Supporting information I

Novel photoinduced squalene cyclic peroxide identified, detected and quantified in human skin surface lipids

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Content:

1. MRM conditions for the method optimized for the analysis of 2-OOH-3-(1,2-dioxane)-SQ:

Table S1. MRM conditions for the method optimized for 2-OOH-3-(1,2-dioxane)-SQ.

	Conditions
	MRM
Source	ESI
Ion polarity	Positive
Declustering potential (V)	75
Entrance potential (V)	10
Temperature (°C)	600
Ion spray voltage (V)	5500
Curtain gas (psi)	20
Collision-activated dissociation gas (psi)	7
Collision energy (V)	25
Collision cell exit potential (V)	20
Ion source gas 1 (psi)	70
Ion source gas 2 (psi)	60

2. Q1 and PIS conditions for the analysis of individual SQ-OOH isomers' secondary oxidation products:

Table S2. Q1 and PIS conditions for the analysis of individual SQ-OOH isomers' secondary oxidation products.

	Q1	**MS/MS**
Source	ESI	ESI
Ion polarity	Positive	Positive
Mass range (***m/z***)	50-700	50-700
End plate offset (V)	-500	-500
Capillary (V)	4500	4500
Nebulizer (bar)	1.6	1.6
Dry gas (L/min)	6	6
Dry heater (°C)	180	180
Funnel 1RF (Vpp)	300	300
Funnel 2RF (Vpp)	400	400
Hexapole RF (Vpp)	400	400
isCID energy	0	0
Ion energy (eV)	3	3
Isolation mass (***m/z***)	300	300
Collision energy (eV)	14	30
Collision (RF) (Vpp)	400	400
Transfer time (μs)	70	70
Peak width	5	5

3. Percentage of individual SQ-OOH isomers among total SQ-OOH isomers in SSLs:

Table S3. Percentage of individual SQ-OOH isomers among total SQ-OOH isomers in SSLs.

Isomer	Subject1	Subject2	Subject3	Subject4	Subject5	Subject6
11-OOH-SQ	11.5%	10.7%	10.5%	11.6%	9.8%	11.9%
7-OOH-SQ	11.2%	11.9%	7.0%	10.2%	9.8%	12.1%
10-OOH-SQ	18.7%	21.2%	29.0%	24.5%	22.2%	23.1%
6-OOH-SQ	17.3%	19.9%	15.6%	18.0%	17.3%	18.1%
3-OOH-SQ	15.0%	14.9%	11.1%	14.2%	12.5%	15.2%
2-OOH-SQ	26.3%	21.4%	26.7%	21.5%	28.4%	19.6%

4. Comparison of the PIS obtained form 6-OOH-SQ and 2-OOH-3-(1,2-dioxane)-SQ, Q1 scan of photooxidized 10-OOH-SQ:

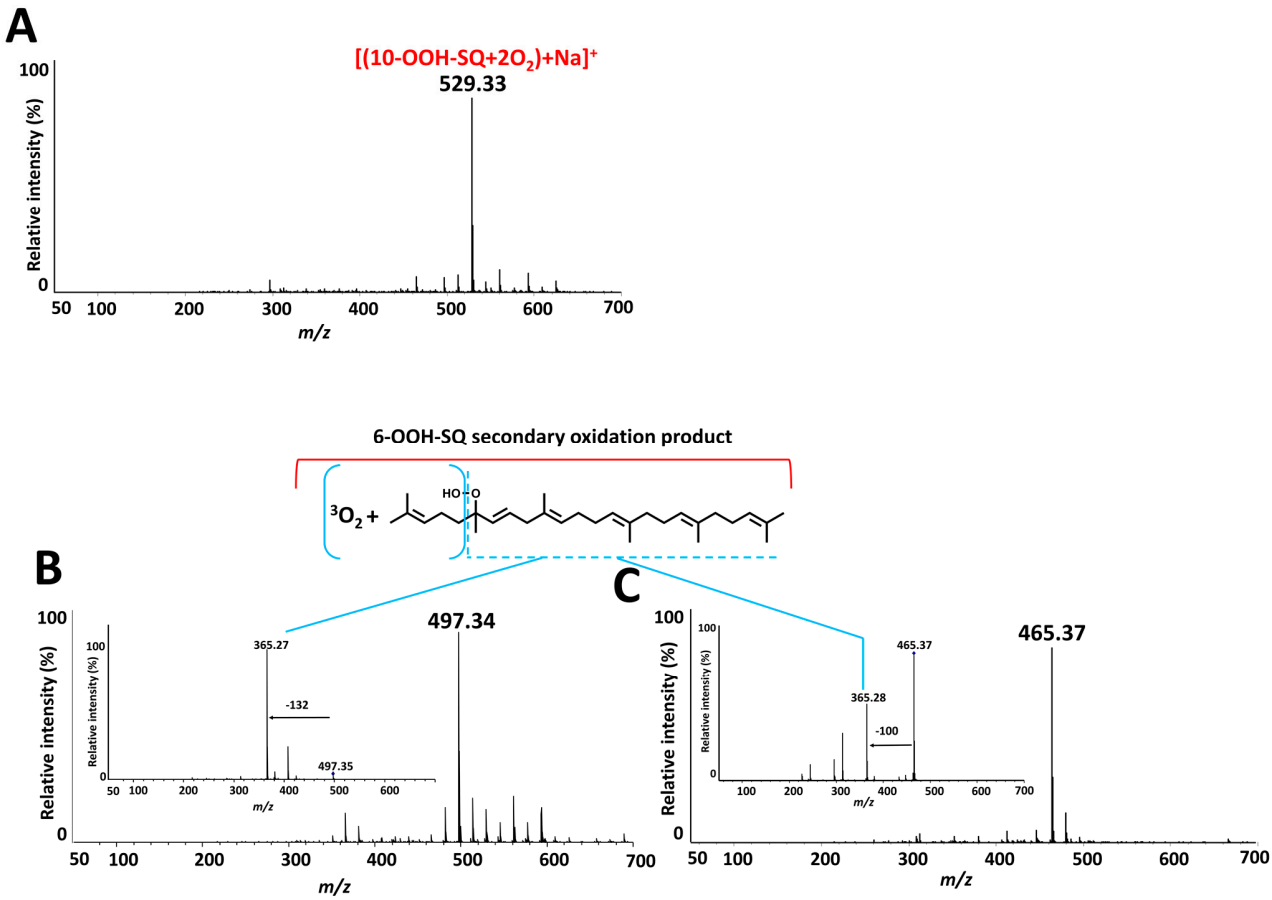
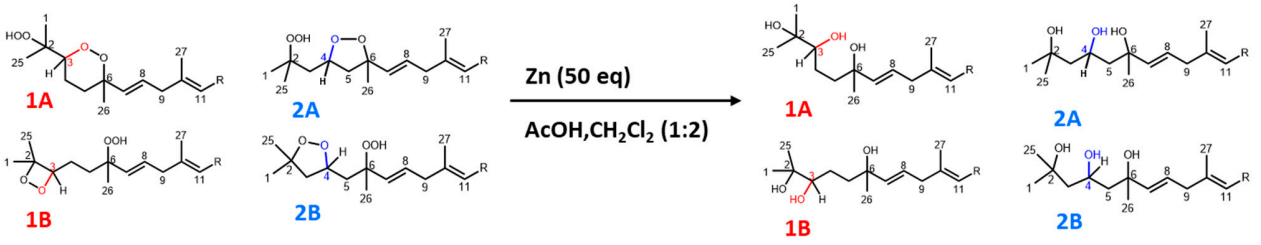


Figure S1. Q1 spectrum of photooxidized 10-OOH-SQ (4 hours) (A) and Q1 spectra and PIS of photooxidized 6-OOH-SQ (B) and unoxidized 6-OOH-SQ (C).

5. Schemes and Q1 scan of the derivatization reactions carried out for the identification of 2-OOH-3-(1,2-dioxane)-SQ:

- **Step1: reduction using Zinc dust**



- **Step2: cleavage of vicinal alcohols using sodium periodate ($NaIO_4$)**

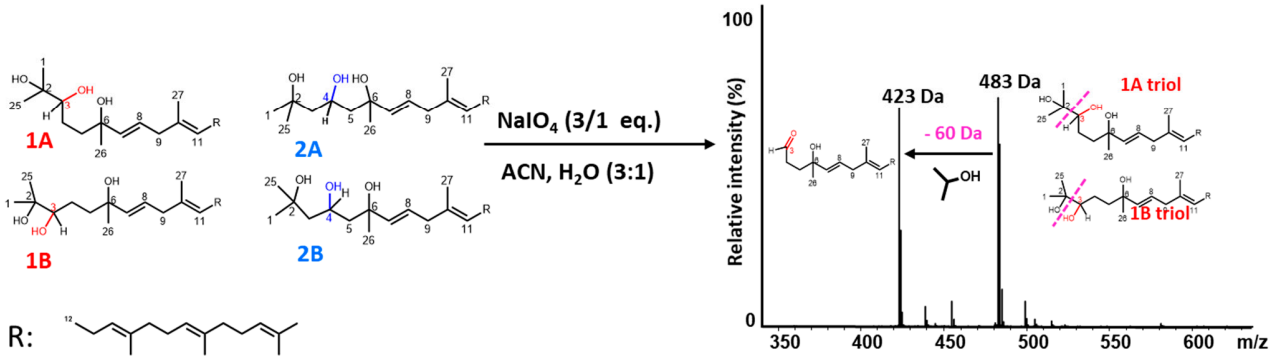


Figure S2. Derivatization reactions of SQ's main secondary oxidation product obtained from photooxidation of 6-OOH-SQ.

6. Q1 scan of the photooxidation of 10-OOH-SQ after 4 hours and 8 hours:

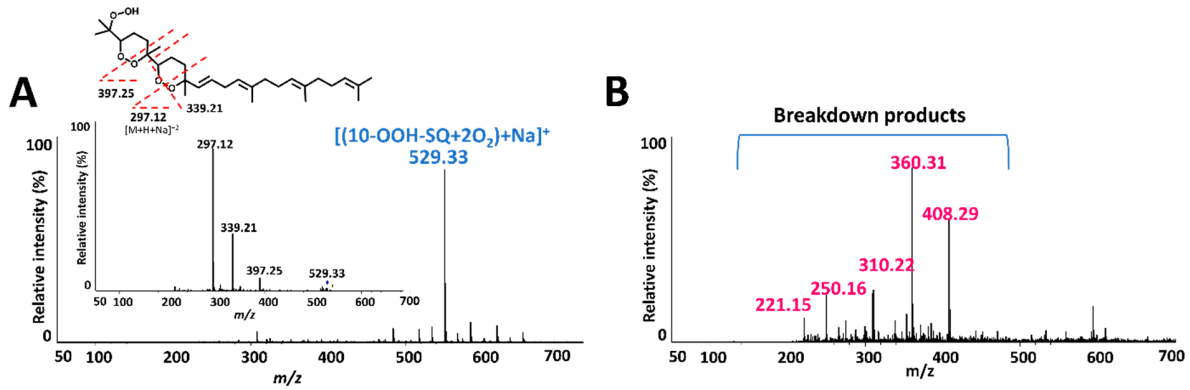


Figure S3. Formation of secondary oxidation product 2-OOH-3,7-di(1,2-dioxane)-SQ after 4 hours of oxidation of 10-OOH-SQ (Q1 + PIS) (A) and decomposition of the secondary oxidation product after 8 hours of oxidation (Q1) (B).

7. Q1 scan of the reaction between Mxp and the main secondary oxidation product of each SQ-OOH isomer.

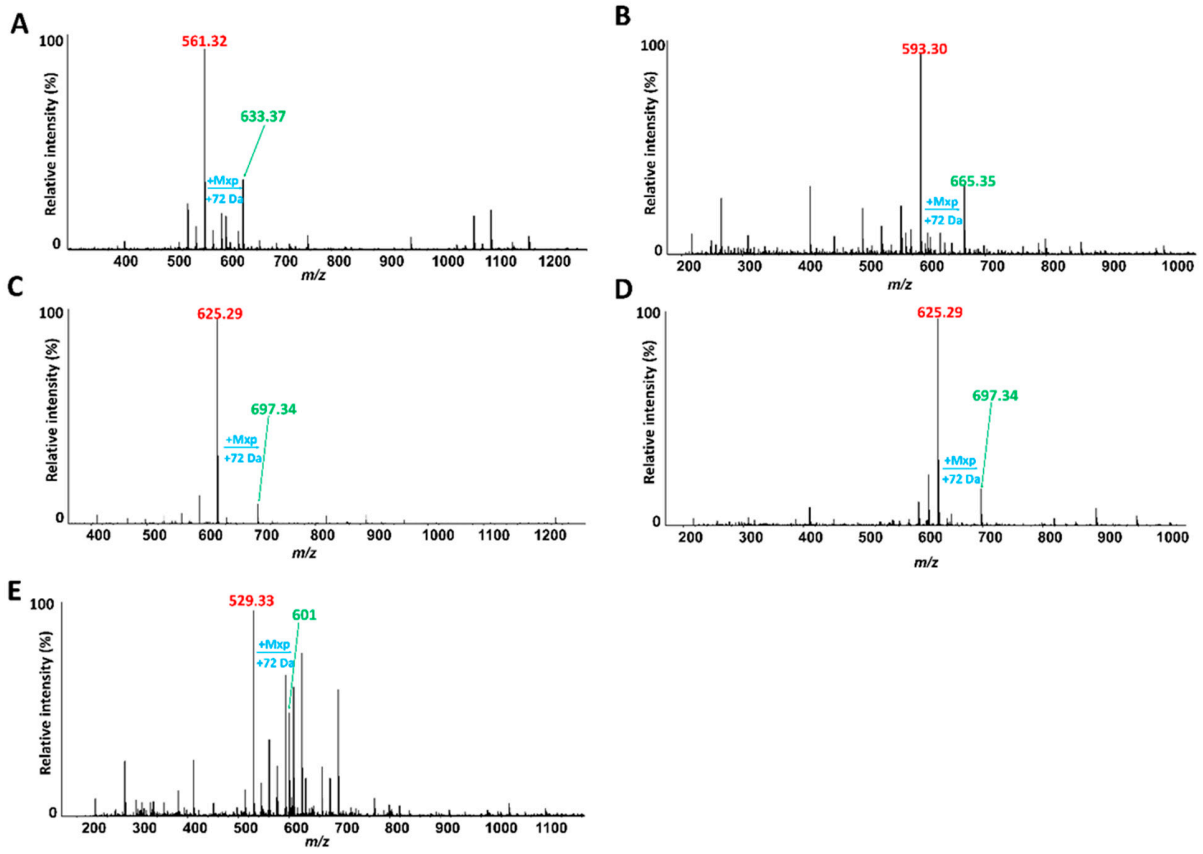


Figure S4. Mxp reaction with the crude sample of the secondary oxidation products obtained from the photooxidation of individual SQ-OOH isomers: (A) 11-OOH-SQ (containing mainly 11-OOH-SQ+3O_2), (B) 7-OOH-SQ (containing mainly 7-OOH-SQ+4O_2), (C) 3-OOH-SQ (containing mainly 3-OOH-SQ+5O_2), (D) 2-OOH-SQ (containing mainly 2-OOH-SQ+5O_2) and (E) 10-OOH-SQ (containing mainly 10-OOH-SQ+2O_2).

8. ^{1}H NMR and ^{13}C NMR spectral data of the major and minor isomers of 2-OOH-3-(1,2-dioxane)-SQ:

Table S4. ^{1}H NMR and ^{13}C NMR spectral data of the major isomer of 2-OOH-3-(1,2-dioxane)-SQ.

Position	1H NMR (CDCl3, 600 M Hz)	13C NMR (CDCl3, 150 M Hz)
1	1.21 (3H, s)	21.0
2	–	83.3
3	4.23 (1H, dd *J* = 10.5 3.3 Hz)	84.7
4	1.58-1.62 (1H, overlapping), 1.80-1.86 (1H, overlapping)	20.4
5	1.72-1.80 (1H, overlapping), 1.86-1.90 (1H, overlapping)	32.9
6	–	80.7
7	5.66 (1H, d, *J* = 15.6 Hz)	134.0
8	5.57 (1H, dt, *J* = 15.6, 7.2 Hz)	129.0
9	2.71 (2H, d, *J* = 6.6 Hz)	42.8
10	–	133.7
11	5.16-5.20 (1H, overlapping)	125.5
12	1.98-2.04 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
13	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
14	5.08-5.16 (1H, overlapping)	124.14, 124.22, or 124.37
15	–	135.2 or 134.9
16	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
17	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
18	5.08-5.16 (1H, overlapping)	124.14, 124.22, or 124.37
19	–	135.2 or 134.9
20	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
21	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
22	5.08-5.16 (1H, overlapping)	124.14, 124.22, or 124.37
23	–	131.3

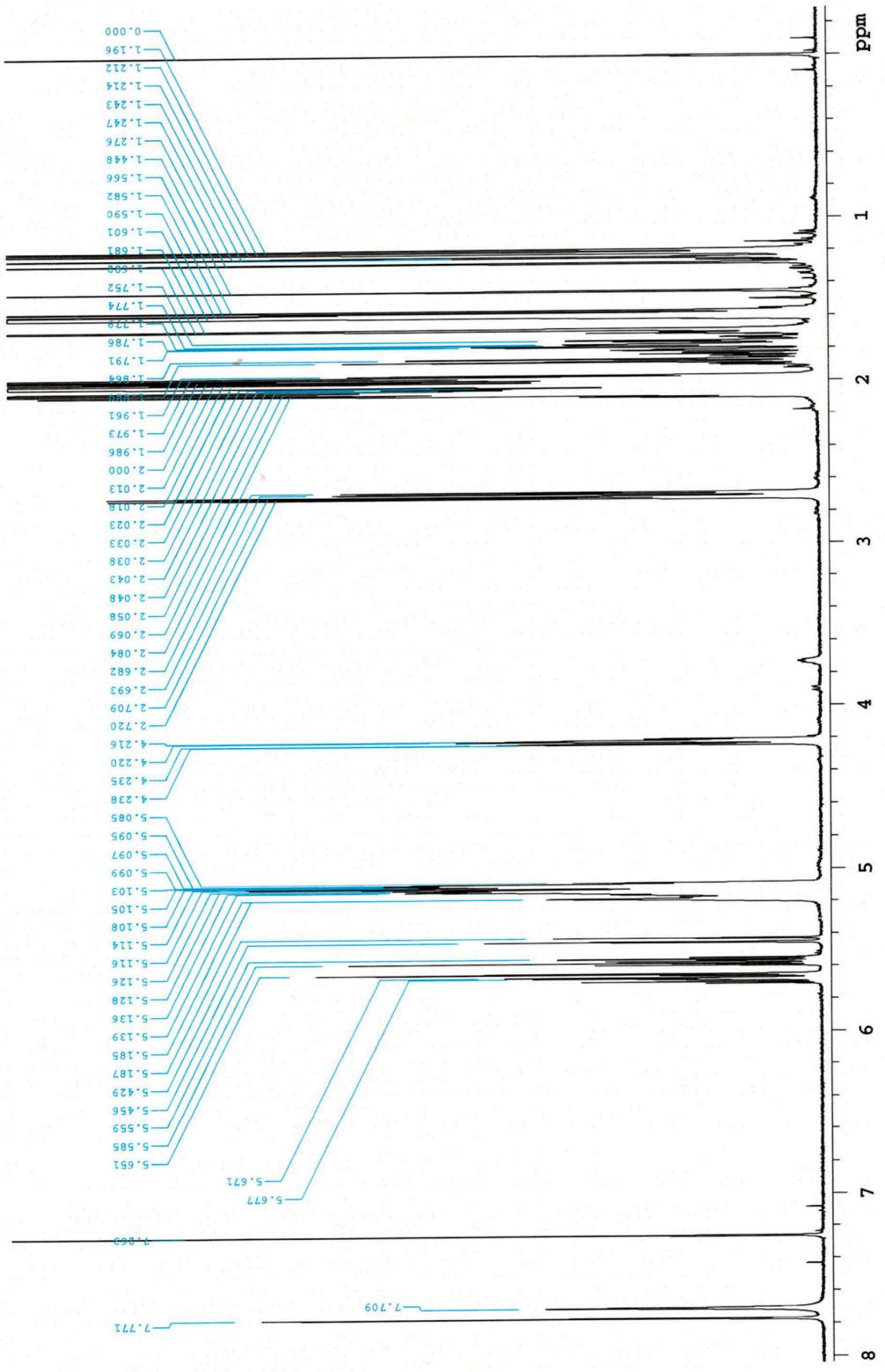
24	1.68 (3H, s)	25.7
25	1.21 (3H, s)	21.0
26	1.20 (3H, s)	26.9
27	1.59 (3H, s)	16.1
28	1.60 (3H, s)	20.9 or 20.3
29	1.60 (3H, s)	20.9 or 20.3
30	1.60 (3H, s)	17.7

Table S5. ^{1}H NMR and ^{13}C NMR spectral data of the minor isomer of 2-OOH-3-(1,2-dioxane)-SQ.

position	**1H NMR (CDCl3, 600 M Hz)**	**13C NMR (CDCl3, 150 M Hz)**
1	1.24 (3H, s)	20.9
2	—	83.2
3	4.22 (1H, dd, *J* = 10.5, 3.3 Hz)	84.7
4	1.66-1.72 (1H, overlapping), 1.84-1.90 (1H, overlapping)	20.4
5	1.72-1.80 (1H, overlapping) 2.02-2.06 (1H, overlapping)	32.7
6	—	79.9
7	5.44 (1H, d, *J* = 16.2 Hz)	134.1
8	5.68 (1H, dt, J = 15.6, 7.2 Hz)	130.4
9	2.69 (2H, d, *J* = 6.6 Hz)	42.8
10	—	133.2
11	5.16-5.20 (1H, overlapping)	125.7
12	1.98-2.04 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
13	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
14	5.08-5.16 (1H, overlapping)	124.10, 124.22, or 124.37
15	–	135.2 or 134.9
16	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4

17	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
18	5.08-5.16 (1H, overlapping)	124.10, 124.22, or 124.37
19	–	135.2 or 134.9
20	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
21	1.90-2.12 (2H, overlapping)	26.6, 26.7, 28.1, 28.2, 28.3, or 28.4
22	5.08-5.16 (1H, overlapping)	124.10, 124.22, or 124.37
23	–	131.3
24	1.68 (3H, s)	25.7
25	1.28 (3H, s)	21.2
26	1.48 (3H, s)	20.9
27	1.59 (3H, s)	16.1
28	1.60 (3H, s)	20.9 or 20.3
29	1.60 (3H, s)	20.9 or 20.3
30	1.60 (3H, s)	17.7

^{1}H NMR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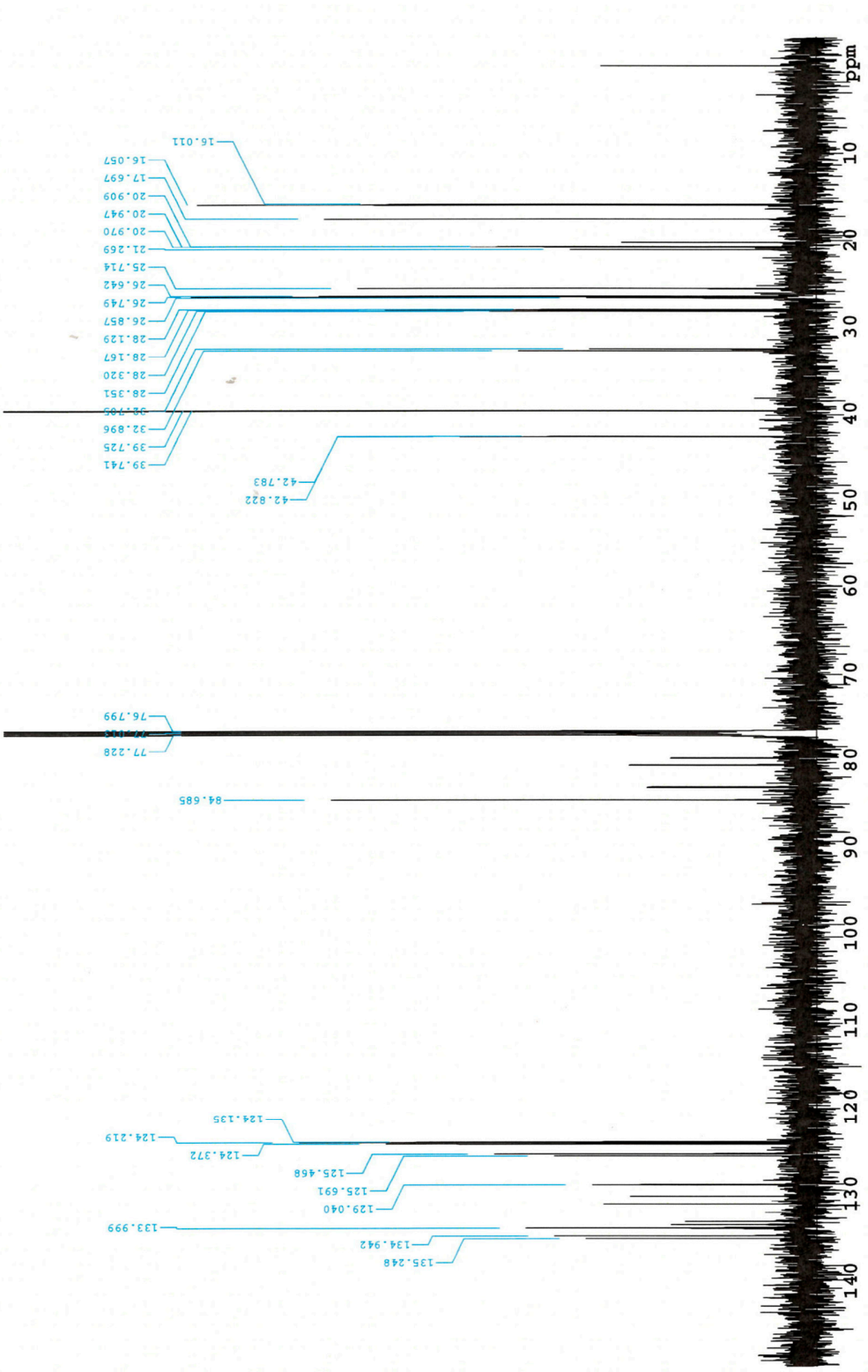
^{13}C NMR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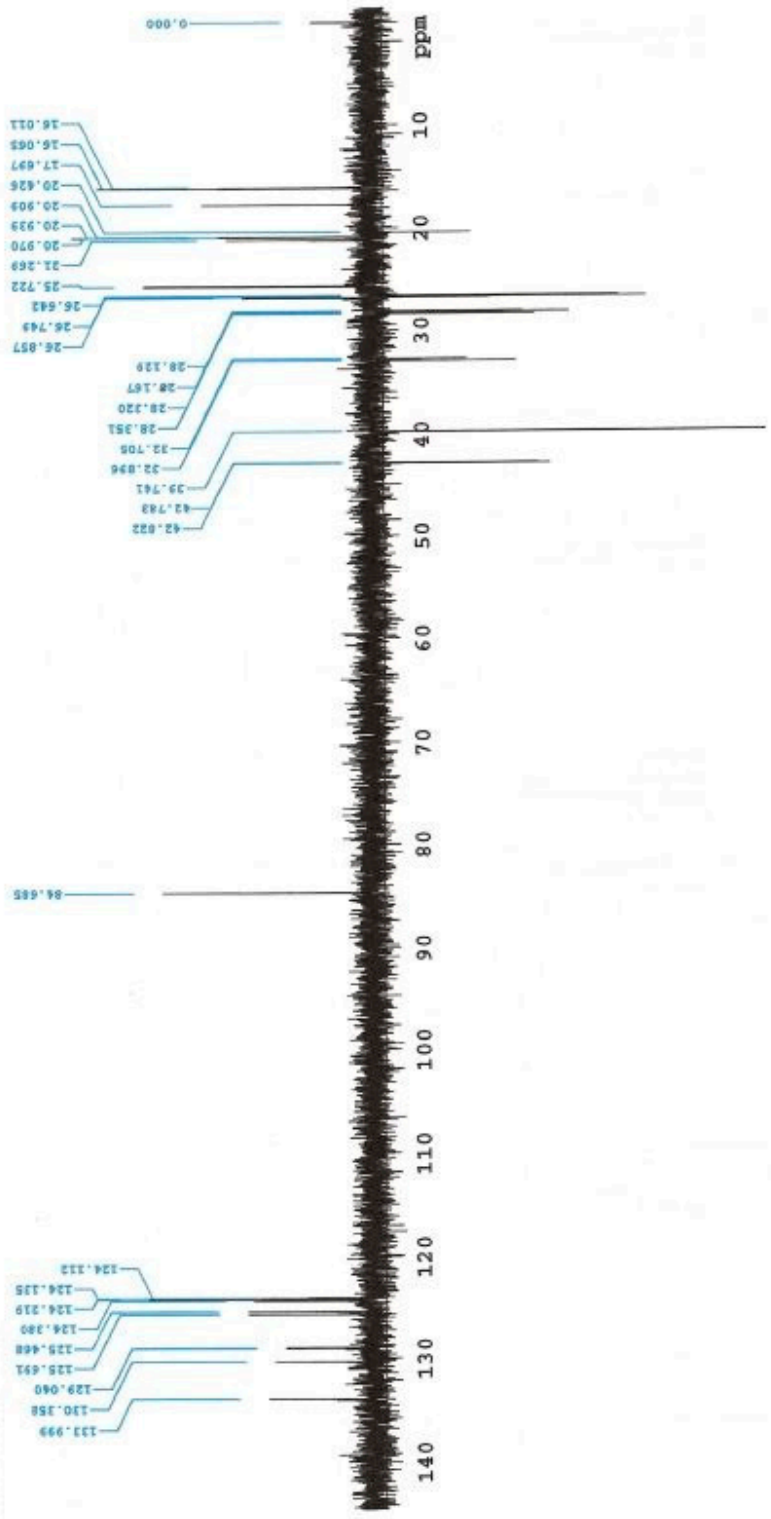
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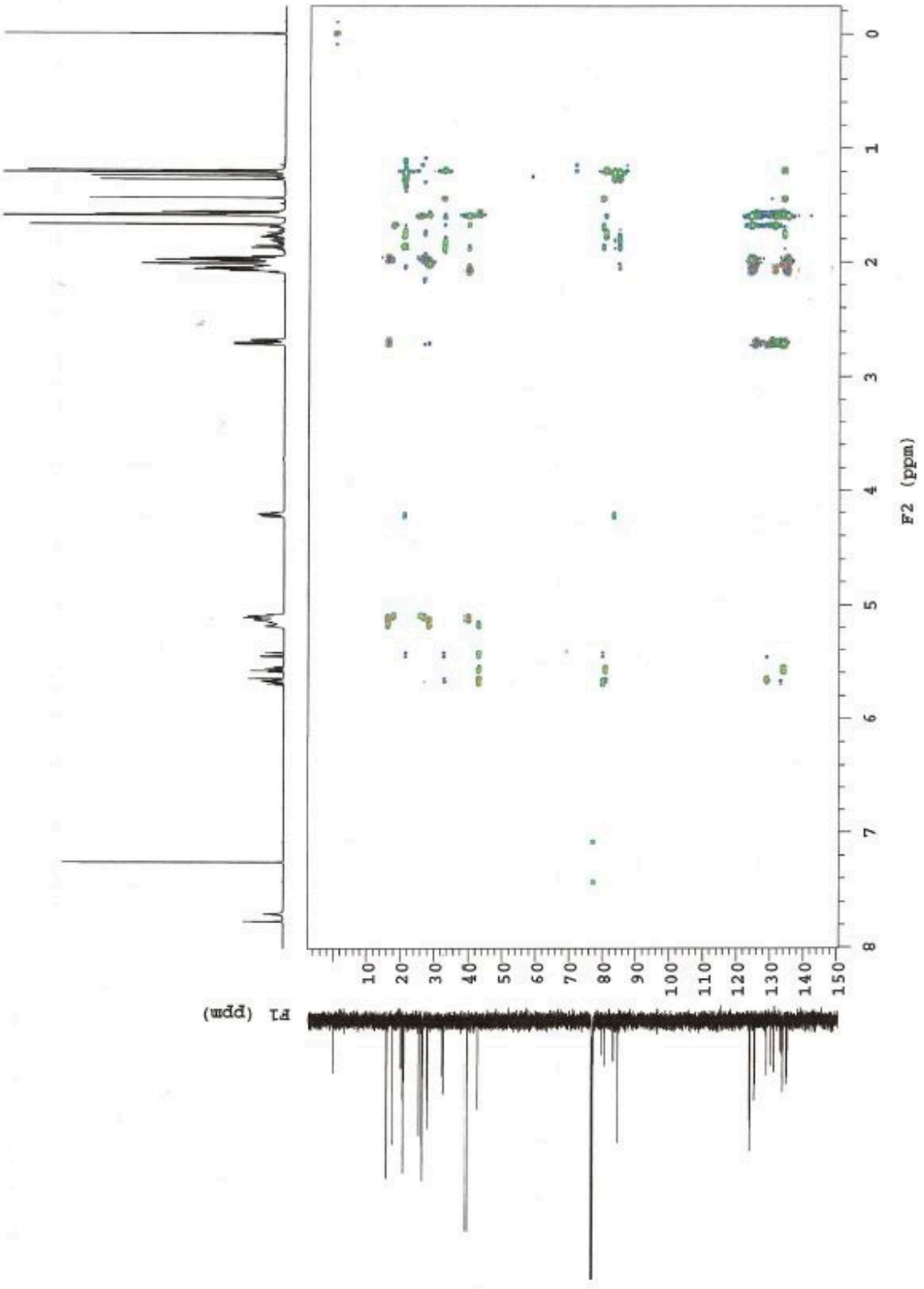

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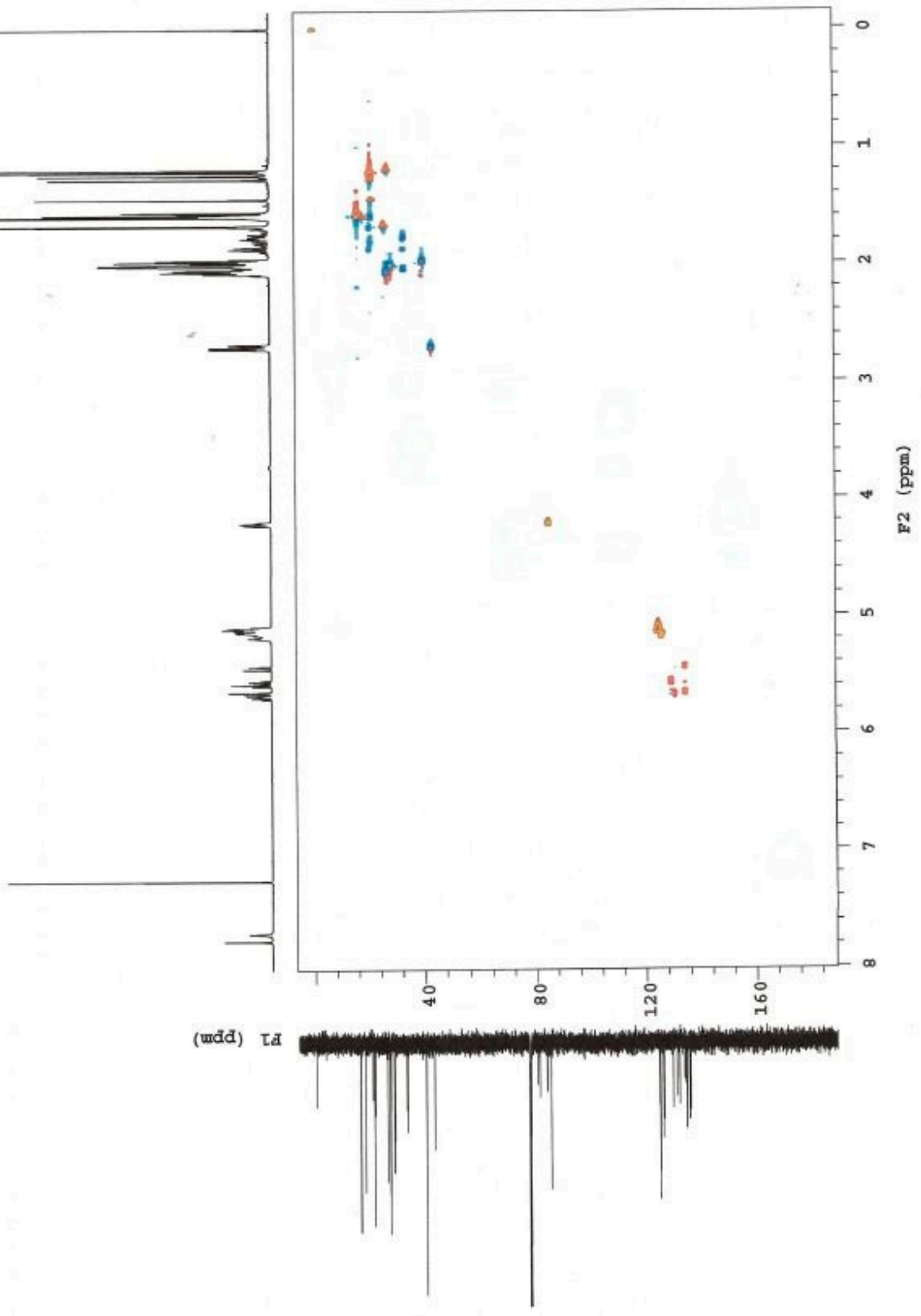

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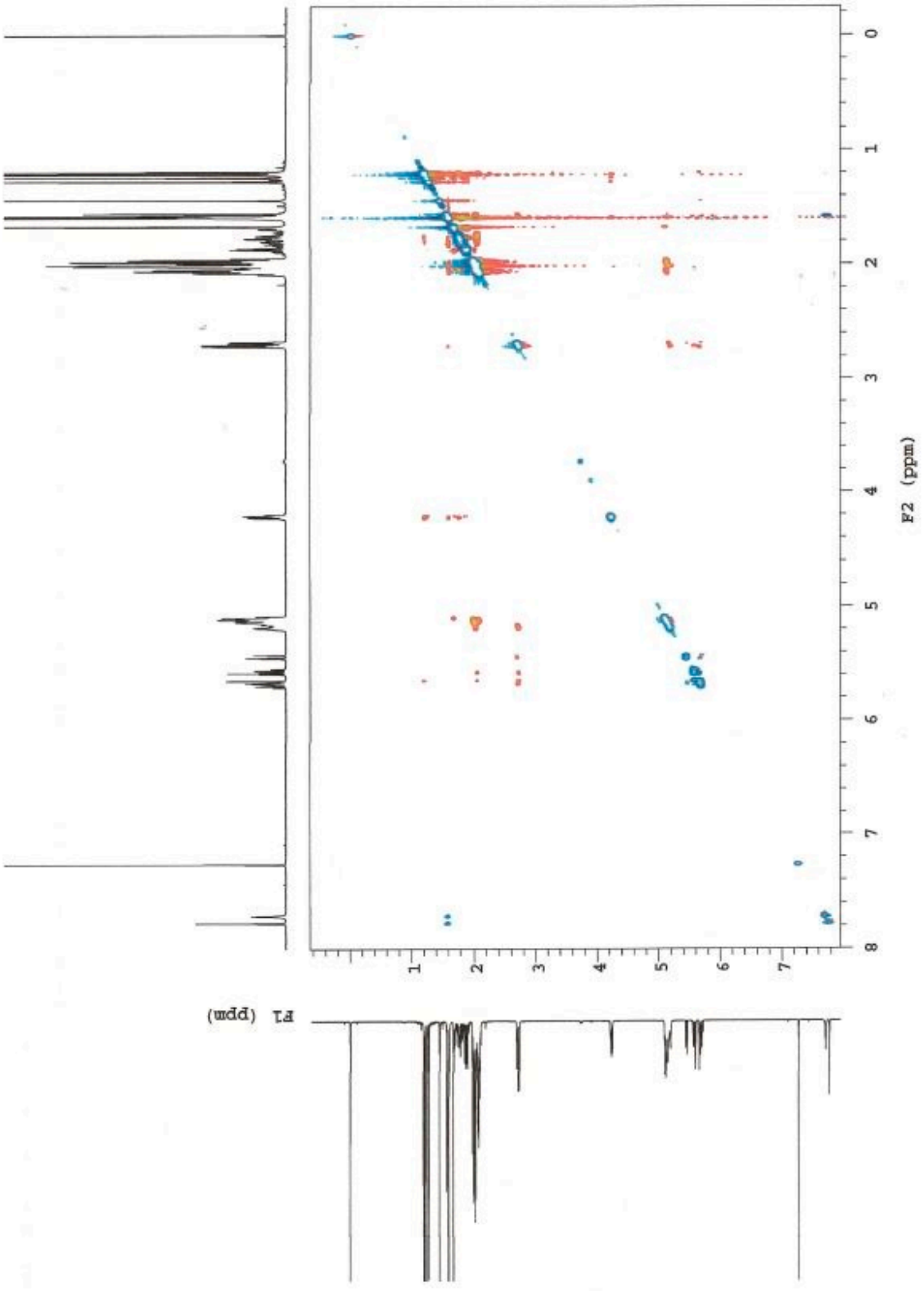

COSY