One-Pot Synthesis of *cis*-Isoquinolonic Acid Derivatives *via* Three-Component Reaction of Homophthalic Anhydride with Aldehydes and Amines using Ytterbium(III) Triflate as Catalyst

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Abstract: Ytterbium(III) triflate efficiently catalyzes the one-pot reaction of homophthalic anhydride with aldehydes and amines at ambient temperature to afford the corresponding *cis*-isoquinolonic acid derivatives in good to excellent yields with high diastereoselectivity. This method provides a novel and much improved modification of the three-component reaction in terms of mild reaction conditions, short reaction times, clean reaction profiles, small quantity of catalyst, and simple work-up procedure. Another important feature of this method is that the catalyst can be easily recovered from the aqueous layer after the reaction and can be reused with no loss of activity.

Keywords: *cis*-isoquinolonic acids, homophthalic anhydride, lanthanide triflates, Lewis acids, one-pot synthesis

Introduction

Tetrahydroisoquinolonic acid derivatives have attracted the attention of synthetic organic chemists due to their potential activity in the field of pharmaceuticals, and exhibit a wide spectrum of biological activities including psychotropic, anti-allergenic, anti-inflammatory and estrogenic behavior.[1] In particular, isoquinolonic acids are useful precursors for the total synthesis of naturally occurring phenanthridine alkaloids[2] such as corynoline, oxocorynoline and epicorynoline as well as indenoisoquinolines[3] possessing significant anti-tumor activity. It is therefore not surprising that many synthetic methods have been developed for these compounds. Cushman and his group first reported that these compounds could be synthesized by a simple cycloaddition reaction of homophthalic anhydrides with imines under mild conditions.[4] The reaction products resulting from the cycloaddition of homophthalic anhydride with imines using a base catalysis or no catalyst under thermal conditions[5] possess two asymmetric centers and are capable of existing as *cis*- and *trans*-diastereoisomers, favoring the *cis*-isomer. As a result, a variety of synthetic approaches have been developed for the synthesis of isoquinolonic acids.[6–8] Recently, room temperature ionic liquids[6] and trimethyl orthoformate have been employed for the synthesis of *cis*-isoquinolonic acids.[7] Gesquiere and his group reported that the efficient procedure using the boron trifluoride diethyl ether complex ($BF_3 \cdot Et_2O$) as a Lewis acid catalyst led to *trans*-isoquinolonic acid derivatives in moderate yields.[9] However, most of these procedures involve stoichiometric amounts of a metal promoter, longer reaction time and give low yields of the products. All of the methods mentioned above require lengthy procedures to prepare the starting materials. In addition, most of the imines are hygroscopic, unstable at high temperatures, and are difficult to purify by distillation or column chromatography, thus generating a lack of efficiency. Therefore, it is of increasing importance to develop simple and efficient synthetic methods towards this type of compounds involving reactions that need not only effective catalysts, but also simple and convenient procedures. Most of the conventional Lewis acids such as $TiCl_4$, $AlCl_3$, $SnCl_4$ and $BF_3 \cdot OEt_2$ are decomposed or deactivated by water that exists during imine formation. Thus we focused on the use of Lewis acid catalysts to increase the reactivities of imine groups in the imino reactions. For this purpose, we selected rare earth metal triflates as catalyst since they have been reported to have excellent catalytic activities as Lewis acids for a variety of reactions. Rare earth metal triflates such as ytterbium triflate

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[$Yb(OTf)_3$] and scandium triflate [$Sc(OTf)_3$] are stable and serve as Lewis acids in water solution. Many nitrogen-containing compounds such as imines and hydrazones are also activated by rare earth metal triflates in both organic and aqueous solvents.[10] Moreover, they can be recovered after the reactions are completed and reused without loss of activity.[11] In continuation of our long-standing interest in lanthanide triflate-catalyzed synthetic reactions,[12] we disclose a simple and efficient procedure using lanthanide triflates as a novel and recyclable catalyst for the synthesis of *cis*-isoquinolonic acids through the one-pot coupling reaction of homophthalic anhydride, aldehydes and amines under mild reaction conditions.

Results and Discussions

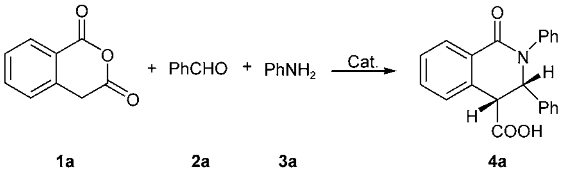
We investigated the reaction of homophthalic anhydride (**1a**) with benzaldehyde (**2a**) and aniline (**3a**) under various conditions (Scheme 1). The results are summarized in Table 1. The reaction proceeded smoothly in the presence of 2 mol % of lanthanide triflates at ambient temperature to afford the corresponding *cis*-1-oxo-2,3-diphenyl-1,2,3,4-tetrahydro-4-isoquinolinecarboxylic acid (**4a**) in high yield. Interestingly, there was no evidence for the formation of any *trans*-diastereoisomer. This showed that the lanthanide triflates did effectively catalyze the cycloaddition reaction. Among the lanthanide triflates screened, $Yb(OTf)_3$ exhibited superior catalytic activity and afforded the corresponding *cis*-compound (**4a**) in 86% yield, which was higher than that with any other lanthanide triflate.

Lanthanide triflates are more soluble in water than in common organic solvents. These catalysts could be recovered almost quantitatively from the aqueous layer after the reactions were completed and they can be reused without attenuated activity. For example, only a catalytic amount of $Yb(OTf)_3$ was enough to complete the reaction, the catalyst could be reused three times without showing any loss of activity (with the yields of the product **4a** being 85%, 84%, 83%, respectively). Further studies showed that increasing the amount of catalyst did not improve the yield of the product. When using 0.5 mol % of $Yb(OTf)_3$, the reaction of benzaldehyde and aniline with homophthalic anhydride gave only a 45% yield even after 12 h. It is obvious that the yield of product was affected by the amount of $Yb(OTf)_3$ catalyst.

Since then, not only $Ln(OTf)_3$ but also other lanthanide compounds such as $YbCl_3$, $DyCl_3$ and $TbCl_3$ were evaluated in this reaction. However, the catalytic activities of $YbCl_3$, $DyCl_3$ and $TbCl_3$ were lower than that of lanthanide triflates in this reaction, and gave lower yields (65%, 55% and 63%) at the first use. Various typical Lewis acid catalysts including $AlCl_3$, $SnCl_4$ and $ZnCl_2$ as well as protic acids (HCl and CH_3COOH), were tested: in most cases the reactions gave extremely lower yields and mixture of *cis*- and *trans*-products or very complicated mixtures.[9] Most of these Lewis acids react rapidly with water rather than the substrates and are decomposed or deactivated, thus, the reactions must be carried out under strictly anhydrous conditions. Furthermore, most of the imines are hygroscopic, unstable at high temperatures, and are difficult to purify by distillation or column chromatography. However, lanthanide triflates can be used as efficient Lewis acids in aqueous media, as their hydrolysis by water is generally slow.

These one-pot procedures have been developed for this transformation using lanthanide triflates as catalysts, and do not require the isolation of unstable imines prior to reaction. It is desirable from a synthetic point of view that the imines, generated *in situ* from aldehydes and amines, be immediately reacted with homophthalic anhydride to afford isoquinolonic acids in one-pot. It was found that the reaction of benzaldehyde, aniline and homophthalic anhydride was efficiently catalyzed by $Yb(OTf)_3$ in the presence of anhydrous $MgSO_4$ or 4 Å molecular sieves, which are added to trap the water generated during the reaction (Scheme 1). The reaction was instantaneous and produced the isoquinolonic acid as expected. On the other hand, the reaction proceeded sluggishly in the presence of anhydrous $MgSO_4$ without any catalyst, and only a trace amount of product was detected after 24 h.

Various solvents were used in the model reaction with 2 mol % $Yb(OTf)_3$ as a catalyst; the results are summarized in Table 1. In this reaction, dichloromethane played an important role for the high yield (86%). When the reaction was carried out in acetonitrile, toluene, ether, methanol, DMF and THF, lower yields were observed (46% in acetonitrile, 19% in toluene, 27% in ether, 33% in methanol, 35% in DMF and 36% in THF). Furthermore, the reaction proceeded smoothly at room temperature in dichloromethane. If proceeding at high temperature (in refluxing dichloromethane), the reaction gave mixtures of *cis*- and *trans*-products along with homophthalic amide. The lower reaction temperature resulted in an improvement of diasteroselective and yields. The use of $Yb(OTf)_3$ as a reaction catalyst for this transformation avoids the use of a moisture-sensitive catalyst and high temperature reaction conditions. $Yb(OTf)_3$ proved to be a efficient catalyst for promoting this reaction under mild conditions.



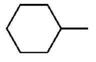
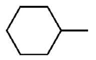
Scheme 1.

Table 1. Reaction of homophthalic anhydride, benzaldehyde and aniline under different reaction conditions.

Entry	Solvent[a]	Catalyst[b]	Additive	Yield [%][c]
1	CH_2Cl_2	None	$MgSO_4$	trace
2	CH_2Cl_2	$YbCl_3$	$MgSO_4$	65
3	CH_2Cl_2	$TbCl_3$	$MgSO_4$	63
4	CH_2Cl_2	$DyCl_3$	$MgSO_4$	55
5	CH_2Cl_2	$Nd(OTf)_3$	$MgSO_4$	73
6	CH_2Cl_2	$Sm(OTf)_3$	$MgSO_4$	74
7	CH_2Cl_2	$Yb(OTf)_3$	$MgSO_4$	86
8	CH_2Cl_2	$Yb(OTf)_3$	4 Å	84
9	CH_3CN	$Yb(OTf)_3$	$MgSO_4$	46
10	toluene	$Yb(OTf)_3$	$MgSO_4$	19
11	Et_2O	$Yb(OTf)_3$	$MgSO_4$	27
12	CH_3OH	$Yb(OTf)_3$	$MgSO_4$	33
13	DMF	$Yb(OTf)_3$	$MgSO_4$	35
14	THF	$Yb(OTf)_3$	$MgSO_4$	36
15	CH_2Cl_2	$Yb(OTf)_3$[d]	$MgSO_4$	85, 84, 83

[a] All reactions were carried out at room temperature for 2 h.
[b] 2 mol % of catalyst was used.
[c] Yield of isolated product.
[d] Catalyst was reused three times.

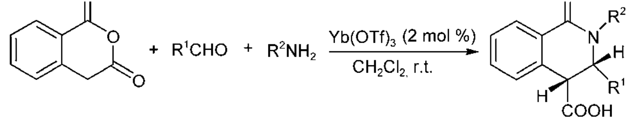
Table 2. One-pot synthesis of *cis* -isoquinolonic acid derivatives catalyzed by $Yb(OTf)_3$.[a]

Entry	R^1(-CHO)	R^2(-NH_2)	Product	Yield [%][b]
1	Ph	Ph	**4a**	86
2	Ph	4-MeC_6H_4	**4b**	80
3	Ph	3,4-$Me_2C_6H_3$	**4c**	84
4	4-$MeOC_6H_4$	4-Me-C_6H_4	**4d**	83
5	4-$MeOC_6H_4$	*i*-C_3H_7	**4e**	85
6	4-$Me_2NC_6H_4$	*i*-C_3H_7	**4f**	92
7	C_3H_7		**4 g**	78
8	Ph		**4 h**	79
9	*i*-C_3H_7	*i*-C_3H_7	**4i**	82
10	2-Me-C_6H_4	4-ClC_6H_4	**4j**	88
11	Ph	4-ClC_6H_4	**4k**	85
12	Ph	4-BrC_6H_4	**4 l**	88
13	2-$NO_2C_6H_4$	Ph	**4 m**	80
14	4-$MeOC_6H_4$	$C_6H_5CH_2$	**4n**	89
15	4-$NO_2C_6H_4$	Ph	**4′o**[c]	93

[a] All reactions were carried out at room temperature in CH_2Cl_2 at for 2 h.
[b] Yield of isolated product.
[c] 2-[*E*-1,2-benzamide-(4-nitrobenzo)ethenyl]benzoic acid.

To examine the scope of this process, several examples for the synthesis of *cis*-isoquinolonic acids were studied in the presence of catalytic amounts (2 mol %) of $Yb(OTf)_3$ and anhydrous $MgSO_4$ in dichloromethane and the results are summarized in Table 2. The three-component one-pot reaction of various aldehydes, amines and homophthalic anhydride was clean and highly diastereoselective, and proceeded smoothly to give the corresponding *cis*-isoquinolonic acids **4** in good to excellent yields (Scheme 2). A variety of substituted aromatic and aliphatic aldehydes carrying either electron-donating or -withdrawing substituents afforded high yields of products. Most importantly, both aromatic and aliphatic amines reacted easily under these conditions to afford the desired *cis*-products in satisfactory yields. In all reactions, the products were obtained as the *cis*-diastereomer, and their structures were confirmed by detailed ^1H NMR analysis.

In theory the most diagnostic parameter for the *cis*- and *trans*-configuration is the scalar coupling constant between protons H-3 and H-4. In the compounds **4a**–**n** the coupling constant $J_{(H\text{-}3,H\text{-}4)} = 4.2–6.0$ Hz is typical for the *cis* configuration. In the *trans* compounds the coupling constant $J_{(H\text{-}3,H\text{-}4)}$ is significantly smaller than for the *cis* configuration (typical value 0–2 Hz).[9]

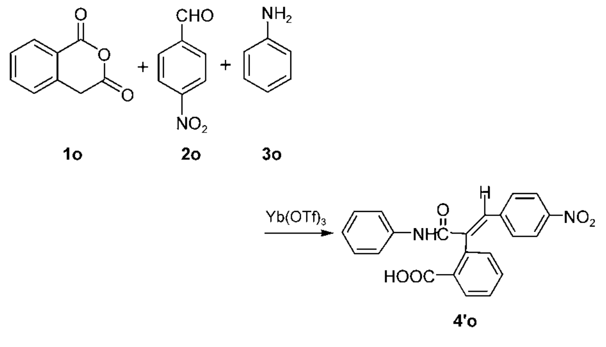


1 2 3 4

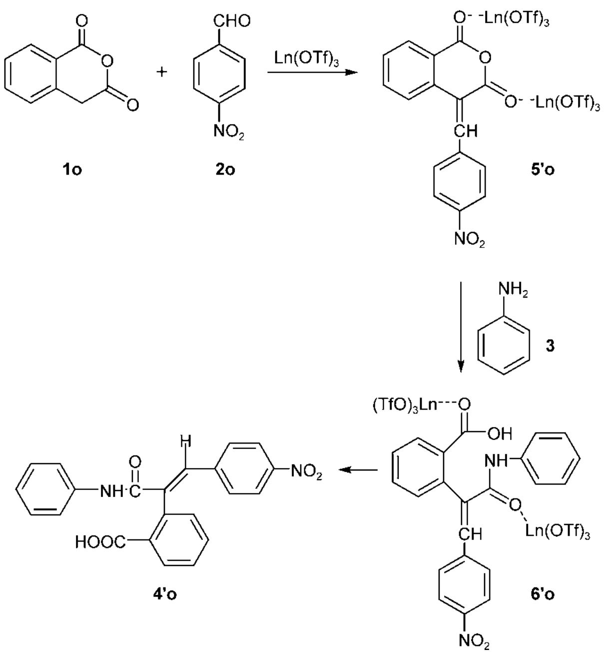
Scheme 2.

Remarkably, the reaction of *p*-nitrobenzaldehyde (**2o**), aniline (**3o**) and homophthalic anhydride did not give the corresponding isoquinolonic acid, but rather afforded 2-[*E*-1,2-benzamide-(4-nitrobenzo)ethenyl]benzoic acid (**4′o)** as the corresponding product (Scheme 3). A possible mechanism to account for the formation of **4′o** is illustrated in Scheme 4. Presumably, *p*-nitrobenzaldehyde is first activated by $Yb(OTf)_3$ because of the strong electron-withdrawing substituent (NO_2) showing a higher reactivity. The reaction may proceed through the $Yb(OTf)_3$-catalyzed aldol condensation reaction of *p*-nitrobenzaldehyde and homophthalic anhydride to yield the 4-(*p*-nitrobenzylidene)homophthalic anhydride intermediate (**5′o**) which is stabilized by the lanthanide, with subsequent acetylization and ring-opening reactions resulting in the formation of 2-[*E*-1,2-benzamide-(4-nitrobenzo)ethenyl]benzoic acid (**4′o**), an X-ray crystallographic analysis of which was performed to confirm the molecular structure (Figure 1). A similar phenomenon has also been reported in the synthesis of optically active aromatic α-hydroxy esters.[13] It appears that the reaction can only proceed with an activated aromatic system such as phenol, since no reaction was observed under the same conditions with alkylbenzenes. Especially, a strong electron-withdrawing group on the phenol ring (e.g., *p*-nitrophenol) significantly deactivated the system and prevented the reaction from happening.

To explore the mechanism of the reaction, we carried out several reactions catalyzed by lanthanide triflate un-



Scheme 3.



Scheme 4.

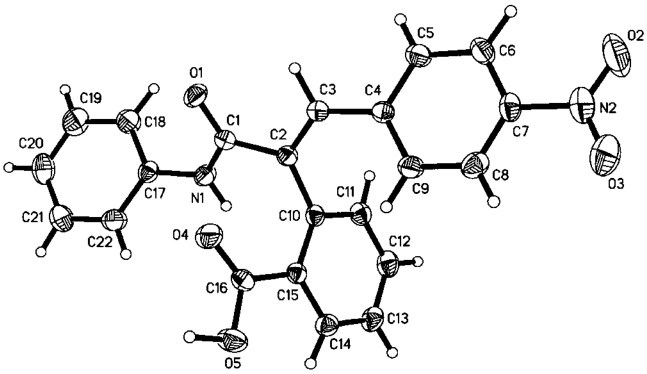
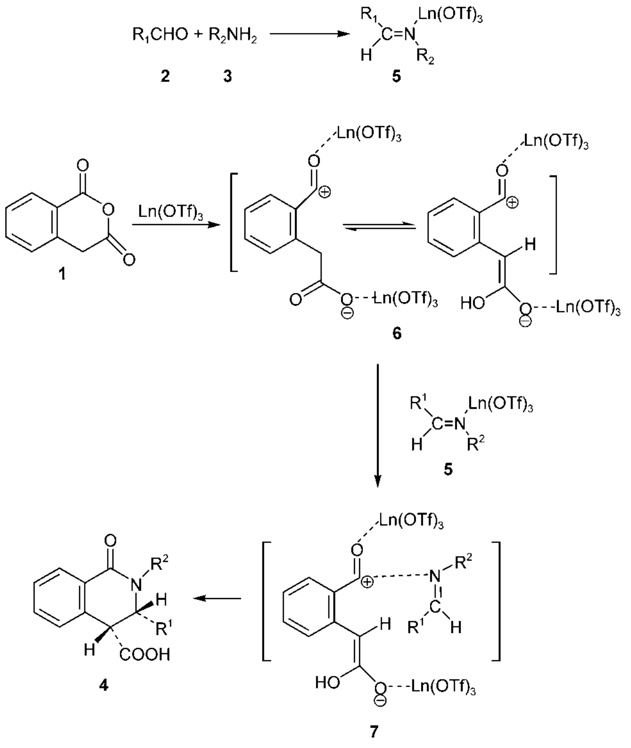


Figure 1. X-ray molecular structure of **4′o** with the atom numbering scheme.



Scheme 5.

der the optimized conditions. First of all, the reaction of homophthalic anhydride and aniline with benzaldehyde, contrary to our expectation, gave an *N*-phenylhomophthalic amide, and the end product was not observed. Besides *p*-nitrobenzaldehyde, the cycloaddition reaction of homophthalic anhydride with benzaldehyde did not occur to give 3,4-dihydroisocoumarin-4-carboxylic acid underwent catalysis by the Lewis acid lanthanide triflate as reported by Gesquiere.[14] Moreover, to prove that the imine was produced, benzaldehyde was reacted with aniline to give the corresponding benzylideneaniline, and the latter was used for the following reaction without purification. Thus, treatment of benzylideneaniline with homophthalic anhydride in the presence of lanthanide triflate resulted in formation of 1-oxo-2,3-diphenyl-1,2,3,4-tetrahydro-4-isoquinolinecarboxylic acid as the expected product.

We have proposed a mechanism similar to that of Cushman[2] and Gesquiere[9] for the lanthanide triflate-catalyzed reaction as shown in Scheme 5. The reaction of the aldehyde **2** with amine **3** first afforded the imine as intermediate **5**, which is stabilized by the lanthanide triflate. Subsequently, the homophthalic anhydride **1** is activated by the lanthanide triflate, leading to a more reactive intermediate **6**, a mobile equilibrium of **6** exists between the ketone and enol tautomers. Nucleophilic attack of the imine nitrogen of the intermediate **5** on the carbonyl carbon of the intermediate **6**, in which steric factors are increased by the lanthanide triflate, gives the less sterically hindered intermediate **7** and finally product **4** as the *cis*-isomer.

Conclusion

In conclusion, lanthanide triflate was found to be a highly efficient and convenient catalyst in the one-pot reaction of homophthalic anhydride, aldehydes and amines to afford *cis*-isoquinolonic acid derivatives in good to excellent yields. This method offers several advantages including mild reaction conditions, enhanced reaction rates, clean reaction profiles, small quantity of catalyst, high diastereoselectivity, no by-products such as homophthalic amides or other side products, operational and experimental simplicity, making it a useful and attractive strategy for the synthesis of *cis*-isoquinolonic acid derivatives. In addition, the catalyst lanthanide triflate can be easily recovered from the aqueous layer after the reaction and can be reused with no loss of activity.

Experimental Section

General Methods

^{1}H NMR spectra were recorded at 500 MHz in $CDCl_3$ using TMS as internal reference. ^{13}C NMR spectral measurements were performed at 75.4 MHz using $CDCl_3$ as an internal standard. IR spectra were obtained on an FTS-185 as neat films. Mass spectra were determined on a Finigan 8230 mass spectrometer.

Catalysts

The rare earth catalysts were prepared by the reported procedure and dried by heating at 200 °C under reduced pressure prior to use.[15] The catalyst $Yb(OTf)_3$ remaining in the aqueous phase after the reaction can be recovered by removing the water through heating and then dying under vacuum at 100 °C for 2 h.

One-Pot Reaction of Aldehydes, Amines and Homophthalic Anhydride; Typical Procedure

Aldehyde **2** (1.0 mmol), amine **3** (1.0 mmol) and homophthalic anhydride **1** (1.2 mmol) in CH_2Cl_2 (1.0 mL) were added to a suspension of $Yb(OTf)_3$ (0.02 mmol, 2 mol %) and $MgSO_4$ (125 mg) in 4.0 mL CH_2Cl_2 at room temperature. The mixture was stirred for 2.0 h at room temperature, and then the CH_2Cl_2 was removed under reduced pressure. Water was added, and the product was extracted with EtOAc. After the organic layer had been dried (Na_2SO_4) and evaporated, the crude product was chromatographed on silica gel to afford the compound **4**.

Characterization data for *cis*-isoquinolonic acid derivatives **4** and the details of the crystallographic study on *cis*-isoquinolonic acid derivative **4′o** are provided in the Supporting Information.

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