Protecting-Group-Free Route to Hydroxylated Pyrrolidine and Piperidine Derivatives through Cu(I)-Catalyzed Intramolecular Hydroamination of Alkenes

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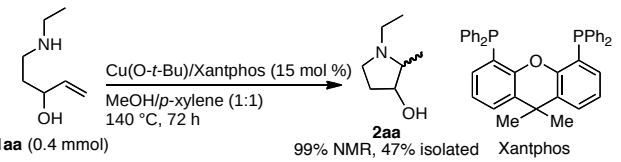
Abstract: An efficient approach to hydroxylated pyrrolidine and piperidine derivatives through the intramolecular hydroamination catalyzed by a Cu(I)–Xantphos system is described. The transformation allows for the short synthesis of *N*-alkylated azasugars without a protection/deprotection event of the hydroxy groups.

Key words: pyrrolidine, piperidine, protecting-group-free synthesis, hydroamination, copper

Polyhydroxylated pyrrolidine and piperidine derivatives, commonly called azasugars, have attracted considerable attention and have been the target of numerous synthetic efforts due to their potent glycosidase and glycosyltransferase inhibitory activities.[1] Intramolecular cyclization of highly hydroxylated aminoalkenes is one of the simplest methods for the construction of these nitrogen heterocycles. However, these synthetic sequences *via* the intramolecular cyclization require intricate protecting group manipulations of the hydroxy groups, which lead to lengthy syntheses and reduced atom economy.[1d] We reported earlier that the Cu(I)–Xantphos system catalyzes the intramolecular hydroamination of unactivated terminal alkenes bearing an aminoalkyl substituent in alcoholic mixed solvents, giving pyrrolidine and piperidine derivatives in excellent yields.[2,3,4,5] Given that alcoholic solvents are used, we anticipated that aminoalkenes with protecting group free hydroxy groups within the carbon chain tethering the amine and alkene moieties may be usable as substrates of the copper-catalyzed hydroamination, which leads directly to hydroxylated nitrogen heterocycles, while the removing the Thorpe-Ingold effect by the geminal substituents within the tethering carbon chain was a challenge. Here we report a protecting-group-free approach to hydroxylated pyrrolidine and piperidine derivatives with various *N*-alkyl substituents through the Cu(I)-catalyzed intramolecular hydroamination of terminal alkenes as a key step.[6,7]

The reaction of ω-alkenic secondary amine **1aa** bearing a hydroxy group at the allylic position proceeded in the presence of Cu(O-*t*-Bu) (15 mol %) and Xantphos (15 mol %) in MeOH/*p*-xylene (1:1) at 140 ˚C, affording the monohydroxy pyrrolidine derivative **2aa** in 99% NMR yield (47% isolated yield, dr 86:14) after 72 h reaction time (Scheme 1). The ^{1}H NMR analysis of the crude mixture indicated that the reaction proceeded cleanly, while the isolated yield remained 47% because of the material loss during Kugelrohr distillation. Relative stereochemistry of the diastereomers is yet to be determined (NOE and coupling constant analyses are ambiguous) (Procedure A).[8]

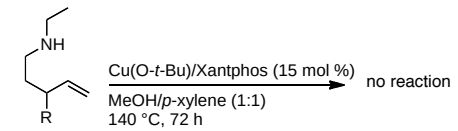


1aa (0.4 mmol) **2aa** 99% NMR, 47% isolated Xantphos

Scheme 1

Since Cu(O-*t*-Bu) is not commercially available, we also examined a copper catalyst system in-situ prepared from commercial sources as more convenient catalyst system, and found that the reaction could also be performed well by using CuOAc (15 mol %) and K(O-*t*-Bu) (23 mol %) instead of Cu(O-*t*-Bu) (99% NMR yield, dr 76:24) (Procedure B).[8] In all cases we examined with different substrates, the both catalyst systems performed almost equally concerning the product yield, while slight deviation in diastereoselectivity was observed.

Interestingly, the aminoalkene (**1a'a**) without the substituents in the linker chain resisted the reaction (Scheme 2).[5] The aminoalkene (**1a''a**) bearing a TBDMS-protected hydroxy group was also unreactive. These results indicate that the free hydroxy group plays an important role in accelerating the intramolecular hydroamination. The impact of the hydroxy group may be comparable to the Thorpe-Ingold-type steric effects observed in our earlier study [*vide infra* (Table 2, entry 6) for similar effect of hydroxy groups at the homoallylic and bishomoallylic positions].[5]



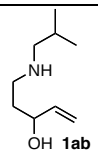
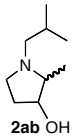
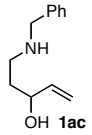
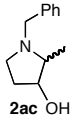
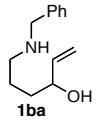
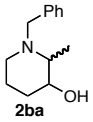
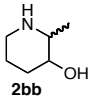
R = H (**1a'a**)
R = OTBDMS (**1a''a**)

Scheme 2

Various monohydroxy aminoalkenes (**1ab**, **ac**, **ba**, **bb**), which are different in the *N*-substituent and in length of the tethering carbon chain were transformed into the corresponding nitrogen heterocycles (**2ab**, **ac**, **ba**, **bb**) in the presence of the Cu–Xantphos system [Cu(O-*t*-Bu)–Xantphos or CuOAc–K(O-*t*-Bu)–Xantphos] (Table 1, Procedures A and B).[8] Thus, the aminopentenes (**1ab**, **ac**) with *N*-*i*-Bu and *N*-Bn groups underwent hydroamination in good yields, giving the corresponding pyrrolidine derivatives **2ab** and **2ac**,[14] respectively (Table 1, entries 1 and 2). Piperidine derivatives were also obtainable by the Cu-catalyzed hydroamination of the substrate with a longer tethering chain (**1ba**) (entry 3). However,

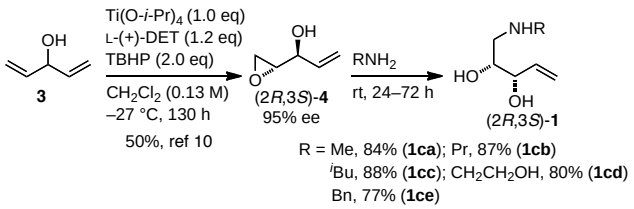
the reaction of the primary amine (**1bb**) to yield the *N*-unsubstituted 2-hydroxy piperidine (**2bb**) resulted in a lower yield (22%, *trans*/*cis* 82:18[9]) (entry 4).

Table 1 Synthesis of Monohydroxylated Pyrrolidines and Piperidines

entry	aminoalkene	product	yield (%)[a,b]	dr[c]
1[d]	 **1ab**	 **2ab**	51 (99)	80:20
2[e]	 **1ac**	 **2ac**	76 (99)	69:31
3[e]	 **1ba**	 **2ba**	61 (99)	73:27
4[f]	 **1bb**	 **2bb**	(22)	82:18

[a]Isolated yield. The yield in parentheses was determined by ^{1}H NMR. [b]The products were isolated by Kugelrohr distillation. [c]Diastereomeric ratio. Determined by ^{1}H NMR. [d]Conditions: CuOAc (15 mol %), Xantphos (15 mol %), K(O-*t*-Bu) (23 mol %), **1** (0.4 mmol), MeOH/*p*-xylene (1:1, 0.8 mL), 140 ˚C, 72 h. [e]Conditions: Cu(O-*t*-Bu) (15 mol %), Xantphos (15 mol %), **1** (0.4 mmol), MeOH/*p*-xylene (1:1, 0.8 mL), 140 ˚C, 72 h. [f]Conditions: Cu(O-*t*-Bu) (15 mol %), Xantphos (15 mol %), **1** (0.4 mmol), MeOH/*p*-xylene (1:1, 1.8 mL), 140 ˚C, 72 h.

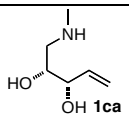
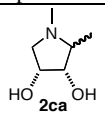
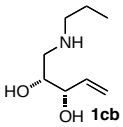
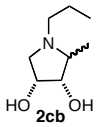
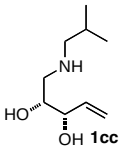
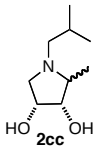
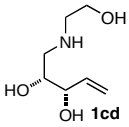
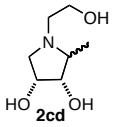
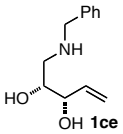
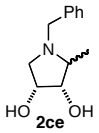
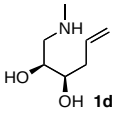
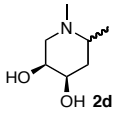
Next, we investigated the synthesis of dihydroxylated *N*-alkylpyrrolidine derivatives. The chiral 3,4-dihydroxylated 1-amino-5-pentene substrates (**1ca**–**ce**) with different *N*-alkyl groups were readily prepared from 1,4-pentadien-3-ol (**3**) without the need for protecting groups (Scheme 3). Thus, according to the literature, (2*R*,3*S*)-1,2-epoxy-4-penten-3-ol (**4**, 95% ee) was prepared through the enantiotopos selective Sharpless oxidation of **3** with the Ti(O-*i*-Pr)$_4$/L-(+)-DET/TBHP (1 eq of Ti) in 50% yield.[10] Subsequent ring-opening with various primary amines provided the aminoalkene substrates (**1ca**–**ce**) with good to high yields.



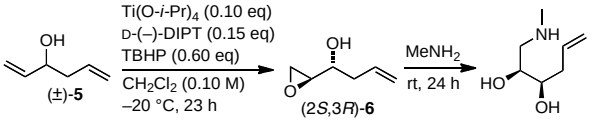
Scheme 3

The dihydroxylated alkene **1ca**–**cd** underwent the hydroamination with an increased catalyst loading (20 mol % Cu), providing dihydroxylated pyrrolidine derivatives (**2ca**–**cd**) with a high diastereoselectivity (>20:1) (Table 2, Procedures A and B).[8,15] Thus, substituents such as Me, Pr, *i*-Bu and hydroxylethyl groups were tolerated at the nitrogen atom (entries 1–4). On the other hand, the reaction of the aminopentene (**1ce**) with an *N*-benzyl group resulted in a low conversion (entry 5).

Table 2 Synthesis of Dihydroxylated Pyrrolidines and Piperidines

entry	aminoalkene	product	yield (%)[a]	dr[b]
1[c]	 **1ca**	 **2ca**	51[e] (99)	>20:1
2[d]	 **1cb**	 **2cb**	47[f] (55)	>20:1
3[d]	 **1cc**	 **2cc**	43[f] (45)	>20:1
4[c]	 **1cd**	 **2cd**	(56)	>20:1
5[c]	 **1ce**	 **2ce**	trace	–
6[d]	 **1d**	 **2d**	41[e] (99)	62:38

[a]Isolated yield. The yield in parentheses was determined by ^{1}H NMR. [b]Diastereomeric ratio. Determined by ^{1}H NMR. [c]Conditions: Cu(O-*t*-Bu) (20 mol %), Xantphos (20 mol %), **1** (0.4 mmol), MeOH/*p*-xylene (1:1, 0.8 mL), 140 ˚C, 72 h. [d]Conditions: CuOAc (20 mol %), Xantphos (20 mol %), K(O-*t*-Bu) (30 mol %), **1** (0.4 mmol), MeOH/*p*-xylene (1:1, 0.8 mL), 140 ˚C, 72 h. [e]The product was isolated by Kugelrohr distillation. [f]The product was isolated by PTLC (silica gel, MeOH).

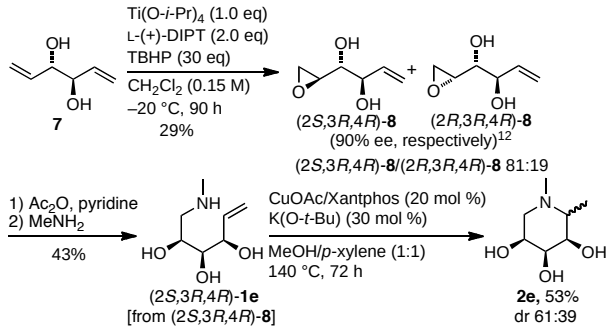


Scheme 4

Extension of the protecting-group-free protocol to the synthesis of a piperidine derivative, 3,4-dihydroxy-1,6-dimethylpiperidine (**2d**) was feasible by replacing the epoxidation substrate **3** with its one-carbon homologue (±)-**5** (Scheme 4 and Table 1, entry 6). Thus, the Sharpless kinetic resolution[11] of dienyl alcohol (±)-**5** with Ti(O-*i*-Pr)$_4$/D-(–)-DIPT/TBHP (0.1 eq of Ti) system afforded (2*S*,3*R*)-1,2-epoxy-5-hexen-3-ol (**6**) with 99% ee in 35% yield [based on (±)-**5**]. Subsequent ring-opening with methylamine provided the hydroamination precursor (2*S*,3*R*)-**1d** in 65% yield (Scheme 4). The Cu-

catalyzed hydroamination of (2*S*,3*R*)-**1d** afforded the corresponding piperidine derivatives (**2d**) as 62:38 diastereomer mixture (Table 1, entry 6, Procedure B).[8,16] The successful intramolecular hydroamination of **1d** indicates that the effect of a free hydroxy group to accelerate cyclization can operate even at the homoallylic or bishomoallylic positions, which are virtually not electronically associated with the alkene moiety. Hence, the effect of the hydroxy groups is likely to be due to an entropic factor.

A route to a trihydroxy-*N*-methylpiperidine derivative (**2e**) is outlined in Scheme 5. The Sharpless asymmetric oxidation of *meso*-1,2-divinylethylene glycol (**7**) with Ti(O-*i*-Pr)$_4$/L-(+)-DIPT/TBHP (1 eq of Ti) system afforded a diastereomeric mixture (dr 81:19) of optically active epoxides (2*S*,3*R*,4*R*)-**8** (90% ee) and (2*R*,3*R*,4*R*)-**8** (90% ee).[12] Temporary diacetylation of the diol epoxides allowed for the isolation of the major isomer by silica gel chromatography. The treatment of the diacetoxy epoxide with MeNH$_2$ caused epoxide ring-opening and simultaneous deacetylation to provide the chiral aminotriol [(2*S*,3*R*,4*R*)-**1e**] with a terminal alkene moiety. The copper-catalyzed hydroamination of **1e** under the conditions identical to those for Table 2, entries 2–4 and 6 furnished the corresponding trihydroxylated piperidine derivative (**2e**) in 53% yield (dr 61:39) after extraction with H$_2$O followed by concentration to dryness (Procedure C).[13,17,18]



Scheme 5

In summary, we have developed protecting-group-free routes to a variety of hydroxylated pyrrolidine and piperidine derivatives by way of the Cu(I)-catalyzed intramolecular hydroamination of aminoalcohols with a terminal alkene moiety. The presence of one or more free hydroxy groups in the tethering chain connecting the amine and alkene moieties was beneficial for the cyclization to proceed efficiently. Having flexibility in introducing different *N*-alkyl groups in the substrate preparation and a broad tolerance of the copper catalysis toward various *N*-alkyl groups, the present approach would possibly be a useful alternative to the existing methods for the preparation of *N*-alkylazasugars.

Acknowledgement

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References and Notes

(1) For reviews: (a) *Iminosugars as Glycosidase Inhibitors-Nojirimycin and Beyond*; Stütz, A. E., Ed.; Wiley-VCH: Weinheim Germany, **1999**. (b) Asano, N.; Nash, R. J.; Molyneux, R. J.; Fleet, G. W. *Tetrahedron: Asymmetry.* **2000**, *11*, 1645–1680. (c) Lillelund, V. H.; Jensen, H. H.; Liang, X.; Bols, M. *Chem. Rev*. **2002**, *102*, 515–553. (d) Pearson, M. S. M.; Mathe-Allainmat, M.; Fargeas, V.; Lebreton, J. *Eur. J. Org. Chem.* **2005**, 2159–2191.

(2) For reviews on the hydroamination of alkenes and alkynes, see: (a) Müller, T. E.; Beller, M. *Chem. Rev*. **1998**, *98*, 675–703. (b) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev*. **2008**, *108*, 3795–3892.

(3) For late transition metal catalyzed intramolecular hydroaminations of aminoalkenes bearing a protecting-group-free hydroxy group, see: Rh: (a) Liu, Z.; Hartwig, J. F. *J. Am. Chem. Soc*. **2008**, *130*, 1570–1571. Pt: (b) Han, X.; Widenhoefer, R. A. *Angew. Chem Int. Ed*. **2006**, *45*, 1747–1749. Pd: (c) Michael, F. E.; Cochran B. M. *J. Am. Chem. Soc*. **2006**, *128*, 4246–4247.

(4) For intramolecular amidomercurations of amidoalkenes bearing a protecting-group-free free hydroxy group, see: (a) Singh, S.; Chikkanna, D.; Singh, O. V.; Han, H. *Synlett* **2003**, 1279–1282. (b) Chikkanna, D.; Han, H. *Synlett* **2004**, 2311–2314. See also ref 2.

(5) Ohmiya, H.; Moriya, T.; Sawamura, M. *Org. Lett.* **2009**, *11*, 2145–2147.

(6) For reviews on the protecting-group-free synthesis, see: (a) Hoffmann, R. W. *Synthesis* **2006**, 3531–3541. (b) Young, I. S.; Baran, P. S. *Nature Chem.* **2009**, *1*, 193–205.

(7) For a synthesis of hydroxypyrrolidines without protecting groups, see: Dangerfield, E. M.; Timmer, M. S. M.; Stocker, B. L. *Org. Lett.* **2009**, *11*, 535–538.

(8) **General Procedure for the Cu(I)-Catalyzed Hydroamination of Aminoalkene [Procedure A with Cu(O-*t*-Bu)–Xantphos, Scheme 1, Tables 1 and 2].** In a glove box, Cu(O-*t*-Bu) (0.06 mmol, 8.2 mg or 0.08 mmol, 10.9 mg) and Xantphos (0.06 mmol, 34.7 mg or 0.08 mmol, 46.3 mg) were placed in a screw vial. Anhydrous, degassed mixed solvent, MeOH/*p*-xylene (1:1, 0.4 mL) was added and stirred at room temperature for 10 min to give a pale yellow solution. A solution of a hydroxylated aminoalkene (0.4 mmol) in MeOH/*p*-xylene (1:1, 0.4 mL) was added. The vial was sealed with a screw cap, and was removed from the glove box. The mixture was stirred and heated at 140 °C for 72 h. The reaction mixture was cooled to room temperature and concentrated. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product was determined by ^{1}H NMR. Purification by Kugelrohr distillation or preparative thin-layer chromatography (silica gel, MeOH) gave the desired product in a practically pure form. **General Procedure for the Cu(I)-Catalyzed Hydroamination of Aminoalkene [Procedure B with CuOAc–K(O-*t*-Bu)–Xantphos, Tables 1 and 2].** In a

glove box, CuOAc (0.06 mmol, 7.4 mg or 0.08 mmol, 9.8 mg), Xantphos (0.06 mmol, 34.7 mg or 0.08 mmol, 46.3 mg) and K(O-*t*-Bu) (0.09 mmol, 12.3 mg or 0.12 mmol, 16.4 mg) were placed in a screw vial. Anhydrous, degassed mixed solvent, MeOH/*p*-xylene (1:1, 0.4 mL) was added and stirred at room temperature for 10 min to give a pale yellow solution. The following procedure is identical to that described above.

(9) The relative stereochemistry of **2bb** was assigned according to the literature. See: Andrés, J. M.; Pedrosa, R.; Pérez-Encabo, A. *Eur. J. Org. Chem.* **2007**, 1803–1810.

(10) The enantiomeric excess of (2*R*,3*S*)-**4** (95% ee) was determined by chiral HPLC analysis of the *p*-nitrobenzoate derivative. See: Jäger, V.; Hümmer, W.; Stahl, U.; Gracza, T. *Synthesis* **1991**, 769–776.

(11) The ee value of (2*S*,3*R*)-**6** (99% ee) was determined by the Mosher's NMR spectroscopic method. See: Crimmins, M. T.; Powell, M. T. *J. Am. Chem. Soc.* **2003**, *125*, 7592–7595.

(12) The epoxides **8** were prepared according to the reported procedure. The enantiomeric excess of **8** has not been determined in our hand. See: Takano, S.; Iwabuchi, Y.; Ogasawara, K. *J. Am. Chem. Soc.* **1991**, *113*, 2786–2787.

(13) The isolated **2e** was contaminated with unidentified materials. See experimental procedure in Note 17.

(14) **1-Benzyl-3-hydroxy-2-methylpyrrolidine (2ac) (69:31 mixture of diastereomers).** Viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) For major isomer: δ 1.22 (d, *J* = 6.3 Hz, 3H), 1.66 (m, 1H), 1.97–2.16 (m, 2H), 2.30 (m, 1H), 2.93 (ddd, *J* = 11.1, 8.4, 2.1 Hz, 1H), 3.10 (d, *J* = 12.9 Hz, 1H), 4.02 (d, *J* = 12.9 Hz, 1H), 4.03 (m, 1H), 7.23–7.35 (m, 5H). For minor isomer: δ 1.18 (d, *J* = 6.3 Hz, 3H), 1.53 (m, 1H), 1.97–2.16 (m, 2H), 2.41 (m, 1H), 2.79 (ddd, *J* = 11.4, 8.7, 2.4 Hz, 1H), 3.29 (d, *J* = 12.9 Hz, 1H), 3.89 (m, 1H), 3.94 (d, *J* = 12.9 Hz, 1H), 7.23–7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.84 16.25, 32.22, 32.84, 50.89, 51.24, 57.51, 57.77, 63.85, 67.26, 74.31, 78.22, 126.98, 127.01, 128.27 (×2), 128.98, 129.03, 138.99, 139.04. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{12}H_{18}ON$, 192.1382; found, 192.1381.

(15) **(3*S*,4*R*)-3,4-Dihydroxy-1,2-dimethylpyrrolidine (2ca) (>20:1 mixture of diastereomers).** Viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.6 Hz, 3H), 2.26 (s, 3H), 2.31 (m, 1H), 2.42 (dd, *J* = 11.0, 6.9 Hz, 1H), 2.97 (dd, *J* = 11.0, 2.7 Hz, 1H), 4.00 (dd, *J* = 6.3, 5.2 Hz, 1H), 4.22 (ddd, *J* = 6.9, 6.3, 2.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.27, 39.84, 63.42, 65.02, 69.53, 73.37. HRMS-FAB (m/z): $[M+H]^+$ calcd for $C_6H_{13}O_2N$, 131.0946; found, 132.1032. $[\alpha]_D^{27}$ +37.0 (*c* 0.6, MeOH).

(16) **(4*R*,5*S*)-4,5-Dihydroxy-1,2-dimethylpiperidine (2d) (62:38 mixture of diastereomers).** Viscous oil. ^{1}H NMR (300 MHz, CD_3OD) For major isomer: δ 1.10 (d, *J* = 6.3 Hz, 3H), 1.54–1.67 (m, 2H), 2.18–2.41 (m, 2H), 2.19 (s, 3H), 2.91 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.55 (m, 1H), 3.77 (m, 1H). For minor isomer: δ 1.04 (d, *J* = 6.3 Hz, 3H), 1.44 (ddd, *J* = 14.7, 11.8, 2.7 Hz, 1H), 1.77 (dt, *J* = 14.7, 3.6 Hz, 1H), 2.18–2.41 (m, 2H), 2.27 (s, 3H), 2.62 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.65 (m, 1H), 3.90 (m, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ 19.38, 20.25, 37.71, 40.50, 42.57, 43.15, 53.45, 57.39, 58.89, 61.80, 68.61, 69.61, 69.70, 70.95. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_7H_{15}O_2N$, 145.1103; found, 146.1179. $[\alpha]_D^{27}$ +19.8 (*c* 1.0, MeOH).

(17) **Procedure for the synthesis of trihydroxylated piperidine 2e (Procedure C, Scheme 5).** In a glove box, CuOAc (0.04 mmol, 4.9 mg), Xantphos (0.04 mmol, 23.1 mg) and K(O-*t*-Bu) (0.06 mmol, 8.2 mg) were placed in a screw vial. Anhydrous, degassed mixed solvent, MeOH/*p*-xylene (1:1, 0.2 mL) was added and stirred at room temperature for 10 min to give a pale yellow solution. A solution of **1e** (0.2 mmol) in MeOH/*p*-xylene (1:1, 0.2 mL) was added. The vial was sealed with a screw cap, and was removed from the glove box. The mixture was stirred and heated at 140 °C for 72 h. The reaction mixture was cooled to room temperature and concentrated. The residue was dissolved in ethyl acetate (5 mL) and H_2O (5 mL). The mixture was extracted with H_2O (5 mL×3). The combined aqueous layers were evaporated under reduced pressure to give a pale yellow oil (25.5 mg). ^{1}H NMR analysis of the material using *t*-BuOH as an internal standard indicated that the yield and purity of **2e** were 53% (17.7 mg) and 67%, respectively.

(18) **(3*R*,4*S*,5*S*)-3,4,5-Trihydroxy-1,2-dimethylpiperidine (2e) (61:39 mixture of diastereomers).** Oil. ^{1}H NMR (600 MHz, D_2O) For major isomer: δ 1.14 (d, *J* = 6.6 Hz, 3H), 2.25 (m, 1H), 2.28 (s, 3H), 2.41 (m, 1H), 2.66 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.26 (m, 1H), 3.72 (m, 1H), 4.02 (m, 1H). For minor isomer: δ 1.17 (d, *J* = 6.6 Hz, 3H), 2.19 (s, 3H), 2.25 (m, 1H), 2.35 (d, *J* = 12.6 Hz, 1H), 2.41 (m, 1H), 2.96 (m, 1H), 3.72 (m, 1H), 3.97 (m, 1H). HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_7H_{16}O_3N$, 162.11247; found, 162.11242.