

## **Supplementary Data**

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Table S1. NMR Spectral Data of **1** in CDCl<sub>3</sub>.

No.	$\delta_{\text{H}}^{\text{a}}$	( <i>J</i> in Hz)	<sup>1</sup> H- <sup>1</sup> H COSY	NOE	$\delta_{\text{C}}$		HMBC (C) <sup>b</sup>
1 $\beta$	5.05	brd (6.4)	2 $\alpha$ , 2 $\beta$		70.7	d	2, 3, 5, 9, 30, 1'
2 $\alpha$	3.11	dd (6.4, 15.8)	1, 2 $\beta$	19, 29	35.3	t	1, 3, 10
2 $\beta$	3.24	brd (15.8)	1, 2 $\alpha$				1, 3, 10
3					169.1	s	
4					84.4	s	
5	2.62	dd (3.9, 15.8)	6 $\alpha$ , 6 $\beta$	9	51.1	d	19, 29, 30
6 $\alpha$	2.60	dd (3.9, 15.8)	5, 6 $\beta$		38.6	t	4, 7, 8, 10
6 $\beta$	2.78	t (15.8)	5, 6 $\alpha$	19, 29, 30			4, 5, 7, 10
7					206.5	s	
8					53.1	s	
9	2.44	d	11 $\alpha$ , 11 $\beta$		44.3	d	5, 7, 8, 10, 12, 30
10					44.1	s	
11 $\alpha$	1.70	m	9, 11 $\beta$ , 12 $\alpha$ , 12 $\beta$		17.3	t	8, 9
11 $\beta$	1.66	m	9, 11 $\alpha$ , 12 $\alpha$ , 12 $\beta$	30			13
12 $\alpha$	1.29	m	11 $\alpha$ , 11 $\beta$ , 12 $\beta$		32.0	t	13, 14, 17
12 $\beta$	2.02	dd (7.9, 13.0)	11 $\alpha$ , 11 $\beta$ , 12 $\alpha$	17, 21			9, 11, 13, 14, 17, 18
13					37.7	s	
14					65.0	s	
15	3.70	brs		18	52.6	d	14, 16
16					165.5	s	
17	5.34	brs		12 $\beta$ , 21	78.1	d	12, 13, 14, 18, 20, 21, 22
18	1.11	s		2'	21.4	q	12, 13, 14, 17
19	1.34	s		2 $\beta$ , 6 $\beta$	16.64	q	1, 5, 9, 10
20					162.5	s	
21	5.99	m		12 $\beta$ , 17	97.4	d	
22	6.30	m			123.2	d	17, 21, 23
23					168.9	s	
28	1.48	s		6 $\alpha$	33.4	q	4, 5, 29
29	1.56	s		2 $\beta$ , 6 $\beta$	23.4	q	4, 5, 28
30	1.16	s		6 $\beta$ , 11 $\beta$	16.66	q	7, 8, 9, 14
1'					169.6	s	
2'	2.10	s		18	20.9	q	1'

<sup>a</sup> <sup>1</sup>H chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants (*J*/Hz).

<sup>b</sup> Long range <sup>1</sup>H-<sup>13</sup>C correlation from H to C observed in the HMBC experiment.

Table S2. NMR Spectral Data of **2** in (CD<sub>3</sub>)<sub>2</sub>CO.

No.	$\delta_{\text{H}}^{\text{a}}$	( <i>J</i> in Hz)	<sup>1</sup> H- <sup>1</sup> H COSY	NOE	$\delta_{\text{C}}$	HMBC (C) <sup>b</sup>
1	4.97	d (7.1)	2 $\alpha$ , 2 $\beta$		72.0	d 2, 3, 5, 10, 19, 1'
2 $\alpha$	2.98	dd (7.1, 15.8)	1, 2 $\beta$		36.0	t 3, 10
2 $\beta$	3.50	dd (1.2, 15.8)	1, 2 $\alpha$	29		3, 10
3					169.5	s
4					84.7	s
5	2.69	dd (3.5, 14.7)	6 $\alpha$ , 6 $\beta$	9	51.7	d 4, 6, 10, 19, 29
6 $\alpha$	2.51	dd (3.5, 14.7)	5, 6 $\beta$		39.6	t 5, 7, 8, 10
6 $\beta$	3.10	t (14.7)	5, 6 $\alpha$	19		4, 5, 7, 10
7					208.3	s
8					53.2	s
9	2.61	dd (2.4, 11.8)	11 $\alpha$ , 11 $\beta$	5, 18	44.8	d 5, 8, 10, 12, 19, 30
10					45.1	s
11 $\alpha$	1.63	m	9, 12 $\alpha$ , 12 $\beta$		17.44	t
11 $\beta$	1.73	m	9, 12 $\alpha$ , 12 $\beta$	19, 30		
12 $\alpha$	1.16	m	11 $\alpha$ , 11 $\beta$ , 12 $\beta$		30.6	t 18, 30
12 $\beta$	2.10	m	11 $\alpha$ , 12 $\alpha$	17, 30		
13					39.0	s
14					66.8	s
15	3.95	s		18	54.5	d 16
16					166.9	s
17	5.32	t (1.1)	22, 23	12 $\alpha$	76.2	d 13, 14, 18, 20, 21, 22
18	1.20	s		9, 19	20.4	q 12, 13, 14, 17
19	1.47	s		18	16.1	q 1, 5, 9, 10
20					134.0	s
21					169.80	s
22	7.48	t (1.1)	17, 23		150.9	d 17, 20, 21, 23
23	6.02	t (1.1)	17, 22		103.5	d 20, 21, 23-OCH <sub>3</sub>
28	1.39	s			33.9	q 4, 5, 29
29	1.64	s		2 $\beta$ , 19	23.3	q 4, 5, 28
30	1.28	s		11 $\beta$ , 12 $\beta$	17.49	q 7, 8, 9, 14
1'					169.82	s
2'	2.00	s			20.7	q 1'
23-OCH <sub>3</sub>	3.45	s			56.9	q 23

<sup>a</sup> <sup>1</sup>H chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants (*J*/Hz).

<sup>b</sup> Long range <sup>1</sup>H-<sup>13</sup>C correlation from H to C observed in the HMBC experiment.

Table 3S. NMR Spectral Data of **3** in CDCl<sub>3</sub>+1 drop CD<sub>3</sub>OD.

No.	$\delta_{\text{H}}^{\text{a}}$ ( $J$ in Hz)	$^1\text{H}$ - $^1\text{H}$ COSY	NOE	$\delta_{\text{C}}$	HMBC (C) <sup>b</sup>
1	6.54 brs	2A	2B, 19, 28, 29	76.3	d
2	A 2.35 m	1, 2B	9	35.4	t
	B 2.82 m	2A	1, 5, 9		3
3				172.0	s
4				74.1	s
5	2.01 m	6 $\alpha$ , 6 $\beta$	2B, 9	53.0	
6	$\alpha$ 2.46 dd (5.3, 14.9)	6 $\beta$		38.9	t 5, 7, 8
	$\beta$ 2.80 t (14.9)	6 $\alpha$	19		4, 5, 7, 8
7				210.0	s
8				52.5	s
9	2.14 d (11.4)	11 $\alpha$ , 11 $\beta$	2A, 2B, 18	44.4	d 5, 7, 8, 12, 30
10				46.1	s
11	$\alpha$ 2.49 m	9, 11 $\beta$ , 12 $\alpha$ , 12 $\beta$		19.0	t
	$\beta$ 1.72 m	9, 11 $\alpha$ , 12 $\alpha$ , 12 $\beta$	19, 30		8, 12
12	$\alpha$ 1.61 m	11 $\alpha$ , 12 $\beta$		31.6	t 14
	$\beta$ 2.01 m	11 $\alpha$ , 12 $\alpha$	17		11, 17
13				37.5	s
14				65.0	s
15	3.64 s			52.5	d 14, 16
16				166.3	s
17	5.33 d (1.5)	22	12 $\beta$	78.6	d 14, 20, 22
18	1.10 s		9, 21, 22	21.4	q 14, 17
19	1.31 s		6 $\beta$ , 2'	16.7	q 1, 5, 9, 10, 12, 13
20				163.6	s
21	6.00 brs		18	98.2	d 22, 23
22	6.29 brs	17	18	122.7	d 17, 21, 23
23				169.8	s
28	1.35 s			33.6	q 4, 5, 29
29	1.34 s			27.5	q 4, 5, 28
30	1.14 s		11 $\beta$	16.3	q 7, 8, 9, 14
1'				170.8	s
2'	2.08 s		19	21.1	q 1'
3-OCH <sub>3</sub>	3.67 s			52.3	q 3

<sup>a</sup>  $^1\text{H}$  chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants ( $J/\text{Hz}$ ).

<sup>b</sup> Long range  $^1\text{H}$ - $^{13}\text{C}$  correlation from H to C observed in the HMBC experiment.

Table S4. NMR Spectral Data of **4** in CDCl<sub>3</sub>.

No.	$\delta_{\text{H}}^{\text{a}}$ ( <i>J</i> in Hz)	<sup>1</sup> H- <sup>1</sup> H COSY	NOE	$\delta_{\text{C}}$		HMBC (C) <sup>b</sup>
1	4.03 brd (4.2)	2 $\alpha$ , 2 $\beta$		79.2	d	3
2 $\alpha$	2.66 dd (1.7, 16.8)	1, 2 $\alpha$	19 $\alpha$	35.6	t	3
2 $\beta$	2.98 dd (4.2, 16.8)	1, 2 $\beta$				1, 3, 10
3				168.9	s	
4				80.3	s	
5	2.22 m	6 $\alpha$ , 6 $\beta$	9	60.4	d	4, 6, 9, 10, 14, 28
6 $\alpha$	2.47 dd (3.5, 14.6)	5, 6 $\beta$	28	36.3	t	7, 10
6 $\beta$	2.84 dd (14.6, 15.8)	5, 6 $\alpha$	19 $\beta$ , 30			5, 7, 10
7				206.1	s	
8				51.1	s	
9	2.50 ddd (3.3, 12.7)		5 $\alpha$	48.0	d	10
10				45.8	s	
11	1.77 m (2H)			18.5	t	
12 $\alpha$	1.40 ddd (7.3, 9.1, 14.4)	11, 12 $\beta$		28.7	t	11, 13, 14, 18
12 $\beta$	2.24 m	11, 12 $\alpha$	17			
13				38.6	s	
14				65.7	s	
15	4.12 s		18	53.8	d	14, 16
16				166.0	s	
17	5.43 t (1.5)			75.2	d	13, 14, 18, 20, 21, 22
18	1.18 s		9	20.0	q	12, 13, 14, 17
19 $\alpha$	4.46 d (13.2)		2 $\alpha$ , 30	65.1	t	5, 9
19 $\beta$	4.74 d (13.2)		6 $\beta$ , 29, 30			1, 3, 5, 10
20				133.8	s	
21				168.8	s	
22	7.25 t (1.5)			149.1	d	17, 20, 21, 23
23	5.77 t (1.5)			102.5	d	20, 21, 23-OMe
28	1.29 s		6 $\alpha$	30.2	q	4, 5, 29
29	1.18 s		19 $\beta$	21.2	q	4, 5, 28
30	1.09 s		6 $\beta$ , 19 $\alpha$ , 19 $\beta$	17.8	q	7, 8, 9, 14
23-OMe	3.60 s			57.8	q	23

<sup>a</sup> <sup>1</sup>H chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants (*J*/Hz).

<sup>b</sup> Long range <sup>1</sup>H-<sup>13</sup>C correlation from H to C observed in the HMBC experiment.

Table S5. NMR Spectral Data of **5** in (CD<sub>3</sub>)<sub>2</sub>CO.

No.	$\delta_{\text{H}}^{\text{a}}$	( <i>J</i> in Hz)	<sup>1</sup> H- <sup>1</sup> H COSY	NOE	$\delta_{\text{C}}$		HMBC (C) <sup>b</sup>
1	4.27	dt (1.2, 3.8)	2 $\alpha$ , 2 $\beta$	2 $\alpha$ , 2 $\beta$	80.1	d	3, 9, 19
2 $\alpha$	2.87	dd (1.5, 16.7)	1, 2 $\beta$	1, 19 $\alpha$	36.5	t	1, 3
2 $\beta$	2.73	dd (4.1, 16.4)	1, 2 $\alpha$	1			1, 3, 10
3					170.0	s	
4					80.7	s	
5	2.60	dd (3.6, 15.9)	6 $\alpha$ , 6 $\beta$	9	59.8	d	4, 6, 7, 9, 10, 19, 28, 29
6 $\alpha$	2.40	dd (3.5, 15.0)	5, 6 $\beta$	19 $\beta$ , 30	37.1	t	5, 7, 8, 10
6 $\beta$	3.16	t (5.2)	5, 6 $\alpha$	19 $\beta$ , 30			4, 5, 7, 10
7					208.2	s	
8					51.7	s	
9	2.83	m	11 $\alpha$ , 11 $\beta$	5, 18	48.2	d	8, 10, 11, 12, 19
10					46.7	s	
11 $\alpha$	1.96	m	9, 11 $\beta$ , 12 $\alpha$ , 12 $\beta$		18.8	t	8, 9, 12, 13
11 $\beta$	2.07	m	9, 11 $\alpha$ , 12 $\alpha$ , 12 $\beta$	19 $\alpha$ , 30			8, 9, 13
12 $\alpha$	1.44	m	11 $\alpha$ , 11 $\beta$ , 12 $\beta$		29.0	t	11, 13, 14, 18, 23
12b	2.06	m	11 $\alpha$ , 11 $\beta$ , 12 $\alpha$	17			12, 17, 18
13					39.9	s	
14					67.6	s	
15	4.19	s		18, 30	55.2	d	14, 16
16					167.3	s	
17	5.35	d (1.2)	22, 23	12 $\beta$	76.6	d	12, 13, 14, 18, 20, 21, 22
18	1.27	s		9, 22	19.7	s	12, 13, 14, 17
19 $\alpha$	4.65	d (13.5)	19 $\beta$	2 $\alpha$ , 11 $\beta$ , 30	65.7	t	5, 9, 10
19 $\beta$	4.97	d (13.5)	19 $\alpha$	6 $\beta$ , 29			1, 3, 5, 10
20					129.6	s	
21					173.1	s	
22	7.85	dd (1.7, 2.9)	17, 23	30	154.4	d	17, 20, 21, 23
23	4.99	dd (1.7, 3.5)	17, 22		71.9	t	20, 21, 22
28	1.13	s			21.8	s	4, 5, 28
29	1.24	s		6 $\beta$ , 19 $\beta$	30.3	s	4, 5, 29
30	1.18	s		11 $\beta$ , 19 $\beta$	18.2	s	7, 8, 9, 14

<sup>a</sup> <sup>1</sup>H chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants (*J*/Hz).

<sup>b</sup> Long range <sup>1</sup>H-<sup>13</sup>C correlation from H to C observed in the HMBC experiment.

Fig. S1.  $^1\text{H}$ -NMR spectrum of compound **1**.

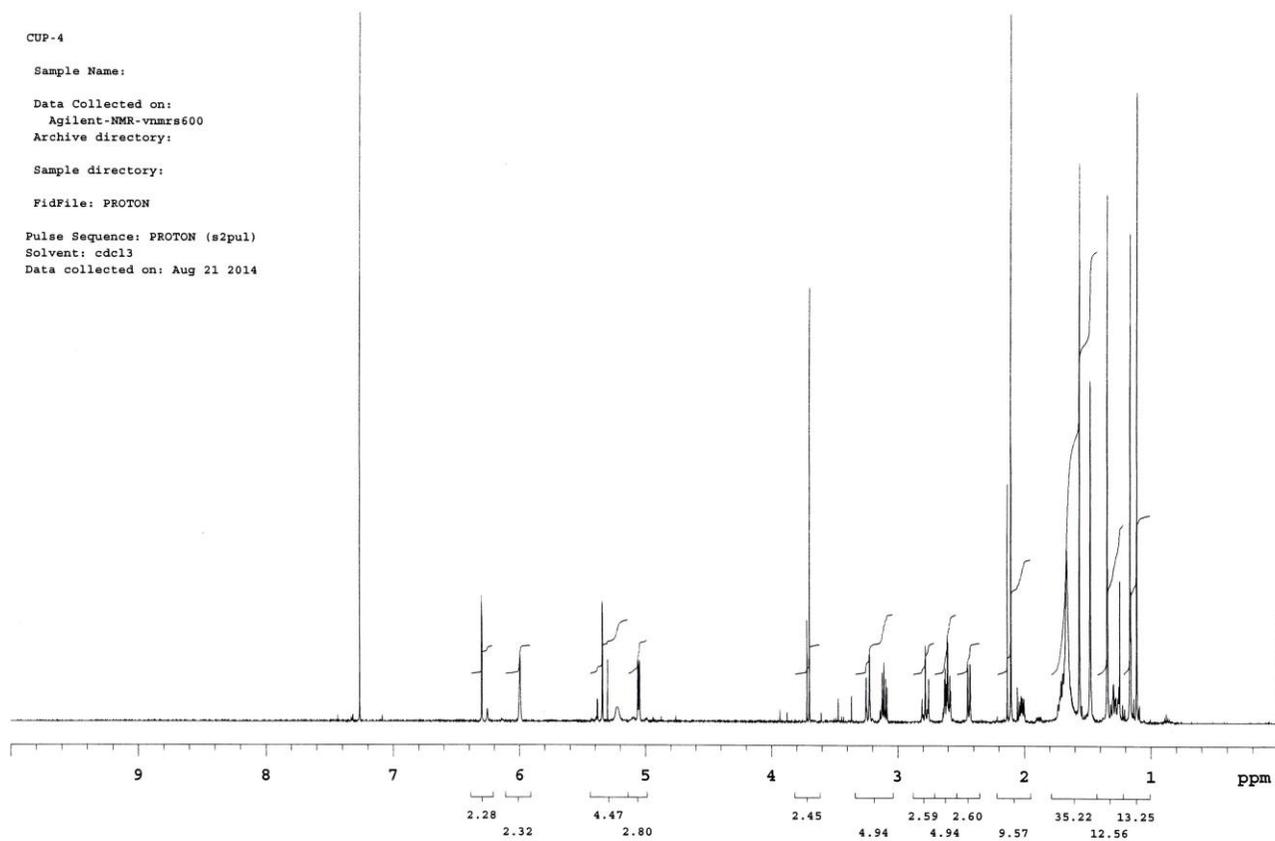


Fig. S2.  $^{13}\text{C}$ -NMR spectrum of compound **1**.

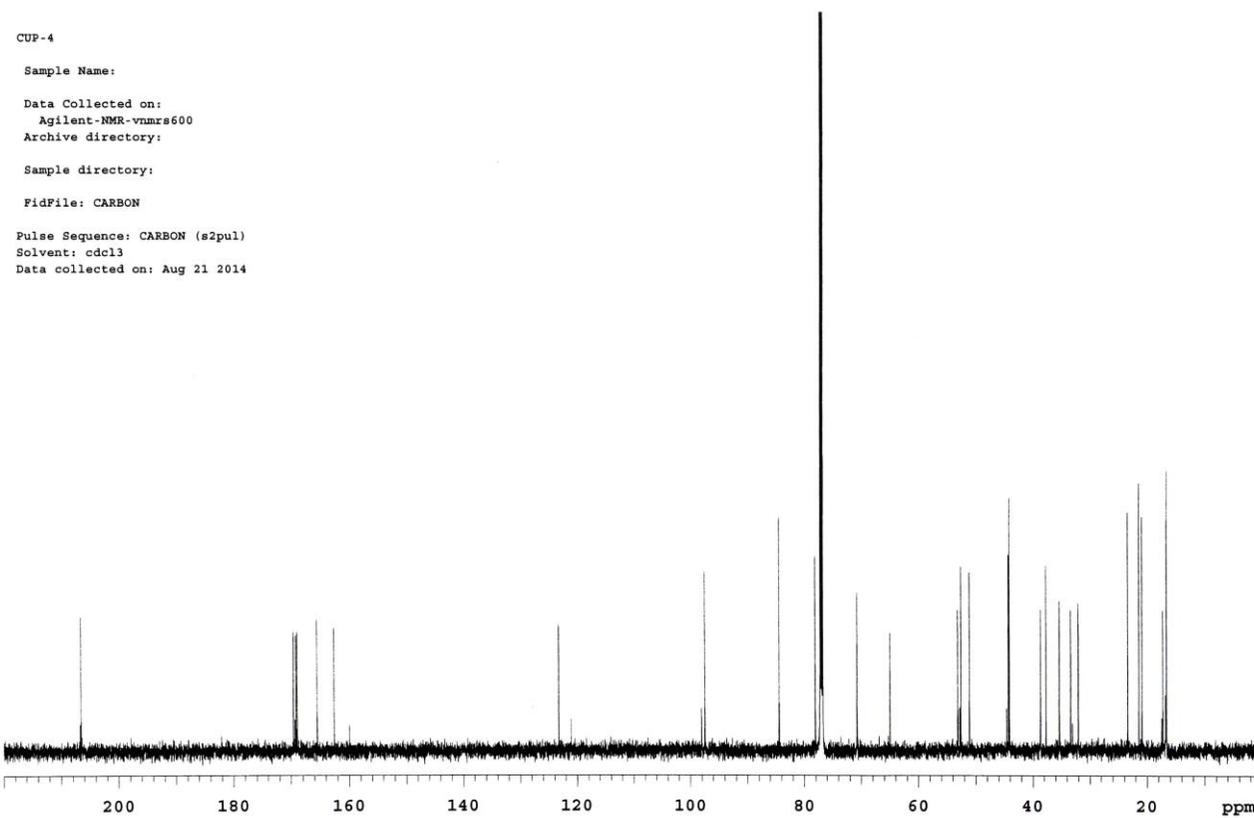


Fig. S3. HSQC spectrum of compound 1.

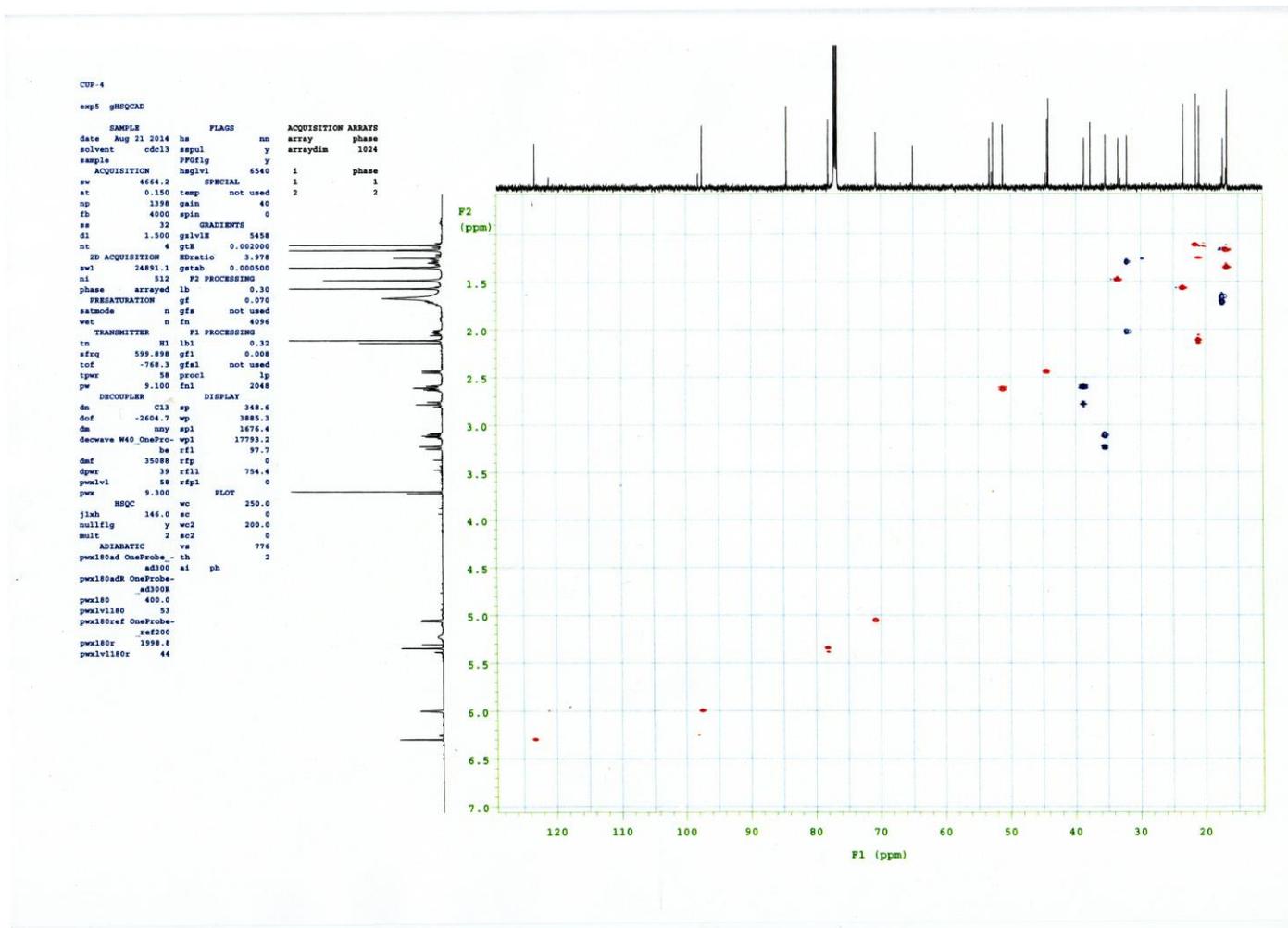


Fig. S4. HMBC spectrum of compound 1.

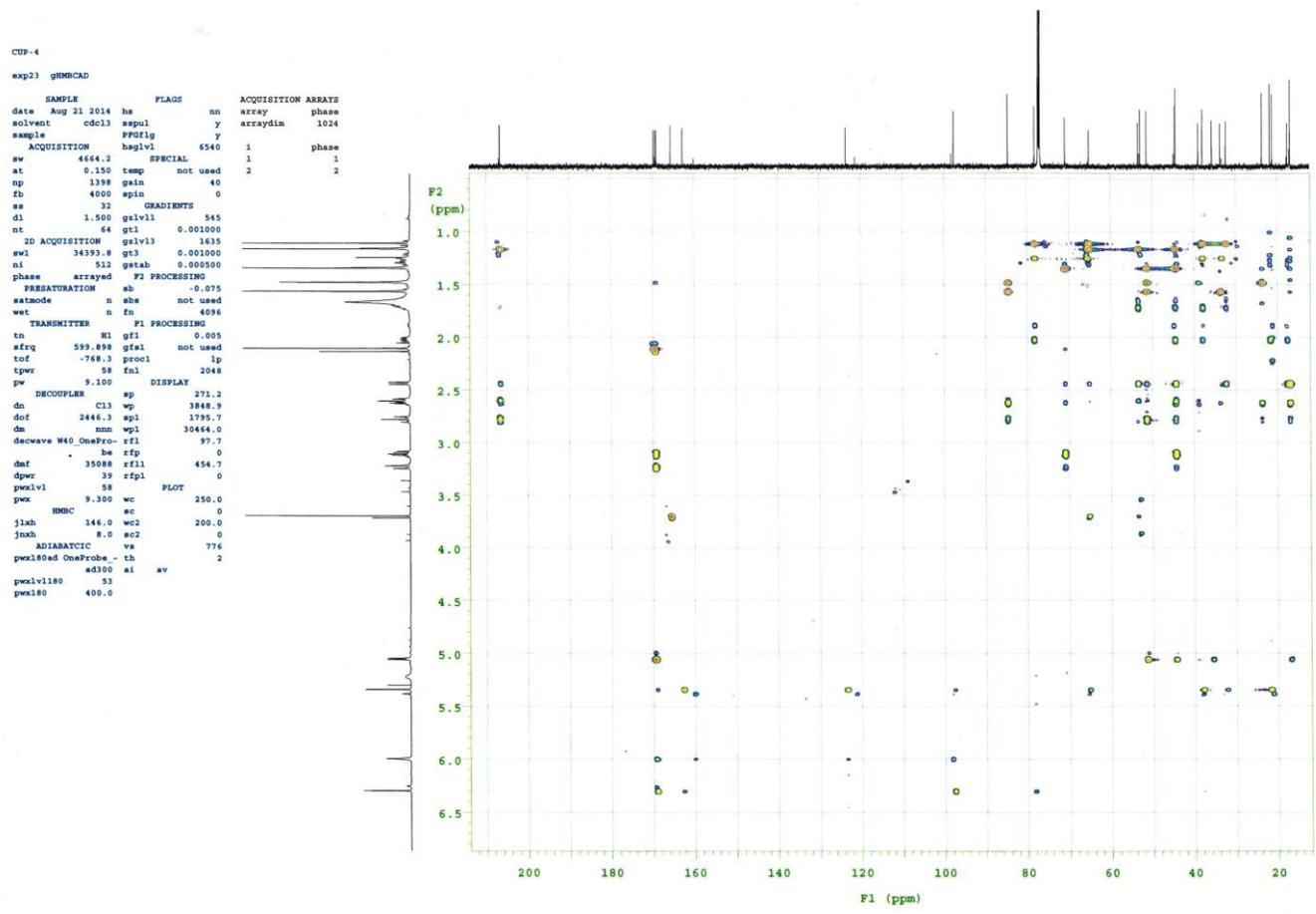


Fig. S5.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 1.

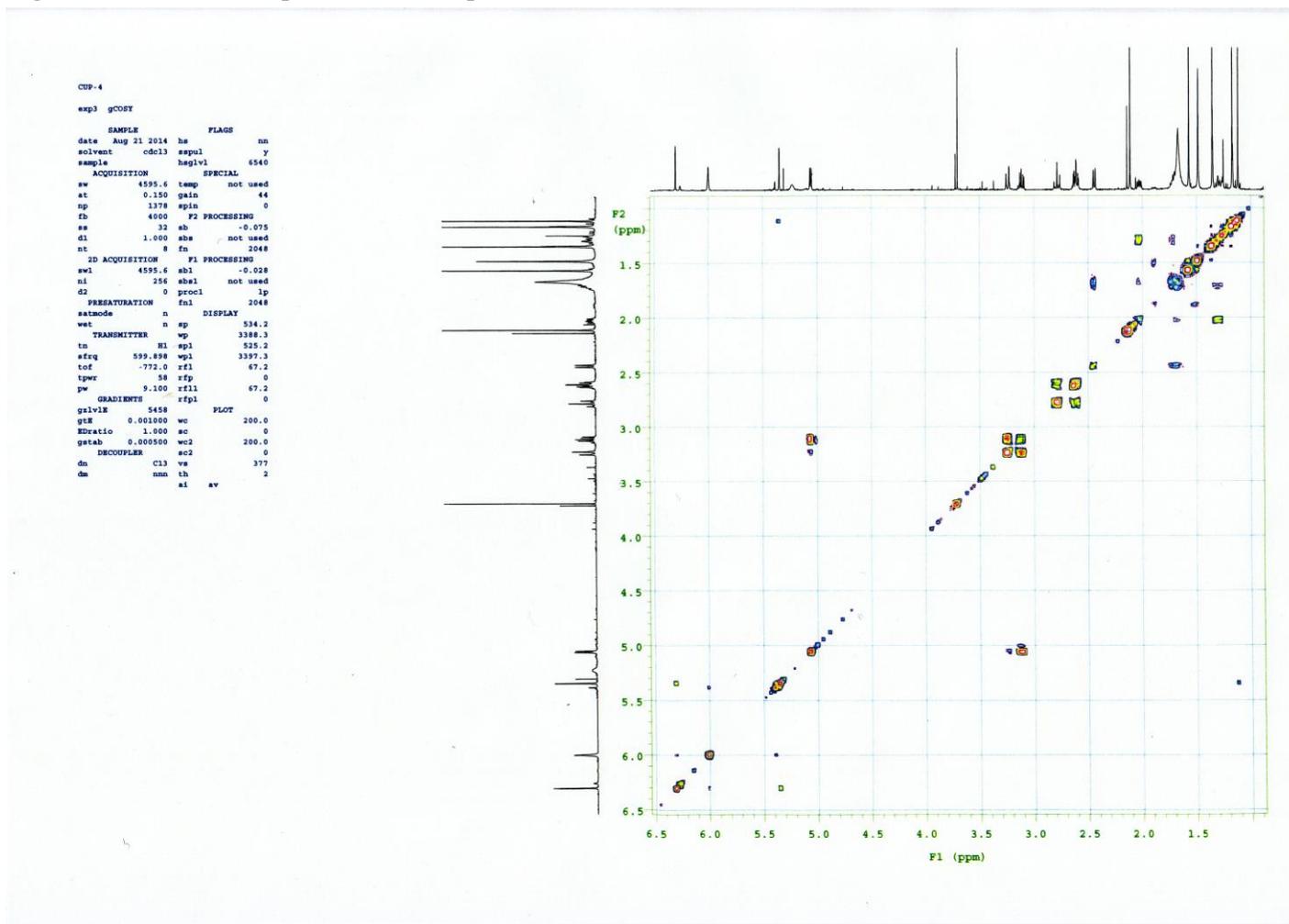


Fig. S6. NOESY spectrum of compound 1.

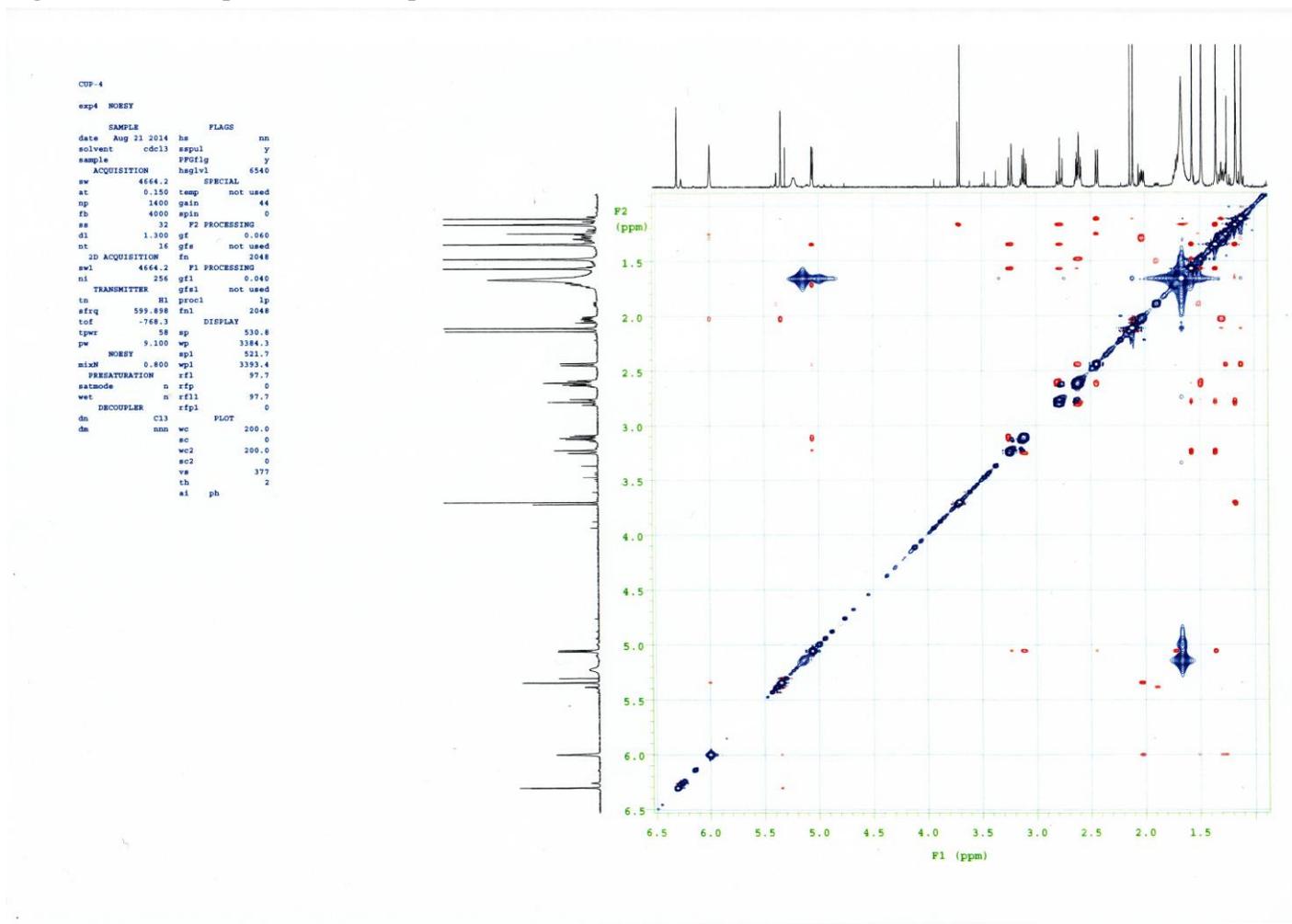


Fig. S7.  $^1\text{H-NMR}$  spectrum of compound **2**.

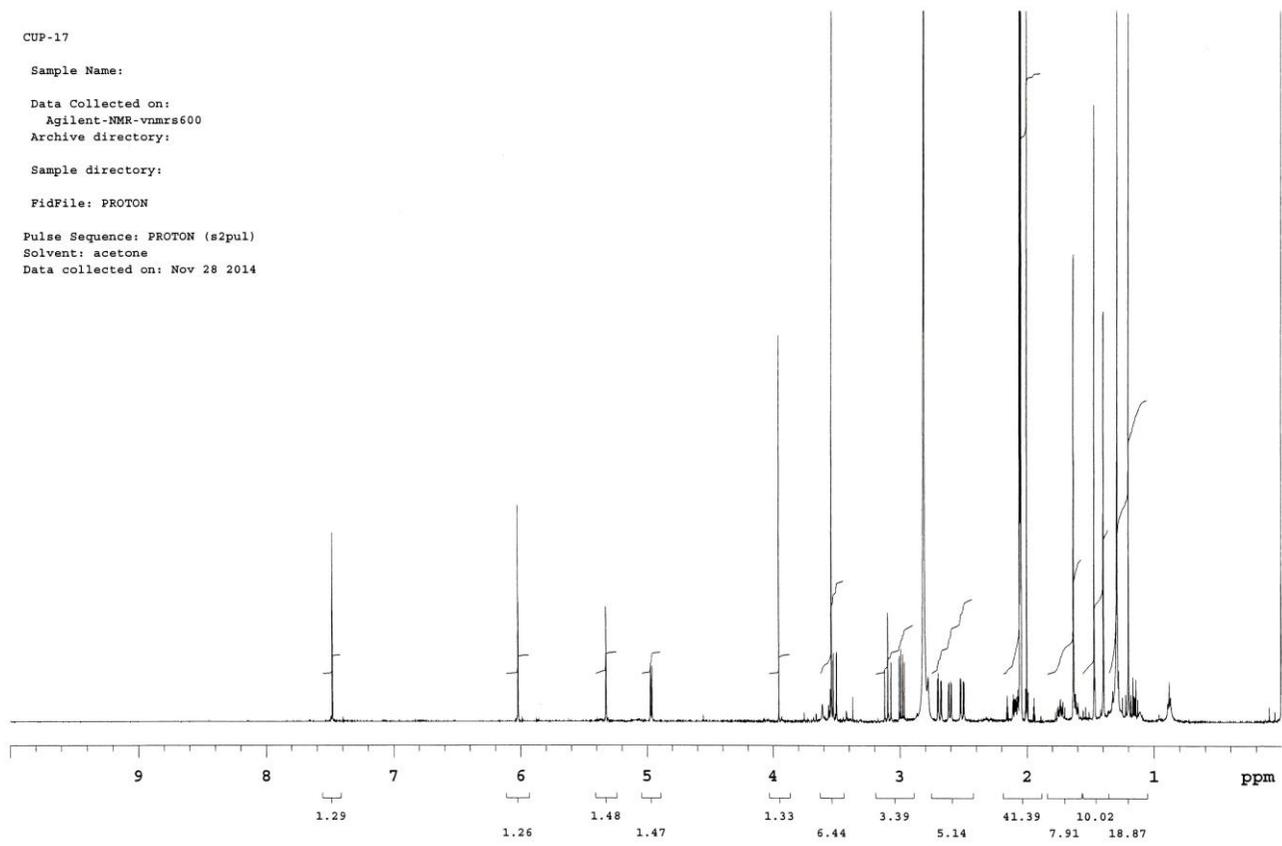


Fig. S8.  $^{13}\text{C}$ -NMR spectrum of compound 2.

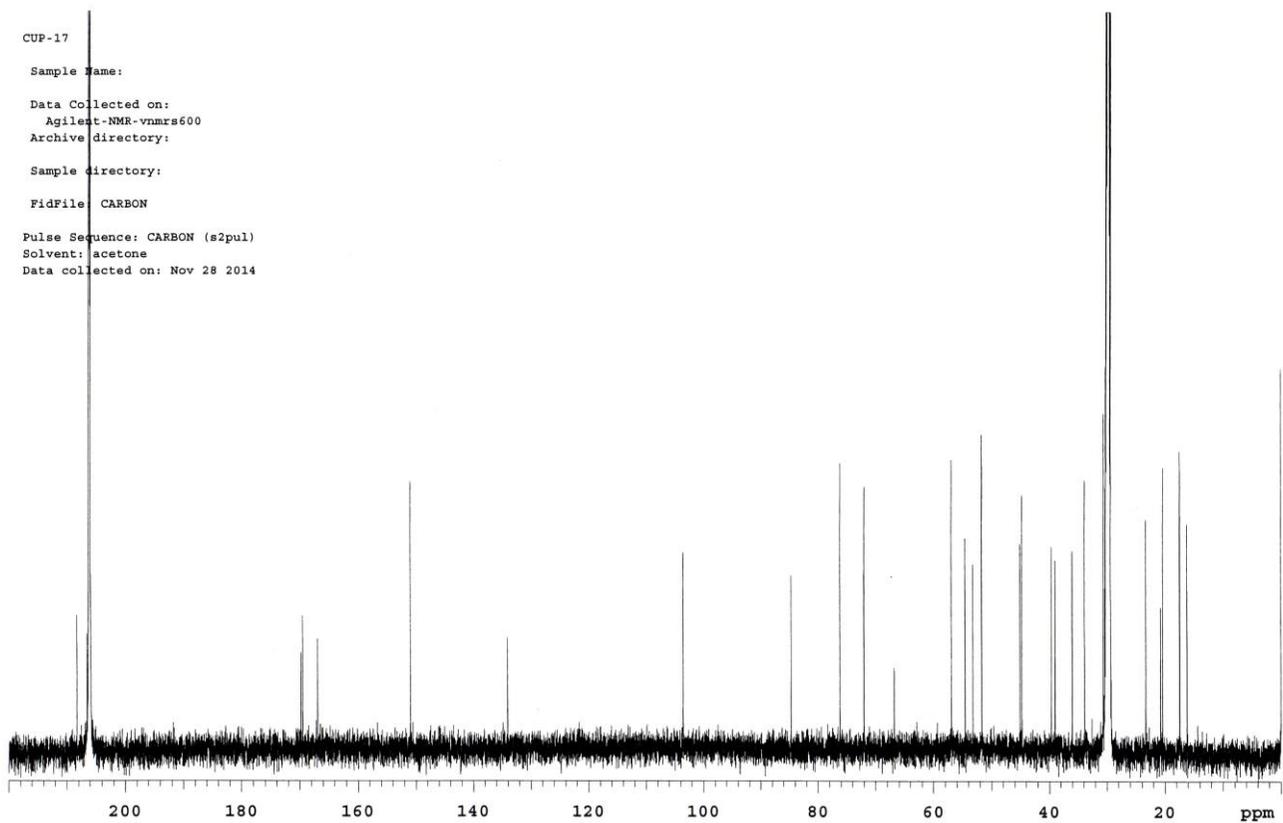


Fig. S9. HSQC spectrum of compound 2.

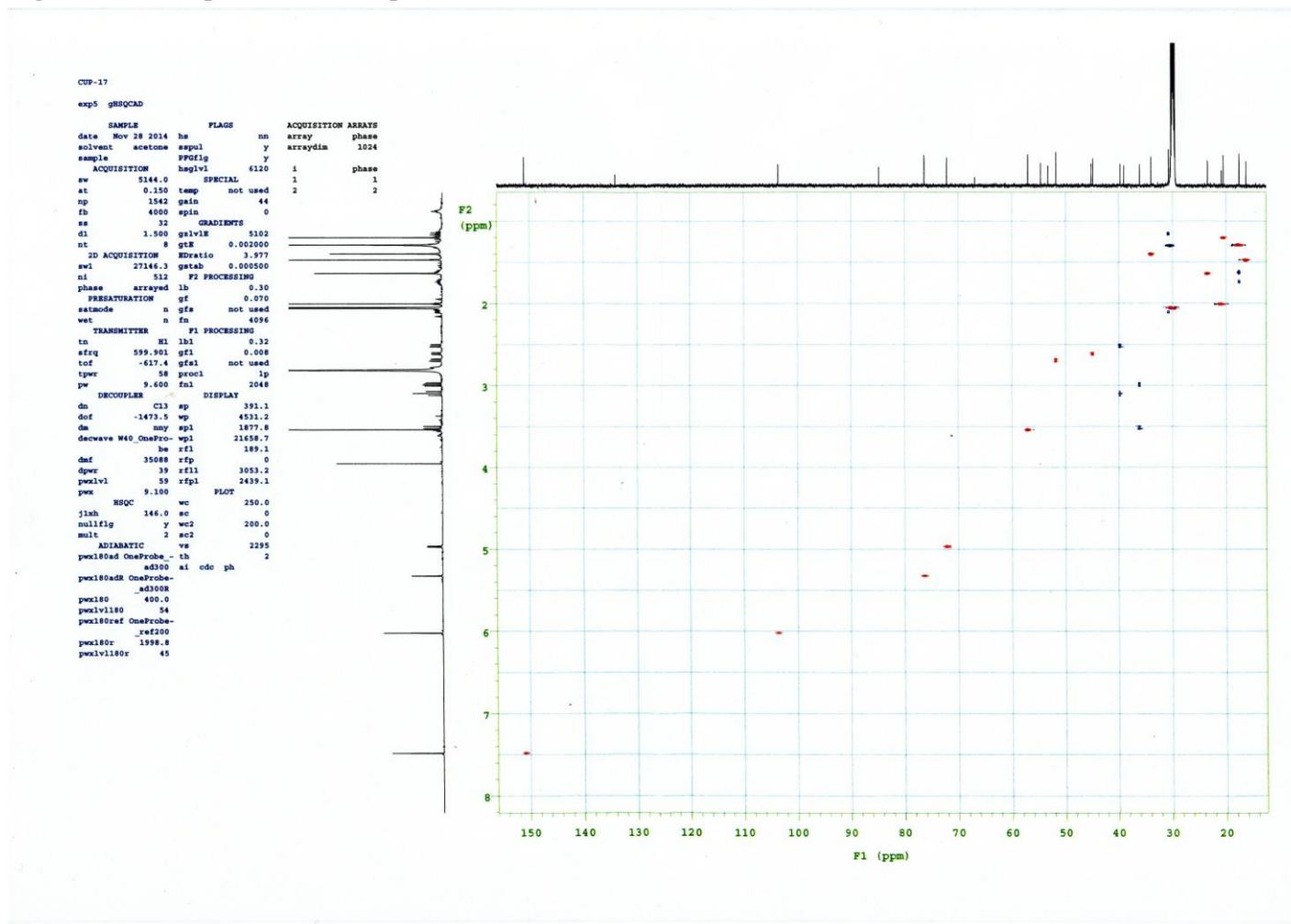


Fig. S10. HMBC spectrum of compound 2.

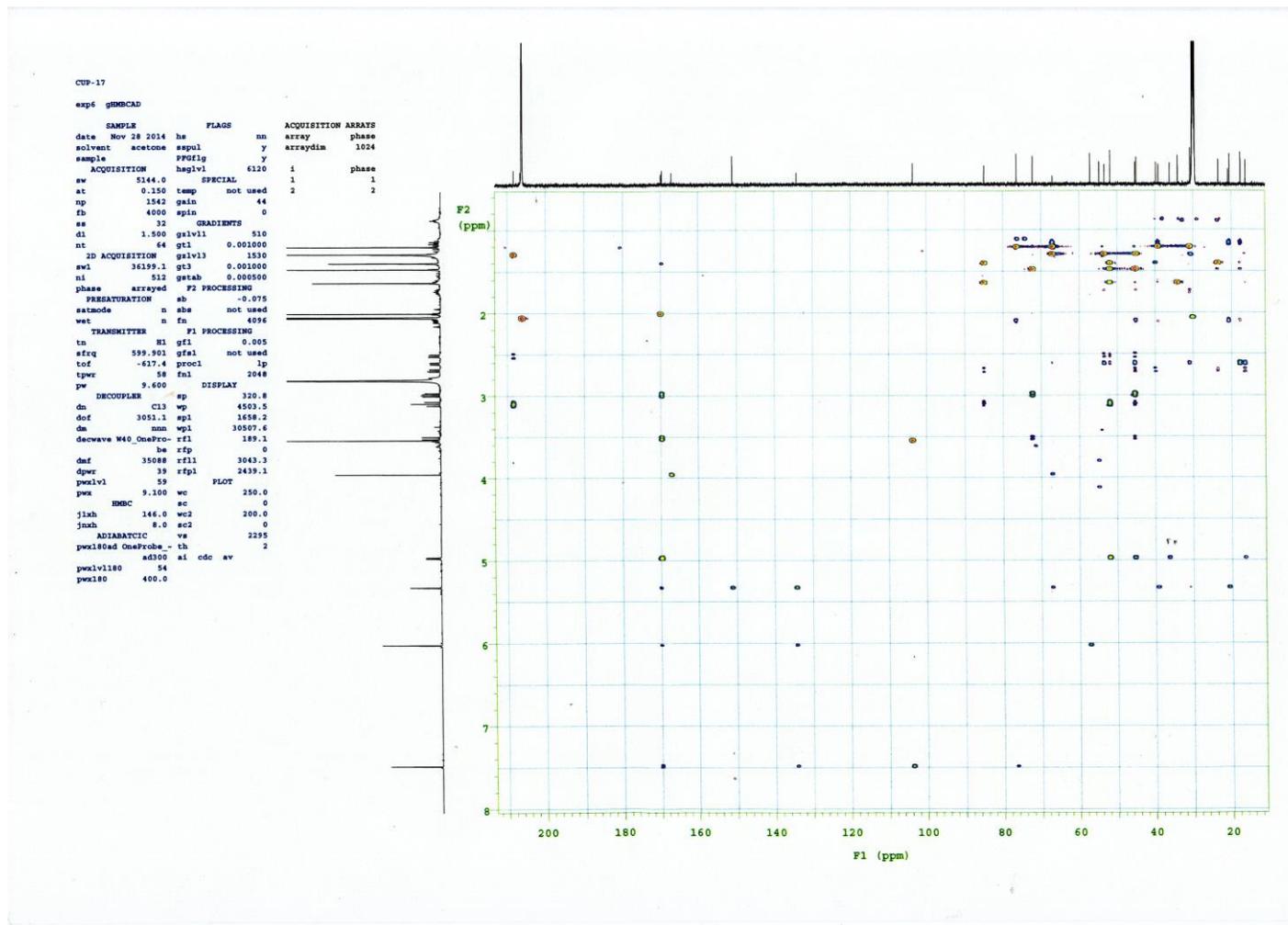


Fig. S11.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 2.

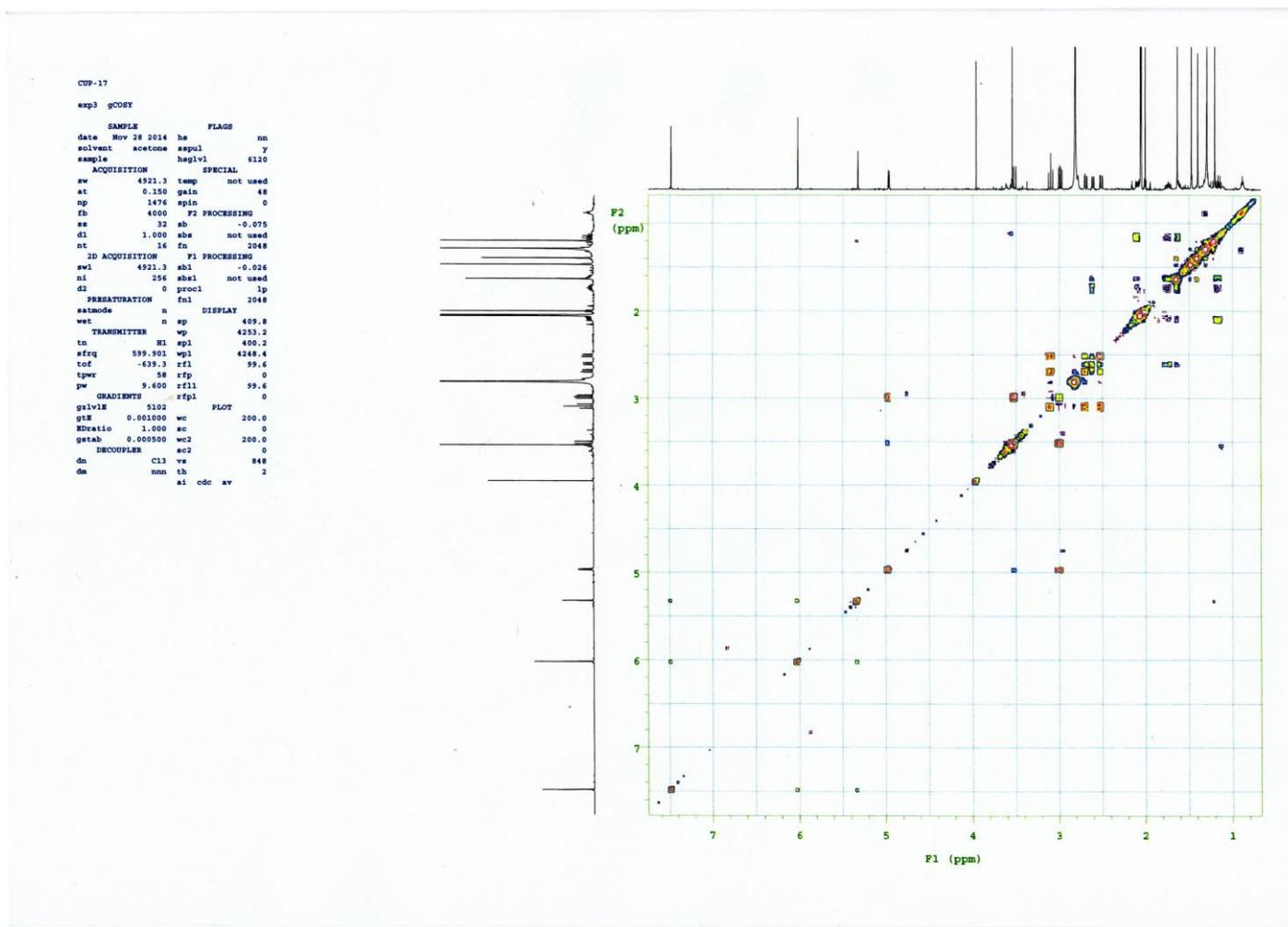


Fig. S12. NOESY spectrum of compound 2.

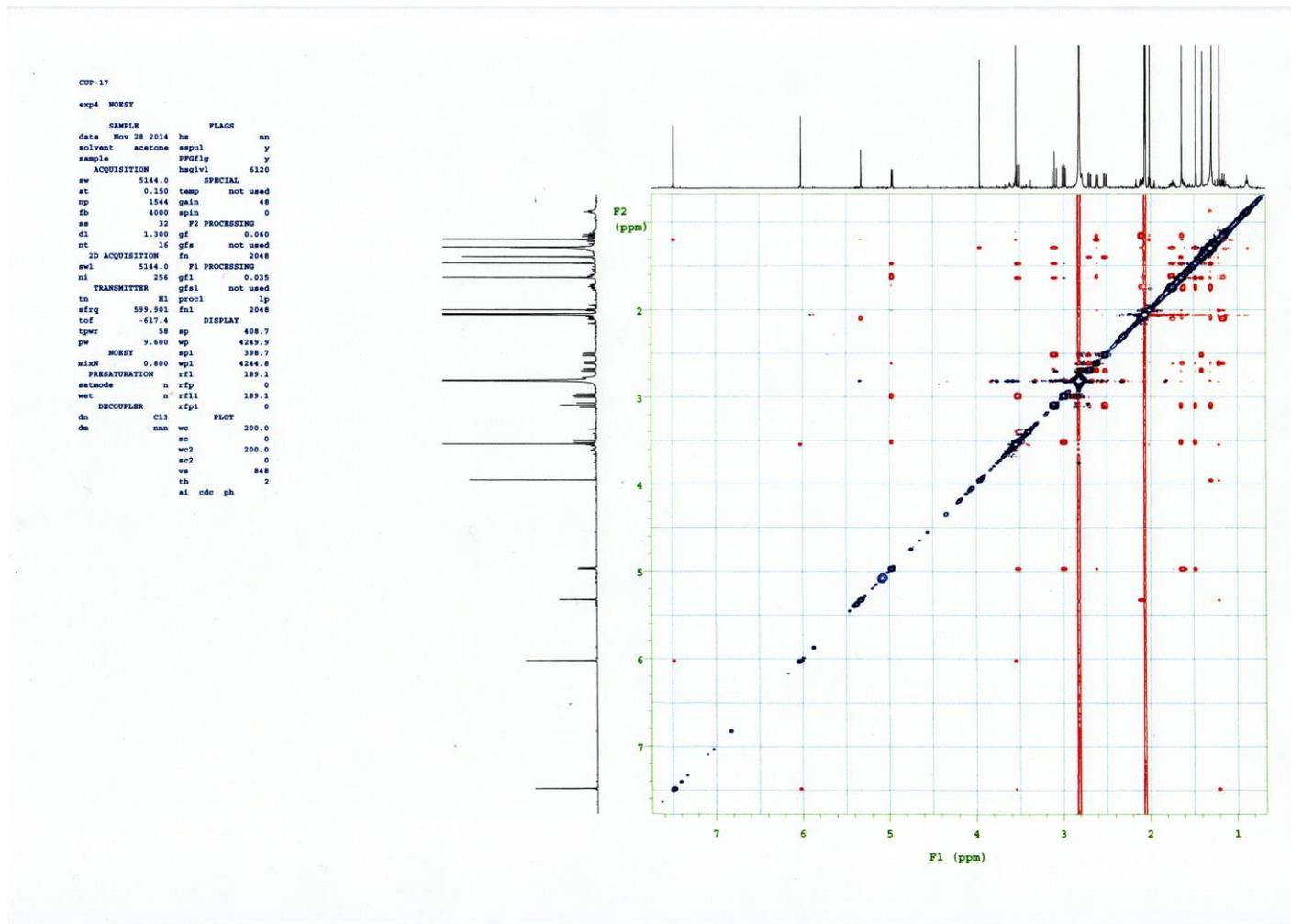


Fig. S13. <sup>1</sup>H-NMR spectrum of compound 3.

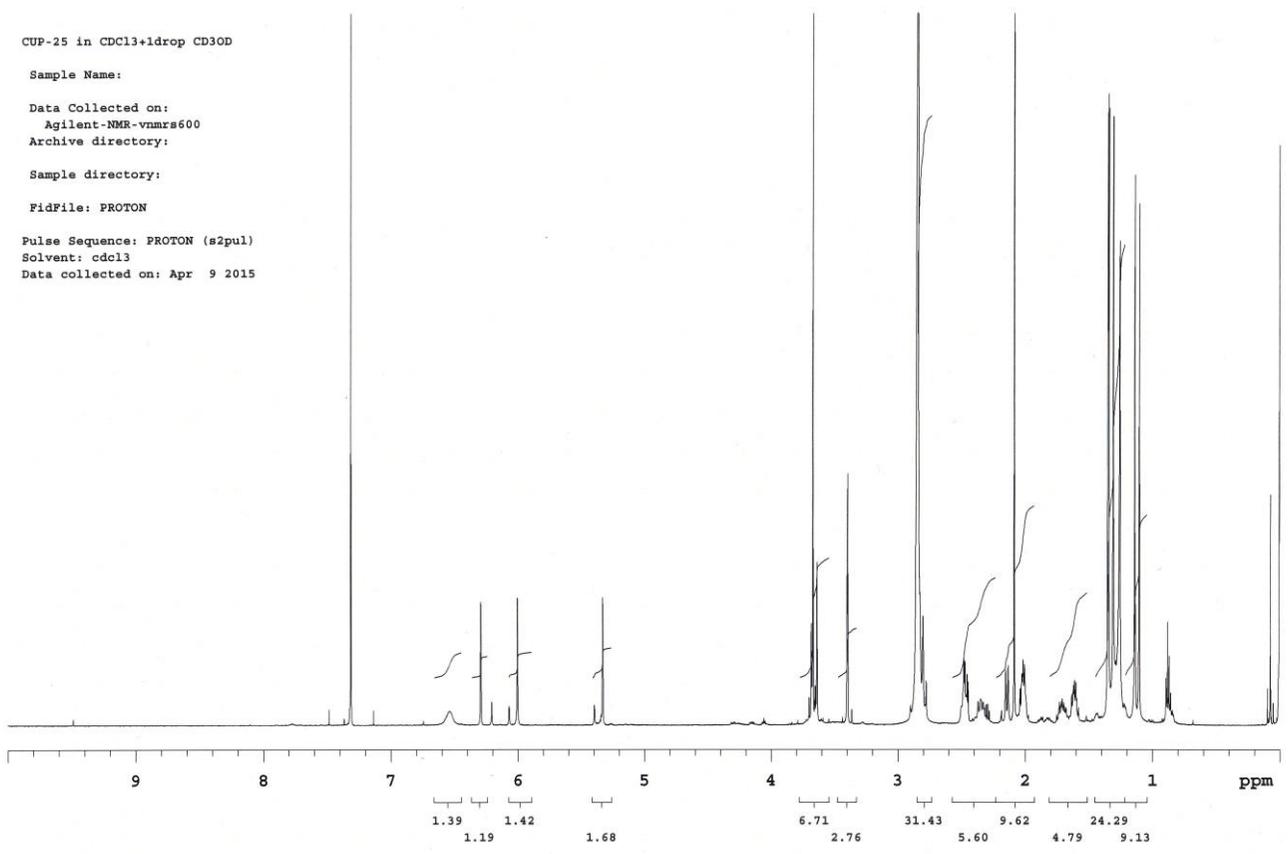


Fig. S14.  $^{13}\text{C}$ -NMR spectrum of compound **3**.

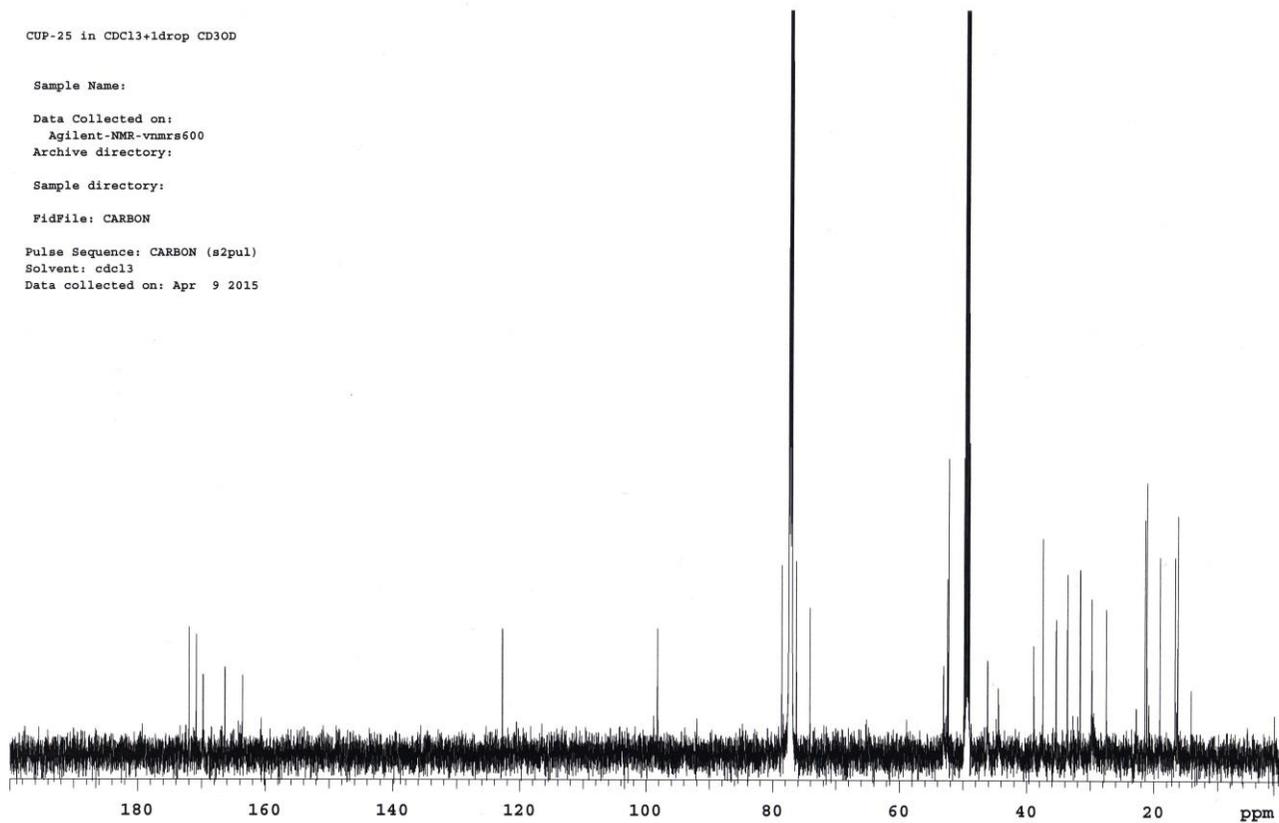


Fig. S15. HSQC spectrum of compound 3.

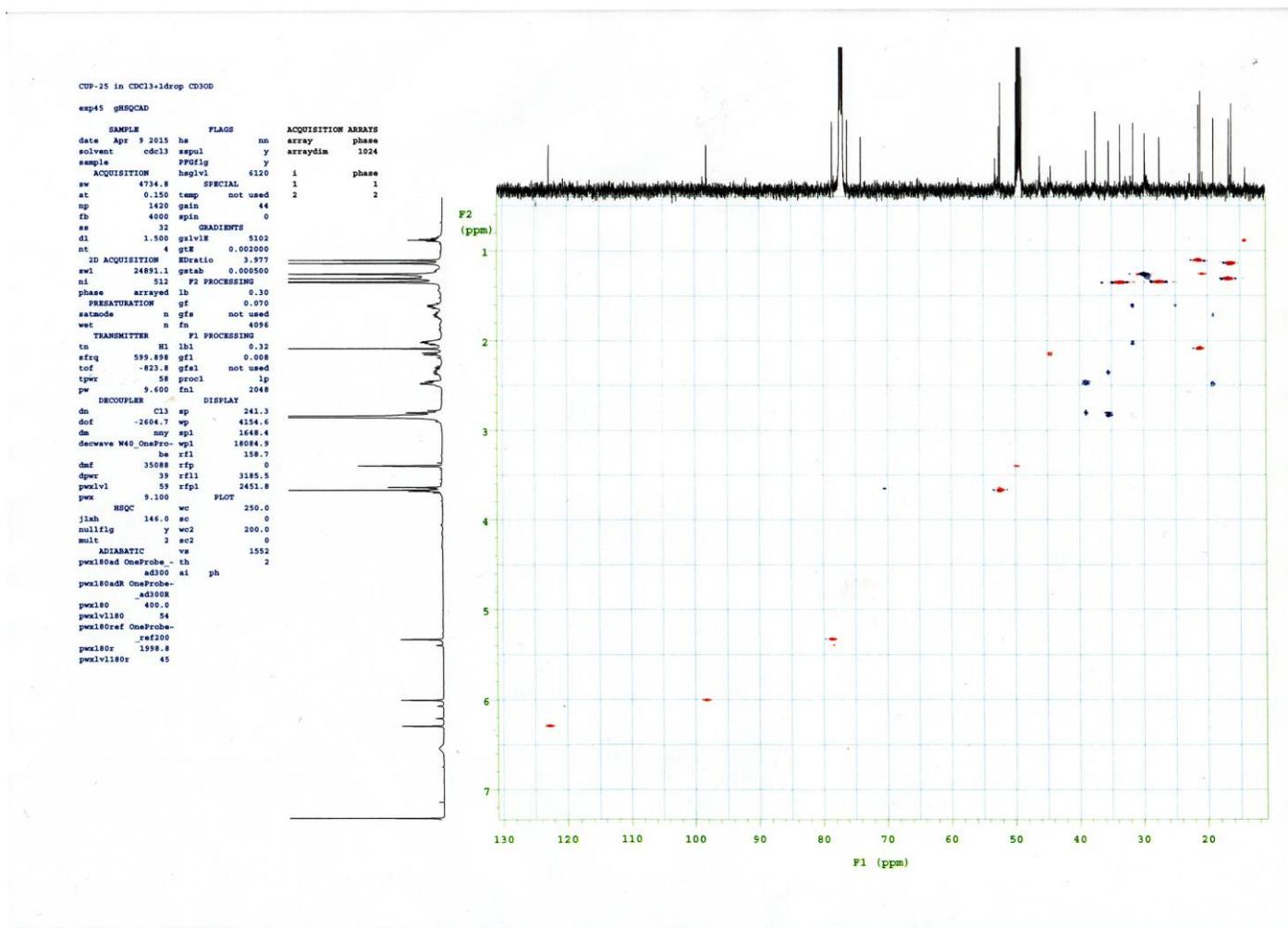


Fig. S16. HMBC spectrum of compound 3.

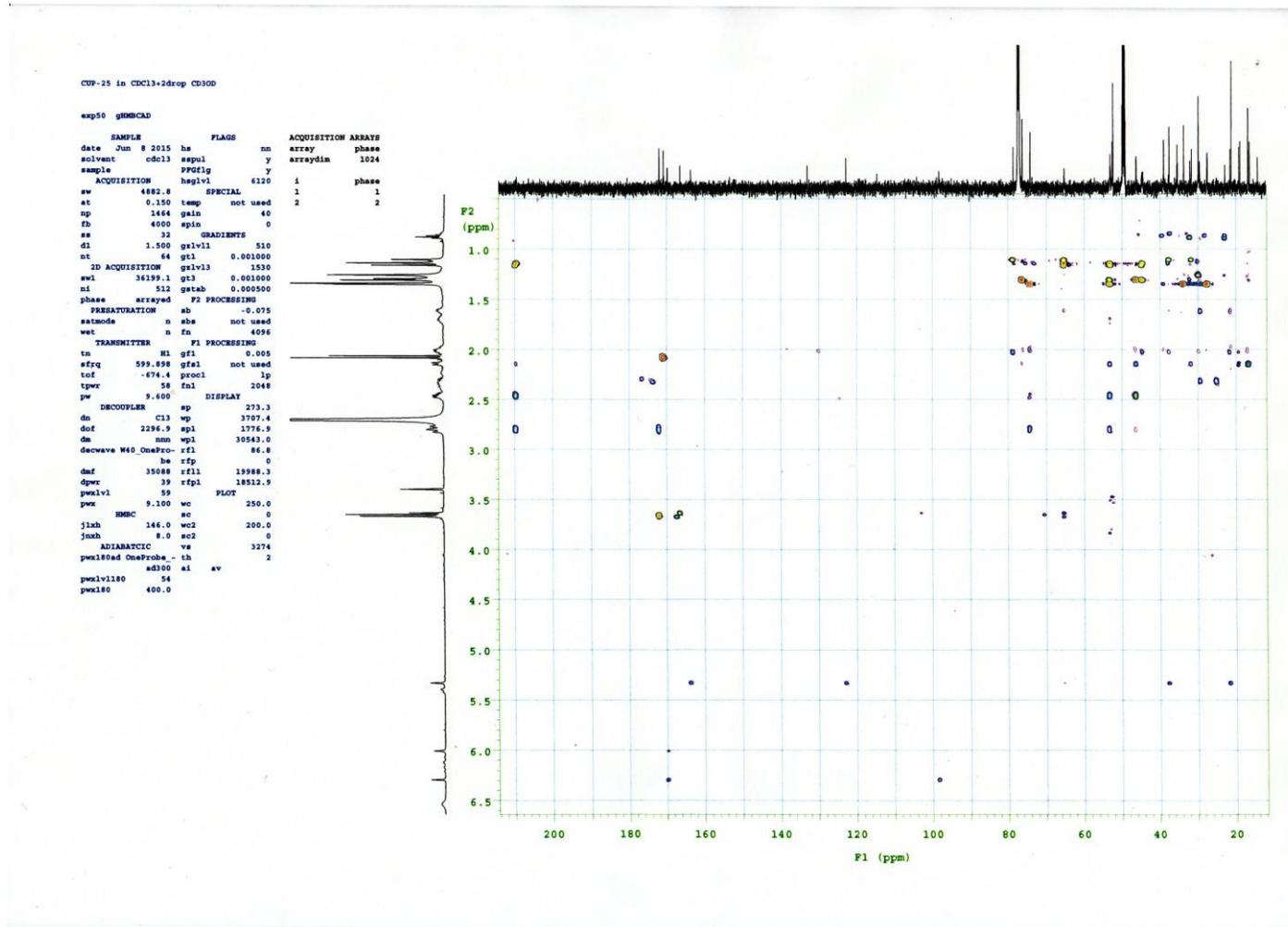


Fig. S17.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 3.

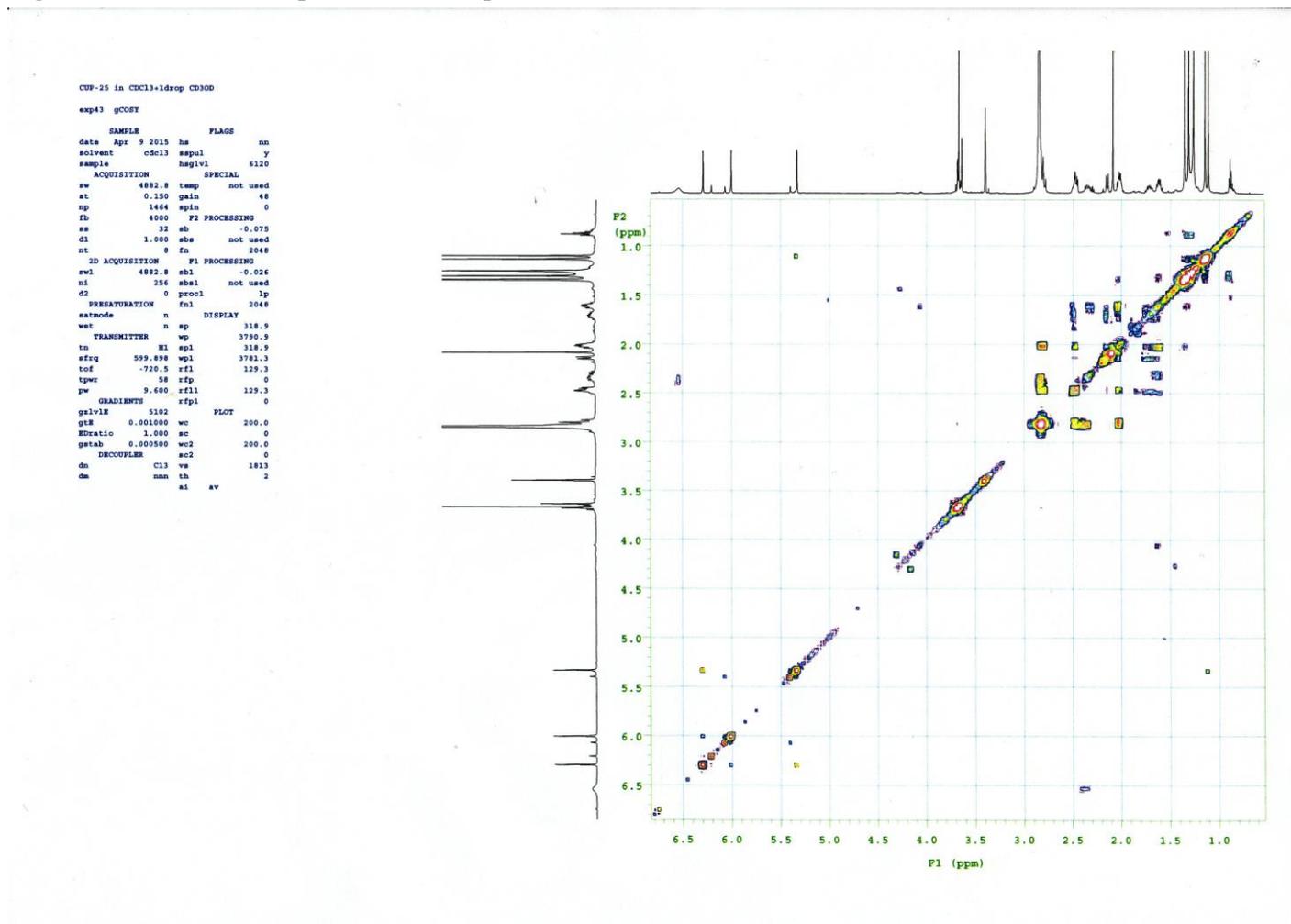


Fig. S18. NOESY spectrum of compound 3.

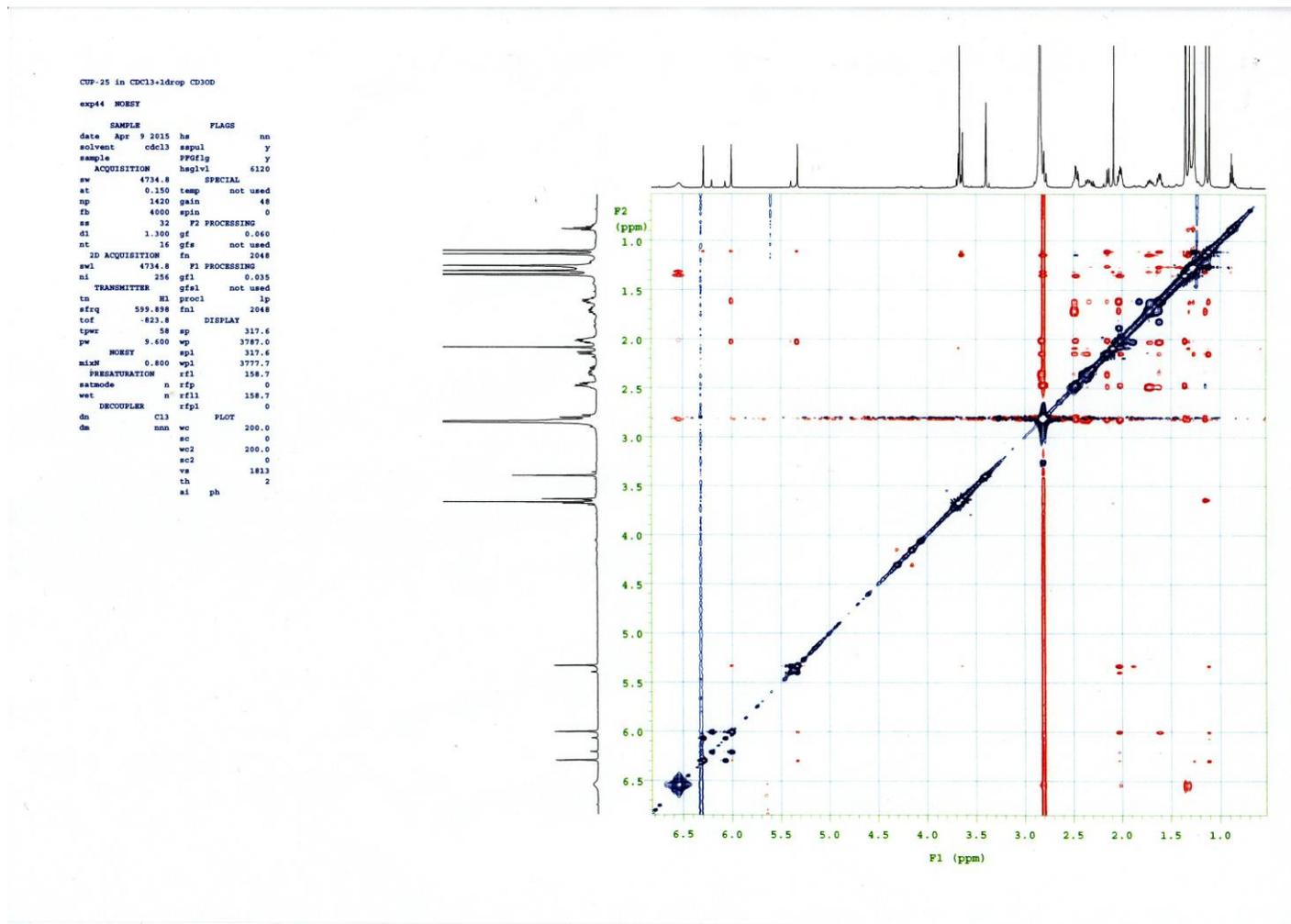


Fig. S19. <sup>1</sup>H-NMR spectrum of compound 4.

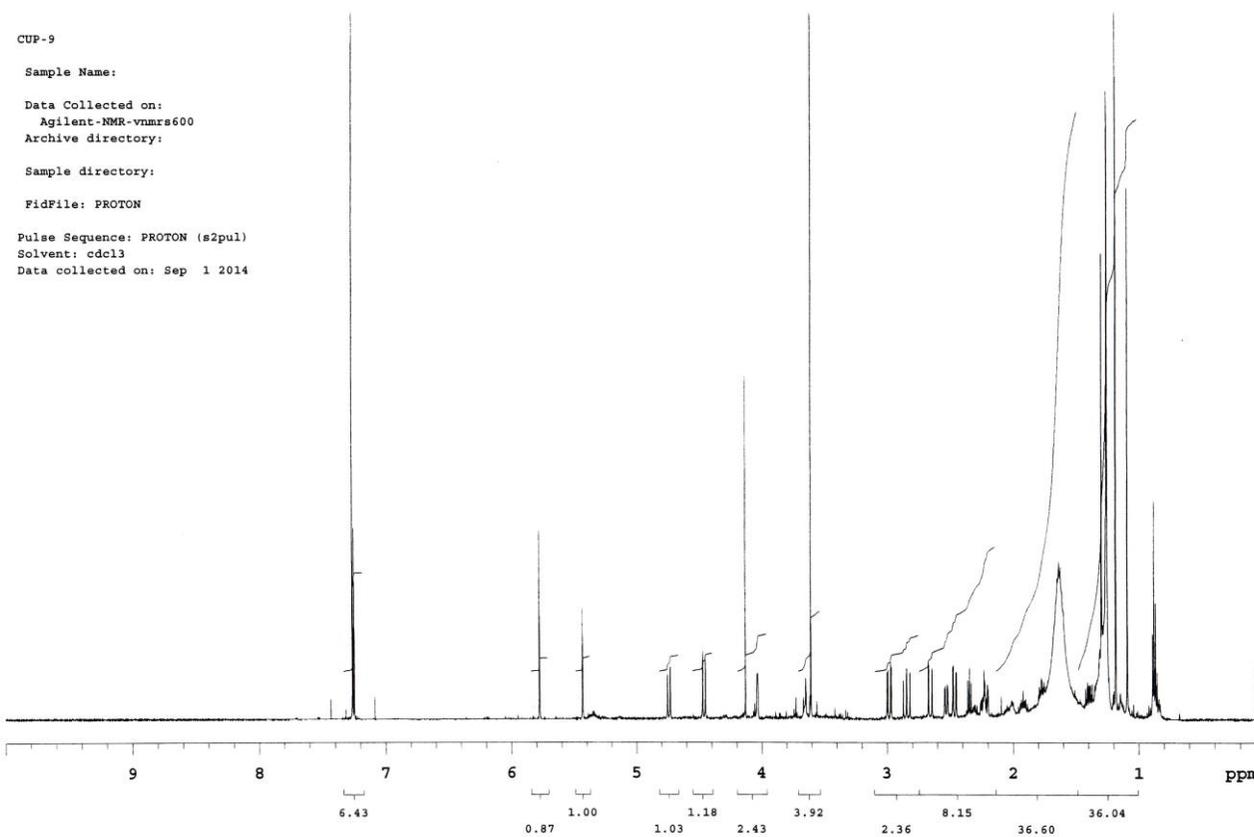


Fig. S20.  $^{13}\text{C}$ -NMR spectrum of compound **4**.

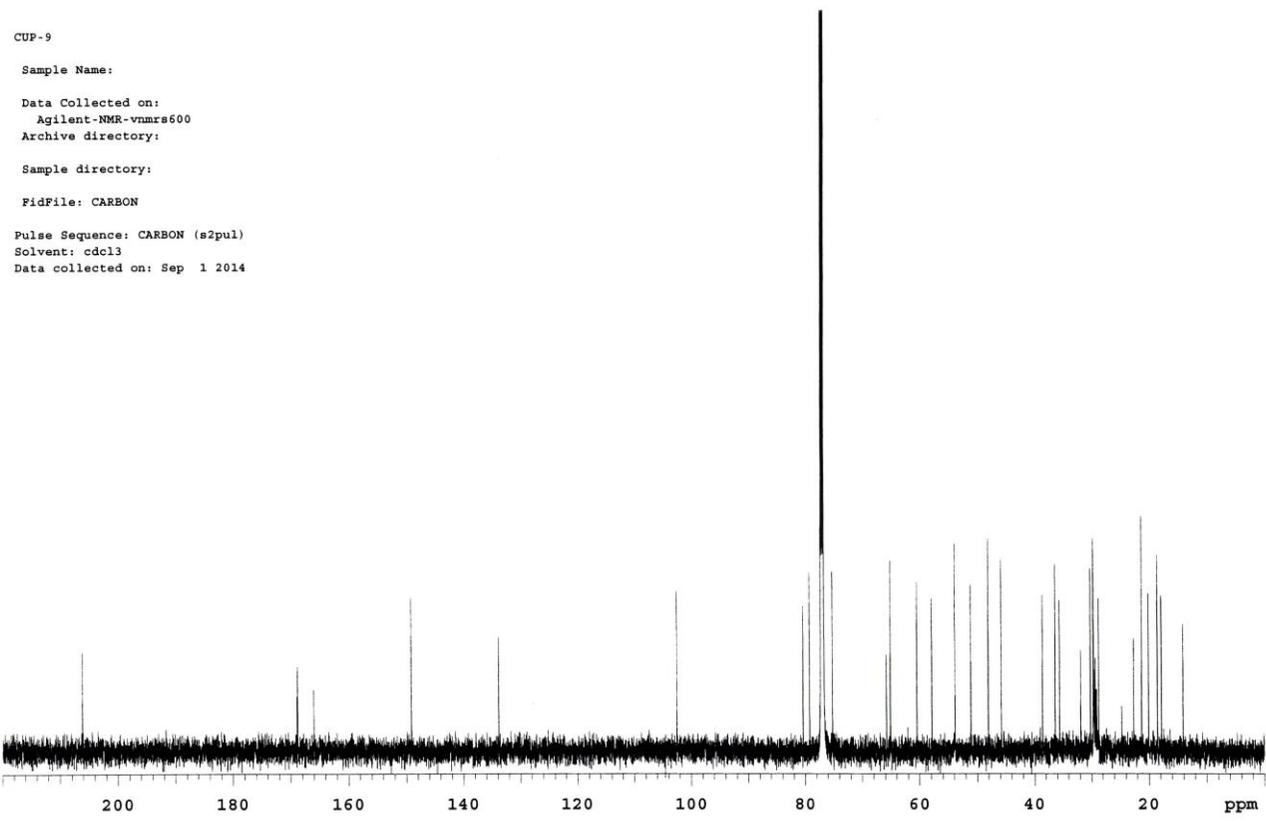


Fig. S21. HSQC spectrum of compound 4.

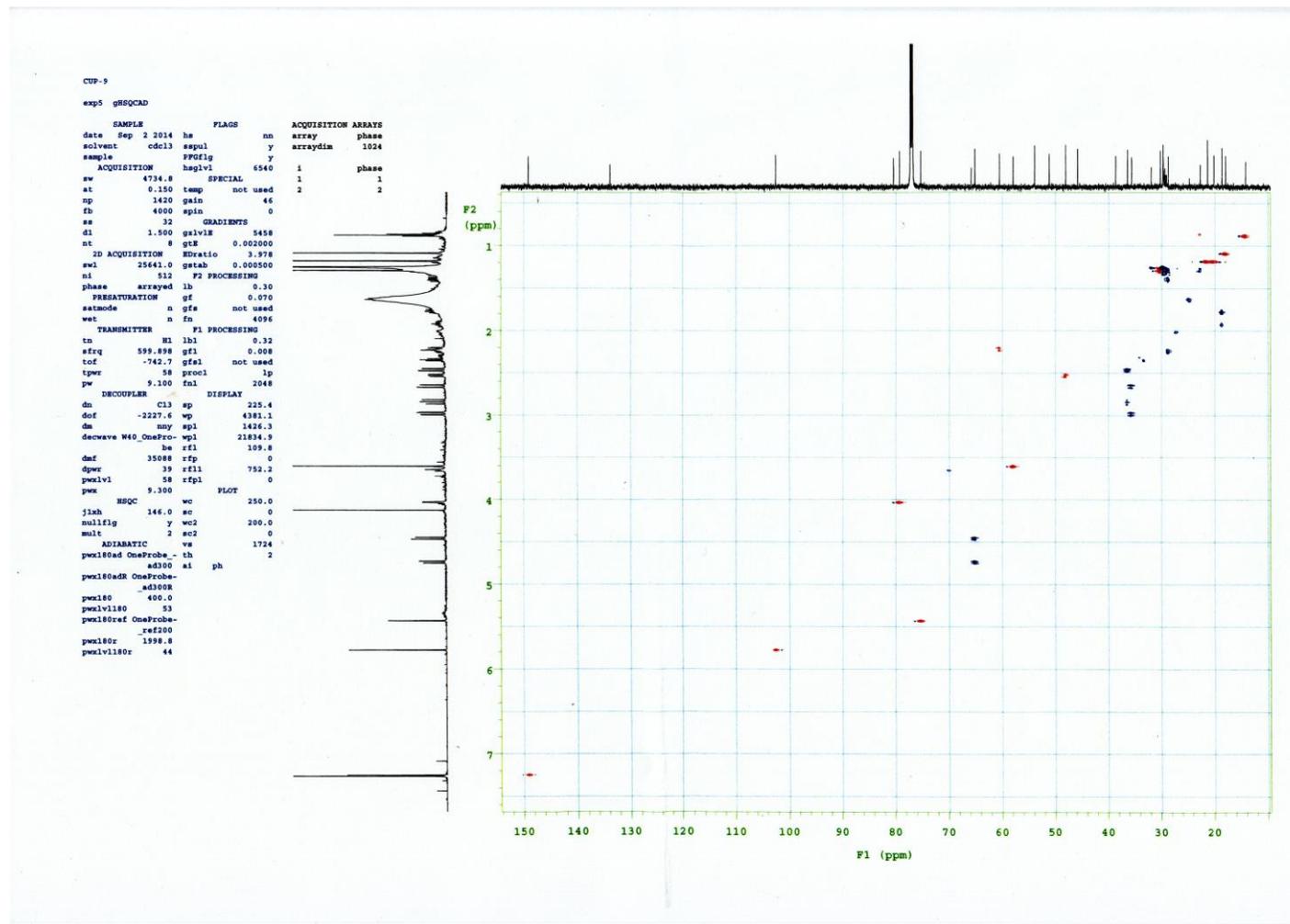


Fig. S22. HMBC spectrum of compound 4.

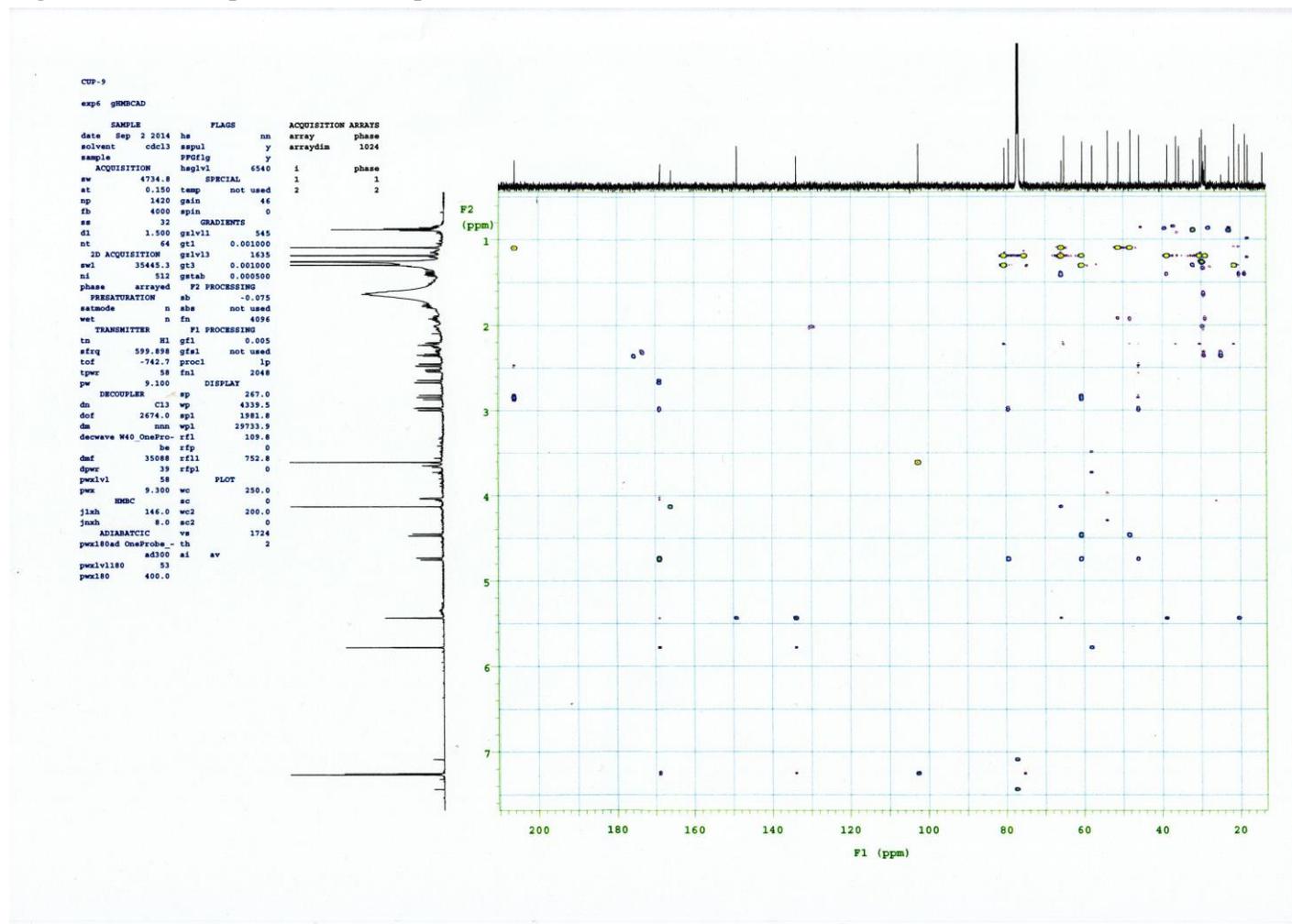


Fig. S23.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 4.

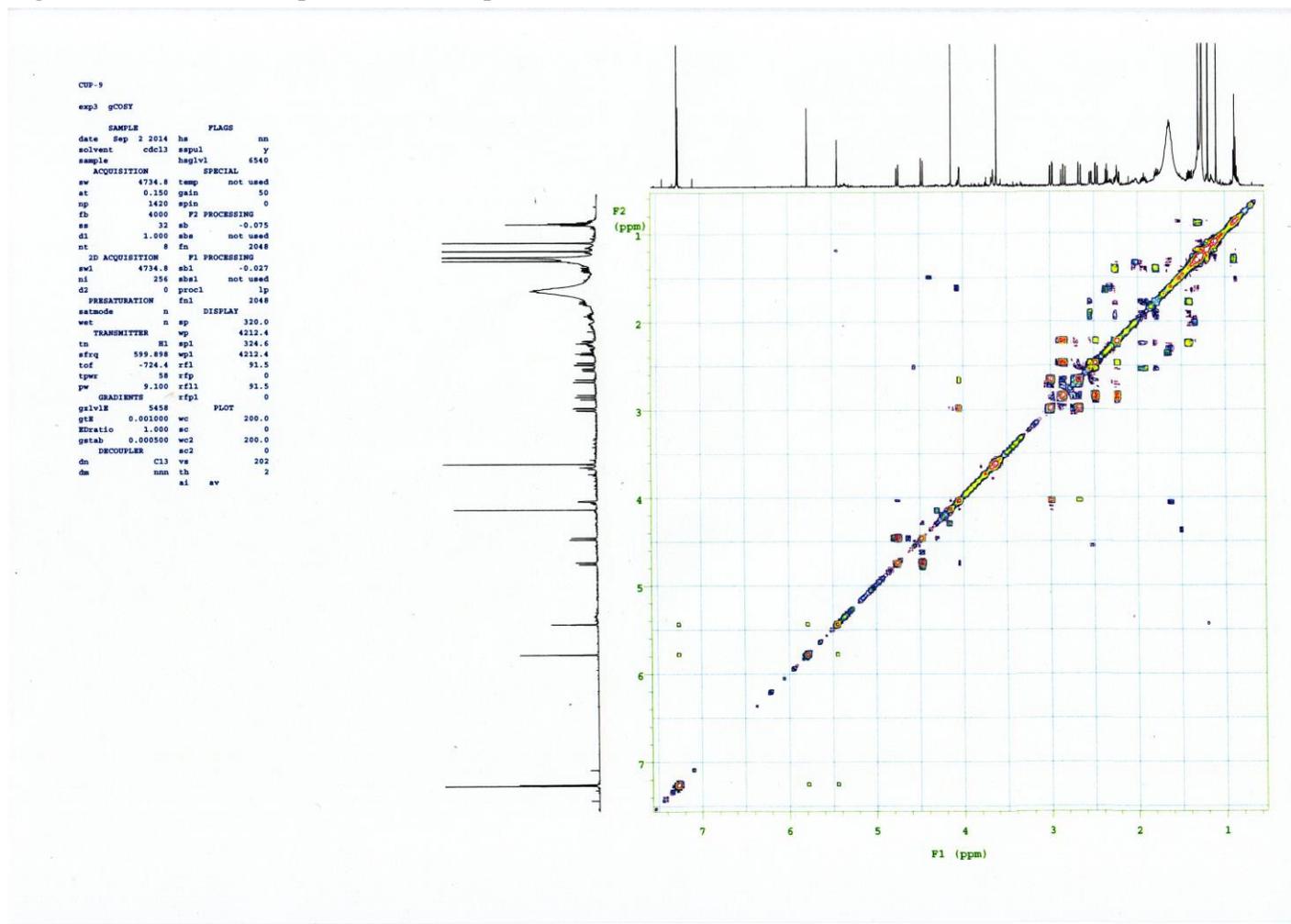


Fig. S24. NOESY spectrum of compound 4.

```
CUP-9
exp4 NOESY
SAMPLE          FLAGS
date Sep 2 2014 ha nn
solvent cdcl3 sspol y
sample FFGISig y
ACQUISITION    hsp1v1 6540
aw 4734.8 SPECIAL
at 0.150 temp not used
ap 1420 gain 50
fb 4000 spin 0
se 32 F2 PROCESSING
dl 1.300 gf 0.060
nt 16 gfs not used
2D ACQUISITION fn 2048
awl 4734.8 F1 PROCESSING
nl 256 gf1 0.040
TRANSMITTER    gf1 not used
to N1 ptocl lp
sfrq 599.898 fnl 2048
tof -742.7 DISPLAY
tpwr 58 sp 315.6
pw 9.100 wp 4212.4
NOESY          sp1 320.2
mixN 0.800 wp1 4212.4
PRESATURATION rfl 109.8
satmode n rfp 0
wet n rfl1 109.8
DECOUPLER      rfp1 0
dn C13 PLOT
dm nmn wc 200.0
sc 0
wc2 200.0
sc2 0
ve 202
th 2
al ph
```

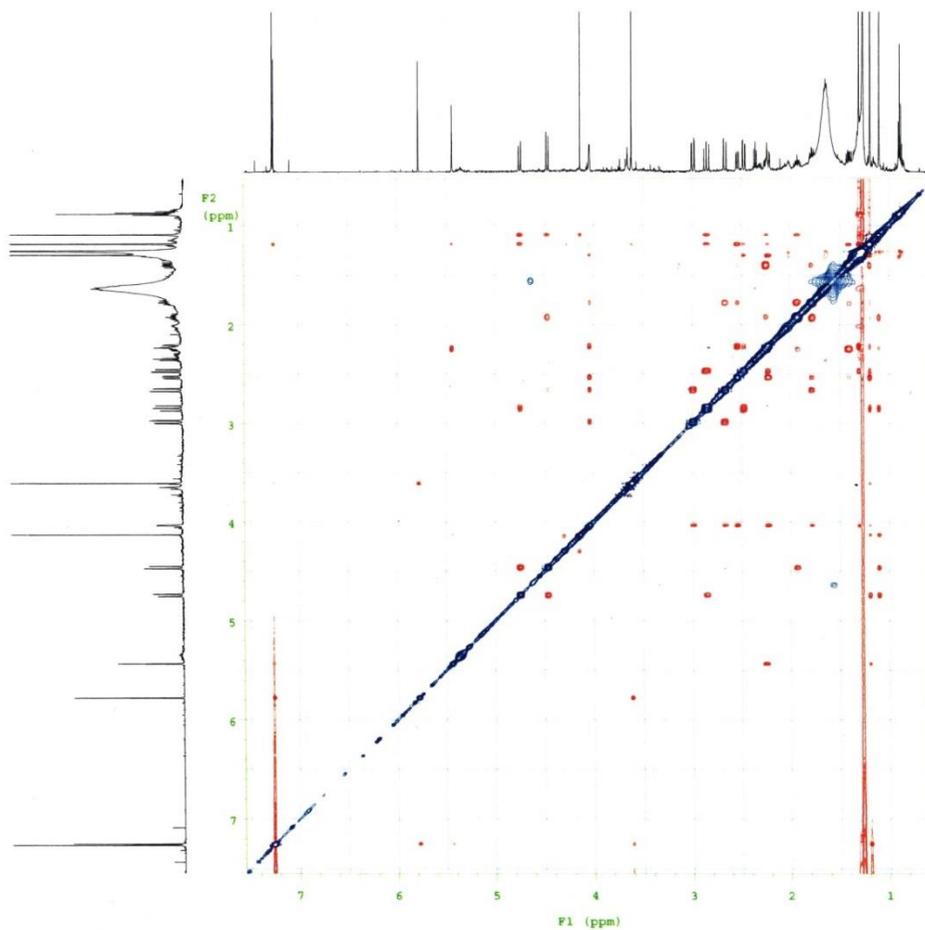


Fig. S25. <sup>1</sup>H-NMR spectrum of compound 5.

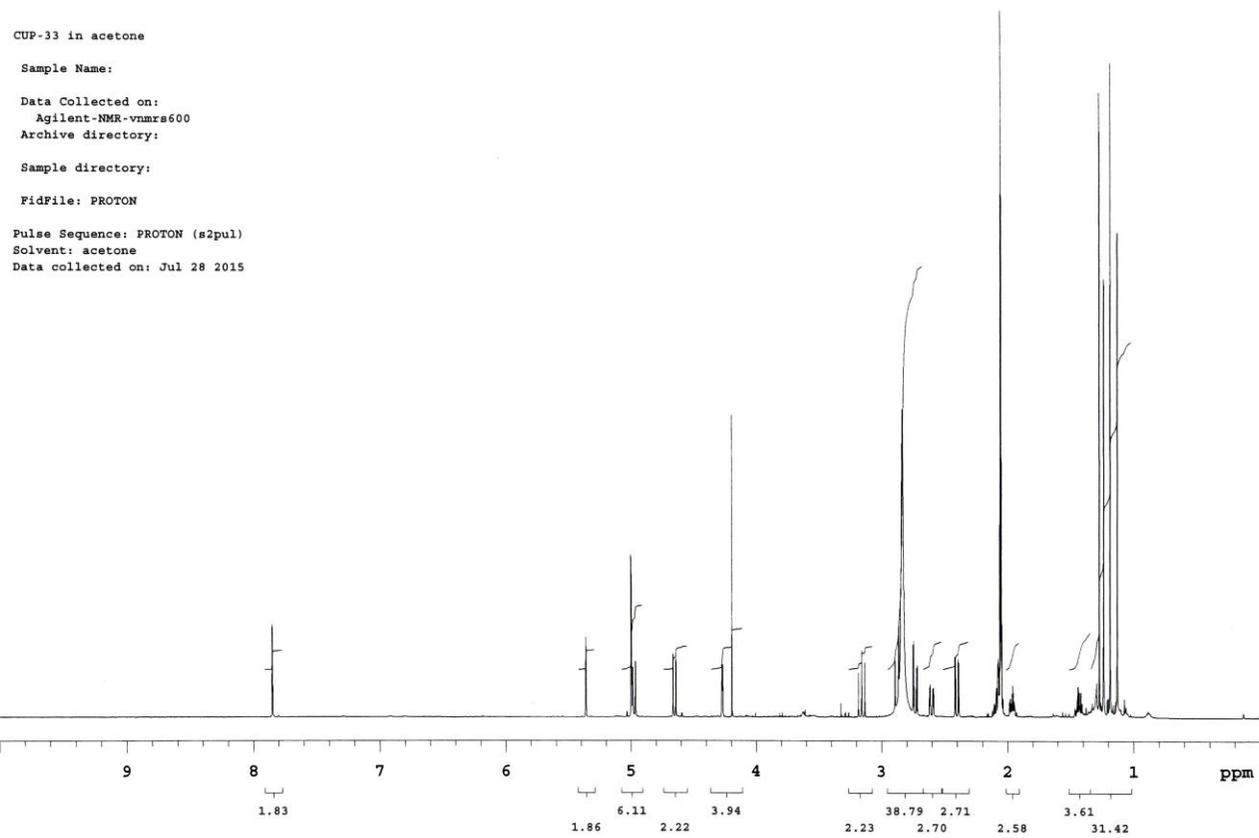


Fig. S26.  $^{13}\text{C}$ -NMR spectrum of compound 5.

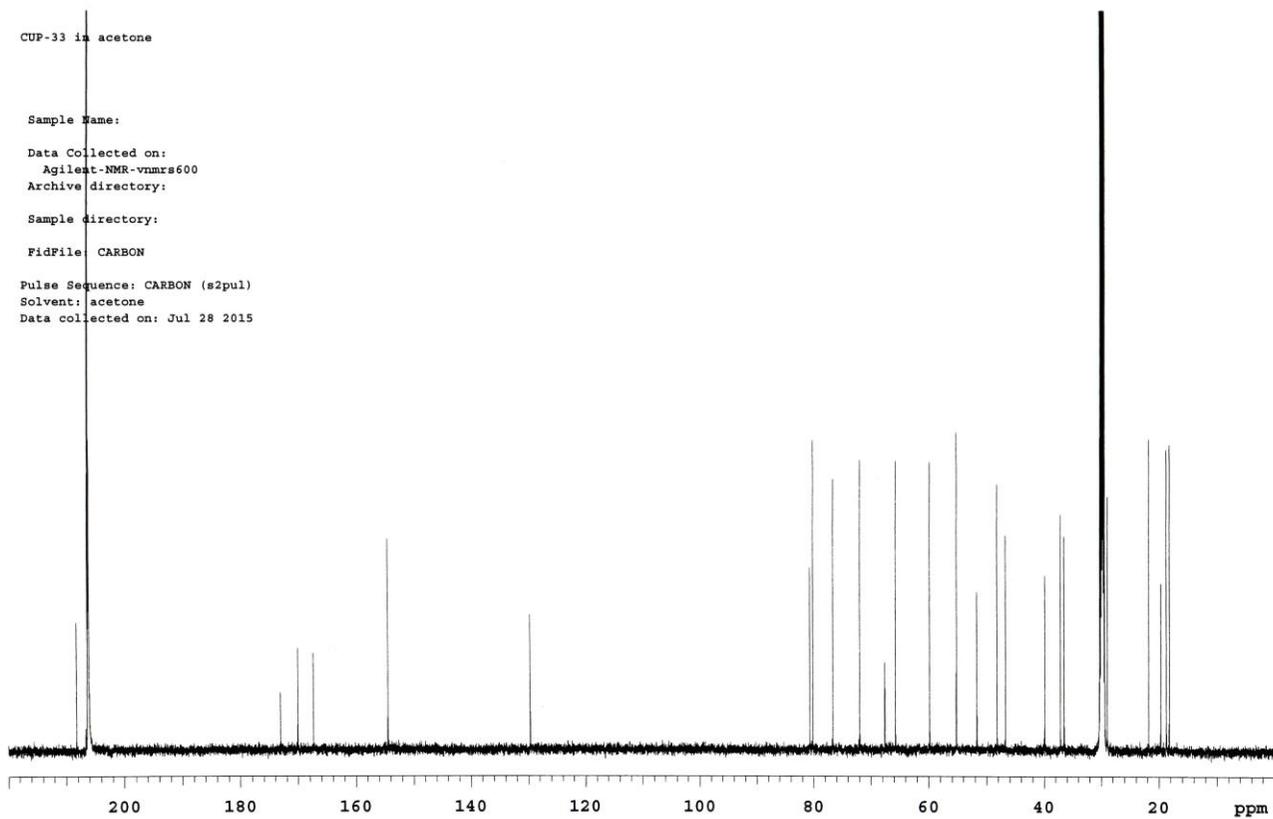




Fig. S28. HMBC spectrum of compound 4.

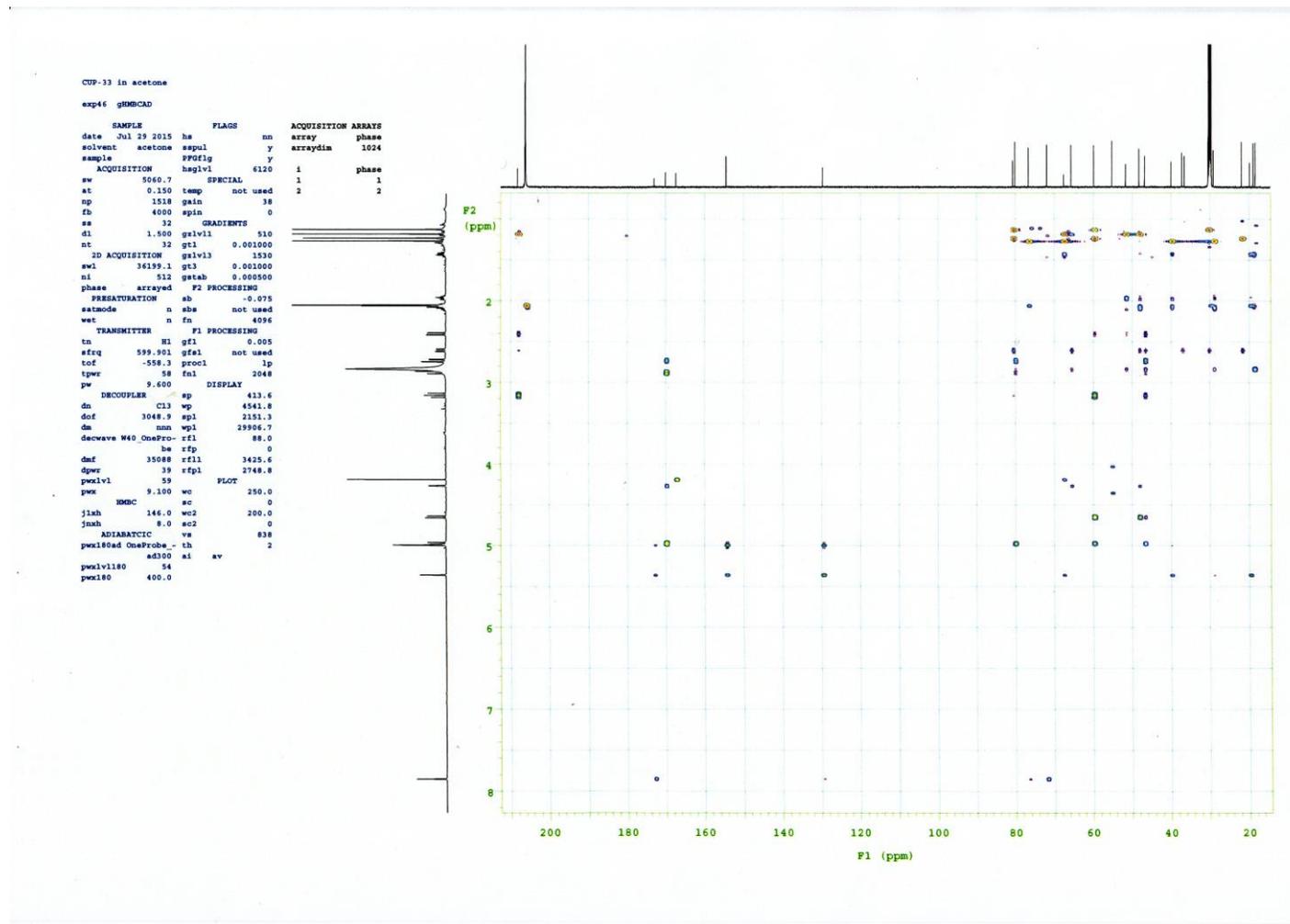


Fig. S29.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 4.

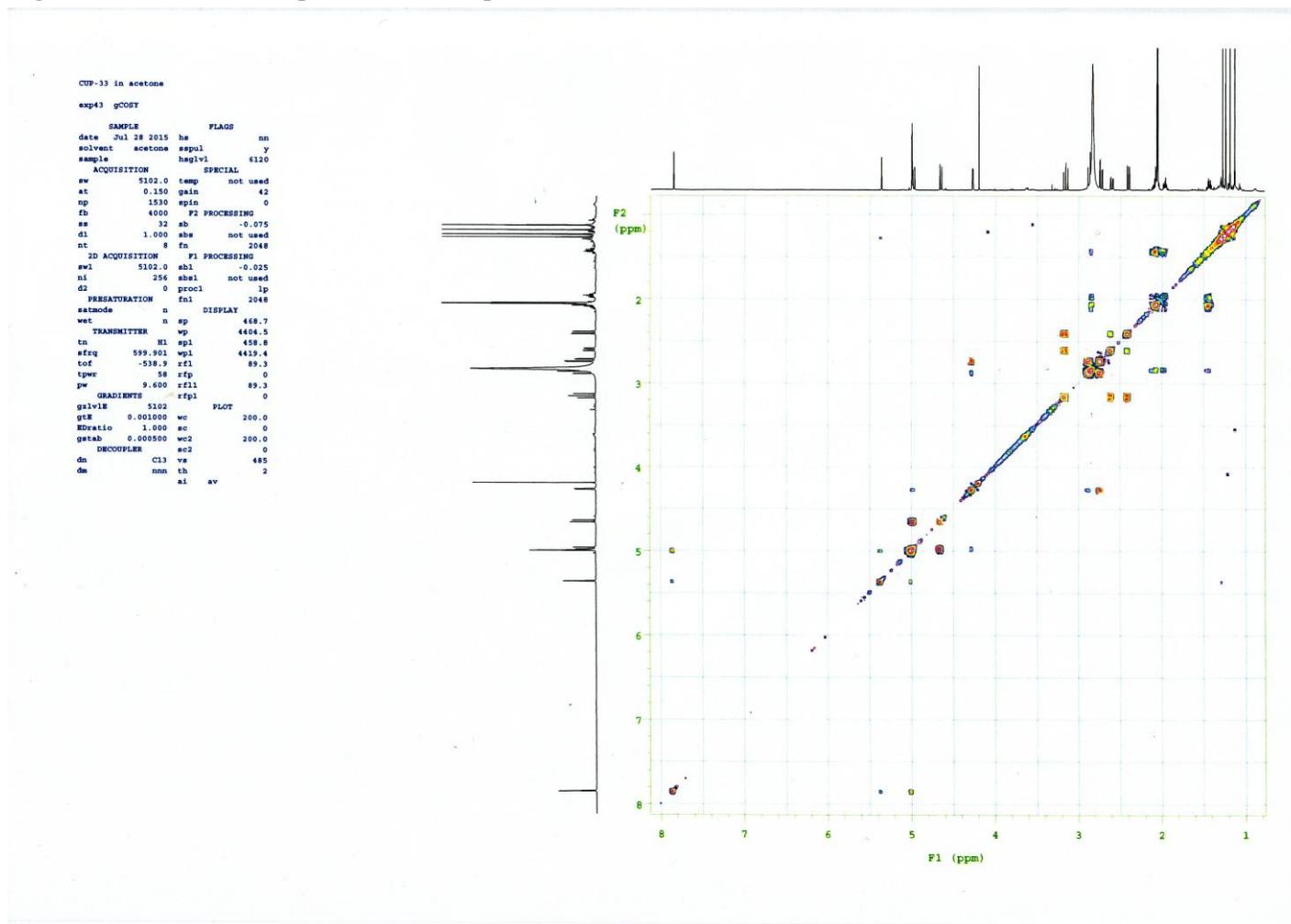


Fig. S30. NOESY spectrum of compound 5.

