

Supplementary Materials

Stonikacidin A, an Antimicrobial 4-Bromopyrrole Alkaloid Containing L-Idonic Acid Core from the Northwestern Pacific Marine Sponge *Lissodendoryx papillosa*

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Content

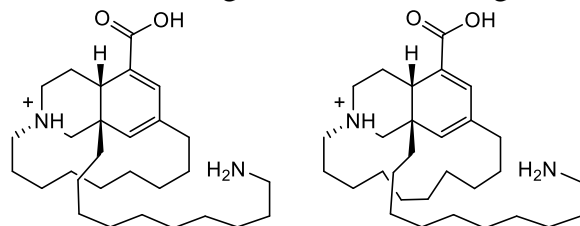
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List of previously described metabolites from genus *Lissodendoryx*

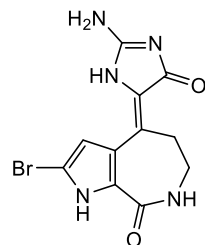
A: N-Containing metabolites from genus *Lissodendoryx*



lissodendoric acid A

lissodendoric acid B

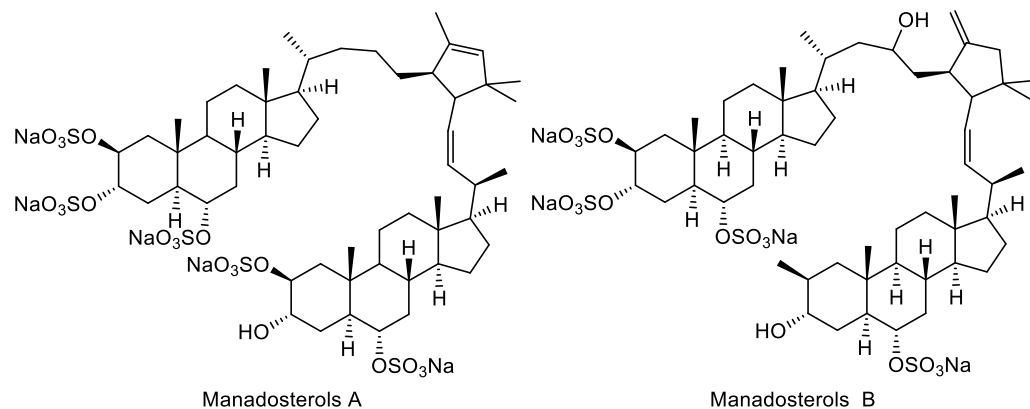
Lyakhova, E.G.; Kolesnikova, S.A.; Kalinovskiy, A.I.; Berdyshev, D.V.; Pislyagin, E.A.; Kuzmich, A.S.; Popov, R.S.; Dmitrenok, P.S.; Makarieva, T.N.; Stonik, V.A. Lissodendoric Acids A and B, Manzamine-Related Alkaloids from the Far Eastern Sponge *Lissodendoryx florida*. *Org. Lett.* **2017**, *19*(19), 5320–5323. DOI: [10.1021/acs.orglett.7b02608](https://doi.org/10.1021/acs.orglett.7b02608).



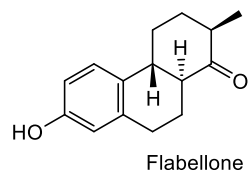
Pyrrololactam

Francis, J.; Schmitz, F.J.; Sarath, P.; Gunasekera, S.P.; Lakshmi, V.; Tillekeratne, L.M.V. Marine Natural Products: Pyrrololactams from several sponges. *Nat. Prod. Res.* **2012**, *26*(13), 1240–1248. <https://doi.org/10.1021/np50037a008>.

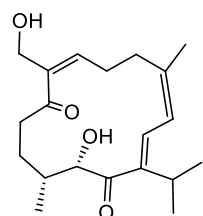
B: Non N-Containing metabolites



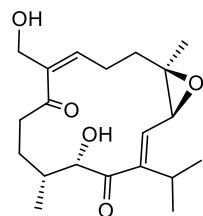
Ushiyama, Sh.; Umaoka, H.; Kato, H.; Suwa, Y.; Morioka, H.; Rotinsulu, H.; Losung, F.; Mangindaan, R.E.P.; de Voogd, N.J.; Yokosawa, H.; Tsukamoto, S. Manadosterols A and B, sulfonated sterol dimers inhibiting the Ubc13–Uev1A interaction, isolated from the marine sponge *Lissodendryx fibrosa*. *J. Nat. Prod.* **2012**, 75(8), 1495–1499. <https://doi.org/10.1021/np300352u>.



Cutignano, A.; De Palma, R.; Fontana, A. A chemical investigation of the Antarctic sponge *Lyssodendoryx flabellate*. *Nat. Prod. Res.* **2012**, 26(13), 1240–1248. <https://doi.org/10.1080/14786419.2011.561493>.



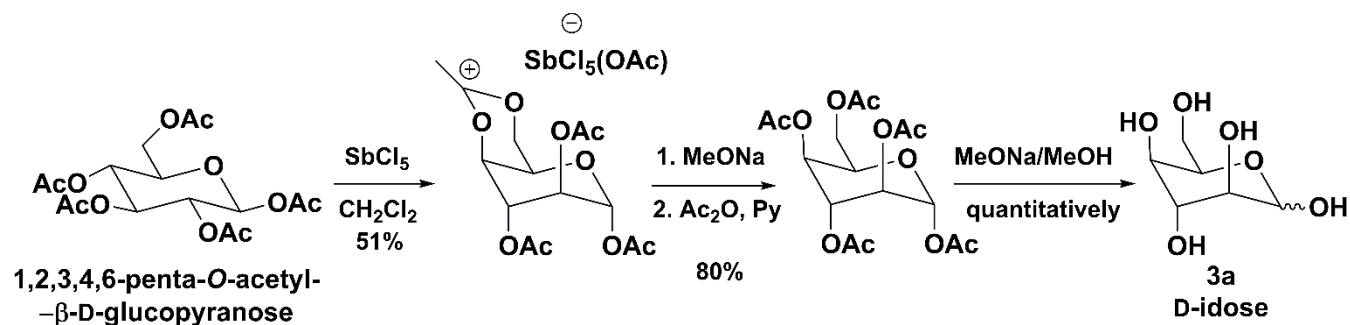
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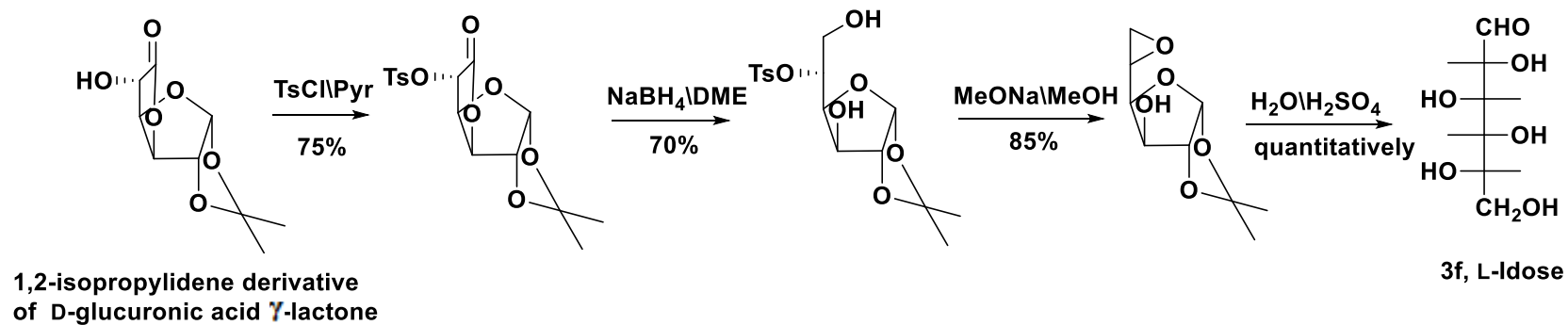
Flabellatene B'

Fontana, A.; Ciavatta, M.L.; Amodeo, P.; Cimino, G. Single solution phase conformation of new antiproliferative cembranes. *Tetrahedron* **1999**, 55, 1143–1152. doi: 10.1016/S0040-4020(98)01092-8.

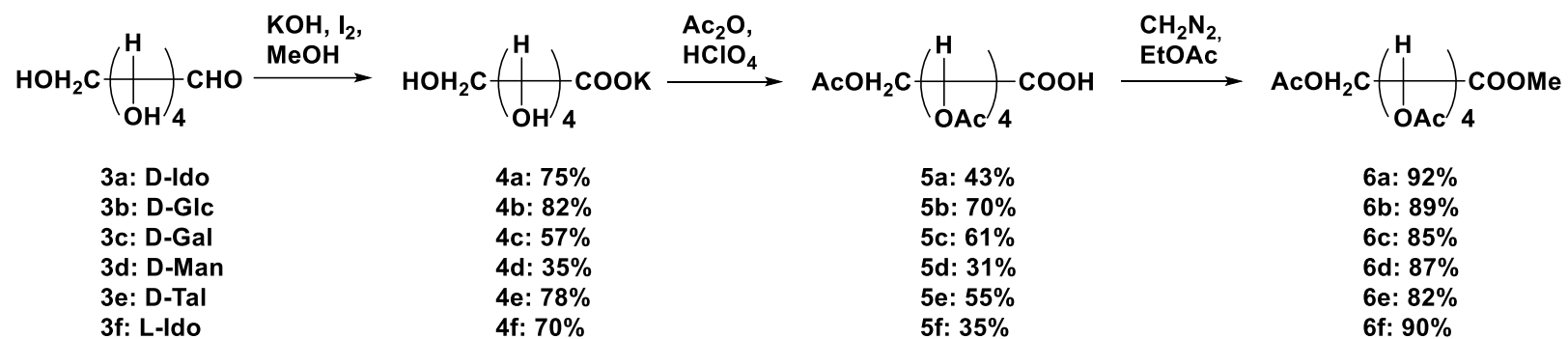
Reaction schemes



Scheme S1. Synthesis of D-idose **3a** from peracetyl-D-glucopyranose.



Scheme S2. Synthesis of L-idose **3f** from 1,2-isopropylidene derivative of D-glucuronic acid γ -lactone.



Scheme S3. Synthesis of acetylated methyl aldonates **6a-6f**.

Tables and Figures

Figure S1. (–)HRESIMS spectrum of stonikacidin A (**1**).

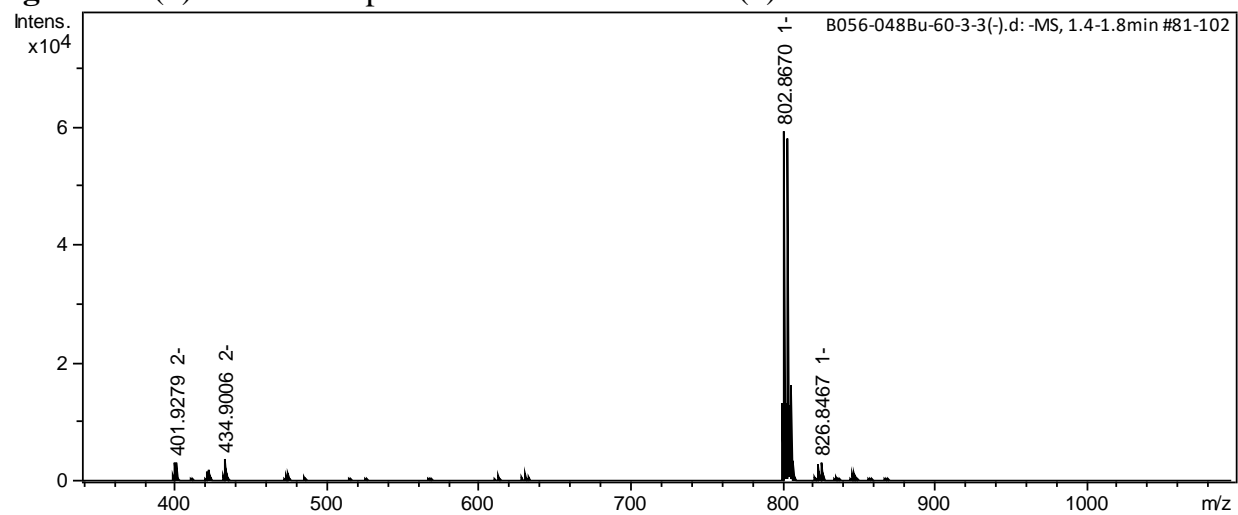


Figure S2. Isotope pattern of deprotonated molecule ion peak $[M - H]^-$ of stonikacidin A (**1**) showing the isotope distribution characteristic for ions with three bromine atoms (m/z calcd 800.8684 for $[C_{26}H_{20}^{79}Br_3N_4O_{11}]^-$, found 800.8683, error 0.1 ppm)

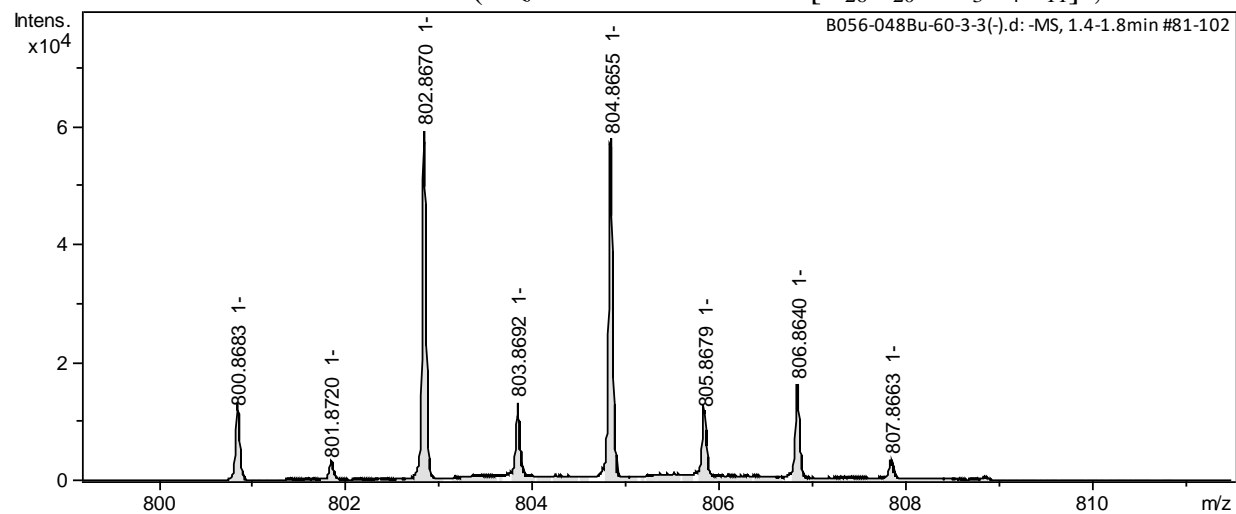


Table S1. Isotopes of deprotonated molecule ion peak of stonikacidin A (**1**) and corresponding formulas of the major isotopologues.

N	Measured peak		Calculated peak		Δ (ppm)	Molecular formula of the major isotopologues of the ion
	m/z	I %	m/z	I %		
1	800.8683	20.0	800.8684	32.9	0.1	$[^{12}\text{C}_{26}\text{H}_{20}^{79}\text{Br}_3\text{N}_4\text{O}_{11}]^-$
2	801.8720	5.1	801.8715	10.0	-0.6	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{79}\text{Br}_3\text{N}_4\text{O}_{11}]^-$
3	802.8670	100.0	802.8665	98.3	-0.6	$[^{12}\text{C}_{26}\text{H}_{20}^{79}\text{Br}_2^{81}\text{BrN}_4\text{O}_{11}]^-$
4	803.8692	22.3	803.8695	29.4	0.4	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{79}\text{Br}_2^{81}\text{BrN}_4\text{O}_{11}]^-$
5	804.8655	97.3	804.8648	100.0	-0.8	$[^{12}\text{C}_{26}\text{H}_{20}^{79}\text{Br}^{81}\text{Br}_2\text{N}_4\text{O}_{11}]^-$
6	805.8679	19.4	805.8677	29.3	-0.3	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{79}\text{Br}^{81}\text{Br}_2\text{N}_4\text{O}_{11}]^-$
7	806.8640	27.3	806.8636	36.7	-0.5	$[^{12}\text{C}_{26}\text{H}_{20}^{81}\text{Br}_3\text{N}_4\text{O}_{11}]^-$
8	807.8663	6.0	807.8661	10.2	-0.3	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{81}\text{Br}_3\text{N}_4\text{O}_{11}]^-$

Figure S3. (–)ESIMS/MS spectrum of $[M - H]^-$ precursor ion of stonikacidin A (**1**).

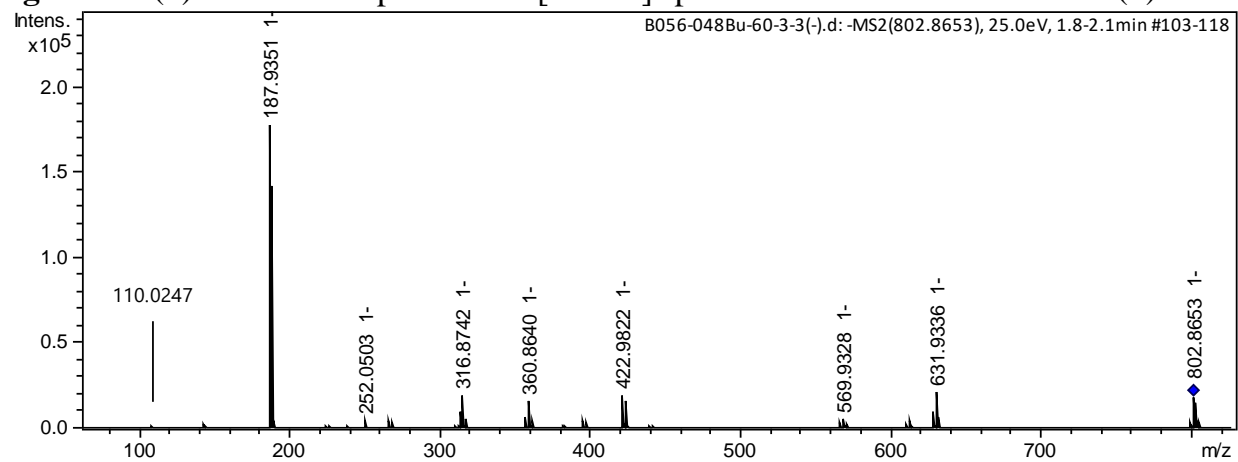


Figure S4. (+)HRESIMS spectrum of stonikacidin A (**1**).

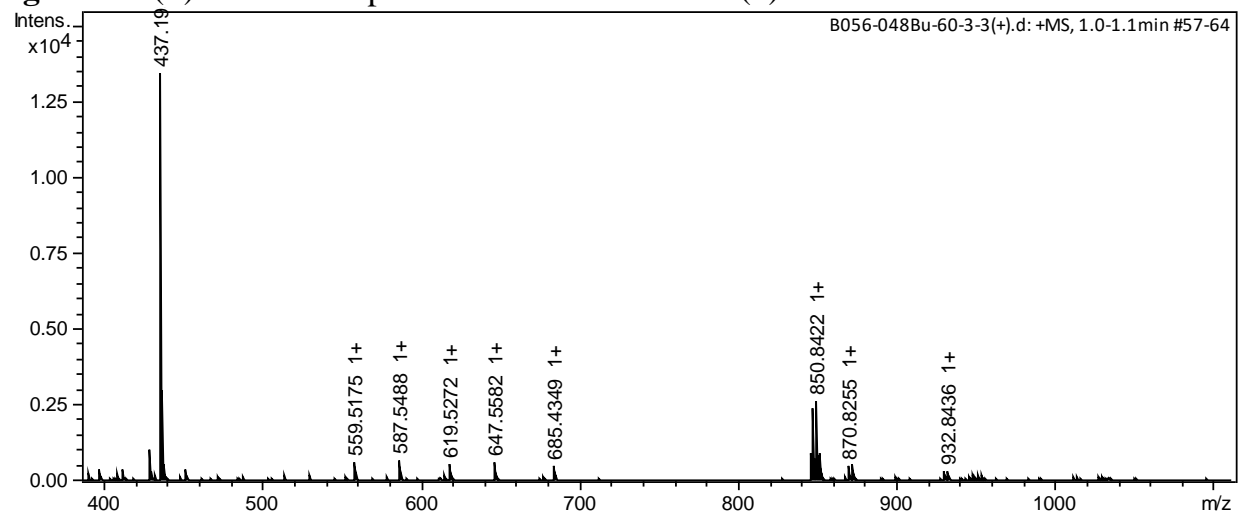


Figure S5. Isotope pattern of $[M + 2Na - H]^+$ ion of stonikacidin A (**1**) showing the characteristic isotope pattern with three bromine atoms (m/z calcd 846.8469 for $[C_{26}H_{20}^{79}Br_3N_4O_{11}Na_2]^+$, found 846.8463, error 0.7 ppm)

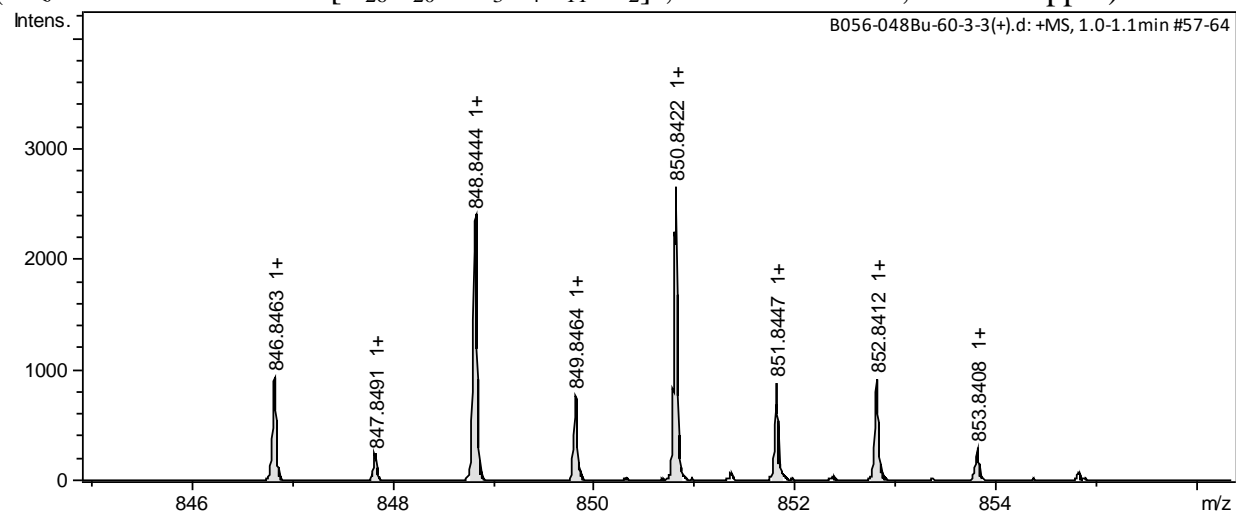


Table S2. Isotopes of $[M + 2Na - H]^+$ ion of stonikacidin A (**1**) and corresponding formulas of the major isotopologues.

N	Measured peak		Calculated peak		Δ (ppm)	Molecular formula of the major isotopologues of the ion
	m/z	I %	m/z	I %		
1	846.8463	35.5	846.8469	32.9	0.7	$[^{12}\text{C}_{26}\text{H}_{20}^{79}\text{Br}_3\text{N}_4\text{Na}_2\text{O}_{11}]^+$
2	847.8491	8.6	847.8499	10.0	1.0	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{79}\text{Br}_3\text{N}_4\text{Na}_2\text{O}_{11}]^+$
3	848.8444	90.3	848.845	98.3	0.7	$[^{12}\text{C}_{26}\text{H}_{20}^{79}\text{Br}_2^{81}\text{BrN}_4\text{Na}_2\text{O}_{11}]^+$
4	849.8464	29.0	849.848	29.4	1.9	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{79}\text{Br}_2^{81}\text{BrN}_4\text{Na}_2\text{O}_{11}]^+$
5	850.8422	100.0	850.8433	100.0	1.2	$[^{12}\text{C}_{26}\text{H}_{20}^{79}\text{Br}^{81}\text{Br}_2\text{N}_4\text{Na}_2\text{O}_{11}]^+$
6	851.8447	33.3	851.8461	29.3	1.6	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{79}\text{Br}^{81}\text{Br}_2\text{N Na}_2\text{O}_{11}]^+$
7	852.8412	34.4	852.8421	36.7	1.0	$[^{12}\text{C}_{26}\text{H}_{20}^{81}\text{Br}_3\text{N}_4\text{Na}_2\text{O}_{11}]^+$
8	853.8408	11.3	853.8445	10.2	4.4	$[^{12}\text{C}_{25}^{13}\text{CH}_{20}^{81}\text{Br}_3\text{N}_4\text{Na}_2\text{O}_{11}]^+$

Figure S6. (+)ESIMS/MS spectrum of $[M + 2Na - H]^+$ precursor ion of stonikacidin A (**1**).

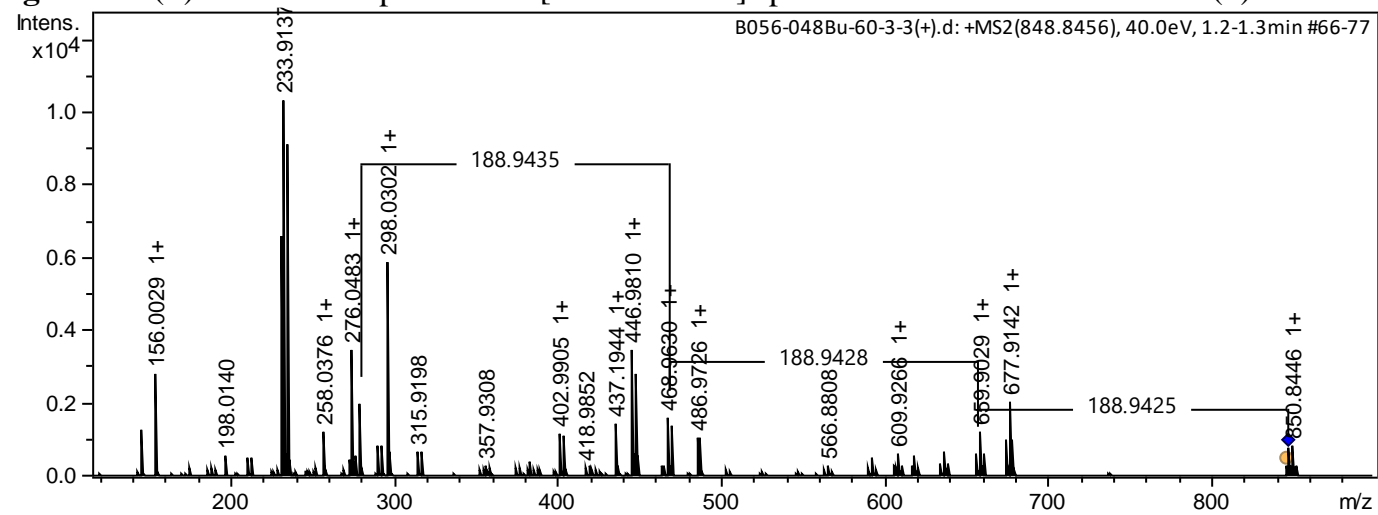


Figure S7. Fragmentation of $[M + 2Na - H]^+$ precursor ion of stonikacidin A (**1**) in the collision-induced dissociation (CID) (+)ESIMS/MS.

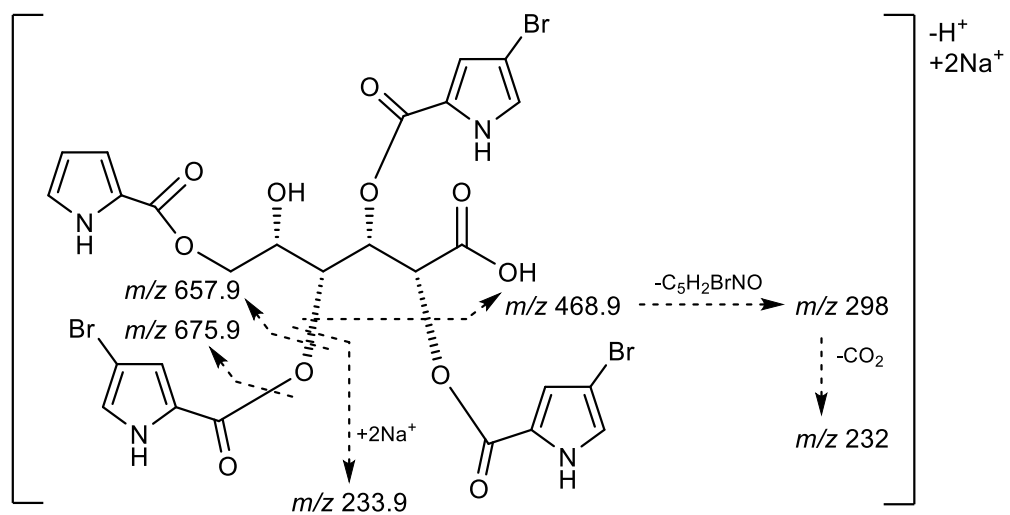


Figure S8. ^1H NMR spectrum of stonikacidin A (**1**) in CD_3OD (700 MHz).

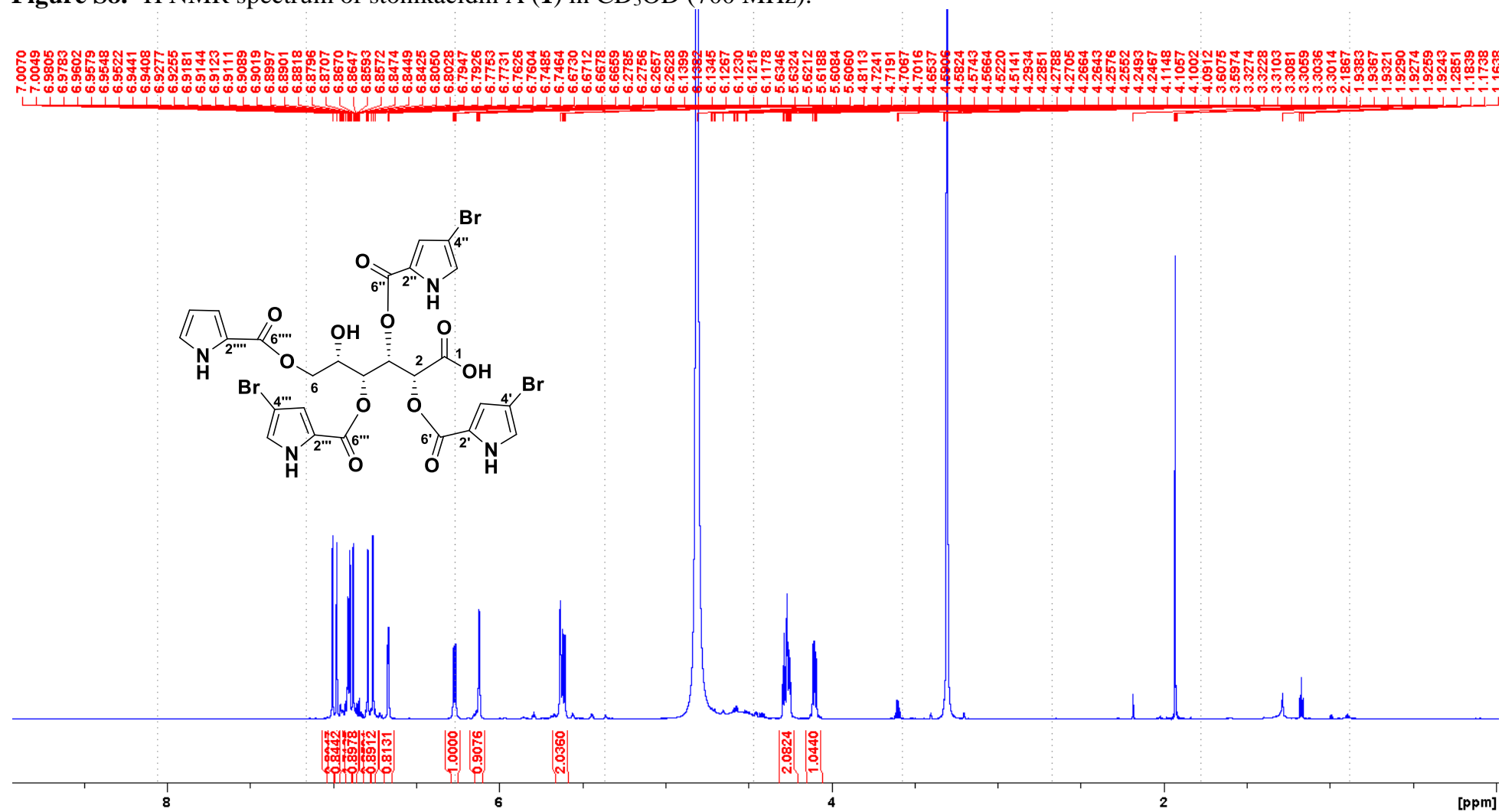


Figure S9. ^{13}C NMR spectrum of stonikacidin A (**1**) in CD_3OD (175 MHz).

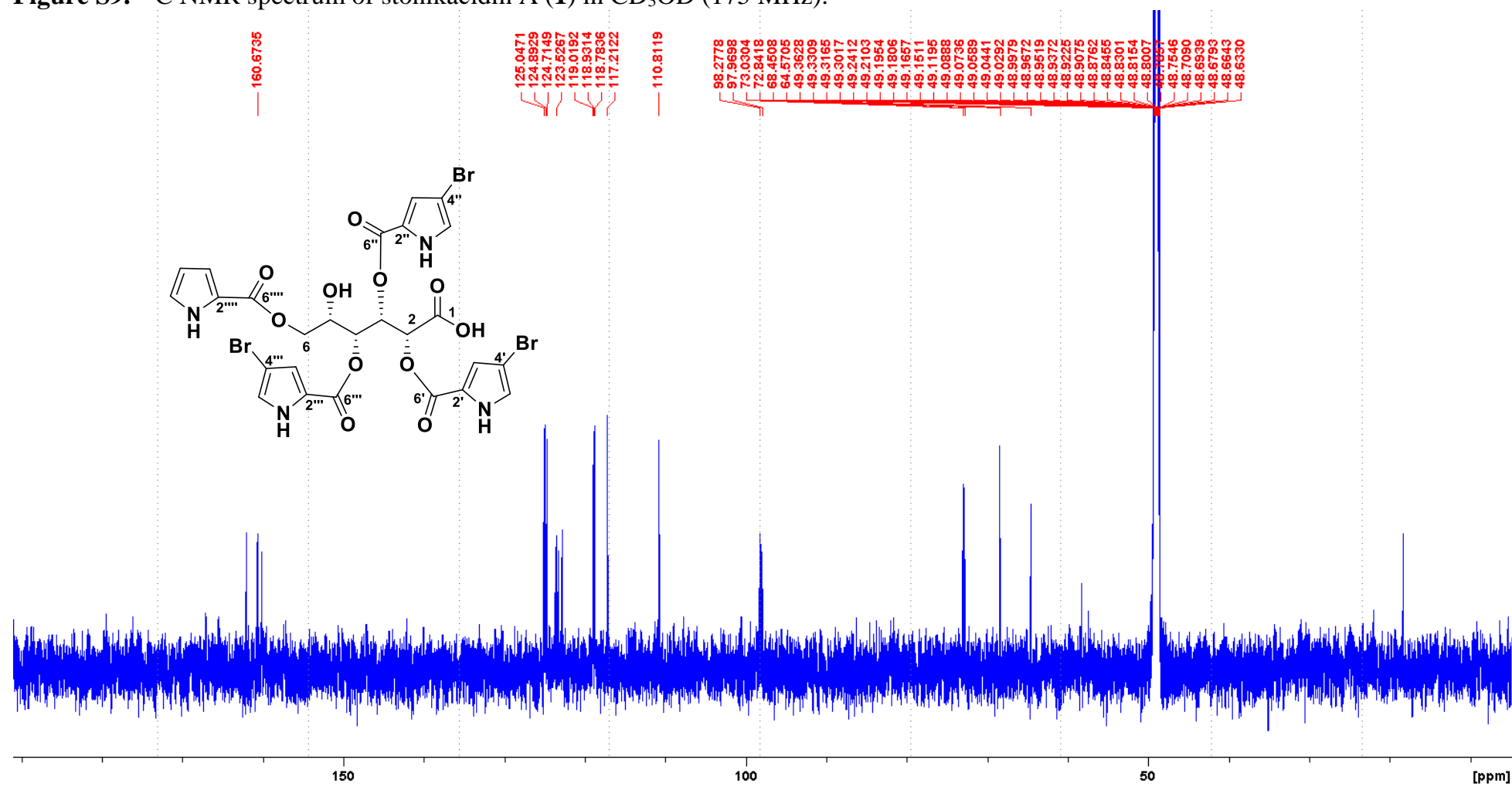


Figure S10. COSY spectrum of stonikacidin A (**1**) in CD₃OD (700 MHz).

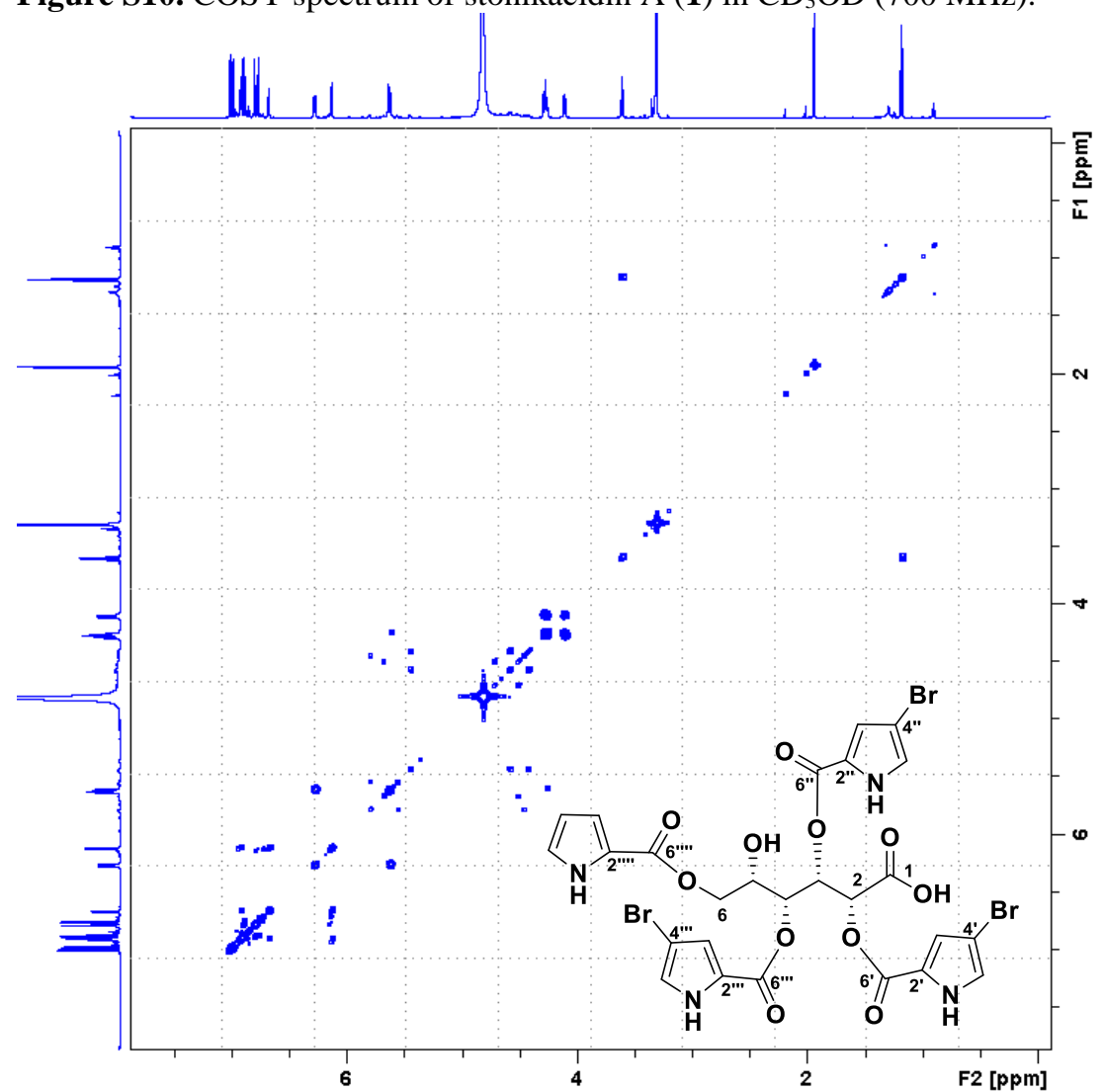


Figure S11. HSQC spectrum of stonikacidin A (**1**) in CD₃OD (700 MHz).

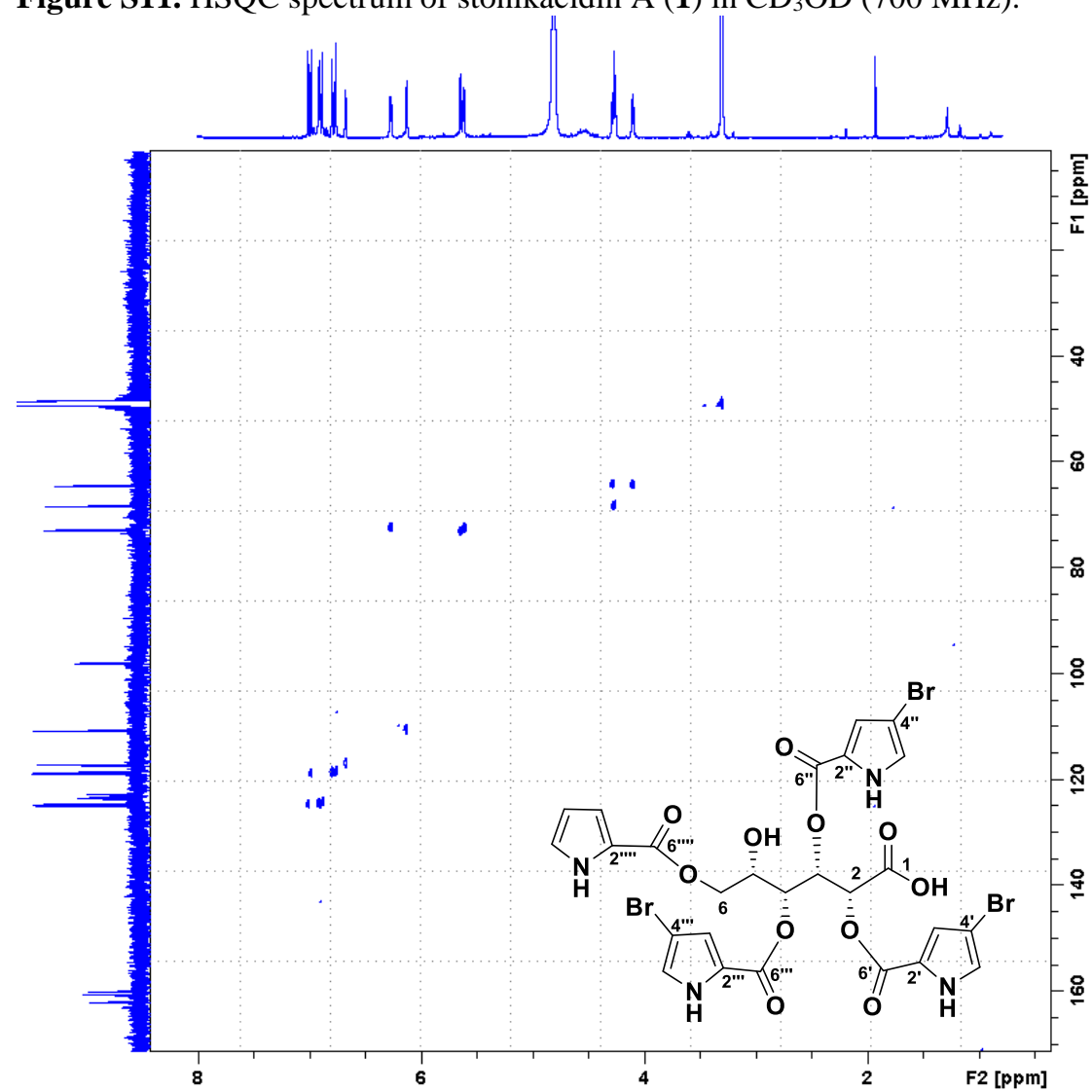


Figure S12. HMBC spectrum of stonikacidin A (**1**) in CD₃OD (700 MHz).

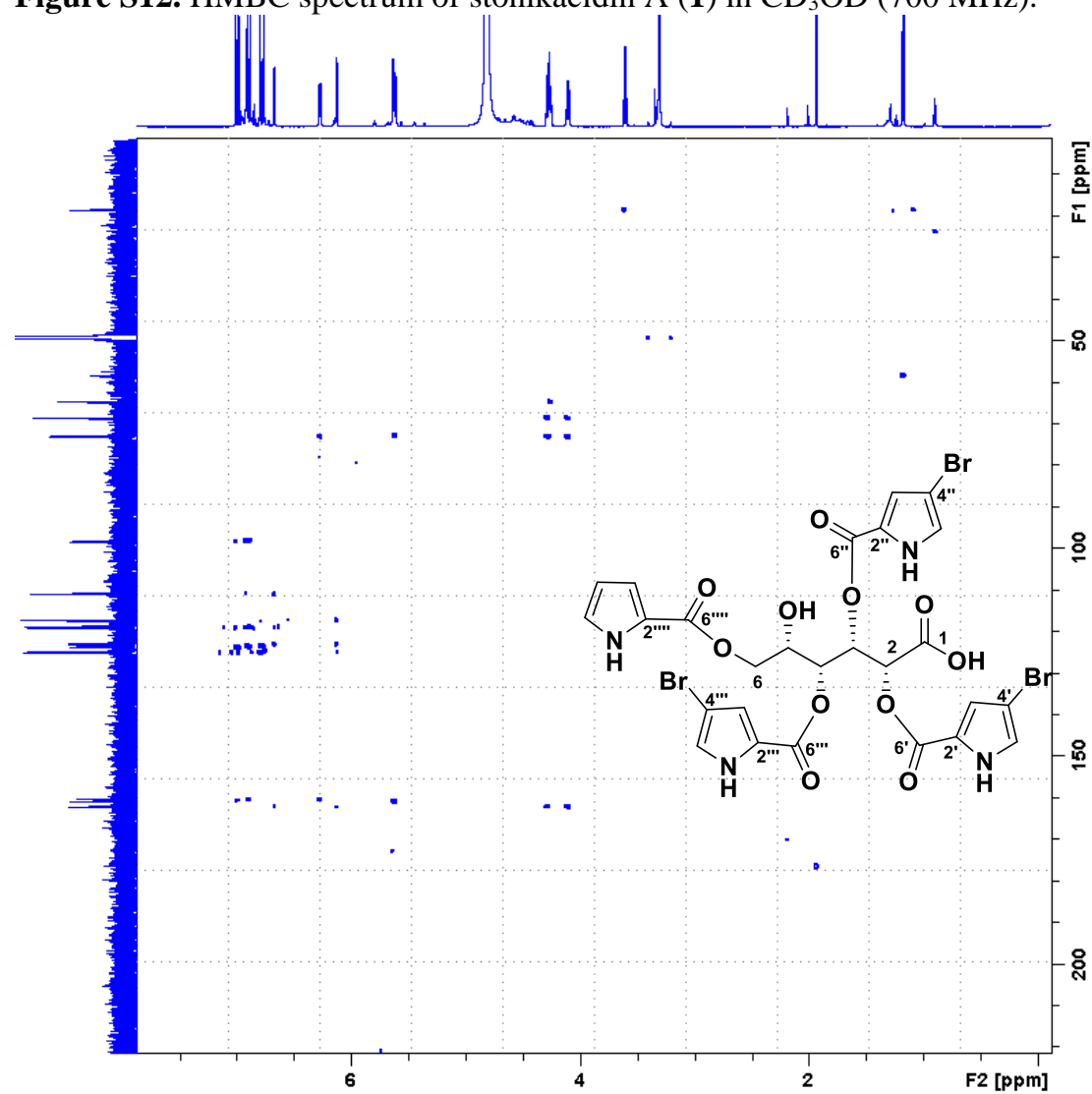


Figure S13. IR spectrum of stonikacidin A (**1**) in KBr.

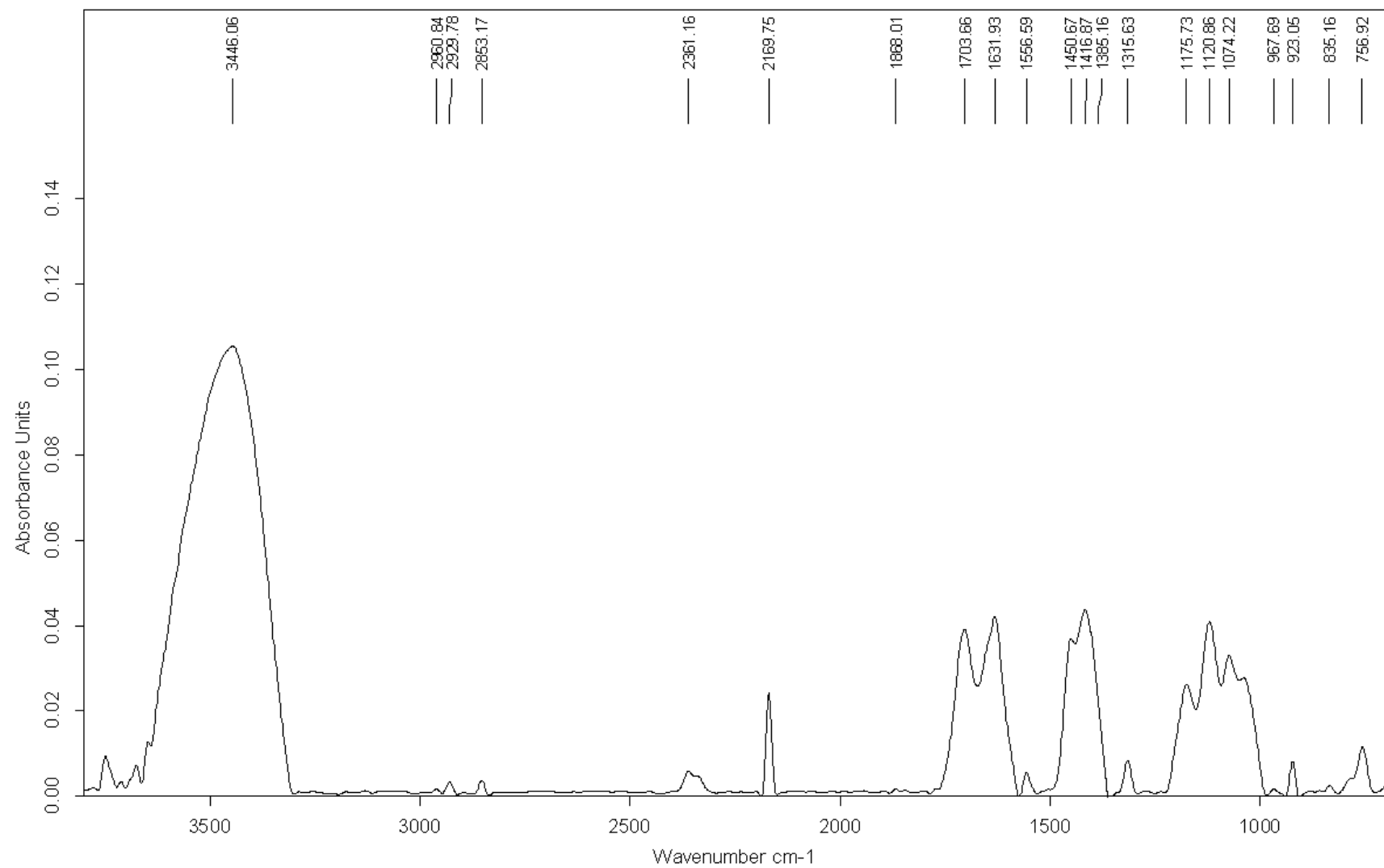


Figure S14. UV spectrum of stonikacidin A (**1**) in MeOH.

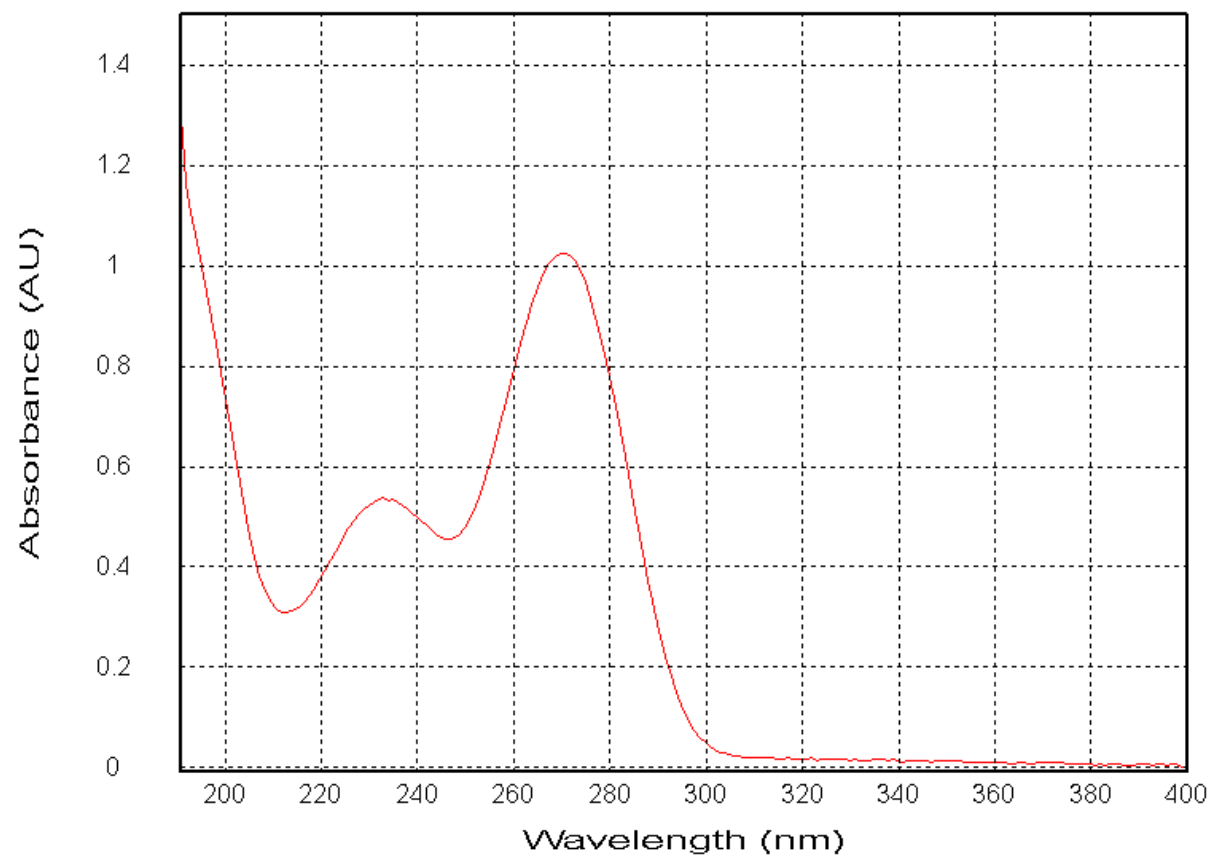


Figure S15. ECD spectrum of stonikacidin A (**1**) in MeOH.

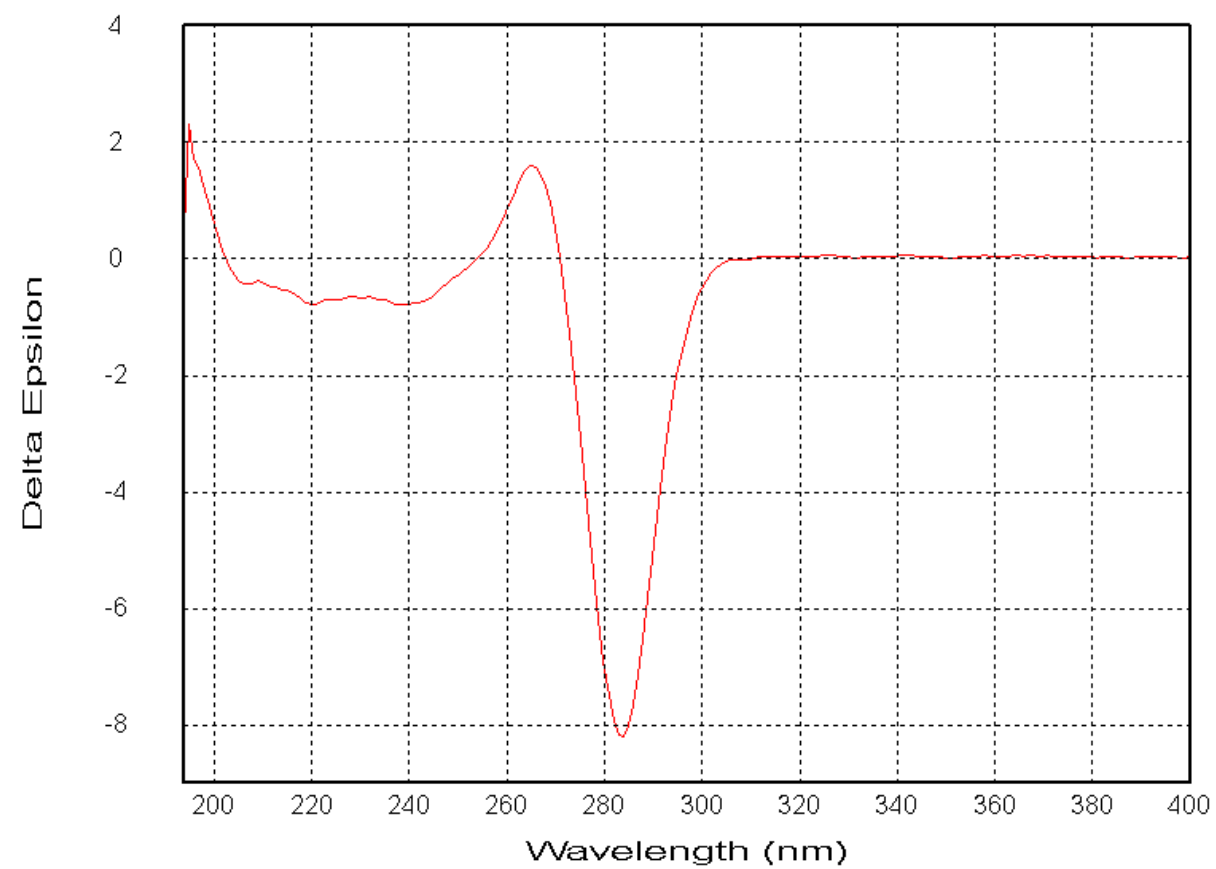
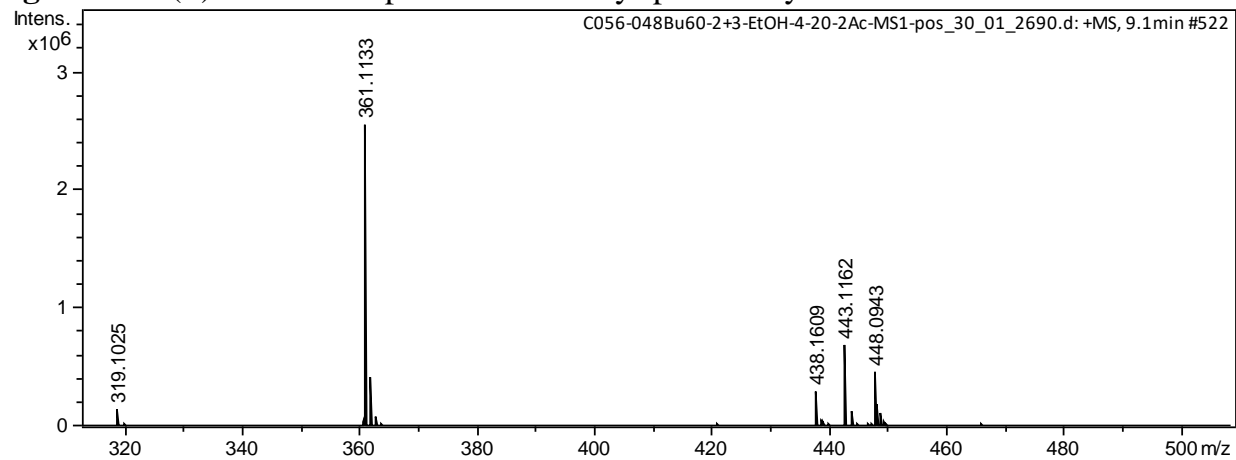
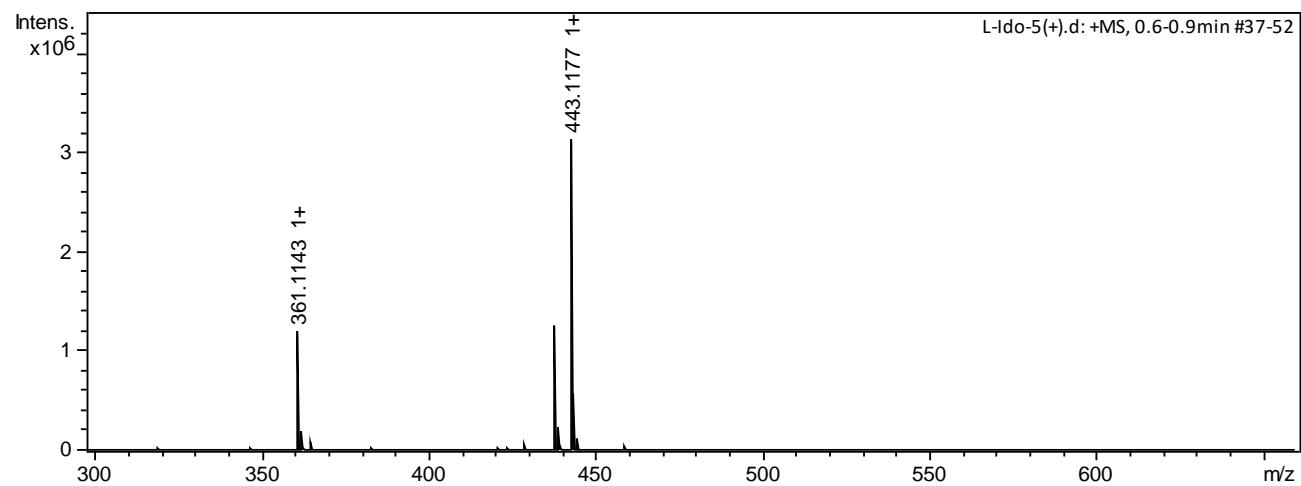


Figure S16. (+)HRESIMS spectrum of methyl-pentaacetyl-L-idonate **2**.



	found	calcd	Δ (ppm)	
$[M + H - AcOH]^+$	361,1133	361,1129	-1,1	-
				$[C_{15}H_{21}O_{10}]^+$
$[M + Na]^+$	443,1162	443,116	-0,5	

Figure S17. (+)HRESIMS spectrum of methyl-pentaacetyl-L-idonate **6f**.



	found	calcd	Δ (ppm)	
$[M + H - AcOH]^+$	361,1143	361,1129	-3,9	-
				$[C_{15}H_{21}O_{10}]^+$
$[M + Na]^+$	443,1177	443,116	-3,8	

Figure S18. ^1H NMR spectrum of methyl-pentaacetyl-L-idonate **2** in CDCl_3 (700 MHz).

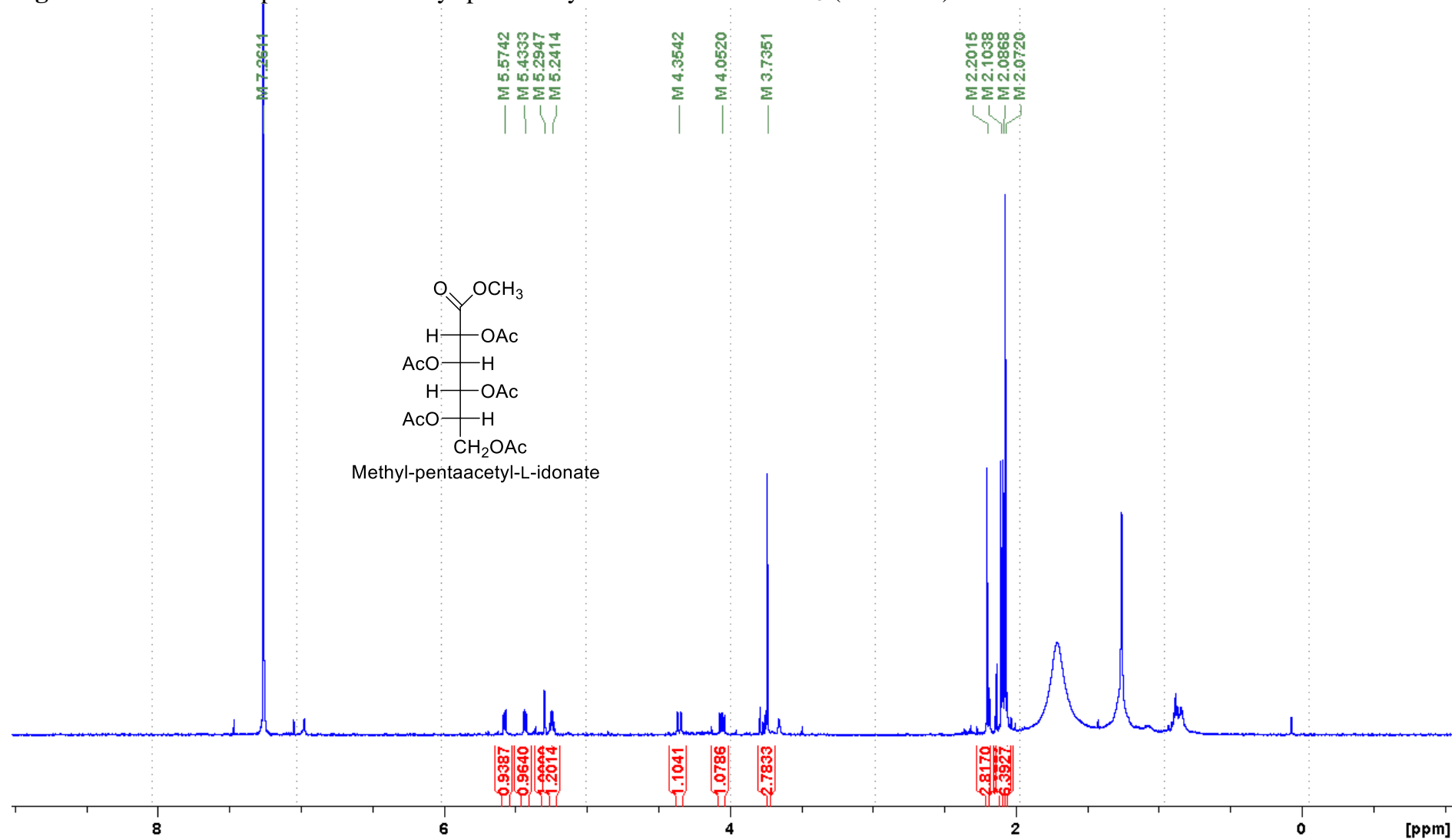


Figure S19. ^1H NMR spectrum of methyl-pentaacetyl-D-idonate **6a** in CDCl_3 (700 MHz).

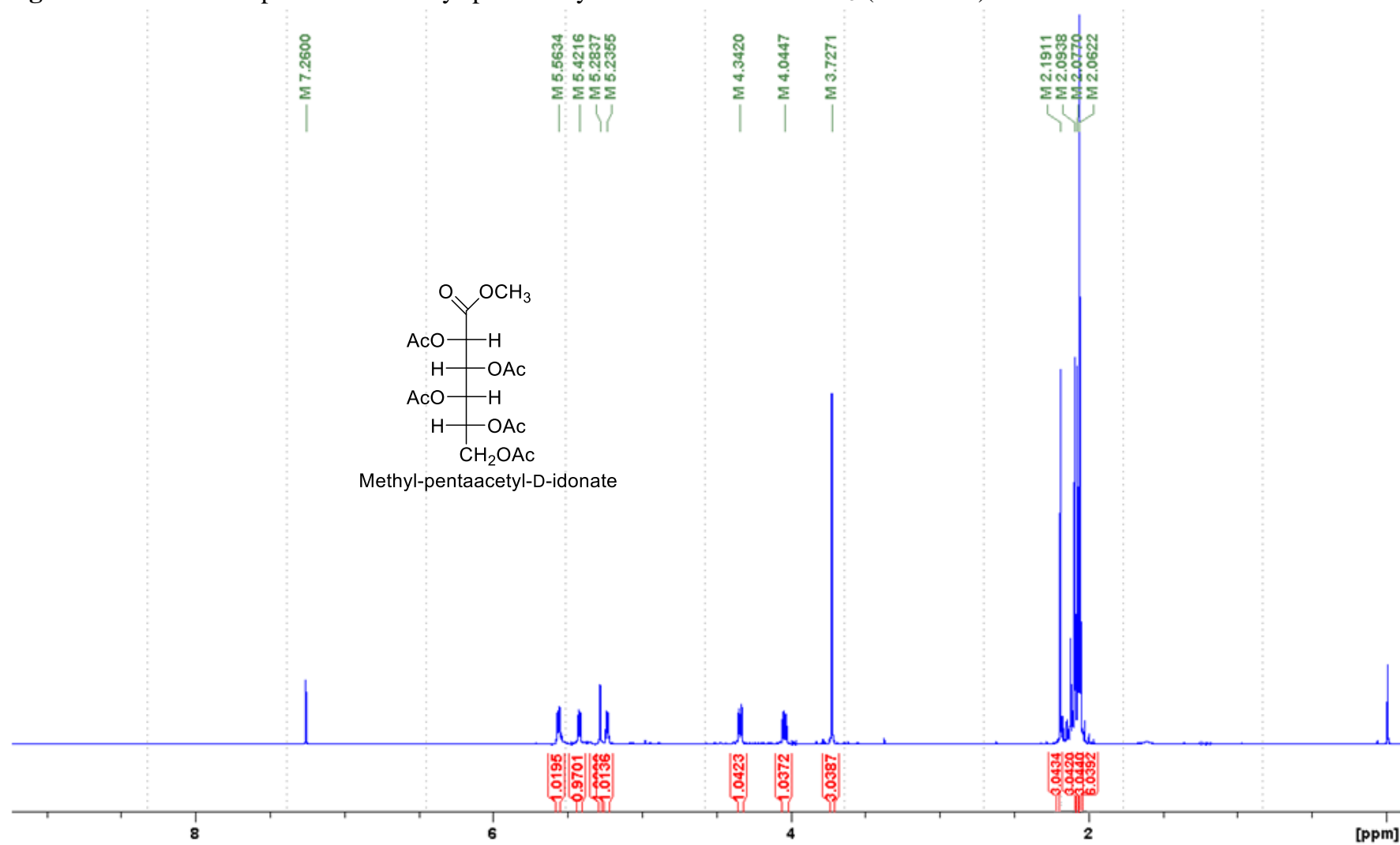


Figure S20. ^{13}C NMR spectrum of methyl-pentaacetyl-D-idonate **6a** in CDCl_3 (175 MHz).

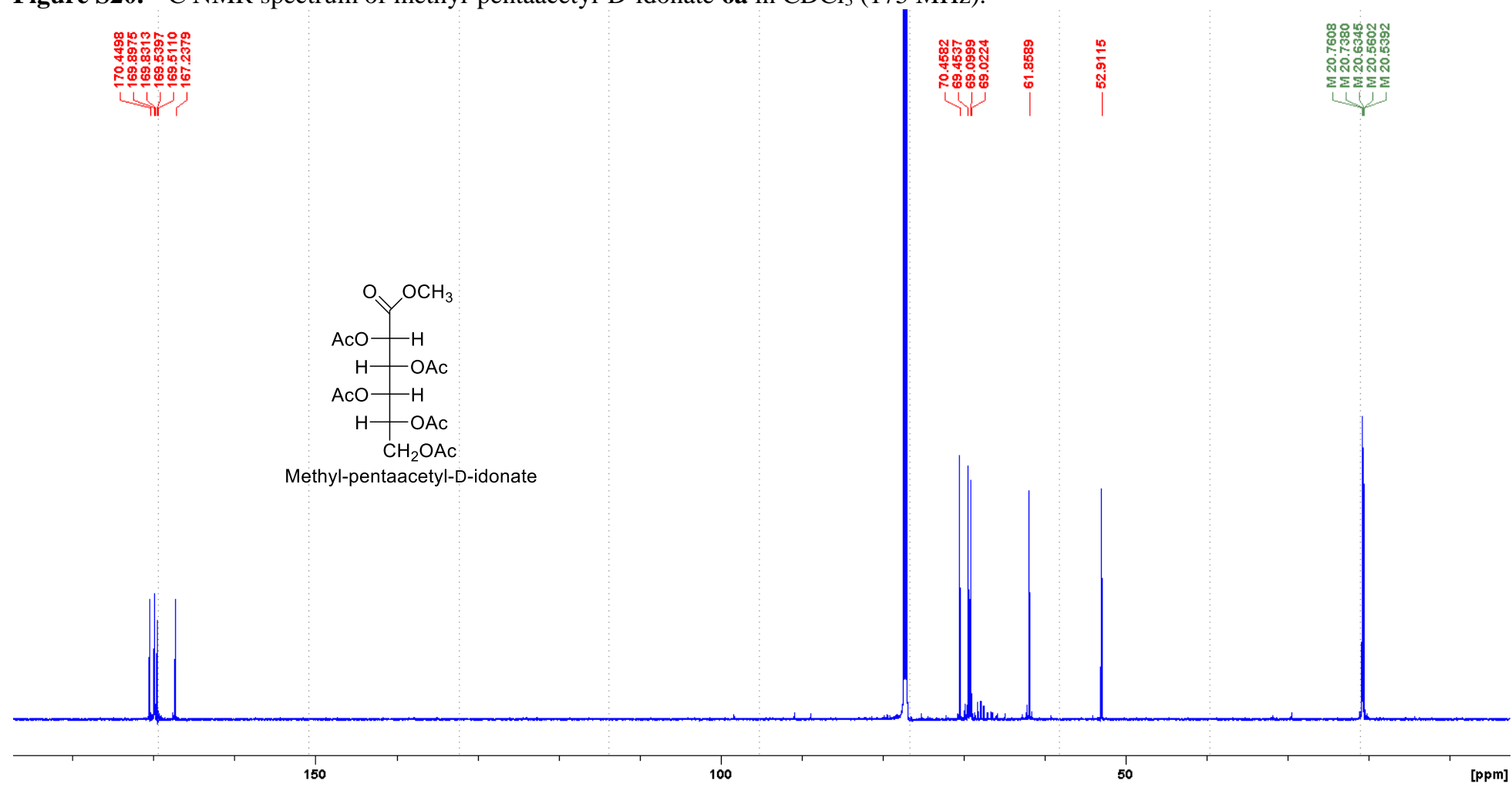


Figure S21. ^1H NMR spectrum of methyl-pentaacetyl-D-gluconate **6b** in CDCl_3 (500 MHz).

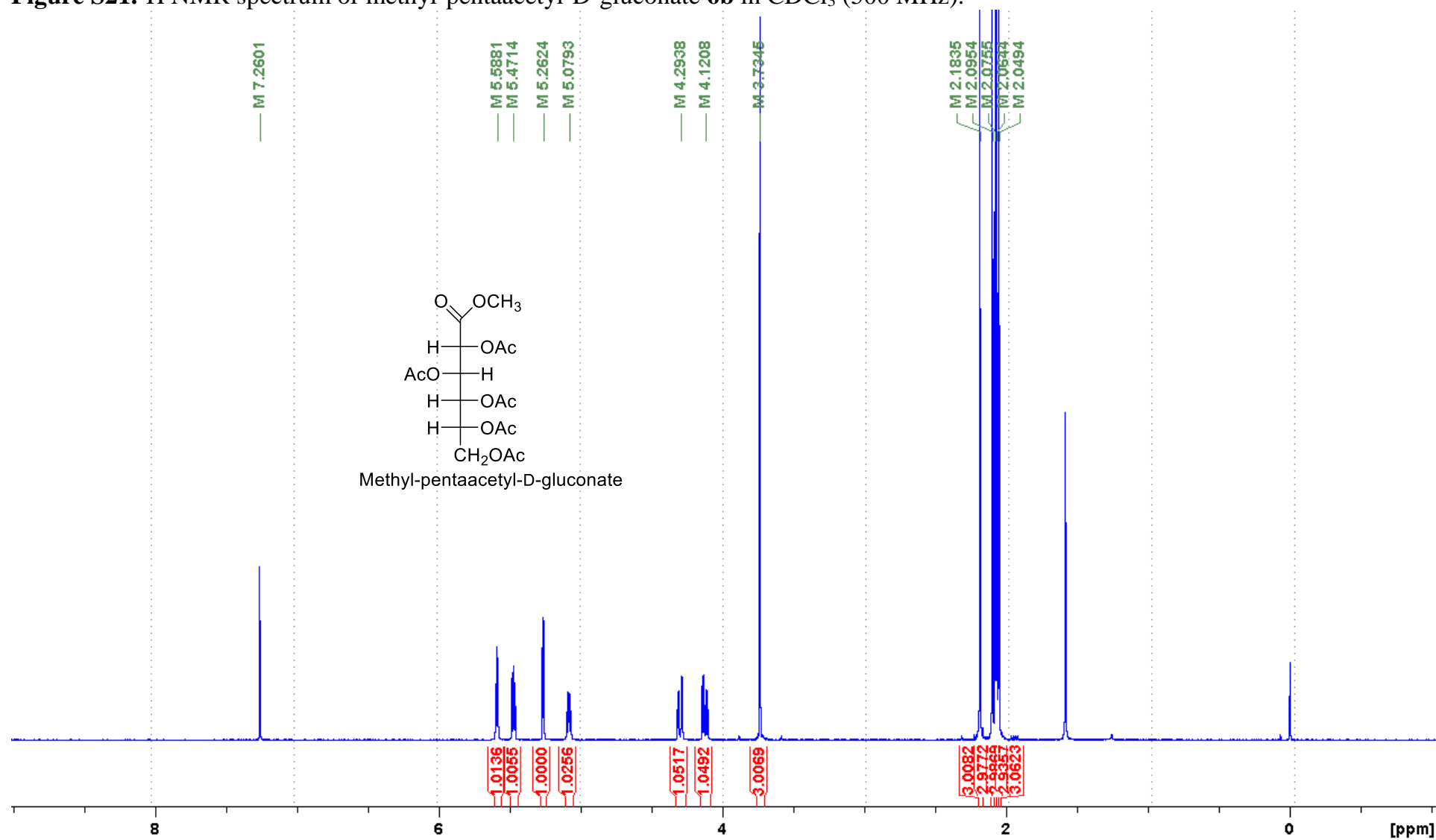


Figure S22. ^{13}C NMR spectrum of methyl-pentaacetyl-D-gluconate **6b** in CDCl_3 (125 MHz).

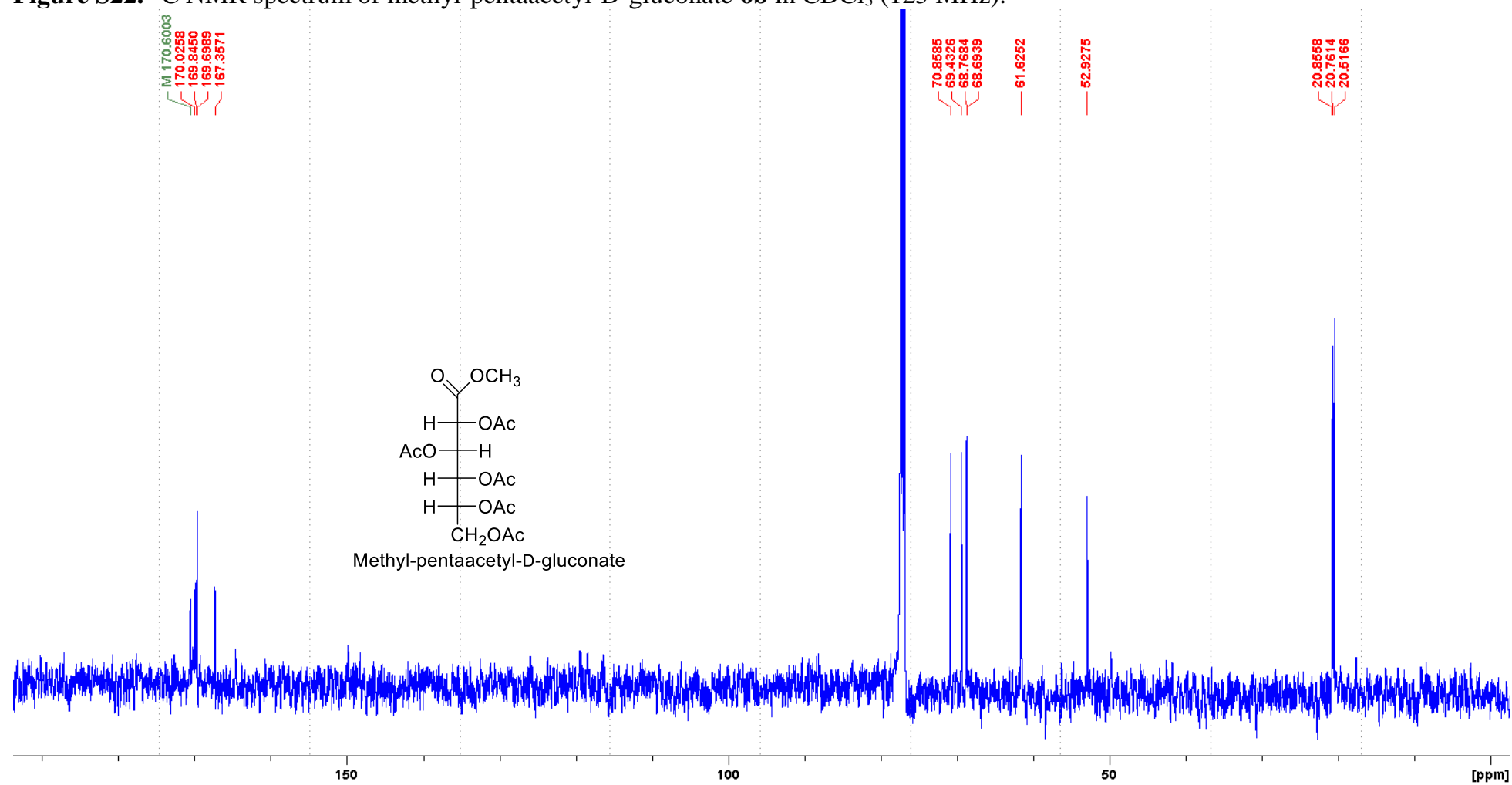


Figure S23. ^1H NMR spectrum of methyl-pentaacetyl-D-galactonate **6c** in CDCl_3 (500 MHz).

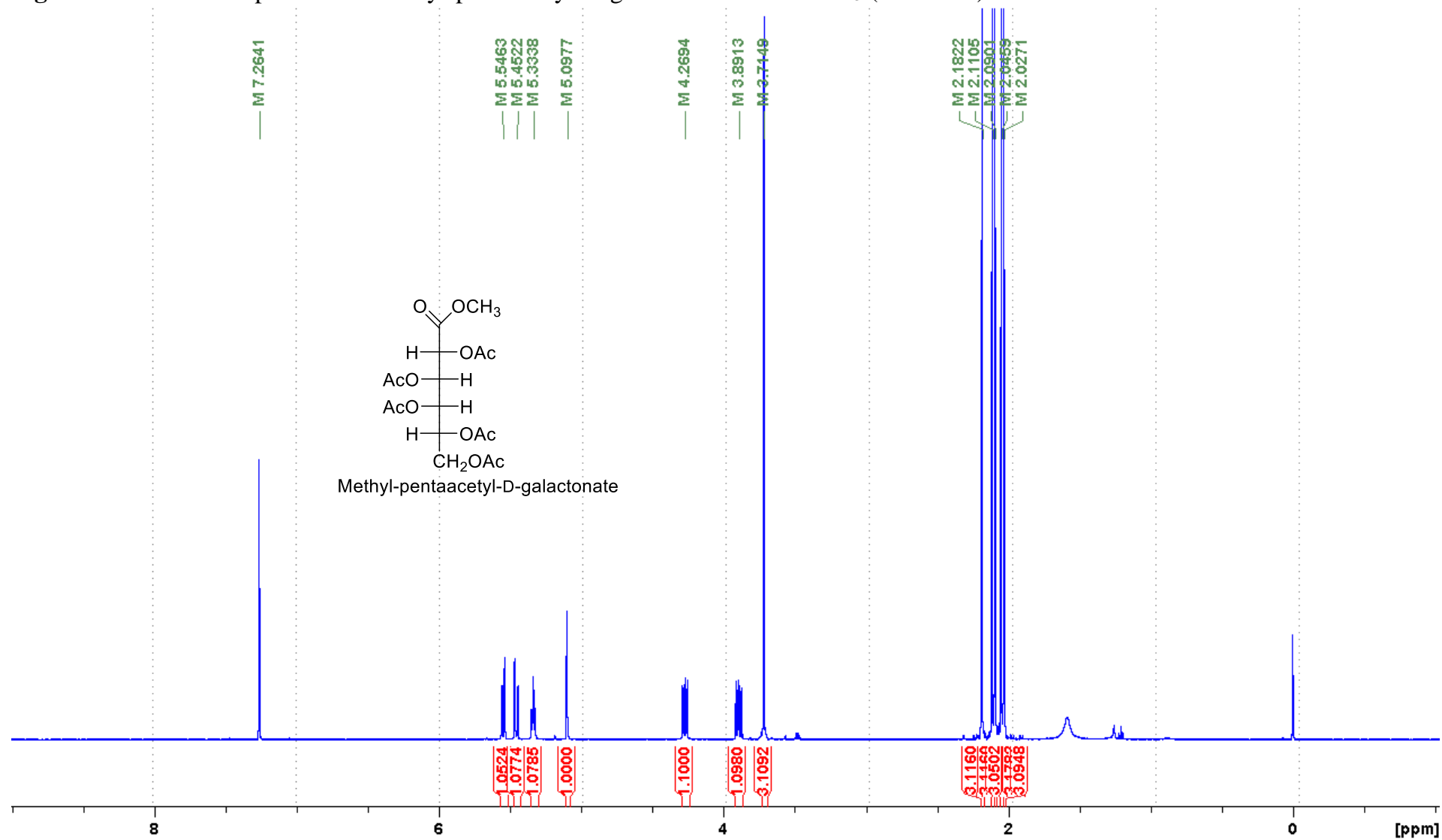


Figure S24. ^{13}C NMR spectrum of methyl-pentaacetyl-D-galactonate **6c** in CDCl_3 (125 MHz).

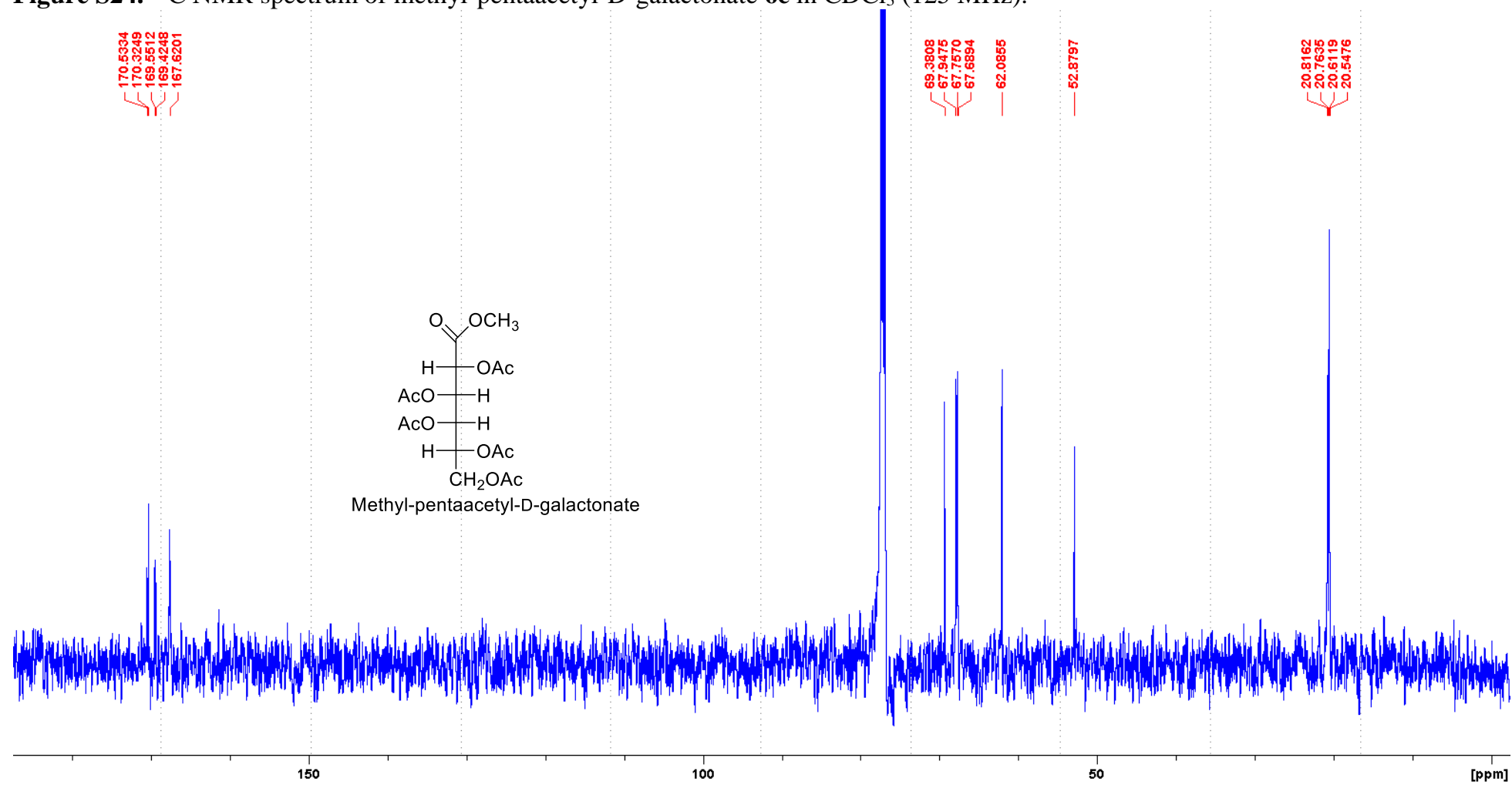


Figure S25. ^1H NMR spectrum of methyl-pentaacetyl-D-mannonate **6d** in CDCl_3 (500 MHz).

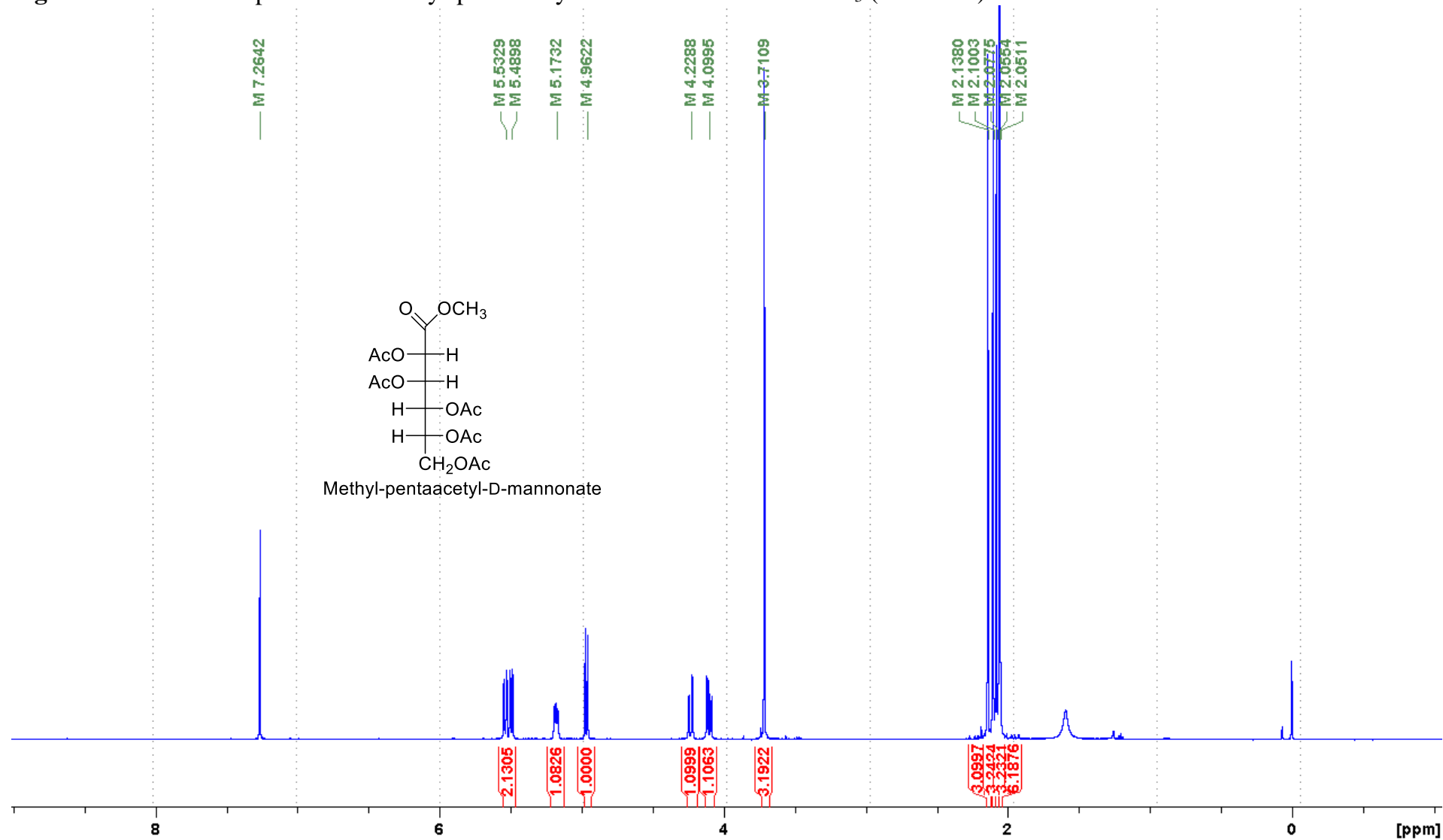


Figure S26. ^{13}C NMR spectrum of methyl-pentaacetyl-D-mannonate **6d** in CDCl_3 (125 MHz).

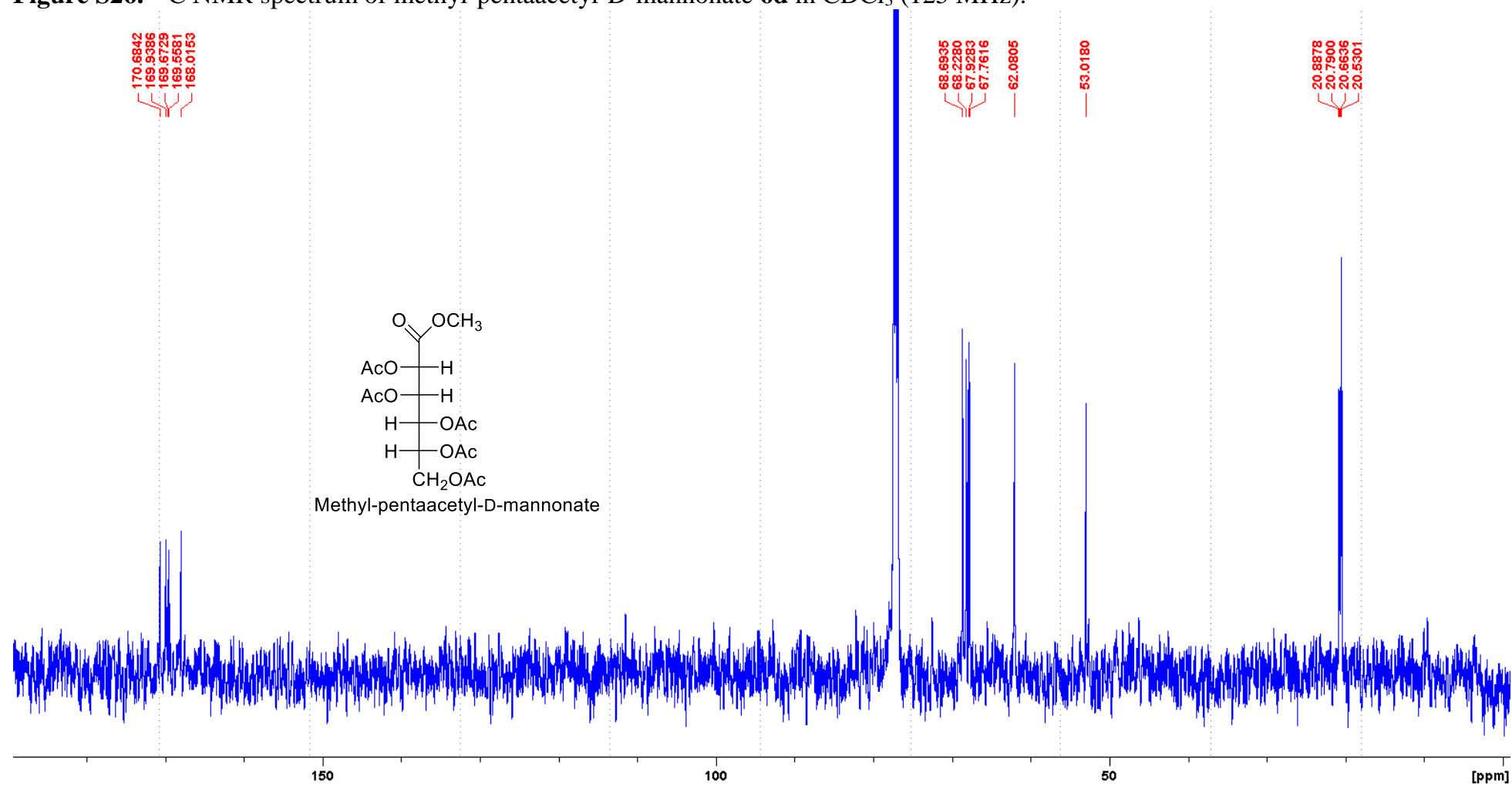


Figure S27. ^1H NMR spectrum of methyl-pentaacetyl-D-talonate **6e** in CDCl_3 (700 MHz).

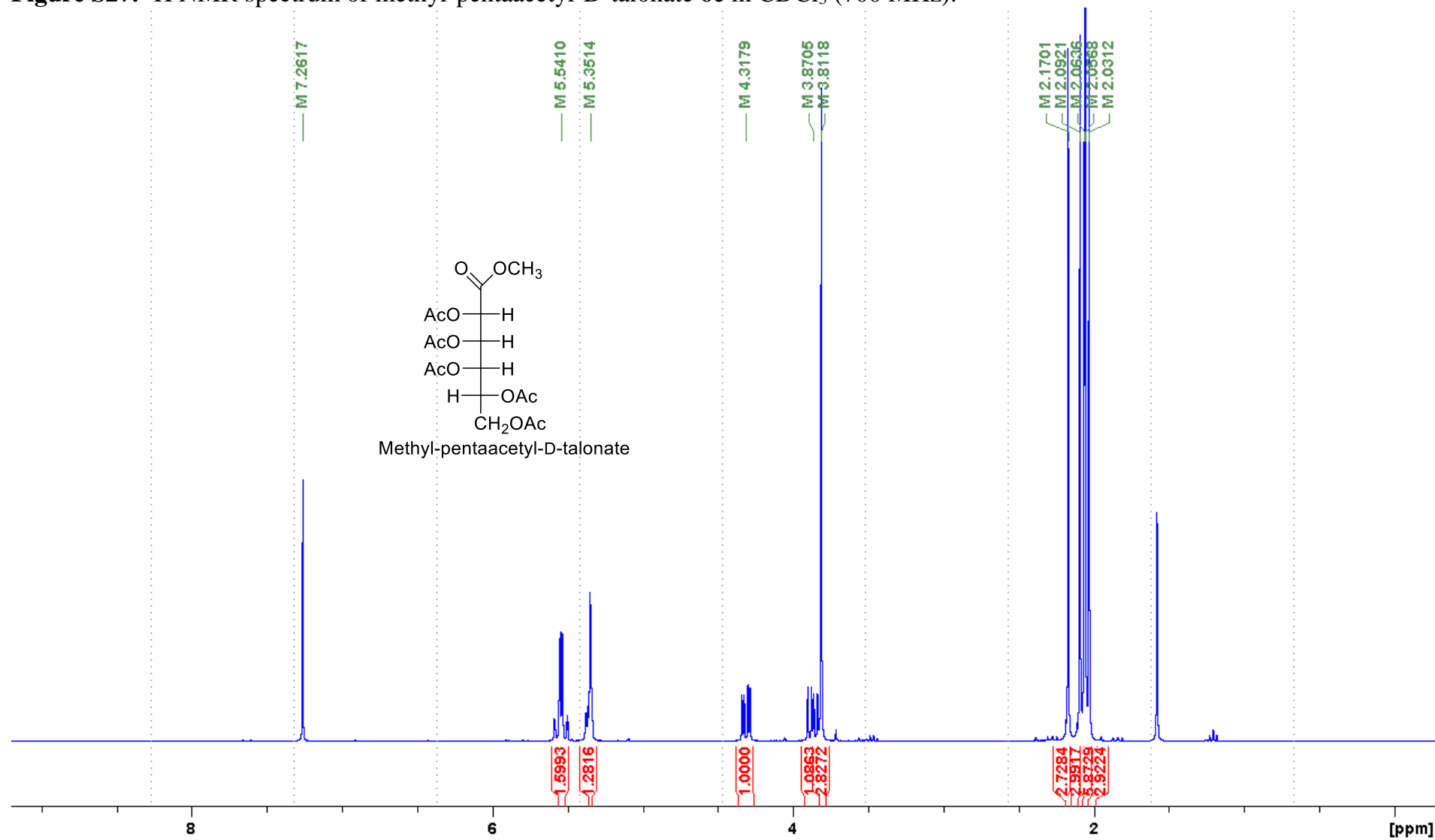


Figure S28. ^{13}C NMR spectrum of methyl-pentaacetyl-D-talonate **6e** in CDCl_3 (175 MHz).

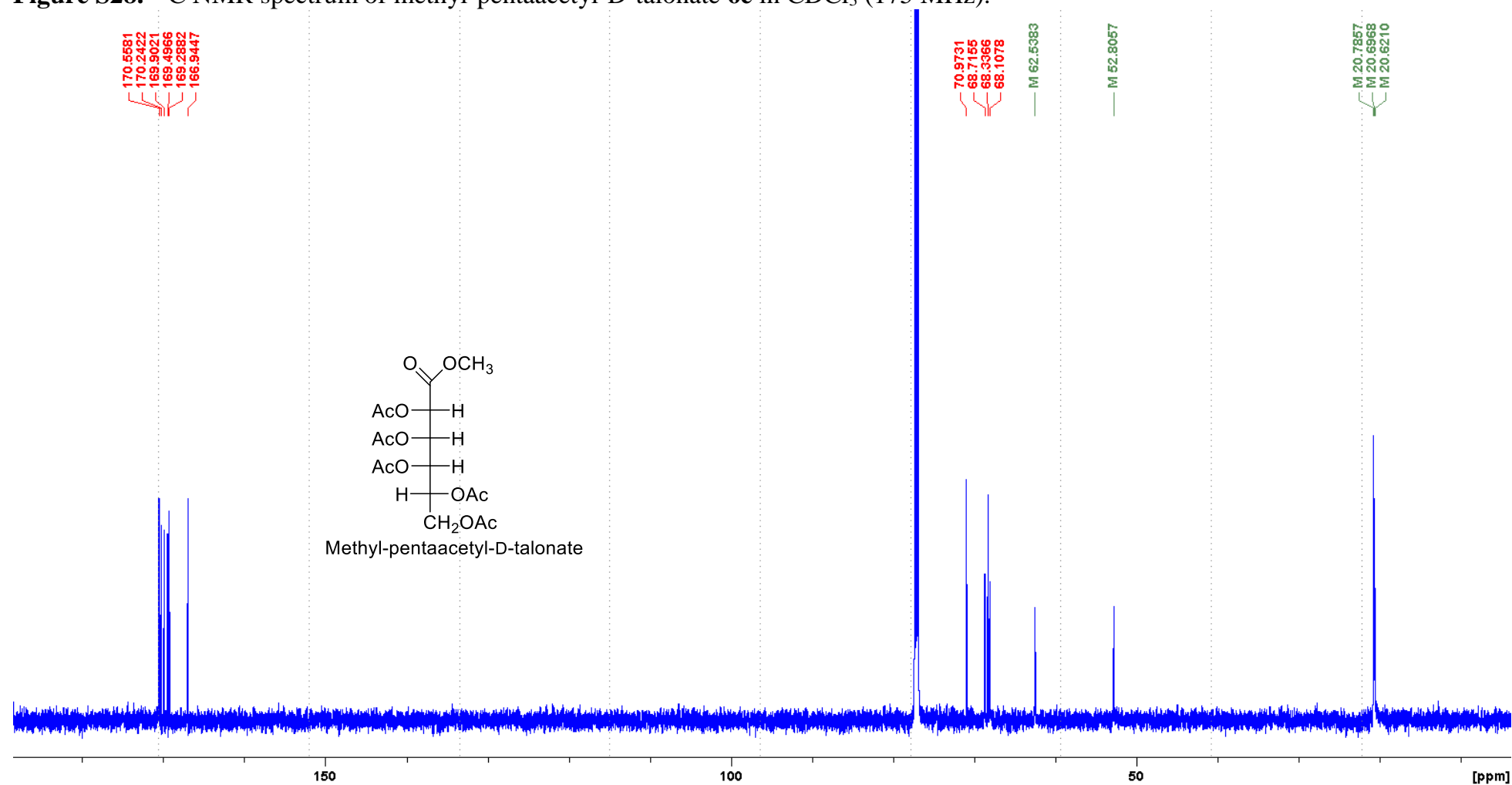


Figure S29. ^1H NMR spectrum of methyl-pentaacetyl-L-idonate **6f** in CDCl_3 (500 MHz).

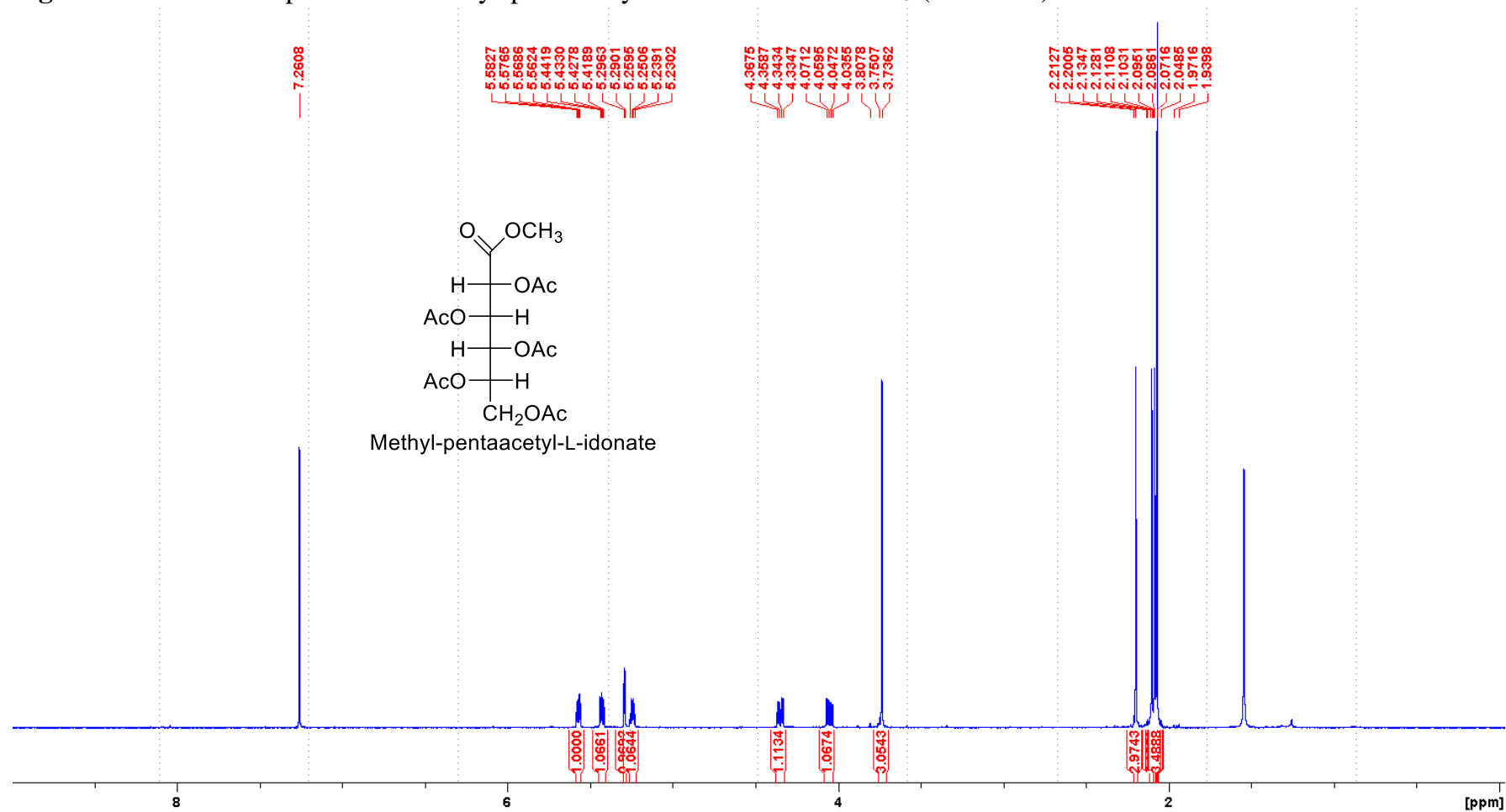


Figure S30. ^{13}C NMR spectrum of methyl-pentaacetyl-L-idonate **6f** in CDCl_3 (175 MHz).

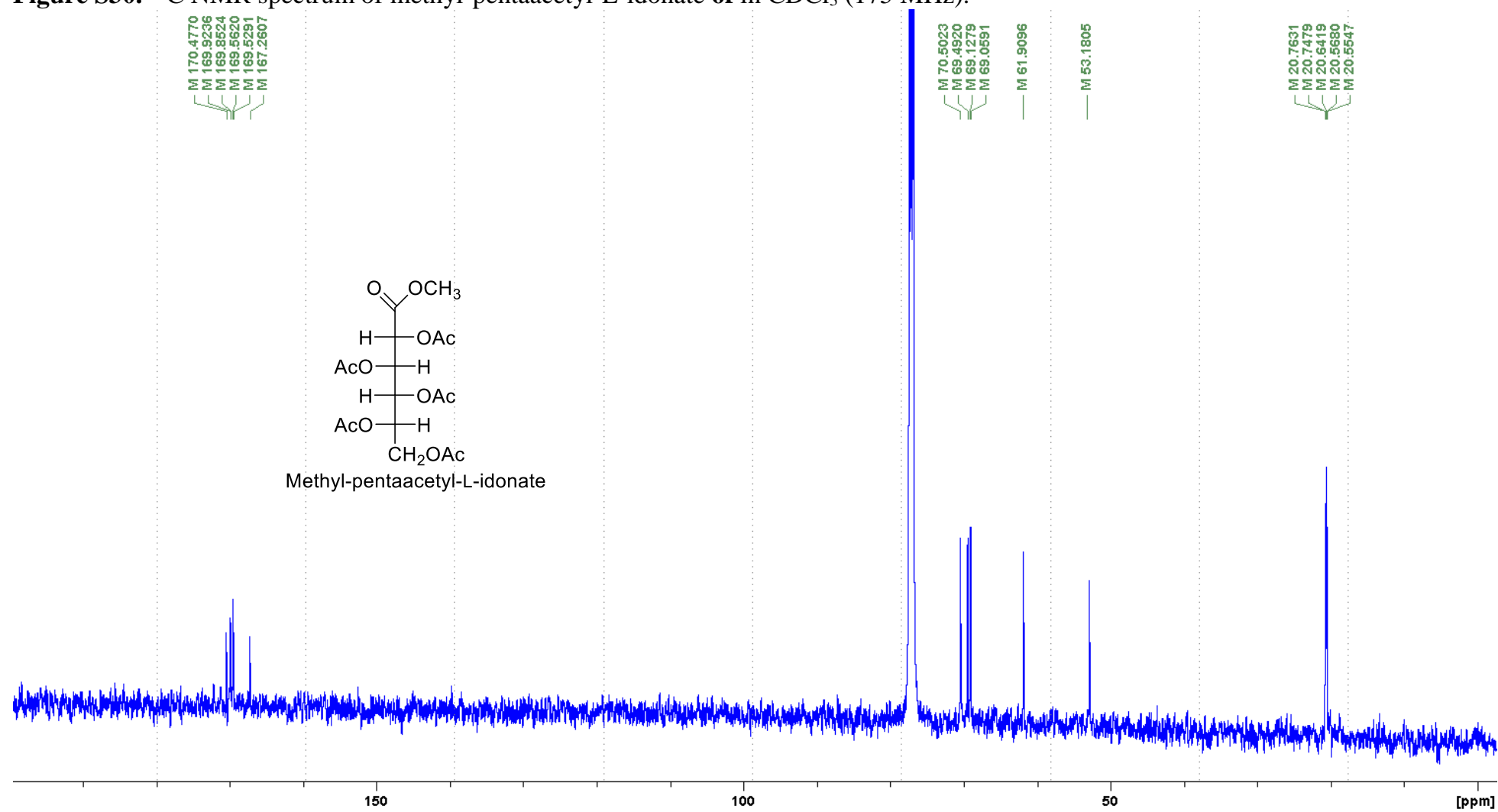
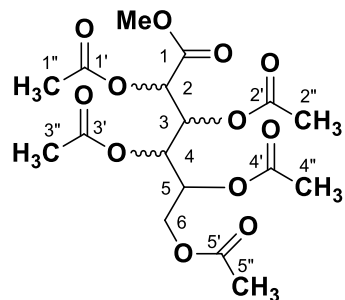


Table S3. NMR data for compounds **2**, and **6a–6f**.



No.	2	6a		6b		6c		6d		6e		6f	
	δ_{H} , mult (<i>J</i> in Hz)	δ_{H} , mult (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult (<i>J</i> in Hz)	δ_{C}	δ_{H} , mult (<i>J</i> in Hz)	δ_{C}
1			167.2		167.4		167.6		168.0		166.9		167.2
2	5.29 d (3.0)	5.28 d (3.0)	70.5	5.26 d (4.1)	70.9	5.10 d (1.7)	69.4	4.96 d (8.9)	68.7	5.35 d (1.9)	71.0	5.29 d (3.0)	70.5
3	5.57 dd (3.0, 7.0)	5.56 dd (3.0, 7.0)	69.4	5.59 dd (4.1, 5.1)	68.8	5.54 dd (1.7, 10.0)	67.9	5.49 dd (2.3, 8.9)	68.2	5.52 dd (1.9, 9.8)	68.7	5.57 dd (3.0, 7.0)	69.4
4	5.43 dd (4.5, 7.0)	5.42 dd (4.5, 7.0)	69.1	5.47 dd (5.0, 6.5)	69.4	5.45 dd (1.9, 10.0)	67.8	5.53 dd (2.3, 9.1)	67.8	5.56 dd (2.0, 9.8)	68.1	5.43 dd (4.5, 7.0)	69.1
5	5.25 m	5.24 m	69.0	4.08 m	68.7	5.33 m	67.7	5.17 m	67.9	5.36 m	68.3	5.25 m	69.0
6a	4.35 dd (4.3, 12.0)	4.34 dd (4.3, 12.0)	61.9	4.12 dd (5.5, 12.2)	61.6	3.89 dd (7.4, 11.6)	62.1	4.23 dd (2.7, 12.5)	62.1	4.31 dd (4.5, 11.8)	62.5	4.35 dd (4.3, 12.0)	61.9
6b	4.05 dd (5.8, 12.0)	4.04 dd (5.8, 12.0)		4.30 dd (3.9, 12.2)		4.27 dd (5.3, 11.6)		4.10 dd (5.2, 12.5)		3.88 dd (7.7, 11.8)		4.05 dd (5.8, 12.0)	
MeO-	3.74 s	3.73 s	52.9	3.73 s	52.9	3.71 s	52.9	3.71 s	53.0	3.81 s	52.8	3.74 s	52.9

1'			170.4		170.6		170.5		170.7		170.6		170.4
2'			169.9		170.0		170.3		169.9		170.2		169.9
3'			169.8		169.8		170.3		169.9		169.9		169.8
4'			169.5		169.7		169.6		169.7		169.5		169.5
5'			169.5		169.7		169.4		169.6		169.3		169.5
1"	2.20 s	2.19 s	20.5	2.18 s	20.5	2.18 s	20.5	2.14 s	20.5	2.16 s	20.6	2.20 s	20.6
2"	2.10 s	2.09 s	20.5	2.10 s	20.5	2.11 s	20.5	2.10 s	20.5	2.09 s	20.7	2.10 s	20.6
3"	2.09 s	2.08 s	20.6	2.08 s	20.8	2.09 s	20.6	2.08 s	20.7	2.06 s	20.8	2.09 s	20.7
4"	2.07 s	2.06 s	20.7	2.06 s	20.8	2.05 s	20.7	2.06 s	20.8	2.05 s	20.8	2.07 s	20.8
5"	2.07 s	2.06 s	20.8	2.05 s	20.9	2.03 s	20.8	2.05 s	20.9	2.03 s	20.8	2.07 s	20.8

Figure S31. GC analysis for methyl-pentaacetyl-L-idonate **2**.

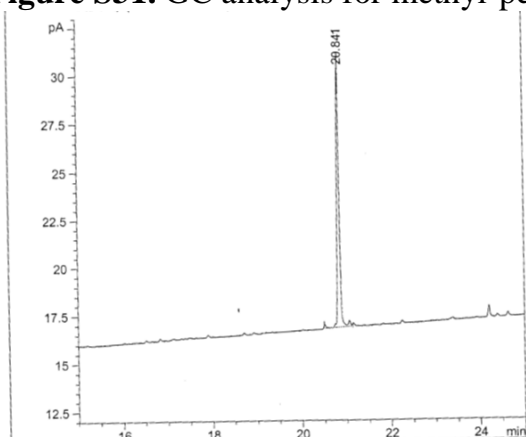


Figure S32. GC analysis for methyl-pentaacetyl-D-idonate **6a**.

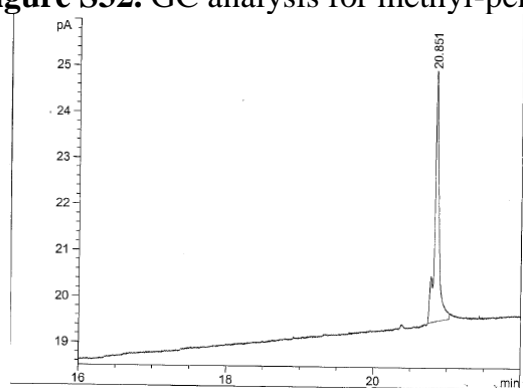


Figure S33. GC analysis with co-injected of methyl-pentaacetyl-L-idonate **2** and methyl-pentaacetyl-D-idonate **6a**. The coincidence of the retention times of methyl-pentaacetyl-L-idonate **2** and methyl-pentaacetyl-D-idonate **6a** and the increased peak intensity when they were co-injected.

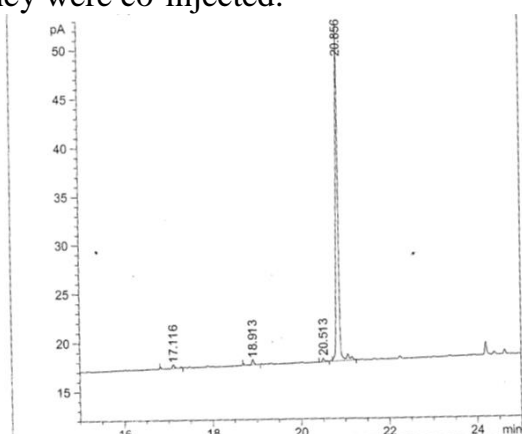


Figure S34. GC analysis with co-injected of methyl-pentaacetyl-L-idonate **2** and methyl-pentaacetyl-D-gluconate **6b**.

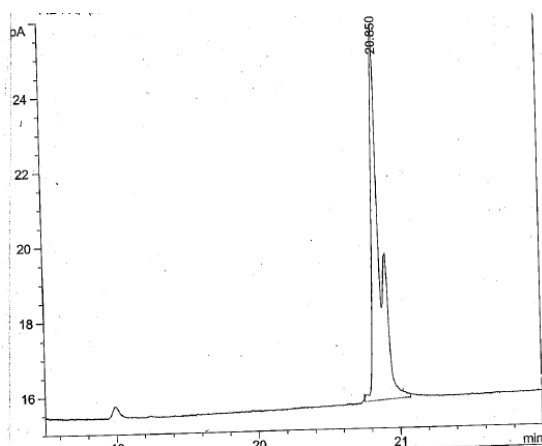


Figure S35. GC analysis with co-injected of methyl-pentaacetyl-L-idonate **2** and methyl-pentaacetyl-D-galactonate **6c**.

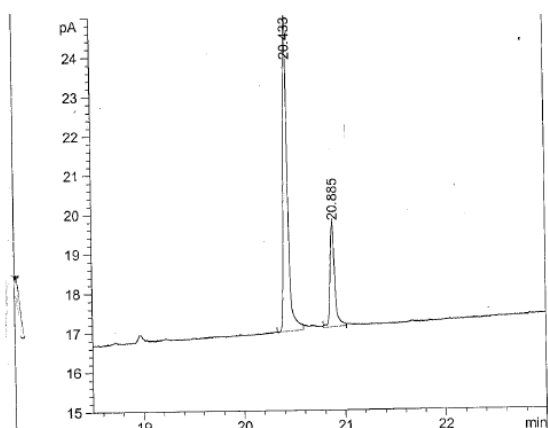


Figure S36. GC analysis with co-injected of methyl-pentaacetyl-L-idonate **2** and methyl-pentaacetyl-D-mannonate **6d**.

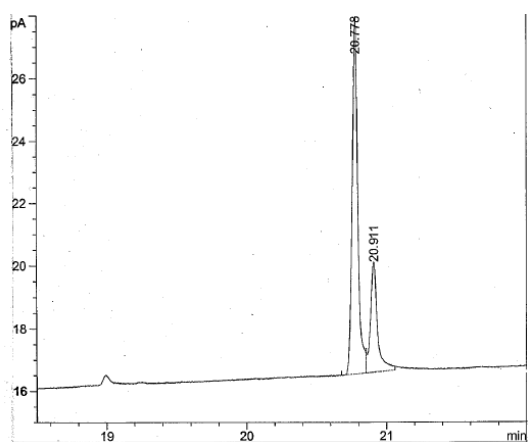


Figure S37. GC analysis with co-injected of methyl-pentaacetyl-L-idonate **2** and methyl-pentaacetyl-D-talonate **6e**.

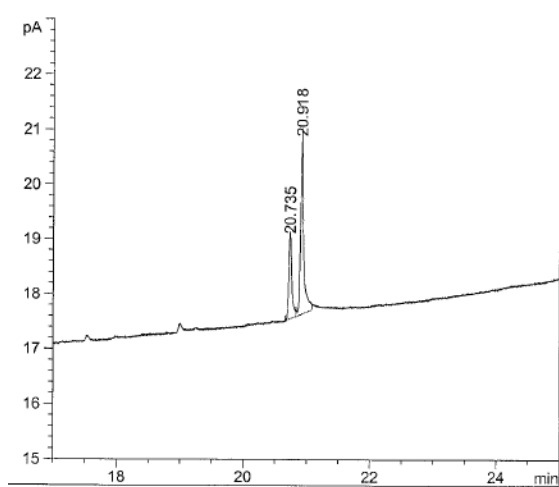


Figure S38. Fragments of GC chromatograms for: **a** – pentaacetate of (*S*)-2-butyl ester of **2**; **b** – pentaacetate of (*S*)-2-butyl ester of L-idonate; **c** – pentaacetate of (*S*)-2-butyl ester of D-idonate.

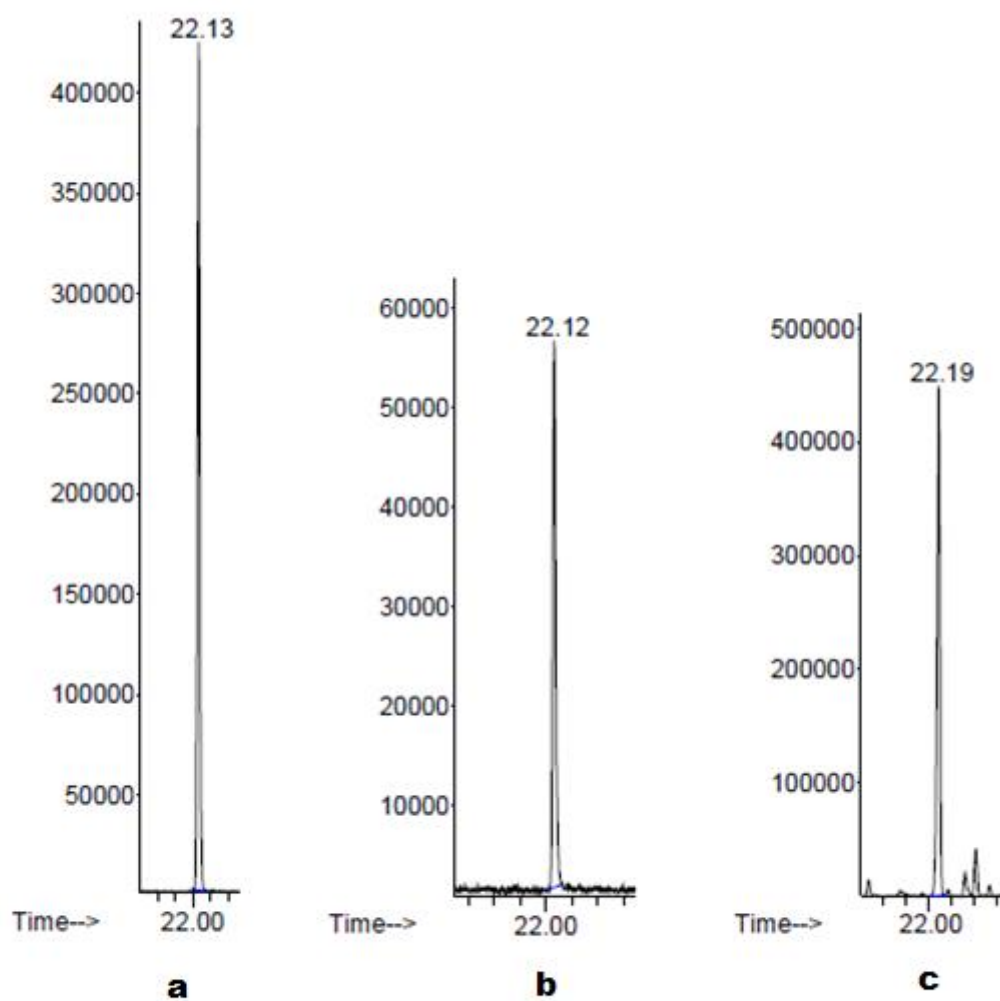
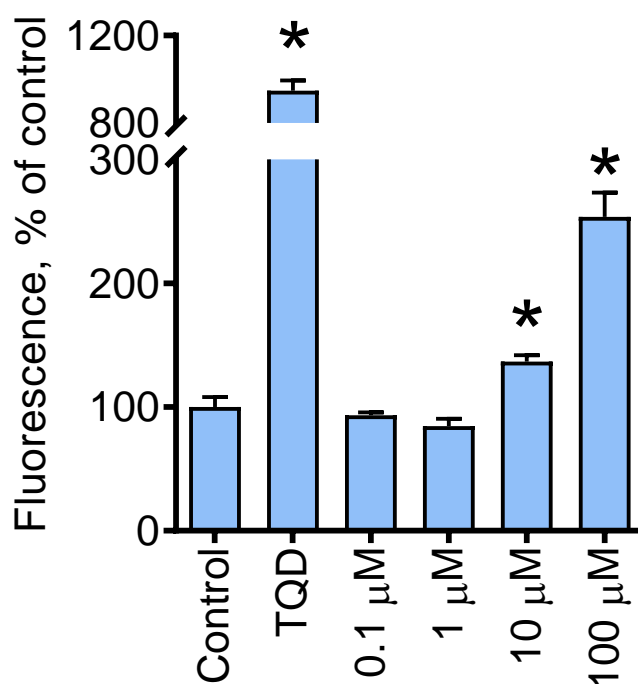


Figure S39. Effect of stonikacidin A (**1**) on p-glycoprotein activity.



PC3-DR cells were treated with **1** for 30 min followed by incubation with calcein-AM. Increased intracellular levels of the calcein dye, measured by fluorescence, indicated inhibition of p-gp. Tariquidar (TQD, 50 nM) was used as a positive control. Statistically significant differences from the control are indicated by * ($p < 0.05$, ANOVA test).