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Frustrated Lewis Acid/Brønsted Base Catalysts for Direct Enantioselective α-Amination of Carbonyl Compounds

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Supporting Information

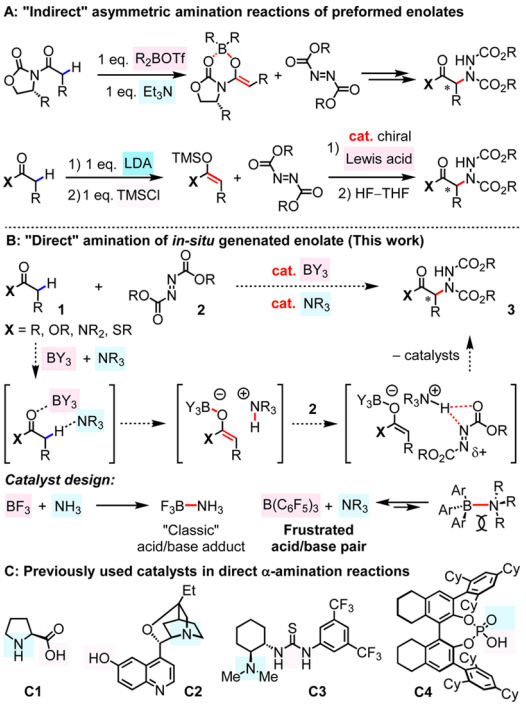
ABSTRACT: A method for enantioselective direct α-amination reaction catalyzed by a sterically "frustrated" Lewis acid/Brønsted base complex is disclosed. Cooperative functioning of the Lewis acid and Brønsted base components gives rise to in situ enolate generation from monocarbonyl compounds. Subsequent reaction with hydrogen-bond activated dialkyl azodicarboxylates delivers α-aminocarbonyl compounds in high enantiomeric purity.

Stereoselective synthesis of C−N bonds, which can be found in a large number of biologically active molecules, represents a frontier endeavor in chemistry.[1−6] Electrophilic amine sources such as dialkyl azodicarboxylates, nitrosoarenes, and oxaziridines have been used extensively in the diastereo- or enantio-controlled generation of amine-bearing stereogenic centers through reaction with preformed enolate equivalents (Scheme 1A).[3−6] Recently, enantioselective "direct" amination of carbonyl compounds involving in situ nucleophile generation has emerged as an atom- and step-economical approach for preparation of these important molecules (Scheme 1B,C).[2,7,8] One strategy entails the use of a cooperative Lewis acid/Brønsted base catalyst which promotes both deprotonation of a carbonyl pronucleophile to generate an enolate equivalent and its enantioselective reaction with the amination reagent.[2,9−11] However, a key unsolved issue in enantioselective cooperative catalysis is that mutual quenching can occur to inhibit the desired transformation. To address this complication, the majority of bifunctional catalysts (e.g., **C2**-**C4**) have been equipped with mildly to moderately acidic and basic groups that only allow for deprotonation of preactivated substrates with acidic C−H bonds (e.g., 1,3-dicarbonyl and α-arylcarbonyl compounds).[10] With stronger chiral acid and/or base catalysts, self-quenching can be problematic.[7,8]

While contemplating the design of an enantioselective cooperative acid/base catalyst capable of promoting reactions between N-based electrophiles and unactivated carbonyl pronucleophiles, we considered a system that would contain an unquenched and more strongly Lewis acidic fragment along with a hindered Brønsted base unit (Scheme 1B). The frustrated Lewis pairs (FLPs) pioneered by Stephan and Erker consist of acidic and basic fragments that are not able to associate easily because of steric factors.[12] However, FLP-catalyzed enantioselective processes remain limited in large extent to hydrogenation or hydrosilylation processes.[12−14] By exploiting strongly acidic $B(C_6F_5)_3$ and hindered 1,2,2,6,6-pentamethylpiperidine (PMP), we recently demonstrated that these catalysts can overcome the self-quenching problem and promote the direct Mannich-type reaction.[15] Herein, we disclose the development of enantioselective direct α-amination of unactivated carbonyl compounds catalyzed by a readily accessible class of chiral frustrated $B(C_6F_5)_3$/amine complexes.

We envisioned a set of transformations that would begin by a boron-based Lewis acid binding to carbonyl pronucleophiles to enhance the acidity of an α-C−H bond. Ensuing deprotonation by a hindered ("soft") amine would then result in the formation of a tightly bound ionic pair consisting of a boron enolate and an ammonium cation;[16] the latter component may then serve as a Brønsted acid to activate electrophilic amination reagent **2** while precisely positioning it for reaction with the enolate component to afford aminocarbonyl products **3** (Scheme 1B). A critical advantage of the proposed strategy is that tethering of acidic and basic catalyst components is not necessary, allowing for facile and

Scheme 1. "Indirect" and "Direct" α-Amination Reactions



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independent modification of each component for optimization of reaction efficiency and/or enantioselectivity.

We began by examining the ability of achiral Lewis acid/Brønsted base catalysts to promote the desired transformation. α-Tetralone (**1a**) and dialkyl azodicarboxylates (**2**) were reacted with $B(C_6F_5)_3$/amines serving as potential catalysts (Table 1).

Table 1. Evaluation of Reaction Parameters[a,b]

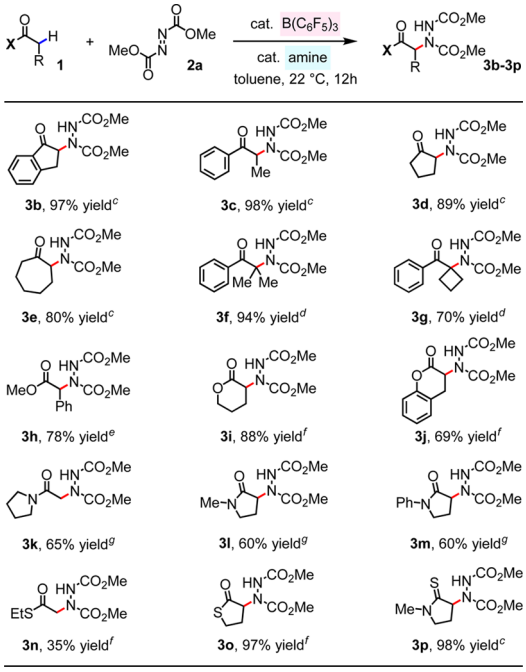
entry	Lewis acid	Brønsted base	$RCO_2N{=}NCO_2R$ (2)	yield (%)
1	$B(C_6F_5)_3$	none	$MeCO_2N{=}NCO_2Me$	0
2	none	PMP[c]	$MeCO_2N{=}NCO_2Me$	0
3	$B(C_6F_5)_3$	Et_3N	$MeCO_2N{=}NCO_2Me$	32
4	$B(C_6F_5)_3$	*i*-Pr_2NEt	$MeCO_2N{=}NCO_2Me$	90
5	$B(C_6F_5)_3$	$PhNMe_2$	$MeCO_2N{=}NCO_2Me$	<5
6	$B(C_6F_5)_3$	DBU[c]	$MeCO_2N{=}NCO_2Me$	12
7	$B(C_6F_6)_3$	Barton's base[c]	$MeCO_2N{=}NCO_2Me$	<5
8	$B(C_6F_5)_3$	TMP[c]	$MeCO_2N{=}NCO_2Me$	84
9	$B(C_6F_5)_3$	PMP[c]	$MeCO_2N{=}NCO_2Me$	>95
10	$B(C_6F_5)_3$	PMP[c]	$EtCO_2N{=}NCO_2Et$	80
11	$B(C_6F_5)_3$	PMP[c]	$BnCO_2N{=}NCO_2Bn$	22
12	$B(C_6F_5)_3$	PMP[c]	*t*-$BuCO_2N{=}NCO_2$*t*-Bu	0

[a]Conditions: α-tetralone (0.2 mmol), dialkyl azodicarboxylate (0.3 mmol), acid (5 mol %), base (10 mol %), toluene (1.0 mL), under N_2, 22 °C, 12 h. [b]Yields were determined by ^1H NMR analysis of unpurified reaction mixtures with mesitylene as the internal standard. [c]DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, Barton's base =2-*tert*-butyl-1,1,3,3-tetramethylguanidine, TMP = 2,2,6,6-tetramethylpiperidine, PMP = 1,2,2,6,6-pentamethylpiperidine.

No product was formed in the absence of an amine or $B(C_6F_5)_3$ (entries 1, 2). With 5.0 mol % of $B(C_6F_5)_3$ and 10 mol % of Et_3N the reaction between **1a** and dimethyl azodicarboxylate (**2a**, DMAD) in toluene at 22 °C afforded **3a** in 32% yield (Table 1, entry 3). With the less basic *N*,*N*-dimethylaniline there was hardly any product obtained (entry 5, <5% yield) and with DBU and Barton's base, yields were low as well (entries 6, 7). In contrast, the transformation proceeded efficiently when PMP was employed (entry 9, >95%). These observations are consistent with the hypothesis that highly acidic $B(C_6F_5)_3$ and sterically hindered PMP can serve as an effective catalyst combination for the direct α-amination reaction. Alkyl-substituents of azodicarboxylate were found to have a strong influence on efficiency, as use of the more hindered diethyl, benzyl and *tert*-butyl-substituted electrophiles led to diminished yields (entries 10–12). The reaction was higher yielding in a nonpolar solvent (e.g., toluene), which is consistent with the hypothesis that ionic and H-bonding interactions are likely critical (Scheme 1B).[8,16]

Cyclic as well as acyclic ketones participate effectively in direct α-amination reactions with **2a** catalyzed by 5 mol % of $B(C_6F_5)_3$ and 10 mol % of PMP (Table 2, 3b–e). Cyclopentanone and cycloheptanone which lack a fused aromatic group gave **3d** in 89% yield and **3e** in 80% yield. Using 10 mol % of $B(C_6F_5)_3$ and 20 mol % of less hindered *N*-methylmorphiline, α,α′-disubstituted aminoketones **3f** and **3g** were obtained in 94% and 70% yield, respectively. Lactone containing **3i** and **3j** were isolated in 88% and 69% yield in the presence of 10 mol % of $B(C_6F_5)_3$ and 20 mol % of PMP. The more basic Barton's base was required for deprotonation of amides. Acyclic and cyclic amides were readily transformed to the corresponding products

Table 2. Catalytic Amination of Different Pronucleophiles[a,b]



[a]Conditions: pronucleophile (0.2 mmol), dimethyl azodicarboxylate (0.3 mmol), $B(C_6F_5)_3$, amine, toluene (1.0 mL), under N_2, 22 °C, 12 h. [b]Yield of isolated and purified products. [c]$B(C_6F_5)_3$ (5 mol %) and PMP (10 mol %) were used. [d]$B(C_6F_5)_3$ (10 mol %) and *N*-methylmorpholine (20 mol %) were used. [e]$B(C_6F_5)_3$ (10 mol %) and PMP (10 mol %) were used. [f]$B(C_6F_5)_3$ (10 mol %) and PMP (20 mol %) were used. [g]$B(C_6F_5)_3$ (10 mol %) and Barton's base (20 mol %) were used.

in 60–65% yield (**3k–m**). Thioesters could be deprotonated by PMP, delivering **3n** and **3o** in 35% and 97% yield, respectively. α-Amination of 2-pyrrolidinethione proceeded to afford **3p** in quantitative yield.

We then focused on the development of an enantioselective version of the catalytic process with **1a** serving as the model substrate (Scheme 2 and Table 3). Chiral amine catalysts were easily prepared from commercial chiral amines, and their derivatization, storage and handling are less complicated compared to chiral boron-based Lewis acids.[12,13] Therefore, we chose to center our initial studies on the development of catalysts that consist of $B(C_6F_5)_3$ and chiral amine catalysts (Scheme 2).

The tertiary amine moiety of **C-mono** was expected to play the role of a Brønsted base in deprotonation of $B(C_6F_5)_3$-activated **1a**; after deprotonation, the amine group would be transformed into a Brønsted acid that could associate with a basic moiety of **2a** by a single H-bonding interaction (**A**). Catalyst-activated enolate and DMAD fixed within the catalyst framework would undergo enantiodetermining C–N bond formation to give **3a**. However, transformations between α-tetralone **1a** and DMAD **2a** with chiral amine catalysts such as **C5**, **C6** and (−)-sparteine (**C7**) afforded *rac*-**3a** (Table 3). Accordingly, we posited that a single H-bonding interaction between chiral ammonium ion and **2a** might not be sufficient for promoting a highly enantioselective C–N bond forming process (Scheme 2, A).[8,16] For a more directional catalyst–electrophile binding, we decided to evaluate the dual H-bond donors derived from the amine groups of **C-di**. We surmised that the second N–H unit of **C-di**, attached to an electron-withdrawing substituent, would function as an additional H-bond donor (**B**). Dual H-bonding interactions could as a

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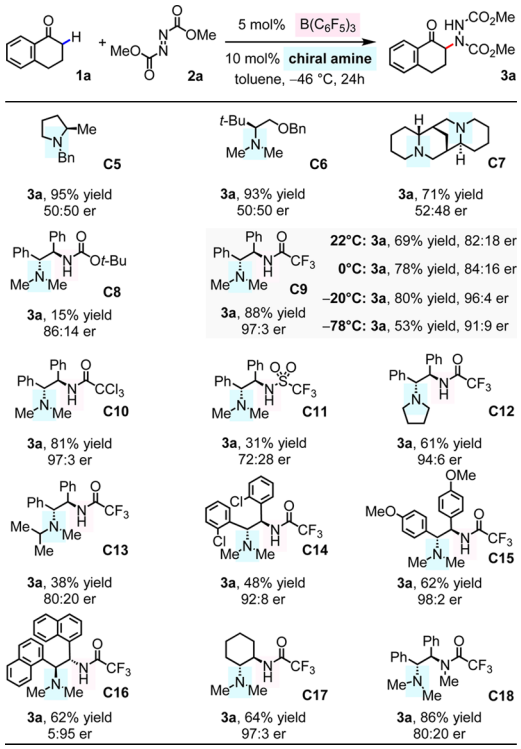
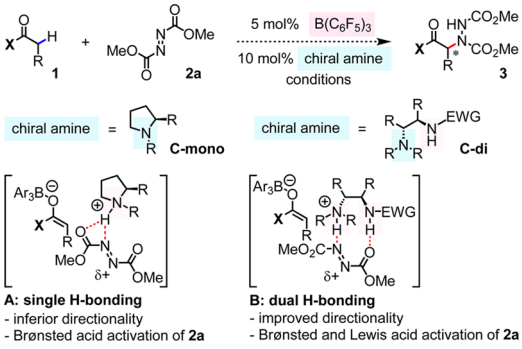
Table 3. Evaluation of Chiral Amine Catalysts[a,b]



[a]Conditions: α-tetralone (0.2 mmol), dimethyl azodicarboxylate (0.3 mmol), acid (5 mol %), base (10 mol %), toluene (1.0 mL), under N_2, −46 °C, 24 h. [b]Yields were determined by ^{1}H NMR analysis of unpurified reaction mixtures with mesitylene as the internal standard. Er was determined by HPLC analysis of the purified product.

Scheme 2. Designing of Chiral Amine Catalysts

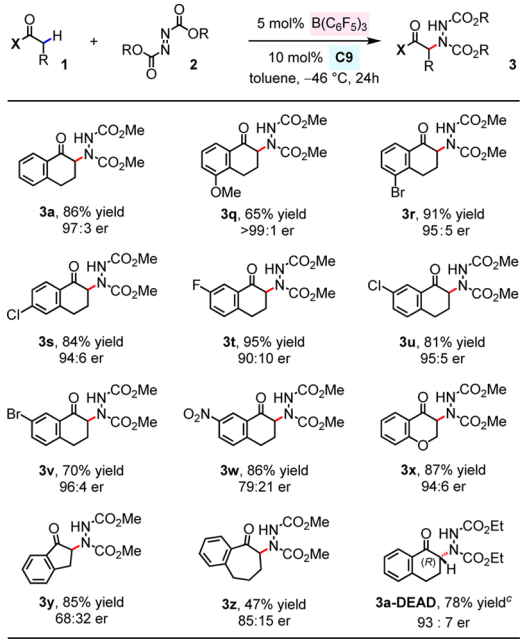


result offer additional electrophile activation, accelerating the enantioselective C−N bond formation by increasing conformational restriction (vs single H-bonding in panel A).[8]

(1*R*,2*R*)-(+)-1,2-Diphenylethylenediamine was converted into diamine catalysts (**C8**−**C13**). *N*-Boc-substituted **C8** generated **3a** inefficiently (15% yield) but in a promising 86:14 er. Yield as well as enantioselectivity were improved (88% and 97:3 er) when the more electron-withdrawing and less hindered *N*-trifluoroacetyl-substituted **C9** was utilized. Enantioselectivity proved to be highly dependent on the reaction temperature: **3a** was obtained in 82:18 er at 22 °C, 84:16 er at 0 °C, and 96:4 er at −20 °C (69−80% yield); at −78 °C, **3a** was obtained in 53% yield and 91:9 er. Diamines containing *N*-trichloroacetyl (**C10**) and *N*-triflyl (**C11**) groups gave **3a** in 97:3 and 72:28 er, respectively. Installation of other *N*,*N*,-dialkyl groups to diamine catalysts (**C12**, **C13**) resulted in lower yield and er. Chiral 1,2-diarylethylenediamines were converted to **C14**, **C15** and **C16**. *ortho*-Chlorophenyl (**C14**) and 1-naphthyl (**C16**)-substituted catalysts were less enantioselective. The highest enantioselectivity (98:2 er) was observed with **C15** but at the cost of diminished yield (62%). Reaction with cyclohexyldiamine **C17** generated **3a** in 64% yield and 97:3 er. With **C18**, prepared by *N*-methylation of **C9**, **3a** was formed in 80:20 er (vs 97:3 er with **C9**). These results clearly point to the effectiveness of dual H-bonding strategy.

A range of cyclic ketones are suitable for enantioselective direct α-amination reactions catalyzed by 5 mol % $B(C_6F_5)_3$ and 10 mol % **C9** (Table 4). Methoxy, fluoro-, chloro- and bromo-substituted

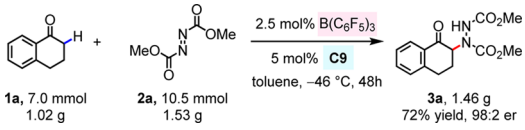
Table 4. Direct Enantioselective α-Amination Reactions[a,b]



[a]Conditions: pronucleophile (0.2 mmol), dialkyl azodicarboxylate (0.3 mmol), $B(C_6F_5)_3$ (5 mol %), **diamine C9** (10 mol %), toluene, under N_2, −46 °C, 24 h. [b]Yields of purified products. Er was determined by HPLC analysis. [c]The absolute configuration of **3a-DEAD** was determined to be *R* (see ref 17).

α-tetralone derivatives **3q**−**3v** were converted to the corresponding products in 90:10 to >99:1 er. Nitro-substituted **3w** was generated in 86% yield and 79:21 er, probably due to competing H-bonding by the nitro group. Chroman-4-one was converted to **3x** in 87% yield and 94:6 er; **3y** (85% yield, 68:32 er) and **3z** (47% yield, 85:15 er) were prepared through reactions with α-indanone and 1-benzosuberone. Using more hindered diethyl azodicarboxylate (DEAD), **3a-DEAD** was obtained in 78% yield and 93:7 er.[17] The catalytic protocol is scalable, as highlighted by the gram-scale synthesis of **3a** (72% yield, 98:2 er) in the presence of 2.5 mol % $B(C_6F_5)_3$ and 5 mol % **C9** (Scheme 3). However, our studies indicate that the tertiary amine moiety of **C9** is not sufficiently basic for efficient deprotonation of esters, amides and

Scheme 3. Gram Scale Synthesis of 3a



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thioesters. To address this latter reactivity issue and to expand the scope of the enantioselective method, we are evaluating the effectiveness of a number of catalysts that contain a more basic guanidine derivative.

In summary, we have developed a catalytic method for $B(C_6F_5)_3$/amine-catalyzed direct α-amination reaction that provides access to an assortment of α-aminocarbonyl compounds with ketones, esters, amides, thioesters and thioamides serving as suitable pronucleophiles. We have also been able to develop an efficient enantioselective variant of the process. Based on our mechanistic hypothesis, it should be possible to broaden the scope of this enantioselective addition reaction through design of more potent chiral Lewis acid/Brønsted base catalyst combinations. Investigations along these lines are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11908.

Experimental procedures and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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