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C_2-Symmetric Cyclic Selenium-Catalyzed Enantioselective Bromoaminocyclization

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Supporting Information

ABSTRACT: A catalytic asymmetric bromocyclization of trisubstituted olefinic amides that uses a C_2-symmetric mannitol-derived cyclic selenium catalyst and a stoichiometric amount of *N*-bromophthalimide is reported. The resulting enantioenriched pyrrolidine products, which contain two stereogenic centers, can undergo rearrangement to yield 2,3-disubstituted piperidines with excellent diastereoselectivity and enantiospecificity.

Electrophilic halogenation of olefins is a widely used fundamental organic transformation.[1] However, the development of its asymmetric variant, in particular the catalytic version, remains a challenging task despite the significant effort devoted to this area.[2] On the basis of Brown's studies, degenerate halogen exchange of halonium ion with the olefin causes racemization of the halonium intermediate, which is believed to be the major obstacle to the development of an asymmetric halogenation reaction.[3]

In the literature, there are a number of reports dealing with the use of bifunctional catalyst systems in asymmetric halocyclization processes. Such bifunctionality appears to be an essential requirement for catalyst design in order to achieve high reactivity and useful levels of enantioselectivity.[4−6] Recently, our research group focused on the development of an amino−thiocarbamate bifunctional organocatalytic system and its application to the asymmetric bromocyclization of olefinic substrates. The Lewis basic sulfur-containing thiocarbamate is believed to activate the halogen in the electrophilic cyclization reaction.[7]

In Denmark's recent reports, a number of monofunctional Lewis basic selenium catalysts that showed excellent catalytic ability in halolactonization reactions were studied.[8] In addition, it has been shown that those monofunctional Lewis basic selenium catalysts can significantly affect the inherent site selectivity (through a tight Lewis base−halonium pair intermediate) in the halolactonization reaction, suggesting that Lewis basic selenium can potentially be used as a catalyst in the enantioselective halogenation.[8,9] Although there are several elegant reports on the use of stoichiometric monofunctional chiral Lewis bases as promoters in enantioselective halogenation processes,[4c,10] the application of monofunctional Lewis basic catalysts in asymmetric halogenation processes remains unknown.[11] Herein we are pleased to report the use of a sugar alcohol-derived C_2-symmetric monofunctional cyclic selenium species as a Lewis basic catalyst (substoichiometric amount) in the enantioselective bromoaminocyclization of trisubstituted olefinic amides. To the best of our knowledge, this represents the first case of a monofunctional Lewis basic selenium-catalyzed enantioselective bromocyclization process.

We initially examined **2**, the selenium analogue of amino−thiocarbamate catalyst **1** (Figure 1), which was readily obtained

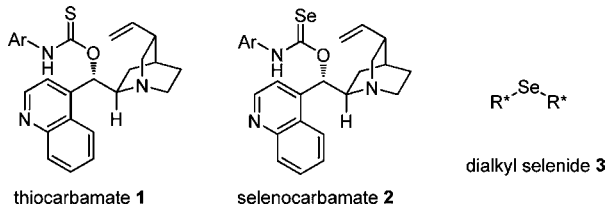

Figure 1. Lewis Basic Sulfur and Selenium Catalysts.

by a one-step coupling between isoselenocyanate and cinchona alkaloid. When 4-phenyl-4-pentenoic acid was used as the model substrate, selenocarbamate **2** was found to be a useful catalyst that offered not only appreciable ee but also a high reaction rate comparable to that of the thiocarbamate-catalyzed reaction.[12,13] However, it was found that the catalyst was unstable and decomposed during the reaction. In addition, **2** gradually turns reddish brown if it is not stored under an inert, anhydrous atmosphere. This could be a result of oxidative decomposition accompanied by the release of elemental selenium.[14]

To obtain a stable Lewis basic selenium catalyst that is resistant to decomposition, we decided to incorporate the selenium atom into a dialkyl-substituted system (**3**). A sugar alcohol-derived system was chosen in this study since it offers a well-defined chiral scaffold. Bulky substituents can also be introduced onto the hydroxyl handles for catalyst optimization. Mannitol was used in the synthesis, as it is inexpensive and commercially available. The C_2 symmetry of the scaffold also simplified the catalyst design and modification. Moreover, different substituents could be introduced to fine-tune the steric hindrance. The corresponding cyclic selenium catalysts **7** were readily obtained using a modified literature procedure (Scheme 1).[15] Epoxide **4** was treated with different phenols under basic conditions to yield diols **5**. At this stage, the steric side arms were introduced. Subsequent mesylation followed by nucleophilic selenium substitution afforded catalysts **7**.

The monofunctional selenium catalysts **7** were then employed in the underexploited asymmetric haloaminocycliza-

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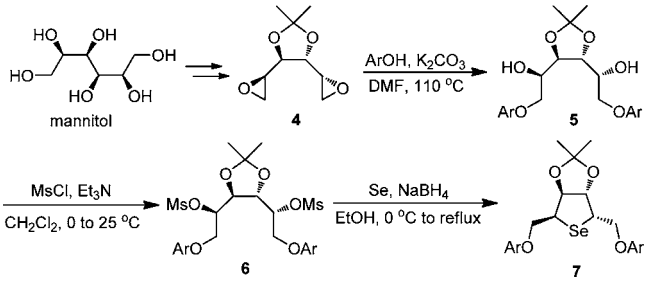
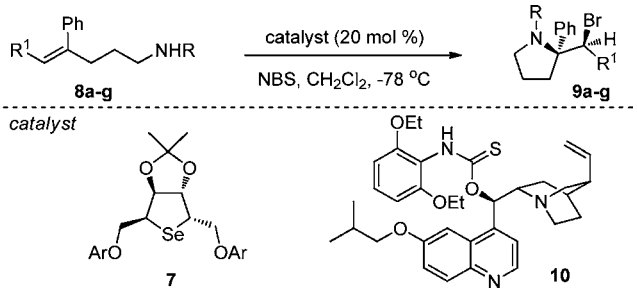
Scheme 1. Synthesis of Cyclic Selenium Catalysts 7



tion reaction. The paucity of related reports suggests the high difficulty of this class of reaction.[5,7c,e,h] Trisubstituted olefinic amides **8** (R^1 = alkyl) were chosen for study because their asymmetric cyclization remains a very challenging task. One of the major obstacles is the sluggishness of the reaction compared with the O-type halocyclization (also see Table 1). The resulting pyrrolidines can be transformed to valuable and unusual substituted piperidine building blocks (vide infra).

A preliminary investigation was performed using catalyst **7a** and 1,1-disubstituted olefinic amide. We were surprised after some screening to find that the 3-nitrobenzenesulfonamide (3-nosylamide) was far superior to the corresponding 2- and 4-nosyl analogues (Table 1, entries 1−3).[16] An examination of

Table 1. Haloaminocyclization of 8 Using 7[a]



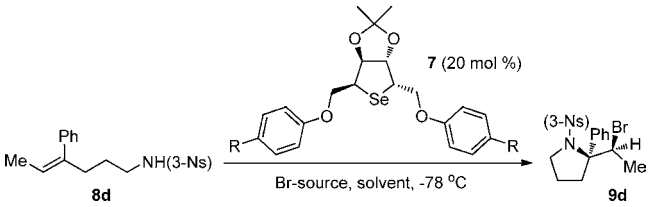
entry	amide, R,[b] R^1	catalyst, Ar	time (days)	yield (%),[c] ee (%)
1	**8a**, 4-Ns, H	**7a**, Ph	0.5	71, 11
2	**8b**, 3-Ns, H	**7a**, Ph	0.5	67, 41
3	**8c**, 2-Ns, H	**7a**, Ph	0.5	82, 1
4	**8b**, 3-Ns, H	**7b**, 4-MePh	0.5	62, 41
5	**8b**, 3-Ns, H	**7c**, 3,5-Me_2Ph	0.5	80, 37
6	**8b**, 3-Ns, H	**7d**, 4-^{t}BuPh	0.5	77, 49
7[d]	**8b**, 3-Ns, H	**7d**, 4-^{t}BuPh	2	88, 71
8[e]	**8b**, 3-Ns, H	**7d**, 4-^{t}BuPh	0.5	NR
9[f]	**8b**, 3-Ns, H	**7d**, 4-^{t}BuPh	0.5	14, 15
10	**8d**, 3-Ns, Me	**7d**, 4-^{t}BuPh	4	90, 79
11	**8d**, 3-Ns, Me	**10**	4	21, 65
12	**8e**, 4-Ns, Me	**10**	4	28, 78

[a]Reactions were carried out with amide **8** (0.03 mmol), catalyst **7** (0.006 mmol), and NBS (0.033 mmol) in CH_2Cl_2 (1.0 mL) in the absence of light. [b]Ns = nosyl. [c]Isolated yields. [d]1:1 CH_2Cl_2/toluene was used as the solvent. [e]NCS was used as the halogen source. [f]NIS was used as the halogen source.

different Ar substituents in **7** showed that a 4-*tert*-butylphenoxy unit gave 49% ee (entries 4−6). Changing the solvent from CH_2Cl_2 to 1:1 CH_2Cl_2/toluene gave the desired product with 71% ee (entry 7). Changing the halogen source from *N*-bromosuccinimide (NBS) to *N*-chlorosuccinimide (NCS) or *N*-iodosuccinimide (NIS) resulted in sluggish reactions with low enantioselectivity (entries 8 and 9). After this brief study of 1,1-disubstituted olefinic amides, we embarked on the cyclization of the challenging trisubstituted substrates. To our delight, the desired product **9d** was obtained in 90% yield with 79% ee (entry 10). It is noteworthy that only one diastereomer was detected exclusively. We also examined substrates **8d** and **8e** using thiocarbamate **10**, a catalyst that gave good yields and ee in the haloaminocyclization of 1,1-disubstituted olefinic amide;[7c] although good ee was obtained, the reaction was sluggish (entries 11 and 12). This result shows that the monofunctional cyclic selenium catalysts **7** are more reactive than the bifunctional amino−thiocarbamate catalyst.[12]

A systematic screen of different physical parameters was performed (Table 2). Among different brominating reagents,

Table 2. Optimization of the 7-Catalyzed Bromocyclization Reaction[a]



entry	Br source	solvent	catalyst, R	time (days)	yield (%),[b] ee (%)
1	NBS	CH_2Cl_2	**7d**, ^{t}Bu	4	90, 79
2	NBP	CH_2Cl_2	**7d**, ^{t}Bu	4	90, 80
3	DBH	CH_2Cl_2	**7d**, ^{t}Bu	4	92, 71
4	NBP	CH_2Cl_2/PhMe (1:1)	**7d**, ^{t}Bu	5	90, 89
5	NBP	CH_2Cl_2/nC_6H_{14} (1:1)	**7d**, ^{t}Bu	5	87, 81
6[c]	NBP	CH_2Cl_2/PhMe (1:1)	**7d**, ^{t}Bu	5	90, 90
7[d]	NBP	CH_2Cl_2/PhMe (1:1)	**7d**, ^{t}Bu	5	90, 88
8[c]	NBP	CH_2Cl_2/PhMe (1:1)	**7e**, ^{i}Pr	5	85, 84
9[c]	NBP	CH_2Cl_2/PhMe (1:1)	**7f**, CMe_2Et	5	90, 92

[a]Reactions were carried out with **8d** (0.03 mmol), **7** (0.006 mmol), and the Br source (0.033 mmol) in the solvent (0.03 M) in the absence of light. [b]Isolated yields. [c]The reaction was conducted at a concentration of 0.02 M. [d]The reaction was conducted at a concentration of 0.015 M.

N-bromophthalimide (NBP) offered the best enantioselectivity (entry 2). In the solvent screen, a CH_2Cl_2/toluene solvent blend (1:1, 0.02 M) was found to be optimal, giving the desired pyrrolidine **9d** with 90% ee (entry 6). Further fine-tuning of the catalyst bulkiness showed that the 1,1-dimethylpropyl-substituted catalyst **7f** gave **9d** with up to 92% ee (entry 9).

With the optimized conditions in hand, we further expanded the substrate scope (Table 3). Substrates with various R^1 substituents returned good yields and ees (entries 1−7). In addition, the reaction was readily scalable without diminishing the enantioselectivity (entry 3). Substrates **8k** and **8l** containing multiple double bonds also furnished the desired pyrrolidine products (entries 8 and 9), in sharp contrast to the results for other simple catalytic systems. With simple Lewis bases such as 1,4-diazabicyclo[2.2.2]octane and triphenylphosphine sulfide, no reaction was observed at low temperature. At room temperature, the reaction was sluggish and accompanied by

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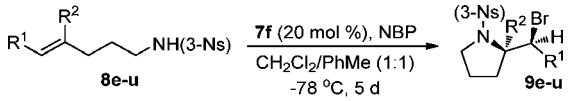
Table 3. Bromoaminocyclization of 8 Using 7f[a]



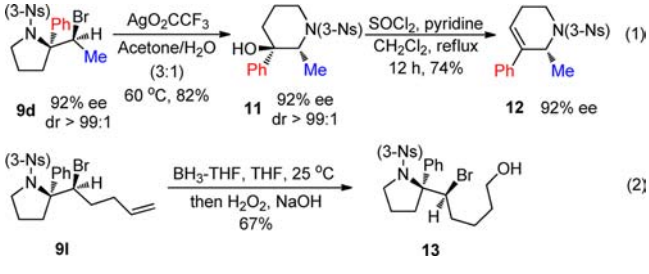
entry	amide	R^1	R^2	yield (%),[b] ee (%)
1	**8e**	Et	Ph	93, 91
2	**8f**	^{n}Pr	Ph	90, 90
3[c,d]	**8f**	^{n}Pr	Ph	82, 91
4	**8g**	^{n}Bu	Ph	91, 90
5	**8h**	^{i}Bu	Ph	91, 83
6[d]	**8i**	Bn	Ph	70, 60
7	**8j**	EtPh	Ph	92, 83
8[d]	**8k**	allyl	Ph	66, 84
9	**8l**	homoallyl	Ph	91, 90
10	**8m**	Ph	Ph	15, 79
11	**8n**	Me	4-ClPh	62, 59
12	**8o**	Me	3-ClPh	85, 83
13	**8p**	Me	4-FPh	61, 79
14	**8q**	Me	4-CF_3Ph	43, 29
15	**8r**	Me	2-MePh	92, 95
16	**8s**	Me	3-MePh	89, 51
17	**8t**	Me	4-MePh	90, 75
18	**8u**	Me	4-MeOPh	11, 2

[a]Reactions were carried out with **8** (0.03 mmol), **7f** (0.006 mmol), and NBP (0.033 mmol) in 1:1 CH_2Cl_2/PhMe (1.6 mL) in the absence of light. [b]Isolated yields. [c]The reaction was conducted on a 0.3 mmol scale. [d]The reaction time was 6 days.

the formation of multiple side products.[17] This suggests that the cyclic selenium catalyst **7** offers not only good control of the enantioselectivity but also high positional selectivity. For substrate **8m**, for which $R^1 = R^2 =$ Ph, the exo-cyclized product was obtained exclusively with 79% ee despite the low reaction rate (entry 10).[18] Some substrates with different R^2 substituents were also examined and returned good to excellent ee's (entries 11−13 and 15−17). Relatively strong electron-rich and electron-poor aryl R^2 groups, however, gave disappointing ee's (entries 14 and 18). Notably, the reactions were highly diastereoselective, as products **9** were obtained exclusively with dr >99%. The absolute configurations of **9** were established by an X-ray crystallographic study of **9d**.[13]

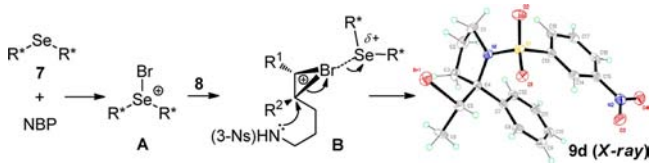
The cyclized products **9** could be further manipulated to form various interesting building blocks. For instance, treatment of **9d** with silver trifluoroacetate in 3:1 acetone/water at 60 °C gave 2,3-disubstituted piperidine **11** (Scheme 2, eq 1).[19] This rearrangement was found to be highly diastereoselective and enantiospecific.[18] Subsequent dehydration of **11** furnished unsaturated piperidine **12**. On the other hand, hydroboration of the olefin in **9l** gave multifunctional pyrrolidine **13** (Scheme 2, eq 2). These motifs resemble many interesting bioactive compounds.[20]

Scheme 2. Syntheses of 11−13



We speculate that the mechanism of this cyclic-selenium-catalyzed bromocyclization reaction may involve the following sequence (Scheme 3): (1) Coordination of the Lewis basic selenium **7** to NBP would form activated electrophilic brominating species **A**. (2) Subsequent interaction between **A** and the olefinic substrate **8** would then give a tight selenium-coordinated bromonium intermediate species, **B**. We suspect that the tight pair may help mitigate the halogen degeneration and racemization (without the use of a bifunctional pocket that could encapsulate the halonium intermediate), which may explain the high enantioselectivity. (3) Se−Br−olefin intermediate[8c] **B** would then undergo S_N2 attack by the sulfonamide to give the desired product **9** with regeneration of catalyst **7**. The dominant role of the bromonium intermediate **B** would explain the excellent regioselectivity (Markonikov type) and stereoselectivity (anti relationship of Br and Ns).

Scheme 3. Proposed Mechanism of the Lewis Basic Selenium-Catalyzed Bromoaminocyclization



In summary, we have developed the first Lewis basic selenium-catalyzed asymmetric bromocyclization of trisubstituted olefinic amides. The enantioenriched pyrrolidine products, which contain two stereogenic centers, can undergo rearrangement to yield the corresponding 2,3-disubstituted piperidines with excellent diastereoselectivity and enantiospecificity. Further studies of the mechanism and applications of this class of catalysts to other asymmetric halogenation processes are underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, CIF files, and spectroscopic and analytical data for 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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(12) When selenocarbamate **2** (Ar = *p*-MeOPh) was used as the catalyst, the desired lactone was obtained in 92% yield with 31% ee in 2 h. The reaction rate was higher than with the corresponding sulfur analogue of the catalyst (ref 7a). For details, see Scheme S1 in the Supporting Information (SI).

(13) For details, see the SI.

(14) In our previous related study, it was found that in the presence of halogen sources and trace amounts of water, some sulfur-containing catalysts were unstable. See: Tan, C. K.; Chen, F.; Yeung, Y.-Y. *Tetrahedron Lett.* **2011**, *52*, 4892.

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(16) We also examined a 1,2-disubstituted olefinic substrate. For details, see Scheme S2 in the SI.

(17) The side products were inseparable by flash column chromatography. For example, when **8k** was used as the substrate, one of the major products in the mixture with the same mass as **9k** (by LC−MS analysis) was observed. We suspect that the compound may result from cyclization at the terminal olefin. For details, see Table S1 in the SI.

(18) The structures of products **9m** and **11** were confirmed by X-ray crystallography.

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