Iridium-Catalyzed Synthesis of Primary Allylic Amines from Allylic Alcohols: Sulfamic Acid as Ammonia Equivalent**

Christian Defieber, Martin A. Ariger, Patricia Moriel, and Erick M. Carreira*

A large range of building blocks are accessible thanks to the impressive advances in homogeneous catalysis. Many reactions require the use of preactivated reactants with the exception of simple atom-transfer processes, such as epoxidation or hydrogenation. Additionally, the protected products must be subjected to further chemical steps prior to their actual application. The rapid and direct access to building blocks without additional processing being required is scarce despite the fact that such processes would be of great use.^[1] We have been interested in these types of transformations for some time;^[2,3] we have focused our attention on the development of nitrogen nucleophiles that would give access to unprotected primary amines.^[4]

Herein we report the use of sulfamic acid (H_2NSO_3H) as an inexpensive, commercially available ammonia equivalent in allylic substitutions to afford directly allylic amines in excellent regioselectivity and synthetically useful yields.^[5] The process employs a commercially available iridium catalyst precursor as well as a novel phosphoramidite–olefin ligand,^[6] which can be synthesized in one step. A welcome side effect is the fact that allylic alcohols can be directly employed as the starting materials for the transformation without the need for prior activation [Eq. (1); cod = cycloocta-l,5-diene]. amines can be accessed in excellent yields and stereoselectivities, primary amines can only be prepared through the use of protected forms of ammonia.^[11] In this respect, Helmchen and co-workers has recently reported the use of *o*-nosylamides and *N*,*N*-diacylamides in enantioselective Ir-catalyzed allylic amination reactions.^[12]

To increase the practicality and atom economy^[13] of the Ircatalyzed allylic amination reaction to give primary amines, we have investigated the chemistry of sulfamic acid and specifically its capacity to serve as an ammonia equivalent. Sulfamic acid is a crystalline, inexpensive solid that has found limited applications in organic synthesis,^[14] primarily as an acid catalyst.^[15] However, to the best of our knowledge, sulfamic acid has never been employed as a nitrogen source in a process, despite its many potential advantages (low toxicity, non-corrosive, non-odorous, low molecular weight).

At the outset of our studies, we examined the reaction of *tert*-butyl cinnamyl carbonate (1) as a test substrate with sulfamic acid in the presence of a catalyst derived from the Feringa phosphoramidite ligand L1 and Ir^{I} (Scheme 1).^[3,16]



Scheme 1. Test substrates and ligands for the Ir-catalyzed allylic amination reaction with sulfamic acid.

However, all experiments conducted in THF, CH_2Cl_2 , CH_3CN , EtOH, MeOH, or acetone were hampered by the low solubility of sulfamic acid, which led to recovery of starting material **1**. Although sulfamic acid is soluble in dipolar aprotic solvents such as *N*,*N*-dimethylformamide (DMF), dimethylacetamide (DMA), or dimethyl sulfoxide (DMSO), no conversion into the desired amine product or its derivatives (that is, secondary sulfamate) was observed.



One of the most convenient methods for the synthesis of allylic amines is the Ir-catalyzed allylic substitution pioneered by the research groups of Takeuchi,^[7] Hartwig,^[8] Helmchen^[9] and Alexakis.^[10] However, whereas secondary and tertiary

[*] C. Defieber, M. A. Ariger, P. Moriel, Prof. Dr. E. M. Carreira	
Laboratorium für Organische Chemie	
ETH Zürich, HCI H335	
8093 Zürich (Switzerland)	
Fax: (+41) 44 632-1328	
E-mail: carreira@org.chem.ethz.ch	

- [**] This research was supported by the ETH Zürich and the Swiss National Science Foundation. P.M. wishes to thank MEC of Spain for a predoctoral fellowship. The authors acknowledge the English translation of Ref. [26b] by Dr. Nicka Chinkov.
 - Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Angew. Chem. Int. Ed. 2007, 46, 3139-3143

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Communications

The first set of promising results were achieved with branched tert-butyl carbonate 2 as the substrate in DMF (15% conversion). Of greater significance, however, was the subsequent observation that alcohol 3 could be employed directly under otherwise identical conditions (15% conversion). This finding was key to the further optimization of the process. In transition-metal catalyzed allylic substitution reactions, activated allylic substrates (for example, halides, esters, carbonates, or carbamates) are usually required to facilitate the formation of the crucial allyl-metal intermediate.^[17] Alternatively, reagents such as Et₃B or metal catalysts (Bi^{III}) can provide the in situ activation of a free alcohol.^[18] The discovery of a process that involved the direct use of allylic alcohols was an unexpected bonus. Moreover, to the best of our knowledge, no transition-metal-mediated process in which a single reagent serves as both the ammonia source and in situ activator of a hydroxy group has been previously reported.

We further investigated the influence of various ligands. The nitrogen-based pyridylbis(oxazoline) (pybox) ligand only displayed decreased reactivity (5% conversion).^[19] No amination was observed with the use of PPh₃ and P(NMe₂)₃ (<5% conversion) but we obtained 25% conversion with P(OPh)₃. Using 1.5 mol% of [{Ir(cod)Cl}₂] and 3 mol% of the achiral phosphoramidite ligand **L2**, we achieved 30% conversion of **3** (DMF, 24 h, 23 °C).

Based on our interest in alkenes as ligands in transitionmetal catalysis,^[20] we investigated the olefin ligand L3 in the substitution process. Ligand L3 can easily be synthesized from inexpensive 2,2'-biphenol, PCl₃, and 5*H*-dibenzo-[*b*,*f*]azepine.^[21] The reaction with this ligand was remarkably clean (>99% conversion, DMF, 24 h, 23 °C). When we used the saturated analogue, ligand L4, only 20% conversion of alcohol **3** was achieved.^[22,23]

It is worth noting that the Ir-catalyzed transformation proceeds with complete regioselectivity.^[24] Furthermore, neither di- nor triallylated amines could be observed in the unpurified reaction mixture. With the optimal conditions in hand, we investigated the scope of the reaction [Eq. (2),

$$\begin{array}{c} & & & & & \\ & & & & \\ & & & \\ R^{1} & + & H_{3}^{+}N^{-}SO_{3}^{-} & \underbrace{(3 \text{ mol}\%)}_{[\{IrCl(cod)\}_{2}]} & & \\ R^{1} & & & \\ 1 \text{ equiv} & 1 \text{ equiv} & \underbrace{(1.5 \text{ mol}\%)}_{DMF, 50 \ ^{\circ}C, 3 \text{ h}} \end{array}$$
(2)

Table 1]. A convenient way to isolate the amine products is through the precipitation of their hydrochloride salts. However, a salient feature of the process results from the use of an ammonia equivalent, in which the amine can be subsequently protected in situ as the benzamide (entry 2, Bz = benzoyl), the Boc-carbamate (entry 3, Boc = tert-butoxycarbonyl), or the trifluoroacetamide (entry 4). In fact, the protection can facilitate the isolation of the product for certain lowmolecular-weight substances produced on small scale. Various

Table 1: Investigation of the substrate scope.



[a] Yield of product isolated after purification by chromatography. Regioselectivity was >99:1 as shown and determined by ¹H NMR spectroscopy of the unpurified reaction mixtures. [b] Isolated as the hydrochloride salt by treatment of the purified amine with 2 M HCl in diethyl ether. [c] Treatment of the unpurified reaction mixture with Et₃N, BzCl. [d] Treatment of the unpurified reaction mixture with 0.5 M aq NaOH, Boc₂O. [e] Treatment of the unpurified reaction mixture with K₂CO₃, (CF₃CO)₂O. For further experimental details, see the Experimental Section and the Supporting Information.

substituents are permitted in the substrate including phenyl-(entry 5), cylohexyl- (entry 6), as well as benzyloxymethylsubstituted allylic amines (entry 7, Bn = benzyl). Noteworthy is also the isolation of hexa-1,5-dien-3-amine hydrochloride (entry 8) in 75% yield without any isomerization of the double bond.

To get further insight in this interesting process, the course of the reaction was followed using time-dependent ¹H NMR spectroscopy in $[D_7]DMF$, in which the signal corresponding to H-3 of our test alcohol 3 was monitored.^[25] In analogy to the reaction on preparative scale, the NMR experiments showed the clean transformation of **3** (δ (H-3) = 4.04 ppm) into the corresponding amine 4 (δ (H-3) = 3.88 ppm) within three hours (Scheme 2). In a separate experiment, we investigated the influence of an excess of sulfamic acid (2 equiv). The desired amine 4 was generated after two hours as shown by the appearance of the corresponding signal of the amine. When the reaction was allowed to continue over 8 h, amine 4 is observed to undergo partial conversion into another product with a characteristic signal at $\delta = 4.46$ ppm. To assign a structure for this product, we conducted additional experiments in [D₇]DMF: Treatment of alcohol 3 with two equivalents of sulfamic acid after eight hours gave quantita-



Scheme 2. Selected results from the spectroscopic experiments in $[D_{7}]DMF$.

tive sulfate ester **5** (δ (H-3) = 4.72 ppm) which is consistent to what is known in the literature.^[5] The more potent commercially available sulfating agent sulfur trioxide-*N*,*N*-dimethyl-formamide performs sulfation in an analogous way to deliver **5** already after 1 h. When amine **4** is treated under the same conditions, sulfamate **6** could be obtained along with side products after nine hours.

These spectroscopic observations allow us to make the following conclusions:

- When an excess of sulfamic acid was employed in the Ircatalyzed process, the amine 4 initially produced underwent partial sulfamation with the second equivalent of sulfamic acid to form 6. This sulfamation only began after 3 had been entirely transformed into 4.
- 2) Throughout the course of the Ir-catalyzed process, no signals corresponding to the sulfate ester 5 were observed. Given the long reaction time required to perform the sulfation with sulfamic acid (eight hours), it is unlikely that the sulfate ester 5 serves as activated intermediate in the Ir-catalyzed reaction.
- 3) The absence of signals corresponding to 6 leads us to suspect that sulfamic acid does not act as a nucleophile in the catalytic process.

Based on these observations, we developed a working model shown in Scheme 3. It has been suggested in the literature that N,N-dimethylformamide undergoes a condensation reaction with sulfamic acid^[26] to form a Vilsmeier-like intermediate **7**.^[27] We speculate that this reactive intermediate is generated here, and that it subsequently reacts with the



Scheme 3. Proposed working model. L=ligand.

Angew. Chem. Int. Ed. 2007, 46, 3139–3143

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

allylic alcohol to form **8**.^[28] This activated species then can participate in an oxidative addition reaction with the iridium complex.^[29] The resulting iridium–allyl species **9** is sufficiently electrophilic to undergo a nucleophilic attack by ammonia, thus liberating the primary protonated allylic amine product.

Our aim was to apply the unique aspects of sulfamic acid chemistry to a catalytic asymmetric process. The modular structure of phosphoramidite ligand **L3** allows the incorporation of a wide range of chiral diol backbones. For example, the integration of (*S*)-binol in place of 2,2'-biphenol resulted in the chiral ligand **L5**, which, in combination with Ir^I, can be used in the reaction of 1-cyclohexylprop-2-en-1-ol to provide (*S*)-1-cyclohexylprop-2-en-1-amine hydrochloride in 70% yield and 70% *ee*.^[30] [Eq. (3); coe = cyclooctene] Although



this result is far from optimal, it represents the first example of direct generation of a primary enantiomerically enriched allylic amine from an allylic alcohol.^[31]

In conclusion, we demonstrate for the first time the direct Ir-catalyzed conversion of an allylic alcohol into an allylic amine with the use of sulfamic acid. This method does not require either separate prior activation or protecting group operations and thus the process is attractive both economically and ecologically. Also, promising preliminary results towards the development of an asymmetric process have been achieved. Further mechanistic investigations as well as the fine-tuning of ligands are underway. The fact that sulfamic acid can serve as an ammonia equivalent is intriguing and may have an application in other transformations that invlove the conversion of OH into NH_2 groups.

Experimental Section

Representative procedure: A Schlenk flask under argon was charged with [{Ir(cod)Cl}₂] (10.1 mg, 15 µmol, 1.5 mol%) and L3 (12.2 mg, 30 µmol, 3 mol%). DMF (2 mL) was added and the reaction mixture was stirred at 23 °C for 15 min. The allylic alcohol (1.00 mmol, 1 equiv) was added by syringe, followed by solid sulfamic acid (97 mg, 1.00 mmol, 1 equiv). The resulting reaction mixture was heated to 50 °C. After completion of the reaction (usually 3-4 h, as monitored by TLC), the solvent was evaporated at high vacuum. The resulting brown residue was dissolved in CH2Cl2 (10 mL) and sat. aq NaHCO3 solution (10 mL) and stirred for 10 min. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na2SO4) and concentrated under reduced pressure to afford the crude allylic amine. The ratio of regioisomers was determined by ¹H NMR analysis of the unpurified sample. The desired amine was obtained after purification of the residue by flash chromatography on basic or neutral alumina using $CH_2Cl_2/MeOH$ as eluent. As some amines proved to be unstable and/or volatile, they were obtained through precipitation of their more-stable hydrochloride salts by addition of 2 M HCl in Et₂O.

Received: January 12, 2007 Published online: March 12, 2007

Keywords: alcohols \cdot allylation \cdot allylic compounds \cdot amines \cdot iridium

- a) Comprehensive Asymmetric Catalysis I-III (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**;
 b) Asymmetric Catalysis on Industrial Scale (Eds.: H. U. Blaser, E. Schmidt), Wiley-VCH, Weinheim, **2003**; c) H.-U. Blaser, B. Pugin, F. Spindler, J. Mol. Catal. A **2005**, 231, 1–20.
- [2] a) E. M. Carreira, W. Lee, R. A. Singer, J. Am. Chem. Soc. 1995, 117, 3649–3650; b) D. E. Frantz, R. Fässler, E. M. Carreira, J. Am. Chem. Soc. 2000, 122, 1806–1807; c) N. K. Anand, E. M. Carreira, J. Am. Chem. Soc. 2001, 123, 9687–9688.
- [3] I. Lyothier, C. Defieber, E. M. Carreira, Angew. Chem. 2006, 118, 6350-6353; Angew. Chem. Int. Ed. 2006, 45, 6204-6207.
- [4] M. Johannsen, K. A. Jorgensen, Chem. Rev. 1998, 98, 1689– 1708.
- [5] For reviews on the chemistry of sulfamic acid, see: a) G. A. Benson, W. J. Spillane, *Chem. Rev.* **1980**, *80*, 151–186; b) B. Wang, *Synlett* **2005**, 1342–1343. Sulfamic acid can be purchased from a number of commercial suppliers, for example, from Fluka Switzerland (5 kg for 58 € = 78 \$, 2007).
- [6] For applications of bidentate phosphorus-olefin ligands in asymmetric catalysis, see: a) R. Shintani, W. L. Duan, T. Nagano, A. Okada, T. Hayashi, Angew. Chem. 2005, 117, 4687-4690; Angew. Chem. Int. Ed. 2005, 44, 4611-4614; b) R. Shintani, W. L. Duan, K. Okamoto, T. Hayashi, Tetrahedron: Asymmetry 2005, 16, 3400-3405; c) C. Thoumazet, L. Ricard, H. Grützmacher, P. Le Floch, Chem. Commun. 2005, 1592-1594; d) E. Piras, F. Läng, H. Rüegger, D. Stein, M. Wörle, H. Grützmacher, Chem. Eur. J. 2006, 12, 5849-5858; e) G. Mora, S. van Zutphen, C. Thoumazet, X. F. Le Goff, L. Ricard, H. Grützmacher, P. Le Floch, Organometallics 2006, 25, 5528-5532; f) T. M. Douglas, J. Le Nôtre, S. K. Brayshaw, C. G. Frost. A. S. Weller, Chem. Commun. 2006, 3408-3410; g) P. Kasák, V. B. Arion, M. Widhalm, Tetrahedron: Asymmetry 2006, 17, 3084-3090.
- [7] a) R. Takeuchi, M. Kashio, Angew. Chem. 1997, 109, 268-270; Angew. Chem. Int. Ed. Engl. 1997, 36, 263-265; b) R. Takeuchi, M. Kashio, J. Am. Chem. Soc. 1998, 120, 8647-8655; c) R. Takeuchi, N. Ue, K. Tanabe, K. Yamashita, N. Shiga, J. Am. Chem. Soc. 2001, 123, 9525-9534; d) R. Takeuchi, Synlett 2002, 1954-1965; e) R. Takeuchi, S. Kezuka, Synthesis 2006, 3349-3366.
- [8] a) A. Leitner, C. Shu, J. F. Hartwig, *Proc. Natl. Acad. Sci. USA* 2004, 101, 5830-5833; b) C. Shu, A. Leitner, J. F. Hartwig, *Angew. Chem.* 2004, 116, 4901-4904; *Angew. Chem. Int. Ed.* 2004, 43, 4797-4800; c) A. Leitner, C. Shu, J. F. Hartwig, *Org. Lett.* 2005, 7, 1093-1096; d) A. Leitner, S. Shekhar, M. J. Pouy, J. F. Hartwig, *J. Am. Chem. Soc.* 2005, 127, 15506-15514; e) S. Shekhar, B. Trantow, A. Leitner, J. F. Hartwig, *J. Am. Chem. Soc.* 2006, 128, 11770-11771.
- [9] a) G. Lipowsky, G. Helmchen, *Chem. Commun.* 2004, 116-117;
 b) C. Welter, O. Koch, G. Lipowsky, G. Helmchen, *Chem. Commun.* 2004, 896-897; c) C. Welter, A. Dahnz, B. Brunner, S. Streiff, P. Dübon, G. Helmchen, *Org. Lett.* 2005, *7*, 1239-1242;
 d) R. Weihofen, A. Dahnz, O. Tverskoy, G. Helmchen, *Chem. Chem.*

Commun. **2005**, 3541–3543; e) C. Welter, R. M. Moreno, S. Streiff, G. Helmchen, *Org. Biomol. Chem.* **2005**, *3*, 3266–3268.

- [10] a) K. Tissot-Croset, D. Polet, A. Alexakis, Angew. Chem. 2004, 116, 2480-2482; Angew. Chem. Int. Ed. 2004, 43, 2426-2428;
 b) D. Polet, A. Alexakis, Org. Lett. 2005, 7, 1621-1624; c) D. Polet, A. Alexakis, K. Tissot-Croset, C. Corminboeuf, K. Ditrich, Chem. Eur. J. 2006, 12, 3596-3609.
- [11] Ammonia is not an effective nucleophile for π-allyl metal complexes; see: S. A. Godleski in *Comprehensive Organic Synthesis* (Eds: B. M. Trost, I. Fleming) Pergamon, Amsterdam, **1991**, pp. 585–633.
- [12] R. Weihofen, O. Tverskoy, G. Helmchen, Angew. Chem. 2006, 118, 5673-5676; Angew. Chem. Int. Ed. 2006, 45, 5546-5549.
- [13] a) B. M. Trost, Science 1991, 254, 1471–1477; b) B. M. Trost, Angew. Chem. 1995, 107, 285–307; Angew. Chem. Int. Ed. Engl. 1995, 34, 259–281.
- [14] Traditionally, sulfamic acid has been used as a scavenger for hypochlorous acid in Lindgren oxidations; see: B. O. Lindgren, T. Nilsson, *Acta Chem. Scand.* **1973**, *27*, 888–890. Sulfamic acid finds widespread use in the electroplating industry, as a decalcifier, for disinfection in swimming pools, and many other applications. For a more detailed overview, see Ref. [5].
- [15] For selected examples, see: a) P. R. Sing, D. U. Singh, S. D. Samant, *Synlett* 2004, 1909–1912; b) B. Wang, Y. L. Gu, G. Y. Luo, T. Yang, Y. M. Yang, J. S. Suo, *Tetrahedron Lett.* 2004, 45, 3369–3372; c) J. S. Yadav, H. Ather, P. Purushothama Rao, R. Srinivasa Rao, K. Nagaiah, A. R. Prasad, *Catal. Commun.* 2006, 7, 797–801.
- [16] a) B. L. Feringa, Acc. Chem. Res. 2000, 33, 346–353; b) L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. De Vries, R. Naasz, B. L. Feringa, Tetrahedron 2000, 56, 2865–2878; c) A. Alexakis, S. Rosset, J. Allamand, S. March, J. Guillen, C. Benhaim, Synlett 2001, 1375–1378.
- [17] a) B. M. Trost, C. Lee in *Catalytic Asymmetric Synthesis*, 2nd ed.
 (Ed.: I. Ojima), Wiley, New York, **2000**, 593; b) A. Pfaltz, M. Lautens in *Comprehensive Asymmetric Catalysis I–III* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, p. 833.
- [18] For reviews on the Pd-catalyzed formation of C–N bonds from alcohols, see: a) J. Muzart, *Tetrahedron* 2005, 61, 4179-4212;
 b) Y. Tamaru, *Eur. J. Org. Chem.* 2005, 2647-2656. For selected recent examples of direct substitution reactions, see: c) F. Ozawa, H. Okamaoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.* 2002, 124, 10968-10969; d) K. Manabe, S. Kobayashi, *Org. Lett.* 2003, 5, 3241-3244; e) H. Kinoshita, H. Shinokubo, K. Oshima, *Org. Lett.* 2004, *6*, 4085-4088; f) K. Manabe, K. Nakada, N. Aoyama, S. Kobayashi, *Adv. Synth. Catal.* 2005, 347, 1499-1503; g) H. Qin, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Angew. Chem.* 2007, 119, 413-417; *Angew. Chem. Int. Ed.* 2007, 46, 409-413.
- [19] For an example in which (*R*,*R*)-pybox was used in an allylic amination reaction catalyzed by Ir, see: H. Miyabe, A. Matsumara, K. Moriyama, Y. Takemoto, Org. Lett. 2004, 6, 4631–4634.
- [20] a) C. Fischer, C. Defieber, T. Suzuki, E. M. Carreira, J. Am. Chem. Soc. 2004, 126, 1628-1629; b) C. Defieber, J.-F. Paquin, S. Serna, E. M. Carreira, Org. Lett. 2004, 6, 3873-3876; c) J.-F. Paquin, C. Defieber, C. R. J. Stephenson, E. M. Carreira, J. Am. Chem. Soc. 2005, 127, 10850-10851; d) J.-F. Paquin, C. R. J. Stephenson, C. Defieber, E. M. Carreira, Org. Lett. 2005, 7, 3821-3824.
- [21] 5H-Dibenzo[b,f]azepine (iminostilbene) is a precursor in the synthesis of the antiepileptic drug carbamazepine (Novartis) and is commercially available from Fluka Switzerland (25 g for 64 € = 86 \$, 2007); P. C. Fuenfschilling, W. Zaugg, U. Beutler, D. Kaufmann, O. Lohse, J.-P. Mutz, U. Onken, J.-L. Reber, D. Shenton, Org. Process Res. Dev. 2005, 9, 272–277.



- [22] During the course of the reaction with ligand L5, the color of the reaction mixture changed from light yellow to dark brown. TLC indicated the partial decomposition of the ligand.
- [23] We speculate that the presence of the olefin in L4 may at least stabilize some of the various intermediate complexes that are part of the catalytic cycle. The bent structure of 5*H*-dibenzo-[*b*,*f*]azepine reduces the amount of conjugation and renders the olefin unit more susceptible to coordination with a transition metal. The central azepine unit in 5*H*-dibenzo[*b*,*f*]azepine is known to adopt a boat conformation; see: G. M. Kuramshina, T. Mogi, H. Takahashi, J. Mol. Struct. 2003, 661, 121–140. For a similar ligand from the (tropylidene)phosphane (tropp) family, see: a) J. Thomaier, S, Boulmaâz, H. Schönberg, H. Rüegger, A. Currao, H. Grützmacher, H. Hillebrecht, H. Pritzkow, New J. Chem. 1998, 22, 947–958; b) P. Maire, S. Deblon, F. Breher, J. Geier, C. Böhler, H. Rüegger, H. Schönberg, H. Grützmacher, *Chem. Eur. J.* 2004, *10*, 4198–4205; c) see also Ref. [6c–e].
- [24] This result is different from the regioselectivity problems ($S_N 2$ vs. $S_N 2'$) seen in the Mitsunobu-type conversion of allyl derivatives. For a study, see: J. Mulzer, G. Funk, *Synthesis* **1995**, 101–112.
- [25] For individual spectra and experimental conditions, see the Supporting Information.

- [26] For previous studies into the solvolysis of sulfamic acid in DMF, see: a) K. Nagasawa, H. Yoshidome, *Chem. Pharm. Bull.* 1969, 17, 1316–1323; b) Y. B. Kagan, G. M. Pakhomova, N. A. Shimanko, A. Y. Koshevnik, M. V. Shishkina, R. G. Lokteva, *Kinet. Katal.* 1974, 15, 23–29.
- [27] DMF-SO₃ adducts can be regarded as Vilsmeier adducts; see: M. L. Wolfrom, T. M. Shen Han, J. Am. Chem. Soc. 1959, 81, 1764–1766.
- [28] For a recent example of the activation of alcohols with Vilsmeier reagents, see: Y. Kawano, N. Kenko, T. Mukaiyama, *Chem. Lett.* 2005, 34, 1612–1613.
- [29] For the transition-metal-catalyzed oxidative addition of allylic imidates, see: T. G. Schenck, B. Bosnich, J. Am. Chem. Soc. 1985, 107, 2058–2066.
- [30] The resulting amine was trapped in situ with benzoyl chloride and triethylamine to obtain the UV-active benzamide. The enantioselectivity was determined by HPLC on a chiral stationary phase. The *ee* value was not dependent on the type of starting material used (carbonate or alcohol).
- [31] Cinnamyl alcohol did not serve as substrate under our current reaction conditions, even when the Hartwig catalyst-activation protocol (Ir¹ and L1) was employed; see Ref. [8d].