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Larger Scale Photochemical Bromination of Toluene, 1-Methylnaphthalene and Acetophenone in Aqueous Biphasic System and Applications of the Crude Products in Synthesis

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Abstract

Photochemical bromination of toluene up to 300 mmol per run in aqueous biphasic system formed benzyl bromide of sufficient purity to be used directly for benzylations without any purification. 1-Methylnaphthalene and acetophenone react similarly. An approach to (R) and (S) 1-O-triphenylmethyl-glycerol is presented based on L- and D-xylose.

Subject Areas

Organic Chemistry

Keywords

Alkylation, Anticancer, Photochemical Bromination, Phase Transfer Catalysis

1. Introduction

Benzyl bromide is frequently used in Organic Chemistry. Even though the compound is available commercially, many methods to synthesize it have been published. The selected literature shows the procedures to get benzyl bromide with variable degrees of complexity starting form benzaldehyde dialkyl acetals ($SnBr_2$, AcBr, Et_3SiH) [1], benzene (H_2CO, HBr) [2], benzyl acetate (1,1-dibromomethyl methyl ether) [3], benzyl alcohol (P_2O_5-KBr [4], TMSBr [5], NH_4Br-ionic liquid-microwave [6], pyridinium bromide ionic liquid-pTSA [7], $SOBr_2$-perfulorohexane [8], PBr_3 [9], $(COBr)_2$-Ph_3PO [10], CH_2Br_2-Et_3SiH-$PdCl_2$ [11]), benzyl chloride

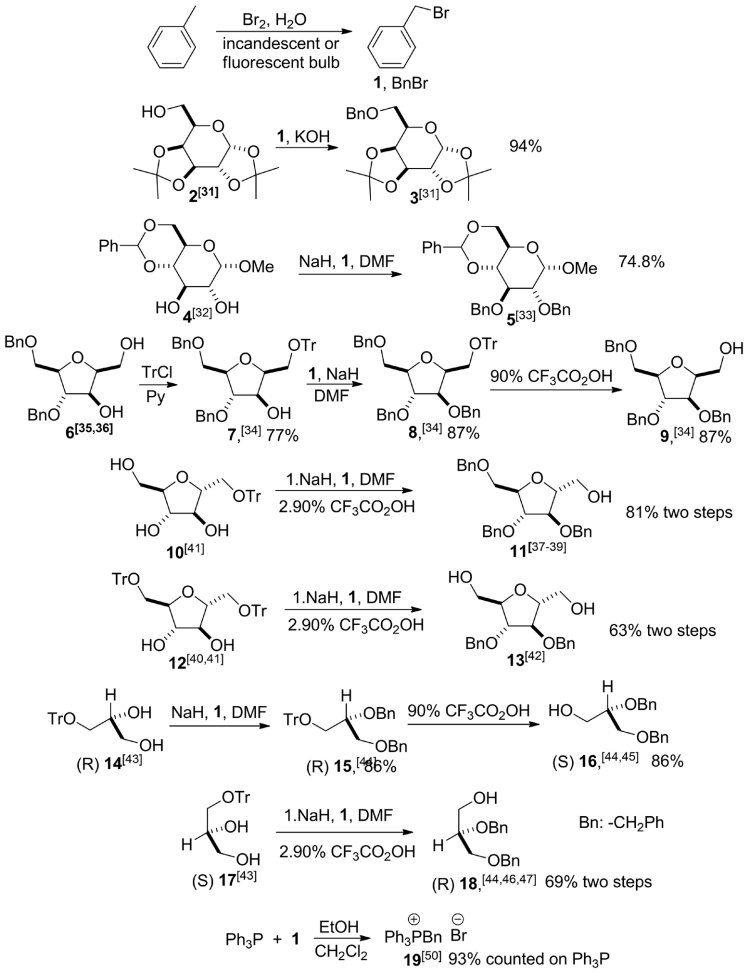
($MgBr_2$, $ZnBr_2$) [12], benzyl phenyl ether (BBr_3) [13], benzyl thiol (Ph_3PBr_2) [14], dibromomethyl benzene (Et_3N, light) [15], phenylacetic acid (bromoisocyanuronate) [16] and toluene (bromoisocyanuronate [17], n-bromosaccharin-$(BzO)_2$ [18], tetrabromodiphenylglycoluril [19], KBr-H_2O_2-Mn(VIII) [20], Me_4NBr_3 [21], manganese/graphite composite, air and light [22], $NaBrO_3$-AIBN or $(BzO)_2$ [23], NaBr-$K_2S_2O_8$-sodium 2-anthraquinone sulfonate [24], Br_2-CCl_4 [25], HBr-H_2O_2-light [26], NBS [27], N,N-dibromobenzenesulfonamide [28], and KBr-oxone [29]). The standard textbook procedure presents a photochemical pathway of bromination of toluene together with the calculations of the energies of the bonds which are broken and formed to show, that the entire process is exothermic. A practical drawback of this method is a release of gaseous HBr, which is toxic and highly corrosive. A small-scale (ca 10 mmol) procedure has been published [30] which employs incandescent bulb irradiation of the toluene-bromine-water mixture. The HBr formed is absorbed in water, which simplifies the process since an HBr-absorbing set-up is not necessary. The benzyl bromide thus formed was purified by separation from the water phase followed by vacuum distillation.

2. Results and Discussion

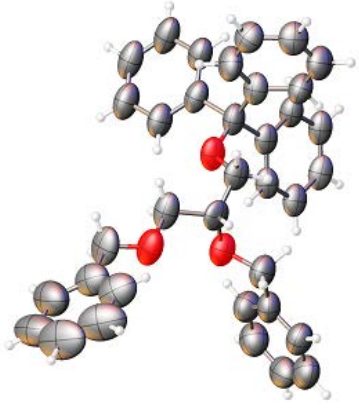
The objective of the present communication is to show, that the photochemical biphasic bromination mentioned above can be scaled-up to ca 300 mmol of toluene per run and that the crude benzyl bromide (BnBr) **1** obtained after separation from the water phase can be used in further transformations without distillation. This facilitates the procedure thanks to limitation to minimum the exposure to very lachrymogenic BnBr.

The procedure was validated by obtention of a series of derivatives as shown in Scheme 1. Monobenzylation of 1,2;3,4-di-O-isopropylidene-*α*-D-galactopyranose **2** [31] using liquid-liquid phase-transfer catalysis conditions furnished the known 6-O-benzyl ether **3** [31] in 94% yield at the 10 g scale of the hydroxylic component. It is necessary to stress that during benzylations excess of the benzylating reagents (chloride or bromide) is used so a purity of the crude **1** is not so important. The same holds for the other alkylations presented here.

Methyl 4,6-O-benzylidene-*α*-D-glucopyranoside **4** [32] was converted to its 2,3-di-O-benzyl derivative **5** [33] using NaH/DMF. Likewise, benzylation of 2,5-anhydro-4,6-di-O-benzyl-1-O-triphenylmethyl-D-glucitol **7** [34] furnished **8** [34], which was 1-O-deprotected to yield the known 2,5-anhydro-3,4,6-tri-O-benzyl-D-glucitol **9** [34]. The intermediate **7** was prepared by selective triphenylmethylation of the known **6** [35] [36]. The 2,5-anhydro-3,4,6-tri-O-benzyl-D-mannitol **11** [37]-[39] was obtained by triple benzylation of 2,5-anhydro-1-O-triphenylmethyl-D-mannitol **10** [40] [41] followed by removal of the Tr group. The 2,5-anhydro-1,6-di-O-triphenylmethyl-D-mannitol **12** [40] [41] was transformed to the 2,5-anhydro-3,4-di-O-benzyl-D-mannitol **13** [42] by consecutive benzylation and detritylation. **13** was obtained in better yield then published (63% vs. 30% [42]). Next, the benzylation of (R) 1-O-trityl glycerol **14** [43] furnished **15** [44] whose structure was confirmed by X-ray crystallography as shown in Picture 1.



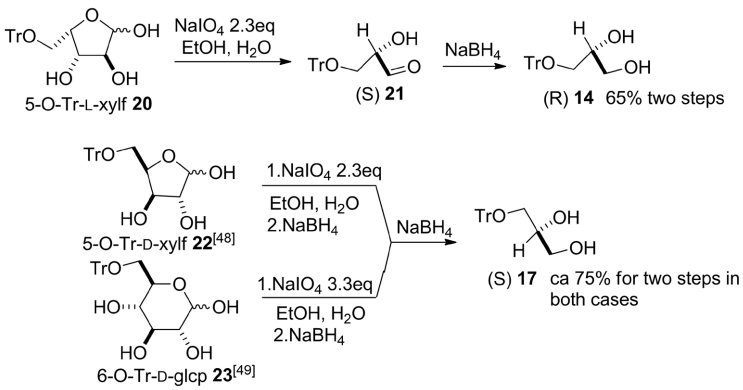
Scheme 1. Photochemical formation of benzyl bromide **1** in toluene-water system and applications of the crude product.



Picture 1. Molecular structure of (R) 2,3-di-O-benzyl-1-O-triphenylmethyl glycerol **15** with thermal ellipsoids drawn at 50% probability. The relevant parameters were deposited in the Cambridge Crystallographic Data Centre under no. 2039449.

15 was subsequently de-tritylated to yield the (S) 2,3-di-O-benzyl glycerol **16** [44] [45]. For the preparative reasons, it was easier to skip the isolation of **15** and to

perform de-tritylation directly on the crude benzylation mixture since the difference between chromatographic mobilities of the unreacted **1** and the de-tritylated product **16** is much greater than this of **1** and **15** which facilitates isolation. The (R) 2,3-di-O-benzylglycerol **18** [44] [46] [47] was obtained using the (S) 1-O-tritylglycerol **17** [43] by the same way. Both doubly benzylated glycerols **16** and **18** were previously obtained from D-mannitol via longer pathways [44]. The substrates **14** and **17** are known [43] but for the purpose of the present communication they were obtained from 5-O-trityl-L-xylofuranose **20** to get (R) **14**, or from 5-O-trityl-D-xylofuranose **22** [48] and from 6-O-trityl-D-glucopiranose **23** [49] to get (S) **17** by $NaIO_4$ cleavage and $NaBH_4$ reduction as shown in the Scheme 2. The only stereogenic center in **14** and **17** is this of the carbon atom C4 present if the furanoses **20** and **22**, or the atom C5 present in the pyranose **23**. The compound L-**20** was prepared following the directions published for the D enantiomer **22** [48].



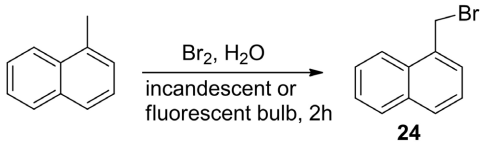
Scheme 2. Synthesis of 1-O-trityl (R)- and (S)-glicerols from tritylated L-xylose, D-glucose and D-xylose.

Finally, crude **1** was used to get benzyltriphenylphosphonium bromide **19** [50] in 93% yield (counted on Ph_3P).

All these examples and the yields obtained favor the idea to use the crude benzyl bromide **1** without any purification.

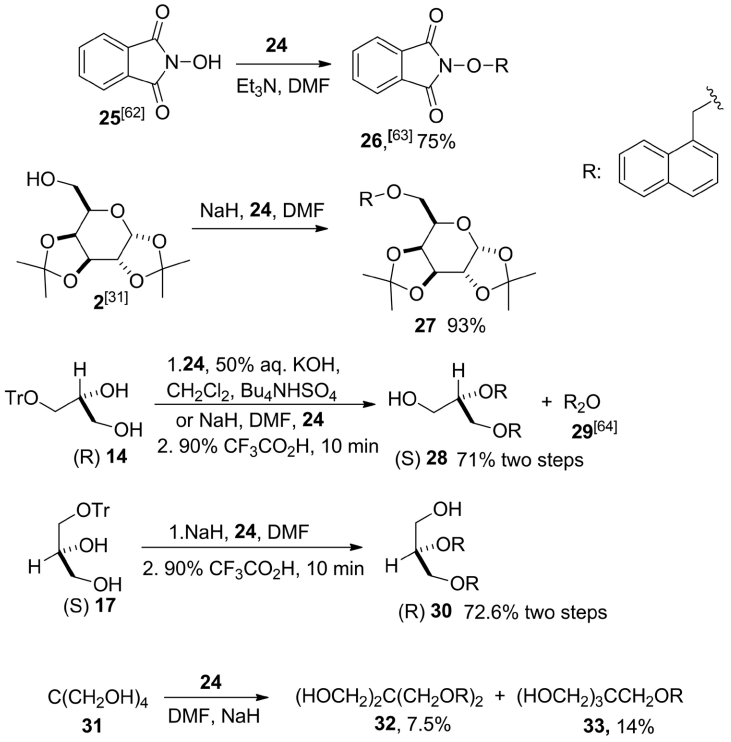
Next, we used 1-methylnaphthalene as a substrate for biphasic photochemical bromination in the same way as described for **1** to get 1-(bromomethyl)naphthalene **24** (Scheme 3). Pure **24** is a low melting point solid (45˚ - 56˚ [51]) and is reported to be extremely lachrymogenic [51]. In the case of the preparation presented here, no effort has been made to obtain **24** in a pure form. Instead, a crude bromination mixture was used to show that **24** was indeed formed in preparatively acceptable yield. **24** was obtained in a liquid form and was probably contaminated with unreacted 1-methylnaphthalene. The alternative procedures to get **24** include bromomethylation of naphthalene (trioxane, HBr) [52], application of 1-(dimethoxymethyl)-naphthalene ($SnBr_2$, AcBr, Et_3SiH) [1], (1-hydroxymethyl)-naphthalene ($SOBr_2$, perfluorohexane) [8], N,N-dialkyl-1-bromo-2-methyl-1-propenylamines [53], hexabromoacetone-Ph_3Ph [54], α,α-dibromo-β-dicarbonyl compounds-PPh_3 [55], 1-methylnaphthalene (Br_2, microwaves [56], NBS-benzoyl peroxide [57], Br_2-

$La(OAc)_2$ [58], benzyltrimethylammonium tribromide-AIBN [59], N,N,N',N'-tetrabromobenzene-1,3-disulfonamide [60], tribromoisocyanuric acid [17] and 1-(trimethylsilylmethyl)naphthalene (NBS-UV) [61].



Scheme 3. Photochemical bromination of 1-methyinaphthalene in biphasic system.

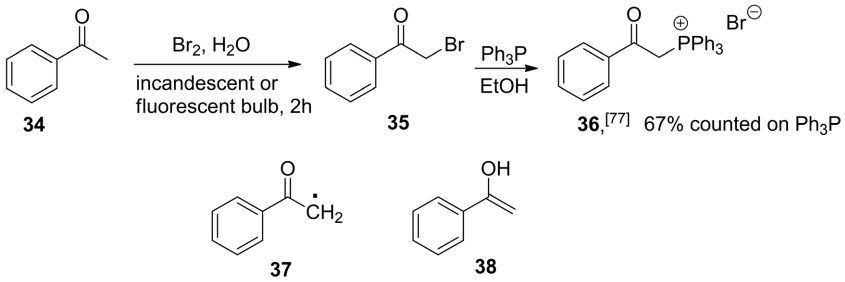
The first compound used for alkylation with **24** was N-hydroxyphthalimide **25** [62] to furnish the known **26** [63] as shown in **Scheme 4**. Likewise, the crude **24** was used to alkylate the diacetone galactose **2** [31] to furnish **27**. The bromide **24** was then used to doubly alkylate **14** and **17** to furnish both enantiomeric products **28** and **30** after removal of the triphenylmethyl protection, in *ca* 72% yields for two steps. These alkylations were performed using either NaH as a base or a phase-transfer catalysis (50% aq. KOH, Bu_4NHSO_4). In both cases variable quantities of the bis (1-methylnaphthyl) ether **29** [64] were also formed. Finally, alkylation of the pentaerythritol **31** with **24** in DMF/NaH system furnished doubly alkylated compound **32** and monoalkylated compound **33**. Both yields were low presumably due to limited solubility of the substrate **31**. No reaction occurred when the liquid-liquid phase-transfer catalysis was used (50% aq. KOH-CH_2Cl_2-$CH_3(CH_2)_{15}NMe_3Br$. The compounds **27**, **28**, **30** and **32** and **33** have not been described before.



Scheme 4. Alkylation of **2**, **14**, **17**, **25** and **31** using crude 1-(bromomethyl)naphthalene **24**.

The last compound brominated in the biphasic photochemical system was acetophenone **34** to get the phenacyl bromide **35** as shown in Scheme 5. In this case, it is unclear if the entire process is photochemical. One can suppose that the bromination proceeds initially via radical pathway and that the resonance stabilized free radical **37** is indeed formed, but after release of HBr enolization of **34** takes place and the bromination proceeds via the enol **38**. May be both processes occur in parallel. Phenacyl bromide **35** can be alternatively prepared via various methods starting from acetophenone (Br_2-$AlCl_3$ [65], Br_2-AcOH [66], KBr-H_2O_2-V(V)-$HClO_4$ [67], $CuBr_2$ [68], dibromination-photochemical debromination [69], 1-bromoethenylbenzene (Bu_4NBr-O_2-light) [70], 1-bromoethyl benzene (NBS-Fe(III)-O_2 [71], *t*BuOOH-Fe(III) [72]), 1-(bromomethyl)ethenyl benzene (O_2-Mn oxo species, light) [73], 2-bromoethynylbenzene (H_2SO_4-H_2O-ionic liquid) [74], ethenyl benzene ($HCBr_3$-O_2-$PhI(OAc)_2$-light) [75], or ethylbenzene (NaBr-$NaBrO_3$-H_2SO_4) [76].

To confirm that **35** was indeed formed, the crude bromination mixture was reacted with triphenylphosphine to furnish the known crystalline salt **36** [77].



Scheme 5. Formation of bromoacetophenone **35** and its reaction with Ph_3P.

3. Conclusion

In conclusion, scaled-up procedure to brominate toluene, 1-methylnaphthalene and acetophenone in aqueous biphasic system under photochemical conditions is shown to furnish benzyl bromide **1**, 1-bromomethylnaphthalene **24** [78] and phenacyl bromide **35** [79] of sufficient purity to be used without any purification. This greatly simplifies the experimental conditions by minimization of exposure to the toxic and lachrymogenic reagents. It should be pointed out that TiO_2, the known photosensitizer [80], can be applied in the above-mentioned reactions to speed them up. This however necessitates its subsequent removal via filtration through a pad of celite (data not shown), which complicates a workout and runs counter a basic premise of this project. Additionally, the compounds **28**, **30** and **32** display interesting antiproliferative activities *in vitro* in the human cervical carcinoma HeLa, human colon adenocarcinoma HT-29 and mouse fibroblast L929 cell lines, being as active as doxorubicin amply used in medicine to treat various neoplasms [81].

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Authors' Contributions

KKdML, HNLdS, ECdS and BD: synthesis;
AYN: X-ray analysis;
BD: idealized the project and wrote the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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Experimental Appendix

All experiments were conducted in efficient hood using protective gloves. Thin layer chromatography (TLC) was performed on a 0.2 mm silica aluminum-coated plates from Fluka. Silica gel for column chromatography (70 - 230 mesh) was from Fluka. All solvents were distilled. The NMR spectra were recorded using Varian spectrometer operating at 200, 300 or 400 MHz in $CDCl_3$ solutions unless otherwise stated. Optical rotations were recorded using a Kruss automatic polarimeter at 28˚C. Exact mass measurements were performed using the Exactive Plus HCD, Thermo Scientific, in electrospray mode.

Benzyl bromide 1.

To a round-bottom flask containing a mixture of toluene, 20 ml, 17.4 g 189 mmol, and water, 60 ml, was added bromine 10.2 ml, 31.6 g, 200 mmol portion wise (~1 ml) during 10 min while maintaining magnetic stirring and irradiation with either incandescent (60 W) or fluorescent (15 W) bulb localized approximately 2 cm from the surface of the flask. To avoid excessive warming, the flask can be cooled in water in a crystallizing dish. Bromine can be alternatively added in one portion. After a total of 40 min the reaction mixture was transferred to a separatory funnel and the flask was washed with water, 10 ml, to remove as much of the product as possible. The lower phase was drained directly to another separatory funnel and minimum volume of aqueous Na_2SO_3 was added just to discolor the liquid, which was subsequently drained to a small Erlenmeyer flask charged with $MgSO_4$. The crude **1** obtained in this way was used for all benzylations listed below. The procedure can be repeated using 30 ml of toluene and proportional amount of bromine.

6-O-Benzyl-1,2;3,4-di-O-isopropylidene-*α*-D-galactopyranose 3.

The mixture of **2** [31] 10.1 g, 38.8 mmol, in toluene 60 ml, 9 ml of crude **1**, Bu_4NHSO_4, 0.5 g, and 100 ml of 40% KOH in water was vigorously stirred overnight. TLC showed that all **2** disappeared (R_f 0.28 hexane - EtOAc 2:1) to form less polar **3** (R_f 0.68, hexane - EtOAc 3:1). The organic layer was separated, washed with water, dried ($MgSO_4$), passed through a sintered glass funnel and the volatile was evaporated. The product **3** was isolated by column chromatography using a gradient of hexane - EtOAc 20: 1→10: 1→5: 1 to give **3**, 12.8 g, 94% as a syrup; α_D −67, c 3 $CHCl_3$; lit. [78] α_D −68, c 6.7 $CHCl_3$.

Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-*α*-D-glucopyranoside 5.

The known methyl 4,6-O-benzylidene-*α*-D-glucopyranopyside **4** [32] 0.9 g, 3.1 mmol was solubilized in CH_2Cl_2, 20 ml, and crude **1**, 1 ml, 40% KOH in water, 20 ml and 0.1 g of hexadecyltrimethylammonium bromide were added and the whole was magnetically stirred for 24 h. TLC indicated disappearance of **4** (R_f 0.12, hexane - EtOAc 1: 1) and formation of less polar **5** (R_f 0.33 hexane - EtOAc 6: 1). The organic phase was separated, washed with water, dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by chromatography using hexane - EtOAc 4:1 as eluent to furnish **5** 0.9 g, 74.8% as a colorless solid compound; mp 66˚ - 68˚ (cryst. from hexane - EtOAc); α_D + 19.1 c 1.5 CH_2Cl_2. Lit. [33] mp. 67˚ -

68˚, α_D + 20.0 c 0.885 CH_2Cl_2.

^1H (400 MHz): 7.50 - 7.27 (H aromatic, 15H), 5.54 (s, 1H), 4.91 (d, J = 11.1 Hz, 1H), 4.85 (d, J = 4.9 Hz, 1H), 4.82 (d, J = 4.6 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 3.7 Hz, 1H), 4.26 (dd, J = 4.6 Hz, 9.9 Hz,1H), 4.05 (t, J = 9.2 Hz, 1H), 3.81 (dd, J = 4.6 Hz, 9.7 Hz, 1H), 3.70 (t, J = 10.1 Hz, 1H), 3.60 (t, J = 9.4 Hz, 1H), 3.55 (dd, J = 3.1 Hz, 9.3 Hz, 1H), 3.39 (s, 3H).

^{13}C: 138.4, 137.2, 128.8, 128.2, 128.1, 127.9, 127.6, 125.9, 105.1, 101.0, 82.1, 81.4, 80.7, 75.1, 74.9, 68.7, 65.8, 57.3.

2,5-Anhydro-4,6-di-O-benzyl-1-O-triphenylmethyl-D-glucitol 7.

To a solution of 2,5-anhydro-4,6-di-O-benzyl-D-glucitol **6** [35] [36] 2.3 g, 6.7 mmol in pyridine, 25 ml, was added triphenylmethyl chloride, 5.6 g, 20 mmol under Ar and the mixture was incubated for three days at rt. TLC showed that the starting diol (R_f 0.35 in $CHCl_3$ - MeOH 10:0.2) disappeared to form a less polar **7** (R_f 0.62 in hexane - EtOAc 2:1). Ten drops of water were added to destroy the remaining TrCl and 1.5 h later extraction was performed (CH_2Cl_2 - H_2O). The organic phase was drained, the solvent was evaporated, and the residue was co-evaporated with xylenes. The product was obtained by silica gel chromatography (gradient: hexane - EtOAc 10:1 → 4:1) to furnish 3.0 g, 77% of **7** [34] a glassy material.

^1H (300 MHz): 7.58 - 7.29 (H aromatic), 4.70 (d, J = 12 Hz, 1H), 4.62 (t, J-11.4 Hz, 1H), 4.30 - 4.19 (unresolved, 3H), 3.98 (d, J = 1.8 Hz, 1H), 3.75 (dd, J = 2.6 Hz, 9.8 Hz, 1H), 3.70 (d, J = 9.2 Hz, 1H), 3.65 (dd, J = 2.6 Hz, 9.8 Hz, 1H), 3.50 (ddd, J = 4.7 Hz, 9.2 Hz, 14.6 Hz, 2H).

^{13}C: 143.8, 137.7, 137.1, 128.7, 128.4 (two lines), 127.9, 127.4, 127.6, 126.9, 86.9, 86.5, 83.0, 81.1, 74.9, 73.7, 71.7, 70.4, 62.3.

HRMS: cacl. for $C_{39}H_{38}O_5$ + Na^+ = 609.2612; found: 609.2598.

2,5-Anhydro-3,4,6-tri-O-benzyl-1-O-triphenylmethyl-D-glucitol 8.

To magnetically stirred solution of the compound **7**, 3.1 g, 5.3 mmol in DMF, 30 ml was added NaH (60% suspension in mineral oil), 2.3 g under Ar blanket. One hour later **1**, 3 ml was added via a syringe. Next day TLC showed a spot of less polar **8** (R_f 0.51 in hexane-EtOAc 4:1). Conventional extraction followed by chromatographic purification using hexane - EtOAc 8:1 furnished **8**, 3.1 g, 87% of the known [34] glassy material.

^1H (300 MHz): 7.66 - 7.25 (H aromatic, 30H), 4.76 - 4.48 (m, 7H), 4.35 (dt, J = 2.5 Hz, 6.0 Hz, 6.0 Hz, 1H), 4.21 (d, J = 3.4 Hz, 1H), 4.00 (d, J = 2.4 Hz, 1H), 3.77 (dd, J = 6.4 Hz, 10.1 Hz, 1H), 3.72 (t, J = 3.5 Hz, 1H), 3.68 (dd, J = 6.4 Hz, 9.2 Hz, 1H), 3.52 (dd, J = 5.8 Hz, 9.0 Hz, 1H).

^{13}C: 143.9, 138.1, 137.8, 137.7, 128.6, 128.3, 128.2, 127.6, 127.5, 127.4, 127.3, 126.8, 86.6, 83.8, 82.6, 82.1, 80.4, 73.1, 71.3, 71.2, 70.5, 61.6.

2,5-Anhydro-3,4,6-tri-O-benzyl-D-glucitol 9.

To a solution of the trityl ether **8**, 4.9 g, 6.1 mmol in CH_2Cl_2, 5 ml, was added 90% CF_3CO_2H, 20 ml. After 10 min TLC showed a spot of the new compound having R_f 0.17 (hexane-EtOAc 13:7). Extraction (CH_2Cl_2 - H_2O) and conventional

work-up followed by silica gel chromatography (gradient, hexane-EtOAc 7:3→3:2) furnished **9**, 2.7 g, 87% as oil. Lit. [34]: data unavailable.

α_D + 17.2 c 1.6 $CHCl_3$.

^1H (300 MHz): 7.27 - 7.15 (H aromatic, 15H), 4.76 - 4.44 (unresolved, 5H), 4.32 (d, J = 11.7 Hz, 1H), 4.04 - 3.97 (unresolved, 4H), 3.75 - 3.73 (unresolved, 2H), 3.52 - 3.50 (unresolved, 2H), 2.38 (bs, OH).

^{13}C: 137.8, 137.7, 137.3, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 83.8, 82.9, 81.7, 80.1, 73.3, 71.8, 71.7, 69.9, 61.9.

Detritylation using 90% AcOH at 100˚ furnished mixture of **9** and variable quantities of its 1-O-acetate (data not shown).

2,5-Anhydro-3,4,6-tri-O-benzyl-D-mannitol 11.

The known 2,5-anhydro-1-O-triphenylmethyl-D-mannitol **10** [40] [41] 2.1 g, 5.2 mmol was solubilized in DMF, 60 ml and cooled in ice-water bath under a blanket of Ar. NaH (60% suspension in mineral oil), 2 g was added and the whole was magnetically stirred for 1 h, whereupon crude **1**, 5 ml was added using a syringe. The mixture was allowed to reach rt during 1 h and stirring was continued over the weekend. TLC showed that all **10** (R_f 0.44 CH_2Cl_2 - MeOH 10:1 reacted to from a less polar intermediate 2,5-anhydro-3,4,6-tri-O-benzyl-1-O-triphenylmethyl-D-mannitol having R_f 0.31 (hexane - EtOAC 7:1). Extraction (CH_2Cl_2 - aq citric acid) and evaporation of the solvent furnished yellowish oil, which was treated with 90% trifluoroacetic acid, 15 ml, for 12 min. TLC at this point showed the spot of **11** R_f 0.35 in hexane - EtOAc 3:2. Extraction was performed using CH_2Cl_2 - water. The organic phase was washed with water, dried ($MgSO_4$), the solids were filtered and the solvent was evaporated. The known [37]-[39] compound **11** was obtained by chromatography (gradient of hexane - EtOAC 4:1→3:1→2:1) to furnish 1.82 g, 81% over two steps of yellowish oil.

α_D + 14.7 c 0.9 $CHCl_3$

^1H (200 MHz): 7.37 - 7.24, H aromatic, 4.55 (s, 2H), 4.53 (s, 4H), 4.30 - 4.20 (m, 1H), 4.17 - 4.07 (unresolved, 3H), 3.70 (t, J = 7.2 Hz, J = 7.2 Hz, 2H), 3.57 (dd, J = 3.3 Hz, J = 8.7 Hz, 2H).

^{13}C: 138.0, 137.6, 137.5, 128.4, 128.3, 127.81, 127.78, 127.7, 127.6, 84.5, 84.0, 83.2, 81.8, 73.3, 72.0, 71.8, 70.0, 62.6.

2,5-Anhydro-3,4-di-O-benzyl-D-mannitol 13.

To a solution of 2,5-anhydro-1,6-di-O-triphenylmethyl-D-mannitol **12** [40] [41], 6.4 g, 9.9 mmol in CH_2Cl_2, 40 ml, was added a 45% solution of KOH in water, 50 ml, 1 g of hexadecyltrimethylammonium bromide and 5 ml of crude **1**. The whole was magnetically stirred during 8 h. TLC showed that all 0 R_f 0.33 (hexane - EtOAc 3: 2) reacted to form a less polar compound having R_f 0.55 (hexane - EtOAc 6: 1). Unreacted **1** was also present (weakly UV absorbing spot R_f ca 0.8). The organic phase was washed with water and without drying the solvent was evaporated. To the residual brownish oil was added 90% trifluoroacetic acid, 20 ml. The mixture immediately turned yellow. TLC run 10 min later showed that hydrolysis was complete and that the more polar diol **13** (R_f 0.29, hexane - EtOAc

1: 4) was formed. Extraction (CH_2Cl_2 - water), drying the organic phase ($MgSO_4$), filtration through a sintered glass funnel, evaporation of the solvent and chromatography (gradient: hexane - EtOAc 1:1→1:4) furnished the known **13**, 2.18 g, 63% over two steps. **13** spontaneously solidified; mp 72˚ - 75˚; α_D + 36.8 c 2 $CHCl_3$; lit. [42]: mp 76˚ - 78˚, α_D + +40 c 1 $CHCl_3$.

^1H (300 MHz): 7.36 - 7.24 (H aromatic, 10H), 4.53 (s, 6H), 4.16 - 4.11 (apparent q, J = 4.4 Hz, 2H), 4.00 (dd, J~ 1 Hz, J = 3 Hz, 2H), 3.66 (d, J = 5.1 Hz, 4H).

^{13}C: 137.4, 128.4, 127.7, 83.9, 83.3, 72.0, 62.6.

(R) 1-O-Triphenylmethylglycerol 14.

The compound **20** (see below), 2.03 g, 5.18 mmol, in 20 ml of 96% EtOH was cooled in ice-bath and $NaIO_4$, 2.44 g, 11.39 mmol in H_2O 15 ml was added while maintain magnetic stirring. Cooling bath was removed. White precipitate started to appear immediately. After ca 5 min stirring became impossible. 2 h later TLC showed that all **20** (R_f 0.32 in CH_2Cl_2 - MeOH 95: 5) reacted to form less polar intermediate (R_f 0.77 in the same system). Glycerol 0.3 ml was added to destroy excess of $NaIO_4$ and 15 min later the solid material was removed by filtration through sintered glass funnel. The solids were washed with EtOH and combined solutions were cooled in ice-water bath and $NaBH_4$ 1 g was added. 1h later TLC showed the product **14** having R_f 0.45 (CH_2Cl_2 - MeOH 95: 5) together with minor impurities. Extraction (CH_2Cl_2 - brine), drying of the organic phase ($MgSO_4$), filtration of the solid material, evaporation of the volatiles and chromatography in CH_2Cl_2 - MeOH 95: 5 furnished (R) **14** 1.73 g, 65% over two steps; mp 97˚ - 100˚ (cryst. from CH_2Cl_2), α_D +8.9 c 4, dioxane; lit. [43] mp. 98˚ - 100˚, α_D +9.2 c 5.5, dioxane, for the compound obtained from L-arabinose.

(R) 2,3-Di-O-benzyl-1-O-triphenylmethylglycerol 15.

Compound **14**, 1.28 g, 3.8 mmol in DMF, 30 ml, was cooled in ice-bath under a blanket of Ar and NaH, 60% suspension, 1 g was added. After 30 min of magnetic stirring crude **1**, 1 ml was added. After 5 h TLC showed that all **14** R_f 0.45 (CH_2Cl_2 - MeOH 95: 5) reacted to form less polar **15** R_f 0.37 (hexane-EtOAc 10:1). Extraction (CH_2Cl_2 - water), conventional work-up and chromatography using hexane-EtOAC 10: 1 furnished 1.7 g, 86% of **15**. α_D +6.5 c 1.7 $CHCl_3$, mp 83˚C - 85˚C; lit. [44] α_D +8.8, c 2.5 $CHCl_3$, mp 83.5˚C - 84.5˚C. Enantiomeric (S) 2,3-Di-O-benzyl-1-O-triphenylmethylglycerol obtained from (S) **17** obtained by the same procedure (data not shown) has α_D −7.7 c 6 $CHCl_3$, mp 83˚C - 85˚C. Lit. [44]: mp 81˚ - 83˚, α_D -8.6 c 2.5 $CHCl_3$.

^1H: (400 MHz, DMSO-*d6*): 7.41 - 7.21 (H aromatic), 4.60 (s, 2H), 4.445 (s, 2H), 3.76 (m of 5 lines, J = 5.0 Hz, 5.0 Hz, 9.8 Hz, 1H), 3.58 (d, J = 5.2 Hz, 2H), 3.17 (dd, J = 4.3 Hz, 10.4 Hz, 1H), 3.12(dd, J = 5.5 Hz, 9.5 Hz, 1H).

^{13}C: 143.7, 138.7, 138.3, 128.2, 128.1 two signals, 127.8, 127.4, 127.3, 127.2, 126.9, 85.0, 76.9, 72.1, 71.1, 69.4, 63.4.

(S) 2,3-Di-O-benzylglycerol 16.

A. From the isolated **15**.

The compound **15**, 1.5 g, 2.9 mmol, was solubilized in CH_2Cl_2, 5 ml, and 5 ml

of 90% trifluoroacetic acid was added. 10 min later TLC showed the spot of more polar **16**, R_f 0.33 (hexane - EtOAc 65: 35). Extraction (CH_2Cl_2 - water), conventional workup and chromatography using hexane - EtOAc 3:2 furnished **16**, 0.68 g, 86%, as oil.

B. From **14** without isolation of the intermediate **15**.

To a cold (ice-water bath) solution of the diol **14**, 2.1 g, 6.3 mmol in DMF, 40 ml, was added 2.1 g NaH (60%) under a blanket of Ar. After 30 min of magnetic stirring, crude **1**, 2.5 ml was added. After 3 h extraction (CH_2Cl_2 - water) was performed, followed by conventional work-up, to furnish yellowish oil after evaporation of the solvent. This oil was treated with 90% trifluoroacetic acid, 25 ml during 10 min. Workup as above and chromatographic separation furnished **16**, 1.2 g, 73% over two steps. α_D -19.2 c 3.7 $CHCl_3$. Lit. [79] α_D -17.2 c 1 $CHCl_3$.

^1H (300 MHz): 7.35 - 7.25 (H aromatic, 10H), 4.71 (d, J = 12 Hz, 1H), 4.61 (d, J = 12 Hz, 1H), 4.54 (s, 2H), 3.78 - 3.59 (unresolved, 5H).

^{13}C: 137.9, 128.4, 127.8, 127.6, 78.0, 73.5, 72.2, 70.2, 62.9.

(S) 1-Triphenylmethylglycerol 17.

This compound was obtained from 5-O-triphenylmethyl-D-xylose **22** using the same procedure as described for the (R) enantiomer **14** obtained form 5-O-triphenylmethyl-L-xylofuranose **20**, or from the 6-O-triphenylmethyl-D-glucose **23** as follows.

To a cold (ice-bath) solution of **23**, 6.4 g, 15.2 mmol, in 96% EtOH, 120 ml, was added portion wise (*ca* 2 ml) a solution of $NaIO_4$, 11.7 g, 54.6 mmol in 50 ml of water while maintaining magnetic stirring. Cooling bath was removed after the end of addition and semi-solid mixture was kept at room temp. for 2 h more counting from the end of addition. Total of reaction time was 140 min. Glycerol, 0.6 ml, was added and 10 min. later the solid material was removed by filtration through sintered glass and the solids were washed with EtOH. The resulting opaque solution was cooled in ice-bath and $NaBH_4$, 1.5 g, was added while maintaining magnetic stirring. Extraction (CH_2Cl_2 - brine) 2 h later, conventional work-up and chromatography in hexane - EtOAc 1: 1 or in CH_2Cl_2 - MeOH 95: 5 furnished (S) **17**, 3.9 g, 77% over two steps, mp 97˚ - 100˚ (from EtOAc - hexane); α_D −9.5 c 4, dioxane; lit. [43] mp 98˚ - 100˚, α_D −9.1 c 5.1 dioxane.

(R) 2,3-Di-O-benzylglycerol 18.

(R) **18** was obtained from (S) **17** following the same procedure as described for the (R) **16**, procedure B, in 69% yield. α_D +18.7 c 3.9 $CHCl_3$. Lit. [47] α_D +15.7 c 1 $CHCl_3$.

Benzyltriphenylphosphonium bromide 19.

Bromination of toluene, 2.3 ml, 2.0 g, 21.7 mmol with Br_2, 1.2 ml, 3.86 g, 24 mmol in water, 20 ml during 30 min was conducted as described for **1**. The whole content was transferred to a separatory funnel with the aid of minimum volume of CH_2Cl_2. The lower phase was drained to another separatory funnel and washed with diluted Na_2SO_3. The lower phase was added to Ph_3P, 4.4 g, 16.8 mmol previously solubilized in CH_2Cl_2, 15 ml, and 96% EtOH, 15 ml. Slight warming took

place. After 36 h the volatiles were removed under vacuum and the residue was stored in a refrigerator overnight. Cold 96% EtOH was added to break the mass of crystals. Filtration on a sintered glass funnel, washing with cold EtOH and drying under vacuum furnished 6.8 g, 93% of **19**. The yield is counted on Ph_3P. Mp 269˚C - 275˚C; lit. [77] mp 274˚C - 5˚C (from EtOH).

5-O-Triphenylmethyl-L-xylofuranose 20.

This compound was obtained in 45% yield as published for the D-enantiomer [48].

^{1}H (300 MHz, DMSO-d*6*): 7.55 - 7.40 (H aromatic, 15H), 5.22 (d, J = 5.3 Hz, 1H, exchangeable), 4.92 (d, J = 4.7 Hz, 1H, exchangeable), 4.74 (d, J = 4.8 Hz,, 1H, exchangeable), 3.81 (d, J = 7.6 Hz, 1H), 3.38 - 3.28 (m, superimposed on H_2O), 3.25 - 3.16 (m, 2H), 2.89 (dt, J = 4.2 Hz, J = 8.2 Hz, J = 8.2 Hz, 1H).

^{13}C: 144.5, 128.8, 127.3, 126.9, 98.8, 86.9, 76.9, 73.5, 69.5, 65.0.

HRMS: calc. for $C_{24}H_{24}O_5 + Na^+$ = 415.1516; found: 415.1520.

5-O-Triphenylmethyl-D-glucopyranose 23.

To a slurry of D-glucose, 5.2 g, 28.9 mmol, in pyridine, 120 ml, was added triphenylmethyl chloride 10.1 g, 36.3 mmol in one portion under Ar blanket. The mixture was magnetically stirred during 48 h at rt. TLC showed the product **23** which has R_f 0.35 (CH_2Cl_2 - MeOH 9:1). Extraction (CH_2Cl_2 - water), washing the organic phase with aq citric acid, water again, drying ($MgSO_4$), filtration of the solids (sintered glass funnel) and evaporation of the solvent furnished a semi-solid material which was applied on top of the silica gel column. Elution with CH_2Cl_2 - MeOH 9: 1 furnished the known **23**, 7.11 g, 58.3% as a glassy material; α_D + 19.0 c 5.2, MeOH, after 5min of preparation of the solution. Lit. [49] foam; α_D not given. HRMS: calc. for $C_{25}H_{26}O_6 + Na^+$ = 445.1622; found: 445.163.

^{1}H (300 MHz, DMSO-d*6*): 7.43 - 7.22, four groups of m, H aromatic, 6.66 (d, J = 4.9 Hz) and 6.30 (d, J = 3.3 Hz) both exchangeable, 4.98 (t, J = 3.1 Hz, J = 3.1 Hz, [after D_2O exchange: s]), 4.85 (dd, J = 2.0 Hz, J = 3.3 Hz) and 4.80 (d, J = 3.9 Hz) and 4.66 (d, J = 3.5 Hz) and 4.47 (d, J = 5.5 Hz) all exchangeable, 4.34 (dd, J = 5.5 Hz, J = 5.9 Hz) [after D_2O exchange: d, J = 5.8 Hz], 3.83 (ddd, J = ca 0.8 Hz, J = 4.2 Hz, J = 7.6 Hz), 3.43 (dt, J = 3.5 Hz, J = 6.7 Hz, J = 6.7 Hz), 3.37 - 3.30 partially superimposed on H_2O)3.27 (dd, J = 1.5 Hz, J = 7.5 Hz), 3.21 - 3.02 (unresolved), 2.92 (dt, J = 3.6 Hz, J = 6.0 Hz).

^{13}C: 126.3, 127.7, 126.8, 96.9, 92.3, 85.6, 85.5, 78.5, 76.6, 75.1, 74,8 73.3, 72.3, 70.5, 70.4, 68.3, 68.6.

1-(Bromomethyl)naphthalene 24.

1-Methylnaphthalene, 5 ml, 5.1 g, 35.2 mmol in 30 ml of water and 6.2 g, 2 ml, 39.3 mmol of bromine in a round-bottom flask, was stirred magnetically under incandescent or fluorescent bulb irradiation during 90 min. The bulb was localized 2 - 5 cm from the surface of the flask. The warm mixture was transferred to a small separatory funnel with the aid of small volume of water and a solution of sodium bisulfite was added just to discolor the mixture. The lower phase was drained to a small Erlenmeyer flask charged with $MgSO_4$. The resulting crude **24**,

evidently contaminated with unreacted 1-methylnaphthalene, was used for the alkylations shown below. No effort has been done to obtain **24** in a solid state or to purify it; published mp: 55˚ or 45˚ - 56˚ [51] and references cited therein.

N-((1-Methoxy)naphthalene)phthalimide 26.

N-Hydroxyphthalimide **25** [62], 2.8 g, 17.2 mmol, was solubilized in DMF, 20 ml, and Et_3N 2.4 ml, 1.74 g, 17.2 mmol was added. The solution turned deep red. Crude **24**, 3 ml, was added. After overnight incubation at room temp. (ca 28˚C) the mixture turned colorless. TLC showed that all **25** reacted (R_f 0.51 CH_2Cl_2 - MeOH 10: 0.5) to form **26**, R_f 0.84 in the same system, or R_f 0.34 in hexane-EtOAc 2: 1. Extraction was performed (CH_2Cl_2 - H_2O) and after conventional work-up, the product crystallized during evaporation of the solvent. More **26** was obtained after silica gel purification of the mother liquor using hexane-EtOAc 3:2 as eluent. Total yield was 3.9 g, 75%. Mp 125˚C - 128˚C, lit. [63] mp 127˚C - 130˚C.

^1H (400 M Hz): 8.62 (d, J = 8.5 Hz, 1H), 7.87 (t, J = 7.5 Hz, 2H), 7.79 (dd, J = 3.2 Hz, 5.5 Hz, 2H), 7.69 (dd, J = 3.2 Hz, 5.5 Hz, 2H), 7.66 - 7.63 (unresolved, 1H), 7.59 (dd, J < 1 Hz, 8.7 Hz, 1H), 7.52 (dt, J = 1 Hz, 7.1 Hz, 1H), 7.42 (dd, J = 7.1 Hz, 8.2 Hz, 1H), 5.63 (s, 2H).

^{13}C: 163.6, 134.5, 133.7, 132.5, 129.6, 129.5, 128.9, 128.5, 127.0, 126.2, 125.1, 124.5, 123.5, 78.2.

1,2;3,4-Di-O-isopropylidene-6-O-(2-methylnaphthyl)-*α*-D-galactopyranose 27.

To a solution of the compound **2** [31], 2.3 g, 8.8 mmol, in DMF, 30 ml, under a blanket of Ar was added 1.5 g of NaH (60% suspension). After 30 min of magnetic stirring, crude **24**, 3.5 ml, was added. TLC showed 3 h later that all **2** reacted to form a less polar product **27** (hexane - EtOAc 4:1, R_f 0.11 and 0.42, respectively). Methanol, 3 ml, was added to destroy the remaining NaH and the whole mixture was transferred to a separatory funnel to perform the extraction (CH_2Cl_2 - water). The organic phase was consecutively dried ($MgSO_4$), filtered and the solvent was evaporated. The residual oil was purified by chromatography using hexane-EtOAc 4:1 as an eluent to furnish 3.3g, 93% of **27** as a syrup.

α_D - 64.8 c 1.1 $CHCl_3$.

^1H (300 MHz): 8.15 - 8.12 (1H), 7.93 - 7.67 (2H), and 7.57 - 7.45 (4H), H aromatic; 5.48 (d, J = 4.7 Hz, 1H), 4.95 (apparent t, J = 2.1 Hz, 2H), 4.58 (dd, J = 2.4 Hz, 7.8 Hz, 1H), 4.34 (dd, J = 2.2 Hz, 5.1 Hz, 1H), 4.23 (dd, J = 1.7 Hz, 7.7 Hz, 1H), 3.93 (ddd, J = 2.1 Hz, 4.7 Hz, 6.8 Hz, 1H), 3.70 (dd, J = 4.9 Hz, 10.4 Hz, 1H), 3.58 (dd, J = 7.3 Hz, 10.4 Hz, 1H), 1.41 (s, 3H), 1.53 (s, 3H), 1.28 (s, 6H).

^{13}C: 133.8, 133.2, 126.2, 126.1, 125.8, 125.2, 124.2, 108.2, 107.7, 95.6, 70.8, 70.5, 70.0, 69.7, 68.9, 66.5.

HRMS: calc. for $C_{23}H_{28}O_6 + Na^+$ = 423.1778. Found: 423.1780.

(S) 2,3-di-O-(1-methylnaphthyl)glycerol 28 and bis(1-methylnaphthyl) ether 29.

To magnetically stirred ice-cold solution of the (R) **14** (obtained from L-arabinose **20**) 1.3 g, 3.9 mmol, in DMF, 25 ml, was added 0.9 g of NaH (60%) under Ar

atmosphere. Half an hour later crude **24**, 1.8 ml, was added and stirring was maintained for 2.5 h. TLC showed that all **14** reacted to form the 2,3-di-O-(1-naphthylmethyl)-3-O-triphenylmethyl glycerol (R_f 0.46, hexane-EtOAc 9:1) together with a spot R_f 0.63 of the ether **29**. Extraction was performed (CH_2Cl_2 - H_2O) and after usual work-up, the oil remaining after evaporation of the solvent was treated with 90% CF_3CO_2H during 10 min. The spot corresponding to the detritylated product **28** showed R_f 0.24 (hexane - EtOAc 3:1). Extraction was performed (CH_2Cl_2 - H_2O) and after usual work-up the product **28** was obtained as a syrup by column chromatography using a gradient of hexane - EtOAc (4:1→7:3); 1.03 g, 71% over two steps. From the fore-fractions small quantity of the ether **29** crystallized.

Similar results were obtained using liquid-liquid phase transfer catalysis (50% KOH in water, Bu_4NHSO_4, CH_2Cl_2).

α_D -11.5, c 8, $CHCl_3$.

28: ^{1}H (400 MHz): 8.20 - 816 (m, 2H), 7.95 - 7.85 (m, 4H), 7.60 - 7.44 (m, 8H), 5.21 (d, J = 11.6 Hz, 1H), 5.06 (d, J = 11.6 Hz, 1H), 5.05 (d, J = 12.4 Hz, 1H), 5.01 (d, J = 12.4 Hz, 1H), 3.85 (dq, J = 3.0 Hz, J = 5.3 Hz, J = 5.3 Hz, J = 5.3 Hz, 1H), 3.78 (d, J = 10.4 Hz, 1H), 3.77 (d, J = 8.3 Hz, 1H), 3.74 (d, J = 7.9 Hz, 1H), 3.73 (d, J = 10.1 Hz, 1H).

^{13}C: 133.9 two signals, 133.8, 133.5, 131.8, 131.7, 128.9, 128.8, 128.7, 128.6, 126.8, 126.6, 126.4, 126.3, 125.9, 125.3, 125.2, 124.1, 78.3, 72.2, 70.8, 70.3, 62.9.

HRMS: calc. for $C_{25}H_{24}O_3 + Na^+$ = 395.1618. Found: 395.162.

29: mp 124˚C - 127˚C (spontaneous cryst. from hexane-EtOAc); lit.[64] mp. 120.5˚C - 121˚C.

^{1}H (300 MHz): 8.16 - 8.13, 7.93 - 7.85 and 7.59 - 746 (three groups of m, H aromatic), 5.10 (s, 4H).

^{13}C: 133.7, 131.8, 128.7, 128.5, 126.7, 126.1, 125.7, 124.2, 70.7.

(R) 2,3-di-O-(1-methylnaphthyl)glycerol 30.

From 1.52 g of (S) **17** (obtained from D-xylose **22** or from D-glucose **23**), 1.23 g, 72.6% (over two steps) of (R) **30** was obtained following the same procedure as shown above for the (S) enantiomer **28**.

α_D +9.8, c 7, $CHCl_3$.

HRMS: calc. for $C_{25}H_{24}O_3 + Na^+$ = 395.1618. Found: 395.1606.

Bis(1-methylnaphtyl)pentaerythritol 32 and (1-methylnaphtyl)pentaerythritol 33.

Pentaerythritol **31**, 2.04 g, 15 mmol, in DMF, 30 ml under argon was magnetically stirred with NaH, 60% suspension in mineral oil, 0.5 g, for 1 h, whereupon crude **24**, 2 ml, was added. Stirring was maintained for 48 h. TLC showed the doubly alkylated compound **32** (R_f 0.53, hexane-EtOAc 3: 7) and the monoalkylated compound **33** (R_f 0.19 in the same system, or R_f 0.36 in EtOAc neat). Conventional aqueous work-up and chromatography (gradient, hexane-EtOAc 3: 7→EtOAc neat) furnished **32**, 0.48 g, 7.5%. Eluted next was **33**, which was re-purified by chromatography using neat EtOAc, to furnish **33**, 0.59 g, 14%.

32: mp 108˚C - 110˚C, spontaneous cryst. from hexane-EtOAc.

^{1}H (400 MHz, DMSO-*d6*): 8.09 - 8.06, 7.93 - 7.90, 7.87 - 7.85, 7.54 - 7.43 four groups of signals, total 19H, 4.85 (s, 4H), 4.36 (t, J = 2 Hz, interchangeable with D_2O), 3.53 - 3.44 (partially superimposed on the signal of H_2O, 8H).

^{13}C: 134.7, 133,7, 131.7, 128.8, 128.6,126.5, 126.3, 126.2, 125.7, 124.5, 71.6, 69.9, 61.1,46.2.

HRMS: calculated for $C_{27}H_{28}O_4 + Na^+$ = 439.1879 ; found: 439.1879.

33: syrup

^{1}H: (400 MHz, DMSO-*d6*): 8.11 - 8.09, 7.95 - 7.93, 7.88 - 7.86, 7.56 - 7.45 (four groups of signals, 7H), 4.89 s, 20, 4.28 (bs, interchangeable with D_2O), 3.52 - 3.40 (partially superimposed on the H_2O signal, 8H).

^{13}C: 134.8, 135.7, 131.7, 128.8, 128.5, 126.5, 126.3, 126.2, 125.8, 124.6, 77.7, 70.1, 61.4, 46.2.

HRMS: calculated for $C_{16}H_{20}O_4 + Na^+$ = 299.1254 ; found: 299.1253.

(2-oxo-2-phenylethyl)triphenylphosphonium bromide 36.

Magnetically stirred mixture of phenylethanone (acetophenone) **34**, 5 ml, 5.16 g, 43 mmol, water, 50 ml and bromine, 2.3 ml, 7.16 g, 45 mmol was irradiated during 2.5 h as described for **1**. The mixture was transferred to a small separatory funnel with the aid of 5 ml of CH_2Cl_2 and lower phase was drained to another separatory funnel. Water was added followed by small volume of sodium bisulfide solution to reduce any remaining bromine. No effort has been made to isolate **35** which is a solid, mp 50˚C [66]. The organic phase was drained to a round bottom flask and a solution of triphenylphosphine, 9 g, 34.4 mmol solubilized in 15 ml of CH_2Cl_2 and 15 ml of 96% EtOH was added. The mixture was left for three days at rt. Some solid material was already present. Evaporation of the solvents furnished a mass of crystals which was triturated with cold 96% EtOH and filtered on a sintered glass funnel. Washing with cold EtOH followed by hexane and vacuum drying furnished 9.9 g, 67% of **36** (the yield is counted on Ph_3P).

Mp. 265˚C - 270˚C (cryst. from water). Lit. [77] mp. 269˚C - 271˚C (cryst. from water).