Asymmetric Conjugate Addition

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Highly Enantioselective Aza-Michael Reaction between Alkyl Amines and β-Trifluoromethyl β-Aryl Nitroolefins

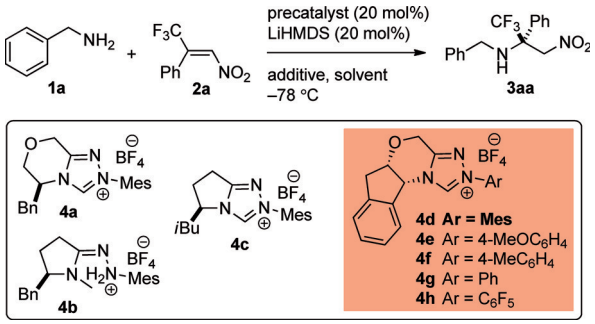
*Leming Wang, Jiean Chen, and Yong Huang**

Abstract: *The aza-Michael addition reaction is a vital transformation for the synthesis of functionalized chiral amines. Despite intensive research, enantioselective aza-Michael reactions with alkyl amines as the nitrogen donor have not been successful. We report the use of chiral N-heterocyclic carbenes (NHCs) as noncovalent organocatalysts to promote a highly selective aza-Michael reaction between primary alkyl amines and β-trifluoromethyl β-aryl nitroolefins. In contrast to classical conjugate-addition reactions, a strategy of HOMO-raising activation was used. Chiral trifluoromethylated amines were synthesized in high yield (up to 99%) with excellent enantioselectivity (up to 98% ee).*

The asymmetric aza-Michael reaction is arguably one of the most straightforward methods for the synthesis of important 1,2-difunctionalized chiral building blocks, such as 1,2-diamines.[1] Many successful combinations of nitrogen nucleophiles and electron-deficient olefins have been reported, with either Lewis acid catalysts[2] or organocatalysts.[3] However, two key problems remain largely unsolved: the use of alkyl amines as the nitrogen source, and the construction of tertiary stereocenters with a nitrogen substituent. Simple alkyl amines tend to form stable complexes with Lewis acids, which not only deactivates the catalyst, but also renders the aza-Michael reaction reversible.[4] In the case of organocatalysis, primary and secondary amines interfere with both LUMO-lowering iminium activation (competing imine/iminium formation) and proton catalysis (acid–base neutralization). As a result, research efforts have been mostly concentrated on modulating the basicity of the donor nitrogen atom (Scheme 1). For example, MacMillan and co-workers used *N*-silyloxycarbamates as a nonbasic nitrogen source for aza-Michael reactions of α,β-unsaturated aldehydes.[5] Jørgensen and co-workers reported the use of 1,2,4-triazoles as good amine surrogates for secondary-amine-catalyzed enantioselective aza-Michael reactions with α,β-unsaturated aldehydes.[6] Nonbasic benzotriazoles,[7] 5-phenyltetrazoles,[8] hydroxylamines,[9] hydrazones,[10] azides,[11] anilines,[12] hydrazides,[13] imides,[14] and imines[15] have also been reported as valid nitrogen sources for asymmetric aza-Michael reactions under iminium catalysis. Ooi and co-workers reported a unique arylaminophosphonium-catalyzed asymmetric addition of 2,4-dimethoxyanilines to nitroolefins.[16]

The only reaction of this type involving a basic amine was reported by Sundararajan and Prabagaran, who used a polymer-supported Lewis acid as the catalyst and found that benzyl amine reacted with ethyl cinnamate to give the product with 81% *ee*.[17] However, the arguably more useful reaction of unactivated alkyl amines has not been reported. Furthermore, nearly all aza-Michael reactions rely on LUMO-lowering activation mechanisms with Lewis acids, amine catalysts, or Brønsted acids. Herein, we report an enantioselective aza-Michael reaction between primary alkyl amines and β-trifluoromethyl β-aryl nitroolefins for the

Table 1: Optimization of the reaction conditions.[a]



Entry	Catalyst	Additive	Solvent	Yield [%][b]	*ee* [%][c]
1	**4a**	HFIP, 4 Å MS	toluene	88	−13
2	**4b**	HFIP, 4 Å MS	toluene	85	−16
3	**4c**	HFIP, 4 Å MS	toluene	90	2
4	**4d**	**HFIP, 4 Å MS**	**toluene**	**99**	**91**
5	**4e**	HFIP, 4 Å MS	toluene	80	51
6	**4f**	HFIP, 4 Å MS	toluene	90	28
7	**4g**	HFIP, 4 Å MS	toluene	70	7
8	**4h**	HFIP, 4 Å MS	toluene	50	0
9[d]	**4d**	HFIP, 4 Å MS	toluene	83	15
10	**4d**	HFIP, 5 Å MS	toluene	57	52
11	**4d**	HFIP, 4 Å MS	CH_2Cl_2	70	3
12	**4d**	HFIP, 4 Å MS	THF	99	0
13	**4d**	HFIP, 4 Å MS	Et_2O	70	76
14	**4d**	HFIP, 4 Å MS	MTBE	85	36
15	**4d**	4 Å MS	toluene	23	87
16	**4d**	HFIP	toluene	25	4

[a] Reaction conditions, unless otherwise specified: **1a** (0.1 mmol), **2a** (0.05 mmol), NHC precatalyst (20 mol%), HFIP (40 mol%), 4 Å MS (100 mg), solvent (1.2 mL), −78 °C, 36 h. [b] The yield was determined by GC with biphenyl as an internal standard. [c] The *ee* value was determined by HPLC on a chiral stationary phase. [d] The reaction was performed at −40 °C with 10 mol% of the catalyst. HFIP = hexafluoroisopropanol, Mes = mesityl, MTBE = *tert*-butyl methyl ether.

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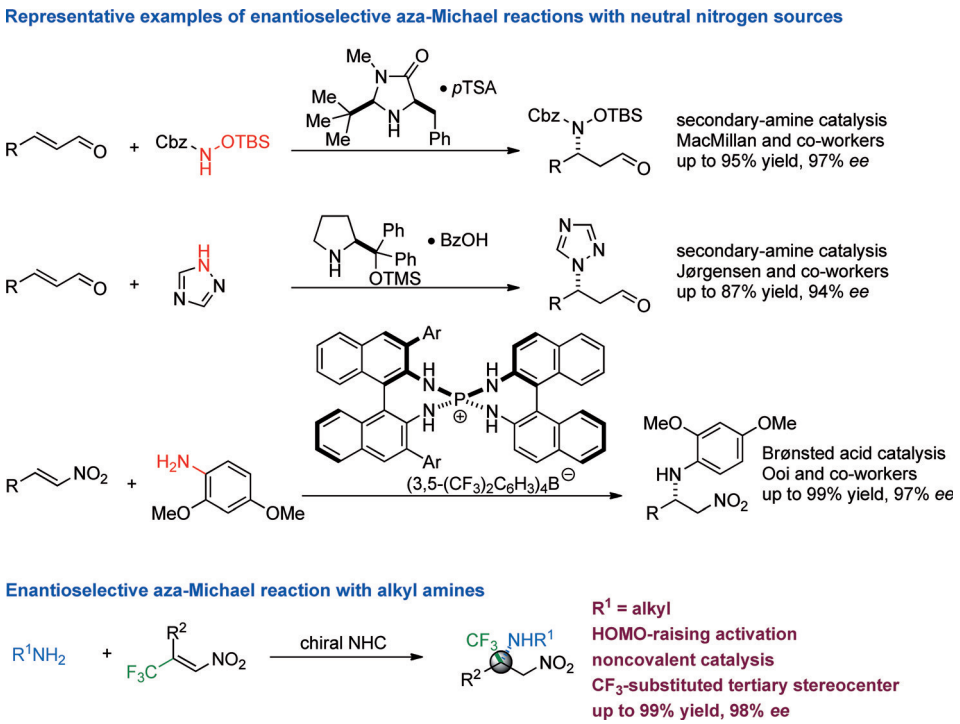


Scheme 1. Examples of enantioselective aza-Michael reactions, which were previously limited to the use of nonbasic nitrogen nucleophiles, and our approach with alkyl amines. Bz = benzoyl, Cbz = carboxybenzyl, TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl, *p*TSA = *p*-toluenesulfonic acid.

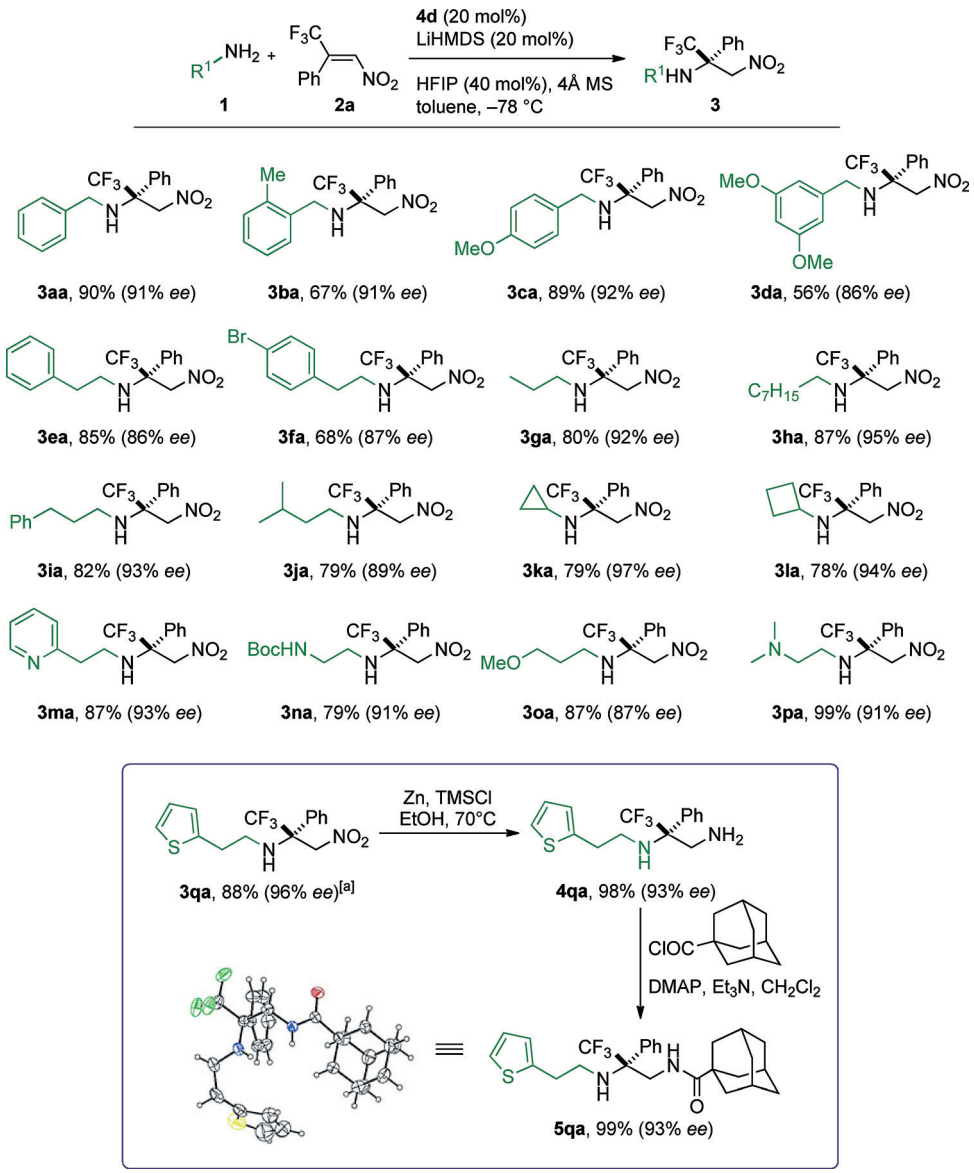
synthesis of chiral trifluoromethylated amines through HOMO-raising activation with a chiral NHC as a noncovalent catalyst. Although Brønsted base catalysis by NHCs has been described previously, asymmetric C–N bond formation in the presence of an NHC by this particular generic mode of catalysis has not been reported.[18,19]

Trifluoromethylated amines are popular amide isosteres for peptide medicinal chemistry.[20] Therefore, they have long been an important synthetic target for synthetic-method development. Chiral trifluoromethylated amines are accessed primarily through asymmetric Strecker-type reactions.[21] However, the synthesis of CF_3-containing 1,2-diamine scaffolds, a privileged motif in medicinal chemistry, often requires the use of toxic cyanides.[21b,g–i] The asymmetric aza-Michael reaction of β-CF_3-substituted nitroolefins is a straightforward alternative. Despite the intensive utilization of nitroolefins in aza-Michael reactions,[7a,d,13,15,16,22] enantioselective C–N bond formation has not been described for nitroolefins bearing a β-CF_3 substituent.[23] We envisioned that an enantioselective reaction between alkyl amines and β-trifluoromethyl β-aryl nitroolefins would offer a divergent route to 1,2-diamines bearing a CF_3-containing tertiary stereocenter.

Traditionally, aza-Michael reactions have been catalyzed by a LUMO-lowering pathway. Encouraged by our recent discovery of noncovalent catalysis with NHCs, we decided to explore the orthogonal approach of the HOMO-raising activation of basic alkyl amines through hydrogen bonding.[24] We initially investigated a reaction with benzylamine, as this compound is considerably less basic than simple alkyl amines. (*E*)-1-Phenyl-1-trifluoromethyl-2-nitroethene (**2a**) was used as the electrophile. The aza-Michael reaction occurred without any catalyst at room temperature, and the racemic product was obtained quantitatively. The reaction slowed down noticeably at a low temperature. Various NHCs derived from triazolium salts catalyzed this reaction at −78 °C, but only the aminoindanol-derived scaffold afforded a good level of enantioselectivity (Table 1, entries 1–4). The mesityl substituent on the catalyst was essential for asymmetric induction (Table 1, entries 4–8). The use of both THF and CH_2Cl_2 as solvents led to very poor enantioselectivity (Table 1, entries 11 and 12). In sharp contrast, toluene afforded high selectivity under otherwise identical conditions. Both molecular sieves (MS) and a proton shuttle (HFIP) were required. In the absence of molecular sieves, the racemic product was formed in low yield (Table 1, entry 16). Without HFIP, the enantioselectivity was little affected, but the yield was low (Table 1, entry 15). A catalytic amount of HFIP was sufficient to promote catalyst turnover.

Having established a protocol for the asymmetric aza-Michael reaction, we next examined the scope of the reaction in terms of the amine nucleophile. Reactions of substituted benzyl amines were effective: *ortho*, *meta*, and *para* substituents were all tolerated (Scheme 2). We were very pleased to find that simple primary amines are excellent substrates for the aza-Michael reaction. Both high yields and high *ee* values were observed across the board. Cyclic primary amines were found to be particularly selective. Cyclopropylamine and cyclobutylamine were converted into the desired products with 97% and 94% *ee*, respectively. Interestingly, a basic pyridine or tertiary amine substituent on the amine did not compromise selectivity, despite the presence of a potentially interfering basic site. Other functional groups, such as carbamate, ether, and thienyl groups, were all tolerated. The absolute configuration of product **3qa** was determined by single-crystal X-ray crystallography of its 1,2-diamine analogue **5qa**. We also treated one of the products **3aa** with a different amine in a cross-over experiment and found that the C–N bond-forming reaction was not reversible under our reaction conditions. Unfortunately, secondary amines do not participate in this reaction owing to steric hindrance.

The scope of the reaction with respect to the Michael acceptor was examined subsequently (Scheme 3). Various β-aryl β-trifluoromethyl nitroolefins reacted with primary amines to yield the trifluoromethyl-substituted amine products in good yield with good enantioselectivity. Substituents



Scheme 2. Scope of the reaction with respect to the amine nucleophile. Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), **4d** (20 mol%), HFIP (40 mol%), 4 Å MS (100 mg), toluene (1.2 mL), −78 °C, 36 h. Yields are for the isolated product. The *ee* values were determined by HPLC on a chiral stationary phase. [a] Compound **3qa** was obtained from a reaction carried out on a 1.0 mmol scale. Boc = *tert*-butoxycarbonyl, DMAP = 4-dimethylaminopyridine, HMDS = hexamethyldisilazide.

on the β-aryl moiety had a moderate electronic effect on the enantioselectivity. For example, the presence of a *p*-methoxy substituent resulted in higher enantioselectivity than that observed with less electron rich *p*-CF_3, *p*-F, and *p*-Cl groups. This observation is consistent with a weak π–π stacking interaction between the electrophile and the catalyst in the transition state.[19b,24] Reactions of β-heteroaryl and β-naphthyl substrates proceeded equally well. High selectivity was observed consistently with various cyclic and acyclic primary amines. In the case of β-alkyl substrates, the products were obtained in good yield, but with poor enantioselectivity.

The reaction of **1a** and **2a** was also carried out on a 1 mmol scale. Product **3aa** was isolated in 78% yield with 91% *ee* (Scheme 4). The nitro group can be conveniently reduced with zinc under acidic conditions to give versatile 1-trifluoromethyl-1,2-diamines.[25] These important building blocks, especially those bearing an *N*-alkyl group, are very difficult to access by the Strecker reaction. The chiral cyclic urea **6aa** was obtained by treating **4aa** with triphosgene.[26] Dihydroimidazole **7aa** was prepared by an oxidative cyclization with benzaldehyde in the presence of *N*-bromosuccinimide (NBS).[27] Both heterocycles contain a unique tertiary stereocenter bearing a CF_3, an aryl, and a nitrogen substituent.

We propose an H-bonding/π–π stacking dual interaction mechanism (Figure 1). Owing to the relatively high pK_a values of alkyl amines, deprotonation by the NHC catalyst is not possible. Presumably, the nucleophilicity of the nitrogen atom is enhanced by the formation of a hydrogen-bonded complex between the amine and the NHC. A chiral pocket is created in this complex in such a way that only one prochiral face of the bulky β-trifluoromethyl β-aryl nitroolefin can approach the nucleophile, whereby the CF_3 group is oriented away from the large mesityl substituent of the catalyst to avoid steric repulsion. A linear free-energy relationship (LFER) study suggested a weak π–π interaction between the β-aryl group and the positively charged NHC

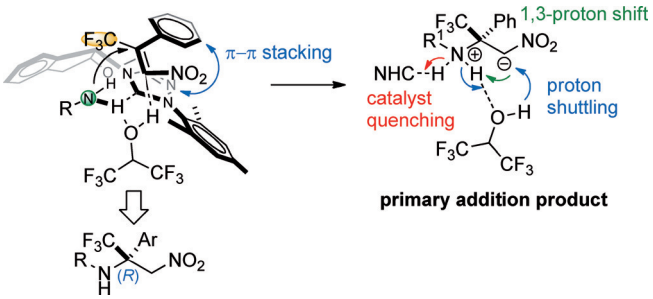
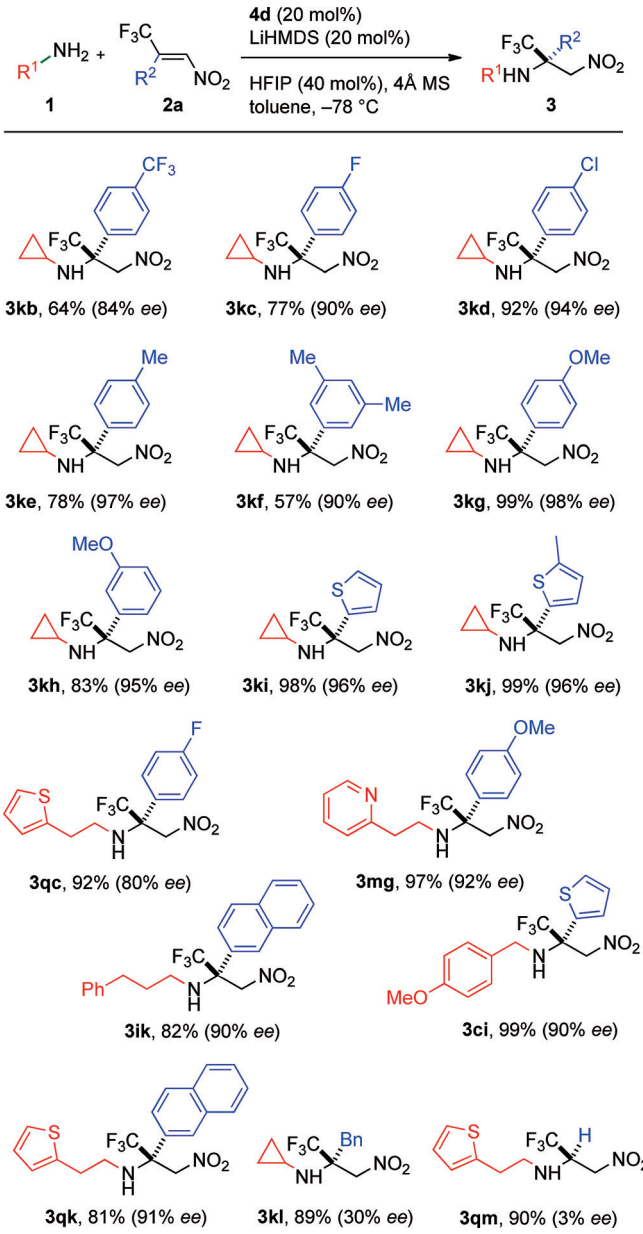
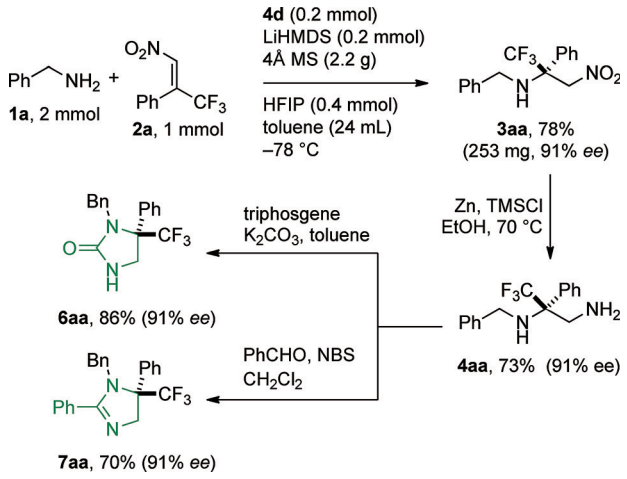


Figure 1. Proposed transition state and proton-shuttling mechanism.



Scheme 3. Scope of the reaction with respect to the nitroalkene. Reaction conditions: **1a** (0.1 mmol), **2a** (0.05 mmol), NHC precatalyst (20 mol%), HFIP (40 mol%), 4 Å MS (100 mg), toluene (1.2 mL), −78 °C, 36 h. Yields are for the isolated product. The *ee* values were determined by HPLC on a chiral stationary phase.

heterocycle (see the Supporting Information). The primary conjugate-addition adduct contains an acidic ammonium cation. In the absence of HFIP, this acidic species would quench the much more basic NHC rapidly (p*K*a 9.3 vs. 17.4; Figure 1, red arrow).[28] The competing 1,3-proton shift from the ammonium center to the nitroenolate is probably slow and reversible owing to similar pK_a values (9.3 vs. 8.9). As a result, reactions effectively shut down without an external proton-transfer agent (Table 1, entry 15). HFIP, with a nearly identical pK_a value (9.3), acts as an efficient shuttle to bridge proton transfer from the ammonium center to the nitroenolate (Figure 1, blue arrows).



Scheme 4. Synthesis of CF_3-containing chiral heterocycles.

In summary, we have developed the first highly enantioselective aza-Michael reaction of simple aliphatic amines. 1,2-Diamine analogues with a unique CF_3-bearing tertiary stereocenter can be prepared in high yield with high enantioselectivity. The noncovalent, HOMO-raising activation of the NHC overcomes the intrinsic problem of using a basic amine in LUMO-lowering catalysis. Furthermore, an acidic proton shuttle is used to prevent catalyst quenching and retain turnover. A dual role of the NHC is proposed: activation by hydrogen bonding and π–π stacking. We expect that this generic HOMO-raising noncovalent activation mode by NHCs will find wide application in enantioselective catalysis and cascade reactions.

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