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Iodine(III)-Promoted Intermolecular Diamination of Alkenes

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Abstract: A rapid and productive vicinal diamination of alkenes takes place in the presence of a hypervalent iodine(III) reagent and bissulfonimides as nitrogen sources. A total of more than 60 examples are presented. The reaction is characterized by its robustness and its wide substrate scope: it proceeds selectively with both terminal and internal alkenes and tolerates a range of functional groups.

Keywords: alkenes · diamines · iodine · oxidation · synthesis

Introduction

Hypervalent iodine(III) reagents represent powerful reagents for the oxidation of organic molecules and they have been employed as an attractive tool for this purpose.[1] Usually, they react under mild conditions, are safe to handle, and do not pose major toxicity problems. Where appropriate, they have arisen as an attractive alternative to transition metal-promoted oxidation reactions, especially for applications where metal contamination is an issue.

In the particular area of alkene oxidation,[2] a series of dioxygenation[3] and amination[4] reactions of alkenes was developed using these reagents. Still, related oxidative intermolecular carbon-nitrogen bond formation aided by iodine (III) reagents is rather unexplored.

We recently reported on an unexpected enantioselective 1,2-diamination reaction of styrenes that proceeds in the presence of a defined chiral hypervalent iodine(III) reagent and bissulfonimides as nitrogen sources.[5] This work originated from our general interest in the synthesis of 1,2-diamines from alkenes.[6,7] Such a reaction traditionally requires the application of a metal promoter, and historic developments described thallium,[8] mercury,[9] osmium,[10] palladium[11], and copper[12] for this purpose.

Starting in 2005, the important development of 1,2-diamination of butadienes was reported for palladium[13] and copper[14] catalysts. In parallel, our group and others reported intramolecular diamination reactions using catalytic amounts of palladium,[15] nickel,[16] gold[17], and copper,[18] which were recently extended to palladium-catalyzed intermolecular and regioselective diamination of alkenes.[19] These latter reactions require specific palladium catalyst precursors. In their absence, an entirely different oxidative diamination reaction was discovered to take place,[5] in which alkenes are converted into the corresponding 1,2-diamines through incorporation of two bissulfonimide units. Control experiments in the absence of any palladium salt showed the diamine products to originate from an oxidation that is exclusively promoted by the iodine(III) reagent itself. This by the time unprecedented observation led us to develop the first enantioselective diamination of styrenes.[5]

However, the scope for iodine(III)-mediated diamination of alkenes is significantly larger than initially anticipated. We here wish to give a full account on this novel diamination reaction that allows for a rapid, selective, and productive intermolecular vicinal diamination of a series of alkenes.

Results and Discussion

As reported previously, styrenes constitute a particularly efficient class of alkenes for our novel transformation (Table 1). Hence, in the presence of a 2:1 ratio of bistosylimide as nitrogen source and iodosobenzene diacetate as oxidant, a clean diamination reaction of styrenes is accomplished (entries 1–12). Examples comprise styrenes containing various *para* (entries 2–7) and *meta* substituents (entries 8–11) with both donor and acceptor properties. Overall, reactions proceed with reasonable rate at room temperature and with good isolated yields. As an example of a large-scale transformation, the diamination of **1a** was conducted on a 10 mmol scale. Reduction of the reaction volume and addition of methanol led to product precipitation and direct isolation upon filtration (78 % isolated yield). *Ortho* substitution remains problematic in some cases (entry 12). For example, diamination of 2-methyl styrene **1l** proceeds rather slowly and gives rise to vicinal diamine **2l** in a low yield of 20 %.

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The reaction is not limited to terminal alkenes of this class, but also works very well for internal 1-aryl alkenes. For example, β-methyl styrene reacts in a clean manner to give the corresponding vicinal diamine as the only product (entries 13,14). While the *E* isomer **1m** leads to the (2*S*,3*R*/2*R*,3*S*)-product, the opposite (2*R*,3*R*/2*S*,3*S*)-diastereomer is formed as the major product from oxidation of the corresponding *Z* isomer **1n** (ratio **2n**/**2m** = 2.65:1). The relative configuration of **2m** was unambiguously assured from X-ray analysis (Figure 1).[20]

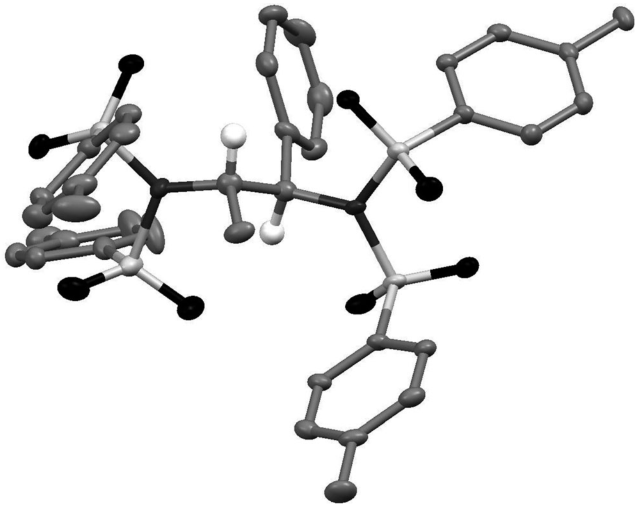


Figure 1. Crystal structure of **2m**. C gray, S light gray, N dark gray, O black, hydrogen white. Except for the stereogenic centers, hydrogen atoms are omitted for clarity.

Symmetric (*E*)-stilbenes **1o** and **1p** yield the corresponding *meso* derivatives as single isomers (entries 15,16). A slightly higher reaction temperature is required for this class of substrates in order to reach full conversion within less than 24 hours. Attempts to carry out the diamination of (*Z*)-stilbene led again to formation of the *meso* product (50% isolated yield), probably due to a rapid isomerization of the double bond under the reaction conditions. However, chiral diamine products can be obtained from the oxidation of unsymmetrically substituted stilbenes such as **1q** (entry 17).

The same process can be conducted with bismesylimide as nitrogen source as well. Table 2 shows representative examples of this diamination reaction. It was noticed that the mixture of iodosobenzene diacetate and bismesylimide led to the quick formation of $PhI(OAc)NMs_2$ as a white solid,[5] which was insoluble and thus led to dramatically reduced conversion. Attempts to accelerate the reaction through additives were not successful, and finally, this problem could be overcome by employing microwave irradiation. Under such conditions, clean diamination of styrenes was accomplished, although for some styrenes the reaction time had to be significantly increased.

Abstract in Spanish: Se presenta un método eficiente y rápido para llevar a cabo la diaminación de alquenos promovido por especies de iodo(III) hipervalente en presencia de bissulfonilimidas. Una serie de mas de 60 olefinas, tanto en posición terminal como interna, con distinta sustitución demuestran la robustez del método y la elevada tolerancia a grupos funcionales.

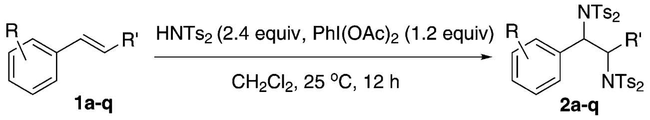
Para-substituted styrenes are preferred substrates (entries 3–10), and several substituents are tolerated, which include the benzyl chloride derivative (entry 5). In two cases, it was found that thermal conditions could compete well with microwave irradiation (entries 6,8). As expected, *meta*-substitution proceeds equally well (entries 11–13). It is particularly interesting to note that with bismesylimide as nitrogen source, diamination of *ortho*-substituted styrenes proceeds readily (entries 14,15), probably due to the lower steric demand of the bismesylimide in comparison to bistosylimide.

The advantage of the bismesyl substitution is evident from its convenient deprotection. Thus, single treatment with sodium bis(2-methoxyethoxy)aluminumhydride (Red-Al) leads to complete removal of all four mesyl substituents within a single step. While the work-up readily provides the free diamines, conversion into the corresponding bisbenzamides was found to be more convenient with regard to characterization (Table 3). In total, the reported two-step procedure includes the manipulation or formation of six amide bonds and proceeds with excellent overall yields of 69–95%. In summary, 1-aryl ethylenediamines are now available through a rapid, productive diamination of the respective styrenes in a robust low-step approach.

Despite the broad scope of the presented diamination reactions of styrenes (Tables 1 and 2), substrates displaying high electron density such as *para*-methoxystyrene usually lead to formation of enimides. This is particularly the case for the oxidation with $PhI(OAc)_2/HNTs_2$, which resulted in **4a** as the only isolated product (74% isolated yield). By contrast, the combination of $PhI(OAc)_2$ with $HNMs_2$ gives the desired diamine **2y** in 20% yield as the minor product. The major product is again the elimination product **4b**, which is obtained in 72% yield (Scheme 1), providing a 3.6:1 ratio of the enimide to the diamine product.

Intermolecular diamination of terminal alkenes **5** that do not contain an aryl substituent has so far remained elusive except for one report on palladium catalysis.[19a] Again, the simple reagent combination of bissulfonimide and $PhI(OAc)_2$ provides convenient access to this type of transformation, although a reaction temperature of 50°C is required. Since bismesylimide results in diamine products lacking any UV activity, exploration on the scope of this transformation is carried out with bistosylimide (Table 4). Hydrocarbons such as 1-hexene, 1-octene, 1-decene, and 1-dodecene all give the corresponding diamines **6a**–**d** as the only oxidation products in very good yields (entries 1–4), as does the α-branched vinylcyclohexane **5e** (entry 5). For octane **5b** the reaction was scaled up to a 5 mmol reaction, which again proceeded in a straight-forward manner to pro-

Table 1. Vicinal diamination of styrenes with bistosylimide.



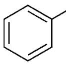
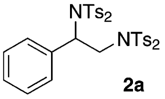
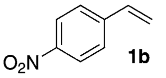
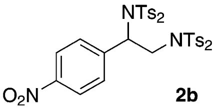
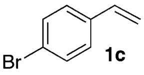
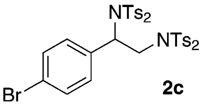
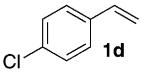
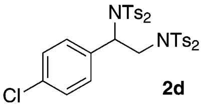
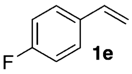
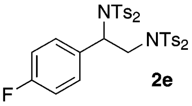
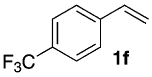
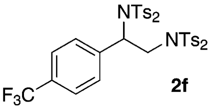
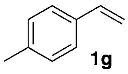
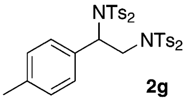
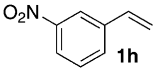
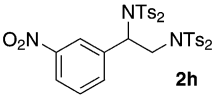
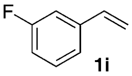
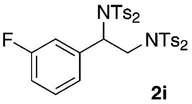
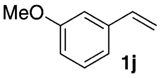
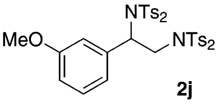
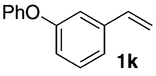
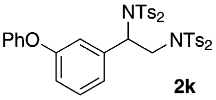
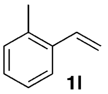
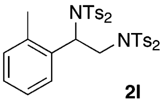
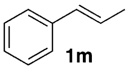
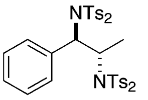
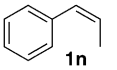
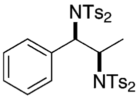
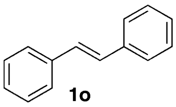
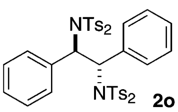
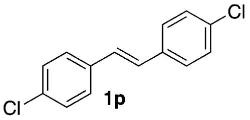
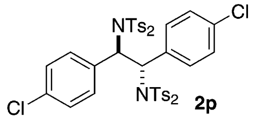
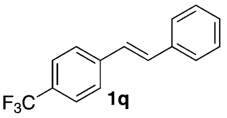
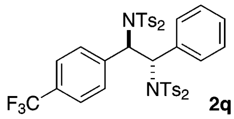
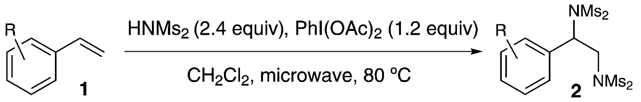
Entry	Alkene	Diamine	Yield [%][a]
1	 **1a**	 **2a**	80
2	 **1b**	 **2b**	70
3	 **1c**	 **2c**	80
4	 **1d**	 **2d**	69
5	 **1e**	 **2e**	66
6	 **1f**	 **2f**	79
7	 **1g**	 **2g**	42
8[b]	 **1h**	 **2h**	77
9	 **1i**	 **2i**	40
10	 **1j**	 **2j**	77
11	 **1k**	 **2k**	81
12	 **1l**	 **2l**	20
13	 **1m**	 **2m**	70
14[c]	 **1n**	 **2n**	61[d]
15[b]	 **1o**	 **2o**	56

Table 1. (Continued)

Entry	Alkene	Diamine	Yield [%][a]
16[b,e]	 1p	 2p	67
17[b,e]	 1q	 2q	56

[a] Isolated yields after purification. Scale, 0.5 mmol. [b] Reaction at 50 °C. [c] 7.2 equiv $HNTs_2$, 3.6 equiv $PhI(OAc)_2$, CH_2Cl_2, 25 °C, 36 h. [d] Together with 23 % **2m**. [e] 96 h reaction time.

Table 2. Vicinal diamination of styrenes with bismesylimide.



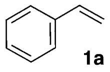
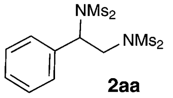
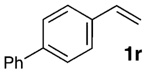
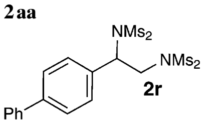
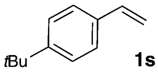
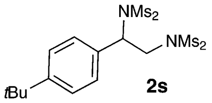
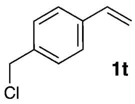
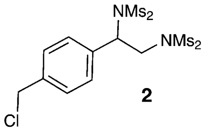
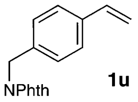
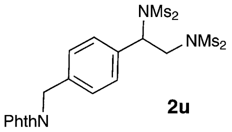
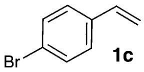
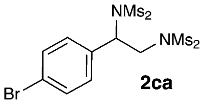
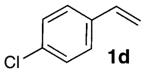
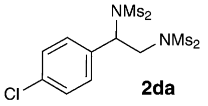
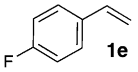
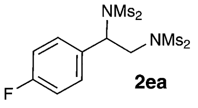
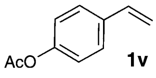
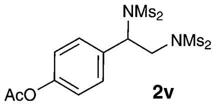
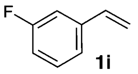
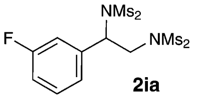
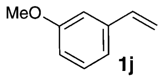
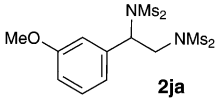
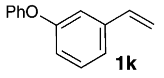
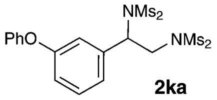
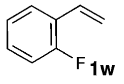
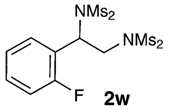
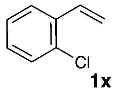
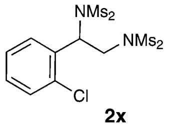
Entry	Alkene	t [h]	Diamine	Yield [%][a]
1	 1a	0.5	 2aa	62
2	**1a**	1	**2aa**	72
3	 1r	0.25	 2r	74
4	 1s	0.25	 2s	62
5	 1t	1.5	 2	58
6[b]	 1u	2.5	 2u	83
7	 1c	3	 2ca	67
8[b]	 1d	4	 2da	64
9	 1e	1	 2ea	54
10	 1v	1.5	 2v	60
11	 1i	14	 2ia	76

Table 2. (Continued)

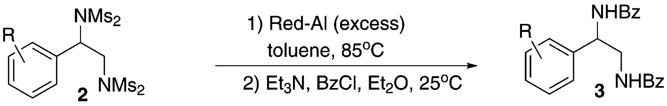
Entry	Alkene	t [h]	Diamine	Yield [%][a]
12	 1j	0.25	 2ja	65
13	 1k	3	 2ka	56
14	 1w	14	 2w	45
15	 1x	26	 2x	53

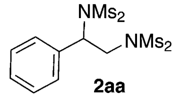
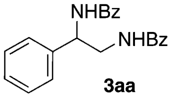
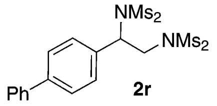
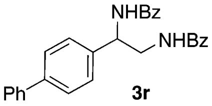
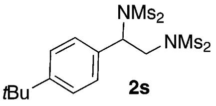
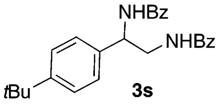
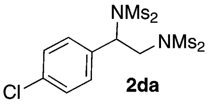
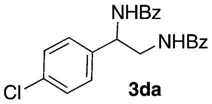
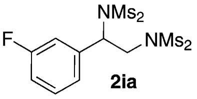
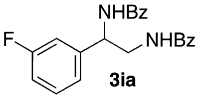
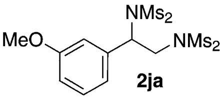
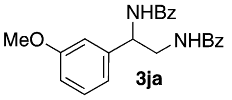
[a] Isolated yields after purification. Scale, 0.5 mmol. [b] Thermal reaction with external oil bath.

vide vicinal diamine **6b** in 81 % isolated yield. For 4-phenyl butene, the corresponding diamine **6f** was obtained in an excellent yield, and in this case, replacement of the nitrogen source for bismesylimide verifies that this nitrogen source is also feasible (entries 6,7).

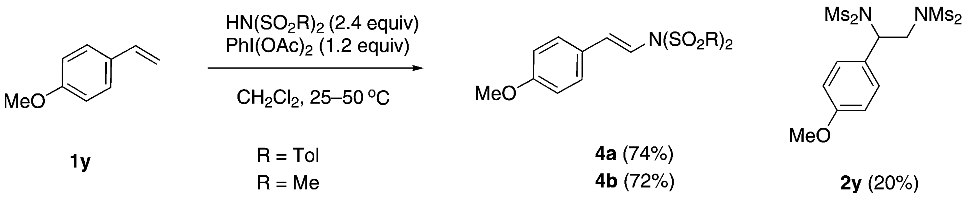
Allyl benzene **5g**, which represents a difficult substrate in metal catalysis due to double-bond isomerization, was cleanly converted into diamine **6g** in 90 % yield (entry 8). Selective monodiamination of 1,7-octadiene **5h** gave rise to the single product **6h** (entry 9), and methylvinylketone **5i** underwent an unprecedented diamination of an α,β-unsaturated ketone to provide **6i** (entry 10). A series of common functional groups were tolerated under the reaction conditions, including an ester, alkylbromide of different chain length, nitrile, phthalimide, and sulfone (entries 11–17). The yields equal or surpass those obtained by us using palladium-catalyzed diamination of alkenes.[19a] Alcohols are usually found to suffer from oxidation; however, when placed in suitable proximity to the alkene, they can participate in the oxidative difunctionalization. For example, 5-hexenol **5q** gives rise to amination product **6q** under concomitant formation of a tetrahydropyran ring (entry 18).

Table 3. Deprotection of diamines **2**.



Entry	Substrate	Product	Yield [%][a]
1	 **2aa**	 **3aa**	83
2	 **2r**	 **3r**	73
3	 **2s**	 **3s**	69
4	 **2da**	 **3da**	95
5	 **2ia**	 **3ia**	73
6	 **2ja**	 **3ja**	70

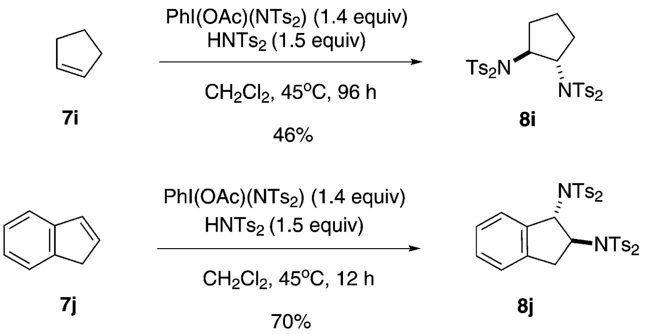
[a] Isolated yield after all steps and purification. Scale, 0.1 mmol.



Scheme 1. Oxidation of *para*-methoxystyrene **1y** with the $PhI(OAc)_2/HNR_2$ system.

Internal non-conjugated alkenes are usually beyond the scope of metal-catalyzed reactions. The present protocol leads to very good oxidation of internal (*E*)-configured alkenes **7** as well, provided that the preformed iodine(III) reagent $PhI(OAc)NTs_2$[5] is employed at a reaction temperature of 50 °C. Under such conditions, the expected diamination products **8** are generated selectively. Table 5 shows examples for this type of transformation. These include the diamination of simple unsaturated hydrocarbons **7a-e**, in which symmetric alkenes **7a** and **7b** give the corresponding *meso*-diamines **8a** and **8b**, respectively (entries 1,2). This outcome matches the one from the diamination of styrenes (Table 1, entries 15,16), and the stereochemistry of **8b** had been previously confirmed by X-ray analysis.[5] Nonsymmetric 2-octene and 2-heptene provide the corresponding diamines **8c,d** in excellent yield (entries 3,4), while 3-octene forms diamine **8e** in lower yield (entry 5). As in the case of terminal alkenes, the conditions for diamination of internal alkenes are compatible with common functional groups. For example, oxidation of alkenes **7f–h** bearing bromine, mesylate, or phthalimide, respectively, leads to the corresponding vicinal diamines as the only isolated products (entries 6–8). The superiority of the preformed reagent $PhI(OAc)NTs_2$ is obvious from a comparison with the in situ generated reagent using $PhI(OAc)_2/HNTs_2$. For **7b** and **7c**, incomplete conversion took place and the reaction time had to be increased to 36 hours. Even then, lower yields of 41 and 43 % were obtained for **8b** and **8c**, respectively.

We also investigated cyclic alkenes in our reaction. While cyclohexene and cyclooctene are beyond the scope of the present conditions, cyclopentene **7i** undergoes a clean diamination reaction to yield **8i** as the only product in 46 % yield (Scheme 2). This is a remarkable transformation that gives rise to a derivative of diaminocyclopentane, a chiral C_2-symmetric diamine that has so far received significantly less attention than the widely acclaimed diaminocyclohexane.[21] This fact certainly stems from its more difficult availability, although some multi-step approaches are known.[22] Certainly, direct vicinal diamination represents a convenient synthetic approach to this compound. To unambiguously confirm the C_2-symmetry of **8i**, its structure was secured by X-ray analysis (Figure 2).

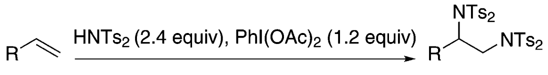


Scheme 2. Synthesis of C_2-symmetric vicinal diamine **8i**.

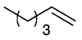
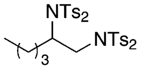
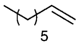
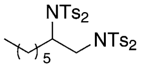
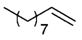
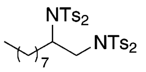
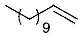
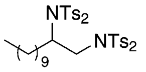
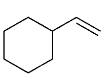
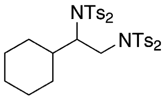
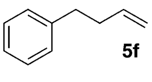
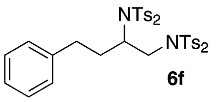
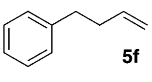
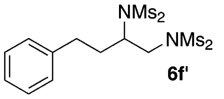
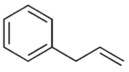
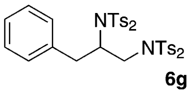
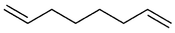
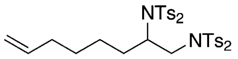
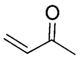
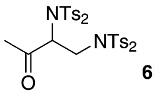
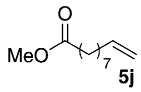
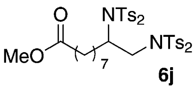
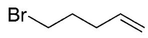
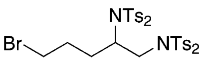
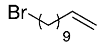
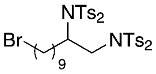
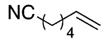
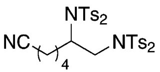
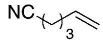
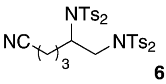
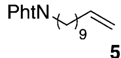
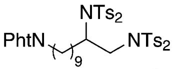
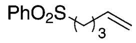
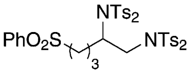
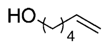
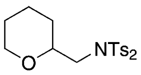
An attempt to carry out the enantioselective diamination of **7i** was not successful. However, indene **7j**, which as a styrene derivative represents a priviledged substrate, was successfully submitted to enantioselective diamination under conditions described previously.[5] In the present case, **7j** was transferred into the corresponding diamines **8j** and **8ja** using bistosylimide and bismesylimide, respectively, as nitrogen source (Scheme 3). As expected, the latter one proved superior in both yield and enantiomeric induction. Although the *ee* does not reach values as high as for related noncyclic substrates, the feasibility of enantioselective diamination of cyclic alkenes has now been demonstrated for the first time.[23]

Regarding these diamination reactions of (*Z*)-alkenes, the observed relative stereochemistry of **8i** and **8j**/**8ja** is in

Table 4. Diamination of terminal alkenes.

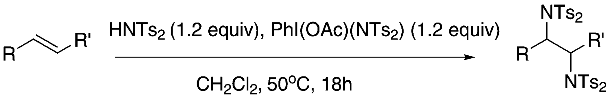


5a-q **6a-q, 6f'**

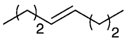
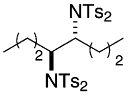
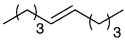
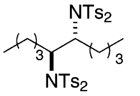
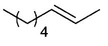
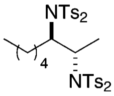
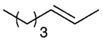
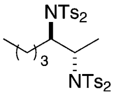
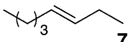
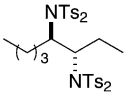
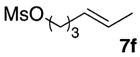
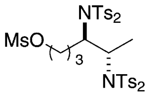
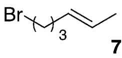
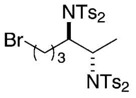
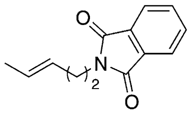
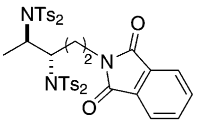
Entry	Alkene	Diamine	Yield [%][a]
1	 **5a**	 **6a**	60
2	 **5b**	 **6b**	80
3	 **5c**	 **6c**	80
4	 **5d**	 **6d**	68
5	 **5e**	 **6e**	53
6	 **5f**	 **6f**	87
7	 **5f**	 **6f'**	57[b]
8	 **5g**	 **6g**	90
9	 **5h**	 **6h**	74
10	 **5i**	 **6i**	53
11	 **5j**	 **6j**	70
12	 **5k**	 **6k**	88
13	 **5l**	 **6l**	89
14	 **5m**	 **6m**	91
15	 **5n**	 **6n**	82
16	 **5o**	 **6o**	67
17	 **5p**	 **6p**	69
18	 **5q**	 **6q**	71

[a] Isolated yields after purification. Scale, 0.5 mmol. [b] Isolated yield at 70% conversion.

Table 5. Diamination of internal alkenes.



7a-h **8a-h**

Entry	Alkene	Diamine	Yield [%][a]
1	 **7a**	 **8a**	54
2	 **7b**	 **8b**	54 (41)[b]
3	 **7c**	 **8c**	70 (43)[b]
4	 **7d**	 **8d**	80
5	 **7e**	 **8e**	54
6	 **7f**	 **8f**	66
7	 **7g**	 **8g**	47
8	 **7h**	 **8h**	52

[a] Isolated yields after purification. Scale, 0.5 mmol. [b] Yields in brackets refer to reactions with 1.2 equiv $PhI(OAc)_2$ and 2.4 equiv $HNTs_2$ at 50 °C for 36 h.

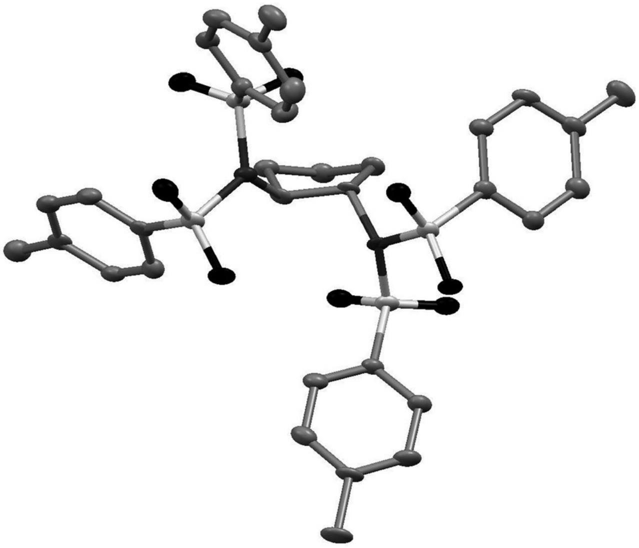
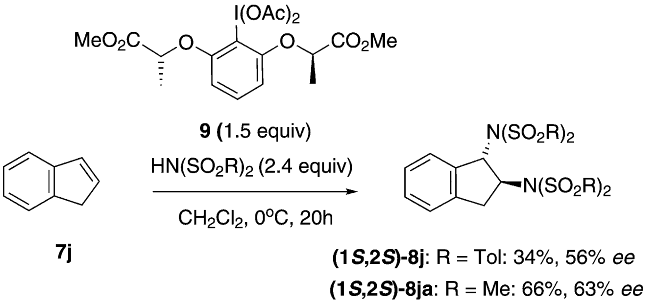


Figure 2. Crystal structure of **8i**. C gray, S light gray, N dark gray, O black. Hydrogen atoms are omitted for clarity.



Scheme 3. Enantioselective diamination of **7j**.

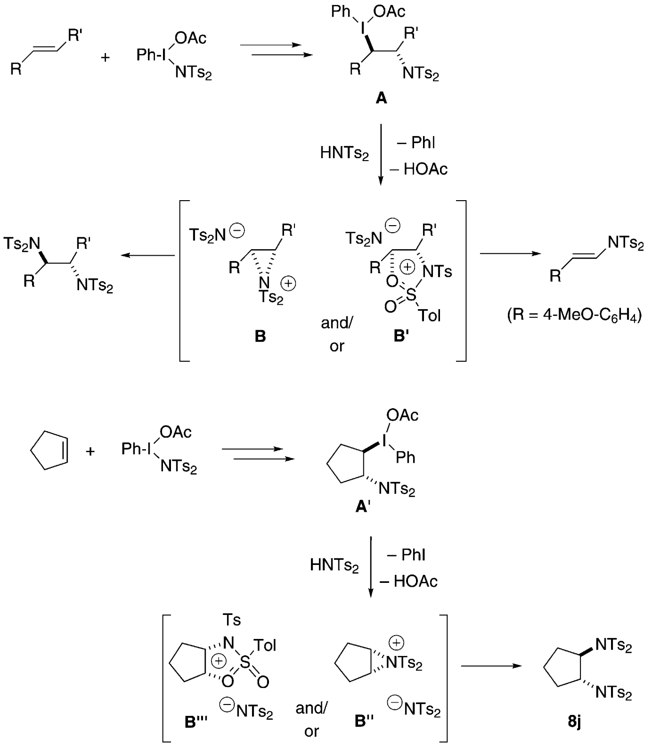


Figure 3. Proposed mechanism.

agreement with our earlier mechanistic proposal of an aziridinium intermediate **B** (Figure 3) that is generated from an aminoiodination intermediate **A** following an intramolecular reductive elimination of iodobenzene.[5] This aziridinium intermediate was postulated to be involved in enantioselective diamination reactions with bismesylimide taking into account stereochemical arguments.[5,3n] For the present reactions with the sterically more demanding bistosylimides this may not always be feasible, and stabilization may involve a bridging oxygen from the sulfonyl substituent. Opening of these intermediary stages **B**/**B′** gives rise to the final diamine products. For (*E*)-substituted alkenes (R′ = alkyl, aryl), this mechanism explains the observed relative stereochemistry (Table 1, entries 13,15–17 and Table 5), as well as the corresponding opposite diastereoselectivity in the major pathway for (*Z*)-β-methyl styrene **1n** (Table 1, entry 14). These reactions generally proceed stereospecifically as all postulated steps are expected to proceed with clean inversion of configuration. For styrenes possessing a rather strong donor substituent such as **1y** (R = 4-MeOPh, R’ = H), nucleophilic attack at the benzylic position of **B**/**B′** is less favorable due to strong mesomeric stabilization. As a consequence, elimination becomes the dominating pathway (Scheme 1). The same steps explain the observed C_2-symmetry for **8i** as a result of an aminoiodination of **7i** to **A′** followed by formation of intermediates **B″**/**B‴** and subsequent nucleophilic opening.

Finally, an acyclic alkene, (*Z*)-2-heptene **7k**, was submitted to diamination (Scheme 4). In this case, two isomeric vicinal diamines were obtained in a 2:1 ratio. The major diastereoisomer was identified to be the *anti*-product **8k** by NMR correlation with previously obtained *anti*-products, and the minor one was consequently assigned to be the corresponding *syn*-isomer **8k’**.

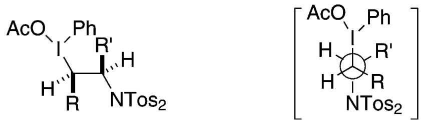
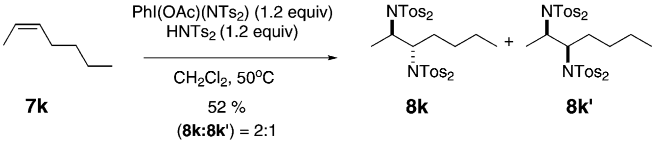


Figure 4. *Anti*-aminoiodinated intermediate from **7k** and its Newmann projection. R, R’ = CH_3, n-C_4H_9.

We believe that this unexpected major product is due to a higher activation barrier in the transition state for the formation of the aziridinium intermediate, in which R and R′ groups should be placed in a gauche conformation (Figure 4); as a result, a direct S_N2-type substitution by the generated NTs_2 anion starts to become competitive. However, a partial *Z* to *E* isomerization of the double bond of **7k** over the course of the reaction cannot be excluded. This would explain the major isomer **8k** to derive from a diamination of the (*E*)-alkene in agreement with the mechanism shown in Figure 3.



Scheme 4. Diamination reaction of (*Z*)-2-heptene **7k**.

Conclusions

We have described a robust reagent combination for the rapid and productive diamination of alkenes. A total of over 60 examples demonstrate the broad applicability of this new methodology that proceeds under metal-free conditions.

Experimental Section

General Procedure for Diamination of Terminal Alkenes

To a solution of $PhI(OAc)_2$ (0.18 g, 0.55 mmol) in CH_2Cl_2 (1.25 mL) was added $HNTs_2$ (0.36 g, 1.10 mmol) and the corresponding terminal alkene (0.50 mmol). The reaction mixture was heated at 25–50 °C in a sealed pyrex tube and the conversion was monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexanes/EtOAc, 6:1, v/v).

General Procedure for Diamination of Internal Alkenes

To a suspension of the preformed iodine reagent $PhI(OAc)NTs_2$ (0.35 g, 0.60 mmol) in CH_2Cl_2 (1.25 mL) was added $HNTs_2$ (0.20 g, 0.60 mmol) and the corresponding internal alkene (0.50 mmol). The reaction mixture was heated at 50 °C in a sealed pyrex tube and the conversion was monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexanes/EtOAc, 6:1, v/v).

Acknowledgements

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[1] For reviews on iodine(III)-reagents: a) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299; b) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523; c) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123; d) T. Dohi, Y. Kita, *Chem. Commun.* **2009**, 2073; e) M. Uyanik, K. Ishihara, *Chem. Commun.* **2009**, 2086; f) M. Ngatimin, D. W. Lupton, *Aust. J. Chem.* **2010**, *63*, 653; g) V. V. Zhdankin, *ARKIVOC* **2009**, *1*, 1; h) *Hypervalent Iodine in Organic Chemistry: Chemical Transformations* (Eds.: R. M. Moriarty, O. Prakash), Wiley-Interscience, New York, **2008**; i) M. A. Ciufolini, N. A. Braun, S. Canesi, M. Ousmer, J. Chang, D. Chai, *Synthesis* **2007**, 3759; j) M. Ochiai, *Chem. Rec.* **2007**, *7*, 12; k) *Top. Curr. Chem.*, *Vol. 224* (Ed.: T. Wirth), Springer, Berlin, **2003**.

[2] For the general case of 1,2-difunctionalization of alkenes: G. F. Koser, *Top. Curr. Chem.* **2000**, *208*, 137.

[3] Diacetoxylation: a) M. Fujita, W. Wakita, T. Sugimura, *Chem. Commun.* **2011**, *47*, 3983; b) Y.-B. Kang, L. H. Gade, *J. Am. Chem. Soc.* **2011**, *133*, 3658; ditosylation: c) L. Rebrovic, G. F. Koser, *J. Org. Chem.* **1984**, *49*, 2462; d) T. Wirth, U. H. Hirt, *Tetrahedron: Asymmetry* **1997**, *8*, 23; e) U. H. Hirt, B. Spingler, T. Wirth, *J. Org. Chem.* **1998**, *63*, 7674; f) U. H. Hirt, M. F. H. Schuster, A. N. French, O. G. Wiest, T. Wirth, *Eur. J. Org. Chem.* **2001**, 1569; g) I. Tellitu, E. Domínguez, *Tetrahedron* **2008**, *64*, 2465; h) W. Zhong, J. Yang, X. Mang, Z. Li, *J. Org. Chem.* dx.doi.org/10.1021/jo201752y; oxylactonization: i) M. Fujita, Y. Yoshida, K. Miyata, A. Wakisaka, T. Sugimura, *Angew. Chem.* **2010**, *122*, 7222; *Angew. Chem. Int. Ed.* **2010**, *49*, 7068; tetrahydrofuranation: j) M. Fujita, S. Okuno, H. J. Lee, T. Sugimura, T. Okuyama, *Tetrahedron Lett.* **2007**, *48*, 8691; k) M. Fujita, Y. Ookubo, T. Sugimura, *Tetrahedron Lett.* **2009**, *50*, 1298; oxybromination: l) D. C. Braddock, G. Cansell, S. A. Hermitage, *Chem. Commun.* **2006**, 2483; m) D. C. Whitehead, M. Fhaner, B. Borhan, *Tetrahedron Lett.* **2011**, *52*, 2288; for a related dichlorination: n) K. C. Nicolaou, N. L. Simmons, Y. Ying, P. M. Heretsch, J. S. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 8134; for recent advances in related Kita spirolactonization: o) M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem.* **2010**, *122*, 2221; *Angew. Chem. Int. Ed.* **2010**, *49*, 2175; p) T. Dohi, A. Maruyama, N. Takenaga, K. Senami, Y. Minamitsuji, H. Fujioka, S. B. Caemmerer, Y. Kita, *Angew. Chem.* **2008**, *120*, 3847; *Angew. Chem. Int. Ed.* **2008**, *47*, 3787.

[4] Aziridination: a) A. Yoshimura, V. N. Nemykin, V. V. Zhdankin, *Chem. Eur. J.* **2011**, *17*, 10538; b) R. D. Richardson, M. Desaize, T. Wirth, *Chem. Eur. J.* **2007**, *13*, 6745; c) J. Li, J.-L. Liang, P. W. H. Chan, C.-M. Che, *Tetrahedron Lett.* **2004**, *45*, 2685; d) J. Li, P. W. H. Chan, C.-M. Che, *Org. Lett.* **2005**, *7*, 5801; e) R. M. Moriarty, S. Tyagi, *Org. Lett.* **2010**, *12*, 364; f) M. M. Hoque, K. Miyamoto, N. Tada, M. Shiro, M. Ochiai, *Org. Lett.* **2011**, *13*, 5428; g) J. Hernández-Toribio, M. M. Hussain, K. Cheng, P. J. Carroll, P. J. Walsh, *Org. Lett.* **2011**, *13*, 6094; h) R. Fan, D. Pu, J. Gan, B. Wang, *Tetrahedron Lett.* **2008**, *49*, 4925; bisazidation: i) R. Chung, E. Yu, C. D. Incarvito, D. J. Austin, *Org. Lett.* **2004**, *6*, 3881; aminooxygenation: j) B. M. Cochran, F. E. Michael, *Org. Lett.* **2008**, *10*, 5039; k) D. J. Wardrop, E. G. Bowen, R. E. Forslund, A. D. Sussman, S. L. Weerasekera, *J. Am. Chem. Soc.* **2010**, *132*, 1188; l) H. M. Lovick, F. E. Michael, *J. Am. Chem. Soc.* **2010**, *132*, 1249; m) A. Correa, I. Tellitu, E. Domínguez, R. SanMartin, *J. Org. Chem.* **2006**, *71*, 8316; For oxidative installation of a spiro carbon-nitrogen bond: n) T. Dohi, A. Maruyama, Y. Minamitsuji, N. Takenaga, Y. Kita, *Chem. Commun.* **2007**, 1224.

[5] C. Röben, J. A. Souto, Y. González, A. Lishchynskyi, K. Muñiz, *Angew. Chem.* **2011**, *123*, 9650; *Angew. Chem. Int. Ed.* **2011**, *50*, 9478.

[6] a) K. Muñiz, C. H. Hövelmann, J. Streuff, E. Campos-Gómez, *Pure Appl. Chem.* **2008**, *80*, 1089; b) K. Muñiz, *New J. Chem.* **2005**, *29*, 1371.

[7] a) F. Cardona, A. Goti, *Nat. Chem.* **2009**, *1*, 269; b) R. M. de Figueiredo, *Angew. Chem.* **2009**, *121*, 1212; *Angew. Chem. Int. Ed.* **2009**, *48*, 1190; c) K. Muñiz in *Science of Synthesis: Stereoselective Synthesis, Vol. I*, Thieme, Stuttgart, **2011**, 5–67.

[8] V. Gómez Aranda, J. Barluenga, F. Aznar, *Synthesis* **1974**, 504.

[9] a) J. Barluenga, L. Alonso-Cires G. Asensio, *Synthesis* **1979**, 962; b) J. Barluenga, F. Aznar, M. C. S. de Mattos, W. B. Kover, S. García-Granda, E. Pérez-Carreño, *J. Org. Chem.* **1991**, *56*, 2930.

[10] a) K. Muñiz, *Chem. Soc. Rev.* **2004**, *33*, 166; b) A. O. Chong, K. Oshima, K. B. Sharpless, *J. Am. Chem. Soc.* **1977**, *99*, 3420; c) J. T. Anhaus, T. P. Kee, M. H. Schofield R. R. Schrock, *J. Am. Chem. Soc.* **1990**, *112*, 1642; M. H. Schofield, T. P. Kee, J. T. Anhaus, R. R. Schrock, K. H. Johnson, W. M. Davis, *Inorg. Chem.* **1991**, *30*, 3595; d) K. Muñiz, A. Iesato M. Nieger, *Chem. Eur. J.* **2003**, *9*, 5581; e) D. V. Deubel, K. Muñiz, *Chem. Eur. J.* **2004**, *10*, 2475; f) K. Muñiz, *Eur. J. Org. Chem.* **2004**, 2243; g) K. Muñiz, M. Nieger, *Synlett* **2003**, 0211; h) K. Muñiz, M. Nieger, *Chem. Commun.* **2005**, 2729; i) K. Muñiz, M. Nieger, H. Mansikkamäki, *Angew. Chem.* **2003**, *115*, 6140; *Angew. Chem. Int. Ed.* **2003**, *42*, 5958.

[11] a) J.-E. Bäckvall, *Tetrahedron Lett.* **1975**, *16*, 2225; b) J.-E. Bäckvall, *Tetrahedron Lett.* **1978**, *19*, 163; c) J.-E. Bäckvall, *Acc. Chem. Res.* **1983**, *16*, 335.

[12] a) T. P. Zabawa, D. Kasi, S. R. Chemler, *J. Am. Chem. Soc.* **2005**, *127*, 11250; b) T. P. Zabawa, S. R. Chemler, *Org. Lett.* **2007**, *9*, 2035.

[13] For reports on palladium-catalyzed synthesis of diamines from oxidation of butadienes or from allylic and homoallylic C−H activation, see ref. [7] and a) G. L. J. Bar, G. C. Lloyd-Jones, K. I. Booker-Milburn, *J. Am. Chem. Soc.* **2005**, *127*, 7308; b) H. Du, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 762; c) H. Du, W. Yuan, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7496; d) H. Du, W. Yuan, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 11688; e) B. Wang, H. Du, Y. Shi, *Angew. Chem.* **2008**, *120*, 8348; *Angew. Chem. Int. Ed.* **2008**, *47*, 8224; f) H. Du, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 8590; g) L. Xu, Y. Shi, *J. Org. Chem.* **2008**, *73*, 749; h) B. Zhao, H. Du, S. Cui, Y. Shi, *J. Am. Chem. Soc.* **2010**, *132*, 3523.

[14] a) B. Zhao, H. Du, Y. Shi, *J. Org. Chem.* **2009**, *74*, 8392; b) W. Yuan, H. Du, B. Zhao, Y. Shi, *Org. Lett.* **2007**, *9*, 2589; c) H. Du, B. Zhao, W. Yuan, Y. Shi, *Org. Lett.* **2008**, *10*, 4231; d) B. Zhao, X. Peng, S. Cui, Y. Shi, *J. Am. Chem. Soc.* **2010**, *132*, 11009; e) R. G. Cornwall, B. Zhao, Y. Shi, *Org. Lett.* **2011**, *13*, 434.

[15] a) J. Streuff, C. H. Hövelmann, M. Nieger, K. Muñiz, *J. Am. Chem. Soc.* **2005**, *127*, 14586; b) K. Muñiz, C. H. Hövelmann, J. Streuff, *J.*

Am. Chem. Soc. **2008**, *130*, 763; c) K. Muñiz, *J. Am. Chem. Soc.* **2007**, *129*, 14542; d) C. H. Hövelmann, J. Streuff, L. Brelot, K. Muñiz, *Chem. Commun.* **2008**, 2334; e) K. Muñiz, C. H. Hövelmann, E. Campos-Gómez, J. Barluenga, J. M. González, Jan Streuff, M. Nieger, *Chem. Asian J.* **2008**, *3*, 776; f) K. Muñiz, J. Streuff, P. Chávez, C. H. Hövelmann, *Chem. Asian J.* **2008**, *3*, 1248; g) P. A. Sibbald, F. E. Michael, *Org. Lett.* **2009**, *11*, 1147; h) P. A. Sibbald, C. F. Rosewall, R. D. Swartz, F. E. Michael, *J. Am. Chem. Soc.* **2009**, *131*, 15945.

[16] K. Muñiz, J. Streuff, C. H. Hövelmann, A. Nuñez, *Angew. Chem.* **2007**, *119*, 7255; *Angew. Chem. Int. Ed.* **2007**, *46*, 7125.

[17] A. Iglesias, K. Muñiz, *Chem. Eur. J.* **2009**, *15*, 10563.

[18] a) Y. Wen, B. Zhao, Y. Shi, *Org. Lett.* **2009**, *11*, 2365; b) B. Zhao, H. Du, Y. Shi, *Org. Lett.* **2008**, *10*, 1087; c) B. Zhao, W. Yuan, H. Du, Y. Shi, *Org. Lett.* **2007**, *9*, 4943.

[19] a) A. Iglesias, E. G. Pérez, K. Muñiz, *Angew. Chem.* **2010**, *122*, 8286; *Angew. Chem. Int. Ed.* **2010**, *49*, 8109; b) K. Muñiz, J. Kirsch, P. Chávez, *Adv. Synth. Catal.* **2011**, *353*, 689.

[20] Supplementary crystallographic data for this paper is available citing the following identification codes: CCDC 811769 (**2m**) and CCDC 847987 (**8i**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] J.-C. Kizirian, *Chem. Rev.* **2008**, *108*, 140.

[22] For selected approaches, see: a) C. Peña, J. González-Sabín, F. Rebolledo, V. Gotor, *Tetrahedron: Asymmetry* **2008**, *19*, 751; b) J. González-Sabín, V. Gotor, F. Rebolledo, *J. Org. Chem.* **2007**, *72*, 1309; c) A. Luna, I. Alfonso, V. Gotor, *Org. Lett.* **2002**, *4*, 3627; d) A. M. Daly, D. G. Gilheany, *Tetrahedron: Asymmetry* **2003**, *14*, 127; e) D. Kuppert, J. Sander, C. Roth, M. Worle, T. Weyhermuller, G. J. Reiss, U. Schilde, I. Muller, K. Hegetschweiler, *Eur. J. Inorg. Chem.* **2001**, 2525.

[23] For a previous approach to diamino indane via resolution, see: M. J. Palmer, J. A. Kenny, Jennifer T. Walsgrove, A. M. Kawamoto, M. Wills, *J. Chem. Soc. Perkin Trans. 1* **2002**, 416.

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