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Palladium-catalyzed asymmetric hydrogenation of simple ketones activated by Brønsted acids

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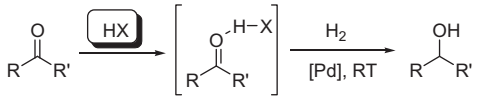
ABSTRACT

Homogeneous $Pd(OCOCF_3)_2$/(*R*)-C_4-TunePhos has been successfully applied in the asymmetric hydrogenation of simple ketones activated by catalytic amount of Brønsted acid with up to 88% ee.

Transition-metal-catalyzed asymmetric reduction of prochiral ketones using molecular hydrogen represents the most simple and powerful method for the preparation of a variety of enantiomerically enriched secondary alcohols due to its low cost and complete atom efficiency.[1] A series of efficient systems have been successfully developed for the asymmetric hydrogenation of ketones with chiral Ru,[2] Rh,[3] Ir,[4] Os,[5] Fe[6] and Cu[7] complexes. Much less attention has been devoted to other transition-metal based systems.

Recently, Pd-based catalytic systems have been developed for asymmetric carbon–carbon and carbon-heteroatom coupling reactions.[8] Although many successful examples of heterogeneous asymmetric hydrogenation reactions catalyzed by Pd(0) have been well documented in the literature, very little attention has been paid to Pd-catalyzed homogeneous asymmetric hydrogenation reactions.[9–14] The first Pd-catalyzed asymmetric hydrogenation of α-fluorinated iminoesters in 2,2,2-trifluoroethanol (TFE) was described by Amii and co-workers with a $Pd(OCOCF_3)_2$/BINAP complex with up to 91% ee.[9a,c] Afterward, Pd-catalyzed asymmetric hydrogenation of *N*-diphenylphosphinyl ketimines and *N*-tosylimines were successively reported by us[10b] and Zhang[11] group, respectively. Then, chiral palladium complexes have been successfully applied to asymmetric hydrogenation of some other activated imines in our laboratory[10c–e] with high reactivities and enantioselectivities. In 2009, Rubio-Perez et al. reported the highly enantioselective one-pot reductive amination of simple ketones catalyzed by chiral palladium complexes with up to 99% ee,[12] and very low reactivity was observed for hydrogenation of ketones. Most recently, we have reported Pd-catalyzed asymmetric hydrogenation of simple fluorinated imines[10g] under mild conditions with up to 94% ee and unfunctionalized ketoimines[10h] activated by Brønsted acid with up to 95% ee, respectively. However, there were few reports on Pd-catalyzed asymmetric hydrogenation of ketones. Raja[13] and co-workers reported the heterogeneous hydrogenation of α-ketoesters with chiral catalyst Pd(allyl)diamino triflate anchored to the inner wall of mesoporous with 67% ee, but in homogeneous form, only 55% ee was obtained. In 2005, highly enantioselective hydrogenation of α-phthalimide ketones was developed by us[10a] using chiral $Pd(OCOCF_3)_2$/DuPhos complex, and the asymmetric hydrogenation of simple ketone was also tried using the above catalyst, but low reactivity and moderate 52% ee were obtained. Goulioukina[14] et al. reported asymmetric hydrogenation of α-keto phosphonates using $Pd(OCOCF_3)_2$/MeO-BiPhep as catalyst with up to 55% ee under atmospheric pressure of hydrogen and 80 °C. Very recently, an efficient Pd-catalyzed asymmetric hydrogenation of simple indoles was developed by us[10f] with the Brønsted acid as activator and up to 96% ee was obtained. Although much work has been devoted to the development of Pd-catalyzed asymmetric hydrogenation of activated imines and functionalized



Scheme 1. Activation strategy for hydrogenation of simple ketones.

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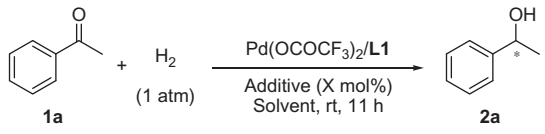
ketones, the development of Pd-catalyzed asymmetric hydrogenation of simple ketones is still a challenge.

Recently, Brønsted acid is found to be very crucial for asymmetric hydrogenation of imines and heteroaromatic compounds.[10h,15,16] Inspired by these examples, we envisioned that catalytic amount of Brønsted acid may play as activator, in this case hydrogen bonding interactions, in the Pd-catalyzed asymmetric hydrogenation of simple ketones (Scheme 1). Herein, we report our preliminary results on Pd-catalyzed asymmetric hydrogenation of simple ketones activated by catalytic amount of Brønsted acid, and up to 88% ee was achieved.

Table 1
The effect of the additives and solvents[a]



Entry	Solvent	Additive (X mol %)	Convn.[b] (%)	Ee[b] (%)
1	TFE	none	39	55
2	TFE	**3a** (10)	>95	59
3	TFE	**3b** (10)	10	49
4	TFE	**3c** (10)	22	49
5	TFE	TFA (10)	15	46
6	TFE	$TsOH{\cdot}H_2O$ (10)	23[c]	N/A
7	**TFE**	**3d (10)**	**>95**	**61**
8	TFE	**3d** (5)	88	59
9	TFE	**3d** (20)	92	56
10	TFE	**3d** (50)	73	56
11	EtOH	**3d** (10)	<5	N/A
12	Benzene	**3d** (10)	<5	N/A
13	THF	**3d** (10)	<5	N/A
14	CH_2Cl_2	**3d** (10)	<5	N/A

Compound **3a**: benzoic acid; **3b**: tartaric acid; **3c**: 2-hydroxy-iso-butanoic acid; **3d**: salicylic acid.

[a] Conditions: 1 atm of H_2, 0.25 mmol Ketone, $Pd(OCOCF_3)_2$ (2 mol %), (*S*)-SynPhos (2.4 mol %), 2 mL solvent, rt, 11 h.

[b] Determined by GC.

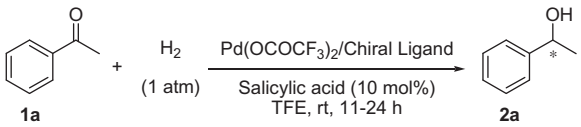
[c] The product was ether **4**: 1-(1-(2,2,2-trifluoroethoxy)ethyl)benzene.

Acetophenone **1a** was chosen as model substrate, the initial experiment was carried out under 1 atm of hydrogen and at room temperature in TFE with $Pd(OCOCF_3)_2$/(*S*)-SynPhos system, but only 39% conversion and 55% ee were obtained (Table 1, entry 1). Gratifyingly, the catalytic activity was improved dramatically in the presence of 10 mol % Brønsted acid, benzoic acid **3a,** full conversion and 59% enantioselectivity was obtained (Table 1, entry 2).

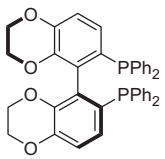
Following this encouraging result, the effect of Brønsted acid on reactivity and enantioselectivity was investigated (Table 1, entries 2–7,). In the case of aliphatic carboxylic acids, **3b** and **3c**, surprisingly, the catalytic activity and enantioselectivity decreased apparently compared to no additive (entries 3 and 4). The stronger acids (entries 5 and 6), such as trifluoroacetic acid and *p*-toluenesulfonic acid, displayed no more positive impact. Aryl carboxylic acids are the most effective additives for the reactivity and enantioselectivity, salicylic acid (**3d**) gave full conversion and the highest enantioselectivity (61% ee, entry 7). Therefore, salicylic acid was chosen as the additive for further study. The lower conversion and enantioselectivity (88% conversion and 59% ee, entry 8) were observed when **3d** was reduced to 5 mol %. As the ratio increasing from 10 to 50 mol %, the conversion and enantioselectivity decreased (73% conversion and 65% ee, entry 10). These results showed 10 mol % amount of salicylic acid is appropriate.

Subsequently, the effects of solvent, hydrogen pressure, reaction temperature and ligand were studied; a strongly solvent-dependent effect was observed (Table 1, entries 7, 11–14), EtOH, benzene, THF and CH_2Cl_2 led to very low reactivity, only TFE was found to be the efficient solvent, which was in accordance with the Pd-catalyzed asymmetric hydrogenation of activated imines

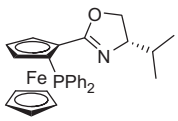
Table 2
The effect of chiral ligands on the reactivity and enantioselectivity[a]



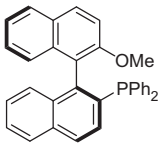
Entry	Ligand	*T* (h)	Convn.[b] (%)	Ee[b] (%)
1	**L1**	11	>95	61 (*S*)
2	**L2**	24	<5	N/A
3	**L3**	24	<5	N/A
4	**L4**	24	8	35 (*R*)
5	**L5**	24	48	65 (*S*)
6	**L6**	24	>95	64 (*S*)
7	**L7**	**11**	**>95**	**67 (*R*)**
8	**L8**	24	>95	61 (*S*)



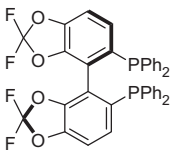
L1 (*S*)-SynPhos



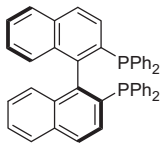
L2



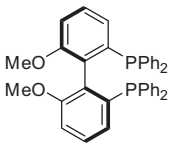
L3 (*S*)-MOP



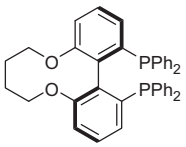
L4 (*R*)-Difluorphos



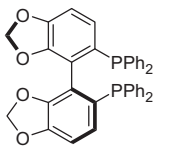
L5 (*S*)-BINAP



L6 (*S*)-MeO-BiPhep



L7 (*R*)-C_4-TunePhos

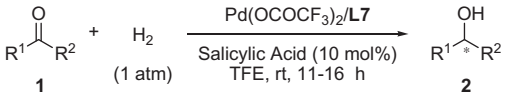


L8 (*S*)-SegPhos

[a] Conditions: 1 atm of H_2, 0.25 mmol ketone, $Pd(OCOCF_3)_2$ (2 mol %), chiral ligand (2.4 mol %), 2 mL TFE, rt.

[b] Determined by GC.

Table 3
Asymmetric hydrogenation of simple ketones[a]



Entry	R^1/R^2	Yield[b] (%)	Ee[c] (%)
1	C_6H_5/CH_3 (**1a**)	93	67 (*R*)
2	4-F-C_6H_4/CH_3 (**1b**)	84	59 (*R*)
3	C_6H_5/Et (**1c**)	94	72 (*R*)
4	C_6H_5/*n*-Pr (**1d**)	85	71 (*R*)
5	C_6H_5/*n*-Bu (**1e**)	99	69 (*R*)
6	C_6H_5/*i*-Pr (**1f**)	81	71 (*R*)
7	C_6H_5/*t*-Bu (**1g**)	93	88 (*R*)
8	$C_6H_5/C_6H_5CH_2CH_2$ (**1h**)	85	59 (*R*)
9	$C_6H_5/C_6H_5CH_2C(CH_3)_2$ (**1i**)	93	72 (*R*)
10	C_6H_5/Cyclohexyl (**1j**)	96	70 (*R*)
11[d]	*n*-Decanyl/CH_3 (**1k**)	83	10 (*R*)

[a] Conditions: 1 atm of H_2, 0.25 mmol ketone, $Pd(OCOCF_3)_2$ (2 mol %), (R)-C4-TunePhos (2.4 mol %), 2 mL TFE, rt.
[b] Isolated yield.
[c] Determined by HPLC or GC.
[d] The reaction time: 48 h and the enantioselectivity was determined by HPLC in the form of benzoate ester.

and functionalized ketones.[9–12] The reaction temperature and H_2 pressure had no dramatic impact on enantioselectivity of product **2a**.

Then, several commercially available chiral ligands were also examined under the above optimized conditions, as summarized in Table 2. *P,N*-ligand **L2**, monophosphine ligand MOP **L3** and electron-withdrawing bisphosphine ligand Difluorphos **L4** had almost no catalytic activity (Table 2, entries 2–4). (*S*)-BINAP **L5** gave 48% conversion and 65% ee. The best result was achieved with (*R*)-C_4-TunePhos **L7**, 67% ee and full conversion was observed (entry 7).

Under the optimized conditions, a variety of substituted simple ketones **1** were hydrogenated, as shown in Table 3. In most cases, the products were obtained in full conversions and moderate to good enantioselectivities. Substitution of the aromatic ring in the ketones has a detrimental effect on the selectivity and enantioselectivity. Substrates bearing the electron-donating *p*-methyl or *p*-methoxy group in the benzene ring of aromatic ketones led to a significant amount of racemic trifluoroethyl ether as byproduct, which may be formed via the acid catalyzed etherification of the corresponding alcohols and solvent trifluoroethanol. Aromatic ketone **1b** with electron-deficient fluoro group (entry 2) could be hydrogenated smoothly, the enantioselectivity decreased to 59%.

Alkyl phenyl ketones **1c–1i** can be hydrogenated smoothly with 59–88% ee (entries 3–10), the bulky pivalophenone **1g** gave the highest 88% ee (entry 7). To probe the generality of the catalytic system, the hydrogenation of dialkyl ketone **1k** was also examined (entry 11), the reaction was completed in 48 h, affording the corresponding product **2k** with full conversion but poor enantioselectivity (Determined by HPLC in the form of benzoate ester).

In summary, a homogeneous Pd-catalyzed asymmetric hydrogenation of simple ketones activated by catalytic amount of Brønsted acid was successfully developed using the $Pd(OCOCF_3)_2$/(*R*)-C_4-TunePhos as catalyst with up to 88% ee. In order to provide the mechanism understanding to rational design of new asymmetric palladium catalysts, the role of salicylic acid and TFE in the reaction is under progress.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.03.057.

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