

## Supplementary Materials

# New diterpenes with a fused 6-5-6-6 ring system isolated from the metabolites of a marine sponge-derived fungus *Trichoderma harzianum*

Takeshi Yamada<sup>1,\*</sup>, Ayano Fujii<sup>1</sup> and Takashi Kikuchi<sup>1</sup>

### The Table of Contents

Table S1	Spectral data including 2D NMR data for 1	2
Table S2	Spectral data including 2D NMR data for 2	3
Table S3	Spectral data including 2D NMR data for 3	4
Table S4	Spectral data including 2D NMR data for 4	5
Table S5	Spectral data for 2a and 2b	6
Figure S1	<sup>1</sup> H NMR spectrum of 1 in CDCl <sub>3</sub>	7
Figure S2	<sup>13</sup> C NMR spectrum of 1 in CDCl <sub>3</sub>	12
Figure S3	<sup>1</sup> H- <sup>1</sup> H COSY of 1	16
Figure S4	NOESY of 1	18
Figure S5	HMQC of 1	20
Figure S6	HMBC of 1	22
Figure S7	FABMS of 1	24
Figure S8	<sup>1</sup> H NMR spectrum of 2 in CDCl <sub>3</sub>	26
Figure S9	<sup>13</sup> C NMR spectrum of 2 in CDCl <sub>3</sub>	30
Figure S10	<sup>1</sup> H- <sup>1</sup> H COSY of 2	34
Figure S11	NOESY of 2	36
Figure S12	HMQC of 2	38
Figure S13	HMBC of 2	40
Figure S14	FABMS of 2	42
Figure S15	<sup>1</sup> H NMR spectrum of 3 in CDCl <sub>3</sub>	44
Figure S16	<sup>13</sup> C NMR spectrum of 3 in CDCl <sub>3</sub>	48
Figure S17	<sup>1</sup> H- <sup>1</sup> H COSY of 3	52
Figure S18	NOESY of 3	54
Figure S19	HMQC of 3	56

<b>Figure S20</b>	<b>HMBC of 3</b>	<b>58</b>
<b>Figure S21</b>	<b>FABMS of 3</b>	<b>60</b>
<b>Figure S22</b>	<b><math>^1\text{H}</math> NMR spectrum of 4 in <math>\text{CDCl}_3</math></b>	<b>62</b>
<b>Figure S23</b>	<b><math>^{13}\text{C}</math> NMR spectrum of 4 in <math>\text{CDCl}_3</math></b>	<b>67</b>
<b>Figure S24</b>	<b><math>^1\text{H}</math>-<math>^1\text{H}</math> COSY of 4</b>	<b>71</b>
<b>Figure S25</b>	<b>NOESY of 4</b>	<b>73</b>
<b>Figure S26</b>	<b>HMQC of 4</b>	<b>75</b>
<b>Figure S27</b>	<b>HMBC of 4</b>	<b>77</b>
<b>Figure S28</b>	<b>FABMS of 4</b>	<b>80</b>
<b>Figure S29</b>	<b><math>^1\text{H}</math> NMR spectrum of 2a in <math>\text{CDCl}_3</math></b>	<b>82</b>
<b>Figure S30</b>	<b><math>^1\text{H}</math>-<math>^1\text{H}</math> COSY of 2a</b>	<b>87</b>
<b>Figure S31</b>	<b>NOESY of 2a</b>	<b>89</b>
<b>Figure S32</b>	<b>FABMS of 2a</b>	<b>91</b>
<b>Figure S33</b>	<b><math>^1\text{H}</math> NMR spectrum of 2b in <math>\text{CDCl}_3</math></b>	<b>93</b>
<b>Figure S34</b>	<b><math>^1\text{H}</math>-<math>^1\text{H}</math> COSY of 2b</b>	<b>98</b>
<b>Figure S35</b>	<b>NOESY of 2b</b>	<b>100</b>
<b>Figure S36</b>	<b>FABMS of 2b</b>	<b>102</b>

Table S1 NMR spectral data of **1** in CDCl<sub>3</sub>

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	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
18ax	0.99	s			6, 7 $\alpha$ , 12, 13 $\alpha$	25.7 (q)	4, 5, 6, 19
19eq	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

a  $^1\text{H}$  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. b The correlations with geminal and vicinal protons are removed. c Long range  $^1\text{H}-^{13}\text{C}$  correlations from H to C observed in the HMBC experiment.

Table S2 NMR spectral data of **2** in CDCl<sub>3</sub>

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 $\alpha$	2.54	ddd	15.0 (1 $\alpha$ ), 11.4 (2), 11.4 (6)	2, 6	19		36.5 (t)	2, 3, 6, 7
1 $\beta$	1.68	m		2, 6	20			2, 5, 6, 7
2	4.30	ddd	11.4 (1 $\beta$ ), 7.2 (3), 6.6 (1 $\alpha$ )	1 $\alpha$ , 2 $\alpha$ , 3	17, 19		74.2 (d)	1, 3, 17
3	1.98	qd	7.2 (17), 7.2 (2)	2, 17	11, 14 $\beta$ , 20		37.9 (d)	2, 4, 5, 12, 17
4							40.8 (s)	
5							39.0 (s)	
6	1.62	m		1 $\alpha$ , 1 $\beta$ , 7 $\alpha$ , 7 $\beta$	18, 19		41.8 (d)	
7 $\alpha$	1.71	dd	13.2 (7 $\beta$ ), 4.2 (6)	6, 7 $\beta$	9 $\alpha$ , 12, 18		42.5 (t)	1, 6, 8, 9
7 $\beta$	1.56	dd	13.2 (7 $\alpha$ ), 3.0 (6)	6, 7 $\alpha$	20			5, 8, 12, 20
8							39.7 (s)	
9 $\alpha$	1.02	m		9 $\beta$ , 10 $\alpha$ , 10 $\beta$	7 $\alpha$ , 12		43.9 (t)	
9 $\beta$	1.43	m		9 $\alpha$ , 10 $\alpha$ , 10 $\beta$	20			11, 12, 20
10 $\alpha$	1.60	m		9 $\alpha$ , 9 $\beta$ , 10 $\beta$ , 11	12, 16		21.6 (t)	11, 15
10 $\beta$	1.81	m		9 $\alpha$ , 9 $\beta$ , 10 $\alpha$ , 11				9
11	1.85	m		10 $\alpha$ , 10 $\beta$ , 12	3, 20		44.4 (d)	10, 12, 15, 16
12	1.30	d	13.2 (11)	11	7 $\alpha$ , 9 $\alpha$ , 10 $\alpha$ , 16, 18		51.9 (d)	3, 4, 5, 8, 9, 10, 11, 15, 20
13 $\alpha$	1.18	ddd	13.8 (13 $\beta$ ), 13.8 (14 $\beta$ ), 3.6 (14 $\alpha$ )	13 $\beta$ , 14 $\alpha$ , 14 $\beta$	18, 19		26.4 (t)	12
13 $\beta$	1.68	m		13 $\alpha$ , 14 $\alpha$ , 14 $\beta$	17			
14 $\alpha$	1.62	m		13 $\alpha$ , 13 $\beta$ , 14 $\beta$			41.2 (t)	
14 $\beta$	1.46	ddd	13.8 (12 $\alpha$ ), 13.8 (13 $\alpha$ ), 3.0 (13 $\beta$ )	13 $\alpha$ , 13 $\beta$ , 14 $\alpha$	3, 17			
15							73.8 (s)	
16	1.18	s			10 $\alpha$ , 12		20.4 (q)	11, 14, 15
17	1.19	d	7.8 (3)	3	2, 13 $\beta$ , 14 $\beta$ , 19		20.4 (q)	2, 3, 4
18ax	0.95	s			6, 7 $\alpha$ , 12, 13 $\alpha$		25.3 (q)	4, 5, 6, 19
19eq	0.96	s			2, 6, 13 $\alpha$ , 17		25.4 (q)	4, 5, 6, 18
20	1.13	s			1 $\beta$ , 3, 7 $\beta$ , 9 $\beta$ , 11		20.3 (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 S3 NMR spectral data of **3** in CDCl<sub>3</sub>

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	4.20	dd	9.6 (2 $\alpha$ ), 5.4 (2 $\beta$ )	2 $\alpha$ , 2 $\beta$ , 6	7 $\beta$ , 20		72.6 (d)	5, 7
2 $\alpha$	2.66	ddd	16.2 (2 $\beta$ ), 9.6 (1), 9.6 (3)	1, 2 $\beta$ , 3	17, 19		41.8 (t)	1, 3, 17
2 $\beta$	1.45	m		1, 2 $\alpha$ , 3	20			1, 3, 4, 6
3	2.10	m		2 $\alpha$ , 2 $\beta$ , 17	11, 20		26.7 (d)	2, 4, 5, 12, 17
4							38.9 (s)	
5							39.0 (s)	
6	1.41	dd	4.2 (7 $\alpha$ ), 3.0 (7 $\beta$ )	1, 7 $\alpha$ , 7 $\beta$	18		52.2 (d)	
7 $\alpha$	1.69	dd	13.8 (7 $\beta$ ), 4.2 (6)	6	12, 18		41.3 (t)	1, 5, 6, 20
7 $\beta$	1.65	dd	13.8 (7 $\alpha$ ), 3.0 (6)	6	1, 20			1, 5, 12, 20
8							38.8 (s)	
9	1.48	m		10	20		52.2 (t)	8, 10, 11, 12, 20
10	4.38	ddd	7.8 (9), 4.8 (11), 1.2 (9)	9, 11	12, 16		72.9 (d)	8, 15
11	1.85	dd	13.8 (12), 4.8 (10)	10, 12	3, 20		55.0 (d)	10, 12, 15, 16
12	1.28	d	13.8 (11)	11	7 $\alpha$ , 10, 18		50.6 (d)	3, 4, 5, 8, 9, 10, 11, 15, 20
13 $\alpha$	1.19	ddd	14.0 (13 $\beta$ ), 14.0 (14 $\beta$ ), 3.0 (14 $\alpha$ )	13 $\beta$ , 14 $\alpha$ , 14 $\beta$	18		25.9 (t)	4, 12, 14
13 $\beta$	1.74	ddd	14.0 (13 $\alpha$ ), 3.0 (14 $\beta$ ), 3.0 (14 $\alpha$ )	13 $\alpha$ , 14 $\alpha$ , 14 $\beta$	17, 19			
14 $\alpha$	1.60	ddd	14.0 (12 $\beta$ ), 3.0 (13 $\alpha$ ), 3.0 (13 $\beta$ )	13 $\alpha$ , 13 $\beta$ , 14 $\beta$	16		41.0 (t)	13
14 $\beta$	1.50	ddd	14.0 (12 $\alpha$ ), 14.0 (13 $\alpha$ ), 3.0 (13 $\beta$ )	13 $\alpha$ , 13 $\beta$ , 14 $\alpha$				4, 15, 16
15							73.1 (s)	
16	1.22	s			10, 14 $\alpha$		21.5 (q)	11, 14, 15
17	1.09	d	6.6 (3)	3	2 $\alpha$ , 13 $\beta$		22.4 (q)	2, 3, 4
18ax	0.97	s			6, 7 $\alpha$ , 12, 13 $\alpha$		25.8 (q)	4, 5, 6, 19
19eq	1.14	s			2 $\alpha$ , 13 $\beta$		24.9 (q)	4, 5, 6, 18
20	1.17	s			1, 2 $\beta$ , 3, 7 $\beta$ , 9, 11		21.4 (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 S4 NMR spectral data of **4** in CDCl<sub>3</sub>

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	4.24	dd	10.2 (2 $\alpha$ ), 6.0 (2 $\beta$ )	2 $\alpha$ , 2 $\beta$ , 17	7 $\beta$ , 20	72.1 (d)	5, 7
2 $\alpha$	2.74	ddd	16.2 (2 $\beta$ ), 10.2 (1), 10.2 (3)	1, 2 $\beta$ , 3	19	36.9 (t)	1, 3, 4, 6
2 $\beta$	1.64	ddd	16.2 (2 $\alpha$ ), 6.0 (1), 3.6 (3)	1, 2 $\alpha$ , 3			17
3	1.88	dddd	10.2 (2 $\alpha$ ), 10.2 (17A), 3.6 (2 $\beta$ ), 3.6 (17B)	2 $\alpha$ , 2 $\beta$ , 17A	11, 20	34.0 (d)	
4						38.9 (s)	
5						38.5 (s)	
6	1.45	dd	4.8 (7 $\alpha$ ), 3.6 (7 $\beta$ )	7 $\alpha$ , 7 $\beta$	18	52.2 (d)	
7 $\alpha$	1.74	dd	13.8 (7 $\beta$ ), 4.8 (6)	6, 7 $\beta$	9 $\alpha$ , 18	40.9 (t)	1, 6, 8, 9, 20
7 $\beta$	1.68	dd	13.8 (7 $\alpha$ ), 3.6 (6)	6, 7 $\alpha$	1, 20		5, 12
8						39.2 (s)	
9 $\alpha$	1.03	m		10 $\alpha$	7 $\alpha$	43.5 (t)	
9 $\beta$	1.43	m		10 $\beta$	20		8, 11
10 $\alpha$	1.59	m		9 $\alpha$ , 11	16	21.5 (t)	
10 $\beta$	1.80	m		9 $\beta$	20		
11	1.88	ddd	13.2 (12), 10.2 (10), 6.0 (10)	10 $\alpha$ , 12	3, 14 $\beta$ , 20	44.1 (d)	12, 15
12	1.28	d	13.2 (11)	11	16, 18	52.0 (d)	3, 4, 5, 8, 9, 11, 15, 20
13 $\alpha$	1.28	m		13 $\beta$ , 14 $\alpha$ , 14 $\beta$		25.5 (t)	
13 $\beta$	1.52	m		13 $\alpha$ , 14 $\alpha$ , 14 $\beta$	17, 19		
14 $\alpha$	1.67	m		13 $\alpha$ , 13 $\beta$ , 14 $\beta$		40.87 (t)	4
14 $\beta$	1.50	m		13 $\alpha$ , 13 $\beta$ , 14 $\alpha$	11		15, 16
15						73.6 (s)	
16	1.18	s			10 $\alpha$ , 12	20.5 (q)	11, 14, 15
17A	3.60	dd	10.2 (3), 10.2 (17B)	3	13 $\beta$ , 19	68.1 (t)	2, 3
17B	3.95	dd	10.2 (17A), 3.6 (3)		13 $\beta$		2
18ax	0.99	s			6, 7 $\alpha$ , 12	25.7 (q)	4, 5, 6, 19
19eq	1.13	s			2 $\alpha$ , 13 $\beta$ , 17A	25.5 (q)	4, 5, 6, 18
20	0.92	s			1, 3, 7 $\beta$ , 9 $\beta$ , 10 $\beta$ , 11	19.5 (q)	7, 8, 9, 12

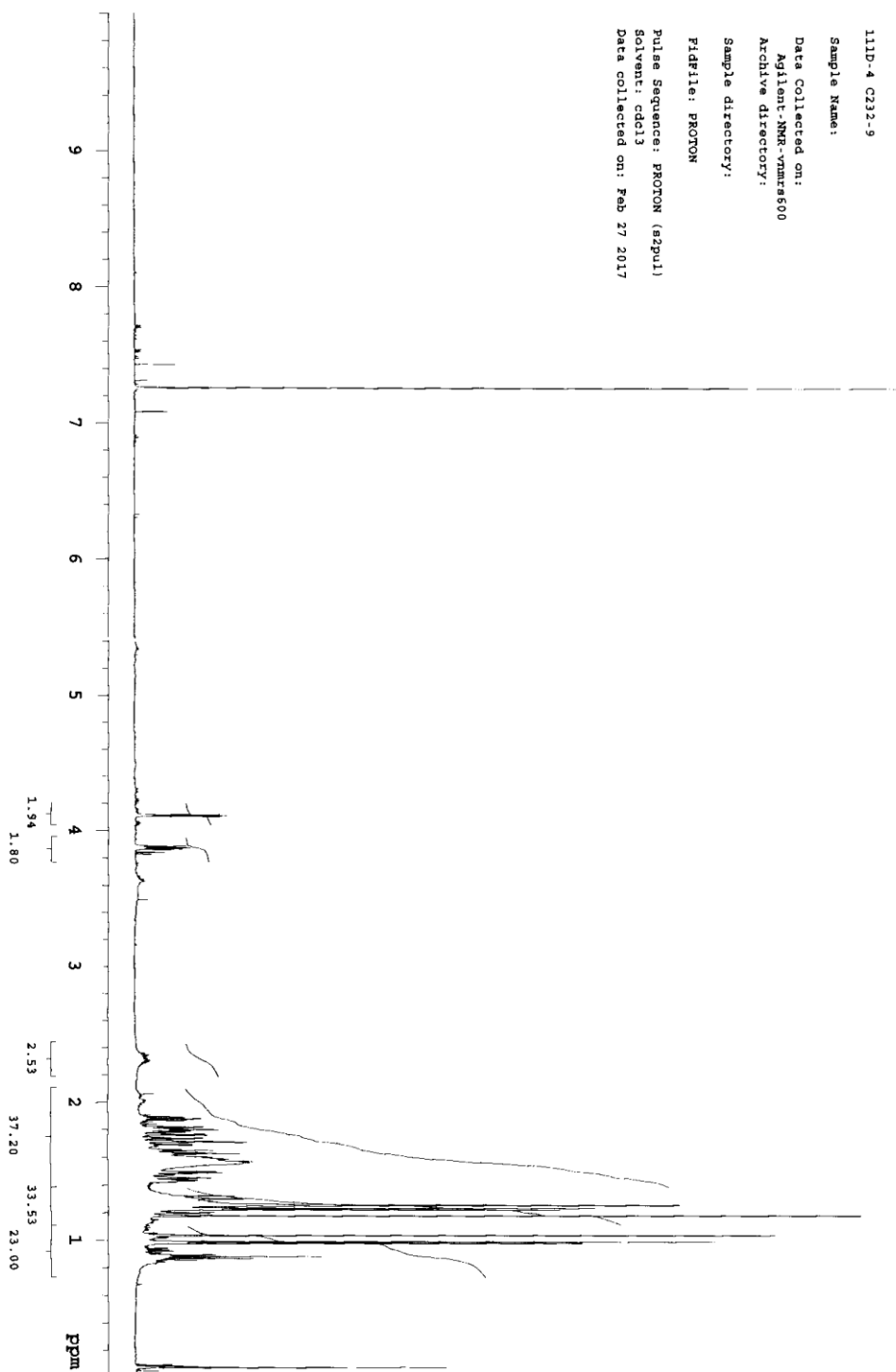
a  $^1\text{H}$  chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants ( $J/\text{Hz}$ ). Figures in parentheses indicate the proton coupling with that position. b The correlations with geminal and vicinal protons are removed. c Long range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

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

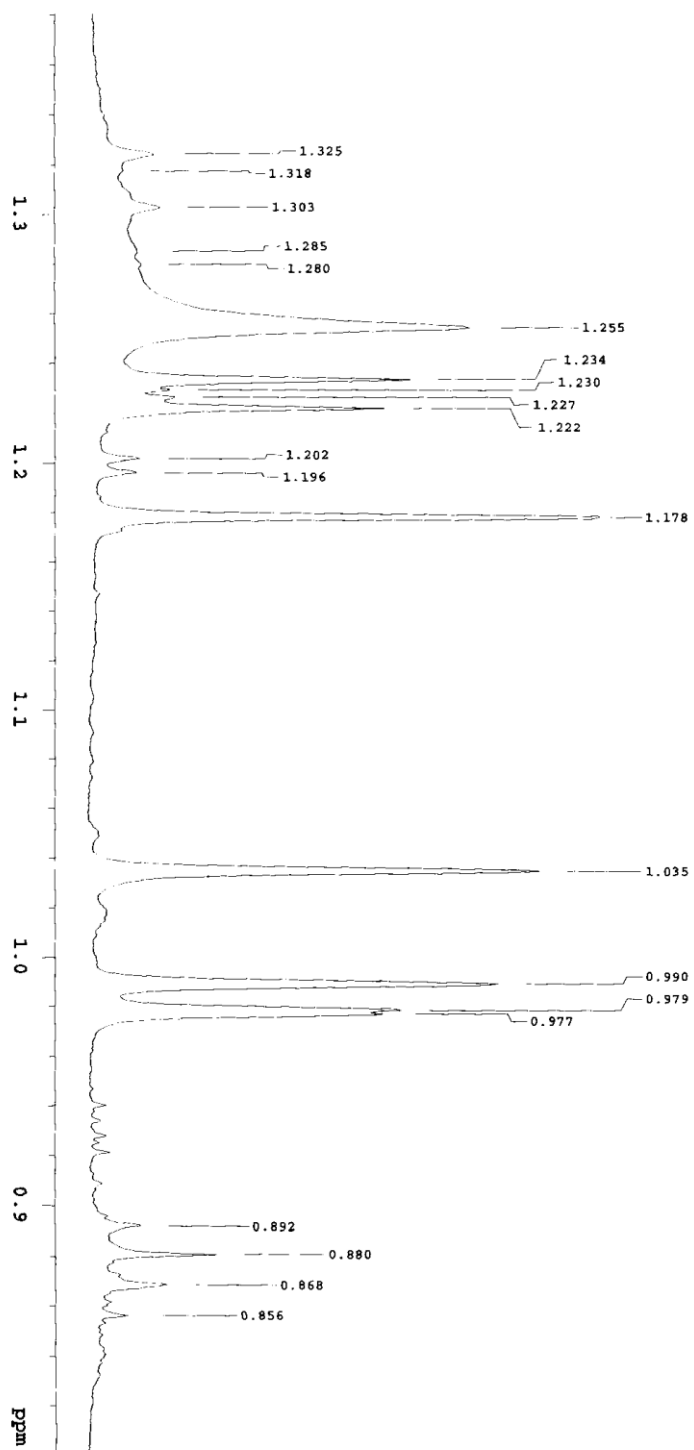
Position	$\delta_{\text{H}}^{\text{a}}$		$J/\text{Hz}$	$\delta_{\text{H}}^{\text{a}}$		$J/\text{Hz}$
	<b>2a</b>			<b>2b</b>		
1 $\alpha$	2.82	ddd	16.2 (1 $\alpha$ ), 10.8 (2), 10.8 (6)	2.85	ddd	15.0 (1 $\alpha$ ), 11.4 (2), 11.4 (6)
1 $\beta$	1.52	m		1.66	m	
2	5.25	ddd	11.4 (1 $\beta$ ), 6.6 (3), 6.6 (1 $\alpha$ )	5.28	ddd	11.4 (1 $\beta$ ), 7.2 (3), 6.6 (1 $\alpha$ )
3	2.21	qd	7.2 (17), 7.2 (2)	2.17	qd	7.2 (17), 7.2 (2)
4						
5						
6	1.64	m		1.64	m	
7 $\alpha$	1.68	m		1.72	dd	16.2 (7 $\beta$ ), 4.2 (6)
7 $\beta$	1.46	dd	13.8 (7 $\alpha$ ), 3.0 (6)	1.53	dd	16.2 (7 $\alpha$ ), 3.0 (6)
8						
9 $\alpha$	1.00	m		1.02	m	
9 $\beta$	1.36	m		1.42	m	
10 $\alpha$	1.58	m		1.60	m	
10 $\beta$	1.79	m		1.81	m	
11	1.81	m		1.81	m	
12	1.28	d	12.6 (11)	1.29	d	12.6 (11)
13 $\alpha$	1.20	ddd	14.4 (13 $\beta$ ), 14.4 (14 $\beta$ ), 3.0 (14 $\alpha$ )	1.19	m	
13 $\beta$	1.70	m		1.68	m	
14 $\alpha$	1.62	m		1.62	m	
14 $\beta$	1.42	m		1.40	m	
15						
16	1.17	s		1.17	s	
17	1.13	d	7.2 (3)	1.02	d	7.2 (3)
18ax	0.97	s		0.98	s	
19eq	1.01	s		1.01	s	
20	0.75	s		0.97	s	
OCH <sub>3</sub>	3.57	s		3.53	s	
Ar.H	7.38-7.41	m		7.39-7.41	m	
Ar.H	7.53	m		7.53	m	

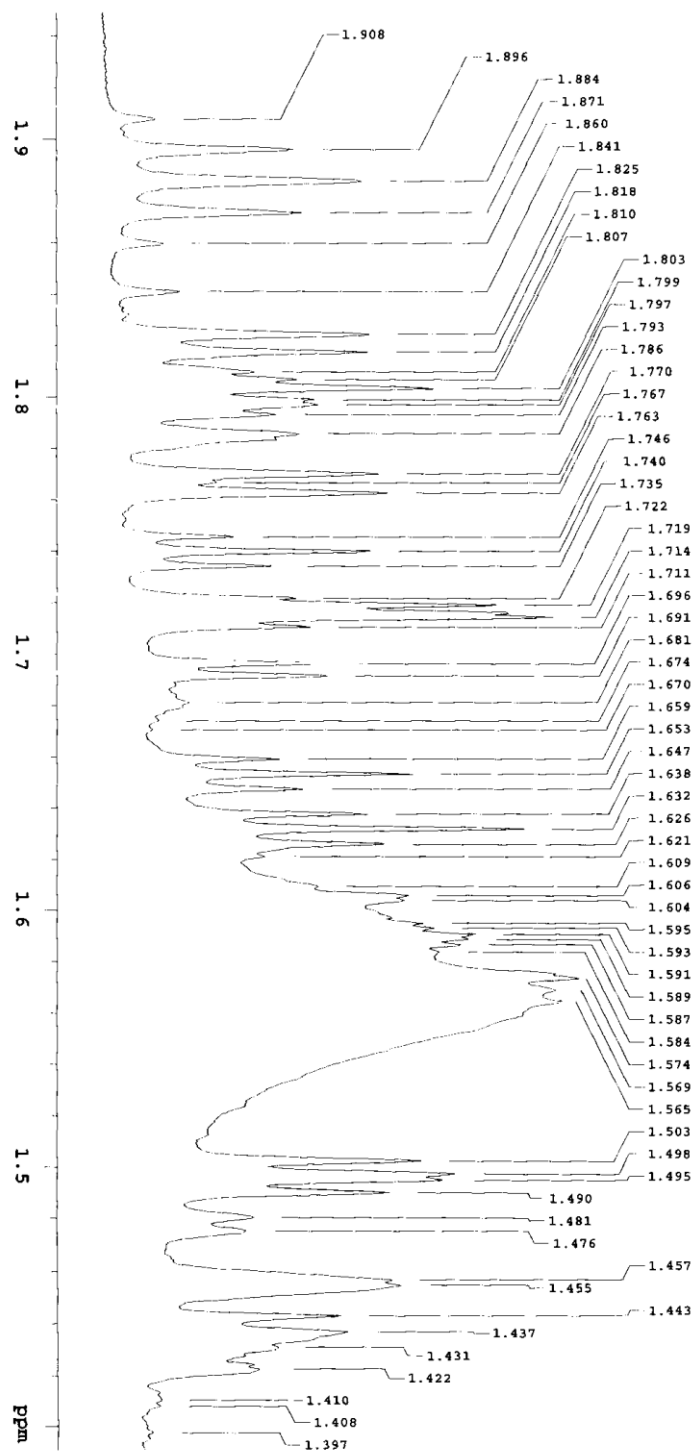
<sup>a</sup> <sup>1</sup>H chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) followed by multiplicity and then the coupling constants (J/Hz). Figures in parentheses indicate the proton coupling with that position.

Figure S1  $^1\text{H}$  NMR spectrum of 1 in  $\text{CDCl}_3$



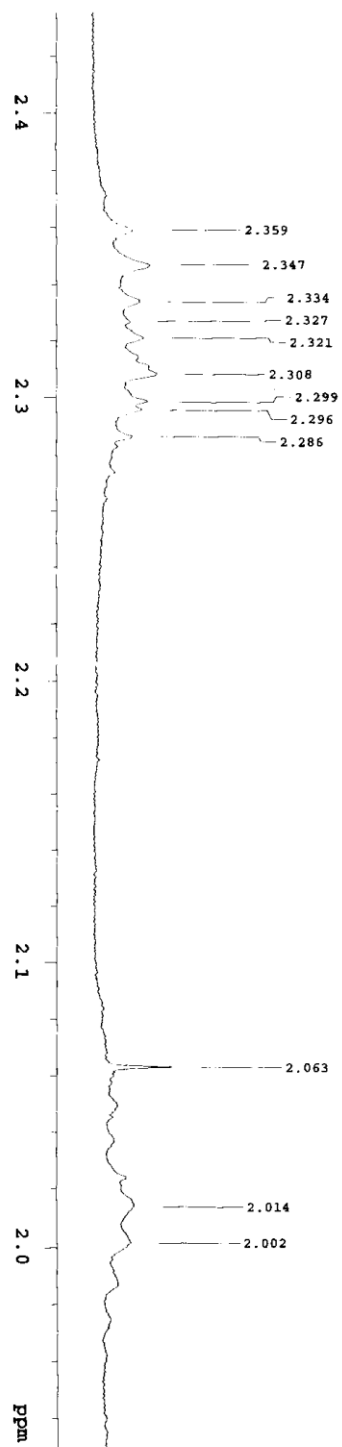






11ID-4 C232-9

111D-4 C232-9



111D-4 C232-9

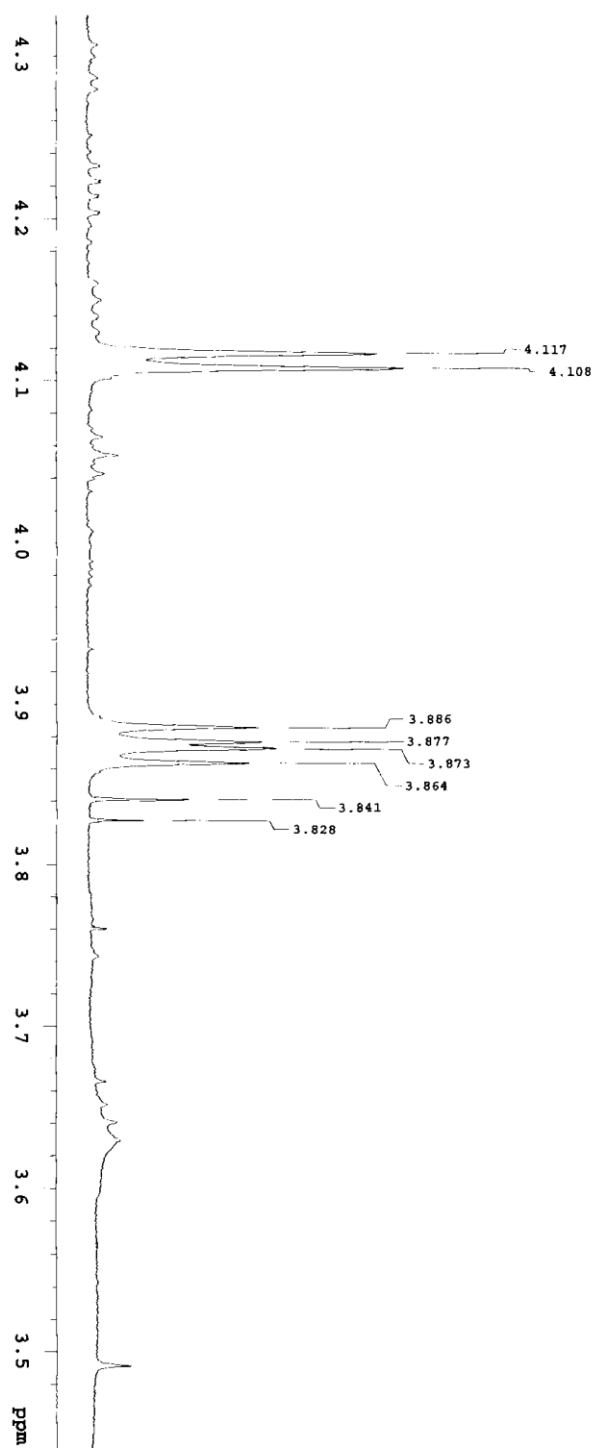
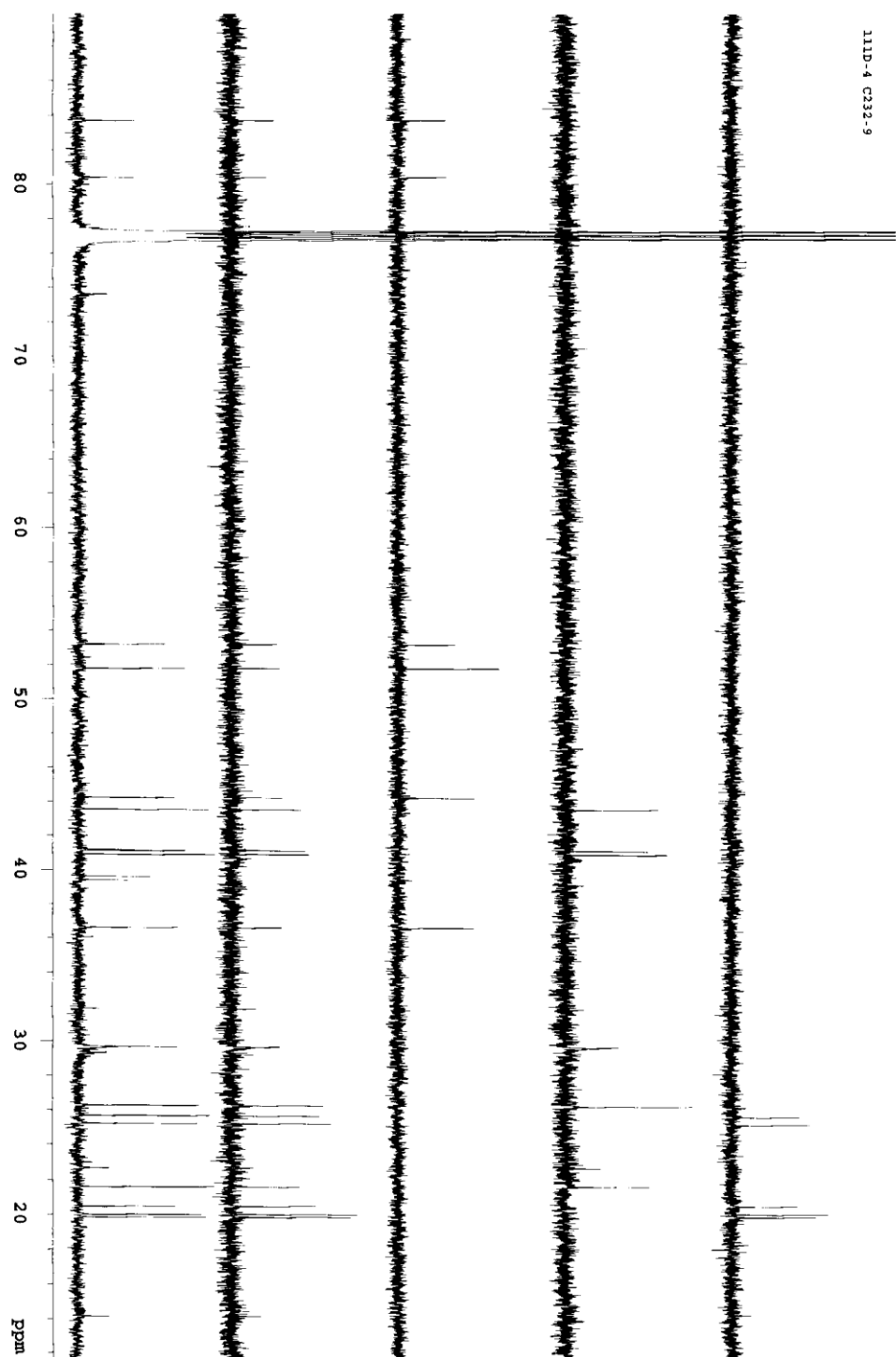


Figure S2  $^{13}\text{C}$  NMR spectrum of 1 in  $\text{CDCl}_3$

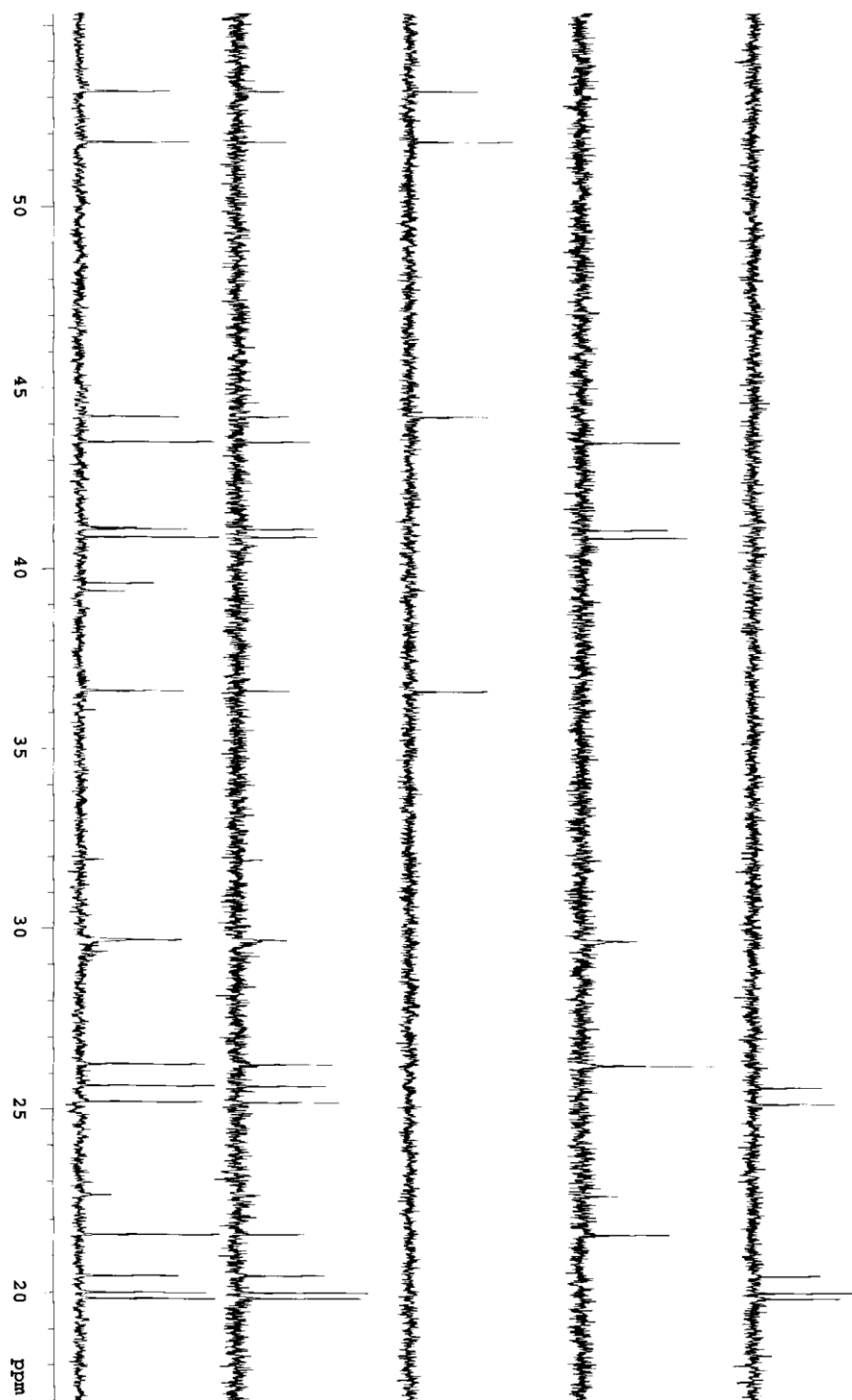


11D-4 C232-9			
INDEX	FREQUENCY	PPM	HEIGHT
1	12623.0	83.682	21.9
2	12124.8	80.380	21.7
3	11647.3	77.215	2875.2
4	11615.0	77.000	3162.6
5	11582.6	76.785	2979.1
6	11104.0	73.613	11.2
7	8022.2	53.182	34.3
8	7810.7	51.780	41.4
9	6669.7	44.216	37.3
10	6564.6	43.519	50.5
11	6208.5	41.159	21.4
12	6201.6	41.113	41.0
13	6168.1	40.890	52.5
14	5973.9	39.603	27.6
15	5940.3	39.381	19.3
16	5523.0	36.614	39.1
17	4814.4	31.917	9.5
18	4479.2	29.694	38.4
19	4428.3	29.357	11.0
20	3962.5	26.269	46.9
21	3872.3	25.671	50.7
22	3804.1	25.219	46.0
23	3421.5	22.682	112.1
24	3256.2	21.586	52.5
25	3085.1	20.452	37.2
26	3015.7	19.992	47.6
27	2957.5	19.821	50.9
28	2127.9	14.107	14.0

11D-4 C232-9



11ID-4 C232-9





111D-4 C133-S  
expt3 PROCYR

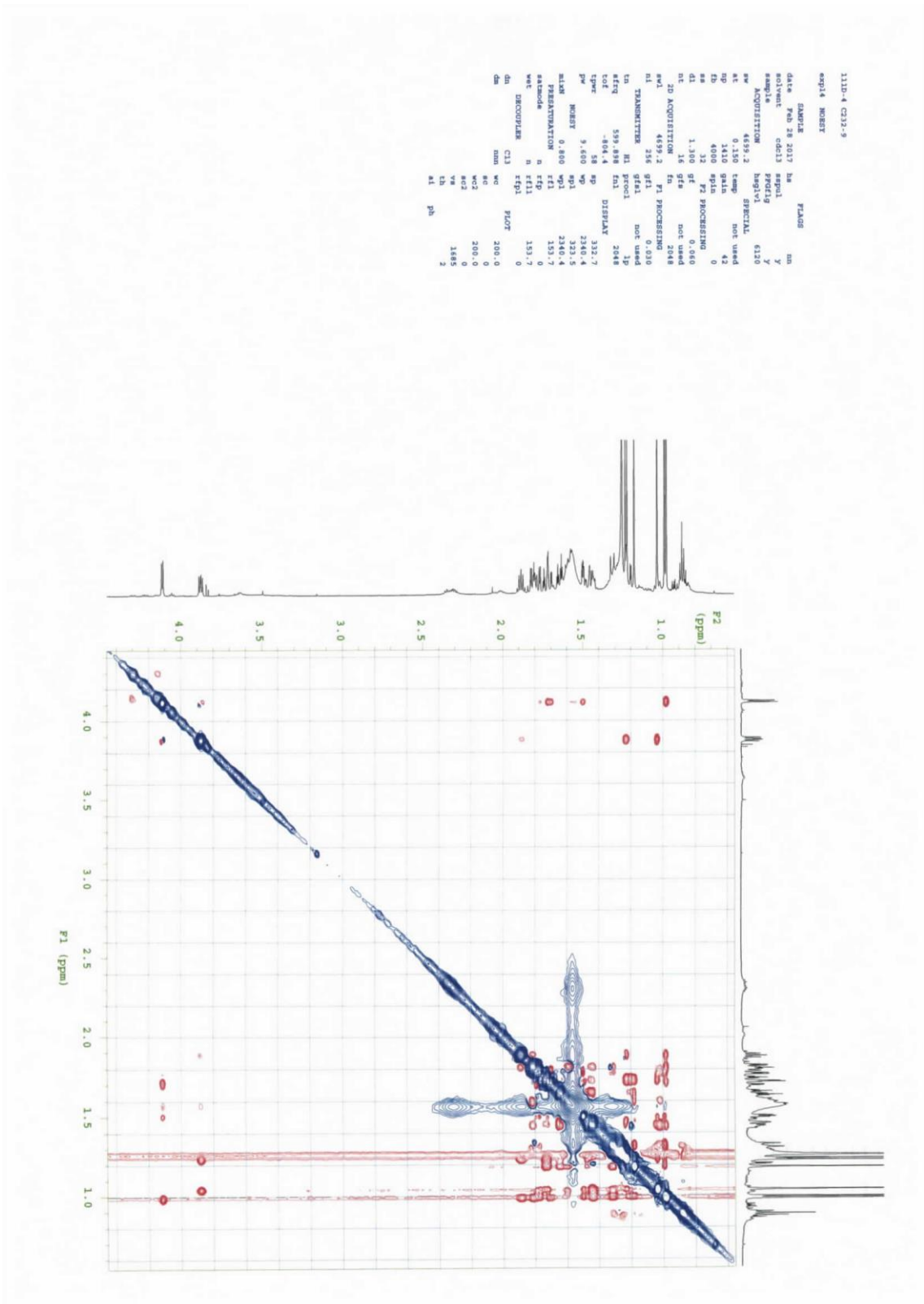
SAMPLE PLANS date Feb 28 2017 ha nm  
NAME COL13 hsqv1 7  
SAMPLE hsqv1 SPECIAL 4120  
ACQUISITION 2934.3 temp not used  
at 0.150 gain 42  
ap 880 spins  
as 4950 F2 PROCESSING 0  
sa 32 ab -0.075  
dl 1.000 abs not used  
nt 15 fn 1024  
2D ACQUISITION F1 PROCESSING  
w1 2934.3 abs -0.044  
w2 4950 F2  
d2 2934.3 not 1d  
PREPARATION 0 proc1  
REFERENCE fcl DISPLAY 1024

WEIGHT TRANSMITTER n ap DISPLAY 335.6  
f1 2934.3  
f2 4950  
freq 599.897 wpl 2344.0  
totl -1867.5 fcl 134.3  
tpr 58 rfp 134.3  
pw 9.600 ffl1 134.3  
pw 9.600 ffl1 0  
g1313E 5102 ffl1 PLOT 200.0  
g13E 0.001800 wc 200.0  
g13E 1.000 ac 200.0  
g13ab 0.000500 wc2 200.0  
dn DECOUPLE CL3 ac2 1685  
cn 2  
cm 13  
ct 1  
cw 2

The figure displays NMR data for sample 111D-4 C133-S. At the top, acquisition parameters are listed, including sample name, date, time, and various technical settings like gain, temperature, and processing options. Below the text, there are two main plots. The left plot is a 2D NMR spectrum with axes labeled F1 (ppm) and F2 (ppm), both ranging from 1.0 to 4.0. It shows a complex pattern of peaks and cross-peaks, typical of a 2D experiment like COSY or HSQC. The right plot is a 1D NMR spectrum, also labeled F2 (ppm), showing several sharp peaks between 1.0 and 2.0 ppm, and some broader features around 3.5 ppm.



Figure S4 NOESY of 1







exp15 ghsqcab

[illegible]



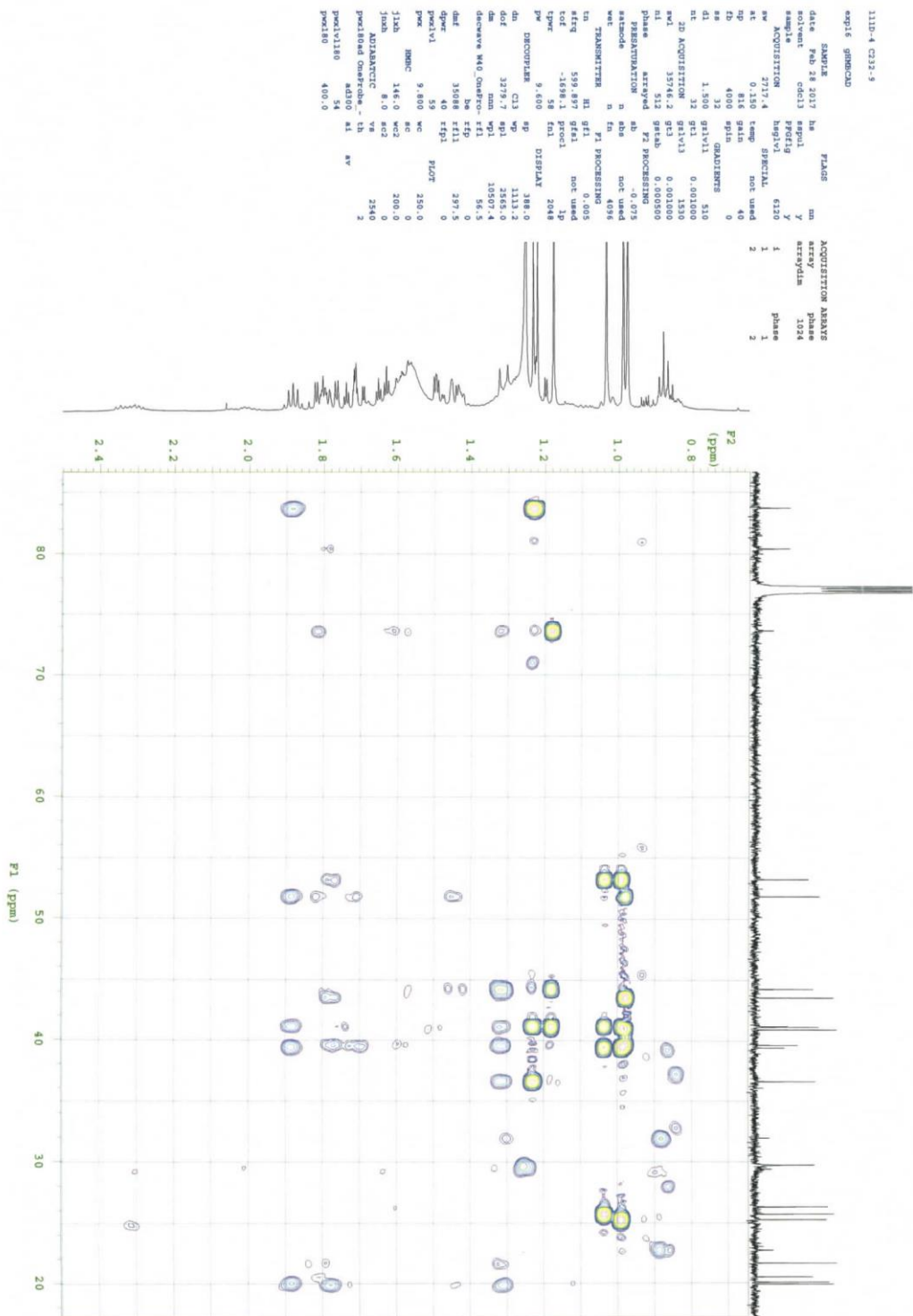
111D-4 C213-9

sample gsmc040

SAMPLE		FLAGS		ACQUISITION		ABASTE	
date	Feb 28 2017	ba		nm	array	phase	
solvent	cdd3	sepal	y		arraylin	1024	
sample		proctig	y				
acq	2117.4	bipvt	g120	1	1	phase	1
at	0.150	tamp	not used	2	2		2
np	816	gate					
fb	4000	apls	0				
as	32	GRADIENTS	510				
cl	1.000	gr1v11	510				
m	32	gr1v13	0.001350				
2d	32	gr1v13	0.001350				
sw1	35746.2	gr3	0.001000				
n1	512	grtab	0.000500				
phase	arrayed	P1 PROCESSING	-0.075				
PREPARATION	ab	dot used					
metabolite	n	not used					
acq	2117.4	not used					
TRANSMITTER	n	P1 PROCESSING					
in	gtf	0.005					
afreq	559.497	gfal	not used				
tof	-1498.1	pfcc1	1p				
tpw	5.600	fol	DIERMAN	1048			
pw	5.600	sp	348.1				
dn	C13	wp	2275.5				
dof	3279.7	wp1	2355.5				
dm	mm	wp1	24284.4				
decouple	wf0	Omeprc	rfl	56.5			
amc	be	rfg	297.0				
dmr	35000	rfl	297.0				
dmr	40	rfl	297.0				
pwctvl	55	rfpl	PLOT				
pwet	5.800	wc	200.0				
j1ch	146.0	rc	0				
j1ch	146.0	wc2	200.0				
j1ch	AUXILIARY	wc2	2540				
postlwd	Omeprc	- lb	2				
ad100	at	av					
pcwl180	54						
pcwl180	400.0						

F2 (ppm)

F1 (ppm)





**Figure S7 FABMS of 1**

[ Elemental Composition ]  
Data : 1703086 Date : 13-Mar-2017 19:27 Page: 1  
Sample: 111D-4 C232-9-XXVII  
Note : Matrix; G  
Inlet : Direct Ion Mode : FAB+  
RT : 7.32 min Scan#: (342,347)  
Elements : C 25/15, H 40/30, O 8/0, Na 1/0  
Mass Tolerance : 20ppm, 1mmu if m/z > 50  
Unsaturation (U.S.) : -1.0 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S. Composition
345.2397	100.0	-2.6 / -0.9	3.5 C 20 H 34 O 3 Na

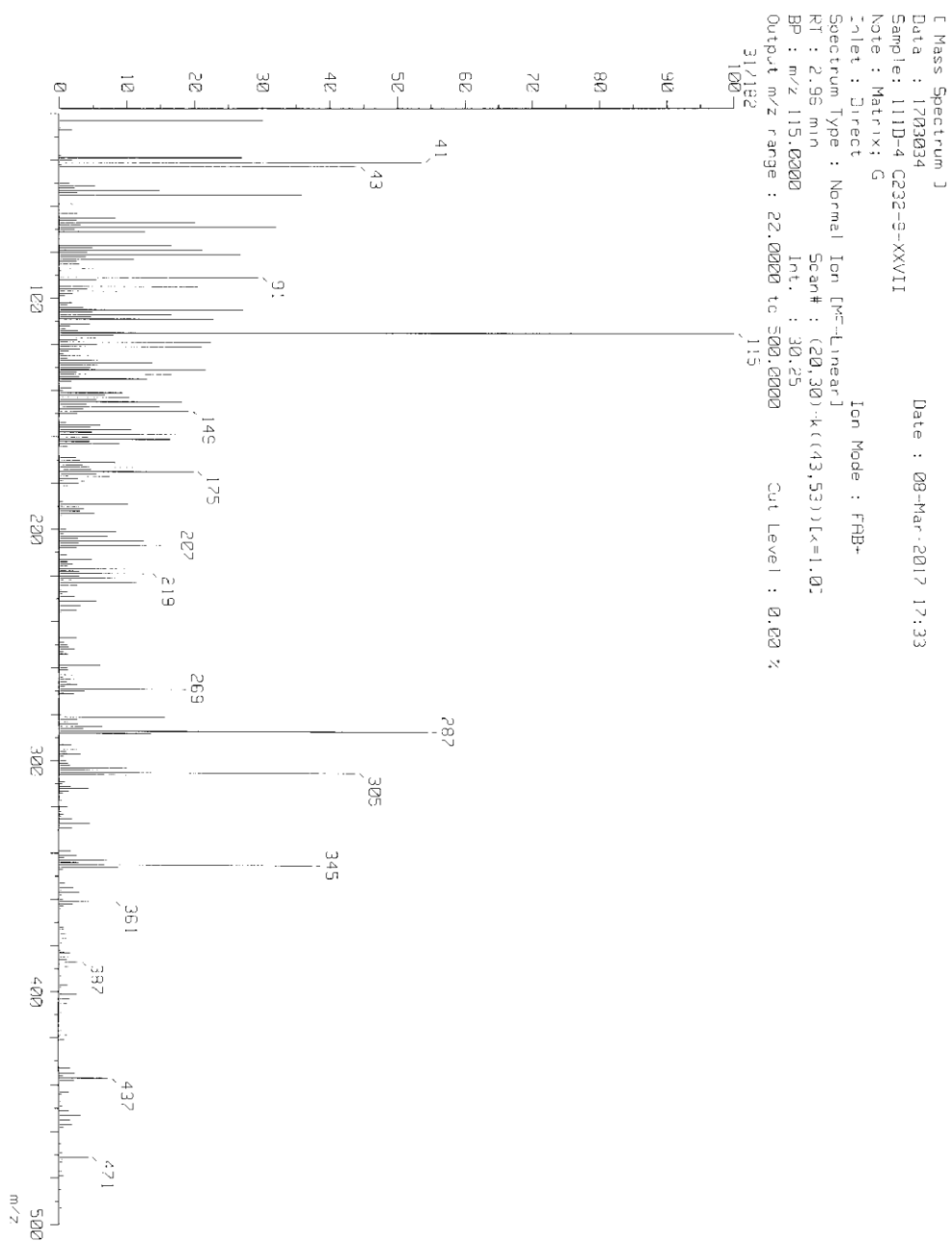
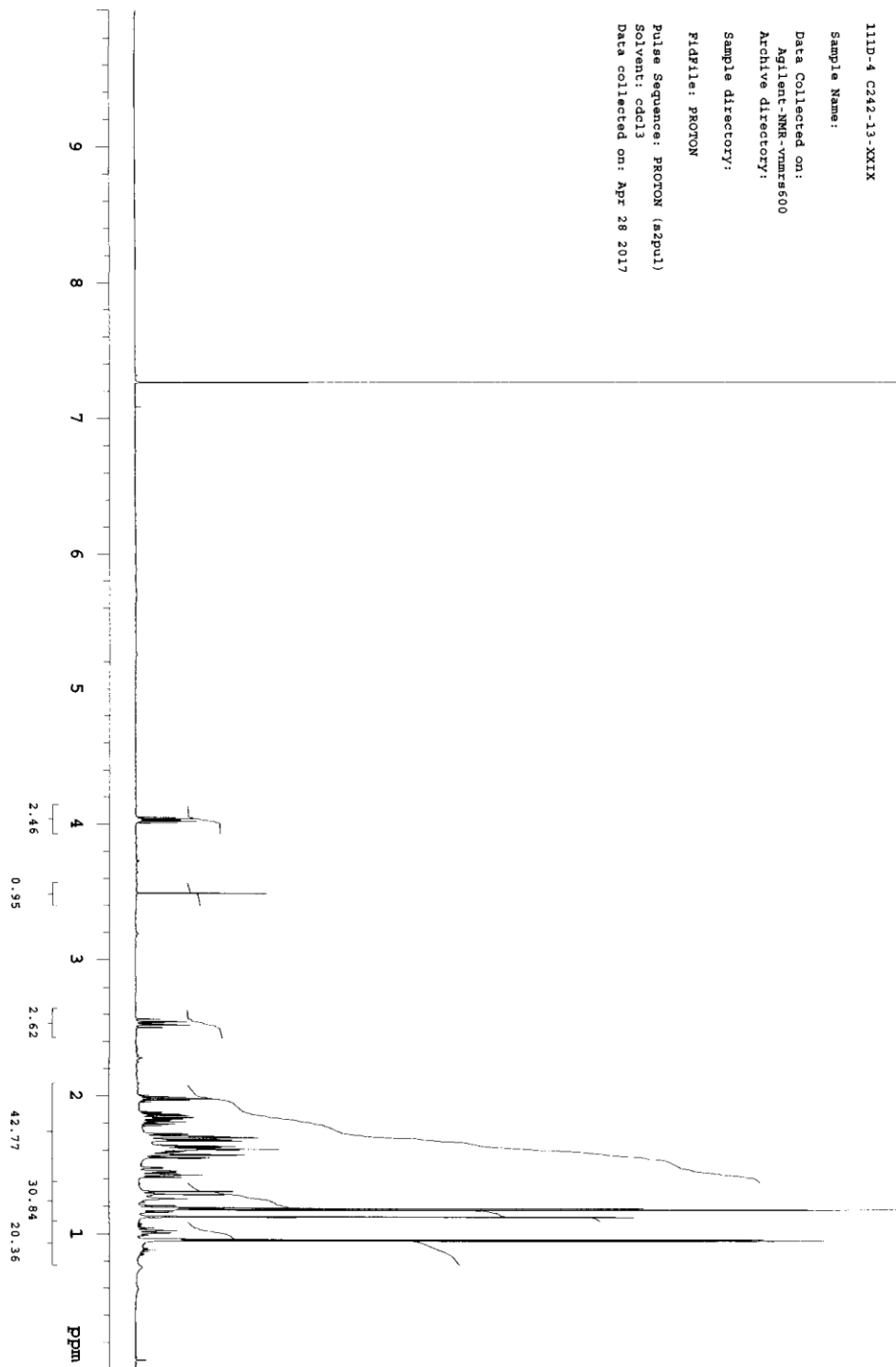
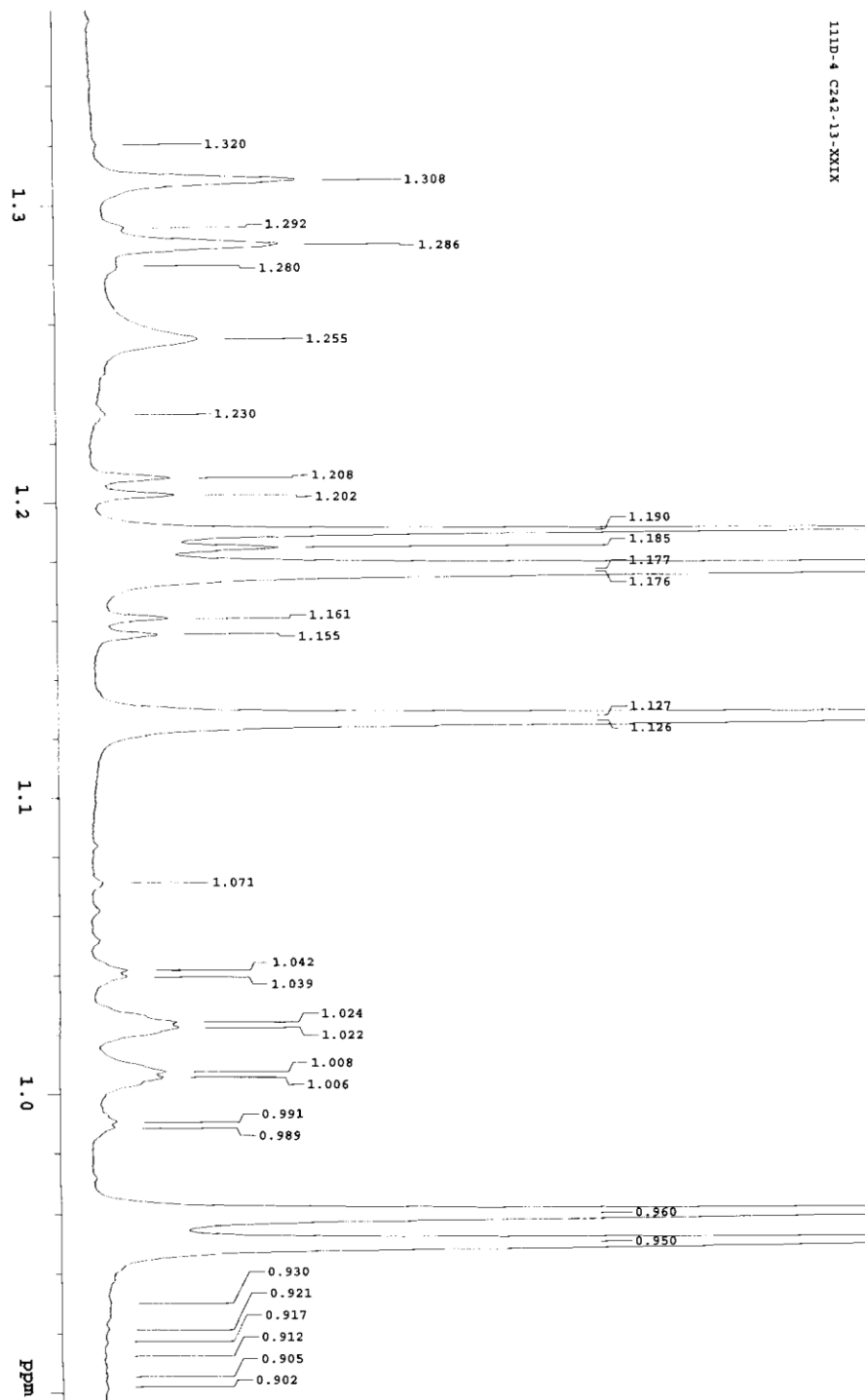
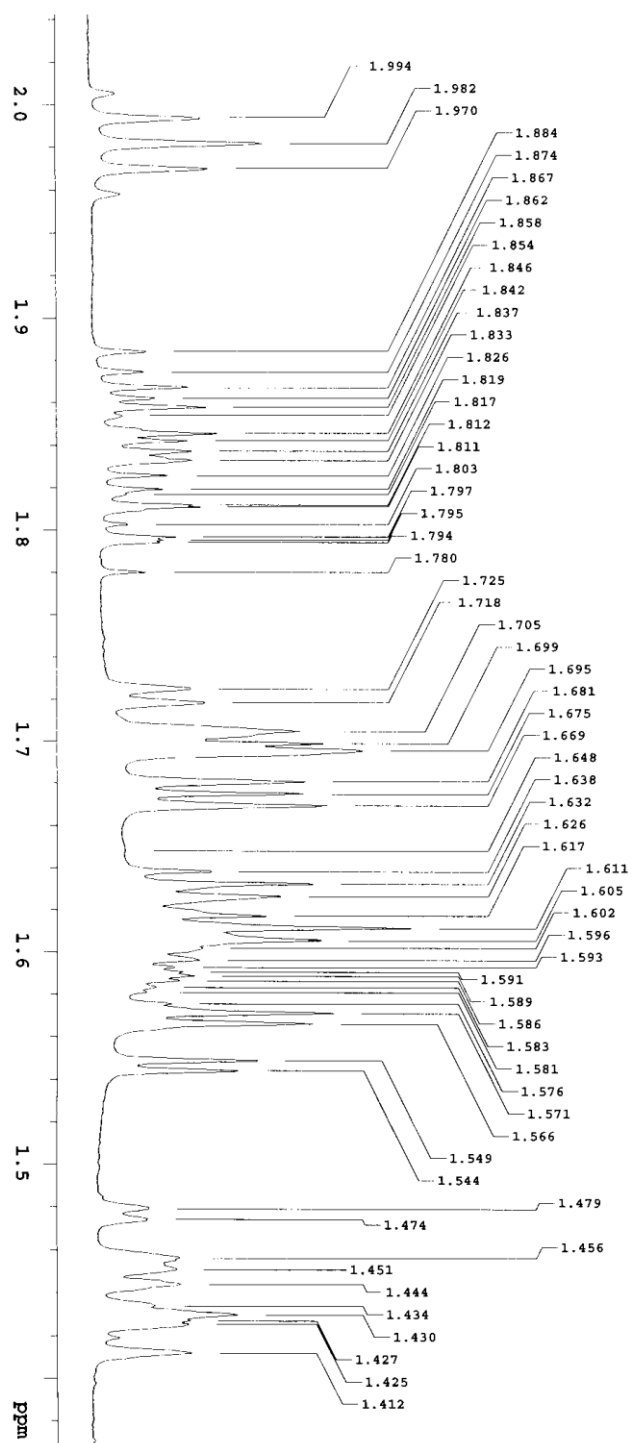


Figure S8  $^1\text{H}$  NMR spectrum of 2 in  $\text{CDCl}_3$







111D-4 C242-13-KXIX

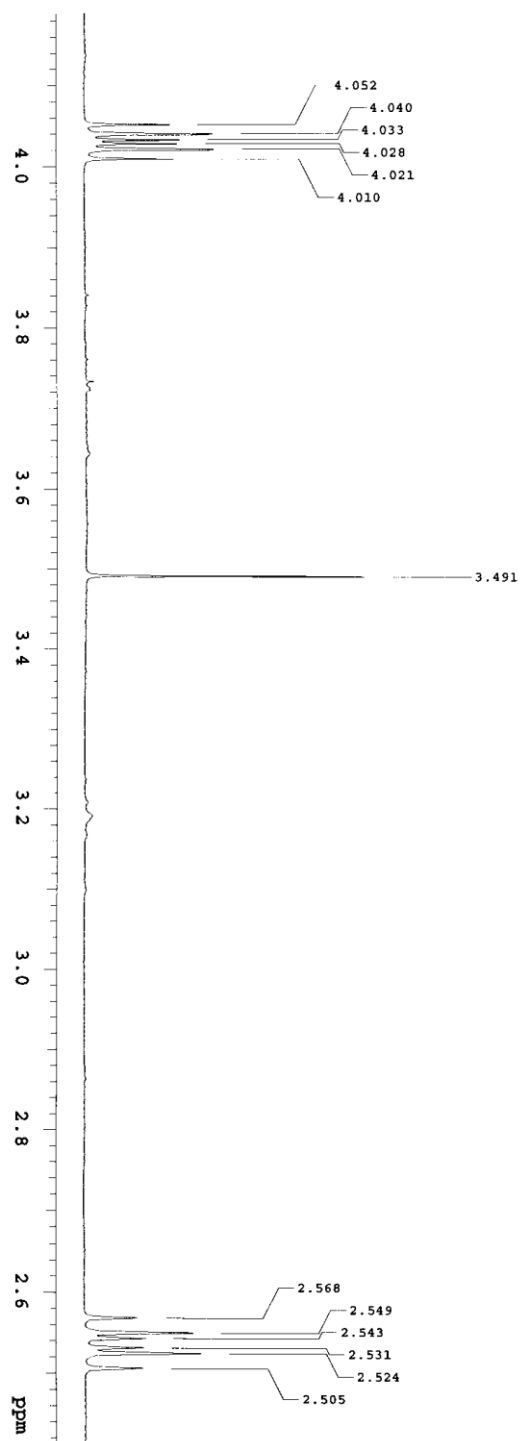
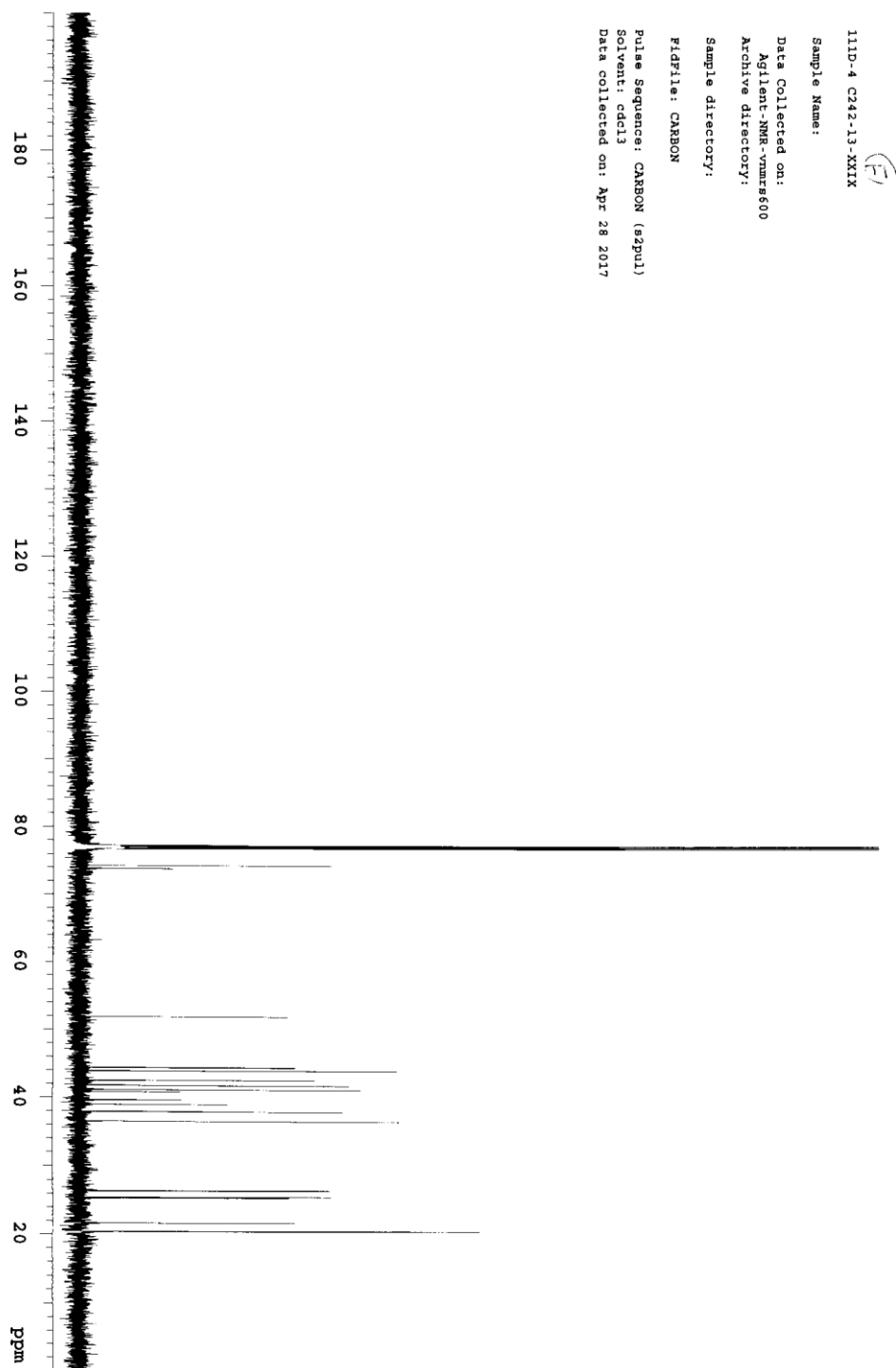
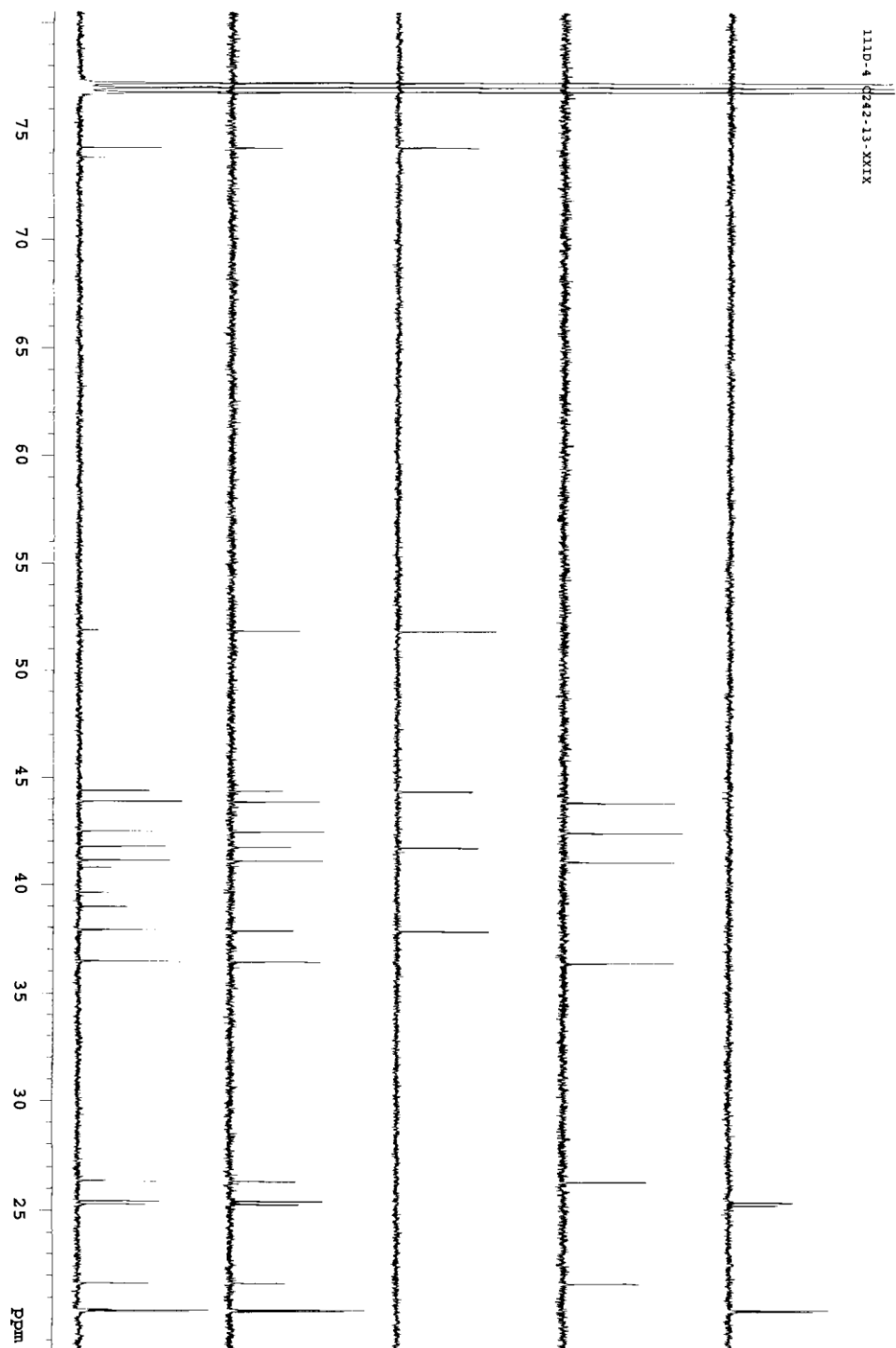


Figure S9  $^{13}\text{C}$  NMR spectrum of 2 in  $\text{CDCl}_3$

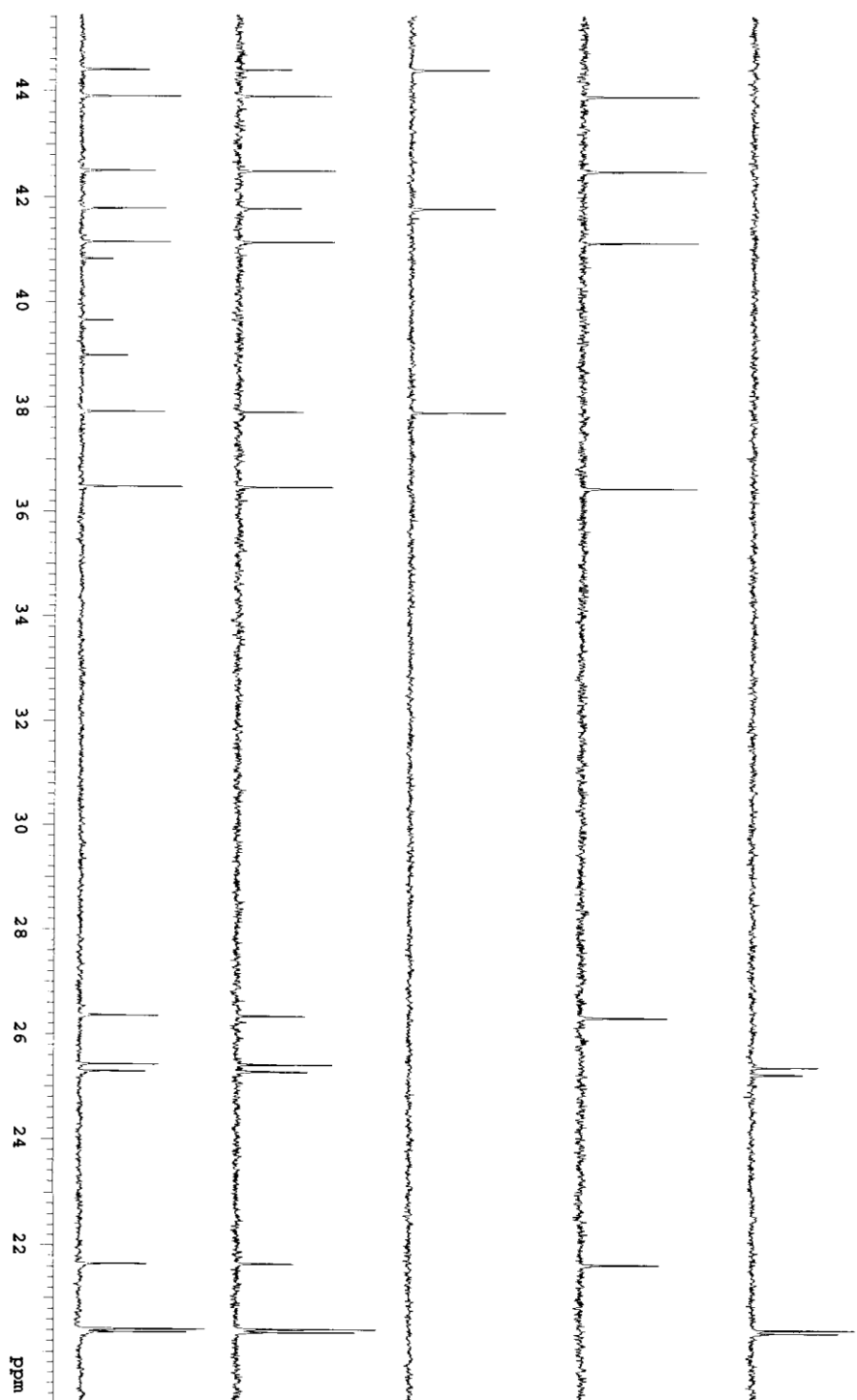


11D-4 C242-13-XXIX			
INDEX	FREQUENCY	PPM	HEIGHT
1	11647.3	77.215	654.5
2	11615.0	77.000	676.4
3	11582.6	76.785	593.0
4	11197.7	74.234	48.8
5	11132.9	73.804	18.2
6	7824.6	51.872	40.5
7	6698.6	44.408	41.9
8	6623.5	43.910	61.6
9	6412.0	42.507	45.6
10	6304.5	41.795	52.3
11	6207.4	41.151	54.9
12	6157.6	40.821	19.5
13	5980.8	39.649	19.8
14	5881.4	38.990	28.7
15	5719.5	37.917	51.1
16	5503.4	36.484	62.5
17	3976.3	26.364	48.4
18	3836.5	25.433	49.1
19	3815.7	25.295	40.6
20	3265.4	21.648	41.8
21	3080.5	20.422	77.7
22	3071.2	20.360	66.4





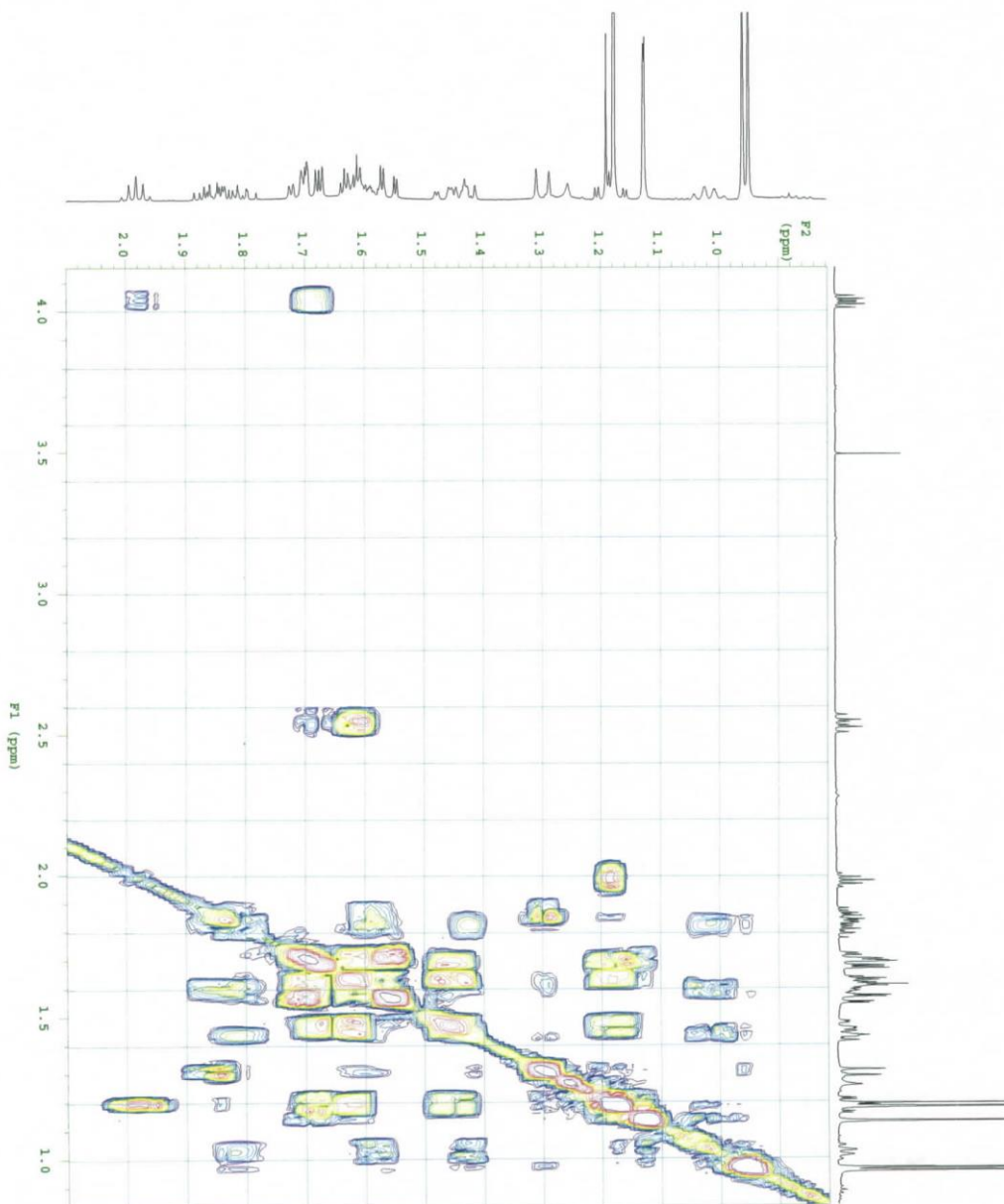
11ID-4 C242-13-XXIX





```
exp) gcost
```

av opo ya







[illegible]

exp5 ghsqcas

pro1v1180r 46





**1D <sup>1</sup>H NMR Spectrum (Top):**

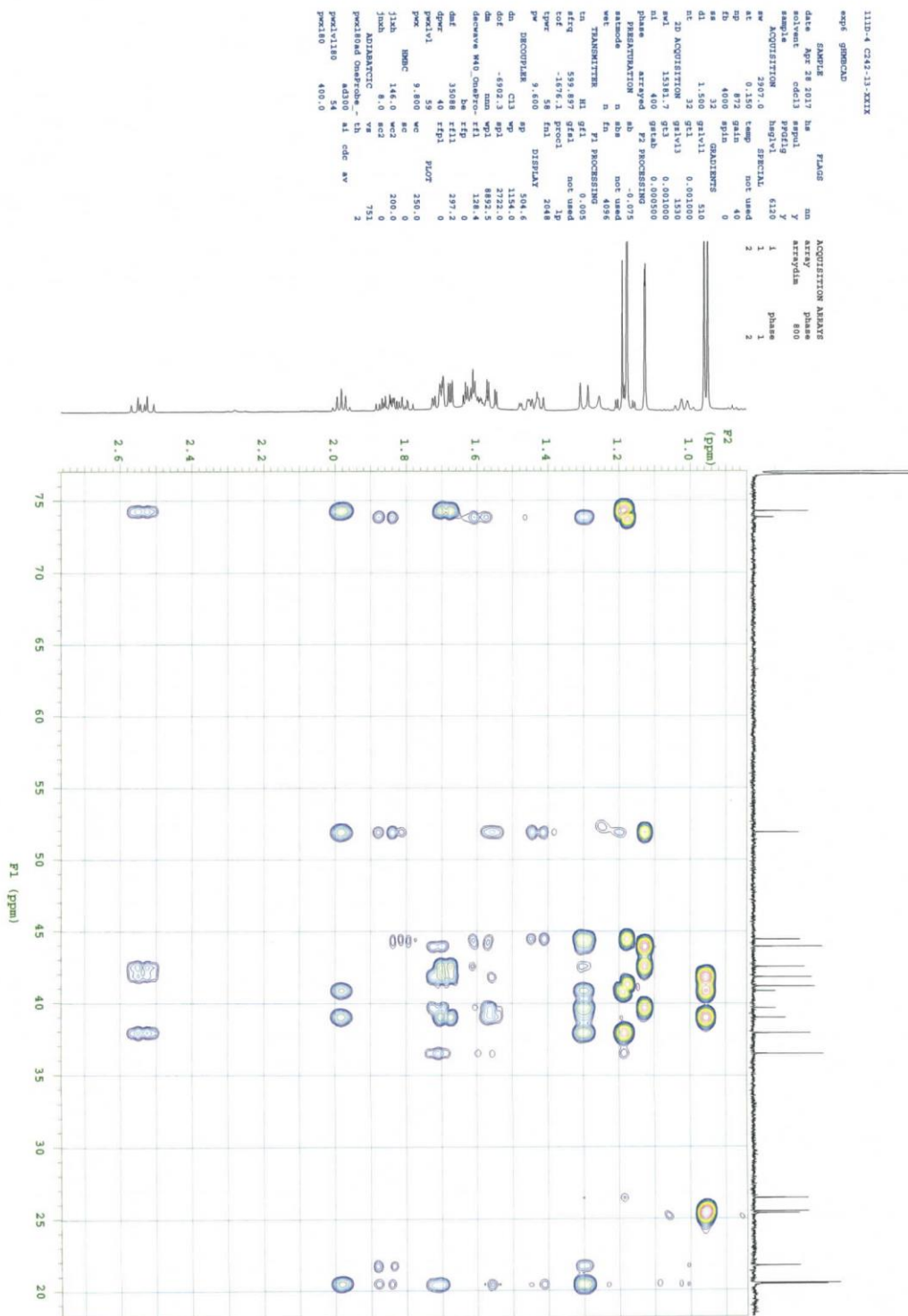
Chemical Shift (ppm)	Assignment
~1.0	CH <sub>3</sub> (multiple)
~1.5	CH <sub>2</sub> (multiple)
~2.0	CH <sub>2</sub> (multiple)
~2.5	CH <sub>2</sub> (multiple)
~3.5	CH <sub>2</sub> (multiple)
~4.0	CH <sub>2</sub> (multiple)

**1D <sup>13</sup>C NMR Spectrum (Right):**

Chemical Shift (ppm)	Assignment
~10	CH <sub>3</sub>
~20	CH <sub>3</sub>
~30	CH <sub>2</sub>
~40	CH <sub>2</sub>
~50	CH <sub>2</sub>
~60	CH <sub>2</sub>
~70	CH <sub>2</sub>
~80	CH <sub>2</sub>
~90	CH <sub>2</sub>
~100	CH <sub>2</sub>
~110	CH <sub>2</sub>
~120	CH <sub>2</sub>
~130	CH <sub>2</sub>
~140	CH <sub>2</sub>
~150	CH <sub>2</sub>
~160	CH <sub>2</sub>
~170	CH <sub>2</sub>
~180	CH <sub>2</sub>
~190	CH <sub>2</sub>
~200	CH <sub>2</sub>
~210	CH <sub>2</sub>
~220	CH <sub>2</sub>
~230	CH <sub>2</sub>
~240	CH <sub>2</sub>
~250	CH <sub>2</sub>
~260	CH <sub>2</sub>
~270	CH <sub>2</sub>
~280	CH <sub>2</sub>
~290	CH <sub>2</sub>
~300	CH <sub>2</sub>
~310	CH <sub>2</sub>
~320	CH <sub>2</sub>
~330	CH <sub>2</sub>
~340	CH <sub>2</sub>
~350	CH <sub>2</sub>
~360	CH <sub>2</sub>
~370	CH <sub>2</sub>
~380	CH <sub>2</sub>
~390	CH <sub>2</sub>
~400	CH <sub>2</sub>
~410	CH <sub>2</sub>
~420	CH <sub>2</sub>
~430	CH <sub>2</sub>
~440	CH <sub>2</sub>
~450	CH <sub>2</sub>
~460	CH <sub>2</sub>
~470	CH <sub>2</sub>
~480	CH <sub>2</sub>
~490	CH <sub>2</sub>
~500	CH <sub>2</sub>
~510	CH <sub>2</sub>
~520	CH <sub>2</sub>
~530	CH <sub>2</sub>
~540	CH <sub>2</sub>
~550	CH <sub>2</sub>
~560	CH <sub>2</sub>
~570	CH <sub>2</sub>
~580	CH <sub>2</sub>
~590	CH <sub>2</sub>
~600	CH <sub>2</sub>
~610	CH <sub>2</sub>
~620	CH <sub>2</sub>
~630	CH <sub>2</sub>
~640	CH <sub>2</sub>
~650	CH <sub>2</sub>
~660	CH <sub>2</sub>
~670	CH <sub>2</sub>
~680	CH <sub>2</sub>
~690	CH <sub>2</sub>
~700	CH <sub>2</sub>
~710	CH <sub>2</sub>
~720	CH <sub>2</sub>
~730	CH <sub>2</sub>
~740	CH <sub>2</sub>
~750	CH <sub>2</sub>
~760	CH <sub>2</sub>
~770	CH <sub>2</sub>
~780	CH <sub>2</sub>
~790	CH <sub>2</sub>
~800	CH <sub>2</sub>
~810	CH <sub>2</sub>
~820	CH <sub>2</sub>
~830	CH <sub>2</sub>
~840	CH <sub>2</sub>
~850	CH <sub>2</sub>
~860	CH <sub>2</sub>
~870	CH <sub>2</sub>
~880	CH <sub>2</sub>
~890	CH <sub>2</sub>
~900	CH <sub>2</sub>
~910	CH <sub>2</sub>
~920	CH <sub>2</sub>
~930	CH <sub>2</sub>
~940	CH <sub>2</sub>
~950	CH <sub>2</sub>
~960	CH <sub>2</sub>
~970	CH <sub>2</sub>
~980	CH <sub>2</sub>
~990	CH <sub>2</sub>
~1000	CH <sub>2</sub>

**2D NMR Spectrum (Main Plot):**

The 2D plot shows correlations between <sup>1</sup>H and <sup>13</sup>C signals. The horizontal axis (F1) represents the <sup>13</sup>C chemical shift (ppm), and the vertical axis (F2) represents the <sup>1</sup>H chemical shift (ppm). The plot contains numerous cross-peaks, indicating scalar coupling between protons and carbons. Key peaks are labeled with their chemical shifts in ppm.



**Figure S14 FABMS of 2**

[ Elemental Composition ]  
Data : 1705110 Date : 17-May-2017 18:16 Page: 1  
Sample: 111D-4 C242-13-XXIX  
Note : Matrix; G  
Inlet : Direct Ion Mode : FAB+  
RT : 4.70 min Scan#: (26,31)  
Elements : C 25/15, H 40/30, O 10/0  
Mass Tolerance : 20ppm, 1mmu if m/z > 50  
Unsaturation (U.S.) : -1.0 - 30.0

Observed m/z	Int%	Err[ppm / mmu]	U.S. Composition
289.2534	88.4	+0.9 / +0.2	4.5 C 20 H 33 O

