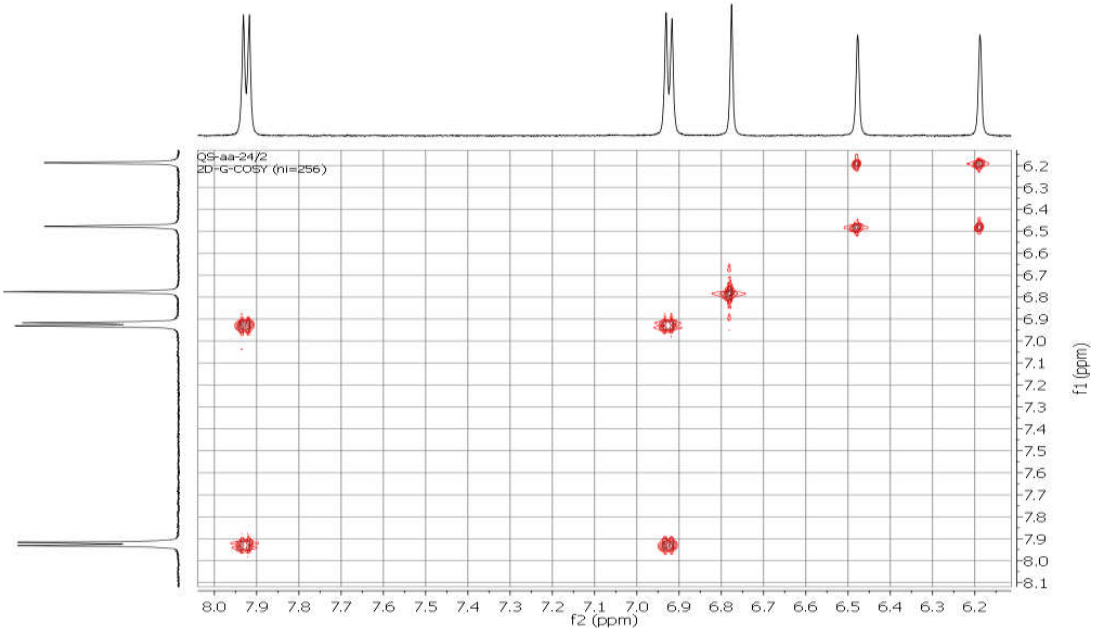
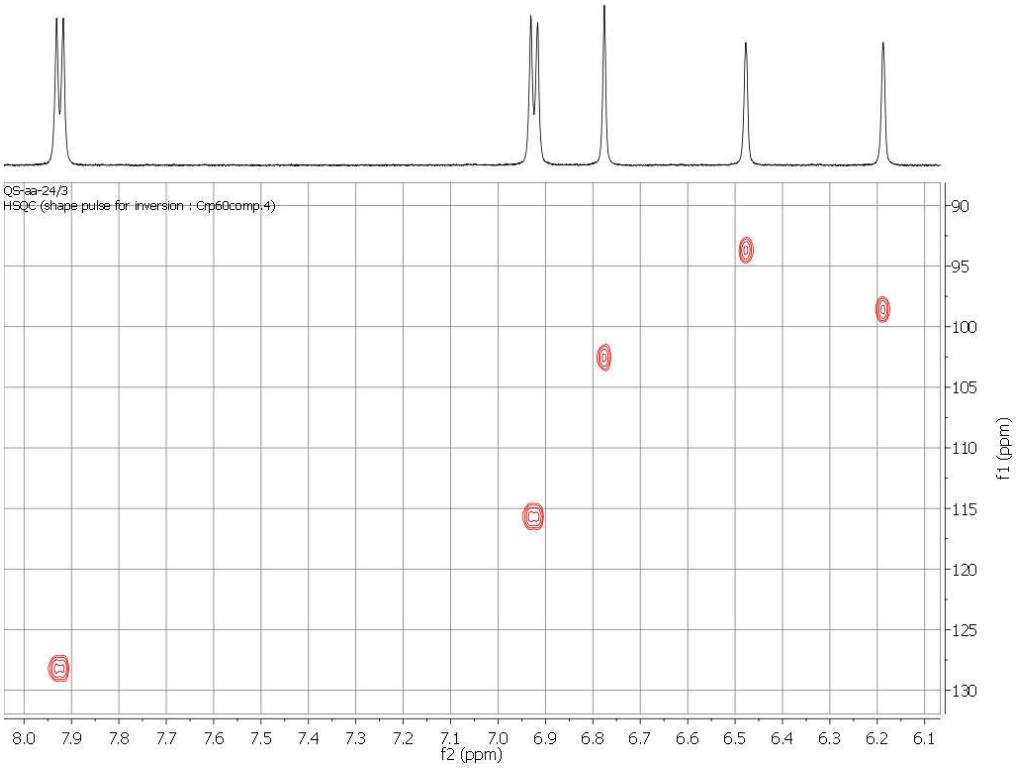
天然药物化学专业波谱分析练习题-2

Question 1: A yellowish compound was isolated from a plant. The IR spectrum exhibited absorption bands at 3323 cm^{-1}, 1655 cm^{-1}, and 1585 and 1478 cm^{-1}. The UV spectrum showed absorption bands at 290 and 337 nm. The mass spectrum showed a molecular ion peak at *m/z* 270 followed by the cleavage of RDA at *m/z* 152 and *m/z* 118. The molecular formula was established as $C_{15}H_{10}O_5$ by HR-MS. The ^1H NMR spectrum showed three exchangeable proton resonances at δ_H 12.86, 9.60 and 9.30 ppm, respectively. The ^1H-^1H COSY and HMQC spectra are presented as following. Please establish the structure and provide your evidence.

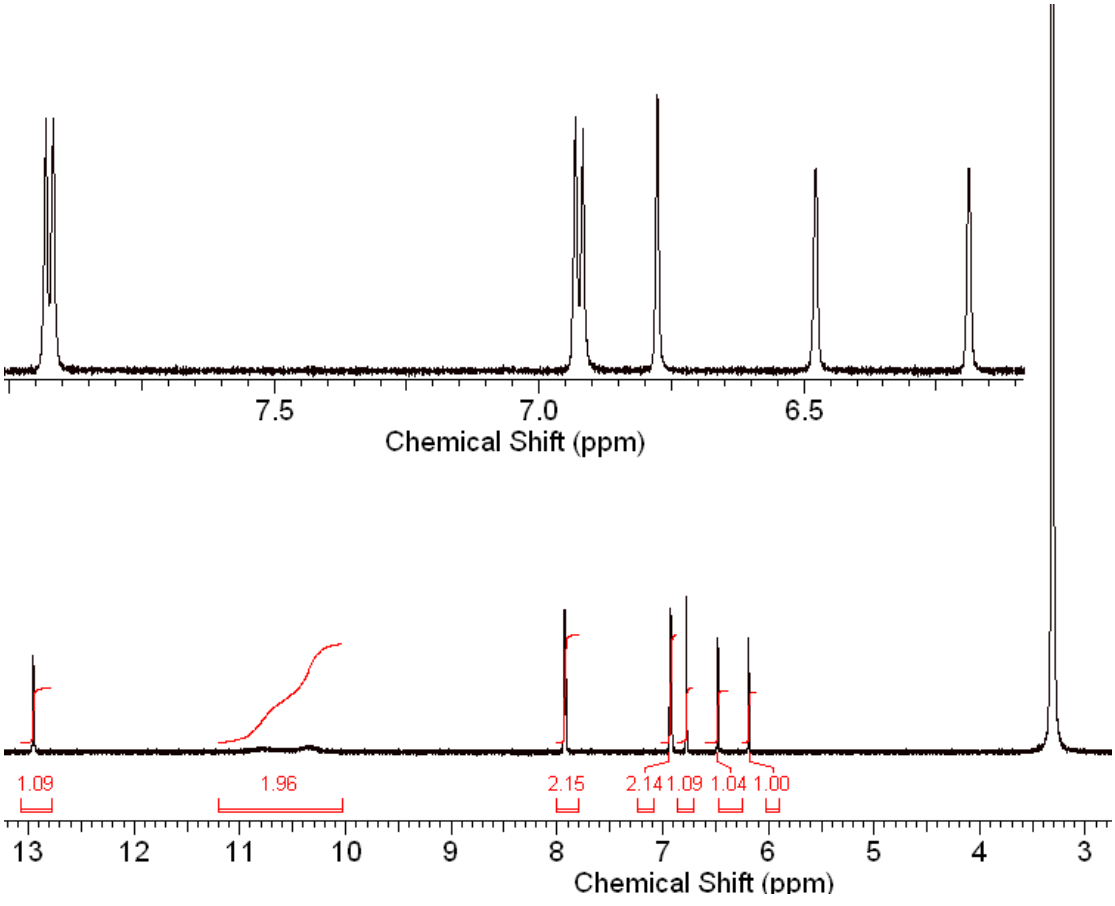
^1H-^1H COSY



HMQC


QS-aa-24/3
HSQC (shape pulse for inversion : Cp60comp.4)
f2 (ppm)
f1 (ppm)

^{1}H-NMR


Chemical Shift (ppm)
1.09
1.96
2.15
2.14
1.09
1.04
1.00
Chemical Shift (ppm)

结 构 测 定 实 例

2. 从小冠花种子中得到一结晶，分子式为$C_9H_6O_3$，呈蓝绿色荧光，$FeCl_3$反应阳性，Gibb's反应阴性，碱水解后Gibbs反应阳性，异羟肟酸铁反应阳性。

UV λ_{max} nm: 257 322 328 (几乎联成一峰)

IR KBr υ_{max} cm^{-1}: 3200 cm^{-1}， 1705 cm^{-1} 。

MS *m/z*: 162 （M^+）, 134， 106。

^{1}H-NMR （$CDCl_3$） δ ppm: 8.22 (1H，S)，
6.21 (1H, d, *J* = 9.5 Hz), 8.15 (1H, d, *J* = 9.5 Hz),
7.70 (1H, d, *J* = 8.0 Hz), 6.95 (1H, dd, *J* = 8.0, 1.2 Hz),
7.00 (1H, d, *J* = 1.2 Hz)。

根据以上提示的信息，写出结构式并说明理由。

- **3. 推测化合物结构**
- 从某药用植物中分离得到一个黄色结晶，HR-MS确定其分子式为C15H10O6。该结晶与FeCl3反应呈暗绿色；与Mg-HCl反应呈紫红色；与ZrOCl2反应呈黄色、再加入枸橼酸后黄色不褪。IR（KBr）（νmax cm-1）：3401，1655，1606，1504；EI-MS 给出离子峰（*m/z*）为286（M+），其余为258，152，134，118，131，103等。
- 其核磁及紫外光谱数据如下：
- 1H-NMR（DMSO-d6，TMS内标）δppm：
- 6.12（1H, d，*J* = 2.0 Hz）， 6.42（1H，d，*J* = 2.0 Hz）
- 6.86（2H, d，*J* = 9.0 Hz）， 8.08（2H，d，*J* = 9.0 Hz）。
- UV（λmax nm）：MeOH: 267，363； NaOMe ： 75，406
- AlCl3 ： 274，420； AlCl3/HCl 276，303，423
- NaOAc/H3BO3 266，300sh，363

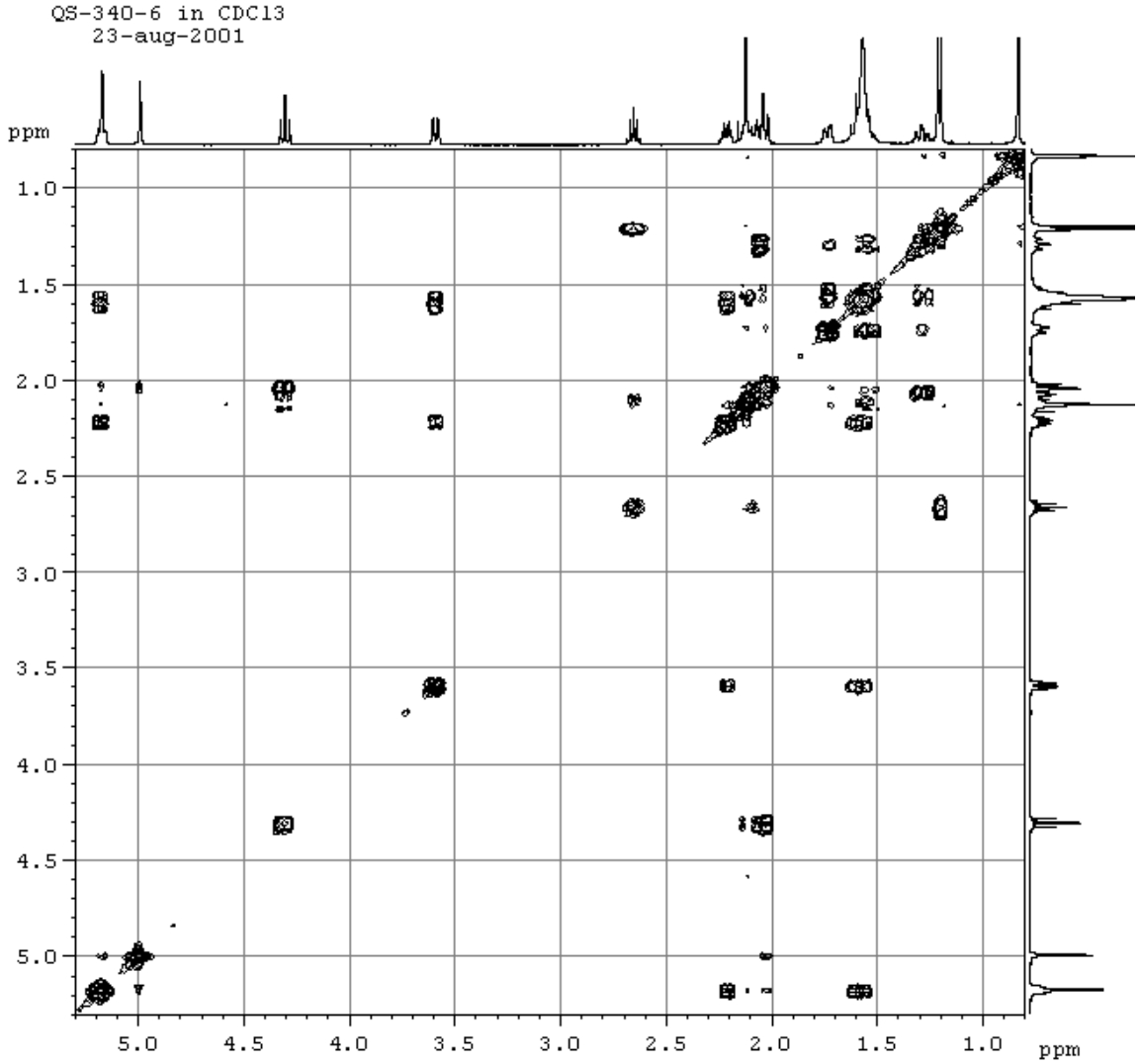
- **请根据以上信息回答下列问题：**
- **1） 该化合物的不饱和度是多少？（1分）**
- **2） “与三氯化铁反应呈暗绿色”说明什么？（1分）**
- **3）“与镁粉-盐酸反应呈紫红色”说明什么？（1分）**
- **4）“与$ZrOCl_2$反应呈黄色、再加入枸橼酸后黄色不褪去”说明什么？（1分）**
- **5）解释IR中在 3401、1655处的吸收峰分别说明什么？（2分）**
- **6） 对所列1H-NMR数据进行归属。（4分）**
- **7） 解释样品-甲醇溶液的UV波谱特征以及加入各种诊断试剂后UV 吸收峰位变化说明什么？（4分）**
- **8） 根据以上信息写出该化合物的结构式。（2分）**

UNKNOWN Compound QS-340-6 isolated from a plant

An unknown compound have been extracted from a medicinal plant. From high resolution FAB-MS, the molecular formula has been found to be $C_{17}H_{24}O_5$. Using all the data provided, propose a structure that matches the data, assign all Protons and Carbon signals you can. Once you have the structure deduce the relative stereochemistry of that compound.

The Carbon-13 line listing (next page) has been extracted from 2D-HSQC and HMBC (as there was not enough sample to acquire a regular 1D-Carbon-13 NMR).

UNKNOWN QS-340-6 : COSY

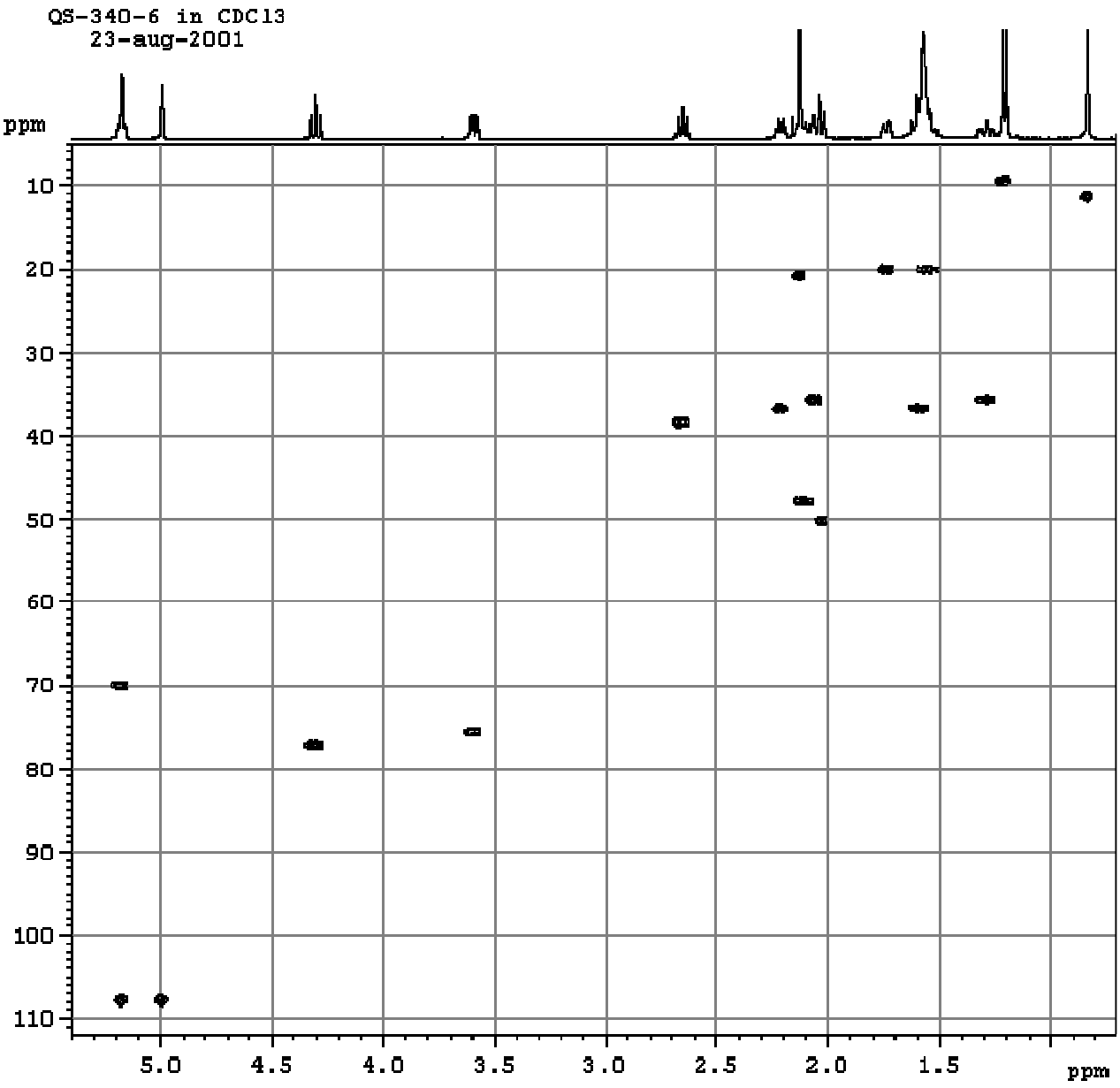


Unknown QS-340-3 Carbon-13 line listing (DEPT multiplicity information)

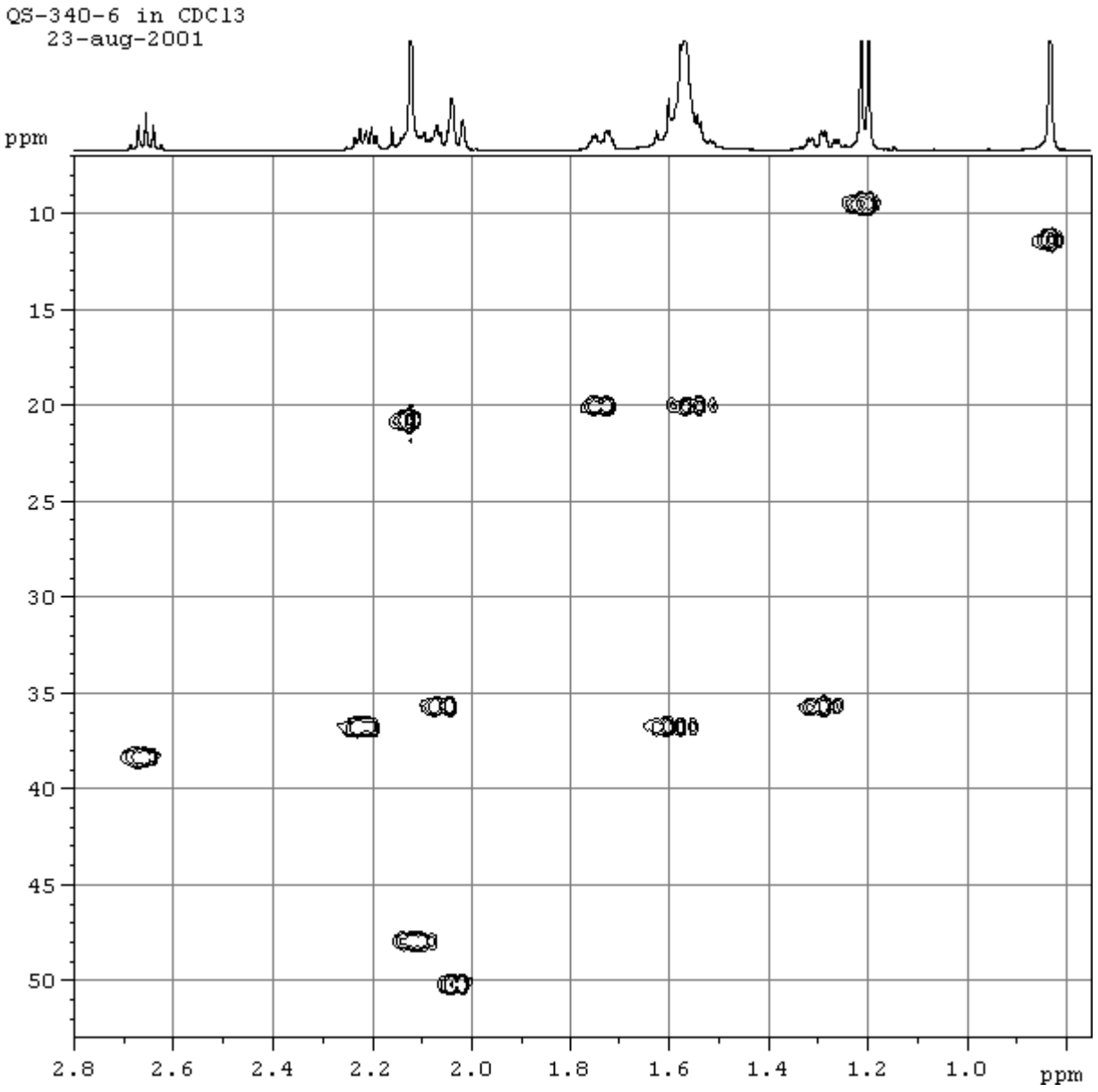
UNKNOWN 340-3

line number	shift PPM	Mult.	line number	shift PPM	Mult.
1	9.5	q	10	50.3	d
2	11.5	q	11	70.1	d
3	20.1	t	12	75.7	d
4	20.9	q	13	77.3	d
5	35.7	t	14	107.8	t
6	36.9	t	15	140.5	s
7	38.5	d	16	169.6	s
8	42.4	s	17	179.6	s
9	48.1	d			

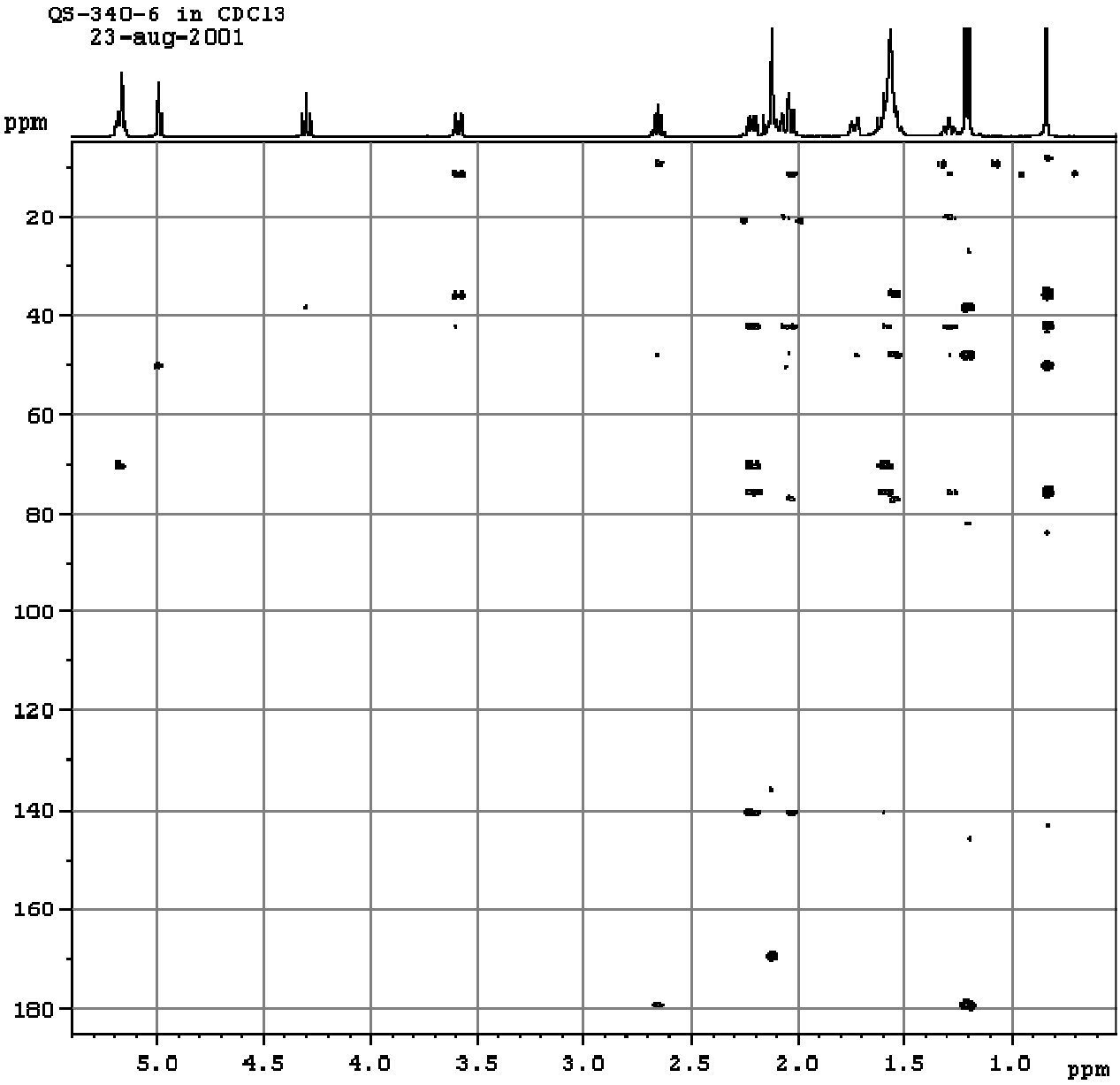
UNKNOWN QS-340-6: HSQC



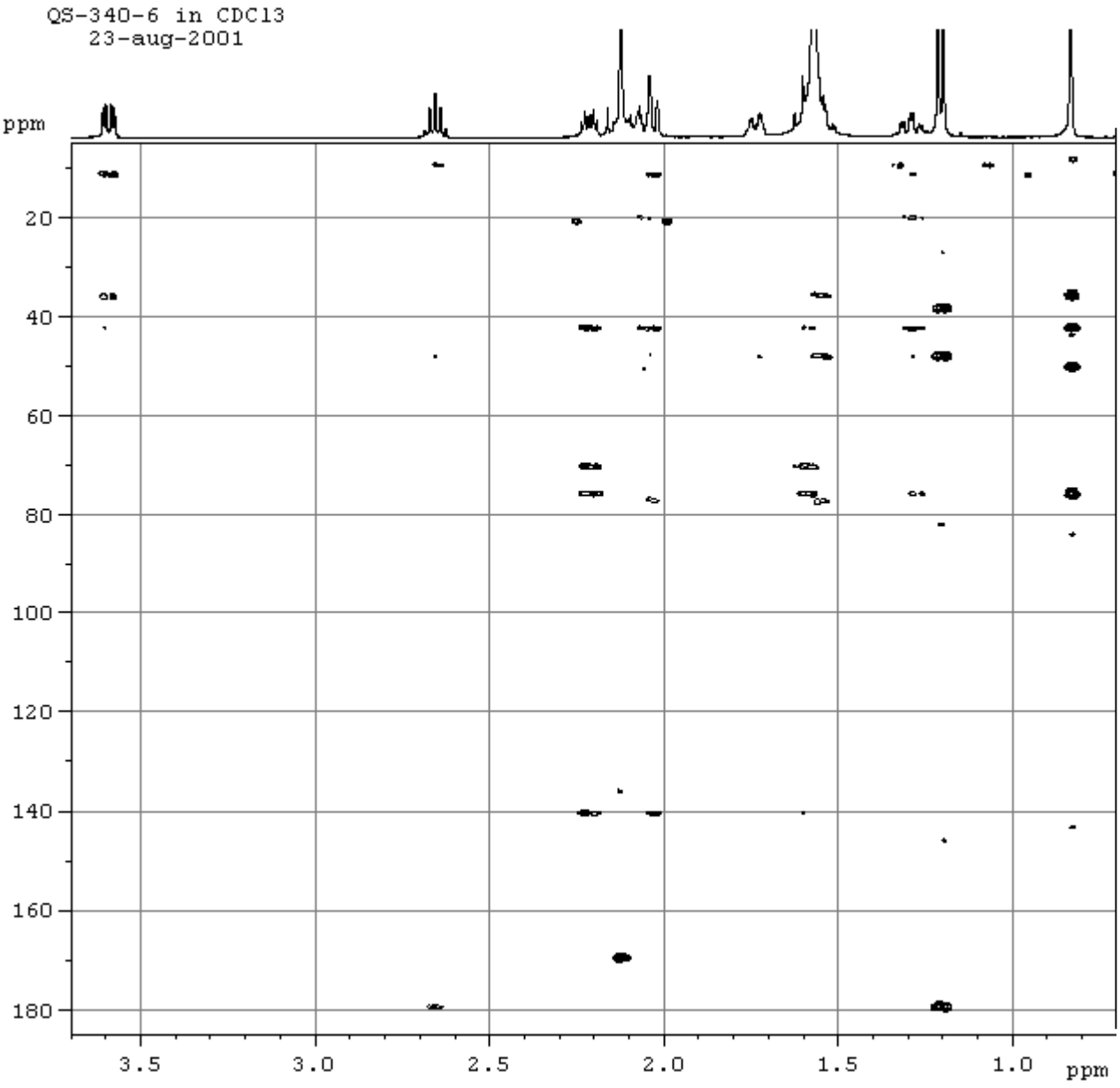
UNKNOWN QS-340-6: HSQC - expansion



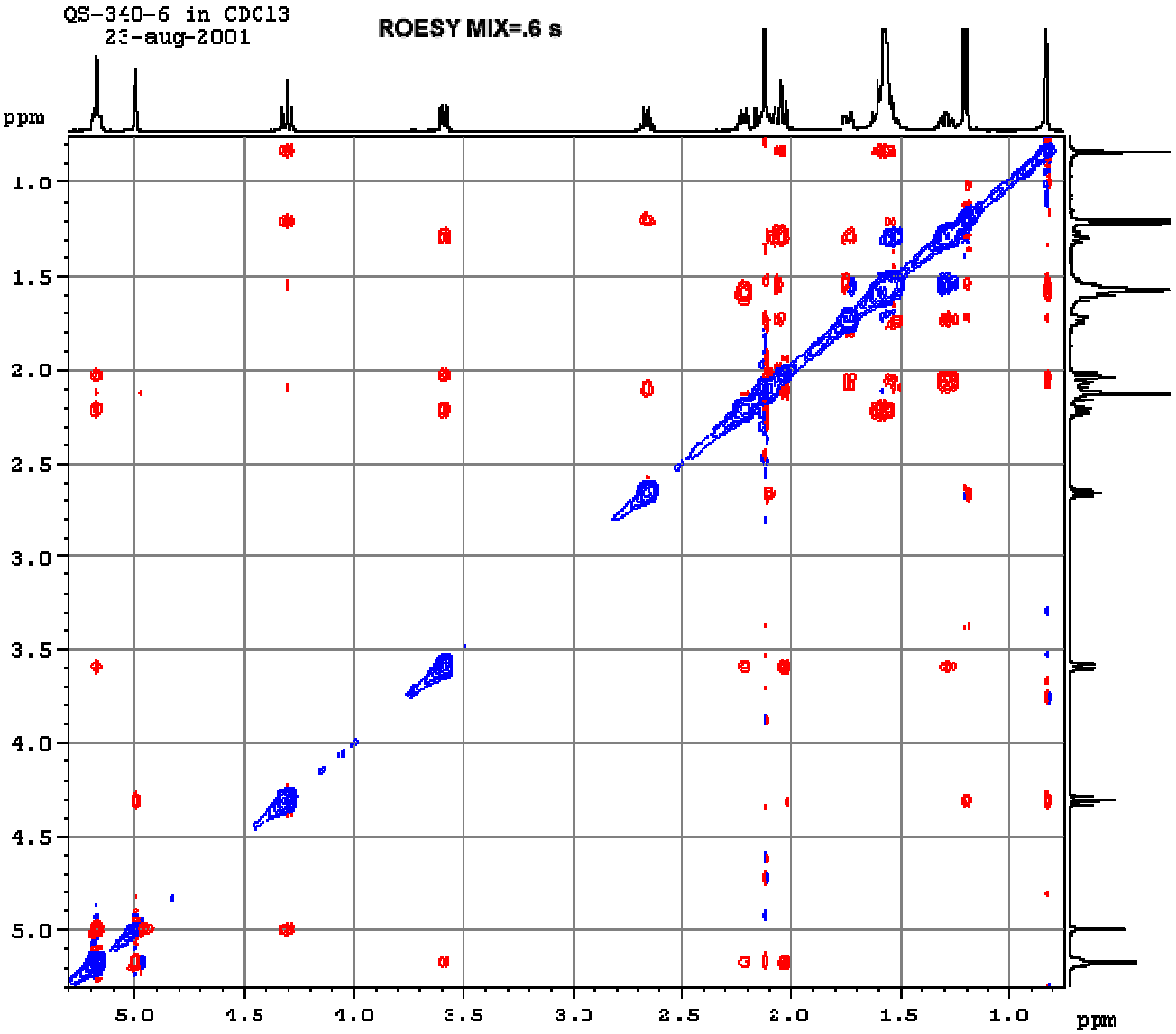
UNKNOWN QS-340-6 : HMBC



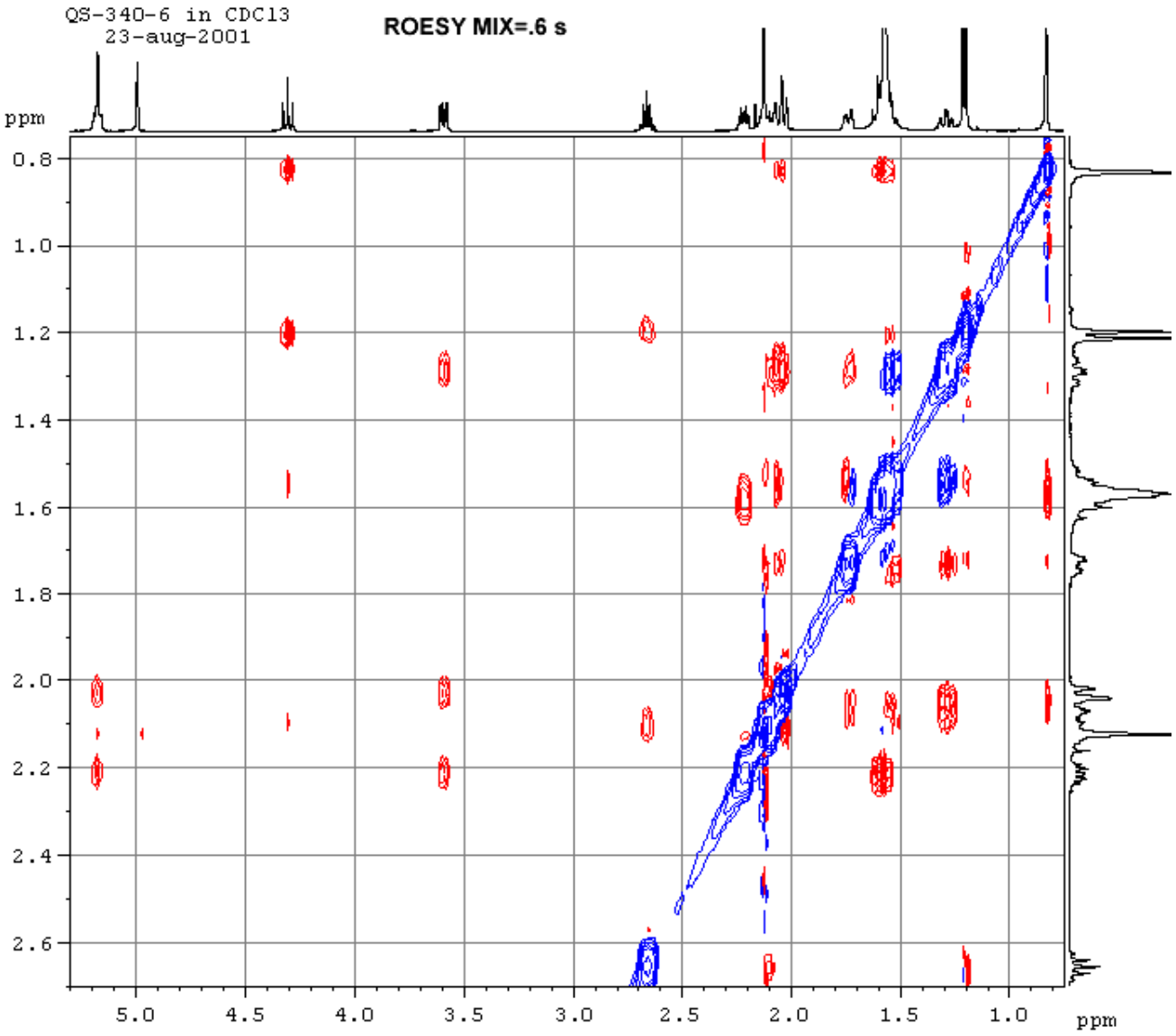
UNKNOWN QS-340-6: HMBC expansion



UNKNOWN QS-340-6: ROESY



UNKNOWN QS-340-6: ROESY expansion

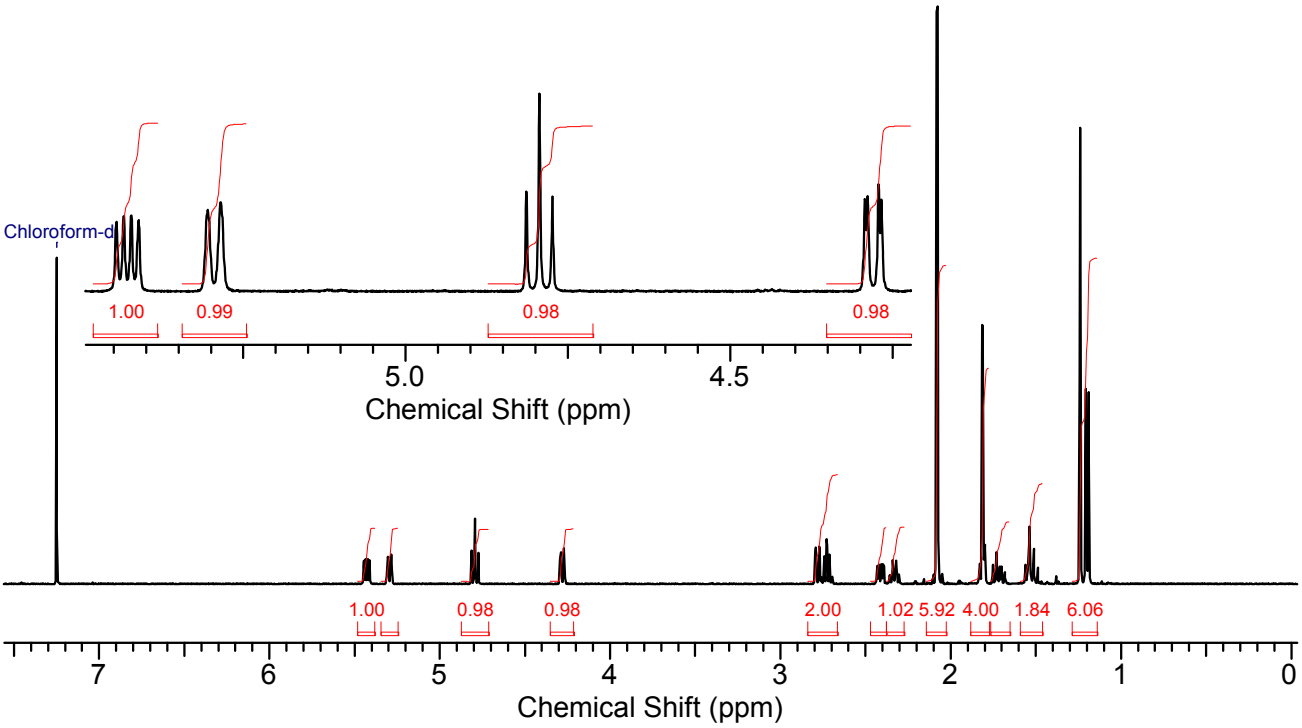


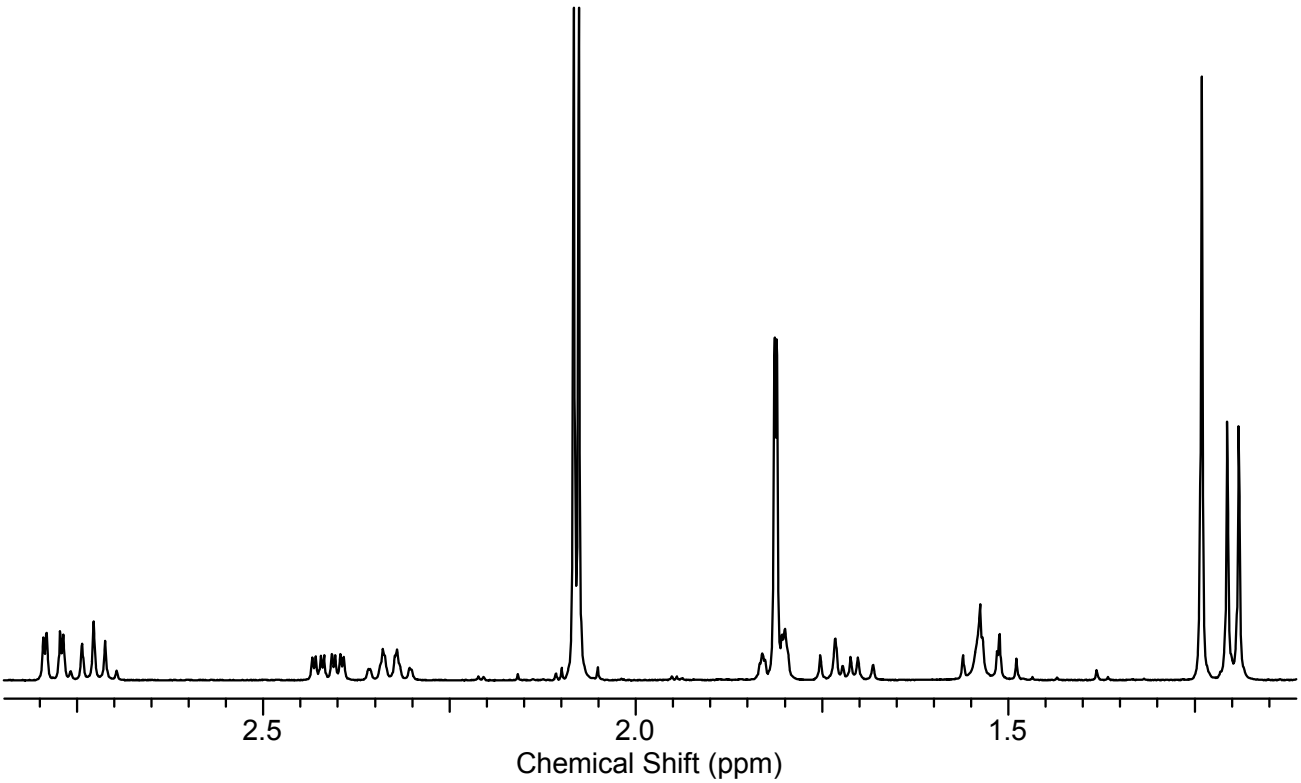
Question 1

A compound labeled QS-103-6 has been extracted from a medicinal plant.

From MS, the molecular formula was established as: **$C_{19}H_{26}O_7$**

The compound (4.1 mg) was dissolved in $CDCl_3$ and various NMR spectra (^{1}H, ^{13}C, COSY, HSQC, HMBC, NOESY) were obtained. Establish the structure and the relative stereochemistry of this compound.



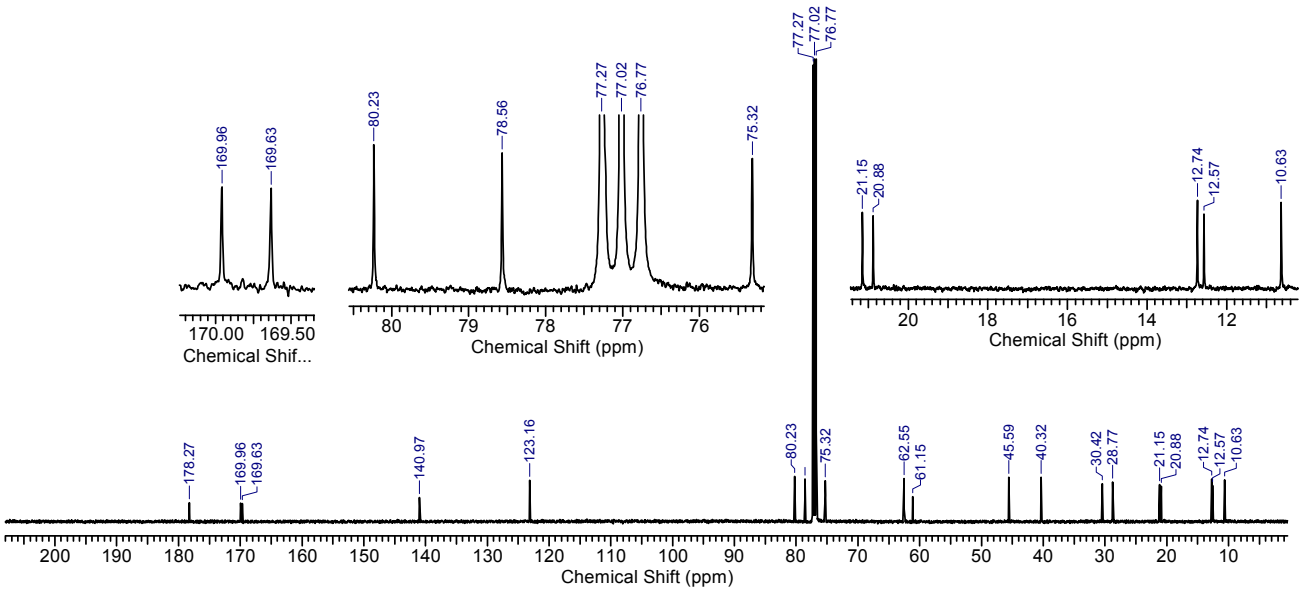

2.5
2.0
1.5
Chemical Shift (ppm)

Line listing H-NMR of QS-103-6

No.	(ppm)	(Hz)	Height
1	1.191	595.48	0.3326
2	1.206	603.18	0.3386
3	1.241	620.42	0.7906
4	1.489	744.58	0.0283
5	1.512	755.95	0.0610
6	1.515	757.60	0.0382
7	1.535	767.51	0.0563
8	1.538	769.07	0.0996
9	1.561	780.44	0.0330
10	1.682	840.78	0.0205
11	1.702	850.96	0.0300
12	1.712	855.91	0.0304
13	1.722	861.13	0.0191
14	1.732	866.18	0.0548
15	1.752	876.26	0.0332
16	1.800	900.02	0.0673
17	1.804	901.85	0.0602
18	1.811	905.52	0.4467
19	1.814	906.89	0.4489
20	1.827	913.40	0.0269
21	1.830	915.15	0.0349
22	1.834	916.89	0.0221
23	2.051	1025.55	0.0173
24	2.077	1038.30	1.0000
25	2.083	1041.69	0.9919
26	2.099	1049.76	0.0167
27	2.304	1151.92	0.0163
28	2.320	1160.26	0.0401
29	2.323	1161.64	0.0325
30	2.340	1169.80	0.0416

No.	(ppm)	(Hz)	Height
31	2.392	1196.12	0.0307
32	2.397	1198.32	0.0344
33	2.404	1201.80	0.0331
34	2.408	1204.00	0.0343
35	2.418	1209.23	0.0328
36	2.423	1211.43	0.0326
37	2.430	1214.92	0.0319
38	2.434	1217.12	0.0297
39	2.712	1356.04	0.0514
40	2.728	1363.84	0.0772
41	2.743	1371.54	0.0478
42	2.768	1384.20	0.0597
43	2.773	1386.40	0.0643
44	2.791	1395.48	0.0625
45	2.795	1397.58	0.0559
46	4.267	2133.58	0.0529
47	4.271	2135.78	0.0616
48	4.288	2144.12	0.0548
49	4.293	2146.32	0.0529
50	4.774	2387.04	0.0542
51	4.794	2397.03	0.1136
52	4.814	2407.03	0.0574
53	5.285	2642.42	0.0511
54	5.411	2705.79	0.0408
55	5.423	2711.38	0.0435
56	5.434	2717.16	0.0431
57	5.446	2722.84	0.0401
58	7.250	3625.09	0.5647

C-13 NMR of QS-103-6

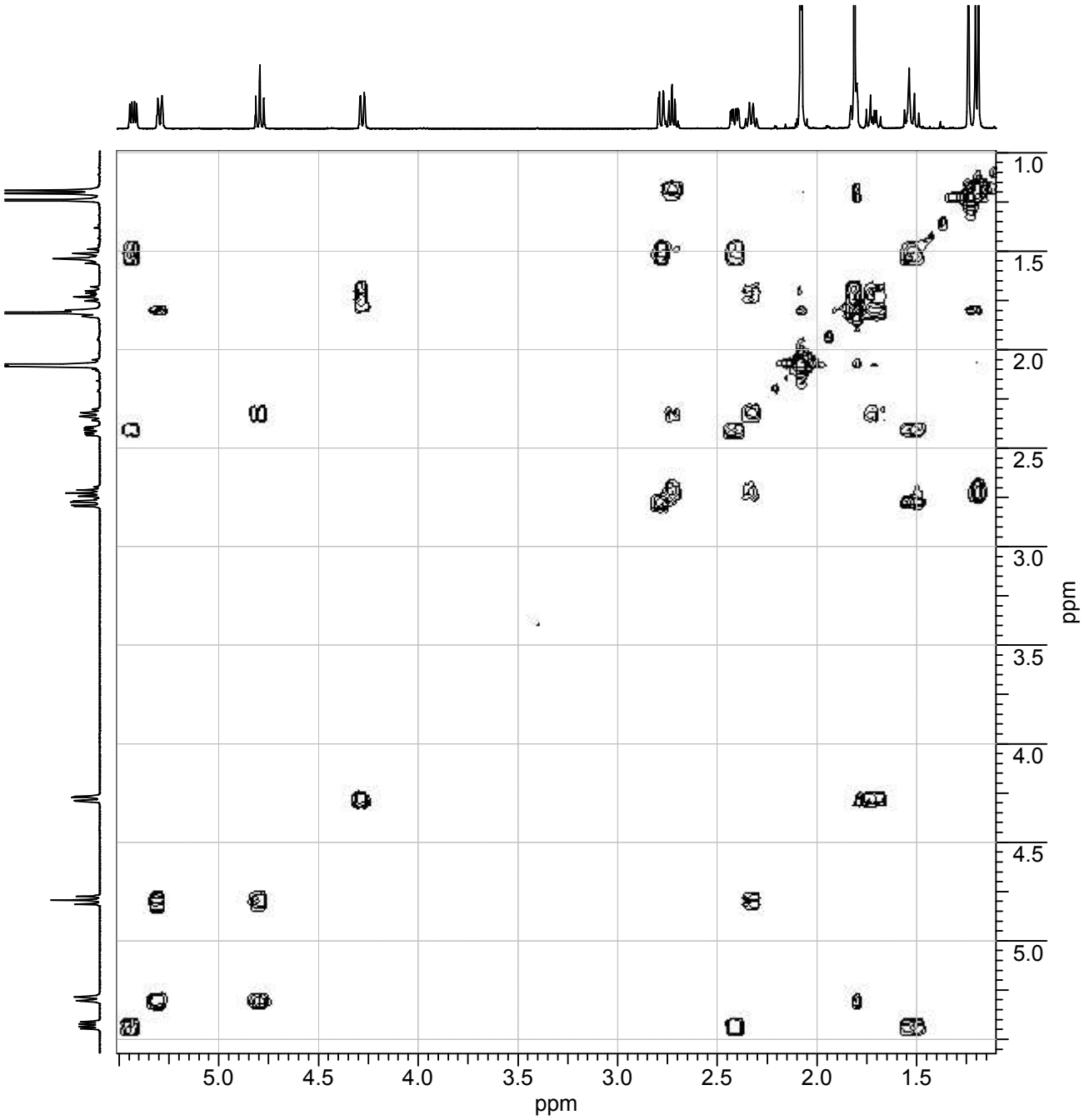


Line Listing C13

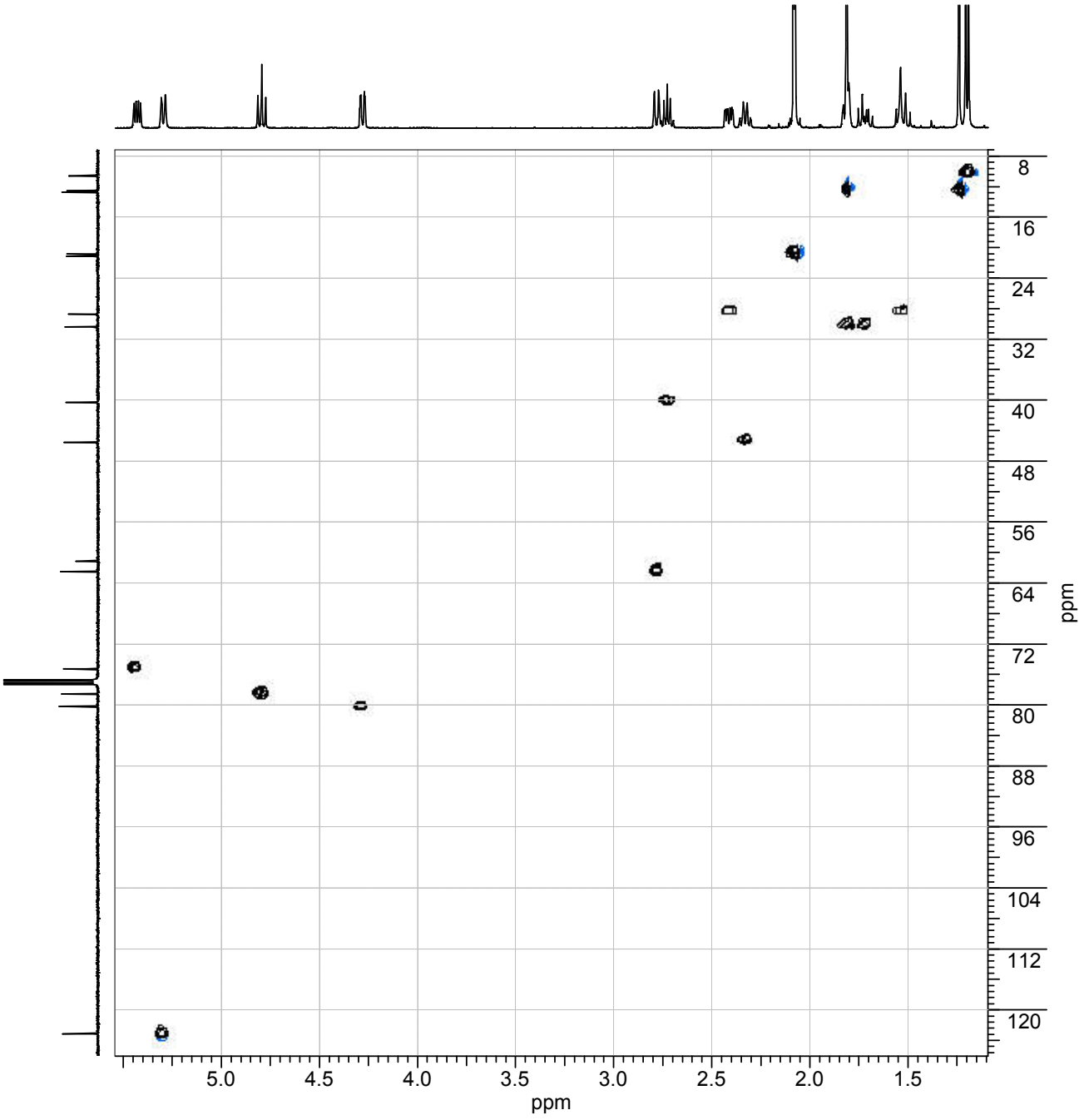
No.	(ppm)	(Hz)	Height
1	10.630	1336.60	0.0901
2	12.568	1580.36	0.0779
3	12.736	1601.47	0.0922
4	20.884	2625.94	0.0762
5	21.151	2659.53	0.0796
6	28.772	3617.78	0.0850
7	30.424	3825.55	0.0822
8	40.319	5069.78	0.0955
9	45.593	5732.93	0.0959
10	61.151	7689.25	0.0535
11	62.548	7864.87	0.0930
12	75.317	9470.43	0.0882
13	76.767	9652.77	0.9997
14	77.019	9684.44	1.0000
15	77.274	9716.59	0.9867
16	78.564	9878.77	0.0917
17	80.232	10088.46	0.0973
18	123.155	15485.74	0.0892
19	140.973	17726.13	0.0520
20	169.632	21329.76	0.0390

21	169.956	21370.54	0.0396
22	178.268	22415.64	0.0405

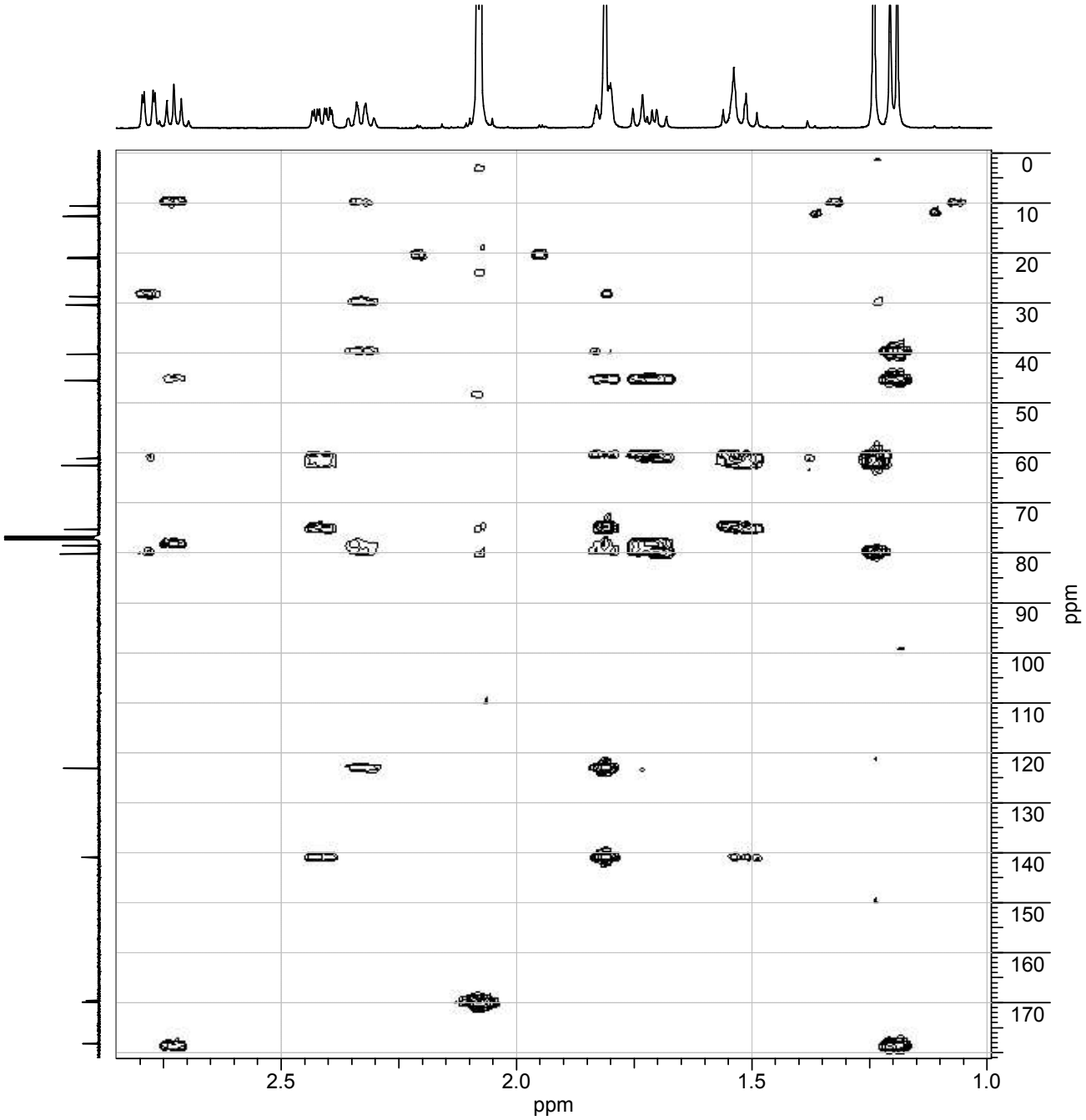
COSY of QS-103-6



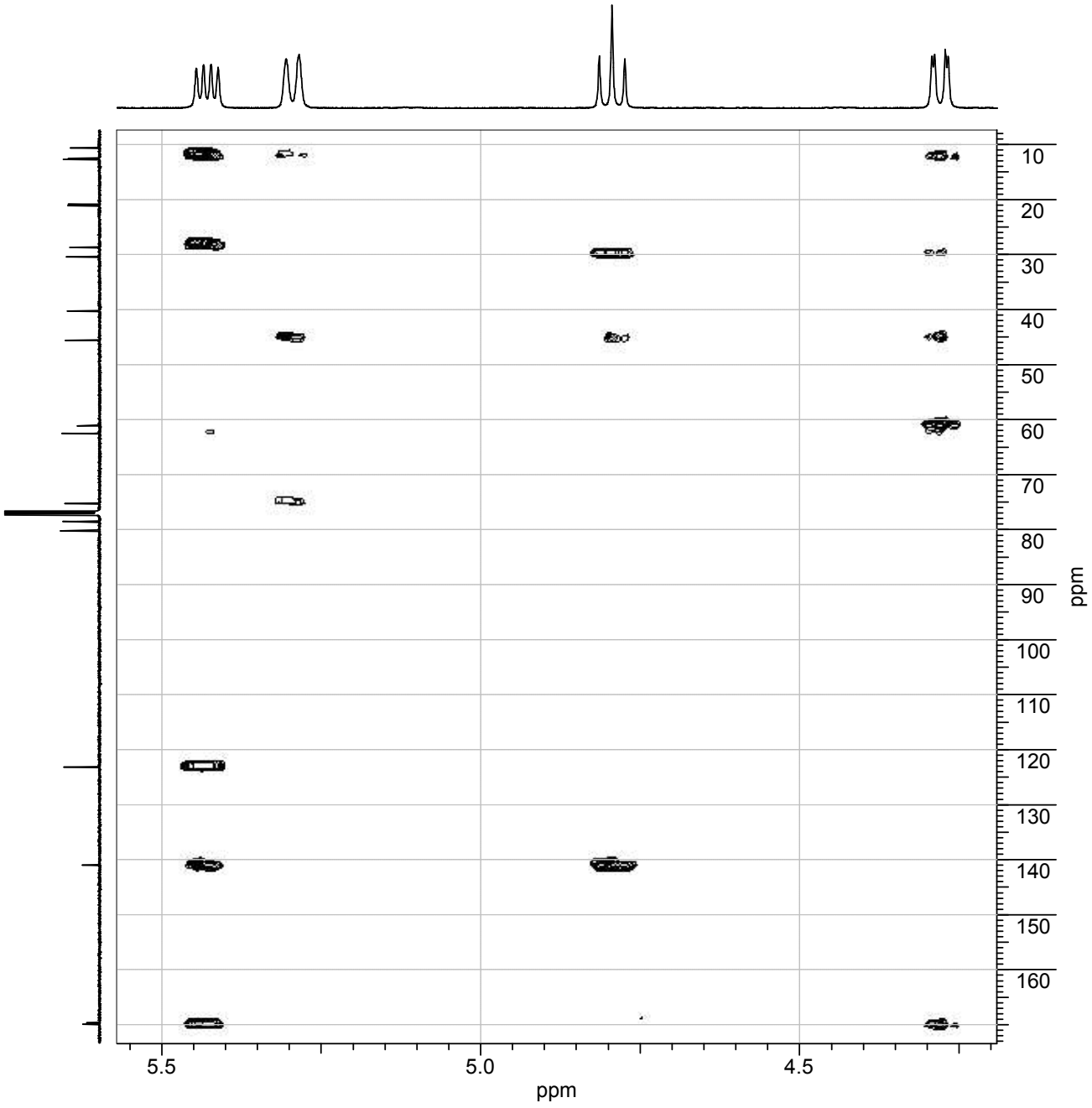
HSQC of QS-103-6



HMBC (high field expansion) of QS-103-6



HMBC (low field expansion) of QS-103-6



NOESY (0.8 sec) of QS-103-6