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Scandium(III)-Catalyzed Enantioselective Allylation of Isatins Using Allylsilanes

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ABSTRACT

The scandium(III)-catalyzed enantioselective Hosomi–Sakurai allylation of isatins with various substituted allylic silanes is described. A catalyst loading as low as 0.05 mol % is utilized at room temperature to afford the 3-allyl-3-hydroxy-2-oxindoles in excellent yields and enantioselectivity up to 99% ee, including a demonstration of a gram-scale reaction. The effects of additives and varying silyl groups were explored to demonstrate the scope and application.

The synthesis of oxindoles continues to be an exciting challenge due to their importance as core structures in natural products and pharmaceutical lead compounds.[1] Enantioenriched 3-hydroxy-2-oxindole structures are key intermediates reported in the synthesis of several natural products and biologically relevant small molecules.[2] In particular, the 3-allyl-3-hydroxy-oxindole is a useful intermediate for synthesis because the alkene provides a functional handle for further transformations.[3,4]

Using chiral Lewis acids with good chelating potential, our research has focused on developing a broadly applicable methodology for the enantioselective addition of π-nucleophiles to isatins.[5] We have previously described the addition of allylstannanes to isatins, which afforded 3-allyl-3-hydroxy-oxindoles with 80% *ee* (at −40 °C).[5a] Allylation reactions with allylic silanes, known as the Hosomi–Sakurai reaction,[6] provide an attractive alternative to allylstannanes because allylsilanes are less toxic and have a reactivity that can be tailored by varying the steric and electronic properties.[7] Allylsilanes have been successfully utilized for the enantioselective allylation of various reactive electrophiles, such as aldehydes and imines;[8] yet, there is only one current example for the enantioselective allylation of isatins using allylsilanes, which proceeds with modest enantioselectivity.[9] Here we report an efficient

(1) For reviews on the synthesis of oxindoles in natural products and drug discovery, see: (a) Badillo, J. J.; Hanhan, N. V.; Franz, A. K. *Curr. Opin. Drug Discovery Dev.* **2010**, *13*, 758–776. (b) Zhou, F.; Liu, Y. L.; Zhou, J. A. *Adv. Synth. Catal.* **2010**, *352*, 1381–1407. (c) Trost, B. M.; Brennan, M. K. *Synthesis* **2009**, 3003–3025. (d) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748–8758.

(2) Peddibhotla, S. *Curr. Bioact. Compd.* **2009**, *5*, 20–38.

(3) (a) Kawasaki, T.; Nagaoka, M.; Satoh, T.; Okamoto, A.; Ukon, R.; Ogawa, A. *Tetrahedron* **2004**, *60*, 3493–3503. (b) Kawasaki, T.; Takamiya, W.; Okamoto, N.; Nagaoka, M.; Hirayama, T. *Tetrahedron Lett.* **2006**, *47*, 5379–5382. (c) Kitajima, M.; Mori, I.; Arai, K.; Kogure, N.; Takayama, H. *Tetrahedron Lett.* **2006**, *47*, 3199–3202.

(4) For syntheses of 3-allyl-3-hydroxy-oxindoles from isatin, see: (a) Alcaide, B.; Almendros, P.; Rodriguez-Acebes, R. *J. Org. Chem.* **2005**, *70*, 3198–3204. (b) Nair, V.; Ros, S.; Jayan, C. N.; Viji, S. *Synthesis* **2003**, 2542–2546. (c) Vyas, D. J.; Frohlich, R.; Oestreich, M. *J. Org. Chem.* **2010**, *75*, 6720–6723. For catalytic asymmetric allylations of isatin, see: (d) Qiao, X. C.; Zhu, S. F.; Zhou, Q. L. *Tetrahedron: Asymmetry* **2009**, *20*, 1254–1261. (e) Itoh, J.; Han, S. B.; Krische, M. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6313–6316. (f) Grant, C. D.; Krische, M. J. *Org. Lett.* **2009**, *11*, 4485–4487. For an example of a catalytic asymmetric hydroxylation of 3-allyl-oxindoles, see: (g) Sano, D.; Nagata, K.; Itoh, T. *Org. Lett.* **2008**, *10*, 1593–1595.

(5) (a) Hanhan, N. V.; Sahin, A. H.; Chang, T. W.; Fettinger, J. C.; Franz, A. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 744–747. (b) Gutierrez, E. G.; Wong, C. J.; Sahin, A. H.; Franz, A. K. *Org. Lett.* **2011**, *13*, 5754–5757.

(6) (a) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673–1675. (b) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200–206.

(7) For reviews on allylsilane reactivity, see: (a) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173–3199. (b) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293–1316. For a comparison of allylsilane nucleophilicity, see: (c) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66–77. (d) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957.

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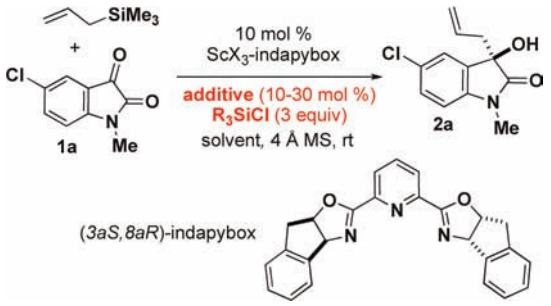
catalytic enantioselective allylation and crotylation of isatins with allylsilanes using a Sc(III)-indapybox complex with a TMSCl activator.[10,11]

We first investigated the allylation of isatin **1a** using a $Sc(OTf)_3$ complex with (*S,R*)-indapybox, which had been identified as the optimal catalyst complex for the addition of indoles and allylstannane.[5a] This complex afforded hydroxy-oxindole **2a** with 71% ee at rt, albeit with extremely low catalytic activity (Table 1, entry 1). We envisioned that additives such as $NaSbF_6$ could be used to enhance the rate of reaction, by either creating a more reactive cationic complex[12] or providing a counterion to stabilize formation of the β-silyl carbocation intermediate.[13] However, the $NaSbF_6$ addition did not improve catalytic activity (entry 2). We then investigated the addition of TMSCl to promote the reaction,[11,14] and a dramatic effect on both the yield and enantioselectivity was observed: hydroxy-oxindole **2a** was isolated with 91% yield and 88% ee (entry 3). Under these reaction conditions, the silylated **2a** (i.e., TMS-ether) product was often isolated in 11−20%. The addition of $NaSbF_6$ (10−30 mol %) with TMSCl afforded hydroxy-oxindole **2a** with 92−99% yield and up to 94% ee (entries 4−6).[15] While, the addition of $NaSbF_6$ is not essential for rate or enantioselectivity, it provides deprotection (in situ or upon workup) of any resulting TMS-ether side product.

Table 1. Optimization for Asymmetric Allylsilane Allylation[a]



entry	X	R_3SiCl	additive (mol %)	time (h)	yield[b] (%)	ee[c] (%)
1	OTf	-	-	24	6	71
2	OTf	-	$NaSbF_6$(10)	24	< 5	-
3[d]	OTf	TMSCl	-	22	91	88
4	OTf	TMSCl	$NaSbF_6$(10)	15	92	94
5	OTf	TMSCl	$NaSbF_6$(20)	17	99	88
6	OTf	TMSCl	$NaSbF_6$(30)	24	99	91
7	OTf	TMSCl	$AgClO_4$(30)	24	99	84
8	OTf	TMSCl	$LiClO_4$(30)	24	99	84
9	OTf	TMSCl	$AgSbF_6$(10)	48	93	87
10	OTf	$PhMe_2SiCl$	$NaSbF_6$(10)	24	87	89
11	OTf	TMSCl	$NaSbF_6$(10)	24	85[e]	78
12[f]	Cl	TMSCl	-	24	17	73
13[f]	Cl	TMSCl	$NaSbF_6$(10)	24	96	79

[a] All reactions performed under Ar using 3 equiv of allylsilane. [b] Isolated yield. [c] Determined by HPLC analysis with chiral AD-H stationary phase. [d] Yield and enantioselectivity reflect an average of two replicates. Under these reactions conditions, the yield varies from 80 to 99% because up to 20% of TMS-ether product is also isolated. [e] Reaction run with CH_2Cl_2, and 14% of the [3 + 2]-annulation product was isolated; see Supporting Information and ref 11. [f] Reaction run with $ScCl_3(THF)_3$. TMS = trimethylsilyl.

Investigating other additives and reaction conditions showed that the Sc(III)-catalyzed allylation maintains a high yield and enantioselectivity under various conditions (Table 1). Reactions with alternate counterion sources

(8) For reviews and selected recent examples of enantioselective allylations using allylsilanes, see: (a) Yus, M.; Gonzalez-Gomez, J. C.; Foubelo, F. *Chem. Rev.* **2011**, *111*, 7774–7854. (b) Denmark, S. E.; Fu, J. P. *Chem. Rev.* **2003**, *103*, 2763–2793. (c) Momiyama, N.; Nishimoto, H.; Terada, M. *Org. Lett.* **2011**, *13*, 2126–2129. (d) Ong, W. W.; Beeler, A. B.; Kesavan, S.; Panek, J. S.; Porco, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7470–7472. (e) Evans, D. A.; Aye, Y.; Wu, J. *Org. Lett.* **2006**, *8*, 2071–2073. (f) Kim, H.; Ho, S.; Leighton, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 6517–6520.

(9) (a) $Hg(ClO_4)_2 \cdot 3H_2O$ has recently been shown to catalyze the addition of allylsilanes to isatins, where the use of (*S*)-BINOL affords 55−63% ee; see: Cao, Z. Y.; Zhang, Y.; Ji, C. B.; Zhou, J. *Org. Lett.* **2011**, *13*, 6398–6401. (b) A racemic $Bi(OTf)_3$-catalyzed addition of allylsilanes to isatins has recently been reported; see: Meshram, H. M.; Ramesh, P.; Reddy, B. C.; Kumar, G. S. *Chem. Lett.* **2011**, *40*, 357–359.

(10) Sc(III)-pybox complexes are effective chiral Lewis acid catalysts with good chelating potential; for example, see: (a) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095–12096. (b) Evans, D. A.; Fandrick, K. R.; Song, H. J.; Scheidt, K. A.; Xu, R. S. *J. Am. Chem. Soc.* **2007**, *129*, 10029–10041. (c) Desimoni, G.; Faita, G.; Mella, M.; Piccinini, F.; Toscanini, M. *Eur. J. Org. Chem.* **2007**, 1529–1534.

(11) We recently reported a Sc(III)-catalyzed enantioselective [3 + 2] allylsilane annulation reaction with isatins using the cationic $ScCl_2(SbF_6)$-pybox complex; see: Hanhan, N. V.; Ball-Jones, N. R.; Tran, N. T.; Franz, A. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 989–992.

(12) The use of $AgSbF_6$ has been reported previously to access cationic metal chloride complexes with scandium, copper, and indium. For examples, see: (a) Evans, D. A.; Kozlowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 669–685. (b) Evans, D. A.; Willis, M. C.; Johnston, J. N. *Org. Lett.* **1999**, *1*, 865–868. (c) Evans, D. A.; Wu, J.; Masse, C. E.; MacMillan, D. W. C. *Org. Lett.* **2002**, *4*, 3379–3382. (d) Zhao, J. F.; Tjan, T. B. W.; Loh, T. P. *Tetrahedron Lett.* **2010**, *51*, 5649–5652. (e) Zhao, J.-F.; Tan, B.-H.; Loh, T.-P. *Chem. Sci* **2011**, *2*, 349.

(13) For descriptions of β-silyl carbocations, see refs 6a, 7, and 8, and also: (a) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867–7868. (b) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677–2689.

(14) (a) Evans, D. A.; Tedrow, J. S.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2002**, *124*, 392–393. (b) Lee, P. H.; Seomoon, D.; Kim, S.; Nagaiah, K.; Damle, S. V.; Lee, K. *Synthesis* **2003**, 2189–2193. (c) Miranda, P. O.; Carballo, R. M.; Martin, V. S.; Padron, J. I. *Org. Lett.* **2009**, *11*, 357–360.

(15) Catalytic activity was not observed with either $NaSbF_6$ or AgOTf when evaluated in the presence of the chiral pybox ligand and TMSCl promoter.

(16) (a) Onishi, Y.; Ito, T.; Yasuda, M.; Baba, A. *Eur. J. Org. Chem.* **2002**, 1578–1581. (b) Saito, T.; Nishimoto, Y.; Yasuda, M.; Baba, A. *J. Org. Chem.* **2006**, *71*, 8516–8522.

(17) Lee, P. H.; Seomoon, D.; Kim, S.; Nagaiah, K.; Damle, S. V.; Lee, K. *Synthesis* **2003**, 2189–2193.

(18) (a) Knolker, H. J.; Foitzik, N.; Goesmann, H.; Graf, R. *Angew. Chem., Int. Ed.* **1993**, *32*, 1081–1083. (b) Organ, M. G.; Dragan, V.; Miller, M.; Froese, R. D. J.; Goddard, J. D. *J. Org. Chem.* **2000**, *65*, 3666–3678.

(19) We have previously noted that selection of the scandium salt (OTf vs Cl) and solvent (MeCN vs CH_2Cl_2) is important to control the allylation vs annulation pathway. The allylation pathway is dominant when using the $Sc(OTf)_3$ complex with MeCN solvent. See ref 11.

(20) For a review and pioneering examples of allyltrichlorosilane activation, see: (a) Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453–3456. (b) Kobayashi, S.; Sugiura, M.; Ogawa, C. *Adv. Synth. Catal.* **2004**, *346*, 1023–1034. (c) Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161–6163.

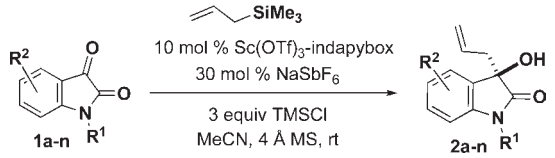
(21) A control experiment demonstrated that the allylation of isatin with allyltrichlorosilane and DMF proceeded without the Sc(III)-pybox catalyst, affording the product with a comparable (71%) yield.

(22) Narayanan, B. A.; Bunnelle, W. H. *Tetrahedron Lett.* **1987**, *28*, 6261–6264.

generally afforded similar yields and enantioselectivities compared to $NaSbF_6$ (entries 7–9). In place of TMSCl, the use of another silyl chloride, such as $PhMe_2SiCl$, was also effective in promoting the reaction (entry 10). The selection of solvent has an important effect on enantioselectivity, and performing the reaction in CH_2Cl_2 afforded **2a** with only 78% ee (entry 11). Under these conditions, we also observed formation of the spirofused tetrahydrofuran product, which was isolated in 14% yield (see Supporting Information).[11] The $ScCl_3$-indapybox catalyst proceeded with lower enantioselectivity compared to the triflate variant, and the cationic $ScCl_2(SbF_6)$ complex was essential for efficient activity (entries 12, 13).[11] When other pybox ligands (e.g., isopropyl, phenyl) were investigated, these reactions proceeded with slower rates and lower enantioselectivity (e.g., 28–61% ee, not shown).

These optimization studies demonstrated that a silyl chloride activator, such as TMSCl, is essential for efficient catalytic activity while the counterion additive had less effect on the rate or the enantioselectivity. Our previous studies using ^1H NMR spectroscopy[11] suggest that interactions of TMSCl with the metal–ligand complex may enhance the Lewis acidity of the catalyst.[16] TMSCl may also serve as a cooperative Lewis acid to preactivate the electrophile, or a transmetalation between TMSCl and the chiral scandium complex is possible.[17]

Table 2. Scope of Isatins with Allyltrimethylsilane[a]



entry	R^1	R^2	time (h)	product	yield[b] (%)	ee[c] (%)
1	Me	5-Cl	17	**2a**	99	91
2	Me	5-Br	20	**2b**	96	86[d]
3	Me	5-F	29	**2c**	89	89
4	Me	4-Cl	20	**2d**	96	87
5	Me	H	23	**2e**	91	89
6	Me	5-OMe	168	**2f**	72	92
7	H	H	72	**2g**	99	85
8	H	5-Br	51	**2h**	99	86
9	H	4-Cl	18	**2i**	99	82
10	H	7-F	27	**2j**	97	81
11	H	5-OMe	216	**2k**	99	80
12	H	5-OCF_3	22	**2l**	99	81
13	Ph	H	47	**2m**	97	89
14	CH_2CCH	5-F	22	**2n**	81	85

[a] All reactions performed under argon using 3 equiv of allylsilane. [b] Isolated yield. [c] Determined by HPLC analysis on chiral stationary phase. [d] Performing the reaction at 6 °C for 24 h afforded 95% yield and 92% ee.

(23) We have also evaluated the reaction of propargylsilane under the optimal reaction conditions, and the reaction affords the racemic allenyl product.

(24) The absolute configuration of product **3a** was assigned as the (*R*)-enantiomer, based on X-ray diffraction analysis (CDCC 866520), which matches the absolute configuration assigned for the addition of allyltributyltin in ref 5a.

We proceeded to investigate the scope of isatins in the allylation reaction, utilizing 30 mol % of $NaSbF_6$ as an optimal condition to ensure reproducible yields with a wide scope of isatins (Table 2). Although the substituents on isatins can affect the reaction rate, the yield and enantioselectivity are maintained within 72–99% yield and 80–91% ee across all isatins tested. The scandium catalyst complex is equally efficient for *N*-substituted and unsubstituted NH isatins, affording high yields and enantioselectivity for both. In many cases, using $NaSbF_6$ was preferred, because it is less hygroscopic and easier to handle.

Various allylsilanes were investigated to identify the ability of the scandium catalyst to control the product ratio (allylation vs annulation) and enantioselectivity for varying steric and electronic effects (Table 3). While bulky allylsilanes are known to promote a [3 + 2] annulation pathway,[18] here allylation is maintained as the major product using the $Sc(OTf)_3$-pybox catalyst. Using an aryldimethylsilyl group afforded the allylation product with overall identical performance to the trimethylsilyl group (entry 1). Although the increased steric bulk of the triisopropylallylsilane did not affect the rate of the reaction, the yield of the reaction was reduced to 66% (entry 2) due to formation of the annulation product.[19]

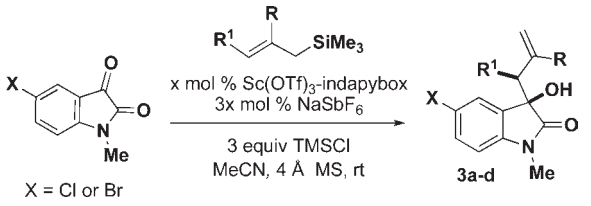
Investigating several electron-deficient allylsilanes demonstrated the limitations of the $Sc(OTf)_3$-pybox catalyst; poor or no reactivity was observed with chloro- and methoxy-substituted allylsilanes (entries 3–5). We proceeded to investigate if the $Sc(OTf)_3$-pybox catalyst would be compatible with a Lewis base additive, such as DMF, which can be used to activate the nucleophilicity of the allyl group by formation of the pentacoordinate siliconate.[20] While the allyltrichlorosilane afforded no product, adding 4 equiv of DMF to the reaction promoted allylation in 74% yield, albeit with no enantioselectivity (compare entry 4 to 6). The formation of the racemic product is attributed to the

Table 3. Reactivity of Silyl Groups for Scandium-Catalyzed Allylation[a]

entry	SiR_3	time (h)	yield[b] (%)	ee[c] (%)
1	$SiMe_2$(Ar)	24	99	87
2	$Si(i\text{-}Pr)_3$	24	66[d]	85
3	$SiMe_2Cl$	46	45	0
4	$SiCl_3$	48	<5	--
5	$Si(OMe)_3$	24	0	--
6	$SiCl_3$/DMF[e]	46	74	0

[a] All reactions performed under argon using 3 equiv of allylsilane. Ar = 4-methoxyphenyl. [b] Isolated yield. [c] Determined by HPLC analysis on chiral stationary phase (Daicel CHIRALPAK AS-H column). [d] The [3 + 2]-annulation product was also isolated in 34% yield with 99% ee. See Supporting Information. [e] Reaction run with 4 equiv of DMF. Without catalyst, this reaction yielded 71% in 48 h.

Table 4. Scope of Substituted Allylsilanes with Isatins[a]



entry	X	R	R^1	mol % catalyst	time (h)	product	yield[b] (%)	ee[c] (%)
1	Br	Me	H	5	0.17	**3a**	95	97
2	Br	Me	H	1	0.83	**3a**	95	97
3	Br	Me	H	0.05[d]	30	**3a**	94	94
4[e]	Cl	Ph	H	10	0.17	**3b**	88	99
5	Cl	C_6H_{11}	H	5	2	**3c**	99	95
6	Cl	H	Me	10	42	**3d**	95[f]	96[g]

[a] All reactions performed under argon; entries 1–5 performed with 3 equiv of allylsilane. [b] Isolated yield. [c] Determined by HPLC analysis on chiral stationary phase. [d] Due to the small scale, reaction was run with 10 equiv of $NaSbF_6$ with respect to $Sc(OTf)_3$. [e] Reaction at 5 mol % procceds with 93% yield and 91% ee in 3 h. [f] The reaction was run with 6 equiv of (*E*)-crotyltrimethylsilane to afford the product as a 5:1 mixture of diastereomers. [g] Reflects % ee of the major product, assigned as the *anti*-product. The *syn*-product was obtained in 80% ee.

enhanced Lewis acidity of the silicon and the six-membered closed transition state that can be accessed by this reaction.[21] The Sc(III)-catalyzed allylation with an allylchlorodimethylsilane reagent also afforded a racemic product (entry 3).

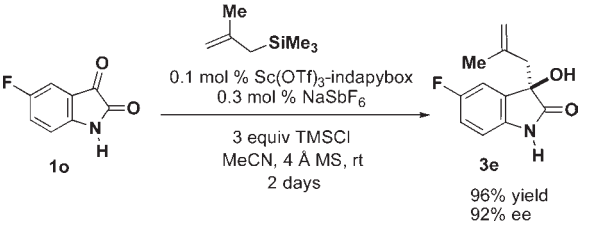
Next, a series of substituted allylic silanes were investigated and shown to proceed with high efficiency and selectivity using the Sc-catalyzed conditions. The 2-methyl-, 2-cyclohexyl-, and 2-phenyl-substituted allylsilanes[22] proceed with high yields (up to 98%) and enantioselectivities up to 99% ee (Table 4, entries 1–5).[23] These reactions were effective with as low as 0.05 mol % of the Sc(III) complex, where a high yield and enantioselectivity were maintained (entry 3).[24] The Sc-catalyzed methodology is also effective for the crotylation of isatins using (*E*)-crotyltrimethylsilane.[25] The crotylation affords *anti*-**3d** with 96% ee, isolated in 95% yield as a 5:1 mixture of diastereomers (entry 6).[26]

(25) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969.

(26) The *anti*-product was assigned as the major diastereomer by analogy with the isatin crotylation products reported in ref 4e.

To test the scalability of the allylation reaction at a low catalyst loading, a gram-scale reaction was performed using a 0.1 mol % catalyst loading (Scheme 1). The addition of methallylsilane to isatin **1o** proceeds with 96% yield and 92% ee in 48 h at rt.

Scheme 1. Gram Scale Reaction with Methallyltrimethylsilane



In conclusion, we have developed a catalytic asymmetric allylation of isatins with allylsilanes that proceeds with high yield and high enantioselectivity. The reaction utilizes a chiral Sc(III)-pybox catalyst with a TMSCl activator and additive such as $NaSbF_6$. The reaction encompasses a wide scope of isatins and various substituted allylic silanes at rt with a catalyst loading as low as 0.05 mol %, which should make this methodology useful for synthetic intermediates and industrial applications.

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Supporting Information Available. Experimental procedures, spectral data for all compounds, and X-ray data for compound **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.