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Communication

Diastereodivergent Intermolecular 1,2-Diamination of Unactivated Alkenes Enabled by Iodine Catalysis

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ABSTRACT: The stereospecific, substrate (nitrogen source)-controlled intermolecular *anti*- and *syn*-1,2-diaminations of unactivated alkenes using the same catalysis (an iodine catalyst) is reported. The combined use of the two potential methods provides access to all of the disastereomeric forms of 1,2-diamines in spite of the availability of *E*- and *Z*-alkenes, and the resulting products can be readily converted into free vicinal diamines.

The 1,2-diamine substructure is a ubiquitous structural motif that is found in a number of natural products, biologically active compounds, ligands for metal-mediated catalysis, and organocatalysts (Figure 1a).[1−8] The development of an efficient methodology for the synthesis of 1,2-diamines with control of the stereochemistry would be highly desirable[9] in terms of preparing useful compounds with a minimum number of steps. Of the various starting materials that are available for the construction of a 1,2-diamine moiety, alkenes represent ideal substrates.[10] Even though the nitrogen atom is a ubiquitous atom that is as important as an oxygen atom in many organic molecules, the nitrogen version of a diastereodivergent dihydroxylation of alkenes, that is, the Prévost[11] and Woodward[12] reactions, remains unexplored. Thus, a versatile method for the robust 1,2-diamination of alkenes promises to contribute to a more rapid drug discovery but also could be utilized in the functionalization of a variety of organic molecules.[13] The stoichiometric, metal-mediated 1,2-diamination of alkenes was developed in the 1970s,[14−20] and it has been applied to some stereoselective reactions.[21,22] The analogous transition-metal-catalyzed intermolecular 1,2-diamination of alkenes has emerged by overcoming the latent capability of vicinal diamines to coordinate to a metal center.[23−36] Since the removal of trace amounts of metal catalysts from the final product would be costly in the synthesis of pharmaceuticals and electronic devices, Muñiz's and Johnston's group, using hypervalent iodine(III), developed the metal-free diamination of alkenes,[37−40] and the former group applied this method to a catalytic system in which styrene derivatives are used as substrates.[41] An alternative metal-free process, namely, electrochemical diamination reactions of alkenes, was also reported,[42,43] although the stereochemical outcome was difficult to control and was dependent on the stability of the structure of the products. During our research, the catalytic and enantioselective *syn*-diamination of styrene derivatives as the main substrates was reported by Denmark's group.[44] The diaminations developed

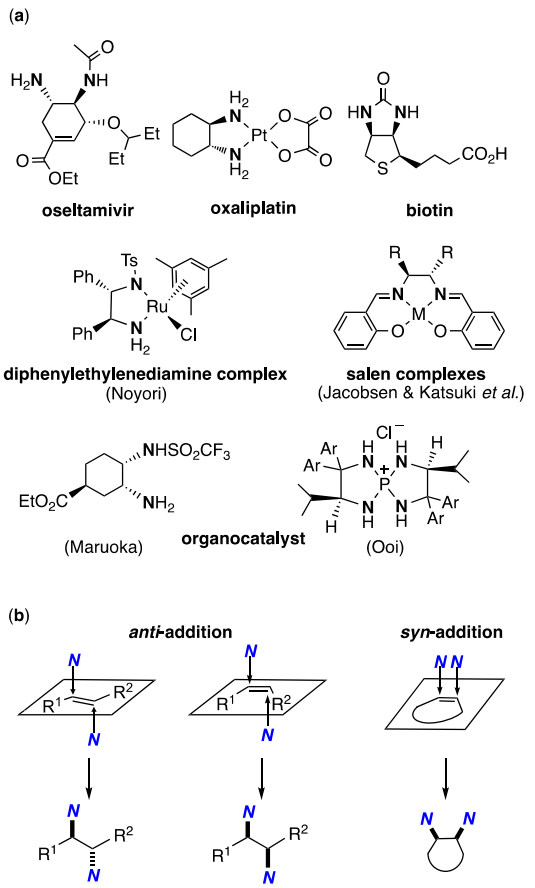

Figure 1. (a) Selected useful compounds containing a 1,2-diamino moiety. (b) Synthetic modes for the synthesis of all of the diastereomers of 1,2-diamino compounds.

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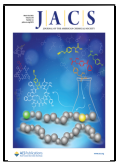

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so far, for the most part, have been confronted with several problematic issues. (i) Transition-metal reagents or catalysts are required. (ii) The generality of such reactions with respect to alkenes as carbon resources remains unsatisfied. (iii) The removal of substituents on the nitrogen moieties of the initially formed products to give free diamines requires multistep reactions and relatively harsh conditions. (iv) An established protocol for producing diverse arrays of 1,2-diamines with the intended stereochemistry remains unexplored. If the complete stereospecific *anti*- and *syn*-1,2-diaminations of acyclic *E*- and *Z*-alkenes as well as cyclic alkenes could be achieved, it would permit all possible diastereomers of 1,2-diamines to be synthesized (Figure 1b).

We previously reported on the development of unique nitrogen transfer reactions for simple organic molecules by utilizing reactive intermediates containing nitrogen-halogen bonds.[45,46] Among these, the molecular iodine-catalyzed aziridination of alkenes with *N*-chloro-*N*-sodio-*p*-toluenesulfonamide (chloramine-T) was found to be a versatile method for the construction of aziridines from various alkenes.[47,48] Even though the resulting aziridine rings are highly strained and the nitrogen source has a certain degree of nucleophilicity, when chloramine-T was used, only a small amount of the ring-opened product was obtained. The characteristics of the strained product and the nucleophilic nitrogen source prompted us to investigate the direct *anti*-diamination of alkenes through reactive aziridine intermediates. A suitable nitrogen source, such as a chloramine salt, could function both for aziridination and ring-opening reactions, resulting in the *anti*-diamination being achieved. From the mechanistic point of view (proposed pathways for *anti*- and *syn*-diamination are depicted in Figure 2), the aziridination proceeds through an

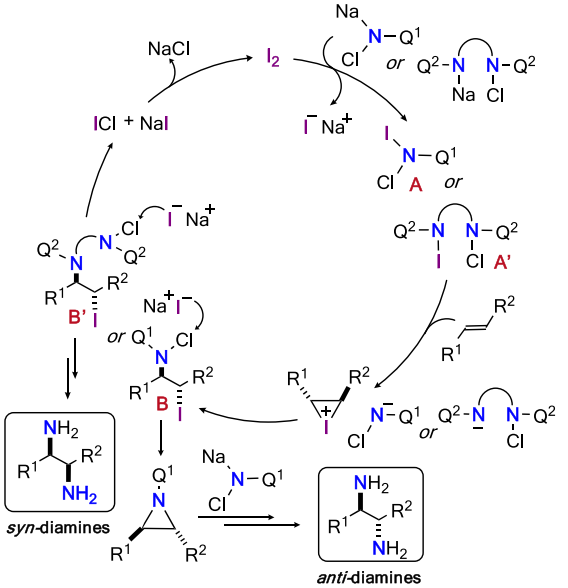
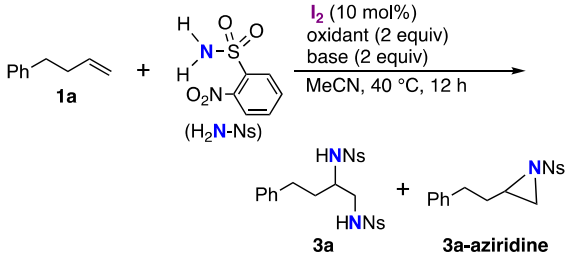


Figure 2. Proposed catalytic cycle for the *anti*- and *syn*-1,2-diamination reactions.

anti-iodoaminated intermediate **B** that is generated from a reactive *N*-chloro-*N*-iodo-amide species **A** and an alkene, followed by a ring-closure reaction. If a nitrogen source could be prepared that contains both electron-withdrawing groups to permit a nitrogen−iodine bond to be easily formed in situ and with two nitrogen moieties within the molecule, the concomitant use of such a nitrogen source and an iodine catalyst might result in the *syn*-diamination of alkenes via the reactive *anti*-iodoaminated intermediate **B′**. Both iodoaminated intermediates **B** and **B′** should be stereospecifically formed via the formation of a three-membered iodonium intermediate generated by the transfer of iodine to the alkene from the *N*-iodinated reactive species **A** and **A′** via the reaction of the chloramine salt with the iodine catalyst.

In initial investigations directed at identifying a suitable nitrogen source, various chloramine salts with different charges on the nitrogen atom were screened for use in the iodine-catalyzed 1,2-diamination. Among these, *N*-chloro-*N*-sodio-*o*-nitrobenzenesulfonamide (chloramine-Ns) was found to be a viable nitrogen source (Table S2). Although chloramine-Ns can be prepared by the reaction of *o*-nitrobenzenesulfonamide (nosylamide) with *tert*-butyl hypochlorite followed by a treatment with NaOH,[49] the in situ generation of chloramine-Ns using nosylamide and a suitable halogen-containing oxidant would be a general, useful, and practical method for the formation of 1,2-diamines. When 4-phenyl-1-butene (**1a**) was treated with nosyl-amide in the presence of I_2 as the catalyst, *tert*-BuOCl, and NaOH in acetonitrile at 40 °C for 12 h, the desired diaminated product was not obtained. The use of *N*-chlorosuccinimide (NCS) instead of *tert*-BuOCl gave the 1,2-diaminated compound **3a** in 23% yield. Although aqueous NaOCl and $Ca(OCl)_2$ were not so effective, sodium hypochlorite pentahydrate ($NaOCl{\cdot}5H_2O$) in the solid form[50] was found to be the most effective oxidant, which provided the 1,2-diaminated product **3a** in 92% isolated yield (Table 1). In fact, chloramine-Ns was smoothly formed in 91%

Table 1. Optimization of the Chlorinating Oxidant for the I_2-Catalyzed 1,2-Diamination from Nosylamide



entry	oxidant	base	yield (%) 3a	yield (%) 3a-aziridine
1	*tert*-BuOCl	NaOH	0	0
2	NCS	NaOH	23	0
3	NaOCl aq		35	0
4	$Ca(OCl)_2$ aq		10	10
5	$NaOCl\ 5H_2O$		92	0

yield under mild conditions by treating the nosylamide with $NaOCl{\cdot}5H_2O$ in acetonitrile (Figure S1), indicating that the chloramine-Ns is initially generated in situ. An additional benefit is that a nosyl group on the nitrogen can be readily detached by Fukuyama's method to furnish the free diaminated products.[51]

This highly practical reaction starting from the commercially available nosylamide, the appropriate oxidant, and an iodine catalyst prompted us to survey the scope of the reaction for a broad range of alkenes. Terminal and cyclic alkenes were successfully converted into 1,2-diamines under conditions I (Table 2 (**a**)). The phenyl group-substituted alkene **1b** could

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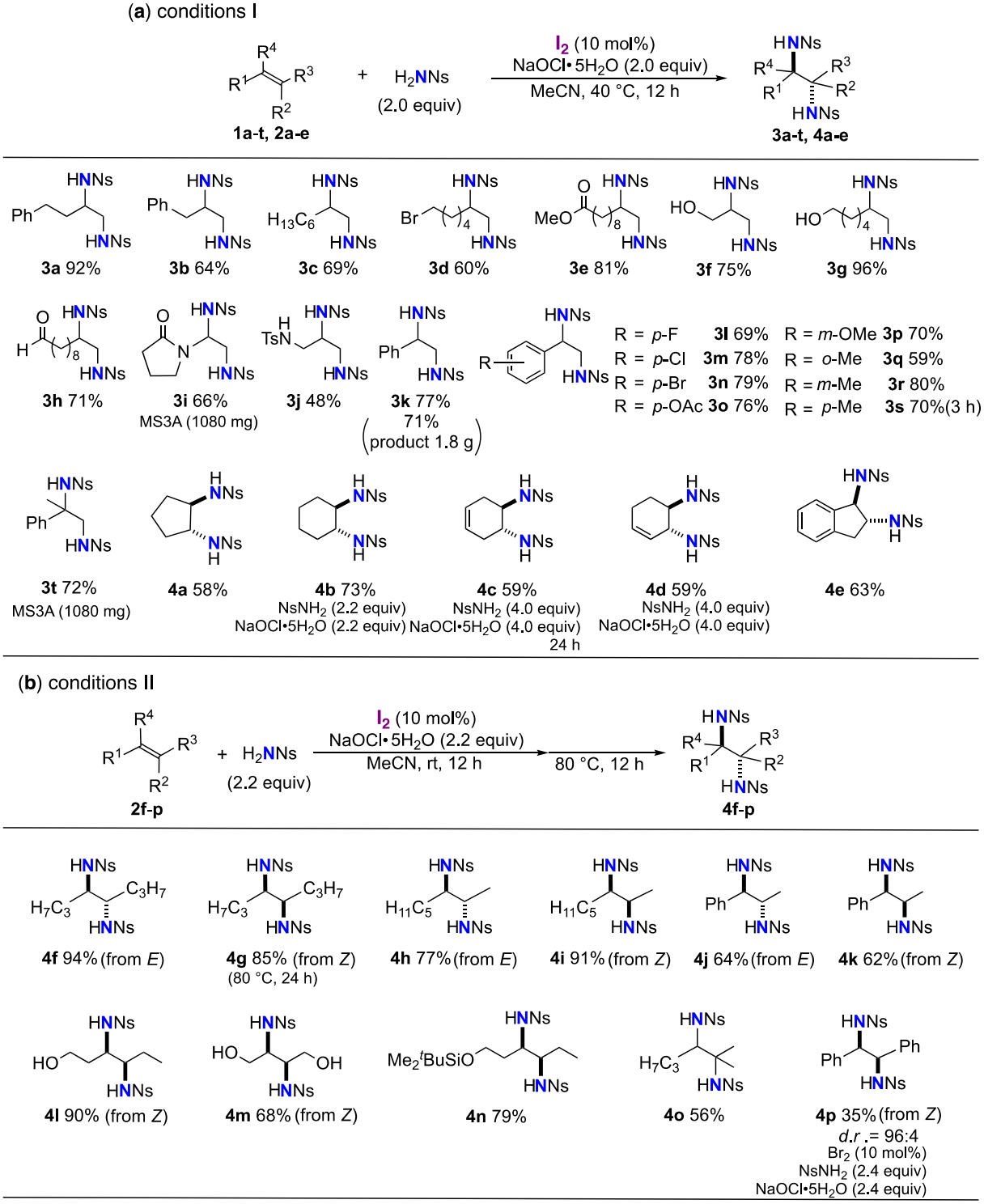
Table 2. Substrate Scope for the I_2-Catalyzed *anti*-1,2-Diamination[a]



[a]Reactions were conducted at a concentration of 0.17 M on a 0.5 mmol scale (alkenes being the limiting reagent, 10 mol % of I_2 catalyst). Yields are the isolated material after purification.

also be converted into **3b** without oxidation at the benzylic and allylic positions. The relatively simple aliphatic terminal alkene **1c** as well as derivatives containing bromo and ester groups **1d** and **1e** could also be used in the diamination reaction. Primary alcohols and formyl groups were well-tolerated, giving **3f**–**3h** in good yields, even in the presence of an oxidant. *N*-Vinylpyrrolidone and allylamine could be transformed into the triaminated compounds **3i** and **3j**. The reaction of various styrene derivatives also afforded the corresponding adducts **3k**–**3t** in good yields. The complete *anti*-selective diamination of five- and six-membered cyclic alkenes proceeded to give **4a** and **4b**. Notably, the use of 1,4-cyclohexadiene (**3c**) selectively provided the *trans*-diaminated product **4c**, which is a versatile synthetic intermediate for the total synthesis of oseltamivir

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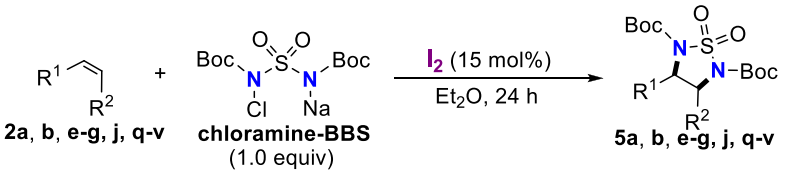
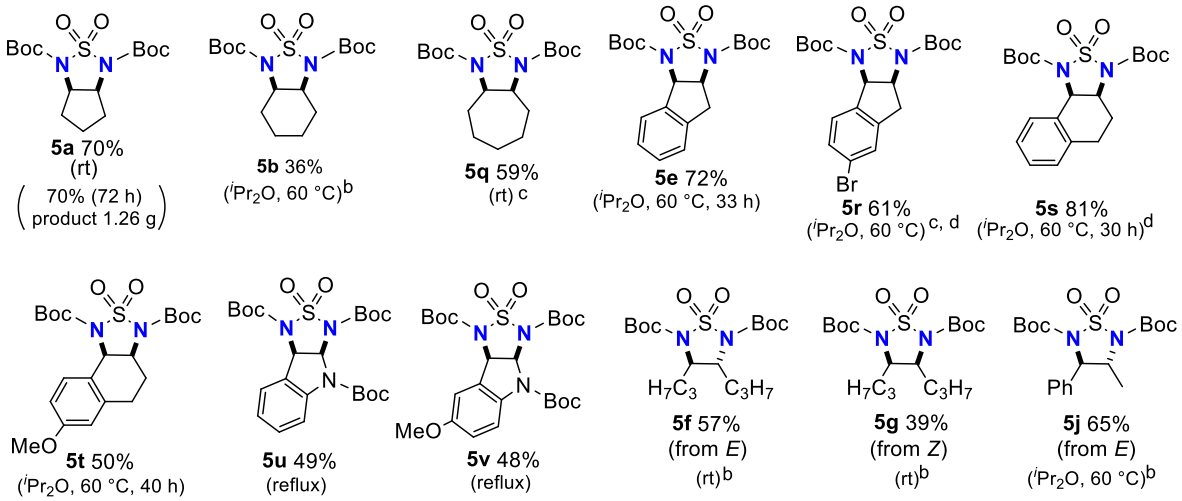
Table 3. Substrate Scope for the *syn*-1,2-Diamination





[a]Reactions were conducted at 0.17 M on a 0.5 mmol scale (with alkenes as the limiting reagent) unless otherwise noted. Yields are the isolated material after purification. [b]I_2: 30 mol %. [c]I_2: 20 mol %. [d]Chloramine-BBS: 1.5 equiv.

(Tamiflu) that was developed by Shibasaki's group.[52] The conjugated cyclic alkenes **4d** and **4e** were also diaminated without any detectable formation of a *syn*-adduct. When the reaction of *E*-4-octene (**2f**) was performed with 2 equiv of H_2NNs under conditions I, no desired diaminated product was formed, but, rather, *trans*-2,3-di-*n*-propylaziridine was obtained. Since the ring opening of the aziridine intermediate would be hampered by the steric hindrance of the two substituents, running the reaction at room temperature for 12 h in order to produce the maximum amount of the intermediate aziridine, followed by heating at 80 °C for an additional 12 h, was found to be the most useful condition for the internal alkene diamination (Table 2 (**b**): conditions II). With the optimal conditions, the desired diamination leading to the formation of **4f**–**4i** in good yields with complete *anti*-selectivity was achieved. The present diamination also proceeded stereospecifically to afford **4j** from *E* and **4k** from *Z*, even when phenyl-conjugated internal alkenes were used. Although the diamination of internal alkenes required heating the reaction at 80 °C, hydroxy and siloxy groups were tolerated, furnishing **4l**–**4n** in good yields. A trisubstituted olefin **2o** and *cis*-stilbene (**2p**) were also applicable to the reaction, but a bromine catalyst was needed, and a small amount of diastereomer was formed in the case of the reaction with *cis*-stilbene. From the results of the product stereochemistry, the present diamination appears to be a stereospecific reaction.

The present 1,2-*anti*-diamination can be used to selectively produce most of the diastereomers of vicinal diamine compounds starting from the appropriate geometric isomer of the alkene. The exception is the preparation of *syn*-diaminated compounds from cyclic alkenes. On the basis of the proposed pathway (Figure 2), we focused on a sulfamide framework containing two *tert*-butoxycarbonyl (Boc) groups, that is, *N*,*N*′-bis(*tert*-butoxycarbonyl)sulfamide (BBS) (Figure S2). Although BBS is a known compound and is used as a stabilizer for anaerobically curable adhesives, its use in organic synthesis is unknown. Although cyclopentene was treated with BBS in the presence of $NaOCl{\cdot}5H_2O$ and the I_2 catalyst at room temperature (conditions I), the desired *syn*-diaminated product was obtained in only a 17% yield, after 45 h. In fact, the chloramine-BBS, which is thought to be an active species, was efficiently formed by the reaction of BBS with $NaOCl{\cdot}5H_2O$ in MeCN, and its structure was confirmed by an X-ray structural analysis (Figures S3 and S4). Since the reason for the low yield might be due to the solvent used in the diamination step, further attempts were made to optimize this aspect (Tables S6 and S7). The reaction of cyclopentene with chloramine-BBS in the presence of the iodine catalyst in Et_2O selectively afforded the *syn*-diaminated product **5a** in good yield, and this reaction could be easily scaled up (Table 3). To verify the utility of this metal-free and catalytic *syn*-diamination, other cyclic as well as acyclic alkenes were examined. Six- and seven-membered alkenes were converted into the corresponding *syn*-adducts **5b** and **5q**. Indenes and 1,2-dihydronaphthalenes were also transformed to **5e** and **5r**–**5t** in good yields. Even when the starting alkenes were heteroaromatic compounds **2u** and **2v**, *N*-boc-indoles, the *syn*-diamination reacted at the 2- and 3-positions,[53] albeit in moderate yields. The acyclic alkenes **2f** and **2g** could be successfully diaminated in a *syn* manner with no *anti* adducts being formed, even in the case of the aromatic-conjugated alkene **2j**. In addition to the *anti* diamination, the use of chloramine-BBS in the iodine-catalyzed diamination was also found to be a stereospecific reaction.

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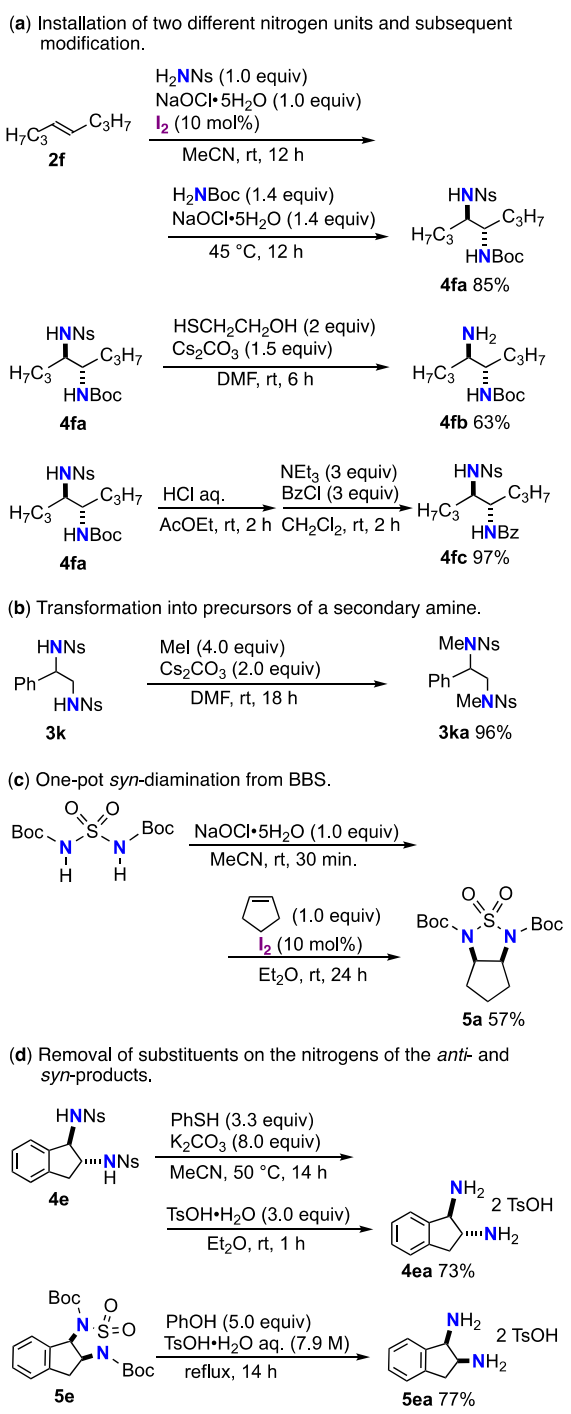
As a unique feature of the *anti*-diamination reaction, two different nitrogen units could be installed in a carbon−carbon double bond in a one-pot reaction. For example, when 1.2 equiv of the *E*-4-octene (**2f**) was treated with nosylamide and $NaOCl·5H_2O$ in the presence of an I_2 catalyst in MeCN at ambient temperature for 12 h, followed by the addition of 1.4 equiv of H_2NBoc and $NaOCl·5H_2O$, followed by stirring at 45 °C for 12 h, the Ns and the Boc-substituted diamine **4fa** were produced in 85% yield. Each of the protected groups of the potential diaminated product **4fa** could be individually transformed (Scheme 1a).[54] Nosyl-substituted amines represent potential precursors of secondary amine derivatives.[55] The treatment of **3k** with 4 equiv of methyl iodide in the presence of cesium carbonate gave the dimethylated product **3ka** in excellent yield (Scheme 1b). The present *syn*-diamination was also applicable for use in a one-pot process, namely, the in situ preparation of chloramine-BBS from BBS and $NaOCl·5H_2O$ in acetonitrile, followed by the removal of the solvents, followed by the addition of cyclopentene and the iodine catalyst successfully gave **5a** (Scheme 1c). The two Ns groups of the *anti*-diaminated product **4e** could be readily detached,[51] leading to the formation of the free diamine, which was isolated as the *p*-toluenesulfonic acid salt **4ea**. The sulfonyl and Boc groups of the *syn*-diaminated product **5e** could then be easily removed to give **5ea** in good yield (Scheme 1d).

Scheme 1. Application of the Present 1,2-Diamination and Transformation of 1,2-Diaminated Products



In conclusion, we report herein on a synthetic strategy that permits various 1,2-diamine derivatives to be produced from unactivated alkenes. The nitrogen sources-controlled stereospecific intermolecular *anti*- and *syn*-1,2-diamination was successfully achieved, which are regarded as catalytic aza-Prévost-Woodward reactions. The present diamination reactions are green-sustainable, because the byproducts that are produced in the reactions are only NaCl and/or H_2O.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00228.

Experimental procedures and spectral data (PDF)

Accession Codes

CCDC 1919391−1919392 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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