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A catalytic enantioselective allylation reaction of aldehydes in an aqueous medium

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Abstract

A modified Yamamoto–Yanagisawa's catalyst (*S*)-Tol-BINAP·$AgNO_3$ was successfully applied to a catalytic enantioselective allylation reaction of aldehydes in an aqueous system. The reactions with aromatic aldehydes afforded the desired products in high yields with good stereoselectivities. © 2000 Published by Elsevier Science Ltd.

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Catalytic enantioselective allylation reactions of aldehydes are valuable C–C bond-formation methods for preparing enantiomerically enriched secondary alcohols. To date several catalysts have been devised to serve this purpose.[1,2] Another research focus among today's synthetic community is performing organic transformations in aqueous media,[3] which entails extraordinary chemical stability and reactivity. Furthermore, extension of catalytic enantioselective transformations to the aqueous media poses additional challenges in catalyst tolerance towards water. Several such examples using catalytic amounts of chemzymes have been reported,[4] but not with the allylation reactions between allylmetal reagents and carbonyl functionalities. Herein, we report our recent progress in this area employing a modified Yamamoto–Yanagisawa's catalyst (*S*)-Tol-BINAP·$AgNO_3$ (Scheme 1).

First, we started with the reaction of benzaldehyde with allyltributyltin in the presence of (*S*)-BINAP·AgOTf, developed by Yamamoto and Yanagisawa in dry THF.[2] The (*S*)-BINAP·AgOTf complex was generated by stirring (*S*)-BINAP and silver(I) triflate in a 1:9 water:ethanol mixed solvent at 25°C for 30 min in the dark. Treatment of the catalyst (5 mol%) with equimolar amounts of benzaldehyde and allyltributyltin and subsequent stirring at 25°C for 14 h in the dark afforded the (*S*)-enriched product in 61% yield with 54% ee. Investigation on the solvent effect (Table 1, entries 1–4) showed that the 1:9 water:ethanol was a superior choice. Other chiral diphosphines **2**–**6** (Scheme 1) were also screened under the same conditions and the highest 66%

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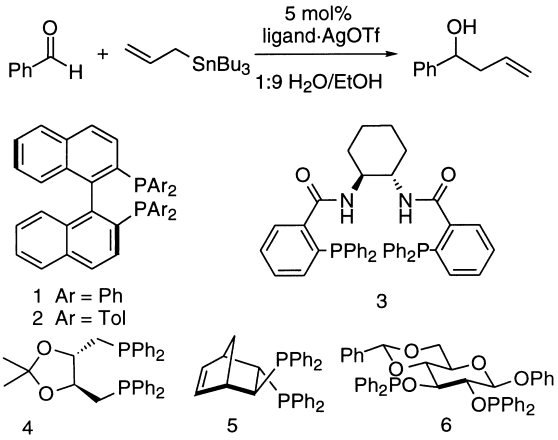

Scheme 1.

Table 1
Enantioselective allylation of benzaldehyde

entry	Ligands	Solvents	Conditions	Results[a]
1	**1**	1:9 H_2O/EtOH	25 °C, 14 h	61%, 54% ee
2	**1**	1:4 H_2O/EtOH	25 °C, 14 h	60%, 54% ee
3	**1**	1:4 H_2O/THF	25 °C, 14 h	60%, 40% ee
4	**1**	1:1.5 H_2O/EtOH	25 °C, 14 h	79%, 45% ee
5	**2**	1:9 H_2O/EtOH	25 °C, 14 h	84%, 66% ee
6	**3**	1:9 H_2O/EtOH	25 °C, 14 h	11%
7	**4**	1:9 H_2O/EtOH	25 °C, 14 h	90%, 2% ee
8	**5**	1:9 H_2O/EtOH	25 °C, 14 h	--[b]
9	**6**	1:9 H_2O/EtOH	25 °C, 14 h	--[b]
10	**2**	1:9 H_2O/EtOH	0 °C, 14 h	84%, 69% ee
11	**2**	1:9 H_2O/EtOH	-20 °C, 14 h	89%, 71% ee
12	**2**	1:9 H_2O/EtOH	-40 °C, 14 h	90%, 75% ee
13	**2**	1:9 H_2O/EtOH	-60 °C, 14 h	2%

[a] Enantioselectivity was determined by HPLC analysis employing a Daicel Chiracel OD column. Absolute configuration was assigned by comparison with literature value of optical rotation.

[b] The ligand did not form a complex with AgOTf to form a homogeneous solution after being stirred at 25 °C for 30 min.

ee was achieved with **2**, (*S*)-Tol-BINAP (entry 5). Lowering the temperature to –40°C further increased the selectivity to 75% ee with a higher isolated yield (entry 12). On the other hand, no reaction was observed at –60°C.

Next we surveyed the catalytic activities of other transition metal salts (Table 2). The experiments were carried out by stirring benzaldehyde, allyltributyltin and 5 mol% pre-formed complexes with (*S*)-Tol-BINAP at –40°C for 14 h. The results are summarised in Table 2. Only silver(I) salts were found to be effective in the catalysis. Furthermore, the reactions with the silver(I) salts exhibited essentially no counterion effect, which is in sharp contrast to those observed in organic solvents.[2] This is probably due to complete ionic dissociation in the aqueous medium. Additionally, increasing

Table 2
Catalytic activities of transition metal salts

Entry	Metal salts	Results
1	$CdCl_2 \cdot H_2O$	--[a]
2	$RuCl_3 \cdot H_2O$	0%
3	$Cu(MeCN)_4PF_6$	10%
4	$Pd(MeCN)_4(BF_4)_2$	2%
5	$Pd(CF_3COO)_2$	1%
6	$Pd(NO_3)_2$[b]	18%, 67% ee
7	$AgClO_4$	95%, 75% ee
8	$AgNO_3$	94%, 75% ee
9	$AgNO_3$[c]	93%, 79% ee

[a] The salt did not complex with (*S*)-Tol-BINAP to form a homogeneous solution after being stirred at 25 °C for 30 min.
[b] The salt was pre-formed *in situ* by stirring 1 equivalent of $PdCl_2$ and 2 equivalents of $AgNO_3$ at 25 °C for 30 min.
[c] The reaction was carried out with 10 mol% of the catalyst.

the amount of (*S*)-Tol-BINAP·$AgNO_3$ to 10 mol% (entry 9) led to a little improvement in the selectivity (79% ee).

With the optimised conditions, (*S*)-Tol-BINAP·$AgNO_3$ was applied to other aldehydes (Table 3). The (*S*)-Tol-BINAP·$AgNO_3$ complex (0.1 mmol) was generated in 10 mL of 1:9 H_2O:EtOH mixed solvent as described above. The colourless catalyst solution was cooled to –40°C and treated with an aldehyde (1 mmol) and allyltributyltin (1 mmol, 310 μL). The reaction mixture was stirred in the dark for several hours as indicated in Table 3. In general, aromatic aldehydes afforded the desired products with good stereocontrol. It is noteworthy that 71% ee was obtained with 3-hydroxybenzaldehyde without protection of its phenolic group. However, only low to moderate stereoselectivity was observed with aliphatic, olefinic and acetylenic aldehydes (entries 8–10).

Table 3
Enantioselective allylation of aldehydes

Entry	Aldehydes	Conditions	$[\alpha]_D^{25}$	Results[a]
1	benzaldehyde	-40 °C, 14 h	-45.0 (*c* 0.80, toluene)	93%, 79% ee(*S*)
2	1-naphthaldehyde	-40 °C, 30 h	-90.4 (*c* 0.45, toluene)	100%, 81% ee(*S*)
3	2-naphthylaldehyde	-40 °C, 18 h	-56.3 (*c* 0.64, toluene)	99%, 79% ee(*S*)
4	3-hydroxybenzaldehyde	-40 °C, 60 h	-19.2 (*c* 1.33, EtOAc)	92%, 71% ee
5	3-chlorobenzaldehyde	-40 °C, 14 h	-50.0 (*c* 1.15, toluene)	95%, 73% ee
6	3-methoxybenzaldehyde	-40 °C, 14 h	-26.8 (*c* 0.88, toluene)	96%, 79% ee
7	5-methyl-2-furyladehyde	-40 °C, 14 h	-25.7 (*c* 0.55, toluene)	88%, 58% ee
8	cinnamaldehyde	-40 °C, 20 h	-45.0 (*c* 0.80, toluene)	98%, 58% ee(*S*)
9	3-phenylpropionaldehyde	-40 °C, 40 h	+12.1 (*c* 0.63, toluene)	70%, 53% ee(*S*)
10	phenylpropiolaldehyde	25 °C, 5 h[b]	-2.1 (*c* 0.66, toluene)	93%, 30% ee(*S*)

[a] Enantioselectivity was determined by HPLC analysis employing a Daicel Chiracel OD or OJ column. Absolute configurations were assigned by comparison with literature value of optical rotation.
[b] No observable change after stirring at -40 °C for 14 h.

In conclusion, the modified Yamamoto–Yanagisawa's catalyst was successfully applied to the enantioselective allylation reaction of aldehydes in an aqueous system. The reactions with aromatic aldehydes usually afforded desired products in high yields with good stereoselectivities. The experiment was easy to perform without the need to exclude moisture or air. In addition, compounds carrying sensitive functional groups need no protection under the reaction conditions. Ligand modification is still underway in our laboratory.

Acknowledgements

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