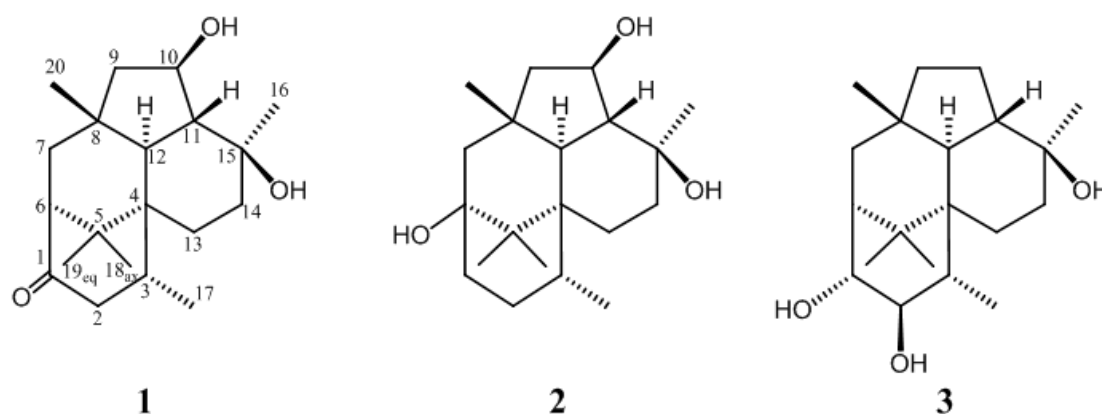


# Supplementary Materials: Trichodermanins C–E, New Diterpenes with a Fused 6-5-6-6 Ring System Produced by a Marine Sponge-Derived Fungus

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Scheme 1. Structures of metabolites in the fungal strain.

Table S1. Spectral data including 2D NMR data for 1.

Position	$\delta_{\text{H}}^{\text{a}}$	$J/\text{Hz}$	$^1\text{H}-^1\text{H}$ COSY	NOESY <sup>b</sup>	$\delta_{\text{C}}$	HMBC (C) <sup>c</sup>
1	-	-	-	-	217.7	1
2 $\alpha$	2.27	dd	20.4 (2 $\beta$ ), 7.2 (3)	17, 19	48.7	2 $\alpha$ 2.27
2 $\beta$	2.91	dd	20.4 (2 $\alpha$ ), 9.0 (3)	20		2 $\beta$ 2.91
3	2.44	dqd	9.0 (2 $\beta$ ), 7.2 (2 $\alpha$ ), 7.2 (17)	11, 14 $\beta$ , 20	26.1	3 2.44
4	-	-	-	-	39.5	4
5	-	-	-	-	38.2	5
6	2.03	dd	3.6 (7 $\alpha$ ), 3.6 (7 $\beta$ )	18, 19	58.0	6 2.03
7 $\alpha$	1.76	dd	13.8 (7 $\beta$ ), 3.6 (6)	9, 12, 18	41.4	7 $\alpha$ 1.76
7 $\beta$	1.92	dd	13.8 (7 $\alpha$ ), 3.6 (6)	9, 20	-	7 $\beta$ 1.92
8	-	-	-	-	39.0	8
9	1.50	m	-	7 $\alpha$ , 7 $\beta$ , 20	53.9	9 1.50
10	4.41	ddd	7.8 (9), 4.8 (11), 1.2 (9)	12, 16	72.6	10 4.41
11	1.95	dd	12.6 (12), 4.8 (10)	3, 20	54.7	11 1.95
12	1.46	d	12.6 (11)	7 $\alpha$ , 10, 16, 18	51.0	12 1.46
13 $\alpha$	1.25	ddd	14.0 (13 $\beta$ ), 14.0 (14 $\beta$ ), 3.0 (14 $\alpha$ )	18	25.9	13 $\alpha$ 1.25
13 $\beta$	1.80	ddd	14.0 (13 $\alpha$ ), 3.0 (14 $\beta$ ), 3.0 (14 $\alpha$ )	17, 19	-	13 $\beta$ 1.80
14 $\alpha$	1.66	ddd	14.0 (12 $\beta$ ), 3.0 (13 $\alpha$ ), 3.0 (13 $\beta$ )	-	40.2	14 $\alpha$ 1.66
14 $\beta$	1.55	ddd	14.0 (12 $\alpha$ ), 14.0 (13 $\alpha$ ), 3.0 (13 $\beta$ )	3, 17	-	14 $\beta$ 1.55
15	-	-	-	-	72.9	15
16	1.26	s	-	10, 12	21.6	16 1.26
17	1.17	d	7.2 (3)	2a, 13b, 14b, 19	21.3	(q) 2, 3, 4
18ax	1.01	s	-	6, 7a, 12, 13a	24.2	(q) 4, 5, 6, 19
19eq	1.03	s	-	2a, 6, 13b, 17	25.1	(q) 4, 5, 6, 18
20	1.05	s	-	2b, 3, 7b, 9, 11	22.0	(q) 7, 8, 9, 12

<sup>a</sup>  $^1\text{H}$  chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants ( $J/\text{Hz}$ ). Figures in parentheses indicate the proton coupling with that position. <sup>b</sup> The correlations with geminal and vicinal protons are removed. <sup>c</sup> Long range  $^1\text{H}-^{13}\text{C}$  correlations from H to C observed in the HMBC experiment.

**Table S2.** Spectral data including 2D NMR data for **2**.

Position	$\delta_{\text{H}}^{\text{a}}$		$J/\text{Hz}$	$^1\text{H}-^1\text{H}$ COSY	NOESY <sup>b</sup>	$\delta_{\text{C}}$		HMBC (C) <sup>c</sup>
1 $\alpha$	1.90	ddd	14.4 (1 $\beta$ ), 2.4 (2 $\alpha$ ), 2.4 (2 $\beta$ )	1 $\beta$ , 2 $\alpha$ , 2 $\beta$	19	35.5	(t)	2, 6, 7
1 $\beta$	1.98	ddd	14.4 (2 $\beta$ ), 10.8 (2 $\alpha$ ), 6.0 (2 $\beta$ )	1 $\alpha$ , 2 $\alpha$ , 2 $\beta$	3, 20	-	-	2, 5, 6, 7
2 $\alpha$	1.64	m	-	1 $\alpha$ , 1 $\beta$ , 2 $\beta$ , 3	17, 19	29.5	(t)	1, 3, 17
2 $\beta$	2.12	m	-	1 $\alpha$ , 1 $\beta$ , 2 $\alpha$ , 3	-	-	-	-
3	2.14	m	-	2 $\alpha$ , 2 $\beta$	1 $\beta$ , 11, 20	26.0	(d)	2, 5, 12, 17
4	-	-	-	-	-	41.0	(s)	-
5	-	-	-	-	-	44.1	(s)	-
6	-	-	-	-	-	74.9	(s)	-
7 $\alpha$	1.56	m	-	7 $\beta$	-	51.2	(t)	1, 6, 8, 9, 20
7 $\beta$	1.62	m	-	7 $\alpha$	20	-	-	1, 5, 6, 8, 12, 20
8	-	-	-	-	-	39.1	(s)	-
9	1.51	m	-	10	20	54.4	(t)	7, 8, 20
10	4.39	ddd	8.4 (9), 4.8 (11), 1.2 (9)	9, 11	12, 16	72.8	(d)	8, 15
11	1.88	dd	12.6 (12), 4.8 (10)	10, 12	3, 20	55.1	(d)	10, 12, 15, 16
12	1.25	d	12.6 (11)	11	10, 18	50.4	(d)	3, 4, 5, 8, 9, 10, 11, 13, 15, 20
13 $\alpha$	1.23	ddd	14.0 (13 $\beta$ ), 14.0 (14 $\beta$ ), 3.0 (14 $\alpha$ )	13 $\beta$ , 14 $\alpha$ , 14 $\beta$	18	26.4	(t)	14, 15
13 $\beta$	1.73	ddd	14.0 (13 $\alpha$ ), 3.0 (14 $\beta$ ), 3.0 (14 $\alpha$ )	13 $\alpha$ , 14 $\alpha$ , 14 $\beta$	17, 19	-	-	14
14 $\alpha$	1.66	m	-	13 $\alpha$ , 13 $\beta$ , 14 $\beta$	-	40.6	(t)	-
14 $\beta$	1.59	m	-	13 $\alpha$ , 13 $\beta$ , 14 $\alpha$	17	-	-	-
15	-	-	-	-	-	73.1	(s)	-
16	1.23	s	-	-	10	21.5	(q)	11, 14, 15
17	1.05	d	6.6 (3)	3	2 $\alpha$ , 13 $\beta$ , 14 $\beta$	22.9	(q)	2, 3, 4
18ax	0.93	s	-	-	12, 13 $\alpha$	18.3	(q)	4, 5, 6, 19
19eq	1.02	s	-	-	1 $\alpha$ , 2 $\alpha$ , 13 $\beta$	19.4	(q)	4, 5, 6, 18
20	1.29	s	-	-	1 $\beta$ , 3, 7 $\beta$ , 9, 11	20.9	(q)	7, 8, 9, 12

<sup>a</sup>  $^1\text{H}$  chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants ( $J/\text{Hz}$ ). Figures in parentheses indicate the proton coupling with that position. <sup>b</sup> The

correlations with geminal and vicinal protons are removed. <sup>c</sup> Long range <sup>1</sup>H-<sup>13</sup>C correlations from H to C observed in the HMBC experiment.

**Table S3.** Spectral data including 2D NMR data for **3**.

Position	$\delta_{\text{H}}^{\text{a}}$		$J/\text{Hz}$	<sup>1</sup> H- <sup>1</sup> H COSY	NOESY <sup>b</sup>	$\delta_{\text{C}}$		HMBC (C) <sup>c</sup>
1	4.11	d	5.4 (2)	2	7 $\beta$ , 20	80.4	(d)	2, 5, 6, 7
2	3.88	dd	7.8 (3), 5.4 (1)	1, 3	17, 19	83.7	(d)	1, 3, 17
3	1.88	qd	7.8 (17), 7.8 (3)	2 $\alpha$ , 2 $\beta$ , 17	11, 20	36.6	(d)	2, 4, 5, 12, 17
4	-	-	-	-	-	41.2	(s)	-
5	-	-	-	-	-	39.4	(s)	-
6	1.50	dd	4.8 (7 $\alpha$ ), 3.0 (7 $\beta$ )	7 $\alpha$ , 7 $\beta$	18, 19	53.2	(d)	4
7 $\alpha$	1.78	dd	13.8 (7 $\beta$ ), 4.8 (6)	6, 7 $\beta$	9 $\alpha$ , 12, 18	40.9	(t)	1, 6, 8, 9, 20
7 $\beta$	1.70	dd	13.8 (7 $\alpha$ ), 3.0 (6)	6, 7 $\alpha$	1, 20	-	-	5, 12
8	-	-	-	-	-	39.6	(s)	-
9 $\alpha$	1.03	m	-	9 $\beta$ , 10 $\alpha$ , 10 $\beta$	7 $\alpha$ , 12	43.5	(t)	-
9 $\beta$	1.43	m	-	9 $\alpha$ , 10 $\alpha$ , 10 $\beta$	20	-	-	20
10 $\alpha$	1.59	m	-	9 $\alpha$ , 9 $\beta$ , 10 $\beta$ , 11	16	21.6	(t)	8, 15
10 $\beta$	1.80	m	-	9 $\alpha$ , 9 $\beta$ , 10 $\alpha$ , 11	-	-	-	-
11	1.81	dd	13.2 (12), 4.2 (10)	10 $\alpha$ , 10 $\beta$ , 12	3, 14 $\beta$ , 20	44.2	(d)	10, 12, 15, 16
12	1.32	d	13.2 (11)	11	7 $\alpha$ , 9 $\alpha$ , 16, 18	51.8	(d)	3, 4, 5, 8, 11, 15, 20
13 $\alpha$	1.23	ddd	13.8 (13 $\beta$ ), 13.8 (14 $\beta$ ), 3.6 (14 $\alpha$ )	13 $\beta$ , 14 $\alpha$ , 14 $\beta$	18	26.3	(t)	-
13 $\beta$	1.72	ddd	13.8 (13 $\alpha$ ), 3.6 (14 $\beta$ ), 3.6 (14 $\alpha$ )	13 $\alpha$ , 14 $\alpha$ , 14 $\beta$	17, 19	-	-	5, 12
14 $\alpha$	1.64	ddd	13.8 (12 $\beta$ ), 3.6 (13 $\alpha$ ), 3.6 (13 $\beta$ )	13 $\alpha$ , 13 $\beta$ , 14 $\beta$	16	41.1	(t)	-
14 $\beta$	1.46	ddd	13.8 (12 $\alpha$ ), 13.8 (13 $\alpha$ ), 3.6 (13 $\beta$ )	13 $\alpha$ , 13 $\beta$ , 14 $\alpha$	11, 17	-	-	11
15	-	-	-	-	-	73.6	(s)	-
16	1.18	s	-	-	10 $\alpha$ , 12, 14 $\alpha$	20.5	(q)	11, 14, 15
17	1.23	d	7.2 (3)	3	2, 13 $\beta$ , 14 $\beta$ , 19	20.0	(q)	2, 3, 4
18 $\alpha$	0.99	s	-	-	6, 7 $\alpha$ , 12, 13 $\alpha$	25.7	(q)	4, 5, 6, 19
19 $\text{eq}$	1.04	s	-	-	2, 6, 13 $\beta$ , 17	25.2	(q)	4, 5, 6, 18
20	0.98	s	-	-	1, 3, 7 $\beta$ , 9 $\beta$ , 11	19.8	(q)	7, 8, 9, 12

<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 ( $J/\text{Hz}$ ). Figures in parentheses indicate the proton coupling with that position. <sup>b</sup> The correlations with geminal and vicinal protons are removed. <sup>c</sup> Long range <sup>1</sup>H-<sup>13</sup>C correlations from H to C observed in the HMBC experiment.



**Table S4.** <sup>1</sup>H NMR spectral data of MTPA esters **1a** and **1b** in CDCl<sub>3</sub>.

Position	$\delta_{\text{H}^a}$		$J/\text{Hz}$	$\delta_{\text{H}^a}$		$J/\text{Hz}$
			<b>1a</b>			<b>1b</b>
1	-	-	-	-	-	-
2 $\alpha$	2.26	dd	19.8 (2 $\beta$ ), 7.2 (3)	2.26	dd	20.4 (2 $\beta$ ), 7.8 (3)
2 $\beta$	2.87	dd	19.8 (2 $\alpha$ ), 7.8 (3)	2.87	dd	20.4 (2 $\alpha$ ), 9.0 (3)
3	2.30	m	-	2.32	m	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	2.04	dd	4.2 (7 $\alpha$ ), 3.0 (7 $\beta$ )	2.03	dd	4.8 (7 $\alpha$ ), 3.6 (7 $\beta$ )
7 $\alpha$	1.78	m	-	1.76	dd	13.8 (7 $\beta$ ), 4.8 (6)
7 $\beta$	1.96	dd	13.8 (7 $\alpha$ ), 3.0 (6)	1.92	dd	13.8 (7 $\alpha$ ), 3.6 (6)
8	-	-	-	-	-	-
9	1.60	m	-	1.55	m	-
10	5.41	dd	7.8 (9), 4.8 (11)	5.41	dd	7.2 (9), 4.8 (11)
11	2.00	dd	14.4 (12), 4.8 (10)	2.09	dd	14.4 (12), 4.8 (10)
12	1.53	d	14.4 (11)	1.51	d	14.4 (11)
13 $\alpha$	1.27	ddd	14.4 (13 $\beta$ ), 14.4 (14 $\beta$ ), 3.6 (14 $\alpha$ )	1.28	ddd	14.4 (13 $\beta$ ), 14.4 (14 $\beta$ ), 3.6 (14 $\alpha$ )
13 $\beta$	1.8	ddd	14.4 (13 $\alpha$ ), 3.6 (14 $\beta$ ), 3.6 (14 $\alpha$ )	1.81	ddd	14.4 (13 $\alpha$ ), 3.6 (14 $\beta$ ), 3.6 (14 $\alpha$ )
14 $\alpha$	1.69	ddd	13.2 (14 $\beta$ ), 3.6 (13 $\alpha$ ), 3.6 (13 $\beta$ )	1.70	ddd	13.2 (14 $\beta$ ), 3.6 (13 $\alpha$ ), 3.6 (13 $\beta$ )
14 $\beta$	1.52	m	-	1.54	m	-
15	-	-	-	-	-	-
16	1.34	s	-	1.34	s	-
17	1.16	d	7.2 (3)	1.16	d	7.2 (3)
18ax	1.02	s	-	1.02	s	-
19eq	1.05	s	-	1.04	s	-
20	0.87	s	-	0.79	s	-
OCH <sub>3</sub>	3.54	s	-	3.57	s	-
Ar.H	7.38-7.43	m	-	7.38-7.43	m	-
Ar.H	7.49-7.57	m	-	7.52-7.61	m	-

<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 ( $J/\text{Hz}$ ). Figures in parentheses indicate the proton coupling with that position.

**Table S5.** <sup>1</sup>H NMR spectral data of MTPA esters **2a** and **2b** in CDCl<sub>3</sub>.

Position	$\delta_{\text{H}}^{\text{a}}$		<i>J</i> /Hz	$\delta_{\text{H}}^{\text{a}}$		<i>J</i> /Hz
			<b>2a</b>			<b>2b</b>
1 $\alpha$	1.89	m	-	1.89	m	-
1 $\beta$	1.97	m	-	1.97	m	-
2 $\alpha$	1.64	m	-	1.64	m	-
2 $\beta$	2.10	m	-	2.10	m	-
3	2.01	m	-	2.02	m	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7 $\alpha$	1.60	m	-	1.57	m	-
7 $\beta$	1.74	d	13.8 (7 $\alpha$ )	1.64	m	-
8	-	-	-	-	-	-
9	1.60	m	-	1.55	m	-
10	5.41	dd	8.4 (9), 4.8 (11)	5.41	dd	8.4 (9), 4.8 (11)
11	1.96	dd	14.4 (12), 4.8 (10)	2.04	dd	14.4 (12), 4.8 (10)
12	1.33	d	14.4 (11)	1.31	d	14.4 (11)
13 $\alpha$		ddd	14.4 (13 $\beta$ ), 14.4 (14 $\beta$ ), 3.6 (14 $\alpha$ )	1.26	ddd	14.4 (13 $\beta$ ), 14.4 (14 $\beta$ ), 3.6 (14 $\alpha$ )
	1.25					
13 $\beta$		ddd	14.4 (13 $\alpha$ ), 3.6 (14 $\alpha$ ), 3.6 (14 $\beta$ )	1.74	ddd	14.4 (13 $\alpha$ ), 3.6 (14 $\alpha$ ), 3.6 (14 $\beta$ )
	1.73					
14 $\alpha$		ddd	14.4 (14 $\beta$ ), 3.6 (13 $\alpha$ ), 3.6 (13 $\beta$ )	1.61	m	-
	1.60					
14 $\beta$		ddd	14.4 (13 $\alpha$ ), 14.4 (14 $\alpha$ ), 3.6 (13 $\beta$ )	1.50	ddd	14.4 (13 $\alpha$ ), 14.4 (14 $\alpha$ ), 3.6 (13 $\beta$ )
	1.48					
15	-	-	-	-	-	-
16	1.31	s	-	1.31	s	-
17	1.04	d	7.2 (3)	1.04	d	7.2 (3)
18ax	0.95	s	-	0.94	s	-
19eq	1.03	s	-	1.02	-	-
20	1.14	s	-	1.06	-	-
OCH <sub>3</sub>	3.56	s	-	3.56	s	-
Ar.H	7.26-7.42	m	-	7.26-7.41	m	-
Ar.H	7.52	m	-	7.55	m	-

<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). Figures in parentheses indicate the proton coupling with that position.

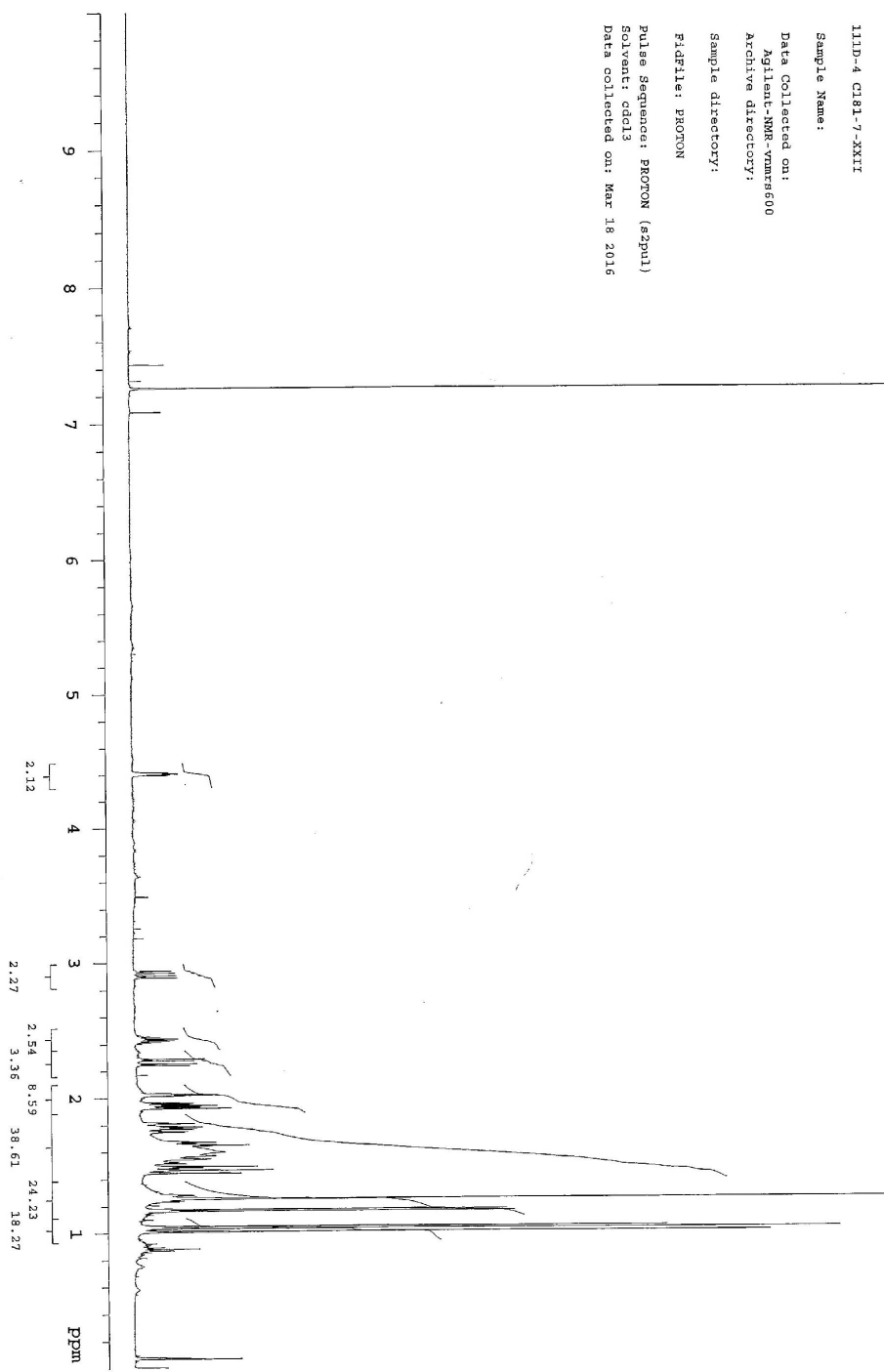


Figure S1. <sup>1</sup>H NMR spectrum of 1.

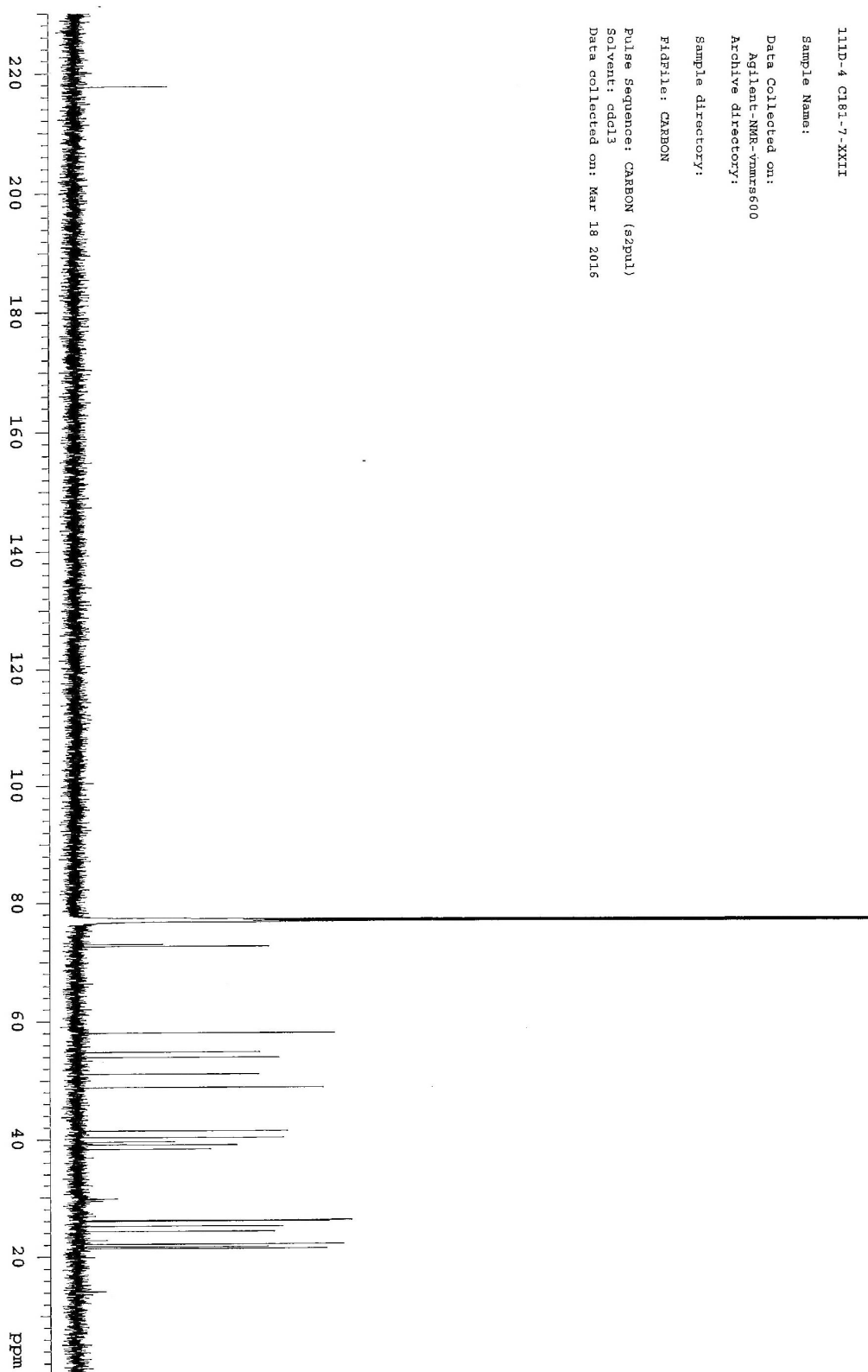


Figure S2. <sup>13</sup>C NMR spectrum of **1** in CDCl<sub>3</sub>.

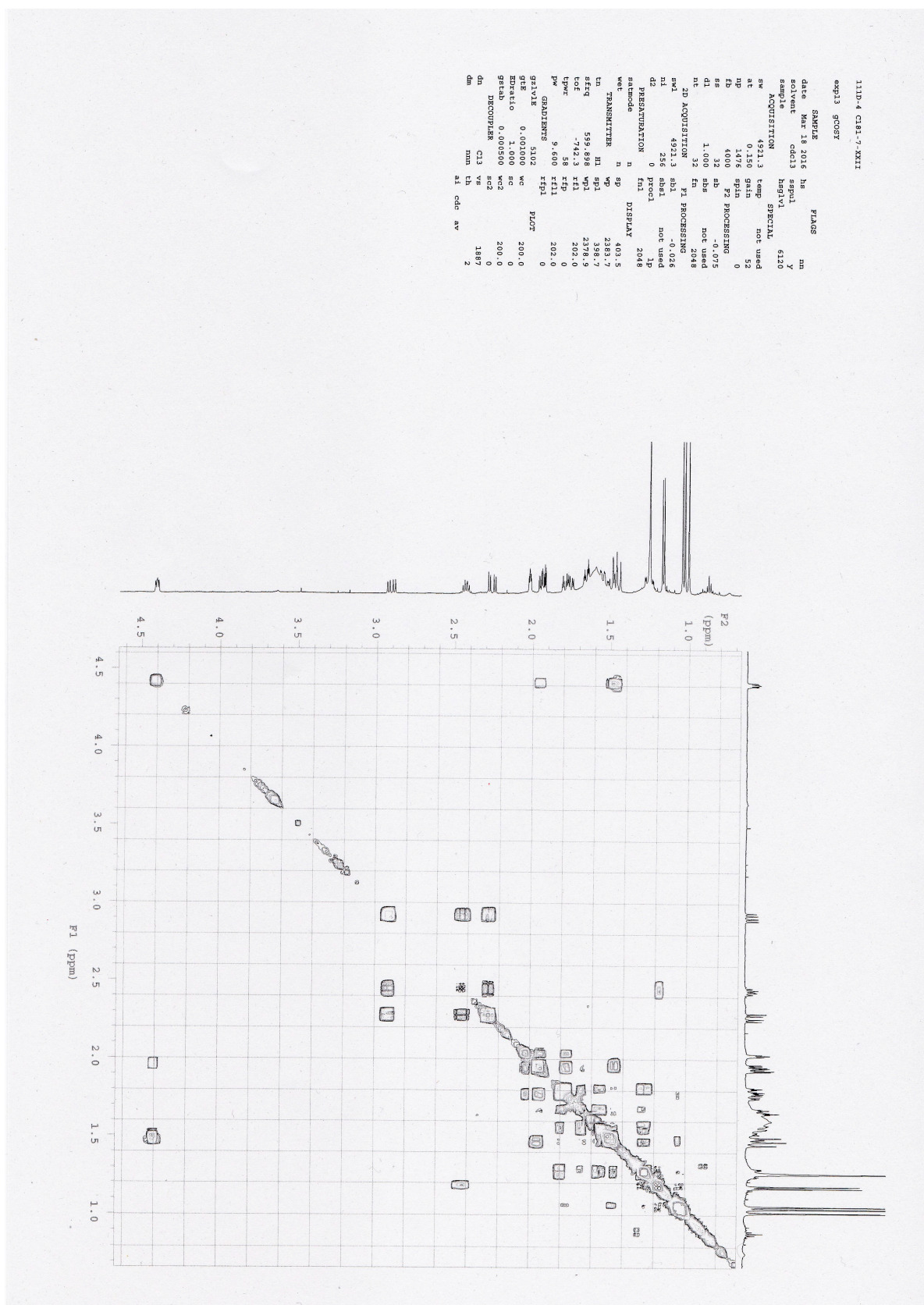
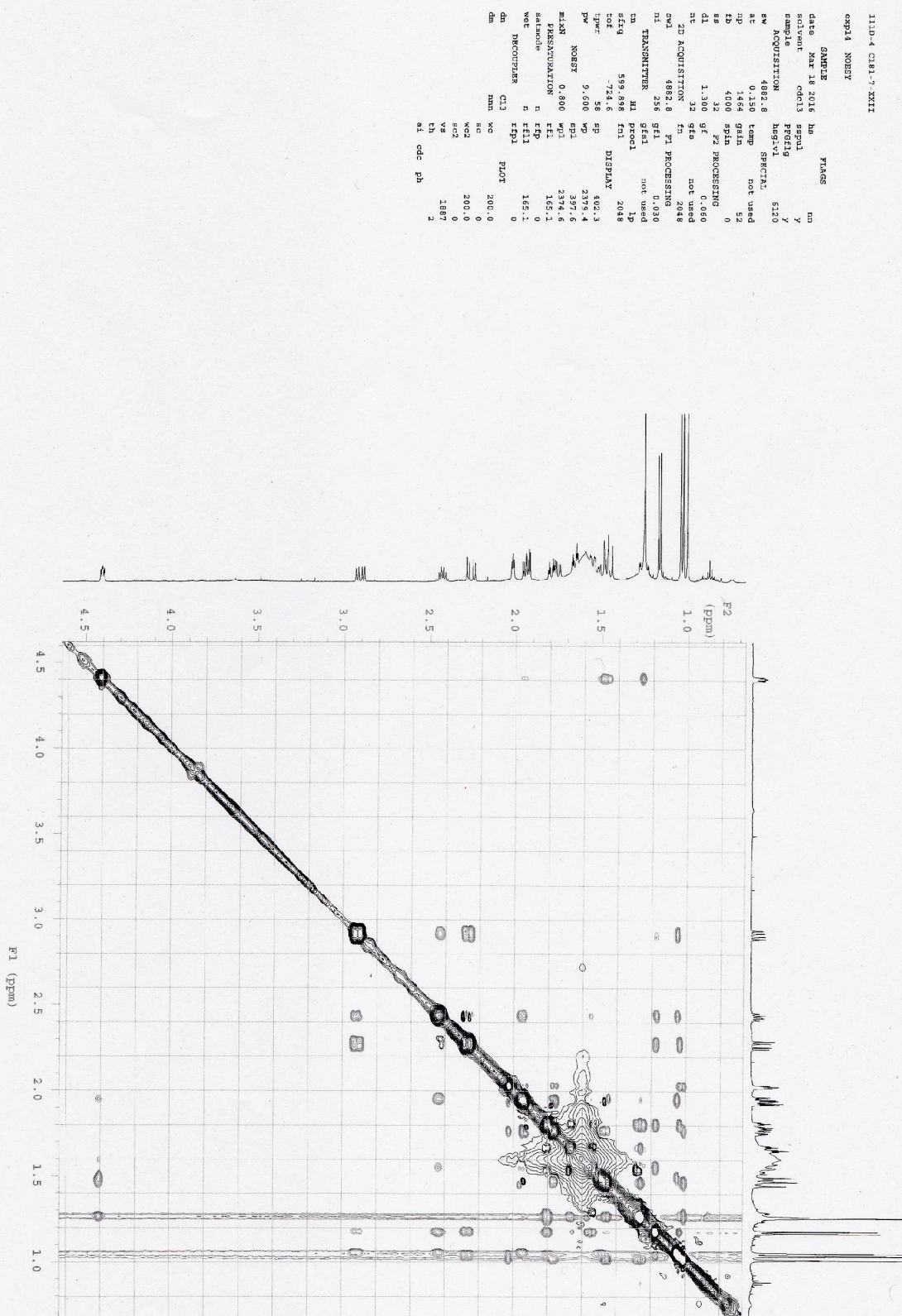


Figure S3.  $^1\text{H}$ - $^1\text{H}$  COSY of 1.













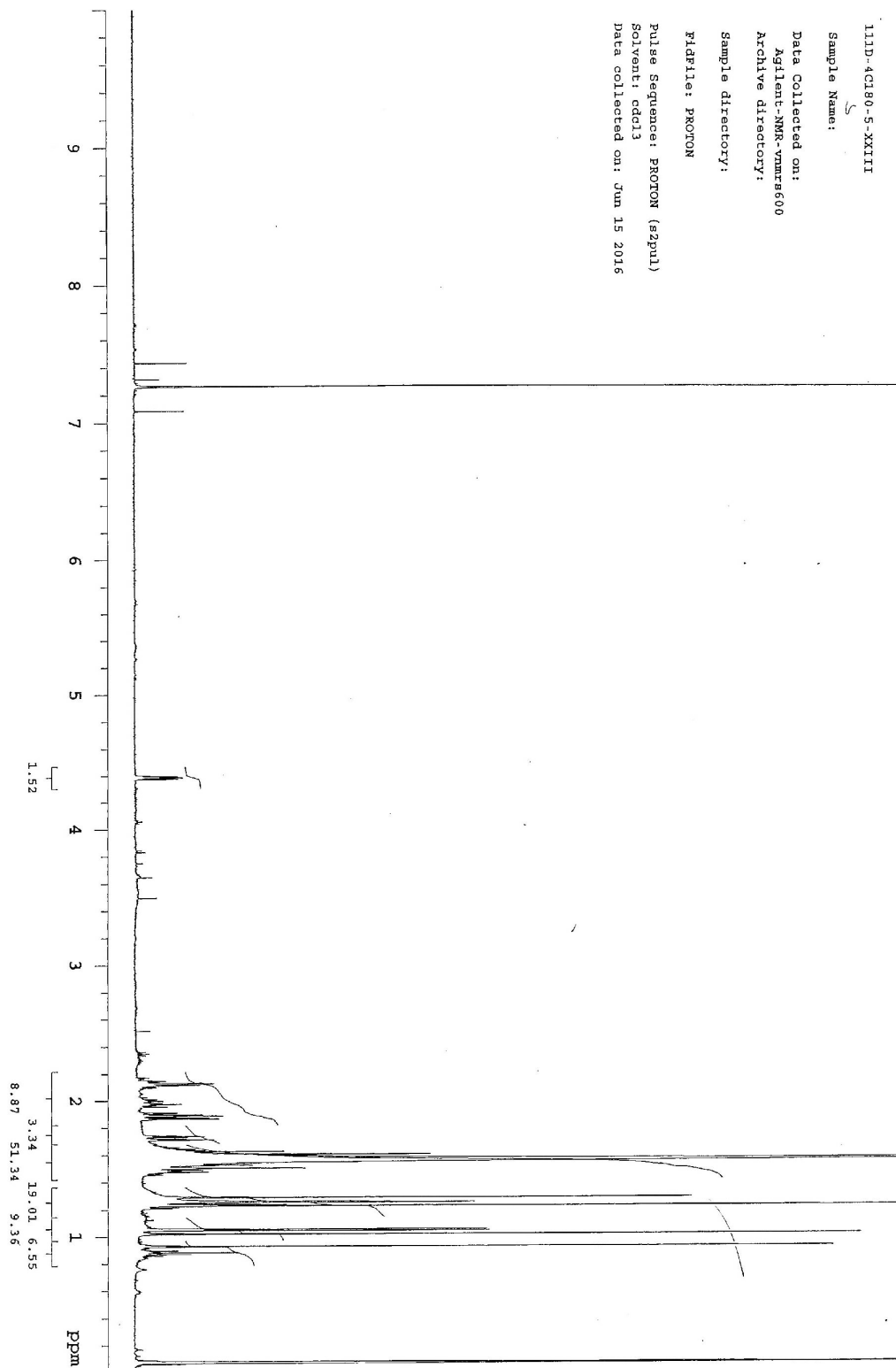


Figure S7. <sup>1</sup>H NMR spectrum of 2 in CDCl<sub>3</sub>.

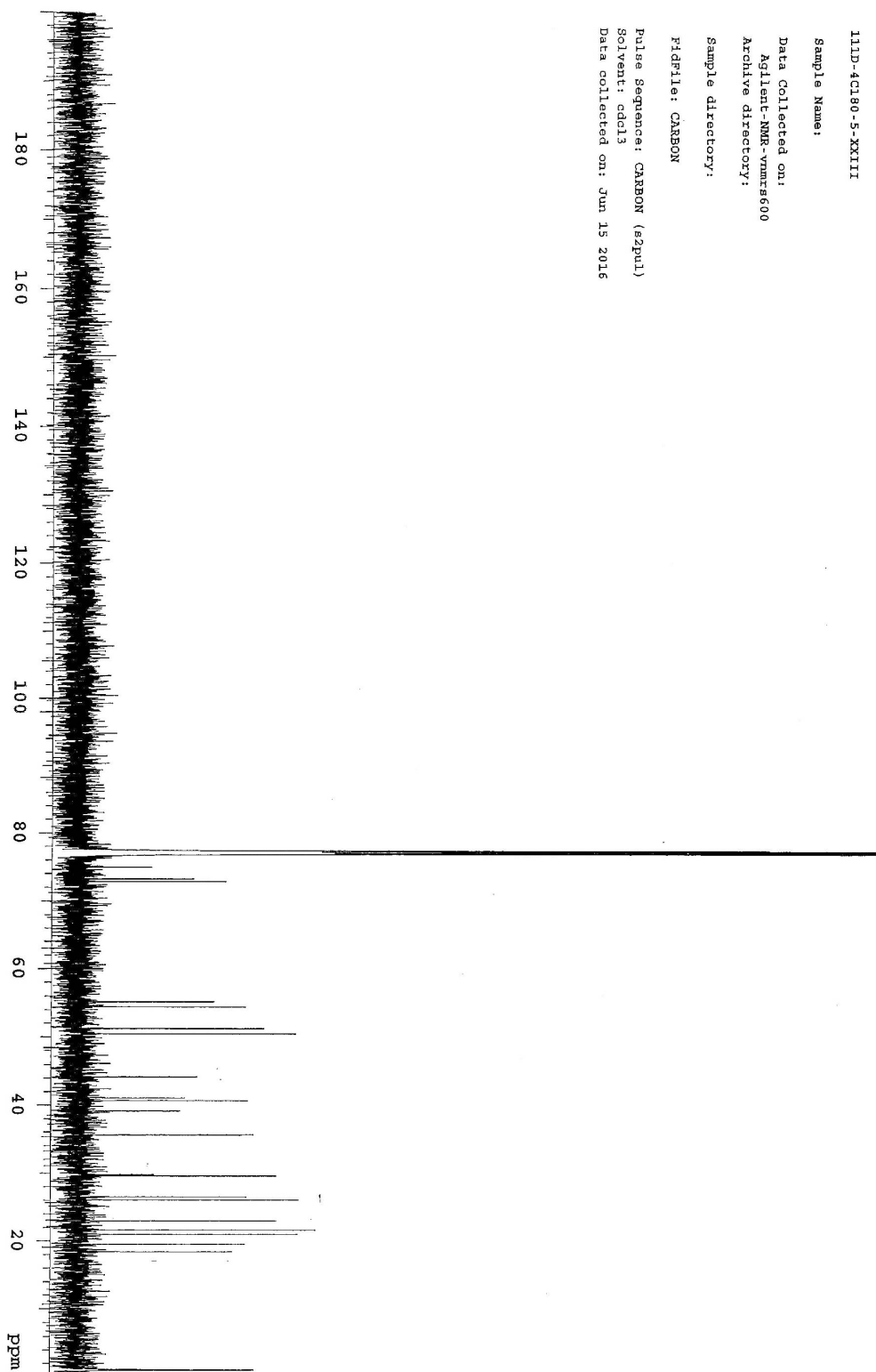


Figure S8. <sup>13</sup>C NMR spectrum of 2 in CDCl<sub>3</sub>.

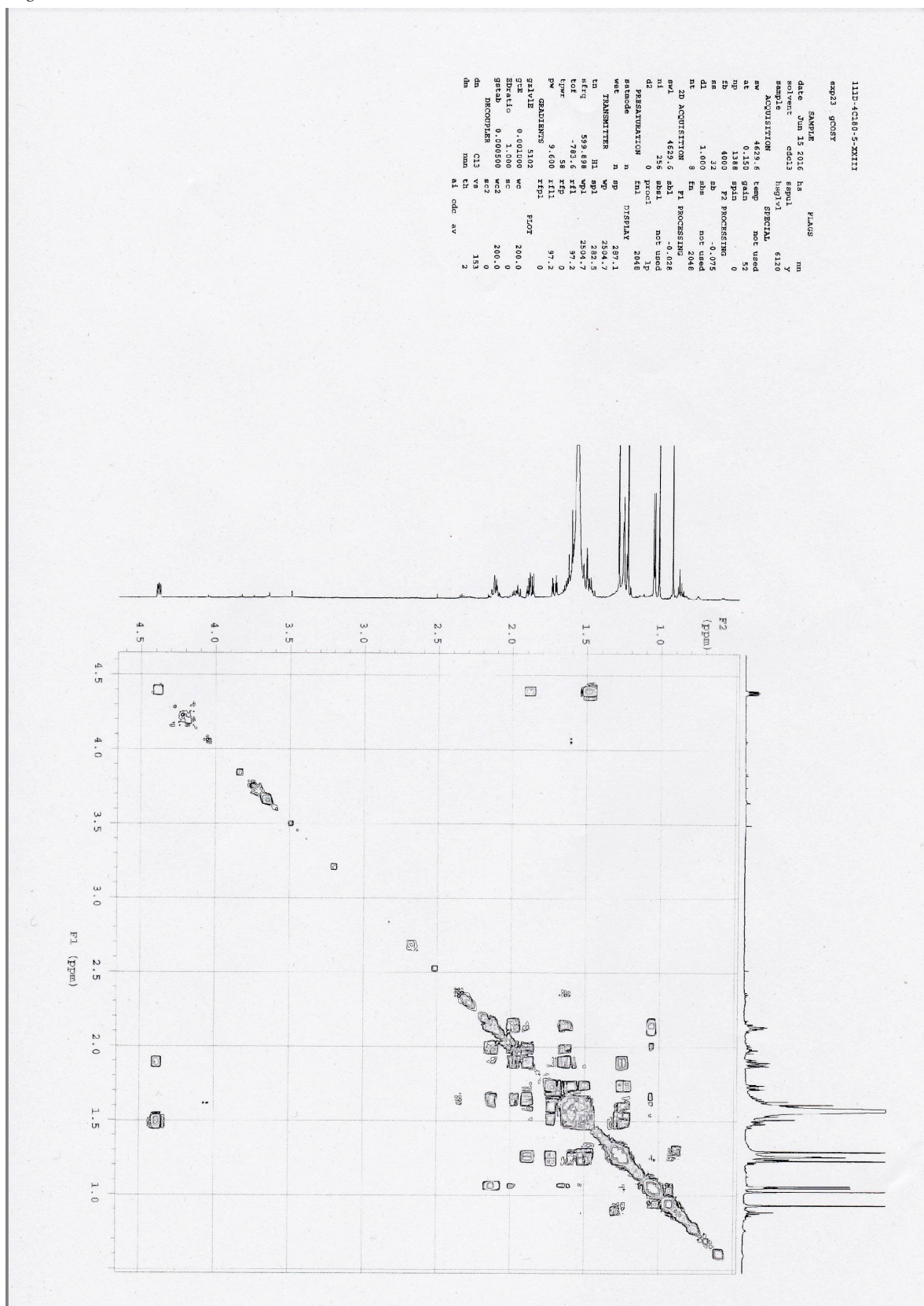


Figure S9.  $^1\text{H}$ - $^1\text{H}$  COSY of 2.







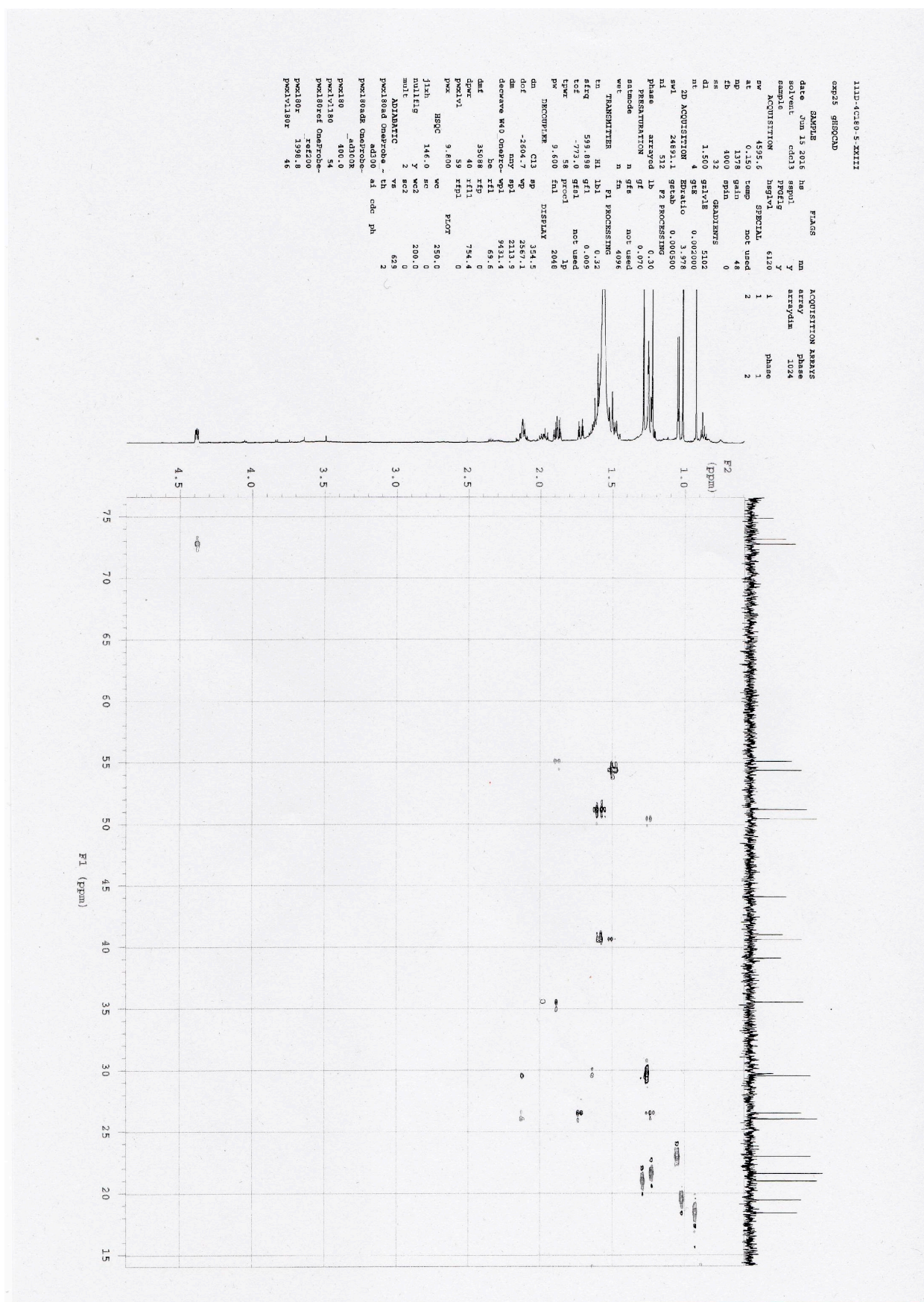


Figure S11. HMQC of 2.





111D-4 C232-9  
Sample Name:  
Data Collected on:  
Agilent-NMR-Vnmr600  
Archive directory:  
Sample directory:  
Fidfile: PROTON  
Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: Feb 27 2017

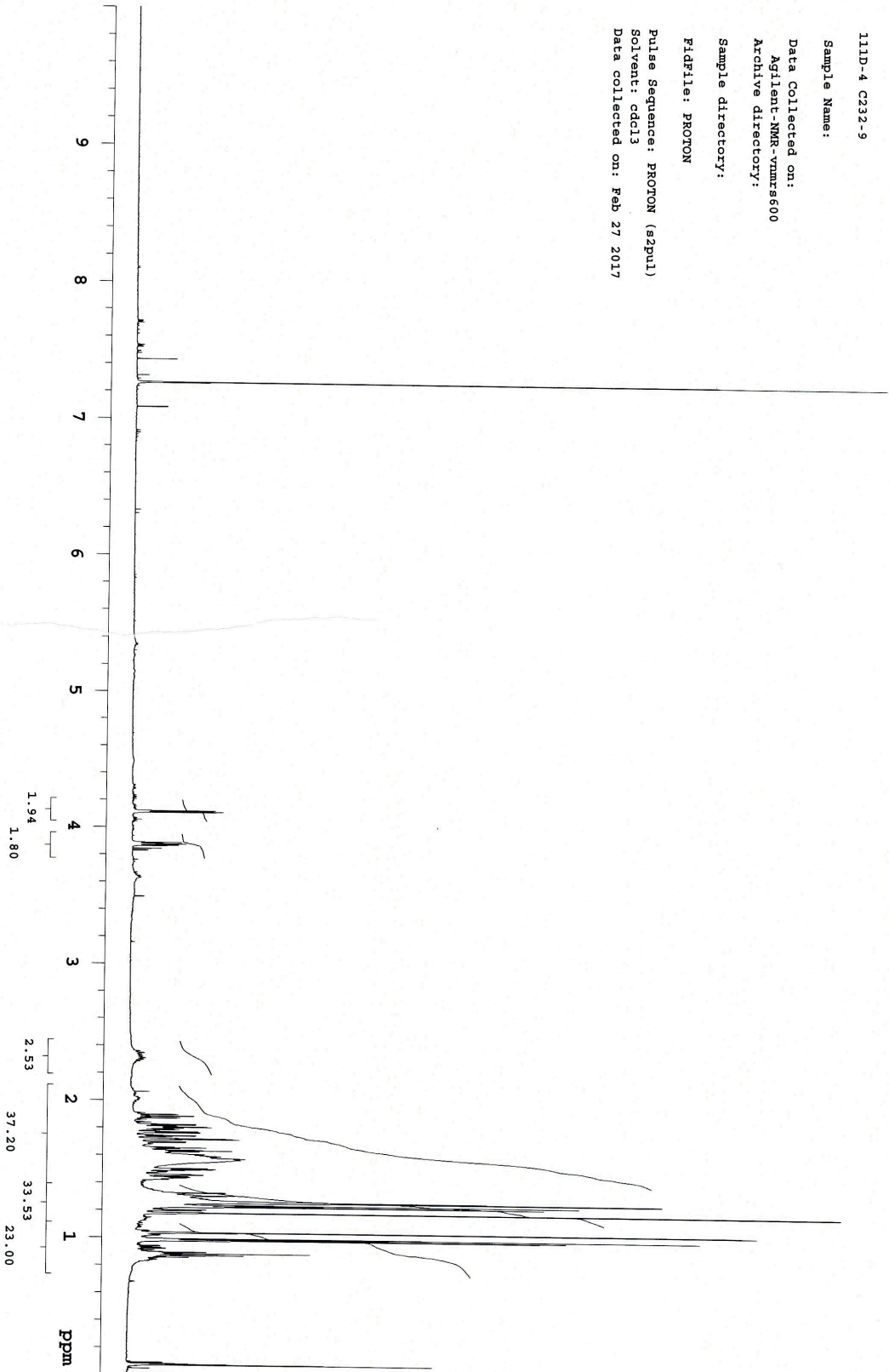


Figure S13. <sup>1</sup>H NMR spectrum of 3 in CDCl<sub>3</sub>.



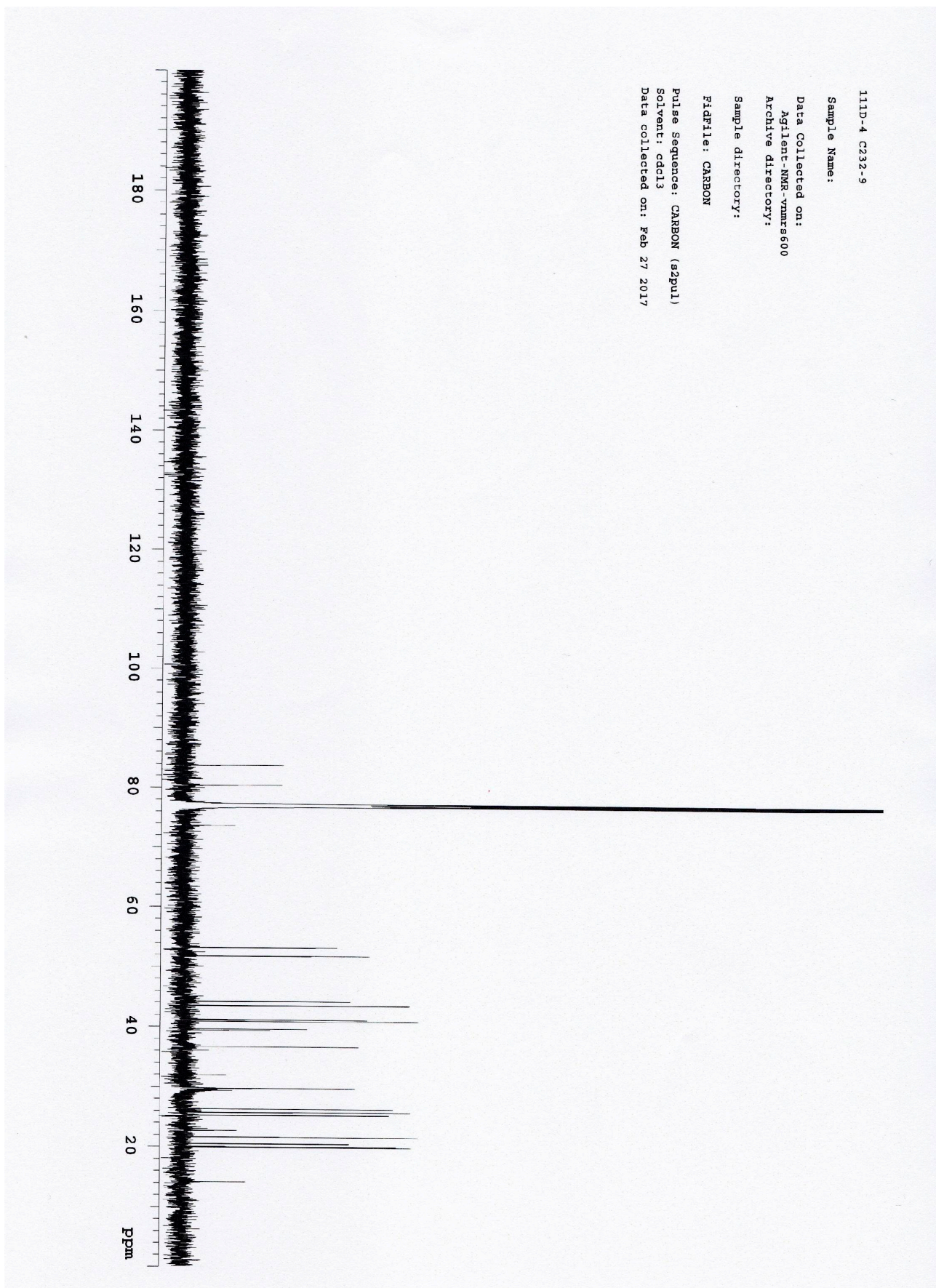


Figure S14. <sup>13</sup>C NMR spectrum of 3 in CDCl<sub>3</sub>.



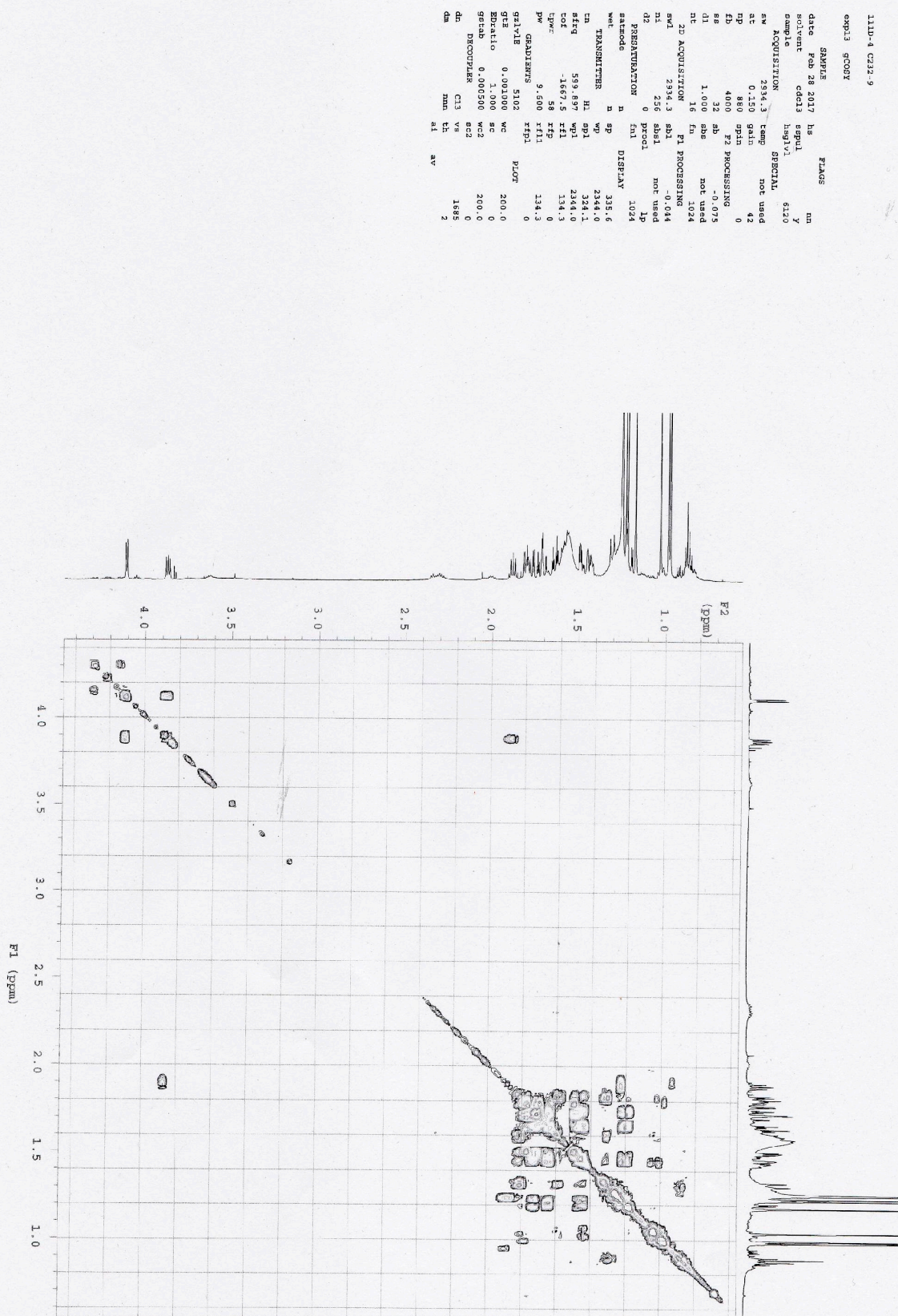


Figure S15. <sup>1</sup>H-<sup>1</sup>H COSY of 3.



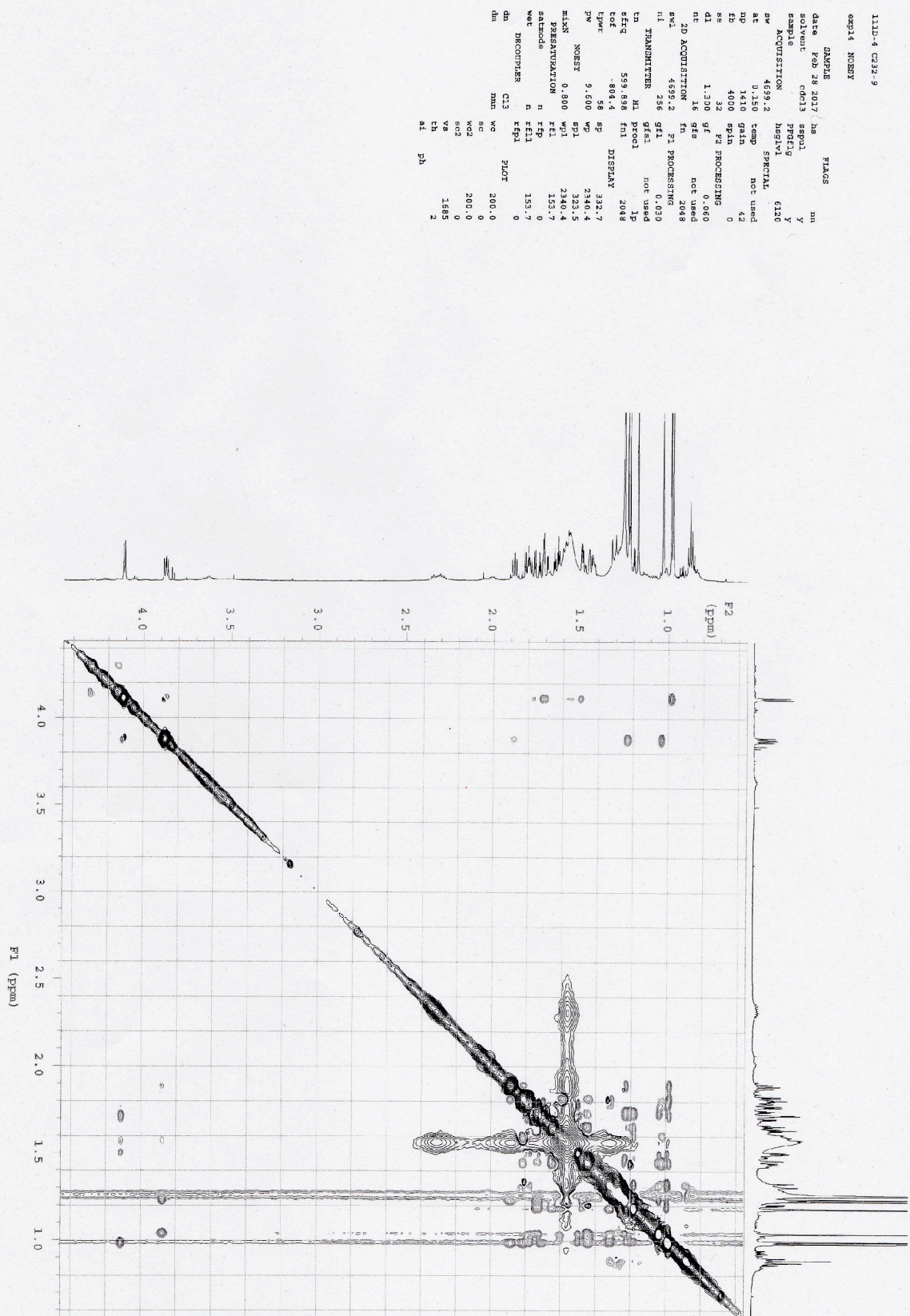


Figure S16. NOESY of 3.







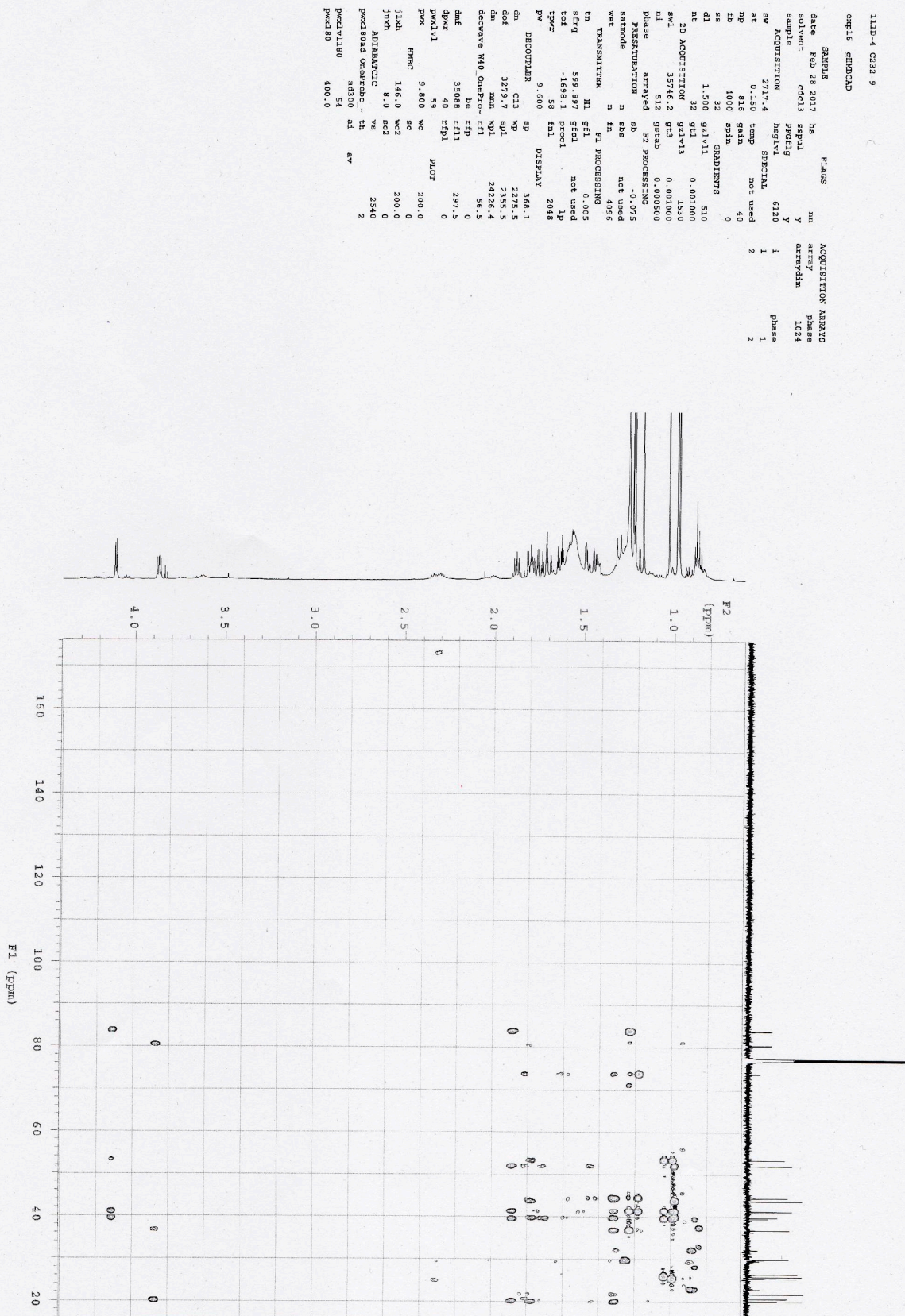


Figure S18. HMBC of 3.

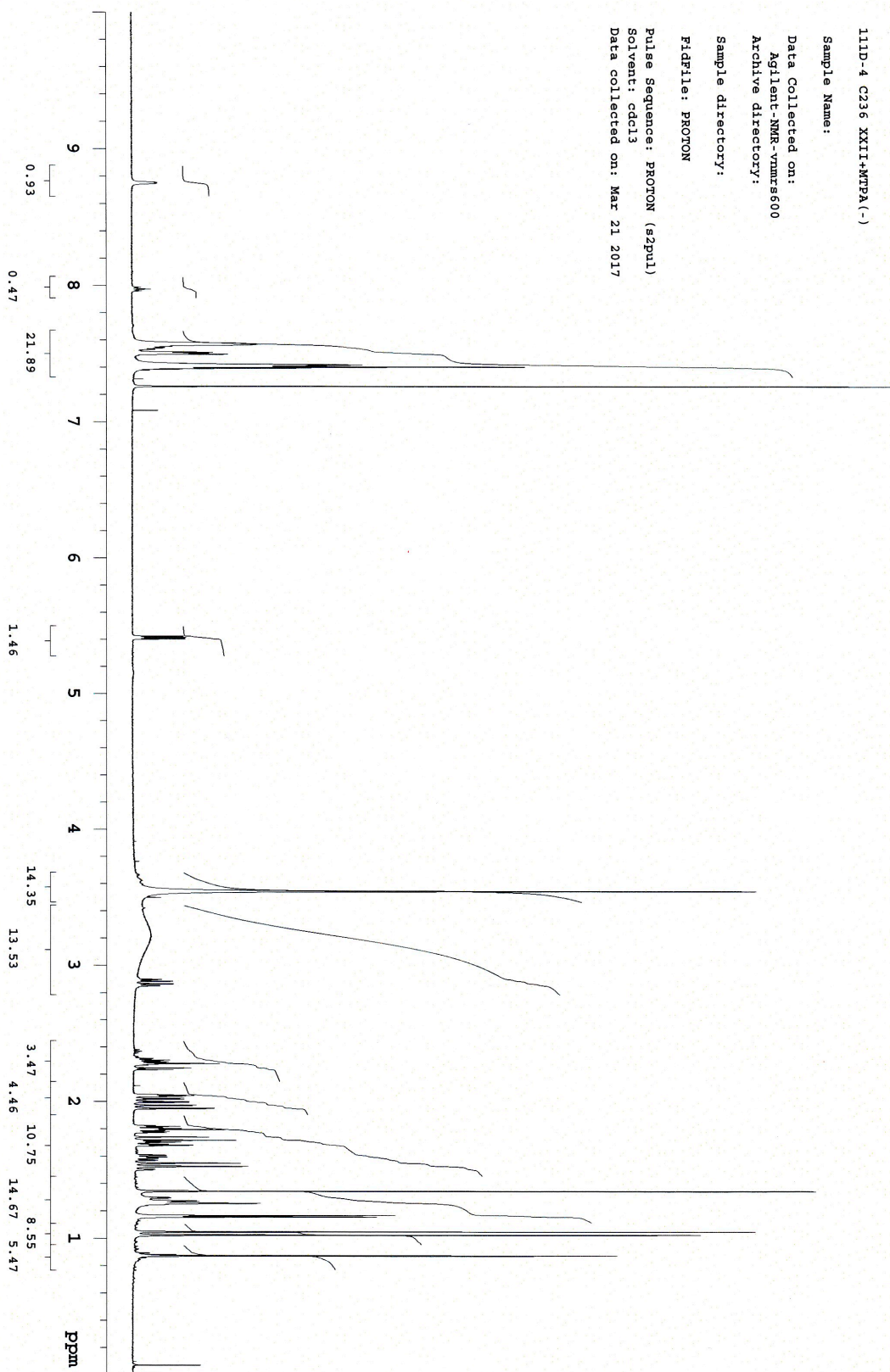


Figure S19. <sup>1</sup>H NMR spectra of 1a in CDCl<sub>3</sub>.



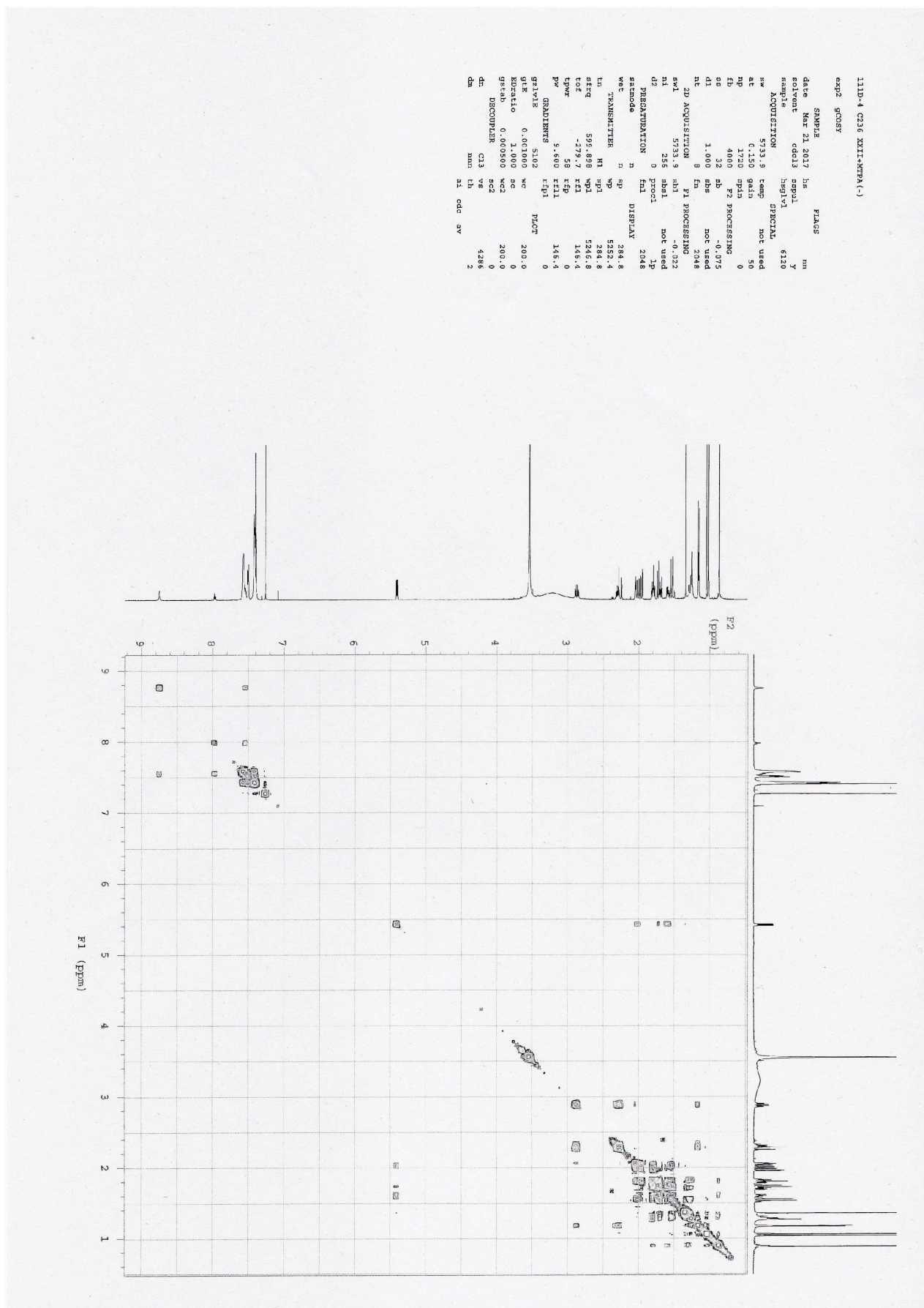


Figure S20. <sup>1</sup>H-<sup>1</sup>H COSY of 1a.



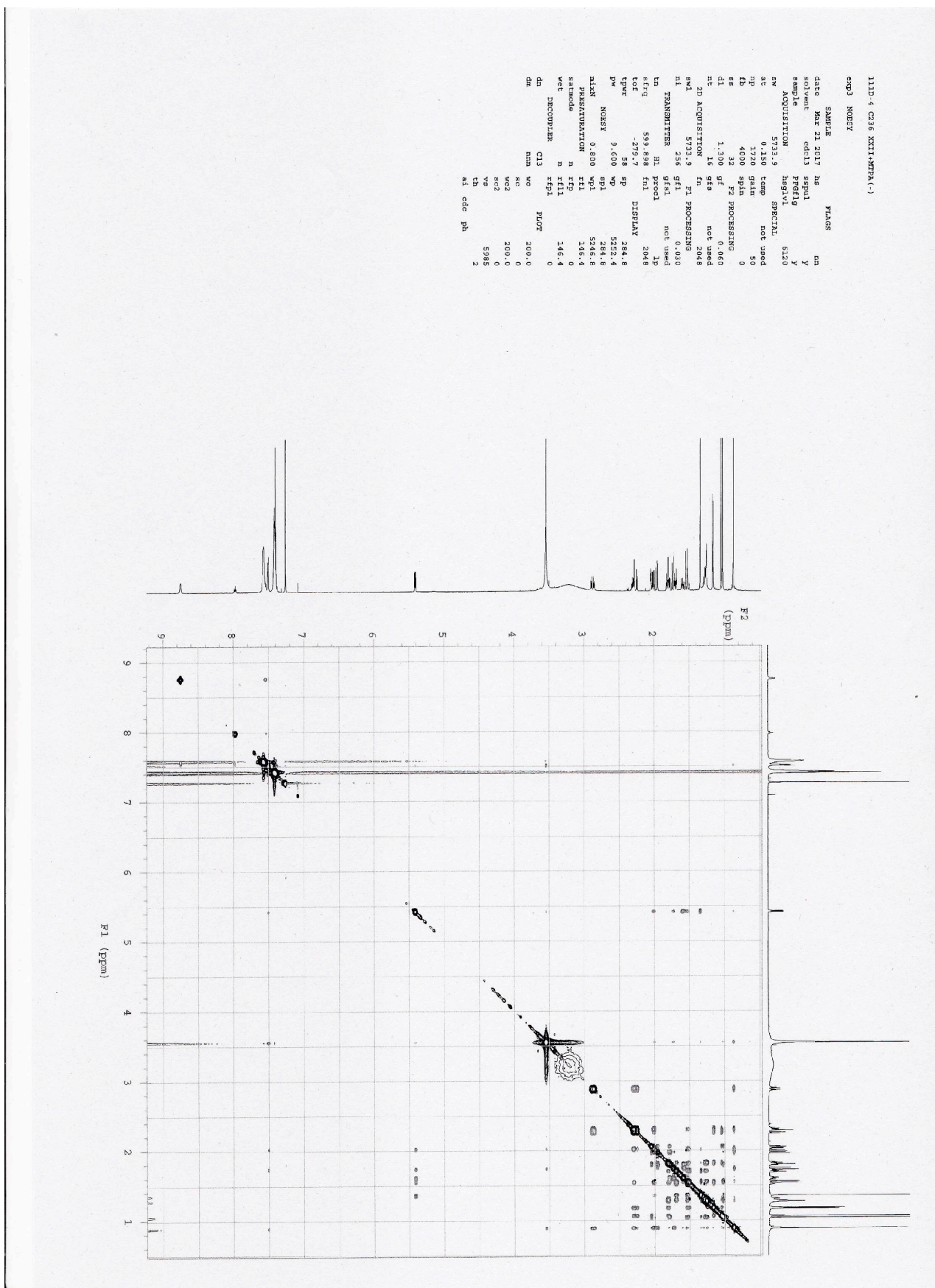


Figure S21. NOESY of 1a.

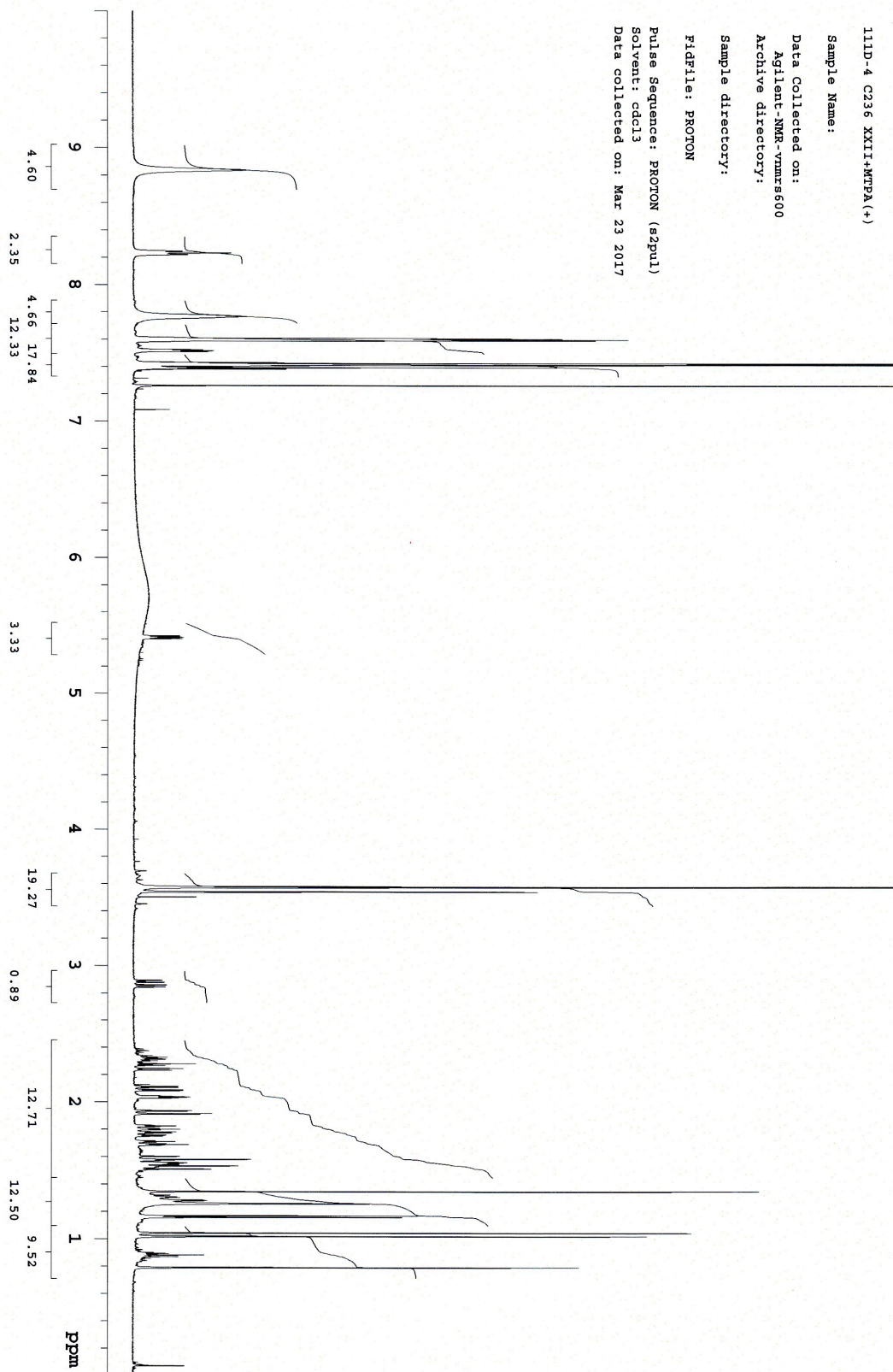


Figure S22. <sup>1</sup>H NMR spectra of **1b** in CDCl<sub>3</sub>.



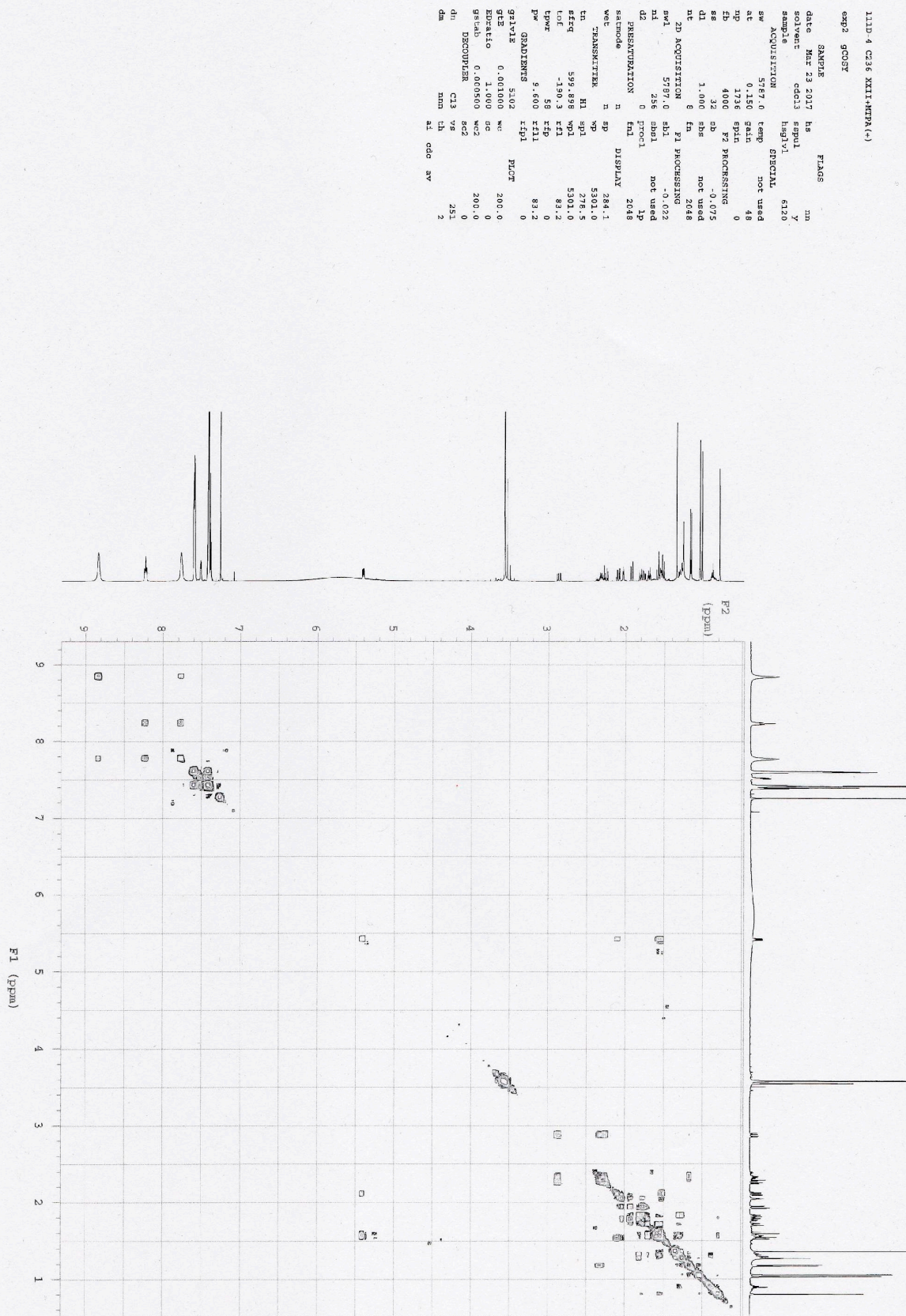


Figure S23. <sup>1</sup>H-<sup>1</sup>H COSY of 1b.

111D-4 C136 X111-N1RA(+)  
 exp3 NOESY

NAME	FLAG
date	Mar 23 2017
solvent	cdcl3
sample	exp19
ACQUISITION	hsqmv1
row	5924.2
at	0.150
ep	1708
sp	32
d1	1.300
nt	16
2D ACQUISITION	F1 PROCESSING
sw1	5924.2
nl	286
TRANSMITTER	HL
ln	599.898
sfreq	-169.7
lpcr	58
pw	9.600
mixr	NOESY
PRESATURATION	WFL
satmode	n
wee	PROCPAR
dm	mm
sc	ec
ec2	ec2
vs	vs
th	th
al	al

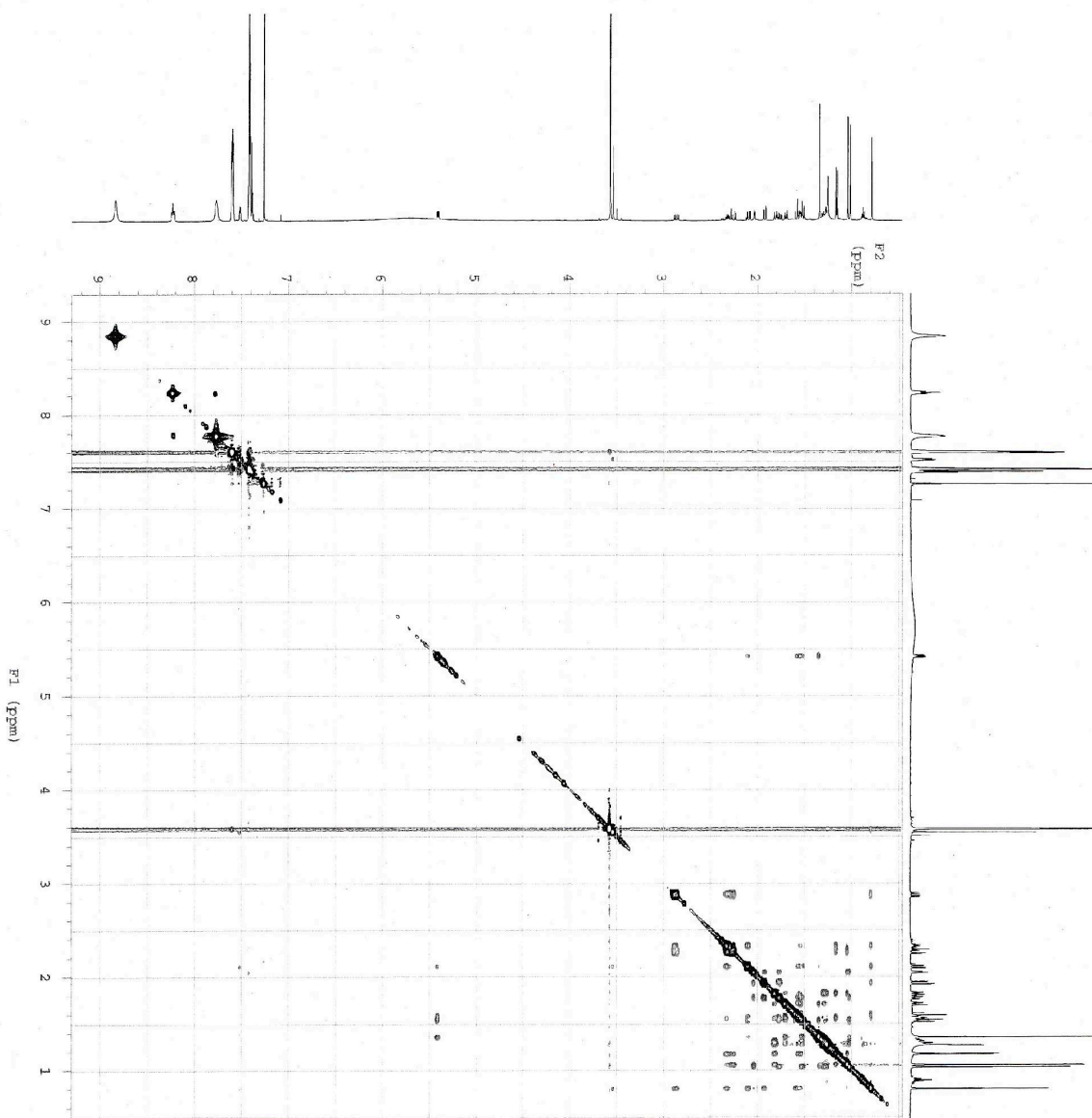


Figure S24. NOESY of 1b.



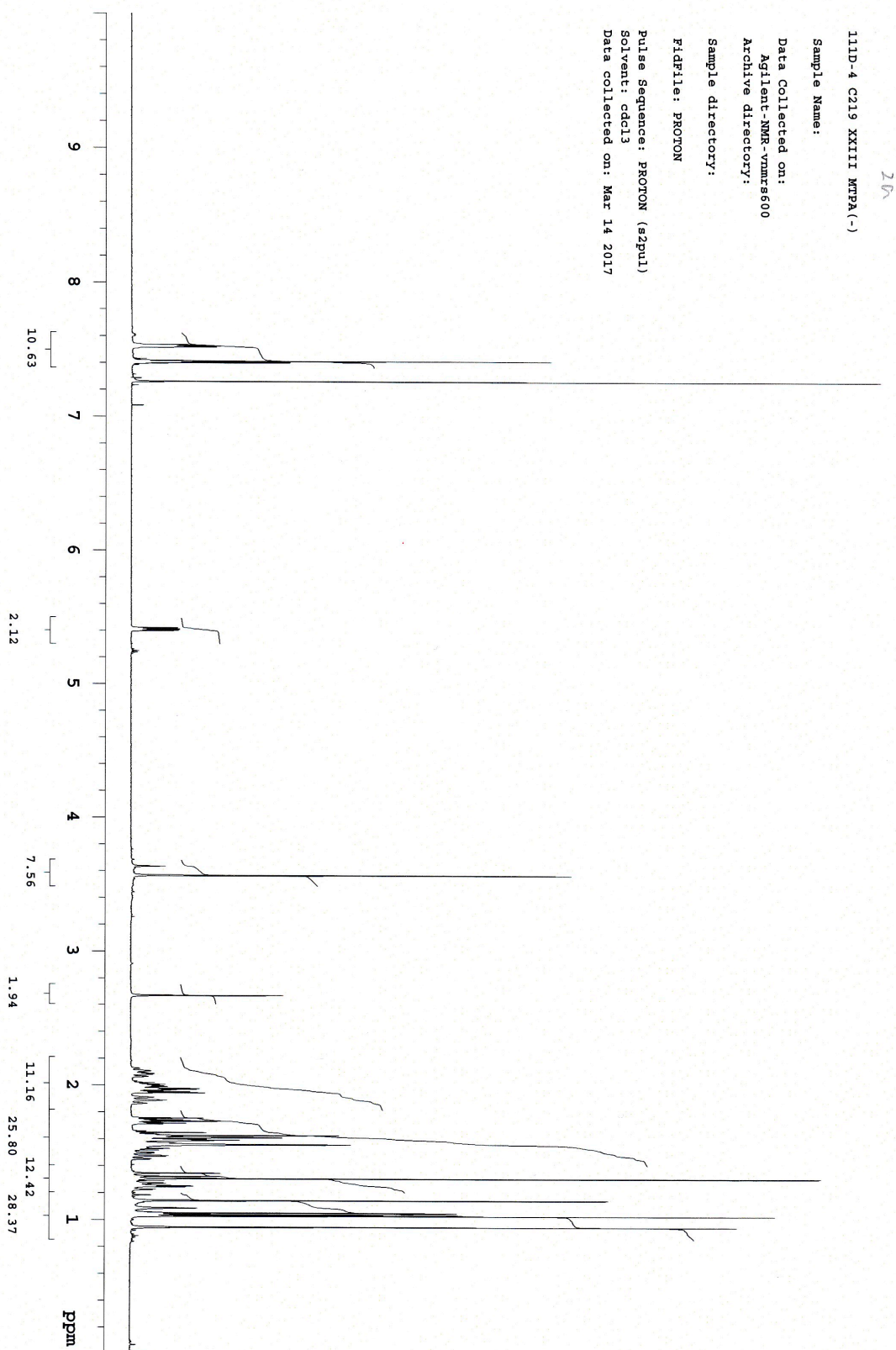


Figure S25. <sup>1</sup>H NMR spectra of 2a in CDCl<sub>3</sub>.

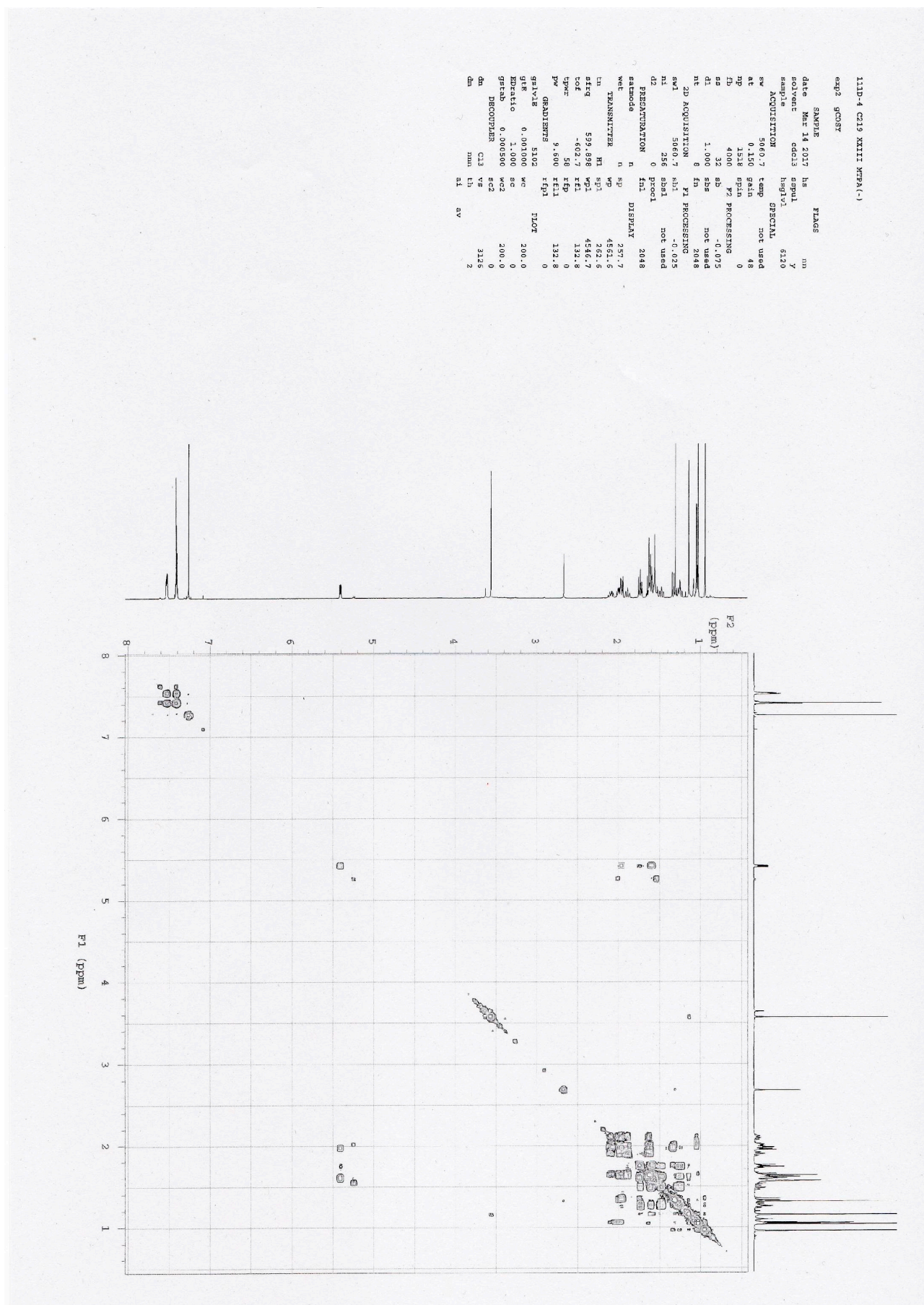


Figure S26. <sup>1</sup>H-<sup>1</sup>H COSY of 2a.





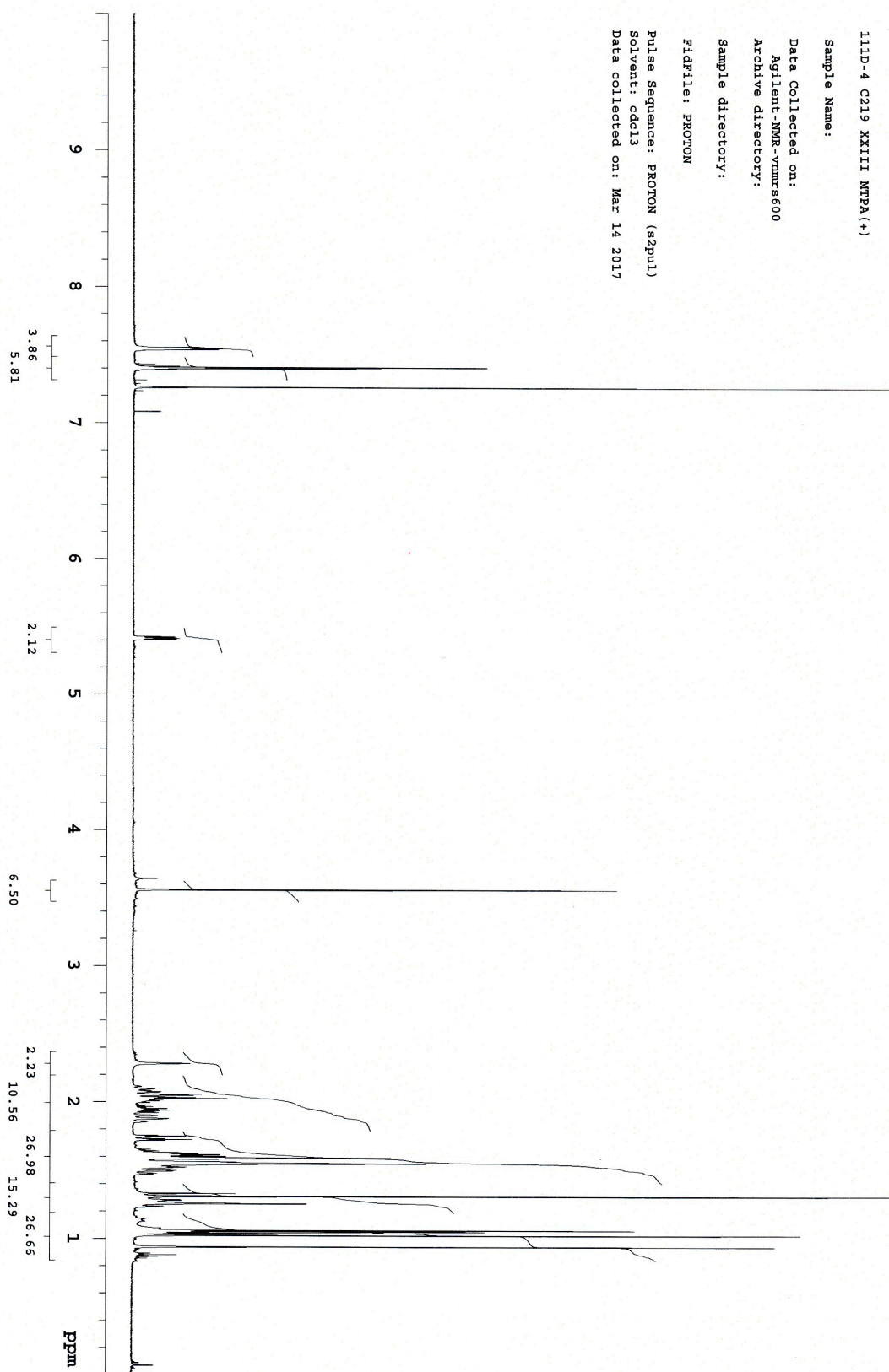


Figure S28. <sup>1</sup>H NMR spectra of **2b** in CDCl<sub>3</sub>.

```

11ID-4-C21D XXIII NMR (-)
exp5 gcosy
=====
date Mar 14 2017 hs
solvent cdcl3
sample Y
SPECTRA 6120
=====
ACQUISITION
sw 5061.3 temp not used
sc 0.130 gain 48
sp 420
fp 4000
ss 32 sb 22 PROCESSING 0
dl 1.000 sbw not used
nt 8 ft 2048
=====
2D ACQUISITION F1 PROCESSING
sw1 5061.3 sb1 -0.025
nl 236 sbal not used
d2 PREPARATION 0 pncol 1p
=====
satmode n sp DISPLAY 2048
wet n sp 262.0
=====
TRANSMITTER H1 W1 4555.2
ca 266.9
freq 599.898 W1 4550.3
foc -564.9 xF1 105.2
cpw 58 xF2 0
pw GRABBERS 9.800 xF1 105.2
=====
gate1 5102 E107 0
gate2 0.001000 w2 200.0
kdratio 1.000 w2 200.0
gate3 0.000500 w2 200.0
DECOUPLER C13 v2 3126
dm mm th sl cdc av 2
    
```

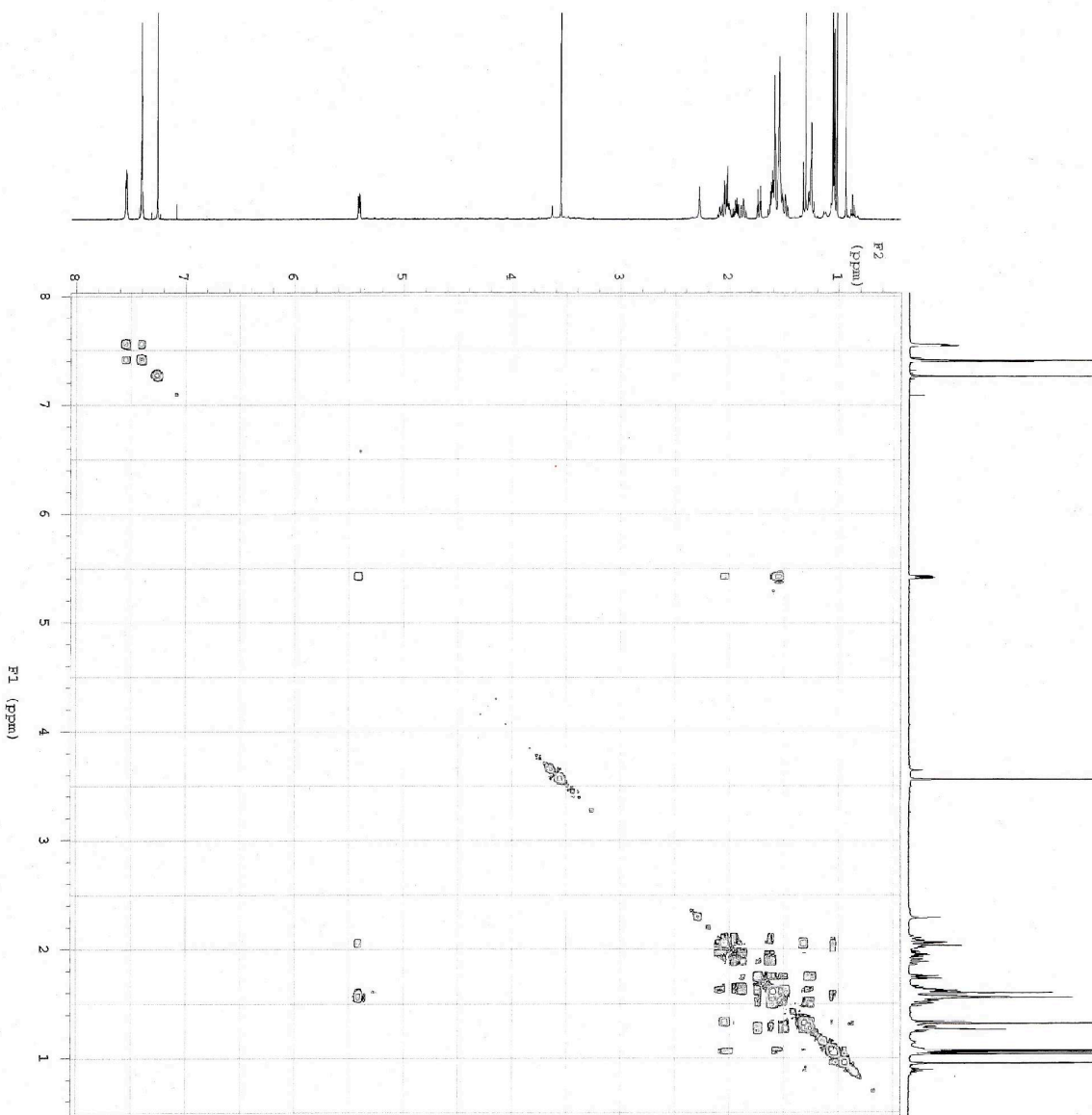


Figure S29.  $^1\text{H}$ - $^1\text{H}$  COSY of 2b.

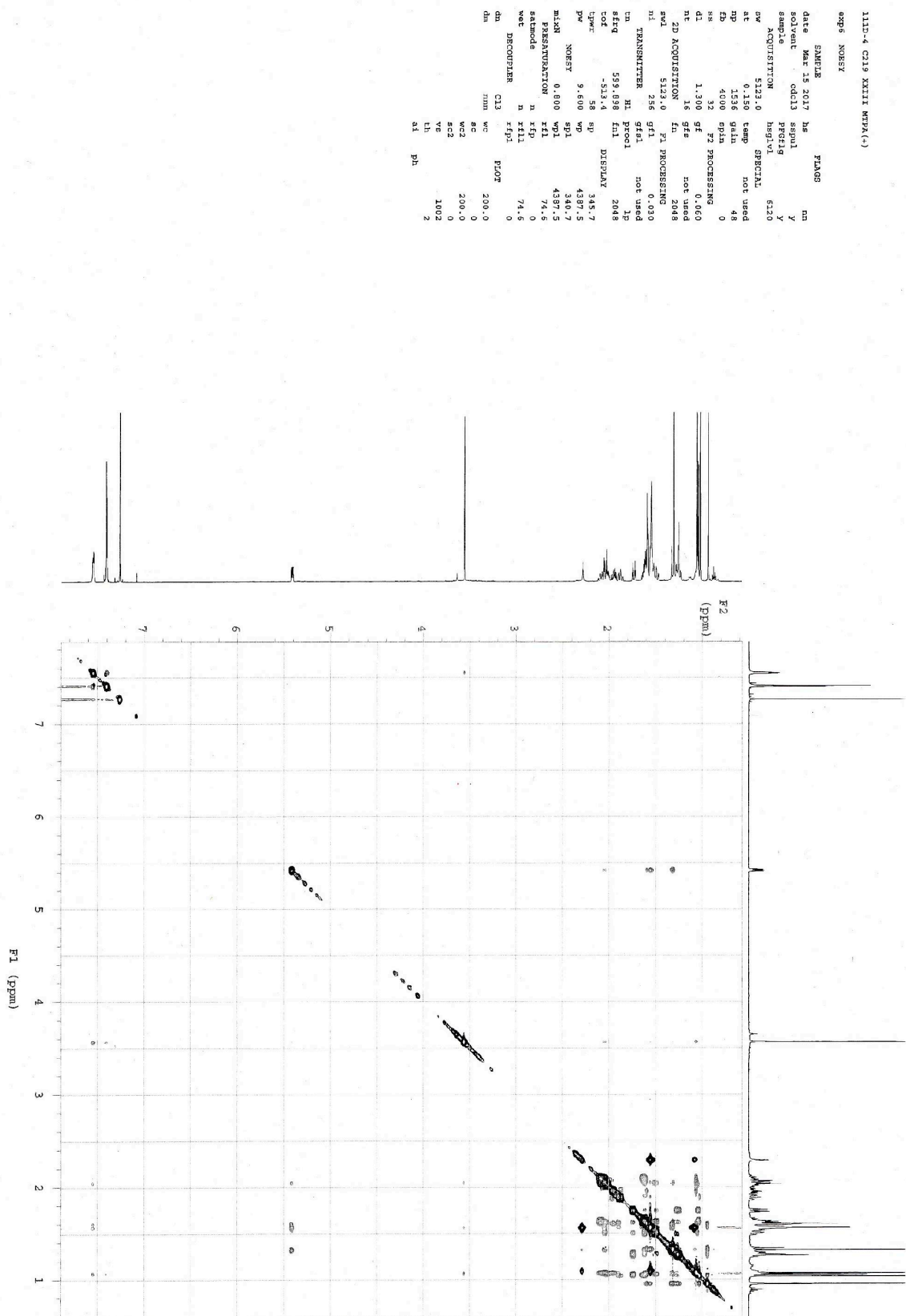


Figure S30. NOESY of 2b.