Supporting Information

Carapanins A–C: New limonoids from andiroba (*Carapa guianensis*) fruit oil

Takashi Kikuchi[a,*] Keiko Akita[a], Hiroki Koike[a], Yasuko In[a], Takeshi Yamada[a], Reiko Tanaka[a]

[a] Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan

Supporting Information

Table S1. NMR data of compound 1 in $CDCl_3$ (δ in ppm, J in Hz).

no.	δ_H	^1H-^1H COSY	NOESY	δ_C		HMBC (H to C)
1	5.70 (1H, d, 10.2)	2	12β, 17, 19, 30β	152.1	d	3, 5, 9
2	5.84 (1H, d, 10.2)	1		126.0	d	1, 4, 10
3				202.7	s	
4				46.0	s	
5	2.86 (1H, dd, 7.2, 3.6)	6A, 6B	9, 11β, 28	42.5	d	4, 6, 7, 9, 10, 29
6	A 2.34 (1H, dd, 16.8, 3.6)	5, 6B	6B, 9, 19	31.3	t	4, 5, 7
	B 2.52 (1H, dd, 16.8, 7.2)	5, 6A	6A, 29			4, 5, 7
7				173.7	s	
8				160.3	s	
9	2.42 (1H, dd, 6.0, 3.6)	11α, 11β	5, 6A, 18, 19, 30α	44.5	d	5, 8, 14
10				42.8	s	
11	α 1.67 (1H, m)	9, 11β, 12α, 12β	18	21.2	t	
	β 1.96 (1H, ddt, 15.0, 6.6, 3.0)	9, 11α, 12α, 12β	5			
12	α 1.33 (1H, m)	11α, 11β, 12β		27.9	t	11
	β 1.78 (1H, td, 12.0, 3.0)	11α, 11β, 12α	1, 17, 21, 22			18
13				39.8	s	
14				136.3	s	
15				173.4	s	
17	5.30 (1H, d, 3.0)	21, 17-OH	1, 12β, 18, 21, 22, 17-OH	71.5	d	20, 21
18	1.34 (3H, s)		5, 9, 11α, 17, 21, 22	20.9	q	12, 13, 14, 17
19	1.13 (3H, s)		1, 6A, 9, 30α, 30β	22.0	q	1, 5, 9, 10
20				126.2	s	
21	7.35 (1H, m)	17	12β, 17, 18	140.3	d	20, 22, 23
22	6.30 (1H, dd, 1.8, 0.6)	23	12β, 17, 18	109.9	d	20, 21, 23
23	7.37 (1H, t, 1.8)	22		142.6	d	20, 21
28	1.10 (3H, s)		5	23.4	q	3, 4, 10, 29
29	1.09 (3H, s)		6B	22.7	q	3, 4, 10, 28
30	α 4.66 (1H, d, 17.4)	30β	9, 19	73.6	t	8, 14, 15
	β 5.02 (1H, d, 17.4)	30α	1, 19			8, 14, 15
1'	3.70 (3H, s)			52.3	q	7
17-OH	2.85 (1H, m)	17	17			

Table S2. NMR data of compound 2 in $CDCl_3$ (δ in ppm, J in Hz).

no.	δ_H	^1H-^1H COSY	NOESY	δ_C	HMBC (H to C)
1				211.5 s	
2				79.3 s	
3	4.82 (1H, s)		28, 29, 2-OH	84.8 d	2, 4, 5, 6, 29, 1'
4				39.6 s	
5	3.50 (1H, d, 9.1)	6A, 6B	28	43.7 d	3, 4, 6, 7, 10, 19, 29
6	A 2.30 (1H, d, 16.7)	5, 6B	19, 29	32.4 t	4, 5, 7, 10
	B 2.38 (1H, dd, 16.7, 9.1)	5, 6A	19, 29		4, 5, 7
7				173.4 s	
8				81.8 s	
9	3.00 (1H, dd, 12.3, 6.8)		19	47.8 d	5, 8, 10, 11, 19, 30
10				48.2 s	
11	α 1.77 (1H, m)	11β, 12β	19	19.4 t	
	β 2.39 (1H, m)	11α, 12α	17, 21, 22		
12	α 1.45 (1H, td, 14.1, 3.8)	11β, 12β	14	34.7 t	11, 13, 18
	β 1.61 (1H, dt, 14.1, 3.2)	11α, 12α	17, 21, 22		14
13				39.8 s	
14	3.24 (1H, d, 9.1)	15α, 15β	12α, 18	42.9 d	8, 12, 13, 15, 16, 17, 18, 30
15	α 2.53 (1H, dd, 19.1, 9.1)	14, 15β	2'''	27.0 t	13, 14, 16
	β 3.01 (1H, d, 19.1)	14, 15α	2''''		8, 13, 14, 16, 30
16				167.0 s	
17	6.33 (1H, s)		11β, 12β, 30	70.9 d	12, 13, 14, 18, 20, 21, 22, 1''''
18	1.21 (3H, s)		14	23.2 q	12, 13, 14, 17
19	1.17 (3H, s)		6A, 6B, 9, 11α, 29	18.9 q	1, 5, 9, 10
20				121.8 s	
21	7.83 (1H, brs)	22, 23	11β, 12β	142.2 d	20, 22, 23
22	6.45 (1H, dd, 1.8, 0.6)	21, 23	11β, 12β	109.7 d	17, 20, 23
23	7.37 (1H, t, 1.8)	21, 22		142.8 d	20, 21, 22
28	0.82 (3H, s)		3, 5, 30	22.9 q	3, 4, 5, 29
29	0.91 (3H, s)		3, 6A, 6B, 19	22.0 q	3, 4, 5, 28
30	5.81 (1H, s)		17, 28	78.7 d	2, 3, 8, 9, 16, 1'''
1'				178.2 s	
2'	2.95 (1H, sept, 7.1)	3', 4'	2''''	33.5 d	1', 3', 4'
3'	1.21 (3H, d, 7.1)	2'	2''''	19.5 q	1', 2', 4'
4'	1.25 (3H, d, 7.1)	2'	2''''	18.8 q	1', 2', 3'
1''	3.76 (3H, s)			52.5 q	7
1'''				170.4 s	
2'''	1.94 (3H, s)		15α	22.6 q	1'''
1''''				169.8 s	
2''''	2.02 (3H, s)		15β, 2', 3', 4'	21.5 q	1''''
2-OH	3.90 (1H, s)		3		1, 2, 3

Table S3. NMR data of compound 3 in $CDCl_3$ (δ in ppm, J in Hz).

no.	δ_H	^1H-^1H COSY	NOESY	δ_C	HMBC (H to C)
1				108.1 s	
2				94.3 s	
3	5.57 (1H, s)		28, 29, 2'	75.8 d	2, 5, 29, 1''
4				39.9 s	
5	2.77 (1H, dd, 10.2, 1.2)	6A, 6B	30	39.7 d	4, 6, 7, 9, 10, 29
6	A 2.26 (1H, dd, 16.2, 1.2)	5, 6B	19	32.1 t	4, 7, 10
	B 2.38 (1H, dd, 16.2, 10.2)	5, 6A	29		4, 7
7				174.2 s	
8				78.2 s	
9	1.48 (1H, m)	11α, 11β	12α, 19	61.0 d	
10				46.5 s	
11	α 1.68 (1H, m)	9, 11β, 12α, 12β		19.3 t	
	β 1.76 (1H, m)	9, 11α, 12α, 12β	17		
12	α 1.34 (1H, m)	11α, 11β, 12β	9, 19	35.3 t	
	β 1.78 (1H, m)	11α, 11β, 12α			
13				35.6 s	
14	2.17 (1H, dd, 7.2, 2.4)	15α, 15β	9, 12α, 18	44.3 d	8, 13, 17
15	2.83 (2H, m)	14	17	27.8 t	8, 14, 16
16				169.9 s	
17	5.34 (1H, s)	21	11β, 15β, 30β	77.7 d	12, 13, 18, 20, 21, 22
18	1.02 (3H, s)		14, 21, 23	22.2 q	12, 13, 14, 17
19	1.10 (3H, s)		6A, 9, 12α, 1-OH	21.1 q	1, 5, 9, 10
20				121.1 s	
21	7.47 (1H, brs)	17, 22, 23	18	140.7 d	20, 22, 23
22	6.40 (1H, dd, 1.8, 1.2)	23, 21	18	109.9 d	20, 21, 23
23	7.44 (1H, t, 1.8)	21, 22		143.2 d	20, 21
28	0.73 (3H, s)		3	24.4 q	3, 4, 5, 29
29	1.35 (3H, s)		3, 1-OH	22.0 q	3, 4, 5, 28
30	α 2.88 (1H, d, 14.4)	30β		39.1 t	3, 9
	β 1.93 (1H, dd, 14.4, 1.2)	30α	5, 11β, 17		2, 8, 9, 14
1'				175.2 s	
2'	2.11 (3H, s)		3, 1-OH	22.3 q	1'
1''				166.9 s	
2''				128.0 s	
3''	6.88 (1H, qq, 7.2, 1.2)	4'', 5''		138.7 d	1'', 4'', 5''
4''	1.82 (1H, dd, 7.2, 1.2)	3''		14.6 q	2'', 3''
5''	1.85 (1H, t, 1.2)	3''		12.3 q	1'', 2'', 3''
1'''	3.69 (3H, s)			51.9 q	7
1-OH	7.42 (1H, s)		3, 19, 29, 2'		1, 2, 10

Figure S1. ^{1}H NMR spectrum of compound **1**.

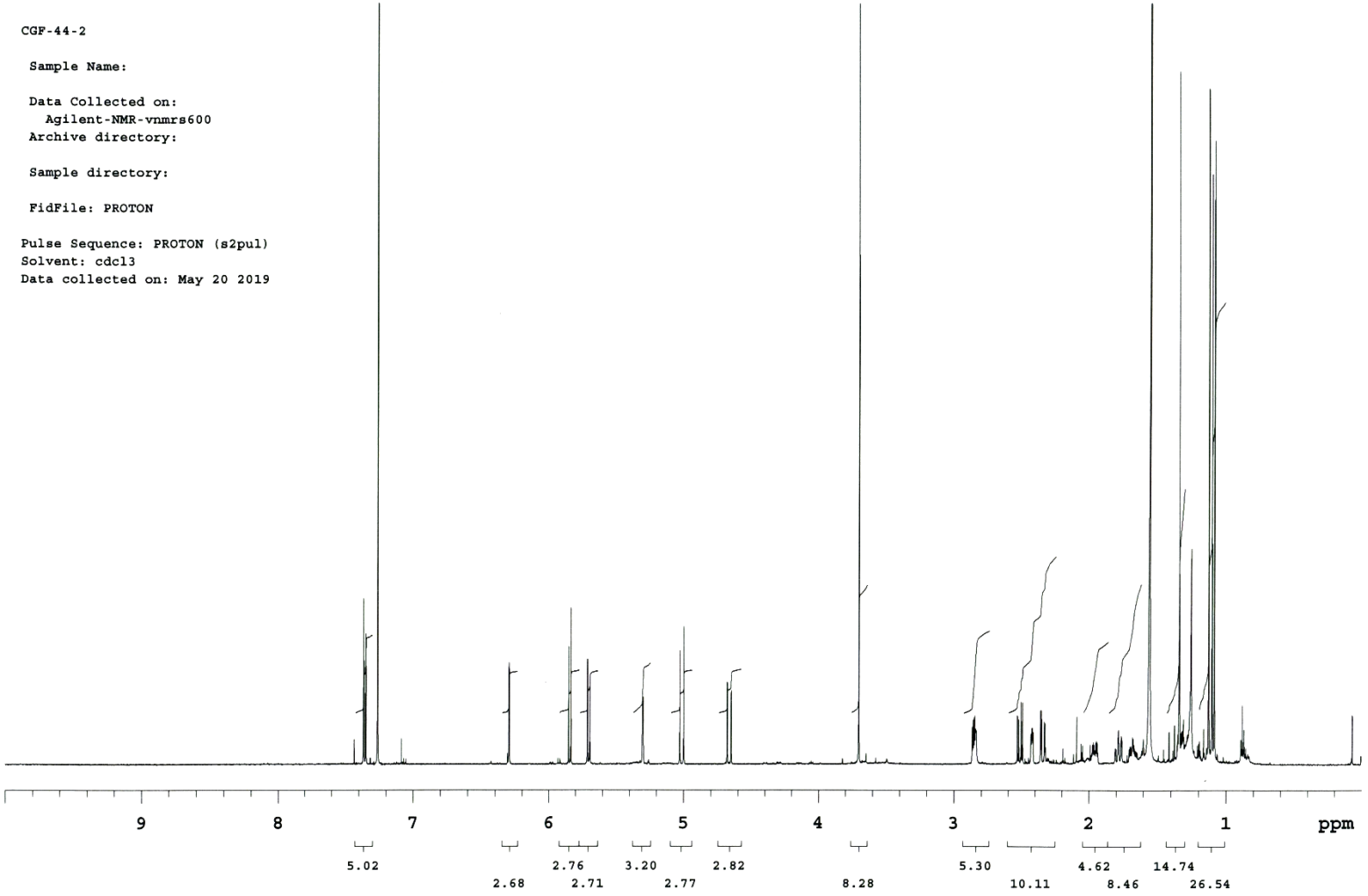


Figure S2. ^{13}C NMR spectrum of compound **1**.

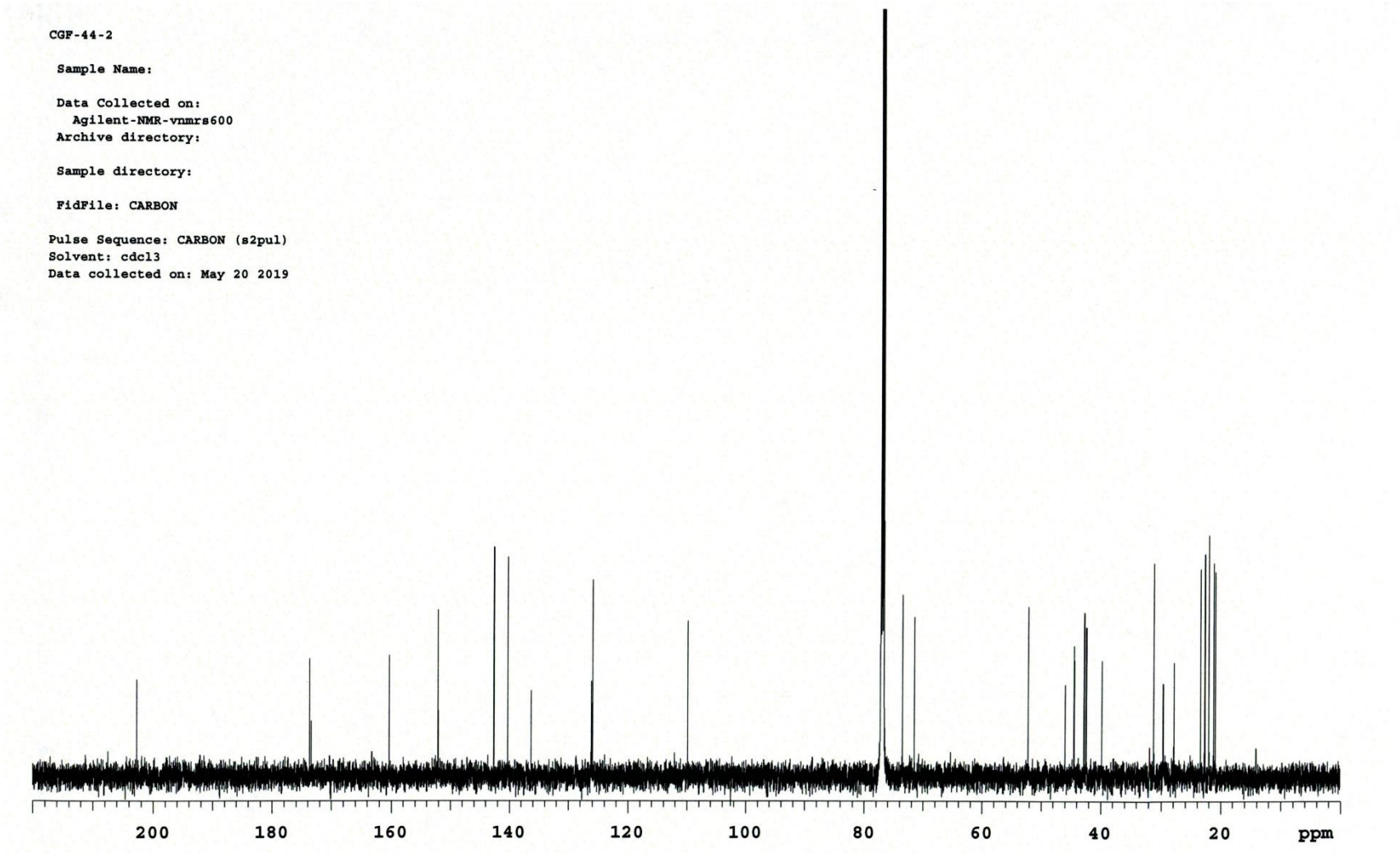


Figure S3. DEPT spectrum of compound **1**.

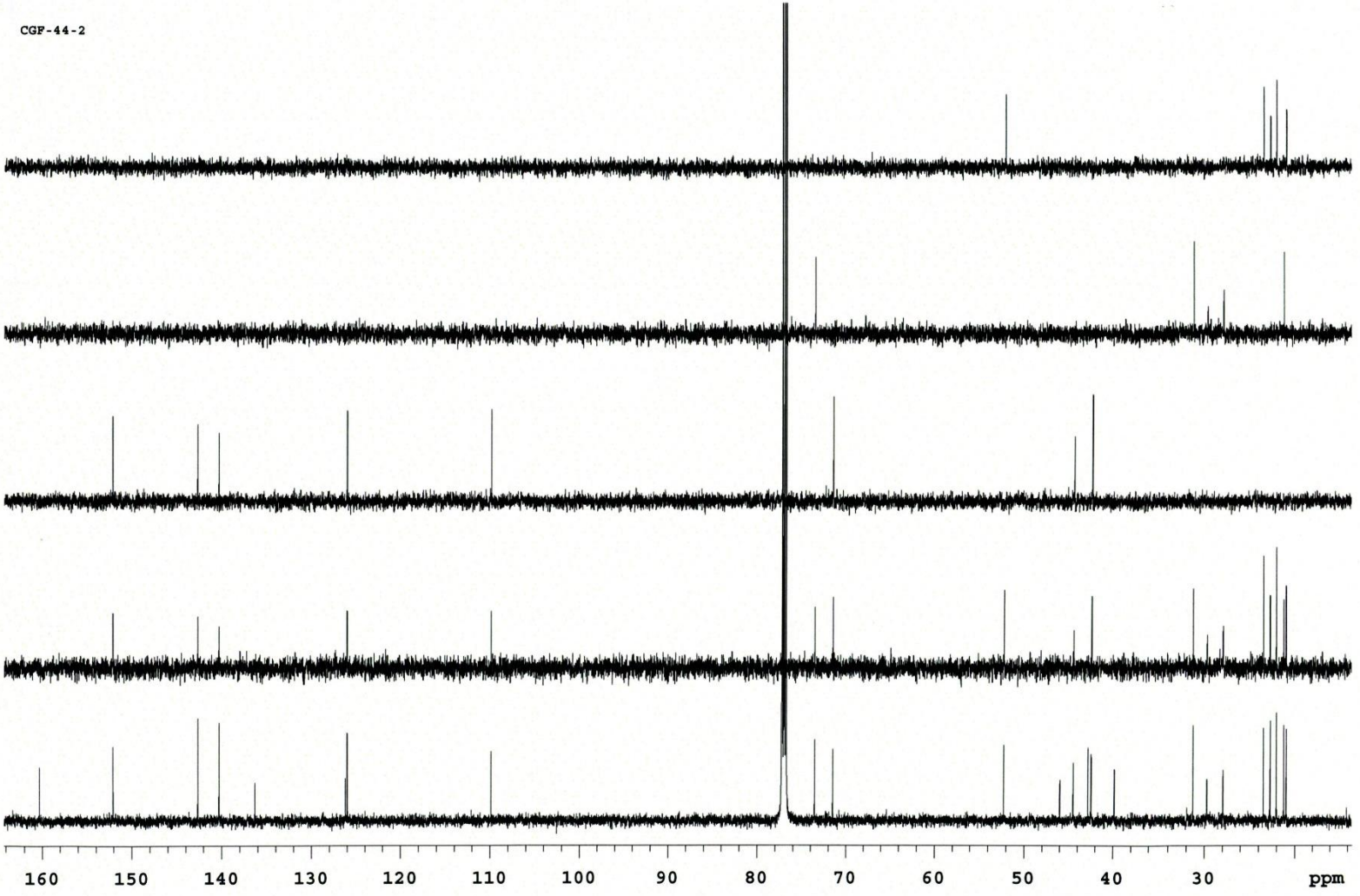


Figure S4. HSQC spectrum of compound **1**.

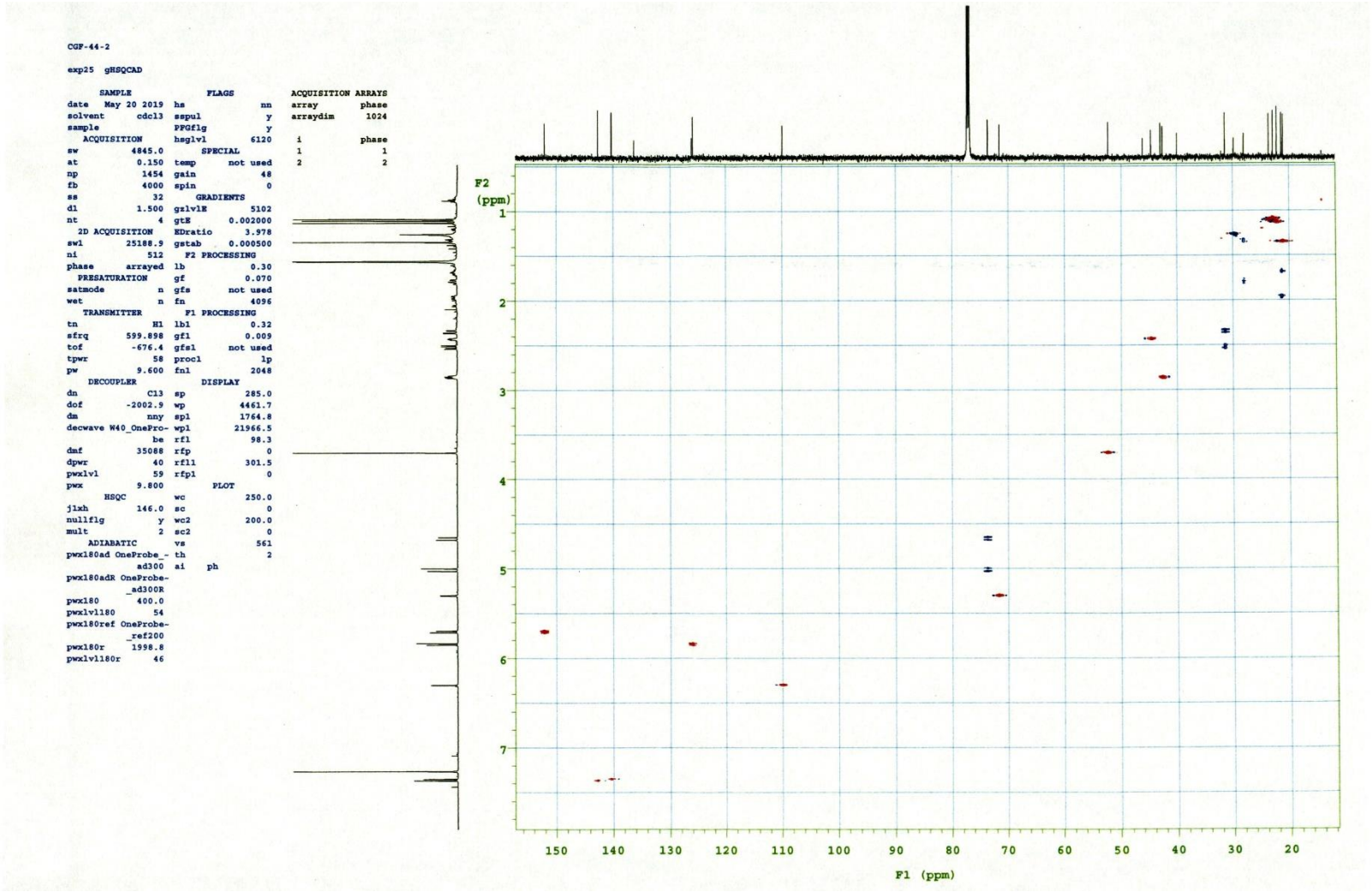


Figure S5. HMBC spectrum of compound **1**.

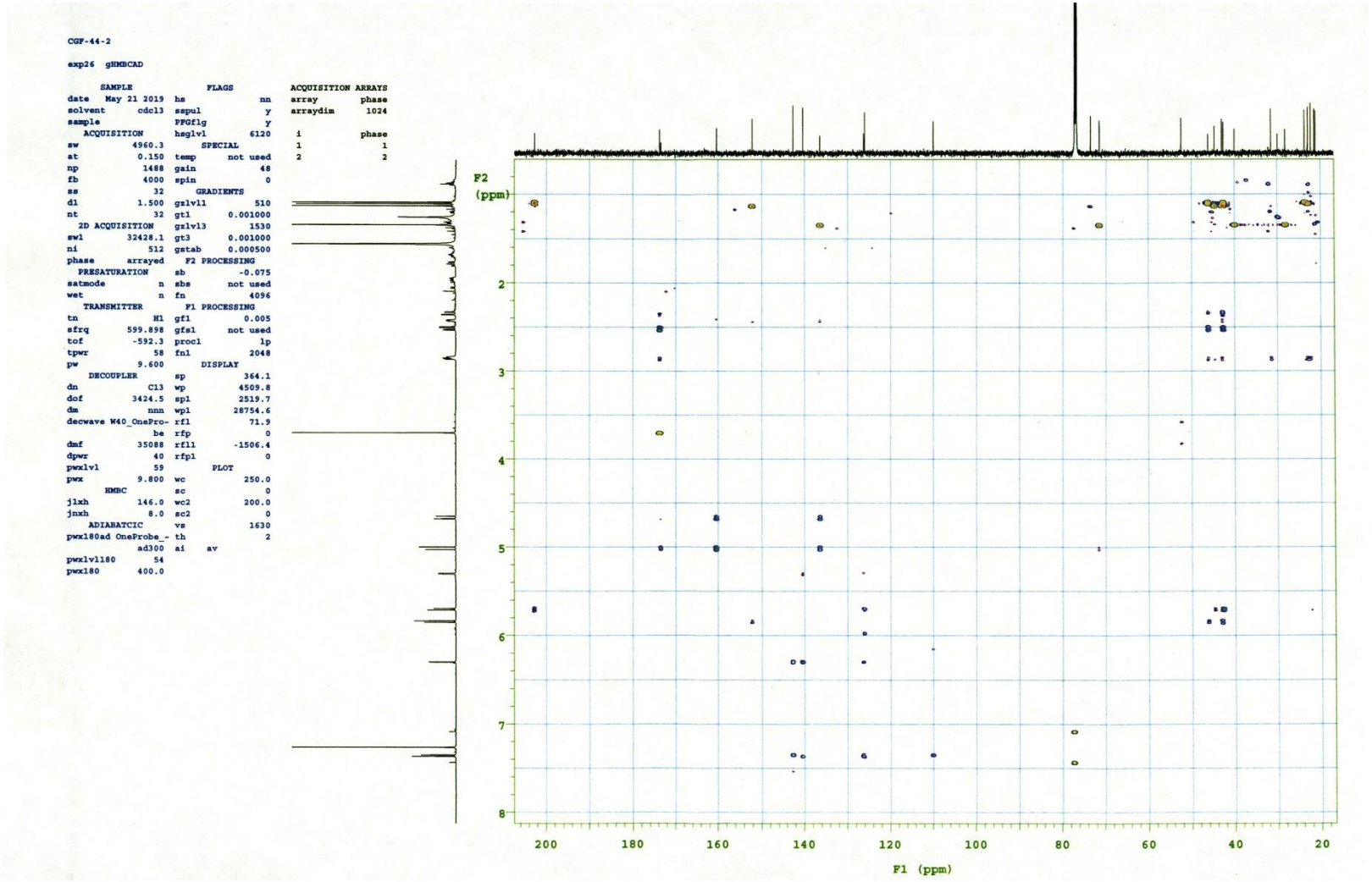


Figure S6. ^{1}H-^{1}H COSY spectrum of compound **1**.

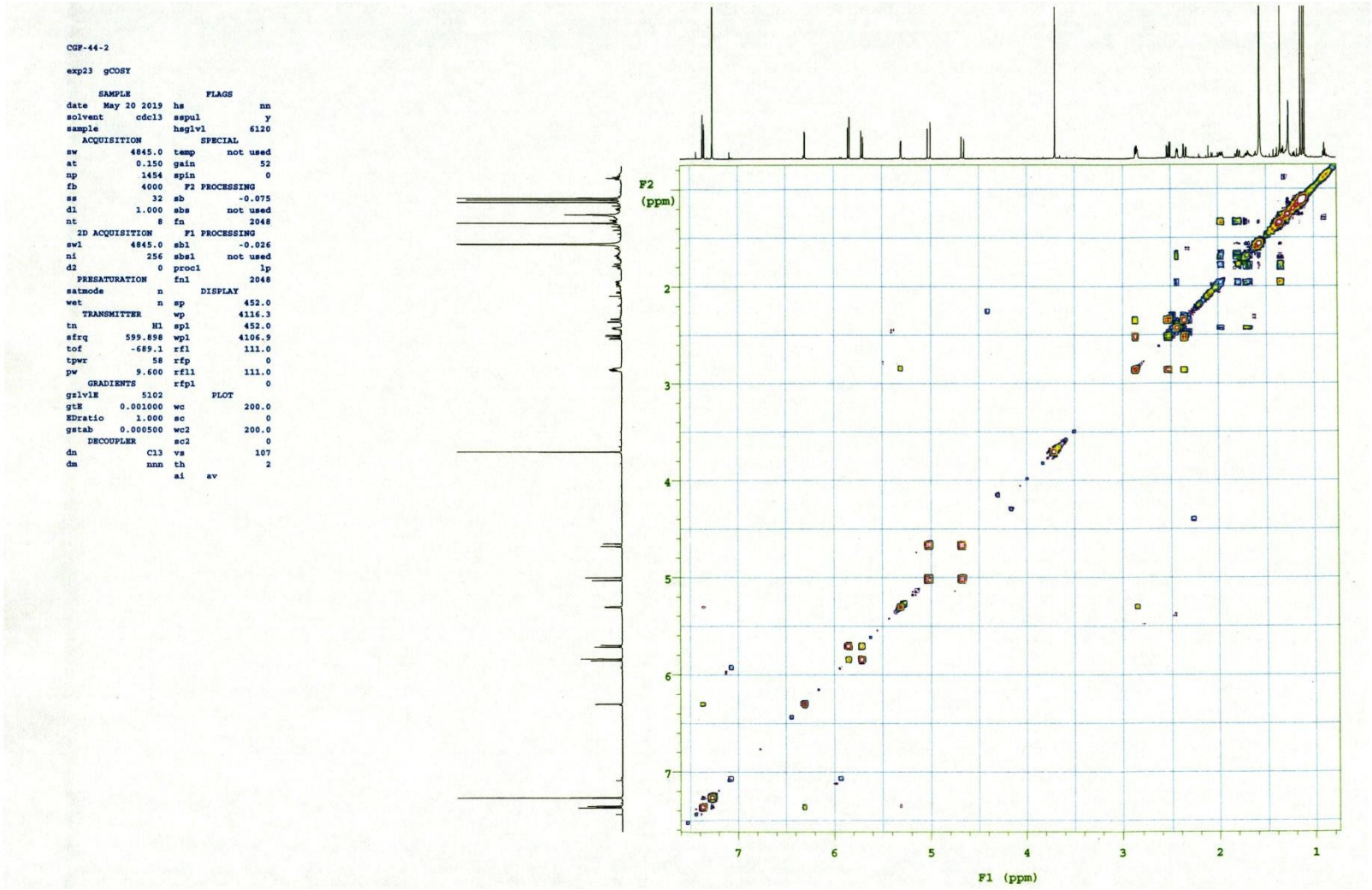


Figure S7. NOESY spectrum of compound **1**.

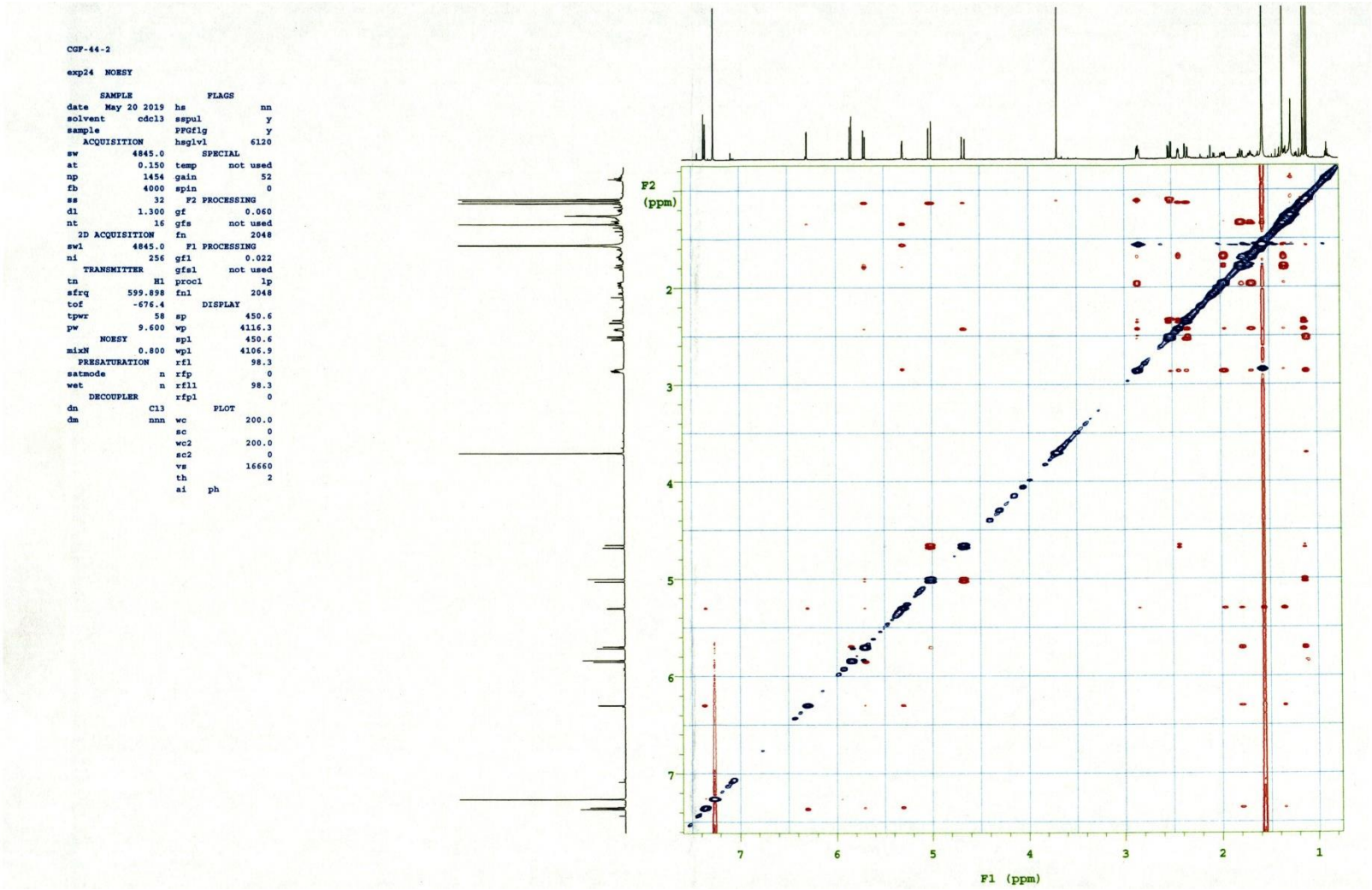


Figure S8. FABMS of compound **1**.

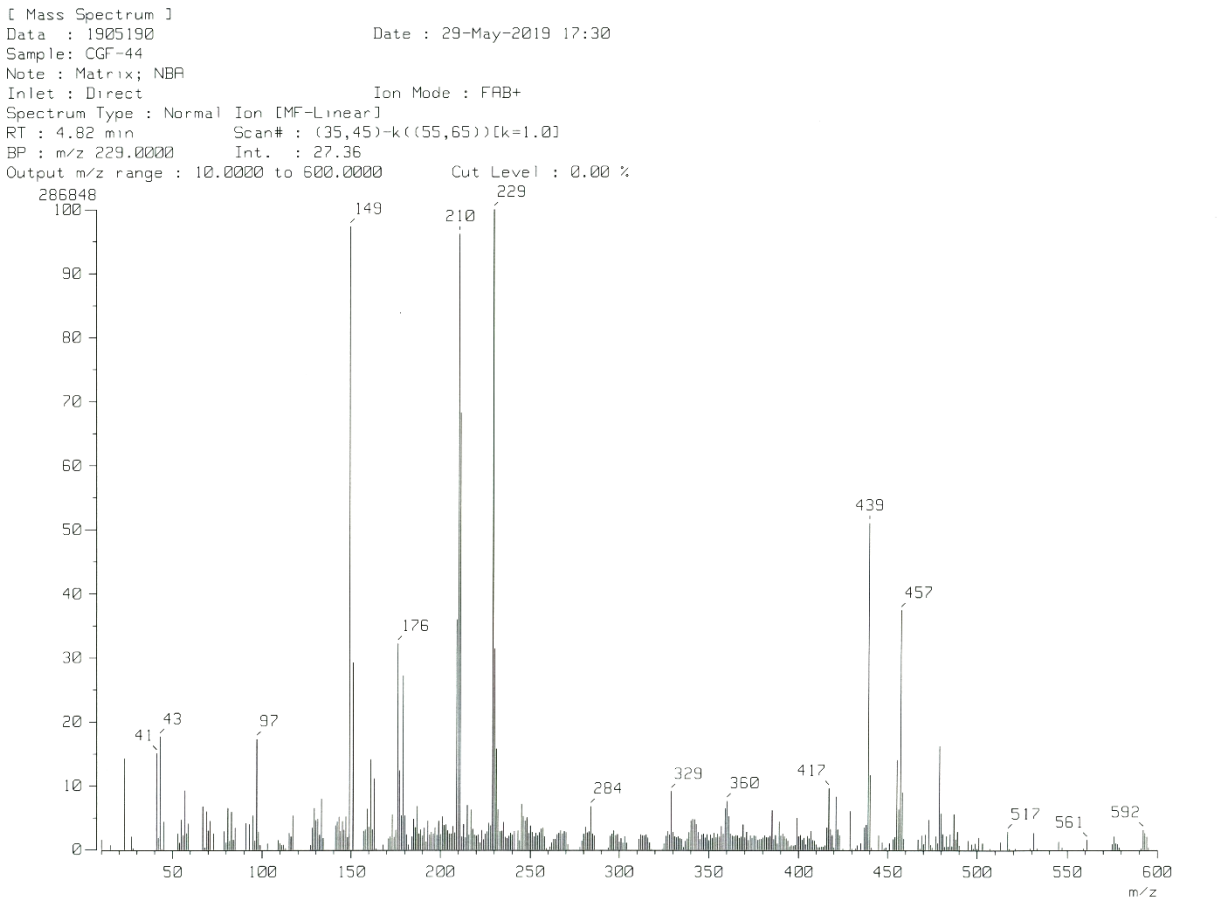
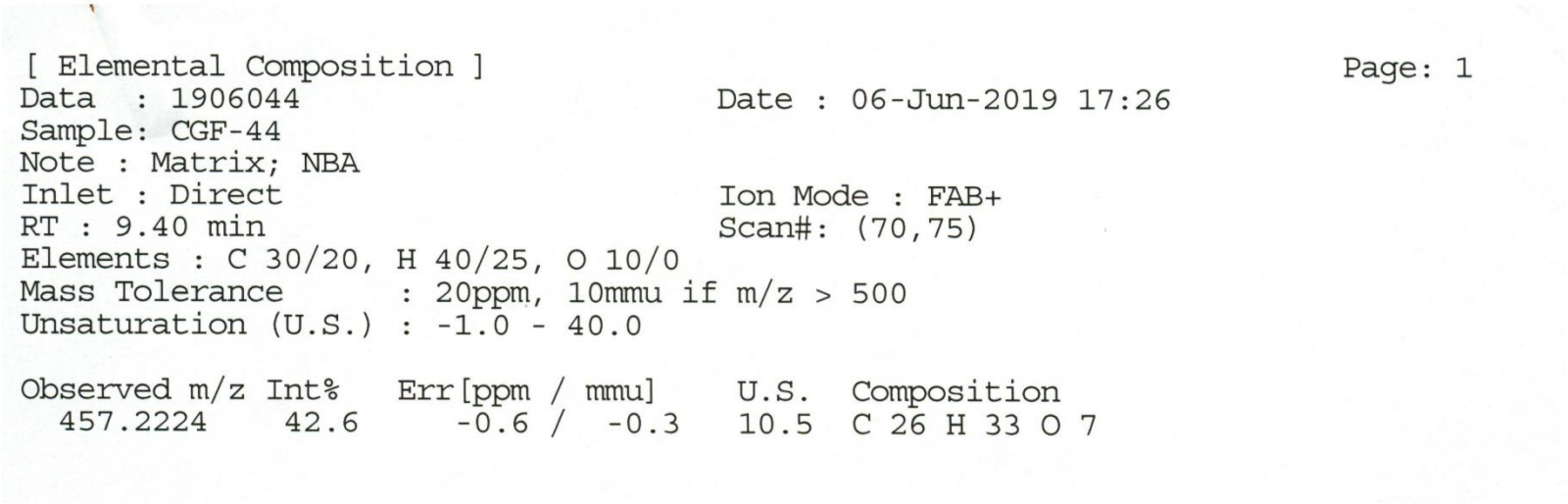


Figure S9. HRFABMS data of compound **1**.



[Elemental Composition] Page: 1
Data : 1906044 Date : 06-Jun-2019 17:26
Sample: CGF-44
Note : Matrix; NBA
Inlet : Direct Ion Mode : FAB+
RT : 9.40 min Scan#: (70,75)
Elements : C 30/20, H 40/25, O 10/0
Mass Tolerance : 20ppm, 10mmu if m/z > 500
Unsaturation (U.S.) : -1.0 - 40.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
457.2224	42.6	-0.6 / -0.3	10.5	C 26 H 33 O 7

Figure S10. IR spectrum of compound **1**.

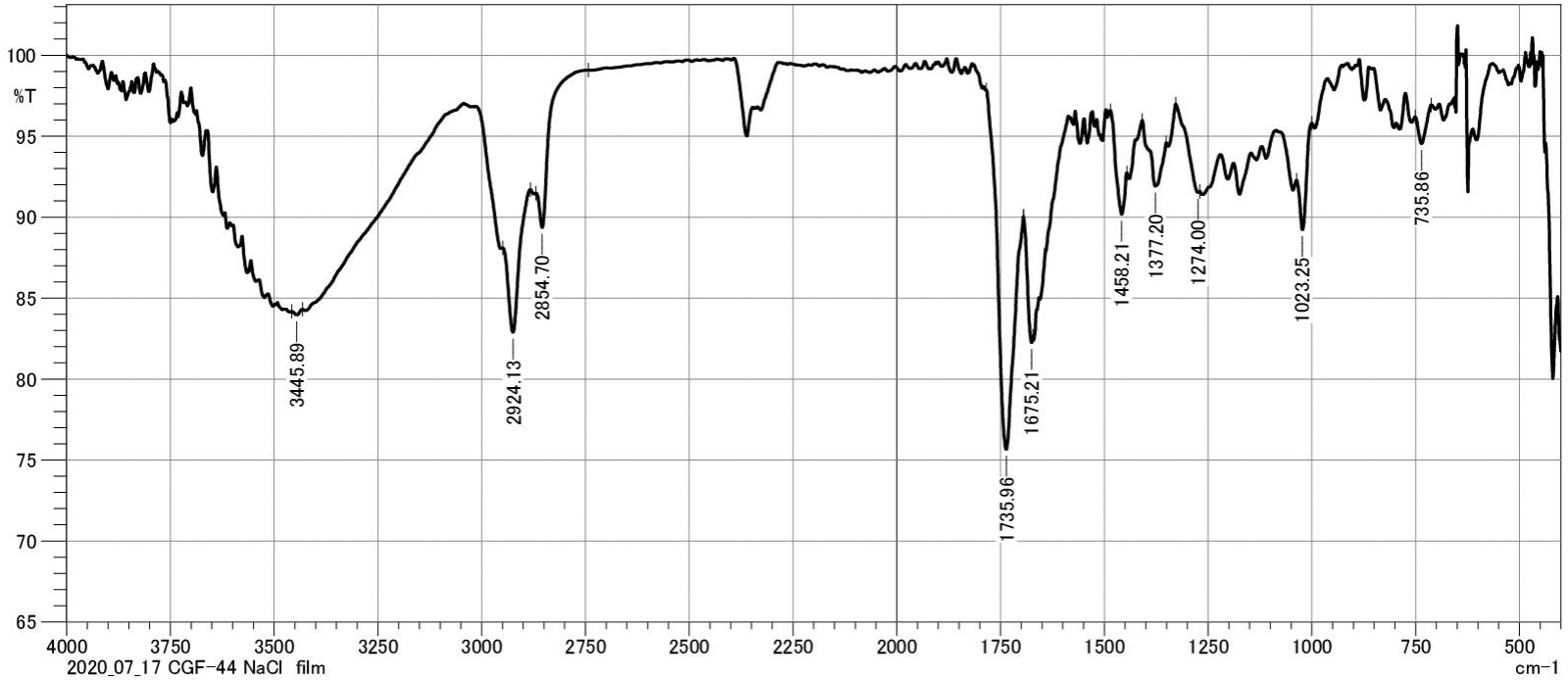


Figure S11. ^{1}H NMR spectrum of compound **2**.

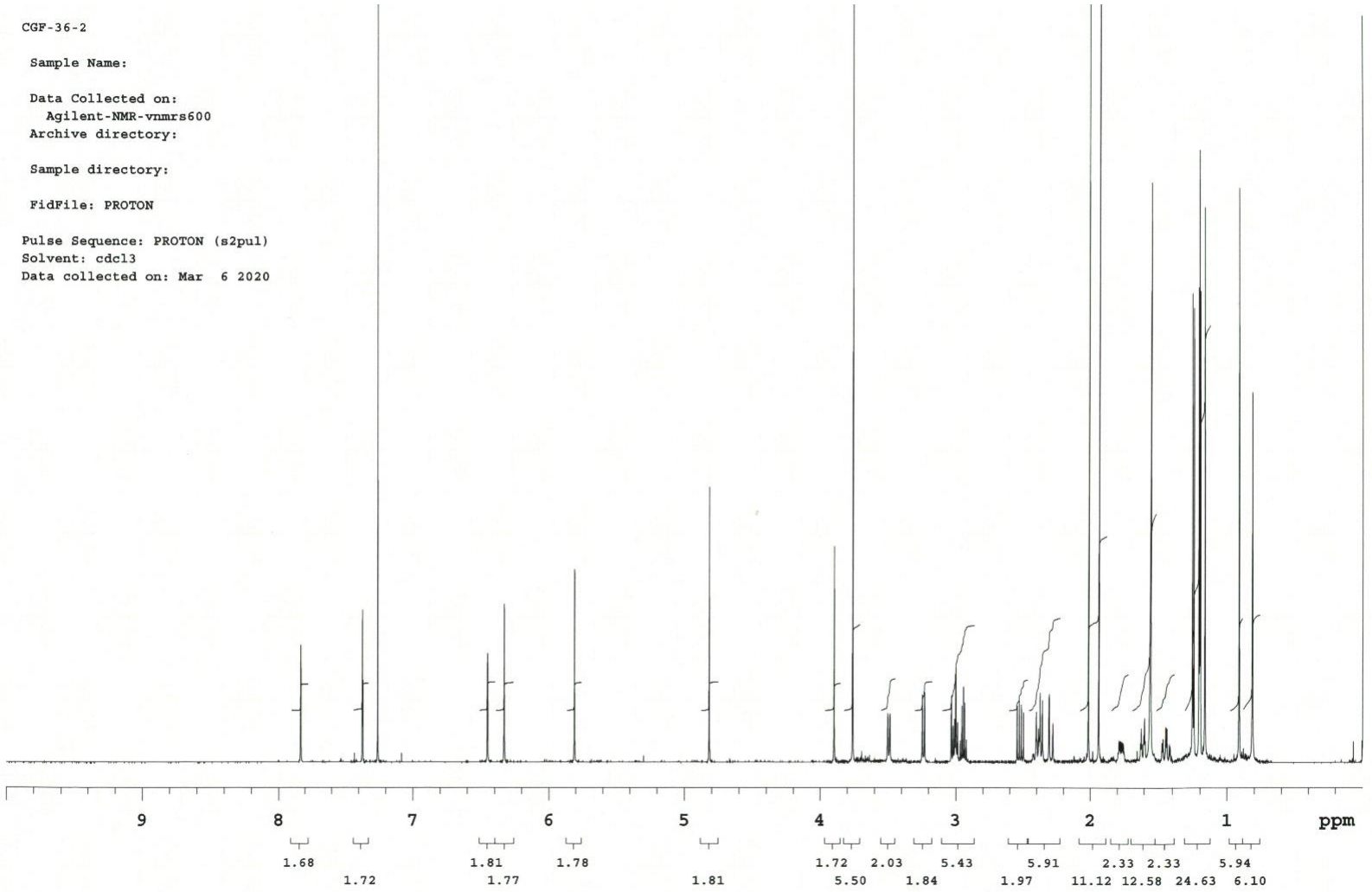


Figure S12. ^{13}C NMR spectrum of compound **2**.

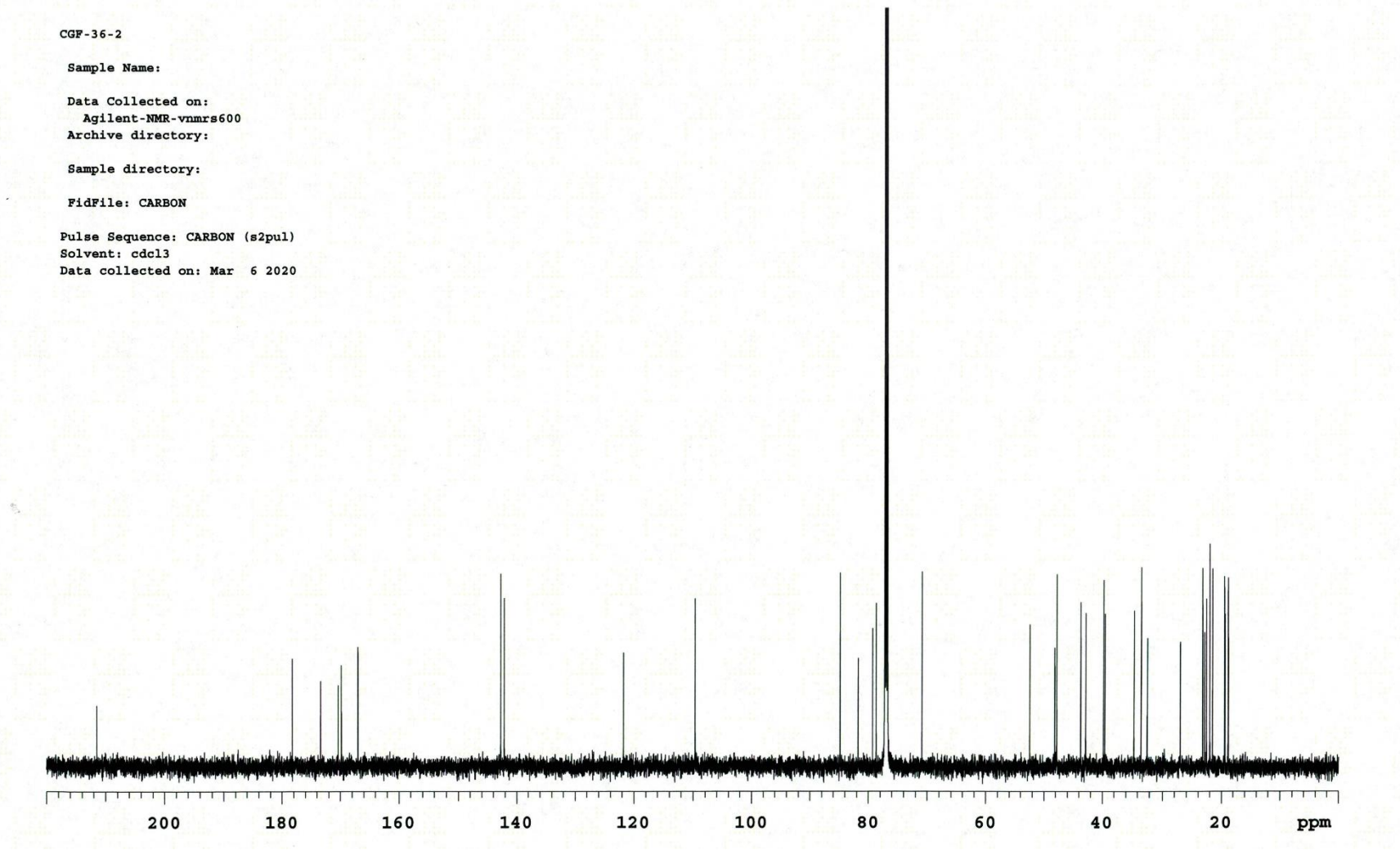


Figure S13. DEPT spectrum of compound **2**.

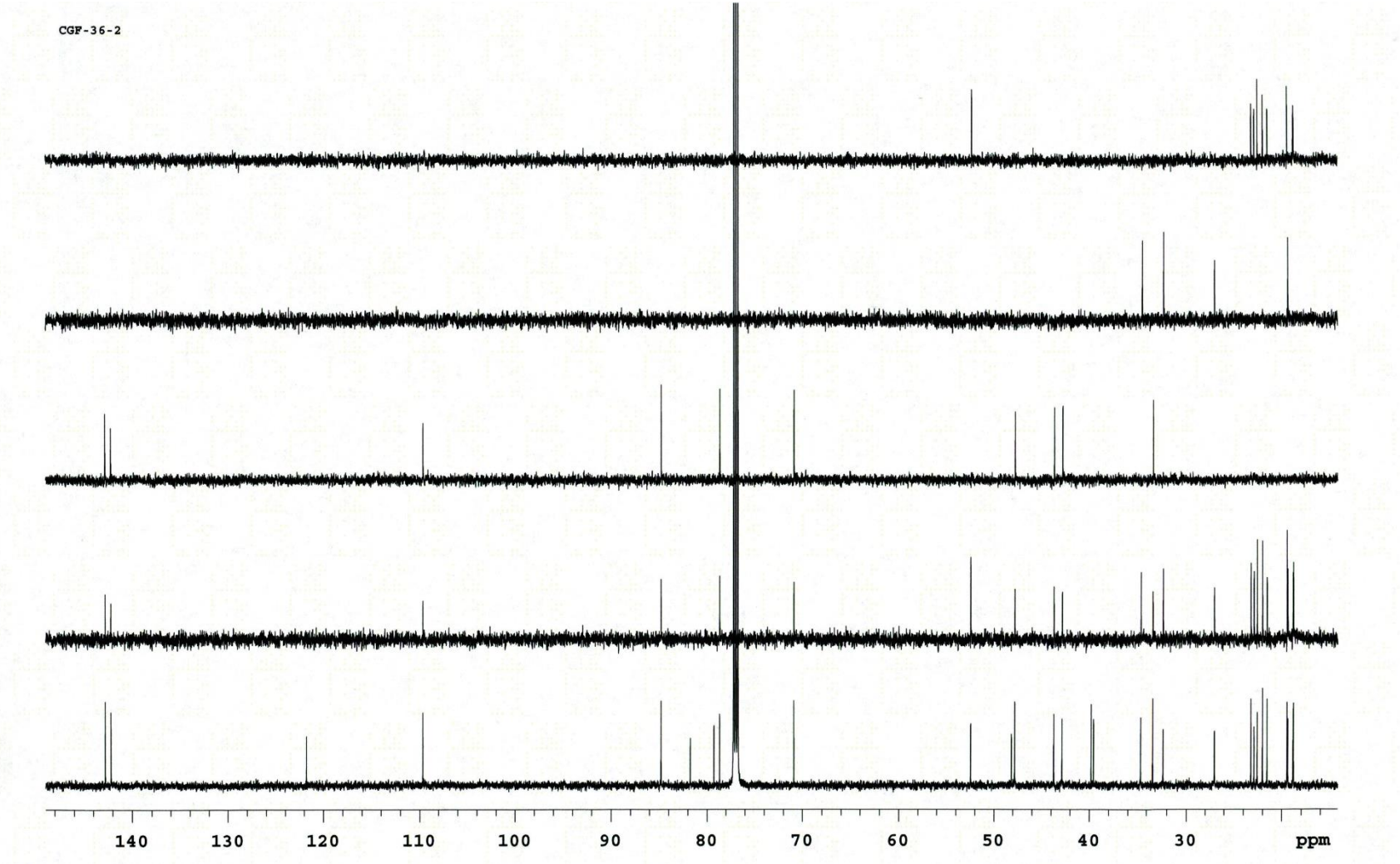


Figure S14. HSQC spectrum of compound **2**.

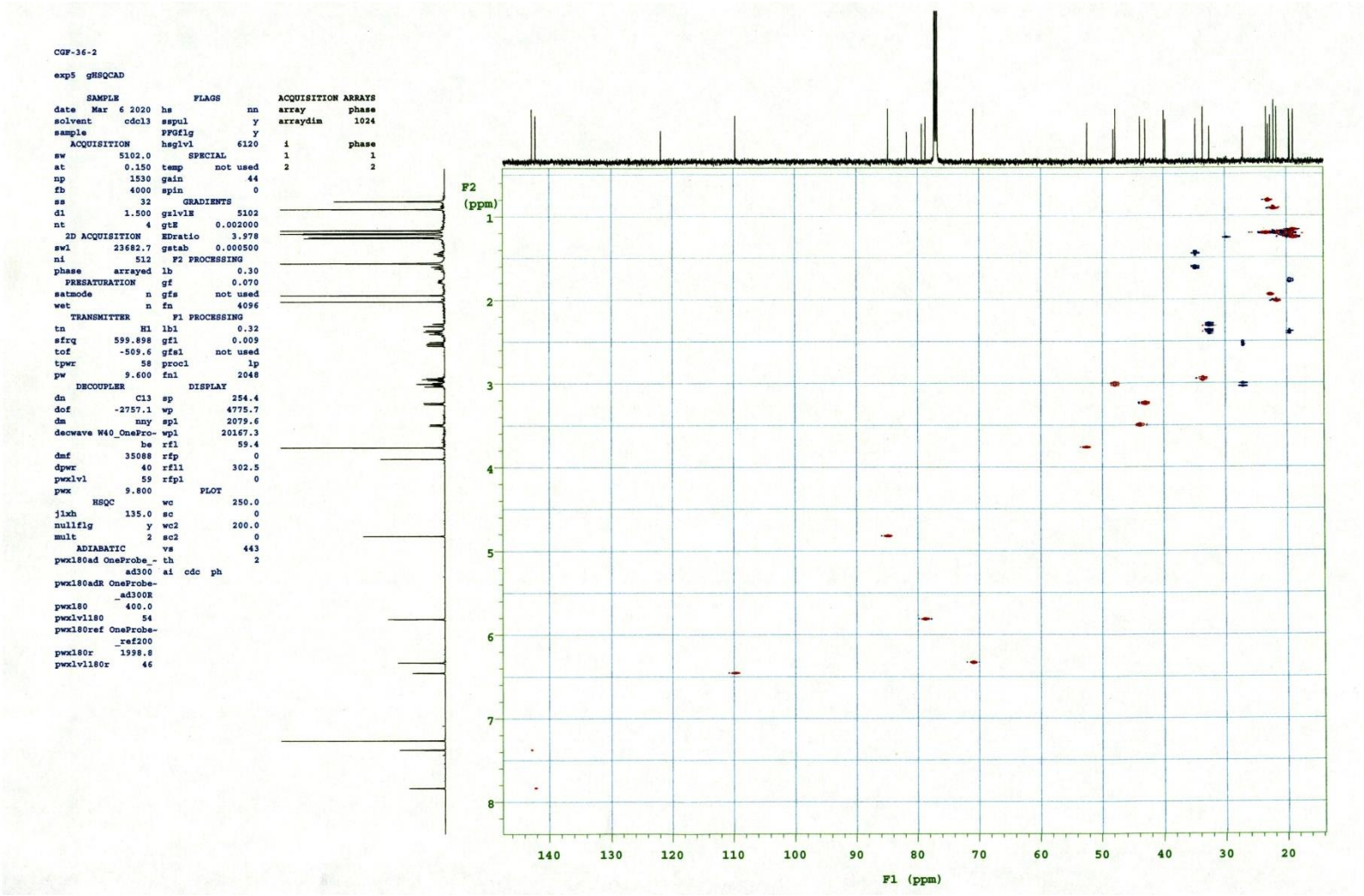


Figure S15. HMBC spectrum of compound **2**.

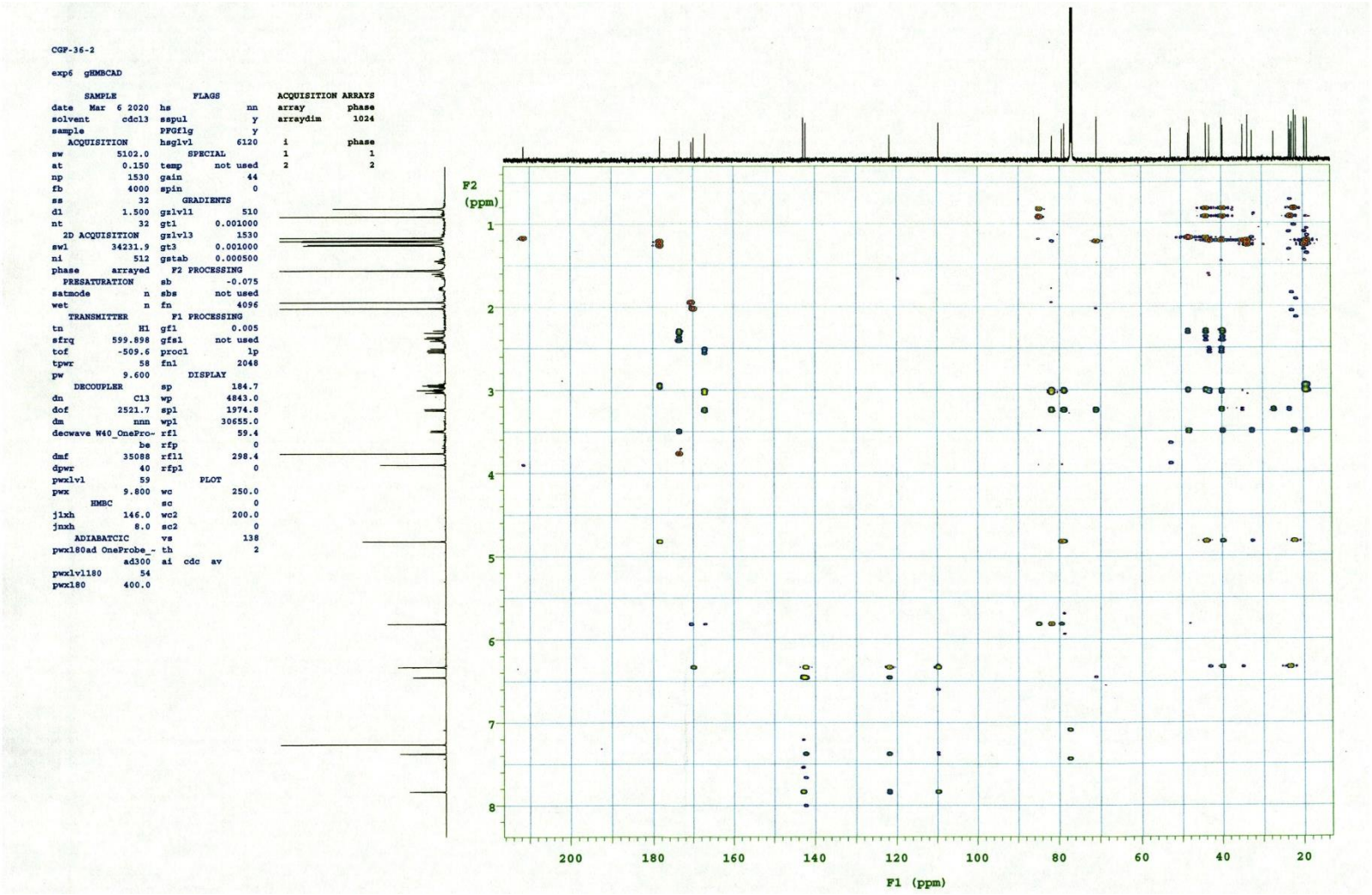


Figure S16. ^{1}H-^{1}H COSY spectrum of compound **2**.

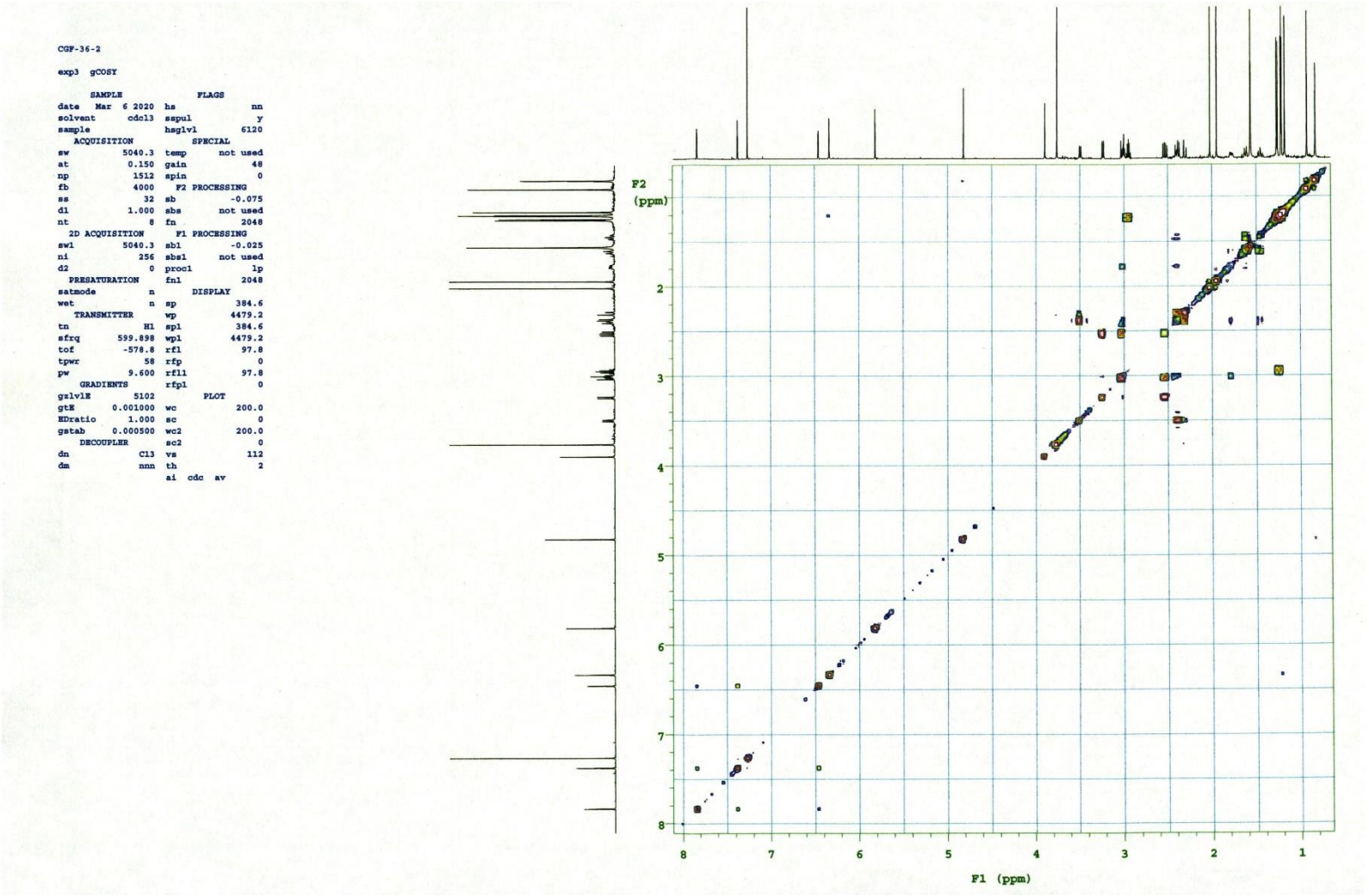


Figure S17. NOESY spectrum of compound **2**.

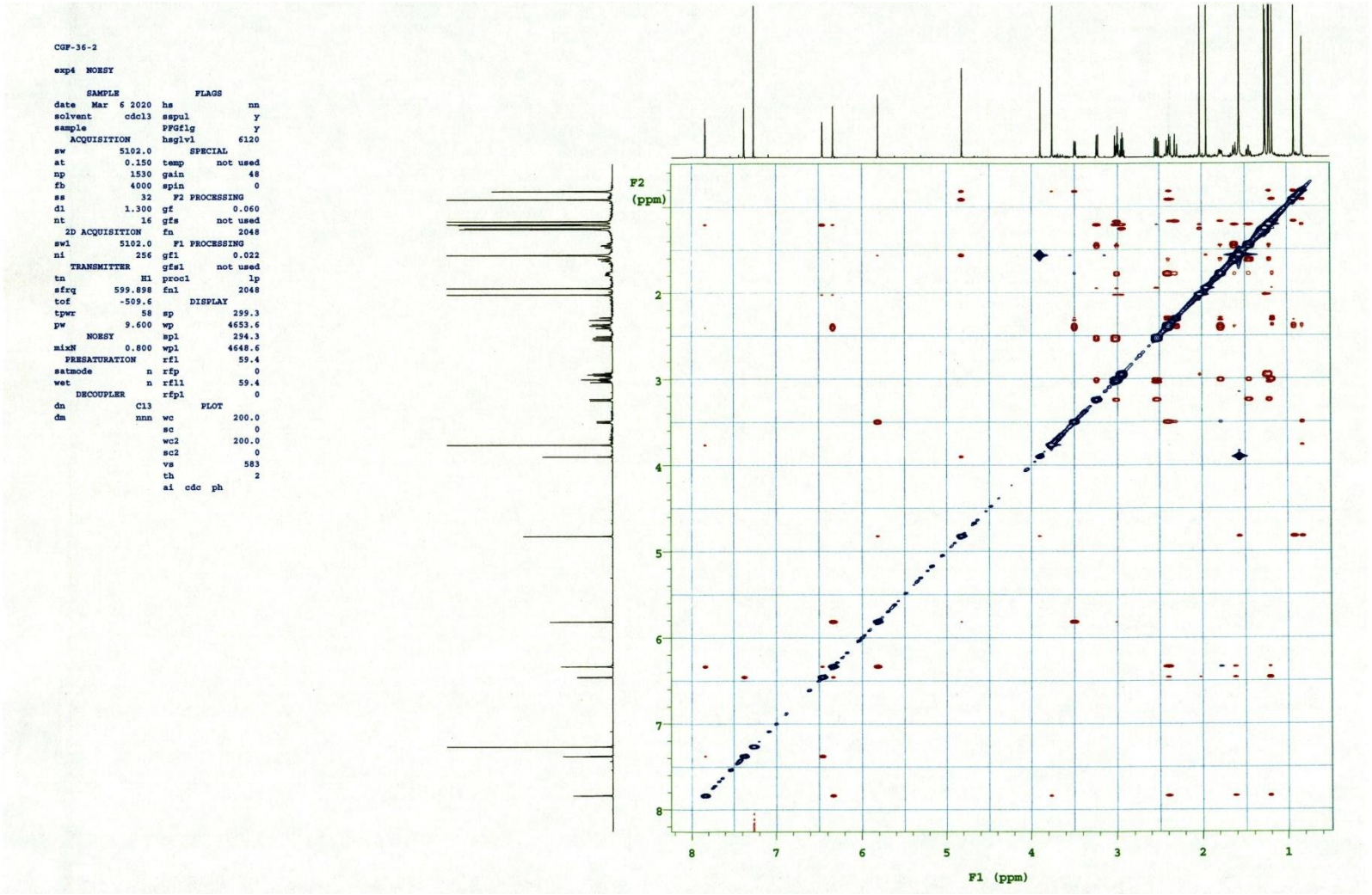


Figure S18. EIMS of compound **2**.

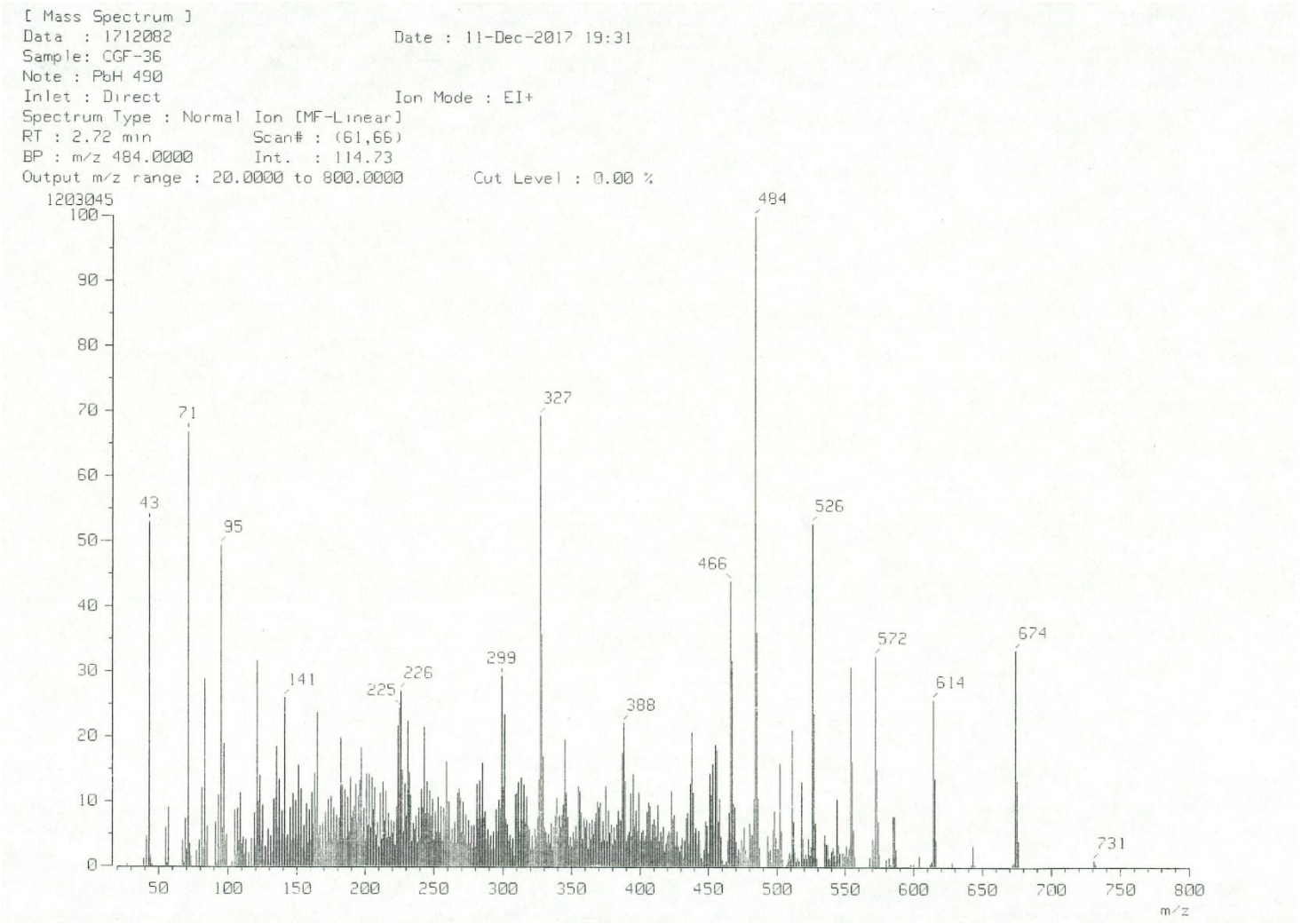
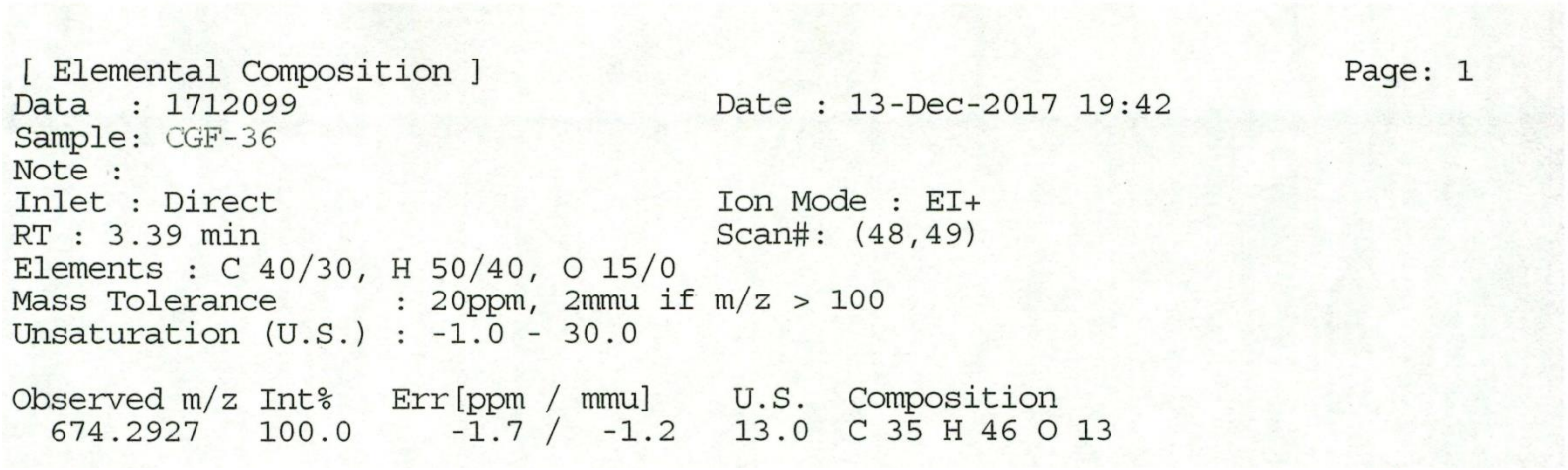


Figure S19. HREIMS data of compound **2**.



```
[ Elemental Composition ]                                    Page: 1
Data  : 1712099                    Date : 13-Dec-2017 19:42
Sample: CGF-36
Note :
Inlet : Direct                     Ion Mode : EI+
RT : 3.39 min                      Scan#: (48,49)
Elements : C 40/30, H 50/40, O 15/0
Mass Tolerance      : 20ppm, 2mmu if m/z > 100
Unsaturation (U.S.) : -1.0 - 30.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  674.2927   100.0     -1.7 /  -1.2   13.0  C 35 H 46 O 13
```

Figure S20. IR spectrum of compound **2**.

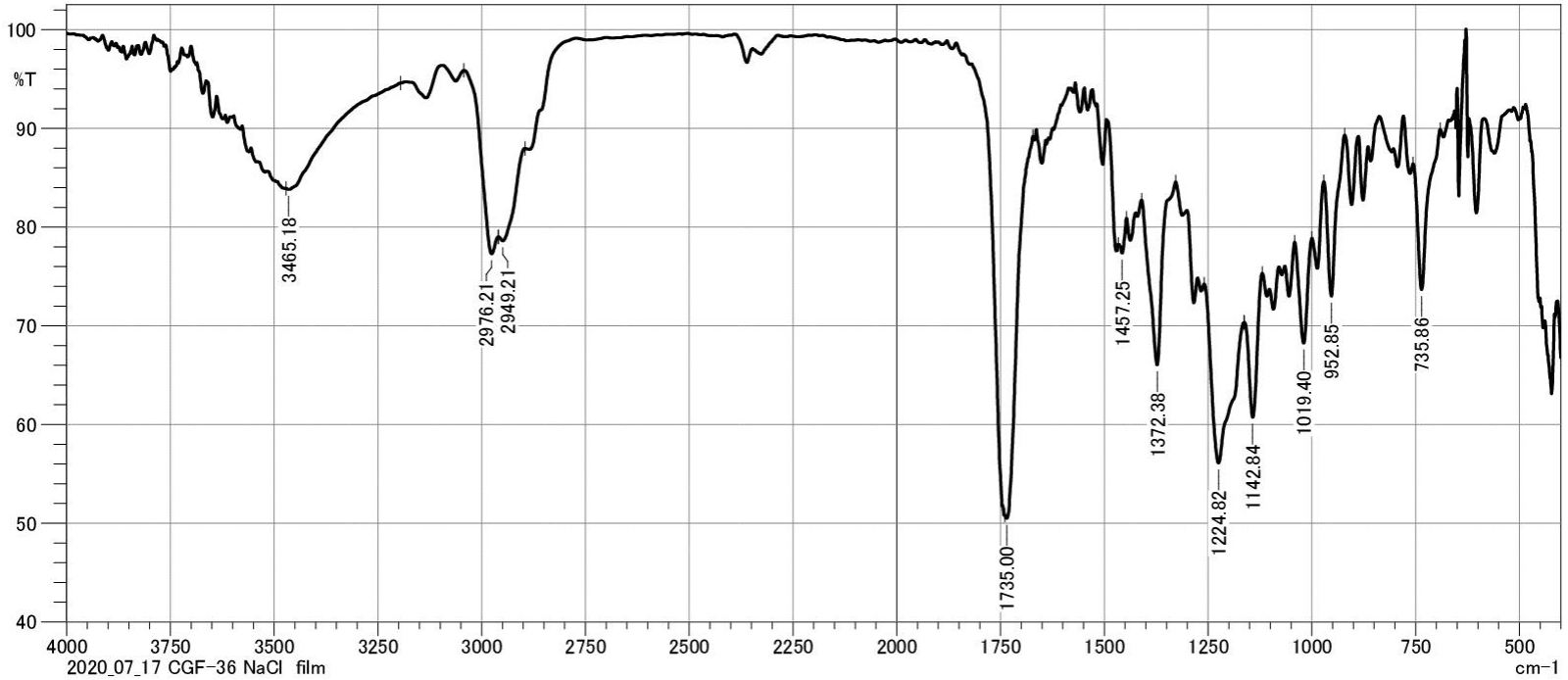


Figure S21. ^{1}H NMR spectrum of compound **3**.

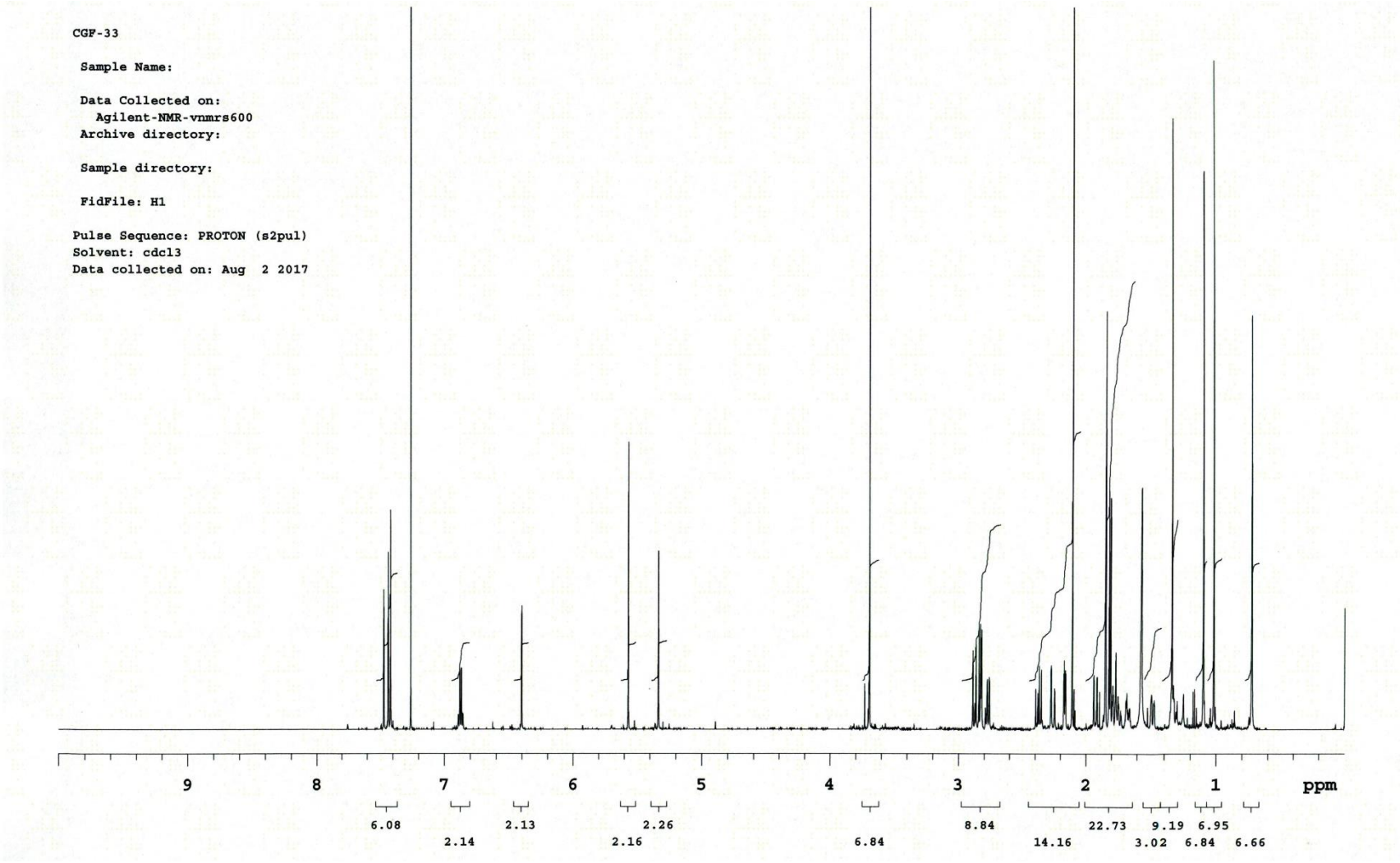


Figure S22. ^{13}C NMR spectrum of compound **3**.

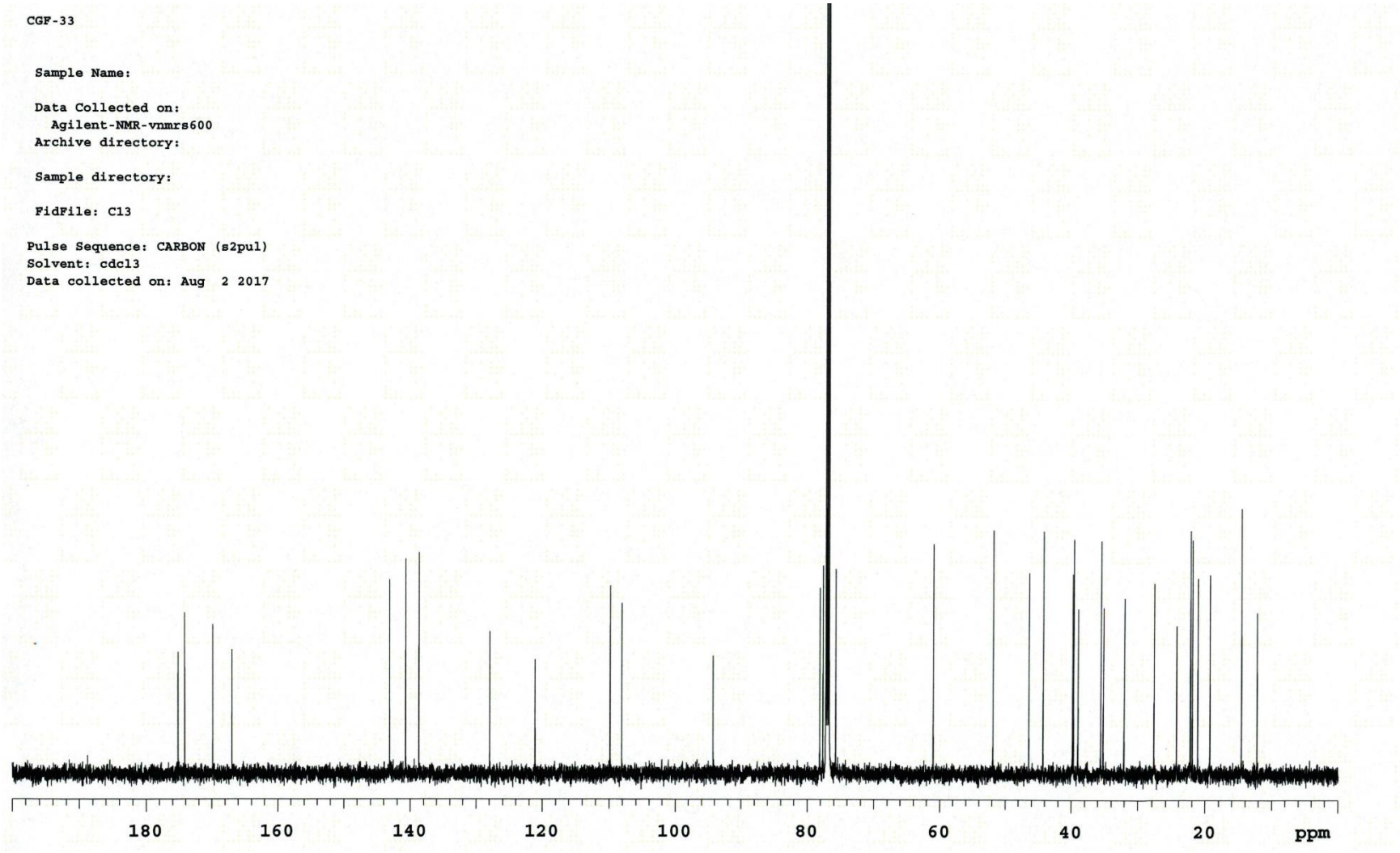


Figure S23. DEPT spectrum of compound **3**.

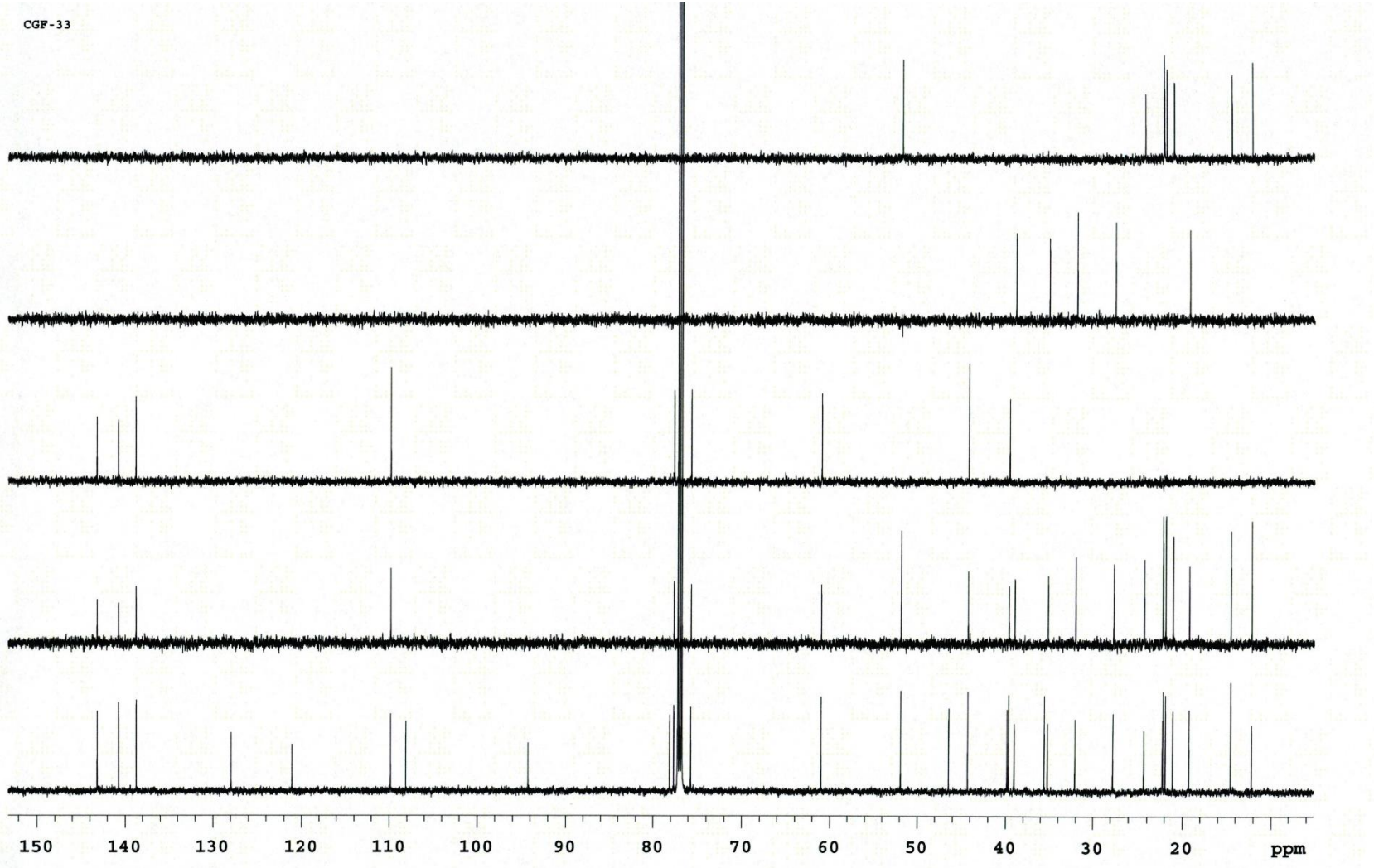


Figure S24. HSQC spectrum of compound **3**.

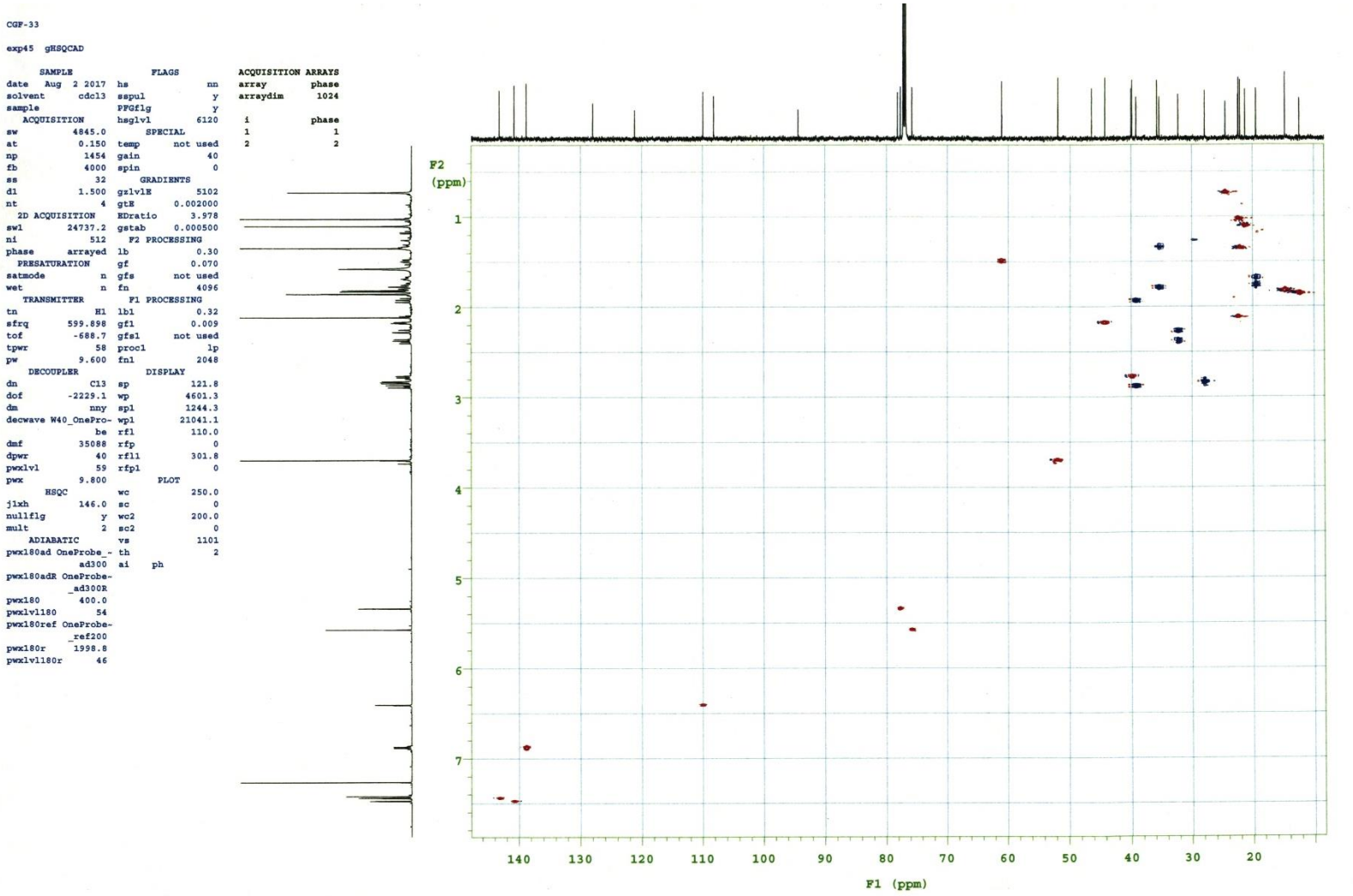


Figure S25. HMBC spectrum of compound **3**.

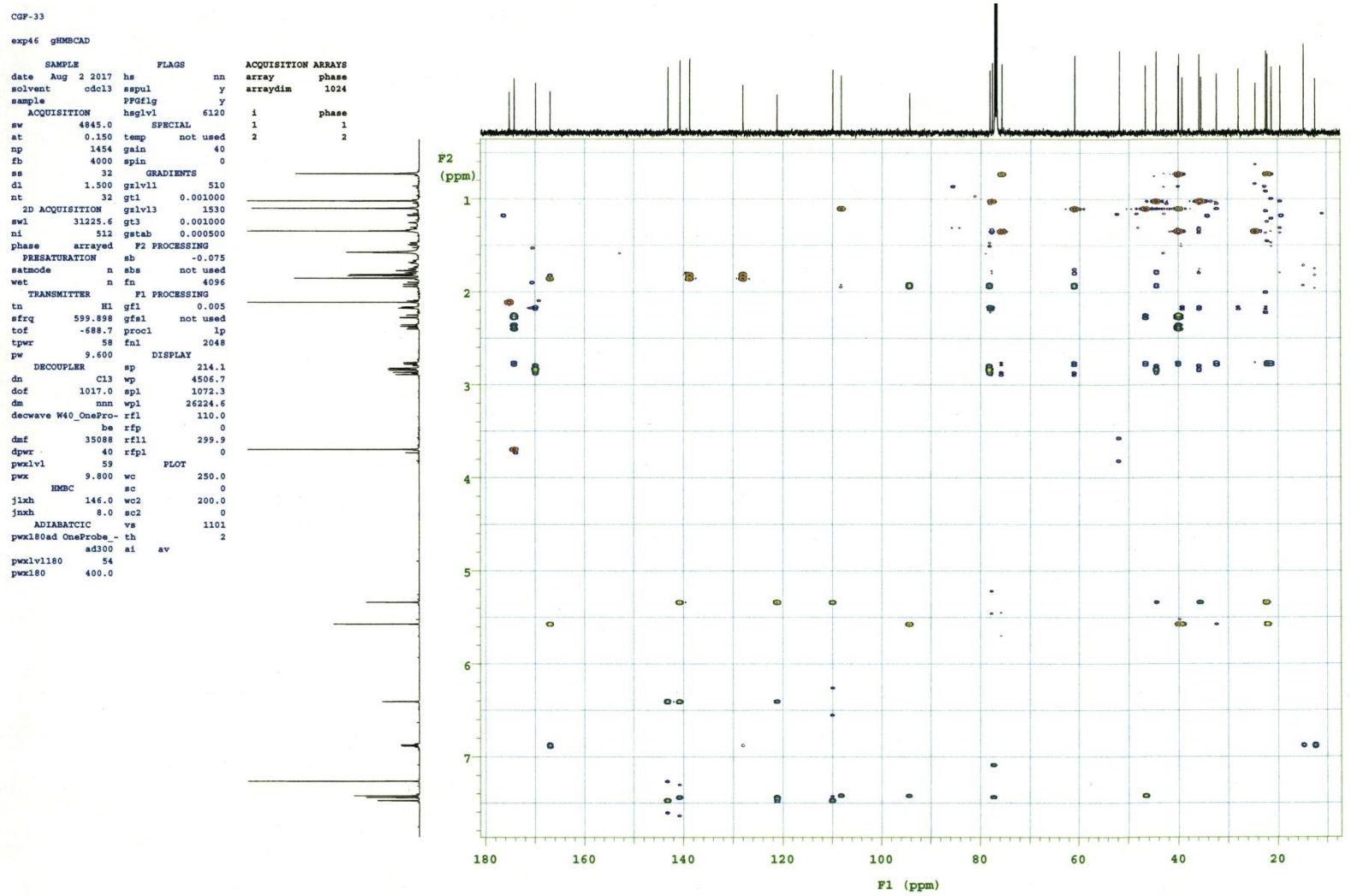


Figure S26. ^{1}H-^{1}H COSY spectrum of compound **3**.

CGF-33

exp43 gCOSY

SAMPLE		FLAGS	
date	Aug 2 2017	hs	nn
solvent	cdcl3	sspul	y
sample		hsglvl	6120
ACQUISITION		SPECIAL	
sw	4960.3	temp	not used
at	0.150	gain	44
np	1488	spin	0
fb	4000	F2 PROCESSING	
ss	32	sb	-0.075
d1	1.000	sbs	not used
nt	8	fn	2048
2D ACQUISITION		F1 PROCESSING	
sw1	4960.3	sb1	-0.026
ni	256	sbs1	not used
d2	0	proc1	lp
PRESATURATION		fn1	2048
satmode	n	DISPLAY	
wet	n	sp	294.2
TRANSMITTER		wp	4558.3
tn	H1	sp1	294.2
sfrq	599.898	wp1	4553.4
tof	-619.2	rf1	98.2
tpwr	58	rfp	0
pw	9.600	rfl1	98.2
GRADIENTS		rfp1	0
gzlvlE	5102	PLOT	
gtE	0.001000	wc	200.0
EDratio	1.000	sc	0
gstab	0.000500	wc2	200.0
DECOUPLER		sc2	0
dn	C13	vs	490
dm	nnn	th	5
		ai av	

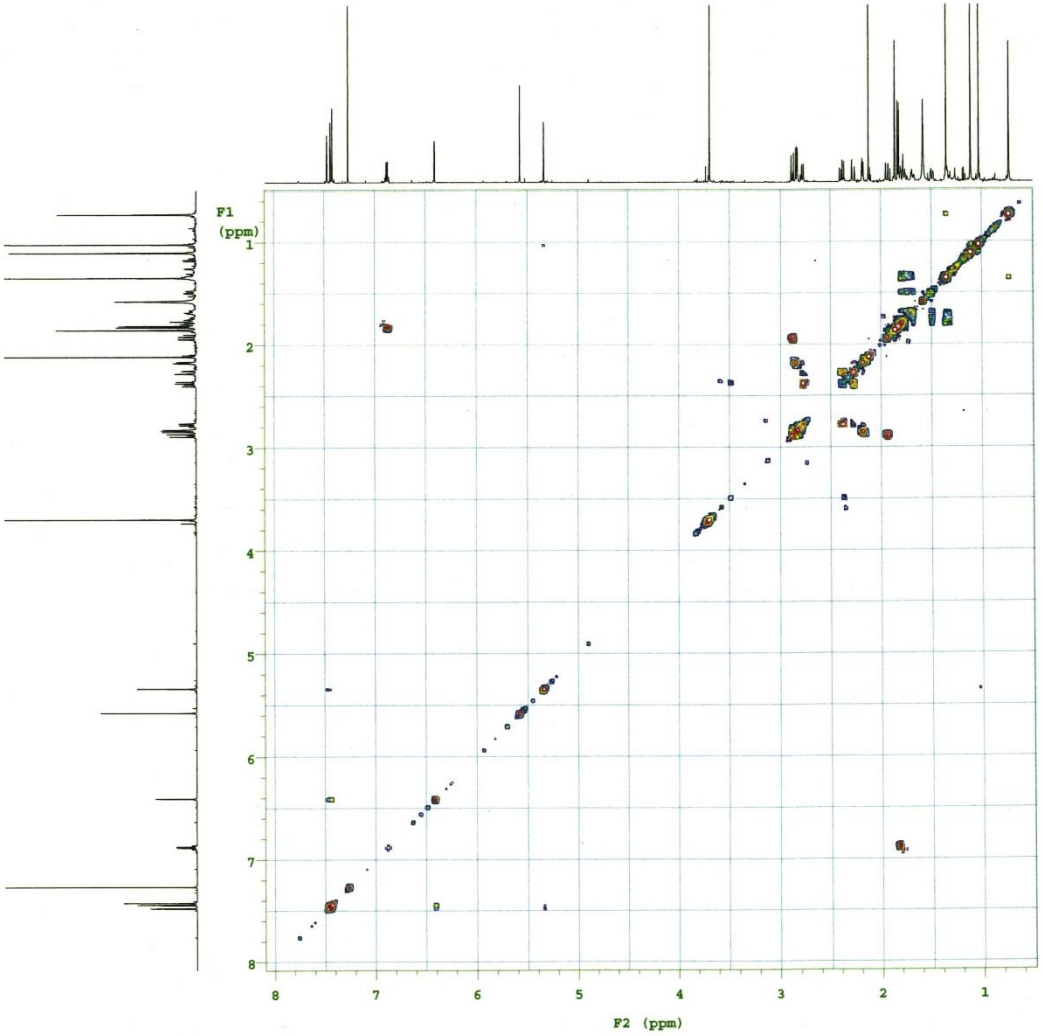
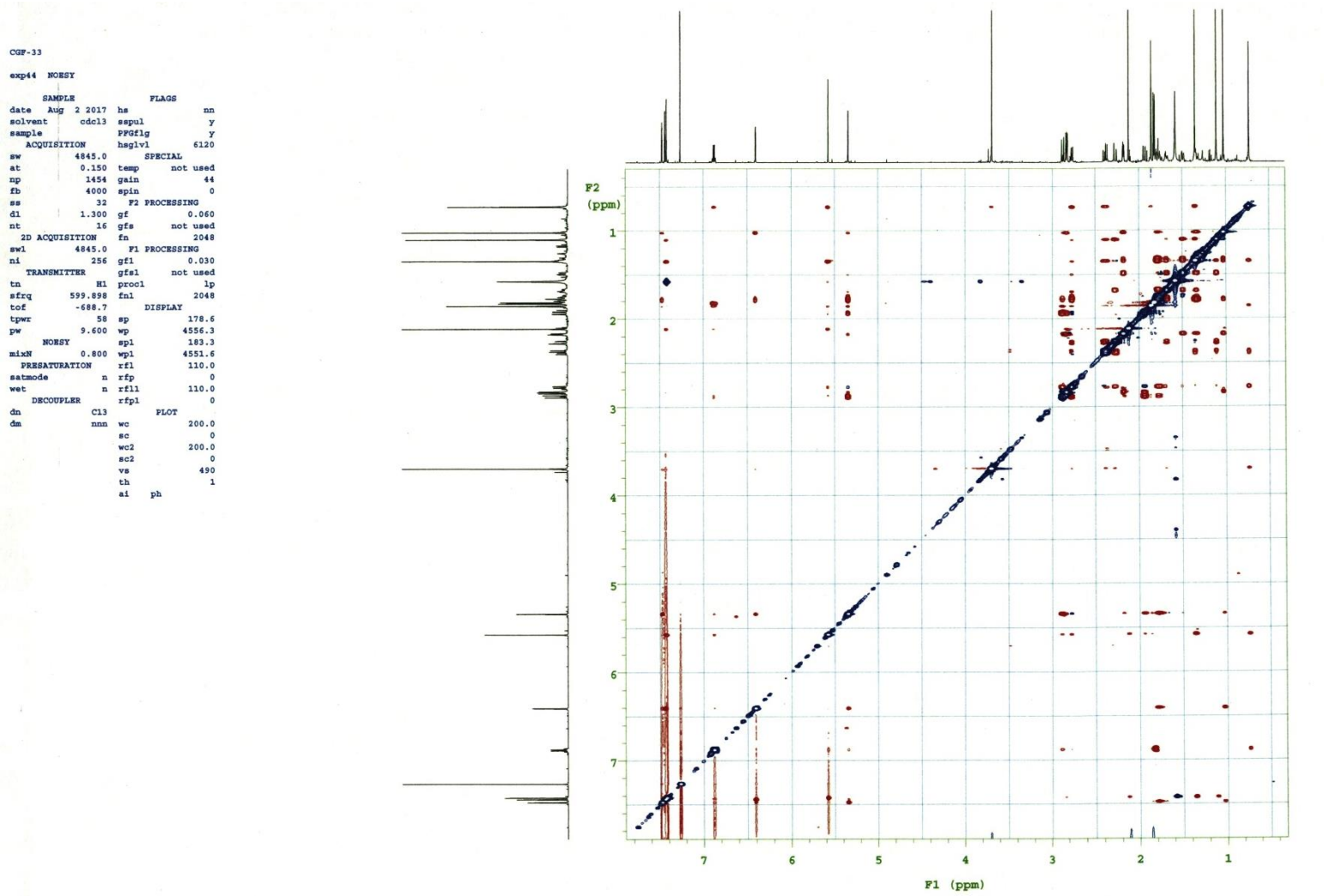


Figure S27. NOESY spectrum of compound **3**.



CGF-33

exp44 NOESY

SAMPLE		FLAGS	
date	Aug 2 2017	hs	nn
solvent	cdcl3	sspul	y
sample		PPGflg	y
ACQUISITION		hsglvl	6120
sw	4845.0	SPECIAL	
at	0.150	temp	not used
np	1454	gain	44
fb	4000	spin	0
ss	32	F2 PROCESSING	
d1	1.300	gf	0.060
nt	16	gfs	not used
2D ACQUISITION		fn	2048
sw1	4845.0	F1 PROCESSING	
ni	256	gf1	0.030
TRANSMITTER		gfs1	not used
tn	H1	proc1	lp
sfrq	599.898	fn1	2048
tof	-688.7	DISPLAY	
tpwr	58	sp	178.6
pw	9.600	wp	4556.3
NOESY		sp1	183.3
mixN	0.800	wp1	4551.6
PRESATURATION		rf1	110.0
satmode	n	rfp	0
wet	n	rf11	110.0
DECOUPLER		rfp1	0
dn	C13	PLOT	
dm	nnn	wc	200.0
		sc	0
		wc2	200.0
		sc2	0
		vs	490
		th	1
		ai ph	

Figure S28. FABMS of compound **3**.

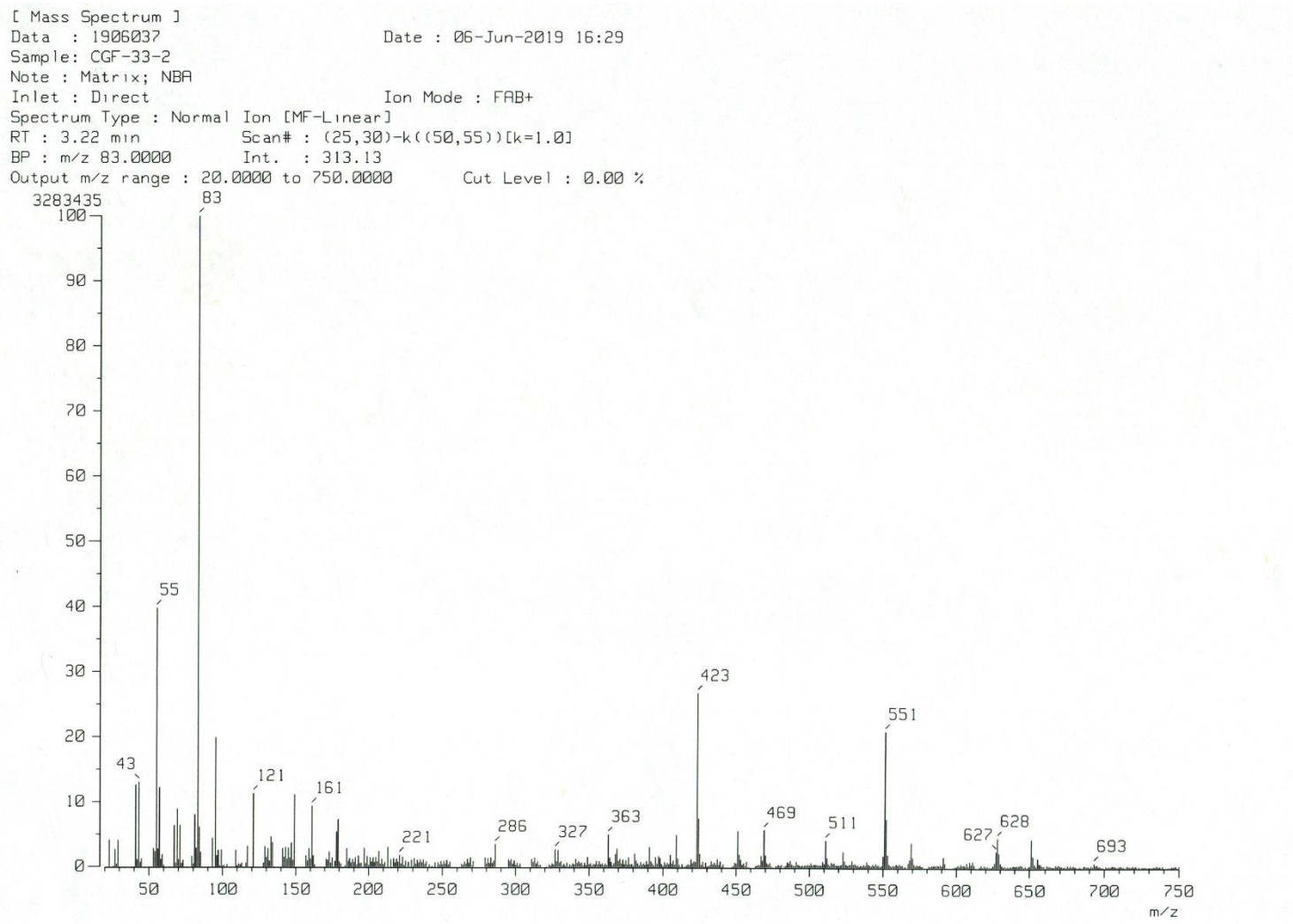
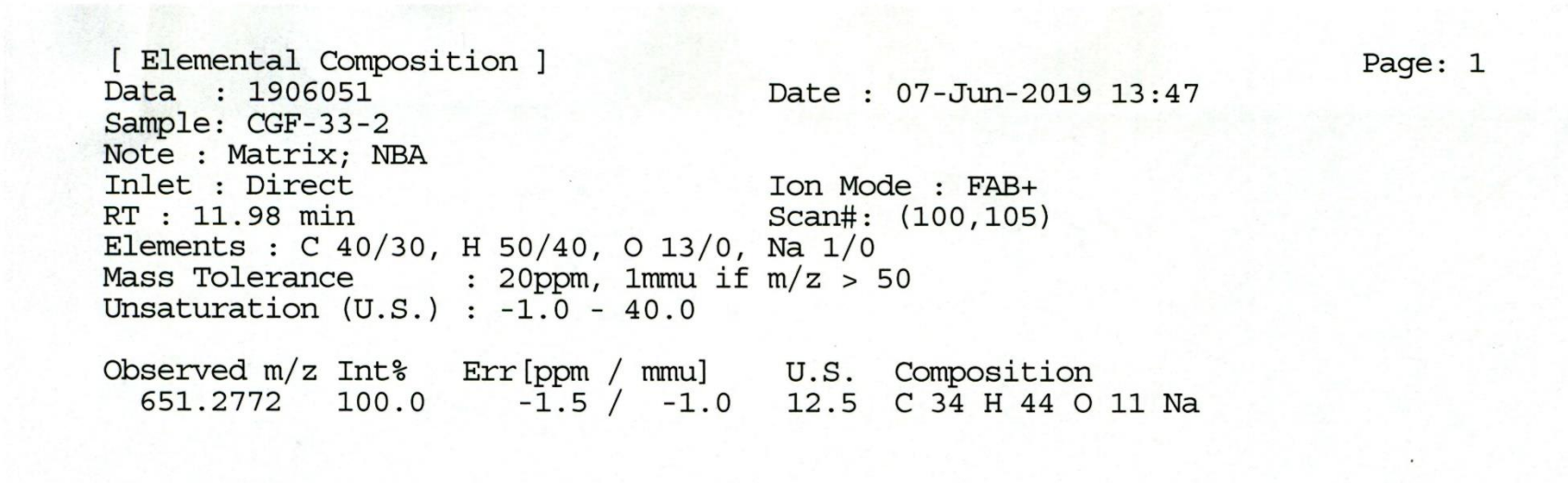


Figure S29. HRFABMS data of compound **3**.



```
[ Elemental Composition ]                                          Page: 1
Data  : 1906051                        Date : 07-Jun-2019 13:47
Sample: CGF-33-2
Note : Matrix; NBA
Inlet : Direct                         Ion Mode : FAB+
RT : 11.98 min                         Scan#: (100,105)
Elements : C 40/30, H 50/40, O 13/0, Na 1/0
Mass Tolerance      : 20ppm, 1mmu if m/z > 50
Unsaturation (U.S.) : -1.0 - 40.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  651.2772   100.0     -1.5 /  -1.0   12.5  C 34 H 44 O 11 Na
```

Figure S30. IR spectrum of compound **3**.