Asymmetric Allylic Amination Catalyzed by Pd-BINAP Complexes

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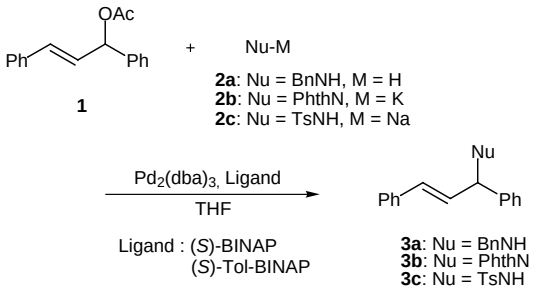
Received 4 December 2000

Abstract: The asymmetric allylic amination of *rac*-1,3-diphenyl-2-propenyl acetate (**1**) with potassium phthalimide (**2b**) has been carried out in the presence of 2.5 mol% $Pd_2(dba)_3$•$CHCl_3$ and 5.0 mol% (*S*)-Tol-BINAP to give the allylic product (**3b**) in 75% yield with 99% ee.

Key words: asymmetric catalysis, aminations, palladium, phosphorus, allyl complexes

The palladium-catalyzed asymmetric allylic amination is a useful synthetic transformation as the resulting amines can be converted into various kinds of chiral compounds including α-amino acid derivatives.[1] Recently, Hayashi and Ito's ferrocenyl phosphine ligands,[1b] Togni's phosphine-pyrazole ligands,[1d] and Helmchen and Pfaltz's phosphino-oxazoline ligand,[1g] have also been reported to be applicable to the palladium-catalyzed allylic amination. As far as we know, there have been a few reports on the allylic alkylation,[2] but there have been no reports on the palladium-catalyzed allylic amination using the chiral ligands with 1,1'-binaphthyl skeleton. A popular chiral bidentate diphosphine ligand, BINAP, has been utilized in the Rh(I)- or Ru(I)-catalyzed asymmetric hydrogenation,[3] double bond isomerization,[4] and Heck addition.[5] Despite the great success that the BINAP ligand has enjoyed over the years, less satisfactory or even poor results have been reported for their application in the palladium(0)-catalyzed allylic substitution.[6] In 1999, Tanaka et al. found that zinc malonates free from other metals can give high ees in allylic alkylations catalyzed by a palladium(0)-BINAP complex.[7] Therefore, we have examined the allylic amination catalyzed by the Pd(0)-BINAP complex.[8]



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The palladium-catalyzed allylic amination was carried out in tetrahydrofuran using a catalyst prepared in situ by mixing 2.5 mol% $Pd_2(dba)_3$•$CHCl_3$ and 5.0 mol% (*S*)-BINAP or (*S*)-Tol-BINAP (Scheme, Table 1). As nitrogen nucleophiles, 2.4 equiv benzylamine, potassium phthalimide, and sodium *p*-toluenesulfonamide were used.

The palladium-catalyzed allylic amination of *rac*-1,3-diphenyl-2-propenyl acetate (**1**) with benzylamine (**2a**) and potassium phthalimide (**2b**) using the (*S*)-BINAP ligand gave the corresponding aminated products *(S)*-**3a** and (*S*)-**3b** in 79% and 41% yield with 39% ee and 90% ee, respectively (Entries 1 and 2, Table 1). Using (*S*)-Tol-BINAP as the ligand for this reaction leads to an increase in the enantioselectivities (Entries 4-6, Table 1). However, by using sodium *p*-toluenesulfonamide (**2c**) as the nucleophile, this reaction did not occur (Entries 3 and 7, Table 1). Moreover, in spite of using 5.0 mol% $Pd_2(dba)_3$•$CHCl_3$ and 10 mol% (*S*)-Tol-BINAP, this reaction did not occur (Entry 8, Table 1).

Next, the effect of an additive was examined for the reaction using the (*S*)-Tol-BINAP ligand (Table 2). The allylic

Table 1 Palladium-BINAP Catalyzed Asymmetric Allylic Amination

Entry	Nucleophile	Product	Ligand	Time (h)	Yield (%)[a]	E.e. (%)[b]
1	**2a**	**3a**	(*S*)-BINAP	48	79	39 (*S*)
2	**2b**	**3b**	(*S*)-BINAP	48	41	90 (*S*)
3	**2c**	**3c**	(*S*)-BINAP	48	N.r.	N.d.
4	**2a**	**3a**	(*S*)-Tol-BINAP	48	85	42 (*S*)
5	**2b**	**3b**	(*S*)-Tol-BINAP	48	40	98 (*S*)
6	**2b**	**3b**	(*S*)-Tol-BINAP	72	75	>99 (*S*)
7	**2c**	**3c**	(*S*)-Tol-BINAP	48	N.r.	N.d.
8[c]	**2c**	**3c**	(*S*)-Tol-BINAP	48	Trace	N.d.

[a]Isolated yield. [b]Determined by HPLC analysis using a DAICEL CHIRALCEL OD-H column. [c]The 5.0 mol% $Pd_2(dba)_3$·$CHCl_3$ catalyst and the 10 mol% *(S)*-Tol-BINAP ligand were used.

Table 2 Effect of Additive on Palladium-catalyzed Asymmetric Allylic Amination

Entry	Nucleophile	Product	Additive	Time (h)	Yield (%)[a]	E.e. (%)[b]
1	**2a**	**3a**	BSA[c]	48	96	78 (*S*)
2	**2b**	**3b**	BSA	48	66	85 (*S*)
3	**2c**	**3c**	BSA	60	40	91 (-)

[a]Isolated yield. [b]Determined by HPLC analysis using a DAICEL CHIRALCEL OD-H column. [c]BSA = *N,O*-bis(trimethylsilyl)acetamide

amination catalyzed by Pd(0)-Tol-BINAP using 1.5 equiv BSA (*N,O*-bis(trimethylsilyl)acetamide) as an additive proceeded more smoothly to give the aminated products ((*S*)-**3a** and (-)-**3c**) than no additive (Entries 1 and 3, Table 2).

In conclusion, the asymmetric allylic amination of *rac*-1,3-diphenyl-2-propenyl acetate (**1**) with potassium phthalimide (**2a**) smoothly proceeded in the presence of 2.5 mol% $Pd_2(dba)_3 \cdot CHCl_3$ and 5.0 mol% (*S*)-Tol-BINAP to give the allylic product (**3a**) in 75% yield with 99% ee. Furthermore, the asymmetric allylic amination of *rac*-1,3-diphenyl-2-propenyl acetate (**1**) with sodium *p*-toluenesulfonamide (**2c**) using BSA proceeded to give **3c** in 40% yield with 91% ee.

Acknowledgement

We thank Dr. Takayuki Yamashita for helpful discussions during the course of this work. This work was partially supported by Doshisha University's Research Promotion Fund and a grant to RCAST at Doshisha University from the Ministry of Education, Japan.

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(8) *A typical procedure for the palladium-catalyzed asymmetric allylic alkylation of rac-1,3-diphenyl-2-propenyl acetate (**1**) with benzylamine (**2a**).*
A solution of *(S)*-Tol-BINAP (0.017 g, 0.025 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (0.013 g, 0.013 mmol) in tetrahydrofuran (2 mL) was stirred at room temperature for 30 min. This solution was successively treated with a solution of *rac*-1,3-diphenyl-2-propenyl acetate (**1**) (0.13 g, 0.50 mmol) in tetrahydrofuran (1 mL) and benzylamine (**2a**) (0.13 g, 1.2 mmol). The reaction mixture was then stirred for 48 h at 50 °C. The reaction mixture was quenched with saturated aqueous ammonium chloride, and then extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness, and the residue was chromatographed on silica gel (ethyl acetate:hexane = 1:4) to give *N*-((*E*)-1,3-diphenyl-2-propenyl)benzylamine ((*S*)-**3a**). $[\alpha]_D^{25}$ = +10.9 (c = 1.7, $CHCl_3$) (Entry 4, Table 1) (lit. $[\alpha]_D^{25}$ = +25 (c = 1.76, $CHCl_3$)[9]). The enantiomeric excess was determined by an HPLC analysis using a DAICEL CHIRALCEL OD-H column (eluent, 1:99 2-propanol–hexane; 0.5 mL/min flow rate; detection, uv 254 nm; retention times, 15.4 min (*R*): 16.2 min (*S*)).
In a similar method, *N*-((*E*)-1,3-diphenyl-2-propenyl)phthalimide ((*S*)-**3b**) was prepared from *rac*-1,3-diphenyl-2-propenyl acetate (**1**) and potassium phthalimide (**2b**) as a nitrogen nucleophile. The work-up, and determination of the enantiomeric excesses and the absolute configurations were performed using the same method described above. $[\alpha]_D^{25}$ = +17.31 (c = 1.7, $CHCl_3$) (Entry 6, Table 1) (lit. $[\alpha]_D^{26}$ = -17 (c = 1.7, $CHCl_3$)[9]). The enantiomeric excess was determined by a DAICEL CHIRALCEL OD-H column (eluent, 1:99 2-propanol–hexane; 0.5 mL/min flow rate; detection, uv 254 nm; retention times, 22.3 min (*S*): 30.8 min (*R*)). Moreover, *N*-((*E*)-1,3-diphenyl-2-propenyl)-*p*-toluenesulfonamide ((-)-**3c**) was prepared from *rac*-1,3-diphenyl-2-propenyl acetate (**1**) and sodium *p*-toluenesulfonamide (**2c**) as a nitrogen nucleophile.
The work-up, and determination of the enantiomeric excesses and the absolute configurations were performed using the same method described above. The enantiomeric excess was determined by a DAICEL CHIRALCEL OD-H column

(eluent, 20:80 2-propanol–hexane; 0.5 mL/min flow rate; detection, uv 254 nm; retention times, 14.9 min (-): 20.0 min (+)).

(9) Moreover, Saigo et al. reported that the amination products were obtained with excellent enantioselectivitiy when acetic acid was added to the reaction system.[10] Therefore, the effect of the addition of acetic acid was examined, but the amination products (**3a-3c**) were not obtained in high yields with excellent enantioselectivities.

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Article Identifier:
1437-2096,E;2001,0,03,0385,0387,ftx,en;Y20100ST.pdf