Regioselective Tosylation of Aldonolactones

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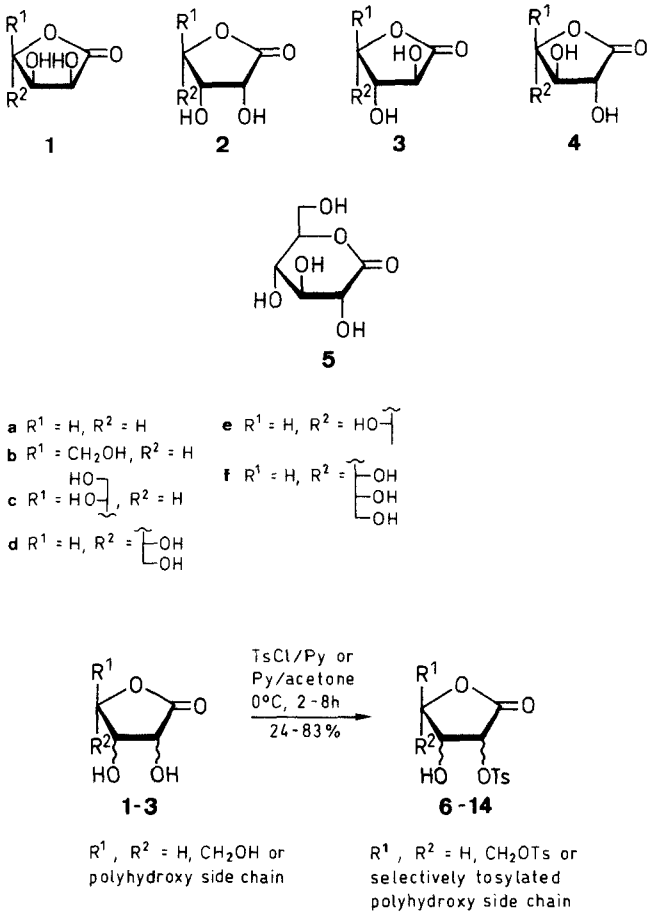
An investigation of the selective di-*O*-acylation with *p*-toluenesulfonyl (tosyl) chloride of the four D-pentono-, the eight D-hexono- and D-*glycero*-D-*gulo*-heptonolactone has been undertaken, and a number of 2,5-, 2,6- and 2,7-di-*O*-tosylated lactones have been prepared. Monotosylation of L-erythrono- and L-rhamnonolactone gave the corresponding 2-*O*-tosylates.

Selective acylation of carbohydrates with a variety of acylating agents has been studied for a long time.[1] In the case of aldonolactones, no systematic studies on such reactions have been undertaken, although some reports have appeared in the literature. Thus, 2,6-di-*O*-benzoyl-D-galactonolactone[2] and 2,5-di-*O*-tosyl-D-ribonolactone[3,4] have both been obtained by selective di-*O*-acylation of the corresponding aldonolactones. Furthermore a mono-*O*-tosylate of D-erythronolactone has been obtained by treatment of the lactone with one equivalent of *p*-toluenesulfonyl chloride,[3] while 2-*O*-mesyl-L-rhamnonolactone has been prepared by a similar monoacylation.[5]

In contrast to the pyranose derivatives[1] it seems to be impossible to acylate aldonolactones selectively at the primary position. Thus, treatment of D-ribono-1,4-lactone (**2b**) with one equivalent of *p*-toluenesulfonyl chloride leads to a mixture of 5-*O*-tosyl-, 2-*O*-tosyl- and 2,5-di-*O*-tosyl-D-ribonolactone.[6] Apparently the primary hydroxy group and the hydroxy group at C-2 are of similar reactivity. This is also confirmed by the fact that protection of the hydroxy groups at C-6 and C-2 in hexonolactones by di-*O*-silylation proceeds smoothly,[7] while attempts to monosilylate OH-7 of D-*glycero*-D-*gulo*-heptonolactone (**2f**) led to substantial amounts of the 2,7-di-*O*-silylated heptonolactone as a side reaction.[8]

We have now undertaken an investigation of the selective di-*O*-tosylation of the four D-pentonolactones **1b–4b**, the eight D-hexonolactones **1c–3c, 1d–4d** and **5**, together with L-erythrono-(**1a**), L-rhamnono-(**2e**) and D-*glycero*-D-*gulo*-heptonolactone (**2f**). The aim was to obtain aldonolactones with leaving groups at the α- and ω-positions. As a continuation of our ongoing work using α-bromo-α-deoxy- or α,ω-dibromo-α,ω-dideoxyaldonolactones as substrates for nucleophilic substitution reactions,[9,10] we wanted to extend the number of stereoisomeric lactones with leaving groups at these positions.

Tosylation of the aldonolactones was performed by dissolving them in pyridine followed by addition at 0 °C of *p*-toluenesulfonyl chloride, either neat or dissolved in acetone. Dilution of the acylating mixture with acetone gave in some cases a slightly better selectivity. Table 1 shows the reaction conditions used for preparation of the selectively tosylated aldonolactones, which could be obtained in good to acceptable yields directly by crystallization (for comments on **12**, see below).



Monotosylation of L-erythronolactone (**1a**)[11] gave the 2-*O*-tosylate **6**. A monotosylated D-erythronolactone has been described[3] but no structure was assigned to the compound. Attempts to lactonize L-threonic acid, obtained from calcium L-threonate,[12] to L-threonolactone (**4a**) were unsuccessful; neither did the acid lactonize under the tosylating conditions. Thus no monotosylated L-threonolactone could be obtained. Selective ditosylation of D-lyxonolactone (**1b**)[11] gave a high yield of the crystalline 2,5-di-*O*-tosylate **7**. D-Ribonolactone (**2b**) also yielded a 2,5-di-*O*-tosylate **8** in a yield similar to that described in the literature,[3,4] but no NMR data have been published to confirm the structure. When D-arabinonolactone (**3b**)[11] was subjected to the reaction conditions, a mixture was obtained from which the 2,5-di-*O*-tosylate **9** could be crystallized. Although D-xylono-1,4-lactone (**4b**) has been reported crystalline,[13] we found that the D-xylonic acid, obtained from the corresponding ammonium salt,[14] could not be lactonized completely in an acceptable yield. This is also in accordance with the literature.[15] Thus, no selective tosylation could be performed.

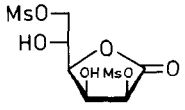
By di-*O*-tosylation of the eight isomeric D-hexonolactones **1c–3c** and **1d–4d** together with **5**, we found that D-mannono- (**1c**),[16] D-talono- (**1d**),[17] D-allono-(**2c**)[18]

and D-gulono-1,4-lactone (**2d**)[19] all gave the corresponding 2,6-di-*O*-tosylate as the main product, as indicated by ^{13}C NMR spectra. The ditosylated derivatives of mannonolactone **10** and of talonolactone **11** could be isolated by crystallization, while the ditosylated gulonolactone **12** was obtained pure by chromatography. The latter was, however, slowly converted into a 3,6-anhydride, as shown by its ^{13}C NMR spectrum. The 2,6-ditosylated allonolactone could not be completely purified by chromatography. Di-*O*-tosylation of D-altrono-(**3c**)[18] and D-idono-1,4-lactone (**3d**)[19] gave both mixtures of three compounds in about equal amounts. Similarly, D-galactono-1,4-lactone (**4d**) gave a mixture of tosyl esters. Finally, D-glucono-1,5-lactone (**5**) gave two compounds by di-*O*-tosylation, as seen from a ^{13}C NMR spectrum obtained directly on the reaction mixture. When water was added in the workup procedure, the compounds were partly hydrolyzed, and the open carboxylic acids could not be isolated by extraction.

Monotosylation of L-rhamnono-1,4-lactone (**2e**)[13] gave a high yield of the 2-*O*-tosylate **13**, while ditosylation of D-*glycero*-D-*gulo*-heptono-1,4-lactone (**2f**) gave the 2,7-di-*O*-tosylate **14** in good yield.

Comparison of the structures of the crystalline α-mono- and α,ω-di-*O*-tosylates prepared in good yields by selective tosylation, reveals that they all have the hydroxy groups at C-2 and C-3 cis-oriented. Furthermore, the selectivity was highest for lactones having also the side chain cis to the two hydroxy groups mentioned, giving the products **6, 7, 10, 13** and **14** (Table 1). When the side chain is trans to the cis-hydroxy groups at C-2 and C-3, the selectivity was lower, and only in the case of D-ribonolactone (**2b**) and D-talonolactone (**1d**) was it possible to crystallize the products, **8** and **11**, respectively. In cases where the 2- and 3-hydroxy groups are trans-oriented, it seems that the selectivity between OH-2 and OH-3 was lower. It was, although, possible to crystallize **9** from the mixture of tosylates obtained by di-*O*-tosylation of D-arabinonolactone (**3b**).

We have also investigated the selective di-*O*-mesylation of D-mannono- (**1c**), D-allono-(**2c**) and D-gulono-1,4-lactone (**2d**). In all three cases it was possible to crystallize directly the 2,6-di-*O*-mesylates **15** (42%), **16** (16%) and **17** (27%). The yields were lower compared to the tosylation reactions, indicating a lower selectivity. This appears to be more general, since the reported yield of 2-*O*-mesyl-L-rhamnonolactone was lower (60%)[5] compared to the yield of the 2-*O*-tosyl-derivatives **13** (83%) found in this work.



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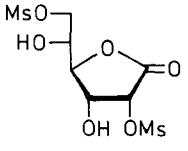

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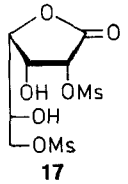

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The structures of the selectively tosylated and mesylated lactones were proven from ^1H and ^{13}C NMR spectra in combination with the CH-correlated spectra (Table 2).

In conclusion, we found that by selective di-*O*-tosylation of aldonolactones the OH-2 and the primary hydroxy group were tosylated at the same rate, and that the selectivity was good for aldonolactones of the type **1** having R^1 as the side chain, and of the type **2** having R^2 as the side chain. Eight crystalline α-mono- and α,ω-di-*O*-tosylated aldonolactones were prepared (Table 1) together with three 2,6-di-*O*-mesylated hexonolactones.

Melting points are uncorrected. Optimal rotations were determined on a Perkin-Elmer 241 polarimeter. NMR spectra were recorded on Bruker AC-250 and AM-500 instruments. All NMR spectra were recorded in acetone-d_6, which was also used as internal reference, $\delta = 29.8$ for ^{13}C NMR spectra, and $\delta = 2.05$ for ^1H NMR spectra. ^{13}C NMR signals were assigned through CH-correlated NMR experiments. Column chromatography was performed on silica gel (40–63 μm, Merck 9385) using the flash technique. Spots were visualised on TLC by charring with sulfuric acid. Microanalyses were performed by Leo Microanalytical Laboratory. Pyridine was kept over KOH, and acetone was kept over $MgSO_4$.

The following lactones are commercially available: D-ribonolactone (**2b**) (Vitaminfabrikken BASF, Grenå, Denmark) D-gluconolactone (**5**) (Fluka); D-galactonolactone (**3d**) (Sigma); and D-*glycero*-D-*gulo*-heptonolactone (**2f**) (Sigma). Literature methods, as indicated in the text and Table 1, were used for preparation of the remaining lactones.

Selective Tosylation of Aldonolactones (Table 1); General Procedure:
The lactone (5.0 g) was dissolved in dry pyridine (25 mL), at 0°C. While stirring, TsCl (amounts given in Table 1) was added during 10 min. The TsCl was added either neat, or as a solution in acetone (25 mL) as indicated in Table 1. The mixture was stirred at 0°C for the period given, after which time 6 M HCl was added until pH 1. Extracting with EtOAc (3 × 30 mL), drying (Na_2SO_4), and concentration gave a residue which was crystallized from $CHCl_3$, and recrystallized from the solvent indicated (Tables 1 and 2).

2,6-Di-*O*-methanesulfonyl-D-mannono-1,4-lactone (15):
Following the general procedure, D-mannonolactone (**1c**)[16] (6.0 g, 0.034 mol) in pyridine (20 mL) and methanesulfonyl chloride (9.5 g, 2.5 eq.) in acetone (20 mL) gave after reaction for 3 h at 0°C and workup, a residue, which crystallized from EtOAc to give **15**; yield: 4.77 g (42%), m.p. 148–149°C and was pure as indicated by ^{13}C NMR. An analytical sample was obtained by recrystallization from acetone/EtOAc; mp 167–168°C; $[\alpha]_D^{20}$ + 37° (*c* = 3, acetone).

$C_8H_{14}O_{10}S_2$	calc.	C 28.74	H 4.22	S 19.18
(334.3)	found	29.13	4.33	18.73

^1H NMR: δ = 3.15, 3.32 (2 s, 3 H each, 2 × CH_3), 4.35 (m, 2 H, H-5,6), 4.50 (dd, 1 H, H-6'), 4.60 (dd, 1 H, $J_{4,5}$ = 9 Hz, H-4), 4.89 (dd, 1 H, $J_{3,4}$ = 3 Hz, H-3), 5.67 (d, 1 H, $J_{2,3}$ = 4 Hz, H-2).

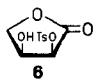
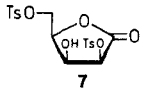
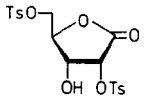
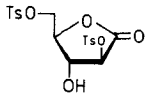
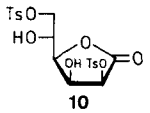
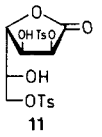
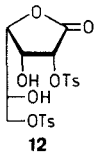
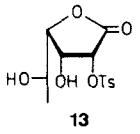
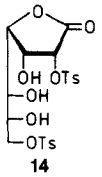
^{13}C NMR: δ = 37.2, 39.1 (2 × CH_3), 66.3 (C-5), 69.2 (C-3), 72.3 (C-6), 77.1 (C-2), 78.8 (C-4), 170.8 (C-1).

2,6-Di-*O*-methanesulfonyl-D-allono-1,4-lactone (16):
D-Allonolactone (**2c**;[18] 5 g, 0.028 mol) was mesylated as described above to give a crude product, which was crystallized from EtOAc to give **16** (1.48 g, 16%), mp 139–140°C, homogeneous according to a ^{13}C NMR spectrum. An analytical sample was obtained by recrystallization from EtOAc/acetone; mp 143–144°C; $[\alpha]_D^{20}$ + 9.4° (*c* = 3, acetone).

$C_8H_{14}O_{10}S_2$	calc.	C 28.74	H 4.22	S 19.18
(334.3)	found	28.87	4.22	19.04

^1H NMR: δ = 3.17, 3.31 (2 s, 3 H each, 2 × CH_3), 4.28 (m, 1 H, H-5), 4.38 (dd, 1 H, $J_{5,6}$ = 6 Hz, H-6), 4.44 (dd, 1 H, $J_{5,6'}$ = 4 Hz, $J_{6,6'}$ = 11 Hz, H-6'), 4.60 (d, 1 H, $J_{3,4}$ = O, $J_{4,5}$ = 4 Hz, H-4), 4.86 (d, 1 H, H-3), 5.59 (d, 1 H, $J_{2,3}$ = 5 Hz, H-2).

Table 1. α-Mono- and α,ω-di-*O*-Tosylaldono-1,4-lactones from Selective Tosylation of Aldonolactones[a]

Substrate	Reaction Conditions: TsCl (equiv)/ Solvent[b]/Time (h)	Product	Yield (%)	mp (°C)[c]	Analytical Sample, mp (°C) (solvent)	$[\alpha]_D^{20}$ (*c*, acetone)	Molecular Formula[d] Lit. mp (°C) or $[\alpha]_D$ (solvent)
1a[11]	1.1/B/3	 **6**	80	167–168	177–179 (EtOAc)	+45° (2.0)	172–173 and 183–184[3] (for the enantiomer)
1b[11]	2.2/A/2	 **7**	76	104–106	128–129 (EtOAc/hexane)	+59° (1.0)	$C_{19}H_{20}O_9S_2$ (456.5)
2b	2.3/B/5	 **8**	45	114–116	119–121 (EtOAc/hexane)	+7.3° (2.0)	122; +2° ($CHCl_3$)[4] 122–125; +9° (EtOH)[3]
3b[11]	2.2/B/8	 **9**	24	111–115	129–131 ($CHCl_3$)	+43° (2.0)	$C_{19}H_{20}O_9S_2$ (456.5)
1c[16]	2.0/A/2	 **10**	77	138–140	142–143 ($CHCl_3$)	+47° (2.0)	$C_{20}H_{22}O_{10}S_2$ (486.5)
1d[17]	2.2/B/3	 **11**	30	116–118	117–118 ($CHCl_3$)	−17° (2.0)	$C_{20}H_{22}O_{10}S_2$ (486.5)
2d[19]	2.3/B/3	 **12**	44	syrup	–	−38° (3.0)	$C_{20}H_{22}O_{10}S_2$[e] (486.5)
2e[13]	1.1/A/2	 **13**	83	178–185	183–185 ($CHCl_3$)	−57° (1.0)	$C_{13}H_{16}O_7S$ (316.3)
2f	2.2/B/3	 **14**	64	132–134	146–147 (acetone/$CHCl_3$)	−38° (2.0)	$C_{21}H_{24}O_{11}S_2$ (516.6)

[a] The tosylations were carried out in 5–10 g seale, except for **2d** (0.5 g).

[b] A: pyridine; B: pyridine/acetone (1 : 1).

[c] Melting point of products obtained by direct crystallization of the crude product from $CHCl_3$. The products were found to be homogeneous according to ^{13}C NMR spectra.

[d] Satisfactory microanalyses obtained: C ±0.2, H ±0.15, S ±0.2.

[e] Not analysed for C, H, S values.

^{13}C NMR: δ = 37.2, 39.2 (2 × CH_3), 68.3 (C-3), 69.2 (C-5), 70.9 (C-6), 75.4 (C-2), 86.4 (C-4), 171.2 (C-1).

2,6-Di-*O*-methanesulfonyl-D-gulono-1,4-lactone (17):
D-Gulonolactone (**2d**;[19] 5 g, 0.028 mol) was mesylated as above to give a crude product which crystallized from EtOAc to give **17**; yield: 2.52 g (27%), mp 128–129°C, homogeneous according to its ^{13}C NMR spectrum. An analytical sample was obtained by recrystallization from acetone/EtOAc; mp 141–142°C; $[\alpha]_D^{20}$ −1.5° (*c* = 3, acetone).

$C_8H_{14}O_{10}S_2$ (334.3)	calc.	C 28.74	H 4.22	S 19.18
	found	28.80	4.28	19.13

^1H NMR: δ = 3.17, 3.32 (2 s, 3 H each, 2 × CH_3), 4.35 (m, 1 H, H-5), 4.46 (dd, 1 H, $J_{5,6}$ = 4 Hz, H-6), 4.47 (dd, 1 H, $J_{5,6'}$ = 4 Hz, H-6'), 4.69 (dd, 1 H, $J_{4,5}$ = 8 Hz, H-4), 4.90 (dd, 1 H, $J_{3,4}$ = 3 Hz, H-3), 5.66 (d, 1 H, $J_{2,3}$ = 5 Hz, H-2).

^{13}C NMR: δ = 37.2, 39.1 (2 × CH_3), 69.0 (C-5), 69.7 (C-3), 71.3 (C-6), 77.0 (C-2), 81.2 (C-4), 170.8 (C-1).

Table 2. NMR-Data of Compounds **6–14** Prepared[a]

Compound	^{1}H NMR (acetone-d_6) δ, J (Hz)	^{13}C NMR (acetone-d_6)
6	4.26 (d, 1H, $J_{3,4}$ = 0, H-4), 4.51 (dd, 1H, $J_{3,4'}$ = 3, $J_{4,4'}$ = 10, H-4'), 4.60 (ddd, 1H, H-3), 5.42 (d, 1H, $J_{2,3}$ = 5, H-2)	68.8 (C-3), 73.2 (C-4), 76.0 (C-2), 170.5 (C-1)
7	4.26 (dd, 1H, H-5), 4.45 (dd, 1H, $J_{5,5'}$ = 11, H-5'), 4.72 (m, 1H, H-3), 4.86 (ddd, 1H, $J_{3,4}$ = 3, $J_{4,5'}$ = 3, $J_{4,5}$ = 8, H-4), 5.50 (d, 1H, $J_{2,3}$ = 4, H-2)	69.1 (C-5), 69.3 (C-3), 76.2 (C-2), 78.5 (C-4), 169.6 (C-1)
8	4.39 (dd, 1H, H-5), 4.46 (dd, 1H, $J_{5,5'}$ = 12, H-5'), 4.50 (ddd, 1H, H-3), 4.68 (ddd, 1H, $J_{3,4}$ = 1, $J_{4,5'}$ = 4, $J_{4,5}$ = 3, H-4), 5.25 (d, 1H, $J_{2,3}$ = 5, H-2)	69.0 (C-3), 69.1 (C-5), 74.6 (C-2), 83.6 (C-4), 169.6 (C-1)
9	4.34 (dd, 1H, H-5), 4.43 (dd, 1H, $J_{5,5'}$ = 12, H-5'), 4.50 (ddd, 1H, H-3), 4.55 (ddd, 1H, $J_{3,4}$ = 8, $J_{4,5'}$ = 2, $J_{4,5}$ = 5, H-4), 5.52 (d, 1H, $J_{2,3}$ = 8, H-2)	68.3 (C-5), 72.0 (C-3), 78.6 (C-4), 80.7 (C-2), 168.0 (C-1)
10	4.08 (dd, 1H, $J_{5,6}$ = 5, H-6), 4.21 (m, 1H, H-5), 4.22 (dd, 1H, $J_{5,6'}$ = 2, $J_{6,6'}$ = 11, H-6'), 4.45 (d, 1H, $J_{4,5}$ = 9, H-4), 4.62 (m, 1H, $J_{3,4}$ = 3, H-3), 5.51 (d, 1H, $J_{2,3}$ = 4, H-2)	66.1 (C-5), 69.1 (C-3), 72.3 (C-6), 76.8 (C-2), 78.5 (C-4), 169.7 (C-1)
11	3.96 (dd, 1H, H-6), 4.12 (dd, 1H, $J_{6,6'}$ = 10, H-6'), 4.29 (m, 1H, $J_{4,5}$ = 1, $J_{5,6'}$ = 5, $J_{5,6}$ = 8, H-5), 4.55 (m, 2H, H-3, 4), 5.42 (d, 1H, $J_{2,3}$ = 5, H-2)	68.8 (C-5), 70.5 (C-6), 70.6 (C-3), 74.9 (C-2), 86.0 (C-4), 170.5 (C-1)
12	4.22–4.24 (m, 3H, H-5, 6, 6'), 4.56, 4.57 (m, 1H each, H-3, 4), 5.50 (d, 1H, $J_{2,3}$ = 4, H-2)	68.6 (C-5), 69.5 (C-3), 71.3 (C-6), 76.6 (C-2), 80.8 (C-4), 169.8 (C-1)
13	1.26 (d, 3H, H-6), 4.13 (m, 1H, $J_{5,6}$ = 6, H-5), 4.19 (dd, 1H, $J_{4,5}$ = 8, H-4), 4.66 (ddd, 1H, $J_{3,4}$ = 3, H-3), 5.45 (d, 1H, $J_{2,3}$ = 4, H-2)	20.4 (C-6), 64.1 (C-5), 69.4 (C-3), 77.1 (C-2), 83.6 (C-4), 170.3 (C-1)
14	3.91 (m, 1H, H-6), 4.01 (ddd, 1H, $J_{5,6}$ = 8, H-5), 4.11 (dd, 1H, $J_{6,7}$ = 6, H-7), 4.30 (dd, 1H, $J_{6,7'}$ = 3, $J_{7,7'}$ = 10, H-7'), 4.71 (d, 1H, $J_{4,5}$ = 5, H-4), 4.77 (d, 1H, $J_{3,4}$ = 3, H-3), 5.50 (d, 1H, $J_{2,3}$ = 4, H-2)	69.8 (C-6), 70.8 (C-5), 71.4 (C-3), 72.6 (C-7), 76.4 (C-2), 79.9 (C-4), 170.1 (C-1)

[a] Acetone-d_6 was also used as internal standard, δ = 2.05 for ^{1}H NMR spectra and δ = 29.8 for ^{13}C NMR spectra. The reiterating signals of the tosyl group are omitted in the ^{1}H (δ = ca. 2.45 for CH_3 and δ = 7.4–7.9 for the aromatic protons) and ^{13}C (δ = 21.5 for CH_3 and δ = 128–147 for the C-aromatic carbons) spectra.

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