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Synthetic Methods

Iodine-Catalyzed Decarboxylative Amidation of β,γ-Unsaturated Carboxylic Acids with Chloramine Salts Leading to Allylic Amides

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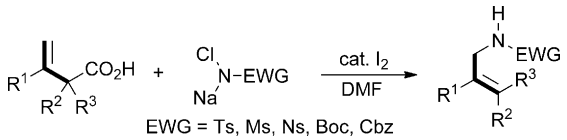
Abstract: The iodine-catalyzed decarboxylative amidation of β,γ-unsaturated carboxylic acids with chloramine salts is described. This method enables the regioselective synthesis of allylic amides from various types of β,γ-unsaturated carboxylic acids containing substituents at the α- and β-positions. In the reaction, *N*-iodo-*N*-chloroamides, generated by the reaction of a chloramine salt with I_2, function as a key active species. The reaction provides an attractive alternative to existing methods for the synthesis of useful secondary allylic amine derivatives.

Allylic amines are a versatile building block for the synthesis of nitrogen-containing organic molecules. Therefore, great efforts have been devoted to the development of new synthetic methodologies for their preparation in the past few decades. The coupling of amine derivatives with an allylic component represents the most straightforward approach for the synthesis of allylic amines. In these reactions, the classical method involves the nucleophilic substitution of an allylic halide by a nitrogen nucleophile.[1a,b] Although this approach is efficient and reliable, it remains limited by a narrow substrate scope, owing to difficulties associated with the regioselective synthesis of allylic halides. In recent years, transition metal-catalyzed allylic substitution of allylic alcohols or their derivatives with nitrogen nucleophiles has emerged as a broadly applicable method and has also been extended to the asymmetric synthesis of allylic amines.[1,2] Most recently, the intra- and intermolecular oxidative allylic C–H aminations of alkenes under transition-metal-catalyzed[3,4] or metal-free[5] conditions have been reported as a novel method to enable direct allylic amination. Although these elegant methods appear to be general and efficient, new synthetic strategies, especially under mild and environmentally benign conditions, are still desirable.[6] In this context, we envisioned that β,γ-unsaturated carboxylic acids[7] could be utilized as a new class of efficient allylating reagents for the synthesis of allylic amines under oxidative conditions, that is, by decarboxylative amination.[8]

Recently, our group reported on the use of hypervalent iodine reagents in the decarboxylative imidation of β,γ-unsaturated carboxylic acids with imide ligands, affording allylic imides.[9] However, the substrate scope and regioselectivity was not ideal. Concurrently, our group continued to investigate oxidative amination reactions, in particular aziridination of alkenes, using inexpensive and readily available chloramine salts in the presence of I_2 as the catalyst.[10,11] In the system, *N*-iodo-*N*-chloroamide is generated in situ by the reaction of a chloramine salt with I_2 and then activates a carbon–carbon double bond in the substrate through the formation of a three-membered iodonium intermediate. As part of our ongoing research efforts in iodine-catalyzed oxidative amination reactions, we herein report on the iodine-catalyzed decarboxylative amidation of β,γ-unsaturated carboxylic acids with chloramine salts that function as a nitrogen source as well as an oxidant (Scheme 1). The method was found to be applicable to



Scheme 1. Decarboxylative amidation of β,γ-unsaturated carboxylic acids.

various types of β,γ-unsaturated carboxylic acids containing substituents at the α- and β-positions to afford synthetically useful secondary allylic amides in a regioselective manner. It is noteworthy that the regioselective synthesis of allylic amides containing a tetrasubstituted alkene moiety, which are difficult to access by conventional protocols, was also achieved.

Our investigation began with the decarboxylative amidation of 3-phenylbut-3-enoic acid (**1a**) as a model substrate with 1.5 equivalents of *N*-chloro-*N*-sodio-*p*-toluenesulfonamide (chloramine-T) in the presence of a catalytic amount of I_2 (Table 1). On the basis of our previous work on chloramine-T/I_2 systems,[10] the reaction was first conducted in MeCN for 2 h at room temperature, and the allylic amide **2a** was produced in 53% yield.[12] Although reactions in other common organic solvents, such as toluene, diethyl ether, dimethoxyethane (DME), and dimethylsulfoxide (DMSO), failed to improve the product yield of **2a** (Table 1, entries 2–5), the use of several polar solvents including *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylacetoamide (DMA), and *N*,*N*-dimethylformamide (DMF) resulted in increased yields of up to 82% (Table 1, entries 6–8). Finally, DMF was identified as the best solvent for this transformation, providing a high yield with high reproducibility (Table 1,

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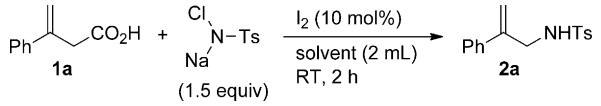
Table 1. Solvent screening.[a]



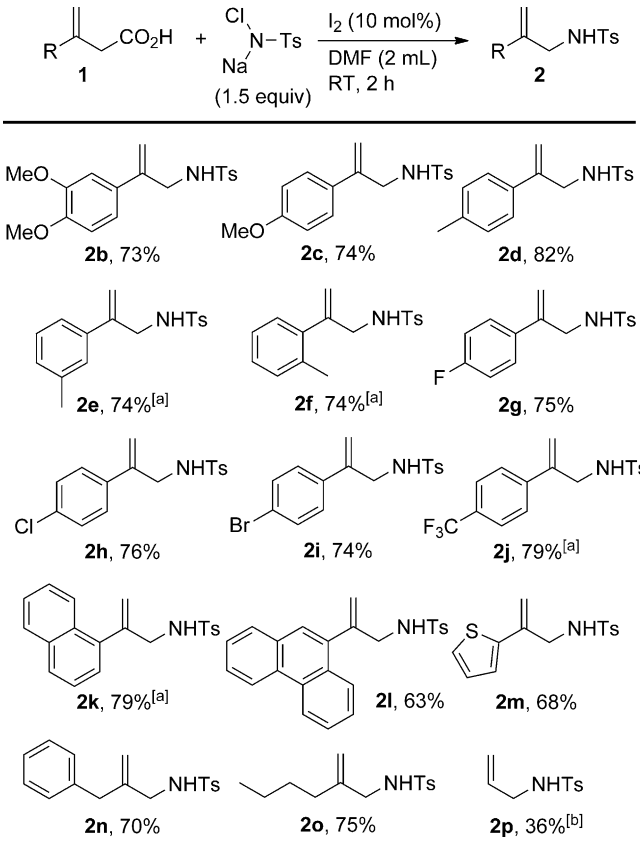
Entry	Solvent	Yield[b] [%]
1	MeCN	53
2	Toluene	7
3	Et_2O	6
4	DME	17
5	DMSO	34
6	NMP	82
7	DMA	79
8	DMF	82 (78)
9[c]	DMF	55

[a] Reaction conditions: **1a** (0.25 mmol), chloramine-T (0.375 mmol), solvent (2 mL), RT, 2 h. [b] Determined by ^{1}H NMR analysis of the crude product using 1,1,2,2-tetrachloroethane as an internal standard. The value in parenthesis is the yield of isolated product. [c] Chloramine-T (1 equiv) was used. Ts = *p*-toluenesulfonyl; DME = dimethoxyethane; DMSO = dimethylsulfoxide; NMP = *N*-methylpyrrolidone; DMA = *N*,*N*-dimethylacetoamide; DMF = *N*,*N*-dimethylformamide.

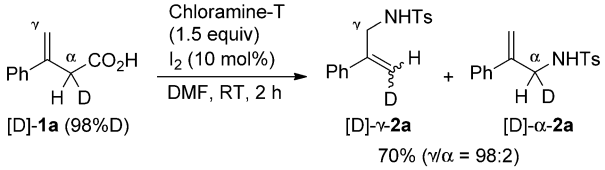
entry 8). Decreasing the amount of chloramine-T from 1.5 to 1 equivalent resulted in a lower yield of **2a** (Table 1, entry 9).

With the optimized conditions in hand, we next investigated the decarboxylative amidation of various β-substituted β,γ-unsaturated carboxylic acids **1** (Scheme 2). Substrates with electron-rich aryl substituents at the β-position effectively provided the amides **2b**–**d** at room temperature without the formation of any overoxidation product. However, in cases with substituents at the *meta* or *ortho* position on the phenyl ring, it was necessary to heat the reaction mixture to achieve satisfactory yields (**2e** and **2f**). Halogen substituents, fluoro (**2g**), chloro (**2h**), and bromo (**2i**) groups, were well tolerated. A highly electron-deficient substrate with a trifluoromethyl group also underwent decarboxylative amidation in good yield at 50 °C (**2j**). Other β-aromatic substrates, including naphthyl (**2k**), phenanthryl (**2l**), and thienyl (**2m**) groups, were efficiently converted into the corresponding amides. In addition, the amidation could also be expanded to substrates that contained β-aliphatic substituents. In those reactions, it is noteworthy that allylic amides containing a terminal alkene moiety (**2n** and **2o**) were produced selectively, where neither the internal alkene isomer nor the oxidation product of benzylic and allylic C–H bonds was observed. A β-unsubstituted substrate, but-3-enoic acid, also underwent decarboxylative amidation to provide **2p**, albeit in low yield. Consequently, this decarboxylative amidation approach was proven to be useful for the synthesis of allylic amides with a substituent at the β-position.

In an attempt to confirm the site of incorporation of the amide group (α- vs. γ-position), the reaction of the α-monodeuterated carboxylic acid [D]-**1a** was examined. Under the standard conditions, the reaction predominantly afforded [D]-γ-**2a**, which contained a deuterium atom at the vinylic position, over the α-product [D]-α-**2a** (γ/α = 98:2; Scheme 3). This result clearly indicates that the amidation proceeds selectively at the γ-position.



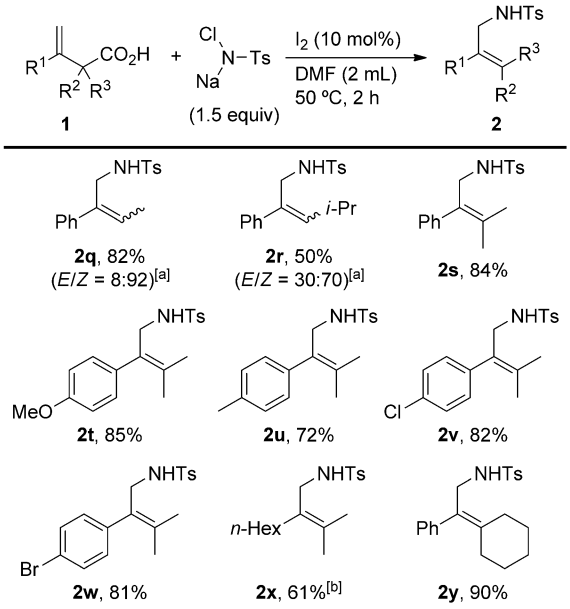
Scheme 2. Scope of β-substituted β,γ-unsaturated carboxylic acids. Unless otherwise noted, the following reaction conditions were employed: **1** (0.25 mmol), chloramine-T (0.375 mmol), DMF (2 mL), RT, 2 h. Yields are for the isolated product. [a] The reaction was conducted at 50 °C. [b] The reaction was conducted at 120 °C for 6 h. Yield was determined by ^{1}H NMR analysis of the crude product.



Scheme 3. Deuterium-labeling experiment for the decarboxylative amidation.

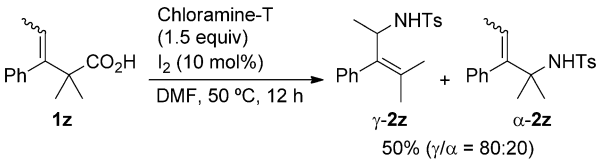
Encouraged by the results described in Scheme 3, we examined the reaction of acids with α-substituents for the regioselective synthesis of allylic amides that contain tri- and tetrasubstituted alkene moieties, which are difficult to prepare in isomerically pure form by conventional methods (Scheme 4).

As expected, the decarboxylative amidation of α-methylated **1q** proceeded with complete selectivity at the γ-position, affording the product **2r** (*E*/*Z* = 8:92) in high yield.[13] The bulkier isopropyl substituent at the α-position resulted in a decreased yield of **2s** as well as a decrease in *E*/*Z* selectivity. Acids with α,α-dimethyl substituents also underwent decarboxylative amidation selectively to give the corresponding products that contained a tetrasubstituted alkene moiety (**2t**–**x**). Moreover, the



Scheme 4. Scope of β,γ-unsaturated carboxylic acids with α- and β-substituents. Unless otherwise noted, the following reaction conditions were employed: **1** (0.25 mmol), chloramine-T (0.375 mmol), DMF (2 mL), 50 °C, 2 h. Yields are for the isolated product. [a] Determined by ^{1}H NMR analysis of the crude product. [b] The reaction was conducted for 12 h.

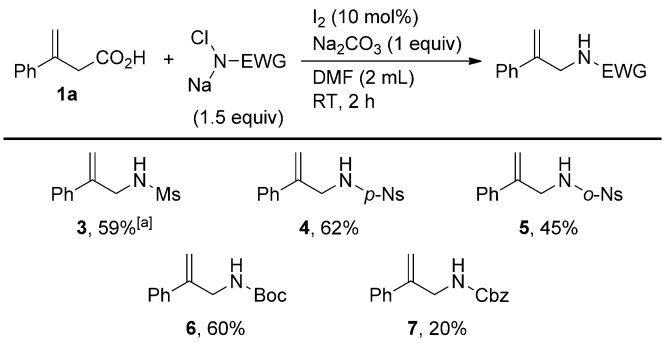
allylic amide **2y**, containing an exocyclic double bond, could be synthesized in high yield using this protocol. However, the reaction of **1z**, which has a methyl group at the γ-position, resulted in the generation of a mixture of regioisomers, γ-**2z** and α-**2z** (γ/α = 80:20; Scheme 5).[14]



Scheme 5. Reaction using a γ-substituted substrate.

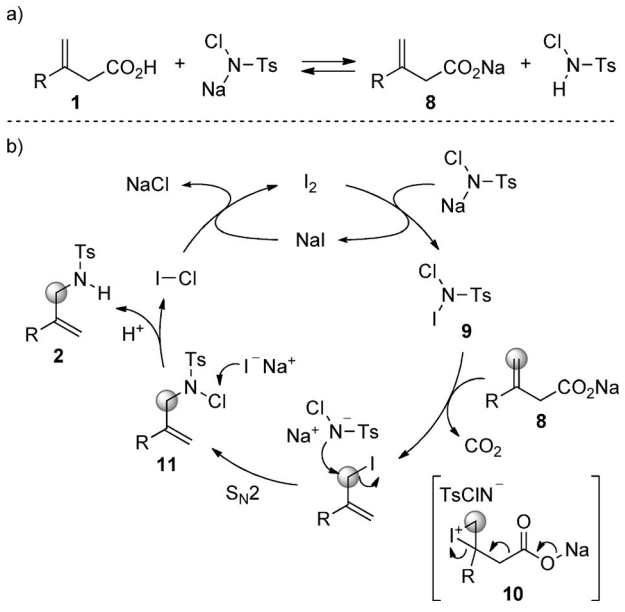
Other types of chloramine salts were employed in the decarboxylative amidation (Scheme 6). Instead of chloramine-T, *N*-chloro-*N*-sodio-methanesulfonamide (chloramine-Ms) was also applicable and gave the corresponding amide **3** in moderate yield. Chloramine salts with a nitrobenzenesulfonyl group (Ns) were also suitable nitrogen sources affording products **4** and **5** in acceptable yields in the presence of Na_2CO_3 as a base. In addition, carbamate-protected chloramine salts such as chloramine-Boc and -Cbz could also participate in the decarboxylative amidation to provide **6** and **7**, respectively, but the latter was produced in low yield.

To obtain further insight into the reaction mechanism, we conducted several additional experiments. When a reaction mixture of **1a** and chloramine-T in [D$_7$]DMF was monitored by ^{1}H NMR spectroscopy, the signal of the acidic OH disappeared and the proton signals of **1a** underwent a slight upfield shift,



Scheme 6. Reactions using various chloramine salts. Unless otherwise noted, the following reaction conditions were employed: **1** (0.25 mmol), chloramine salts (0.375 mmol), Na_2CO_3 (0.25 mmol), DMF (2 mL), RT, 2 h. Yields are for the isolated product. [a] Na_2CO_3 was not added. The reaction was conducted for 4 h. Ms = methanesulfonyl, Ns = nitrobenzenesulfonyl, Boc = *tert*-butoxycarbonyl, Cbz = carboxybenzyl.

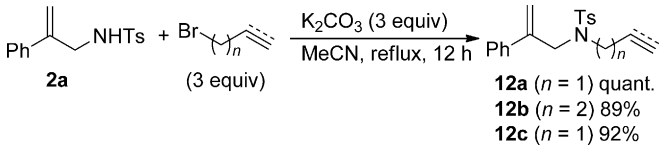
indicating the in situ formation of an equilibrium mixture of the sodium salt **8** (Scheme 7a).[15] In addition, the reaction was run using a mixture of chloramine-T and **1a** in the presence of 10 mol% of I_2 in [D$_7$]DMF and was monitored by NMR spectroscopy. In the ^{1}H NMR spectra of the mixture, characteristic signals, indicating the generation of amide **2a** as well as the allylic chloride **2a′** and iodide **2a″**, were observed immediately.[16] The reaction then reached completion within 1 h to afford the amide **2a** and the allylic chloride **2a′**, whereas the signals indicating allylic iodide **2a″** disappeared. Indeed, when (3-iodoprop-1-en-2-yl)benzene (**2a″**), which was separately prepared, was treated with chloramine-T in DMF, the allylic amide **2a** was produced in high yield.[16] These results strongly suggest that an allylic iodide could be an intermediate in this reaction. Based on the experimental results, the proposed catalytic cycle is shown in Scheme 7b. Initially, chloramine-T reacts with



Scheme 7. Plausible reaction mechanism.

I_2 to provide the *N*-iodo-*N*-chloroamide **9**, which then activates the alkene moiety of **8** via formation of a three-membered iodonium intermediate **10**. The decarboxylation of **10** gives the allylic iodide along with the generation of a chloramine salt. A subsequent S_N2 displacement by the chloramine salt results in the formation of chloramine **11**, which then reacts with NaI, leading to product **2** after protonation. Finally, the resulting iodine monochloride (ICl) serves to oxidize NaI to regenerate I_2.[17] In this reaction, the selective introduction of an amino group is achieved through selective decarboxylative iodination at the γ-position followed by an S_N2-type nucleophilic attack of a chloramine salt. As described in Scheme 5, the regioselectivity was reduced in the reaction of **1z**. This is probably because the steric hidrance at the γ-position retarded the S_N2 displacement, and the stable allylic cation intermediate was partially formed by elimination of the iodide from the allylic iodide, which would lead to the formation of a mixtutre of α- and γ-products.

Finally, we demonstrated the utility of the secondary amide product **2** by its smooth conversion to more synthetically useful compounds (Scheme 8). For example, the reaction of **2a**



Scheme 8. Alkylation of product **2a**.

with allyl bromide and 4-bromobut-1-ene afforded the corresponding products **12a** and **12b**, respectively, which are important precursors for the synthesis of chiral nitrogen-containing heterocycles by ring-closing metathesis followed by asymmetric hydrogenation.[18] Moreover, the enyne **12c** was also synthesized by the reaction using propargyl bromide.[19]

In conclusion, we have reported the development of the iodine-catalyzed decarboxylative amidation of β,γ-unsaturated carboxylic acids with chloramine salts. The reaction enables the efficient and selective synthesis of various secondary allylic amides. Considering the low cost and the availability of iodine and chloramine salts, this metal-free approach represents a highly economical and environmentally benign procedure. Further investigations focused on expanding the scope of this method are currently in progress.

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Keywords: amines · amidation · chloramine salt · decarboxylation · iodine

[1] For selected reviews, see: a) R. B. Cheikh, R. Chaabouni, A. Laurent, P. Mison, A. Nafti, *Synthesis* **1983**, 685 – 700; b) M. Johannsen, K. A. Jørgensen, *Chem. Rev.* **1998**, *98*, 1689 – 1708; c) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921 – 2943; d) G. Helmchen, A. Dahnz, P. Dübon, M. Schelwies, R. Weihofen, *Chem. Commun.* **2007**, 675 – 691; e) J. Muzart, *Eur. J. Org. Chem.* **2007**, 3077 – 3089; f) J. F. Hartwig, M. J. Pouy, *Top. Organomet. Chem.* **2011**, *34*, 169 – 208; g) B. Sundararaju, M. Achard, C. Bruneau, *Chem. Soc. Rev.* **2012**, *41*, 4467 – 4483.

[2] For selected recent examples of metal-catalyzed allylic amination, see: a) T. Nagano, S. Kobayashi, *J. Am. Chem. Soc.* **2009**, *131*, 4200 – 4201; b) D. Banerjee, R. V. Jagadeesh, K. Junge, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 11556 – 11560; *Angew. Chem.* **2012**, *124*, 11724 – 11728; c) J. H. Lee, S. Lee, *Chem. Sci.* **2013**, *4*, 2922 – 2927; d) A. Sharma, J. F. Hartwig, *J. Am. Chem. Soc.* **2013**, *135*, 17983 – 17989; e) D. Banerjee, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 13049 – 13053; *Angew. Chem.* **2014**, *126*, 13265 – 13269; f) J. S. Arnold, E. T. Mwenda, H. M. Nguyen, *Angew. Chem. Int. Ed.* **2014**, *53*, 3688 – 3692; *Angew. Chem.* **2014**, *126*, 3762 – 3766; g) B.-S. Kim, M. M. Hussain, N. Hussain, P. J. Walsh, *Chem. Eur. J.* **2014**, *20*, 11726 – 11739; h) R. L. Grange, E. A. Clizbe, E. J. Counsellb, P. A. Evans, *Chem. Sci.* **2015**, *6*, 777 – 781.

[3] For selected reviews of metal-catalyzed allylic C–H amination, see: a) S. Fantauzzi, A. Caselli, E. Gallo, *Dalton Trans.* **2009**, 5434 – 5443; b) F. Collet, R. H. Dodd, P. Dauban, *Chem. Commun.* **2009**, 5061 – 5074; c) D. N. Zalatan, J. Du Bois, *Top. Curr. Chem.* **2009**, *292*, 347 – 378; d) F. Collet, C. Lescot, P. Dauban, *Chem. Soc. Rev.* **2011**, *40*, 1926 – 1936.

[4] For selected recent examples of metal-catalyzed allylic C–H amination, see: a) K. J. Fraunhoffer, M. C. White, *J. Am. Chem. Soc.* **2007**, *129*, 7274 – 7276; b) S. A. Reed, M. C. White, *J. Am. Chem. Soc.* **2008**, *130*, 3316 – 3318; c) E. Milczek, N. Boudet, S. Blakey, *Angew. Chem. Int. Ed.* **2008**, *47*, 6825 – 6828; *Angew. Chem.* **2008**, *120*, 6931 – 6934; d) G. Liu, G. Yin, L. Wu, *Angew. Chem. Int. Ed.* **2008**, *47*, 4733 – 4736; *Angew. Chem.* **2008**, *120*, 4811 – 4814; e) C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd, P. Dauban, *J. Am. Chem. Soc.* **2008**, *130*, 343 – 350; f) L. Wu, S. Qiu, G. Liu, *Org. Lett.* **2009**, *11*, 2707 – 2710; g) S. A. Reed, A. R. Mazzotti, M. C. White, *J. Am. Chem. Soc.* **2009**, *131*, 11701 – 11706; h) G. T. Rice, M. C. White, *J. Am. Chem. Soc.* **2009**, *131*, 11707 – 11711; i) Y. Shimizu, Y. Obora, Y. Ishii, *Org. Lett.* **2010**, *12*, 1372 – 1374; j) Y. Liu, C.-M. Che, *Chem. Eur. J.* **2010**, *16*, 10494 – 10501; k) G. Yin, Y. Wu, G. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 11978 – 11987; l) M. E. Harvey, D. G. Musaev, J. Du Bois, *J. Am. Chem. Soc.* **2011**, *133*, 17207 – 17216; m) C. Jiang, D. J. Covell, A. F. Stepan, M. S. Plummer, M. C. White, *Org. Lett.* **2012**, *14*, 1386 – 1389; n) I. I. Strambeanu, M. C. White, *J. Am. Chem. Soc.* **2013**, *135*, 12032 – 12037; o) E. T. Hennessy, R. Y. Liu, D. Iovan, R. A. Duncan, T. A. Betley, *Chem. Sci.* **2014**, *5*, 1526 – 1532; p) S. Murru, R. S. Srivastava, *Eur. J. Org. Chem.* **2014**, 2174 – 2181; q) H. Chen, W. Yang, W. Wu, H. Jiang, *Org. Biomol. Chem.* **2014**, *12*, 3340 – 3343.

[5] For selected examples of metal-free allylic C–H amination, see: a) K. B. Sharpless, T. Hori, L. K. Truesdale, C. O. Dietrich, *J. Am. Chem. Soc.* **1976**, *98*, 269 – 271; b) M. Bruncko, T. A. V. Khuong, K. B. Sharpless, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 454 – 456; *Angew. Chem.* **1996**, *108*, 453 – 455; c) J. A. Souto, D. Zian, K. Muñiz, *J. Am. Chem. Soc.* **2012**, *134*, 7242 – 7245; d) Y. Wei, F. Liang, X. Zhang, *Org. Lett.* **2013**, *15*, 5186 – 5189; e) M.-Y. Chang, Y.-C. Chen, C.-K. Chan, *Tetrahedron Lett.* **2014**, *55*, 4767 – 4770; f) X. Zhu, S. Chiba, *Org. Biomol. Chem.* **2014**, *12*, 4567 – 4570.

[6] Other representative examples of the synthesis of allylic amines are shown. For examples of the vinylation of imines, see: a) N. A. Petasis, I. Akritopoulou, *Tetrahedron Lett.* **1993**, *34*, 583 – 586; b) E. P. Kündig, L. H. Xu, B. Schnell, *Synlett* **1994**, 413 – 414; c) P. Merino, S. Anoro, F. Merchan, E. Castillo, T. Tejero, *Tetrahedron: Asymmetry* **1996**, *7*, 1887 – 1890; d) D. Enders, J. Schankat, *Helv. Chim. Acta* **1995**, *78*, 970 – 992. For examples of the reduction of α,β-unsaturated imines, see: e) N. D. Kimpe, E. Stanoeva, R. Verhé, N. Schamp, *Synthesis* **1988**, 587 – 592; f) P. Kocovsky, *Synlett* **1990**, 677 – 679. For examples of the hydroamination of allenes, see: g) L. Besson, J. Goré, B. Cazes, *Tetrahedron Lett.* **1995**, *36*, 3857 – 3860; for a review, see: h) L. Huang, M. Arndt, K. Gooßen, H. Heydt, L. J. Gooßen, *Chem. Rev.* **2015**, *115*, 2596 – 2697. For examples of the coupling of alkynes with zirconocene complexes of imines, see: i) S. L. Buchwald, B. T. Watson, M. W. Wannamaker, J. C. Dewan, *J. Am. Chem. Soc.* **1989**, *111*, 4486 – 4494; j) R. B. Grossman, W. M. Davis, S. L. Buchwald, *J. Am. Chem. Soc.* **1991**, *113*, 2321 – 2322. For example of the coupling of imines with titanium complexes of alkynes, see: k) Y. Gao, K.

Harada, F. Sato, *Tetrahedron Lett.* **1995**, *36*, 5913 – 5916. For examples of the ene reaction of alkynes with iminium species, see: l) A. R. Ofial, H. Mayr, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 143 – 145; *Angew. Chem.* **1997**, *109*, 145 – 147; m) M. Shimizu, H. Itou, T. Iwao, Y. Umeda, *Chem. Lett.* **2009**, *38*, 732 – 733; n) N. Arai, T Ohkuma, *Tetrahedron* **2011**, *67*, 1617 – 1622. For example of the coupling of α-aminoalkyl cuprates with enol triflates, see: o) R. K. Dieter, J. W. Dieter, C. W. Alexander, N. S. Bhinderwala, *J. Org. Chem.* **1996**, *61*, 2930 – 2931. For other methods, also see references [1a] and [1b].

[7] For the decarboxylative difluoromethylation of β,γ-unsaturated carboxylic acids, see: Z. He, M. Hu, T. Luo, L. Li, J. Hu, *Angew. Chem. Int. Ed.* **2012**, *51*, 11545 – 11547; *Angew. Chem.* **2012**, *124*, 11713 – 11715.

[8] For selected examples of decarboxylative C–N bond formation, see: a) A. Boto, R. Hernández, E. Suárez, *Tetrahedron Lett.* **1999**, *40*, 5945 – 5948; b) Y. Zhang, S. Patel, N. Mainolfi, *Chem. Sci.* **2012**, *3*, 3196 – 3199; c) W. Jia, N. Jiao, *Org. Lett.* **2010**, *12*, 2000 – 2003.

[9] K. Kiyokawa, S. Yahata, T. Kojima, S. Minakata, *Org. Lett.* **2014**, *16*, 4646 – 4649.

[10] a) S. Minakata, *Acc. Chem. Res.* **2009**, *42*, 1172 – 1182; b) T. Ando, D. Kano, S. Minakata, I. Ryu, M. Komatsu, *Tetrahedron* **1998**, *54*, 13485 – 13494; c) D. Kano, S. Minakata, M. Komatsu, *J. Chem. Soc. Perkin Trans. 1* **2001**, 3186 – 3188; d) S. Minakata, D. Kano, Y. Oderaotoshi, M. Komatsu, *Angew. Chem. Int. Ed.* **2004**, *43*, 79 – 81; *Angew. Chem.* **2004**, *116*, 81 – 83.

[11] Aziridination of styrene derivatives with iminoiodinane catalyzed by a combination of iodine and ammonium iodide has been also reported. See: K. Kiyokawa, T. Kosaka, S. Minakata, *Org. Lett.* **2013**, *15*, 4858 – 4861.

[12] The corresponding allylic chloride and iodide were also obtained as by-products. See the Supporting Information for details.

[13] The structure of the product was confirmed by X-ray crystallography. See the Supporting Information for details.

[14] The reaction using 2-(3,4-dihydronaphthalen-1-yl)acetic acid also gave the product as a mixture of regioisomers. See the Supporting Information for details.

[15] The pK_a value of *N*-chloro-*p*-toluenesulfonamide (TsNHCl) is estimated to be 4.41 in H_2O. See: H. Dannan, A. Hussain, P. A. Crooks, L. W. Dittert, *J. Pharm. Sci.* **1992**, *81*, 657 – 660.

[16] See the Supporting Information for details.

[17] A mechanism where iodine monochloride (ICl) generated in situ functions as a catalyst instead of I_2 cannot be ruled out.

[18] J. J. Verendel, T. Zhou, J.-Q. Li, A. Paptchikhine, O. Lebedev, P. G. Andersson, *J. Am. Chem. Soc.* **2010**, *132*, 8880 – 8881.

[19] A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785 – 6786.

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