Supplementary Material

Application of Appel reaction to the primary alcohol groups of fructooligosaccharides: Synthesis of 6,6′,6″-trihalogenated 1-kestose derivatives

Zetryana Puteri Tachrim,[a] Tadashi Nakamura,[b] Yasuko Sakihama,[a] Yasuyuki Hashidoko,[a] and Makoto Hashimoto*[a]

[a]Division of Applied Science, Graduate School of Agriculture, Hokkaido University, Sapporo, Japan
[b]Department of Agricultural and Life Science, Obihiro University of Agriculture and Veterinary Medicine, Obihiro, Japan
Email: hasimoto@abs.agr.hokudai.ac.jp

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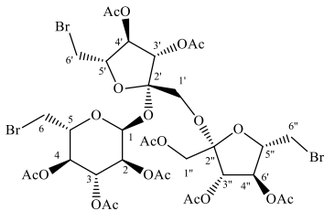
NMR spectrum

1′′,2,3,3′,3′′,4,4′,4′′-Octa-O-acetyl-6,6′,6′′-tribromo-6,6′,6′′-trideoxy-1-kestose (**4**)



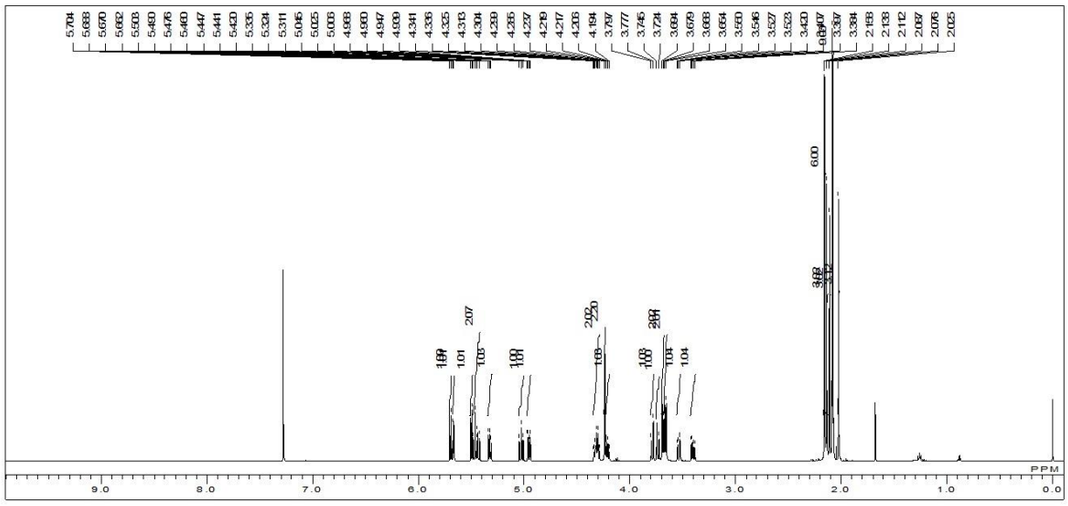


Figure SM-1(a). ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **4**

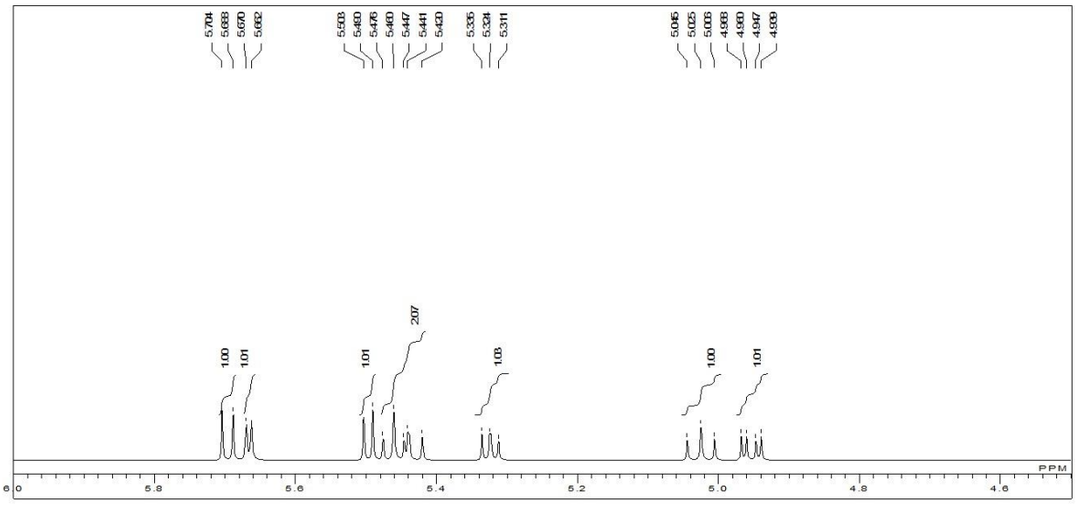


Figure SM-1(b). Selected down field region ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **4**

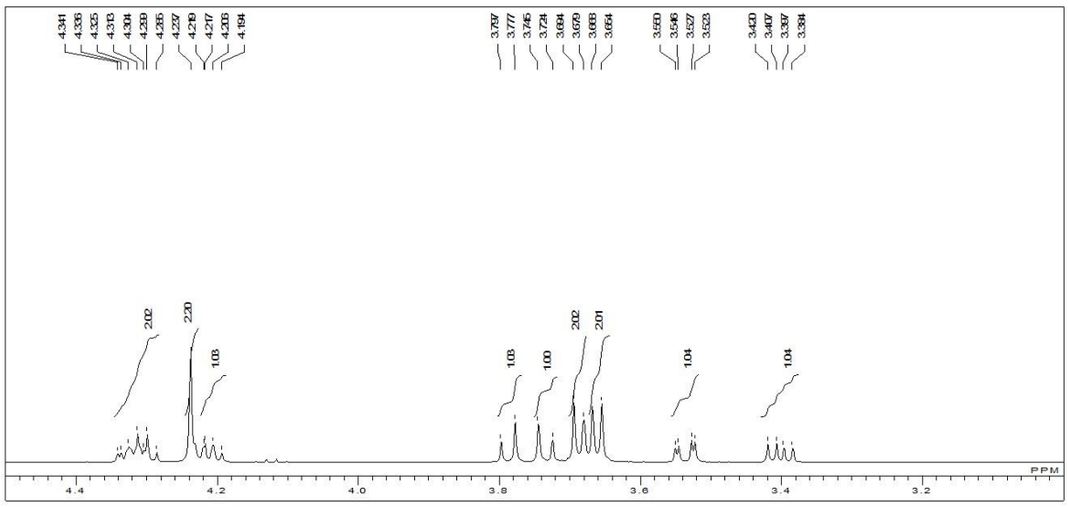


Figure SM-1(c). Selected up field region ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **4**

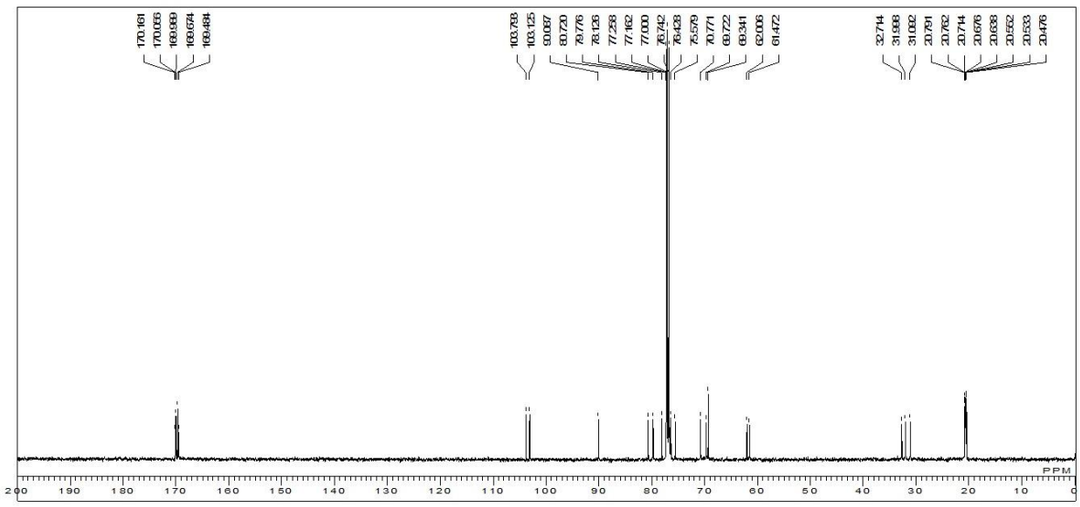


Figure SM-2(a). ^{13}C NMR (125 MHz, $CDCl_3$) of compound **4**

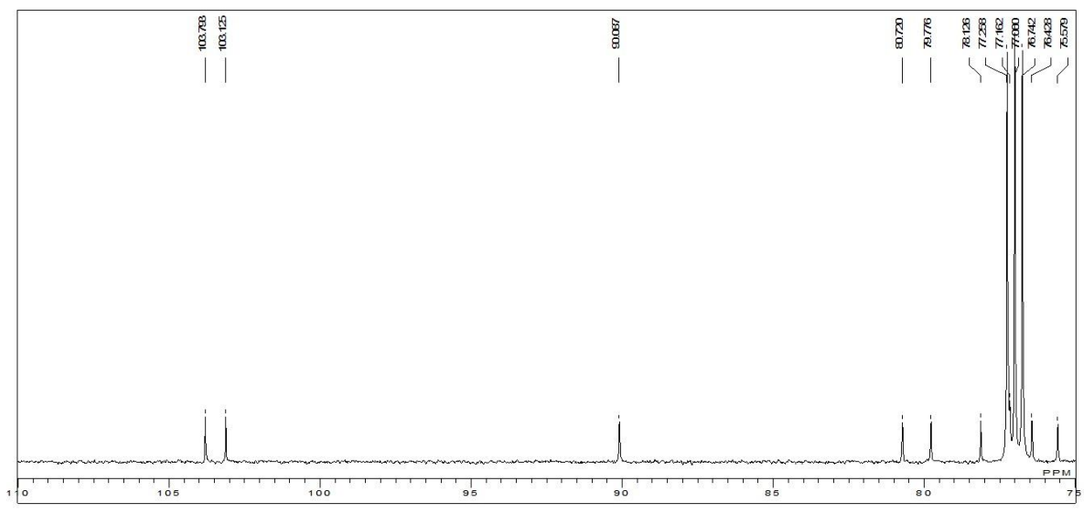


Figure SM-2(b). Selected down field region ^{13}C-NMR (500 MHz, $CDCl_3$) of compound **4**

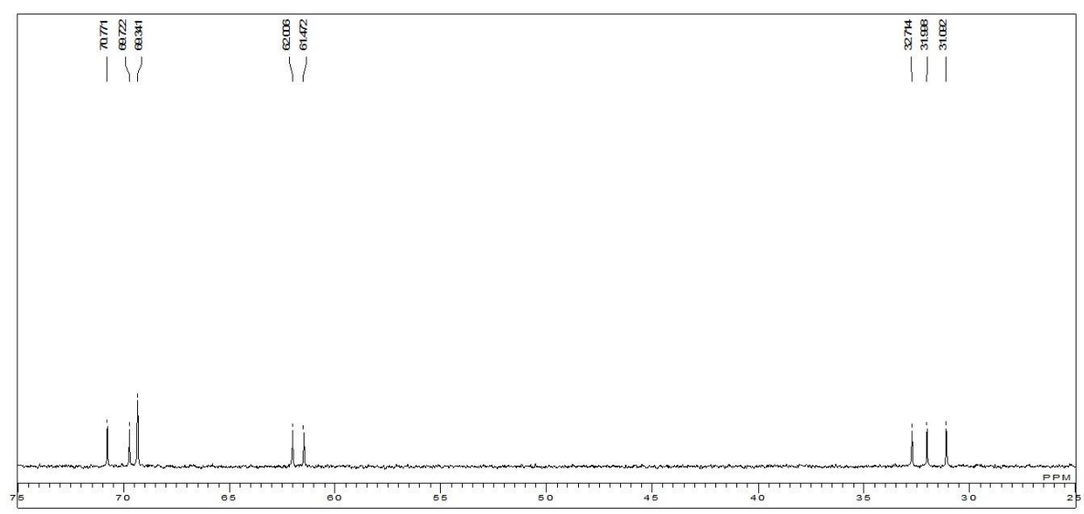


Figure SM-2(c). Selected up field region ^{13}C-NMR (500 MHz, $CDCl_3$) of compound **4**

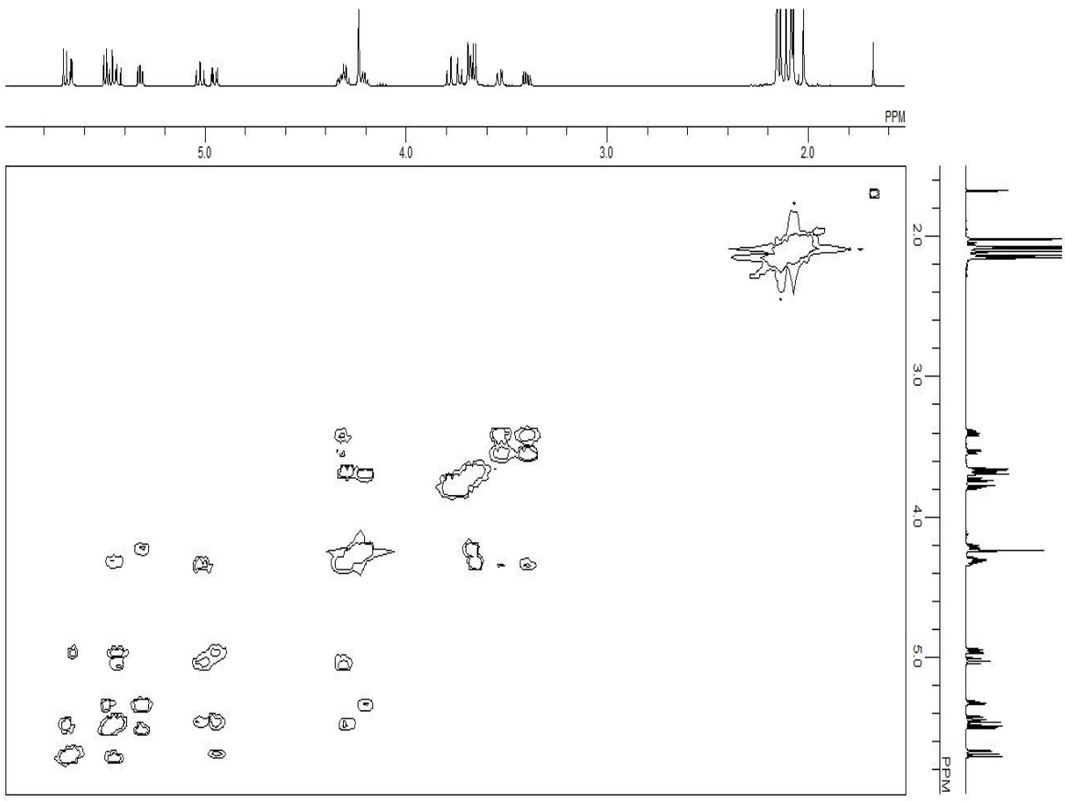


Figure SM-3. ^{1}H-^{1}H COSY 2D-NMR (500 MHz, $CDCl_3$) of compound **4**

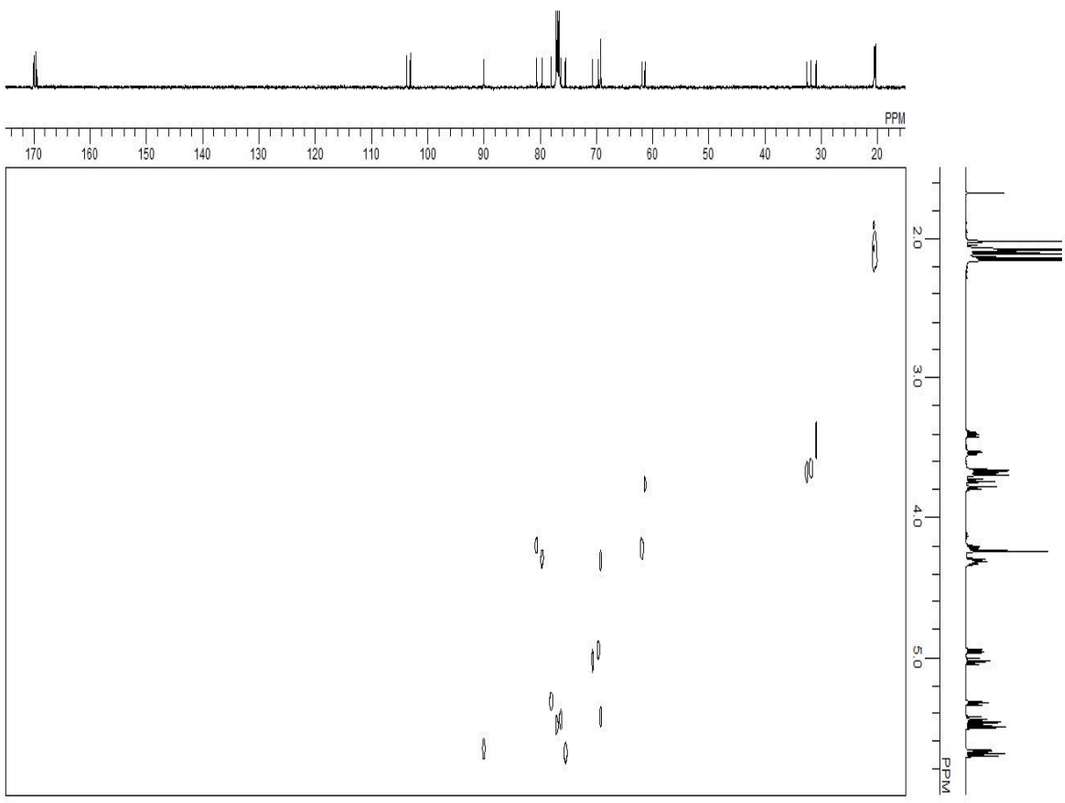


Figure SM-4. ^{13}C-^{1}H HETCOR 2D-NMR (500 MHz, $CDCl_3$) of compound **4**

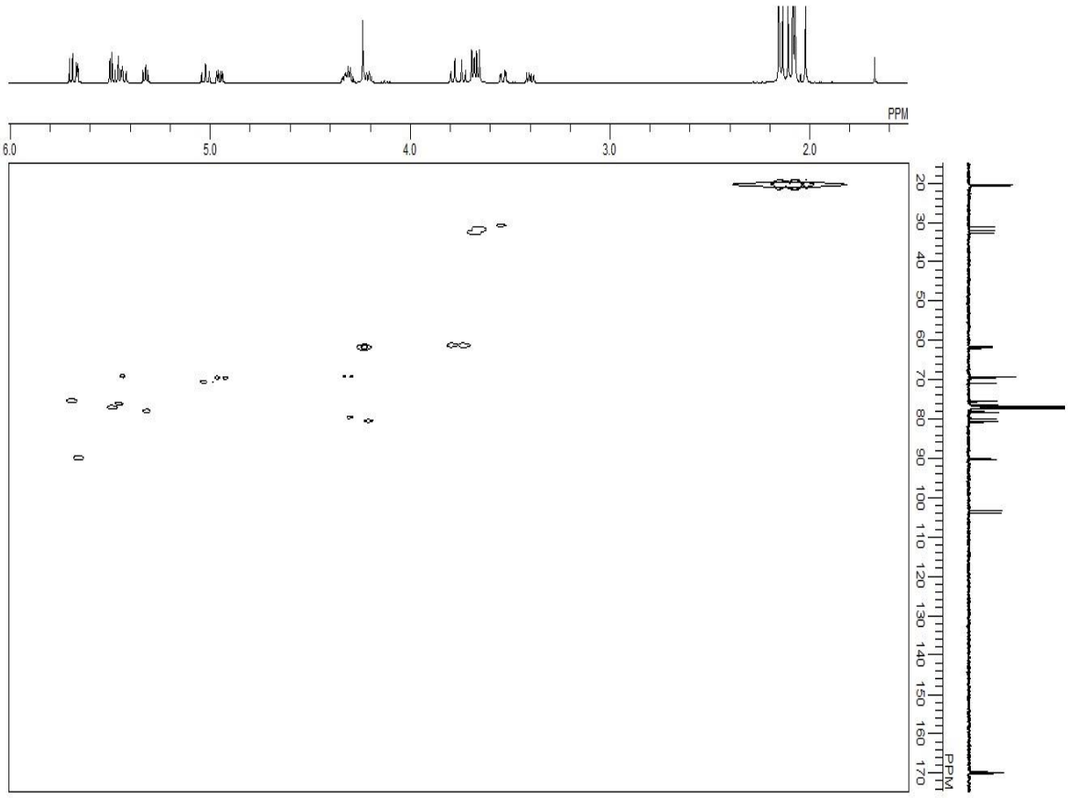


Figure SM-5. ^{1}H-^{13}C HMQC 2D-NMR (500 MHz, $CDCl_3$) of compound **4**

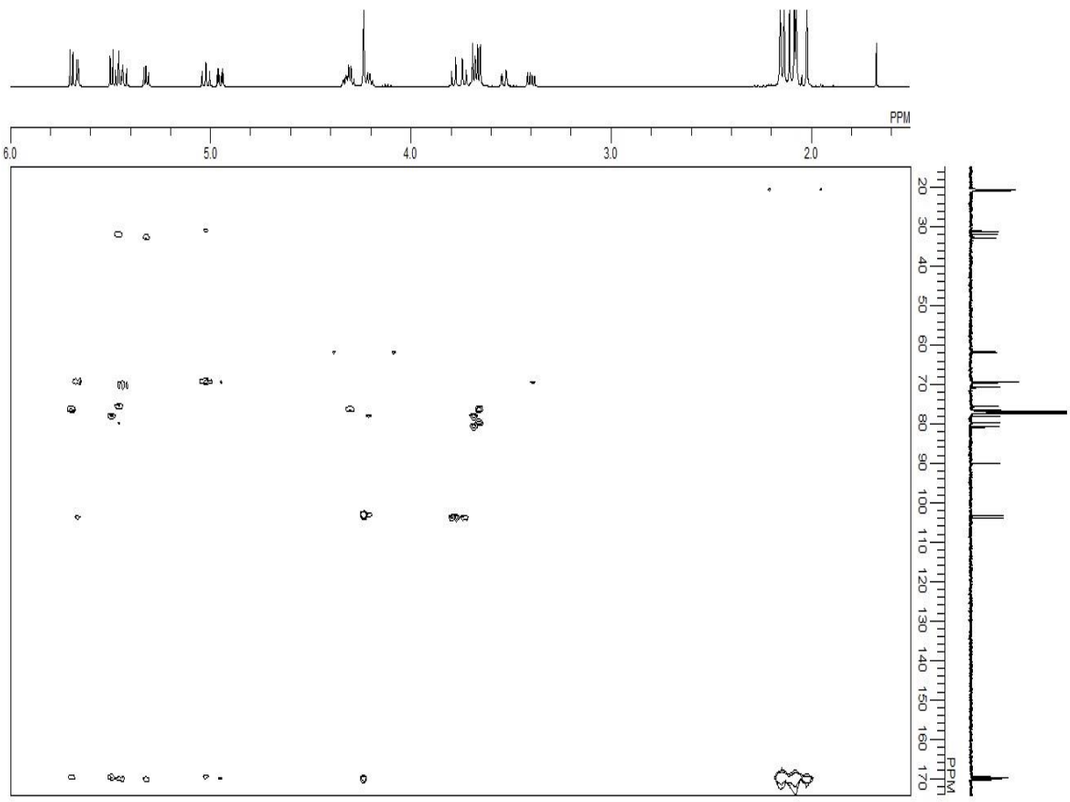


Figure SM-6. ^{1}H-^{13}C HMBC 2D-NMR (500 MHz, $CDCl_3$) of compound **4**

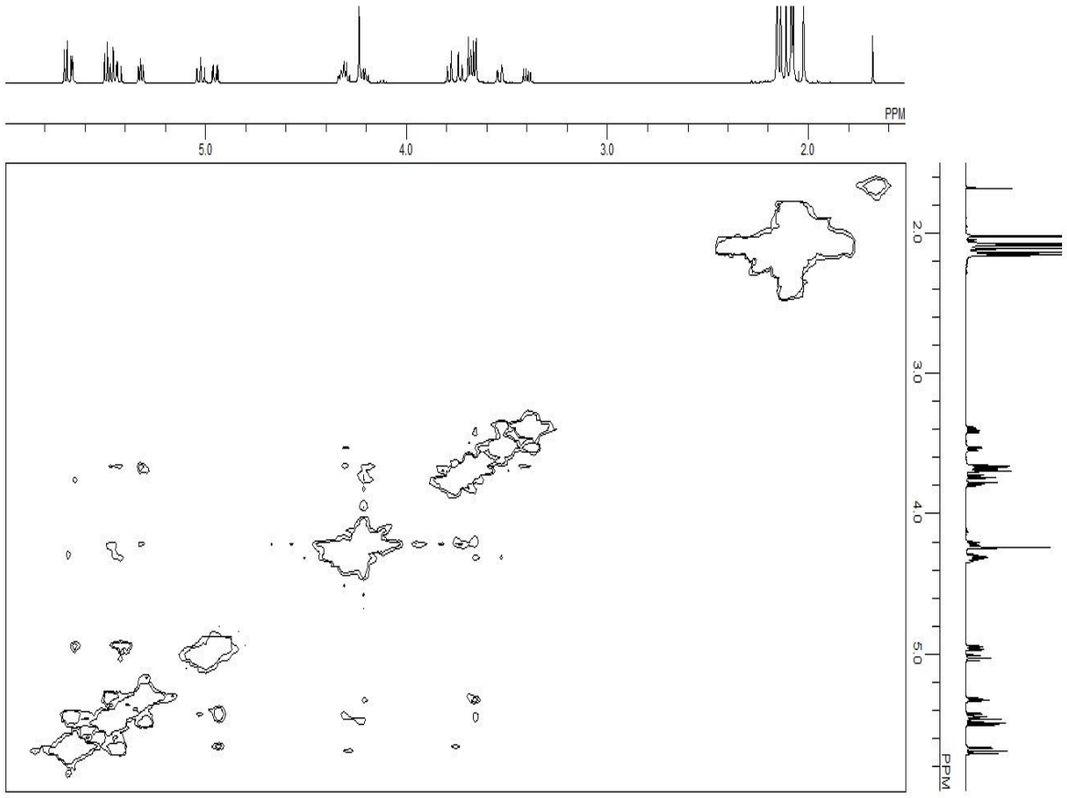


Figure SM-7. ^{1}H-^{1}H NOESY 2D-NMR (500 MHz, $CDCl_3$) of compound **4**

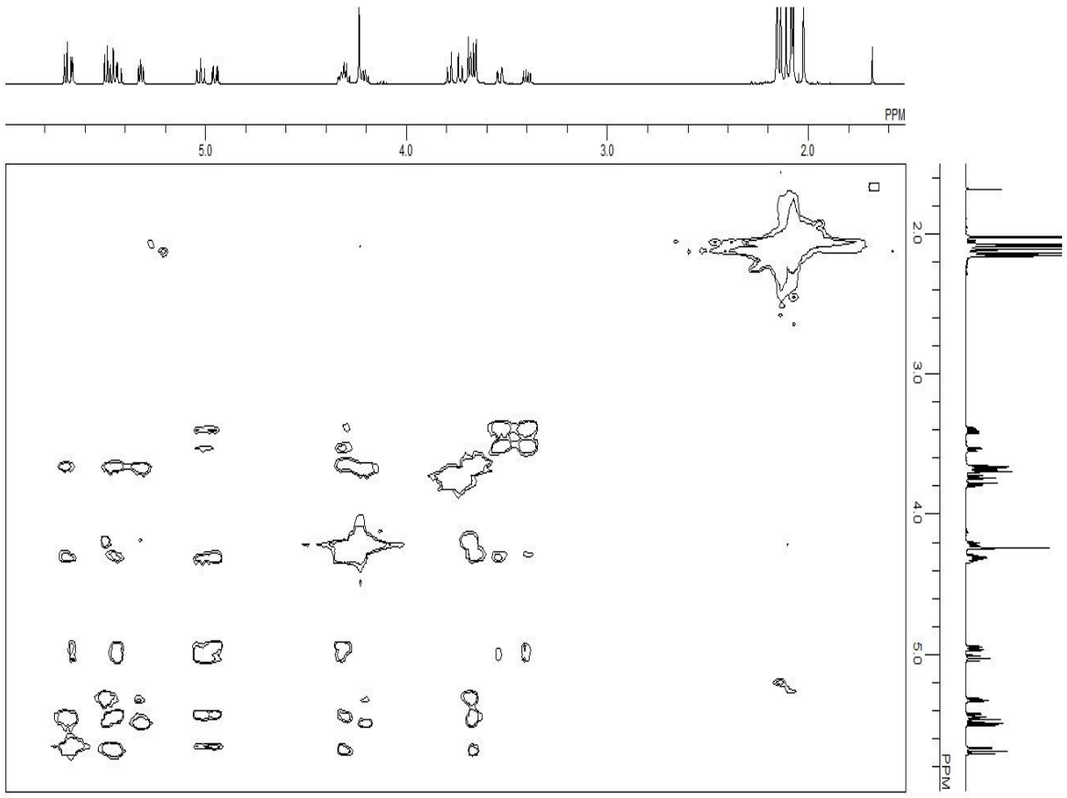
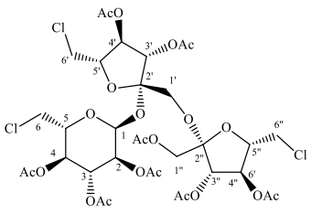


Figure SM-8. ^{1}H-^{1}H TOCSY 2D-NMR (500 MHz, $CDCl_3$) of compound **4**

1′′,2,3,3′,3′′,4,4′,4′′-Octa-O-acetyl-6,6′,6′′-trichloro-6,6′,6′′-trideoxy-1-kestose (**5**)



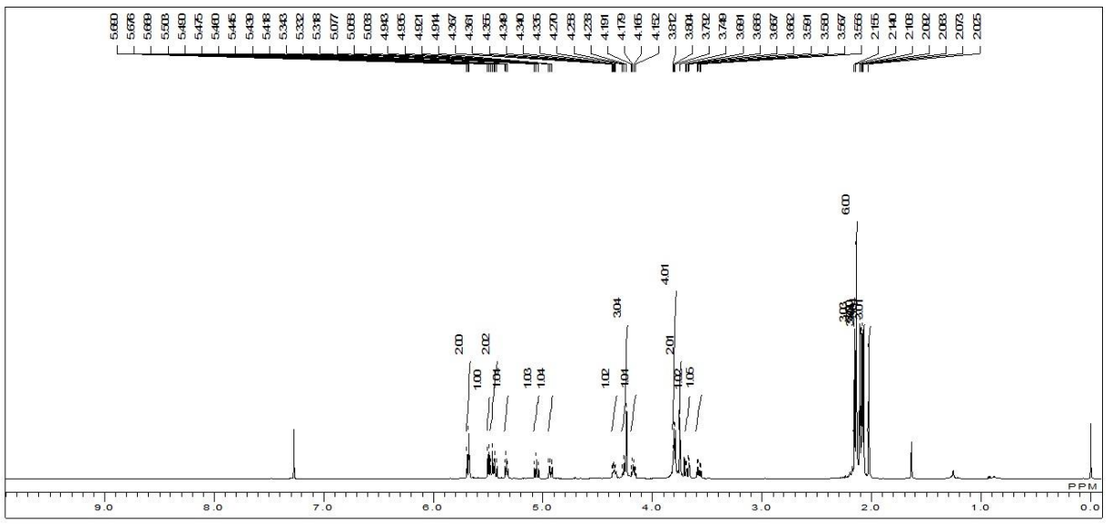


Figure SM-9(a). ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **5**

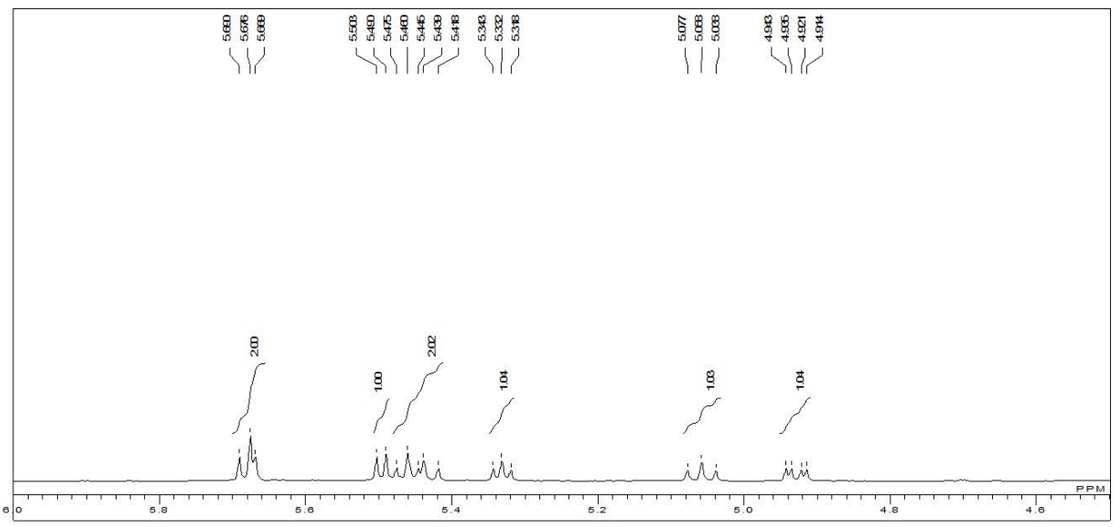


Figure SM-9(b). Selected down field region ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **5**

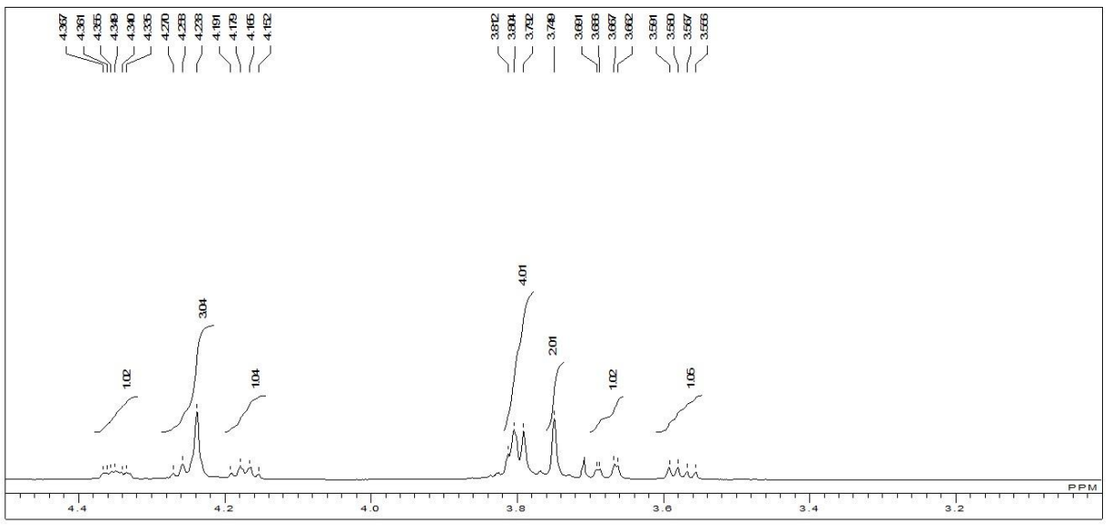


Figure SM-9(c). Selected up field region ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **5**

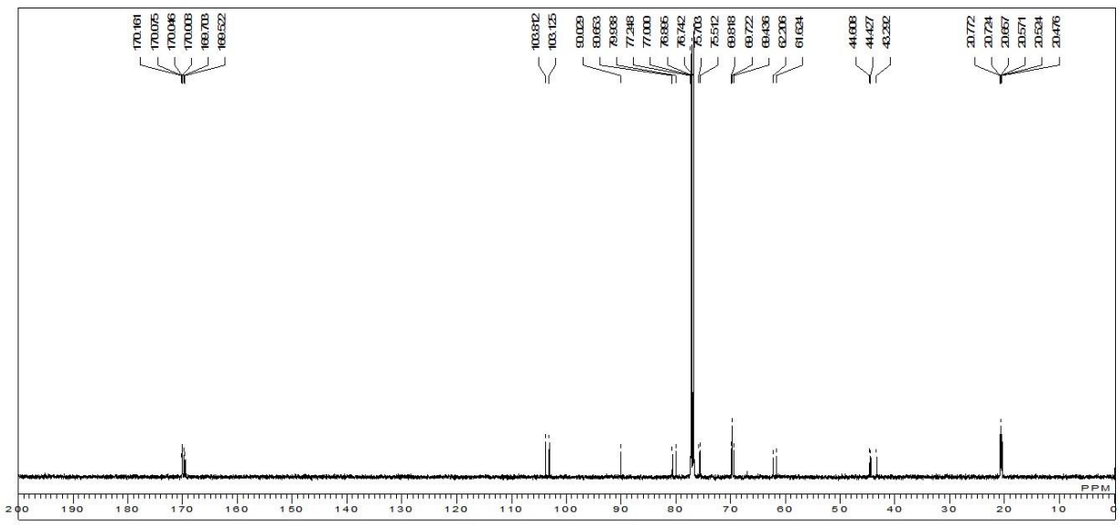


Figure SM-10(a).[13]C NMR (125 MHz, $CDCl_3$) of compound **5**

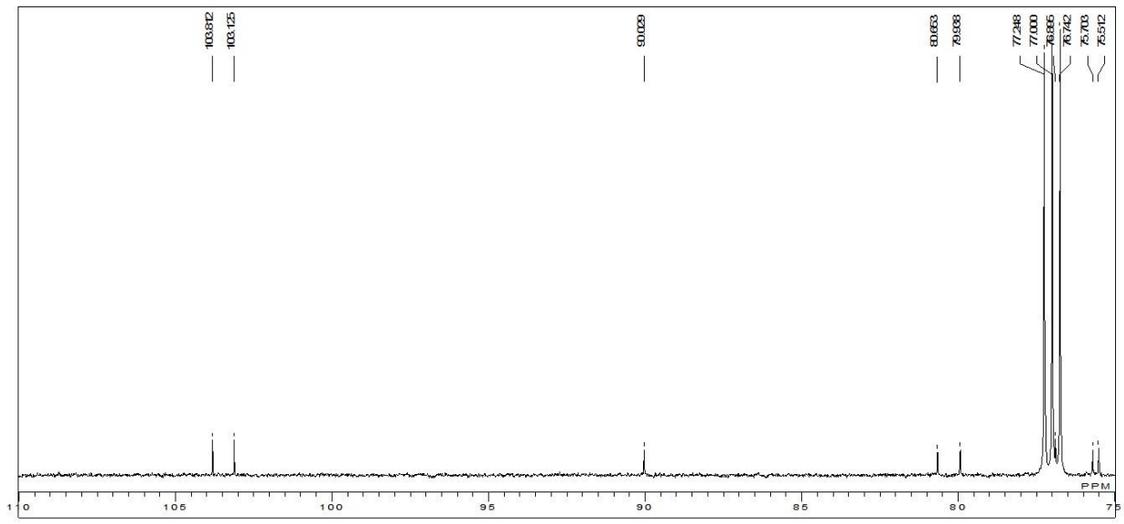


Figure SM-10(b). Selected down field region ^{13}C NMR (125 MHz, $CDCl_3$) of compound **5**

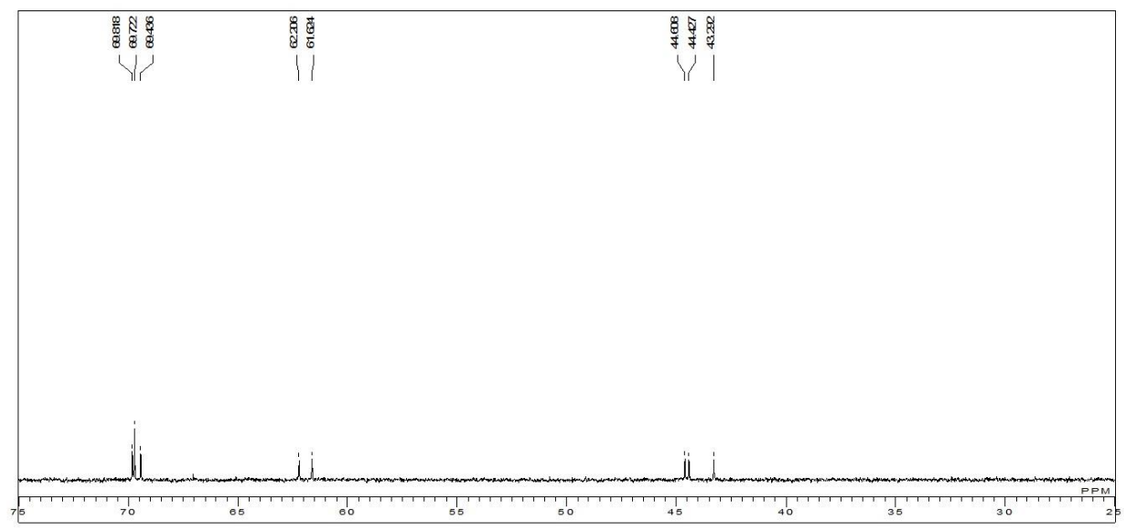


Figure SM-10(c). Selected up field region ^{13}C NMR (125 MHz, $CDCl_3$) of compound **5**

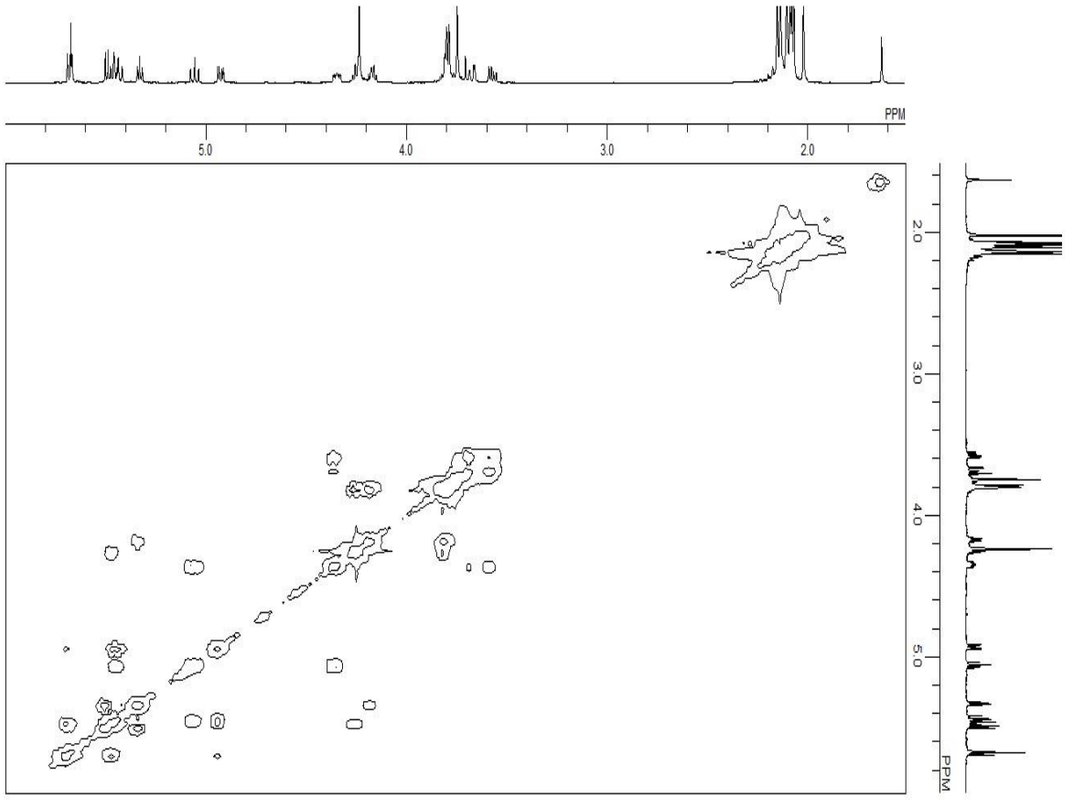


Figure SM-11. ^{1}H-^{1}H COSY 2D-NMR (500 MHz, $CDCl_3$) of compound **5**

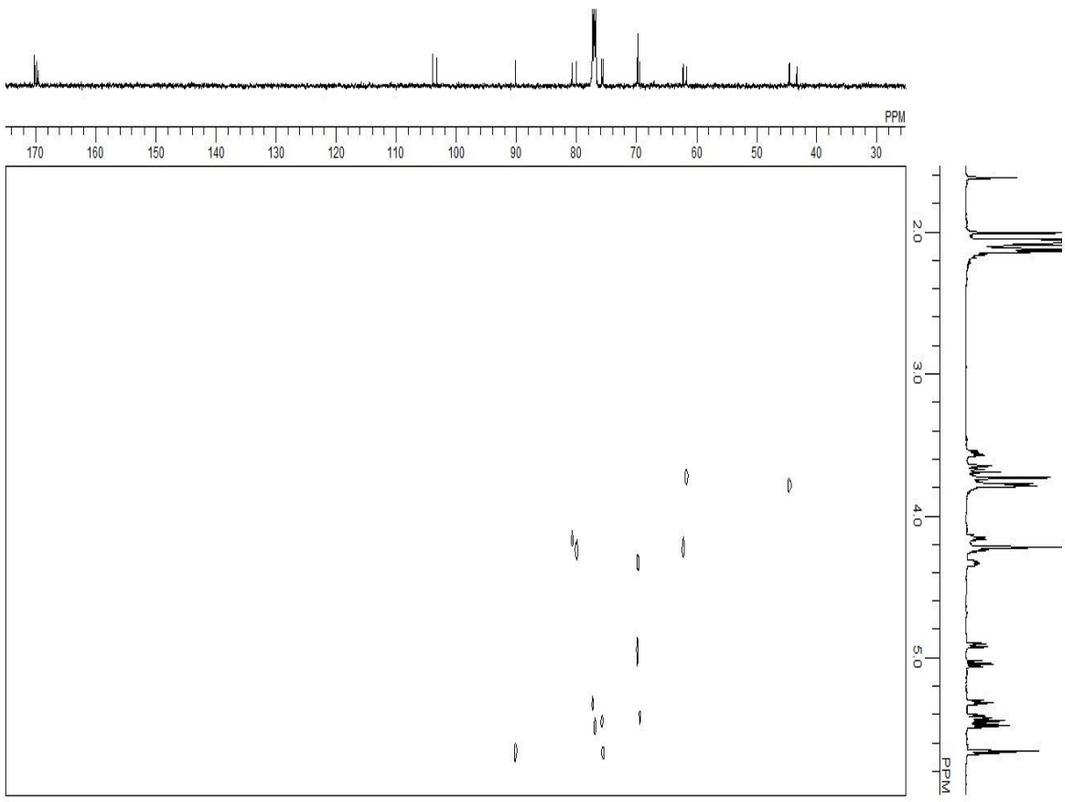


Figure SM-12. ^{13}C-^{1}H HETCOR 2D-NMR (500 MHz, $CDCl_3$) of compound **5**

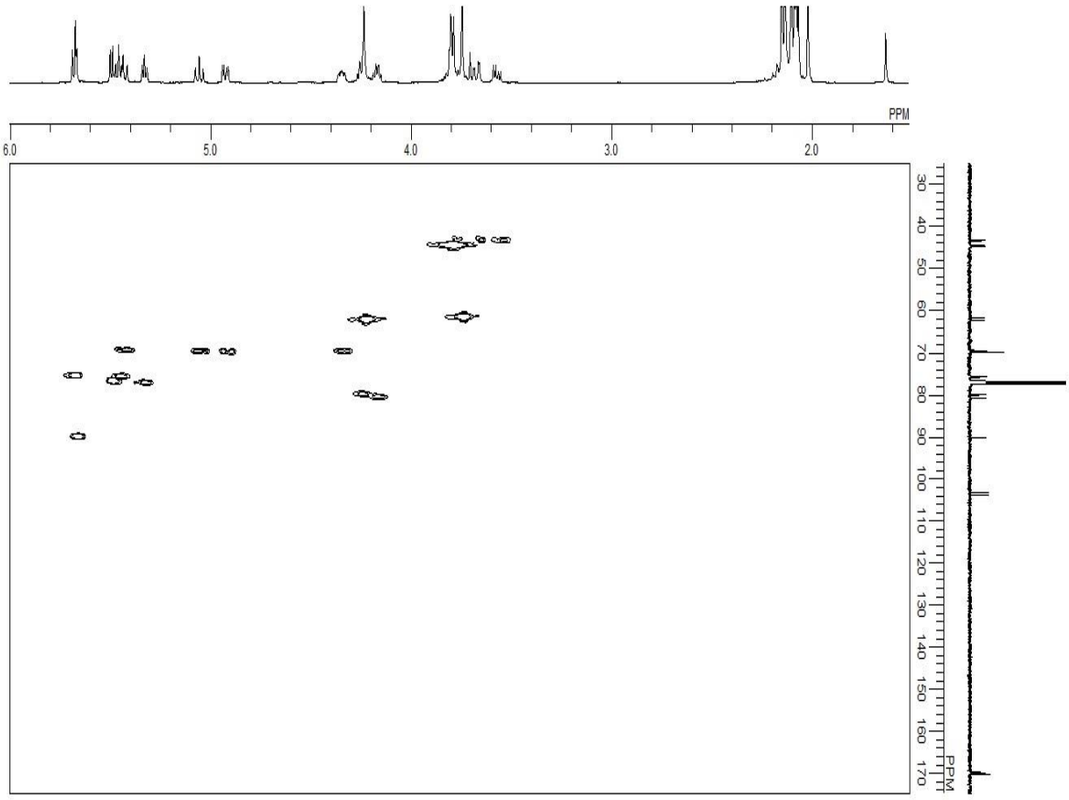


Figure SM-13. ^{1}H-^{13}C HMQC 2D-NMR (500 MHz, $CDCl_3$) of compound **5**

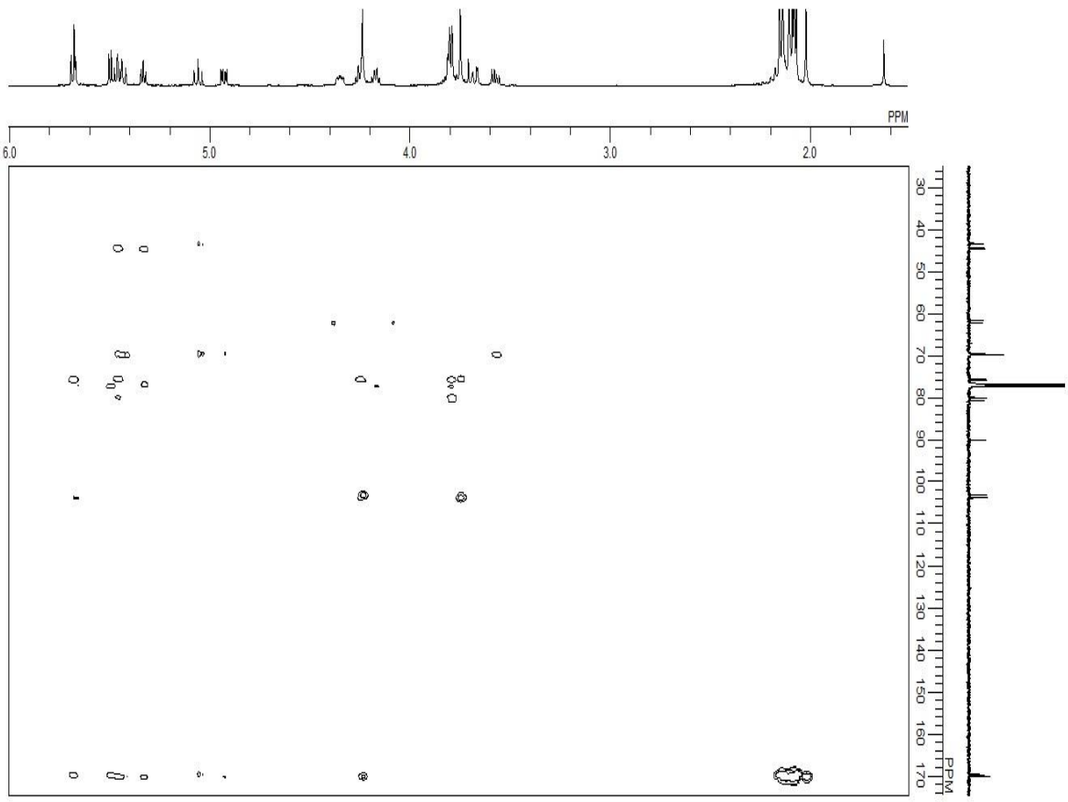


Figure SM-14. ^{1}H-^{13}C HMBC 2D-NMR (500 MHz, $CDCl_3$) of compound **5**

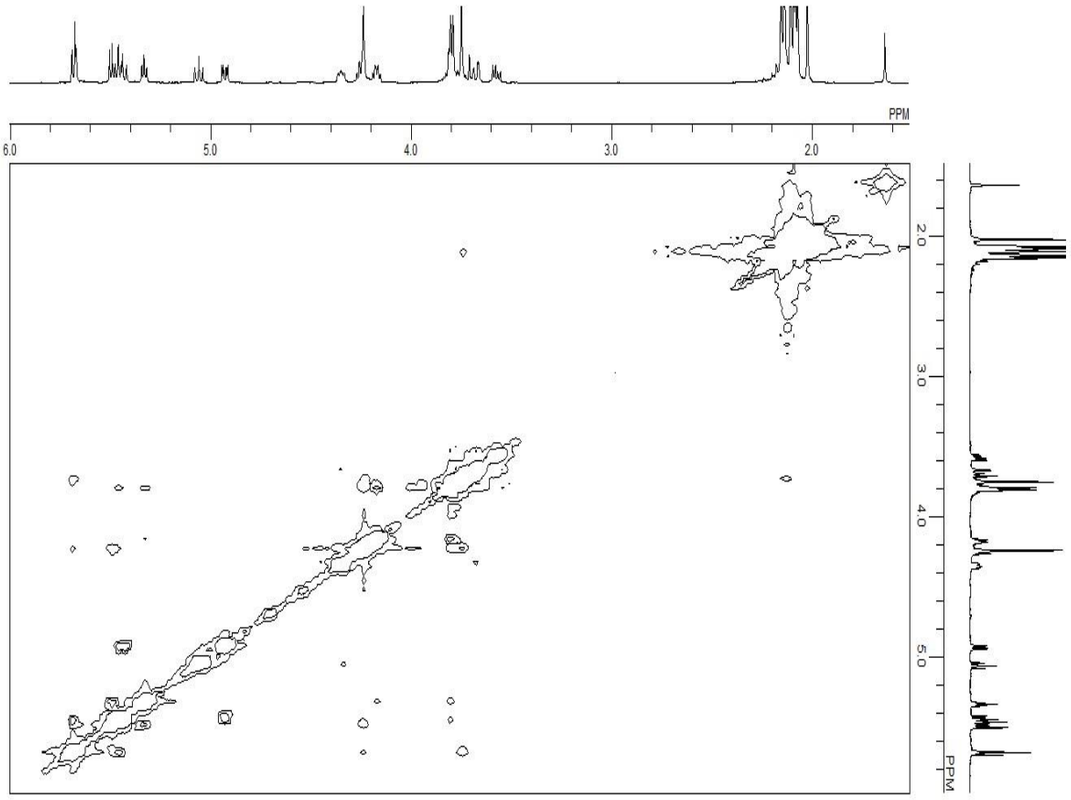


Figure SM-15. ^{1}H-^{1}H NOESY 2D-NMR (500 MHz, $CDCl_3$) of compound **5**

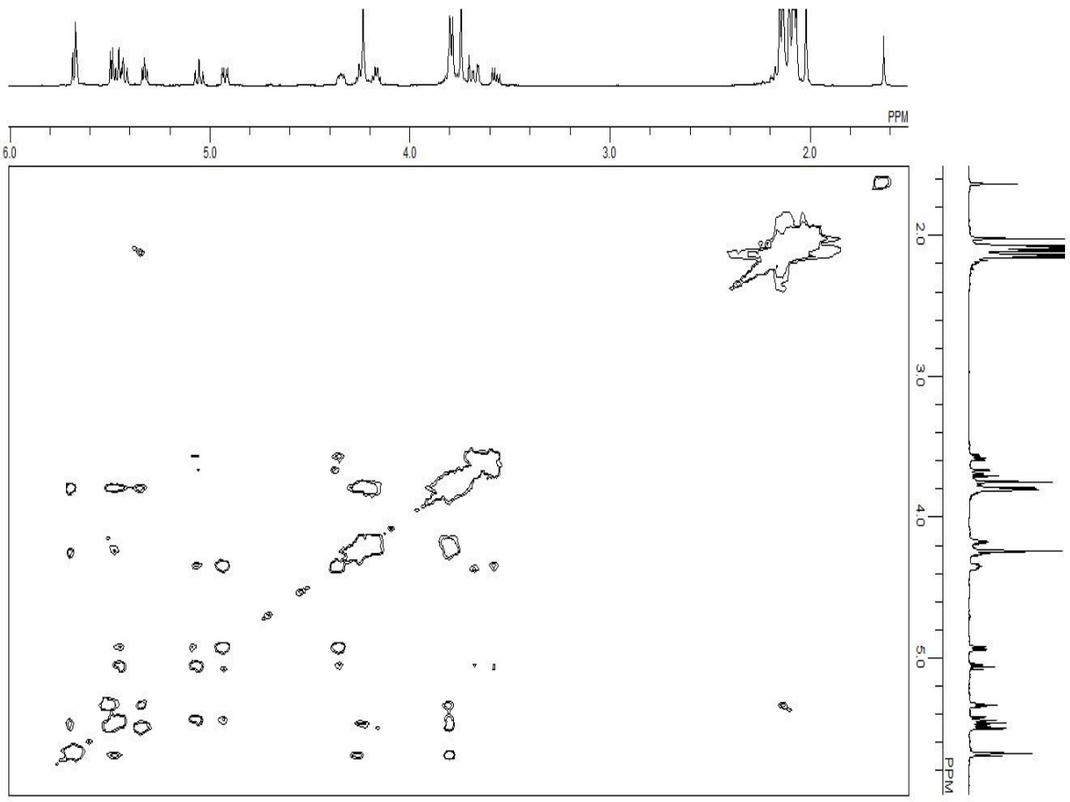
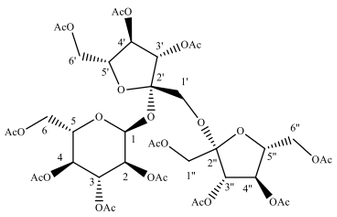


Figure SM-16. ^{1}H-^{1}H TOCSY 2D-NMR (500 MHz, $CDCl_3$) of compound **5**

1′′,2,3,3′,3′′,4,4′,4′′,6,6′,6′′-Undeca-O-acetyl-1-kestose (**3**)



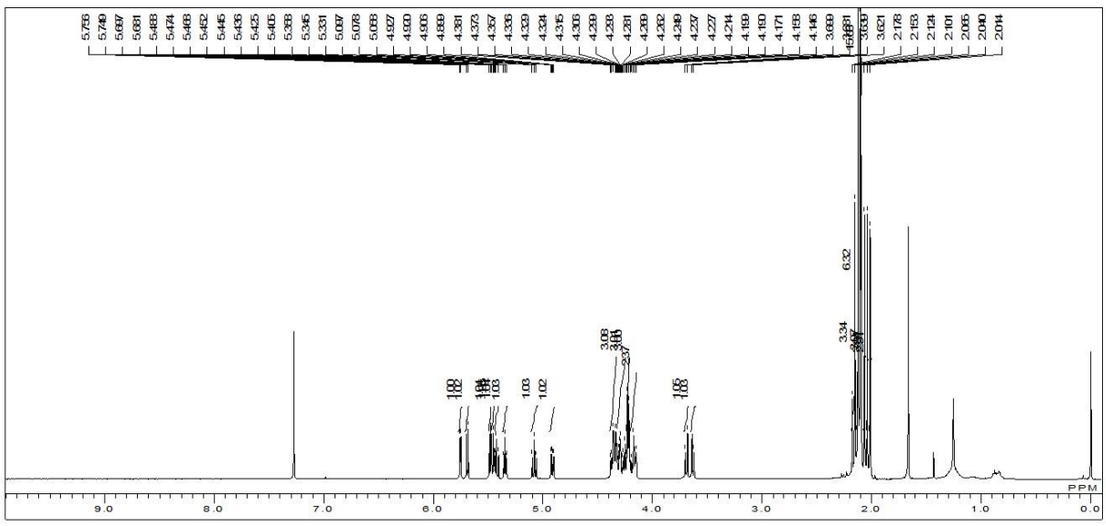


Figure SM-17(a). ^{1}H-NMR (500 MHz, CDCl^{3}) of compound **3**

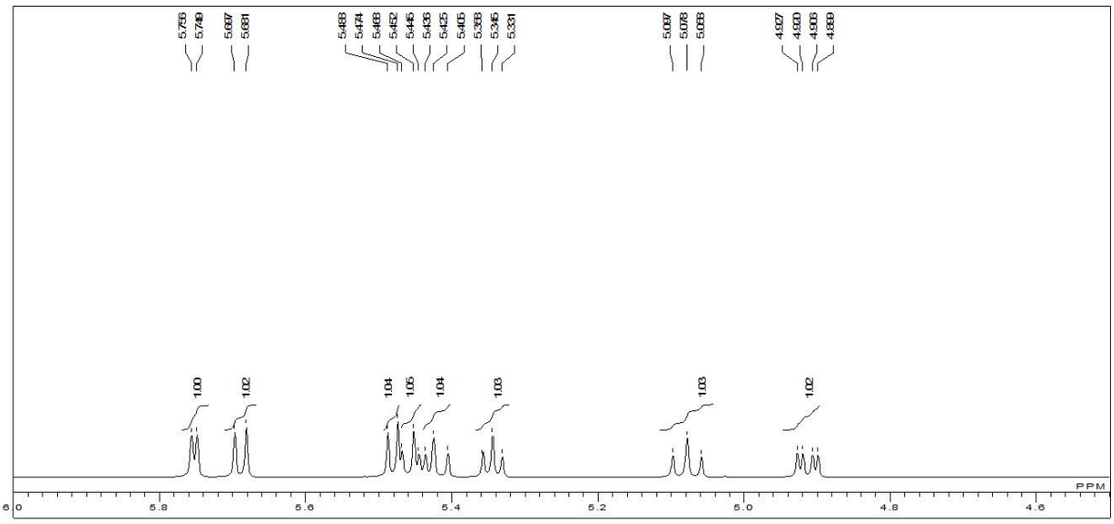


Figure SM-17(b). Selected down field region ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **3**

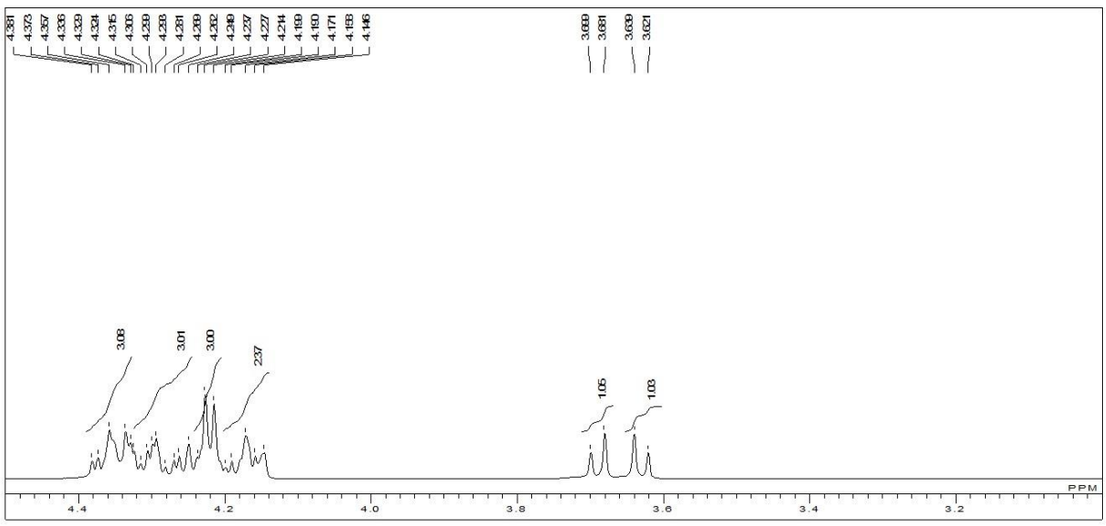


Figure SM-17(c). Selected up filed region ^{1}H-NMR (500 MHz, $CDCl_3$) of compound **3**

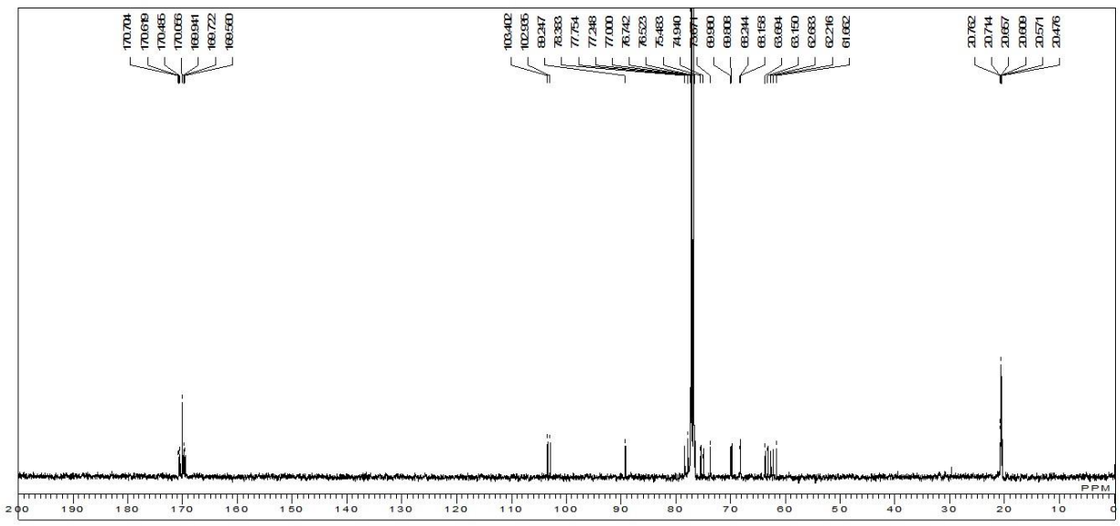


Figure SM-18(a). ^{13}C NMR (125 MHz, $CDCl_3$) of compound **3**

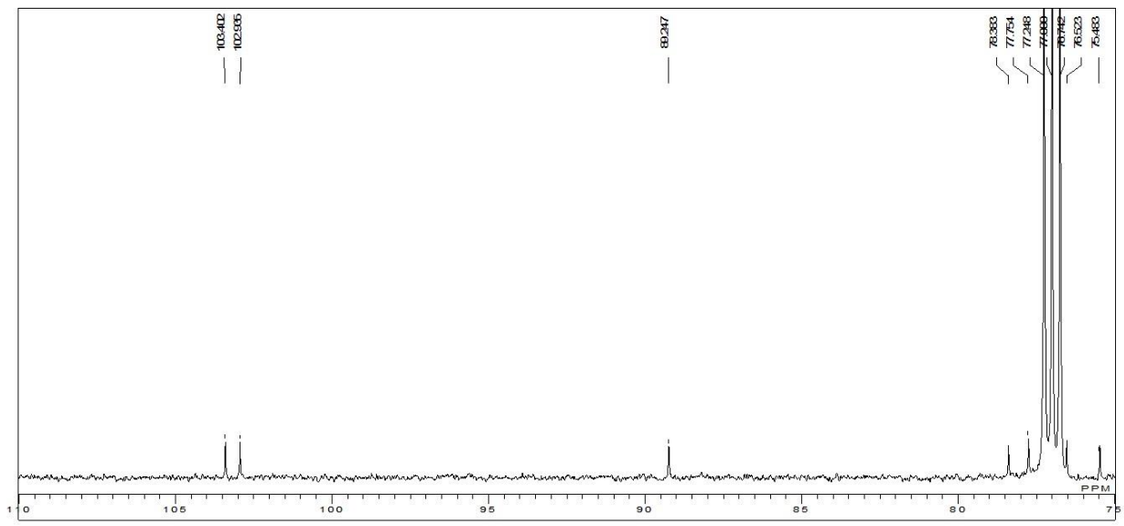


Figure SM-18(b). Selected down field region ^{13}C-NMR (500 MHz, $CDCl_3$) of compound **3**

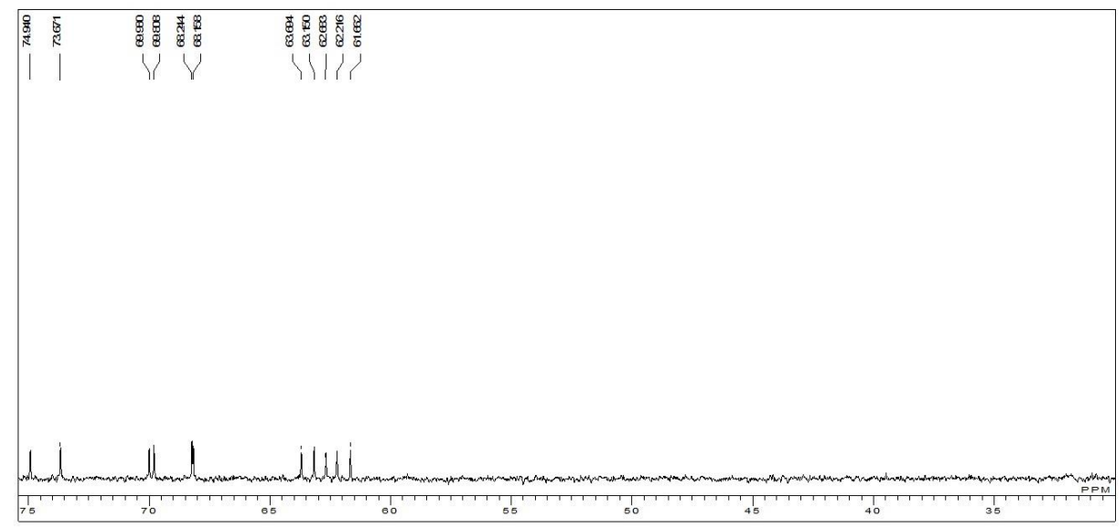


Figure SM-18(c). Selected up filed region ^{13}C-NMR (500 MHz, CDCl3) of compound **3**

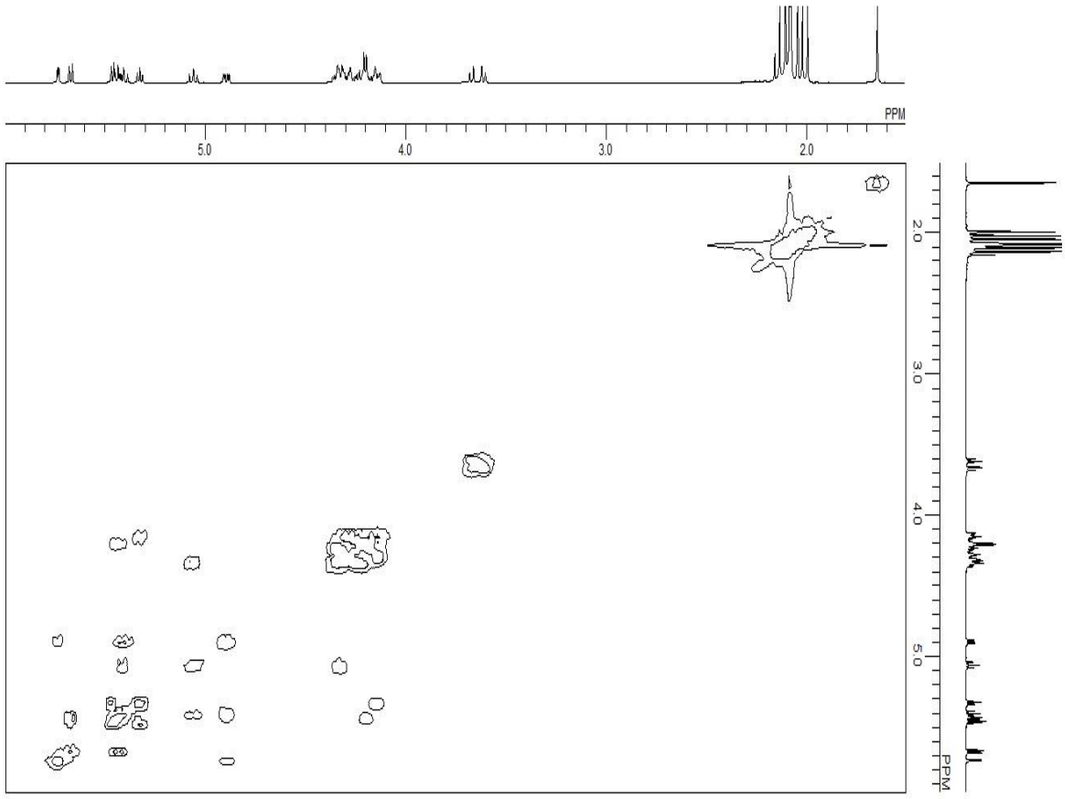


Figure SM-19. ^{1}H-^{1}H COSY 2D-NMR (500 MHz, $CDCl_3$) of compound **3**

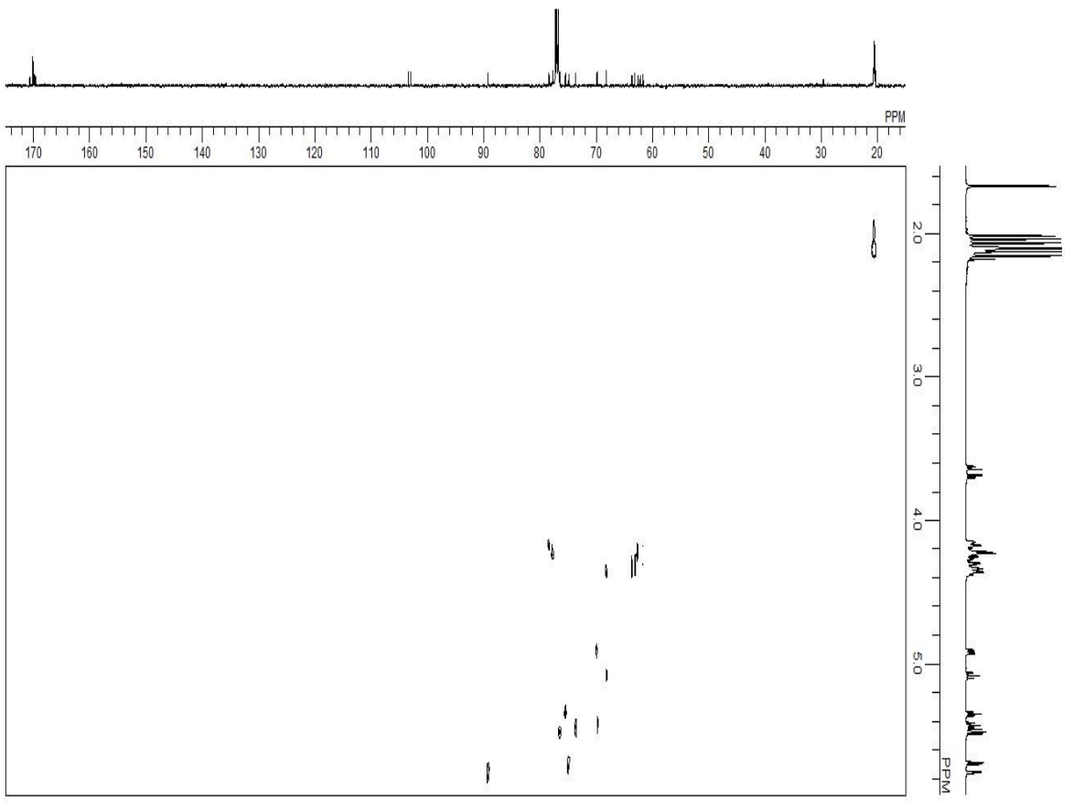


Figure SM-20. ^{13}C-^{1}H HETCOR 2D-NMR (500 MHz, $CDCl_3$) of compound **3**

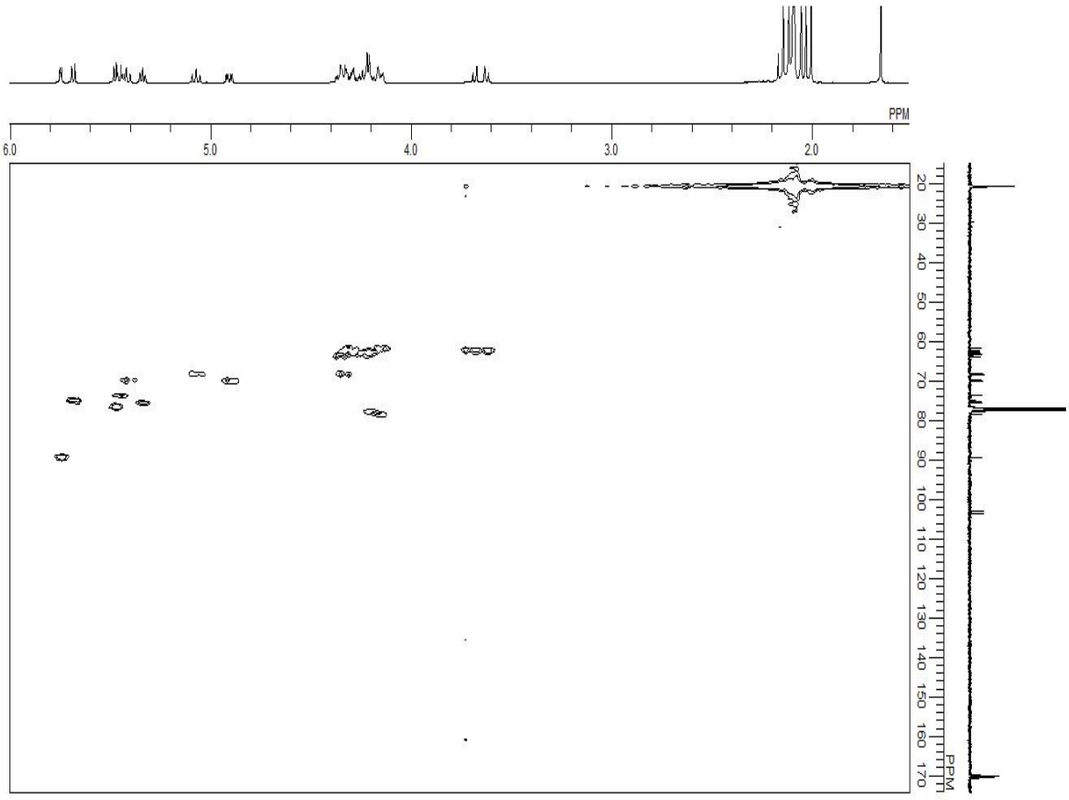


Figure SM-21. ^{1}H-^{13}C HMQC 2D-NMR (500 MHz, $CDCl_3$) of compound **3**

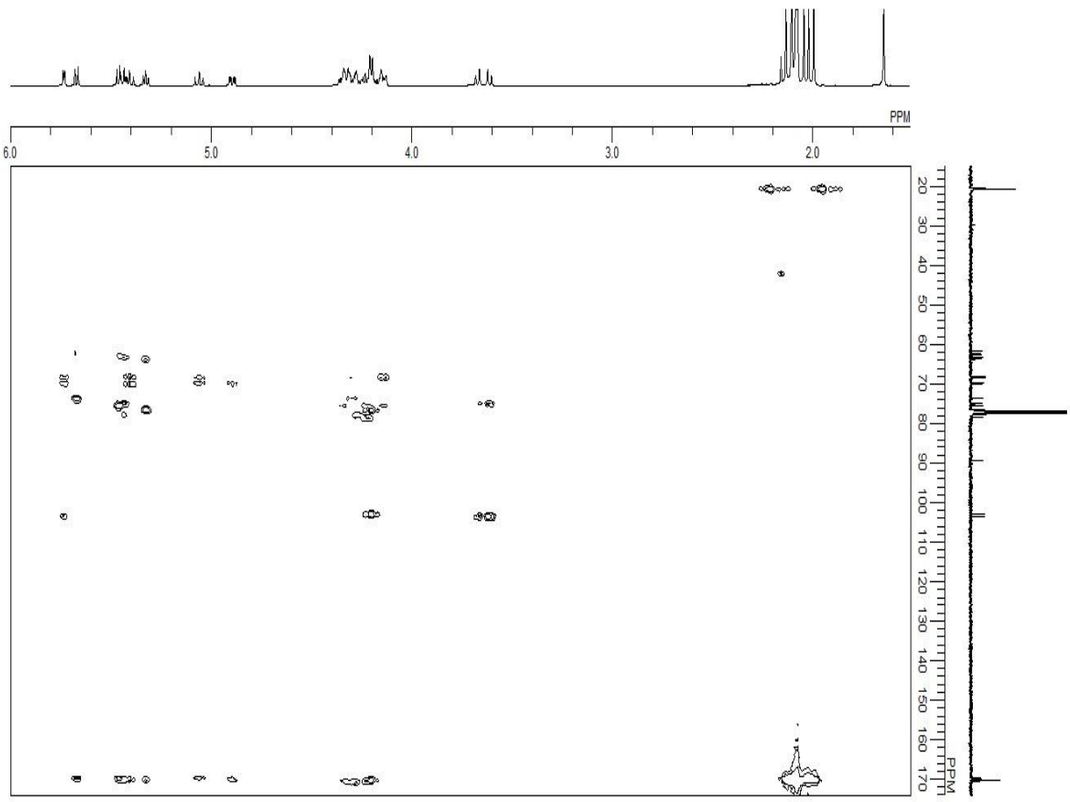


Figure SM-22. ^{1}H-^{13}C HMBC 2D-NMR (500 MHz, $CDCl_3$) of compound **3**

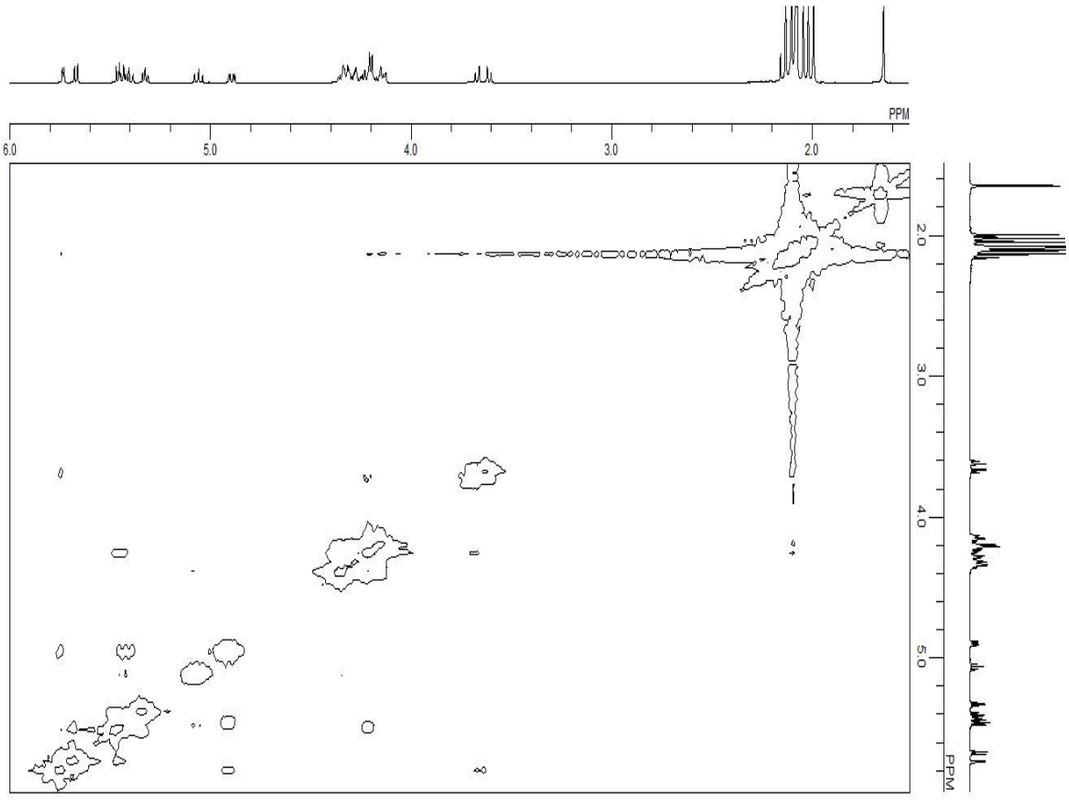


Figure SM-23. ^{1}H-^{1}H NOESY 2D-NMR (500 MHz, $CDCl_3$) of compound **3**

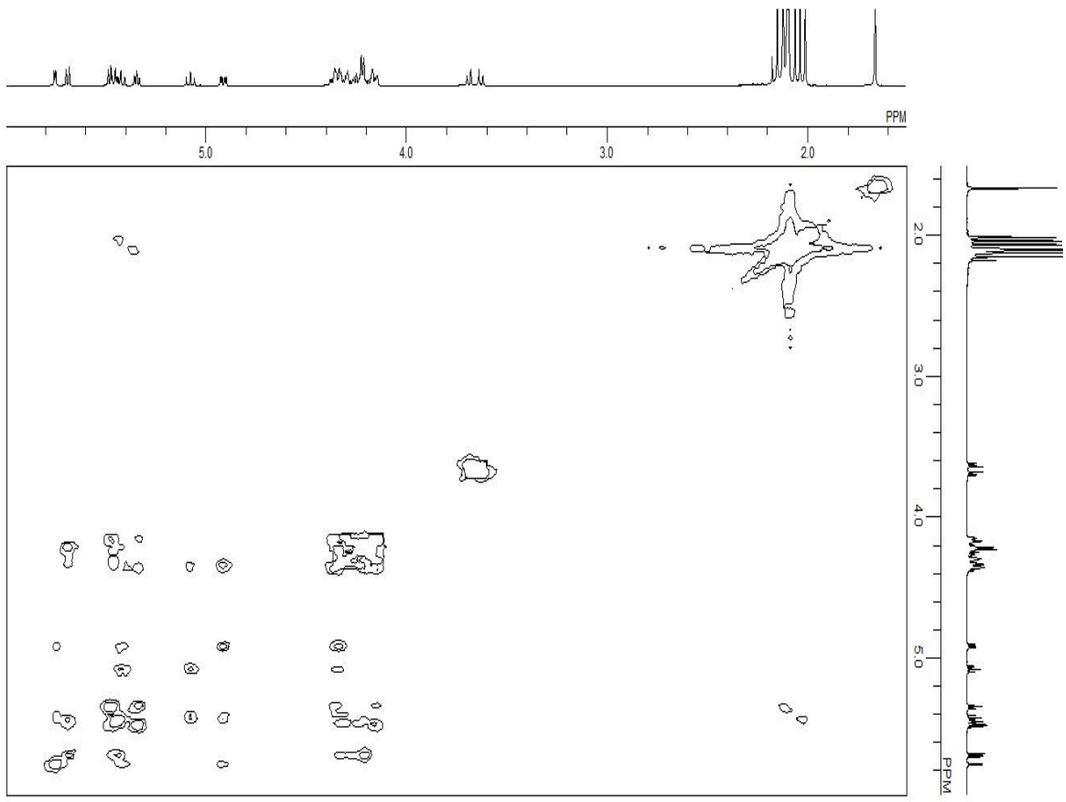
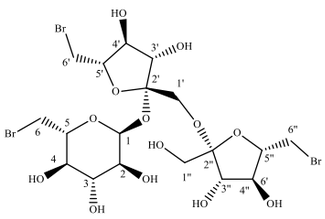


Figure SM-24. ^{1}H-^{1}H TOCSY 2D-NMR (500 MHz, $CDCl_3$) of compound **3**

6,6′,6′′-Tribromo-6,6′,6′′-trideoxy-1-kestose (**6**)



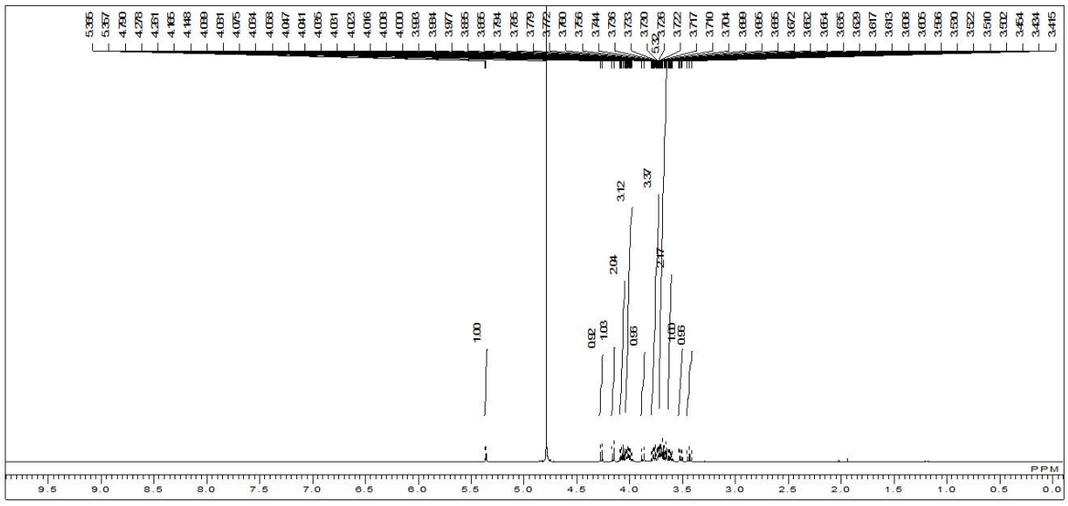


Figure SM-25(a). ^{1}H-NMR (500 MHz, D_2O) of compound **6**

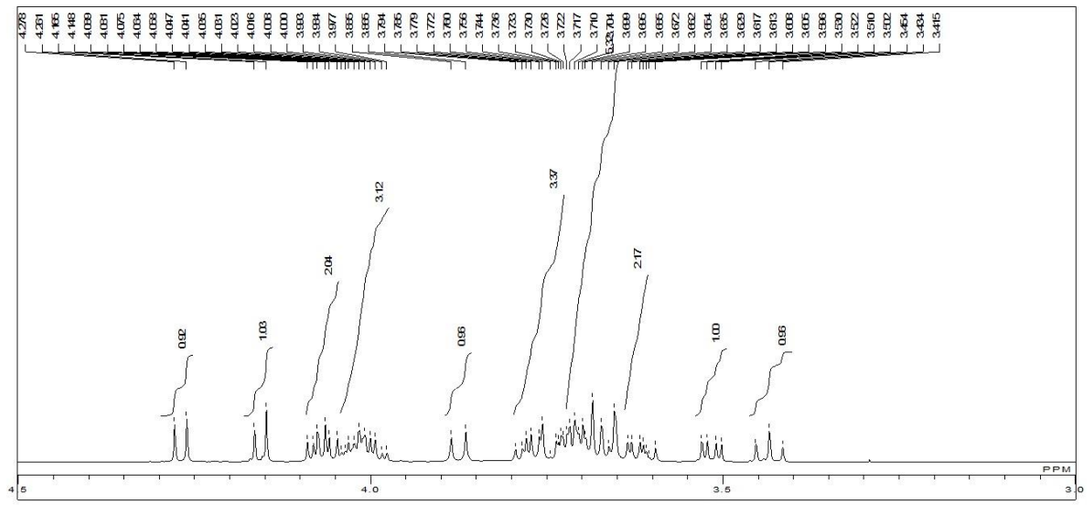


Figure SM-25(b). Selected region ^{1}H-NMR (500 MHz, D_2O) of compound **6**

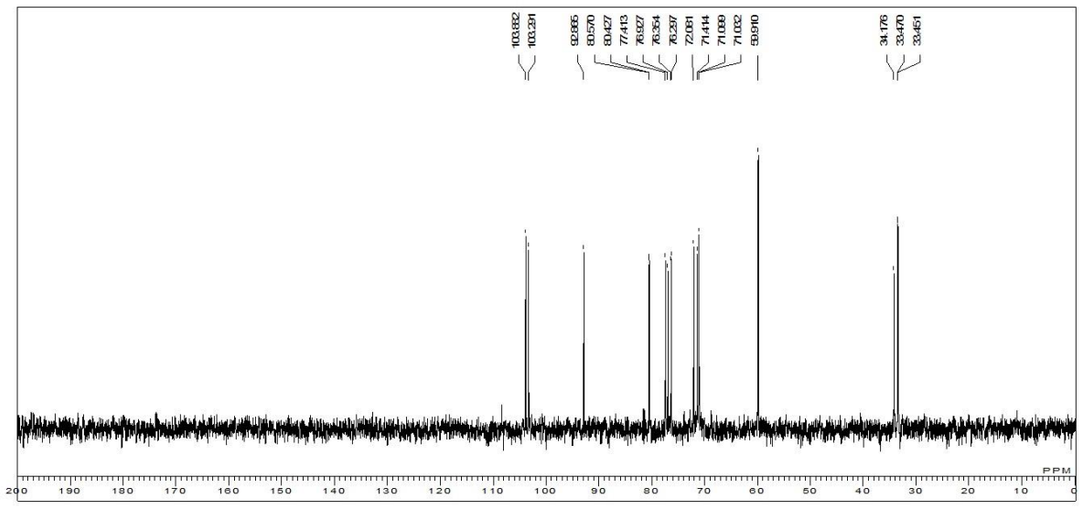


Figure SM-26(a). ^{13}C NMR (125 MHz, D_2O) of compound **6**

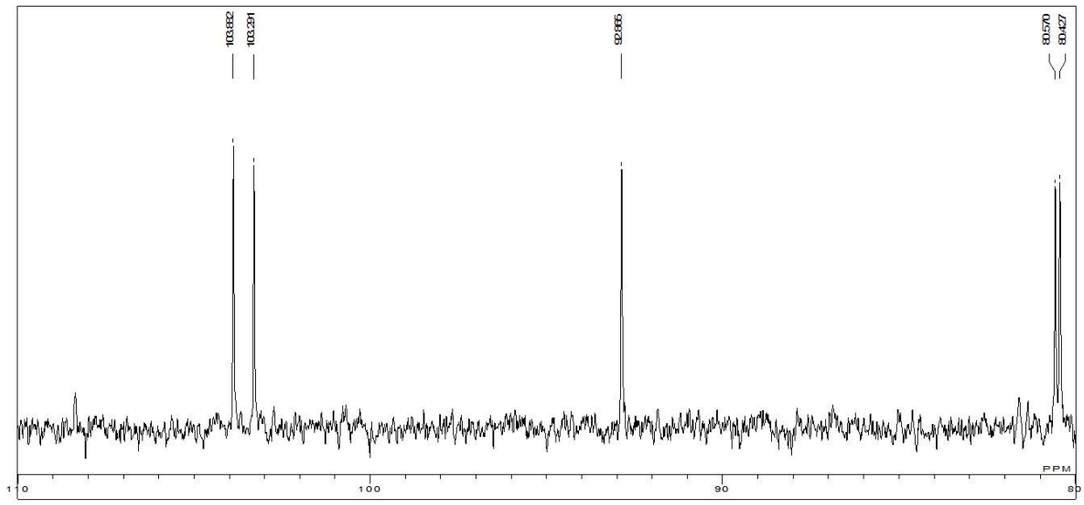


Figure SM-26(b). Selected down field region ^{13}C NMR (125 MHz, D_2O) of compound **6**

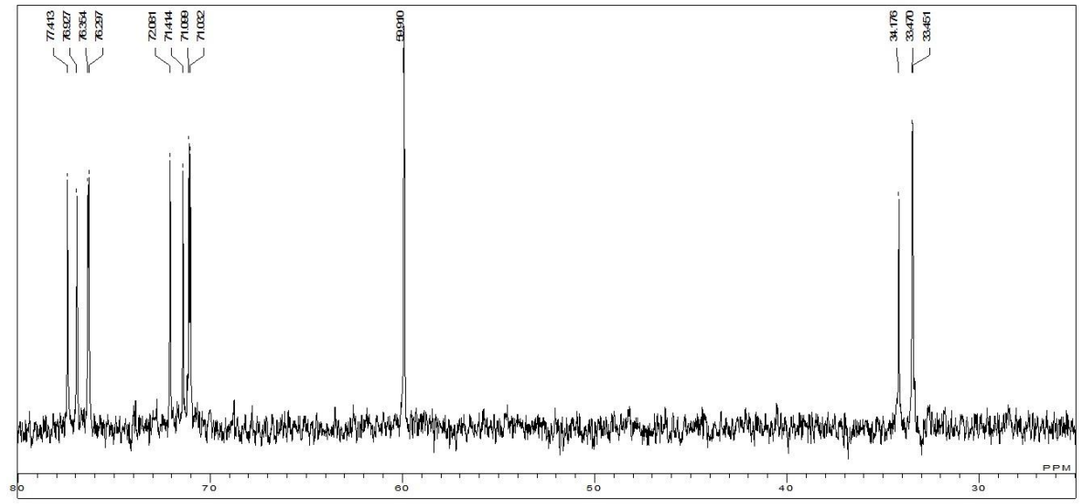


Figure SM-26(c). Selected up field region ^{13}C NMR (125 MHz, D_2O) of compound **6**

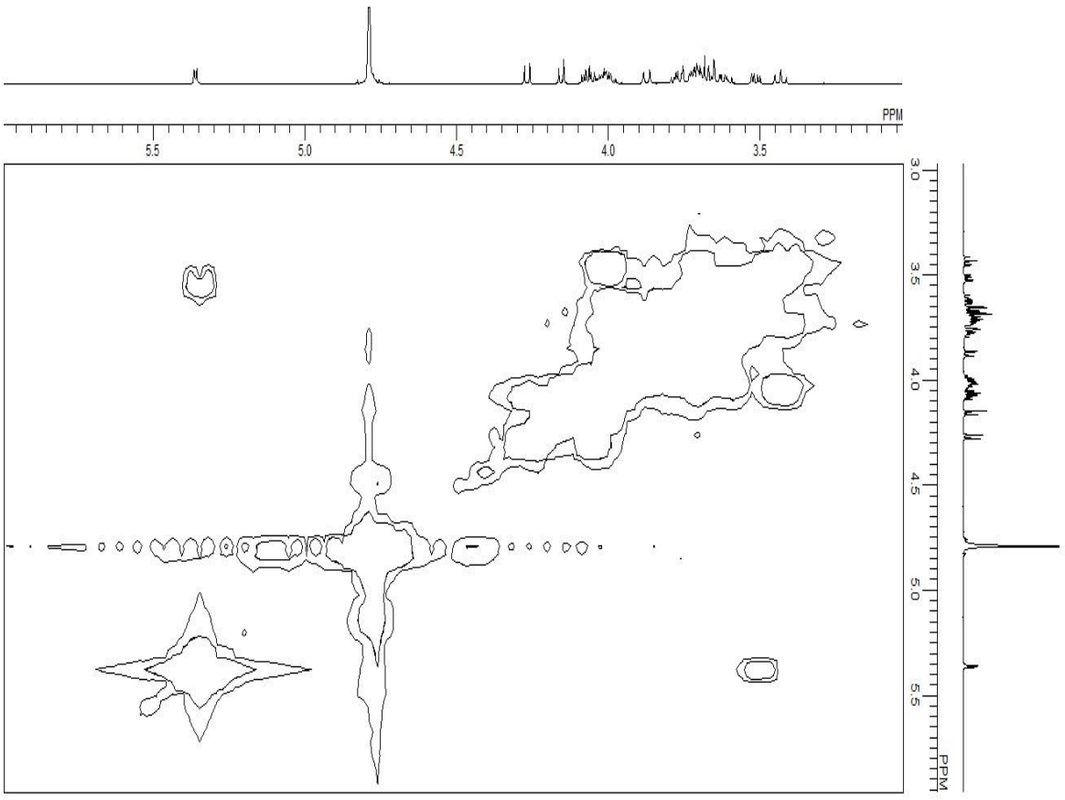


Figure SM-27. ^{1}H-^{1}H COSY 2D-NMR (500 MHz, D_2O) of compound **6**

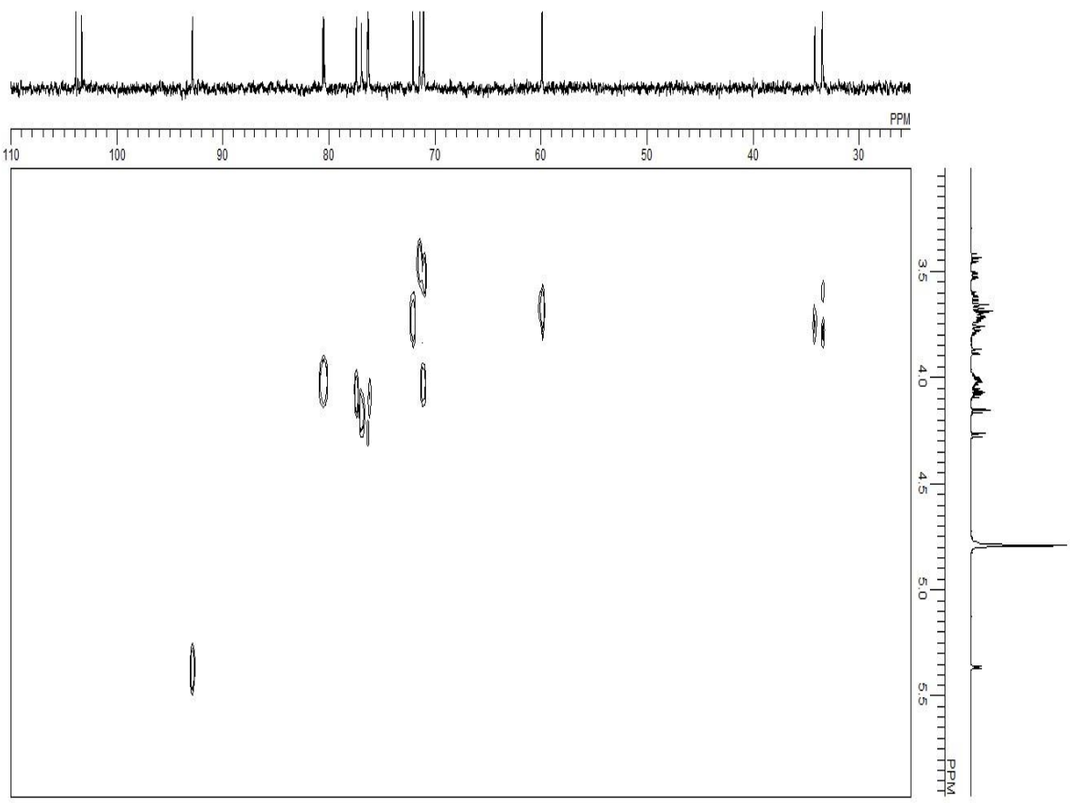


Figure SM-28. ^{13}C-^{1}H HETCOR 2D-NMR (500 MHz, D_2O) of compound **6**

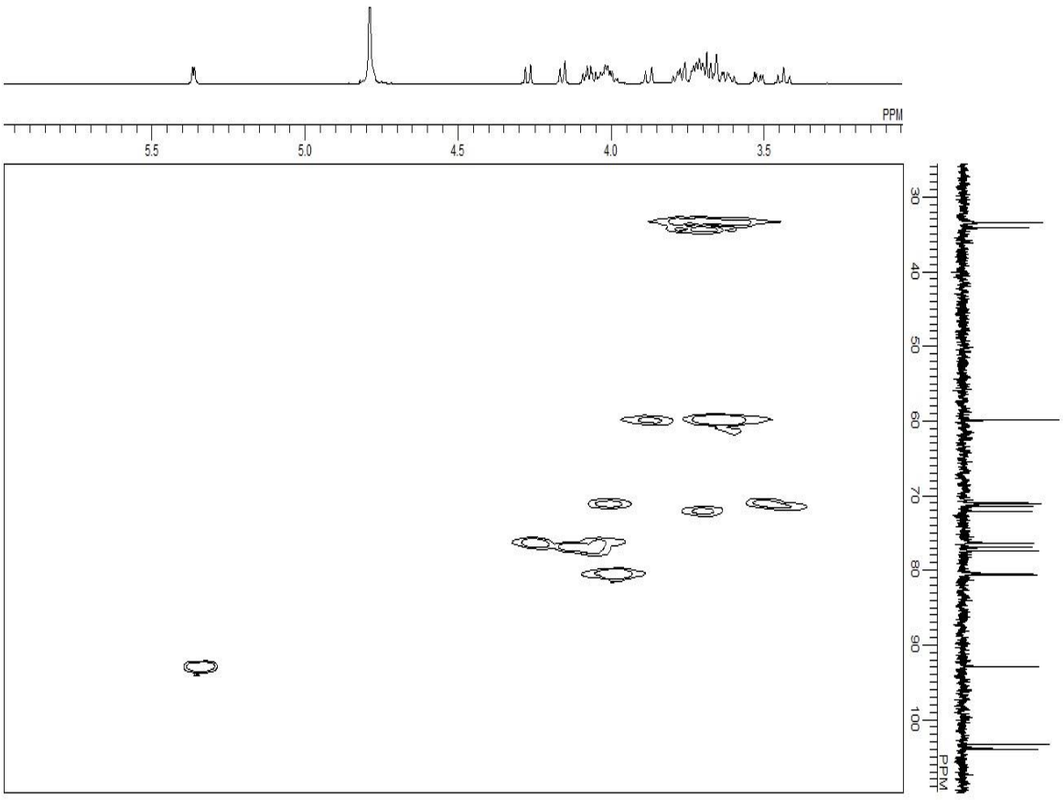


Figure SM-29. ^{1}H-^{13}C HMQC 2D-NMR (500 MHz, D_2O) of compound **6**

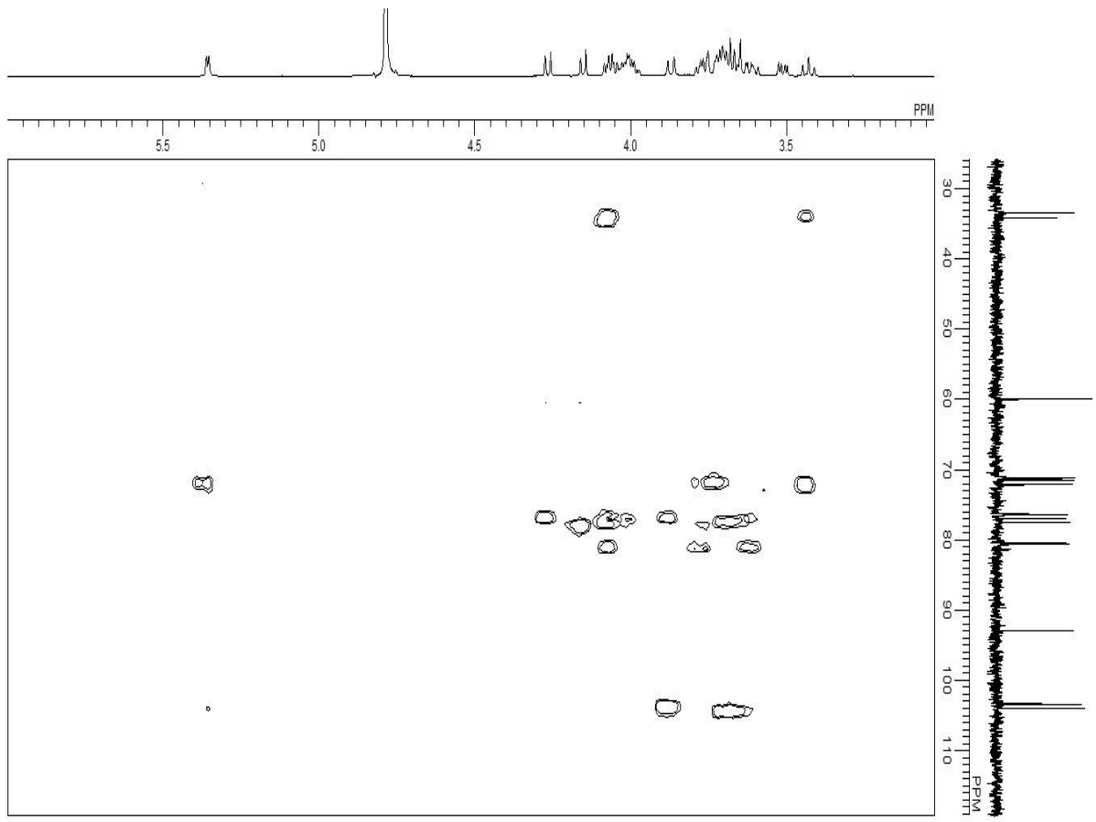


Figure SM-30. ^{1}H-^{13}C HMBC 2D-NMR (500 MHz, D_2O) of compound **6**

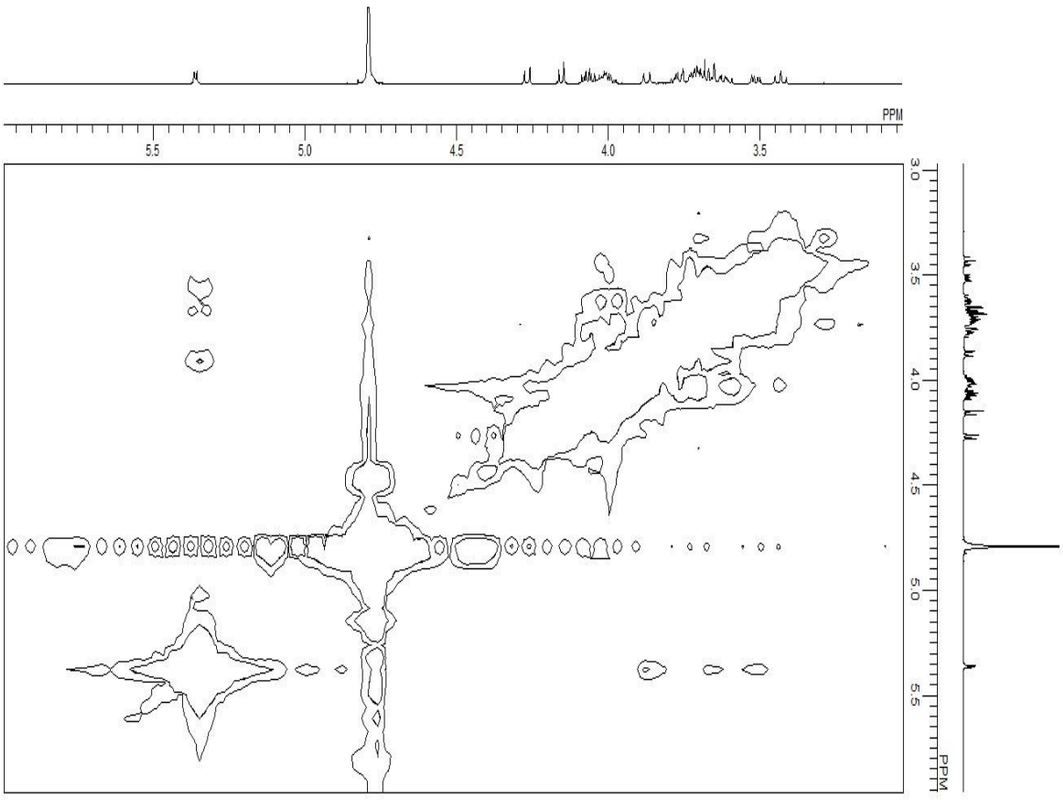


Figure SM-31. ^{1}H-^{1}H NOESY 2D-NMR (500 MHz, D_2O) of compound **6**

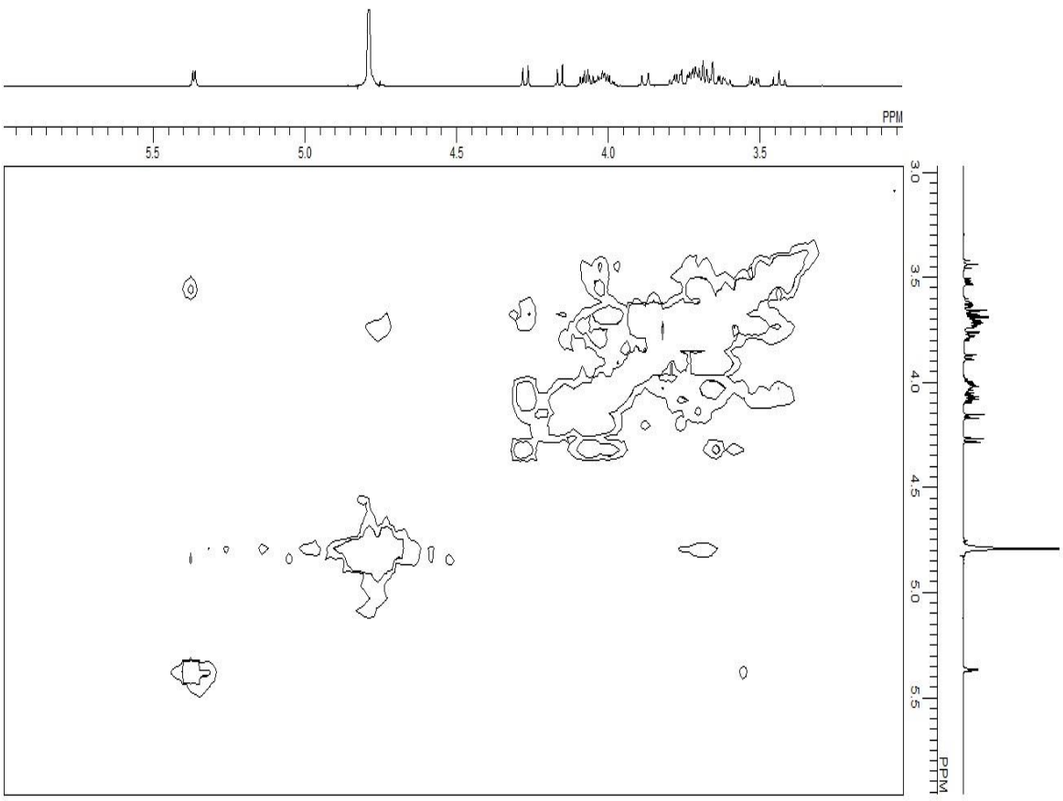
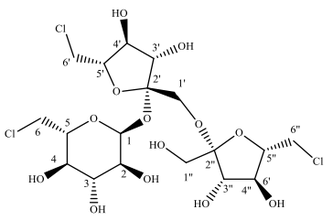


Figure SM-32. ^{1}H-^{1}H TOCSY 2D-NMR (500 MHz, D_2O) of compound **6**

6,6′,6′′-Trichloro-6,6′,6′′-trideoxy-1-kestose (**7**)



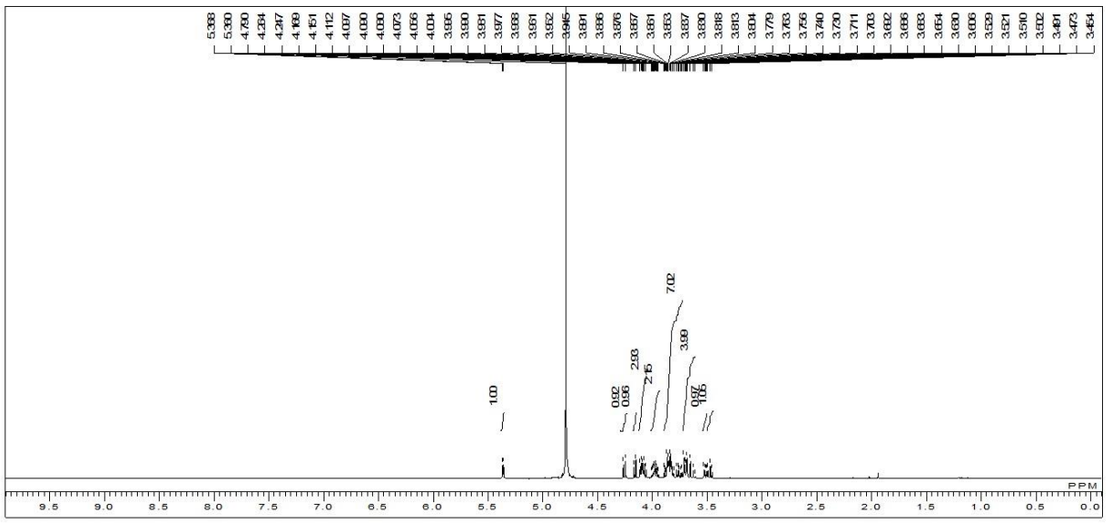


Figure SM-33(a). ^{1}H-NMR (500 MHz, D_2O) of compound **7**

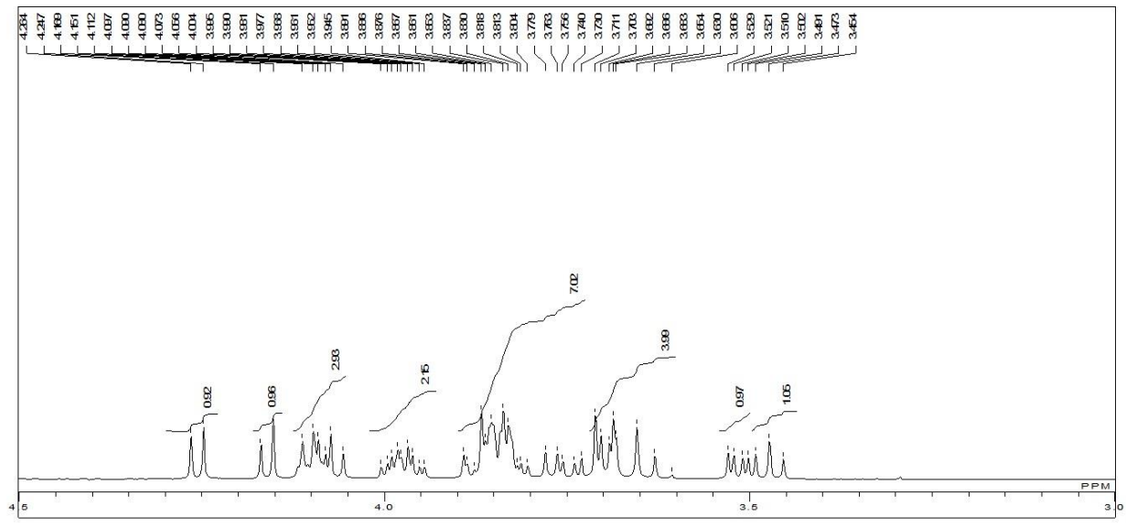


Figure SM-33(b). Selected region ^{1}H-NMR (500 MHz, D_2O) of compound **7**

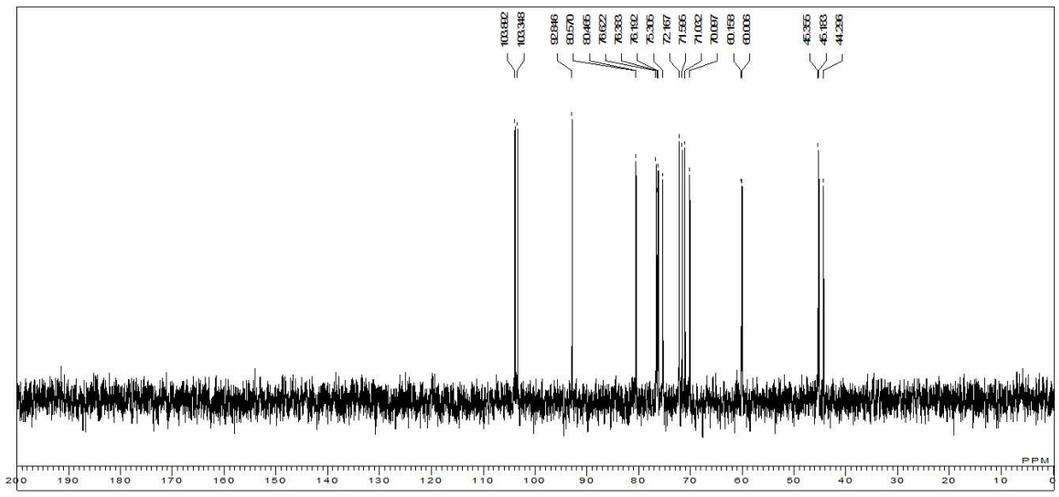


Figure SM-34(a). ^{13}C-NMR (125 MHz, D_2O) of compound **7**

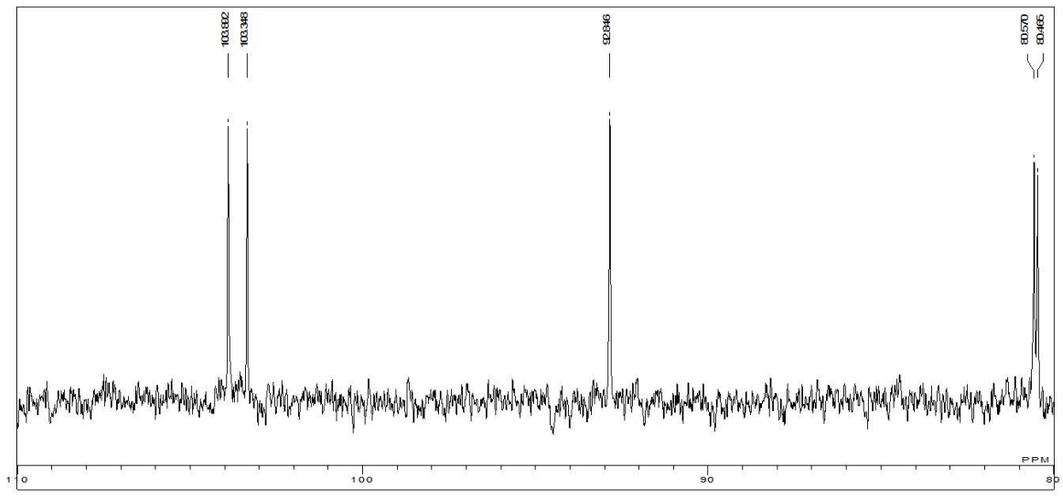


Figure SM-34(b). Selected down field region ^{13}C-NMR (125 MHz, D_2O) of compound **7**

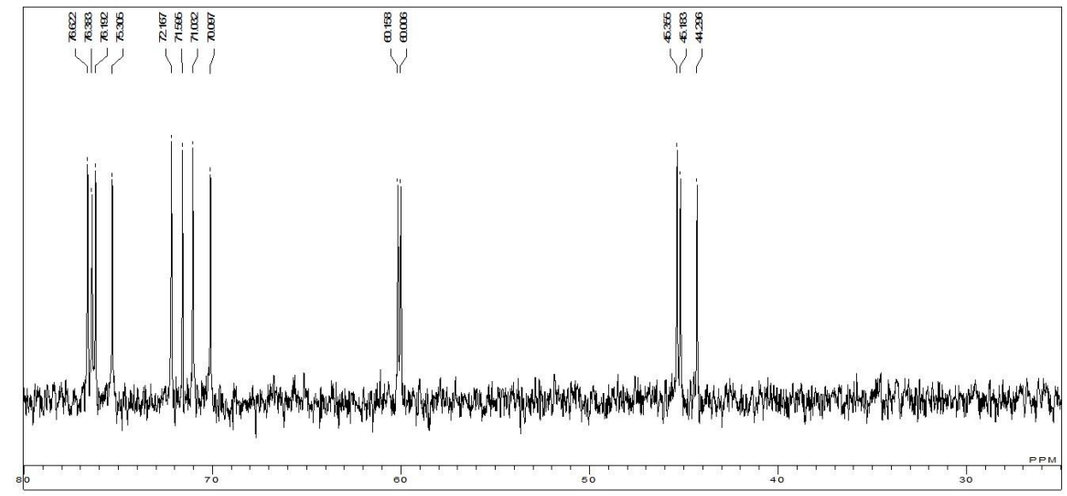


Figure SM-34(c). Selected up field region ^{13}C-NMR (125 MHz, D_2O) of compound **7**

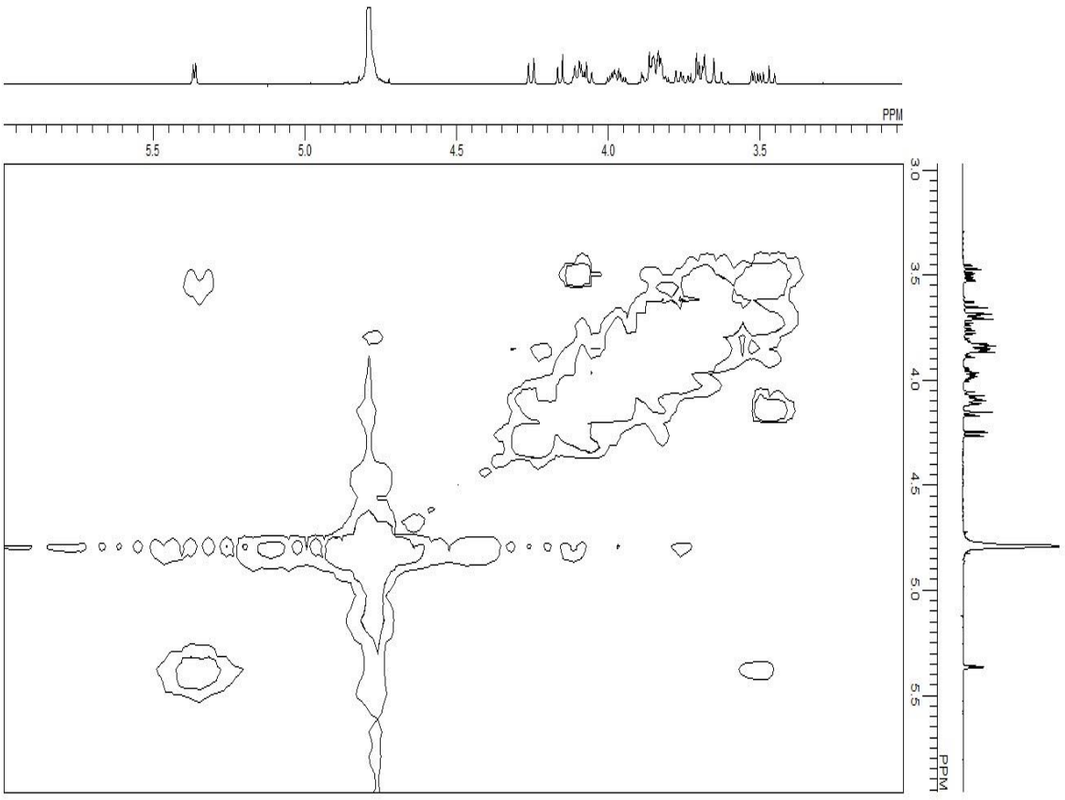


Figure SM-35. ^{1}H-^{1}H COSY 2D-NMR (500 MHz, D_2O) of compound **7**

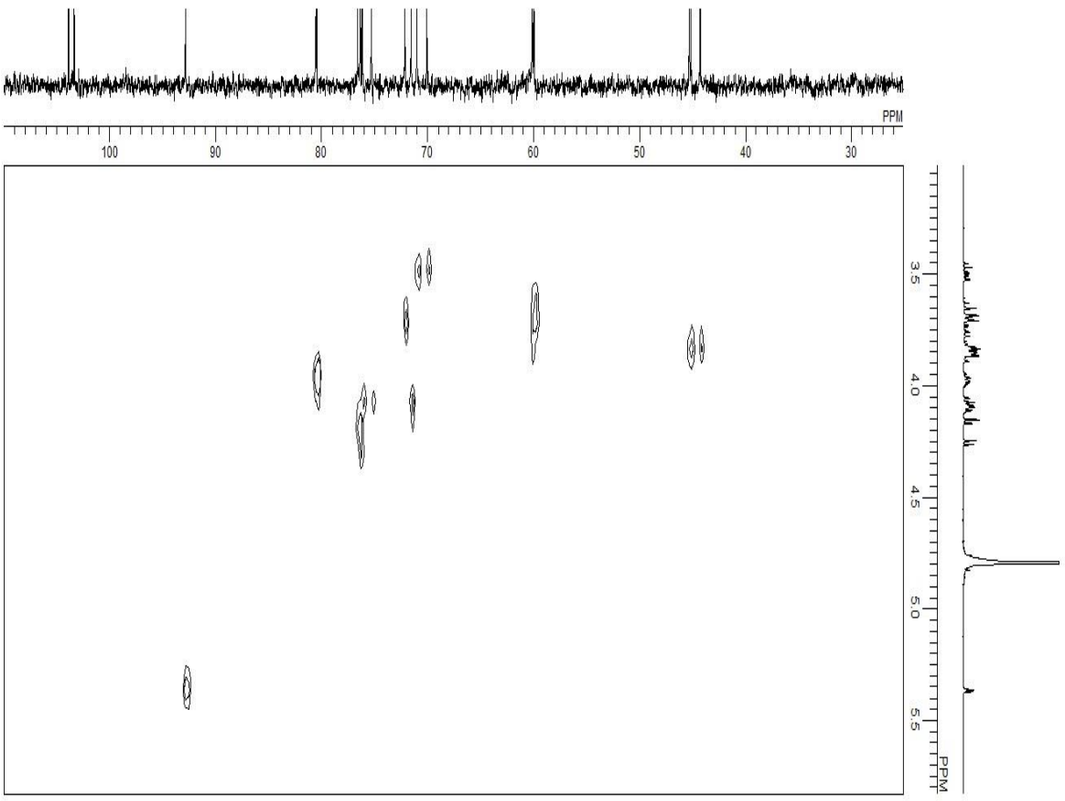


Figure SM-36. ^{13}C-^{1}H HETCOR 2D-NMR (500 MHz, D_2O) of compound **7**

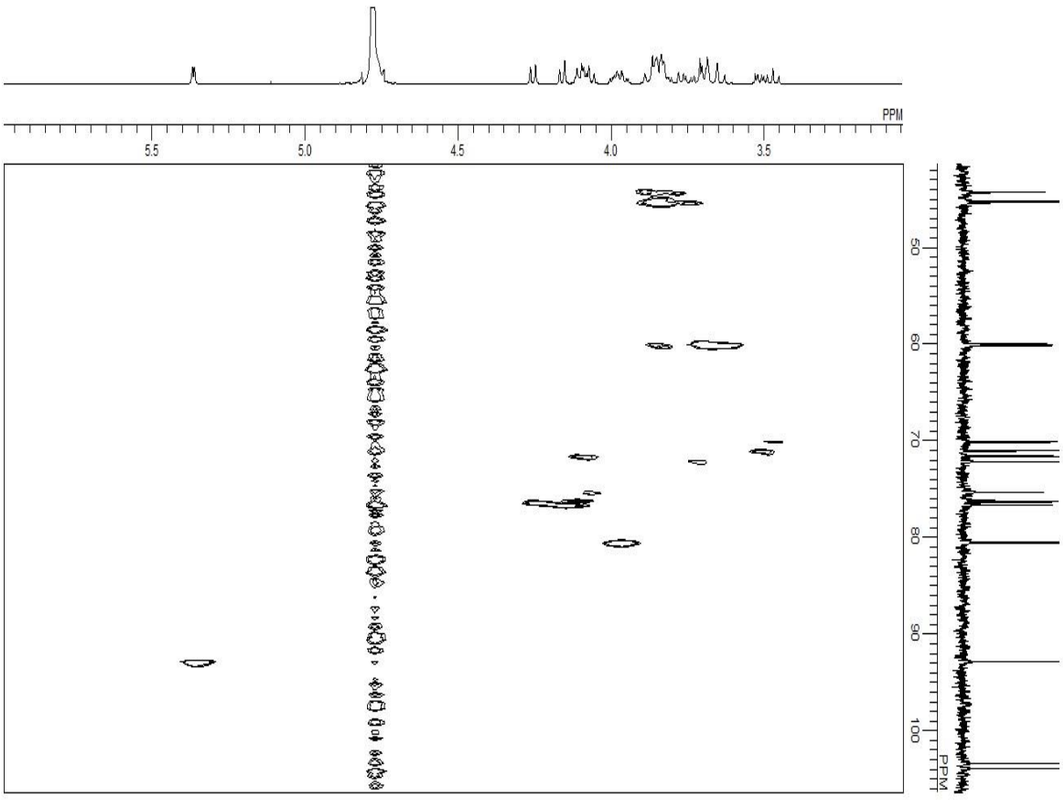


Figure SM-37. ^{1}H-^{13}C HMQC 2D-NMR (500 MHz, D_2O) of compound **7**

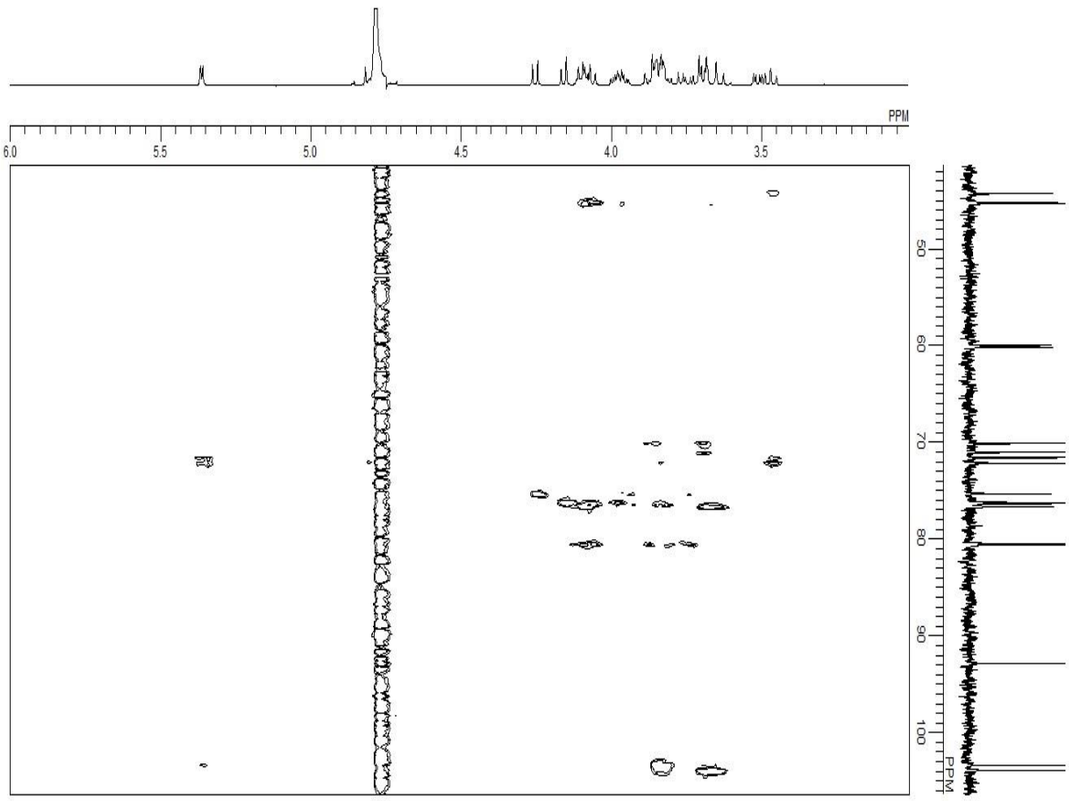


Figure SM-38. ^{1}H-^{13}C HMBC 2D-NMR (500 MHz, D_2O) of compound **7**

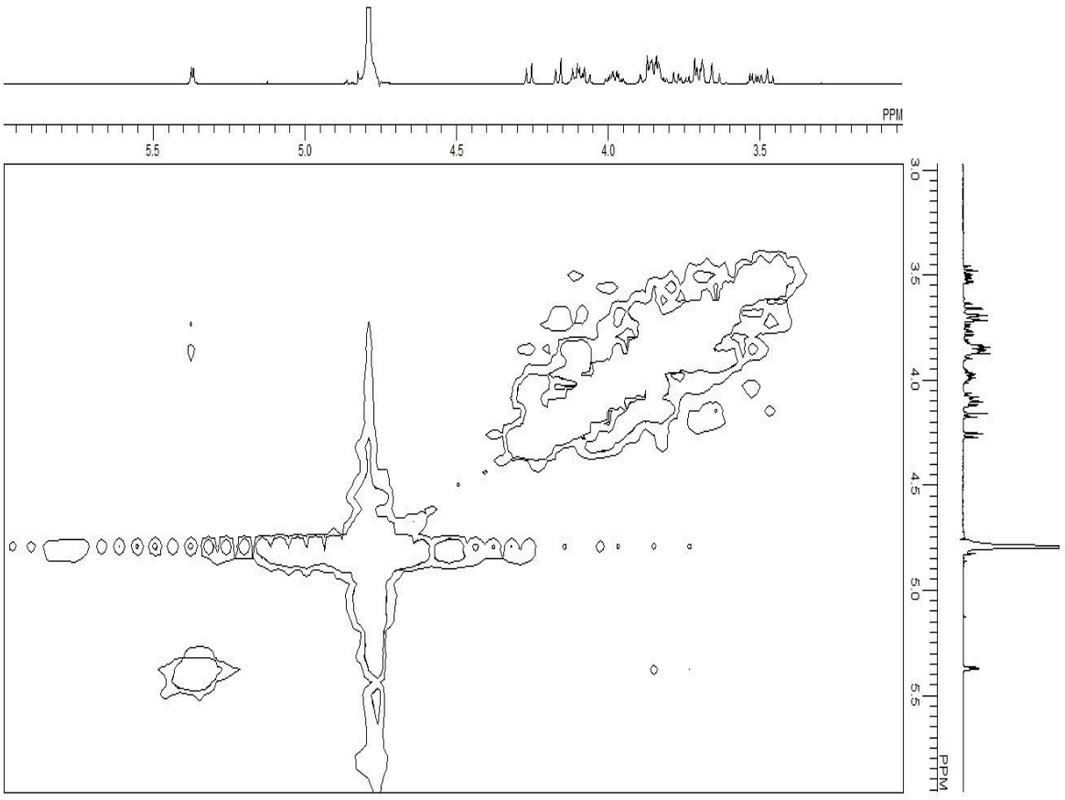


Figure SM-39.^{1}H-^{1}H NOESY 2D-NMR (500 MHz, D_2O) of compound **7**

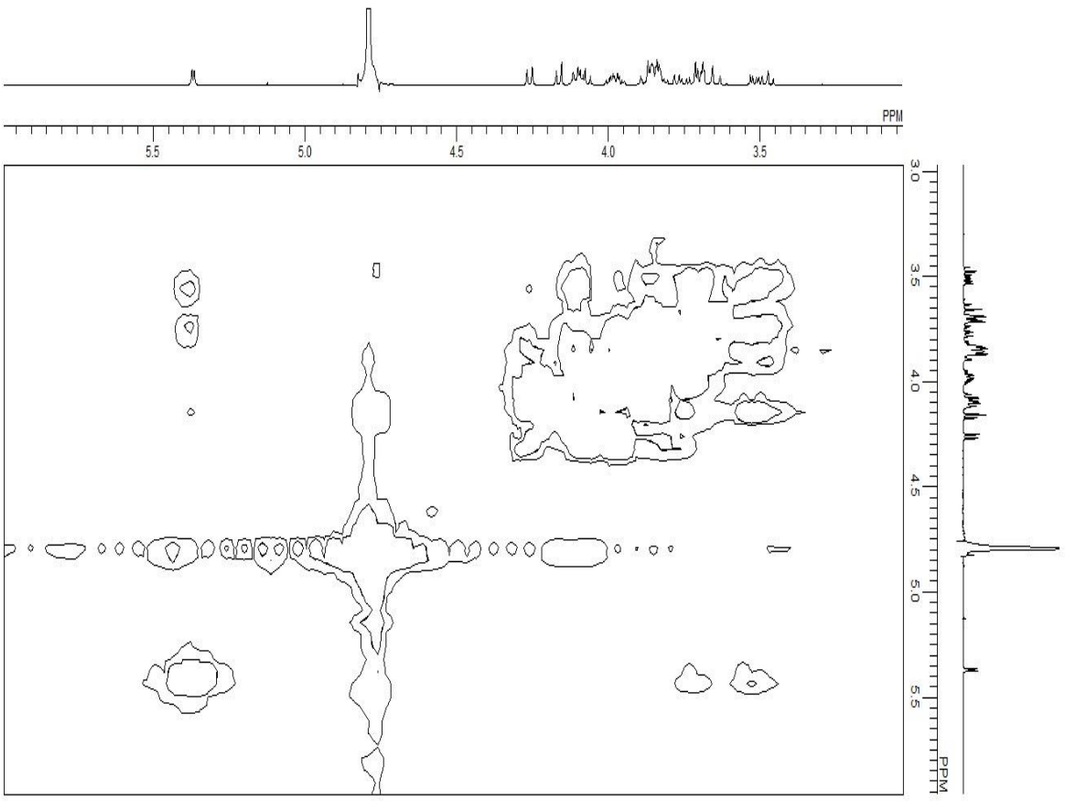
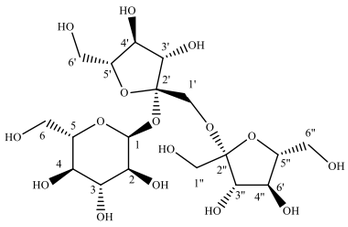


Figure SM-40. ^{1}H-^{1}H TOCSY 2D-NMR (500 MHz, D_2O) of compound **7**

1-kestose (**1**)



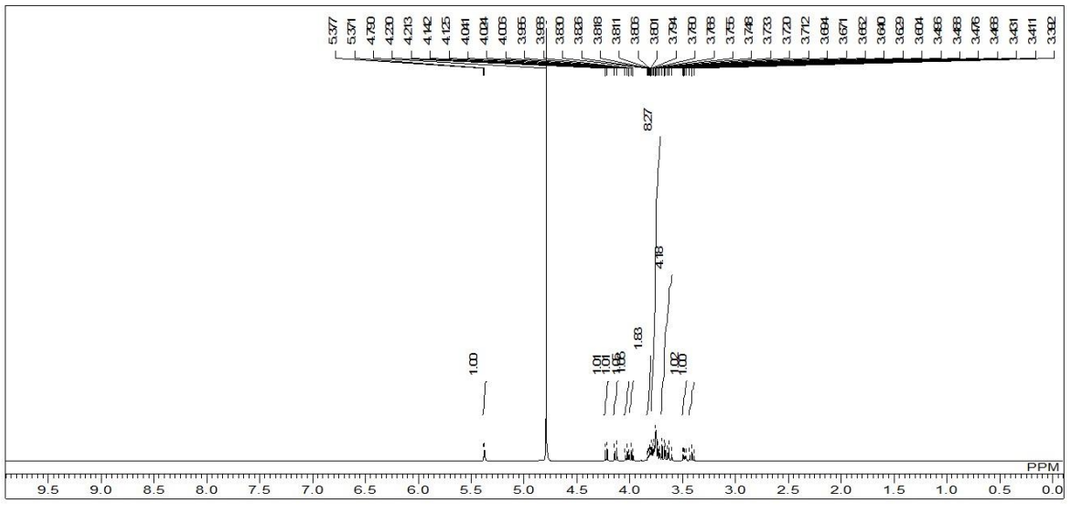


Figure SM-41(a).^{1}H-NMR (500 MHz, D_2O) of compound **1**

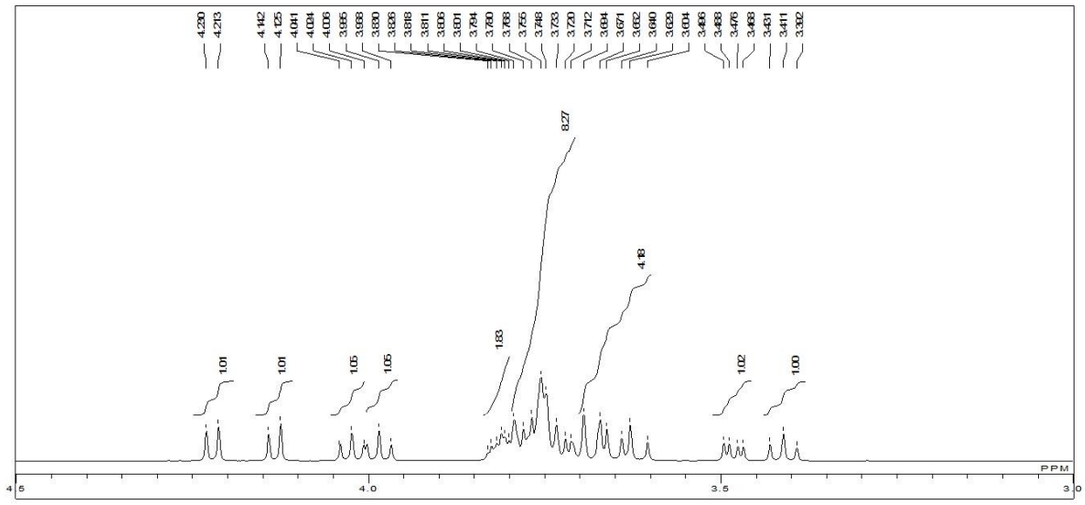


Figure SM-41(b). Selected region ^{1}H-NMR (500 MHz, D_2O) of compound **1**

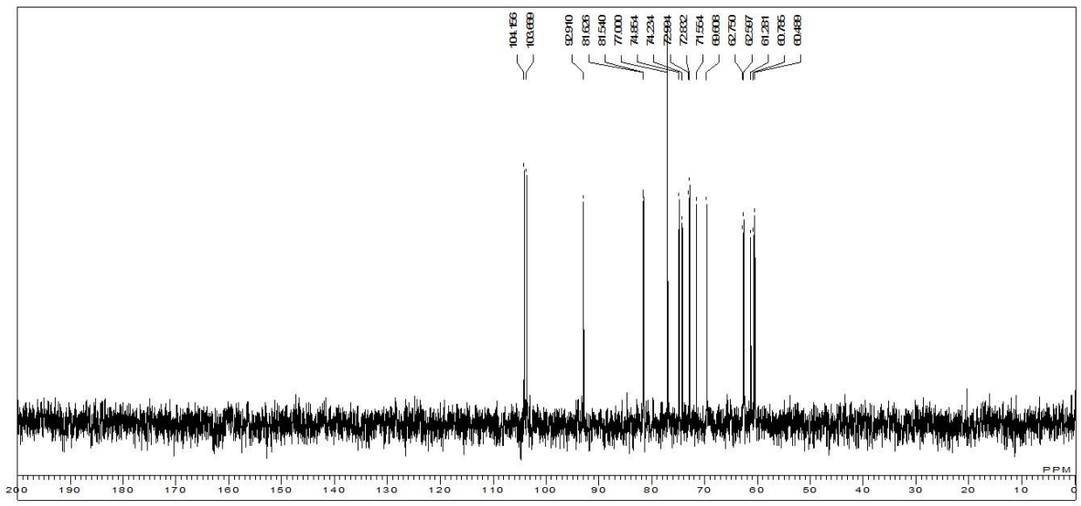


Figure SM-42(a). ^{13}C NMR (125 MHz, D_2O) of compound **1**

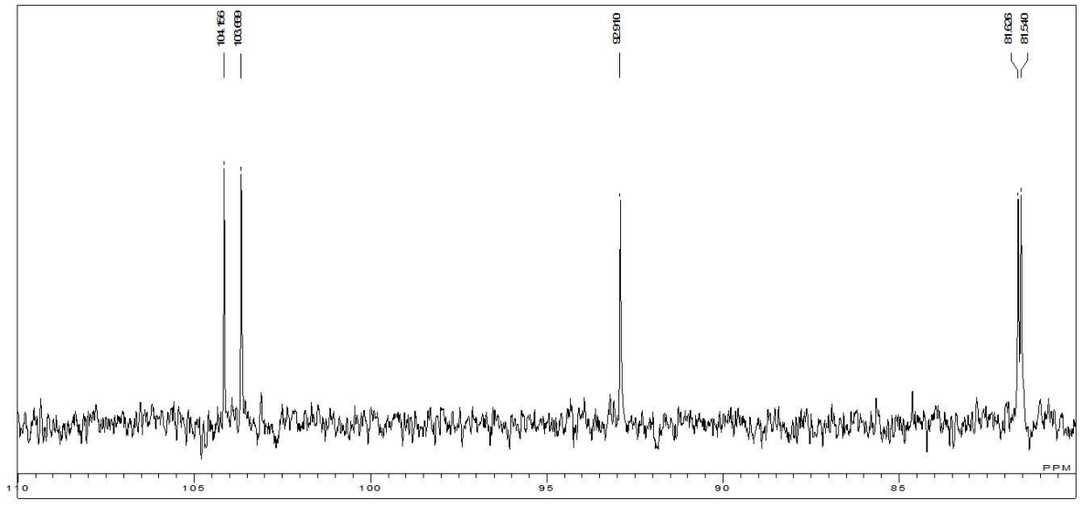


Figure SM-42(b). Selected down field region ^{13}C NMR (125 MHz, D_2O) of compound **1**

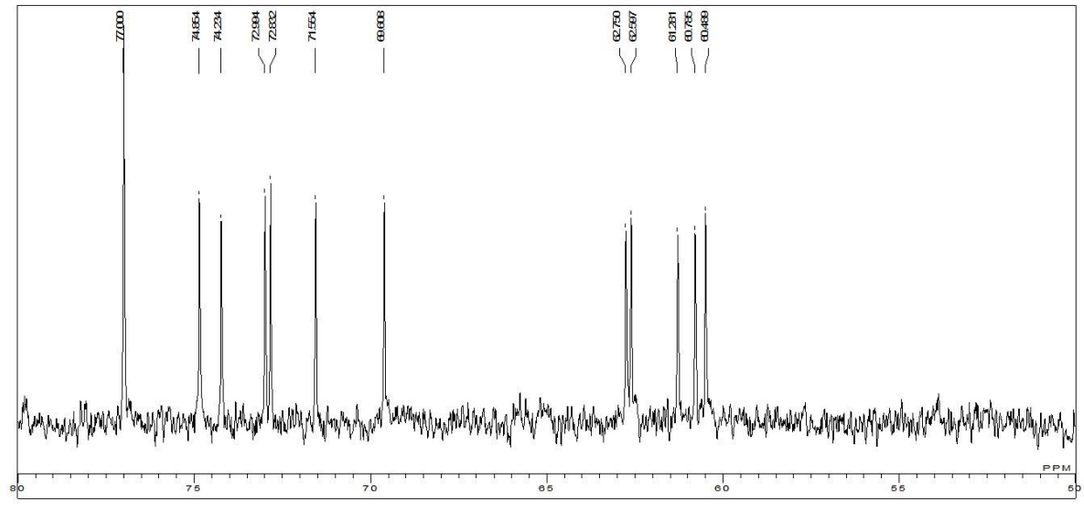


Figure SM-42(c). Selected up field region ^{13}C NMR (125 MHz, D_2O) of compound **1**

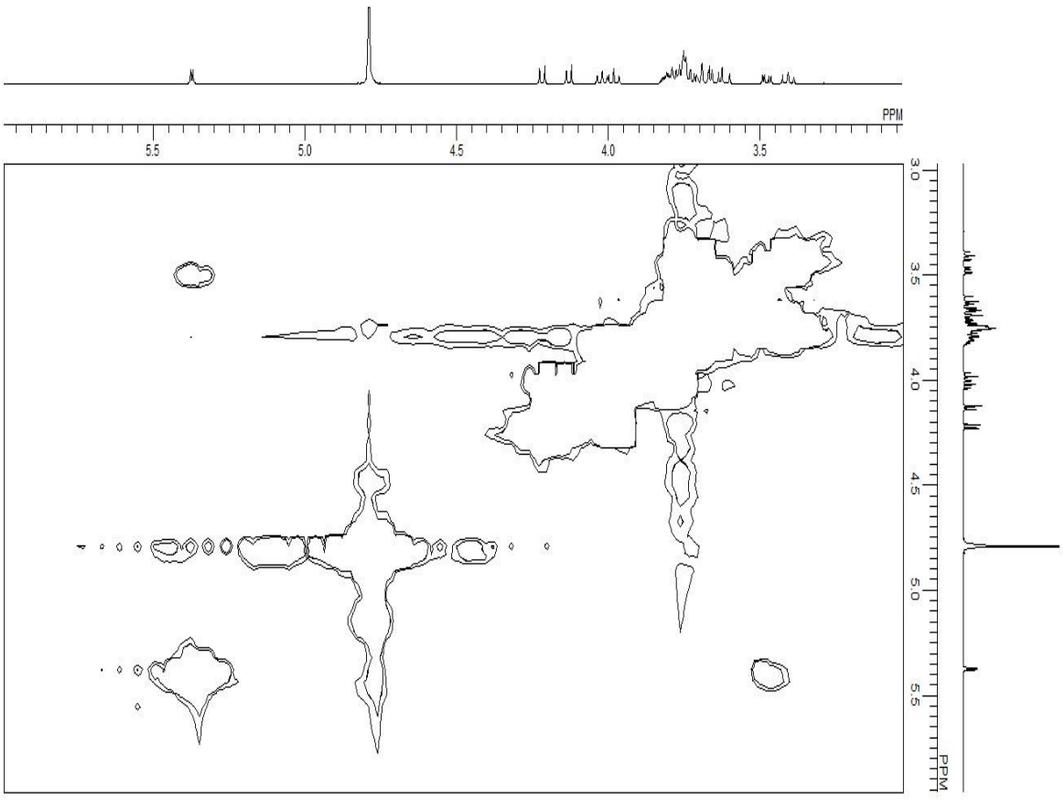


Figure SM-43. ^{1}H-^{1}H COSY 2D-NMR (500 MHz, D_2O) of compound **1**

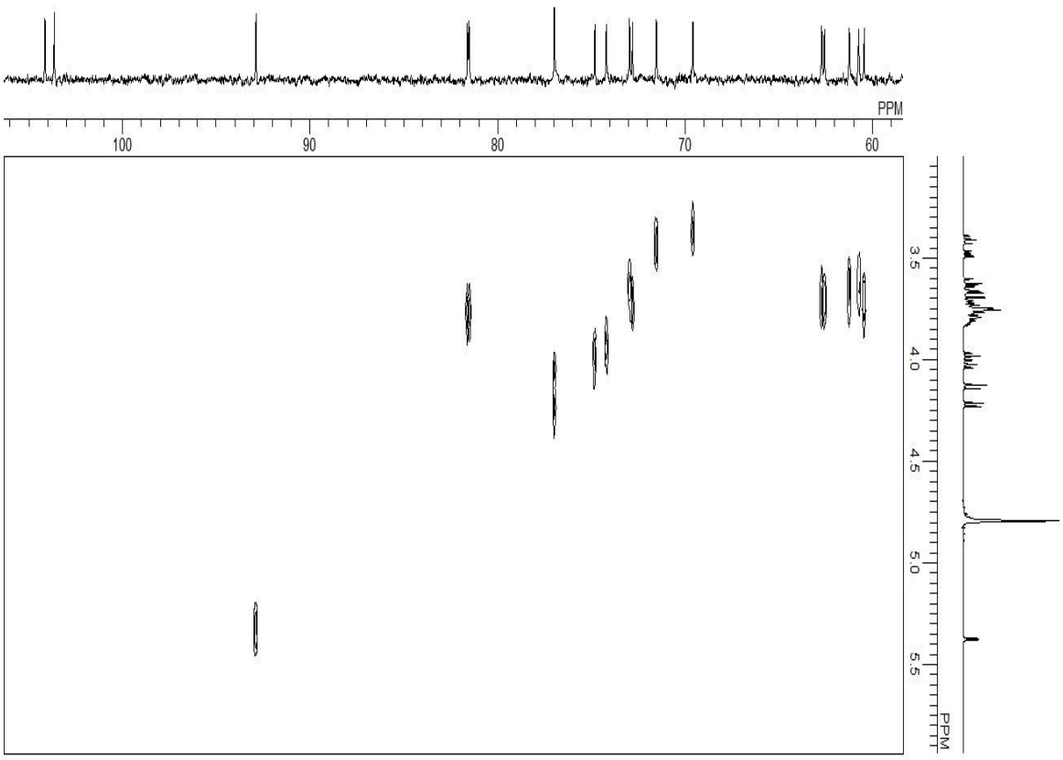


Figure SM-44. ^{13}C-^{1}H HETCOR 2D-NMR (500 MHz, D_2O) of compound **1**

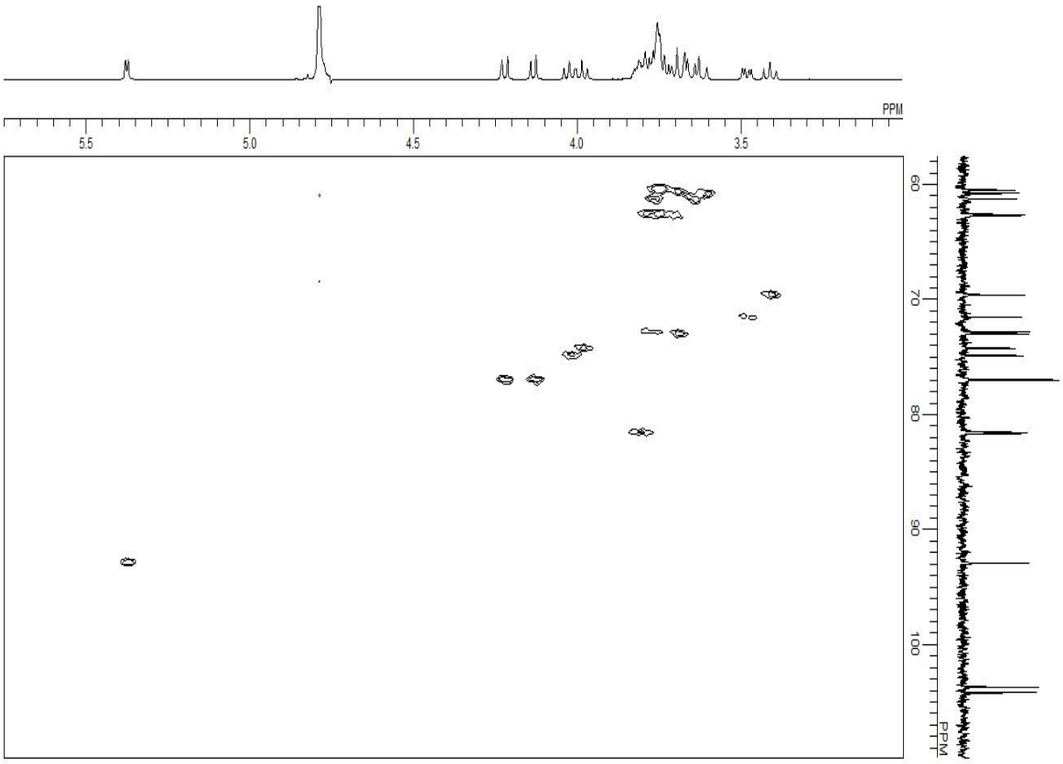


Figure SM-45. ^{1}H-^{13}C HMQC 2D-NMR (500 MHz, D_2O) of compound **1**

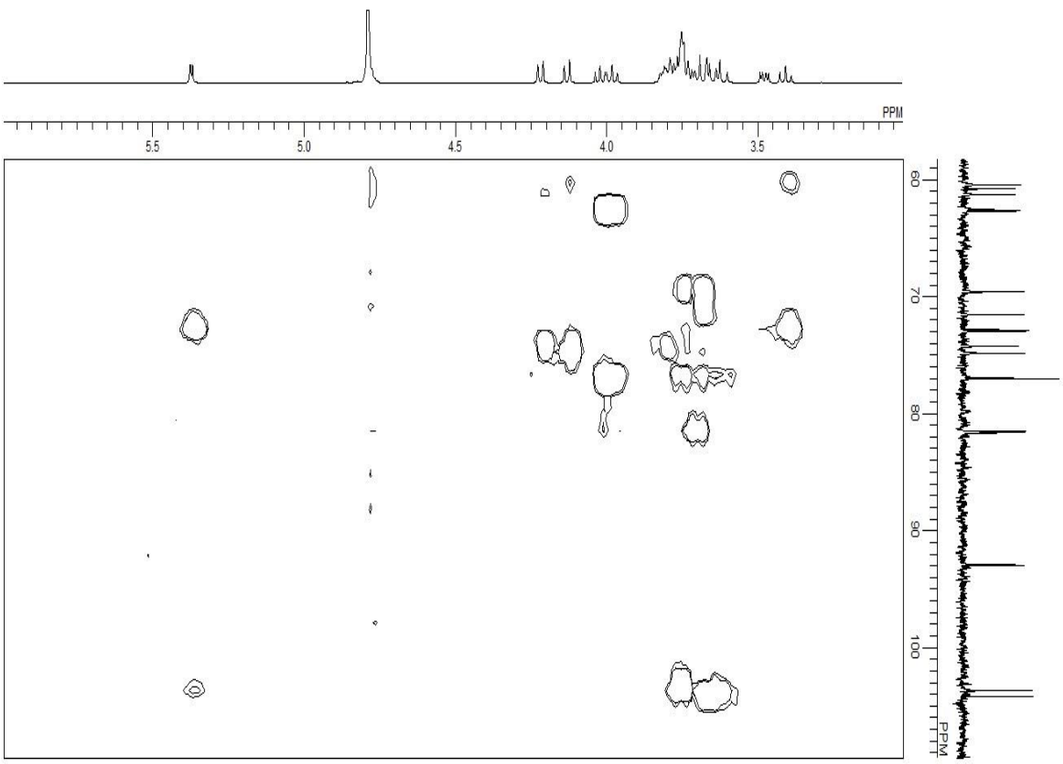


Figure SM-46.^{1}H-^{13}C HMBC 2D-NMR (500 MHz, D_2O) of compound **1**

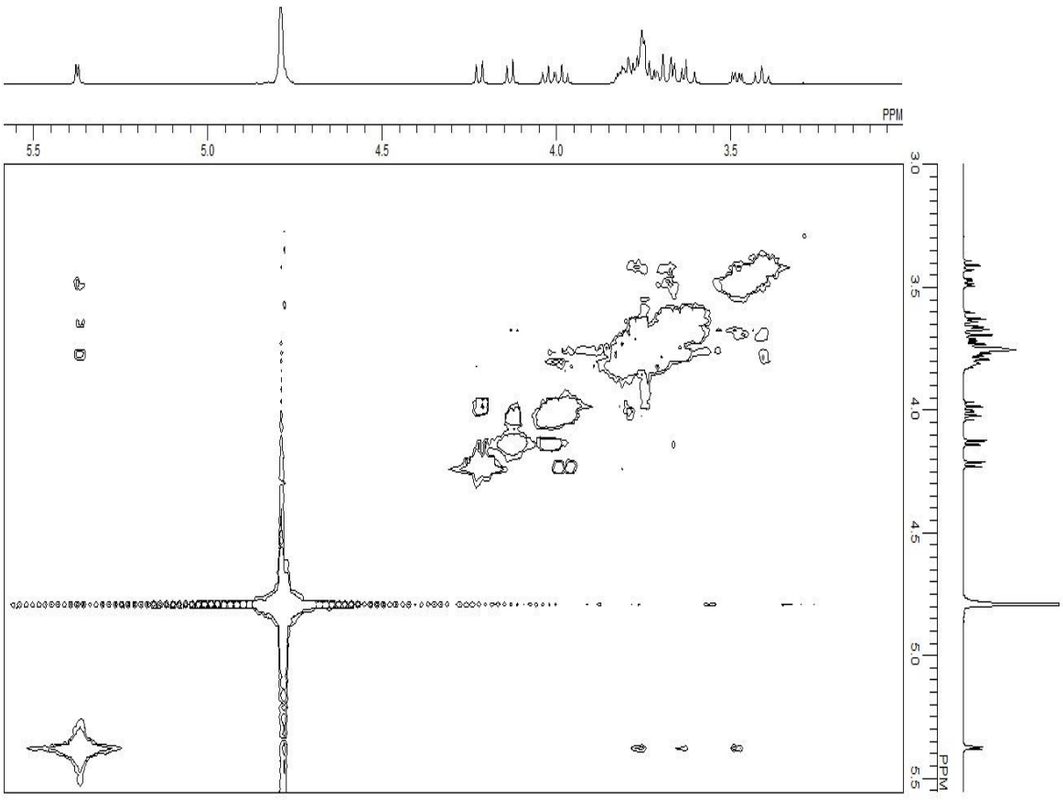


Figure SM-47.^{1}H-^{1}H NOESY 2D-NMR (500 MHz, D_2O) of compound **1**

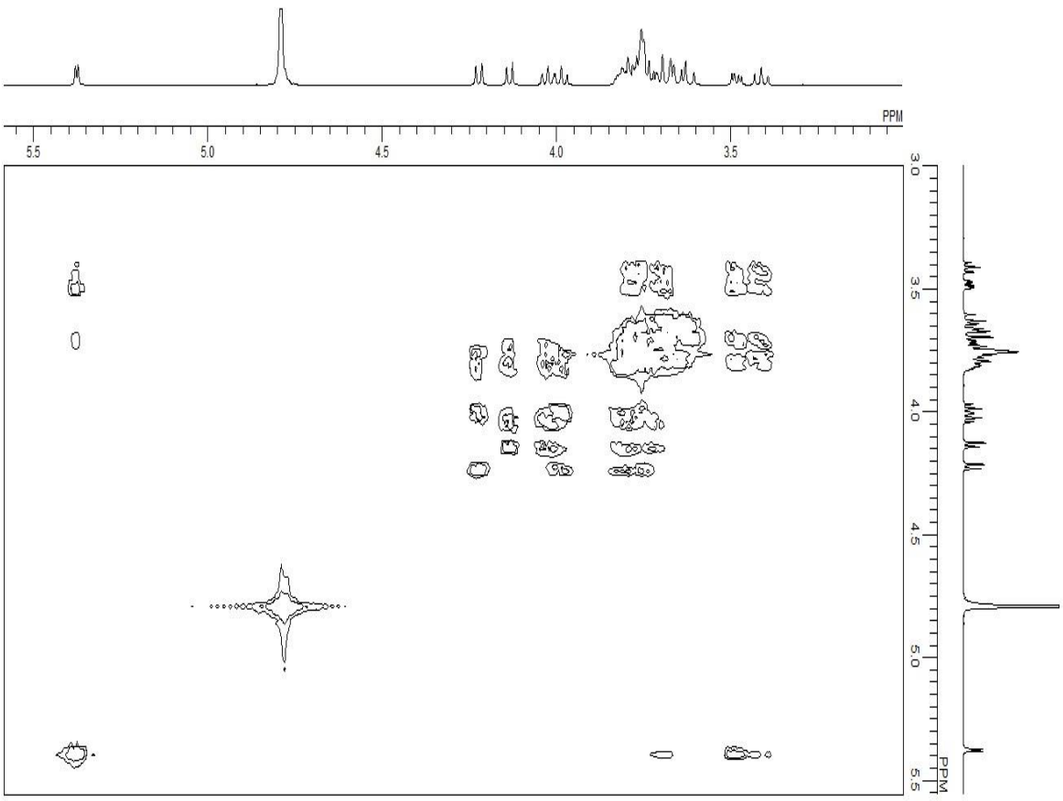


Figure SM-48.^{1}H-^{1}H TOCSY 2D-NMR (500 MHz, D_2O) of compound **1**

^{1}H and 13C NMR literature comparison with observation data

Table SM-1. ^{1}H and ^{13}C NMR literature comparison with observation data of per-O-acetylated 1-kestose and per-O-acetylated halogenated 1-kestose derivatives

Assignment	**1″,2,3,3′,3″,4,4′,4″,6,6′,6″-Undeca-*O*-acetyl-deoxy-1-kestose (3)** CAS: 25101-98-8 (*δ* in ppm and *J* in Hz)						**1″,2,3,3′,3″,4,4′,4″-octa-*O*-acetyl-6,6′,6″-tribromo-6,6′,6′-trideoxy 1-kestose (4)** No CAS (*δ* in ppm and *J* in Hz)		**1″,2,3,3′,3″,4,4′,4″-octa-*O*-acetyl-6,6′,6″-trichloro-6,6′,6″-trideoxy-1-kestose (5)** No CAS (*δ* in ppm and *J* in Hz)	
	Ref [1]		**Ref [2]**		**Observed**		**Observed**		**Observed**	
	δ ^{1}H (CDCl$_3$)	*δ* ^{13}C (100.6 MHz, CDCl$_3$)	*δ* ^{1}H (100 or 220 MHz, CDCl$_3$)	*δ* ^{13}C[a]	*δ* ^{1}H (500 MHz, CDCl$_3$)	*δ* ^{13}C (125 MHz, CDCl$_3$)	*δ* ^{1}H (500 MHz, CDCl$_3$)	*δ* ^{13}C (125 MHz, CDCl$_3$)	*δ* ^{1}H (500 MHz, CDCl$_3$)	*δ* ^{13}C (125 MHz, CDCl$_3$)
1	5.71 (d)	90.3 (d)	5.71		5.75 (d)	89.2	5.67 (d)	90.1	5.70–5.66 (m)	90.0
2	4.88 (dd)	70.3 (d)	4.88		4.91 (dd)	70.0	4.95 (dd)	69.7	4.93 (dd)	69.7
3	5.42 (t)	70.1 (d)	5.42		5.42 (t)	69.8	5.48–5.42 (m)	69.3	5.48–5.41 (m)	69.4
4	5.22 (t)	68.0 (d)	5.04		5.08 (t)	68.2	5.03 (t)	70.8	5.06 (t)	69.7
5	4.40–4.20 (m, overlap 13H signals)	69.0 (d)	4.42–4.07 (11H signals)		4.39–4.33 (m)	68.2	4.35–4.28 (m)	69.3	4.38-4.32 (m)	69.8
6a		59.7 (t)	4.42–4.07 (11H signals)	—	4.33–4.24 (m)	61.7	3.54 (dd)	31.1	3.68 (dd)	43.2
6b			4.42–4.07 (11H signals)		4.20–4.14 (m)		3.40 (dd)		3.57 (dd)	
1′a		63.7 (t)	3.71		3.69 (d)	62.2	3.79 (d)	61.5	3.75 (s)	61.6
1′b			3.62		3.63 (d)		3.73 (d)			
2′	—	104.3 (s)	—		—	103.4	—	103.8	—	103.8
3′	5.37 (d)	76.2 (d)	5.46		5.69 (d)	74.9	5.70 (d)	75.8	5.70–5.66 (m)	75.5
4′	[a]	75.3 (d)	5.32		5.46 (t)	73.7	5.48–5.42 (m)	76.4	5.48–5.41 (m)	75.7

5′	4.40–4.20 (m, overlap 13H signals)	78.1 (d)	4.42–4.07 (11H signals)		4.24–4.20 (m)	77.8	4.35–4.28 (m)	79.8	4.28–4.22 (m)	79.9
6′		62.5 (t)	4.42–4.07 (11H signals)		4.33–4.24 (m)	63.2	3.66 (d)	32.0	3.82–3.78 (m)	44.4
1′′		64.4 (t)	4.42–4.07 (11H signals)		4.24–4.20 (m)	62.7	4.24 (s)	62.0	4.28–4.22 (m)	62.2
2′′	—	103.1 (s)	—		—	102.9	—	103.1	—	103.1
3′′	5.46 (d)	76.6 (d)	5.68		5.48 (d)	76.5	5.50 (d)	77.2	5.50 (d)	76.9
4′′	[a]	76.0 (d)	5.22		5.34 (t)	75.5	5.32 (t)	78.1	5.33 (t)	77.2
5′′	4.40–4.20 (m, overlap 13H signals)	79.1 (d)	4.42–4.07 (11H signals)		4.20–4.14 (m)	78.4	4.22–4.19 (m)	80.7	4.17 (q)	80.6
6′′		62.9 (t)	4.42–4.07 (11H signals)		4.39–4.33 (m)	63.7	3.69 (d)	32.7	3.82–3.78 (m)	44.6
$J_{1,2}$	3.4		3.9		3.4		4.0		3.7	
$J_{2,3}$	10.2		9.0		10.3		10.3		10.6	
$J_{3,4}$	10.2		9.4		9.7		9.7		9.7	
$J_{4,5}$			10.0				2.3		2.3	
$J_{5,6a}$										
$J_{5,6b}$							6.3		5.7	
$J_{6a,6b}$							11.5		12.0	
$J_{1'a,1'b}$					9.2		10.3			
$J_{3',4'}$	8.6		7.0		8.0		8.0			
$J_{4',5'}$			6.0							
$J_{5',6'}$							6.9			
$J_{3'',4''}$	8.6		8.0		6.9		6.3		6.3	
$J_{4'',5''}$			8.0							
$J_{5'',6''}$							7.4		6.5	
CH_3	2.09 (s), 2.12 (s), 2.11 (s), 2.10 (s),	21.5–20.8	2.12 2.09		2.19–2.14 (m), 2.13–2.12 (m),	20.8, 20.7,	2.16–2.15 (m), 2.14 (s),	20.8, 20.8, 20.7, 20.8,	2.16 (s), 2.15–2.13 (m),	20.8, 20.7,

	2.09 (s), 2.08 (s), 2.07 (s), 2.05 (s), 2.02 (s), 2.00 (s)		2.08 2.07 1.99 1.97		2.11–2.09 (m), 2.06 (s), 2.04 (s), 2.01 (s)	20.7, 20.6, 20.6, 20.5	2.11 (s), 2.09-2.07 (m), 2.02 (s)	20.6, 20.5, 20.5, 20.5	2.11 (s), 2.09 (s), 2.08 (s), 2.07 (s), 2.02 (s)	20.7, 20.6, 20.5, 20.5
C=O		170.4–169.7				170.7, 170.6, 170.5, 170.1, 169.9, 169.7, 169.6		170.2, 170.0, 170.0, 169.8, 169.5		170.2, 170.1, 170.0, 170.0, 169.7, 169.5

[1] Pejin, B., Iodice, C., Tommonaro, G., Sabovljevic, M. Bianco, A., Tesevic , V., Vajs, V. De Rosa, S. Sugar composition of the moss *Rhodobryum ontariense* (Kindb.) Kindb. *Nat. Prod. Res*, **2012**, *26*, 209–215. https://doi.org/10.1080/14786419.2010.535163

[2] Binkley, W. W., Horton, D., Bhacca, N. S. Physical studies on oligosaccharides related to sucrose. *Cabohydr. Res*., **1969**, *10*, 245–258. https://doi.org/10.1016/S0008-6215(00)80466-8

[a]Not assign

Table SM-2. ^{1}H and ^{13}C NMR literature comparison with observation data of 1-kestose and halogenated 1-kestose derivatives

Assign-ment	**1-kestose (1)** CAS 562-68-5 (δ in ppm and J in Hz)				**6,6′,6″-Tribromo-6,6′,6″ -trideoxy-1-kestose (6)** No CAS (δ in ppm and J in Hz)		**6,6′,6″-Trichloro-6,6′,6″-trideoxy-1-kestose (7)** No CAS (δ in ppm and J in Hz)	
	Ref [1]		**Observed**		**Observed**		**Observed**	
	^{1}H in ppm (200.13 MHz, D_2O)	^{13}C in ppm (50.32 MHz, D_2O)	^{1}H in ppm (500 MHz, D_2O)	^{13}C in ppm (125 MHz, D_2O)	^{1}H in ppm (500 MHz, D_2O)	^{13}C in ppm (125 MHz, D_2O)	^{1}H in ppm (500 MHz, D_2O)	^{13}C in ppm (125 MHz, D_2O)
1	5.26	93.73	5.37 (d)	92.9	5.36 (d)	92.9	5.36 (d)	92.8
2	3.38	72.39	3.48 (dd)	71.6	3.52 (dd)	71.0	3.52 (dd)	70.1
3	3.59	73.85	3.70–3.60 (m)	73.0	3.72–3.65 (m)	72.1	3.71–3.60 (m)	72.2
4	3.30	70.48	3.41 (t)	69.6	3.43 (t)	71.4	3.47 (t)	71.6
5	3.64 3.68	73.67	3.79–3.71 (m)	72.8	4.04–3.98 (m)	71.1	4.11–4.05 (m)	71.0
6a	3.63	61.40	3.79–3.71 (m)	60.5	3.79–3.72 (m)	34.2	3.89–3.73 (m)	44.3
6b					3.72–3.65 (m)			
1′a	3.54	62.17	3.79–3.71 (m)	61.3	3.87 (d)	59.9	3.89–3.73 (m)	60.2
1′b	3.66		3.70–3.60 (m)		3.72–3.65 (m)		3.71–3.60 (m)	
2′	–	104.50	–	103.7	–	103.3	–	103.3
3′	4.12	77.92	4.22 (d)	77.0	4.27 (d)	76.4	4.26 (d)	76.4
4′	3.88	75.12	3.98 (t)	74.2	4.09–4.05 (m)	76.3	4.11–4.05 (m)	75.3
5′	3.67 3.70	82.46	3.83–3.80 (m)	81.6	4.04–3.98 (m)	80.6	4.01–3.94 (m)	80.6
6′a	3.63	63.44	3.79–3.71 (m)	62.6	3.64–3.59 (m)	33.5	3.89–3.73 (m)	45.2
6′b								
1″a	3.50	61.70	3.70–3.60 (m)	60.8	3.72–3.65 (m)	59.9	3.71–3.60 (m)	60.0
1″b	3.59							

2′′	–	104.96	–	104.2	–	103.9	–	103.9
3′′	4.02	77.94	4.13 (d)	77.0	4.16 (d)	76.9	4.16 (d)	76.6
4′′	3.91	75.74	4.02 (t)	74.9	4.09–4.05 (m)	77.4	4.11–4.05 (m)	76.2
5′′	3.69	82.36	3.83–3.80 (m)	81.5	4.04–3.98 (m)	80.4	4.01–3.94 (m)	80.5
6′′a	3.70	63.59	3.79–3.71 (m)	62.7	3.79–3.72 (m)	33.5	3.89–3.73 (m)	45.4
6′′b	3.64							
$J_{1,2}$			4.0		4.0,		4.0	
$J_{2,3}$			9.7		10.0		9.7	
$J_{3,4}$			9.7		10.0		9.7	
$J_{1'a,1'b}$					10.3			
$J_{3',4'}$			8.6		8.6		8.6	
$J_{3'',4''}$			8.6		8.6		8.6	

[1] Calub, T. M., Waterhouse, A. L., Chatterton, N. J. Proton and carbon chemical-shift assignments for 1-kestose, from two-dimensional nmr-spectral measurements. *Carbohydr. Res*, **1990**, *199*, 11–17. https://doi.org/10.1016/0008-6215(90)84088-C