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Rhodium Catalysed Asymmetric Hydroformylation with Diphosphite Ligands based on Sugar Backbones

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Abstract: Chiral diphosphite ligands (PP) prepared from {(2,2'-biphenyl-1,1'-diyl), (4,4',6,6'-tetra-*t*-butyl-2,2'-biphenyl-1,1'-diyl), 4,4'-di-*t*-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl) and di(2-*t*-butyl, 6-methylphenyl)} phosphorochloridites and sugar backbones {1,2-*O*-isopropylidene-D-xylofuranose, methyl-2,3-*O*-isopropylidene-α-D-mannopyranoside and (methyl-3,6-anhydro)-α-D-mannopyranoside, α-D-glucopyranoside and β-D-galactopyranoside} have been used in the rhodium catalysed asymmetric hydroformylation of styrene. Enantioselectivities up to 64% have been obtained with stable hydridorhodium diphosphite dicarbonyl catalysts (HRhPP(CO)$_2$). High regioselectivities (up to 97%) to the branched aldehyde were found at relatively mild reaction conditions (T = 25-40°C, 9-45 bar of syngas pressure). The solution structures of HRhPP(CO)$_2$ catalysts have been studied by ^{31}P and ^{1}H NMR spectroscopy. Bidentate coordination of the diphosphite ligand to the rhodium centre takes place in a bis-equatorial way. A relation between the trigonal bipyramidal structure and the enantioselectivity of the HRhPP(CO)$_2$ complex is found. Rigid ligands with unsuitable geometries for bidentate coordination probably coordinate as monodentates and give rise to unstable catalysts and low selectivities during catalysis.

INTRODUCTION

Since the early seventies there has been a great deal of interest in the asymmetric hydroformylation of various functionalised alkenes.[1] The formed chiral aldehydes can serve as starting material for the synthesis of high value added organic compounds for e.g. pharmaceutical purposes.[2] Platinum complexes modified with chiral diphosphine ligands have proven to be highly enantioselective hydroformylation catalysts but generally suffer from poor regioselectivity and chemoselectivity to the desired branched chiral aldehydes.[3] In 1983 van Leeuwen and Roobeek reported a very active rhodium hydroformylation catalyst modified with a bulky phosphite ligand.[4] One of the major advantages of phosphites is that they are easy to prepare and are not as sensitive to air as phosphines.[5] With the development of mono and diphosphite ligands, it seemed possible to steer the selectivity of the hydroformylation reaction, if required, to linear or branched products.[6]

We reported on the asymmetric hydroformylation of styrene with chiral diphosphite ligands albeit with low enantiomeric excess (20%).[7a] Hydroformylation of vinyl acetate with chiral diphosphite ligands based on *(R)* and *(S)*-bisnaphthol has been reported by Takaya et al.[8] Highly enantioselective hydroformylation of functionalised alkenes with rhodium/phosphine-phosphite catalysts has been published by the same workers.[9] Union Carbide claimed enantioselectivities up to 90% with a diphosphite ligand based on *(2R,4R)*-pentanediol.[10] Up to now only little attention has been paid to the structure of hydridorhodium diphosphite

dicarbonyl complexes, the putative catalysts in these systems.[11] Solution structures of hydridorhodium diphosphite dicarbonyl catalysts in the asymmetric hydroformylation of styrene have been published recently.[12] It became clear that the structure and the stability of the catalyst plays a crucial role in the asymmetric induction. Spectroscopic studies involving NMR, IR and X-ray carried out in our group[13] revealed a trigonal bipyramidal structure for a hydridorhodium diphosphite hydroformylation catalyst in agreement with that proposed in solution chemistry.[12a] We here report the synthesis and the applicability of diphosphite ligands based on easily accessible sugar derivatives as chiral hydroformylation catalysts. The results are discussed in relation to the solution structures of the hydridorhodium diphosphite dicarbonyl catalysts.

RESULTS AND DISCUSSION

Synthesis

To enlarge the scope of the asymmetric hydroformylation with chiral diphosphite ligands we have used several sugar backbones as starting material. From earlier work it appeared that diphosphite ligands based on 1,3-diols gave rise to relatively stable hydridorhodium diphosphite hydroformylation catalysts, compared to those based on 1,2 and 1,4-diols.[7a,12] 1,2-*O*-Isopropylidene-D-xylofuranose (fig. 1), having a three carbon atom bridge between the hydroxy groups, was among others used as starting material.
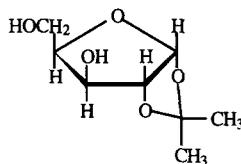

Fig. 1   1,2-*O*-isopropylidene-D-xylofuranose.

As a consequence of the intrinsically higher reactivity of the primary hydroxy group at C_5 compared with the secondary hydroxy group at C_3 toward phosphorochloridites, different substituents could be brought into the molecule. In order to study the effect of small structural changes, a series of ligands have been synthesised in which the steric bulk was varied at the ortho and para positions of the bisphenol phosphorochloridites (**1a**, **1b** and **1c**, fig. 2).
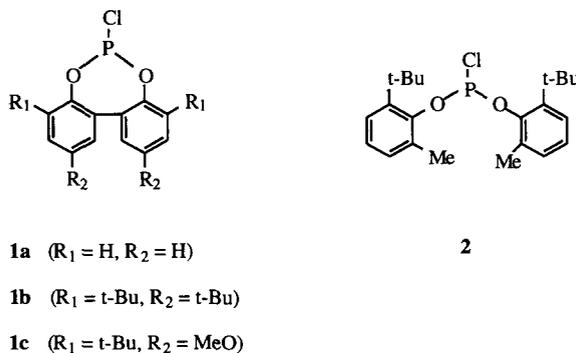

1a   (R₁ = H, R₂ = H)   **2**

1b   (R₁ = t-Bu, R₂ = t-Bu)

1c   (R₁ = t-Bu, R₂ = MeO)

Fig. 2   Variation of steric hindrance in phosphorochloridites.

Di-(2-t-butyl,6-methylphenyl)phosphorochloridite (2), considered to be a very bulky substituent, was used to develop sterically demanding diphosphite ligands. Mono phosphorylated 1,2-O-isopropylidene-D-xylofuranose derivatives **3a** and **3b** (fig. 3) were prepared by reaction with one equivalent of phosphorochloridite **1c** and **2** respectively in the presence of a base.
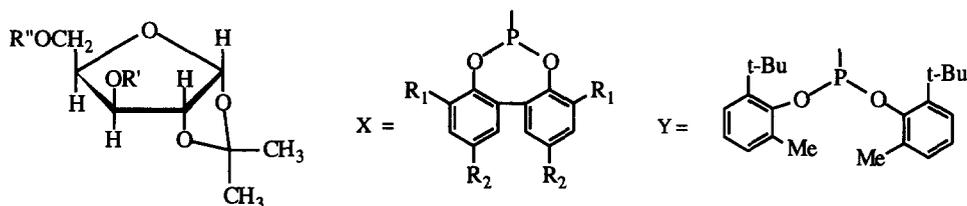
3a R' = H, R" = X: R$_1$ = t-Bu, R$_2$ = OMe

3b R' = H, R" = Y

4 R' = R" = X: R$_1$ = R$_2$ = H

5 R' = R" = X: R$_1$ = R$_2$ = t-Bu

6 R' = R" = X: R$_1$ = t-Bu, R$_2$ = OMe

7 R' = X: R$_1$ = R$_2$ = H , R" = X: R$_1$ = t-Bu, R$_2$ = OMe

8 R' = X: R$_1$ = t-Bu, R$_2$ = OMe, R" = Y
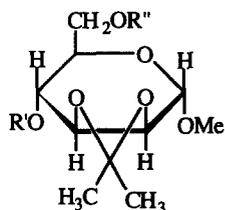
9 R' = R" = X: R$_1$ = R$_2$ = t-Bu
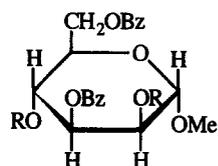
10 R' = R" = X: R$_1$ = t-Bu, R$_2$ = OMe
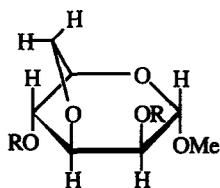
11 R = X: R$_1$ = t-Bu, R$_2$ = OMe
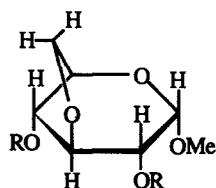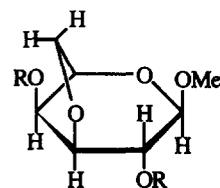
12   **13**   **14**

12, 13, 14 : R = X: R$_1$ = t-Bu, R$_2$ = OMe

Fig. 3 Chiral mono and diphosphites

Diphosphite compounds **4** to **7** were all synthesised from 1,2-*O*-isopropylidene-D-xylofuranose and bisphenol phosphorochloridites with or without *t*-butyl and methoxy groups at the ortho or para positions. For the synthesis of ligand **8**, monophosphite **3b** was substituted with one equivalent of phosphorochloridite **2**. Probably as a consequence of too much steric hindrance, 1,2-*O*-isopropylidene-D-xylofuranose could not be substituted with two equivalents of **2** in the presence of pyridine under reflux conditions. Methyl-2,3-*O*-isopropylidene-α-D-mannopyranoside[14] and methyl-3,6-di*O*-benzoyl-α-D-mannopyranoside[15,16], prepared according to literature procedures, were used as backbones for the synthesis of the six-membered ring compounds **9, 10** and **11** respectively. Ligands **4** to **10** all have one of the phosphorus substituents directly bonded to an oxygen atom at a chiral carbon centre (R') while the other substituent (R") is bonded to an oxygen atom at an achiral CH_2 group. In contrast, ligand **11** shows two phosphorus substituents bonded to oxygen atoms at chiral carbon centres. To reduce flexibility in the 6-membered pyranoside rings, the tricyclic *anhydro* derivatives **12, 13** and **14** were synthesised from methyl 3,6-anhydro-α-D-mannopyranoside[17], methyl 3,6-anhydro-α-D-glucopyranoside[18] and methyl 3,6-anhydro-β-D-galactopyranoside[19] respectively. The ligands were all stable during purification on silica gel under an atmosphere of argon and were isolated as white solids. Rapid ring inversions (atropisomerisation) in bisphenol-phosphorus moieties occurs on the NMR time scale since the expected diastereoisomers could not be detected by low temperature phosphorus NMR (fig. 4).[20] This contrasts with chiral backbones substituted with racemic bisnaphtholphosphorochloridites; the intrinsically hindered rotation around the 2,2'-dinaphthyl linkage gave rise to mixtures of diastereoisomers (unpublished results).
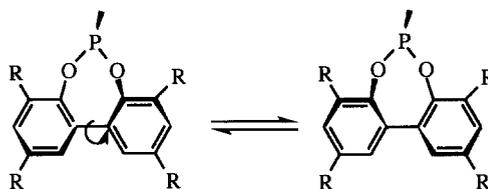

Fig. 4   Rapid ring inversion

Catalysis

Ligands **4** to **14** have been used in the rhodium catalysed asymmetric hydroformylation of styrene under different reaction conditions. Since at low temperatures (below 40 °C) incubation times for the formation of the hydridorhodium diphosphite catalysts are known to be at least 5-10 hours, the catalysts were prepared in situ overnight in 15 hours.[12] An excess of diphosphite ligand was always added to the catalyst precursor $Rh(acac)(CO)_2$ to exclude the formation of $HRh(CO)_4$, which is an active achiral hydroformylation catalyst.[21] After identical catalyst preparation conditions, hydroformylation experiments under different partial CO and H_2 pressures have been carried out (table 1, entries 1 to 6) with ligand **6**. From the results in table 1 it becomes clear that higher partial CO pressures lead to lower initial turnover frequencies (entries 1, 3 and 4).

Table 1. Hydroformylation of Styrene with **6** at Different Partial Pressures.[a]

entry	ligand	p[b]	pCO/pH_2[c]	TOF[d]	% conv.[e]	% branched[f]	% n[f]	% e.e.[g]
1	6	9	1	47	51	92	8	51 *(S)*
2[h]	6	9	1	2	3	91	9	62 *(S)*
3	6	18	3	16	23	92	8	53 *(S)*
4	6	45	9	–	99[i]	92	8	43 *(S)*
5	6	18	0.33	180	98[j]	51	13	48 *(S)*
6	6	45	1	18	21	91	9	53 *(S)*

[a] P/Rh molar ratio is 2.5, styrene/catalyst molar ratio is 421, T= 40 °C, catalyst prepared in situ over a period of 15 hrs, 9 bar of syn gas, 40 °C. [b] Total syn gas pressure. [c] Partial CO/partial H_2 pressure ratio. [d] TOF in mol styrene.mol $Rh^{-1}.hr^{-1}$ determined after 1 hour reaction time by GC. [e] % Conversion of styrene after 5 hours. [f] Selectivity to aldehyde. [g] % Enantiomeric excess. [h] Experiment at 25 °C. [i] Conversion after 70 hours. [j] 34% Hydrogenation to ethyl benzene.

Entry 4 shows no measurable conversion of styrene after one hour although a complete conversion to aldehydes was reached after 70 hours. A negative order in partial CO pressure and a positive order in partial H_2 pressure was observed. [22c] Hydrogenation to ethyl benzene (to an extent of 34%) occurred as a competing side reaction at high partial hydrogen pressure. At 45 bar of syn gas (entry 6, $pCO = pH_2 = 22.5$ bar) the increased partial CO pressure leads to a lower reaction rate in spite of the increased partial H_2 pressure (entry 1, $pCO = pH_2 = 4.5$ bar). Except for entry 5, for which an increased partial hydrogen pressure was used, the selectivity to branched aldehyde always exceeds 90%. Comparison of entries 1 to 6 further shows that the regio and enantioselectivity is not much influenced by varying the partial CO pressure. Generally catalyst decomposition at longer reaction times can be an explanation for the lower enantiomeric excesses found (43%) as illustrated in entry 4.[7a,12b] An increased excess (62%) was obtained at 25 °C (entry 2) but the reaction rate turned to an unpractical, low value. The results of the hydroformylation of styrene with ligands 4 to 8 are given in table 2. For all ligands a good regioselectivity to the branched aldehyde (88-95%) is obtained. Interestingly, the enantioselectivity varies dramatically depending on the substitution of the ligand. The highest enantioselectivities are found for ligands 5 and 6 having bulky *t*-butyl substituents at the ortho positions of the bisphenol moiety (entries 8 and 9). Without *t*-butyl groups at these ortho positions (ligand 4 and 7) hardly any enantioselectivity is induced in the branched product (entries 7 and 10). In all cases the *(S)* absolute configuration is predominantly formed in the branched aldehyde. A very low enantiomeric excess (2%) is obtained for the bulky ligand 8. The absence of the 2,2'-diaryl linkage results in rotational freedom around the phosphorus-oxygen bond and hereby introduces increased flexibility in the catalyst. Probably in this case the bulky *t*-butyl groups can turn away from the rhodium centre giving rise to a low e.e. Monodentate coordination of ligand 8 does not seem very likely because a higher turnover frequency and a lower regioselectivity should have been observed in that case as was shown for bulky mono phosphites.[6a] Further

indication for bidentate coordination of ligand **8** follows from spectroscopic data (*vide infra*). From these results it becomes clear that the asymmetric induction depends on the existence of bulky *t*-butyl groups rigidly kept in position at both bisphenol moieties.

Table 2. Hydroformylation of Styrene with Chiral Rh-Diphosphite Catalysts.[a]

entry	ligand	TOF[b]	% conv.[c]	% branched[d]	% n[d]	% e.e.[e]
7	**4**	150	62	83	17	3 *(S)*
8	**5**	134	47	95	5	40 *(S)*
9	**6**	90	38	94	6	50 *(S)*
10	**7**	88	38	88	12	1 *(S)*
11	**8**	38	16	90	10	2 *(S)*

[a] P/Rh molar ratio is 2.5, styrene/catalyst molar ratio is 1000, T = 40 °C, total syn gas pressure is 25 bar, pCO/pH_2 ratio is 4. [b] TOF in mol styrene.mol $Rh^{-1}.hr^{-1}$ determined after 1 hour reaction time by GC. [c] % Conversion of styrene after 5 hours. [d] Selectivity to aldehyde. [e] % Enantiomeric excess.

The results of the asymmetric hydroformylation with ligands **9** to **11**, based on 6-membered pyranoside rings, are given in table 3. Similar to ligands based on 1,2-*O*-isopropylidene-D-xylofuranose high regioselectivities (93-97%) to branched aldehyde and reasonable e.e.'s are obtained for pyranoside derived ligands (entries 12 to 17). Lowering the reaction temperature from 40 to 25 °C results in higher enantiomeric excesses (up to 64%) but the reaction rate becomes very low (entry 12 vs. 13 and 15 vs. 16). Replacement of *t*-butyl by methoxy substituents at the para positions of the bisphenol moiety gives somewhat higher enantioselectivities (entry 14 vs. 15). Ligands based on methyl-2,3-*O*-isopropylidene-α-D-mannopyranoside predominantly give *(R)*-aldehyde while ligands based on 1,2-*O*-isopropylidene-D-xylofuranose predominantly give *(S)*-aldehyde (see tables 1, 2 and 3). The absolute configuration at C_3 in 1,2-*O*-isopropylidene-D-xylofuranose is *(S)* while the absolute configuration at C_4 in methyl-2,3-*O*-isopropylidene-α-D-mannopyranoside is *(R)* (see fig. 3). Both sugar backbones give rise to the formation of 8-membered phosphorus-rhodium-phosphorus chelate rings in the hydridorhodium diphosphite complexes. Although no X-ray spectroscopic data for the absolute configuration of the catalyst are available at the moment, we think that the inverse absolute configurations at the chiral carbon atoms (C_3 and C_4 in the furanose and pyranose derivatives respectively) results in overall opposite absolute structures of the catalysts and hereby inducing opposite enantioselectivities. Hydroformylation with *dibenzoyl*-**11**, having both phosphorochloridites directly bonded via oxygen atoms to chiral carbon atoms (C_2 and C_4) gave no asymmetric induction at all (table 4, entry 17). From these results it is seen that small structural changes can cause a dramatic effect on the asymmetric induction. The relatively high reaction rate and the absence of asymmetric induction suggests monodentate coordination of the ligand during hydroformylation *(vide infra)*.

Table 3. Hydroformylation of Styrene with Chiral Rh-Diphosphite Catalysts.[a]

entry	ligand	T	p[b]	pCO/pH_2[c]	TOF[d]	% conv.[e]	% branched[f]	% n[f]	% e.e.[g]
12	9	40	40	1	106	67	97	3	31 *(R)*
13	9	25	40	1	3	3	97	3	50 *(R)*
14	9	40	25	4	122	38	96	4	45 *(R)*
15	10	40	25	4	47	42	95	5	53 *(R)*
16	10	25	25	4	–	14[h]	93	7	64 *(R)*

[a]P/Rh molar ratio is 2.5, styrene/catalyst molar ratio is 500, T = 40 °C. [b]Total syn gas pressure. [c]Partial CO/partial H_2 pressure ratio. [d]TOF in mol styrene.mol $Rh^{-1}.hr^{-1}$ determined after 1 hour reaction time by GC. [e]% Conversion of styrene after 5 hours. [f]Selectivity to aldehyde. [g]% Enantiomeric excess. [h]Conversion after 110 hours.

Structurally related *anhydro* compounds were synthesised as rigid chiral sugar backbones for the synthesis of ligands **12** to **14** to reduce flexibility in the catalysts. These ligands only differ in orientation (equatorially/axially) of bulky bisphenol phosphorus substituents at the chiral carbon atoms C_2 and C_4 in the *anhydro* backbones. Results of the hydroformylation of styrene are given in table 4. The structural restrictions in ligands **12** to **14** seem to exert a negative effect on the asymmetric induction in comparison with 1,2-*O*-isopropylidene-D-xylofuranose in which one of the two phosphorus substituents is coordinated to a flexible endocyclic methylene group (C_5).

Table 4. Hydroformylation of Styrene with Anhydro-Diphosphite Catalysts.[a]

entry	ligand	p[b]	pCO/pH_2[c]	TOF[d]	% conv.[e]	% branched[f]	% n[f]	% e.e.[g]
17	11	40	1	692	>99	94	6	~0
18	12	40	1	344	>99	93	7	7 *(S)*
19	13	40	1	77	49	92	8	8 *(S)*
20	14	40	1	252	94	93	7	2 *(S)*

[a]P/Rh molar ratio is 2.5, styrene/catalyst molar ratio is 1000, T = 40 °C. [b]Total syn gas pressure. [c]Partial CO/partial H_2 pressure ratio. [d]TOF in mol styrene.mol $Rh^{-1}.hr^{-1}$ determined after 1 hour reaction time by GC. [e]% Conversion of styrene after 5 hours. [f]Selectivity to aldehyde. [g]% Enantiomeric excess.

Characterisation of HRhPP(CO)₂ complexes and the relation of structure versus selectivity

Hydridorhodium diphosphite dicarbonyl complexes denoted as $HRhPP(CO)_2$ have been prepared to elucidate the solution structures of these catalysts. These complexes were formed by adding one equivalent of ligand (PP) to the catalyst precursor $Rh(acac)(CO)_2$. A displacement of two carbon monoxide molecules by

the ligand results in the formation of Rh(acac)(PP) complexes.[8,12b] Under typical hydroformylation conditions of carbon monoxide and dihydrogen pressure these complexes transform to hydridorhodium diphosphite dicarbonyl complexes.[12a,b] HRhPP(CO)$_2$ complexes were formed quantitatively for nearly all of the ligands. Hydrolysis of the diphosphite ligands to H-phosphonates occurred in some cases as the only side reaction in small amounts (< 5%). NMR spectroscopy was carried out under atmospheric condition and showed no detectable increase in decomposition of the complex. The non bulky ligand 4 was unsuitable for making a stable HRhPP(CO)$_2$ complex. Since we expected comparable results in the NMR for ligands 5 and 6 only the HRhPP(CO)$_2$ complex containing 6 has been made. The proton decoupled phosphorus NMR spectrum (denoted ^{31}P{^{1}H}) showed one doublet caused by a rhodium coupling ($^2J_{Rh-p}$ = 236 Hz). The chemical shifts of both phosphorus atoms accidentally coincide or show fluxional behaviour on the NMR time scale and therefore appeared as a broadened signal in the complex. No $^2J_{P1-P2}$ coupling constant could be measured. The hydride signal was observed as a broadened multiplet caused by a relatively small coupling constant of hydrogen with rhodium and two phosphorus atoms (< 3Hz). As expected for different phosphorus atoms, low temperature (213 K) ^{31}P NMR revealed two phosphorus chemical shifts (160.7 and 160.5 ppm) with the same intensity without discernible $^2J_{P1-P2}$ coupling. These NMR data are consistent with the formation of a rhodium diphosphite dicarbonyl catalyst in which the diphosphite ligand coordinates bis-equatorially to the rhodium centre (fig. 5a). During catalysis, no dependency on selectivity versus partial CO pressure was found (table 1) which makes bidentate coordination of the ligand at different partial CO pressures plausible. These observations are in contrast with results reported with phosphine ligands, for which often competing rhodium species are observed depending on different partial CO pressures.[23a,c] Hydrido complexes of ligands 7 and 8, in which the two phosphorus atoms have rather different substituents gave straightforward ^{31}P and ^{1}H NMR spectra.
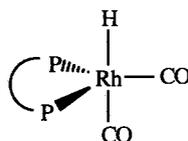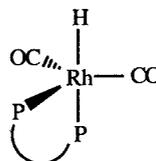

Fig. 5a   eq-eq coordinating ligand   Fig. 5b   eq-ax coordinating ligand

The intrinsically different phosphorus atoms (P$_1$ and P$_2$) have different chemical shifts giving rise to an AB-system with large $^2J_{P1-P2}$ coupling constants (see table 5). An additional $^1J_{Rh-P}$ coupling resulted in a double AB-system (fig. 6a). This is in contrast with C$_2$ symmetric diphosphite ligands which have indistinguishable phosphorus atoms in hydride complexes at room temperature. Only at low temperature these complexes show different ^{31}P chemical shifts caused by a somewhat perturbed trigonal bipyramidal structure of the hydride complex in the slow exchange.[12a,b] Exchange of equatorial positions in C$_2$ symmetric ligands results in the same complex (fig. 7a). This is in contrast with C$_1$ symmetric ligands in which exchange of equatorially positions results in two diastereoisomeric complexes (fig. 7b). HRhPP(CO)$_2$ complexes of ligand 7 and 8 show somewhat broadened signals (fig. 6a, Δ $\omega_{1/2}$ = 150 Hz) at room temperature for the phosphorus atom
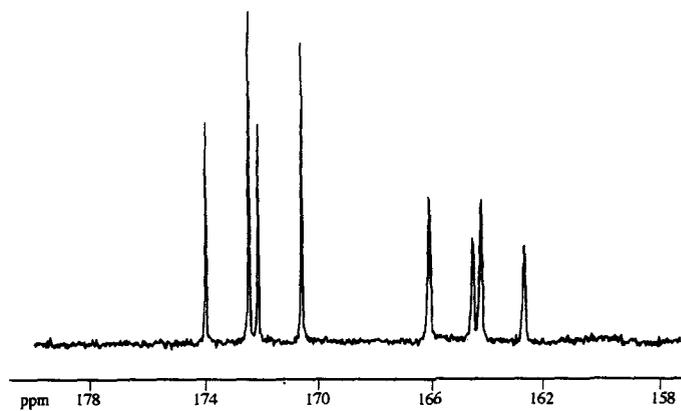
Fig. 6a ^1H decoupled ^{31}P NMR spectrum (HRhPP(CO)$_2$ complex with **7**, see table 5)
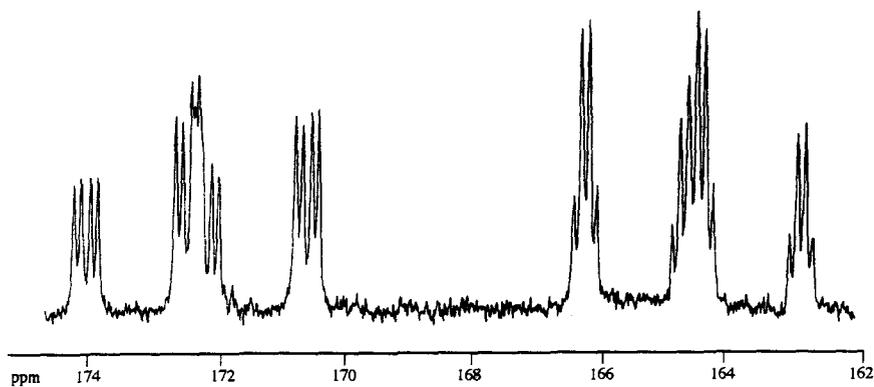

Fig. 6b ^1H coupled ^{31}P NMR spectrum (HRhPP(CO)$_2$ complex with **7**, see table 5)
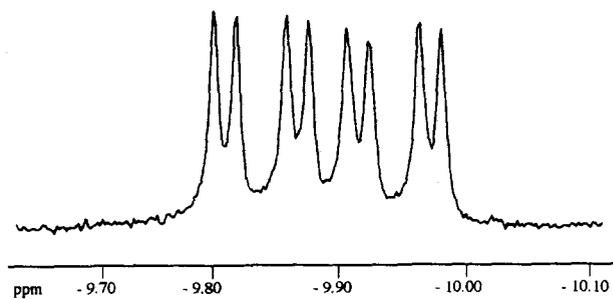

Fig. 6c ^{31}P coupled ^1H NMR spectrum (HRhPP(CO)$_2$ complex with **7**, see table 5)

bonded to the CH_2 -group. Distinction between the two phosphorus atoms (P_1 and P_2) was made on the basis of proton coupled phosphorus NMR (^{31}P-^1H). Additional pseudo quartets on P_2 ($^2J_{P2-H}$ = 17 Hz, $^3J_{P2-Hfuranose}$ = 14 Hz) and double doublets on P_1 ($^2J_{P1-H}$ = 31 Hz, $^3J_{P1-Hfuranose}$ = 14 Hz) were caused by the hydride and protons of the furanose backbone (fig. 6b). ^1H NMR showed a double double doublet for the hydride in the complex with **7** (fig. 6c). The complex containing **8** showed a not completely resolved doublet ($^2J_{P1-H}$ = 24 Hz) with relatively small $^1J_{Rh-H}$ and $^2J_{P2-H}$ coupling constants. Only for the bulky ligand **8**, the low temperature ^{31}P NMR spectrum of HRhPP(CO)$_2$ revealed the existence of another diastereoisomeric complex (25% at 213-203 K) at somewhat shifted ^{31}P chemical shifts (δP_1 = 163.1 ppm, δP_2 = 150.6 ppm). No separate hydride signal could be found for this diastereoisomer at low temperature. The low enantiomeric excesses obtained with hydride complexes of **7** and **8** probably results from not well defined steric surroundings. HRhPP(CO)$_2$ complexes of ligand **9** and **10** showed ^{31}P and ^1H NMR spectra similar to that of **6** (table 5) with somewhat smaller $^1J_{Rh-H}$ and $^2J_{P-H}$ coupling constants (< 3 Hz). The hydride signals appeared as broadened, not completely resolved multiplets in the ^1H NMR spectrum. Ligands **11** to **14**, developed as structurally related rigid compounds, showed different behaviour. Hardly any identifiable HRhPP(CO)$_2$ complexes could be prepared for these ligands. The steric requirements enforced in these ligands (large bite angle) probably impedes bidentate coordination resulting in unstable catalytic species. Simple ball and stick models of ligands **11, 12** and **14** showed that equatorial-equatorial coordination to rhodium in a trigonal bipyramidal (TBP) complex is beyond the reach of the backbones. These results are in agreement with the relatively high turnovers obtained for complexes of **11, 12** and **14** in catalysis (table 4) since they act most likely as monodentates.
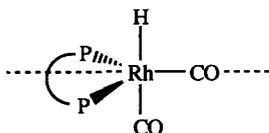

Fig 7 a. Hydrido rhodium diphosphite dicarbonyl complex.
          C$_2$ symmetrical diphosphite ligand (PP) with equivalent phosphorus atoms
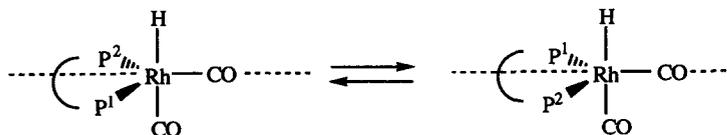

Fig 7 b. Two diastereomeric hydrido rhodium diphosphite dicarbonyl complexes.
          C$_1$ symmetrical diphosphite ligand with inequivalent phosphorus atoms ($P^1 \neq P^2$)

Ligand **13**, having both phosphorus atoms in axial positions of the sugar backbone, the HRhPP(CO)$_2$ complex was formed quantitatively albeit after extended reaction time (15 hr). Under standard reaction conditions (8 hr) the precursor Rh(acac)(PP) was still present for 75% (δP_1 = 139.9 ppm, δP_2 = 136.6 ppm, $^1J_{Rh-P1}$ = 310 Hz,

$^1J_{Rh-P2}$ = 306 Hz, $^2J_{P1-P2}$ = 413.1 Hz). The proton coupled phosphorus NMR spectrum for the HRhPP(CO)$_2$ complex showed a relatively large hydride coupling of about 45 Hz which is indicative of a perturbed trigonal bipyramidal (TBP) hydride complex. The hydride signal appeared as a double double doublet ($^1J_{Rh-H}$ = 5 Hz, $^2J_{P1-H}$ = 41 Hz, $^2J_{P2-H}$ = 47 Hz) in the ^{1}H NMR spectrum. No efforts have been made to distinguish between phosphorus atoms P$_1$ and P$_2$. From the results reported in table 5 it is evident that $^1J_{Rh-P}$ coupling constants vary between 220 and 246 Hz. We think that $^1J_{Rh-P}$ coupling constants close to 236 Hz are typical of equatorially coordinated phosphorus atoms (fig. 5a). These trigonal bipyramidal structures yield $^2J_{Peq-H}$ coupling constants smaller than 3 Hz (hydrido complexes with ligands **6**, **9** and **10**).[12a,b] With these hydridorhodium diphosphite dicarbonyl complexes enantioselectivities up to 64% have been obtained (table 5). In contrast, low enantioselectivities (1-8%, hydrido complexes with ligands **7**, **8** and **13**) resulted from distorted TBP hydridorhodium diphosphite dicarbonyl complexes. Perturbation of the TBP structure presumably results in $^1J_{Rh-P}$ coupling constants other than 236 Hz and larger $^2J_{P-H}$ coupling constants. Relatively large $^2J_{P-H}$ coupling constants (varying between 150 and 220 Hz) in HRhPP(CO)$_2$ complexes are reported in literature but they involve phosphorus ligands coordinating axially to the rhodium centre (large $^2J_{Pax-H}$ coupling constants, fig. 5b).[9a,11,12]

Table 5. NMR data for HRhPP(CO)$_2$ Complexes[a]

PP	δ $^{31}P_1$[b,c]	δ $^{31}P_2$[b,c]	δ ^1H[b,c]	$^2J_{P1-P2}$[d]	$^1J_{Rh-P1}$[d]	$^1J_{Rh-P2}$[d]	$^1J_{Rh-H}$[d]	$^2J_{P1-H}$[d]	$^2J_{P2-H}$[d]	% e.e[i]
6	157.1	157.1	-10.31	–[e]	236	236	< 3	< 3	< 3	51-62
7	172.2	164.4	-9.89	188	224	227	5	31	17	1
8	161.9	149.2	-11.01	300	245	234	6	24	< 3	2
8[f]	163.9	149.9	-10.96	298	243	234	4	21	< 3	–
8[f,g]	163.1	150.6	–[h]	298	246	231	–[h]	–[h]	–[h]	–
9	164.1	161.1	-10.40	277	236	236	< 3	< 3	< 3	31-50
10	165.0	162.4	-10.45	275	235	236	< 3	< 3	< 3	53-64
13	154.0	151.5	-9.87	324	222	220	5	41	47	8

[a] HRh(PP)(CO)$_2$ complexes prepared in tol-$d8$ starting from 0.0194 mmol Rh(acac)(CO)$_2$, 40 °C, 8 h under 15-20 bar of syn gas. [b] ^{31}P{^{1}H}, ^{31}P and ^{1}H spectra recorded in tol-$d8$ under atmospheric conditions at RT. [c] Chemical shifts (δ) in ppm. [d] Coupling constants in Hz. [e] Not measurable. [f] Measured at 213 K. [g] Other diastereoisomeric complex. [h] Not found. [i] Enantioselectivities reported in this article.

CONCLUSIONS

Chiral diphosphites, based on commercially available sugar backbones, can easily be synthesised and used as ligands in the rhodium catalysed asymmetric hydroformylation of styrene. Depending on the steric bulk of the ligand enantiomeric excesses up to 64% have been obtained. From NMR spectroscopy it was

concluded that stable hydridorhodium diphosphite dicarbonyl complexes are formed for most of the sugar derived 1,3-diols reported here. The ligands coordinate bis-equatorially to the rhodium centre. From NMR spectroscopy we have found that the highest enantioselectivities are obtained with undistorted, trigonal bipyramidal hydridorhodium (bis-equatorial) diphosphite dicarbonyl catalysts. Since all ligands are C_1-symmetric, two diastereoisomeric hydrido complexes with different selectivities are possible. Only for one bulky ligand a mixture of two diastereoisomeric HRhPP(CO)$_2$ complexes was observed at low temperature. Hydride complexes of structurally enforced *anhydro* derived diphosphite ligands were not easily accessible under standard reaction conditions and showed poor results in catalysis since they act most likely as monodentates.

Acknowledgement

EXPERIMENTAL

General.

All reactions were carried out in oven-dried glasswork using Schlenk techniques under an atmosphere of argon. Toluene was distilled from sodium/benzophenone. Pyridine was distilled from CaH$_2$ and stored under an atmosphere of argon. PCl$_3$ was distilled before use and stored under an atmosphere of argon. Dichloromethane was dried over P$_2$O$_5$ and distilled from CaH$_2$. Chemicals were purchased from Janssen Chimica and Aldrich Chemical Co. Compounds **1a, 1b, 1c** and **2** were prepared according to literature procedures.[7a,b] For column chromatography Silica gel 60 (230-400 mesh) purchased from Merck was used. Melting points were determined on a Gallenkamp MFB-595 melting point apparatus in open capillaries and are uncorrected. NMR spectra were obtained on a Bruker AMX 300 spectrometer. [31]P and ^{13}C spectra were measured ^{1}H decoupled unless otherwise stated. TMS was used as a standard for ^{1}H and ^{13}C NMR and H$_3$PO$_4$ for ^{31}P NMR. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Gas chromatographic analysis were run on a Carlo Erba GC 6000 Vega Series apparatus (split/splitless injector, J&W Scientific, DB1 30m column, film thickness 3.0 μm, carrier gas: 70 kPa He, F.I.D. detector) equipped with a Hewlett Packard HP 3396 integrator. Enantiomeric excesses were measured after reduction of the aldehydes with NaBH$_4$ to the corresponding alcohols on a Carlo Erba Vega 6000 Gas Chromatograph split/splitless injector, SGE 50m Chiral β-Cyclodextrin column, F.I.D. detector, equipped with a Shimadzu C-R 5A integrator). Absolute configuration determined by comparison of the retention times with optically pure (*R*)-(+)-2-phenyl-1-propanol. Hydroformylation reactions were carried out in a home-made 200 ml stainless steel autoclave. Syn gas 3.0 was purchased from Praxair.

Catalysis.

In a typical experiment the autoclave was dried under reduced pressure at 80 °C for one hour, filled with Rh(acac)(CO)$_2$ (0.031 mmol), diphosphite ligand (0.039 mmol, P/Rh ratio of 2.5) and toluene (15 ml). Subsequently the autoclave was purged three times with syn gas (CO:H$_2$ = 1:1) and pressurised to the appropriate initial pressure with syn gas. After heating the autoclave to the reaction temperature, the reaction mixture was stirred for 15 hours to form the active catalyst. Styrene (1.5 ml, filtered on neutral activated

aluminium oxide) and decane (5 mmol, dried on magnesium sulfate) were brought into the autoclave. During the reaction several samples were taken from the autoclave. After a desired reaction time the autoclave was cooled down, depressurised and vented with nitrogen. The reaction mixture was directly vacuum distilled to remove the catalyst and analysed by Gas Chromatography. A sample of the reaction mixture (containing about 6 mmol of aldehydes) was dissolved in 20 ml of ethanol. Sodium borohydride (12 mmol) was added and the reaction mixture was stirred for 90 minutes at room temperature. After quenching the reaction mixture with water, the mixture was extracted two times with ethyl acetate/hexane (1/1). The organic layers were combined and dried on magnesium sulfate. About 20 µl of reduced reaction mixture was dissolved in 10 ml of ethanol and analysed by GC for determination of the enantiomeric excess.

Preparation of HRhPP(CO)$_2$ complexes

In a typical experiment a 5 ml vessel was filled with Rh(acac)(CO)$_2$ (0.0194 mmol), diphosphite ligand (0.0194 mmol) and toluene-$d8$ (1-2 ml) and placed into the autoclave. Subsequently the autoclave was purged three times with syn gas (CO:H$_2$ = 1:1) and pressurised to the appropriate pressure (15-20 bar). After a reaction time of 8 hours at 40 °C, the autoclave was cooled down and depressurised. Under atmospheric conditions NMR tubes were filled and immediately analysed. No decomposition of HRhPP(CO)$_2$ could be observed during analysis.

5-[(4,4'-Di-t-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-1,2-O-isopropylidene-D-xylofuranose (3a)

In situ formed 1c[7a,b] (5.2 mmol) was dissolved in toluene (15 ml) and pyridine (10 mmol, 0.81 ml). 1,2-O-Isopropylidene-D-xylofuranose (10.0 mmol, 1.90 g) was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (10 ml) to which pyridine (10 mmol, 0.81 ml) was added. The 1,2-O-isopropylidene-D-xylofuranose solution was added in 1.5 hour to the solution of 1c at 0 °C. The reaction mixture was stirred overnight. Filtration followed by evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 25% EtOAc/toluene (v/v), Rf. 0.45). Yield 2.39 g (42%, 4.2 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 136.2 (s), ^{13}C NMR (CDCl$_3$): δ 156.3 (d, C arom, $^2J_{C,P}$ = 2.3 Hz), 142.8 (d, C arom, $^2J_{C,P}$ = 2.3 Hz), 142.2 (d, C arom, $^3J_{C,P}$ = 7.5 Hz), 134.0 (d, C arom, $^3J_{C,P}$ = 7.0 Hz), 115.0 (s, CH arom), 113.4 (s, CH arom), 112.3 (s, C(CH$_3$)$_2$), 105.5 (s, C$_1$H), 85.6 (s, C$_2$H), 79.2 (d, C$_3$H, $^2J_{C,P}$ = 2.3 Hz), 75.3 (s, C$_4$H), 62.1 (s, CH$_2$), 56.1 (s, OCH$_3$), 35.9 (s, C(CH$_3$)$_3$), 31.4 (s, C(CH$_3$)$_3$), 31.3 (s, C(CH$_3$)$_3$), 27.3 (s, CH$_3$), 26.8 (s, CH$_3$), ^{1}H NMR (CDCl$_3$): δ 6.98 (d, 2H, arom, $^4J_{H,H}$= 3.0 Hz), 6.71 (d, 2H, arom, $^4J_{H,H}$= 2.7 Hz), 6.70 (d, 2H, arom, $^4J_{H,H}$= 2.8 Hz), 5.88 (d, 1H, H$_1$, $^3J_{H1,H2}$ = 3.6 Hz), 4.48 (d, 1H, H$_2$, $^3J_{H2,H1}$ = 3.6 Hz), 4.29-4.25 (m, 2H, H$_3$ + H$_4$), 4.10 (dd, 2H, H$_{5,5'}$ $^3J_{H5,P}$ = 7.7 Hz, $^3J_{H5,H4}$ = 6.2 Hz), 3.82 (s, 6H, OCH$_3$), 2.36 (b, 1H, OH), 1.47 (s, 9H, t-Bu), 1.46 (s, 9H, t-Bu), 1.45 (s, 3H, CH$_3$), 1.30 (s, 3H, CH$_3$), Mp.: 73-75 °C, [α]$_D^{22}$ = -19.2 (c = 0.50, CH$_2$Cl$_2$)

5-[Di-(2-t-butyl,6-methylphenyl-diyl)phosphite]-1,2-O-isopropylidene-D-xylofuranose (3b)

To a solution of 1,2-O-isopropylidene-D-xylofuranose (7.5 mmol, 1.43 g) in toluene (10 ml) and pyridine (15 mmol, 1.21 ml) was added a solution of phosphoruschloridite 2[7a,b] (8.0 mmol) in toluene (15 ml) at 0 °C. The reaction mixture was stirred overnight and the formed pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10%

EtOAc/toluene (v/v), Rf. 0.22). Yield 1.53 g (37%, 2.80 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 148.6 (s), ^{1}H NMR (CDCl$_3$): δ 7.30–7.27 (m, 2H, arom), 7.13–6.98 (m, 4H, arom), 5.78 (d, 1H, H$_1$, [3]$J_{H1,H2}$ = 3.5 Hz), 4.37 (d, 1H, H$_2$, [3]$J_{H2,H1}$ = 3.5 Hz), 4.15 (ddd, 1H, H$_5$, [2]$J_{H5,H5'}$ = 9.7 Hz, [3]$J_{H5,H4}$ = 5.1 Hz, [3]$J_{H5,P}$ = 5.1 Hz), 4.03 (m, 1H, H$_4$), 3.86 (m, 1H, H$_{5'}$) , 2.47 (s, 6H, CH$_3$), 1.49 (s, 18H, t-Bu), 1.48 (s, 3H, CH$_3$), 1.29 (s, 3H, CH$_3$), Mp.: 48-50 °C, [α]$_D^{22}$ = -8.6 (c = 0.50, CH$_2$Cl$_2$)

3,5-Bis[(2,2'-biphenyl-1,1'-diyl)phosphite]-1,2-*O*-isopropylidene-D-xylofuranose (4)

1,2-*O*-Isopropylidene-D-xylofuranose (2.0 mmol, 0.38 g) was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (20 ml) to which pyridine (10.0 mmol, 0.81 ml) was added. The solution was added in 30 minutes to a solution of 1a[7a,b] (4.5 mmol, 1.13 g) in 5 ml toluene and 10 mmol pyridine at 0 °C. The reaction mixture was stirred for 2 hours at room temperature. Filtration followed by evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10% EtOAc/toluene (v/v), Rf. 0.36). Yield 0.93 g (75 %, 1.50 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 140.2 (s), 139.2 (s), ^{1}H NMR (CDCl$_3$): δ 7.47–7.16 (m, 16H, arom), 5.92 (d, 1H, H$_1$, [3]$J_{H1,H2}$ = 3.6 Hz), 4.75 (dd, 1H, H$_3$, [3]$J_{H3,H4}$ = 2.6 Hz, [3]$J_{H3,P}$ = 9.9 Hz), 4.64 (d, 1H, H$_2$, [3]$J_{H2,H1}$ = 3.6 Hz), 4.37 (dt, 1H, H$_4$, [3]$J_{H4,H5}$ = 6.4 Hz, [3]$J_{H4,H3}$ = 2.6 Hz), 4.22 (dd, 2H, H$_{5,5'}$ [3]$J_{H5,H4}$ = 6.5 Hz, [3]$J_{H5,P}$ = 7.0 Hz), 1.48 (s, 3H, CH$_3$), 1.31 (s, 3H CH$_3$) , Mp. : 103-105 °C

3,5-Bis[(4,4',6,6'-tetra-*t*-butyl-2,2'-biphenyl-1,1'-diyl)phosphite]-1,2-*O*-isopropylidene-D-xylo-furanose (5)

In situ formed 1b[7a,b] (10.0 mmol) was dissolved in toluene (25 ml) to which pyridine (12.5 mmol, 1.0 ml) was added. 1,2-*O*-Isopropylidene-D-xylofuranose (4.0 mmol, 0.76 g) was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (15 ml) to which pyridine (12.5 mmol, 1.0 ml) was added. The 1,2-*O*-isopropylidene-D-xylofuranose solution in toluene was added in 30 minutes to the solution of 1b at room temperature. The reaction mixture was stirred overnight and the formed pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 5% EtOAc/PE 60-80 °C (v/v), Rf. 0.40). Yield 3.14 g (73.6%, 2.94 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 143.3 (s), 135.0 (s), ^{13}C NMR (CDCl$_3$): δ 147.3 (s, C arom), 147.0 (s, C arom), 146.9 (s, C arom), 146.6 (m, C arom), 146.1 (m, C arom), 140.9 (s, C arom), 140.6 (s, C arom), 140.4 (s, C arom), 133.5 (m, C arom), 133.1 (m, C arom), 127.3 (d, CH arom, $J_{P,C}$ = 4.6 Hz), 127.1 (s, CH arom), 124.8 (s, CH arom), 112.3 (s, $\underline{C}$(CH$_3$)$_2$), 106.2 (s, C$_1$H), 84.8 (s, C$_2$H), 79.5 (s, C$_3$H), 77.0 (s, C$_4$H), 62.8 (s, CH$_2$), 36.0 (s, $\underline{C}$(CH$_3$)$_3$), 35.2 (s, $\underline{C}$(CH$_3$)$_3$), 32.1 (s, C($\underline{C}$H$_3$)$_3$), 31.8 (s, C($\underline{C}$H$_3$)$_3$), 31.6 (s, C($\underline{C}$H$_3$)$_3$), 27.2 (s, CH$_3$), 27.0 (s, CH$_3$), ^{1}H NMR (CDCl$_3$): δ 7.45–7.40 (m, 4H, arom), 7.18–7.15 (m, 4H, arom), 5.55 (d, 1H, H$_1$, [3]$J_{H1,H2}$ = 3.5 Hz), 4.73 (dd, 1H, H$_3$, [3]$J_{H3,P}$ = 7.6 Hz, [3]$J_{H3,H4}$ = 2.6 Hz), 4.27 (dt, 1H, H$_4$, [3]$J_{H4,H5}$ = 6.3 Hz, [3]$J_{H4,H3}$ = 2.6 Hz), 4.01 (dd, 2H, H$_{5,5'}$, [2]$J_{H5,H5'}$ = 7.5 Hz, [3]$J_{H5,H4}$ = 6.4 Hz), 3.96 (d, 1H, H$_2$, [3]$J_{H2,H1}$ = 3.2 Hz), 1.48 (s, 18H, t-Bu), 1.47 (s, 9H, t-Bu), 1.44 (s, 9H, t-Bu), 1.43 (s, 9H, t-Bu), 1.36 (s, 27H, t-Bu), 1.33 (s, 3H, CH$_3$), 1.10 (s, 3H, CH$_3$), Mp.: 127-129 °C, [α]$_D^{22}$ = 79.4 (c = 0.50, CH$_2$Cl$_2$)

3,5-Bis[(4,4'-di-*t*-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-1,2-*O*-isopropylidene-D-xylofuranose (6)

In situ formed 1c[7a,b] (5.0 mmol) was dissolved in toluene (10 ml) to which pyridine (10 mmol, 0.81 ml) was

added. 1,2-O-Isopropylidene-D-xylofuranose (2.0 mmol, 0.38 g) was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (20 ml) to which pyridine (20 mmol, 1.62 ml) was added. The 1,2-O-isopropylidene-D-xylofuranose solution was added in 30 minutes to the solution of 1c at room temperature. The reaction mixture was stirred overnight and the formed pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10% EtOAc/toluene (v/v), Rf. 0.58). Yield 1.01 g (53%, 1.05 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 143.4 (s), 134.8 (s), ^{13}C NMR (CDCl$_3$): δ 156.3 (s, C arom), 156.1 (s, C arom), 156.0 (s, C arom), 143.3 (s, C arom), 143.0 (s, C arom), 142.9 (s, C arom), 142.8 (s, C arom), 142.6 (d, C arom, $J_{P,C}$ = 3.8 Hz), 142.5 (d, C arom, $J_{P,C}$ = 3.8 Hz), 142.1 (d, C arom, $J_{P,C}$ = 4.5 Hz), 142.0 (d, C arom, $J_{P,C}$ = 4.5 Hz), 134.3 (d, C arom, $J_{P,C}$ = 3.8 Hz), 134.2 (d, C arom, $J_{P,C}$ = 3.0 Hz), 134.0 (d, C arom, $J_{P,C}$ = 3.0 Hz), 133.9 (d, C arom, $J_{P,C}$ = 3.0 Hz), 115.0 (d, CH arom, $J_{P,C}$ = 3.0 Hz), 114.8 (s, CH arom), 114.6 (d, CH arom, $J_{P,C}$ = 3.0 Hz), 113.7 (d, CH arom, $J_{P,C}$ = 2.0 Hz), 113.4 (d, CH arom, $J_{P,C}$ = 2.0 Hz), 113.3 (s, CH arom), 112.3 (s, C(CH$_3$)$_2$), 105.3 (s, C$_1$H), 84.4 (s, C$_2$H), 79.4 (s, C$_3$H), 76.6 (s, C$_4$H), 62.2 (s, CH$_2$), 56.1 (s, OCH$_3$), 35.9 (s, C(CH$_3$)$_3$), 31.6 (s, C(CH$_3$)$_3$), 31.4 (s, C(CH$_3$)$_3$), 31.3 (s, C(CH$_3$)$_3$), 27.1 (s, CH$_3$), 26.5 (s, CH$_3$), ^{1}H NMR (CDCl$_3$): δ 6.98 (d, 2H, arom, ^3J = 3.0 Hz), 6.95 (d, 2H, arom, ^3J = 3.0 Hz), 6.70 (d, 2H, arom, ^3J = 3.1 Hz), 6.68 (d, 2H, arom, ^3J = 3.1 Hz), 5.64 (d, 1H, H$_1$, $^3J_{H1,H2}$ = 3.5 Hz), 4.76 (dd, 1H, H$_3$, $^3J_{H3,P}$ = 8.2 Hz, ^3J H3,H4 = 2.5 Hz), 4.29 (dt, 1H, H$_4$, $^3J_{H4,H5}$ = 3.9 Hz, $^3J_{H4,H3}$ = 2.5 Hz), 4.04 (m, 2H, H$_{5,5'}$), 3.92 (d, 1H, H$_2$, $^3J_{H2,H1}$ = 3.5 Hz), 3.82 (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 3.80 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 1.44 (s, 9H, t-Bu), 1.43 (s, 9H, t-Bu), 1.42 (s, 9H, t-Bu), 1.38 (s, 9H, t-Bu), 1.37 (s, 3H, CH$_3$), 1.14 (s, 3H, CH$_3$), Mp.: 100-102 °C, [α]$_D^{22}$ = 68.8 (c = 0.50, CH$_2$Cl$_2$)

3-[(2,2'-Biphenyl-1,1'-diyl)phosphite]-5-[(4,4'-di-t-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-1,2-O-isopropylidene-D-xylofuranose (7)

Monophosphite 3a (1.5 mmol) was dissolved in toluene (10 ml) to which pyridine (5.0 mmol, 0.41 ml) was added. To this solution was added a solution of bisphenoxyphosphorus chloride 1a[7a,b] (1.6 mmol) in toluene (10 ml) at 0 °C. The reaction mixture was stirred overnight and the formed pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10% EtOAc/toluene (v/v), Rf. 0.59). Yield 1.03 g (87%, 1.30 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 140.0 (s), 135.0 (s), ^{13}C NMR (CDCl$_3$): δ 156.3 (s, C arom), 150.1 (d, C arom, $^2J_{C,P}$ = 6.8 Hz), 149.6 (d, C arom, $^2J_{C,P}$ = 4.5 Hz), 142.7 (s, C arom), 142.6 (d, C arom, $^2J_{C,P}$ = 5.3 Hz), 134.0 (s, C arom), 131.5 (d, C arom, $^2J_{C,P}$ = 3.0 Hz), 131.1 (d, C arom, $^2J_{C,P}$ = 3.0 Hz), 130.6 (d, CH arom, $^2J_{C,P}$ = 5.3 Hz), 130.0 (d, CH arom, $^2J_{C,P}$ = 5.3 Hz), 126.0 (s, CH arom), 125.9 (s, CH arom), 122.7 (s, CH arom), 122.4 (s, CH arom), 115.1 (d, CH arom, $^2J_{C,P}$ = 5.3 Hz), 113.5 (d, CH arom, $^2J_{C,P}$ = 7.5 Hz), 112.8 (s, C(CH$_3$)$_2$), 105.4 (s, C$_1$H), 85.0 (s, C$_2$H), 79.5 (s, C$_4$H), 77.5 (d, C$_3$H, $^2J_{C,P}$ = 6.0 Hz), 62.4 (s, CH$_2$), 56.2 (s, OCH$_3$), 36.0 (s, C(CH$_3$)$_3$), 31.5 (s, C(CH$_3$)$_3$), 27.3 (s, CH$_3$), 27.0 (s, CH$_3$), ^{1}H NMR (CDCl$_3$): δ 7.45–7.14 (m, 8H, arom), 6.99 (d, 2H, arom, ^4J = 2.9 Hz), 6.71 (d, 2H, arom, ^4J = 2.6 Hz), 5.85 (d, 1H, H$_1$, ^3J H1,H2 = 3.5 Hz), 4.69 (dd, 1H, H$_3$, $^3J_{H3,P}$ = 9.8 Hz, ^3J H3,H4 = 2.3 Hz), 4.59 (d, 1H, H$_2$, $^3J_{H2,H1}$ = 3.4 Hz), 4.31 (dt, 1H, H$_4$, $^3J_{H4,H5}$ = 6.2 Hz, $^3J_{H4,H3}$ = 2.4 Hz), 4.06 (dd, 2H, H$_{5,5'}$ $^3J_{H5,P}$ = 7.2 Hz, $^3J_{H5,H4}$ = 6.1 Hz), 1.47 (s, 18H, t-Bu), 1.40 (s, 3H, CH$_3$), 1.26 (s, 3H, CH$_3$), Mp.: 96-98 °C, [α]$_D^{22}$ = 8.7 (c = 0.50, CH$_2$Cl$_2$)

3-[(4,4'-Di-t-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-5-[di-(2-t-butyl,6-methylphenyl-

diyl)phosphite]-1,2-*O*-isopropylidene-D-xylofuranose (8)

Monophosphite **3b** (1.0 mmol) was dissolved in toluene (20 ml) to which triethylamine (5.0 mmol, 0.70 ml) was added. To this solution was added a solution of **1c**[7a,b] (1.6 mmol) in toluene (10 ml) at 0 °C. The reaction mixture was stirred overnight at 60 °C and additionally at 100 °C for 1.5 h. The formed triethylamine salts were removed by filtration. Evaporation of the solvent gave a white/yellow foam which was purified by flash column chromatography (eluent: 20% EtOAc/PE 60-80 (v/v), Rf. 0.42). Yield 0.68 g (72%, 0.72 mmol) of a white/yellow powder. ^{31}P NMR (C_6D_6): δ 146.8 (s), 145.3 (s), ^{13}C NMR (C_6D_6): δ 157.0 (s, 2C arom), 156.8 (s, 2C arom), 150.9 (m, 2C arom), 143.3 (d, C arom, $J_{C,P}$ = 2.3 Hz), 142.5 (d, C arom, $J_{C,P}$ = 7.5 Hz), 142.2 (m, 2C arom) 141.8 (d, C arom, $J_{C,P}$ = 4.5 Hz), 135.0 (d, C arom, $J_{C,P}$ = 4.5 Hz), 134.5 (d, C arom, $J_{C,P}$ = 3.8 Hz), 131.1 (d, C arom, $J_{C,P}$ = 3.0 Hz), 130.9 (d, C arom, $J_{C,P}$ = 3.8 Hz), 130.4 (s, 2 CH arom), 126.2 (s, CH arom), 126.1 (s, CH arom), 124.3 (s, 2 CH arom), 115.2 (s, CH arom), 115.0 (s, CH arom), 113.8 (s, 2 CH arom), 112.0 (s, $\underline{C}$(CH$_3$)$_2$), 105.6 (s, C$_1$H), 84.8 (s, C$_2$H), 79.5 (dd, C$_4$H, $^3J_{C,P1}$ = 5.1 Hz, $^3J_{C,P2}$ = 5.1 Hz), 77.2 (s, C$_3$H), 62.9 (d, $^2J_{C,P}$= 18.3 Hz, CH$_2$), 55.4 (s, 2 OCH$_3$), 35.9 (s, $\underline{C}$(CH$_3$)$_3$), 35.8 (s, $\underline{C}$(CH$_3$)$_3$), 35.6 (s, 2 $\underline{C}$(CH$_3$)$_3$), 31.6 (s, 4 C($\underline{C}$H$_3$)$_3$), 27.3 (s, CH$_3$), 26.4 (s, CH$_3$), 20.8 (s, CH$_3$), 20.7 (s, CH$_3$), ^{1}H NMR (C_6D_6): δ 7.23 (m, 2H, arom), 6.92 (m, 6H, arom), 6.71 (d, 2H, arom, ^4J = 3.0 Hz), 6.67 (d, 2H, arom, ^4J = 3.0 Hz), 5.67 (d, 1H, H$_1$, ^3J $_{H1,H2}$ = 3.5 Hz), 4.67 (dd, 1H, H$_3$, $^3J_{H3,P}$ = 8.2 Hz, ^3J $_{H3,H4}$ = 2.5 Hz), 4.35 (m, 2H, H$_{5,5'}$), 4.32 (d, 1H, H$_2$, $^3J_{H2,H1}$ = 3.2 Hz), 4.14 (m, 1H, H$_4$), 3.30 (s, 3H, OMe), 3.28 (s, 3H, OMe), 2.52 (s, 3H, Me), 2.48 (s, 3H, Me), 1.61 (s, 9H, t-Bu), 1.60 (s, 9H, t-Bu), 1.49 (s, 9H, t-Bu), 1.46 (s, 9H, t-Bu), 1.34 (s, 3H, CH$_3$), 0.96 (s, 3H, CH$_3$), Mp.: 68-70 °C, [α]$_D^{22}$ = 49.0 (c = *0.50*, CH$_2$Cl$_2$)

Methyl-4,6-bis[(4,4',6,6'-tetra-*t*-butyl-2,2'-biphenyl-1,1'-diyl)phosphite]-2,3-*O*-isopropylidene-α-D-mannopyranoside (9)

In situ formed **1b**[7a,b] (5.0 mmol) was dissolved in toluene (10 ml). Methyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (2.0 mmol, 0.47 g), prepared according to a literature procedure[14], was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (15 ml) to which pyridine (20 mmol, 1.62 ml) was added. This solution was added to the solution of **1b** at 0 °C. The reaction mixture was stirred overnight at 60 °C. Filtration followed by evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 2.5% EtOAc/toluene (v/v), Rf. 0.71). Yield 1.31 g (59 %, 1.18 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 145.8 (s), 142.9 (s), ^{13}C NMR (CDCl$_3$): δ 146.9–146.0 (C arom), 140.7–140.5 (C arom), 133.8-133.1 (C arom), 127.2-127.0 (CH arom), 124.6 (CH arom), 110.3 (s, $\underline{C}$(CH$_3$)$_2$), 98.5 (s, C$_1$H), 78.0 (s, C$_2$H), 76.4 (s C$_3$H), 73.0 (d, C$_4$H, $^2J_{C,P}$ = 10.7 Hz), 69.1 (s, C$_5$H), 64.3 (d, CH$_2$, $^2J_{C,P}$ = 11.3 Hz), 55.8 (s, OCH$_3$), 36.0-35.9 ($\underline{C}$(CH$_3$)$_3$), 35.2-35.1 ($\underline{C}$(CH$_3$)$_3$), 32.1-31.7 (C($\underline{C}$H$_3$)$_3$), 28.6 (s, CH$_3$), 26.8 (s, CH$_3$), ^{1}H{^{31}P} NMR (CDCl$_3$): δ 7.35–7.32 (m, 4H, arom), 7.10–7.07 (m, 4H, arom), 4.82 (s, 1H, H$_1$), 4.23 (dd, 1H, H$_3$, ^3J $_{H3,H2}$ = 5.6 Hz, ^3J $_{H3,H4}$ = 6.2 Hz), 4.17 (dd, 1H, H$_6$, $^2J_{H6,H6'}$ = 11.4 Hz, $^3J_{H6,H5}$ = 2.1 Hz), 4.06 (d, 1H, H$_2$, $^3J_{H2,H3}$ = 5.6 Hz), 4.02 (m, 1H, H$_4$), 3.90 (dd, 1H, H$_{6'}$, $^2J_{H6',H6}$ = 11.4 Hz, $^3J_{H6',H5}$ = 7.1 Hz), 3.69 (ddd, 1H, H$_5$, $^3J_{H5,H6}$ = 2.1 Hz, $^3J_{H5,H6'}$ = 7.1 Hz, $^3J_{H5,H4}$ = 6.8 Hz), 3.24 (s, 3H, OMe), 1.50 (s, 3H, CH$_3$), 1.45-1.31 (75H, 8xt-Bu and 1xCH$_3$). Mp.: 137-139 °C, [α]$_D^{22}$ = 40.0 (c = *1.00*, CH$_2$Cl$_2$)

Methyl-4,6-bis[(4,4'-di-*t*-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-2,3-*O*-isopropylidene-α-D-mannopyranoside (10)

In situ formed **1c**[7a,b] (3.1 mmol) was dissolved in toluene (10 ml). Methyl-2,3-*O*-isopropylidene-α-D-

mannopyranoside (1.2 mmol, 0.29 g), prepared according to a literature procedure[14], was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (15 ml) to which pyridine (10 mmol, 0.81 ml) was added. This solution was added to the solution of 1c at 0 °C. The reaction mixture was stirred overnight at 60 °C and additionally refluxed for 2 hours. Filtration followed by evaporation of the solvent gave a white foam which was purified twice by flash column chromatography (eluent: 2.5% EtOAc/toluene (v/v), Rf. 0.33). Yield 0.21 g (17%, 0.21 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 145.5 (s), 141.1 (s), ^{1}H$\{^{31}$P$\}$ NMR (CDCl$_3$): δ 6.95 (d, 1H, arom, ^4J = 3.2 Hz), 6.94 (d, 1H, arom, ^4J = 3.2 Hz), 6.93 (d, 1H, arom, ^4J = 3.2 Hz), 6.84 (d, 1H, arom, ^4J = 3.0 Hz), 6.72 (d, 1H, arom, ^4J = 3.0 Hz), 6.70 (d, 1H, arom, ^4J = 3.1 Hz), 6.66 (d, 1H, arom, ^4J = 3.1 Hz), 6.62 (d, 1H, arom, ^4J = 3.1 Hz), 4.88 (s, 1H, H$_1$), 4.18 (dd, 1H, H$_3$, $^3J_{H3,H2}$ = 5.6 Hz, ^3J $_{H3,H4}$ = 6.0 Hz), 4.12 (dd, 1H, H$_6$, $^2J_{H6,H6'}$ = 11.3 Hz, $^3J_{H6,H5}$ = 2.1 Hz), 4.05 (d, 1H, H$_2$, $^3J_{H2,H3}$ = 5.6 Hz), 4.00 (m, 1H, H$_4$), 3.88 (dd, 1H, H$_{6'}$, $^2J_{H6',H6}$ = 11.3 Hz, $^3J_{H6',H5}$ = 7.3 Hz), 3.81(s, 6H, OMe), 3.77 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.69 (m, 1H, H$_5$), 3.33 (s, 3H, OMe), 1.46 (s, 3H, CH$_3$), 1.41 (s, 9H, t-Bu), 1.38 (s, 9H, t-Bu), 1.34 (s, 18H, t-Bu), 1.31(s, 3H, CH$_3$), Mp.: 108-110 °C, [α]$_D^{22}$ = 30.0 (c = 1.00, CH$_2$Cl$_2$)

Methyl-3,6-di-O-benzoyl-2,4-bis[(4,4'-di-t- butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-α-D-mannopyranoside (11)

In situ formed 1c^{7a,b} (2.0 mmol) was dissolved in toluene (10 ml). Methyl-3,6-di-O-benzoyl-α-D-mannopyranoside (1.0 mmol, 0.40 g), prepared according to a literature procedure[15,16], was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (10 ml) to which pyridine (20 mmol, 1.62 ml) was added. This solution was added to the solution of 1c at 0 °C. The reaction mixture was stirred overnight at 60 °C and additionally refluxed for 2 hours. Filtration followed by evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10% EtOAc/toluene (v/v), Rf. 0.65). Yield 0.46 g (39 %, 0.39 mmol) of a white powder. ^{31}P-^{1}H (proton coupled) NMR (benzene-$d6$): δ 148.3 (d, $^3J_{P,H}$ = 9.7 Hz), 144.3 (d, $^3J_{P,H}$ = 9.7 Hz), ^{1}H NMR (CDCl$_3$): δ 8.12 (d, 2H, arom, ^3J = 7.5 Hz), 7.94 (d, 2H, arom, ^3J = 7.5 Hz), 7.53 (t, 1H, arom, ^3J = 7.3 Hz), 7.51 (t, 1H, arom, ^3J = 7.5 Hz), 7.39 (t, 2H, arom, ^3J = 7.7 Hz), 7.32 (t, 2H, arom, ^3J = 7.7 Hz), 6.98 (d, 1H, arom, ^4J = 3.0 Hz), 6.94 (d, 1H, arom, ^4J = 3.0 Hz), 6.90 (d, 1H, arom, ^4J = 3.0 Hz), 6.87 (d, 1H, arom, ^4J = 3.1 Hz), 6.67 (d, 1H, arom, ^4J = 3.0 Hz), 6.60 (d, 1H, arom, ^4J = 3.1 Hz), 6.57 (d, 1H, arom, ^4J = 2.9 Hz), 6.54 (d, 1H, arom, ^4J = 3.0 Hz), 5.40 (dd, 1H, H$_3$, ^3J = 3.2 Hz, ^3J = 9.8 Hz), 5.00 (bd, 1H, H$_4$, $J_{H,P}$ = 14.3 Hz), 4.87 (dd, 1H, H$_6$, $^2J_{H6,H6'}$ = 19.9 Hz, $^3J_{H6,H5}$ = 9.9 Hz), 4.56 (dd, 1H, H$_{6'}$ $^2J_{H6',H6}$ = 11.8 Hz, $^3J_{H6',H5}$ = 1.6 Hz), 4.19-4.12 (m, 2H, H$_1$+H$_2$), 4.04 (m, 1H, H$_5$), 3.80 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.27 (s, 3H, OMe), 1.49 (s, 9H, t-Bu), 1.34 (s, 9H, t-Bu), 1.25 (s, 18H, t-Bu), Mp.: 128-131 °C, [α]$_D^{22}$ = 168.0 (c = 1.00, CH$_2$Cl$_2$)

Methyl-3,6-anhydro-2,4-bis[(4,4'-di-t-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-α-D-mannopyranoside (12)

In situ formed 1c^{7a,b} (5.0 mmol) was dissolved in toluene (15 ml) to which pyridine was added (10 mmol, 0.81 ml). Methyl-3,6-anhydro-α-D-mannopyranoside (2.30 mmol, 0.41g), prepared according to a literature procedure[17], was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (15 ml) and CH$_2$Cl$_2$ (10 ml). This solution was added to the solution of 1c at room temperature and stirred overnight. Filtration followed by evaporation of the solvents gave a white foam which was purified twice by column chromatography (eluent: 20% EtOAc/P.E. 60-80 (v/v) and 2.5% EtOAc/toluene (v/v), Rf. 0.17) Yield. 1.20 g

(55%, 1.26 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 149.6 (s), 133.7 (s), ^{13}C NMR (CDCl$_3$): δ 156.5 (s, C arom), 156.3 (s, C arom), 156.1 (s, C arom), 156.0 (s, C arom), 143.5 (s, C arom), 143,1 (s, C arom), 142.9 (s, C arom), 142.8 (s, C arom), 142.6 (d, C arom, $^3J_{C,P}$ = 6.0 Hz), 142.2 (d, C arom, $^3J_{C,P}$ = 5.3 Hz), 142.1 (d, C arom, $^3J_{C,P}$ = 3.8 Hz), 142.0 (d, C arom, $^3J_{C,P}$ = 4.5 Hz), 134.6 (d, C arom, $^2J_{C,P}$ = 3.8 Hz), 134.1 (d, C arom, $^2J_{C,P}$ = 3.8 Hz), 134.0 (d, C arom, $^2J_{C,P}$ = 3.8 Hz, 133.7 (d, C arom, $^2J_{C,P}$ = 3.8 Hz), 115.0 (s, CH arom), 114.9 (s, CH arom), 114.8 (s, CH arom), 114.7 (s, CH arom), 113.6-113.3 (m, 4 CH arom), 101.6 (s, C$_1$H), 76.9 (d, C$_{4/2}$H, $^2J_{C,P}$ = 4.0 Hz), 74.7 (s, C$_3$H), 74.1 (d, C$_{2/4}$H, $^2J_{C,P}$ = 4.2 Hz), 73.3 (d, C$_5$H, $^3J_{C,P}$ = 17.4 Hz), 69.7 (s, CH$_2$), 56.7 (s, OCH$_3$), 56.1 (m, 4x OCH$_3$), 35.9-35.8 (4 $\underline{C}$(CH$_3$)$_3$), 31.8-31.4 (4 C(CH$_3$)$_3$), ^{1}H{^{31}P} NMR (CDCl$_3$): δ 6.97 (m, 4H, arom), 6.70 (m, 4H, arom), 4.77 (d, 1H, H$_1$, ^3J $_{H1,H2}$ = 6.6 Hz), 4.50 (d, 1H, H$_2$, $^2J_{H2,H1}$ = 6.5 Hz), 4.29 (dd, 1H, H$_5$, $^2J_{H5,H6'}$ = 2.6 Hz, $^3J_{H5,H4}$ = 6.0 Hz), 4.24-4.19 (m, 2H, H$_4$+H$_3$), 3.89 (d, 1H, H$_6$, $^2J_{H6,H6'}$ = 10.6 Hz), 3.77 (s, 6H, OMe), 3.76 (s, 6H, OMe), 3.76 (s, 3H, OMe), 3.64 (dd, 1H, H$_{6'}$, $^2J_{H6',H6}$ = 10.6 Hz, $^3J_{H6',H5}$ = 2.7 Hz), 3.44 (s, 3H, OMe), 1.42 (s, 9H, t-Bu), 1.41 (s, 9H, t-Bu), 1.39 (s, 18H, t-Bu), M.p.: 112-114 °C, [α]$_D^{22}$ = 31.0   (c = *0.10*, CH$_2$Cl$_2$)

Methyl-3,6-anhydro-2,4-bis[(4,4'-di-*t*-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-α-D-glucopyranoside (13)

In situ formed **1c**[7a,b] (5.0 mmol) was dissolved in toluene (15 ml) to which pyridine was added (20 mmol, 1.62 ml). Methyl-3,6-anhydro-α-D-glucopyranoside (2.0 mmol, 0.35 g), prepared according to a literature procedure[18], was azeotropically dried with toluene (3x1 ml) and dissolved in toluene (15 ml). This solution was added to the solution of **1c** at room temperature and stirred overnight. Filtration followed by evaporation of the solvents gave a white foam which was purified by column chromatography (eluent: 10% EtOAc/toluene (v/v), Rf. 0.49) Yield. 0.89 g (47%, 0.94 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 148.1 (s), 134.2 (s), ^{1}H{^{31}P} NMR (CDCl$_3$): δ 6.97 (d, 1H, arom, ^4J = 3.0 Hz), 6.95 (d, 2x1H, arom, ^4J = 2.7 Hz), 6.91 (d, 1H, arom, ^4J = 3.0 Hz), 6.70 (d, 1H, arom, ^4J = 3.0 Hz), 6.66 (d, 2x1H, arom, ^4J = 4.0 Hz), 6.65 (d, 1H, arom, ^4J = 3.6 Hz), 4.83 (d, 1H, H$_1$, ^3J $_{H1,H2}$ = 3.2 Hz), 4.27 (m, 1H, H$_5$), 4.09 (m, 3H, H$_2$+H$_3$+H$_4$), 3.91 (d, 1H, H$_6$, $^2J_{H6,H6'}$ = 10.4 Hz), 3.75 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.73 (s, 6H, OMe), 3.47 (dd, 1H, H$_{6'}$, $^2J_{H6',H6}$ = 10.4 Hz, $^3J_{H6',H5}$ = 2.8 Hz), 3.46 (s, 3H, OMe), 1.47 (s, 9H, t-Bu), 1.45 (s, 9H, t-Bu), 1.43 (s, 9H, t-Bu), 1.27 (s, 9H, t-Bu), M.p.: 138-140 °C, [α]$_D^{22}$ = 88.0   (c = *0.10*, CH$_2$Cl$_2$)

Methyl-3,6-anhydro-2,4-bis[(4,4'-di-*t*-butyl-6,6'-dimethoxy-2,2'-biphenyl-1,1'-diyl)phosphite]-β-D-galactopyranoside (14)

In situ formed **1c**[7a,b] (2.9 mmol) was dissolved in toluene (10 ml) to which pyridine was added (10 mmol, 0.81 ml). Methyl-3,6-anhydro-β-D-galactopyranoside (1.5 mmol, 0.264 g), prepared according to a literature procedure[19], was azeotropically dried with toluene (3x1 ml) and stirred in CH$_2$Cl$_2$ (20 ml). The suspension was added to the solution of **1c** at room temperature and stirred overnight. Filtration followed by evaporation of the solvents gave a white foam which was purified by column chromatography (eluent: 2.5% EtOAc/toluene (v/v), Rf. 0.20) Yield. 0.95 g (67%, 1.00 mmol) of a white powder. ^{31}P NMR (CDCl$_3$): δ 142.1 (s), 138.5 (s), ^{13}C NMR (CDCl$_3$): δ 156.4 (s, C arom), 156.3 (s, C arom), 156.2 (s, C arom), 156.1 (s, C arom), 143.1 (s, C arom), 142.9 (s, C arom), 142.8 (s, C arom), 142.6 (s, C arom), 142.2 (m, 4 C arom), 134.0 (s, 4 C arom), 115.1 (s, CH arom), 114.9 (s, CH arom), 114.8 (s, CH arom), 114.7 (s, CH arom), 113.8 (s, CH arom), 113.5 (s, 2 CH arom), 113.2 (s, CH arom), 101.8 (s, C$_1$H), 79.7 (d, C$_{4/2}$H, $^2J_{C,P}$ = 6.2 Hz), 77.5 (d, C$_{2/4}$H,

$^2J_{C,P}$ = 3.1 Hz), 75.0 (s, C_3H), 74.7 (d, C_5H, $^3J_{C,P}$ = 8.3 Hz), 70.9 (s, CH_2), 56.1 (m, 5 OCH_3), 35.9-35.8 (4 $\underline{C}(CH_3)_3$), 31.6-31.5 (4 $C(CH_3)_3$), ^1H-^{31}P NMR ($CDCl_3$): δ 6.97 (m, 4H, arom), 6.70 (m, 4H, arom), 4.79 (dd, 1H, H_2, $^3J_{H2,H3}$ = 1.5 Hz, $^3J_{H2,P}$ = 7.7 Hz), 4.54 (dd, 1H, H_4, $^3J_{H4,H3}$ = 5.0 Hz, $^3J_{H4,P}$ = 9.8 Hz), 4.36 (d, 1H, H_3, $^3J_{H3,H4}$ = 5.1 Hz), 4.34 (s, 1H, H_1), 4.22 (d, 1H, H_5, $^3J_{H5,H6'}$ = 2.8 Hz), 4.05 (d, 1H, H_6, $^2J_{H6',H6}$ = 9.6 Hz), 3.84 (dd, 1H, $H_{6'}$, $^2J_{H6',H6}$ = 9.6 Hz, $^3J_{H6',H5}$ = 2.8 Hz), 3.83 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.16 (s, 3H, OMe), 1.45 (s, 9H, t-Bu), 1.44 (s, 9H, t-Bu), 1.42 (s, 9H, t-Bu), 1.40 (s, 9H, t-Bu), M.p.: 110-112 °C, $[\alpha]_D^{22}$ = - 58.0 ($c = 0.10$, CH_2Cl_2)

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