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# Rapid Access to 1,6-Anhydro-β-L-hexopyranose Derivatives via Domino Reaction: Synthesis of L-Allose and L-Glucose

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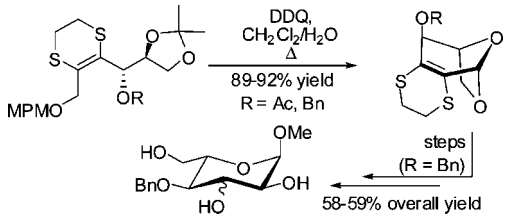


An expeditious and efficient synthesis of 1,6-anhydro-β-L-hexopyranosyl derivatives **3** as valuable building blocks for the preparation of L-sugars is herein reported. This route relies upon the use of a domino reaction involving five synthetic steps from the 5,6-dihydro-1,4-dithiin **4**. As 1,6-anhydro derivatives **3** are obtained, dithioethylene bridge removal and double-bond dihydroxylation give access to protected L-allose and L-glucose in stereoselective fashion and high yields.

1,6-Anhydrohexopyranoses are useful synthons for the synthesis of complex natural products and bioactive molecules.[1] Indeed, their [3.2.1]bicyclic skeleton enables high regio- and stereocontrolled reactions; likewise, it does not require the use of protecting groups at C1 and C6 positions.[2]

From a stereochemical standpoint, one of the most intriguing features of the 1,6-anhydrohexose framework is represented by the locked conformation of the pyranose ring, with stereocenters in opposite orientation compared to the corresponding pyranosides (Figure 1).

Several efficient methods have been devised to gain access to 1,6-anhydro-β-hexopyranoses belonging to D-series, including cyclization of hexose derivatives under acidic[3] or alkaline[4] conditions and Lewis acid[5] or halonium ion[6]-catalyzed intramolecular rearrangement of D-glycal derivatives. Conversely, only a few approaches for the synthesis of L-series 1,6-anhydrosugars are reported;[7] nevertheless, considering their potential use as chiral building blocks in rare sugar-containing natural product synthesis,[8] their preparation still represents a challenging subject of investigation.

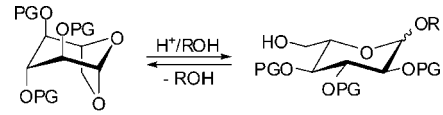


**FIGURE 1.** Chair conformation of 1,6-anhydro-β-L-hexopyranoses ($^4C_1$) and L-hexopyranosides ($^1C_4$).

As part of our efforts working toward the de novo synthesis of L-sugars,[9] a complementary approach to such molecules is herein proposed through the preparation of 1,6-anhydro-β-L-hexopyranoses, taking advantage of their stereochemical features.

We have recently reported[9] a new synthetic methodology for the stereoselective synthesis of L-hexoses, based on the use of our 1,2-bis-thioenol ether synthon **1**, acting as a three-carbon homologating agent[10] and 2,3-*O*-isopropylidene-L-glyceraldehyde (**2**) (Scheme 1). To our regret, although L-*manno*- and L-*altro*-hexopyranosides were easily synthesized, the strategy proved to be unsuitable for the preparation of the remaining epimers with *gluco*-configuration, therefore requiring a different approach. On the other hand, the 1,6-anhydro derivative **3**, which occurred as a byproduct at the beginning of our experiments, holds the favorable stereochemical requirements to be conveniently used for the synthesis of L-*gluco* and L-*allo*-pyranosides. For this purpose, we devoted our efforts to the development of an efficient method for 1,6-anhydrosugar preparation.

A first approach to anhydro compound **3** is depicted in Scheme 2. As the coupling reaction between **1** and **2** was accomplished, the *anti*-adduct was easily separated from its *syn*-diastereomer by flash chromatography.[9] Benzylation or acetylation of the secondary hydroxyl group led almost quantitatively to derivatives **4**. Then, MPM group removal by treatment of **4** with DDQ in a $CH_2Cl_2/H_2O$ emulsion led to alcohols **5**

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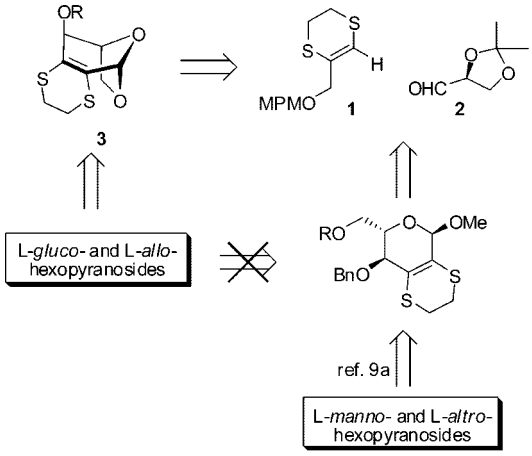
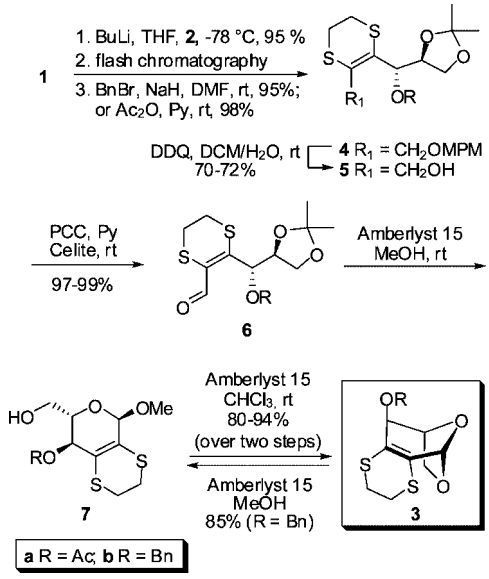
**SCHEME 1. Retrosynthetic Path**




**SCHEME 2. Synthesis of 1,6-Anhydro Compounds 3**




(70−72% yield), which were next oxidized by means of PCC in pyridine, affording the aldehydes **6** (97−99% yield). Subsequently, exposure of **6** to Amberlyst 15 in MeOH afforded bicycle compounds **7** as an $\alpha/\beta$ (85/15) anomeric mixture. The bicycle system resulted fairly unstable even to mild acidic conditions giving degradation products in addition to the stable adducts **3**. Intrigued by this finding, we then directed our efforts on the achievement of the complete conversion of bicycles **7** into the 1,6-anhydrosugar derivatives **3**. Best results were gained by direct treatment of **7** with Amberlyst 15, replacing the nucleophilic methanol with the weakly acidic chloroform. After only 30 min, the desired 1,6-anhydro-$\beta$-L-hexopyranose derivatives **3** were isolated in very good (80−94%) yields (Scheme 2). Interestingly, treatment of **3b** with Amberlyst in MeOH again restored bicycle compound **7b** (85% yield).

Although this route gave access to desired 1,6-anhydro compounds with satisfactory yields (56−65% overall yield), a more rapid and efficient procedure could be planned, considering that (a) the 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a reagent capable of removing the MPM protective group

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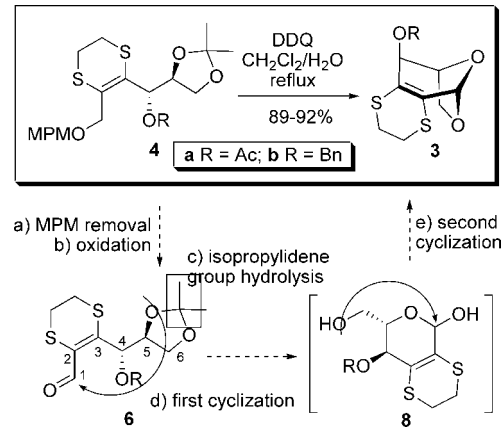
**SCHEME 3. Proposed Path for the Synthesis of 1,6-Anhydro Sugar Derivatives 3 by Domino Reaction**




affording, depending on the conditions used, an alcohol[10] or a formyl[11] function; (b) the use of DDQ in protic solvents generates an acidic environment, owing to the evolution of HCN;[12] and (c) isopropylidene group and formyl function can be respectively removed and activated under such conditions.

On the basis of these realizations, experiments were carried out to establish suitable conditions for a direct double cyclization starting from intermediates **4**, with the aim to obtain the 1,6-anhydrosugar intermediates **3** by a domino reaction.[13] As a result, the use of an excess of DDQ (2.0 equiv) in a refluxing 18:1 $CH_2Cl_2/H_2O$ emulsion[14] and more prolonged reaction times (48−56 h) resulted in a sequence of five synthetic transformations, affording **3** in excellent 89−92% yields. In addition, the reaction was compatible with both acetyl and benzyl derivatives, which displayed similar reactivity. Formally, the following reactions took place (Scheme 3): MPM protecting group removal, oxidation of the resulting primary hydroxyl function to yield aldehyde **6**, isopropylidene group removal with subsequent attack by C5 hydroxyl group on the activated formyl function to give the hemiacetal **8**, and further ring closure by means of the C6 hydroxyl attack on the C1 position. Reaction could be stopped at the stage of aldehyde **6**, which was indeed isolable during the course of the reaction; conversely, hemiacetal **8** could not be detected.

As previously emphasized, compounds **3** represented profitable intermediates to have an easy access to L-hexoses; for this purpose, benzyl ether **3b** was chosen for further elaborations.

Dithioethylene bridge removal by treatment of **3b** with Ni/Ra at 0 °C afforded the unsaturated 1,6-anhydro-$\beta$-L-hexopyranose **9** in 75% yield (Scheme 4). As previously reported[9a,10] for similar substrates, when the desulfurization reaction was carried out with a Raney-Ni excess, the over-reduction product was obtained in satisfactory yield (82%), affording the 2,3-dideoxy-1,6-anhydro-$\beta$-L-hexopyranose **10**.

Double-bond functionalization of olefin **9** provided the desired hexoses **12** and **15**. In particular, stereoselective *syn*-dihydroxylation was first explored. Treatment of **9** with $OsO_4$ in pyridine[2] led to 1,6-anhydro derivative **11** with complete selectivity and

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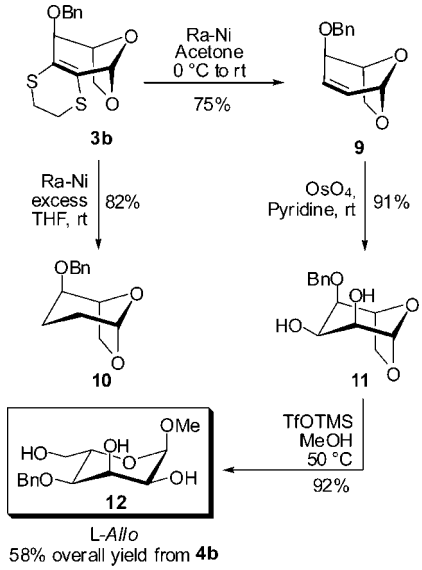
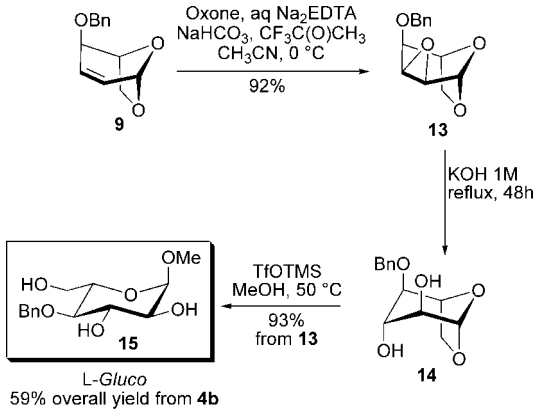
(14) A 10-fold more concentrated mixture with respect to DDQ-mediated MPM removal was also required to accomplish this synthetic sequence.

**SCHEME 4. Dithioethylene Bridge Removal of 3b and *syn*-Dihydroxylation of 9**




**SCHEME 5. *anti*-Dihydroxylation of 9**




in 91% yield, the attack being driven on the less hindered face of the olefin. Hence, stereoselective acetal ring opening was studied. Exposure of **11** to HCl in MeOH provided an anomeric mixture of the resulting methyl pyranosides without significant selectivity,[15] whereas treatment with a weaker acidic agent, such as TFA, did not display any reactivity. Eventually, best results were attained exposing **11** to a catalytic amount of TfOTMS in MeOH, allowing smooth acetal cleavage with complete α-selectivity at the anomeric center and in almost quantitative yield to give the methyl 4-*O*-benzyl-α-L-*allo*-pyranoside (**12**, 58% overall yield from compound **4b**).

Finally, *anti*-dihydroxylation was considered (Scheme 5). The allylic ether **9** was stereoselectively oxidized with in situ generated methyl(trifluoromethyl)dioxirane (TFDO) to afford the 1,6:2,3-dianhydro-*β*-L-hexopyranose **13**, the L-enantiomer of the so-called "Černý epoxide",[1a] in 92% yield. Subsequent 2,3-oxirane ring opening by means of refluxing KOH solution led to dihydroxylated product **14**. The direct treatment of the latter with catalytic TfOTMS in MeOH easily brought on 1,6-anhydro ring cleavage, leading to methyl 4-*O*-benzyl-α-L-*gluco*-hexopyranoside (**15**, Scheme 5) as a single anomer and in excellent yield (93% over two steps, 59% overall yield from compound **4b**).

In summary, a straightforward approach to L-form 1,6-anhydrosugar derivatives **3** has been herein reported. Key to the successful outcome of our procedure has been the use of a domino reaction, formally involving five synthetic steps from derivatives **4** (with yields ranging from 89 to 92%). Considering the relatively short number of synthetic steps and the high yields occurred, this route is to be considered amenable to multigram scale preparation.

In this paper, the intermediate **3b** have been used as building blocks to stereoselectively afford L-*allo*- and L-*gluco*-hexopyranosides **12** and **15**, therefore completing the synthesis of L-hexoses belonging to *gluco* configuration. Likewise, this methodology represents a powerful tool for further synthetic tasks, i.e. the construction of more complex organic molecules in high selectivity for application in medicinal chemistry.

## Experimental Section

**General Procedure 1,6-Anhydrosugar Ring-Closure Compound 3b. Method A.** Amberlyst 15 (5.5 g, previously washed with anhydrous MeOH) was added to a stirred solution of aldehyde **6b** (0.55 g, 1.5 mmol) in methanol (50 mL) at 0 °C. After 10 min, the suspension was warmed to room temperature and stirred for 1 h. Then the solid was filtered off and washed with AcOEt; the organic phase, diluted with AcOEt, was washed with brine until neutral, dried ($Na_2SO_4$), and concentrated under reduced pressure. The crude residue was dissolved in $CHCl_3$ (90 mL), and Amberlyst 15 (5.5 g, previously washed with anhydrous $CHCl_3$) was added in one portion at 0 °C. After 10 min, the suspension was warmed to room temperature and further stirred for 1 h. Then the solid was filtered off and washed with $CHCl_3$, and the resulting solution washed with saturated $NaHCO_3$ solution and brine. The organic layers were dried ($Na_2SO_4$), and the solvent was evaporated. Chromatography of the crude residue over silica gel (hexane/acetone = 90:1) gave the pure **3b** (0.44 g, 94% overall yield).

**Method B.** To a stirred 18:1 $CH_2Cl_2/H_2O$ emulsion (7 mL) containing the ether **4b** (0.48 g, 1.0 mmol) was added DDQ (0.45 g, 2.0 mmol) at room temperature, and then the reaction was warmed until reflux and stirred for 48 h. Then $H_2O$ was added, and the mixture was extracted with $CH_2Cl_2$; the organic layer was dried ($Na_2SO_4$) and the solvent evaporated. Chromatography of the crude residue (hexane/acetone = 9:1) gave pure **3b** (0.28 g, 92% yield): white solid; mp 132.3−134.4 °C (from MeOH); $[\alpha]^{25}_D$ +12.5 (*c* 1.2, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.16−3.29 (m, 4H), 3.56 (dd, $J$ = 2.0 Hz, $J$ = 7.7 Hz, 1H), 3.58 (d, $J$ = 1.0 Hz, 1H), 3.98 (dd, $J$ = 6.8 Hz, $J$ = 7.7 Hz, 1H), 4.72 (s, 2H), 4.80−4.82 (m, 1H), 5.24 (s, 1H), 7.29−7.44 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 27.6, 27.7, 64.0, 70.2, 76.6, 77.0, 98.8, 118.9, 126.8, 127.7, 128.0, 128.3, 137.9. Anal. Calcd for $C_{15}H_{16}O_3S_2$: C, 58.41; H, 5.23; S, 20.79. Found: C, 58.59; H, 5.25; S, 20.71.

***syn*-Dihydroxylation: 1,6-Anhydro-4-*O*-benzyl-*β*-L-*allo*pyranose (11).** To a solution of **9** (0.15 g, 0.69 mmol) in pyridine (5.0 mL), cooled at 0 °C, was added $OsO_4$ (0.17 g, 0.69 mmol), and the resulting mixture was stirred overnight at room temperature; then the reaction was quenched with a saturated $NaHSO_3$ solution and evaporated under reduced pressure. Chromatography of the crude residue over silica gel ($CH_2Cl_2$/MeOH = 95/5) afforded pure **11** (0.16 g, 91% yield) as single diastereomer: white crystals; mp 109.0−110.3 °C (from hexane/acetone); $[\alpha]^{25}_D$ +71.1 (*c* 0.8, $CHCl_3$) [lit.[16] data for *ent*-**11**: mp 113 °C, $[\alpha]^{25}_D$ −79.0 and mp 109−111 °C, $[\alpha]^{25}_D$ −76.0)]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.61 (bs, 1H), 2.82 (bs, 1H), 3.60 (bt, $J$ = 1.8 Hz, 1H), 3.70 (dd, $J$ =

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5.4 Hz, $J$ = 7.4 Hz, 1H), 3.87 (dd, $J$ = 1.8 Hz, $J$ = 5.6 Hz, 1H), 4.02−4.08 (m, 1H), 4.12 (d, $J$ = 7.4 Hz, 1H), 4.57 (bd, $J$ = 5.4 Hz, 1H), 4.62 (d, $J$ = 12.4 Hz, 1H), 4.64 (d, $J$ = 12.4 Hz, 1H), 5.40 (s, 1H), 7.28−7.42 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 64.8, 66.6, 68.8, 71.5, 74.0, 78.2, 101.4, 127.7, 127.9, 128.5, 137.4. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.71; H, 6.41.

**Epoxidation: 1,6:2,3-Dianhydro-4-*O*-benzyl-*β*-L-*allo*pyranose (13).** $Na_2EDTA$ ($4.0 \times 10^{-4}$ M, 3.45 mL) and $CF_3COCH_3$ (0.61 mL) were added to a solution of **9** (0.15 g, 0.69 mmol) in $CH_3CN$ (6.9 mL) at 0 °C. After a few minutes, a mixture of $NaHCO_3$ (0.43 g) and Oxone (1.72 g) was added over 1 h, and the whole resulting mixture was stirred for 30 min at the same temperature. Then the reaction was diluted with $H_2O$ and extracted with $CH_2Cl_2$. The extracts were washed with brine, dried ($Na_2SO_4$), and evaporated under reduced pressure. Chromatography of the crude residue over silica gel (hexane/acetone = 8:2) afforded the pure **13** (0.15 g, 92% yield) as a single diastereoisomer: white solid; mp 74.2−76.0 °C (from MeOH); $[\alpha]^{25}_D$ −117.3 (*c* 1.8, $CHCl_3$) [lit.[17] data for *ent*-**13**: mp 74.0−76.0 °C, $[\alpha]^{25}_D$ +127.0 and mp 75.0−79.0 °C, $[\alpha]^{25}_D$ +119.0]; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.09 (dd, $J$ = 0.9 Hz, $J$ = 4.4 Hz, 1H), 3.29−3.34 (m, 1H), 3.45 (d, $J$ = 4.4 Hz, 1H), 3.62 (dd, $J$ = 1.9 Hz, $J$ = 7.8 Hz, 1H), 3.88 (appt, $J$ = 7.1 Hz, $J$ = 7.8 Hz, 1H), 4.51 (dt, $J$ = 1.9 Hz, $J$ = 7.1 Hz, 1H), 4.74 (d, $J$ = 12.4 Hz, 1H), 4.87 (d, $J$ = 12.4 Hz, 1H), 5.65 (d, $J$ = 0.9 Hz, 1H), 7.28−7.47 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 47.5, 47.8, 65.4, 70.7, 72.3, 75.4, 97.1, 127.8, 127.9, 128.4, 137.6. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.87; H, 6.04.

**1,6-Anhydro-4-*O*-benzyl-*β*-L-*gluco*pyranose (14).** The epoxide **13** (0.14 g, 0.60 mmol) was refluxed for 48 h in a 1 M aqueous solution of KOH (8 mL). Then 1 N HCl was carefully added at 0 °C until neutrality. The white solid was filtered off and washed with AcOEt and the solvent removed under reduced pressure to afford crude **14**, which was directly used in the next reaction. A sample of crude **14** was purified by $SiO_2$ chromatography ($CH_2Cl_2$/MeOH = 95/5) and characterized: white crystals; mp 51−53; $[\alpha]^{25}_D$ +40.2 (*c* 1.5, EtOH) [lit.[18] data for *ent*-**14**: mp 53.0−54.0 °C, $[\alpha]^{25}_D$ −43.0 and mp 50.0−52.0 °C, $[\alpha]^{25}_D$ −41.0]; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.52 (bs, 1H), 2.75 (bs, 1H), 3.45 (s, 1H), 3.55 (bs, 1H), 3.78 (dd, $J$ = 5.4 Hz, $J$ = 7.8 Hz, 1H), 3.94 (bs, 1H), 4.15 (d, $J$ = 7.8 Hz, 1H), 4.63 (bd, $J$ = 7.3 Hz, 1H), 4.66 (d, $J$ = 11.7 Hz, 1H), 4.70 (d, $J$ = 11.7 Hz, 1H), 5.52 (s, 1H), 7.30−7.40 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 65.3, 69.8, 70.4, 71.3, 74.3, 76.6, 102.0, 127.6, 127.8, 128.4, 137.0. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 62.12; H, 6.52.

**Methyl 4-*O*-Benzyl-α-L-*gluco*pyranoside (15).** The crude **14**, coevaporated three times with toluene, was dissolved in MeOH (10 mL), and a catalytic amount of TfOTMS (10.9 $\mu$L, 0.06 mmol) was added. The resulting reaction mixture was stirred at 50 °C for 48 h, and then the reaction was quenched with solid $NaHCO_3$ and the solvent evaporated under reduced pressure. Chromatography of the crude residue over silica gel ($CH_2Cl_2$/MeOH = 9/1) gave the pure **15** (0.16 g, 93% yield from **13**): white crystals; mp 125−127 °C; $[\alpha]^{25}_D$ −144.2 (c 1.2, MeOH) [lit.[19] data for *ent*-**15**: mp 126.0−127.0 °C, $[\alpha]^{25}_D$ +154.0]; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.41 (s, 3H), 3.46 (t, $J$ = 9.5 Hz, 1H), 3.51 (dd, $J$ = 3.1 Hz, $J$ = 9.5 Hz, 1H), 3.65 (dt, $J$ = 3.2 Hz, $J$ = 9.5 Hz, 1H), 3.67−3.73 (m, 1H), 3.76 (dd, $J$ = 3.2 Hz, $J$ = 11.7 Hz, 1H), 3.84 (dd, $J$ = 3.2 Hz, $J$ = 11.7 Hz, 1H), 3.86 (t, $J$ = 9.5 Hz, 1H), 4.73 (d, $J$ = 11.2 Hz, 1H), 4.77 (d, $J$ = 3.1 Hz, 1H), 4.87 (d, $J$ = 11.2 Hz, 1H), 7.25−7.38 (m, 5H); $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ 54.0, 60.8, 61.3, 72.3, 74.0, 74.3, 78.0, 99.7, 127.1, 127.5, 127.7, 138.5. Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 58.95; H, 7.06.

**Acknowledgment.** $^1$H and $^{13}$C NMR spectra were performed at Centro Interdipartimentale di Metodologie Chimico-Fisiche (CIMCF), Università di Napoli Federico II.

**Supporting Information Available:** Experimental procedures, full spectroscopic data, and copies of NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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