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Catalytic Enantioselective Silylation of *N*-Sulfonylimines: Asymmetric Synthesis of α-Amino Acids from CO_2 via Stereospecific Carboxylation of α-Amino Silanes

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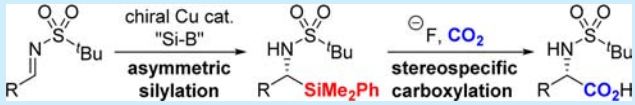
Supporting Information

ABSTRACT: A catalytic enantioselective silylation of *N*-*tert*-butylsulfonylimines using a Cu–secondary diamine complex was demonstrated. The resulting optically active α-amino silanes could be carboxylated under a CO_2 atmosphere (1 atm) to afford the corresponding α-amino acids in a stereoretentive manner. This two-step sequence provides a new synthetic protocol for optically active α-amino acids from gaseous CO_2 and imines in the presence of a catalytic amount of a chiral source.



Catalytic enantioselective silylation has received much attention over the past decade due to the versatility of the resultant optically active silylated compounds. Therefore, several methods have been devised using chiral Rh,[1a−c] Cu,[1d−j] and Pd[2] complexes. Reactive bismetals such as $PhMe_2Si$-Bpin[1,3] and $PhCl_2Si$-$SiMe_3$[2] were usually employed as silylating reagents for these silylations. Although there are many reports on enantioselective 1,4-silylations of α,β-unsaturated carbonyl compounds, examples of 1,2-silylations have been very limited.[1g,4] In 2011 Oestreich et al. reported Cu-catalyzed silylation of imines (racemic version),[4a] and in 2013 Riant et al. developed enantioselective silylation of aldehydes using a Cu–phosphine complex.[1g] However, there had been no report of enantioselective 1,2-silylation of imines until early 2014.[4b] We herein disclose a new entry of catalytic enantioselective silylation of *N*-*tert*-butylsulfonylimines using a Cu–secondary diamine complex.

As a further benefit, the resulting optically active α-amino silanes are expected to be transformed into the corresponding α-amino acids by stereospecific carboxylation with CO_2 by a fluoride under mild conditions.[5] It is well-known that optically active α-amino acids are primal units of proteins and peptides, and they are frequently utilized as chiral building blocks for asymmetric synthesis of natural products and catalysts.[6] Thus, this synthetic strategy is of great importance not only for the utilization of CO_2, an abundant, inexpensive, and relatively nontoxic C1 source,[7] but also for providing a new and alternative method for the synthesis of optically active α-amino acid derivatives via carboxylation of amine derivatives. There are several methods for preparing chiral α-amino acid derivatives via both chemical[6] and biochemical processes,[8] among which the utilization of CO_2 is limited and mostly represented by enantioselective α-carboxylation of α-amino stannanes[9] or alkyl amines[10] using a combination of BuLi and an appropriate chiral amine such as (−)-sparteine. Our group already revealed that optically active *N*-*tert*-butylsulfonyl-α-amido stannanes[11] derived from Ellman's chiral *tert*-butylsulfinamide undergo stereospecific carboxylation with CO_2 using CsF to afford optically active α-amino acid derivatives.[12] In contrast, when optically active *N*-Boc-α-amido stannanes and silanes were utilized as substrates for carboxylation, their optical purity was lost and only racemic products were obtained.[12−14] On the basis of these findings, we considered that *N*-*tert*-butylsulfonyl-α-amido silanes would also be carboxylated in a stereospecific manner even under milder conditions because a Si atom is more prone to activation by fluoride than a Sn atom (bond dissociation energy: 565 kJ/mol for Si–F and 414 kJ/mol for Sn–F).[15]

First, we engaged in the development of a catalytic enantioselective silylation of *N*-*tert*-butylsulfonylimine **1a**. Substantial screening for the combination of a Rh/Cu salt and a chiral phosphine ligand with $PhMe_2Si$-Bpin led to unsatisfying yields and ee's. We next considered employing chiral amine ligands. In 2010, Shibasaki, Kanai, and co-workers reported enantioselective 1,4-borylation using a Cu–secondary diamine **L-b** complex,[16] which actually worked very well for 1,2-silylation of imines **1a**. The reaction of **1a** with $PhMe_2Si$-Bpin (1.2 equiv) in the presence of $CuOTf{\cdot}1/2C_6H_6$ (10 mol %), **L-b** (20 mol %), and *i*-PrOH (2 equiv) proceeded smoothly in DME at 30 °C to afford the optically active α-amino silane **2a** in 93% yield with 83% ee (Table 1, entry 2).

Encouraged by the good performance of the Cu–secondary diamine complex, we screened the structures of ligands (Table 1). When the desired silylation was slow, **1a** was somewhat decomposed to produce sulfonamide **3** and benzaldehyde (**4a**) in addition to the recovery of **1a**. Examination of alkyl substituents (R^1) of 1,2-diphenylethylenediamine showed that the ethyl substitution exhibited the best performance (entries

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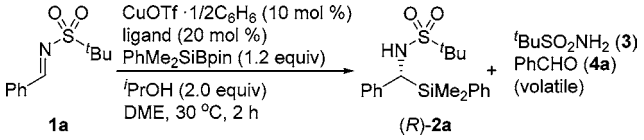
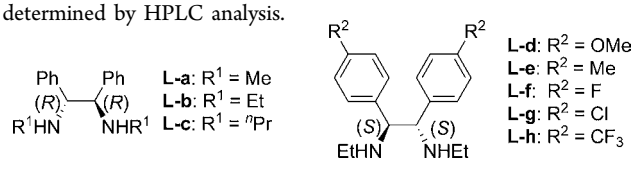
Table 1. Screening of Diamine Ligands



entry	ligand	yield (%)[a] 2a[a]	3[b]	1a rec.[b]	ee of 2a (%)[c]
1	**L-a**	88	2	-	10
2	**L-b**	93	-	-	83
3	**L-c**	65	5	23	77
4	**L-d**	83	2	6	-78
5	**L-e**	86	-	-	-82
6	**L-f**	24	8	57	-78
7	**L-g**	40	12	39	-67
8	**L-h**	34	7	37	-3

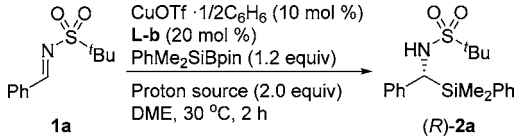
[a]Isolated yield. [b]Yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]Ee's were determined by HPLC analysis.

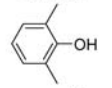
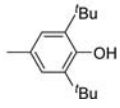


1−3). The electronic effects on the arene part of the ligand were then investigated. When ligands bearing an electron-rich arene were employed, ee's slightly dropped (entries 4 and 5). On the other hand, the substitution of an electron-deficient arene resulted in decreases in both yields and ee's (entries 6−8). Based on these results, **L-b** was selected as a suitable ligand for further investigation.

Next, we examined additive effects (Table 2). Most of the Rh/Cu-catalyzed 1,2- or 1,4-silylations to carbonyl compounds required a proton source such as an alcohol to accelerate the catalyst regeneration step.[1] Without an alcohol, the reaction was sluggish and **2a** was obtained only in 42% yield with 68% ee (entry 1). The addition of an alcohol accelerated the

Table 2. Screening of Proton Sources



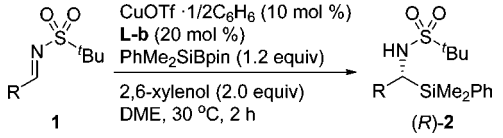
entry	proton source	yield (%) 2a[a]	1a rec.[b]	ee (%) of 2a[c]
1	None	42	54	68
2	MeOH	72	2	83
3	EtOH	84	8	82
4	^{i}PrOH	93	-	83
5	^{t}BuOH	76	9	87
6	PhOH	87	-	81
7		91	-	86
8		45	44	63

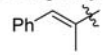
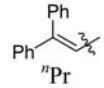
[a]Isolated yield. [b]Yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]Ee's were determined by HPLC analysis.

silylation with higher ee's. Not only aliphatic alcohols (entries 2−5) but also phenol derivatives were effective as proton sources (entries 6−8). In response to the steric bulk of an alcohol, the enantioselectivity of the product increased. However, much bulkiness impeded both the enantioselectivity and yield (entry 8). On the basis of these observations, 2,6-xylenol was the most suitable additive for this 1,2-silylation of imines (91% yield, 86% ee) (entry 7).

With the optimal conditions in hand, the substrate scope was examined (Table 3). Silylations of imines bearing an electron-

Table 3. Substrate Scope



entry	R	product	yield (%)[a]	ee (%)[b]
1	Ph	**2a**	91	86
2	4-F-C_6H_4	**2b**	99	86
3[c]	4-Cl-C_6H_4	**2c**	81	83
4[c]	2-Cl-C_6H_4	**2d**	75	81
5	4-Me-C_6H_4	**2e**	94	87
6	4-OMe-C_6H_4	**2f**	80	88
7	3,4-OMe-C_6H_3	**2g**	90	88
8	3,4,5-OMe-C_6H_2	**2h**	92	88
9	2-Me-C_6H_4	**2i**	100	95
10	2-OMe-C_6H_4	**2j**	83	86
11	2-thienyl	**2k**	97	83
12	2-naphthyl	**2l**	91	87
13		**2m**	75	93
14[c]		**2n**	76	92
15[d]	^{n}Pr	**2o**	27	76

[a]Isolated yields. [b]Ee's were determined by HPLC analysis. [c]Reaction time was 3 h. [d]Reaction was conducted at 0 °C for 13 h.

withdrawing group on the aromatic ring gave slightly lower yields and ee's (entries 2 to 4). In contrast, substitutions of an electron-donating group on the aromatic ring led to higher yields and ee's (entries 5 to 10). The product was obtained with 95% ee when the methyl group was substituted at the *ortho*-position (entry 9). In addition, silylations of the substrates possessing 2-thiophene and 2-naphthalene proceeded with high yields and ee's (entries 11 and 12). α-Alkenyl imines were also applicable in this 1,2-silylation without the generation of 1,4-silylated compounds (entries 13 and 14). α-Amino silane bearing an α-alkyl group was also obtained by this method, albeit in low yield (entry 15).

This enantioselective silylation could be performed on a gram scale (1.5 g) without any difficulties (Scheme 1). After recrystallization twice, optically pure α-amino silane **2a** was obtained in 52% yield. The absolute configuration of **2a** was determined as *R* by X-ray crystallographic analysis of this enantiopure crystal (Figure 1).[17]

Having established an efficient silylation of *N*-*tert*-butylsulfonylimines to obtain enantioenriched α-amino silanes, we next evaluated the stereospecificity of CsF-mediated carboxylation with CO_2 (balloon) (Table 4). Optically active α-amino silanes shown in Table 4 were prepared either by this silylation or diastereoselective silylation of (*R*)-*tert*-butylsulfinylimine with

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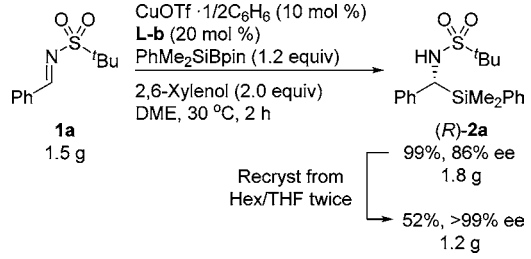
Scheme 1. Gram-Scale Synthesis of α-Amino Silane



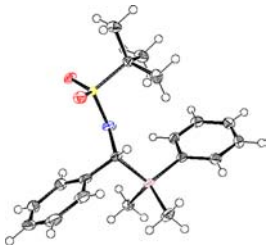
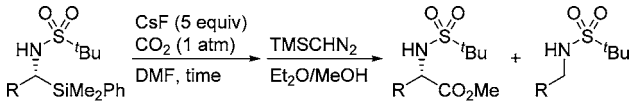


Figure 1. ORTEP figure of α-amino silane **2a** (Flack parameter is 0.00(3).).

Table 4. Stereospecific Carboxylations of α-Amino Silanes



entry	temp (°C)	R	ee of **2** (%)[b]	time (h)	yield (%) **5**[a]	yield (%) **6**[b]	ee of **5** (%)[c]
1[d]	rt	Ph (**2a**)	99	24	53	20	50
2	rt	Ph	99	24	57	5	52
3	-20	Ph	99	46	91	-	85
4	-20	4-F-C_6H_4 (**2b**)	98	46	82	-	85
5	-20	4-Cl-C_6H_4 (**2c**)	97	46	93	-	78
6	-20	4-Me-C_6H_4 (**2e**)	99	46	89	-	86
7	100	^{n}Pr (**2o**)	95	24	-	20	-
8	60	 (**2p**)	99	3	12	1	85
9[e]	60	**2p**	99	3	38	-	84

[a]Isolated yield. [b]Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c]Ee's were determined by HPLC analysis. [d]Triglyme was used as a solvent. [e]10 atm of CO_2.

$LiSiMe_2Ph$[4c] followed by oxidation. Our previous study on carboxylation of *N-tert*-butylsulfonyl-α-amido stannanes demonstrated that triglyme (triethylene glycol dimethyl ether) was a suitable solvent for stereospecific carboxylation at a high temperature (100 °C).[12] However, in the case of α-amino silanes, carboxylation proceeded similarly in both triglyme and DMF even at rt (entries 1 and 2). By using DMF as a solvent, amino acid **5a** was obtained in 57% yield with 52% ee after methyl esterification with $TMSCHN_2$, together with a small amount of protodesilylation byproduct **6a** (entry 2). Furthermore, a decrease in temperature to −20 °C resulted in a higher level of stereospecificity, selectively producing **5a** in 85% ee without the generation of **6a** (entry 3). Moreover, substrates bearing both electron-donating and -withdrawing substituents underwent carboxylations smoothly to afford **5** in high yields with high ee's (entries 4−6). However, α-alkyl substrate **2o** was not tolerable in this carboxylation even at 100 °C and only the protodesilylation product **6o** was selectively produced (entry 7). The use of α-alkenyl α-amino silane **2p** did not promote the desired carboxylation well, but the target amino acid was obtained with high stereospecificity (entry 8). An increase of CO_2 pressure (10 atm) improved the yield with the ee being maintained (entry 9).

The absolute configuration of **5a** was determined as *S* by comparison of the optical rotation value with the reported one.[18] This assignment indicated that the carboxylation of *N-tert*-butylsulfonyl-α-amido silanes proceeded in a stereoretentive manner.[19]

In summary, we successfully developed the asymmetric synthesis of α-amino silanes by a Cu-catalyzed enantioselective silylation of *N-tert*-butylsulfonylimines. *N-tert*-Butylsulfonyl-α-amido silanes thus obtained were converted into optically active α-amino acid derivatives via stereoretentive carboxylation under 1 atm of CO_2 atmosphere. Combined with the silylation and carboxylation, we eventually succeeded in the development of the asymmetric synthesis of α-amino acids using CO_2. Examination of a broader substrate scope including ketoimines to prepare quaternary α-amino acids is in progress.

■ ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures and physical properties of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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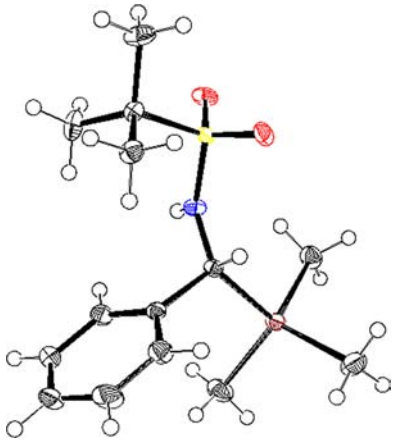
(19) In our previous work (ref 12), (*S*)-*N-tert*-butylsulfonyl-α-$SnBu_3$-benzylamine was prepared according to Chong's procedure (ref 11a), and carboxylation of this amido stannane gave the corresponding product with inversion of the stereogenic center. Thus, we concluded that carboxylation of *N-tert*-butylsulfonyl-α-amido stannanes proceeded in a stereoinvertive manner. However, we doubt the inconsistency of the stereochemical reaction mode between the reaction of α-amino silane (retention) and α-amino stannane (inversion). Therefore, we prepared several *N-tert*-butylsulfonyl-α-amido stannanes according to Chong's procedure in order to clarify the absolute configuration of the α-amido stannanes. Among them, *N-tert*-butylsulfonyl-α-$SnMe_3$-benzylamine was obtained as a single crystal (98% ee), and X-ray crystallographic analysis revealed that the absolute configuration was not *S* but *R* (No. CCDC992530, Flack parameter = −0.008(14)). Carboxylation of the genuine (*R*)-*N-tert*-butylsulfonyl-α-$SnMe_3$-benzylamine gave the product with retention of the stereogenic center, and the absolute configuration of the product was unambiguously determined by comparison of the reported optical rotation value (ref 18). Thus, our previously reported carboxylation of *N-tert*-butylsulfonyl-α-amido stannanes is also considered to proceed in a stereoretentive manner similar to that in the case of *N-tert*-butylsulfonyl-α-amido silanes (see the SI for details).



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