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N-Heterocyclic Carbene-Catalyzed Truce–Smiles Rearrangement of *N*-Arylacrylamides via the Cleavage of Unactivated C(aryl)–N Bonds

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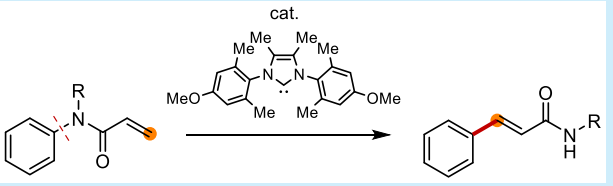
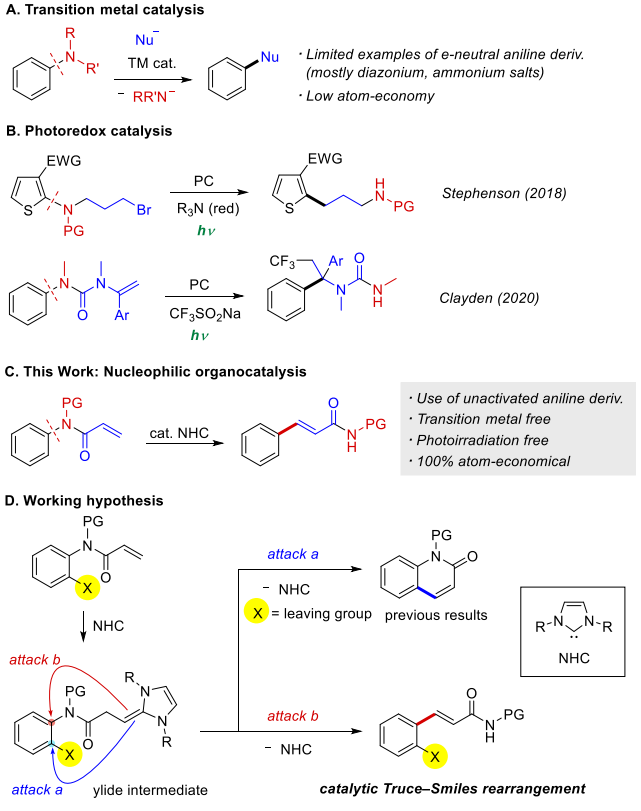
ABSTRACT: We report on the N-heterocyclic carbene (NHC)-catalyzed Truce–Smiles rearrangement of aniline derivatives, in which an unactivated C(aryl)–N bond is cleaved, leading to the formation of a new C(aryl)–C bond. The key to the success of this reaction is the utilization of a highly nucleophilic NHC, which enables the formation of a highly nucleophilic ylide intermediate that is generated from an α,β-unsaturated amide.



The catalytic transformation of C(aryl)–N bonds of aniline derivatives represents a formidable challenge due, in part, to their inertness (the BDE of Ph–NH_2: ca. 103 kcal/mol).[1] In fact, only a limited number of reports on the catalytic transformation of unactivated aniline derivatives have been appeared to date.[2,3] One major approach to this type of catalytic transformation of C(aryl)–N bonds involves the use of transition metal catalysts, which allows for cross-coupling type reactions, although the scope of both the aniline derivatives and the nucleophiles is significantly limited compared with that for the cross-coupling using aryl halides (Scheme 1A).[4,5] The Truce–Smiles rearrangement of aniline derivatives is a unique alternative approach for converting an unactivated C(aryl)–N bond to a C(aryl)–C bond via an intramolecular S_NAr reaction.[6,7] Although the Truce–Smiles rearrangement enables an otherwise difficult bond disconnection, the need for the use of a stoichiometric amount of a strong base (e.g., BuLi, LDA etc.) diminishes its synthetic utility, and therefore catalytic variants would be highly desirable. To date, only two reports have appeared on the catalytic Truce–Smiles rearrangement of aniline derivatives, both of which are based on photoredox catalysis (Scheme 1B). Stephenson reported on the photocatalytic Truce–Smiles rearrangement of aminothiophene derivatives, in which an alkyl radical generated from a pendant alkyl halide moiety mediates the C–N bond cleavage.[8] Clayden reported on a photocatalytic two component coupling that involves the Truce–Smiles rearrangement of aniline derivatives.[9] We report herein that a simple nucleophilic catalysis by an N-heterocyclic carbene can be used to promote the Truce–Smiles rearrangement of readily available aniline derivatives (Scheme 1C). Unlike the radical-based approach, photoirradiation is not required, and no radical precursors are involved, thus allowing for 100% atom economy.[10]

Scheme 1. Catalytic Transformation of C(aryl)–N Bonds



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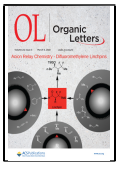

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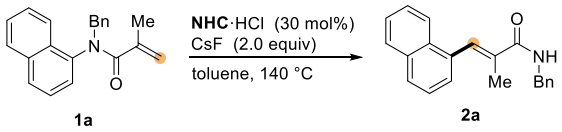
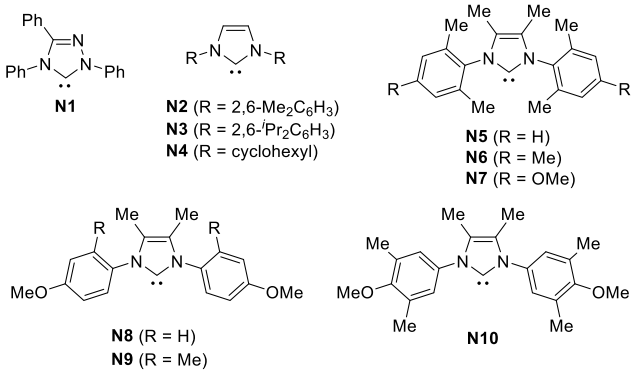
Table 1. Optimization of the Catalyst[a]



1a 2a

entry	NHC	GC yield of **2a** (%)
1	**N1**	0
2	**N2**	0
3	**N3**	0
4	**N4**	0
5	**N5**	16
6	**N6**	9
7	**N7**	26
8	**N8**	0
9	**N9**	0
10	**N10**	0
11	**N7**	>95[b] (79)[c]



[a]Reaction conditions: amide **1a** (0.20 mmol), NHC·HCl (0.060 mmol), CsF (0.40 mmol), and toluene (1.0 mL) in sealed tube at 140 °C for 12 h. [b]Reaction conducted for 40 h in toluene (3.0 mL). [c]Isolated yield of **2a** when conducted on 8 mmol scale (40 h).

We previously reported on the NHC-catalyzed intramolecular concerted nucleophilic aromatic substitution (CS_NAr) of aryl halides bearing an α,β-unsaturated amide moiety,[11] in which a highly nucleophilic ylide species is involved (Scheme 1D, attack a).[12] In these reactions, oxygen-based poor leaving groups, such as a OPh and even an a OMe group, can also participate,[13] although C(aryl)−O bonds are generally assumed to be inert.[14] The broad scope of leaving groups led us to envision that α,β-unsaturated amides without any leaving groups at the *ortho* position would direct the attack of the ylide nucleophile to the most electrophilic *ipso* carbon of the anilide substrate to undergo the Truce−Smiles rearrangement (Scheme 1D, attack b). The key challenges to realizing the nucleophile-initiated Truce−Smiles rearrangement are (i) the low electrophilicity of anilides compared to aryl halides and (ii) difficulties associated with suppressing the competing cleavage of a more reactive C(acyl)−N bond in anilides.

With these challenges in mind, we commenced our study by evaluating various NHC catalysts for the conversion of the anilide **1a** into the rearranged product **2a** (Table 1). Although common triazole-based (**N1**) and imidazole-based NHCs (**N2**, **N3**, and **N4**) did not produce the desired **2a** (entries 1−4), the introduction of methyl groups at the 4,5-positions of the imidazole ring (i.e., **N5**, **N6**, and **N7**) permitted the desired C−N bond cleavage to form **2a** (entries 5−7) with the methoxy-substituted **N7** being among the most effective. Less sterically demanding NHCs, such as **N8**, **N9**, and **N10**, were less effective for promoting the catalytic Truce−Smiles rearrangement of **1a** (entries 8−10). Finally, using **N7** with a prolonged reaction time permitted the complete consumption of **1a** with the quantitative generation of **2a** (entry 11). These conditions were applicable to the reaction on a gram scale (entry 11).

With the optimized reaction conditions in hand, we next examined the scope of substrates (Scheme 2). A range of functional groups, including cyano (**1b**), iodo (**1c**), methoxy (**1d**), and ester (**1e**) groups, were tolerated with the corresponding rearranged products being successfully produced. When *para*-substituted anilides were used, this organocatalytic rearrangement proceeded efficiently with substrates bearing a CH_2Mes group (*i.e.*, **1f**−**1i**), possibly because this bulkier *N*-protecting group suppressed the undesired C(acyl)−N bond cleavage and the associated side reactions. Notably, since this method does not require the use of a strong, nucleophilic base, substrates bearing an enolizable ketone moiety, as in **1i**, were applicable. Sterically demanding *ortho*-substituted anilides **1j**−**1m** also participated in this organocatalytic C−N cleavage reaction. Interestingly, *ortho*-chloro and *ortho*-bromo substituents did not undergo nucleophilic aromatic substitution by the postulated ylide intermediate[11,13] under these conditions, but rather C−N bond substitution occurred exclusively to form the corresponding cinnamamides **2j** and **2k**, respectively. One of the advantages of this organocatalytic method over transition metal and photoredox catalysis is the tolerance of halogen groups, as evidenced in the reactions of **1c**, **1j**, and **1k**, which should serve as a synthetic handle for further functionalization.[15] The heteroaromatic compound **1n** and π-extended arenes **1o** also participated in this catalytic reaction. The electronic properties of the benzyl protecting groups in anilides had no apparent effect on the yield of the products, as evidenced by the reactions of anilides bearing 4-methoxybenzyl (**1p**) and 4-trifluoromethylbenzyl (**1q**) groups.

This organocatalytic C−N bond cleavage is applicable to the transformation of biologically active molecules containing an aniline moiety (Scheme 3, top). For example, the C(aryl)−N bonds in the antimicrobial sulfamethazine **1r** and anesthetic dimethocaine **1s** can be transformed into C(aryl)−C bonds via this NHC-catalyzed rearrangement to provide new amide derivatives **2r** and **2s**, respectively. As mentioned above, an *ortho* bromo group is tolerated in the **N7**-catalyzed Truce−Smiles rearrangement of **1k** to afford a cinnamamide **2k** exclusively. Interestingly, the use of **N9**, instead of **N7**, as a catalyst led to the formation of a cyclized product **3** as a major product, which was produced by catalytic nucleophilic aromatic substution (Scheme 3, bottom).[11,13] These results demonstrate that a catalyst-controlled selectivity between C−N and C−Br bond cleavage is possible.

To gain additional insights into the reaction mechanism, we next investigated the reaction pathway by DFT calculations using *N*-methyl-*N*-(naphthalene-1-yl)methacrylamide as a model substrate. The energy changes at the M06-2X/6-311+G*//M06-2X/6-31+G* level of theory [SCRF (pcm, solvent = toluene)] are shown in kcal/mol (Scheme 4). Because the route from an α,β-unsaturated ester and an NHC catalyst to the ylide intermediate similar to **INT1** was previously calculated,[16] our calculations focused on the critical C−N bond cleavage process via intramolecular nucleophilic substitution. The calculations revealed that this catalytic C−N

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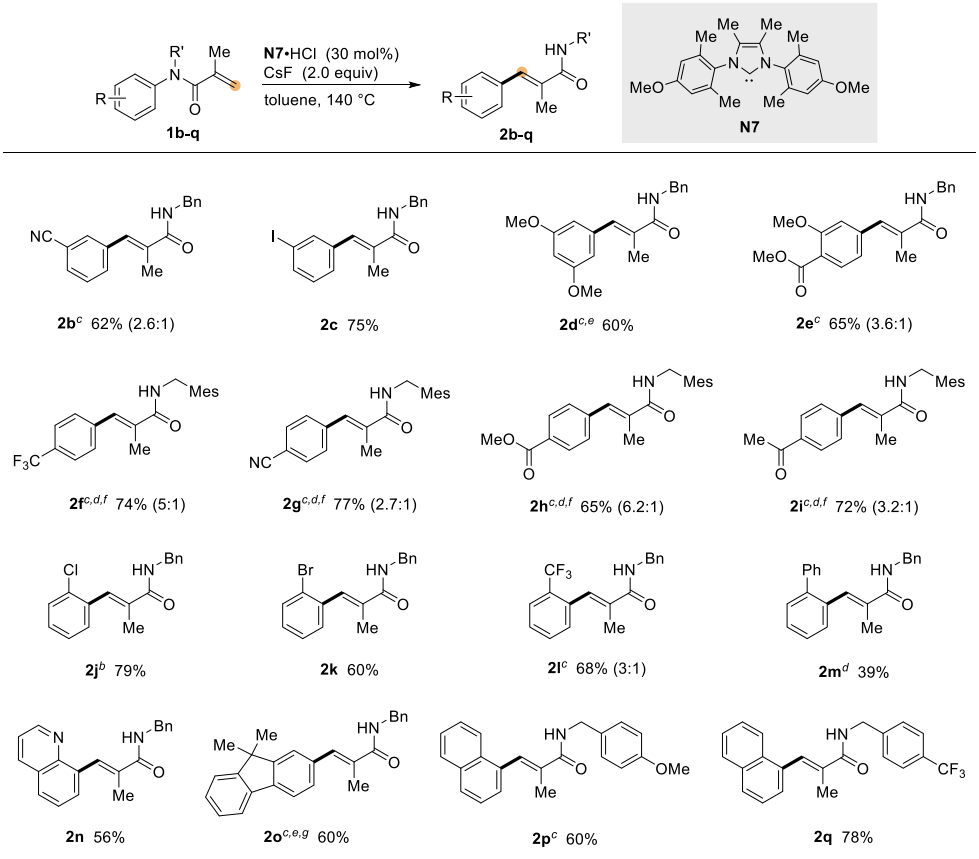
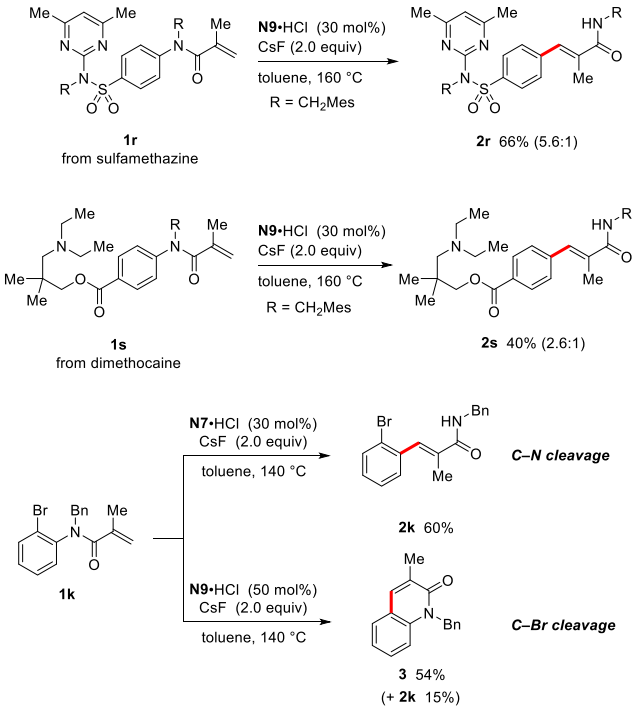
Scheme 2. Scope of Substrates[a]



[a]Reaction conditions: amide **1** (0.20 mmol), **N7**·HCl (0.060 mmol), CsF (0.40 mmol), and toluene (3.0 mL) in sealed tube at 140 °C for 40 h. Isolated yield is shown. For **2f–i**, the yield refers to that determined by NMR due to the formation of inseparable byproducts. Ratio in parentheses refers to that of *E*/*Z* isomers of **2**. [b]For 72 h. [c]At 160 °C. [d]**N9**·HCl was used as a catalyst. [e]For 144 h. [f]For 24 h. [g]50 mol % catalyst was used.

Scheme 3. Synthetic Applications



bond cleavage proceeds through an S_NAr pathway, including a Meisenheimer intermediate **INT2**. Approaching the **TS1** requires a barrier of 22.9 kcal/mol, followed by the formation of the Meisenheimer intermediate **INT2**. The collapse of **INT2** to **INT3** proceeds through **TS2** with a higher activation barrier of 29.6 kcal/mol, which indicates that the cleavage of C–N bond is likely the rate-determining step of this process. Natural population analysis (NPA) of **INT2** revealed that the negative charges were largely distributed on the aromatic ring of an amide substrate (C2, −0.459; C3, −0.230; C4, −0.442) while the positive charges were on the imidazolium ring (see the Supporting Information for details). These results are consistent with the experimental results showing that electron-poor anilides react more efficiently in this Truce–Smiles-type rearrangement.[17]

In summary, we report on the development of the nucleophilic organocatalytic C–N bond cleavage of aniline derivatives. The key to realizing this reaction is the utilization of a highly nucleophilic NHC, which enables the formation of a highly nucleophilic ylide intermediate generated from an *α*,*β*-unsaturated amide. This reaction is applicable to substrates bearing a variety of functional groups and biologically active molecules having an aniline moiety, such as sulfonamide drugs. DFT calculations suggest that this reaction is likely to proceed via the formation of the nonstabilized Meisenheimer intermediate **INT2**. Further investigations of organocatalytic reactions involving the cleavage of strong bonds are currently underway in our laboratory.

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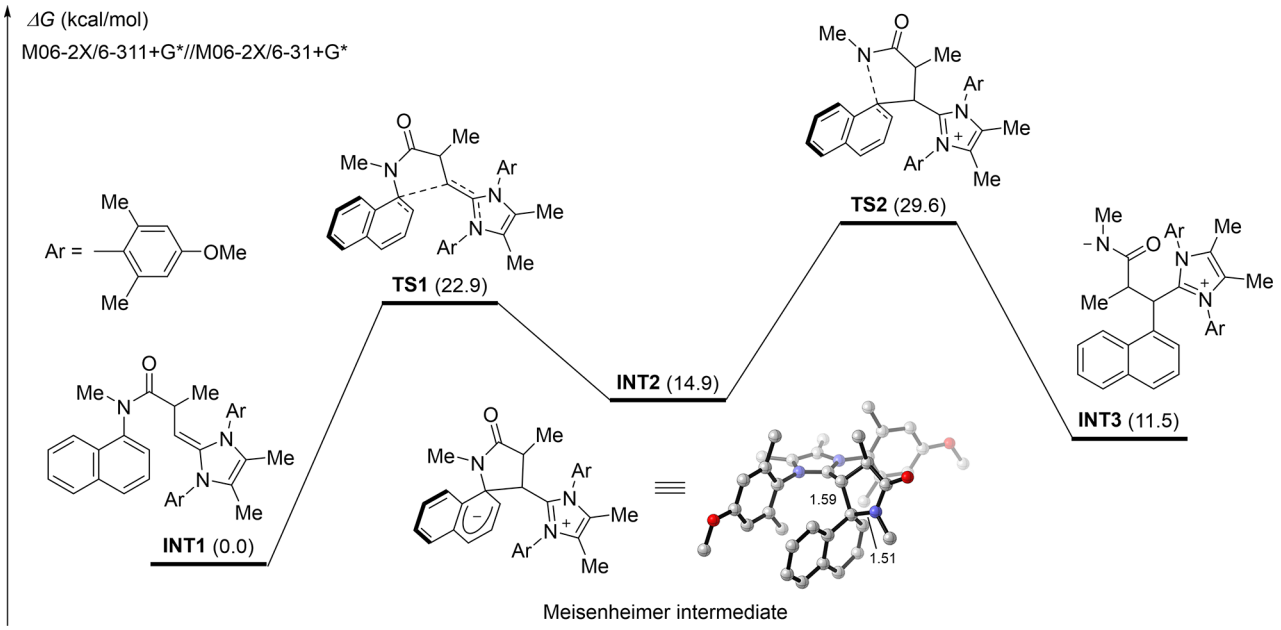
Org. Lett. 2021, 23, 1572–1576

Scheme 4. DFT Calculations



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04281.

Detailed experimental procedures, characterization of new compounds, Cartesian coordinates, NMR spectra, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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(17) We also performed DFT calculations using *N*-methyl-*N*-phenylmethacrylamide, which revealed that a stepwise pathway involving a Meisenheimer intermediate is preferred, rather than a concerted pathway. See the Supporting Information for details.

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