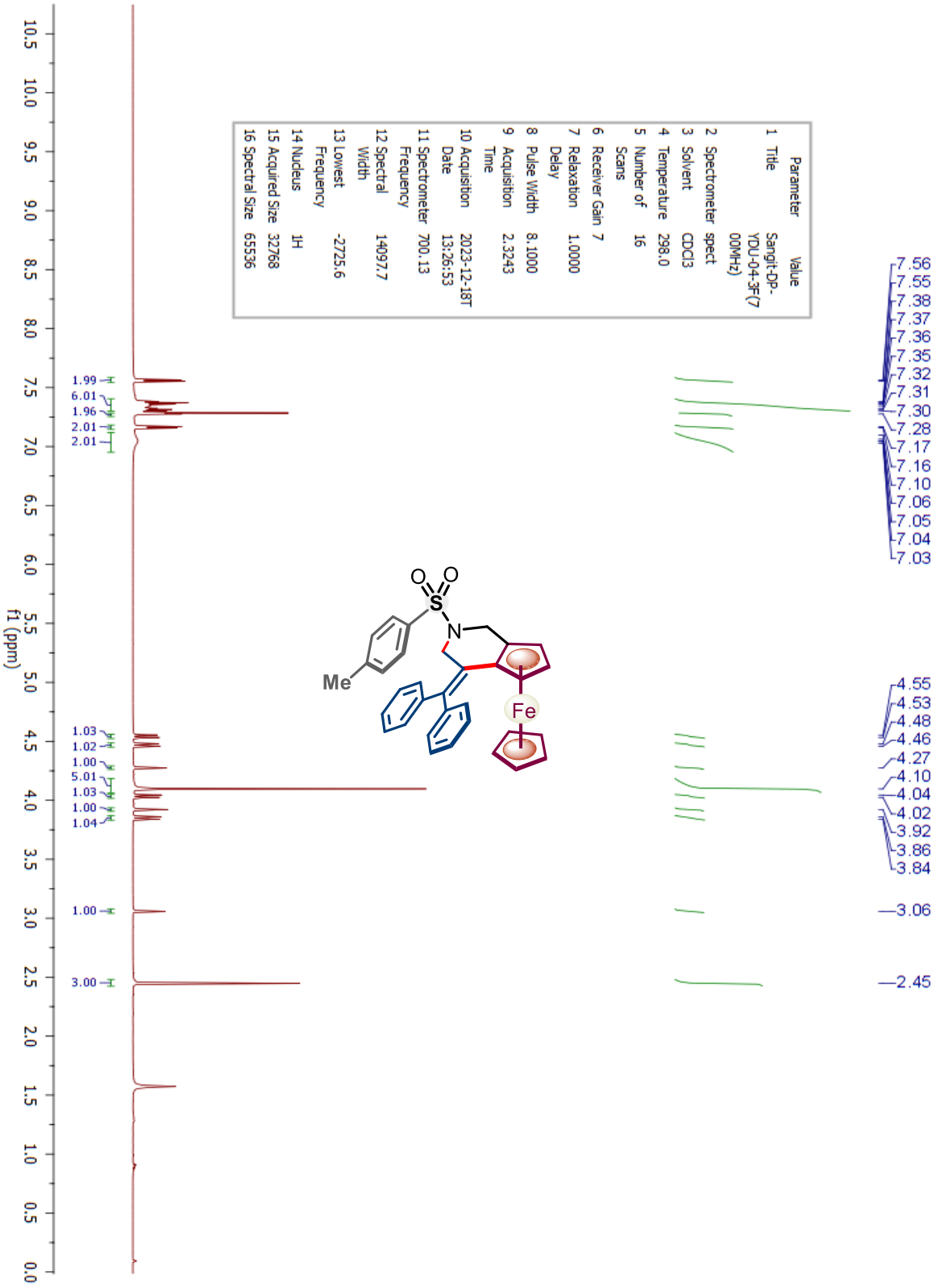
^{1}H NMR Spectrum of **3k**



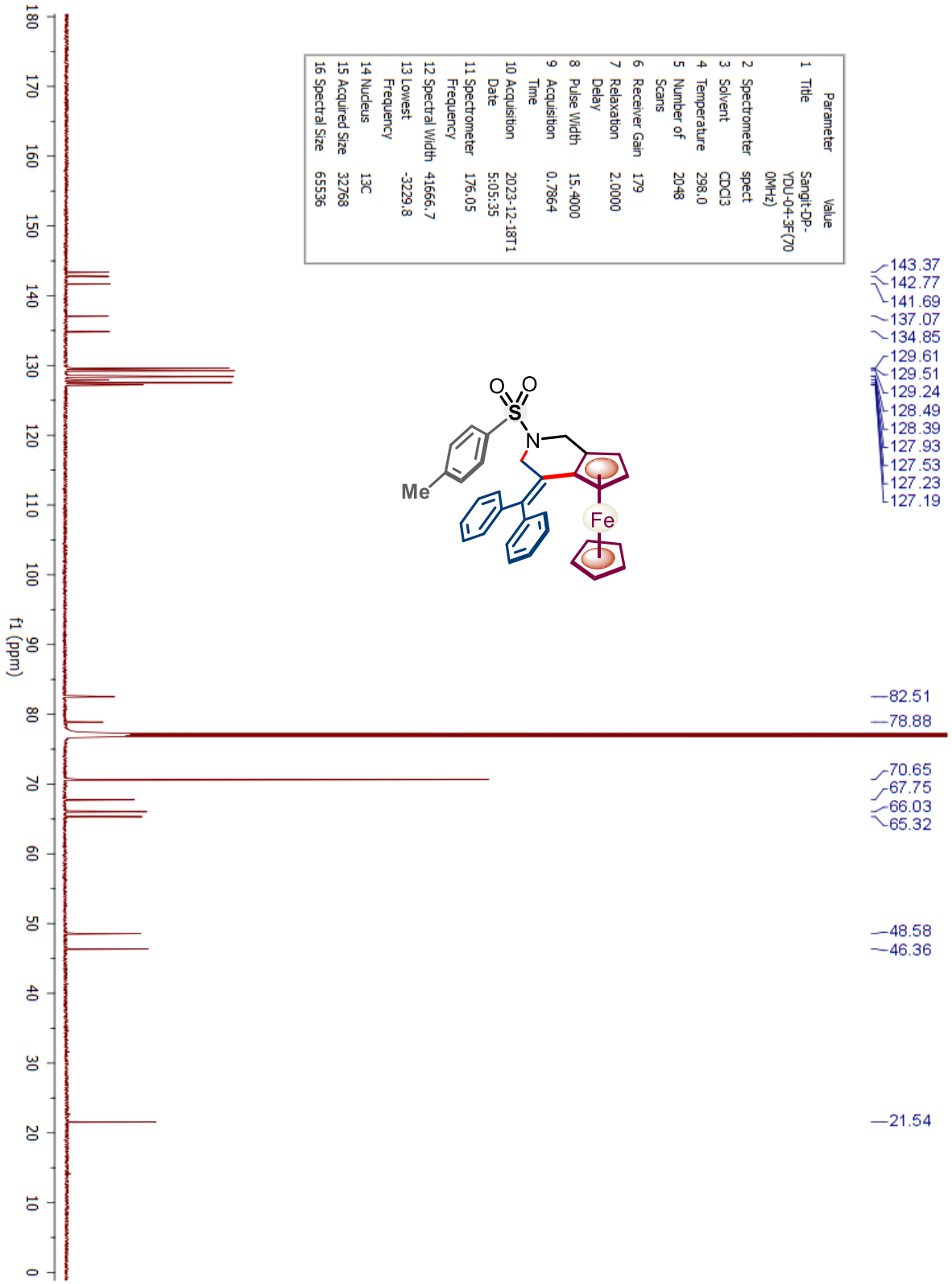
$^{13}C\{^{1}H\}$ NMR Spectrum of **3k**



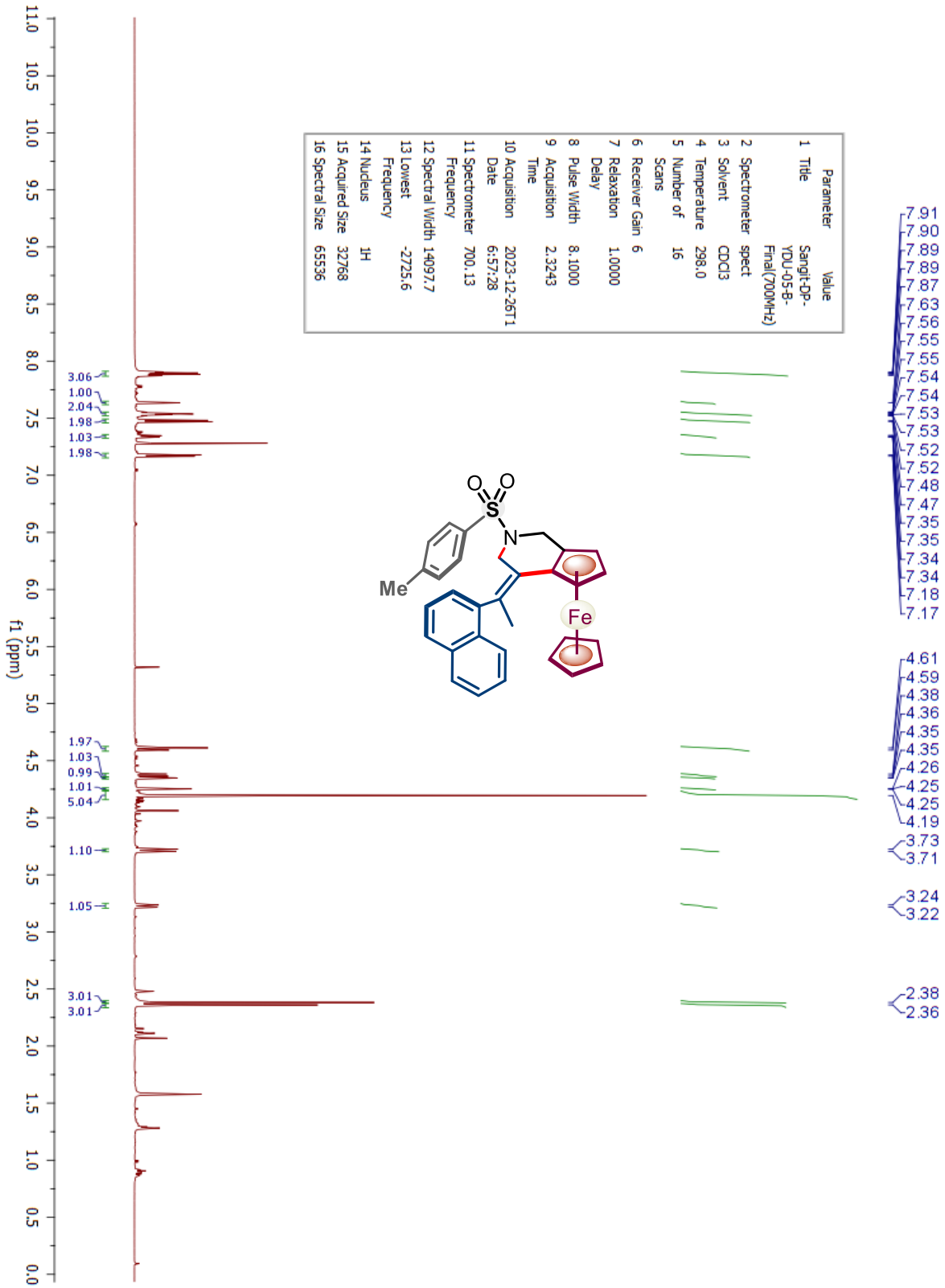
^{1}H NMR Spectrum of **3l**



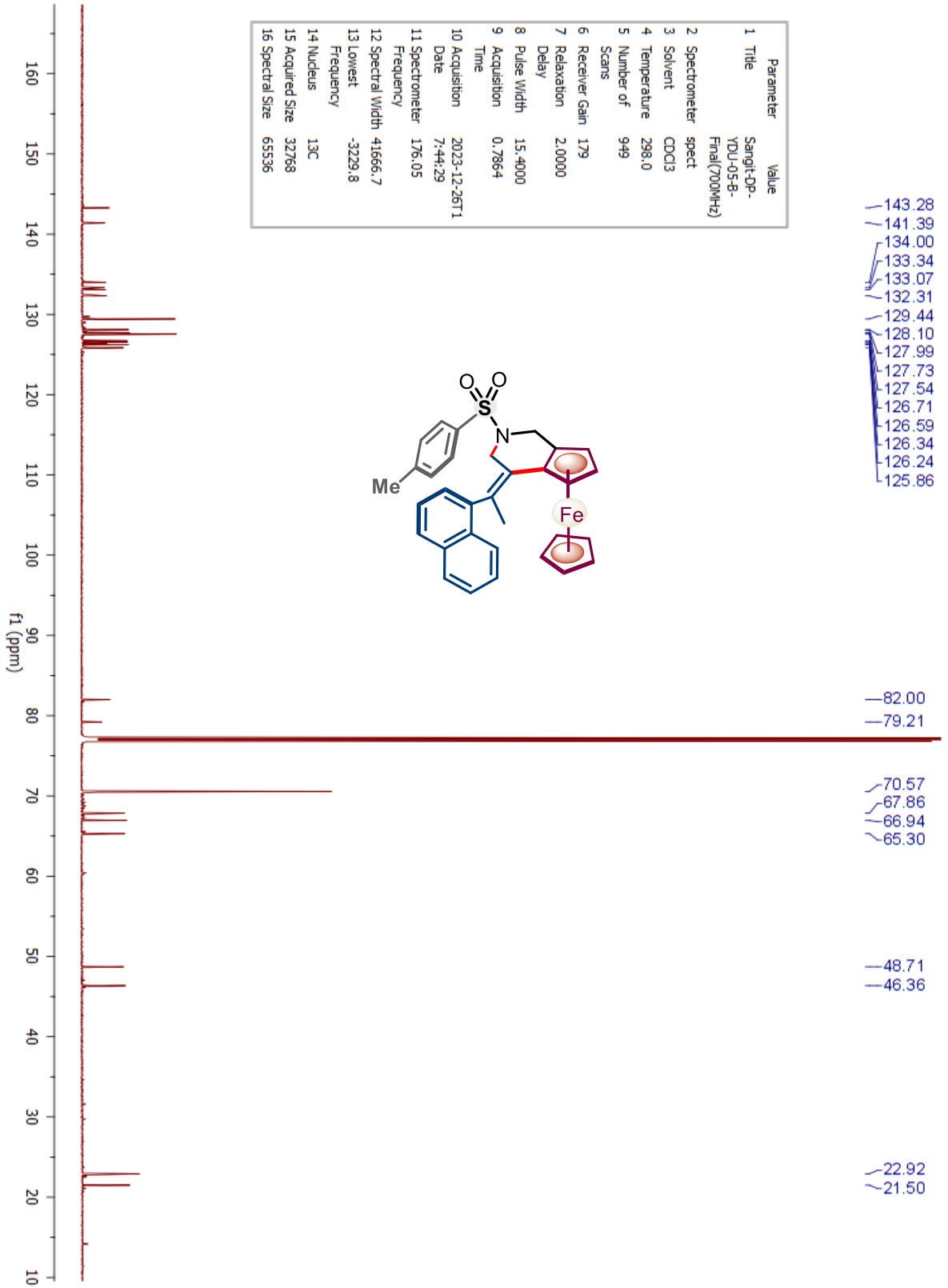
$^{13}C\{^{1}H\}$ NMR Spectrum of **3l**



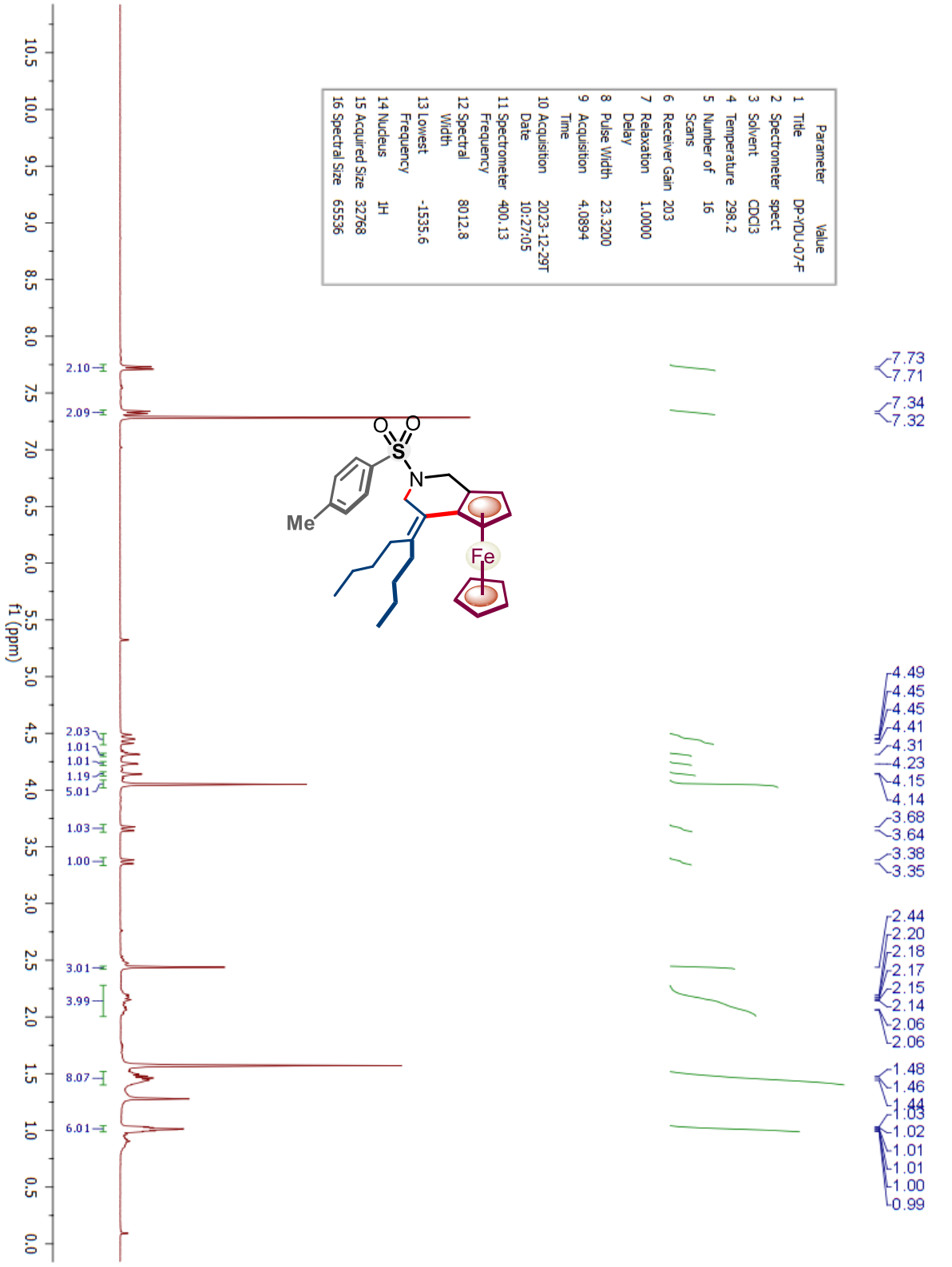
^{1}H NMR Spectrum of **3m**



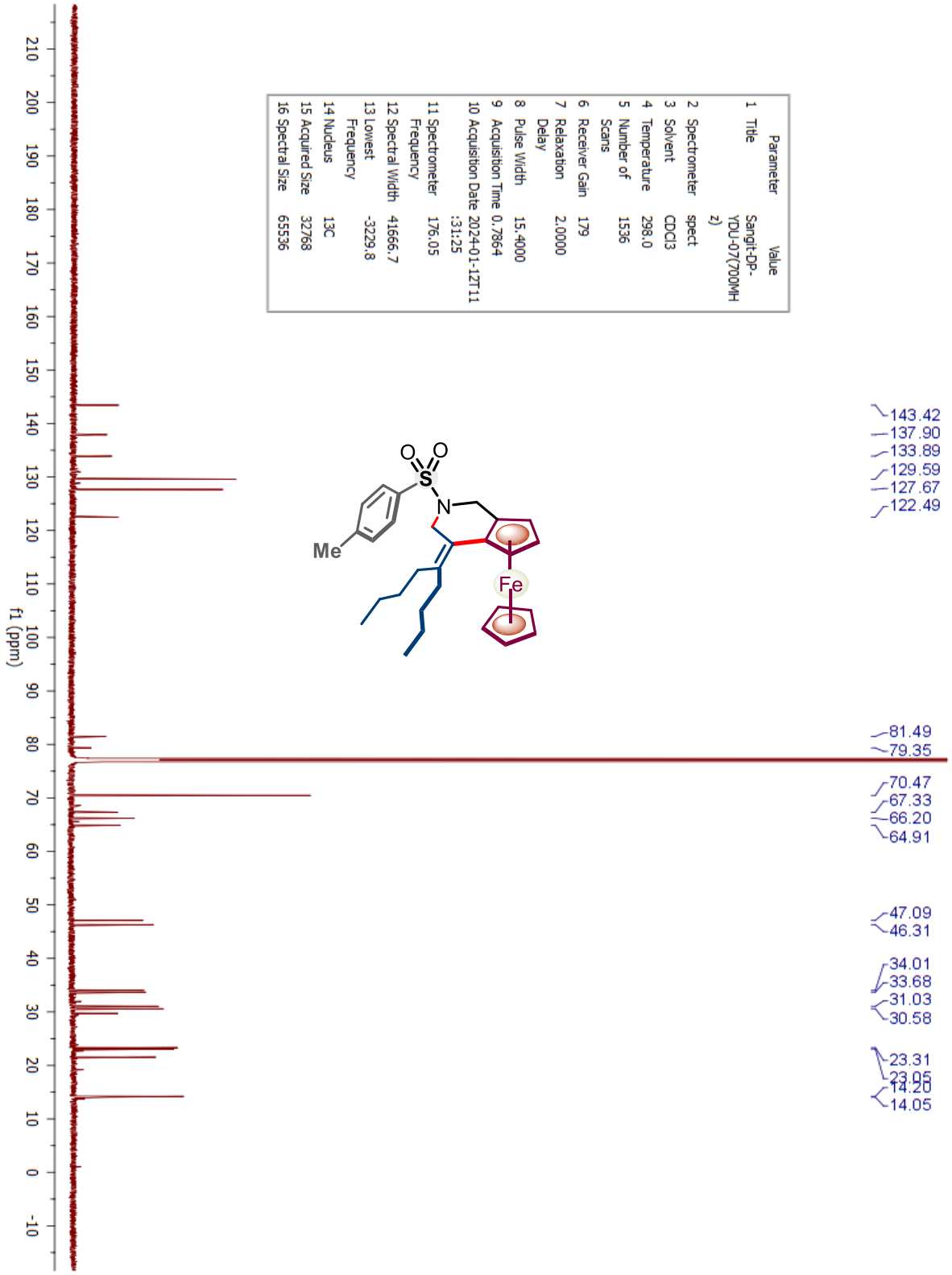
$^{13}C\{^{1}H\}$ NMR Spectrum of **3m**



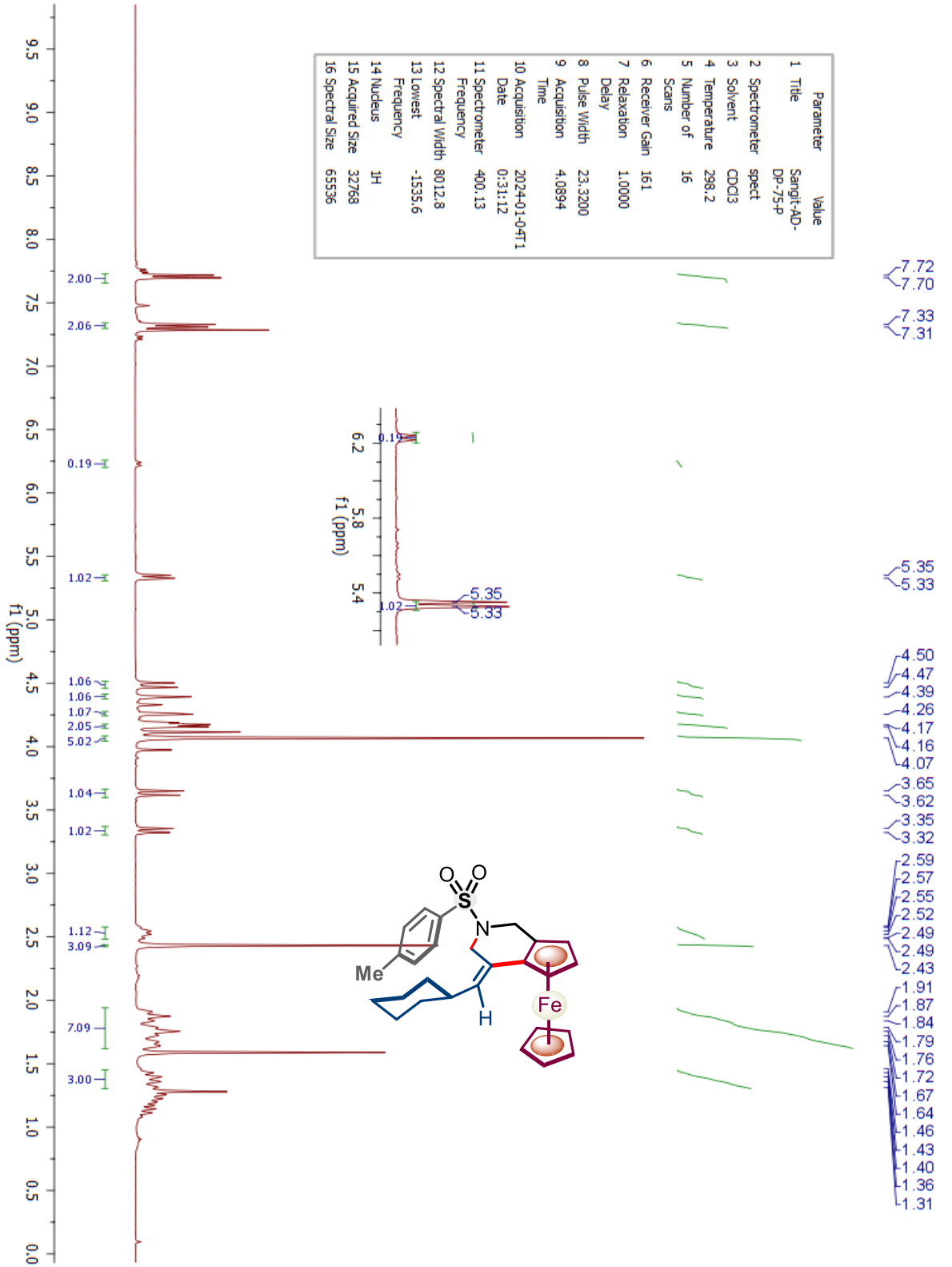
^{1}H NMR Spectrum of **3n**



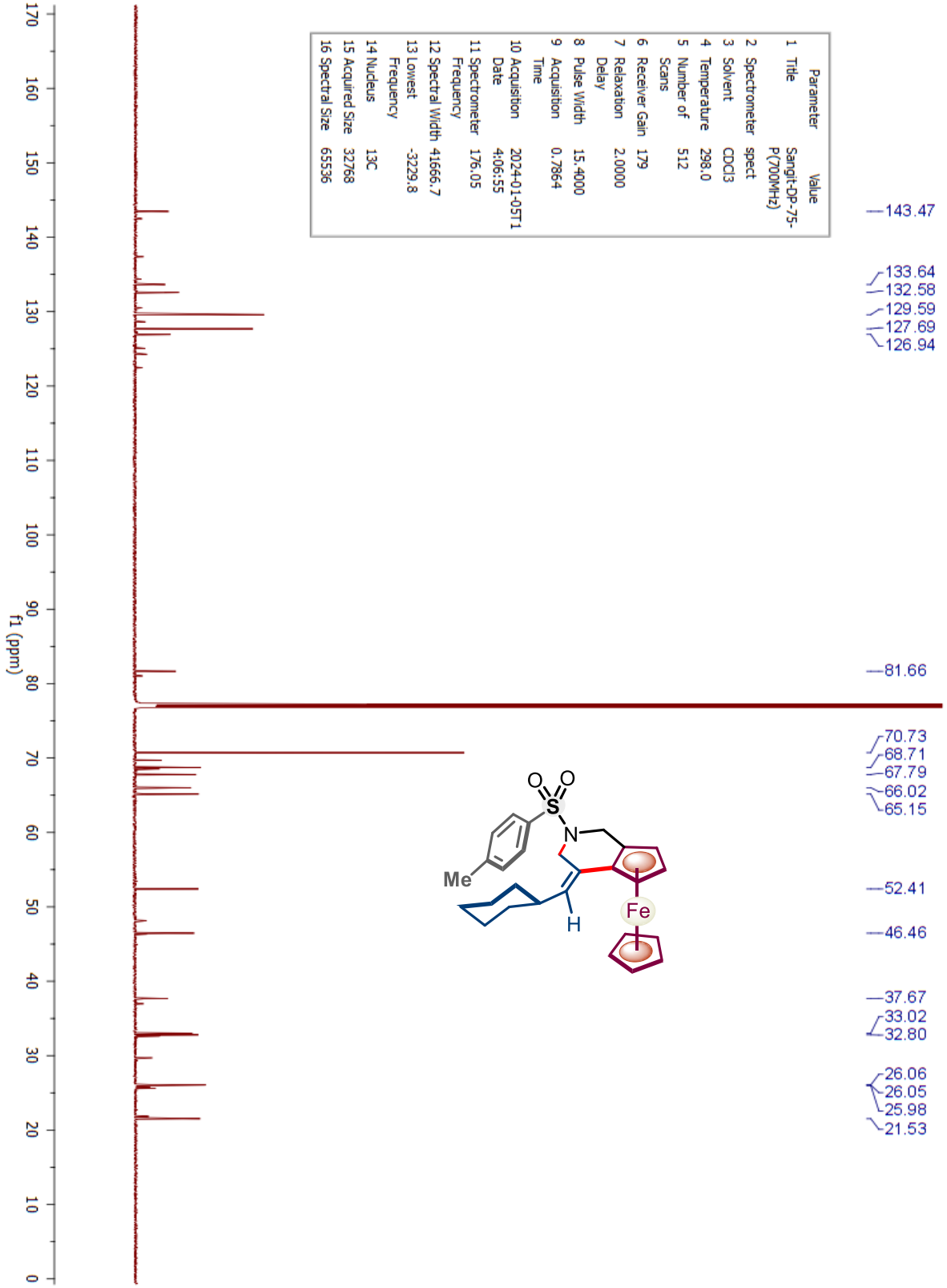
$^{13}C\{^{1}H\}$ NMR Spectrum of **3n**



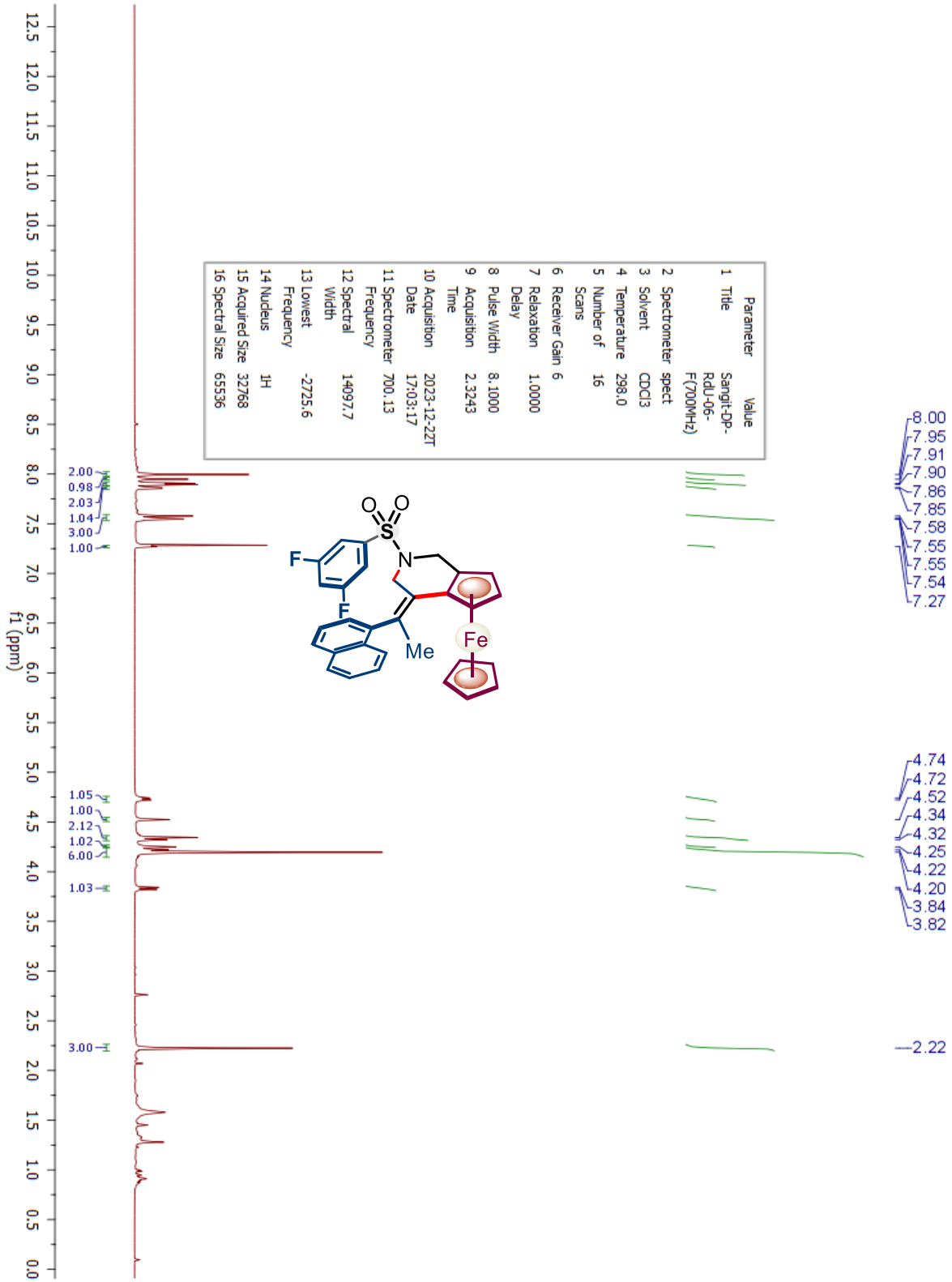
^{1}H NMR Spectrum of **3o**



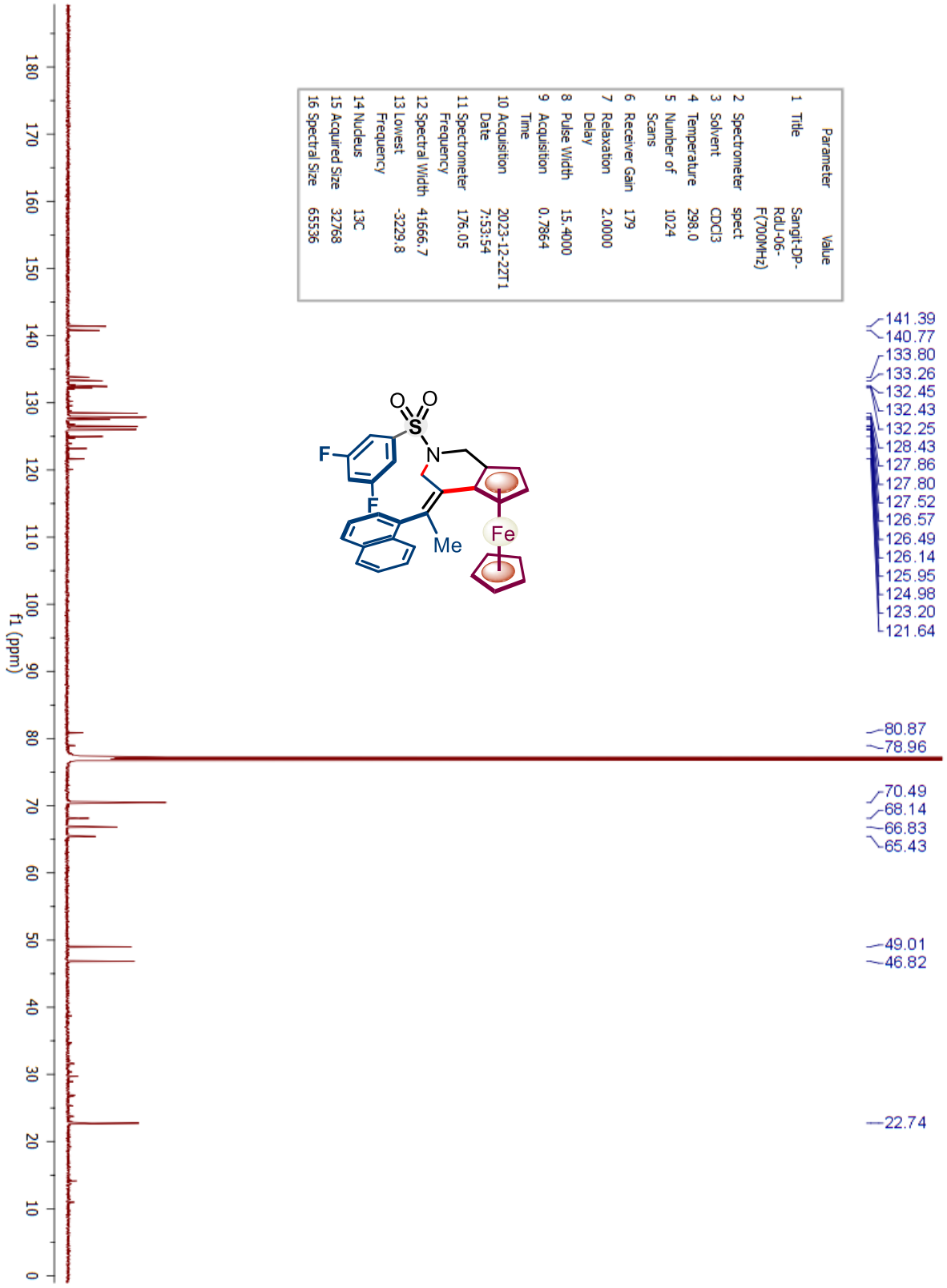
$^{13}C\{^{1}H\}$ NMR Spectrum of **3o**



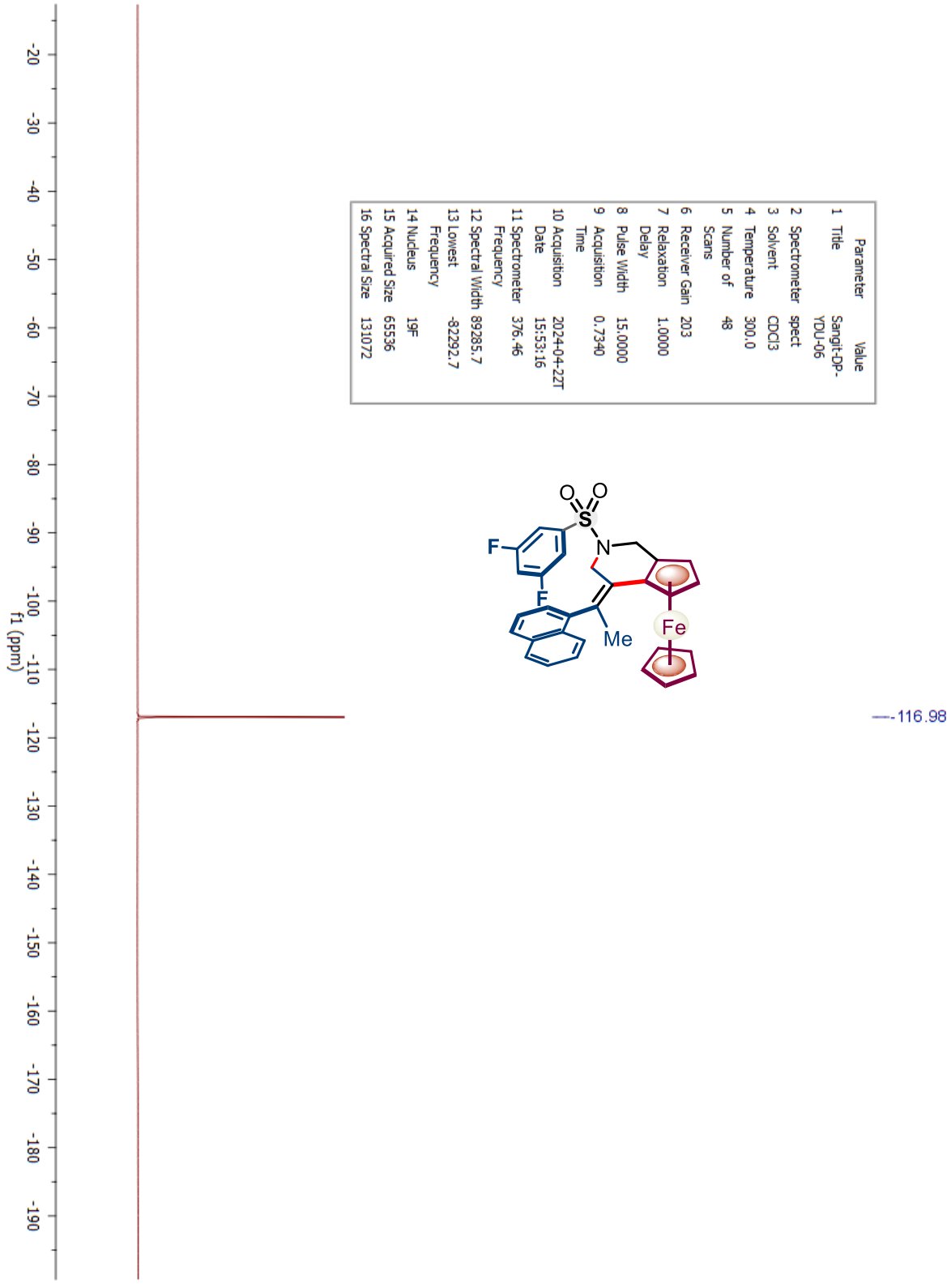
^{1}H NMR Spectrum of **3p**



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

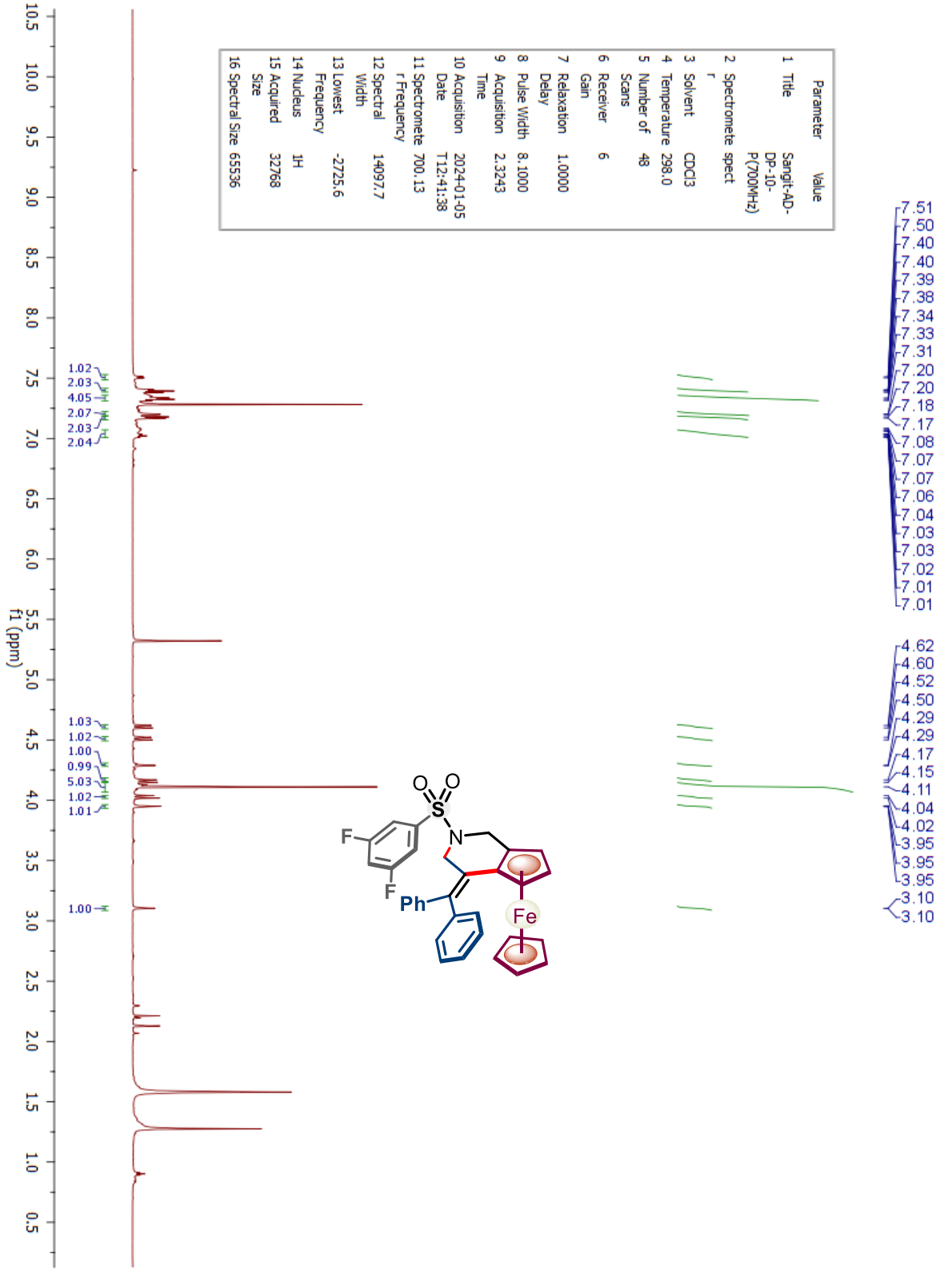


^{19}F NMR Spectrum of **3p**

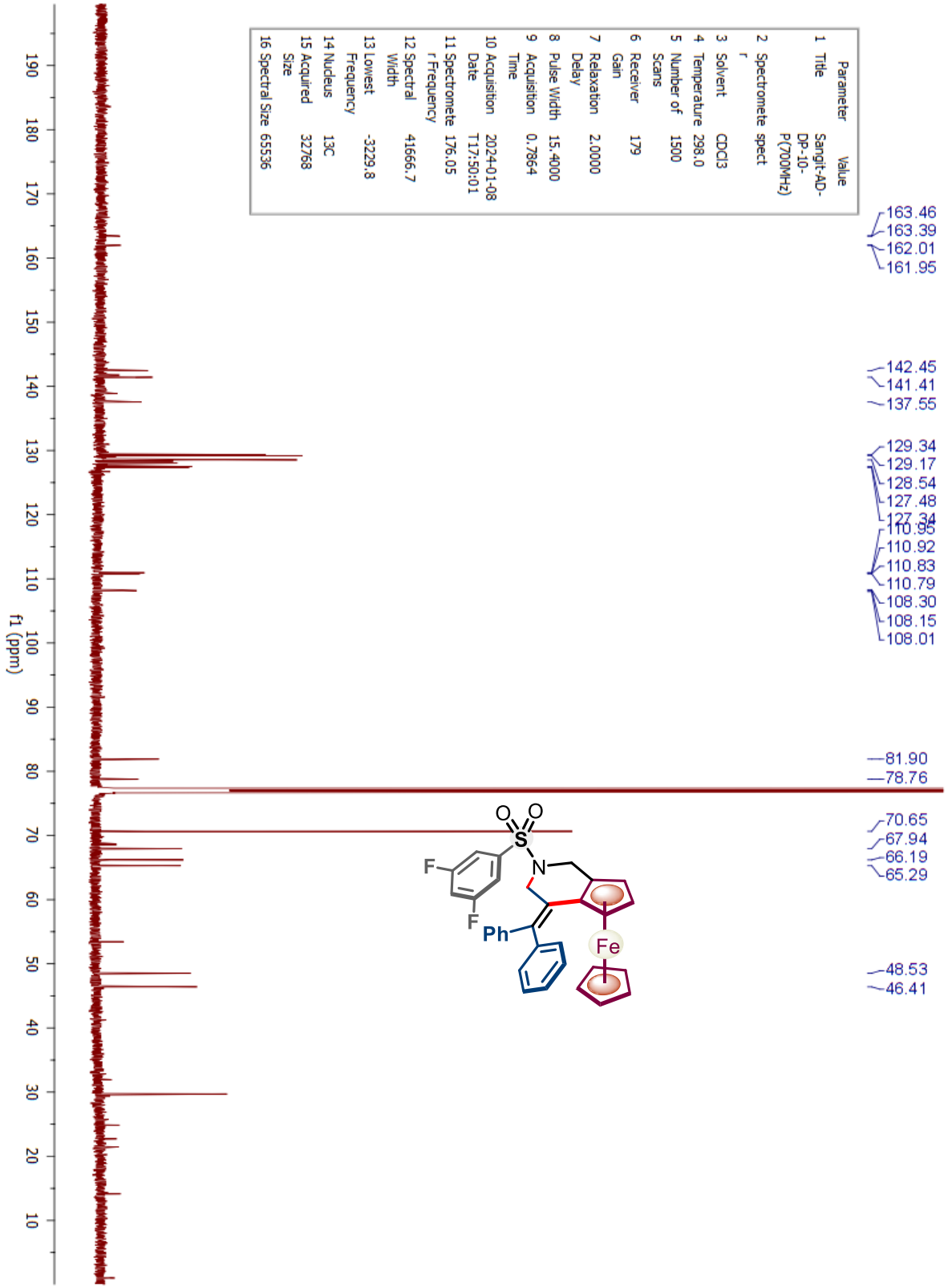


	Parameter	Value
1	Title	Sangit-DP-YDU-06
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	300.0
5	Number of Scans	48
6	Receiver Gain	203
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Acquisition Time	0.7340
10	Acquisition Date	2024-04-22T 15:53:16
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82292.7
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

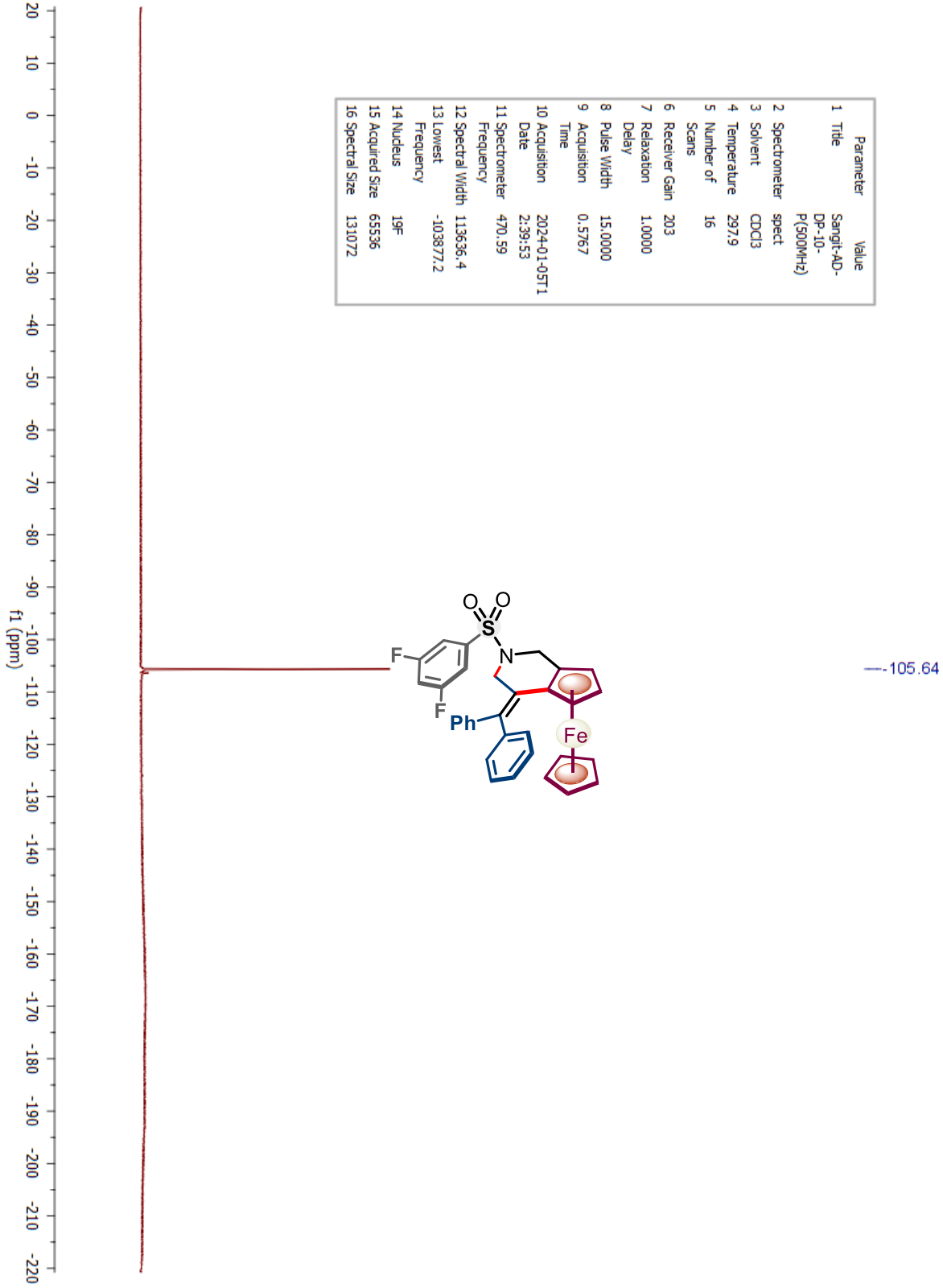
^{1}H NMR Spectrum of **3q**



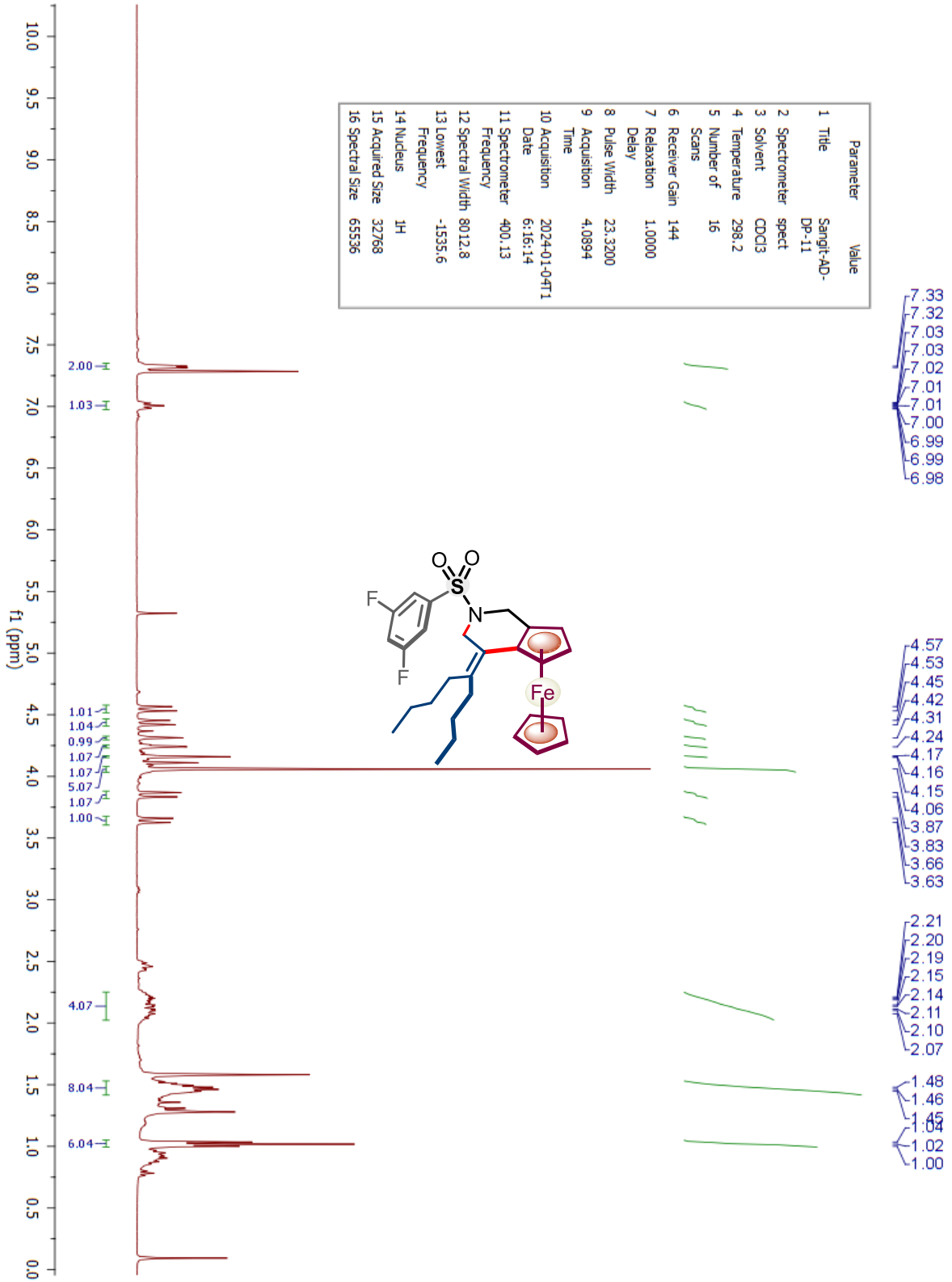
$^{13}C\{^{1}H\}$ NMR Spectrum of **3q**



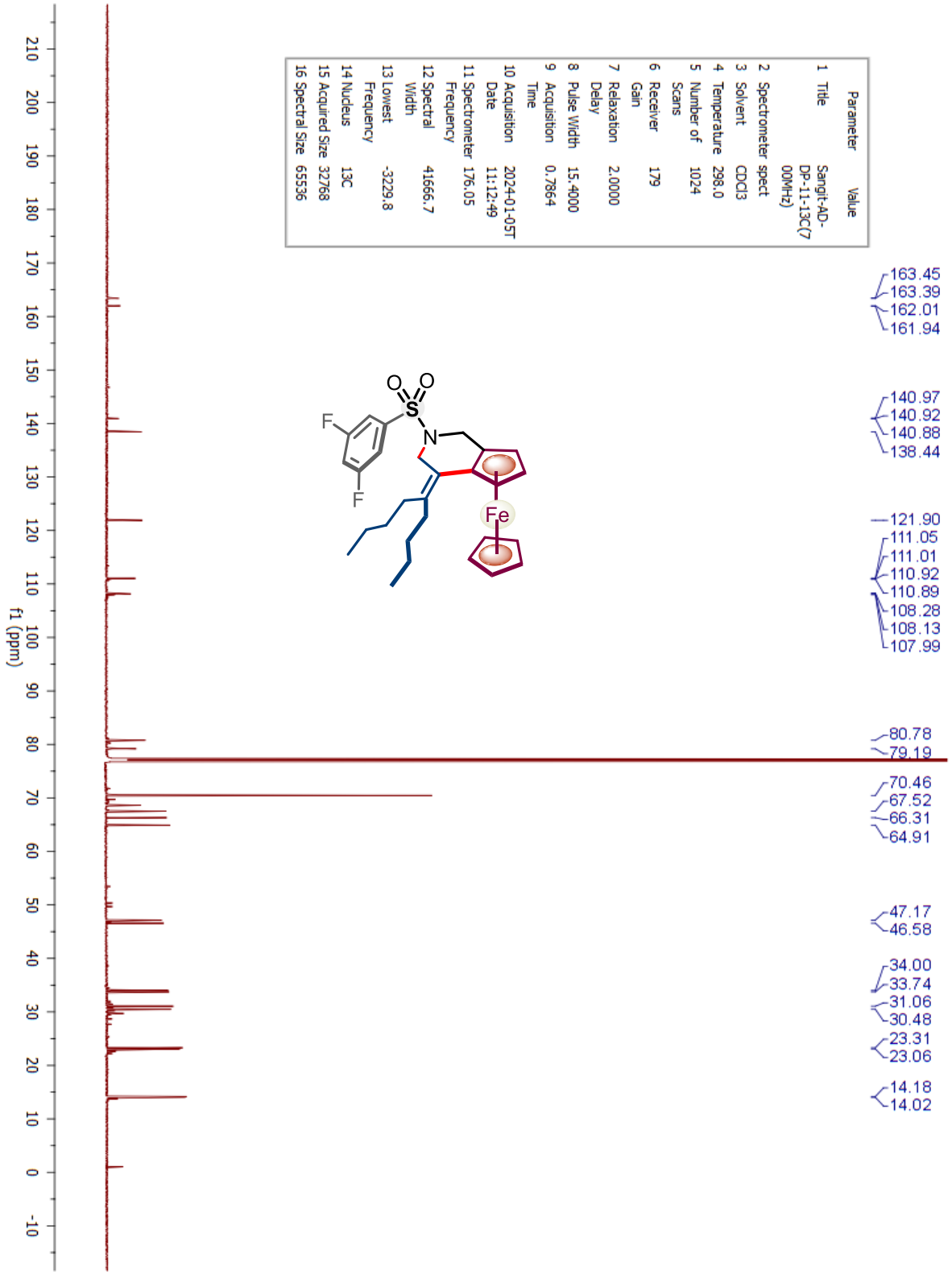
^{19}F NMR Spectrum of **3q**



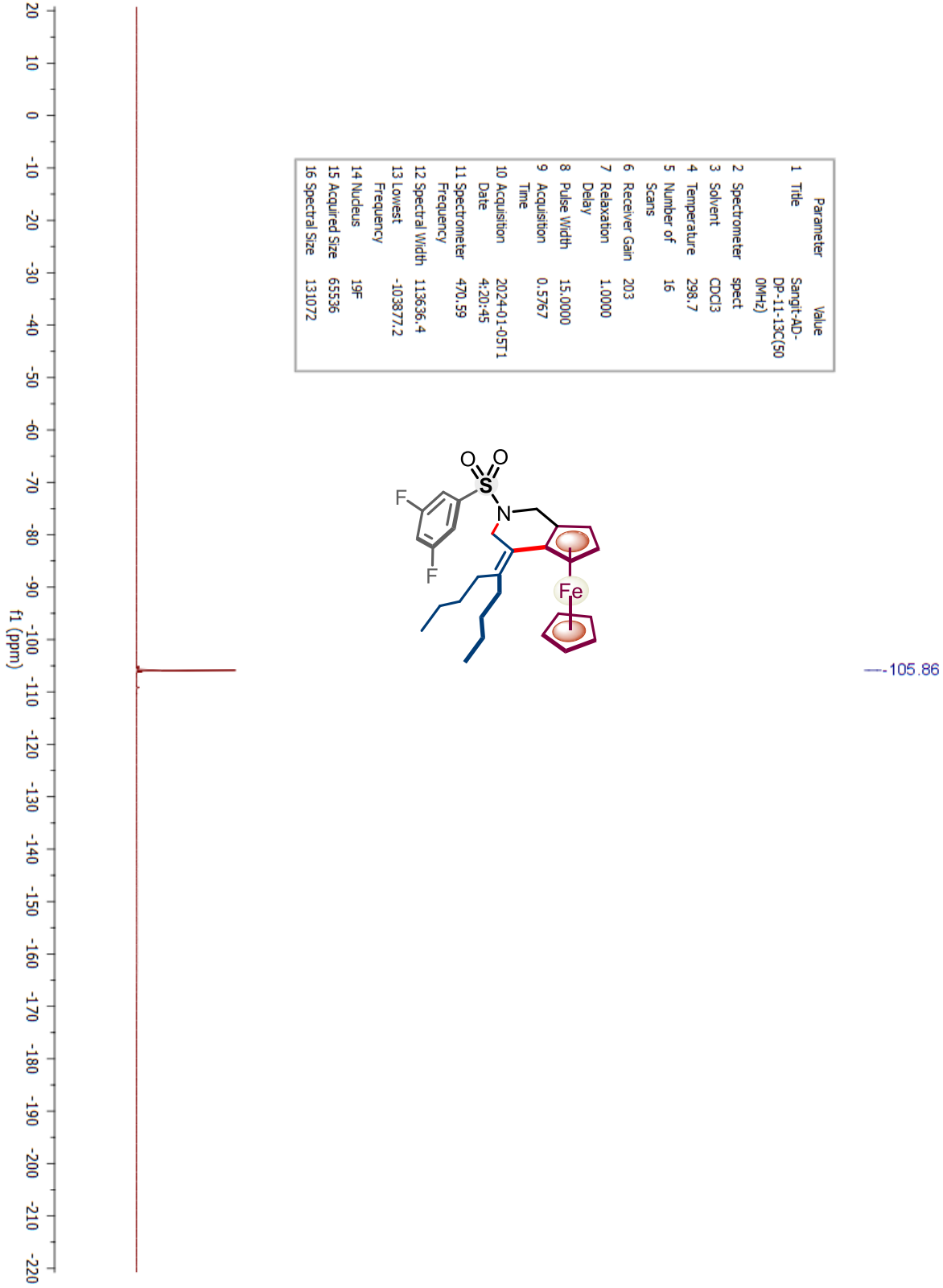
^{1}H NMR Spectrum of **3r**



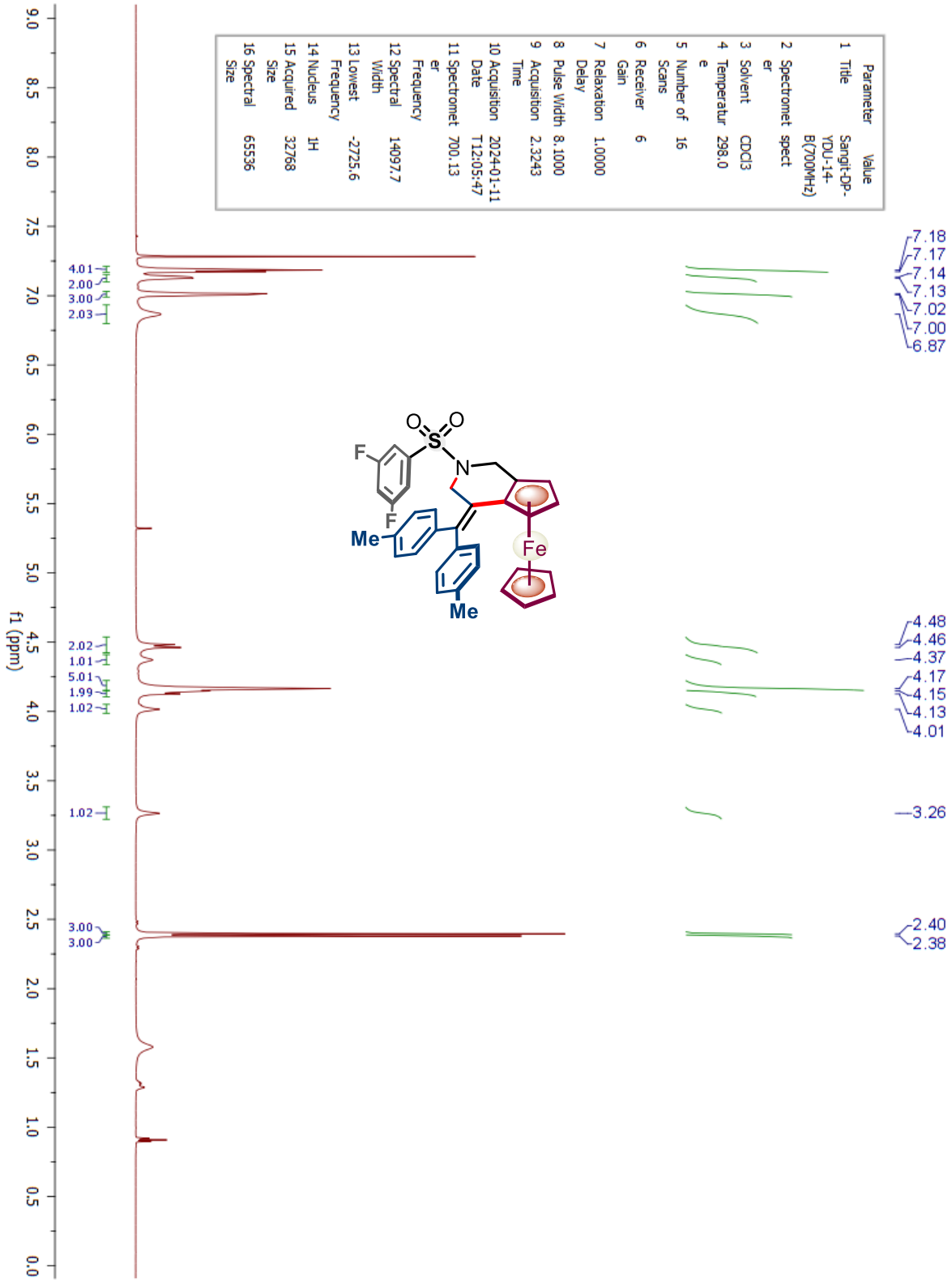
$^{13}C\{^{1}H\}$ NMR Spectrum of **3r**



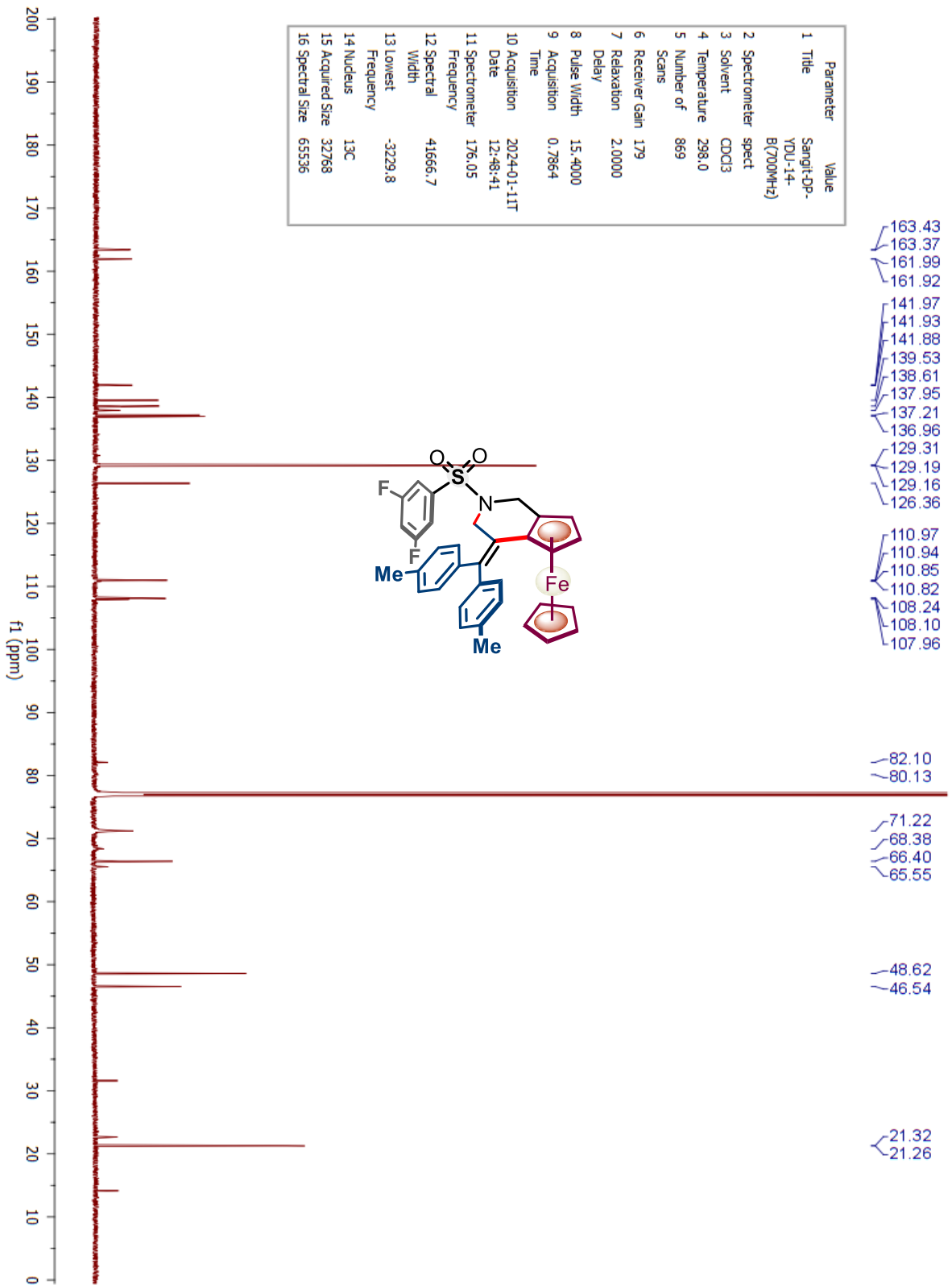
^{19}F NMR Spectrum of **3r**



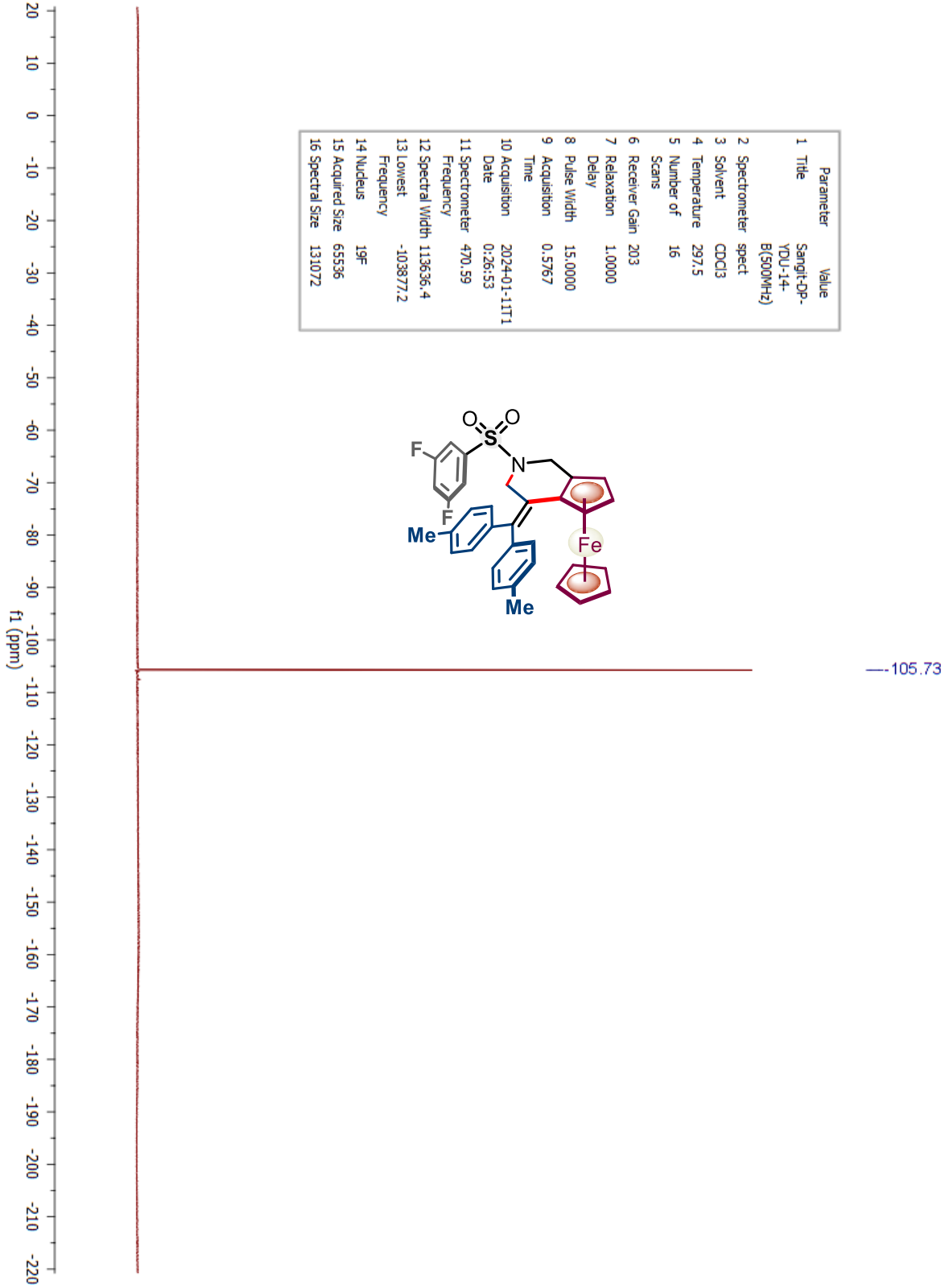
^{1}H NMR Spectrum of **3s**



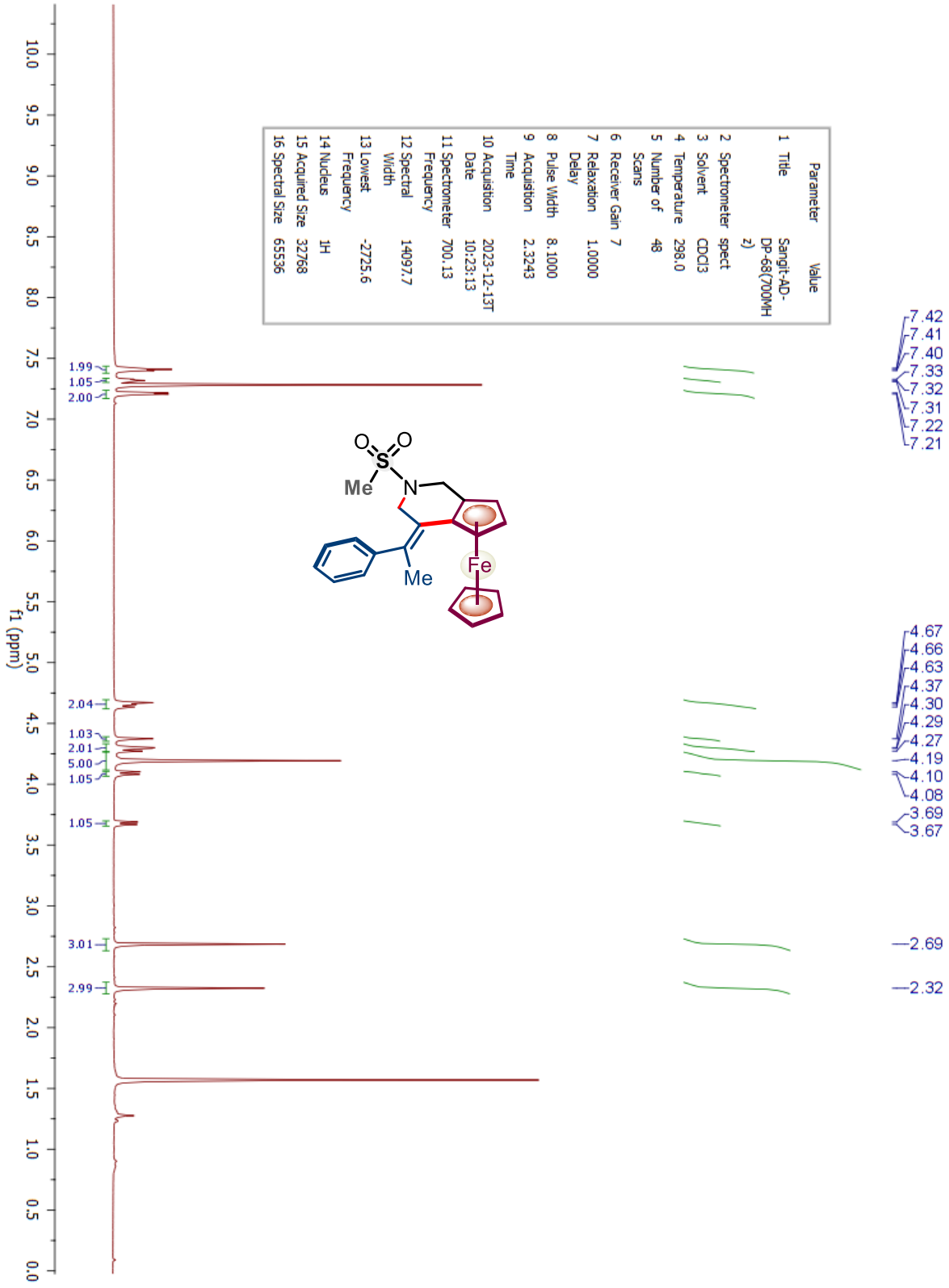
$^{13}C\{^{1}H\}$ NMR Spectrum of **3s**



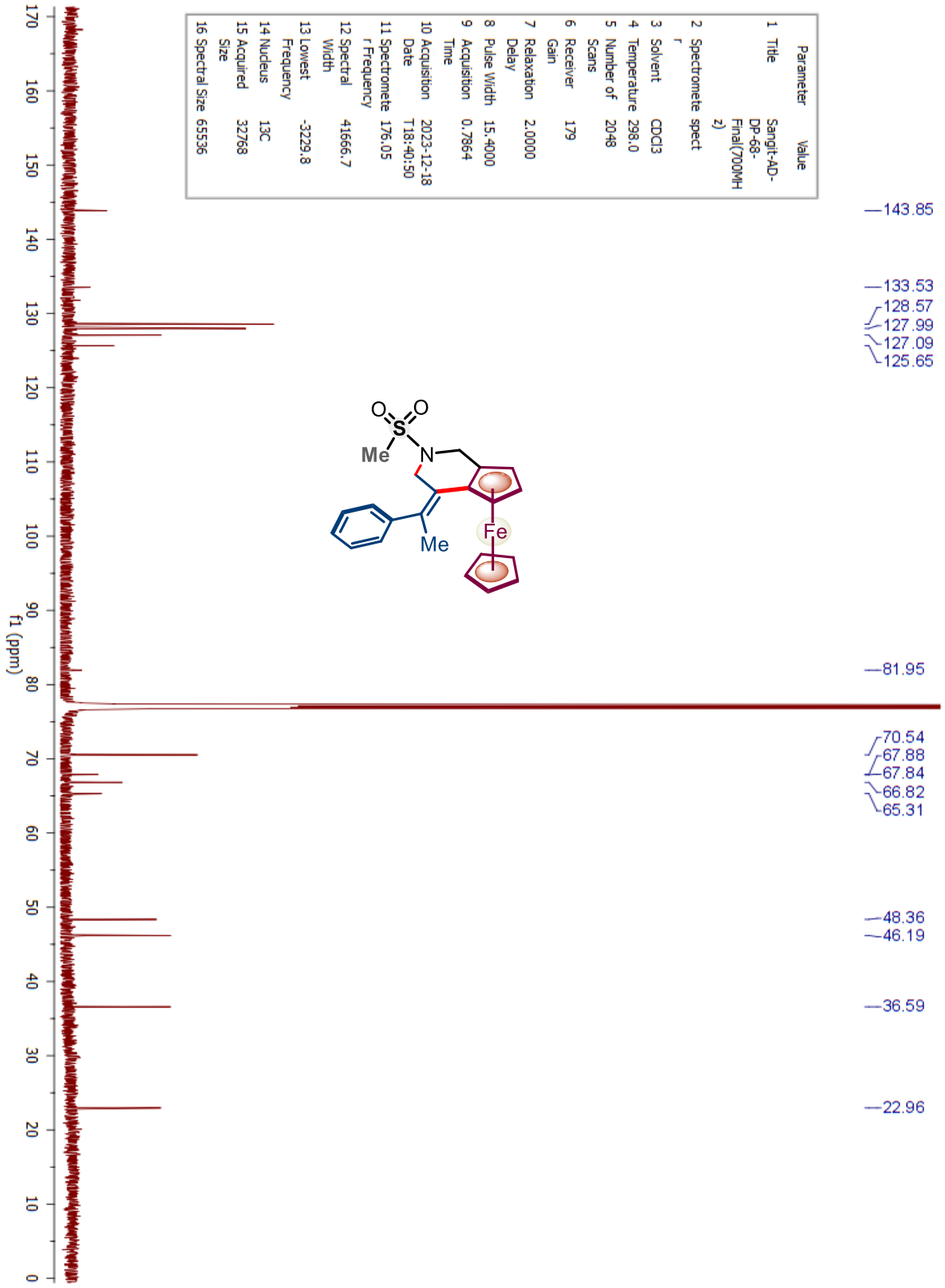
^{19}F NMR Spectrum of **3s**



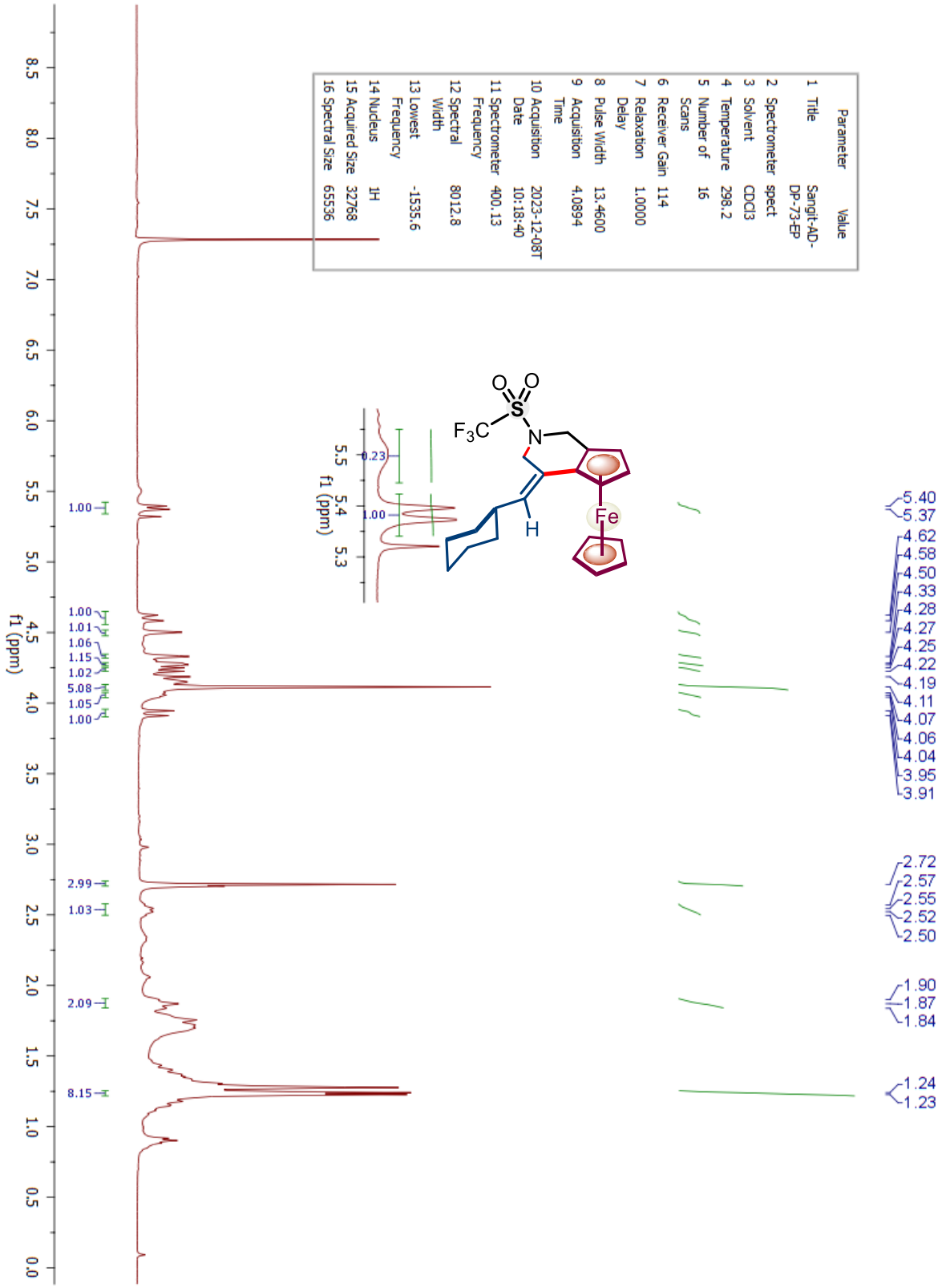
^{1}H NMR Spectrum of **3t**



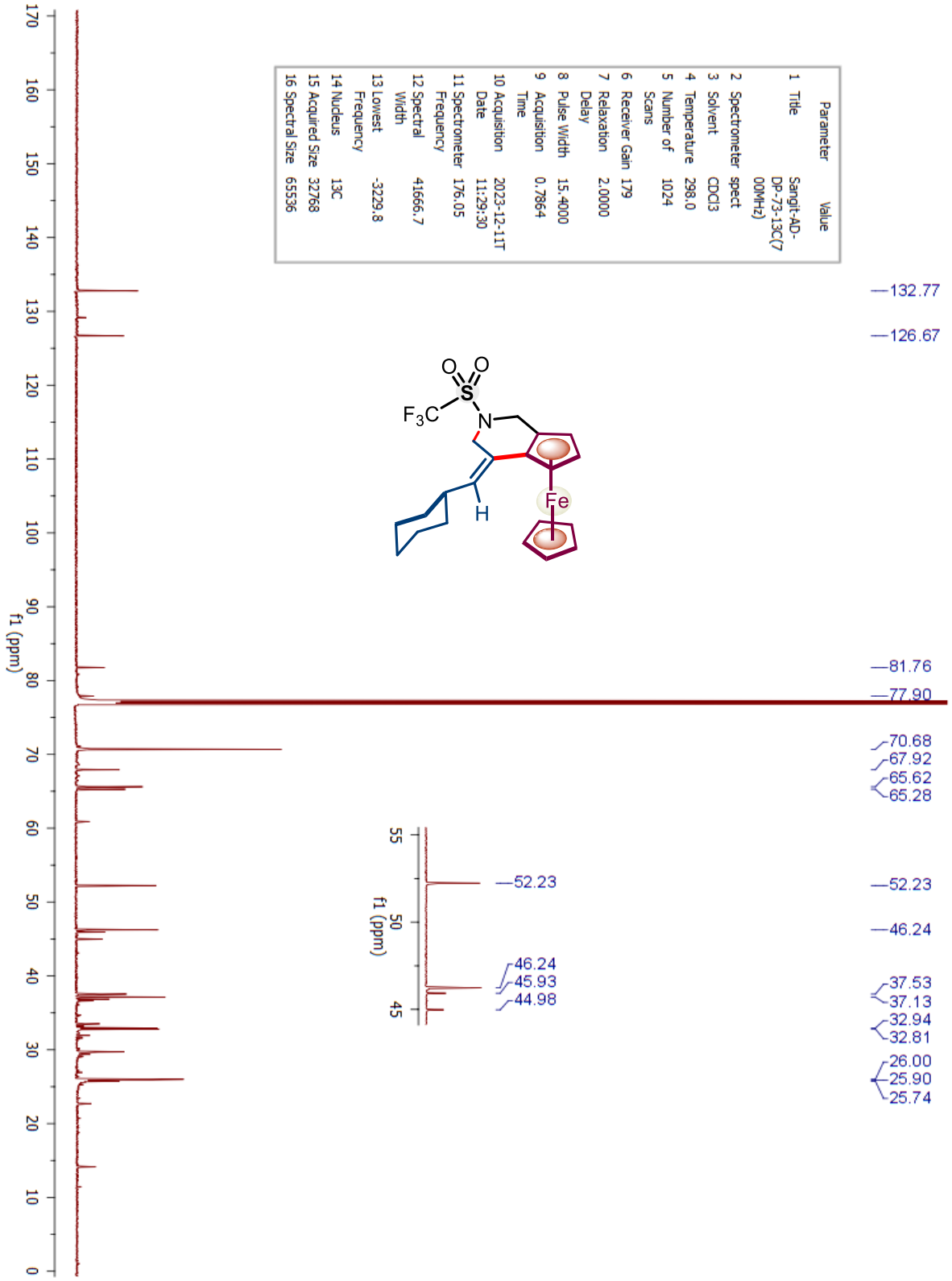
$^{13}C\{^{1}H\}$ NMR Spectrum of **3t**



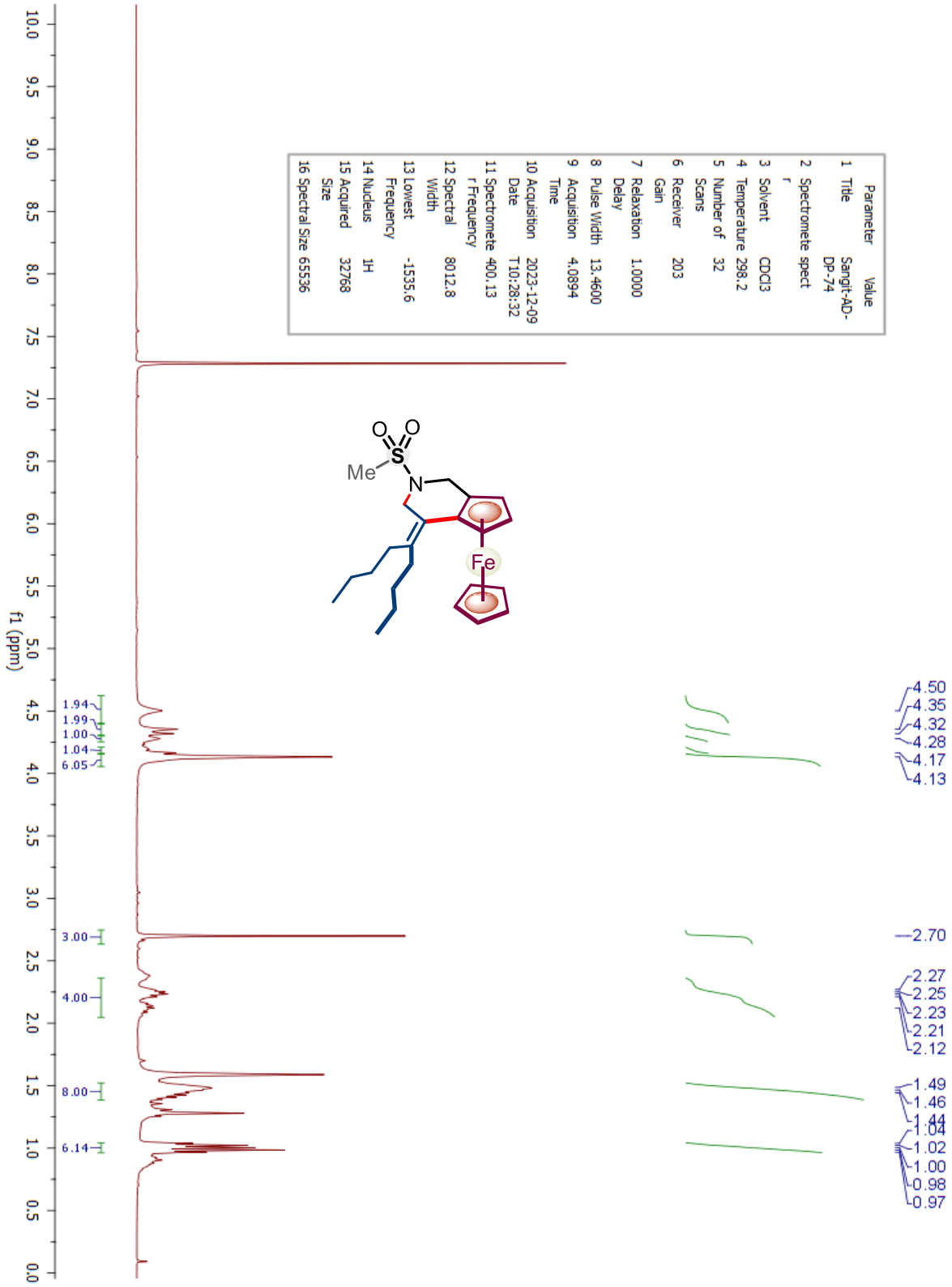
^{1}H NMR Spectrum of **3u**



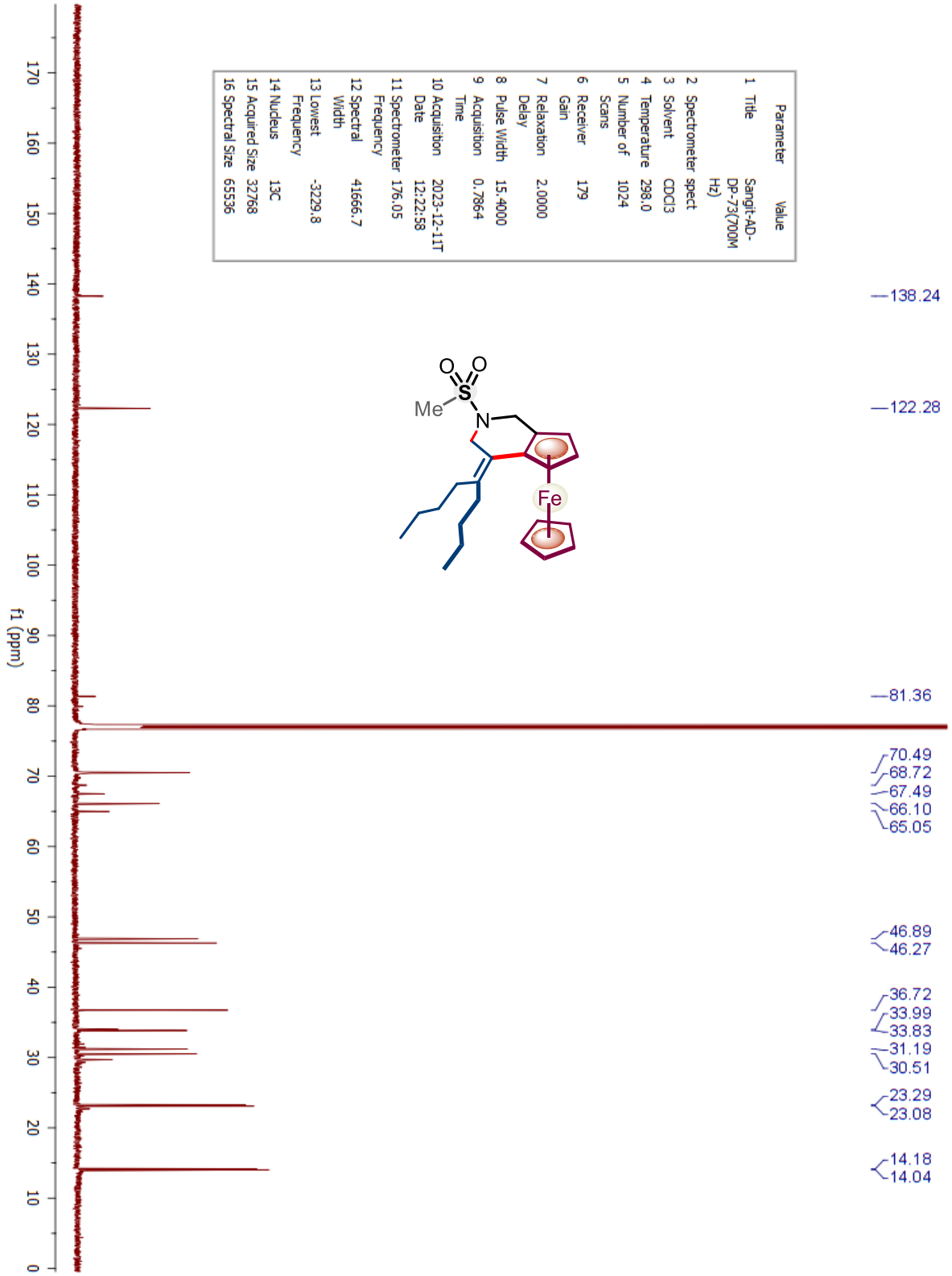
$^{13}C\{^{1}H\}$ NMR Spectrum of **3u**



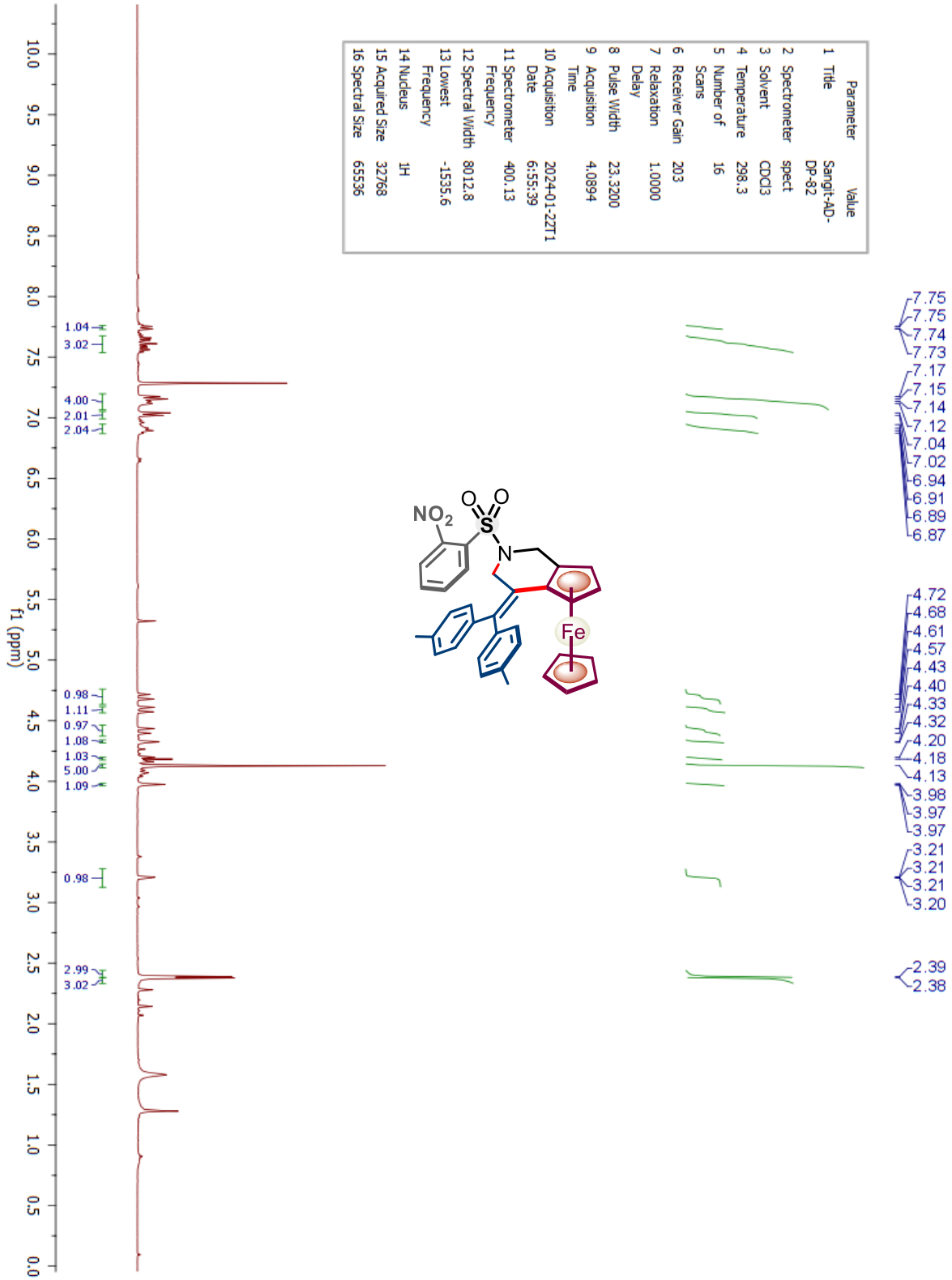
^{1}H NMR Spectrum of **3v**



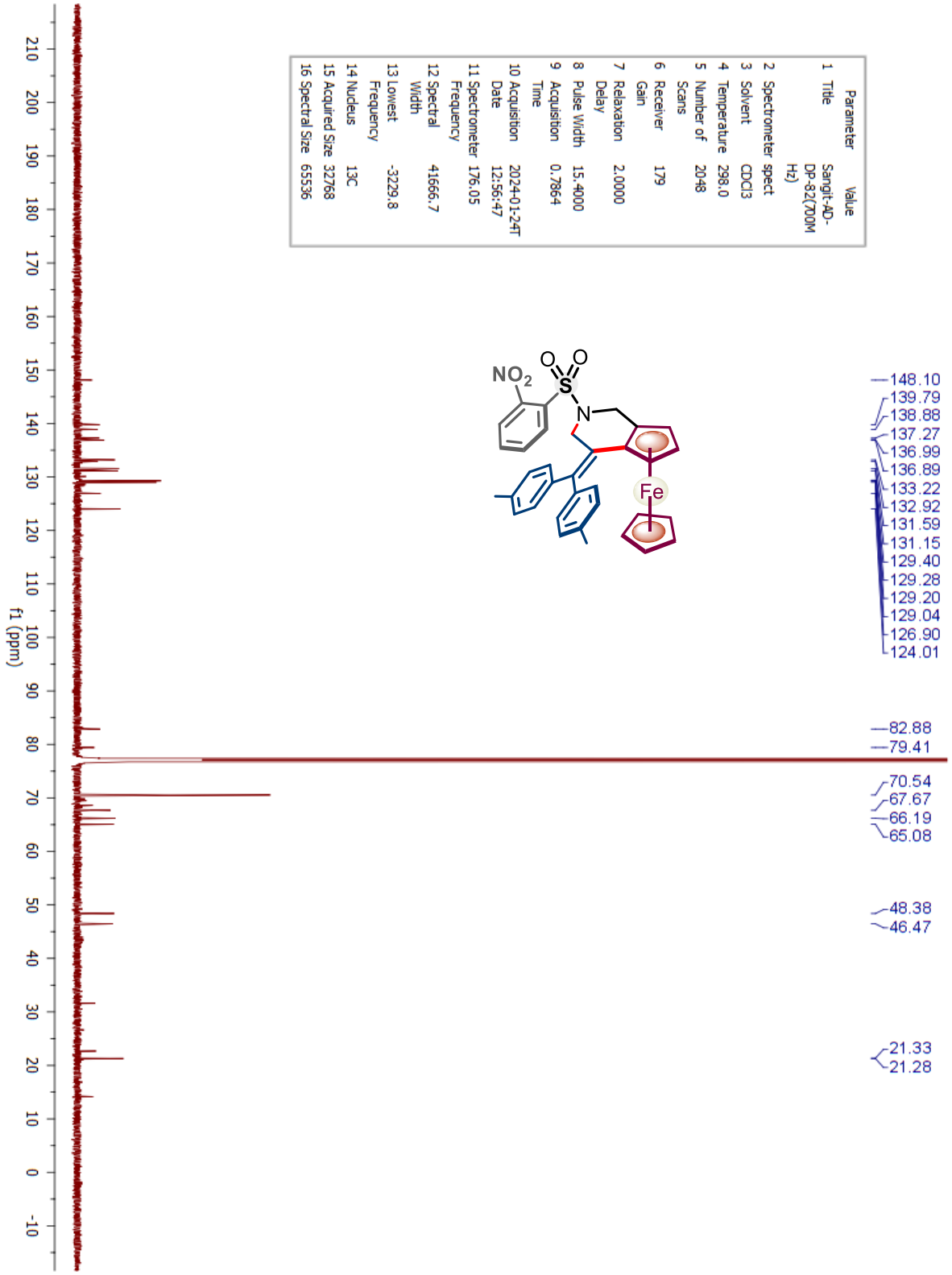
$^{13}C\{^{1}H\}$ NMR Spectrum of **3v**



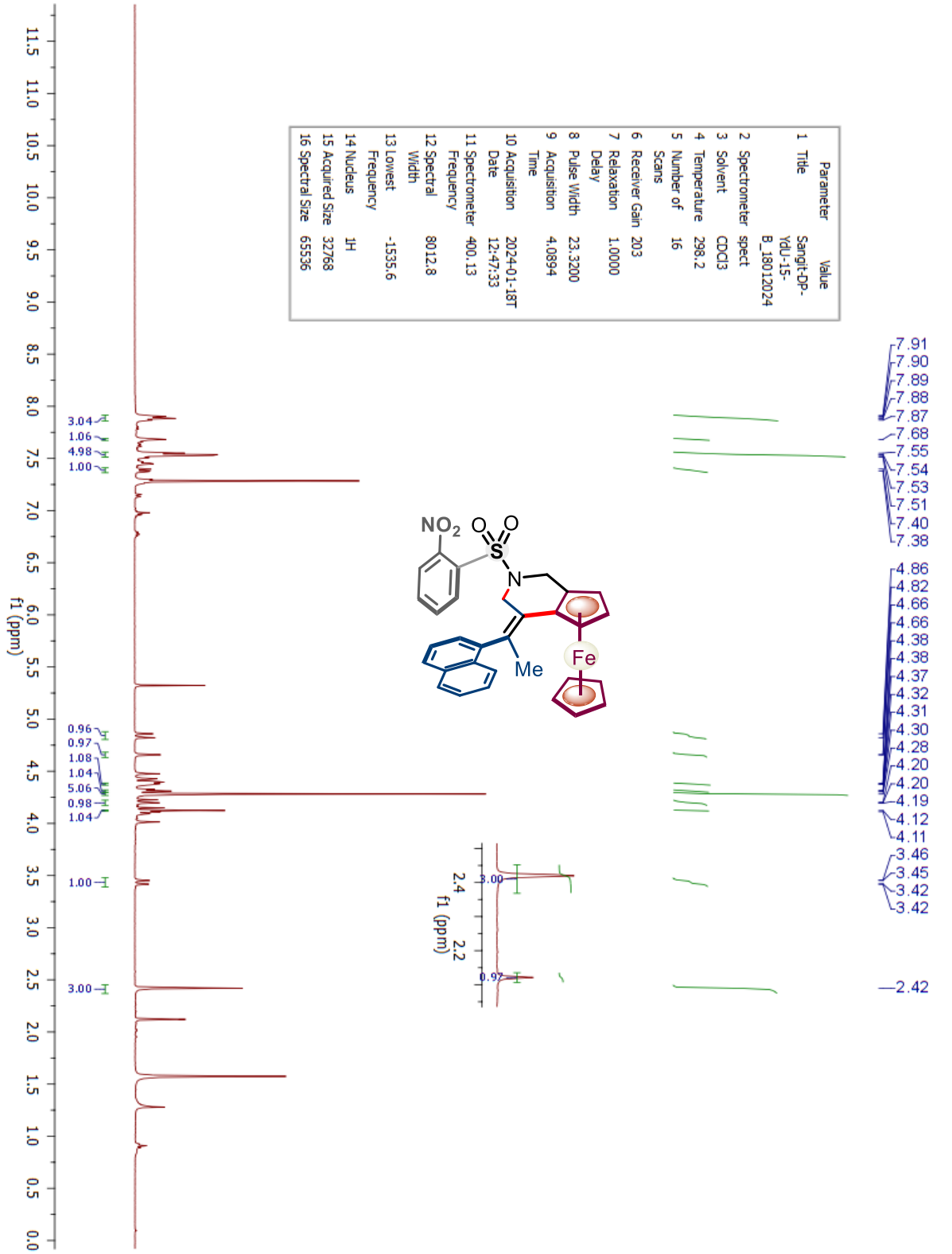
^{1}H NMR Spectrum of **3w**



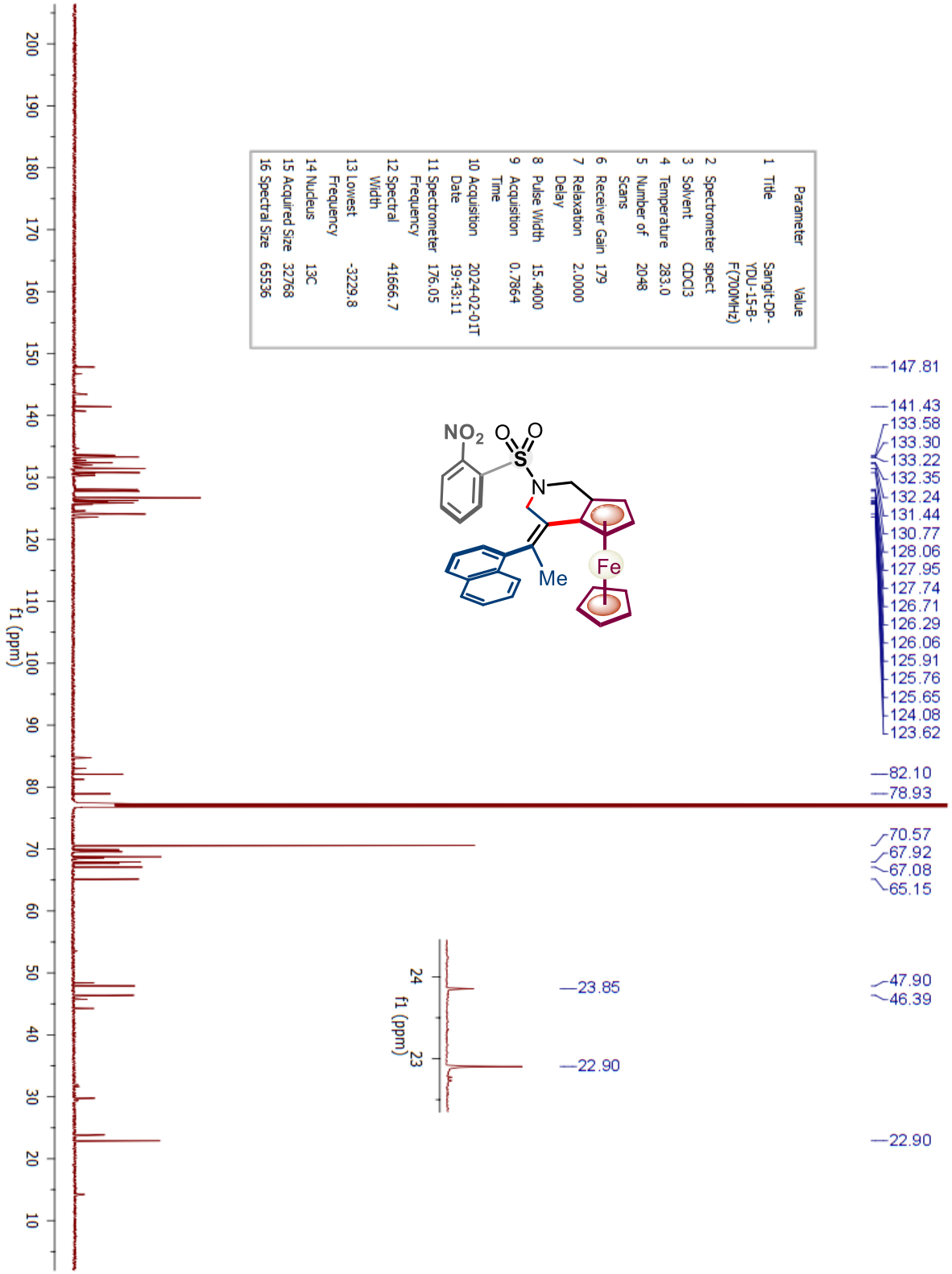
$^{13}C\{^{1}H\}$ NMR Spectrum of **3w**



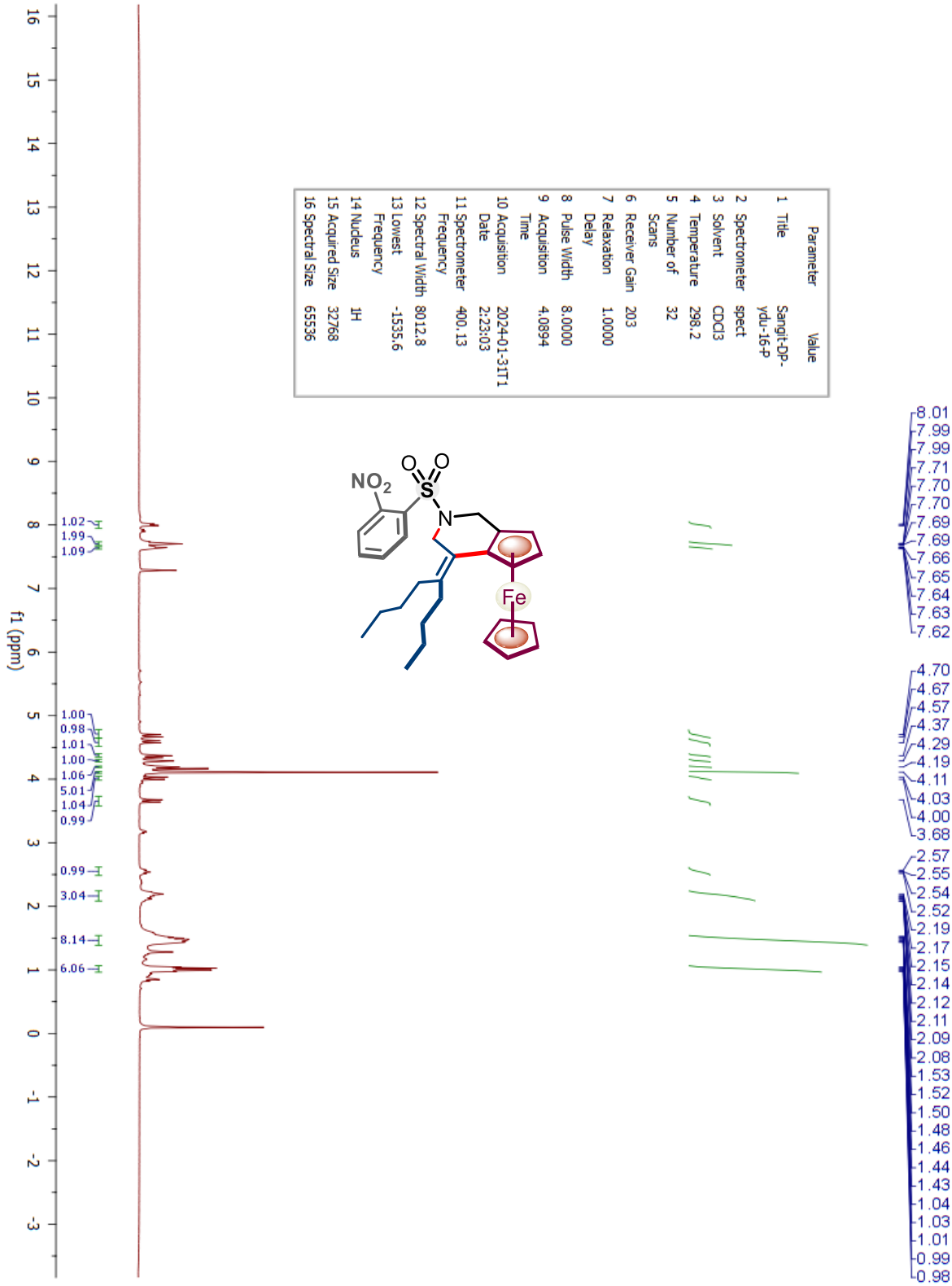
^{1}H NMR Spectrum of **3x**



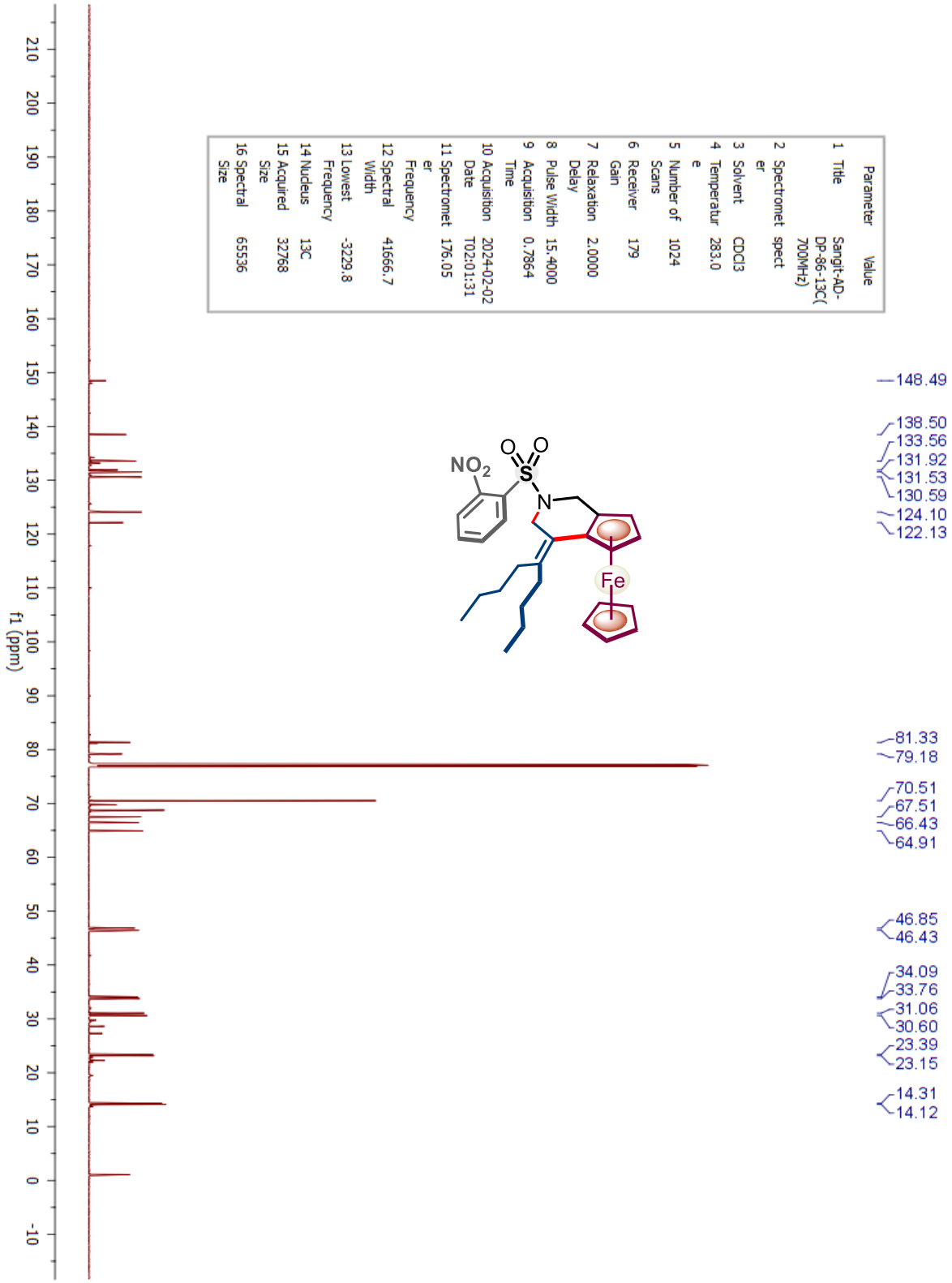
$^{13}C\{^{1}H\}$ NMR Spectrum of **3x**



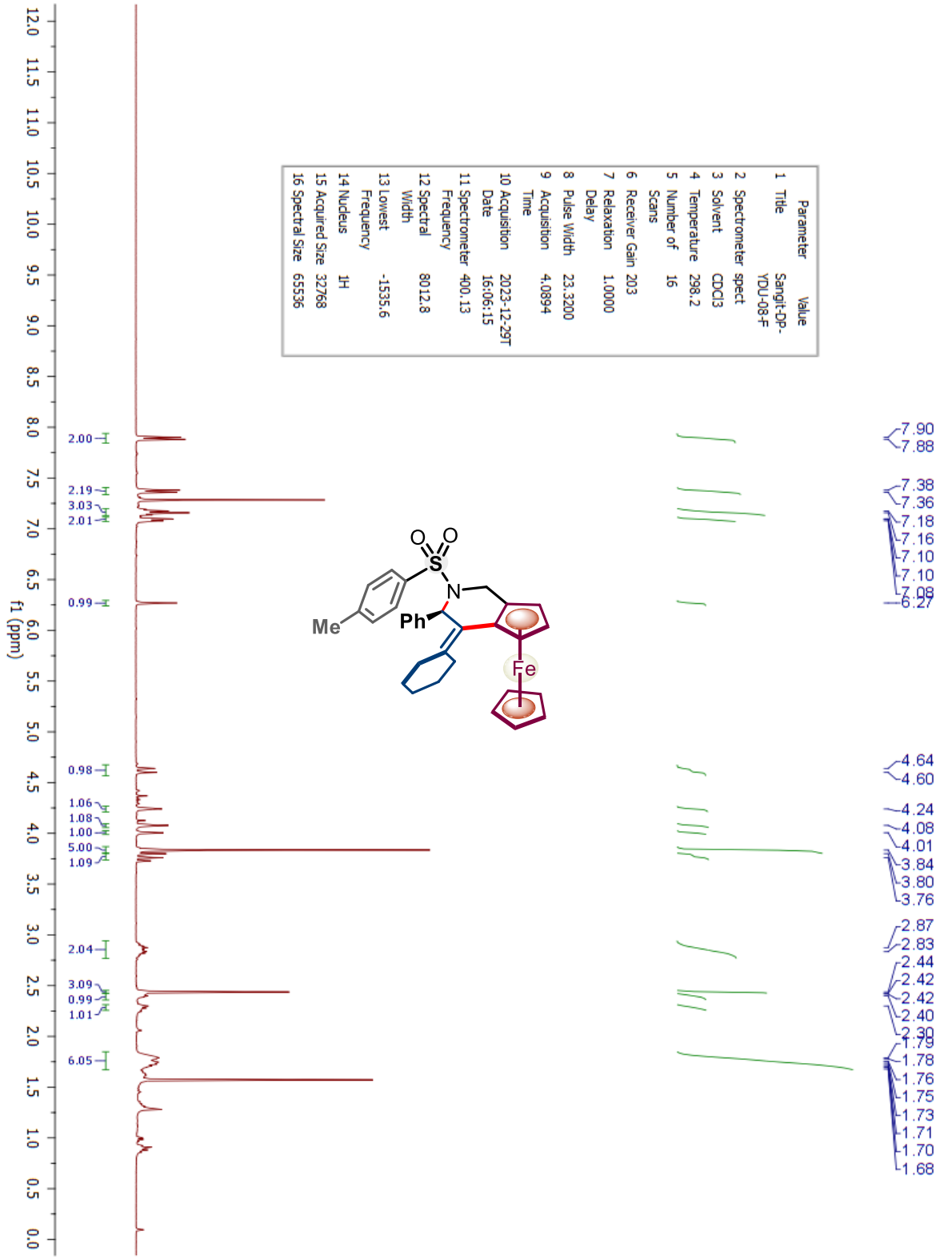
^{1}H NMR Spectrum of **3y**



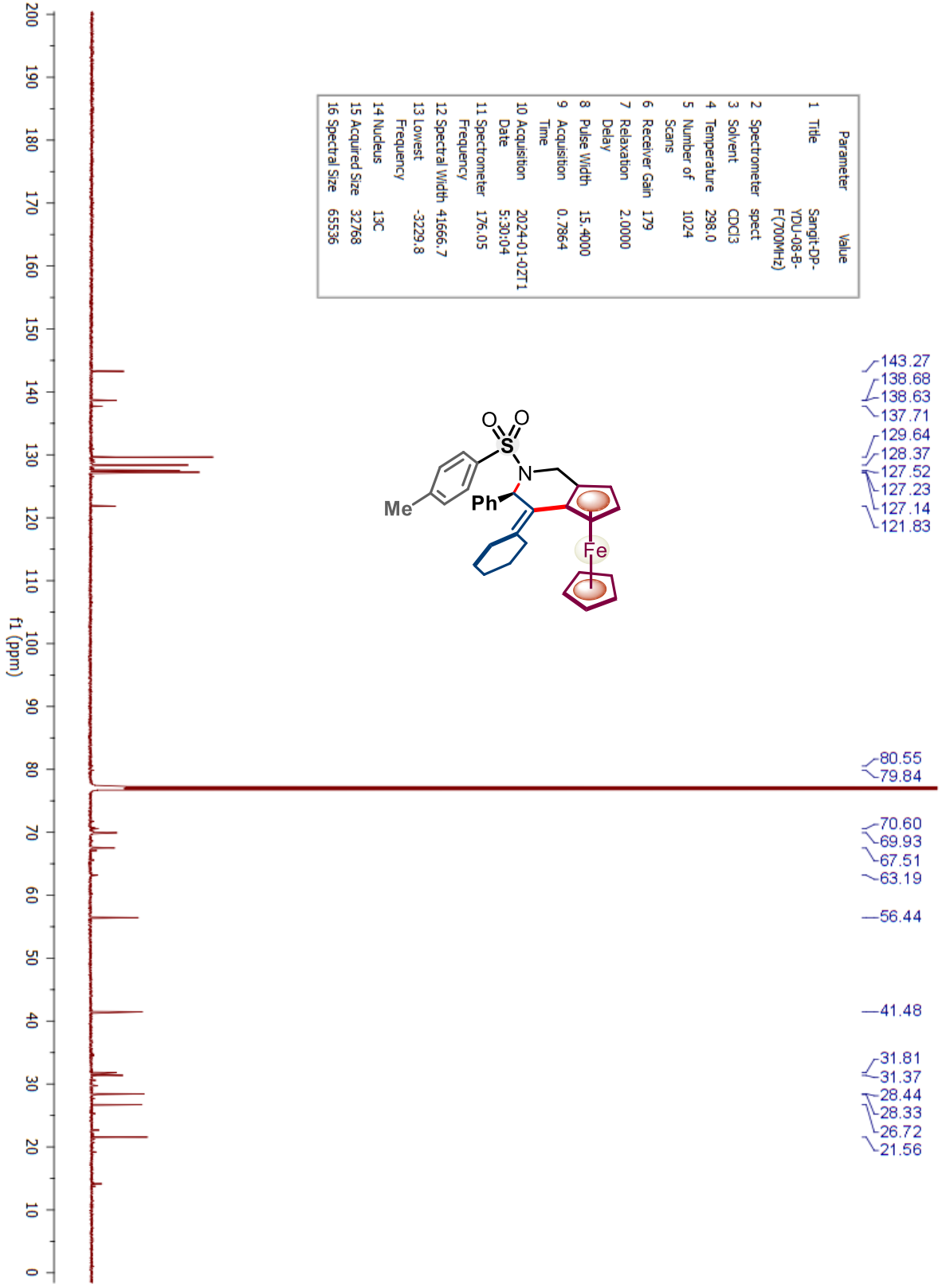
$^{13}C\{^{1}H\}$ NMR Spectrum of **3y**



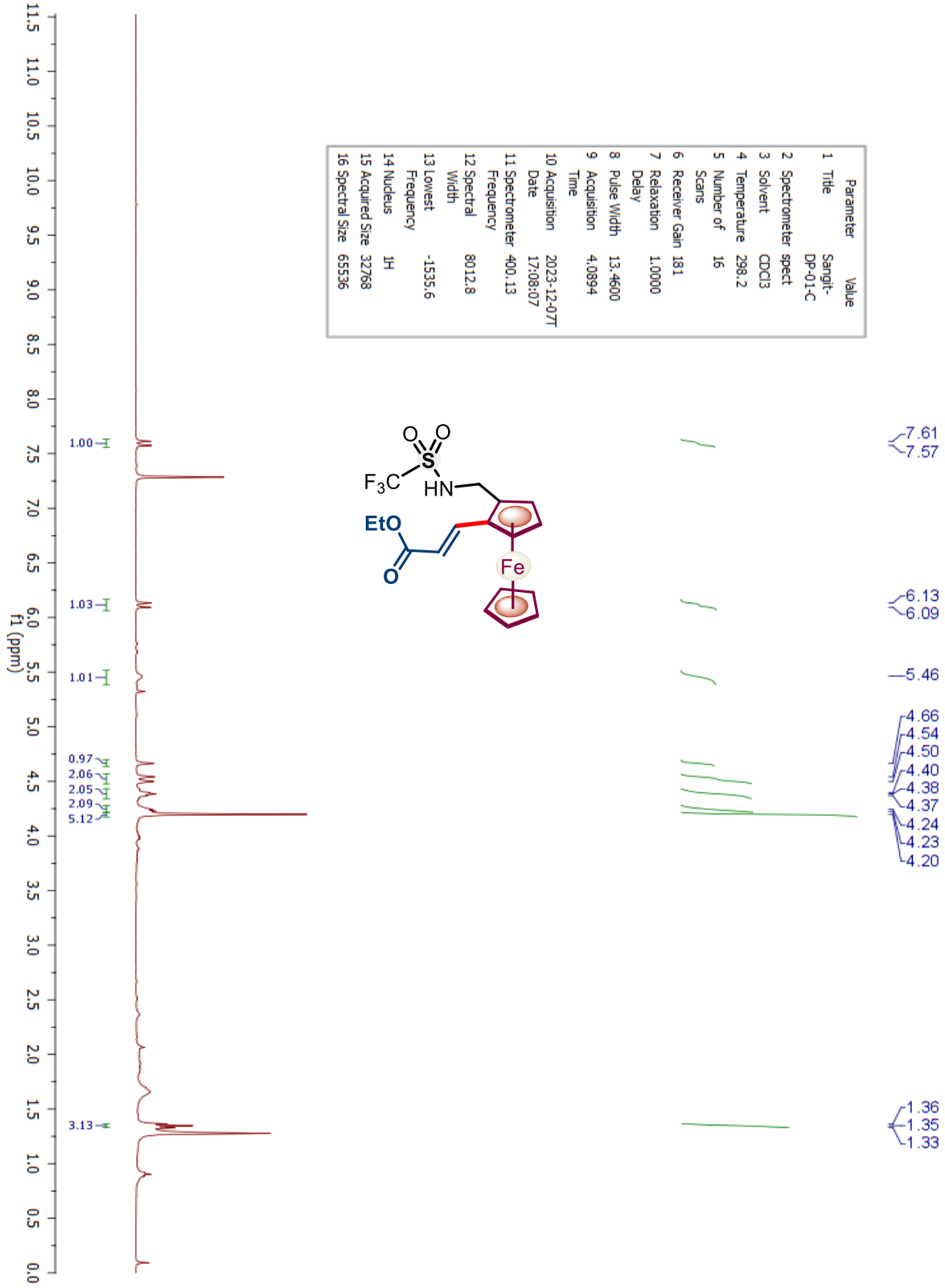
^{1}H NMR Spectrum of **3z**



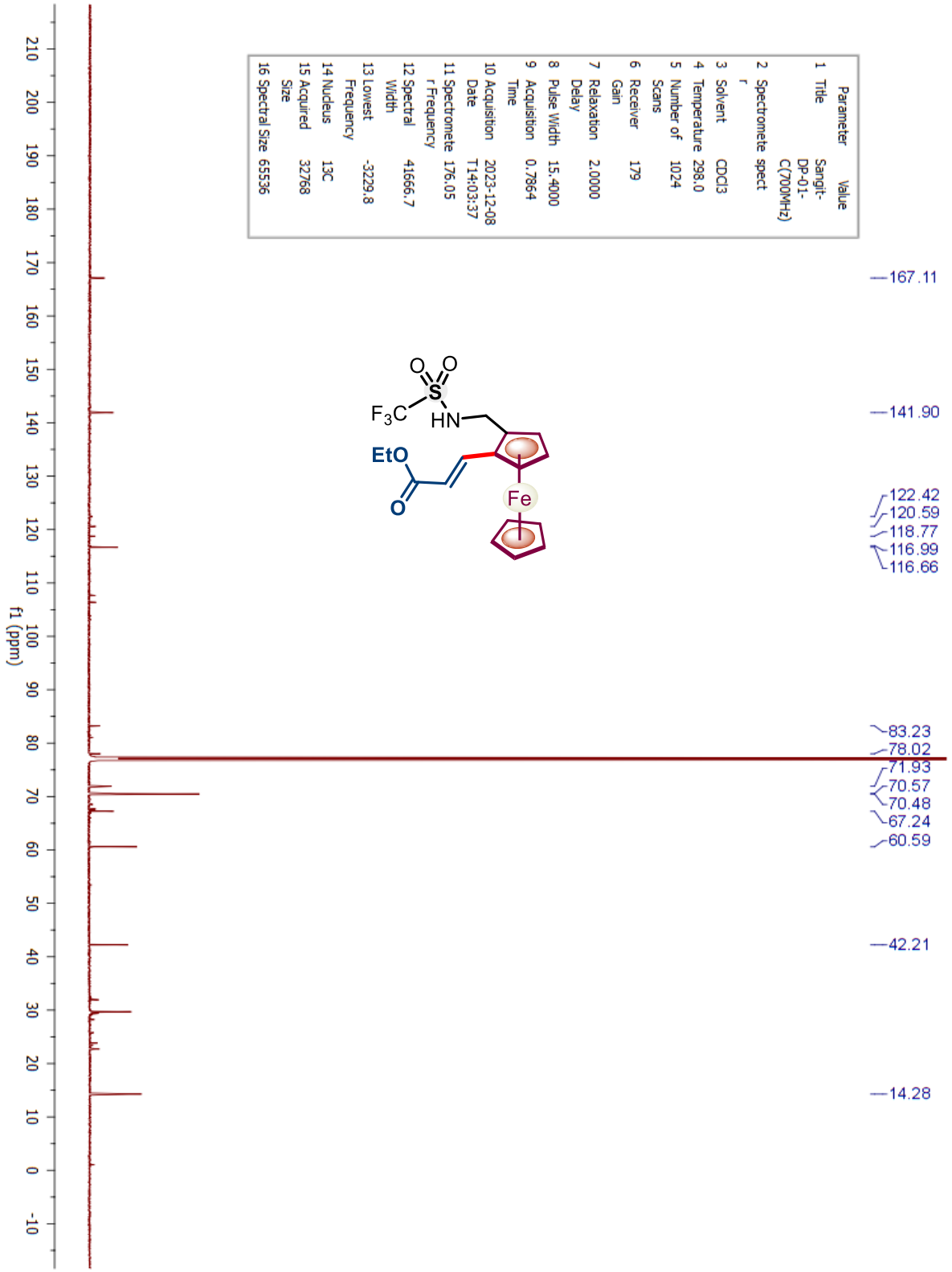
$^{13}C\{^{1}H\}$ NMR Spectrum of **3z**



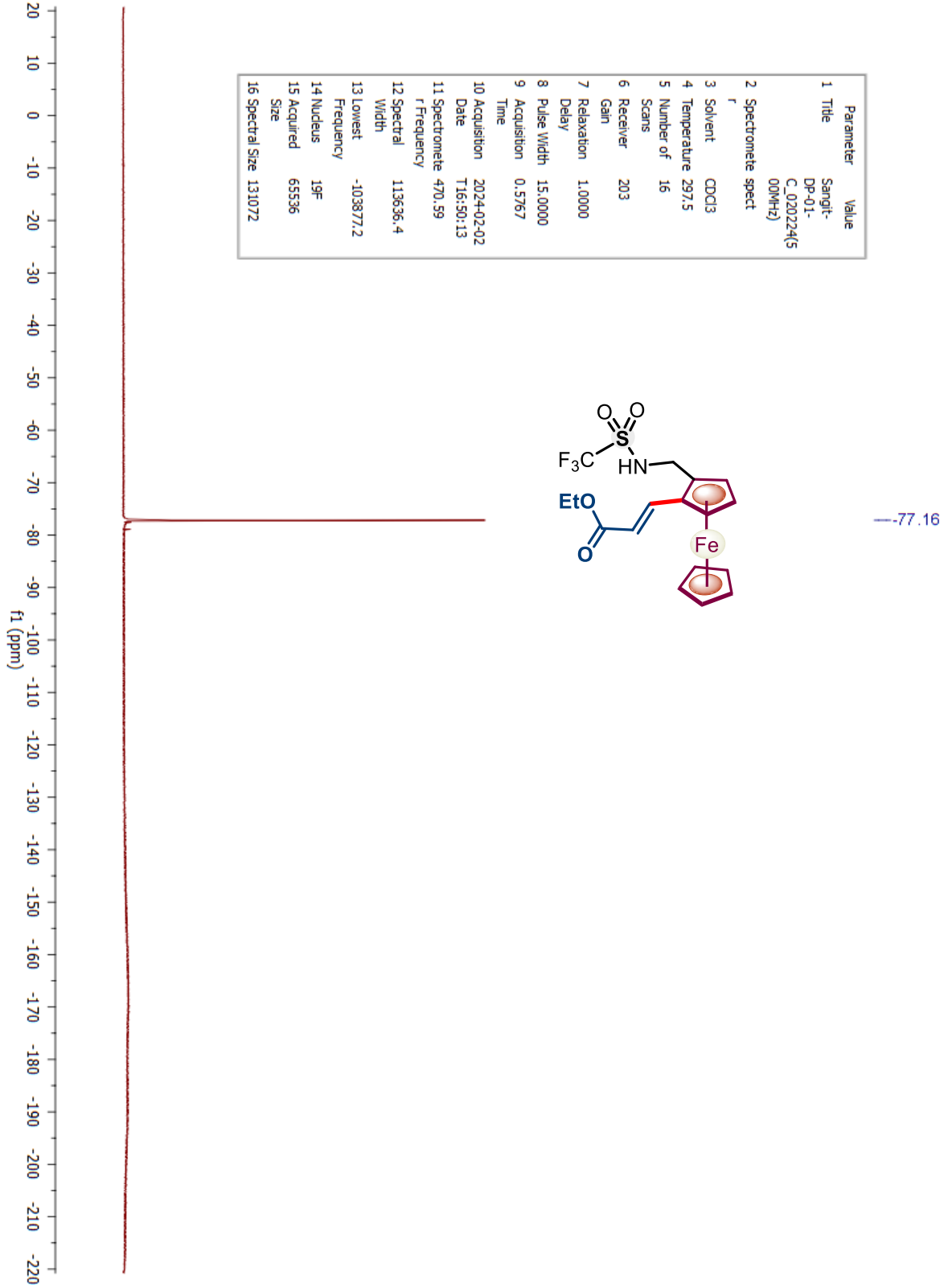
^{1}H NMR Spectrum of **4a**



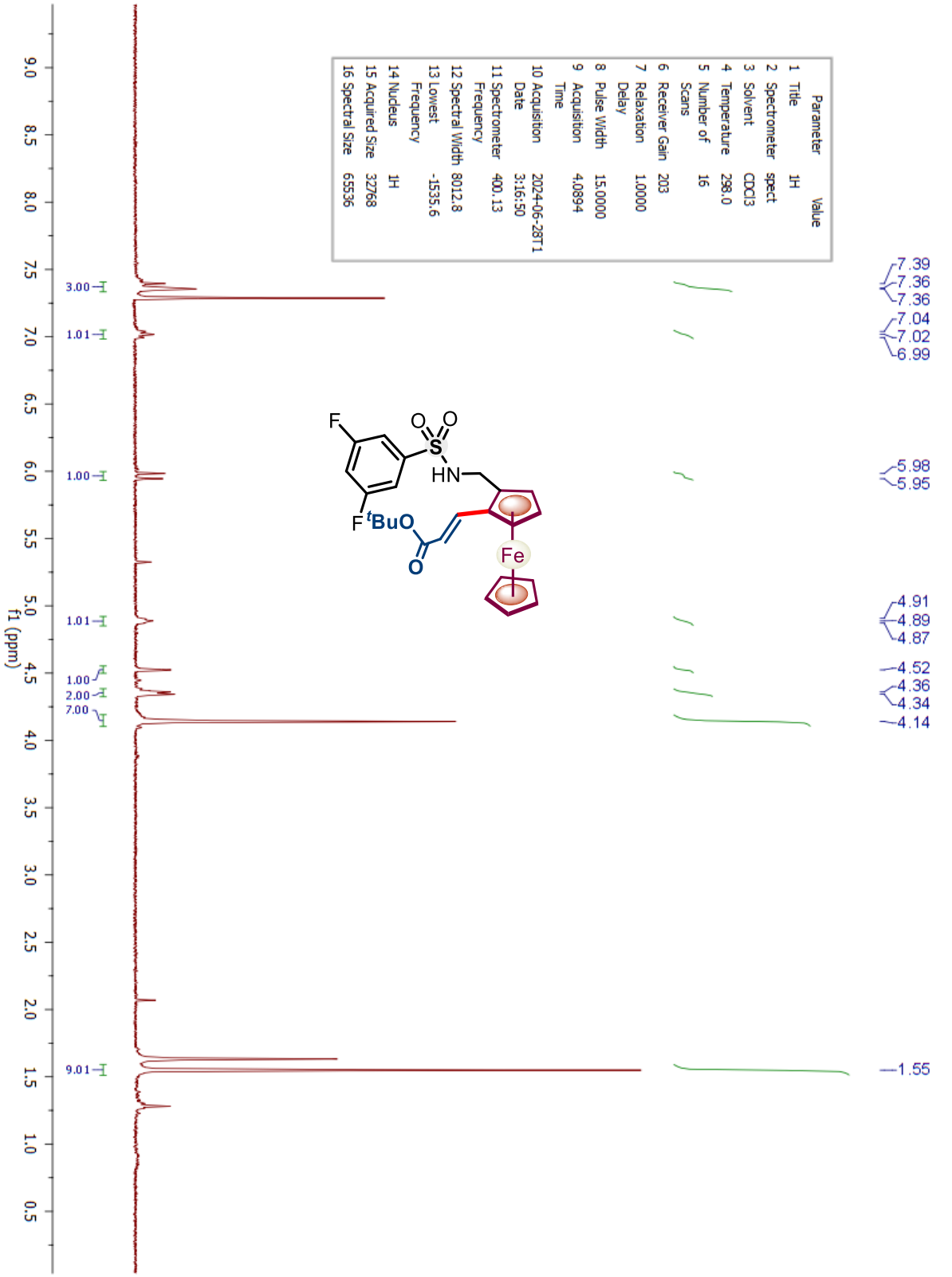
$^{13}C\{^{1}H\}$ NMR Spectrum of **4a**



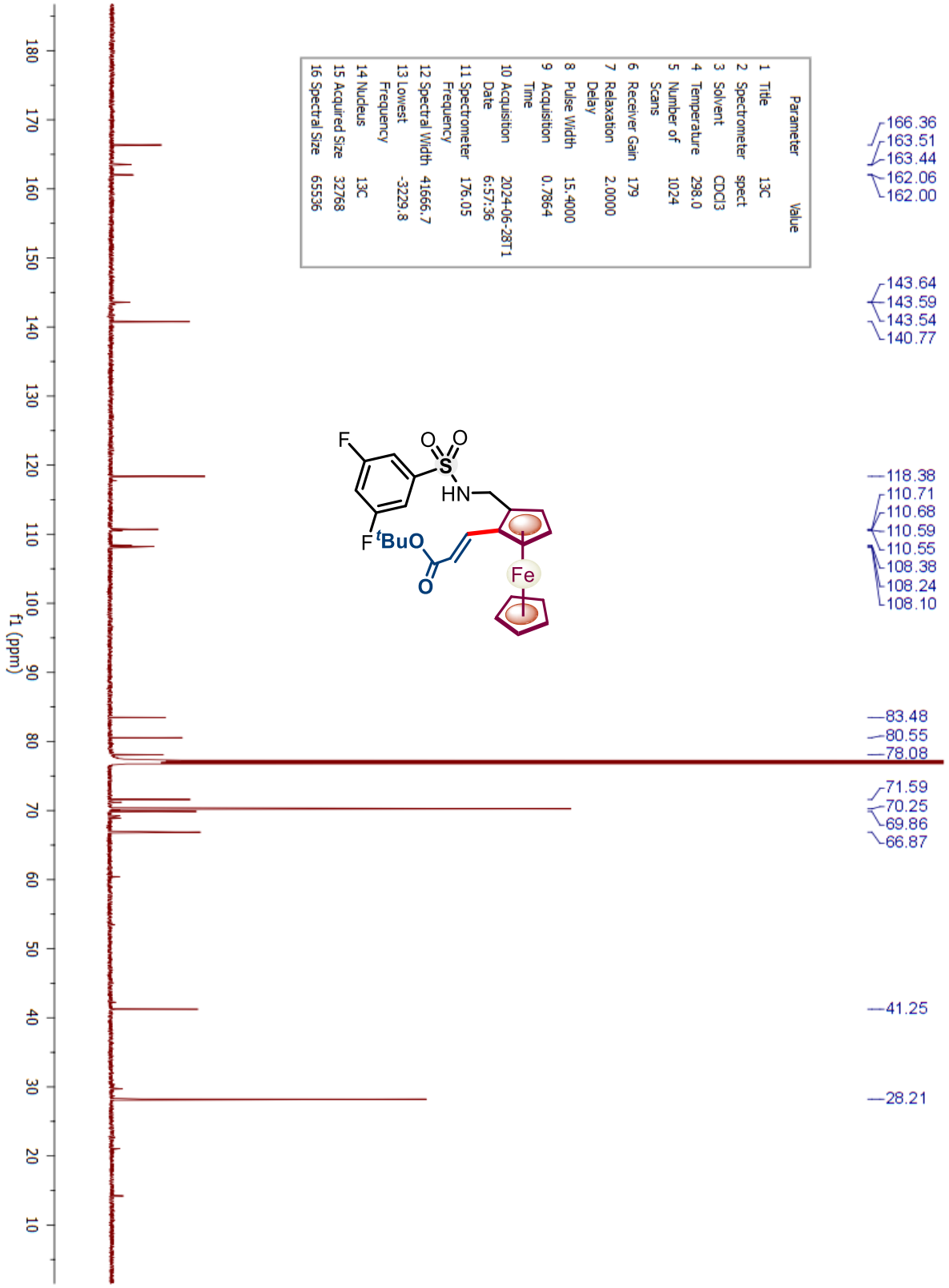
^{19}F NMR Spectrum of **4a**



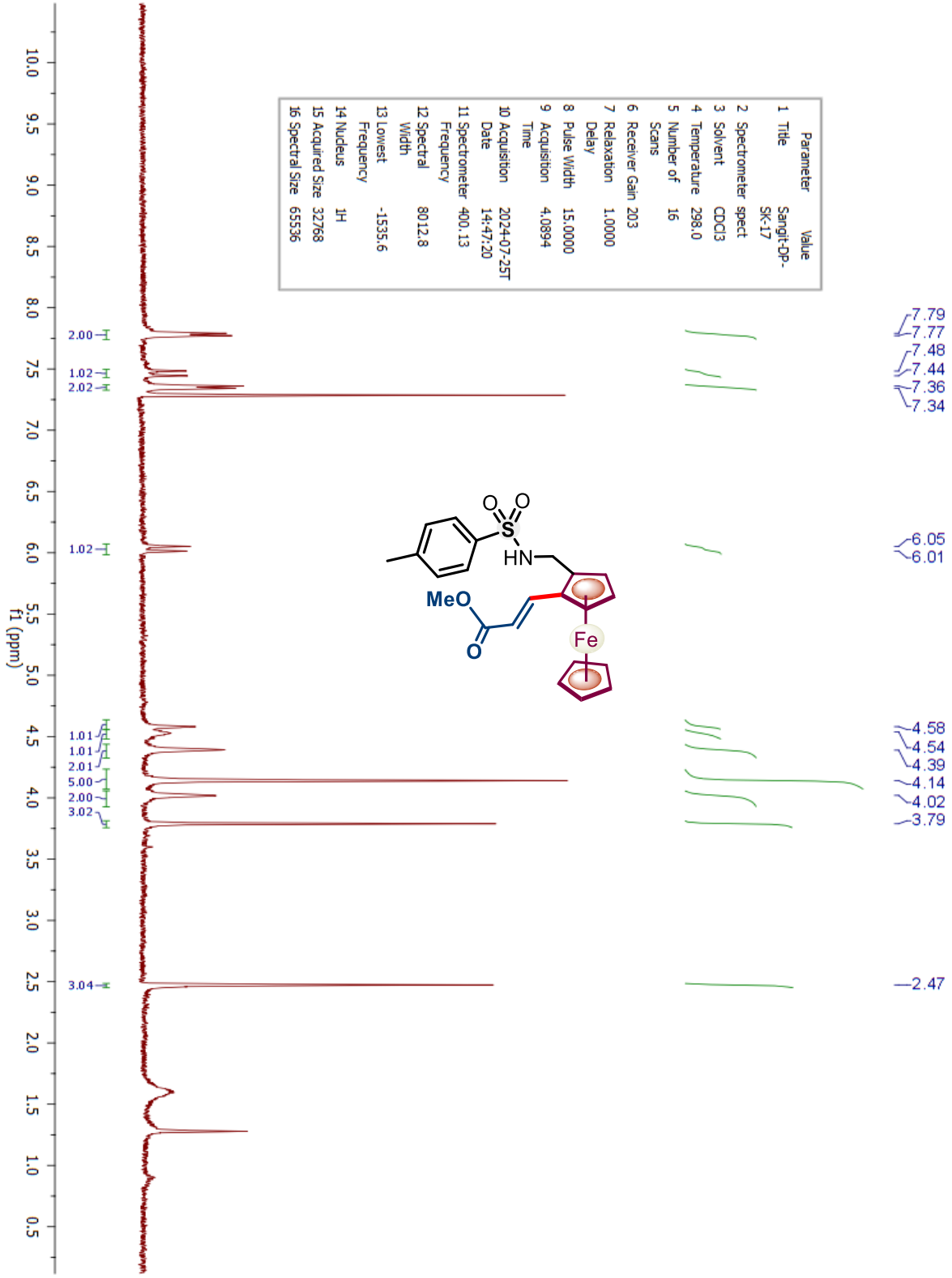
^{1}H NMR Spectrum of **4b**



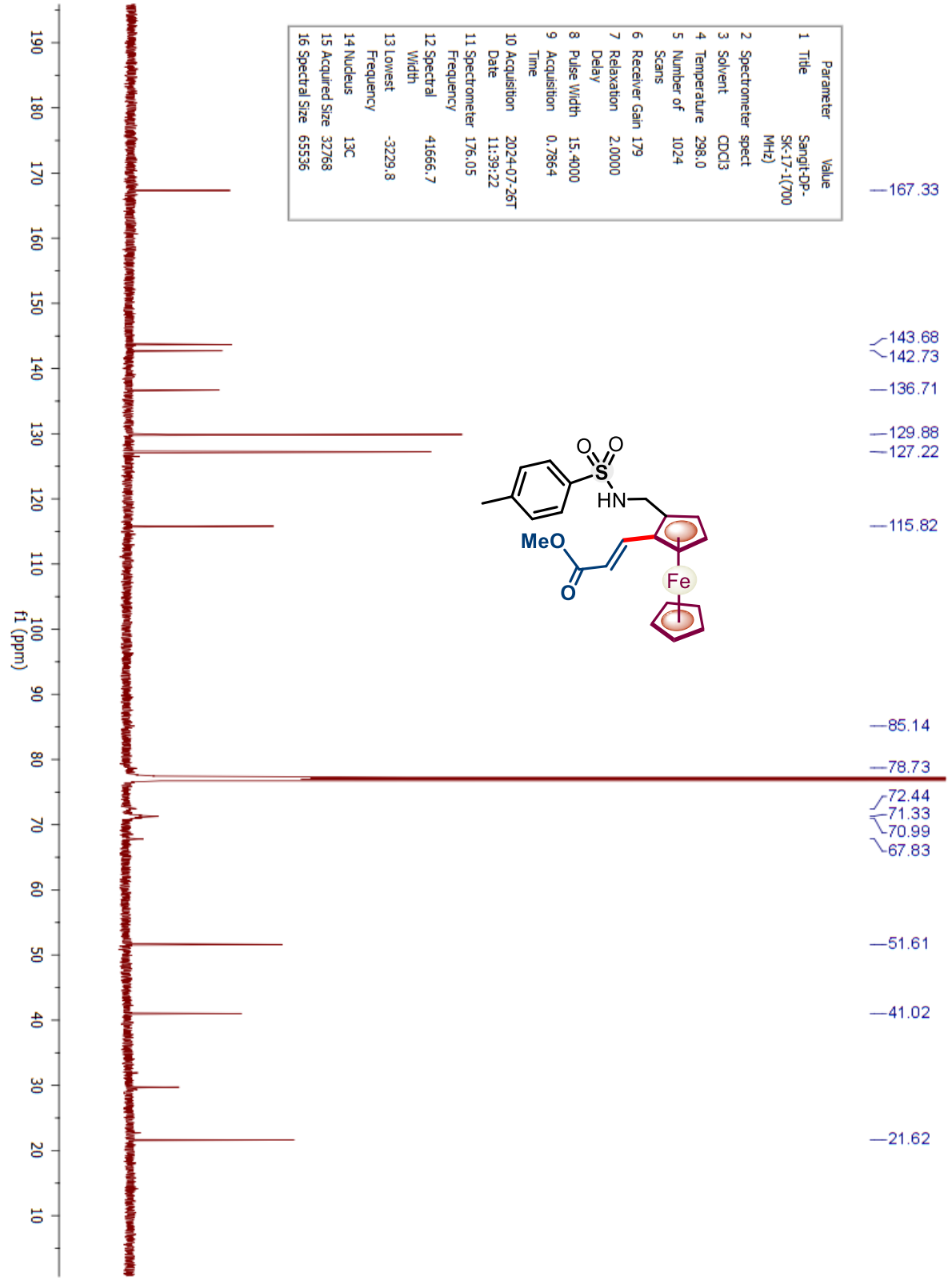
$^{13}C\{^{1}H\}$ NMR Spectrum of **4b**



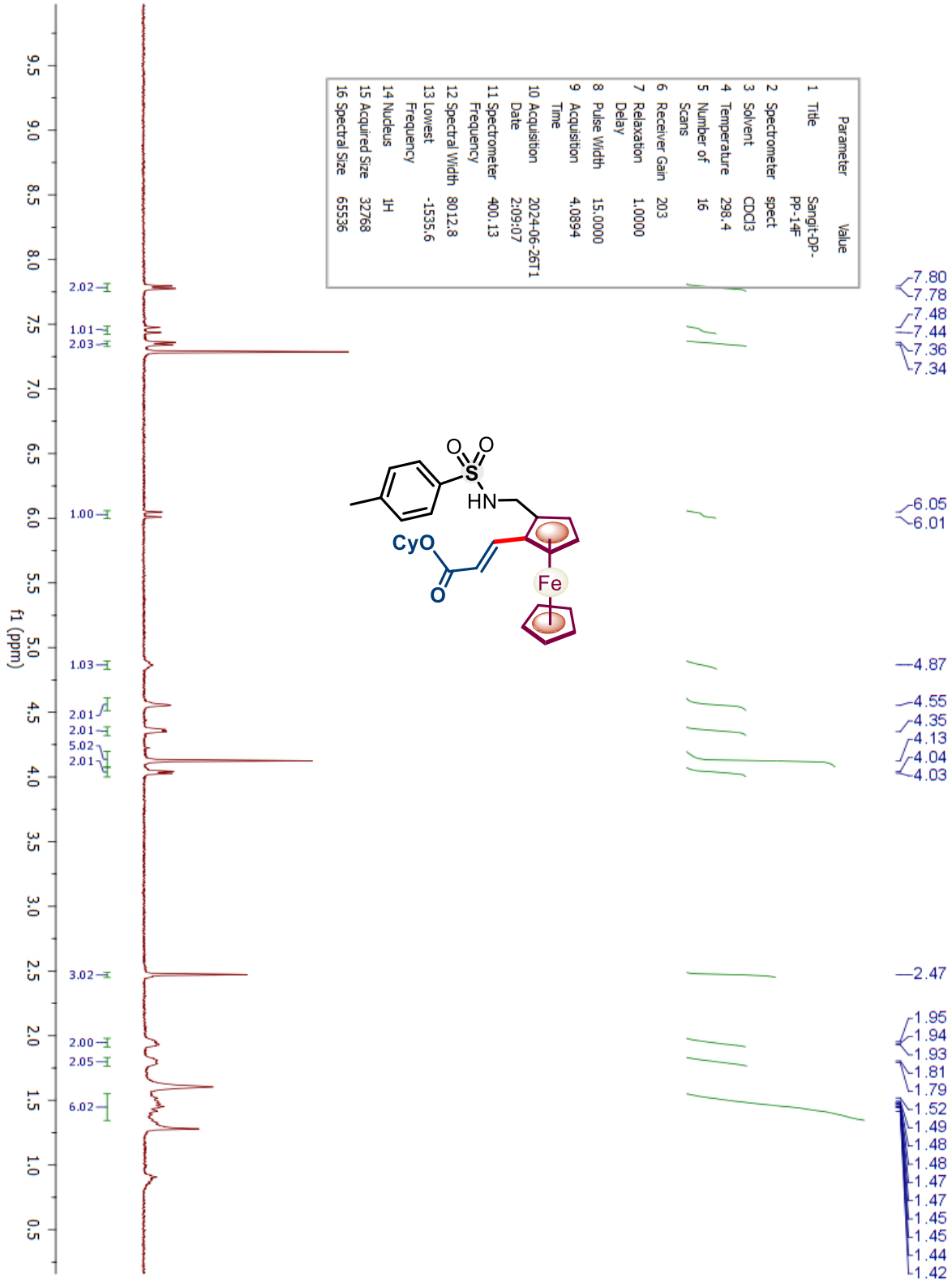
^{1}H NMR Spectrum of **4c**



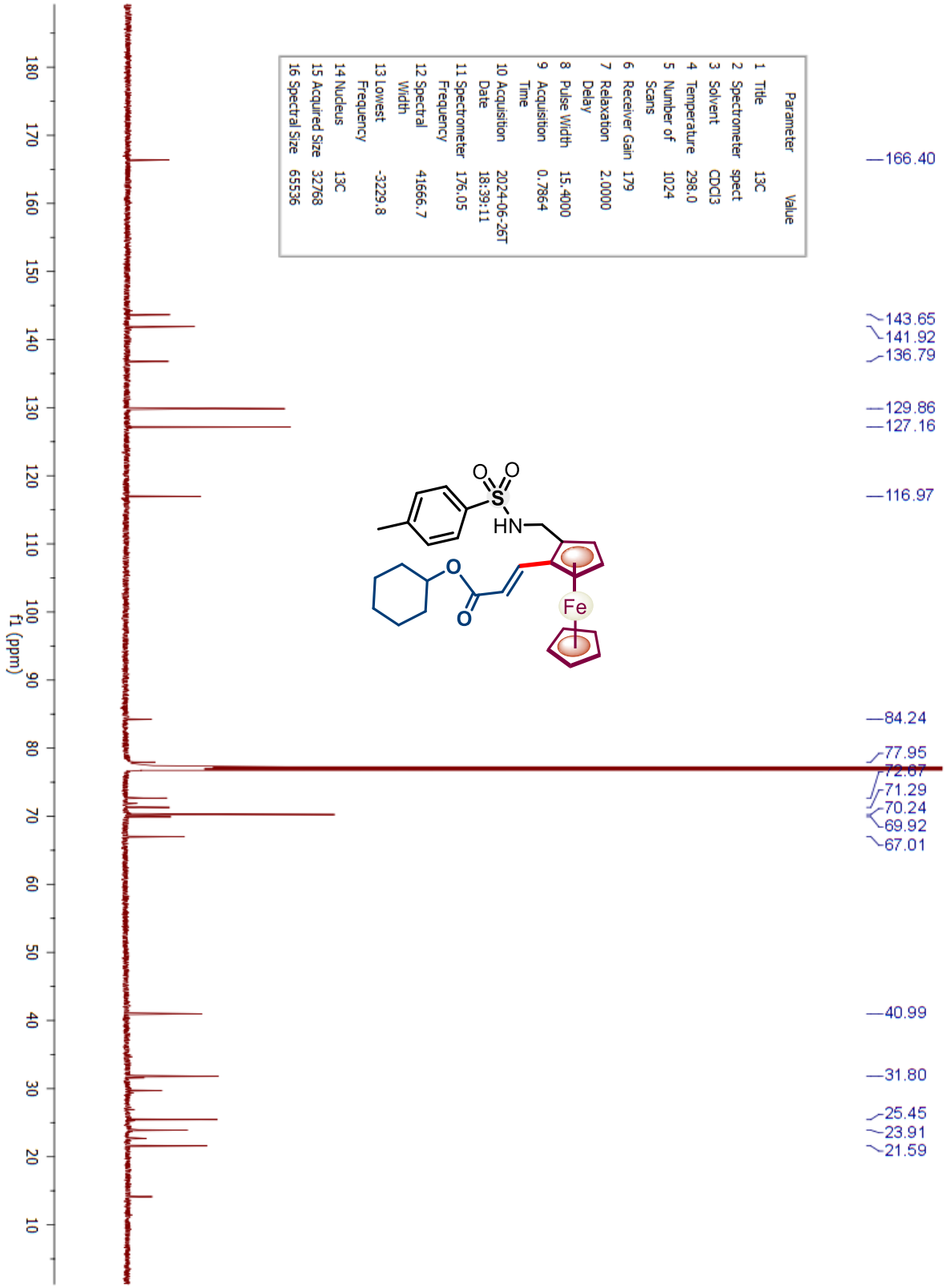
$^{13}C\{^{1}H\}$ NMR Spectrum of **4c**



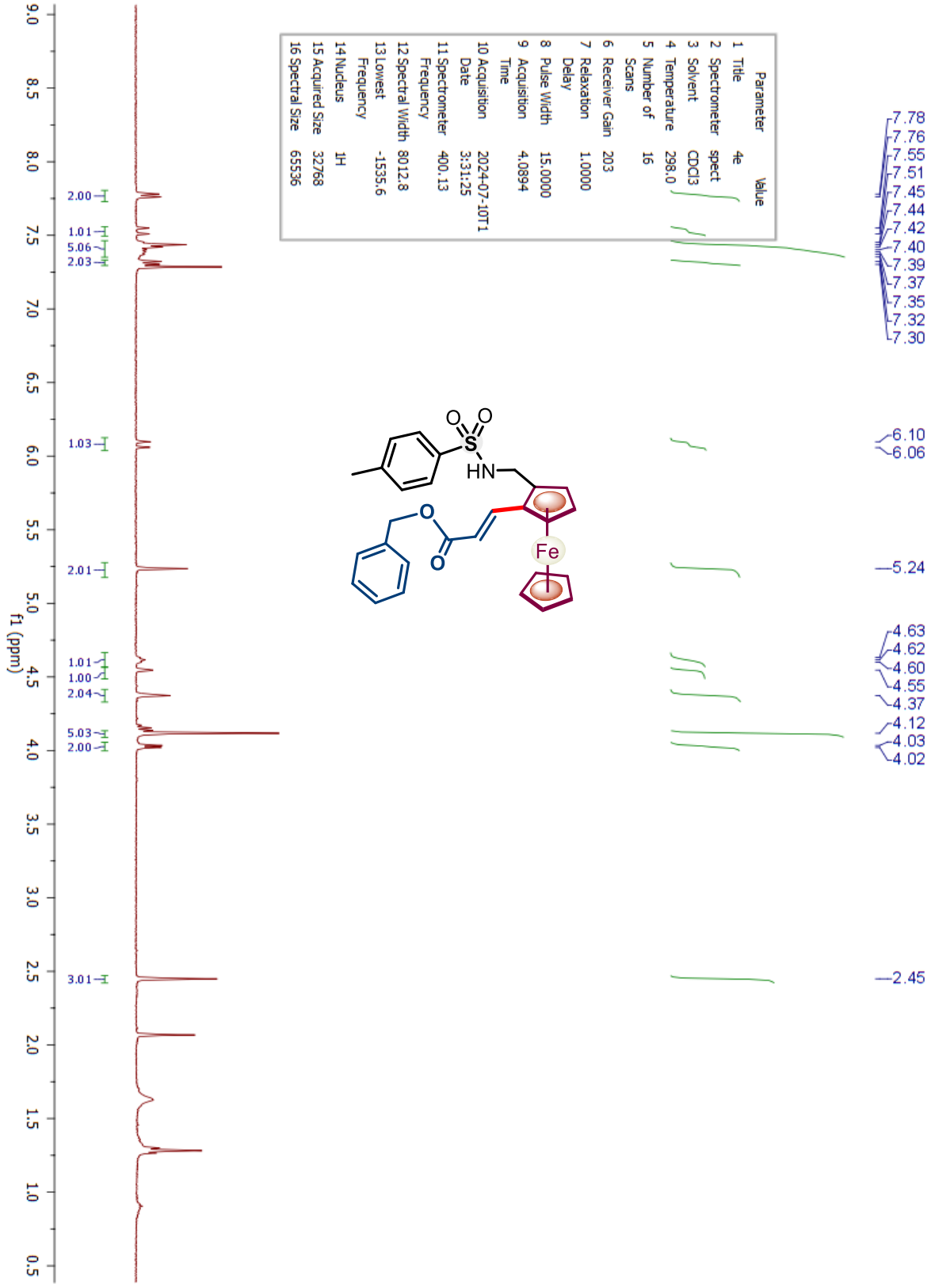
^{1}H NMR Spectrum of **4d**



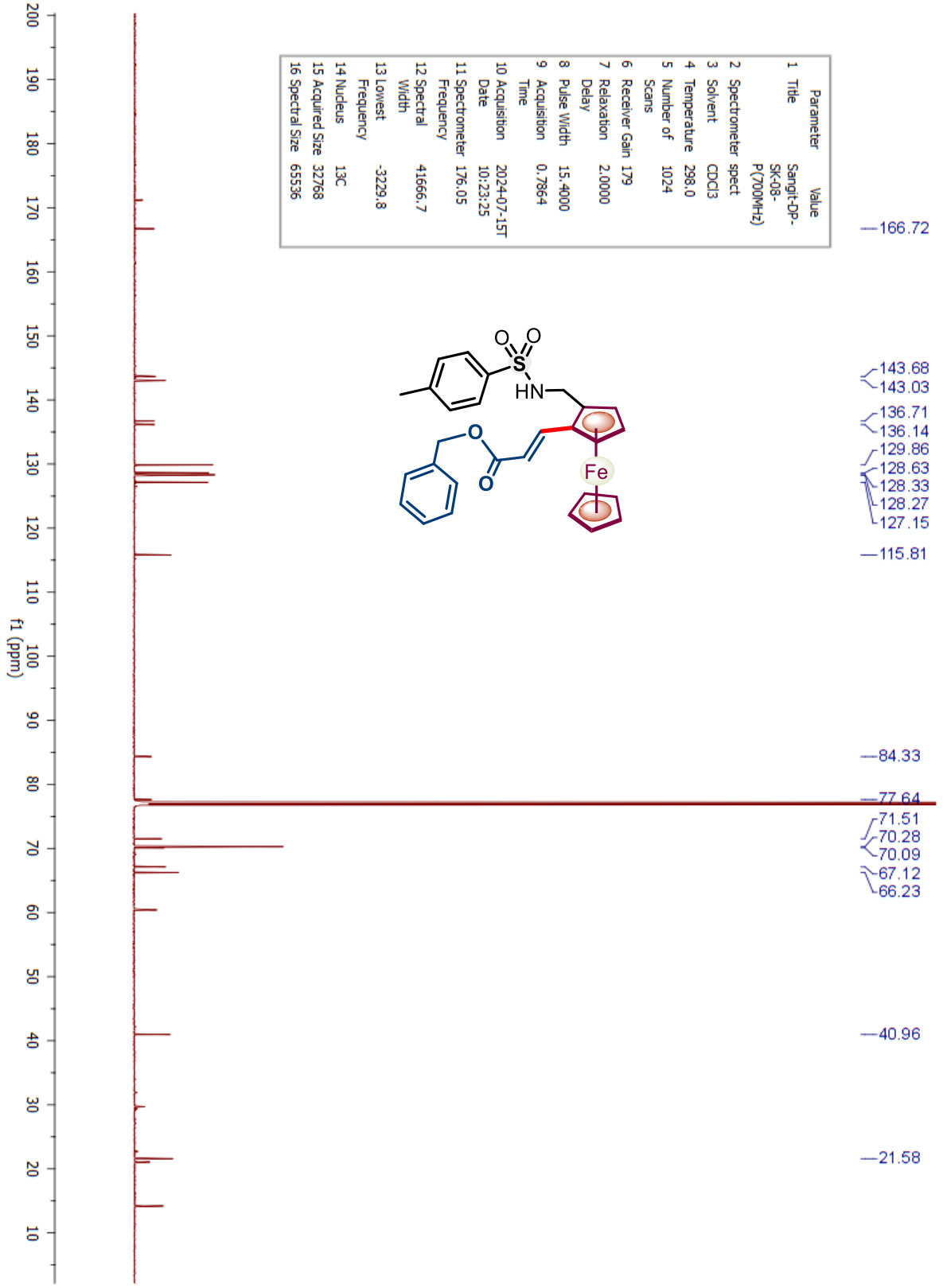
$^{13}C\{^{1}H\}$ NMR Spectrum of **4d**



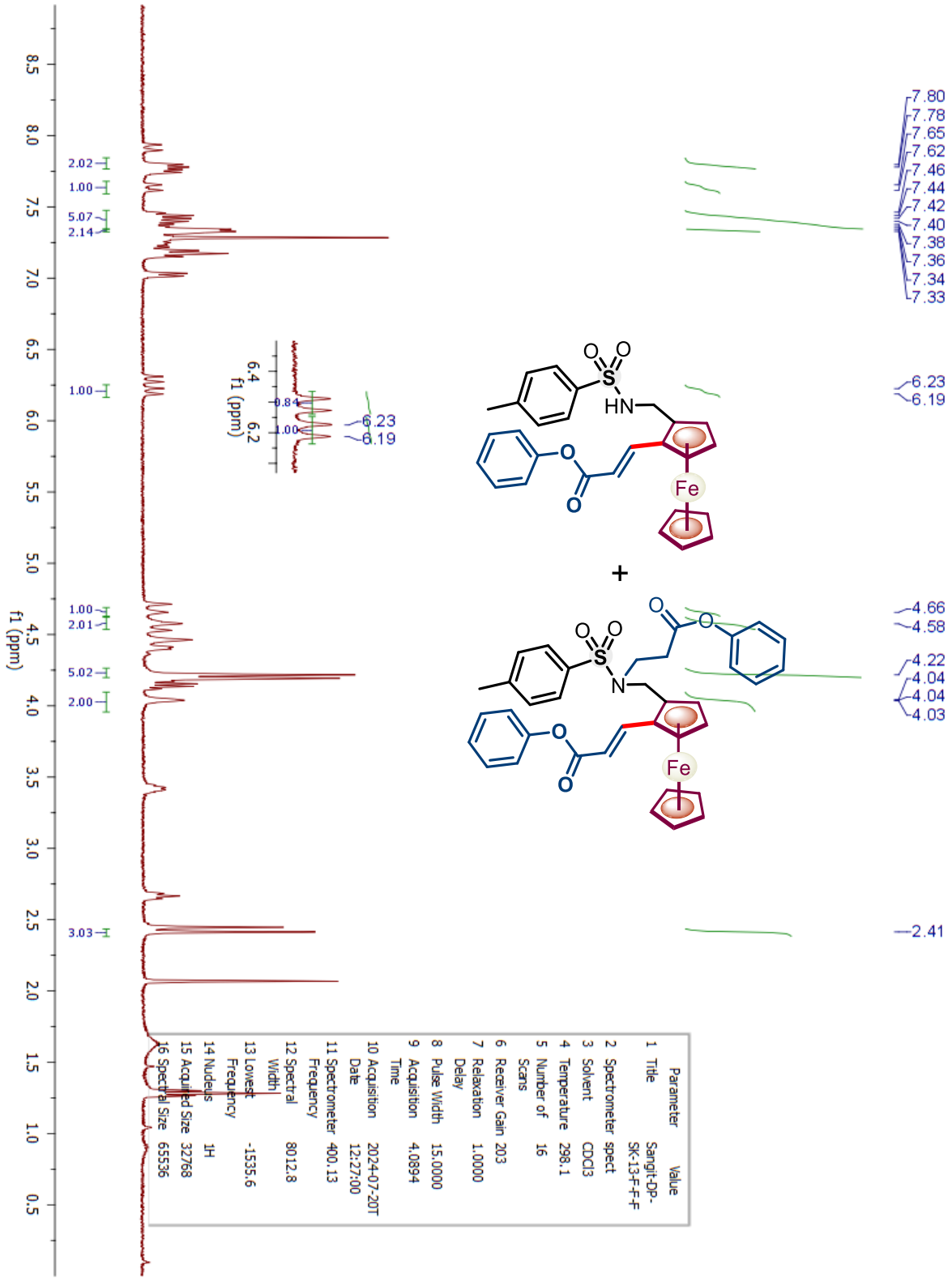
^{1}H NMR Spectrum of **4e**



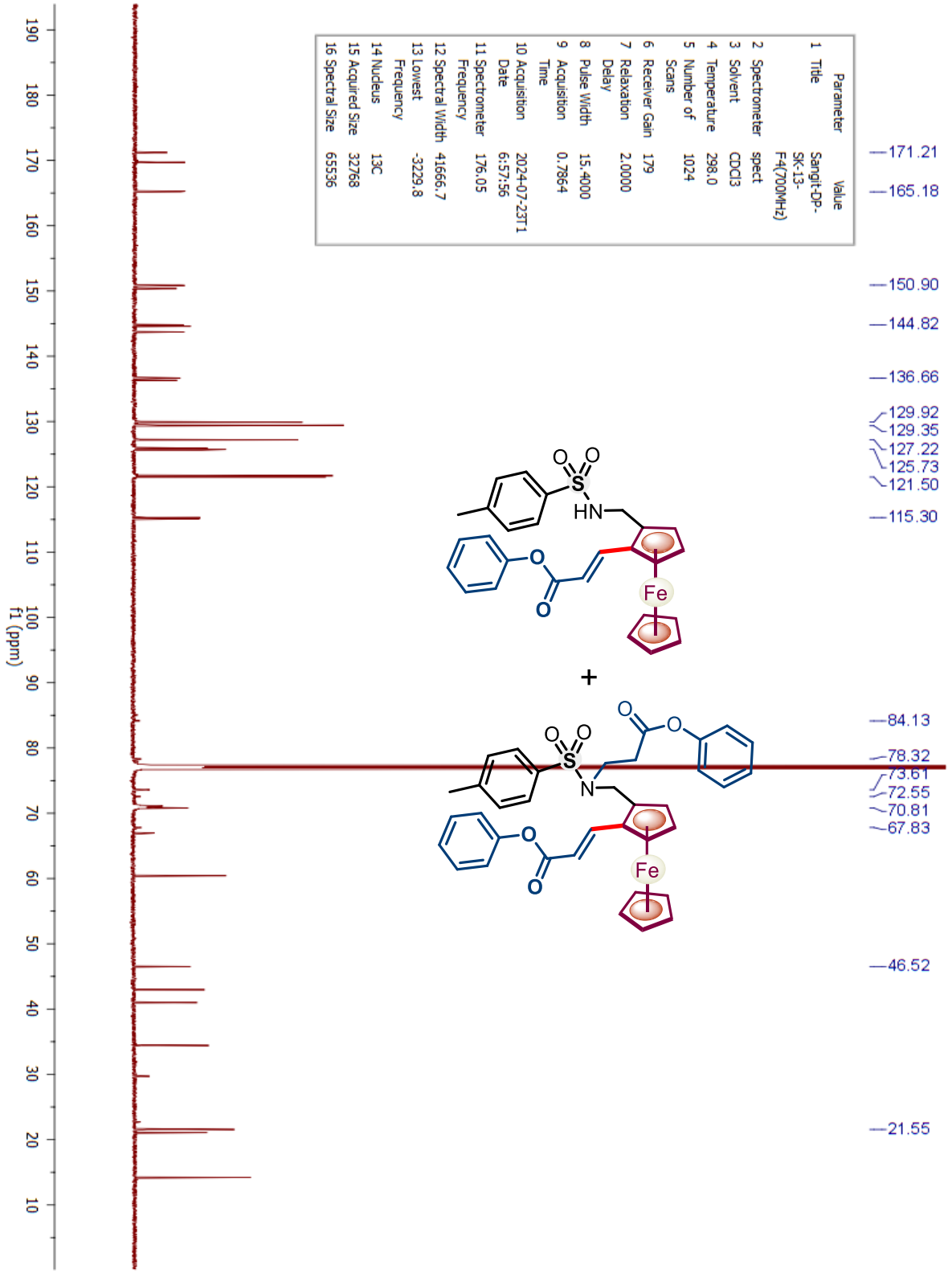
$^{13}C\{^{1}H\}$ NMR Spectrum of **4e**



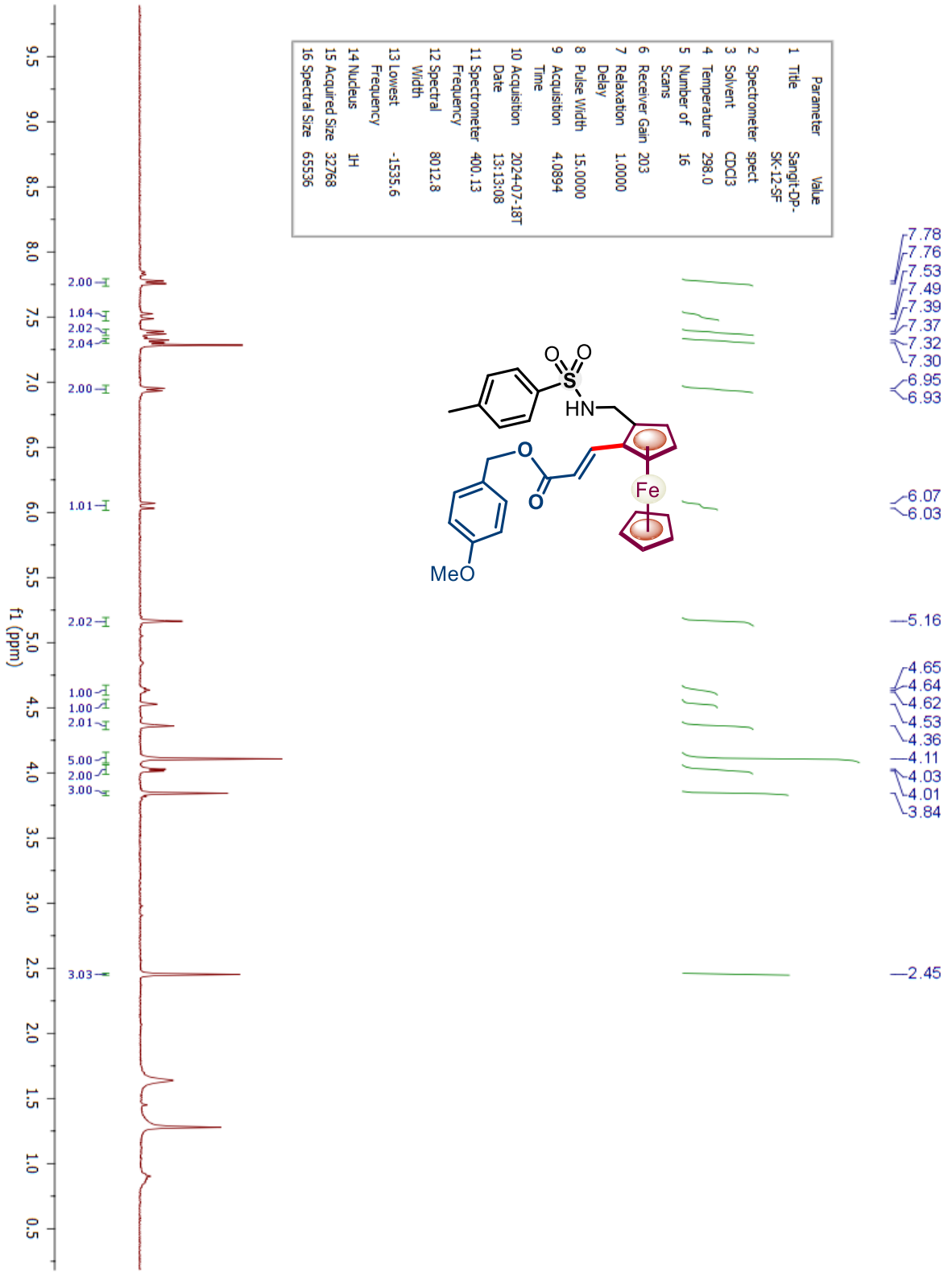
^{1}H NMR Spectrum of **4f**



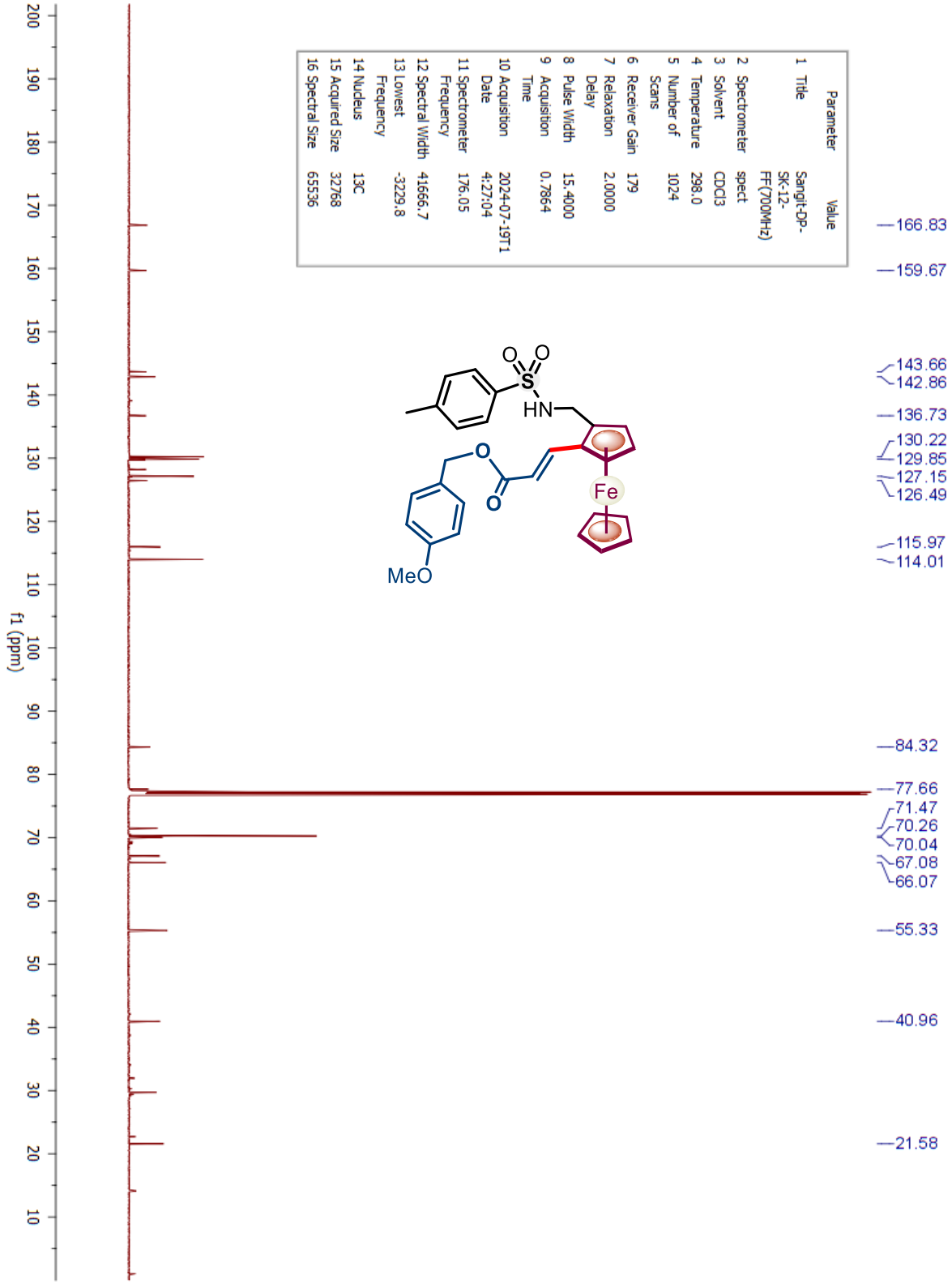
$^{13}C\{^{1}H\}$ NMR Spectrum of **4f**



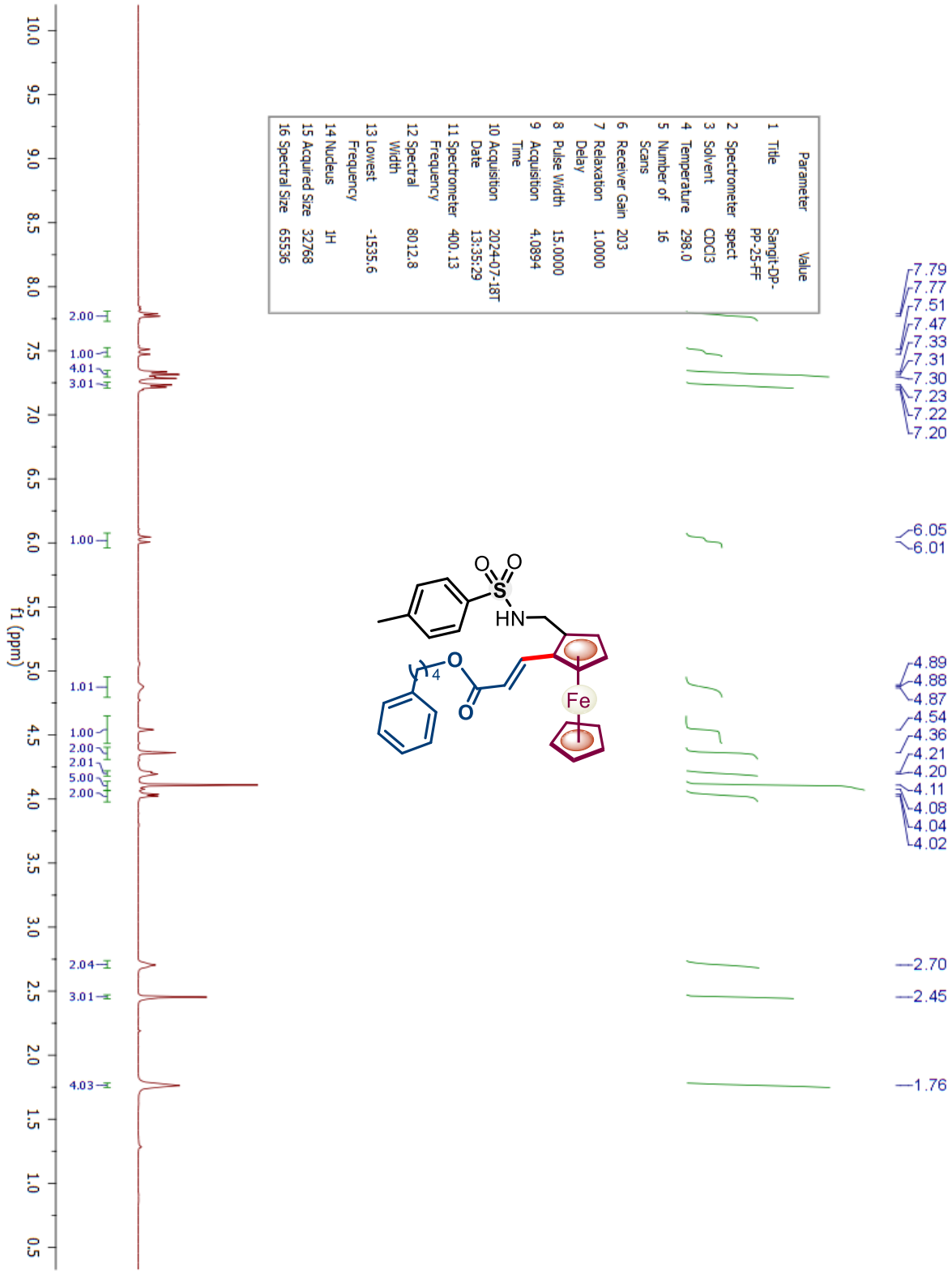
^{1}H NMR Spectrum of **4g**



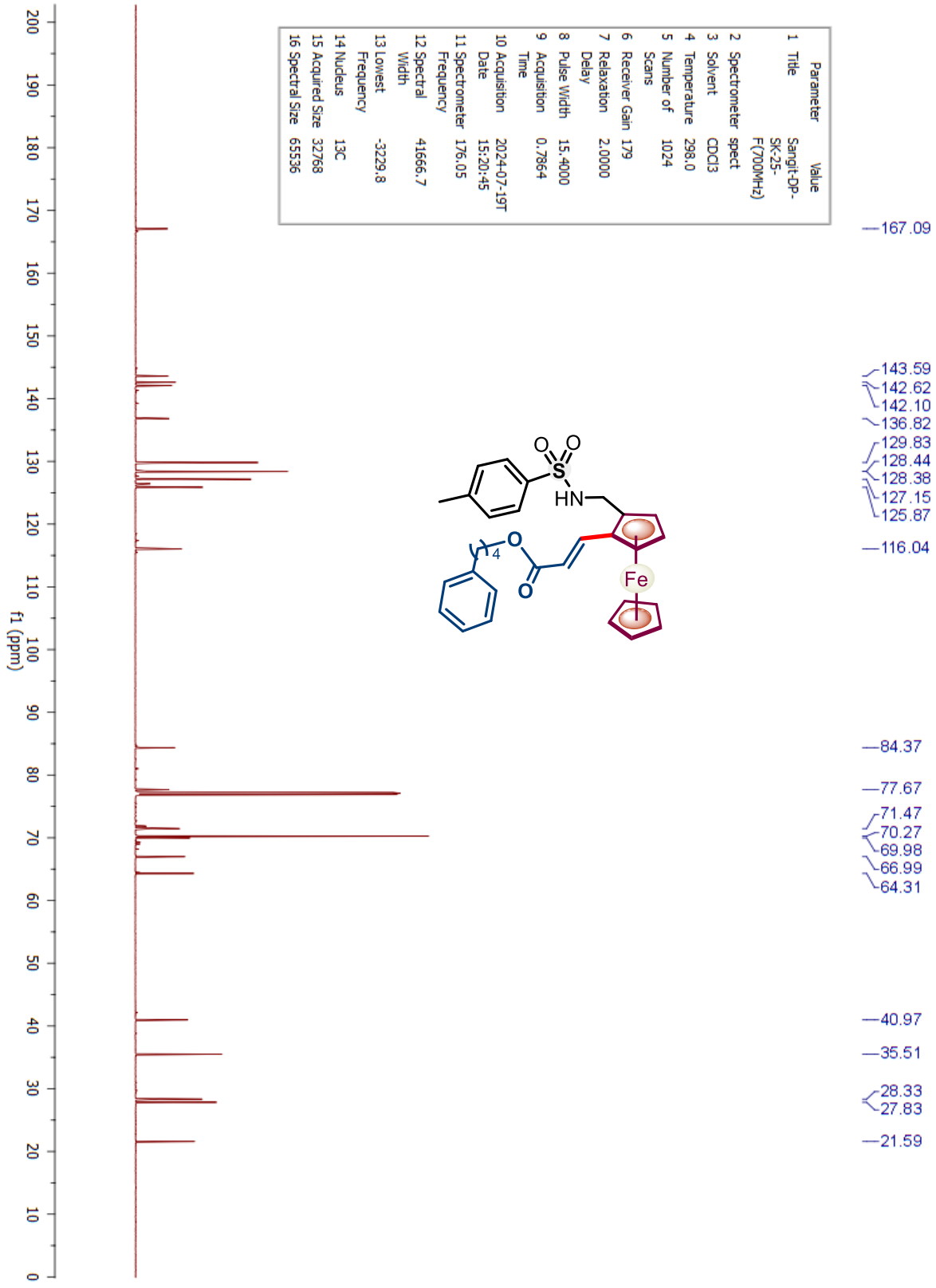
$^{13}C\{^{1}H\}$ NMR Spectrum of **4g**



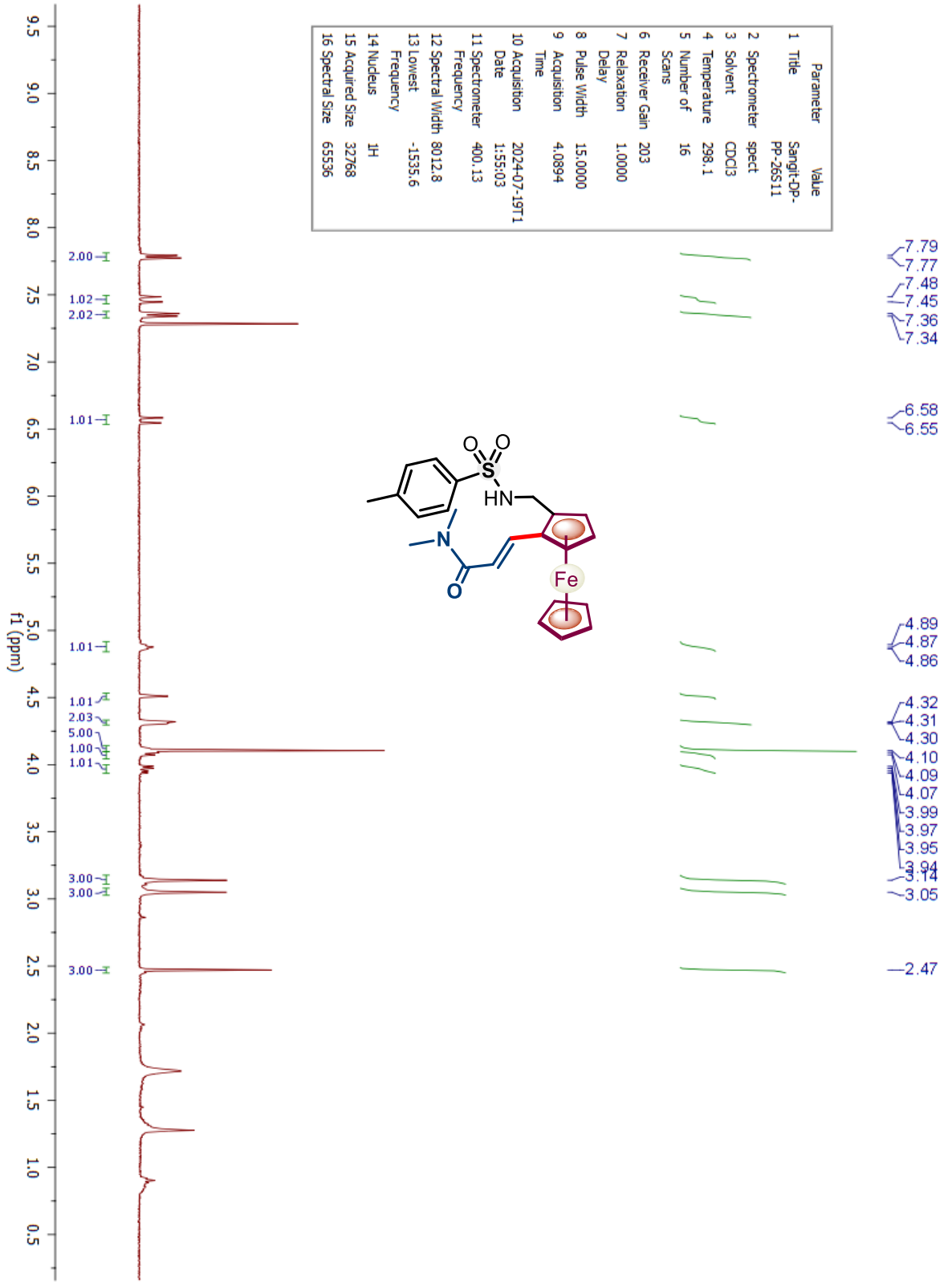
^{1}H NMR Spectrum of **4h**



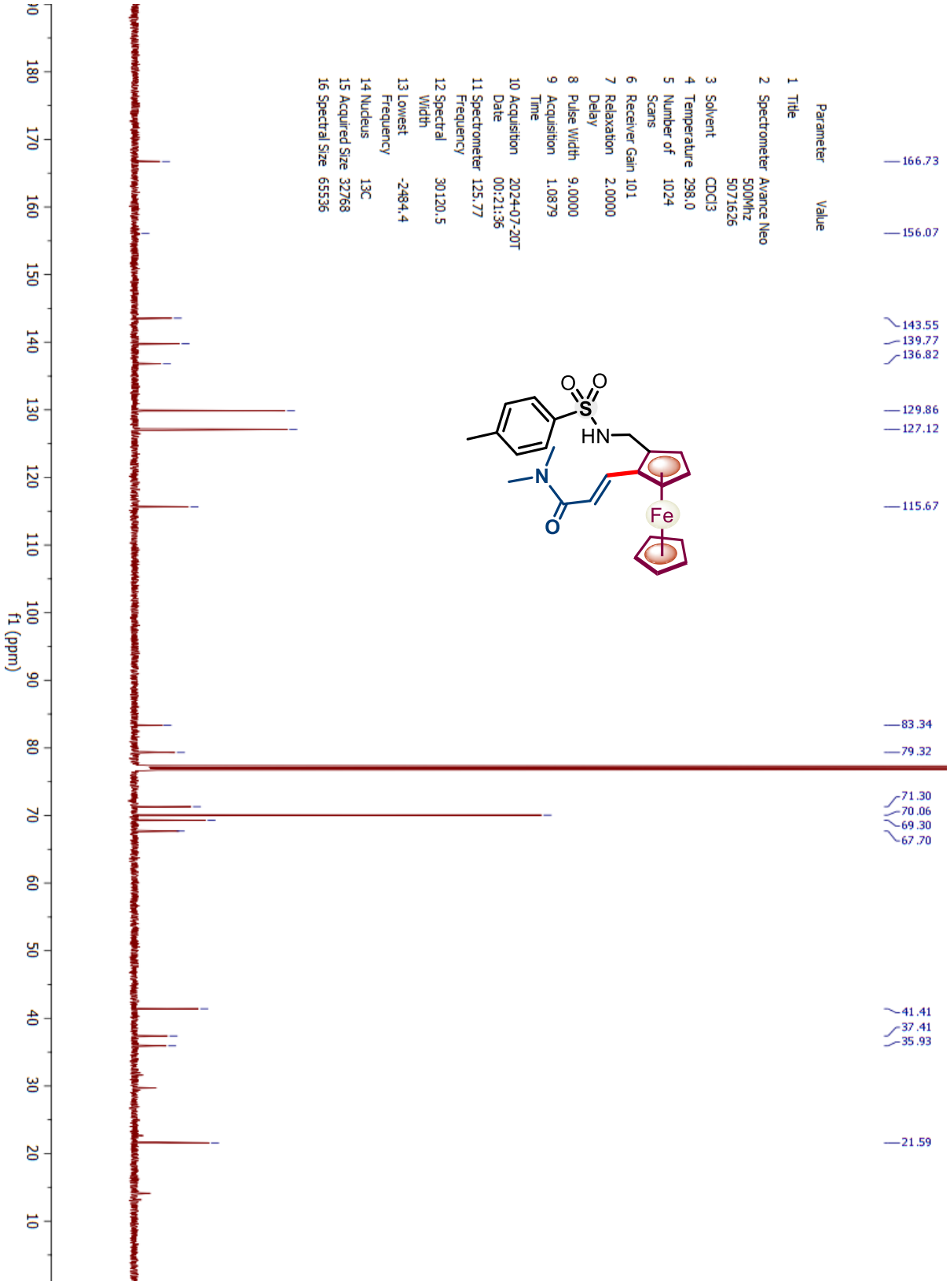
$^{13}C\{^{1}H\}$ NMR Spectrum of **4h**



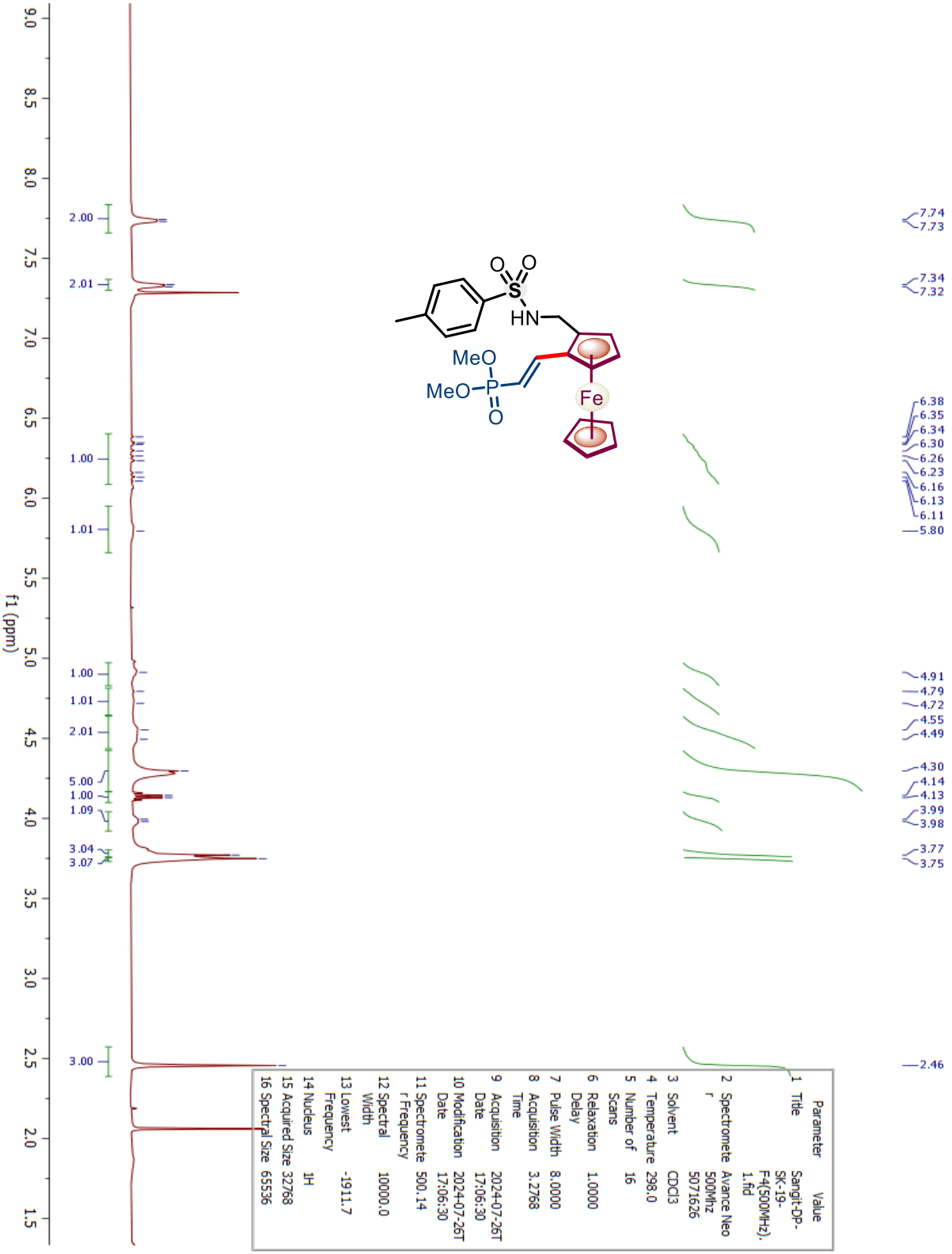
^{1}H NMR Spectrum of **4i**



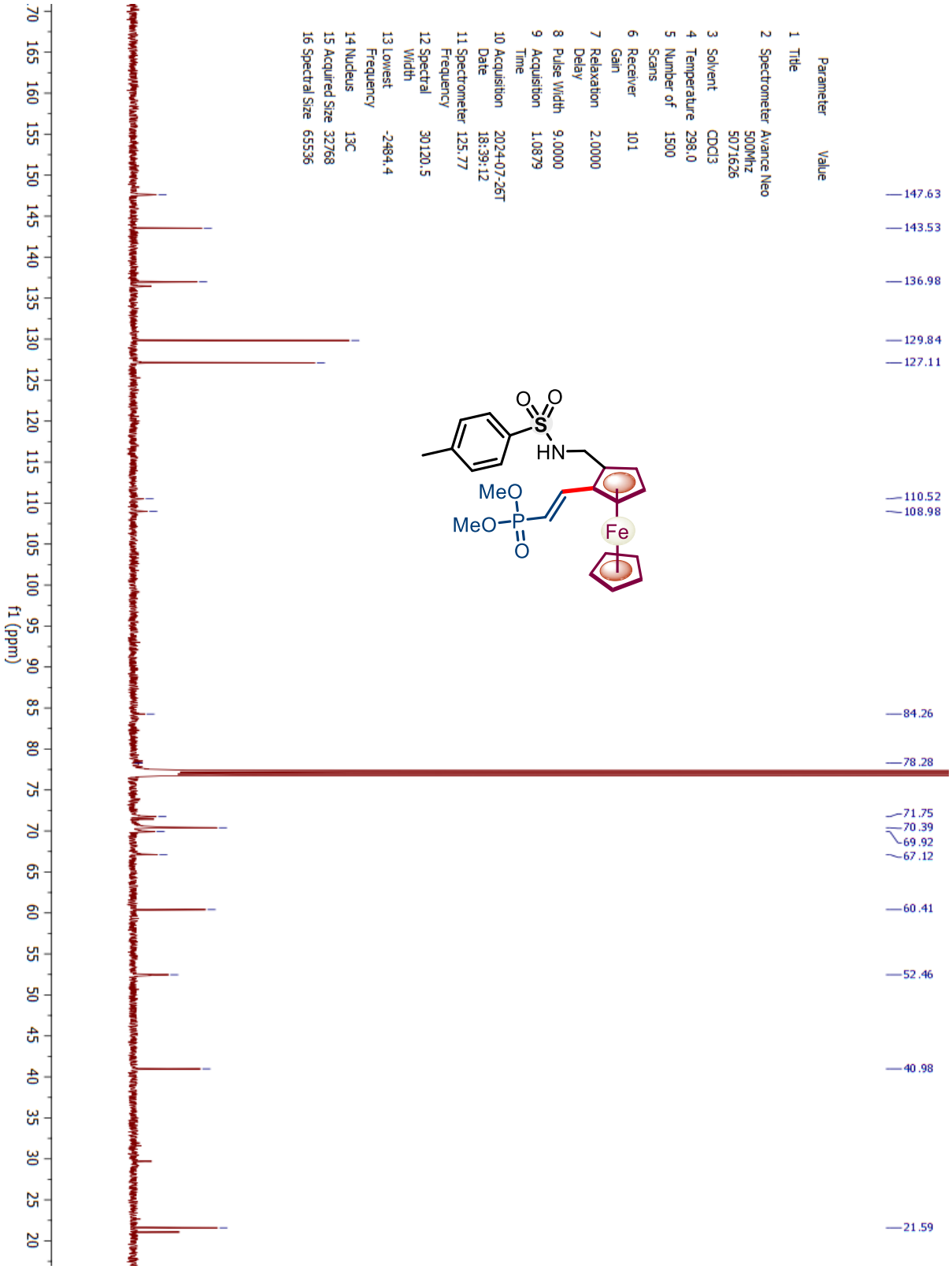
$^{13}C\{^{1}H\}$ NMR Spectrum of **4i**



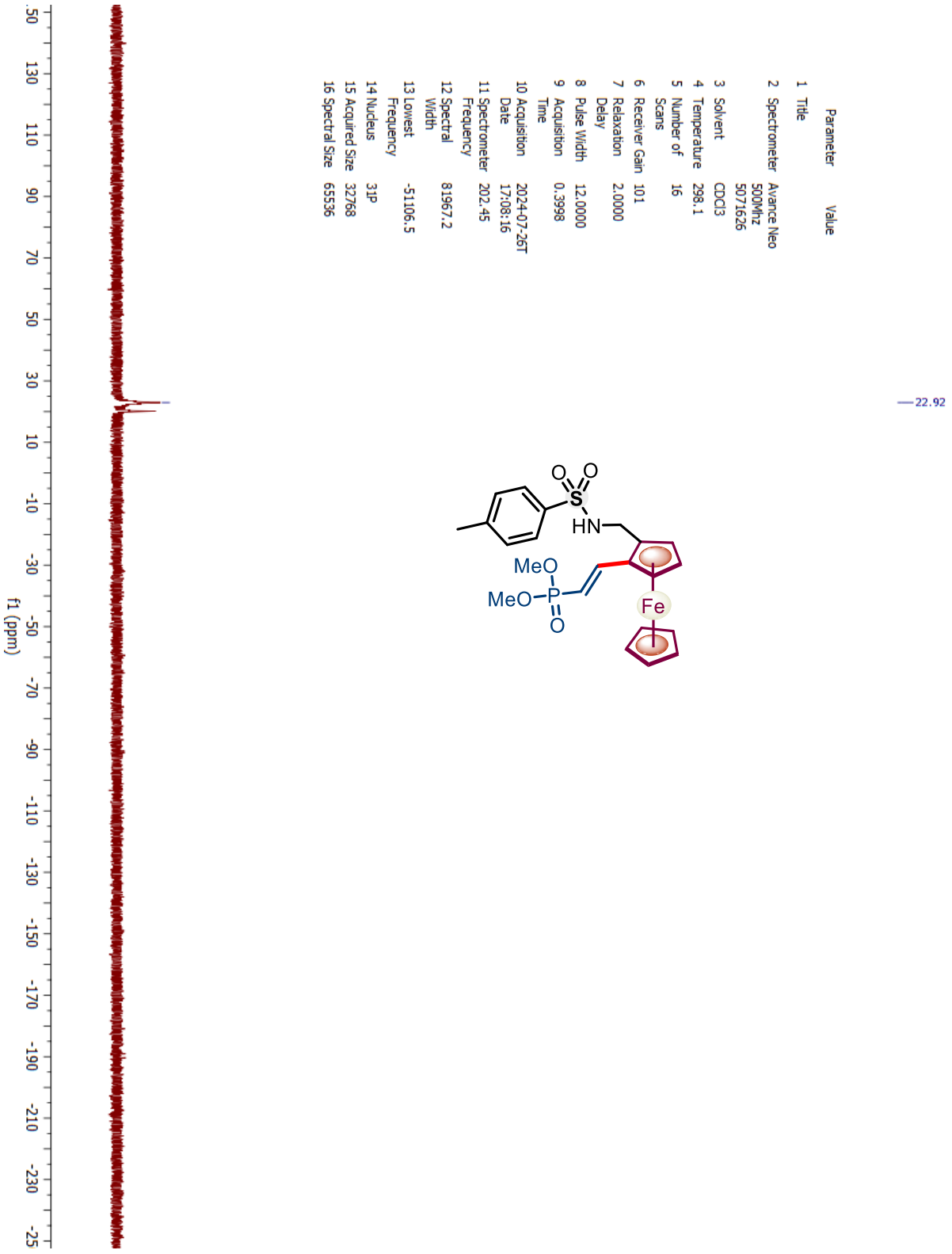
^{1}H NMR Spectrum of **4j**



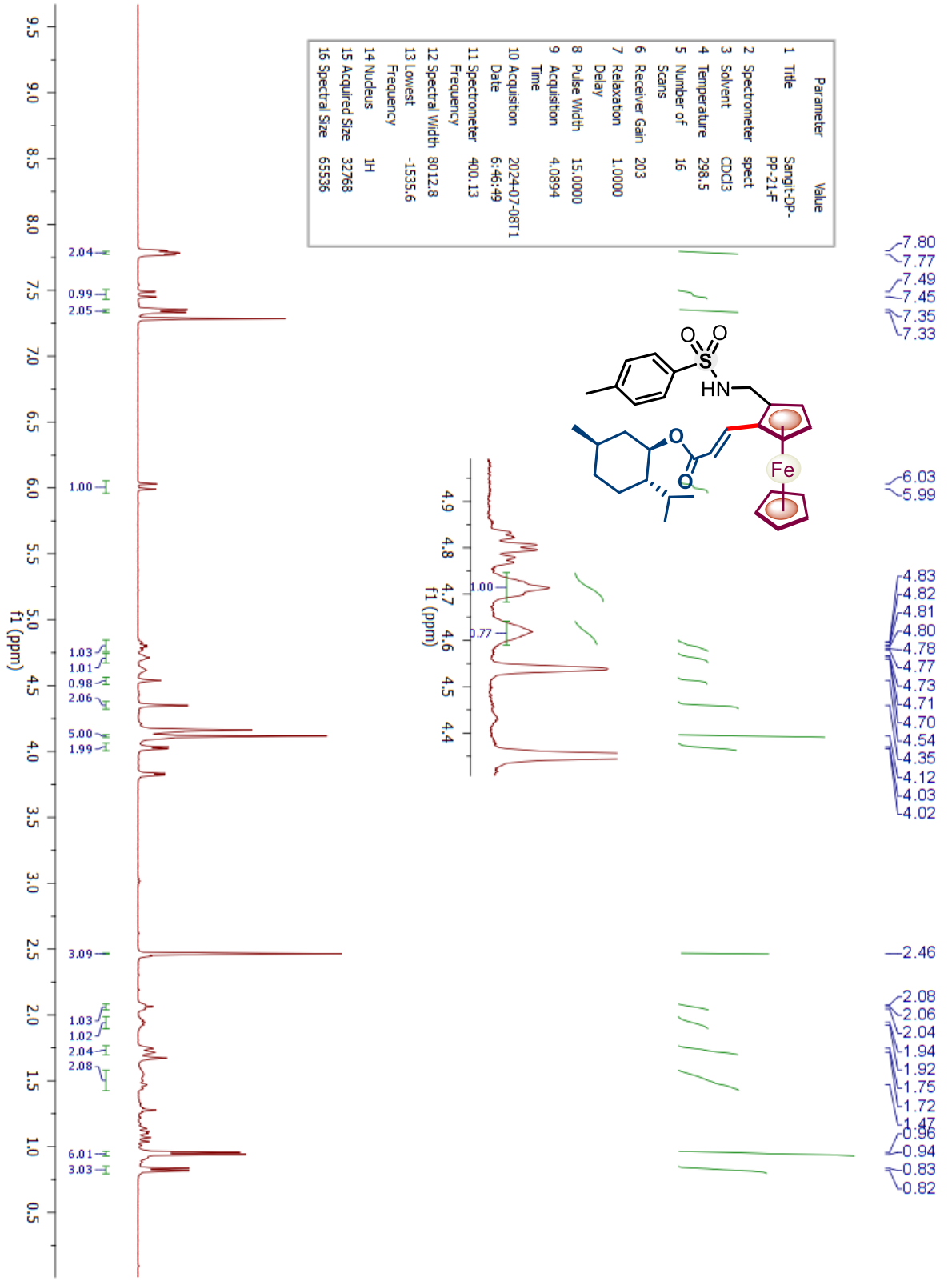
$^{13}C\{^{1}H\}$ NMR Spectrum of **4j**



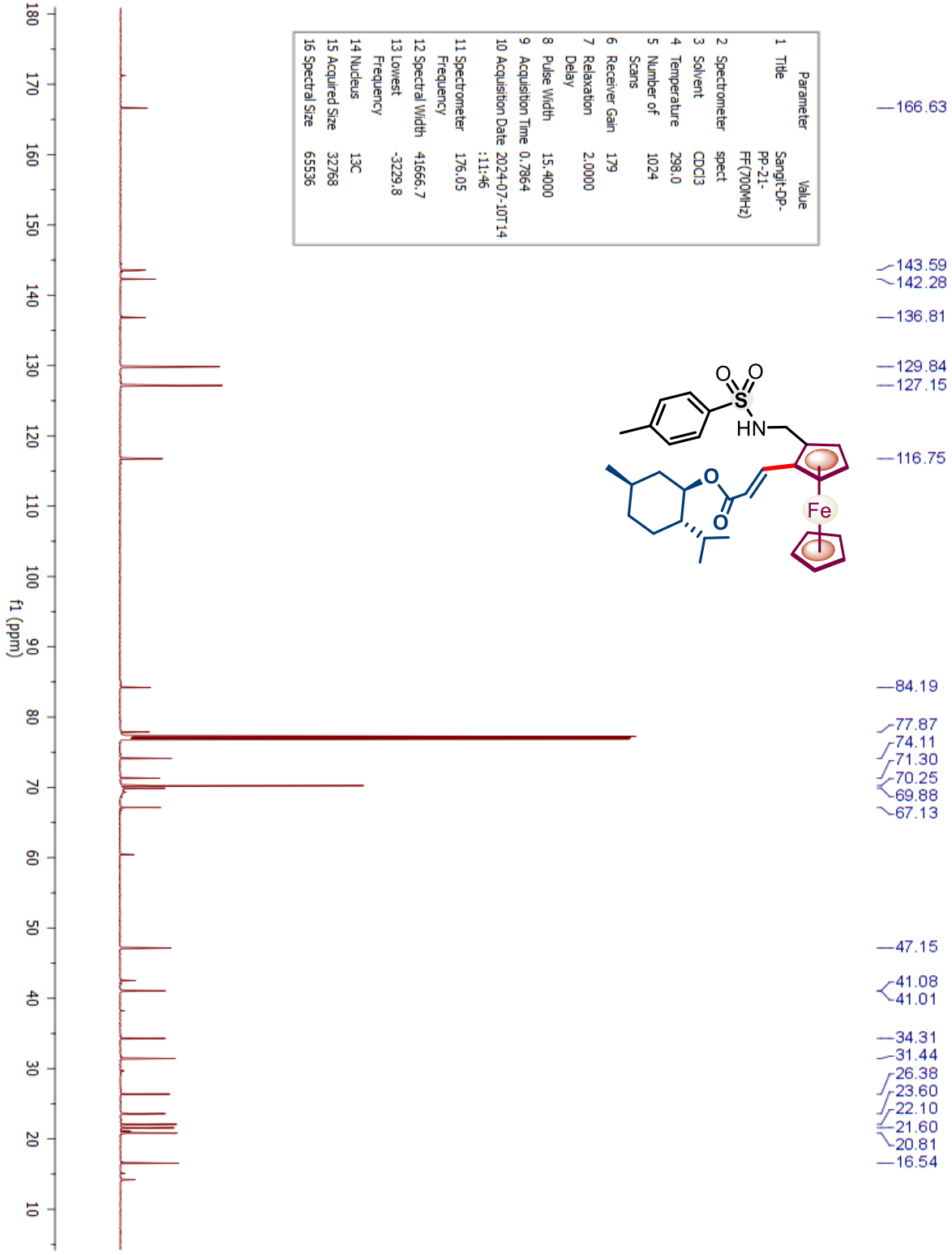
^{31}P NMR Spectrum of **4j**



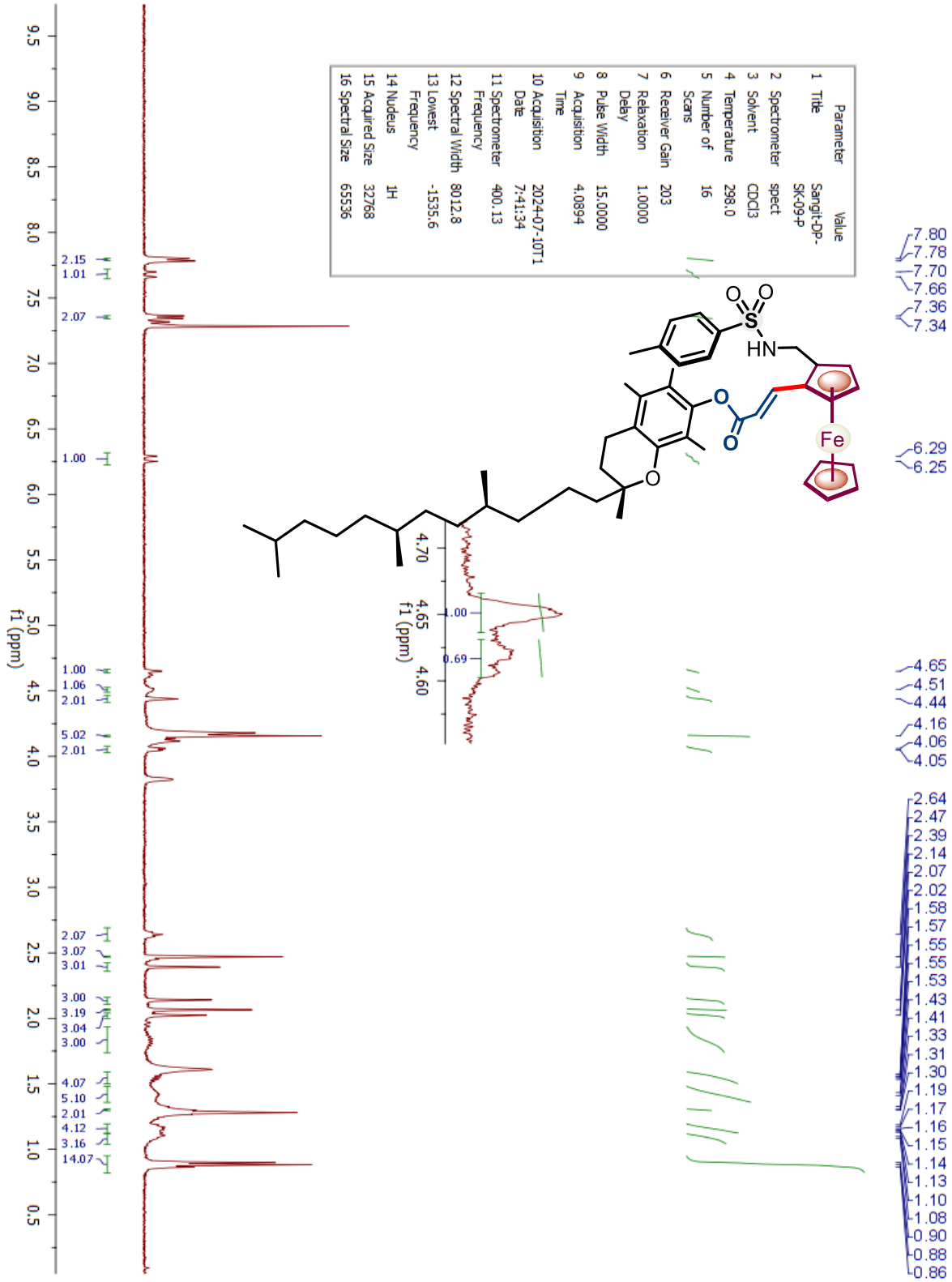
^{1}H NMR Spectrum of **4m**



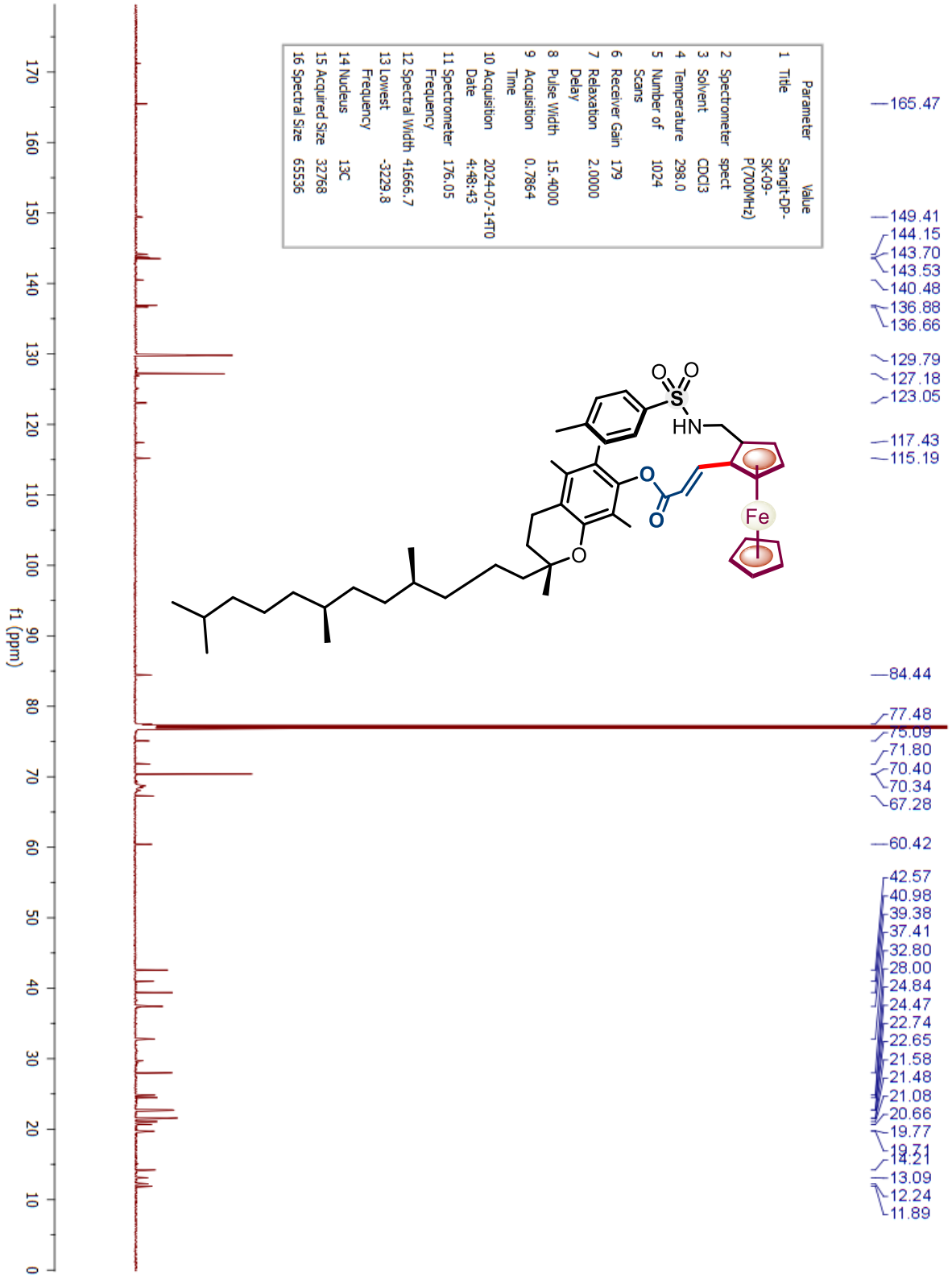
$^{13}C\{^{1}H\}$ NMR Spectrum of **4m**



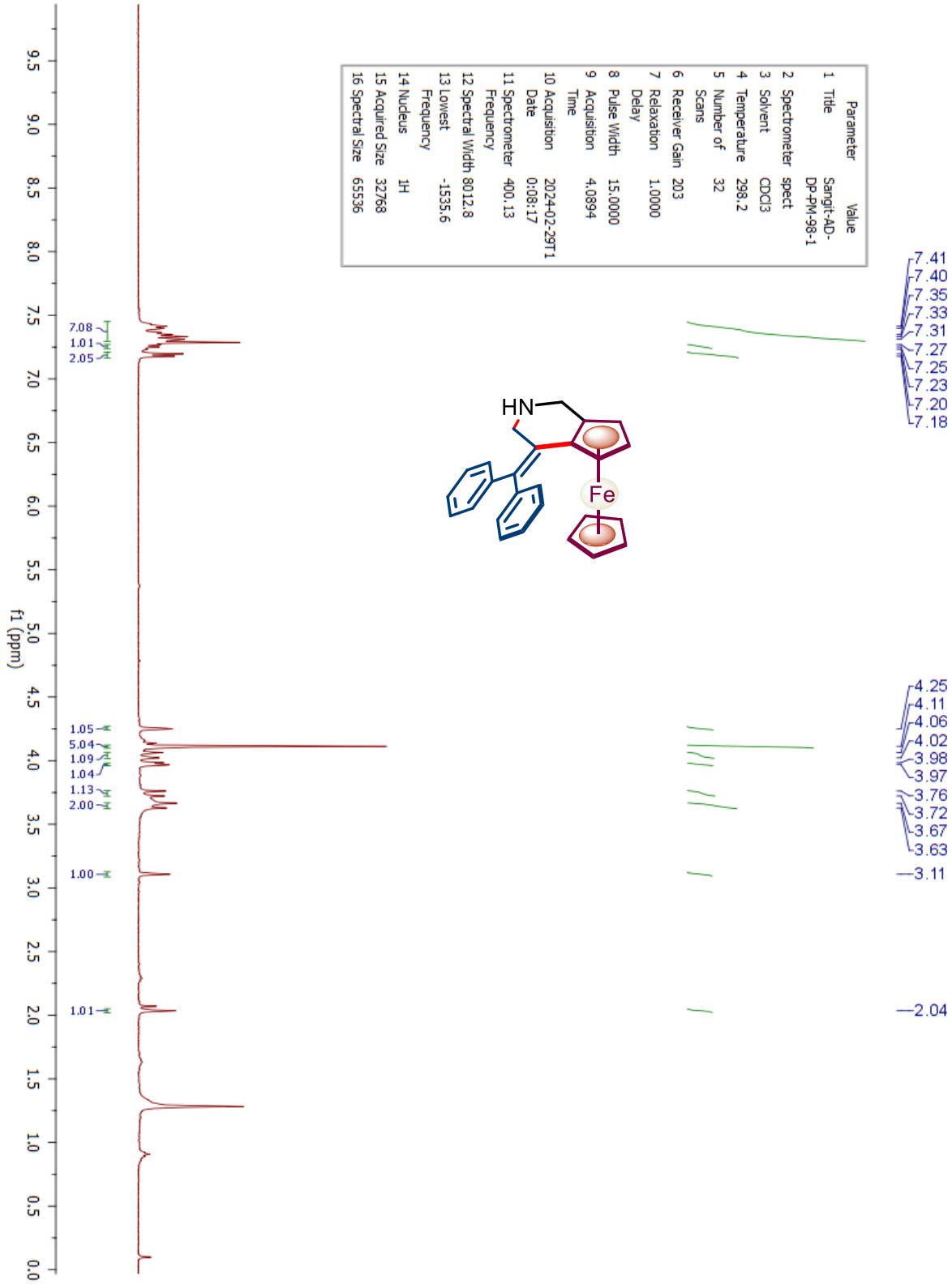
^{1}H NMR Spectrum of **4n**



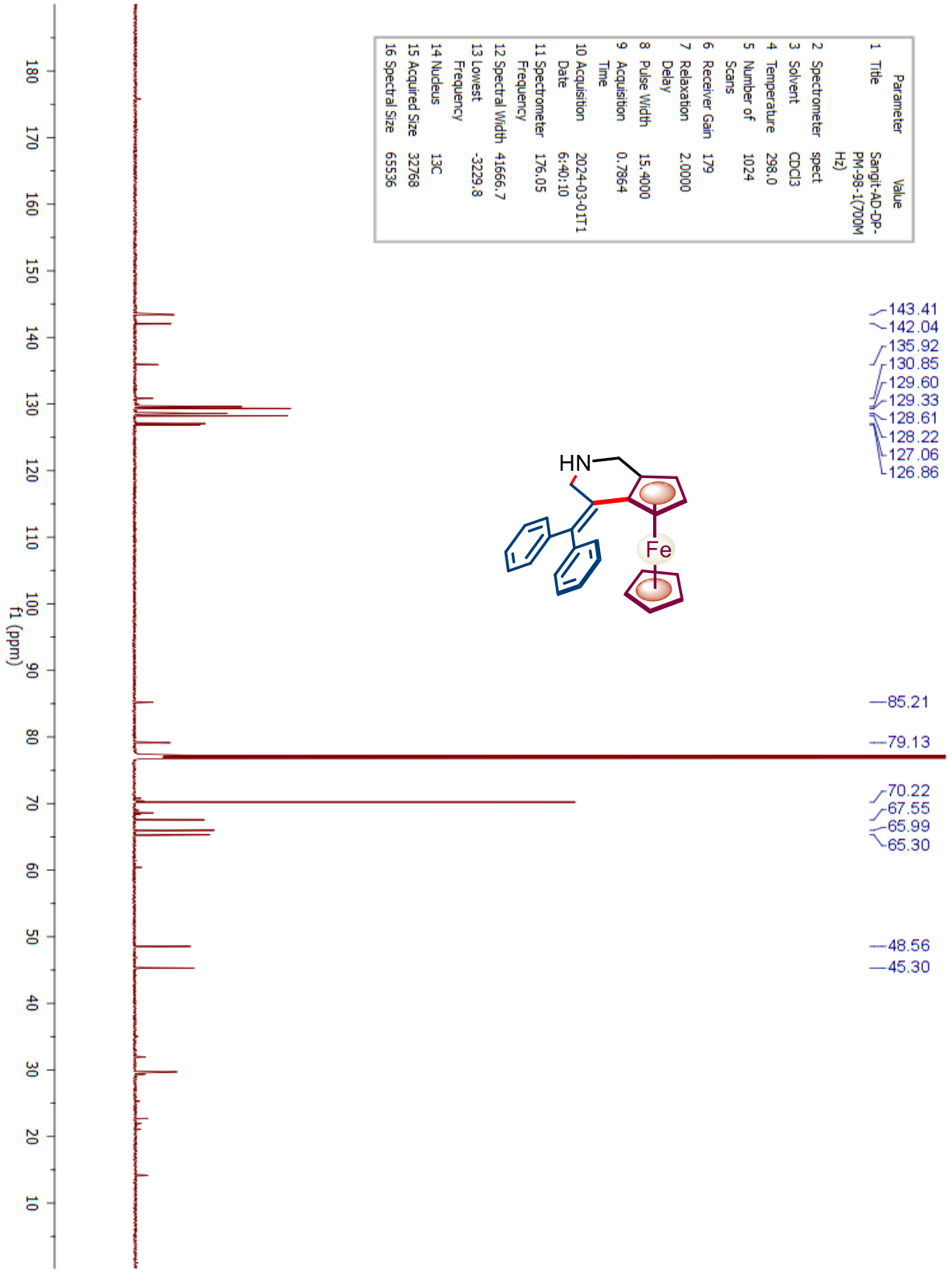
$^{13}C\{^{1}H\}$ NMR Spectrum of **4n**



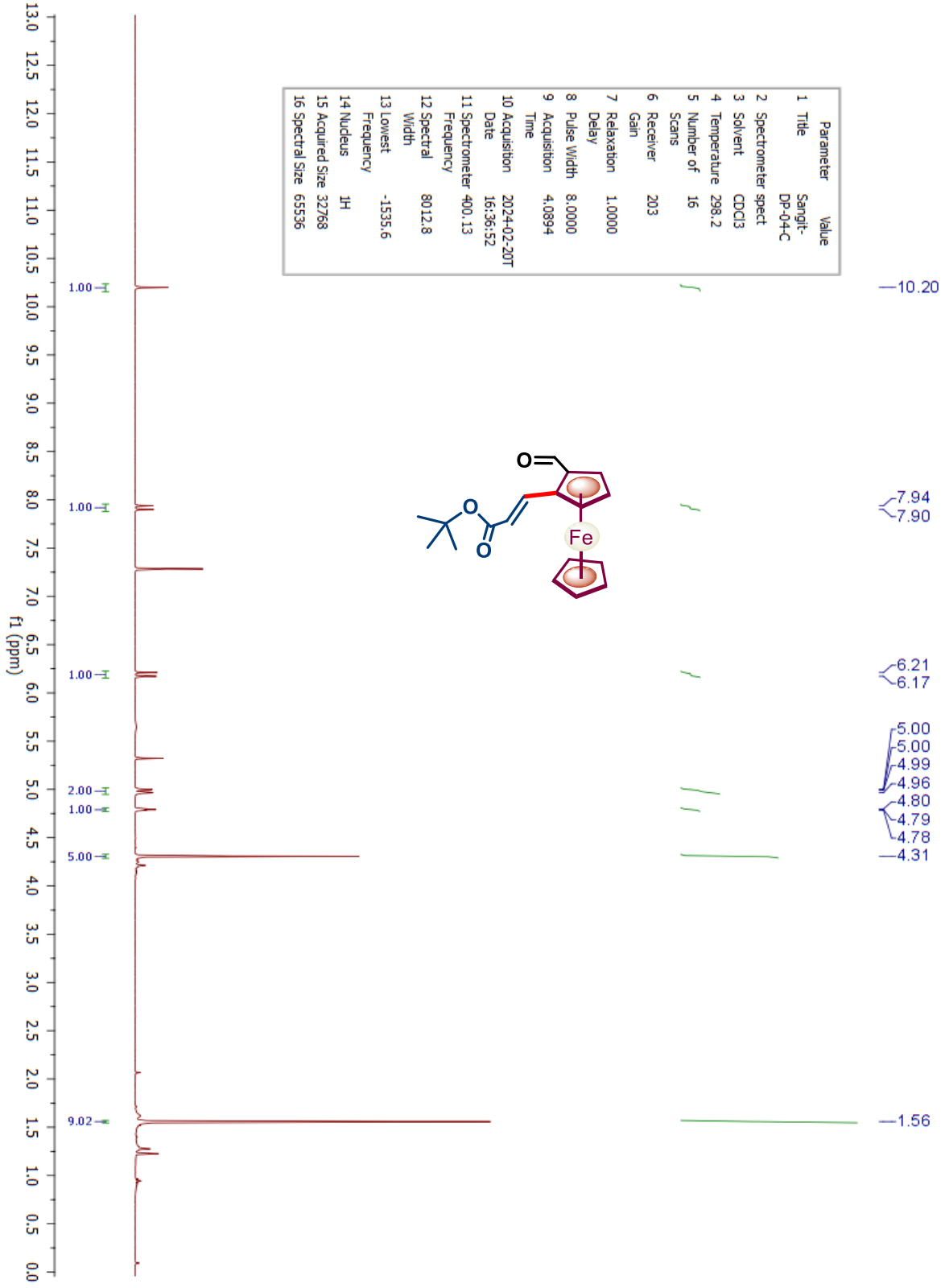
^{1}H NMR Spectrum of **5a**



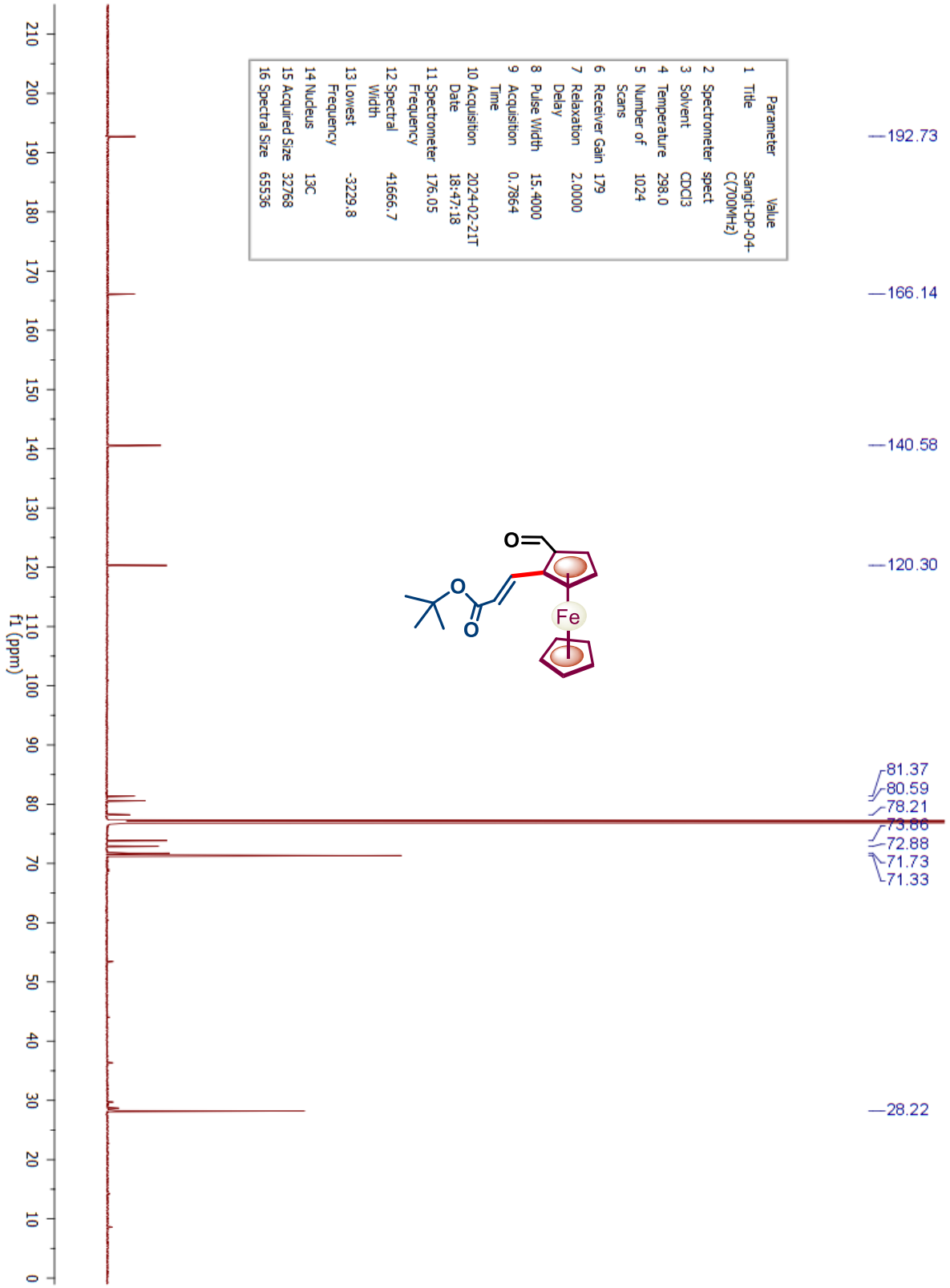
$^{13}C\{^{1}H\}$ NMR Spectrum of **5a**



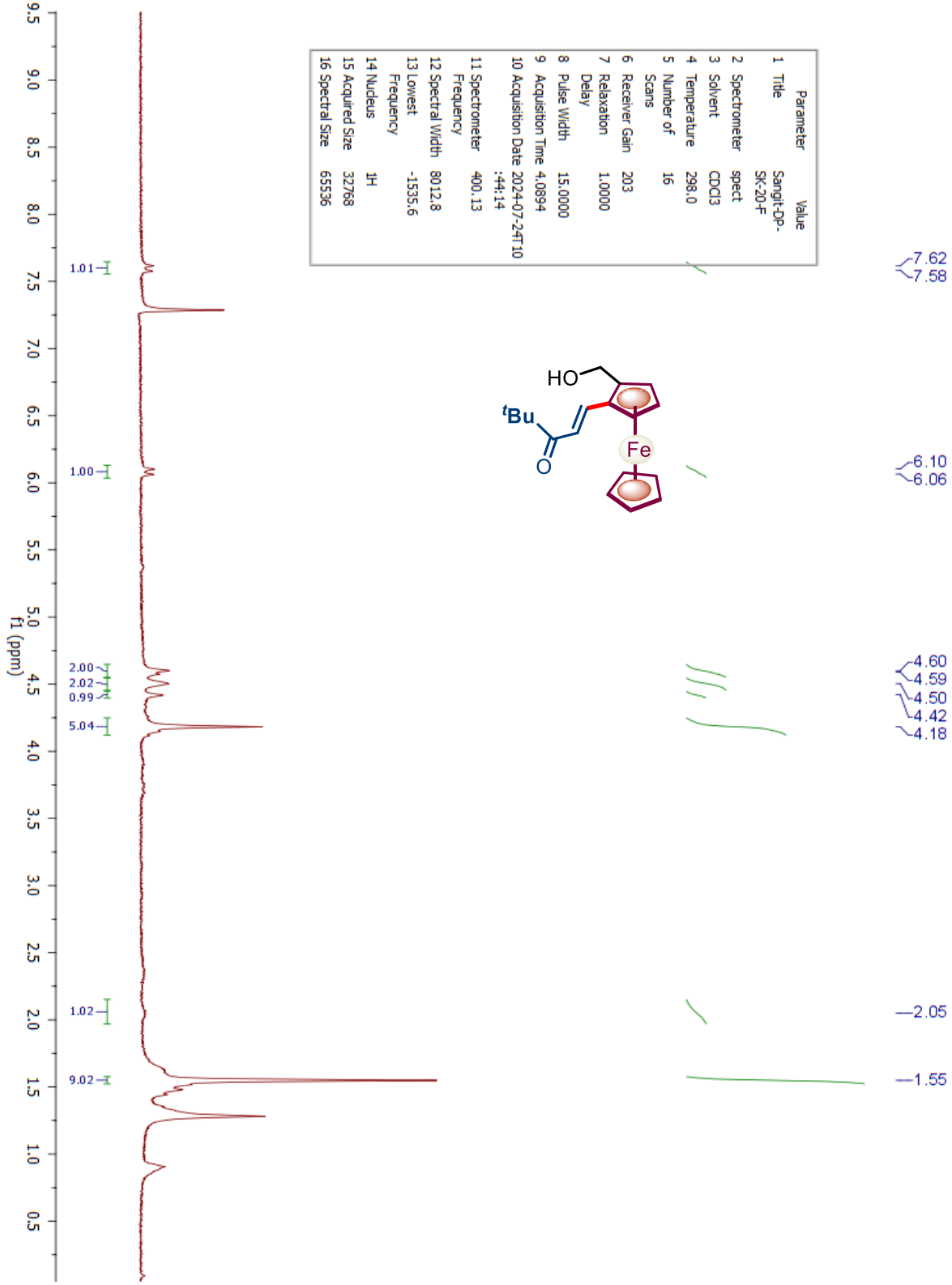
^{1}H NMR Spectrum of **6a**



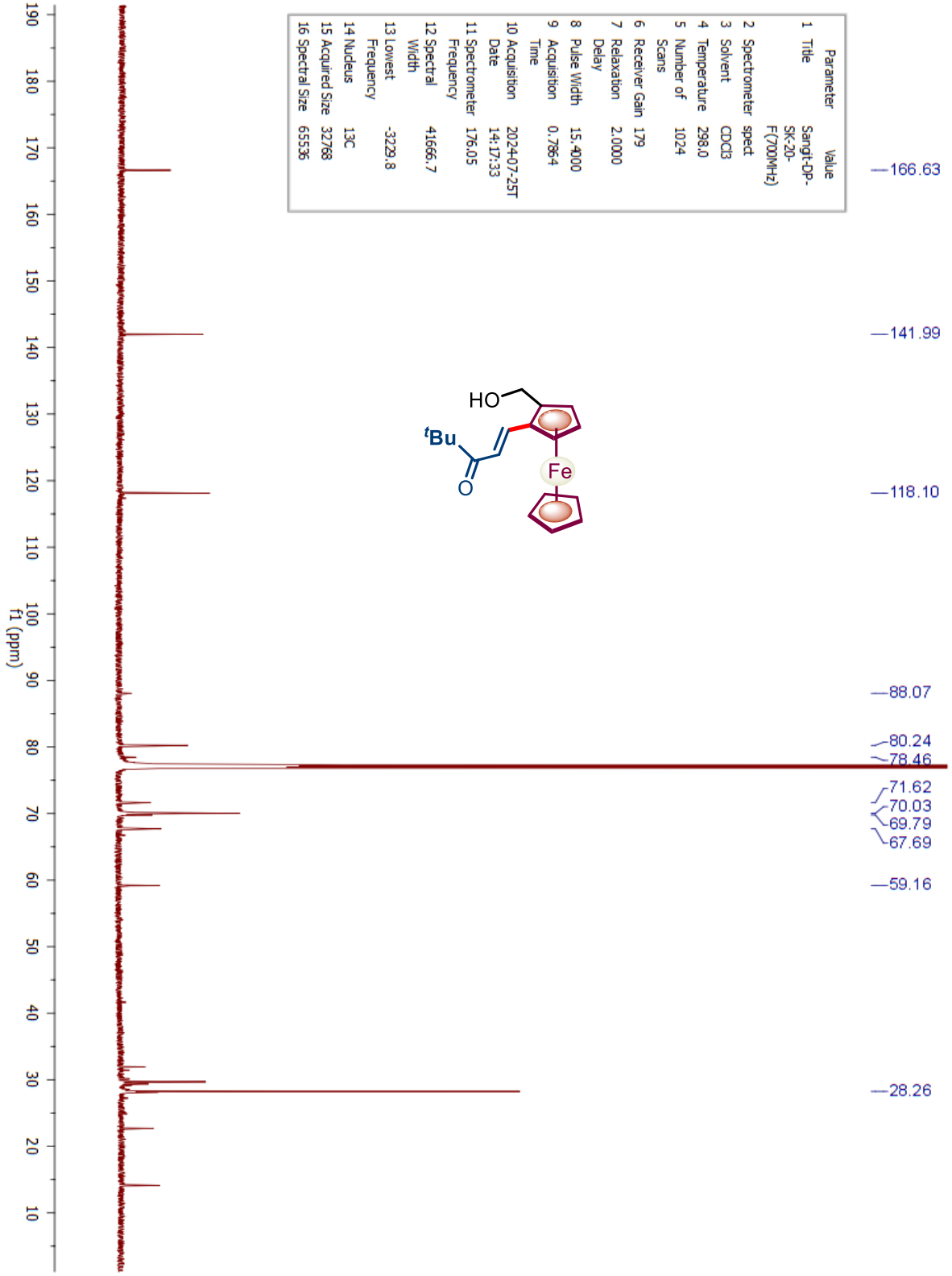
$^{13}C\{^{1}H\}$ NMR Spectrum of **6a**



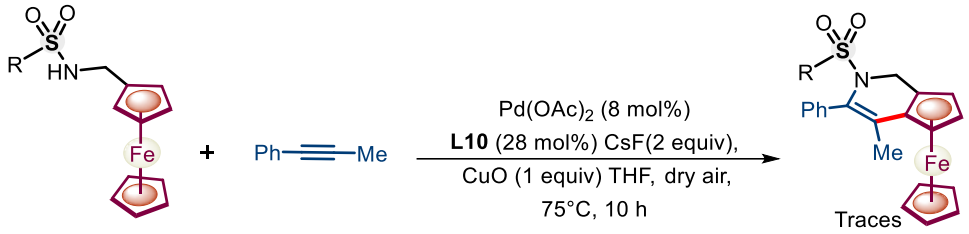
^{1}H NMR Spectrum of **7a**



$^{13}C\{^{1}H\}$ NMR Spectrum of **7a**



Mass spectrum of the reaction with alkyne coupling partner



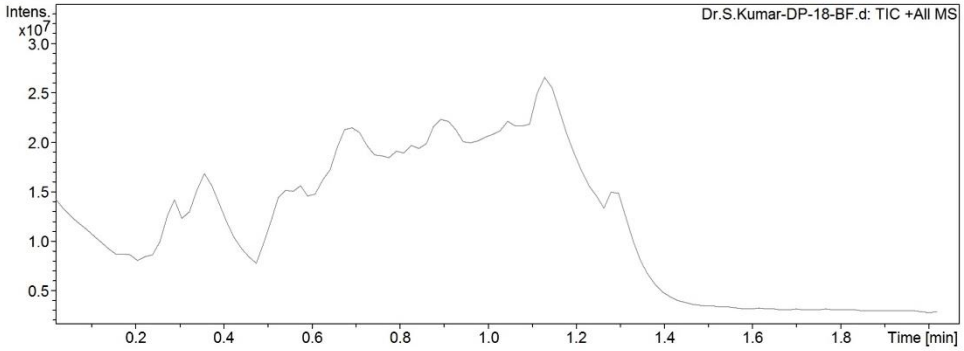
Display Report

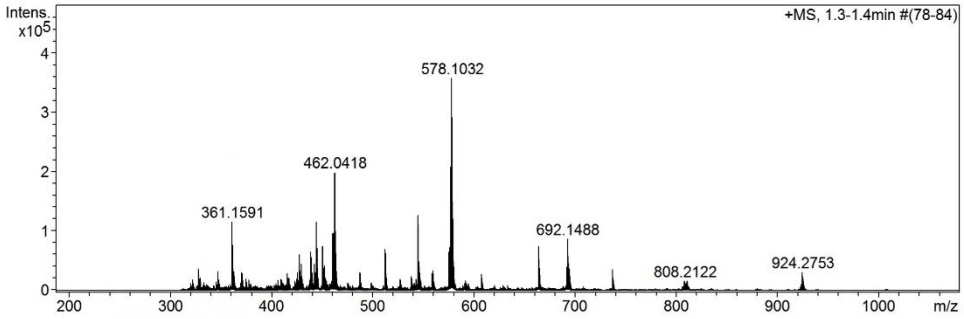
Analysis Info

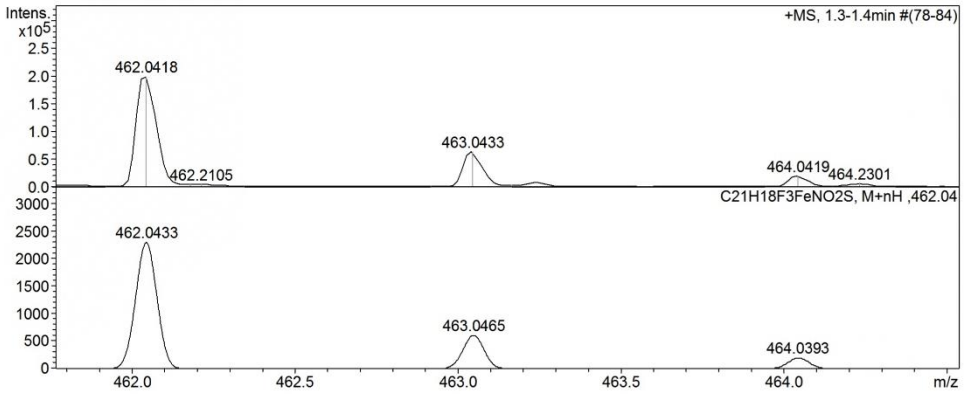
Analysis Name	D:\Data\USER DATA 2023\Oct 23\12-oct\Dr.S.Kumar-DP-18-BF.d	Acquisition Date	12-10-2023 15:52:27
Method	tune_wide _APCI_23.06.m	Operator	Bruker
Sample Name	DP-18-BF	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	2500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste







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