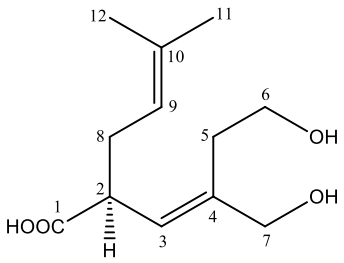
Supplementary Information

Sterepinic acids A–C, new carboxylic acids produced by a marine alga-derived Fungus

Takeshi Yamada * Miwa Matsuda, Mayuko Seki, Megumi Hirose and Takashi Kikuchi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10
9
6
8
5
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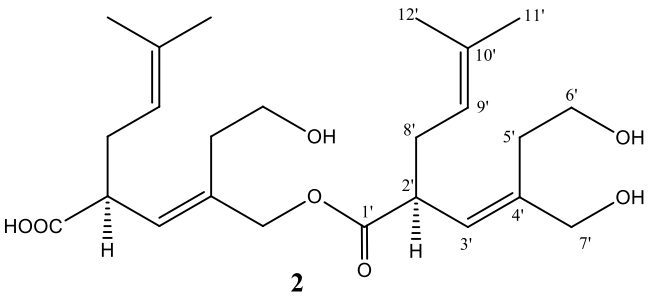
2
1
OH
HOOC
4
3
7
H

1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11'
10'
9'
6'
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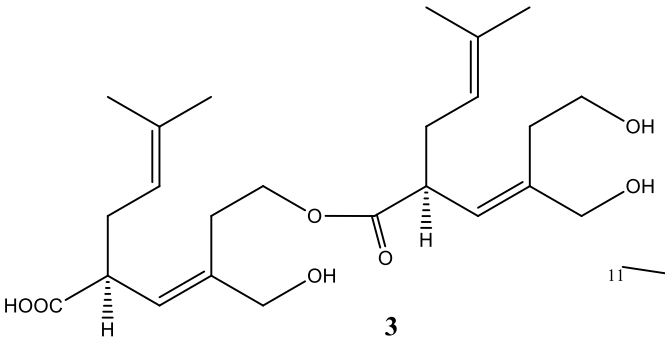
8'
5'
OH
OH
2'
O
1'
HOOC
4'
OH
H
3'
7'
O

2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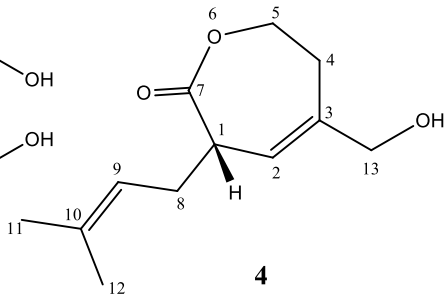
OH
O
O
H
OH
HOOC
H

3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5
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O
7
3
OH
1
9
2
13
H
8
10
11
12

4

Table S1 NMR spectral data of **1** in $CDCl_3$

Position	δ_H[a]		J/Hz	^1H-^1H COSY	NOESY[b]	δ_C		HMBC (C)[c]
1						177.5	(s)	
2	3.27	m		3, 8A, 8B	9, 11, 12	44.9	(d)	1, 3, 4, 8, 9
3	5.50	d	10.2 (2)	2	8A, 8B, 9, 11, 12	127.0	(d)	1, 2, 5, 7, 8
4						138.7	(s)	
5A	2.25	m		5B, 6		31.9	(t)	3, 4, 6, 7
5B	2.49	m		5A, 6				3, 4, 6, 7
6	3.68	br s		5A, 5B	11, 12	61.0	(t)	4
7	4.03	br s			3, 11, 12	66.8	(t)	3, 4, 5
8A	2.20	m		2, 8B, 9	3, 11, 12	30.9	(t)	1, 2, 3, 9, 10
8B	2.44	m		2, 8A, 9	3, 11, 12			1, 2, 3, 9, 10
9	5.04	dd	7.2 (8), 7.2 (8)	8A, 8B	2, 3, 11, 12	120.2	(d)	2, 8, 11, 12
10						134.1	(s)	
11	1.67	s			2, 3, 6, 7, 8A, 8B, 9	25.7	(q)	9, 10, 12
12	1.60	s			2, 3, 6, 7, 8A, 8B, 9	17.8	(q)	9, 10, 11

a ^1H 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 ^1H-^{13}C correlations from H to C observed in the HMBC experiment.

Table S2 NMR spectral data of **2** in $CDCl_3$

Position	δ_H[a]		J/Hz	^{1}H-^{1}H COSY	NOESY[b]	δ_C	HMBC (C)[c]
1						173.5 (s)	
2	3.28	m		3, 8A, 8B	5, 9	45.4 (d)	1, 3, 4, 8, 9
3	5.49	d	10.8 (2)	2	7A, 7B, 8A, 8B	129.3 (d)	2, 5, 7, 8
4						133.9 (s)	
5A	2.18	m		5B, 6A, 6B	2	32.3 (t)	3, 4, 6, 7
5B	2.54	m		5A, 6A, 6B	2		3, 4, 6, 7
6A	3.65	br s		5A, 5B, 6B		61.4 (t)	
6B	3.72	br s		5A, 5B, 6A			
7A	4.48	d	13.2 (7B)	7B	3	67.9 (t)	1, 3, 4, 5
7B	4.62	d	13.2 (7A)	7A	3		1, 3, 4, 5
8A	2.20	m		2, 8B, 9	3, 11, 12	30.8[d1] (t)	1, 2, 3, 9, 10
8B	2.46	m		2, 8A, 9	3, 11, 12		1, 2, 3, 9, 10
9	5.03	m		8A, 8B	2, 11, 12	120.2[d2] (d)	2, 8, 11, 12
10						134.2[d3] (s)	
11	1.67	s			9	25.7 (q)	9, 10, 12
12	1.60	s			8A, 8B, 9	17.8 (q)	9, 10, 11
1'						173.5 (s)	
2'	3.28	m		3', 8'A, 8'B	5', 9'	45.4 (d)	1', 8', 9'
3'	5.52	d	10.2 (2')	2'	7', 8'A, 8'B	127.2 (d)	5', 7'
4'						139.6 (s)	
5'A	2.29	m		5'B, 6'	2'	32.3 (t)	3', 4', 6', 7'
5'B	2.54	m		5'A, 6'	2'		3', 4', 6', 7'
6'	3.72	br s		5'A, 5'B		60.5 (t)	
7'	4.05	br s			3'	67.5 (t)	3', 4', 5'
8'A	2.20	m		2', 8'B, 9'	3', 11', 12'	30.6[d1] (t)	1', 2', 3', 9', 10'
8'B	2.46	m		2', 8'A, 9'	3', 11', 12'		1', 2', 3', 9', 10'
9'	5.03	m		8'A, 8'B	2', 11', 12'	120.3[d2] (d)	2', 8', 11', 12'
10'						134.3[d3] (s)	
11'	1.67	s			9'	25.7 (q)	9', 10', 12'
12'	1.60	s			8'A, 8'B, 9'	17.8 (q)	9', 10', 11'

a 1H che+B14:L36mical shift values (d ppm from SiMe4) 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 1H-13C correlations from H to C observed in the HMBC experiment. d1-d3 interchangeable

Table S3 NMR spectral data of **3** in $CDCl_3$

Position	δ_H[a]		J/Hz	^1H-^1H COSY	NOESY[b]	δ_C		HMBC (C)[c]
1						174.3	(s)	
2	3.28	m		3, 8A, 8B	5, 9	44.9	(d)	1, 8, 9
3	5.55	d	9.6 (2)	2	7, 9	129.3	(d)	5, 7
4						137.9	(s)	
5A	2.30	ddd	14.4 (5B), 5.4 (6), 5.4 (6)	5B, 6	2	27.7	(t)	3, 4, 6, 7
5B	2.54	ddd	14.4 (5B), 5.4 (6), 5.4 (6)	5A, 6	2			3, 4, 6, 7
6	4.20	m		5A, 5B		63.5	(t)	1', 4
7	4.07	m			3	66.5	(t)	3, 4
8A	2.20	m		2, 8B, 9	12	31.4	(t)	1, 2, 3, 9, 10
8B	2.44	m		2, 8A, 9	12			1, 2, 3, 9, 10
9	5.02[d1]	dd	7.2 (8A), 7.2 (8B)	8A, 8B	2, 3, 11	120.2[d2]	(d)	2, 8, 11, 12
10						134.3	(s)	
11	1.67	s			9	25.7	(q)	9, 10, 12
12	1.59[d3]	s			8A, 8B	17.8[d4]	(q)	9, 10, 11
1'						174.3	(s)	
2'	3.28	m		3', 8'A, 8'B	5', 9'	44.9	(d)	1', 3', 4', 8', 9'
3'	5.51	d	9.6 (2')	2'	7', 8'A, 8'B, 9'	127.2	(d)	1', 2', 5', 7', 8'
4'						138.7	(s)	
5'A	2.25	m		5'B, 6'A, 6'B	2'	32.2	(t)	3', 4', 6', 7'
5'B	2.51	m		5'A, 6'A, 6'B	2'			3', 4', 6', 7'
6'A	3.65	br s		5'A, 5'B, 6'B		61.1	(t)	
6'B	3.71	br s		5'A, 5'B, 6'A				
7'	4.02	m			3'	67.4	(t)	3', 4'
8'A	2.20	m		2', 8'B, 9'	12'	31.4	(t)	1', 2', 3', 9', 10'
8'B	2.44	m		2', 8'A, 9'	12'			1', 2', 3', 9', 10'
9'	5.06[d1]	dd	7.2 (8'A), 7.2 (8'B)	8'A, 8'B	2', 3', 11'	120.3[d2]	(d)	11', 12'
10'						134.3	(s)	
11'	1.67	s			9'	25.7	(q)	9', 10', 12'
12'	1.61[d3]	s			8'A, 8'B	17.9[d4]	(q)	9', 10', 11'

a 1H che+B23:L35mical shift values (d ppm from SiMe4) 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 1H-13C correlations from H to C observed in the HMBC experiment. d1-d4 interchangeable

Table S4 NMR spectral data of **4** in $CDCl_3$

Position	δ_H[a]		J/Hz	^1H-^1H COSY	NOESY[b]	δ_C		HMBC (C)[c]
1	3.68	m		2, 8A, 8B	9	40.2	(d)	
2	5.36	br s		1	8A, 8B, 9,13A, 13B	121.2	(d)	4, 7, 8, 13
3						139.2	(s)	
4A	2.45	br d	19.2 (5B)	4B, 5	13A	30.3	(t)	
4B	2.59	m		5A, 5B, 6B	13B			
5α	4.68	ddd	12.6 (4B), 12.6 (5β), 1.8 (4A)	4, 5β		64.4	(t)	3, 4, 7
5β	4.33	ddd	12.6 (5α), 4.8 (4B), 2.4 (4A)	4, 5α				3, 4, 7
6								
7						174.3	(s)	
8A	2.33	ddd	14.4 (8B), 6.6 (1), 6.6 (9)	1, 8B, 9	2, 11	30.1	(t)	1, 2, 7, 9, 10
8B	2.52	ddd	14.4 (8A), 6.6 (1), 6.6 (9)	1, 8A, 9	2, 11			1, 2, 7, 9, 10
9	5.14	dd	6.6 (8A), 6.6 (8B)	8A, 8B	1, 2, 11	120.9	(d)	1, 8, 11, 12
10						134.6	(s)	
11	1.72	s			9	25.8	(q)	9, 10, 12
12	1.67	s			8A, 8B	18.0	(q)	9, 10, 12
13A	3.99	d	13.8 (13B)		2, 4	67.4	(t)	2, 3, 4
13B	4.01	d	13.8 (13A)		2, 4			

a ^1H 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 ^1H-^{13}C correlations from H to C observed in the HMBC experiment.

Figure S1 ^{1}H NMR spectrum of 1

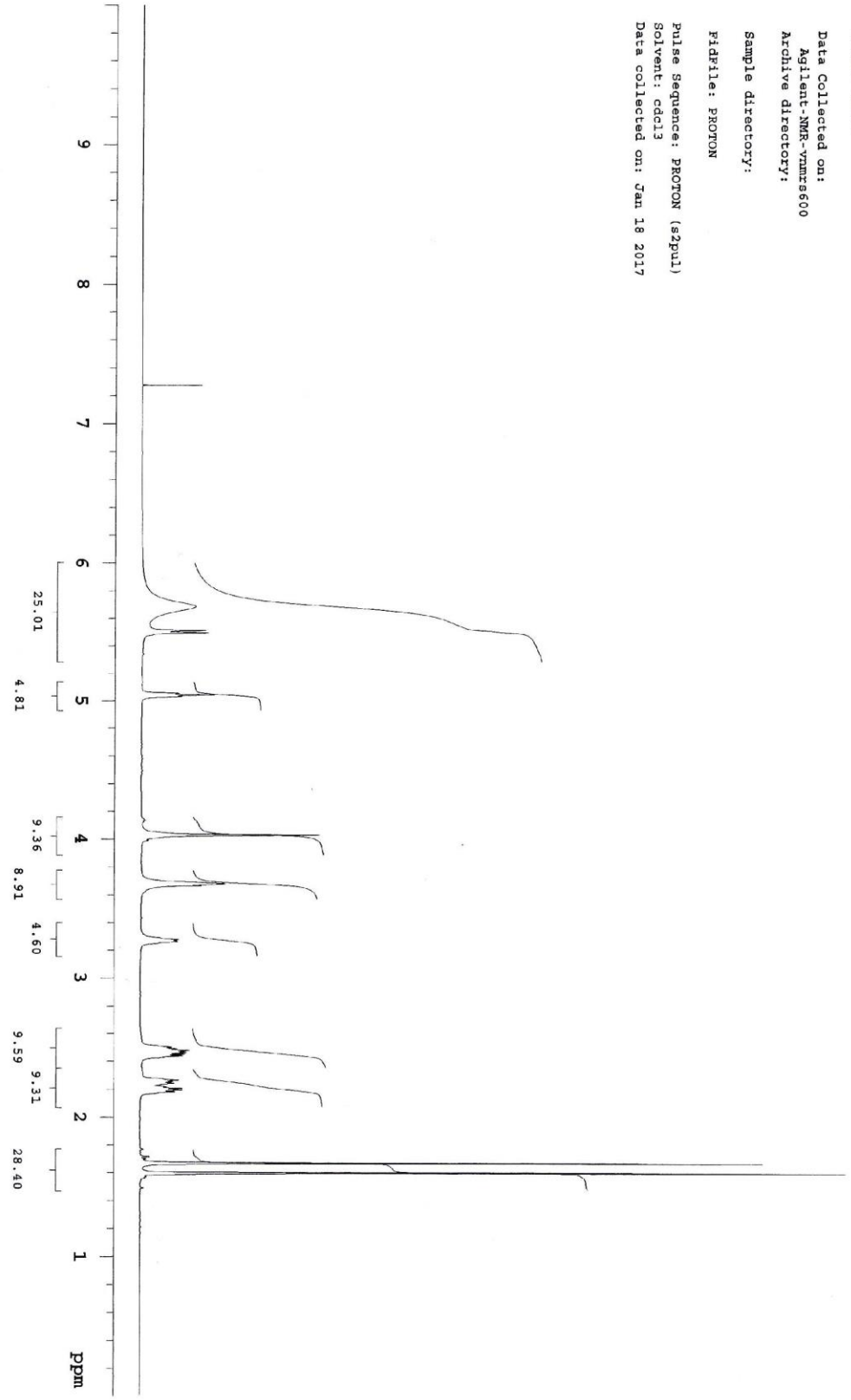

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Figure S2 ^{13}C NMR spectrum of 1 in $CDCl_3$

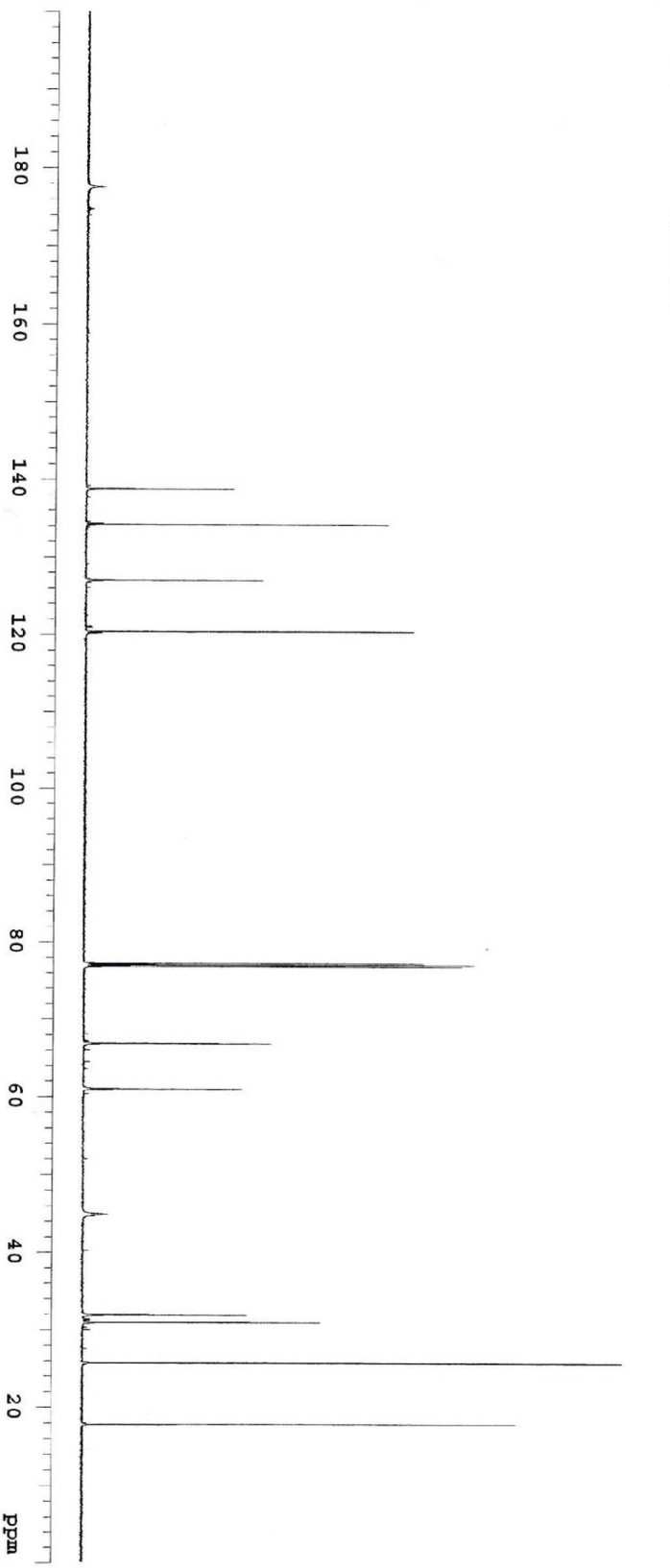
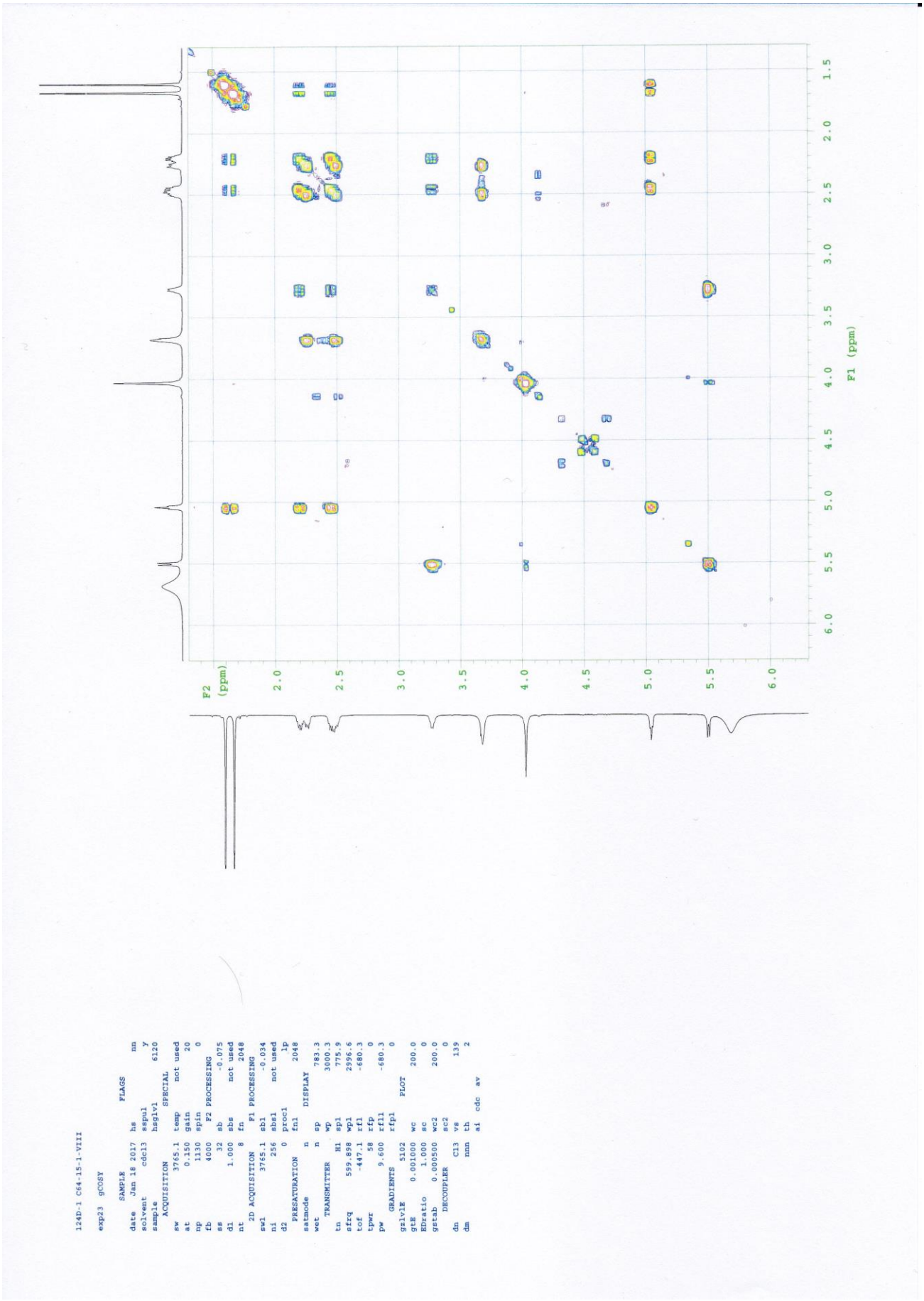


Figure S3 ^{1}H-^{1}H COSY of 1



124D-1 C64-15-1-VIII

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ss 32 sb -0.075
d1 1.000 sbs not used 2048
nt 8 fn
2D ACQUISITION F1 PROCESSING
sw1 3765.1 sb1 -0.034
ni 256 sbs1 not used 1p
d2 0 proc1 2048
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satmode n sp 783.3
wet n wp 3000.3
TRANSMITTER H1 sp1 775.9
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pw 9.600 rfl1 -680.3
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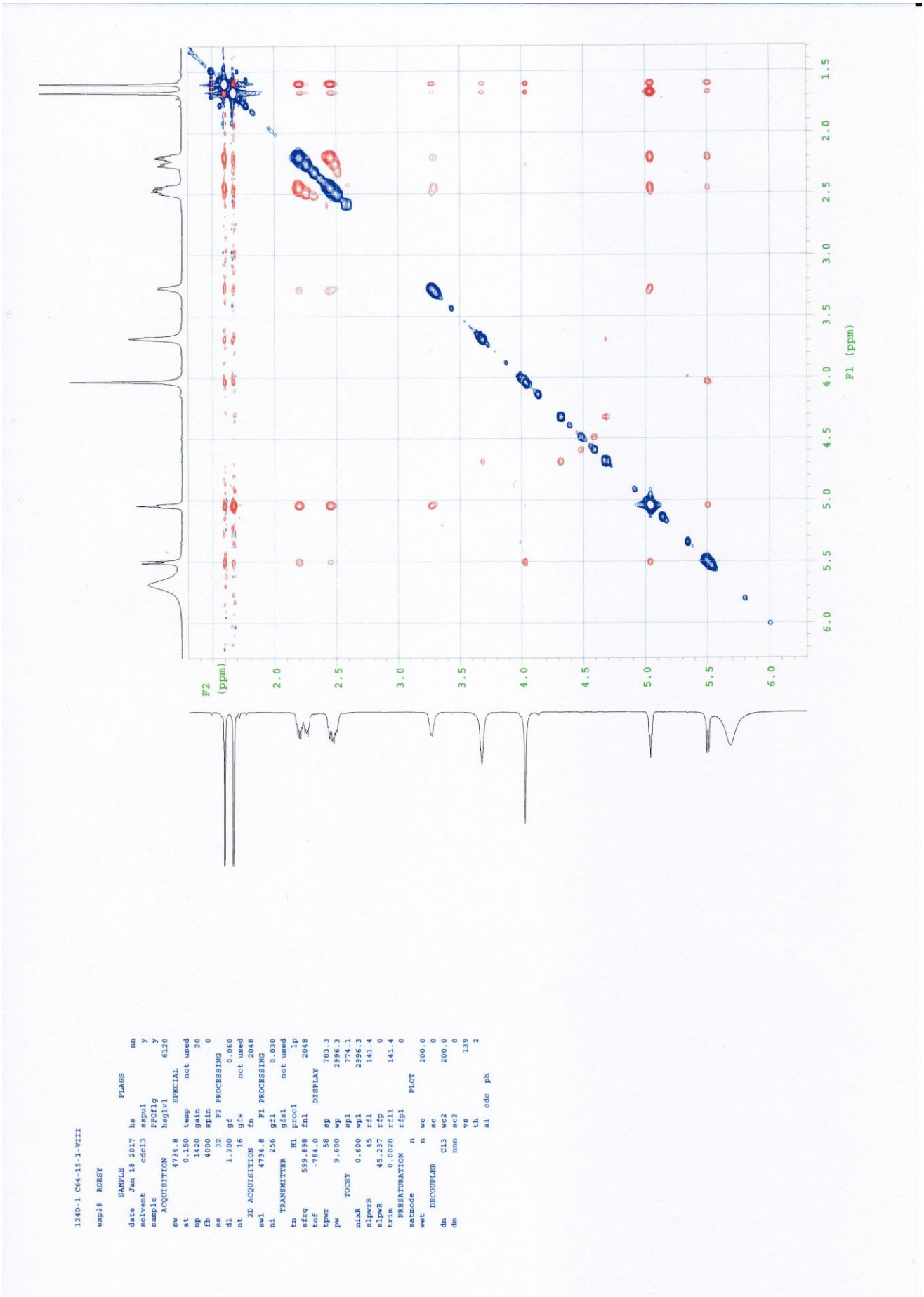
ai cdc av

Figure S4 NOESY of 1



124D-1 C64-15-1-VIII

exp28 ROESY

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fb 4000 spin 0
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d1 1.300 gf 0.060
nt 16 gfs not used
2D ACQUISITION fn 2048
sw1 4734.8 F1 PROCESSING
ni 256 gf1 0.030
TRANSMITTER gfs1 not used
tn H1 procl lp
sfrq 599.898 fn1 2048
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mixR 0.600 wp1 2996.3
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PRESATURATION rfp1 0
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vs 139
th 2
al cdc ph

Figure S5 HMQC of 1

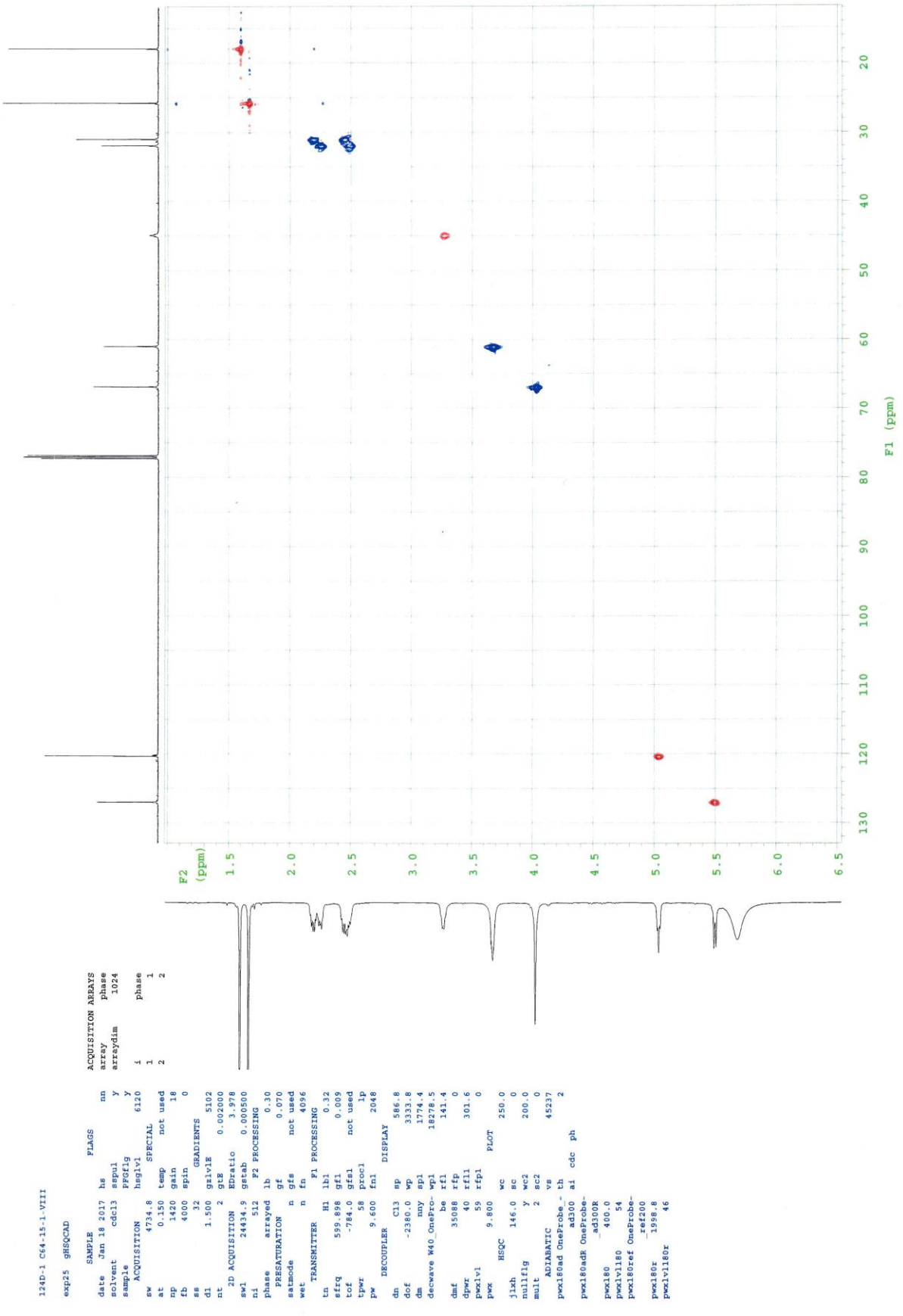


Figure S6 HMBC of 1

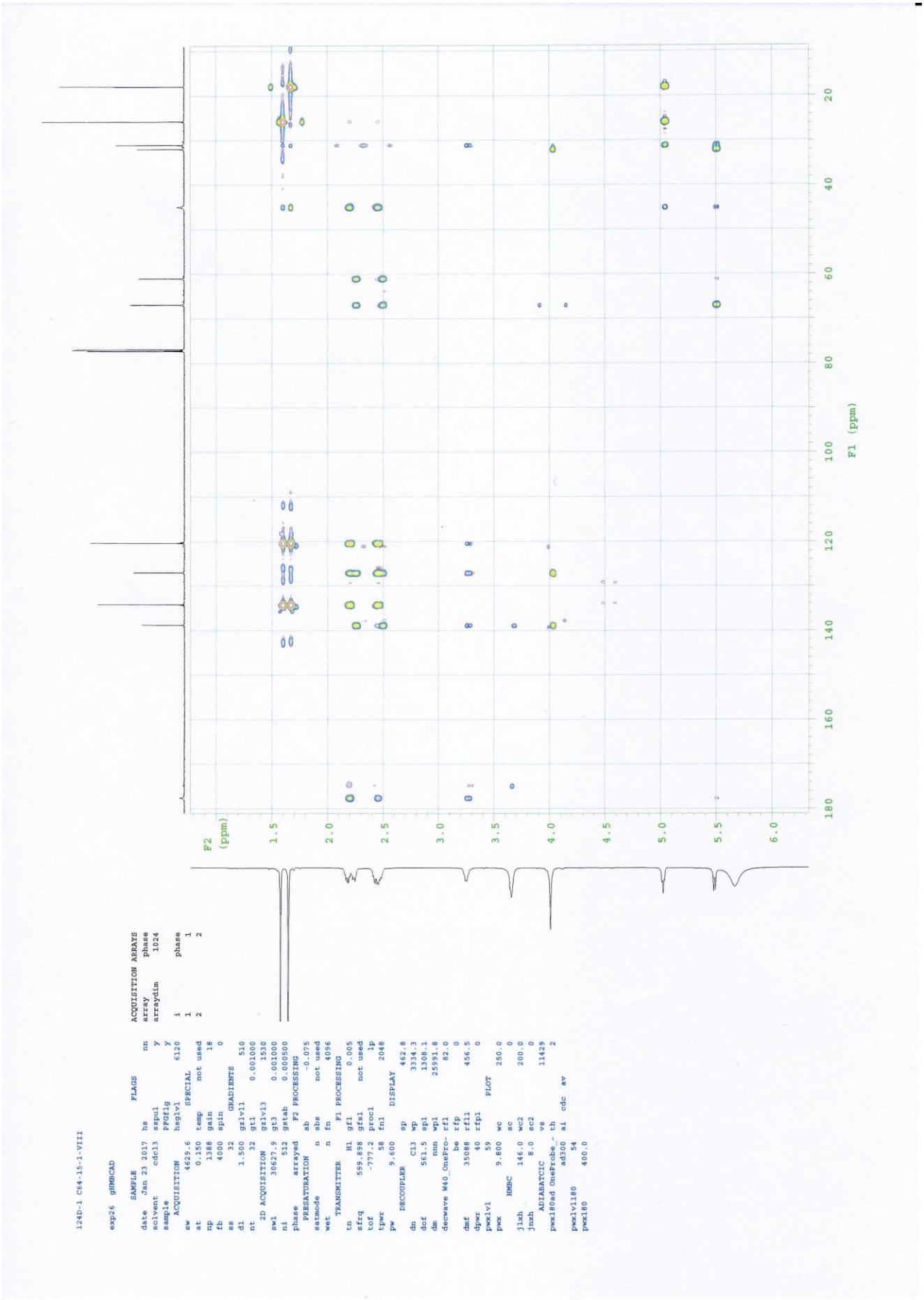


Figure S7 ^{1}H NMR spectrum of 2 in $CDCl_3$

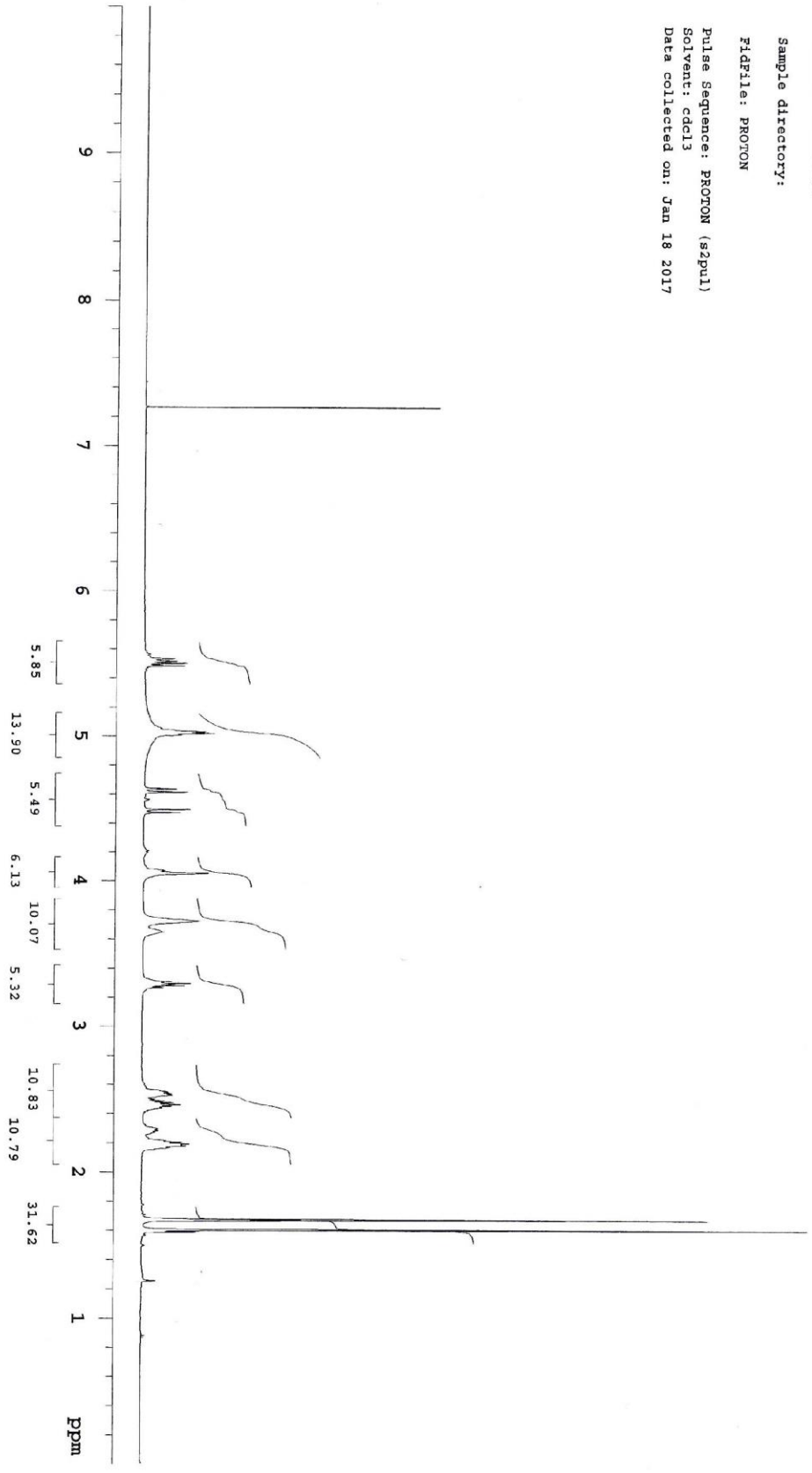


Figure S8 ^{13}C **NMR spectrum of 2 in** $CDCl_3$

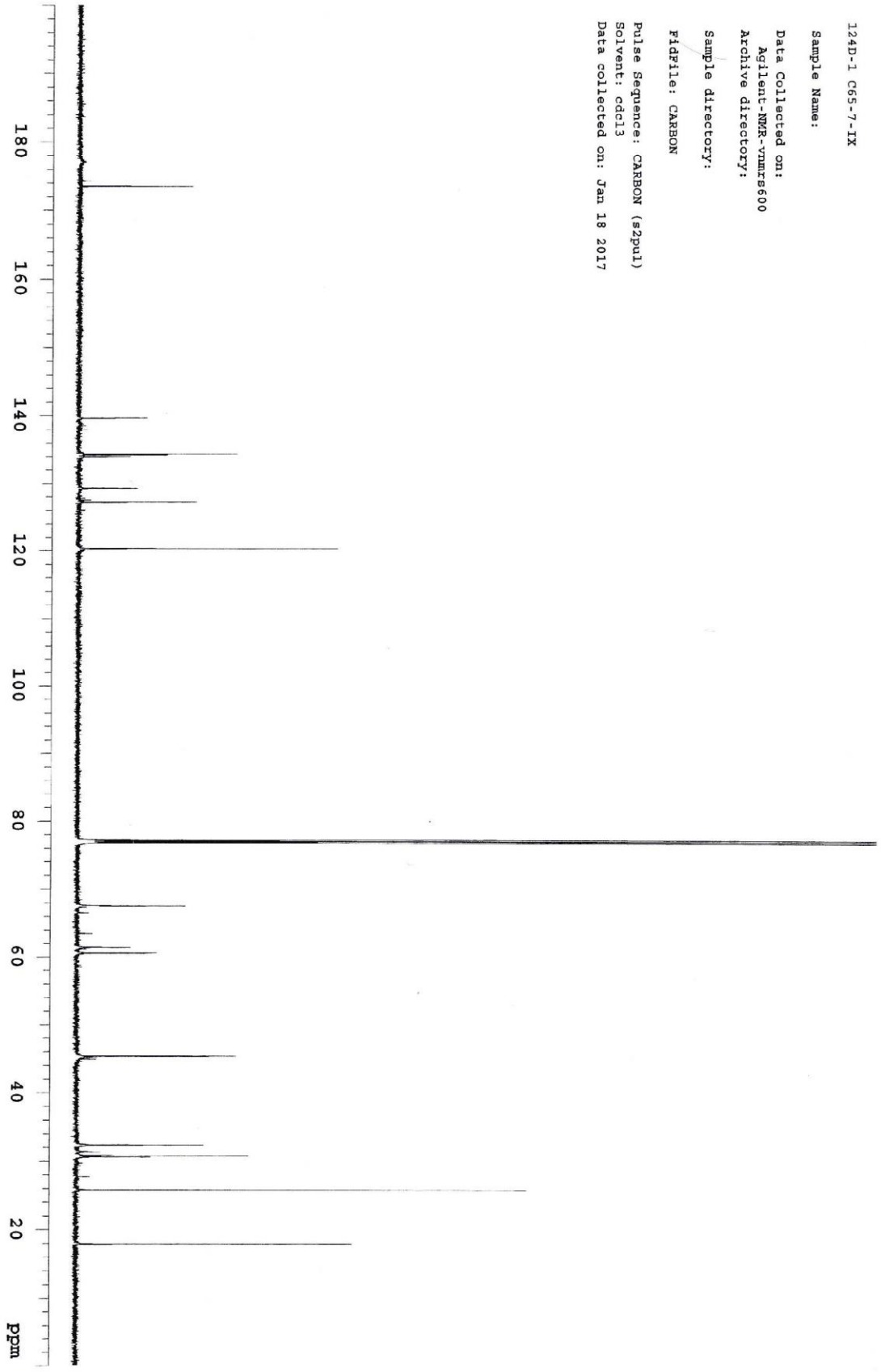
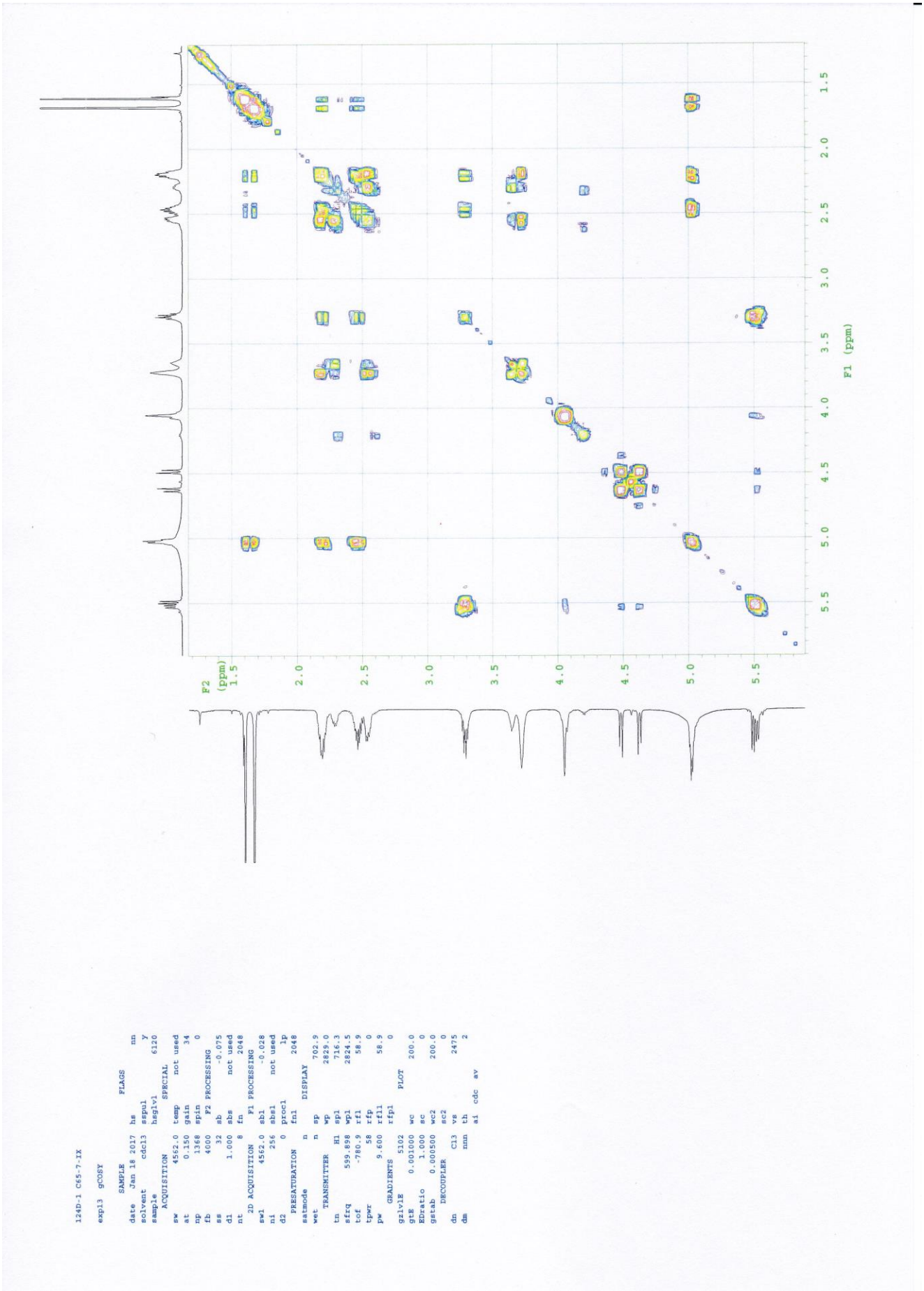


Figure S9 ^{1}H-^{1}H COSY of 2



124D-1 C65-7-IX

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ss 32 ab -0.075
d1 1.000 abs not used
nt 8 fn 2048
2D ACQUISITION F1 PROCESSING
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ni 256 abs1 not used
d2 0 proc1 1p
PRESATURATION fn1 2048
satmode n DISPLAY
wet n sp 702.9
TRANSMITTER wp 2829.0
tn H1 sp1 716.3
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tpwr 58 rfp 0
pw 9.600 rfl1 58.9
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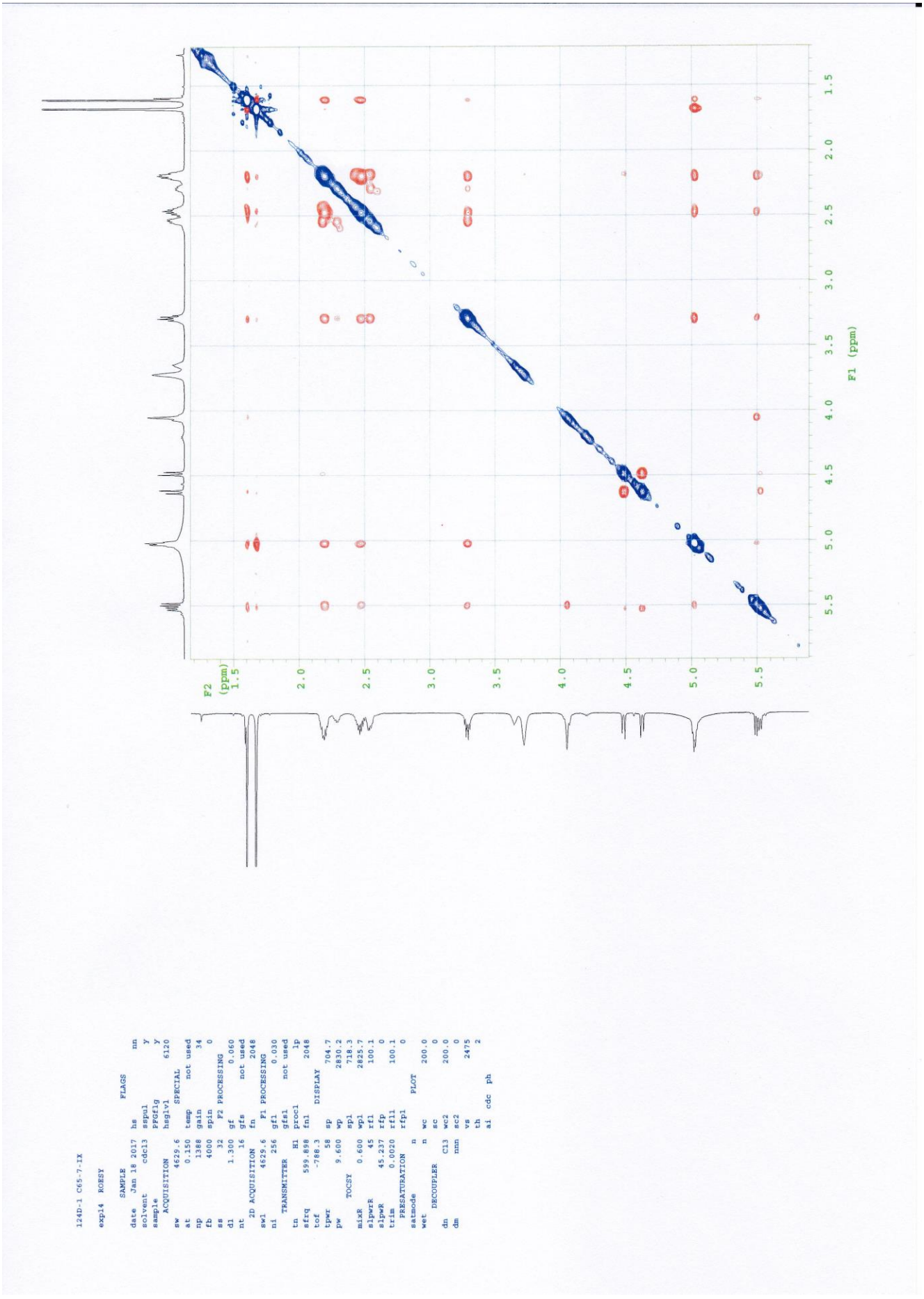
ai cdc av

Figure S10 NOESY of 2

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124D-1 C65-7-IX

exp14  ROESY

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solvent     cdcl3       ssqul                           y
sample                  PFGflg                          y
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    at         0.150      temp        not used
    np          1388      gain              34
    fb          4000      spin               0
    ss            32        F2 PROCESSING
    d1         1.300      gf                  0.060
    nt            16      gfs         not used 2048
  2D ACQUISITION          fn                   2048
    sw1       4629.6        F1 PROCESSING
    ni           256      gf1                 0.030
  TRANSMITTER       H1    gfs1        not used   1p
    tn                    proc1                2048
    sfrq       599.898    fn1
    tof         -788.3        DISPLAY
    tpwr             58     sp                704.7
    pw            9.600     wp               2830.2
        TOCSY               sp1               718.3
    mixR          0.600     wp1              2825.7
    slpwrR           45     rf1               100.1
    slpwR         45.237     rfp                  0
    trim          0.0020     rfl1              100.1
    PRESATURATION            rfp1                 0
    satmode              PLOT
    wet                n     wc               200.0
       DECOUPLER             sc                   0
    dn                C13    wc2              200.0
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                             vs                2475
                             th                   2
                             ai  cdc  ph
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Figure S11 HMQC of 2

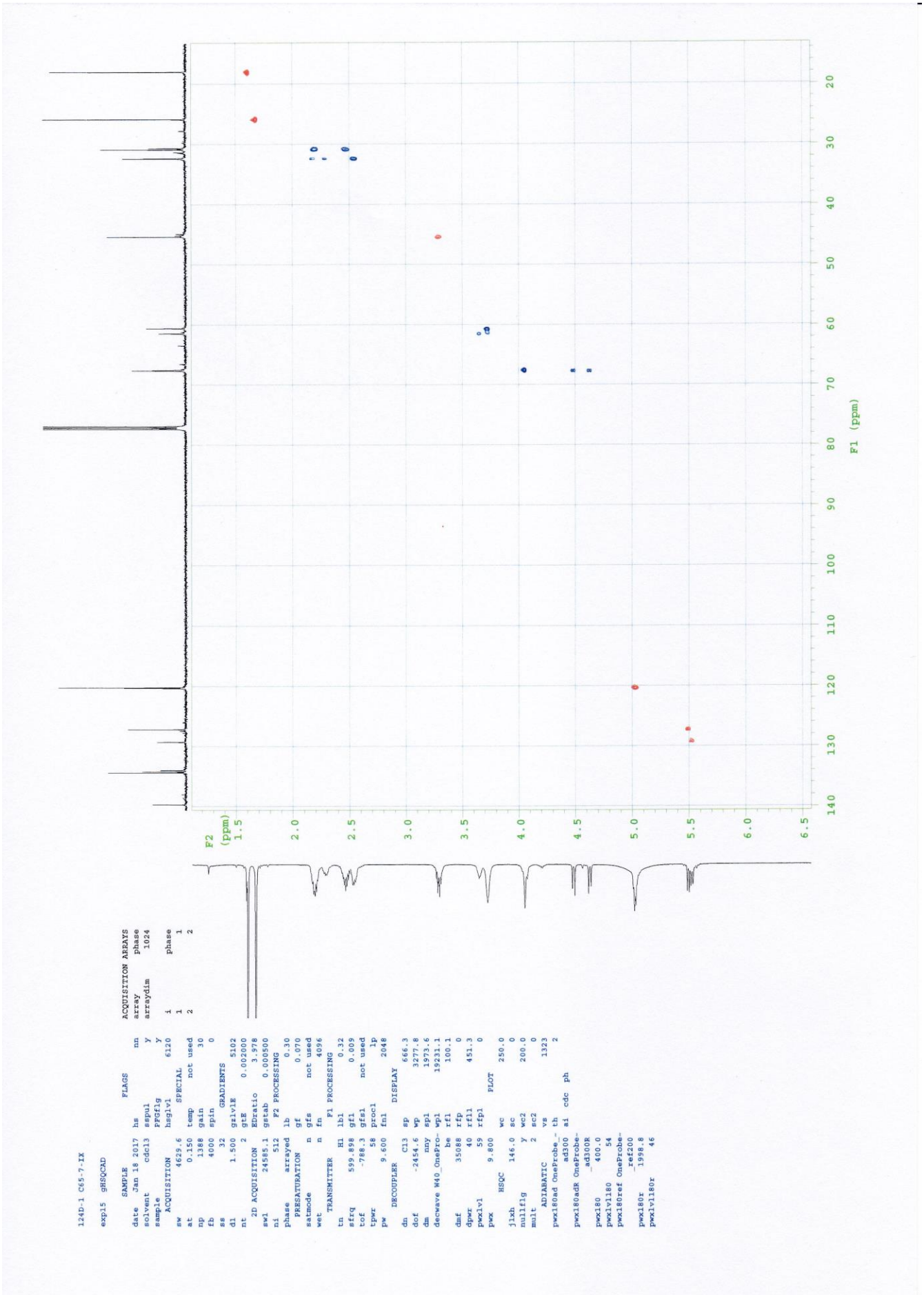


Figure S12 HMBC of 2

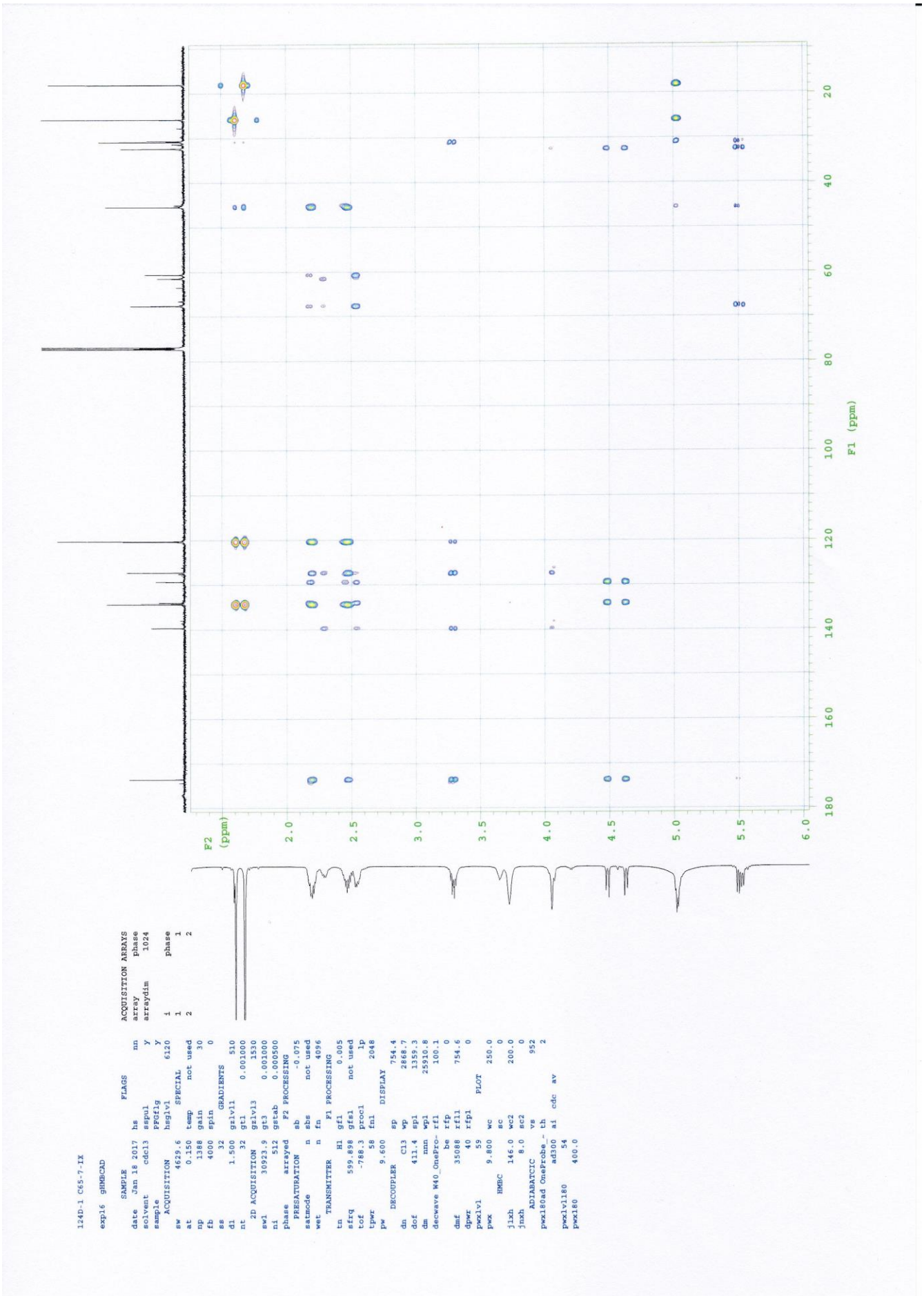


Figure S13 ^{1}H NMR spectrum of 3 in $CDCl_3$

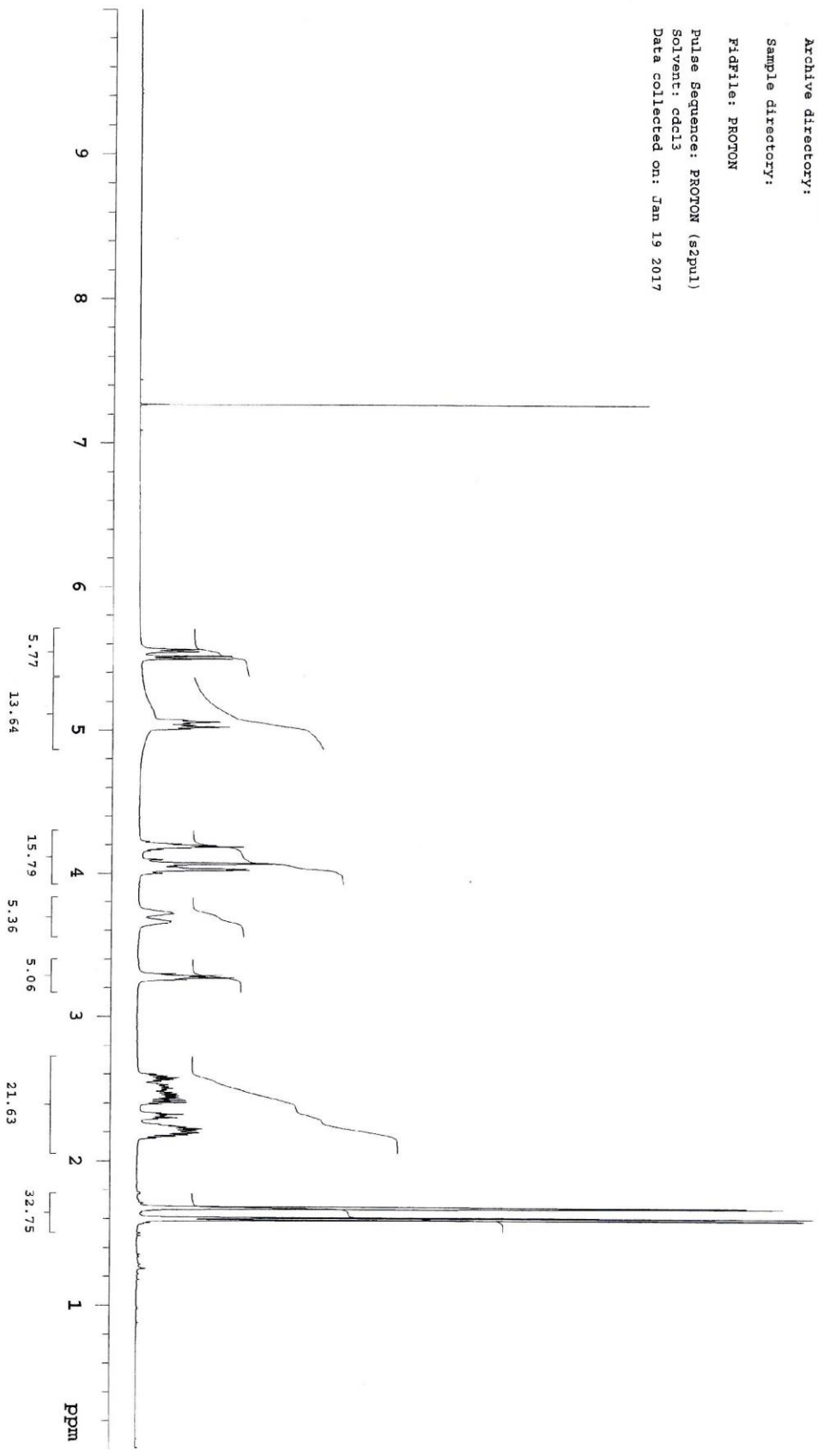


Figure S14 ^{13}C NMR spectrum of 3 in $CDCl_3$

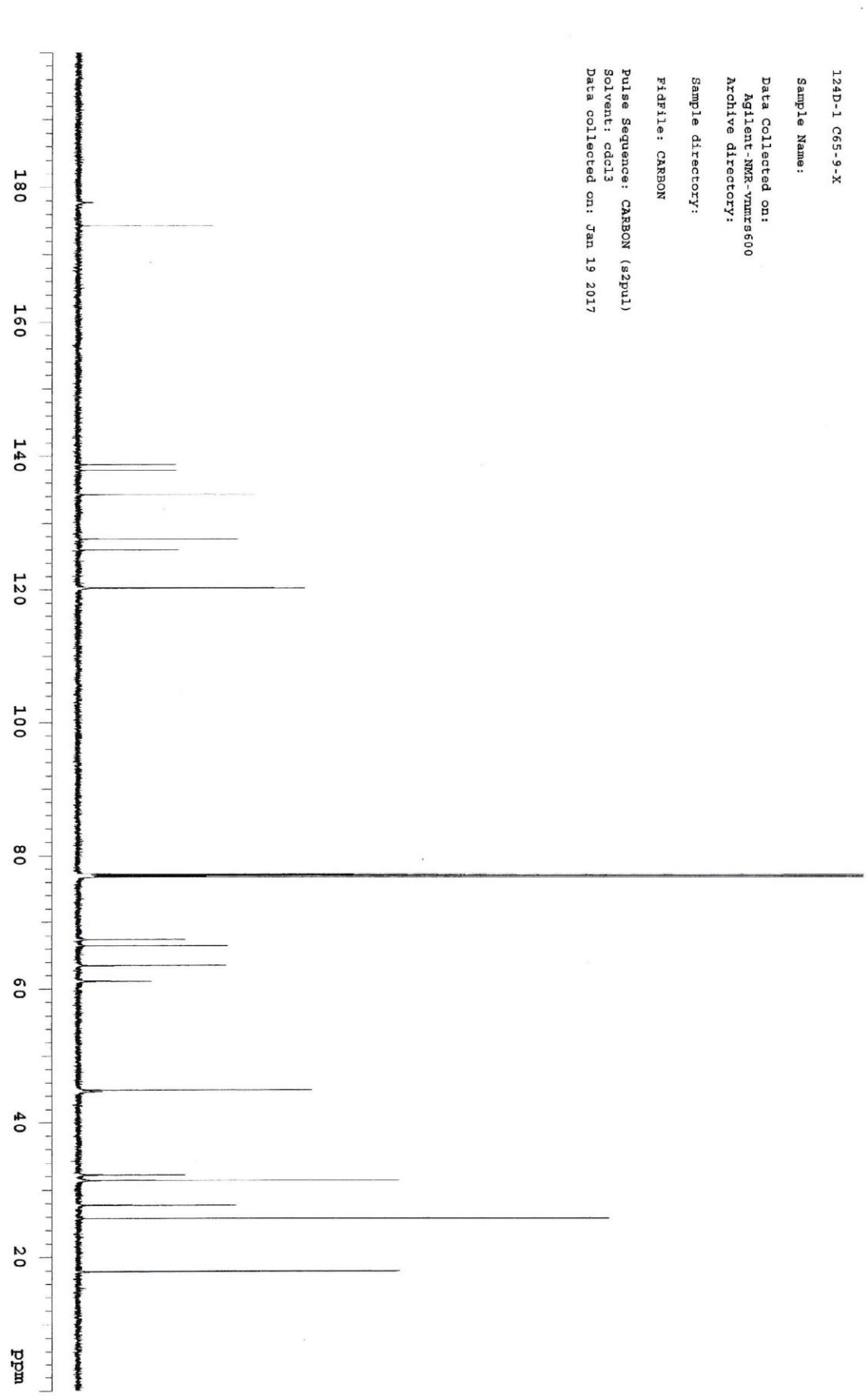


Figure S15 ^{1}H-^{1}H COSY of 3

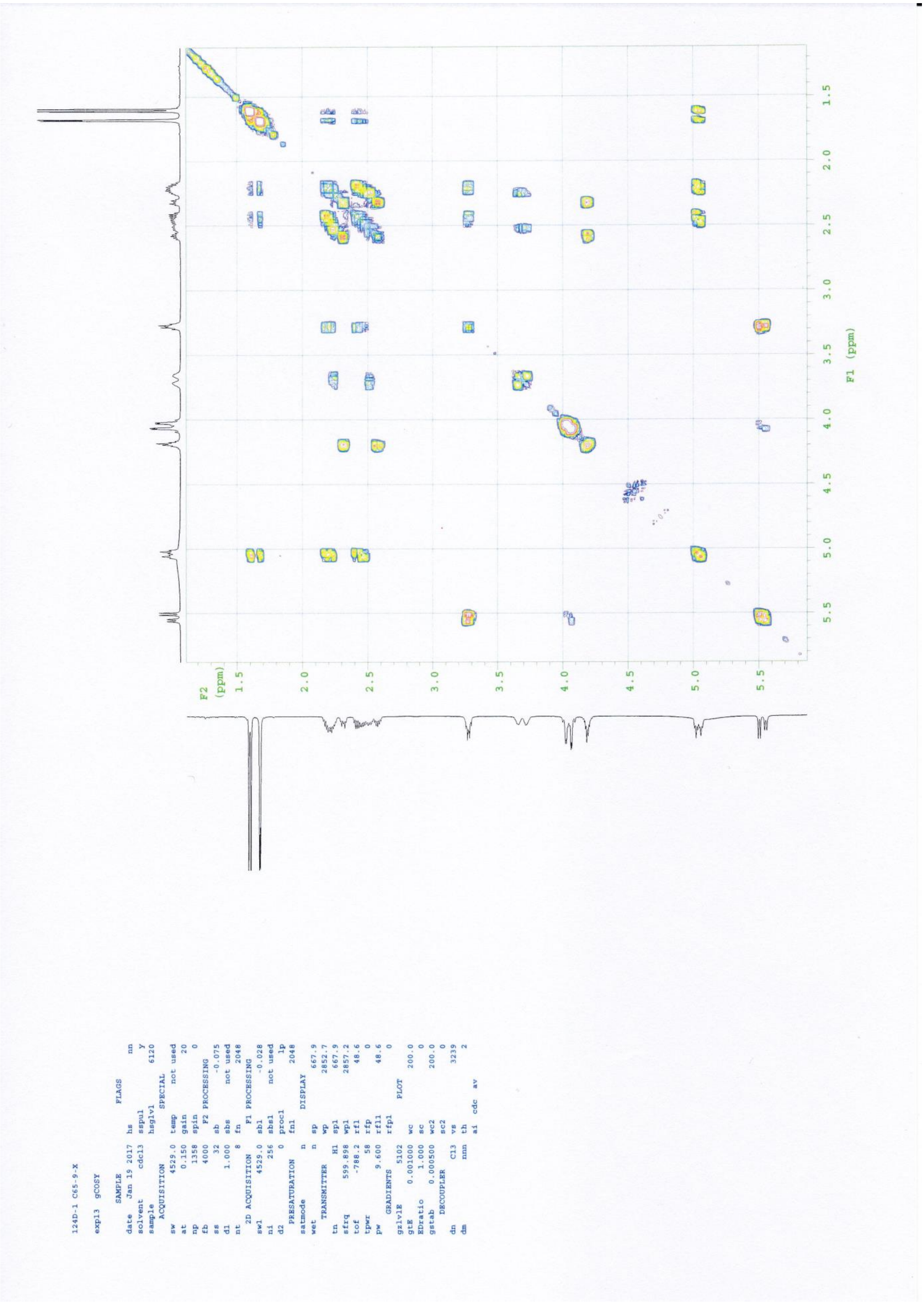
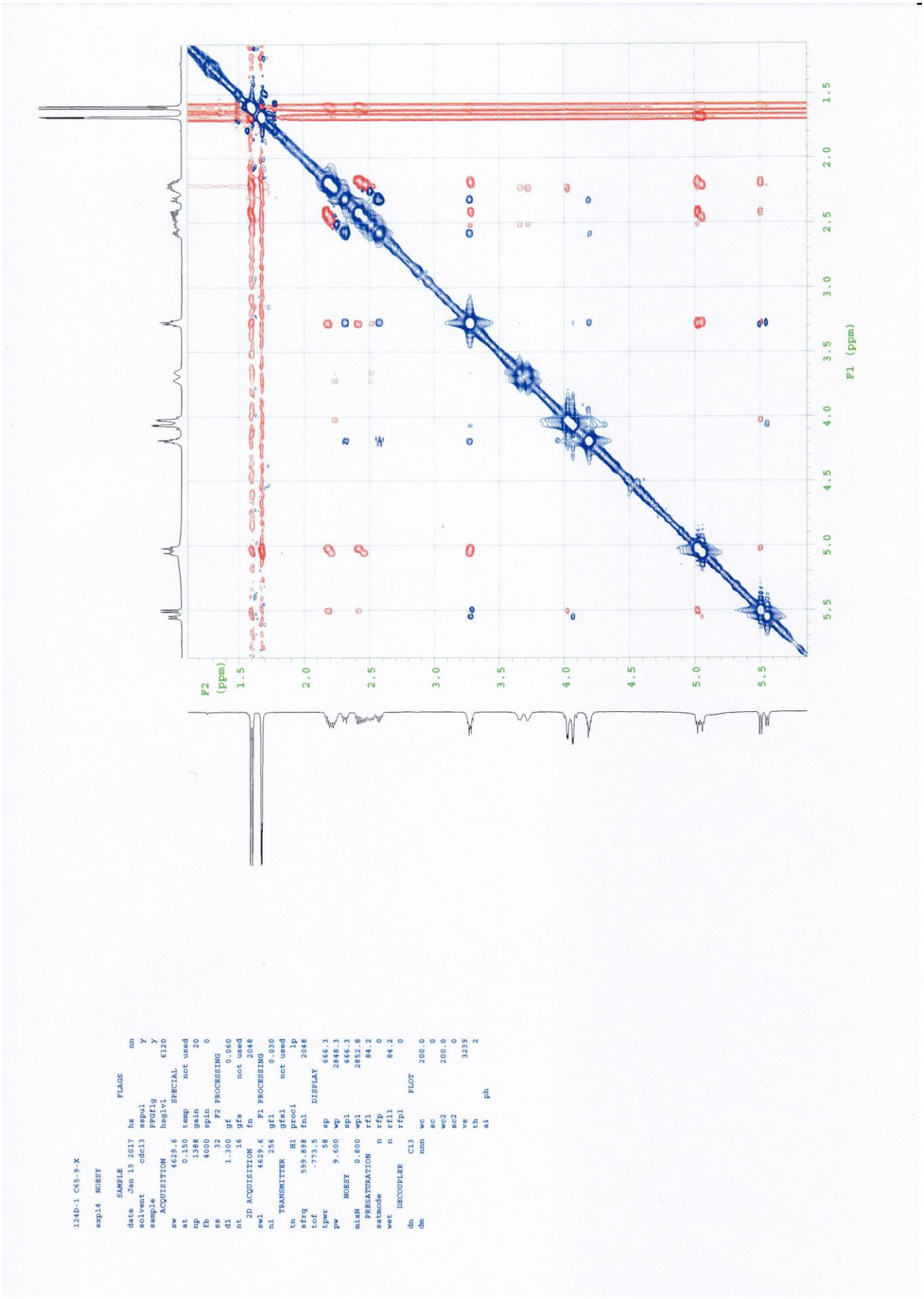


Figure S16 NOESY of 3



124D-1 C65-9-X

exp14 NOESY

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sample PFGflg y
ACQUISITION hsglv1 6120
sw 4629.6 SPECIAL
at 0.150 temp not used
np 1388 gain 20
fb 4000 spin 0
ss 32 F2 PROCESSING
d1 1.300 gf 0.060
nt 16 gfs not used
2D ACQUISITION fn 2048
sw1 4629.6 F1 PROCESSING
ni 256 gf1 0.030
TRANSMITTER gfs1 not used
tn H1 procl lp
sfrq 599.898 fn1 2048
tof -773.5 DISPLAY
tpwr 58 sp 666.3
pw 9.600 wp 2848.3
NOESY sp1 666.3
mixN 0.800 wp1 2852.8
PRESATURATION rf1 84.2
satmode n rfp 0
wet n rfl1 84.2
DECOUPLER rfp1 0
dn C13 PLOT
dm nnn wc 200.0
sc 0
wc2 200.0
sc2 0
vs 3239
th 2
ai ph

Figure S17 HMQC of 3

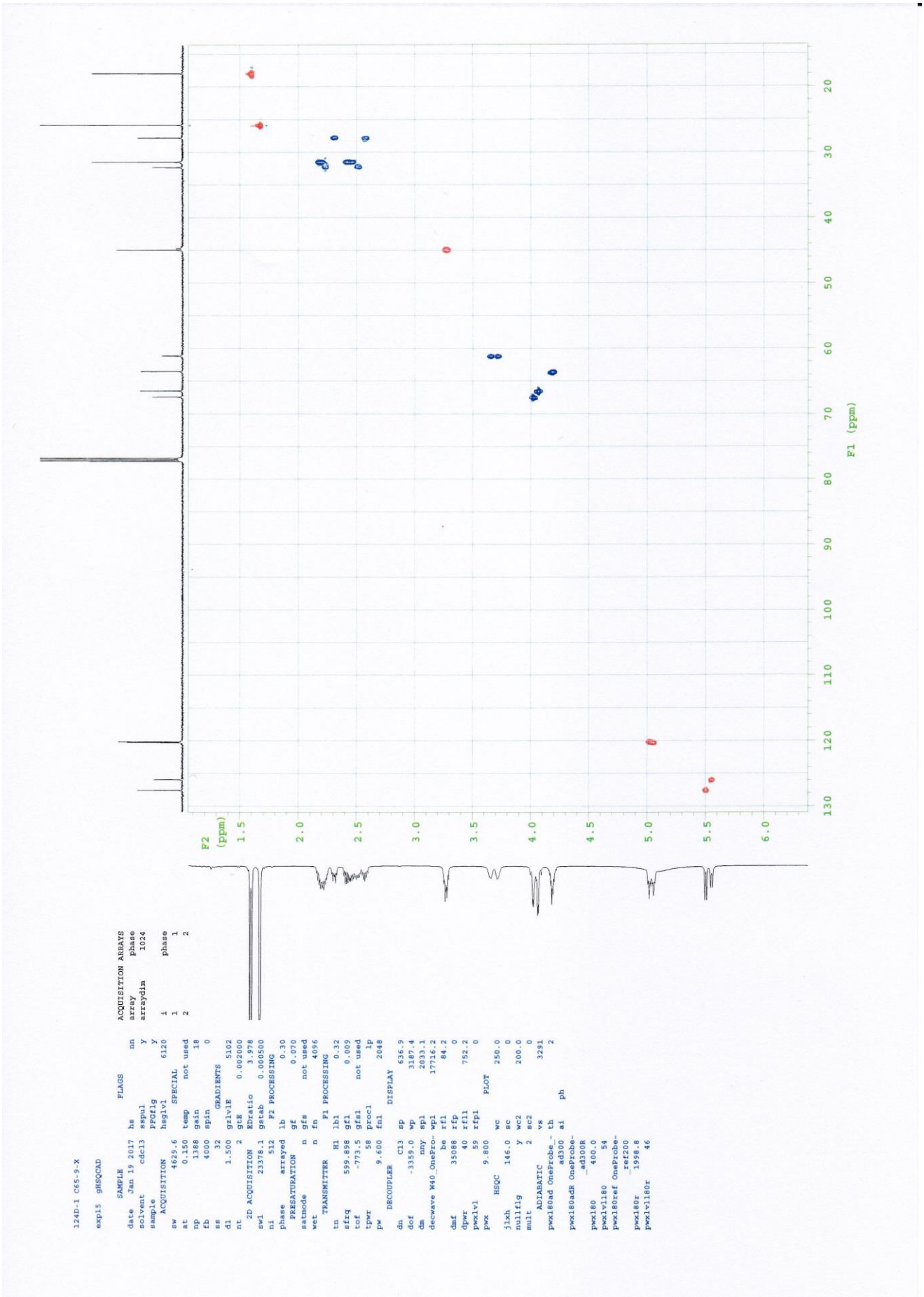

Figure S18 HMBC of 3

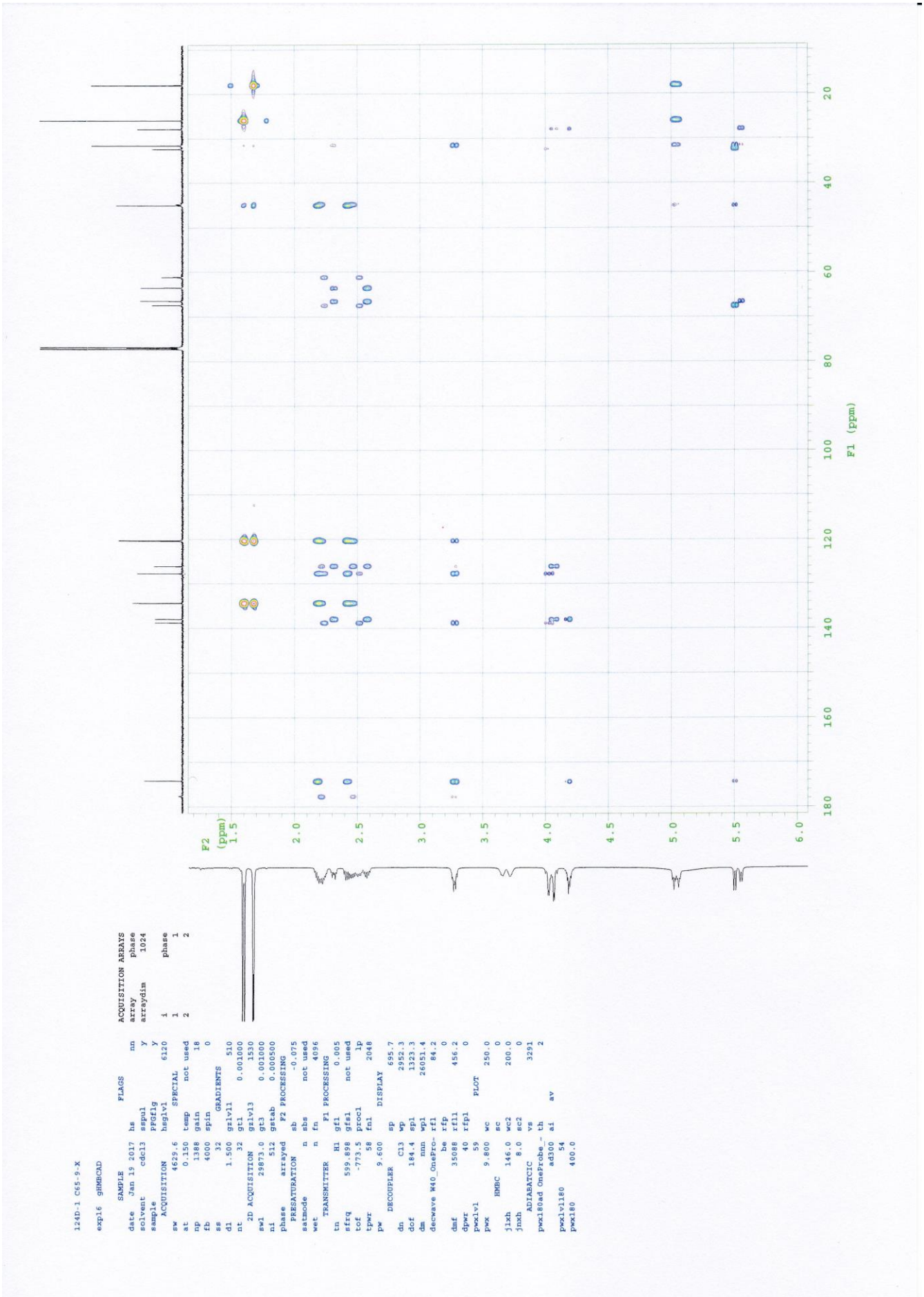

Figure S19 ^{1}H NMR spectra of 4 in $CDCl_3$

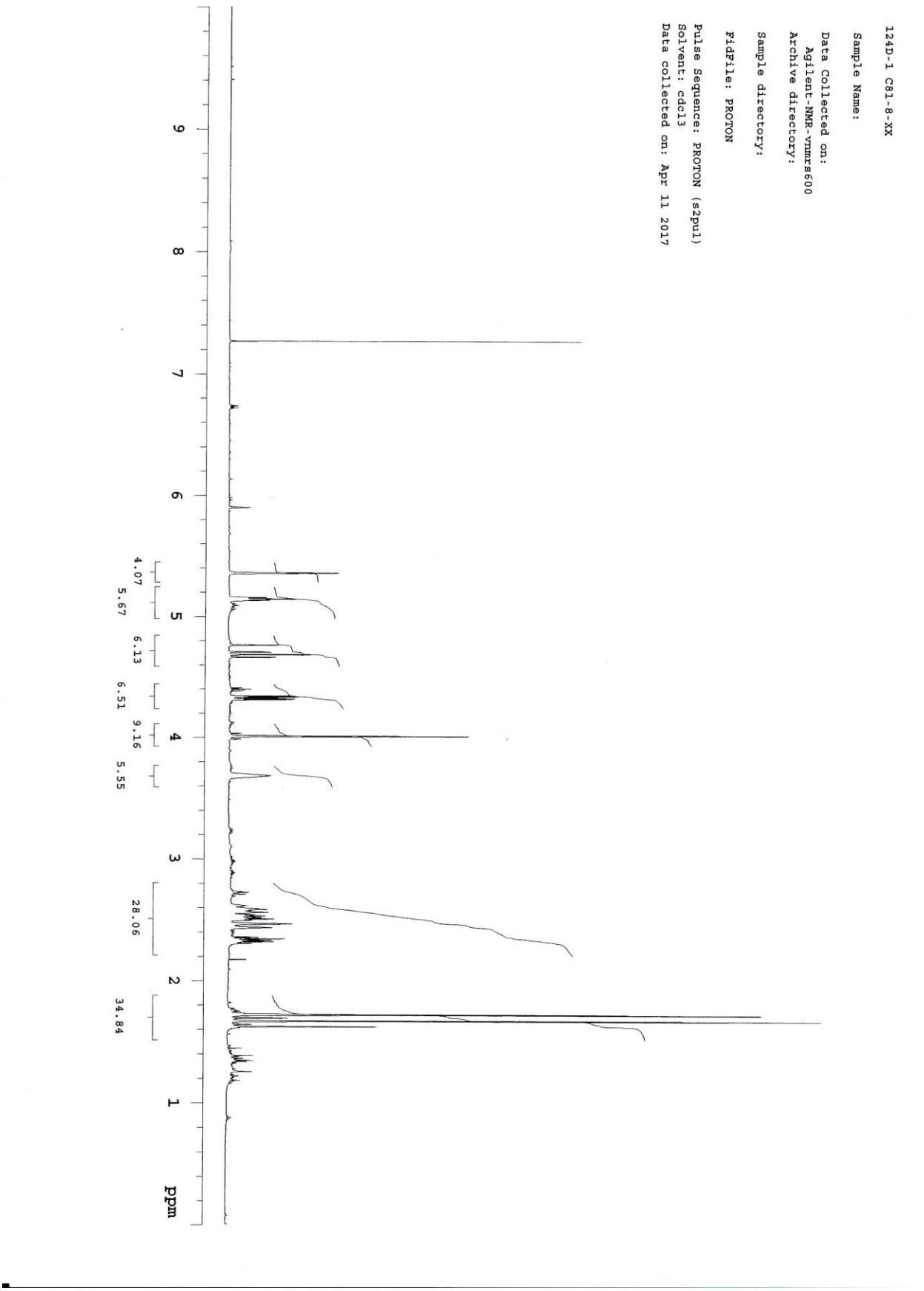

Figure S20 ^{13}C NMR spectra of 4 in $CDCl_3$

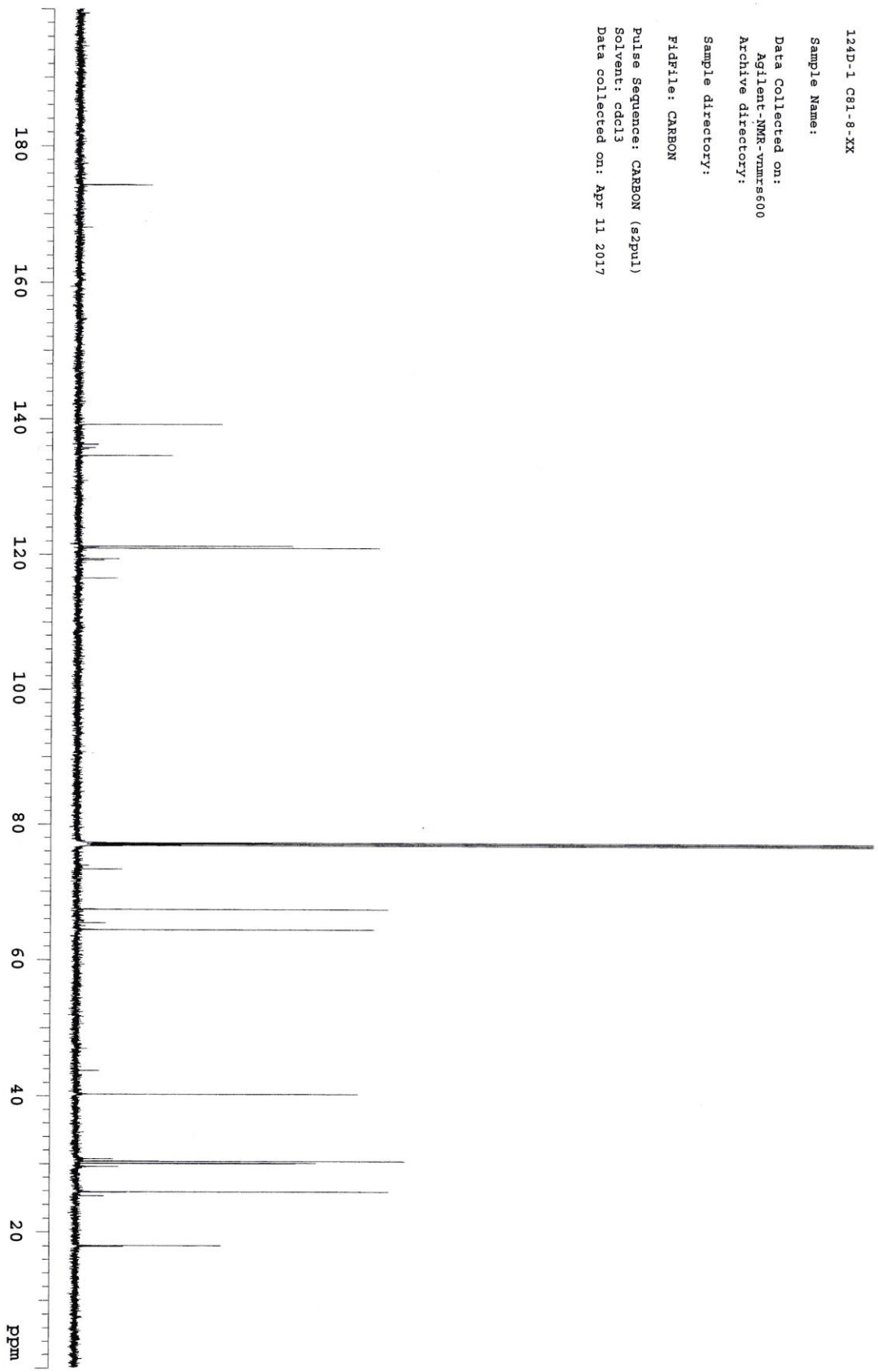

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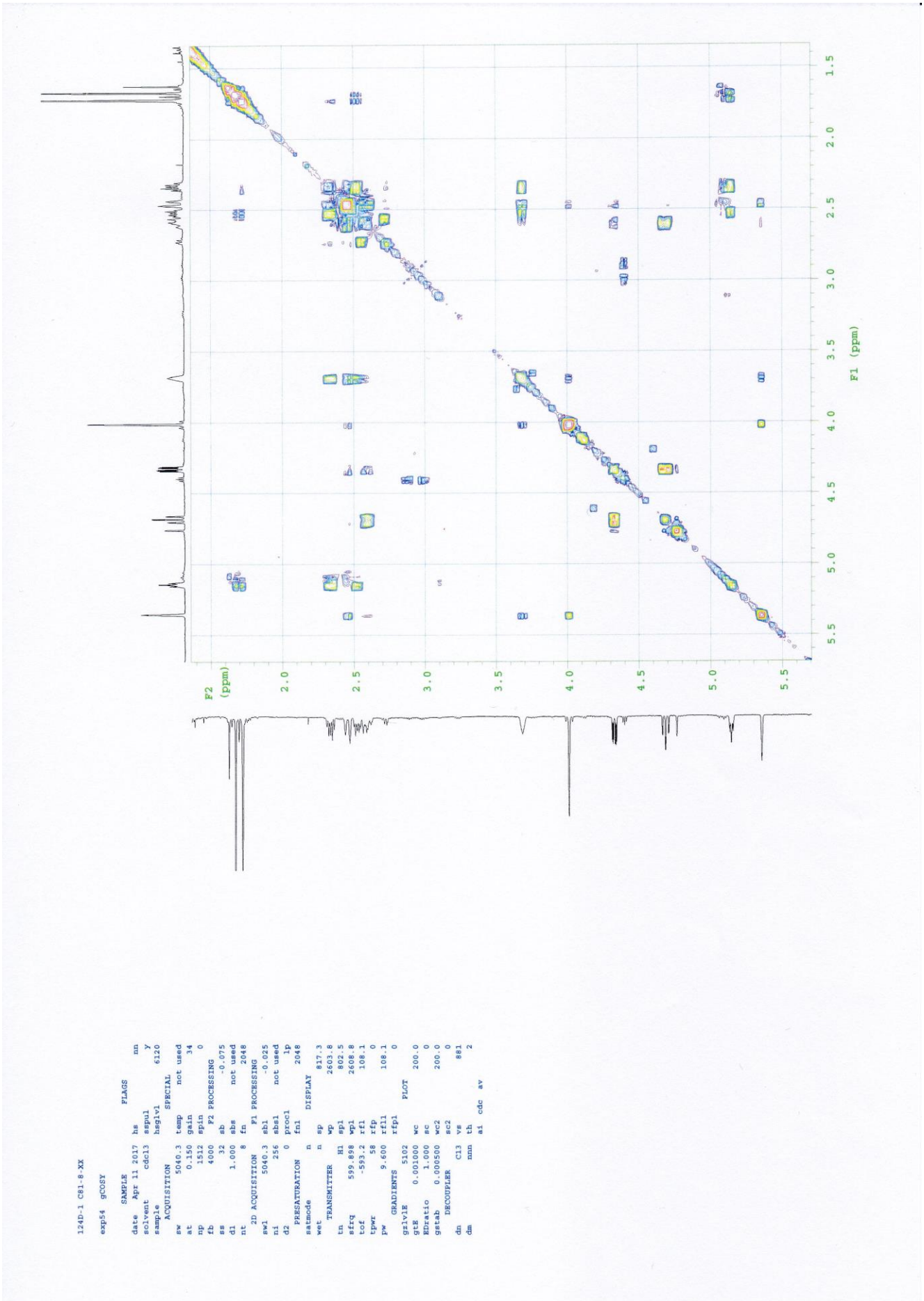
Figure S21 ^{1}H-^{1}H COSY of 4

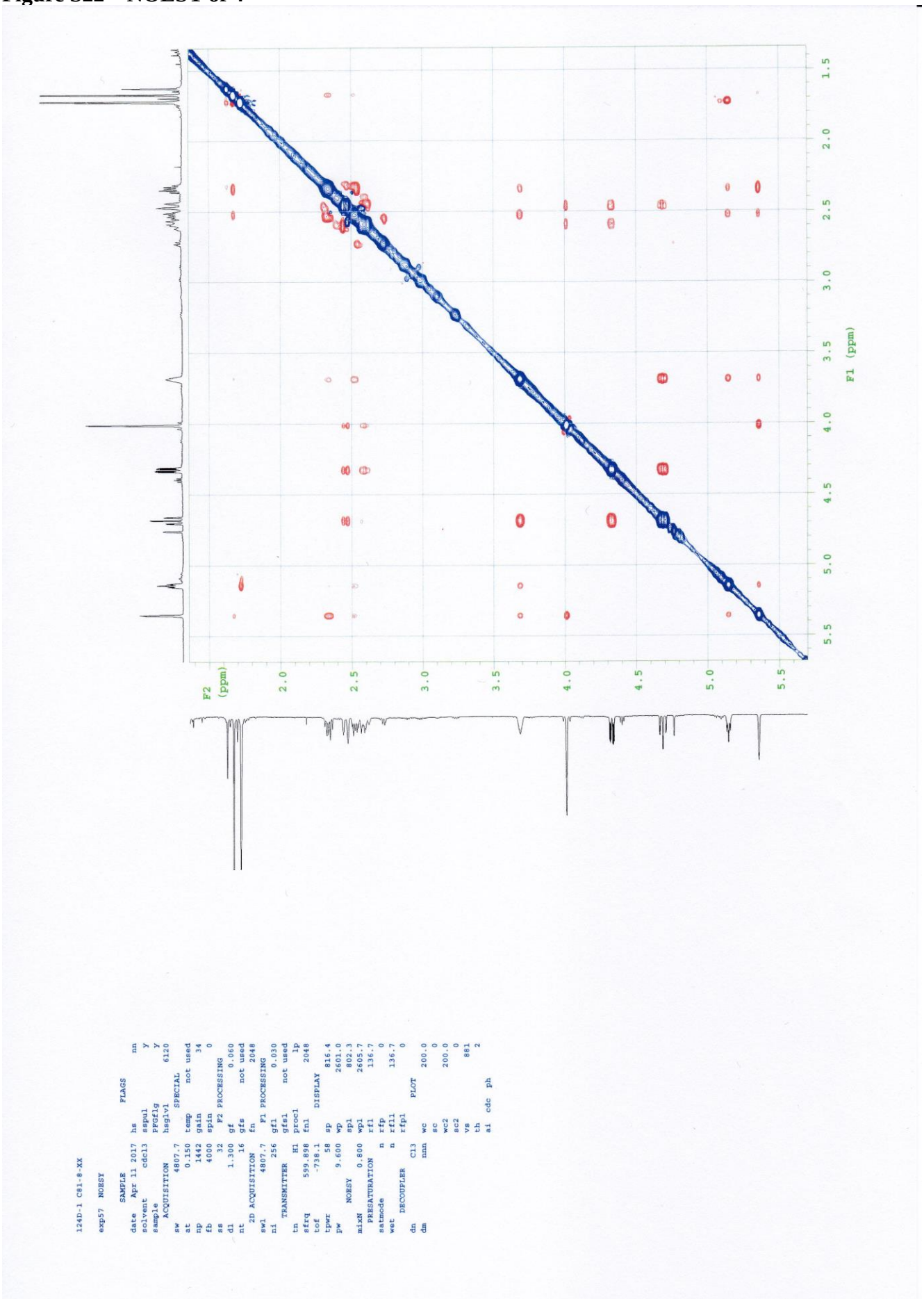



```
124D-1 C81-8-XX

exp54  gCOSY

          SAMPLE                    FLAGS                    nn
  date  Apr 11 2017  hs                        y
  solvent       cdcl3  sspul                  y
  sample              hsglv1                 6120
    ACQUISITION             SPECIAL
  sw          5040.3  temp       not used
  at           0.150  gain             34
  np            1512  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         5040.3  sb1         -0.025
  ni              256  sbs1       not used
  d2                0  proc1            1p
    PRESATURATION           fn1             2048
  satmode             n          DISPLAY
  wet                 n  sp          817.3
    TRANSMITTER             wp         2603.8
  tn                 H1  sp1          802.5
  sfrq        599.898  wp1        2608.8
  tof        -593.2  rf1         108.1
  tpwr             58  rfp             0
  pw           9.600  rfl1        108.1
    GRADIENTS               rfp1            0
  gzlvlE          5102                PLOT
  gtE         0.001000  wc         200.0
  EDratio        1.000  sc              0
  getab       0.000500  wc2        200.0
    DECOUPLER               sc2             0
  dn                C13  vs            881
  dm                nnn  th              2
                         al   cdc  av
```

Figure S22 NOESY of 4 $^{+}$



124D-1 C81-8-XX

exp57 NOESY

SAMPLE FLAGS
date Apr 11 2017 hs nn
solvent cdcl3 ssput y
sample PPG1g y
ACQUISITION hsglv1 6120
sw 4807.7 SPECIAL
at 0.150 temp not used
np 1442 gain 34
fb 4000 spin 0
ss 32 F2 PROCESSING
d1 1.300 gf 0.060
nt 16 gfs not used
2D ACQUISITION fn 2048
sw1 4807.7 F1 PROCESSING
ni 256 gf1 0.030
TRANSMITTER gfs1 not used
tn H1 proc1 lp
sfrq 599.898 fn1 2048
tof -738.1 DISPLAY
tpwr 58 sp 816.4
pw 9.600 wp 2601.0
NOESY sp1 802.3
mixN 0.800 wp1 2605.7
PRESATURATION rf1 136.7
satmode n rfp 0
wet n rfl1 136.7
DECOUPLER rfp1 0
dn C13 PLOT
dm nnn wc 200.0
sc 0
wc2 200.0
sc2 0
vs 881
th 2
ai cdc ph

Figure S23 HMQC of 4

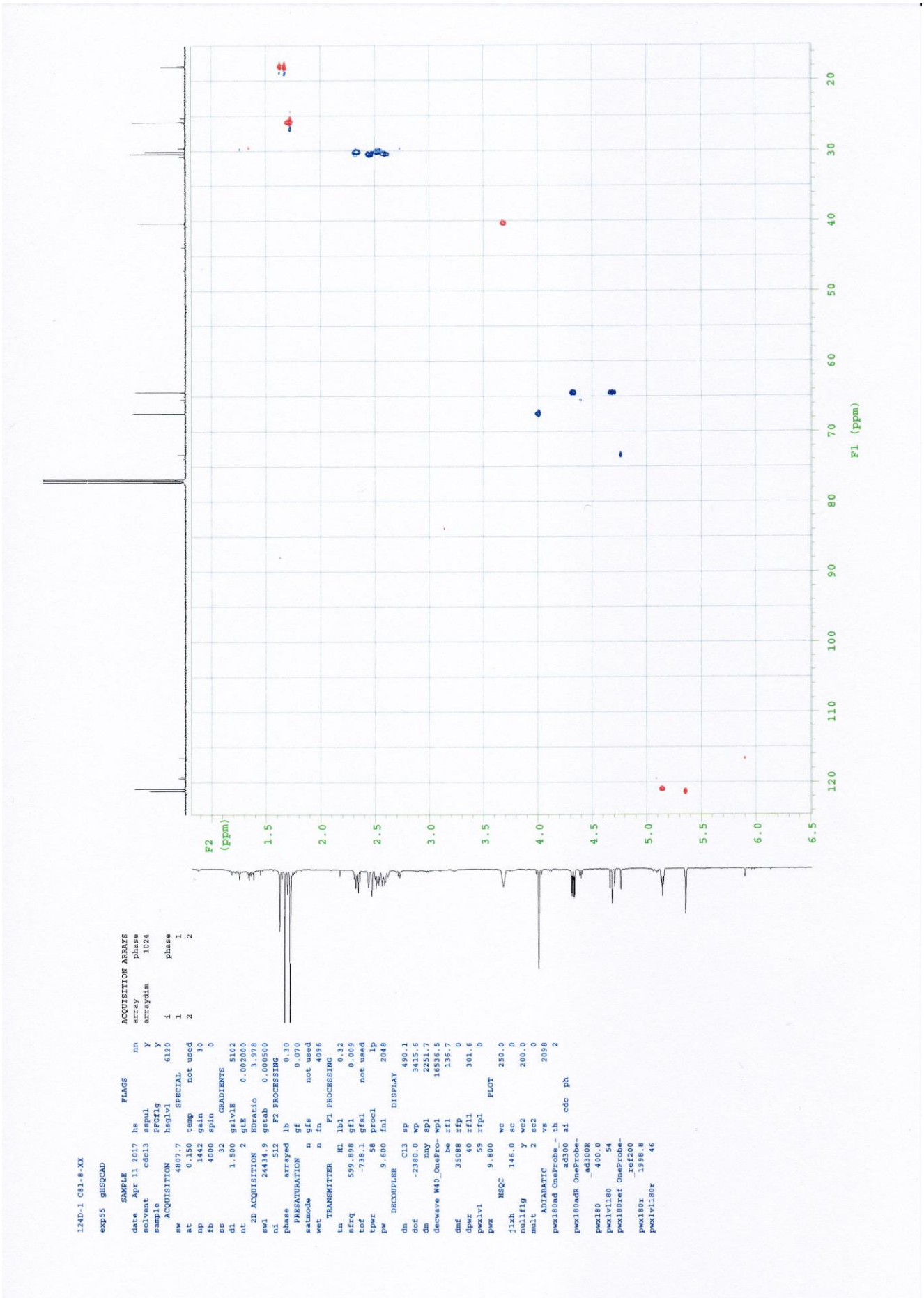


Figure S24 HMBC of 4

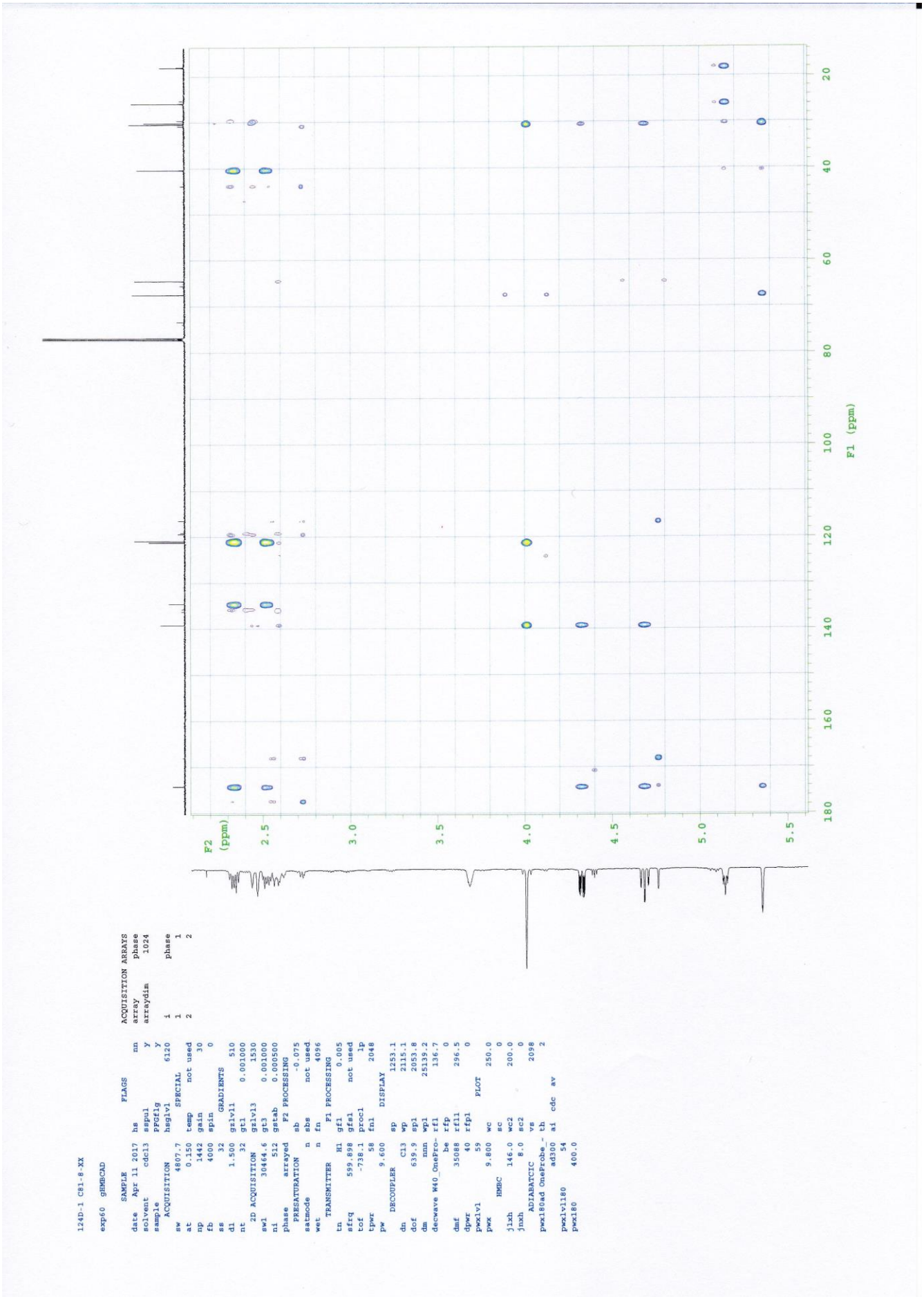
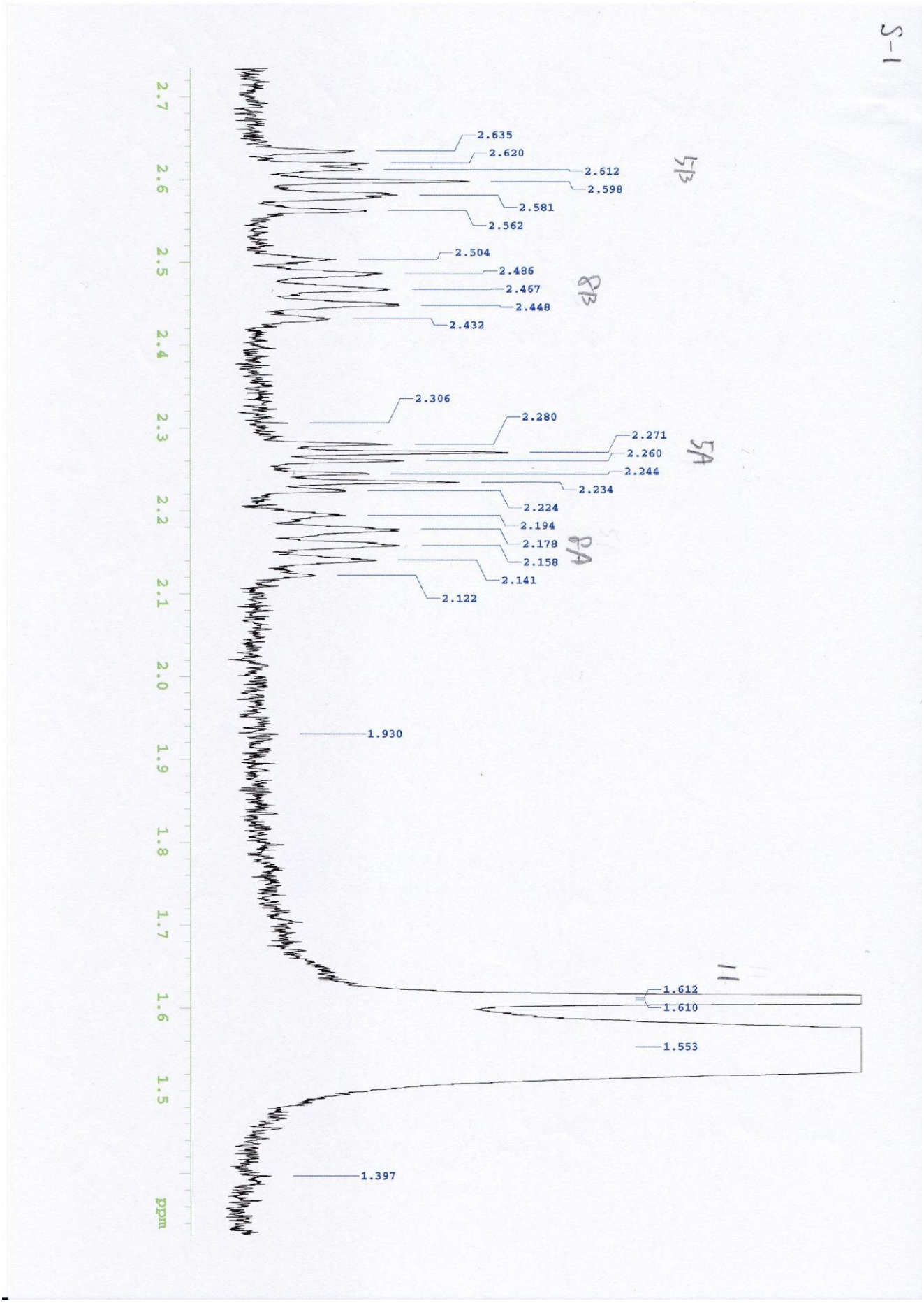
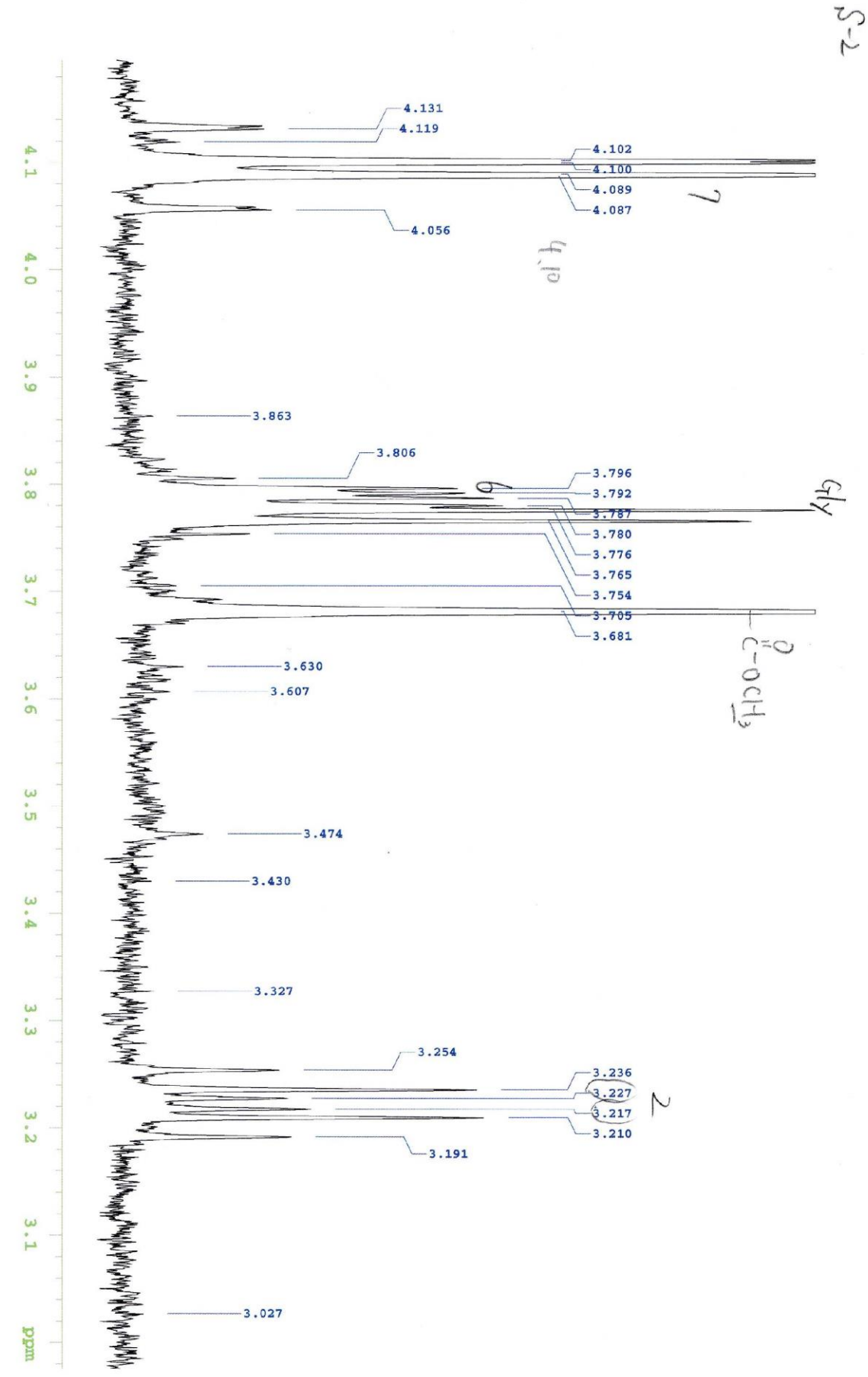
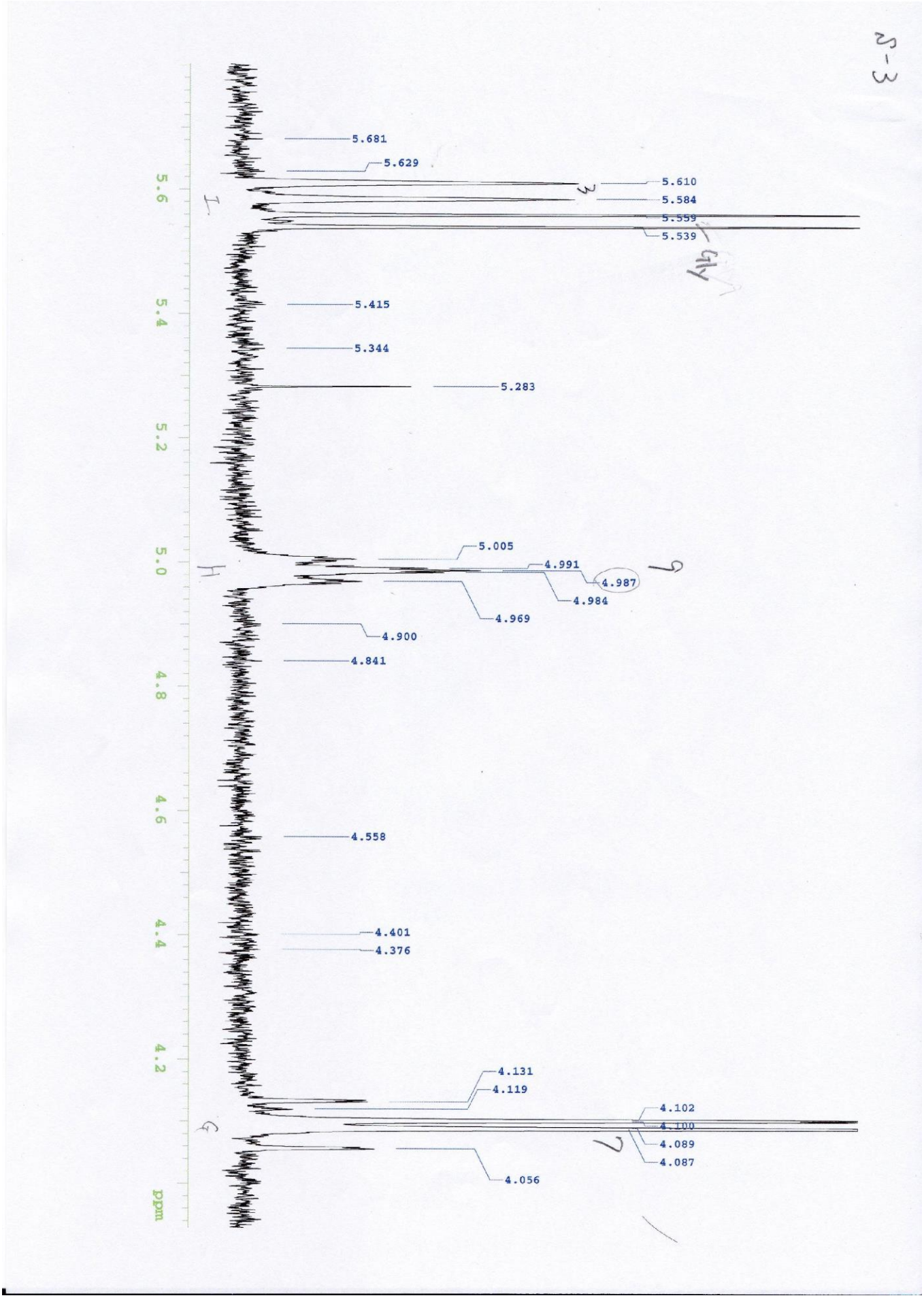


Figure S25 ^{1}H NMR spectra of 1a in $CDCl_3$




S-2
4.131
4.119
4.102
4.100
4.089
4.087
4.056
3.863
3.806
3.796
3.792
3.787
3.780
3.776
3.765
3.754
3.705
3.681
3.630
3.607
3.474
3.430
3.327
3.254
3.236
3.227
3.217
3.210
3.191
3.027
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
ppm
7
6
4
2
C-OCH3


5-3
5.681
5.629
5.610
5.584
5.559
5.539
5.415
5.344
5.283
5.005
4.991
4.987
4.984
4.969
4.900
4.841
4.558
4.401
4.376
4.131
4.119
4.102
4.100
4.089
4.087
4.056
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
ppm

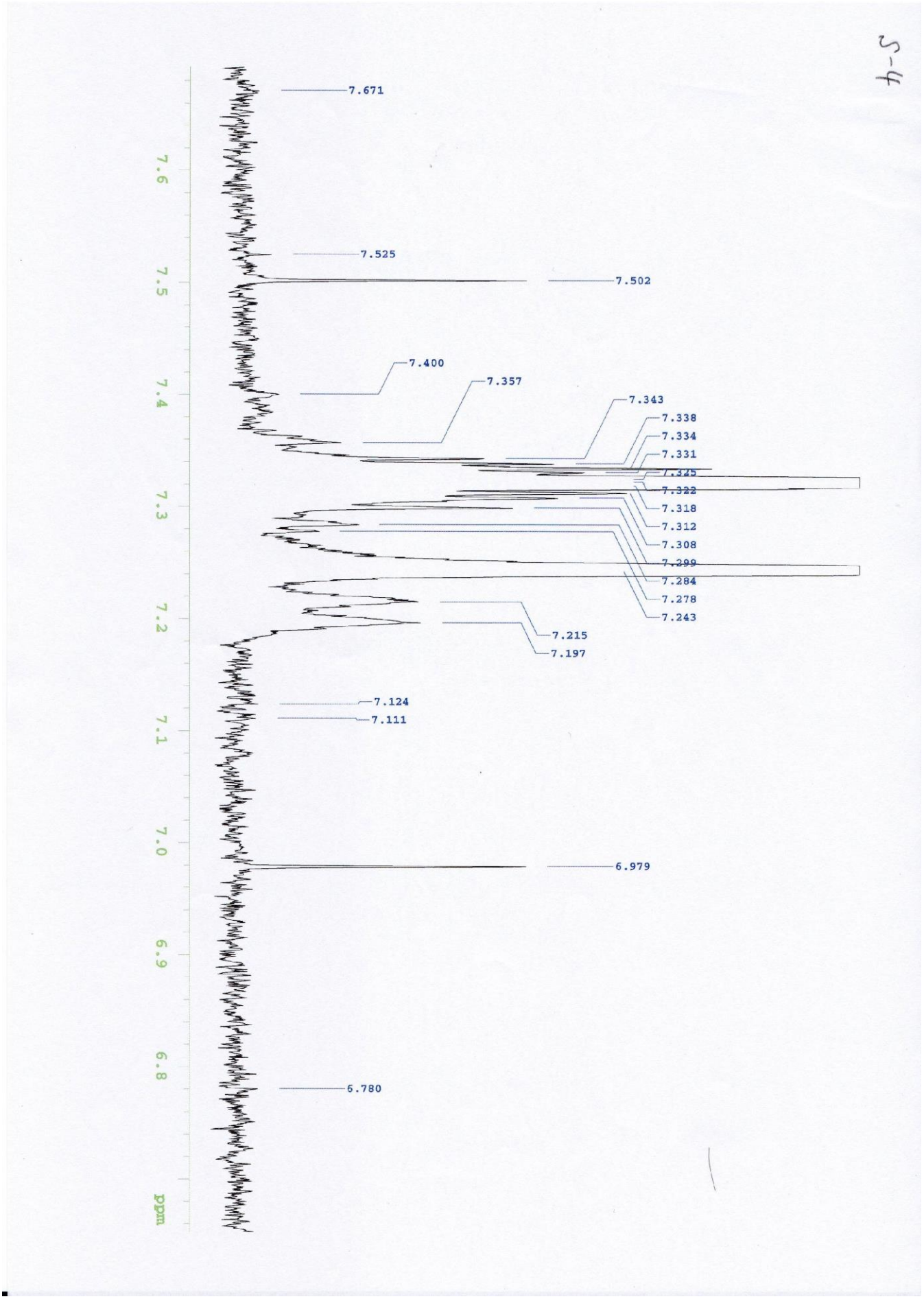
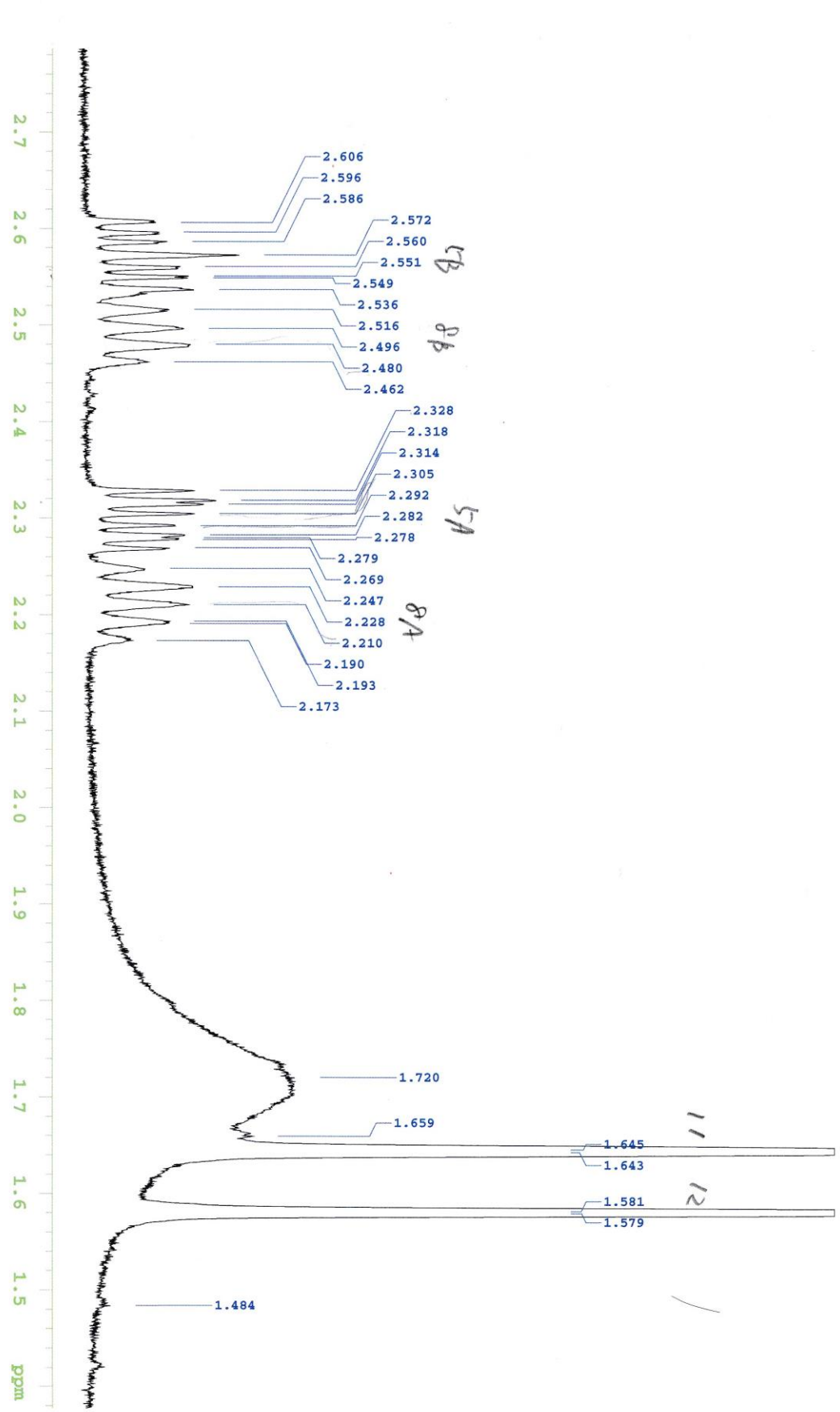
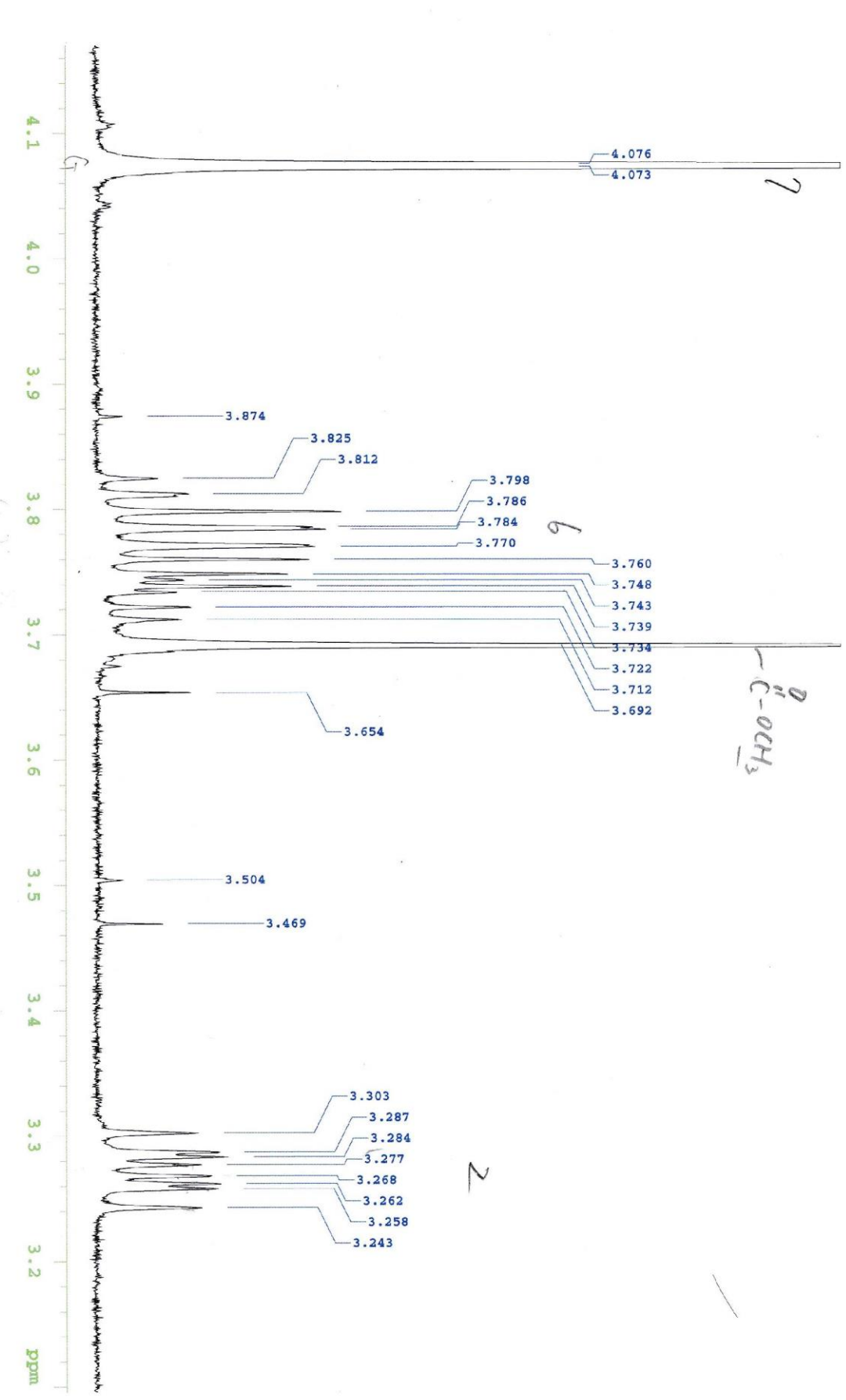

h-5
7.671
7.525
7.502
7.400
7.357
7.343
7.338
7.334
7.331
7.325
7.322
7.318
7.312
7.308
7.299
7.284
7.278
7.243
7.215
7.197
7.124
7.111
6.979
6.780
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
ppm

Figure S26 ^{1}H NMR spectra of 2a in $CDCl_{3+}$




R-2
4.076
4.073
3.874
3.825
3.812
3.798
3.786
3.784
3.770
3.760
3.748
3.743
3.739
3.734
3.722
3.712
3.692
3.654
3.504
3.469
3.303
3.287
3.284
3.277
3.268
3.262
3.258
3.243
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
ppm

R-3

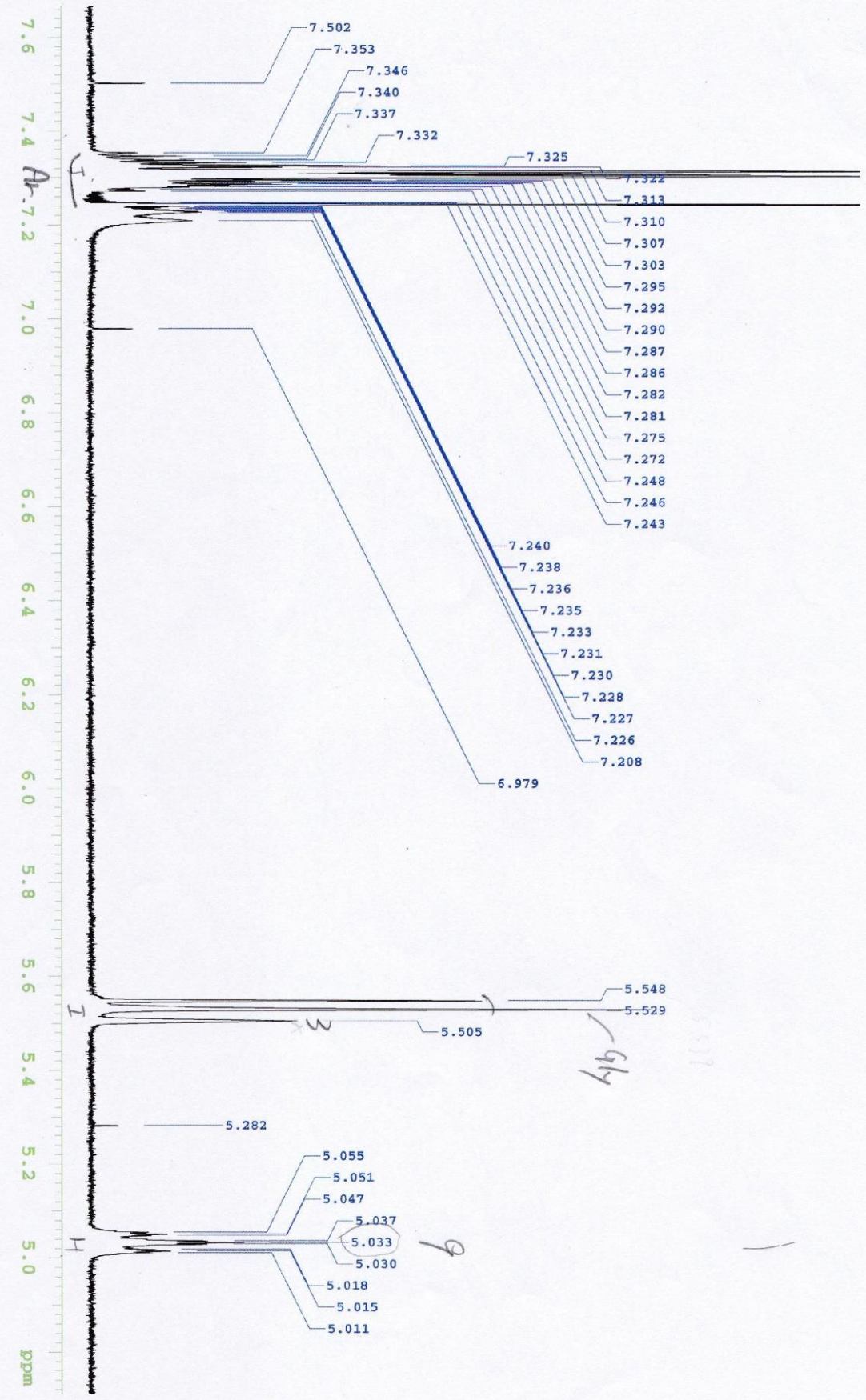

7.502
7.353
7.346
7.340
7.337
7.332
7.325
7.322
7.313
7.310
7.307
7.303
7.295
7.292
7.290
7.287
7.286
7.282
7.281
7.275
7.272
7.248
7.246
7.243
7.240
7.238
7.236
7.235
7.233
7.231
7.230
7.228
7.227
7.226
7.208
6.979
5.548
5.529
5.505
5.282
5.055
5.051
5.047
5.037
5.033
5.030
5.018
5.015
5.011
Ar
ppm

Figure S27 ^{1}H NMR spectra of 2b in $CDCl_3$