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Synthesis of Spirocarbamate Oxindoles via Intramolecular Trapping of a β-Silyl Carbocation by an *N*-Boc Group

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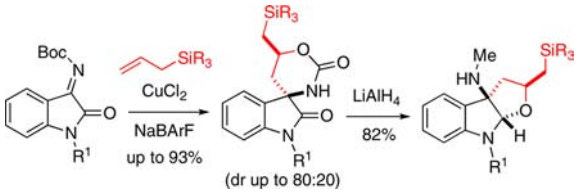
ABSTRACT



We report the Lewis acid catalyzed additions of allylsilanes to *N*-Boc-iminooxindoles and the formation of novel silicon-containing spirocarbamates via intramolecular trapping of a β-silyl carbocation by an *N*-Boc group. Several transformations display the synthetic utility of these spirocarbamate oxindoles, including a reductive cyclization to access new silylated furoindoline derivatives.

Synthetic interest in spirooxindoles has increased over the past decade due to the notable biological activity and occurrence of this class of heterocycles in natural products and pharmaceutical lead compounds.[1] Recent synthetic methods to access spirocyclic 3-aminooxindoles have utilized preformed iminooxindoles[2] and in situ generated iminium ions[3] in various spirocyclization strategies; however, allylsilanes have not previously been investigated for annulations of iminooxindoles. Based on the steric and electronic effects of different silyl groups, allylsilane reagents can exhibit either an allylation (i.e., elimination) or annulation pathway.[4] Both pathways proceed through a transient β-silyl stabilized carbocation intermediate,[5] which can be directly intercepted (as a 1,2-dipole synthon),[6] or a 1,2-silyl migration can occur with interception in a [3 + 2] annulation (as a 1,3-dipole synthon).[7]

Herein we describe the discovery and development of a new Lewis acid catalyzed allylsilane annulation with *N*-Boc-iminooxindoles (**1**) to form spirocyclic carbamates such as **3** (Scheme 1). Previous work from our group has shown that chiral scandium(III)-indapybox complexes catalyze allylsilane additions to isatins to selectively afford

(1) For reviews, see: (a) Ball-Jones, N. R.; Badillo, J. J.; Franz, A. K. *Org. Biomol. Chem.* **2012**, *10*, 5165. (b) Trost, B. M.; Brennan, M. K. *Synthesis* **2009**, 3003. (c) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748. (d) Marti, C.; Carreira, E. M. *Eur. J. Org. Chem.* **2003**, 2209. For selected examples of bioactive nitrogen-containing spirooxindoles, see: (a) Yong, S. R.; Ung, A. T.; Pyne, S. G.; Skelton, B. W.; White, A. H. *Tetrahedron* **2007**, *63*, 5579. (b) Vintonyak, V.; Warburg, K.; Kruse, H.; Grimme, S.; Hübel, K.; Rauh, D.; Waldmann, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 5902. (c) Bhaskar, G.; Arun, Y.; Balachandran, C.; Saikumar, C.; Perumal, P. T. *Eur. J. Med. Chem.* **2012**, *51*, 79. (d) Ding, K.; Lu, Y.; Nikolovska-Coleska, Z.; Wang, G.; Qiu, S.; Shangary, S.; Gao, W.; Qin, D.; Stuckey, J.; Krajewski, K.; Roller, P. P.; Wang, S. *J. Med. Chem.* **2006**, *49*, 3432.

(2) For selected recent examples, see: (a) Lv, H.; Tiwari, B.; Mo, J.; Xing, C.; Chi, Y. R. *Org. Lett.* **2012**, *14*, 5412. (b) Pei, C.; Jiang, Y.; Shi, M. *Eur. J. Org. Chem.* **2012**, *12*, 4206. (c) Zhang, B.; Feng, P.; Sun, L.; Cui, Y.; Ye, S.; Jiao, N. *Chem.—Eur. J.* **2012**, *18*, 9198.

(3) For selected recent examples, see: (a) Badillo, J. J.; Silva-García, A.; Shupe, B. H.; Fettinger, J. C.; Franz, A. K. *Tetrahedron Lett.* **2011**, *52*, 5550. (b) Taghizadeh, M. J.; Arvinnezhad, H.; Samadi, S.; Jadidi, K.; Javidan, A.; Notash, B. *Tetrahedron Lett.* **2012**, *53*, 5148. (c) Shi, F.; Tao, Z.; Luo, S.; Tu, S.; Gong, L. *Chem.—Eur. J.* **2012**, *18*, 6885.

(4) (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (b) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, *15*, 3173. (c) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 9868. (d) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094. (e) Knölker, H.-J.; Foitzik, N.; Graf, R.; Pannek, J.-B. *Tetrahedron* **1993**, *49*, 9955.

(5) (a) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867. (b) Creary, X.; Kochly, E. D. *J. Org. Chem.* **2009**, *74*, 2134. (c) Lambert, J. B.; Zhao, Y.; Emblide, R. W.; Salvador, L. A.; Liu, X.; So, J.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.

(6) (a) Brocherieux-Lanoy, S.; Dhimane, H.; Poupon, J.-C.; Vanucci, C.; Lhommet, G. J. *Chem. Soc. Perkin Trans.* **1997**, *1*, 2163. (b) Angle, S. R.; El-Said, N. A. *J. Am. Chem. Soc.* **1999**, *121*, 10211. (c) Horino, Y.; Kimura, M.; Naito, M.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **2000**, *41*, 3427. (d) Hirashita, T.; Kawai, D.; Araki, S. *Tetrahedron Lett.* **2007**, *48*, 5421. (e) Romero, A.; Woerpel, K. A. *Org. Lett.* **2006**, *8*, 2127. (f) Dressel, M.; Restorp, P.; Somfai, P. *Chem.—Eur. J.* **2008**, *14*, 3072.

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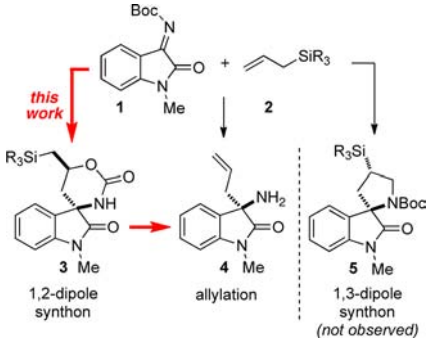
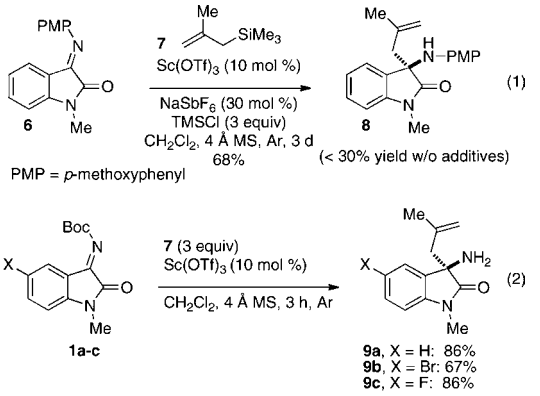
Scheme 1. Annulation Pathways with *N*-Boc-iminooxindoles



either allylation[8] or annulation[9] products in high yields and enantioselectivities. The allylation of iminooxindoles represents a synthetic challenge, and limited examples have been reported.[10,11] We also present methods to access 3-allyl-3-aminooxindoles and furoindolones upon transformation of the spirocarbamate.

Our initial studies compared the reactivity of iminooxindoles **1** and **6** in Lewis acid catalyzed allylation reactions with methallyltrimethylsilane **7** (Scheme 2, eqs 1 and 2). Using the conditions we have previously optimized for isatins (i.e., $Sc(OTf)_3$ with $NaSbF_6$ and TMSCl),[8] the allylation of ketimine **6** afforded the protected 3-aminooxindole **8** in 68% yield after 3 days.[12] In comparison, the electron-deficient *N*-Boc protected ketimines **1**[13] exhibit a significant increase in reactivity compared to *N*-aryl ketimines. The addition of methallyltrimethylsilane **7** to iminooxindoles **1** proceeds rapidly (< 3h) in the presence of catalytic

Scheme 2. Addition of Methallyltrimethylsilane to *N*-Aryl and *N*-Boc-iminooxindoles



$Sc(OTf)_3$. Under these reaction conditions, the Boc group was deprotected to afford amine **9** in high yields (eq 2).[14]

When the addition of unsubstituted allyltrimethylsilane **2a** was investigated, no allylation was observed after 2 days; however, a new annulation product (**3**) was isolated as a 64:36 mixture of diastereomers, albeit in low yield.[15] The low yield was attributed to competing imine hydrolysis promoted by $Sc(OTf)_3$, leading to regeneration of isatin and also subsequent allylation of the isatin. Although we initially hypothesized that a [3 + 2] cyclization could occur to afford spiropyrrolidines such as **5**,[16] this product was not observed. The structure of spirocarbamate **3** was assigned on the basis of mass spectrometry and ^{13}C NMR data and then further confirmed by X-ray crystallography.[17]

These initial results with $Sc(OTf)_3$ prompted us to investigate other Lewis acids to optimize the formation of spirocarbamate **3b** (Table 1).[18] We turned our attention to metal chloride salts as catalysts because we hypothesized that the metal triflates were promoting Boc deprotection and imine hydrolysis.[19] Although we observed the lower conversion for the formation of **3b** with various metal chloride salts (entries 2−5), the formation of byproducts was also reduced. A moderate diastereomeric ratio was observed for all catalysts, and selectivity was relatively unaffected by the choice of metal salt.

Continuing our investigation, we looked toward additives that would enhance catalytic activity and increase the yield for the spirocarbamate product. We initially investigated additives such as $AgSbF_6$ and $NaSbF_6$, which have been shown to enhance the reactivity of metal chloride catalysts by formation of a cationic complex;[20,9] however, the addition of $NaSbF_6$ in this reaction did not improve the yield (entry 5 vs 6). Further investigations revealed that the addition of TMSCl

(7) For selected examples, see references 4c−e, and also see: (a) Akiyama, T.; Kirino, M. *Chem. Lett.* **1995**, *24*, 723. (b) Brengel, G. P.; Meyers, A. I. *J. Org. Chem.* **1996**, *61*, 3230. (c) Akiyama, T.; Sugano, M.; Kagoshima, H. *Tetrahedron Lett.* **2001**, *42*, 3889.

(8) (a) Hanhan, N. V.; Tang, Y. C.; Tran, N. T.; Franz, A. K. *Org. Lett.* **2012**, *14*, 2218. (b) Silverio, D. L.; Torker, S.; Pilyugina, T.; Vieira, E. M.; Snapper, M. L.; Haeffner, F.; Hoveyda, A. H. *Nature* **2013**, *494*, 216.

(9) Hanhan, N. V.; Ball-Jones, N. R.; Tran, N. T.; Franz, A. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 989.

(10) (a) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Eur. J. Org. Chem.* **2010**, *15*, 2845. (b) Lesma, G.; Landoni, N.; Pilati, T.; Sacchetti, A.; Silvani, A. *J. Org. Chem.* **2009**, *74*, 4537.

(11) An allylation of *N*-aryliminooxindoles with allylsilane reagents has been reported previously using mercury(II) salts as catalysts, see: Cao, Z. Y.; Zhang, Y.; Ji, C. B.; Zhou, J. *Org. Lett.* **2011**, *13*, 6398.

(12) See Supporting Information Table S1 for a comparison of reaction conditions and additive effects.

(13) *N*-Boc-protected ketimine oxindoles were prepared using an aza-Wittig reaction: Yan, W.; Wang, D.; Feng, J.; Li, P.; Zhao, D.; Wang, R. *Org. Lett.* **2012**, *14*, 2512.

(14) The reaction was performed using rigorous anhydrous conditions; in all cases the NHBoc product was not observed. When the reaction was run in the presence of 2,6-di-*tert*-butyl-4-methylpyridine, amine **9** was still obtained as the major product. Using $CuCl_2$/NaBArF conditions (vida infra) also provided amine **9** as the major product in 66% yield. See Table S2 in the Supporting Information for details.

(15) Rh(II)-catalyzed oxidative intramolecular spiroannulations of indoles have been reported for the synthesis of spirocarbamate oxindoles, see: (a) Padwa, A.; Stengel, T. *Org. Lett.* **2002**, *4*, 2137. (b) Sato, S.; Shibuya, M.; Kanoh, N.; Iwabuchi, Y. *J. Org. Chem.* **2009**, *74*, 7522. (c) A cyclic carbamate has also been observed as a side product upon reaction of an allylsilane with *N*-Boc-aldimines, see: Ollevier, T.; Li, Z. *Adv. Synth. Catal.* **2009**, *351*, 3251. (d) For the synthesis of cyclic carbamates through in situ imine formation and alkene addition, see: Richter, H.; Fröhlich, R.; Daniliuc, C.; Mancheño, O. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 8656.

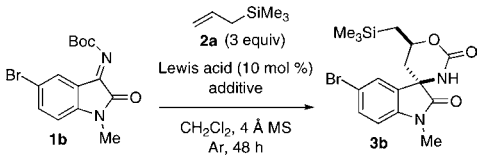
(16) Wu, J.; Zhu, K.; Yuan, P.; Panek, J. S. *Org. Lett.* **2012**, *14*, 3624.

(17) The X-ray structure of spirocarbamate **3i** (CCDC 925542) was solved with a disordered molecule of CH_2Cl_2.

(18) When additional catalysts (e.g., thioureas, phosphoric acids, $MgCl_2$, and $PdCl_2$) were evaluated, no product formation was observed. See Supporting Information Table S3 for a full summary of catalysts and conditions investigated.

(19) Bose, D. S.; Kumar, K. K.; Reddy, A. V. N. *Synth. Commun.* **2003**, *33*, 445.

Table 1. Optimization of Spirocyclization



entry	Lewis acid	additive (mol %)	dr[a]	conversion[b] (% yield)[c]
1	$Sc(OTf)_3$	–	64:36	21
2	$ScCl_3(THF)_3$	–	68:32	3
3	$InCl_3$	–	62:38	6
4	$SnCl_2$	–	70:30	10
5	$CuCl_2$	–	68:32	12
6	$CuCl_2$	$NaSbF_6$ (30)	nd	<5
7	$CuCl_2$	TMSCl (300)	62:38	70 (62)
8	$Sc(OTf)_3$	NaBArF (11)	50:50	39
9	$CuCl_2$	NaBArF (11)	65:35	99 (82)
10	$ScCl_3$	NaBArF (11)	50:50	93 (54)
11	$InCl_3$	NaBArF (11)	62:38	78 (54)
12	$SnCl_2$	NaBArF (11)	55:45	99
13	–	NaBArF (11)	–	no rxn

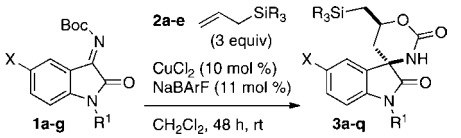
[a] Diastereoselectivity was determined for the unpurified mixture using ^{1}H NMR spectroscopy. [b] Conversion was determined using ^{1}H NMR spectroscopy. [c] Isolated yield.

enhanced the yield of spirocycle **3b** (62%, entry 5 vs 7).[21] Next, we evaluated the addition of sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate (NaBArF),[22,23] where moderate to high conversion to spirocarbamate **3b** was observed with all metal chlorides evaluated (entries 8−12). The combination of $CuCl_2$ with NaBArF resulted in the highest isolated yield (82%, entry 9). A control experiment using only NaBArF (entry 13) confirmed that the NaBArF alone is not a catalyst for this reaction.

With the optimal catalyst system identified, we proceeded to demonstrate the scope of iminooxindoles for this reaction (Table 2). The *N*-acyl substrate (entry 4) exhibited lower reactivity (60% yield) compared to *N*-alkyl substrates, which we attribute to a competitive binding mode for the Lewis acid compared to a 1,2-binding mode of the ketimine oxindole. In other cases, yields of substrates with lower reactivity could be improved by utilizing 22 mol % NaBArF.

To determine the influence of the silyl group on yield and diastereoselectivity, we investigated several aryl and alkyl groups on silicon. The addition of allyltri-isopropylsilane (**2b**) to imines **1b**,**c**,**e** provided increased yields (entries 7−9)

Table 2. Scope of Imines and Allylsilanes



entry	R^1	X	SiR_3 (**2**)	**3**	dr[a]	yield (%)[b]
1[c]	Me	H	$SiMe_3$ (**2a**)	**3a**	60:40	91
2	Me	Br	$SiMe_3$ (**2a**)	**3b**	65:35	82
3[d]	Bn	H	$SiMe_3$ (**2a**)	**3c**	60:40	87
4	Ac	H	$SiMe_3$ (**2a**)	**3d**	66:34	60
5[c]	Ph	H	$SiMe_3$ (**2a**)	**3e**	66:34	74
6[c]	Me	F	$SiMe_3$ (**2a**)	**3f**	60:40	76
7	Me	Br	$Si(i\text{-}Pr)_3$ (**2b**)	**3g**	65:35	93
8	Ac	H	$Si(i\text{-}Pr)_3$ (**2b**)	**3h**	55:45	66
9	Me	F	$Si(i\text{-}Pr)_3$ (**2b**)	**3i**	66:34	76
10	Me	Br	$SiMe_2CHPh_2$ (**2c**)	**3j**	70:30	78
11	Me	OMe	$SiMe_2CHPh_2$ (**2c**)	**3k**	63:37	91
12	Me	H	$SiMe_2CHPh_2$ (**2c**)	**3l**	78:22	83
13	Me	F	$SiMe_2CHPh_2$ (**2c**)	**3m**	75:25	64
14	Ac	H	$SiMe_2CHPh_2$ (**2c**)	**3n**	56:44	51
15	Me	Br	$Si(i\text{-}Pr)_2CHPh_2$ (**2d**)	**3o**	80:20	36
16	Me	F	$Si(i\text{-}Pr)_2CHPh_2$ (**2d**)	**3p**	69:31	37
17	Me	F	$SiPh_2t\text{-}Bu$ (**2e**)	**3q**	75:25	76

[a] Determined based on analysis of ^{1}H NMR spectra of the unpurified reaction mixture. [b] Isolated yield. [c] Reaction was run in the presence of 22 mol % NaBArF. [d] Reaction was run for 72 h.

compared to allylsilane **2a** while maintaining consistent diastereoselectivity. Reactions with silane **2c** also proceeded with high yields (entries 10−14). The bulkier aryl-substituted allylsilane **2d** proceeded with the highest diastereoselectivity (80:20 dr) and also showed the lowest reactivity (36% yield) (entries 15−16). Additionally, the allyl(*tert*-butyl)-diphenylsilane **2e** (entry 17) afforded the spirocarbamate product in good yield and moderate diastereoselectivity (75% yield, 75:25 dr).

The proposed mechanism of spirocyclization (Scheme 3) is initiated upon chelation of the copper(II) catalyst to the iminooxindole (intermediate **I**), which increases the electrophilicity of the imine.[24] Addition of the allylsilane affords a β-silyl stabilized carbocation (intermediate **II**). Although elimination of the silyl group would afford allylation product **4**, the carbocation can be intercepted by the nucleophilic oxygen of the Boc group to afford intermediate **III**. Elimination of 2-methylpropene from intermediate **III** gives rise to spirocarbamate **3**. Two possible roles can be envisioned for the NaBArF additive. First, NaBArF can serve

(20) For examples using $AgSbF_6$ to prepare cationic metal complexes, see: (a) Evans, D., A.; Barnes, D. M.; Johnson, J. S.; Lectka, T.; Matt, P.; Miller, S. J.; Murry, J. A.; Norcross, R. D.; Shaughnessy, E. A.; Campos, K. R. *J. Am. Chem. Soc.* **1999**, *121*, 7582. (b) Evans, D. A.; Rovis, T.; Kozlowski, M. C.; Downey, C. W.; Tedrow, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 9134.

(21) For examples of TMSCl increasing the reactivity of Lewis acids, see: (a) Onishi, Y.; Ito, T.; Yasuda, M.; Baba, A. *Eur. J. Org. Chem.* **2002**, *9*, 1578. (b) Yamanaka, M.; Nishida, A.; Nakagawa, M. *Org. Lett.* **2000**, *2*, 159.

(22) For synthesis and preparation of NaBArF, see: Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.

(23) For use of NaBArF with Lewis acid catalysis, see: (a) Onodera, G.; Yamamoto, E.; Tonegawa, S.; Iezumi, M.; Takeuchi, R. *Adv. Synth. Catal.* **2011**, *353*, 2013. (b) Nomura, N.; Jin, J.; Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 459.

(24) (a) France, S.; Shah, M. H.; Weatherwax, A.; Wack, H.; Roth, J. P.; Lectka, T. *J. Am. Chem. Soc.* **2005**, *127*, 1206. (b) Evans, D. A.; Johnson, D. S. *Org. Lett.* **1999**, *4*, 595. (c) Evans, D. A; Fandrick, K. R.; Song, H. *J. Am. Chem. Soc.* **2005**, *127*, 8942.

(25) For examples of NaBArF creating cationic complexes, see: (a) Schreiber, D. F.; Ortin, Y.; Muller-Bunz, H.; Phillips, A. D. *Organometallics* **2011**, *30*, 5381. (b) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Corzo-Suárez, R.; García-Granda, S.; Miguel, D. *Organometallics* **2002**, *21*, 1540.

(26) For examples of boron anions stabilizing carbocations, see: (a) Cordoneanu, A.; Drewitt, M. J.; Bavarian, N.; Baird, M. C. *New J. Chem.* **2008**, *32*, 1890. (b) Shaffer, T. D.; Ashbaugh, J. R. *J. Polym. Sci.* **1997**, *35*, 329.

Scheme 3. Proposed Mechanism for Spirocyclization

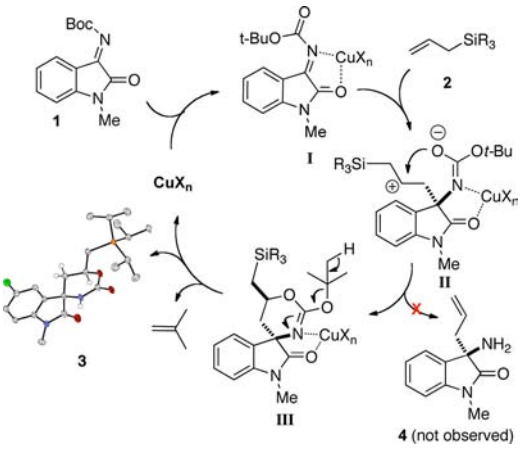
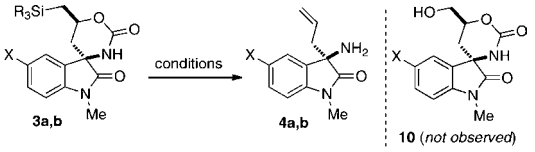


Table 3. Acessing 3-Amino-3-allyloxindoles

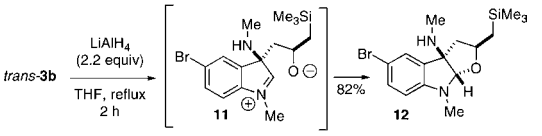


entry	R^1	SiR_3	conditions	product	yield (%)
1	Br	$SiMe_2CHPh_2$	TBAF, 0 °C, 15 min	**4a**	89
2	F	$SiMe_2CHPh_2$	CsF, 24 °C, 16 h	**4b**	89
3	F	$SiMe_3$	TBAF, 24 °C, 2 h	**4b**	77
4	F	$SiMe_3$	CsF, 24 °C, 16 h	**4b**	0
5	F	$Si(i\text{-}Pr)_3$	TBAF, 24 °C, 2 h	**4b**	0
6	Br	$SiMe_2CHPh_2$	NaOH, reflux, 2 h	**4a**	92

as a loosely coordinating anion to promote formation of a cationic copper(II) species.[25] Alternatively, NaBArF can stabilize formation of the β-silyl carbocation.[5,26] Although it is likely that one role of the NaBArF is more dominant, a dual mode of activation may also be occurring in the reaction.

Upon investigating Tamao−Fleming oxidation conditions to modify the silyl group (i.e., to access the corresponding alcohol **10**),[27] we determined that various conditions favored elimination of the silyl group and formation of 3-allyl-3-amino-oxindole **4**. We initially investigated dimethylbenzhydryl spirocycles **3j** and **3m** using TBAF or CsF as the fluoride source (Table 3, entries 1 and 2); however, before addition of the oxidant, elimination of the silyl group was observed, followed by decarboxylation, to give 3-allyl-3-amino-oxindole **4** in high yield. Elimination was also observed upon treatment of the TMS-containing spirocycle **3f** with TBAF conditions, giving amine **4b** in 77% yield (entry 3). In contrast, **3f** did not undergo elimination using CsF conditions (entry 4), and the TIPS group was resistant to elimination with TBAF (entry 5). NaOH hydrolysis conditions to access an amino alcohol,[15d] a substrate that may be more successful for C−Si oxidation, also led to elimination of the silyl group and formation of **4a** in high yield (entry 6).

Scheme 4. Reduction of Spirocarbamate **3** to Furoindoline **12**



The reduction of spirocarbamate **3** with LAH was investigated and determined to be an efficient route for access to tetrahydrofuroindoles (Scheme 4). LAH reduction of *trans*-**3b** afforded a single diastereomer of **12** in high yield. The chemoselective reduction of the carbamate to access the 1,3-amino alcohol was not observed.[15d] The tetrahydrofuroindole product results from a tandem reduction of the carbamate and the oxindole amide to produce an iminium ion (**11**), which is poised for cyclization.[28,29]

In conclusion, we have developed new methodology utilizing allylsilanes and iminooxindoles to access spirocarbamate oxindoles[30] via intramolecular trapping of a transient β-silyl carbocation with the *N*-Boc group. The *N*-Boc-iminooxindole displays significantly increased reactivity compared to *N*-aryl substrates; however, NaBArF is still integral for efficient reactivity. We hypothesize that the noncoordinating borate anion plays a key role to stabilize the β-silyl carbocation and increase the Lewis acidity of the $CuCl_2$ upon formation of a cationic complex. Transformation of the spirocarbamate can be achieved using a fluoride-promoted elimination to afford 3-amino-3-allyloxindole products or upon reduction with LAH to access furoindoline products.

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Supporting Information Available. Experimental procedures and spectral data for all compounds; X-ray crystal structure coordinates and files in CIF format for **3i**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

(27) (a) Jones, G. R.; Landias, Y. *Tetrahedron* **1996**, *52*, 7599. (b) Roberson, C. W.; Woerpel, K. A. *Org. Lett.* **2000**, *2*, 621. (c) Peng, Z.; Woerpel, K. *Org. Lett.* **2000**, *2*, 1379.

(28) Itoh, T.; Ishikawa, H.; Hayashi, Y. *Org. Lett.* **2009**, *17*, 3854.

(29) For an example of the furoindoline core in natural products, see: Sunazuka, T.; Yoshida, K.; Kojima, N.; Shirahata, T.; Hirose, T.; Handa, M.; Yamamoto, D.; Harigaya, Y.; Kuwajima, I.; Omura, S. *Tetrahedron Lett.* **2005**, *46*, 1459.

(30) Preliminary investigations for enantioselective catalysis afforded an enantiomeric ratio of 70:30 using 10 mol % of copper(II) chloride and NaBArF with an isopropyl-bisoxazoline ligand.