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New phosphine-imine and phosphine-amine ligands derived from D-gluco-, D-galacto- and D-allosamine in Pd-catalysed asymmetric allylic alkylation

Izabela Szulc, Robert Kołodziuk, Anna Zawisza*

Department of Organic and Applied Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland

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ABSTRACT

New phosphine-imine and phosphine-amine chiral ligands which were easily prepared from D-gluco-, D-galacto- and D-allosamine 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.

1. Introduction

Catalytic asymmetric synthesis has been one of the most active research areas in modern organic chemistry. To achieve the highest levels of reactivity and selectivity in enantioselective reactions the design of efficient synthetic chiral catalysts is at the center of contemporary studies.

In recent years impressive results have been obtained using carbohydrate-based ligands.[1] These chiral natural derivatives have many advantages: they are readily available, can be easily functionalized, have several stereogenic centers and successfully used in a large number of asymmetric catalytic reactions, such as: hydrogenation,[2] 1,2-addition of nucleophiles to C=O and C=NR,[3] 1,4-addition of nucleophiles to Michael acceptors,[4] hydroformylation,[5] Heck reaction,[6] cyclopropanation[7] and hydrovinylation.[8] Derivatives of the most accessible NH_2-containing sugar, D-glucosamine, have been mainly evaluated as chiral ligands in Pd-catalysed 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. The best results in Pd-catalysed asymmetric allylic alkylation of 1,3-symmetrically disubstituted acetates (ee up to 98%) provided phosphine-oxazoline,[9] phosphinite-oxazoline,[10] phosphite-oxazoline,[11] phosphite-phosphoramidite[12] and phosphine-amide[13] derivatives of D-glucosamine. Just a few phosphine-imine ligands with a pyranoside backbone have been developed for Pd-catalysed allylic substitution.[13c,13d,14] The studies indicated that the presence of the imine-phosphine residue at C2 provides better enantioselectivities than when the residue is at C1 of the pyranoside backbone. Additionally the C2 imine group in ligands has been replaced by an amine group and also provided good results.[13d]

Herein, we report a simple and efficient synthesis of novel phosphine-imine and phosphine-amine chiral ligands derived from D-gluco-, D-galacto- and D-allosamine hydrochloride (Fig. 1) and their application in the Pd-catalysed allylic alkylation reaction with various nucleophiles.

* Corresponding author.
E-mail address: azawisza@chemia.uni.lodz.pl (A. Zawisza).

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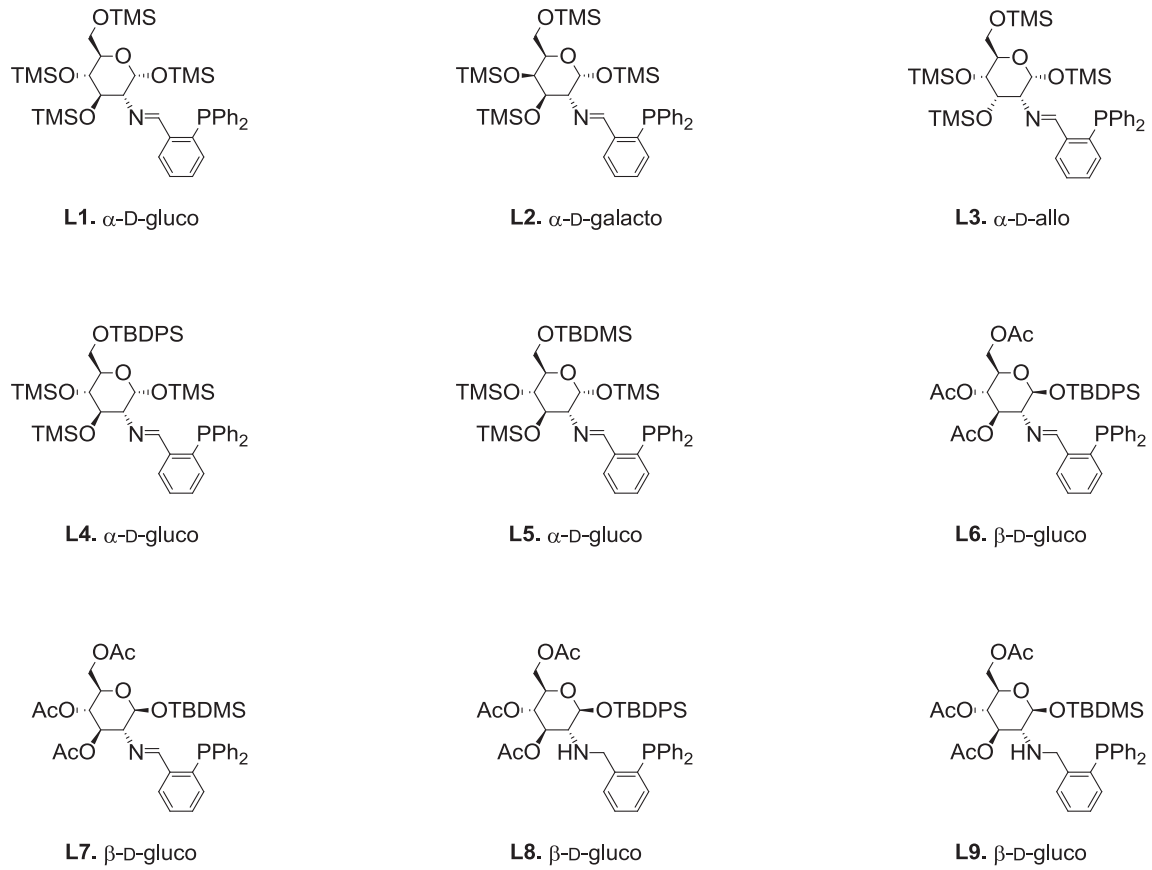


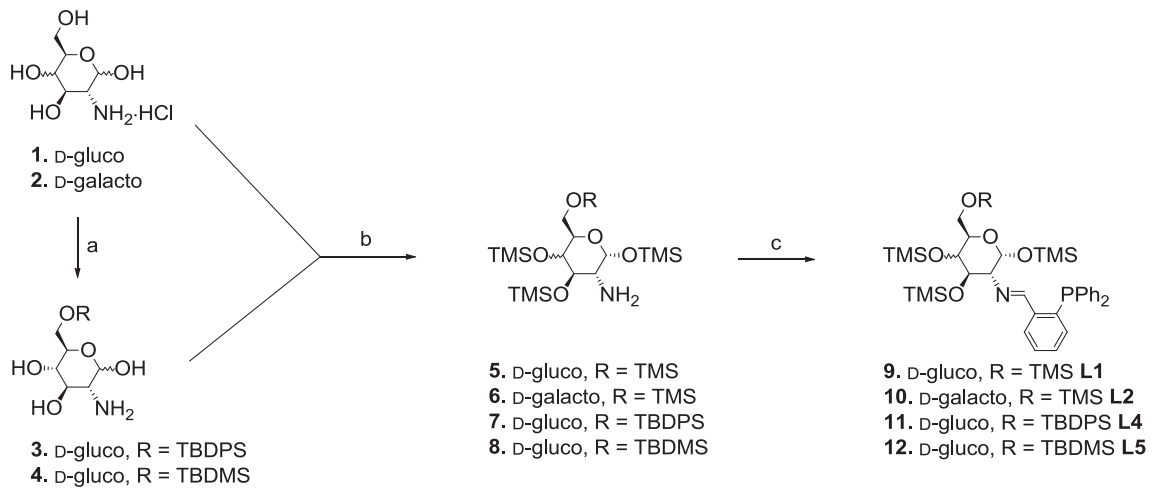
Fig. 1. New *P,N*-ligands used in this work.

2. Results and discussion

2.1. Synthesis of the starting materials

The new phosphine-imine ligands **9**–**12**, derivatives of D-gluco- and D-galactosamine were easily prepared according to Scheme 1.

Glucosamine hydrochloride **1** was first treated with TBDPSCl or TBDMSCl in pyridine to give 6-*O*-silyl protected derivatives **3** and **4** as yellow oil in 63% and 72% yields, respectively. Per-*O*-silyl protected α-derivatives **5**,[15] **6**,[16] **7** and **8** were obtained in 82%, 82%, 55% and 60% yields, respectively, by the reaction of **1**–**4** with trimethylsilyl chloride (TMSCl) and hexamethyl disilazane (HMDS) in pyridine[15,17]. Under these conditions the amino functional group remains unprotected.[15] Condensation of 2-(diphenylphosphino)-benzaldehyde onto D-glucopyranose **5**, **7**–**8** and D-galactopyranose **6** derivatives in toluene furnished the corresponding phosphine-imine derivatives **9**,[18] **10**,[16] **11** and **12** in 77%, 67%, 43% and 45% yields, respectively.



Scheme 1. Synthesis of ligands **L1, L2, L4 and L5**; reagents and conditions: (a) TBDPSCl or TBDMSCl, Py, rt; (b) TMSCl, HMDS, Py, rt; (c) 1,2-Ph_2P-C_6H_4-CHO, toluene, 60 °C.

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The synthesis of phosphine-imine ligand derivative of D-allosamine **21** we started from the inexpensive α-D-glucosamine hydrochloride **1** which was *N*-acetylated to give α-D-*N*-acetylglucosamine **13**[19] (Scheme 2). In the two following steps, 1-*O*-methyl and 4,6-*O*-benzylidene protecting groups were introduced according to known procedures,[20] leaving the 3-hydroxy group of **15** unprotected. The mesylation reaction of this group[20b] followed by the substitution with OH group causes the inversion of configuration at C-3.[20b] Deprotection of 4 and 6[21] positions of the saccharide **17**, as well as 1 and 2[22] in acidic conditions leads to α-D-allosamine hydrochloride **19**. Per-*O*-silylation and condensation with 2-(diphenylphosphino)-benzaldehyde gave the corresponding phosphine-imine D-allo-ligand **21** in 57% yield.

The synthesis of ligands **L6**-**L9** was started by protecting the amino group in α-D-glucosamine hydrochloride **1** with a 2,2,2-trichloroethoxycarbonyl group[23] (Scheme 3). Selective deprotection of the hydroxyl group located on the anomeric carbon with benzylamine leads to **23**,[23] which is easily converted into 1-*O*-silyl protected derivatives **24** and **25**. In the next step, these derivatives reacted with activated Zn dust in glacial acetic acid gave **26** and **27** with free amino groups in 80% and 83% yields, respectively. Condensation with 2-(diphenylphosphino)-benzaldehyde afforded the corresponding phosphine-imine ligands **28** and **29** (75% and 85% yields, respectively). The imino functionality was then reduced with $NaBH_3CN$ to provide phosphine-amines **30** and **31** with quantitative yields.

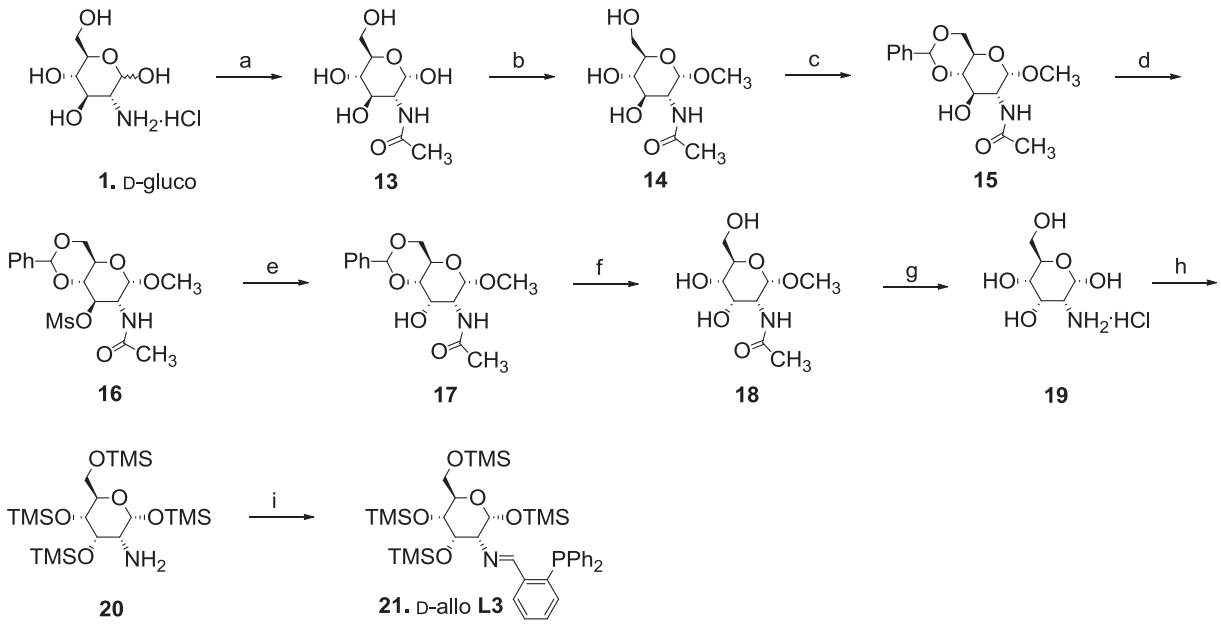
2.2. Application of ligands *L1*–*L9* in the Pd(0)-catalysed asymmetric allylic alkylation

In a previous paper,[16] we examined the influence of base, solvent, Pd/ligand ratio and substrate/nucleophile ratio on the outcome of the asymmetric allylic alkylation using $[(\eta^3\text{-}C_3H_5)PdCl]_2$ as the palladium source and **9** (**L1**) as the ligand. The best results were obtained with a Pd/ligand ratio of 1:2 and substrate/nucleophile ratio of 1:2 in CH_2Cl_2 in the presence of a mixture of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and KOAc as base (Table 1, entries 1–4). Based on these results, we decided under the same conditions, to carry out the palladium-catalysed allylic substitution of 1,3-diphenyl-2-propenyl acetate with various nucleophiles using **L1**-**L7** chiral phosphine-imine ligands and amino-phosphine ligands **L8**-**L9** (Table 1). The activity of some saccharide ligands (**L4**-**L9**), containing other than TMS protective groups, was also investigated in tetrahydrofuran.

Initially, we performed the palladium-catalysed allylic substitution of 1,3-diphenyl-2-propenyl acetate **32** with dimethyl malonate (Table 1, entries 1–22). Ligands **L2** derived from α-D-galactosamine and **L3** derived from α-D-allosamine were the most reactive in these conditions and gave compound **33** with the highest enantiomeric excess – over 99% ee at 0 °C (Table 1, entries 5–8). It should be noted that the configuration of the substituent at the C4 and C3 position of the carbohydrate moiety of the D-galacto ligand **L2** and D-allo ligand **L3** had an influence on the configuration of the alkylation product **33**. The (*R*) configuration of the obtained product was opposite to that observed for the reaction using D-gluco ligand **L2** (Table 1, entries 1–4). The phosphine-imine ligands **L4** and **L5** of the α-D-gluco configuration with the large substituents at the C6 position of a saccharide were less reactive and gave **33** with practically quantitative yield but ee's of 40–56% in favor of the (*R*)-enantiomer (Table 1, entries 9–12). The reactions with β-D-gluco ligands **L6** and **L7** were characterised by excellent yields and high enantioselectivity – up to 93% ee (Table 1, entries 13–18). The obtained results also confirmed that dichloromethane is a better solvent for this type of reaction than tetrahydrofuran. Comparing the results obtained with ligands **L4**-**L7**, we can also conclude that only bulky protecting groups at the C1 position of the sugar have the influence on the course of the reaction and the mode complexation of ligands with palladium whereas such groups in the C6 position show only minimal effect.

Finally, we performed the allylic alkylation reaction using phosphine-amine ligands **L8** and **L9** (Table 1, entries 19–22). The reaction gave **33** in excellent yield but an ee of 10% in favor of the (*S*)-enantiomer in CH_2Cl_2.

In the next step, the effectiveness of the ligands **L1**-**L9** has been



Scheme 2. Synthesis of ligand **L3**; reagents and conditions: (a) $(CH_3CO)_2O$, CH_3ONa, CH_3OH, 40 °C, 24 h; (b) Amberlite IR-120, CH_3OH, reflux, 24 h; (c) $PhCH(OCH_3)_2$, *p*-TsOH, DMF, 40 °C, 48 h; (d) MsCl, Py, 0 °C, 16 h; (e) $CH_3OCH_2CH_2OH$, CH_3COONa, reflux → rt, 12 h; (f) 60% CH_3COOH, 40 °C, 3 h; (g) 2N HCl, 80 °C, 2 h; (h) TMSCl, HMDS, Py, rt, 10 h; (i) 1,2-Ph_2P-C_6H_4-CHO, toluene, 60 °C, 24 h.

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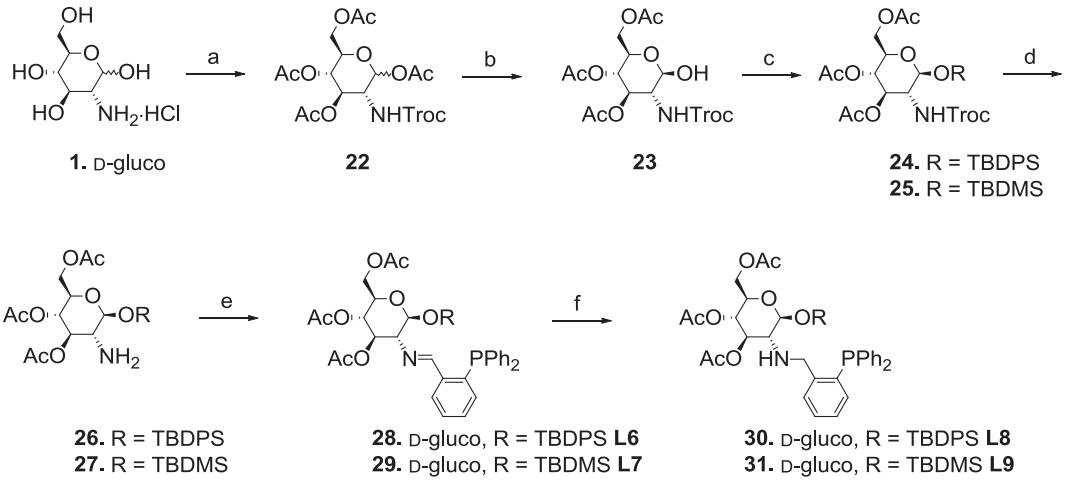

Scheme 3. Synthesis of ligands **L6** – **L9**; reagents and conditions: (a) 1. CCl_3CH_2OCOCl, $NaHCO_3$, H_2O, rt, 2 h; 2. $(CH_3CO)_2O$, Py, rt, 24 h; (b) $BnNH_2$, THF, rt, 24 h; (c) TBDPSCl or TBDMSCl, CH_3CN, rt, 24 h; (d) Zn, CH_3COOH, rt, 24 h; (e) 1,2-Ph_2P-C_6H_4-CHO, toluene, 60 °C, 24 h; (f) $NaBH_3CN$, CH_3COOH, CH_3OH, rt, 0.5 h.

tested in the reaction with other nucleophiles.

The reaction with ligand **L1** and diethyl malonate at 25 °C required longer reaction times and was characterised by low yields (35% conversion) and an ee of 71% (Table 1, entry 23). Increasing the temperature to 36 °C afforded the product in 100% conversion after 24 h but did not improve the selectivity of the reaction (Table 1, entries 23–24). Ligand **L2** was more reactive with the same nucleophile and gave **33** with an improved yield and enantioselectivity; 83% ee at 25 °C and 99% ee at 0 °C in favor of the (*R*)-enantiomer (Table 1, entries 25–26). The α-D-allo-ligand **L3** gave slightly weaker results: 80% ee at 25 °C (Table 1, entry 27). Ligands **L4** and **L5** generate moderate results under the same conditions: 69% ee and 39% ee, respectively. Lowering the temperature to 0 °C did not improve the selectivity of the reaction (Table 1, entries 29–31). However, it should be noted that the ligand **L4** with a larger substituent (TBDPS) in the C6 position of α-D-glucopyranose generated significantly higher enantiomeric excesses than ligand **L5** with TBDMS substituent. The β-D-gluco-ligands **L6** and **L7** in the reaction with diethyl malonate produced results comparable to those obtained for dimethyl malonate (83% and 82% ee's, respectively at 25 °C in CH_2Cl_2), although these reactions required elongation of reaction time to 48 h (Table 1, entries 33–37). Phosphine-amine ligands **L8** and **L9** showed slightly higher efficiency in the reaction with diethyl malonate (Table 1, entries 38–41). In this case, enantioselectivity of 40% for **L8** and 71% for **L9** with a conversion of 100% was observed after a reaction time of 24 h at 25 °C in CH_2Cl_2. The reaction in THF gave comparable results.

Finally, a series of Pd-catalysed asymmetric allylation reactions were performed with 1,3-diphenyl-2-propenyl acetate **32** and dimethyl methylmalonate (Table 1, entries 42–58). The use of trimethylsilyl α-D-glucoside derivative **L1** as the ligand, gave 35% and 85% conversion at 25 °C after 24 and 48 h, respectively (Table 1, entries 42 and 43). The obtained enantioselectivity was 74% and 72% ee in favor of the (*R*)-enantiomer. α-D-Galactoside derivative **L2** gave a more active catalyst, a 98% conversion end 75% ee being obtained at 25 °C and a 87% conversion end 96% ee at 0 °C after 48 h (Table 1, entries 44–45). The α-D-allo ligand **L3** gave moderate results in these conditions – 77% conversion and 52% ee (*R*) (Table 1, entry 46). The phosphine-imine ligands **L4** and **L5** of the α-D-gluco configuration gave quite similar results (Table 1, entries 47–50). However, a total conversion occurred at 25 °C after 24 h, the enantioselectivity was only 56% and 46% ee, respectively in favor of the (*S*)-enantiomer. Lowering the temperature to 0 °C did not result in improving the enantioselectivity of the reaction. The β-D-gluco-ligands **L6** and **L7** in the reaction with dimethyl methylmalonate produced the highest enantiomeric excess: 89% and 75% in THF and 92% and 89% in CH_2Cl_2, respectively (Table 1, entries 51–54). Phosphine-amine ligands **L8** and **L9** were again ineffective in allyl substitution reactions.

The reactions carried out in their presence provided a 60% conversion and an enantiomeric excess not exceeding 20% in favor of the (*S*)-enantiomer.

As reported previously, to determine the mode of complexation of phosphine-imine ligands with palladium, an NMR and IR study of the palladium complex was made using ligand **L2** before and after complexation with palladium.[16] Both ^{1}H NMR and IR spectra excluded the coordination of the imine nitrogen to the palladium metal center. The ^{1}H NMR spectra of free ligand **L2** displayed the imine proton at 9.00 ppm, which was not shifted after chelatation with the metal. The IR spectroscopic data of complex **L2** with palladium did not reveal a batochromic shift with respect to the free ligand,[24] with a $\nu_{C=N}$ stretching vibration band at 1636 cm^{-1}. However, a significant downfield shift of the single ^{31}P resonances of ligand **L2** to 15.86 ppm after complexation compared to −16.57 ppm for the free ligand confirmed coordination of the phosphine moiety to the palladium center.

3. Conclusion

In conclusion, a series of saccharides phosphine-imine and phosphine-amine chiral ligands which were easily prepared from D-gluco-, D-galacto- and D-allosamine have been examined in asymmetric allylic alkylation. We have shown the influence of factors such as sugar configuration, type of solvent or nucleophile on the course of the reaction. The phosphine-imine ligands **L2** derived from α-D-galactosamine and **L3** derived from α-D-allosamine were the most reactive in dichloromethane and gave the substitution product with the highest enantiomeric excess (over 99% ee at 0 °C) while phosphine-amine ligands **L8** and **L9** did not show activity under these conditions. In addition, we have shown that synthesized ligands utilize the chirality of the sugar moiety and induce chirality to the coordination sphere solely by phosphorus atom coordination.

Further work is underway to utilize the obtained *P,N*-ligands in other asymmetric reactions.

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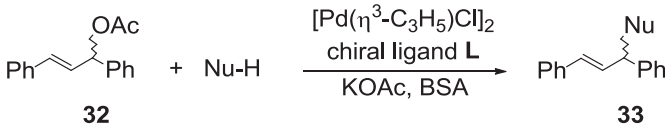
Table 1
Effect of nucleophiles and ligands on Pd^0-catalysed asymmetric allylic alkylation[a].



32 **33**

Entry	Ligand	Nu-H	Solvent	Temp. [°C]	Time [h]	Conv. [%][b]	ee [%][c] (config.)[d]
1	**L1**	$CH_2(CO_2Me)_2$	THF	25	24	100	55 (*S*)
2	**L1**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	73 (*S*)
3	**L1**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	98	81 (*S*)
4	**L1**	$CH_2(CO_2Me)_2$	CH_2Cl_2	−20	24	100	80 (*S*)
5	**L2**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	85 (*R*)
6	**L2**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	98	>99 (*R*)
7	**L3**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	15 min	100	93(*R*)
8	**L3**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	100	>99 (*R*)
9	**L4**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	56 (*R*)
10	**L4**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	100	50 (*R*)
11	**L5**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	44 (*R*)
12	**L5**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	97	40 (*R*)
13	**L6**	$CH_2(CO_2Me)_2$	THF	25	24	100	83 (*S*)
14	**L6**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	89 (*S*)
15	**L6**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	100	93 (*S*)
16	**L7**	$CH_2(CO_2Me)_2$	THF	25	24	100	69 (*S*)
17	**L7**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	83 (*S*)
18	**L7**	$CH_2(CO_2Me)_2$	CH_2Cl_2	0	24	100	86 (*S*)
19	**L8**	$CH_2(CO_2Me)_2$	THF	25	24	100	10 (*S*)
20	**L8**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	10 (*S*)
21	**L9**	$CH_2(CO_2Me)_2$	THF	25	24	100	8 (*S*)
22	**L9**	$CH_2(CO_2Me)_2$	CH_2Cl_2	25	24	100	10 (*S*)
23	**L1**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	78	35	71 (*S*)
24	**L1**	$CH_2(CO_2Et)_2$	CH_2Cl_2	36	24	100	67 (*S*)
25	**L2**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	24	100	83 (*R*)
26	**L2**	$CH_2(CO_2Et)_2$	CH_2Cl_2	0	24	100	>99 (*R*)
27	**L3**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	24	100	80 (*R*)
28	**L4**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	24	100	69 (*R*)
29	**L4**	$CH_2(CO_2Et)_2$	CH_2Cl_2	0	48	100	69 (*R*)
30	**L5**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	24	100	39 (*R*)
31	**L5**	$CH_2(CO_2Et)_2$	CH_2Cl_2	0	24	100	35 (*R*)
32	**L6**	$CH_2(CO_2Et)_2$	THF	25	48	100	81 (*S*)
33	**L6**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	48	100	83 (*S*)
34	**L6**	$CH_2(CO_2Et)_2$	CH_2Cl_2	0	48	36	88 (*S*)
35	**L7**	$CH_2(CO_2Et)_2$	THF	25	48	100	60 (*S*)
36	**L7**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	48	100	82 (*S*)
37	**L7**	$CH_2(CO_2Et)_2$	CH_2Cl_2	0	48	traces	–
38	**L8**	$CH_2(CO_2Et)_2$	THF	25	24	100	40 (*R*)
39	**L8**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	24	100	38 (*R*)
40	**L9**	$CH_2(CO_2Et)_2$	THF	25	24	100	71 (*R*)
41	**L9**	$CH_2(CO_2Et)_2$	CH_2Cl_2	25	24	100	71 (*R*)
42	**L1**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	24	35	74 (*R*)
43	**L1**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	48	78	73 (*R*)
44	**L2**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	48	98	75 (*R*)
45	**L2**	$MeCH(CO_2Me)_2$	CH_2Cl_2	0	48	87	96 (*R*)
46	**L3**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	24	77	52 (*R*)
47	**L4**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	24	100	56 (*S*)
48	**L4**	$MeCH(CO_2Me)_2$	CH_2Cl_2	0	48	76	60 (*S*)
49	**L5**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	24	100	46 (*S*)
50	**L5**	$MeCH(CO_2Me)_2$	CH_2Cl_2	0	24	67	45 (*S*)
51	**L6**	$MeCH(CO_2Me)_2$	THF	25	72	57	89 (*S*)
52	**L6**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	72	54	92 (*S*)
53	**L7**	$MeCH(CO_2Me)_2$	THF	25	72	55	75 (*S*)
54	**L7**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	72	70	89 (*S*)
55	**L8**	$MeCH(CO_2Me)_2$	THF	25	96	62	20 (*S*)
56	**L8**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	96	61	3 (*S*)
57	**L9**	$MeCH(CO_2Me)_2$	THF	25	96	58	17 (*S*)
58	**L9**	$MeCH(CO_2Me)_2$	CH_2Cl_2	25	96	60	13 (*S*)

[a] Reaction conditions: [**7**]:[Nu-H]:[KOAc]:[BSA]:[Pd]:[L] = 1:2:0.05:2:0.05:0.1.
[b] Determined by ^1H NMR analysis.
[c] Enantioselectivity (ee) was measured by chiral stationary phase HPLC on a KROMASIL AD column (25 cm × 4.6 mm); λ = 254 nm, hexane/*i*-propanol (85:15), flow rate = 0.5 mL min^{-1}, t_R = 17.2 min and t_S = 23.8 min for dimethyl malonate; on a Phenomenex - Lux® 5 μm Amylose-1 column (25 cm × 4.6 mm); λ = 254 nm, hexane/*i*-propanol (95:5), flow rate = 0.4 mL min^{-1}, t_R = 32.4 min and t_S = 38.5 min for diethyl malonate and on a Phenomenex - Lux® 5 μm Amylose-1 column (25 cm × 4.6 mm); λ = 254 nm, hexane/*i*-propanol (99:1), flow rate = 0.4 mL min^{-1}, t_R = 22.6 min and t_S = 26.6 min for dimethyl methylmalonate.
[d] Determined by comparison with an authentic sample.

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4. Experimental

4.1. General

All solvents and reagents were purchased from Sigma-Aldrich and were used as supplied, without additional purification. NMR spectra were recorded in $CDCl_3$ on Varian Gemini 2000 (200 MHz for ^1H NMR, 50 MHz for ^{13}C NMR) or Bruker Avance III (600 MHz for ^1H NMR, 150 MHz for ^{13}C NMR), coupling constants are reported in Hz. Chromatographic purification of compounds was achieved with 230–400 mesh size silica gel. The progress of reactions was monitored by silica gel thin layer chromatography plates (Merck TLC Silicagel 60 F_{254}). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric ratio was determined by HPLC (ProStar Varian) employing a KROMASIL AD or Phenomenex - Lux® 5 μm Amylose-1 column (25 cm × 4.6 mm).

4.2. Typical procedure for the synthesis of silyl derivatives **3** and **4**

To a suspension of gluco- or galactosamine hydrochloride (23.2 mmol, 1eq.) in pyridine (80 mL) was added *tert*-butyldiphenylsilylchloride (TBDPSCl) or *tert*-butyldimethylsilylchloride (TBDMSCl) (30.2 mmol, 1.3 eq.). The resulting mixture was stirred at room temp. and monitored via TLC (CH_2Cl_2/CH_3OH, 10: 3). After completion of the reaction (approx. 48 h), the mixture was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

4.2.1. 2-Amino-2-deoxy-6-O-tert-butyldiphenylsilyl-D-glucopyranose hydrochloride **3**

Yellow oil, 6.1 g, 63% yield; $[\alpha]_D^{25} = +27.0$ (*c* 0.5, $CHCl_3$); R_f (CH_2Cl_2/CH_3OH, 10: 3) 0.78; δ_H (600 MHz, $CDCl_3$) 1.00 (s, 9H, OSiC(C**H**$_3$)$_3$), 2.50–2.57 (m, 0.33H, **H**-2β), 2.85 (dd, 0.66H, *J* 10.2, 3.2, **H**-2α), 3.20–4.20 (m, 8H, **H**-3α and β, **H**-4α and β, **H**-5α and β, **H**-6′α and β, **H**-6α and β, 3 × O**H**), 5.31 (d, 0.66H, *J* 3.2, **H**-1α), 5.34 (d, 0.33H, *J* 5.4, **H**-1β), 5.69 (d, 0.66H, *J* 5.3, N**H$_2$**α), 5.85 (d, 0.33H, *J* 5.3, N**H$_2$**β), 7.35–7.50 (m, 6H, C$_6$**H**$_5$), 7.60–7.77 (m, 4H, C$_6$**H**$_5$); δ_C (150 MHz, $CDCl_3$) 18.9 (OSi**C**(CH$_3$)$_3$), 26.6 (OSiC(**C**H$_3$)$_3$), 54.5, 57.3 (**C**-2 α and β), 63.2, 63.4 (**C**-6 α and β), 69.9, 72.0, 72.5 (**C**-4 α and β, **C**-5 α and β), 76.6 (**C**-3 α and β), 89.0, 93.0 (C-1 α and β), 123.8, 127.7, 129.7, 133.2, 133.3, 135.1, 136.1 (**C**$_6$H$_5$); MS-EI (*m*/*z*): 476.2 [(M+Na)$^+$, 100].

4.2.2. 2-Amino-2-deoxy-6-O-tert-butyldimethylsilyl-D-glucopyranose hydrochloride **4**

Yellow oil, 4.9 g, 72% yield; $[\alpha]_D^{25} = +34.0$ (*c* 0.5, $CHCl_3$); R_f (CH_2Cl_2/CH_3OH, 10: 3) 0.78; δ_H (600 MHz, $CDCl_3$) 0.00 (s, 6H, OSiC(C**H**$_3$)$_3$), 0.83 (s, 9H, OSi(C**H**$_3$)$_2$), 2.40 (dd, 0.33H, *J* 10.4, 5.5, **H**-2β), 2.75 (dd, 0.67H, *J* 10.4, 3.3, **H**-2α), 3.00–3.12 (m, 1H, **H**-3α and β), 3.53–3.60 (m, 5H, **H**-4α and β, **H**-5α and β, 3 × O**H**), 3.63 (dd, 0.33H, *J* 11.1, 5.3, **H**-6′β), 3.68 (dd, 0.67H, *J* 11.1, 4.9, **H**-6′α), 3.75 (d, 0.67H, *J* 11.1, **H**-6α), 3.82 (d, 0.33H, *J* 11.1, **H**-6β), 5.16 (d, 0.67H, *J* 3.3, **H**-1α), 5.21 (d, 0.33H, *J* 5.5, **H**-1β), 5.57 (d, 0.67H, *J* 5.2, N**H$_2$**α), 5.70 (d, 0.33H, *J* 5.2, N**H$_2$**β); δ_C (150 MHz, $CDCl_3$) −5.2 (OSi(**C**H$_3$)$_2$), 18.1 (OSi**C**(CH$_3$)$_3$), 25.9 (OSiC(**C**H$_3$)$_3$), 54.5, 57.3 (**C**-2 α and β), 62.6, 62.7 (**C**-6 α and β), 69.8, 69.9, 72.2, 72.7 (**C**-4 α and β, **C**-5 α i β), 76.8 (**C**-3 α and β), 89.0, 93.2 (**C**-1 α and β); MS-EI (*m*/*z*): 352.2 [(M+Na)$^+$, 100].

4.3. Typical procedure for the synthesis of trimethylsilyl derivatives **5**–**8**

To a suspension of gluco- or galactosamine hydrochloride **1**–**4** (11.59 mmol, 1eq.) in pyridine (50 mL), HMDS (24.2 mL, 115.9 mmol, 10 eq.) was added followed by TMSCl (14.7 mL, 115.9 mmol, 10 eq.). The resulting mixture was stirred at rt and the reaction monitored via TLC (petroleum ether/ethyl acetate, 5:1). During the reaction a lot of salt byproduct precipitated. After completion of the reaction (approx. 3 h), the mixture was evaporated *in vacuo* with a cooling trap between rotary evaporator and pump stand. The residue was twice co-evaporated with toluene to remove the residual pyridine. The raw material was then submitted to short column filtration over silica gel (petroleum ether/ethyl acetate) to remove the pyridinium salts.

4.3.1. 2-Amino-2-deoxy-1,3,4,6-tetra-O-trimethylsilyl-α-D-glucopyranose **5**

The analytically pure, colourless solid 2-amino-2- deoxy-1,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranose (**5**) was prepared according to literature[15] in 82%. The spectroscopic data are in accordance to ref.[15]

Mp. 50–52 °C; $[\alpha]_D^{25} = +90.5$ (*c* 0.4, $CHCl_3$); Lit.[15] $[\alpha]_D^{25} = +87.0$ (*c* 3.4, $CHCl_3$); R_f (petroleum ether/ethyl acetate, 5:1) 0.82.

4.3.2. 2-Amino-2-deoxy-1,3,4,6-tetra-O-trimethylsilyl-α-D-galactopyranose **6**

Synthesis and spectral data for 2-amino-2-deoxy-1,3,4,6-tetra-*O*-trimethylsilyl-α-D-galactopyranose **6** see: Szulc, I.; Kołodziuk, R.; Kryczka, B.; Zawisza, A. *Tetrahedron Lett.* **2015**, *56*, 4740–4743.

4.3.3. 2-Amino-2-deoxy-1,3,4-tri-O-trimethylsilyl-6-O-tert-butyldiphenylsilyl-α-D-glucopyranose **7**

Yellow oil, 4.0 g, 55% yield; $[\alpha]_D^{25} = +15.0$ (*c* 0.5, $CHCl_3$); R_f (petroleum ether/ethyl acetate, 5:1) 0.76; δ_H (600 MHz, $CDCl_3$) 0.08 (s, 9H, OSi(C**H**$_3$)$_2$), 0.11 (s, 9H, OSi(C**H**$_3$)$_2$), 0.20 (s, 9H, OSi(C**H**$_3$)$_2$), 1.06 (s, 9H, OSiC(C**H**$_3$)$_3$), 1.52 (s, 2H, N**H$_2$**), 2.55 (dd, 1H, *J* 9.0, 3.2, **H**-2), 3.53–3.57 (m, 2H, **H**-3, **H**-4), 3.63–3.70 (m, 1H, **H**-5), 3.78 (dd, 1H, *J* 11.4, 2.4, **H**-6), 3.85 (dd, 1H, *J* 11.4, 3.9, **H**-6′), 5.10 (d, 1H, *J* 3.2, **H**-1), 7.30–7.45 (m, 6H, C$_6$**H**$_5$), 7.64–7.79 (m, 4H, C$_6$**H**$_5$); δ_C (150 MHz, $CDCl_3$) 0.1 (OSi(**C**H$_3$)$_3$), 0.4 (OSi(**C**H$_3$)$_3$), 1.0 (OSi(**C**H$_3$)$_3$),19.5 (OSi**C**(CH$_3$)$_3$), 27.2 (OSiC(**C**H$_3$)$_3$), 59.8 (**C**-2), 60.6 (**C**-6), 72.7 (**C**-4), 63.5 (**C**-5), 78.3 (**C**-3), 98.8 (**C**-1), 127.6, 127.7, 127.8, 129.7, 129.8, 135.9, 136.0, 136.1, 136.4 (**C**$_6$H$_5$); MS-EI (*m*/*z*): 634.1 [(M+H)$^+$, 100].

4.3.4. 2-Amino-2-deoxy-1,3,4-tri-O-trimethylsilyl-6-O-tert-butyldimethylsilyl-α-D-glucopyranose **8**

Yellow oil, 3.5 g, 60% yield; $[\alpha]_D^{25} = +59.0$ (*c* 0.5, $CHCl_3$); R_f (petroleum ether/ethyl acetate, 5:1) 0.77; δ_H (600 MHz, $CDCl_3$) 0.15 (s, 9H, OSi(C**H**$_3$)$_2$), 0.16 (s, 3H, OSi(C**H**$_3$)$_2$), 0.17 (s, 3H, OSi(C**H**$_3$)$_2$), 0.18 (s, 9H, OSi(C**H**$_3$)$_2$), 0.20 (s, 9H, OSi(C**H**$_3$)$_2$), 0.88 (s, 9H, OSiC(C**H**$_3$)$_3$), 1.45 (s, 2H, N**H$_2$**), 2.51 (dd, 1H, *J* 9.6, 3.2, **H**-2), 3.52 (dd, 1H, *J* 9.4, 8.6, **H**-4), 3.55 (dd, 1H, *J* 9.6, 8.6, **H**-3), 3.57–3.61 (m, 1H, **H**-5), 3.79 (dd, 1H, *J* 11.5, 2.2, **H**-6), 3.79 (dd, 1H, *J* 11.5, 3.9, **H**-6′), 5.10 (d, 1H, *J* 3.2, **H**-1); δ_C (150 MHz, $CDCl_3$) −5.4 (OSi(**C**H$_3$)$_2$), −0.1 (OSi(**C**H$_3$)$_3$), 0.8 (OSi(**C**H$_3$)$_3$), 1.33 (OSi(**C**H$_3$)$_3$), 18.4 (OSi**C**(CH$_3$)$_3$), 25.8 (OSiC(**C**H$_3$)$_3$), 57.5 (**C**-2), 62.3 (**C**-6), 71.5 (**C**-5), 73.1 (**C**-4), 77.6 (**C**-3), 94.6 (**C**-1); found: C, 49.65; H, 10.21; N, 2.69. $C_{21}H_{51}NO_5Si$ requires C, 49.46; H, 10.08; N, 2.75%.

4.4. Typical procedure for the synthesis of phosphine-imine ligands **9**–**12**

In a Schlenk tube under nitrogen, α-D-pyranose **5**–**8** (2.1 mmol) and 2-(diphenylphosphino)benzaldehyde (621 mg, 2.1 mmol) were stirred in toluene (40 mL) at 60 °C for 12 h. After concentration, the residue was purified by flash column chromatography on silica gel.

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4.4.1. 1,3,4,6-Tetra-O-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]imino}-α-D-glucopyranose ***9 (L1)***

Synthesis and spectral data for *1,3,4,6-tetra-O-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]imino}-α-D-glucopyranose* **9** see: Olszewska, B.; Szulc, I.; Kryczka, B.; Kubiak, A.; Porwański, S.; Zawisza, A. *Tetrahedron: Asymmetry* **2013**, 24, 212–216.

4.4.2. 1,3,4,6-Tetra-O-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]imino}-α-D-galactopyranose ***10 (L2)***

Synthesis and spectral data for 1,3,4,6-tetra-*O*-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl]imino}-α-D-galactopyranose **10** see: Szulc, I.; Kołodziuk, R.; Kryczka, B.; Zawisza, A. *Tetrahedron Lett.* **2015**, *56*, 4740–4743.

4.4.3. 1,3,4,-Tri-O-trimethylsilyl-6-O-tert-butyldiphenylsilyl-2-deoxy-2-{[2-(diphenyl-phosphino)benzoyl]imino}-α-D-glucopyranose ***11 (L4)***

Yellow oil, 0.8 g, 43% yield; $[\alpha]_D^{25} = +8.0$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 24:1) 0.72; δ_H (600 MHz, $CDCl_3$) −0.07 (s, 9H, OSi(C**H**$_3$)$_3$), 0.00 (s, 9H, OSi(C**H**$_3$)$_3$), 0.01 (s, 9H, OSi(C**H**$_3$)$_3$), 1.06 (s, 9H, OSiC(C**H**$_3$)$_3$), 3.03 (dd, 1H, *J* 8.7, 7.3, **H**-2), 3.42 (d, 1H, *J* 8.5, **H**-4), 3.50 (ddd, 1H, *J* 8.5, 7.3, 1.7, **H**-5), 3.68 (dd, 1H, *J* 10.8, 7.3, **H**-6′), 3.89 (dd, 1H, *J* 10.8, 1.7, **H**-6), 3.93 (dd, 1H, *J* 8.7, 8.5, **H**-3), 4.76 (d, 1H, *J* 7.3, **H**-1), 7.26–7.38 (m, 24H, C_6**H**$_5$), 9.05 (d, 1H, *J* 5.8, NC**H**); δ_C (150 MHz, $CDCl_3$) 0.1 (OSi(**C**H$_3$)$_3$), 0.8 (OSi(**C**H$_3$)$_3$), 1.4 (OSi(**C**H$_3$)$_3$), 19.2 (OSi**C**(CH$_3$)$_3$), 26.9 (OSiC(**C**H$_3$)$_3$), 64.4 (**C**-2), 72.4 (**C**-6), 77.6, 77.9 (**C**-4, **C**-5), 79.4 (**C**-3), 95.8 (**C**-1), 128.5128.6, 128.7, 128.8, 128.9, 129.1, 129.5, 130.4, 133.8, 133.9, 134.0, 134.1, 135.8, 135.9, 136.7 (**C**$_6$H$_5$), 162.3 (d, *J* = 25.5, N**C**H); found: C, 66.34; H, 7.70; N, 1.47. $C_{50}H_{68}NO_5PSi_4$ requires C, 66.26; H, 7.56; N, 1.55%.

4.4.4. 1,3,4,-Tri-O-trimethylsilyl-6-O-tert-butyldimethylsilyl-2-deoxy-2-{[2-(diphenyl-phosphino)benzoyl]imino}-α-D-glucopyranose ***12 (L5)***

Yellow oil, 0.7 g, 45% yield; $[\alpha]_D^{25} = +15.6$ (*c* 0.5, $CHCl_3$); R_f (CH_2Cl_2/CH_3OH, 12: 1) 0.89; δ_H (600 MHz, $CDCl_3$) −0.04 (s, 9H, OSi(C**H**$_3$)$_3$), 0.00 (s, 9H, OSi(C**H**$_3$)$_3$), 0.19 (s, 9H, OSi(C**H**$_3$)$_3$), 0.09 (s, 3H, OSi(C**H**$_3$)$_2$), 0.10 (s, 3H, OSi(C**H**$_3$)$_2$), 0.92 (s, 9H, OSiC(C**H**$_3$)$_3$), 3.00 (dd, 1H, *J* 9.0, 7.3, **H**-2), 3.32 (ddd, 1H, *J* 9.2, 5.0, 1.9, **H**-5), 3.61 (t, 1H, *J* 9.2, **H**-4), 3.77 (dd, 1H, *J* 11.2, 5.0, **H**-6′), 3.86 (dd, 1H, *J* 11.2, 1.9, **H**-6), 3.94 (dd, 1H, *J* 9.2, 9.0, **H**-3), 4.70 (d, 1H, *J* 7.3, **H**-1), 6.97–6.99 (m, 1H, C_6**H**$_5$), 7.23–7.39 (m, 13H, C_6**H**$_5$), 9.05 (d, 1H, *J* 5.6, NC**H**); δ_C (150 MHz, $CDCl_3$) −5.3 (OSi(**C**H$_3$)$_2$), 0.1 (OSiC(**C**H$_3$)$_3$), 0.9 (OSiC(**C**H$_3$)$_3$), 1.4 (OSiC(**C**H$_3$)$_3$), 18.4 (OSi**C**(CH$_3$)$_3$), 26.0 (OSiC(**C**H$_3$)$_3$), 62.8 (**C**-6), 71.7 (**C**-4), 77.1 (**C**-5), 77.9 (**C**-3), 79.4 (**C**-2), 95.9 (**C**-1), 127.3, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 130.3, 133.7, 133.8, 133.9, 134.2, 136.8, 137.6 (**C**$_6$H$_5$), 162.3 (d, *J* = 26.4, N**C**H); found: C, 61.25; H, 7.94; N, 2.05. $C_{40}H_{64}NO_5PSi_4$ requires C, 61.41; H, 8.25; N, 1.79%.

4.5. Synthesis of 1,3,4,6-tetra-O-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino) benzoyl]imino}-α-D-allopyranose ***21 (L3)***

4.5.1. 2-Acetamido-2-deoxy-α-D-glucopyranose ***13***

The synthesis and spectroscopic data for 2-acetamido-2-deoxy-α-D-glucopyranose **13** are in accordance to ref.[25]

Colorless solid, 78% yield; m.p. 202.0–204.0 °C; Lit.[26] m.p. 203.0–205.0 °C; $[\alpha]_D^{25} = +66.0$ (*c* 0.5, H_2O); Lit.[27] $[\alpha]_D^{25} = +70.0$ (*c* 0.5, H_2O); R_f (CH_2Cl_2/CH_3OH, 10: 3) 0.57.

4.5.2. Methyl 2-acetamido-2-deoxy-α-D-glucopyranoside ***14***

The synthesis and spectroscopic data for methyl 2-acetamido-2-deoxy-α-D-glucopyranoside **14** are in accordance to ref.[28]

Yellow solid, 70% yield; m.p. 190.0–192.0 °C; Lit. m.p.[29] 184.0–185.0 °C; $[\alpha]_D^{25} = +128.0$ (*c* 0.5, H_2O); Lit.[30] $[\alpha]_D^{25} = +127.0$ (*c* 1.0, H_2O); R_f (CH_2Cl_2/CH_3OH, 10: 3) 0.75.

4.5.3. Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside ***15***

The synthesis and spectroscopic data for methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside **15** are in accordance to ref.[31]

Colorless solid, 50% yield; m.p. 200.0–202.0 °C; Lit.[32] m.p. 199.0–200.0 °C; $[\alpha]_D^{25} = +15.6$ (*c* 0.5, $CHCl_3$); Lit.[33] $[\alpha]_D^{25} = +32.0$ (*c* 1.0, CH_2Cl_2); R_f (CH_2Cl_2/CH_3OH, 8: 1) 0.82.

4.5.4. Methyl 2-acetamido-4,6-O-benzylidene-3-O-mesyl-2-deoxy-α-D-glucopyranoside ***16***

The synthesis and spectroscopic data for methyl 2-acetamido-4,6-*O*-benzylidene-3-*O*-mesyl-2-deoxy-α-D-glucopyranoside **16** are in accordance to ref.[31]

Colorless solid, 75% yield; m.p. 187.0–190.0 °C; Lit.[31] m.p. 196 °C, $[\alpha]_D^{25} = +42.6$ (*c* 0.5, $CHCl_3$); Lit.34 $[\alpha]_D^{25} = +42.0$ (*c* 1.0, $CHCl_3$); R_f (CH_2Cl_2/CH_3OH, 8: 1) 0.90.

4.5.5. Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside ***17***

The synthesis and spectroscopic data for methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside **17** are in accordance to ref.[31]

Colorless solid, 84% yield; m.p. 194.0–195.5 °C; Lit.[31b] m.p. 196 °C, $[\alpha]_D^{25} = +66.4$ (*c* 1.0, $CHCl_3$); Lit.[34] $[\alpha]_D^{25} = +64.0$ (*c* 0.5, $CHCl_3$); R_f (ethyl acetate/CH_3OH, 40: 1) 0.39.

4.5.6. Methyl 2-acetamido-2-deoxy-α-D-allopyranoside ***18***

The synthesis and spectroscopic data for methyl 2-acetamido-2-deoxy-α-D-allopyranoside **18** are in accordance to ref.[35]

Colorless oil, 93% yield; $[\alpha]_D^{25} = +76.6$ (*c* 0.5, H_2O); Lit.[35] $[\alpha]_D^{25} = +77.9$ (*c* 0.7, H_2O); R_f (ethyl acetate/CH_3OH, 8: 1) 0.19.

4.5.7. 2-Amino-2-deoxy allosamine hydrochloride ***19***

Procedure for the synthesis of 2-amino-2-deoxy allosamine hydrochloride **19** see ref.[34]

Yellow solid, 100% yield; m.p. 145.0–147.5 °C; Lit.36 m.p. 145–148 °C, $[\alpha]_D^{25} = +15.4$ (*c* 1.0, H_2O); Lit.[36] $[\alpha]_D^{25} = +16.0$ (*c* 1.4, H_2O); R_f (CH_2Cl_2/CH_3OH, 8: 3) 0.26; δ_H (600 MHz, $CDCl_3$) 2.89 (m, 1H, **H**-2), 3.30–3.80 (m, 4H, **H**-4, **H**-5, **H**-6, **H**-6′), 4.07 (s, 1H, **H**-3), 4.88 (d, 1H, *J* 8.3, **H**-1), 8.00 (s, 2H, N**H$_2$**); δ_C (150 MHz, $CDCl_3$) 54.3 (**C**-2), 61.0 (**C**-6), 66.8 (**C**-5), 67.9 (**C**-3), 74.4 (**C**-4), 90.9 (**C**-1).

4.5.8. 2-Amino-2-deoxy-1,3,4,6-tetra-O-trimethylsilyl-α-D-allopyranose ***20***

Procedure for the synthesis of 2-amino-2-deoxy-1,3,4,6-tetra-*O*-trimethylsilyl-α-D-allopyranose **20** see **4.3**.

Colorless oil, 2.3 g, 40% yield; $[\alpha]_D^{25} = +38.6$ (*c* 0.5, $CHCl_3$); R_f (petroleum ether/ethyl acetate, 5: 1) 0.62; δ_H (600 MHz, $CDCl_3$) 0.11 (s, 9H, OSi(C**H**$_3$)$_3$), 0.13 (s, 9H, OSi(C**H**$_3$)$_3$), 0.14 (s, 9H, OSi(C**H**$_3$)$_3$), 0.18 (s, 9H, OSi(C**H**$_3$)$_3$), 1.48 (s, 2H, N**H$_2$**), 2.38 (dd, 1H, *J* 7.6, 2.3, **H**-2), 3.52 (dd, 1H, *J* 9.1, 2.2, **H**-4), 3.58 (dd, 1H, *J* 10.9, 5.8, **H**-6′), 3.70–3.75 (m, 2H,**H**-5, **H**-6), 4.01 (s, 1H, **H**-3), 4.64 (d, 1H, *J* 7.6, **H**-1); δ_C (150 MHz, $CDCl_3$) −0.2 (OSi(C**H**$_3$)$_3$), 0.5 (OSi(C**H**$_3$)$_3$), 0.6 (OSi(C**H**$_3$)$_3$), 0.9 (OSi(C**H**$_3$)$_3$), 57.7 (**C**-2), 62.7 (**C**-6), 70.4 (**C**-4), 74.4 (**C**-5), 75.3 (**C**-3), 97.7 (**C**-1); found: C, 46.20; H, 9.50; N, 3.19. $C_{18}H_{45}NO_5PSi_4$ requires C, 46.21; H, 9.69; N, 2.99%.

4.5.9. 1,3,4,6-Tetra-O-trimethylsilyl-2-deoxy-2-{[2-(diphenylphosphino)benzoyl] imino}-α-D-allopyranose ***21 (L3)***

Procedure for the synthesis of 1,3,4,6-tetra-*O*-trimethylsilyl-2-

Please cite this article in press as: Szulc I, et al., New phosphine-imine and phosphine-amine ligands derived from D-gluco-, D-galacto- and D-allosamine in Pd-catalysed asymmetric allylic alkylation, Tetrahedron (2018), https://doi.org/10.1016/j.tet.2018.02.009

deoxy-2-{[2-(diphenylphosphino)benzoyl] imino}-α-D-allopyranose **21** (**L3**) see **4.4**.

Yellow oil, 0.9 g, 57% yield; $[\alpha]_D^{25} = +16.8$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 5: 1) 0.82; δ_H (600 MHz, $CDCl_3$) 0.03 (s, 9H, OSi(C**H**$_3$)$_3$), 0.08 (s, 9H, OSi(C**H**$_3$)$_3$), 0.12 (s, 9H, OSi(C**H**$_3$)$_3$), 0.14 (s, 9H, OSi(C**H**$_3$)$_3$), 2.97 (dd, 1H, *J* 7.4, 2.0, **H**-2), 3.57 (dd, 1H, *J* 9.4, 2.4, **H**-4), 3.66 (dd, 1H, *J* 11.2, 5.9, **H**-6′), 3.74–3.82 (m, 2H, **H**-5, **H**-6), 3.99 (dd, 1H, *J* 2.4, 2.0, **H**-3), 5.23 (d, 1H, *J* 7.4, **H**-1), 7.15–7.70 (m, 13H, C_6H_5), 8.15–8.19 (m, 1H, C_6H_5), 9.04 (d, 1H, *J* = 5.6, NC*H*); δ_C (150 MHz, $CDCl_3$) −0.2, 0.3, 0.4, 0.8 (4OSi(*C*H$_3$)$_3$), 57.5 (C-2), 62.9 (C-6), 69.3 (C-4), 74.5 (C-5), 76.5 (C-3), 93.8 (C-1), 127.0 (d, *J* 4.4, C_6H_5), 128.6, 128.7, 128.8, 129.0, 129.1, 130.4, 130.6, 132.1, 133.7, 133.9, 134.0 (C_6H_5), 134.1 (d, *J* 5.5, C_6H_5), 137.0 (d, *J* 9.8, C_6H_5), 137.9 (d, *J* 18.7, C_6H_5), 160.8 (d, *J* = 26.7, NCH); found: C, 60.14; H, 7.94; N, 1.78. $C_{37}H_{58}NO_5PSi_4$ requires C, 60.04; H, 7.90; N, 1.89%.

4.6. Synthesis of ligands ***L6-L9***

4.6.1. 1,3,4,6-Tetra-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α,β-D-glucopyranoside ***22***

The synthesis and spectroscopic data for 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranoside **22** are in accordance to ref.[37]

Colorless oil, 74% yield; R_f (petroleum ether/ethyl acetate, 1: 1) 0.73.

4.6.2. 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α,β-D-glucopyranose ***23***

The synthesis and spectroscopic data for 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α,β-D-glucopyranose **23** are in accordance to ref.[37]

Yellow solid, 84% yield; m.p. 172.0–175.0 °C; R_f (petroleum ether/ethyl acetate, 1: 1) 0.60.

4.6.3. 1-O-tert-Butyldiphenylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside ***24***

The synthesis and spectroscopic data for 1-*O*-*tert*-butyldiphenylsilyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside **24** are in accordance to ref.[37]

Colorless solid, 75% yield; m.p. 147.0–149.0 °C; $[\alpha]_D^{25} = +9.6$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 3: 1) 0.44.

4.6.4. 1-O-tert-Butyldimethylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside ***25***

To a magnetically stirred solution of **23** (2.5 g, 5.0 mmol) in anhydrous CH_3CN (30 mL) at room temperature, solid imidazole (0.78 g, 11.5 mmol) was added in one portion, followed by *tert*-butyldimethylchlorosilane (TBDPSCl) (1.7 mL, 11.5 mmol), added dropwise. After 24 h the solvent was removed under reduced pressure. The crude residue was dissolved in $CHCl_3$ and the solution was washed with brine until neutral, dried (Na_2SO_4), and the solvents evaporated under vacuum. The final product was isolated by flash column chromatography on silica gel.

Colorless solid, 2.6 g, 84% yield; m.p. 160.0–162.0 °C; $[\alpha]_D^{25} = +4.4$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 3: 1) 0.42; δ_H (600 MHz, $CDCl_3$) 0.10, 0.12 (s, 6H, 2 × Si-C**H**$_3$), 0.89 (s, 9H, C(C**H**$_3$)$_3$), 2.01, 2.03, 2.06 (s, 9H, 3 × C**H**$_3$), 3.57–3.63 (m, 1H, **H**-2), 3.68–3.74 (m, 1H, **H**-5), 4.14 (dd, 1H, *J* 11.7, 2.2, **H**-6$_a$), 4.21 (dd, 1H, *J* 11.7, 5.8, **H**-6$_b$), 4.62 (d, 1H, *J* 11.8, **H**$_a$-Troc), 4.75 (d, 1H, *J* 11.8, **H**$_b$-Troc), 4.83 (d, 1H, *J* 7.8, **H**-1), 5.05 (dd, 1H, *J* 9.6, 9.6, **H**-3), 5.15 (d, 1H, *J* 8.3, N**H**), 5.27 (dd, 1H, *J* 9.6, 9.6, **H**-4); δ_C (150 MHz, $CDCl_3$) −5.2, −4.4 (Si-**C**H$_3$), 17.8 ((CH$_3$)$_3$**C**), 20.7, 20.7, 20.8 (**C**H$_3$CO), 25.7 ((**C**H$_3$)$_3$C), 58.4 (**C**-2), 62.6 (**C**-6), 69.2 (**C**-4), 71.8 (**C**-3), 72.3 (CCl$_3$**C**H$_2$OCO), 74.5 (**C**-5), 95.2 (**C**Cl$_3$CH$_2$OCO), 96.3 (**C**-1), 154.2 (CCl$_3$CH$_2$O**C**O), 169.6, 170.7, 170.8 (CH$_3$**C**O); MS-EI (*m*/*z*): 616.3 [(M+Na)$^+$, 100]; found: C, 42.49; H, 5.64; N, 2.23. $C_{21}H_{34}Cl_3NO_{10}Si$ requires C, 42.39; H, 5.76; N, 2.35%.

4.6.5. 1-O-tert-Butyldiphenylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-amino-β-D-glucopyranoside ***26***

The synthesis and spectroscopic data for 1-*O*-*tert*-butyldiphenylsilyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-amino-β-D-glucopyranoside **26** are in accordance to ref.[37]

Colorless oil, 80% yield; $[\alpha]_D^{25} = +4.7$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 1: 2) 0.65.

4.6.6. 1-O-tert-Butyldimethylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-amino-β-D-glucopyranoside ***27***

To a solution of compound **25** (2,0 g, 3.4 mmol) in glacial acetic acid (100 mL), activated Zn dust (4.6 g, 70.0 mmol) [washed with aq 2 M HCl, water, acetone, diethyl ether, and then dried under vacuum] was added in one portion and the mixture was vigorously stirred for 24 h (TLC monitoring) at room temperature. The solid was then filtered off and most of acetic acid was evaporated under reduced pressure. The residue was diluted with AcOEt and the resulting solution was shaken with saturated aq $NaHCO_3$, washed with brine until neutral, dried (Na_2SO_4). The solvents were evaporated under reduced pressure and the crude residue was purified by flash column chromatography on silica gel.

Colorless solid, 1.3 g, 83% yield; m.p. 61.0–63.0 °C; $[\alpha]_D^{25} = +21.8$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 1: 2) 0.50; δ_H (600 MHz, $CDCl_3$) 0.14, 0.15 (s, 6H, 2 × Si-C**H**$_3$), 0.95 (s, 9H, C(C**H**$_3$)$_3$), 1.54 (s, 2H, N**H**$_2$), 2.03, 2.08, 2.08 (s, 9H, 3 × C**H**$_3$), 2.81–2.88 (m, 1H, **H**-2), 3.66–3.72 (m, 1H, **H**-5), 4.13 (dd, 1H, *J* 12.0, 2.5, **H**-6$_a$), 4.21 (dd, 1H, *J* 12.0, 6.1, **H**-6$_b$), 4.52 (d, 1H, *J* 7.5, **H**-1), 4.91–4.98 (m, 2H, **H**-3, **H**-4); δ_C (150 MHz, $CDCl_3$) −5.2, −4.3 (Si-**C**H$_3$), 18.2 ((CH$_3$)$_3$**C**), 20.7, 20.8, 20.9 (**C**H$_3$CO), 25.6 ((**C**H$_3$)$_3$C), 57.7 (**C**-2), 62.8 (**C**-6), 69.3 (**C**-4), 72.2 (**C**-3), 75.3 (**C**-5), 99.2 (**C**-1), 169.9, 170.7, 170.7 (CH$_3$**C**O); MS-EI (*m*/*z*): 420.2 [(M+H)$^+$, 100]; found: C, 51.48; H, 7.96; N, 3.42. $C_{18}H_{33}NO_8Si$ requires C, 51.53; H, 7.93; N, 3.34%.

4.6.7. 1-O-tert-Butyldiphenylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-amino-{[2-(diphenylphosphino)benzoyl] imino}- β -D-glucopyranose ***28 (L6)***

Procedure for the synthesis of 1-*O*-*tert*-butyldiphenylsilyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-amino-{[2-(diphenylphosphino)benzoyl] imino}- β -D-glucopyranose **28** (**L6**) see **4.4**.

Yellow solid, 1.1 g, 75% yield; m.p. 58.0–67.0 °C; $[\alpha]_D^{25} = +17.1$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 2: 1) 0.54; δ_H (600 MHz, $CDCl_3$) 0.98 (s, 9H, C(C**H**$_3$)$_3$), 1.65, 1.97, 2.01 (s, 9H, 3 × C**H**$_3$), 3.41 (dd, 1H, *J* 9.8, 7.5, **H**-2), 3.48 (ddd, 1H, *J* 9.8, 5.4, 2.3, **H**-5), 3.99 (dd, 1H, *J* 12.0, 2.3, **H**-6$_a$), 4.13 (dd, 1H, *J* 12.0, 5.6, **H**-6$_b$), 4.88 (d, 1H, *J* 7.5, **H**-1), 5.03 (dd, 1H, *J* 9.8, 9.8, **H**-4), 5.21 (dd, 1H, *J* 9.8, 9.8, **H**-3), 6.91–6.95 (m, 1H, C$_6$**H**$_5$), 7.19–7.22 (m, 6H, C$_6$**H**$_5$), 7.24–7.40 (m, 12H, C$_6$**H**$_5$), 7.55–7.60 (m, 2H, C$_6$**H**$_5$), 7.67 7.69 (m, 2H, C$_6$**H**$_5$), 8.03–8.07 (m, 1H, C$_6$**H**$_5$), 9.10 (d, 1H, *J* 5.6, N=C**H**); δ_C (150 MHz, $CDCl_3$) 19.3 ((CH$_3$)$_3$**C**), 20.4, 20.8, 20.8 (**C**H$_3$CO), 26.9 ((**C**H$_3$)$_3$C), 62.3 (**C**-6), 69.2 (**C**-4), 71.6 (**C**-5), 73.4 (**C**-3), 76.3 (**C**-2), 96.9 (**C**-1), 127.2–139.4 (**C**$_6$H$_5$), 162.9 (d, *J* 30.6 N=**C**H), 169.9, 169.9, 170.7 (CH$_3$**C**O); MS-EI (*m*/*z*): 816.4 [(M+H)$^+$, 100]; found: C, 69.03; H, 6.18; N, 1.52. $C_{47}H_{50}NO_8PSi$ requires C, 69.03; H, 6.18; N, 1.72%.

4.6.8. 1-O-tert-Butyldimethylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-amino-{[2-(diphenylphosphino)benzoyl] imino}- β -D-glucopyranose ***29 (L7)***

Procedure for the synthesis of 1-*O*-*tert*-butyldimethylsilyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-amino-{[2-(diphenylphosphino)benzoyl] imino}- β -D-glucopyranose **29** (**L7**) see **4.4**.

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Yellow solid, 1.4 g, 85% yield; m.p. 49.0–57.0 °C; $[\alpha]_D^{25} = -7.5$ (*c* 0.5, $CHCl_3$); R_f (hexane/ethyl acetate, 2: 1) 0.54; δ_H (600 MHz, $CDCl_3$) −0.08, −0.02, (s, 6H, 2 × Si-C**H**$_3$), 0.74 (s, 9H, C(C**H**$_3$)$_3$), 1.63, 1.96, 2.03 (s, 9H, 3 × C**H**$_3$), 3.18 (dd, 1H, *J* 9.7, 7.6, **H**-2), 3.71 (ddd, 1H, *J* 9.8, 5.2, 2.2, **H**-5), 4.03 (dd, 1H, *J* 11.9, 2.2, **H**-6$_a$), 4.20 (dd, 1H, *J* 11.9, 5.2, **H**-6$_b$), 4.81 (d, 1H, *J* 7.5, **H**-1), 4.92 (dd, 1H, *J* 9.8, 9.8, **H**-4), 5.28 (dd, 1H, *J* 9.8, 9.8, **H**-3), 6.77–6.85 (m, 1H, C_6**H**$_5$), 7.13–7.35 (m, 12H, C_6**H**$_5$), 7.92–7.99 (m, 1H, C_6**H**$_5$), 8.99 (d, 1H, *J* 5.5, N=C**H**); δ_C (150 MHz, $CDCl_3$) −5.3, −4.4 (Si-**C**H$_3$), 18.0 ((CH$_3$)$_3$**C**), 20.4, 20.7, 20.8 (**C**H$_3$CO), 25.5 ((**C**H$_3$)$_3$C), 62.7 (**C**-6), 69.1 (**C**-4), 71.8 (**C**-5), 73.2 (**C**-3), 76.2 (**C**-2), 96.6 (**C**-1), 127.7–139.4 (C_6H$_5$), 162.9 (d, *J* 25.4, N=**C**H), 169.9, 170.0, 170.7 (CH$_3$**C**O); MS-EI (*m*/*z*): 692.3 [(M+H)$^+$, 100]; found: C, 64.25; H, 6.91; N, 1.91. $C_{37}H_{46}NO_8PSi$ requires C, 64.24; H, 6.70; N, 2.02%.

4.7. Typical procedure for the synthesis of phosphine-amine ligands *30*–*31*

The phosphine-imine derivative **28** or **29** (0.26 mmol) was dissolved in a mixture of methanol (7.5 mL) and acetic acid (0.75 mL). $NaBH_3CN$ (0.123 g, 1.95 mmol) was added to the previous solution, and the mixture was stirred at room temperature for 15 min before adding water (30 mL) in order to stop the reaction. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic phase was washed with a saturated solution of $NaHCO_3$ and then of brine, dried with Na_2SO_4, and concentrated. The phosphine-amine compounds **30** and **31** were obtained in quantitative yield without further purification.

4.7.1. 1-O-tert-butyldiphenylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-{[2-(diphenylphosphino) benzyl]amino}-β-D- glucopyranose *30 (L8)*

Colorless, 0.2 g, quantitative yield; m.p. 56.0–67.0 °C; $[\alpha]_D^{25} = +8.6$ (*c* 0.5, $CHCl_3$); R_f (petroleum ether/ethyl acetate, 5: 1) 0.33; δ_H (600 MHz, $CDCl_3$) 1.00 (s, 9H, C(C**H**$_3$)$_3$), 1.50 (s, 1H, N**H**), 1.80 (s, 3H, C**H**$_3$CO), 1.86 (s, 6H, 2xC**H**$_3$CO), 2.83 (dd, 1H, *J* 9.7, 7.7, **H**-2), 3.17 (ddd, 1H, *J* 8.8, 5.2, 2.4, **H**-5), 3.72 (dd, 1H, *J* 12.0, 2.4, **H**-6a), 3.87 (dd, 1H, *J* 12.0, 5.2, **H**-6b), 4.02–4.04 (m, 2H, C**H**$_2$NH), 4.43 (d, 1H, *J* = .7, **H**-1), 4.82, (dd, 1H, *J* 9.2, 9.7, **H**-3), 4.85 (dd, 1H, *J* 9.2, 8.8, **H**-4), 6,76 (ddd, 1H, *J* 7.6, 4.3, 0.8, C_6**H**$_5$), 7.06 (dt, 1H, *J* 7.6, 1.0, C_6**H**$_5$), 7.10–7.15 (m, 4H, C_6**H**$_5$), 7.19–7.26 (m, 11H, C_6**H**$_5$), 7.29–7.36 (m, 3H, C_6**H**$_5$), 7.60–7.64 (m, 4H, C_6**H**$_5$); δ_C (150 MHz, $CDCl_3$) 19.3 ((CH$_3$)$_3$**C**), 20.8, 21.1, 21.2 (3x**C**H$_3$CO), 27.2 ((**C**H$_3$)$_3$C), 51.3 (d, *J* 23.2, **C**H$_2$), 62.4 (**C**-6), 63.9 (**C**-2), 69.6 (**C**-4), 71.4 (**C**-5), 75.0 (**C**-3), 98.9 (**C**-1), 127.7 (C_6H$_5$), 128.6 (d, *J* 6.7, C_6H$_5$), 128,8 (C_6H$_5$), 128,9 (d, *J* 5.7, C_6H$_5$), 129.2 (C_6H$_5$), 129.9 (d, *J* 18.5, C_6H$_5$), 133.2 (C_6H$_5$), 135.5 (d, *J* 5.9, C_6H$_5$), 133.9 (d, *J* 10.7, C_6H$_5$), 134.0 (d, *J* 10.2, C_6H$_5$), 136.0, 136.2 (C_6H$_5$), 136.8 (d, *J* 10.4, C_6H$_5$), 136.9 (d, *J* 10.5, C_6H$_5$), 145.0 (d, *J* 23.9, C_6H$_5$), 169.9, 170.7, 171.0 (3xCH$_3$**C**O); MS-EI (*m*/*z*): 818.4 [(M+H)$^+$, 100]; found: C, 68.82; H, 6.25; N, 1.78. $C_{47}H_{52}NO_8PSi$ requires C, 69.01; H, 6.41; N, 1.71%.

4.7.2. 1-O-tert-butyldimethylsilyl-3,4,6-tri-O-acetyl-2-deoxy-2-{[2-(diphenylphosphino) benzyl]amino}-β-D- glucopyranose *31 (L9)*

Colorless, 0.18 g, quantitative yield; m.p. 47.0–58.0 °C; $[\alpha]_D^{25} = +11.1$ (*c* 0.5, $CHCl_3$); R_f (petroleum ether/ethyl acetate, 5: 1) 0.33; δ_H (600 MHz, $CDCl_3$) 0.13 (s, 3H, Si(C**H**$_3$)$_2$), 0.14 (s, 3H, Si(C**H**$_3$)$_2$), 0.90 (s, 9H, C(C**H**$_3$)$_3$), 1.70 (s, 1H, N**H**), 1.92, 2.00, 2.05 (3s, 9H, 3xC**H**$_3$CO), 2.76 (dd, 1H, *J* 10.1, 7.7, **H**-2), 3.64 (ddd, 1H, *J* 9.7, 6,1, 2.5, **H**-5), 4.03 (dd, 1H, *J* 13.7, 2.5, **H**-6$_a$), 4.06–4.12 (m, 2H, C**H**$_2$NH), 4.15 (dd, 1H, *J* 12.0, 6.2, **H**-6$_b$), 4.60 (d, 1H, *J* 7.7, **H**-1), 4.93 (dd, 1H, *J* 9.9, 9.7, **H**-4), 5.02 (dd, 1H, *J* 10.1, 9.9, **H**-3), 6.83 (ddd, 1H, *J* 7.6, 4.4, 0.7, C_6**H**$_5$), 7.13 (t, 1H, *J* 7.4, C_6**H**$_5$), 7.19–7.24 (m, 4H, C_6**H**$_5$), 7.28–7.35 (m, 7H, C_6**H**$_5$), 7.48 (dd, 1H, *J* 7.3, 4.6, C_6**H**$_5$); δ_C (150 MHz, $CDCl_3$) −4.7 (SiC**H**$_3$), −4.1 (SiC**H**$_3$), 18.2 ((CH$_3$)$_3$**C**), 20.8, 20.8, 21.1 (3x**C**H$_3$CO), 26.0 ((**C**H$_3$)$_3$C), 51.1 (d, *J* 22,2, **C**H$_2$), 62.9 (**C**-6), 63.8 (**C**-2), 69.8 (**C**-4), 71.8 (**C**-5), 74.7 (**C**-3), 99.4 (**C**-1), 127.4 (C_{ar}), 128.7 (d, *J* 6.4, C_6H$_5$), 128,8 (d, *J* 5.9, C_6H$_5$), 128,9 (d, *J* 5.5, C_6H$_5$), 129.2 (C_6H$_5$), 133.9 (d, *J* 2.9, C_6H$_5$), 134.0 (d, *J* 2.2, C_6H$_5$), 135.3 (d, *J* 14.1, C_6H$_5$), 136.8 (d, *J* 9.8, C_6H$_5$), 136.9 (d, *J* 9.8, C_6H$_5$), 145.0 (d, *J* 18.7, C_6H$_5$), 169.9, 170.7, 171.0 (3xCH$_3$**C**O); MS-EI (*m*/*z*): 694.3 [(M+H)$^+$, 100]; found: C, 63.81; H, 6.95; N, 1.99. $C_{37}H_{48}NO_8PSi$ requires C, 64.05; H, 6.97; N, 2.02%.

4.8. Typical procedure for the Pd^0-catalysed reaction

The catalytic system was prepared by stirring $[Pd(C_3H_5)Cl]_2$ (3.6 mg, 9.9 μmmol) and the ligand (19.8 μmmol) in an appropriate anhydrous solvent (3 mL) for 0.5 h in a Schlenk tube under argon. This solution was added, under argon, to a Schlenk tube containing the 1,3-diphenyl-2-propenyl acetate **32** (50 mg, 0.198 mmol), KOAc (0.97 mg, 9.9 μmmol), and BSA (0.1 mL, 0.4 mmol) and NuH (0.4 mmol) in an appropriate anhydrous solvent (3 mL). The solution was stirred at 25 °C (0 °C or − 20 °C). After an appropriate period of time, removal of the solvent followed by column chromatography gave the corresponding product.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.02.009.

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