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ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 7133–7141

Influence on the enantioselectivity in allylic alkylation of the anomeric position of the phosphine-amide ligands derived from D-glucosamine

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Received 22 March 2007; revised 26 April 2007; accepted 27 April 2007
Available online 3 May 2007

Abstract—The synthesis of a new series of chiral phosphine amides derived from D-glucosamine is described. The palladium-catalyzed asymmetric allylic alkylations of racemic (*E*)-1,3-diphenyl-2-propenyl acetate with dimethyl malonate using these ligands have been investigated. The results obtained and the NMR studies of free ligands and of their Pd-complexes obtained from dimer $[(\eta^3\text{-}C_3H_5)PdCl]_2$ revealed the mode of complexation and the influence of the configuration and of the nature of the substituent at the anomeric position on the enantioselectivity of the studied asymmetric allylic alkylation reactions.

1. Introduction

Palladium-catalyzed allylic substitutions have been developed as fundamentally important cross-coupling reactions.[1] Since the first example by Trost and Strege in 1977,[2] many asymmetric catalytic systems have been described. The best ones are Trost's *P,P* ligand[3] and Pfaltz's *P,N* ligand[4] with enantioselectivities up to 95% being obtained using these ligands.

During the last 10 years, carbohydrates have appeared as good sources of chiral ligands for asymmetric catalysis. Indeed, these chiral natural derivatives can be easily functionalized, and can be used as precursors of ligands used in a large number of catalytic asymmetric reactions.[5] These ligands have been mainly synthesized from carbohydrates including xylose, glucose, galactose, mannitol, and trehalose backbones. Few examples of ligands derived from D-glucosamine are described in the literature. In addition to Mn-catalyzed epoxidation of styrene,[6] Ni-catalyzed hydrovinylation of styrene,[7] V-catalyzed oxidation of thioanisole,[8] and Zn-catalyzed alkynylation of aldehydes,[9] the D-glucosamine has been used as precursor of ligands in Pd-catalyzed Suzuki–Miyaura,[10] Heck,[10a,11] and allylic substitution reactions. In the last Pd-catalyzed reaction, four types of ligands derived from D-glucosamine have been described: diphenylphosphinoaryloxazoline **1**,[12] phosphinite-oxazoline **2**,[13] phosphite-oxazoline **3**[14] and phosphine-amide **4**,[15] and **5**[16] ligands (Fig. 1).

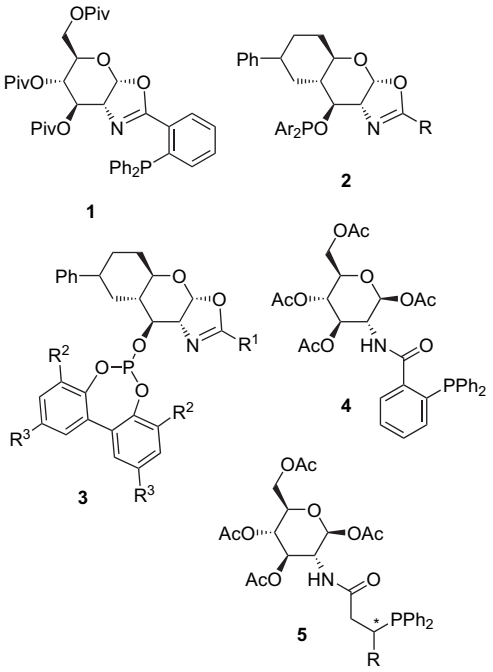

Figure 1. Ligands based on D-glucosamine used in allylic alkylation.

Keywords: D-Glucosamine; Phosphine amides; Allylic alkylation; NMR studies.
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doi:10.1016/j.tet.2007.04.098

The *P,N* ligands based on oxazoline **1**–**3**[12–14] gave enantioselectivities up to 98% in the allylic alkylation of 1,3-symmetrically disubstituted acetates. In 2003, we have reported the potential of the phosphine-amide ligands **4** derived from D-glucosamine.[15] With the phosphine-amide ligand **4**, enantioselectivities up to 97% have been obtained in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with various nucleophiles. We have shown that the enantioselectivity was higher with a ligand/palladium ratio of 1/1 than 2/1, corresponding probably to two different types of chelation: *P,O*-chelation versus *P,P*-coordination, respectively.[15] This difference in enantioselectivity could be explained by a more rigid *P,O*-chelated complex. We have also shown that the influence of the carbohydrate moiety on the enantioselectivity seemed to be the most important factor in this asymmetric reaction.[16]

In this context, we decided to prepare new phosphine-amide ligands derived from D-glucosamine by modification of the configuration and the nature of the substituent at the anomeric position. In this paper, we report the synthesis of these new phosphine-amide ligands **6**–**8** (Fig. 2), and compare the results obtained in the palladium-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenylprop-2-enyl acetate with dimethyl malonate, using the catalysts prepared from ligand **4** and also ligands **6**–**8**.

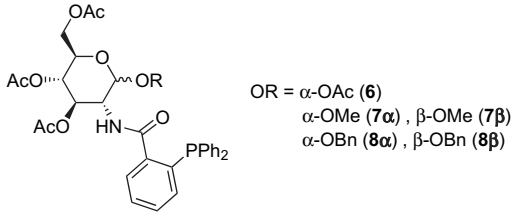


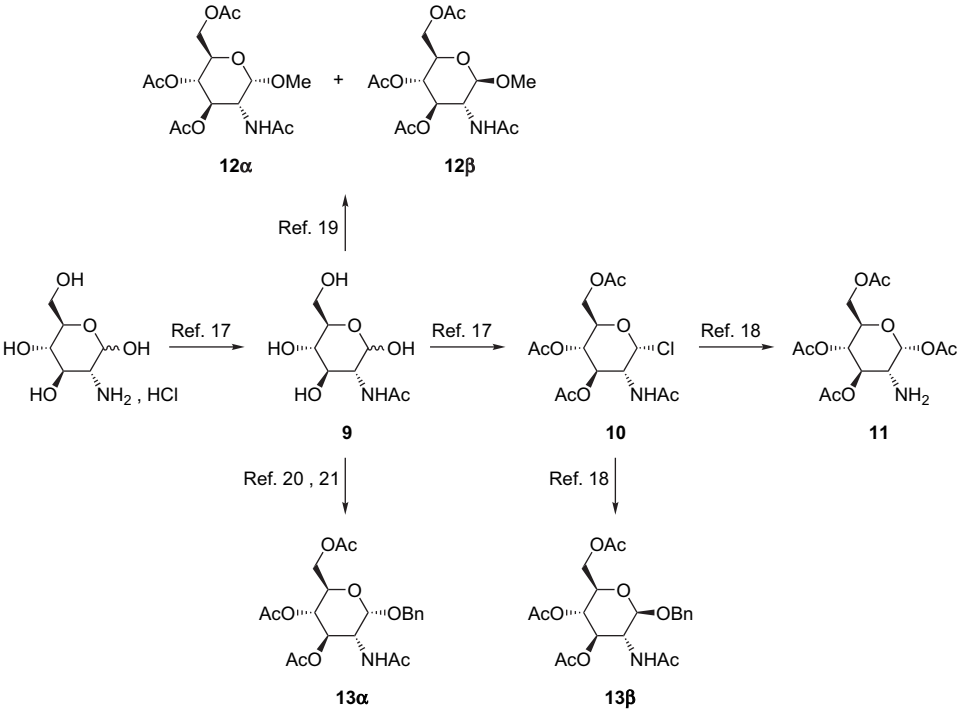
Figure 2. New phosphine-amide ligands **6**–**8** derived from D-glucosamine.

2. Results and discussion

2.1. Synthesis of ligands

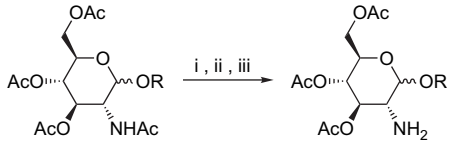
Ligands **6**–**8** were prepared from commercial D-glucosamine hydrochloride (Schemes 1 and 2). According to the literature, the amino group of D-glucosamine hydrochloride was selectivity protected giving acetamide **9**. Then the peracetylation of the hydroxyl functions followed by the replacement of the acetyl group at the anomeric position by a chlorine afforded 3,4,6-tri-*O*-acetyl-2-acetylamino-2-deoxy-α-D-glucopyranosyl chloride **10**.[17] Treatment of derivative **10** with water in the presence of benzyltriethylammonium chloride in nitromethane led to the stereospecific formation of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl hydrochloride **11** as described by Pertel et al.[18]

The anomeric mixture of *N*-acetyl-D-glucosamine **9** was treated with 5% sulfuric acid/methanol to give, after acetylation of the remaining three hydroxyl functions, an anomeric mixture of methyl 3,4,6-tri-*O*-acetyl-2-acetylamino-2-deoxy-D-glucopyranoside **12** in an α/β ratio of 1.5 to 1, as reported by Oshima et al.[19] The two anomers **12α** and **12β** were separated on silica gel. The same procedure, but using benzyl alcohol instead of methanol, gave benzyl 3,4,6-tri-*O*-acetyl-2-acetylamino-2-deoxy-α-D-glucopyranoside **13α** in 52% yield after purification by column chromatography, as reported by Shulman and Khorlin,[20] or by Paul et al.[21] The anomer **13β** was obtained using the 1,2-*trans*-glycosaminide synthesis described by Pertel et al.[18] In the presence of benzyl alcohol and benzyltriethylammonium chloride, an



Scheme 1.

anomeric mixture of benzyl glycoside **13** was obtained in an α/β ratio of 1 to 9, in 77% yield; a simple crystallization afforded pure benzyl 3,4,6-tri-*O*-acetyl-2-acetylamino-2-deoxy-β-D-glucopyranoside **13β**.



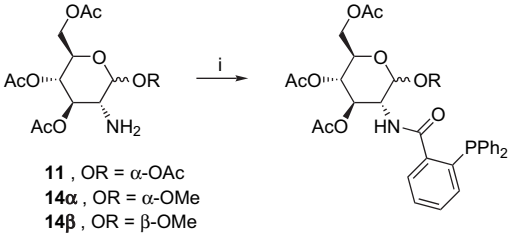
12α , OR = α-OMe
12β , OR = β-OMe
13α , OR = α-OBn
13β , OR = β-OBn

14α , OR = α-OMe
14β , OR = β-OMe
15α , OR = α-OBn
15β , OR = β-OBn

Scheme 2. (i) Boc_2O, DMAP, THF, Δ, 14 h; (ii) $NH_2NH_2 \cdot H_2O$, MeOH, rt, 5 h; (iii) CF_3CO_2H.

Aminocarbohydrates **14** and **15** (Scheme 2) were obtained from the two anomers of alkyl 3,4,6-tri-*O*-acetyl-2-acetylamino-2-deoxy-D-glucopyranosides **12** and **13**, using usual methods[22] of protection and deprotection. Derivatives **12α**,**β** and **13α**,**β** were treated with di-*tert*-butyl dicarbamate, and immediately after, with hydrazine monohydrate in methanol to give the corresponding carbamate derivatives, as reported by Burk and Allen in the case of acetamido compounds based on commercial amino-esters and in the case of methyl glycoside **12α**.[23] Without purification, trifluoroacetic acid was added in order to cleave the Boc function. Methyl and benzyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-D-glucopyranosides **14α**,**β** and **15α**,**β** were isolated after column chromatography in 40 or 43% yield in the case of the anomer α, and in 45 or 55% yield in the case of the anomer β, respectively.

In order to obtain the desired phosphine-amide derivatives **6–8**, a condensation reaction between derivatives **11**, **14α**,**β**, and **15α**,**β**, based on D-glucosamine, and 2-(diphenylphosphino)benzoic acid was required in the last step (Scheme 3). The reaction was performed in a CH_2Cl_2/THF mixture in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) and 1-hydroxybenzotriazole (HOBT) as coupling reagents. After washing and purification by flash chromatography, the phosphine-amide derivatives **6**, **7α**,**β**, and **8α**,**β** were isolated in 55, 40, 42, 53, and 65% yield, respectively.



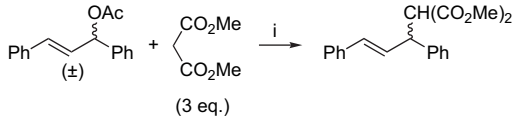
11 , OR = α-OAc
14α , OR = α-OMe
14β , OR = β-OMe
15α , OR = α-OBn
15β , OR = β-OBn

6 , OR = α-OAc
7α , OR = α-OMe
7β , OR = β-OMe
8α , OR = α-OBn
8β , OR = β-OBn

Scheme 3. (i) 2-(Diphenylphosphino)benzoic acid, EDC/HOBT, THF/CH_2Cl_2, rt, 48 h.

2.2. Application of ligands 6–8 in the allylic alkylations

The ligands **6–8** were examined in the palladium-catalyzed asymmetric allylic alkylation of racemic (*E*)-1,3-diphenyl-2-propenyl acetate with dimethyl malonate using $[(\eta^3\text{-}C_3H_5)PdCl]_2$ as the palladium source (Scheme 4). The results were compared to those obtained previously using ligand **4** (Table 1).[15] The reaction was performed in THF or CH_2Cl_2 (0.125 M) at 25 or 60 °C, using 2 mol % of $[(\eta^3\text{-}C_3H_5)PdCl]_2$, 4 mol % of monophosphine **6–8**, 3 equiv of dimethyl malonate, and NaH (3 equiv) or a mixture of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (3 equiv) and KOAc (2 mol %), as the base.



Scheme 4. (i) $[(\eta^3\text{-}C_3H_5)PdCl]_2$ of 2 mol %, 4 mol % ligand, solvent (0.125 M), base (3 equiv).

We first examined the results obtained using BSA/KOAc as the base[24] in THF. The use of carbohydrate derivative **6**, having the α-configuration, as the ligand gave no reaction at 25 °C and only 46% conversion, with no enantioselectivity at 60 °C (Table 1, entries 2 and 3). The use of methyl α-D-glycoside derivative **7α** as the ligand, gave 57 and 100% conversion at 60 °C after 24 and 48 h, respectively (entries 4 and 5). However, the obtained enantioselectivity was only 30 and 27% ee in favor of the (*S*)-enantiomer. Methyl β-D-glycoside derivative **7β** gave a more active catalyst, a total conversion being obtained at 60 °C after 24 h; however, the enantioselectivity was only 31% ee in favor of the

Table 1. Palladium-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenylprop-2-enyl acetate with dimethyl malonate[a]

Entry	Ligand	Base	*T* (°C)	*T* (h)	Conversion[b] (%)	Yield[c] (%)	ee[d] (%)	Configuration[e]
1[f]	**4**	BSA/	25	24	100	98	83	*R*
2	**6**	KOAc	25	24	0	—	—	—
3	**6**		60	24	46	35	0	—
4	**7α**		60	24	57	41	30	*S*
5	**7α**		60	48	100	93	27	*S*
6	**7β**		25	24	17	—	nd	—
7	**7β**		60	24	100	91	31	*S*
8	**8α**		25	24	<10	—	nd	—
9	**8α**		60	72	100	80	25	*S*
10	**8β**		25	24	23	—	14	*S*
11	**8β**		60	72	100	93	32	*S*
12[f]	**4**	NaH	25	24	78	—	25	*R*
13	**6**		25	24	100	96	36	*S*
14[g]	**7α**		25	24	100	91	27	*S*
15[g]	**7β**		25	48	47	39	0	—
16	**8α**		25	48	32	—	21	*S*
17	**8α**		60	72	100	89	21	*S*
18	**8β**		25	48	100	96	34	*S*

[a] [Substrate]/[$CH_2(CO_2Me)_2$]/[base]/[Pd]/[ligand]=25/75/75/1/1.
[b] Conversion determined by GC analysis.
[c] Isolated pure product after column chromatography.
[d] Enantiomeric excess determined by HPLC analysis (column Chiralpak AD 0.46×25 cm).
[e] The absolute configuration was determined by comparison with an authentic sample (see Ref. 25).
[f] See Ref. 15.
[g] Reaction performed in CH_2Cl_2.

(*S*)-enantiomer (entry 7). It is to be noticed that the low conversion (17%) observed at 25 °C could be due to the low solubility of the complex in THF. The benzyl α-D-glycoside derivative **8α** and β-D-glycoside derivative **8β** gave quite similar results. Low conversions were observed when the reaction was performed at 25 °C (entries 8 and 10), whereas a total conversion occurred at 60 °C (entries 9 and 11). However, in each case, the obtained enantioselectivities were low: 25 and 32% in favor of (*S*)-enantiomer, respectively.

In the second time, the same study was performed changing the base BSA/KOAc by NaH (Table 1, entries 12–18). After 24 h at 25 °C, using phosphine-amide based carbohydrates **6**, **7α**, or **8β**, a total conversion and a chemical yield up to 91% were obtained with enantiomeric excesses of 36, 27, or 34% always in favor of the (*S*)-enantiomer, respectively (entries 13, 14, and 18). In the case of ligand **7β** derived from methyl β-D-glycoside, the reaction has to be performed in CH_2Cl_2 in order to solubilize the palladium-complex (entry 15). After 48 h at 25 °C, a conversion of only 47% was obtained with no enantiomeric excess. A low conversion was also obtained using catalyst prepared from benzyl α-D-glycoside **8α**, when the reaction was run at 25 °C (entry 16). However, a total conversion, with a chemical yield of 89%, and an enantiomeric excess of 21% in favor of the (*S*)-enantiomer were obtained after 72 h when the reaction was performed at 60 °C (entry 17).

2.3. NMR study

Previously we proposed for the phosphine-amide derivative **4** based on D-glucosamine, an equilibrium between two complexes resulting from a bidentate *P,O*-chelation mode and a monodentate *P,P*-chelation mode.[15] In the case of a ligand/palladium ratio of 1/1, the *P,O*-chelation mode was the major one, inducing a higher enantioselectivity due to the rigidity of the complex formed from $[(\eta^3\text{-}C_3H_5)PdCl]_2$. We were unable to isolate monocrystals of the complexes based on ligands **4** or **6**–**8**. In order to get an insight into the possible *P,O*-chelation mode between these ligands and the palladium, we performed a NMR study of the ligands and of the corresponding complexes. Pregosin has studied the structures of complexes obtained from *N,S*-oxazoline-thioglucose[26] or diphenylphosphinoferrocenyl-ethylthioether-glucose,[27] and 1,3-diphenylallyl-palladium-chloro dimer. The pertinent ^1H and ^{13}C NMR spectra revealed the existence of different diastereomeric complexes. Unfortunately, our NMR study of the Pd-complexes based on the ligands **4**, **6**–**8**, and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ did not allow for similar interpretation. So we focused our NMR study on the chemical shifts of the carbon of the carbonyl groups of the ligand before and after the complexation. The assignment of each carbonyl group was made using ^1H–^{13}C HMBC NMR sequence (the spectrum of ligand **4** is shown as an example in Fig. 3).

In the case of β-D-glycopyranose **4**, the five signals corresponding to carbonyl groups linked to C-3, C-6, C-1, C-4, and NH of the carbohydrate skeleton were detected at δ 171.7, 171.1, 170.2, 169.6, and 169.1 ppm, respectively (Fig. 4a). After complexation with $[(\eta^3\text{-}C_3H_5)PdCl]_2$, three signals were modified (Fig. 4b). The signal of carbonyl group of the amido function moved from δ 169.1 to 167.9 ppm with a lower intensity. The chemical shifts of

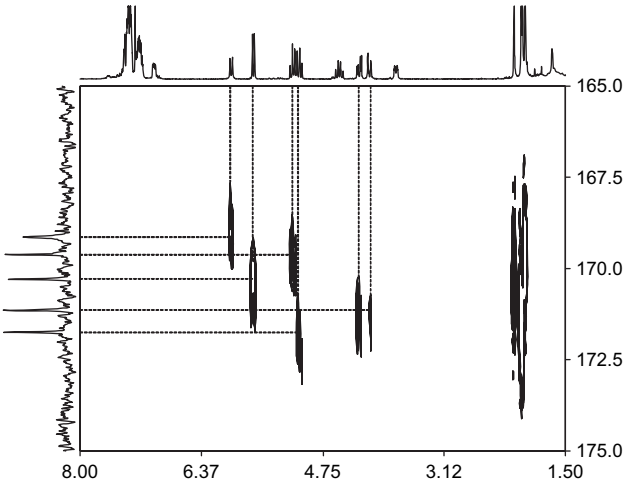


Figure 3. ^1H–^{13}C HMBC NMR ($CDCl_3$) between δ 8.00–1.50 ppm and δ 175.0–165.0 ppm for ligand **4**.

the four other signals were not modified, however, the intensity of the signals of the carbonyl groups of the two acetoxy groups linked to C-3 and C-1 decreased almost completely. The α-D-glycopyranose **6** gave the NMR spectra quite similar to the spectrum of the derivative **4**, having the β-configuration. For ligand **6**, before complexation with palladium, five signals were detected at δ 172.0, 171.1, 169.5, 169.0, and 168.9 ppm, corresponding to carbonyl groups linked to C-3, C-6, C-1, C-4, and NH of D-glucosamine, respectively (Fig. 4c). After complexation with palladium, the same three signals, than in the case of ligand **4**, were modified (Fig. 4d). The intensity of the signals of the carbonyl groups linked to C-3 and C-1 at δ 172.0 and 169.0 ppm decreased almost completely, and the signal of the carbonyl group of the amido group moved from δ 168.9 to 169.4 ppm with lower intensity. No change was observed for the two other signals at δ 171.1 and 169.5 ppm, corresponding to the carbonyl groups linked to C-6 and C-4, respectively. For methyl or benzyl D-glycosides **7** and **8**, the NMR studies gave quite similar results when the same anomers were compared. In the case of methyl β-D-glycoside **7β**, the signals of the four carbonyl groups linked to C-3, C-6, C-4, and NH of sugar were at δ 171.2, 171.1, 169.9, and 169.4 ppm, respectively, before complexation with palladium (Fig. 4e). After addition of $[(\eta^3\text{-}C_3H_5)PdCl]_2$, the signals of the two carbonyl groups linked to C-6 and C-4 were not modified (δ 171.1 and 169.8 ppm, respectively), the intensity of the carbonyl group linked to C-3 at δ 171.2 ppm decreased almost totally, and the signal of the acetamido group moved from δ 169.4 to 168.5 ppm, with a lower intensity (Fig. 4f). In the case of benzyl β-D-glycoside **8β**, the signals of the four carbonyl groups linked to C-3, C-6, C-4, and NH of the carbohydrate moiety were at δ 171.4, 171.2, 169.8, and 169.3 ppm, respectively (Fig. 4i). After complexation with palladium, the signals of the two carbonyl groups linked to C-6 and C-4 were not modified (δ 171.2 and 169.8 ppm, respectively), the intensity of the carbonyl group linked to C-3 at 171.4 ppm decreased almost totally, and the signal of the acetamido group moved from δ 169.3 to 168.3 ppm, with a lower intensity (Fig. 4j). In the case of methyl α-D-glycoside **7α**, the signals of the four carbonyl groups linked to C-3, C-6, C-4, and NH of D-glucosamine were at δ 171.7, 171.1, 169.7, and 168.9 ppm,

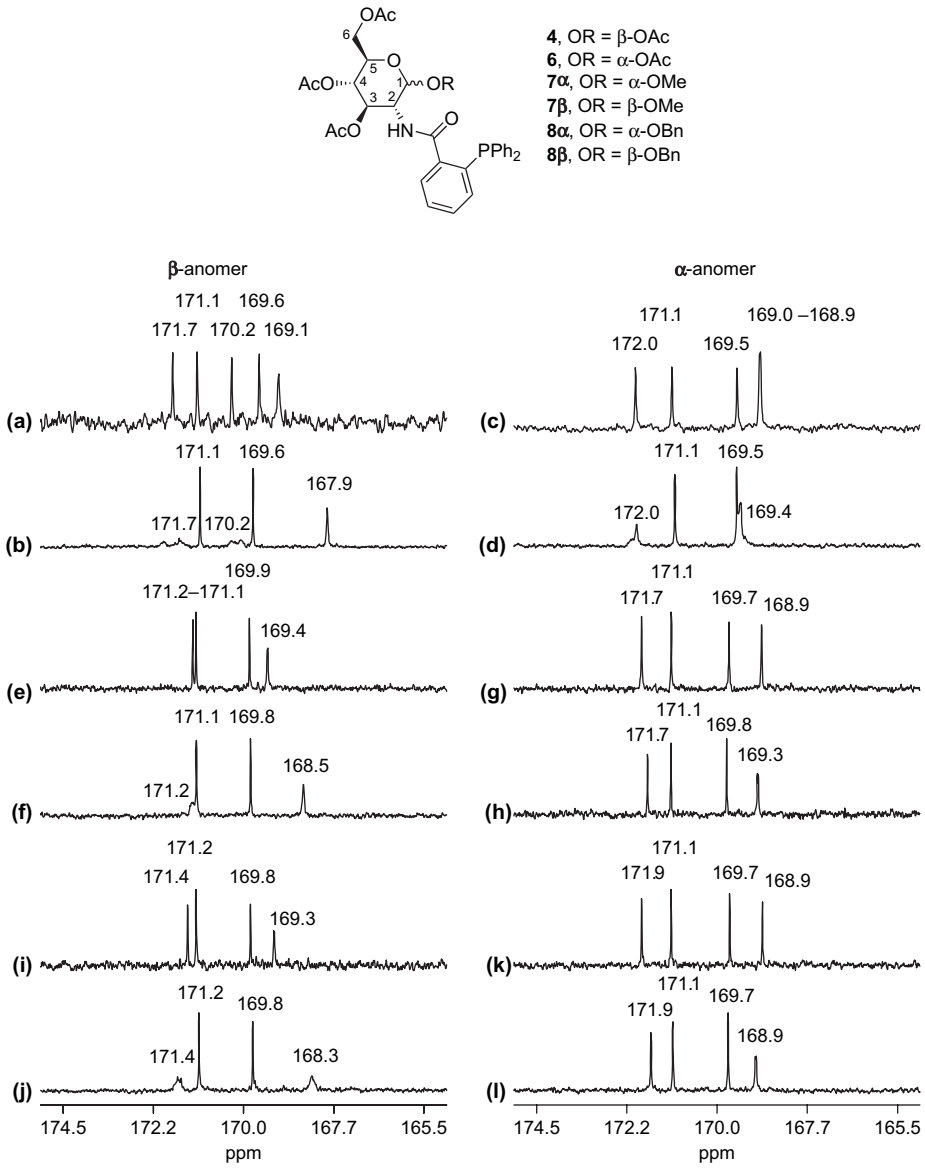


Figure 4. ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum between δ 175.0 and 165.0 ppm of the ligands and the corresponding Pd-complexes: (a), (c), (e), (g), (i) and (k) for ligands **4**, **6**, **7β**, **7α**, **8β** and **8α**, respectively; (b), (d), (f), (h), (j) and (l) for the Pd-complexes of ligands **4**, **6**, **7β**, **7α**, **8β** and **8α**, respectively.

respectively (Fig. 4g). After complexation with palladium, no modification was observed except for the acetamido group signal moving from δ 168.9 to 169.3 ppm, with a lower intensity (Fig. 4h). And finally, in the case of benzyl α-D-glycoside **8α**, the signals of the four carbonyl groups linked to C-3, C-6, C-4, and NH of carbohydrate skeleton were at δ 171.9, 171.1, 169.7, and 168.9 ppm, respectively (Fig. 4k). After complexation with palladium, no change was observed except for the signal of the acetamido group decreasing in intensity (Fig. 4l).

The chelation of the palladium by the phosphorus atom was confirmed by ^{31}P NMR (see Supplementary data). Before complexation, the chemical shifts of the phosphorus atom of the ligands **4**, **6**, **7α**, **7β**, **8α**, and **8β** were at δ −10.3, −9.3, −8.5, −10.3, −8.6, −10.5 ppm, respectively. In the case of the complex derived from β-D-glycopyranose **4**, two close and thin signals were detected at δ 29.8 and 29.6 ppm. These two signals were integrated with the same intensity. From the α-D-glycopyranose **6**, two signals were recorded at δ 29.3 and 28.4 ppm for the corresponding Pd-complex, the signal at δ 28.4 ppm being more intensive. In the case of the Pd-complex based on methyl α-D-glycoside **7α**, two signals at δ 26.6 and 26.0 ppm were observed with an integration of 1.0 and 1.1, respectively. In the case of methyl β-D-glycoside **7β**, the resulting Pd-complex showed also two signals at δ 28.8 and 28.3 ppm with an equal intensity. The NMR spectra of the Pd-complex derived from benzyl α-D-glycoside **8α** showed two signals at δ 27.1 and 26.3 ppm, with an integration of 1.0 and 1.2, respectively, whereas, in the case of the Pd-complex based on benzyl β-D-glycoside **8β**, only one signal was observed at δ 28.9 ppm. Since for this type of phosphine-amide derivatives, the chemical shifts of the corresponding oxides are over δ 35 ppm, the observed values corresponded to the chemical shifts of various conformers of amidophosphine chelated to palladium. In order to confirm that the palladium was not chelated to the nitrogen atom of the D-glucosamine

moiety, a ^{1}H–^{15}N HMBC NMR sequence was made for some ligands and the corresponding Pd-complexes (see Supplementary data). In the case of ligands **4** and **8β**, before complexation, the chemical shifts of nitrogen atom were at δ 113.5 and 113.7 ppm, and after complexation, at δ 107.9 and 112.0 ppm, respectively. In the case of Pd-complex based on ligand **8α**, the chemical shift of nitrogen atom was at δ 113.4 ppm. These values confirm that no complexation of the nitrogen occurred with the palladium.

This NMR study shows that the complexes obtained from the ligands and the palladium are bidentate. The palladium is chelated to the phosphorus atom, and also to the oxygen atom of one (or more) carbonyl group(s). The *P*,*O*-coordination of Pd-allyl involving carbonyl group has already been suggested for the Trost-type ligand systems.[28] In the case of α- and β-D-glycopyranoses **6** and **4**, the palladium is probably coordinated to the oxygen atoms of the carbonyl groups linked to C-3, C-1, or NH of the carbohydrate skeleton, these complexes being in equilibrium. In the case of methyl and benzyl α-D-glycosides **7α** and **8α**, only the oxygen atom of the acetamido group of the D-glucosamine seems to be chelated to the palladium, affording only one complex for each ligand. In the case of methyl and benzyl β-D-glycosides **7β** and **8β**, the chelated oxygen atoms are probably the carbonyl groups linked to C-3 or NH of the sugar, affording an equilibrium between these two complexes for each ligand. According to the results obtained in enantioselectivity, it seems that the enantiomeric excess of the allylic substitution is dependent on the formed *P*,*O*-complexes. Only in the case of the use of β-D-glycopyranose **4** as the chiral ligand, an enantioselectivity over 80% was obtained. The only difference between this ligand and the five others is the presence of an acetoxy group on the β-position at the anomeric center. It seems that the presence of this group is crucial for obtaining high enantioselectivity in this studied Pd-catalyzed allylic alkylations.

3. Conclusions

In conclusion, new chiral phosphine amides derived from D-glucosamine were easily prepared, and were used in the palladium-catalyzed asymmetric allylic alkylation. The influence of the D-glucosamine moiety on the enantioselectivity of the product of allylic alkylation was studied by modifying the configuration and the nature of the substituent at the anomeric position. It seems that in order to obtain enantiomeric excess up to 85%, it is necessary to have an acetoxy group at the anomeric center in a β-position. In the case of alkyl α- or β-D-glycosides, the size of the alkyl group (methyl or benzyl) seems to have no influence on the enantiomeric excess. Work is currently in progress in order to obtain monocrystal of the different complexes for X-ray structure.

4. Experimental section

4.1. General

Solvents were purified by standard methods and dried if necessary. All commercially available reagents were used as received. All reactions were monitored by TLC (TLC plates GF_{254} Merck). Air and moisture sensitive reactions were performed under the usual inert atmosphere techniques. Reactions involving organometallic catalysis were carried out in a Schlenk tube under an inert atmosphere. Column chromatography was performed on silica gel 60 (230–240 mesh, Merck). All melting points were determined with a Büchi apparatus and are uncorrected. Optical rotations were recorded using Perkin–Elmer 241 polarimeter. NMR spectra were recorded with a Bruker AMX 300 spectrometer and referenced as follows: ^{1}H, internal $SiMe_4$ at δ 0.00 ppm; ^{13}C, internal $CDCl_3$ at δ 77.2 ppm; ^{31}P, external 85% H_3PO_4 at δ 0.0 ppm. Conversion was determined by GC using a Quadrex OV1 column (30 m×0.25 mm), and enantiomeric excess was determined by HPLC with a Chiralpak AD column (25 cm×4.6 mm) using hexane/2-PrOH as the eluant, the flow rate being 0.5 mL/min, and the detection being done by UV at 225 nm.

4.2. Synthesis of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-α-D-glucopyranose 6 and alkyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-D-glucopyranoside 7 and 8

Carbohydrate derivative **11**, **14α**,**β**, or **15α**,**β** (1.44 mmol), 2-(diphenylphosphino)benzoic acid (462 mg, 1.51 mmol), EDC·HCl (326 mg, 1.70 mmol), HOBT (230 mg, 1.70 mmol), and $NaHCO_3$ (171 mg, 2.04 mmol) were dissolved in a mixture of CH_2Cl_2 (10 mL) and THF (20 mL) in a Schlenk tube. After being stirred for 48 h at rt, the solvents were evaporated. The residue was dissolved in ethyl acetate (10 mL), and then washed with 5% NaOH (5 mL) and 0.5 M HCl (5 mL) solutions. After drying and evaporation of the solvents under reduced pressure, the crude residue was purified by flash chromatography on silica gel to give phosphine-amide derivatives **6**–**8**.

4.2.1. 1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-α-D-glucopyranose 6. White solid (yield 55%); mp=152–154 °C; R_f=0.57 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +73.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.45–7.15 (m, 13H, H_{arom}), 6.98–6.92 (m, 1H, H_{arom}), 6.17 (br d, *J*=9.4 Hz, 1H, NH), 6.06 (d, *J*=3.7 Hz, 1H, H-1), 5.32 (dd, *J*=9.8, 9.4 Hz, 1H, H-3), 5.21 (dd, *J*=9.6, 9.4 Hz, 1H, H-4), 4.65 (ddd, *J*=9.8, 9.4, 3.7 Hz, 1H, H-2), 4.24 (dd, *J*=12.3, 4.1 Hz, 1H, H-6), 4.07 (dd, *J*=12.3, 2.2 Hz, 1H, H-6), 3.99 (ddd, *J*=9.6, 4.1, 2.2 Hz, 1H, H-5), 2.14 (s, 3H, Me), 2.08 (s, 3H, Me), 2.07 (s, 3H, Me), 2.04 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 172.0, 171.1, 169.5, 169.0, 168.9, 140.6 (d, *J*=26.0 Hz), 137.0 (d, *J*=10.5 Hz), 136.9 (d, *J*=9.9 Hz), 136.8 (d, *J*=21.1 Hz), 134.7, 134.3 (d, *J*=7.2 Hz), 134.0 (d, *J*=5.0 Hz), 131.0, 129.3, 129.1 (d, *J*=6.8 Hz), 128.9 (d, *J*=6.8 Hz), 127.9 (d, *J*=4.9 Hz), 91.4, 71.1, 70.1, 68.0, 61.9, 51.3, 21.5, 21.4, 21.1, 21.0; ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): δ −9.3 ppm; HRMS (ESI) calcd for $C_{33}H_{35}NO_{10}P$ $[M+H]^+$: 636.1999, found: 636.1999.

4.2.2. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-α-D-glucopyranoside 7α. White solid (yield 40%); mp=67–69 °C; R_f=0.50 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +39.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.30–7.18 (m, 13H, H_{arom}),

6.97–6.94 (m, 1H, H_{arom}), 6.12 (br d, J=9.4 Hz, 1H, NH), 5.26 (dd, J=10.0, 9.9 Hz, 1H, H-3), 5.11 (dd, J=10.0, 9.9 Hz, 1H, H-4), 4.53 (d, J=3.6 Hz, 1H, H-1), 4.45 (ddd, J=10.0, 9.4, 3.6 Hz, 1H, H-2), 4.21 (dd, J=12.2, 4.5 Hz, 1H, H-6), 4.10 (dd, J=12.2, 2.5 Hz, 1H, H-6), 3.90 (ddd, J=10.0, 4.5, 2.5 Hz, 1H, H-5), 3.30 (s, 3H, OMe), 2.09 (s, 3H, Me), 2.04 (s, 3H, Me), 2.02 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.7, 171.1, 169.7, 168.9, 140.7 (d, J=24.8 Hz), 137.9 (d, J=11.2 Hz), 137.6 (d, J=11.2 Hz), 137.5 (d, J=22.3 Hz), 134.8, 134.2 (d, J=8.5 Hz), 134.1 (d, J=6.2 Hz), 131.0, 129.3, 129.1 (d, J=7.8 Hz), 128.9 (d, J=7.8 Hz), 127.9 (d, J=4.9 Hz), 98.6, 71.6, 68.6, 68.1, 62.4, 55.7, 52.3, 21.4, 21.2, 21.0; ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): δ −8.5 ppm; HRMS (ESI) calcd for $C_{32}H_{35}NO_9P$ $[M+H]^+$: 608.2050, found: 608.2072; calcd for $C_{32}H_{34}NO_9NaP$ $[M+Na]^+$: 630.1869, found: 630.1855.

4.2.3. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-β-D-glucopyranoside 7β. White solid (yield 42%); mp=129–131 °C; R_f=0.44 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +38.0 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.55–7.50 (m, 1H, H_{arom}), 7.40–7.20 (m, 12H, H_{arom}), 6.99–6.94 (m, 1H, H_{arom}), 6.01 (br d, J=8.2 Hz, 1H, NH), 5.34 (dd, J=10.2, 9.6 Hz, 1H, H-3), 5.08 (dd, J=9.6, 9.4 Hz, 1H, H-4), 4.59 (d, J=8.5 Hz, 1H, H-1), 4.27 (dd, J=12.0, 4.3 Hz, 1H, H-6), 4.14 (dd, J=12.0, 2.3 Hz, 1H, H-6), 4.00 (ddd, J=10.2, 8.5, 8.2 Hz, 1H, H-2), 3.70 (ddd, J=9.4, 4.3, 2.3 Hz, 1H, H-5), 3.45 (s, 3H, OMe), 2.08 (s, 3H, Me), 2.05 (s, 3H, Me), 2.02 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.2, 171.1, 169.9, 169.4, 142.0 (d, J=29.1 Hz), 137.6 (d, J=11.2 Hz), 137.3 (d, J=10.5 Hz), 136.1 (d, J=21.0 Hz), 135.1, 134.1 (d, J=7.2 Hz), 134.1 (d, J=5.0 Hz), 134.0 (d, J=6.2 Hz), 130.8, 129.4, 129.1 (d, J=6.8 Hz), 129.0 (d, J=10.5 Hz), 128.9 (d, J=8.1 Hz), 128.1 (d, J=5.6 Hz), 101.8, 72.5, 72.1, 69.2, 62.5, 57.2, 55.2, 21.4, 21.2, 21.1; ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): δ −10.3 ppm; HRMS (ESI) calcd for $C_{32}H_{34}NO_9NaP$ $[M+Na]^+$: 630.1869, found: 630.1872.

4.2.4. Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-α-D-glucopyranoside 8α. White solid (yield 53%); mp=53–56 °C; R_f=0.80 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +70.0 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.40–7.20 (m, 18H, H_{arom}), 7.00–6.90 (m, 1H, H_{arom}), 6.18 (br d, J=9.4 Hz, 1H, NH), 5.31 (dd, J=10.3, 9.8 Hz, 1H, H-3), 5.14 (dd, J=9.8, 9.8 Hz, 1H, H-4), 4.85 (d, J=3.6 Hz, 1H, H-1), 4.66 (d, J=11.8 Hz, 1H, OCH_2Ph), 4.50 (ddd, J=10.3, 9.4, 3.6 Hz, 1H, H-2), 4.49 (d, J=11.8 Hz, 1H, OCH_2Ph), 4.20 (dd, J=12.2, 4.1 Hz, 1H, H-6), 4.01 (dd, J=12.2, 2.2 Hz, 1H, H-6), 3.95 (ddd, J=9.8, 4.1, 2.2 Hz, 1H, H-5), 2.09 (s, 3H, Me), 2.05 (s, 3H, Me), 2.02 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.9, 171.1, 169.7, 168.9, 140.7 (d, J=25.4 Hz), 137.7 (d, J=12.4 Hz), 137.5 (d, J=10.5 Hz), 137.0, 134.9, 134.3, 134.0, 130.9, 129.2–128.6 (area with nine peaks), 127.3 (d, J=4.3 Hz), 97.2, 71.6, 70.7, 68.6, 68.5, 62.2, 52.2, 21.5, 21.1, 21.0; ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): δ −8.6 ppm; HRMS (ESI) calcd for $C_{38}H_{39}NO_9P$ $[M+H]^+$: 684.2363, found: 684.2365; calcd for $C_{38}H_{38}NO_9NaP$ $[M+Na]^+$: 706.2182, found: 706.2176.

4.2.5. Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]amino}-β-D-glucopyranoside 8β. White solid (yield 65%); mp=60–63 °C; R_f=0.84 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +29.5 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.42–7.20 (m, 18H, H_{arom}), 7.06–7.02 (m, 1H, H_{arom}), 5.84 (br d, J=8.7 Hz, 1H, NH), 5.26 (dd, J=10.3, 9.4 Hz, 1H, H-3), 5.10 (dd, J=9.8, 9.4 Hz, 1H, H-4), 4.84 (d, J=12.0 Hz, 1H, OCH_2Ph), 4.67 (d, J=8.3 Hz, 1H, H-1), 4.64 (d, J=12.0 Hz, 1H, OCH_2Ph), 4.27 (dd, J=12.2, 4.5 Hz, 1H, H-6), 4.17 (dd, J=12.2, 2.6 Hz, 1H, H-6), 4.16 (ddd, J=10.3, 8.7, 8.3 Hz, 1H, H-2), 3.64 (ddd, J=9.8, 4.5, 2.6 Hz, 1H, H-5), 2.10 (s, 3H, Me), 2.05 (s, 3H, Me), 2.01 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.4, 171.2, 169.8, 169.3, 142.0 (d, J=29.6 Hz), 137.9 (d, J=11.5 Hz), 137.5 (d, J=10.4 Hz), 137.3, 136.5 (d, J=21.4 Hz), 135.3, 134.2 (d, J=12.0 Hz), 134.0 (d, J=8.8 Hz), 133.8 (d, J=8.8 Hz), 130.7, 129.3, 129.0–128.3 (area with eight peaks), 127.6 (d, J=6.0 Hz), 99.8, 72.6, 72.2, 71.0, 69.2, 62.5, 54.9, 21.5, 21.1, 21.0; ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): δ −10.5 ppm; HRMS (ESI) calcd for $C_{38}H_{39}NO_9P$ $[M+H]^+$: 684.2363, found: 684.2357.

4.3. General procedure for deprotection of the acetamido function

The three steps (Boc protection, deacetylation, and cleavage of the Boc group) have been performed without intermediate purification. The acetamido derivatives **12α,β** or **13α,β** (1.15 mmol) and *N*,*N*-dimethyl-4-aminopyridine (28 mg, 0.23 mmol) were dissolved in THF (3 mL). Di-*tert*-butyl dicarbonate (0.80 mL, 752 mg, 3.45 mmol) was added and the mixture was refluxed for 14 h. The solution was cooled to rt, methanol (3 mL) added, and the mixture treated with monohydrate hydrazine (0.15 mL, 230 mg, 4.60 mmol) for 4 h. The mixture was then poured into CH_2Cl_2 (10 mL), the organic solution washed with 1 M HCl, $CuSO_4$, and $NaHCO_3$ solutions, dried, and concentrated under reduced pressure. CF_3CO_2H (6 mL) was added and the mixture stirred at rt for 14 h. After evaporation, the residue was dissolved in CH_2Cl_2 (10 mL) and washed with 10% Na_2CO_3 (2×5 mL). The aqueous phase was extracted with CH_2Cl_2 (3×5 mL), and the combined organic phases were dried and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to give the corresponding amino derivatives **14α,β** and **15α,β**.

4.3.1. Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranoside 14α. Colorless oil (yield 40%); R_f=0.57 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +141.5 (c 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 5.12 (dd, J=9.8, 9.8 Hz, 1H, H-3), 4.95 (dd, J=9.8, 9.4 Hz, 1H, H-4), 4.76 (d, J=3.5 Hz, 1H, H-1), 4.28 (dd, J=12.2, 4.7 Hz, 1H, H-6), 4.07 (dd, J=12.2, 1.7 Hz, 1H, H-6), 3.96 (ddd, J=9.4, 4.7, 1.7 Hz, 1H, H-5), 3.42 (s, 3H, OMe), 2.93 (br d, J=7.9 Hz, 1H, H-2), 2.09 (s, 3H, Me), 2.07 (s, 3H, Me), 2.02 (s, 3H, Me), 1.53 (br, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.1, 170.9, 170.0, 100.8, 70.0, 69.1, 67.8, 62.5, 55.7, 54.8, 21.1, 21.0, 20.9; Anal. Calcd for $C_{13}H_{21}NO_8$: C 48.90, H 6.62; found: C 48.83, H 6.53.

4.3.2. Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside 14β. White solid (yield 45%);

mp=133–135 °C; R_f=0.43 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +16.2 (*c* 1.0, MeOH), lit. $[\alpha]_D^{22}$ +14 (*c* 1.0, MeOH)[29] or $[\alpha]_D^{27}$ +15 (*c* 1.0, MeOH)[30]; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 5.02 (dd, *J*=9.6, 9.4 Hz, 1H, H-3), 4.47 (dd, *J*=9.4, 9.4 Hz, 1H, H-4), 4.30 (dd, *J*=12.2, 4.7 Hz, 1H, H-6), 4.16 (d, *J*=7.9 Hz, 1H, H-1), 4.12 (dd, *J*=12.2, 2.2 Hz, 1H, H-6), 3.68 (ddd, *J*=9.4, 4.7, 2.2 Hz, 1H, H-5), 3.56 (s, 3H, OMe), 2.91 (dd, *J*=9.6, 7.9 Hz, 1H, H-2), 2.08 (s, 3H, Me), 2.07 (s, 3H, Me), 2.03 (s, 3H, Me), 1.44 (br, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.1, 171.0, 170.1, 105.4, 75.7, 72.2, 69.2, 62.5, 57.8, 56.3, 21.2, 21.1, 21.0; the ^{1}H NMR spectrum is in agreement with the literature.[30]

4.3.3. Benzyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranoside 15α. Colorless oil (yield 43%); R_f=0.40 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ +102.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.50–7.29 (m, 5H, H_{arom}), 5.16 (dd, *J*=9.8, 9.6 Hz, 1H, H-3), 4.99 (d, *J*=3.6 Hz, 1H, H-1), 4.98 (dd, *J*=9.8, 9.4 Hz, 1H, H-4), 4.73 (d, *J*=11.6 Hz, 1H, OCH_2Ph), 4.57 (d, *J*=11.6 Hz, 1H, OCH_2Ph), 4.27 (dd, *J*=11.8, 4.1 Hz, 1H, H-6), 4.04–3.98 (m, 2H, H-5+H-6), 2.97 (dd, *J*=9.6, 3.6 Hz, 1H, H-2), 2.10 (s, 3H, Me), 2.07 (s, 3H, Me), 2.01 (s, 3H, Me), 1.68 (br, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.3, 171.1, 170.2, 137.2, 129.1, 128.9, 128.5, 99.4, 75.2, 70.6, 69.2, 68.3, 62.5, 55.0, 21.3, 21.1, 21.0; Anal. Calcd for $C_{19}H_{25}NO_8$: C 57.77, H 6.37; found: C 57.36, H 6.55.

4.3.4. Benzyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside 15β. White solid (yield 55%); mp=233–235 °C; R_f=0.40 ($CHCl_3$/MeOH 10/1); $[\alpha]_D^{25}$ −37.0 (*c* 0.6, $CHCl_3$), lit. $[\alpha]_D^{20}$ −31.8 (*c* 0.7, $CHCl_3$)[31]; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.32–7.26 (m, 5H, H_{arom}), 5.04 (dd, *J*=9.4, 9.4 Hz, 1H, H-3), 4.95 (dd, *J*=9.4, 9.4 Hz, 1H, H-4), 4.93 (d, *J*=11.7 Hz, 1H, OCH_2Ph), 4.63 (d, *J*=11.7 Hz, 1H, OCH_2Ph), 4.32 (d, *J*=7.8 Hz, 1H, H-1), 4.30 (dd, *J*=12.2, 4.9 Hz, 1H, H-6), 4.15 (dd, *J*=12.2, 2.4 Hz, 1H, H-6), 3.67 (ddd, *J*=9.4, 4.9, 2.4 Hz, 1H, H-5), 2.98 (dd, *J*=9.4, 7.8 Hz, 1H, H-2), 2.11 (s, 3H, Me), 2.10 (s, 3H, Me), 2.07 (s, 3H, Me), 1.25 (br, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 171.2, 171.1, 170.2, 137.1, 128.9, 128.7, 128.6, 103.1, 75.7, 72.3, 71.6, 69.3, 62.7, 56.3, 21.2, 21.1; Anal. Calcd for $C_{19}H_{25}NO_8$: C 57.77, H 6.37; found: C 58.19, H 6.52; the ^{1}H NMR spectrum is in agreement with the literature.[31]

4.4. General procedure for the allylic alkylation

In a Schlenk tube $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (8.8 mg, 24 μmol) and the ligand (48 μmol) were dissolved in THF or CH_2Cl_2 (1 mL). After being stirred for 1 h at 25 °C, a solution of racemic (*E*)-1,3-diphenyl-2-propenyl acetate (302 mg, 1.2 mmol) in THF or CH_2Cl_2 (1 mL) was added. After 30 min, this solution was transferred to a Schlenk tube containing dimethyl malonate (475 mg, 3.6 mmol), and the base [NaH (87 mg, 3.6 mmol) or BSA (732 mg, 3.6 mmol)/KOAc (2.5 mg, 24 μmol)] in THF or CH_2Cl_2 (2 mL). The reaction mixture was stirred at the desired temperature for the indicated time. The conversion was determined by GC analysis. The mixture was then diluted with diethyl ether (15 mL) and water (5 mL). The organic phase was washed with brine and dried over $MgSO_4$. Evaporation of the solvents gave a residue, which was purified by chromatography (petroleum ether/ethyl acetate 10/1). The enantiomeric excesses of dimethyl[(*E*)-1,3-diphenyl-prop-2-en-1-yl]malonate were determined by HPLC analysis using a Daicel Chiralpak AD column and eluting with hexane/*i*-PrOH (85/15), t_R 18 min for (*R*)-isomer and t_R 24 min for (*S*)-isomer. The absolute configurations of the enantiomers were determined by comparison of the retention times with that of an authentic sample[25] and by measurement of the optical rotation of the product.

Acknowledgements

K.G. thanks the MENSR for fellowship.

Supplementary data

The supplementary NMR data is available on the online version. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.098.

References and notes

1. Pfaltz, A.; Lautens, M. *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, Heidelberg, 1999; pp 833–886.
2. Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649–1651.
3. Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327–9343.
4. (a) Von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566–568; (b) Williams, J. M. J. *Synlett* **1996**, 705–710; (c) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203–214.
5. (a) Dieguez, M.; Pamies, O.; Claver, C. *Chem. Rev.* **2004**, *104*, 3189–3215; (b) Dieguez, M.; Pamies, O.; Ruiz, A.; Diaz, Y.; Castillon, S.; Claver, C. *Coord. Chem. Rev.* **2004**, *248*, 2165–2192.
6. Borriello, C.; Del Litto, R.; Panunzi, A.; Ruffo, F. *Tetrahedron: Asymmetry* **2004**, *15*, 681–686.
7. Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2002**, *124*, 734–735.
8. Cucciolito, M. E.; Del Litto, R.; Roviello, G.; Ruffo, F. *J. Mol. Catal. A: Chem.* **2005**, *236*, 176–181.
9. (a) Bauer, T.; Tarasiuk, J.; Pasnicek, K. *Tetrahedron: Asymmetry* **2002**, *13*, 77–82; (b) Emmerson, D. P. G.; Villard, R.; Mugnaini, C.; Batsanov, A.; Howard, J. A. K.; Hems, W. P.; Tooze, R. P.; Davis, B. G. *Org. Biomol. Chem.* **2003**, *1*, 3826–3838; (c) Emmerson, D. P. G.; Hems, W. P.; Davis, B. G. *Tetrahedron: Asymmetry* **2005**, *16*, 213–221; (d) Emmerson, D. P. G.; Hems, W. P.; Davis, B. G. *Org. Lett.* **2006**, *8*, 207–210.
10. (a) Beller, M.; Krauter, J. G. E.; Zapf, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 772–774; (b) Parisot, S.; Kolodziuk, R.; Goux-Henry, C.; Iourtchenko, A.; Sinou, D. *Tetrahedron Lett.* **2002**, *43*, 7397–7400; (c) Kolodziuk, R.; Penciu, A.; Tollabi, M.; Framery, E.; Goux-Henry, C.; Iourtchenko, A.; Sinou, D. *J. Organomet. Chem.* **2003**, *687*, 384–391; (d) Konovets, A.; Penciu, A.; Framery, E.; Percina, N.; Goux-Henry, C.; Sinou, D. *Tetrahedron Lett.* **2005**, *46*, 3205–3208.

11. (a) Yonehara, K.; Mori, K.; Hashizume, T.; Chung, K.-G.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2000**, *603*, 40–49; (b) Mata, Y.; Dieguez, M.; Pamies, O.; Claver, C. *Org. Lett.* **2005**, *7*, 5597–5599.
12. Glaser, B.; Kunz, H. *Synlett* **1998**, 53–55.
13. (a) Yonehara, K.; Hashizume, T.; Mori, K.; Ohe, K.; Uemura, S. *Chem. Commun.* **1999**, 415–416; (b) Yonehara, K.; Hashizume, T.; Mori, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 9374–9380; (c) Hashizume, T.; Yonehara, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2000**, *65*, 5197–5201.
14. Mata, Y.; Dieguez, M.; Pamies, O.; Claver, C. *Adv. Synth. Catal.* **2005**, *347*, 1943–1947.
15. Tollabi, M.; Framery, E.; Goux-Henry, C.; Sinou, D. *Tetrahedron: Asymmetry* **2003**, *14*, 3329–3333.
16. Konovets, A.; Glegola, K.; Penciu, A.; Framery, E.; Jubault, P.; Goux-Henry, C.; Pietrusiewicz, K. M.; Quirion, J.-C.; Sinou, D. *Tetrahedron: Asymmetry* **2005**, *16*, 3183–3187.
17. Cunha, A. C.; Pereira, L. O. R.; de Souza, R. O. P.; de Souza, M. C. B. V.; Ferreira, V. F. *Nucleosides Nucleotides Nucleic Acids* **2001**, *20*, 1555–1569.
18. Pertel, S. S.; Chirva, V. Y.; Kadun, A. L.; Kakayan, E. S. *Carbohydr. Res.* **2000**, *329*, 895–899.
19. Kikuchi, H.; Saito, Y.; Komiya, J.; Takaya, Y.; Honma, S.; Nakahata, N.; Ito, A.; Oshima, Y. *J. Org. Chem.* **2001**, *66*, 6982–6987.
20. Shulman, M. L.; Khorlin, A. Ya. *Carbohydr. Res.* **1973**, *27*, 141–147.
21. Paul, B.; Bernacki, R. J.; Korytnyk, W. *Carbohydr. Res.* **1980**, *80*, 99–115.
22. See: Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley and Sons: New York, NY, 1999.
23. Burk, M. J.; Allen, J. G. *J. Org. Chem.* **1997**, *62*, 7054–7057.
24. El Gihani, M. T.; Heaney, H. *Synthesis* **1998**, 357–375.
25. Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769–1772.
26. Boog-Wick, K.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 3254–3264.
27. Boog-Wick, K.; Pregosin, P. S.; Trabesinger, G. *Magn. Reson. Chem.* **1998**, *36*, 5189–5194.
28. (a) Butts, C. P.; Crosby, J.; Lloyd-Jones, G. C.; Stephen, S. C. *Chem. Commun.* **1999**, 1707–1708; (b) Fairlamb, I. J. S.; Lloyd-Jones, G. C. *Chem. Commun.* **2000**, 2447–2448; (c) Amatore, C.; Jutand, A.; Mensah, L.; Ricard, L. *J. Organomet. Chem.* **2007**, *692*, 1457–1464.
29. Yamasaki, T.; Kubota, Y.; Tsuchiya, T.; Umezawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3190–3192.
30. Billing, J. F.; Nilsson, U. J. *Tetrahedron* **2005**, *61*, 863–874.
31. Kraska, U.; Pougny, J.-P.; Sinaÿ, P. *Carbohydr. Res.* **1976**, *50*, 181–190.