Palladium(II)-Catalyzed Highly Regio- and Diastereoselective Cyclization of Difunctional Allylic *N*-Tosylcarbamates. A Convenient Synthesis of Optically Active 4-Vinyl-2-oxazolidinones and Total Synthesis of 1,4-Dideoxy-1,4-imino-L-xylitol

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A Pd(II)-catalyzed cyclization of difunctional allylic *N*-tosyl carbamates in the presence of halide ions was developed with high regio- and diastereoselectivity. The reaction involves aminopalladation of alkene and β-heteroatom elimination to regenerate Pd(II) species. When the readily available homochiral alcohols were used as substrates, highly optically active 4-vinyl-2-oxazolidinones were easily obtained. The utility of this method was exemplified by the convenient synthesis of 1,4-dideoxy-1,4-imino-L-xylitol.

Introduction

In recent years, a number of palladium(0)-catalyzed reactions that proceed by way of π-allylpalladium have been extensively studied.[1] However, the attack of nucleophiles to the unsymmetric π-allyl moiety often leads to a mixture of regioisomers.[1a,2] Thus, the control of regioselectivity of the π-allylic substitution has been a major challenge.[3] Furthermore, nucleophilic substitutions on difunctional substrates such as **I** are more complicated. Two kinds of π-allylpalladium intermediates may arise (**II** in path a and **III** in path b), and each further affords two products, making the regioselectivity of this reaction more complicated (Scheme 1).[4]

As we know, instead of forming π-allylpalladium intermediates, the palladium(II) catalyst can coordinate with the carbon−carbon double bond and the latter can be attacked by nucleophiles.[5] Two paths may arise, which are simpler than those of the π-allyls (Scheme 2).

We have been interested in using Pd(II)-catalyzed reaction to control the regioselectivity of difunctional substrates such as **I**. Here, we wish to report a palladium(II)-catalyzed cyclization of 1-substituted butenylene di(*N*-tosylcabamates)[6] giving 4-vinyl-2-oxazolidinones with high regio- and diastereoselectivity.

Results and Discussion

On the basis of our previous work on Pd(II)-catalyzed reactions, the carbon−palladium bond was quenched by β-heteroatom elimination to regenerate Pd(II) species.[7] Treatment of compound **1a** with $Pd(OAc)_2$ (5 mol %) and LiBr (4 equiv) in THF at room temperature for 10 min afforded product **2a** in 97% yield. Similar results were obtained with **1b**−**d** (Scheme 3).

It was observed that halide ions were extremely important for the process. Reactions with excess chloride ion gave similar results with bromide ion (Scheme 3). No reaction occurred in the absence of halide ions. While no reaction occurred under the catalysis of $PdCl_2(PhCN)_2$,

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(4) For the excellent illustration of this point related to transition metals using the difunctional reagents such as **I** with different leaving groups, see: (a) Bäckvall, J. E.; Nystrom, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676. (b) Ferroud, D.; Genet, J. P.; Kiolle, R. *Tetrahedron Lett.* **1986**, *27*, 23. (c) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *26*, 2779. (d) Colobert, F.; Genet, J. P. *Tetrahedron Lett.* **1984**, *25*, 3579. (e) Tanigawa, Y.; Nishimura, K.; Lawashaki, A.; Murahashi, S. *Tetrahedron Lett.* **1982**, *23*, 5549. When the two leaving groups are the same, excellent results were obtained, see: (f) Trost, B. M.; Tometzki, G. B.; Hung, M. H. *J. Am. Chem. Soc.* **1987**, *109*, 2176.

(5) (a) Hirai, Y.; Watanabe, J.; Nozaki, T.; Yokoyama, H.; Yamaguchi, S. *J. Org. Chem.* **1997**, *62*, 776. (b) Yokoyama, H.; Otaya, K.; Kobayashi, H.; Miyazawa, M.; Yamaguchi, S.; Hirai, Y. *Org. Lett.* **2000**, *2*, 2427. (c) Hirai, Y.; Nagatsu, M. *Chem. Lett.* **1994**, 21. (d) Hirai, Y.; Terada, T.; Amemiya, Y.; Momose, T. *Tetrehedron Lett.* **1992**, *33*, 7893. (e) Lei, A.; Lu, X. *Org. Lett.* **2000**, *2*, 2357.

(6) *N*-Tosyl carbamates could be used as the efficient nucleophiles in the aminopalladation reaction of alkenes or alkynes under Pd(0) catalysis. (a) Trost, B. M.; Vranken, D. L.-V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 228. (b) Tamaru, Y.; Kimura, M. *Synlett* **1997**, 749. (c) Bando, T.; Harayama, H.; Fukazawa, Y.; Shiro, M.; Fugami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1994**, *59*, 1465. (d) Kimura, M.; Wakamiya, Y.; Horino, Y.; Tamaru, Y. *Tetrahedron Lett.* **1997**, *38*, 3963. (e) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1988**, *110*, 3994.

(7) (a) Mailtis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 1, p 79. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93−99. (c) Kaneda, K.; Uchiyama, T.; Fujiwarka, Y.; Teranishi, S. *J. Org. Chem.* **1979**, *44*, 55. (d) Yanagihara, N.; Lambert, C.; Iritani, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2753. (e) Lu, X.; Zhu, G.; Wang, Z. *Synlett.* **1998**, 115. (f) Lu, X.; Ma, S. In *New Age of Divalent Palladium Catalysis, in Transition Metal Catalyzed Reaction*; Murahashi, S.-I., Davies, S. G., Eds.; Blackwell Science: Oxford, 1999; Chapter 6, p 133. (g) Zhang, Q.; Lu, X. *J. Am. Chem. Soc.* **2000**, *122*, 7604.

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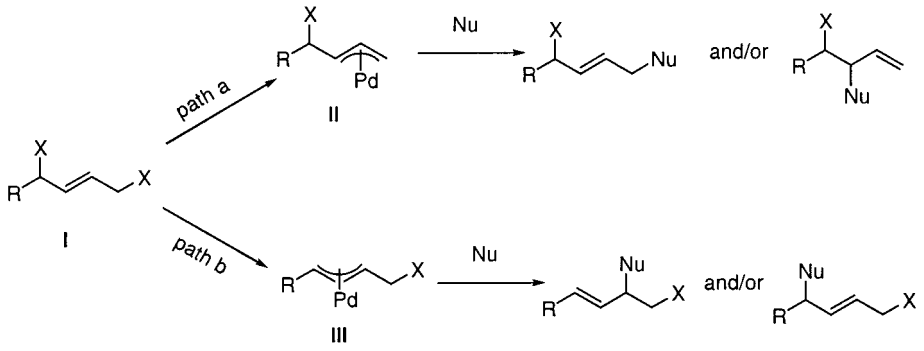
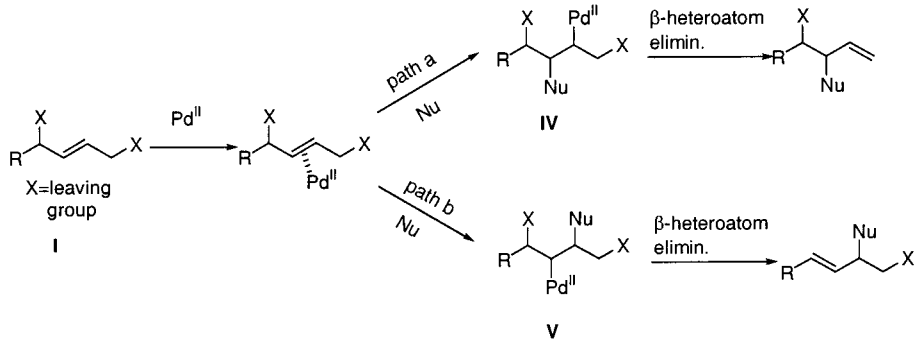
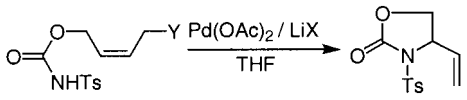
Scheme 1



Scheme 2

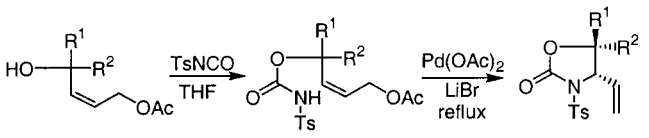


Scheme 3



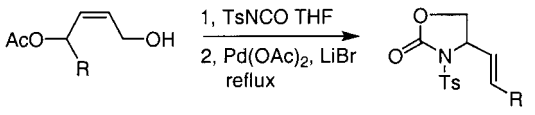
X = **Br**	**1a**: Y = OCONHTs	**2a** (97%)
	1b: Y =OAc	**2a** (95%)
	1c: Y = OCOOMe	**2a** (78%)
	1d: Y = Cl	**2a** (96%)
X = Cl	**1b**: Y =OAc	**2a** (90%)

Scheme 4



3	**1**	**2** (yield%)
Z-**3e** R^1= R^2= Me	**1e**	**2e**(80%)
Z-**3f** R^1= Me, R^2=H	**1f**	*trans*-**2f** (79%)
Z-**3g** R^1= *n*-C_5H_{11}, R^2=H	**1g**	*trans*-**2g** (98%)
Z-**3h** R^1= *i*-Pr, R^2=H	**1h**	*trans*-**2h** (92%)

Scheme 5



4	**5**
***Z*-4a**: R= Me	**5a** (88% yield) ***E*:*Z***=93:7
***Z*-4b**: R=*i*-Pr	**5b** (84% yield) ***E*:*Z***>97:3

the reaction proceeded smoothly on adding excess LiCl. The reaction did not take place using $PdCl_2(PPh_3)_2$ as the catalyst even in the presence of LiCl. Some ionic palladium species, such as $[Pd(PPh_3)_2]^{2+}[(BF_4)_2]^{2-}$, $[Pd(PPh_3)_2]^{2+}[(OTf)_2]^{2-}$, and $[Pd(bpy)]^{2+}[(BF_4)_2]^{2-}$, were ineffective for this reaction.

The reaction can be carried out in one pot using the corresponding allylic alcohol and TsNCO (1.1 equiv) to yield the carbamate first,[8] followed by the catalytic reaction in the presence of $Pd(OAc)_2$ and LiBr at reflux temperature to yield the product. For the 1-substituted allylic alcohols (*Z*)-**3**, only one diastereomer **2** with trans substituents was obtained (Scheme 4).[9]

When 4-substituted allylic alcohols (*Z*)-**4** (**4a**, **4b**) were used as the starting materials, the reaction under the same conditions also gave cyclization products **5** with high yield and high stereoselectivity of the vinyl group (Scheme 5). These results indicated that both reactions of substituted allylic alcohols **3** and **4**, catalyzed by $Pd(OAc)_2$/LiBr, proceeded smoothly regardless of the substituent on the 1 or 4 position (Schemes 4 and 5).

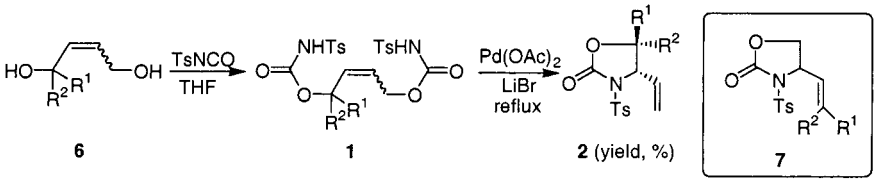
Surprisingly, the reactions of 1-substituted butenylene dicarbamates (**1i**−**m**) also gave **2** as sole product with high regioselectivity, although both nitrogen atoms of butenylene dicarbamates **1** can attack the Pd(II)-coordinated alkene. No regioisomer **7** was detected. Reactions of 1-substituted butenylene dicarbamates **1**, formed in situ from the corresponding diol **6** with TsNCO (2.2 equiv), gave products with high regioselectivity and good yields under the catalysis of $Pd(OAc)_2$/LiBr in THF at reflux (Scheme 6).

The reactions of (*E*)-configuration butenylene dicarbamates gave similar results; e.g., the reactions of (*E*)-**1a** and (*E*)-**1l**, catalyzed by $Pd(OAc)_2$/LiBr in THF, gave

(8) Tamaru, Y.; Kimura, M.; Tanaka, S.; Kure, S.; Yoshida, Z.-I. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2838.

(9) The structure and stereochemistry of products were characterized by comparison with the data reported by Tamaru; see: Kimura, M.; Tanaka, S.; Tamaru, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1689.

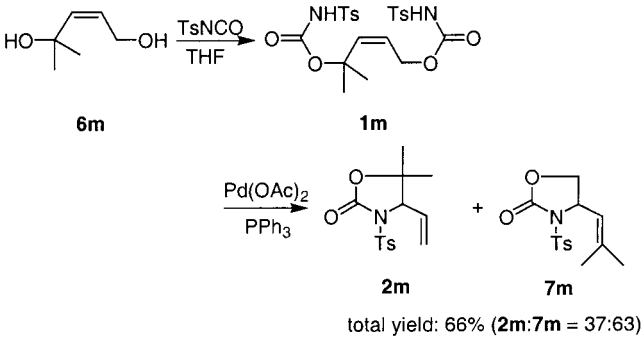
Scheme 6



(*Z*)-**6i** R^1= Me, R^2=H	(*Z*)-**1i**	*trans*-**2f** (65%)
(*Z*)-**6j** R^1= *n*-C_5H_{11}, R^2=H	(*Z*)-**1j**	*trans*-**2g** (92%)
(*Z*)-**6k** R^1= *i*-Pr, R^2=H	(*Z*)-**1k**	*trans*-**2h** (91%)
(*Z*)-**6l** R^1= CH_2OBn R^2=H	(*Z*)-**1l**	*trans*-**2l** (93%)
(*Z*)-**6m** R^1=R^2=Me	(*Z*)-**1m**	**2e** (82%)
(*E*)-**6a** R^1= R^2= H	(*E*)-**1a**	**2a** (79%)
(*E*)-**6l** R^1= CH_2OBn R^2=H	(*E*)-**1l**	*trans*-**2l** (82%)

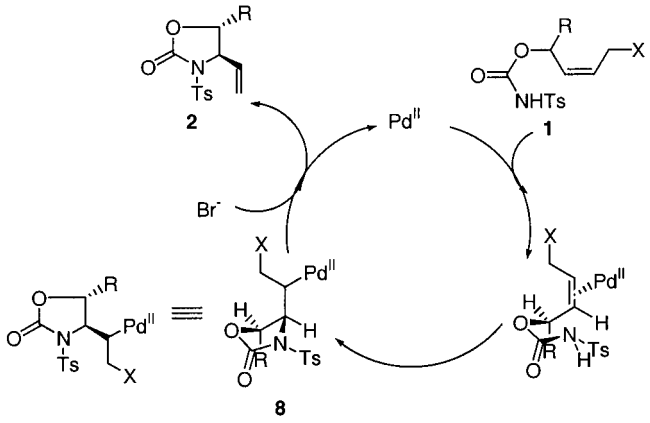
not detected

Scheme 7

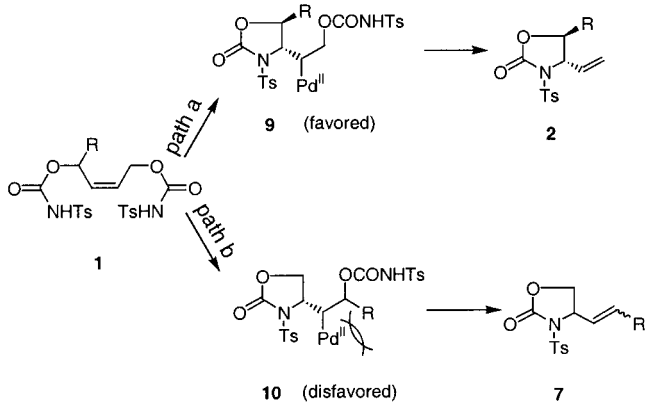


total yield: 66% (**2m**:**7m** = 37:63)

Scheme 8



Scheme 9



2a and *trans*-**2l** with yields of 79% and 82%, respectively (Scheme 6).

Before the mechanism of the reaction was speculated, the reaction of **1b** was tried using $Pd_2(dba)_3$·$CHCl_3$ as the catalyst, no reaction occurred but only the Pd black precipitated out. Again, the reactions of **1b** and **1c** were tried with $Pd(OAc)_2$ (5 mol %)/PPh_3 (20 mol %), which was regarded as the precursor of the Pd(0) species.[10] Both reactions are more complicated than those catalyzed by $Pd(OAc)_2$/LiBr, yielding **2a** as the sole product. Moreover, the reaction of **1m** catalyzed by $Pd(OAc)_2$ (5 mol %)/PPh_3 (20 mol %) gave a mixture of products **2m** and **7m** with poor regioselectivity (Scheme 7, compare with the reaction of **1m** in Scheme 6). The reaction of substrate similar to that of **1m** with Pd(0) has been reported in the literature.[11]

From the different results obtained from the reactions in the presence of different additives (LiBr or PPh_3) in addition to the fact that the yields of the reaction were influenced by the halide ions, it is most probably that the reaction proceeds through the Pd(II) mechanism,[12] although the Pd(0) mechanism cannot be completely ruled out. Thus, a mechanism is speculated as follows: first, the Pd(II) species coordinates with the olefinic double bond, then trans attack of the nitrogen atom to the double bond forms intermediate **8** from the opposite side (aminopalladation),[5,6] followed by β-heteroatom elimination in the presence of the halide ions[7,12] to form the product **2** with high stereoselectivity and regeneration of the Pd(II) species (Scheme 8). Here, excess halide ions effectively inhibit the β-hydride elimination,[12] making the reaction with high yield. Different from quenching the carbon−palladium bond by β-hydride elimination or reductive elimination,[1a] oxidants are not necessary in this reaction.

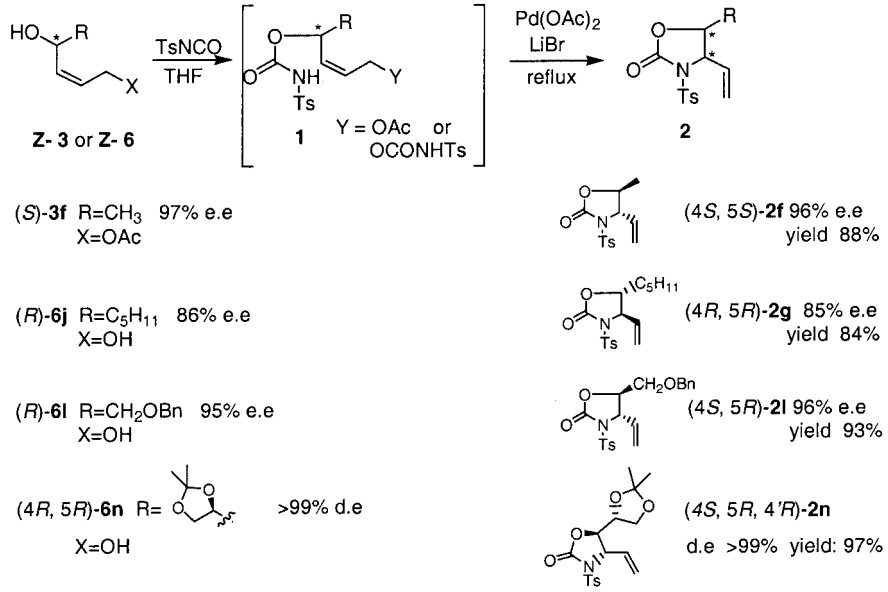
According to the speculated mechanism, for reactions of 1-substituted butenylene dicarbamates (Scheme 6), the intermediate **9** (Scheme 9, path a) will be formed preferentially over **10** (Scheme 9, path b) during the amino-

(10) $Pd(OAc)_2$/PPh_3 was regarded as the precursor of Pd(0) species due to the in situ reduction of Pd(II) to Pd(0) by PPh_3; see: (a) Amatore, C.; Jutand, A.; Barki, M. A. *Organometallics*. **1992**, *11*, 3009. (b) Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett*. **1992**, 2177. (c) Hayashi, T.; Kubo, A.; Ozawa, F. *Pure Appl. Chem*. **1992**, *64*, 421.

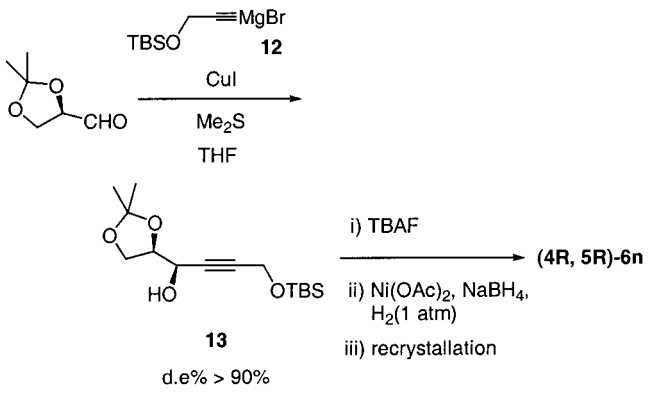
(11) Cyclization of *N*-phenyl-1-substituted butenyl dicarbamates catalyzed by Pd(0) gave poor regioselectivity; see: Hayashi, T.; Yamamoto, A.; Ito, A. *Tetrahedron Lett*. **1987**, *28*, 4837.

(12) The excess halide ions can effectively inhibit the β-hydride elimination; see: (a) Wang, Z.; Zhang, Z.; Lu, X. *Organometallics*. **2000**, *19*, 775. (b) Zhang, Z.; Lu, X.; Xu, Z.; Zhang, Q.; Han, X. *Organometallics*, **2001**, *20*, 3724.

Scheme 10



Scheme 11



palladation step due to the steric effect, making the reaction highly regioselective.

With the readily available homochiral butenylene alcohols (*S*)-**3f**, (*R*)-**6j**, and (*R*)-**6l,** highly optically active 4-vinyl-2-oxazolidinones (4*S*, 5*S*)-**2f**, (4*R*, 5*R*)-**2g**, and (4*S*, 5*R*)-**2l** were obtained, respectively (Scheme 10).[13] Treatment of chiral diol (4*R*,5*R*)-**6n**, which can be easily synthesized (Scheme 11),[14] gave optically pure (4*S*,5*R*,4′*R*)-**2n** also with high yield (Scheme 10), indicating that the effect of the substituent on the 1-position was not obvious.

These optically active 4-vinyl-2-oxazolidinones are important precursors for useful products. The convenient transformation of optically pure compound **2l** to the homochiral α-amino alcohol has been reported.[15] Furthermore, the conversion of (4*S*,5*R*,4′*R*)-**2n** to 1,4-dideoxy-1,4-imino-L-xylitol **11**[16] was examined.

1,4-Dideoxy-1,4-imino-L-xylitol **11**, as the 2-epimer of 1,4-dideoxy-1,4-imino-D-arabinitol which was isolated from *Arachniodes Standishii* and *Angylocalyx boutiqueanus*, has been proven to be a potential glycosidase inhibitor.[16d] Starting from (4*S*,5*R*,4′*R*)-**2n** prepared by our method, **11** can be easily synthesized (Scheme 12). First, isopropylidene group was removed by treatment of (4*S*,5*R*,4′*R*)-**2n** with $CuCl_2 \cdot 2H_2O$ in CH_3CN[17] to give the diol **14** in 93% yield. The diol **14** was protected with toluenesulfonyl chloride in the prensence of a catalytic amount of Bu_2SnO.[18] Surprisingly, **15** was formed with 91% yield accompanied by the transfer of the cyclic carbamate to cyclic carbonate.[19] Instead of giving the nitrogen heterocyclic derivative **17**, the reactions of **15** with bases, such as NaH and Bu[t]OK, were very complex. To hydrolyze the cyclic carbonate **15**, the reaction proceeded smoothly in a dilute solution of sodium hydroxide in a mixture of H_2O and dioxane with the simultaneous formation of the nitrogen heterocycle **18**[20] by eliminating TsOH. Compound **18** has been used as an important chiral building block for the preparation of nitrogen-containing natural products. Reaction of **18** with ozone followed by reduction with $NaBH_4$ gave **19**. Treatment of **19** with $NaNH_2$ in liquid ammonia afforded target compound **11** in moderate yield.

In conclusion, we developed a Pd(II)-catalyzed cyclization of difunctional allylic *N*-tosyl carbamates in the presence of halide ions with high regio- and diastereoselectivity involving aminopalladation of alkene, and β-heteroatom elimination to regenerate Pd(II) species.

(13) (a) Ando, K. *J. Org. Chem*. **1997**, *62*, 1934. (b) Taylor, E. C.; Doetzer, R. *J. Org. Chem*. **1991**, *56*, 1818. (c) Zhu, G.; Lu, X. *J. Org. Chem*. **1995**, *60*, 1087.

(14) Sato, F.; Takahashi, O.; Chiba, T.; Takeda, Y.; Kusakabe, M. *J. Chem. Soc., Chem. Commun*. **1985**, 1636.

(15) Olofesson, B.; Khamrai, U.; Somfai, P. *Org. Lett*. **2000**, *2*, 4087.

(16) (a) Buchanan, J. G.; Lumbard, K. W.; Sturgeon, R. J.; Thompson, D. K.; Wightman, R. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 699. (b) Meng, Q. C.; Hesse, M. *Helv. Chim. Acta*. **1991**, *74*, 445. (c) Huang, Y.; Dalton, D. R. *J. Org. Chem*. **1997**, *62*, 372. (d) Kim, J. H.; Yang, M. S.; Lee, W. S.; Park, K. H. *J. Chem. Soc., Pekin Trans. 1* **1998**, 2877. (e) Lee, B. W.; Jeong, I.; Yang, M. S.; Choi, S. U.; Park, K. H. *Synthesis* **2000**, 1305.

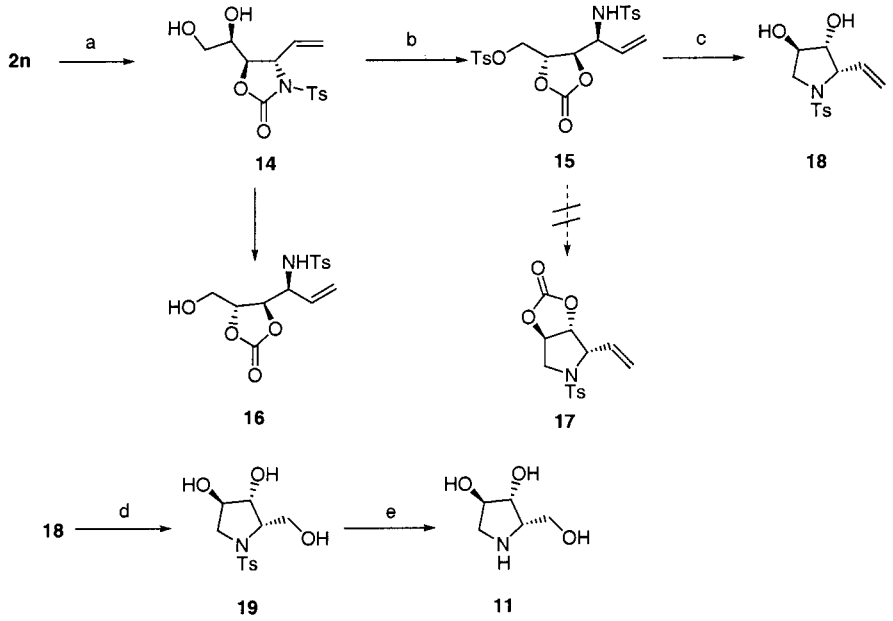
(17) Saravanan, P.; Chandrasekhar, M.; Anand, R. V.; Singh, V. K. *Tetrahedron Lett*. **1998**, *39*, 3091.

(18) Martinell, M. J.; Nayyar, N. K.; Moher, E. D.; Dhokte, U. P.; Pawlak, J. M.; Vaidyanathan, R. *Org. Lett*. **1999**, *1*, 447.

(19) We found that the transfer of cyclic carbamate to cyclic carbonate occurred also in the prensence of Et_3N to give compound **16** with high yield.

(20) The stereostructure of compound **18** was determined by X-ray analysis. Crystallographic data for **18**: $C_{13}H_{17}O_4NS$, FW = 283.34, orthorhombic, space group $P2_12_12_1$(#19), a = 8.552(2) Å, b = 19.575(3) Å, c = 8.406(2) Å, V = 1407.2(5) Å^3, Z = 4, density (calcd) = 1.337 g/cm^3; F(000) = 600.00, T = 293 K, μ(Mo Kα) = 2.39 cm^{-1}. The intensity data were collected on a Rigaku AFC7R diffractometer with Mo Kα radiation (λ = 0.710 69 Å, graphite monochromator), and a 12 kW rotating anode generator. The maximum $2\theta_{max}$ value was 55.0°; 1893 unique reflections were observed. The 1596 reflection with $I = 2.00\sigma(I)$ were used in refinement; R (Rw) = 0.040 (0.050).

Scheme 12[a]



[a] Reaction conditions: (a) $CuCl_2$, MeCN, reflux, 93%; (b) Bu_2SnO (4 mol %), TsCl, Et_3N, 91%; (c) 0.5N NaOH, H_2O, dioxane; (d) O_3, MeOH, −78 °C, $NaBH_4$, 86%; (e) $NaNH_2$, liquid NH_3, THF, 65%.

When the readily available homochiral alcohols were used as substrates, highly optically active products 4-vinyl-2-oxazolidinones were easily obtained. 1,4-Dideoxy-1,4-imino-L-xylitol was synthesized conveniently using this cyclization as a key step.

Experimental Section

General Methods. Melting points were uncorrected. ^{1}H NMR spectra were obtained at 300 or 400 MHz. Optical rotations were measured with a Perkin-Elmer model 341 polarimeter. HPLC was conducted on a Waters 515 pump/2487 instrument. LiBr and LiCl were dried under vacuum by heating at 120 °C for 24 h in the presence of P_2O_5.

Materials. Homochiral butenylene alcohol (*S*)-**3f** was synthesized from ethyl L-(−)-lactate;[13a] (*R*)-**6l** from L-tartaric acid;[13b] (*R*)-**6j** from propargyl alcohol.[13c]

Typical Procedure for the Synthesis of Compound 1. Compound **1** was easily prepared from the corresponding allylic alcohol with *p*-toluenesulfonyl isocyanate according to the literature.[9]

(*Z*)-2-Butene-1,4-diol ditosylcarbamate (1a): colorless crystal; mp 176.0−176.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 5.66 (t, J = 5.2 Hz, 2H), 4.61 (d, J = 5.2 Hz, 4H), 2.45 (s, 6H); IR (neat) ν 3247, 2954, 2925, 1729, 1598, 1494, 1453, 1361, 1222, 1210, 1171, 1090, 857, 813, 769, 704, 666, 550 cm^{-1}; MS *m/e* 288, 268, 216, 197, 171, 155, 139, 107, 91, 65. Anal. Calcd for $C_{20}H_{22}N_2O_8S_2$: C, 49.78; H, 4.60; N, 5.81. Found: C, 49.63; H, 4.57; N, 5.81.

(*Z*)-4-Acetoxybut-2-enyl tosylcarbamate (1b): oil; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.72 (dt, J = 13.0, 6.4 Hz, 1H), 5.61 (dt, J = 13.9, 6.5 Hz, 1H), 4.67 (d, J = 6.4 Hz, 2H), 4.61 (d, J = 6.5 Hz, 2H), 2.44 (s, 3H), 2.05 (s, 3H); IR (neat) ν 3236, 1743, 1451, 1353, 1225, 1162, 1091 cm^{-1}; MS *m/e* 268 (M^+ − OAc), 171, 155, 108, 107, 91, 89, 65, 43. Anal. Calcd for $C_{14}H_{17}NO_6S$: C, 51.37; H, 5.23; N, 4.28. Found: C, 51.77; H, 5.22; N, 4.28.

(*Z*)-4-Methoxycarbonyloxybut-2-enyl tosylcarbamate (1c): oil; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.77 (ttd, J = 0.9, 6.7, 12.2 Hz, 1H), 5.68 (ttd, J = 1.1, 6.7, 12.3 Hz, 1H), 4.69−4.66 (m, 4H), 3.79 (s, 3H), 2.45 (s, 3H); IR (neat) ν 3236, 2961, 1752, 1598, 1448, 1356, 1272, 1223, 1162, 1091 cm^{-1}; MS *m/e* 268 (M^+ − OCO_2Me), 155, 91, 70, 69, 65, 43, 42, 41. Anal. Calcd for $C_{14}H_{17}NO_7S$: C, 48.97; H, 4.99; N, 4.08. Found: C, 49.04; H, 4.70; N, 4.15.

(*Z*)-4-Chlorobut-2-enyl tosylcarbamate (1d): colorless solid; mp 83−84 °C; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 5.85 (m, 1H), 5.64 (m, 1H), 4.67 (d, J = 7.0 Hz, 2H), 4.06 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H); IR (neat) ν 3213, 1732, 1600, 1477, 1367, 1241, 1162, 1091 cm^{-1}; MS *m/e* 287 (M^+), 268, 197, 155, 91, 81, 65, 41. Anal. Calcd for $C_{12}H_{14}ClNO_4S$: C,47.45; H, 4.65; N, 4.61. Found: C, 47.55; H, 4.67; N, 4.46.

Typical Procedure for the Synthesis of Compounds 3, 4, and 6. The (*Z*)- and (*E*)-alk-2-ene-1,4-diols **6** were obtained from the alk-2-yne-1,4-diols that were synthesized by alkynylation of an aldehyde,[21] followed by hydrogenation[22] or reduction with $LiAlH_4$.[23] Compounds **3** and **4** were prepared from **6** according to the literature.[24]

Compounds (*Z*)-**3e**,[25] (*Z*)-**3f**,[25] (*Z*)-**3g**,[24] (*Z*)-**4a**,[26] (*Z*)-**4b**,[26] (*Z*)-**6i**,[27] (*Z*)-**6j**,[28] (*Z*)-**6k**,[27] and (*Z*)-**6m**[29] were synthesized according to the literature.

(*Z*)-1-Acetoxy-4-hydroxy-5-methylhex-2-ene (3h): oil; ^{1}H NMR ($CDCl_3$) δ 5.69−5.59 (m, 2H), 4.86−4.74 (m, 2H), 4.54 (dd, J = 4.4, 12.9 Hz, 1H), 4.16−4.10 (m, 1H), 2.07 (s, 3H), 1.76−1.69 (m, 1H), 0.97 (d, J = 6.7 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); IR (neat) ν 3474, 2965, 2877, 1741, 1374, 1240, 1028, 978 cm^{-1}; MS *m/e* 155, 112, 95, 76, 71, 56, 55, 43. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.44; H, 9.52.

(*Z*)-5-Benzyloxypent-2-ene-1,4-diol ((*Z*)-6l): oil; ^{1}H NMR ($CDCl_3$) δ 7.37−7.29 (m, 5H), 5.79 (dt, J = 11.3, 6.2 Hz, 1H), 5.51 (dd, J = 11.3, 7.8 Hz, 1H), 4.64 (dt, J = 6.4, 6.2 Hz, 1H), 4.55 (s, 2H), 4.22 (dd, J = 7.0, 6.2 Hz, 1H), 4.11 (m, 1H), 3.43

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(d, J = 6.7 Hz, 2H), 3.20 (s br, 1H), 2.90 (s br, 1H); IR (neat) ν 3370, 3030, 1454, 1103, 1028, 739, 699 cm^{-1}; MS *m/e* 209 ($M^+ + 1$), 181, 173, 143, 129, 91(100), 83, 69; HRMS ($M - H_2O$) calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.1010.

(*E*)-5-Benzyloxypent-2-ene-1,4-diol ((*E*)-6l): oil; ^{1}H NMR ($CDCl_3$) δ 7.35−7.25 (m, 5H), 5.79 (dt, J = 15.6, 5.2 Hz, 1H), 5.51 (dd, J = 15.6, 5.9 Hz, 1H), 4.57 (s, 2H), 4.38 (m, 1H), 4.15 (s, 2H), 3.53 (dd, J = 9.6, 3.2 Hz, 1H), 3.36 (m, 1H), 2.55 (s br, 1H), 1.63 (s br, 1H); IR (neat) ν 3370, 3032, 2864, 1454, 1098, 1003, 740, 699 cm^{-1}; MS *m/e* 208 (M^+), 190, 177, 145, 107, 91 (100), 87, 69; HRMS ($M - H_2O$) calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0983.

(*Z*)-(4*R*,5*R*)-5,6-*O*-isopropylidenehex-2-ene-1,4-diol (6n). To a solution of CuI (13.6 g, 72 mmol) in a mixture of THF (100 mL) and Me_2S (20 mL) was added the Grignard reagent **12** (60 mmol) in THF (30 mL) at −78 °C, and the mixture was stirred for 5 min at −78 °C under argon. (*R*)-2,3-Isopropylideneglyceraldehyde (6.3 g, 48 mmol) was then added, and the mixture was gradually warmed to room temperature. After the mixture was stirred for 2 h, saturated NH_4Cl (30 mL) solution was added, and the mixture was extracted with ethyl acetate. The combined extracts were dried ($MgSO_4$), filtered, and evaporated. The crude oil was purified by column chromatography on silica gel (ethyl acetate/petrolum ether = 1/5) to give **13** (12.3 g, yield 86%) as an oil: ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 2H), 4.20 (d, J = 1.4 Hz, 1H), 4.06 (ddd, J = 6.5, 5.4, 1.4 Hz, 1H), 3.98 (dd, J = 6.5, 8.5 Hz, 1H), 3.77 (dd, J = 5.4, 8.5 Hz, 1H), 2.35 (s, br, 1H), 1.34 (s, 3H), 1.26 (s, 3H), 0.79 (s, 9H), 0.01 (s, 6H); IR (neat) ν 3439, 1473, 1464, 1373, 1256, 1074, 838, 780 cm^{-1}; MS *m/e* 285, 185, 111, 101, 75 (100), 59, 43. Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 59.64; H, 9.07.

To a solution of **13** (12 g, 40 mmol) in THF (100 mL) was added dropwise TBAF (40 mL, 1.0 M) in THF at room temperature, and the mixture was stirred. After the reaction was complete as monitored by TLC, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to give the alkynediol. The alkynediol was hydrogenated with $Ni(OAc)_2$/$NaBH_4$ to give **6n** using the literature method.[22] After purification by column chromatography on silica gel (ethyl acetate/petrolum ether = 1/1), optically pure (4*R*,5*R*)-**6n** was obtained by recrystallization (ethyl acetate/petroleum ether) at −20 °C as a colorless solid: mp 25−26 °C; $[\alpha]^{20}_D$ = −5.1 (c = 1.30, EtOH); ^{1}H NMR ($CDCl_3$) δ 5.88 (ddt, J = 5.7, 1.4, 1.2 Hz, 1H), 5.53 (ddt, J = 11.4, 8.0, 1.4 Hz, 1H), 4.41 (ddd, J = 8.0, 6.4, 1.2 Hz, 1H), 4.32 (ddd, J = 6.6, 5.7, 1.4 Hz, 1H), 4.21 (ddd, J = 6.6, 5.7, 1.4 Hz, 1H), 4.09 (dt, J = 6.4, 6.0 Hz, 1H), 4.00 (dd, J = 8.4, 6.4 Hz, 1H), 3.76 (dd, J = 8.4, 5.7 Hz, 1H), 2.85 (s, br, 1H), 2.64 (s, br, 1H), 1.46 (s, 3H), 1.37 (s, 3H); IR (neat) ν 3371, 1442, 1383, 1258, 1063, 864, 679 cm^{-1}; MS *m/e* 173, 101 (100), 95, 83, 73, 67, 59, 55, 43. Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.15; H, 8.32.

Typical Procedure for the Reaction of 1. Compound **1** (0.5 mmol) was added to a solution of $Pd(OAc)_2$ (5 mol %) and LiBr (2 mmol) in THF, and the mixture was stirred at room temperature. After the reaction was complete as monitored by TLC, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to give product **2a**.

Typical Procedure for the Reaction of 3 and 4. Compound **3** (0.5 mmol) was reacted with TsNCO (0.55 mmol) in THF (5 mL) for 10 min at room temperature under N_2. Then $Pd(OAc)_2$ (5 mol %) and LiBr (2 mmol) were added, and the mixture was heated to reflux. After the reaction was complete as monitored by TLC, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate) to give product **2**. Products **5** were obtained from **4** using the same procedure.

Compounds **2a**,[9] **2e**,[30] *trans*-**2f**,[9] *trans*-**2h**,[9] and **5a**[9] are known compounds, and their spectroscopic data matched those in the literature.

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***N*-(*p*-Toluenesulfonyl)-5-pentyl-4-vinyl-2-oxazolidinone (2g):** mp 61.0−61.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.79−5.67 (m, 1H), 5.37 (d, J = 17.1 Hz, 1H), 5.30 (d, J = 10.1 Hz, 1H), 4.45 (dd, J = 4.3, 8.2 Hz, 1H), 4.14 (dt, J = 6.4, 4.4 Hz, 1H), 2.38 (s, 3H), 1.61−1.19 (m, 8H), 0.81 (t, J = 6.8 Hz, 3H); IR (neat) ν 2958, 2931, 2862, 1784, 1371, 1175, 665 cm^{-1}; MS (*m/e*) 338 (M^++1), 173, 155, 119, 108, 91, 82, 65, 41. Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.41; H, 6.75; N, 4.09.

(*E*)-*N*-(*p*-Toluenesulfonyl)-4-(2′-isopropylvinyl)-2-oxazolidinone (5b): oil; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 5.90 (dd, J = 6.2, 15.3 Hz, 1H), 5.30 (ddd, J = 15.4, 9.0, 1.4 Hz, 1H), 4.89 (dt, J = 3.4, 8.3 Hz, 1H), 4.49 (t, J = 8.7 Hz, 1H), 4.02 (dd, J = 3.4, 8.7 Hz, 1H), 2.45 (s, 3H), 2.40−2.30 (m, 1H), 0.99 (d, J = 6.8 Hz, 6H); IR (neat) ν 1785, 1598, 1372, 1174, 1092, 815, 667, 580 cm^{-1}; MS *m/e* 310 ($M^+ + 1$), 266, 240, 202, 155, 139, 110, 91 (100), 65. Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N,4.53. Found: C, 58.23; H, 6.08; N, 4.55.

Typical Procedure for the Reaction of 6. Compound **6** (0.5 mmol) was reacted with TsNCO (1.10 mmol) in THF (5 mL) for 10 min at room temperature under N_2. Then $Pd(OAc)_2$ (5 mol %) and LiBr (2 mmol) were added, and the mixture was heated to reflux. After the reaction was complete as monitored by TLC, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate) to give product **2**.

***N*-(*p*-Toluenesulfonyl)-5-benzyloxymethyl-4-vinyl-2-oxazolidinone (2l):** oil; ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H), 7.38−7.29 (m, 5H), 7.25 (d, J = 8.3 Hz, 2H), 5.84 (ddd, J = 7.7, 10.0, 17.0 Hz, 1H), 5.45 (d, J = 17.0 Hz, 1H), 5.37 (d, J = 10.0 Hz, 1H), 4.81 (dd, J = 7.7, 3.9 Hz, 1H), 4.47 (s, 2H), 4.25 (dt, J = 3.9, 3.5 Hz, 1H), 3.57 (t, J = 3.5 Hz, 2H), 2.40 (s, 3H); IR (neat) ν 1782, 1364, 1272, 1174, 1091, 815, 666, 567 cm^{-1}; MS (*m/e*) 388 ($M^+ + 1$), 387, 181, 155, 126, 91 (100), 82, 65; HRMS calcd for $C_{20}H_{21}NO_5S$ 387.1100, found 387.1140.

(4*S*,5*R*,4′*R*)-*N*-(*p*-Toluenesulfonyl)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-vinyl-2-oxazolidinone (2n): mp 120−121 °C; $[\alpha]^{20}_D$ = −14.5 (c = 2.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.93 (ddd, J = 7.7, 10.0, 17.0 Hz, 1H), 5.53 (d, J = 17.0 Hz, 1H), 5.41 (d, J = 10.0 Hz, 1H), 4.84 (dd, J = 7.7, 3.4 Hz, 1H), 4.18 (dt, J = 7.7, 1.9 Hz, 1H), 4.14 (dd, J = 3.4, 1.9 Hz, 1H), 4.04 (dd, J = 8.6, 6.8 Hz, 1H), 3.84 (dd, J = 8.6, 6.8 Hz, 1H), 2.45 (s, 3H), 1.27 (s, 3H), 1.10 (s, 3H); IR (neat) ν 1769, 1569, 1373, 1352, 1171, 1152, 1051, 820, 665 cm^{-1}; MS (*m/e*) 352, 248, 171, 155, 146, 101, 91(100), 65, 43. Anal. Calcd for $C_{17}H_{21}NO_6S$: C, 55.66; H, 5.92; N, 4.10. Found: C, 55.57; H, 5.76; N, 3.81.

(4*S*,5*R*,1′*R*)-*N*-(*p*-Toluenesulfonyl)-5-(1′,2′-dihydroxylethyl)-4-vinyl-2-oxazolidinone (14). $CuCl_2 \cdot 2H_2O$ (340 mg, 2.0 mmol) was added to a solution of **2n** (367 mg, 1.0 mmol) in CH_3CN (4 mL), and the solution was refluxed for ∼5 h. After the reaction was complete as monitored by TLC, water (10 mL) was added. The mixture was extracted with ethyl acetate (4 × 15 mL). The combined extracts were dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give product **14 (**310 mg, yield 93%) as an oil: $[\alpha]^{20}_D$ = −40.8 (c = 2.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.86 (ddd, J = 8.0, 10.1, 17.9 Hz, 1H), 5.50 (d, J = 17.9 Hz, 1H), 5.38 (d, J = 10.1 Hz, 1H), 4.94 (dd, J = 8.0, 4.2 Hz, 1H), 4.24 (dd, J = 4.2, 2.4 Hz, 1H), 3.79 (d, J = 4.7 Hz, 1H), 3.67 (s, br, 2H), 3.61 (d, J = 4.7 Hz, 1H), 3.07 (s, br, 1H), 2.42 (s, 3H); IR ν (neat) 3519, 3410, 1781, 1597, 1370, 1174, 815, 668 cm^{-1}; MS *m/e* 327, 210, 172, 155, 112, 91 (100), 68, 65. Anal. Calcd for $C_{14}H_{17}NO_6S$: C, 51.64; H, 5.45; N, 4.05. Found: C, 51.37; H, 5.23; N, 4.28.

(4*R*,5*R*,1′*S*)-*N*,*O*-Di(*p*-toluenesulfonyl)-5-(1′-aminoallyl)-4-hydroxymethyl-1,3-dioxolan-2-one (15). To a solution of **14** (310 mg, 0.93 mmol), Bu_2SnO (15 mg, 0.04 mmol), and Et_3N (110 mg, 1.1 mmol) in dry CH_2Cl_2 (15 mL) was added *p*-toluenesulfonyl chloride (188 mg, 1 mmol), and then the mixture was stirred at room temperature. After the reaction was complete as monitored with TLC, the mixture was evaporated under vacuum and purified by column chromatog-

raphy on silica gel (petroleum ether/ethyl acetate = 2/1) to give product **15** (405 mg, yield 91%) as a colorless crystal: mp 120−121 °C; $[\alpha]^{20}_D = +31.0$ ($c = 1.25$, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.3$ Hz, 2H), 5.64 (d, $J = 8.6$ Hz, 1H), 5.53 (ddd, $J = 17.2$, 10.5, 6.7 Hz, 1H), 5.03 (d, $J = 10.5$ Hz, 1H), 4.97 (dt, $J = 5.3$, 2.3 Hz, 1H), 4.92 (d, $J = 17.2$ Hz, 1H), 4.64 (dd, $J = 5.3$, 2.3 Hz, 1H), 4.28 (d, $J = 2.3$ Hz, 2H), 3.98 (t, $J = 6.7$ Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H); IR (neat) ν 3271, 1808, 1598, 1367, 1178, 1094, 667 cm^{-1}; MS *m*/*e* 481 (M^+), 212, 210 (100), 155, 91, 89, 65. Anal. Calcd for $C_{21}H_{23}NO_8S_2$: C, 52.02; H, 5.15; N, 2.68. Found: C, 52.38; H, 4.81; N, 2.91.

(4*R*,5*R*,1′*S*)-*N*-(*p*-Toluenesulfonyl)-5-(1′-aminoallyl)-4-hydroxymethyl-1,3-dioxolan-2-one (16). The mixture of **14** (167 mg, 0.50 mmol) and Et_3N (50 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature. After the reaction was complete as monitored by TLC, the mixture was evaporated under vacuum and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give product **16** (154 mg, yield: 92%) as a colorless crystal: mp 128−129 °C, $[\alpha]^{20}_D = +46.0$ ($c = 0.79$, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 5.89 (d, $J = 8.9$ Hz, 1H), 5.58 (ddd, $J = 17.2$, 10.3, 6.5 Hz, 1H), 5.05 (d, $J = 10.3$ Hz, 1H), 4.96 (d, $J = 17.2$ Hz, 1H), 4.82 (dt, $J = 5.9$, 2.8 Hz, 1H), 4.75 (dd, $J = 5.9$, 2.8 Hz, 1H), 3.99 (m, 2H), 3.77 (m, 1H), 3.2 (t, $J = 6.1$ Hz, 1H), 2.45 (s, 3H); IR (neat) ν 3449, 3247, 1783, 1597, 1330, 1163, 1091, 672 cm^{-1}; MS *m*/*e* 210 (100), 155, 139, 128, 91, 89, 65. Anal. Calcd for $C_{14}H_{17}NO_6S$: C, 51.37; H, 5.23; N, 4.28. Found: C, 51.64; H, 5.27; N, 4.28.

(2*S*,3*R*,4*R*)-*N*-(*p*-Toluenesulfonyl)-2-vinyl-3,4-dihydroxypyrrolidine (18). To a mixture of aqueous NaOH (0.5N, 10 mL) and H_2O/dioxane (1:1, 20 mL) was added **15** (240 mg, 0.5 mmol), and the mixture was stirred at room temperature for about 20 min. After the reaction was complete as monitored with TLC, the mixture was extracted with ethyl acetate (6 × 15 mL). The combined extracts were dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate =1/1) to give product **18** (124 mg, yield 89%) as a colorless crystal; mp: 122−123 °C; $[\alpha]^{20}_D = +77.5$ ($c = 0.55$, MeOH), ^1H NMR ($CDCl_3$) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H), 5.88 (ddd, $J = 17.3$, 10.4, 6.9 Hz, 1H), 5.42 (d, $J = 17.3$ Hz, 1H), 5.38 (d, $J = 10.4$ Hz, 1H), 4.24 (t, $J = 5.8$ Hz, 1H), 4.12 (m, 1H), 3.90 (m, 1H), 3.77 (dd, $J = 11.6$, 4.6 Hz, 1H), 3.33 (dd, $J = 3.0$, 1.4 Hz, 1H), 2.43 (s, 3H), 2.01 (s, br, 1H), 1.84 (s, br, 1H); IR (neat) ν 3487, 3398, 1599, 1332, 1155, 1089, 926, 821, 667 cm^{-1}; MS (*m*/*e*) 283 (M^+), 240, 155, 128, 91, 68 (100), 65, 56, 41. Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.11; H, 6.05; N, 4.94. Found: C, 54.93; H, 6.09; N, 4.84. The stereostructure of **18** was confirmed by X-ray crystallography.[20]

(2*S*,3*R*,4*R*)-*N*-(*p*-Toluenesulfonyl)-2-hydroxymethyl-3,4-dihydroxypyrrolidine (19). Ozone was introduced into a solution of **18** (347 mg, 1.2 mmol) in MeOH (20 mL) using Sudan III as an indicator at −78 °C. When the red solution turned to colorless, $NaBH_4$ (90 mg, 2.4 mmol) was added to the mixture for 10 min at −78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. Saturated NH_4Cl solution (2 mL) was added, and the mixture was concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate) to give product **19** (305 mg, yield 86%) as a colorless crystal. **19**: mp 142−143 °C; $[\alpha]^{20}_D = +19.3$ ($c = 1.30$, EtOH); ^1H NMR (CD_3COCD_3) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 4.07 (dt, $J = 4.0$, 4.2 Hz, 1H), 4.01−3.86 (m, 3H), 3.67−3.56 (m, 2H), 3.30 (s, 3H), 3.20 (dd, $J = 3.6$, 11.0 Hz, 1H), 2.42 (s, 3H); IR (neat) ν 3309, 1599, 1460, 1342, 1154, 1035, 809, 664 cm^{-1}; MS (*m*/*e*) 288 ($M^+ + 1$), 256 (100), 238, 156, 155, 192, 91, 65. Anal. Calcd for $C_{12}H_{17}NO_5S$: C, 50.16; H, 5.96; N, 4.87. Found: C, 50.13; H, 5.87; N, 4.84.

1,4-Dideoxy-1,4-imino-L-xylitol (11). To a solution of $NaNH_2$ (2 mmol) in liquid ammonia (10 mL) was added **19** (62 mg, 0.22 mmol) in THF (1 mL). After the reaction was stirred at −33 °C for 30 min, a saturated NH_4Cl solution (2 mL) was added. The mixture was treated with Dowex 50-8X to give **11** (17 mg, yield 63%) as an oil. **11**: oil; $[\alpha]^{20}_D = -4.0$ ($c = 0.10$, H_2O); ^1H NMR (D_2O) δ 4.07 (m, 1H), 4.01 (m, 1H), 3.68 (ddd, $J = 11.3$, 5.4, 1.2 Hz, 1H), 3.56 (ddd, $J = 11.3$, 7.1, 1.2 Hz, 1H), 3.21 (m, 2H), 2.66 (d, $J = 12.5$ Hz, 1H); ^{13}C NMR (75 MHz, D_2O) δ 79.46, 79.07, 63.66, 62.35, 53.33; MS (*m*/*e*) 134 ($M^+ + 1$), 102, 91, 73, 60, 57, 55 (100), 43; HRMS calcd for $C_5H_{11}NO_3$ 133.0739, found 133.0720.

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Supporting Information Available: ^1H NMR spectrum of compounds **2l**, (*E*)-**6l**, and (*Z*)-**6l**, ^1H NMR and ^{13}C NMR spectra of **11**, and X-ray crystallographic data for **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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