

SUPPLEMENTARY INFORMATION FOR

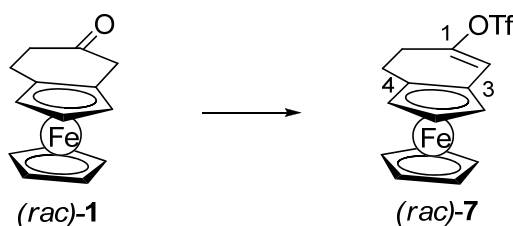
Synthesis and Chiroptical Properties of Ferrocene[4]Helicenequinones: Kinetic Resolution of a Planar-Chiral Diene

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Experimental Procedures

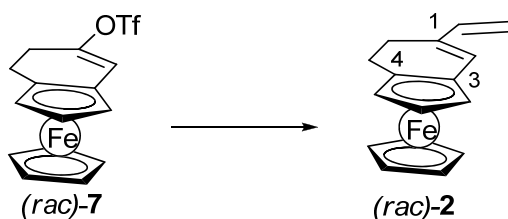
General. Melting points were obtained in open capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 at 300 and 75 MHz, respectively. UV/Vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. The spectra were measured in CH_2Cl_2 in a quartz cuvette (1 cm) at 298 °K. Circular dichroism spectra were measured with a JASCO J-810 spectropolarimeter. All reactions were monitored by thin layer chromatography that was performed on pre-coated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. Ethyl ether, CH_2Cl_2 , THF and CH_3CN were dried over 4\AA molecular sieves. All other reagent quality solvents were used without further purification. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2 , and solvent drying with MgSO_4 .

(±)-3,4-Ferrocene-1-trifluoromethanesulphonyloxycyclohexene (7).



To a solution of 3,4-ferrocenecyclohexanone (*rac*)-**1**¹ (15 mg, 0.06 mmol) and *N*-phenylbis(trifluoromethanesulfonimide) (23 g, 0.06 mmol) in dry THF (2.5 mL) was slowly added a solution of KHMDS 0.5M in THF (155 μ L, 0.078 mmol) at -78 °C, under argon. The mixture was stirred for 1 h and quenched with H₂O at -78 °C. After warming to room temperature, workup and flash chromatography with silica deactivated with 10% of water (eluent CH₂Cl₂/hexane 1:4), enol triflate (*rac*)-**7** was obtained as an orange oil, in 65% yield: ¹H NMR δ 2.47-2.93 (m, 4H), 4.17 (broad s, 8H), 6.30 (d, $J = 2.8$ Hz, 1H); ¹³C NMR δ 22.8, 27.8, 65.9, 66.7, 67.4, 69.8, 76.4, 82.4, 117.7, 146.5; MS (ESI): m/z (%) 253 (22), 282 (15), 386 (M⁺, 15); HRMS (ESI) calcd. for C₁₅H₁₃O₃F₃FeS (M⁺) 386.1671, found 386.9881.

(\pm)-3,4-Ferrocene-1-vinylcyclohexene (**2**).



To a mixture of enol triflate (*rac*)-**7** (55 mg, 0.142 mmol), LiCl (28 mg, 0.71 mmol) and Pd(PPh₃)₄ (9 mg, 5% mol) in THF (1.4 mL), vinyltributylstannane (44 μ L, 0.142 mmol) was added, under argon. The reaction mixture was heated at 90 °C for 45 min, filtered over celite and washed with water. After workup and flash chromatography (eluent CH₂Cl₂/hexane 2:1), diene (*rac*)-**2** was obtained as a red oil, in 58% yield; ¹H NMR δ 2.31-2.49 (m, 2H), 2.61-2.74 (m, 2H), 4.09 (s, 5H), 4.13 (broad s, 3H), 5.02 (d, $J = 10.8$ Hz, 1H), 5.25 (d, $J = 17.4$ Hz, 1H), 6.25 (broad s, 1H), 6.42 (dd, $J = 10.8$ and 17.4 Hz, 1H); ¹³C NMR δ 22.3, 23.4, 64.6, 66.3, 66.4, 69.5, 79.9, 85.1, 109.9, 126.7, 134.9, 139.2; MS (ESI): m/z (%) 264 (M⁺, 55); HRMS (ESI) calcd. for C₁₆H₁₆Fe (M⁺) 264.0601 found 264.0595.

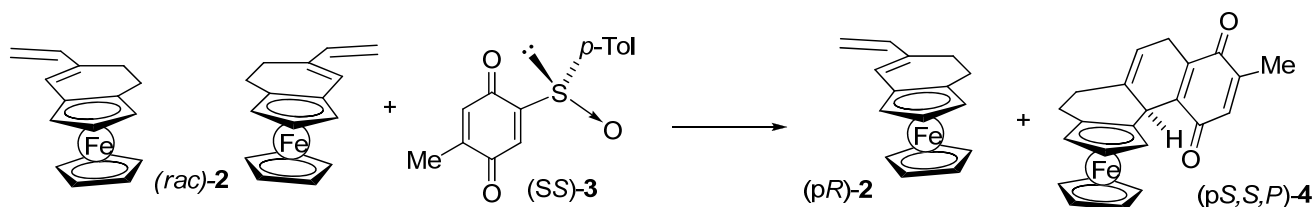
Representative Procedure for Kinetic Resolutions

To a solution of diene (*rac*)-**2** (33 mg, 0.12 mmol) in CH₂Cl₂ (7.6 mL) at -78 °C, a solution of (*SS*)-5-methyl-2-(*p*-tolylsulfinyl)-1,4-benzoquinone (**3**)² (see Table for conditions) in CH₂Cl₂ (7.6 mL)

(1) S. Siegel, H. G. Schmalz, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2456–2458.

(2) M. C. Carreño, J. L. García Ruano, A. Urbano, *Synthesis*, 1992, 651–653.

was rapidly added under argon. The reaction was slowly warmed up to room temperature and the solvent eliminated. After flash chromatography (eluent CH₂Cl₂), unreacted optically active diene (*pR*)-**2** (see Table for yields and optical purities) and tetracyclic ferrocene (*pS,S,P*)-**4** (see Table for yields and optical purities), were respectively obtained.



entry	T (° C)	(<i>SS</i>)- 3 (equiv)	(<i>pR</i>)- 2 (% yield / % <i>ee</i>)	(<i>pS,S,P</i>)- 4 (% yield / % <i>ee</i>)
1	-78 to rt	2.0		(56 / 55)
2	-78 to rt	0.5	(50 / 63)	(34 / 93)
3	-78 to rt	0.9	(28 / 99)	(46 / 73)
4	-10	0.5	(32 / 47)	(45 / 97)

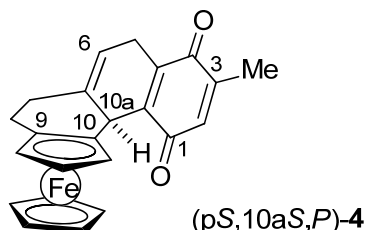
(*pR*)-3,4-Ferrocene-1-vinylcyclohexene (**2**).



Compound (*pR*)-**2** (99% *ee*)³ was obtained from kinetic resolution of diene (*rac*)-**2** with 0.9 equiv of (*SS*)-**4** (entry 3), as a red oil, in 28% yield: $[\alpha]_{\text{D}}^{20} = -1455$ (*c* 0.022, CHCl₃).

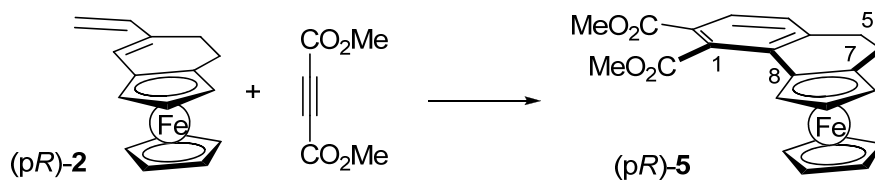
(3) The enantiomeric excess of optically active diene (*pR*)-**2** was determined from optical purity of tricyclic ferrocenyl diester (*pR*)-**5** (see below).

(pS,10aS,P)-9,10-Ferrocene-3-methyl-5,7,8,10a-tetrahydrophenantrene-1,4-quinone (4)



Compound (pS,10aS,P)-4 (97% *ee*)⁴ was obtained from kinetic resolution of diene (*rac*)-2 with 0.5 equiv of (*SS*)-3 at -10 °C for 3 h, as a dark blue solid, in 45% yield: m.p. 270 °C; ¹H NMR δ 2.04 (d, *J* = 1.5 Hz, 3H), 2.37-2.54 (m, 2H), 2.68-2.89 (m, 2H), 2.94-3.15 (m, 2H), 3.68 (broad s, 1H), 3.91 (dd, *J* = 2.4 and 2.5 Hz, 1H), 3.95 (m, 1H), 4.22 (s, 5H), 4.9 (t, *J* = 6.7 Hz, 1H), 5.49 (broad s, 1H), 6.66 (d, *J* = 1.5 Hz, 1H); ¹³C NMR δ 15.7, 25.2, 28.4, 32.5, 36.0, 65.2, 66.0, 66.8, 70.3, 84.4, 88.0, 114.6, 133.3, 136.1, 136.5, 138.7, 140.6, 145.1, 188.0 (2C).

(pR)-Dimethyl 7,8-ferrocene-5,6-dihydronaphthalene-1,2-dicarboxylate (5).



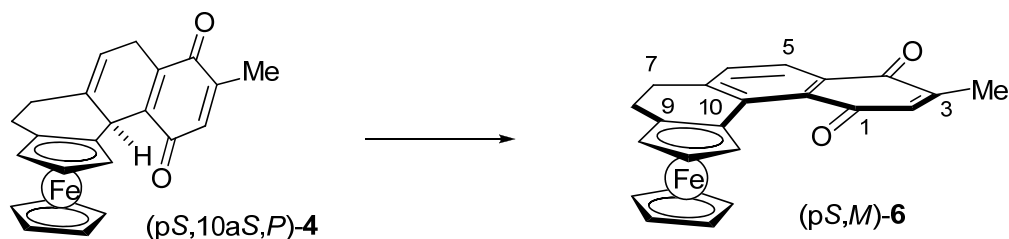
To a solution of diene (pR)-2 (99% *ee*, 15 mg, 0.056 mmol) in toluene (1.5 mL), dimethyl acetylenedicarboxylate (40 μL, 6 mmol) was added. The reaction mixture was heated to 110 °C for 3 h and the solvent evaporated. The residue was solved in CH₂Cl₂ (7.5 mL) and DDQ (10 mg, 0.045 mmol) was added. The reaction mixture was stirred for 15 min and washed with a saturated aqueous solution of sodium bicarbonate. After workup and flash chromatography (eluent hexane/EtOAc 1:1), pure tricyclic ferrocenyl diester (pR)-5 was obtained as a yellow solid, in 63% yield: mp 134-135 °C; [α]_D²⁰ = +283 (*c* 0.012, CHCl₃), 99% *ee*; ⁵ ¹H NMR δ 2.34 (ddd, *J* = 5.4, 14.1 and 14.5 Hz, 1H), 2.59 (ddd, *J* = 2.0, 14.1 and 15.6 Hz, 1H), 3.03 (ddd, *J* = 2.0, 5.4 and 15.6 Hz, 1H), 3.32 (ddd, *J* = 6.5, 14.1 and 15.6 Hz, 1H), 3.88 (s, 3H), 4.00 (s, 3H), 4.06 (s, 5H), 4.30-4.31 (m, 2H), 4.51 (broad s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H); ¹³C NMR δ 22.3, 31.8, 52.3, 52.6, 63.1, 67.7, 68.0,

(4) Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min⁻¹, 254 nm, *R*_t = 7.3 min, *T* = 25 °C.

(5) Chiral HPLC: Daicel Chiralpak AS-H, hexane/2-propanol 90:10; 0.8 mL min⁻¹, 254 nm, *R*_t = 13.3 min, *T* = 25 °C

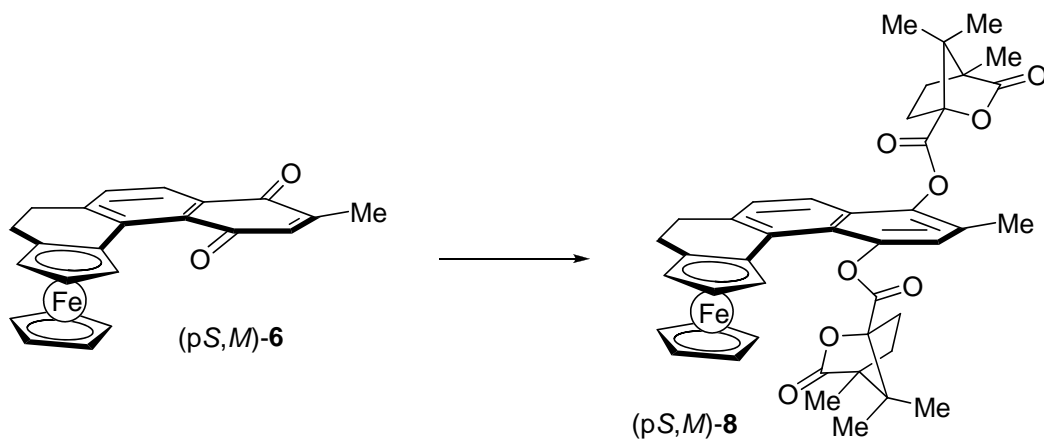
69.9, 77.2, 88.2, 125.9, 127.2, 129.1, 131.3, 133.7, 142.4, 166.1, 170.9; MS (ESI): m/z (%) 404 (M^+ , 100), 405 ($M^+ + 1$, 18); HRMS (ESI) calcd. for $C_{22}H_{20}O_4Fe$ (M^+) 404.0712, found 404.0711.

(p*S*,*M*)-9,10-Ferrocene-3-methyl-7,8-dihydrophenantrene-1,4-quinone (6).



To a solution of tetrahydroaromatic ferrocene (*pS*,10*aS*,*P*)-(4) (97% *ee*, 12 mg, 0.031 mmol) in CH_2Cl_2 (1.2 mL) at room temperature, DDQ (7 mg, 0.031 mmol) was added. The reaction mixture was stirred for 15 min and washed with a saturated aqueous solution of sodium bicarbonate. After workup and flash chromatography, pure dihydroaromatic helical ferrocene (*pS*,*M*)-6 was obtained as a dark green solid, in 72% yield: mp 270 °C; $\{[\alpha]_D^{20} = +1704$ ($c = 0.001$ in $CHCl_3$), 97% *ee*;⁶ 1H NMR δ 2.14 (d, $J = 1.4$ Hz, 3H), 2.41 (dt, $J = 5.4$ and 14.0 Hz, 1H), 2.60 (ddd, $J = 1.9$, 6.6 and 14.0 Hz, 1H), 3.03 (ddd, $J = 1.9$, 5.4 and 16.1 Hz, 1H), 4.67 (d, $J = 2.2$ Hz, 1H), 6.80 (d, $J = 1.4$ Hz, 1H), 7.39 (d, $J = 7.7$ Hz, 1H), 7.89 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR δ 15.7, 22.0, 32.5, 67.6, 67.8, 67.9, 70.2, 77.7, 90.7, 124.4, 130.0, 132.3, 133.0, 138.0, 138.7, 145.1, 145.2, 185.4, 186.5; MS (ESI): m/z (%) 382 (M^+ , 24), 383 ($M^+ + 1$, 39); HRMS (ESI) calcd. for $C_{23}H_{18}FeO_2$ (M^+) 382.2328, found 382.0650.

Bis(-)-camphanate (p*S*,*M*)-8.



(6) Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min⁻¹, 254 nm, $R_t = 11.6$ min, $T = 25$ °C.

Et₃N (60 μL) and CH₂Cl₂ (1 mL) were added to a mixture of dihydroaromatic helical ferrocene (*pS,M*)-**6** (7.7 mg, 0.02 mmol), activated Zn (17 mg, 0.25 mmol), (–)-camphanoyl chloride (22 mg, 0.1 mmol) and DMAP (1.15 mg, 0.01 mmol), under argon. The mixture was refluxed 1.5 h and filtrated through celite, aided by several ethyl acetate washes, to remove remaining Zn. The organic solution was washed with saturated aqueous NaHCO₃, 2% HCl and water. After workup and flash chromatography (hexane/EtOAc 2:1), the corresponding pure *bis*-(–)-camphanate (*pS,M*)-**8** was obtained as a red solid, in 48% yield; m.p. decomposes over 220 °C; [α]_D²⁰ = –400 (*c* = 0.028 in CHCl₃); ¹H NMR δ 0.84 (s, 3H), 1.02 (s, 3H), 1.08 (s, 3H), 1.21 (s, 3H), 1.24 (s, 3H), 1.25 (s, 3H), 1.46-1.60 (m, 2H), 1.72-1.91 (m, 3H), 2.01-2.10 (m, 1H), 2.34 (s, 3H), 2.34-2.42 (m, 2H), 2.56-2.73 (m, 2H), 3.07 (dd, *J* = 4.8 and 16.2 Hz, 1H), 3.43-3.57 (m, 1H), 3.87 (s, 5H), 4.28 (s, 1H), 4.32 (broad s, 1H), 5.00 (broad s, 1H), 6.96 (s, 1H), 7.31 and 7.59 (AB System, *J* = 8.5 Hz, 2H); ¹³C NMR (125 MHz) δ 9.7, 9.8, 16.4, 16.6, 16.7, 17.0, 17.2, 20.2, 20.8, 24.5, 29.0, 29.1, 30.4, 31.5, 33.5, 43.7, 53.8, 54.4, 54.5, 55.0, 55.1, 55.2, 90.6, 91.1, 118.4, 121.2, 123.3, 125.3, 128.1, 128.5, 130.9, 142.3, 143.8, 170.0, 172.7, 178.0, 178.5. MS (ESI): *m/z* (%) 744 (M⁺, 61), 745 (M⁺+1, 100); HRMS (ESI) calcd. for C₄₃H₄₄O₈Fe (M⁺) 744.6497, found 744.2380.

(*pR,P*)-9,10-Ferrocene-3-methyl-7,8-dihydrophenantrene-1,4-quinone (6).

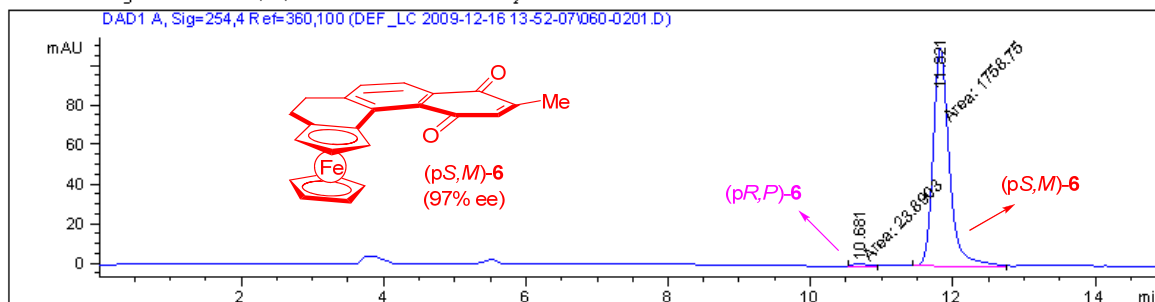


To a solution of diene (*pR*)-**2** (95% *ee*, 8.5 mg, 0.032 mmol) in CH₂Cl₂, a solution of (±)-5-methyl-2-(*p*-tolylsulfonyl)-1,4-benzoquinone (*rac*)-**3**² (17 mg, 0.062 mmol) in CH₂Cl₂ (1 mL) was rapidly added, under argon. After stirring for 2 h, DDQ (7.2 mg, 0.032 mmol) was added and the resulting solution was stirred for 15 min and washed with a saturated solution of sodium bicarbonate. After workup and flash chromatography (eluent CH₂Cl₂), helical ferrocene (*pR,P*)-**6** was obtained as a dark green solid, in 68% yield: [α]_D²⁰ = –1660 (*c* = 0.001 in CHCl₃), 95% *ee*.⁷

(7) Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min⁻¹, 254 nm, *R*_t = 10.5 min, *T* = 25 °C

CHIRAL HPLC

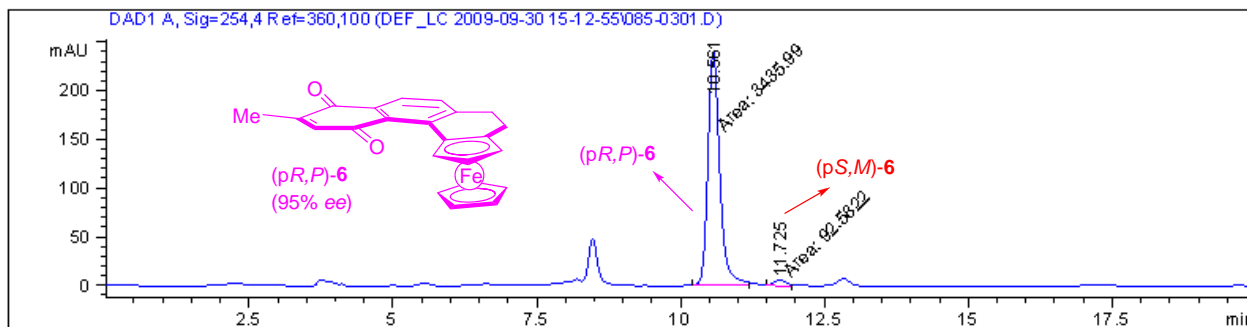
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.681	MM	0.2725	23.89025	1.46137	1.3402
2	11.821	MM	0.2665	1758.75159	109.97760	98.6598

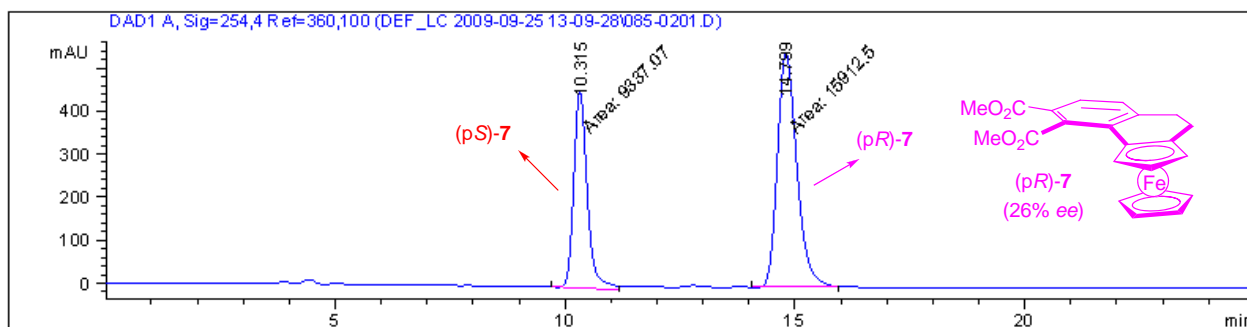
Totals : 1782.64184 111.43897



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

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1	10.561	MM	0.2383	3435.99194	240.27887	97.3762
2	11.725	MM	0.2549	92.58223	6.05382	2.6238

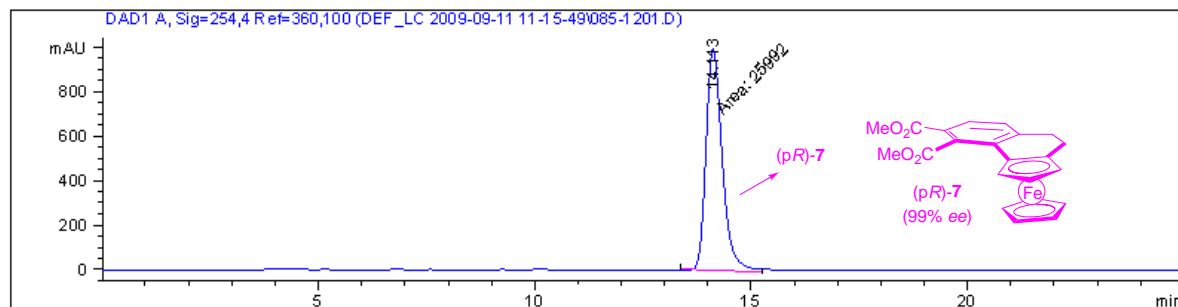
Totals : 3528.57417 246.33269



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.315	MM	0.3401	9337.07129	457.60422	36.9791
2	14.799	MM	0.4884	1.59125e4	542.99731	63.0209

Totals : 2.52496e4 1000.60153

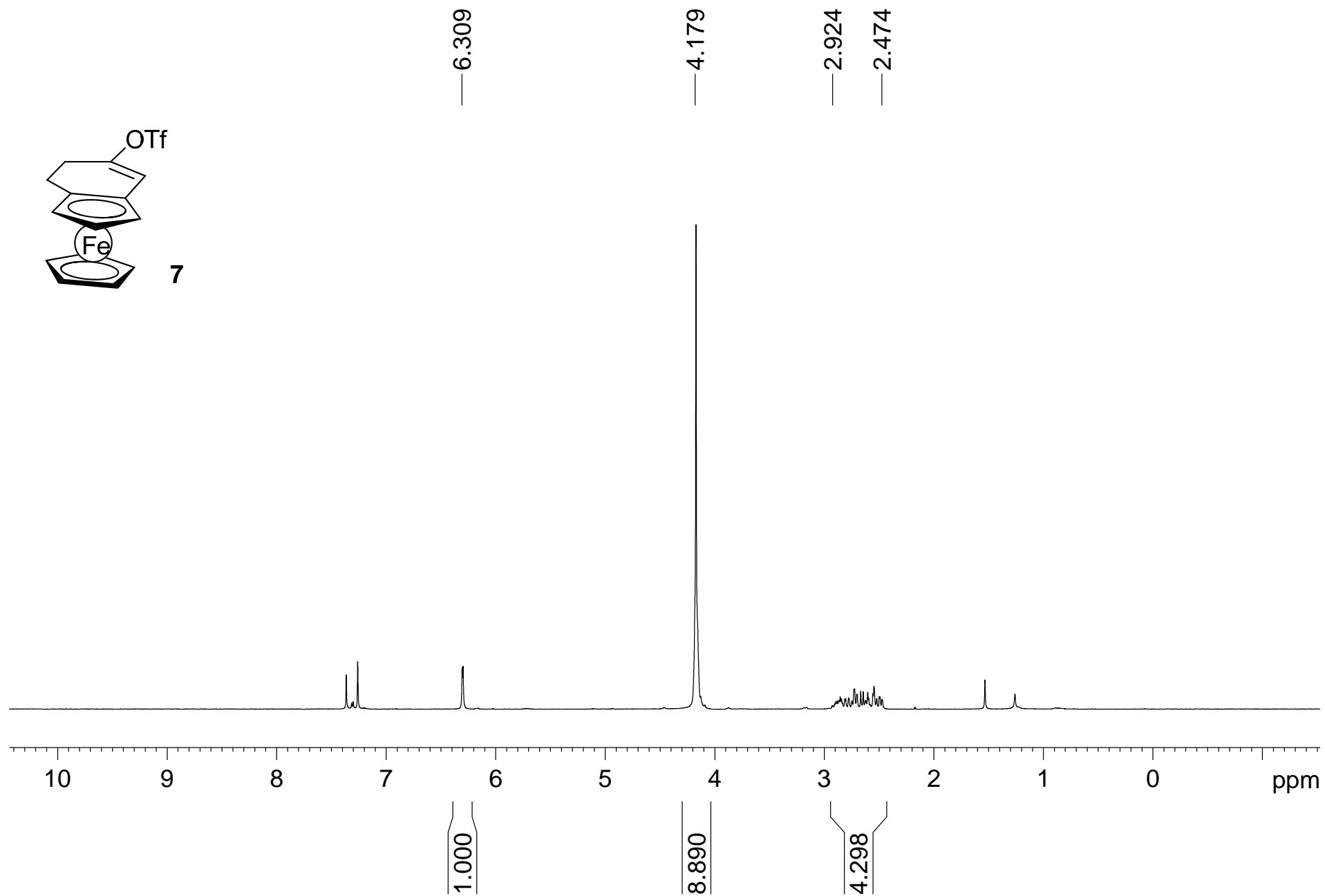


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

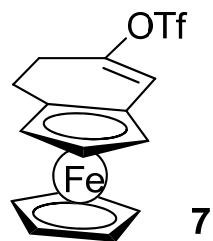
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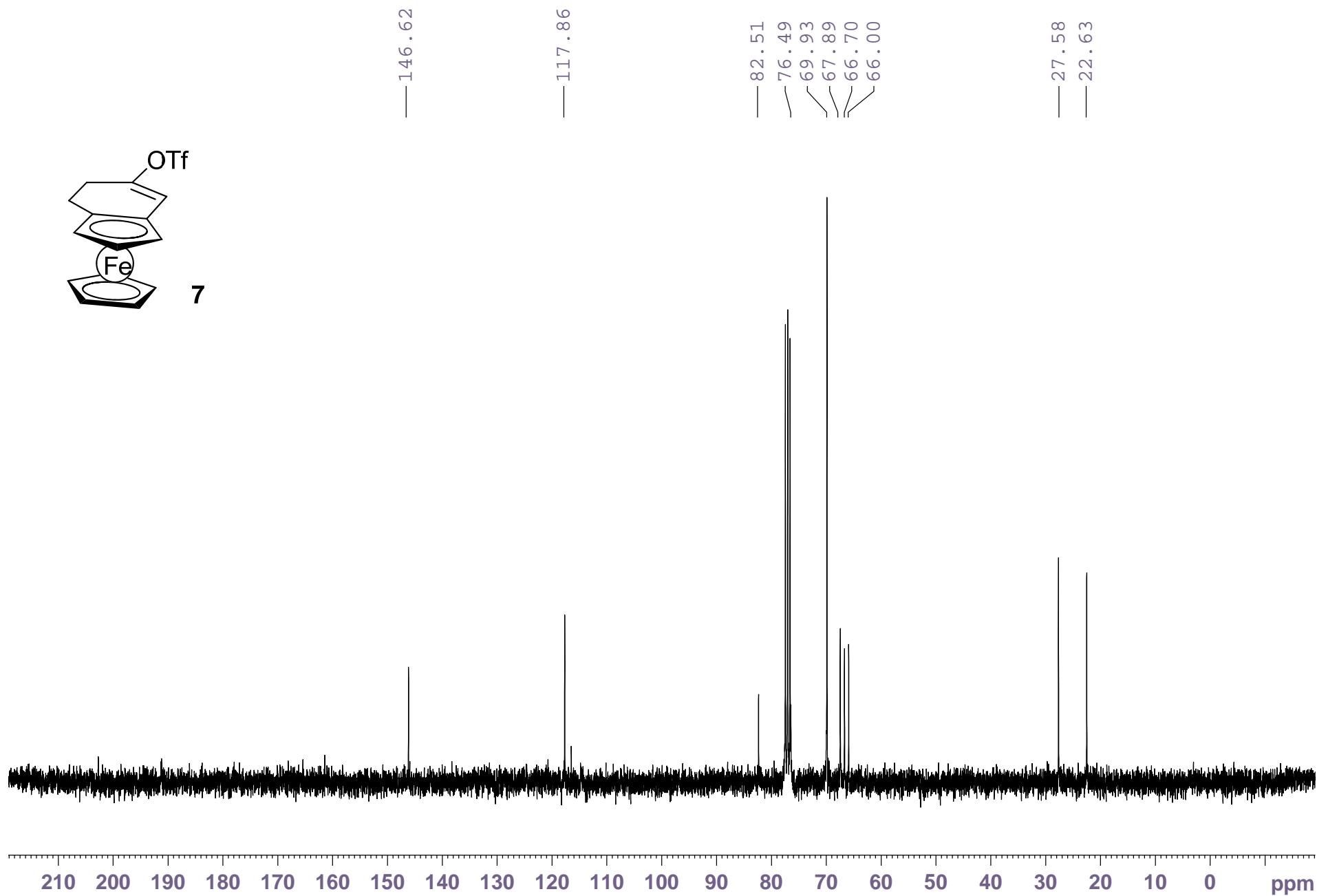
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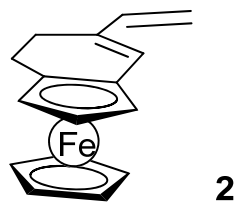
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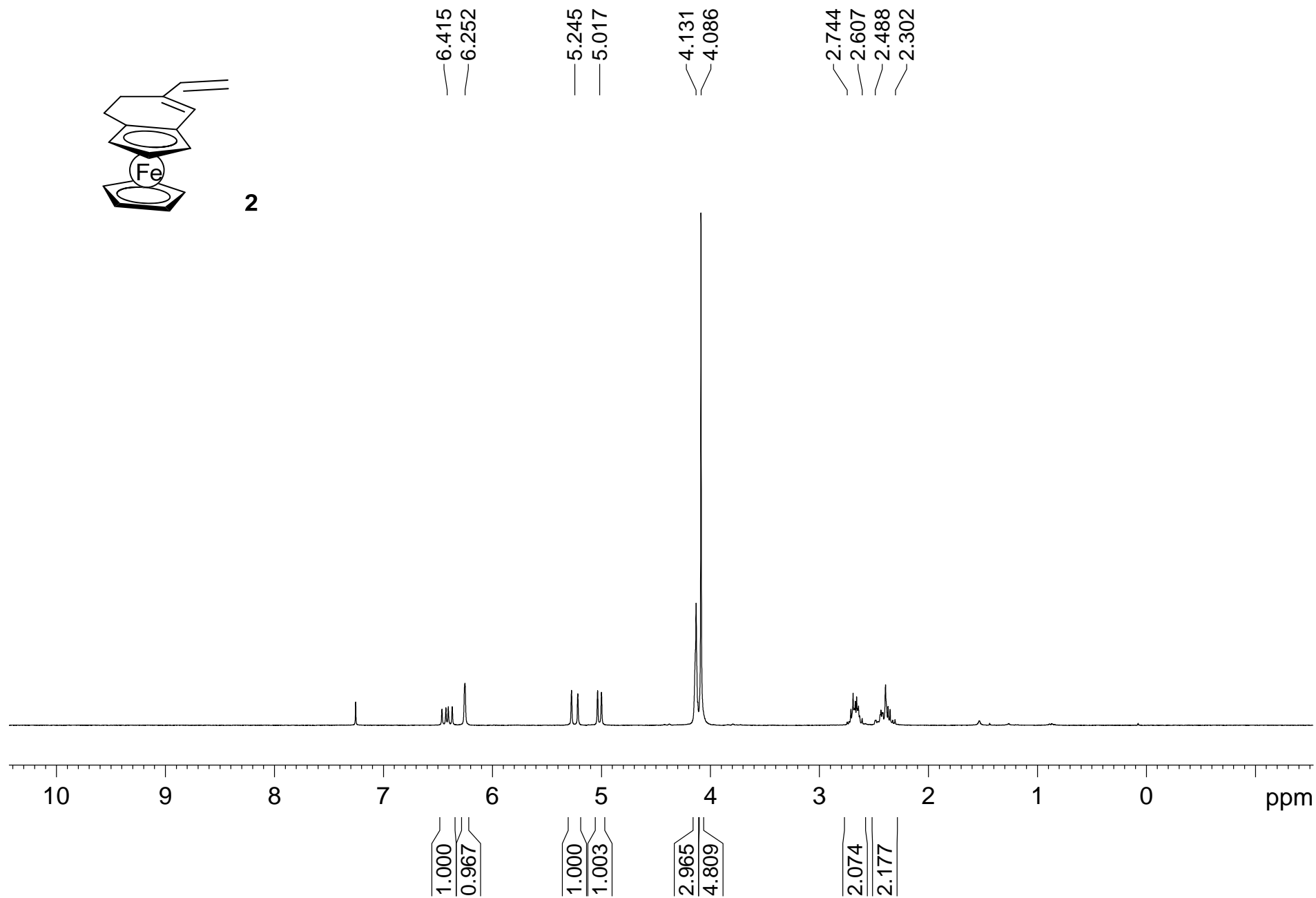
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S-11



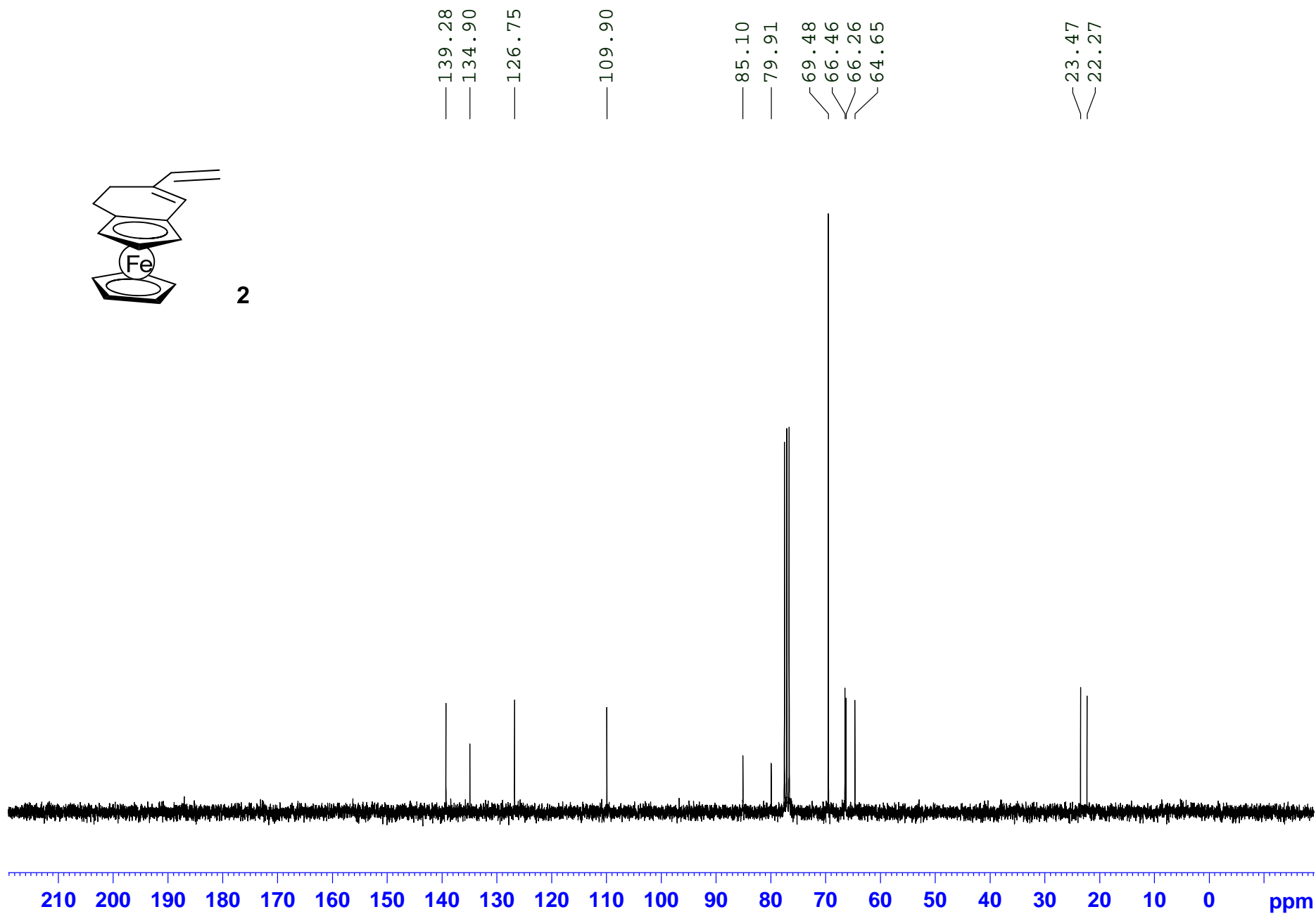
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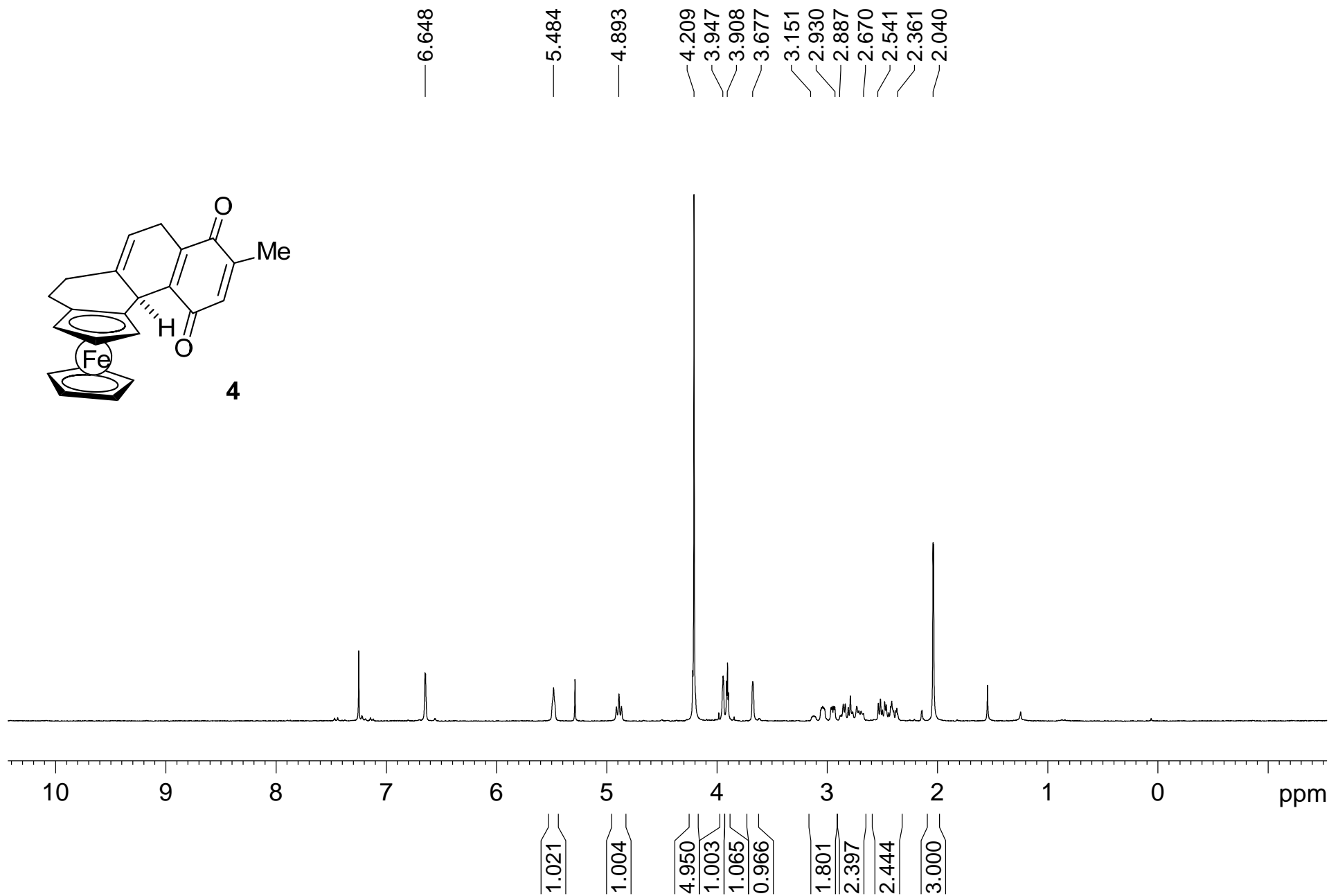
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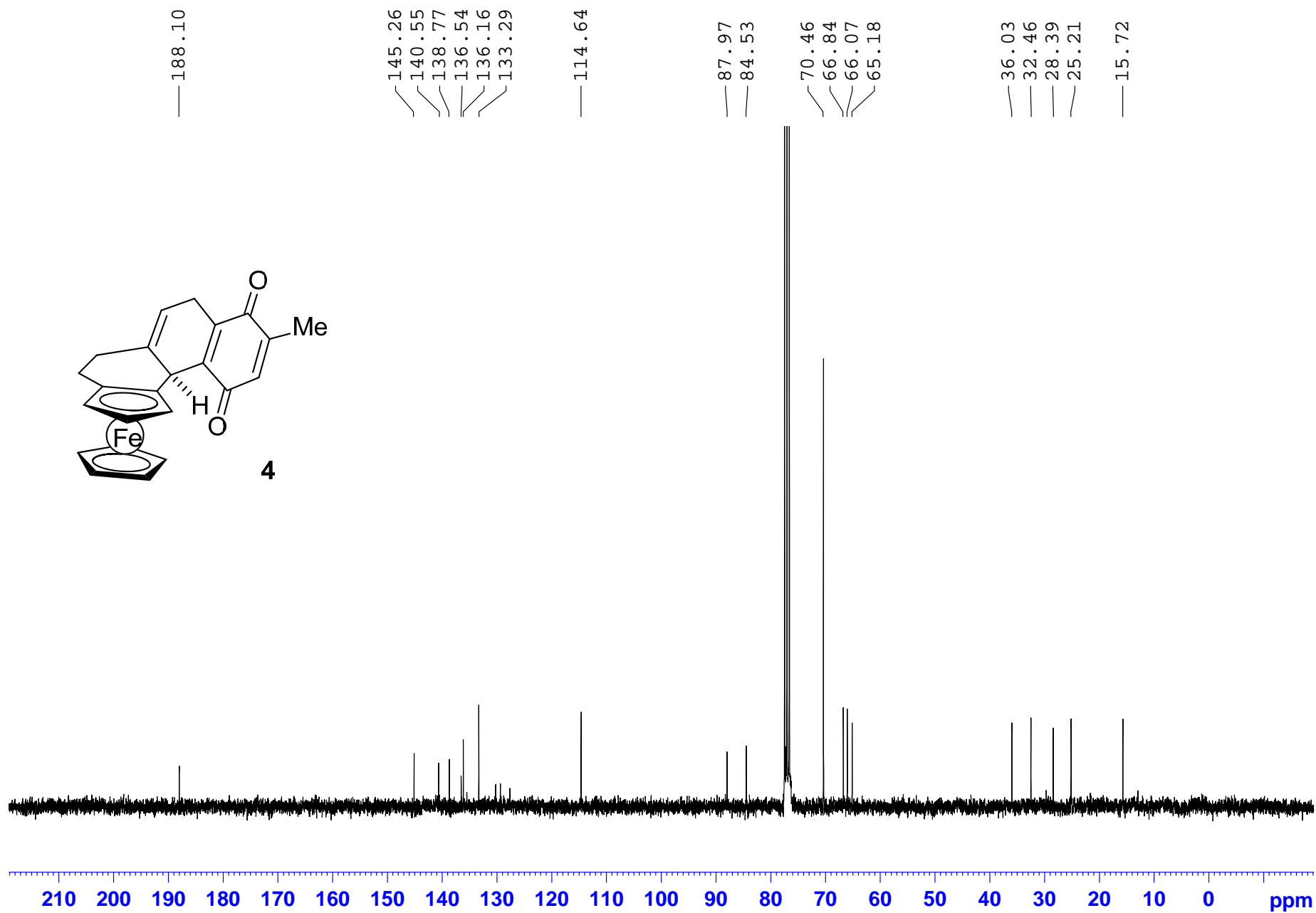
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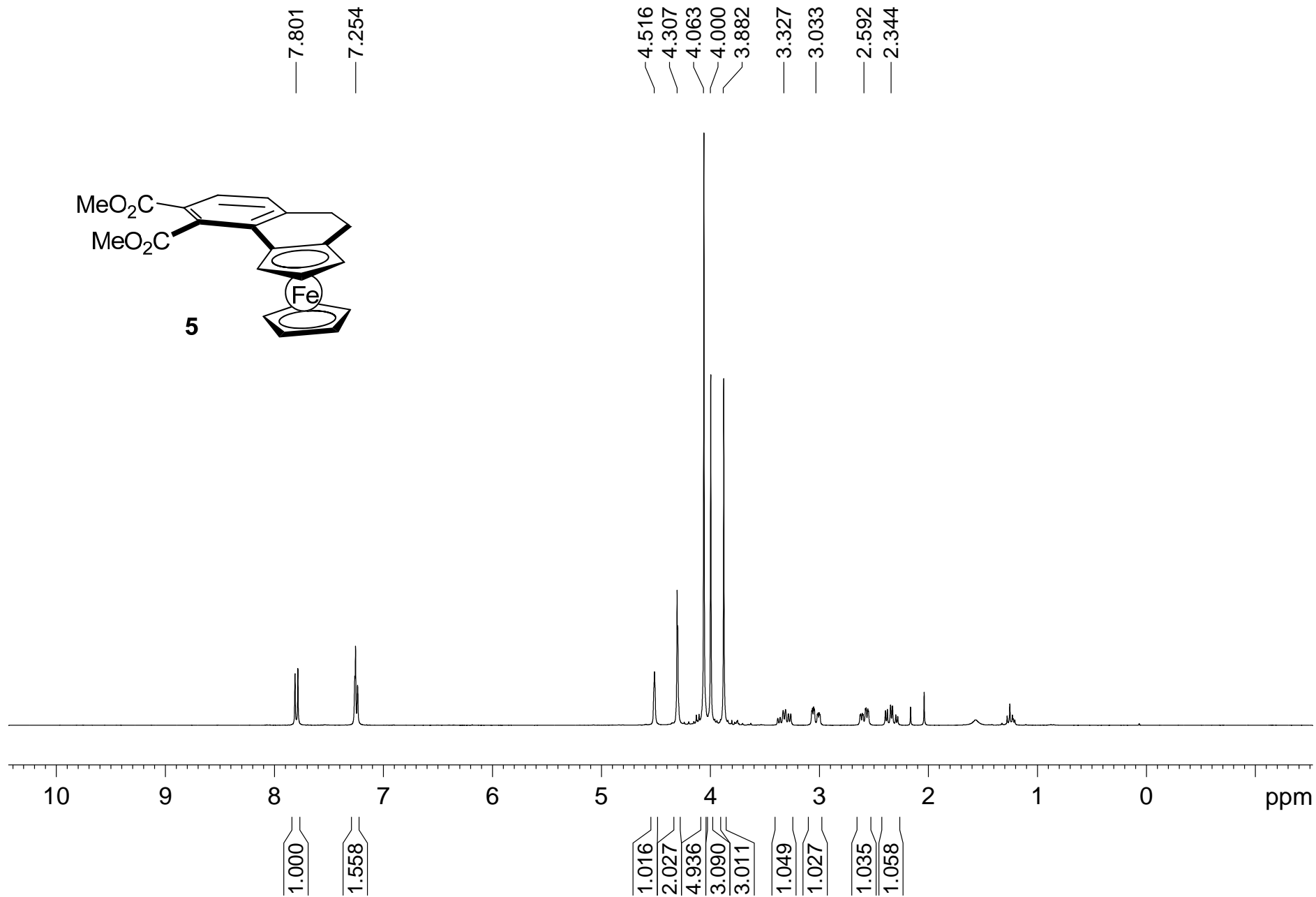
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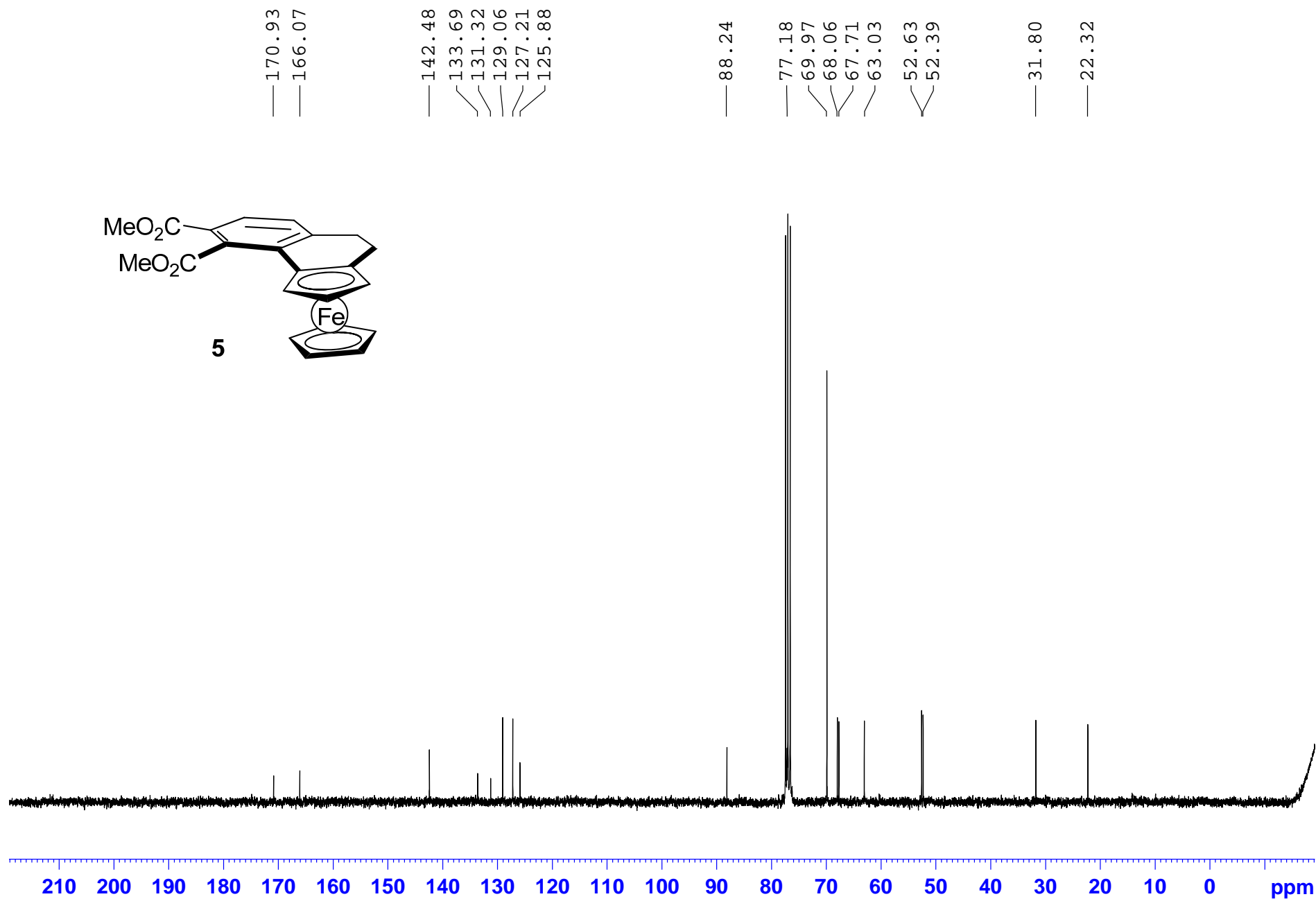
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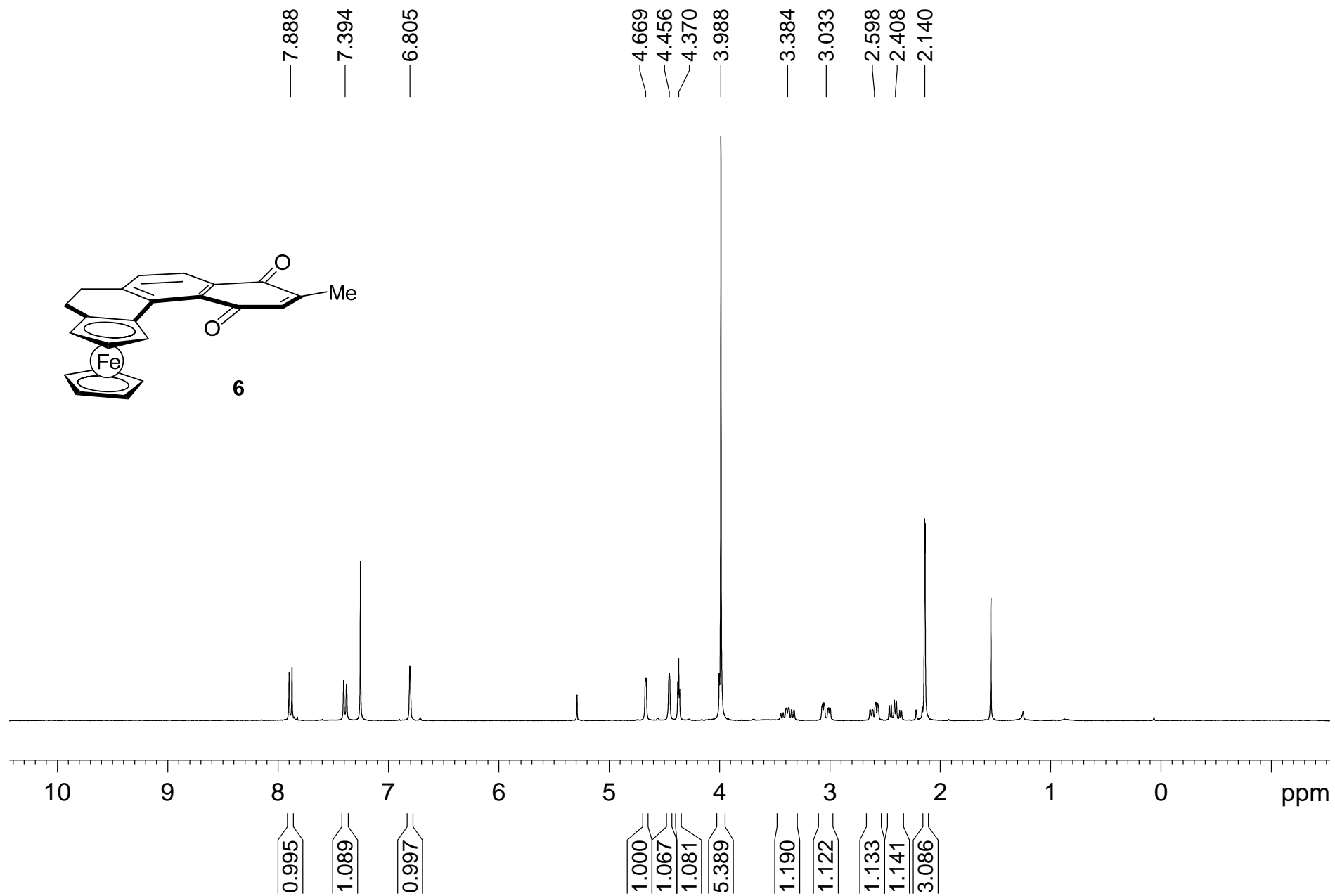
S-15



S-16



S-17



S-18

