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Profiling of Secondary Metabolites in Aerial Parts of *Phanera bracteata*

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Abstract

The flavonoid 4',5,7-trihydroxy-6,8-dimethylflavanone (farresol) and 3',4',-4trihydroxy chalcone (isoliquiritigenin) together with triterpenoid (friedelin) were isolated from the aerial parts of *P. bracteata*. The structure of these compounds was determined on the basis of spectroscopic data including UV, IR, 1-D and 2-D, NMR and mass spectral analysis. This is the first report on the occurrence of these compounds in this plant.

Keywords

Fabaceae, *Phanera bracteata*, Flavonoids

1. Introduction

One of the largest plant families is Fabaceae or Leguminosae dispersed in approximately 650 genera and 18,000 species [1], which are found in several areas of the world especially the tropics. There are three sub families of Fabaceae: Mimosoideae, Faboideae and Caesalpinoideae [1]. Many of these species are applied as folk medicine and feed in remote areas all over the world [1]. Phytochemical investigation of the Fabaceae family has been widely accomplished by different groups and the presence of flavonoids [1], alkaloids [2], stilbene [3], terpenoids [4], phenolic compounds [5], acylated triterpene glycosides [6] and nitro compounds [7] has been reported. Many of these constituents were found to show antimalarial [8], antitumour [9], anti-inflammatory [10] [11], antihyperlipidemic [12], anti-cancer [13], antibacterial [14], insecticidal [15] and antimicrobial activities [16]. *Phanera bracteata* Benth or *Bauhinia bracteata* (Graham ex Benth.) Baker is a woody climber tree native of the tropical area, located mainly in the Southeast Asian region [17]. The vine of *P. bracteata* is used in folk medi-

cine for the treatment of irritated skin and as a rash ointment. There has been no previous report on the chemical investigation for this species. In the present study, we report herein the isolation and characterization of friedelin (1), farresol (2) and isoliquiritigenin (3) from the aerial parts of *P. bracteata*.

2. Materials and Methods

2.1. General Procedures

Melting points were determined on a Büchi 322 micro melting point apparatus and remain uncorrected. Infrared spectra (IR) were recorded on KBr pellets with a Shimadzu 8900 FT-IR spectrophotometer. Silica gel 60 H (E. Merck. 70 - 230 mesh ASTM, cat. No. 7734) and Sephadex LH-20 (20 - 150 μm) were used for column chromatography. TLC analysis was performed on aluminium sheets of silica gel 60 PF_{254} and the compounds were visualized under ultraviolet light. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ and CD_3OD solutions on a BrÜker AV-500 spectrometer. Chemical shifts are in δ (ppm) with tetramethylsilane (TMS) as an internal standard. Low resolution mass spectra were recorded on a Thermo Finnigan Polaris Q mass spectrometer at 70 eV (probe) and EIMS were measured with a BrÜker Esquire apparatus.

2.2. Plant Material

The aerial parts (fully grown trees) of *P. bracteata* were collected in May 2016 from tropical dry dipterocarp forest, Huai Yang Waterfall National Park, Prachuap Khiri Khan Province and authenticated by Mr. Narong Nuntasaen. The aerial parts were air-dried for one week and ground to a powder. A voucher specimen (BKF No. 147626) was deposited at the Forest Herbarium, Department of National Park, Wildlife and Plant Conservation, Ministry of Natural Resources and Environment, Bangkok, Thailand.

2.3. Extraction and Isolation

The air-dried powdered aerial parts of *P. bracteata* (12 kg) were percolated with hexane (25 litters × 3 days × 5 times) and then extracted with ethyl acetate (25 litters × 3 days × 5 times) at room temperature, respectively, followed by filtration (cotton wool). The filtrates were combined and evaporated under reduced pressure to afford the hexane (31.21 g) and ethyl acetate extracts (314.40 g) respectively.

The hexane extract was chromatographed on a silica gel column with gradient mixtures of hexane: ethyl acetate (100:0 to 70:30). Fractions were collected and combined on the basis of TLC characteristic technique. The solvents were evaporated to dryness to afford four fractions (F_1-F_4). F_2 (2.88 g) was recrystallized from 95% ethanol to give compound (1) (470 mg) as white needles.

The ethyl acetate extract was subjected to column chromatography over silica gel, eluted with hexane, gradually enriched with ethyl acetate (100:0 to 0:100) to give fractions $F_1' - F_{10}'$. Fraction F_4' (4.17 g) showed similar TLC characteristic to fraction F_5' (4.79 g), hence they were combined and subjected to column

chromatography over silica gel eluted with a gradient hexane:ethyl acetate (95:5 to 80:20) to yield seven subfractions (B_1-B_7). Fraction B_2 was separated on a silica gel column eluted with a gradient of hexane:ethyl acetate (90:10 to 10:90) to obtain six subfractions (C_1-C_6). Fraction C_4 (1.71 g) was fractionated by Sephadex LH-20 (methanol) to afford six subfractions (An_1-An_6). Then, An_5 was recrystallized from 95% ethanol to provide compound (2) (107 mg) as yellow needles. Fraction F_6' (4.75 g) was purified by column chromatography over silica gel, eluted with various proportions of hexane: ethyl acetate (100:0 to 40:60) to give four subfractions (E_1-E_4). Fraction E_2 (0.24 g) was subjected to column chromatography over silica gel, eluted with hexane:ethyl acetate (100:0 to 50:50), followed by methanol in ethyl acetate (10:90) to afford three subfractions (G_1-G_3). Fraction G_2 (0.70 g) was subjected to repeated column chromatography by Sephadex LH-20 (methanol) to give three subfractions (Bn_1-Bn_3). Subfraction Bn_2 was recrystallized from 95% ethanol to yield compound (3) (89 mg) as pale yellow needles.

3. Results

Chromatographic separations of the hexane and ethyl acetate extracts from the aerial parts of *P. bracteata* afforded compound (1)-(3) respectively. The structure of these compounds was elucidated by comparison of ^{1}H and ^{13}C NMR spectral data with those in previous reports [18] [19] [20] [21] [22].

4. Discussion

Compound (1) was obtained from the crude hexane extract as white needles (470 mg) with m.p. 253˚C - 254˚C. The EI-MS gave the molecular ion peak at m/z 426, which indicated the molecular formula $C_{30}H_{50}O$. Comparison of the NMR spectral data with those in the literature [18] suggested that the compound (1) is a pentacyclic triterpene substituted by an oxo group at position 3 and by methyl groups at the 4, 5, 9, 13, 14, 17, and 20-positions. The ^{13}C-NMR spectrum showed thirty carbons resonances. The DEPT spectrum indicated the presence of a ketone carbonyl at δ 213.2, eight methyl, eleven methylene, four methine and six quaternary carbons. By comparison of the ^{13}C-NMR spectral data with previous reported spectral data [18], the Compound (1) was identified as friedelin. Compound (2) was isolated from the crude ethyl acetate extract of *P. bracteata* as yellow needles (107 mg) with m.p. 210˚C - 211˚C. The EI-MS gave the molecular ion peak at m/z 300, which indicated the molecular formula $C_{17}H_{16}O_5$. The ^{1}H NMR spectral data of (2) showed resonances at δ 12.29 (OH), 7.35 (2H), 6.85 (2H), 5.31 (1H) 3.07 (1H), 2.72 (1H) 2.02 (3H), and 2.00 (3H) in agreement with the reported spectral data [18]. The ^{13}C NMR spectral data of (2) showed seventeen carbons resonances, which were assigned to a ketone carbonyl at δ 197.0, four oxygenated carbon atoms at 157.4, 157.9, 158.9 and 162.7, four aromatic carbon atoms at δ 114.9 and 127.4, one methylene at δ 42.7, one oxymethine carbon atoms at δ 78.6, four quaternary aromatic carbon atoms at δ 101.9, 102.7, 103.4 and 130.1 and two methyl carbon atoms for the remaining signals at δ 6.0

and 6.7 respectively. The ^{1}H and ^{13}C NMR spectral data of compound (2) were consistent with those of farresol [18], hence the structure of compound (2) was determined to be farresol. Furthermore, compound (3) was obtained from the crude ethyl acetate as yellow needles (89 mg) with m.p. 192˚C - 193˚C and considered to be characteristic flavonoidal chalcone constituents of the Leguminosae family [23]. The EI-MS of (3) gave the M+1 peak at m/z 256, which indicated the molecular formula $C_{15}H_{11}O_4$. The ^{1}H NMR spectral date of (3) showed signals δ 8.00 (1H), 7.81 (1H), 7.65 (2H), 7.64 (1H), 6.87 (2H), 6.44 (1H), and 6.31 (1H). The ^{13}C NMR spectral data of (3) showed fifteen carbon resonances, which were assigned to a ketone carbonyl at δ 192.2, three oxygenated carbon atoms at 160.1, 165.0 and 166.1, seven aromatic carbon atoms at δ 102.4, 107.8, 115.5, 130.4 and 132.0, two methine carbon atoms at δ 117.0 and 144.2 and two quaternary aromatic carbon for the remaining signals at δ 113.3 and 126.5 respectively. The ^{1}H and ^{13}C NMR spectral data of compound (3) were consistent with those of isoloiquiritigenin [19] [20] [21] [22], hence the structure of compound (3) was determined to be isoliquiritigenin.

Friedelin (1)

White needles (EtOH). $C_{30}H_{50}O$, m.p. = 253˚C - 254˚C [18], EI-MS (m/z 426 $[M]^+$ (20), 273 (48), 231 (83), 91 (100). ^{1}H NMR ($CDCl_3$, 500 MHz): was in agreement with [18], ^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.2 (C-3), 59.6 (C-10), 58.3 (C-4), 53.3 (C-8), 43.0 (C-18), 42.3 (C-5), 41.7 (C-2), 41.4 (C-6), 39.8 (C-13), 39.4 (C-22), 38.4 (C-14), 37.6 (C-9), 36.2 (C-16), 35.8 (C-11), 35.5 (C-19), 35.2 (C-29), 32.9 (C-21), 32.6 (C-15), 32.2 (C-28), 31.9 (C-30), 30.6 (C-12), 30.2 (C-17), 28.3 (C-20), 22.4 (C-1), 20.4 (C-26), 18.8 (C-27), 18.3 (C-7), 18.1 (C-25), 14.8 (C-24), 6.9 (C-23).

4',5,7-Trihydroxy-6,8-dimethylflavanone (Farresol) (2)

Yellow needles (MeOH). $C_{17}H_{16}O_5$, m.p. = 210˚C - 211˚C [19], EI-MS (m/z) 300 $[M]^+$ (17), 299 (100), 282 (12), 207 (27), 194 (60), 180 (75), 167 (28), 152 (76), 124 (51), 95 (33), 77 (21). UV (MeOH) λ_{max} (log ε): 416 (4.15), 317 (4.34), 214 (4.70), 210 (4.66) nm. IR (KBr) ν_{max} 3794, 3448, 1637, 1600, 1521, 1323, 1191, 1176, 1124, 974, 945 cm^{-1}. ^{1}H NMR (CD_3OD, 500 MHz): δ 12.29 (br s, 5-OH), 7.35 (AA'BB', J6'5' = 8.6, H-6'), 7.35 (AA'BB', J2'3' = 8.6, H-2'), 6.85 (AA'BB', J5'6' = 8.6, H-5'), 6.85 (AA'BB', J3'2' = 8.6, H-3'), 5.31 (dd, J = 3.0, 12.9, H-2), 3.07 (dd, J = 12.9, 17.0, H-3ax), 2.72 (dd, J = 3.0, 17.0, H-3eq), 2.02 (s, 6-CH_3), 2.00 (s, 8-CH_3), ^{13}C NMR (CD_3OD, 125 MHz): δ 197.0 (C-4), 162.7 (C-7), 158.9 (C-5), 157.9 (C-4'), 157.4 (C-9), 130.1 (C-1'), 127.4 (C-2', 6'), 114.9 (C-3', 5'), 103.4 (C-6), 102.7 (C-8), 101.9 (C-10), 78.6 (C-2), 42.7 (C-3), 6.7 (8-CH_3), 6.0 (6-CH_3), HMBC correlations, H/C: 7.35 (H-6')/C-5', 4', 2', 2; 7.35 (H-2')/C-6', 4', 3', 2; 6.85 (H-5')/4', 3', 1'; 6.85 (H-3')/5', 4', 1'; 5.31 (H-2)/C-6', 4, 2', 1'; 3.07 (H-3ax)/C-4, 2, 1'; 2.72 (H-3eq)/C-4, 1'; 2.02 (6-CH_3)/C-7, 5); 2.00 (8-CH_3)/C-9. COSY correlations, H/H: 3'/2'; 5'/6'; 2ax/3ax, 3eq; 3ax/3eq.

3',4',4-Trihydroxychalcone (Isoliquiritigenin) (3)

Pale yellow needles (EtOH). $C_{15}H_{11}O_4$, m.p. = 192˚C - 193˚C [19], EI-MS (m/z) 256 $[M+1]^+$ (100), 241 (20), 164 (43), 152 (51), 138 (44), 121(31), 91 (34),

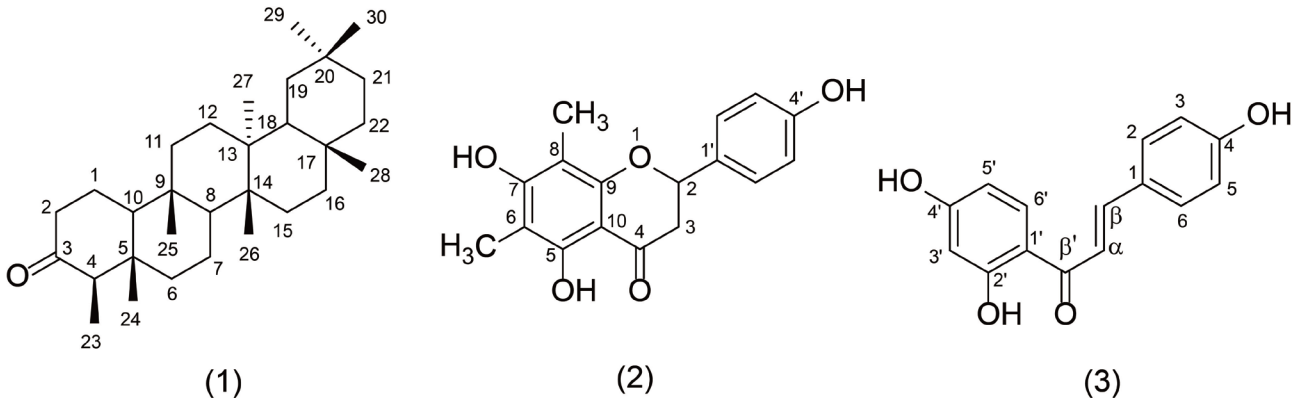

Figure 1. Chemical structure of Friedelin (1), Farresol (2) and Isoliquiritigenin (3).

65 (21), UV (MeOH) λ_{max} (log ε): 380 (1.86), 245 (1.15) nm. IR (KBr) ν_{max} 3457, 1610, 1500, 1363, 1261, 1215, 1170, 1122, 520 cm^{-1}. ^{1}H NMR (CD_3OD, 500 MHz): δ 8.00 (d, J = 9.2, H-6'), 7.81 (d, J = 15.2, H-β), 7.65 (AA'BB', J2,3 = 8.7, H-2), 7.65 (AA'BB', J6,5 = 8.7, H-6), 7.64 (d, J = 15.2, H-α), 6.87 (AA'BB', J3,2 = 8.7, H-3), 6.87 (AA'BB', J5,6 = 8.7, H-5), 6.44 (dd, J = 2.7, 9.2, H-5'), 6.31 (d, J = 2.7, 3'), ^{13}C NMR (CD_3OD, 125 MHz): δ 192.2 (C = O), 166.1 (C-2'), 165.0 (C-4'), 160.1 (C-4), 144.2 (C-β), 132.0 (C-6'), 130.4 (C-2, C-6), 126.5 (C-1), 117.0 (C-α), 115.5 (C-3, C-5), 113.3 (C-1'), 107.8 (C-5'), 102.4 (C-3'), HMBC correlations, H/C: 8.00 (H-6')/C-1', 2', 4', 5', β'; 7.81 (H-β)/C-1, 2, 6, α, β'; 7.65 (H-2)/C-1, 3, 4, 6, β; 7.65 (H-6)/C-1, 4, β; 7.64 (H-α)/C-1, β, β'; 6.87 (H-3)/C-1, 4, 5; 6.87 (H-5)/C-1, 3, 4; 6.44 (H-5')/C-1', 3', 4'; 6.31 (H-3')/C-1', 2', 4', 5'. COSY correlaions, H/H: 5'/6'; β/α; 2/3; 6/5; 5'/3' (**Figure 1**).

We have thus added two more flavonoids to the flavonoid constituents of *P. bracteata*. It is notable that flavonoids were found in the aerial part of this plant. The occurrence of flavonoids and chalcones may be a characteristic useful for further chemotaxonomic studies of the genus Phanera.

5. Conclusion

Our study of the aerial parts of *P. bracteata* (Fabaceae) led to the isolation and characterization of three compounds. These results reinforce the previous studies showing that the genus Phanera is considered a good source of flavonoids. We would like to note here that Friedelin (1), Farresol (2) and Isoliquiritigenin (3) were isolated for the first time from this genus. (Appendix)

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Appendix Figures

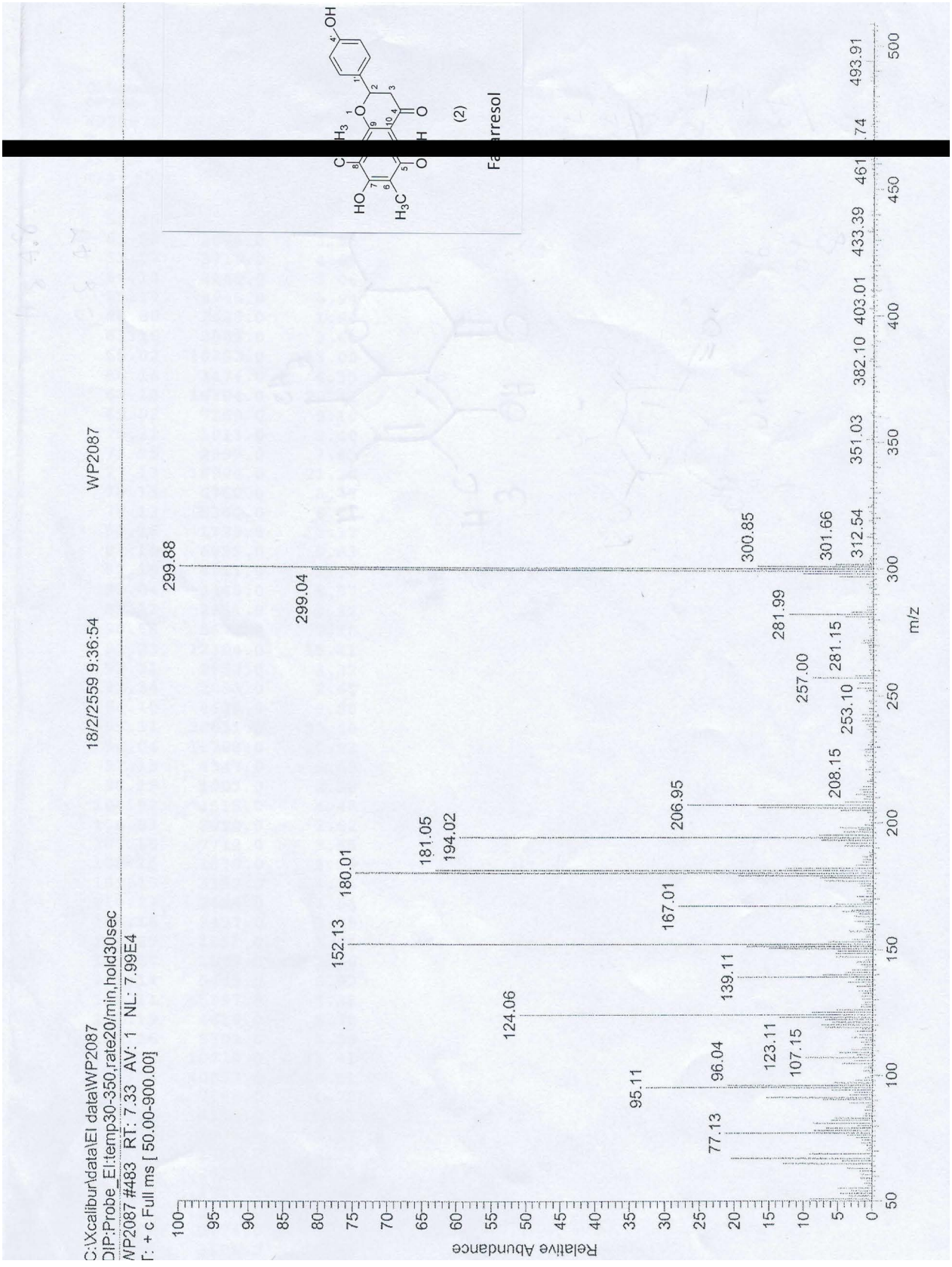
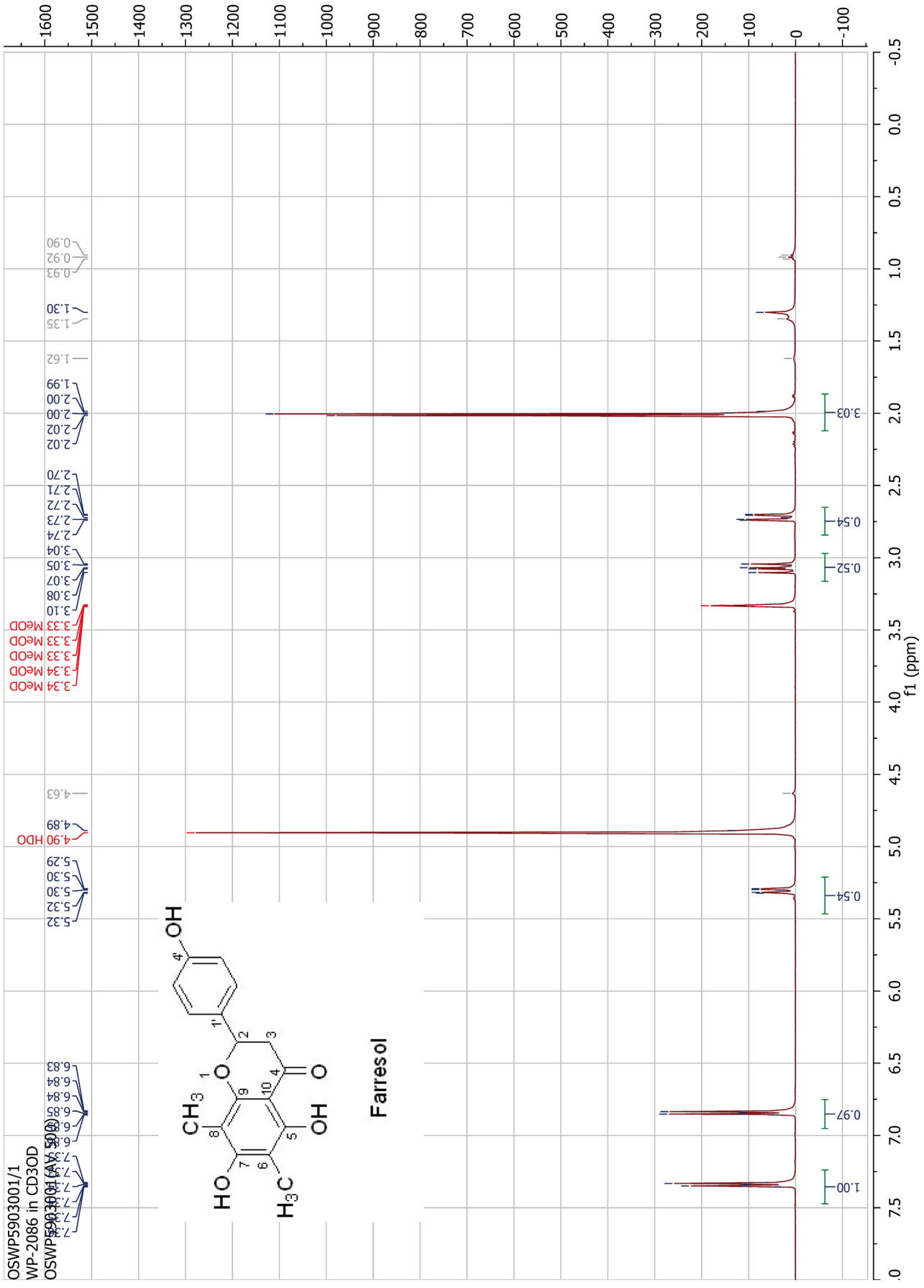


Figure S1. Farresol-MS spectrum.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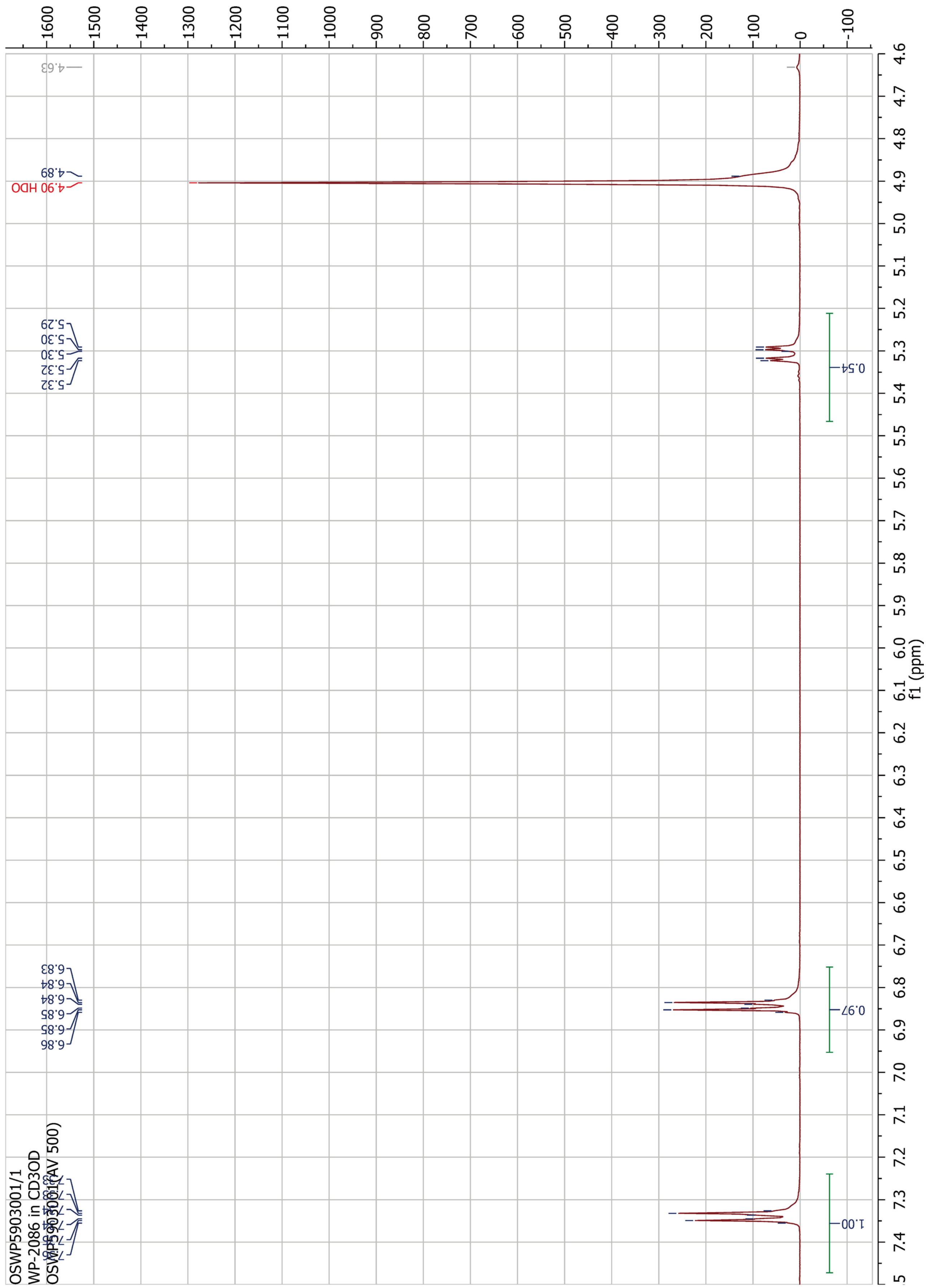
Farresol
f1 (ppm)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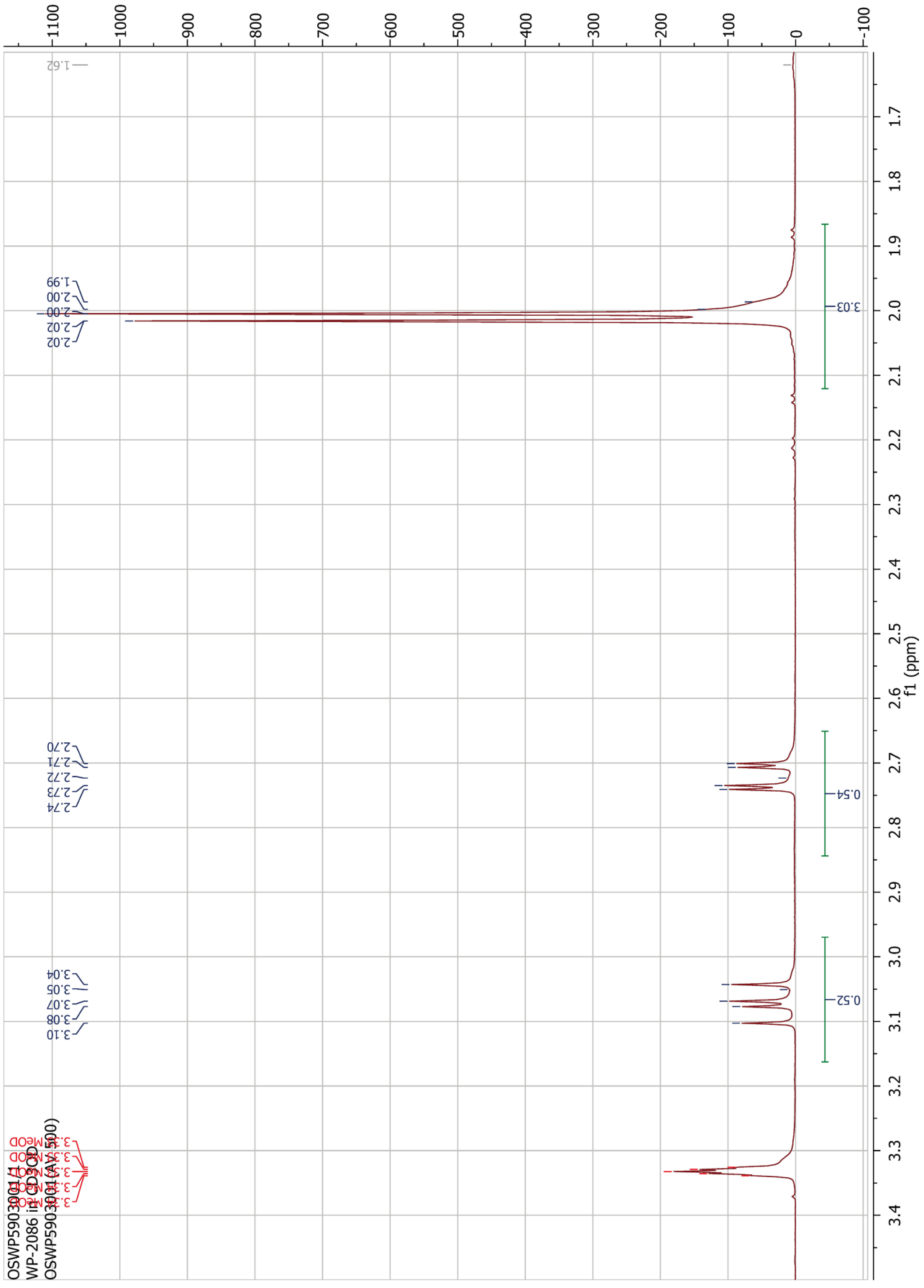
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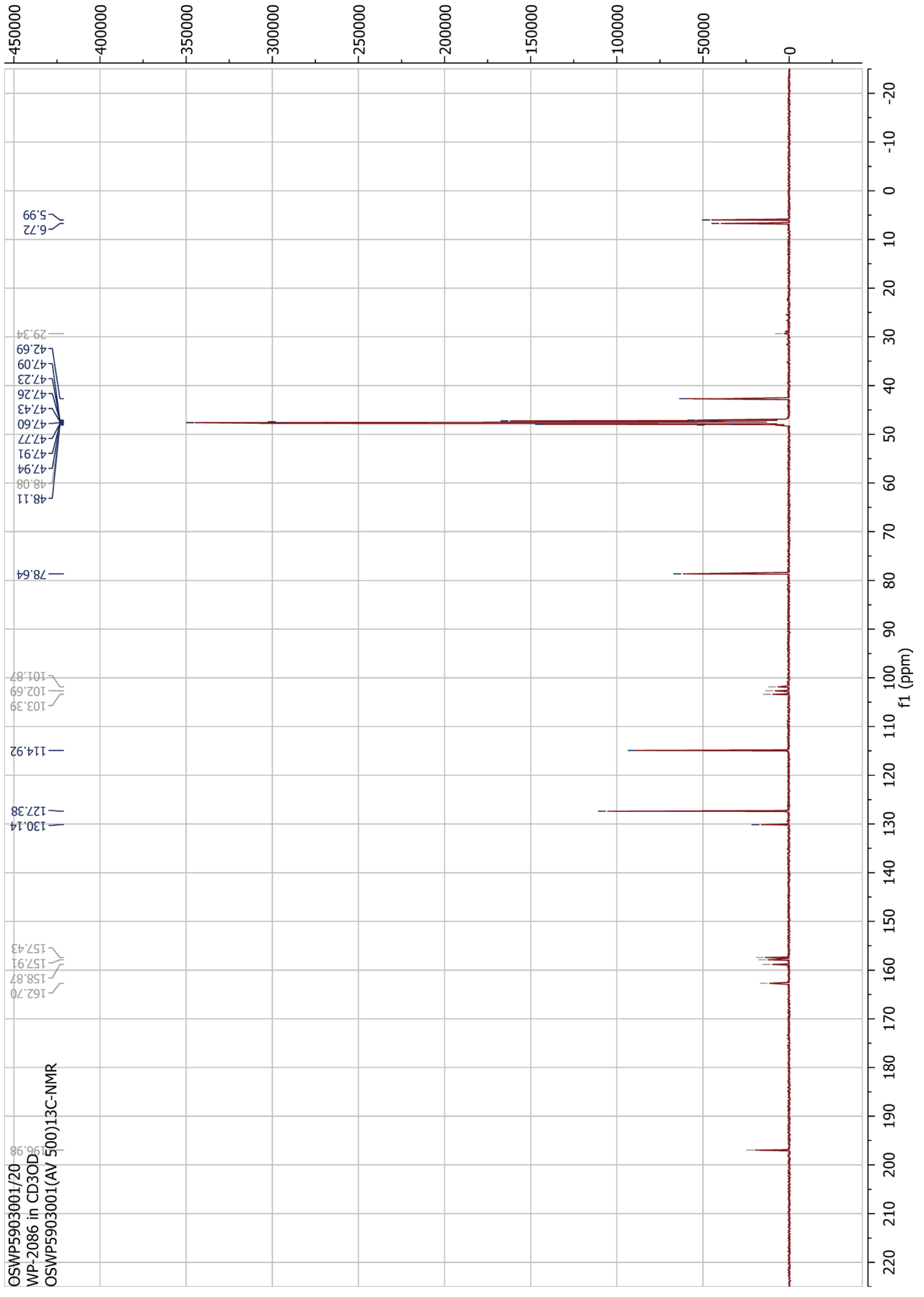
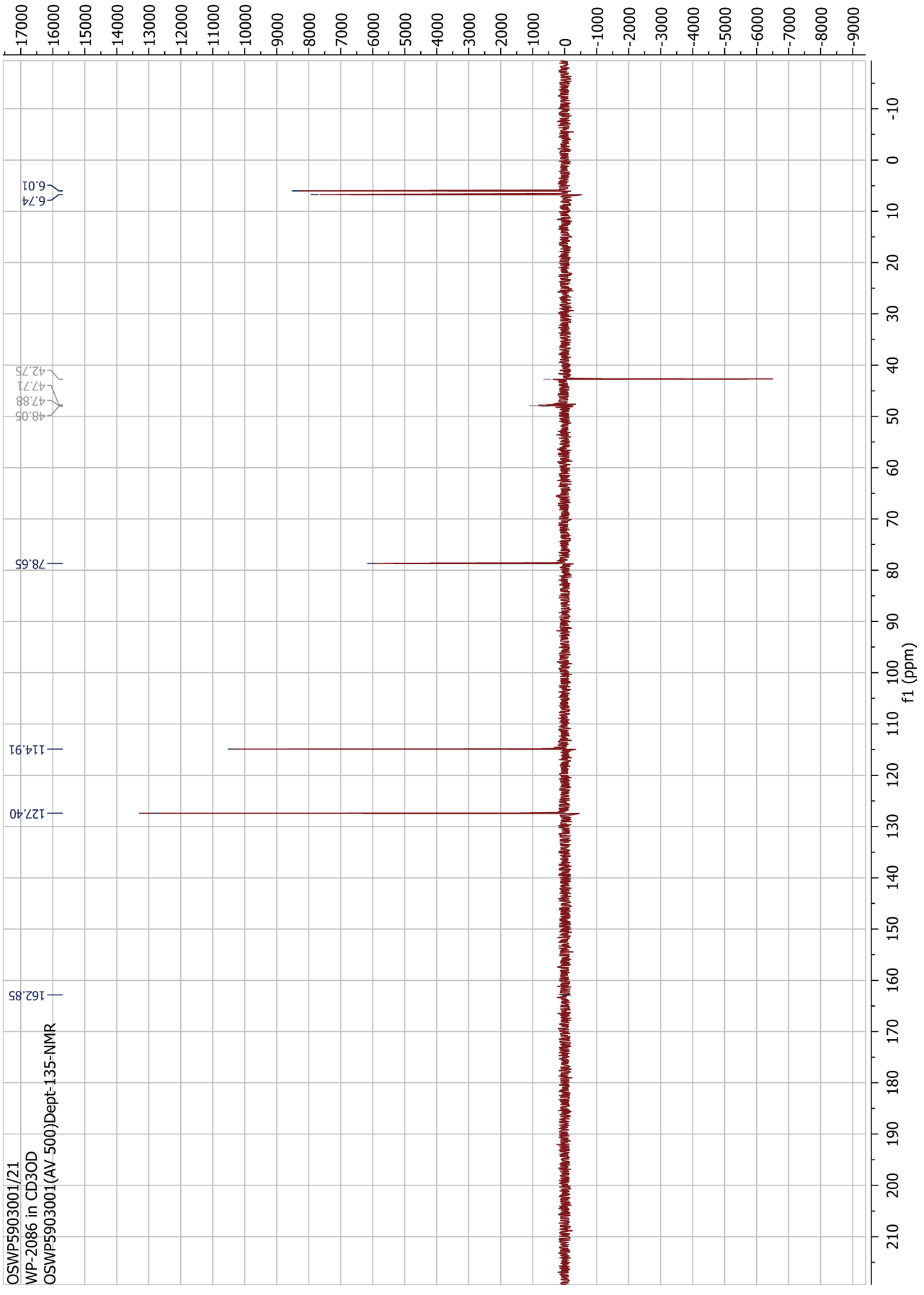
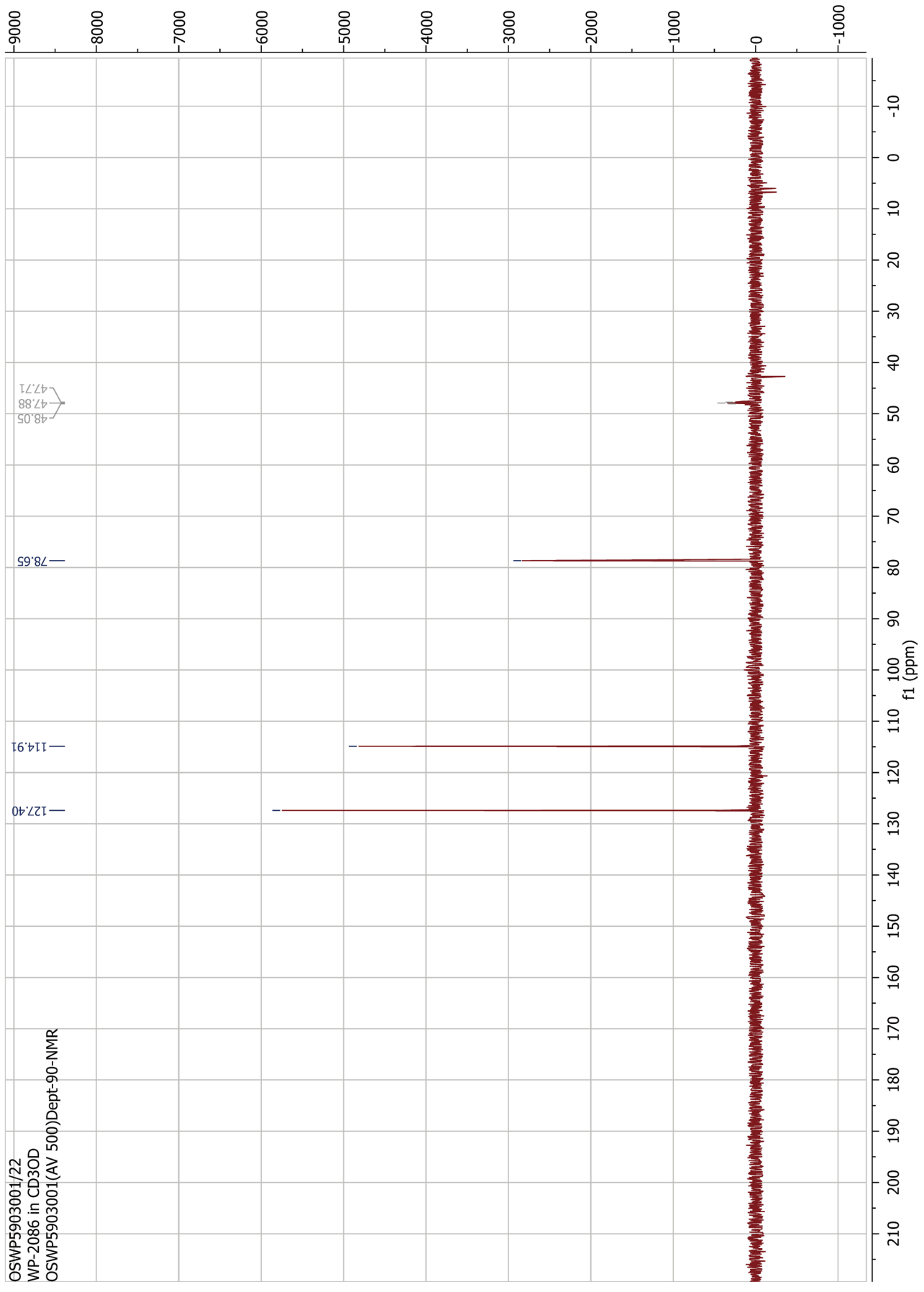
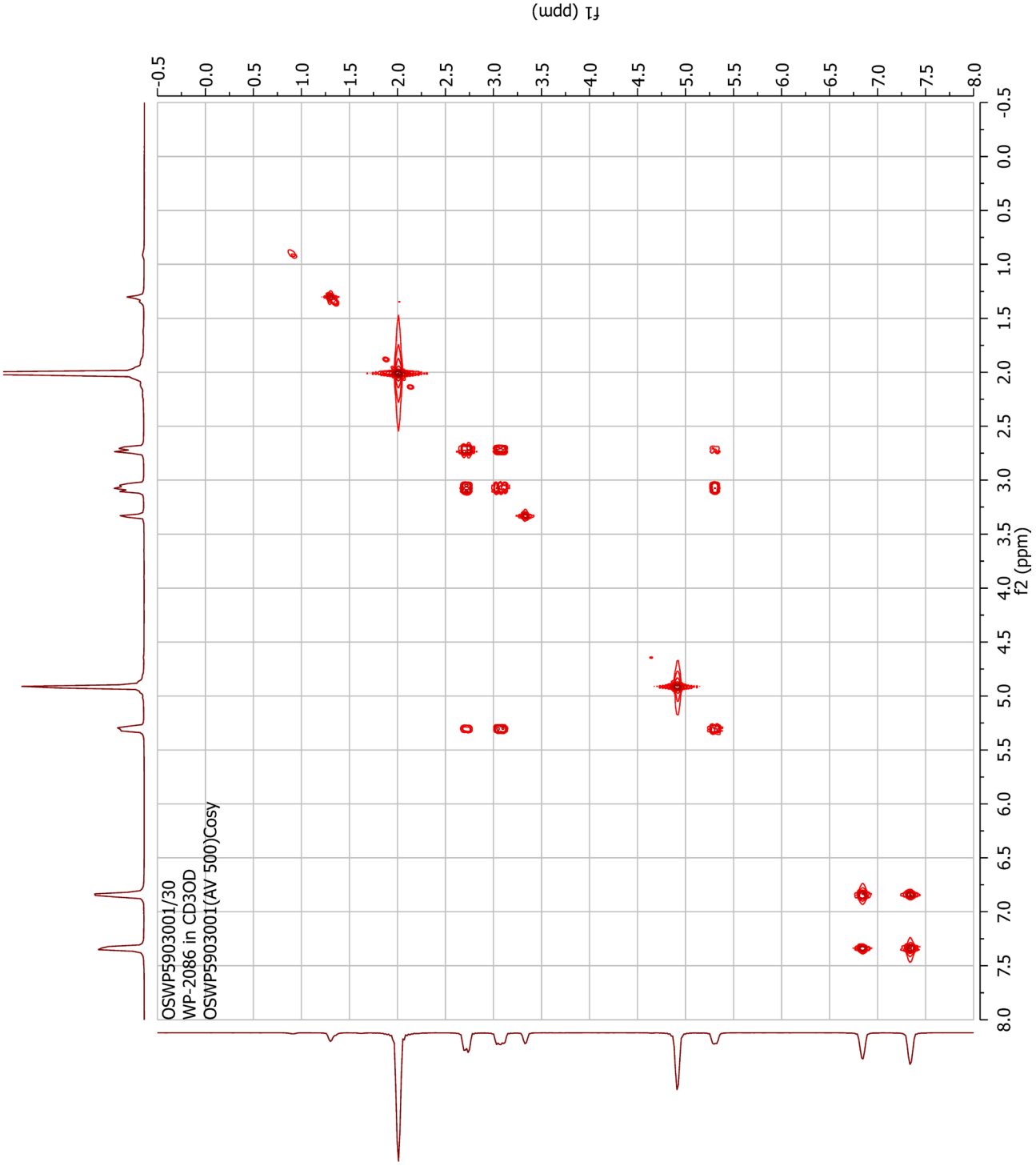
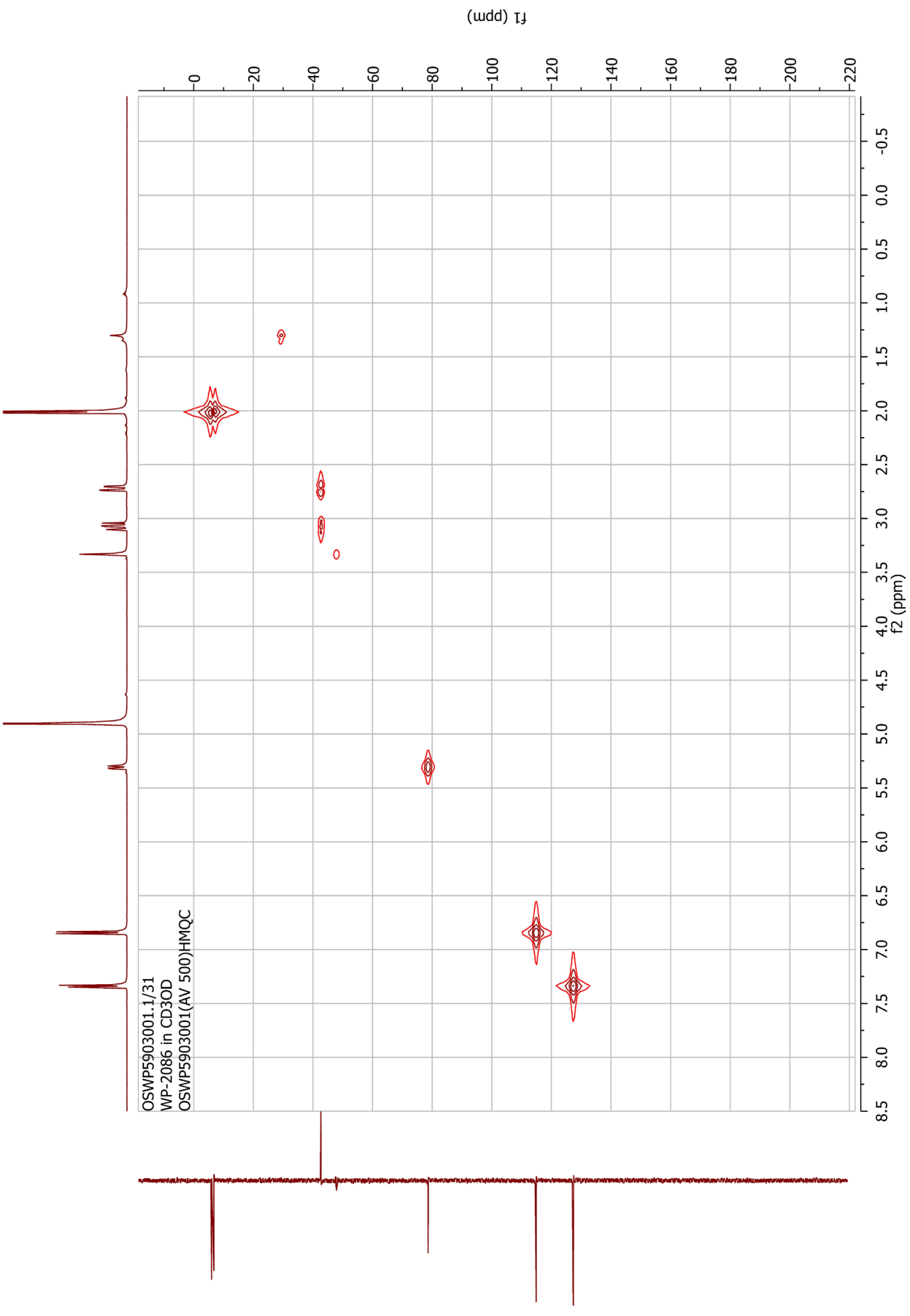
0.54
0.52


OSWP5903001/20
WP-2086 in CD3OD
OSWP5903001(AV 500)13C-NMR
f1 (ppm)


OSWP5903001/21
WP-2086 in CD3OD
OSWP5903001(AV-500)Dept-135-NMR
162.85
127.40
114.91
78.65
48.05
47.88
47.71
42.75
6.74
6.01
f1 (ppm)


OSWP5903001/22
WP-2086 in CD3OD
OSWP5903001(AV 500)Dept-90-NMR
127.40
114.91
78.65
48.05
47.88
47.71
f1 (ppm)


f1 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f2 (ppm)
OSWP5903001/30
WP-2086 in CD3OD
OSWP5903001(AV 500)Cosy


f1 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
f2 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
OSWP5903001.1/31
WP-2086 in CD3OD
OSWP5903001(AV 500)HMQC

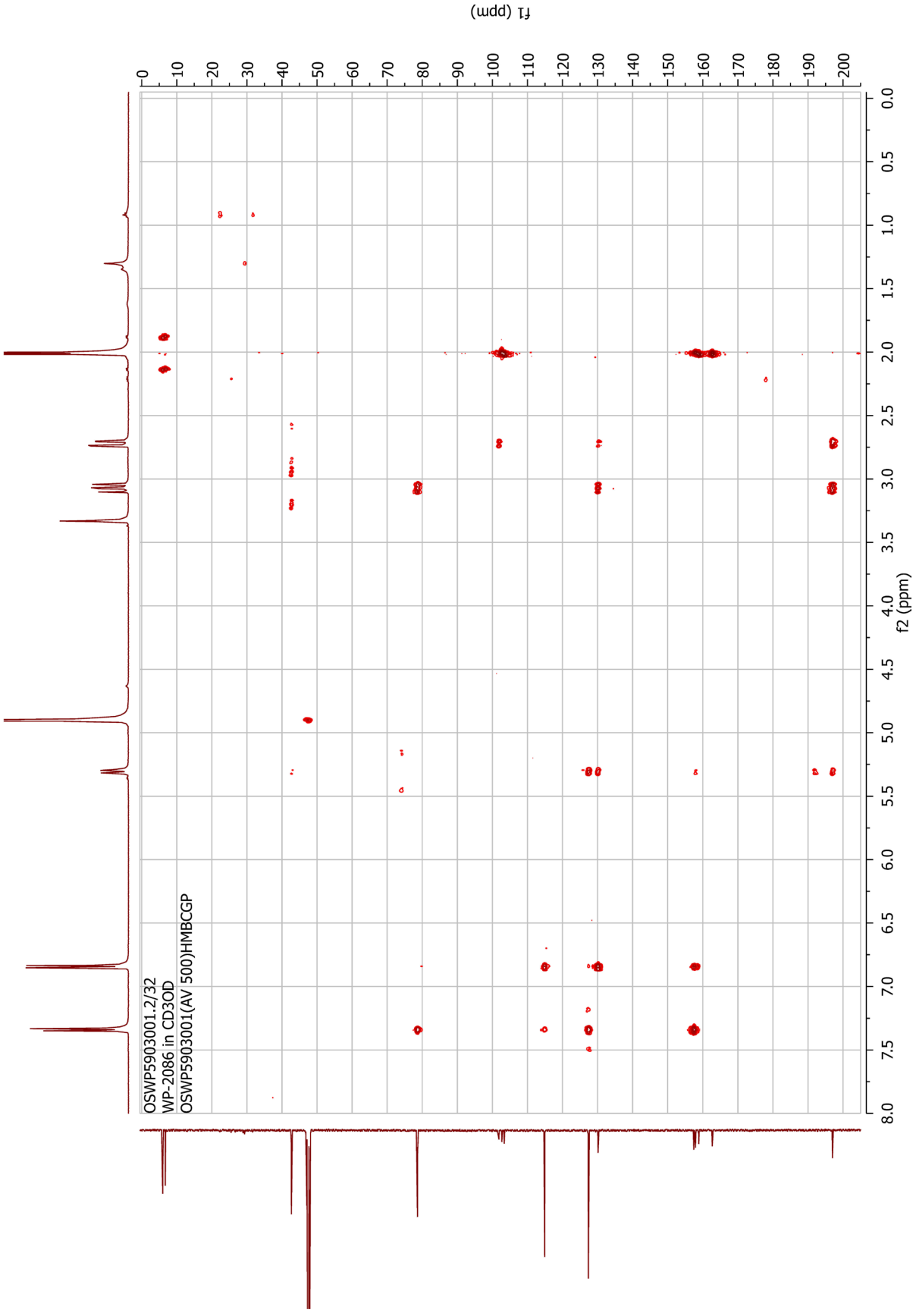
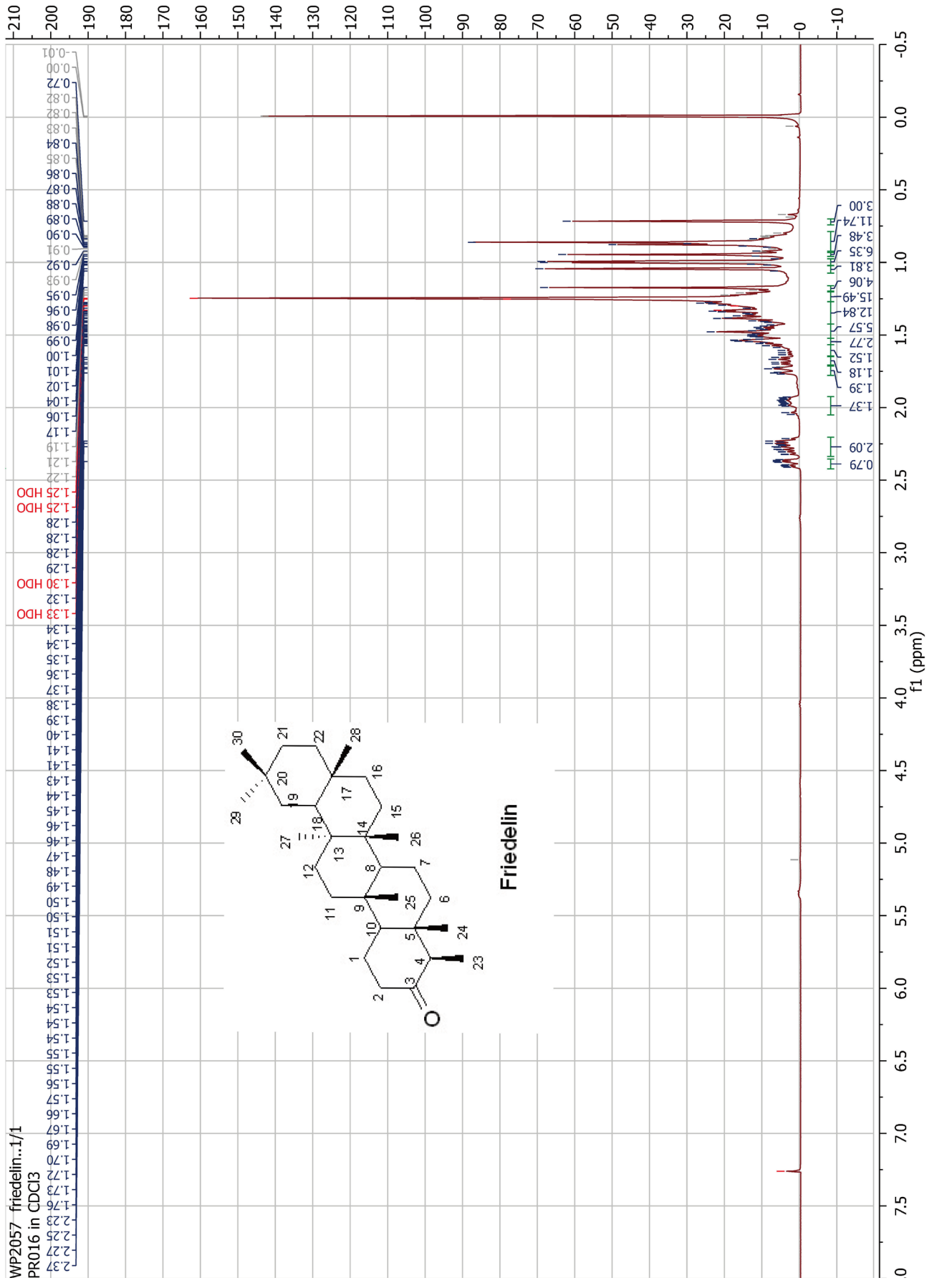
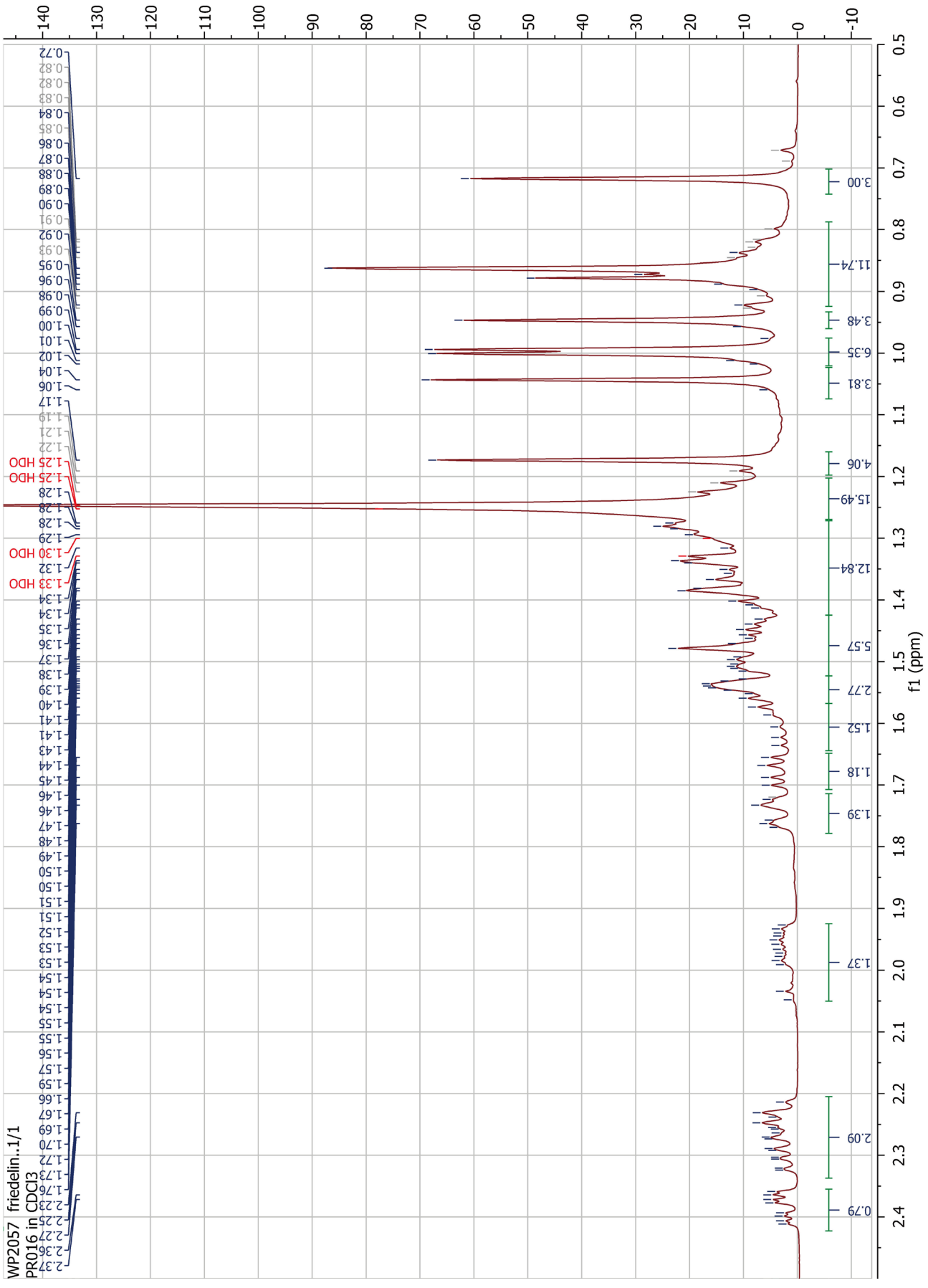
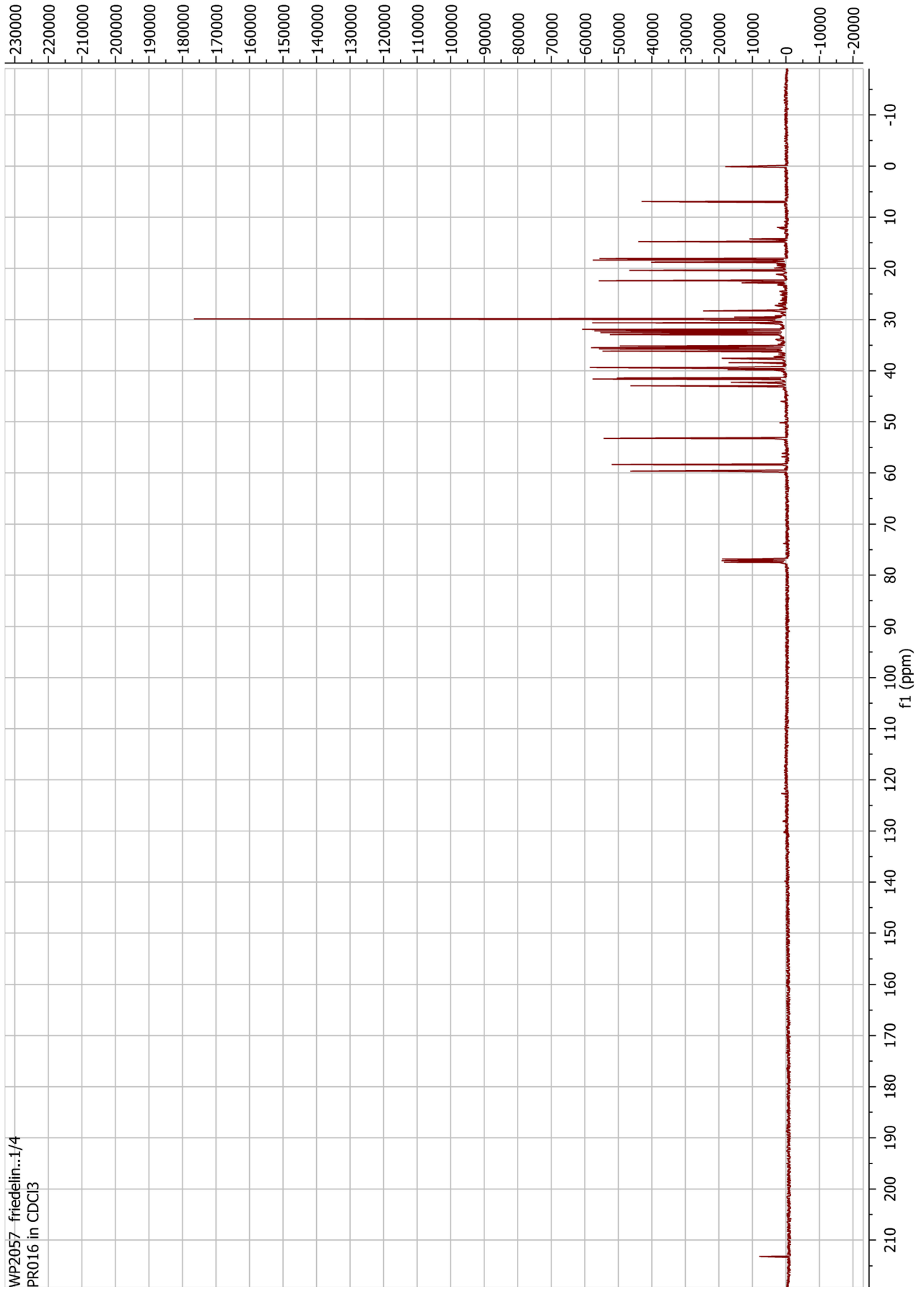
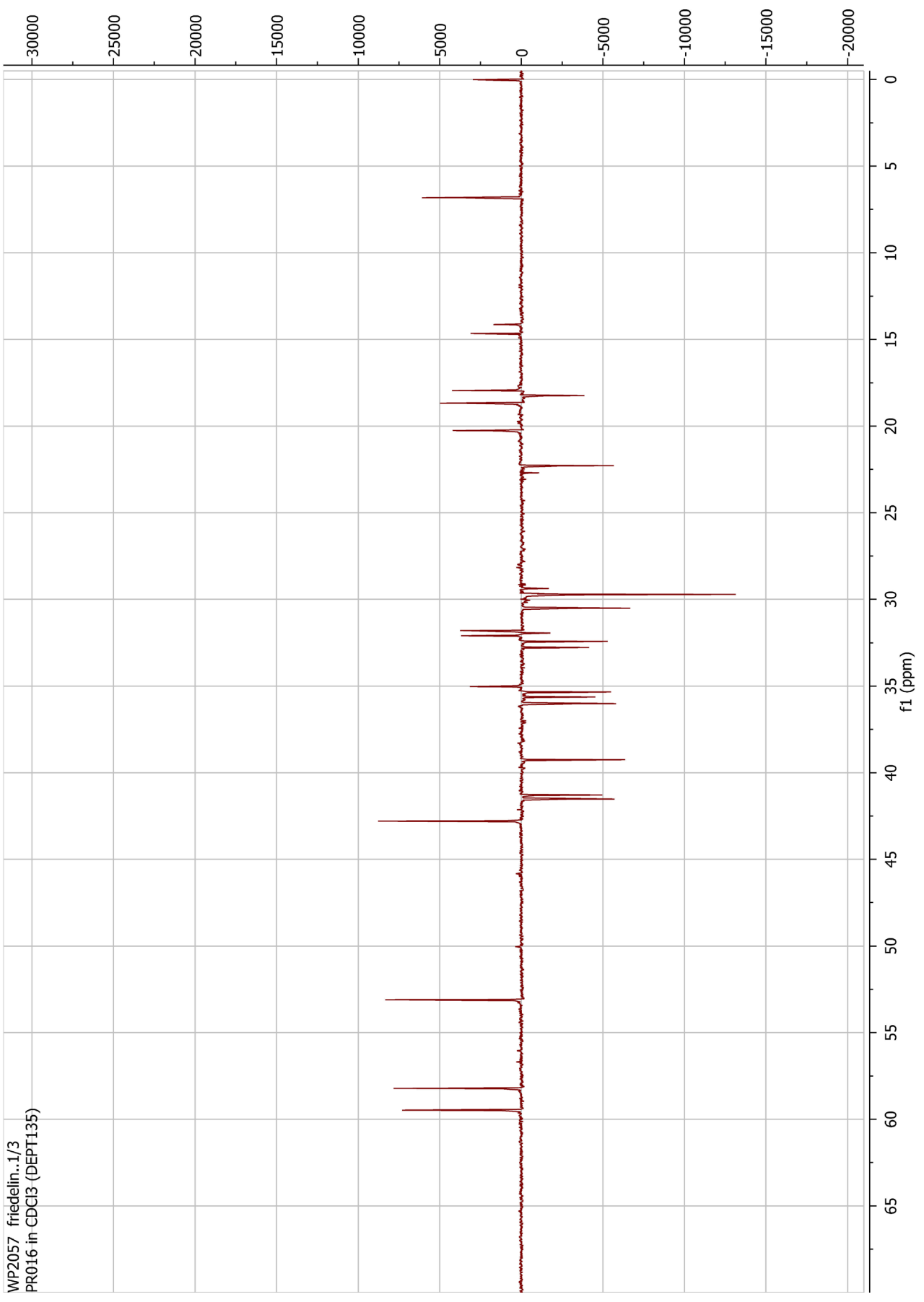


Figure S2. Farresol-NMR spectrums.


WP2057 friedelin..1/1
PR016 in CDCl3
Friedelin
f1 (ppm)


WP2057 friedelin..1/1
PR016 in CDCl3
f1 (ppm)
3.00
11.74
3.48
6.35
3.81
4.06
15.49
12.84
5.57
2.77
1.52
1.18
1.39
1.37
2.09
0.79
1.25 HDO
1.30 HDO
1.33 HDO


WP2057 friedelin..1/4
PR016 in CDCl3
f1 (ppm)


WP2057 friedelin..1/3
PR016 in CDCl3 (DEPT135)
f1 (ppm)

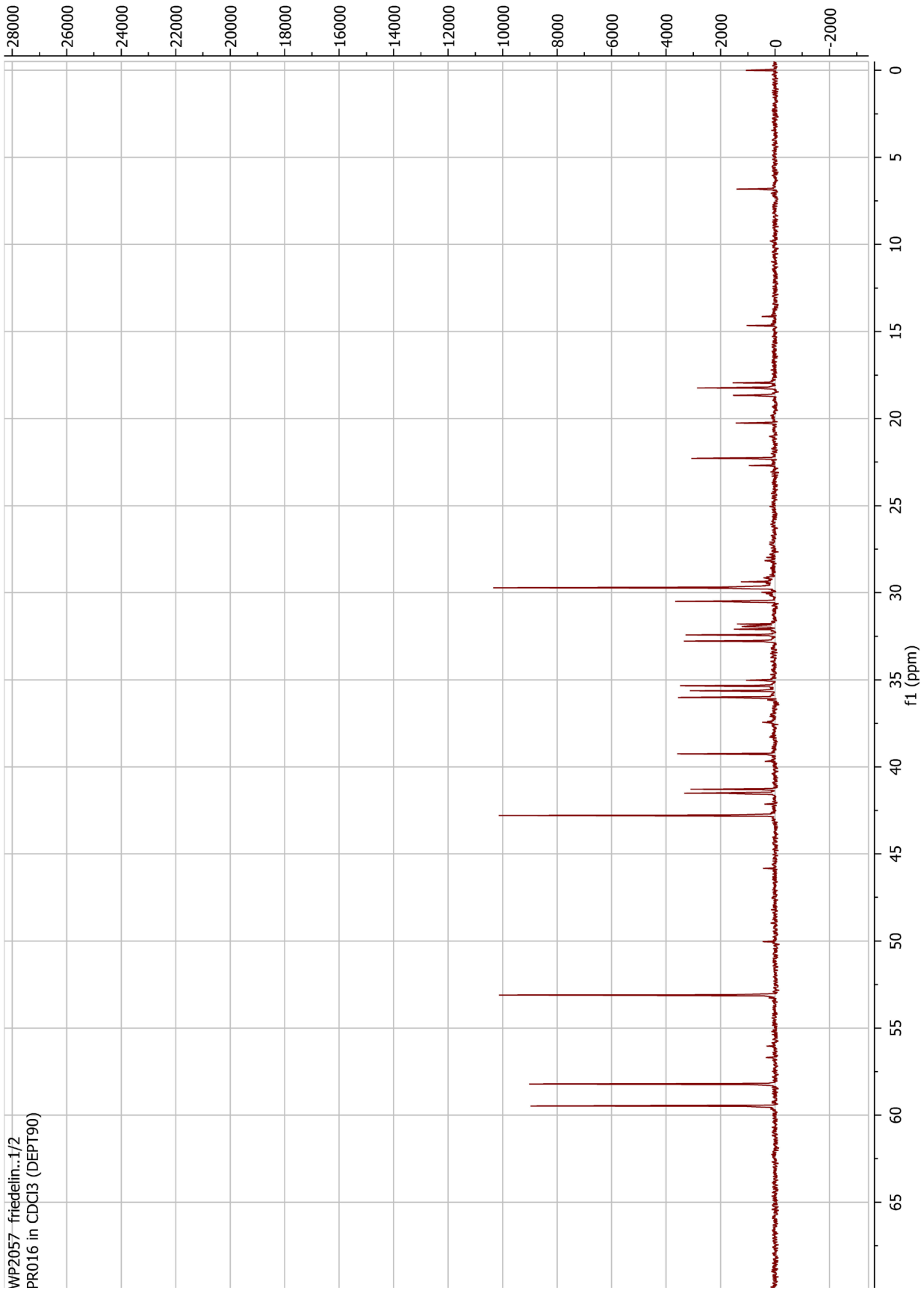


Figure S3. Fridelin-NMR spectrums.

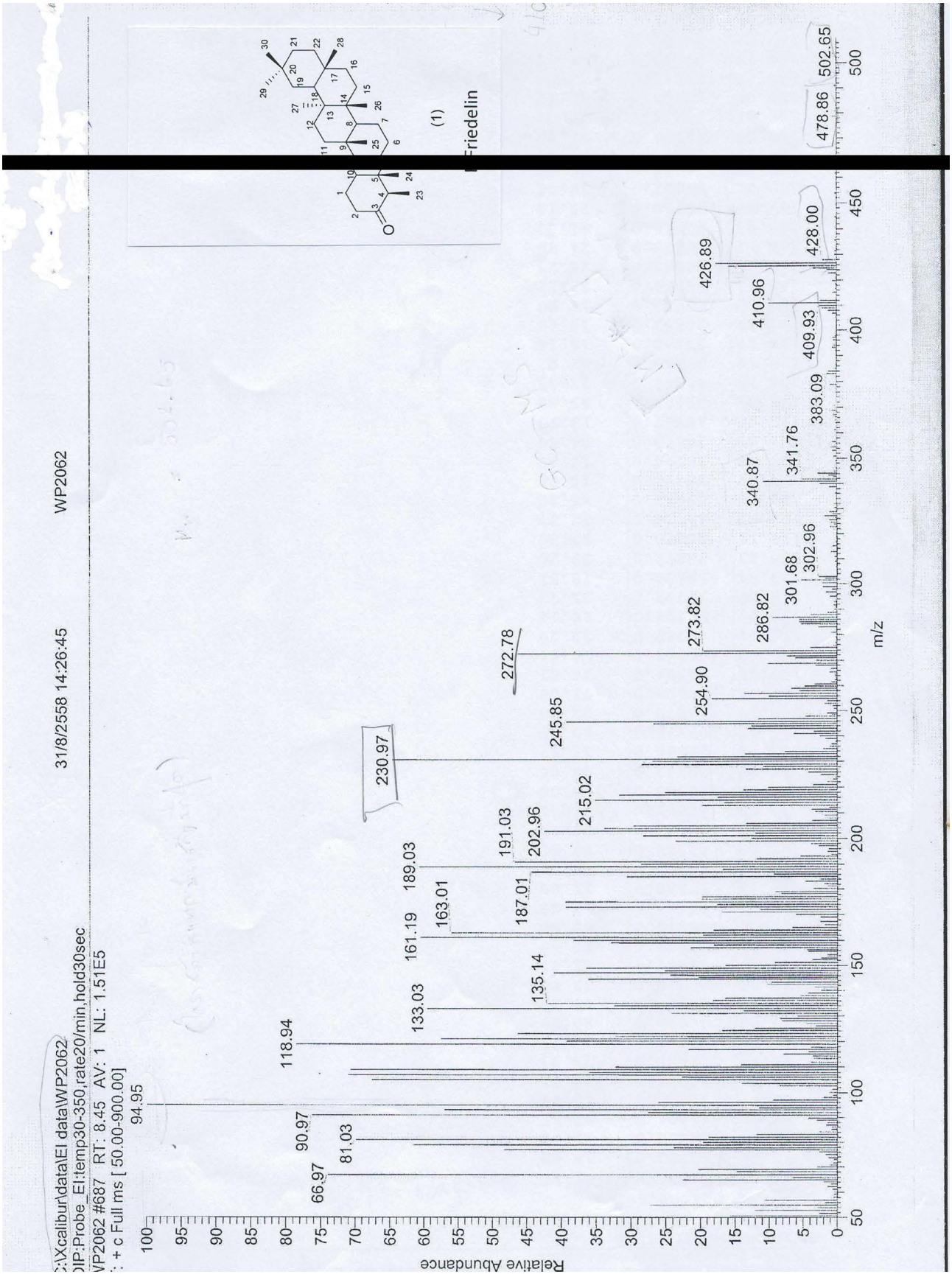


Figure S4. Friedelin-MS-spectrum.

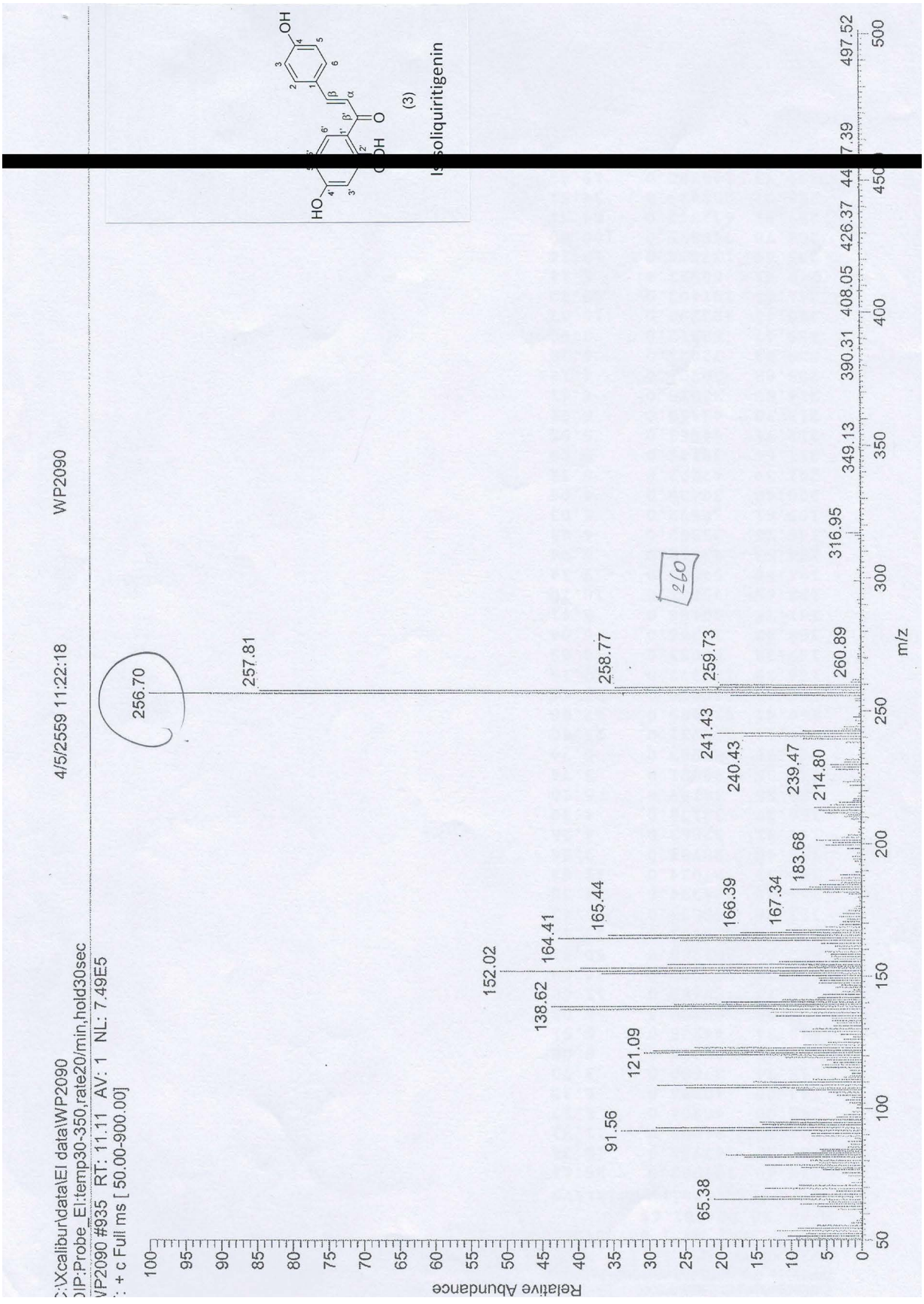
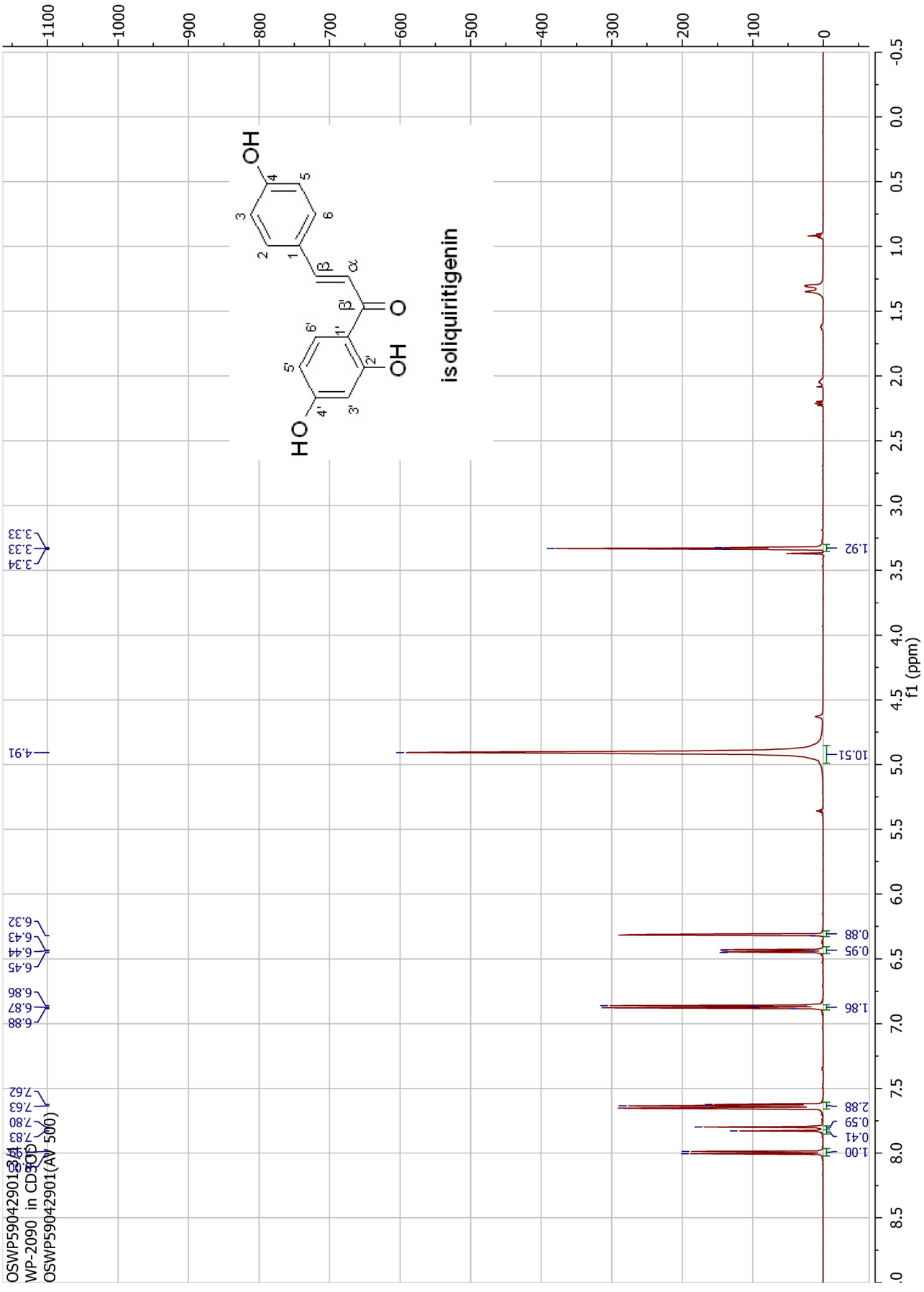
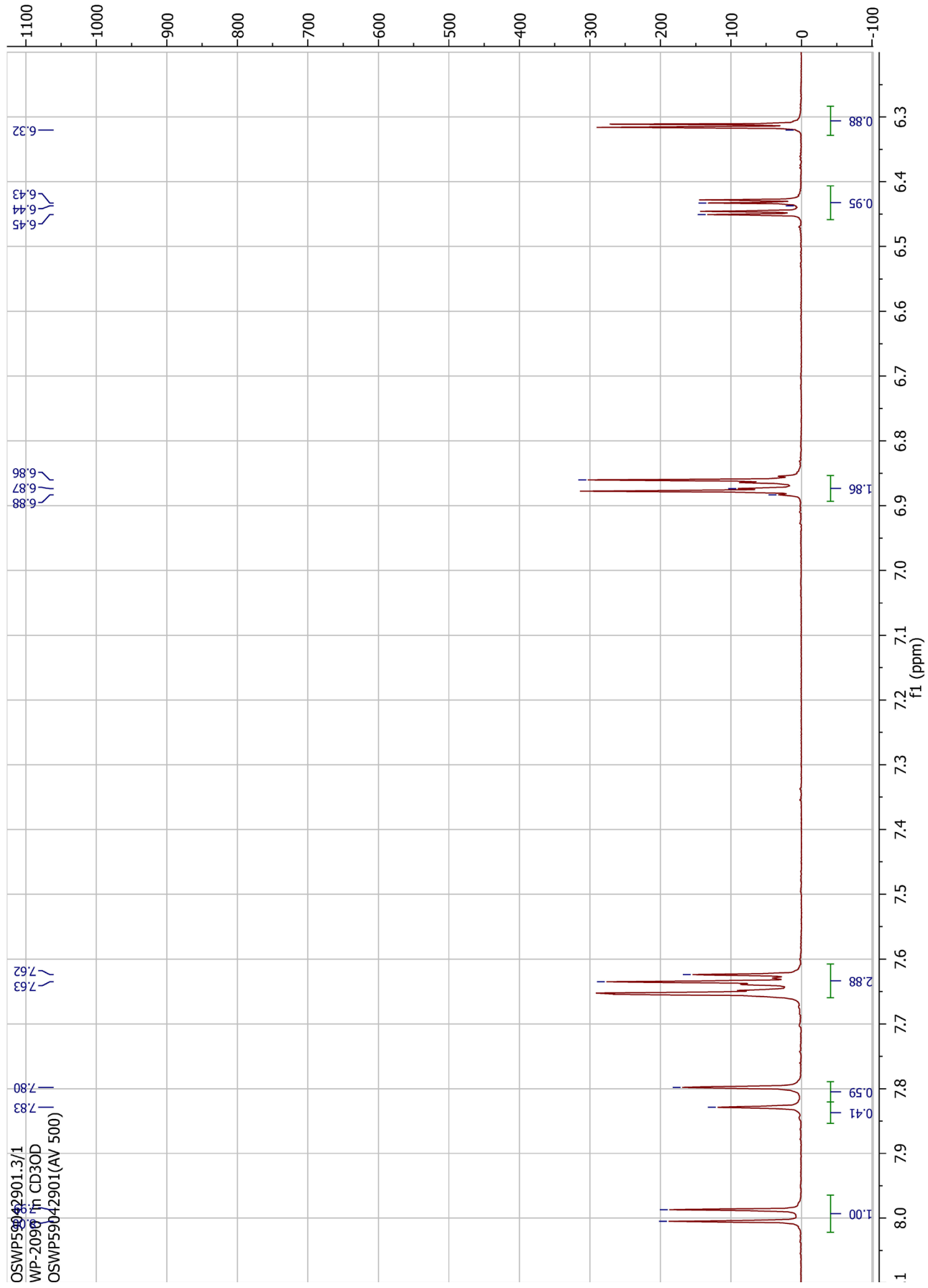
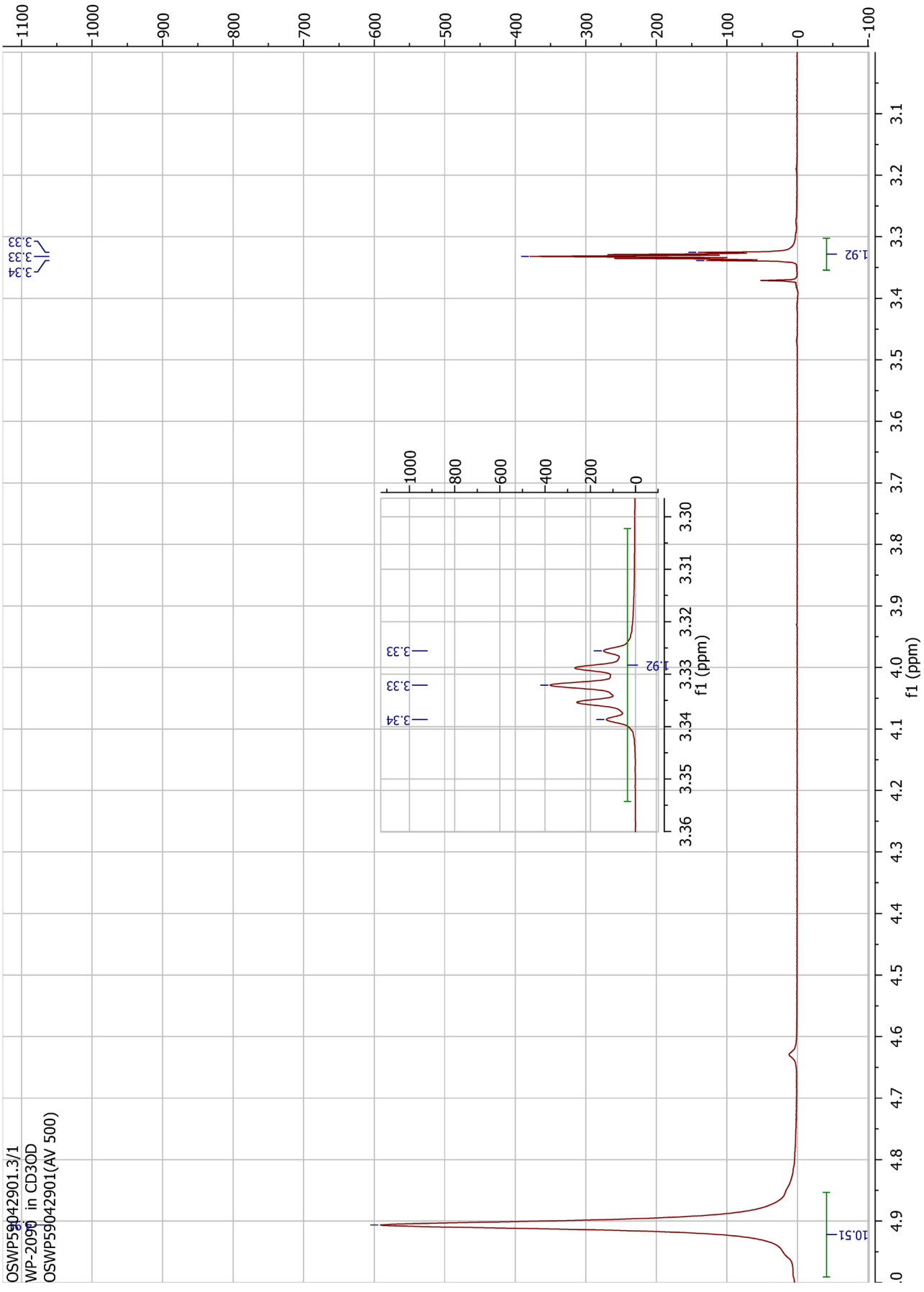
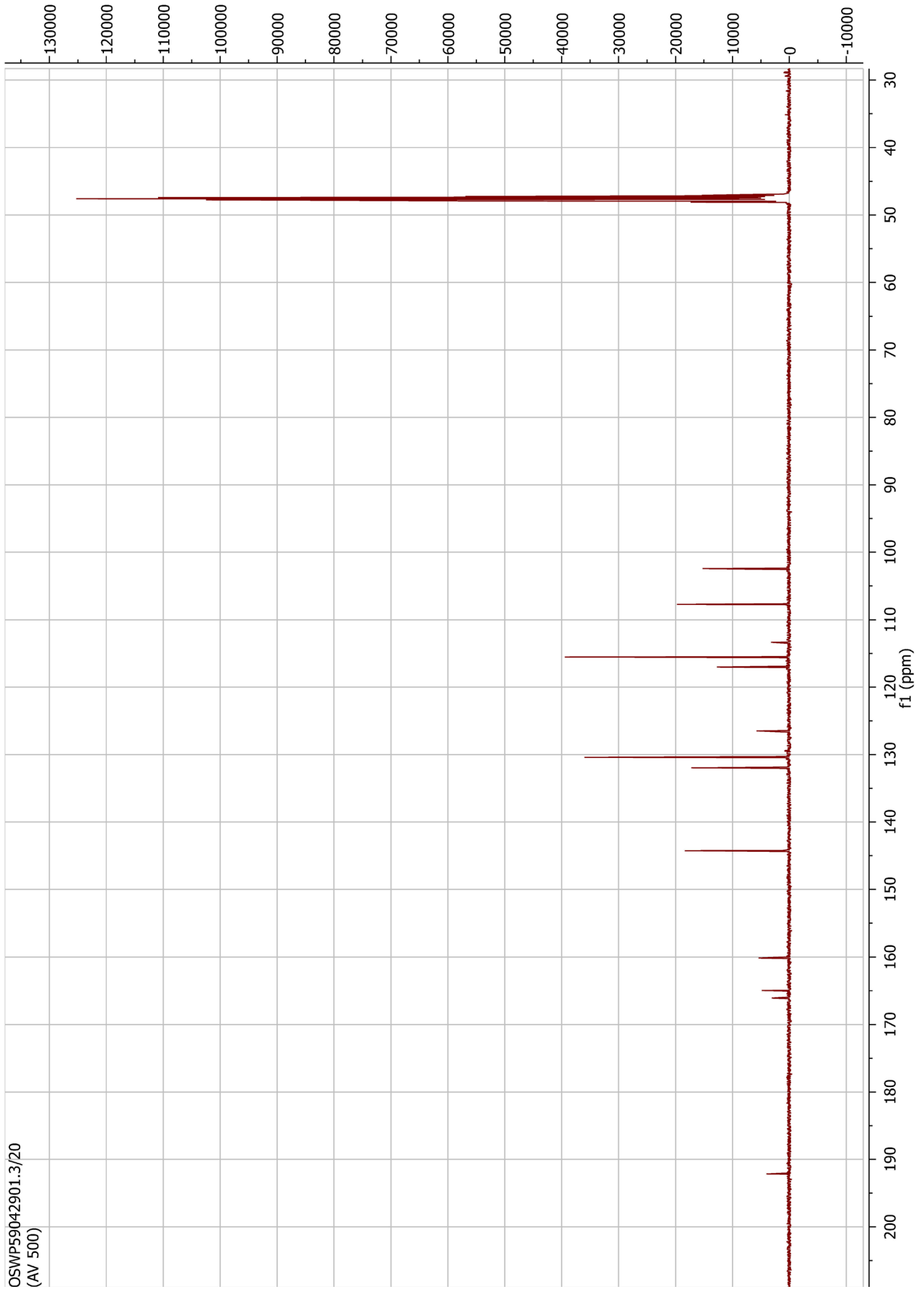


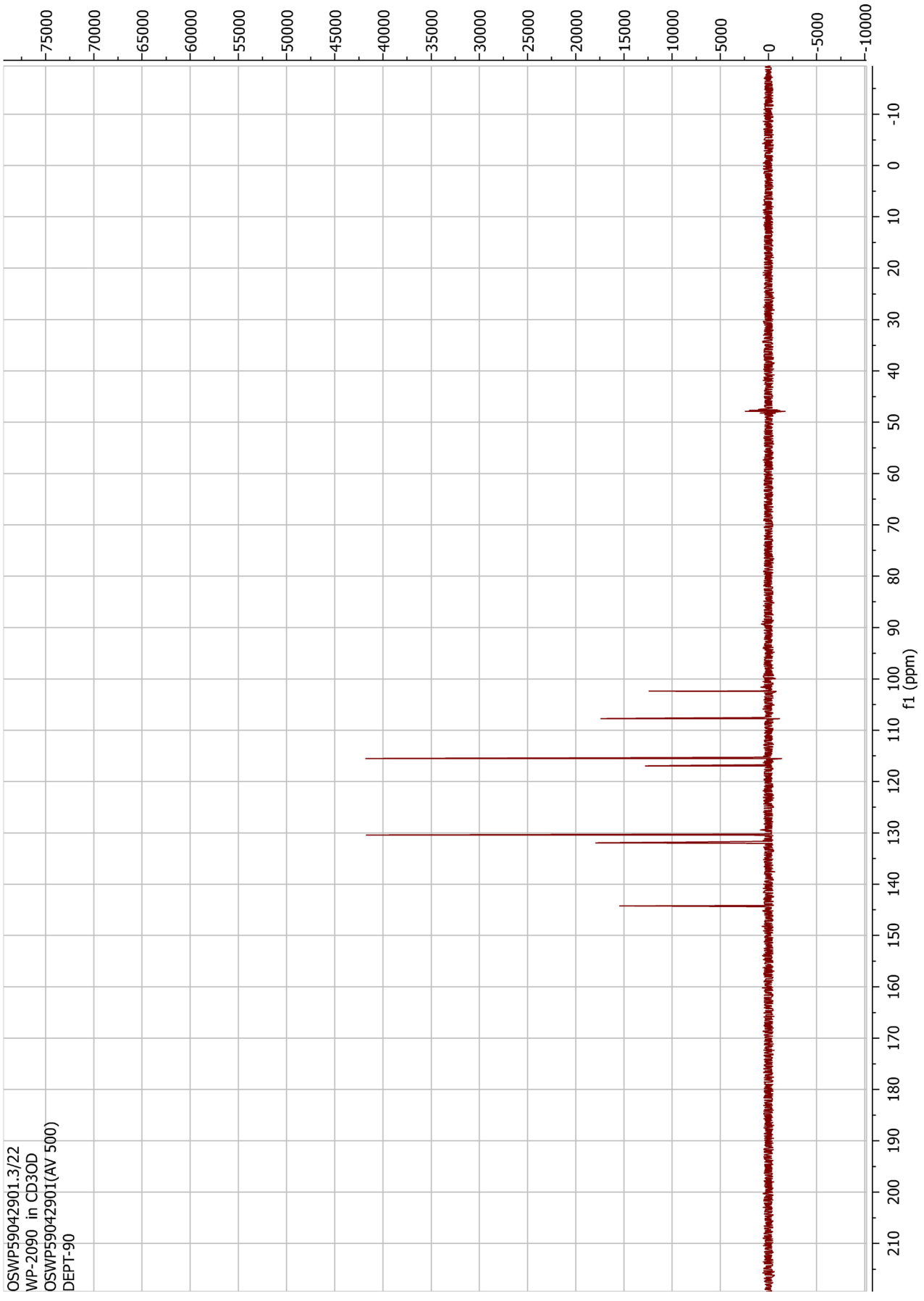
Figure S5. Isoliquiritigenin-MS spectrum.

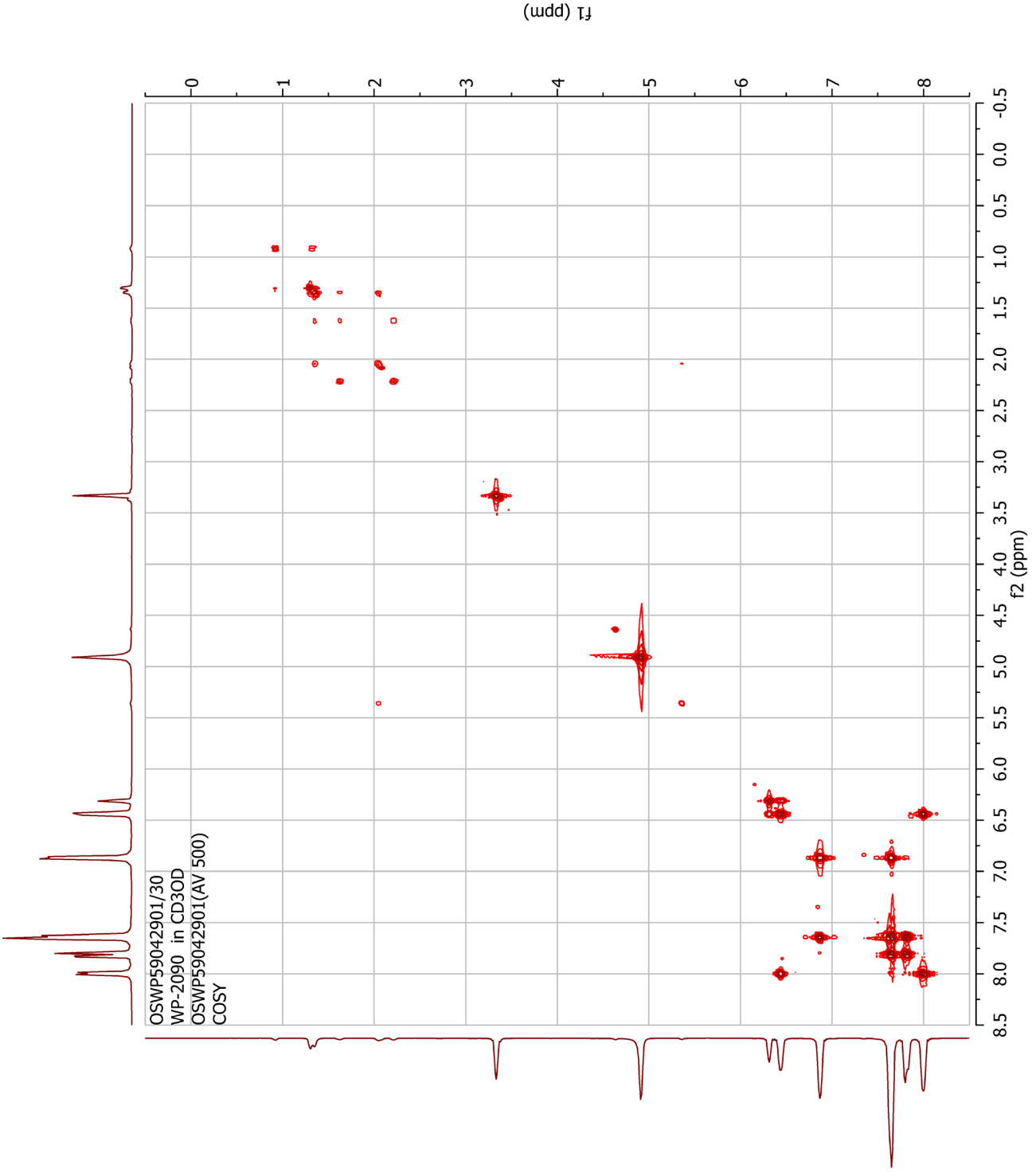

isoliquiritigenin
OH
HO
O
OH
OSWP59042901(AV 500)
WP-2090 in CD3OD
OSWP59042901(AV 500)
f1 (ppm)

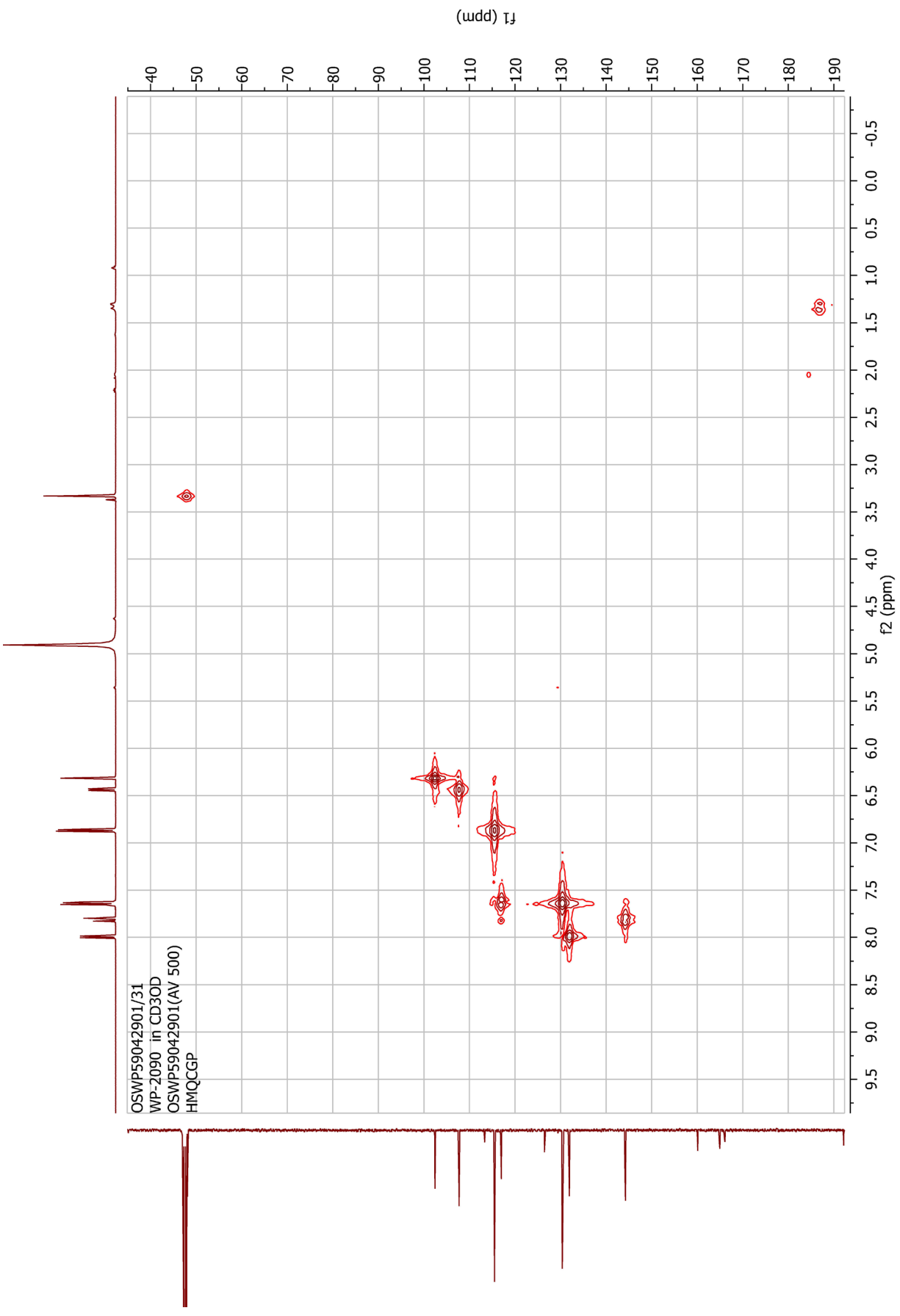

OSWP59042901.3/1
WP-2098 in CD3OD
OSWP59042901(AV 500)
6.32
6.43
6.44
6.45
6.86
6.87
6.88
7.62
7.63
7.80
7.83
0.88
0.95
1.86
2.88
0.59
0.41
1.00
f1 (ppm)

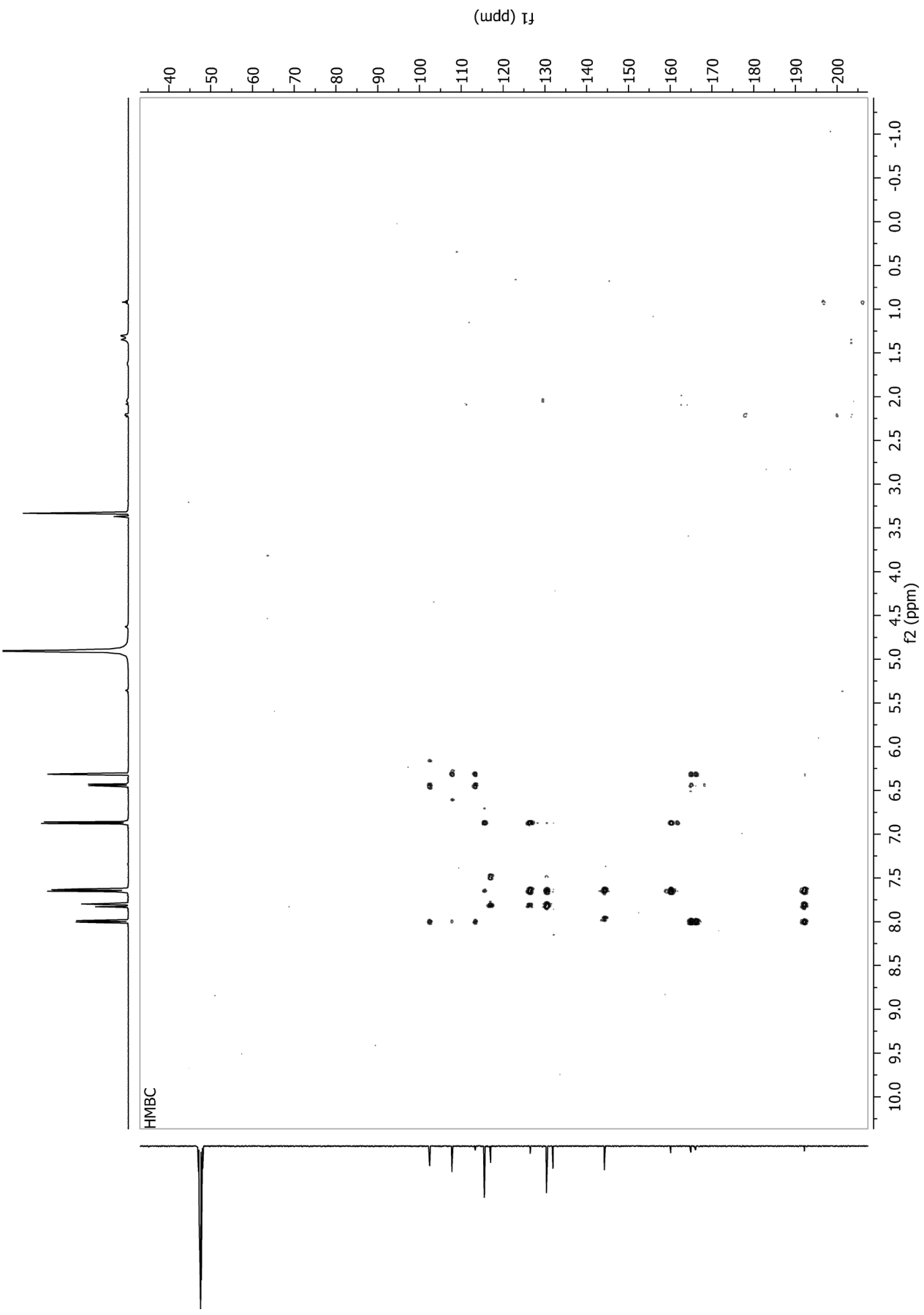

OSWP59042901.3/1
WP-2090 in CD3OD
OSWP59042901(AV 500)
10.51
1.92
3.34
3.33
3.33
f1 (ppm)

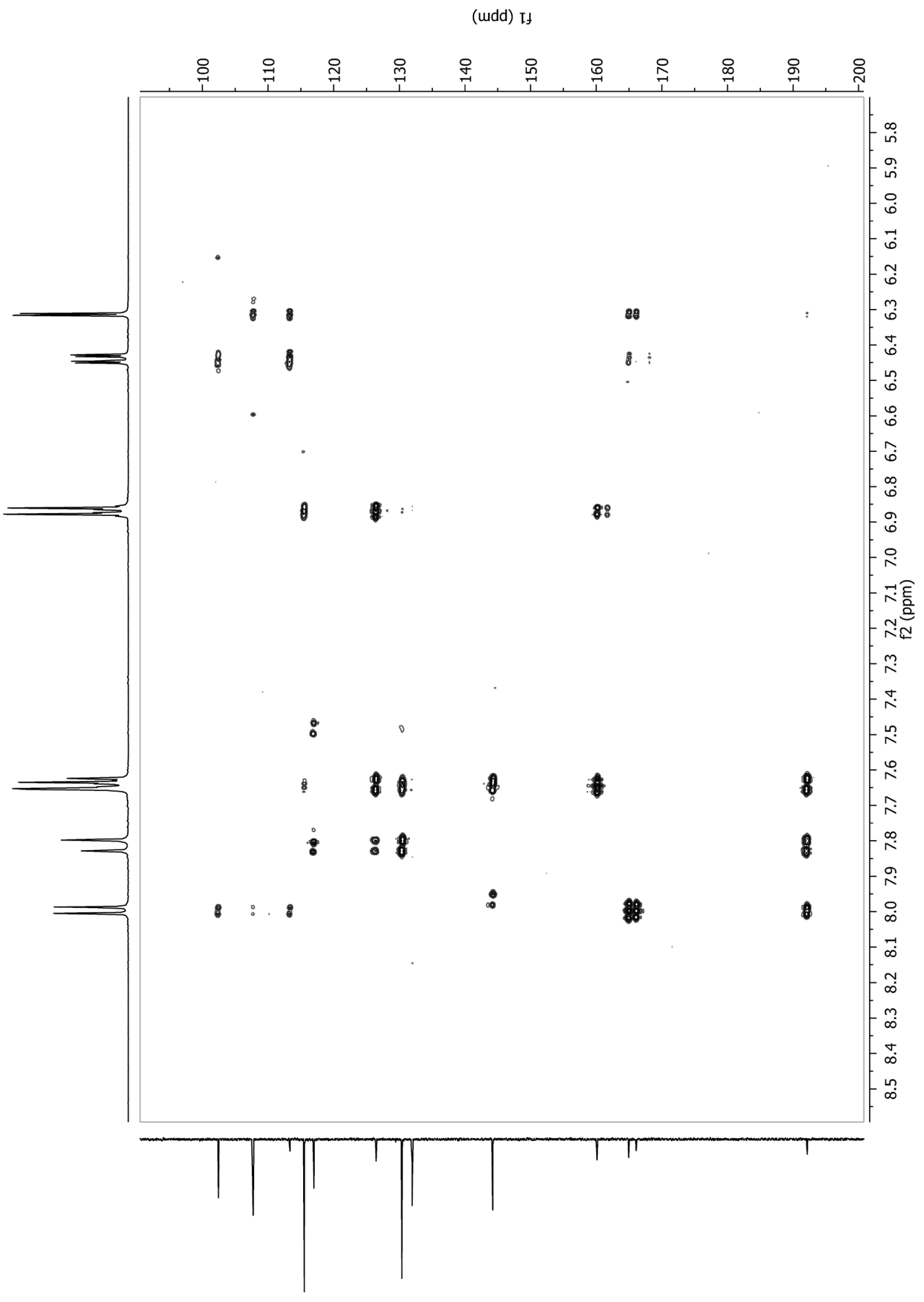

OSWP59042901.3/20
(AV 500)
f1 (ppm)

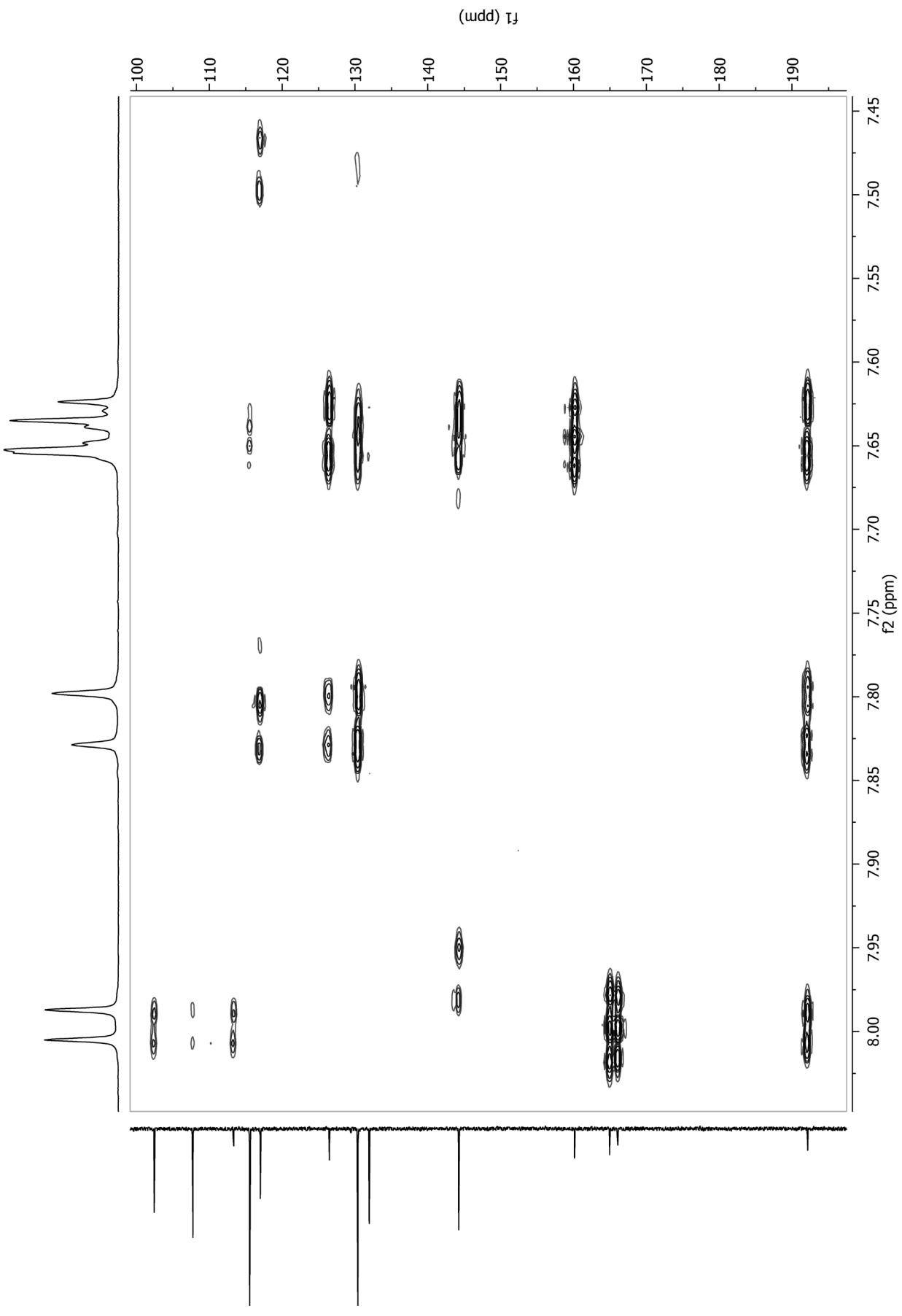

OSWP5942901.3/22
WP-2090 in CD3OD
OSWP5942901(AV 500)
DEPT-90
f1 (ppm)


f1 (ppm)
f2 (ppm)
OSWP59042901/30
WP-2090 in CD3OD
OSWP59042901(AV 500)
COSY


f1 (ppm)
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f2 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
OSWP59042901/31
WP-2090 in CD3OD
OSWP59042901(AV 500)
HMQCGP


HMBC
f2 (ppm)
f1 (ppm)


f1 (ppm)
100
110
120
130
140
150
160
170
180
190
200
f2 (ppm)
5.8
5.9
6.0
6.1
6.2
6.3
6.4
6.5
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5


f1 (ppm)
100
110
120
130
140
150
160
170
180
190
f2 (ppm)
7.45
7.50
7.55
7.60
7.65
7.70
7.75
7.80
7.85
7.90
7.95
8.00

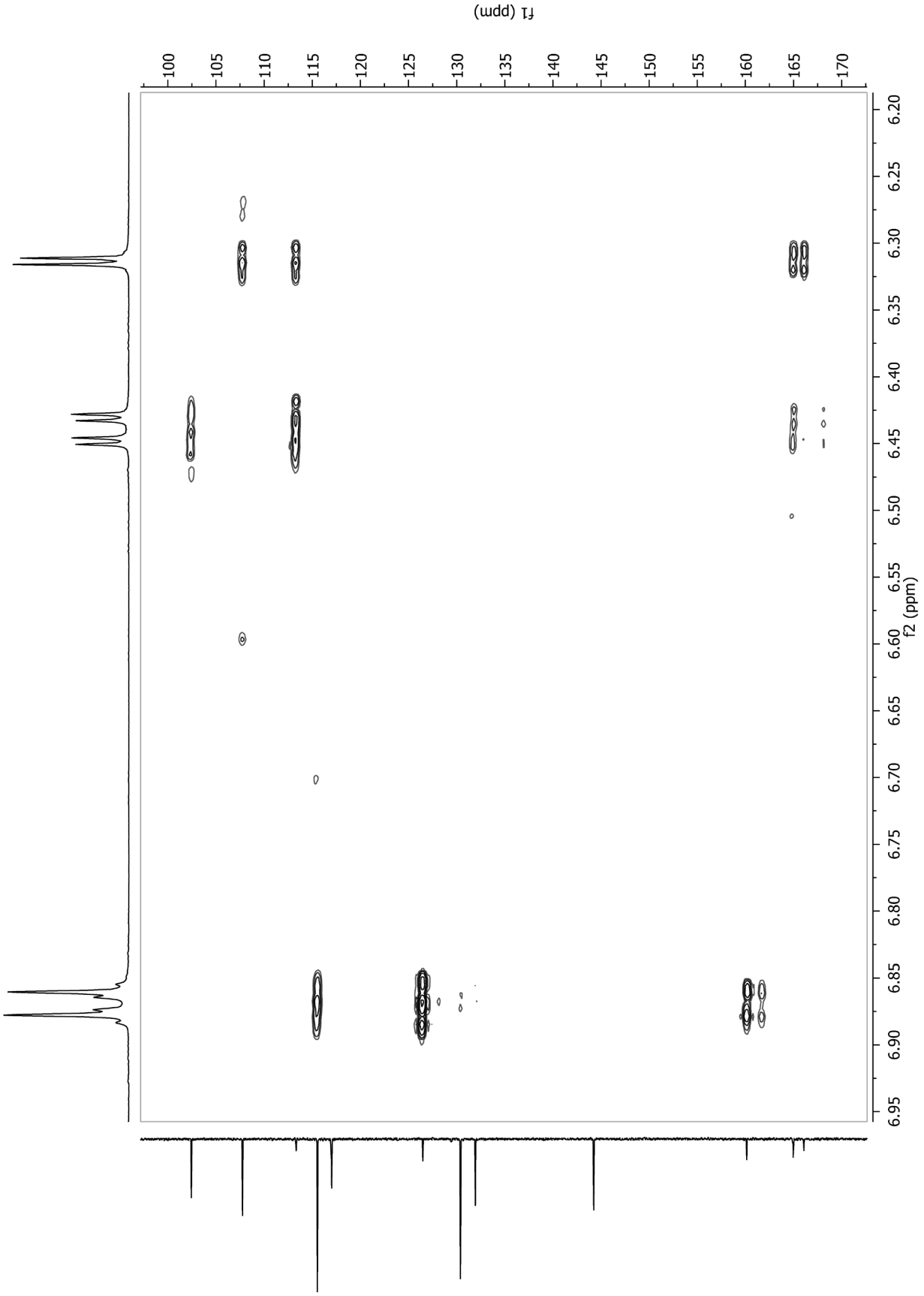


Figure S6. Isoliquiritigenin-NMR spectrum.