

## *Supporting Information*

### **Total Synthesis of Mangiferin, Homomangiferin, and Neomangiferin**

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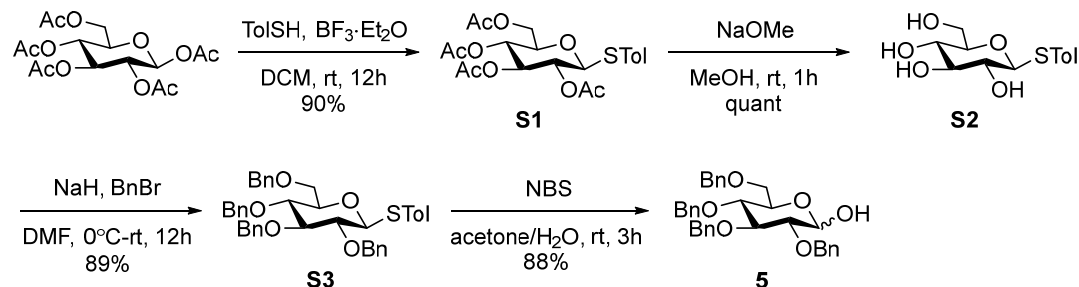
## 1. *General Information:*

Melting points were uncorrected. Nuclear magnetic resonance spectra (NMR spectra) were recorded using 400 MHz equipments (400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ). All spectra obtained in  $\text{CDCl}_3$  were referenced to tetramethylsilane at 0.00 *ppm* for  $^1\text{H}$  spectra and 77.16 *ppm* for  $^{13}\text{C}$  spectra. Spectra obtained in  $\text{DMSO-}d_6$  were referenced to DMSO at 2.50 *ppm* for  $^1\text{H}$  spectra and 39.52 *ppm* for  $^{13}\text{C}$  spectra. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet, br d: broad doublet. High resolution mass spectra (HRMS) data were performed with an ionization mode of ESI (electron spray ionization). Optical rotations were measured using sodium D line. Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F<sub>254</sub> precoated on aluminium plates, with detection by fluorescence and (or) by staining with 5% concentrated sulfuric acid in ethanol. Flash column chromatography was performed using Silica gel (230~400 mesh) with solvents distilled prior to use.

Unless otherwise noted, all the reagents were obtained from commercial suppliers and used without further purification. The following abbreviations are used: **PE**: petroleum ether (*b.p.* 60~90°); **EtOAc**: ethyl acetate; **DCM**: dichloromethane; **THF**: tetrahydrofuran; **DMSO**: dimethyl sulfoxide; **DMF**: *N,N*-dimethylformamide; **NBS**: N-bromosuccinimide; **DIPEA**: *N,N*-diisopropyl ethyl amine; **TMSOTf**: trimethylsilyl trifluoromethanesulfonate; **TBAB**: tetrabutyl ammonium bromide.

## 2. Experimental Section

### 2,3,4,6-Tetra-*O*-benzyl- $\alpha/\beta$ -D-glucopyranoside (**5**).



Building block **5** was obtained from commercial suppliers or prepared following the above synthetic route.

1) Glucose pentaacetate (10.0 g, 25.6 mmol) and *p*-thiocresol (4.8 g, 38.4 mmol) were dissolved in anhydrous DCM (200 mL) under atmosphere of nitrogen, and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (4.2 mL, 33.3 mmol) was added. After being stirred overnight at room temperature, the reaction mixture was diluted with DCM and washed with saturated  $\text{NaHCO}_3$  (aq), 1N HCl (aq) and brine. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , concentrated, and purified by flash column chromatography (PE-EtOAc, 1:1), affording **S1** (10.4 g, 90%) as a white solid.

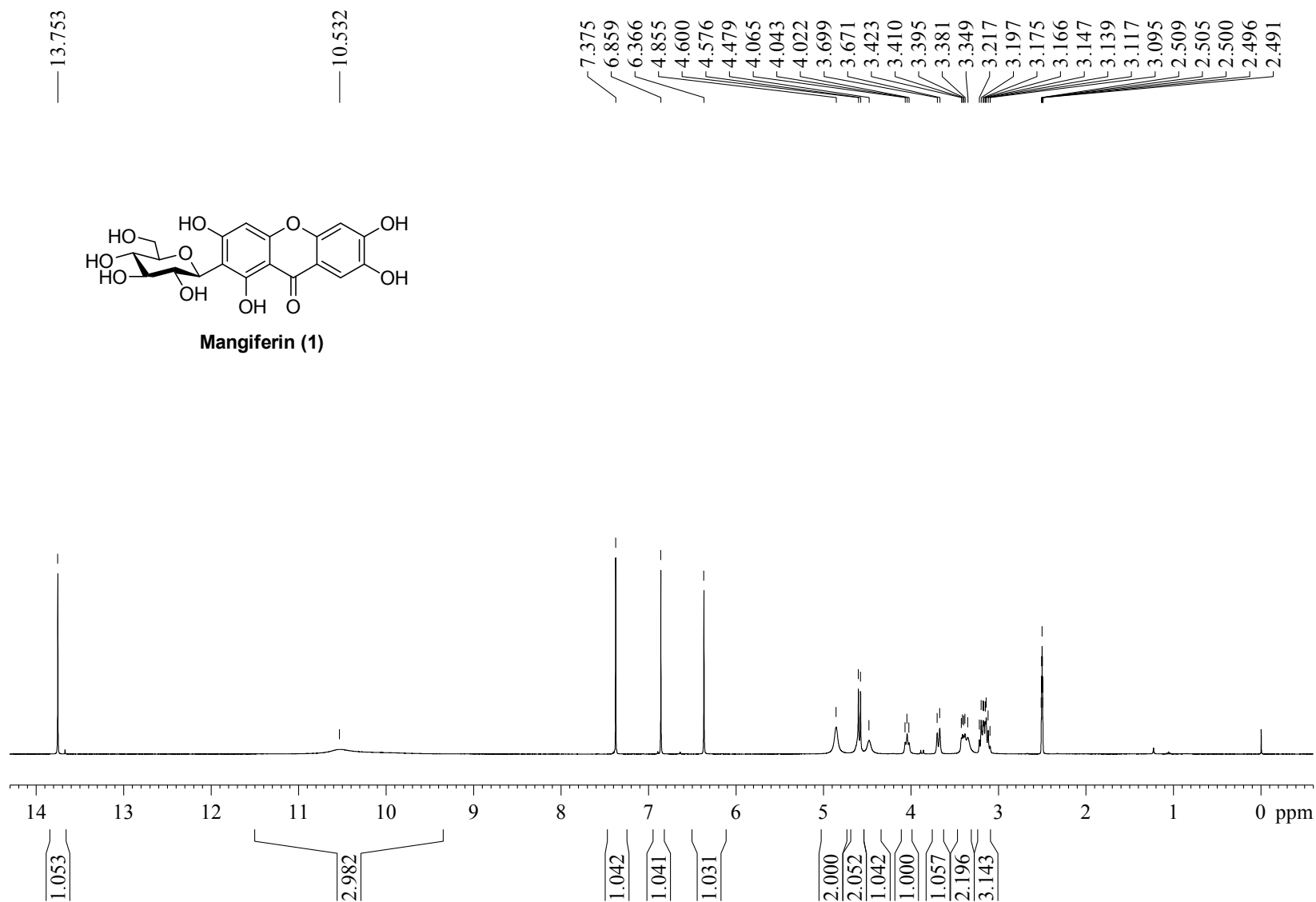
2) To a solution of thioglycoside **S1** (10.4 g, 22.8 mmol) in methanol (100 ml) was added appropriate amount of sodium at room temperature, adjusting pH to 11~12. After being stirred for 1 h, the reaction mixture was neutralized with DOWEX 50WX8-400 resin ( $\text{H}^+$  form), filtered, and evaporated in vacuo, affording **S2** (6.6 g, quant) as a white solid without purification.

3) The obtained **S2** was dissolved in DMF (200 mL) and cooled to 0 °C, and NaH (60%, 5.8 g) was added gradually in portions. When no gas generating, BnBr (16 mL, 136.6 mmol) was added dropwise with a funnel, and the suspension was then allowed to warm to room temperature. After being stirred overnight, appropriate amount of methanol was added to quench the reaction, and the solvent was

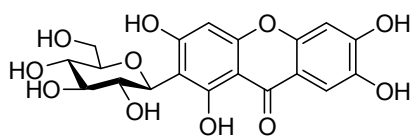
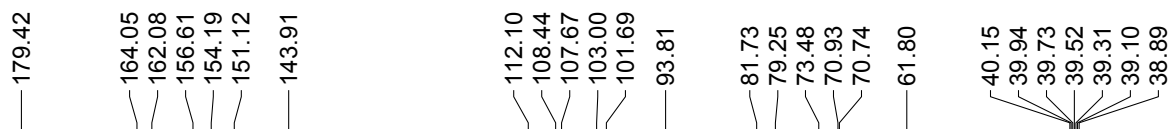
removed under reduced pressure. The residue was washed with brine and extracted with EtOAc. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by flash column chromatography (PE-EtOAc, 15:1) to afford **S3** (13.2 g, 89%) as a yellow syrup: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 6.95 (m, 24H), 5.02 – 4.67 (m, 5H), 4.67 – 4.48 (m, 4H), 3.85 – 3.57 (m, 4H), 3.49 (m, 2H), 2.29 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.5, 138.4, 138.2, 138.1, 137.8, 132.8, 129.9, 129.8, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 87.7, 86.9, 80.9, 79.2, 77.9, 75.9, 75.5, 75.1, 73.5, 69.1, 21.2 ppm.

4) To a solution of benzylated thioglycoside **S3** (1.0 g, 1.55 mmol) in acetone/H<sub>2</sub>O (16 mL, 9:1 v/v) was added NBS (0.83 g, 4.66 mmol) under exclusion of light. After being stirred for 3 h at rt, the reaction mixture was neutralized with appropriate amount of Et<sub>3</sub>N and evaporated under reduced pressure. The residue was washed with brine and extracted with DCM, and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by flash column chromatography (PE-acetone, 5:1) to afford **5** (738 mg, 88%) as a white solid: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.08 (m, 20H), 5.22 (t, *J* = 3.0 Hz, 0.8H), 4.98 – 4.43 (m, 8.2H), 4.07 – 3.49 (m, 6H), 3.44 – 3.34 (m, 0.2H), 3.10 (d, *J* = 2.4 Hz, 0.8H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.8/138.7, 138.5/138.4, 138.1/138.0, 137.9, 130.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 97.6/91.4, 84.7/83.3, 81.9/80.1, 78.0/77.9, 75.8, 75.1/74.8, 73.6, 73.3, 70.4, 69.1/68.8 ppm.

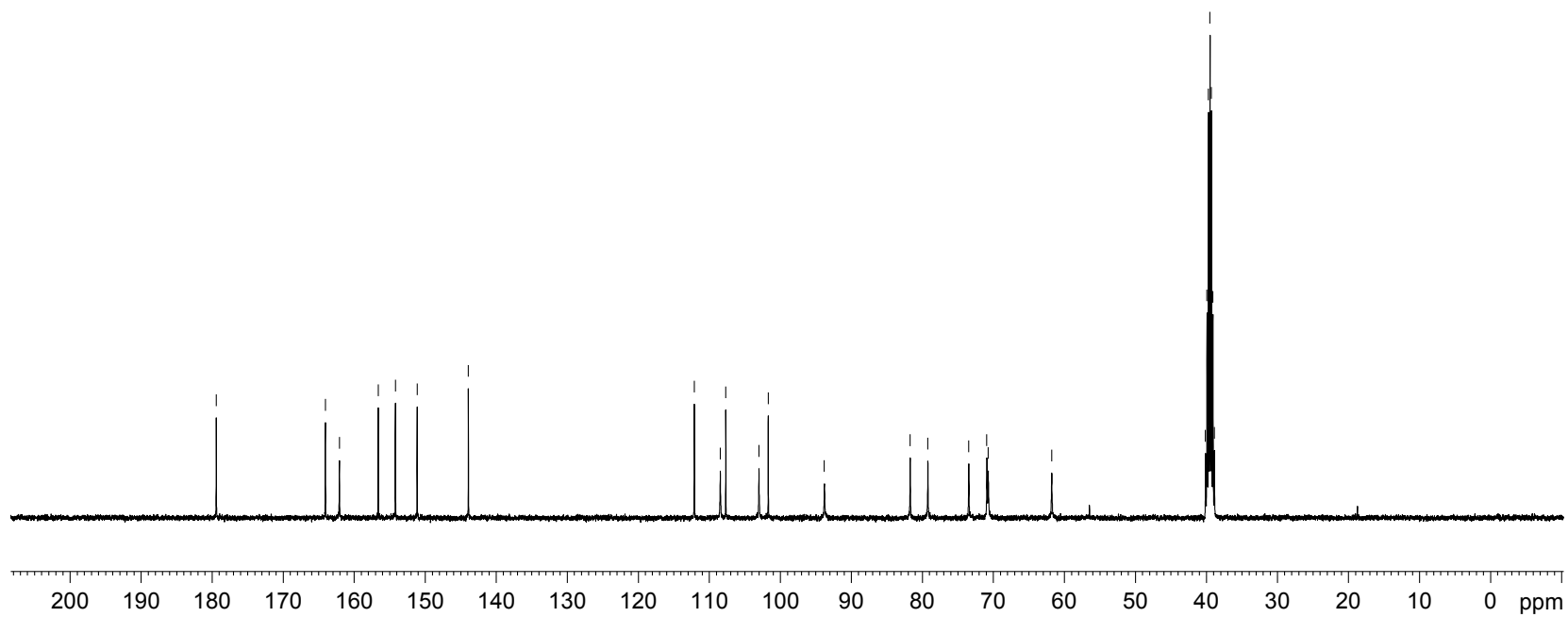
**<sup>1</sup>H NMR spectrum of Synthetic Mangiferin 1 (DMSO-d<sub>6</sub>, 400 MHz)**



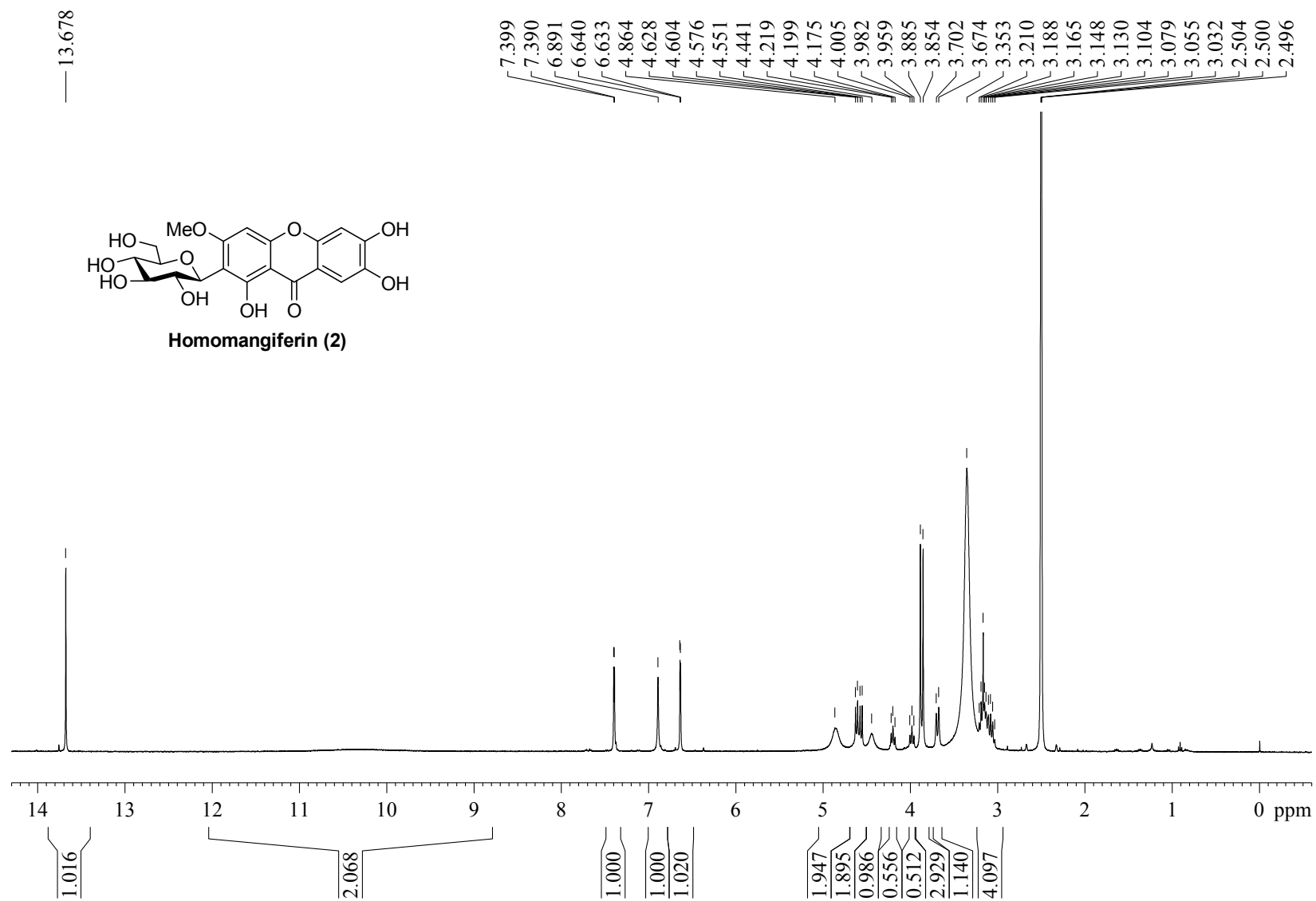
**<sup>13</sup>C NMR spectrum of Synthetic Mangiferin 1 (DMSO-*d*<sub>6</sub>, 100 MHz)**



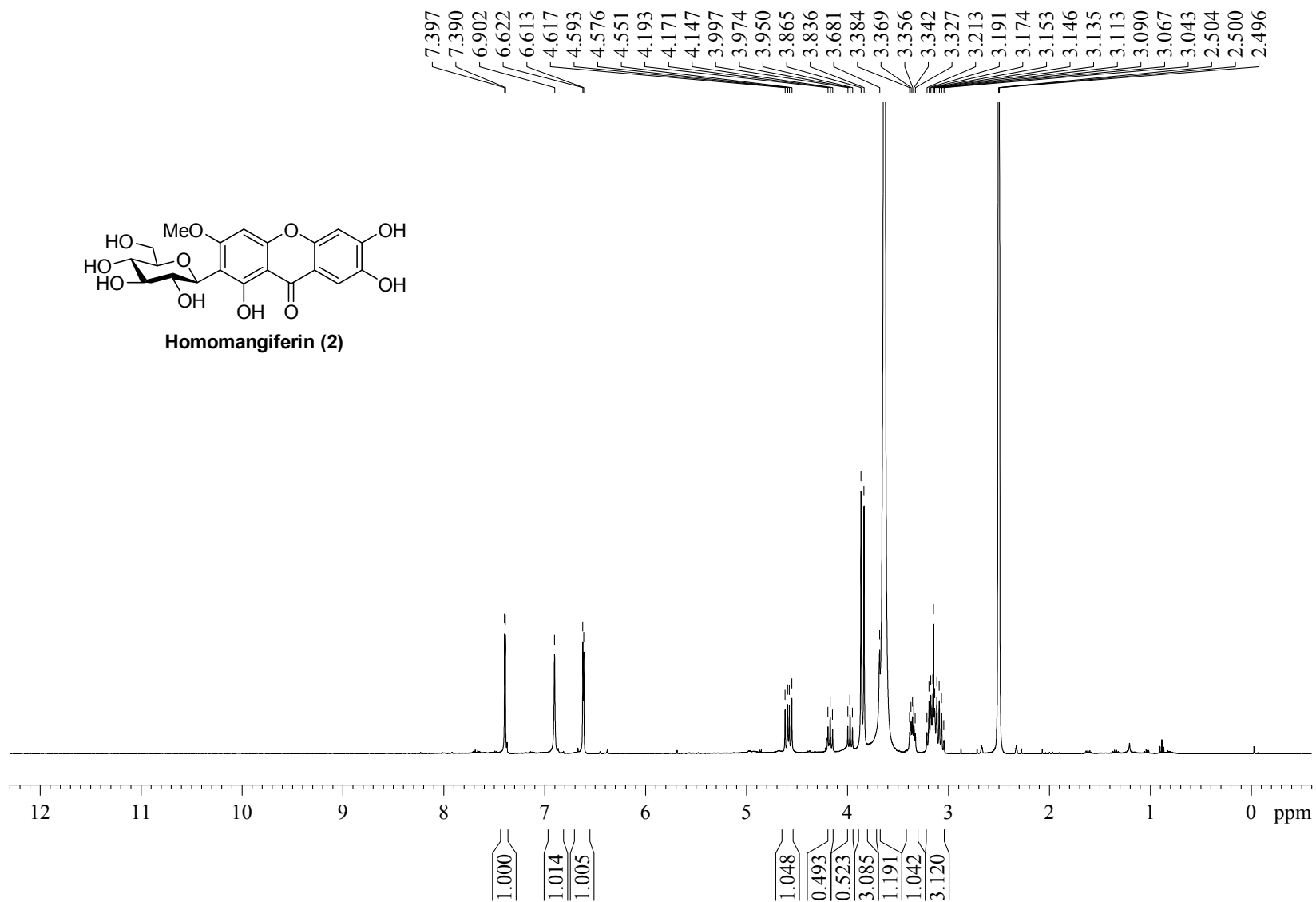
**Mangiferin (1)**



<sup>1</sup>H NMR spectrum of Synthetic Homomangiferin 2 (DMSO-d<sub>6</sub>, 400 MHz)



**<sup>1</sup>H NMR spectrum of Synthetic Homomangiferin 2 (DMSO-*d*<sub>6</sub>+D<sub>2</sub>O, 400 MHz)**

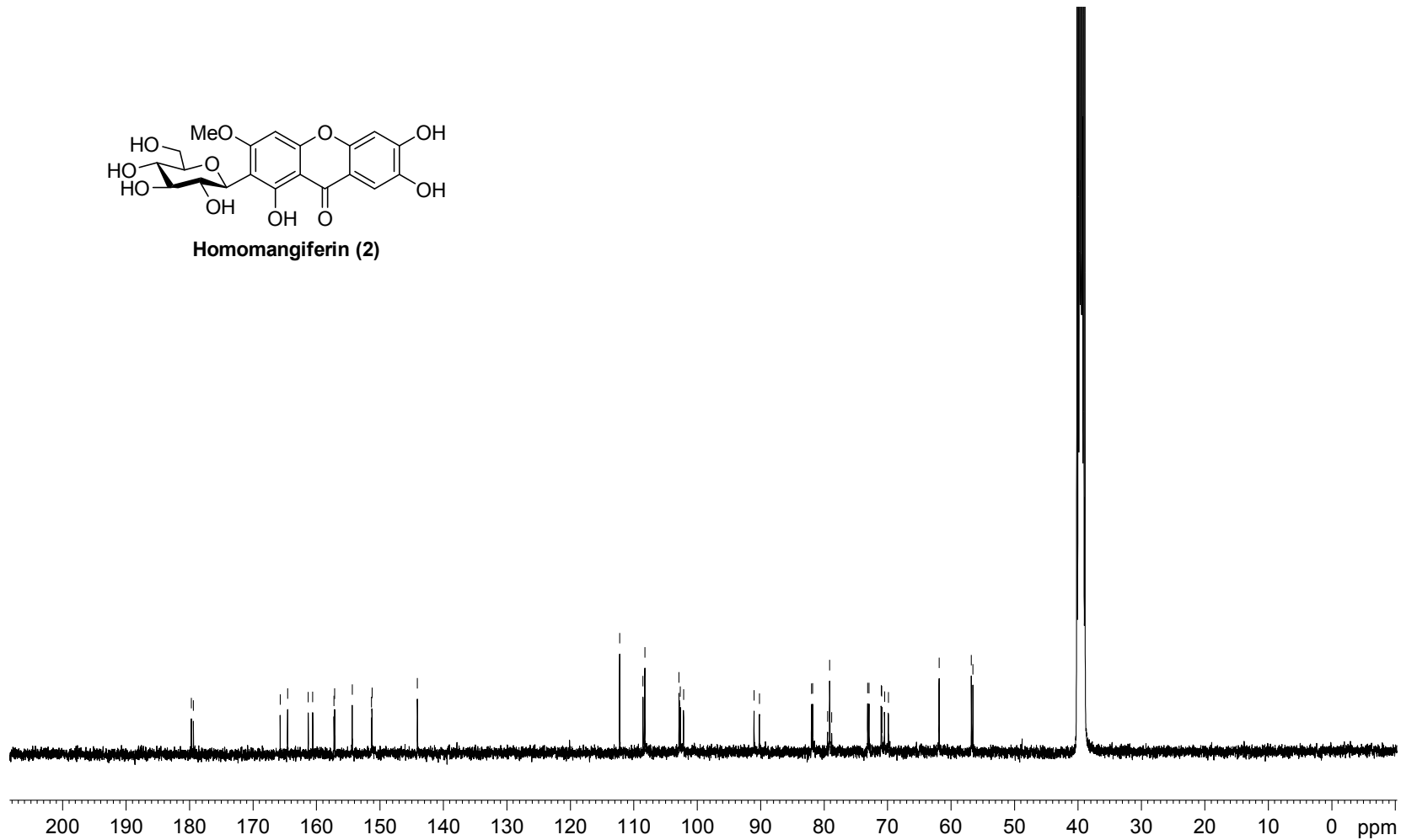
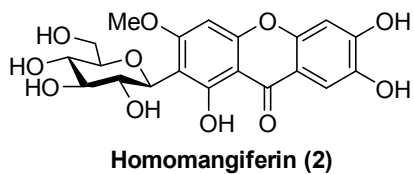




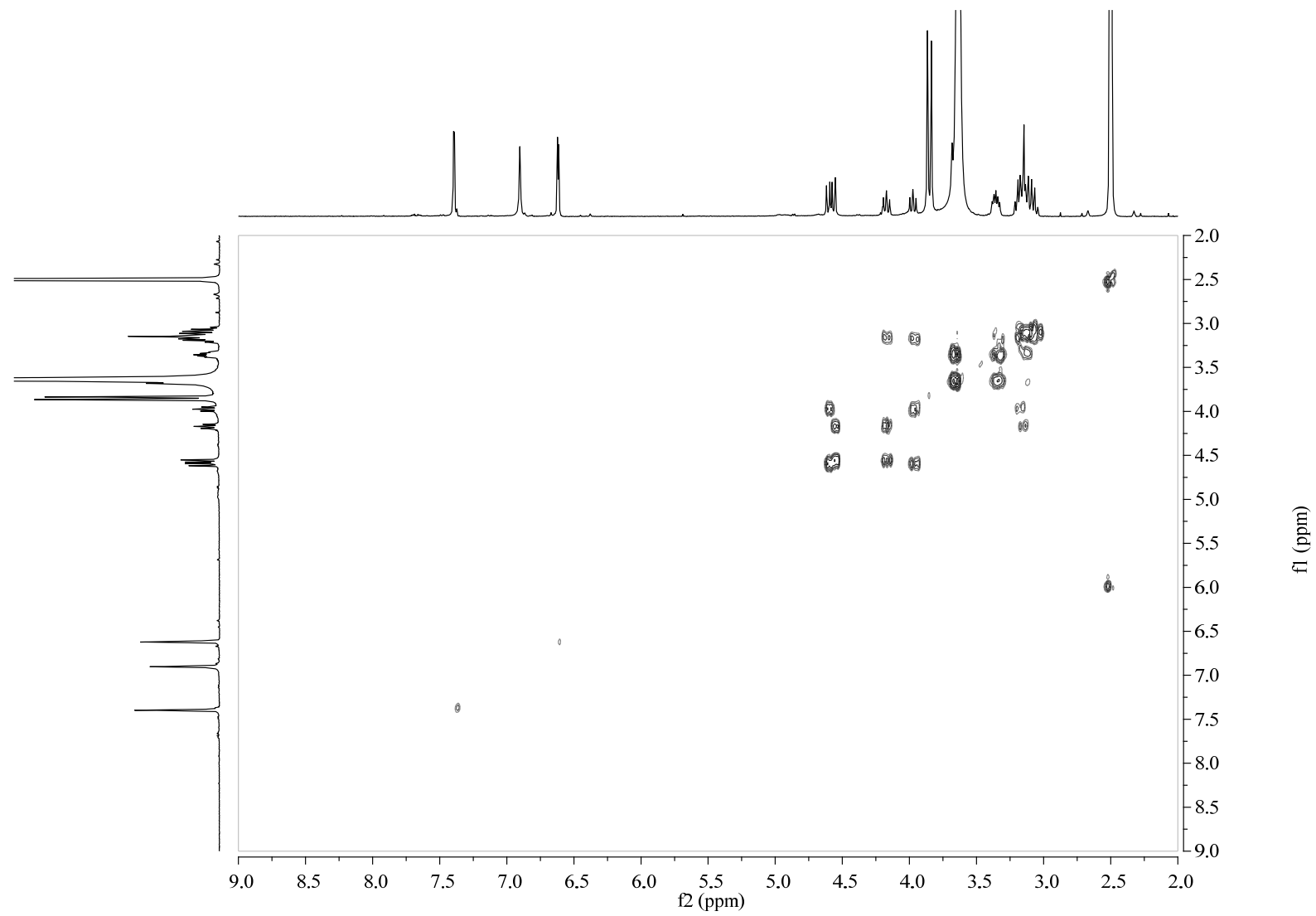
**<sup>13</sup>C NMR spectrum of Synthetic Homomangiferin 2 (DMSO-*d*<sub>6</sub>+D<sub>2</sub>O, 100 MHz)**

179.71  
179.39  
165.71  
164.54  
161.30  
160.59  
157.22  
157.12  
154.36  
151.31  
151.24  
144.08

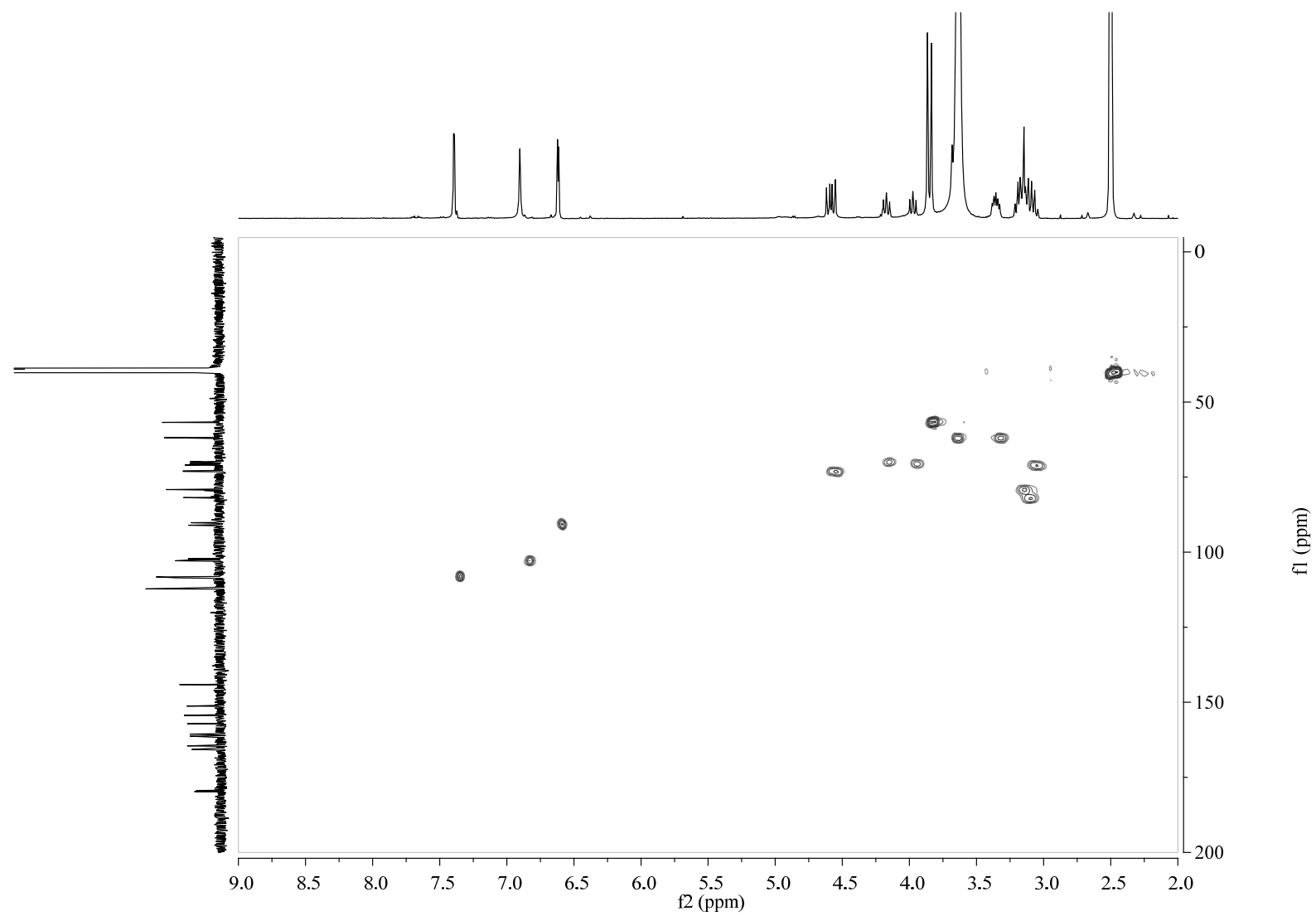
112.22  
108.55  
108.25  
102.86  
102.64  
102.15  
91.03  
90.21  
81.97  
81.82  
79.46  
79.13  
78.80  
73.13  
72.92  
71.00  
70.92  
70.47  
69.88  
61.87  
56.79  
56.54  
40.15  
39.94  
39.73  
39.52  
39.31  
39.10  
38.89



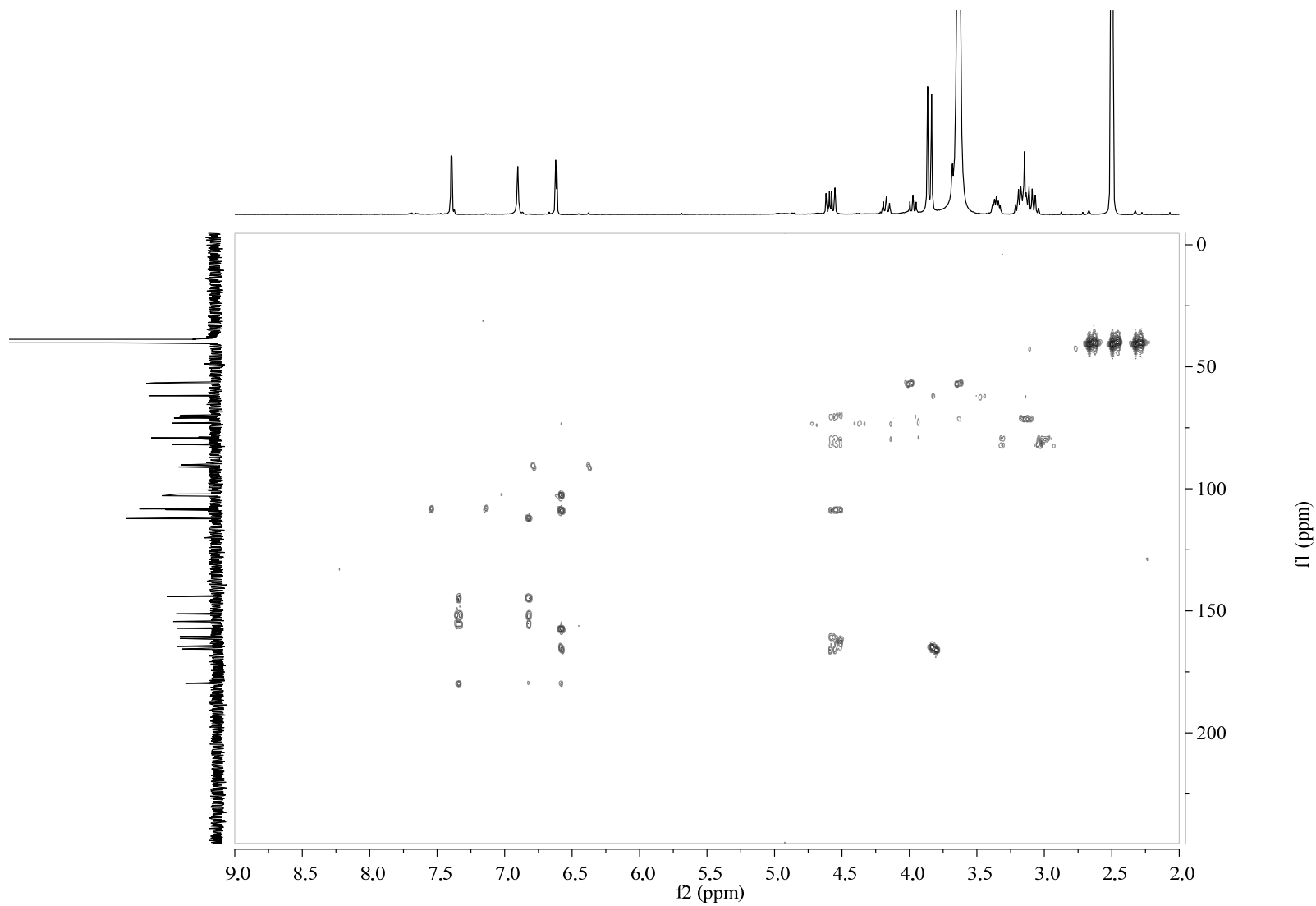
**$^1\text{H}$ - $^1\text{H}$  COSY spectrum of Synthetic Homomangiferin 2 (DMSO- $d_6$ +D $_2$ O)**



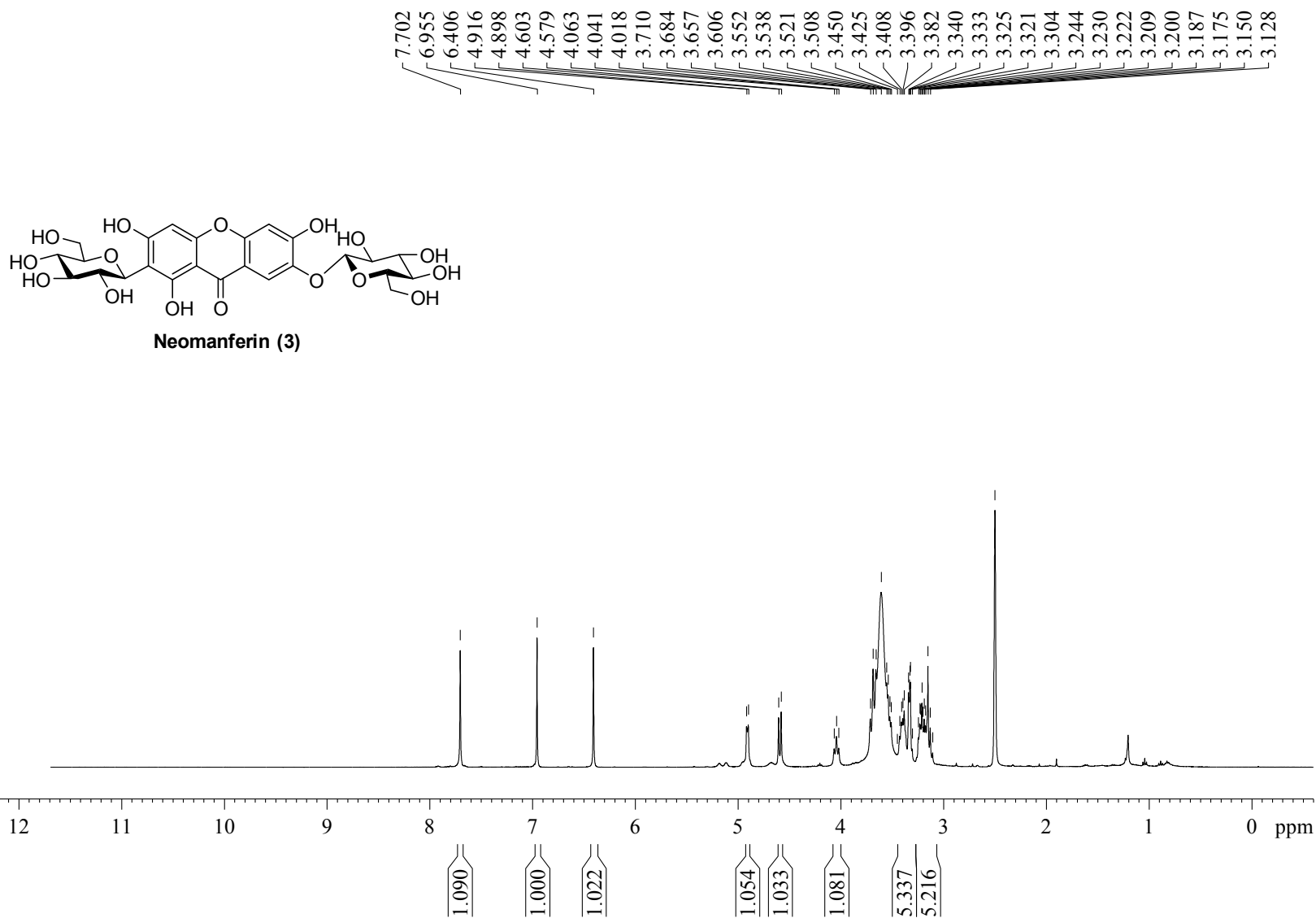
### HSQC spectrum of Synthetic Homomangiferin 2 (DMSO- $d_6$ +D $_2$ O)



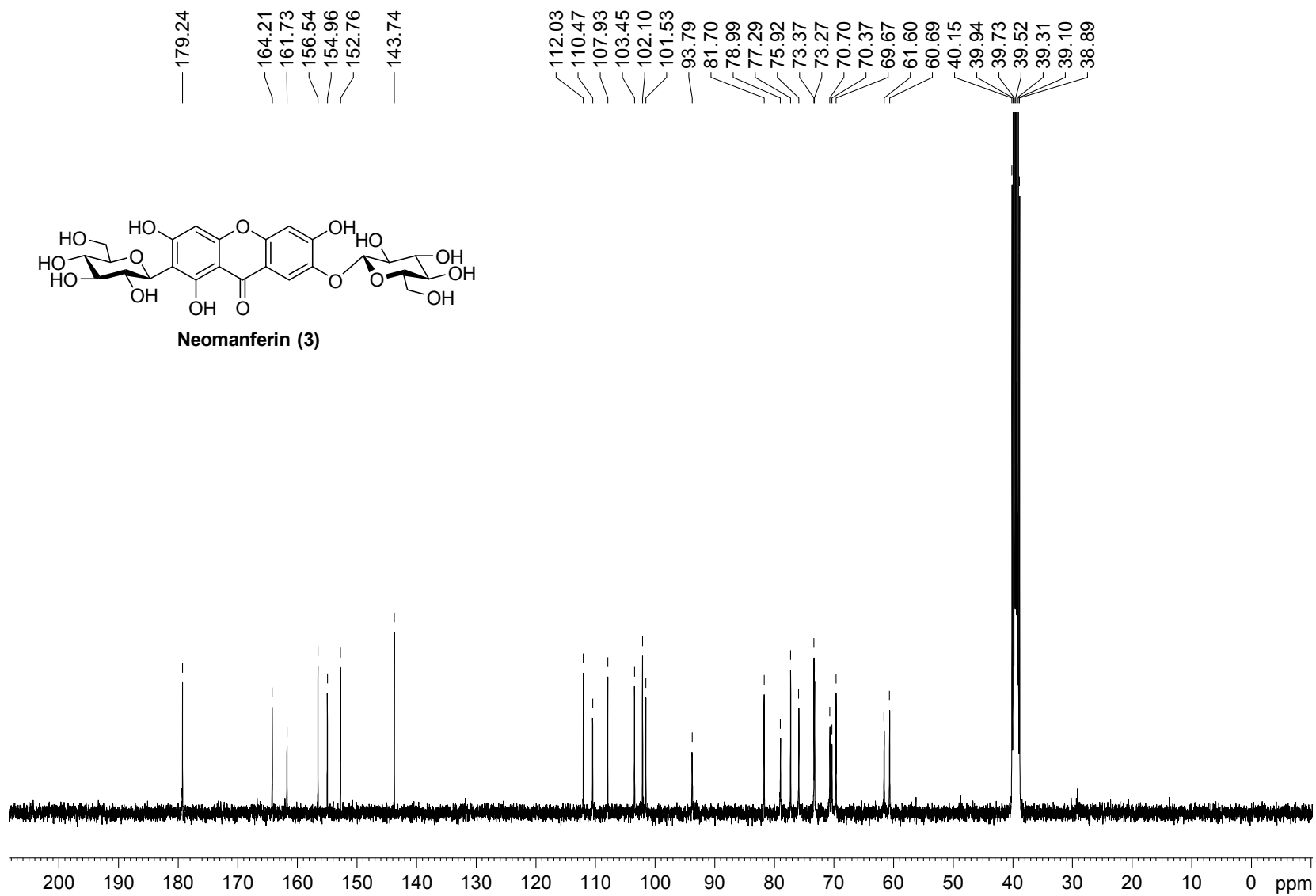
HMBC spectrum of Synthetic Homomangiferin 2 (DMSO- $d_6$ +D $_2$ O)



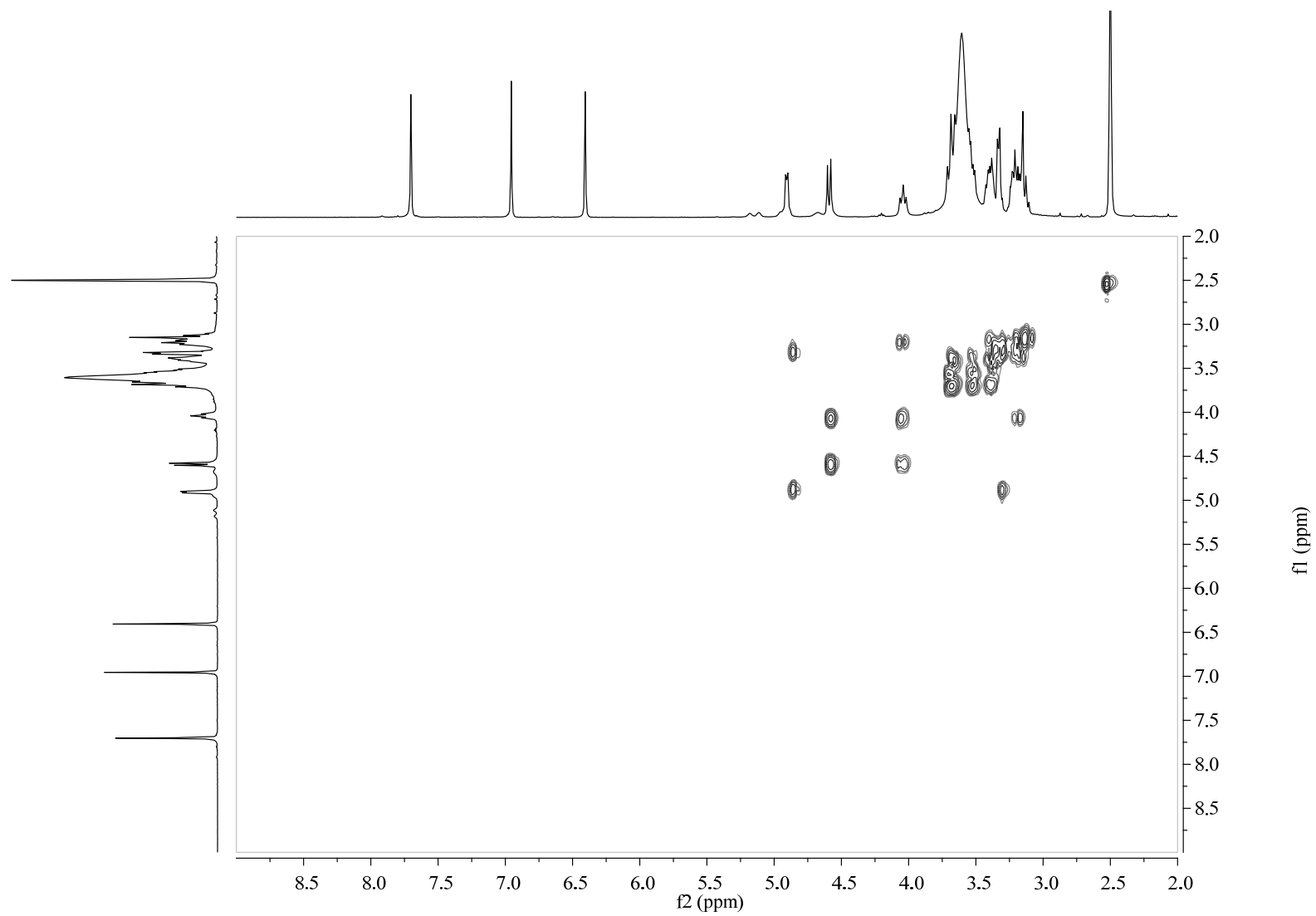
**<sup>1</sup>H NMR spectrum of Synthetic Neomangiferin 3 (DMSO-d<sub>6</sub>+D<sub>2</sub>O, 400 MHz)**



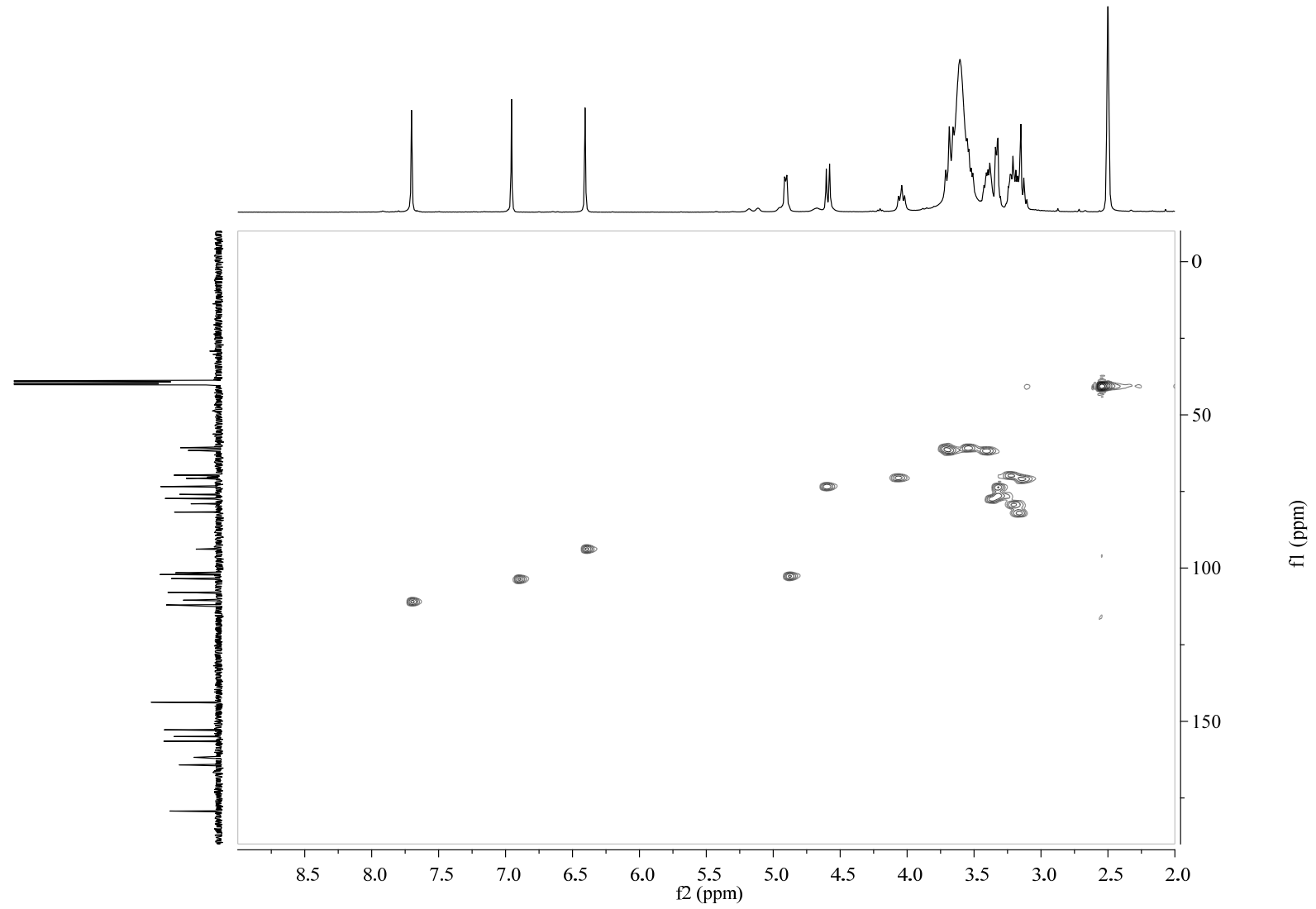
**<sup>13</sup>C NMR spectrum of Synthetic Neomangiferin 3 (DMSO-*d*<sub>6</sub>+D<sub>2</sub>O, 100 MHz)**



**$^1\text{H}$ - $^1\text{H}$  COSY spectrum of Synthetic Neomangiferin 3 (DMSO- $d_6$ +D $_2$ O)**

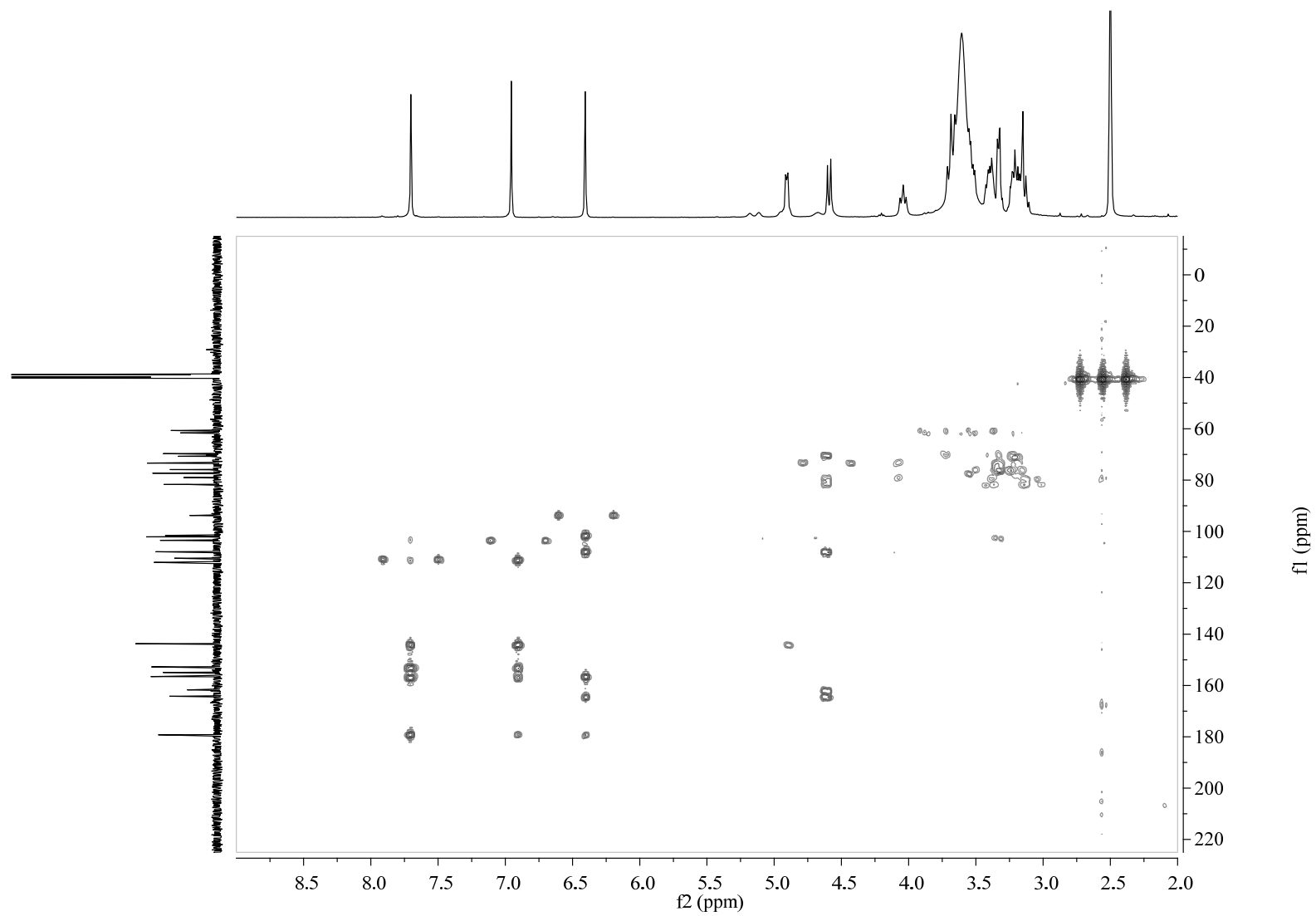


HSQC spectrum of Synthetic Neomangiferin 3 (DMSO- $d_6$ +D $_2$ O)



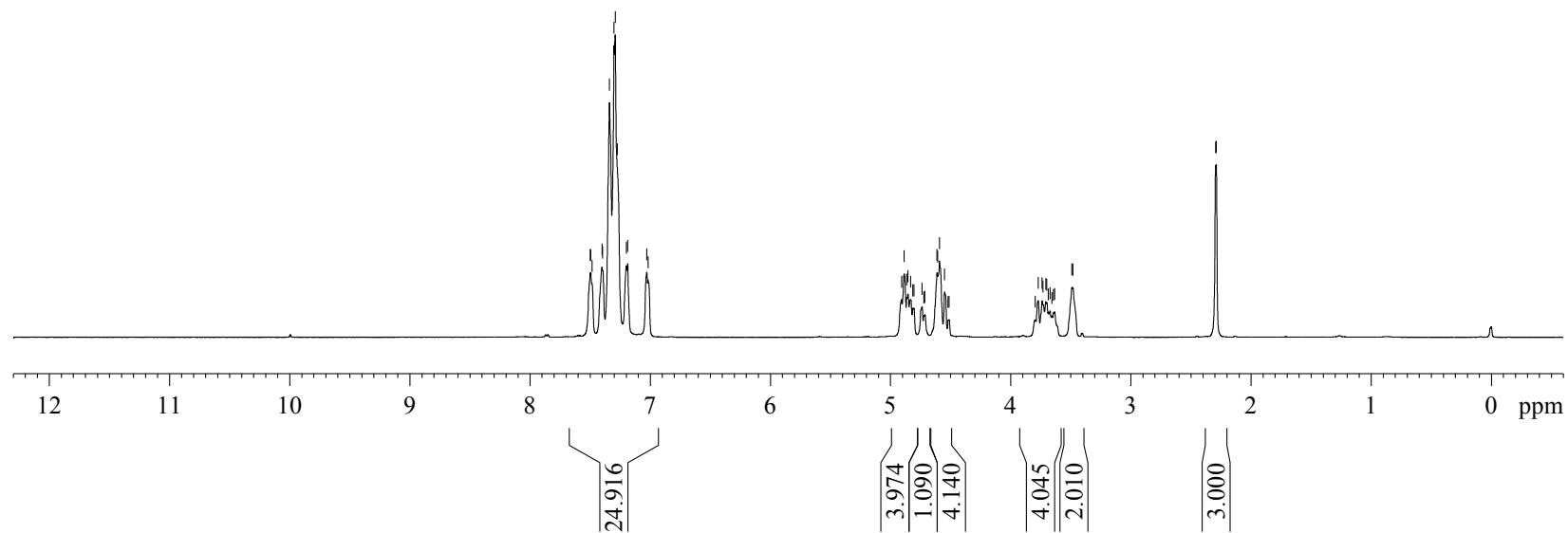
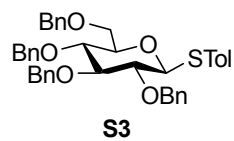


### HMBC spectrum of Synthetic Neomangiferin 3 (DMSO- $d_6$ +D $_2$ O)



**<sup>1</sup>H NMR spectrum of Compound S3 (CDCl<sub>3</sub>, 400 MHz)**

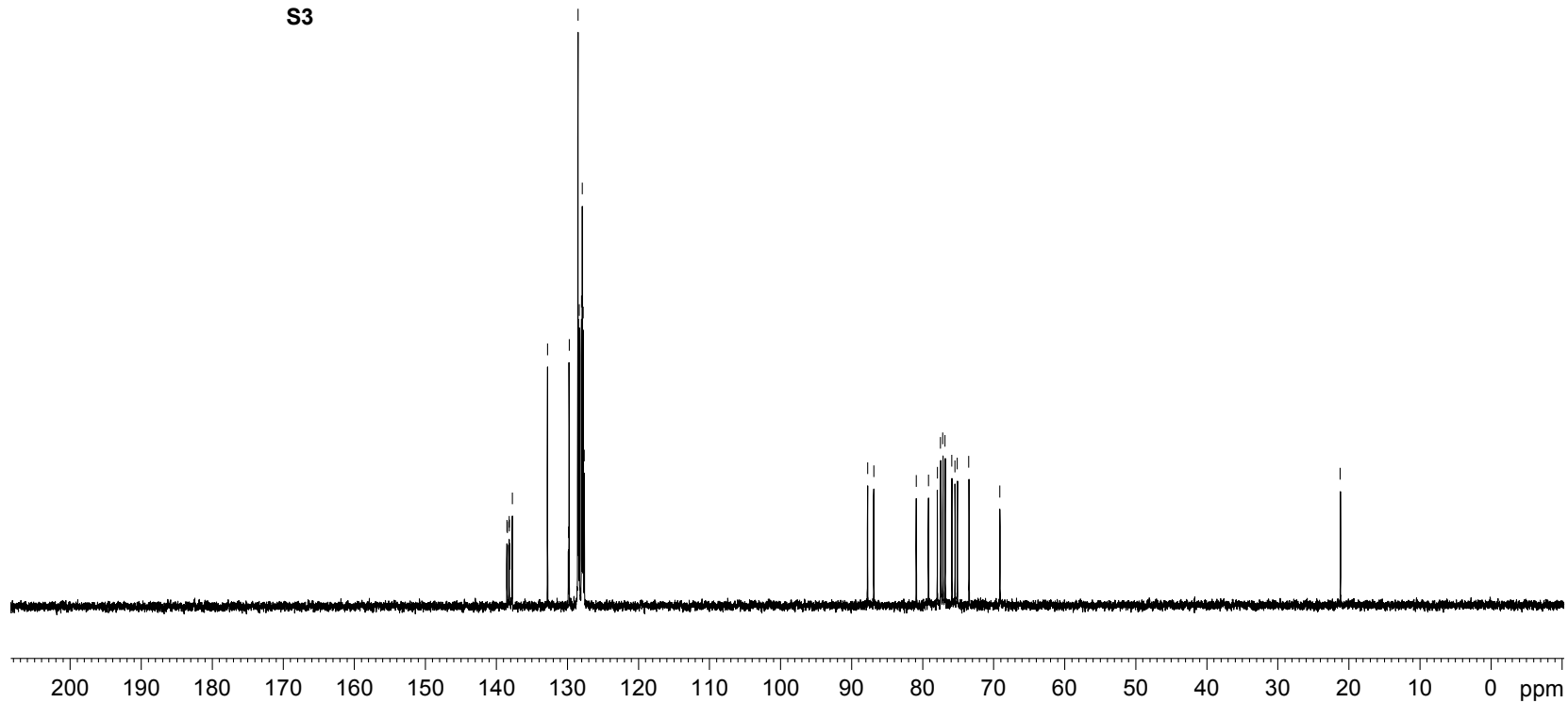
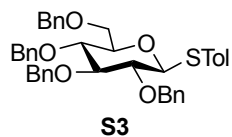
7.497  
7.492  
7.482  
7.400  
7.394  
7.338  
7.300  
7.290  
7.272  
7.197  
7.186  
7.027  
7.017  
4.908  
4.885  
4.864  
4.853  
4.830  
4.814  
4.805  
4.737  
4.722  
4.712  
4.612  
4.605  
4.592  
4.549  
4.520  
4.511  
3.795  
3.770  
3.737  
3.730  
3.708  
3.698  
3.686  
3.671  
3.655  
3.644  
3.633  
3.490  
3.481  
2.293  
2.288



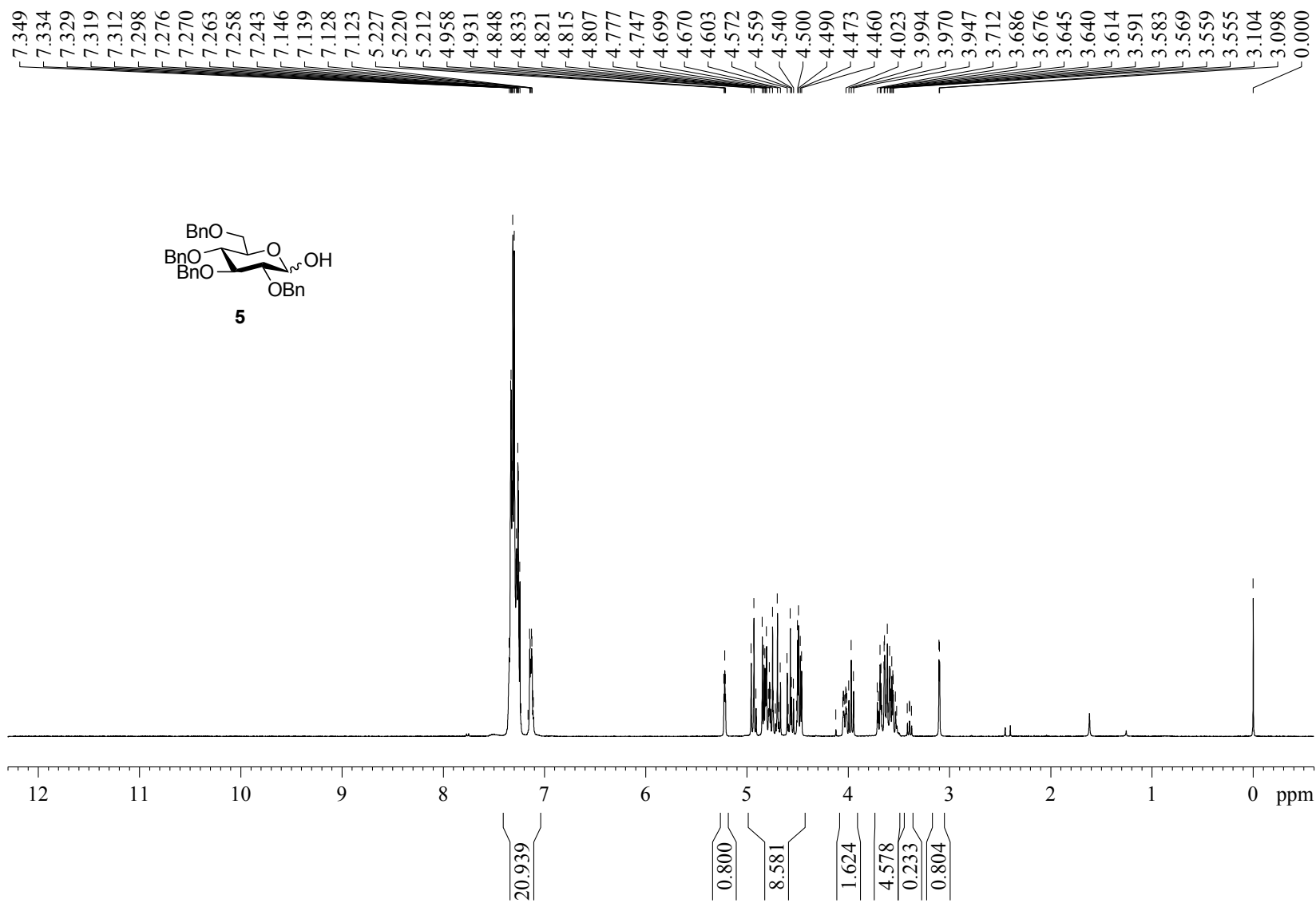
**<sup>13</sup>C NMR spectrum of Compound S3 (CDCl<sub>3</sub>, 100 MHz)**

138.51  
138.45  
138.21  
138.16  
137.75  
132.79  
129.85  
129.75  
128.52  
128.43  
128.31  
128.03  
127.93  
127.90  
127.79  
127.75  
127.62  
87.74  
86.86  
80.89  
79.17  
77.92  
77.48  
77.16  
76.84  
75.91  
75.46  
75.13  
73.50  
69.14

— 21.21

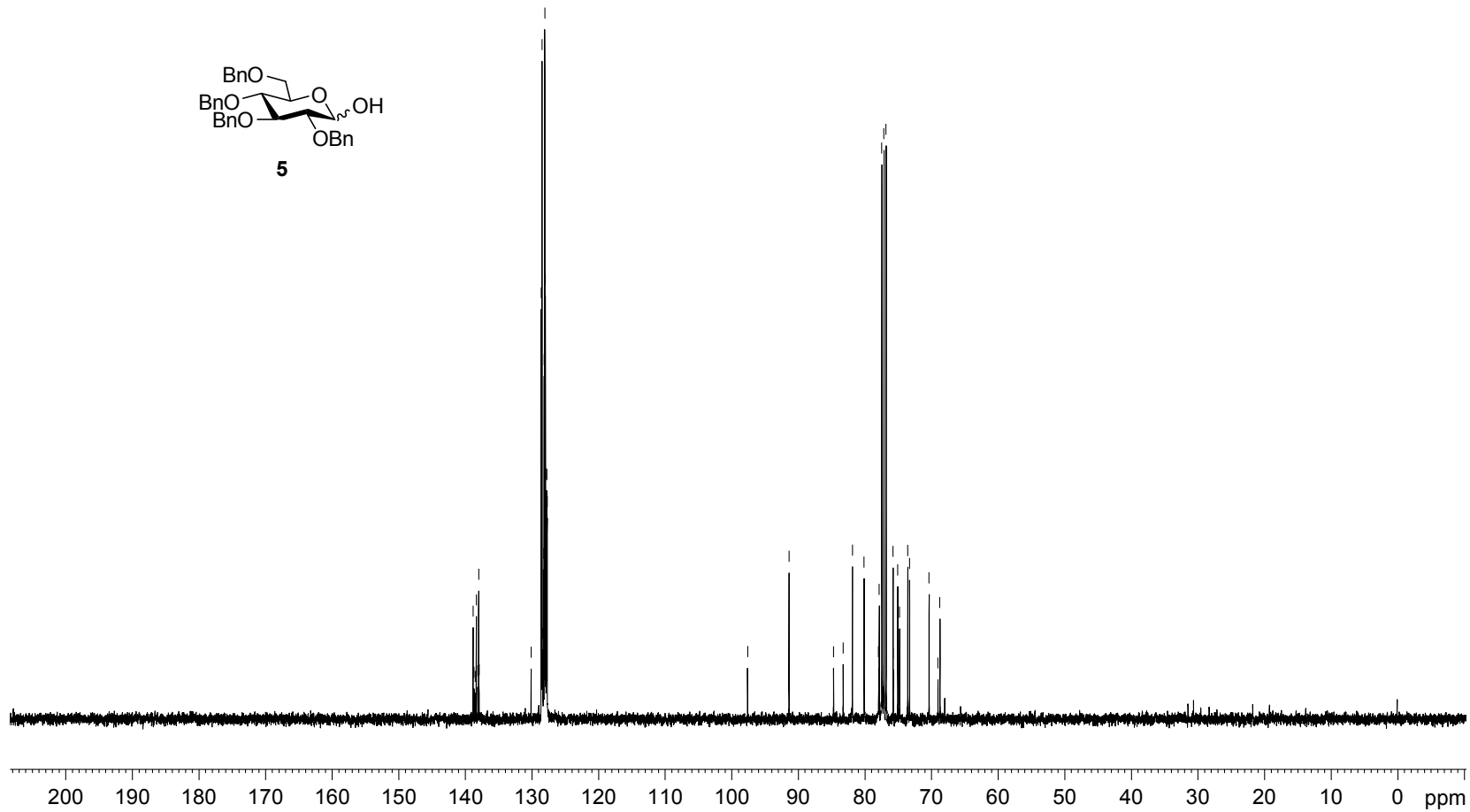
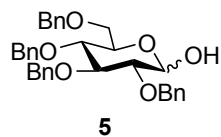


**<sup>1</sup>H NMR spectrum of Compound 5 (CDCl<sub>3</sub>, 400 MHz)**

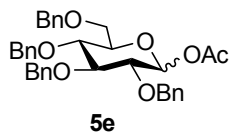
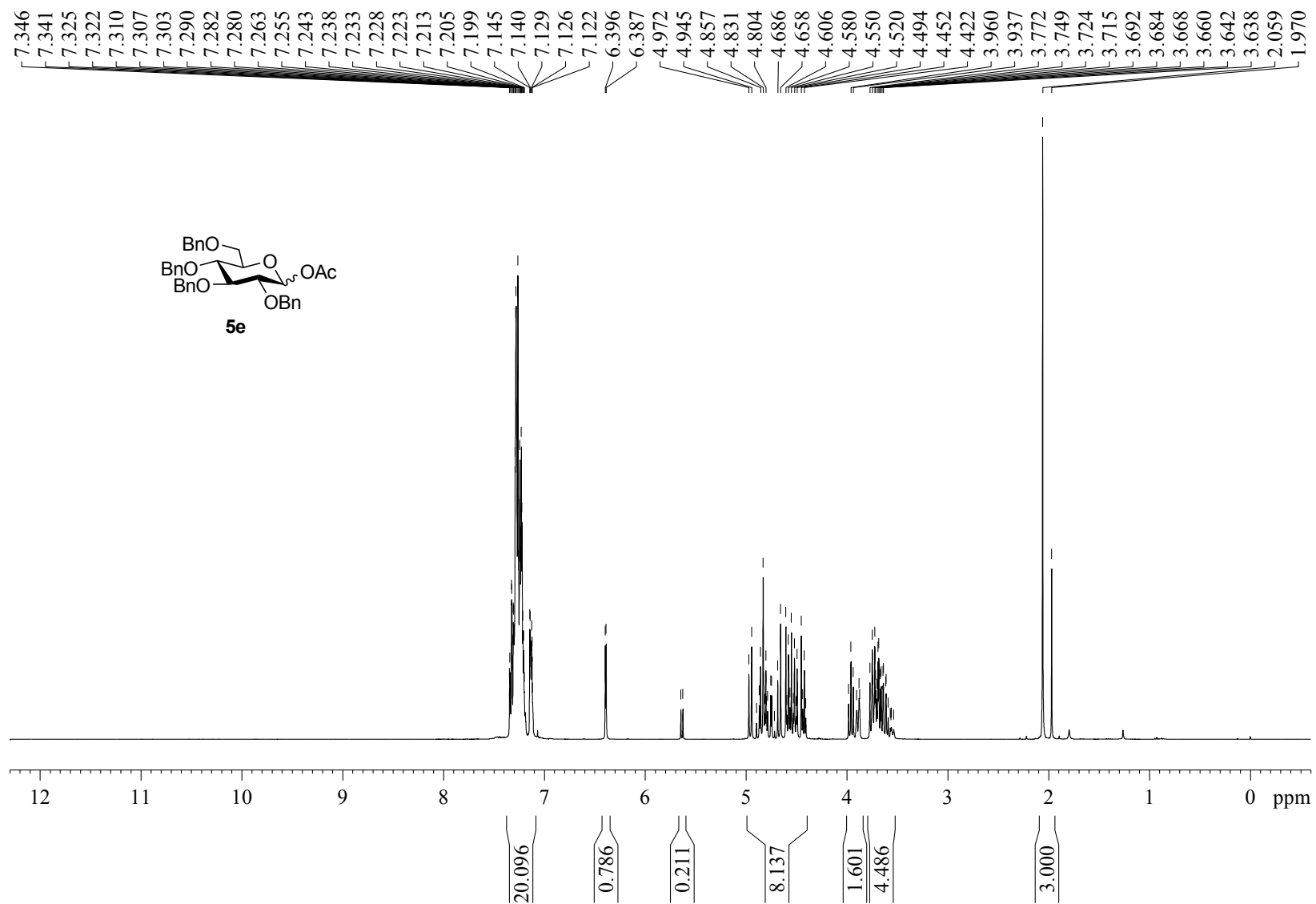


**<sup>13</sup>C NMR spectrum of Compound 5 (CDCl<sub>3</sub>, 100 MHz)**

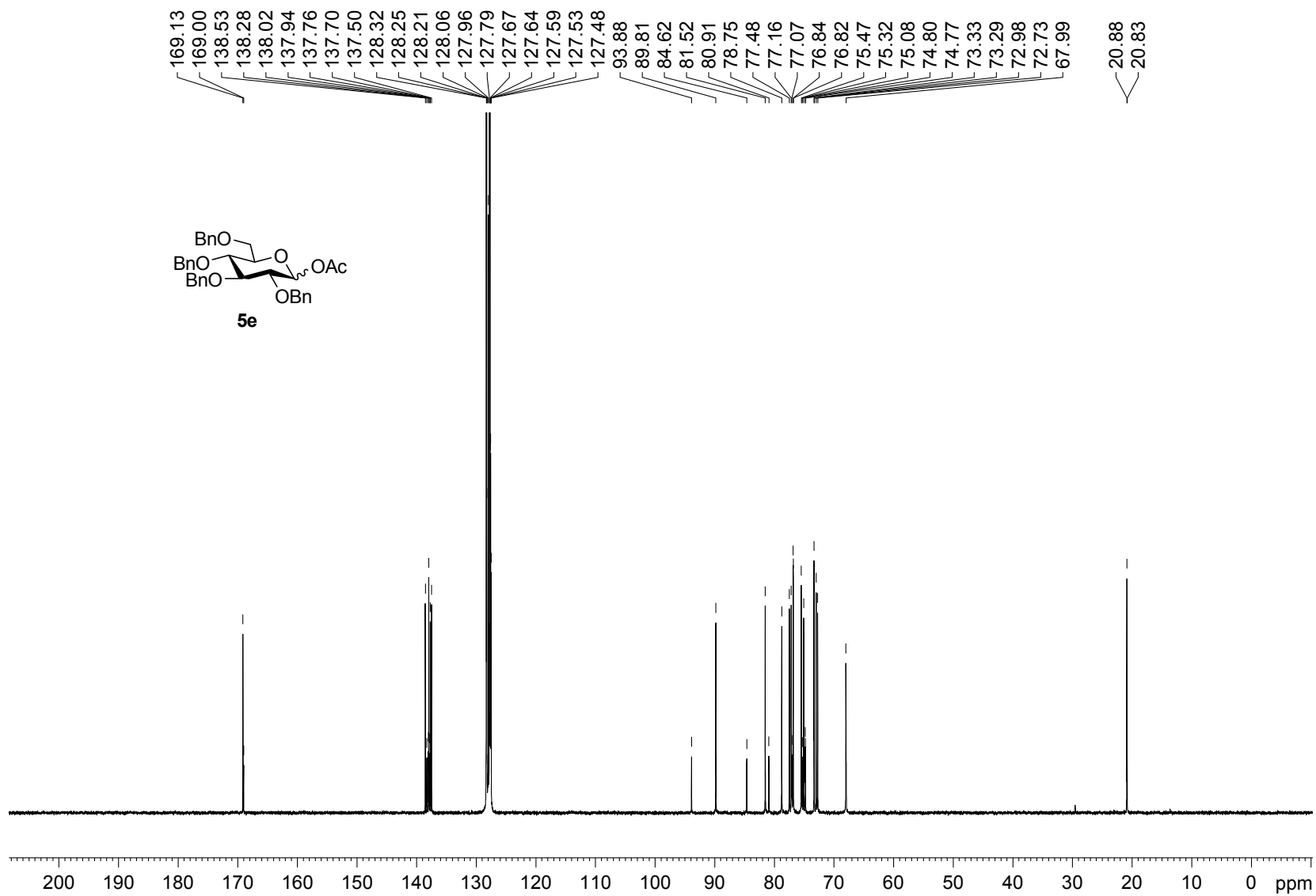
138.83  
138.67  
138.51  
138.35  
138.12  
138.00  
137.93  
130.13  
128.60  
128.48  
128.36  
128.24  
128.15  
128.06  
128.03  
127.96  
127.88  
127.83  
127.80  
127.78  
127.71  
97.62  
91.38  
84.71  
83.26  
81.87  
80.14  
77.97  
77.87  
77.48  
77.36  
77.16  
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74.82  
73.59  
73.32  
70.40  
69.06  
68.76



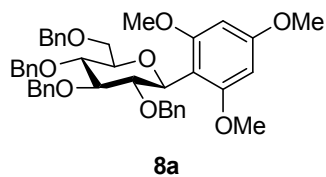
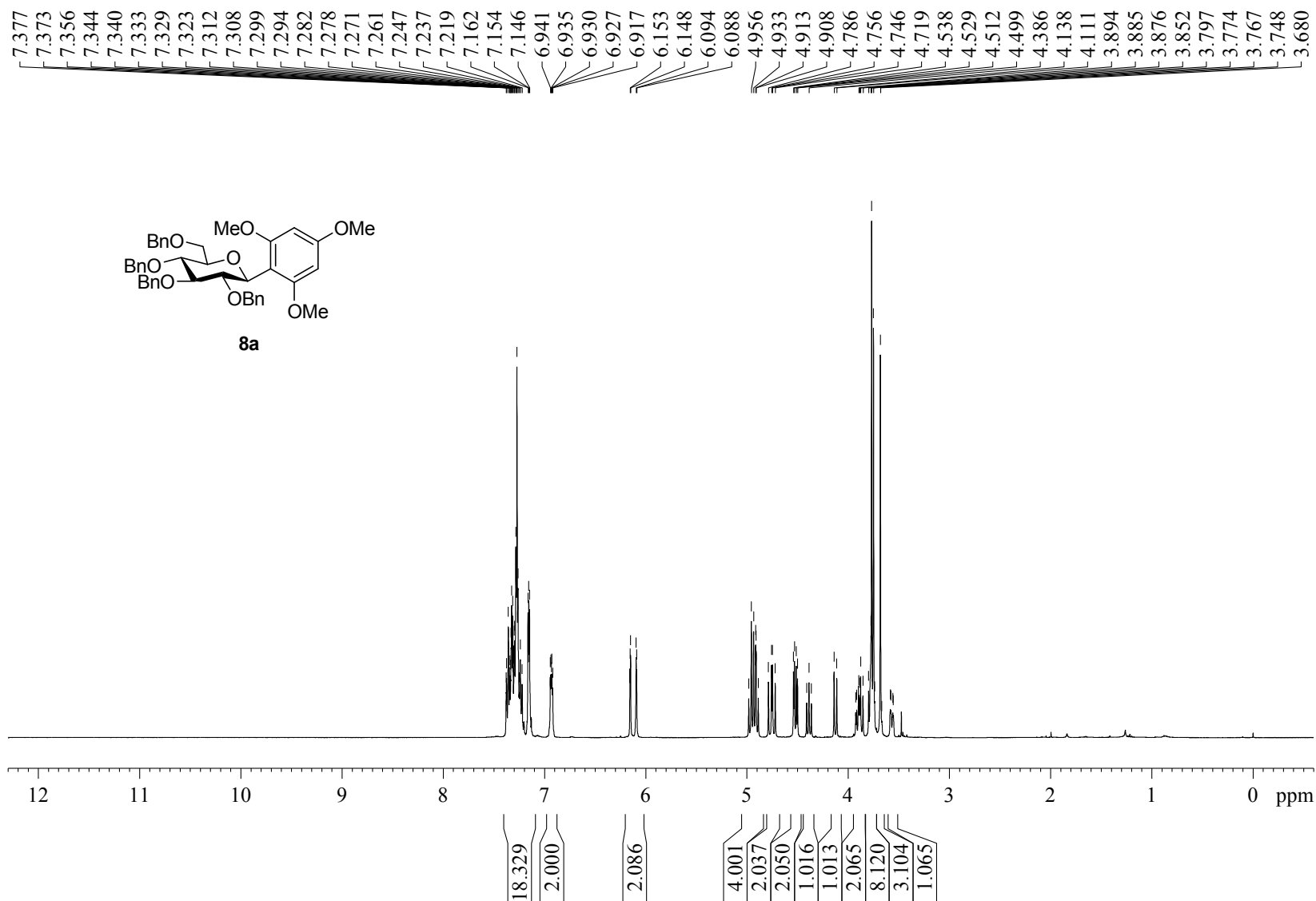
**<sup>1</sup>H NMR spectrum of Compound 5e (CDCl<sub>3</sub>, 400 MHz)**



<sup>13</sup>C NMR spectrum of Compound 5e (CDCl<sub>3</sub>, 100 MHz)



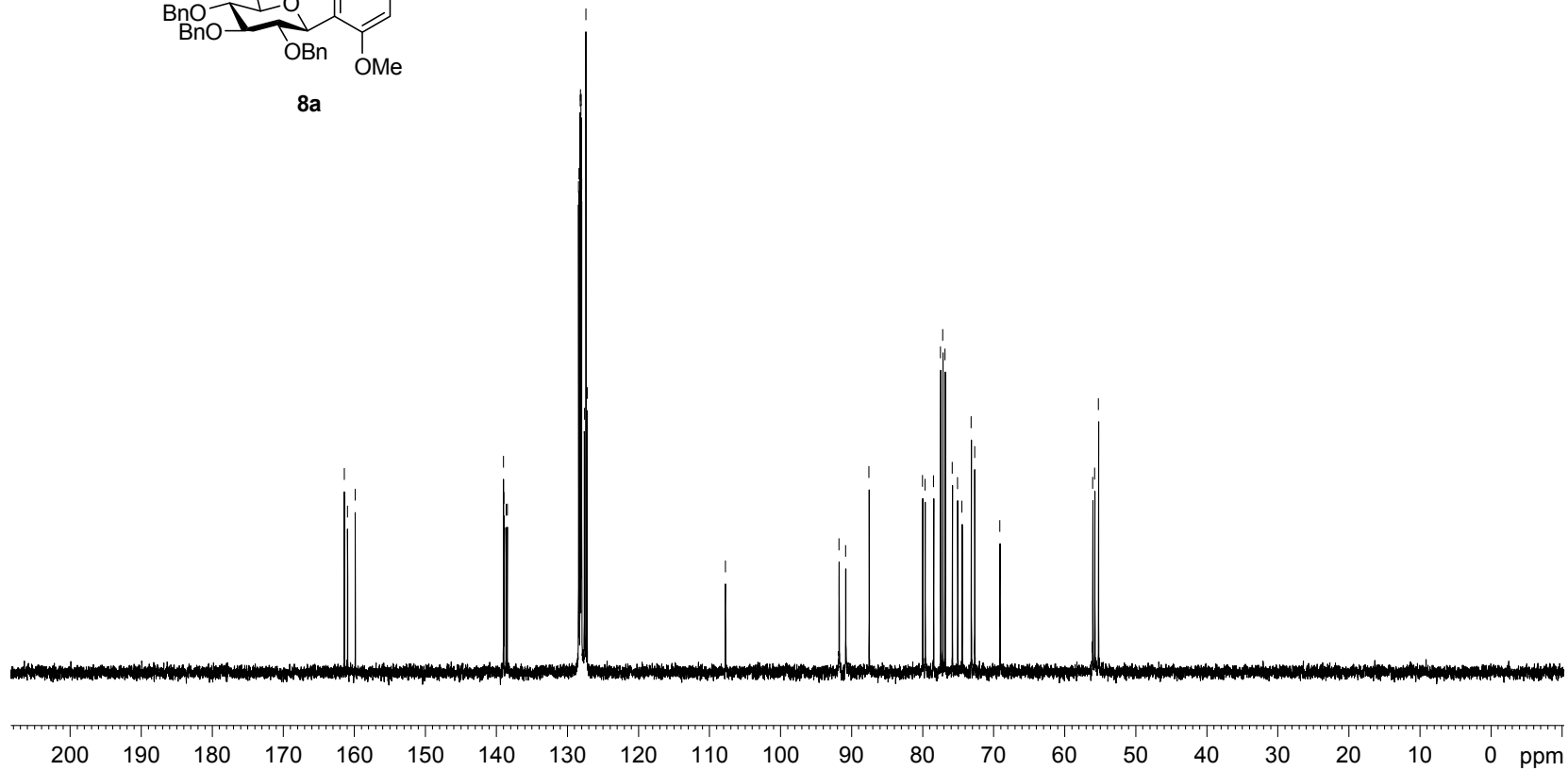
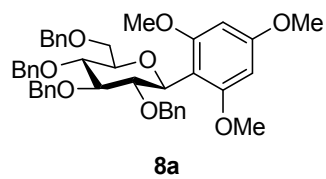
**<sup>1</sup>H NMR spectrum of Compound 8a (CDCl<sub>3</sub>, 400 MHz)**



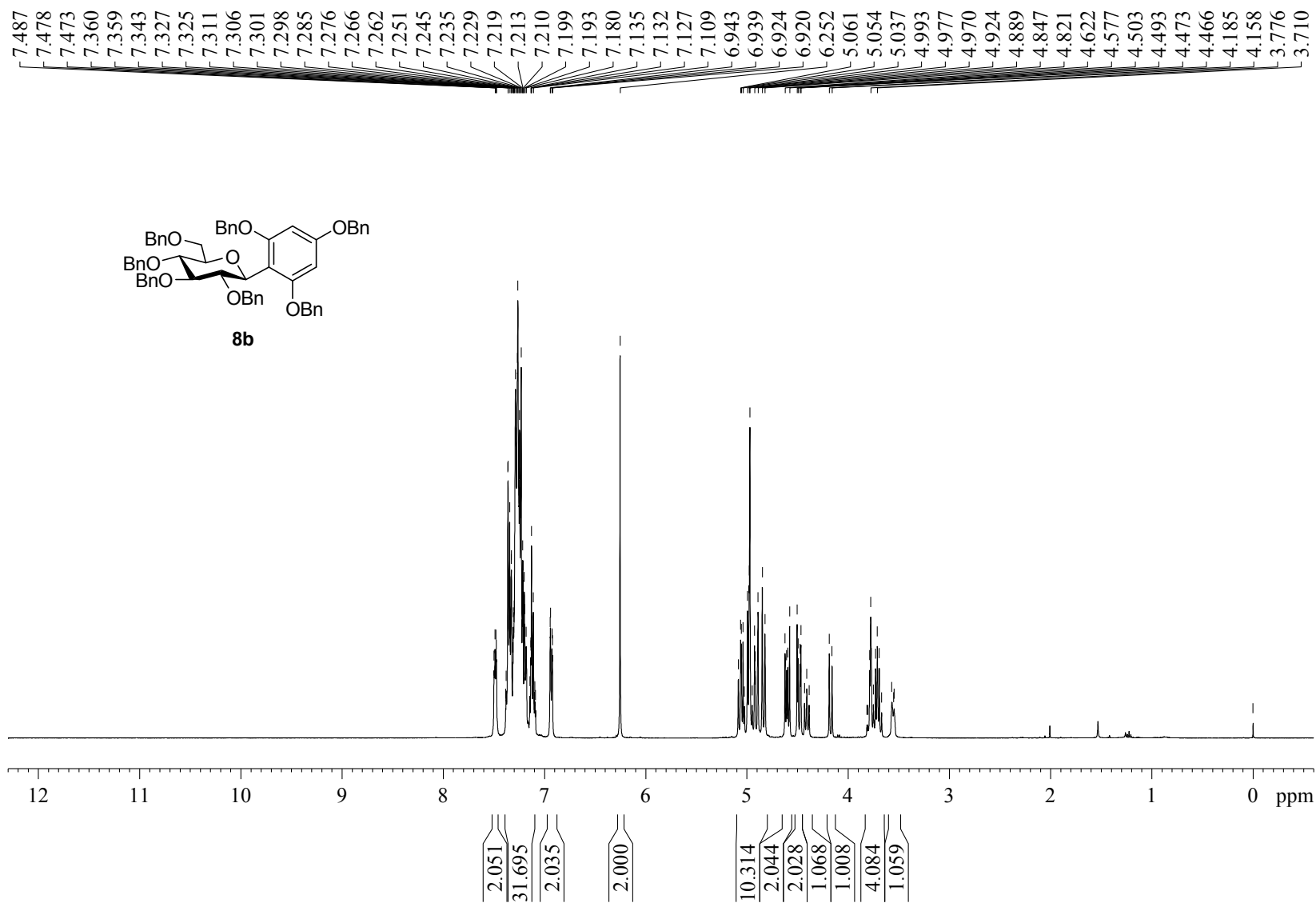


**<sup>13</sup>C NMR spectrum of Compound 8a (CDCl<sub>3</sub>, 100 MHz)**

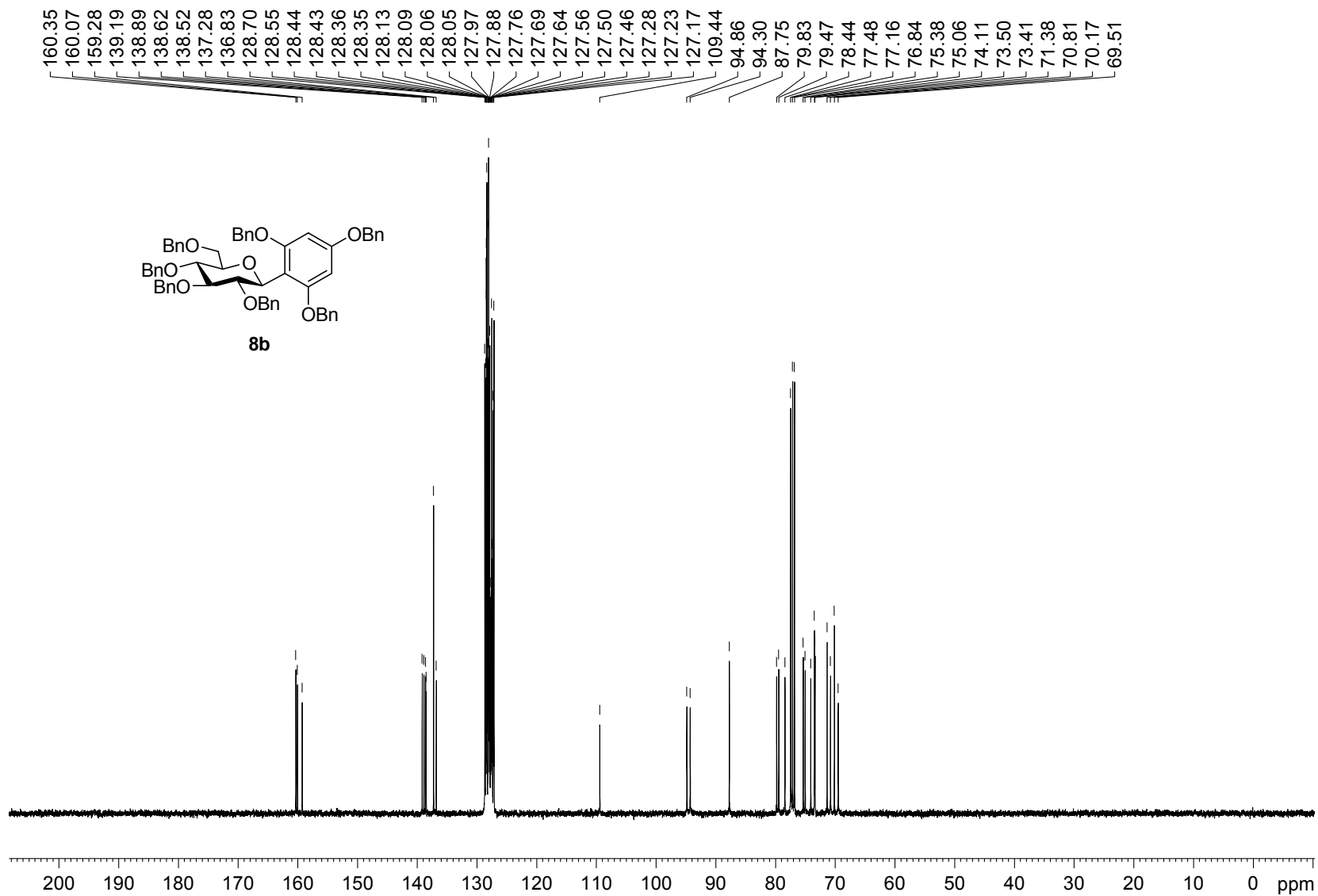
161.39  
160.94  
159.85  
139.00  
138.95  
138.64  
138.45  
128.42  
128.37  
128.20  
128.17  
128.08  
128.03  
127.98  
127.61  
127.38  
127.21  
107.75  
91.77  
90.84  
87.55  
80.02  
79.66  
78.46  
77.48  
77.16  
76.84  
75.83  
75.08  
74.45  
73.16  
72.69  
69.12  
56.06  
55.77  
55.25



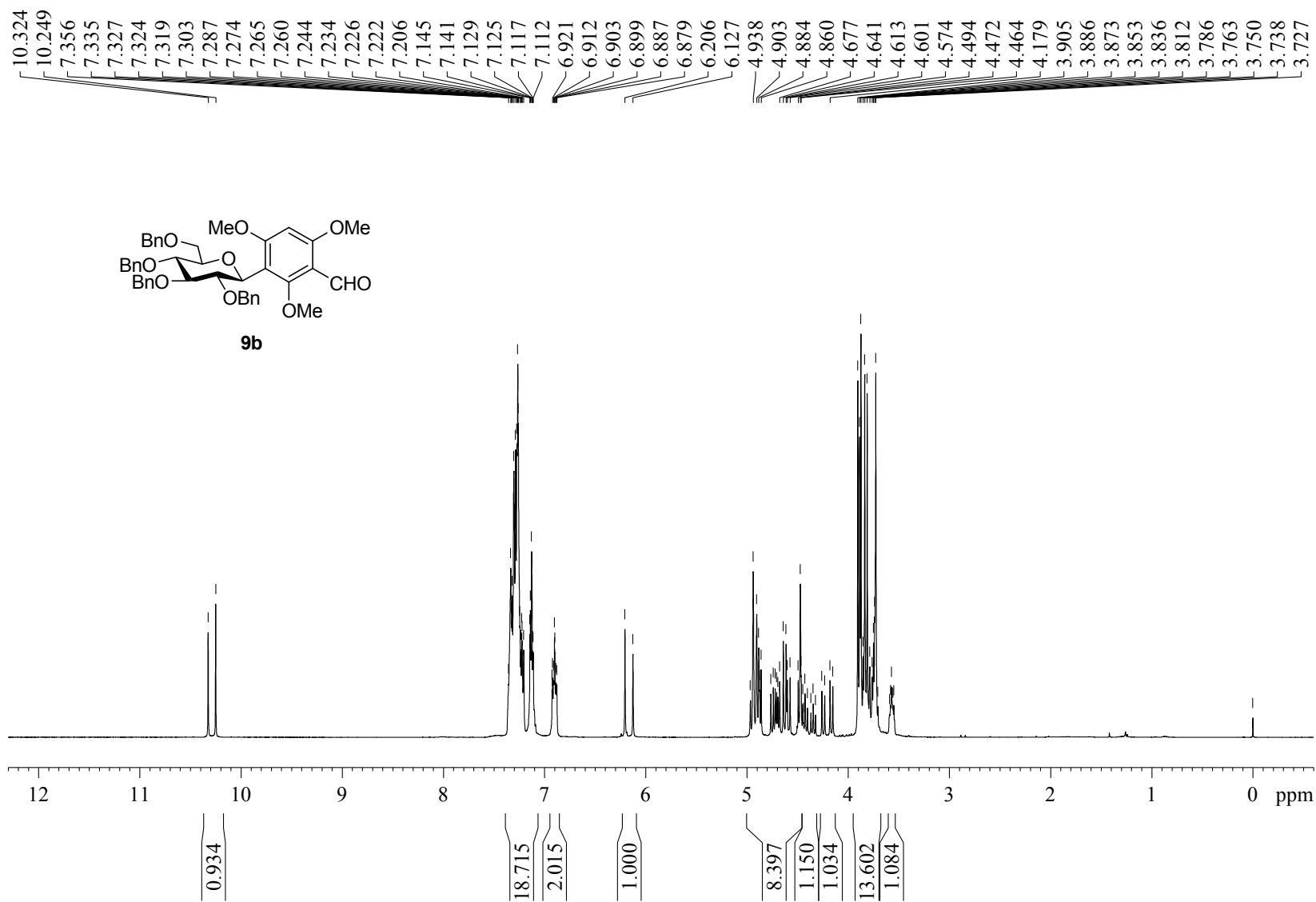
**<sup>1</sup>H NMR spectrum of Compound 8b (CDCl<sub>3</sub>, 400 MHz)**



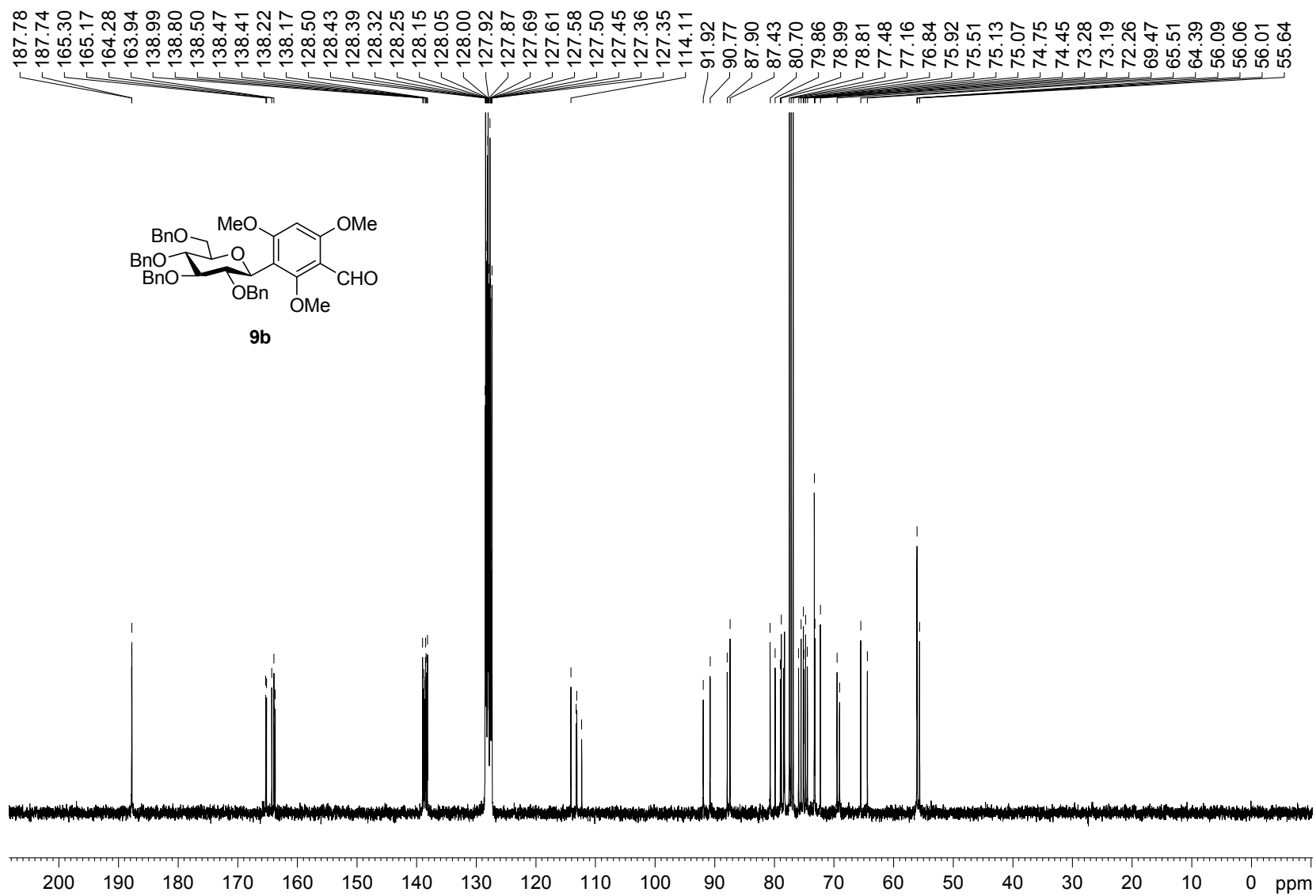
**<sup>13</sup>C NMR spectrum of Compound 8b (CDCl<sub>3</sub>, 100 MHz)**



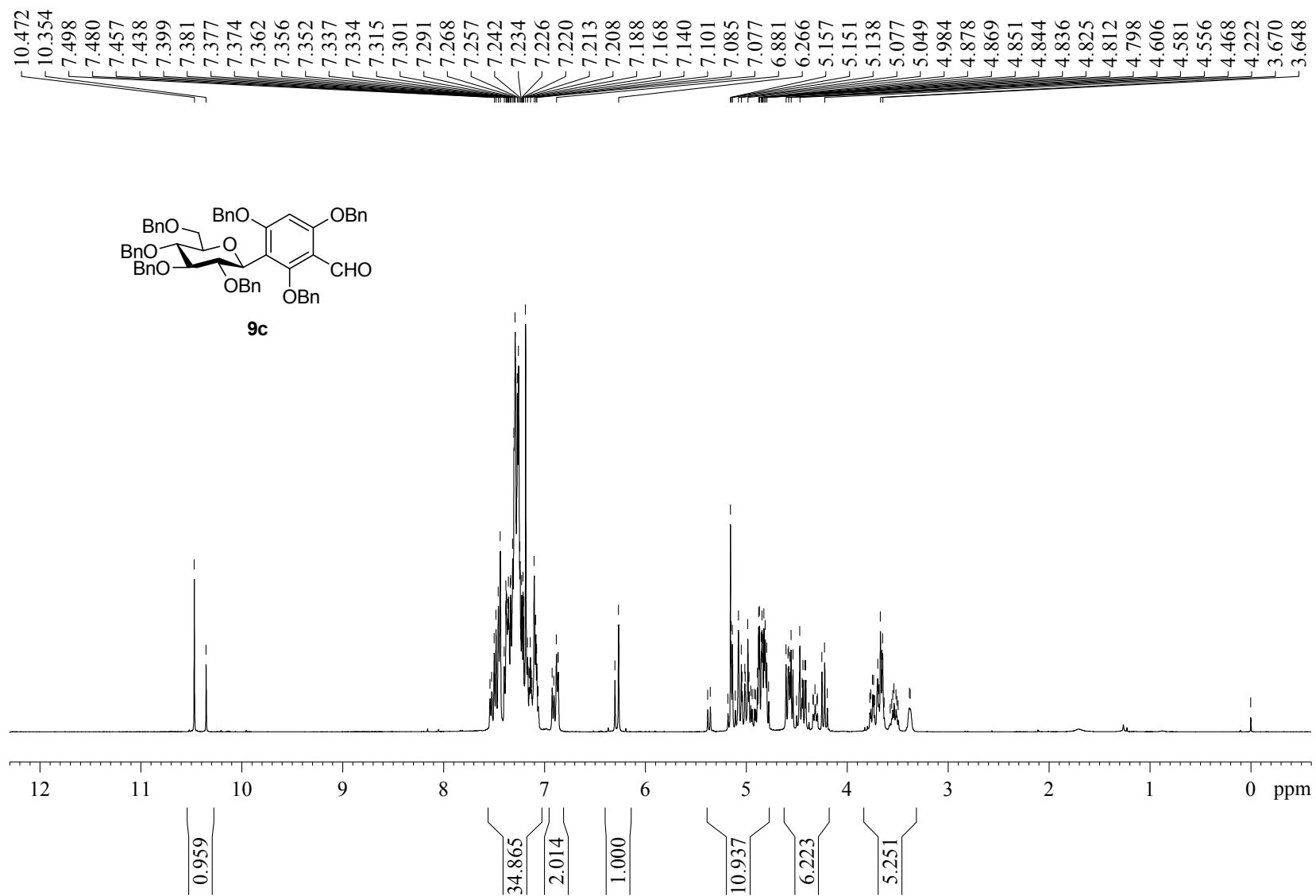
**<sup>1</sup>H NMR spectrum of Compound 9b (CDCl<sub>3</sub>, 400 MHz)**



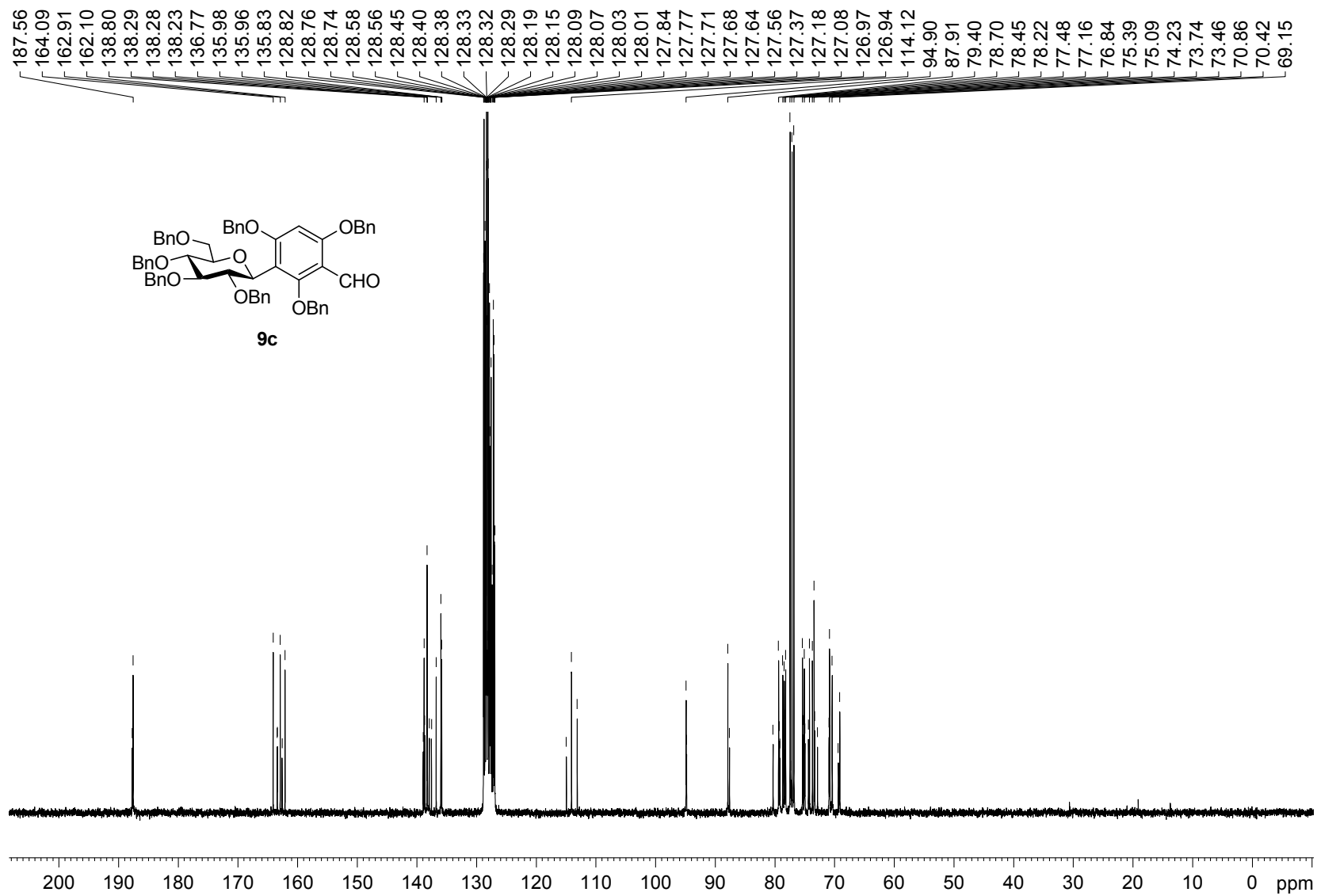
**<sup>13</sup>C NMR spectrum of Compound 9b (CDCl<sub>3</sub>, 100 MHz)**



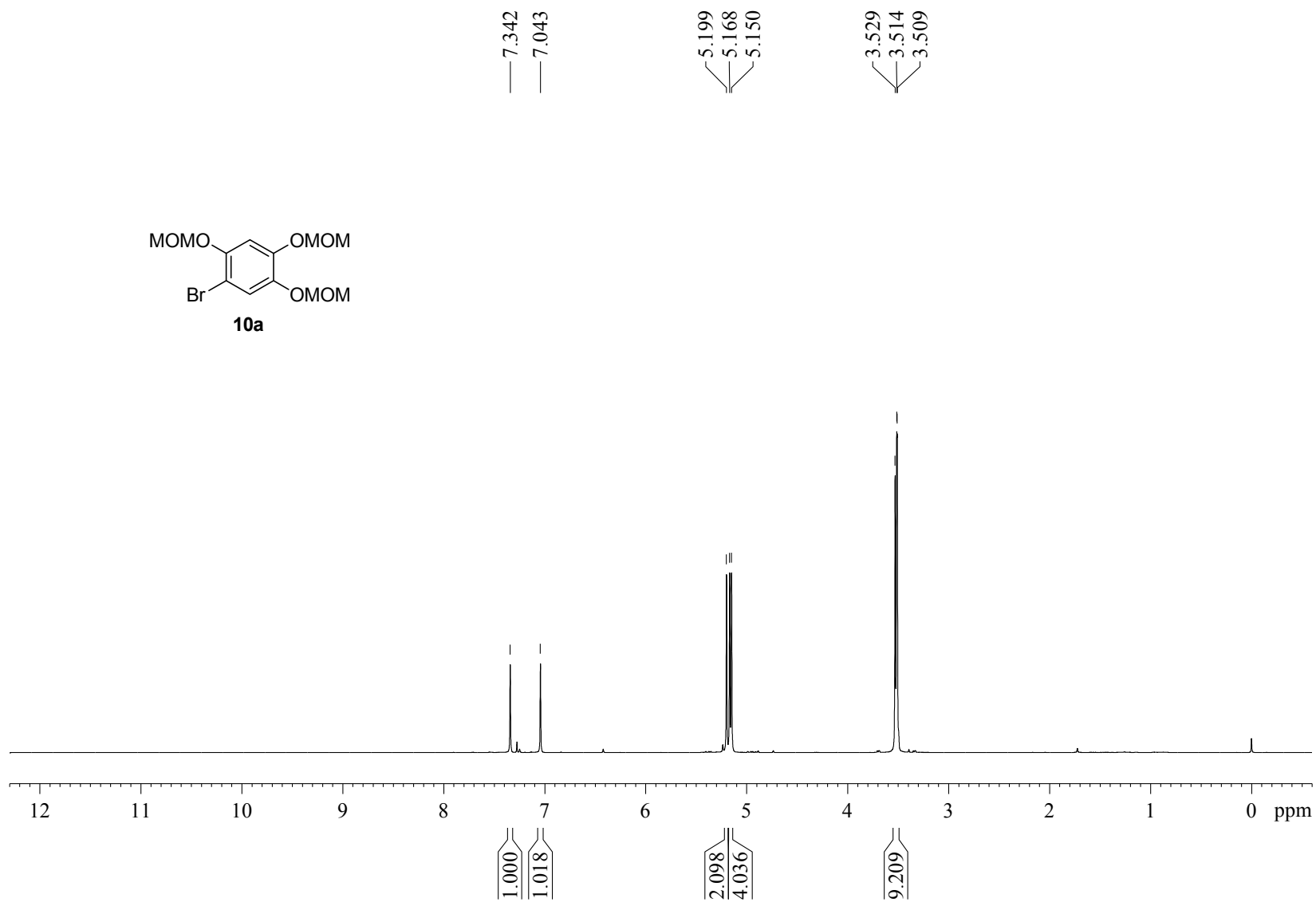
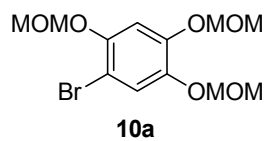
**<sup>1</sup>H NMR spectrum of Compound 9c (CDCl<sub>3</sub>, 400 MHz)**



**<sup>13</sup>C NMR spectrum of Compound 9c (CDCl<sub>3</sub>, 100 MHz)**



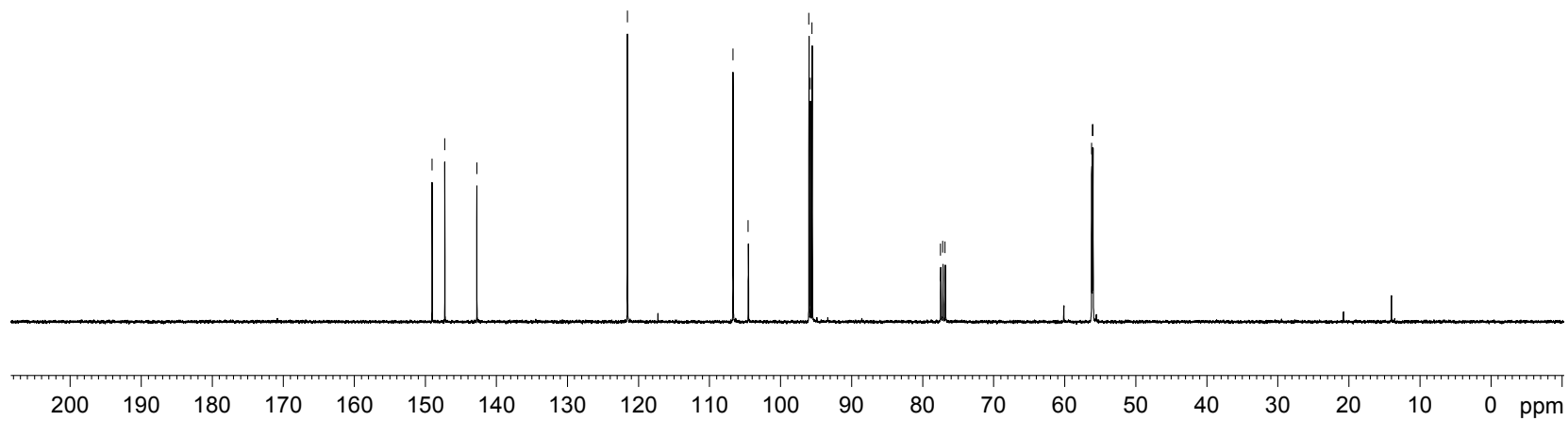
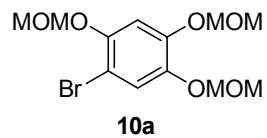
**<sup>1</sup>H NMR spectrum of Compound 10a (CDCl<sub>3</sub>, 400 MHz)**



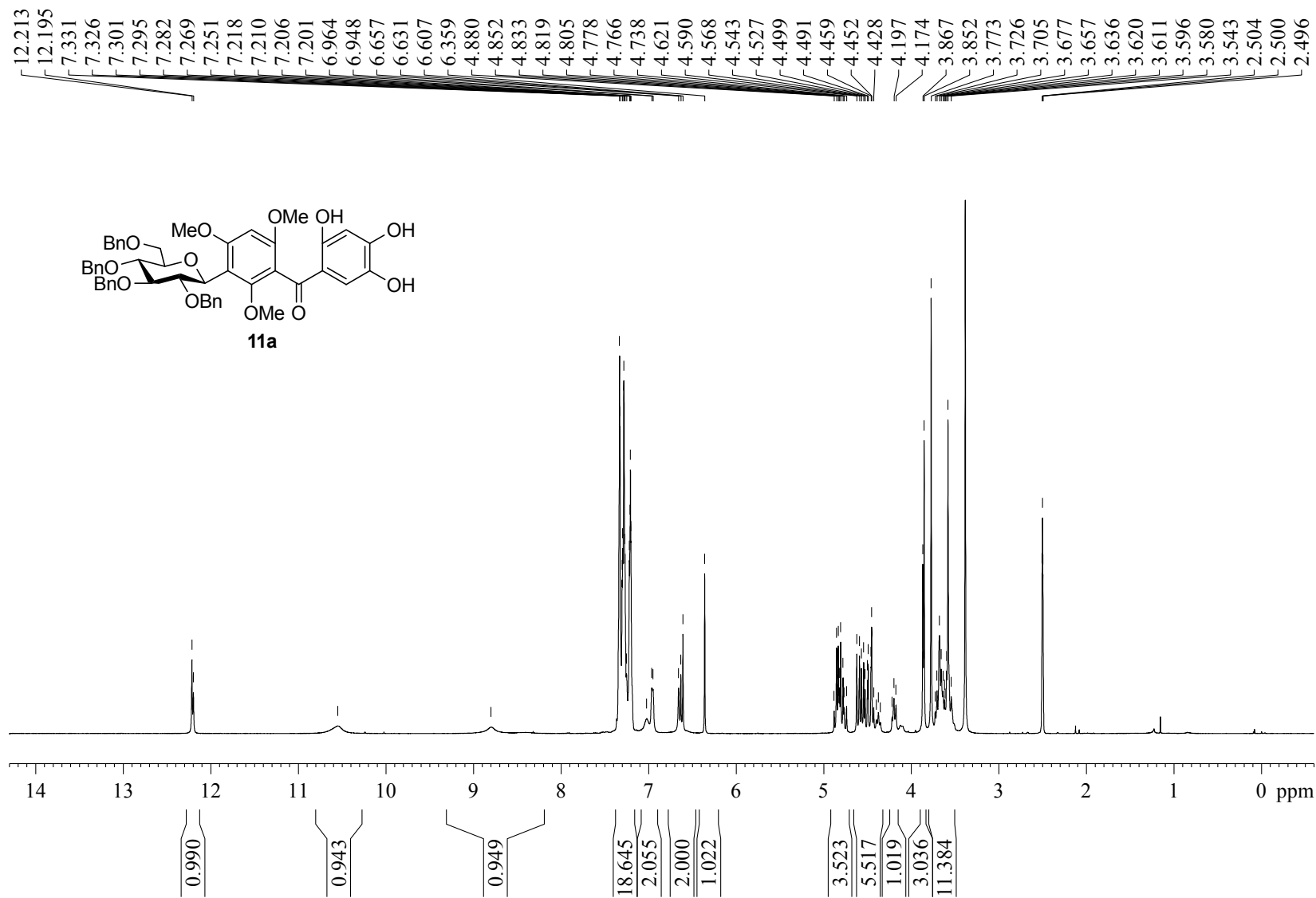


**<sup>13</sup>C NMR spectrum of Compound 10a (CDCl<sub>3</sub>, 100 MHz)**

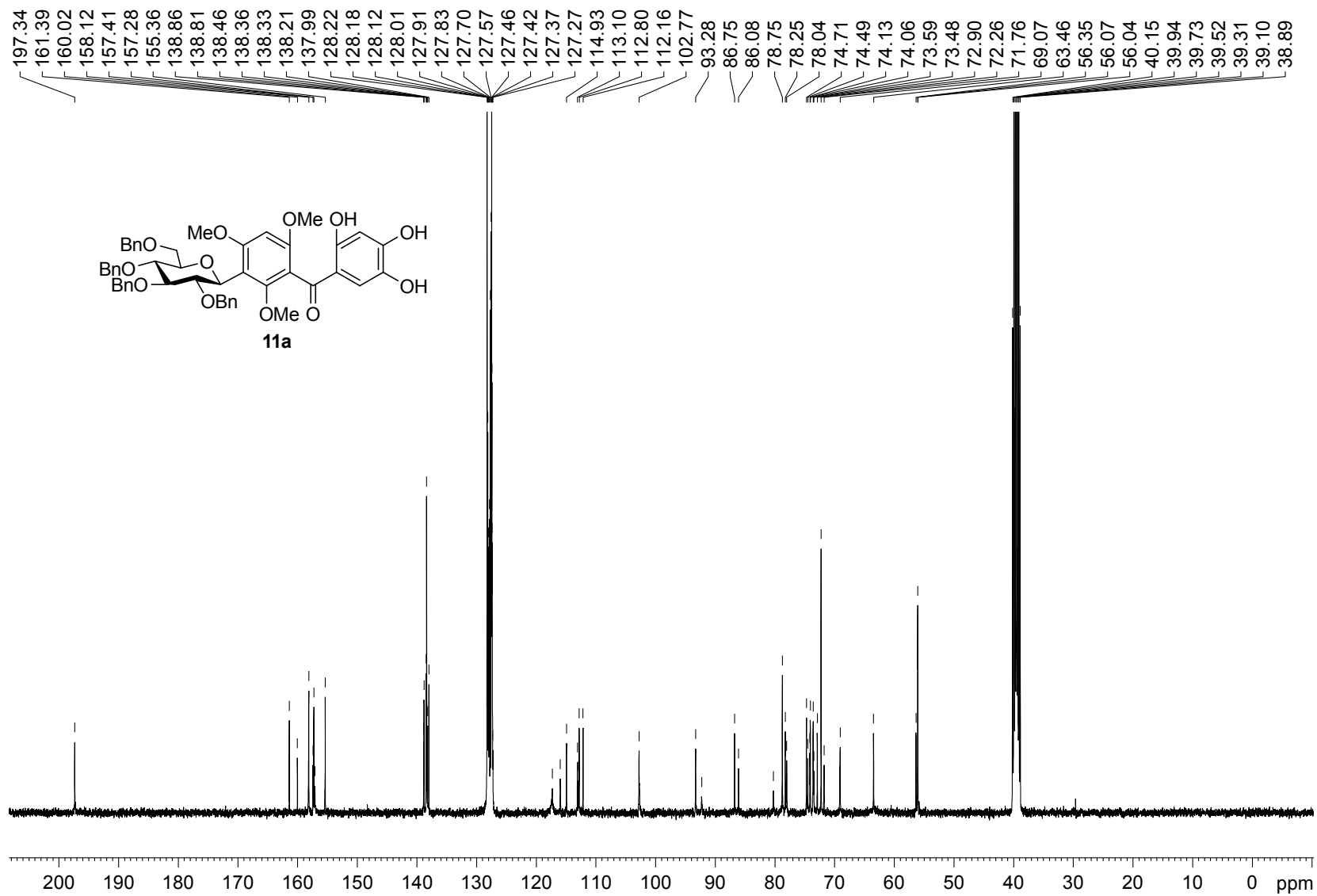
149.03  
147.25  
142.73  
121.54  
106.71  
104.54  
96.02  
95.80  
95.56  
77.48  
77.16  
76.84  
56.21  
56.11  
56.02



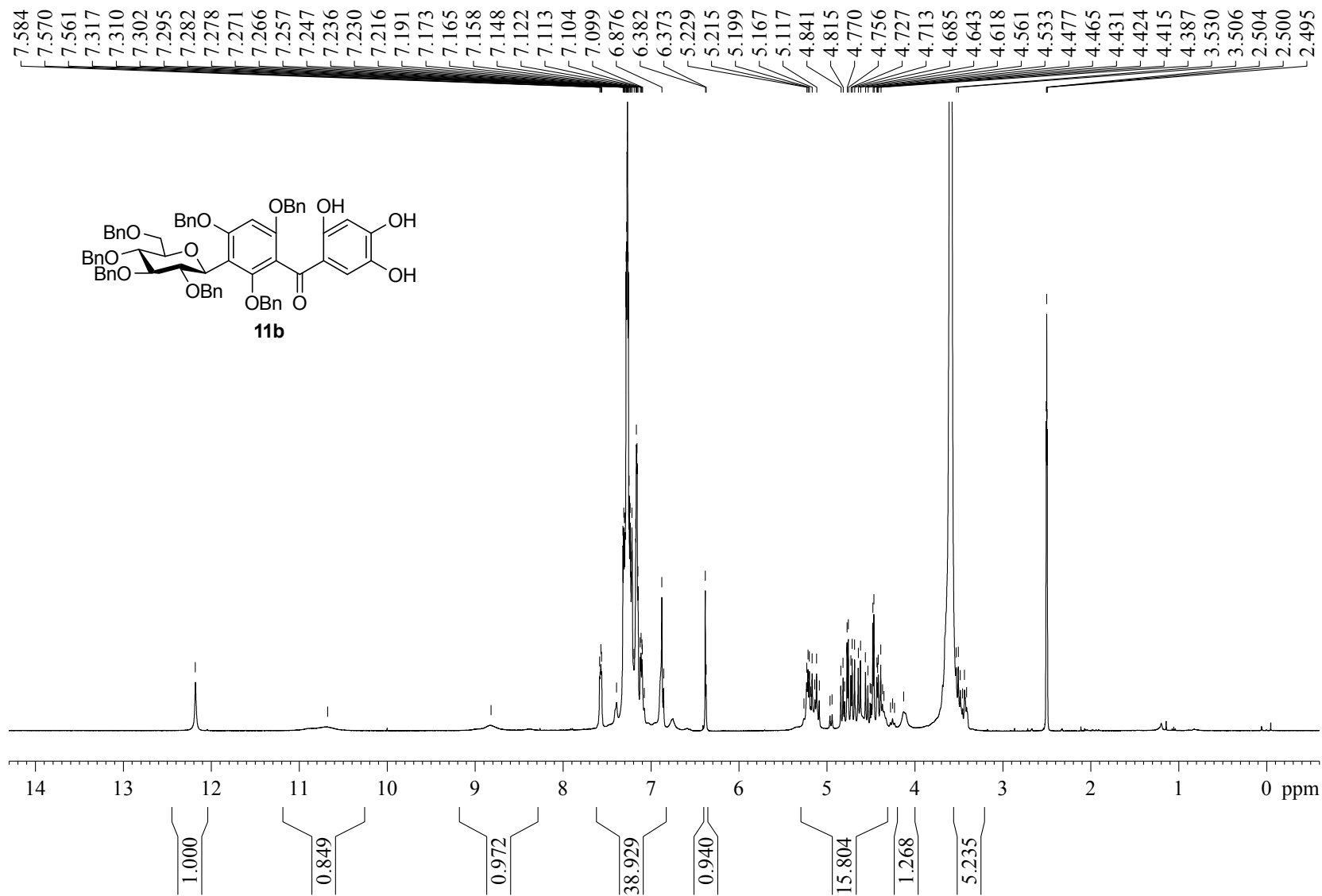
**<sup>1</sup>H NMR spectrum of Compound 11a (DMSO-d<sub>6</sub>, 400 MHz)**



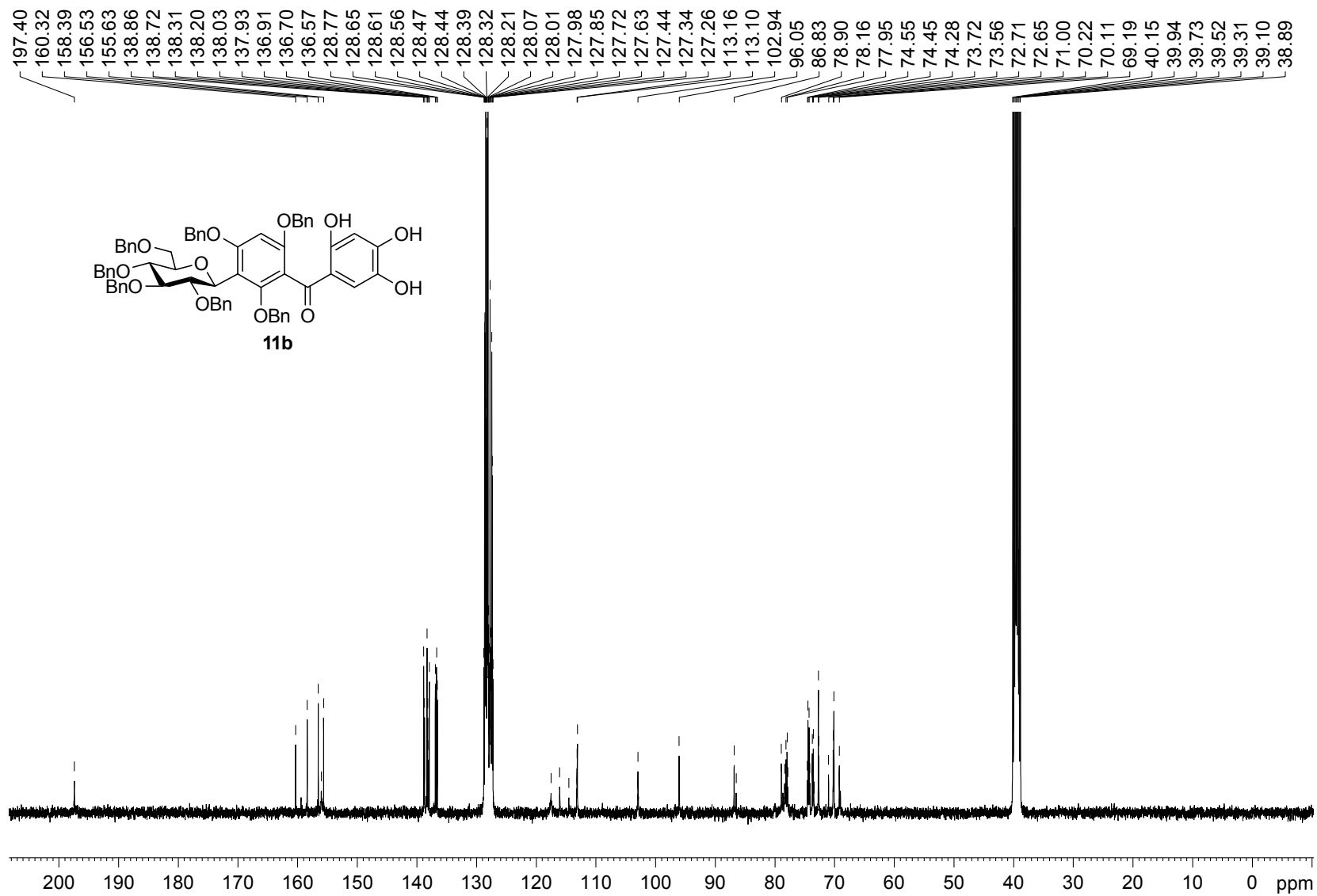
**<sup>13</sup>C NMR spectrum of Compound 11a (DMSO-*d*<sub>6</sub>, 100 MHz)**



**<sup>1</sup>H NMR spectrum of Compound 11b (DMSO-d<sub>6</sub>, 400 MHz)**

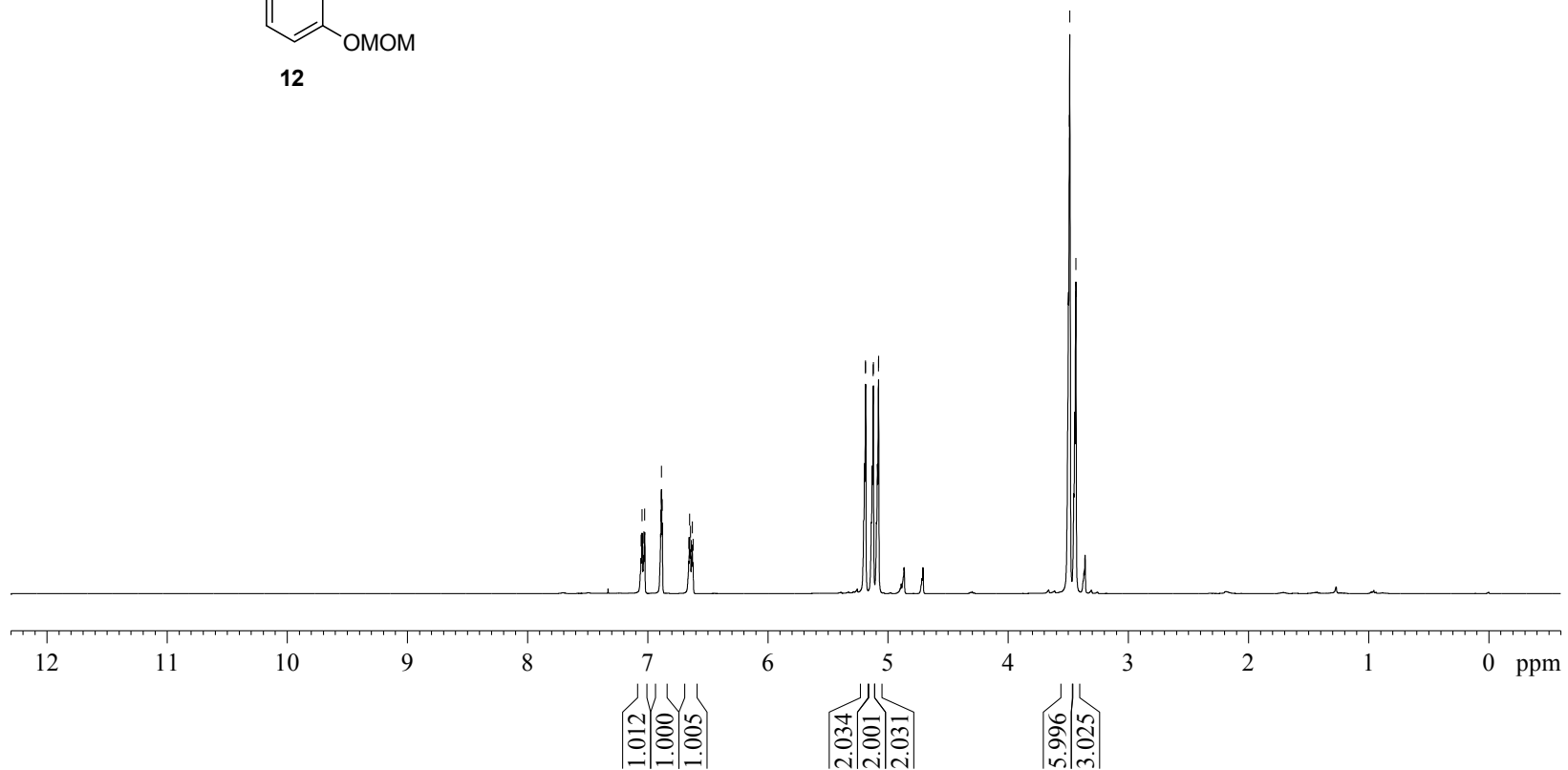
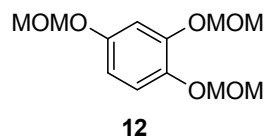


**<sup>13</sup>C NMR spectrum of Compound 11b (DMSO-*d*<sub>6</sub>, 100 MHz)**



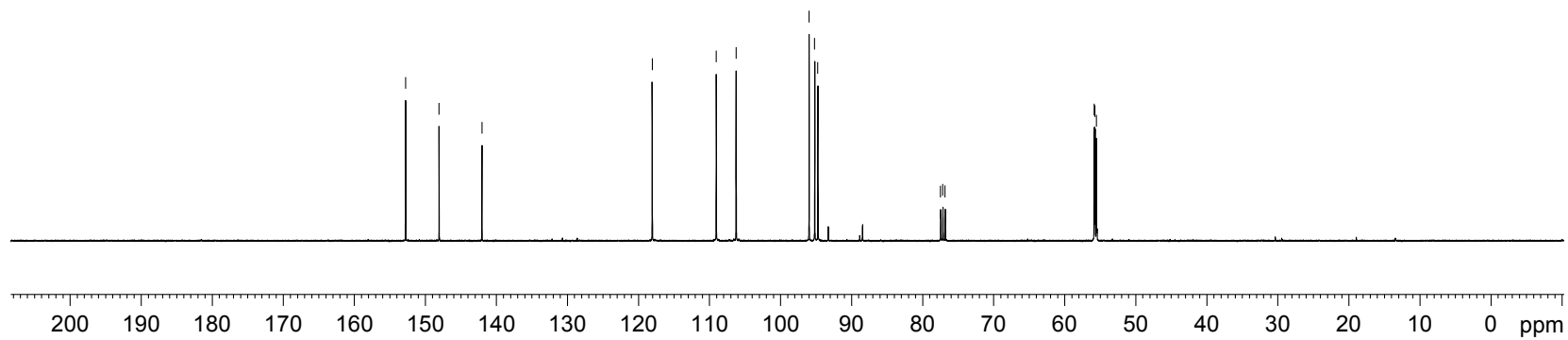
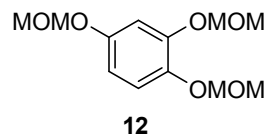
**<sup>1</sup>H NMR spectrum of Compound 12 (CDCl<sub>3</sub>, 400 MHz)**

7.054  
7.045  
7.039  
7.032  
7.024  
6.891  
6.884  
6.878  
6.657  
6.651  
6.643  
6.635  
6.628  
6.622  
5.186  
5.185  
5.123  
5.121  
5.079  
5.078  
3.489  
3.486  
3.435

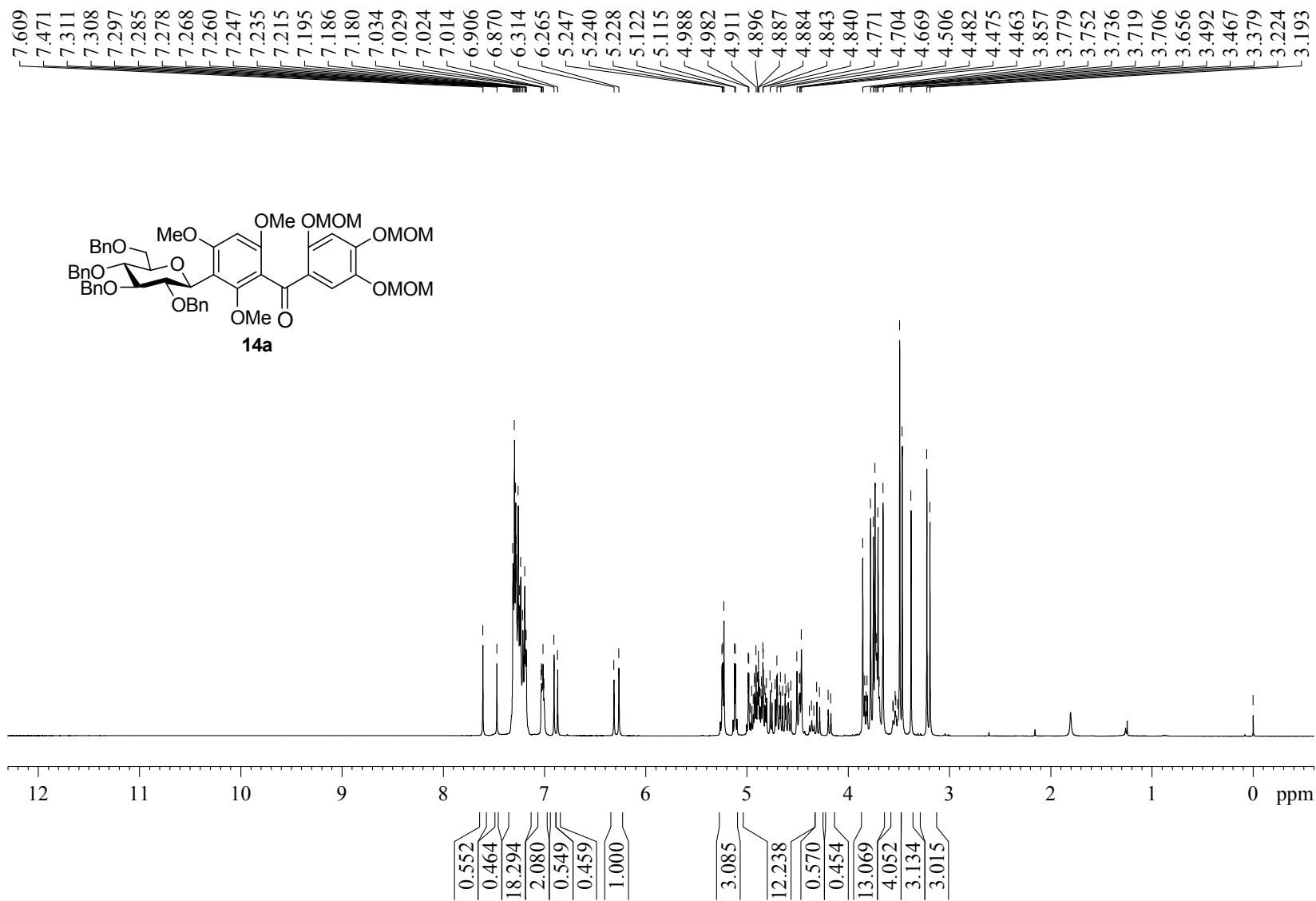


**<sup>13</sup>C NMR spectrum of Compound 12 (CDCl<sub>3</sub>, 100 MHz)**

152.76  
148.05  
142.03  
  
118.06  
109.04  
106.24  
96.00  
95.21  
94.75  
77.48  
77.16  
76.84  
55.86  
55.75  
55.55

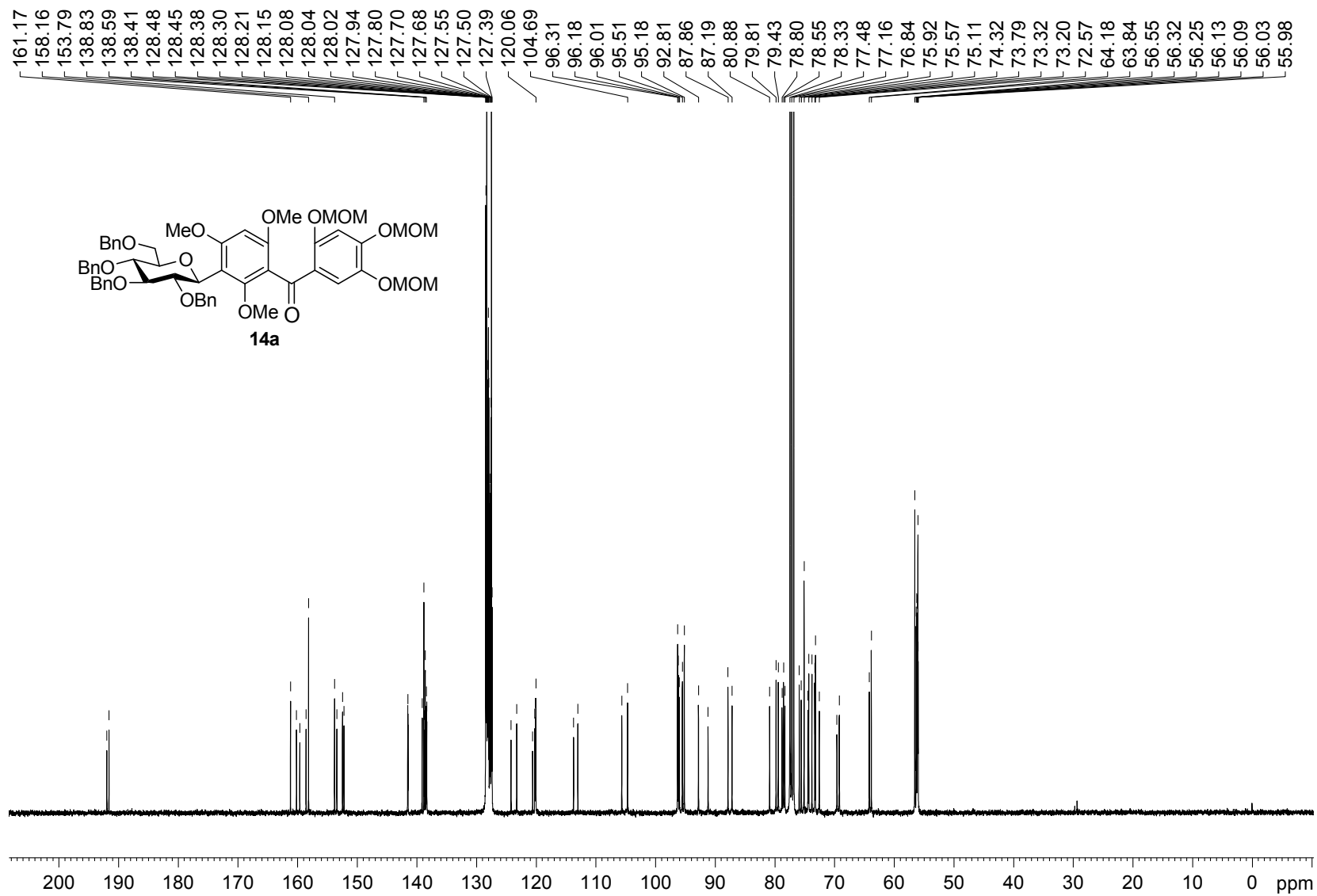


**<sup>1</sup>H NMR spectrum of Compound 14a (CDCl<sub>3</sub>, 400 MHz)**

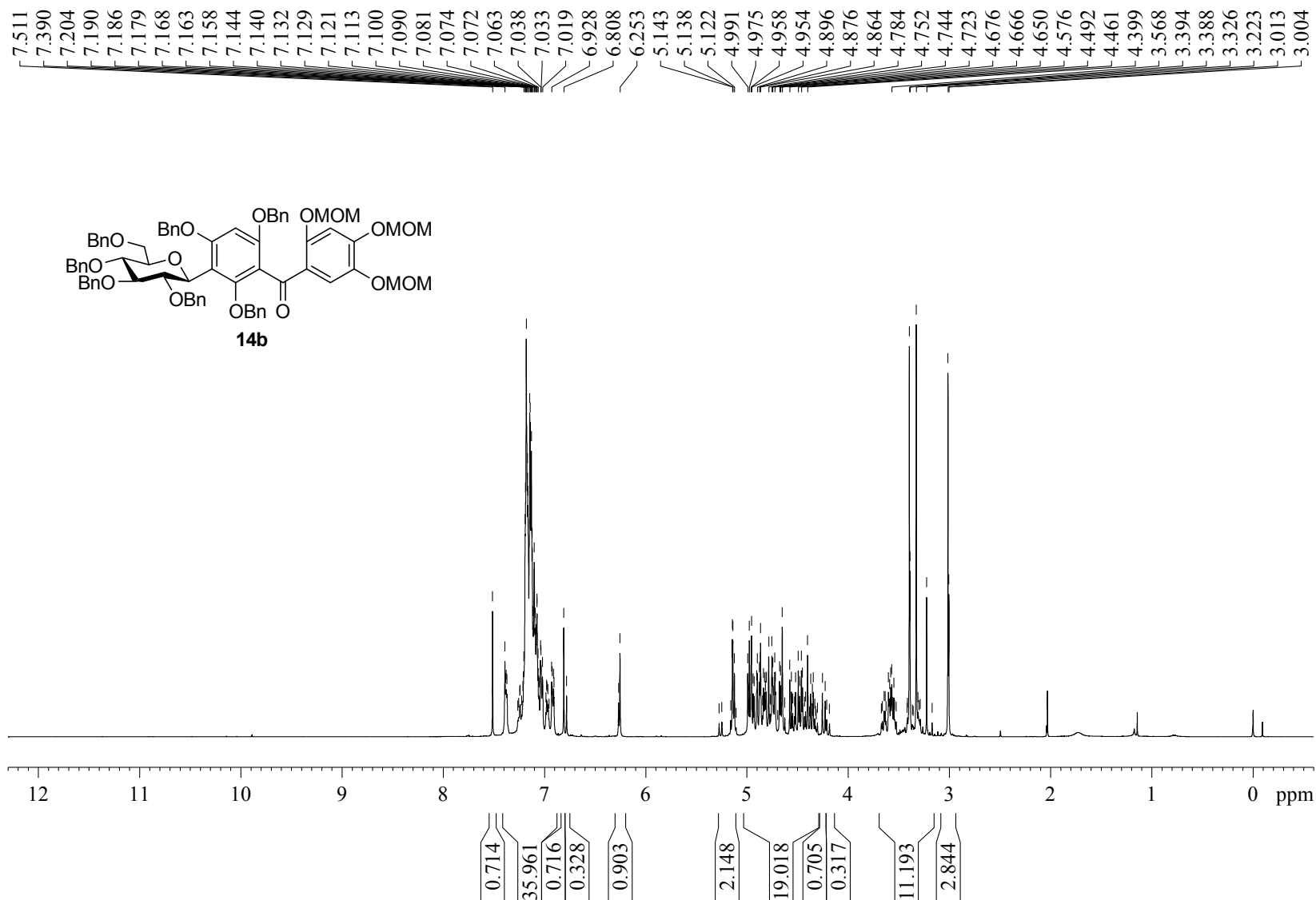




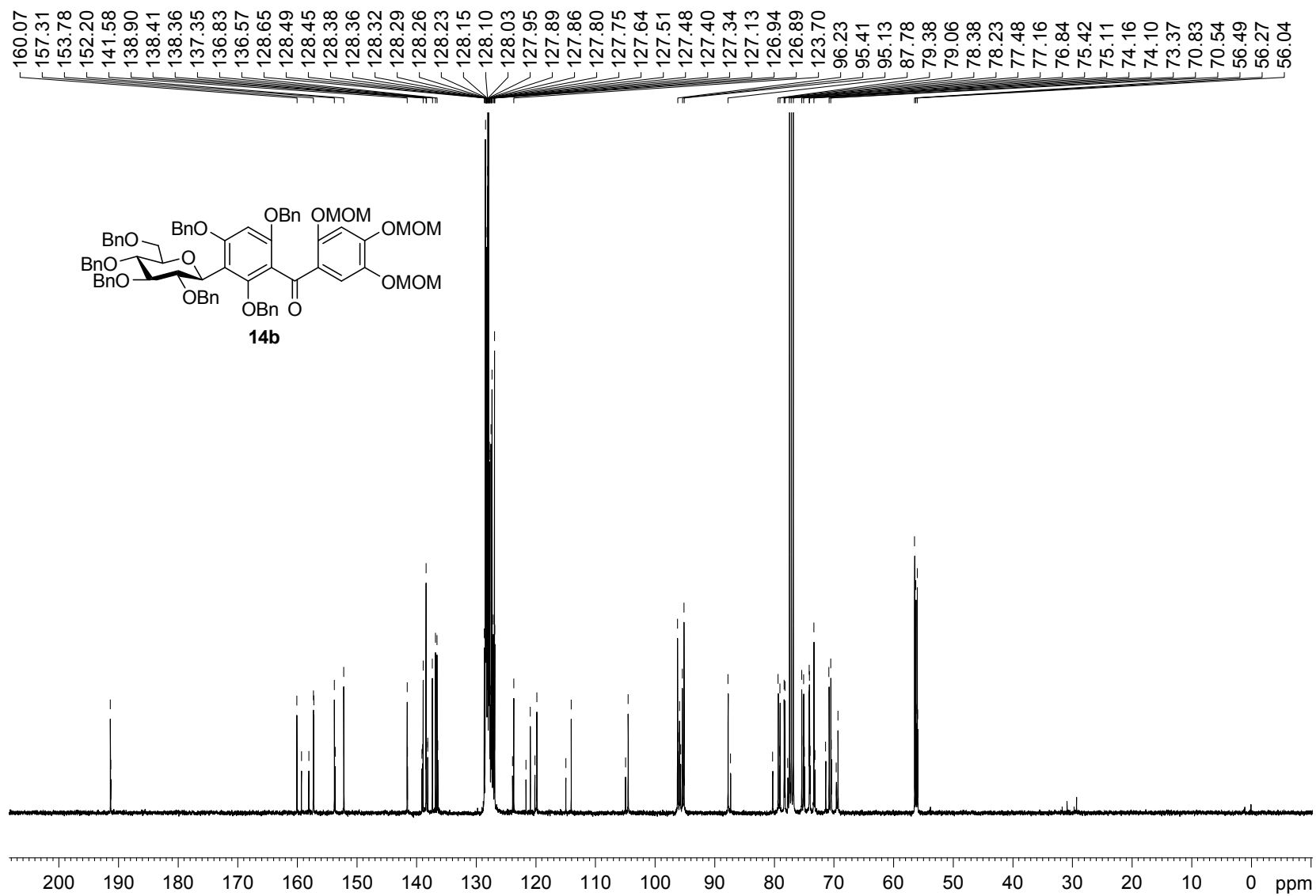
<sup>13</sup>C NMR spectrum of Compound 14a (CDCl<sub>3</sub>, 100 MHz)



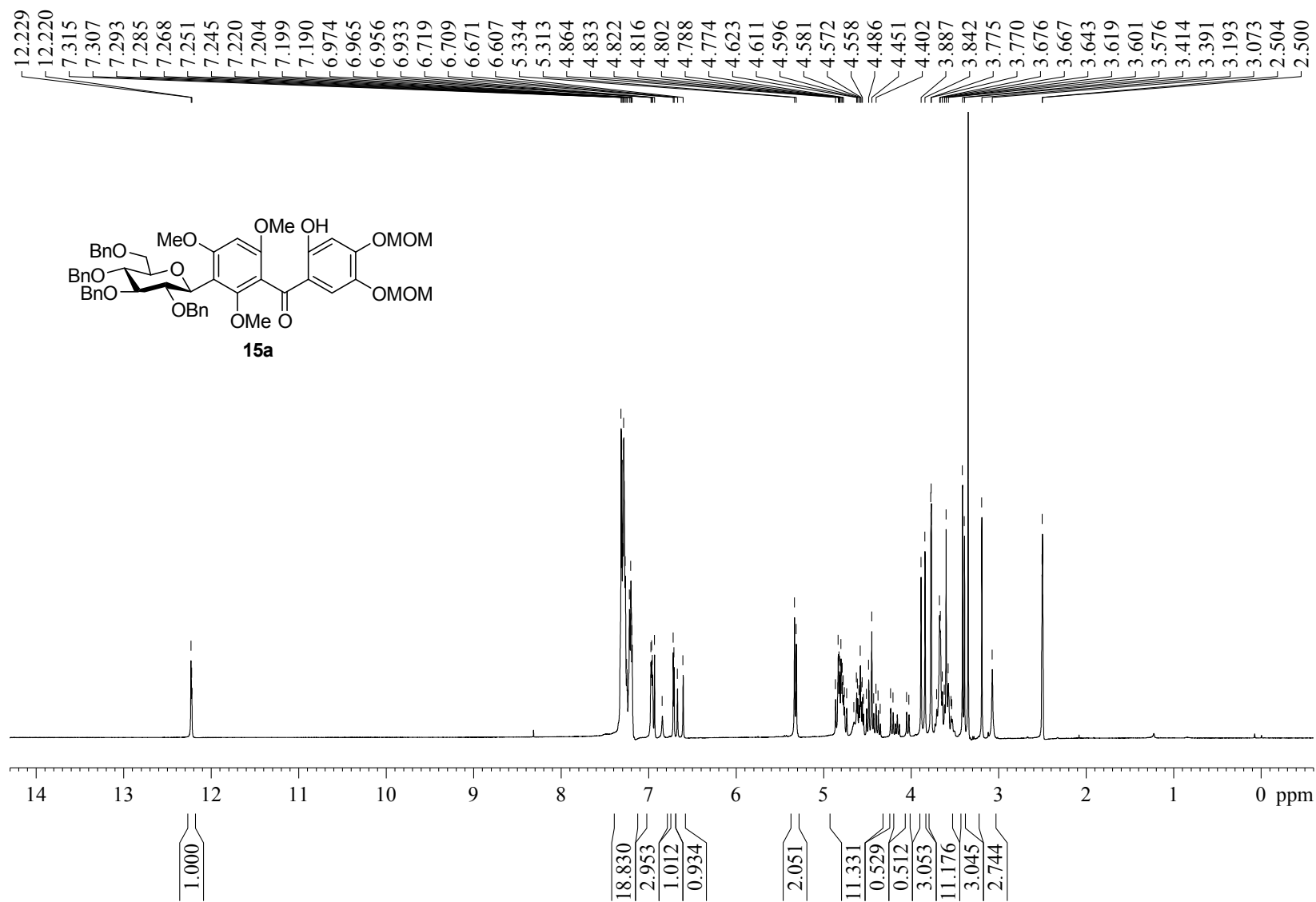
**<sup>1</sup>H NMR spectrum of Compound 14b (CDCl<sub>3</sub>, 400 MHz)**



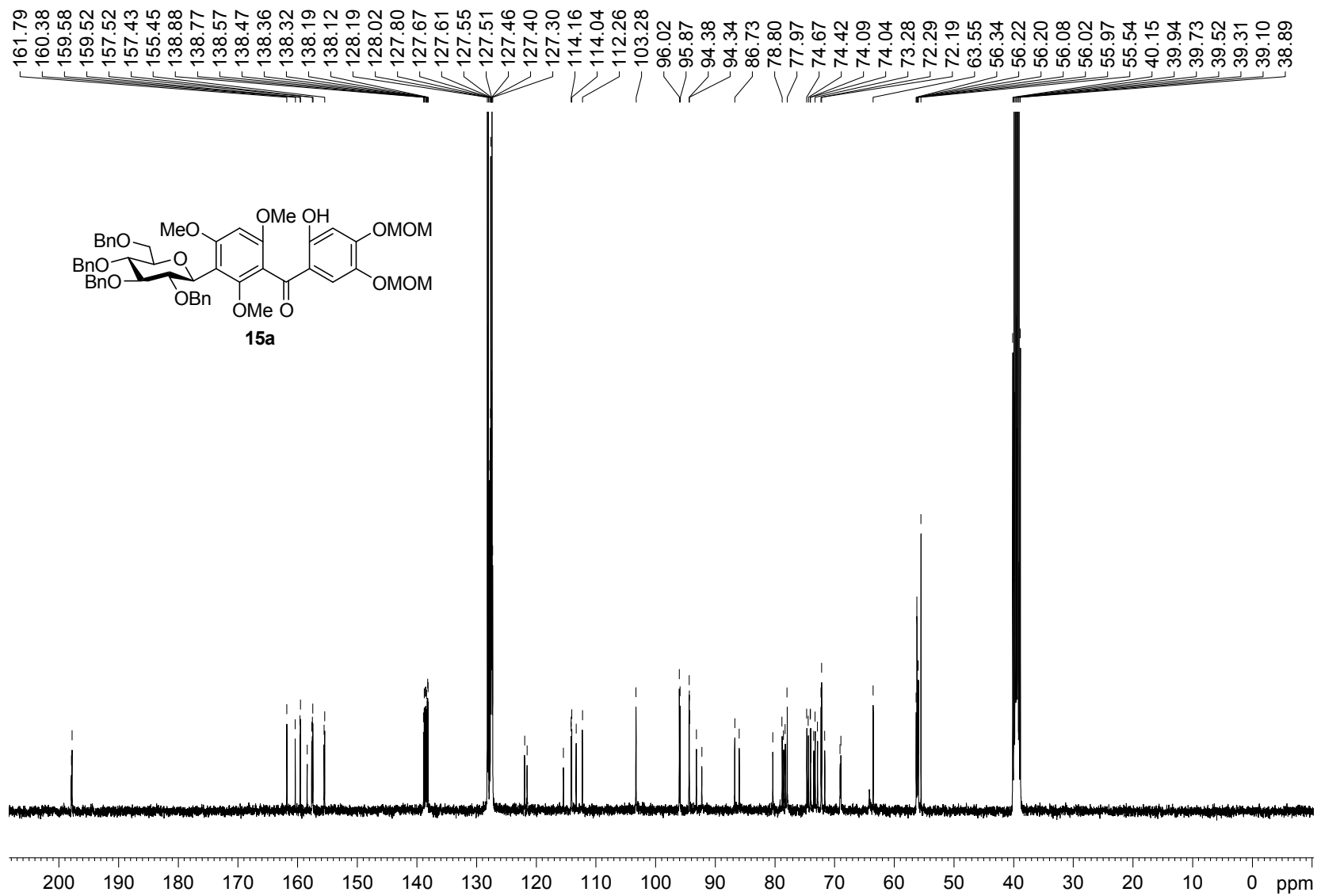
**<sup>13</sup>C NMR spectrum of Compound 14b (CDCl<sub>3</sub>, 100 MHz)**



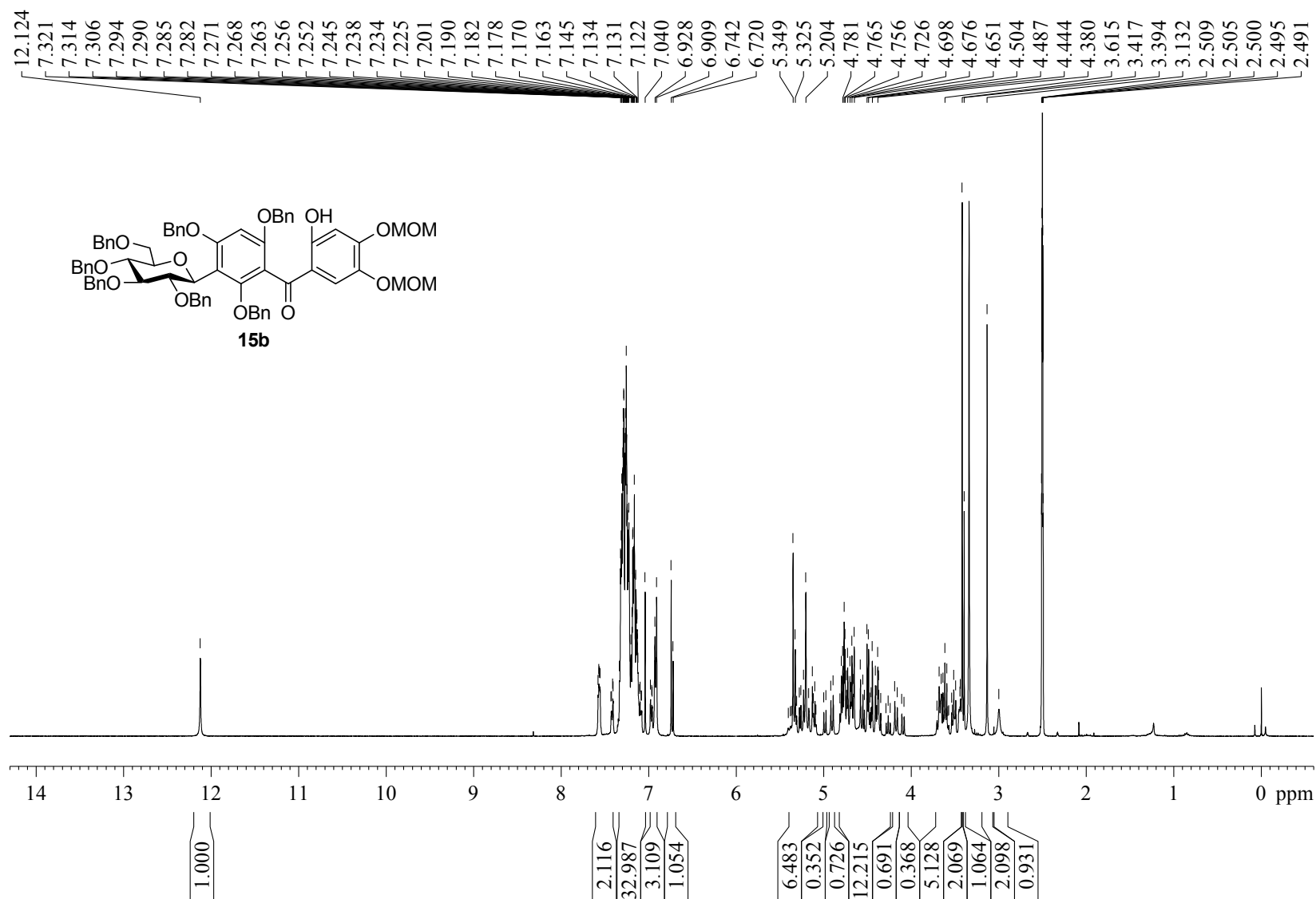
**<sup>1</sup>H NMR spectrum of Compound 15a (DMSO-d<sub>6</sub>, 400 MHz)**



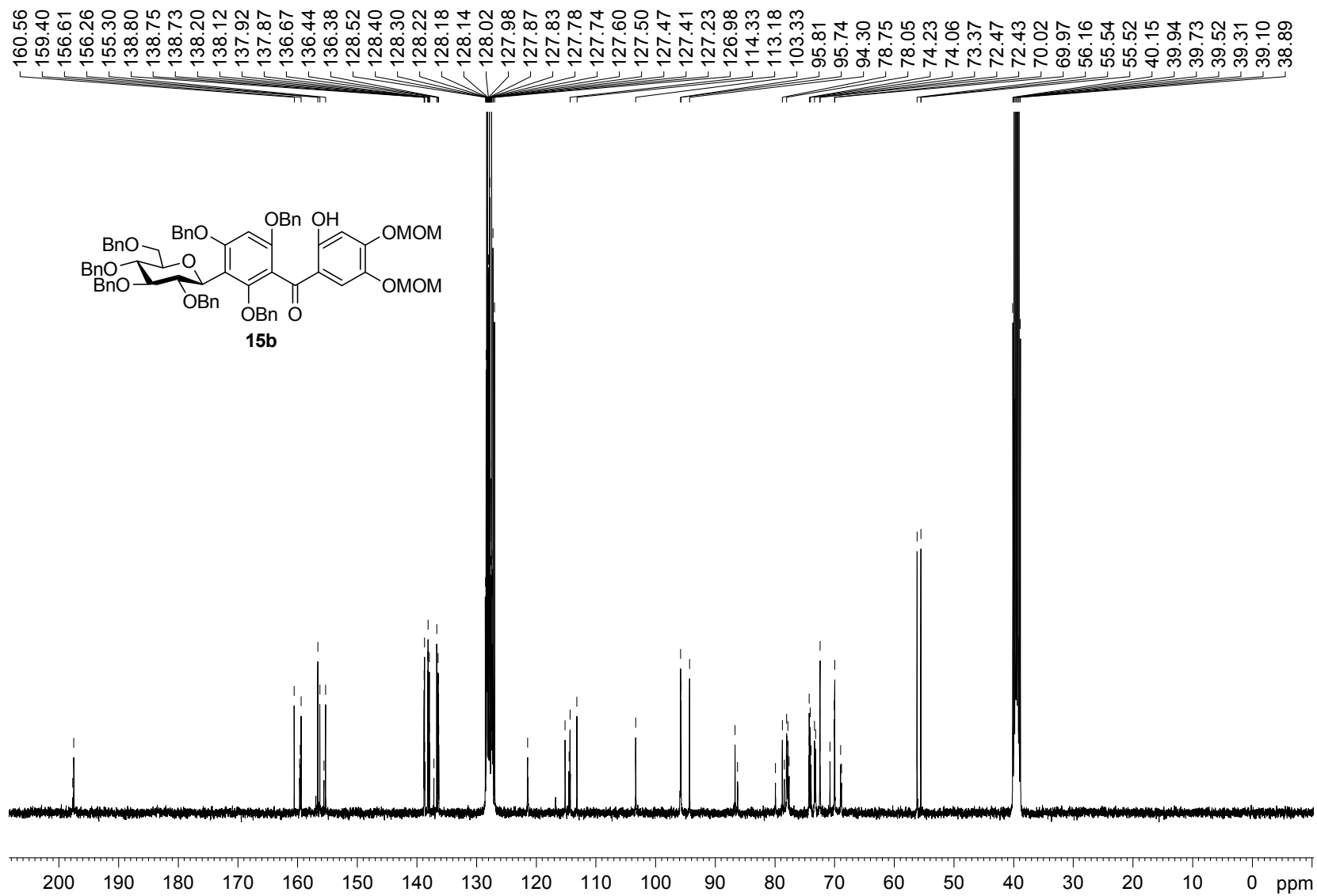
**<sup>13</sup>C NMR spectrum of Compound 15a (DMSO-*d*<sub>6</sub>, 100 MHz)**



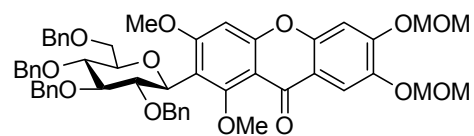
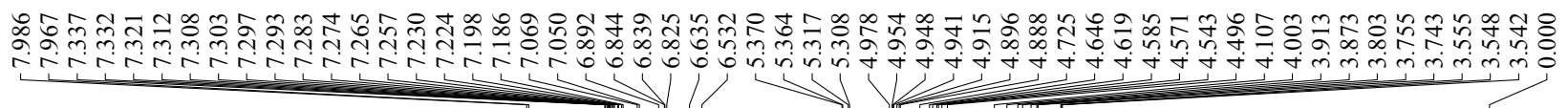
**<sup>1</sup>H NMR spectrum of Compound 15b (DMSO-d<sub>6</sub>, 400 MHz)**



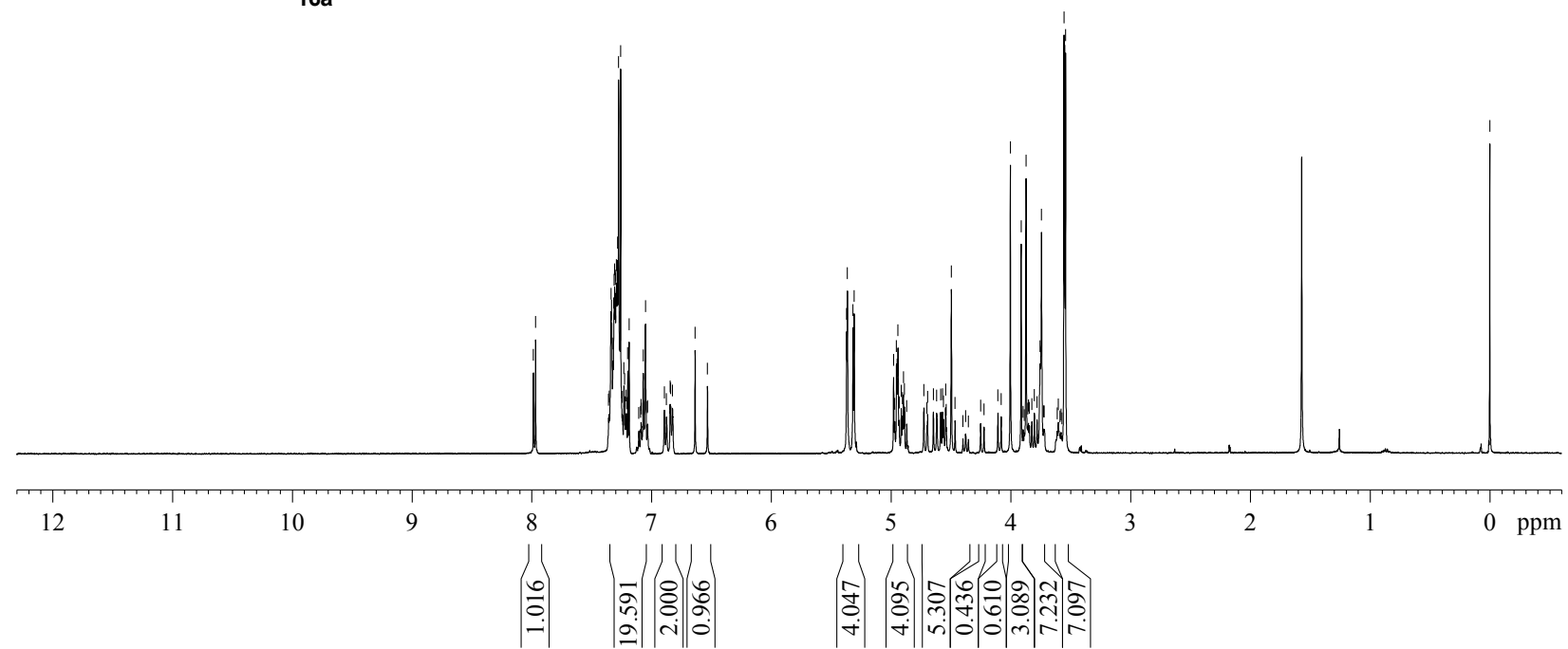
**<sup>13</sup>C NMR spectrum of Compound 15b (DMSO-*d*<sub>6</sub>, 100 MHz)**



**<sup>1</sup>H NMR spectrum of Compound 16a (CDCl<sub>3</sub>, 400 MHz)**

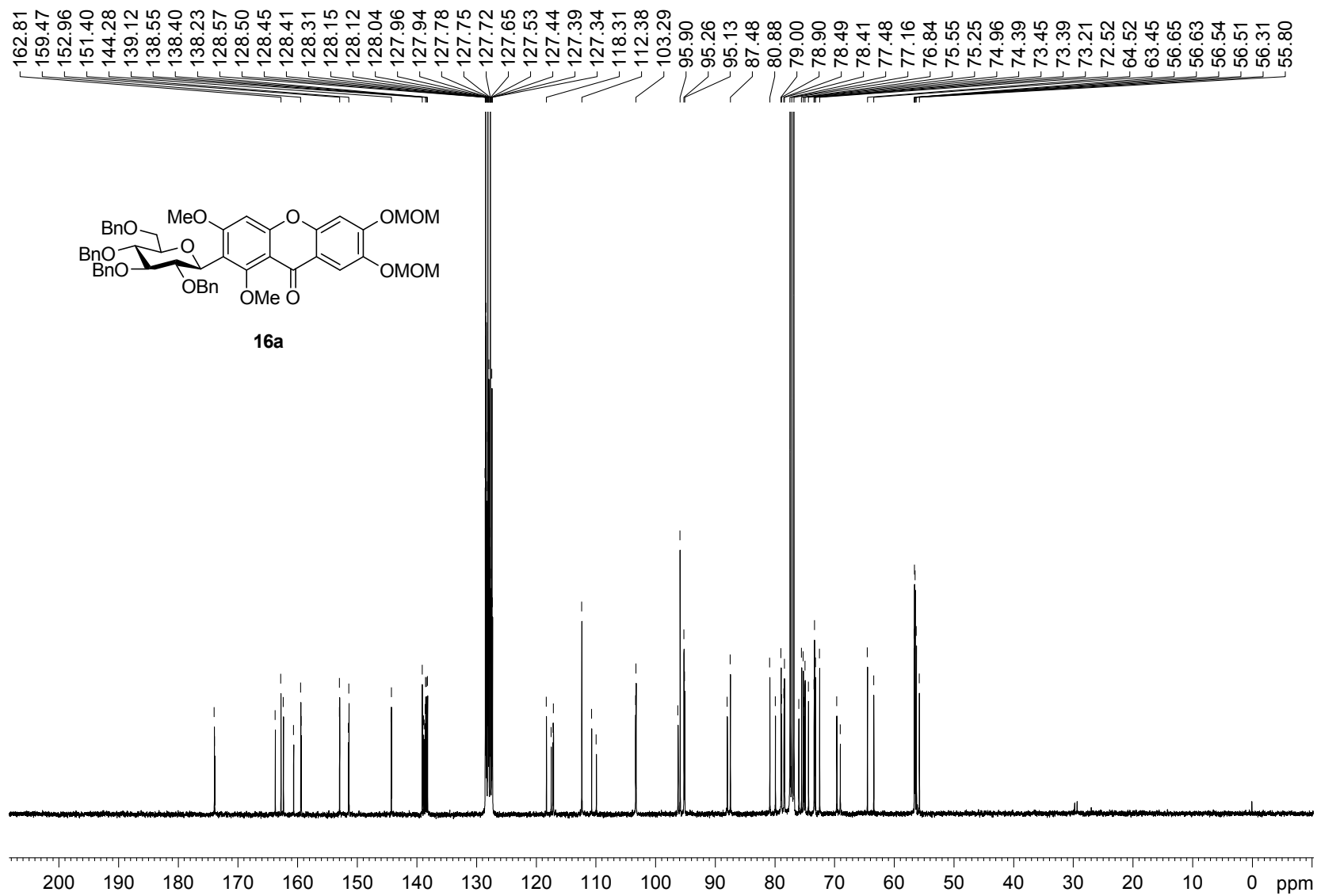


**16a**

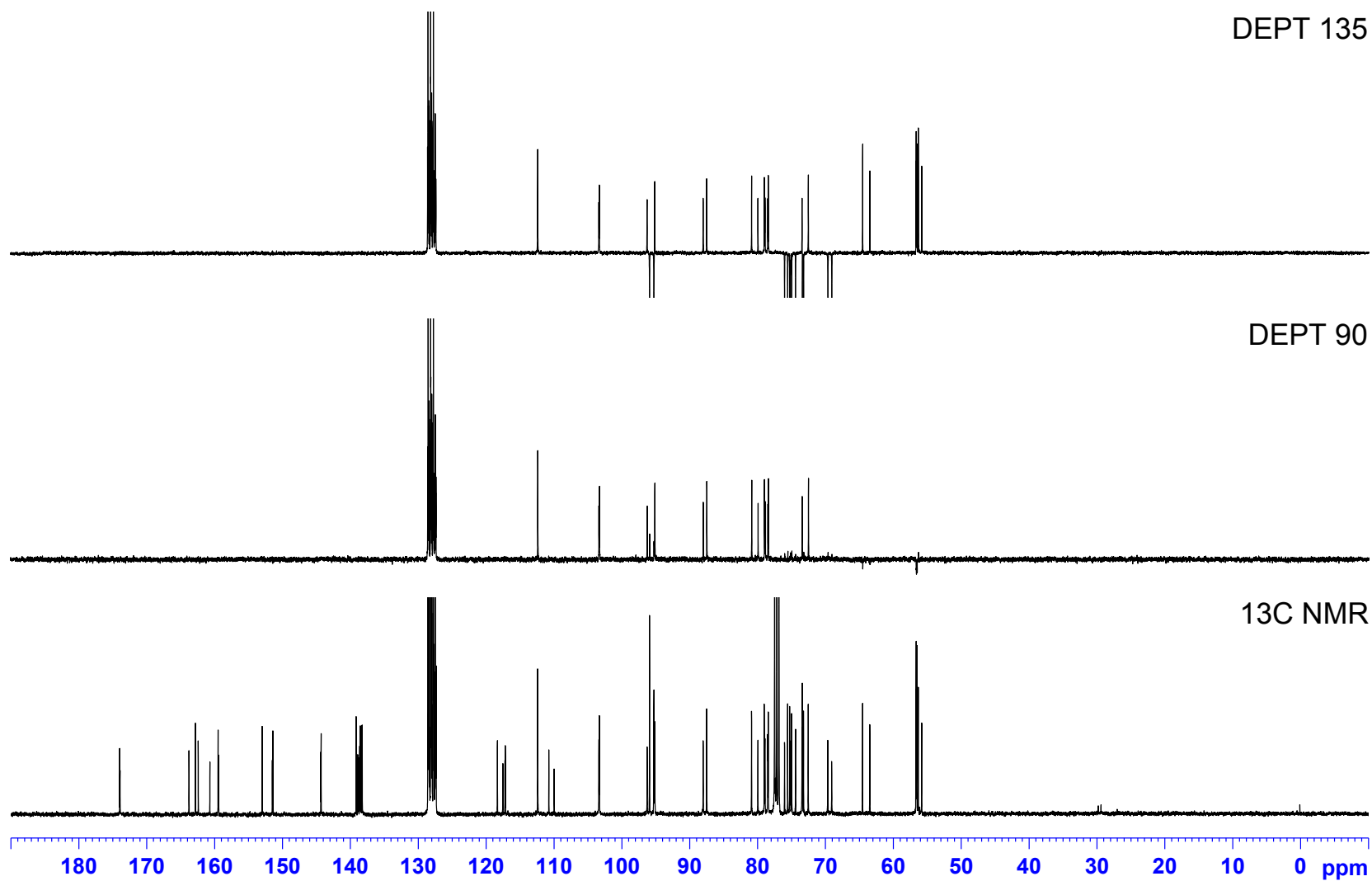




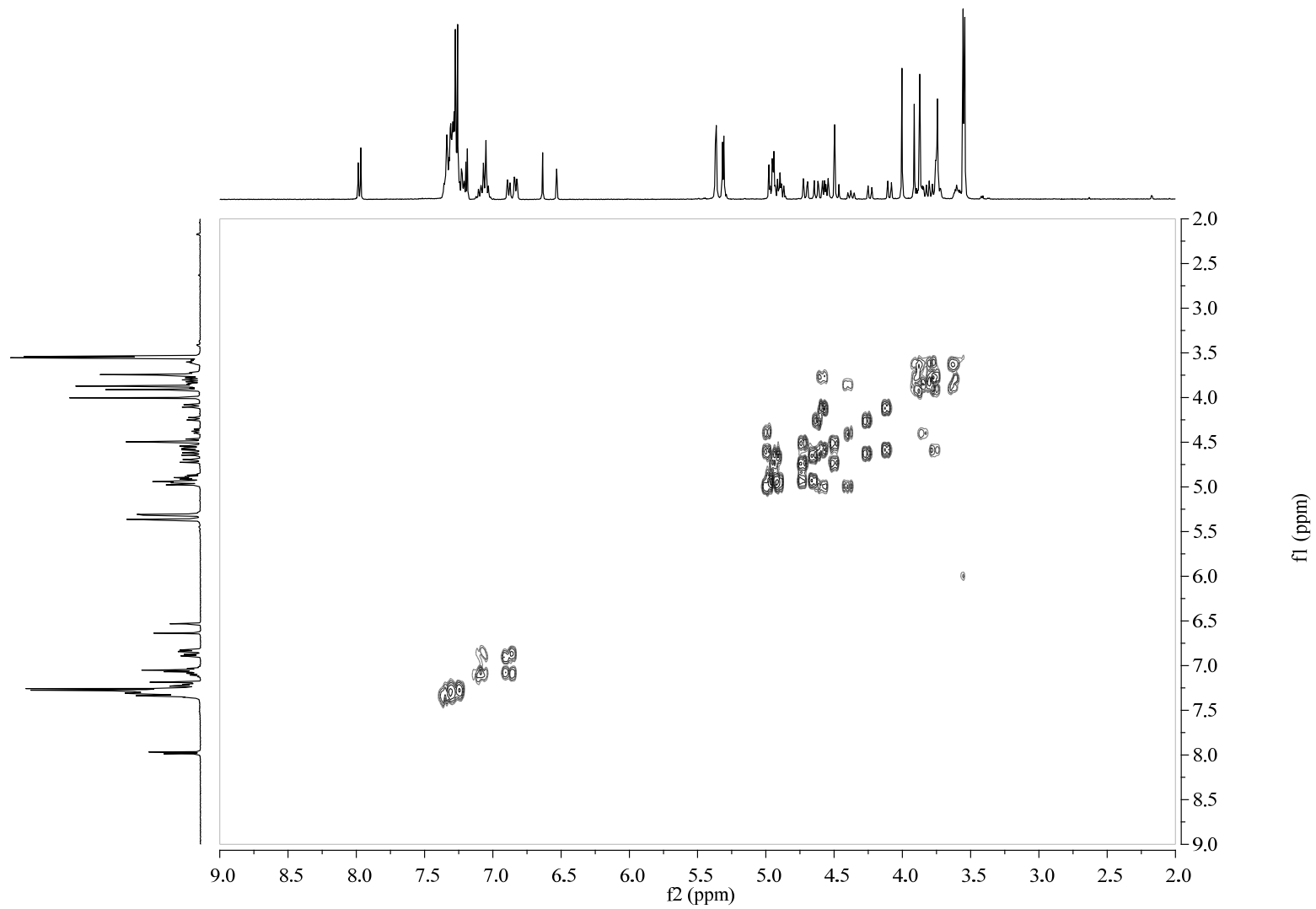
**<sup>13</sup>C NMR spectrum of Compound 16a (CDCl<sub>3</sub>, 100 MHz)**



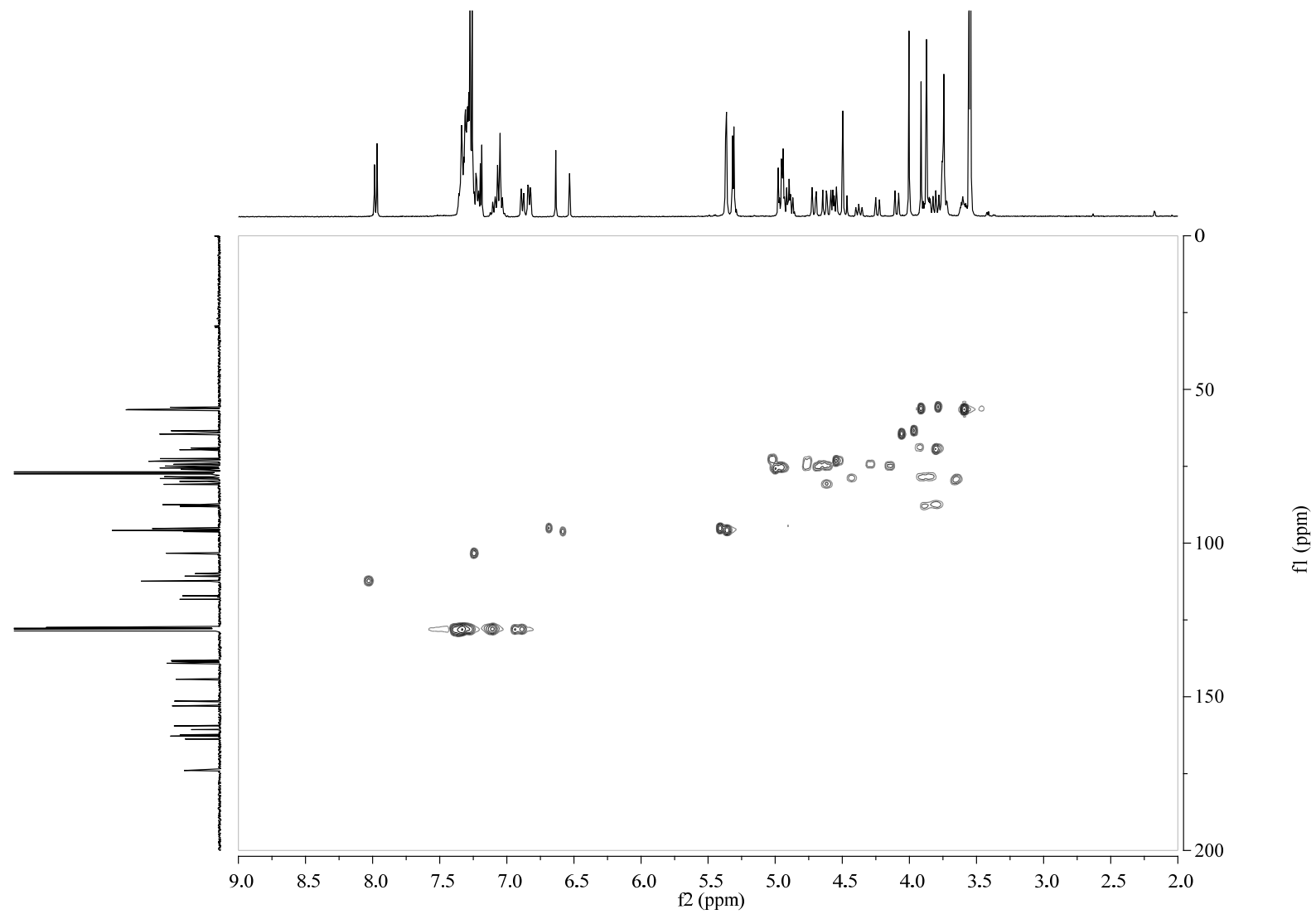
DEPT spectrum of Compound 16a (CDCl<sub>3</sub>, 100 MHz)



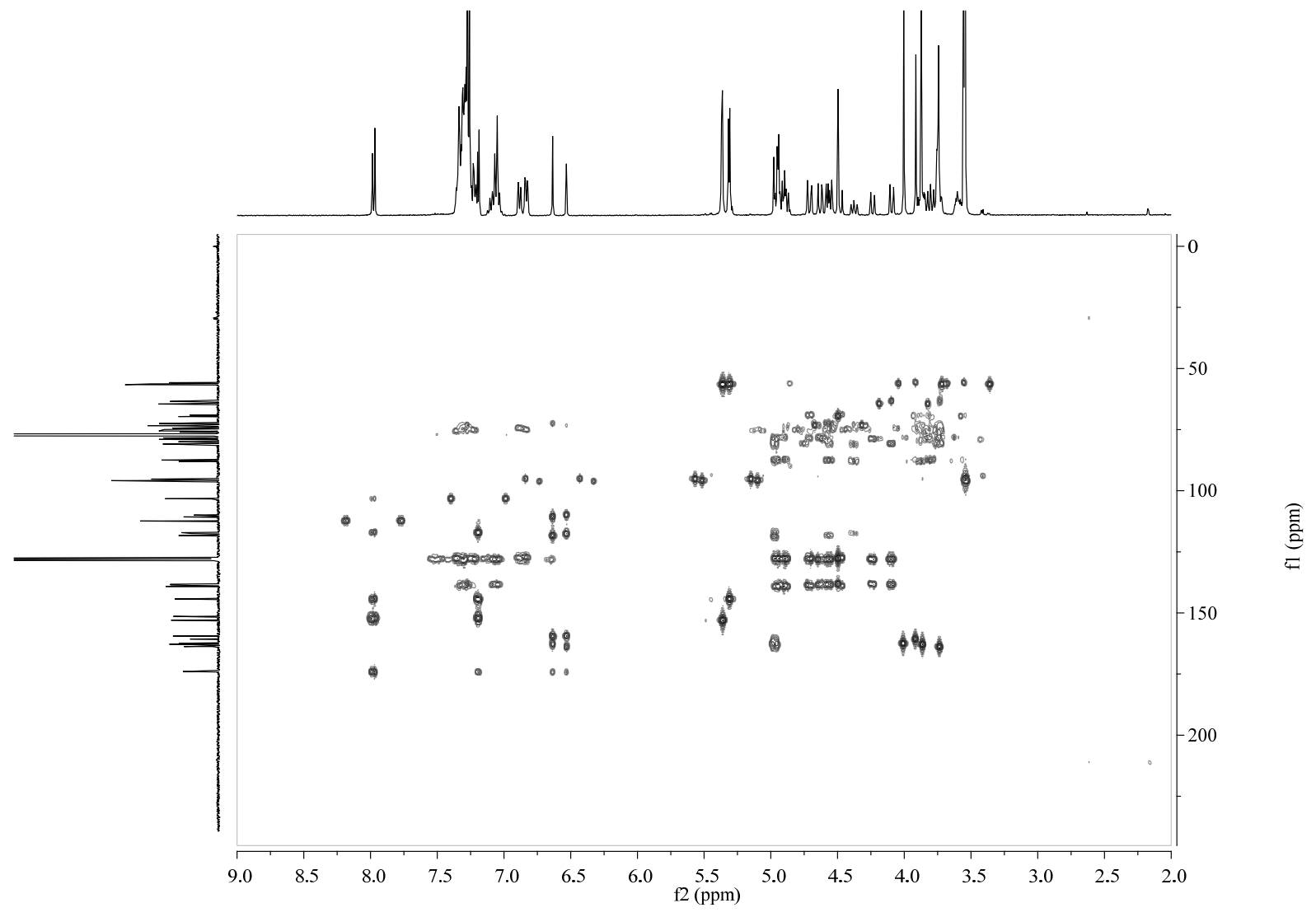
**$^1\text{H}$ - $^1\text{H}$  COSY spectrum of Compound 16a ( $\text{CDCl}_3$ )**



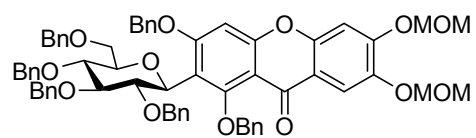
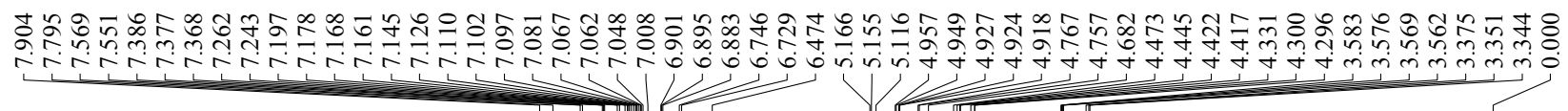
HSQC spectrum of Compound 16a (CDCl<sub>3</sub>)



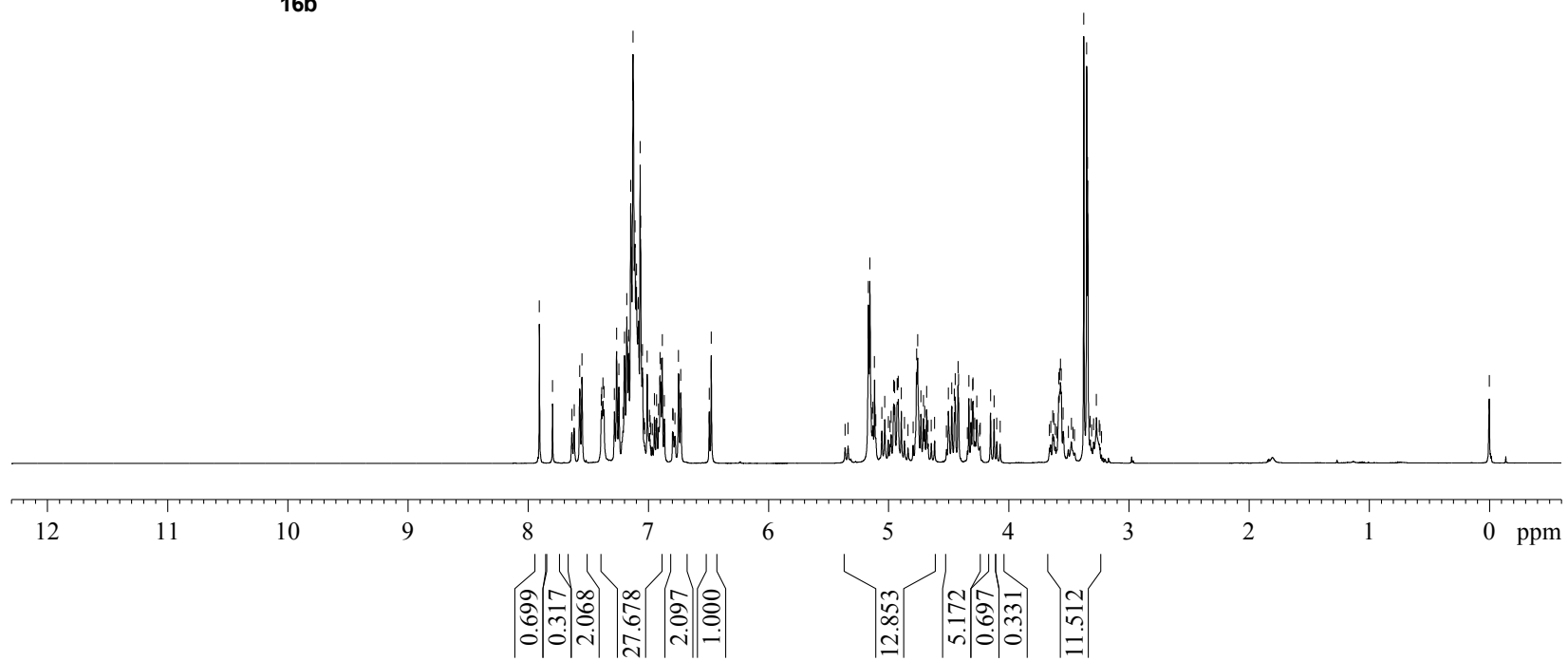
HMBC spectrum of Compound 16a (CDCl<sub>3</sub>)



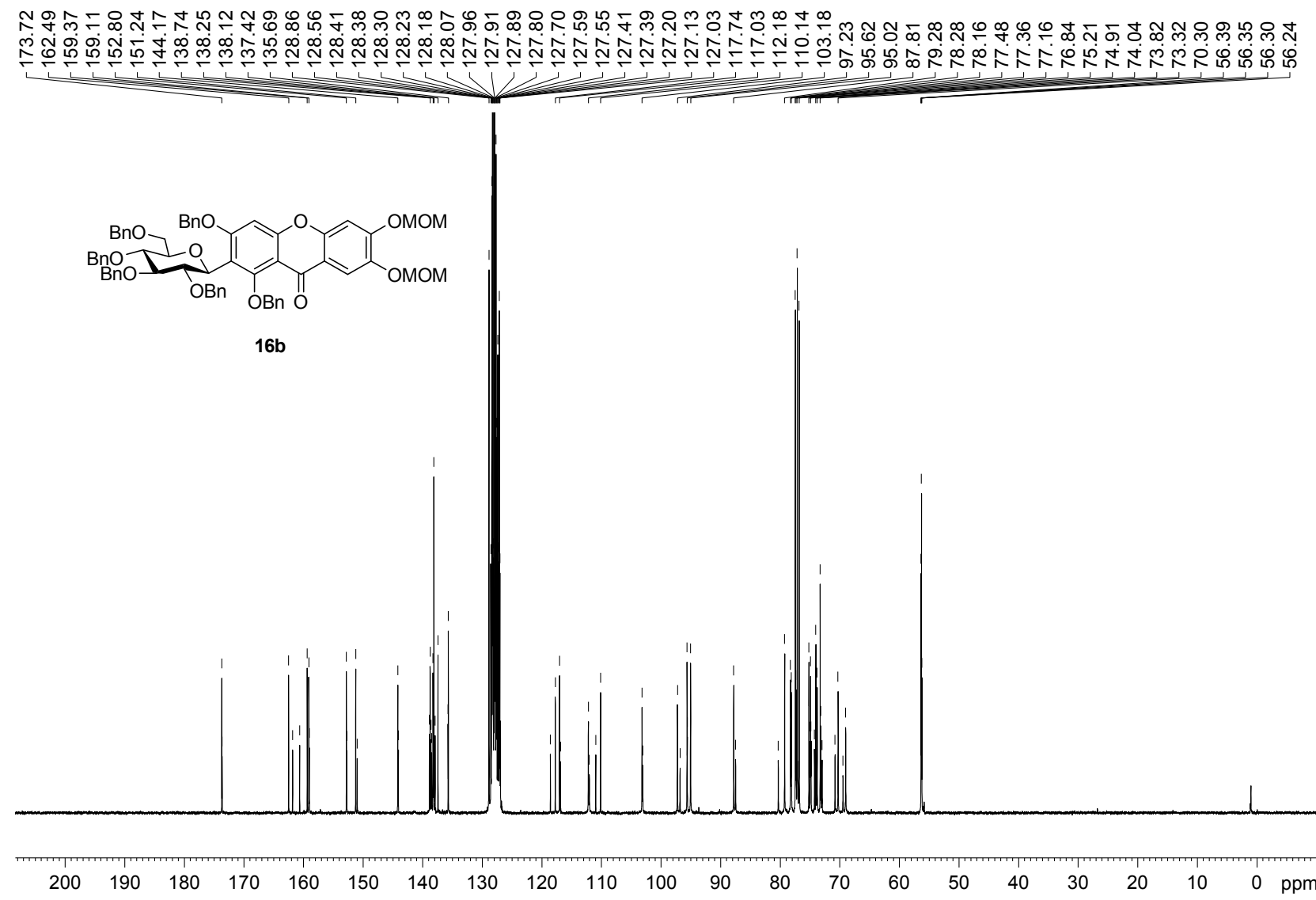
**<sup>1</sup>H NMR spectrum of Compound 16b (CDCl<sub>3</sub>, 400 MHz)**



**16b**

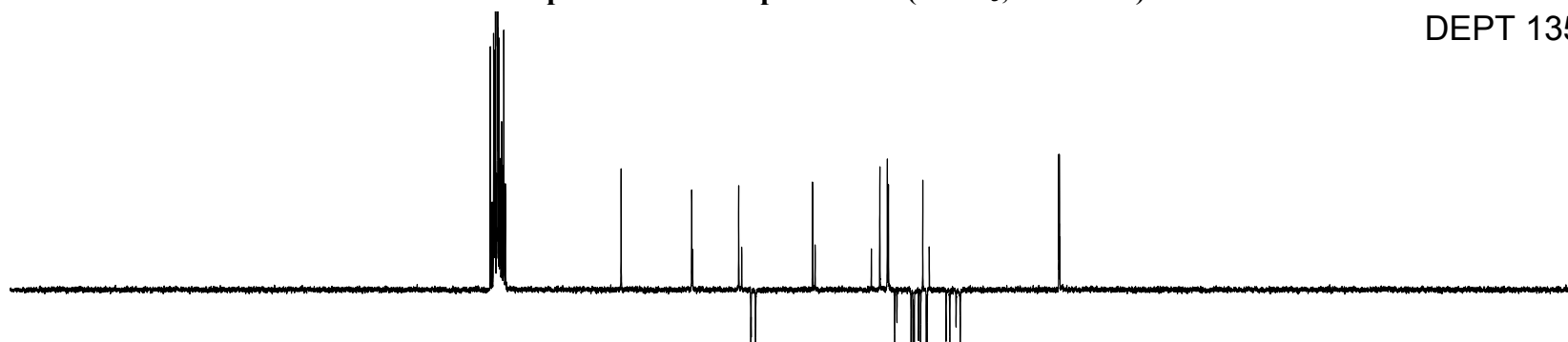


**<sup>13</sup>C NMR spectrum of Compound 16b (CDCl<sub>3</sub>, 100 MHz)**

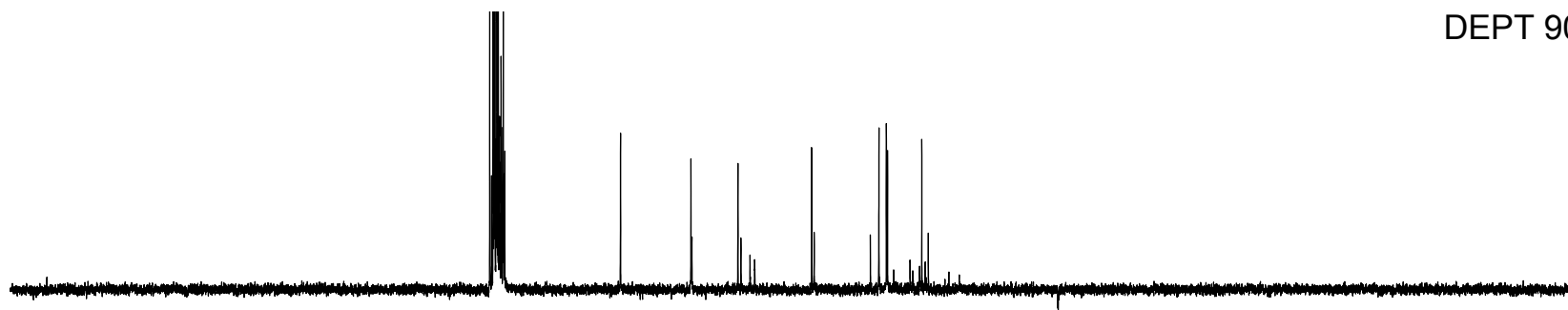


DEPT spectrum of Compound 16b (CDCl<sub>3</sub>, 100 MHz)

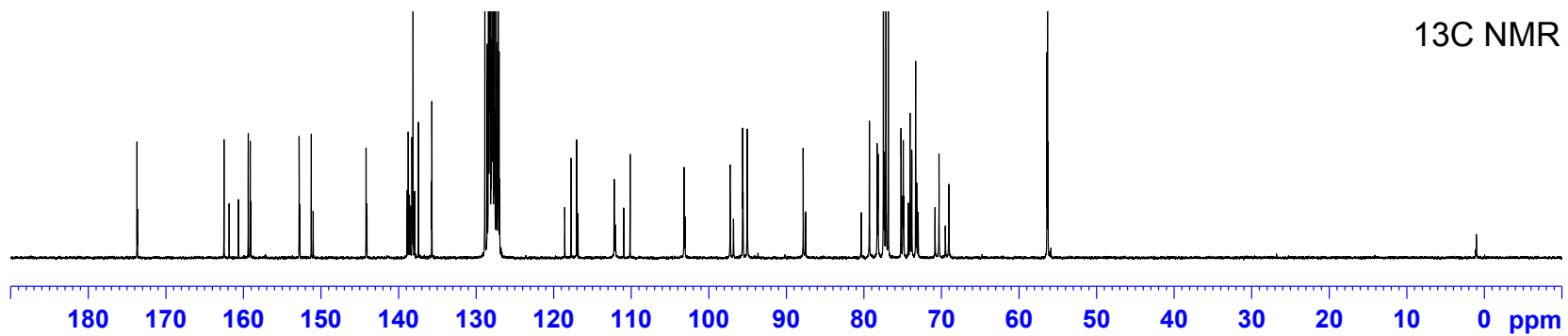
DEPT 135



DEPT 90

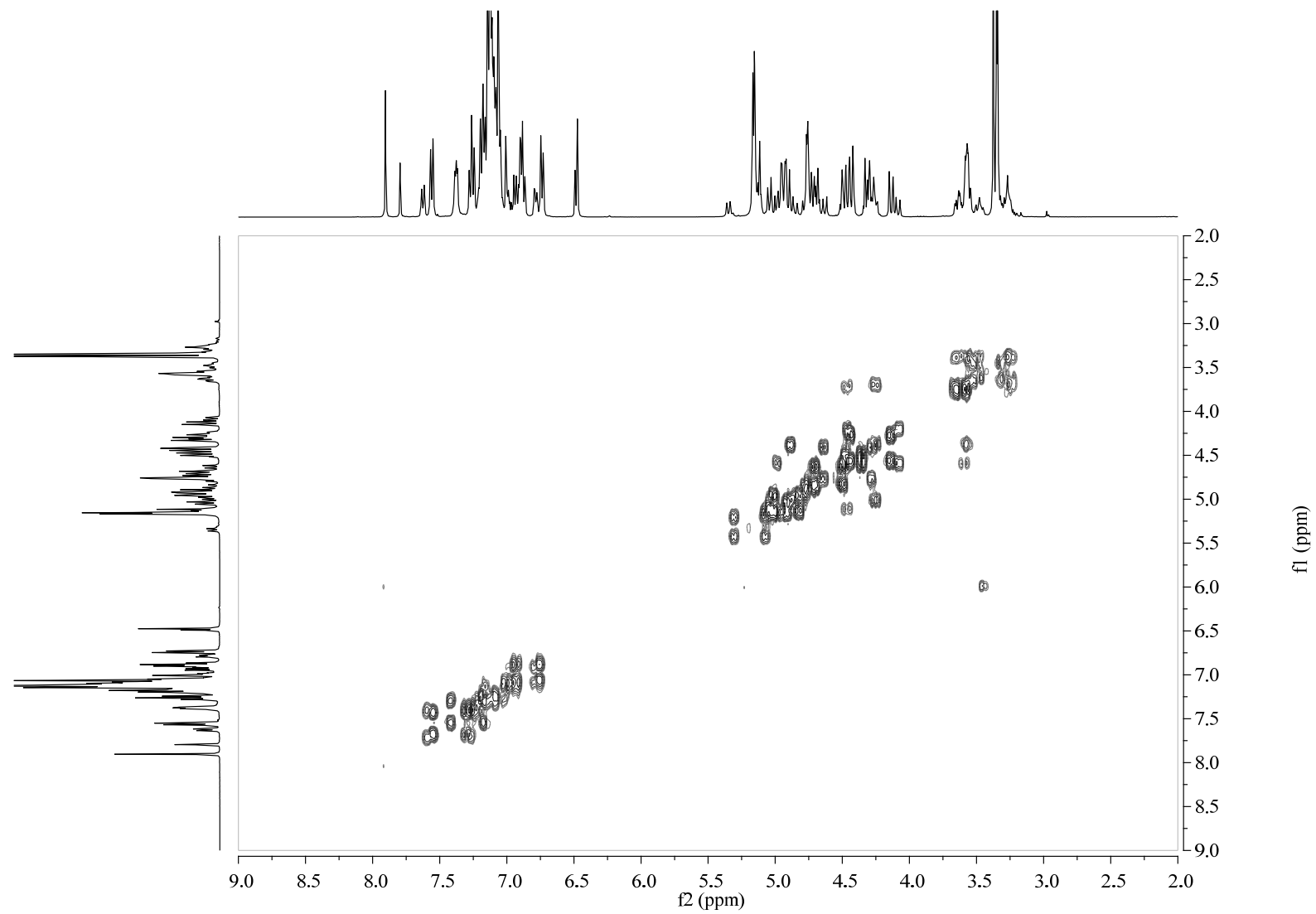


<sup>13</sup>C NMR

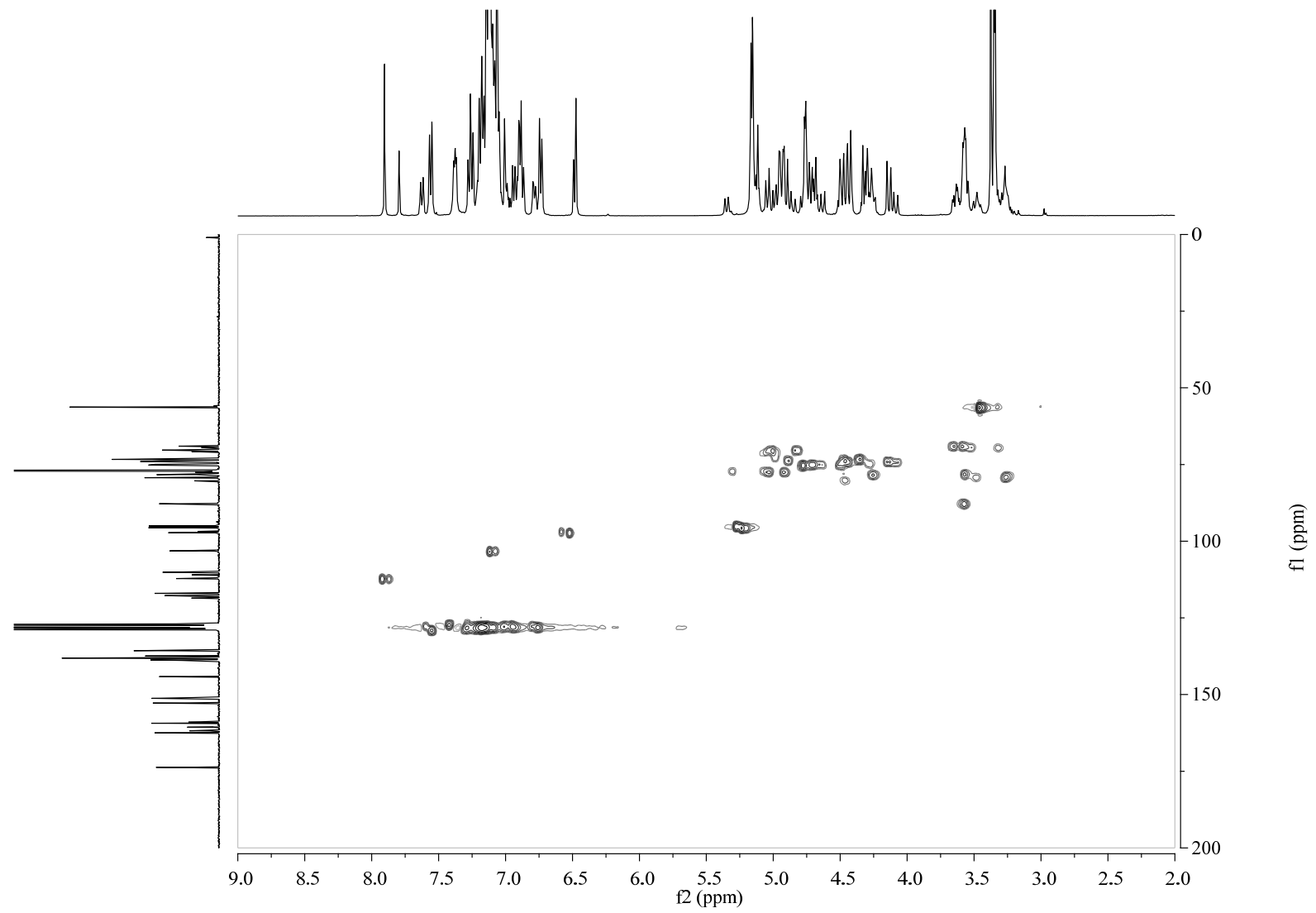




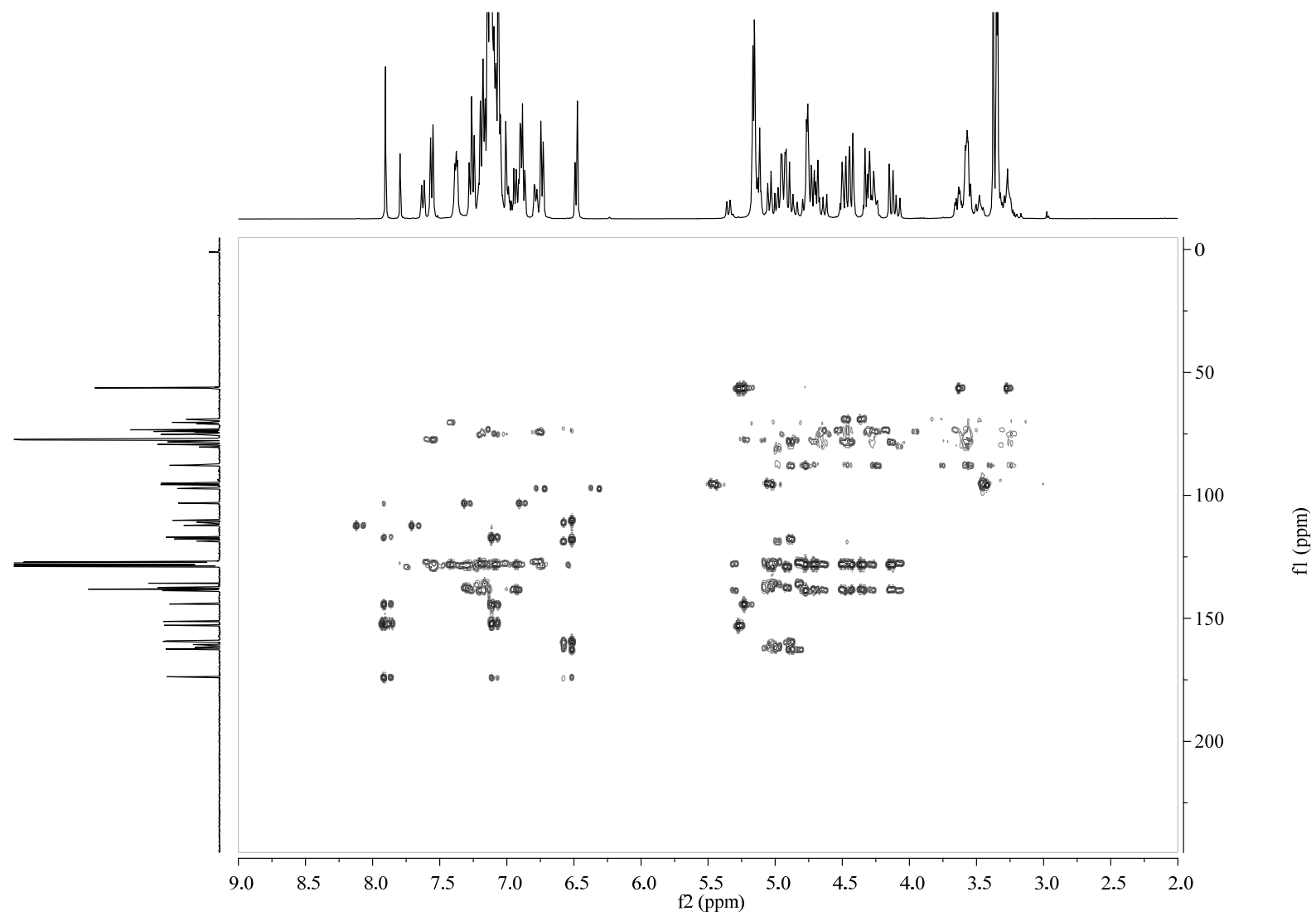
**$^1\text{H}$ - $^1\text{H}$  COSY spectrum of Compound 16b ( $\text{CDCl}_3$ )**



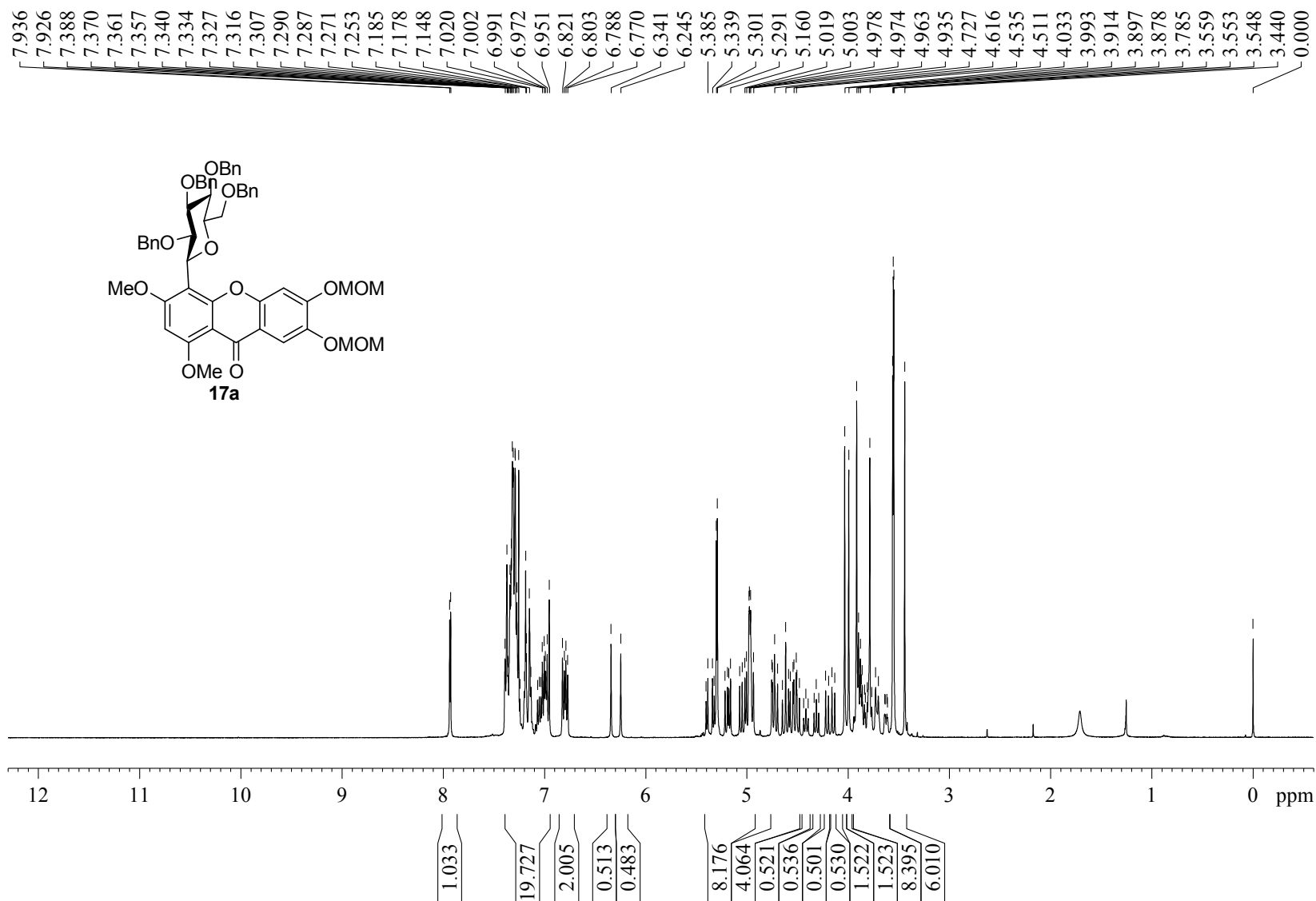
HSQC spectrum of Compound 16b (CDCl<sub>3</sub>)



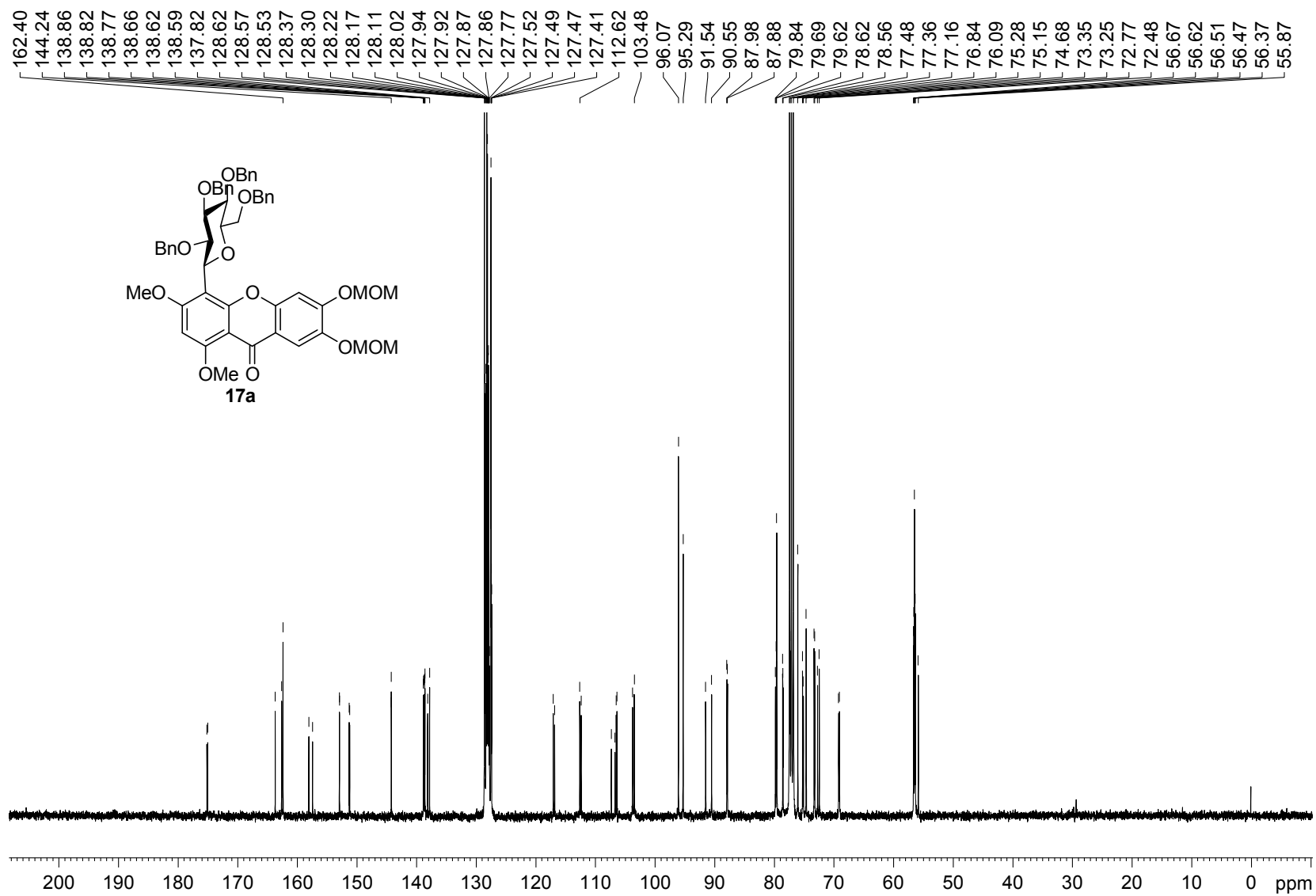
HMBC spectrum of Compound 16b (CDCl<sub>3</sub>)



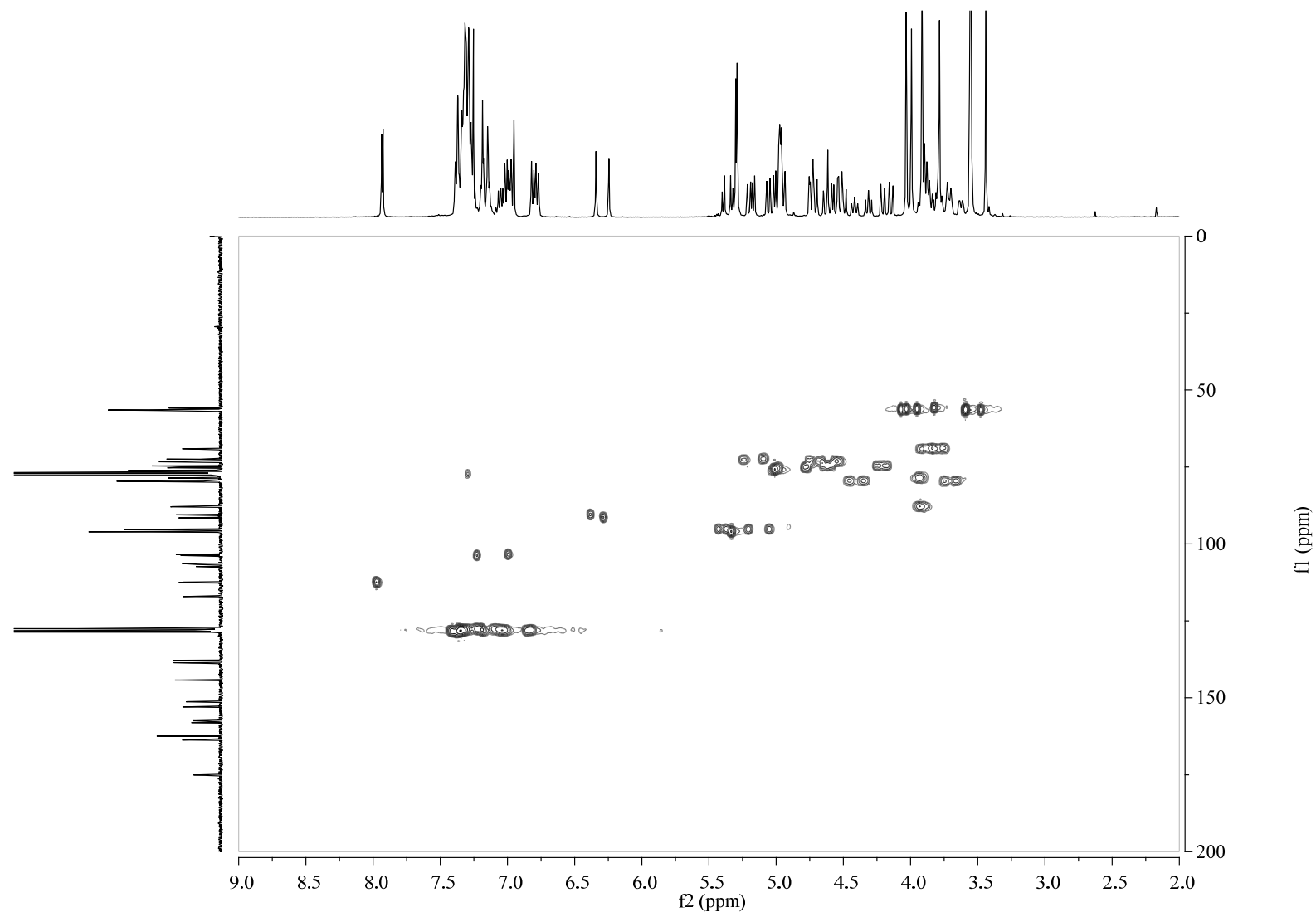
**<sup>1</sup>H NMR spectrum of Compound 17a (CDCl<sub>3</sub>, 400 MHz)**



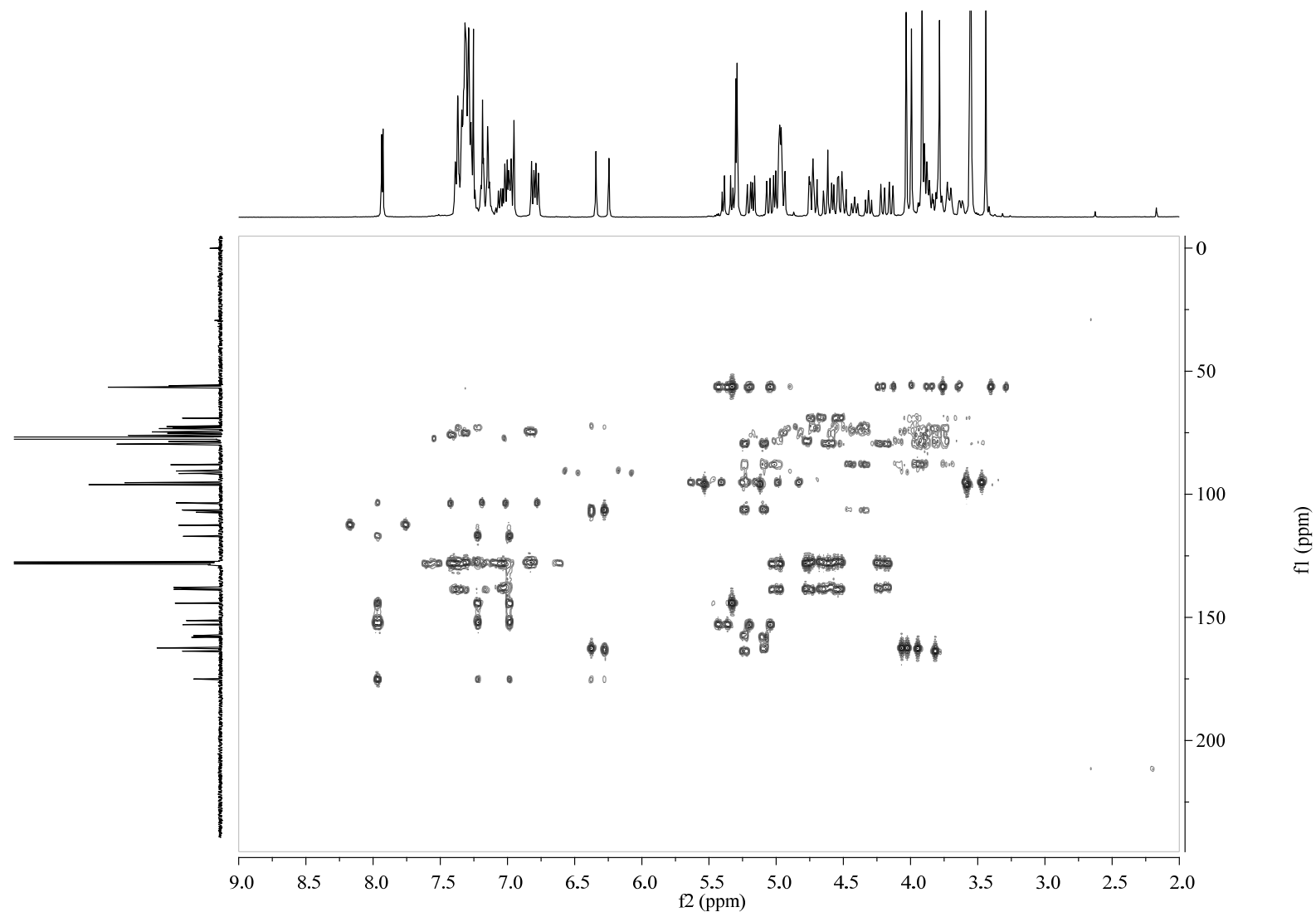
**<sup>13</sup>C NMR spectrum of Compound 17a (CDCl<sub>3</sub>, 100 MHz)**



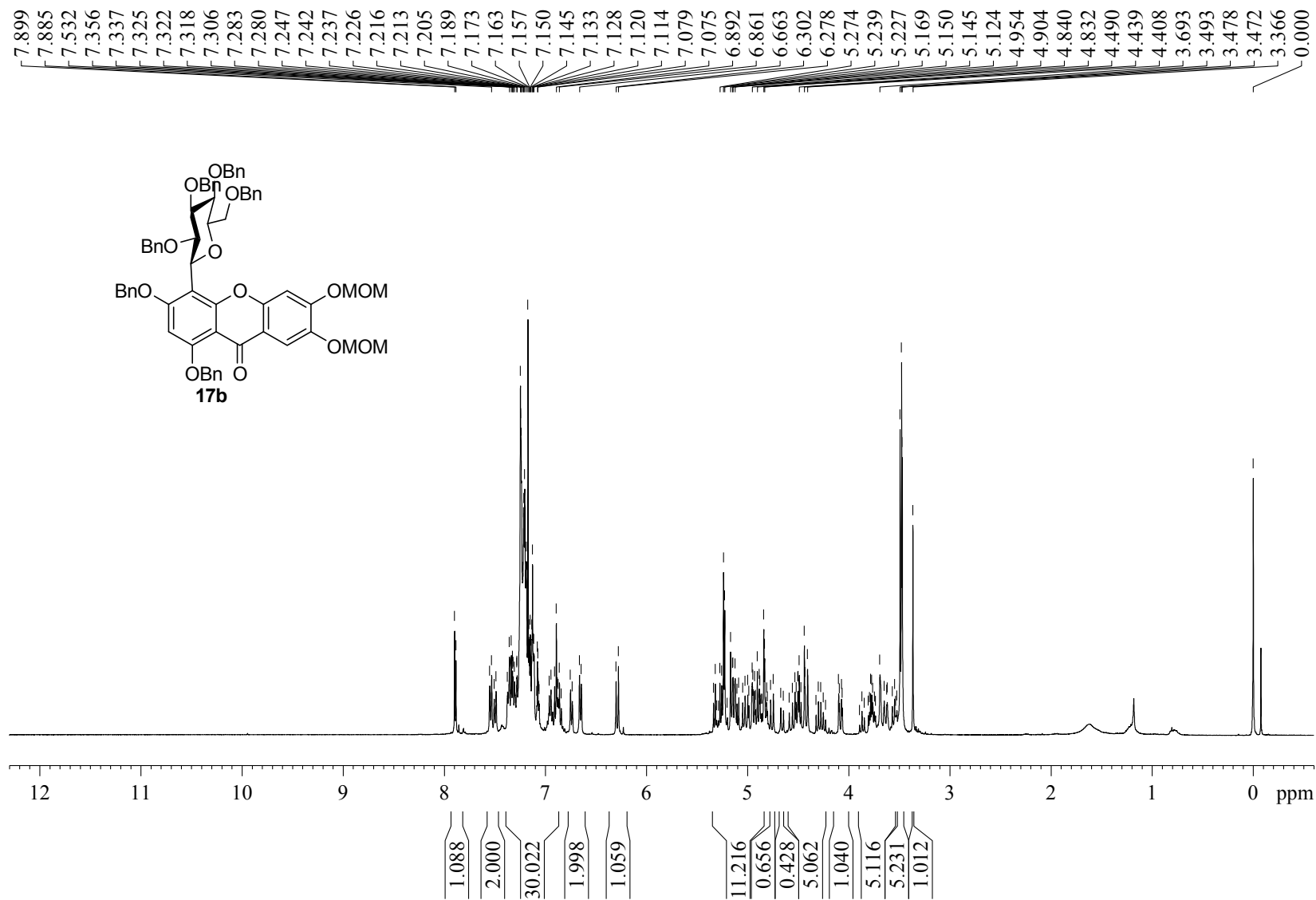
HSQC spectrum of Compound 17a (CDCl<sub>3</sub>)



HMBC spectrum of Compound 17a (CDCl<sub>3</sub>)

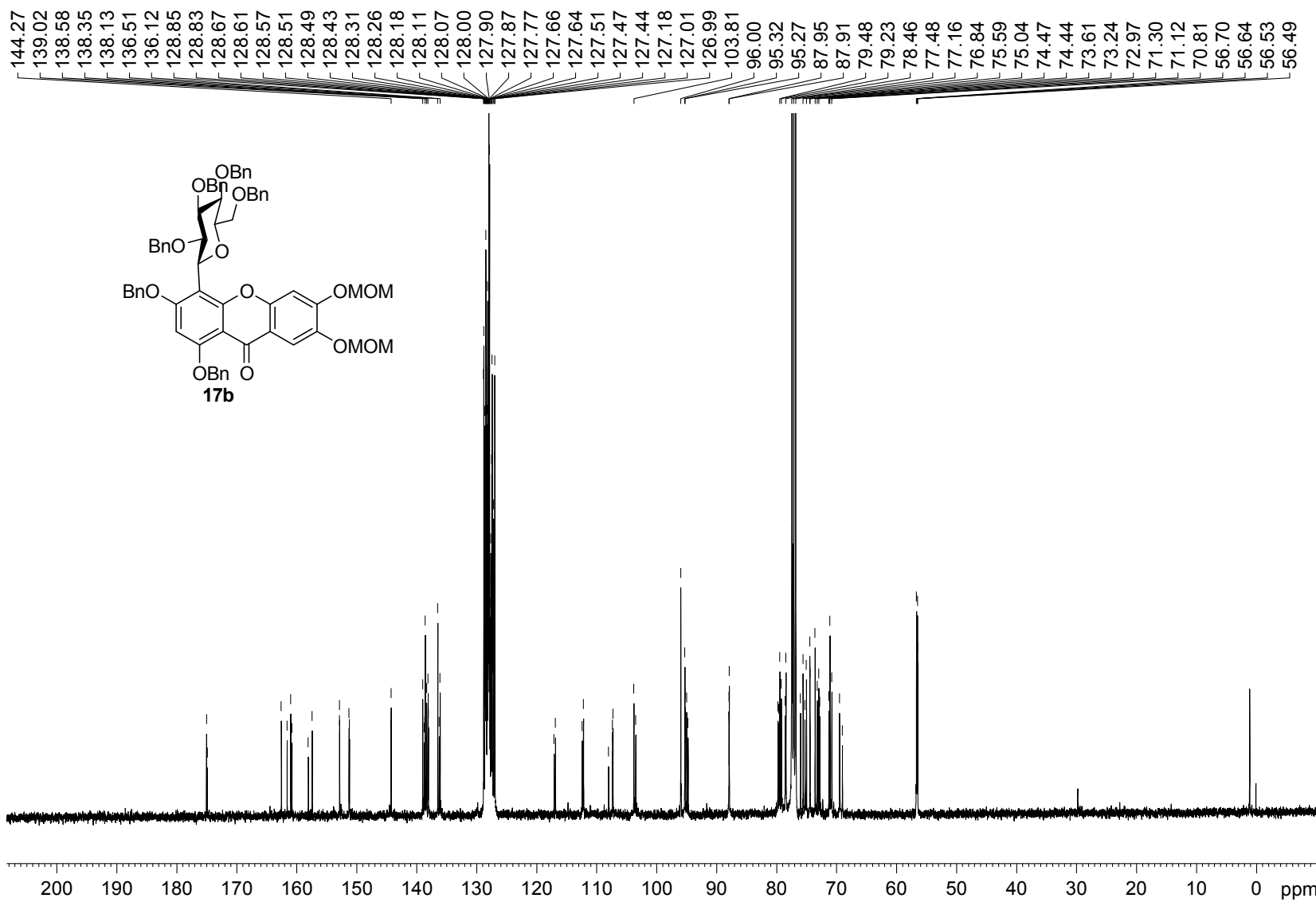


**<sup>1</sup>H NMR spectrum of Compound 17b (CDCl<sub>3</sub>, 400 MHz)**

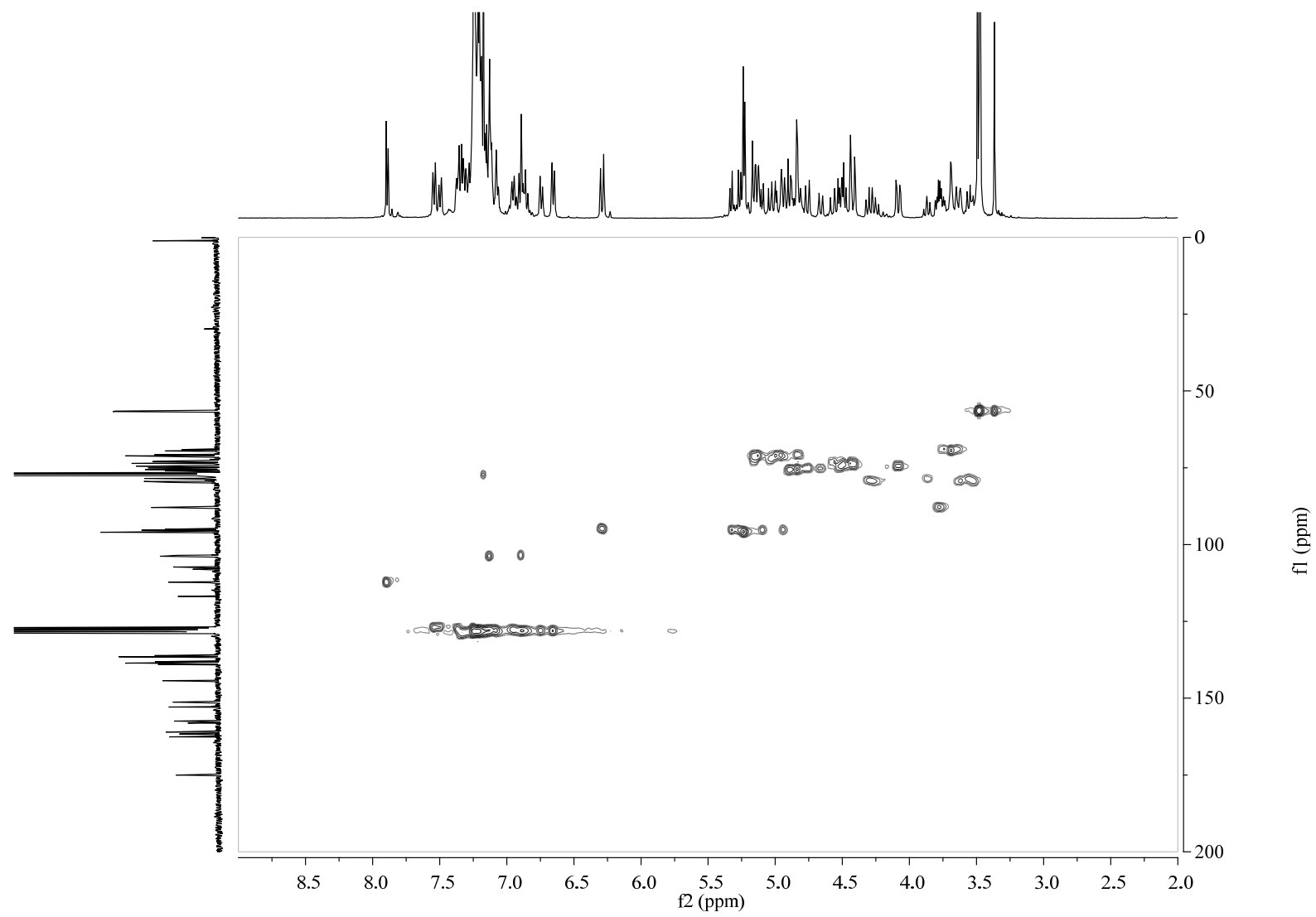




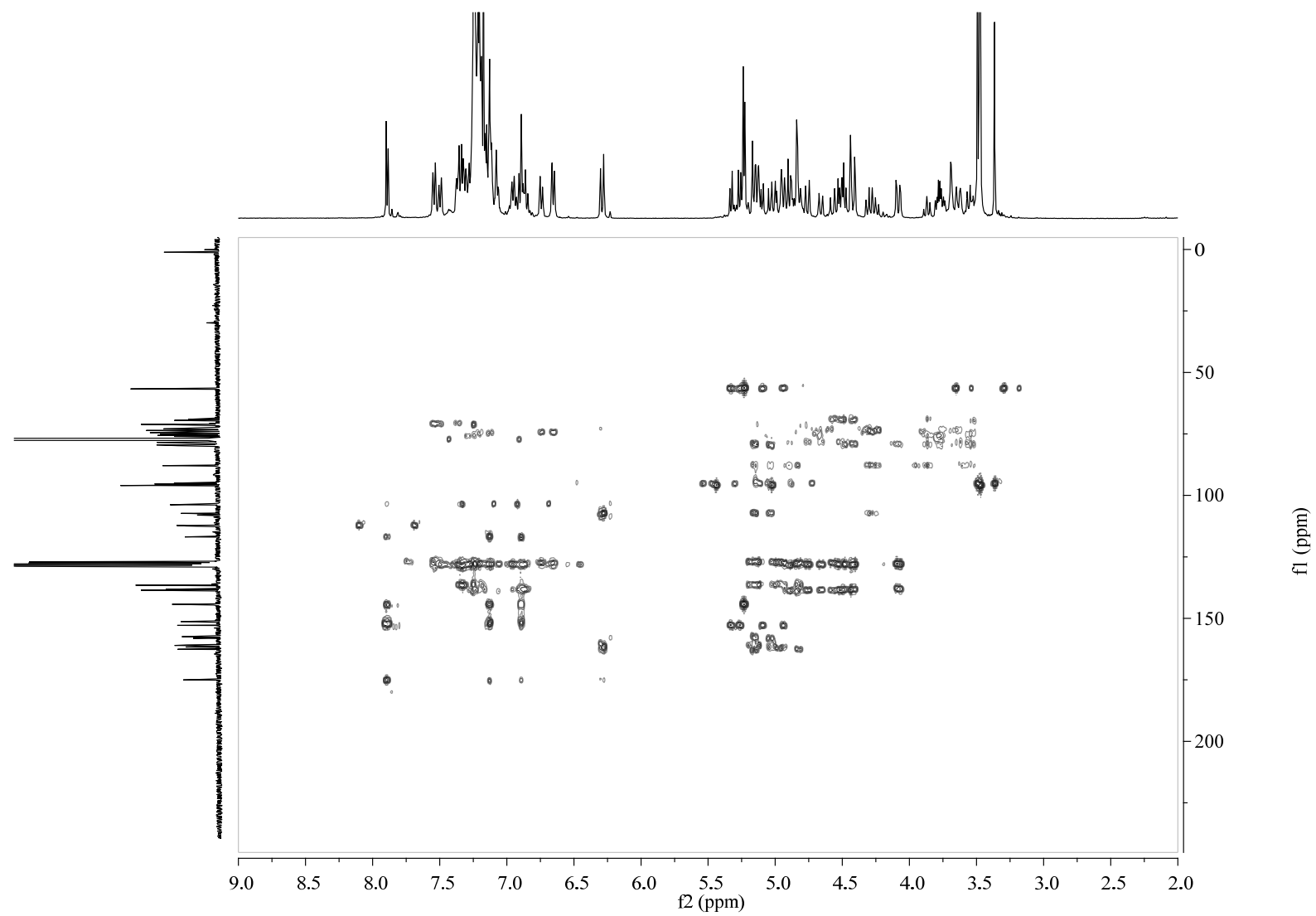
**<sup>13</sup>C NMR spectrum of Compound 17b (CDCl<sub>3</sub>, 100 MHz)**



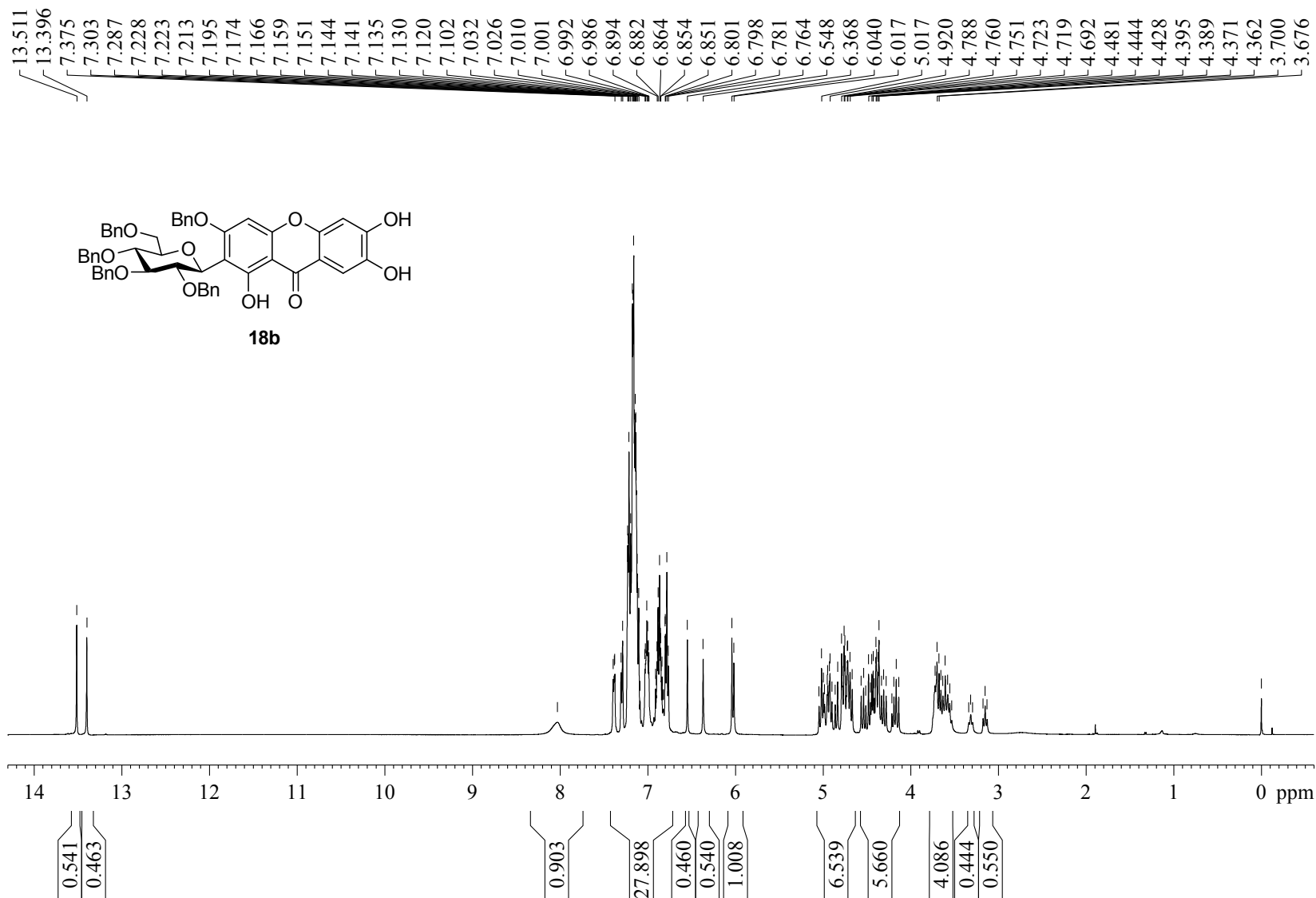
HSQC spectrum of Compound 17b (CDCl<sub>3</sub>)



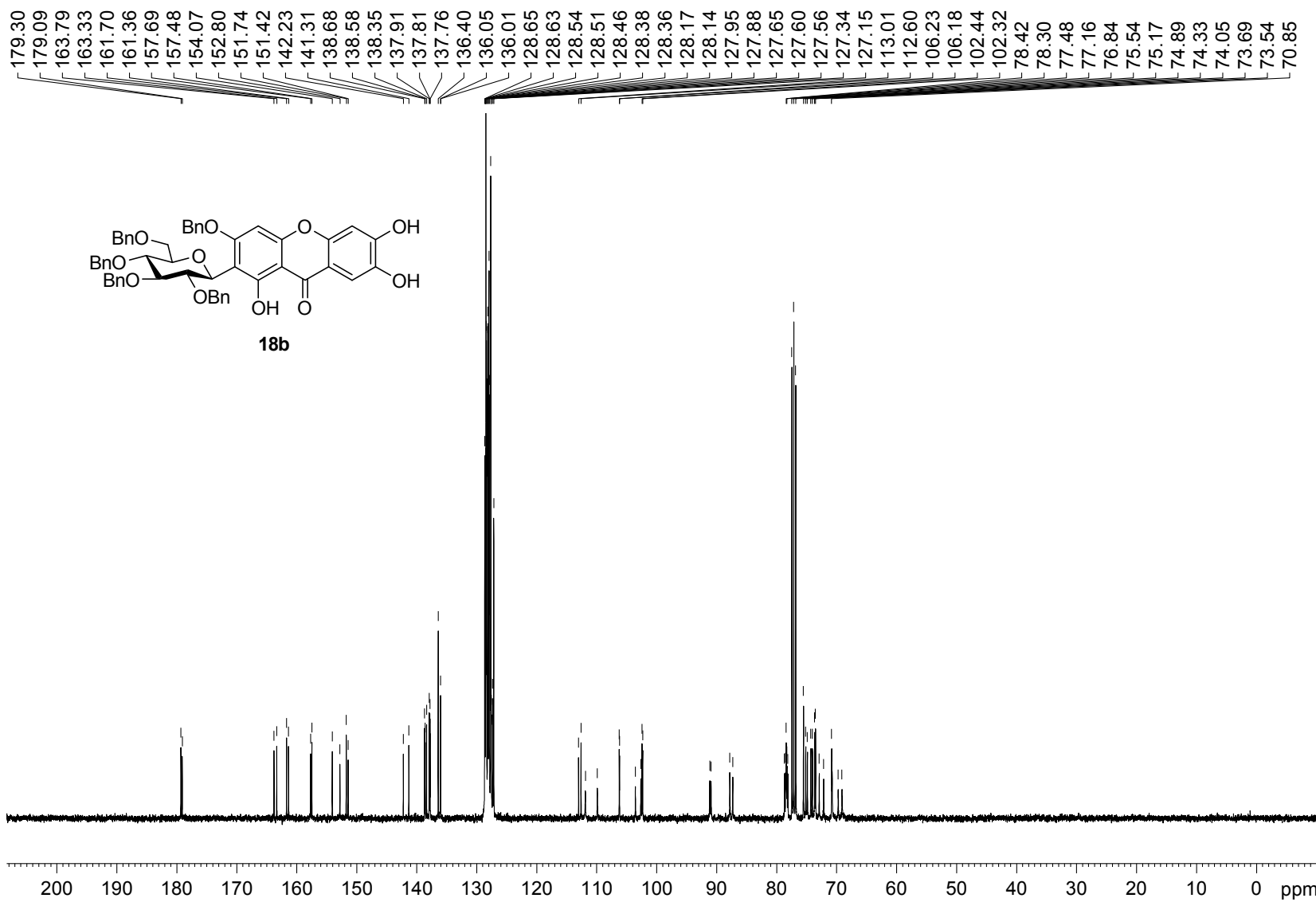
### HMBC spectrum of Compound 17b (CDCl<sub>3</sub>)



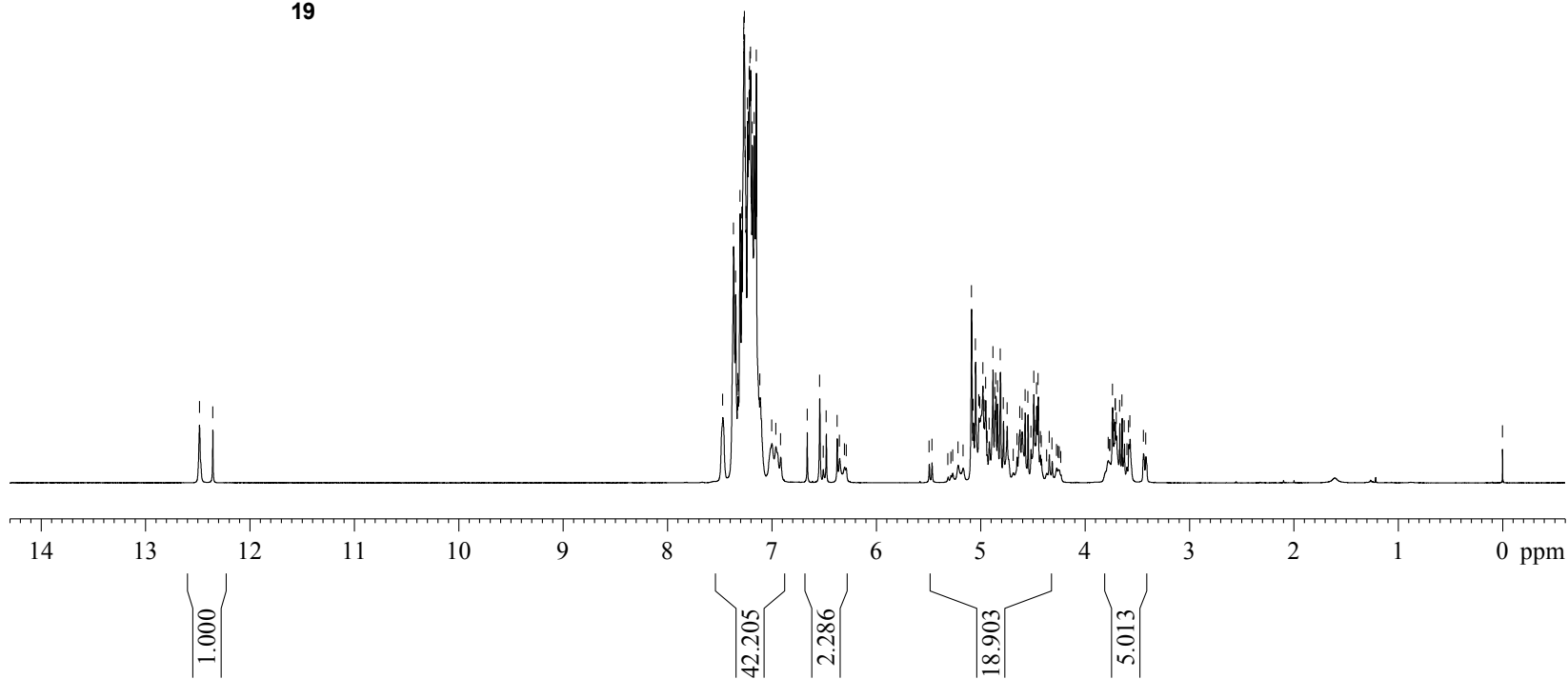
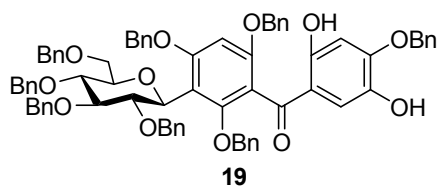
**<sup>1</sup>H NMR spectrum of Compound 18b (CDCl<sub>3</sub>, 400 MHz)**



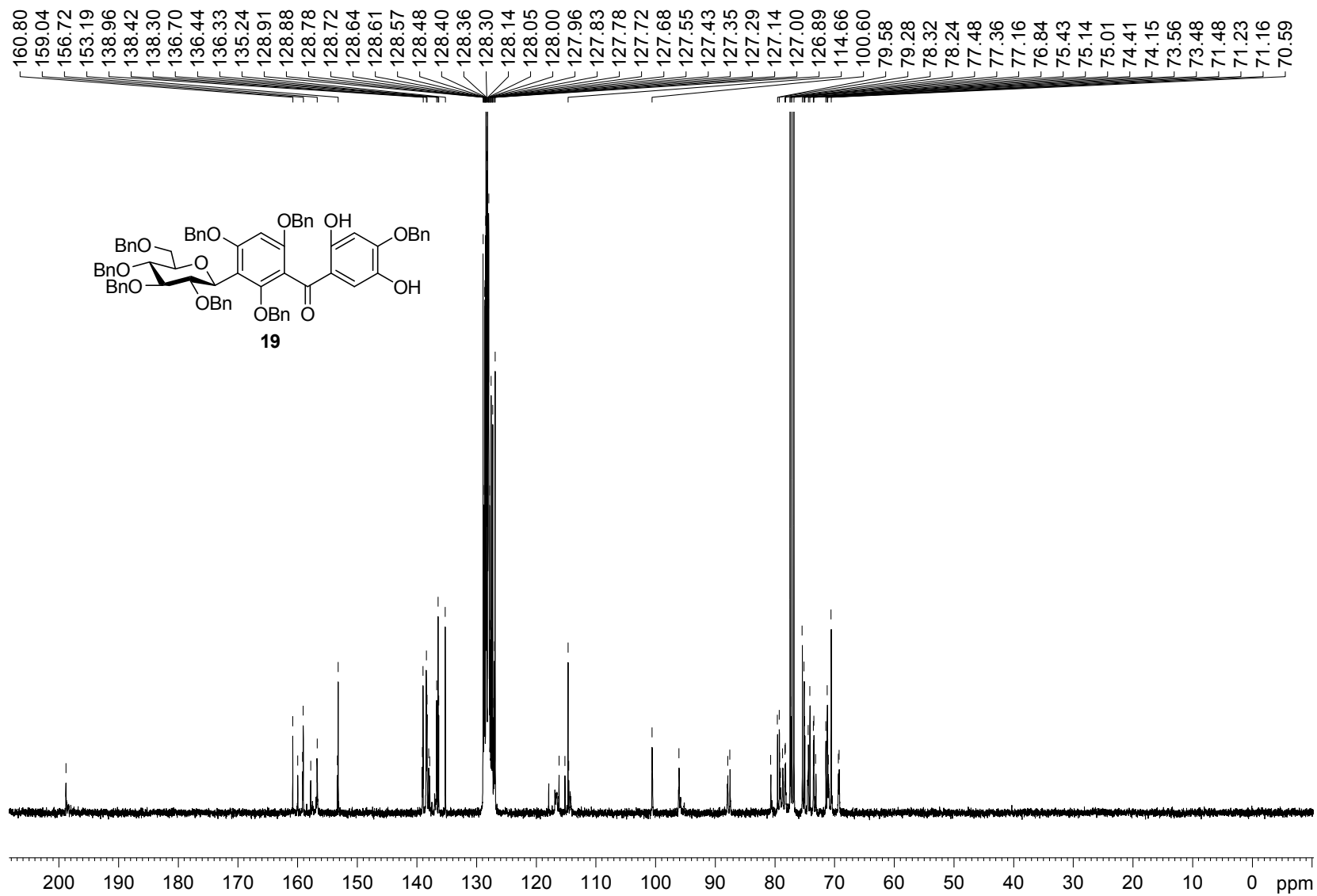
**<sup>13</sup>C NMR spectrum of Compound 18b (CDCl<sub>3</sub>, 100 MHz)**



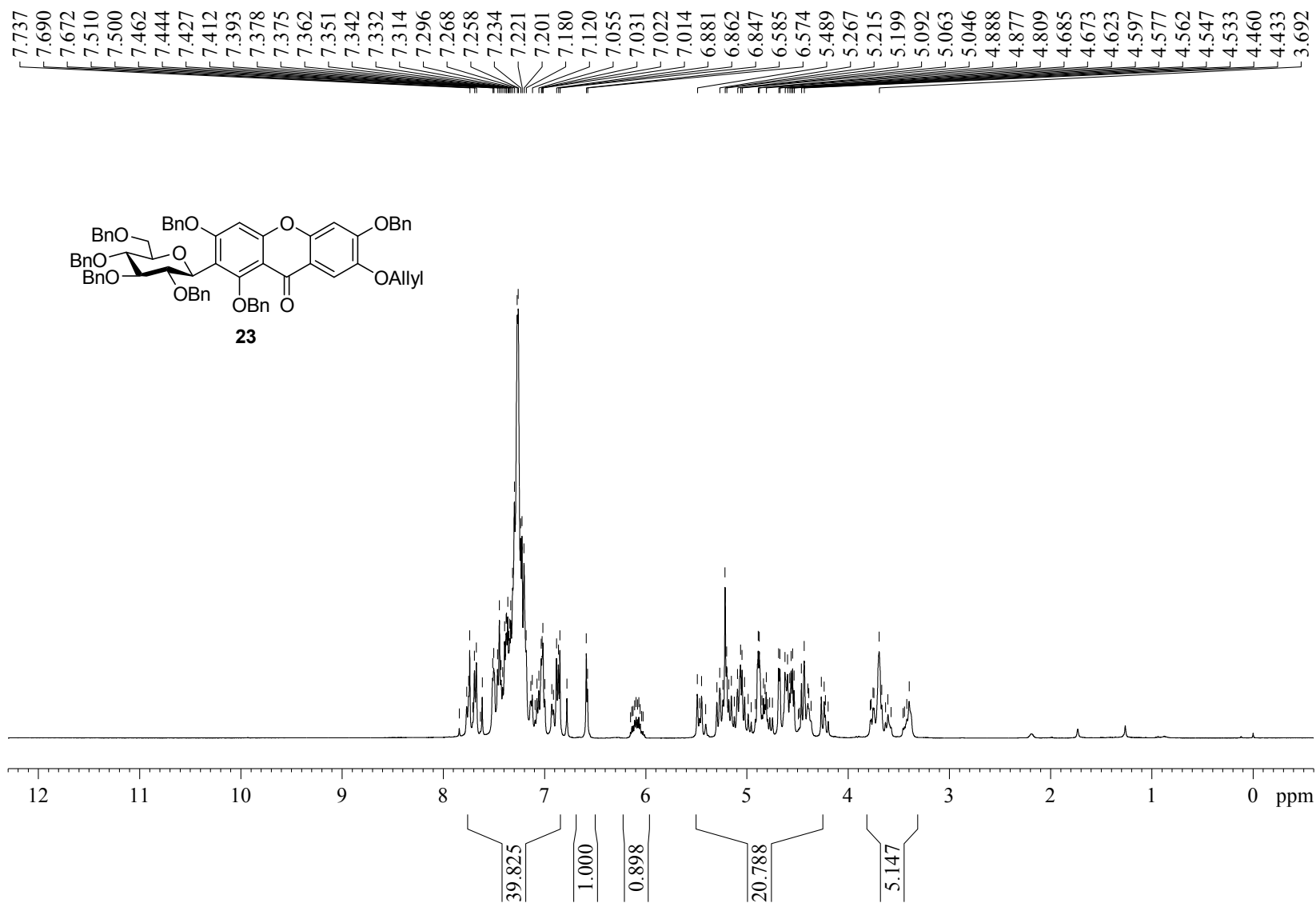
**<sup>1</sup>H NMR spectrum of Compound 19 (CDCl<sub>3</sub>, 400 MHz)**



<sup>13</sup>C NMR spectrum of Compound 19 (CDCl<sub>3</sub>, 100 MHz)

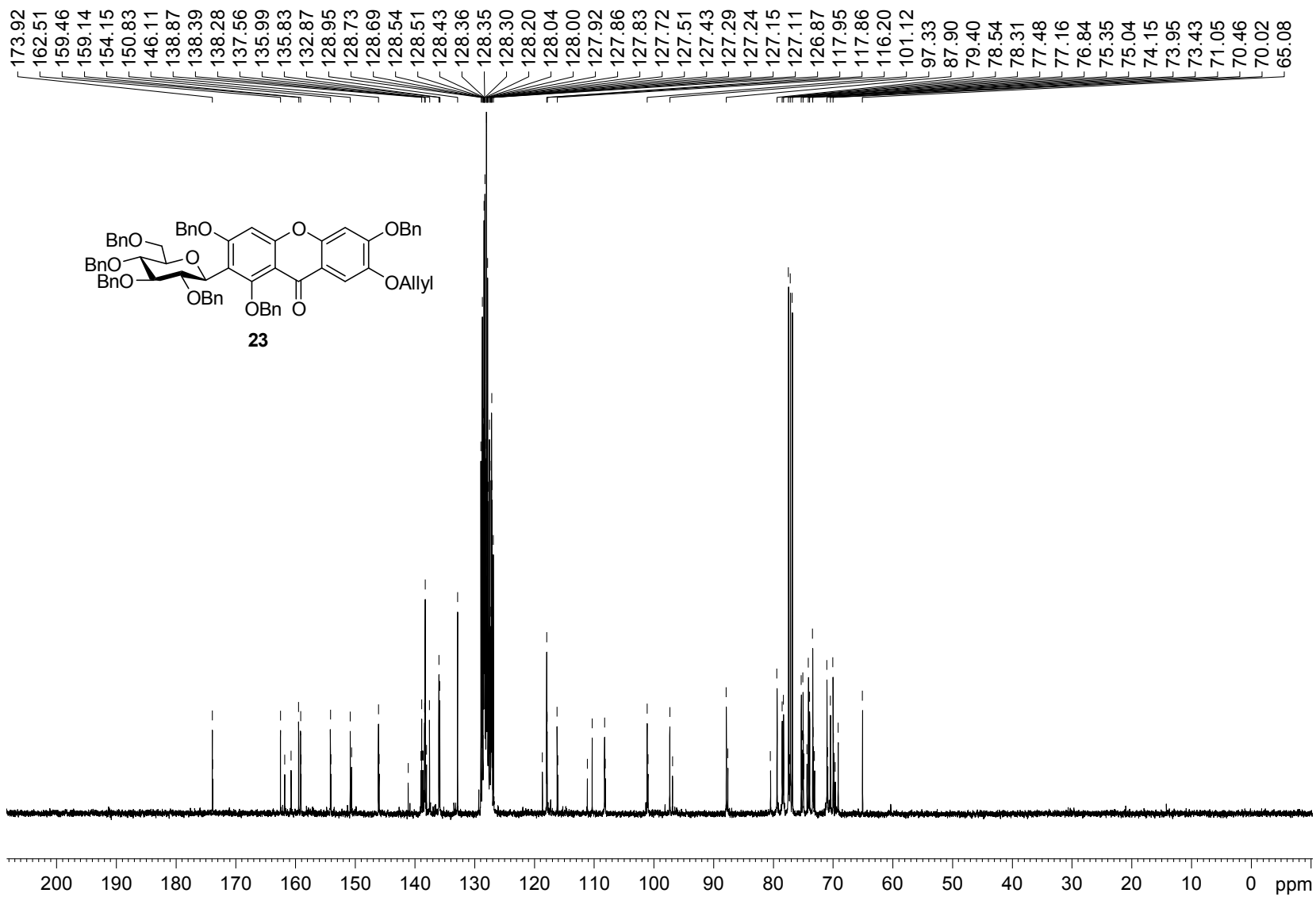


**<sup>1</sup>H NMR spectrum of Compound 23 (CDCl<sub>3</sub>, 400 MHz)**

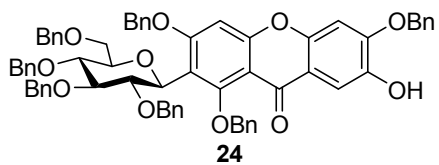
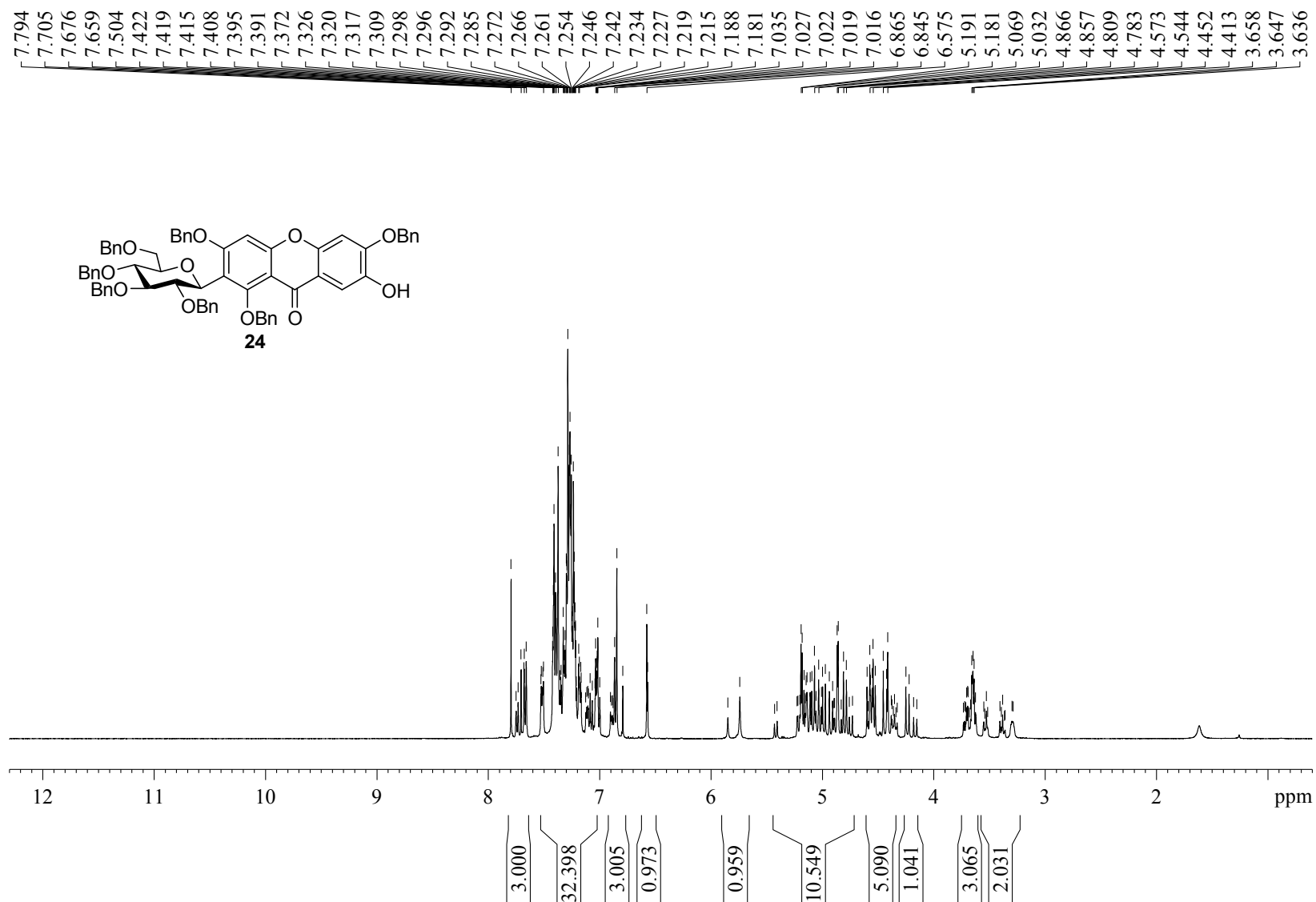




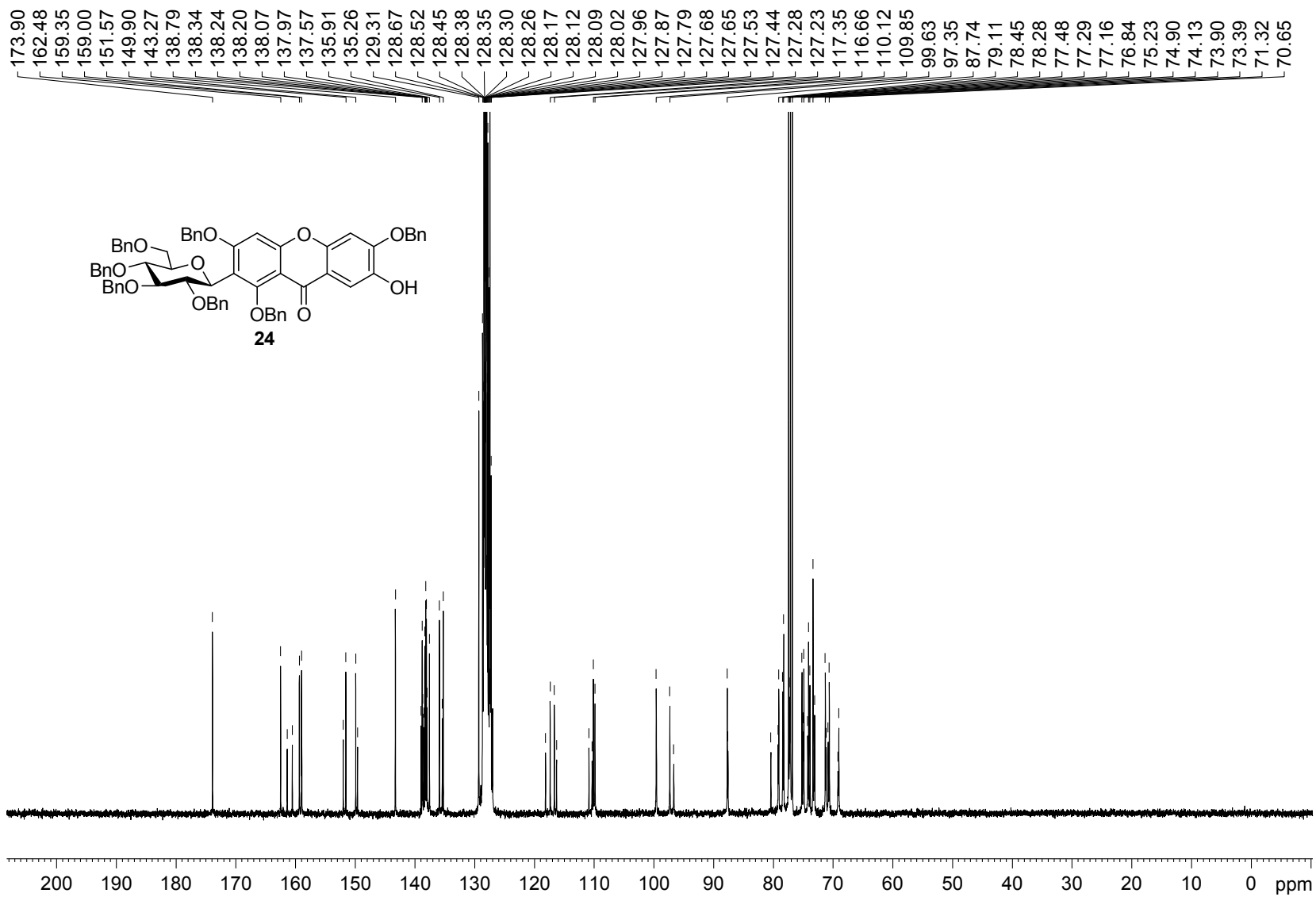
**<sup>13</sup>C NMR spectrum of Compound 23 (CDCl<sub>3</sub>, 100 MHz)**



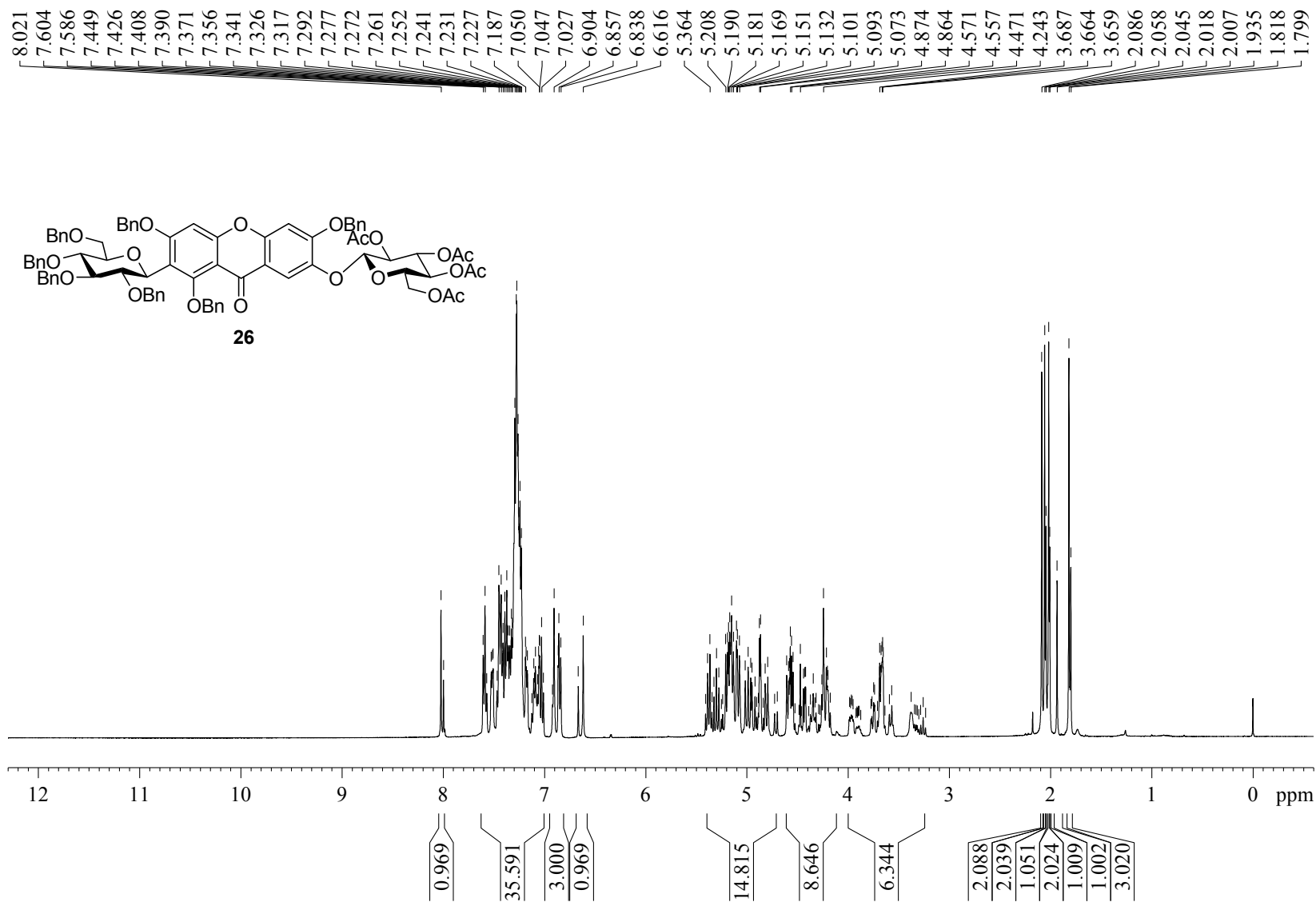
**<sup>1</sup>H NMR spectrum of Compound 24 (CDCl<sub>3</sub>, 400 MHz)**



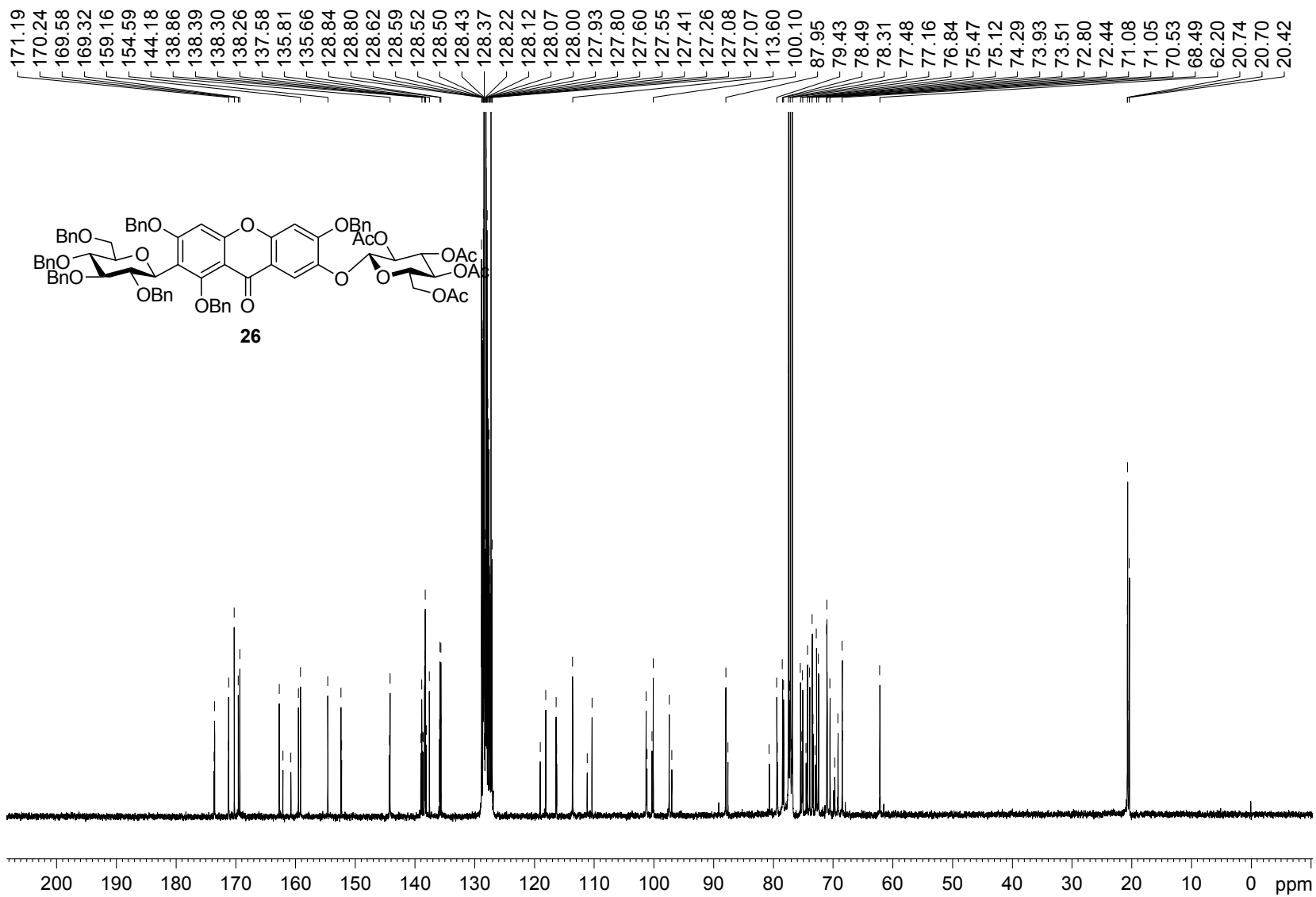
**<sup>13</sup>C NMR spectrum of Compound 24 (CDCl<sub>3</sub>, 100 MHz)**



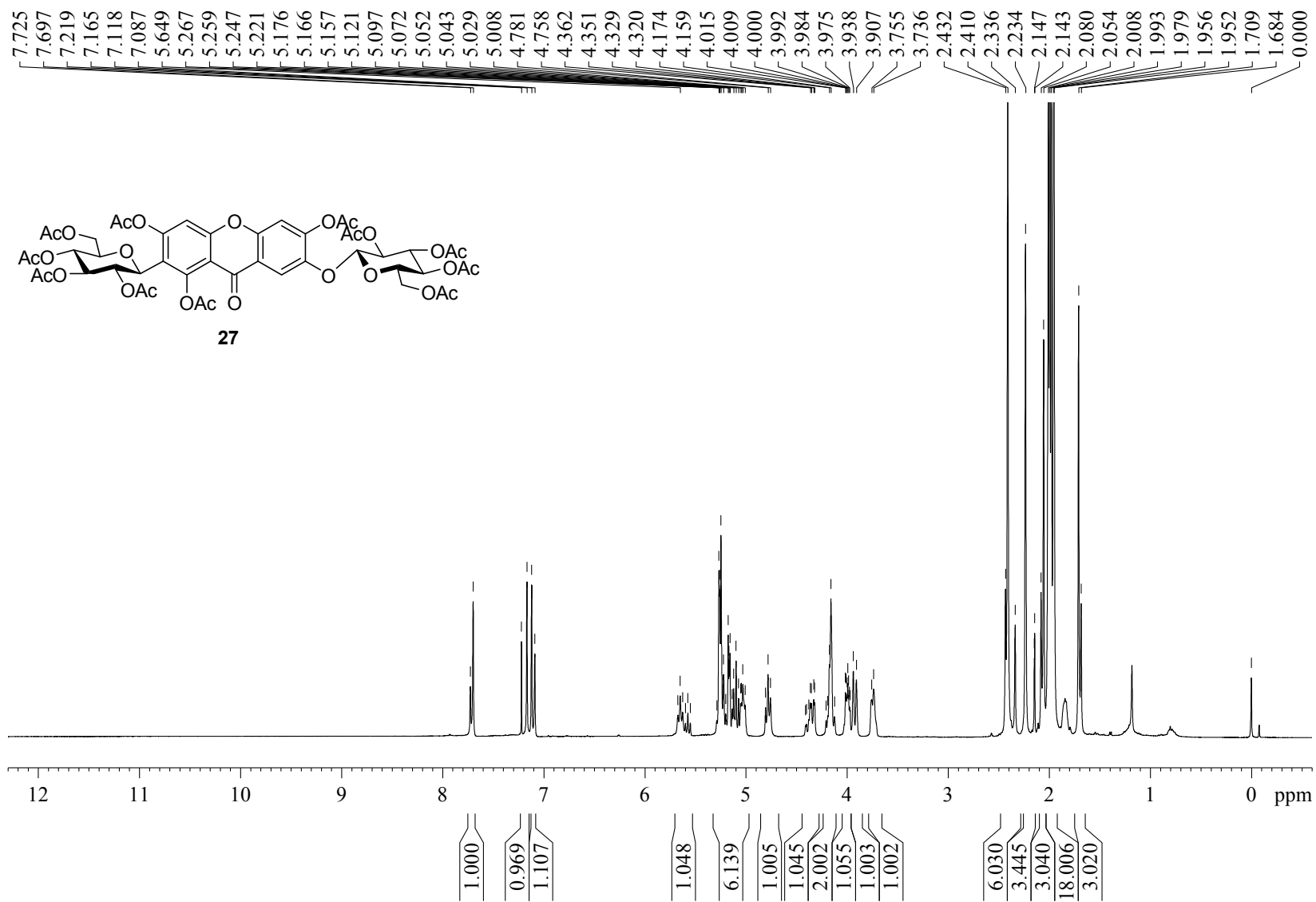
**<sup>1</sup>H NMR spectrum of Compound 26 (CDCl<sub>3</sub>, 400 MHz)**



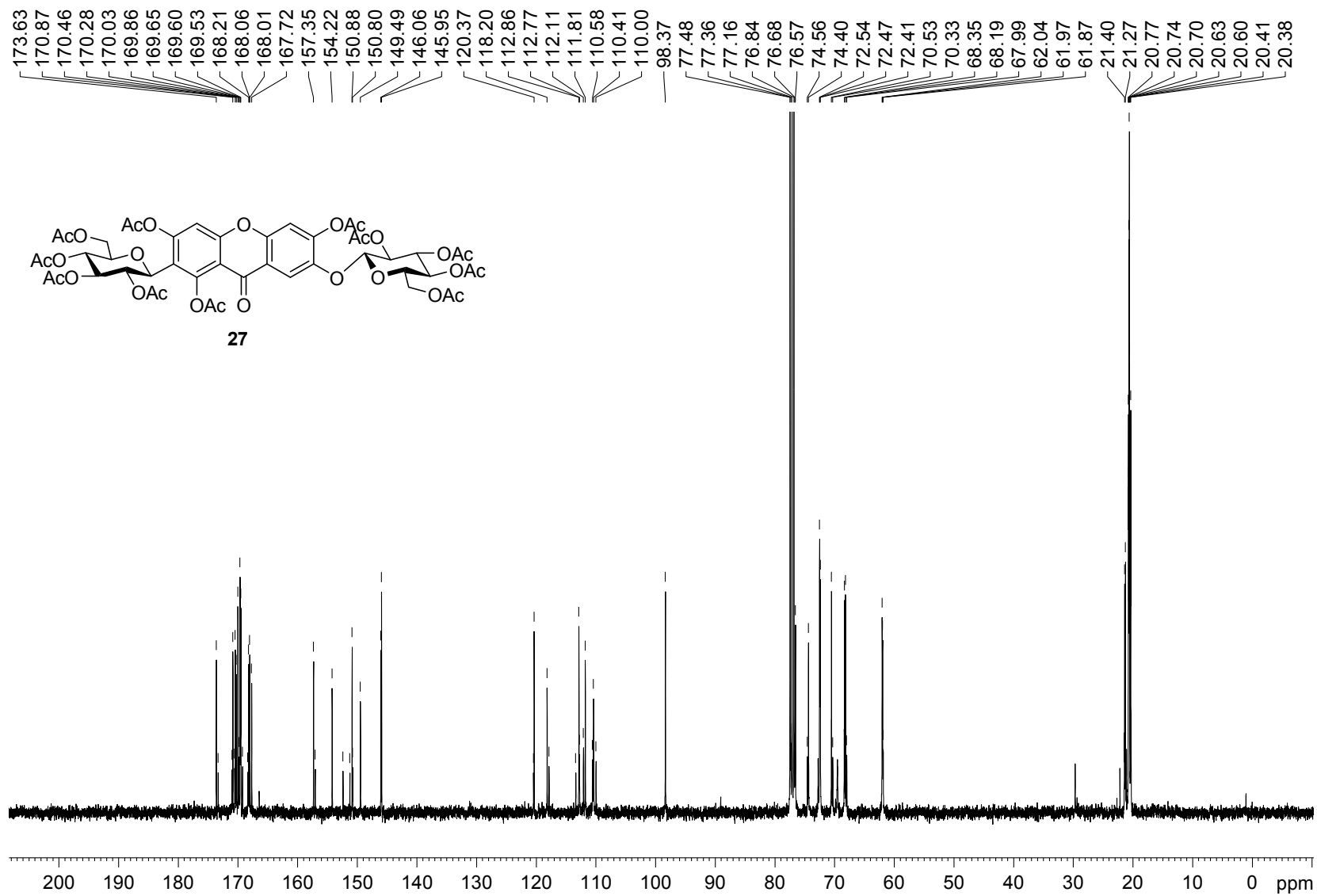
**<sup>13</sup>C NMR spectrum of Compound 26 (CDCl<sub>3</sub>, 100 MHz)**



**<sup>1</sup>H NMR spectrum of Compound 27 (CDCl<sub>3</sub>, 400 MHz)**



**<sup>13</sup>C NMR spectrum of Compound 27 (CDCl<sub>3</sub>, 100 MHz)**



**<sup>1</sup>H NMR spectrum data for natural and synthetic Mangifein**

Assignments	Natural	Synthetic
	Mangiferin	Mangiferin
	DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub>
	400 MHz	400 MHz
HO-1	13.70(s)	13.75 (s, 1H)
HO-6	10.70(s)	
HO-3	10.60(s)	10.53 (br s, 3H)
HO-7	9.78(s)	
H-8	7.35(s)	7.38(s, 1H)
H-5	6.83(s)	6.86 (s, 1H)
H-4	6.34(s)	6.37 (s, 1H)
H-1'	4.60(d, <i>J</i> = 9.6 Hz)	4.59 (d, <i>J</i> = 9.6 Hz, 1H)



**<sup>13</sup>C NMR spectrum data for natural and synthetic Mangifein**

Assignments	Natural	Synthetic	Assignments	Natural	Synthetic
	Mangiferin	Mangiferin		Mangiferin	Mangiferin
	DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub>		DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub>
	100 MHz	100 MHz		100 MHz	100 MHz
1	162.5	162.1	C-1'	73.8	73.5
2	108.3	107.7	C-2'	71.3	70.9
3	164.5	164.1	C-3'	79.7	79.3
4	94.0	93.8	C-4'	70.9	70.7
4a	156.9	156.6	C-5'	82.3	81.7
5	103.3	103.0	C-6'	62.2	61.8
6	154.7	154.2			
7	144.4	143.9			
8	112.4	112.1			
8a	108.7	108.4			
9	179.8	179.4			
9a	102.0	101.7			
10a	151.4	151.1			

**<sup>1</sup>H NMR spectrum data for natural and synthetic Homomangifein**

Assignments	Natural	Synthetic
	Homomangiferin	Homomangiferin
	DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub> + D <sub>2</sub> O
	400 MHz	400 MHz
HO-1	13.66(s)	13.66/13.65(s)
H-8	7.39(s)	7.39/7.38(s)
H-5	6.88(s)	6.89(s)
H-4	6.66(s)	6.62/6.61(s)
H-1'	4.57(d)	4.61/4.56(d)
H-3'	3.98(m)	4.19/3.98(t)
H-6'	3.70/3.33(m)	3.35(m)
H-5'	3.16(m)	
H-2'	3.10(m)	3.23-3.02(m)
H-4'	3.07(m)	
CH <sub>3</sub> O	3.88(s)	3.86/3.84(s)

**<sup>13</sup>C NMR spectrum data for natural and synthetic Homomangifein**

Assignments	Natural	Synthetic	Assignments	Natural	Synthetic
	Homomangiferin	Homomangiferin		Homomangiferin	Homomangiferin
	DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub> + D <sub>2</sub> O		DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub> + D <sub>2</sub> O
	100 MHz	100 MHz		100 MHz	100 MHz
1	161.8	161.3/160.6	C-1'	73.1	73.1/72.9
2	108.9	108.3	C-2'	82.2	82.0/81.8
3	164.7	165.7/164.5	C-3'	70.8	70.5/69.9
4	90.2	91.0/90.2	C-4'	71.4	71.0
4a	157.3	157.2/157.1	C-5'	79.6	79.1
5	103.0	102.9	C-6'	62.2	61.8
6	154.7	154.4	CH <sub>3</sub> O	56.7	56.8/56.5
7	144.4	144.1			
8	108.5	108.6			
8a	112.3	112.2			
9	179.6	179.7/179.4			
9a	102.3	102.6/102.2			
10a	151.4	151.2			

**<sup>1</sup>H NMR spectrum data for natural and synthetic Neomangifein**

Assignments	Natural	Synthetic
	Neomangiferin	Neomangiferin
	DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub> + D <sub>2</sub> O
	400 MHz	400 MHz
H-4	6.37(s)	6.41(s)
H-5	6.93(s)	6.96(s)
H-8	7.69(s)	7.70(s)
2-Glc, H-1'	4.57(d)	4.59(d)
7-Glc, H-1''	4.87(d)	4.91(d)

**<sup>13</sup>C NMR spectrum data for natural and synthetic Neomangifein**

Assignments	Natural	Synthetic	Assignments	Natural	Synthetic
	Neomangiferin	Neomangiferin		Neomangiferin	Neomangiferin
	DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub>		DMSO- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub>
	100 MHz	100 MHz		100 MHz	100 MHz
1	162.5	161.7	2-Glc		
2	108.3	107.9	C-1'	73.8	73.4
3	164.5	164.2	C-2'	71.3	70.7
4	94.0	93.8	C-3'	79.7	79.0
4a	154.7	155.0	C-4'	71.0	70.4
5	103.3	102.1	C-5'	82.2	81.7
6	156.9	156.5	C-6'	61.4	61.6
7	144.4	143.7	(7-Glc)C-1''	103.4	103.4
8	112.4	112.0	C-2''	73.5	73.3
8a	108.8	110.5	C-3''	76.1	75.9
9	179.8	179.2	C-4''	69.6	69.7
9a	102.0	101.5	C-5''	77.3	77.3
10a	151.5	152.8	C-6''	60.7	60.7