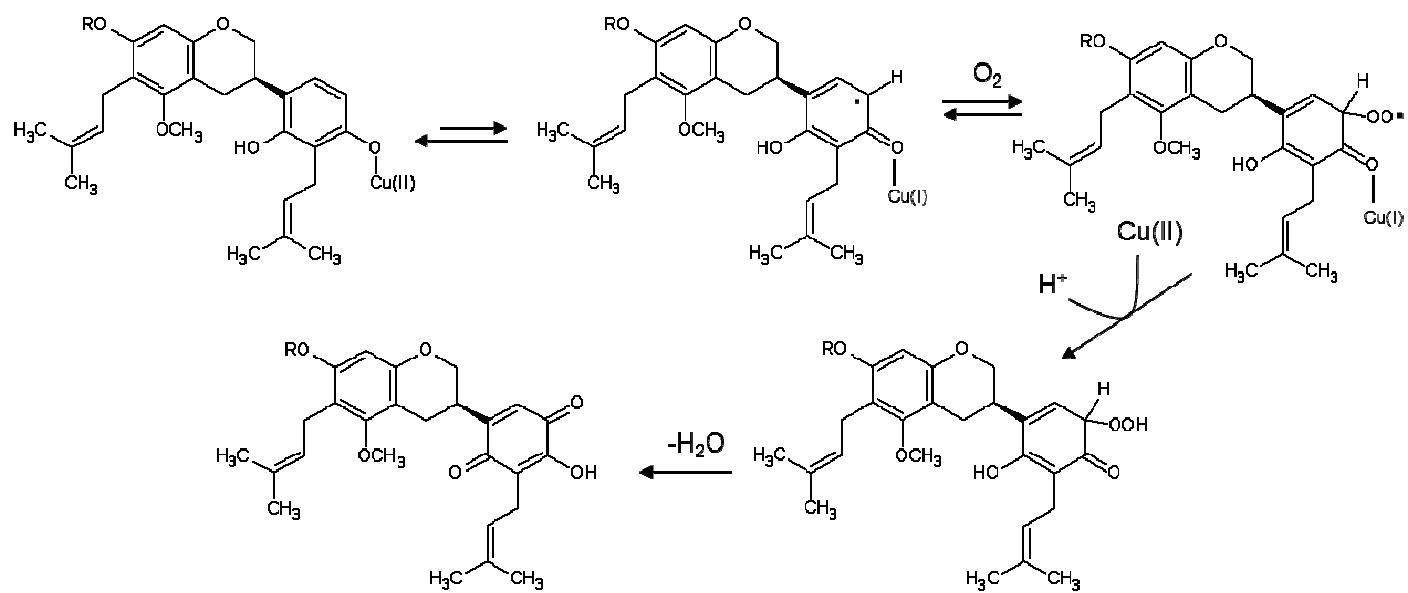
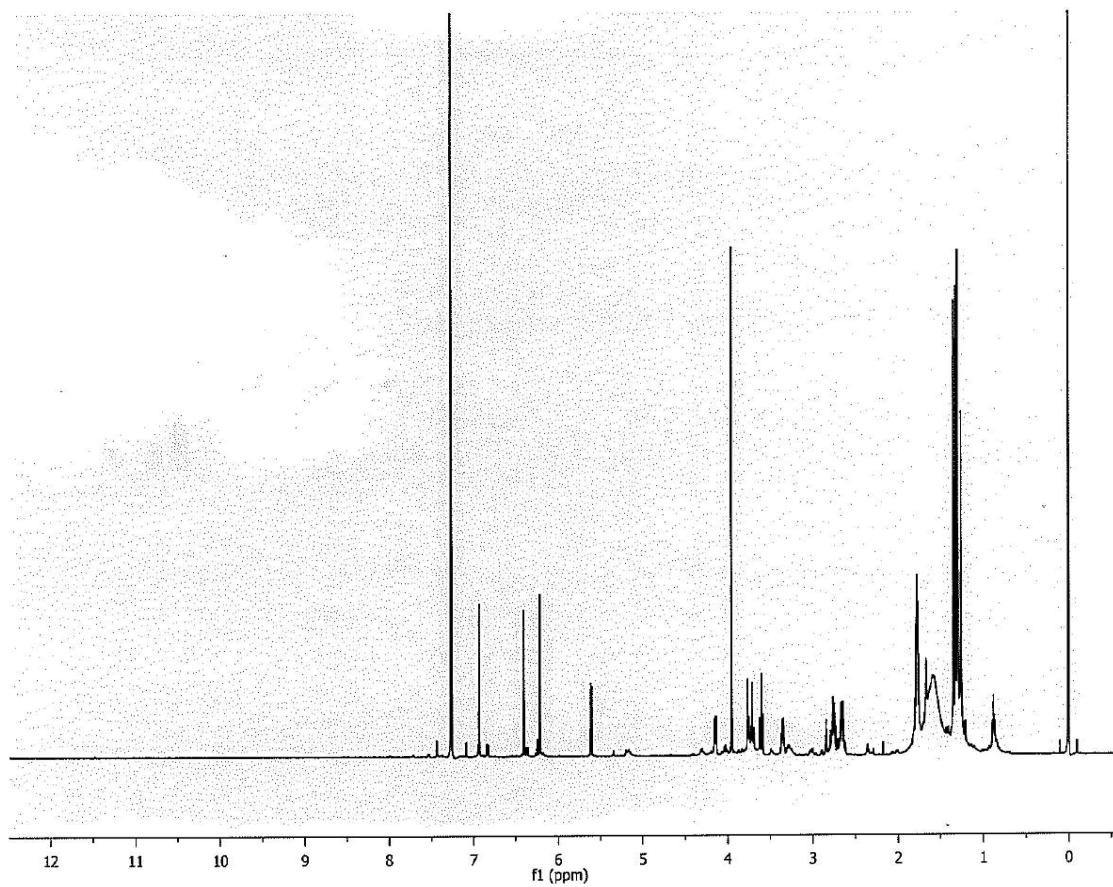


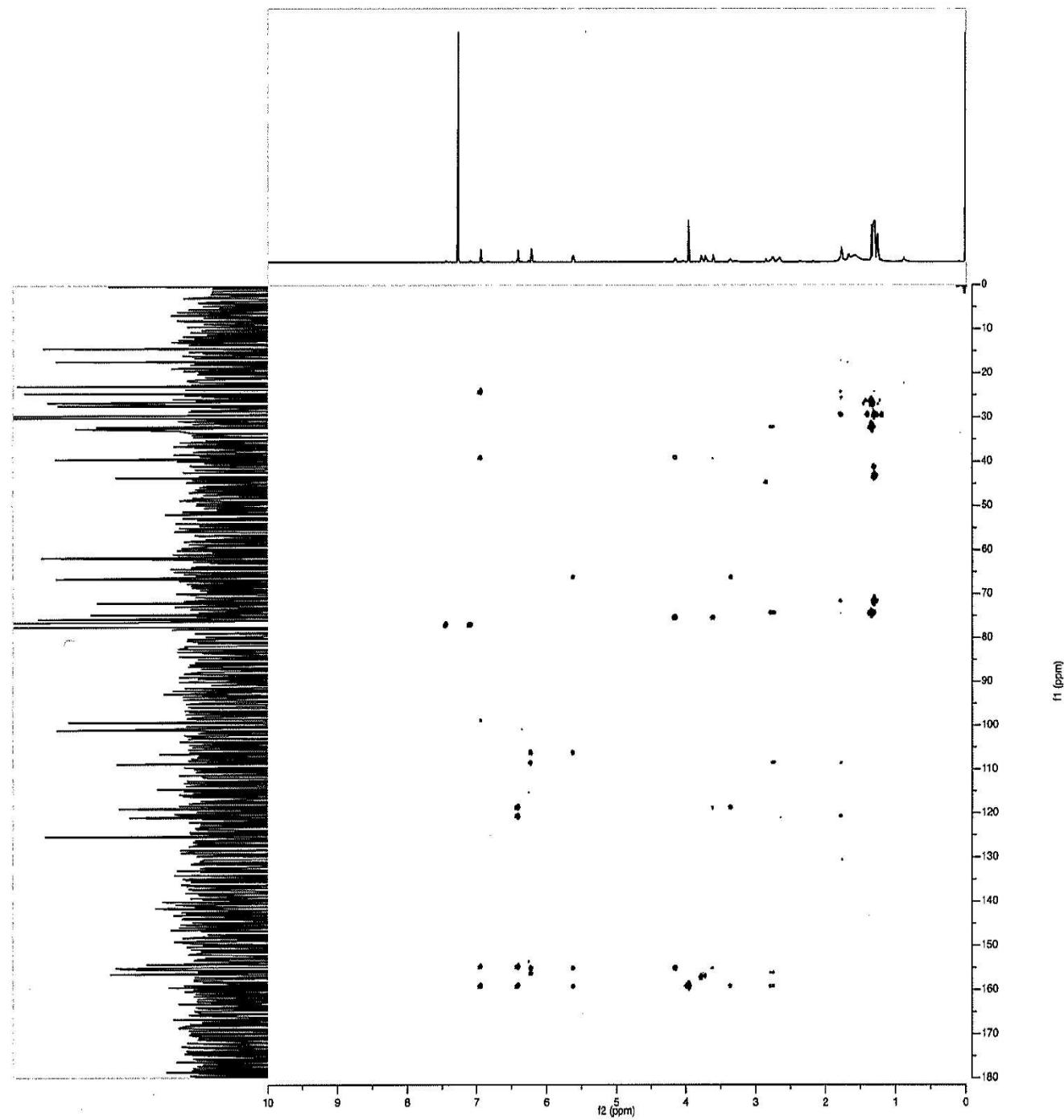
Figure S1



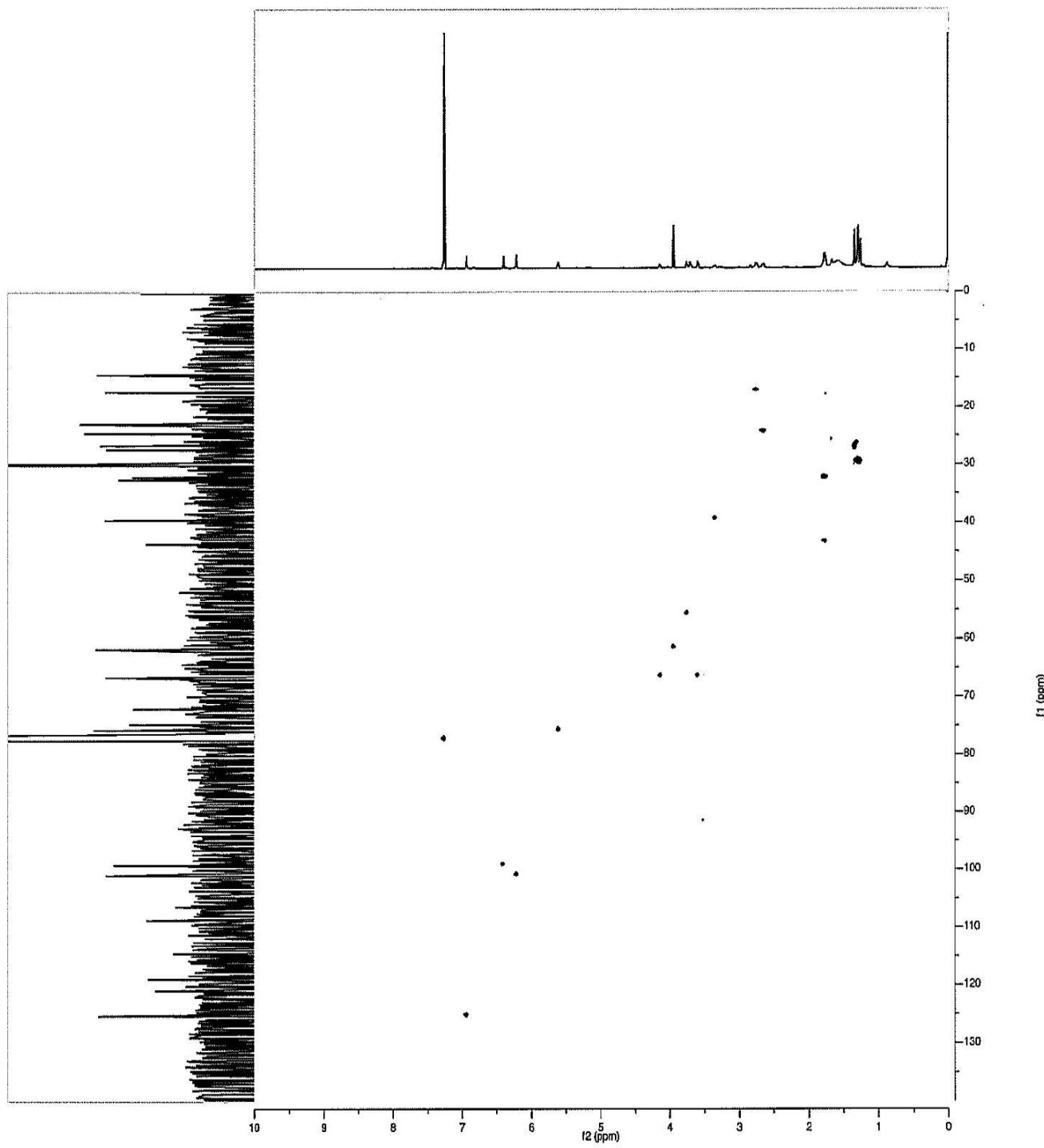
Copper-mediated oxidation of **1** (R = H) and **2** (R = CH₃), modified after Ling *et al.*³¹ There are two possible starting copper(II)-isoflavans: coordination of copper to either the 2'- or to the 4'-hydroxy group. However, the outcome of the reaction will be the same.

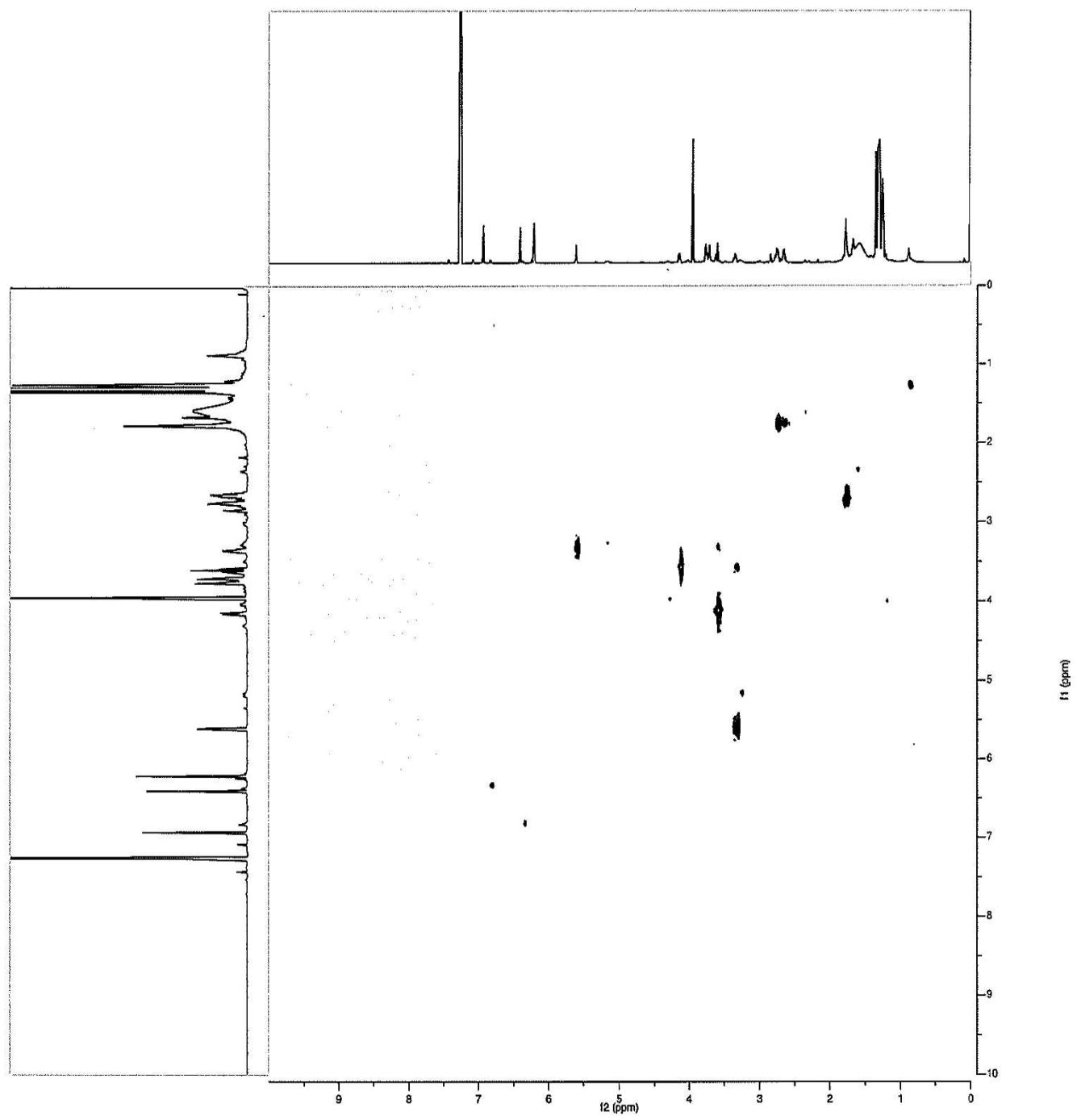


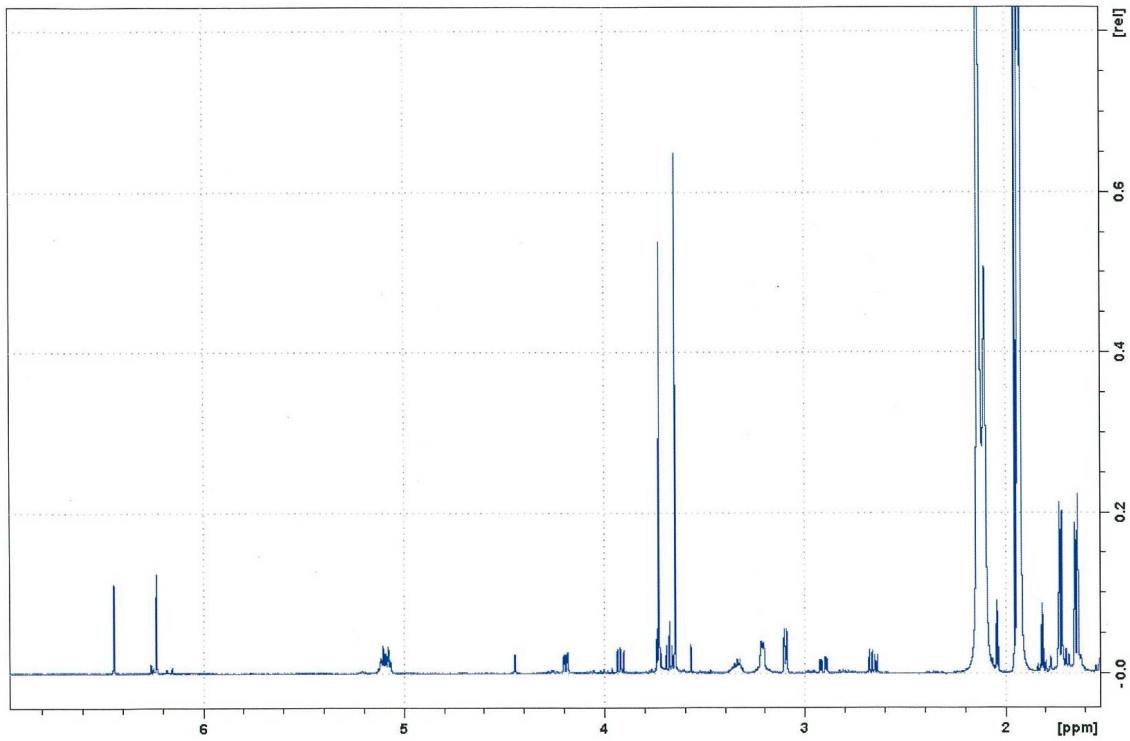
^1H NMR spectrum of **7** (CDCl_3 , 600 MHz).



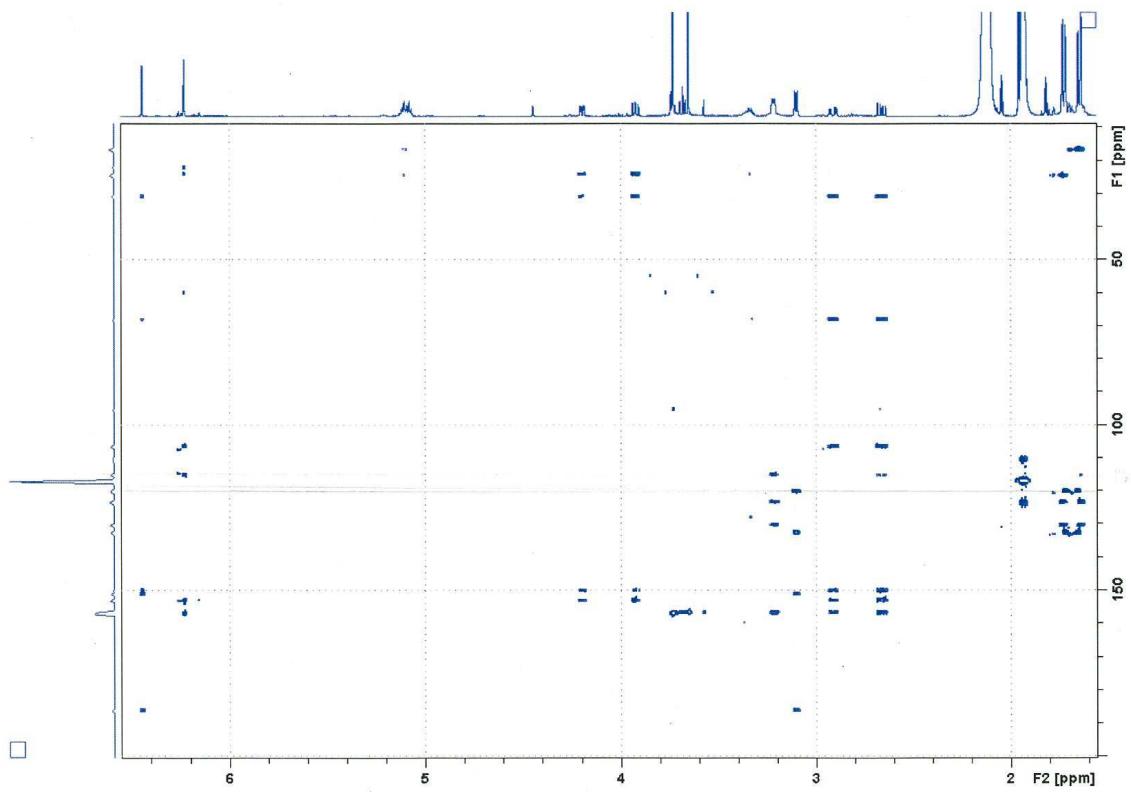
HMBC spectrum of **7** (CDCl_3 , 600 MHz).



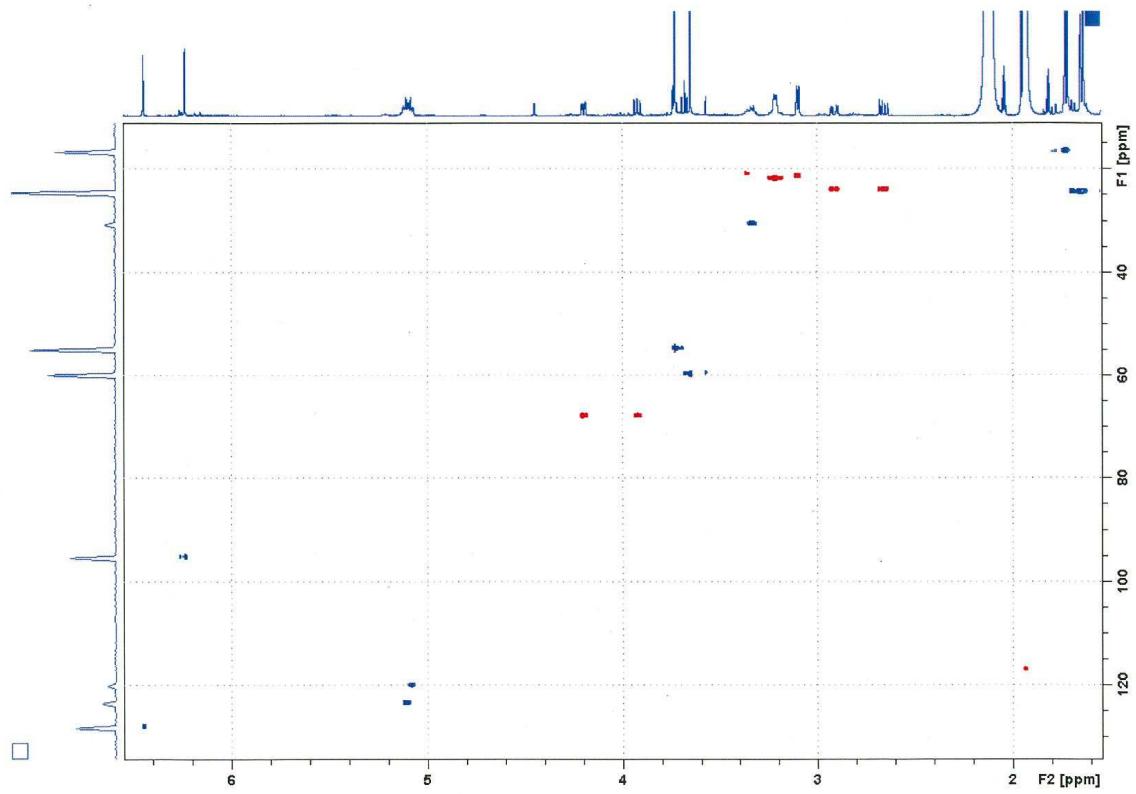




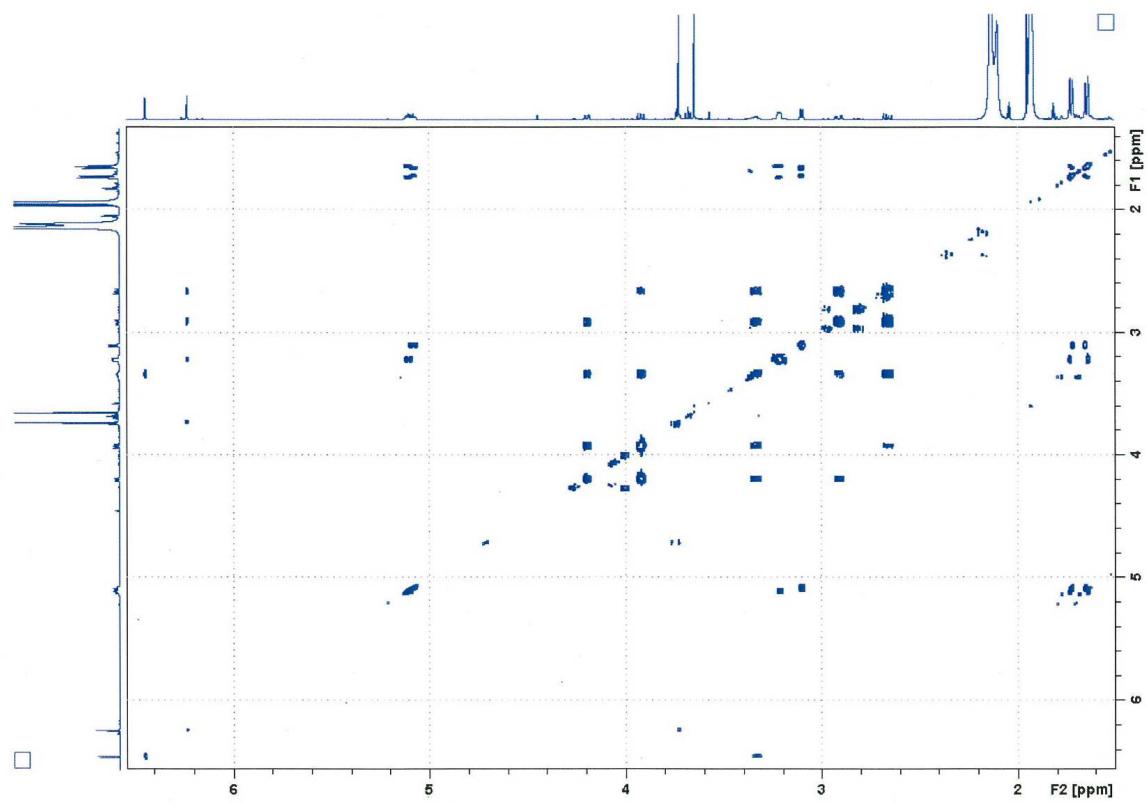
¹H NMR spectrum of **8** (CD₃CN, 600 MHz).



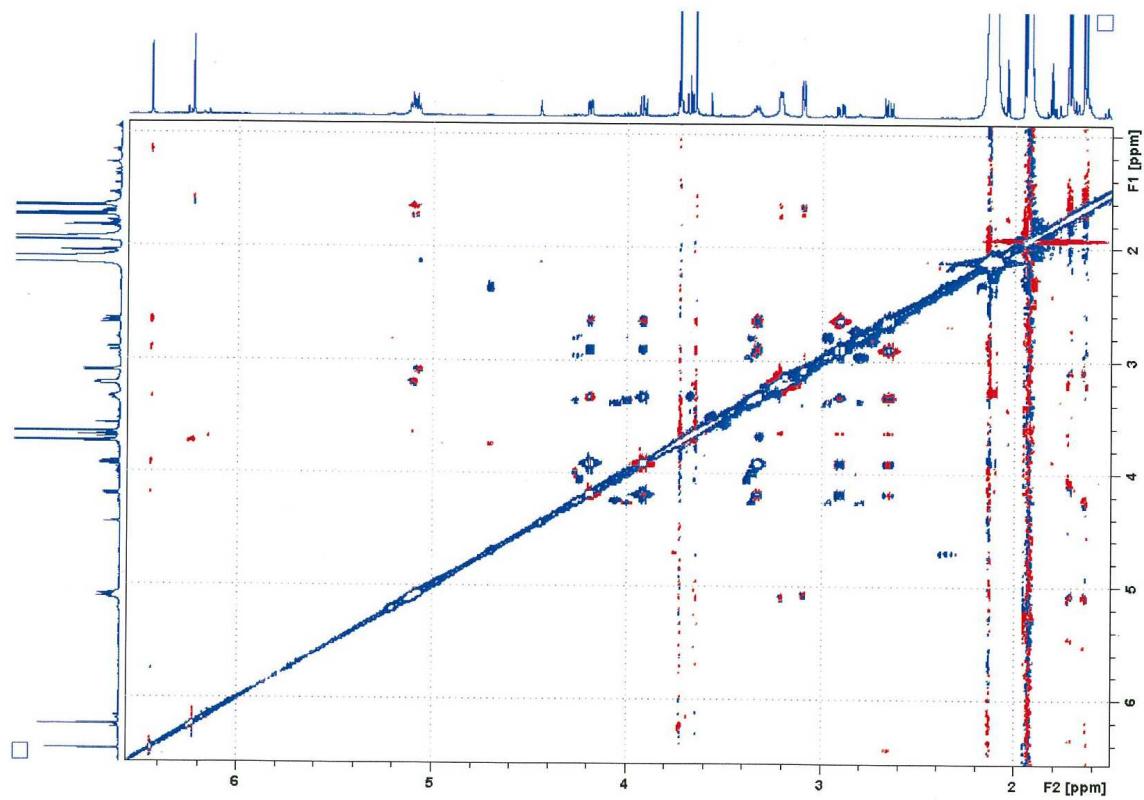
HMBC spectrum of **8** (CD_3CN , 600 MHz).



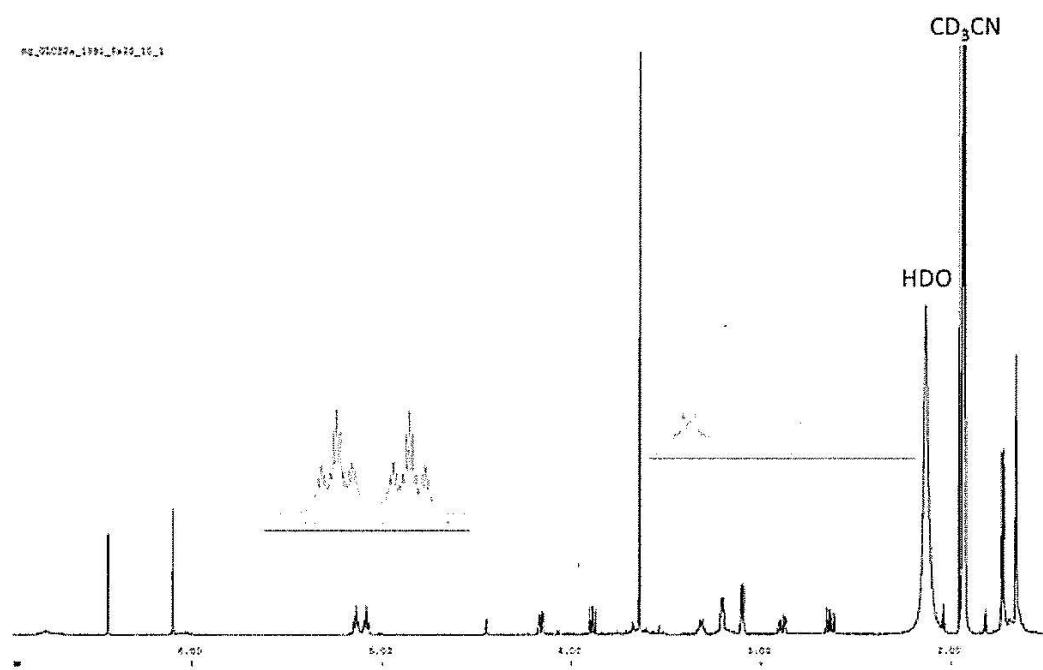
HSQC spectrum of **8** (CD_3CN , 600 MHz).



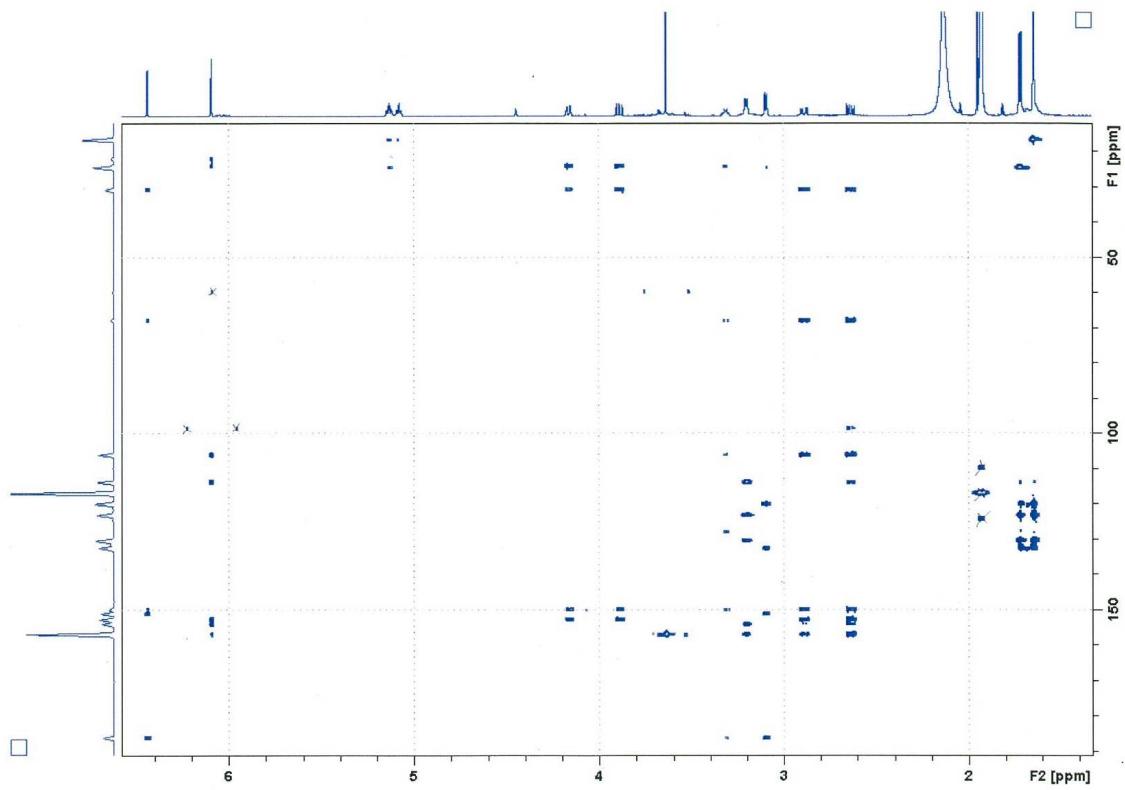
COSY spectrum of **8** (CD_3CN , 600 MHz).



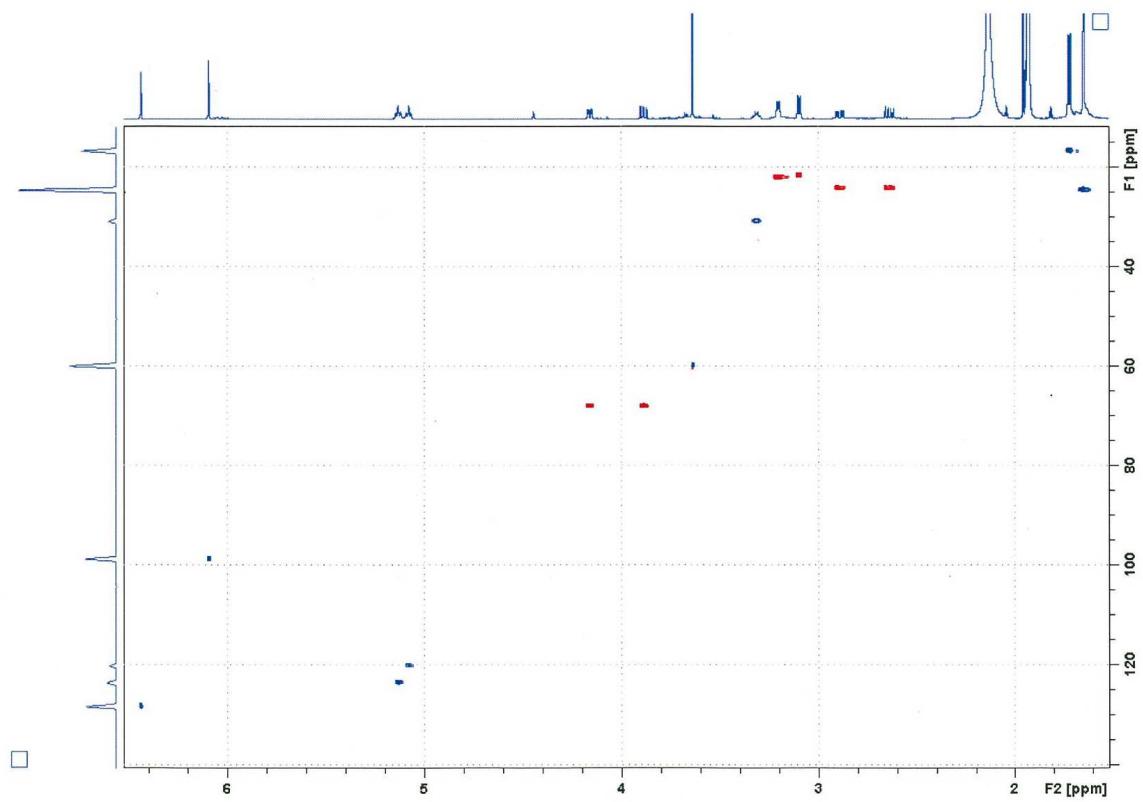
ROESY spectrum of **8** (CD_3CN , 600 MHz).

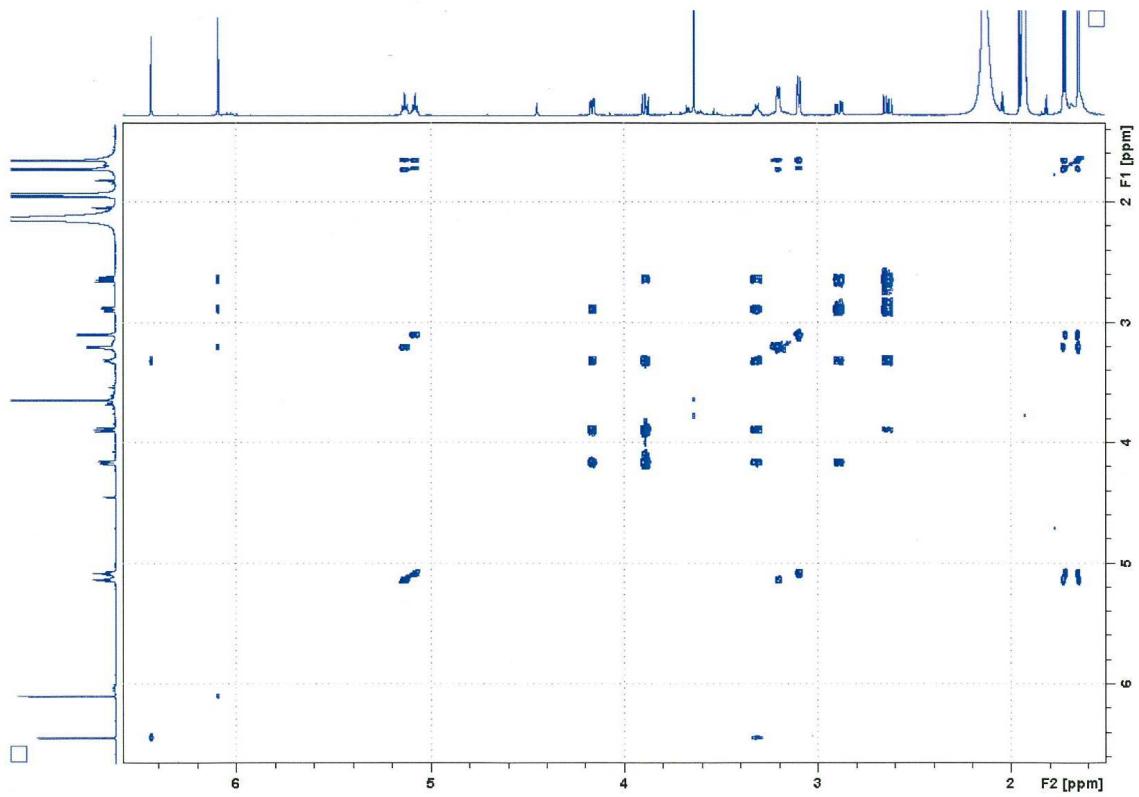


¹H NMR spectrum of **9** (CD₃CN, 600 MHz).

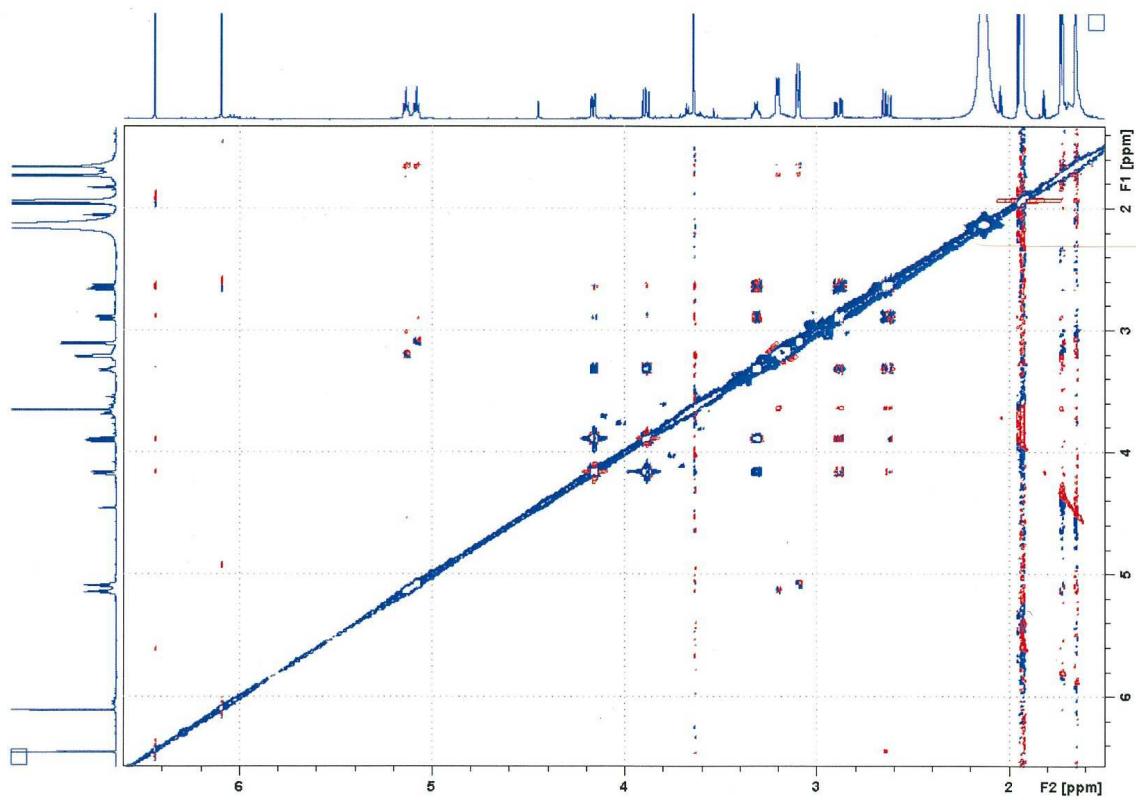


HMBC spectrum of **9** (CD₃CN, 600 MHz).





COSY spectrum of **9** (CD_3CN , 600 MHz).



ROESY spectrum of **9** (CD_3CN , 600 MHz).

Isolation

For the initial fractionation, the extract (414 mg) was separated using MPLC (460 x 36 mm id, 15 μ m) on Luna C-18(2) material (Phenomenex, Torrance, CA) with MeOH–H₂O (62:38) to yield **1** (17 mg) and **2** (21 mg). A second MPLC column (460 x 26 mm id, 100 Å) starting with 115 mg extract on Merck LiChroprep C-18 material (Merck, Darmstadt, Germany) using MeOH–H₂O (70:30) yielded **1** (15 mg), **2** (13 mg), and 1-methoxyficifolinol (13 mg). Another MPLC column using the same LiChroprep stationary phase and MeOH–H₂O (84:16), followed by semi-preparative HPLC on a Zorbax SB C-18 column (250 x 9.4 mm i.d., 5 μ m) using MeOH (0.005% TFA) – H₂O (0.005% TFA) (78:22) as mobile phase afforded kanzonol P (1.1 mg) and 1-methoxyficifolinol (6.1 mg). A number of fractions containing **1** from the previous three MPLC separations were combined and separated by MPLC on LiChroprep C-18 using MeCN (0.005% TFA)–H₂O (0.005% TFA). Combined fractions 2-4 were subsequently subjected to semi-preparative HPLC on a Zorbax SB C-18 column (250 x 9.4 mm, 5 μ m) with MeOH (0.001% TFA)–H₂O (0.001% TFA) (72:28) to yield **1** (10 mg), **3** (1.3 mg), and **5** (1.4 mg).

For the isolation of the additional minor components, 615 mg extract was separated on a large scale MPLC column (460 x 76 cm i.d., 15 μ m) using Luna C-18(2) as stationary phase and MeOH (0.005% TFA) – H₂O (0.005% TFA) as eluent, giving 11 fractions. Fraction 1 contained pure liquiritigenin (8.0 mg). Fraction 5 was subjected semi-preparative HPLC on a Zorbax SB C-18 column (250 x 9.4 mm, 5 μ m) using MeOH (0.001% TFA)–H₂O (0.001% TFA) (58:42) as mobile phase, affording vestitol (0.68 mg), medicarpin (1.9 mg), dihydrolicoisoflavone (1.2 mg), glyasperin F (1.4 mg), glyasperin C (1.9 mg), licoarylcoumarin (1.7 mg), licocoumarone (1.0 mg), and semilicoisoflavone B (1.6 mg). Fraction 6 was subjected to semi-preparative HPLC on a Zorbax SB C-18 column (250 x 9.4 mm, 5 μ m) using MeOH (0.001% TFA)–H₂O (0.001% TFA) (68:32) as solvent. From this separation, medicarpin (0.12 mg),

edudiol (0.95 mg), licoricone (0.87 mg), **4** (1.7 mg), and **6** (3.6 mg) were obtained. Fraction 10 was separated by semi-preparative HPLC on a Zorbax SB C-18 column (250 x 9.4 mm, 5 μ m) using MeOH (0.001% TFA)–H₂O (0.001% TFA) (72:28), yielding **1** (1.9 mg), licoricone (1.2 mg), and gancaonin I (0.88 mg).

MPLC fraction 11 was subjected to gel filtration on Sephadex LH-20 with MeOH–CH₂Cl₂ (1:1) to give five fractions. Fractions 1 and 2 were purified using semi-preparative HPLC on the Zorbax SB C-18 column using MeOH (0.001% TFA)–H₂O (0.001% TFA) (68:32) as mobile phase. This led to the isolation of **2** (5.2 mg), **7** (1.5 mg), and **8** (2.1 mg).

Data processing and evaluation

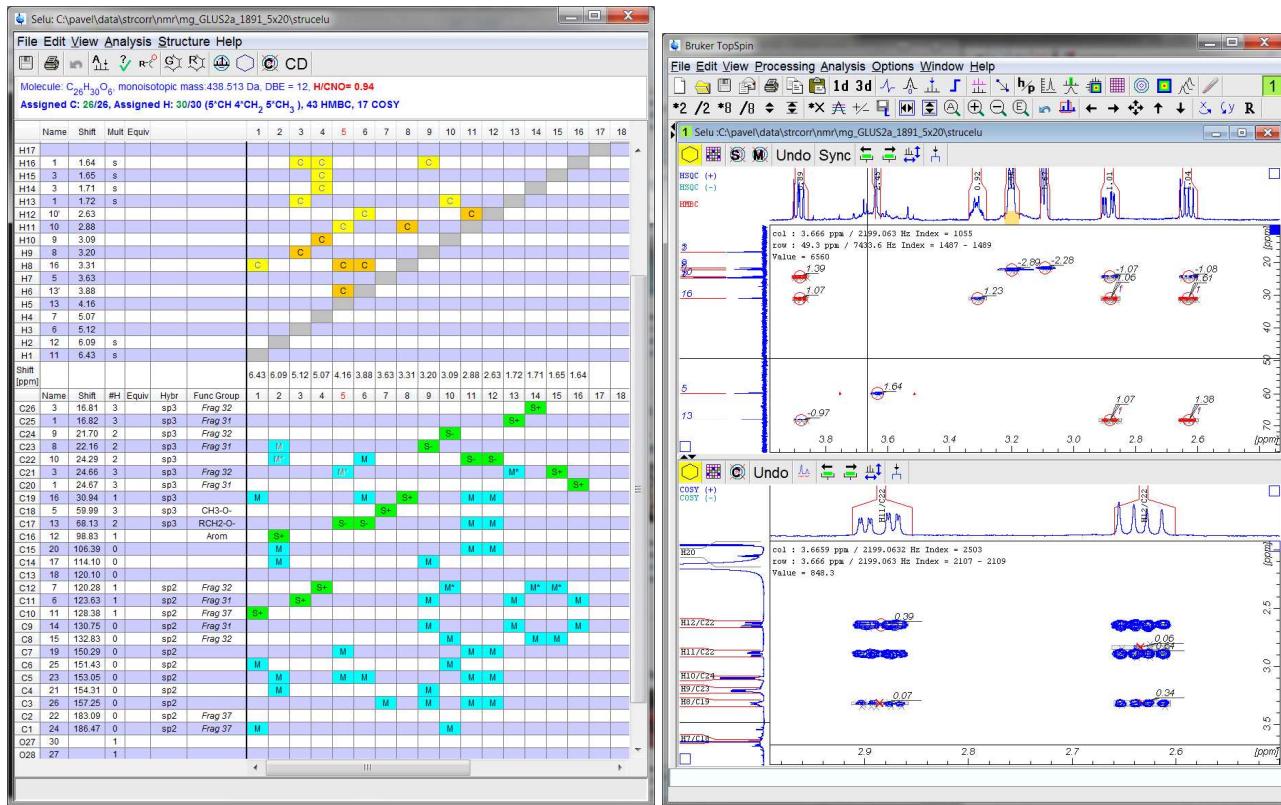
The NMR data acquired were processed according to the general experimental procedures. Bruker structure elucidation package SELU (Topspin 3.1) was used to get the peak and multiplet lists in a fully automated way. This procedure is parameter free – all required information, e.g. the signal to noise ratio, is calculated from the spectra. The multiplet lists are collected to a spreadsheet-like correlation table.

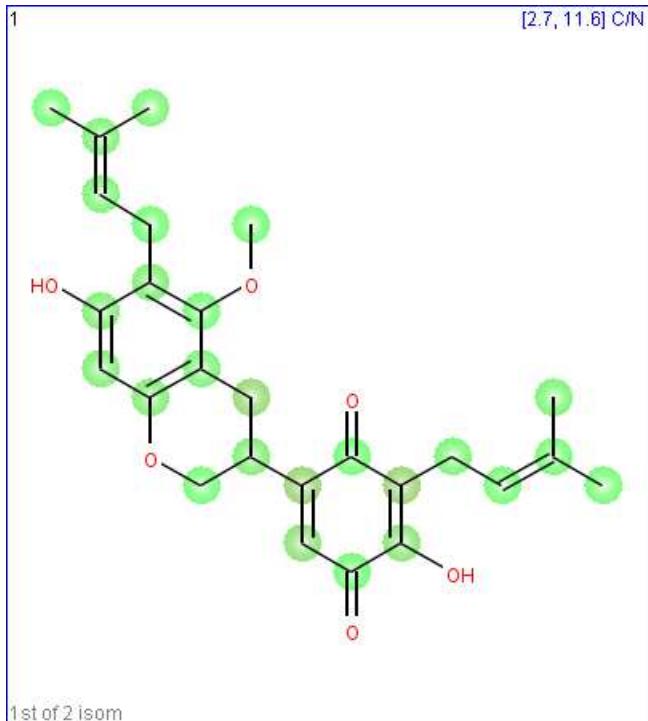
The automatic step is usually followed by short visual inspection of the results. The SELU module contains combined display linking the correlation table and the spectra display. This allows fast inspection and correction of generated HSQC, HMBC and COSY multiplet lists [Figure]. Necessary modifications (e.g. add or remove multiplet) may be done either in the correlation table, or directly in the spectrum.

The next step was the structure generator run. The first trial without further information delivered too many proposals. Additional constraints were necessary to reduce the number of structure candidates.

The UV spectra confirmed the presence of at least one aromatic moiety, the two quaternary carbons at 183 and 186 ppm show typical shifts for a quinone. This additional information was sufficient to reduce the number of structure candidates to only one. Two independent C13 chemical shift prediction methods were used to validate the result. Both predictors (Perch and Modcrafts NMRPredict), which are part of

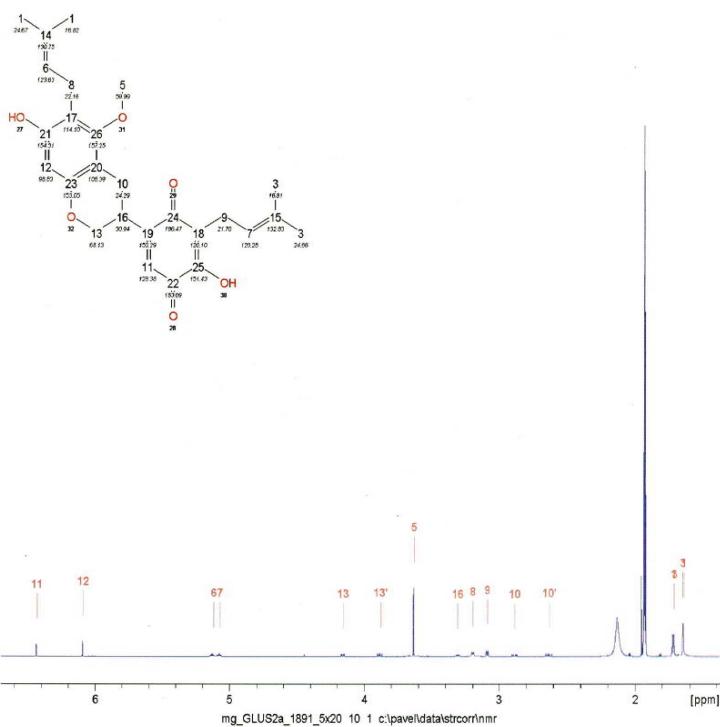
the SELU software, confirmed the correctness of the structure. Additional visual inspection of long range HMBC peaks which were skipped by automatic peak picking did not allow any contradiction between the NMR data and proposed structure.





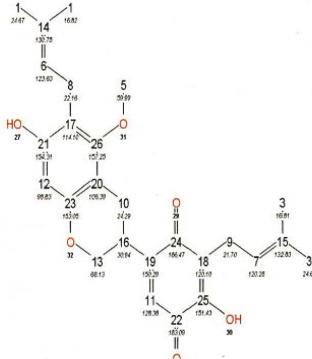
¹H table of assignments

Atom	Shift [ppm]	Multiplicity	Bound to	selu Atom
1	1.64	s	1 (C20)	H16
3	1.65	s	3 (C21)	H15
3	1.71	s	3 (C26)	H14
1	1.72	s	1 (C25)	H13
10'	2.63		10 (C22)	H12
10	2.68		10 (C22)	H11
9	3.09		9 (C24)	H10
8	3.20		8 (C23)	H9
16	3.31		16 (C19)	H8
5	3.63		5 (C18)	H7
13'	3.88		13 (C17)	H6
13	4.16		13 (C17)	H5
7	5.07		7 (C12)	H4
6	5.12		6 (C11)	H3
12	6.09	s	12 (C16)	H2
11	6.43	s	11 (C10)	H1



¹H NMR assignments obtained for **9** with the SELU structure elucidation program.

mg_GLUS2a_1891_5x20

¹H table of assignmentsSum formula: C₂₆H₃₀O₆

Solvent: CD3CN

Description:

¹³C table of assignments. User assigned shifts are shown in italic.

Atom	Shift [ppm]	Multiplicity	Bound to	selu Atom
1	1.64	s	1 (C20)	H16
3	1.65	s	3 (C21)	H15
3	1.71	s	3 (C26)	H14
1	1.72	s	1 (C25)	H13
10'	2.63		10 (C22)	H12
10	2.88		10 (C22)	H11
9	3.09		9 (C24)	H10
8	3.20		8 (C23)	H9
16	3.31		16 (C19)	H8
5	3.63		5 (C18)	H7
13'	3.88		13 (C17)	H6
13	4.16		13 (C17)	H5
7	5.07		7 (C12)	H4
6	5.12		6 (C11)	H3
12	6.09	s	12 (C16)	H2
11	6.43	s	11 (C10)	H1

Atom	Shift [ppm]	# H's	selu Atom
3	16.81	3	C26
1	16.82	3	C25
9	21.70	2	C24
8	22.16	2	C23
10	24.29	2	C22
3	24.66	3	C21
1	24.67	3	C20
16	30.94	1	C19
5	59.99	3	C18
13	68.13	2	C17
12	98.83	1	C16
20	106.39	0	C15
17	114.10	0	C14
18	120.10	0	C13
7	120.28	1	C12
6	123.63	1	C11
11	128.38	1	C10
14	130.75	0	C9
15	132.83	0	C8
19	150.29	0	C7
25	151.43	0	C6
23	153.05	0	C5
21	154.31	0	C4
26	157.25	0	C3
22	163.09	0	C2
24	166.47	0	C1

¹³C NMR assignments obtained for **9** with the SELU structure elucidation program.