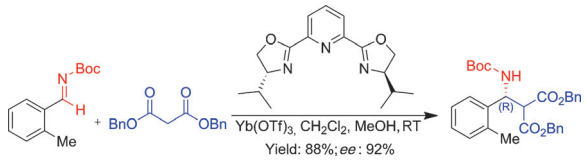

Go Mannich! A highly efficient and enantioselective method for the direct asymmetric reaction of dibenzyl malonate with *N*-*tert*-butoxycarbonyl aldimines in the presence of $Yb(OTf)_3$ and *i*Pr-pybox complexes is described (see scheme; pybox = pyridine bisoxazoline).

Asymmetric Synthesis

B. Karimi, E. Jafari,*
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Highly Efficient Catalytic Enantioselective Mannich Reaction of Malonates with *N*-*tert*-Butoxycarbonyl Imines by Using $Yb(OTf)_3$/Pybox Catalysts at Room Temperature

CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc
Europe

DOI: 10.1002/chem.201300241

Highly Efficient Catalytic Enantioselective Mannich Reaction of Malonates with *N*-*tert*-Butoxycarbonyl Imines by Using $Yb(OTf)_3$/Pybox Catalysts at Room Temperature

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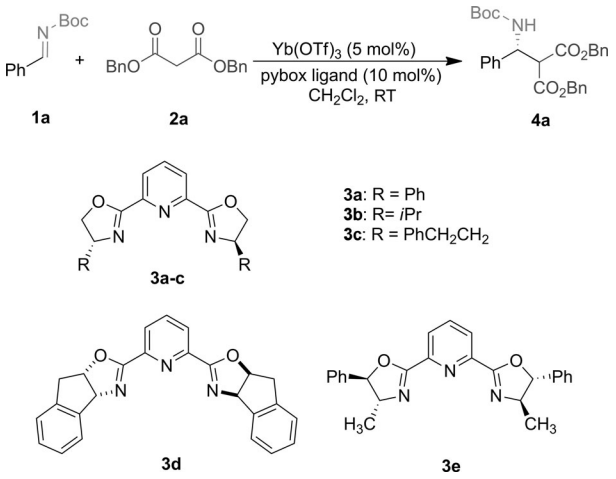
The enantioselective catalytic Mannich reaction is a powerful synthetic method for the preparation of β-amino carbonyl compounds, an important class of chiral building blocks of pharmaceutically and agrochemically relevant target molecules.[1,2] In particular, the use of malonate derivatives as nucleophiles in the Mannich reaction of imines is certainly preferable, as it avoids the preformation of enolates or the naked enolate step to access β-amino carbonyl adducts.[3] Although much attention has been devoted to the development of a diverse array of chiral organocatalysts for the asymmetric addition of malonates to imines, the number of approaches involving chiral metal complexes are quite limited.[4] Moreover, the enantioselective Mannich reaction of imines by using chiral Yb^{III} catalysts has been unexplored, in contrast to the fact that Yb^{III} chiral complexes have given remarkable results in several asymmetric synthetic transformations.[5] It is also worth mentioning that most of the metal-catalyzed asymmetric Mannich reactions require a very low temperature to produce satisfactory enantioselectivities.[6] While excellent advances have been achieved, many of the reported protocols have limitations, such as high catalyst loading, limited substrate scope, or difficult preparation of catalyst. Therefore, there is still substantial room for the development of new versions of catalytic asymmetric Mannich reactions.

Very recently, we have successfully employed a novel chiral $Yb(OTf)_3$/pybox (pybox = pyridine bisoxazoline) complex in the catalytic asymmetric Strecker hydrocyanation of various types of *N*-benzhydryl imines to afford the corresponding α-aminonitriles in good to excellent conversions with enantiomeric excess (*ee*) values of up to 98%.[5a] In continuation to these studies, herein we describe a highly enantioselective direct Mannich-type reaction of malonate esters with both aromatic and aliphatic imines by employing a $Yb(OTf)_3$/pybox catalyst system at room temperature.

At the beginning of our research, we started with the model reaction of *N*-*tert*-butoxycarbonyl (*N*-Boc) aldimine **1a** with dibenzylmalonate **2a** in CH_2Cl_2 at room temperature in the presence of various $Yb(OTf)_3$/pybox complexes, generated in situ from commercially available $Yb(OTf)_3$ and pybox ligands **3a–e** (Scheme 1; Table 1, entries 1–5).



Scheme 1. Enantioselective addition of dibenzyl malonate (**2a**) to *N*-Boc imine (**1a**) in the presence of various chiral pybox ligands.

Interestingly, while in all cases the reaction proceeded smoothly by employing 5 mol% of $Yb(OTf)_3$ and 10 mol% of pybox ligands at room temperature (25 °C) to give the β-amino carbonyl compounds **4a** in high yields, the catalyst system comprising of the pybox ligand **3b** (with an *i*Pr group) furnished the product with the highest *ee* value of 68% (Table 1, entry 2).

To further optimize the reaction conditions, several metal triflates, such as $Sc(OTf)_3$, $Cu(OTf)_2$, $In(OTf)_3$, and $Zn(OTf)_2$, in addition to $Yb(OTf)_3$ were then screened and the later was found to be superior with regard to reaction enantioselectivity under the same conditions (Table 1, entries 2 vs. 6–9). In our recent work, we found that in the course of catalytic enantioselective Strecker reactions of imines using a $Yb(OTf)_3$/pybox catalyst, both enantioselectivities and product yields were remarkably improved upon the addition of stoichiometric amounts of a protic additive to the reac-

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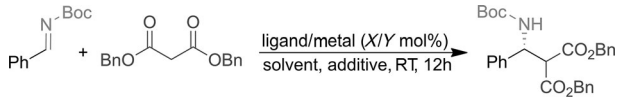
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300241

Table 1. Effect of various reaction parameters in the enantioselective Mannich reaction of benzyl malonate **2a** with benzaldehyde *N*-Boc imine **1a** at room temperature.[a]



1a **2a** **4a**

Run	Ligand/metal	Solvent	Additive	Yield (*ee*) [%][b,c]
1	**3a**/Yb(OTf)$_3$	CH_2Cl_2	–	81 (46)
2	**3b**/Yb(OTf)$_3$	CH_2Cl_2	–	83 (68)
3	**3c**/Yb(OTf)$_3$	CH_2Cl_2	–	88 (50)
4	**3d**/Yb(OTf)$_3$	CH_2Cl_2	–	79 (10)
5	**3e**/Yb(OTf)$_3$	CH_2Cl_2	–	82 (61)
6	**3b**/Sc(OTf)$_3$	CH_2Cl_2	–	87 (37)
7	**3b**/Cu(OTf)$_2$	CH_2Cl_2	–	88 (7)
8	**3b**/In(OTf)$_3$	CH_2Cl_2	–	77 (13)
9	**3b**/Zn(OTf)$_2$	CH_2Cl_2	–	65 (25)
10	**3b**/Yb(OTf)$_3$	CH_2Cl_2	MeOH (0.5 equiv)	85 (70)
11	**3b/Yb(OTf)$_3$**	**CH_2Cl_2**	**MeOH (1 equiv)**	**91 (95)**
12	**3b**/Yb(OTf)$_3$	CH_2Cl_2	MeOH (1.5 equiv)	93 (61)
13	**3b**/Yb(OTf)$_3$	CH_2Cl_2	HFIP (1 equiv)	95 (79)
14	**3b**/Yb(OTf)$_3$	CH_2Cl_2	*i*PrOH (1 equiv)	80 (71)
15	**3b**/Yb(OTf)$_3$	THF	MeOH (1 equiv)	73 (5)
16	**3b**/Yb(OTf)$_3$	toluene	MeOH (1 equiv)	86 (40)
17	**3b**/Yb(OTf)$_3$	CH_3CN	MeOH (1 equiv)	69 (10)
18[d]	**3b**/Yb(OTf)$_3$	CH_2Cl_2	MeOH (1 equiv)	74 (35)
19[e]	**3b**/Yb(OTf)$_3$	CH_2Cl_2	MeOH (1 equiv)	89 (60)
20[f]	**3b**/Yb(OTf)$_3$	CH_2Cl_2	MeOH (1 equiv)	82 (77)

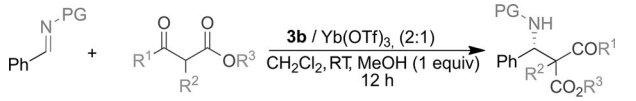
[a] Conditions: Yb(OTf)$_3$ (5 mol%), pybox (10 mol%), **1a** (1 equiv), **2** (1.1 equiv). The reaction was performed at room temperature for 12 h. [b] Isolated yield. [c] Enantiomeric excesses were determined by HPLC analysis on a CHIRALPAK AS column. [d] Yb(OTf)$_3$ (2.5 mol%), pybox (5 mol%). [e] Yb(OTf)$_3$ (10 mol%), pybox (10 mol%). [f] Yb(OTf)$_3$ (5 mol%), pybox (7.5 mol%).

tion mixture.[4a] In the present study, it was also revealed that the protic additives exhibited more or less the same significant effect on the observed enantioselectivities (entries 10–14), although the yields were comparable to the reaction in the absence of protic additives (entry 2).

Among the protic additives investigated, MeOH (1 equiv) was the best, giving **4a** in 91% yield with an excellent *ee* value of 95% (Table 1, entry 11). Higher or lower MeOH loading also afforded **4a** in comparable yields, albeit with much inferior enantioselectivities (entries 10–13). We are currently working towards the mechanistic insight into the effect of protic additive and the results will be appearing in due course.

In the next stage, the effect of solvent and additive together, Yb(OTf)$_3$/**3b** ratio, and amount of the catalyst were evaluated in the reaction. As can be clearly seen, this reaction was sensitive to solvent, and CH_2Cl_2 was the optimum choice (Table 1, entries 11 vs. 15–17). We also found that the reaction still reached completion by changing either the catalyst loading or the Yb(OTf)$_3$/**3b** ratio, although significant loss of enantioselectivity was observed in all cases (entries 11 vs. 18–20). These results also highlight the notion that a 2:1 ratio of **3b** ligand to Yb(OTf)$_3$ is very important for obtaining high enantioselectivities. Facing the challenge of achieving higher enantioselevities, we next examined the influence of other protecting groups at the imine nitrogen atom under the reaction conditions in Table 1, entry 11. The results revealed that no reaction proceeded when using benzaldimine bearing a protecting group, such as *N*-4-methylphenyl, *N*-phenyl, or *N*-2-hydroxyphenyl instead of **1a**, which implied that the presence of the *N*-Boc moiety is crucial for attaining high enantioselectivities (Table 2, entries 1–4). On the other hand, we found that among a variety of alternative malonate esters investigated, the benzyl ester variant delivered the Mannich adducts with the highest selectivity of 95% (entry 1), whereas those of methyl and ethyl esters, 2-substituted malonates, and also β-keto esters led to much lower enantioselectivities (entries 5–8). With the optimal conditions in hand (Table 2, entry 1), we next

Table 2. Effect of *N*-substituent and malonate alkyl group on the enantioselective Mannich reaction of benzaldimine catalyzed by Yb(OTf)$_3$/pybox complexes.[a]



1 **2a-c** **4**

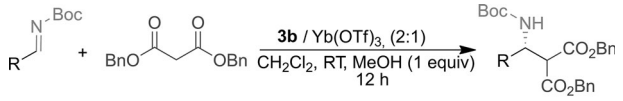
Run	PG	R^1, R^3	Yield [%][b]	*ee* [%][c,d]
1[e]	**Boc**	**OBn, Bn**	**91**	**95**
2[e]	4-tolyl	OBn, Bn	trace	n.d.
3[e]	Ph	OBn, Bn	trace	n.d.
4[e]	2-(OH)Ph	OBn, Bn	trace	n.d.
5[e]	Boc	OMe, Me	89	45
6[e]	Boc	OEt, Et	88	69
7[e]	Boc	Ph, Et	89	68
8[f]	Boc	OBn, Bn	87	66

[a] Conditions: Yb(OTf)$_3$ (5 mol%)/pybox **3b** (10 mol%), 1 (1 equiv), **2a** (1.1 equiv), MeOH (1 equiv), The reaction was performed at room temperature for 12 h in dichloromethane. [b] Isolated yields. [c] Enantiomeric excesses were determined by HPLC analysis on a CHIRALPAK AS column. [d] Absolute configuration was determined to be *R* according to the literature data.[7] [e] R^2=H. [f] R^2=Me.

managed to examine further the scope and limitations of this novel asymmetric Mannich reaction. A survey of electronically and sterically varied aryl and heteroaryl *N*-Boc imines revealed a high degree of sterochemical consistency in their reaction with benzyl malonate **2a**, giving excellent enantioselectivities of >95% *ee* in most cases at room temperature (Table 3).

Apparently, the position and electronic nature of the substituent on the aromatic ring has a very limited influence on the enantioselectivities. In particular, the reaction was successfully applicable to the electron-rich aldimines, which are known to be less prone to the nucleophilic addition reaction, furnishing the corresponding Mannich adducts in high yields (83–92%) with good to excellent enantioselectivities of up to 99% (Table 3, entries 7–11). Noticeably, up to a 93% *ee* was still obtained even for the challenging *ortho*-substitued substrates and 1-naphthyl *N*-Boc aldimines without any significant drop in both selectivities and the product yields irrespective to the electronic properties of the substituents at

Table 3. Scope of the enantioselective Mannich reaction of benzyl malonate with *N*-Boc imines catalyzed by $Yb(OTf)_3$/**3b** at room temperature.[a]



1a-n **2a** **4a-n**

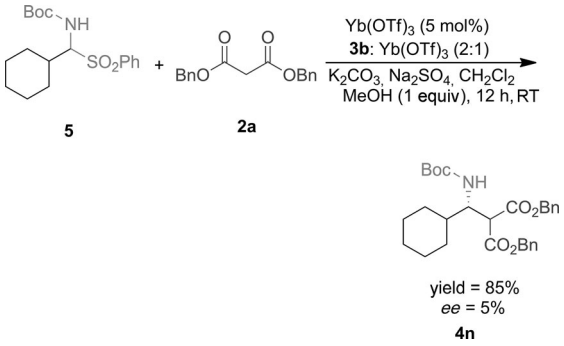
Run	R	Yield [%][b]	*ee* [%][c,d]
1	Ph (**1a**)	91	95
2	2-Br-C_6H_4 (**1b**)	88	93
3	3-Br-C_6H_4(**1c**)	95	97
4	4-Br-C_6H_4(**1d**)	94	98
5	2-Cl-C_6H_4(**1e**)	91	93
6	4-Cl-C_6H_4(**1f**)	95	96
7	2-Me-C_6H_4(**1g**)	88	92
8	3-Me-C_6H_4(**1h**)	88	95
9	4-Me-C_6H_4(**1i**)	92	99
10	4-MeO-C_6H_4(**1j**)	83	98
11	4-*iso*-propyl(**1k**)	92	93
12	1-naphthyl(**1l**)	85	89
13	2-furyl(**1m**)	91	96
14	cyclohexyl(**1n**)	59	69

[a] Conditions: $Yb(OTf)_3$ (5 mol%)/pybox **3b** (10 mol%), **1** (1 equiv), **2a** (1.1 equiv), MeOH (1equiv). The reaction was performed at room temperature for 12 h in dichloromethane. [b] Isolated yields. [c] Enantiomeric excesses were determined by HPLC analysis on a CHIRALPAK AS column. [d] Absolute configuration was determined to be *R* according to the literature data.[7]

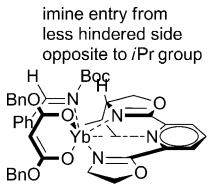
the aromatic rings (entries 2, 5, 7, and 12). Another interesting feature of this protocol is the remarkable tolerance for heteroaryl *N*-Boc aldimines since excellent yield (91%) and enatioselectivity (96% *ee*) was still attained in the reaction of 2-furyl *N*-Boc imine as a model substrate (entry 13). On the other hand, both the yield and the enantioselectivity were sacrificed to some extent when aliphatic aldehyde-derived *N*-Boc imines were employed. The low yield (59%) and low enantioselectivity (69% *ee*) was attributed in the case of aliphatic *N*-Boc imines to isomerization of the imine to the corresponding enamine form under the reaction conditions.[7]

Following the interesting discovery of Ricci and others,[8] we reasoned that it might be possible to circumvent this problem by employing α-amido sulfone **5** for the in situ preparation of the corresponding *N*-Boc imine under the reaction conditions, in which it would be gradually condensed with nucleophilic malonate through our described asymmetric Mannich protocol (Scheme 2). However, while this approach led to the corresponding Mannich adduct in high yield (85%), the selectivity was rather disappointing. We are currently working on this topic to improve the results.

At this stage, the precise explanation and exact mechanistic feature for this reaction is unclear for us. However, we have performed three typical experiments in order to gain more insight into the actual catalyst species and hopefully find a reasonable explanation for the higher loading of ligand in our protocol (2:1 pybox/$Yb(OTf)_3$; 10:5 mol%), which is necessary in obtaining high enatioselectivities of the products. To obtain a reliable result, in the first two experiments, the asymmetric Mannich reaction of benzylmalonate to benzaldehyde-*N*-Boc imine **1a** using 1:1 pybox/$Yb(OTf)_3$ and 2:1 pybox/$Yb(OTf)_3$ was quenched at an early stage after 2 h and the yields and *ee* values of the Mannich products were compared accordingly. It was found that the reaction using 1:1 pybox/$Yb(OTf)_3$ (5 mol%) is not only much slower than the other reactions using 2:1 pybox/$Yb(OTf)_3$ (10:5 mol%) catalyst system (29 vs. 48% yields after 2 h), but it also resulted in much inferior enantioselectivity of the Mannich products (35 vs. 89% *ee* values after 2 h). On the other hand, for the purpose of comparison we have also tested the same reaction by using 1:1 pybox/$Yb(OTf)_3$ (5 mol%) by adding 10 mol% triethylamine (Et_3N) as an exogenous base. Interestingly, we found that by adding 10 mol% Et_3N to a 1:1 pybox/$Yb(OTf)_3$ (5 mol%) catalyst system a significant improvement was observed in the final enantioselectivity after 12 h, giving the corresponding Mannich adducts in 88% yield with 79% *ee*. Based on these observation, we may conclude that in the present protocol, an additional 5 mol% of ligand is most likely acting as a chiral Brønsted base catalyst. Therefore, the proposed transition state of this reaction is outlined in Scheme 3 (front *i*Pr group has been omitted for simplicity). Further studies to clarify the actual mechanism of this reaction in which the role of MeOH in improving the enantioselectivity of the described reaction is being investigated are currently ongoing in our laboratories.



Scheme 2. Asymmetric one-pot Mannich reaction of **5** with **2a**.



Scheme 3. Proposed transition state for the enantioselective Mannich reaction of benzyl malonate with *N*-Boc imines catalyzed by $Yb(OTf)_3$/**3b** at room temperature. The front *iso*-propyl group has been omitted for simplicity.

In conclusion, we have developed a highly efficient catalytic enantioselective Mannich reaction of dibenzyl malonate with *N*-Boc aldimines employing the readily available

ytterbium complex prepared from $Yb(OTf)_3$ and chiral pybox ligand as a catalyst. Using the current protocol, various aldimines including heteroaryl *N*-Boc aldimines could be converted to the corrsponding β-amino carbonyl products in high yields with good to excellent enantioselectivities at room temperature. To the best our knowledge this method can be considered as the first example of a highly enantioselective metal-catalyzed Mannich reaction of malonate esters at room temperature. Further investigations aimed at developing new applications of this catalyst system in other important asymmetric transformations are currently underway in our laboratory.

Experimental Section

General catalytic procedure of the asymmetric Mannich reaction: A well-dried glass tube was charged with $Yb(OTf)_3$ (30 mg, 0.048 mmol) and the corresponding pybox ligand (44 mg, 0.096 mmol) under Argon atmosphere. After dichloromethane (1.0 mL) had been added to the mixture, it was stirred vigorously at room temperature for 1 h until the reaction became homogeneous. The corresponding imine (1 mmol) and dibenzylmalonate (neat, 0.312 g, 1.1 mmol) was added in dichloromethane to a solution of complex, under an Argon atmosphere. After that methanol (1 mmol) was injected in one portion to the reaction mixture. After 12 h, the reaction mixture was purified by flash chromatography through a short column of silica gel by using hexane/ethyl acetate as an eluent to obtain the corresponding products.

Acknowledgements

The authors acknowledge the IASBS research council and Iranian National Science Foundation (INSF) for support of this work.

Keywords: asymmetric catalysis · enantioselectivity · imines · Mannich reactions · pybox · $Yb(OTf)_3$

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Received: January 22, 2013
Revised: May 7, 2013
Published online: ■■ ▮▮, 0000

