

Regioselective solid-phase synthesis of *N*-mono-hydroxylated and *N*-mono-methylated acylpolyamine spider toxins using an 2-(*ortho*-nitrophenyl)ethanal-modified resin

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Supplementary material

Spectra of the final products

AG395a (*4-OH-Bz3(OH)334*):

¹ H NMR (400 MHz) and ¹³ C NMR (100 MHz)	p. 3
COSY	p. 4
HSQC	p. 5
HMBC	p. 6

AG432g (*IndAc3(OH)334*):

¹ H NMR (600 MHz) and ¹³ C NMR (150 MHz)	p. 7
COSY	p. 8
HSQC	p. 9
HMBC	p. 10

4-OH-Bz3(OH)433:

¹ H NMR (400 MHz) and ¹³ C NMR (100 MHz)	p. 11
COSY	p. 12
HSQC	p. 13
HMBC	p. 14

LF448A (*PhAcAsn3(Me)43*):

¹ H NMR (500 MHz) and ¹³ C NMR (125 MHz)	p. 15
COSY	p. 16
HSQC	p. 17
HMBC	p. 18

LF487A (*IndAcAsn3(Me)43*):

¹ H NMR (500 MHz) and ¹³ C NMR (125 MHz)	p. 19
COSY	p. 20
HSQC	p. 21
HMBC	p. 22

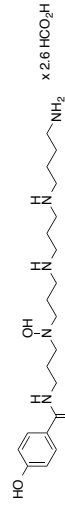
Spectra of the precursors of the final products

Compound **29**

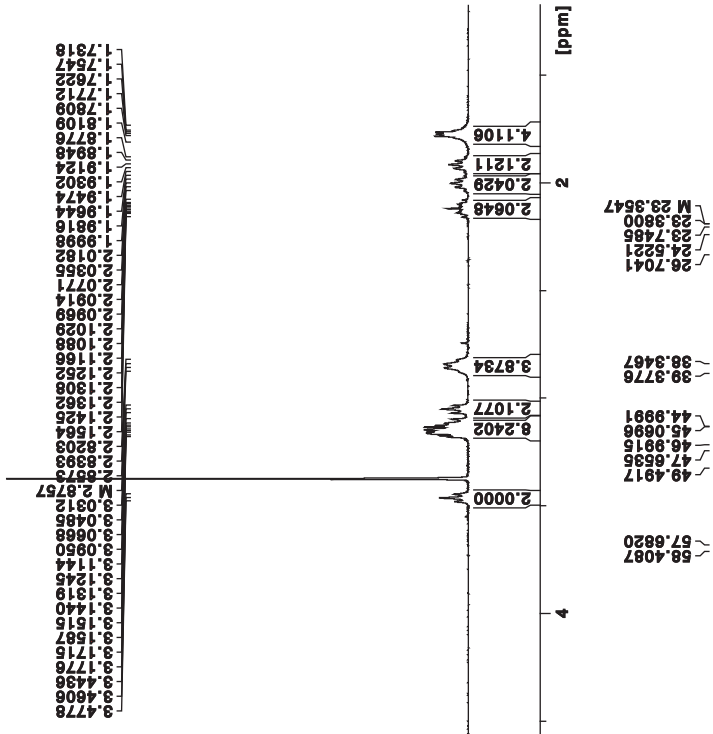
¹ H NMR (400 MHz)	p. 23
¹³ C NMR (100 MHz)	p. 24
COSY	p. 55
HSQC	p. 26

Compound 30	
¹ H NMR (400 MHz)	p. 27
¹³ C NMR (100 MHz)	p. 28
COSY	p. 29
HSQC	p. 30
Compound 31	
¹ H NMR (400 MHz)	p. 31
¹³ C NMR (100 MHz)	p. 32
COSY	p. 33
HSQC	p. 34
Compound 40	
¹ H NMR (500 MHz)	p. 35
¹³ C NMR (125 MHz)	p. 36
COSY	p. 37
HSQC	p. 38
HMBC	p. 39
Compound 41	
¹ H NMR (500 MHz)	p. 40
¹³ C NMR (125 MHz)	p. 41
COSY	p. 42
HSQC	p. 43
HMBC	p. 44
Chromatographic and comparisons of the natural and synthetic toxins LF448A and LF487A of <i>L. folium</i>	
Chromatograms	p. 45
ESI-MS/MS	p. 46

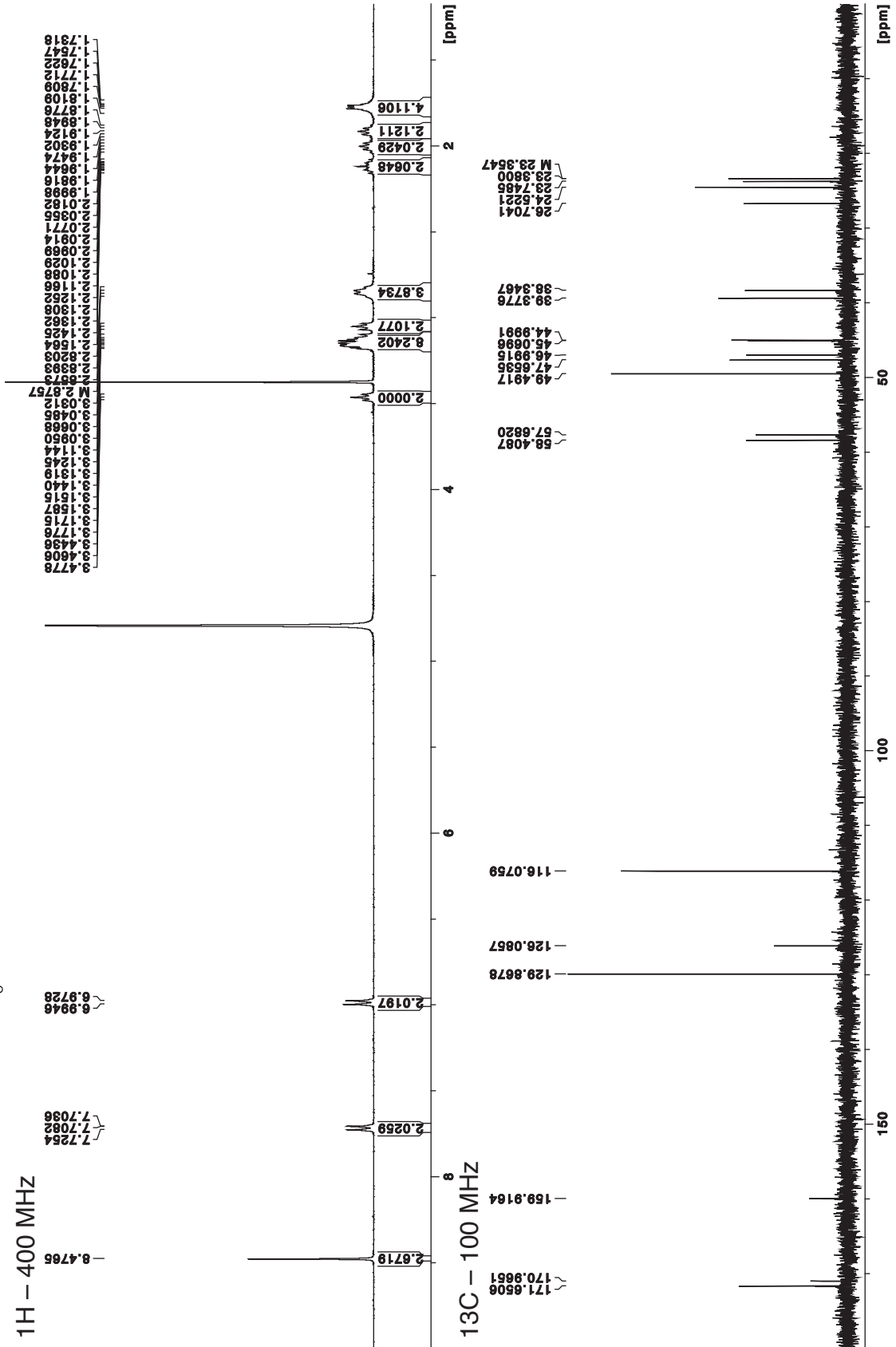
Compound **AG395a**:

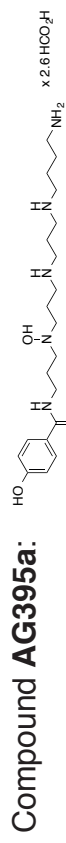


$^1\text{H} - 400 \text{ MHz}$

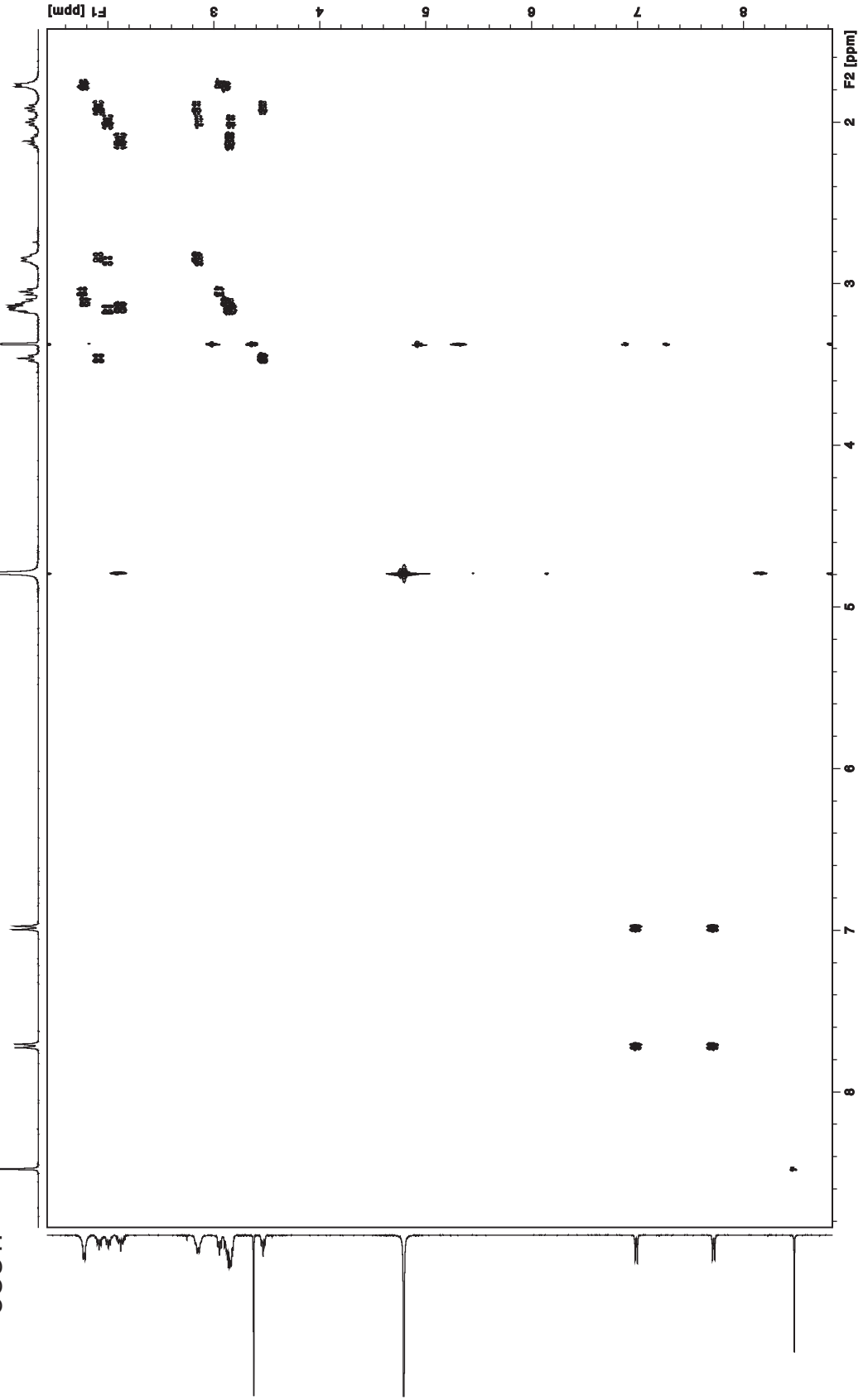


$^{13}\text{C} - 100 \text{ MHz}$



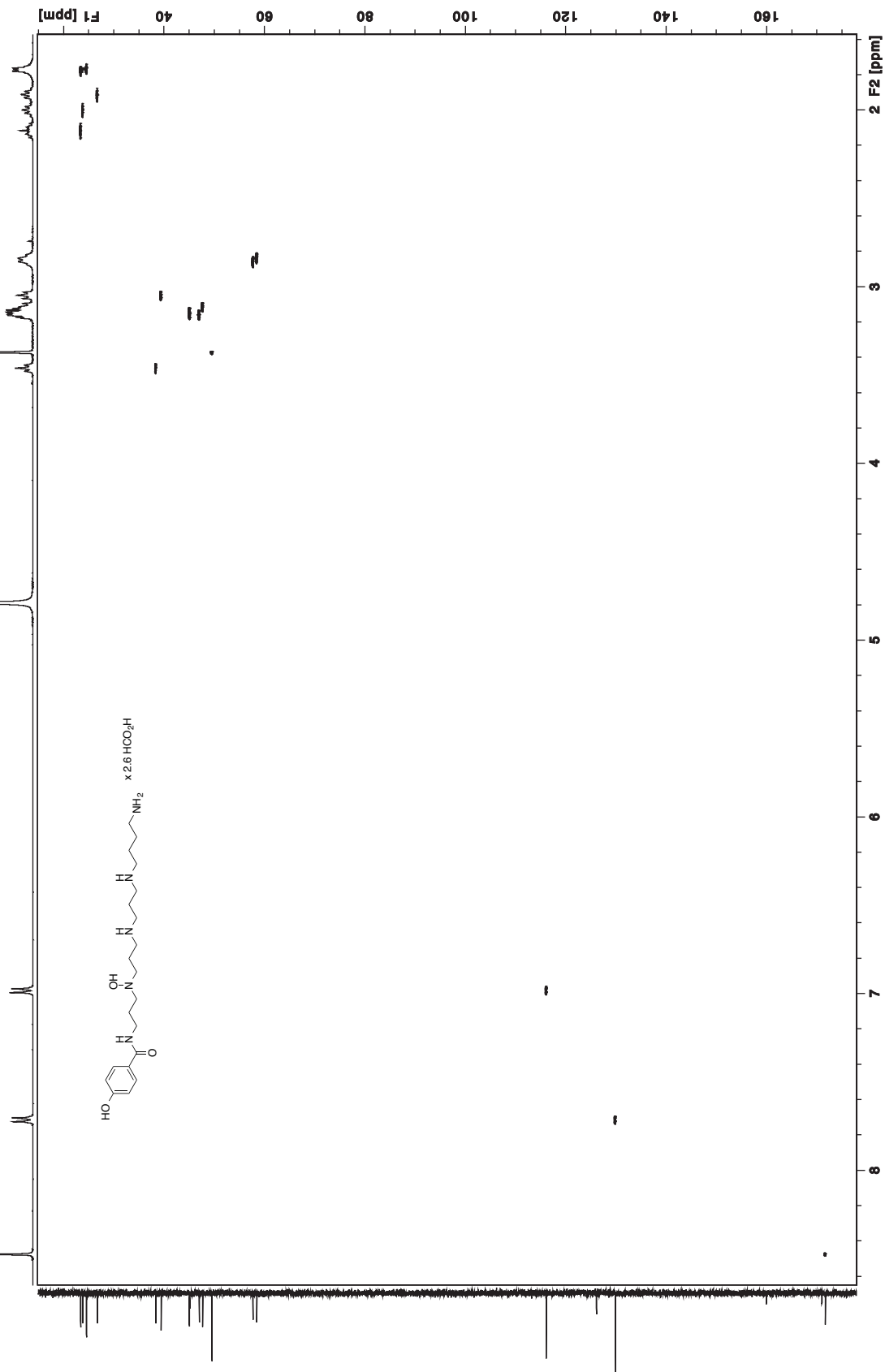


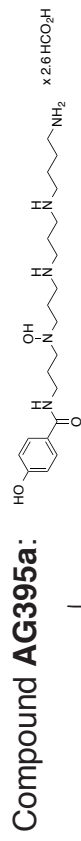
COSY:



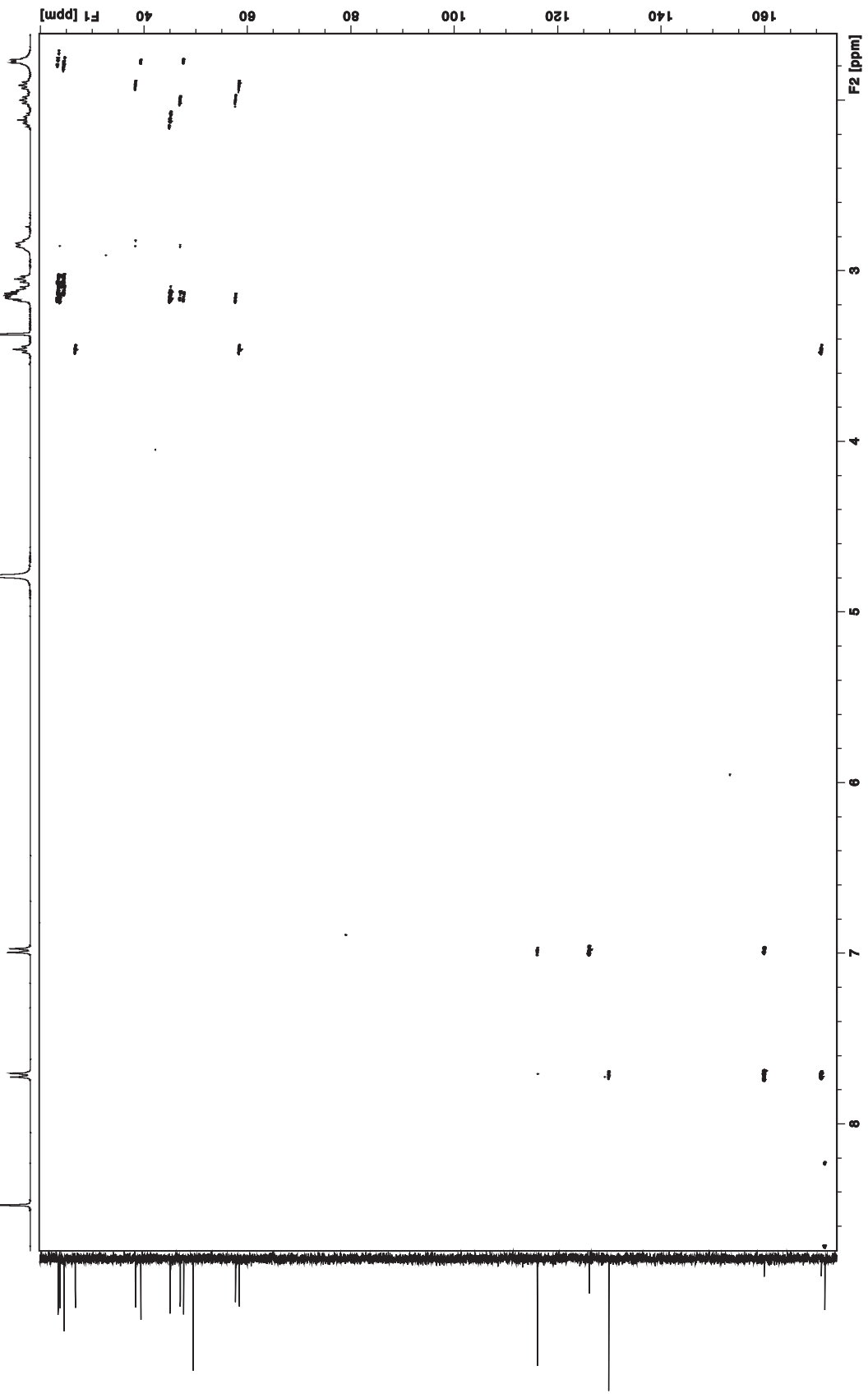
Compound **AG395a**:

HSQC:



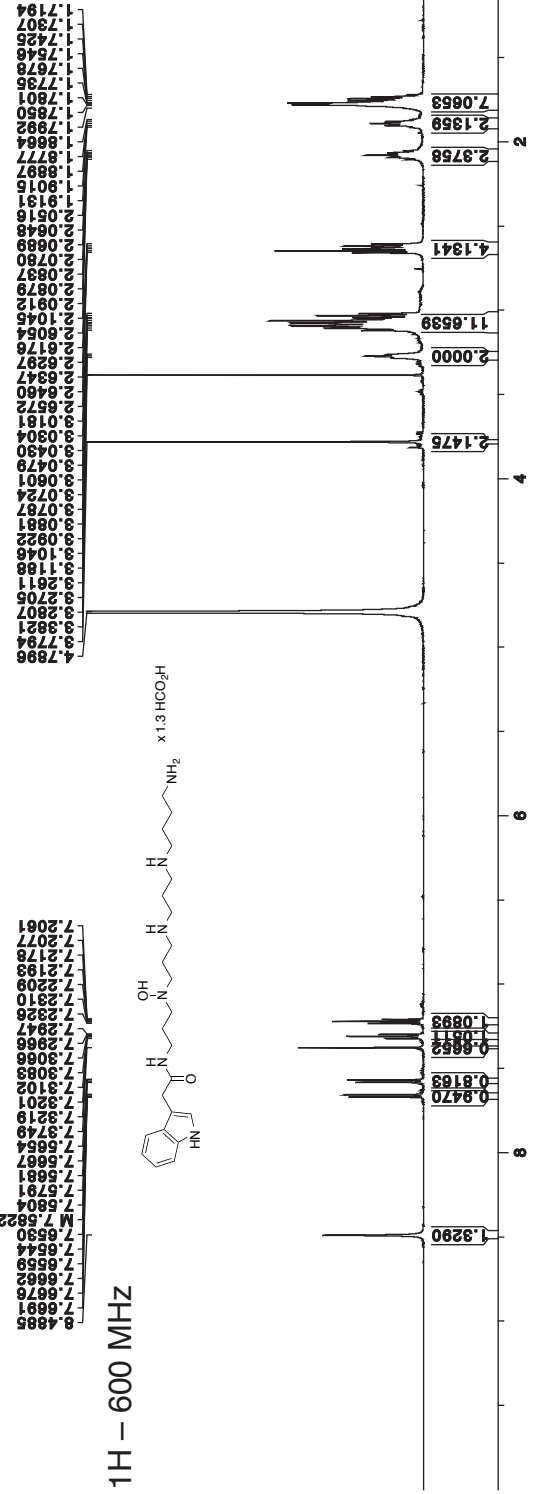


HMBC:

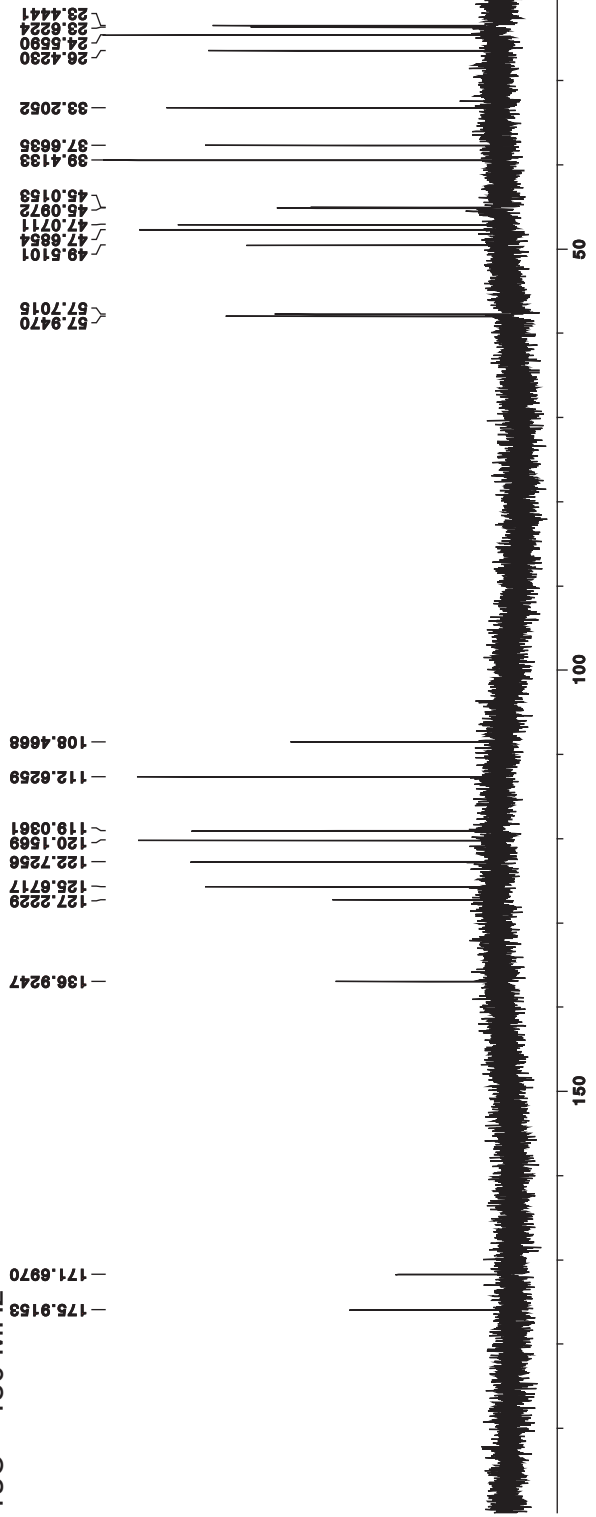


Compound AG432g

1H - 600 MHz

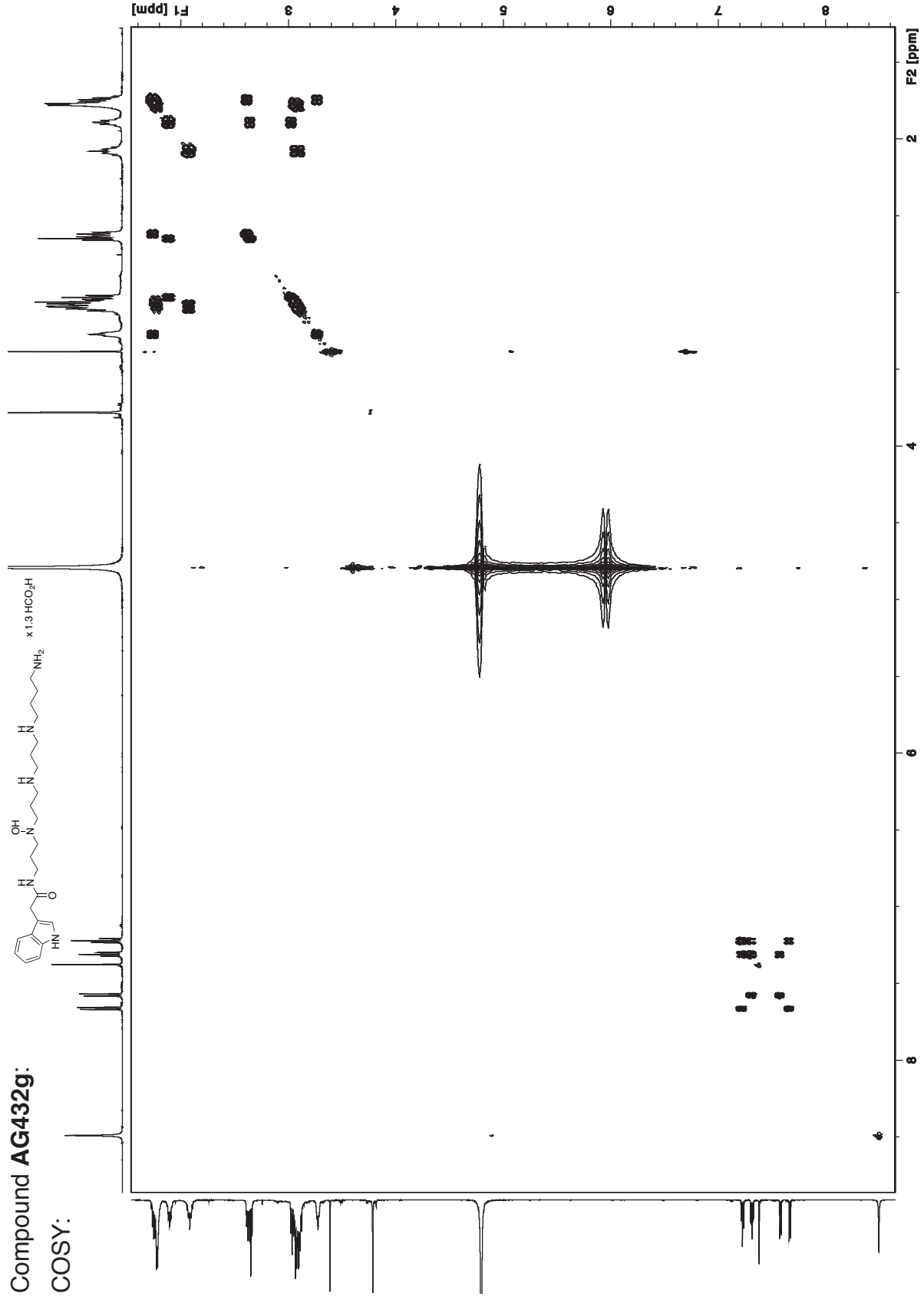


13C - 150 MHz



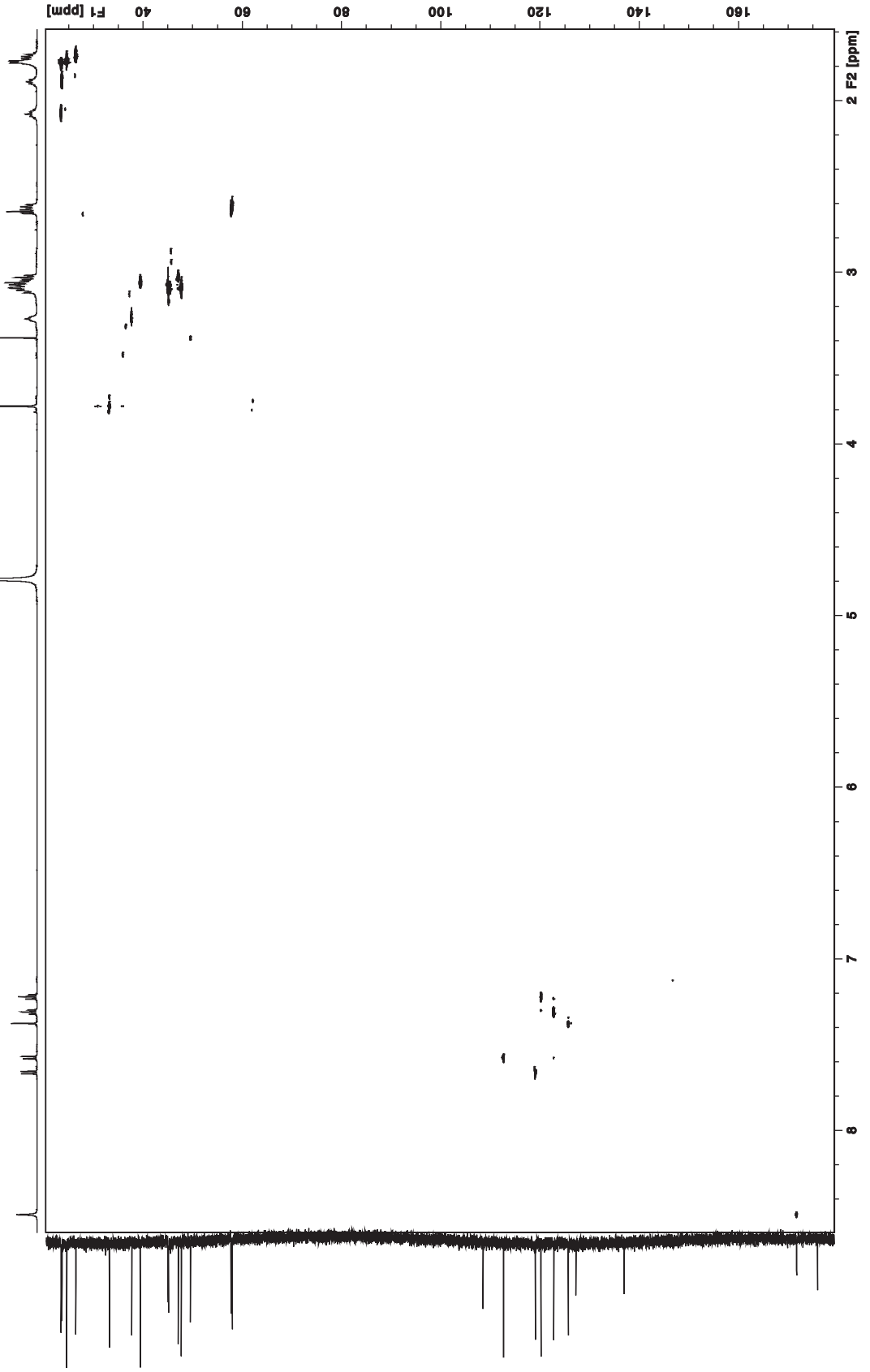
Compound **AG432g**:

COSY:



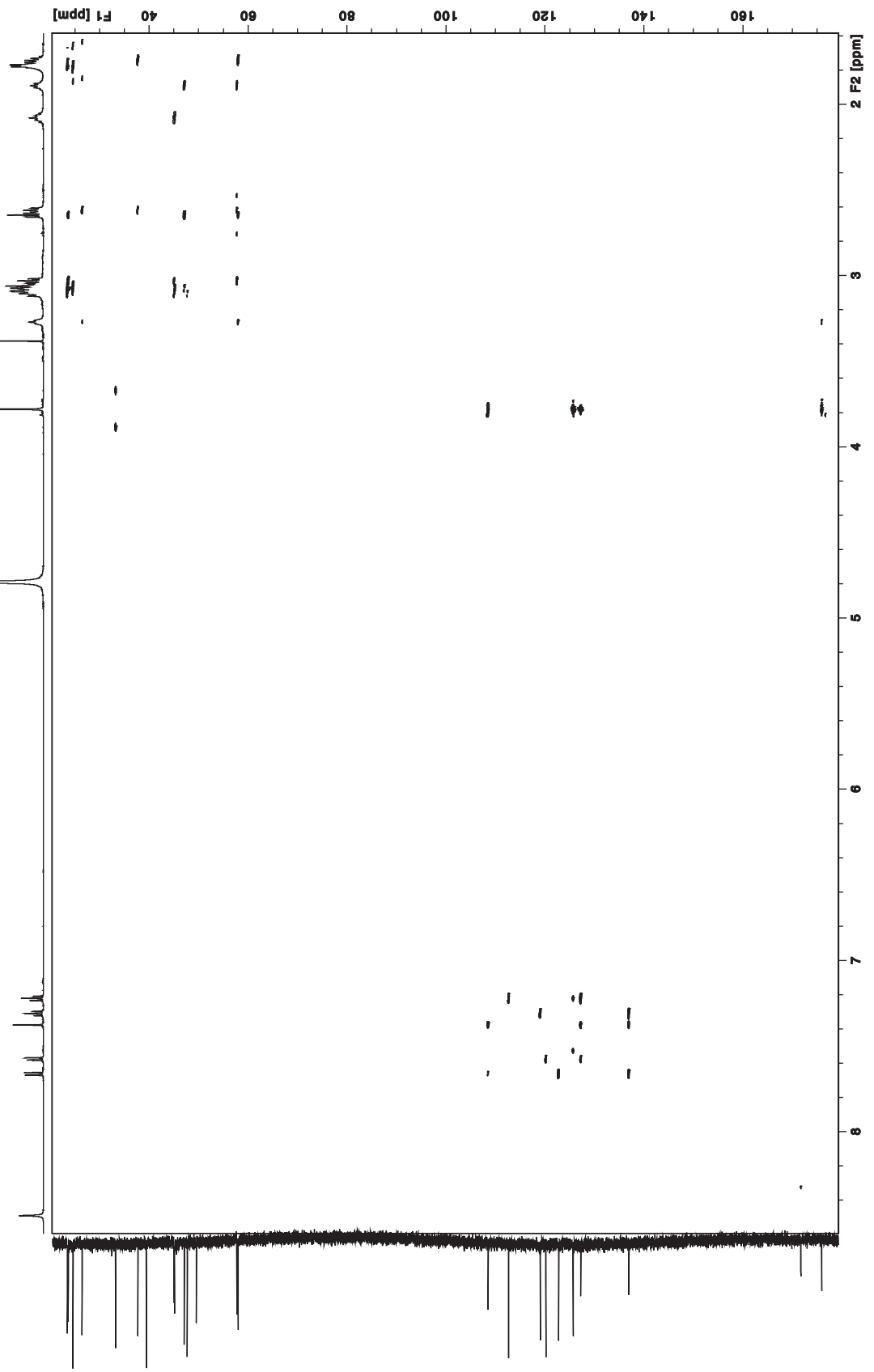
Compound **AG432g**:

HSQC:



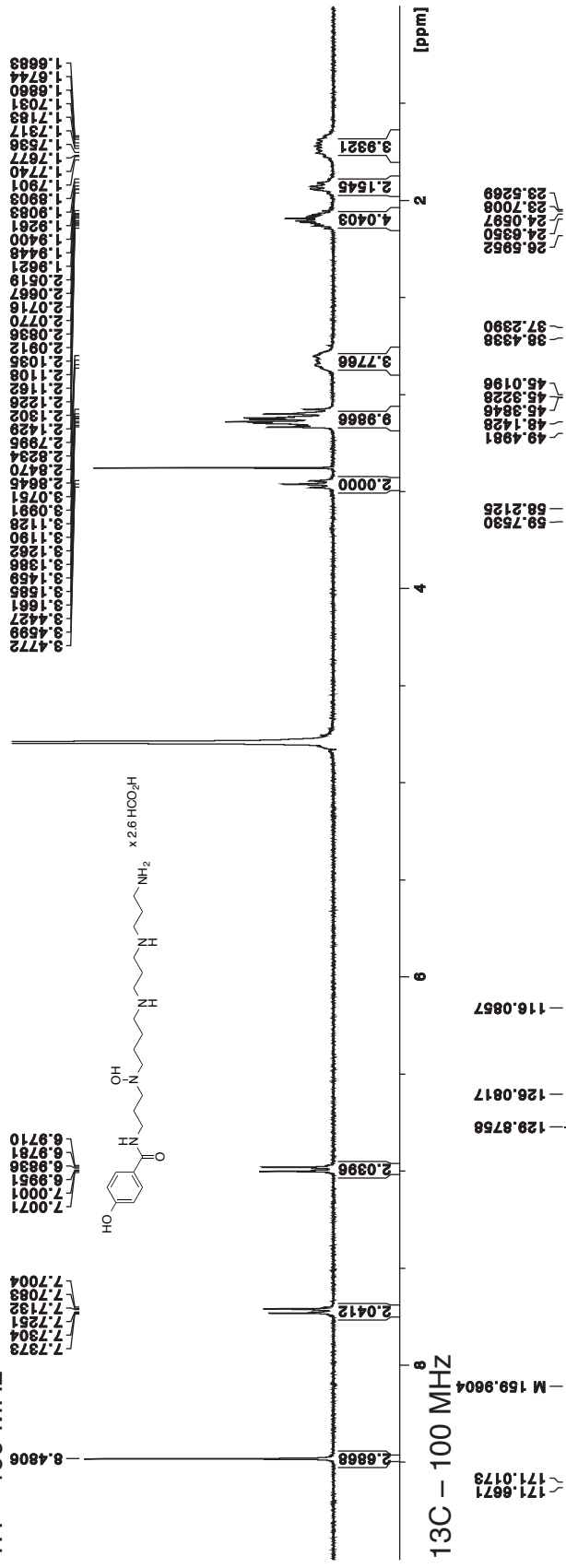
Compound **AG432g**:

HMBC:

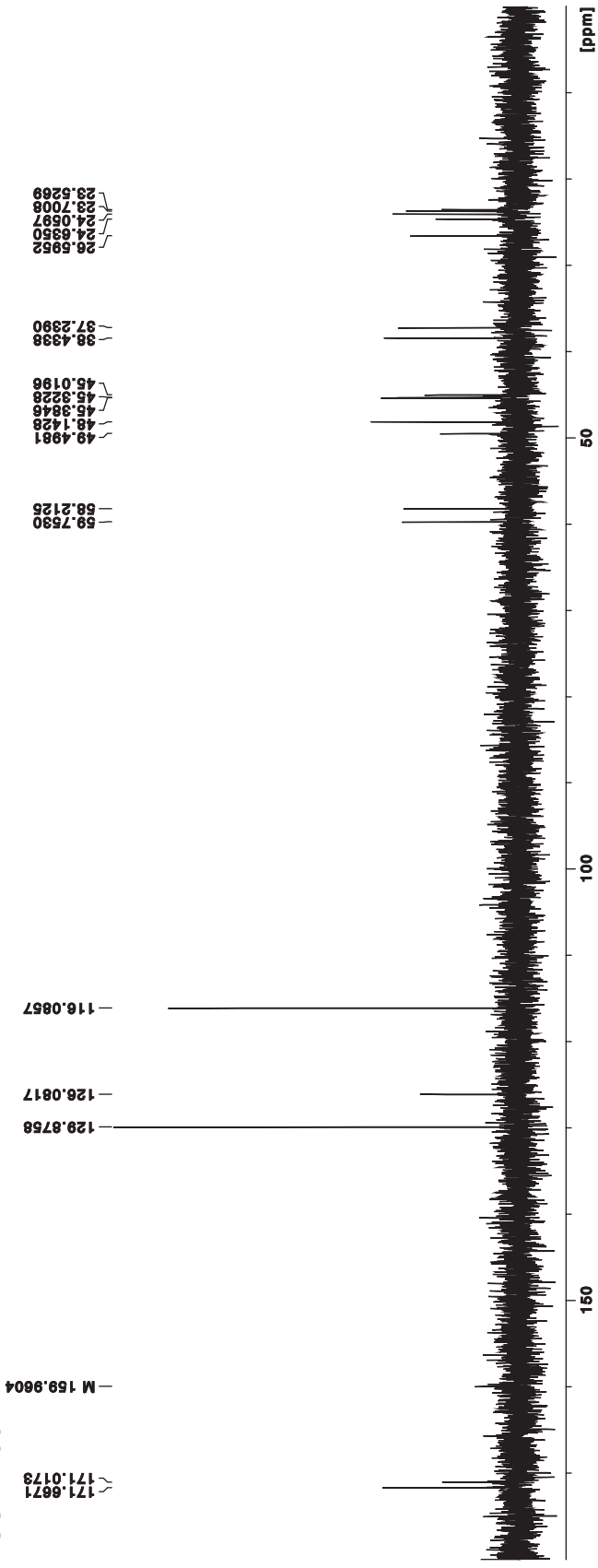


4-OH-Bz3(OH)433

1H - 400 MHz



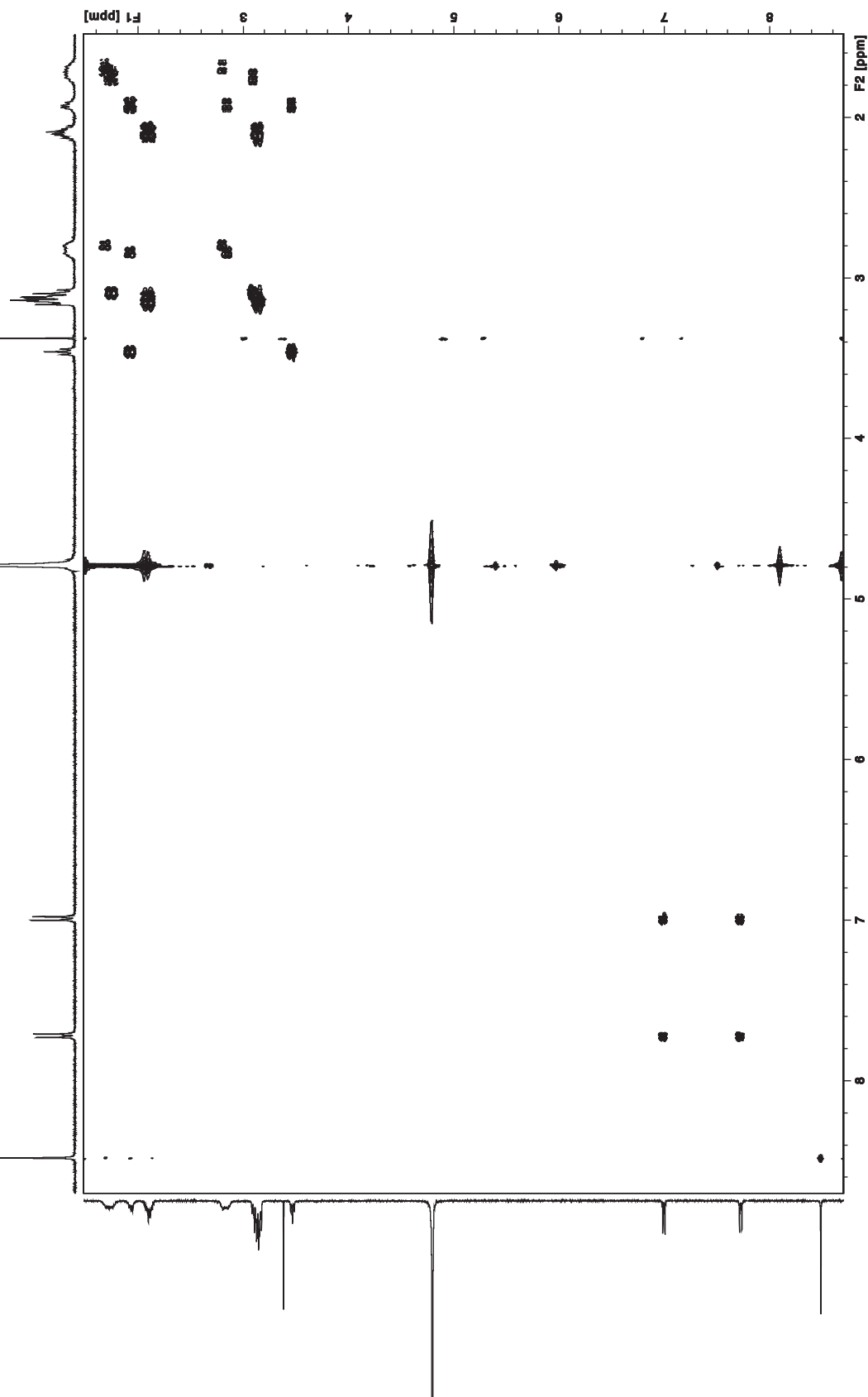
13C - 100 MHz



4-OH-Bz3(OH)433



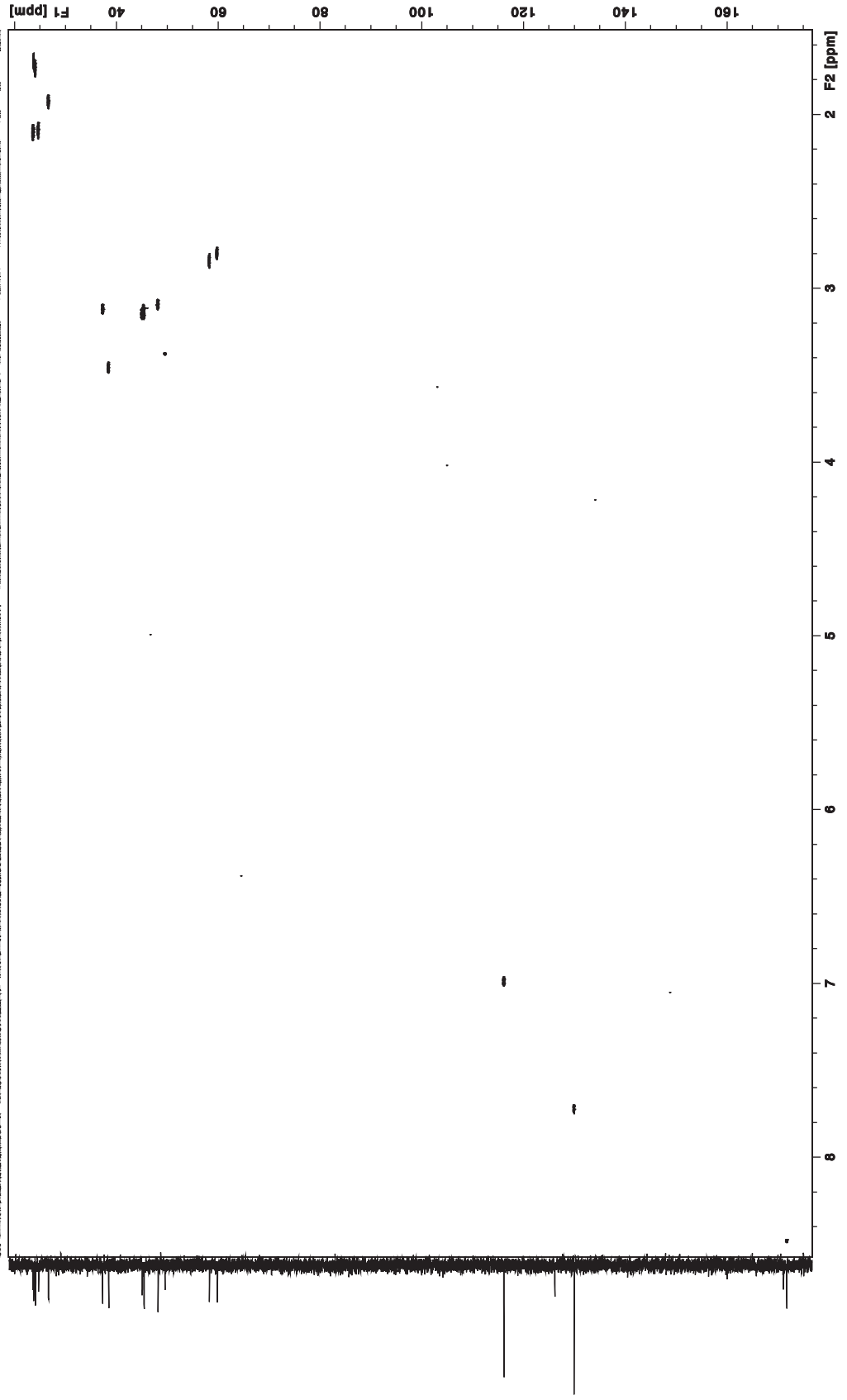
COSY:



4-OH-Bz3(OH)433:

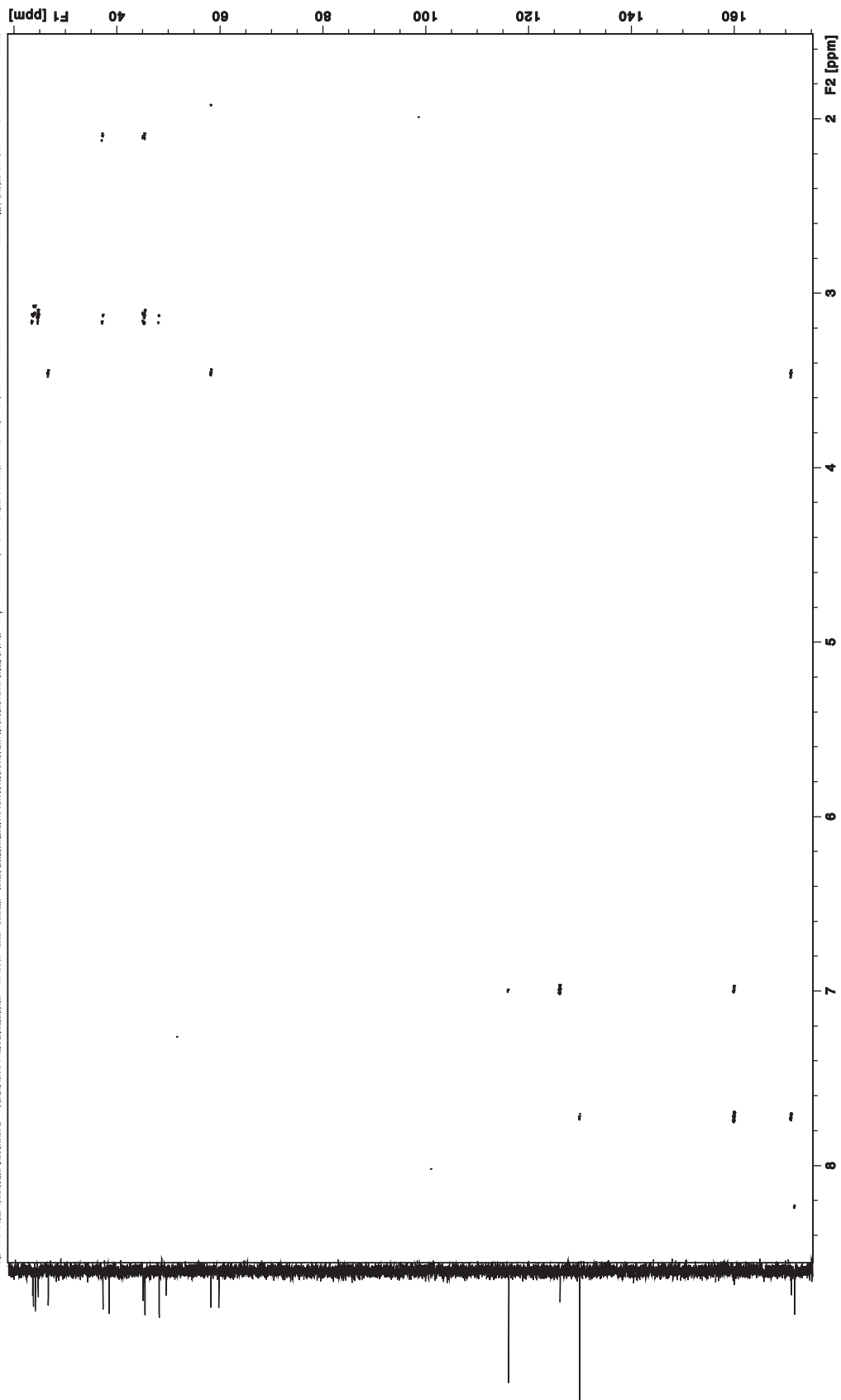
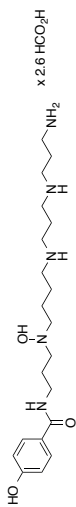


HSQC:



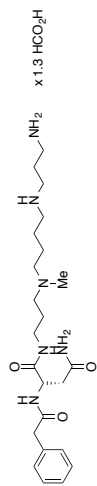
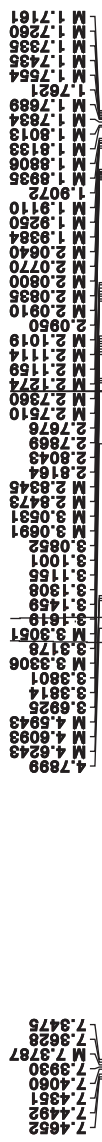
4-OH-Bz3(OH)433

HMBC:



LF448A

1H - 500 MHz

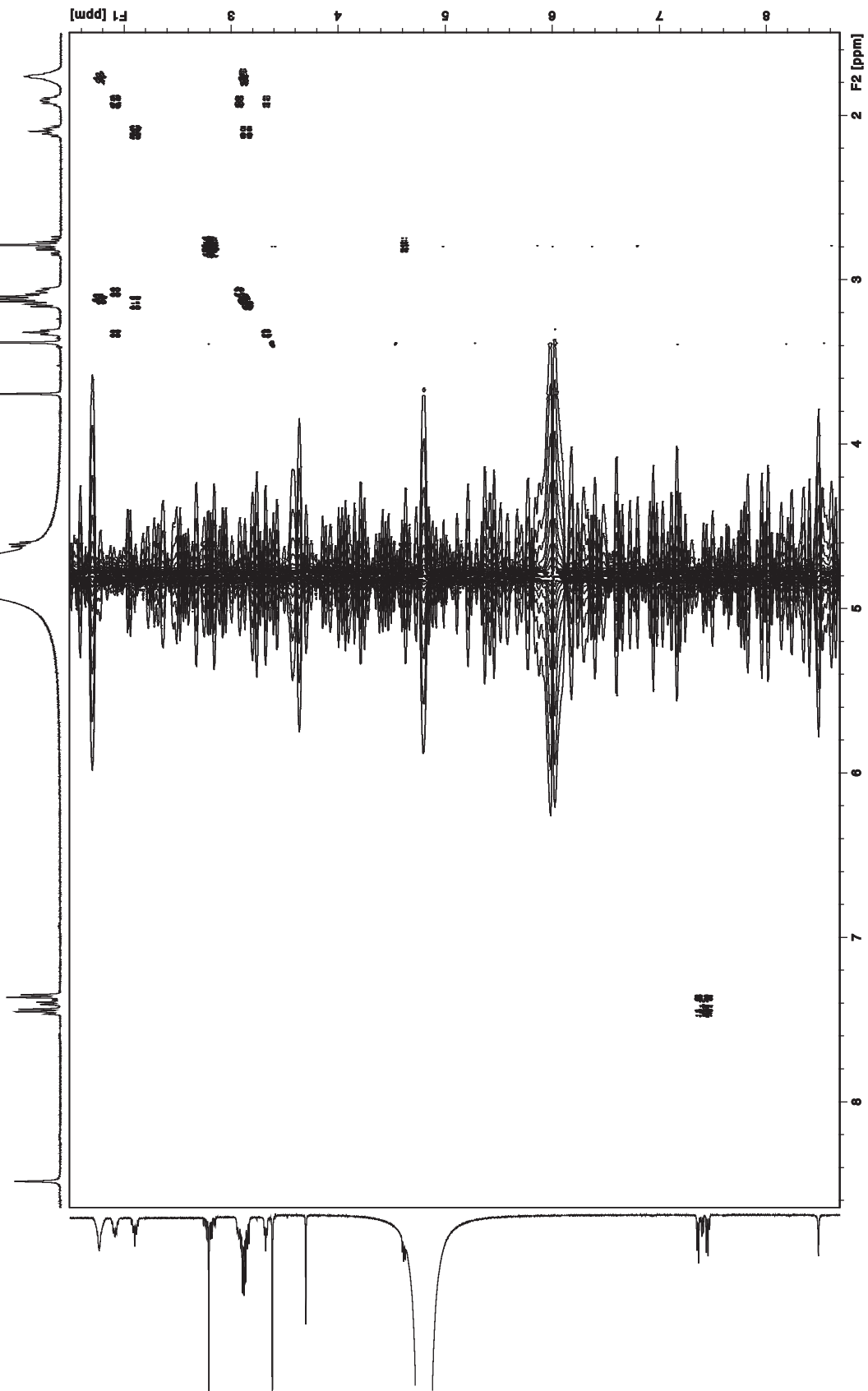
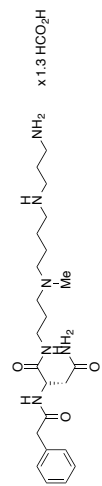


13C - 125 MHz



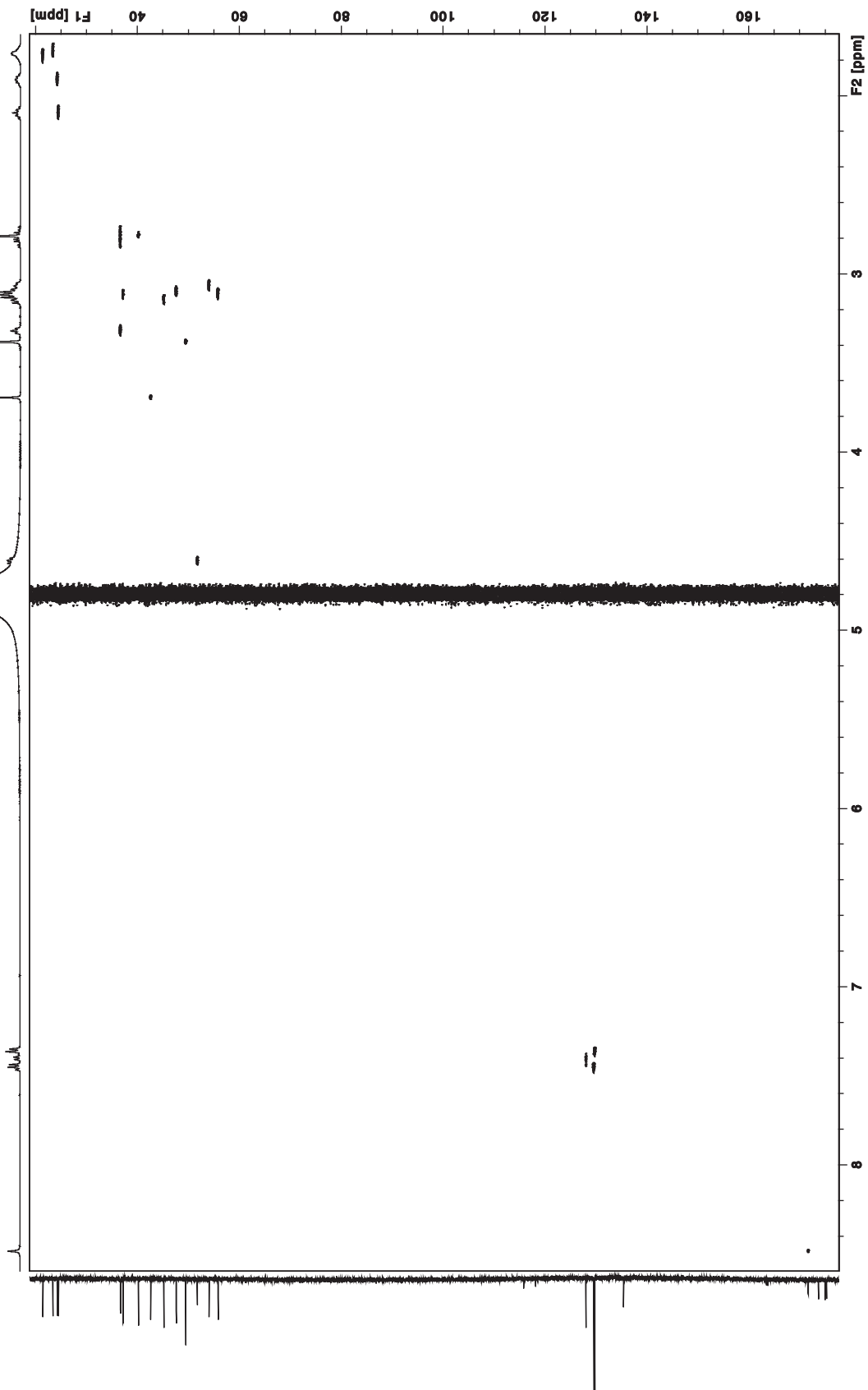
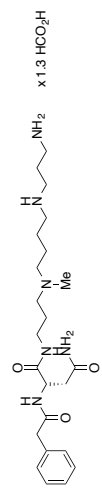
LF448A

COSY:



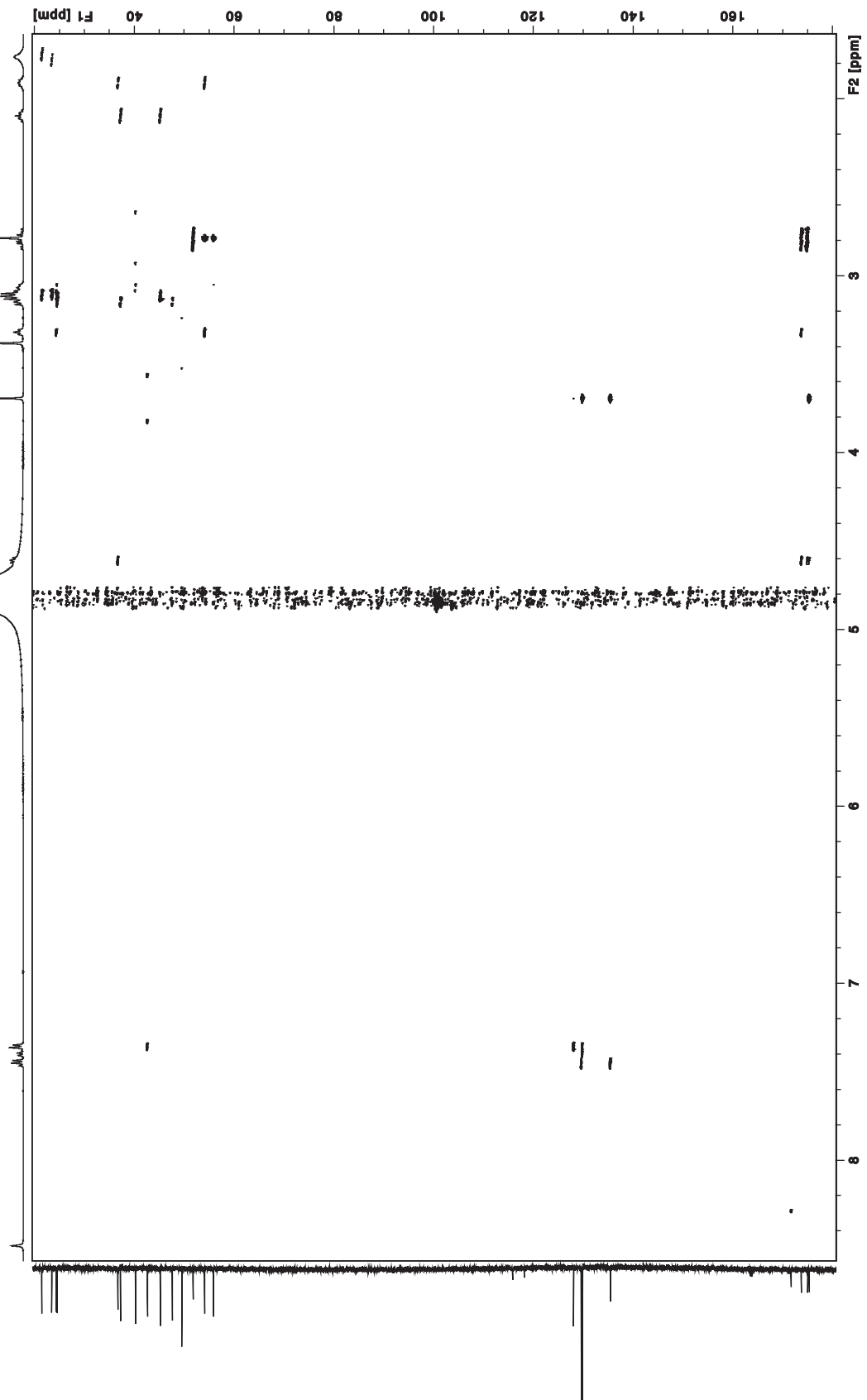
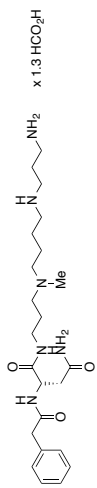
LF448A

HSQC:



LF448A

HMBC:



LF487A

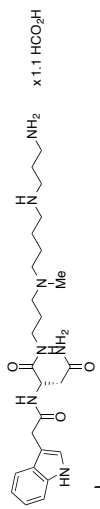
1H - 500 MHz



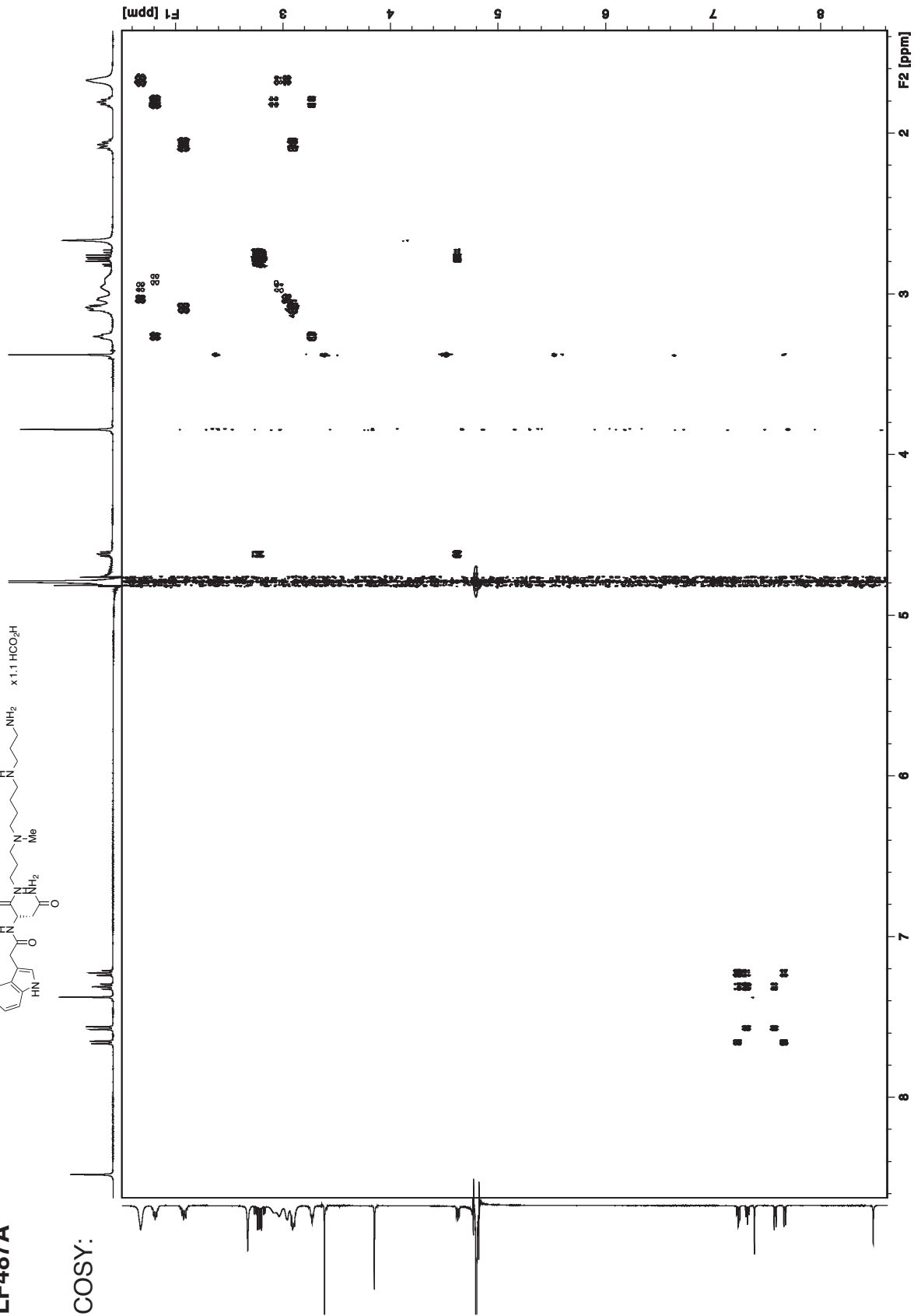
13C - 125 MHz



LF487A

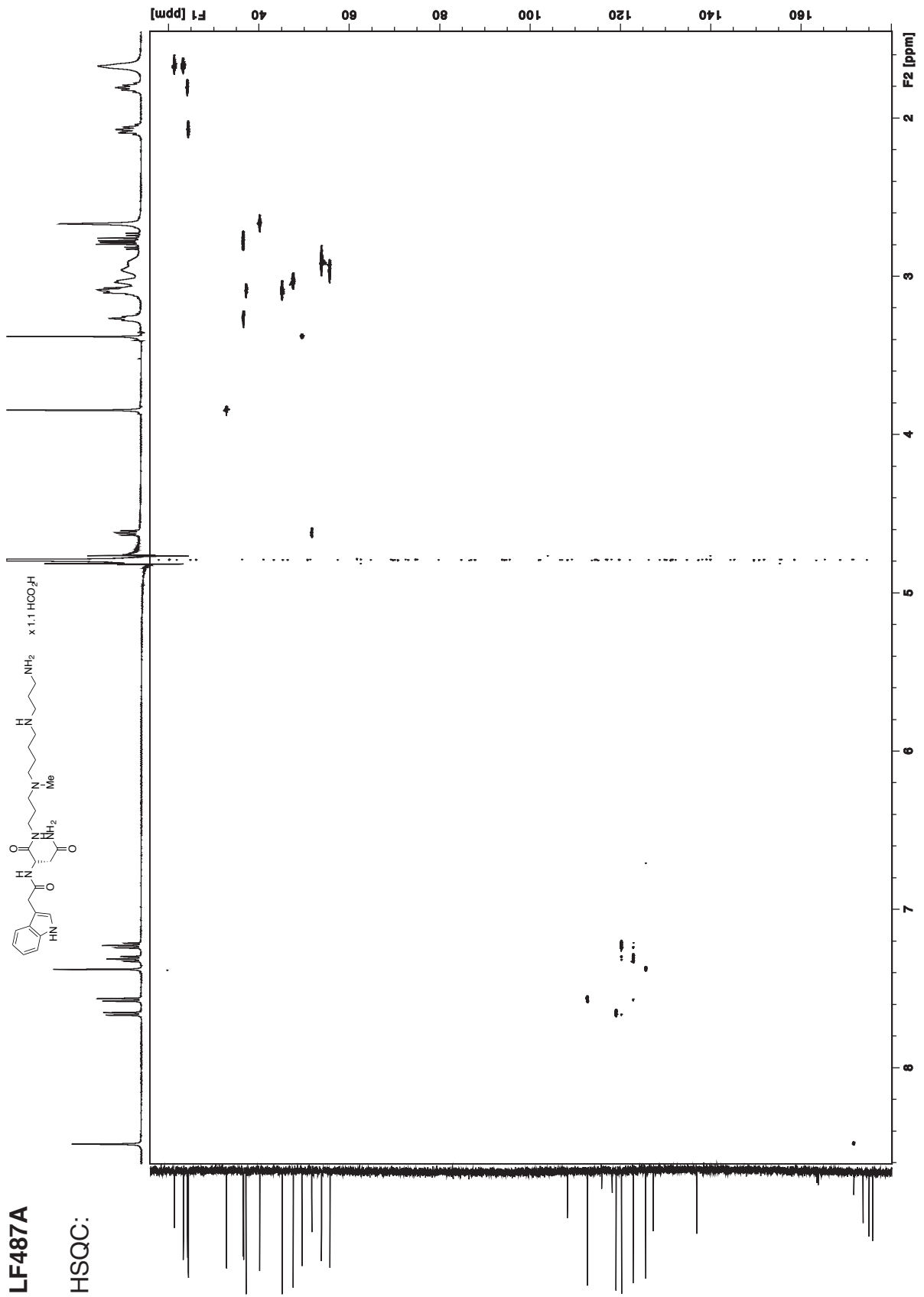


COSY:

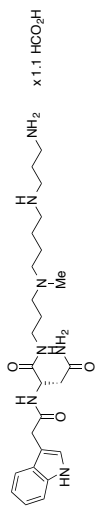


LF487A

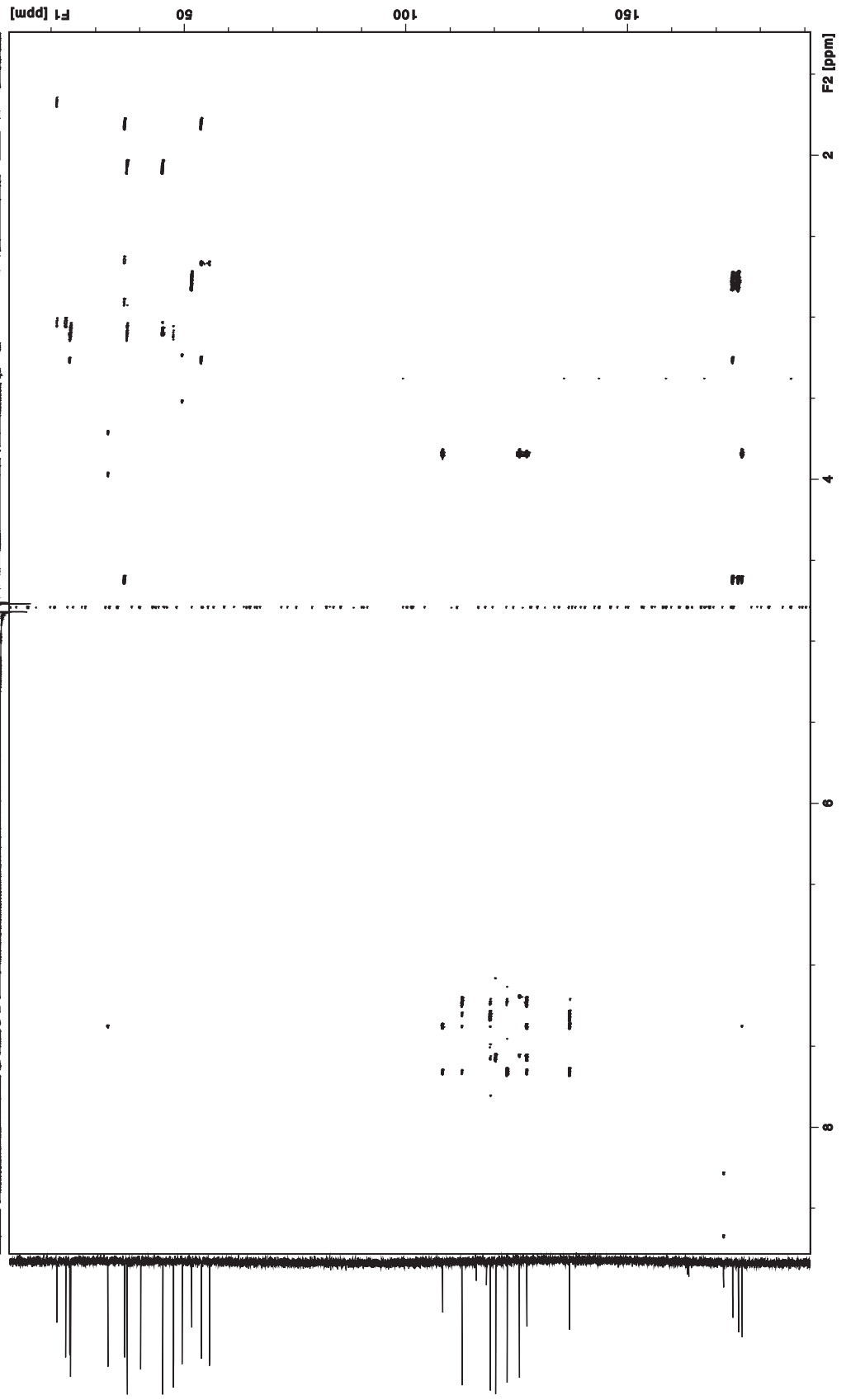
HSQC:



LF487A



HMBC:



Compound **29**

¹H – 400 MHz



7.7226

7.7015

6.9689

6.9475

- M 4.7216

3.5422

3.5269

3.5123

3.4968

3.2566

3.2441

3.1398

3.1116

3.0912

3.0762

2.8065

2.7863

2.6808

1.9074

1.8742

1.8420

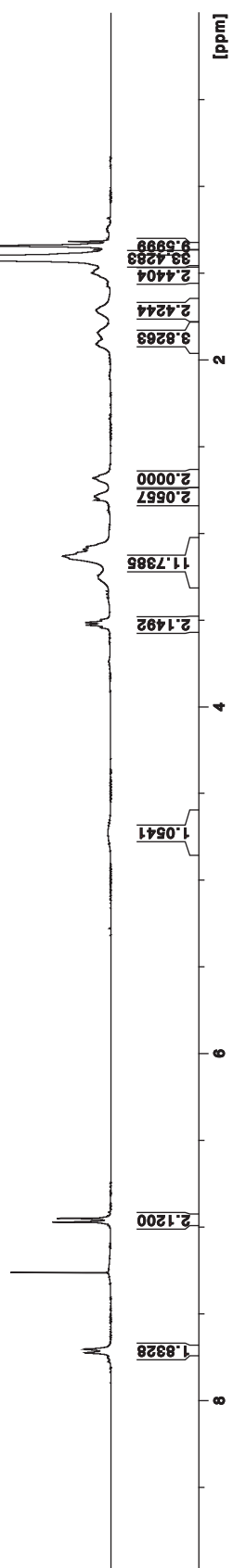
1.7128

1.4973

1.4180

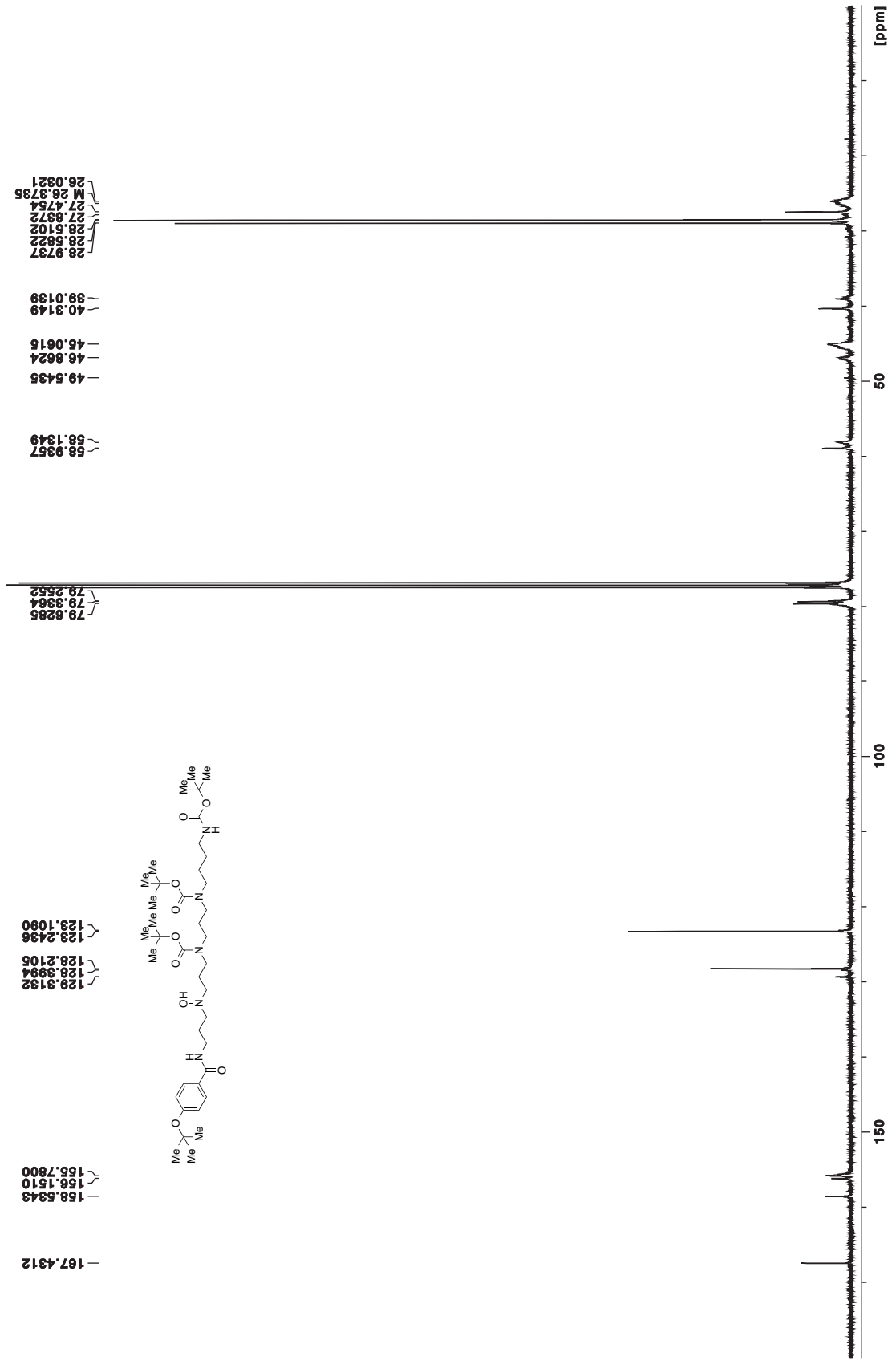
1.4087

1.3408



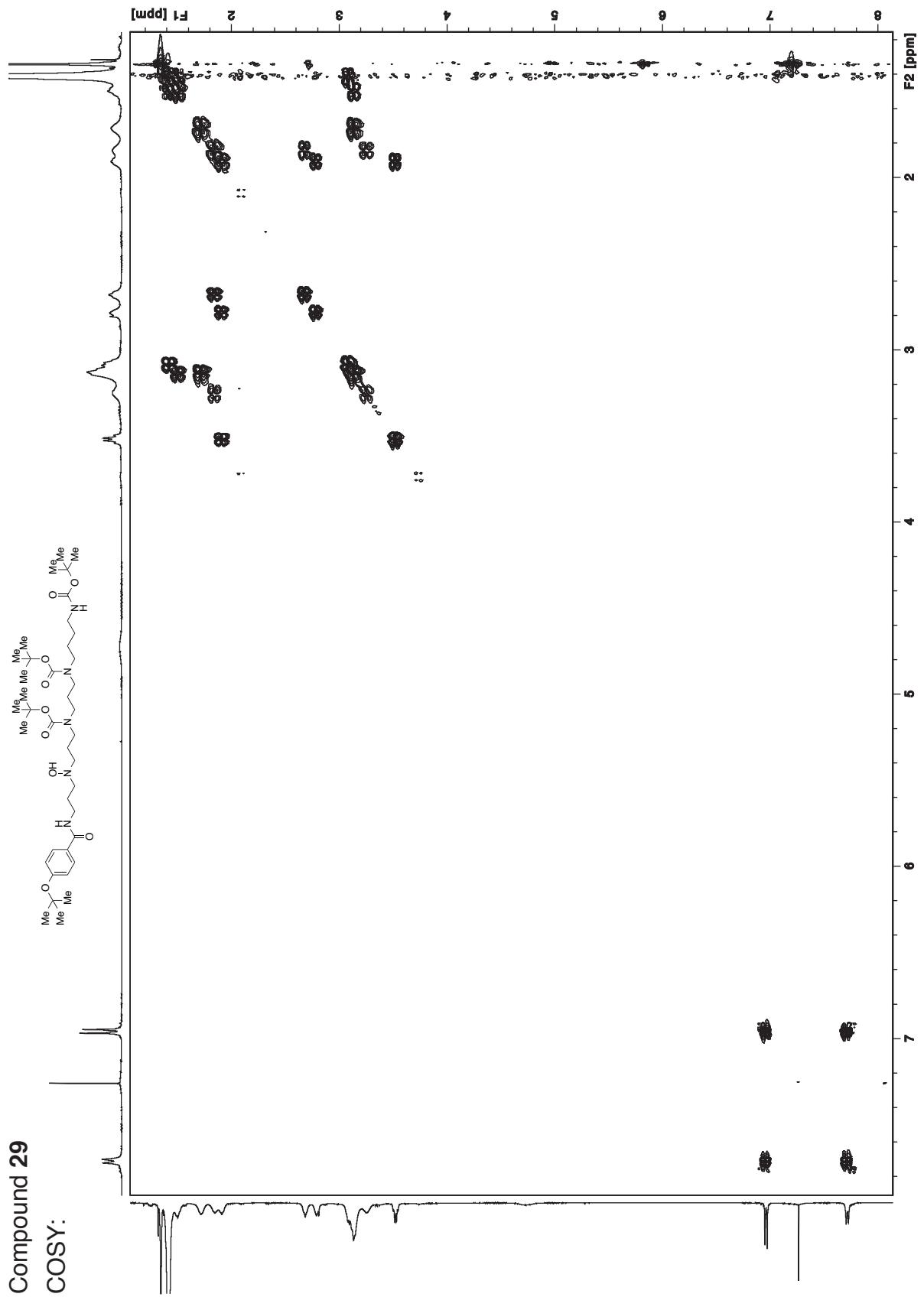
Compound 29

13C – 100 MHz



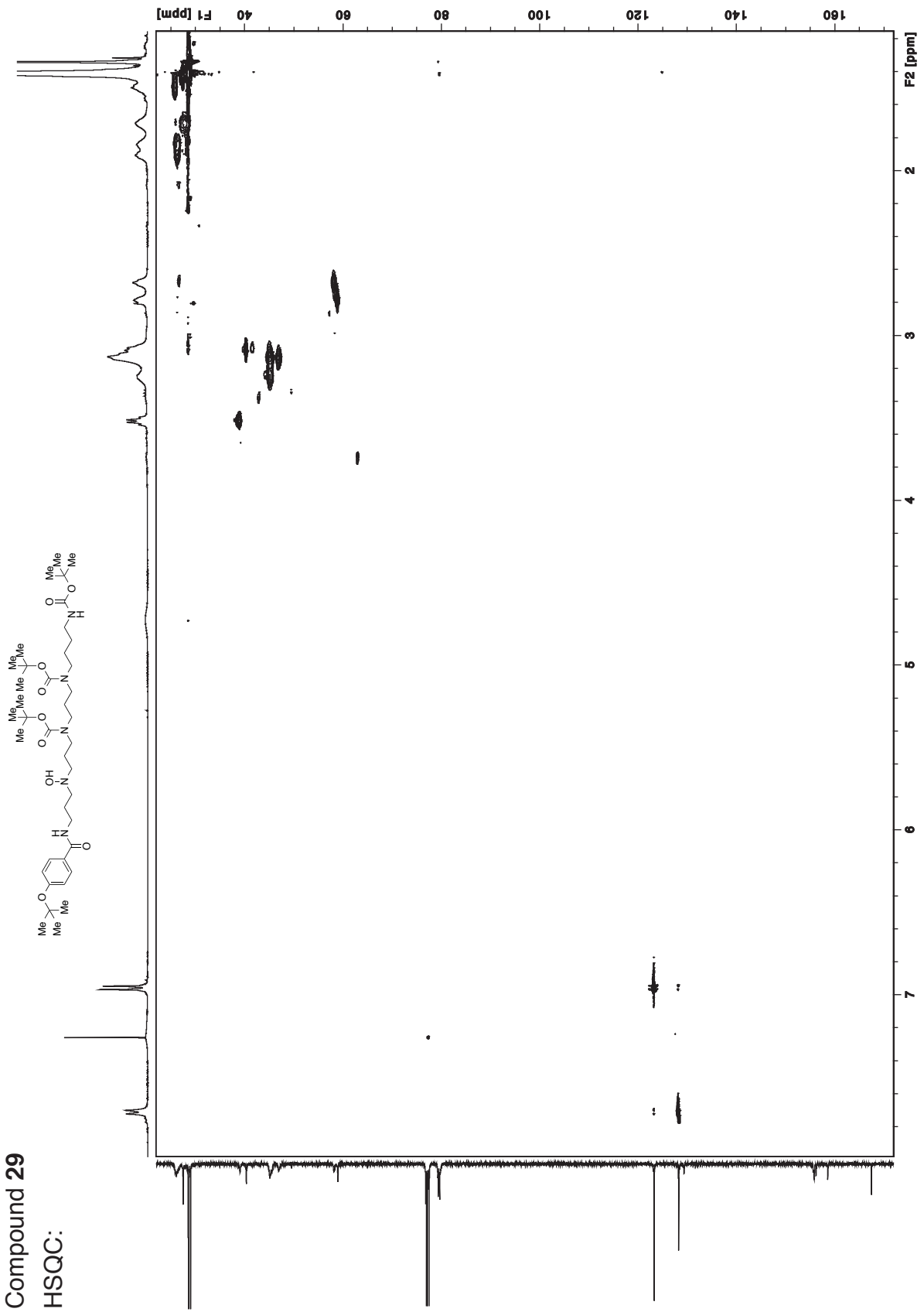
Compound 29

COSY:



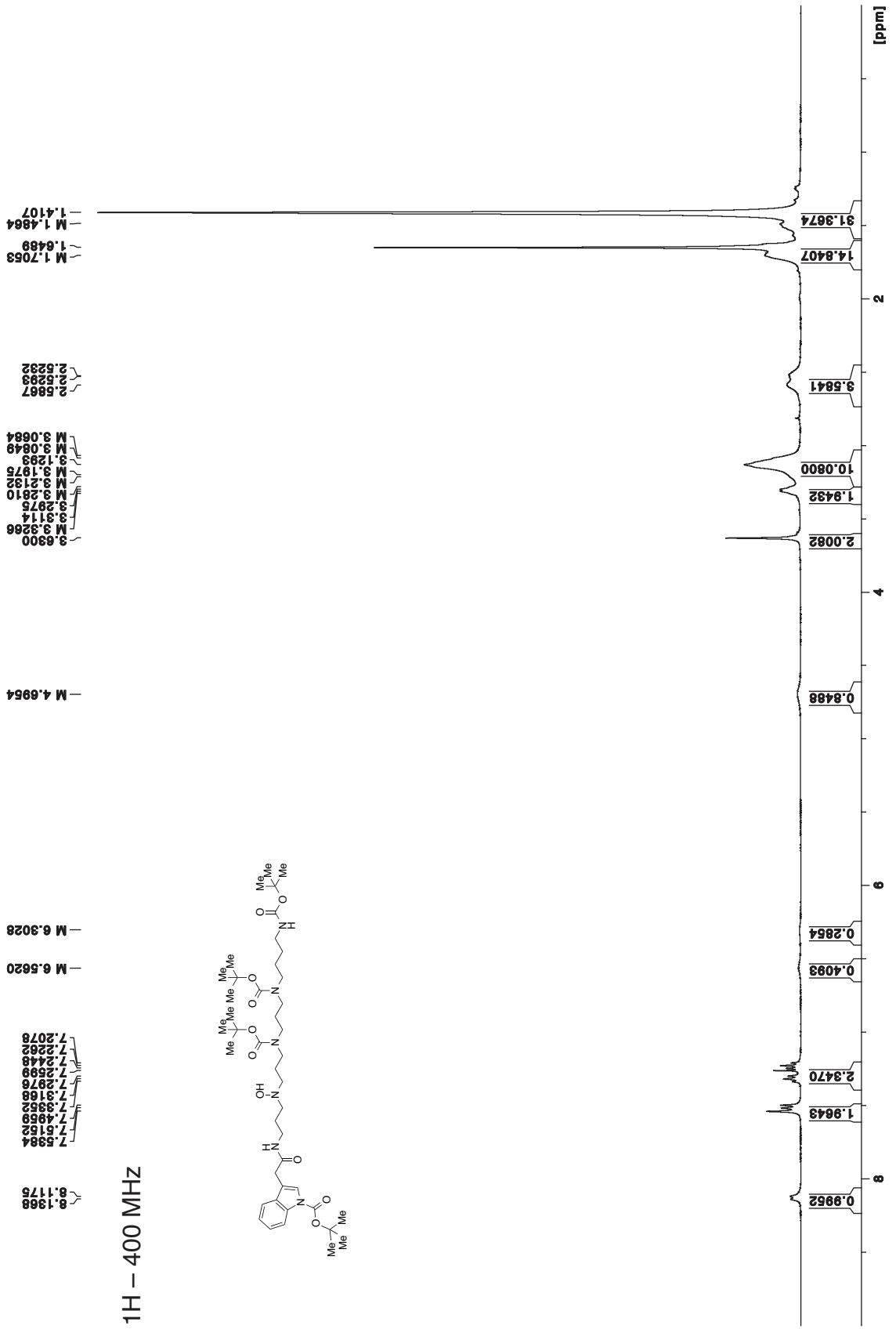
Compound 29

HSQC:



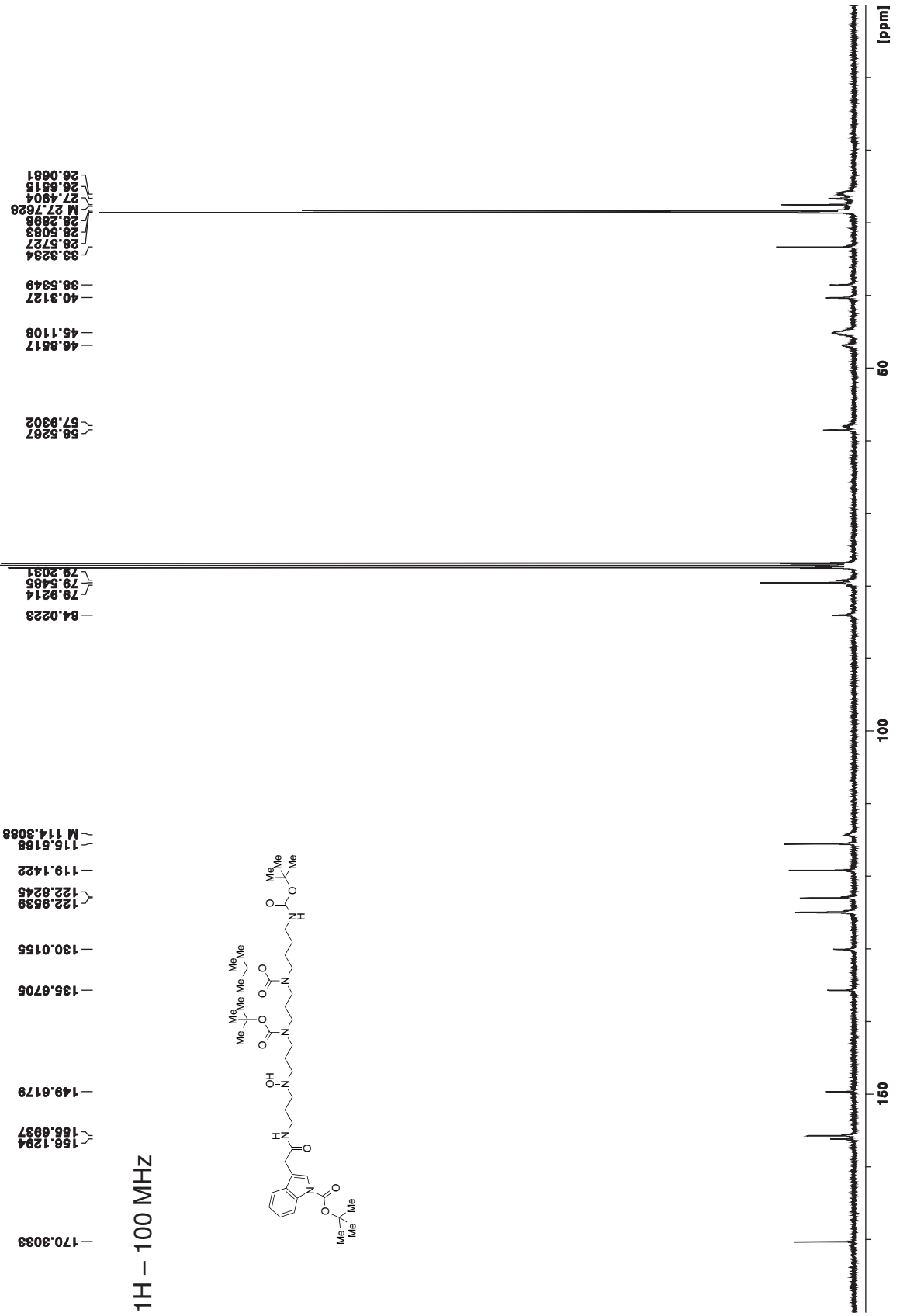
Compound 30

¹H – 400 MHz



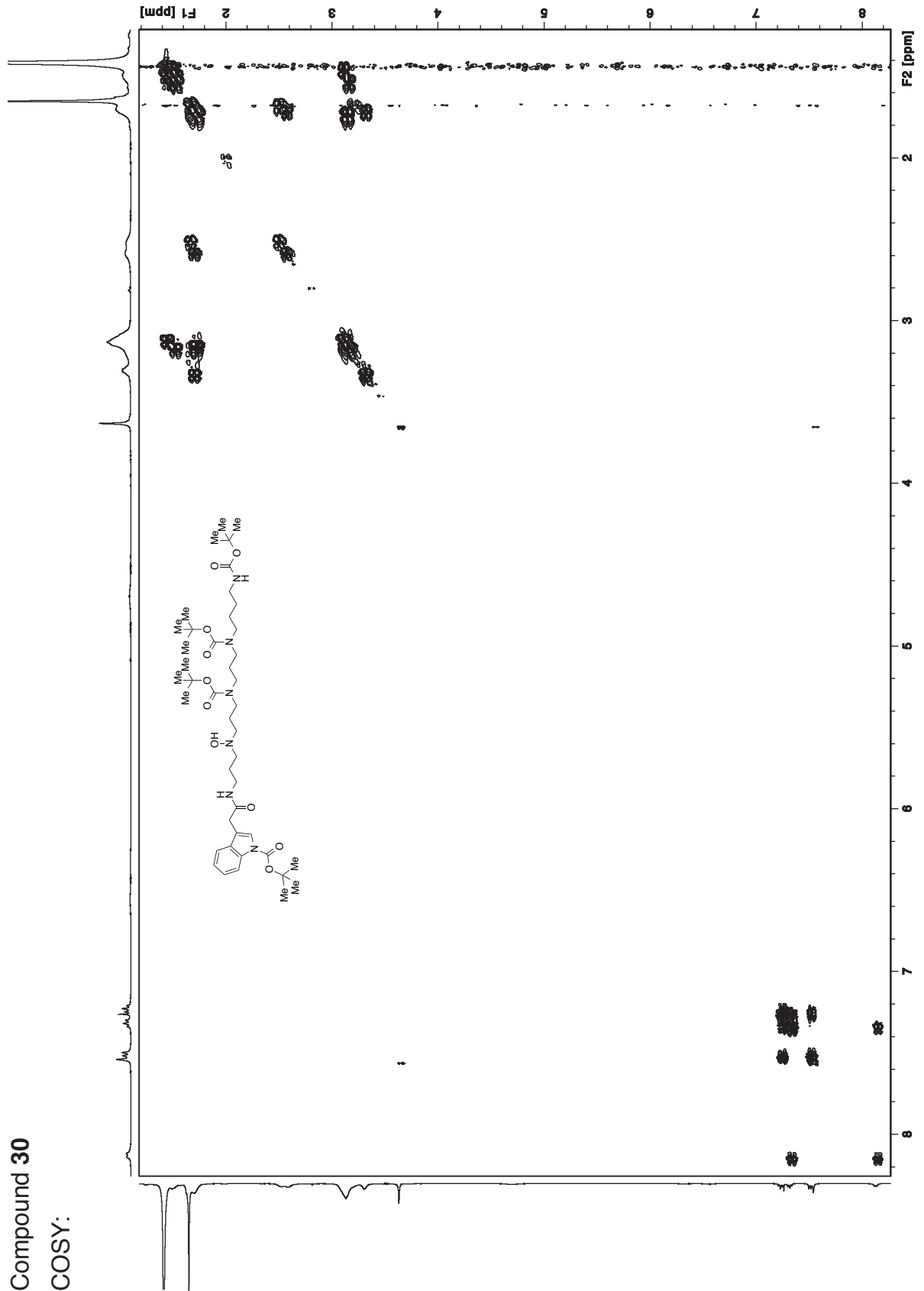
Compound 30

¹H – 100 MHz



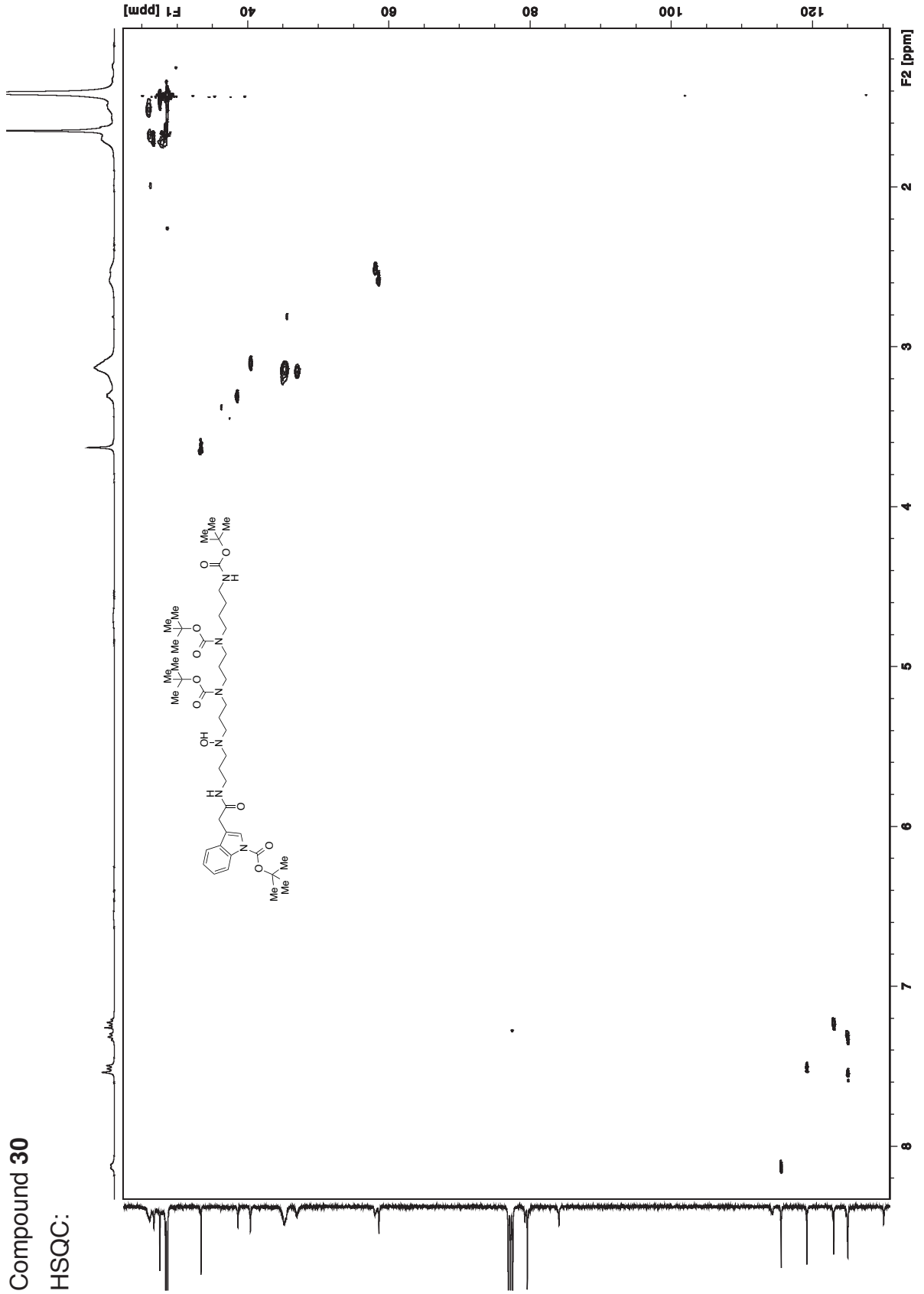
Compound 30

COSY:



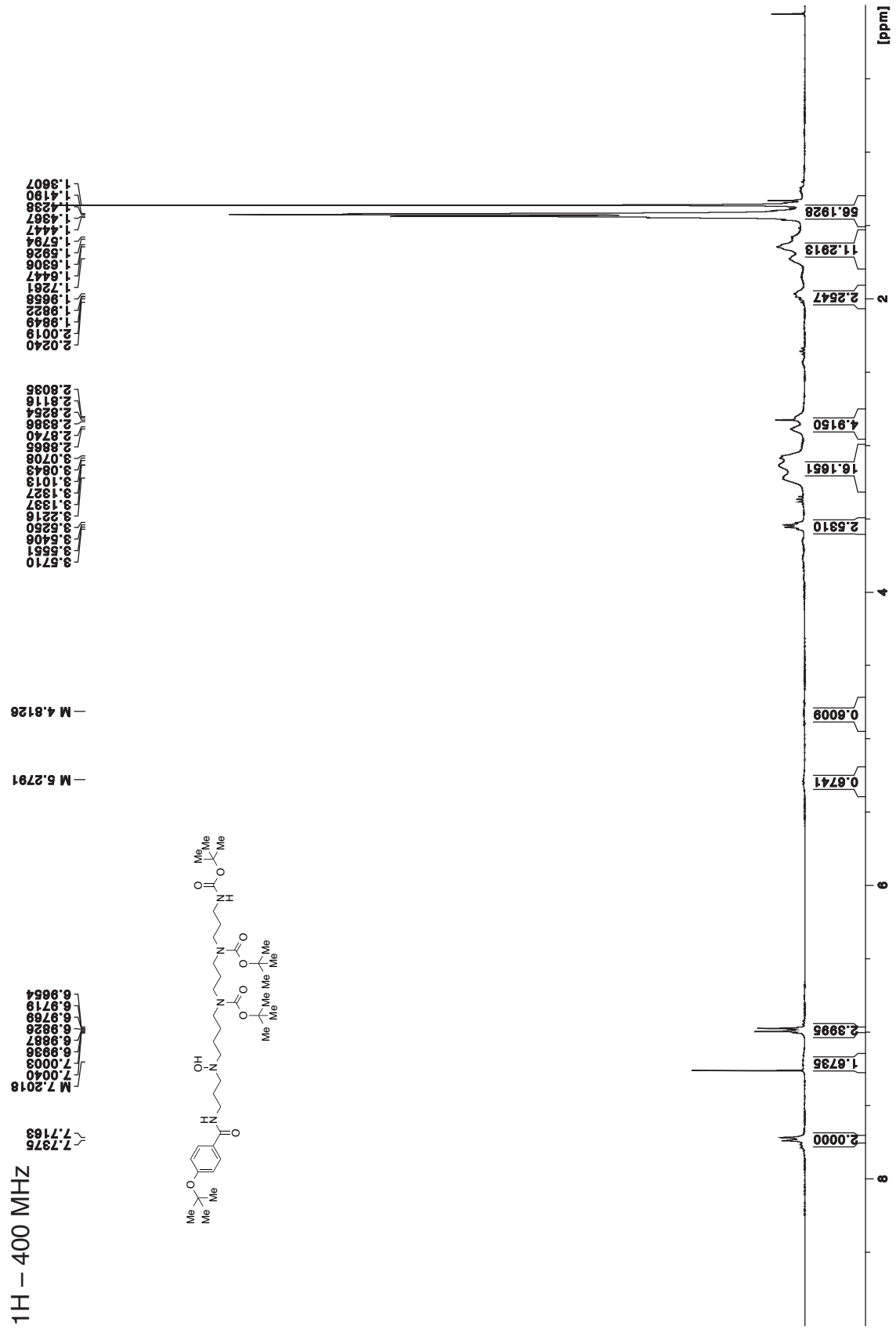
Compound 30

HSQC:

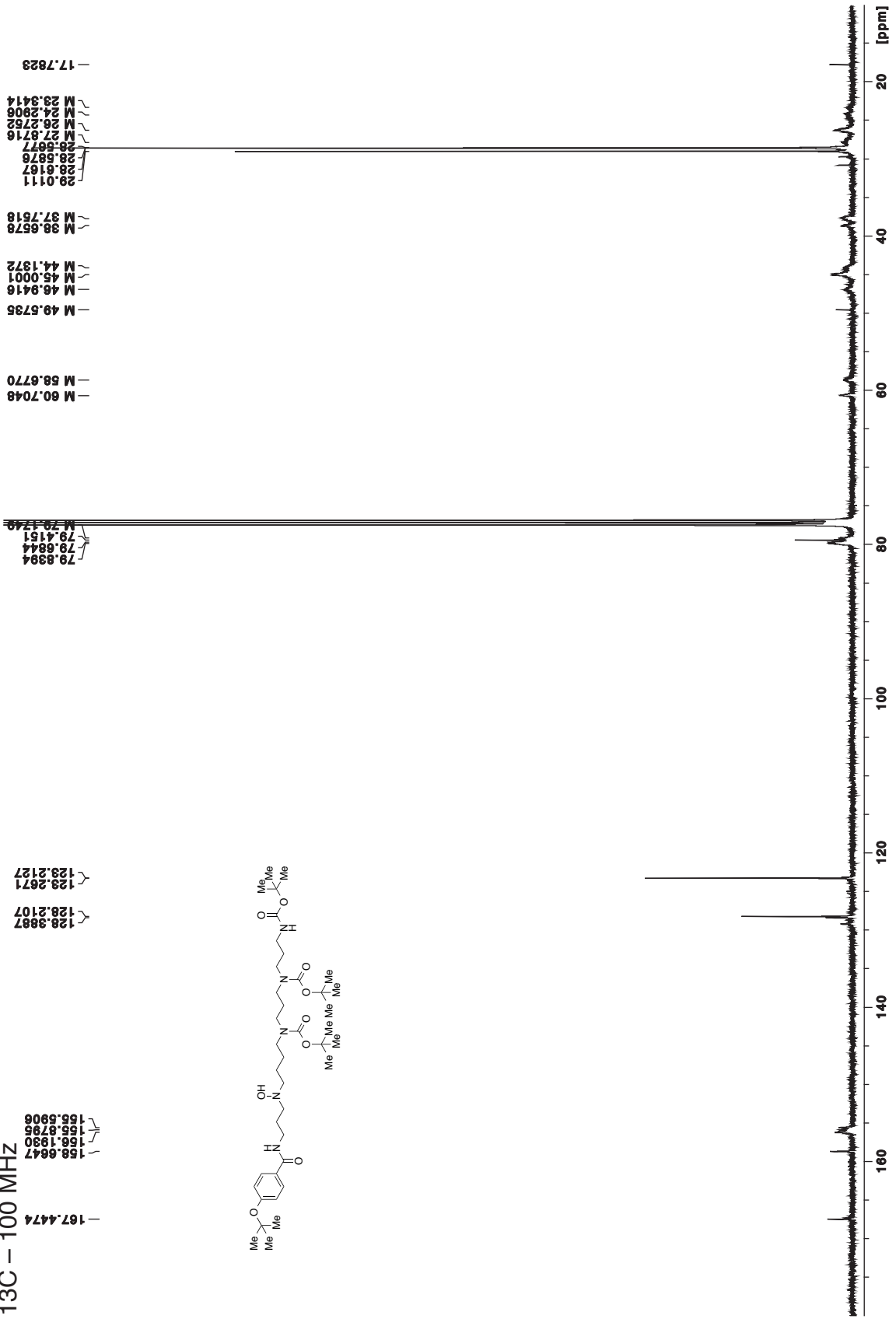


Compound **31**

¹H – 400 MHz



Compound 31
13C — 100 MHz



187.4474

158.6647

155.1930

155.8795

155.5908

129.9897

129.2127

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17.7823

29.0111

28.6167

28.5876

28.5877

27.8719

26.2752

24.2906

23.3414

17.7823

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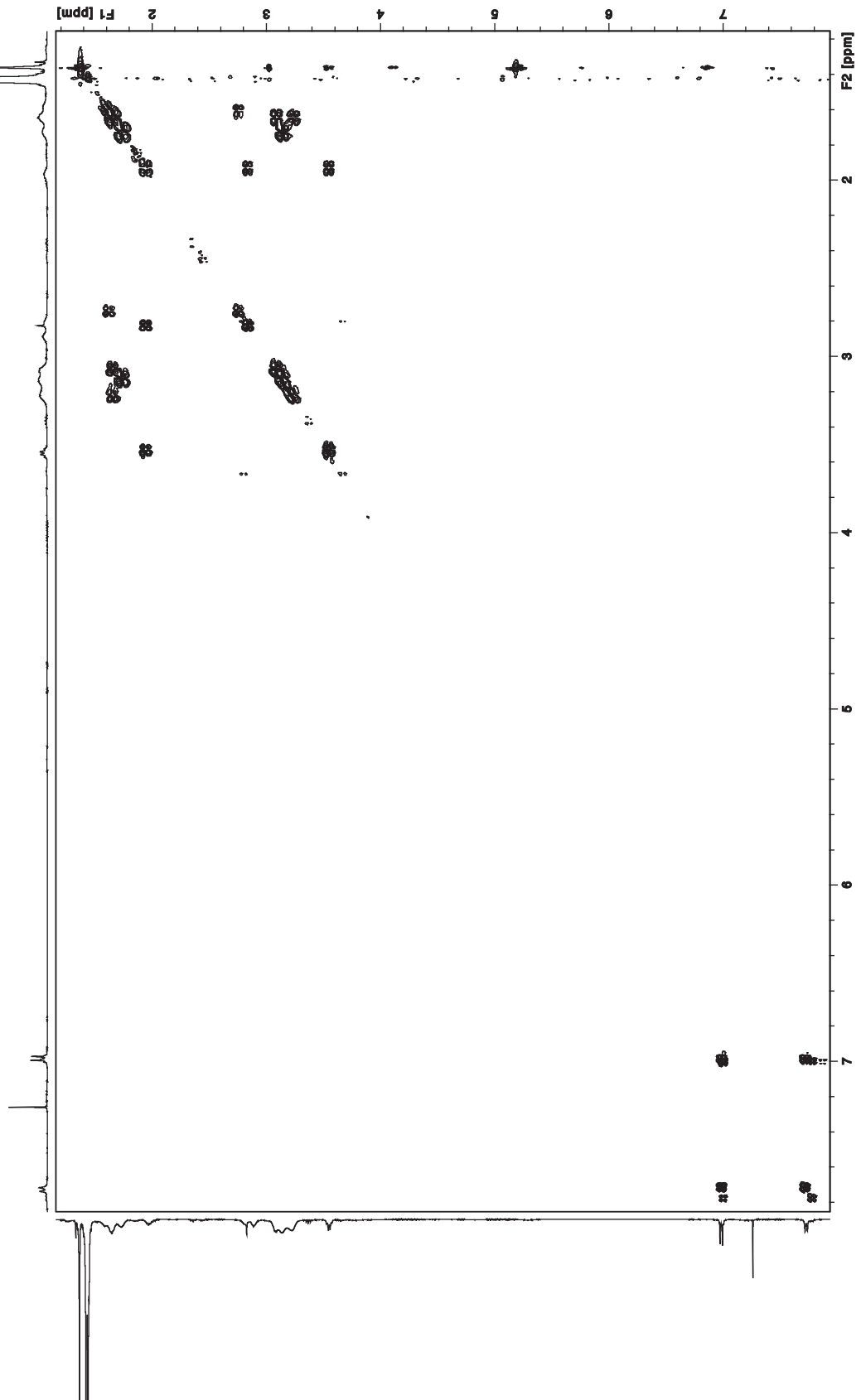
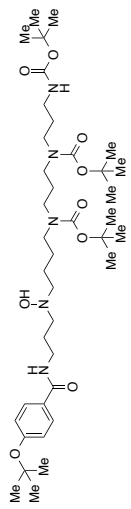
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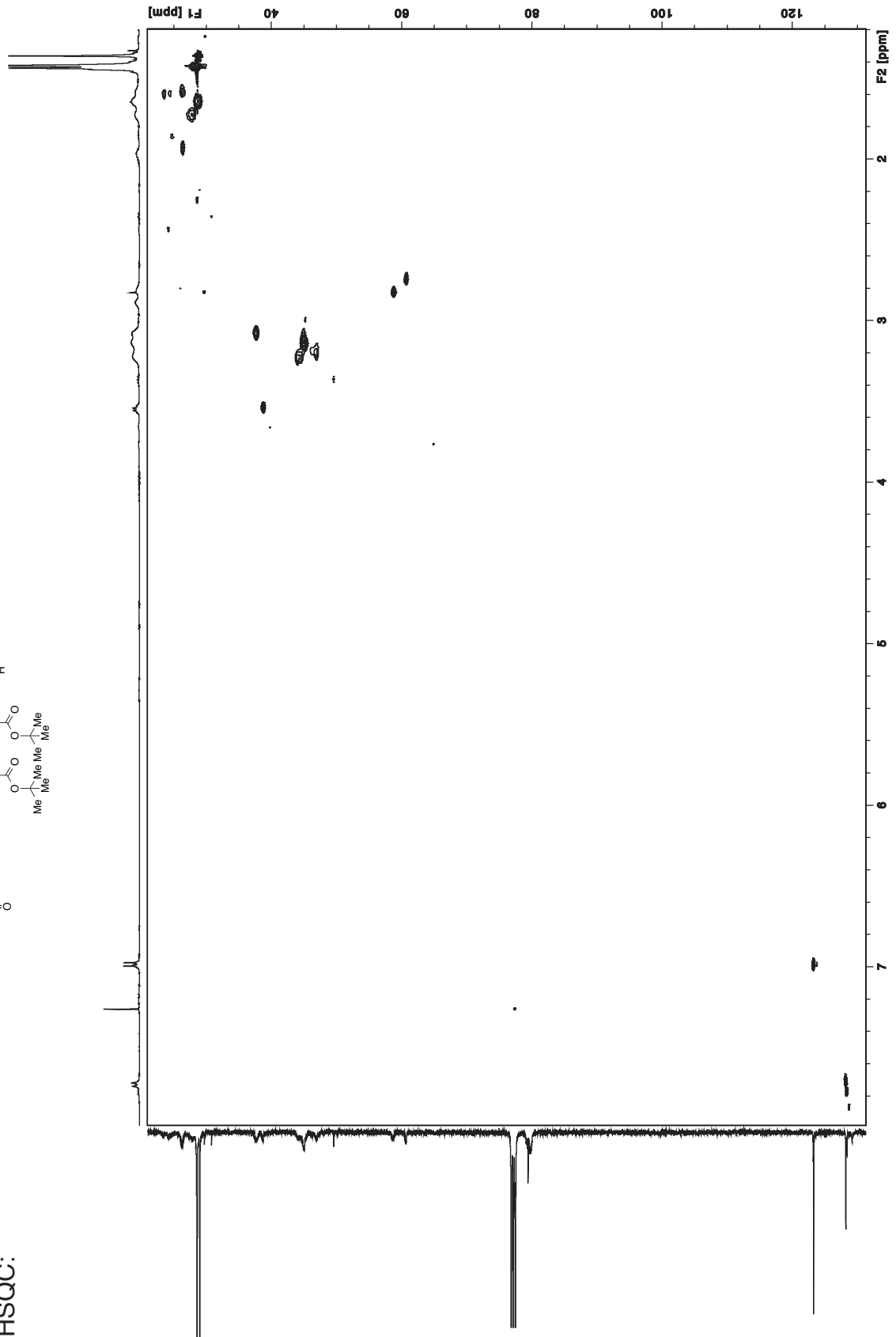
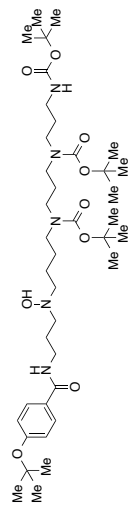
Compound **31**

COSY:



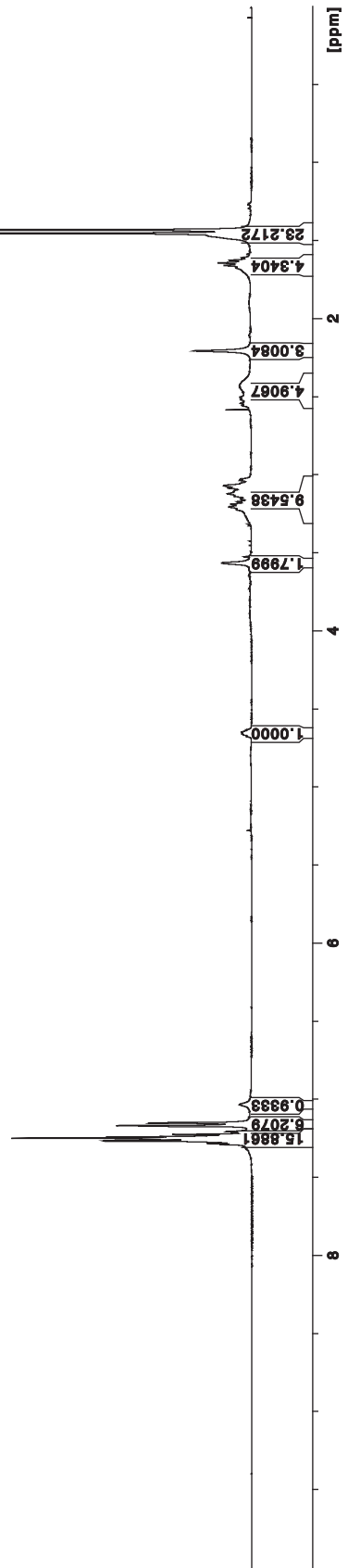
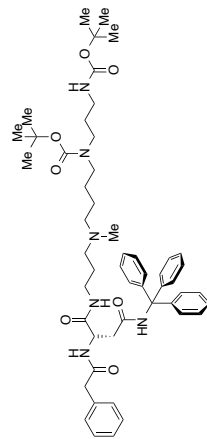
Compound 31

HSQC:



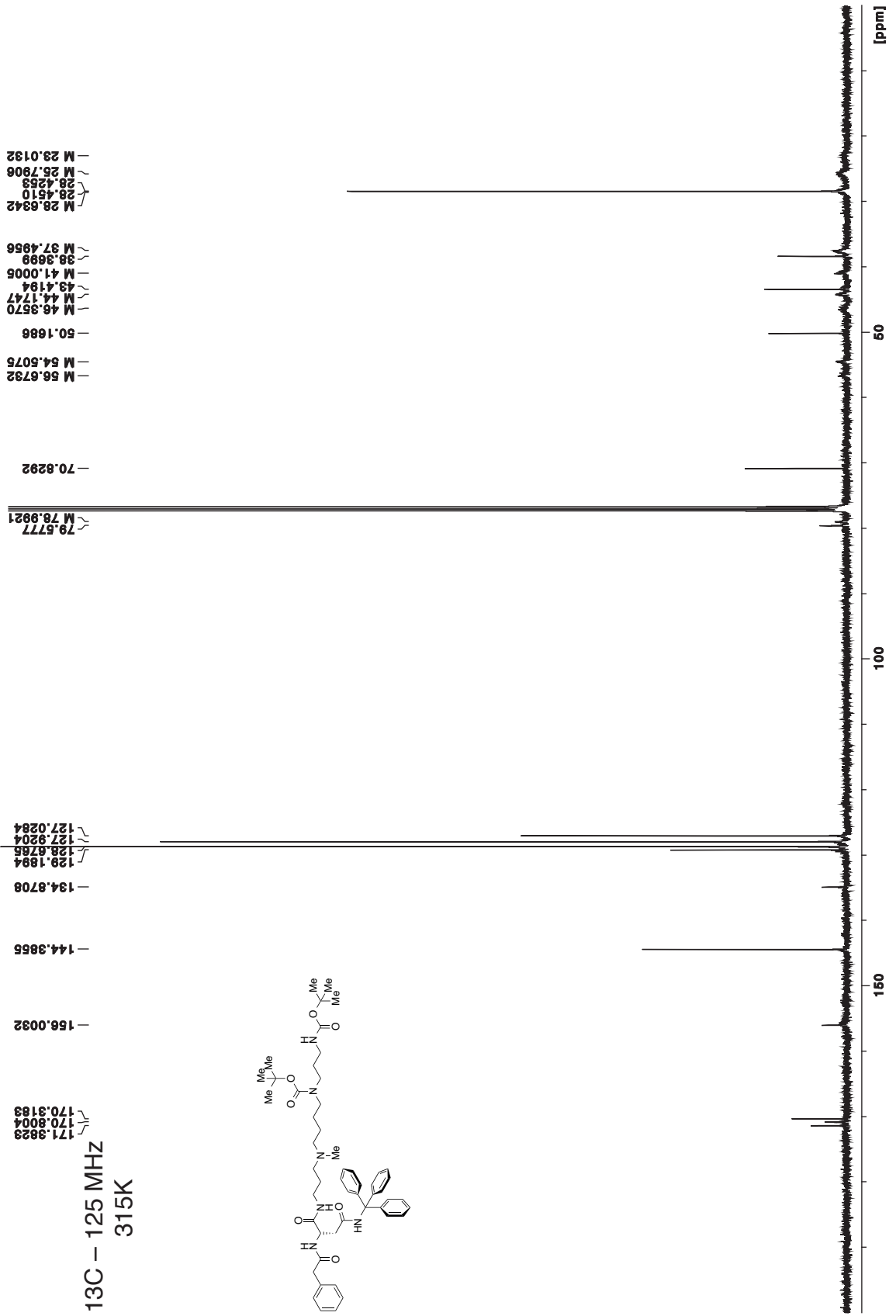
Compound 40

¹H – 500 MHz
315K



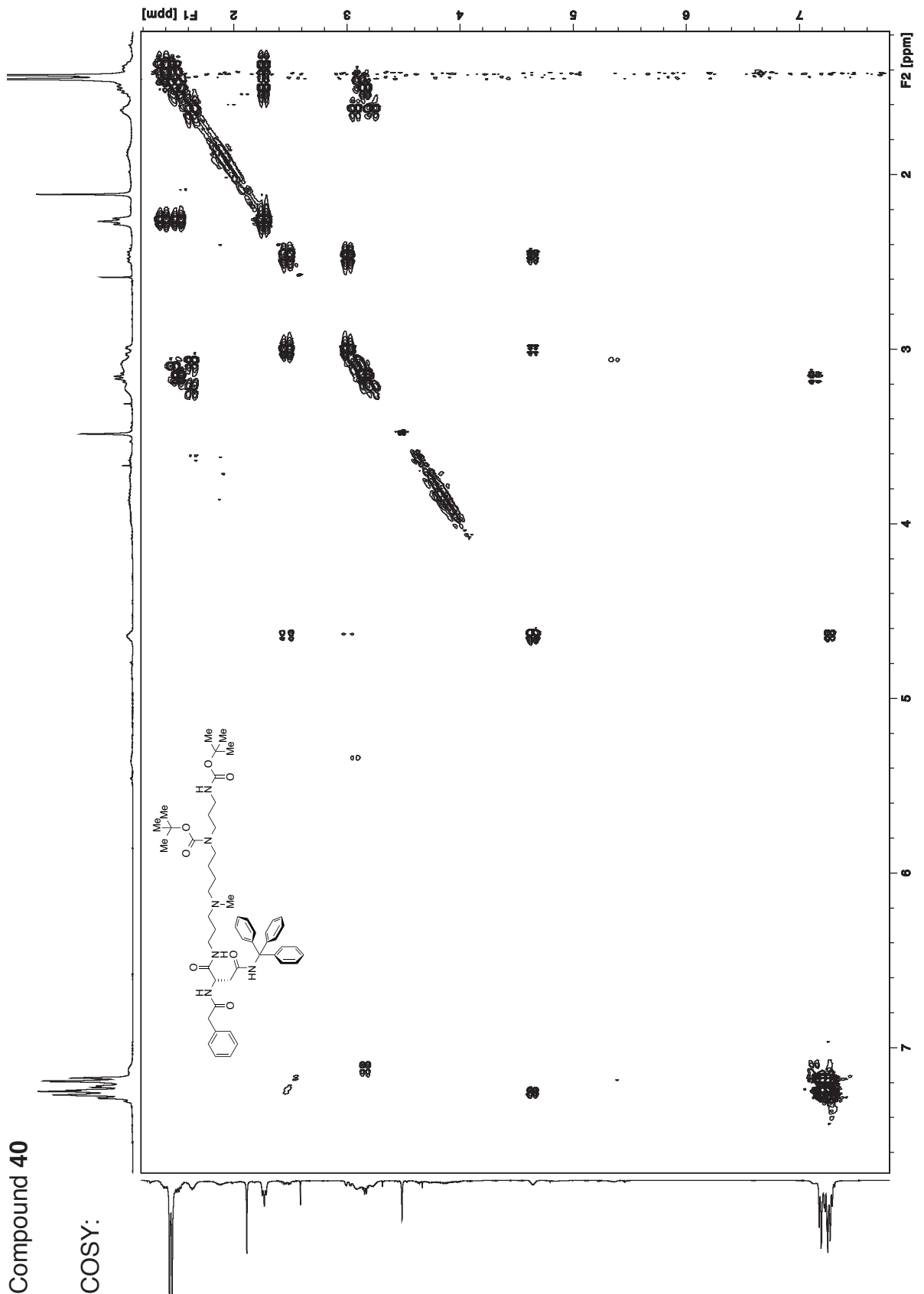
Compound 40

13C – 125 MHz
315K



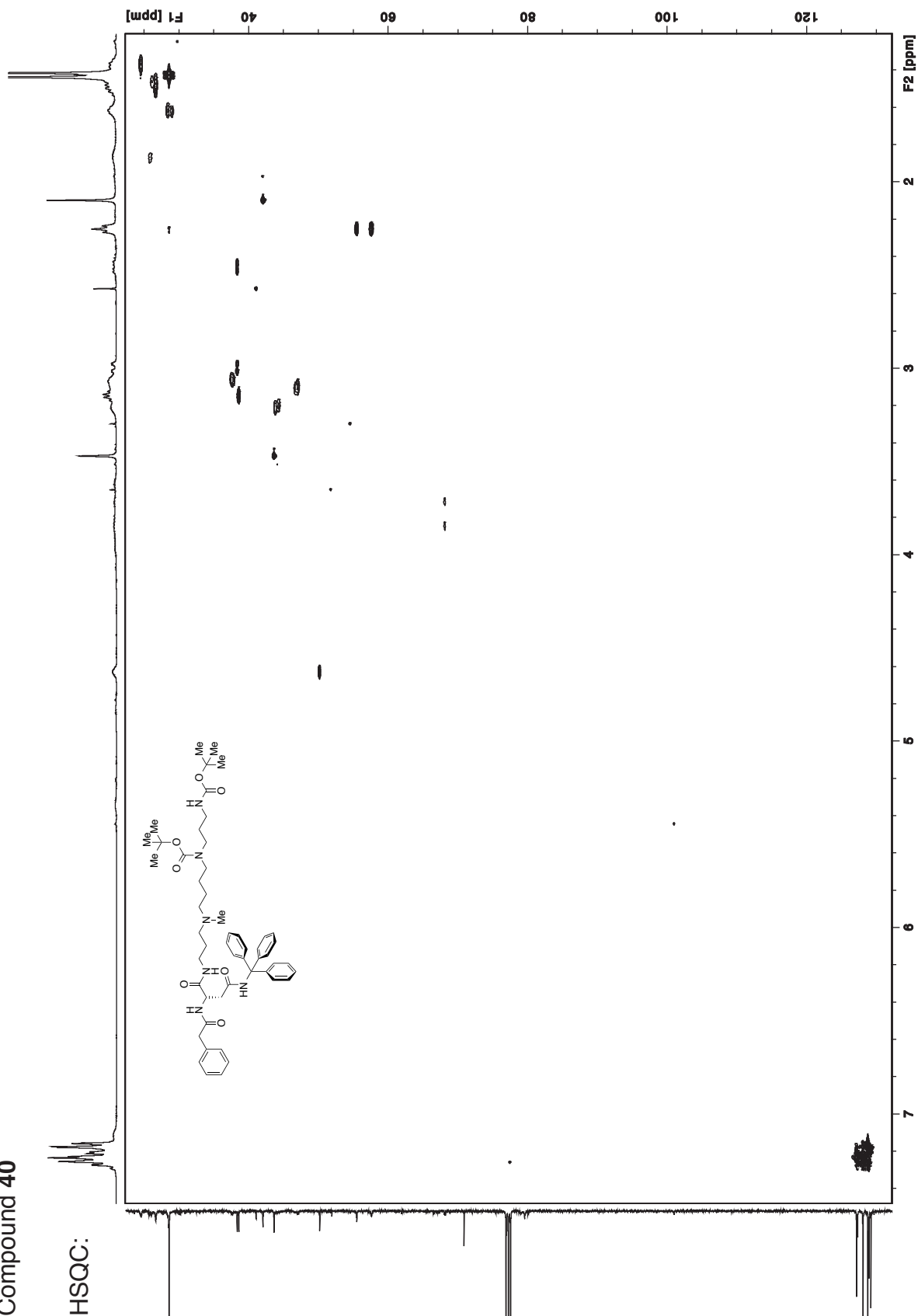
Compound 40

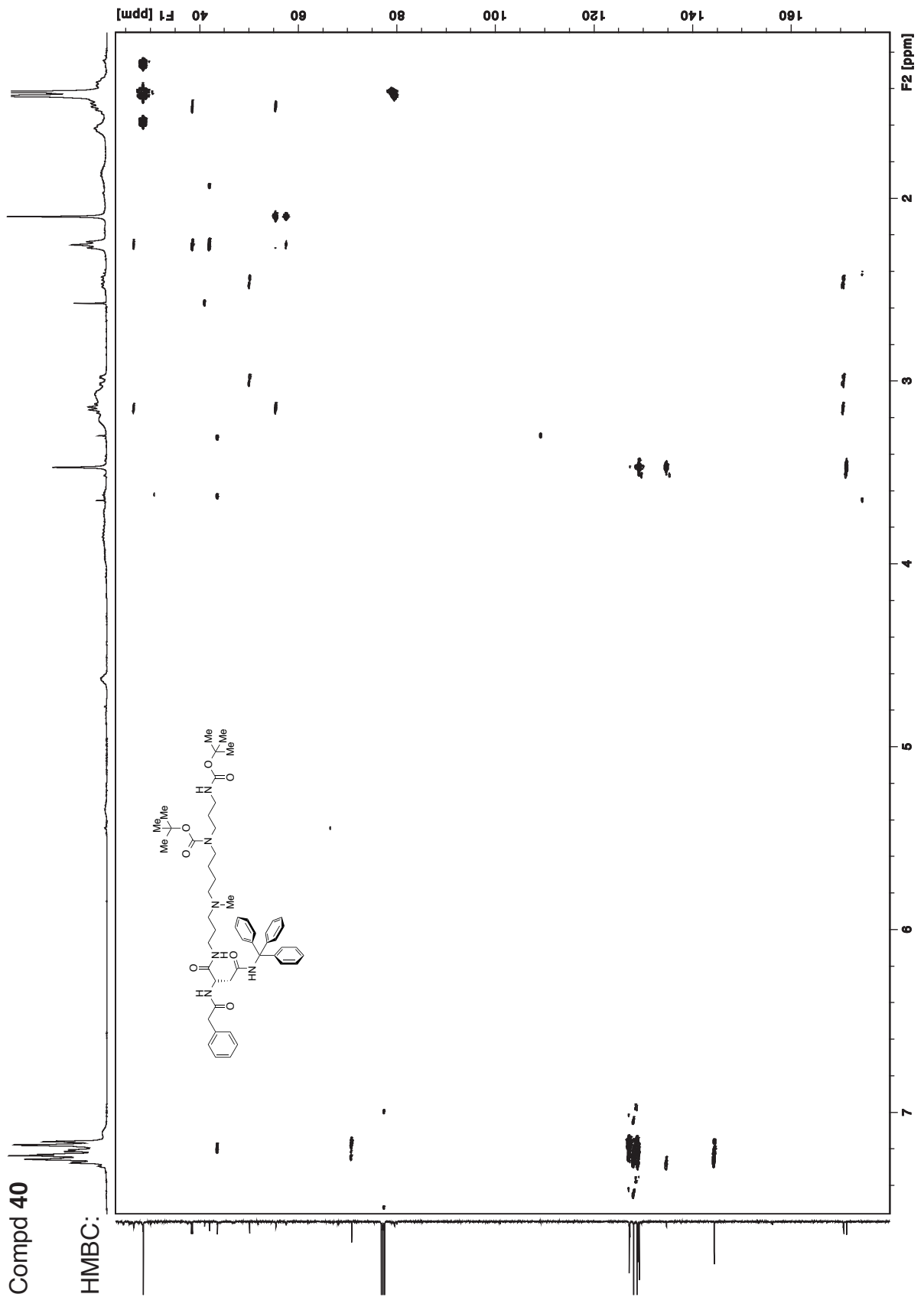
COSY:



Compound 40

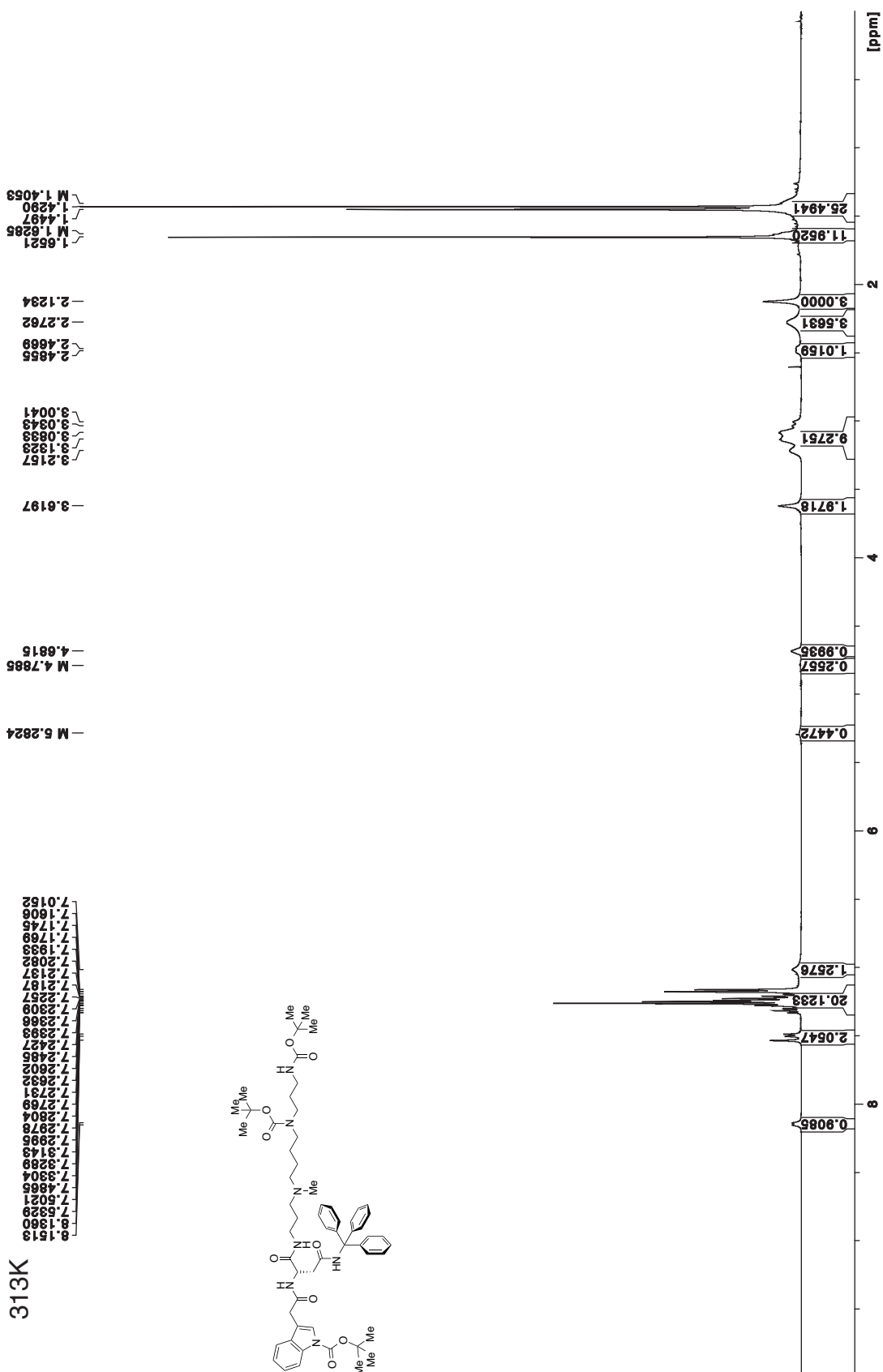
HSQC:



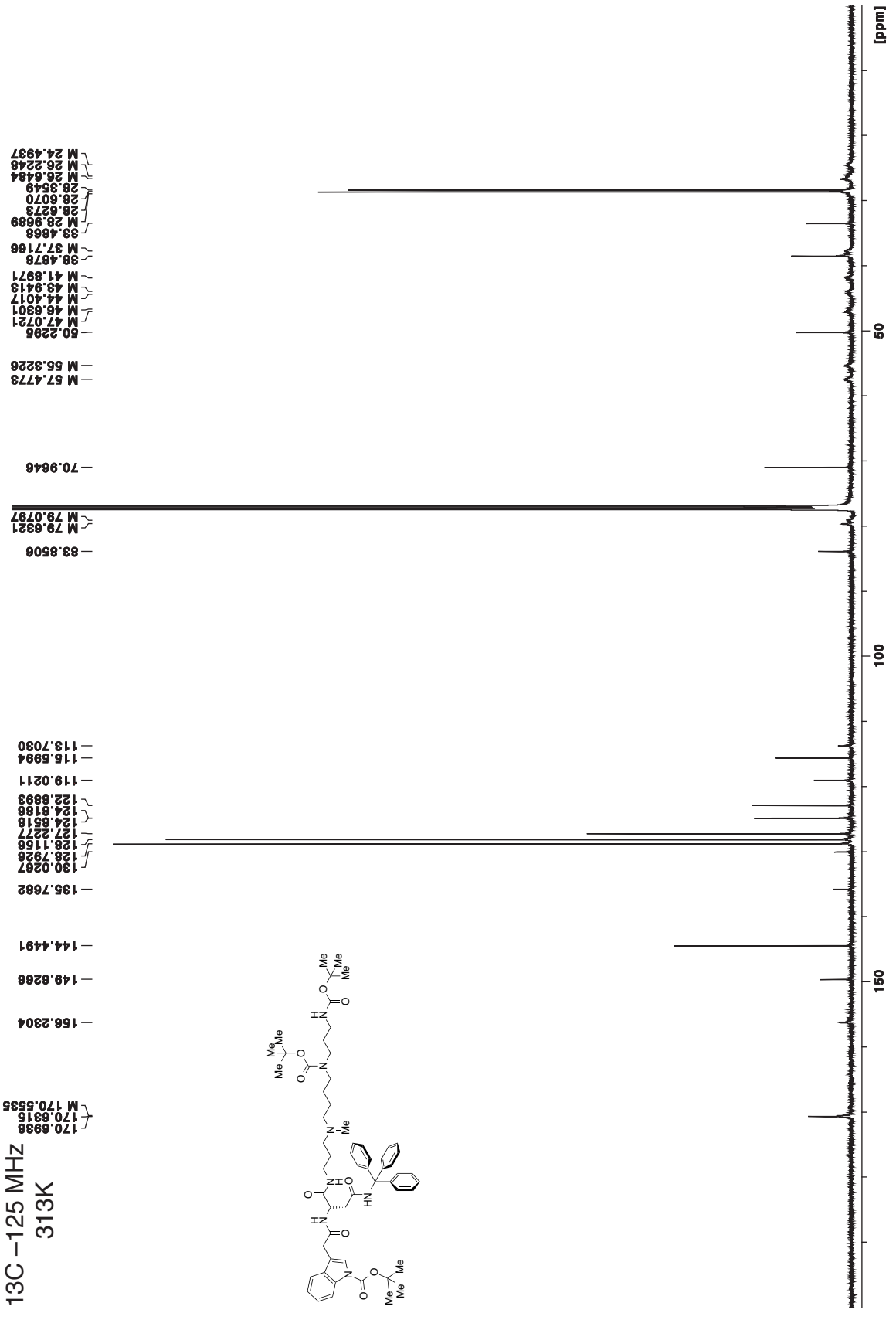


Compound 41

¹H – 500 MHz
313K

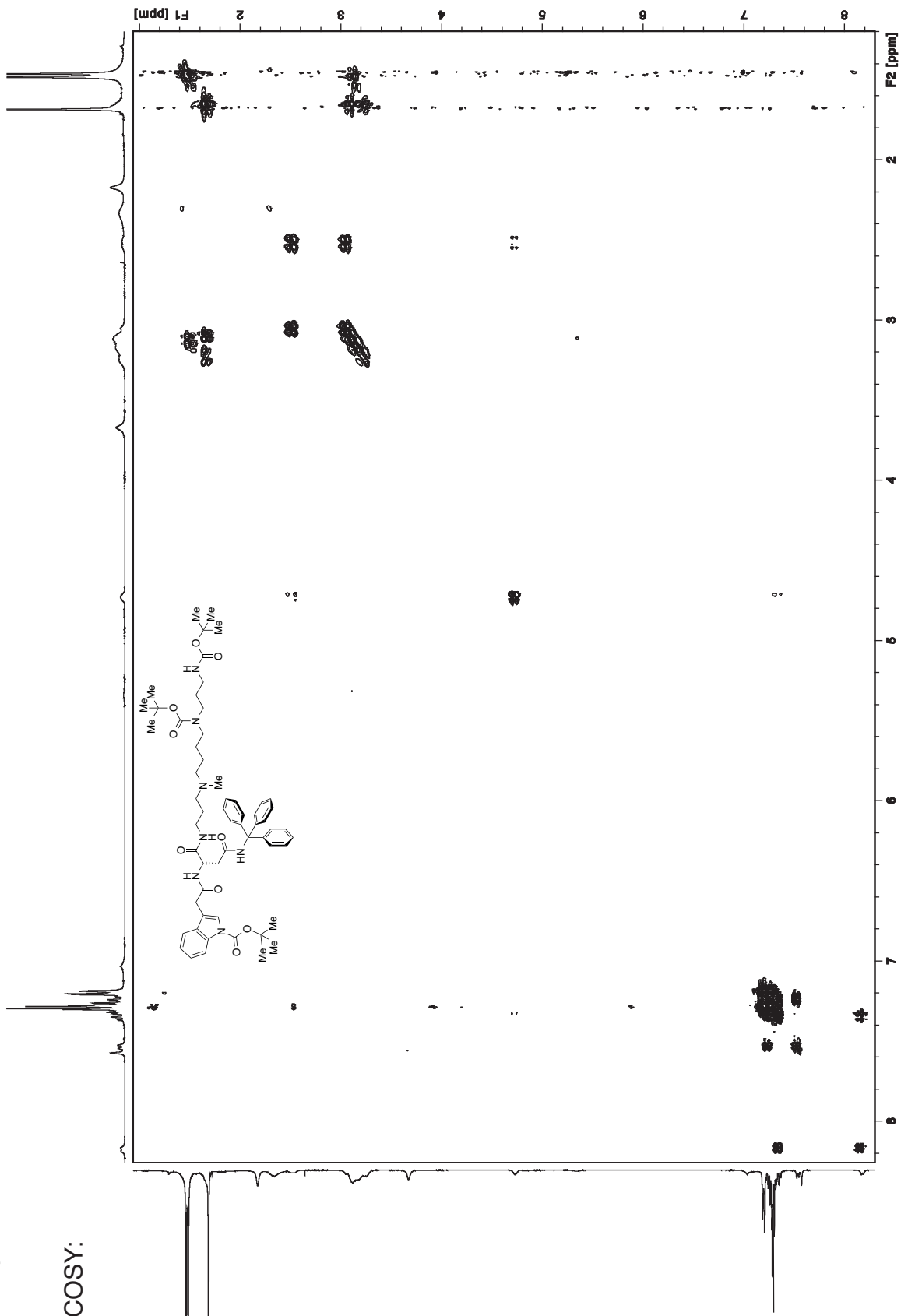


Compound 41
 13C -125 MHz
 313K



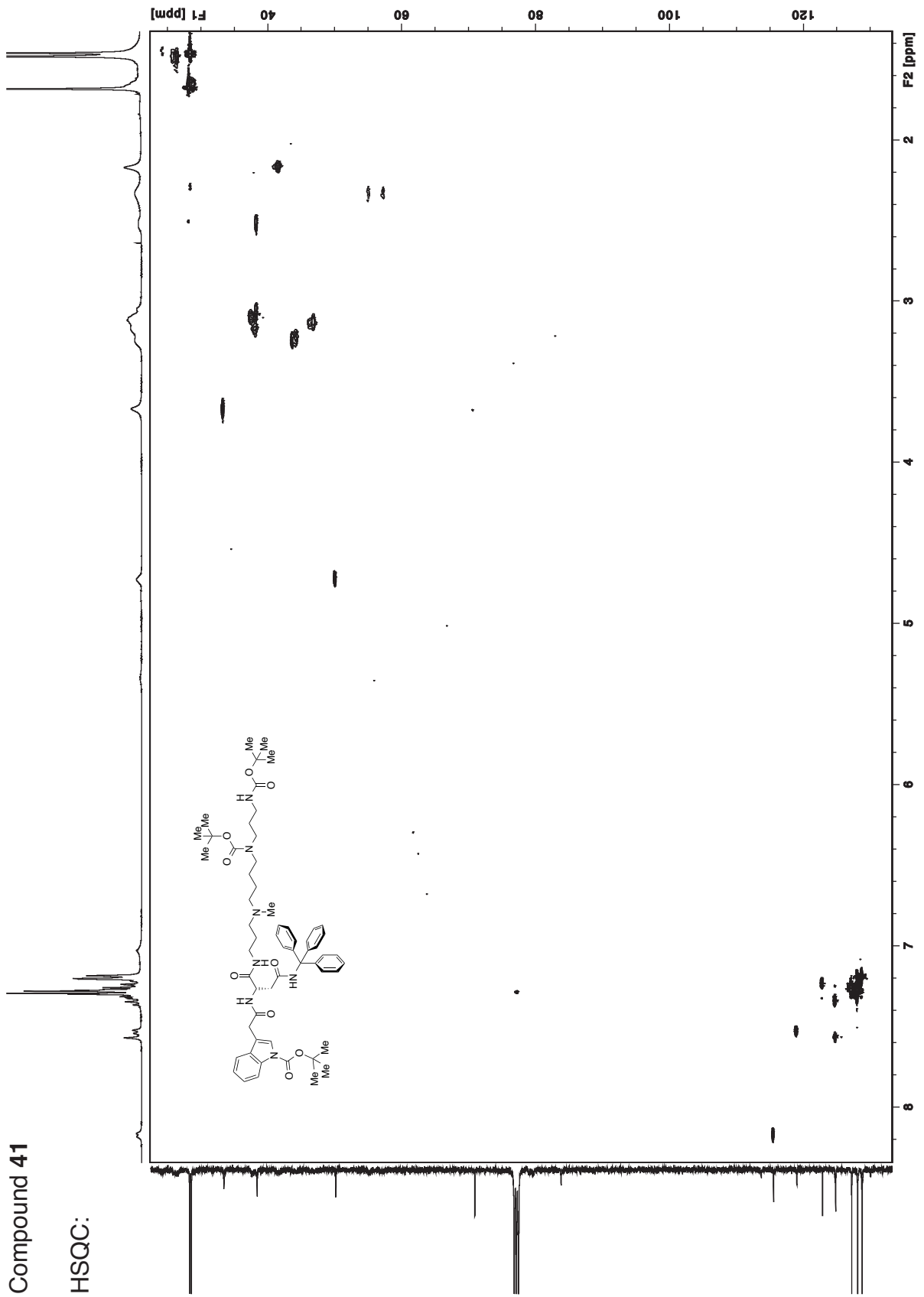
Compound 41

COSY:



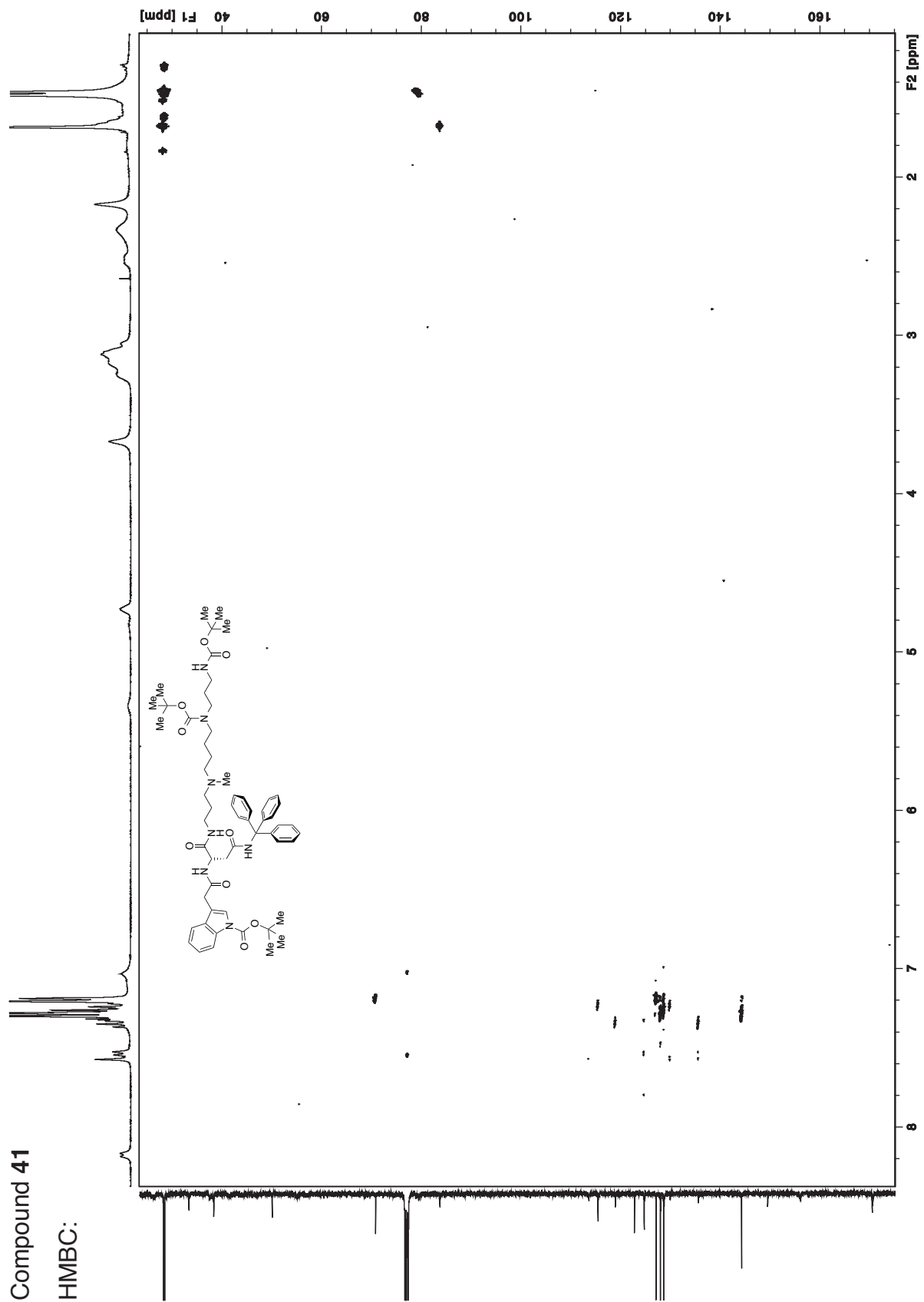
Compound 41

HSQC:

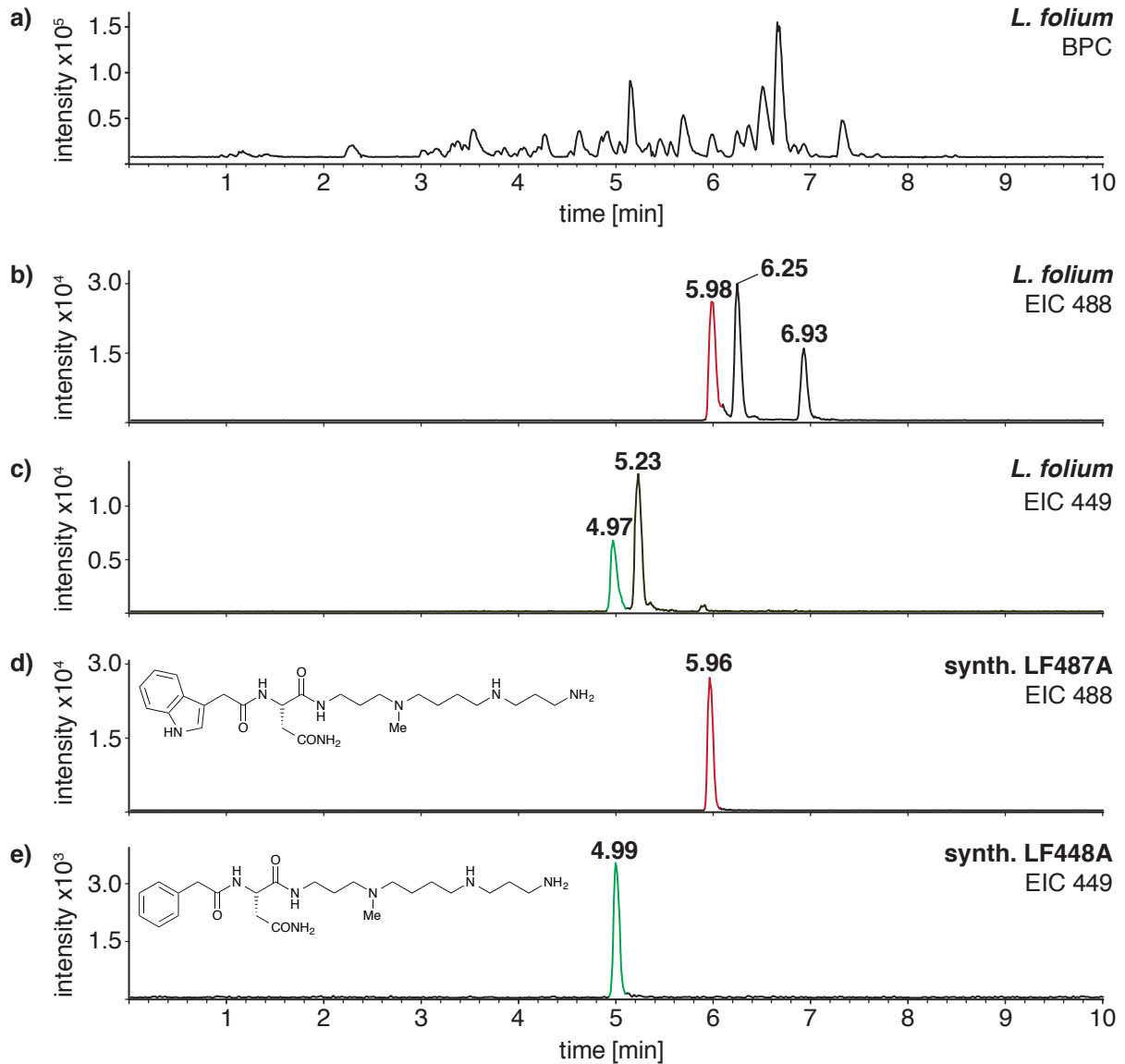


Compound 41

HMBC:



Comparison of the chromatographic behavior of the toxins of *L. folium* and the synthetic toxins **LF448A** and **LF487A**.



Comparison of the MS/MS of the natural toxins of *L. folium* and the synthetic samples.

