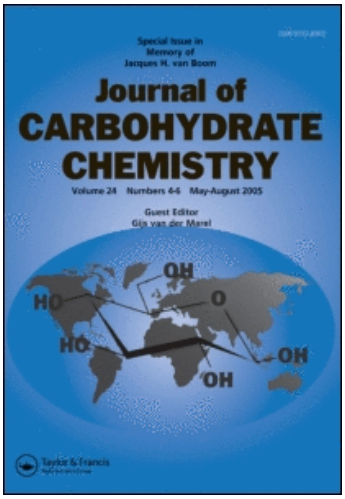

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Synthesis of Some Specifically Deoxygenated D-Hexopyranosyl Phosphates

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Synthesis Of Some Specifically Deoxygenated D-Hexopyranosyl Phosphates [1]

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ABSTRACT

A number of diphenyl α-glucopyranosyl and xylopyranosyl phosphates (**4**, **7**, **11**, **15**, **19**, and **25**) were prepared from their respective glycosyl chlorides by reaction with silver diphenyl phosphate. These sugar phosphates are of interest as enzyme substrates in deoxy sugar biosynthesis.

INTRODUCTION

Deoxy sugars are widely distributed in plant tissue, bacterial cell walls and secondary metabolites. A program presently underway in this laboratory is concerned with deoxy sugar biosynthesis in bacteria. Our interest focuses on the nucleoside diphosphosugar dehydratases, a set of bottleneck enzymes in the pathway of deoxy sugars. Therefore, structural modifications at positions C-4 and C-6 of the hexosyl moiety should lead to inhibitors, whereas modifications at C-2 and C-3 are more likely to give co-substrates.

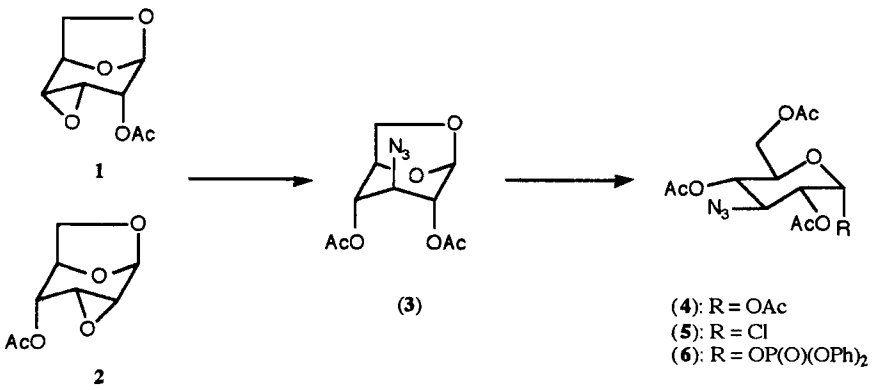
The literature contains a considerable body of papers concerned with the synthesis of phosphates and deoxy sugars from the acetates,[2] 1-OH deblocked hexoses,[3] glycosyl orthoesters,[4] and trichloroacetimidates.[5] However, in this paper we present procedures

which are optimized for particular deoxy sugars and which also describe preparation of sufficient quantities of these sugars for their biochemical evaluation as enzyme substrates.

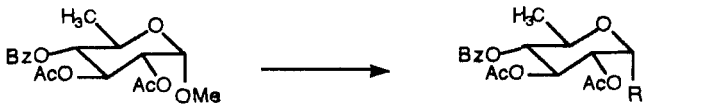
RESULTS AND DISCUSSION

The kanosamine derivative **4** could be easily prepared by azide ion attack on the mixture of epoxides **1** and **2**, obtained from levoglucosan by a method devised by Cerny and co-workers.[6] Although the preparation of **4** has been published by various authors, the method applied here was found to be more effective than techniques following a double inversion of C-3 in *gluco*-configured derivatives[7,8] or by recyclization using a nitromethane condensation.[9] *Trans*-diaxial epoxide ring-opening of **1** and **2** followed by regiospecific acetylation gave **3** as a single product in 55% yield. The per-*O*-acetate **4** was obtained after acetolysis. Treatment of **4** in refluxing dichloromethyl methyl ether in the presence of freshly fused zinc chloride[10] gave the glycosyl chloride **5** in 73% yield as a stable, yellow syrup.

The phosphate group was introduced stereoselectively by reaction of **5** with diphenyl phosphate.[11] Under these reaction conditions the formation of traces of a by-product, presumably the β-configured phosphate was observed. However, due to their reduced stability only the α-configured products were isolated after chromatography. Phosphate **6** was obtained in 50% yield following this protocol.



Methyl 2,3-di-*O*-acetyl-4-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (**7**)[12] could also be transformed into its corresponding chloride **8** (47% yield), which in turn was coupled with silver diphenyl phosphate to give 6-deoxy phosphate **9** (36% yield). The lower yield is mainly due to the formation of various side products, which could be reduced slightly by refluxing the mixture of silver diphenyl phosphate and chloride **8** under an argon atmosphere.



7

(**8**): R = Cl
(**9**): R = $OP(O)(OPh)_2$

All 4-deoxy *gluco*- and *xylo*-configured pyranosides **11**, **15**, **19**, and **24** could be synthesized in similar fashion: Selective benzoylation of D-galactose or D-fucose at -40 °C yielded sufficient amounts of the respective 4-OH unprotected galactopyranoses, either **10** or **23**. Although the synthesis of **10** has been reported by Garegg and co-workers,[13] it was observed to be essential to keep the reaction mixture exactly at -40 °C in order to obtain reasonable amounts of partially benzoylated galactose. This is in accord with the benzoylation of L-fucose by Thiem et al.[14] After esterification with triflic anhydride, either iodide or azide-attack at the corresponding *galacto*-configured triflates gave the 4-azido and 4-iodo-glucopyranoses **11**, **19**, and **24** respectively, in yields between 57% and 81% after flash chromatography. Reduction of **11** and **24** to **15** and **25**, respectively, was achieved, without decomposition of the relatively labile 4-deoxy sugar by hydrogenation in a mixture of dichloromethane/ethanol/equimolar aqueous $NaHCO_3$. This procedure, due to a facile workup, was found to be superior to that employing equimolar amounts of triethylamine. The resulting ^1H NMR spectrum of **25** showed H-4_{eq} and H-4_{ax} signals in the upfield region (2.6 to 2.1 ppm) with ddd and dd-multiplicities, respectively. The data for **25** were in complete accordance with those reported for the L-enantiomer.[14]

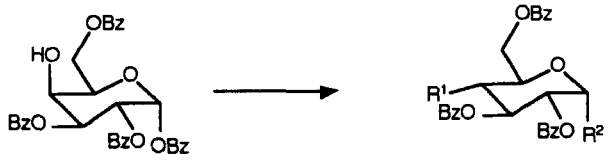
All glucopyranoses **11**, **15**, **19**, and **25** were transformed into their glycosyl chlorides and the pyranosyl phosphates as described above. The yields ranged from 30 to 49%, with 4-iodide **12** as the least reactive glycosyl donor.

The anomerically deblocked glycopyranoses **13**, **17**, and **21** were obtained in good yields from the respective glycosyl chlorides with silver carbonate in refluxing acetone / water with traces of acetic acid and are now at hand for further phosphorylation studies involving phosphite reagents as proposed by van Boom and co-workers.[15]

The α-configuration of all phosphates, **6**, **9**, **14**, **18**, **22**, and **27** was determined from their respective proton-phosphorus and carbon-phosphorus couplings.

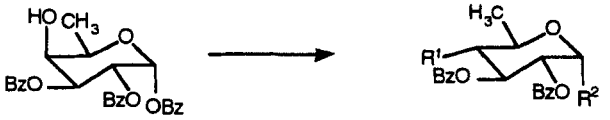
Both ^1H NMR and ^{13}C NMR spectra proved the presence of a phosphate group at C-1 in these compounds. Anomeric proton signals appear as doublets of doublets with a $^3J_{H\text{-}1,P}$ (6.5 Hz) and a $J_{1,2}$ coupling, confirming a *syn*-clinal equatorial-axial relationship between both hydrogens. Furthermore, a $^4J_{H\text{-}2,P}$ coupling of about 3.0 Hz was observed throughout (in general $^4J_{H,P}$<1Hz for the β-*gluco*-case [16,17]) which gave strong evidence for an α-configuration at C -1. The ^{13}C-NMR assignments were made by ^{13}C-^1H-

correlation. In addition C-1 and C-2 could be determined from their phosphorus couplings $^2J_{C\text{-}1,P} = 4.8$ - 5.7 Hz and a $^3J_{C\text{-}2,P} = 6.7$ -7.6 Hz.



(10)

#	R^1	R^2	#	R^1	R^2	#	R^1	R^2
11	I	OBz	**15**	H	OBz	**19**	N_3	OBz
12	I	Cl	**16**	H	Cl	**20**	N_3	Cl
13	I	OH	**17**	H	OH	**21**	N_3	OH
14	I	OP(O)(OPh)$_2$	**18**	H	OP(O)(OPh)$_2$	**22**	N_3	OP(O)(OPh)$_2$



(23)

#	R^1	R^2
24	I	OBz
25	H	OBz
26	H	Cl
27	H	OP(O)(OPh)$_2$

For further biological evaluation a set of deoxygenated glycosyl phosphates is now at hand which is stable on storage at 0 °C. We are presently engaged in both the enzymic and chemical syntheses of deoxythymidine diphosphates of various deoxy sugars.

EXPERIMENTAL

All reactions were monitored by TLC on silica gel plates (Merck, GF_{254}), visualized by spraying with a solution of 1% 4-methoxybenzaldehyde in ethanol containing 0.1% (v/v) of sulfuric acid and subsequent charring. Column chromatography was performed by "flash" technique on silica gel (230-400 mesh, particle size 0.040-0.063mm, Merck). NMR spectra were recorded on Bruker instruments CA-250 (62.90 MHz for ^{13}C) and

AMX-400 (100.7 MHz for ^{13}C) with tetramethylsilane or $CDCl_3$ as internal references. Micronanalyses were carried out at the Institut für Organische Chemie, Hamburg. Optical rotations were measured with a Perkin-Elmer polarimeter 243 (λ = 589 nm, d=10 cm). Chemicals were purchased from Merck, Aldrich or Sigma and were analytical grade. Solvents were dried by standard procedures.

General Procedures

Acetylation (A). To a solution of the alcohol (2 mmol) in anhyd pyridine (40 mL) was added acetic anhydride (20 mL) and the reaction mixture stirred at room temperature for 4-8 h. After addition of methanol (40 mL) the mixture was concentrated *in vacuo* and co-distilled with toluene. The product was isolated after flash chromatography with the solvents specified below.

Synthesis of Glycosyl Chloride (B). The glycoside or glycosyl acetate was refluxed under nitrogen with a catalytic amount of freshly fused $ZnCl_2$ in dichloromethyl methyl ether. After completion of the reaction, excess ether was evaporated, the residue taken up in dichloromethane (50 mL) and filtered. The organic layer was washed twice with a cold solution of satd $NaHCO_3$ (30 mL) and filtered through a layer of $MgSO_4$ before evaporation of the solvent. The yellow/brown oil was either processed without further purification or flash-chromatographed with the solvent listed below.

Diphenyl Phosphates (C). The α-hexopyranosyl chloride (1 mmol) was heated to a given temperature in anhyd toluene with an equimolar amount of silver diphenyl phosphate in a nitrogen atmosphere. After phosphorylation was complete the reaction mixture was cooled to room temperature, filtered, the solvent evaporated and the residue purified by flash chromatography.

Anomerically Deblocked Hexoses (D). The α-hexopyranosyl chloride (1 mmol) was dissolved in 20 mL acetone/water (5:1) and to the solution was added 150 μL of acetic acid and 100 mg of Ag_2CO_3. The mixture was heated under reflux for 2-4 h until TLC indicated a slower moving product.

1,6:3,4-Dianhydro-2-*O*-acetyl-β-D-allopyranose (1) and **1,6:2,3-Dianhydro-4-*O*-acetyl-β-D-allopyranose (2).** Following a literature procedure,[6] a solution of 1,6-anhydro-2,4-di-*O*-benzyloxycarbonyl-3-*O*-methanesulfonyl-β-D-glucopyranose (5.6 g, 11.0 mmol) in dichloromethane (50 mL) was added at 5 °C to a solution of 2.29 g (99.6 mmol) of sodium in 28 mL anhyd methanol before the mixture was allowed to attain room temperature. After 8 h TLC (toluene/ethyl acetate) showed no starting material and indicated the formation of a more polar product. The mixture was neutralized with 2N HCl, diluted with acetone (100 mL) and concentrated. The residue was taken up in ethyl acetate and filtered through a 5 cm layer of silica gel. The filtrate was concentrated and co-distilled several times with *p*-xylene to remove traces of water before

the oily residue was acetylated. Flash-chromatography yielded the product mixture as colourless crystals. Yield 1.73g (84%). Lit.[6]: 74% for the non-acetylated material.

1,6-Anhydro-2,4-di-*O*-acetyl-3-azido-3-deoxy-β-D-glucopyranose (3). The above mixture **1** and **2** (1.50 g, 8.1 mmol) was dissolved in 90 mL of anhyd *N,N*-dimethyl formamide To the solution was added 4.20 g (64.8 mmol) of sodium azide and the reaction mixture heated to 140 °C for 4 h. The solvent was evaporated, the dark brown residue taken up in dichloromethane and the mixture filtered. The filtrate was again concentrated, finally by co-distillation with *p*-xylene and the residue acetylated following procedure A. After chromatographing the reaction mixture (toluene/ethyl acetate, 2:1), the product was isolated as an amorphous white solid. Yield: 1.20g (55%); mp 85-87 °C; $[\alpha]_D^{20}$ -41.1° (*c* 1.0, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 5.40 (s, H-1), 4.57 (mc, 3H, H-2, H-3, H-4), 4.07 (d, H-6a), 3.73 (mc, 2H, H-5, H-6b), 2.18 (2×s, each 3H, each OAc); $J_{5,6a}$=7.6, $J_{6a,6b}$=9.0 Hz; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.3, 169.9 (C=O), 100.1 (C-1), 74.8 (C-5), 72.8 (C-4), 71.6 (C-2), 66.4 (C-6), 59.1 (C-3), 20.9, 20.8 (2×CO<u>C</u>H$_3$). (Assignments were made by COLOC spectroscopy and by comparison to spectral values found for the mono-acetylated material, cf. ref.[18])

Anal. Calcd for $C_{10}H_{13}N_3O_6$ (271.2): C, 44.28; H, 4.83; N, 15.49. Found: C, 44.39; H, 4.90; N, 15.57.

1,2,4,6-Tetra-*O*-acetyl-3-azido-3-deoxy-α-D-glucopyranose (4). Compound **3** (1.14 g, 4.2 mmol) was dissolved in acetic anhydride (50 mL) and to the solution was added 2 drops of perchloric acid at 0 °C. After the reaction was left 12 h at room temperature the mixture was poured onto ice and the mixture extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered and the filtrate chromatographed after concentration (*n*-hexane/ethyl acetate, 1:1) to yield a yellow oil: 1.43g (91%); $[\alpha]_D^{20}$ +60.1° (*c* 0.9, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 6.30 (d, H-1), 5.03 (dd, H-4), 4.95 (dd, H-2), 4.20 (dd, H-6a), 4.07 (mc, 2H, H-5, H-6b), 3.97 (dd, H-3), 2.21 - 2.0 (4×s, 4× 3H, 4× OAc); $J_{1,2}$=3.6, $J_{2,3}$=10.6, $J_{3,4}$=10.2, $J_{4,5}$=10.0, $J_{5,6a}$=4.4, $J_{6a,6b}$=12.6 Hz; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.3, 169.9 (2×s, 2×C=O), 100.1 (C-1), 74.8 (C-5), 72.8 (C-2), 71.6 (C-4), 66.4 (s, C-6), 59.1 (C-3), 20.9, 20.8 (2×s, 2×CO<u>C</u>H$_3$).

Anal. Calcd for $C_{14}H_{19}N_3O_9$ (373.3): C, 45.04; H, 5.13; N, 11.26. Found C, 44.92; H, 5.20; N, 10.50. A better value for N could not be obtained.

2,4,6-Tri-*O*-acetyl-3-azido-3-deoxy-α-D-glucopyranosyl chloride (5). Compound **4** (1.34 g, 3.59 mmol) was treated as described in procedure B for 3 h. Chromatography (toluene/ethyl acetate, 2:1) yielded a light yellow syrup (920 mg, 73%): ^1H NMR (400 MHz, $CDCl_3$) δ 6.29 (d, H-1), 5.01 (dd, H-4), 4.87 (dd, H-2), 4.24 (mc~dd and ddd, 2H, H-6a and H-5), 4.08 (mc~dd and dd, 2H, H-6b and H-3), 2.18,

2.15 and 2.09 (3×s, 3×3H, 3×OAc); $J_{1,2}$=4.0, $J_{2,3}$=10.0, $J_{3,4}$=10.0, $J_{5,6a}$=3.0, $J_{6a,6b}$=13.8 Hz; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.5 and 169.1 (3×s, 3×C=O), 90.2 (C-1), 71.6, 70.5, 67.2 (C-6), 61.2, 60.6, 20.5 (3×s, 3×$COCH_3$).

Diphenyl (2,4,6-Tri-*O*-acetyl-3-azido-3-deoxy-α-D-glucopyranosyl) Phosphate (6). Compound **5** (910 mg, 2.62 mmol) was reacted following procedure C to give, after chromatography (toluene/ethyl acetate, 2:1), pure α-phosphate **6** as a colourless syrup: 740 mg (50%); $[\alpha]_D^{20}$ +86.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.20 (m, 10H, aryl-H), 6.30 (dd, H-1), 5.20 (dd, H-4), 4.86 (dd, H-2), 4.15 (dd, H-6a), 4.04 (ddd, H-5), 3.97 (dd, H-3), 3.91 (dd, H-6b), 2.08, 2.05, 2.00 (3×s, 3×3H, 3×OAc); $J_{1,2}$=3.3, $J_{1,P}$=6.5, $J_{2,3}$=11.0, $J_{2,P}$=3.0, $J_{3,4}$=10.0, $J_{4,5}$=10.0, $J_{5,6a}$=4.0, $J_{5,6b}$=2.5, $J_{6a,6b}$=12.5 Hz; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.53, 169.6, 169.1 (3×s, 3×C=O), 130.0 - 120.0 (aryl-C), 94.6 (d, C-1), 70.6 (d, C-2), 69.9 (C-5), 67.3 (C-4), 61.1 (C-6), 60.4 (C-3), 20.6 - 20.3 (3×s, 3×CO$\underline{C}H_3$); $J_{C\text{-}1,P}$=5.72, $J_{C\text{-}2,P}$= 7.63 Hz.

Anal. Calcd for $C_{22}H_{26}N_3O_{11}P$ (539.4): C, 48.99; H, 4.86; N, 7.79. Found: C, 48.46; H, 4.90; N, 7.75.

2,3-Di-*O*-acetyl-4-*O*-benzoyl-6-deoxy-α-D-glucopyranosyl chloride (8). Following procedure B, compound **7**[12] was refluxed for 6 h to give **8**, after flash chromatography (toluene/ethyl acetate, 7:1) as a hygroscopic amorphous white solid, characterized by NMR: yield: 1.41g (47%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.42 (m, 5H, aryl-H), 6.32 (d, H-1), 5.73 (dd, H-4), 5.13 (dd, H-3), 5.05 (dd, H-2), 4.36 (dq, H-5), 2.07, 1.92 (2×s, 6H, 2×OAc), 1.30 (d, 3H, H-6); $J_{1,2}$=4.0, $J_{2,3}$=10.0, $J_{3,4}$=10.0, $J_{4,5}$=10.0, $J_{5,6}$=6.0 Hz.

Diphenyl (2,3-Di-*O*-acetyl-4-*O*-benzoyl-6-deoxy-α-D-glucopyranosyl) Phosphate (9). Compound **8** (670 mg, 1.72 mmol) was treated following procedure C for 2 h under reflux. After chromatography (toluene/ethyl acetate, 5:1) **9** was obtained as a light yellow oil: 370 mg (36%); $[\alpha]_D^{20}$ +33.7° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 - 7.16 (m, 15H, aryl-H), 6.07 (dd, H-1), 5.68 (dd, H-4), 5.10 (dd, H-3), 5.05 (ddd, H-2), 4.11 (dq, H-5), 2.16 (s, 6H, 2×CH_3CO), 1.14 (d, H-6); $J_{1,2}$=3.5, $J_{1,P}$=6.5, $J_{2,3}$=10.0, $J_{2,P}$=3.0, $J_{3,4}$=10.0, $J_{4,5}$=10.0, $J_{5,6}$=6.0 Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 169.9, 169.8, and 165.4 (3×s, 3×C=O), 150.4 - 120.1 (aryl-C), 95.2 (d, C-1), 70.3 (d, C-2), 73.2 (C-5), 68.9 (C-4), 68.2 (C-3), 20.6, 20.3 (2×CH_3CO), 17.1 (C-6); $J_{C1,P}$=4.8, $J_{C2,P}$=6.7 Hz.

Anal. Calcd for $C_{27}H_{29}O_{11}P$ (560.5): C, 57.86; H, 5.22. Found: C, 58.02; H, 5.31.

1,2,3,6-Tetra-*O*-benzoyl-α-D-galactopyranose (10). A procedure described in the literature [13] was adapted for 10.0 g (55.51 mmol) of D-galactose except for the fact

that benzoyl chloride was added at -40 °C within 6-8 h under a nitrogen atmosphere: yield 7.60 g (23%); $[\alpha]_D^{20}$ +144.2 (*c* 1.0, $CHCl_3$); Lit.[13]: $[\alpha]_D^{20}$ +147.0 (*c* 0.8, $CHCl_3$); Lit.[19]: $[\alpha]_D^{25}$ +179.4 (*c* 0.5, $CHCl_3$). All ^1H and ^{13}C NMR spectra were in accordance to those given in reference [19].

1,2,3,6-Tetra-*O*-benzoyl-4-deoxy-4-iodo-α-D-glucopyranose (11). Under a nitrogen atmosphere, 2.50 g (4.20 mmol) of **10** were dissolved in anhyd dichloromethane and 3.6 mL of anhyd pyridine. At -20 °C a solution of 3.3 mL (20.18 mmol) of trifluoromethanesulfonic acid anhydride in 15 mL of dichloromethane was added dropwise before the reaction was allowed to reach ambient temperature. After the reaction was complete (TLC, toluene/ethyl acetate, 3:1), 30 mL of dichloromethane were added, the mixture was poured onto ice and quickly extracted twice with 30 mL portions of dichloromethane. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*, the water bath temperature not exceeding 30 °C. After several co-evaporations with toluene the oily residue was immediately subjected to the following procedures. The complete amount was dissolved in anhyd *N,N*-dimethylformamide and this solution was added 667 mg (4.45 mmol) of sodium iodide. The reaction mixture was stirred at room temperature for 8 h, 30 mL of dichloromethane were added to the mixture, which was washed subsequently with 10% $Na_2S_2O_3$ and water. The organic layer was dried over $MgSO_4$, concentrated and purified by chromatography (toluene/ ethyl acetate, 30:1) to yield **11**: 2.13g (72%); $[\alpha]_D^{20}$ +135.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 - 7.12 (m, aryl-H), 6.85 (d, H-1), 6.28 (dd, H-3), 5.51 (dd, H-2), 4.88 - 4.83 (m, 2H, H-6a, H-6b), 4.67 (ddd, H-5), 4.47 (dd, H-4); $J_{1,2}$=3.5, $J_{2,3}$=10.5, $J_{3,4}$=10.5, $J_{4,5}$=11.0, $J_{5,6a}$=2.6, $J_{5,6b}$=2.8 Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.9, 165.3, 165.2, and 164.4 (4×C=O), 137.9 - 125.3 (aryl-C), 90.4 (C-1), 73.6 (C-2), 72.6 (C-5), 70.9 (C-3), 65.1 (C-6), 23.2 (C-4).

Anal. Calcd for $C_{34}H_{27}IO_9$ (706.5): C, 57.8; H, 3.85. Found: C, 57.1; H, 3.79.

2,3,6-Tri-*O*-benzoyl-4-deoxy-4-iodo-α-D-glucopyranosyl chloride (12). Compound **11** (1.10 g, 1.9 mmol) was treated under reflux for 4 h following procedure B to give, after flash-chromatography (toluene/ethyl acetate, 40:1), **12** as a white, air sensitive solid: 700 mg (76%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 - 7.2 (m, aryl-H), 6.54 (d, H-1), 6.20 (dd, H-3) 5.33 (dd, H-2), 4.91 - 4.84 (m, H-6a, H-6b), 4.81 (ddd, H-5), 4.37 (dd, H-4); $J_{1,2}$=4.0, $J_{2,3}$=10.0, $J_{3,4}$=11.0, $J_{4,5}$=11.0, $J_{5,6a}$=2.8, $J_{5,6b}$=2.8Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.9, 165.3, 165.0 (3×s, 3×C=O), 133.8 - 125.3 (m, aryl-C), 89.7 (C-1), 74.1 (C-2), 72.0 (C-5), 71.9 (C-3), 64.8 (C-6), 22.4 (C-4).

2,3,6-Tri-*O*-benzoyl-4-deoxy-4-iodo-α-D-glucopyranose (13). Compound **11** (800 mg, 1.13 mmol) was successively reacted as described in procedures

B and D to yield 510 mg of product (87%, 5:1 α/β ratio, judged by integration of the respective H-1 signals) after flash chromatography (toluene/ethyl acetate, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 - 7.15 (m, aryl-H), 5.78 (d, H-1), 5.17 (dd, H-2), 6.20 (dd, H-3), 4.32 (dd, H-4), 4.88 (m, H-5), 4.80 (m, 2H, H-6a, H-6b), 3.16 (d, 1-OH); $J_{1,2}$=3.5, $J_{2,3}$=10.0, $J_{3,4}$=10.5, $J_{4,5}$=10.5Hz. Due to signal overlap, the signals from the β-configured anomer could not be assigned. ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 166.2, 165.7, 165.4 (3×s, 3×C=O), 145.6 - 127.1 (m, aryl-C), 85.3 (C-1$_\beta$), 90.6 (C-1$_\alpha$), 73.0, 72.5, 70.6 (C-2, C-3, C-5), 65.5 (C-6), 24.9 (C-4).

Anal. Calcd for $C_{20}H_{23}IO_8$ (518.3): C, 46.35; H, 4.47. Found: C, 45.94; H, 4.60.

Diphenyl (2,3,6-Tri-*O*-benzoyl-4-deoxy-4-iodo-α-D-glucopyranosyl) Phosphate (14). Compound **12** (400 mg, 0.8 mmol) was treated following procedure C. TLC (toluene/ethyl acetate, 7:1) indicated no further turnover of starting material after 3.5 h. Product **14** was isolated by flash-chromatography with the same solvent (R_F 0.4) as an amorphous, white solid: yield 100 mg (30%). $[\alpha]_D^{20}$ +88.1° (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 - 7.02 (aryl-H), 6.37 (ddd, H-1), 6.15 (dd, H-3), 5.32 (ddd, H-2), 4.72 (dd, H-6a), 4.62 (dd, H-6b), 4.50 (ddd, H-5), 4.35 (dd, H-4); $J_{1,2}$=3.5, $J_{1,P}$=6.5, $J_{2,3}$=10.0, $J_{2,P}$=3.5, $J_{3,4}$=11.0, $J_{4,5}$=11.0, $J_{5,6a}$=3.5, $J_{5,6b}$=2.0, $J_{6a,6b}$=12.5 Hz; ^{13}C NMR (110.67, $CDCl_3$) δ 165.9, 165.3, 165.0 (3×s, 3×C=O), 133.5 - 120.0 (m, aryl-C), 95.6 (d, C-1), 73.3 (d, C-2), 71.7 (C-5), 71.1 (C-3), 64.8 (C-6), 22.6 (C-4); $J_{C\text{-}1,P}$ 5.7, $J_{C\text{-}2,P}$ 8.6 Hz.

Anal. Calcd for $C_{37}H_{32}IO_{11}$ (779.6): C, 57.01; H, 4.14. Found: C, 57.50; H, 4.20.

1,2,3,6-Tetra-*O*-benzoyl-4-deoxy-α-D-xylohexopyranose (15). Compound **11** (1.0 g, 1.4 mmol) was dissolved in 50 mL of dichloromethane/ethanol (1:1). This solution was added to $NaHCO_3$ (750 mg) in water (20 mL), containing 120 mg palladium catalyst (10% on charcoal). The resulting mixture was degassed in an ultrasonifier and hydrogenated under vigorous stirring for 24 h at ambient pressure. Some batches required a longer reaction time, as detected by the incomplete conversion of starting material (TLC, toluene/ethyl acetate, 20:1; starting mat. R_F 0.3, product R_F 0.2). The solid was removed by filtration and the mixture co-evaporated several times with toluene to leave a yellow gum. This was taken up in 100 mL dichloromethane, and and the organic layer washed successively with $Na_2S_2O_3$ (10% in water), water and brine. The organic layer was dried over $MgSO_4$, the solvent evaporated and the residue applied to chromatography (toluene/ethyl acetate, 20:1) to yield a white foam (598 mg, 93%) after evaporation and drying *in vacuo*: $[\alpha]_D^{20}$ +186° (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 7.21 (m, 20H, aryl-H), 6.80 (d, H-1), 5.91 (ddd, H-3), 5.65 (dd, H-2), 4.59 (mc≈dddd, H-5), 4.46 (mc, 2H, H-6a, H-6b), 2.62 (ddd, H-4eq), 2.08 (dd, H-4ax);

$J_{1,2}$=3.5, $J_{2,3}$=10.5, $J_{3,4ax}$=11.0, $J_{3,4eq}$=5.0, $J_{4eq,4ax}$=12.0, $J_{4ax,5}$=11.5, $J_{4eq,5}$=2.5 Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 166.2, 165.9, 165.6, and 164.6 (4×s, 4×C=O), 133.7 - 128.4 (m, aryl-C), 91.2 (C-1), 70.9 (C-2), 68.5 (C-3), 68.3 (C-5), 65.6 (C-6), 32.9 (C-4).

Anal. Calcd for $C_{24}H_{28}O_9$ (460.5): C, 62.60; H, 6.13. Found: C, 62.76; H, 6.24.

2,3,6-Tri-*O*-benzoyl-4-deoxy-α-D-xylohexopyranosyl Chloride (16). Compound **15** (300 mg, 0.52 mmol) was treated under reflux for 2 h following procedure B to give, after flash-chromatography (toluene/ethyl acetate, 7:1) **16** as a colourless, air sensitive syrup, 230 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 - 7.30 (m, ≈15H, aryl-H), 6.50 (d, H-1), 5.86 (ddd, H-3), 5.47 (dd, H-2), 4.71 (m_c, H-5), 4.49 (m, 2H, H-6a, 6b), 2.56 (ddd, H-4eq), 2.00 (dd, H-4ax); $J_{1,2}$=4.0, $J_{2,3}$=10.5, $J_{3,4ax}$=11.0, $J_{3,4eq}$=5.5, $J_{4ax,4eq}$=12.5, $J_{4ax,5}$=5.5, $J_{4eq,5}$=2.5 Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.5, 165.1, 165.08 (3×s, 3×C=O), 133.0 - 127.8 (m, aryl-C), 91.4 (C-1), 71.3 (C-2), 68.4 (C-3), 67.2 (C-5), 64.6 (C-6), 31.8 (C-4).

2,3,6-Tri-*O*-benzoyl-4-deoxy-α/β-D-xylohexopyranose (17). Compound **16** (200 mg, 0.4 mmol) was reacted as described in procedure D. After 2 h (TLC, toluene/ethyl acetate, 7:1) showed no starting material. After flash chromatography (toluene/ethyl acetate, 10:1) the product could be isolated as an amorphous, colourless material, α/β-ratio = 2:1 (as estimated from ^{1}H-NMR integrations): yield 168 mg (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 - 7.30 (m, 15H, aryl-H), 5.85 (sext., ≈ddd, H-3_α), 5.87 (d, H-1_α), 5.51 (ddd, H-3_β), 5.32 (dd, H-2_α), 5.23 (dd, H-2_β), 4.90 (d, H-1_β), 4.62 (m_c, H-5_α), 4.49 (m_c, H-5_β), 4.43 (m_c, 2H, H-$6a_\alpha$, H-$6b_\alpha$), 4.10 (m_c, 2H, H-$6a_\beta$, H-$6b_\beta$), 2.47 (m_c, H-$4eq_\alpha$, H-$4eq_\beta$), 1.91 (m_c, H-$4ax_\alpha$, H-$4ax_\beta$); $J_{1\alpha,2\alpha}$=3.5, $J_{2\alpha,3\alpha}$=11.0, $J_{3\alpha,4ax\alpha}$=11.0, $J_{3\alpha,4eq\alpha}$=5.0, $J_{1\beta,2\beta}$=8.0, $J_{2\beta,3\beta}$=9.5, $J_{3\beta,4ax\beta}$=10.0, $J_{3\beta,4eq\beta}$=5.0 Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 166.5, 165,2, 165.0 (3×s, 3×C=O), 133.5 - 125.3 (m, aryl-C), 96.1 (C-1β), 91.4 (C-1α), 75.3 (C-2β), 72.8 (C-2α), 70.7 (C-3β), 70.0 (C-6β), 68.1 (C-3α), 66.1 (C-6α), 65.8 (C-5β), 65.6 (C-5α), 33.3 (C-4α), 33.1 (C-4β).

Anal. Calcd for $C_{28}H_{24}O_8$ (488.5): C 68.85; H, 4.95. Found: C 68.90; H, 4.91.

Diphenyl (2,3,6-Tri-*O*-benzoyl-4-deoxy-α-D-xylohexopyranosyl) Phosphate (18). Compound **16** (200 mg, 0.4 mmol) was treated following procedure C until TLC (toluene/ethyl acetate, 7:1) showed complete disappearance of starting material. The product was isolated by flash chromatography with the same solvent to give **18** as a colourless oil: yield 139 mg (49%); $[\alpha]_D^{20}$ +92° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 - 7.30 (m, aryl-H), 6.27 (dd, H-1), 5.72 (ddd, H-3), 5.46 (ddd, H-2), 4.60 (m_c, H-5), 4.30 (m_c, 2H, H-6a, H-6b), 2.34 (ddd, H-4_{eq}), 1.91 (dd, H-4_{ax});

$J_{1,2}$=3.8, $J_{1,P}$=6.4, $J_{2,P}$=3.5, $J_{3,4ax}$=11.0, $J_{3,4eq}$=5.4, $J_{4ax,4eq}$=12.0, $J_{4eq,5}$=2.5, $J_{4ax,5}$=5.5Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.4, 165.0, 164.95 (3×σ, 3×C=O), 133.0 - 120.0 (m, aryl-C), 98.2 (d, C-1), 70.8 (d, C-2), 67.7 (C-3), 67.0 (C-5), 64.7 (C-6), 31.9 (C-4); $J_{C\text{-}1,P}$=5.3, $J_{C\text{-}2,P}$=8.2Hz.

Anal. Calcd for $C_{39}H_{33}O_{11}P$ (708.7): C, 66.10; H, 4.69; P, 4.37. Found: C, 65.94; H, 4.73.

1,2,3,6-Tetra-*O*-benzoyl-4-azido-4-deoxy-α-D-glucopyranose (19). To a solution of **10** (2.5 g, 3.55 mmol) in 125 mL anhyd dichloromethane and 25 mL anhyd pyridine was added dropwise a solution of 2.75 mL (167.5 mmol) triflic anhydride in dichloromethane at -20 °C under a nitrogen atmosphere. After 30 min the reaction mixture was allowed to reach room temperature, stirred for aditional 30 min, diluted with 100 mL of dichloromethane and the resulting solution poured onto ice. The aqueous layer was separated and extracted twice with 50 mL of dichloromethane. The combined organic layers were washed with satd $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated to leave a yellow foam, which was dried shortly *in vacuo*. The foam was dissolved in 50 mL anhydr DMF, and NaN_3 (3.4 g, 52.5 mmol) and tetramethylurea (300 μL) were added to the solution. The reaction mixture was stirred at room temperature until TLC (*n*-hexane/ethyl acetate, 3:1) indicated no further conversion. Water (100 mL) was added to the mixture which was then filtered and the filtrate extracted twice with 100 mL portions of dichloromethane. The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated. The resulting oil was purified by flash-chromatography (*n*-hexane/ethyl acetate, 5:1) to give, after solvent evaporation, a white foam: yield 1.25g (57%); $[\alpha]_D^{20}$ +215.5° (*c* 0.9; $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 7.25 (m, ≈20H, aryl-H), 6.78 (d, H-1), 6.13 (dd, H-3), 5.66 (dd, H-2), 4.67 (m, 2H, H-6a, H-6b), 4.23 (sext.≈ddd, H-5), 4.06 (dd, H-4); $J_{1,2}$=4.0, $J_{2,3}$=10.0, $J_{3,4}$=10.0, $J_{4,5}$=10.5, $J_{5,6a}$=10.5, $J_{5,6b}$=3.0Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.7, 165.3 (2×s, 2×C=O), 165.0 (m, 2×C=O), 133.1 - 127.9 (m, aryl-C), 90.0 (C-1), 71.5 (C-2), 70.1 (C-3), 67.6 (C-5), 62.6 (C-6), 60.4 (C-4).

Anal. Calcd for $C_{34}H_{27}N_3O_9$ (621.6): C, 65.70; H, 4.38; N, 6.76; C, 65.62; H, 4.30; N, 6.41.

2,3,6-Tri-*O*-benzoyl-4-azido-4-deoxy-α-D-glucopyranose (21). Compound **19** (1.0 g, 1.61 mmol) was treated for 4 h following procedure B to give, after flash chromatography (*n*-hexane/ethyl acetate, 7:1) **20** as a light yellow syrup, yield 750 mg (86%). This product was processed without further purification. The 4-azido compound **20** (250 mg, 0.4 mmol), without purification, was then reacted by procedures B and D. After flash chromatography (toluene/ethyl acetate, 7:1) **21** was isolated as a light yellow syrup: yield 153 mg (74%), α/β ratio 4:1 as estimated from ^{1}H NMR; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 8.20 - 7.35 (m, 15H, aryl-H), 5.68 (dd, H-3_α), 5.75 (dd, H-3_β), 5.68 (d, H-1_α), 5.20 (dd and d, H-2_α and H-1_β), 4.95 (dd, br., H-2_β), 4.72 (m≈dd, H-$6a_\alpha$, H-$6a_\beta$), 4.61 (m≈ddd, H-$6b_\alpha$, H-$6b_\beta$), 4.33 (ddd, H-5_α), 4.16 (m_c, H-5_β), 3.92 (dd, H-4_β), 3.90 (dd, H-4_α), 3.31 (d, br., 1-O<u>H</u>); $J_{1\alpha,2\alpha}$=3.5, $J_{2\alpha,3\alpha}$=10.5, $J_{3\alpha,4\alpha}$=10.0, $J_{5\alpha,6a\alpha}$=3.5, $J_{5\alpha,6b\alpha}$=2.5, $J_{6a\alpha,6b\alpha}$=12.0, $J_{1\alpha,1\text{-O}\underline{H}}$=3.0, $J_{1\beta,2\beta}$=8.5, $J_{2\beta,3\beta}$=9.5Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.7, 165.3, 165.1 (3×s, 3×C=O), 133.1 - 127.9 (m, aryl-C), 95.4 (C-1_β), 72.3 (m_c, C-2_β, C-3_β, C-5_β), 71.5, 70.1, 67.6 (C-2_α, C-3_α, C-5_α), 62.3 (C-6_β), 62.6 (C-6_α), 60.1 (C-4_β), 60.4 (C-4_α).

Anal. Calcd for $C_{27}H_{23}N_3O_8$ (517.5): C, 62.67;H, 4.48; N, 8.12. Found: C, 62.21; H, 4.31; N, 7.75. A better value for N could not be obtained.

Diphenyl (2,3,6-Tri-*O*-benzoyl-4-azido-4-deoxy-α-D-glucopyranosyl) Phosphate (22). Compound **20** (700 mg, 1.31 mmol) was treated following procedure C until TLC showed no further reaction (approx. 2.5 h). Product **22** was isolated after flash chromatography as a colourless oil: yield 403mg (41%); $[\alpha]_D^{20}$ +84.4° (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 - 7.20 (m, aryl-H), 6.41 (dd, H-1), 6.02 (dd, H-3), 5.62 (ddd, H-2), 4.50 (m, 2H, H-6a, H-6b), 4.12 (ddd, H-5), 4.02 (dd, H-4); $J_{1,2}$=4.0, $J_{1,P}$=6.7, $J_{2,3}$=10.0, $J_{2,P}$=3.6, $J_{3,4}$=10.0, $J_{4,5}$=10.5, $J_{5,6a}$=10.5, $J_{5,6b}$=2.8Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 166.0, 165.8, 165.0 (m, ≈3×C=O), 133.0 - 126.5 (m, aryl-C), 97.6 (d, C-1), 72.0 (d, C-2), 69.3 (C-3), 67.0 (C-5), 62.5 (C-6), 60.5 (C-4); $J_{C\text{-}1,P}$=5.6, $J_{C\text{-}2,P}$=7.9Hz.

Anal. Calcd for $C_{41}H_{32}N_3O_{11}P$ (773.7): C, 63.65; H, 4.17; N, 5.43. Found: C, 63.14; H, 4.22; N, 6.02.

1,2,3-Tri-*O*-benzoyl-6-deoxy-α-D-galactopyranose (23). Following a literature procedure[14] a solution of D-fucose (5 g, 30.5 mmol) was reacted to give **23** (10.9 g, 75%) as a white foam: $[\alpha]_D^{20}$ +156° (*c* 1.2, $CHCl_3$); Lit[14] $[\alpha]_D^{20}$ -160° (c 3.15, $CHCl_3$) for the L-enantiomer; ^1H NMR (400 MHz, $CDCl_3$) δ 820 - 7.20 (m, aryl-H), 6.72 (d, H-1), 5.99 (dd, H-2), 5.84 (dd, H-3), 4.45 (q, br. ≈ dq, H-5), 4.29 (s, br. ≈ d, H-4), 1.39 (d, 3H, H-6); $J_{1,2}$=3.5, $J_{2,3}$=10.5, $J_{3,4}$=3.0, $J_{4,5}$ < 1.0, $J_{5,6}$=6.0 Hz; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 166.0, 165.6, 164.7 (3×s, 3×C=O), 134.5 - 125.3 (m, aryl-C), 90.9 (C-1), 71.5 (C-2), 69.0 (C-3), 68.0 (C-4), 67.7 (C-5), 16.2 (C-6).

Anal. Calcd for $C_{27}H_{24}O_8$ (476.5): C, 68.06; H 5.08. Found C, 67.98; H, 5.01.

1,2,3-Tri-*O*-benzoyl-4,6-dideoxy-4-iodo-α-D-glucohexopyranose (24). Following the procedure described for preparation of compound **11**, **23** (2.17 g, 4.55 mmol) was reacted to give **24** (2.17g, 81%): $[\alpha]_D^{20}$ +128° (*c* 1.0, $CHCl_3$), lit.[14] $[\alpha]_D^{20}$ -123° (*c* 0.29, $CHCl_3$) for the L-enantiomer. All ^1H and ^{13}C NMR spectra were in accordance with the data published for the L-configured enantiomer.

1,2,3-Tri-*O*-benzoyl-4,6-dideoxy-α-D-xylohexopyranose (25). Compound **24** (1.07 g, 1.97 mmol) was hydrogenated as described for compound **15** to give **25** (670 mg, 74%); $[\alpha]_D^{20}$ +218° (*c* 1.1, CH_2Cl_2); lit[14] $[\alpha]_D^{20}$ -223° (*c* 1.0, CH_2Cl_2) for the L-enantiomer. All NMR data were identical with those listed for the L-enantiomer.

2,3-Di-*O*-benzoyl-4,6-dideoxy-α-D-xylohexopyranosyl Chloride (26). Compound **25** (1.0 g, 2.17 mmol) was reacted as described in procedure B. After 2 h no starting material was detected (TLC, *n*-hexane/ethyl acetate, 5:1) and the reaction was worked up. The product can either be used with or without further purification. Yield after chromatography: 714 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 7.30 (m, aryl-H), 6.43 (d, H-1), 5.80 (ddd, H-3), 5.41 (dd, H-2), 4.25 (dq, br., H-5), 2.42 (ddd, H-4eq), 1.72 (ddd≈q, H-4ax), 1.30 (d, 3H, H-6); $J_{1,2}$=3.0, $J_{2,3}$=10.0, $J_{3,4eq}$=5.0, $J_{3,4ax}$=11.0, $J_{4eq,5}$=2.0, $J_{4ax,5}$=11.5, $J_{4eq,4ax}$=12.5, $J_{5,6}$=6.0 Hz. ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 165.8, 165.7 (2×s, 2×C=O), 133.7 - 128.4 (m, aryl-C), 92.5 (C-1), 72.2 (C-2), 68.2 (C-3), 67.3 (C-5), 37.7 (C-4), 20.4 (C-6).

Diphenyl 2,3-Di-*O*-benzoyl-4,6-dideoxy-α-D-xylohexopyranosyl Phosphate (27). Compound **26** (500 mg, 1.37 mmol) was treated under reflux following procedure C for 3 h. After solvent evaporation, chromatography (*n*-hexane/ethyl acetate, 6:1) compound **27** was obtained: yield 355mg (44%); $[\alpha]_D^{20}$ +41.5° (*c* 1.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 - 7.20 (m, aryl-H), 6.12 (dd, H-1), 5.74 (ddd, H-3), 5.38 (ddd, H-2), 4.12 (dq, H-5), 2.38 (ddd, H-4eq), 1.65 (ddd≈q, H-4ax), 1.18 (d, 3H, H-6); $J_{1,2}$=3.0, $J_{1,P}$=6.5, $J_{2,3}$=10.0, $J_{2,P}$=3.0, $J_{3,4eq}$=5.0, $J_{3,4ax}$=10.5, $J_{4eq,5}$=2.0, $J_{4ax,5}$=11.5, $J_{4eq,4ax}$=12.0, $J_{5,6}$=6.0Hz; ^{13}C NMR (100.7MHz, $CDCl_3$) δ 165.8, 165.6 (2×s, 2×C=O), 133.8 - 128.4 (m, aryl-C), 98.0 (d, C-1), 72.1 (d, C-2), 68.0 (C-5), 67.5 (C-3), 36.4 (C-4), 18.7 (C-6); $J_{C-1,P}$=5.0, $J_{C-2,P}$=7.0Hz.

Anal. Calcd for $C_{32}H_{29}O_9P$ (588.6): C, 65.31; H, 4.97; Found: C, 65.90; H, 5.02.

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