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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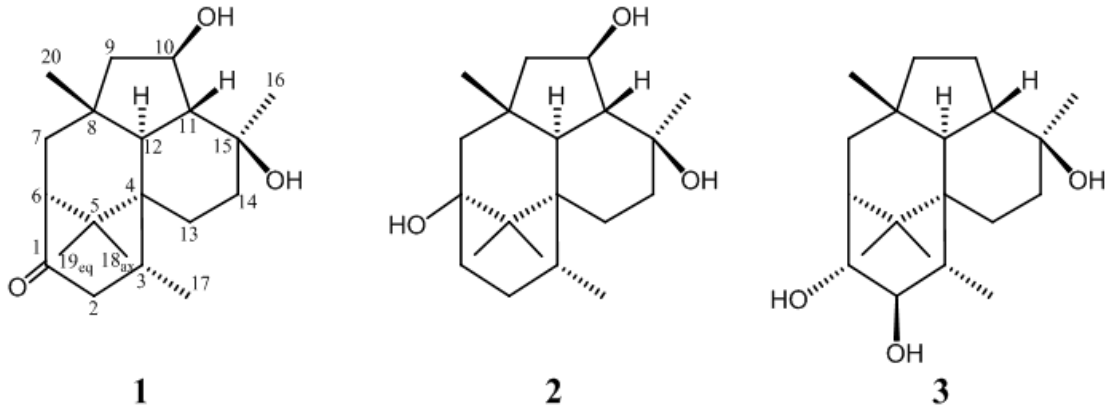

Scheme 1. Structures of metabolites in the fungal strain.

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

Position	δ_H [a]		*J*/Hz	^{1}H-^{1}H COSY	NOESY [b]	δ_C		HMBC (C) [c]
1	-	-	-	-	-	217.7	1	-
2α	2.27	dd	20.4 (2β), 7.2 (3)	2β, 3	17, 19	48.7	2α	2.27
2β	2.91	dd	20.4 (2α), 9.0 (3)	2α, 3	20		2β	2.91
3	2.44	dqd	9.0 (2β), 7.2 (2α), 7.2 (17)	2α, 2β, 17	11, 14β, 20	26.1	3	2.44
4	-	-	-	-	-	39.5	4	-
5	-	-	-	-	-	38.2	5	-
6	2.03	dd	3.6 (7α), 3.6 (7β)	7α, 7β	18, 19	58.0	6	2.03
7α	1.76	dd	13.8 (7β), 3.6 (6)	6, 7β	9, 12, 18	41.4	7α	1.76
7β	1.92	dd	13.8 (7α), 3.6 (6)	6, 7α	9, 20	-	7β	1.92
8	-				-	39.0	8	-
9	1.50	m		10	7α, 7β, 20	53.9	9	1.50
10	4.41	ddd	7.8 (9), 4.8 (11), 1.2 (9)	9, 11	12, 16	72.6	10	4.41
11	1.95	dd	12.6 (12), 4.8 (10)	10, 12	3, 20	54.7	11	1.95
12	1.46	d	12.6 (11)	11	7α, 10, 16, 18	51.0	12	1.46
13α	1.25	ddd	14.0 (13β), 14.0 (14β), 3.0 (14α)	13β, 14α, 14β	18	25.9	13α	1.25
13β	1.80	ddd	14.0 (13α), 3.0 (14β), 3.0 (14α)	13α, 14α, 14β	17, 19	-	13β	1.80
14α	1.66	ddd	14.0 (12β), 3.0 (13α), 3.0 (13β)	13α, 13β, 14β	-	40.2	14α	1.66
14β	1.55	ddd	14.0 (12α),14.0 (13α), 3.0 (13β)	13α, 13β, 14α	3, 17	-	14β	1.55
15	-	-	-	-	-	72.9	15	-
16	1.26	s	-	-	10, 12	21.6	16	1.26
17	1.17	d	7.2 (3)	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

[a] ^{1}H chemical shift values (δ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants (*J*/Hz). Figures in parentheses indicate the proton coupling with that position. [b] The correlations with geminal and vicinal protones are removed. [c] Long range ^{1}H-^{13}C correlations from H to C observed in the HMBC experiment.

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

Position	δ_H [a]		J/Hz	^{1}H-^{1}H COSY	NOESY [b]	δ_C		HMBC (C) [c]
1α	1.90	ddd	14.4 (1β), 2.4 (2α), 2.4 (2β)	1β, 2α, 2β	19	35.5	(t)	2, 6, 7
1β	1.98	ddd	14.4 (2β), 10.8 (2α), 6.0 (2β)	1α, 2α, 2β	3, 20	-	-	2, 5, 6, 7
2α	1.64	m	-	1α, 1β, 2β, 3	17, 19	29.5	(t)	1, 3, 17
2β	2.12	m	-	1α, 1β, 2α, 3	-	-	-	-
3	2.14	m	-	2α, 2β	1β, 11, 20	26.0	(d)	2, 5, 12, 17
4	-	-	-	-	-	41.0	(s)	-
5	-	-	-	-	-	44.1	(s)	-
6	-	-	-	-	-	74.9	(s)	-
7α	1.56	m	-	7β	-	51.2	(t)	1, 6, 8, 9, 20
7β	1.62	m	-	7α	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
13α	1.23	ddd	14.0 (13β), 14.0 (14β), 3.0 (14α)	13β, 14α, 14β	18	26.4	(t)	14, 15
13β	1.73	ddd	14.0 (13α), 3.0 (14β), 3.0 (14α)	13α, 14α, 14β	17, 19	-	-	14
14α	1.66	m	-	13α, 13β, 14β	-	40.6	(t)	-
14β	1.59	m	-	13α, 13β, 14α	17	-	-	-
15	-	-	-	-	-	73.1	(s)	-
16	1.23	s	-	-	10	21.5	(q)	11, 14, 15
17	1.05	d	6.6 (3)	3	2α, 13β, 14β	22.9	(q)	2, 3, 4
18ax	0.93	s	-	-	12, 13α	18.3	(q)	4, 5, 6, 19
19eq	1.02	s	-	-	1α, 2α, 13β	19.4	(q)	4, 5, 6, 18
20	1.29	s	-	-	1β, 3, 7β, 9, 11	20.9	(q)	7, 8, 9, 12

[a] ^{1}H chemical shift values (δ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants (J/Hz). Figures in parentheses indicate the proton coupling with that position. [b] The

correlations with geminal and vicinal protones are removed. [c] Long range ^{1}H-^{13}C correlations from H to C observed in the HMBC experiment.

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

Position	δ_H [a]		*J*/Hz	^{1}H-^{1}H COSY	NOESY [b]	δ_C		HMBC (C) [c]
1	4.11	d	5.4 (2)	2	7β, 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)	2α, 2β, 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 (7α), 3.0 (7β)	7α, 7β	18, 19	53.2	(d)	4
7α	1.78	dd	13.8 (7β), 4.8 (6)	6, 7β	9α, 12, 18	40.9	(t)	1, 6, 8, 9, 20
7β	1.70	dd	13.8 (7α), 3.0 (6)	6, 7α	1, 20	-	-	5, 12
8	-	-	-	-	-	39.6	(s)	-
9α	1.03	m	-	9β, 10α, 10β	7α, 12	43.5	(t)	-
9β	1.43	m	-	9α, 10α, 10β	20	-	-	20
10α	1.59	m	-	9α, 9β, 10β, 11	16	21.6	(t)	8, 15
10β	1.80	m	-	9α, 9β, 10α, 11	-	-	-	-
11	1.81	dd	13.2 (12), 4.2 (10)	10α, 10β, 12	3, 14β, 20	44.2	(d)	10, 12, 15, 16
12	1.32	d	13.2 (11)	11	7α, 9α, 16, 18	51.8	(d)	3, 4, 5, 8, 11, 15, 20
13α	1.23	ddd	13.8 (13β), 13.8 (14β), 3.6 (14α)	13β, 14α, 14β	18	26.3	(t)	-
13β	1.72	ddd	13.8 (13α), 3.6 (14β), 3.6 (14α)	13α, 14α, 14β	17, 19	-	-	5, 12
14α	1.64	ddd	13.8 (12β), 3.6 (13α), 3.6 (13β)	13α, 13β, 14β	16	41.1	(t)	-
14β	1.46	ddd	13.8 (12α), 13.8 (13α), 3.6 (13β)	13α, 13β, 14α	11, 17	-	-	11
15	-	-	-	-	-	73.6	(s)	-
16	1.18	s	-	-	10α, 12, 14α	20.5	(q)	11, 14, 15
17	1.23	d	7.2 (3)	3	2, 13β, 14β, 19	20.0	(q)	2, 3, 4
18αx	0.99	s	-	-	6, 7α, 12, 13α	25.7	(q)	4, 5, 6, 19
19eq	1.04	s	-	-	2, 6, 13β, 17	25.2	(q)	4, 5, 6, 18
20	0.98	s	-	-	1, 3, 7β, 9β, 11	19.8	(q)	7, 8, 9, 12

[a] ^{1}H chemical shift values (δ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants (*J*/Hz). Figures in parentheses indicate the proton coupling with that position. [b] The correlations with geminal and vicinal protones are removed. [c] Long range ^{1}H-^{13}C correlations from H to C observed in the HMBC experiment.

Table S4. ^{1}H NMR spectral data of MTPA esters **1a** and **1b** in $CDCl_3$.

Position	δ_H[a]		*J*/Hz	δ_H[a]		*J*/Hz
	1a			**1b**		
1	-	-	-	-	-	-
2α	2.26	dd	19.8 (2β), 7.2 (3)	2.26	dd	20.4 (2β), 7.8 (3)
2β	2.87	dd	19.8 (2α), 7.8 (3)	2.87	dd	20.4 (2α), 9.0 (3)
3	2.30	m	-	2.32	m	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	2.04	dd	4.2 (7α), 3.0 (7β)	2.03	dd	4.8 (7α), 3.6 (7β)
7α	1.78	m		1.76	dd	13.8 (7β), 4.8 (6)
7β	1.96	dd	13.8 (7α), 3.0 (6)	1.92	dd	13.8 (7α), 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)
13α	1.27	ddd	14.4 (13β), 14.4 (14β), 3.6 (14α)	1.28	ddd	14.4 (13β), 14.4 (14β), 3.6 (14α)
13β	1.8	ddd	14.4 (13α), 3.6 (14β), 3.6 (14α)	1.81	ddd	14.4 (13α), 3.6 (14β), 3.6 (14α)
14α	1.69	ddd	13.2 (14β), 3.6 (13α), 3.6 (13β)	1.70	ddd	13.2 (14β), 3.6 (13α), 3.6 (13β)
14β	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_3	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	-

[a] ^{1}H chemical shift values (δ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants (J/Hz). Figures in parentheses indicate the proton coupling with that position.

Table S5. ^{1}H NMR spectral data of MTPA esters **2a** and **2b** in $CDCl_3$.

Position	δ_H [a]		*J*/Hz	δ_H [a]		*J*/Hz
	2a			**2b**		
1α	1.89	m	-	1.89	m	-
1β	1.97	m	-	1.97	m	-
2α	1.64	m	-	1.64	m	-
2β	2.10	m	-	2.10	m	-
3	2.01	m	-	2.02	m	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7α	1.60	m	-	1.57	m	-
7β	1.74	d	13.8 (7α)	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)
13α	1.25	ddd	14.4 (13β), 14.4 (14β), 3.6 (14α)	1.26	ddd	14.4 (13β), 14.4 (14β), 3.6 (14α)
13β	1.73	ddd	14.4 (13α), 3.6 (14α), 3.6 (14β)	1.74	ddd	14.4 (13α), 3.6 (14α), 3.6 (14β)
14α	1.60	ddd	14.4 (14β), 3.6 (13α), 3.6 (13β)	1.61	m	-
14β	1.48	ddd	14.4 (13α), 14.4 (14α), 3.6 (13β)	1.50	ddd	14.4 (13α), 14.4 (14α), 3.6 (13β)
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_3	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	-

[a] ^{1}H chemical shift values (δ ppm from $SiMe_4$) followed by multiplicity and then the coupling constants (J/Hz). Figures in parentheses indicate the proton coupling with that position.

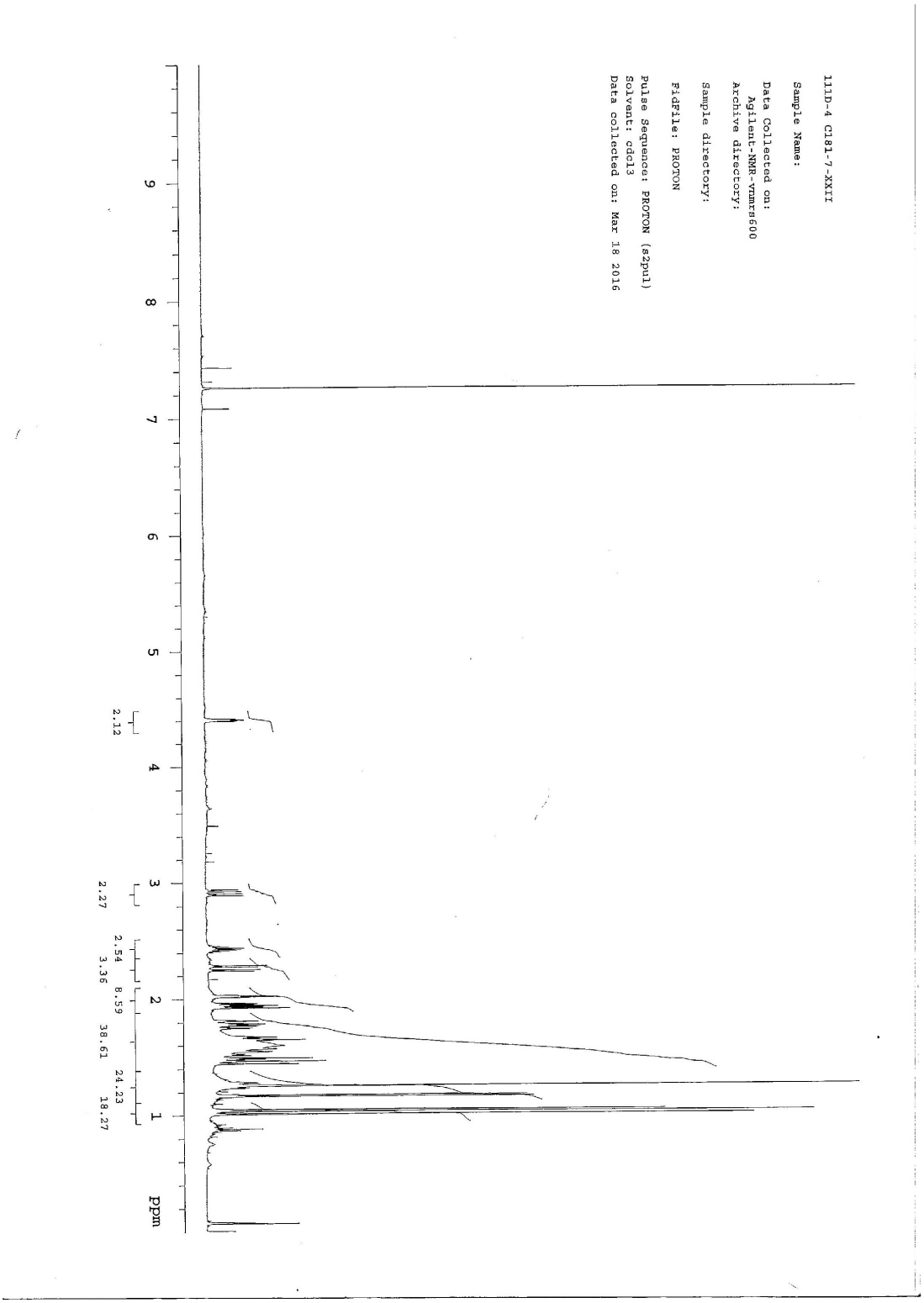

Figure S1. ^{1}H NMR spectrum of **1**.

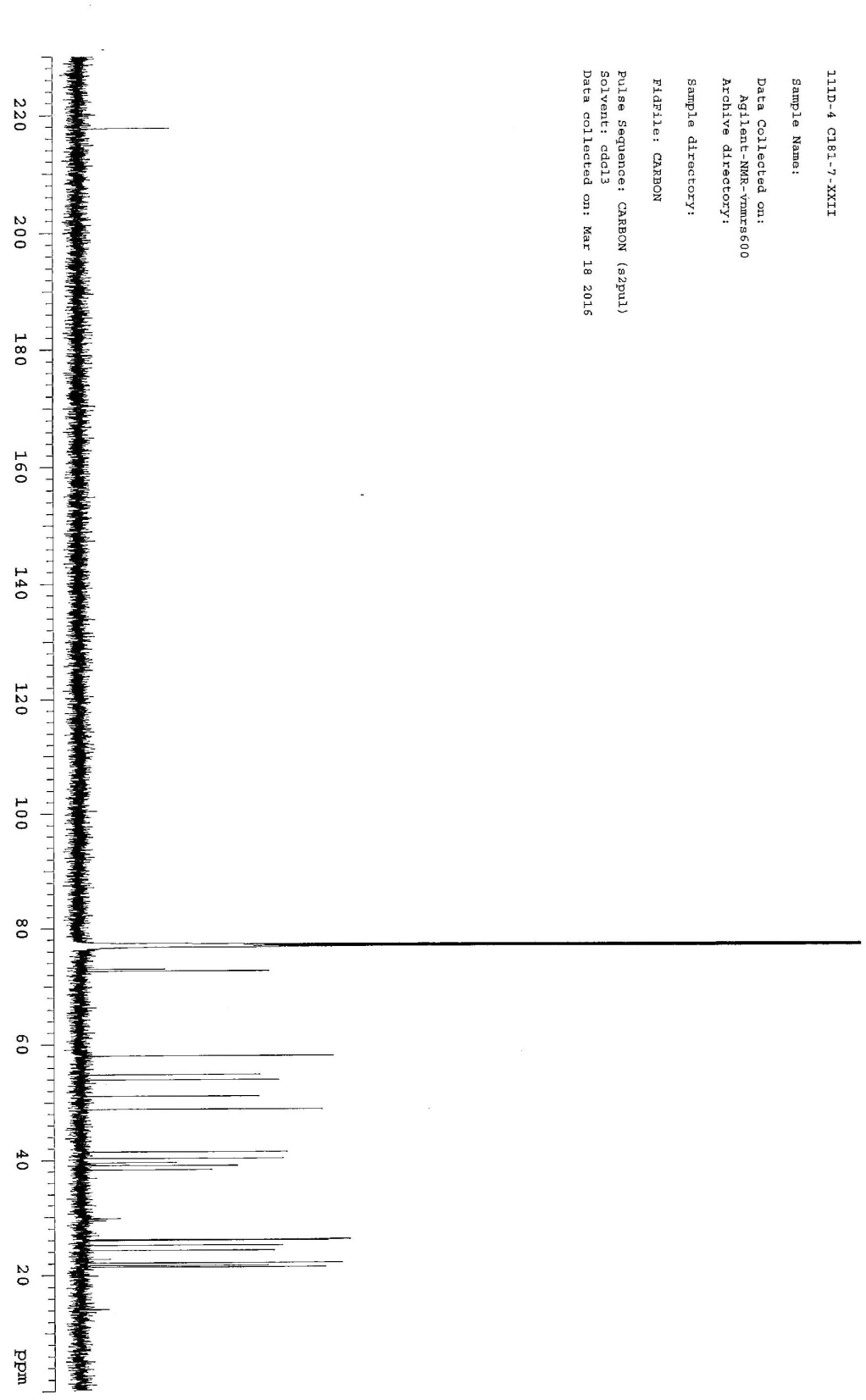

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

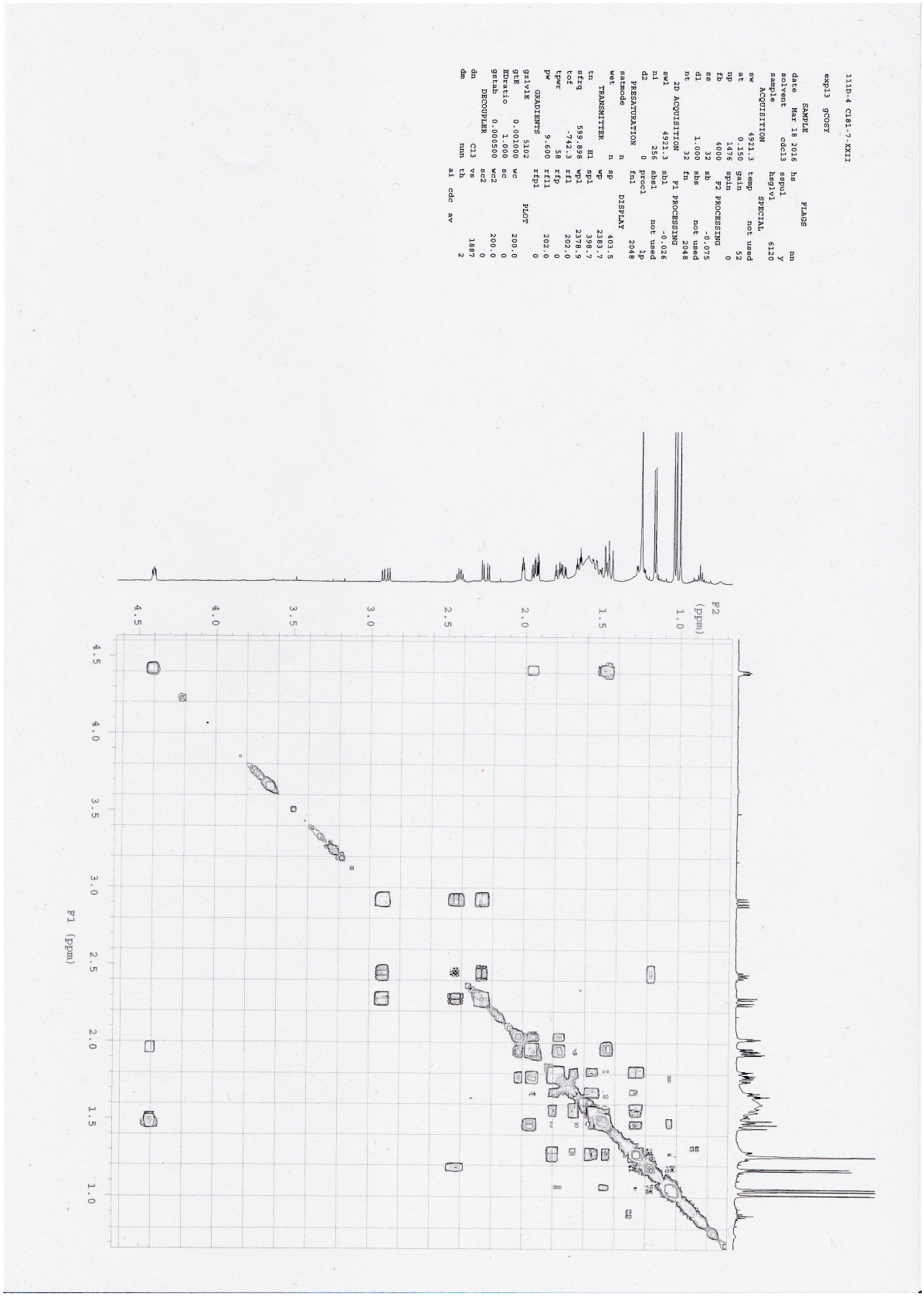

Figure S3. ^{1}H-^{1}H COSY of **1**.

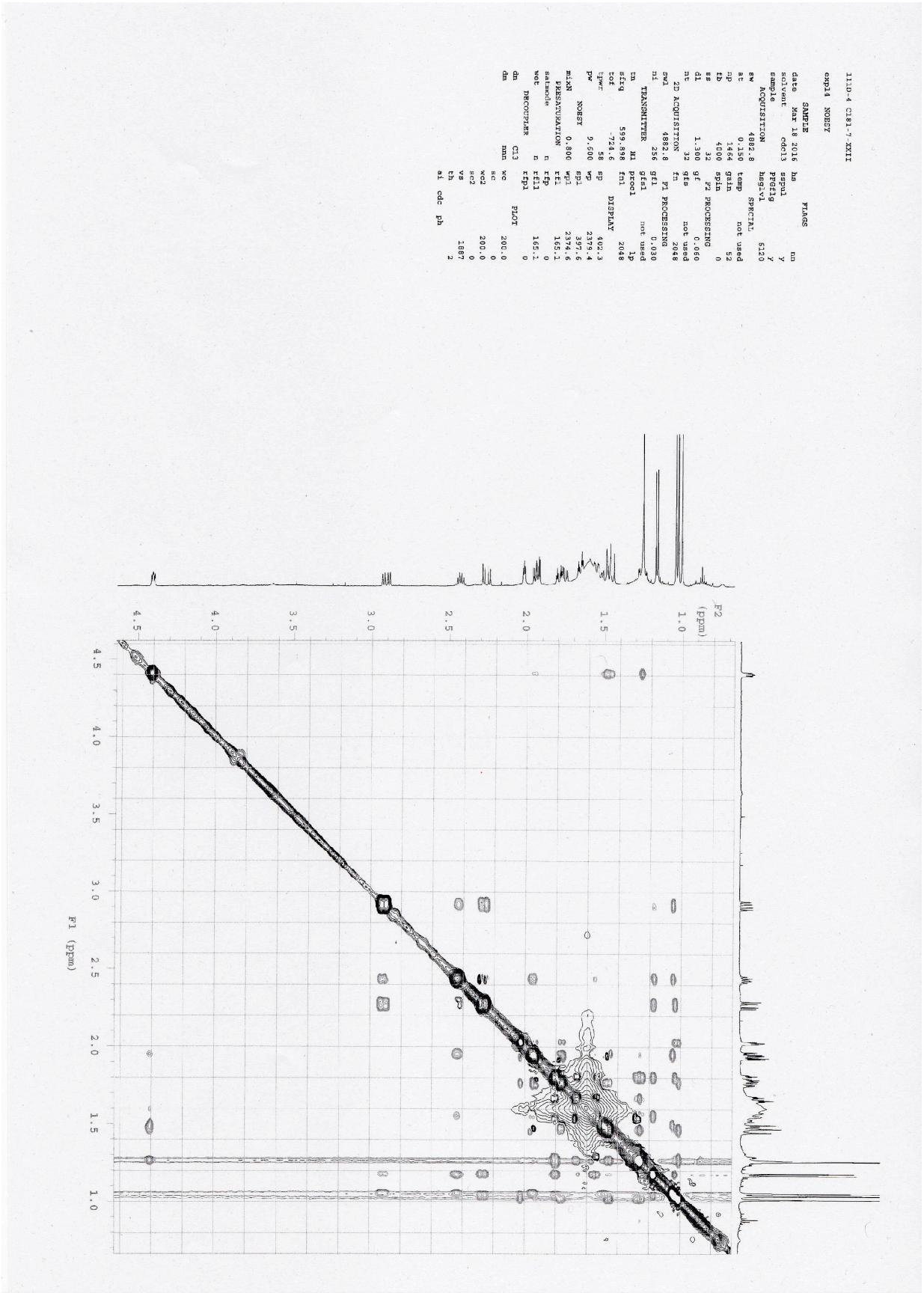

Figure S4. NOESY of 1.

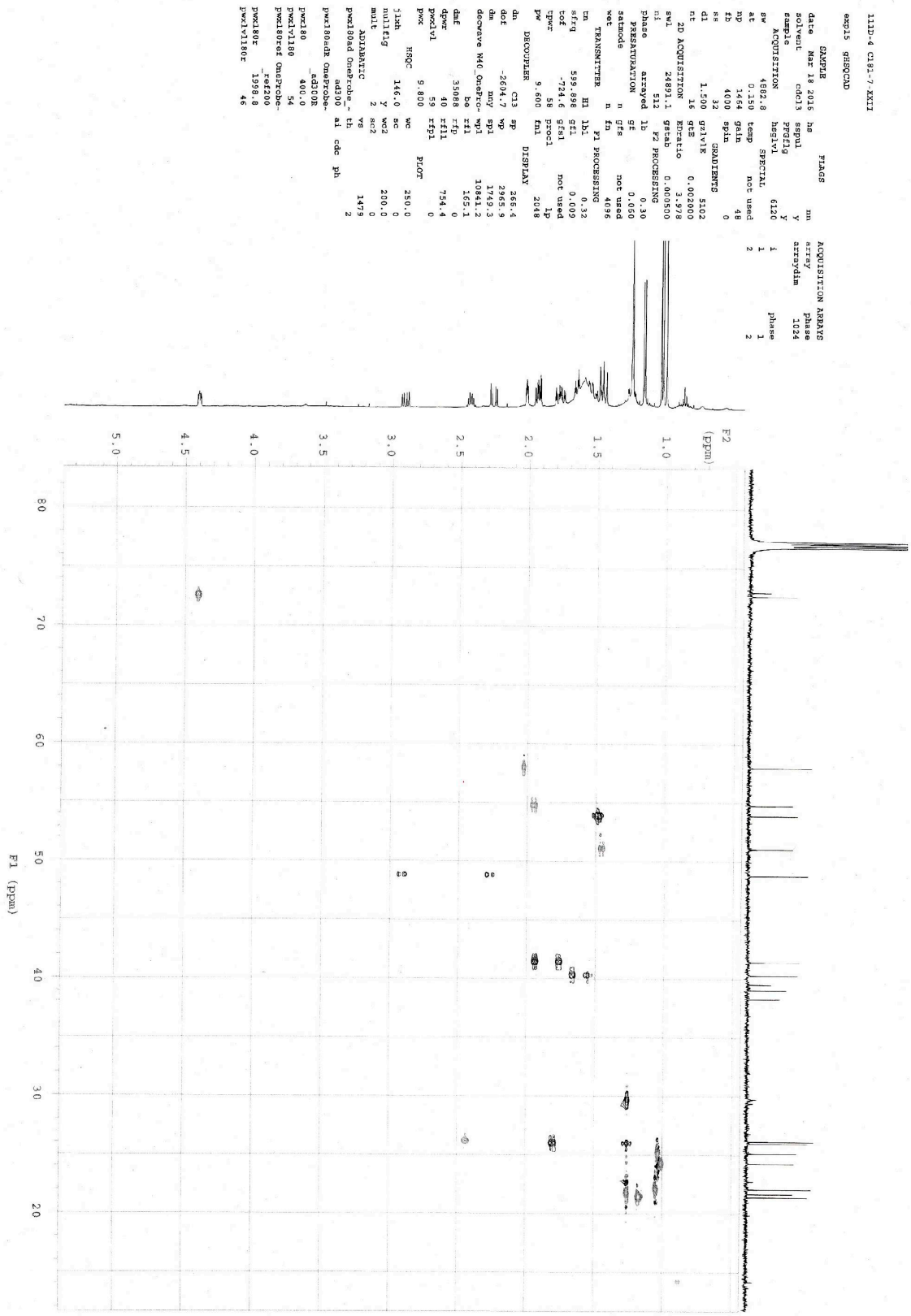

Figure S5. HMQC of **1**.

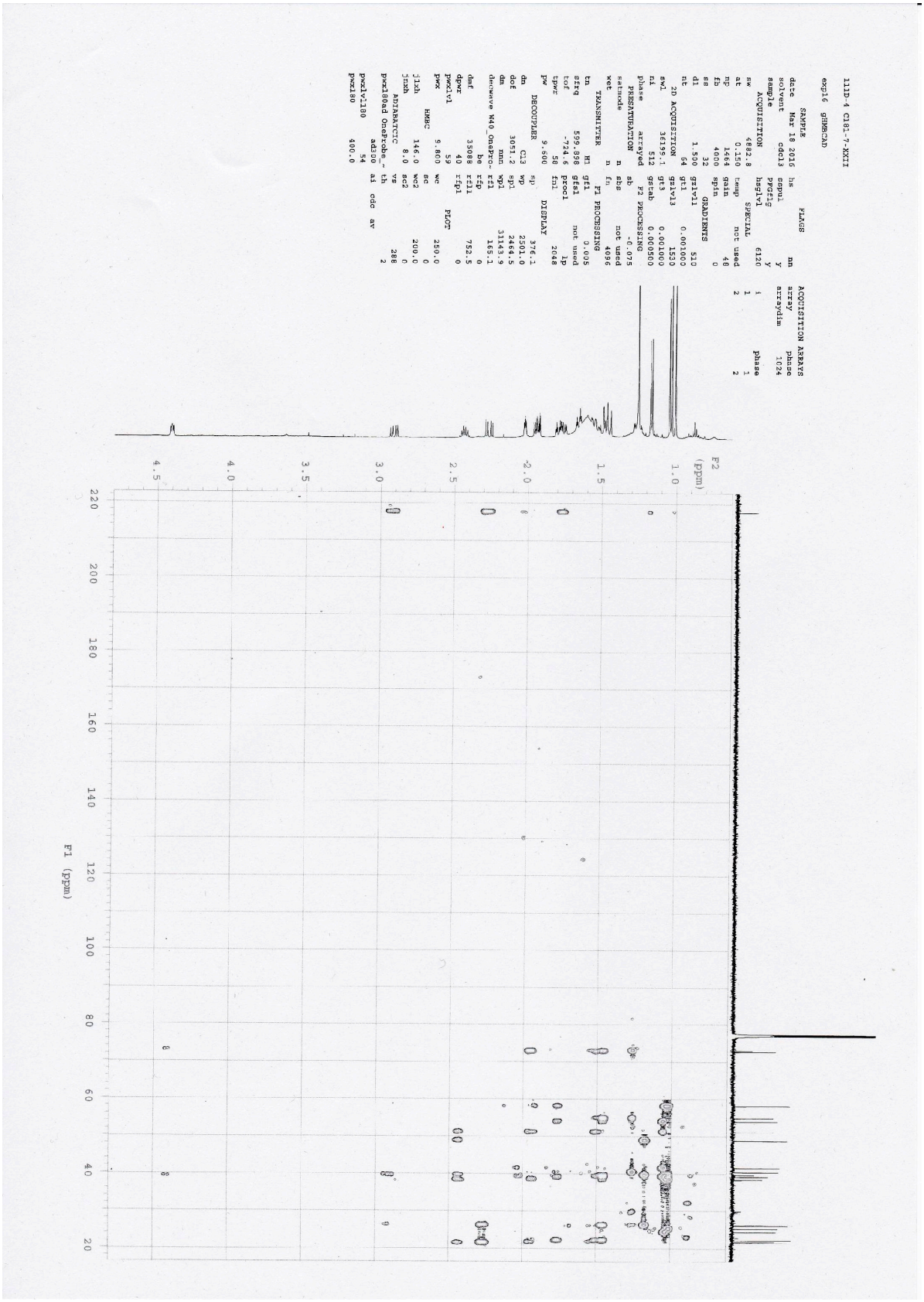

Figure S6. HMBC of 1.

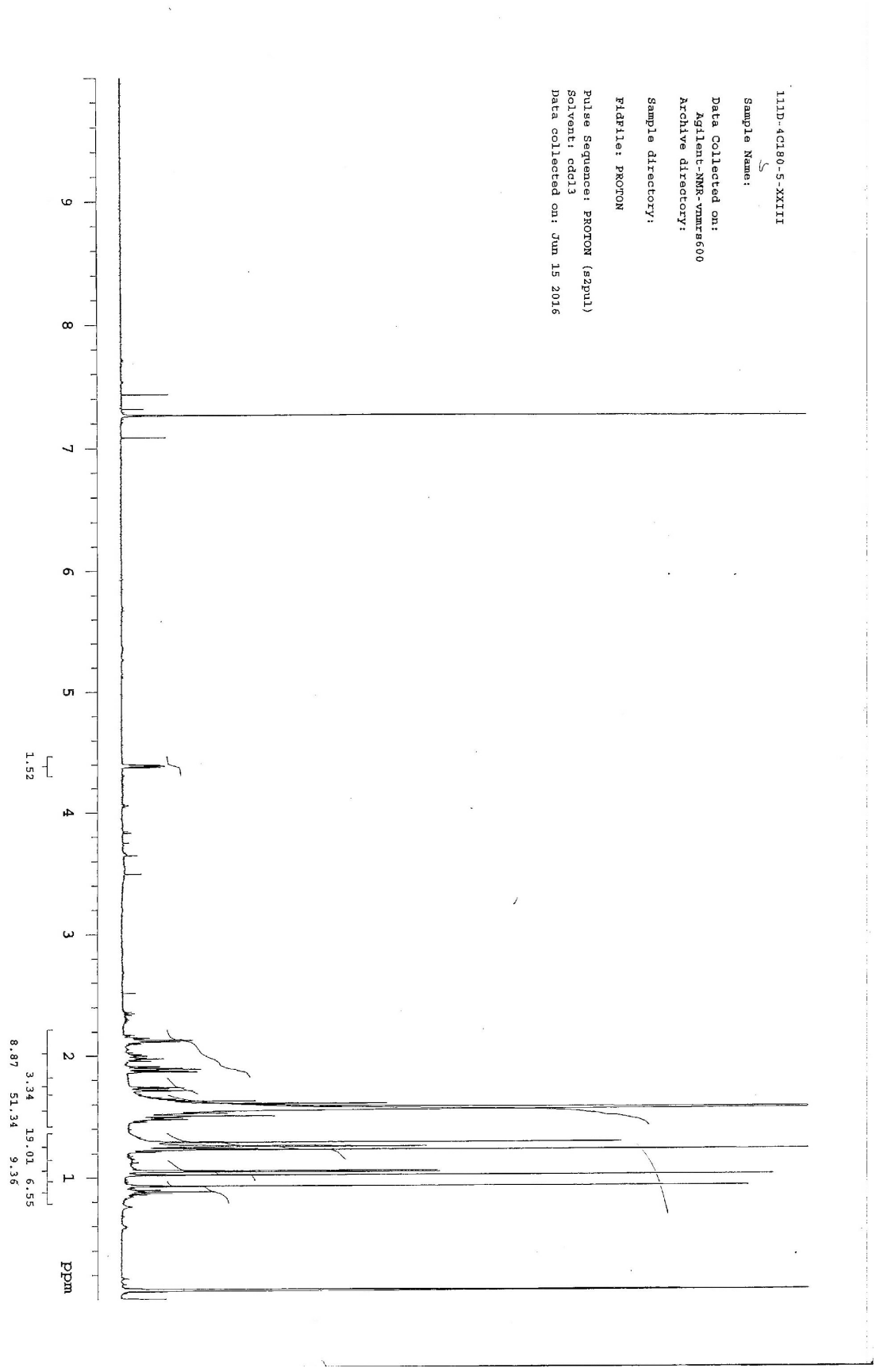

Figure S7. ^{1}H NMR pectrum of **2** in $CDCl_3$.

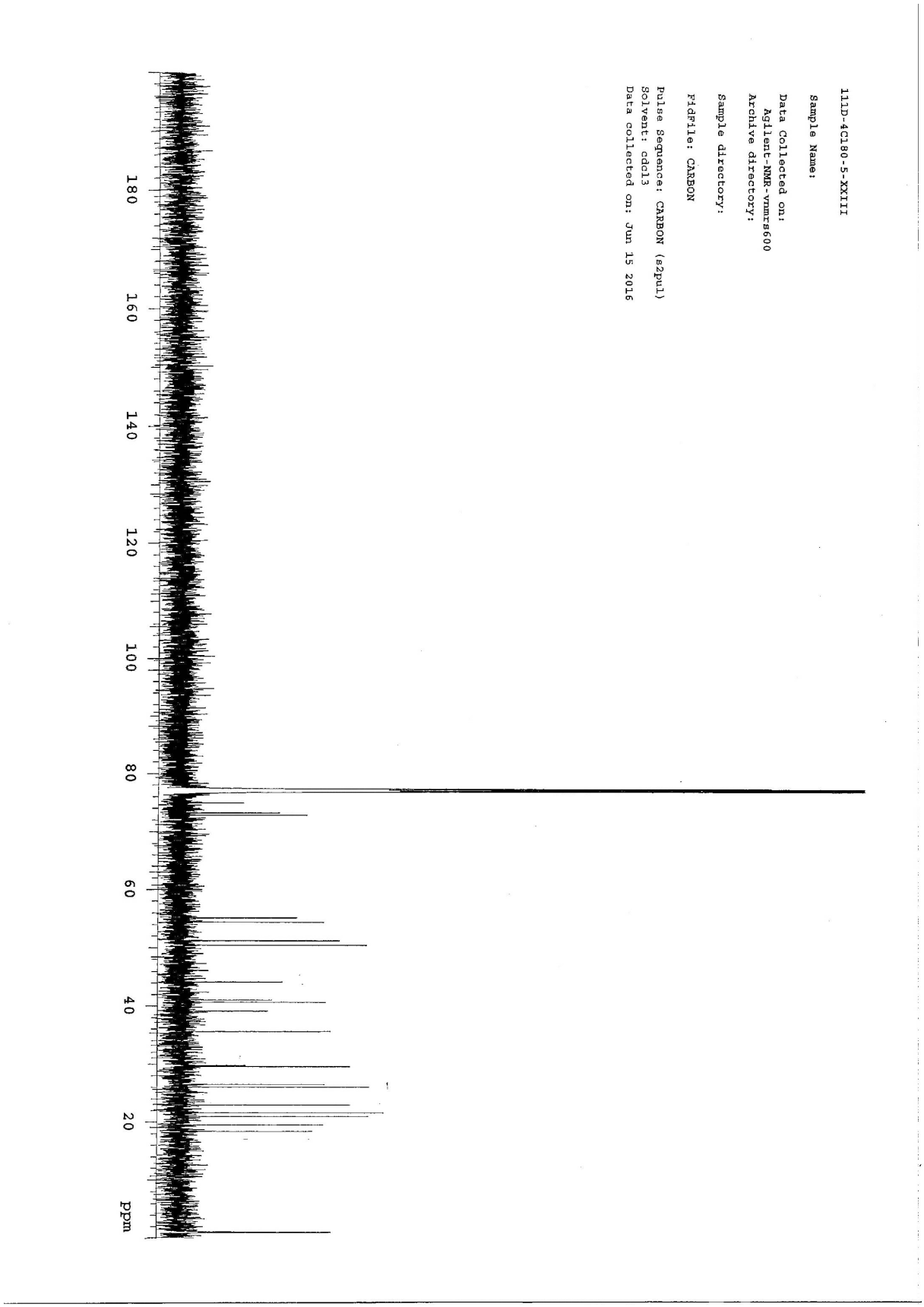

Figure S8. ^{13}C NMR spectrum of 2 in $CDCl_3$.

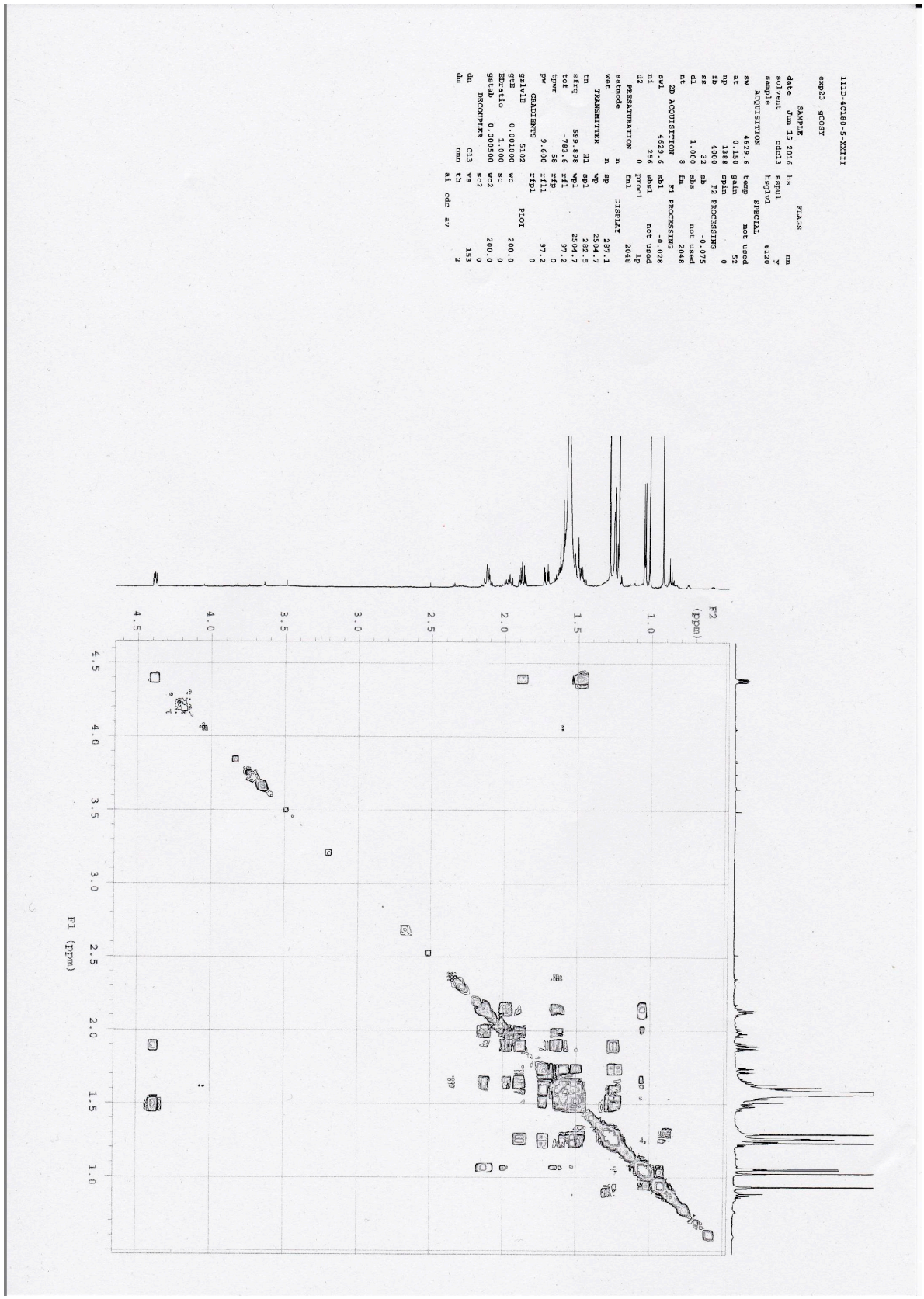

Figure S9. ^{1}H-^{1}H COSY of **2**.

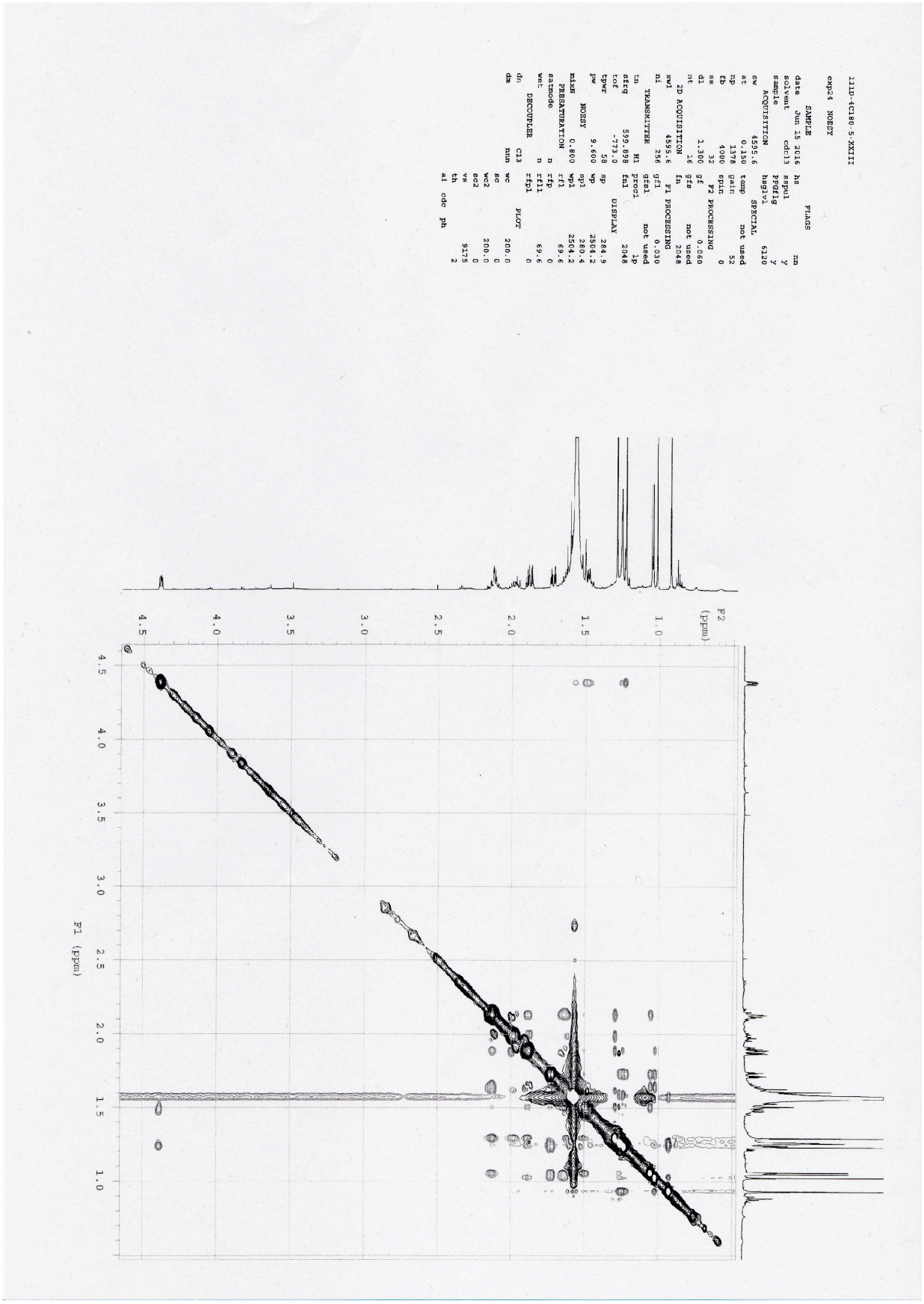

Figure S10. NOESY of **2**.

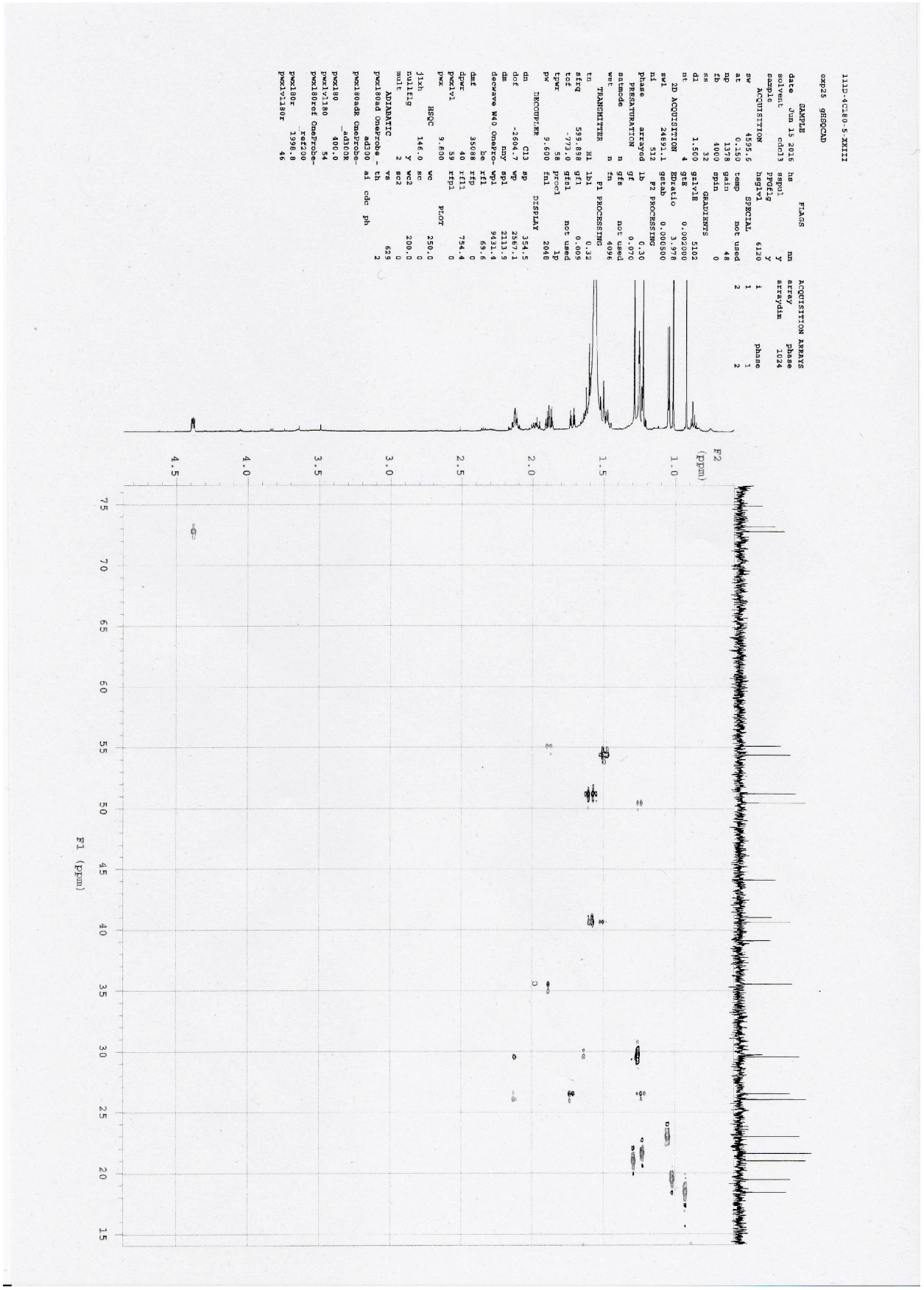

Figure S11. HMQC of **2**.

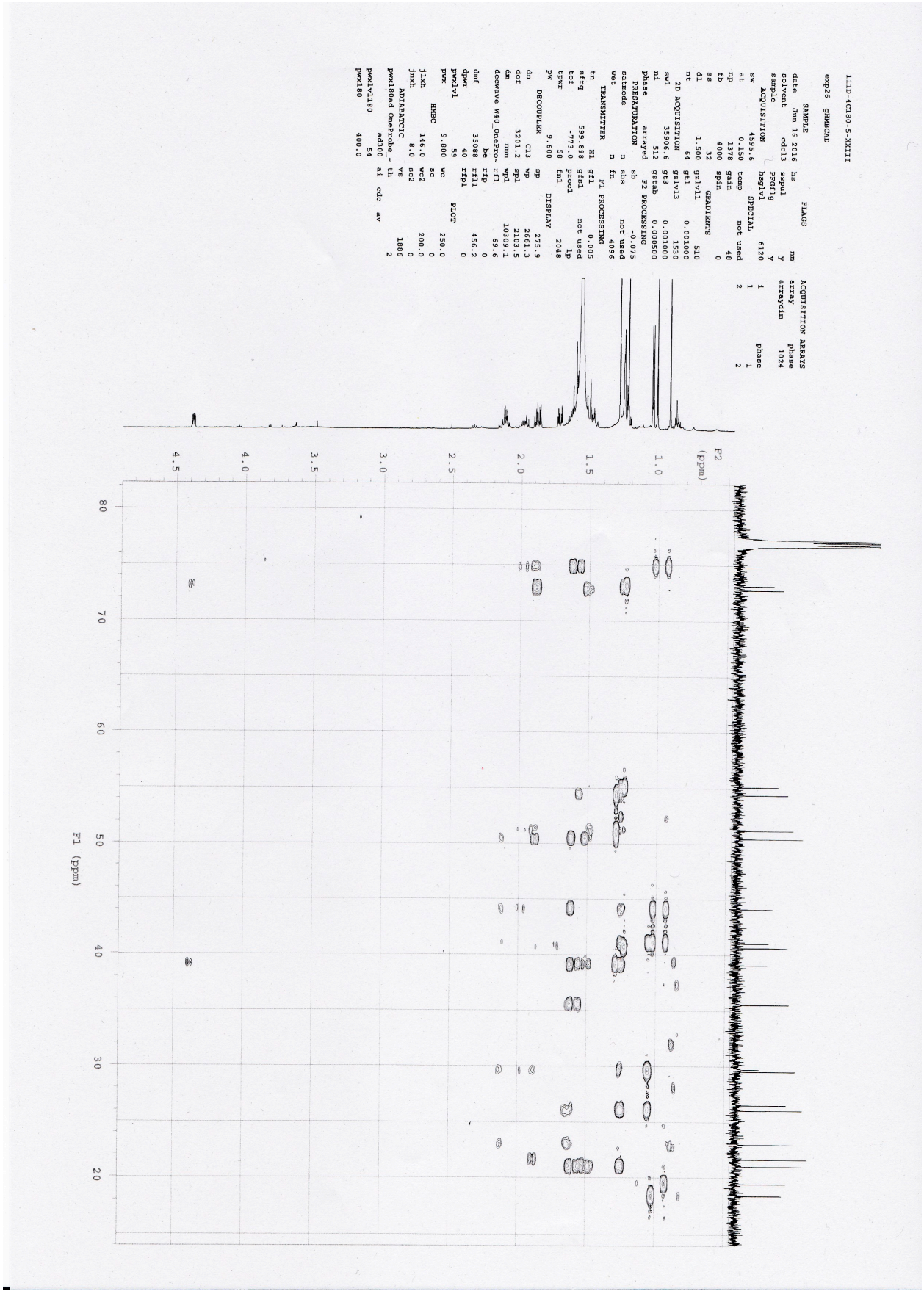

Figure S12. HMBC of **2**.

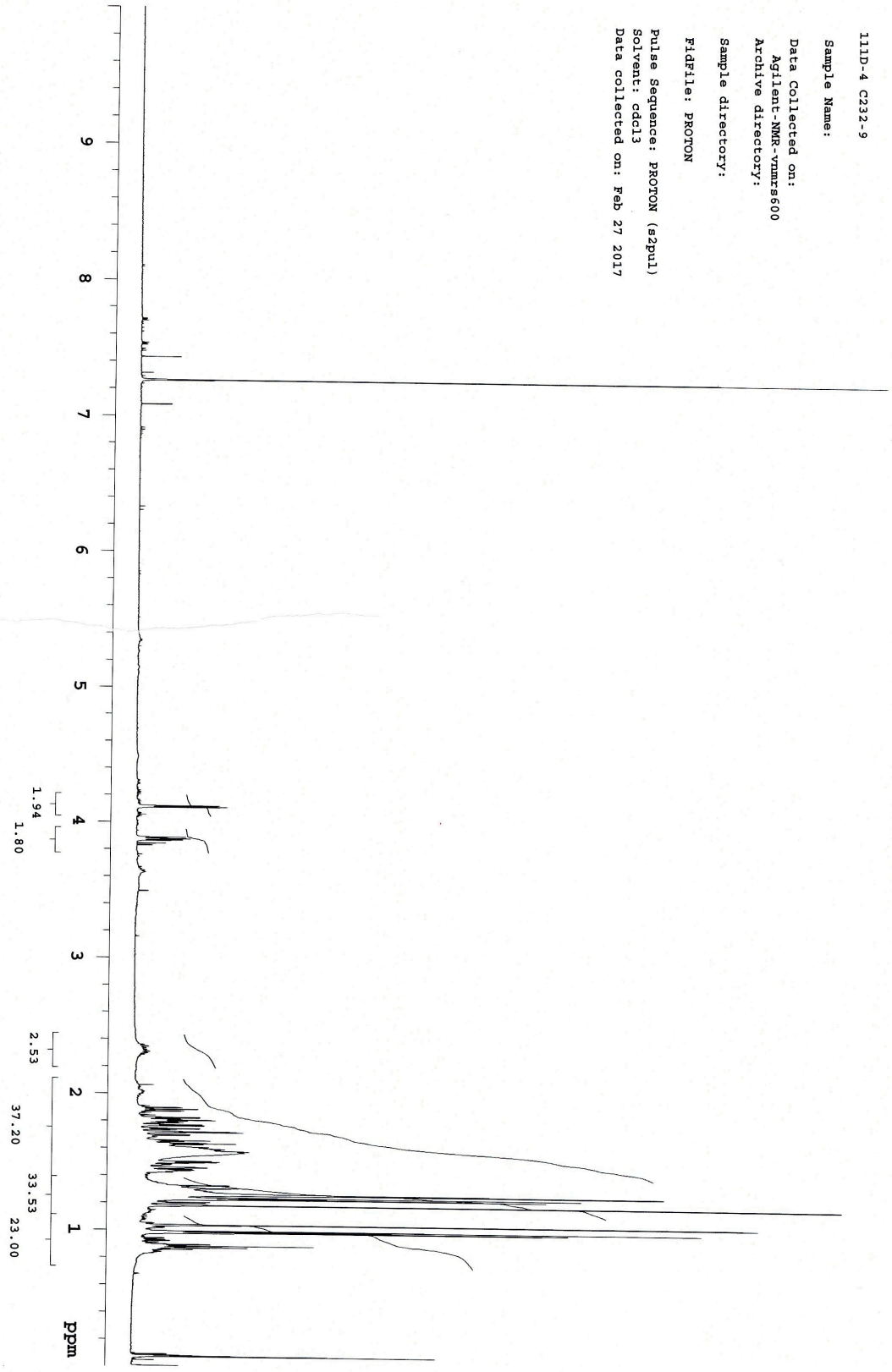

Figure S13. ^{1}H NMR spectrum of **3** in $CDCl_3$.

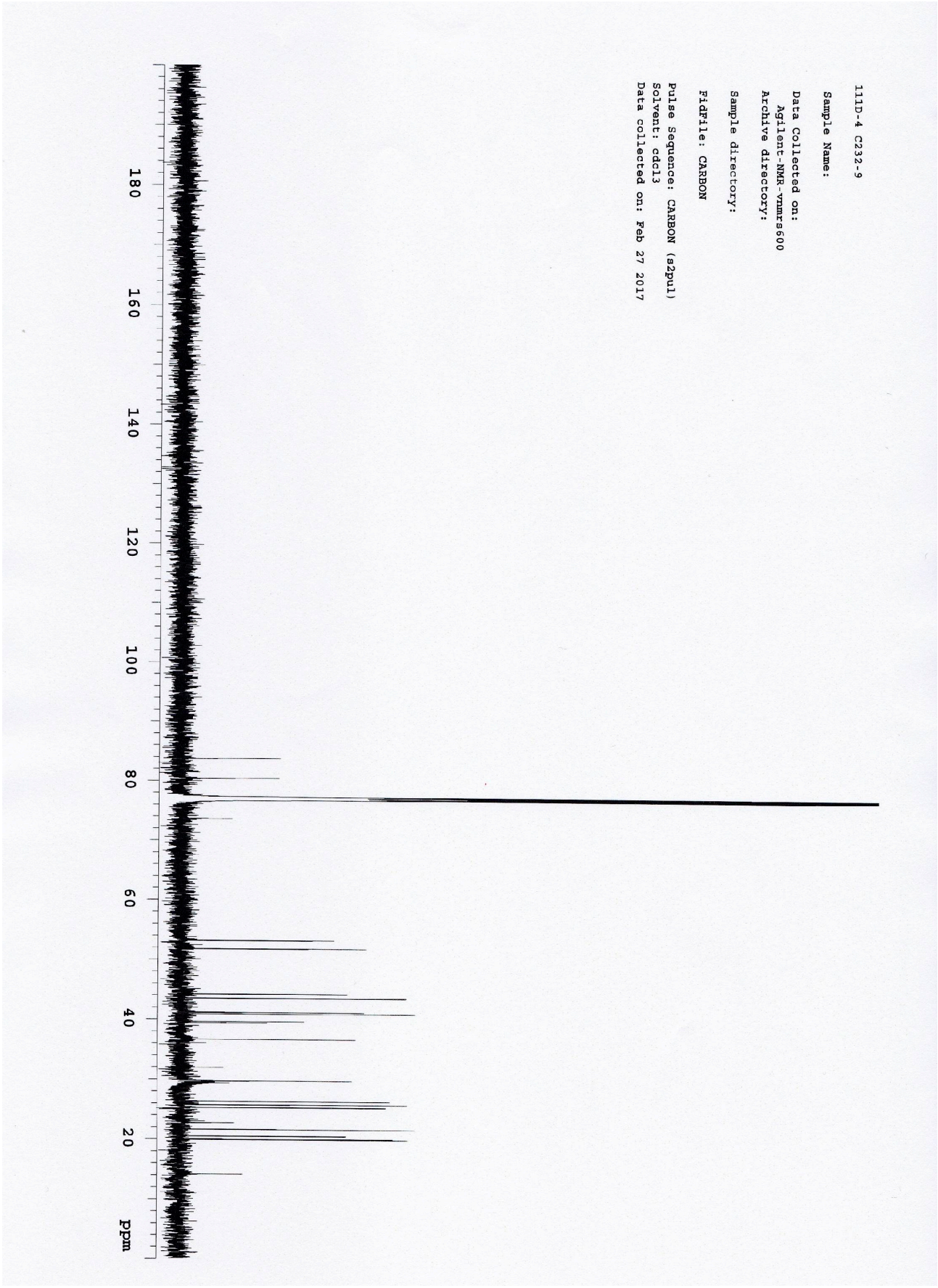

Figure S14. ^{13}C NMR spectrum of **3** in $CDCl_3$.

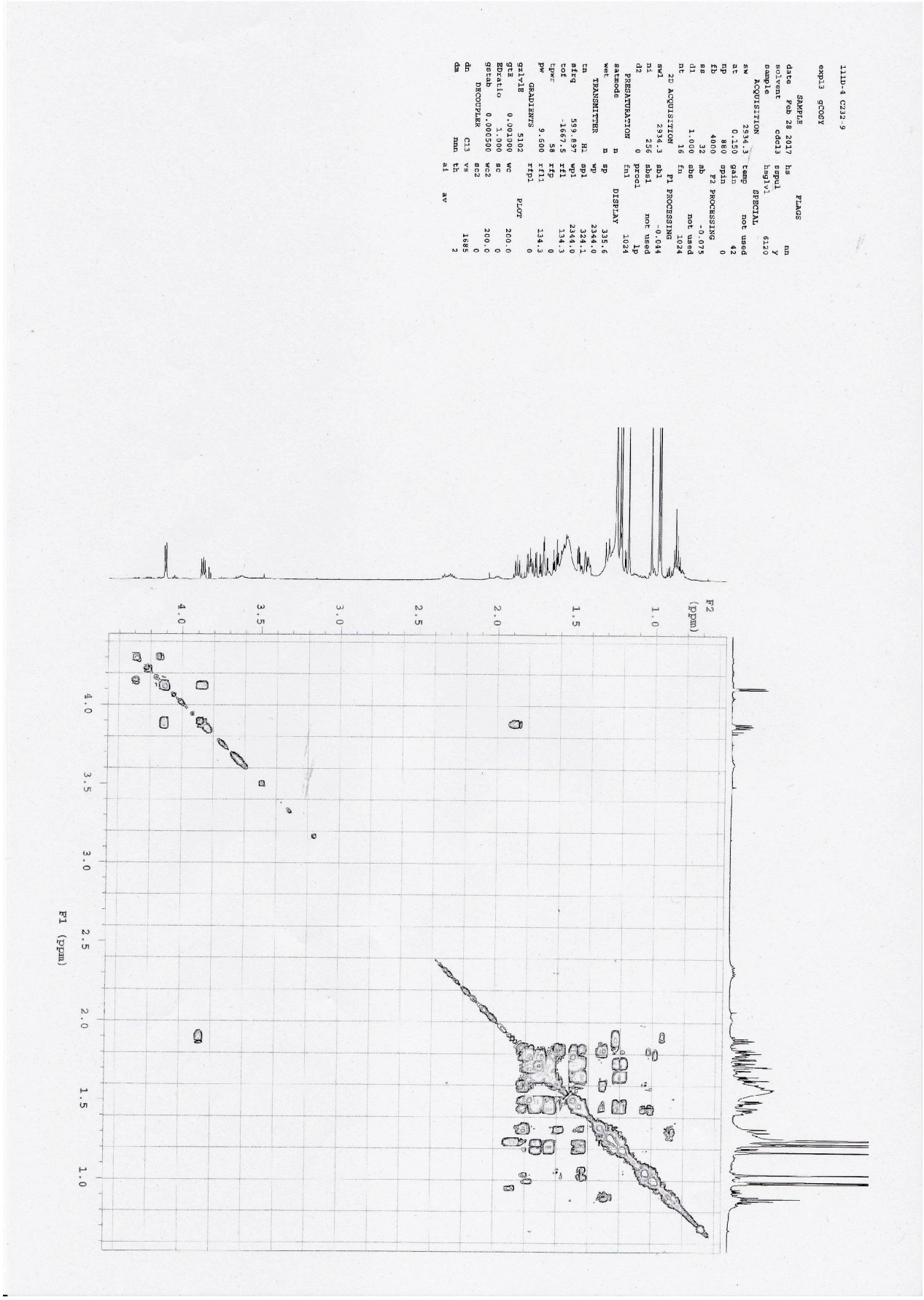

Figure S15. ^{1}H-^{1}H COSY of **3**.

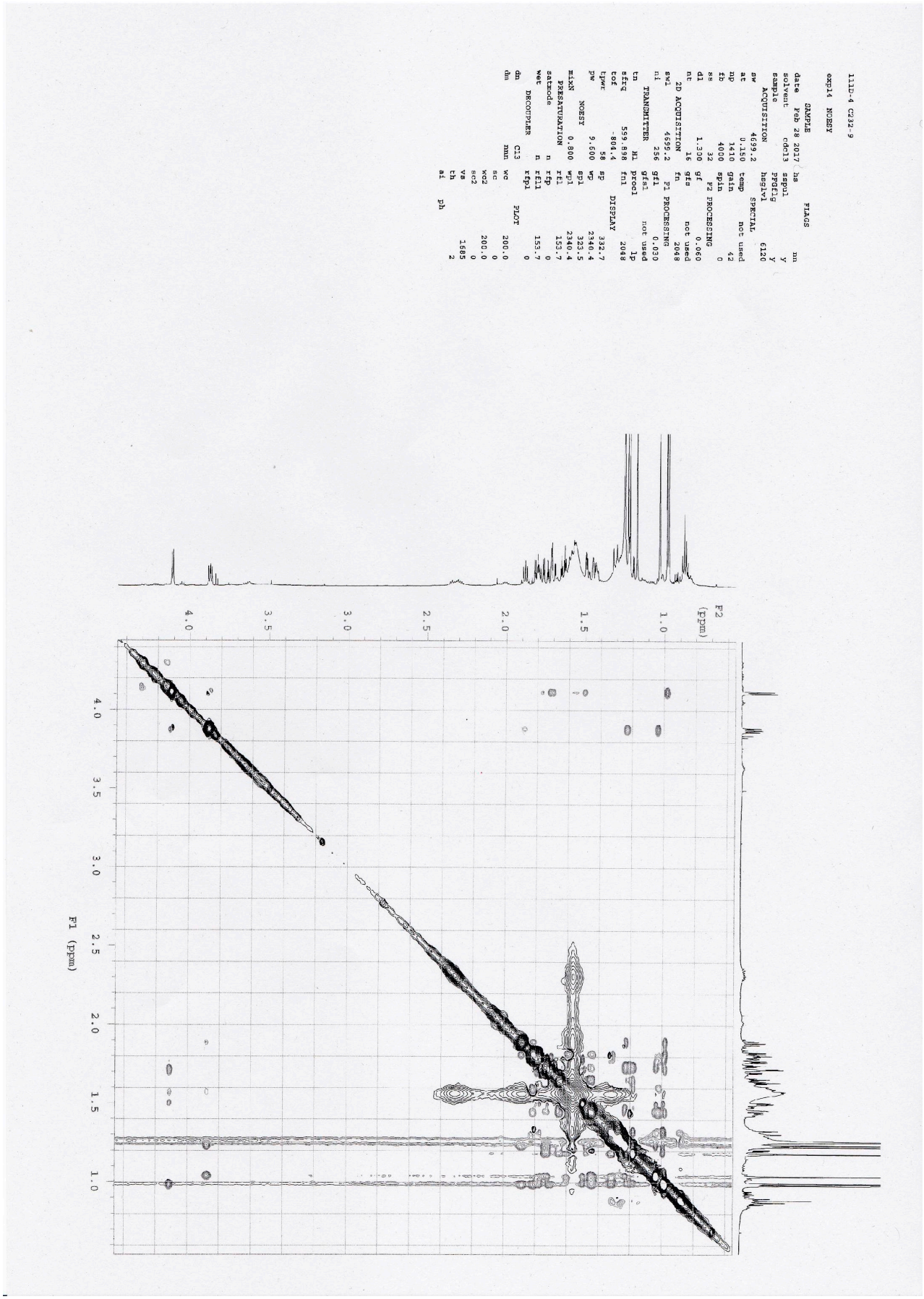

Figure S16. NOESY of **3**.

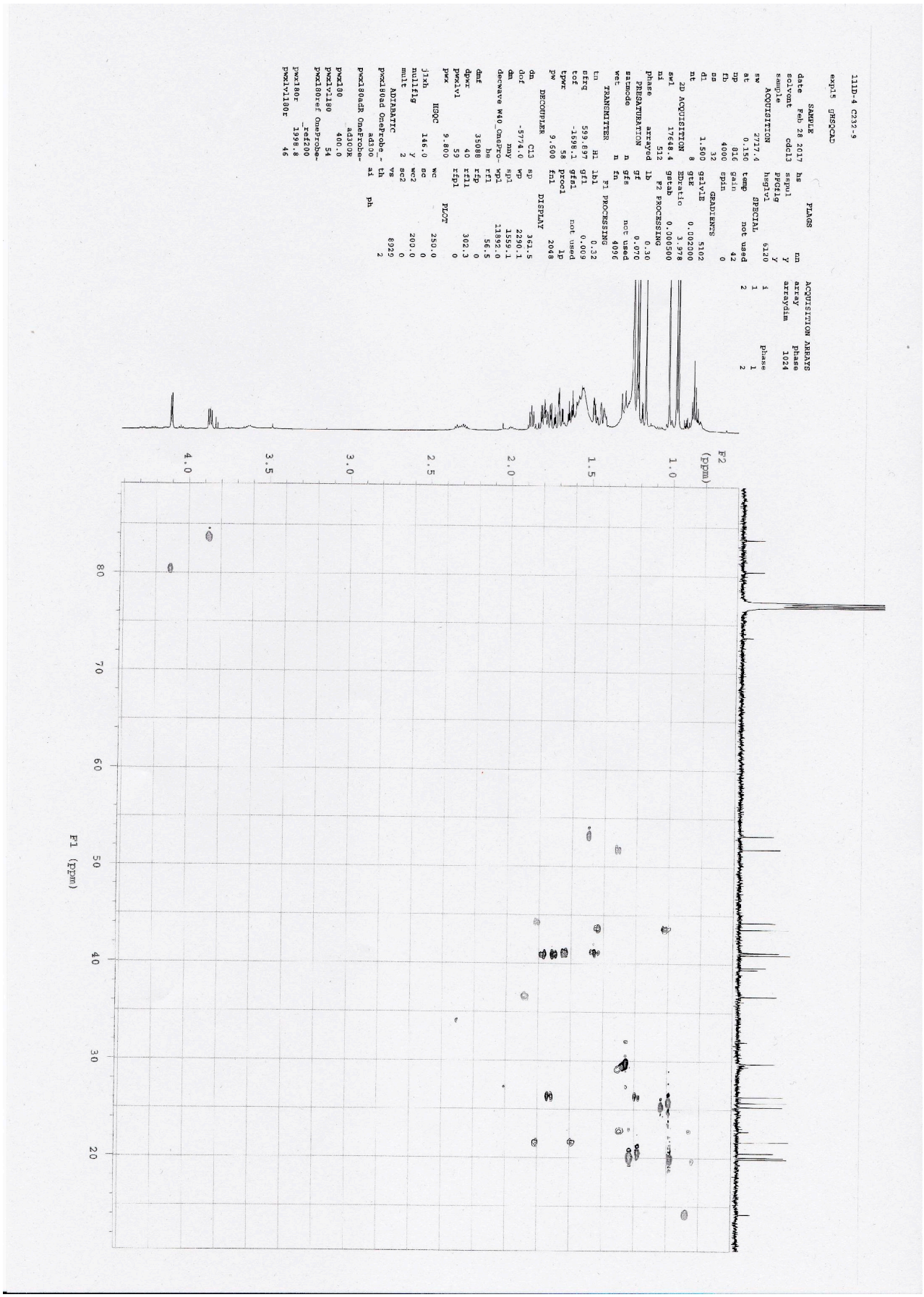

Figure S17. HMQC of **3**.

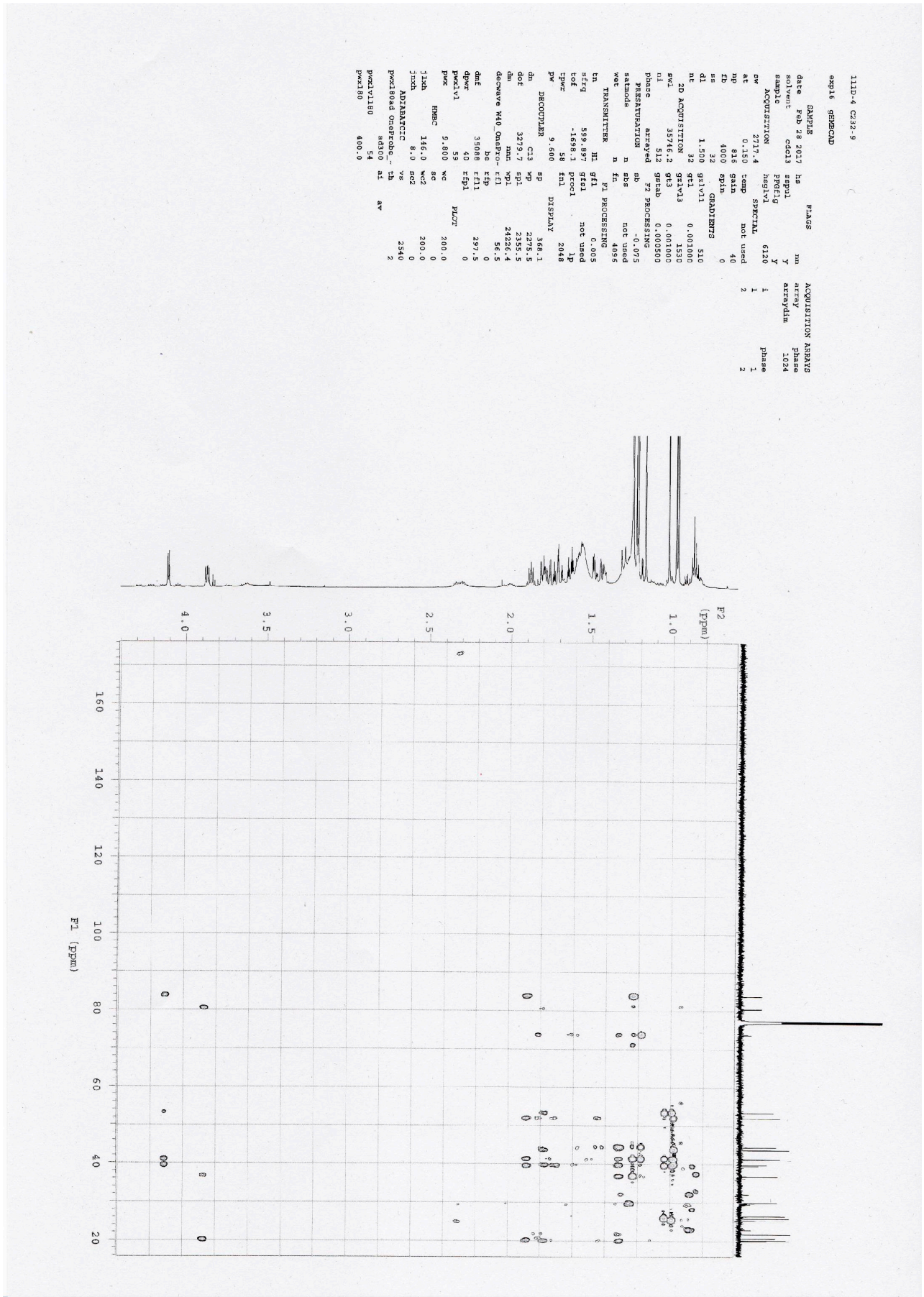

Figure S18. HMBC of **3**.

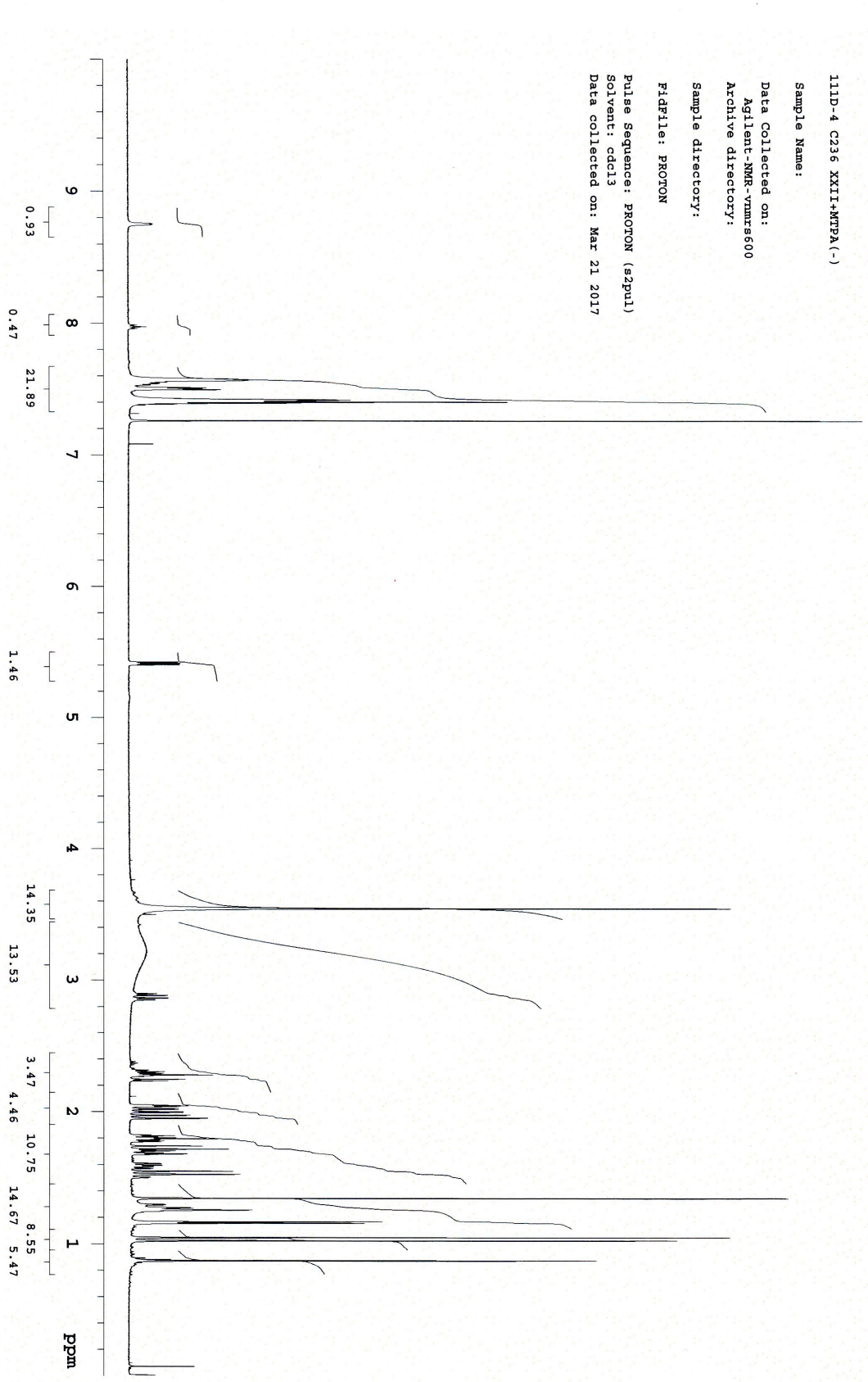

Figure S19. ^{1}H NMR spectra of **1a** in $CDCl_3$.

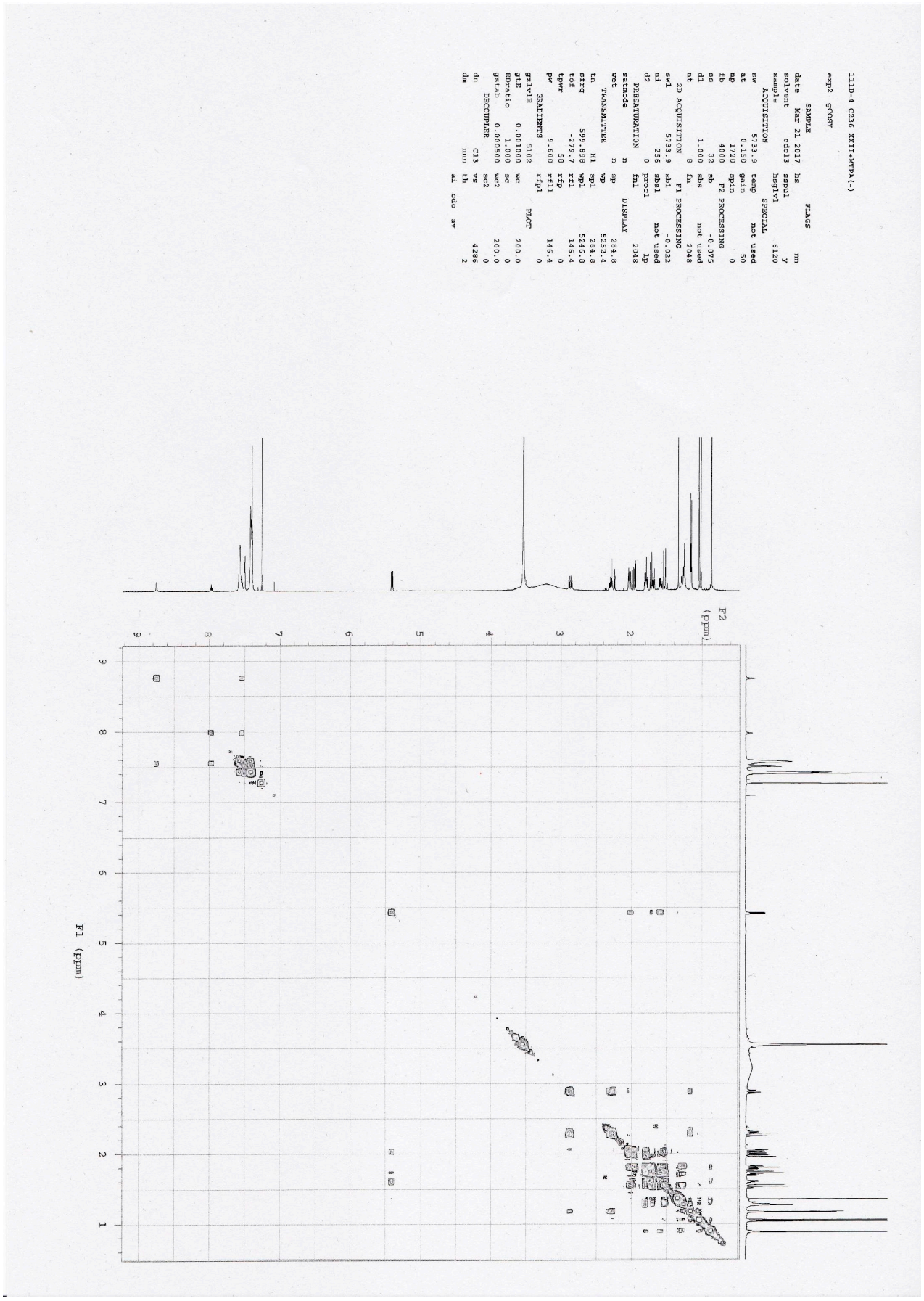

Figure S20. ^{1}H-^{1}H COSY of **1a**.

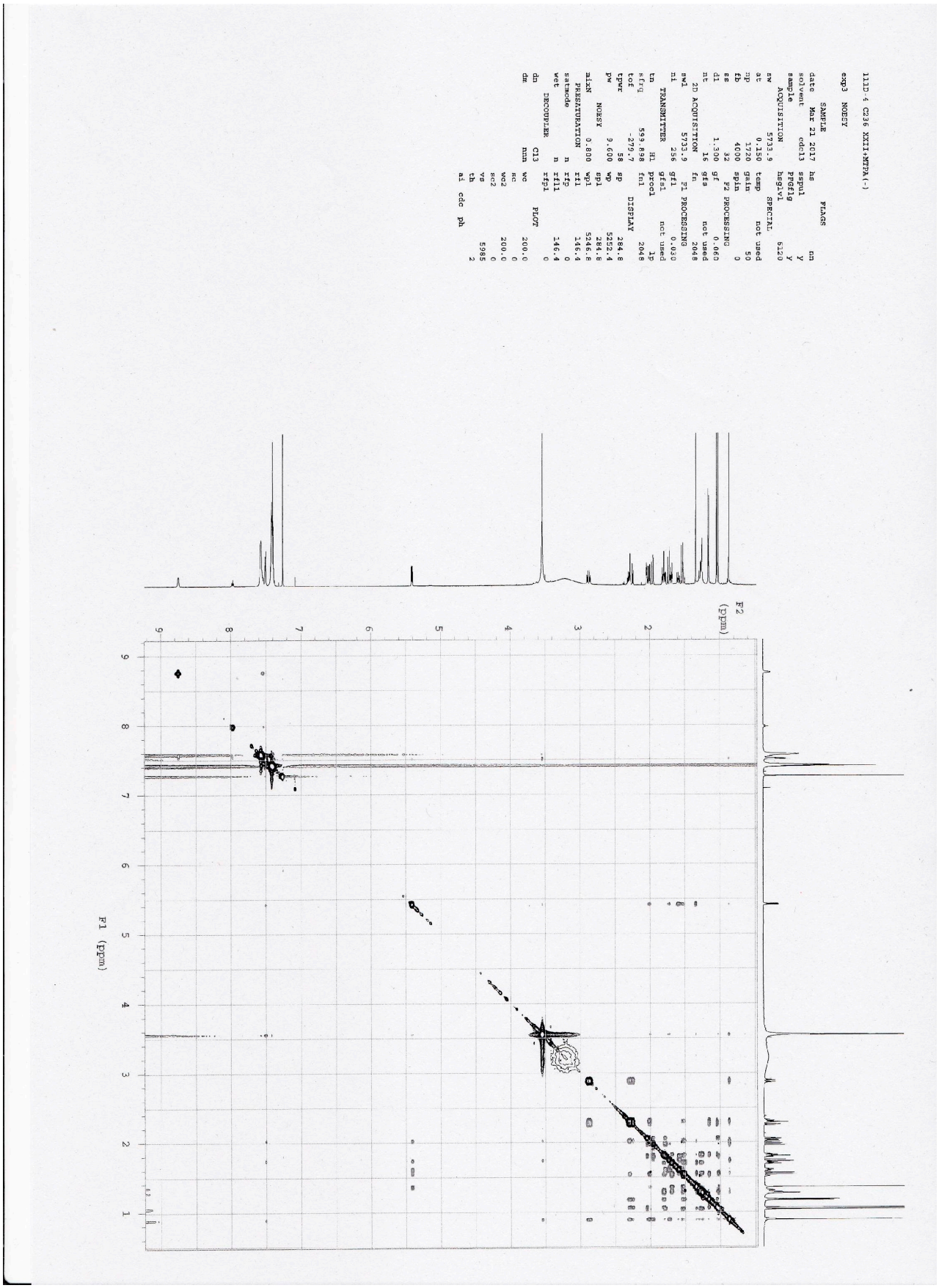

Figure S21. NOESY of **1a**.

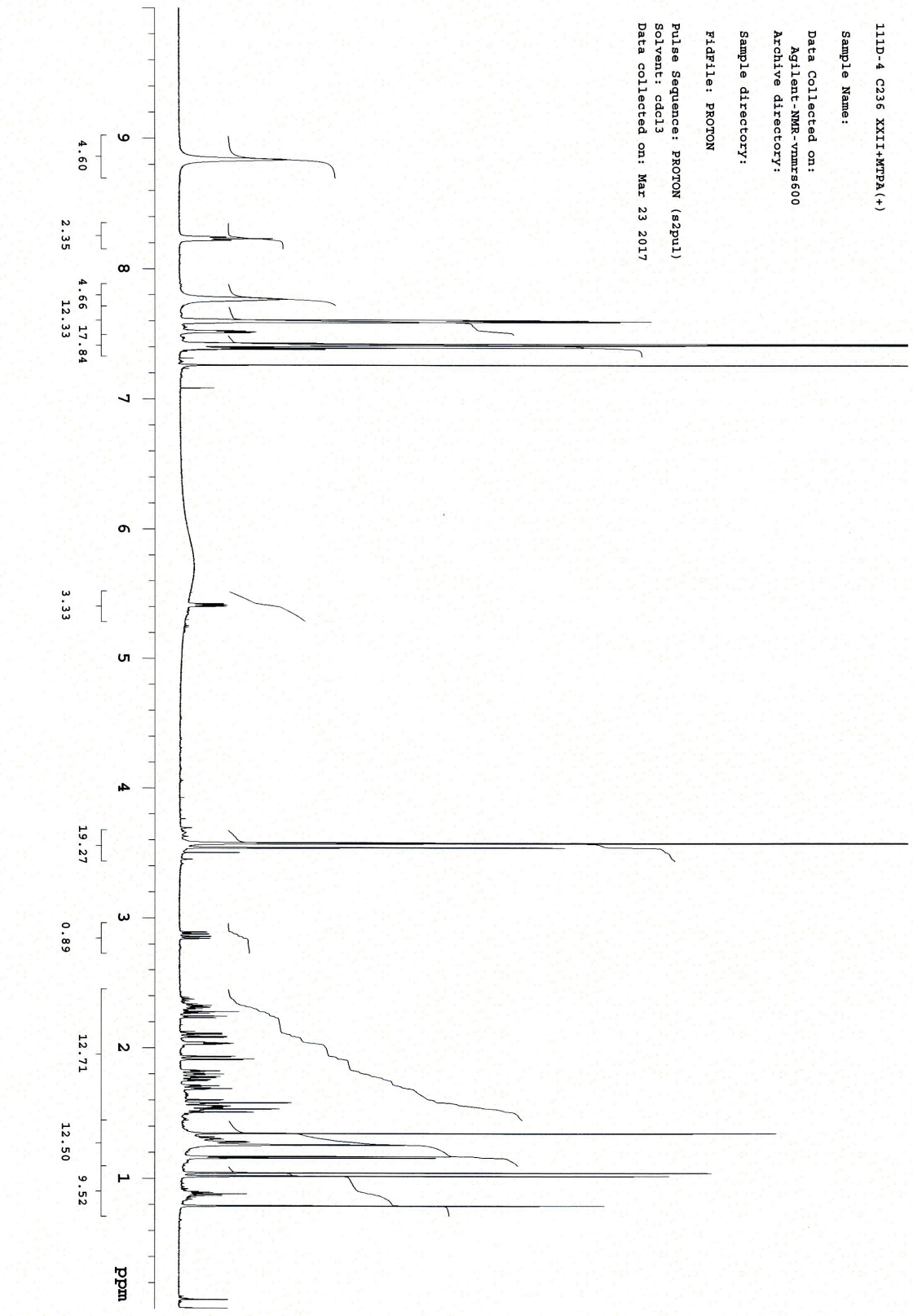

Figure S22. ^{1}H NMR spectra of **1b** in $CDCl_3$.

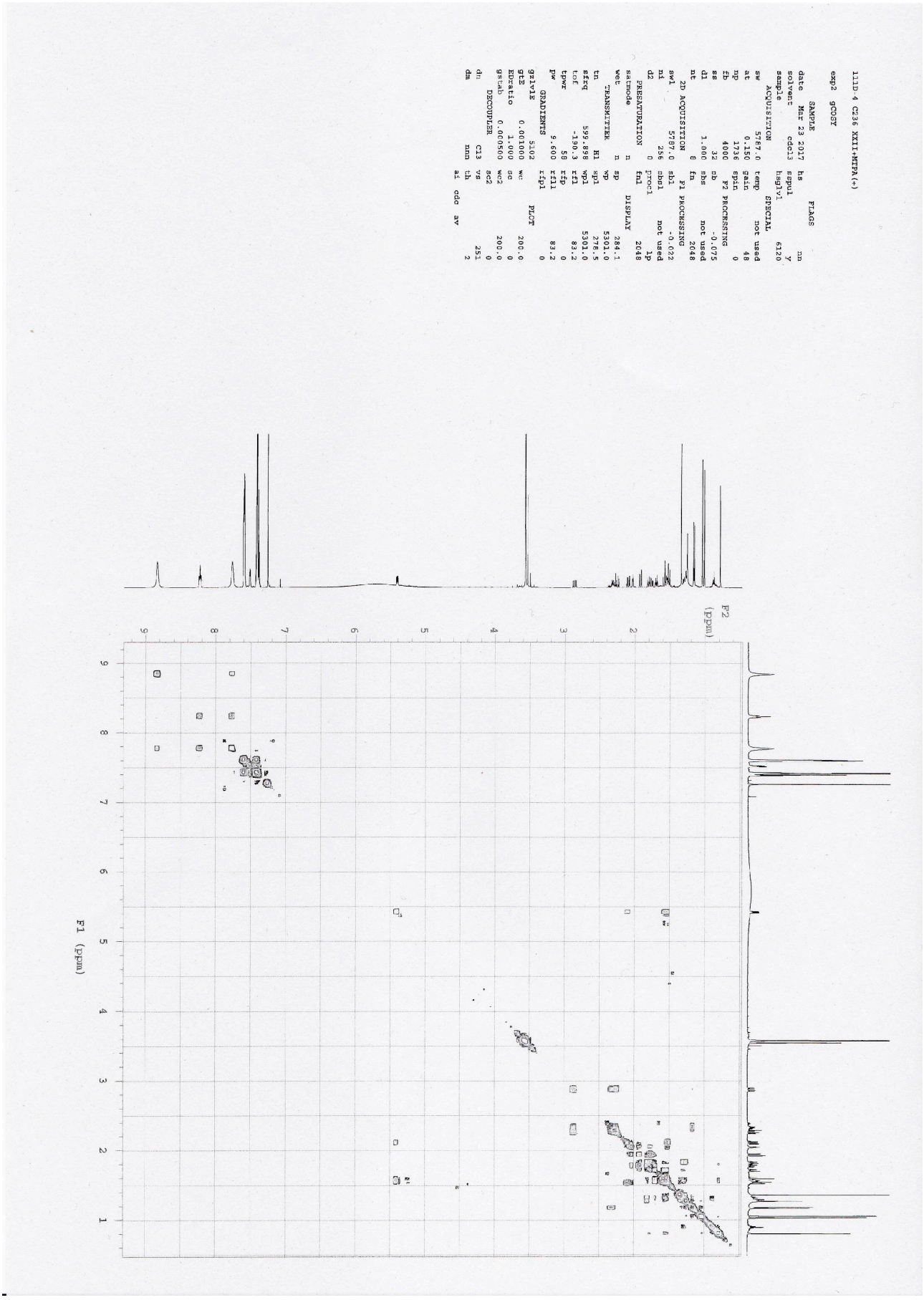

Figure S23. ^{1}H-^{1}H COSY of **1b**.

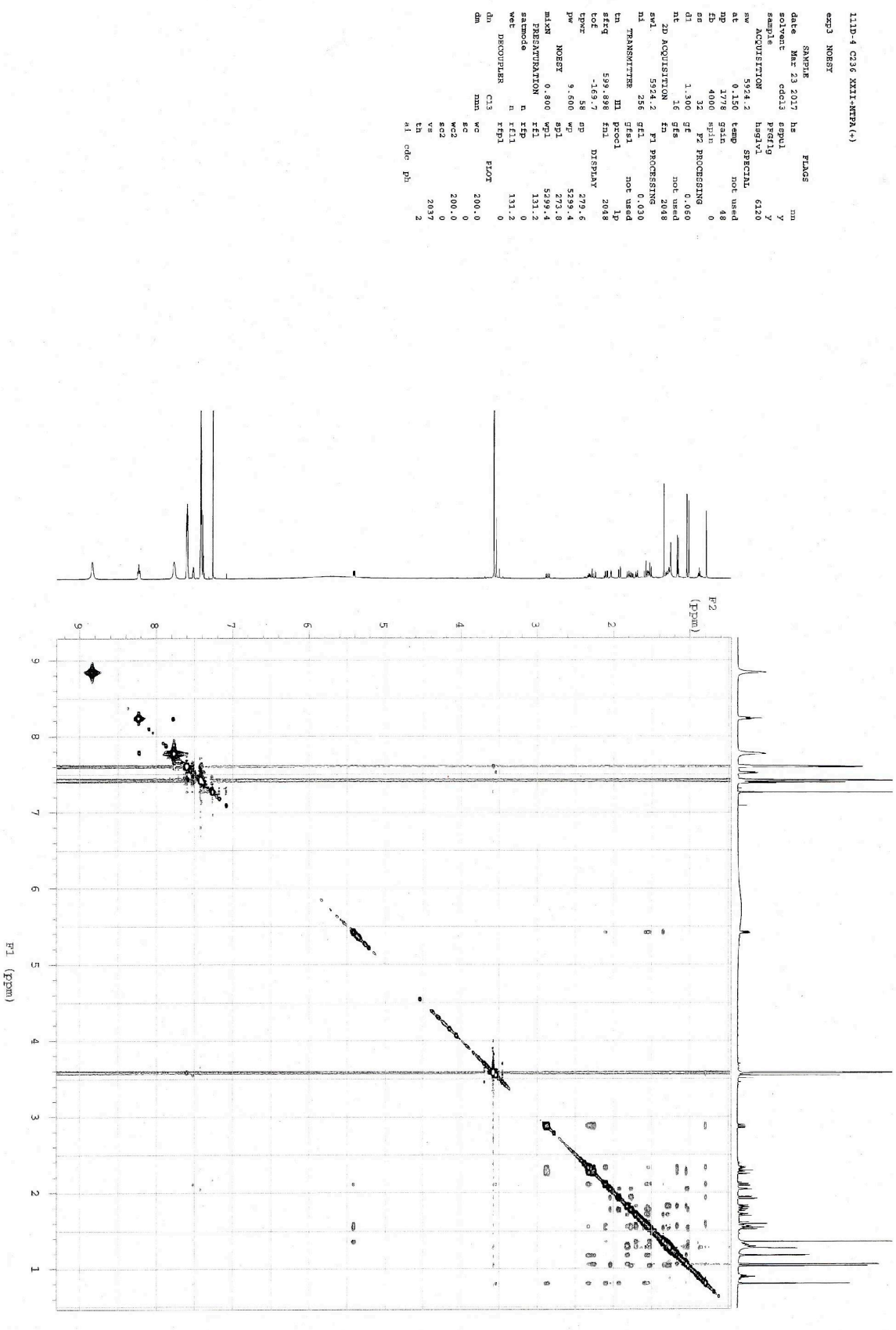

Figure S24. NOESY of **1b**.

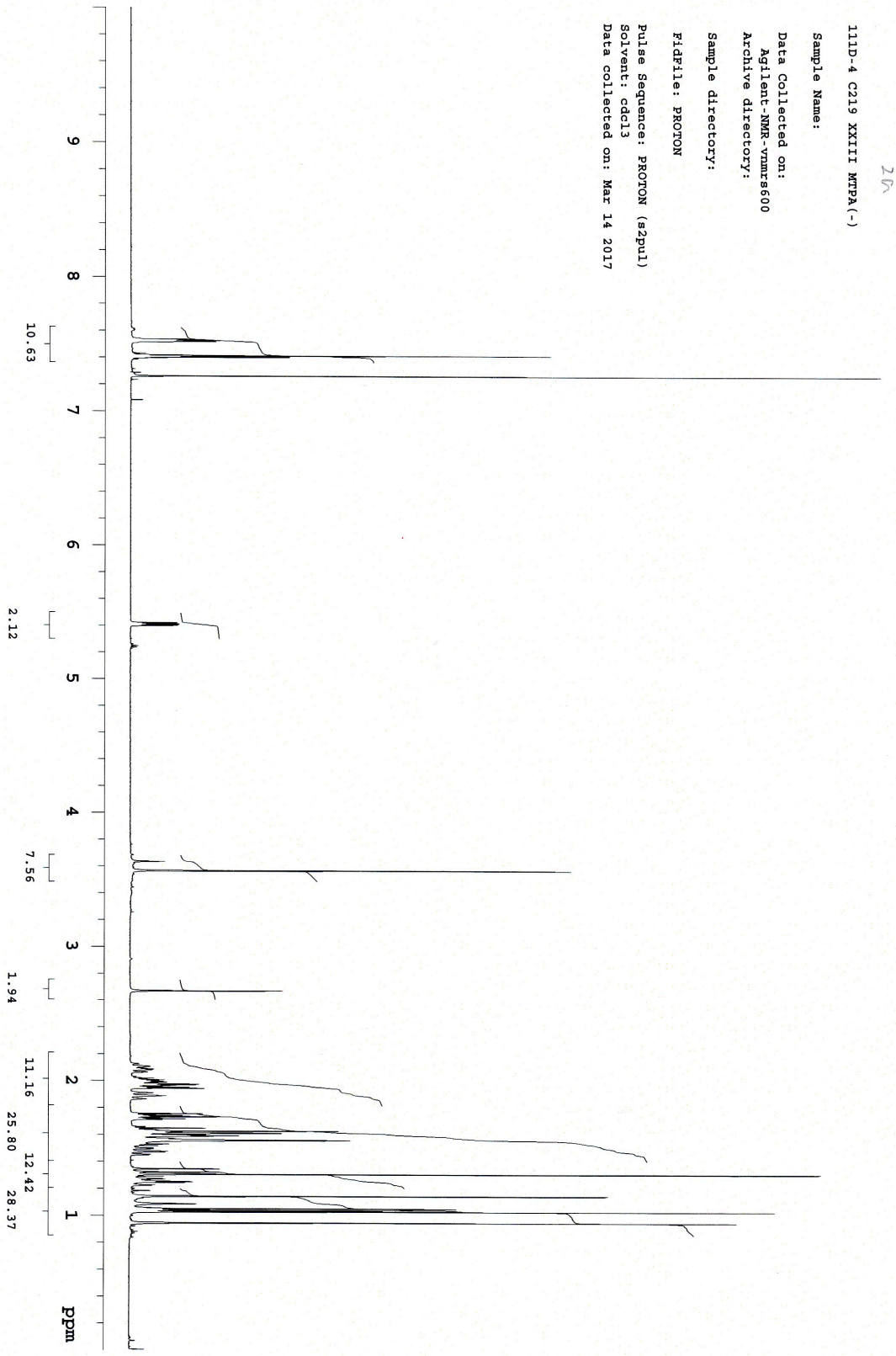

Figure S25. ^{1}H NMR spectra of **2a** in $CDCl_3$.

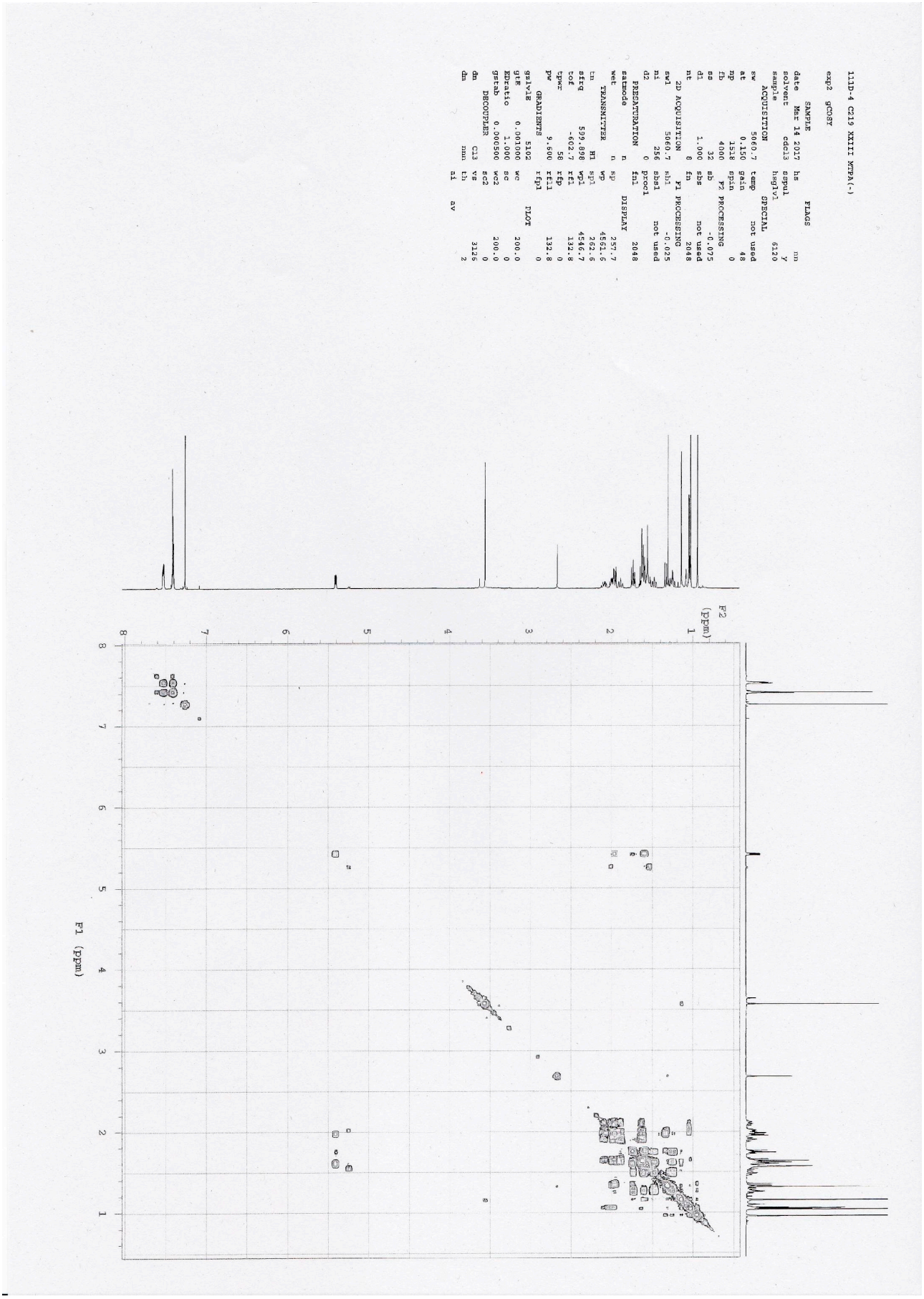

Figure S26. ^{1}H-^{1}H COSY of **2a**.

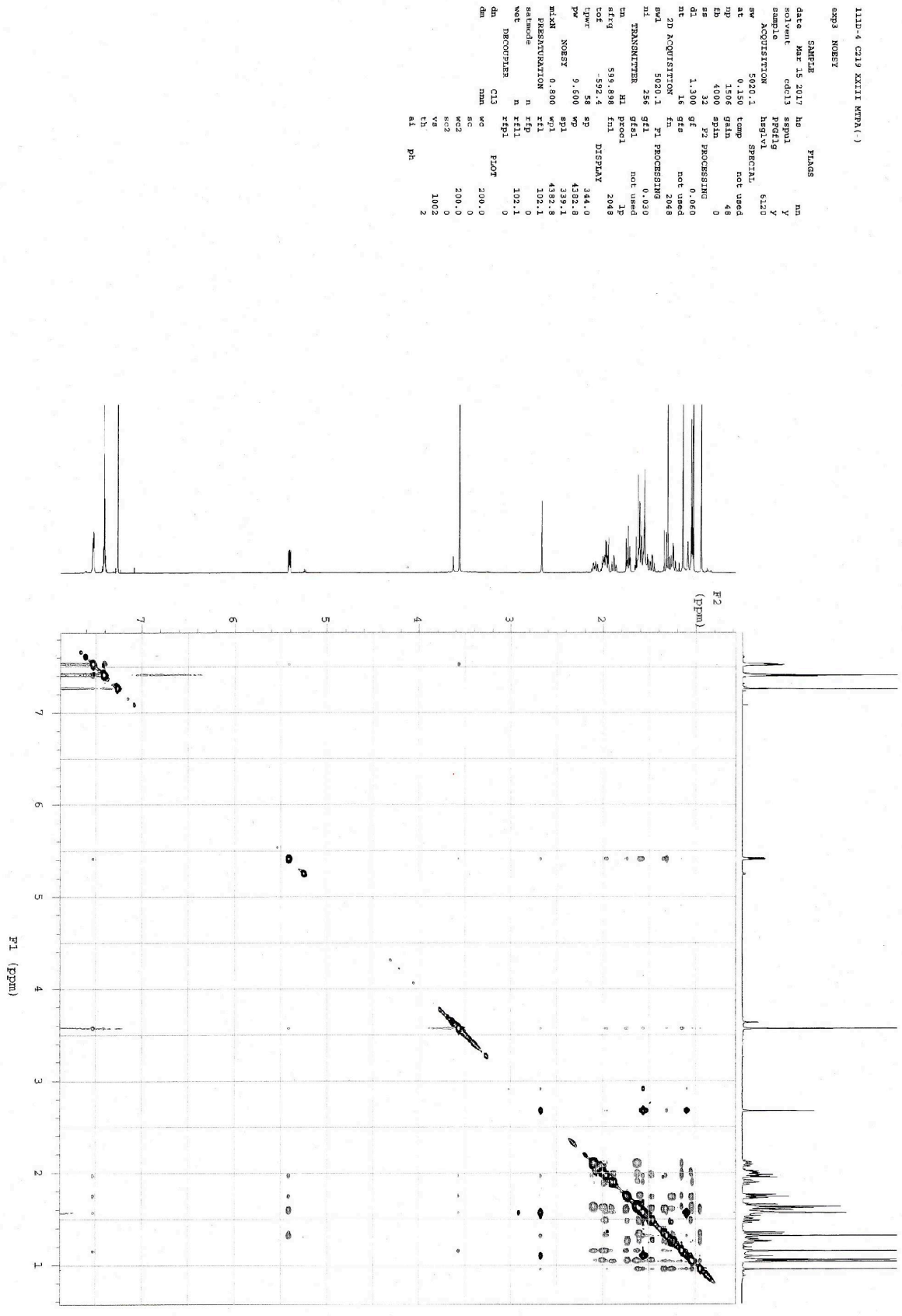

Figure S27. NOESY of **2a**.

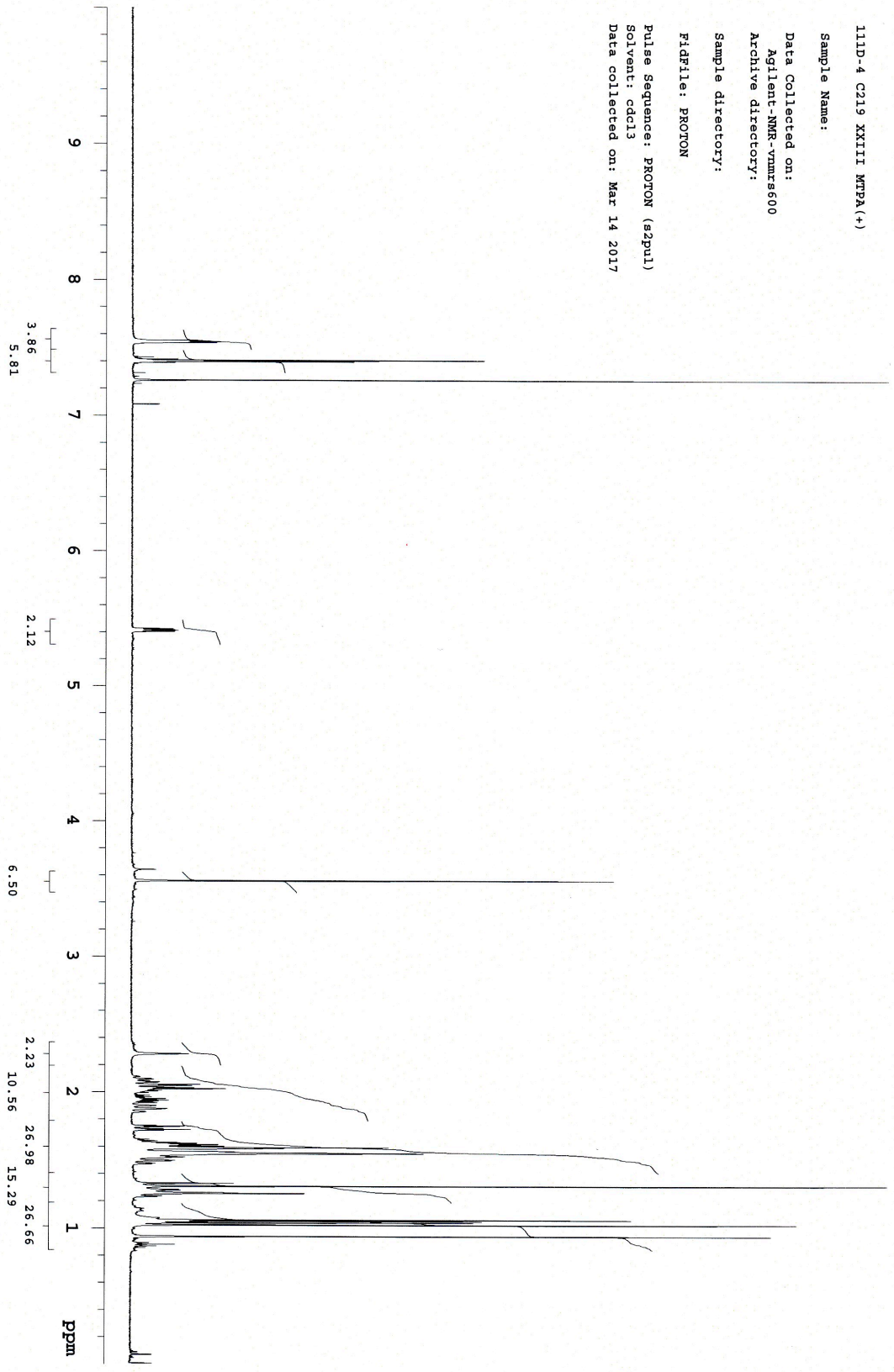

Figure S28. ^{1}H NMR spectra of **2b** in $CDCl_3$.

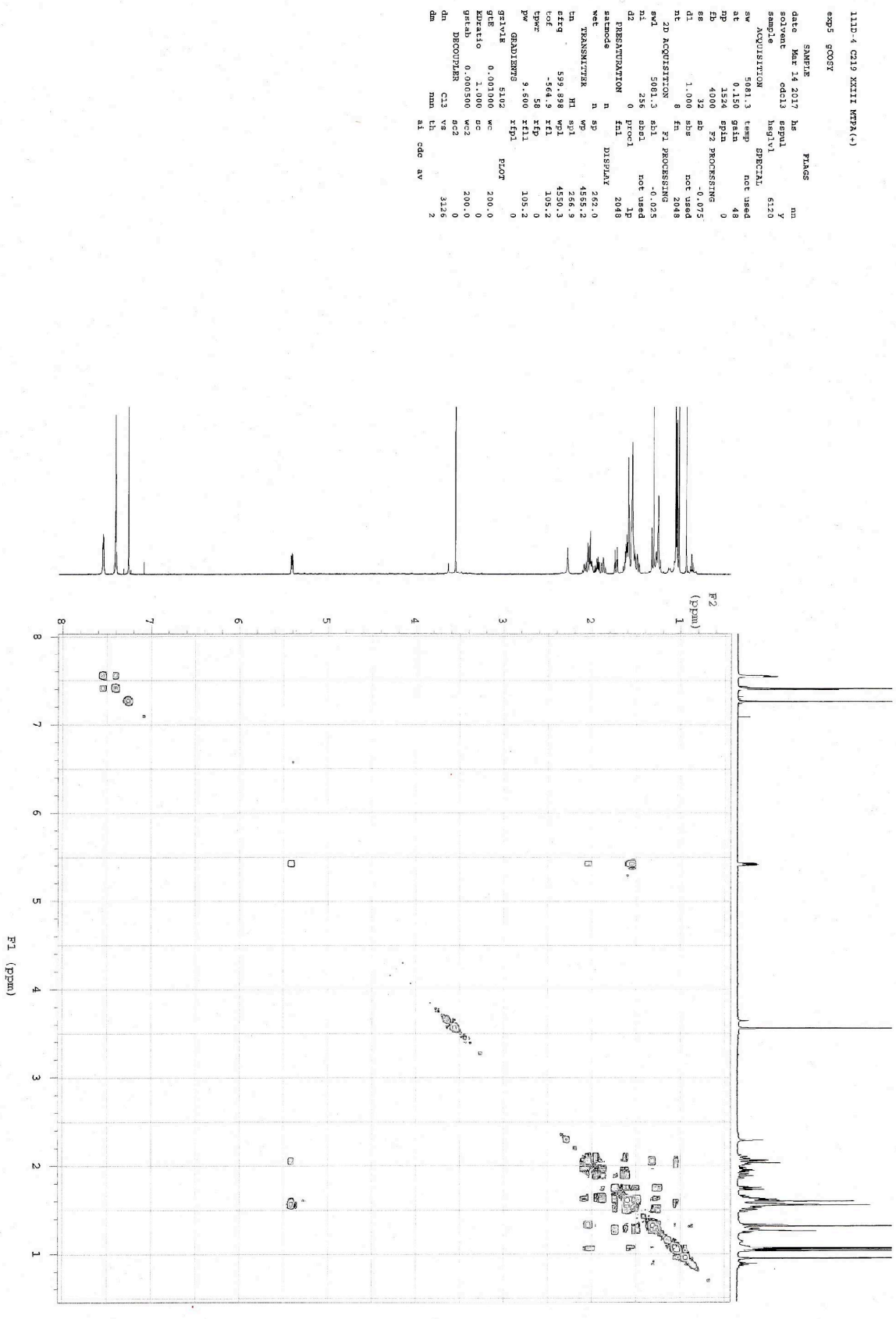

Figure S29. ^{1}H-^{1}H COSY of **2b**.

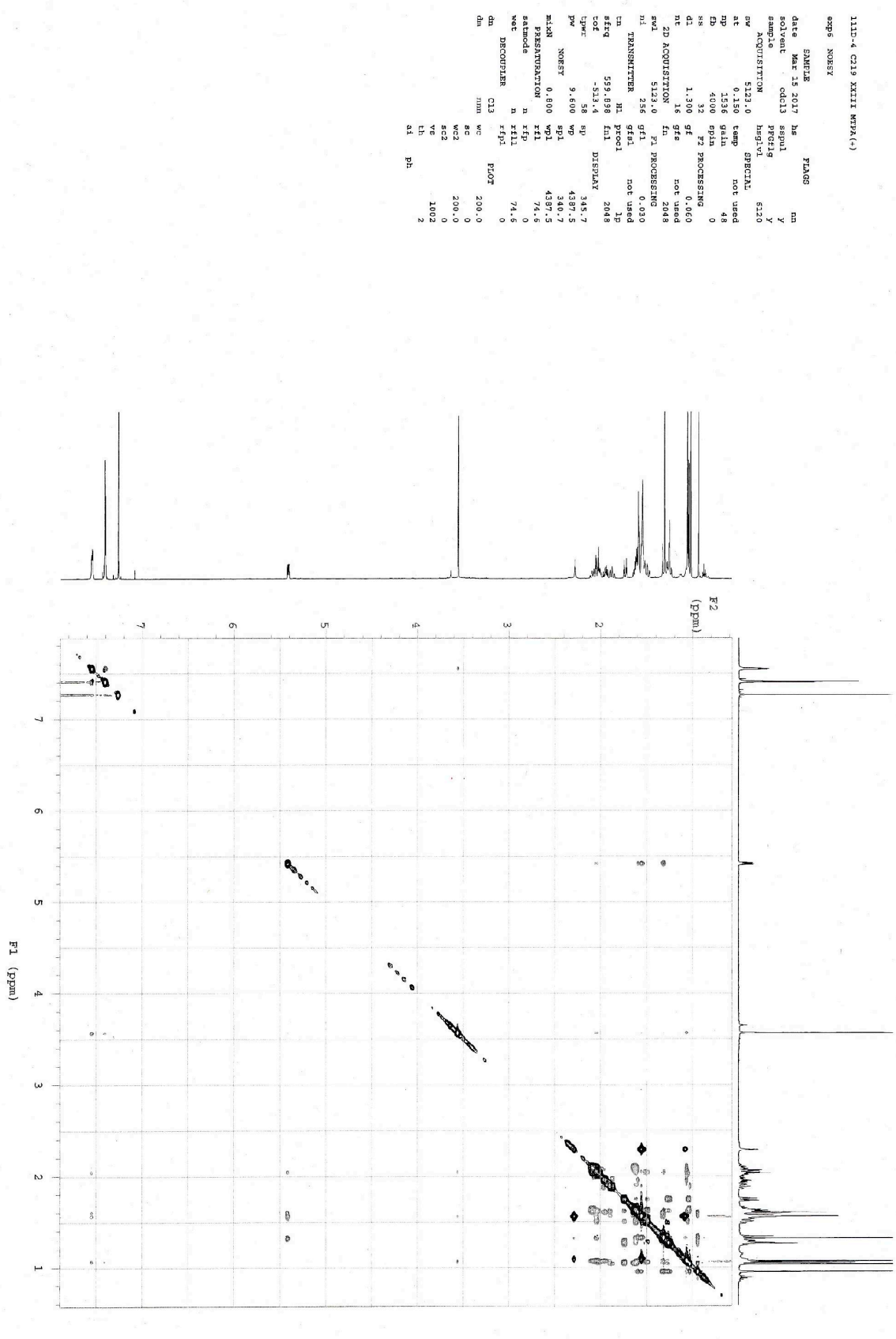

Figure S30. NOESY of **2b.**