Asymmetric Synthesis

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Enantioselective Metal-Free Diamination of Styrenes**

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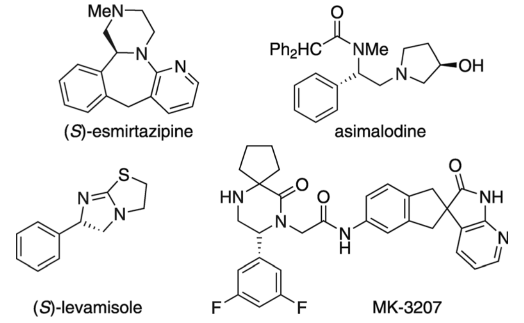
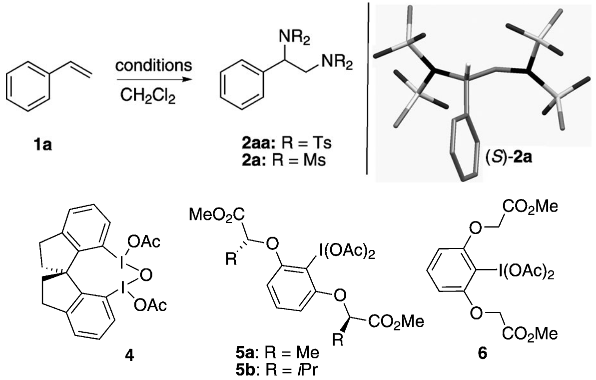
Hypervalent iodine(III) compounds represent powerful reagents for the oxidation of organic molecules and they have been employed as an attractive alternative to the more common transition-metal-promoted oxidation reactions.[1] In particular, the emergence of chiral derivatives has allowed for the development of a series of efficient asymmetric oxidative transformations,[2] including several oxygenation reactions of alkenes.[3–5] In contrast, the potential of iodine(III) reagents in oxidative intermolecular carbon–nitrogen bond formation remains widely unexplored.[6] Herein, we describe the first enantioselective transfer of two nitrogen atoms onto the prochiral face of styrene, promoted by a chiral iodine(III) reagent.



Scheme 1. Pharmaceuticals incorporating the 1-aryl ethylene diamine unit.

Table 1: Discovery and optimization of the intermolecular enantioselective diamination of styrenes.



Entry	Conditions[a]	Prod.	Yield [%][b]	*ee* [%][c]
1	5 mol% $(MeCN)_2PdCl_2$, $HNTs_2$ (1.4 equiv), saccharin (1.1 equiv), **3** (1.2 equiv), RT	**2aa**	45	–
2	$HNTs_2$ (1.4 equiv), **3** (1.2 equiv), RT	**2aa**	42	–
3	$HNTs_2$ (2.4 equiv), **3** (1.2 equiv), RT	**2aa**	85	–
4	$HNTs_2$ (2.4 equiv), **4** (1.2 equiv), RT	**2aa**	55	32
5	$HNTs_2$ (2.4 equiv), **5a** (1.2 equiv), RT	**2aa**	76	50
6	$HNMs_2$ (2.4 equiv), **3** (1.2 equiv), RT	**2a**	24	–
7	$HNMs_2$ (2.4 equiv), **6** (1.2 equiv), RT	**2a**	77	–
8	$HNMs_2$ (2.4 equiv), **5a** (1.2 equiv), RT	**2a**	87	66
9[d]	$HNMs_2$ (2.4 equiv), **5a** (1.2 equiv), 0°C	**2a**	86	85 (99)[e]
10	$HNMs_2$ (2.4 equiv), **5b** (1.2 equiv), 0°C	**2a**	30	84

[a] Reaction carried out on a 0.5 mmol scale. [b] Yield of isolated product after purification. [c] Determined by HPLC on a chiral stationary phase. [d] Reaction on 5 mmol scale. [e] The *ee* value after crystallization is in brackets. Ms = methanesulfonyl, Ts = *p*-toluenesulfonyl.

The diamination reaction of alkenes has recently emerged as a useful synthetic approach to this important class of compounds.[7–9] Within this context, we have recently described the first protocols for the palladium-catalyzed intermolecular and regioselective diamination of terminal alkenes.[10] Styrenes represent a particularly attractive substrate class for the diamination of alkenes[8j–l] as a number of pharmaceutically interesting molecules display the 1-aryl ethylene diamine moiety (Scheme 1). When we applied our previous palladium-catalyzed reaction[10a] to styrene (**1a**), an entirely different oxidative diamination reaction took place. In this case, the alkene was converted into the new 1,2-diamine **2aa** through the incorporation of two bistosylimide units (Table 1, entry 1). A control experiment performed in the absence of the palladium salt showed that the diamine product originated from an oxidation that is promoted by the iodine(III) reagent itself (Table 1, entry 2). Furthermore, a combination of iodosobenzene diacetate ($PhI(OAc)_2$, **3**) and bistosylimide (Ts_2NH), in the correct stoichiometric ratio, efficiently provided the unprecedented intermolecular diamination of styrene in high yield (Table 1, entry 3).[11,12] This reaction proceeded equally well on a 10 mmol scale, and represents a significant advance in the intermolecular diamination of alkenes as it requires just two components and proceeds under metal-free conditions.[13]

When replacing **3** by chiral iodine(III) reagents, we were able to devise reaction conditions for an enantioselective

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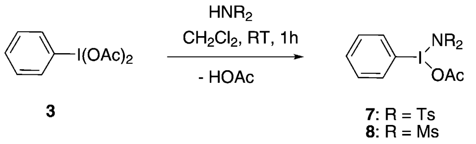
reaction. Using the known spiro derivative **4**[2d] the reaction proceeded at a comparably low rate, but gave a product with 32% *ee* (Table 1, entry 4). This result demonstrated the feasibility of the enantioselective diamination of styrene using a chiral iodine(III) reagent. An increase in the *ee* value to 50% was obtained with the iodine(III) reagent **5a**, which bears two lactate groups (Table 1, entry 5). This compound was recently introduced for enantioselective oxygenation reactions.[2b,4d,e,5] Changing the nitrogen source to bismesylimide initially resulted in a significantly reduced conversion (Table 1, entry 6). By introduction of the new reagent **6** a significant improvement was achieved and diamination of styrene produced **2a** in 77% yield upon isolation (Table 1, entry 7). The reaction with the corresponding chiral reagent **5a** gave significantly enhanced enantiomeric excess (Table 1, entry 8). Notably, product **2a** could be obtained with 85% *ee* at 0°C on a 5 mmol scale (Table 1, entry 9), while the sterically more congested reagent **5b** led to a significantly diminished reaction rate (Table 1, entry 10). Enantiomerically pure diamine **2a** was obtained after a single crystallization. The absolute *S* configuration of diamine **2a** was established by X-ray crystal analysis (Table 1).[13,14]

Direct intermolecular diamination reactions of nonfunctionalized alkenes are still rare[9k–m,10] and enantioselective versions constitute an entirely unexplored field. The present procedure is particularly important as it solves both these quests with the additional benefit that it requires no metal catalyst.

We were able to isolate new hypervalent iodine(III) reagents **7** and **8**, which are formed under ligand-exchange conditions (Scheme 2). The solid-state structure of compound **7** is depicted in Figure 1 and unambiguously proves the existence of an $\mathrm{I^{III}}$–N covalent bond.[15,16] A 1:1 mixture of **7** and $\mathrm{Ts_2NH}$ promoted the diamination of styrene with an outcome that was identical to those reactions that employed the in situ reaction conditions from Table 1, entry 3. This result demonstrates an unprecedented reactivity originating from the $\mathrm{I^{III}}$–N bond. The irreversible formation of this bond may be due to the acidic nature of the bissulfonylimide, which could also contribute to the alkene oxidation.[17]



Scheme 2. Synthesis of iodine(III) compounds **7** and **8** with an I–N bond.

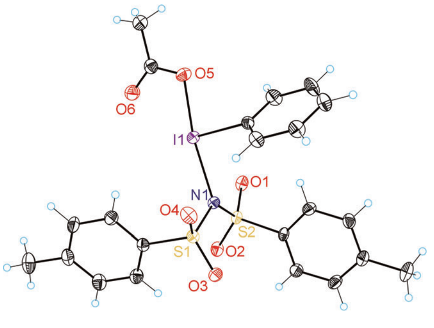
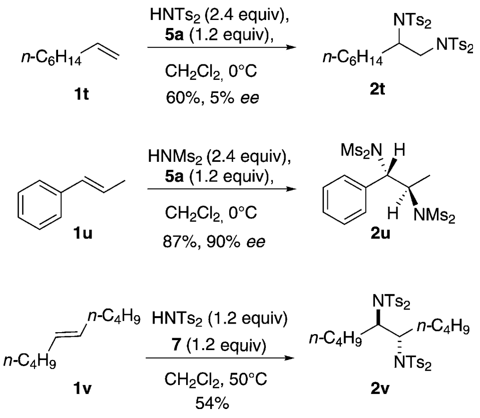


Figure 1. Structure of **7** in the solid state (thermal elipsoids drawn at the 50% probability level).

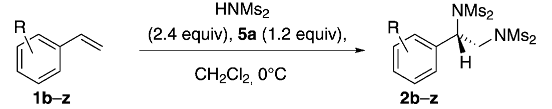
A series of different styrenes were converted into the corresponding diamines using iodine(III) reagent **5a** as the oxidant[18] and bismesylimide as the nitrogen source (Table 2). All of these reactions proceeded with good yields and high asymmetric induction. Representative examples are depicted in Table 2 and include compounds with *para* substitution (entries 1–9), *meta* substitution (entries 10–12), and *ortho* substitution (entries 13,14) as well as symmetric and nonsymmetric higher substitution patterns (entries 15–18). In all these cases, very good enantioselection, with up to 95% *ee*, was observed. A single crystallization led to enantiopure material in almost all cases. The *S* configuration for products **2** was further confirmed with additional X-ray crystal structures of compounds **2g**, **2o**, and **2p**.[14] All products **2a**–**s** display spectroscopic data that are in agreement with the expected vicinal diamine motif. These reactions represent the first examples of enantioselective intermolecular carbon–nitrogen bond-forming reactions using the chiral hypervalent $\mathrm{I^{III}}$ reagent **5a**. Importantly, the products' high crystallinity, resulting from the two bissulfonyl groups, usually enabled enantiomerically pure diamines to be obtained after a single crystallization.

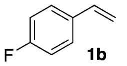
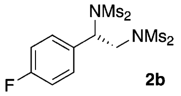
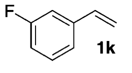
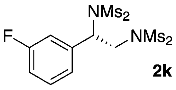
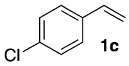
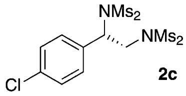
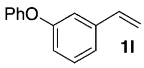
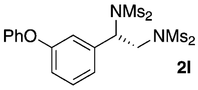
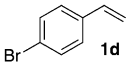
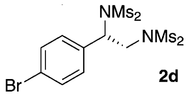
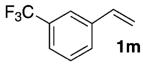
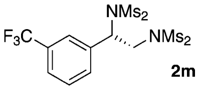
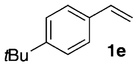
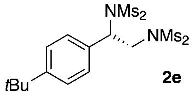
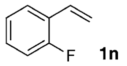
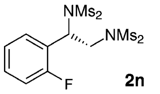
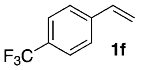
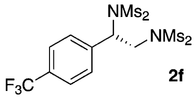
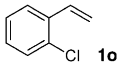
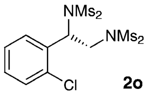
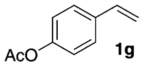
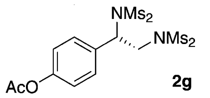
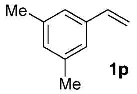
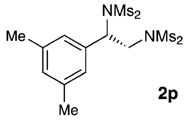
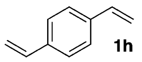
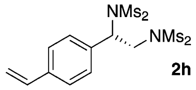
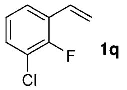
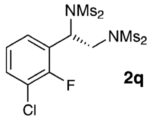
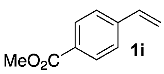
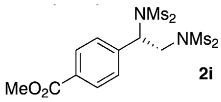
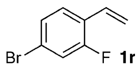
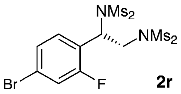
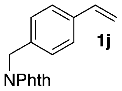
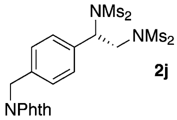
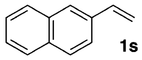
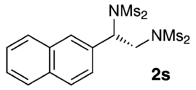
The present diamination conditions work well with a series of other alkenes as well. However, styrenes represent a privileged substrate class with respect to enantioselective induction. Scheme 3 shows three additional reactions. First, when 1-octene (**1t**) was subjected to the standard reaction conditions the corresponding diamination product **2t** was obtained in 60% yield but with a low *ee* value of 5%. Next, the diamination of (*E*)-β-methyl styrene (**1u**) led to a single diastereomer **2u**, which was isolated in 87% yield and 90% *ee* (99% *ee* after recrystallization). X-ray crystal analysis of this compound revealed an unexpected 1*S*,2*R* configuration.[14] The same stereochemical outcome was observed for a diamination reaction of 5-decene, thus giving *meso* diamine **2v** as a single product.[14] The observed stereochemistry for **2u** and **2v** does not agree with the generally accepted mechanism for the related 1,2-dioxygenation of alkenes.[3,4d,19]



Scheme 3. Diamination reactions of alkenes **1t–v**.

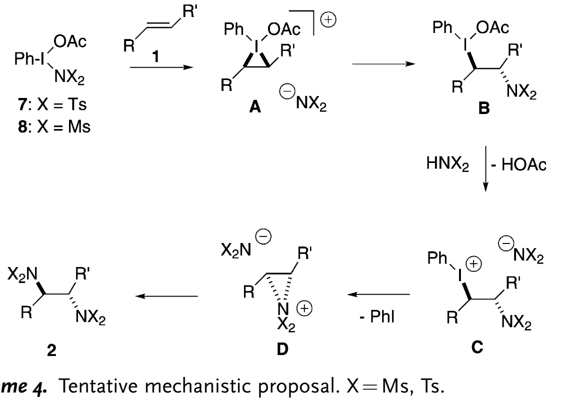
Table 2: Intermolecular enantioselective diamination of styrenes.[a]



Entry	Styrene	Diamine	Yield [%][b]	*ee* [%][c,d]	Entry	Styrene	Diamine	Yield [%][b]	*ee* [%][c,d]
1	 **1b**	 **2b**	67	91 (99)	10[e]	 **1k**	 **2k**	73	90
2	 **1c**	 **2c**	66	82 (99)	11	 **1l**	 **2l**	60	86
3	 **1d**	 **2d**	75	88 (99)	12	 **1m**	 **2m**	55	88
4	 **1e**	 **2e**	72	78 (99)	13	 **1n**	 **2n**	64	86 (99)
5	 **1f**	 **2f**	50	86 (99)	14[e]	 **1o**	 **2o**	71	95 (99)
6	 **1g**	 **2g**	72	88 (99)	15	 **1p**	 **2p**	70	78 (99)
7	 **1h**	 **2h**	44	74 (99)	16[e]	 **1q**	 **2q**	65	92 (99)
8	 **1i**	 **2i**	60	79 (99)	17[e]	 **1r**	 **2r**	69	85 (99)
9	 **1j**	 **2j**	64	90 (99)	18	 **1s**	 **2s**	64	86 (99)

[a] Reaction carried out on a 0.5 mmol scale. [b] Yield of isolated product after purification. [c] Determined by HPLC on a chiral stationary phase. [d] The *ee* values obtained after crystallization are in brackets. [e] With $HNMs_2$ (3.6 equiv), **5a** (2.5 equiv). HNPhth = phthalimide.

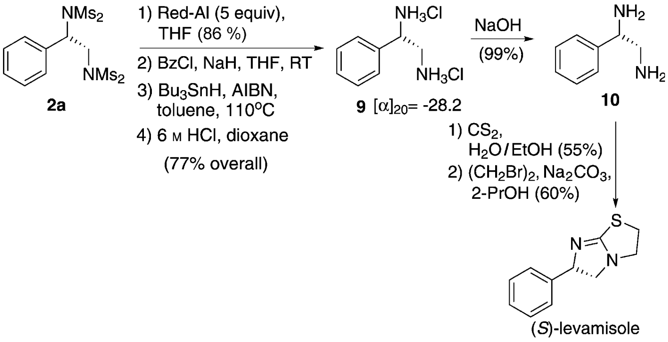
Therefore, we propose the following tentative mechanism for the present transformation (Scheme 4). An initial interaction between the iodine(III) reagent **8** and the alkene **1**, which proceeds via a previously postulated[4d,12a,19a] intermediate **A**, leads to the vicinal *anti* iodo(III) amine **B** through the common literature pathway.[3,4d,19,20] Removal of acetic acid by protonolysis generates the ion pair **C**.[19a] Since direct *anti* C–N bond formation generates the incorrect stereochemistry, we postulate the formation of an intermediary aziridinium **D**,[20] which undergoes nucleophilic opening to the final product **2**. The involvement of **D** corresponds to a related intermediate in the dioxygenation reaction using acetate.[5] Furthermore, it permits the rationalization of enantioinduction in the enantioselective transformation. In the absence of the iodine as the primary chiral source at stage **D**, high enantiomeric excess can only be preserved through regioselective aziridinium opening. While this is apparently the case for styrenes (R = aryl, R′ = H or CH_3), the absence of a benzylic position leads to lower regioselectivity and hence,



Scheme 4. Tentative mechanistic proposal. X = Ms, Ts.

results in decreased enantiomeric excess as observed for **2t**. For reactions with identical substituents ($R = R'$) involvement of intermediate **D** explains the observed *meso* product **2v**.

We have found reductive reaction conditions for the removal of all four methylsulfonyl groups of **2a** (Scheme 5).[13] The observed optical rotation for **9** is in agreement with literature data.[21] Free (*S*)-1-phenyl ethylene diamine **10** could be readily converted into the known anthelmintic (*S*)-levamisole.[22]



Scheme 5. Conversion of product **2a** into free diamine **10** and synthesis of (*S*)-levamisole.

To conclude, we have developed the first example of an intermolecular enantioselective diamination of alkenes. This new oxidation reaction transforms styrenes into their corresponding diamine derivatives under metal-free conditions using a chiral iodine(III) reagent and bismesylimide as the nitrogen source. The reaction proceeds under mild reaction conditions and with very high enantiomeric excess and originates from a reagent containing an $\mathrm{I^{III}}$–N bond of unprecedented reactivity.

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