An Enantioselective Synthesis of Optically Pure Azaferrocenyl Anions – First General and Practical Approach to Chiral Azaferrocenes

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Supporting Information

I. General Information

All reactions were carried out under an atmosphere of nitrogen in flame- or oven-dried glassware with magnetic stirring. All solvents were distilled prior to use. THF was distilled from sodium/benzophenone under nitrogen. *t*-BuLi (1.7M solution in pentane), *n*-BuLi (1.6M solution in hexane), *n*-Bu_3SnCl, Me_3SiCl, Ph_2PCl, iodine and paraformaldehyde were purchased from Aldrich and used without further purification. Compound **1** and **2** were prepared according to litterature.[12] Purification of reaction products was carried out by flash chromatography using Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh). Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} plates. Azaferrocenes could be seen directly as yellow-brown spots. ^{1}H-NMR (300MHz) and ^{13}C-NMR (75MHz) spectra were recorded on a Varian Gemini 300 (300 MHz) NMR spectrometer at ambient temperature. Chemical shifts are reported in ppm using undeuterated solvent residues as internal standard (benzene-d_6 ^{13}C at 128.06 ppm and ^{1}H at 7.16 ppm). Multiplicity (br = broad, s = singlet, d = doublet, t=triplet, dd=doublet of doublets, m = multiplet), integration and coupling constants are reported. Electron Impact (EI) Mass Spectra were recorded on a VG Trio-2 single quadropole instrument. Analytical high performance liquid chromatography (HPLC) was performed on a Varian 9012 HPLC with a Varian 9065 Polychrom detector using a 0.46cm x 25cm Daicel Chiralpak AD, Chiralcel OD-H or Chiralcel OJ column. Optical rotation was measured on a Perkin Elmer 241 Polarimeter at ambient temperature.

[1] Ruble, J. C.; Fu, G. C. *J. Org. Chem.*, **1996**, 61, 7230.
[2] Solladié, G. *Synthesis* **1981**, 185.

II. Synthesis of Azaferrocene Derivatives

(S_S,S_P)-2-*p*-Tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocene (S_S,S_P)-3 and **(S_S,R_P)-2-*p*-tolylsulfinyl 1',2',3',4',5'-Pentamethyl azaferrocene (S_S,R_P)-3:**

1',2',3',4',5'-Pentamethyl azaferrocene **1** (514 mg, 2.00 mmol) was dissolved in dry THF (4 mL) in an oven-dried schlenk tube and cooled to 0 ^oC. 1.1 eq. of *n*-BuLi (2.20 mmol, 1.38 mL, 1.6M) was added dropwise via syringe and the mixture stirred for 30 min. after which time it had become a deep red suspension of the 2-lithio salt. The mixture was cooled to –78 ^oC and 1.2 eq. of (-)-(*1R,2S,5R)*-menthyl (*S*)-*p*-toluene sulfinate **2** (711 mg, 2.4 mmol) was added in one portion to the deep red solution. After 2 min the cooling bath was removed and stirring was continued until the reaction had reached rt (15-20 min) and the solution had become homogeneous. The major part of the solvent was evaporated *in vacuo* and the residue then immediately worked up on a standard flash column (25% CH_2Cl_2,, 25% Et_2O, 50% pentane >> 50% CH_2Cl_2, 50% Et_2O). The yellow-brown (S_S,S_P)-**3** isomer is contained in the first fractions using the low polarity solvent mixture. After elution of the first diastereoisomer the solvent mixture is changed to the more polar mixture and the second product (S_S,R_P)-**3** elutes (second yellow-brown band on the column). Occasionally a third weak yellow band of **1** elutes between the two diastereoisomers. The solvent is evaporated immediately after column chromatography since some minor precipitation occurs in the fractions containing (S_S,R_P)-**3** on prolonged standing. The two are products are obtained as yellow-brown solids in a total yield of 62%: (S_S,S_P)-**3** 226 mg (0.57 mmol, 29%) with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in Hexane, 0.5 mL/min; t_r (major) = 12.1, t_r (minor) = 10.9 (according to racemic sample, the enantiomer was not observed), (S_S,R_P)-**3** 263 mg (0.67 mmol, 33%) with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrO in Hexane, 0.5 mL/min; t_r (minor) = 23.0 (according to racemic sample, the enantiomer was not observed), t_r (major) = 26.9. Crystals suitable for X-ray analysis were obtained from a Et_2O-pentane solution stored at –15 ^oC.

(S_S,S_P)-**3**: ^{1}H-NMR (300 MHz, benzene-d_6) δ 7.78 (d, 2H, J=8.01 Hz), 6.77 (d, 2H, J=7.76 Hz), 4.78 (s, 1H), 4.73 (s, 1H), 3.80 (s, 1H), 1.90 (s, 15H), 1.83 (s, 3H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 144.94, 140.32, 129.73, 124.29, 113.52, 94.37, 82.74, 76.29, 69.06, 21.02, 10.94. MS (EI): *m/z* (%) 395 (M+, 41), 379 (53), 314 (32), 189 (57), 133 (57), 119 (100), 91 (62). $[\alpha]^{20}_D$ = +315 ^{o} (benzene, c = 0.24).

(S_S,R_P)-**3**: ^{1}H-NMR (300 MHz, benzene-d_6) δ 7.67 (d, 2H, J=7.83 Hz), 6.77 (d, 2H, J=7.86 Hz), 4.81 (s, 1H), 4.10 (s, 1H), 3.77 (s, 1H), 1.90 (s, 15H), 1.85 (s, 3H). ^{13}C-NMR (75 MHz, benzene-d_6)

δ 144.28, 140.29, 129.63, 125.01, 112.69, 94.67, 83.17, 76.27, 73.59, 21.07, 11.12. MS (EI): *m/z* (%) 395 (16), 379 (79), 314 (14), 189 (60), 133 (48), 119 (100), 91 (59). $[\alpha]^{20}_{D}$ = +625 ^{o} (benzene, c = 0.13).

In a similar manner the racemates of the two diastereoisomers were prepared using a 50:50 mixture of (+)- and (-)-**2**.

General Procedure for the Synthesis of Racemic Azaferrocene Derivatives:

1',2',3',4',5'-Pentamethyl azaferrocene **1** (50 mg, 0.194 mmol) was dissolved in dry THF (1 mL) in an oven-dried Schlenk tube and cooled to 0 ^{o}C. *n*-BuLi (0.15 mL 1.6 M in hexane, 0.23 mmol, 1.2 eq.) was added dropwise via syringe and the solution stirred for 30 min. after which time the electrophile was added (1.2 eq.) either neat (*n*-Bu_3SnCl, $ClPPh_2$, TMSCl) or as a solution/suspension in dry THF (0.5 mL) (I_2, $(HCHO)_n$). The reaction mixture was stirred for a further 30 min. at 0 ^{o}C after which time the product was worked up by flash column chromatography (20-50% Et_2O/pentane for **4a-d** and $Et_2O/CHCl_3$/MeOH 70/20/10 for **4e**).

2-Iodo-1',2',3',4',5'-pentamethylazaferrocene (4a):

Yield: 32.3 mg (0.084mmol, 43%). ^{1}H-NMR (300 MHz, benzene-d_6) δ 4.69 (s, 1H), 3.96 (s, 1H), 3.60 (s, 1H), 1.70 (s, 15H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 93.43, 82.09, 80.28, 75.94, 65.77, 10.38. MS (EI): *m/z* (%) 383 (M+, 100), 255 (13), 134 (78), 119 (91).

2-(Tri-*n*-butylstannyl)-1',2',3',4',5'-pentamethylazaferrocene (4b):

Yield: 62.8 mg (0.115 mmol, 59%). ^{1}H-NMR (300 MHz, benzene-d_6) δ 5.19 (s, 1H), 4.04 (dd, 1H, J=0.96 Hz, 2.21 Hz), 3.93 (d, 1H, J=2.18 Hz), 1.86 (s, 15H), 1.74 (m, 6H), 1.45 (m, 6H), 1.30 (m, 6H), 0.97 (t, 9H, J=7.37Hz). ^{13}C-NMR (75 MHz, benzene-d_6) δ 99.09, 96.83, 80.92, 80.30, 76.13, 29.73, 27.88, 14.02, 11.61, 10.85. MS (EI): *m/z* (%) 547 (M+, 41), 545 (34), 543 (20), 490 (37), 488 (28), 486 (15), 376 (100), 374 (82), 372 (41), 257 (63), 255 (33), 253 (26), 186 (39), 184 (25), 182 (15), 133 (54), 119 (28).

2-(Diphenylphosphinyl)-1',2',3',4',5'-pentamethylazaferrocene (4c):

Yield: 35 mg (0.080 mmol, 41%). ^{1}H-NMR (300MHz, benzene-d_6) δ 8.00 (m, 2H), 7.70 (m, 2H), 7.18 (m, 6H), 5.25 (s, 1H), 4.14 (s, 1H), 4.11 (s, 1H), 1.84 (s, 15H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 140.52, 140.35, 139.47, 139.37, 134.97, 134.71, 134.61, 134.34, 128.76, 128.68, 128.50,

128.21 (C_{para}-hidden in solvent signals), 96.38, 96.32, 81.36, 78.85, 78.62, 76.86, 11.15. MS (EI): *m/z* (%) 441 (M+, 100), 307 (24), 256 (26), 229 (20), 173 (25), 133 (37).

2-(Trimethylsilyl)-1',2',3',4',5'-pentamethylazaferrocene (4d):
Yield: 38.4 mg (0.117 mmol, 60%). ^{1}H-NMR (300 MHz, benzene-d_6) δ 5.14 (s, 1H), 4.00 (s, 1H), 3.91 (s, 1H), 1.80 (s, 15H), 0.41 (s, 9H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 97.75, 97.45, 78.77, 77.13, 11.54, -0.25. MS (EI): *m/z* (%) 329 (M+, 100), 190 (66), 188 (53), 174 (30), 133 (25).

2-(Hydroxymethyl)-1',2',3',4',5'-pentamethylazaferrocene (4e):
Yield: 27.5 mg (0.096 mmol, 49%). ^{1}H-NMR (300 MHz, benzene-d_6) δ 5.03 (br s, 1H), 4.80 (d, 1H, J=12.35 Hz), 4.68 (s, 1H), 4.66 (d, 1H, J=12.14 Hz), 3.86 (d, 1H, 2.15 Hz), 3.72 (d, 1H, J=2.14 Hz), 1.77 (s, 15H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 105.67, 91.54, 81.05, 75.73, 72.68, 59.85, 10.92. MS (EI): *m/z* (%) 287 (M+, 24), 269 (68), 190 (100), 188 (48), 174 (20), 134 (26), 119 (26).

General Procedure for the Synthesis of Enantiopure Azaferrocene Derivatives:

(-)-(S_P)-2-Iodo-1',2',3',4',5'-pentamethylazaferrocene, (-)-(S_P)-4a:
(S_S,S_P)-**3** (36 mg, 0.091 mmol) was dissolved in dry THF in an oven-dried schlenk tube and cooled to –78 ^{o}C. 2.5 eq. of *t*-BuLi (0.23 mmol, 134 μL, 1.7M) was added dropwise via syringe and the brownish suspension stirred 5 min before adding iodine (57.8 mg, 0.23 mmol in 0.5 mL THF). The brown-black homogeneous solution was worked up by flash column chromatography (20%-50% Et_2O in pentane). Yield: (-)-(S_P)-**4a** 18.0 mg (0.047 mmol, 52%) with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in Hexane, 0.5 mL/min; t_r (minor) = 11.1, t_r (major) = 13.7).
^{1}H-NMR (300 MHz, benzene-d_6) δ 4.69 (s, 1H), 3.96 (s, 1H), 3.60 (s, 1H), 1.70 (s, 15H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 93.43, 82.09, 80.28, 75.94, 65.77, 10.38. MS (EI): *m/z* (%) 383 (M+, 100), 255 (13), 134 (78), 119 (91). $[\alpha]^{20}_D$ = -88 ^{o} (benzene, c = 0.35).

(+)-(R_P)-2-Iodo-1',2',3',4',5'-pentamethylazaferrocene, (+)-(R_P)-4a:
(S_S,R_P)-**3** (36 mg, 0.091 mmol) was used in the synthesis giving 23.6 mg (0.062 mmol, 68%) of (+)-(R_P)-**4a** with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in Hexane, 0.5 mL/min; t_r (major) = 10.8, t_r (minor) = 13.7). (+)-(R_P)-**4a**: $[\alpha]^{20}_D$ = +77 ^{o} (benzene, c = 0.12).

(+)-(S_P)-2-Hydroxymethyl-1',2',3',4',5'-pentamethylazaferrocene, (+)-(S_P)-4e:

(S_S,S_P)-**3** (30mg, 0.076 mmol) was used in the synthesis giving 12.6 mg (0.044 mmol, 58%) of (+)-(S_P)-**4e** with 98% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in Hexane, 0.5 mL/min; t_r (major) = 11.4, t_r (minor) = 20.1).

^{1}H-NMR (300 MHz, benzene-d_6) δ 5.03 (br s, 1H), 4.80 (d, 1H, J=12.35 Hz), 4.68 (s, 1H), 4.66 (d, 1H, J=12.14 Hz), 3.86 (d, 1H, 2.15 Hz), 3.72 (d, 1H, J=2.14 Hz), 1.77 (s, 15H). ^{13}C-NMR (75 MHz, benzene-d_6) δ 105.67, 91.54, 81.05, 75.73, 72.68, 59.85, 10.92. MS (EI): *m/z* (%) 287 (M+, 24), 269 (68), 190 (100), 188 (48), 174 (20), 134 (26), 119 (26). $[\alpha]^{20}_D$ = +50 ^{o} (benzene, c = 0.11).

X-Ray Crystallographic data for compounds (S_S,S_P)-3 and (S_S,R_P)-3:

Table 1. Crystallographic Data for Compounds (S_s, S_p)-**3** and (S_s, R_p)-**3**

	(S_s, S_p)-**3**	(S_s, R_p)-**3**
formula	$C_{21}H_{25}$ Fe N O S	$C_{21}H_{25}$Fe N O S
fw	395.33	395.33
temp *T*/K	120(2)	120(2)
cryst system	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
a/Å	7.2192(9)	8.351(2)
b/Å	35.183(4)	11.496(2)
c/Å	8.3476(11)	19.620(4)
∃/E	115.226(12)	
V/Å^3	1918.0(4)	1883.5(7)
Z	4	4
D_x/g cm^{-3}	1.369	1.394
$\mu_{(MoK\forall)}$/mm^{-1}	0.903	0.920
cryst colour	yellow-brown	yellow-brown
cryst size/mm	0.30 × 0.18 × 0.08	0.40 × 0.18 × 0.12
2-range/^{o}	1.16-29.69	2.05-29.54
meas. reflns	13484	13083
unique reflns	8895	4811
reflns with [I>2Φ(I)]	8406	4535
R(int)	0.0220	0.0213
transm factors	1.0000-0.8119	1.0000-0.8181
Flack param	0.006(11)	0.001(11)
refined param	451	226
$R1$[a] (obs.data)	0.0355	0.0241
$wR2$[b] (all data)	0.0792	0.0639
goodness-of-fit	1.069	1.033
max, min)κ/e Å^{-3}	!0.359 and 0.605	!0.262 and 0.293

[a]$R1$ = E**F_o*-*F_c**/E*F_o*.[b]wR2 = [Ew*F^2_o-F^2_c*^{2}/EwF_o^4]$^{1/2}$

Table 2. Fractional atomic coordinates and equivalent isotropic thermal paramters (in Å^2). for compound (S_s, S_p)-**3**

Atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	0.05141(5)	0.640727(10)	0.96252(4)	0.01408(8)
S(1)	0.37885(11)	0.60055(2)	1.34036(9)	0.02155(14)
O(1)	0.2314(3)	0.59533(6)	1.4208(3)	0.0295(5)
N(1)	0.3082(4)	0.61112(7)	0.9919(3)	0.0196(5)
C(1)	0.0823(4)	0.68829(7)	1.1139(3)	0.0167(5)
C(2)	0.2336(5)	0.69625(9)	1.3016(4)	0.0254(7)
C(3)	-0.1158(4)	0.67143(7)	1.0626(3)	0.0160(5)
C(4)	-0.2023(4)	0.65742(10)	1.1869(4)	0.0239(6)
C(5)	-0.2148(4)	0.67064(8)	0.8727(3)	0.0174(5)
C(6)	-0.4241(4)	0.65472(9)	0.7616(4)	0.0233(6)
C(7)	-0.0789(4)	0.68710(8)	0.8085(3)	0.0183(5)
C(8)	-0.1207(5)	0.69204(9)	0.6173(4)	0.0269(7)
C(9)	0.1043(4)	0.69803(8)	0.9579(4)	0.0185(5)
C(10)	0.2851(5)	0.71769(9)	0.9510(4)	0.0277(6)
C(11)	0.2292(4)	0.59850(8)	1.1086(3)	0.0186(5)
C(12)	0.0266(4)	0.58460(7)	1.0197(4)	0.0194(5)
C(13)	-0.0233(4)	0.58871(8)	0.8366(4)	0.0217(6)
C(14)	0.1511(4)	0.60459(8)	0.8249(4)	0.0196(5)
C(15	0.5113(4)	0.55646(8)	1.3634(4)	0.0210(5)
C(16)	0.4175(5)	0.52266(9)	1.3711(5)	0.0344(7)
C(17)	0.5247(5)	0.48860(10)	1.3937(5)	0.0370(8)
C(18)	0.7222(5)	0.48816(9)	1.4088(4)	0.0305(7)
C(19)	0.8344(6)	0.45094(11)	1.4336(5)	0.0444(9)
C(20)	0.8133(5)	0.52254(10)	1.4017(4)	0.0338(7)
C(21)	0.7096(5)	0.55686(9)	1.3796(4)	0.0274(6)
Fe(2)	0.78859(5)	0.844893(10)	0.70053(4)	0.01432(8)
S(2)	0.82978(12)	0.88631(2)	1.07449(9)	0.02208(14)
O(2)	1.0553(3)	0.89229(6)	1.1543(3)	0.0302(5)
N(2)	0.5582(4)	0.87451(7)	0.7263(3)	0.0200(5)
C(22)	0.9116(4)	0.79858(7)	0.8606(3)	0.0167(5)
C(23)	0.9411(5)	0.79205(9)	1.0477(4)	0.0235(6)
C(24)	1.0566(4)	0.81511(7)	0.8065(3)	0.0162(5)
C(25)	1.2619(4)	0.83068(9)	0.9281(4)	0.0221(6)
C(26)	0.9699(4)	0.81403(8)	0.6167(3)	0.0166(5)
C(27)	1.0701(5)	0.82829(10)	0.5025(4)	0.0256(6)
C(28)	0.7716(4)	0.79731(8)	0.5545(3)	0.0174(5)
C(29)	0.6289(5)	0.79067(10)	0.3631(4)	0.0280(7)
C(30)	0.7353(4)	0.78746(8)	0.7051(4)	0.0181(5)
C(31)	0.5506(5)	0.76804(9)	0.7051(4)	0.0254(6)
C(32)	0.7504(4)	0.88765(8)	0.8410(3)	0.0180(5)
C(33)	0.8667(4)	0.90113(8)	0.7522(4)	0.0197(5)
C(34)	0.7357(4)	0.89634(8)	0.5689(4)	0.0210(6)
C(35)	0.5517(4)	0.88027(8)	0.5596(4)	0.0212(6)
C(36)	0.7156(5)	0.93022(8)	1.0947(4)	0.0224(6)

C(37)	0.8120(6)	0.96448(9)	1.0974(5)	0.0355(8)
C(38)	0.7247(6)	0.99781(9)	1.1180(5)	0.0361(8)
C(39)	0.5424(5)	0.99772(9)	1.1369(4)	0.0287(6)
C(40)	0.4512(6)	1.03492(11)	1.1593(5)	0.0428(9)
C(41)	0.4501(5)	0.96322(10)	1.1342(4)	0.0321(7)
C(42)	0.5349(5)	0.92942(9)	1.1134(4)	0.0279(6)

[a] $U_{eq} = \frac{1}{3} \varphi_i \varphi_j U_{ij} a^*_i a^*_j \boldsymbol{a}_i \forall \boldsymbol{a}_j$

Table 2a. Fractional atomic coordinates and isotropic thermal parameters (in $Å^2$) for compound (S_s, S_p)-**3**

Atom	*x*	*y*	*z*	*U*
H(21)	0.2152(5)	0.67767(9)	1.3811(4)	0.030
H(22)	0.2108(5)	0.72192(9)	1.3352(4)	0.030
H(23)	0.3731(5)	0.69433(9)	1.3107(4)	0.030
H(41)	-0.2436(4)	0.67917(10)	1.2375(4)	0.029
H(42)	-0.0980(4)	0.64264(10)	1.2824(4)	0.029
H(43)	-0.3218(4)	0.64130(10)	1.1219(4)	0.029
H(61)	-0.5240(4)	0.67548(9)	0.7212(4)	0.028
H(62)	-0.4620(4)	0.63681(9)	0.8325(4)	0.028
H(63)	-0.4226(4)	0.64149(9)	0.6589(4)	0.028
H(81)	0.0050(5)	0.68721(9)	0.6028(4)	0.032
H(82)	-0.1674(5)	0.71808(9)	0.5798(4)	0.032
H(83)	-0.2270(5)	0.67407(9)	0.5445(4)	0.032
H(101)	0.2641(5)	0.74526(9)	0.9469(4)	0.033
H(102)	0.3002(5)	0.70954(9)	0.8449(4)	0.033
H(103)	0.4092(5)	0.71112(9)	1.0566(4)	0.033
H(12)	-0.0578(4)	0.57466(7)	1.0714(4)	0.023
H(13)	-0.1492(4)	0.58210(8)	0.7405(4)	0.026
H(14)	0.1595(4)	0.61008(8)	0.7168(4)	0.023
H(16)	0.2814(5)	0.52265(9)	1.3611(5)	0.041
H(17)	0.4604(5)	0.46535(10)	1.3988(5)	0.044
H(191)	0.9760(6)	0.45579(11)	1.4526(5)	0.053
H(192)	0.7661(6)	0.43518(11)	1.3277(5)	0.053
H(193)	0.8341(6)	0.43763(11)	1.5366(5)	0.053
H(20)	0.9496(5)	0.52260(10)	1.4122(4)	0.041
H(21)	0.7741(5)	0.58015(9)	1.3757(4)	0.033
H(231)	0.9942(5)	0.76633(9)	1.0848(4)	0.028
H(232)	0.8096(5)	0.79488(9)	1.0545(4)	0.028
H(233)	1.0388(5)	0.81067(9)	1.1259(4)	0.028
H(251)	1.3098(4)	0.84818(9)	0.8624(4)	0.027
H(252)	1.3598(4)	0.80973(9)	0.9755(4)	0.027
H(253)	1.2505(4)	0.84430(9)	1.0259(4)	0.027
H(271)	1.1236(5)	0.80670(10)	0.4610(4)	0.031
H(272)	1.1828(5)	0.84546(10)	0.5718(4)	0.031
H(273)	0.9690(5)	0.84199(10)	0.4004(4)	0.031
H(291)	0.4871(5)	0.79069(10)	0.3492(4)	0.034
H(292)	0.6598(5)	0.76606(10)	0.3251(4)	0.034
H(293)	0.6468(5)	0.81092(10)	0.2904(4)	0.034
H(311)	0.5136(5)	0.77996(9)	0.7936(4)	0.030
H(312)	0.5814(5)	0.74110(9)	0.7342(4)	0.030
H(313)	0.4361(5)	0.77035(9)	0.5877(4)	0.030
H(33)	1.0018(4)	0.91113(8)	0.8034(4)	0.024
H(34)	0.7659(4)	0.90268(8)	0.4720(4)	0.025
H(35)	0.4373(4)	0.87416(8)	0.4520(4)	0.025
H(37)	0.9370(6)	0.96492(9)	1.0853(5)	0.043

H(38)	0.7902(6)	1.02131(9)	1.1193(5)	0.043
H(401)	0.4050(6)	1.04962(11)	1.0493(5)	0.051
H(402)	0.5550(6)	1.04944(11)	1.2562(5)	0.051
H(403)	0.3345(6)	1.02981(11)	1.1868(5)	0.051
H(41)	0.3254(5)	0.96270(10)	1.1469(4)	0.039
H(42)	0.4695(5)	0.90592(9)	1.1119(4)	0.033

Table 2b. Anisotropic thermal parameters for compound (S_s, S_p)-**3**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0151(2)	0.0132(2)	0.0134(2)	-0.00047(13)	0.00563(13)	-0.00077(14)
S(1)	0.0247(3)	0.0168(3)	0.0174(3)	-0.0007(2)	0.0036(3)	0.0022(3)
O(1)	0.0379(12)	0.0306(12)	0.0220(10)	0.0037(9)	0.0146(9)	0.0111(10)
N(1)	0.0178(11)	0.0176(11)	0.0244(11)	0.0012(9)	0.0099(9)	0.0029(8)
C(1)	0.0174(12)	0.0140(13)	0.0154(12)	-0.0027(9)	0.0039(10)	0.0009(10)
C(2)	0.0234(15)	0.021(2)	0.0210(14)	-0.0057(11)	-0.0012(12)	-0.0004(11)
C(3)	0.0172(12)	0.0162(13)	0.0137(11)	-0.0011(9)	0.0059(10)	0.0007(10)
C(4)	0.0232(14)	0.033(2)	0.0179(13)	0.0014(11)	0.0110(11)	0.0010(12)
C(5)	0.0177(13)	0.0197(13)	0.0131(11)	-0.0023(10)	0.0049(10)	0.0018(10)
C(6)	0.0191(13)	0.027(2)	0.0189(13)	-0.0031(11)	0.0038(11)	-0.0008(11)
C(7)	0.0233(14)	0.0157(13)	0.0156(12)	0.0029(10)	0.0080(10)	0.0053(10)
C(8)	0.037(2)	0.030(2)	0.0180(14)	0.0072(12)	0.0160(13)	0.0094(13)
C(9)	0.0206(13)	0.0123(13)	0.0236(13)	-0.0001(10)	0.0103(11)	0.0003(10)
C(10)	0.027(2)	0.0181(15)	0.044(2)	0.0015(12)	0.0208(14)	-0.0020(12)
C(11)	0.0213(13)	0.0152(13)	0.0176(12)	0.0012(10)	0.0065(10)	0.0021(10)
C(12)	0.0236(14)	0.0152(13)	0.0191(13)	-0.0007(10)	0.0089(11)	-0.0034(10)
C(13)	0.0253(14)	0.0166(14)	0.0200(13)	-0.0040(10)	0.0064(11)	-0.0042(11)
C(14)	0.0240(13)	0.0171(13)	0.0199(12)	-0.0019(10)	0.0116(10)	0.0007(10)
C(15)	0.0223(13)	0.0185(14)	0.0179(12)	0.0005(10)	0.0045(10)	0.0026(10)
C(16)	0.0228(15)	0.023(2)	0.055(2)	0.0007(15)	0.0142(14)	-0.0005(12)
C(17)	0.032(2)	0.022(2)	0.053(2)	0.0030(14)	0.014(2)	0.0018(13)
C(18)	0.034(2)	0.030(2)	0.0256(15)	0.0006(12)	0.0100(13)	0.0086(13)
C(19)	0.050(2)	0.034(2)	0.049(2)	0.001(2)	0.021(2)	0.019(2)
C(20)	0.026(2)	0.042(2)	0.037(2)	0.0055(15)	0.0173(14)	0.0074(14)
C(21)	0.0265(15)	0.025(2)	0.032(2)	0.0026(12)	0.0132(13)	-0.0002(12)
Fe(2)	0.0163(2)	0.0142(2)	0.0129(2)	0.00099(14)	0.00661(13)	-0.00038(14)
S(2)	0.0349(4)	0.0155(3)	0.0178(3)	0.0008(2)	0.0132(3)	0.0040(3)
O(2)	0.0336(12)	0.0293(12)	0.0209(10)	-0.0030(8)	0.0051(9)	0.0108(9)
N(2)	0.0215(12)	0.0160(12)	0.0254(12)	0.0020(9)	0.0128(10)	0.0020(9)
C(22)	0.0225(13)	0.0140(13)	0.0155(12)	0.0018(9)	0.0100(10)	0.0020(10)
C(23)	0.038(2)	0.0181(15)	0.0206(14)	0.0015(11)	0.0185(13)	0.0060(12)
C(24)	0.0188(13)	0.0160(13)	0.0140(11)	0.0018(9)	0.0071(10)	0.0019(10)
C(25)	0.0185(13)	0.0273(15)	0.0159(12)	-0.0001(10)	0.0028(10)	-0.0013(11)
C(26)	0.0192(13)	0.0197(13)	0.0120(11)	0.0007(9)	0.0076(10)	0.0017(10)
C(27)	0.0254(15)	0.036(2)	0.0185(13)	0.0037(12)	0.0125(11)	0.0008(12)
C(28)	0.0210(13)	0.0130(13)	0.0177(12)	-0.0025(10)	0.0076(10)	0.0014(10)
C(29)	0.027(2)	0.032(2)	0.0187(14)	-0.0029(12)	0.0035(12)	-0.0016(13)
C(30)	0.0208(13)	0.0139(13)	0.0216(13)	-0.0001(10)	0.0110(11)	0.0008(10)
C(31)	0.0242(15)	0.0197(15)	0.037(2)	-0.0010(12)	0.0173(13)	-0.0034(11)
C(32)	0.0230(13)	0.0150(12)	0.0171(11)	0.0009(10)	0.0095(10)	0.0021(10)
C(33)	0.0227(14)	0.0133(13)	0.0225(13)	0.0010(10)	0.0091(11)	-0.0030(10)
C(34)	0.0253(14)	0.0185(14)	0.0199(13)	0.0054(10)	0.0105(11)	0.0018(11)
C(35)	0.0219(14)	0.0193(14)	0.0189(12)	0.0002(10)	0.0054(11)	0.0004(10)
C(36)	0.032(2)	0.0185(14)	0.0182(13)	0.0009(10)	0.0119(11)	0.0047(11)
C(37)	0.042(2)	0.019(2)	0.060(2)	-0.0025(15)	0.035(2)	-0.0020(14)

C(38)	0.046(2)	0.0158(15)	0.057(2)	-0.0001(14)	0.032(2)	0.0010(14)
C(39)	0.035(2)	0.025(2)	0.0257(14)	0.0015(12)	0.0119(13)	0.0105(13)
C(40)	0.051(2)	0.033(2)	0.048(2)	-0.001(2)	0.025(2)	0.016(2)
C(41)	0.0238(15)	0.035(2)	0.038(2)	-0.0034(14)	0.0141(13)	0.0040(13)
C(42)	0.028(2)	0.027(2)	0.0289(15)	-0.0035(12)	0.0120(13)	-0.0052(12)

Table 3. Bond lengths (in Å) and bond angles in (E) for compound (S_s, S_p)-**3**

Fe(1)-C(11)	2.002(3)
Fe(1)-C(5)	2.033(3)
Fe(1)-C(14)	2.039(3)
Fe(1)-C(7)	2.042(3)
Fe(1)-C(3)	2.044(3)
Fe(1)-N(1)	2.048(2)
Fe(1)-C(1)	2.051(3)
Fe(1)-C(9)	2.055(3)
Fe(1)-C(12)	2.057(3)
Fe(1)-C(13)	2.064(3)
S(1)-O(1)	1.493(2)
S(1)-C(11)	1.770(3)
S(1)-C(15)	1.789(3)
N(1)-C(14)	1.391(3)
N(1)-C(11)	1.395(3)
C(1)-C(9)	1.420(4)
C(1)-C(3)	1.435(4)
C(1)-C(2)	1.506(4)
C(3)-C(5)	1.435(3)
C(3)-C(4)	1.505(4)
C(5)-C(7)	1.426(4)
C(5)-C(6)	1.504(4)
C(7)-C(9)	1.430(4)
C(7)-C(8)	1.503(4)
C(9)-C(10)	1.500(4)
C(11)-C(12)	1.416(4)
C(12)-C(13)	1.420(4)
C(13)-C(14)	1.418(4)
C(15)-C(21)	1.379(4)
C(15)-C(16)	1.383(4)
C(16)-C(17)	1.395(5)
C(17)-C(18)	1.377(5)
C(18)-C(20)	1.390(5)
C(18)-C(19)	1.507(4)
C(20)-C(21)	1.391(4)
Fe(2)-C(32)	1.998(3)
Fe(2)-C(35)	2.036(3)
Fe(2)-C(26)	2.040(3)
Fe(2)-C(24)	2.041(3)
Fe(2)-C(28)	2.044(3)
Fe(2)-N(2)	2.050(2)
Fe(2)-C(33)	2.052(3)
Fe(2)-C(22)	2.054(3)
Fe(2)-C(30)	2.060(3)
Fe(2)-C(34)	2.067(3)
S(2)-O(2)	1.488(2)
S(2)-C(32)	1.782(3)
S(2)-C(36)	1.793(3)

N(2)-C(35)	1.386(4)
N(2)-C(32)	1.387(4)
C(22)-C(24)	1.428(4)
C(22)-C(30)	1.431(4)
C(22)-C(23)	1.502(4)
C(24)-C(26)	1.435(3)
C(24)-C(25)	1.498(4)
C(26)-C(28)	1.425(4)
C(26)-C(27)	1.508(4)
C(28)-C(30)	1.431(4)
C(28)-C(29)	1.505(4)
C(30)-C(31)	1.499(4)
C(32)-C(33)	1.418(4)
C(33)-C(34)	1.425(4)
C(34)-C(35)	1.415(4)
C(36)-C(42)	1.378(4)
C(36)-C(37)	1.387(4)
C(37)-C(38)	1.376(4)
C(38)-C(39)	1.390(4)
C(39)-C(41)	1.380(5)
C(39)-C(40)	1.512(4)
C(41)-C(42)	1.382(4)
C(11)-Fe(1)-C(5)	150.30(12)
C(11)-Fe(1)-C(14)	65.91(11)
C(5)-Fe(1)-C(14)	128.31(11)
C(11)-Fe(1)-C(7)	168.60(12)
C(5)-Fe(1)-C(7)	40.96(11)
C(14)-Fe(1)-C(7)	108.78(11)
C(11)-Fe(1)-C(3)	118.70(11)
C(5)-Fe(1)-C(3)	41.19(10)
C(14)-Fe(1)-C(3)	166.16(11)
C(7)-Fe(1)-C(3)	68.98(11)
C(11)-Fe(1)-N(1)	40.26(10)
C(5)-Fe(1)-N(1)	166.50(10)
C(14)-Fe(1)-N(1)	39.79(10)
C(7)-Fe(1)-N(1)	129.23(11)
C(3)-Fe(1)-N(1)	151.84(10)
C(11)-Fe(1)-C(1)	110.91(11)
C(5)-Fe(1)-C(1)	69.05(10)
C(14)-Fe(1)-C(1)	152.12(11)
C(7)-Fe(1)-C(1)	68.65(11)
C(3)-Fe(1)-C(1)	41.01(10)
N(1)-Fe(1)-C(1)	119.08(10)
C(11)-Fe(1)-C(9)	131.56(11)
C(5)-Fe(1)-C(9)	68.85(11)
C(14)-Fe(1)-C(9)	119.21(11)
C(7)-Fe(1)-C(9)	40.86(11)
C(3)-Fe(1)-C(9)	68.66(11)
N(1)-Fe(1)-C(9)	109.59(11)
C(1)-Fe(1)-C(9)	40.45(11)

C(11)-Fe(1)-C(12)	40.80(11)
C(5)-Fe(1)-C(12)	114.85(12)
C(14)-Fe(1)-C(12)	67.59(11)
C(7)-Fe(1)-C(12)	148.30(12)
C(3)-Fe(1)-C(12)	106.70(11)
N(1)-Fe(1)-C(12)	69.39(10)
C(1)-Fe(1)-C(12)	129.60(11)
C(9)-Fe(1)-C(12)	168.85(11)
C(11)-Fe(1)-C(13)	67.23(11)
C(5)-Fe(1)-C(13)	105.68(11)
C(14)-Fe(1)-C(13)	40.43(11)
C(7)-Fe(1)-C(13)	115.95(11)
C(3)-Fe(1)-C(13)	127.21(12)
N(1)-Fe(1)-C(13)	68.70(11)
C(1)-Fe(1)-C(13)	166.70(11)
C(9)-Fe(1)-C(13)	150.50(11)
C(12)-Fe(1)-C(13)	40.32(11)
O(1)-S(1)-C(11)	105.47(13)
O(1)-S(1)-C(15)	107.21(13)
C(11)-S(1)-C(15)	97.56(13)
C(14)-N(1)-C(11)	104.2(2)
C(14)-N(1)-Fe(1)	69.74(15)
C(11)-N(1)-Fe(1)	68.08(14)
C(9)-C(1)-C(3)	108.2(2)
C(9)-C(1)-C(2)	126.5(3)
C(3)-C(1)-C(2)	125.2(3)
C(9)-C(1)-Fe(1)	69.9(2)
C(3)-C(1)-Fe(1)	69.25(15)
C(2)-C(1)-Fe(1)	129.3(2)
C(5)-C(3)-C(1)	107.6(2)
C(5)-C(3)-C(4)	126.7(2)
C(1)-C(3)-C(4)	125.7(2)
C(5)-C(3)-Fe(1)	68.99(15)
C(1)-C(3)-Fe(1)	69.74(15)
C(4)-C(3)-Fe(1)	126.9(2)
C(7)-C(5)-C(3)	108.0(2)
C(7)-C(5)-C(6)	126.2(2)
C(3)-C(5)-C(6)	125.8(2)
C(7)-C(5)-Fe(1)	69.8(2)
C(3)-C(5)-Fe(1)	69.81(15)
C(6)-C(5)-Fe(1)	125.3(2)
C(5)-C(7)-C(9)	108.1(2)
C(5)-C(7)-C(8)	126.0(3)
C(9)-C(7)-C(8)	126.0(3)
C(5)-C(7)-Fe(1)	69.2(2)
C(9)-C(7)-Fe(1)	70.1(2)
C(8)-C(7)-Fe(1)	126.3(2)
C(1)-C(9)-C(7)	108.2(2)
C(1)-C(9)-C(10)	125.9(3)
C(7)-C(9)-C(10)	125.9(3)

C(1)-C(9)-Fe(1)	69.6(2)
C(7)-C(9)-Fe(1)	69.0(2)
C(10)-C(9)-Fe(1)	128.7(2)
N(1)-C(11)-C(12)	112.5(2)
N(1)-C(11)-S(1)	120.7(2)
C(12)-C(11)-S(1)	126.9(2)
N(1)-C(11)-Fe(1)	71.66(15)
C(12)-C(11)-Fe(1)	71.7(2)
S(1)-C(11)-Fe(1)	124.74(15)
C(11)-C(12)-C(13)	105.1(2)
C(11)-C(12)-Fe(1)	67.50(15)
C(13)-C(12)-Fe(1)	70.1(2)
C(14)-C(13)-C(12)	106.8(2)
C(14)-C(13)-Fe(1)	68.8(2)
C(12)-C(13)-Fe(1)	69.6(2)
N(1)-C(14)-C(13)	111.4(2)
N(1)-C(14)-Fe(1)	70.46(15)
C(13)-C(14)-Fe(1)	70.7(2)
C(21)-C(15)-C(16)	120.8(3)
C(21)-C(15)-S(1)	119.1(2)
C(16)-C(15)-S(1)	120.1(2)
C(15)-C(16)-C(17)	119.4(3)
C(18)-C(17)-C(16)	121.0(3)
C(17)-C(18)-C(20)	118.5(3)
C(17)-C(18)-C(19)	119.8(3)
C(20)-C(18)-C(19)	121.7(3)
C(18)-C(20)-C(21)	121.5(3)
C(15)-C(21)-C(20)	118.8(3)
C(32)-Fe(2)-C(35)	65.57(11)
C(32)-Fe(2)-C(26)	150.63(11)
C(35)-Fe(2)-C(26)	129.14(11)
C(32)-Fe(2)-C(24)	118.34(11)
C(35)-Fe(2)-C(24)	166.49(11)
C(26)-Fe(2)-C(24)	41.16(10)
C(32)-Fe(2)-C(28)	168.21(12)
C(35)-Fe(2)-C(28)	109.52(11)
C(26)-Fe(2)-C(28)	40.86(11)
C(24)-Fe(2)-C(28)	69.08(11)
C(32)-Fe(2)-N(2)	40.05(10)
C(35)-Fe(2)-N(2)	39.67(10)
C(26)-Fe(2)-N(2)	166.95(10)
C(24)-Fe(2)-N(2)	151.30(10)
C(28)-Fe(2)-N(2)	129.33(11)
C(32)-Fe(2)-C(33)	40.96(11)
C(35)-Fe(2)-C(33)	67.65(11)
C(26)-Fe(2)-C(33)	115.24(11)
C(24)-Fe(2)-C(33)	106.21(11)
C(28)-Fe(2)-C(33)	148.93(11)
N(2)-Fe(2)-C(33)	69.53(10)
C(32)-Fe(2)-C(22)	110.20(10)

C(35)-Fe(2)-C(22)	152.26(12)
C(26)-Fe(2)-C(22)	68.77(10)
C(24)-Fe(2)-C(22)	40.83(10)
C(28)-Fe(2)-C(22)	68.74(11)
N(2)-Fe(2)-C(22)	118.72(10)
C(33)-Fe(2)-C(22)	128.64(11)
C(32)-Fe(2)-C(30)	130.86(11)
C(35)-Fe(2)-C(30)	119.54(12)
C(26)-Fe(2)-C(30)	68.67(11)
C(24)-Fe(2)-C(30)	68.80(11)
C(28)-Fe(2)-C(30)	40.83(10)
N(2)-Fe(2)-C(30)	109.30(11)
C(33)-Fe(2)-C(30)	168.08(11)
C(22)-Fe(2)-C(30)	40.72(10)
C(32)-Fe(2)-C(34)	67.18(11)
C(35)-Fe(2)-C(34)	40.35(11)
C(26)-Fe(2)-C(34)	106.51(11)
C(24)-Fe(2)-C(34)	127.33(11)
C(28)-Fe(2)-C(34)	116.73(11)
N(2)-Fe(2)-C(34)	68.66(10)
C(33)-Fe(2)-C(34)	40.48(11)
C(22)-Fe(2)-C(34)	166.27(12)
C(30)-Fe(2)-C(34)	151.06(11)
O(2)-S(2)-C(32)	105.46(13)
O(2)-S(2)-C(36)	107.18(13)
C(32)-S(2)-C(36)	97.68(13)
C(35)-N(2)-C(32)	103.9(2)
C(35)-N(2)-Fe(2)	69.6(2)
C(32)-N(2)-Fe(2)	67.95(15)
C(24)-C(22)-C(30)	108.2(2)
C(24)-C(22)-C(23)	126.3(3)
C(30)-C(22)-C(23)	125.4(3)
C(24)-C(22)-Fe(2)	69.11(15)
C(30)-C(22)-Fe(2)	69.88(15)
C(23)-C(22)-Fe(2)	128.9(2)
C(22)-C(24)-C(26)	107.7(2)
C(22)-C(24)-C(25)	125.6(2)
C(26)-C(24)-C(25)	126.7(2)
C(22)-C(24)-Fe(2)	70.1(2)
C(26)-C(24)-Fe(2)	69.38(15)
C(25)-C(24)-Fe(2)	126.0(2)
C(28)-C(26)-C(24)	108.1(2)
C(28)-C(26)-C(27)	125.8(2)
C(24)-C(26)-C(27)	126.0(2)
C(28)-C(26)-Fe(2)	69.7(2)
C(24)-C(26)-Fe(2)	69.46(15)
C(27)-C(26)-Fe(2)	126.2(2)
C(26)-C(28)-C(30)	108.1(2)
C(26)-C(28)-C(29)	125.3(3)
C(30)-C(28)-C(29)	126.6(3)

C(26)-C(28)-Fe(2)	69.44(15)
C(30)-C(28)-Fe(2)	70.21(15)
C(29)-C(28)-Fe(2)	126.9(2)
C(28)-C(30)-C(22)	107.8(2)
C(28)-C(30)-C(31)	127.3(3)
C(22)-C(30)-C(31)	124.9(2)
C(28)-C(30)-Fe(2)	69.0(2)
C(22)-C(30)-Fe(2)	69.4(2)
C(31)-C(30)-Fe(2)	128.3(2)
N(2)-C(32)-C(33)	113.0(2)
N(2)-C(32)-S(2)	120.5(2)
C(33)-C(32)-S(2)	126.5(2)
N(2)-C(32)-Fe(2)	72.00(15)
C(33)-C(32)-Fe(2)	71.6(2)
S(2)-C(32)-Fe(2)	124.16(14)
C(32)-C(33)-C(34)	104.6(2)
C(32)-C(33)-Fe(2)	67.5(2)
C(34)-C(33)-Fe(2)	70.3(2)
C(35)-C(34)-C(33)	106.5(2)
C(35)-C(34)-Fe(2)	68.6(2)
C(33)-C(34)-Fe(2)	69.2(2)
N(2)-C(35)-C(34)	111.9(2)
N(2)-C(35)-Fe(2)	70.72(15)
C(34)-C(35)-Fe(2)	71.0(2)
C(42)-C(36)-C(37)	120.6(3)
C(42)-C(36)-S(2)	119.2(2)
C(37)-C(36)-S(2)	120.2(2)
C(38)-C(37)-C(36)	119.3(3)
C(37)-C(38)-C(39)	121.2(3)
C(41)-C(39)-C(38)	118.3(3)
C(41)-C(39)-C(40)	122.0(3)
C(38)-C(39)-C(40)	119.7(3)
C(39)-C(41)-C(42)	121.5(3)
C(36)-C(42)-C(41)	119.2(3)

Table 4. Fractional atomic coordinates and equivalent isotropic thermal paramters (in Å^2). for compound (S_s, R_p)-**3**

Atom	*x*	*y*	*z*	U_{eq}[a]
Fe	0.45181(2)	0.74604(2)	0.181264(9)	0.01876(6)
S	0.08439(5)	0.70538(4)	0.24573(2)	0.02627(9)
O	0.0665(2)	0.58110(12)	0.22572(6)	0.0375(3)
C(1)	0.4474(2)	0.84428(13)	0.09494(8)	0.0218(3)
C(2)	0.4071(2)	0.97133(15)	0.09125(9)	0.0322(4)
C(3)	0.3371(2)	0.7497(2)	0.08862(7)	0.0218(3)
C(4)	0.1614(2)	0.7602(2)	0.07531(8)	0.0299(3)
C(5)	0.4250(2)	0.64371(14)	0.09622(8)	0.0210(3)
C(6)	0.3532(2)	0.5249(2)	0.09389(9)	0.0295(4)
C(7)	0.5901(2)	0.67301(14)	0.10643(8)	0.0214(3)
C(8)	0.7265(2)	0.5888(2)	0.11326(9)	0.0296(4)
C(9)	0.6039(2)	0.79703(14)	0.10584(8)	0.0209(3)
C(10)	0.7546(2)	0.8657(2)	0.11420(10)	0.0306(4)
N	0.4056(2)	0.65132(13)	0.26800(7)	0.0261(3)
C(11)	0.2916(2)	0.73608(15)	0.25678(7)	0.0225(3)
C(12)	0.3600(2)	0.8497(2)	0.25600(9)	0.0300(4)
C(13)	0.5258(3)	0.8326(2)	0.26716(9)	0.0361(5)
C(14)	0.5481(2)	0.7126(2)	0.27407(8)	0.0337(4)
C(15)	0.0268(2)	0.71618(14)	0.33358(7)	0.0213(3)
C(16)	0.0029(2)	0.82603(14)	0.36155(8)	0.0234(3)
C(17)	-0.0389(2)	0.83416(14)	0.42978(8)	0.0242(3)
C(18)	-0.0612(2)	0.73529(14)	0.46977(7)	0.0224(3)
C(19)	-0.1055(2)	0.7462(2)	0.54437(8)	0.0306(3)
C(20)	-0.0414(2)	0.62675(14)	0.43981(8)	0.0232(3)
C(21)	0.0027(2)	0.61644(14)	0.37150(8)	0.0232(3)

[a] $U_{eq} = \frac{1}{3} \varphi_i \varphi_j U_{ij} a^*_i a^*_j \boldsymbol{a}_i \forall \boldsymbol{a}_j$

Table 4a. Fractional atomic coordinates and isotropic thermal parameters (in Å^2) for compound (S_s, R_p)-**3**

Atom	*x*	*y*	*z*	*U*
H(21)	0.4074(2)	0.99653(15)	0.04353(9)	0.039
H(22)	0.4868(2)	1.01604(15)	0.11687(9)	0.039
H(23)	0.3007(2)	0.98438(15)	0.11093(9)	0.039
H(41)	0.1424(2)	0.7623(2)	0.02604(8)	0.036
H(42)	0.1210(2)	0.8320(2)	0.09605(8)	0.036
H(43)	0.1057(2)	0.6933(2)	0.09511(8)	0.036
H(61)	0.4303(2)	0.4683(2)	0.11170(9)	0.035
H(62)	0.3264(2)	0.5051(2)	0.04667(9)	0.035
H(63)	0.2559(2)	0.5233(2)	0.12177(9)	0.035
H(81)	0.7816(2)	0.5814(2)	0.06937(9)	0.035
H(82)	0.6851(2)	0.5127(2)	0.12718(9)	0.035
H(83)	0.8019(2)	0.6173(2)	0.14770(9)	0.035
H(101)	0.7292(2)	0.9421(2)	0.13348(10)	0.037
H(102)	0.8060(2)	0.8757(2)	0.06969(10)	0.037
H(103)	0.8275(2)	0.8242(2)	0.14491(10)	0.037
H(12)	0.3059(2)	0.9216(2)	0.24940(9)	0.036
H(13)	0.6060(3)	0.8911(2)	0.26950(9)	0.043
H(14)	0.6492(2)	0.6771(2)	0.28199(8)	0.040
H(16)	0.0150(2)	0.89399(14)	0.33449(8)	0.028
H(17)	-0.0528(2)	0.90880(14)	0.44971(8)	0.029
H(191)	-0.1714(2)	0.8158(2)	0.55101(8)	0.037
H(192)	-0.0077(2)	0.7526(2)	0.57178(8)	0.037
H(193)	-0.1659(2)	0.6773(2)	0.55857(8)	0.037
H(20)	-0.0581(2)	0.55857(14)	0.46622(8)	0.028
H(21)	0.0160(2)	0.54192(14)	0.35135(8)	0.028

Table 4b. Anisotropic thermal parameters for compound (S_s, R_p)-**3**

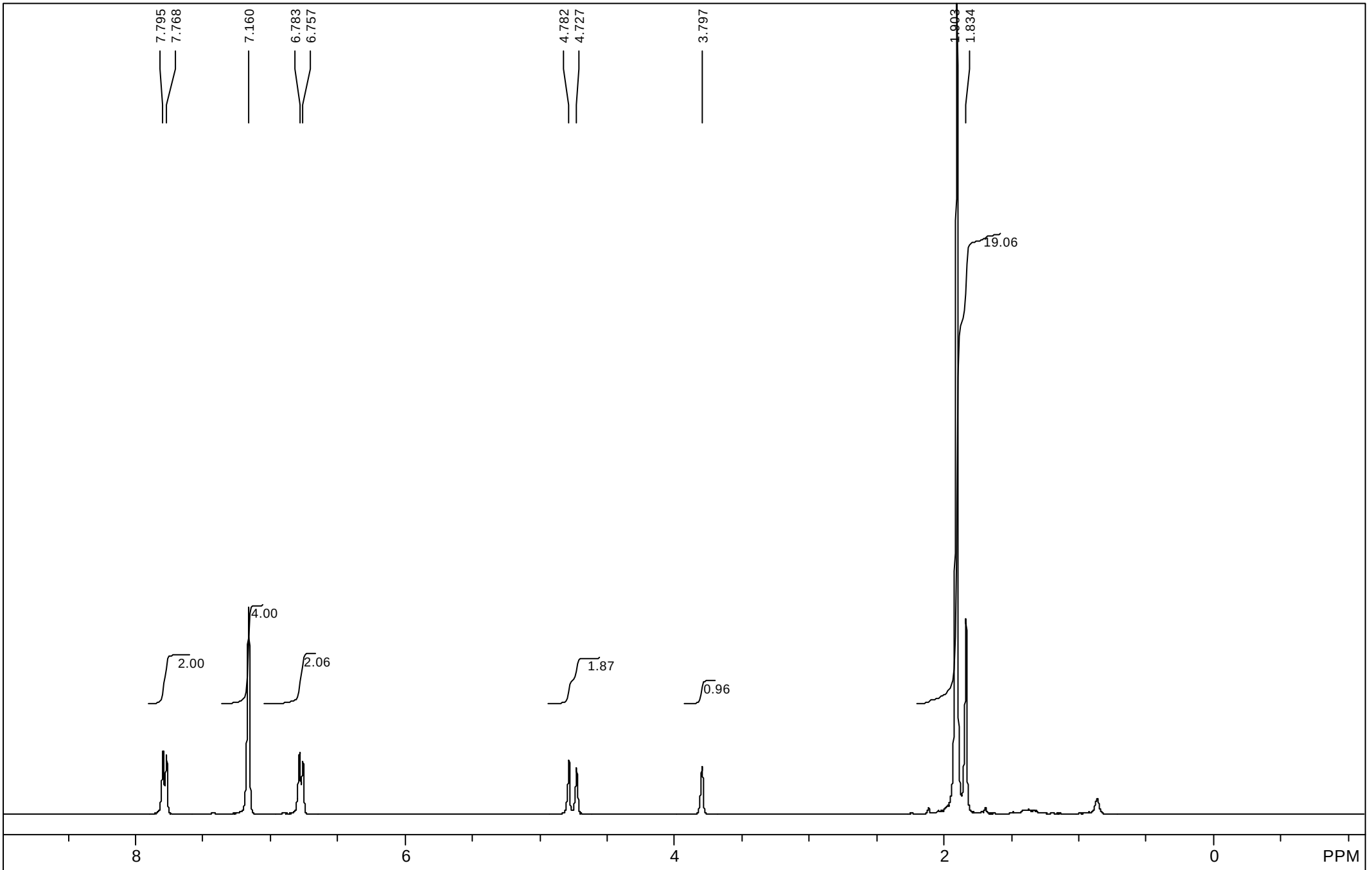
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.01925(10)	0.02368(10)	0.01334(9)	-0.00057(9)	0.00029(7)	-0.00260(9)
S	0.0226(2)	0.0399(2)	0.0163(2)	-0.0016(2)	0.00011(15)	0.0000(2)
O	0.0351(7)	0.0478(7)	0.0296(6)	-0.0169(5)	0.0042(6)	-0.0137(6)
C(1)	0.0250(8)	0.0245(7)	0.0159(6)	0.0012(5)	0.0022(7)	0.0013(7)
C(2)	0.0388(10)	0.0280(8)	0.0298(9)	0.0037(7)	-0.0005(8)	0.0031(7)
C(3)	0.0211(6)	0.0306(7)	0.0137(6)	0.0004(6)	0.0009(5)	-0.0014(8)
C(4)	0.0211(7)	0.0491(10)	0.0194(7)	0.0008(8)	-0.0025(5)	-0.0018(8)
C(5)	0.0226(8)	0.0257(7)	0.0146(6)	-0.0017(5)	0.0012(6)	-0.0023(6)
C(6)	0.0378(10)	0.0285(8)	0.0222(8)	-0.0036(6)	0.0028(7)	-0.0095(7)
C(7)	0.0229(8)	0.0246(7)	0.0165(7)	0.0003(6)	0.0016(6)	-0.0001(6)
C(8)	0.0276(9)	0.0332(9)	0.0278(9)	-0.0002(7)	0.0003(7)	0.0072(7)
C(9)	0.0194(7)	0.0271(8)	0.0161(6)	0.0022(6)	0.0020(6)	-0.0016(6)
C(10)	0.0243(8)	0.0367(9)	0.0306(9)	0.0038(8)	0.0006(7)	-0.0079(7)
N	0.0265(8)	0.0347(8)	0.0172(6)	0.0049(5)	0.0008(6)	0.0004(6)
C(11)	0.0242(6)	0.0286(8)	0.0146(6)	-0.0021(6)	0.0025(5)	-0.0020(6)
C(12)	0.0430(10)	0.0280(9)	0.0190(8)	-0.0057(7)	0.0072(8)	-0.0042(7)
C(13)	0.0393(11)	0.0502(11)	0.0187(8)	-0.0078(7)	0.0018(7)	-0.0201(9)
C(14)	0.0250(8)	0.0587(11)	0.0173(7)	0.0030(7)	-0.0028(7)	-0.0046(8)
C(15)	0.0169(7)	0.0294(7)	0.0178(6)	0.0003(5)	-0.0006(5)	0.0009(6)
C(16)	0.0257(8)	0.0223(7)	0.0223(7)	0.0044(6)	0.0003(6)	0.0017(6)
C(17)	0.0251(8)	0.0226(7)	0.0249(7)	-0.0009(6)	0.0010(7)	0.0046(6)
C(18)	0.0170(6)	0.0305(8)	0.0199(6)	0.0014(6)	0.0011(5)	0.0006(7)
C(19)	0.0331(8)	0.0370(9)	0.0215(7)	-0.0003(8)	0.0071(6)	0.0001(8)
C(20)	0.0221(8)	0.0249(7)	0.0226(7)	0.0035(6)	-0.0011(6)	-0.0022(6)
C(21)	0.0210(7)	0.0224(7)	0.0262(8)	-0.0018(6)	-0.0011(6)	0.0010(6)

Table 5. Bond lengths (in Å) and bond angles in (E) for compound (S_s, R_p)-**3**

Fe-C(11)	1.9994(14)
Fe-C(14)	2.027(2)
Fe-C(1)	2.036(2)
Fe-C(9)	2.036(2)
Fe-C(12)	2.039(2)
Fe-C(7)	2.048(2)
Fe-C(13)	2.052(2)
Fe-C(5)	2.054(2)
Fe-C(3)	2.0551(14)
Fe- N	2.0570(14)
S-O	1.4892(13)
S-C(11)	1.779(2)
S-C(15)	1.7939(15)
C(1)-C(3)	1.430(2)
C(1)-C(9)	1.431(2)
C(1)-C(2)	1.501(2)
C(3)-C(5)	1.430(2)
C(3)-C(4)	1.494(2)
C(5)-C(7)	1.434(2)
C(5)-C(6)	1.492(2)
C(7)-C(9)	1.430(2)
C(7)-C(8)	1.501(2)
C(9)-C(10)	1.495(2)
N-C(11)	1.380(2)
N-C(14)	1.388(2)
C(11)-C(12)	1.426(2)
C(12)-C(13)	1.415(3)
C(13)-C(14)	1.399(3)
C(15)-C(21)	1.382(2)
C(15)-C(16)	1.391(2)
C(16)-C(17)	1.387(2)
C(17)-C(18)	1.394(2)
C(18)-C(20)	1.389(2)
C(18)-C(19)	1.515(2)
C(20)-C(21)	1.395(2)
C(11)-Fe-C(14)	65.73(7)
C(11)-Fe-C(1)	129.50(7)
C(14)-Fe-C(1)	149.26(8)
C(11)-Fe-C(9)	166.47(7)
C(14)-Fe-C(9)	117.38(7)
C(1)-Fe-C(9)	41.15(7)
C(11)-Fe-C(12)	41.34(7)
C(14)-Fe-C(12)	67.31(8)
C(1)-Fe-C(12)	105.49(7)
C(9)-Fe-C(12)	126.06(7)
C(11)-Fe-C(7)	152.26(7)
C(14)-Fe-C(7)	110.02(8)
C(1)-Fe-C(7)	68.97(7)

C(9)-Fe-C(7)	41.00(6)
C(12)-Fe-C(7)	165.24(7)
C(11)-Fe-C(13)	67.70(7)
C(14)-Fe-C(13)	40.11(9)
C(1)-Fe-C(13)	114.80(7)
C(9)-Fe-C(13)	105.64(7)
C(12)-Fe-C(13)	40.46(8)
C(7)-Fe-C(13)	128.15(8)
C(11)-Fe-C(5)	119.75(7)
C(14)-Fe-C(5)	131.63(8)
C(1)-Fe-C(5)	68.89(6)
C(9)-Fe-C(5)	69.05(7)
C(12)-Fe-C(5)	151.40(7)
C(7)-Fe-C(5)	40.92(7)
C(13)-Fe-C(5)	167.89(8)
C(11)-Fe-C(3)	110.16(6)
C(14)-Fe-C(3)	169.48(8)
C(1)-Fe-C(3)	40.93(7)
C(9)-Fe-C(3)	69.03(6)
C(12)-Fe-C(3)	116.66(7)
C(7)-Fe-C(3)	68.74(6)
C(13)-Fe-C(3)	148.93(8)
C(5)-Fe-C(3)	40.74(7)
C(11)-Fe-N	39.74(6)
C(14)-Fe-N	39.73(7)
C(1)-Fe-N	168.10(7)
C(9)-Fe-N	150.55(6)
C(12)-Fe-N	69.15(6)
C(7)-Fe-N	118.81(6)
C(13)-Fe-N	68.52(8)
C(5)-Fe-N	110.40(6)
C(3)-Fe-N	130.93(6)
O)-S)-C(11)	108.68(8)
O)-S)-C(15)	107.02(7)
C(11)-S)-C(15)	97.47(7)
C(3)-C(1)-C(9)	108.22(13)
C(3)-C(1)-C(2)	126.2(2)
C(9)-C(1)-C(2)	125.6(2)
C(3)-C(1)-Fe	70.25(8)
C(9)-C(1)-Fe	69.43(8)
C(2)-C(1)-Fe	125.74(11)
C(5)-C(3)-C(1)	107.93(12)
C(5)-C(3)-C(4)	126.2(2)
C(1)-C(3)-C(4)	125.9(2)
C(5)-C(3)-Fe	69.58(8)
C(1)-C(3)-Fe	68.82(8)
C(4)-C(3)-Fe	127.86(10)
C(3)-C(5)-C(7)	107.94(14)
C(3)-C(5)-C(6)	124.8(2)
C(7)-C(5)-C(6)	127.3(2)

C(3)-C(5)-Fe	69.67(8)
C(7)-C(5)-Fe	69.32(9)
C(6)-C(5)-Fe	126.36(11)
C(9)-C(7)-C(5)	108.1(2)
C(9)-C(7)-C(8)	125.7(2)
C(5)-C(7)-C(8)	126.22(15)
C(9)-C(7)-Fe	69.06(10)
C(5)-C(7)-Fe	69.76(9)
C(8)-C(7)-Fe	128.93(12)
C(7)-C(9)-C(1)	107.84(15)
C(7)-C(9)-C(10)	126.4(2)
C(1)-C(9)-C(10)	125.80(14)
C(7)-C(9)-Fe	69.94(10)
C(1)-C(9)-Fe	69.42(9)
C(10)-C(9)-Fe	126.68(12)
C(11)-N-C(14)	104.29(14)
C(11)-N-Fe	67.88(8)
C(14)-N-Fe	68.99(9)
N-C(11)-C(12)	111.88(15)
N-C(11)-S)	123.37(12)
C(12)-C(11)-S)	124.75(13)
N-C(11)-Fe	72.38(8)
C(12)-C(11)-Fe	70.83(9)
S)-C(11)-Fe	124.87(8)
C(13)-C(12)-C(11)	105.2(2)
C(13)-C(12)-Fe	70.27(11)
C(11)-C(12)-Fe	67.83(9)
C(14)-C(13)-C(12)	106.4(2)
C(14)-C(13)-Fe	68.98(10)
C(12)-C(13)-Fe	69.28(11)
N-C(14)-C(13)	112.2(2)
N-C(14)-Fe	71.28(9)
C(13)-C(14)-Fe	70.90(11)
C(21)-C(15)-C(16)	121.34(14)
C(21)-C(15)-S	119.93(12)
C(16)-C(15)-S	118.70(12)
C(17)-C(16)-C(15)	118.56(14)
C(16)-C(17)-C(18)	121.47(15)
C(20)-C(18)-C(17)	118.59(14)
C(20)-C(18)-C(19)	120.82(14)
C(17)-C(18)-C(19)	120.59(14)
C(18)-C(20)-C(21)	120.96(14)
C(15)-C(21)-C(20)	119.03(14)



(S,S)-2-p-Tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocen, (S,S)-3

USER: -- DATE: Oct 10

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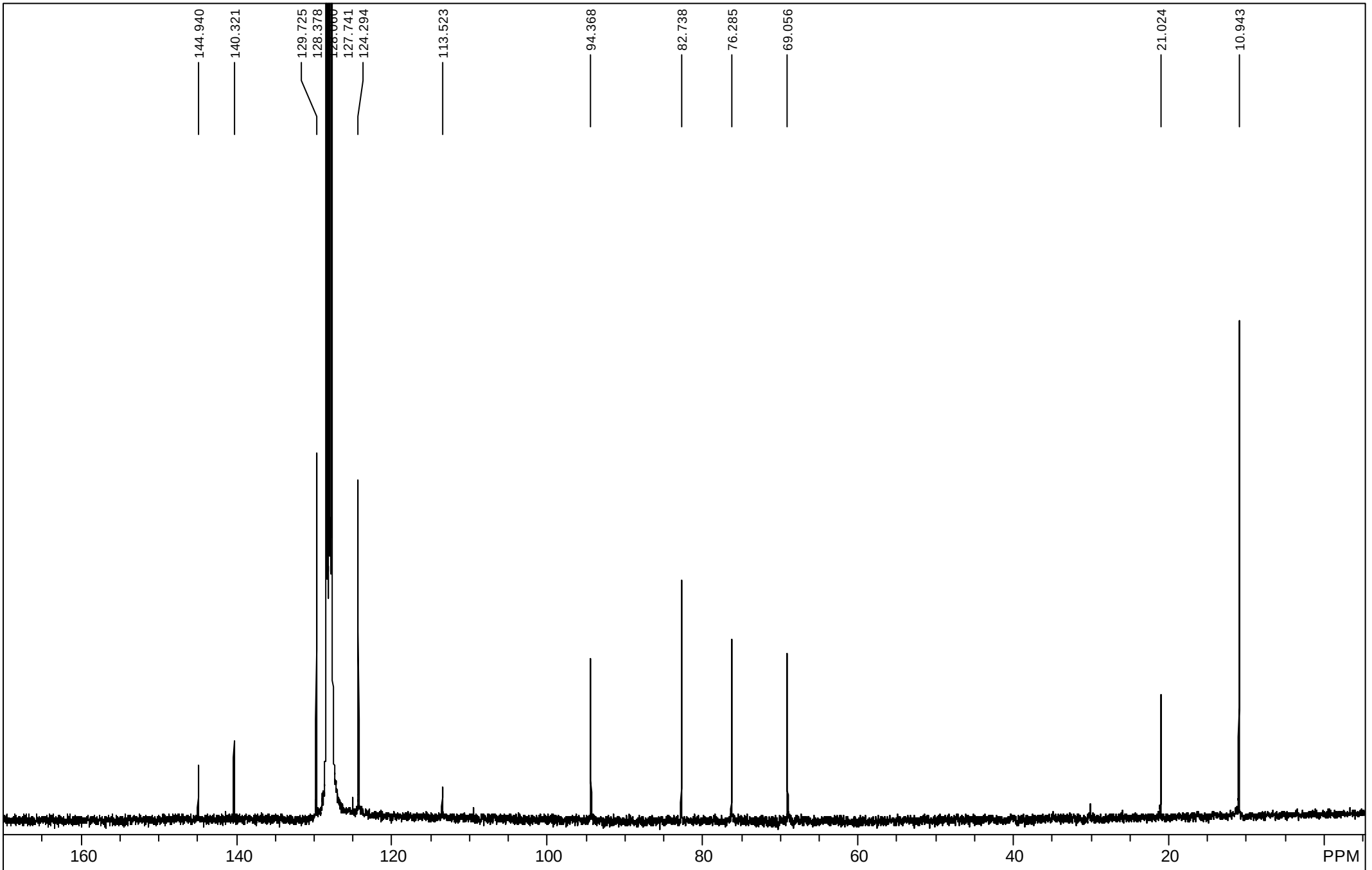
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - stof1H

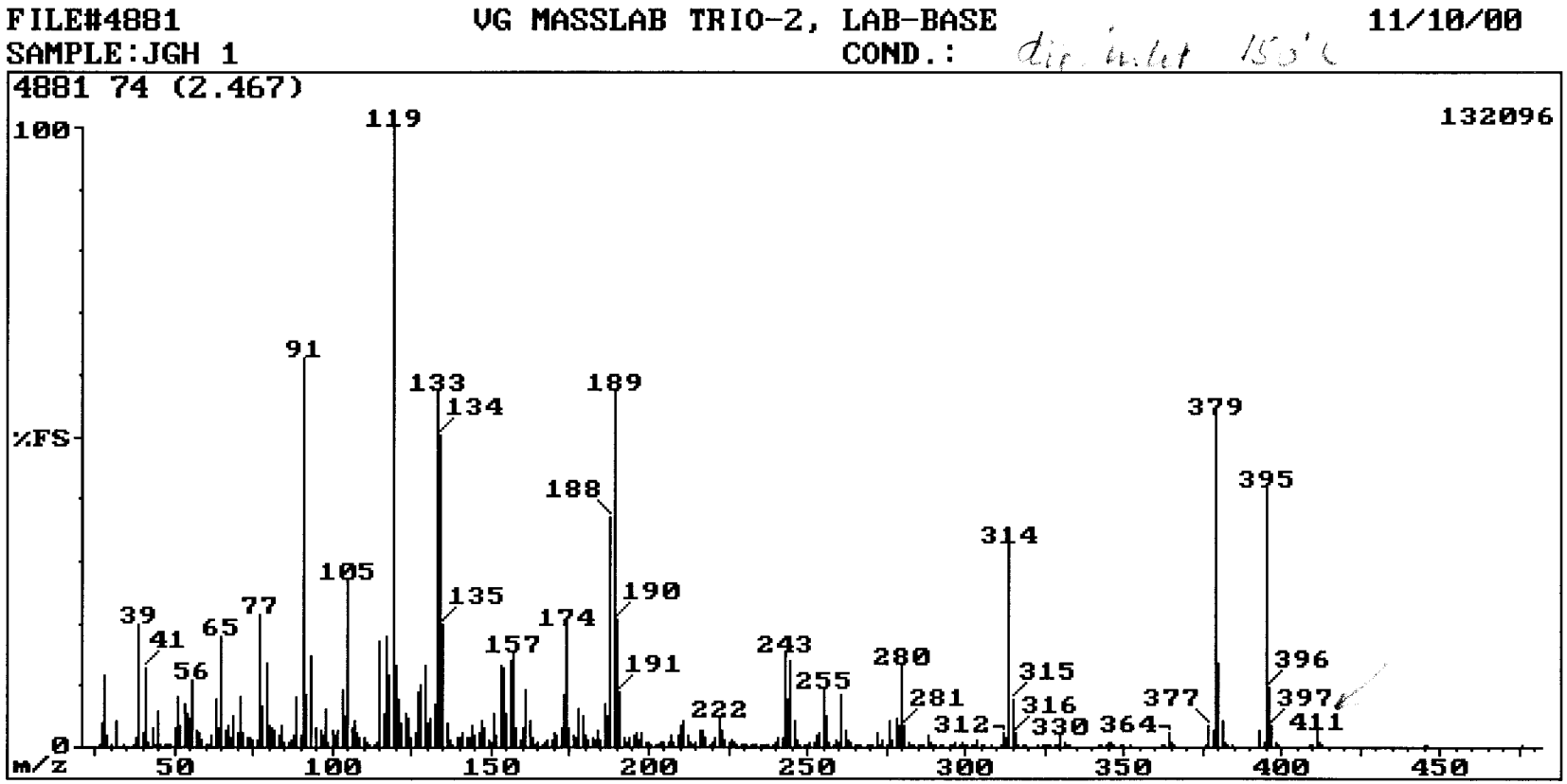


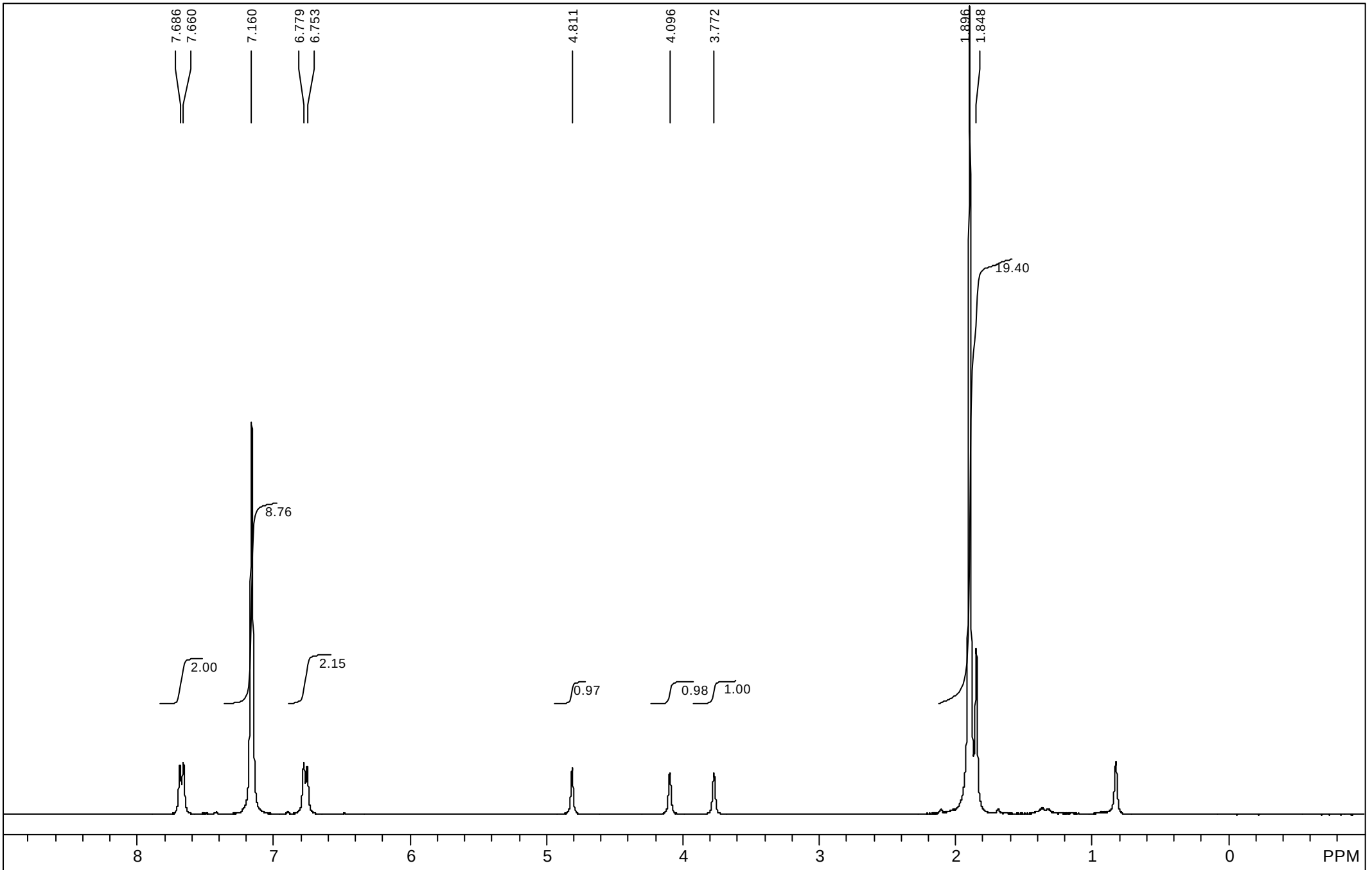
(S,S)-2-p-Tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocene, (S,S)-3

USER: -- DATE: Aug 18

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8064.3		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 1.0 sec	NA: 15000	LB: 1.0		WinNuts - stof1C

(S_S,S_P)-2-p-Tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocene, (S_S,S_P)-**3**

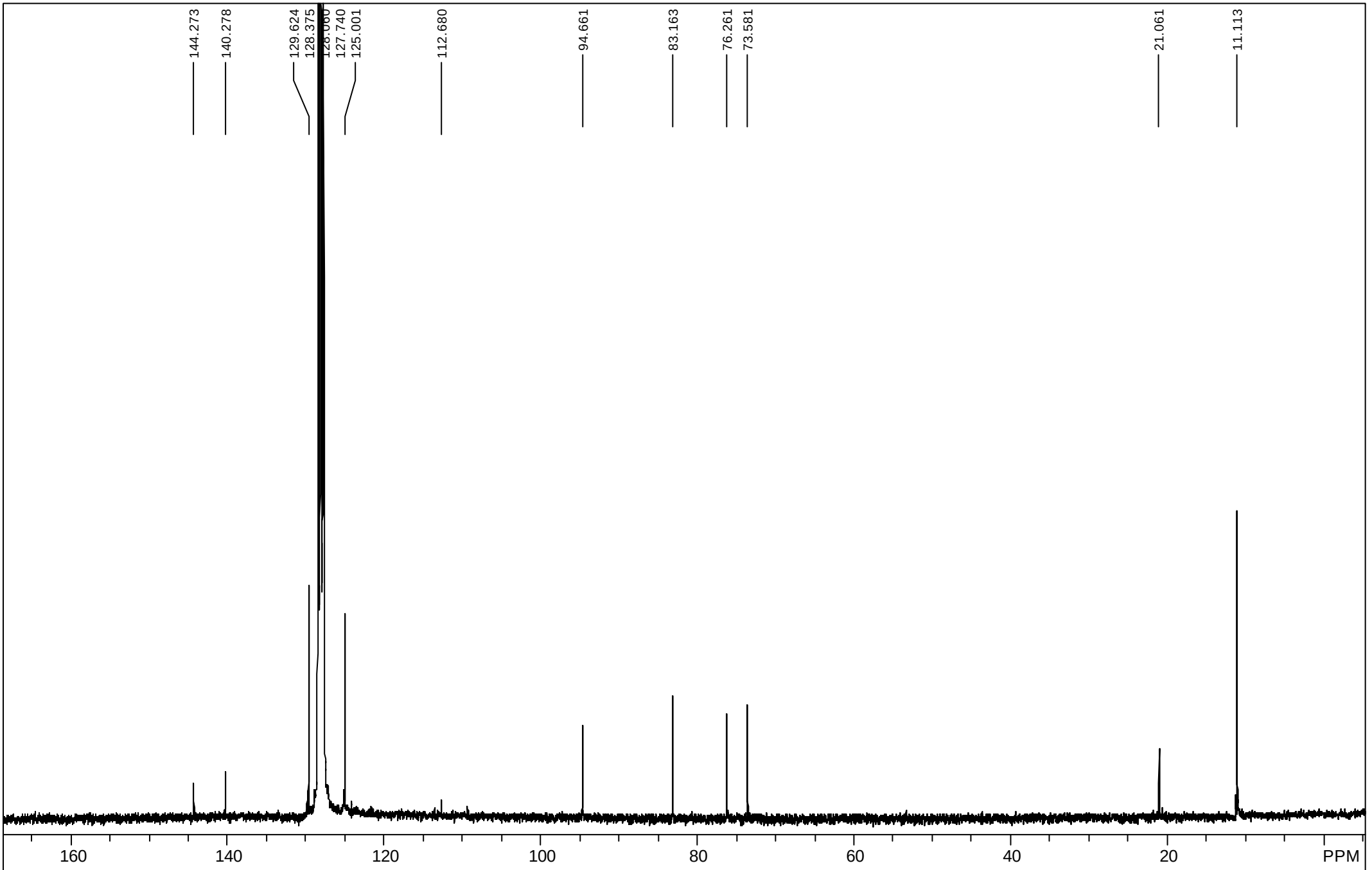




(S,R)-2-p-tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocene, (S,R)-3

USER: -- DATE: Oct 10

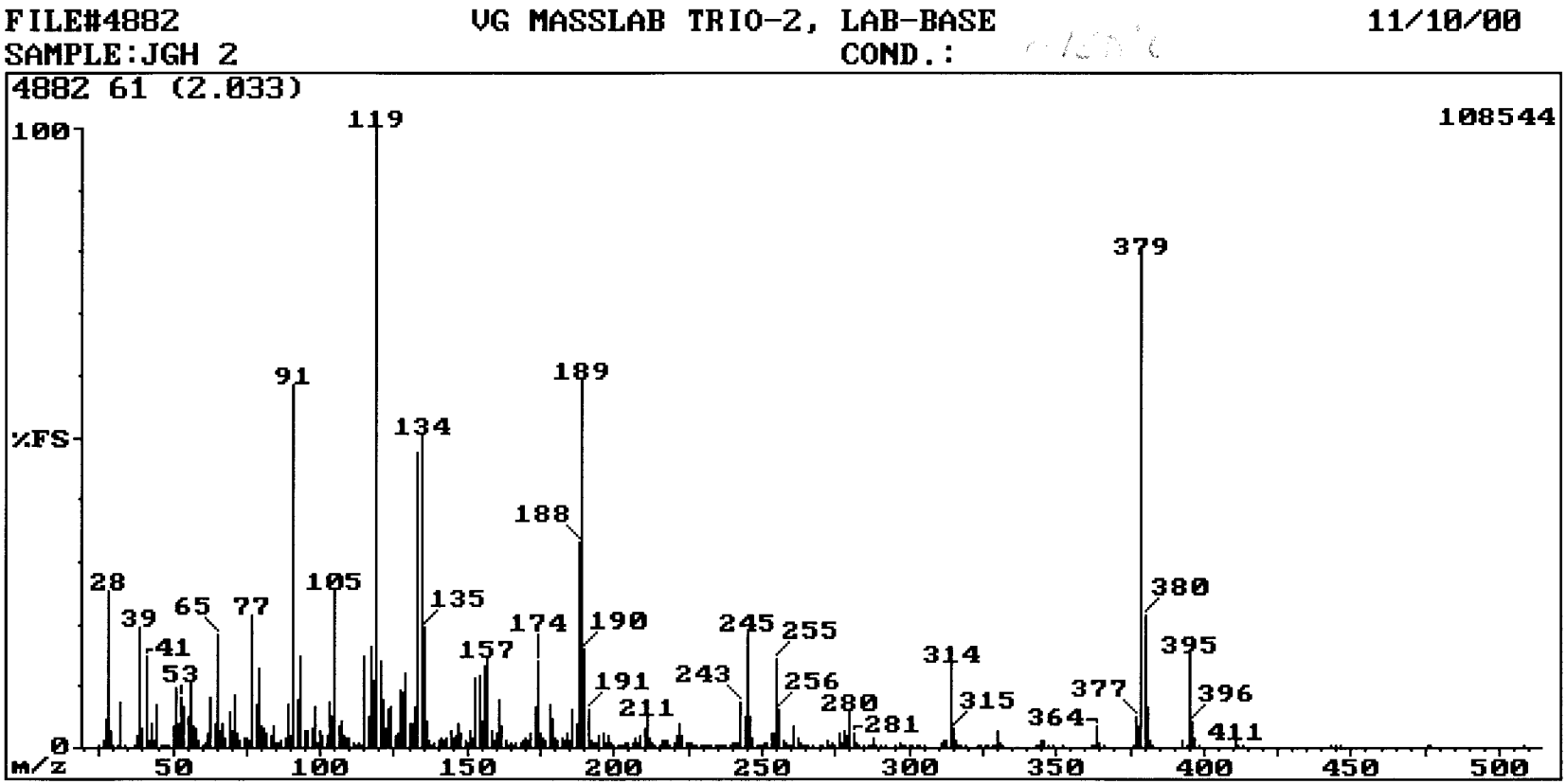
F1: 300.059	F2: 75.457	SW1: 6000		OF1: 1458.9		PTS1d: 32768	
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - stof2H

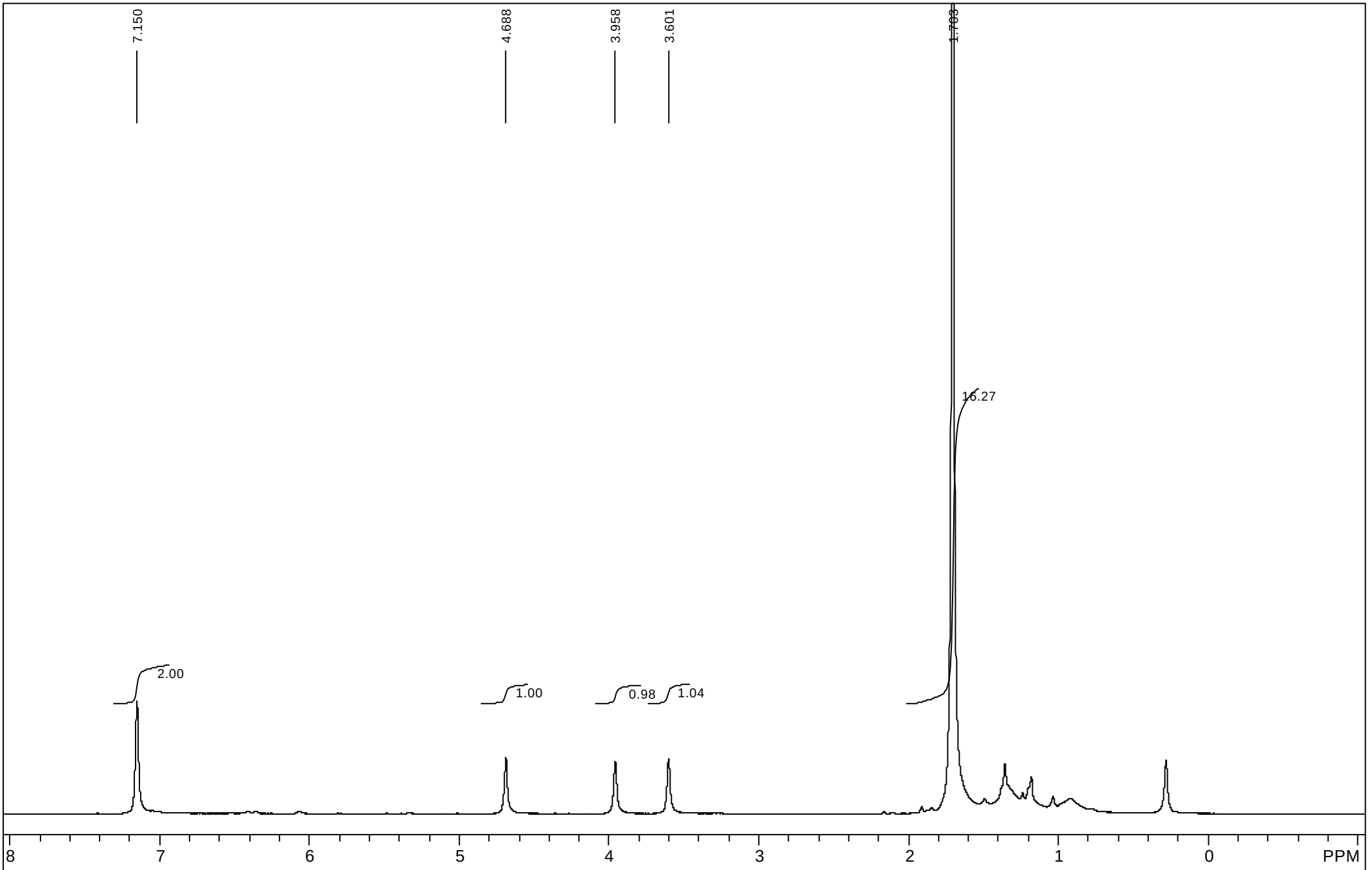


(S,R)-2-p-Tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocene, (S,R)-3 USER: -- DATE: Aug 22

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8064.2		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 1.0 sec	NA: 10000	LB: 1.0		WinNuts - stof2C

(S_S,R_P)-2-p-Tolylsulfinyl-1',2',3',4',5'-pentamethyl azaferrocene, (S_S,R_P)-**3**

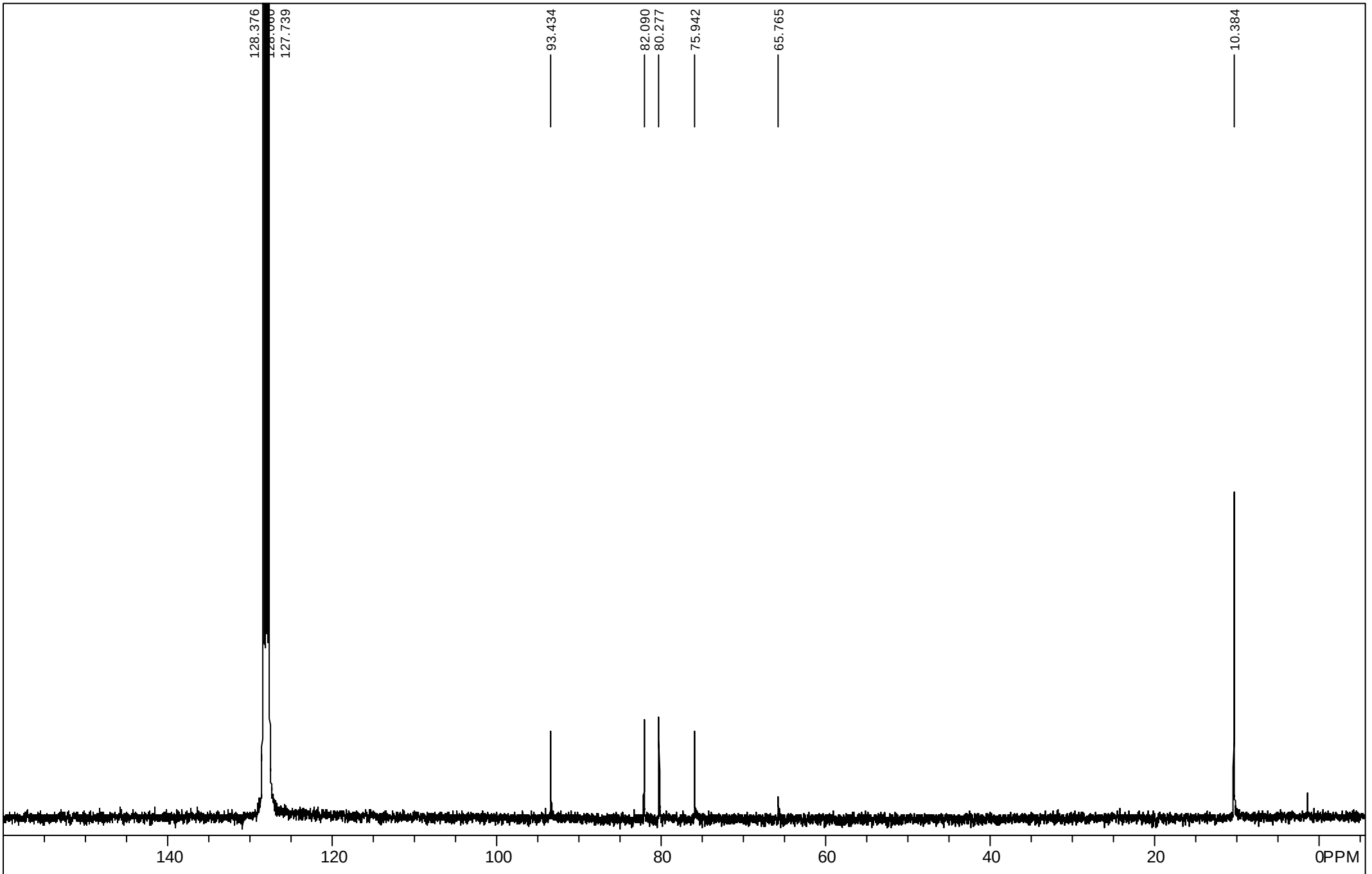




2-Iodo-1',2',3',4',5'-pentamethyl azaferrocene, 4a

USER: -- DATE: Oct 3

F1: 300.059	F2: 75.457	SW1: 6000		OF1: 1455.9		PTS1d: 32768	
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - jgh17 I-azaH

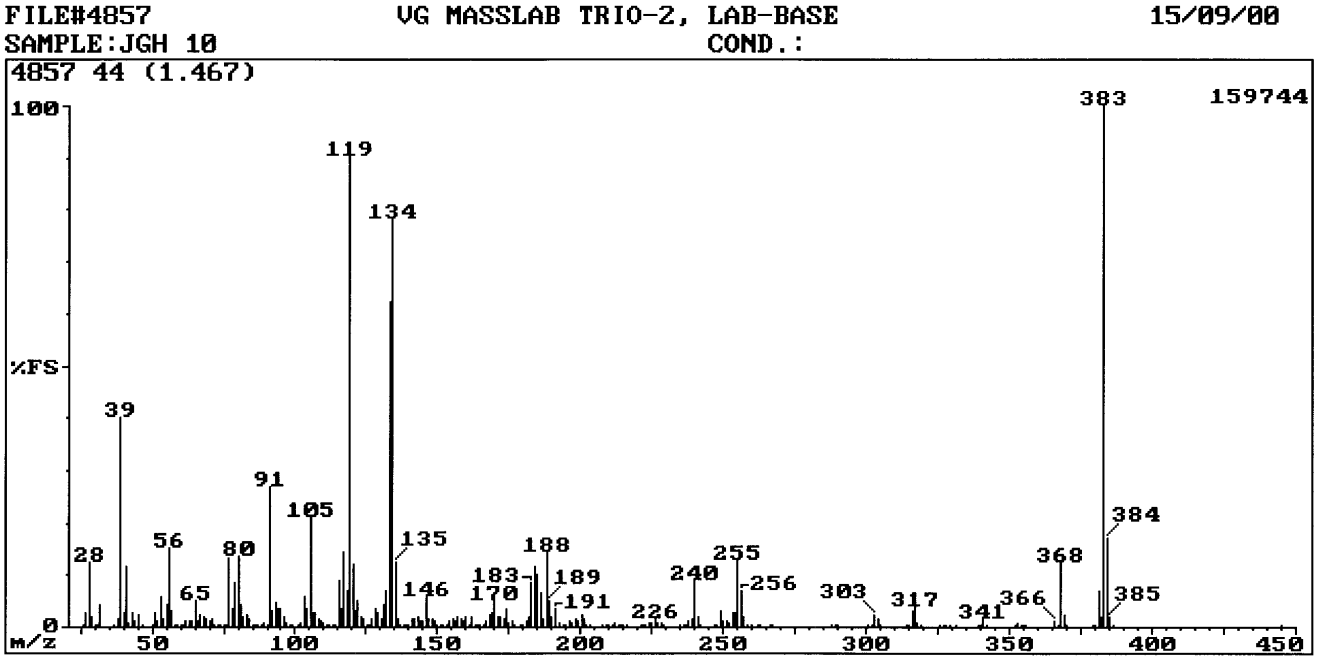


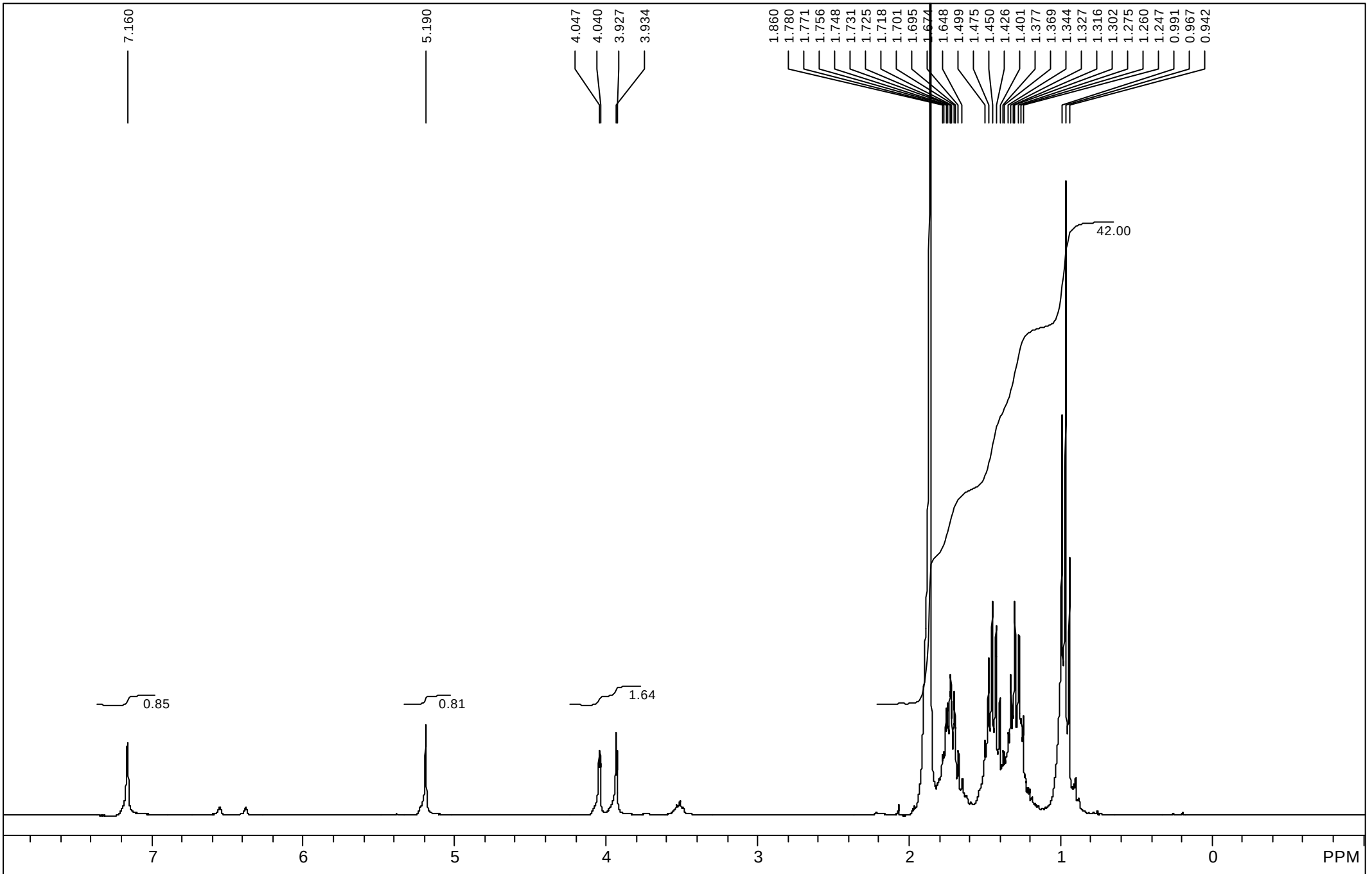
2-Iodo-1',2',3',4',5'-pentamethyl azaferrocene, 4a

USER: -- DATE: Oct 3

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8063.7		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 5.0 sec	NA: 1024	LB: 1.0		WinNuts - jgh17 I-azaC1

2-Iodo-1’,2’,3’,4’,5’-pentamethylazaferrocene, **4a**

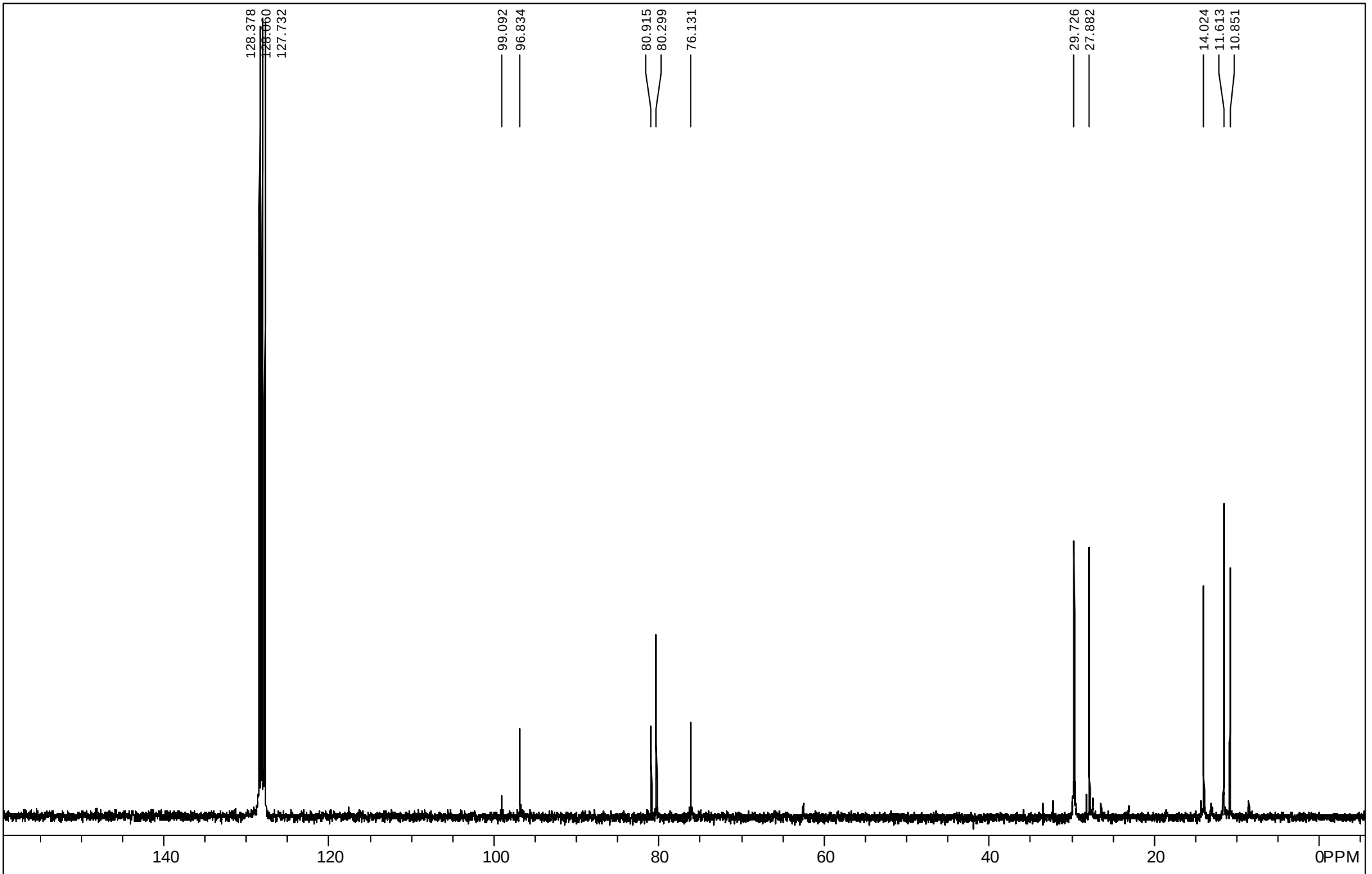




2-(tri-n-butylstannyl)-1',2',3',4',5'-pentamethyl azaferrocene, 4b

USER: -- DATE: Sep 4

F1: 300.059	F2: 75.457	SW1: 6000		OF1: 1459.5		PTS1d: 32768	
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - jgh6aH

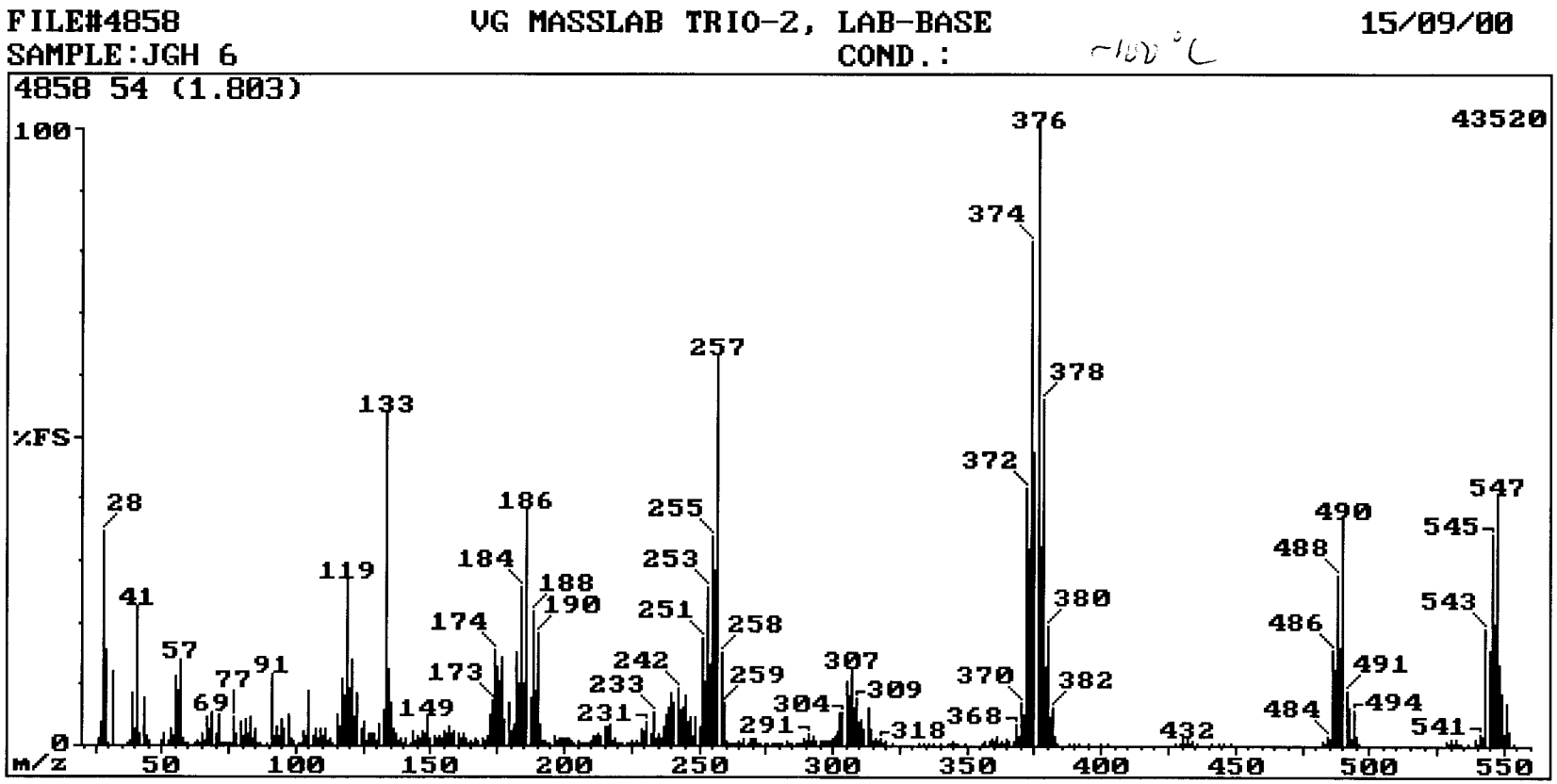


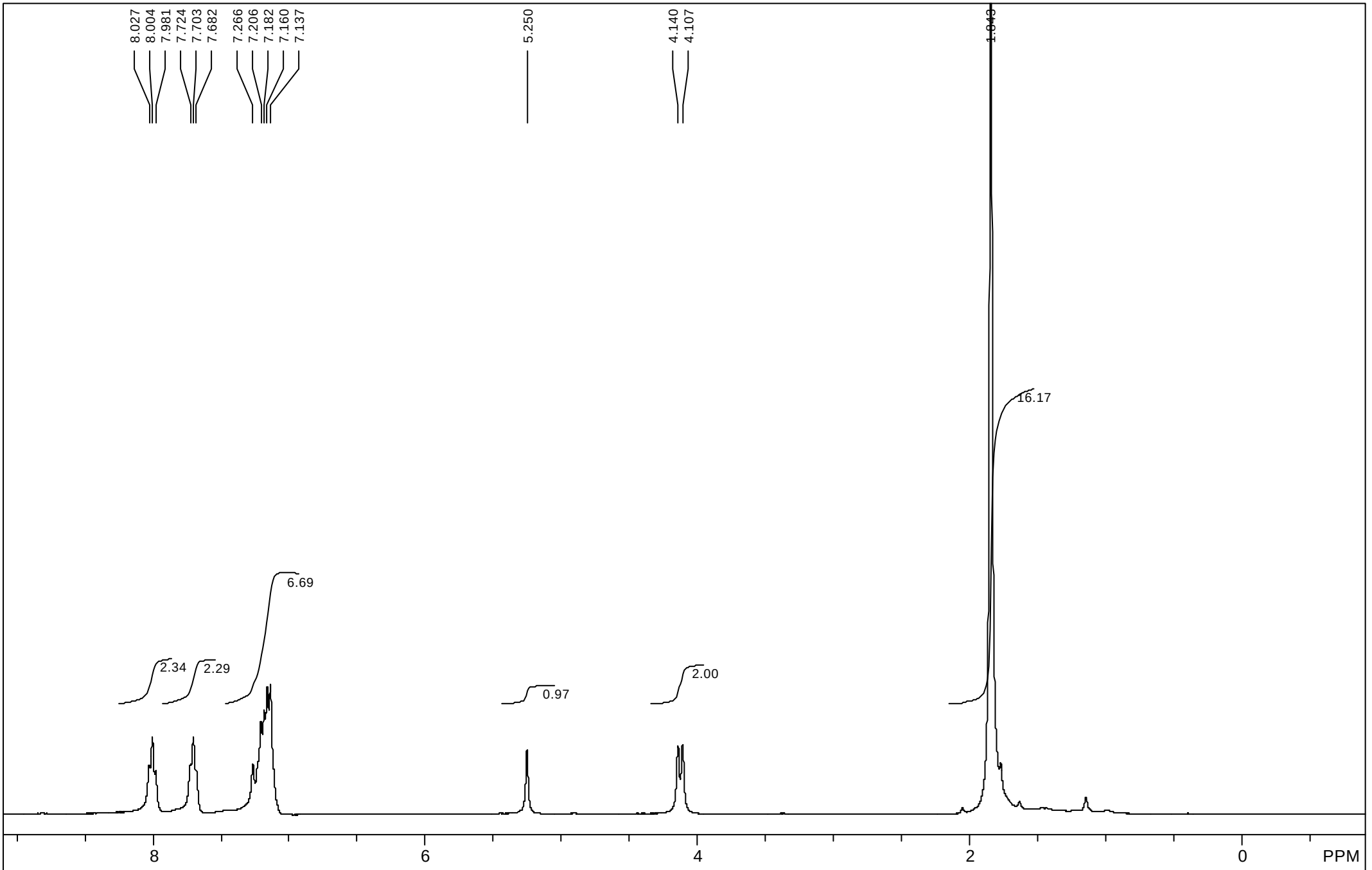
2-(tri-n-butylstannyl)-1',2',3',4',5'-pentamethyl azaferrocene, 4b

USER: -- DATE: Sep 4

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8064.4		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 1.0 sec	NA: 256	LB: 1.0		WinNuts - jgh6aC

2-(Tri-*n*-butylstannyl)-1',2',3',4',5'-pentamethylazaferrocene, **4b**

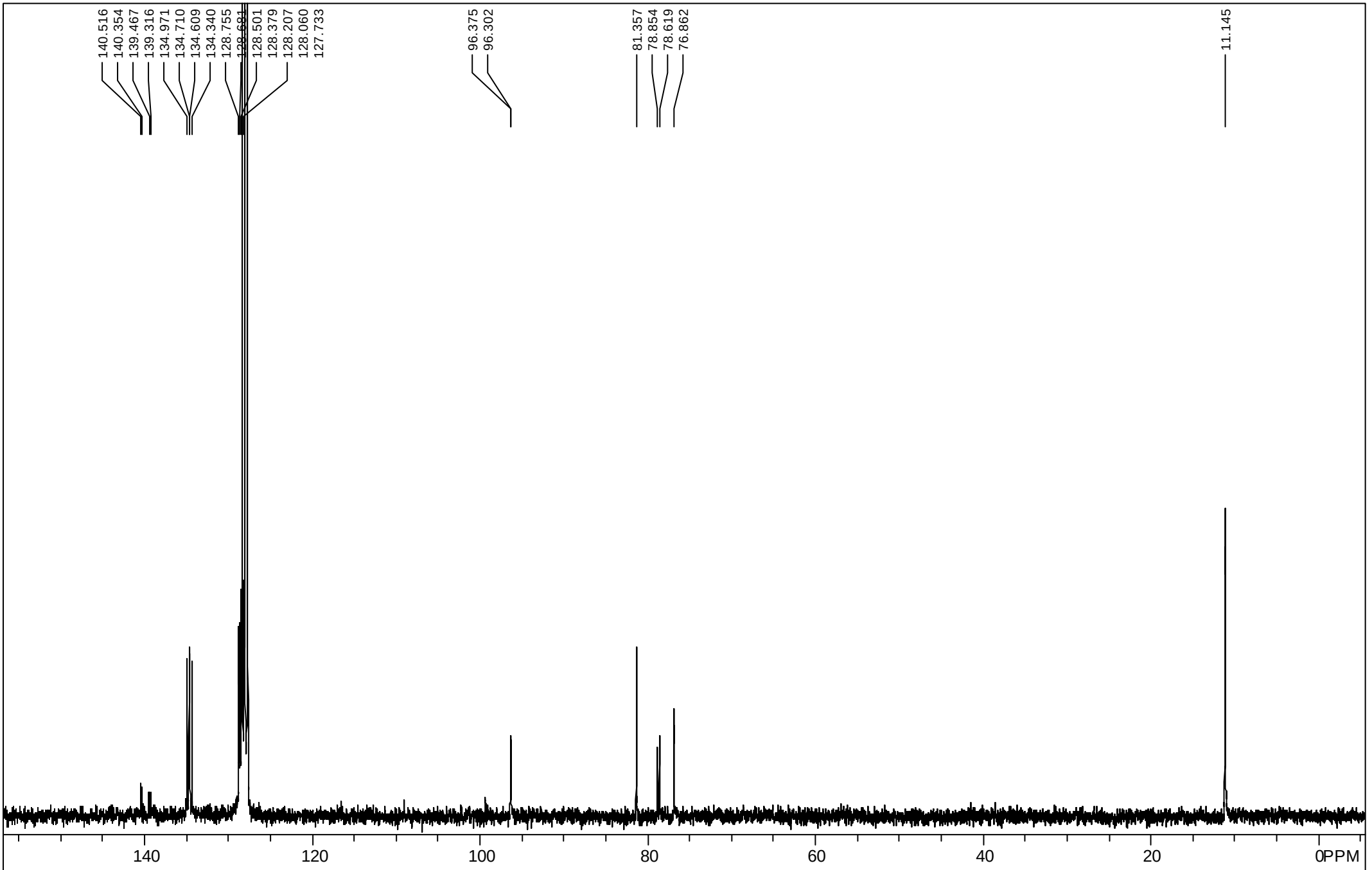




2-(diphenylphosphinyl)-1',2',3',4',5'-pentamethyl azaferrocene, 4c

USER: -- DATE: Sep 7

F1: 300.059	F2: 75.457	SW1: 6000		OF1: 1490.1		PTS1d: 32768	
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - jgh9aH

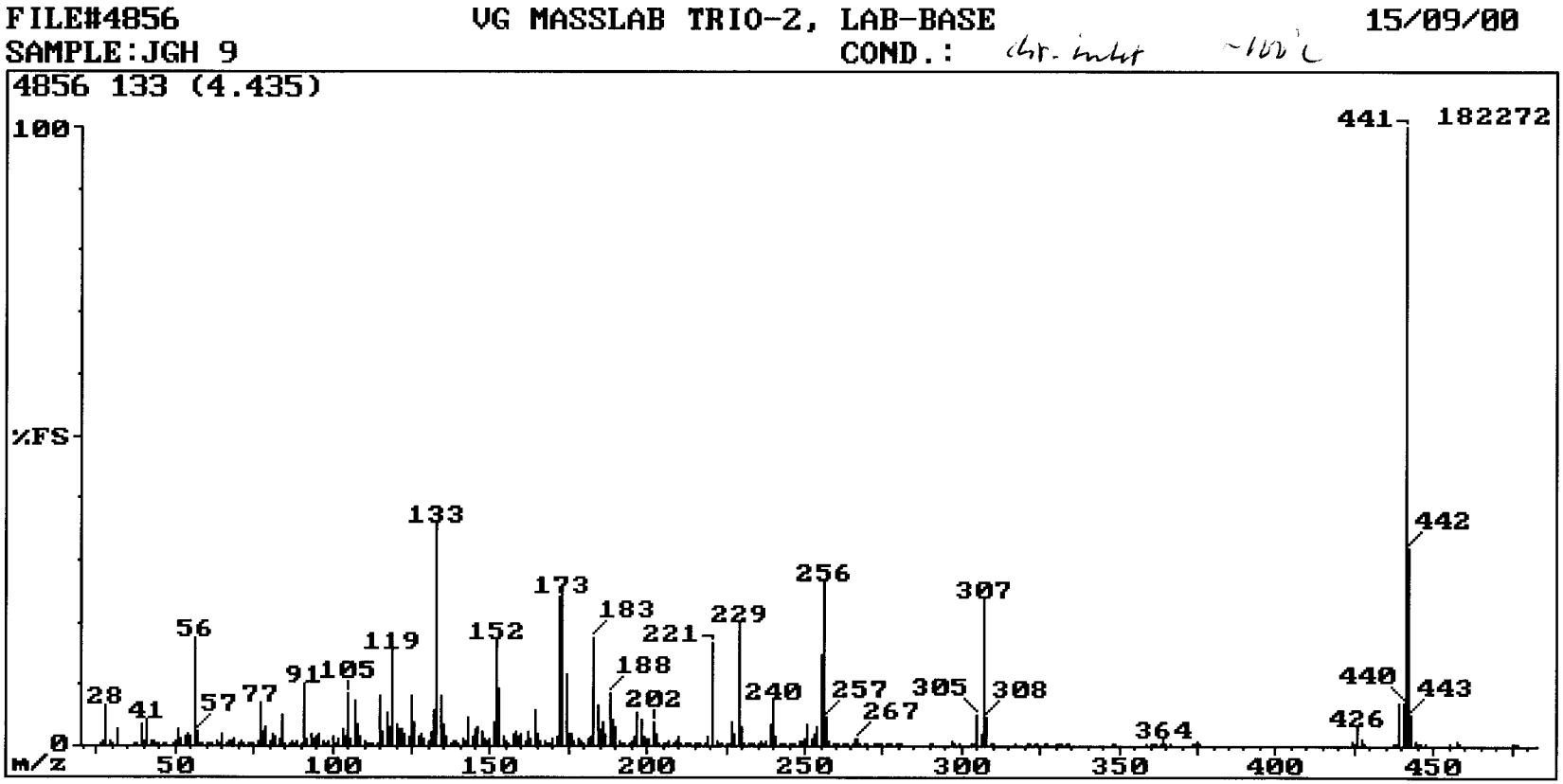


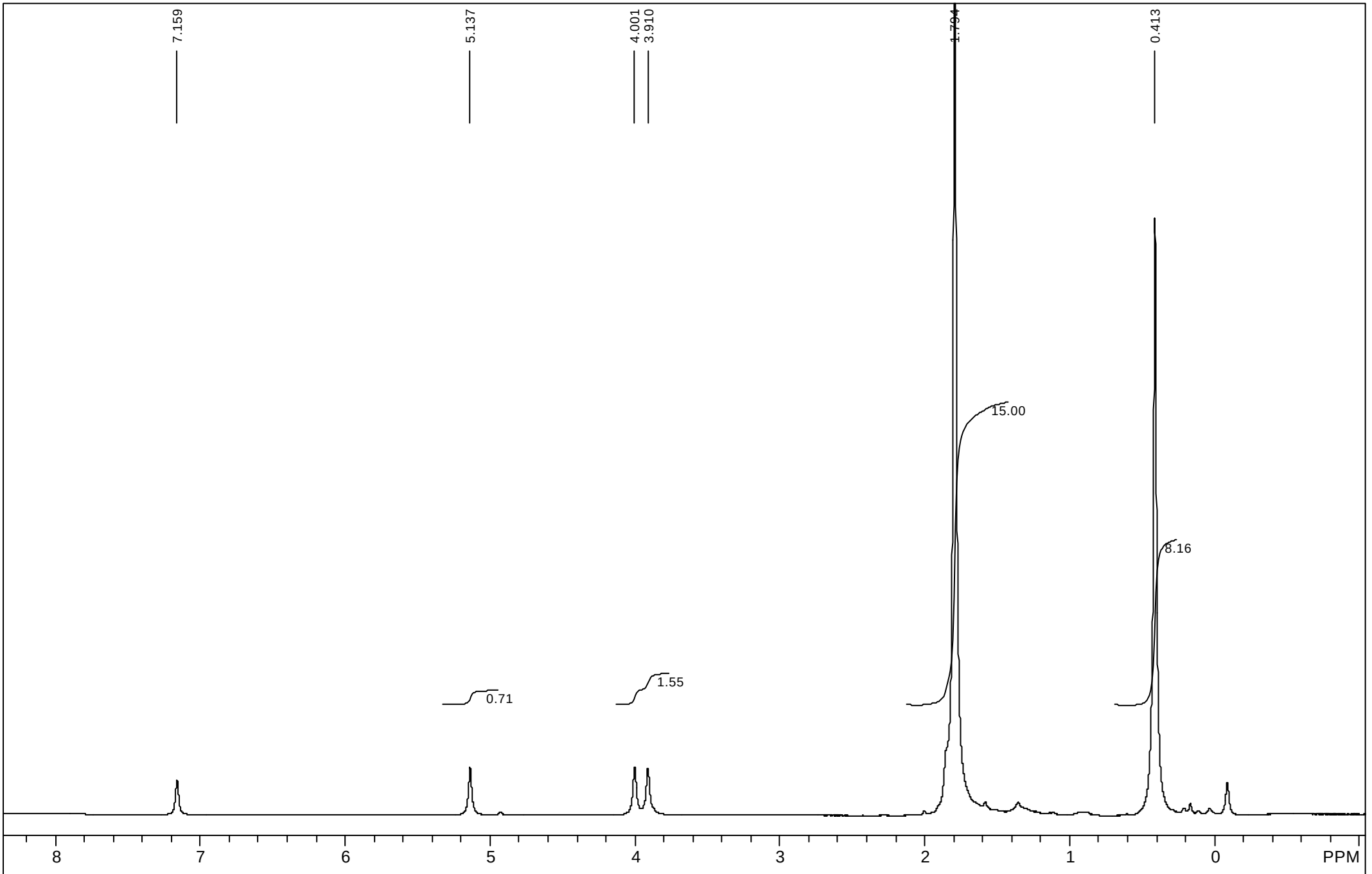
2-(diphenylphosphinyl)-1',2',3',4',5'-pentamethylazaferrocene, 4c

USER: -- DATE: Sep 7

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8063.9		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 1.0 sec	NA: 256	LB: 1.0		WinNuts - jgh9aC

2-(Diphenylphosphinyl)-1',2',3',4',5'-pentamethylazaferrocene, **4c**

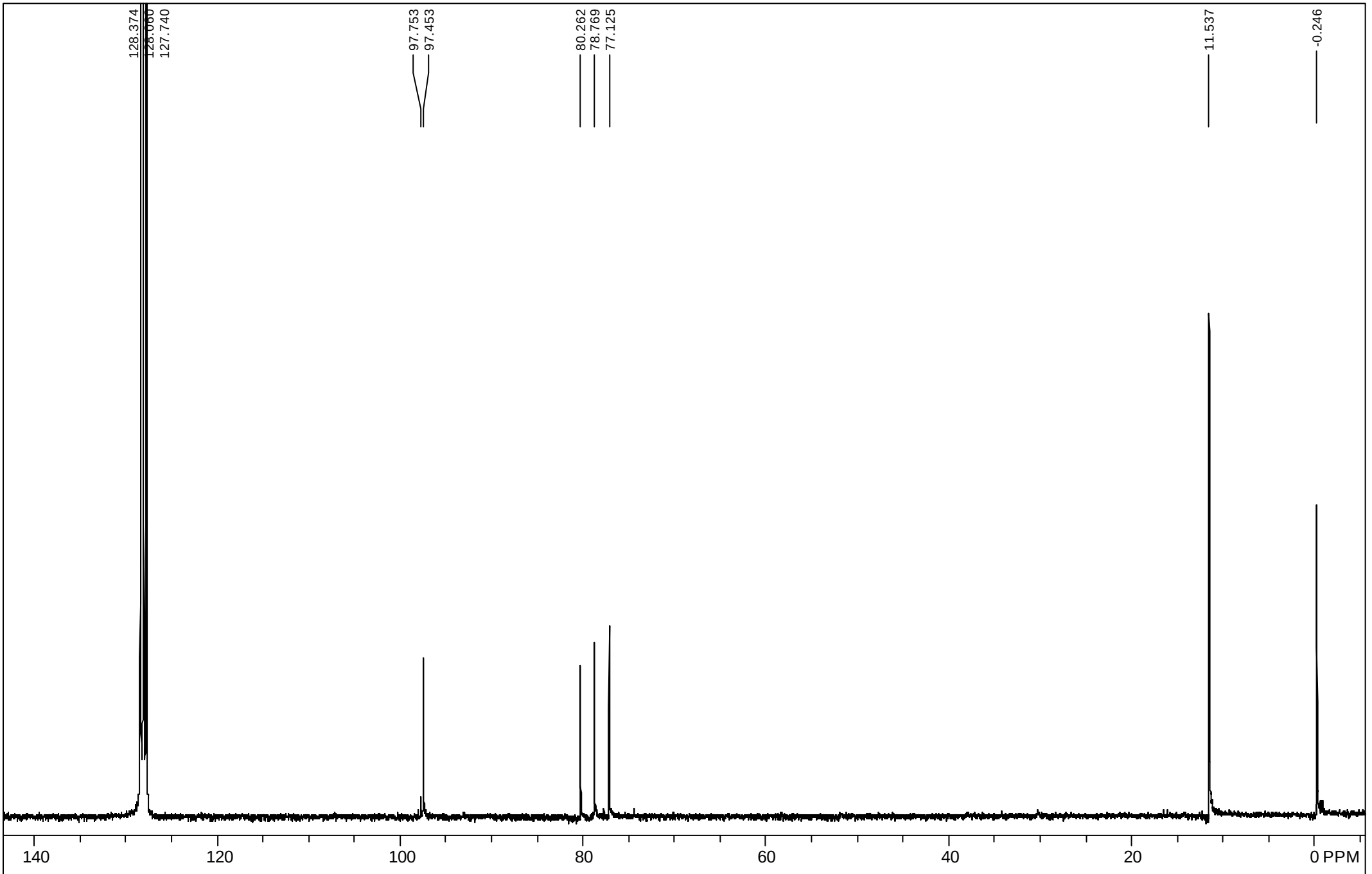




2-(trimethylsilyl)-1',2',3',4',5'-pentamethyl azaferrocene, 4d

USER: -- DATE: Sep 7

F1: 300.059	F2: 75.457	SW1: 6000		OF1: 1458.7		PTS1d: 32768	
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - jgh7bH

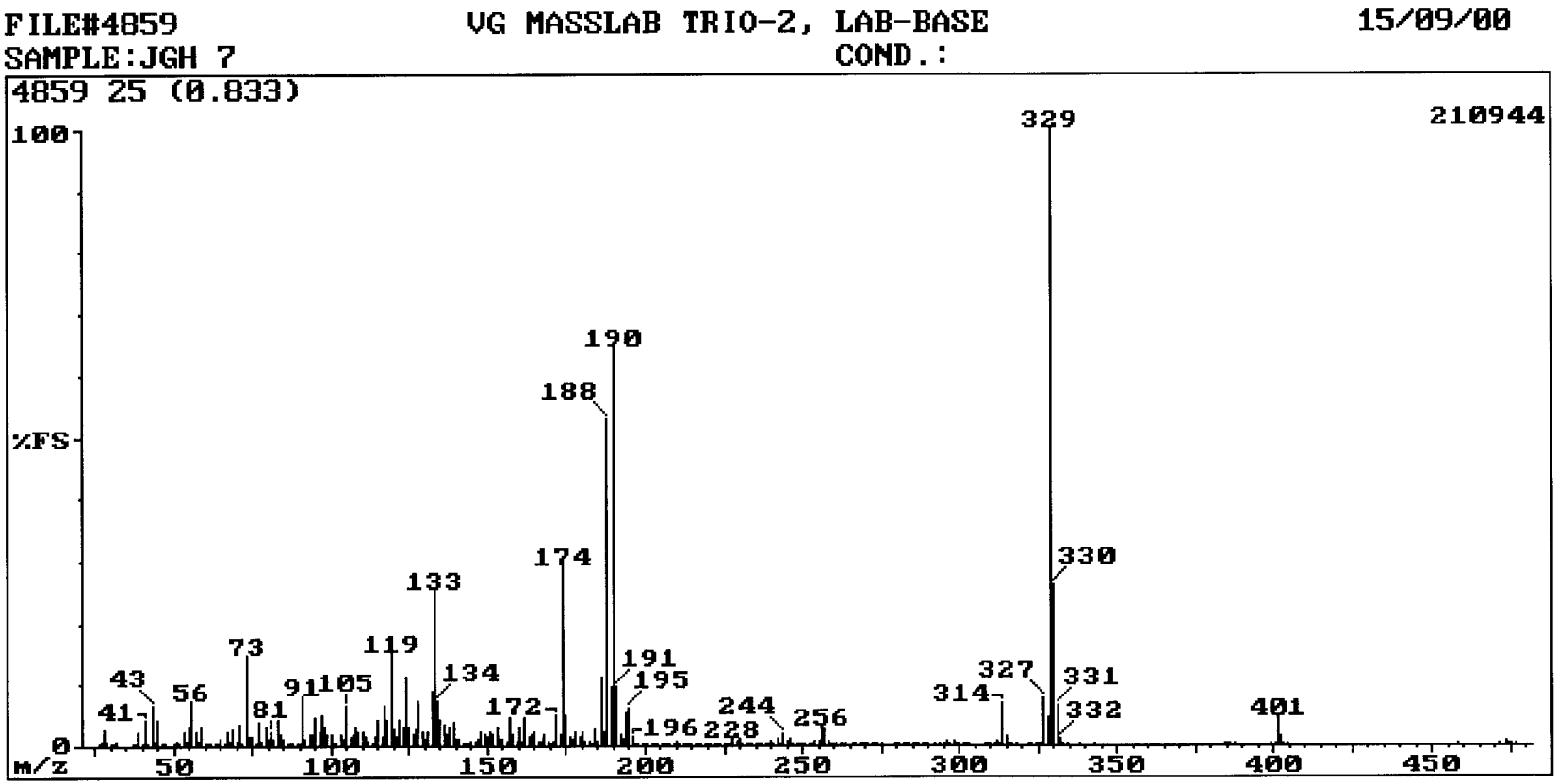


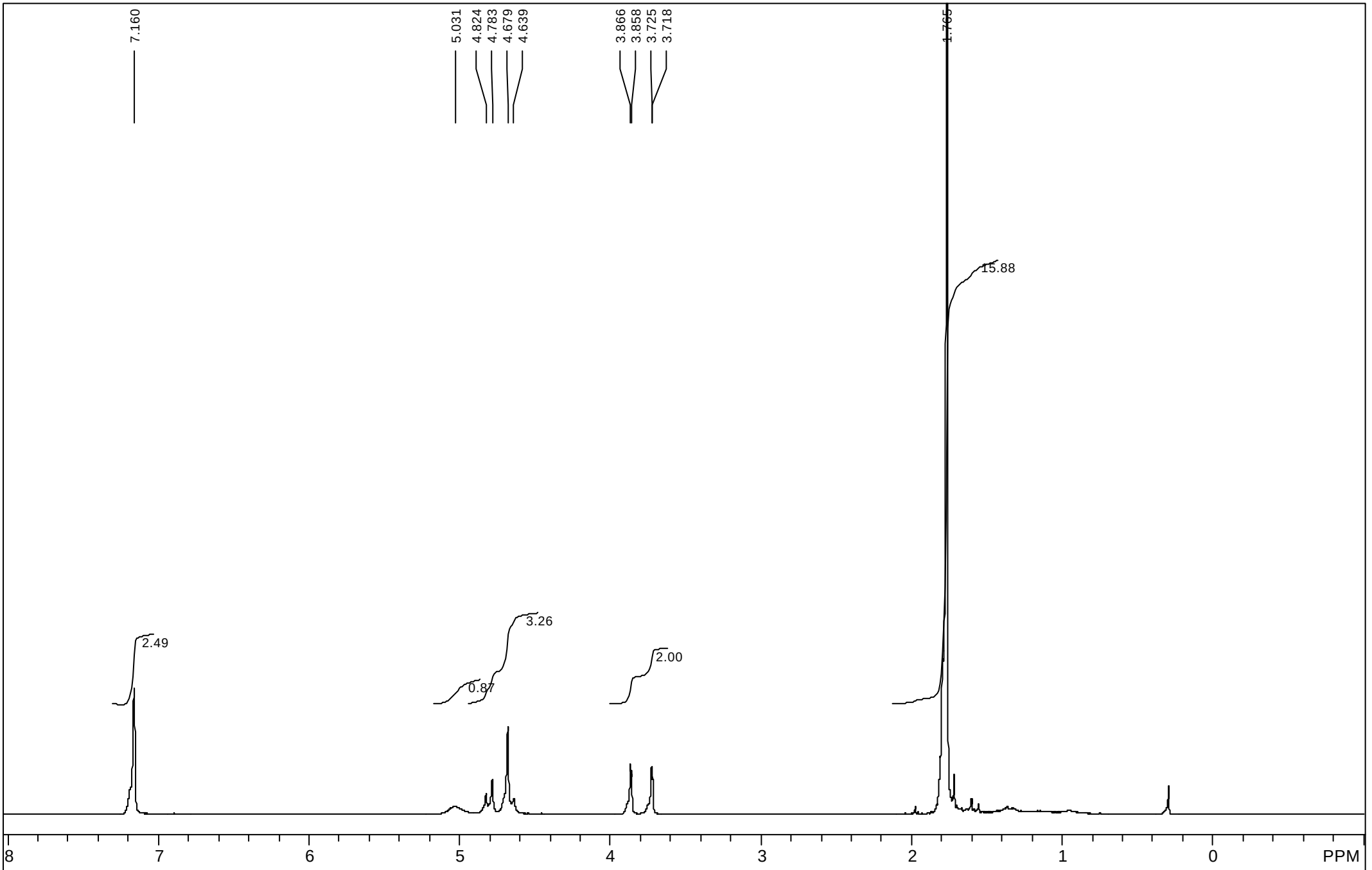
2-(trimethylsilyl)-1',2',3',4',5'-pentamethyl azaferrocene, 4d

USER: -- DATE: Sep 7

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8064.7		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 1.0 sec	NA: 2000	LB: 1.0		WinNuts - jgh7bC

2-(Trimethylsilyl)-1’,2’,3’,4’,5’-pentamethylazaferrocene, **4d**

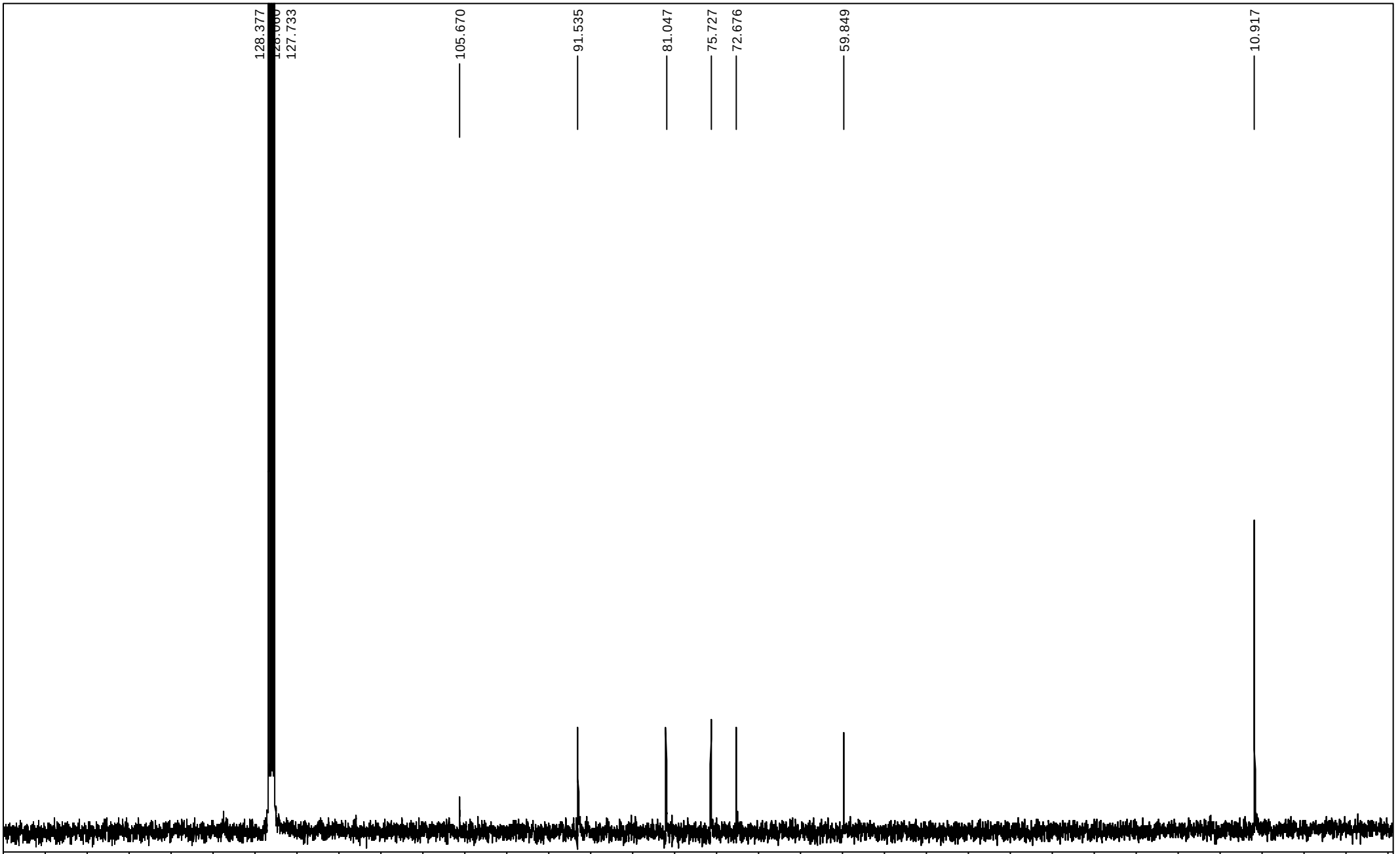




2-Hydroxymethyl-1',2',3',4',5'-pentamethyl azaferrocene, 4e

USER: -- DATE: Oct 5

F1: 300.059	F2: 75.457	SW1: 6000		OF1: 1459.2		PTS1d: 32768	
EX: s2pul		PW: 4.7 usec	PD: 1.0 sec	NA: 8	LB: 0.3		WinNuts - jgh18aH



2-Hydroxymethyl-1',2',3',4',5'-pentamethyl azaferrocene, 4e

USER: -- DATE: Oct 4

F1: 75.458	F2: 300.059	SW1: 17000		OF1: 8063.9		PTS1d: 32768	
EX: s2pul		PW: 5.7 usec	PD: 1.0 sec	NA: 256	LB: 1.0		WinNuts - jgh18aC

2-(Hydroxymethyl)-1’,2’,3’,4’,5’-pentamethylazaferrocene, **4e**