Asymmetric N1 Unit Transfer to Olefins with a Chiral Nitridomanganese Complex: Novel Stereoselective Pathways to Aziridines or Oxazolines

Masaaki Nishimura, Satoshi Minakata,* Toru Takahashi, Yoji Oderaotoshi, and Mitsuo Komatsu*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

komatsu@ap.chem.eng.osaka-u.ac.jp

Received September 25, 2001

Chiral nitridomanganese complex **1** was found to be a highly potential N1 unit source for the asymmetric synthesis of aziridines and 2-oxazolines from olefins such as styrene and its derivatives. When sulfonyl chlorides were employed as activators of the complex in the presence of pyridine, pyridine *N*-oxide, and a silver salt, the reaction of olefins with complex **1** proceeded smoothly to afford the N-sulfonylated aziridines. The aziridination of styrene derivatives with complex **1** using 2-trimethylsilylethanesulfonyl chloride (SESCl) gave the *N*-SES-aziridines, which were easily converted into chiral N-unsubstituted aziridines. It was found that the reaction was applicable to the asymmetric synthesis of 2-oxazolines from olefins when acyl chlorides were employed as activators. Complex **1** provided an effective asymmetric environment for trans-disubstituted styrenes in the reaction (up to 92% ee). This is the first example of a direct asymmetric synthesis of 2-oxazolines from olefins. Additional experiments, conducted during the course of this investigation, suggest that the isomerization of the *N*-acylaziridine intermediate is involved in this reaction.

Introduction

Asymmetric heteroatom transfer reactions to carbon−carbon double bonds using catalytic or stoichiometric amounts of transition-metal complexes have recently attracted considerable interest for use in the synthesis of chiral three-membered heterocycles.[1,2] This class of heterocycles represents a useful chiral building block and is also found in a large number of natural products as well as biologically active compounds.[3,4] A variety of oxygen atom transfer reactions have been described, and some highly stereoselective reactions have been reported. On the other hand, during the past decade, N1 unit transfer reactions have been developed by employing some nitrogen sources such as [*N*-(*p*-toluenesulfonyl)-imino]phenyliodinane (PhI═NTs)[2,5] and Chloramine-T,[6] as well as others,[7] and these reagents have also been applied to asymmetric reactions.[2,7a−c] As an alternative approach, nitrido complexes, which contain a metal−nitrogen triple bond unit, have been utilized for nitrogen atom transfer reactions.[8,9] One of the earliest examples of a nitrogen atom transfer using a nitrido complex was

(1) (a) Johnson, R. A.; Sharpless, K. B. In *Comprehensive Organic Synthesis*; Ley, S. V., Ed.; Pergamon: Oxford, 1991; Vol. 7, pp 389−436. (b) Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 1097−1176. (c) Katsuki, T. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 287−325.

(2) (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M.; *J. Am. Chem. Soc.* **1991**, *113*, 726−728. (b) Lowenthal, R. E.; Masamune, S. *Tetrahedron Lett.* **1991**, *32*, 7373−7376. (c) O'Connor, K. J.; Wey, S.-J.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001−1004. (d) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326−5327. (e) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328−5329. (f) Noda, K.; Hosoya, N.; Irie, R.; Ito, Y.; Katsuki, T. *Synlett* **1993**, 469−471. (g) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889−5890. (h) Nishikori, H.; Katsuki, T. *Tetrahedron Lett.* **1996**, *37*, 9245−9248. (i) Sanders, C. J.; Gillespie, K. M.; Bell, D.; Scott, P. *J. Am. Chem. Soc.* **2000**, *122*, 7132−7133.

(3) (a) Rossiter, B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: Orlando, 1985; Vol. 5, pp 193−246. (b) Erden, I. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: Oxford, 1996; Vol. 1A, pp 97−171.

(4) (a) Kasai, M.; Kono, M. *Synlett* **1992**, 778−790. (b) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599−619. (c) Pearson, W. H.; Lian, B. W.; Bergmeier, S. C. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: Oxford, 1996; Vol. 1A, pp 1−66. (d) Rai, K. M. L.; Hassner, A. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: Oxford, 1996; Vol. 1A, pp 61−96.

(5) (a) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161−1163. (b) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517−1524. (c) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *Tetrahedron Lett.* **1988**, *29*, 1927−1930. (d) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744−6746. (e) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742−2753. (f) Knight, J. G.; Muldowney, M. P. *Synlett* **1995**, 949−951. (g) Müller, P.; Baud, C.; Jacquier, Y. *Can. J. Chem.* **1998**, *76*, 738−750. (h) Jeon, H.-J.; Nguyen, S. T. *Chem. Commun.* **2001**, 235−236.

(6) (a) Ando T.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **1998**, *39*, 309−312. (b) Ando, T.; Kano, D.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron* **1998**, *54*, 13485−13494. (c) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844−6845. (d) Albone, D. P.; Aujla, P. S.; Taylor, P. C.; Challenger, S.; Derrick, A. M. *J. Org. Chem.* **1998**, *63*, 9569−9571. (e) Ali, S. I.; Nikalje, M. D.; Sudalai, A. *Org. Lett.* **1999**, *1*, 705−707. (f) Chanda, B. M.; Vyas, R.; Bedekar, A. V. *J. Org. Chem.* **2001**, *66*, 30−34.

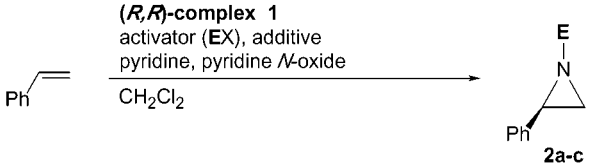
(7) (a) Atkinson, R. S.; Coogan, M. P.; Cornell, C. L. *J. Chem. Soc., Chem. Commun.* **1993**, 1215−1216. (b) Atkinson, R. S.; Claxton, T. A.; Lochrie, I. S. T.; Ulukanli, S. *Tetrahedron Lett.* **1998**, *39*, 5113−5116. (c) Atkinson, R. S.; Ayscough, A. P.; Gattrell, W. T.; Raynham, T. M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2783−2793 and references therein. (d) Rudchenko, V. F.; Ignatov, S. M.; Kostyanovsky, R. G. *J. Chem. Soc., Chem. Commun.* **1990**, 261−262. (e) Vedejs, E.; Sano, H. *Tetrahedron Lett.* **1992**, *33*, 3261−3264. (f) Pereira, M. M.; Santos, P. P. O.; Reis, L. V.; Lobo, A. M.; Prabhakar, S. *J. Chem. Soc., Chem. Commun.* **1993**, 38−40. (g) Fioravanti, S.; Pellacani, L.; Stabile, S.; Tardella, P. A.; Ballini, R. *Tetrahedron* **1998**, *54*, 6169−6176. (h) Au, S.-M.; Fung, W.-H.; Cheng, M.-C.; Che, C.-M.; Peng, S.-M. *Chem. Commun.* **1997**, 1655−1656. (i) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120−9132.

10.1021/jo016146d CCC: $22.00
Published on Web 03/08/2002

reported by Groves's group for the aziridination of cyclooctene in the presence of trifluoroacetic anhydride (TFAA),[8a] but they mentioned no other olefins in their paper. Several years ago, Carreira and co-workers extended this type of reaction to the amination of silyl enol ethers and glycals with new types of nitridomanganese complexes.[8c−e] More recently, we reported the first example of the asymmetric aziridination of olefins using a chiral nitridomanganese complex with good to high yields and excellent enantioselectivities.[9a] In this reaction, *p*-toluenesulfonic anhydride (Ts_2O) played an important role as an activator of the complex to achieve the aziridination. An appropriate choice of activator might be important in controlling the reactivity, stereoselectivity, and product selectivity. To extend the utility of the present nitrogen atom transfer reactions, which use a nitridomanganese complex, we investigated the reaction of olefins with the chiral complex using sulfonyl chlorides or acyl chlorides, which constitute readily available activators of the complex. Moreover, the employment of an acyl chloride would be expected to lead directly to chiral 2-oxazolines from olefins, since it is known that *N*-acylaziridines isomerize to oxazolines under, for example, Lewis acidic conditions.[10] Optically active oxazolines are found as components of a variety of natural products and biologically active compounds.[11,12] It has also been revealed in the past decade that they act as potential chiral ligands for asymmetric synthesis.[13] The reagent-controlled synthesis of chiral 2-oxazolines is a useful method, but only a few examples have been reported to date.[14]

In this paper, we report the asymmetric nitrogen atom transfer to olefins using a chiral nitridomanganese complex in the presence of readily available activators. Asymmetric aziridination was found to proceed smoothly when a sulfonyl chloride was employed as an activator in the presence of a silver salt, while the first example of the direct asymmetric synthesis of 2-oxazolines from olefins was achieved using an acyl chloride as an activator.

Table 1. Asymmetric Aziridination of Styrene with Complex 1 Using Sulfonyl Chlorides[a]



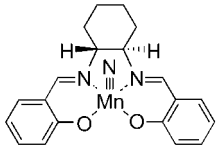
2a-c

entry	activator (**E**X)	additive	conditions	product	yield (%)	ee[b] (%)
1	TsCl	none	rt, 24 h	**2a**	76	26[c]
2	TsCl	$AgClO_4$	rt, 3 h	**2a**	77	38[c]
3	TsCl	$AgClO_4$	0 °C, 6 h	**2a**	78	40[c]
4	NsCl	$AgClO_4$	0 °C, 3 h	**2b**	46	43[d]
5	MsCl	$AgClO_4$	0 °C, 18 h	**2c**	87	42[d]
6	Ts_2O	none	0 °C, 3 h	**2a**	78	41[c]

[a] Reaction conditions: (*R*,*R*)-complex **1** (1 equiv), EX (1.2 equiv), additive (1.2 equiv), pyridine (0.5 equiv), pyridine *N*-oxide (1.2 equiv), styrene (10 equiv). [b] Enantiomeric excesses were determined by HPLC analysis using a Daicel Chiralcel OJ column. [c] Absolute configurations were determined to be (*R*) by comparison of the measured optical rotations with reported values.[15c] [d] Absolute configurations were established as (*R*) by a comparison of the measured optical rotations with that of **2a**.

Results and Discussion

Asymmetric Aziridination Using Sulfonyl Chlorides as Activators. As mentioned above, the asymmetric aziridination has been achieved by the reaction of olefins with complex **1** in the presence of Ts_2O as the activator of the complex.



(*R*,*R*)-complex 1

Although Ts_2O is an effective reagent for aziridination, it is relatively expensive and other sulfonyl anhydrides are not readily available. Thus, sulfonyl chlorides were applied to the aziridination, since they are more readily available and the diversity of substituents on the nitrogen of the formed aziridines is expanded. The results are summarized in Table 1. *p*-Toluenesulfonyl chloride (TsCl) was initially employed in the reaction in an attempt to verify whether sulfonyl chlorides are able to act as an activator or not. When styrene was treated with complex **1** at room temperature for 24 h in the presence of pyridine, pyridine *N*-oxide, and TsCl, *N*-(*p*-toluenesulfonyl)-2-phenylaziridine (**2a**) was obtained in 76% yield with 26% ee. While the aziridination took place even

(8) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073−2074. (b) Groves, J. T.; Takahashi, T.; Butlar, W. M. *Inorg. Chem.* **1983**, *22*, 884−887. (c) Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915−916. (d) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 3179−3180. (e) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M.; Day, M. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1645−1647. (f) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364−372. (g) Svenstrup, N.; Bøgevig, A.; Hazell, R. G.; Jørgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1559−1565. (h) Ho, C. T.; Lau, T. C.; Kwong, H. L.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1999**, 2411−2413.

(9) (a) Minakata, S.; Ando, T.; Nishimura, M.; Ryu, I.; Komatsu, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3392−3394. (b) Nishimura, M.; Minakata, S.; Thongchant, S.; Ryu, I.; Komatsu, M. *Tetrahedron Lett.* **2000**, *41*, 7089−7092.

(10) (a) Ferraris, D.; Drury, W. J., III; Cox, C.; Lectka, T. *J. Org. Chem.* **1998**, *63*, 4568−4569. (b) Tomasini, C.; Vecchione, A. *Org. Lett.* **1999**, *1*, 2153−2156.

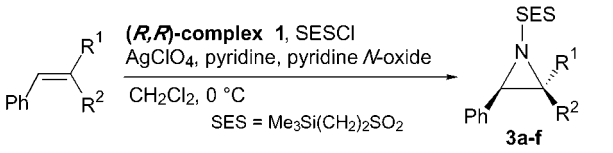
(11) (a) Davidson, B. S. *Chem. Rev.* **1993**, *93*, 1771−1791. (b) Michael, J. P.; Pattenden, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1−23. (c) Sone, H.; Kigoshi, H.; Yamada, K. *Tetrahedron* **1997**, *53*, 8149−8154. (d) Rudi, A.; Aknin, M.; Gaydou, E. M.; Kashman, Y. *Tetrahedron* **1998**, *54*, 13203−13210. (e) Boden, C. D. J.; Norley, M.; Pattrnden, G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 883−888 and references therein.

(12) For reviews on 2-oxazolines: (a) Frump, J. A. *Chem. Rev.* **1971**, *71*, 483−505. (b) Meyers, A. I.; Mihelich, E. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 270−281. (c) Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837−860. (d) Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297−2360. (e) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835−875.

(13) For recent reviews: (a) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1−45. (b) Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325−335. (c) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336−345.

(14) (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405−6406. (b) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857−871. (c) Soloshonok, V. A.; Hayashi, T. *Tetrahedron Lett.* **1994**, *35*, 2713−2716. (d) Sawamura, M.; Nakayama, Y.; Kato, T.; Ito, Y. *J. Org. Chem.* **1995**, *60*, 1727−1732. (e) Soloshonok, V. A.; Kacharov, A. D.; Hayashi, T. *Tetrahedron* **1996**, *52*, 245−254. (f) Suga, H.; Ikai, K.; Ibata, T. *Tetrahedron Lett.* **1998**, *39*, 869−872. (g) Suga, H.; Ikai, K.; Ibata, T. *J. Org. Chem.* **1999**, *64*, 7040−7047. (h) Evans, D. A.; Janey, J. M.; Magomedov, N.; Tedrow, J. S. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1884−1888.

Table 2. Asymmetric Aziridination of Styrene and Its Derivatives with Complex 1 Using SESCl[a]



entry	R^1	R^2	time (h)	product	yield(%)	ee (%)[b]
1	H	H	9	**3a**	60	40[c]
2	Me	H	12	**3b**	70	83[d]
3	*n*-Pr	H	12	**3c**	50	85[e]
4	*i*-Pr	H	12	**3d**	62	90[e]
5	*c*-Hex	H	12	**3e**	62	93[e]
6	H	Me	24	**3f**	37	24[f]

[a] Reaction conditions: (*R*,*R*)-complex **1** (1 equiv), SESCl (1.2 equiv), $AgClO_4$ (1.2 equiv), pyridine (0.5 equiv), pyridine *N*-oxide (1.2 equiv), olefin (10 equiv). [b] Enantiomeric excesses were determined by HPLC analysis. [c] Absolute configuration was determined to be (*R*) from that of **4a**. [d] Absolute configuration was determined to be (2*R*,3*R*) from that of **4b**. [e] Absolute configurations were established to be (2*R*,3*R*) by comparison of the measured optical rotations with that of **3b**. [f] Absolute configuration was determined to be (2*S*,3*R*) from that of **4f**.

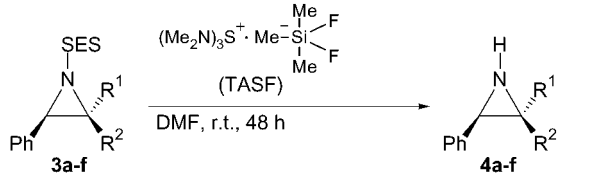
when TsCl was used instead of Ts_2O, the enantioselectivity was rather low compared to that for Ts_2O. Several additives were examined in an attempt to improve the enantiomeric excess. The addition of silver perchlorate ($AgClO_4$) was found to increase the enantioselectivity and decrease the reaction time. The use of $AgClO_4$ at 0 °C afforded the same results as those found for Ts_2O. These results prompted us to employ other sulfonyl chlorides in the reaction. The aziridination was performed with *p*-nitrobenzensulfonyl chloride (NsCl) to furnish the desired product in moderate yield. An alkyl sulfonyl chloride, methanesulfonyl chloride, was found to function as an activator of the complex to afford *N*-mesylaziridine **2c** in good yield. It turned out that sulfonyl chlorides also acted as activators of the complex in the presence of a silver salt to perform the aziridination, and the enantioselectivities were not influenced by the nature of the sulfonyl moiety of the activators.

Although *N*-sulfonyl groups attached to the nitrogen of aziridines can be removed under reductive conditions, undesirable reactions such as the ring-opening of aziridines sometimes occur.[15] To obtain N-unsubstituted aziridines more readily,[8h] the successful introduction of an alkyl sulfonyl group to the nitrogen of an aziridine led us to synthesize *N*-(2-trimethylsilylethanesulfonyl)-aziridines (*N*-SES-aziridine), the SES group of which can be easily removed under mild conditions.[16] 2-Trimethylsilylethanesulfonyl chloride (SESCl) was employed in the aziridination using $AgClO_4$ (Table 2). When styrene was treated with complex **1** in the presence of SESCl and $AgClO_4$, *N*-SES-aziridine **3a** was obtained in 60% yield with 40% ee. The aziridination of *trans*-*β*-methylstyrene afforded the corresponding aziridine **3b** with 83% ee. Other trans-disubstituted styrene derivatives were also smoothly aziridinated with excellent enantioselectivities. *cis*-*β*-Methylstyrene was transformed to *cis*-aziridine **3f** with no detectable formation of the trans-isomer. The

(15) (a) Bellos, K.; Stamm, H.; Speth, D. *J. Org. Chem.* **1991**, *56*, 6846−6849. (b) Vedejs, E.; Lin, S. *J. Org. Chem.* **1994**, *59*, 1602−1603. (c) Alonso, D. A.; Andersson, P. G. *J. Org. Chem.* **1998**, *63*, 9455−9461.

(16) (a) Weinreb, S. M.; Chase, C. E.; Wipf, P.; Venkatraman, S. *Org. Synth.* **1998**, *75*, 161−169. (b) Dauban, P.; Dodd, R. H. *J. Org. Chem.* **1999**, *64*, 5304−5307.

Table 3. Desulfonylation of *N*-SES-Aziridines 3[a]



entry	R^1	R^2	*N*-SES-aziridine	product	yield (%)	ee[b] (%)
1	H	H	**3a** (40% ee)	**4a**	65	40[c]
2	Me	H	**3b** (83% ee)	**4b**	79	83[d]
3	*n*-Pr	H	**3c** (85% ee)	**4c**	80	85[e]
4	*i*-Pr	H	**3d** (90% ee)	**4d**	81	90[e]
5	*c*-Hex	H	**3e** (93% ee)	**4e**	85	93[e]
6	H	Me	**3f** (24% ee)	**4f**	72	24[f]

[a] Reaction conditions: *N*-SES-aziridine **3** (1 equiv) and TASF (4 equiv). [b] Enantiomeric excesses were determined by HPLC analysis. [c] Absolute configuration was determined to be (*R*) by comparison of HPLC analysis of the *N*-tosyl derivative with that of **2a**. [d] Absolute configuration was determined to be (2*R*,3*R*) by comparison of the measured optical rotation with reported values.[24] [e] Absolute configurations were established to be (2*R*,3*R*) by comparison of the measured optical rotations with that of **4b**. [f] Absolute configuration was determined to be (2*S*,3*R*) by comparison of the measured optical rotation with reported values.[25]

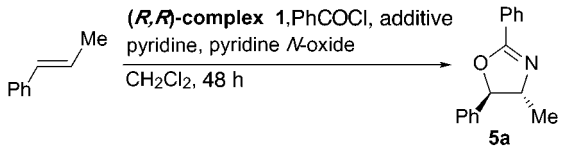
removal of the SES group was performed under conditions using tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) to provide N−H aziridines **4** with no change in optical purity (Table 3).

Asymmetric Synthesis of 2-Oxazolines Using Acyl Chlorides as Activators. Sulfonyl chlorides were found to be good activators of a nitridomanganese complex for achieving asymmetric aziridination. To extend the scope of the N1 unit transfer using a nitridomanganese complex, acyl chlorides were employed as activators. As described in the Introduction, acyl chlorides might be potent candidates as activators for the reaction leading to *N*-acylaziridines and/or 2-oxazolines.[17]

Benzoyl chloride was initially applied to the reaction of olefins with complex **1**. As a model substrate for optimization of the reaction conditions, *trans*-*β*-methylstyrene was selected for the reaction because it gave good results in the previously described aziridination method.[9a] When *trans*-*β*-methylstyrene was treated with complex **1** at room temperature for 48 h in the presence of pyridine, pyridine *N*-oxide, and benzoyl chloride, 4-methyl-2,5-diphenyl-2-oxazoline (**5a**) was obtained in 77% yield with 81% ee (Table 4, entry 1). Although the reaction proceeded at 0 °C with good enantioselectivity (86% ee), the chemical yield of **5a** was lower than the yield at room temperature. To obtain a higher chemical yield at 0 °C while retaining the enantioselectivity, additives for this reaction were investigated (Table 4, entries 3−10). The addition of a silver salt such as $AgClO_4$ or $AgBF_4$ was found to dramatically improve the chemical yield with no significant loss in enantioselectivity. However, the use of $AgNO_3$ reduced the chemical yield of **5a**, indicating that counteranions might be a key determinant in this reaction. The same reactions in the presence of sodium salts ($NaClO_4$ and $NaBF_4$) proceeded in moderate yields. The addition of a lithium or magnesium salt had no effect on the course of the reaction. A reaction conducted in the presence of $AgBF_4$ but without

(17) Carreira et al. reported that the use of $(CF_3CO)_2O$ as an activator for a nitrido complex leads to the formation of ring-opening products, amino alcohols; see: ref 8e.

Table 4. Asymmetric Synthesis of Oxazoline 5a from *trans*-β-Methylstyrene and Complex 1[a]

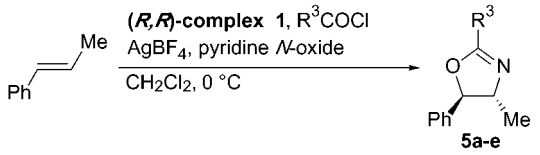


5a

entry	additive	temp	yield (%)	ee (%)[b,c]
1	none	rt	77	81
2	none	0 °C	34	86
3	$AgClO_4$	0 °C	65	87
4	$AgBF_4$	0 °C	77	87
5	$AgNO_3$	0 °C	15	84
6	$NaClO_4$	0 °C	56	86
7	$NaBF_4$	0 °C	50	86
8	$LiClO_4$	0 °C	29	87
9	$Mg(ClO_4)_2$	0 °C	23	86
10[d]	$AgBF_4$	0 °C	81	86

[a] Reaction conditions: (*R*,*R*)-complex **1** (1 equiv), PhCOCl (1.2 equiv), additive (1.2 equiv), pyridine (0.5 equiv), pyridine *N*-oxide (1.2 equiv), *trans*-β-methylstyrene (10 equiv). [b] Enantiomeric excesses were determined by HPLC analysis using a Daicel Chiralcel OD column. [c] Absolute configurations were determined to be (4*R*,5*R*) by a comparison of the measured optical rotations with reported values.[26] [d] Reaction was run without pyridine.

Table 5. Effect of Acid Chlorides on the Reaction of *trans*-β-Methylstyrene with Complex 1[a]



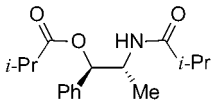
5a-e

entry	R^3	time (h)	oxazoline	yield (%)	ee (%)[b]
1	Ph	48	**5a**	81	86[c]
2	*p*-$CF_3C_6H_4$−	24	**5b**	88	86[d]
3	*p*-$MeOC_6H_4$−	168	**5c**	80	86[d]
4	*t*-Bu	48	**5d**	75	85[e]
5	*i*-Pr	24	**5e**	45[f]	87[g]

[a] Reaction conditions: (*R*,*R*)-complex **1** (1 equiv), PhCOCl (1.2 equiv), $AgBF_4$ (1.2 equiv), pyridine *N*-oxide (1.2 equiv), *trans*-β-methylstyrene (10 equiv). [b] Enantiomeric excesses were determined by HPLC analysis using a Daicel Chiralcel OD column or a Chiralpak AD column. [c] Absolute configuration was determined to be (4*R*,5*R*).[26] [d] Absolute configurations were established to be (4*R*,5*R*) by comparison of the measured optical rotations with that of **5a**. [e] Absolute configuration was determined to be (4*R*,5*R*) using the corresponding amino alcohol derived from **5d**. [f] Compound **6** was obtained in 25% yield with 86% ee. [g] Absolute configuration was established as (4*R*,5*R*) by comparison of the measured optical rotation with that of **5d**.

pyridine afforded the best result.[18] These results represent the first example of the direct asymmetric synthesis of an oxazoline from an olefin. Although *N*-aroylnitrenes generally add to olefins to give aziridines,[19] oxazoline **5a** was selectively produced with no detectable formation of the corresponding *N*-benzoylaziridine. Moreover, the reaction gave *trans*-oxazolines exclusively with the conservation of the stereochemistry of the starting olefins.

To investigate the influence of activators of complex **1** on the synthesis of oxazolines, several acyl chlorides were examined, and the results are listed in Table 5. When *p*-(trifluoromethyl)benzoyl chloride was employed in the reaction, *trans*-β-methylstyrene was found to react smoothly and the corresponding oxazoline was obtained in 88% yield with 86% ee. Although a considerable length of time was required to complete the reaction in the case of *p*-methoxybenzoyl chloride, the yield and enantiomeric excess of the produced oxazoline were the same as those for the product obtained via the use of benzoyl chloride. These results show that an electron-deficient substituent on the phenyl ring of an acyl chloride enhances the reaction rate. Aliphatic acyl chlorides such as pivaloyl chloride and isobutyryl chloride are also applicable to the reaction, yielding the corresponding oxazolines in moderate to good yields with high ee. From these results, the enantioselectivities in the synthesis of oxazolines do not appear to be dependent on the structure of the acyl chlorides. The ee value of compound **6** obtained in entry 5 was the same as that of **5e**, suggesting that the byproduct might not be formed via the ring-opening of an *N*-acylaziridine intermediate but, rather, by the hydrolysis of the acylated oxazoline or the acylation of the hydrolyzed oxazoline. The acylation of **5e** proceeded more easily in comparison with that of **5d** because of the less bulky environment around the nitrogen on **5e** to provide compound **6**.



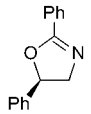
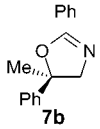
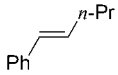
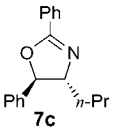
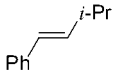
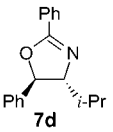
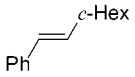
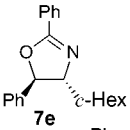
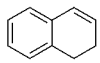
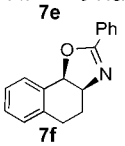
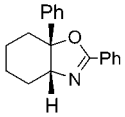
6

The present reaction was successfully applied to the synthesis of oxazolines from styrene and its derivatives, as shown in Table 6. When styrene, a simple olefin, was treated with complex **1** using benzoyl chloride under optimal conditions, oxazoline **7a** was obtained in 74% yield, albeit with a lower enantioselectivity. In the case of α-methylstyrene, the corresponding oxazoline was produced in a better yield with low enantioselectivity. The fact that the use of *trans*-β-methylstyrene resulted in high enantioselectivity (vide ante) encouraged us to investigate the reaction of other trans-disubstituted styrene derivatives with complex **1**. The reaction of *trans*-1-phenyl-1-pentene with **1** afforded the desired oxazoline in good yield with high enantioselectivity. *trans*-3-Phenyl-1-methyl-2-butene and *trans*-β-cyclohexylstyrene were transformed to the corresponding oxazolines in over 90% ee, respectively. In these reactions, the *trans*-oxazolines were obtained as the sole products and no cis-isomers were detected. Although the present reaction permitted the conversion of cyclic olefins such as 1,2-dihydronaphthalene and 1-phenylcyclohexene to the polycyclic compounds, the yields and enantioselectivities were moderate. The complex was found to be a good chiral source for inducing high enantioselectivities when trans-substituted styrene derivatives were used as substrates. The tendency of a substituent effect on enantiomeric excesses in the reactions is similar to that observed for the aziridination of these styrene derivatives using complex **1** and Ts_2O.

(18) When *trans*-β-methylstyrene was treated with (*S*,*S*)-complex **1**, (4*S*,5*S*)-**5a** was obtained (82% yield, 85% ee).

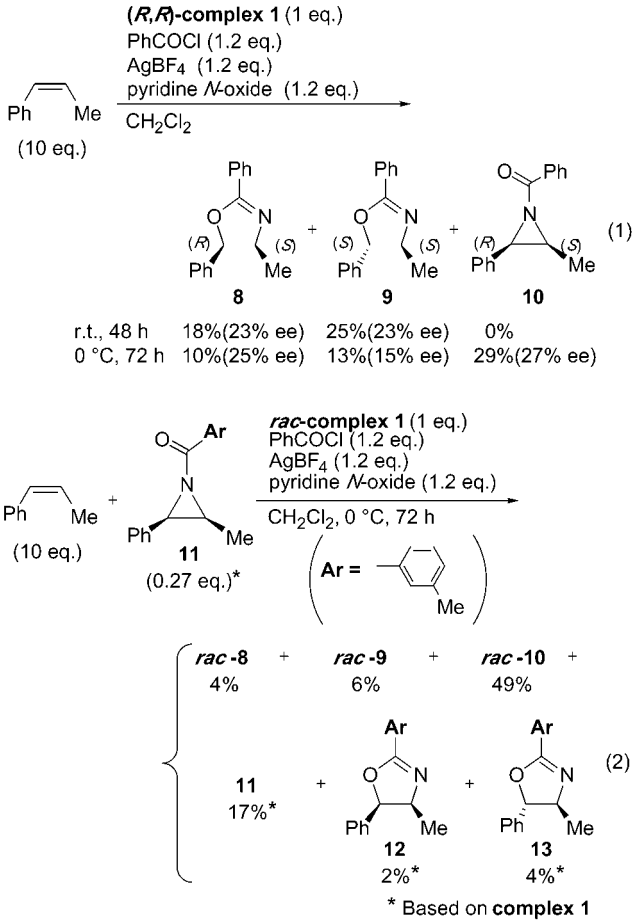
(19) (a) Mishra, A.; Rice, S. N.; Lwowski, W. *J. Org. Chem.* **1968**, *33*, 481−486. (b) Hayashi, Y.; Swern, D. *J. Am. Chem. Soc.* **1973**, *95*, 5205−5210. (c) Semenov, V. P.; Khusainova, A. K.; Studenikov, A. N.; Ogloblin, K. A. *Zh. Org. Khim.* **1977**, *13*, 963−968. (d) Semenov, V. P.; Studenikov, A. N.; Bespalov, A. D.; Ogloblin, K. A. *Zh. Org. Khim.* **1977**, *13*, 2202−2207. (e) Semenov, V. P.; Studenikov, A. N.; Prosypkina, A. P.; Ogloblin, K. A. *Zh. Org. Khim.* **1977**, *13*, 2207−2212. (f) Semenov, V. P.; Studenikov, A. N.; Ivanov, B. B.; Ogloblin, K. A. *Zh. Org. Khim.* **1990**, *26*, 331−335. (g) Buck, K.; Jacobi, D.; Plögert, Y.; Abraham, W. *J. Prakt. Chem.* **1994**, *336*, 678−685.

Table 6. Asymmetric Synthesis of Oxazolines from Styrene and Its Derivatives Using Complex 1[a]

entry	olefin	time (h)	oxazoline	yield (%)	ee (%)[b]
1		48	 **7a**	74	16[c]
2		48	 **7b**	86	6[d]
3		24	 **7c**	85	88[e]
4		24	 **7d**	85	90[e]
5		36	 **7e**	75	92[e]
6		72	 **7f**	55	11[d]
7		48	 **7g**	53	32[d]

[a] Reaction conditions: (*R*,*R*)-complex **1** (1 equiv), PhCOCl (1.2 equiv), $AgBF_4$ (1.2 equiv), pyridine *N*-oxide (1.2 equiv), olefin (10 equiv), CH_2Cl_2, 0 °C. [b] Enantiomeric excesses were determined by HPLC analysis using a Daicel Chiralcel OD column or a Chiralpak AD column. [c] Absolute configuration was determined to be (*R*) by comparison of the measured optical rotation with reported values.[27] [d] Absolute configurations were not determined. [e] Absolute configurations were established to be (4*R*,5*R*) by comparison of the measured optical rotations with that of **5a**.

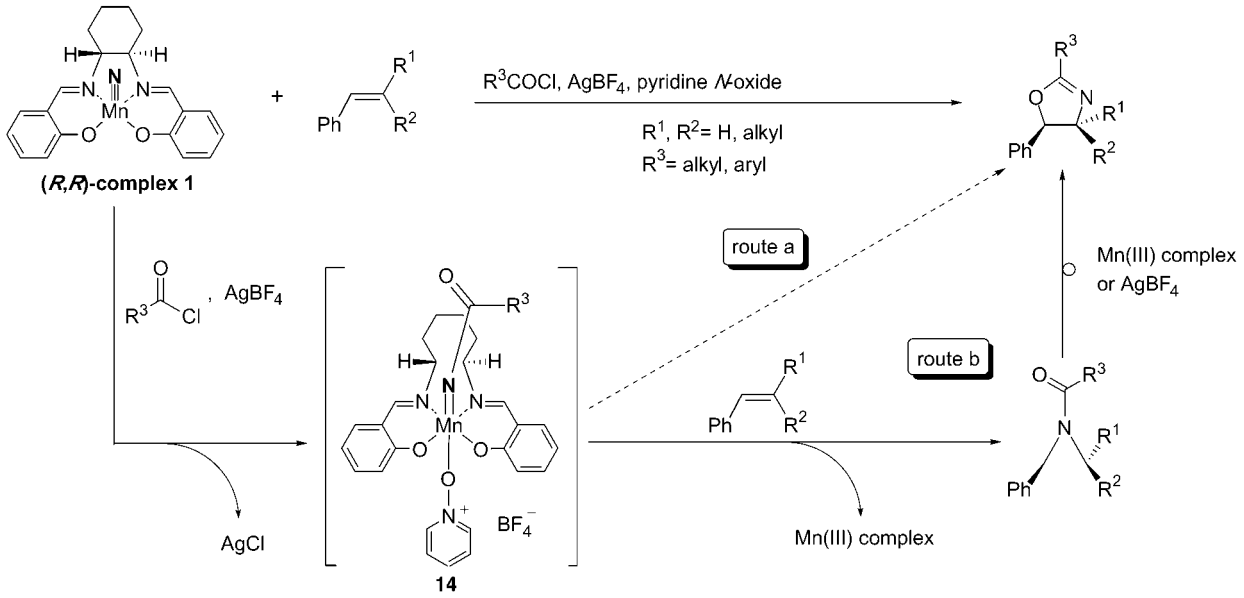
To study the stereospecificity of this reaction, *cis*-*β*-methylstyrene was employed in the synthesis of oxazoline using benzoyl chloride. When *cis*-*β*-methylstyrene was treated with **1** at room temperature for 48 h, *cis*-(4*S*,5*R*)-oxazoline **8** was obtained along with a larger amount of *trans*-(4*S*,5*S*)-oxazoline **9** (eq 1). Thus, stereospecificity was not observed in the synthesis of oxazolines from *trans*- and *cis*-*β*-methylstyrene in contrast to the aziridination of these compounds using Ts_2O.[9a] On the other hand, *cis*-(2*S*,3*R*)-aziridine **10** was formed as a major product along with oxazolines **8** and **9** at 0 °C. These results are consistent with the present reactions proceeding via aziridine intermediates. To determine whether such intermediates are in fact involved, the reaction of *cis*-*β*-methylstyrene with racemic complex **1** was carried out at 0 °C in the presence of *cis*-aziridine **11**[20] labeled with an *m*-toluoyl group on the nitrogen (eq 2). As a consequence, the yield of the produced aziridine **10** was increased and those of oxazolines **8** and **9** were decreased compared to the reaction in the absence of aziridine **11**. In addition, a portion of the labeled aziridine **11** was clearly converted to the *cis*- and *trans*-oxazolines **12** and **13**, respectively. These experiments indicate that an aziridine intermediate is involved in the reaction under the conditions employed herein.



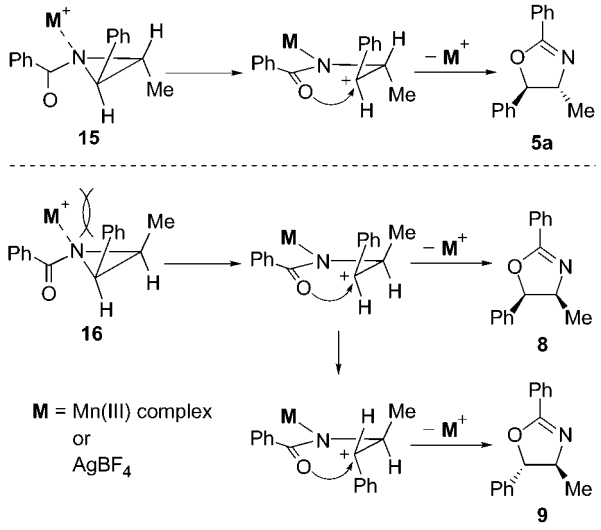
Given these results, a proposal for the most likely pathway for the present reaction using acyl chlorides is shown in Scheme 1. Initially, acyl chlorides, activated by $AgBF_4$, react with complex **1** to generate the imido complex **14**, the formation of which was proposed by Groves on the basis of spectral analysis.[8a] The different efficiencies of metal salts shown in Table 4 can be explained as follows. It is clear that Ag^+ has a good ability to activate acyl chlorides compared to Na^+, Li^+, and Mg^+. The counteranions of the metal salts result in those of the pyridinium ion of pyridine *N*-oxide acting as an axial ligand.[9a,21] The reason for the low yield in the case where $AgNO_3$ is used can be explained by assuming that the coordination of a nitrate anion might disturb that of pyridine *N*-oxide. In the next step, the N−COR units are transferred from intermediate **14** to olefins to afford *N*-acylaziridines and/or 2-oxazolines. The fact that an electron-deficient acyl chloride accelerated the reaction (Table 5) is consistent with the proposed mechanism. Namely, the acyl chloride reacts with complex **1** more smoothly, and in addition, complex **14**, activated by the acyl chloride, which is a type of metal nitrenoid, is more reactive toward olefins. Two routes are conceivable for the formation of oxazolines from olefins and **14**. One is a

(20) Werry, J.; Stamm, H.; Lin, P.-Y.; Falkenstein, R.; Gries, S.; Irngartinger, H. *Tetrahedron* **1989**, *45*, 5015−5028.
(21) Irie, R.; Ito, Y.; Katsuki, T. *Synlett* **1991**, 265−266.

Scheme 1

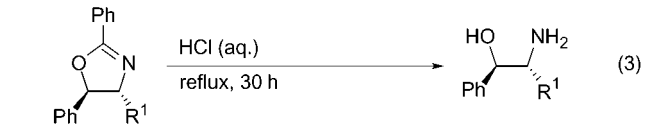


Scheme 2



direct [3 + 2]-type addition between the N−COR unit of complex **14** and an olefin (route a), and the other involves the isomerization of an aziridine intermediate (route b). Evidence for the existence of the aziridine intermediate can be obtained from eqs 1 and 2 as described above. Moreover, the ee values of the oxazolines produced from trans-substituted styrene derivatives were the same as those of aziridines from the reaction when Ts_2O was used as an activator. These results provide strong support for a scenario where the reactions of olefins with **14** proceed via aziridination and a subsequent Lewis acid-promoted isomerization by $AgBF_4$ or the Mn(III) complex generated from **1**. Although we speculate that the reactions of *cis*- and *trans*-*β*-methylstyrene occur via the same mechanism, the former gave oxazolines **8** and **9** and aziridine **10** and the latter gave oxazoline **5a** as the sole product. The difference can be explained as follows (Scheme 2). *trans*-*N*-Benzoylaziridine **15**, coordinated by the metal acting as a Lewis acid, isomerizes to the oxazoline more readily than *cis*-aziridine **16**, because of steric repulsion between the metal and the substituents on the *cis*-**16**. As a consequence, the reaction of *cis*-*β*-methylstyrene affords *cis*-aziridine **10** along with oxazolines. The formation of a mixture of *cis*- and *trans*-oxazolines from *cis*-*β*-methylstyrene can be accounted for by the generation of a benzylic cation and free rotation about the C−C bond to a more stable intermediate, in which a trans relationship exists between the Me and Ph groups. The difference in ee values between produced oxazolines **8** and **9** and aziridine **10** suggests that a chiral manganese complex might be involved in the isomerization as a Lewis acid. This isomerization mechanism through a benzylic cation intermediate supports the observed low enantioselectivities in the case of styrene and α-methylstyrene.

The produced oxazolines could be easily converted into *β*-amino alcohols (eq 3). Optically active *β*-amino alcohols are useful synthetic tools for the preparation of natural products and chiral ligands and have been found in wide variety of biologically important compounds.[12e,22] When oxazoline **5a** was treated with 1.2 N HCl at reflux for 30 h, norpseudoephedrine (**17**) was obtained in good yield with retention of the stereochemistry. The hydrolysis of oxazoline **7e** also took place under similar conditions to give the non-natural *β*-amino alcohol **18** in high yield.



(3)

5a: R^1 = Me (86% ee) **17**: 93% yield (86% ee)
7e: R^1 = *c*-Hex (92% ee) **18**: 88% yield (92% ee)

Conclusions

We have shown here that the chiral nitridomanganese complex is an effective reagent for asymmetric N1 unit transfer reaction to olefins to give chiral aziridines or 2-oxazolines. The asymmetric aziridination of olefins was achieved by using sulfonyl chlorides as activators of the complex in the presence of a silver salt. 2-Trimethylsilylethanesulfonyl chloride (SESCl) also served as an activator for the reaction to give the corresponding

(22) (a) Shioiri, T.; Hamada, Y. *Heterocycles* **1988**, *27*, 1035−1050. (b) Sasai, H.; Itoh, N.; Suzuki, T.; Shibasaki, M. *Tetrahedron Lett.* **1993**, *34*, 855−858 and references therein.

aziridines, which were readily converted to N-unsubstituted aziridines. On the other hand, chiral 2-oxazolines were directly produced from olefins when acyl chlorides were employed as activators of the complex. The reaction of trans-substituted styrene derivatives gave rise to *trans*-2-oxazolines stereoselectively in good yields with high enantioselectivities. These results represent the first example of a three-component coupling to chiral oxazolines. The reaction of *cis*-*β*-methylstyrene and related experiments suggest that the present reaction proceeds via aziridination and subsequent isomerization by Lewis acids.

Experimental Section

General Methods. Melting points were determined on a Yanaco melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 68 MHz, respectively. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Products were purified by chromatography on silica gel FL60D (Fuji Silysia Chemical Co.) or silica gel 60N (spherical, neutral) (Kanto Chemical Co.) and, if necessary, further purified by Recycling Preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) equipped with a GPC column (JAIGEL-1H, 2H) using chloroform as an eluent. Analytical thin-layer chromatography was performed on precoated silica gel glass plates (silica gel 60 F_{254}, 0.25 mm thickness) (Merck Co.). Visualization was accomplished with UV light or treatment with an ethanolic solution of phosphomolybdic acid followed by heating. All reactions were carried out under an atmosphere of nitrogen, unless otherwise noted. Organic solvents were dried and distilled prior to use.

General Procedure for Asymmetric Aziridination of Olefins. Pyridine (0.15 mmol), olefin (3.0 mmol), and sulfonyl chloride (0.36 mmol) were added to a mixture of **1** (0.3 mmol), silver salt (0.36 mmol), and pyridine *N*-oxide (0.36 mmol) in CH_2Cl_2 (3 mL) at the indicated temperature. After the mixture was stirred for the indicated time, pentane (20 mL) was added. The mixture was then passed through a 3-cm pad of silica gel using diethyl ether (125 mL) as the eluent. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc). Enantiomeric excesses of the aziridines were determined by chiral HPLC analysis.

(*R*)-*N*-(*p*-Toluenesulfonyl)-2-phenylaziridine (2a):[15c] white solid; TLC R_f 0.40 (hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.38 (d, 1H, J = 4.5 Hz), 2.43 (s, 3H), 2.98 (d, 1H, J = 7.3 Hz), 3.77 (dd, 1H, J = 4.5, 7.3 Hz), 7.19−7.35 (m, 7H), 7.87 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.7, 36.0, 41.1, 126.5, 127.8, 128.2, 128.4, 129.6, 134.9, 134.9, 144.5; $[\alpha]^{31}_D$ −41.9 (*c* 1.10, $CHCl_3$) (40% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 7:3, 0.7 mL/min, 254 nm, 30 °C) t = 16.0 (*S*) and 19.1 min (*R*).

(*R*)-*N*-(*p*-Nitrobenzenesulfonyl)-2-phenylaziridine (2b):[23] white solid; TLC R_f 0.40 (hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.51 (d, 1H, J = 4.6 Hz), 3.12 (d, 1H, J = 7.3 Hz), 3.90 (dd, 1H, J = 4.6, 7.3 Hz), 7.18−7.24 (m, 2H), 7.28−7.35 (m, 3H), 8.19 (d, 2H, J = 9.1 Hz), 8.38 (d, 1H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 36.6, 41.9, 124.2, 126.3, 128.6, 129.1, 129.1, 134.0, 143.8, 150.5; $[\alpha]^{29}_D$ −31.4 (*c* 0.784, $CHCl_3$) (43% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 1:1, 0.7 mL/min, 254 nm, 30 °C) t = 36.7 (*S*) and 52.5 min (*R*).

(*R*)-*N*-(Methanesulfonyl)-2-phenylaziridine (2c):[6b] colorless oil; TLC R_f 0.28 (hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.44 (d, 1H, J = 4.3 Hz), 2.98 (d, 1H, J = 7.3 Hz), 3.11 (s, 1H), 3.72 (dd, 1H, J = 4.3, 7.3 Hz), 7.26−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 35.5, 39.8, 40.8, 126.4, 128.5, 128.6, 134.7; $[\alpha]^{28}_D$ −88.8 (*c* 1.08, $CHCl_3$) (42% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 1:1, 0.5 mL/min, 254 nm, 30 °C) t = 19.2 (*S*) and 25.4 min (*R*).

(*R*)-*N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-phenylaziridine (3a):[16b] colorless oil; TLC R_f 0.51 (hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.03 (s, 9H), 1.09−1.16 (m, 2H), 2.42 (d, 1H, J = 4.3 Hz), 2.97 (d, 1H, J = 7.3 Hz), 3.08−3.16 (m, 2H), 3.70 (dd, 1H, J = 4.3, 7.3 Hz), 7.27−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ −2.0, 9.8, 35.2, 40.5, 49.1, 126.4, 128.3, 128.6, 135.0; $[\alpha]^{30}_D$ −59.8 (*c* 0.704, $CHCl_3$) (40% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 97:3, 1.0 mL/min, 254 nm, 30 °C) t = 13.8 (*S*) and 17.7 min (*R*).

(2*R*,3*R*)-*N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-methyl-3-phenylaziridine (3b): colorless oil; TLC R_f 0.49 (hexane/EtOAc, 2:1); IR (neat) 2953, 1323, 1252, 1171, 1146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ −0.05 (s, 9H), 0.91−1.17 (m, 2H), 1.80 (d, 3H, J = 6.1 Hz), 2.89 (dt, 1H, J = 4.3, 6.1 Hz), 2.97−3.12 (m, 2H), 3.64 (d, 1H, J = 4.3 Hz), 7.23−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ −2.0, 10.0, 14.5, 48.5, 49.3, 51.5, 126.1, 128.2, 128.5, 135.7; MS (CI, methane) *m*/*z* (relative intensity, %) 298 (M^+ + H, 100); $[\alpha]^{21}_D$ −101.7 (*c* 1.18, $CHCl_3$) (83% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 98:2, 0.5 mL/min, 254 nm, 25 °C) t = 16.5 (2*R*,3*R*) and 20.4 min (2*S*,3*S*); HRMS (CI, methane) calcd for $C_{14}H_{24}NO_2SSi$ (M + H)$^+$ 298.1296, found 298.1291. Anal. Calcd for $C_{14}H_{23}NO_2SSi$: C, 56.52; H, 7.79; N, 4.71. Found: C, 56.48; H, 7.84; N, 4.70.

(2*R*,3*R*)-*N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-phenyl-3-propylaziridine (3c): colorless oil; TLC R_f 0.55 (hexane/EtOAc, 2:1); IR (neat) 2956, 1325, 1252, 1171, 1146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ −0.05 (s, 9H), 0.89−1.19 (m, 2H), 0.99 (t, 3H, J = 7.4 Hz), 1.42−1.74 (m, 2H), 1.83−1.99 (m, 1H), 2.23−2.38 (m, 1H), 2.77 (dt, 1H, J = 4.5, 9.0 Hz), 2.98−3.12 (m, 2H), 3.64 (d, 1H, J = 4.5 Hz), 7.24−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ −2.0, 10.1, 13.8, 21.3, 30.8, 49.0, 51.4, 52.9, 126.1, 128.1, 128.6, 135.8; MS (CI, methane) *m*/*z* (relative intensity, %) 326 (M^+ + H, 100); $[\alpha]^{22}_D$ −101.1 (*c* 1.47, $CHCl_3$) (85% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 99:1, 0.5 mL/min, 254 nm, 25 °C) t = 19.0 (2*S*,3*S*) and 21.6 min (2*R*,3*R*); HRMS (CI, methane) calcd for $C_{16}H_{28}NO_2SSi$ (M + H)$^+$ 326.1608, found 326.1621. Anal. Calcd for $C_{16}H_{27}NO_2SSi$: C, 59.03; H, 8.36; N, 4.30. Found: C, 59.09; H, 8.34; N, 4.41.

(2*R*,3*R*)-*N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-isopropyl-3-phenylaziridine (3d): white solid; mp 50−52 °C; TLC R_f 0.55 (hexane/EtOAc, 2:1); IR (KBr) 2968, 1313, 1250, 1178, 1146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ −0.06 (s, 9H), 0.93−1.16 (m, 2H), 1.09 (d, 3H, J = 6.7 Hz), 1.30 (d, 3H, J = 6.7 Hz), 2.17−2.35 (m, 1H), 2.65 (dd, 1H, J = 4.5, 9.6 Hz), 2.95−3.05 (m, 2H), 3.64 (d, 1H, J = 4.5 Hz), 7.25−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ −2.0, 10.1, 21.3, 21.7, 29.1, 48.2, 51.2, 59.5, 126.4, 128.2, 128.6, 135.5; MS (CI, methane) *m*/*z* (relative intensity, %) 326 (M^+ + H, 100); $[\alpha]^{20}_D$ −92.9 (*c* 1.02, $CHCl_3$) (90% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 97:3, 0.5 mL/min, 254 nm, 25 °C) t = 13.2 (2*S*,3*S*) and 17.5 min (2*R*,3*R*); HRMS (CI, methane) calcd for $C_{16}H_{28}NO_2SSi$ (M + H)$^+$ 326.1608, found 326.1632.

(2*R*,3*R*)-*N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-cyclohexyl-3-phenylaziridine (3e): white solid; mp 104−106 °C; TLC R_f 0.65 (hexane/EtOAc, 2:1); IR (KBr) 2953, 2925, 2851, 1318, 1247, 1165, 1143 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ −0.06 (s, 9H), 0.92−1.45 (m, 7H), 1.62−2.04 (m, 5H), 2.31−2.44 (m, 1H), 2.67 (dd, 1H, J = 4.3, 9.4 Hz), 2.93−3.08 (m, 2H), 3.64 (d, 1H, J = 4.3 Hz), 7.23−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ −2.0, 10.1, 25.4, 25.7, 26.1, 31.6, 32.2, 37.9, 47.9, 51.2, 58.2, 126.3, 128.1, 128.5, 135.6; MS (CI, methane) *m*/*z* (relative intensity, %) 366 (M^+ + H, 64); $[\alpha]^{29}_D$ −57.0 (*c* 1.34, $CHCl_3$) (93% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 97:3, 1.0 mL/min, 254 nm, 30 °C) t = 7.8 (2*S*,3*S*) and 10.8 min (2*R*,3*R*); HRMS (CI, methane) calcd for $C_{19}H_{32}NO_2SSi$ (M + H)$^+$ 366.1921, found 366.1909. Anal. Calcd for $C_{19}H_{31}NO_2SSi$: C, 62.42; H, 8.55; N, 3.83. Found: C, 62.35; H, 8.56; N, 3.85.

(2*S*,3*R*)-*N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-methyl-3-phenylaziridine (3f): colorless oil; TLC R_f 0.51 (hexane/EtOAc, 2:1); IR (neat) 2954, 1325, 1252, 1171, 1144 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.05 (s, 9H), 1.10 (d, 3H, J = 5.9 Hz), 1.12−1.22 (m, 2H), 3.08−3.22 (m, 3H), 3.90 (d, 1H, J = 7.3 Hz), 7.27−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ −1.9, 9.9, 12.0, 41.0, 45.7, 49.1, 127.5, 127.9, 128.3, 132.7; MS (CI,

isobutane) *m*/*z* (relative intensity, %) 298 ($M^+ + H$, 3); $[\alpha]^{28}_D$ −31.2 (*c* 1.07, $CHCl_3$) (24% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 97:3, 0.5 mL/min, 254 nm, 30 °C) t = 13.8 (2*R*,3*S*) and 18.7 min (2*S*,3*R*); HRMS (CI, methane) calcd for $C_{14}H_{24}NO_2SSi$ $(M + H)^+$ 298.1296, found 298.1288. Anal. Calcd for $C_{14}H_{23}NO_2SSi$: C, 56.52; H, 7.79; N, 4.71. Found: C, 56.80; H, 7.98; N, 4.64.

(*R*)-2-Phenylaziridine (4a).[16b] A solution of aziridine **3a** (41.2 mg, 0.15 mmol, 40% ee) and TASF (162.5 mg, 0.59 mmol) in DMF (1 mL) was stirred at room temperature for 48 h. The mixture was purified by flash column chromatography on silica gel (hexane/Et_2O, 1:1) and Kugelrohr distillation (70 °C, 5 mmHg) to afford a colorless oil of **4a** (11.2 mg, 65% yield, 40% ee). The enantiomeric excess was determined by HPLC analysis of the *N*-tosyl derivative. **4a**: colorless oil; TLC R_f 0.26 (hexane/EtOAc, 1:2); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.22 (br s, 1H), 1.81 (d, 1H, J = 3.3 Hz), 2.22 (d, 1H, J = 5.9 Hz), 3.02 (dd, 1H, J = 3.3, 5.9 Hz), 7.21−7.38 (m, 5H); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 7:3, 0.5 mL/min, 254 nm, 30 °C) t = 16.0 (*S*) and 19.1 min (*R*).

(2*R*,3*R*)-2-Methyl-3-phenylaziridine (4b).[24] A solution of aziridine **3b** (64.6 mg, 0.22 mmol, 83% ee) and TASF (242.2 mg, 0.88 mmol) in DMF (1 mL) was stirred at room temperature for 48 h. The mixture was purified by flash column chromatography on silica gel (hexane/Et_2O, 1:1) and Kugelrohr distillation (70 °C, 5 mmHg) to afford a colorless oil of **4b** (22.8 mg, 79% yield, 83% ee). **4b**: colorless oil; TLC R_f 0.08 (hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.22 (br s, 1H), 1.37 (d, 3H, J = 5.4 Hz), 2.07−2.22 (m, 1H), 2.66 (d, 1H, J = 2.8 Hz), 7.15−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 19.7, 37.1, 40.5, 125.4, 126.8, 128.3, 140.3; $[\alpha]^{22}_D$ +50.8 (*c* 0.378, $CHCl_3$) (83% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 25 °C) t = 12.4 (2*S*,3*S*) and 15.2 min (2*R*,3*R*).

(2*R*,3*R*)-2-Phenyl-3-propylaziridine (4c). A solution of aziridine **3c** (81.8 mg, 0.25 mmol, 85% ee) and TASF (277.5 mg, 1.01 mmol) in DMF (1 mL) was stirred at room temperature for 48 h. The mixture was purified by flash column chromatography on silica gel (hexane/Et_2O, 7:3) and Kugelrohr distillation (120 °C, 2 mmHg) to afford a colorless oil of **4c** (32.3 mg, 80% yield, 85% ee). **4c**: colorless oil; TLC R_f 0.22 (hexane/EtOAc, 2:1); IR (neat) 3242, 2958, 2927, 2872, 1606, 1497, 1458 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.93−1.04 (m, 4H), 1.45−1.65 (m, 4H), 2.00−2.13 (m, 1H), 2.69 (d, 1H, J = 2.8 Hz), 7.15−7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 14.1, 20.9, 36.8, 39.6, 42.0, 125.4, 126.8, 128.3, 140.4; MS (EI) *m*/*z* (relative intensity, %) 161 (M^+, 13); $[\alpha]^{22}_D$ +47.1 (*c* 0.512, $CHCl_3$) (85% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm, 25 °C) t = 14.5 (2*S*,3*S*) and 19.2 min (2*R*,3*R*); HRMS (EI) calcd for $C_{11}H_{15}N$ $(M)^+$ 161.1204, found 161.1206.

(2*R*,3*R*)-2-Isopropyl-3-phenylaziridine (4d). A solution of aziridine **3d** (74.7 mg, 0.23 mmol, 90% ee) and TASF (255.3 mg, 0.92 mmol) in DMF (1 mL) was stirred at room temperature for 48 h. The mixture was purified by flash column chromatography on silica gel (hexane/Et_2O, 7:3) and Kugelrohr distillation (120 °C, 2 mmHg) to afford a colorless oil of **4d** (29.9 mg, 81% yield, 90% ee). **4d**: colorless oil; TLC R_f 0.25 (hexane/EtOAc, 2:1); IR (neat) 3238, 2958, 2868, 1603, 1497, 1458 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.00−1.48 (m, 8H), 1.90 (dd, 1H, J = 2.8, 7.6 Hz), 2.73 (d, 1H, J = 2.8 Hz), 7.15−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 20.2, 20.4, 33.5, 38.8, 48.6, 125.4, 126.8, 128.3, 140.5; MS (EI) *m*/*z* (relative intensity, %) 161 (M^+, 25); $[\alpha]^{22}_D$ +29.5 (*c* 0.464, $CHCl_3$) (90% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm, 25 °C) t = 13.8 (2*S*,3*S*) and 17.6 min (2*R*,3*R*); HRMS (EI) calcd for $C_{11}H_{15}N$ $(M)^+$ 161.1204, found 161.1198.

(2*R*,3*R*)-2-Cyclohexyl-3-phenylaziridine (4e). A solution of aziridine **3e** (63.7 mg, 0.17 mmol, 93% ee) and TASF (198.3 mg, 0.72 mmol) in DMF (1 mL) was stirred at room temperature for 48 h. The mixture was purified by flash column chromatography on silica gel (hexane/EtOAc, 8:2) to afford a white solid of **4e** (29.8 mg, 85% yield, 93% ee). **4e**: white solid; mp 35−37 °C; TLC R_f 0.30 (hexane/EtOAc, 2:1); IR (KBr) 3284, 2924, 2848, 1605, 1495, 1448 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.94−1.40 (m, 7H), 1.58−2.01 (m, 6H), 2.74 (d, 1H, J = 3.0 Hz), 7.13−7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 25.8, 25.9, 26.3, 30.8, 31.0, 38.4, 43.0, 47.3, 125.5, 126.8, 128.4, 140.8; MS (EI) *m*/*z* (relative intensity, %) 201 (M^+, 100); $[\alpha]^{31}_D$ +53.3 (*c* 0.666, $CHCl_3$) (93% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 °C) t = 10.4 (2*S*,3*S*) and 14.6 min (2*R*,3*R*); HRMS (EI) calcd for $C_{14}H_{19}N$ $(M)^+$ 201.1517, found 201.1525. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.40; H, 9.67; N, 6.88.

(2*S*,3*R*)-2-Methyl-3-phenylaziridine (4f).[25] A solution of aziridine **3f** (55.1 mg, 0.19 mmol, 24% ee) and TASF (201.2 mg, 0.73 mmol) in DMF (1 mL) was stirred at room temperature for 48 h. The mixture was purified by flash column chromatography on silica gel (hexane/EtOAc, 7:3) and Kugelrohr distillation (70 °C, 5 mmHg) to afford a white solid of **4f** (17.8 mg, 72% yield, 24% ee). The enantiomeric excess was determined by HPLC analysis of the *N*-benzoyl derivative. **4f**: white solid; TLC R_f 0.20 (hexane/EtOAc, 2:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.92 (d, 3H, J = 5.6 Hz), 1.36 (br s, 1H), 2.42 (dq, 1H, J = 5.6, 6.6 Hz), 3.25 (d, 1H, J = 6.6 Hz), 7.18−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 13.7, 32.3, 37.2, 126.5, 127.7, 127.8, 137.5; $[\alpha]^{30}_D$ −14.7 (*c* 0.334, $CHCl_3$) (24% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 97:3, 0.5 mL/min, 254 nm, 30 °C) t = 15.2 (2*R*,3*S*) and 18.9 min (2*S*,3*R*).

General Procedure for Asymmetric Synthesis of 2-Oxazolines from Olefins. Pyridine (0.15 mmol), olefin (3.0 mmol), and acyl chloride (0.36 mmol) were added to a mixture of **1** (0.3 mmol), silver salt (0.36 mmol), and pyridine *N*-oxide (0.36 mmol) in CH_2Cl_2 (3 mL) at the indicated temperature. After the mixture was stirred for the indicated time, pentane (20 mL) was added. The mixture was then passed through a 3-cm pad of silica gel using diethyl ether (125 mL) as the eluent. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc). Enantiomeric excesses of the oxazolines were determined by chiral HPLC analysis.

(4*R*,5*R*)-4-Methyl-2,5-diphenyl-2-oxazoline (5a):[26] colorless oil; TLC R_f 0.40 (hexane/EtOAc, 2:1); IR (neat) 2966, 2926, 1650, 1497, 1450, 1331, 1059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.49 (d, 3H, J = 6.6 Hz), 4.21 (dq, 1H, J = 6.6, 7.7 Hz), 5.10 (d, 1H, J = 7.7 Hz), 7.30−7.54 (m, 8H), 8.00−8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.5, 70.9, 88.1, 125.5, 127.6, 128.2, 128.2, 128.2, 128.7, 131.3, 140.3, 162.6; MS (EI) *m*/*z* (relative intensity, %) 237 (M^+, 6); $[\alpha]^{25}_D$ −60.4 (*c* 1.07, MeOH) (86% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm, 30 °C) t = 9.7 (4*S*,5*S*) and 17.4 min (4*R*,5*R*); HRMS (EI) calcd for $C_{16}H_{15}NO$ $(M)^+$ 237.1154, found 237.1138.

(4*R*,5*R*)-2-[(*p*-Trifluoromethyl)phenyl]-4-methyl-5-phenyl-2-oxazoline (5b): colorless oil; TLC R_f 0.45 (hexane/EtOAc, 2:1); IR (neat) 2968, 2929, 1653, 1414, 1324, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.51 (d, 3H, J = 6.6 Hz), 4.25 (dq, 1H, J = 6.6, 7.7 Hz), 5.14 (d, 1H, J = 7.7 Hz), 7.31−7.44 (m, 5H), 7.70 (d, 2H, J = 8.2 Hz), 8.14 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.4, 71.1, 88.5, 123.7 (q, J_{C-F} = 272 Hz), 125.3, 125.5, 128.4, 128.6, 128.8, 131.0, 132.9 (q, J_{C-F} = 33 Hz), 139.9, 161.4; MS (EI) *m*/*z* (relative intensity, %) 305 (M^+, 0.8); $[\alpha]^{24}_D$ −47.3 (*c* 2.58, $CHCl_3$) (86% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 170:1, 0.5 mL/min, 254 nm, 30 °C) t = 14.8 (4*R*,5*R*) and 20.8 min (4*S*,5*S*); HRMS (EI) calcd for $C_{17}H_{14}F_3NO$ $(M)^+$ 305.1027, found 305.1036. Anal. Calcd for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62; N, 4.59. Found: C, 66.66; H, 4.78; N, 4.58.

(4*R*,5*R*)-2-(*p*-Methoxyphenyl)-4-methyl-5-phenyl-2-oxazoline (5c): colorless oil; TLC R_f 0.25 (hexane/EtOAc, 2:1); IR (neat) 2962, 2927, 1649, 1608, 1512, 1257, 1171 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.48 (d, 3H, J = 6.6 Hz), 3.85 (s, 3H), 4.18 (dq, 1H, J = 6.6, 7.7 Hz), 5.07 (d, 1H, J = 7.7 Hz), 6.93 (d, 2H, J = 8.9 Hz), 7.29−7.42 (m, 5H), 7.97 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.5, 55.4, 70.9, 88.1, 113.6, 120.1, 125.5, 128.1, 128.6, 130.0, 140.5, 162.0, 162.4; MS (EI) *m*/*z* (relative intensity, %) 267 (M^+, 23); $[\alpha]^{24}_D$ −81.6 (*c* 1.04, $CHCl_3$) (86% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 °C) t = 11.2 (4*R*,5*R*)

and 18.5 min (4*S*,5*S*); HRMS (EI) calcd for $C_{17}H_{17}NO_2$ $(M)^+$ 267.1258, found 267.1257.

(4*R*,5*R*)-2-*tert*-Butyl-4-methyl-5-phenyl-2-oxazoline (5d): colorless oil; TLC R_f 0.37 (hexane/EtOAc, 2:1); IR (neat) 2974, 2927, 2872, 1660, 1456, 1363, 1300, 1250, 1140 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.30 (s, 9H), 1.37 (d, 3H, J = 6.6 Hz), 3.96 (dq, 1H, J = 6.6, 7.3 Hz), 4.87 (d, 1H, J = 7.3 Hz), 7.24−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.7, 27.9, 33.3, 70.6, 87.7, 125.2, 127.9, 128.6, 141.0, 172.3; MS (EI) *m*/*z* (relative intensity, %) 217 (M^+, 1); $[\alpha]^{24}_D$ +13.7 (*c* 0.346, $CHCl_3$) (85% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 170:1, 0.5 mL/min, 254 nm, 30 °C) t = 12.1 (4*S*,5*S*) and 16.6 min (4*R*,5*R*); HRMS (EI) calcd for $C_{14}H_{19}NO$ $(M)^+$ 217.1466, found 217.1453.

(4*R*,5*R*)-4-Methyl-2-isopropyl-5-phenyl-2-oxazoline (5e): colorless oil; TLC R_f 0.25 (hexane/EtOAc, 2:1); IR (neat) 2972, 2926, 1668, 1456, 1200, 1147 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.28 (d, 6H, J = 6.9 Hz), 1.37 (d, 3H, J = 6.6 Hz), 2.67 (qq, 1H, J = 6.9, 6.9 Hz), 3.97 (dq, 1H, J = 6.6, 7.6 Hz), 4.88 (d, 1H, J = 7.6 Hz), 7.25−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 19.8, 21.6, 28.4, 70.3, 87.7, 125.3, 128.0, 128.6, 140.8, 170.7; MS (EI) *m*/*z* (relative intensity, %) 203 (M^+, 1); $[\alpha]^{26}_D$ +24.9 (*c* 0.716, $CHCl_3$) (87% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 200:1, 0.5 mL/min, 254 nm, 30 °C) t = 11.8 (4*S*,5*S*) and 14.1 min (4*R*,5*R*); HRMS (EI) calcd for $C_{13}H_{17}NO$ $(M)^+$ 203.1309, found 203.1322.

(1*R*,2*R*)-2-Isobutyrylamino-1-isobutyryloxy-1-phenylpropane (6): white solid; mp 75−77 °C; TLC R_f 0.25 (hexane/EtOAc, 2:1); IR (KBr) 3323, 2970, 2933, 1732, 1647, 1539, 1269, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.01−1.22 (m, 15H), 2.28 (qq, 1H, J = 6.9, 6.9 Hz), 2.61 (qq, 1H, J = 6.9, 6.9 Hz), 4.40−4.55 (m, 1H), 5.54 (br s, 1H), 5.73 (d, 1H, J = 7.3 Hz), 7.27−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) 17.9, 19.0, 19.1, 19.5, 19.6, 34.2, 35.8, 48.8, 126.8, 128.2, 128.4, 137.3, 175.9, 176.3; MS (EI) *m*/*z* (relative intensity, %) 291 (M^+, 1); $[\alpha]^{22}_D$ −31.8 (*c* 0.630, $CHCl_3$) (86% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 98:2, 0.5 mL/min, 254 nm, 30 °C) t = 14.8 (1*S*,2*S*) and 19.4 min (1*R*,2*R*); HRMS (EI) calcd for $C_{17}H_{25}NO_3$ $(M)^+$ 291.1833, found 291.1835. Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.92; H, 8.50; N, 4.67.

(*R*)-2,5-Diphenyl-2-oxazoline (7a):[27] colorless oil; TLC R_f 0.32 (hexane/EtOAc, 2:1); ^1H NMR ($CDCl_3$, 270 MHz) δ 4.00 (dd, 1H, J = 7.9, 14.8 Hz), 4.49 (dd, 1H, J = 10.2, 14.8 Hz), 5.67 (dd, 1H, J = 7.9, 10.2 Hz), 7.32−7.51 (m, 8H), 8.00−8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 63.1, 81.0, 125.6, 127.5, 128.2, 128.2, 128.3, 128.7, 131.3, 140.9, 163.8; $[\alpha]^{26}_D$ −27.3 (*c* 1.08, $CHCl_3$) (16% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 °C) t = 11.8 (*S*) and 35.5 min (*R*).

5-Methyl-2,5-phenyl-2-oxazoline (7b):[28] colorless oil; TLC R_f 0.25 (hexane/EtOAc, 2:1); IR (neat) 2929, 2868, 1649, 1497, 1448, 1348, 1267, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.80 (s, 3H), 4.15 (s, 2H), 7.25−7.54 (m, 8H), 8.02−8.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 28.3, 69.0, 86.7, 124.2, 127.3, 128.0, 128.1, 128.3, 128.5, 131.3, 145.4, 162.9; MS (EI) *m*/*z* (relative intensity, %) 237 (M^+, 16); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 °C) t = 9.2 and 13.7 min; HRMS (EI) calcd for $C_{16}H_{15}NO_3$ $(M)^+$ 237.1154, found 237.1152.

(4*R*,5*R*)-2,5-Diphenyl-4-propyl-2-oxazoline (7c): colorless oil; TLC R_f 0.55 (hexane/EtOAc, 2:1); IR (neat) 2958, 2929, 2872, 1651, 1450, 1330, 1062 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.97 (t, 3H, J = 7.3 Hz), 1.45−1.90 (m, 4H), 4.16 (dt, 1H, J = 6.7, 7.2 Hz), 5.18 (d, 1H, J = 7.2 Hz), 7.28−7.53 (m, 8H), 8.00−8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 14.2, 19.2, 38.4, 75.4, 86.3, 125.6, 127.7, 128.1, 128.2, 128.2, 128.7, 131.2, 141.0, 162.4; MS (EI) *m*/*z* (relative intensity, %) 265 (M^+, 13); $[\alpha]^{28}_D$ −36.2 (*c* 0.418, $CHCl_3$) (88% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 99:1, 0.5 mL/min, 254 nm, 30 °C) t = 10.7 (4*S*,5*S*) and 16.0 min (4*R*,5*R*); HRMS (EI) calcd for $C_{18}H_{19}NO$ $(M)^+$ 265.1466, found 265.1458.

(4*R*,5*R*)-4-Isopropyl-2,5-diphenyl-2-oxazoline (7d): white solid; mp 51−53 °C; TLC R_f 0.53 (hexane/EtOAc, 2:1); IR (KBr) 2958, 2931, 2872, 1653, 1450, 1333, 1063 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.01 (d, 3H, J = 6.6 Hz), 1.07 (d, 3H, J = 6.9 Hz), 1.90−2.12 (m, 1H), 4.04 (dd, 1H, J = 6.3, 6.3 Hz), 5.28 (d, 1H, J = 6.3 Hz), 7.27−7.54 (m, 8H), 8.00−8.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 18.2, 18.6, 32.9, 81.0, 83.2, 125.5, 127.6, 127.9, 128.1, 128.2, 128.6, 131.1, 141.6, 162.2; MS (EI) *m*/*z* (relative intensity, %) 265 (M^+, 2); $[\alpha]^{26}_D$ −46.3 (*c* 0.816, $CHCl_3$) (90% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 99:1, 0.5 mL/min, 254 nm, 30 °C) t = 19.8 (4*S*,5*S*) and 24.9 min (4*R*,5*R*); HRMS (EI) calcd for $C_{18}H_{19}NO$ $(M)^+$ 265.1467, found 265.1490. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.28; H, 7.02; N, 5.16.

(4*R*,5*R*)-4-Cyclohexyl-2,5-diphenyl-2-oxazoline (7e): white solid; mp 90−92 °C; TLC R_f 0.41 (hexane/EtOAc, 9:1); IR (KBr) 2926, 2852, 1647, 1452, 1383, 1333, 1174, 1068 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.05−1.40 (m, 5H), 1.60−1.88 (m, 5H), 1.88−2.00 (m, 1H), 4.03 (dd, 1H, J = 6.1, 6.6 Hz), 5.33 (d, 1H, J = 6.6 Hz), 7.26−7.53 (m, 8H), 8.01−8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 26.2, 26.2, 26.6, 29.0, 29.4, 43.0, 80.5, 83.4, 125.7, 127.7, 128.0, 128.2, 128.3, 128.6, 131.2, 141.7, 162.2; MS (EI) *m*/*z* (relative intensity, %) 305 (M^+, 24); $[\alpha]^{26}_D$ −18.6 (*c* 0.878, $CHCl_3$) (92% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 150:1, 0.5 mL/min, 254 nm, 30 °C) t = 22.8 (4*S*,5*S*) and 31.7 min (4*R*,5*R*); HRMS (EI) calcd for $C_{21}H_{23}NO$ $(M)^+$ 305.1778, found 305.1790. Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.41; H, 7.66; N, 4.45.

***cis*-2-Phenyl-3a,4,5,9b-tetrahydronaphtho[2,1-*d*]oxazole (7f):** colorless oil; TLC R_f 0.32 (hexane/EtOAc, 2:1); IR (neat) 2929, 2850, 1647, 1495, 1450, 1344, 1084, 1065 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.87−2.18 (m, 2H), 2.53−2.64 (m, 1H), 2.72−2.87 (m, 1H), 4.74 (dt, 1H, J = 4.9, 9.6 Hz), 5.68 (d, 1H, J = 9.6 Hz), 7.05−7.55 (m, 7H), 7.91−7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 25.8, 28.7, 64.8, 78.9, 126.5, 127.6, 128.1, 128.2, 128.3, 128.4, 130.4, 131.2, 132.6, 139.7, 164.0; MS (EI) *m*/*z* (relative intensity, %) 249 (M^+, 2); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 °C) t = 10.2 and 20.6 min; HRMS (EI) calcd for $C_{17}H_{15}NO$ $(M)^+$ 249.1153, found 249.1138.

2,7a-Diphenyl-3a,4,5,6,7,7a-hexahydrobenzoxazole (7g): white solid; mp 80−82 °C; TLC R_f 0.40 (hexane/EtOAc, 2:1); IR (KBr) 2927, 2850, 1633, 1448, 1344, 1064 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.52−1.73 (m, 4H), 1.98−2.10 (m, 4H), 4.38 (t, 1H, J = 4.6 Hz), 7.24−7.52 (m, 8H), 8.03−8.08 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 17.4, 18.3, 26.7, 33.5, 70.7, 87.7, 124.3, 127.2, 128.1, 128.2, 128.2, 128.3, 131.2, 145.7, 162.7; MS (EI) *m*/*z* (relative intensity, %) 277 (M^+, 96); $[\alpha]^{29}_D$ −39.4 (*c* 0.898, $CHCl_3$) (32% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm, 30 °C) t = 22.7 and 31.4 min; HRMS (EI) calcd for $C_{19}H_{19}NO$ $(M)^+$ 277.1466, found 277.1467. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.02; H, 6.95; N, 4.84.

(4*S*,5*R*)-4-Methyl-2,5-diphenyl-2-oxazoline (8):[29] colorless oil; TLC R_f 0.34 (hexane/EtOAc, 2:1); IR (neat) 2976, 2929, 1651, 1495, 1450, 1342, 1099, 1066 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.89 (d, 3H, J = 6.9 Hz), 4.67 (dq, 1H, J = 6.9, 9.9 Hz), 5.77 (d, 1H, J = 9.9 Hz), 7.25−7.56 (m, 8H), 8.03−8.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 17.8, 65.4, 83.9, 125.9, 127.5, 127.6, 128.1, 128.1, 128.2, 131.2, 136.9, 162.8; $[\alpha]^{24}_D$ −81.1 (*c* 0.724, $CHCl_3$) (23% ee); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 °C) t = 10.2 and 24.3 min.

(2*S*,3*R*)-*N*-Benzoyl-2-methyl-3-phenylaziridine (10):[20] colorless oil; TLC R_f 0.50 (hexane/EtOAc, 2:1); IR (neat) 3062, 2929, 1678, 1450, 1414, 1317, 1286 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.18 (d, 3H, J = 5.6 Hz), 2.96 (dq, 1H, J = 5.6, 6.6 Hz), 3.77 (d, 1H, J = 6.6 Hz), 7.28−7.59 (m, 8H), 8.03 (d, 2H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 12.6, 40.1, 44.2, 127.4, 127.6, 128.1, 128.3, 128.9, 132.6, 132.8, 134.6, 179.5; $[\alpha]^{28}_D$ −58.5 (*c* 0.242, $CHCl_3$) (27% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 97:3, 0.5 mL/min, 254 nm, 30 °C) t = 15.2 (2*R*,3*S*) and 18.9 min (2*S*,3*R*).

Reaction of *cis*-β-Methylstyrene with Complex 1 in the Presence of *cis*-*N*-(*m*-Toluoyl)-2-methyl-3-phenylaziridine (11) (eq 2). *cis*-β-Methylstyrene (354.5 mg, 0.3 mmol), benzoyl chloride (50.6 mg, 0.36 mmol), and aziridine **11** (20.7

mg, 0.27 mmol) were added to a mixture of **1** (118.1 mg, 0.3 mmol), silver tetrafluoroborate (70.1 mg, 0.36 mmol), and pyridine *N*-oxide (34.2 mg, 0.36 mmol) in CH_2Cl_2 (3 mL) at 0 °C. After the mixture was stirred for 72 h, pentane (20 mL) was added. The mixture was then passed through a 3-cm pad of silica gel using diethyl ether (125 mL) as the eluent. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 98:2) to afford *cis*-oxazoline **8** (2.8 mg, 4%), *trans*-oxazoline **9** (4.1 mg, 6%), aziridine **10** (35.6 mg, 49%), aziridine **11** (13.2 mg, 17%), *cis*-2-(*m*-tolyl)-4-methyl-5-phenyl-2-oxazoline (1.3 mg, 2%), and *trans*-2-(*m*-tolyl)-4-methyl-5-phenyl-2-oxazoline (2.7 mg, 4%). ***cis*-*N*-(*m*-Toluoyl)-2-methyl-3-phenylaziridine (11)**: colorless oil; TLC R_f 0.54 (hexane/EtOAc, 2:1); IR (neat) 3030, 2927, 1678, 1454, 1414, 1306, 1284 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.18 (d, 3H, J = 5.9 Hz), 2.35 (s, 3H), 2.94 (dq, 1H, J = 5.9, 6.3 Hz), 3.76 (d, 1H, J = 6.3 Hz), 7.27−7.45 (m, 7H), 7.81 (d, 1H, J = 7.3 Hz), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 12.7, 21.4, 40.2, 44.2, 126.1, 127.4, 127.6, 128.1, 128.2, 129.6, 132.8, 133.4, 134.7, 138.1, 179.8; MS (EI) *m*/*z* (relative intensity, %) 251 (M^+, 4); HRMS (EI) calcd for $C_{17}H_{17}NO$ $(M)^+$ 251.1309, found 251.1319. ***cis*-2-(*m*-Tolyl)-4-methyl-5-phenyl-2-oxazoline (12)**: colorless oil; TLC R_f 0.40 (hexane/EtOAc, 2:1); IR (neat) 2974, 2927, 1651, 1454, 1342, 1192, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.89 (d, 3H, J = 6.9 Hz), 2.41 (s, 3H), 4.66 (dq, 1H, J = 6.9, 9.6 Hz), 5.76 (d, 1H, J = 9.6 Hz), 7.23−7.41 (m, 7H), 7.81−7.86 (m, 1H), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 17.9, 21.3, 65.4, 84.0, 125.3, 126.1, 127.4, 127.7, 128.2, 128.2, 128.8, 132.1, 137.0, 138.1, 163.1; MS (EI) *m*/*z* (relative intensity, %) 251 (M^+, 2); HRMS (EI) calcd for $C_{17}H_{17}NO$ $(M)^+$ 251.1309, found 251.1314. ***trans*-2-(*m*-Tolyl)-4-methyl-5-phenyl-2-oxazoline (13)**: colorless oil; TLC R_f 0.47 (hexane/EtOAc, 2:1); IR (neat) 2964, 2924, 1651, 1454, 1325, 1194, 1061 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.49 (d, 3H, J = 6.6 Hz), 2.39 (s, 3H), 4.20 (dq, 1H, J = 6.6, 7.6 Hz), 5.09 (d, 1H, J = 7.6 Hz), 7.29−7.42 (m, 7H), 7.80−7.84 (m, 1H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.3, 21.5, 70.9, 88.1, 125.3, 125.5, 127.5, 128.2, 128.2, 128.6, 128.8, 132.1, 138.0, 140.4, 162.7; MS (EI) *m*/*z* (relative intensity, %) 251 (M^+, 1); HRMS (EI) calcd for $C_{17}H_{17}NO$ $(M)^+$ 251.1309, found 251.1305.

(1*R*,2*R*)-2-Amino-1-phenylpropanol ((−)-Norpseudoephedrine) (17).[26] A solution of oxazoline (4*R*,5*R*)-**5a** (75.5 mg, 0.32 mmol, 86% ee) in 1.2 M hydrochloric acid (2.4 mL) was stirred at reflux for 30 h. After cooling to room temperature, the mixture was filtrated. Aqueous 5% sodium hydroxide solution (10 mL) was added to the filtrate, and the aqueous layer was extracted with CH_2Cl_2 (5 × 10 mL). The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo to give **17** (44.7 mg, 93% yield, 86% ee). The enantiomeric excess was determined by a comparison of the optical rotation with the reported value.[30] **17**:[31] white solid; TLC R_f 0.10 ($MeOH/CH_2Cl_2$, 2:1); ^1H NMR ($CDCl_3$, 270 MHz) δ 1.04 (d, 3H, J = 6.3 Hz), 1.99 (br s, 3H), 2.94−3.11 (m, 1H), 4.24 (d, 1H, J = 6.6 Hz), 7.21−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 20.5, 52.9, 78.6, 126.4, 127.4, 128.2, 142.6; $[\alpha]^{28}_D$ −26.5 (*c* 0.554, MeOH) (86% ee).

(1*R*,2*R*)-2-Amino-2-cyclohexyl-1-phenylethanol (18). A mixture of oxazoline (4*R*,5*R*)-**7e** (52.0 mg, 0.17 mmol, 92% ee) and 12 M hydrochloric acid (0.6 mL) in EtOH (1 mL) and water (2.5 mL) was stirred at reflux for 30 h. After cooling to room temperature, the mixture was washed with Et_2O (10 mL). The aqueous layer was made basic via the addition of an aqueous 5% sodium hydroxide solution (10 mL) and then extracted with CH_2Cl_2 (5 × 10 mL). The organic layer was dried over Na_2SO_4 and evaporated in vacuo to give a white solid of **18** (32.9 mg, 88% yield, 92% ee). The enantiomeric excess was determined by HPLC analysis of the *N*-benzoyl derivative. **18**: white solid; mp 81−83 °C; TLC R_f 0.20 ($MeOH/CH_2Cl_2$, 2:1); IR (KBr) 3332, 3269, 2918, 2850, 1605, 1448, 1348, 1061, 993 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.95−1.35 (m, 7H), 1.55−1.80 (m, 6H), 2.64 (dd, 1H, J = 5.3, 5.6 Hz), 4.55 (d, 1H, J = 5.6 Hz), 7.20−7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 26.2, 26.3, 26.5, 27.6, 30.8, 39.2, 62.3, 73.2, 126.2, 127.1, 128.2, 143.1; MS (CI, isobutane) *m*/*z* (relative intensity, %) 220 (M^+ + H, 100); $[\alpha]^{29}_D$ −6.64 (*c* 0.354, $CHCl_3$) (92% ee); HPLC (Daicel Chiralpak AD, hexane/2-propanol, 8:2, 0.5 mL/min, 254 nm, 30 °C) t = 13.0 (1*R*,2*R*) and 16.5 min (1*S*,2*S*); HRMS (CI, isobutane) calcd for $C_{14}H_{22}NO$ $(M + H)^+$ 220.1700, found 220.1715. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.46; H, 9.62; N, 6.39.

Acknowledgment. This work was supported, in part, by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and The Naito Foundation. We also acknowledge the Instrumental Analysis Center, Faculty of Engineering, Osaka University.

JO016146D

(23) Müller, P.; Baud, C.; Jacquier, Y. *Tetrahedron* **1996**, *52*, 1543−1548.

(24) (a) Tomie, M.; Sugimoto, H.; Yoneda, N. *Chem. Pharm. Bull.* **1976**, *24*, 1033−1039. (b) Poelert, M. A.; Hof, R. P.; Peper, N. C. M. W.; Kellogg, R. M. *Heterocycles* **1994**, *37*, 461−475.

(25) Galindo, A.; Orea, F. L.; Gnecco, D.; Enríquez, R. G.; Toscano, R. A.; Reynolds, W. F. *Tetrahedron: Asymmetry* **1997**, *8*, 2877−2879.

(26) Colman, B.; de Sousa, S. E.; O'Brien, P.; Towers, T. D.; Watson, W. *Tetrahedron: Asymmetry* **1999**, *10*, 4175−4182.

(27) Meyers, A. I.; Hanagan, M. A.; Trefonas, L. M.; Baker, R. J. *Tetrahedron* **1983**, *39*, 1991−1999.

(28) Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *J. Org. Chem.* **1987**, *52*, 2523−2530.

(29) Kamata, K.; Agata, I.; Meyers, A. I. *J. Org. Chem.* **1998**, *63*, 3113−3116.

(30) Kalm, M. J. *J. Org. Chem.* **1960**, *25*, 1929−1937.

(31) Tlahuext, H.; Contreras, R. *Tetrahedron: Asymmetry* **1992**, *3*, 727−730.