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New phosphine–imine ligands derived from D-gluco- and D-galactosamine in Pd-catalysed asymmetric allylic alkylation

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ABSTRACT

New phosphine–imine chiral ligands which were easily prepared from D-gluco- and D-galactosamine furnished a high level of enantiomeric excess (up to 99%) in the Pd(0)-catalysed asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with malonates.

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The preparation of new and efficient enantiopure ligands for asymmetric catalysis is a continued research focus for many groups. Impressive results have been obtained in a wide range of catalytic asymmetric reactions using carbohydrate derived ligands.[1] Derivatives of the most accessible NH_2-containing sugar, D-glucosamine, have been evaluated as chiral ligands in the asymmetric allylic substitution reaction which is a fundamental transformation in organic synthesis and one of the most powerful tools for the formation of carbon–carbon and carbon–heteroatom bonds. In particular, D-glucosamine based phosphorus–oxazoline[2] and phosphine–amide[3] ligands have produced excellent results. Several phosphine–imine ligands with a pyranoside backbone have also been developed for the Pd-catalysed allylic substitution of 1,3-diphenyl-2-propenyl acetate (Fig. 1).[4,3c,d]

Previous studies have indicated that having the imine–phosphine residue at C2 provides better enantioselectivities than when the residue is located at the C1 position of the pyranoside backbone. Additionally replacement of the C2 by an amine group has also provided good results.[3c]

Herein, we report the simple and efficient synthesis of novel phosphine–imine chiral ligands from commercially available D-gluco and D-galactosamine hydrochloride and their application in the Pd-catalysed allylic alkylation reaction with various nucleophiles.

The ligands **5** and **6** were easily prepared in two steps according to Scheme 1.

Glucosamine hydrochloride **1** and galactosamine hydrochloride **2** were first treated with trimethylsilylchloride (TMSCl) and hexamethyl disilazane (HMDS) in pyridine[5] to yield per-*O*-silyl protected α-derivatives **3**[5b] and **4**[6] as colourless oil. Under these conditions the amino functional group remained unprotected.[5b] Condensation of 2-(diphenylphosphino)-benzaldehyde onto D-glucopyranose **3** and D-galactopyranose **4** derivatives in toluene furnished the corresponding phosphine–imine derivatives **5**[7] and **6**[8] in 77% and 67% yield, respectively.

Initially, we investigated the palladium-catalysed allylic substitution of 1,3-diphenyl-2-propenyl acetate **7** with dimethylmalonate as a model system using the chiral D-glucosamine derived phosphine–imine ligand **5** (Table 1, entries 1–9).

Using NaH as base and THF as the solvent; the yield was only 50% after 24 h, with a low enantioselectivity (34% ee) in favour of the (*R*)-enantiomer (Table 1, entry 1). The use of a mixture of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and KOAc as base afforded (*S*)-**8** in higher yields and enantioselectivity (Table 1, entries 2–9). These results indicated that enantioselectivity depends on the reaction conditions. We found it difficult to explain this 'chiral switching' when the bases were changed, which was discovered by Li,[9] Beller[10] and Wang.[1f] Additionally, we examined the influence of solvent (THF or CH_2Cl_2), Pd/ligand ratio and substrate/nucleophile ratio on the outcome of the asymmetric allylic alkylation. The best results were obtained with a Pd/ligand ratio

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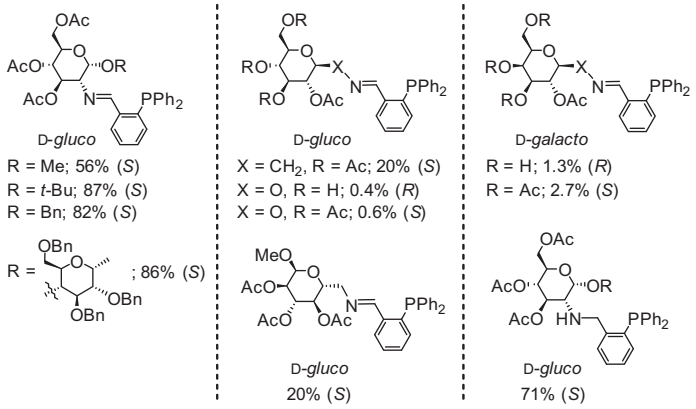
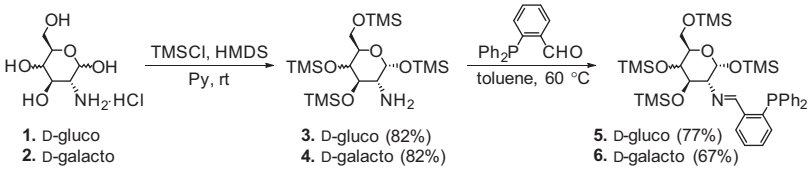
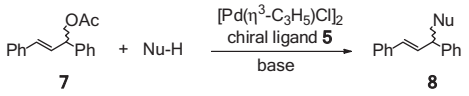


Figure 1. Phosphine–imine ligands and enantioselectivities obtained in the Pd(0)-catalysed asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate.



Scheme 1. Synthesis of ligands **5** and **6**.

Table 1
Optimisation of reaction conditions for ligand **5**[a]



Entry	Nu–H	Nu–H (equiv)	Pd/L ratio	Base	Solvent	Temp (°C)	Yield[b] (%)	ee[c] (%) config.[d]
1	$CH_2(CO_2Me)_2$	3	1:2	NaH	THF	25	50	34 (*R*)
2	$CH_2(CO_2Me)_2$	3	1:2	KOAc, BSA	THF	25	98	49 (*S*)
3	$CH_2(CO_2Me)_2$	3	1:2	KOAc, BSA	CH_2Cl_2	25	96	40 (*S*)
4	$CH_2(CO_2Me)_2$	2	1:1	KOAc, BSA	THF	25	97	55 (*S*)
5	$CH_2(CO_2Me)_2$	2	1:1	KOAc, BSA	CH_2Cl_2	25	98	70 (*S*)
6	$CH_2(CO_2Me)_2$	2	1:2	KOAc, BSA	THF	25	97	55 (*S*)
7	$CH_2(CO_2Me)_2$	2	1:2	KOAc, BSA	CH_2Cl_2	25	97	73 (*S*)
8	$CH_2(CO_2Me)_2$	2	1:2	KOAc, BSA	CH_2Cl_2	0	96	81 (*S*)
9	$CH_2(CO_2Me)_2$	2	1:2	KOAc, BSA	CH_2Cl_2	−20	97	80 (*S*)

[a] Reaction conditions: [**7**]:[NaH]:[Pd] = 1:3:0.05; [**7**]:[KOAc]:[BSA]:[Pd] = 1:0.05:2 or 3:0.05.
[b] Isolated product.
[c] Determined by HPLC analysis (column Chiralcel OJ-H 0.46 × 25 cm).
[d] Determined by comparison with an authentic sample.[1e]

of 1:2 and substrate/nucleophile ratio of 1:2 in CH_2Cl_2. In this case, an enantioselectivity of 73% with a yield of 97% was observed after a reaction time of 24 h at 25 °C (Table 1, entry 7). Lowering the temperature to 0 °C and −20 °C improved the selectivity of the reaction, giving an ee of 81% and 80%, respectively (Table 1, entries 8 and 9).

Ligand **6** derived from D-galactosamine was more reactive under the same conditions and gave compound **8** with higher enantioselectivity; 85% ee at 25 °C and 99% ee at 0 °C (Table 2, entries 1 and 2). It should be noted that the configuration of the substituent at the C4 position of the carbohydrate moiety of the D-galacto ligand **6** also had an influence on the configuration of the alkylation product **8**. The (*R*) configuration of the obtained product was opposite to that observed for the reaction using ligand **5** (Table 2, entries 1 and 2).

The phosphine–imine ligands D-gluco **5** and D-galacto **6** were also applied to allylic alkylation and allylic amination reactions using nucleophiles such as: diethyl malonate, dimethyl methylmalonate, benzylamine and isopropylamine (Table 2, entries 3–11). The reaction with ligand **5** and diethyl malonate at 25 °C required longer reaction times and was characterised by low yields (30%) and an ee of 71%. Increasing the temperature to 36 °C afforded the product in an improved yield of 96% after 24 h but did not improve the selectivity of the reaction (Table 2, entries 3 and 4). Ligand **6** was more reactive with the same nucleophile and gave **8** with an improved yield and enantioselectivity; 83% ee at 25 °C and 99% ee at 0 °C in favour of the (*R*)-enantiomer (Table 2, entries 5 and 6). A similar correlation was observed for the reactions with dimethyl methylmalonate (Table 2, entries 7–9) however, in this reaction, both ligands **5** and **6** gave the

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