Supporting Information

Pennelliisides A-C, 2,3,4-Trisubstituted Acyl Glucoses Isolated from *Solanum pennellii*

Tenki Nakashima, Yurika Nambu, Yutaka Inoue, Masimbula Rishni, and Hideyuki Matsuura

Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

Pennelliisides A-C, 2,3,4-Trisubstituted Acyl Glucoses Isolated from *Solanum pennellii*

Table S1. ^{1}H (500 MHz) and ^{13}C (67.5 MHz) NMR Spectroscopic Data for Compound **4** in C_6D_6

	position	δ_C	type	δ_H, mult. (*J* in Hz)
glucose moiety	1	99.5	CH	4.36, d (6.3)
	2	72.9	CH	5.45, dd (8.6, 6.3)
	3	71.3	CH	5.43, dd (9.3, 8.6)
	4	69.2	CH	5.29, dd (9.3, 9.1)
	5	73.5	CH	3.39, m
	6	69.2	CH_2	3.47, m
benzyl moiety	1a′	70.7	CH_2	4.74, d (12.8)
	1b′			4.73, d (12.8)
	2′	137.4	C	
	3′	128.2	CH	7.24, d (7.5)
	4′	128.1-127.4	CH	7.11-7.19, m
	5′	128.1-127.4	CH	7.07, t (7.3)
	6′	128.1-127.4	CH	7.11-7.19, m
	7′	128.2	CH	7.24, d (7.5)
acyl moiety	A-1	174.4	C	
	A-2	33.9	CH	2.41, m (7.0)
	A-3	18.5-18.7	CH_3	1.07, d (7.0)
	A-4	18.5-18.7	CH_3	1.07, d (7.0)
	B-1	175.5	C	
	B-2	33.9	CH	2.39, m (7.1)
	B-3	18.5-18.7	CH_3	1.06, d (7.1)
	B-4	18.5-18.7	CH_3	1.06, d (7.1)
	C-1	174.6	C	
	C-2	33.9	CH	2.30, m (7.0)
	C-3	18.6 [a]	CH_3[a]	1.01. d (7.0) [b]
	C-4	18.5 [a]	CH_3[a]	0.97, d (7.0) [b]
benzyl moiety	1a″	73.2	CH_2	4.33, d (12.3)
	1b″			4.30, d (12.3)
	2″	138.3	C	
	3″	128.2	CH	7.27, d (7.3)
	4″	128.1-127.4	CH	7.11-7.19, m
	5″	128.1-127.4	CH	7.07, t (7.3)
	6″	128.1-127.4	CH	7.11-7.19, m
	7″	128.2	CH	7.27, d (7.3)

a), b): values are interchangeable in each other

Table S2. ^{1}H (500 MHz) and ^{13}C (67.5 MHz) NMR Spectroscopic Data for Compound **5** in C_6D_6

	position	δ_C	type	δ_H, mult. (*J* in Hz)
glucose moiety	1	99.4	CH	4.39, d (7.7)
	2	71.3	CH	5.46, dd (9.0, 7.7)
	3	72.8	CH	5.49, dd (9.2, 9.0)
	4	69.3	CH	5.31, dd (9.2, 9.1)
	5	73.5	CH	3.43, m
	6	69.1	CH_2	3.48, m
benzyl moiety	1a′	69.9	CH_2	4.75, d (12.2)
	1b′			4.46, d (12.2)
	2′	137.3	C	
	3′	128.5-127.0	CH	7.24, d (7.7)
	4′	128.5-127.0	CH	7.11-7.19, m
	5′	128.5-127.0	CH	7.07, t (7.3)
	6′	128.5-127.0	CH	7.11-7.19, m
	7′	128.5-127.0	CH	7.24, d (7.7)
acyl moiety	A-1	174.5	C	
	A-2	33.8	CH	2.45, m (6.9)
	A-3	18.5 [a]	CH_3	1.12, d (6.9)
	A-4	18.6 [a]	CH_3	1.12, d (6.9)
	B-1	172.3	C	
	B-2	33.9	CH_2	2.22, t (7.6)
	B-3	24.7	CH_2	1.58, m
	B-4	29.5	CH_2	1.20-1.15, m
	B-5	29.0	CH_2	1.20-1.15, m
	B-6	27.0	CH_2	1.20, m
	B-7	38.9	CH_2	1.10, m
	B-8	27.8	CH	1.47, m
	B-9	22.4	CH_3	0.88, d (6.5)
	B-10	22.4	CH_3	0.88, d (6.5)
	C-1	174.6	C	
	C-2	33.7	CH	2.34, m (6.9)
	C-3	18.5 [b]	CH_3	1.05. d (6.9) [c]
	C-4	18.4 [b]	CH_3	1.00, d (6.9) [c]
benzyl moiety	1a″	73.1	CH_2	4.35, d (12.3)
	1b″			4.31, d (12.3)
	2″	138.2	C	
	3″	128.5-127.0	CH	7.27, d (7.3)
	4″	128.5-127.0	CH	7.11-7.19, m
	5″	128.5-127.0	CH	7.07, t (7.3)
	6″	128.5-127.0	CH	7.11-7.19, m
	7″	128.5-127.0	CH	7.27, d (7.3)

a), b), c): values are interchangeable in each other

Table S3. ^{1}H (500 MHz) and ^{13}C (67.5 MHz) NMR Spectroscopic Data for Compound **6** in C_6D_6

	position	δ_C	type	δ_H, mult. (*J* in Hz)
glucose moiety	1	99.4	CH	4.39, d (7.3)
	2	71.3	CH	5.47, dd (9.7, 7.3)
	3	72.8	CH	5.49, dd (9.7, 9.6)
	4	69.2	CH	5.32, dd (9.6, 9.1)
	5	73.5	CH	3.43, m
	6	69.1	CH_2	3.48, m
benzyl moiety	1a′	69.9	CH_2	4.75, d (12.1)
	1b′			4.45, d (12.1)
	2′	137.3	C	
	3′	128.2-127.1	CH	7.24, d (7.5)
	4′	128.2-127.1	CH	7.11-7.19, m
	5′	128.2-127.1	CH	7.07, t (7.3)
	6′	128.2-127.1	CH	7.11-7.19, m
	7′	128.2-127.1	CH	7.24, d (7.5)
acyl moiety	A-1	174.5	C	
	A-2	33.8	CH	2.45, m (7.4)
	A-3	18.6 [a]	CH_3	1.14-0.98, d (7.4)
	A-4	18.5 [a]	CH_3	1.14-0.98, d (7.4)
	B-1	172.3	C	
	B-2	33.9	CH_2	2.22, t (7.3)
	B-3	24.7	CH_2	1.59, m
	B-4	29.1	CH_2	1.20, m
	B-5-B-7	29.4- 29.1	CH_2	1.35-1.75, m
	B-8	31.8	CH_2	1.22, m
	B-9	22.6	CH_2	1.28, m
	B-10	13.9	CH_3	0.90, t (6.8)
	C-1	174.6	C	
	C-2	33.7	CH	2.34 m (6.9)
	C-3	18.5 [b]	CH_3	1.14-0.98, d (6.9)
	C-4	18.4 [b]	CH_3	1.14-0.98, d (6.9)
benzyl moiety	1a″	73.1	CH_2	4.35, d (12.3)
	1b″			4.31, d (12.3)
	2″	138.2	C	
	3″	128.2-127.1	CH	7.27, d (7.5)
	4″	128.2-127.1	CH	7.11-7.19, m
	5″	128.2-127.1	CH	7.07, t (7.3)
	6″	128.2-127.1	CH	7.11-7.19, m
	7″	128.2-127.1	CH	7.27, d (7.5)

a), b): values are interchangeable in each other

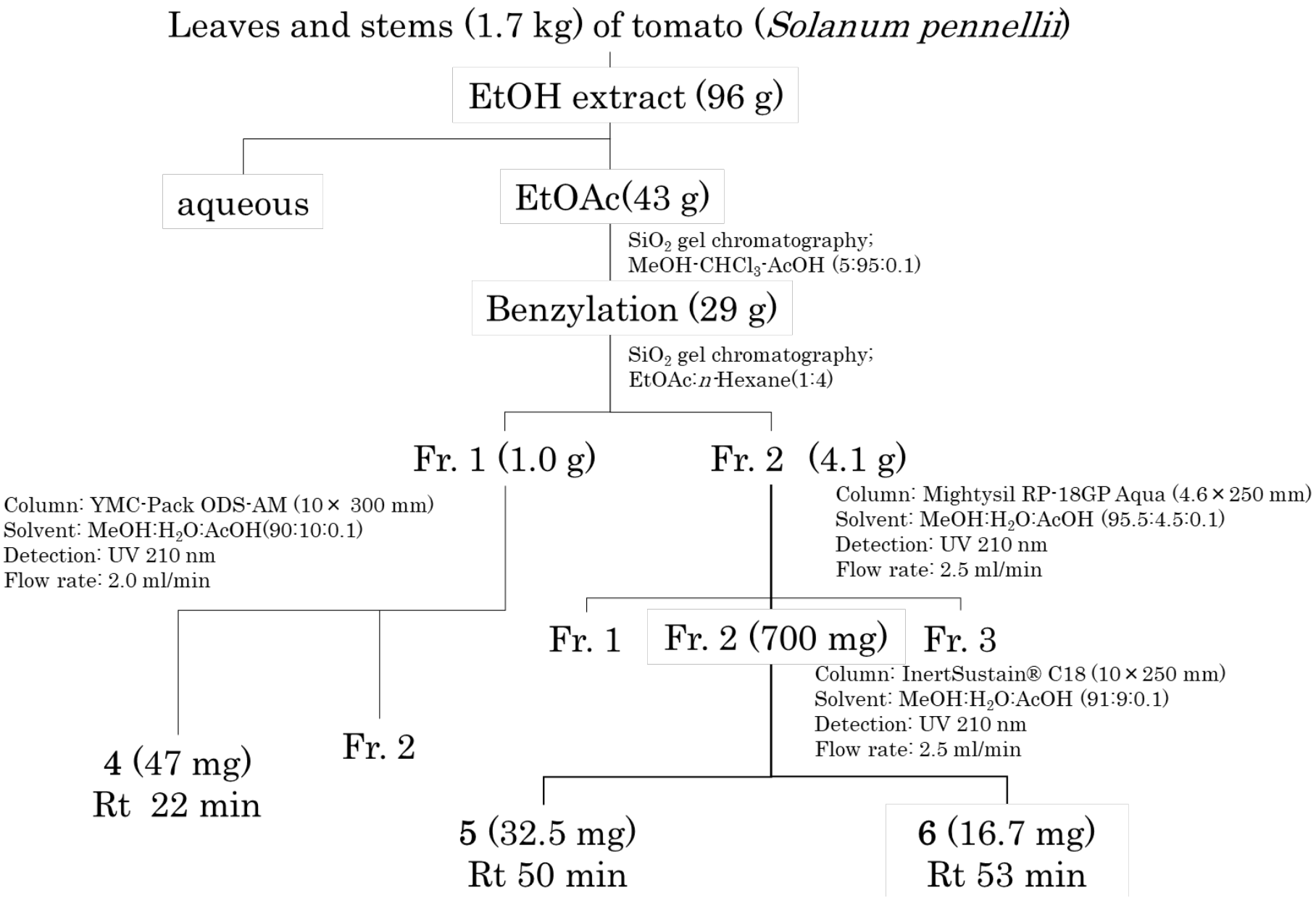

Figure S1. Extraction and isolation.

Figure S2. HRFD-MS spectrum of **4**.

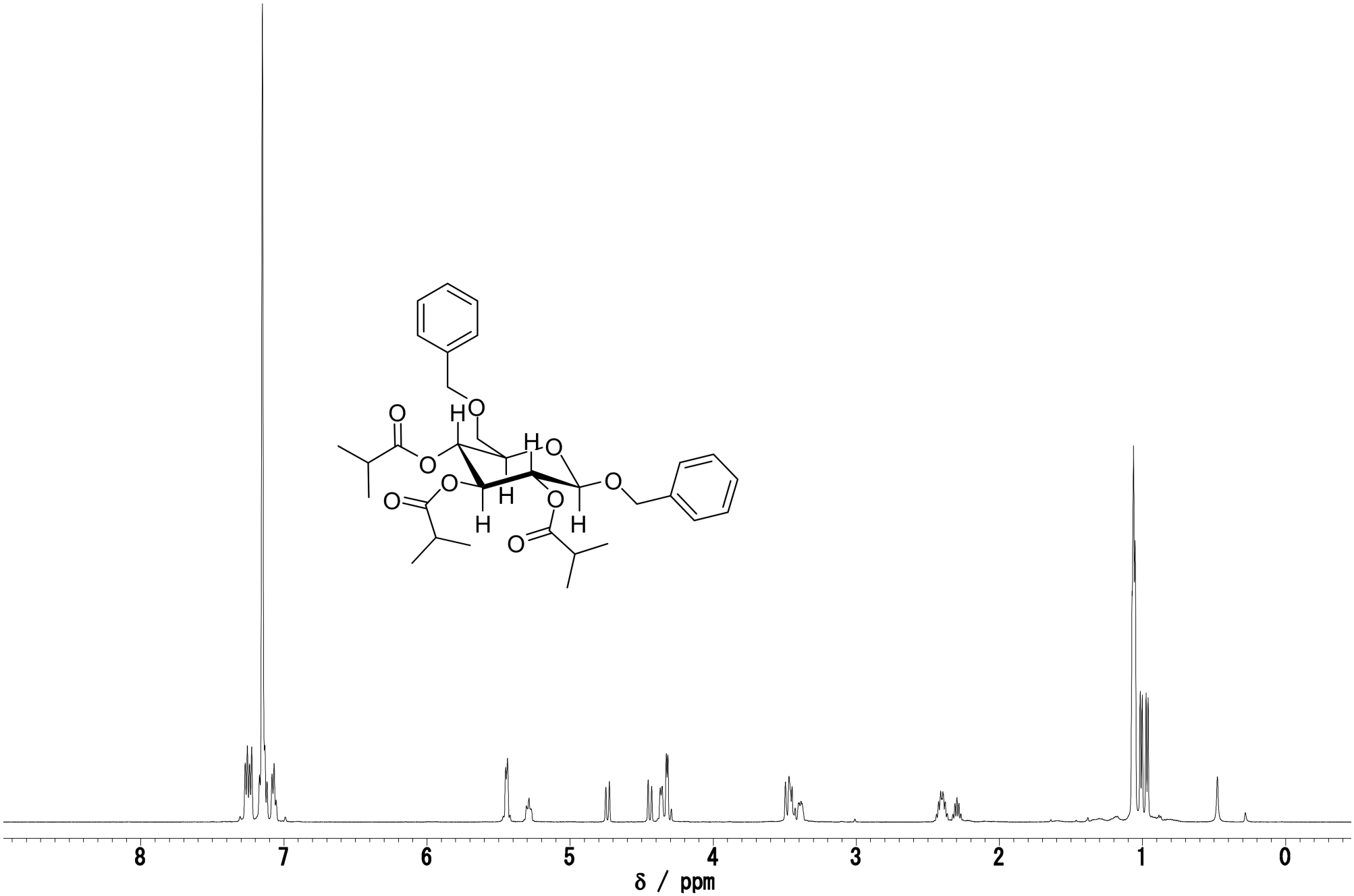

Figure S3. ^{1}H NMR spectrum of **4** (500 MHz, C_6D_6).

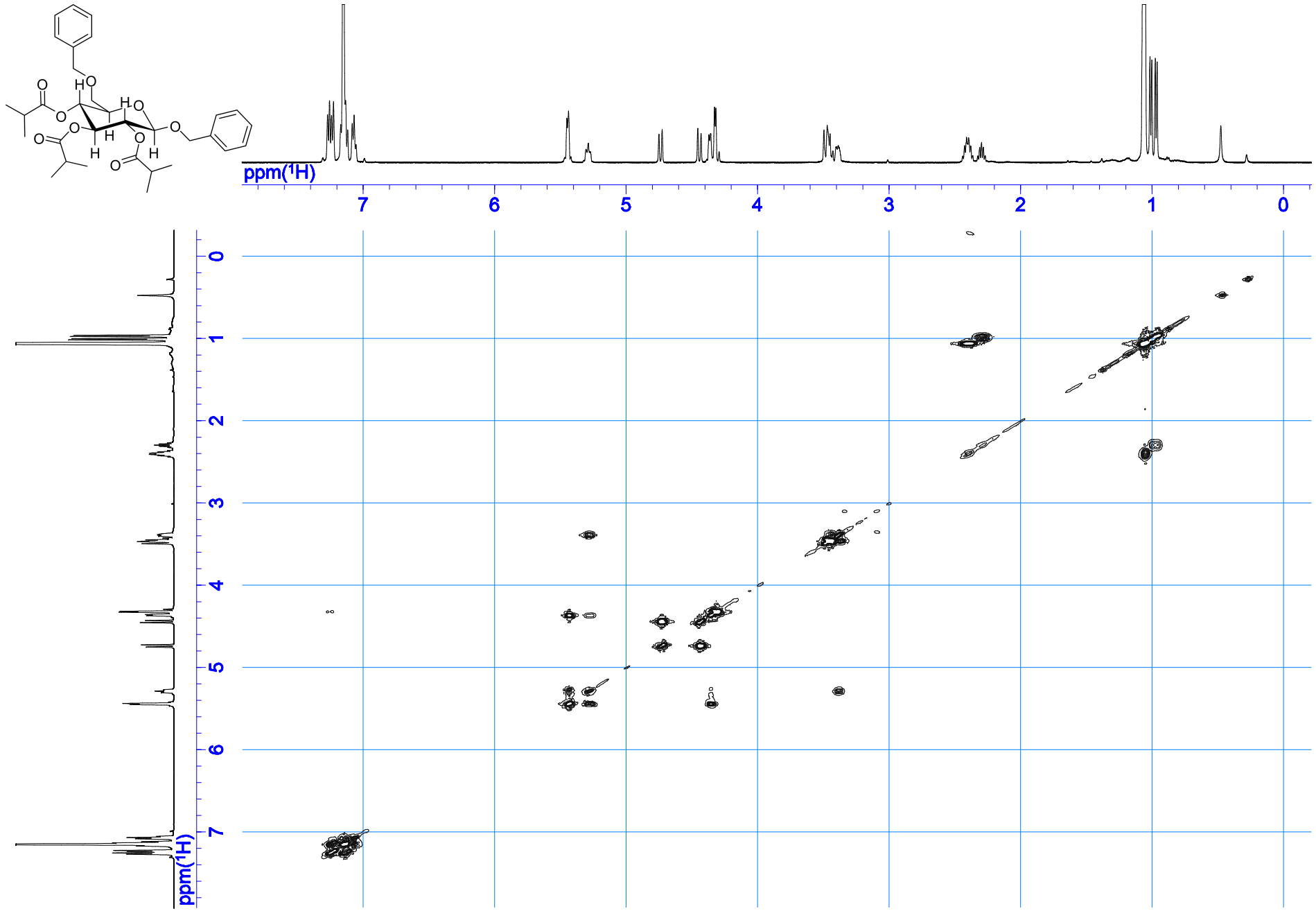

Figure S4. COSY spectrum of **4** (500 MHz, C_6D_6).

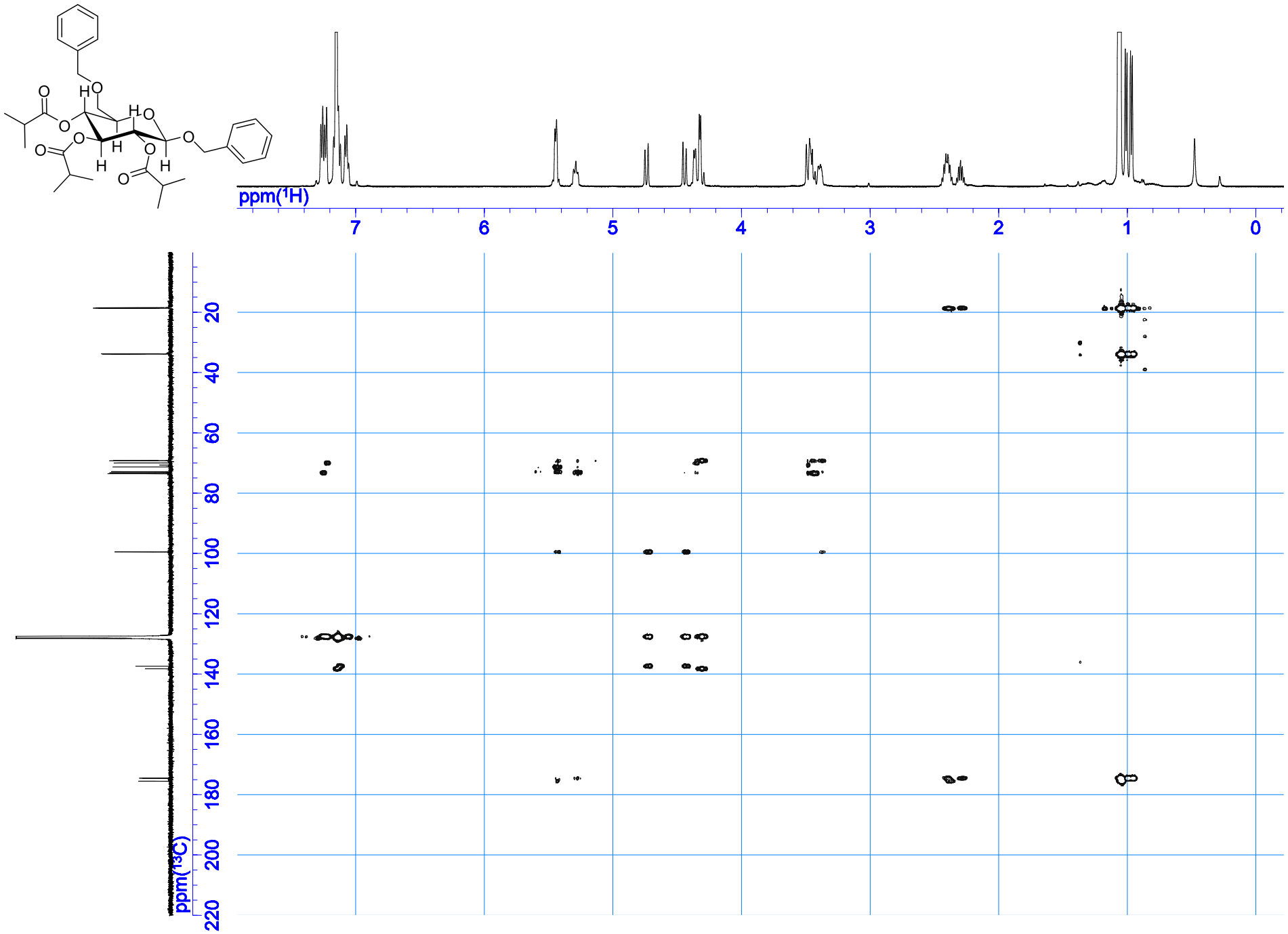

Figure S5. HMBC spectrum of **4** (500 MHz, C_6D_6).

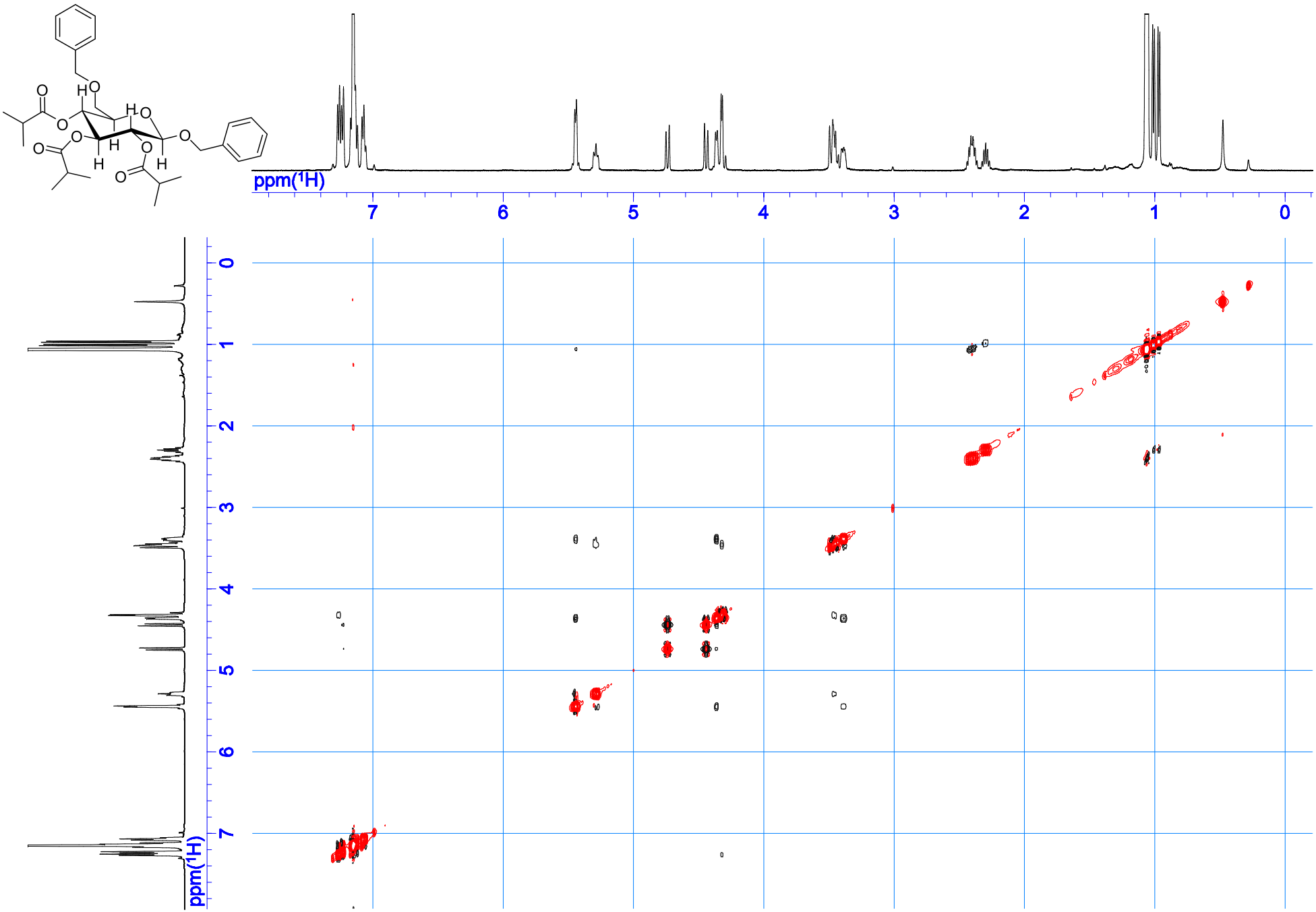

Figure S6. NOESY spectrum of **4** (500 MHz, C_6D_6).

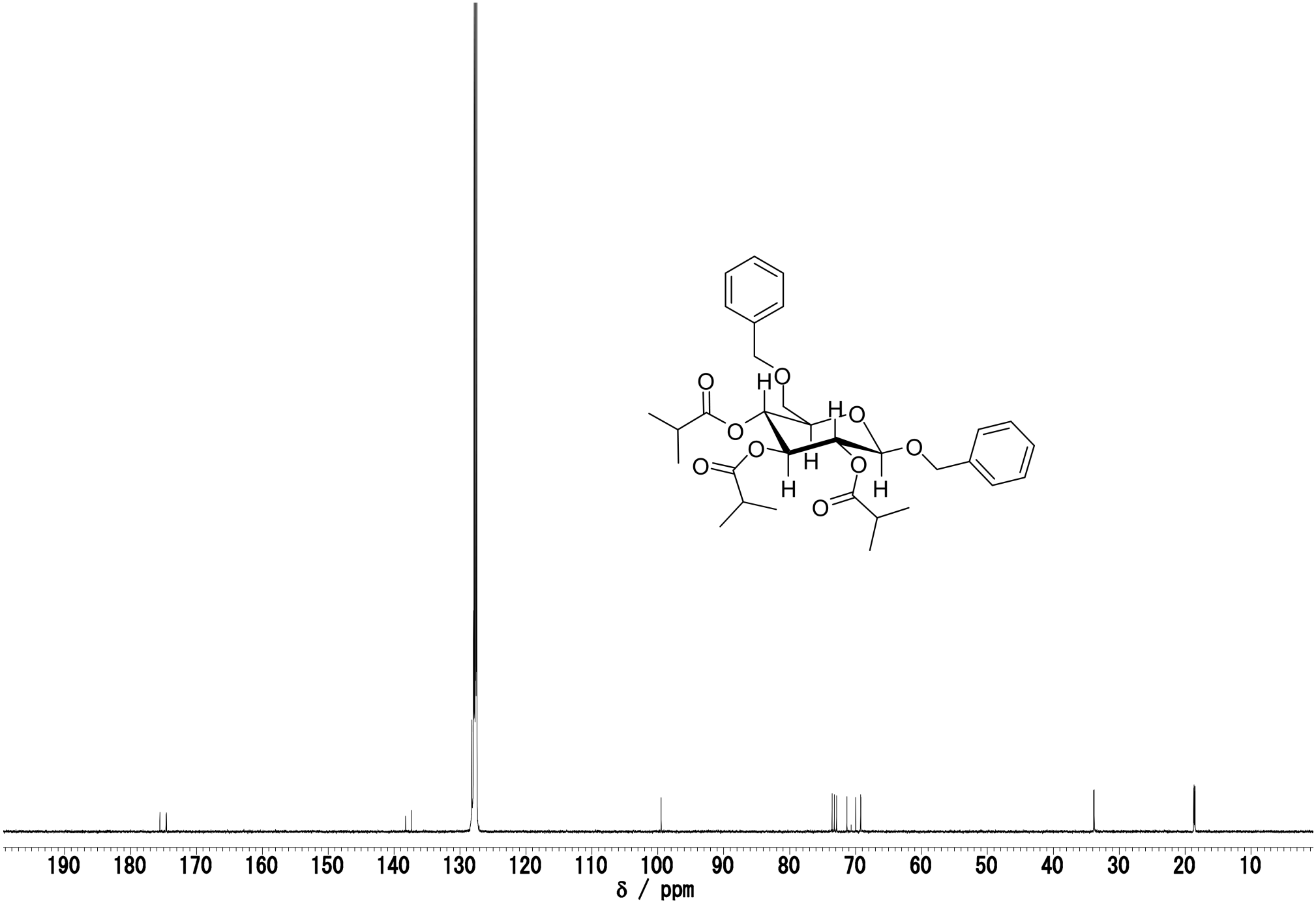

Figure S7. ^{13}C NMR spectrum of **4** (500 MHz, C_6D_6).

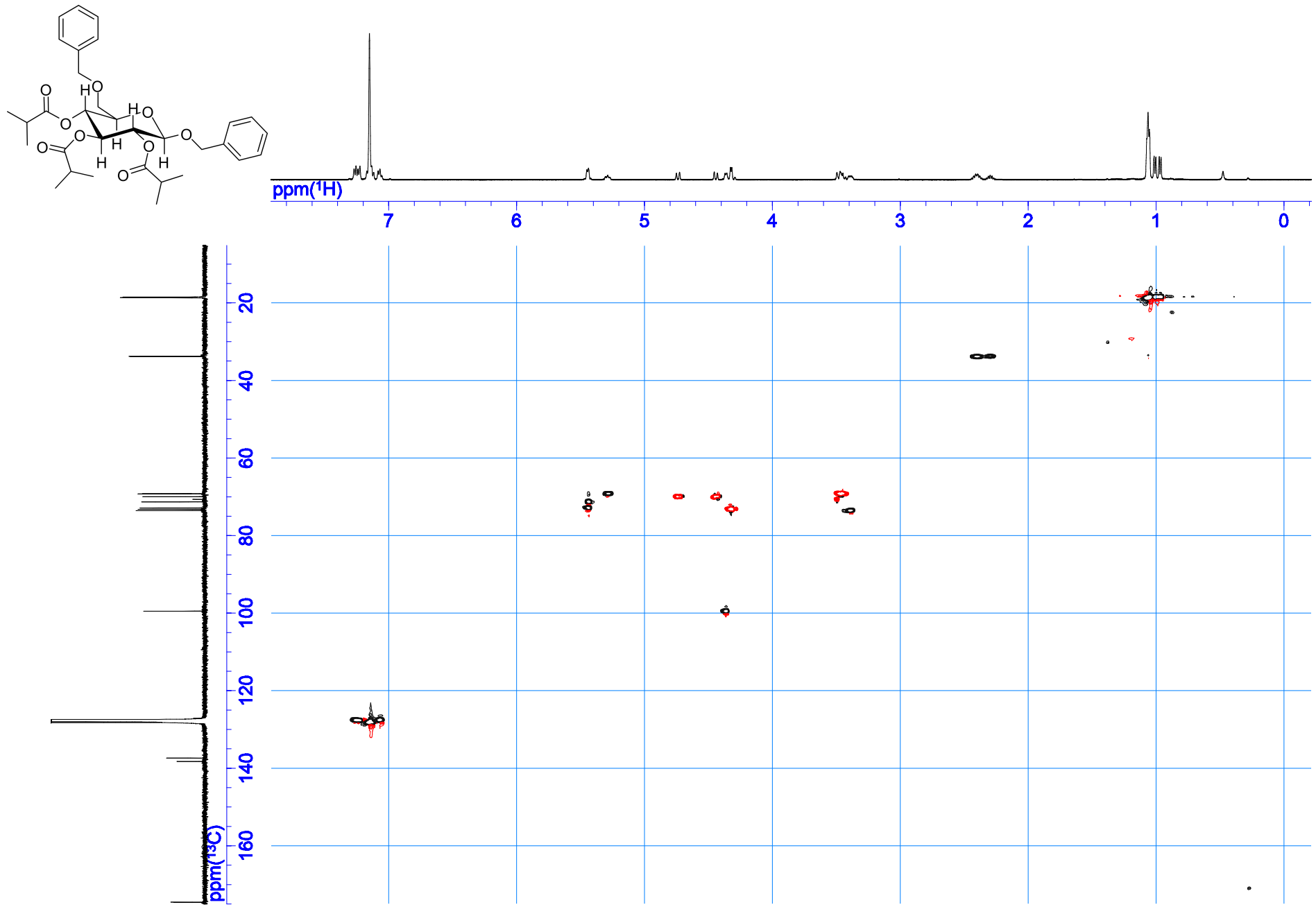

Figure S8. HSQC spectrum of **4** (500 MHz, C_6D_6).

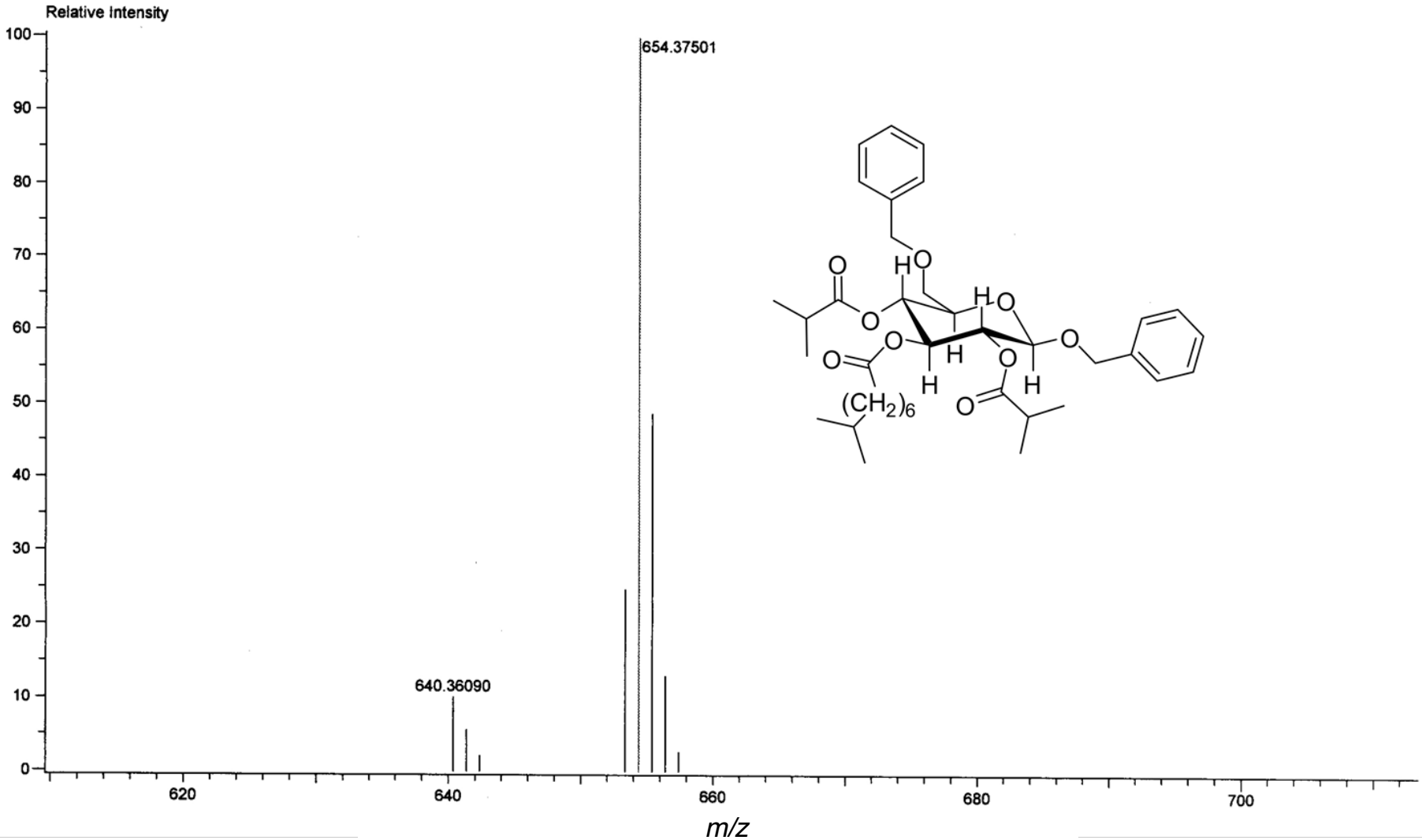

Figure S9. HRFD-MS spectrum of **5**.

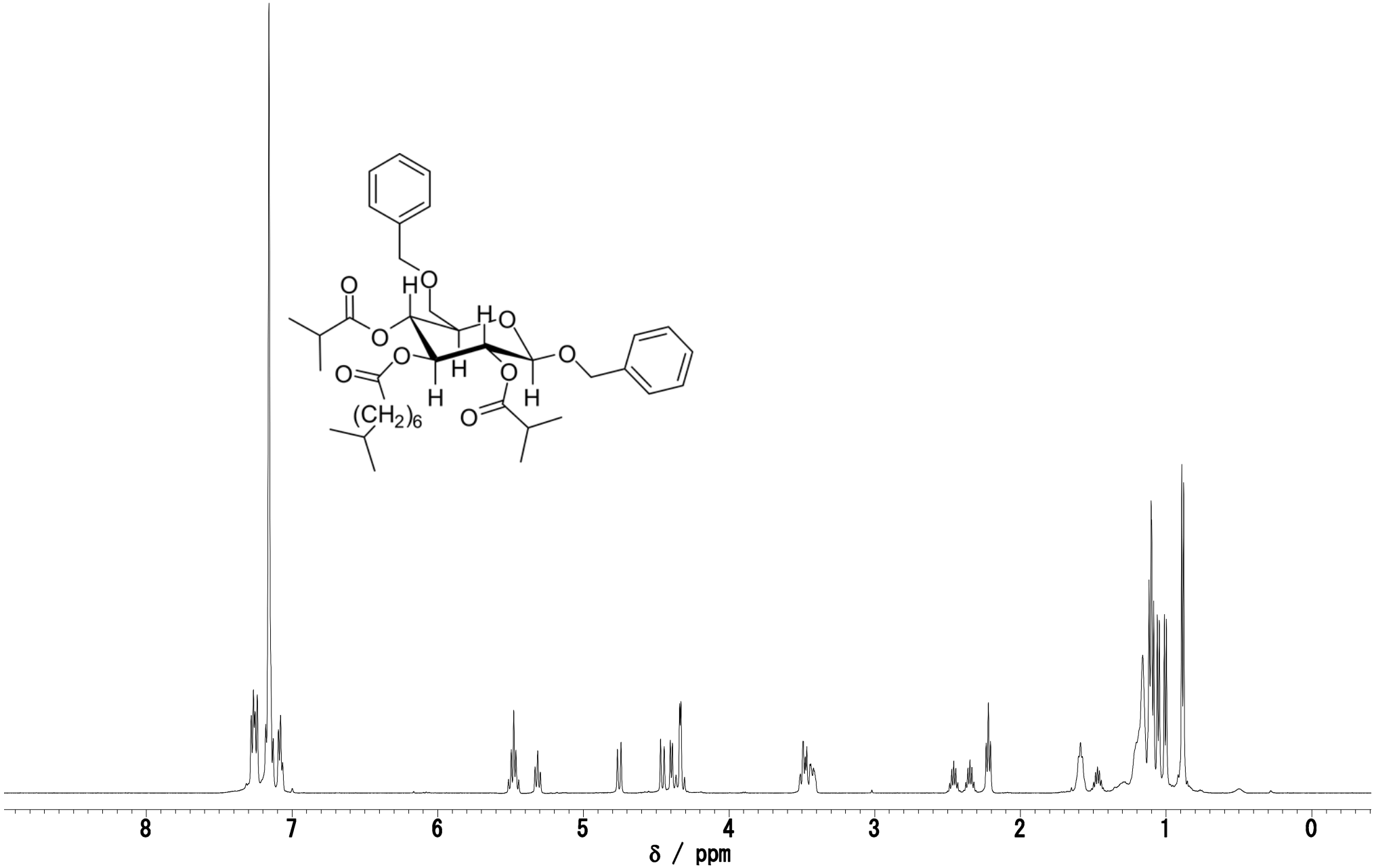

Figure S10. ^{1}H NMR spectrum of **5** (500 MHz, C_6D_6).

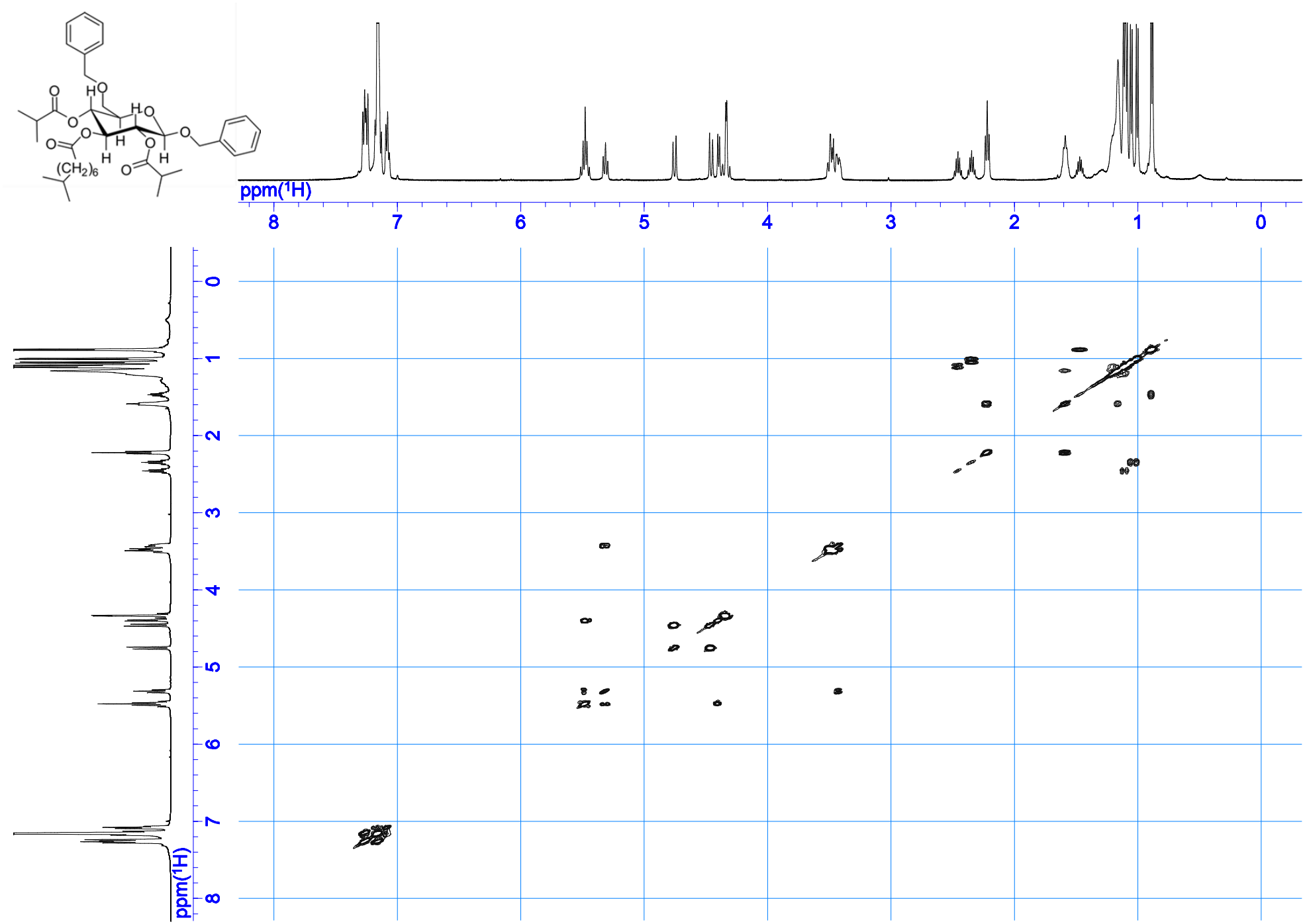

Figure S11. COSY spectrum of **5** (500 MHz, C_6D_6).

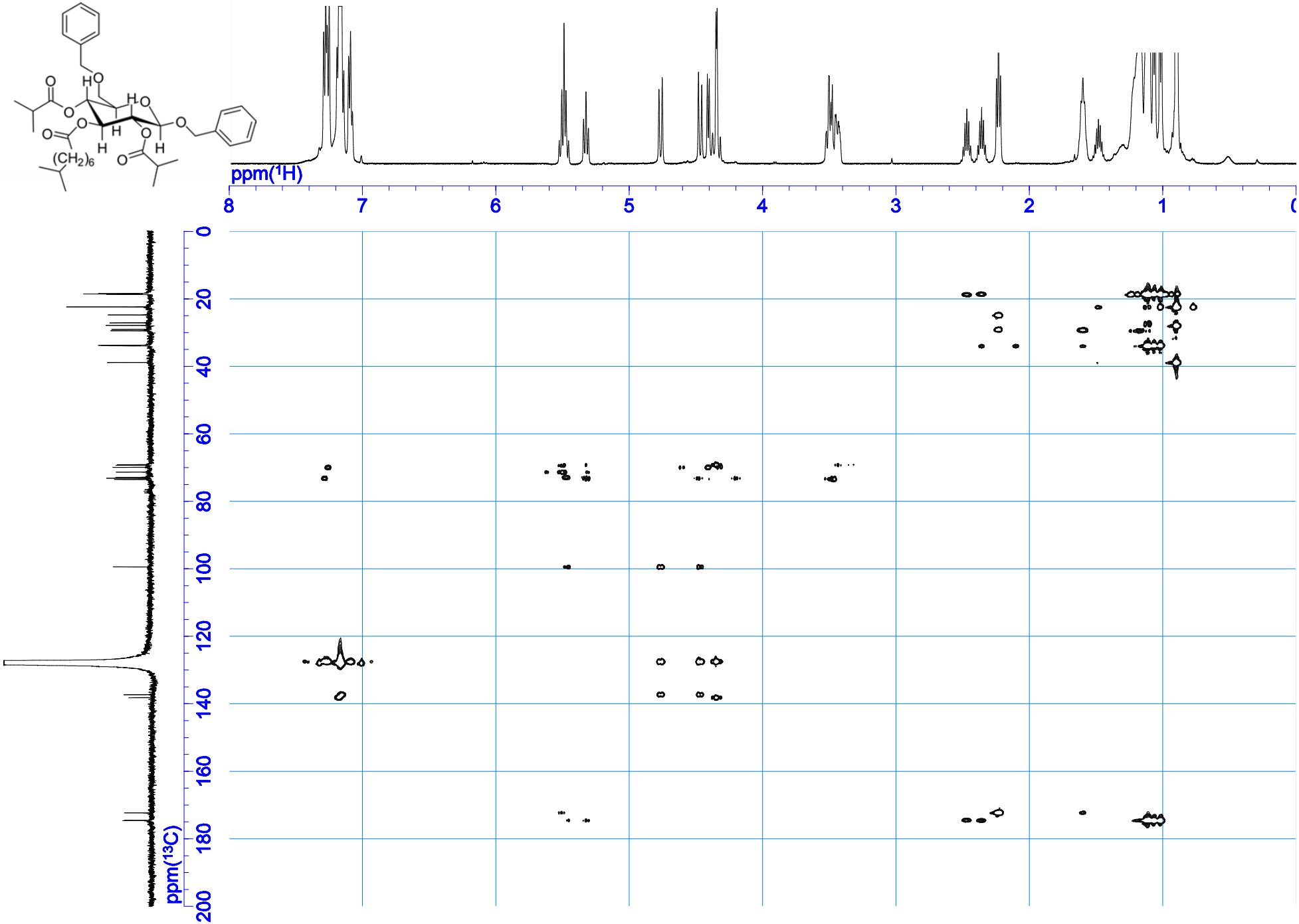

Figure S12. HMBC spectrum of **5** (500 MHz, C_6D_6).

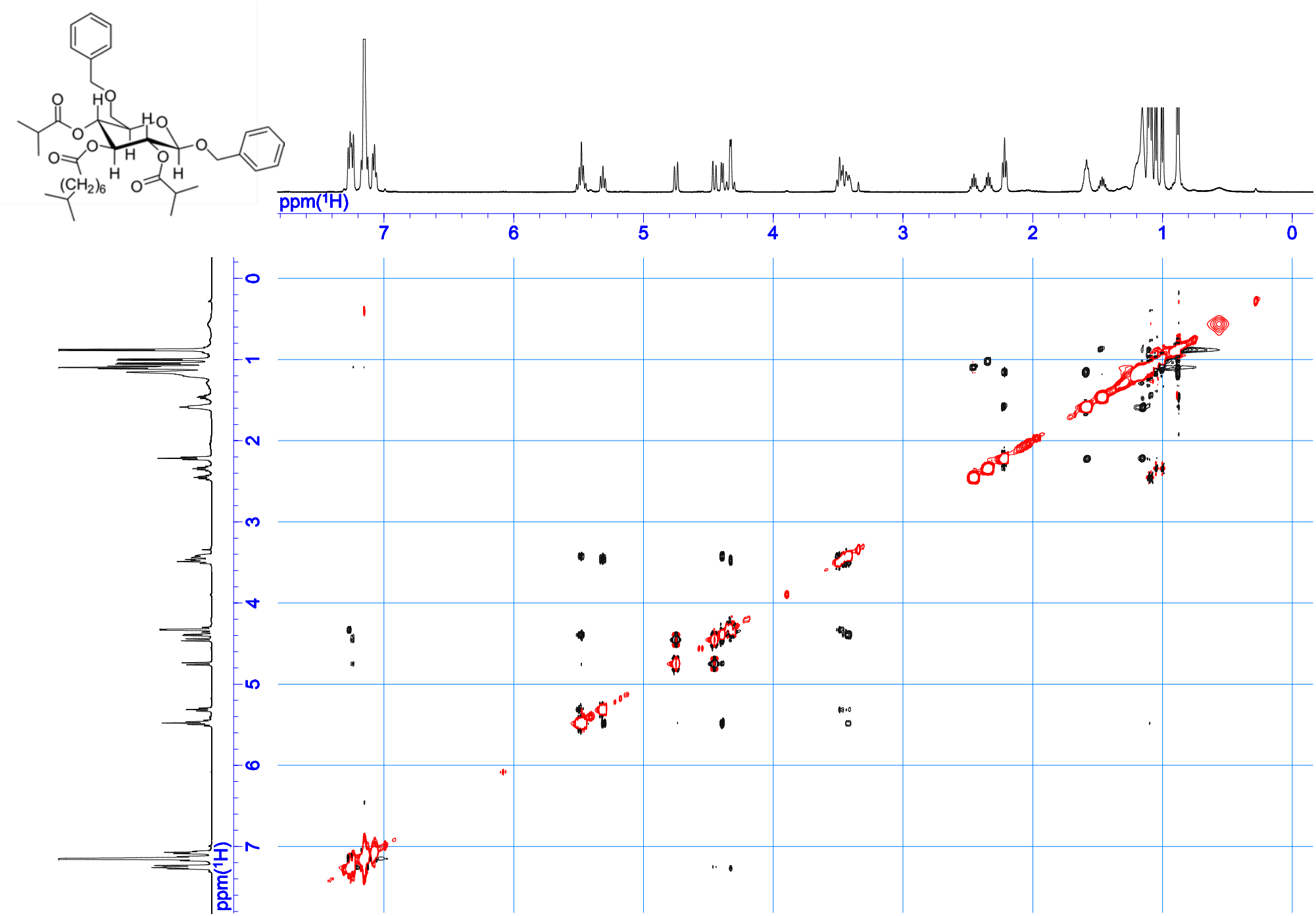

Figure S13. NOESY spectrum of **5** (500 MHz, C_6D_6).

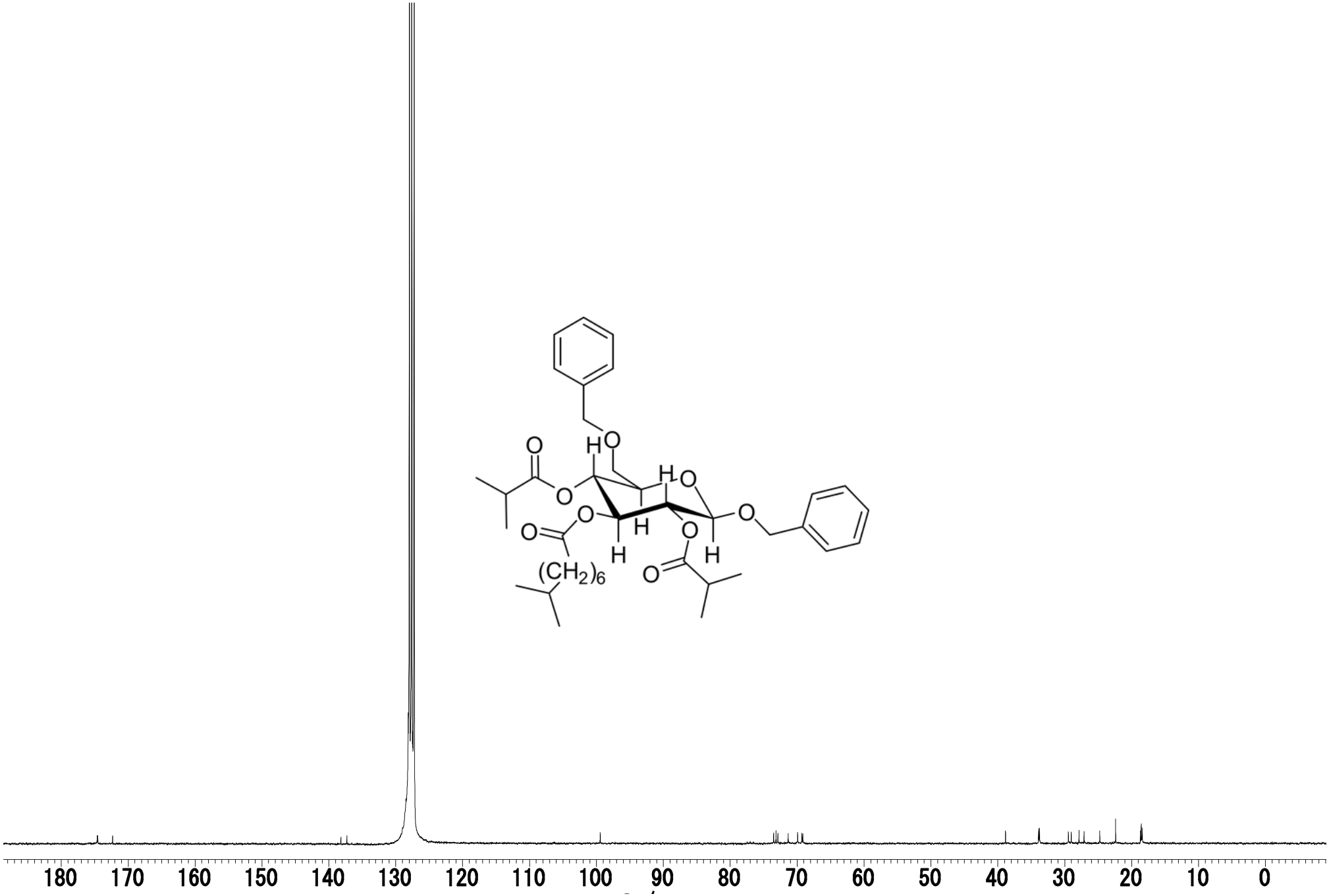

Figure S14. ^{13}C NMR spectrum of **5** (270 MHz, C_6D_6).

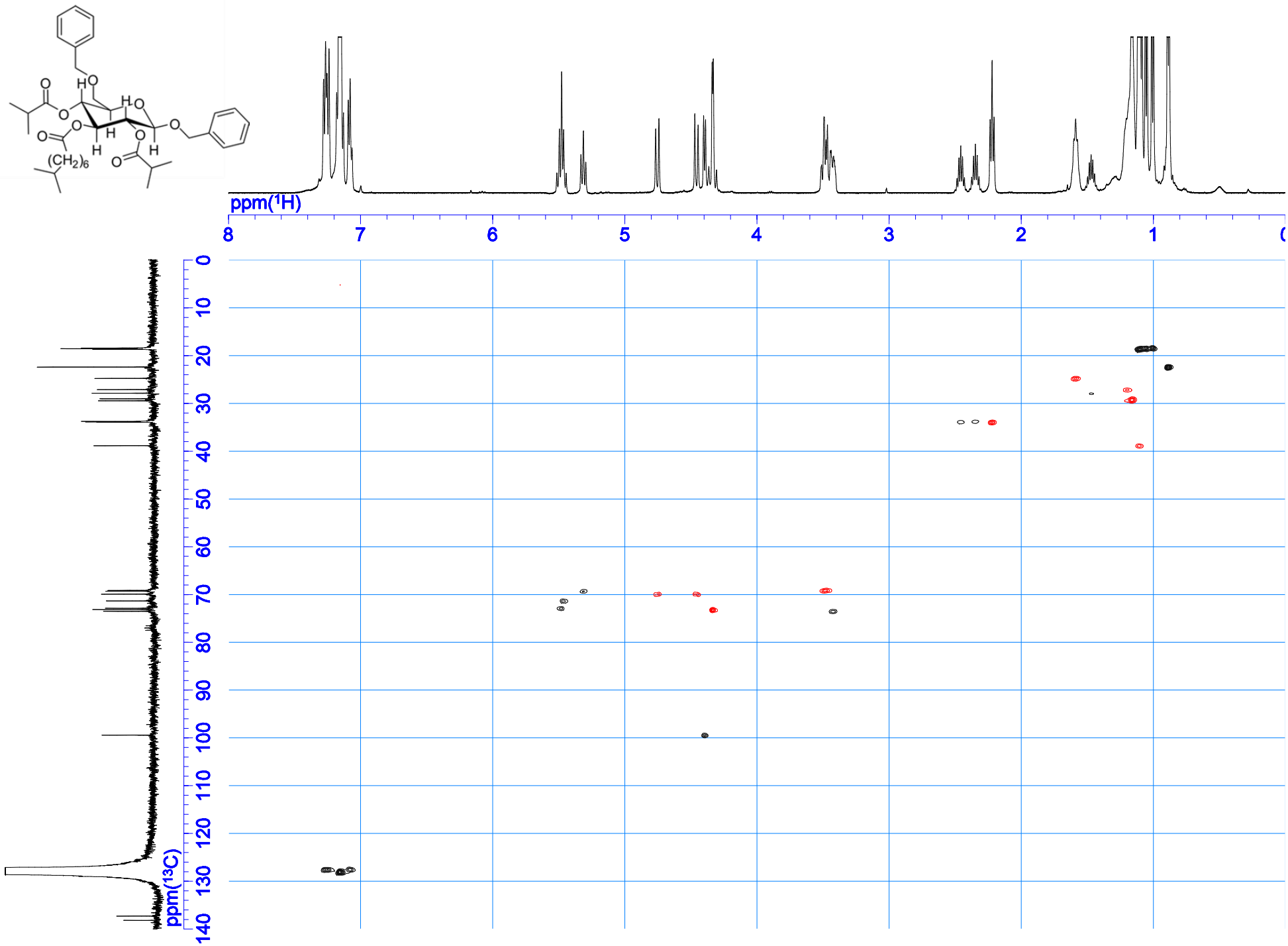

Figure S15. HMQC spectrum of **5** (500 MHz, C_6D_6).

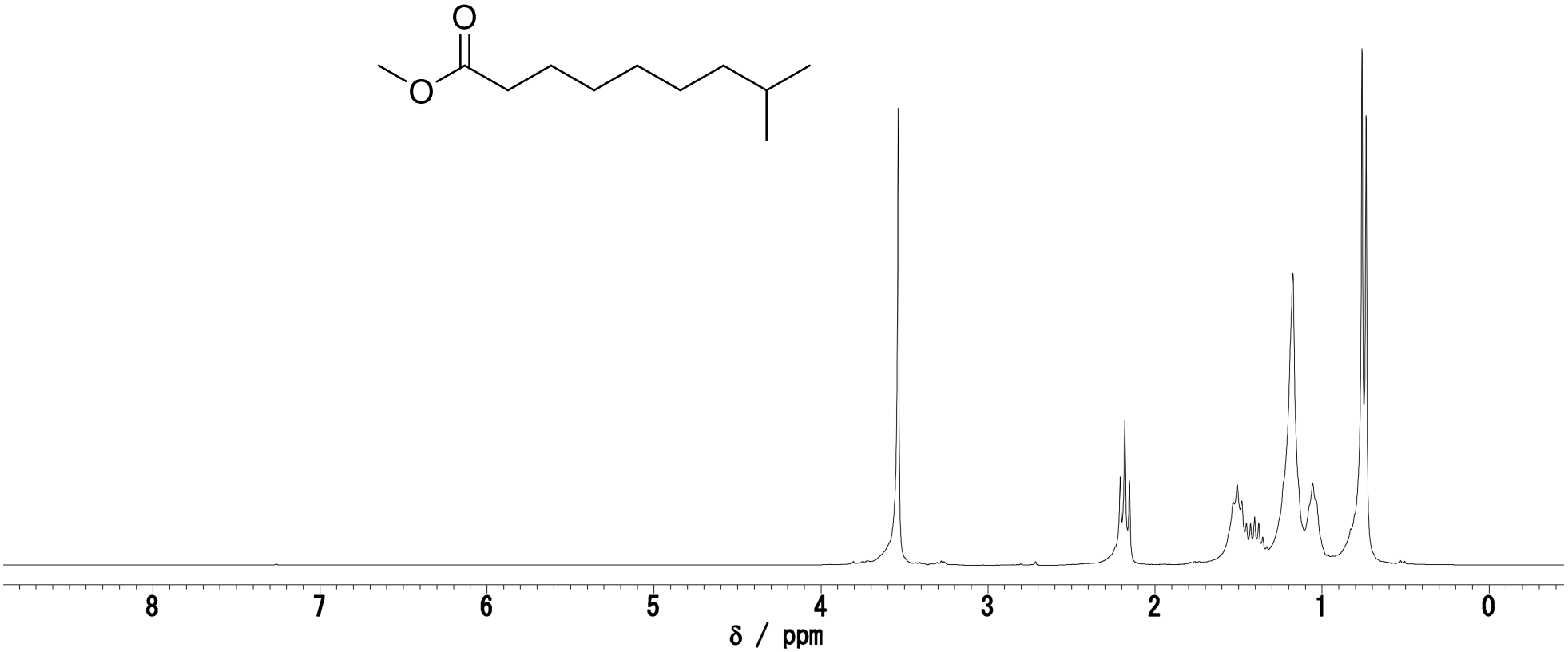

Figure S16. ^{1}H NMR spectrum of 8-methylnonanoate (**7**) (270 MHz, $CDCl_3$).

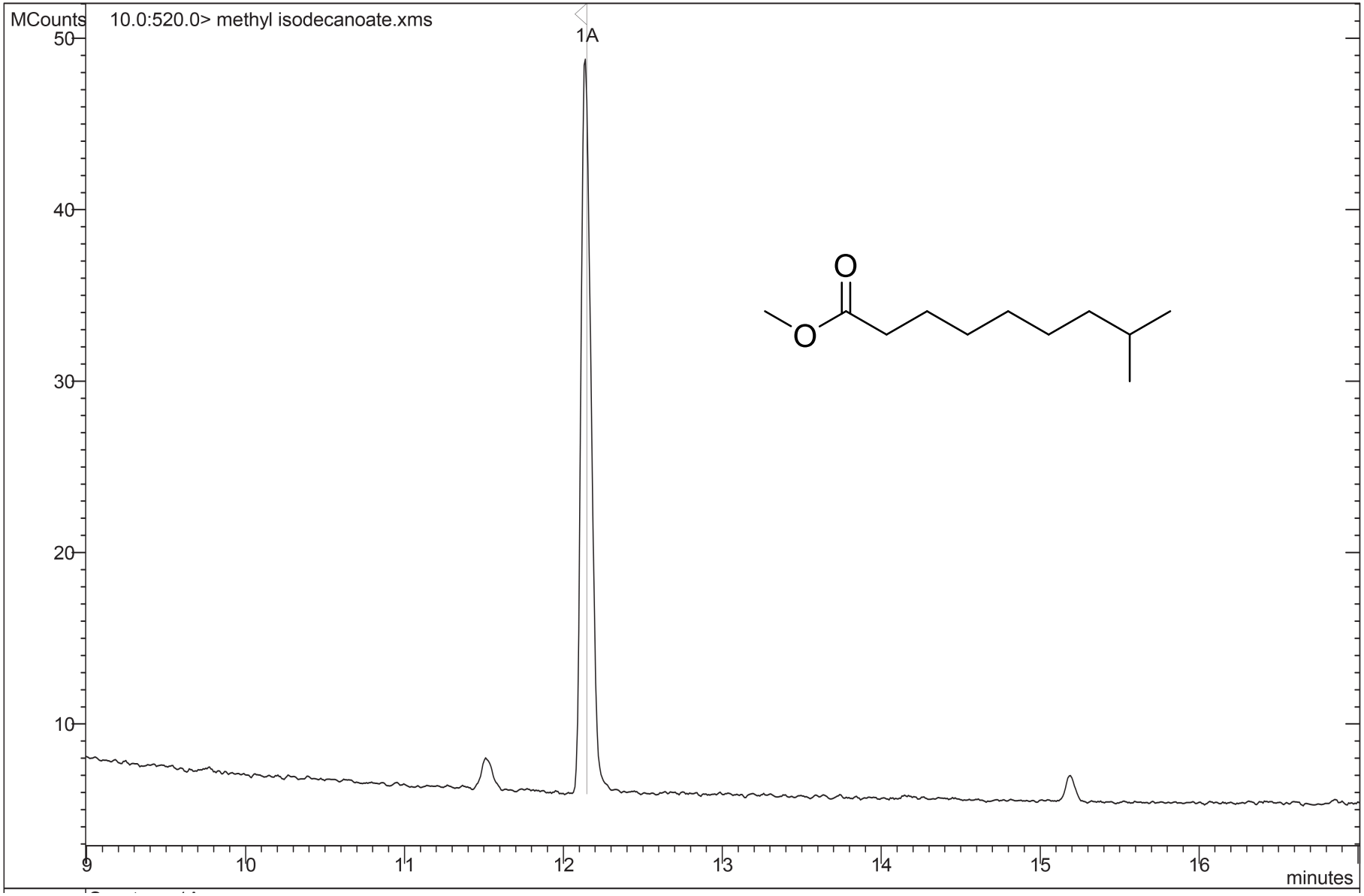

Figure S17. GC-MS chromatogram of 8-methylnonanoate (**7**).

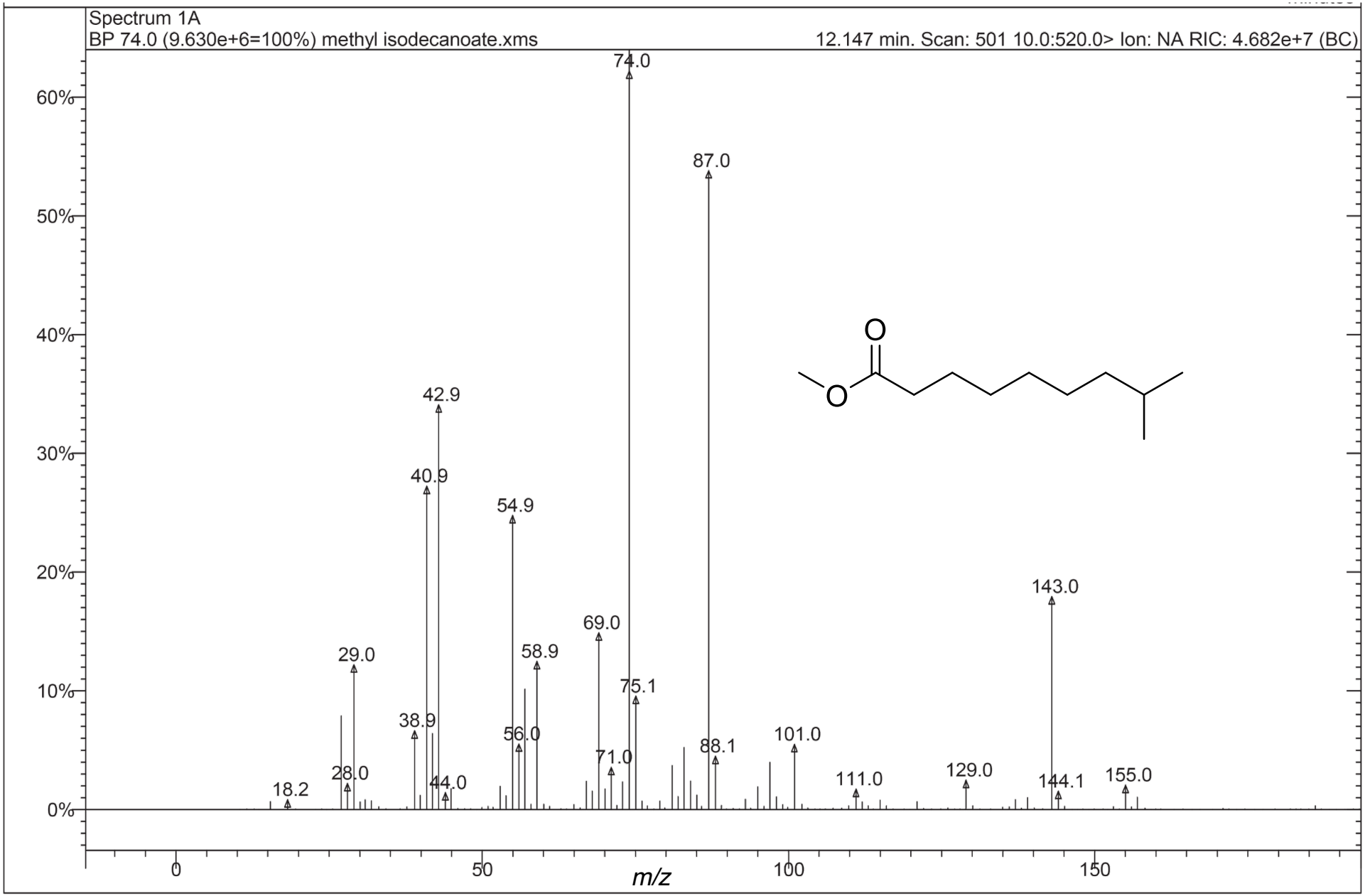

Figure S18. Fragmentation pattern of the MS peak for 8-methylnonanoate (**7**) having Rt. of 12.1 min in the chromatogram of Figure S17.

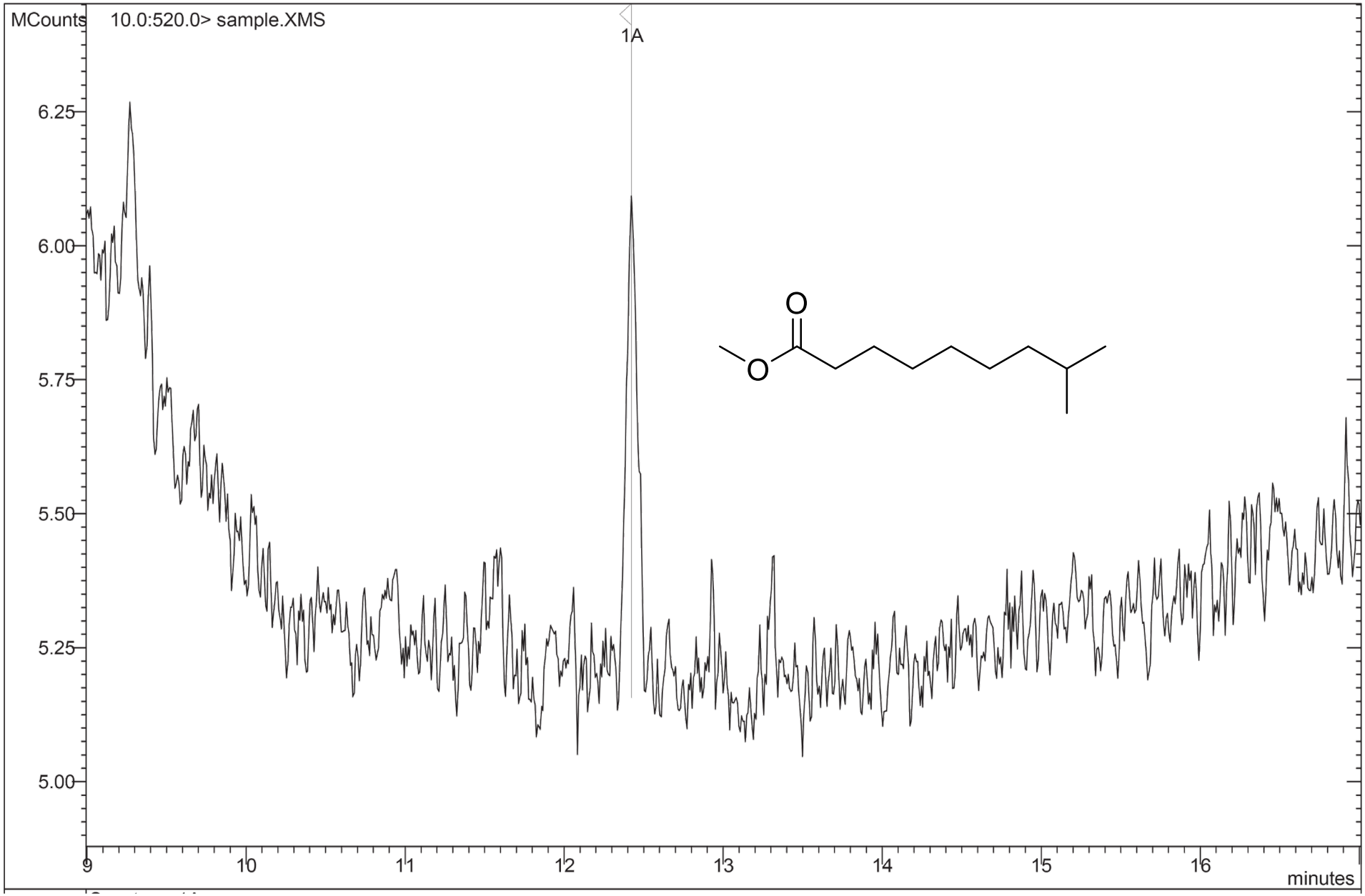

Figure S19. GC-MS chromatogram of methylated acyl moiety of **5.**

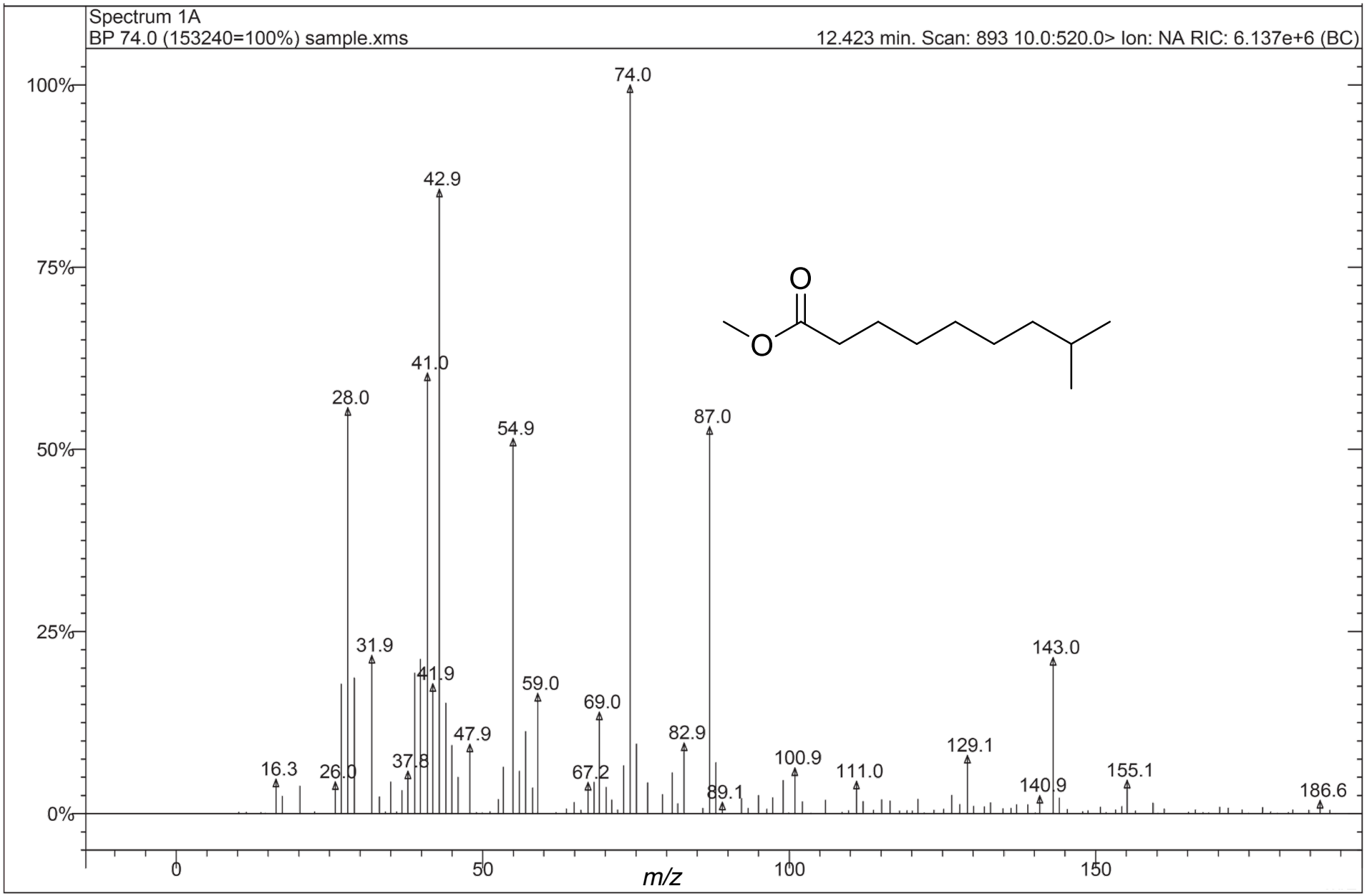

Figure S20. Fragmentation pattern of the MS peak for methylated acyl moiety of **5** having Rt. of 12.4 min in the chromatogram of Figure S19.

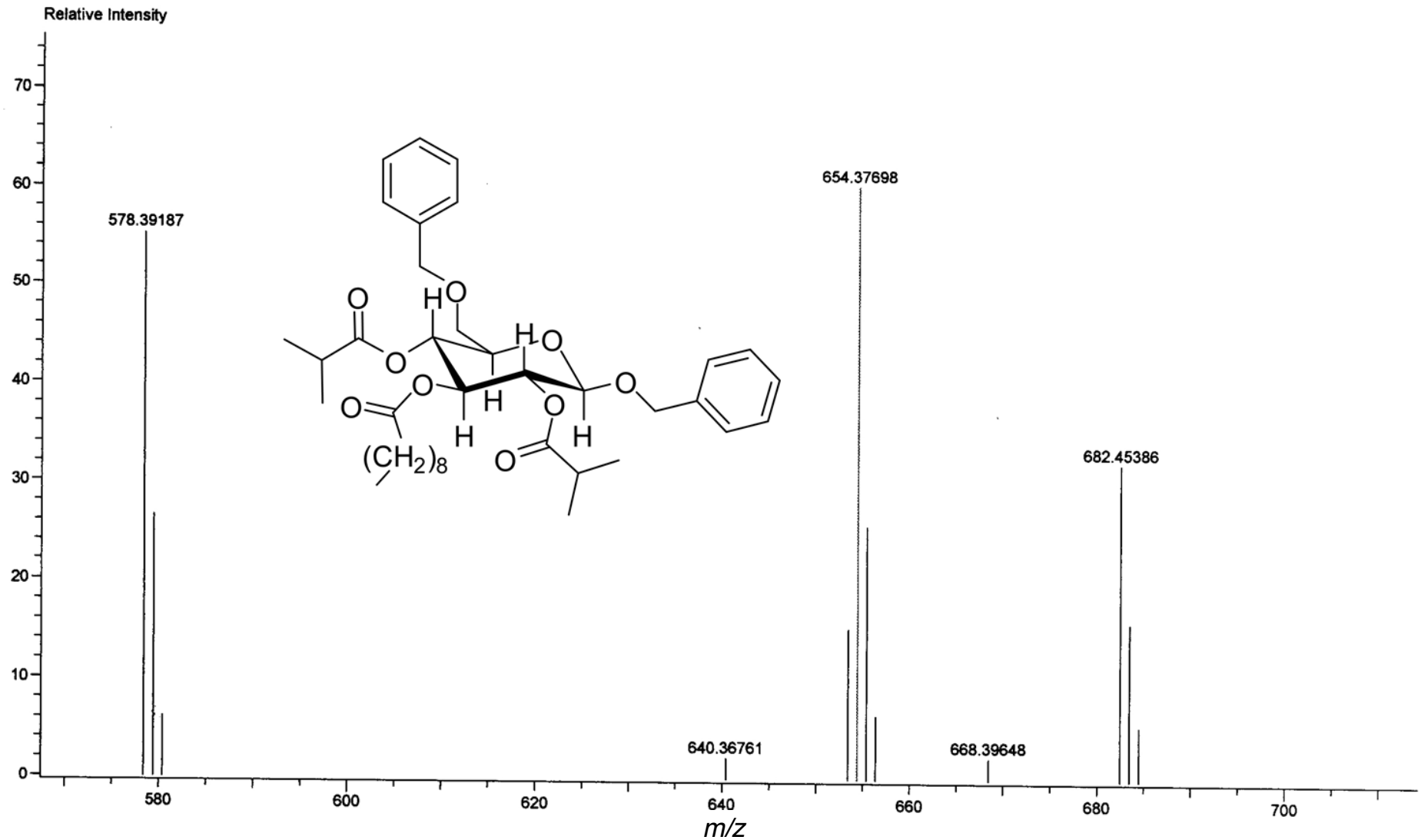

Figure S21. HRFD-MS spectrum of **6**.

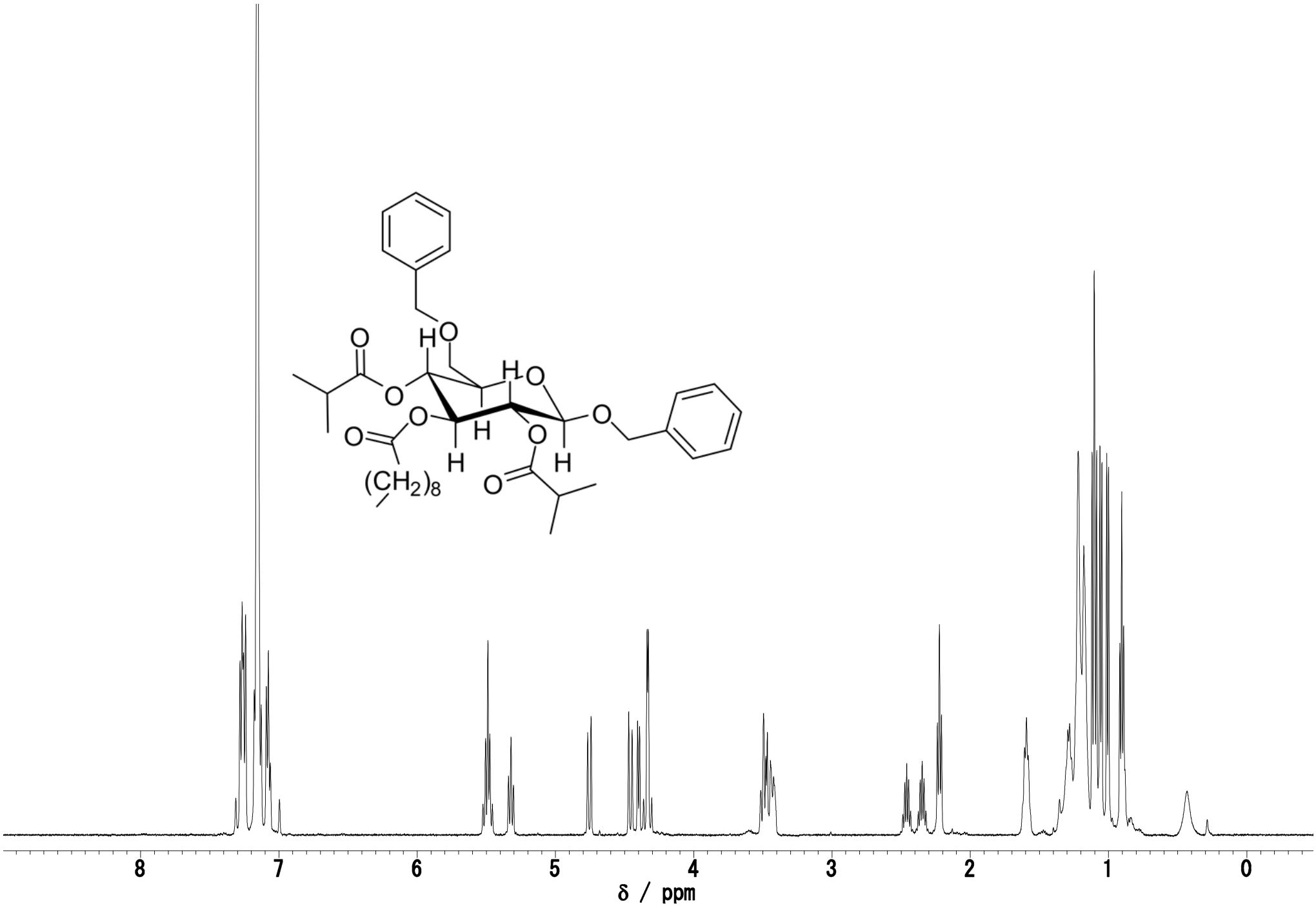

Figure S22. ^{1}H NMR spectrum of **6** (500 MHz, C_6D_6).

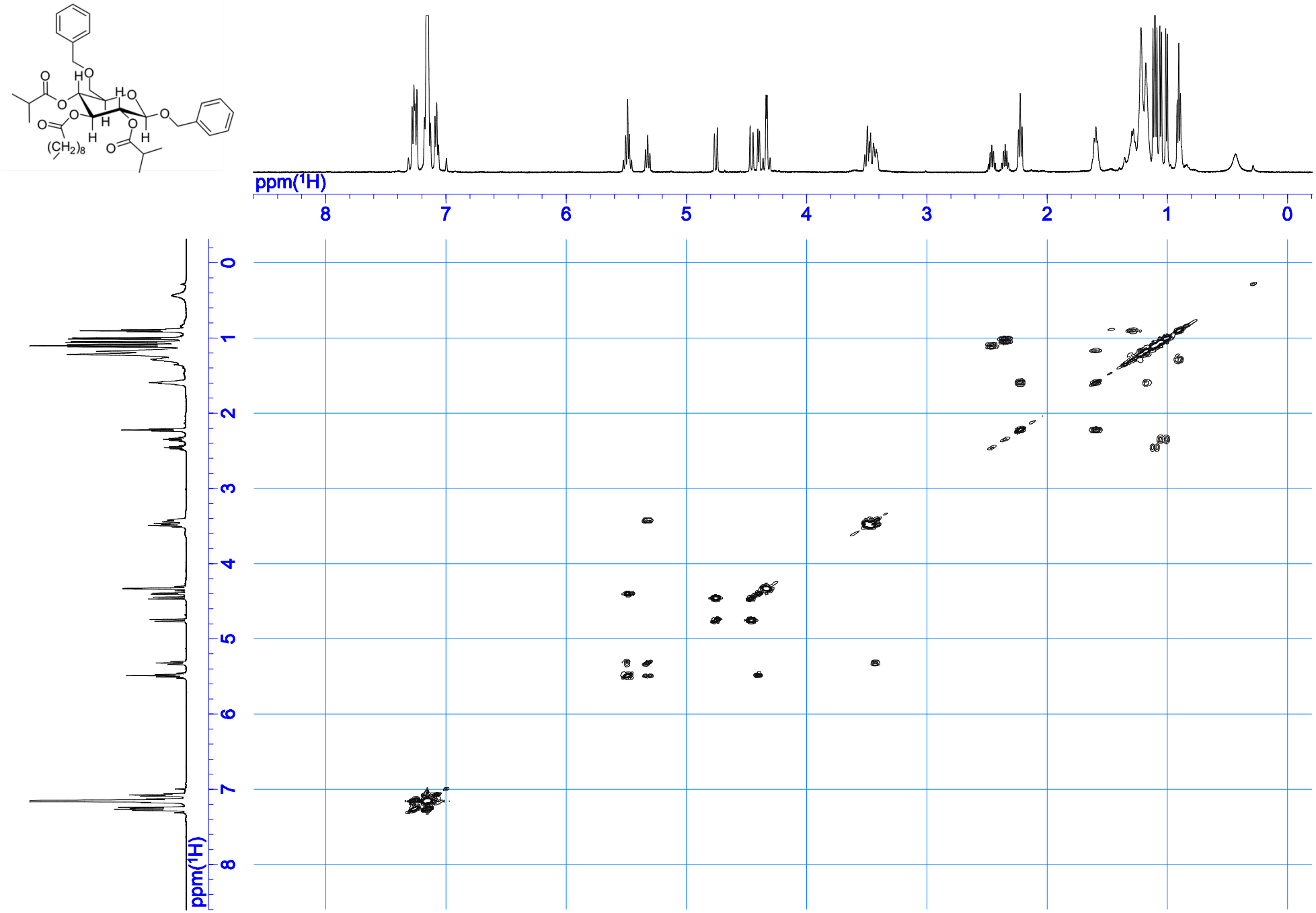

Figure S23. COSY spectrum of **6** (500 MHz, C_6D_6).

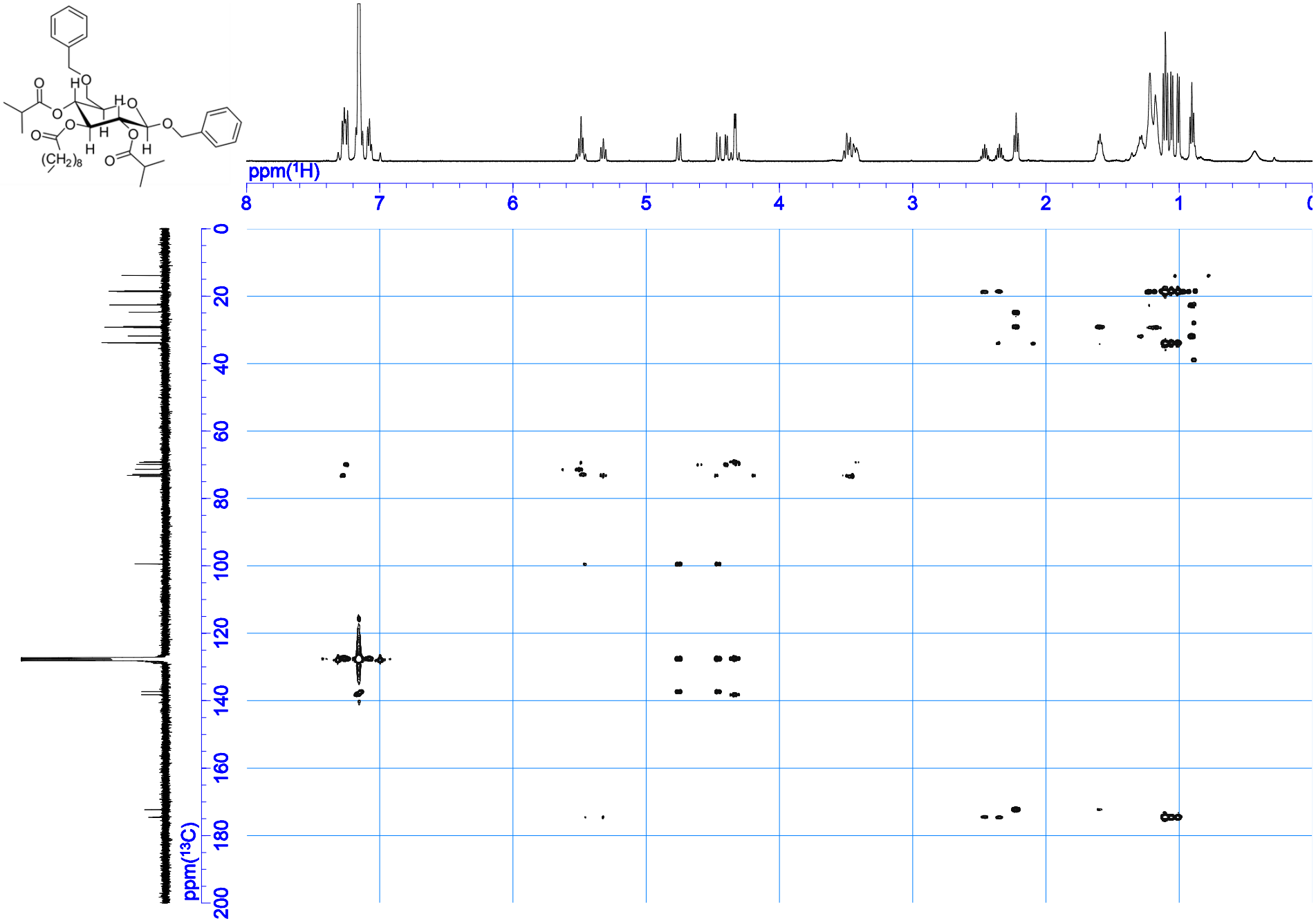

Figure S24. HMBC spectrum of **6** (500 MHz, C_6D_6).

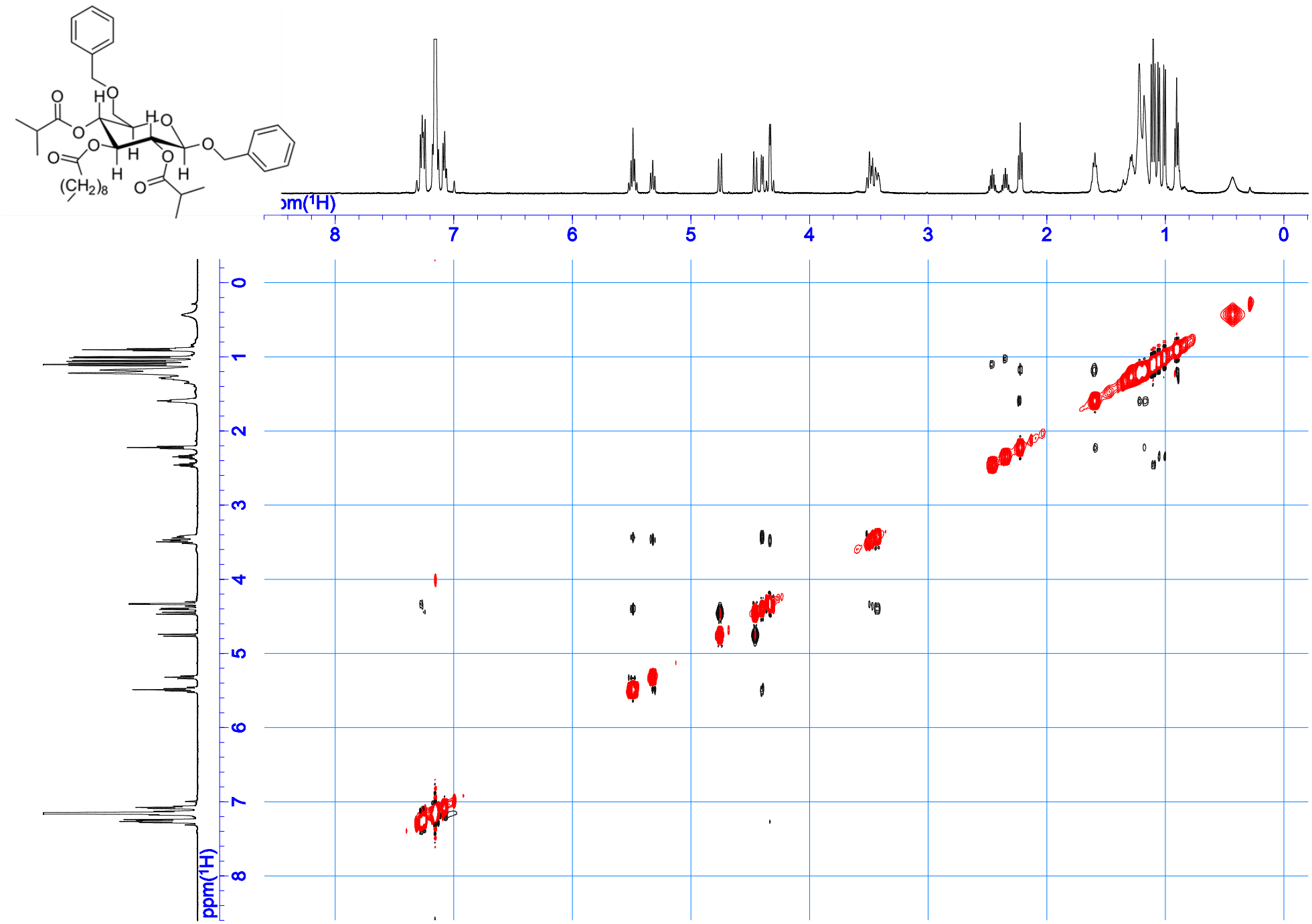

Figure S25. NOESY spectrum of **6** (500 MHz, C_6D_6).

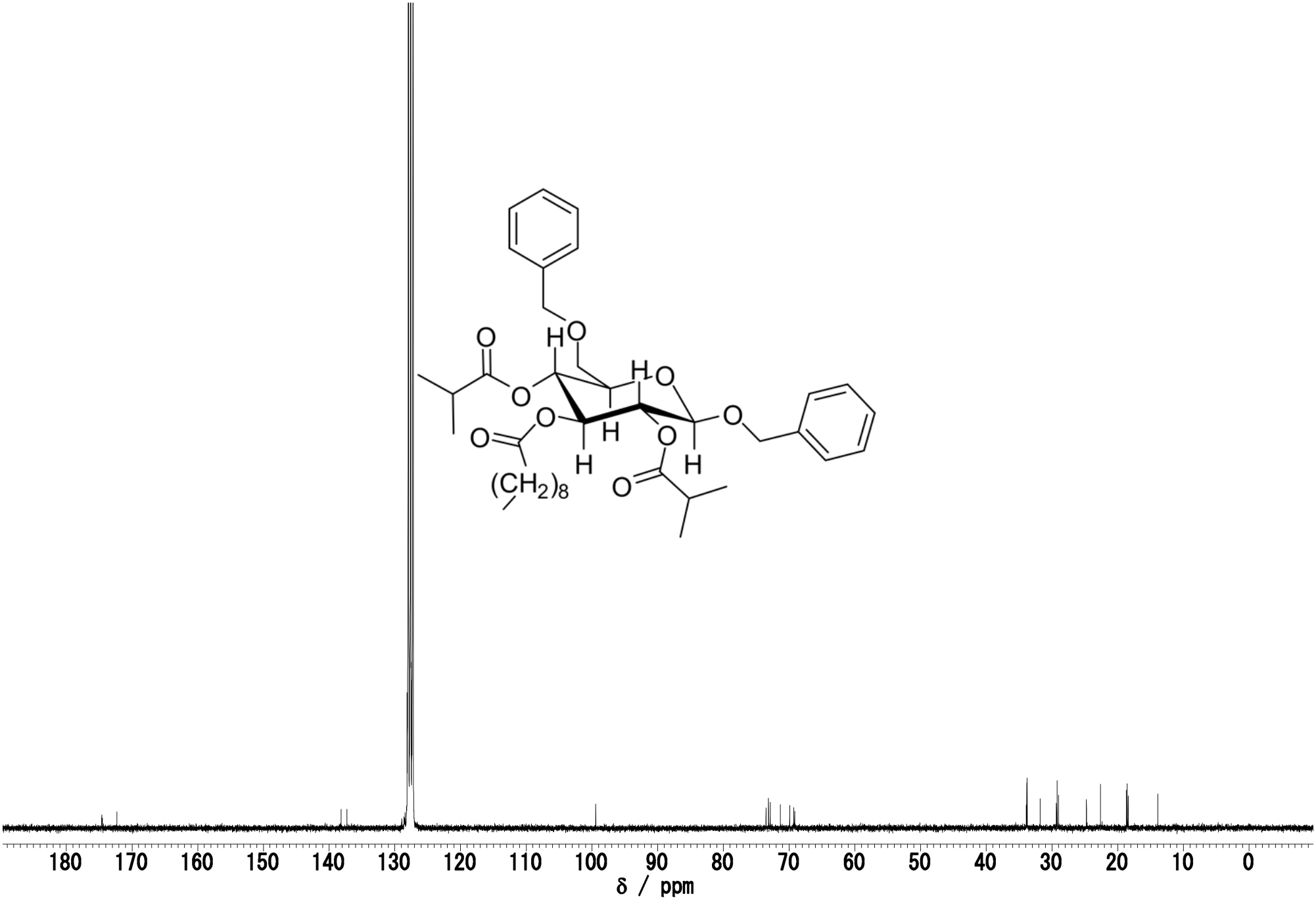

Figure S26. ^{13}C NMR spectrum of **6** (270 MHz, C_6D_6).

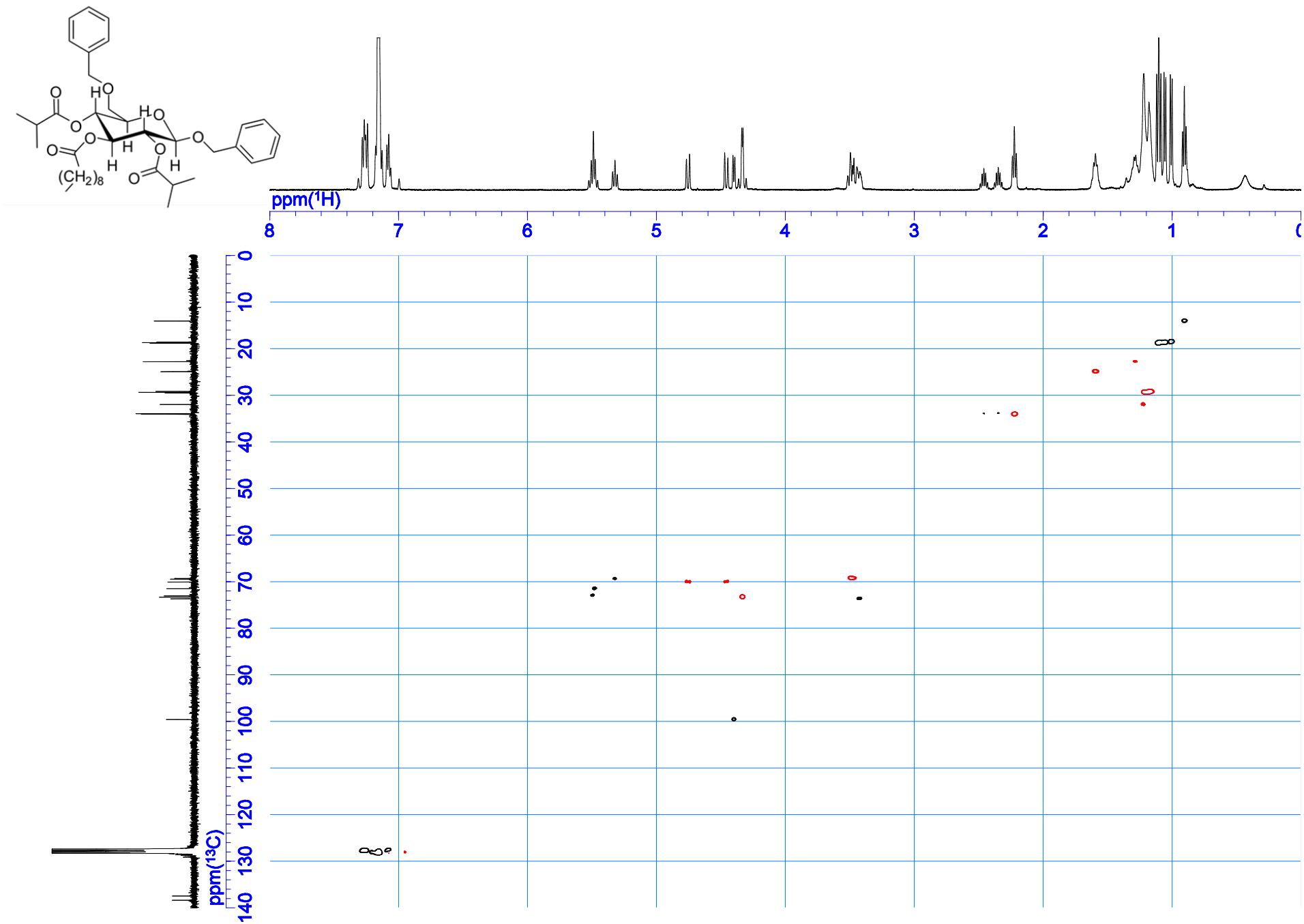

Figure S27. HMQC spectrum of **6** (500 MHz, C_6D_6).

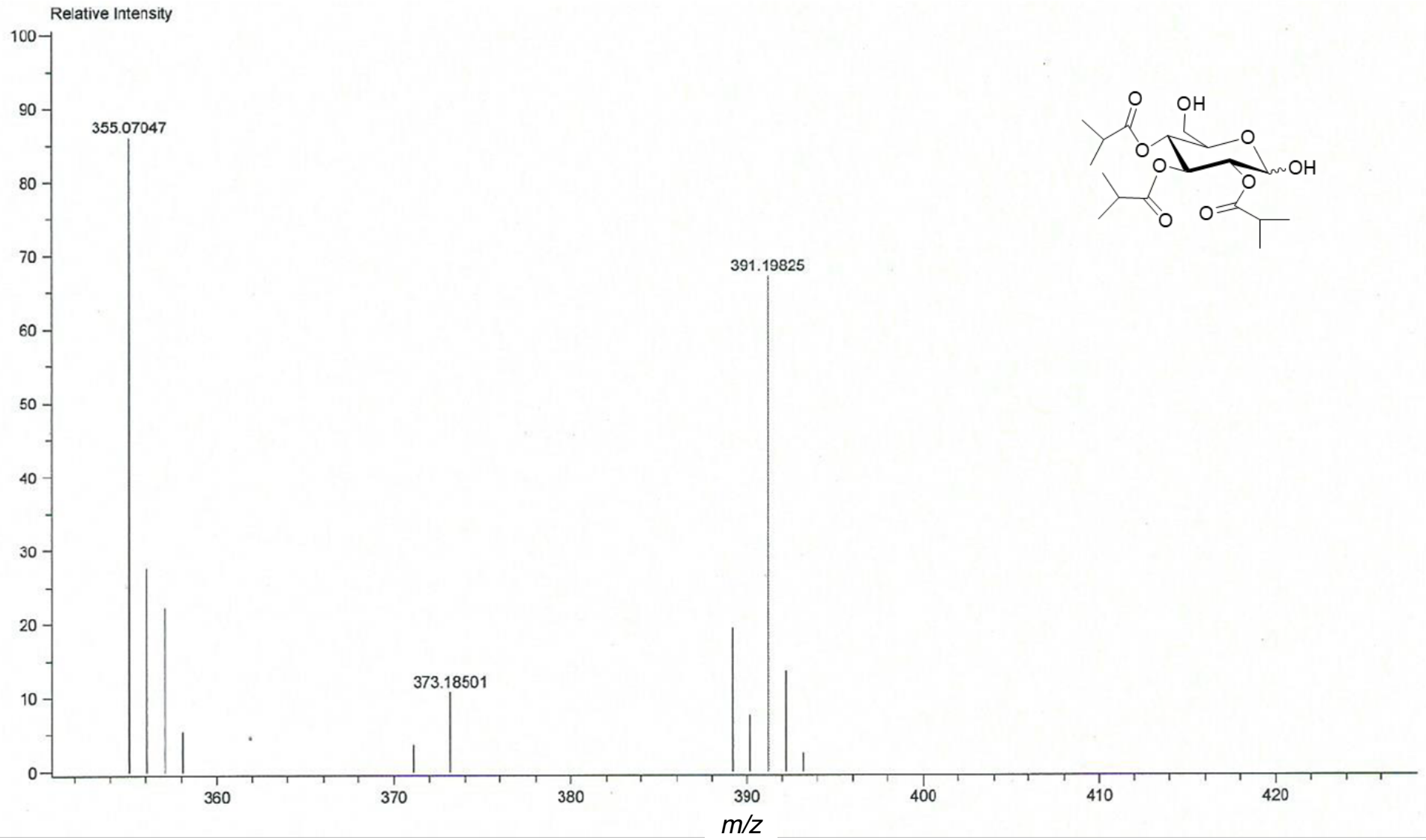

Figure S28. HRFD-MS spectrum of **1**.

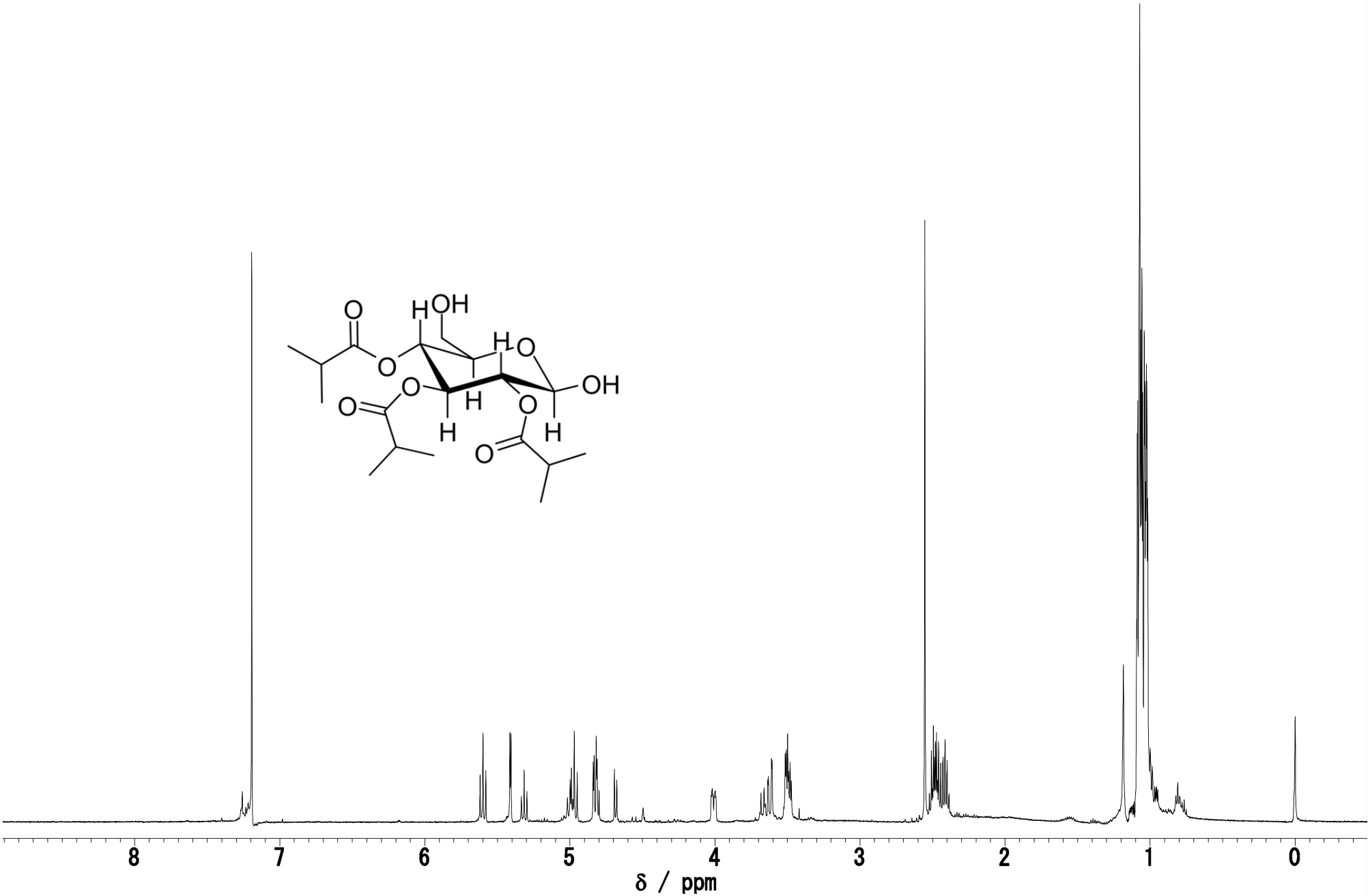

Figure S29. ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$).

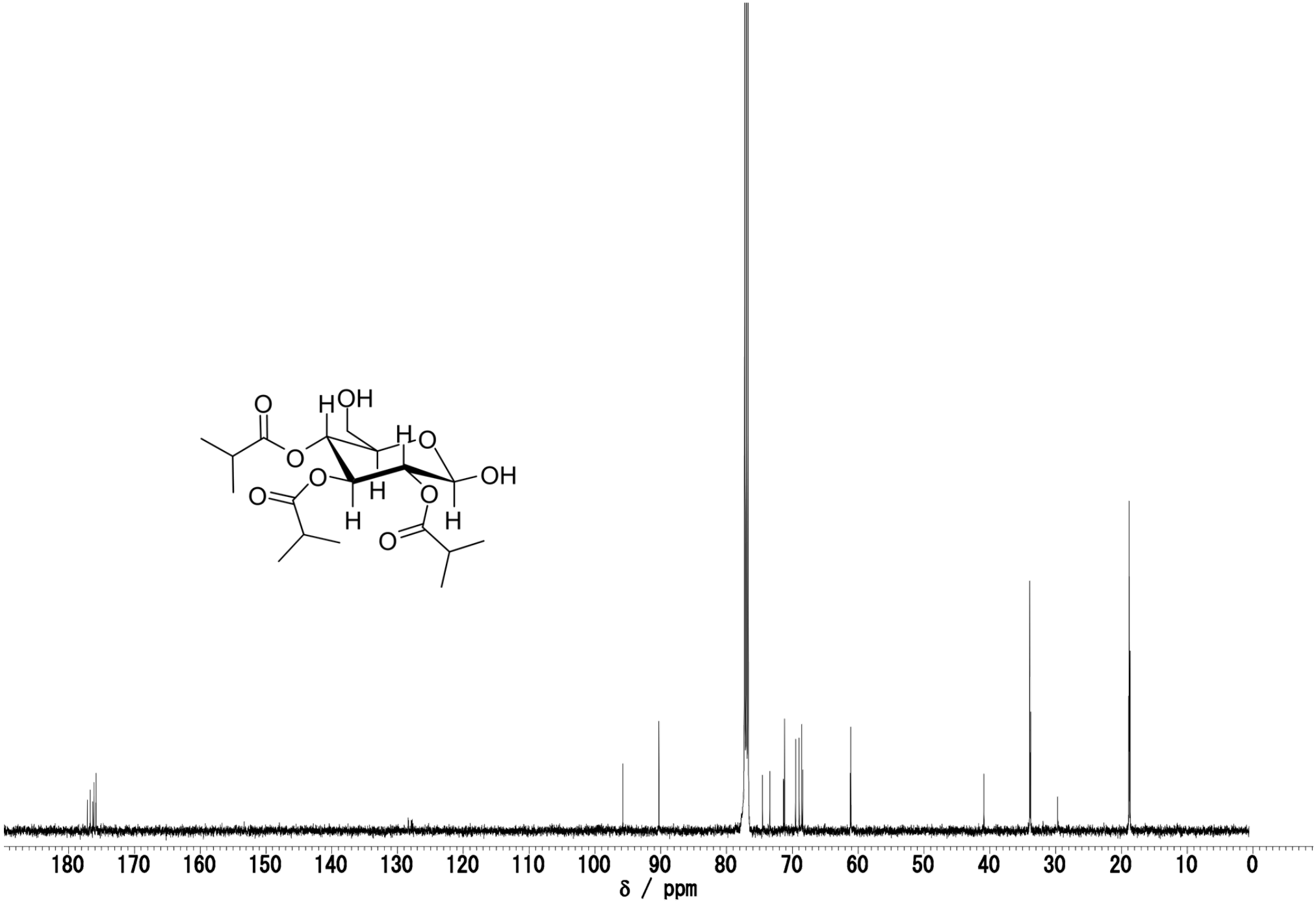

Figure S30. ^{13}C NMR spectrum of **1** (500 MHz, $CDCl_3$).

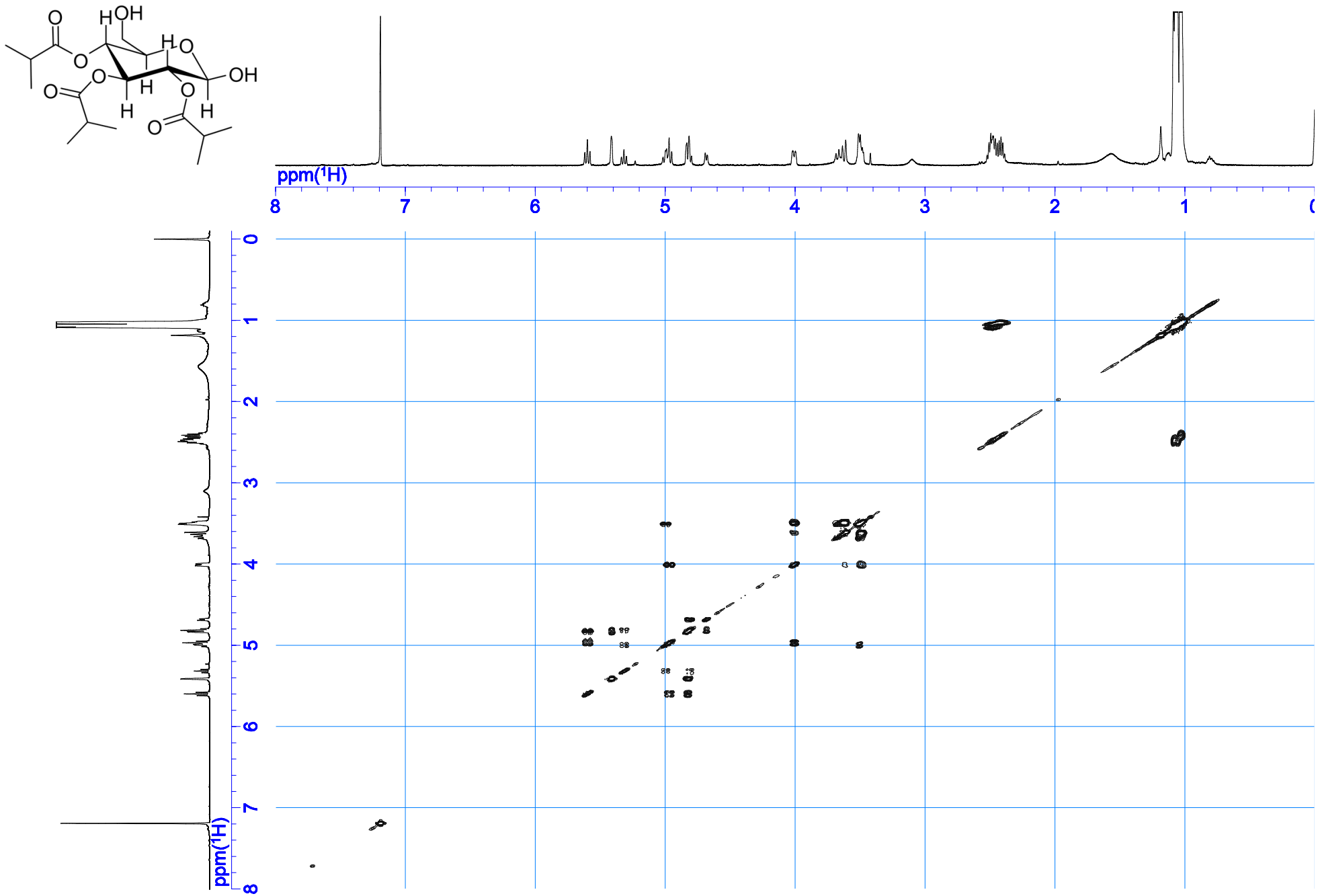

Figure S31. COSY spectrum of **1** (500 MHz, $CDCl_3$).

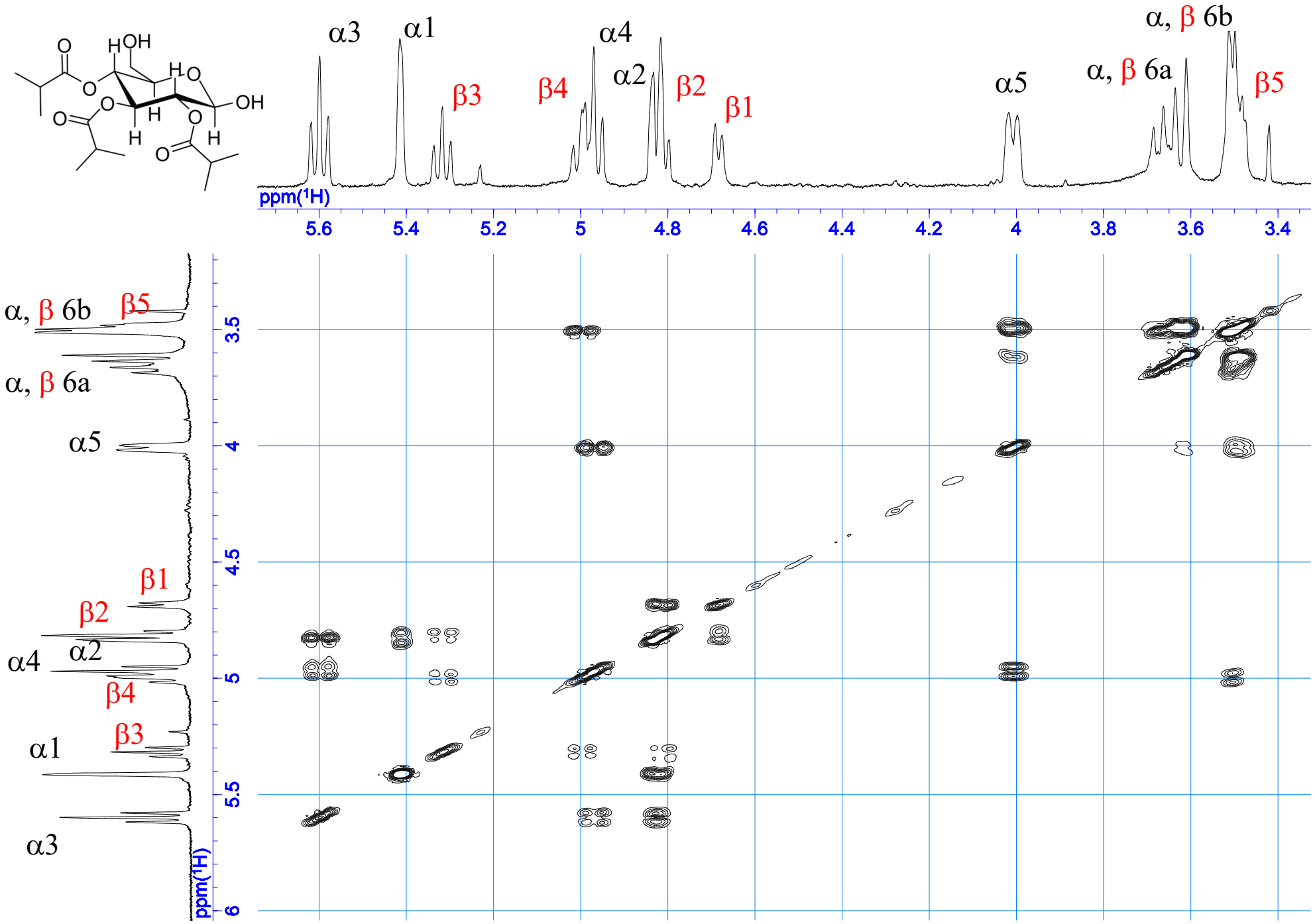

Figure S32. COSY spectrum of **1** (500 MHz, $CDCl_3$).

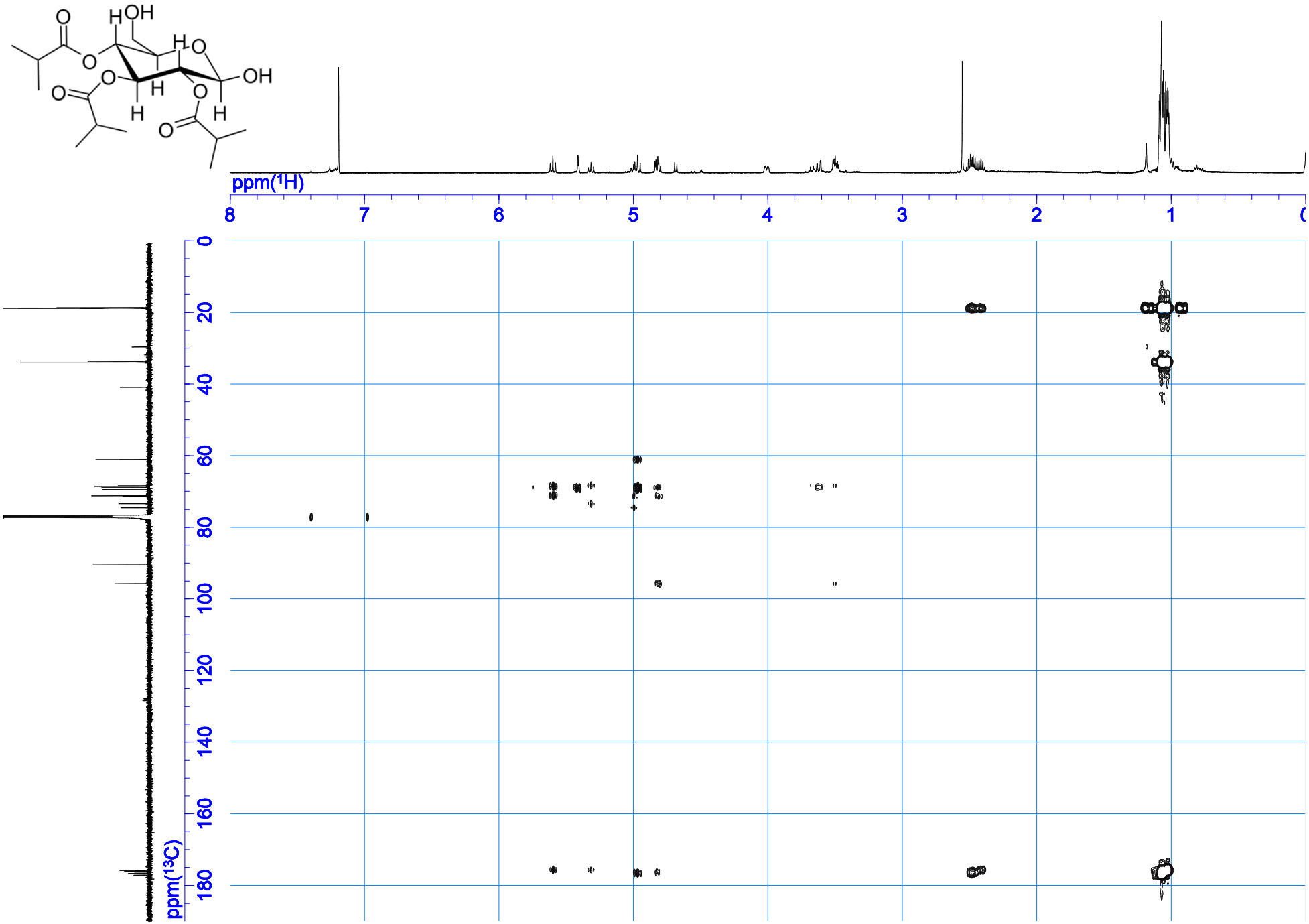

Figure S33. HMBC spectrum of **1** (500 MHz, $CDCl_3$).

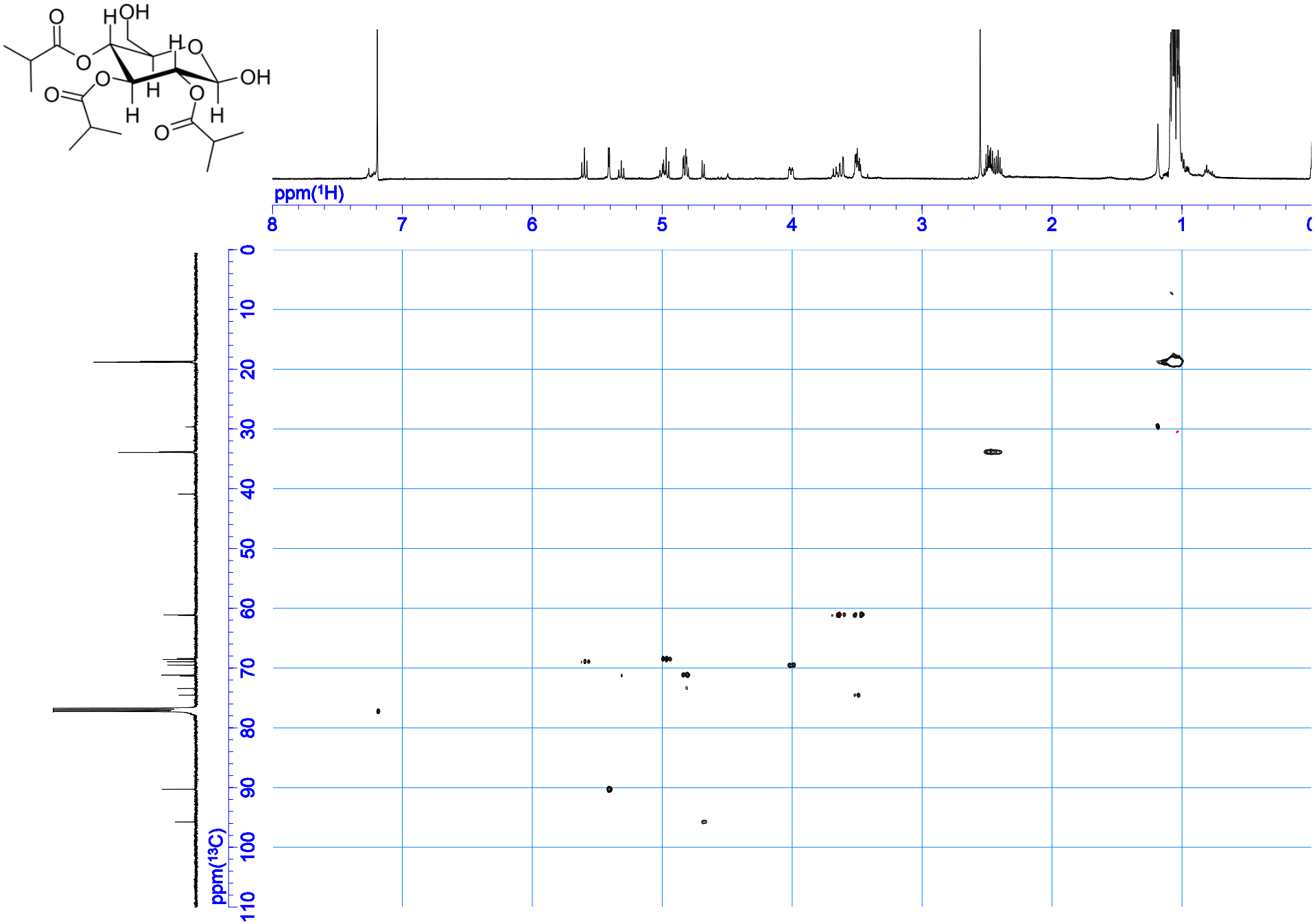

Figure S34. HMQC spectrum of **1** (500 MHz, $CDCl_3$).

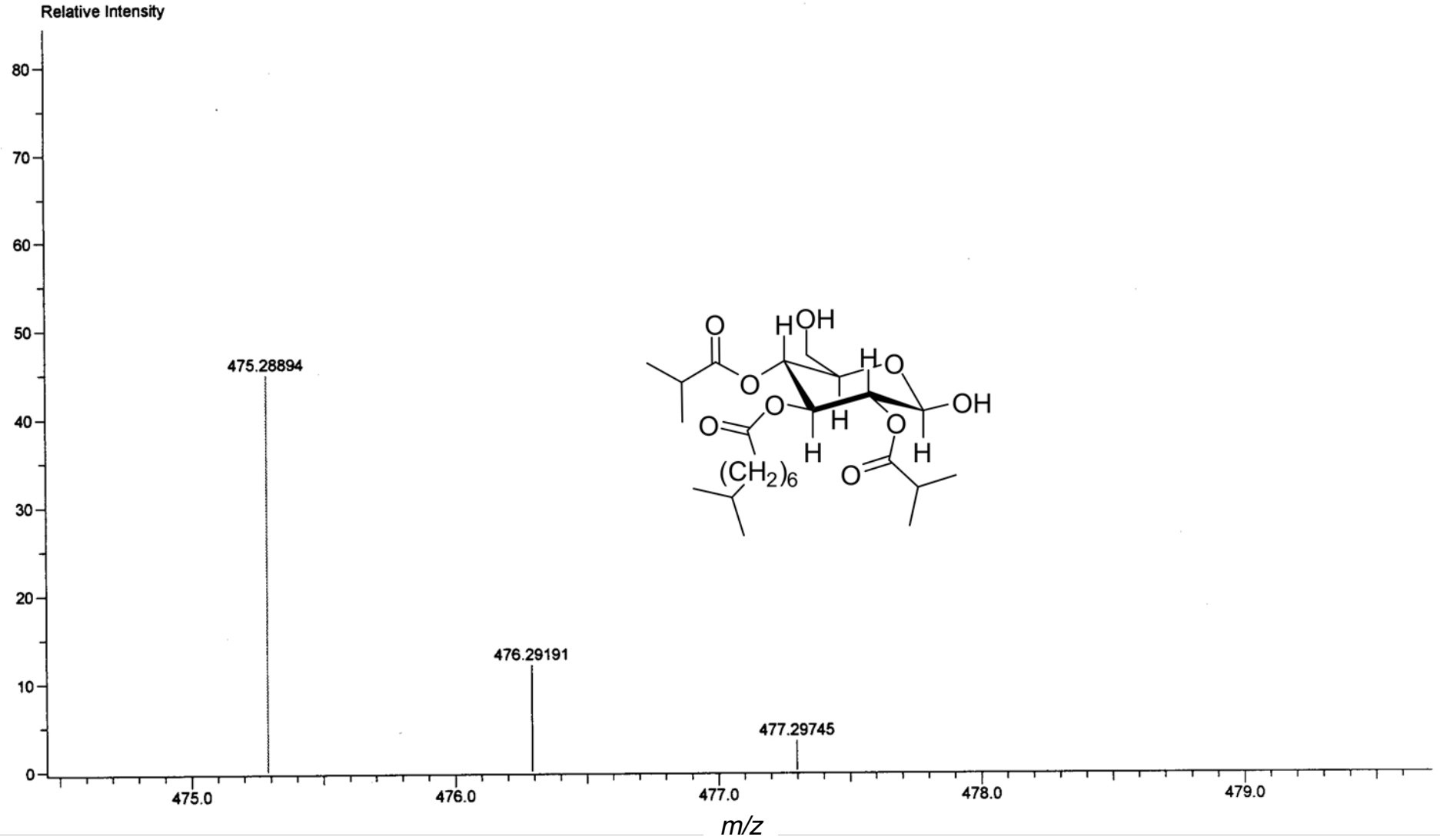

Figure S35. HRFD-MS spectrum of **2**.

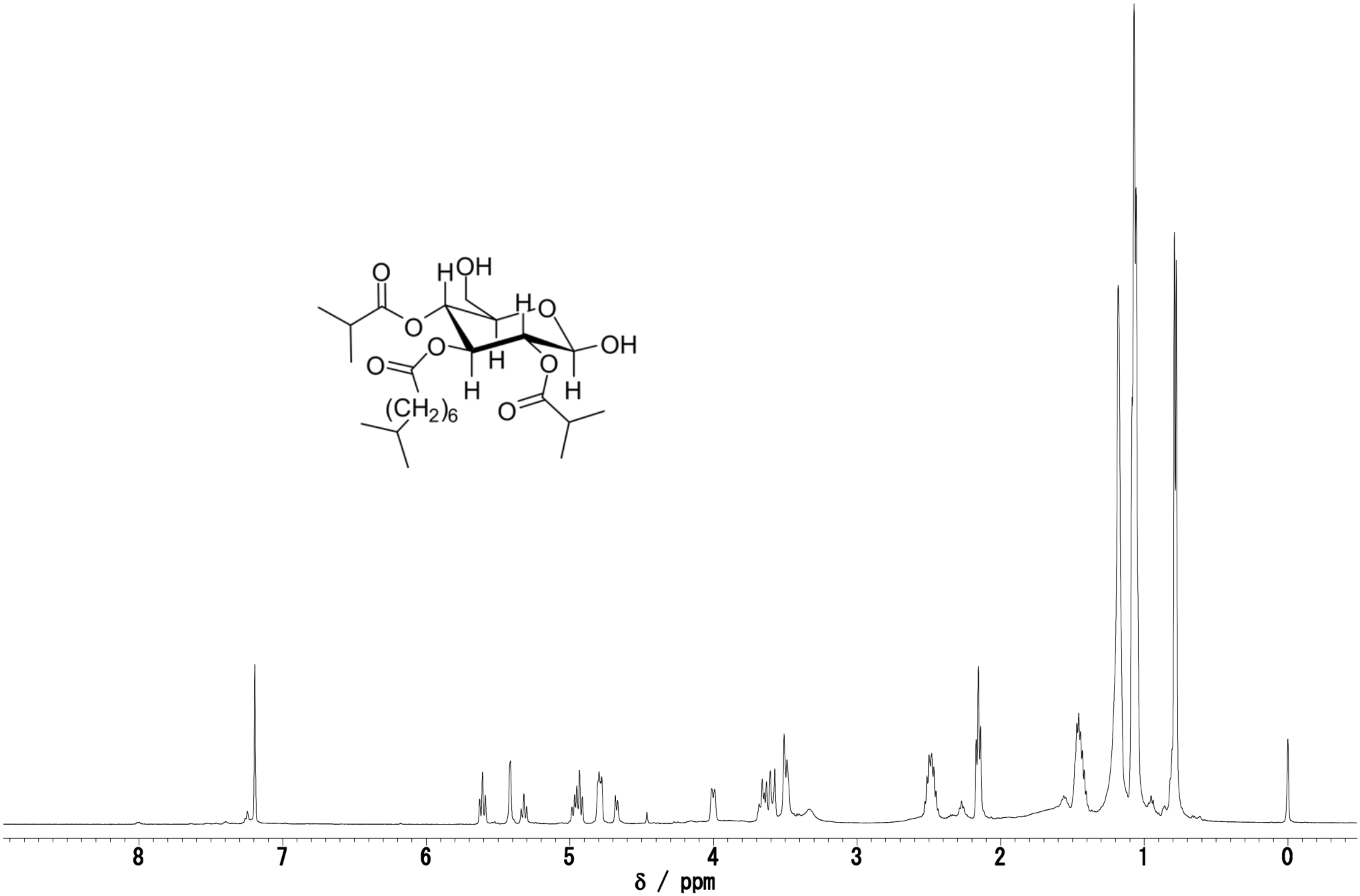

Figure S36. ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$).

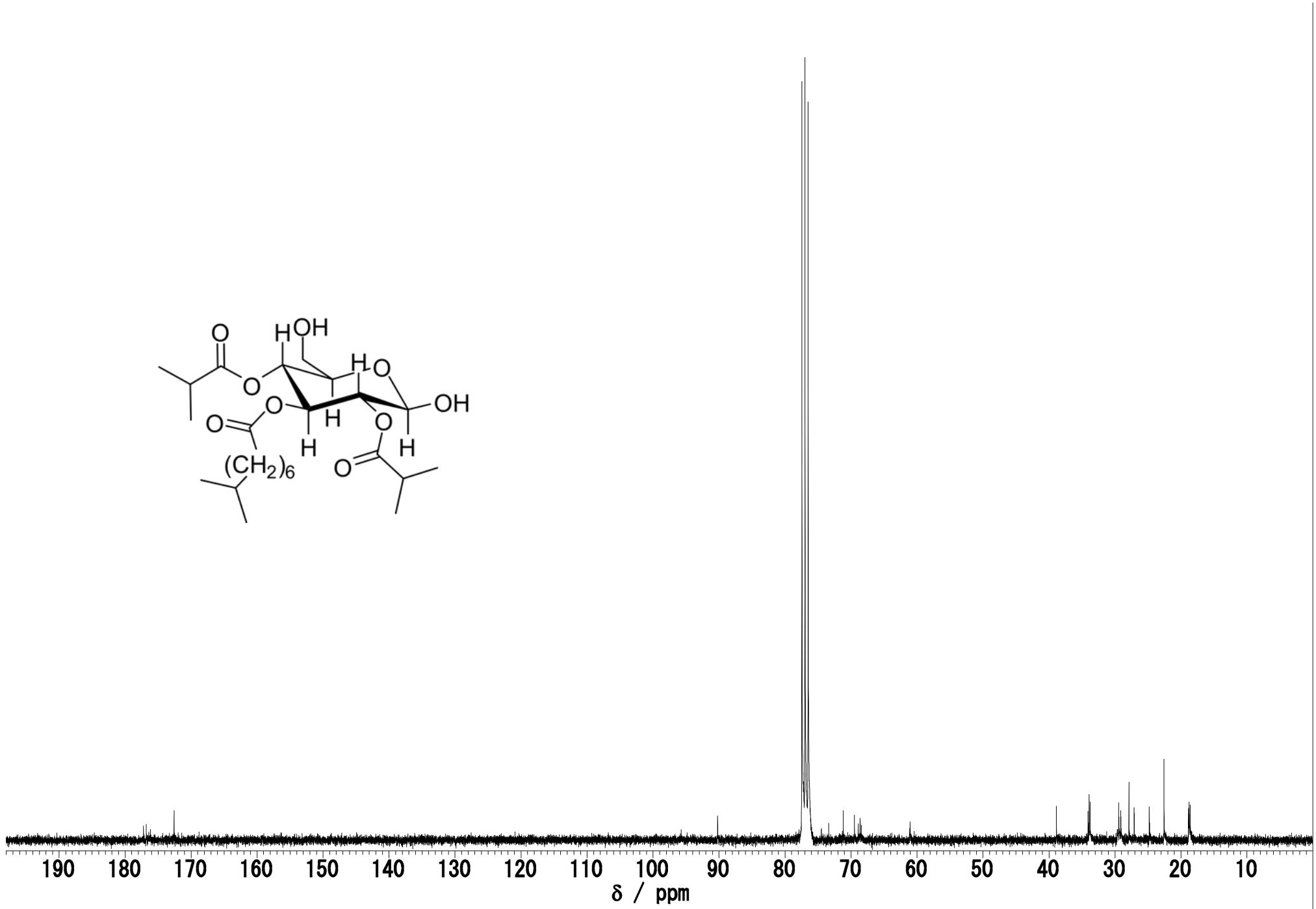

Figure S37. ^{13}C NMR spectrum of **2** (270 MHz, $CDCl_3$).

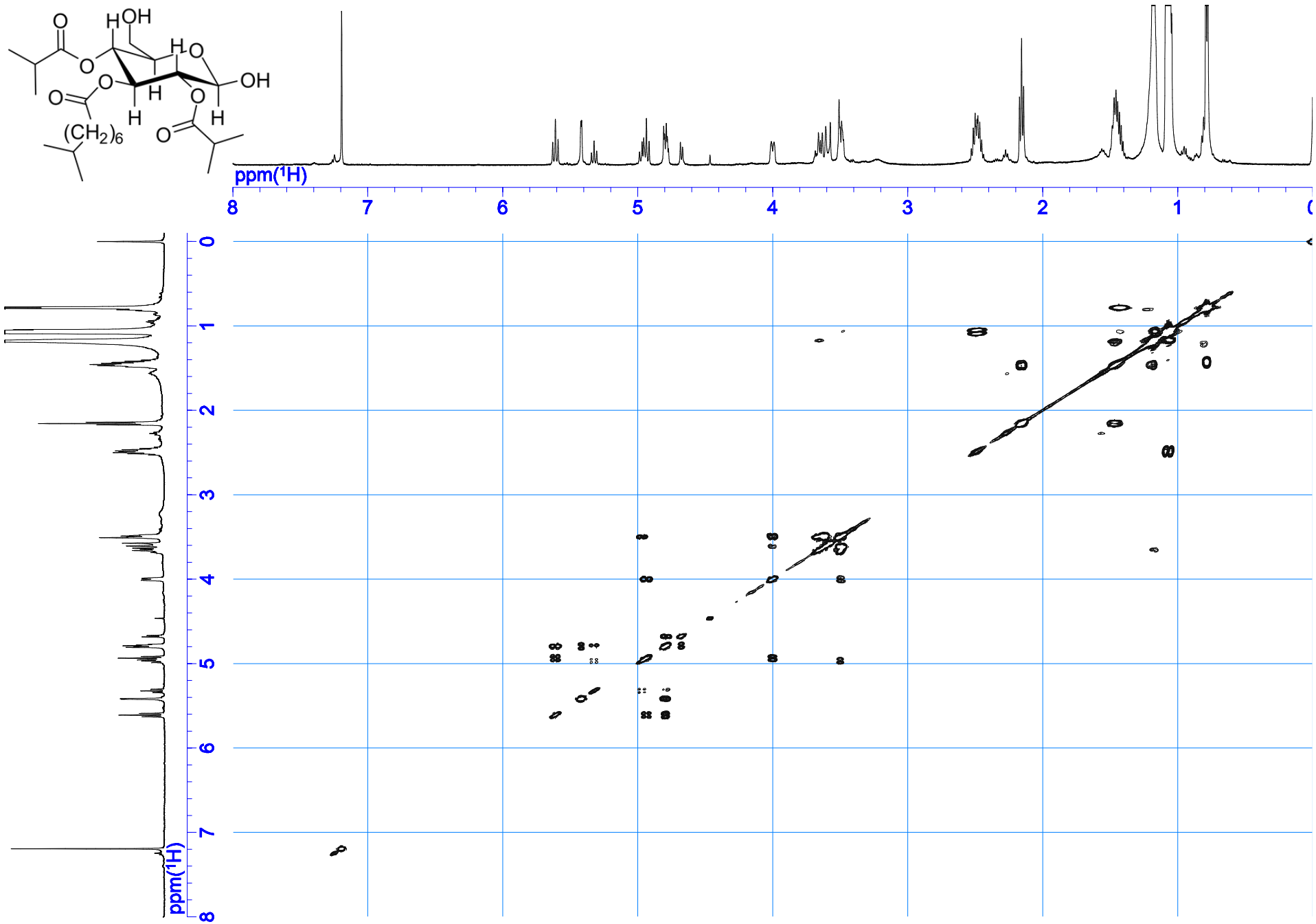

Figure S38. COSY spectrum of **2** (500 MHz, $CDCl_3$).

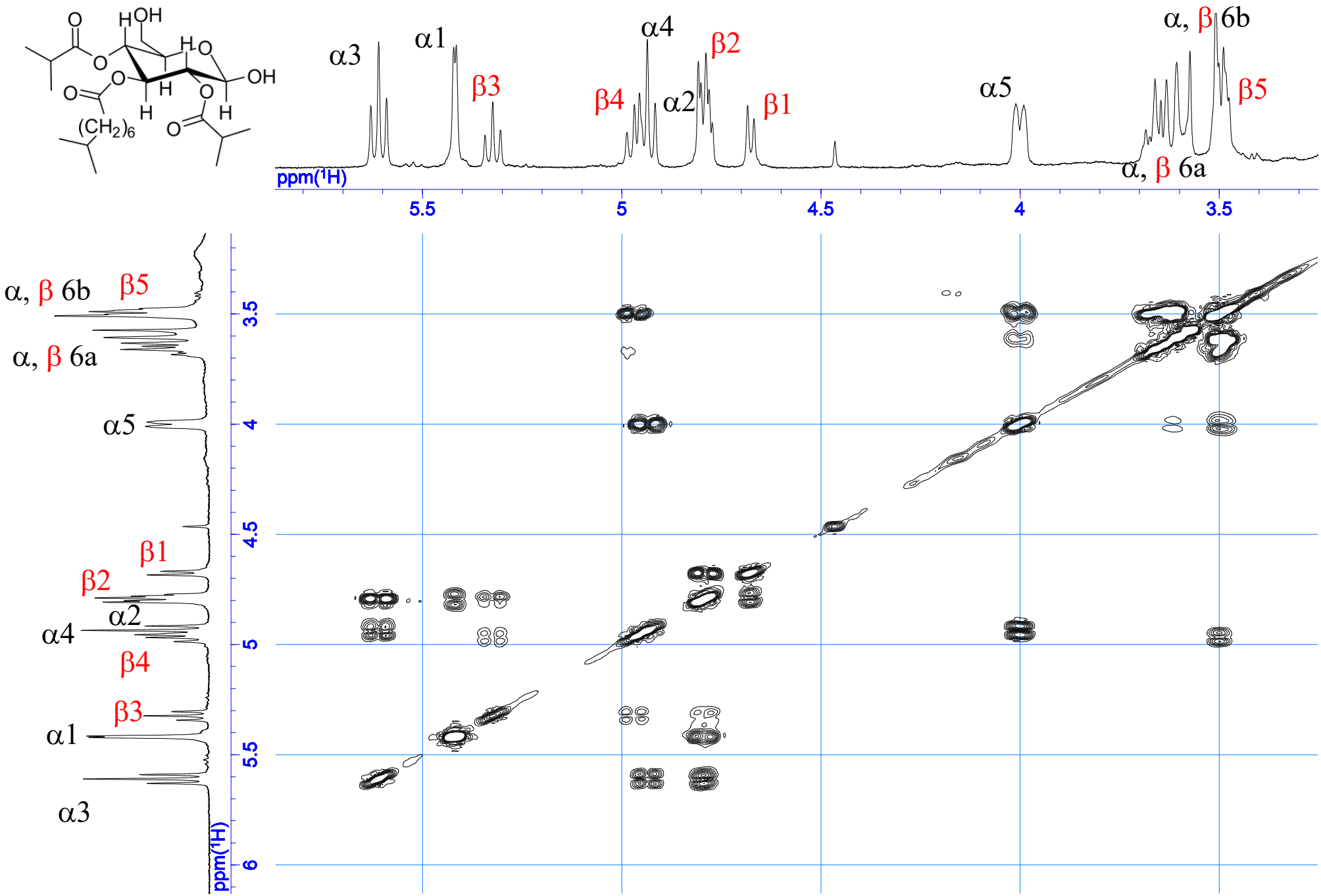

Figure S39. Partial COSY spectrum of **2** (500 MHz, $CDCl_3$).

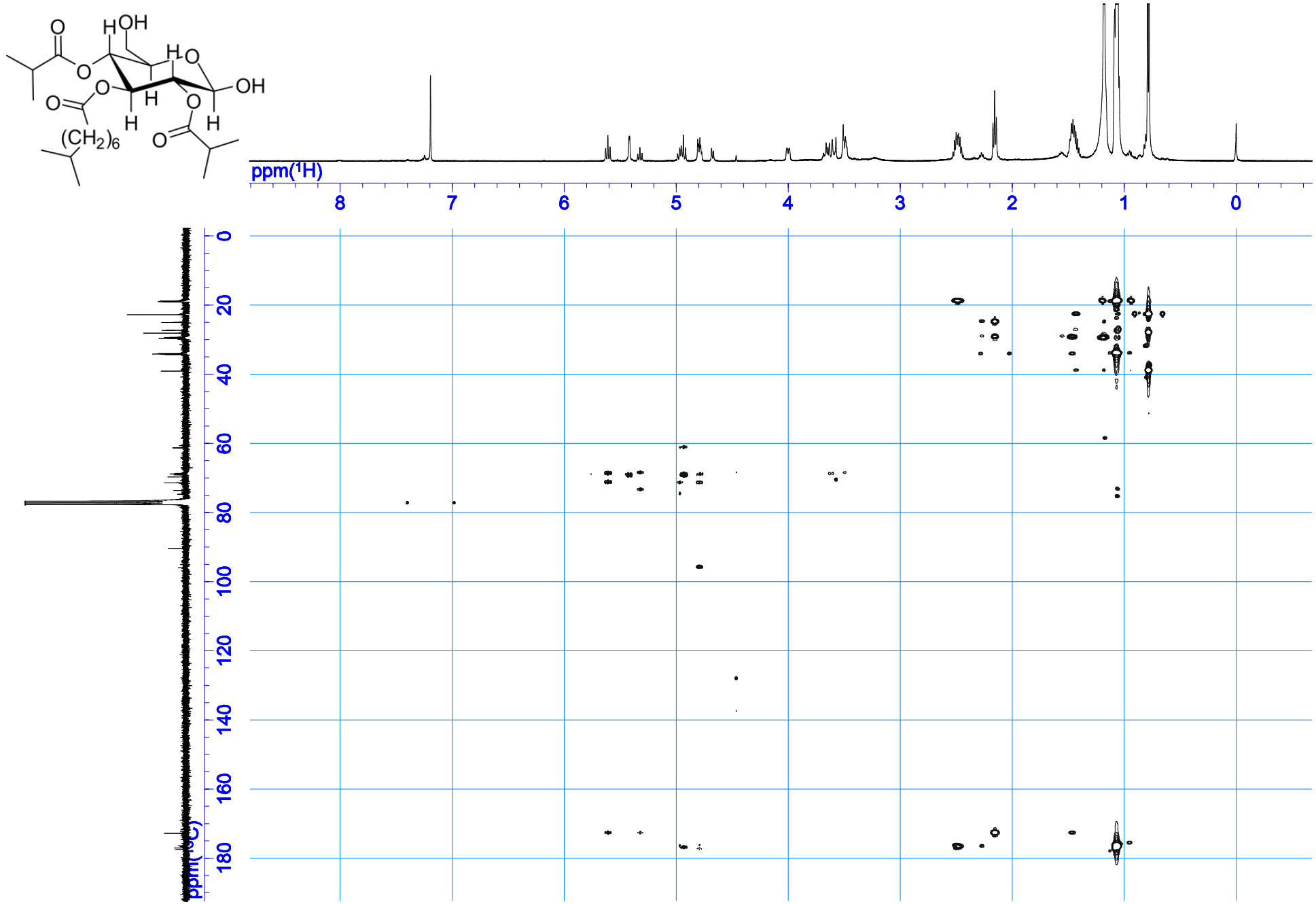

Figure S40. HMBC spectrum of **2** (500 MHz, $CDCl_3$).

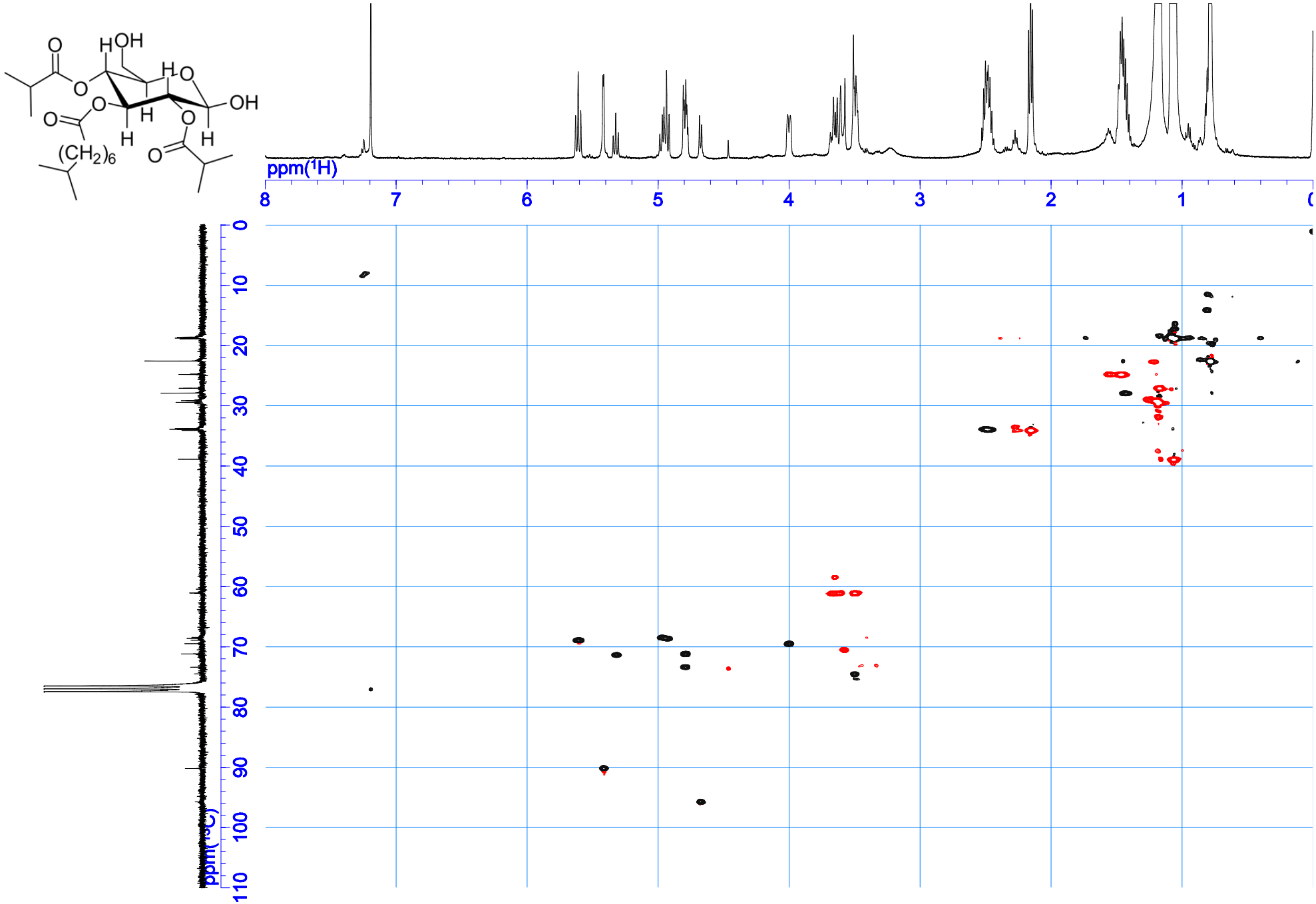

Figure S41. HMQC spectrum of **2** (500 MHz, $CDCl_3$).

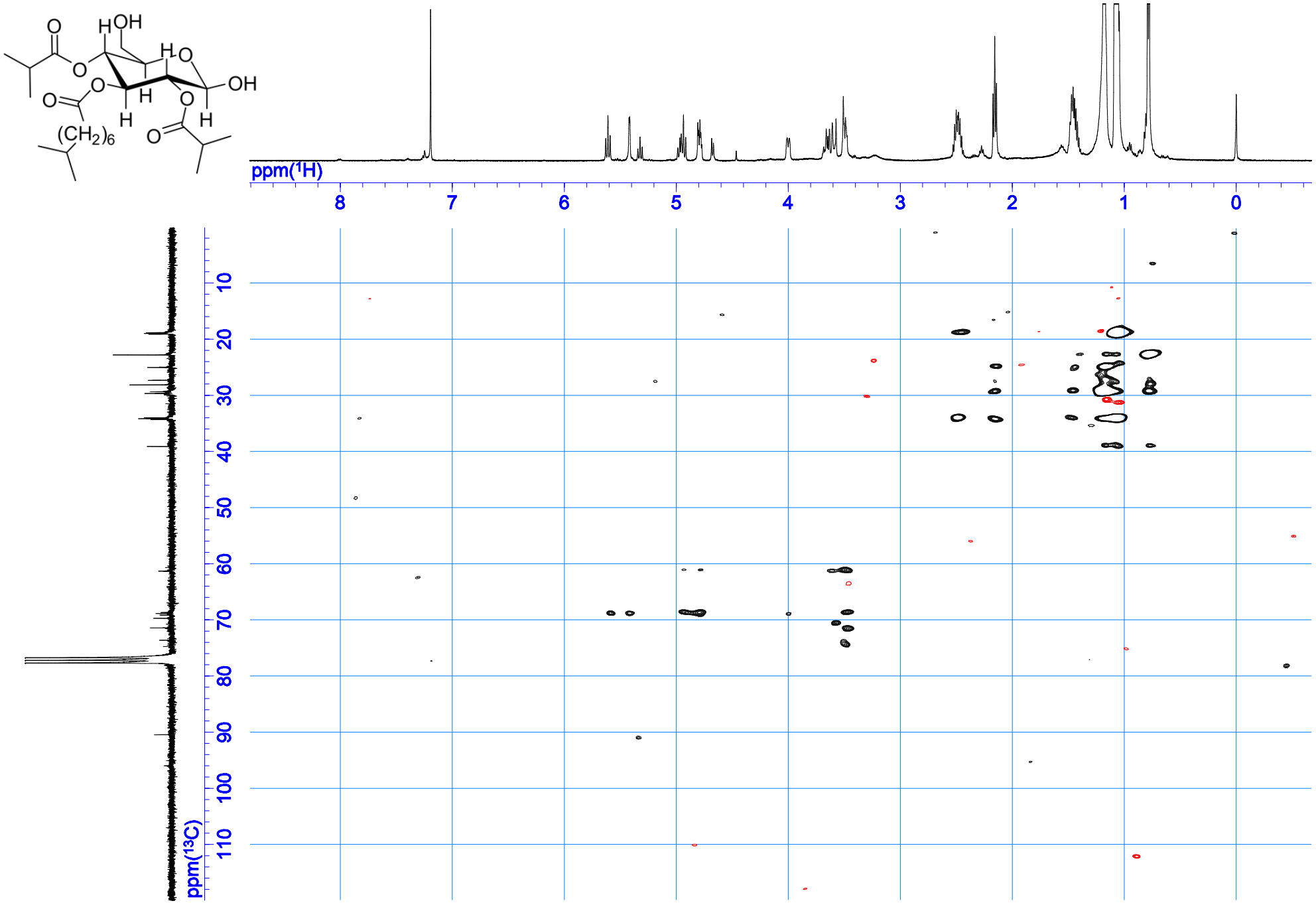

Figure S42. HSQC-TQCSY spectrum of **2** (500 MHz, $CDCl_3$).

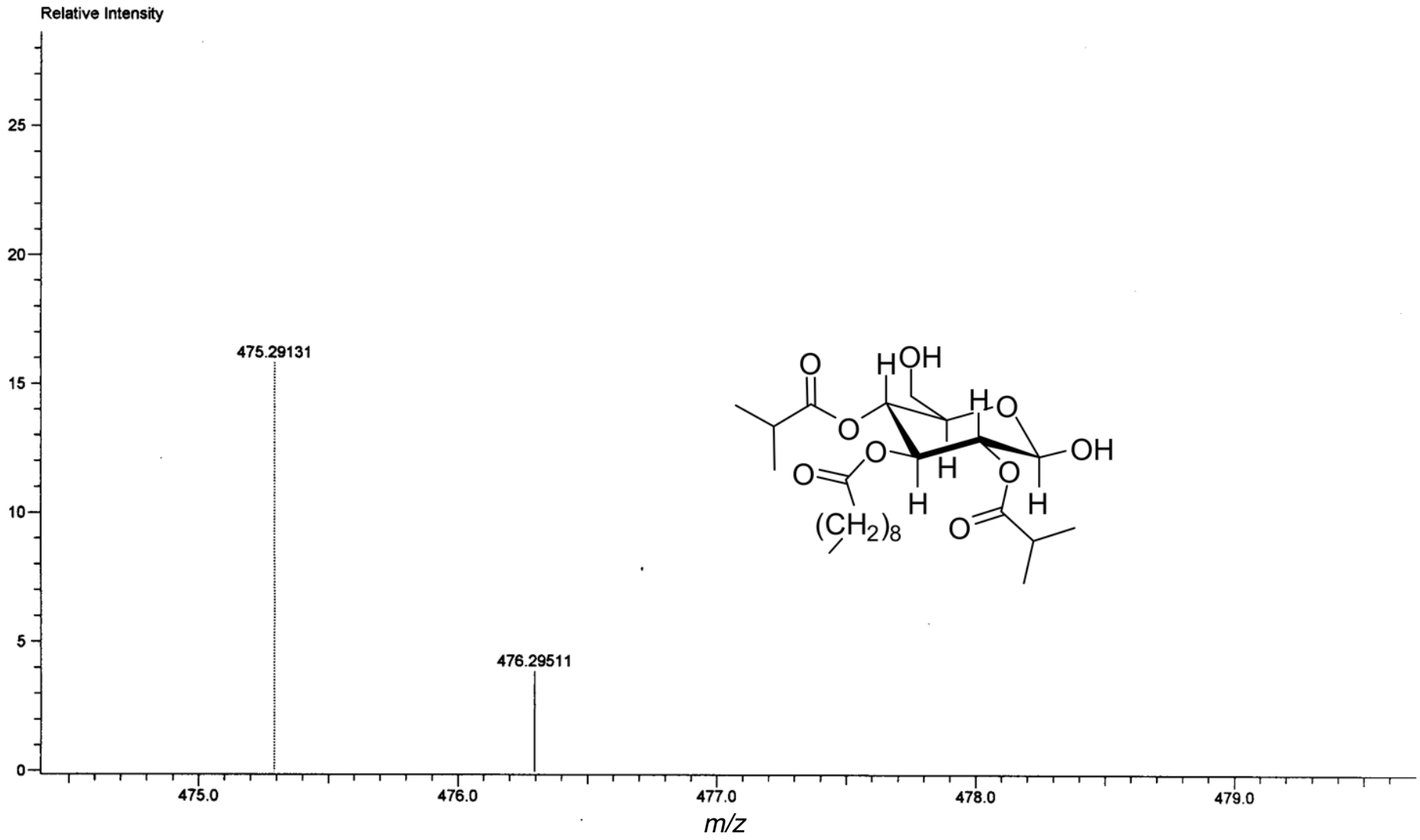

Figure S43. HRFD-MS spectrum of **3**.

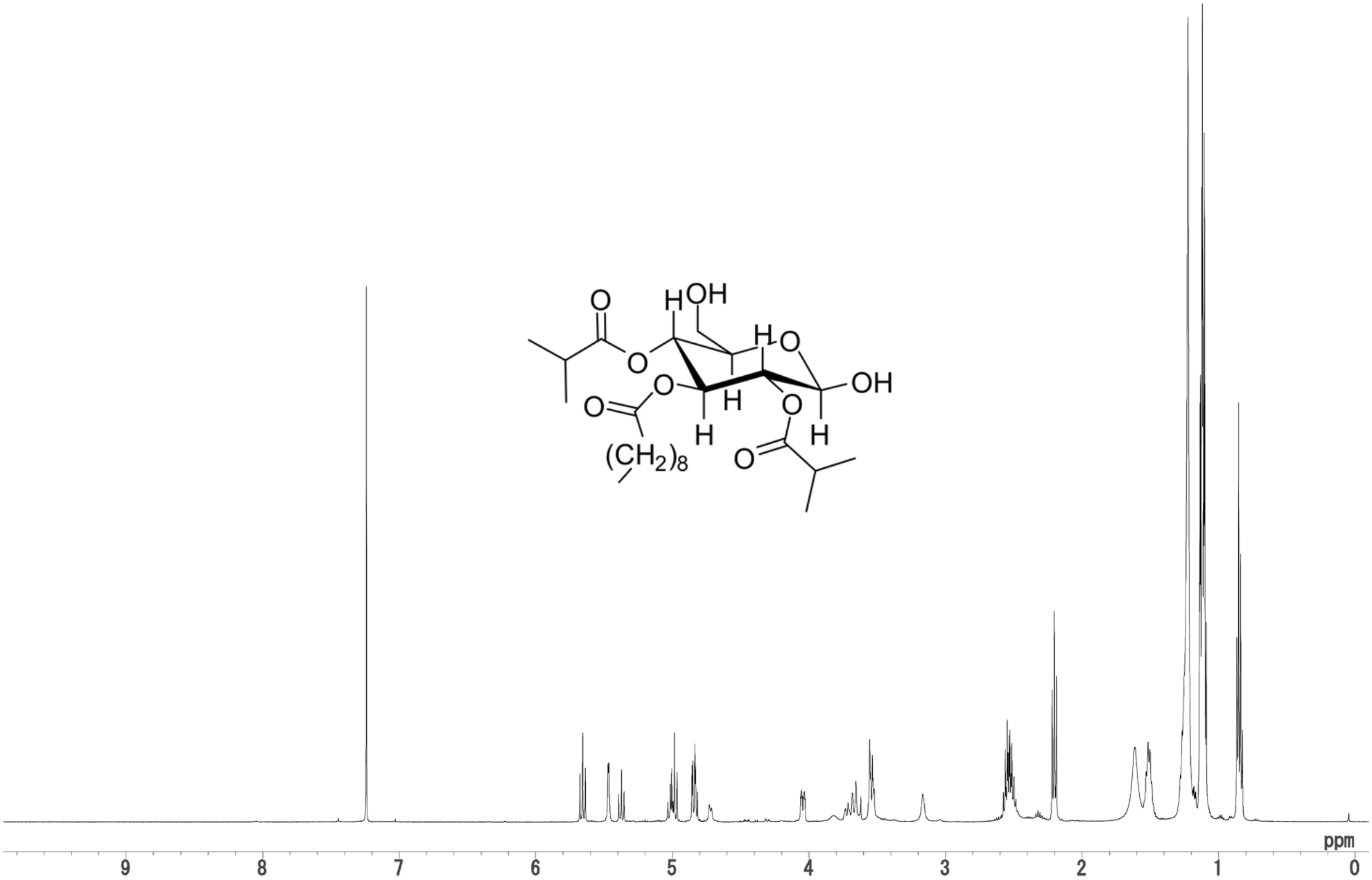

Figure S44. ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$).

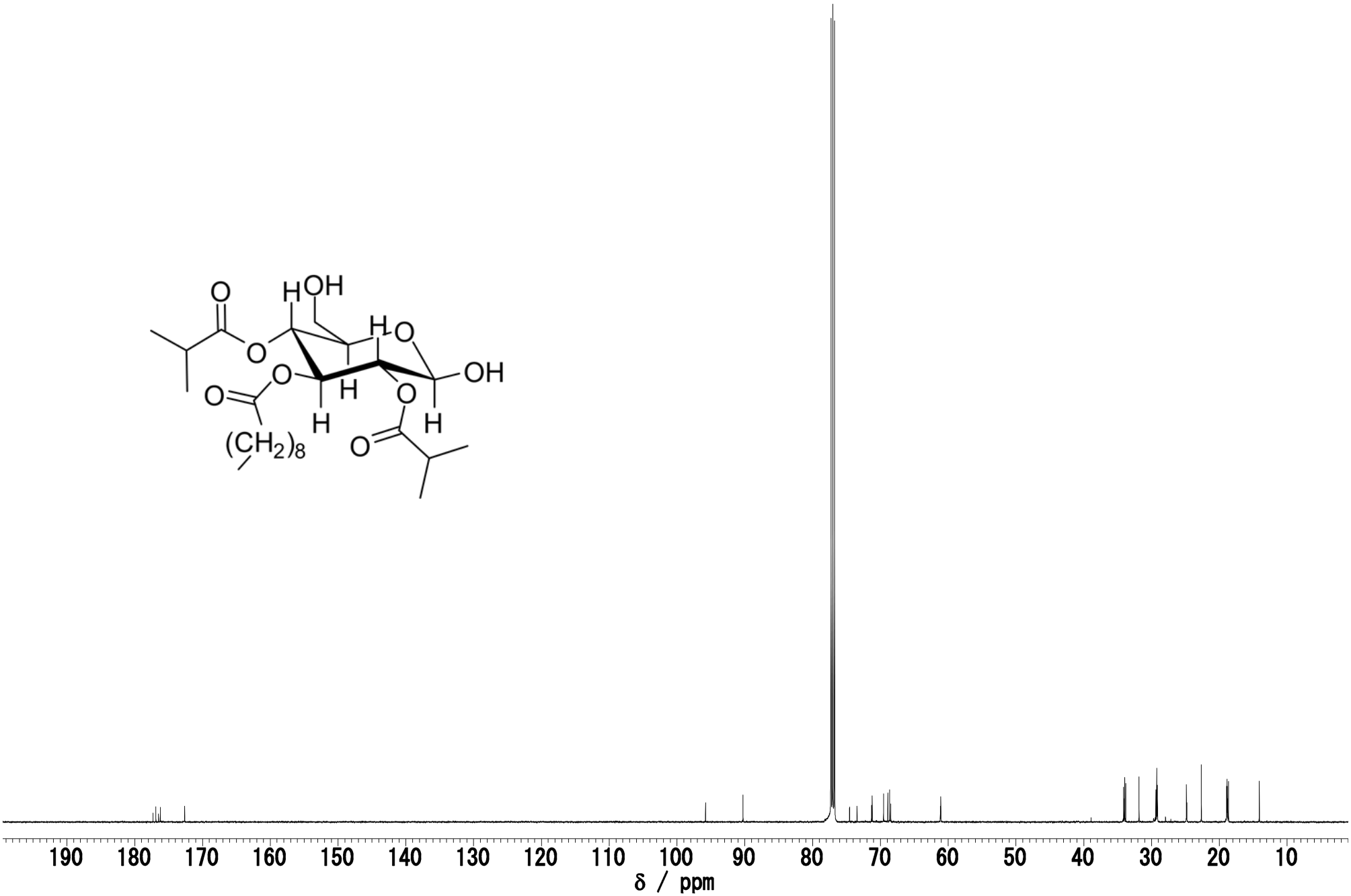

Figure S45. ^{13}C NMR spectrum of **3** (500 MHz, $CDCl_3$).

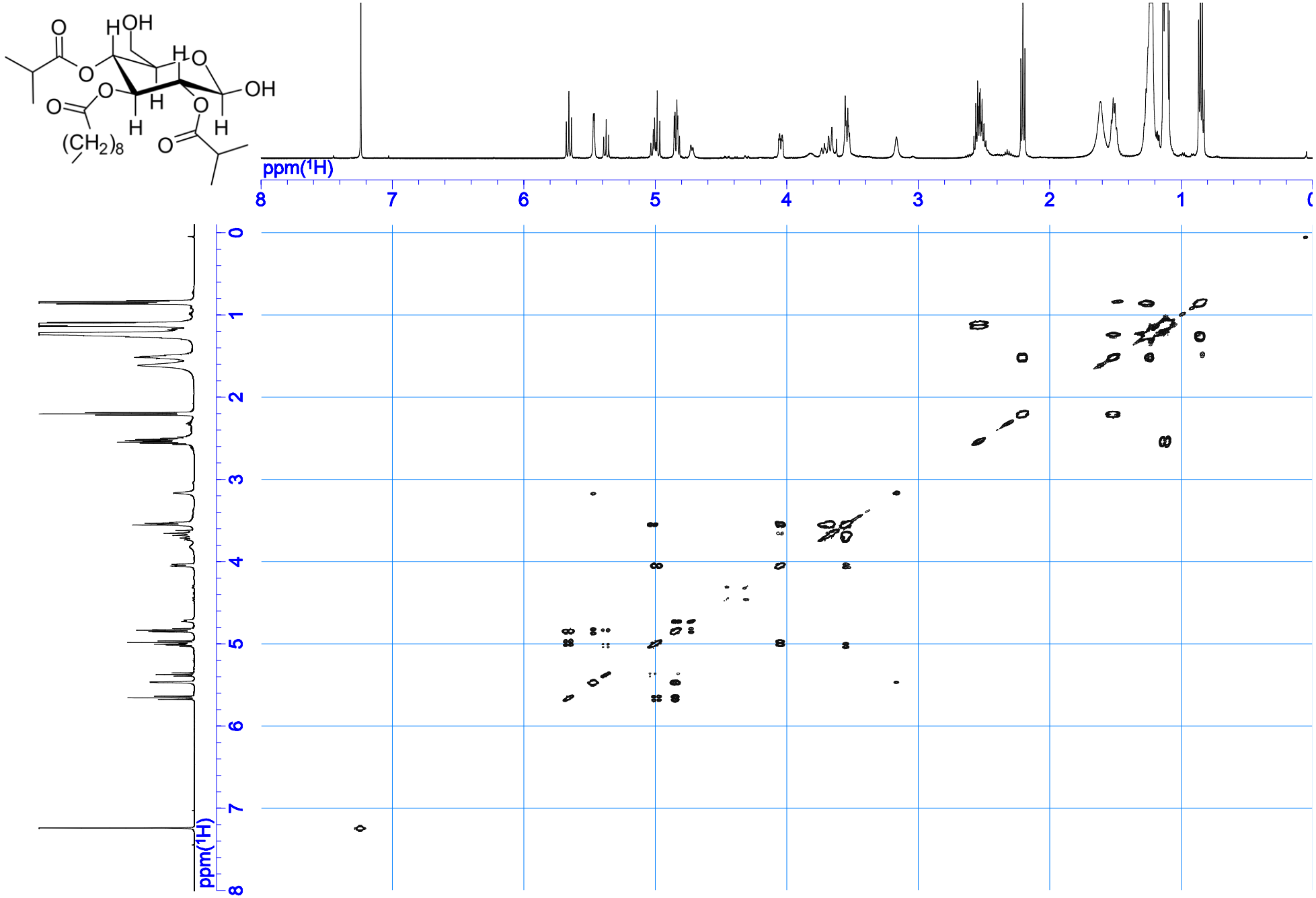

Figure S46. COSY spectrum of **3** (500 MHz, $CDCl_3$).

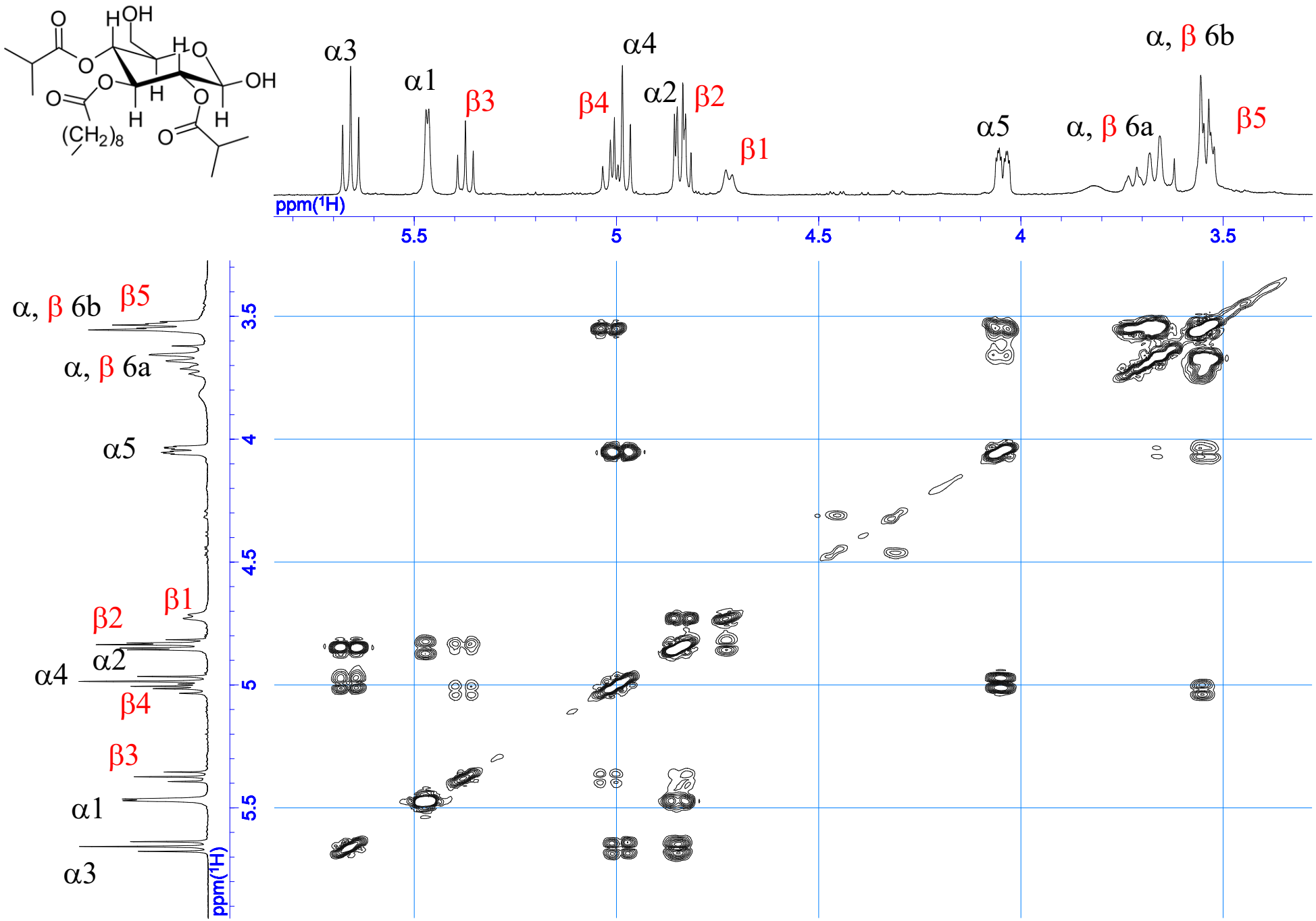

Figure S47. Partial COSY spectrum of **3** (500 MHz, $CDCl_3$).

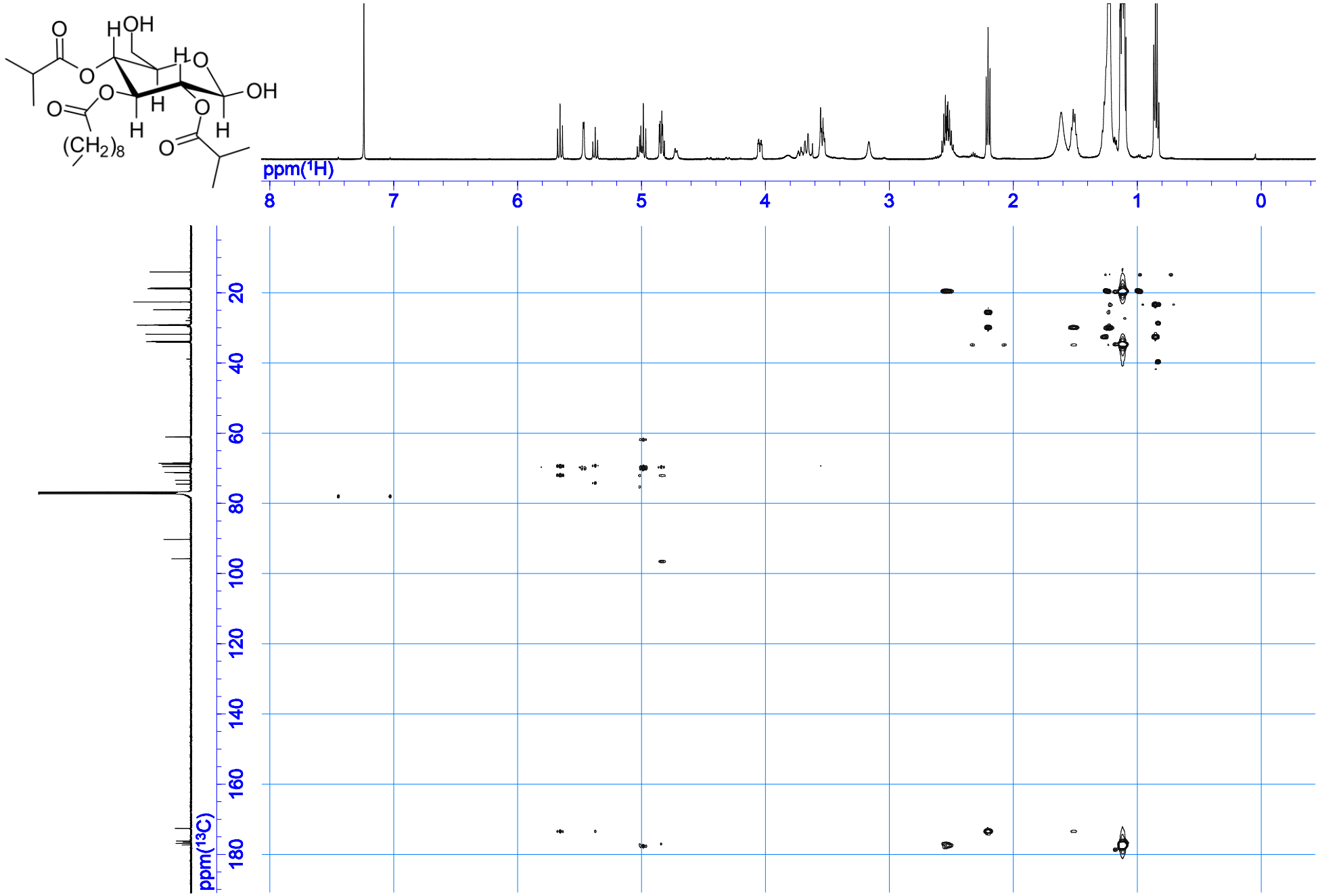

Figure S48. HMBC spectrum of **3** (500 MHz, $CDCl_3$).

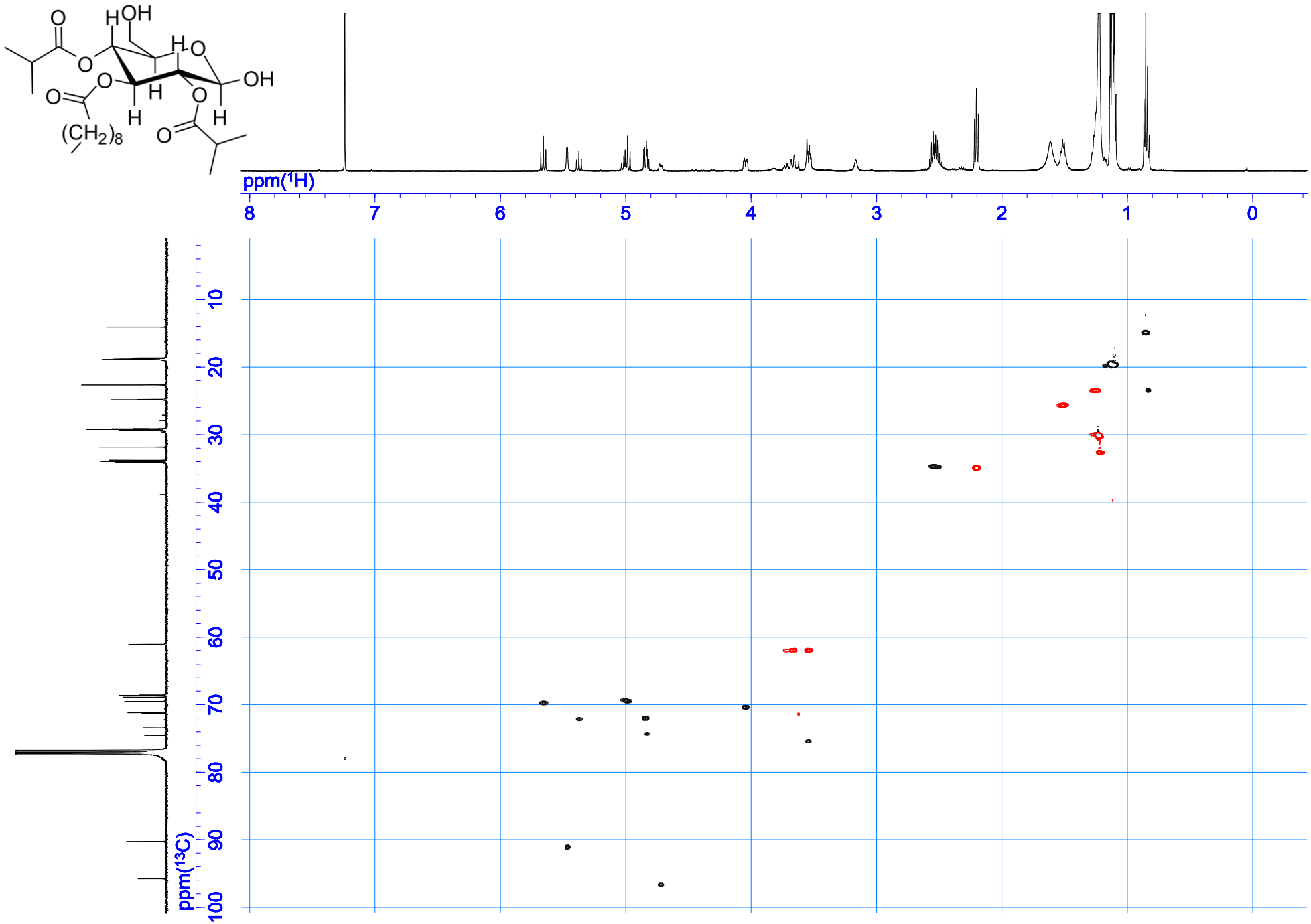

Figure S49. HMQC spectrum of **3** (500 MHz, $CDCl_3$).

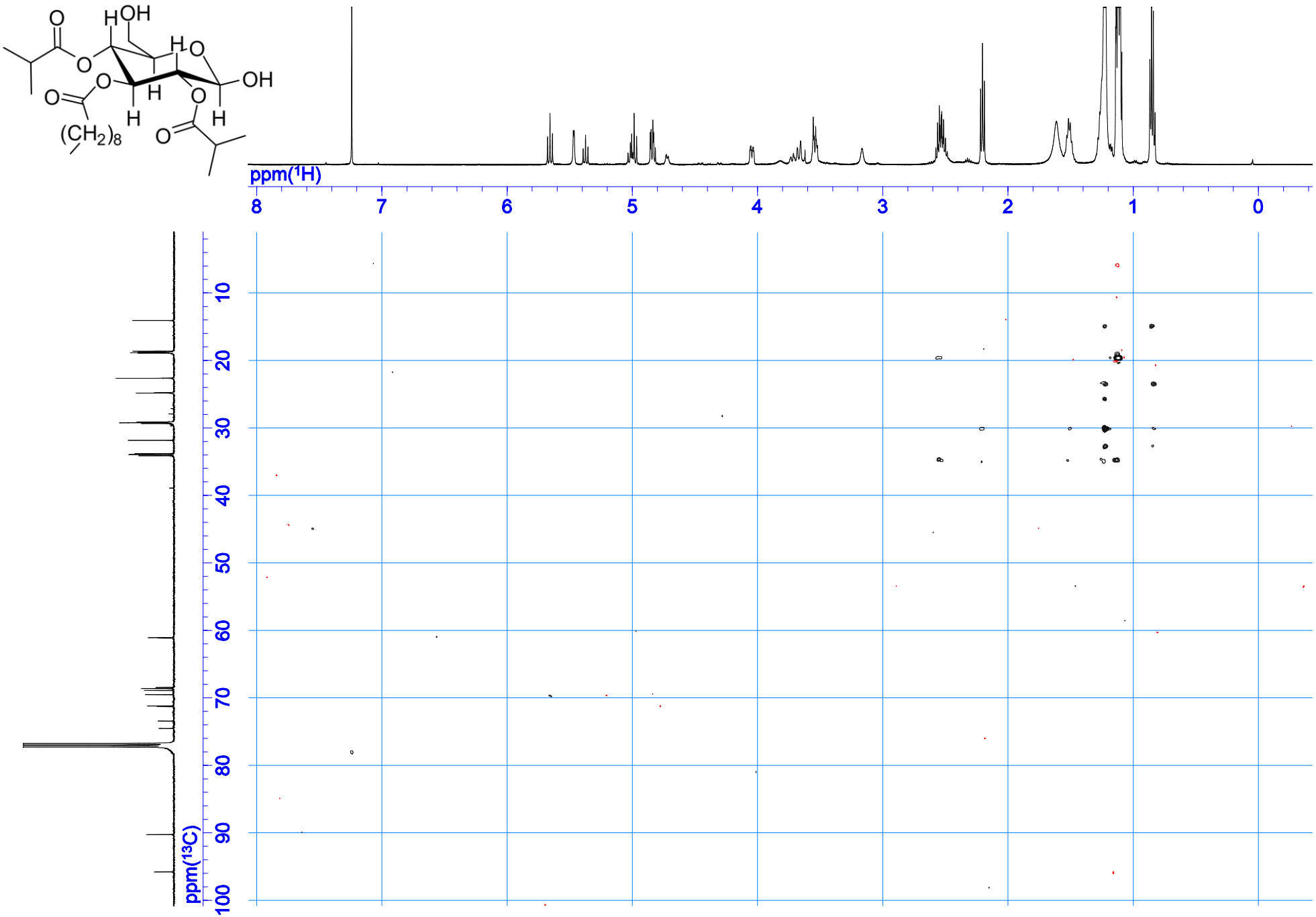

Figure S50. HSQC-TQCSY spectrum of **3** (500 MHz, $CDCl_3$).

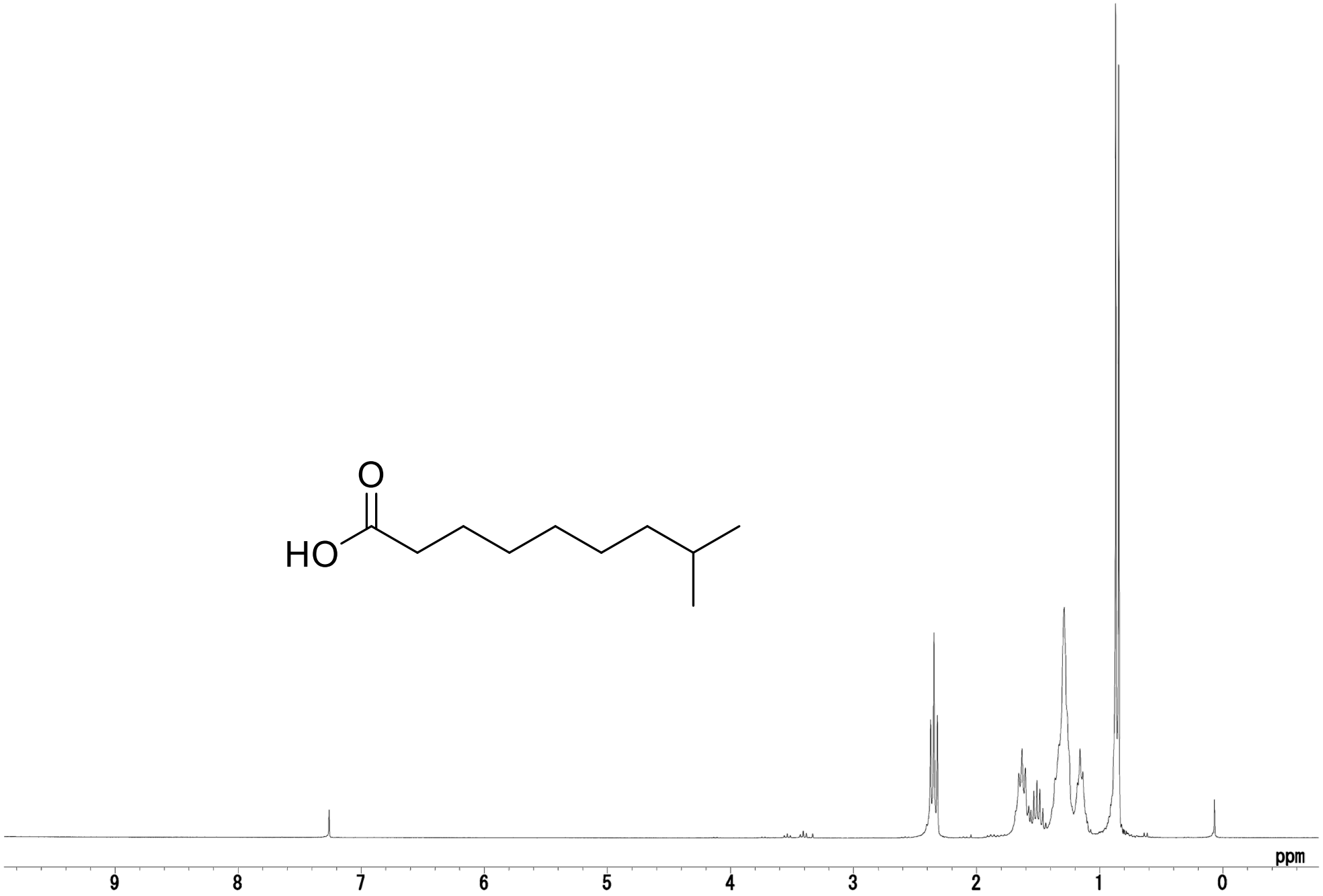

Figure S51. ^{1}H NMR spectrum of 8-methylnonanoic acid (**9**) (270 MHz, $CDCl_3$).

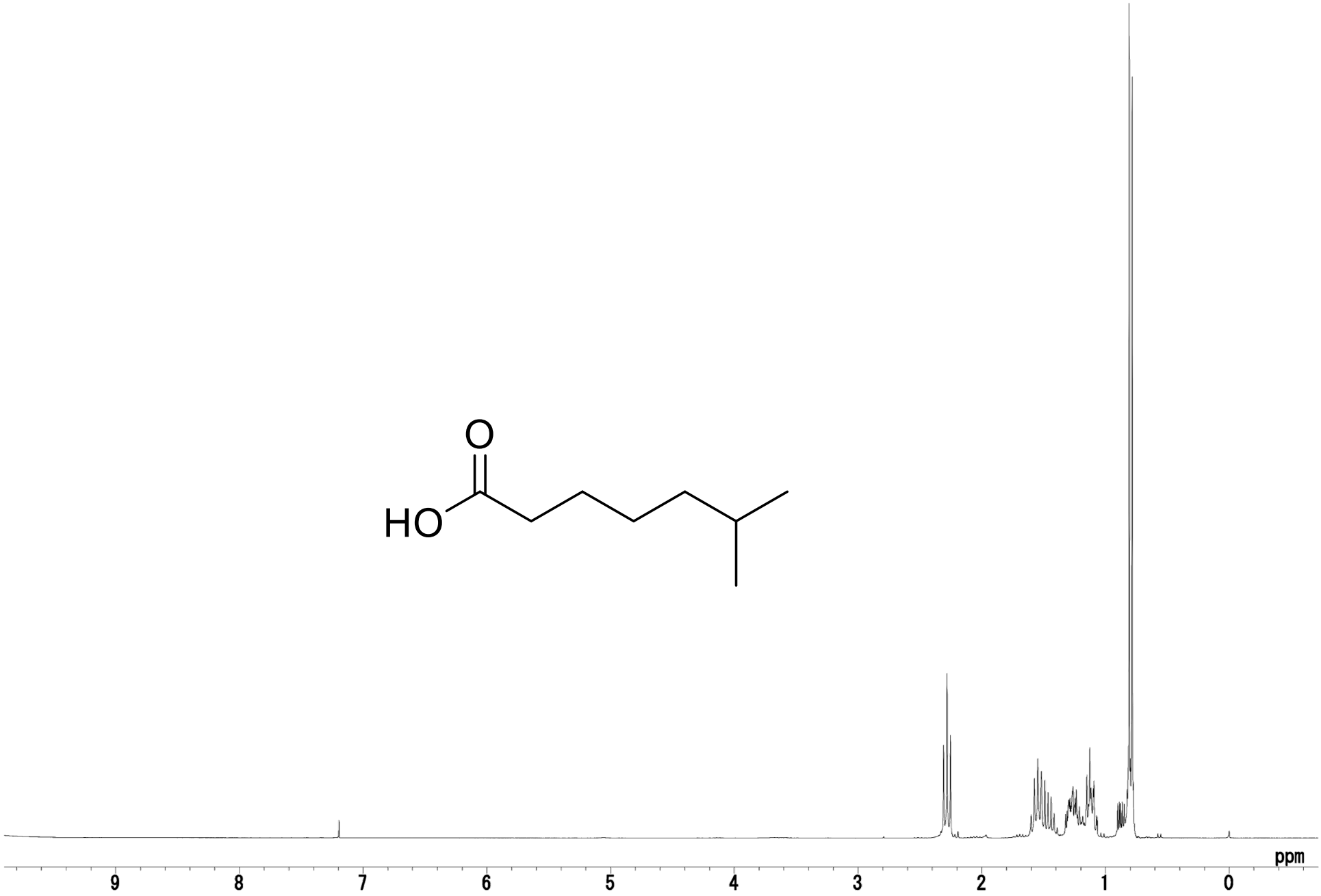

Figure S52. ^{1}H NMR spectrum of 6-methylheptanoic acid (**14**) (270 MHz, $CDCl_3$).

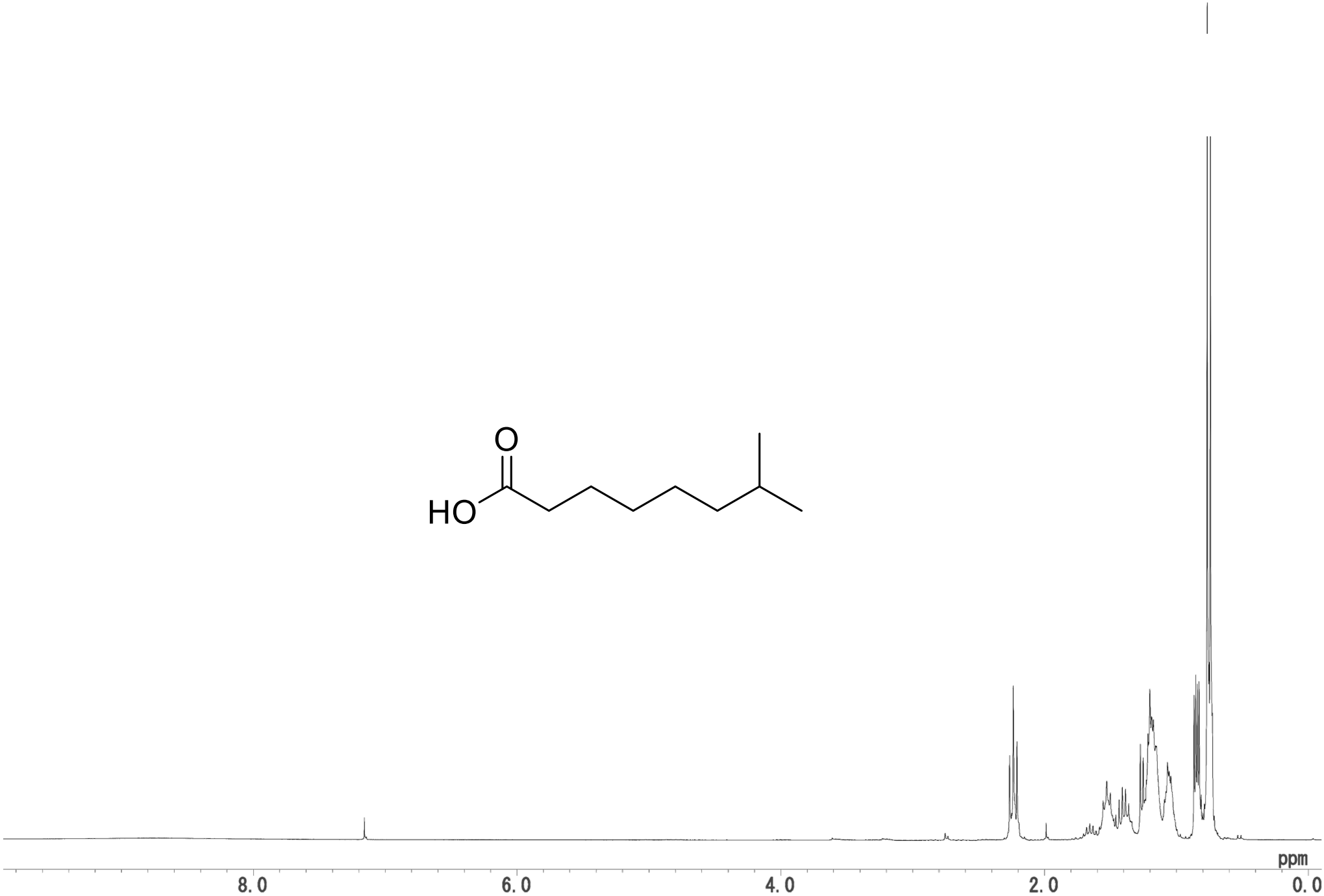

Figure S53. ^{1}H NMR spectrum of 7-methyloctanoic acid (**15**) (270 MHz, $CDCl_3$).