Supporting Information

Roxbin B is Cuspinin; Structural Revision and Total Synthesis

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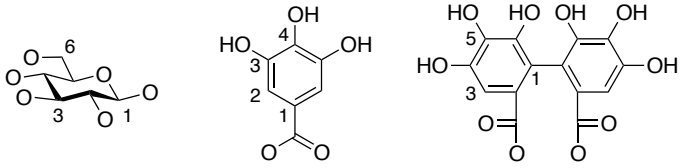
Contents

1. Comparison of literature data (^{1}H and ^{13}C NMR spectra) of natural roxbin B and cuspinin

Literature data (^{1}H and ^{13}C NMR spectra) for roxbin B[1] and cuspinin[2] are summarized in Table S1 and Table S2. Although the data of the two compounds are not identical, they are in good agreement. In the ^{1}H NMR spectra (Table S1), the peak assigned as H-6 of roxbin B (5.30 ppm) is not described for cuspinin. The chemical shifts 5.21 ppm for roxbin B and 5.23 ppm for cuspinin are close, but the assignments are different. The coupling pattern and constants of H-6 of cuspinin (5.23 ppm) are similar to those of the signal at 5.30 ppm of roxbin B. In the ^{13}C NMR spectra (Table S2), despite of the several differences in picking peaks and despite of the difference of the solvents, the two spectra are in good agreement. Position numbers for the assignment are different in each literature; of which the numbers made for roxbin B are adopted here.



Position numbers for the assignments

Table S1. ^{1}H NMR

Roxbin B[1]			$\Delta\delta_{(\text{roxbin B}-\text{cuspinin})}$	Cuspinin[2]		
Assignment	Coupling pattern and constant (Hz)	δ in acetone-d_6		δ in acetone-d_6	Coupling pattern and constant (Hz)	Assignment
Galloyl group	s	7.27	0.01	7.26	s	Galloyl group
HHDP group	s	7.14	0.02	7.12	s	HHDP group
	s	6.80	0.00	6.80	s	
	s	6.73	0.01	6.72	s	
	s	6.60	0.00	6.60	s	
Glucose H-1	d J=8.5	6.08	–0.02	6.10	d J=9	Glucose H-1
Glucose H-6	dd J=13, 6.5	5.30				
Glucose H-3	t J=9.7	5.21	–0.02	5.23	dd J=13, 6	Glucose H-6
Glucose H-2	dd J=9.7, 8.5	4.90	0.00	4.90	t J=9	Glucose H-2
Glucose H-4	dd J=10, 9.7	4.89	–0.01	4.90	t J=9	Glucose H-4
Glucose H-5	ddd J=10, 6.5, 1.5	4.40	0.00	4.40	dd J=9, 6	Glucose H-5
Glucose H-6	dd J=13, 1.5	3.80	0.00	3.80	d J=13	Glucose H-6

Table S2. ^{13}C NMR

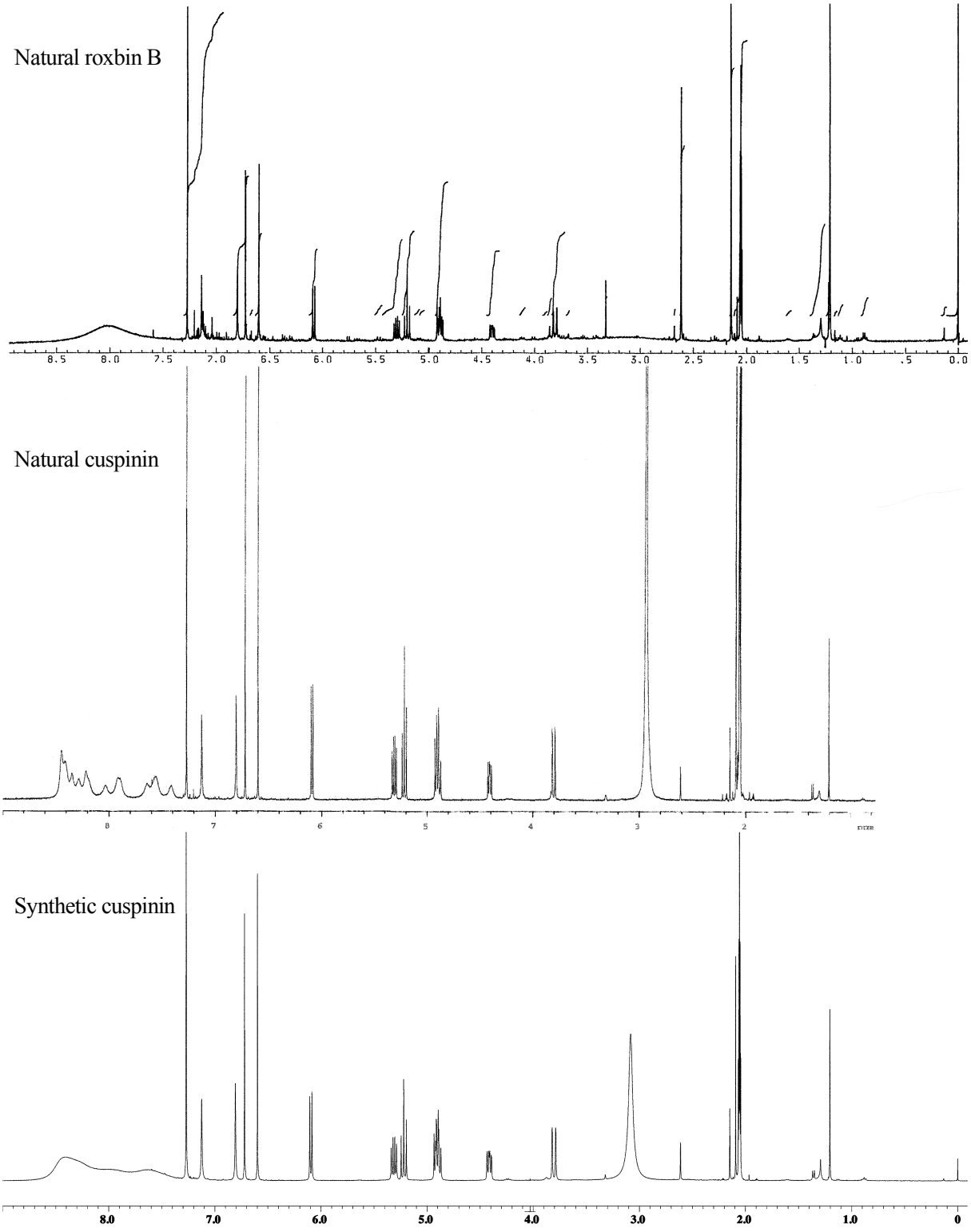
Roxbin B[1]			$\Delta\delta_{(\text{roxbin B}-\text{cuspinin})}$	Cuspinin[2]		
Assignment	Remarks	δ in acetone-d_6		δ in acetone-d_6 + D_2O	Remarks	Assignment
C=O		168.26	–0.24	168.5		C=O
C=O		167.98	–0.12	168.1		C=O
C=O		167.81	–0.19	168.0		C=O
C=O		167.16	–0.14	167.3		C=O
C=O		164.85	–0.15	165.0		C=O
Galloyl C-3	2C	146.17	–0.03	146.2		Galloyl C-3
HHDP C-4, 4', 6, 6'		145.57	–0.03	145.6		HHDP C-4, 4', 6, 6'
HHDP C-4, 4', 6, 6'		145.33				
HHDP C-4, 4', 6, 6'		145.23				
HHDP C-4, 4', 6, 6'		145.08	–0.32	145.4		HHDP C-4, 4', 6, 6'
HHDP C-4, 4', 6, 6'		145.00	0.00	145.0		HHDP C-4, 4', 6, 6'
HHDP C-4, 4', 6, 6'		144.86	0.26	144.6		HHDP C-4, 4', 6, 6'
HHDP C-4, 4', 6, 6'		144.45	–0.05	144.5		HHDP C-4, 4', 6, 6'
HHDP C-4, 4', 6, 6'		144.29	–0.01	144.3		HHDP C-4, 4', 6, 6'
Galloyl C-4		139.84	–0.16	140.0		HHDP C-5, 5'
HHDP C-5, 5'		138.58	–0.02	138.6		Galloyl C-4
HHDP C-5, 5'		137.24	–0.06	137.3		HHDP C-5, 5'
HHDP C-5, 5'		136.46	–0.04	136.5		HHDP C-5, 5'
HHDP C-5, 5'		136.44				
HHDP C-2, 2'		126.37	0.17	126.2		HHDP C-2, 2'
HHDP C-2, 2'		126.11	0.11	126.0		HHDP C-2, 2'
HHDP C-2, 2'	2C	122.23	0.33	121.9		Galloyl C-1
Galloyl C-1		120.05	0.05	120.0		HHDP C-2, 2'
				119.8		HHDP C-2, 2'
HHDP C-1, 1'		117.64	–0.16	117.8		HHDP C-1, 1'
HHDP C-1, 1'		117.44	–0.06	117.5		HHDP C-1, 1'
HHDP C-1, 1'		115.86	0.06	115.8		HHDP C-1, 1'
HHDP C-1, 1'		115.70				
				111.1		HHDP C-1, 1'
Galloyl C-2	2C	110.51	0.01	110.5		Galloyl C-2
HHDP C-3, 3'		110.37				
HHDP C-3, 3'		110.16				
HHDP C-3, 3'		108.37	0.17	108.2		HHDP C-3, 3'
HHDP C-3, 3'		108.03				
Glucose C-1		92.51	0.11	92.4		Glucose C-1
Glucose C-3		78.22	0.02	78.2		Glucose C-3
Glucose C-2		77.24	0.04	77.2		Glucose C-2
Glucose C-5		73.24	0.04	73.2		Glucose C-5
Glucose C-4		69.62	0.02	69.6		Glucose C-4
Glucose C-6		63.03	–0.07	63.1		Glucose C-6

(1) Yoshida, T.; Chen, X.-M.; Hatano, T.; Fukushima, M.; Okuda, T. *Chem. Pharm. Bull*. **1987**, *35*, 1817–1822.

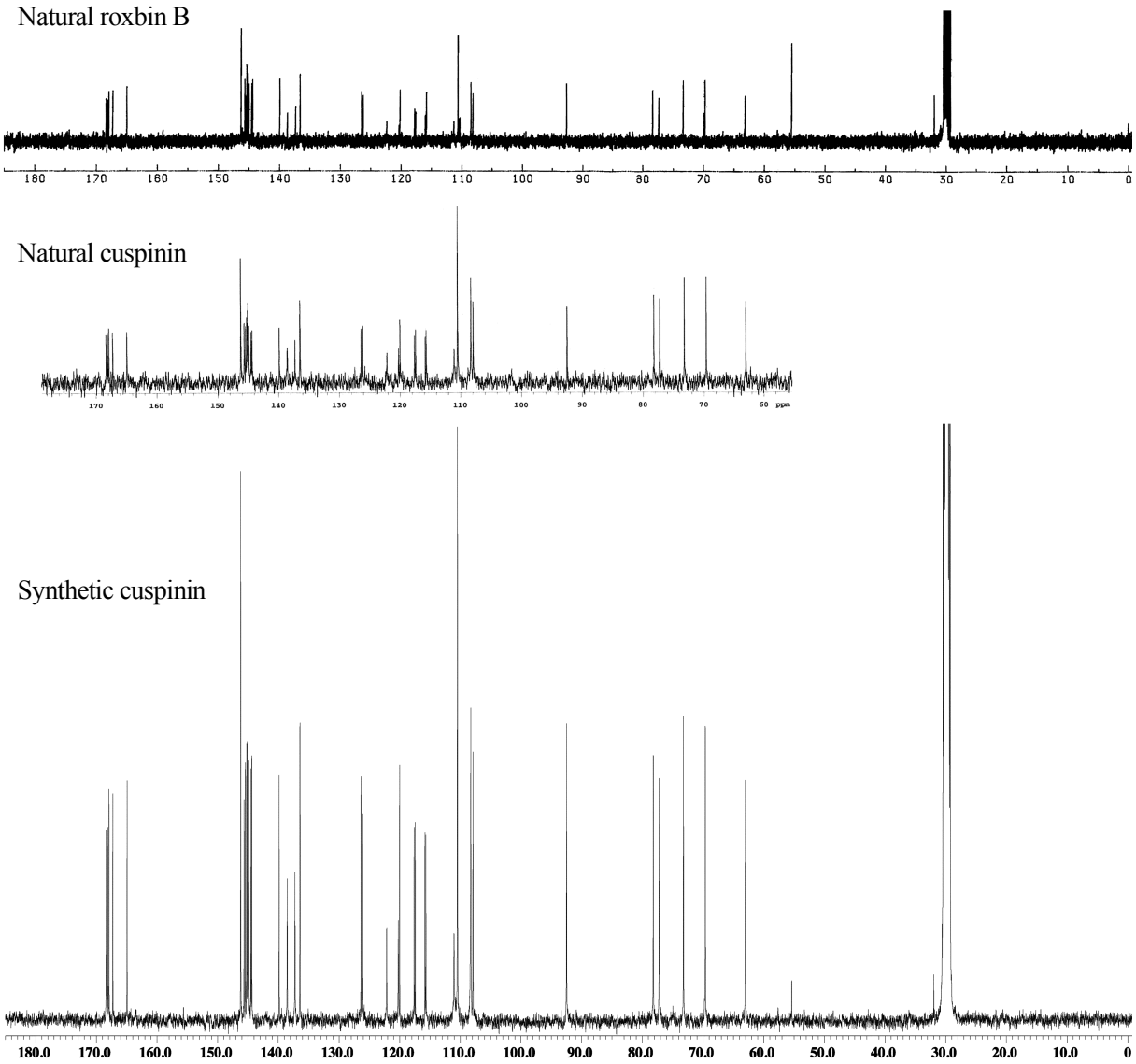
(2) Nonaka, G.-I.; Ishimatsu, M.; Ageta, M.; Nishioka, I. *Chem. Pharm. Bull*. **1989**, *37*, 50–53.

2. Comparison of NMR spectra of natural roxbin B, natural cuspinin, and synthetic cuspinin

^{1}H NMR in acetone-d_6

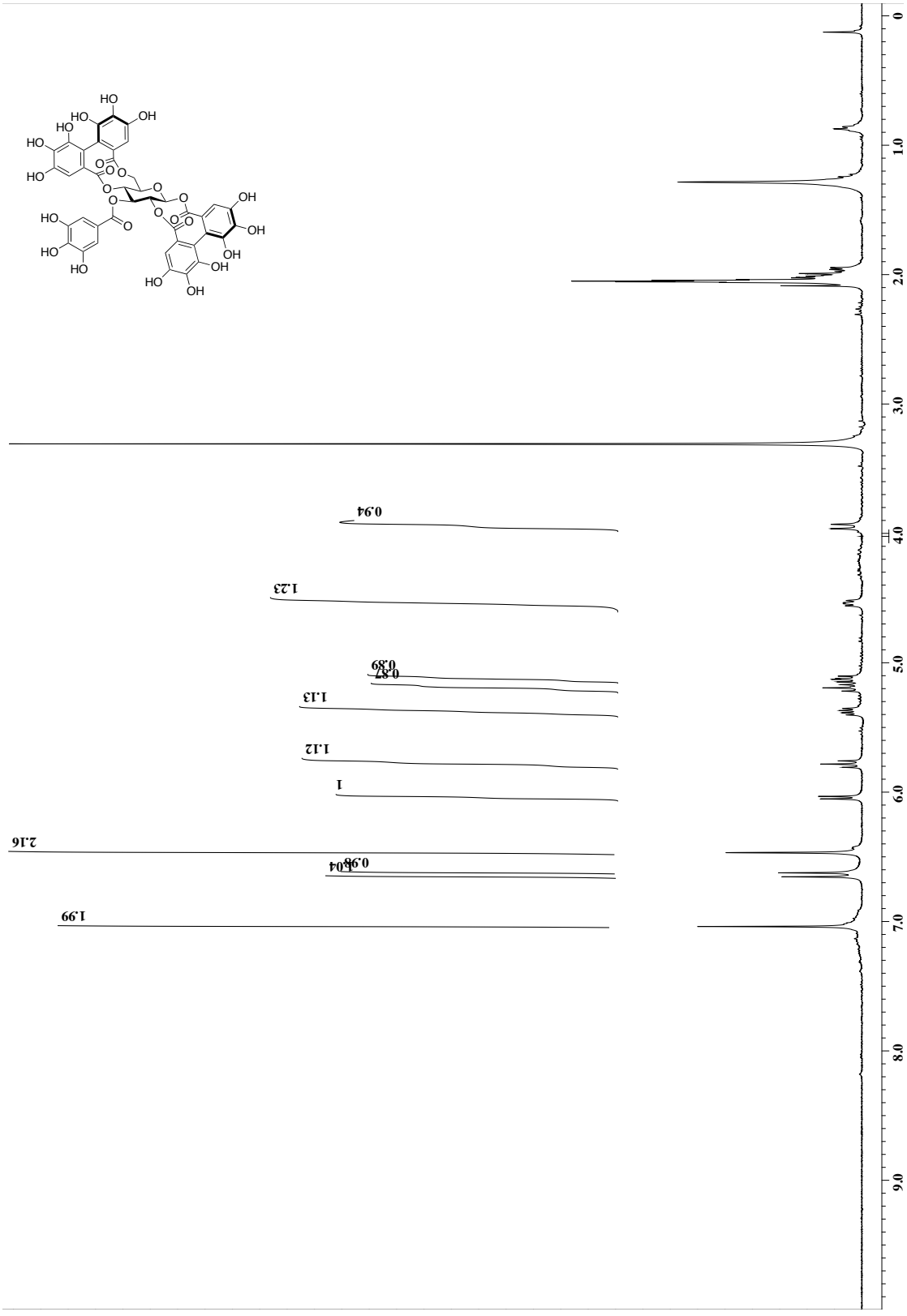


^{13}C NMR in acetone-d_6

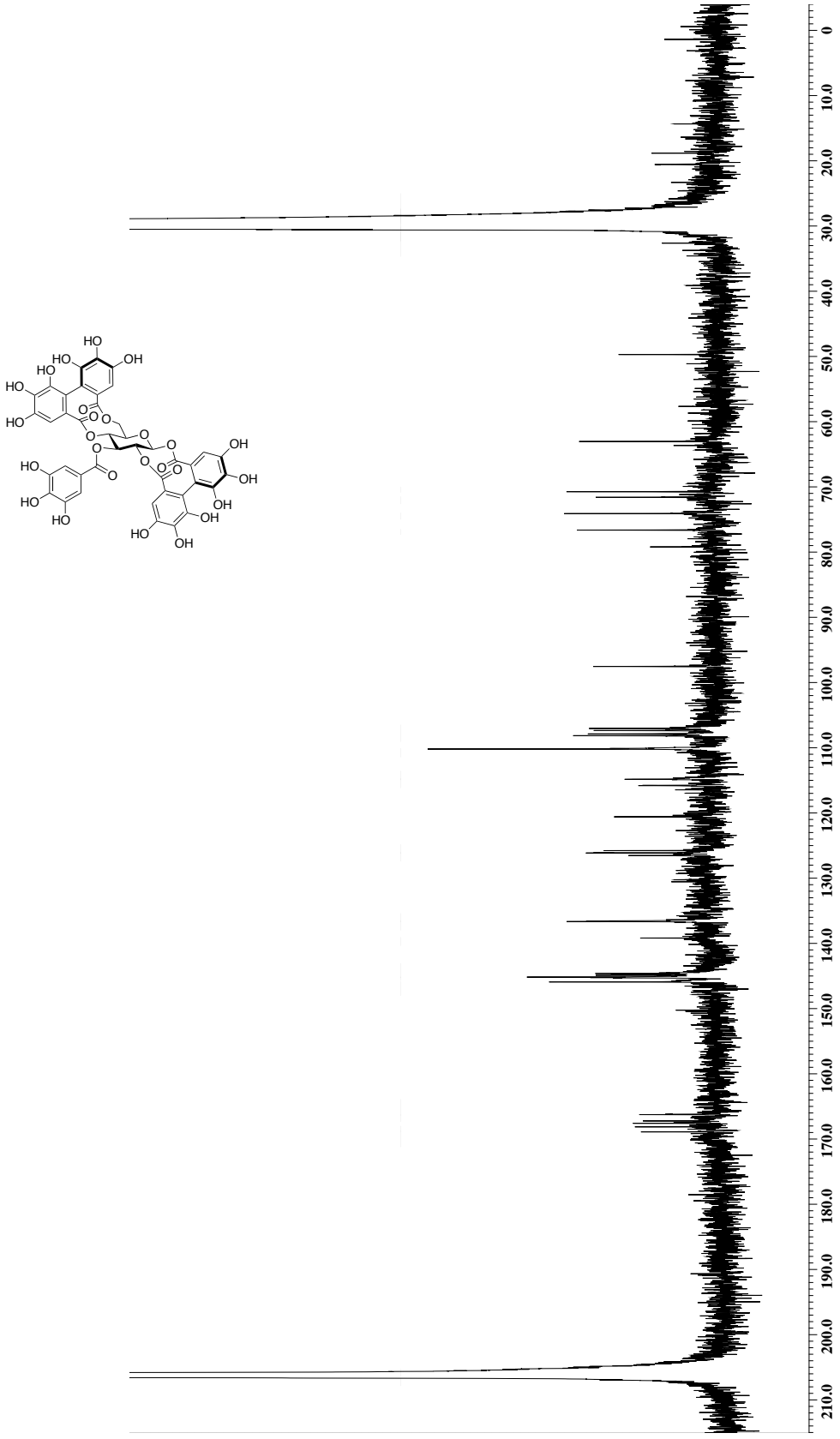


3. NMR data

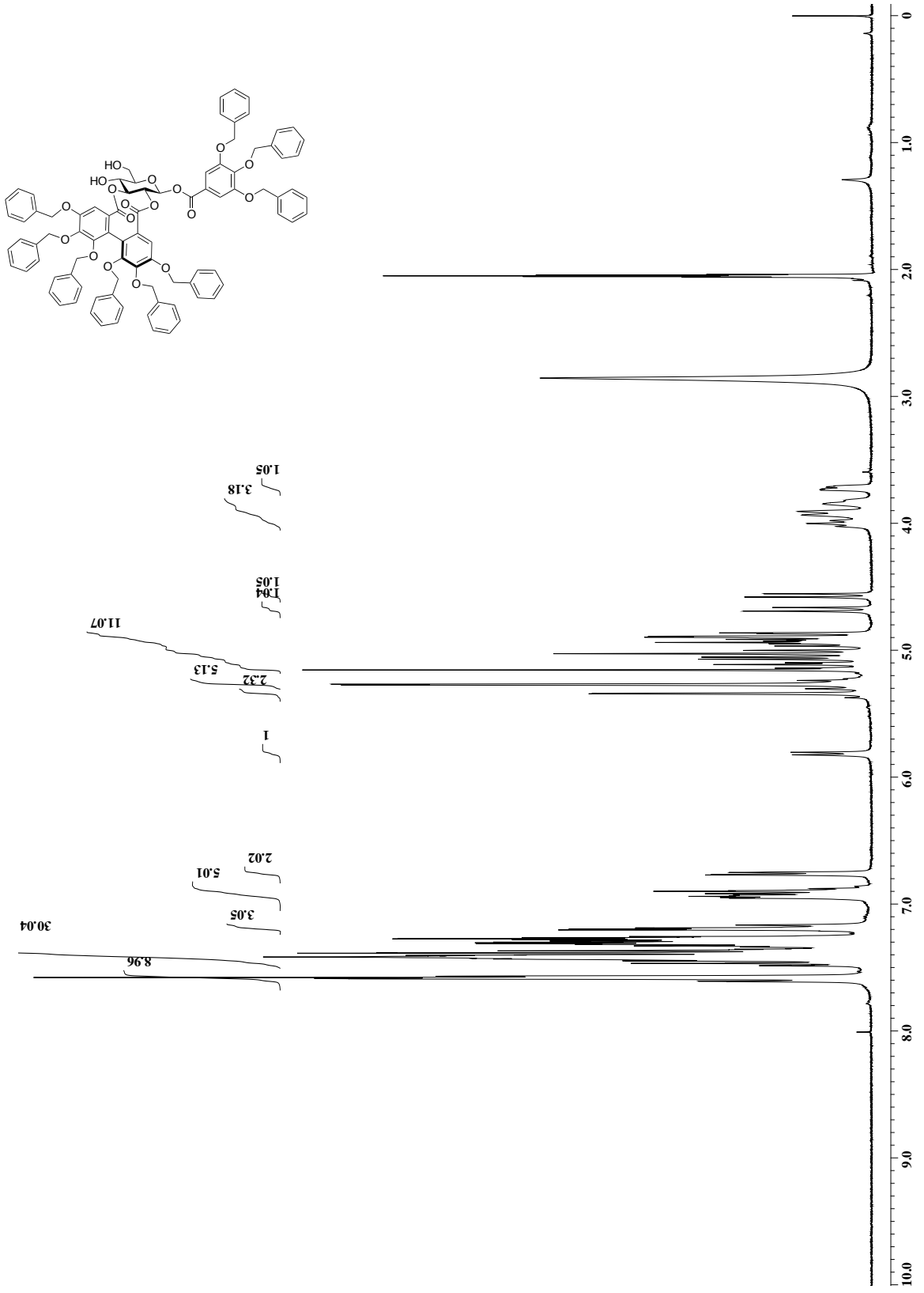
3.1. Compound 6 (^{1}H NMR, 400 MHz, acetone-d_6)



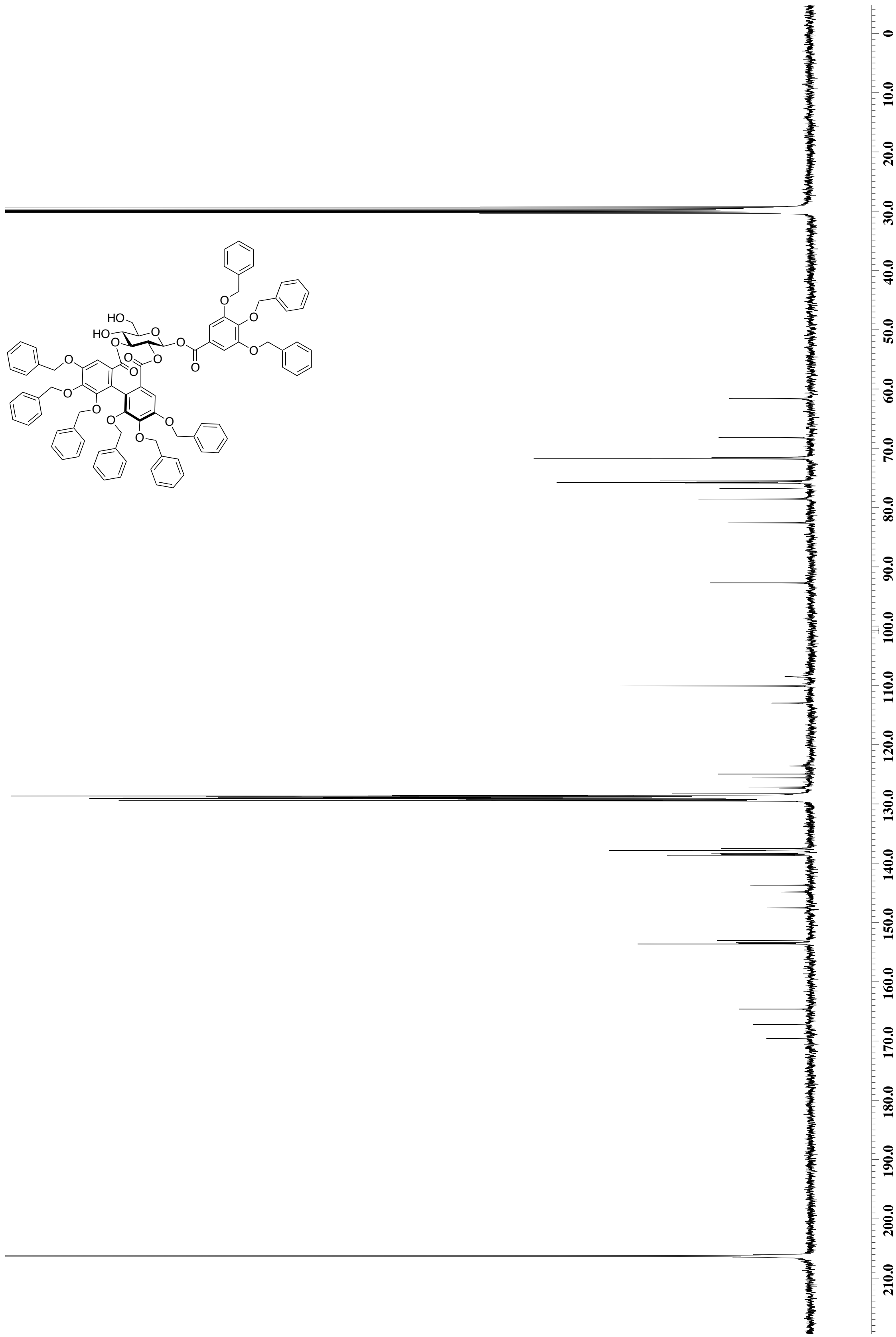
(^{13}C NMR, 100 MHz, acetone-d_6)



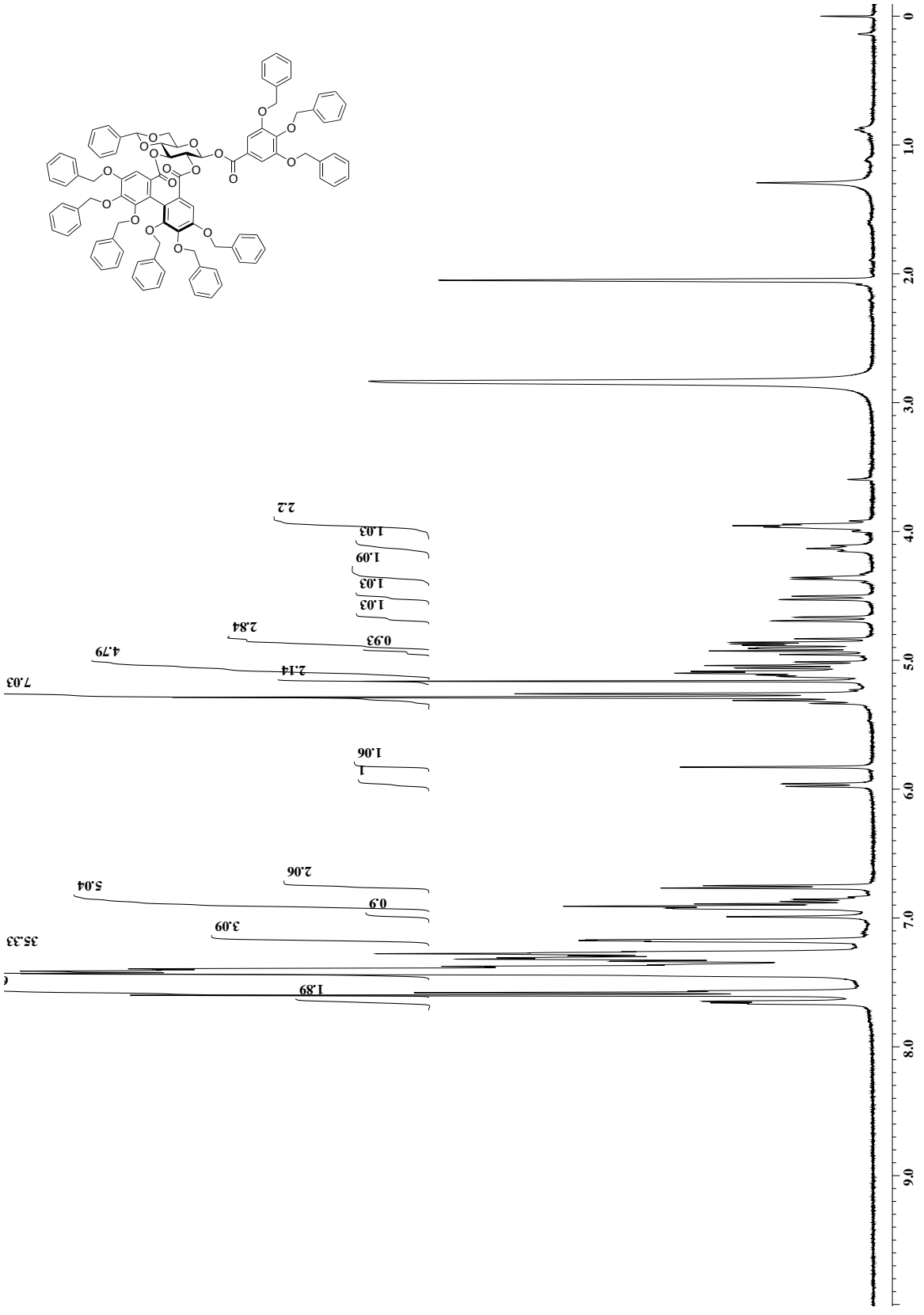
3.2. Compound 7 (^{1}H NMR, 400 MHz, acetone-d_6)



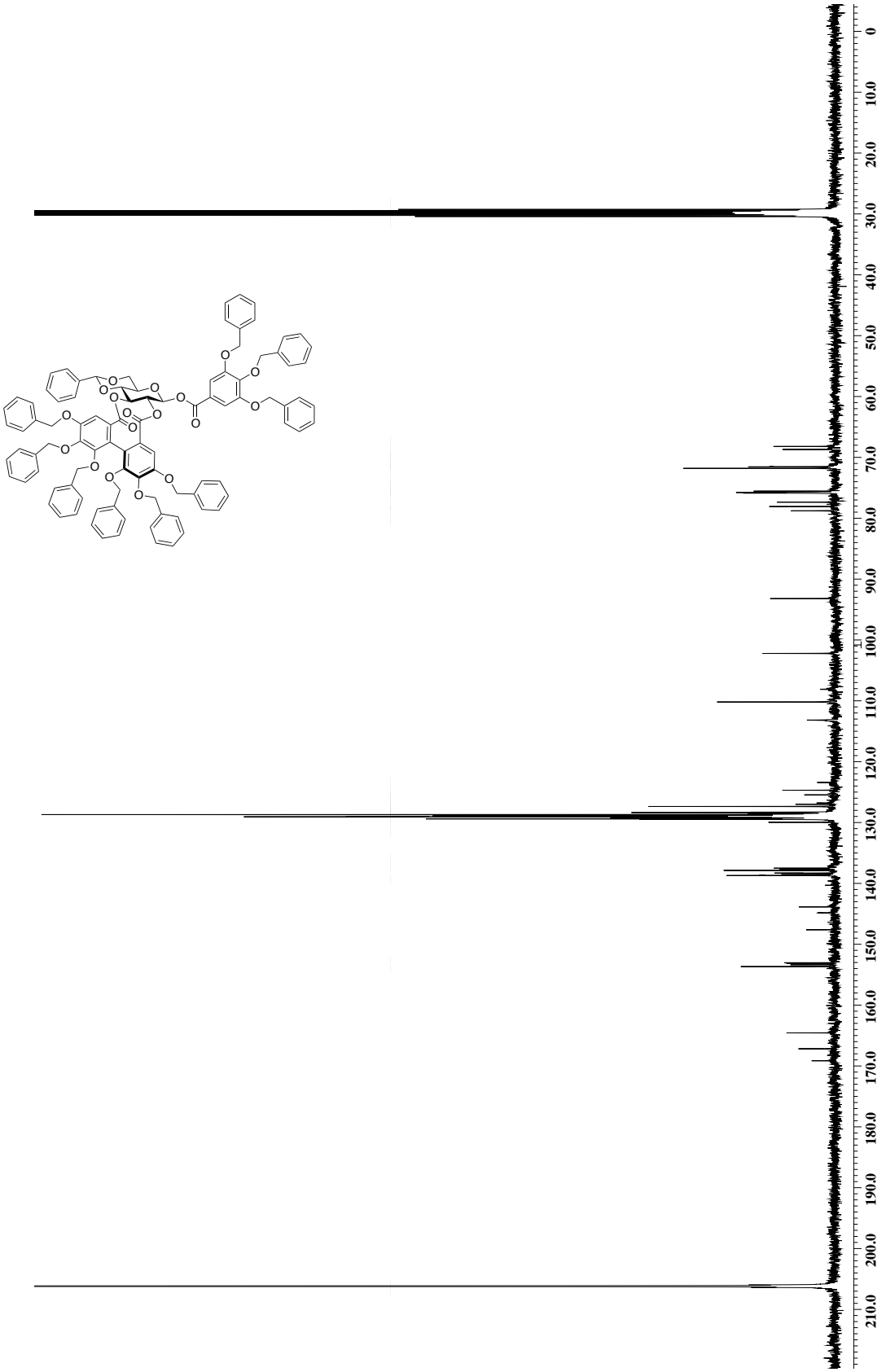
(^{13}C NMR, 100 MHz, acetone-d_6)



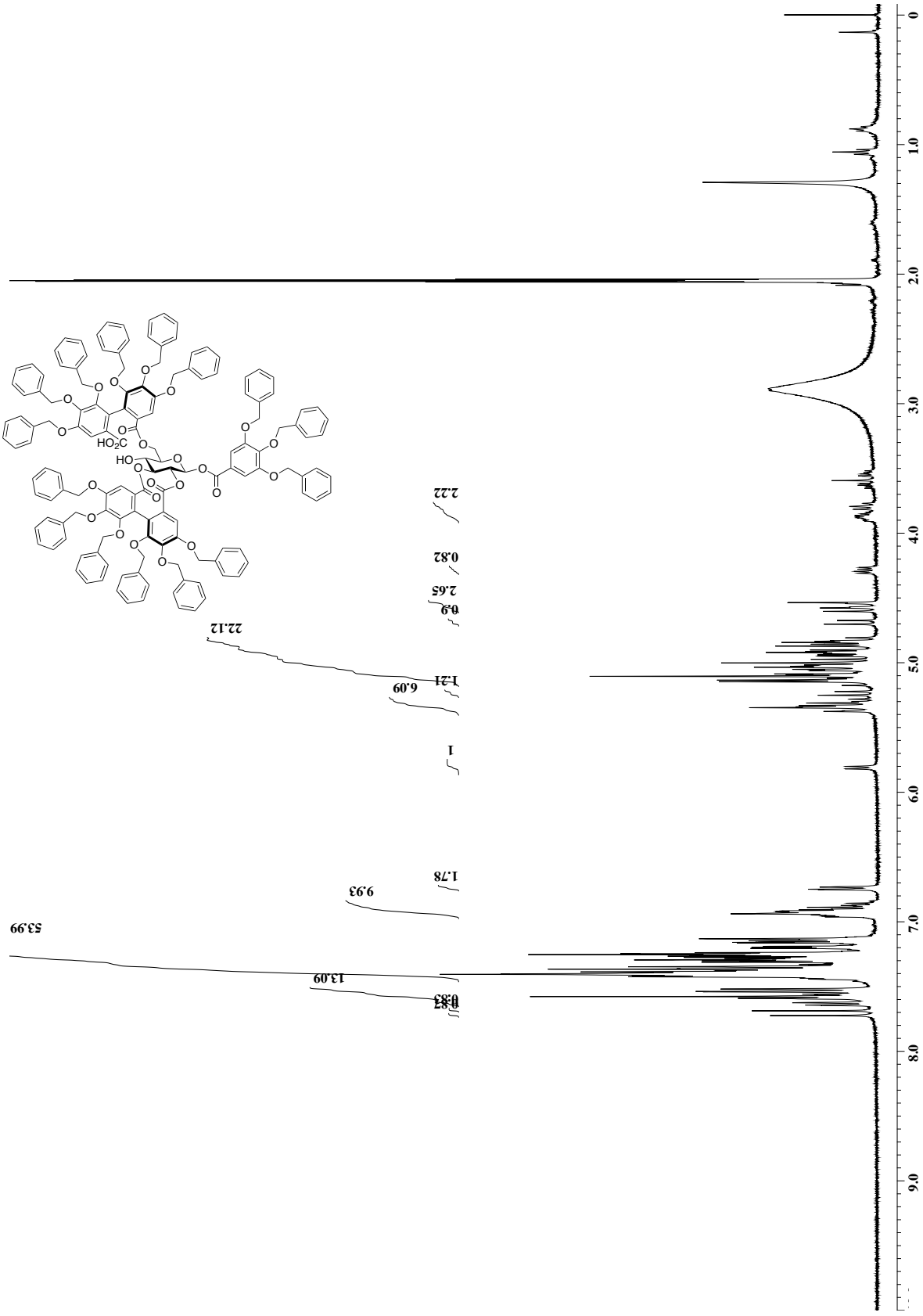
3.3. Compound 11 (^{1}H NMR, 400 MHz, acetone-d_6)



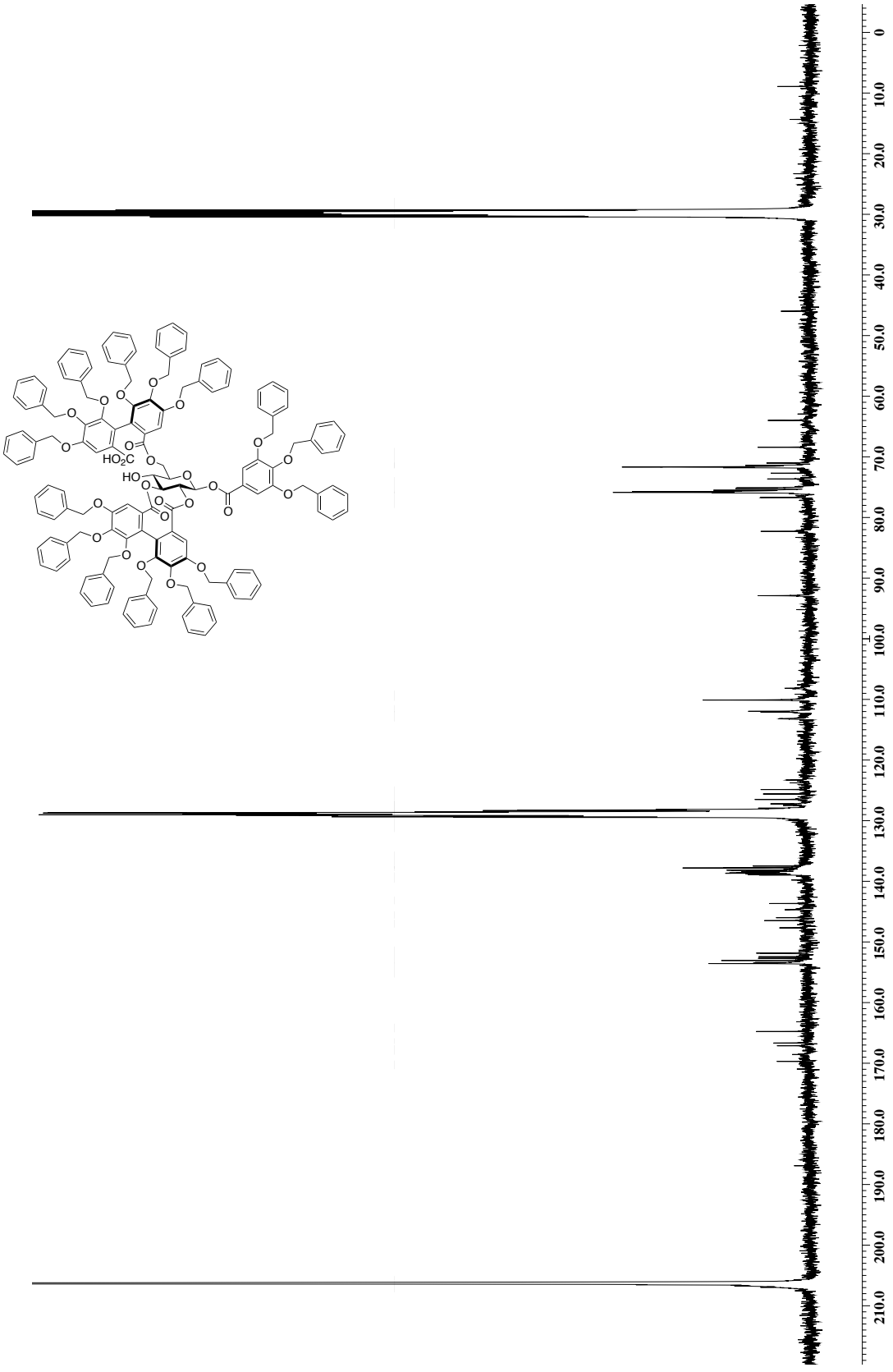
(^{13}C NMR, 100 MHz, acetone-d_6)



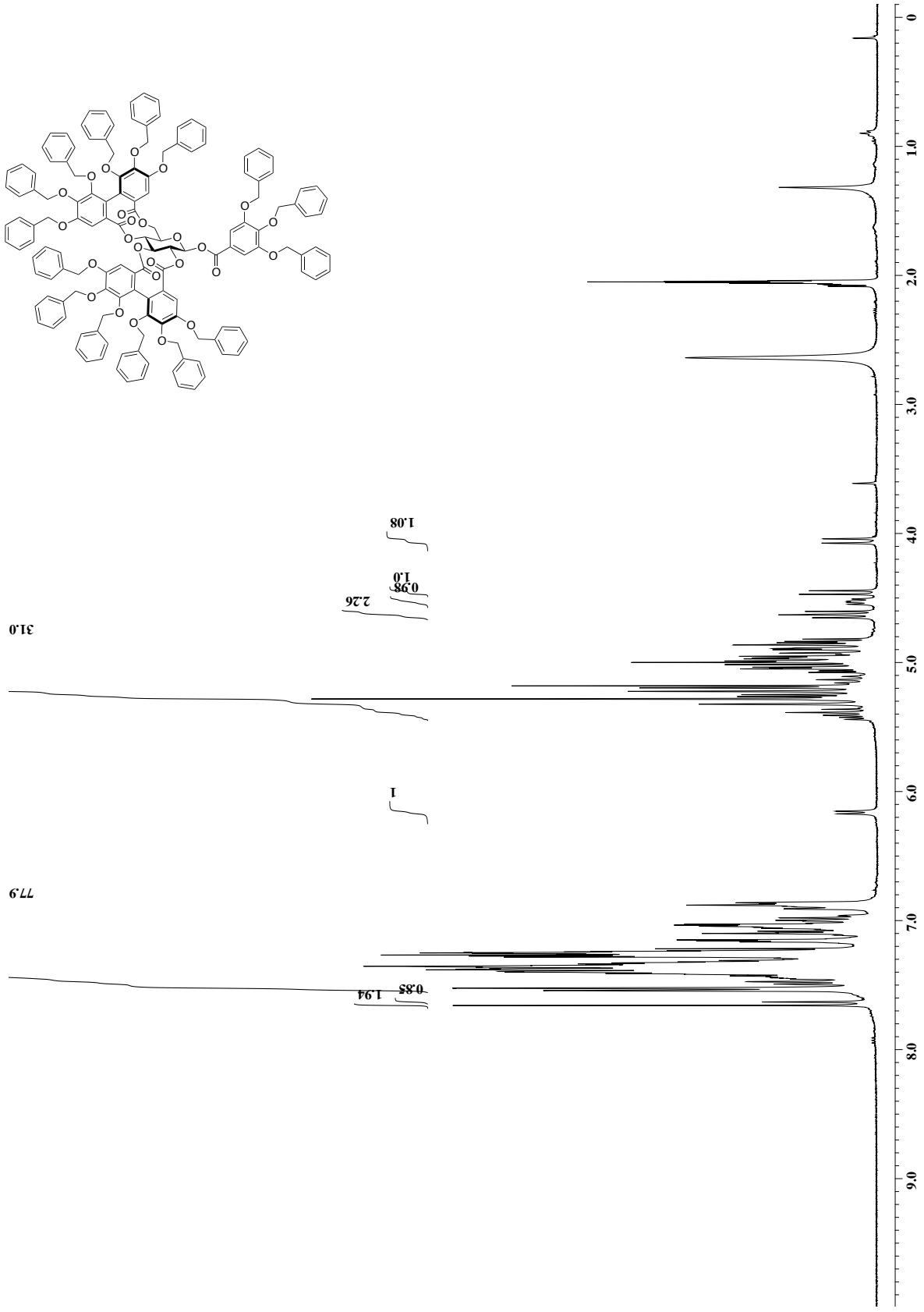
3.4. Compound 13 (^{1}H NMR, 400 MHz, acetone-d_6)



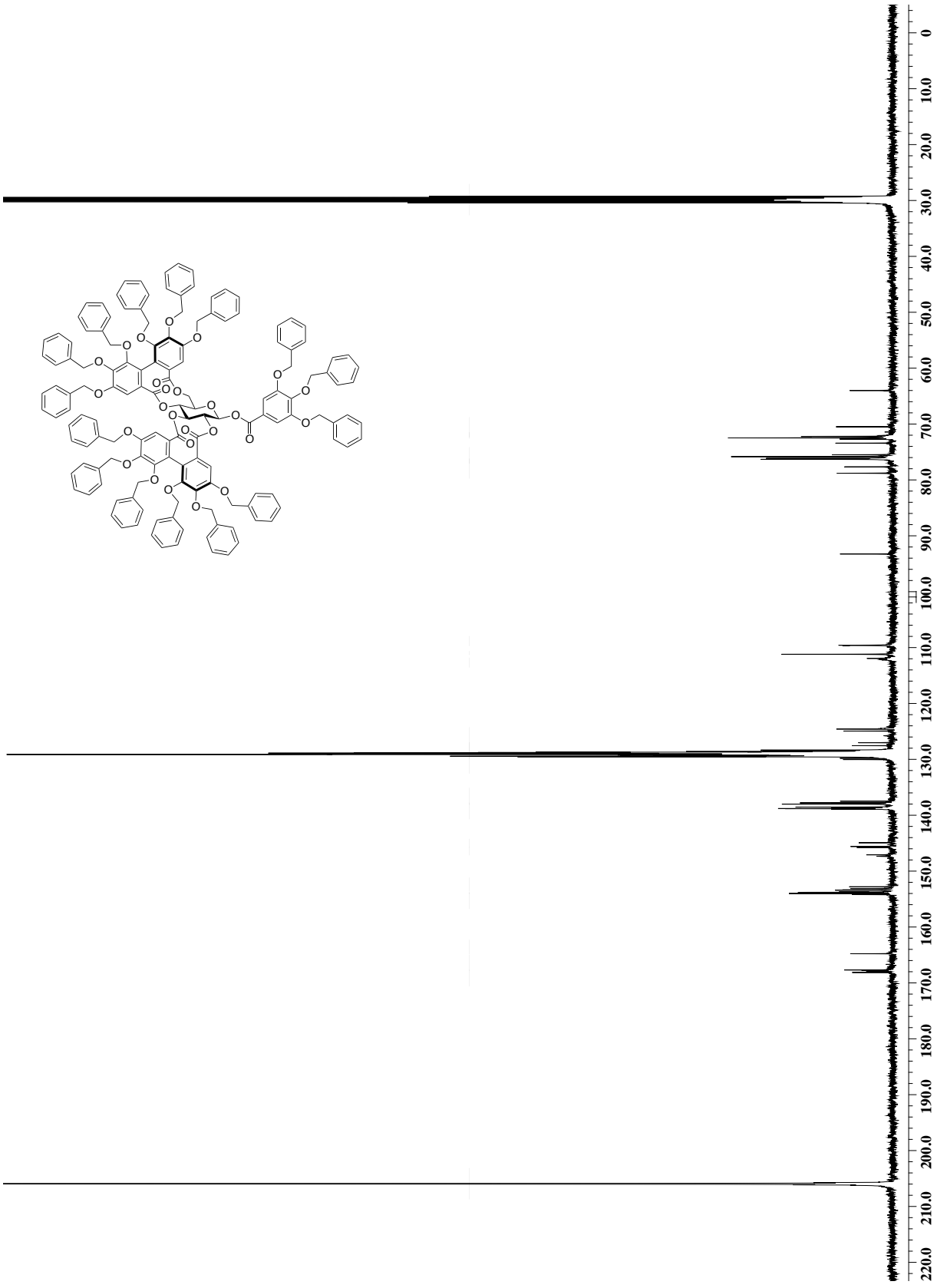
(^{13}C NMR, 100 MHz, acetone-d_6)



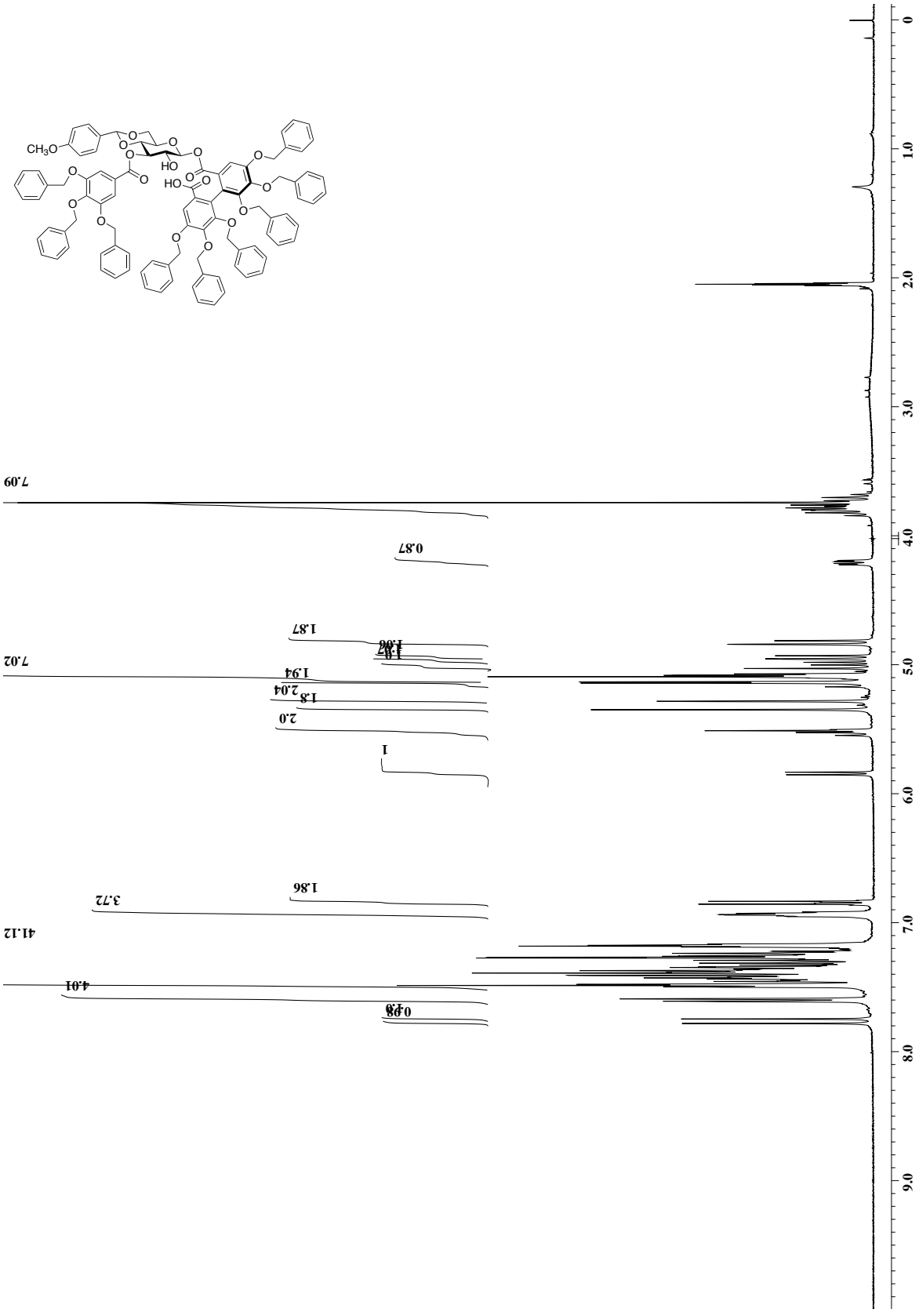
3.5. Compound 14 (^{1}H NMR, 400 MHz, acetone-d_6)



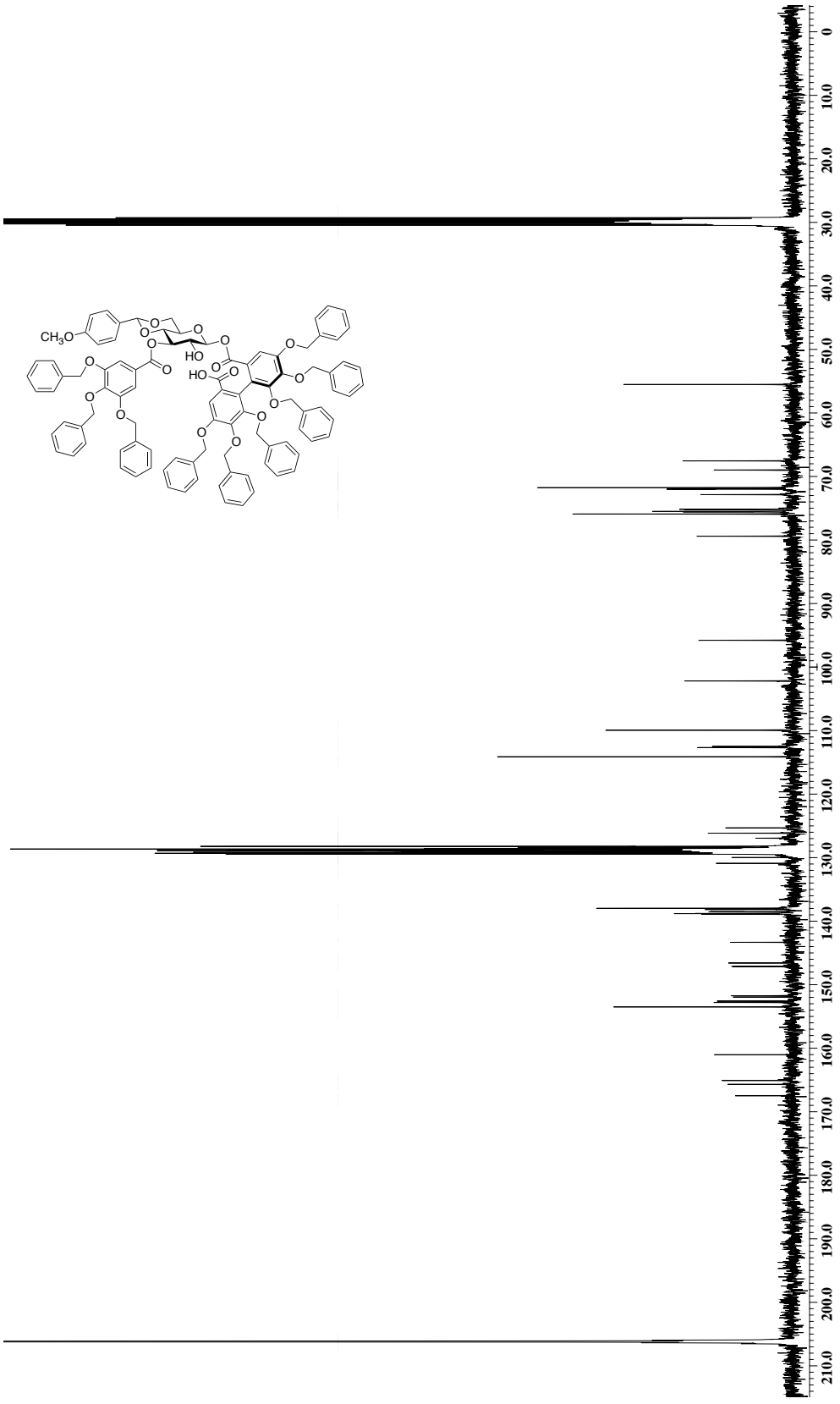
(^{13}C NMR, 100 MHz, acetone-d_6)



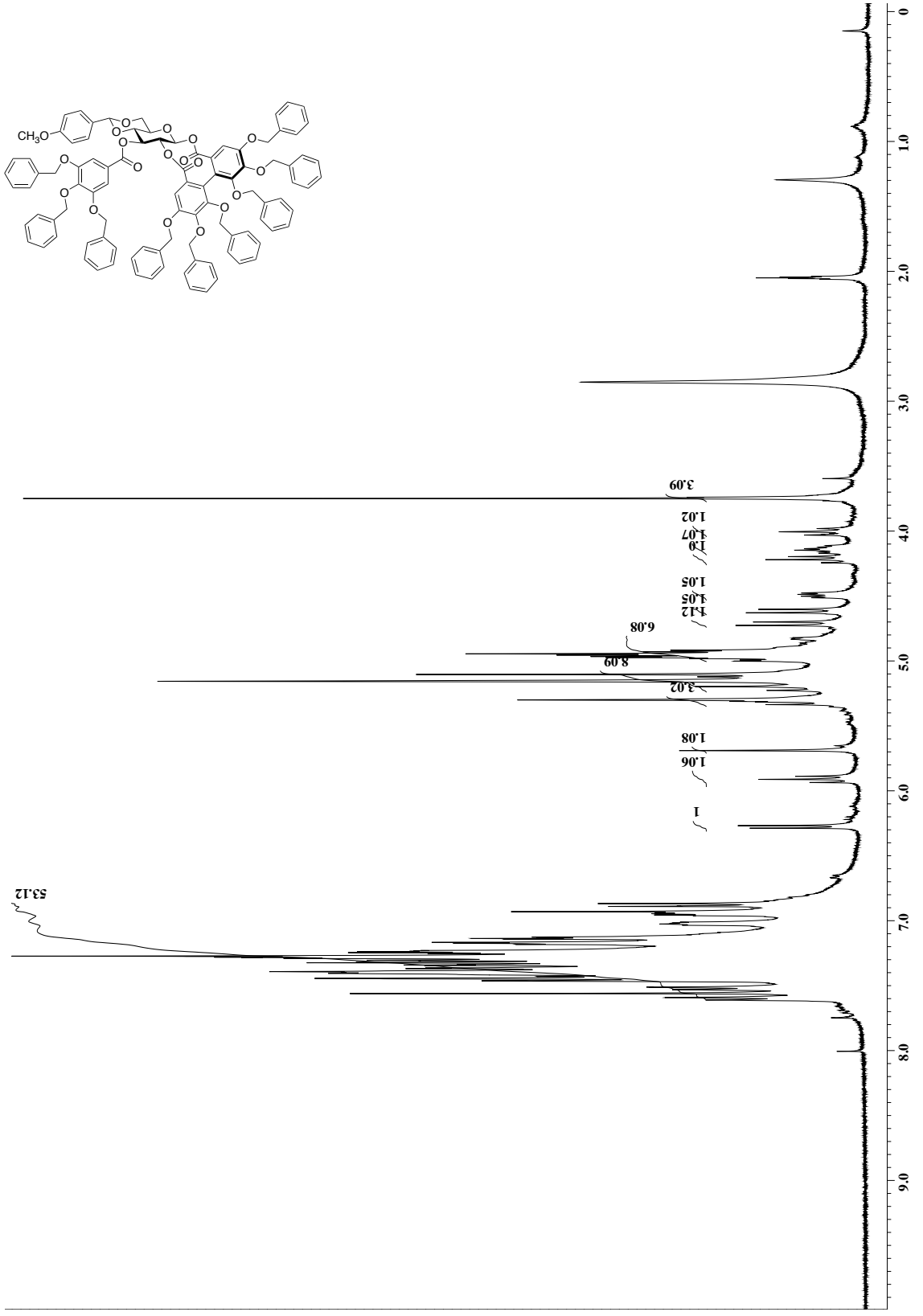
3.6. Compound 16 (^{1}H NMR, 400 MHz, acetone-d_6)



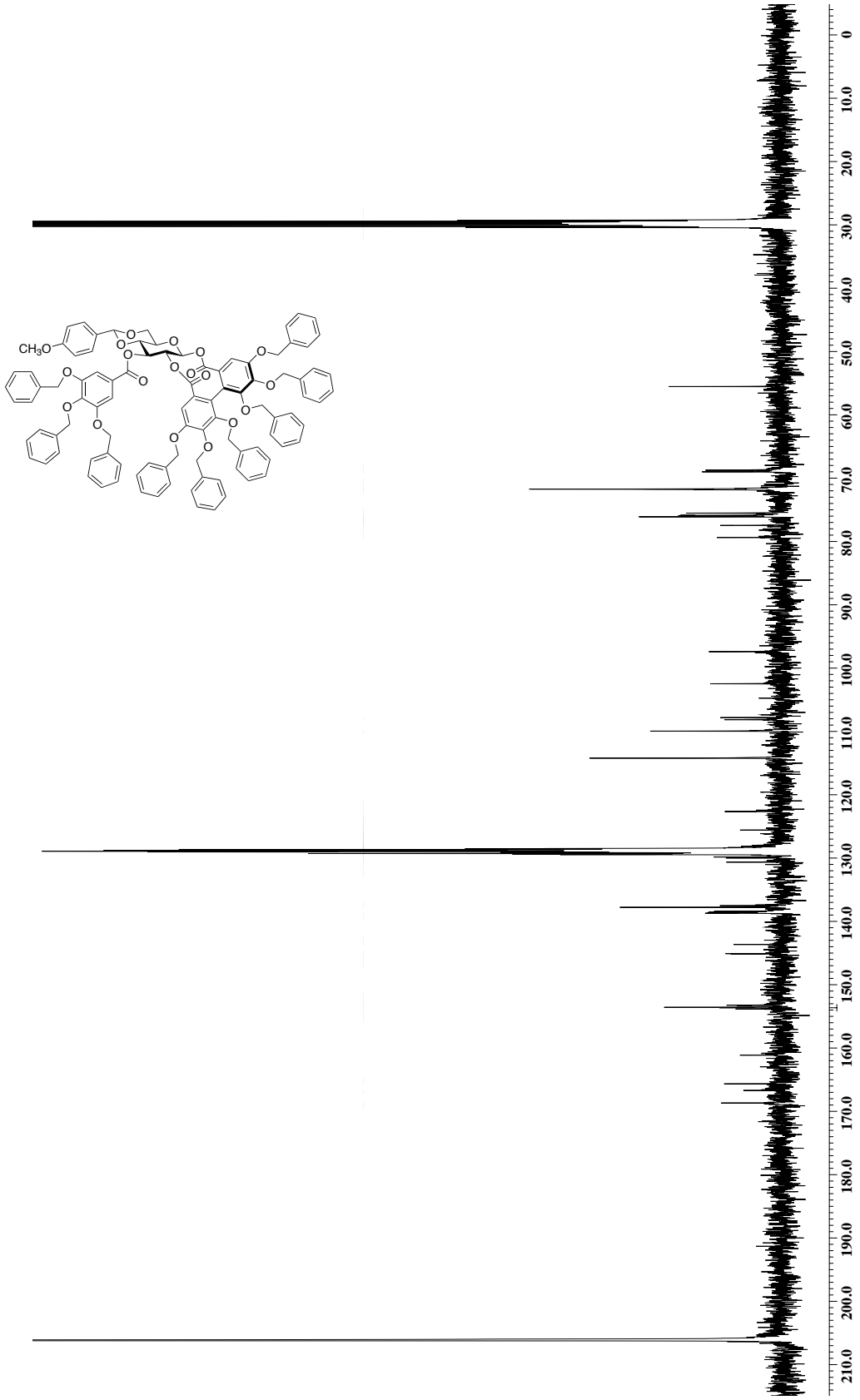
(^{13}C NMR, 100 MHz, acetone-d_6)



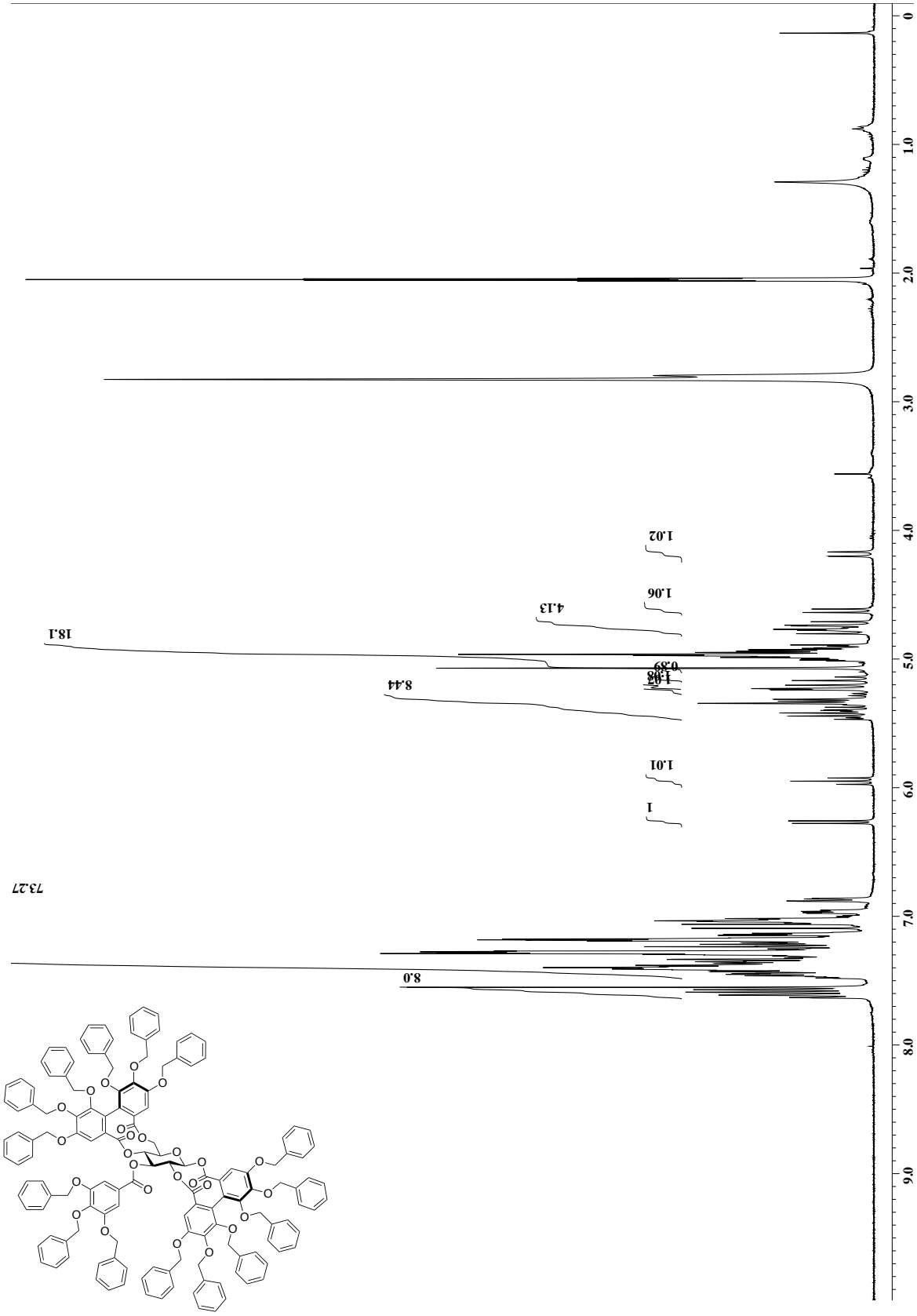
3.7. Compound 17 (^{1}H NMR, 400 MHz, acetone-d_6)



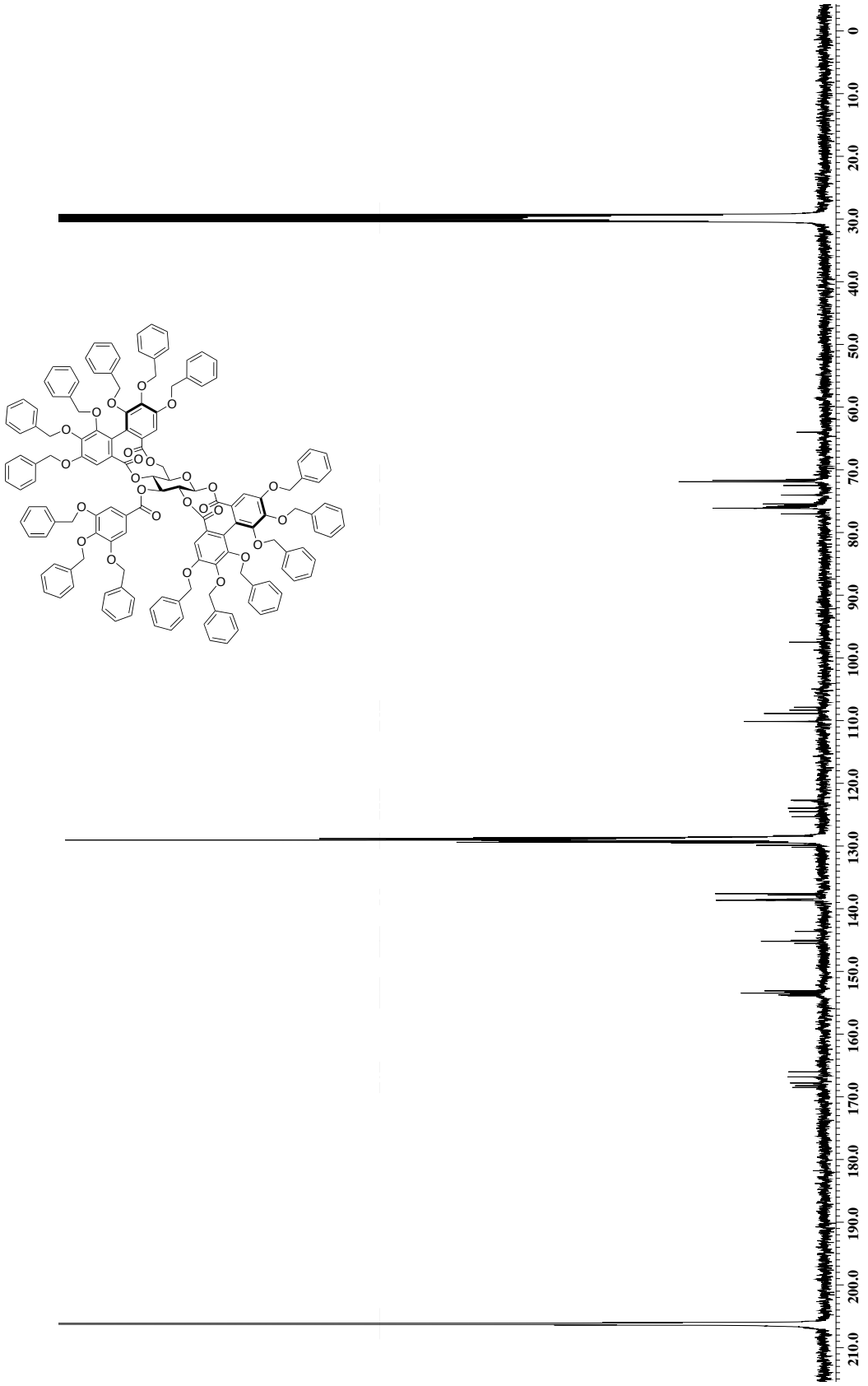
(^{13}C NMR, 100 MHz, acetone-d_6)



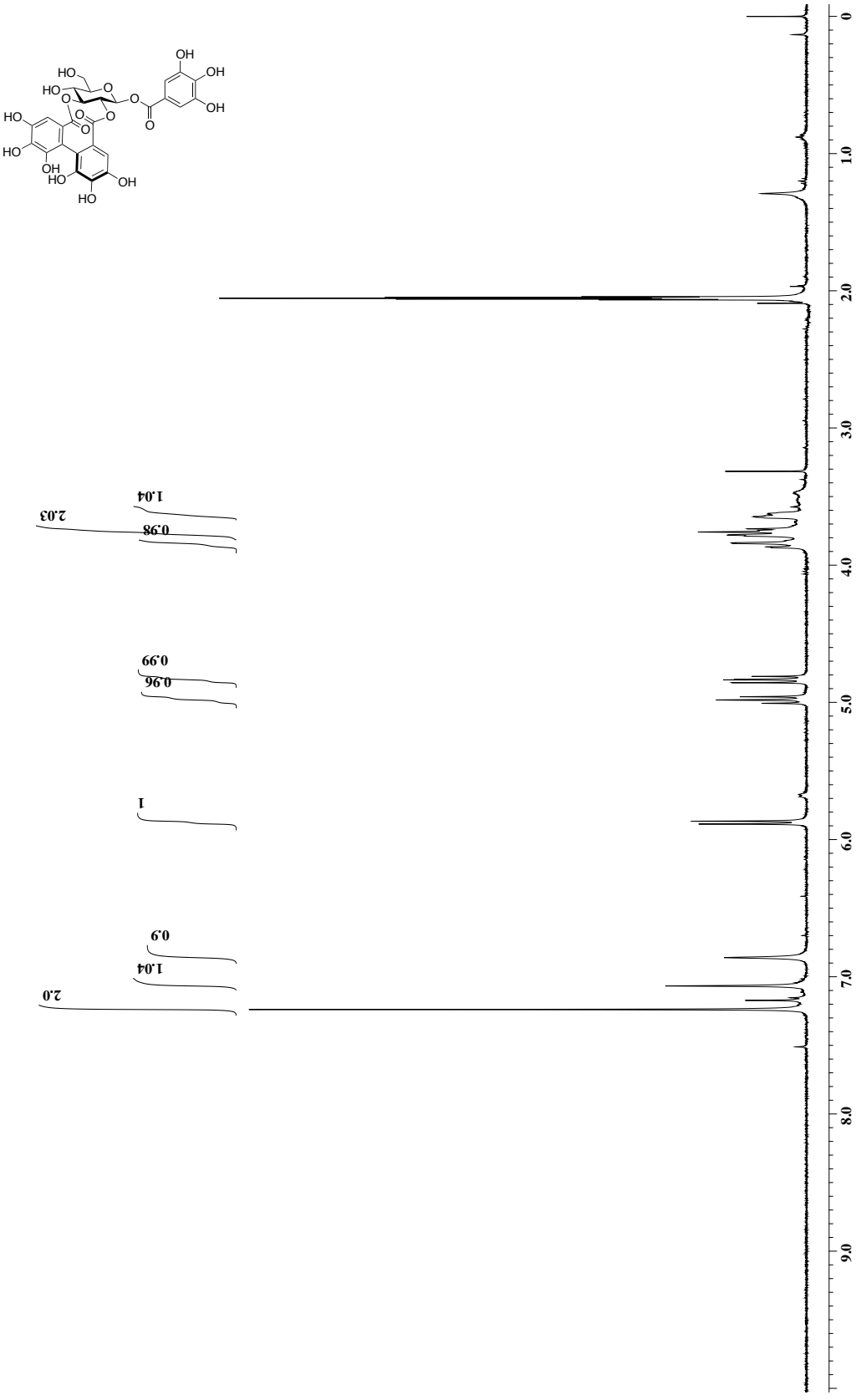
3.8. Compound 18 (^{1}H NMR, 400 MHz, acetone-d_6)



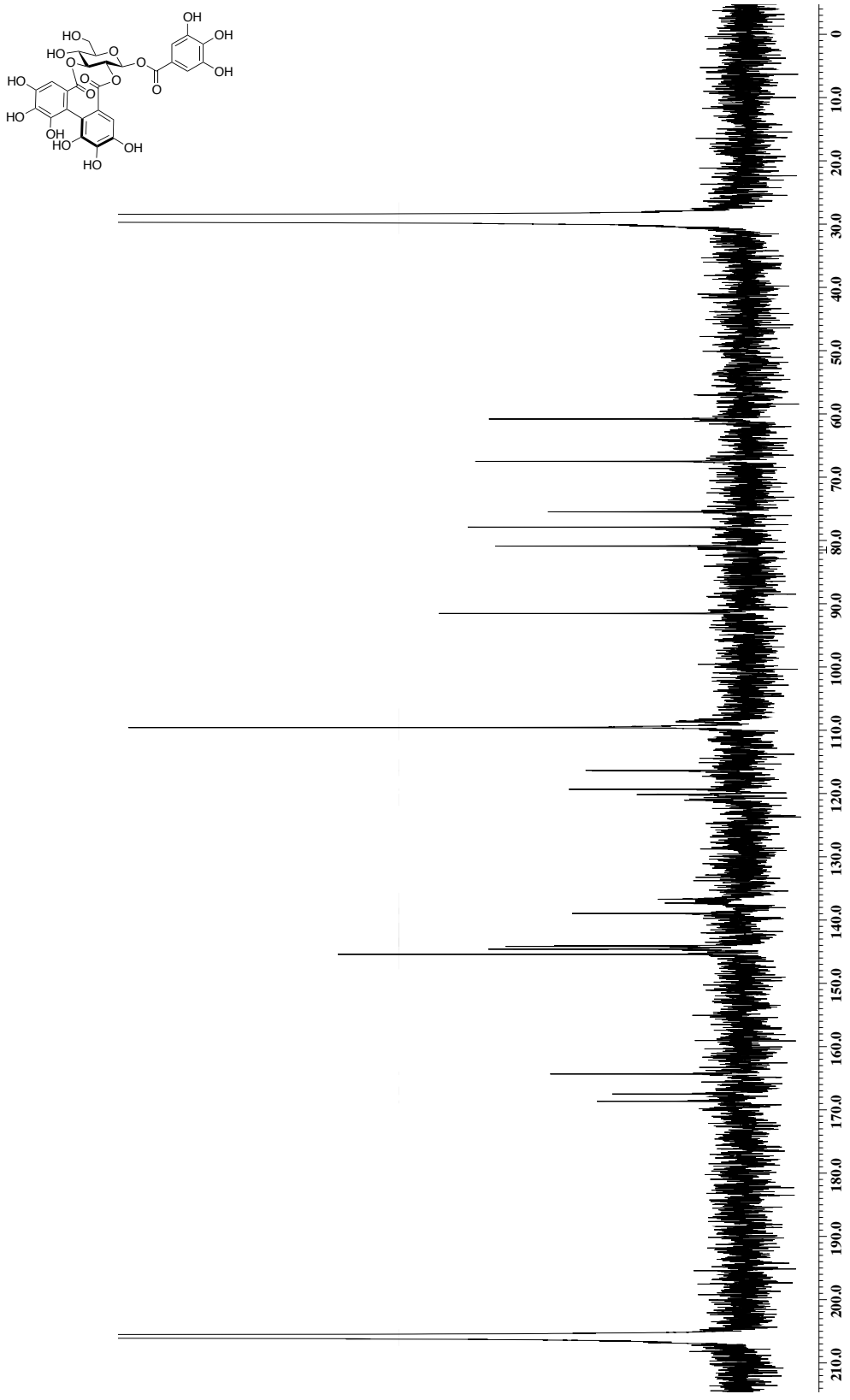
(^{13}C NMR, 100 MHz, acetone-d_6)



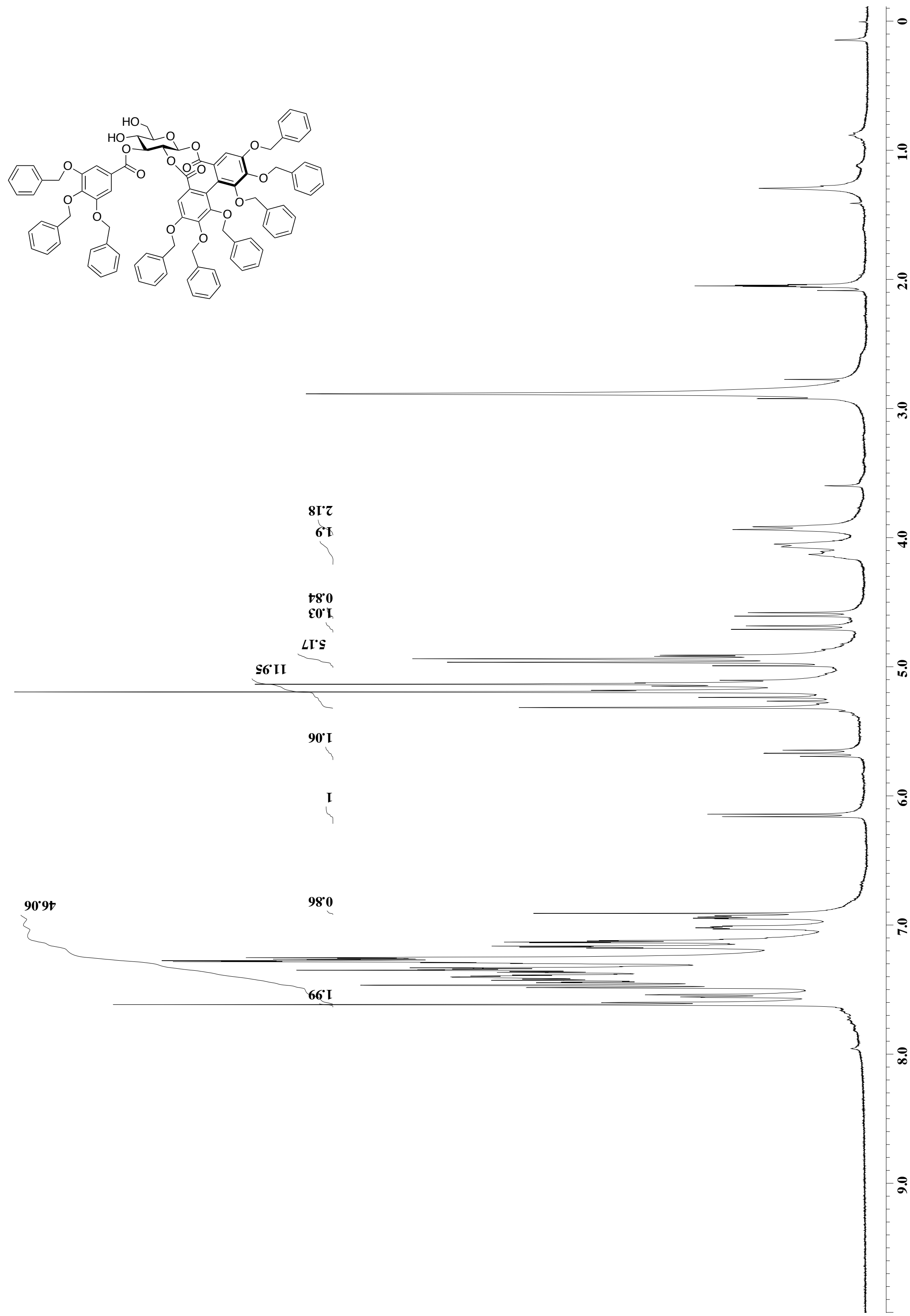
3.9. Compound 19 (^{1}H NMR, 400 MHz, acetone-d_6)



(^{13}C NMR, 100 MHz, acetone-d_6)



3.10. Compound 20 (^{1}H NMR, 400 MHz, acetone-d_6)



(^{13}C NMR, 100 MHz, acetone-d_6)