A Concise Synthesis of (2*S*,3*S*,4*S*)-2-(Hydroxymethyl)pyrrolidine-3,4-diol (LAB1)

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Abstract: The synthesis of (2*S*,3*S*,4*S*)-2-(hydroxymethyl)pyrrolidine-3,4-diol (LAB1) from Garner's aldehyde is described using the Sharpless asymmetric dihydroxylation as the key step.

Key words: Garner's aldehyde, Wittig reaction, diastereoselectivity, alkaloid, azasugars, pyrrolidine

Hydroxylated pyrrolidines constitute one of the main classes of naturally occurring sugar mimics having nitrogen in the ring.[1] Among them, 1,4-dideoxy-1,4-imino-D-arabinose and -D-ribose are naturally occurring imino sugars exhibiting activity as glycosidase inhibitors.[2] Much attention has been focused on this class of compounds because of their potential for therapeutic applications and also their role as glycosidase inhibitors.[3]

α-Amino aldehydes are versatile building blocks that are frequently used in the synthesis of natural products.[4] Adducts of α-amino aldehydes and acetylenic compounds are easily transformed into a variety of chiral natural products containing many contiguous stereogenic centers. Among these products are glycosidic antibiotics,[5] cytostatic,[6] antihelmintic,[7] as well as antiviral compounds.[8]

Various synthetic methods for the synthesis of hydroxy-substituted pyrrolidines have been reported either from carbohydrates,[9] as a chiral pool starting material, or from other sources.[10] The syntheses of target molecule LAB1 (**1**) described in the literature use either carbohydrate,[11a,b] enzyme,[11c] amino acid,[11d] tartaric acid,[11e] or miscellaneous approaches.[11f] Surprisingly there has been no report of its synthesis from Garner's aldehyde. As part of our research on the enantioselective synthesis of naturally occurring amino alcohols,[12] we aimed to synthesize an intermediate such as LAB1 from an α-amino aldehyde, which could be useful in the synthesis of variety of compounds, such as **2**–**5**, of biological interest (Figure 1).

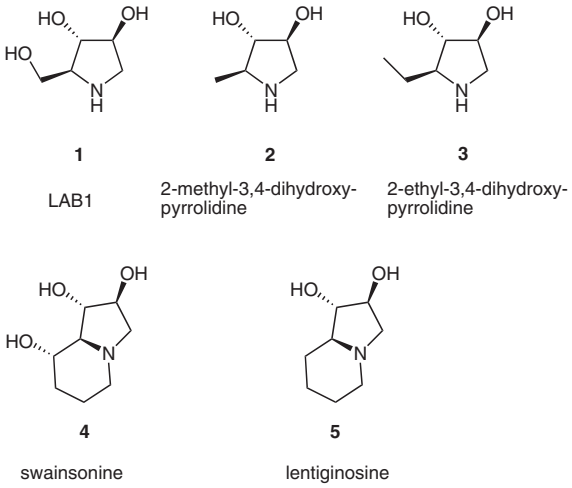
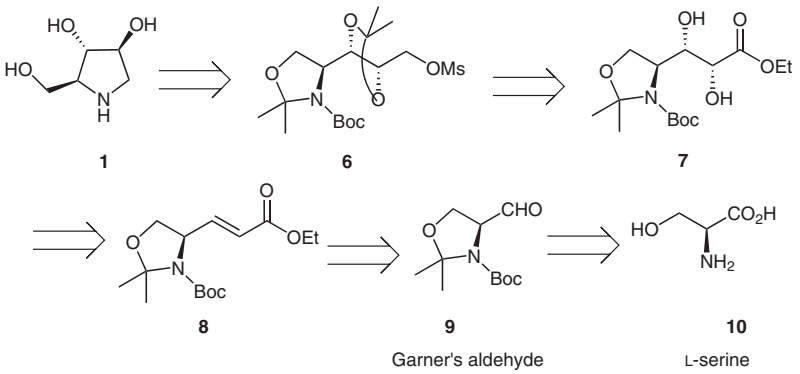


Figure 1 Structures of polyhydroxylated pyrrolidine and indolizidine alkaloids

A synthetic approach for the synthesis of (2*S*,3*S*,4*S*)-2-(hydroxymethyl)pyrrolidine-3,4-diol (1,4-dideoxy-1,4-imino-L-arabinitol, LAB1, **1**) was envisioned via the synthetic route shown in Scheme 1.



Scheme 1 Retrosynthetic analysis of LAB1 (**1**)

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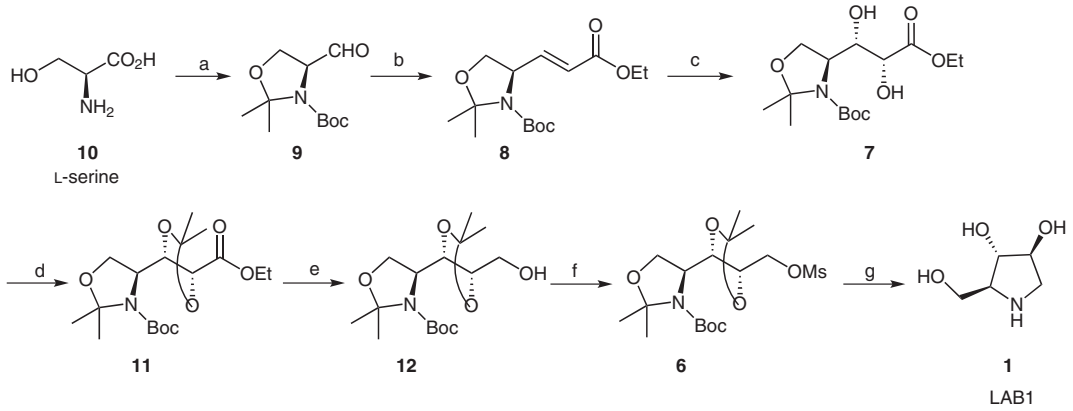

Scheme 2 Synthesis of LAB1 (**1**). *Reagents and conditions*: (a) (i) Boc_2O, 1 M NaOH, dioxane, H_2O, 0 °C to r.t., 3.5 h; (ii) MeI, K_2CO_3, DMF, 0 °C to r.t., 2 h, 86%; (iii) 2,2-DMP, acetone, $BF_3{\cdot}OEt_2$, 2 h, 90%; (iv) DIBAL-H, –78 °C, anhyd toluene, 1–2 h, 75%; (b) $Ph_3P{=}CHCO_2Et$, anhyd THF, 60 °C, 5 h, 90%; (c) OsO_4, $(DHQ)_2PHAL$, $K_3Fe(CN)_6$, K_2CO_3, $MsNH_2$, *t*-BuOH–H_2O, 0 °C, 24 h, 92%; (d) 2,2-DMP, TsOH, anhyd toluene, reflux, 30 min, 96%; (e) $LiAlH_4$, anhyd THF, 0 °C to r.t., 1 h, 75%; (f) MsCl, Et_3N, DMAP, anhyd CH_2Cl_2, 0 °C, 2 h, 81%; (g) 2 M HCl, EtOAc, 0 °C, 3 h, then sat. $NaHCO_3$ soln (to pH 8), 1 h, 69%.

As depicted in Scheme 1, the target molecule LAB1 (**1**) could be obtained from mesylate **6**, which in turn could be accessed from α,β-diol ester **7**. Compound **7** would be prepared by dihydroxylation of olefin **8**, which in turn could be synthesized from Garner's aldehyde **9** derived from L-serine (**10**).

The synthesis of target molecule LAB1 (**1**) began from commercially available chiral pool starting material L-serine (Scheme 2). Following the literature procedure, Garner's aldehyde **9** was prepared from L-serine in 58% overall yield.[13] The freshly prepared Garner's aldehyde **9** was subjected to two-carbon homologation by Wittig reaction to give the olefinic ester **8** in 90% yield. We carried out dihydroxylation reaction under Sharpless asymmetric conditions[14] using $(DHQ)_2PHAL$ ligand and osmium tetroxide to produce dihydroxy ester **7** in 92% yield.[15] Acetonide protection of compound **7** with 2,2-dimethoxypropane (2,2-DMP) in the presence of a catalytic amount

Biographical Sketches

Puspesh Kumar Upadhyay was born in India in 1976. He obtained his B.Sc. and M.Sc. degrees from Purvanchal University, Jaunpur (UP), India. After that, he gained research experience as a project assistant in various projects in the group of Dr. Pradeep Kumar at the National Chemical Laboratory, Pune, India, from 2001–2004. Subsequently he joined the same group as a senior research scholar for his doctoral thesis in 2005. He obtained his Ph.D. degree from Pune University, Pune, India in 2010 under the supervision of Dr. Pradeep Kumar. At present (since February 2010) he is working in the Laxai Pharma Company, Hyderabad in the Discovery Division as an Associate Scientist.

Pradeep Kumar was born and grew up in India. He received his B.Sc. and M.Sc degrees from Gorakhpur University. In 1981, he obtained his Ph.D. degree under the supervision of the late Professor Arya K. Mukerjee. Subsequently he joined the National Chemical Laboratory, Pune, India in 1982. He has been working in the Organic Chemistry Division as Scientist G since 2008. He visited Germany and worked in the group of Professor H. J. Bestmann at the Institute of Organic Chemistry, University of Erlangen, Nuremberg during 1988–1990 as a DAAD fellow and later as an Alexander von Humboldt fellow with Professor Richard R. Schmidt at the University of Konstanz, Germany (1996–1997), with Professor Martin E. Maier at the University of Tuebingen, Germany (2003), with Professor J. Rademann at Leibniz Institute for Molecular Pharmacology (FMP), Berlin, Germany (2006 and 2010). He has published over 140 papers and a few review articles in international journals of repute. He is a fellow of the National Academy of Sciences of India. He is recipient of the bronze medal (2009–2010) of chemical research society of India. His research interest includes the development of new methodologies, synthesis of biologically active natural products, and solid catalyst induced synthetic organic transformation.

of 4-toluenesulfonic acid furnished **11** in essentially quantitative yield. The ester moiety of compound **11** was reduced with lithium aluminum hydride to give the amino alcohol **12** in 75% yield, which on treatment with methanesulfonyl chloride using a catalytic amount of 4-(dimethylamino)pyridine gave the mesylated compound **6** in 81% yield.

Finally, global deprotection of **6** with 2 M hydrochloric acid followed by subsequent cyclization gave the target molecule **1** in 69% yield. The spectral properties (^{1}H and ^{13}C NMR) of **1** were in full agreement with those reported in the literature.[11f]

In summary, we have achieved a short synthesis of (2*S*,3*S*,4*S*)-2-(hydroxymethyl)pyrrolidine-3,4-diol (LAB1) in seven steps in 19% overall yield starting from L-serine and using the Sharpless asymmetric dihydroxylation as the key step.

All reactions were carried out under argon or N_2 in oven-dried glassware using standard gas-light syringes, cannulas, and septa. Solvents and reagents were purified and dried by standard methods prior to use. The progress of all the reactions was monitored by TLC using aluminum plates precoated with silica gel 60 F254 (0.25 mm, Merck). Column chromatography was performed on silica gel (60–120 mesh) using petroleum ether–EtOAc mixtures as the eluent. Petroleum ether (PE) refers to the fraction with bp 60–80 °C. Optical rotations were measured on a Jasco DIP-360 digital polarimeter at 25 °C. IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200, AC-400, and AC-500 spectrometer at 200 MHz, 400 MHz, or 500 MHz (^{1}H) and at 50 MHz, 100 MHz, or 125 MHz (^{13}C) with $CDCl_3$ as internal standard. ESI-MS were obtained using an API-Q-Star Applied Biosystems spectrometer. Elemental analysis was carried out on a Carlo Erba CHNSO analyzer.

Ethyl (*E*)-3-[(*R*)-3-(*tert*-Butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl]propenoate (8)

To a soln of $Ph_3P{=}CHCO_2Et$ (1.83 g, 5.24 mmol) in anhyd THF (15 mL) was added a soln of freshly prepared Garner's aldehyde **9** (0.8 g, 3.45 mmol) in anhyd THF (5 mL). The mixture was stirred at 60 °C for 5 h. It was then concentrated and purified by column chromatography (silica gel, PE–EtOAc, 9.5:0.5) to give **8** as a yellow oil; yield: 0.94 g (90%).

$[\alpha]_D^{25}$ –44.02 (*c* 1.09, $CHCl_3$) [Lit.[15] $[\alpha]_D^{20}$ –44.3 (*c* 1.09, $CHCl_3$)].

IR ($CHCl_3$): 1712 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.08 Hz, 3 H), 1.40–1.61 (m, 15 H), 3.74–3.80 (m, 1 H), 4.03–4.11 (m, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 4.39–4.52 (m, 1 H), 5.87 (d, *J* = 15.4 Hz, 1 H), 6.75–6.86 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.5, 25.1, 28.2, 60.5, 65.7, 72.3, 80.2, 105.5, 121.2, 137.1, 150.5, 165.8.

Ethyl (2*R*,3*S*)-3-[(*S*)-3-(*tert*-Butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl]-2,3-dihydroxypropanoate (7)

To a mixture of $K_3Fe(CN)_6$ (6.94 g, 21.1 mmol), K_2CO_3 (2.91 g, 21.1 mmol), and $(DHQ)_2PHAL$ (60 mg, 1 mol%) in *t*-BuOH–H_2O (1:1, 35 mL) cooled to 0 °C was added 1 M OsO_4 in toluene (0.3 mL, 0.4 mol%) followed by $MsNH_2$ (0.7 g, 7.02 mmol). The mixture was stirred at 0 °C for 5 min and then the olefin **8** (2.10 g, 7.02 mmol) was added in one portion. The mixture was stirred at 0 °C for 24 h and then quenched with solid Na_2SO_3 (10.5 g). Stirring was continued for an additional 45 min, and then the soln was extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with 10% KOH soln and brine, dried (Na_2SO_4), and concentrated. The crude product was subjected to column chromatography (silica gel, PE–EtOAc, 80:20) to give **7** as a colorless syrupy liquid; yield: 2.15 g (92%).

$[\alpha]_D^{25}$ –22.03 (*c* 0.82, $CHCl_3$) [Lit.[15] $[\alpha]_D^{20}$ –21.2 (*c* 0.82, $CHCl_3$)].

IR ($CHCl_3$): 3435, 1719 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.20 Hz, 3 H), 1.48–1.56 (m, 15 H), 3.86–3.94 (m, 2 H), 3.99–4.05 (m, 1 H), 4.14–4.20 (m, 2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.73 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 23.8, 28.1, 58.6, 61.3, 65.2, 70.4, 72.8, 81.7, 94.0, 154.3, 171.4.

MS (ESI): *m*/*z* = 334 (M^+ + 1), 356 (M^+ + Na), 372.3 (M^+ + K).

Ethyl (2*R*,3*S*)-3-[(*S*)-3-(*tert*-Butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl]-2,3-(isopropylidenedioxy)propanoate (11)

To a soln of the diol **7** (0.5 g, 1.51 mmol) in anhyd toluene (16 mL) was added 2,2-dimethoxypropane (5 mL) and $TsOH{\cdot}H_2O$ (6.3 mg, 0.03 mmol). The mixture was refluxed for 30 min and then treated with sat. aq $NaHCO_3$ (10 mL). The separated organic layer was dried (Na_2SO_4) and the solvent was concentrated in vacuo. The crude residue was chromatographed (silica gel, PE–EtOAc, 95:0.5) to give **11** as a white solid; yield: 0.54 g (96%); mp 52–54 °C (Lit.[15] 54–56 °C).

$[\alpha]_D^{25}$ –15.21 (*c* 1.04, $CHCl_3$) [Lit.[15] $[\alpha]_D^{20}$ –15.4 (*c* 1.04, $CHCl_3$)].

IR ($CHCl_3$): 2984, 1746 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.2 Hz, 3 H), 1.39–1.56 (m, 21 H), 3.89–3.97 (m, 1 H), 4.04–4.20 (m, 4 H), 4.9 (d, *J* = 6.2 Hz, 1 H), 4.27–4.32 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 25.8, 27.0, 28.2, 59.4, 61.1, 65.2, 78.7, 80.5, 93.9, 94.5, 110.5, 111.2, 153.1, 170.8.

MS (ESI): *m*/*z* = 396 (M^+ + Na), 411.9 (M^+ + K).

(2*S*,3*S*)-3-[(*S*)-3-(*tert*-Butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl]-2,3-(isopropylidenedioxy)propan-1-ol (12)

To a soln of $LiAlH_4$ (0.23 g, 6.1 mmol) in anhyd THF (20 mL) was added a soln of ester **11** (1.5 g, 4.04 mmol) in anhyd THF at 0 °C through a syringe and resulting mixture was stirred at r.t. for 1 h (TLC showed complete consumption of starting material). The mixture was quenched with sat. aq Na_2SO_4 soln (0.2 mL) at 0 °C and then filtered through a Celite pad and the filtrate was concentrated. The crude residue was purified by column chromatography (silica gel, PE–EtOAc, 8:2) to give **12** as a colorless oil; yield: 1.0 g (75%).

$[\alpha]_D^{25}$ –22 (*c* 0.8, $CHCl_3$).

IR ($CHCl_3$): 3500, 2938 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37–153 (m, 21 H), 2.38 (br s, 1 H), 3.52 (m, 1 H), 3.73–3.92 (m, 3 H), 4.06–4.26 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 26.8, 28.1, 58.9, 62.0, 65.2, 79.2, 80.6, 93.7, 108.2, 153.0.

Anal. Calcd for $C_{16}H_{29}NO_6$: C, 57.99; H, 8.82; N, 4.23. Found: C, 58.04; H, 8.90; N 4.26.

(2*S*,3*S*)-3-[(*S*)-3-(*tert*-Butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl]-2,3-(isopropylidenedioxy)-1-(mesyloxy)propane (6)

To a soln of alcohol **12** (0.6 g, 1.81 mmol) in anhyd CH_2Cl_2 (5 mL) at 0 °C was added Et_3N (0.4 mL, 2.72 mmol). The mixture was stirred for 10 min, MsCl (0.2 mL, 2.17 mmol) and DMAP (0.27 g, 2.72 mmol) were added and resulting mixture was stirred at 0 °C for 2 h (TLC showed complete consumption of starting material). The mixture was quenched with ice pieces and extracted with CH_2Cl_2 (3 × 15 mL), then washed with brine (10 mL), dried (Na_2SO_4), and concentrated. The crude residue was purified by column chroma-

tography (silica gel, PE–EtOAc, 9:1) to give **6** as a white sticky compound; yield: 0.6 g (81%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H), 1.47–1.53 (m, 15 H), 3.03 (s, 3 H), 3.84 (t, *J* = 8.5 Hz, 1 H), 3.90–3.93 (m, 1 H), 4.06–4.15 (m, 3 H), 4.32 (d, *J* = 11.3 Hz, 1 H), 4.52 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.9, 27.0, 28.3, 37.7, 62.3, 69.1, 75.6, 80.3, 110.1, 120.0, 155.8.

(2*S*,3*S*,4*S*)-2-(Hydroxymethyl)pyrrolidine-3,4-diol (1)

To a soln of mesylate **5** (0.1 g, 0.24 mmol) in EtOAc (2.0 mL) was added 2 M HCl (0.05 mL, 0.61 mmol) at 0 °C and the reaction mixture was stirred for 3 h. The mixture was neutralized to pH 8 with sat. $NaHCO_3$ soln (1.0 mL) and stirred for 1 h. The mixture was extracted with EtOAc (3 × 10 mL), then the combined extracts were dried (Na_2SO_4) and concentrated. The crude compound was purified by flash column chromatography (silica gel, CH_2Cl_2–MeOH, 1:1) to give **1** as a pale yellow oil; yield: 22 mg (69%).

$[\alpha]_D^{25}$ –11.4 (*c* 0.2 MeOH) [Lit.[11f] $[\alpha]_D^{25}$ –12.0 (*c* 0.21 MeOH)].

^{1}H NMR (500 MHz, CD_3OD): δ = 3.17–3.52 (m, 3 H), 3.67–3.72 (m, 4 H), 3.87 (m, 4 H).

^{13}C NMR (125 MHz, CD_3OD): δ = 54.4, 66.8, 77.7, 78.0, 78.2.

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References

(1) Asano, N.; Nash, R. J.; Molyneux, R. J.; Fleet, G. W. J. *Tetrahedron: Asymmetry* **2000**, *11*, 1645.
(2) El Ashry, E. S. H.; Rashed, N.; Shobier, A. H. S. *Pharmazie* **2000**, *55*, 331.
(3) El Nemr, A. *Tetrahedron* **2000**, *56*, 8579.
(4) (a) Coppola, G. M.; Huster, H. F. *Asymmetric Synthesis, Construction of Chiral Molecules Using Amino Acids*; Wiley: New York, **1987**. (b) Jurczak, J.; Golebiowski, A. *Chem. Rev.* **1989**, *89*, 149. (c) Golebiowski, A.; Jurczak, J. *Total Synthesis of Linocomycin and Related Chemistry,* In *Recent Progress in the Chemical Synthesis of Antibiotics*; Springer: Berlin, **1990**. (d) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1531. (e) Dondoni, A. *Carbohydrate Synthesis via Thiazoles,* In *Modern Synthetic Reactions*, Vol. 2; Scheffold, R., Ed.; Verlag Helvetica Chimica Acta: Basel, **1992**, 377.
(5) Jurczak, J.; Golebiowski, A. *The Synthesis of Antibiotic Amino Sugars from α-Amino Aldehydes,* In *Antibiotics and Antiviral Compounds, Chemical Synthesis and Modification*; Krohn, K.; Kirst, H.; Maag, H., Eds.; VCH: Weinheim, **1993**.
(6) Jurczak, J.; Golebiowski, A. *From α-Amino Acids to Amino Sugars,* In *Studies in Natural Products Chemistry*, Vol. 4; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, **1989**.
(7) Golebiowski, A.; Jurczak, J. *Synlett* **1993**, 241.
(8) Kiciak, K.; Jacobsson, U.; Golebiowski, A.; Jurczak, J. *Pol. J. Chem.* **1993**, *67*, 685.
(9) (a) Fleet, G. W. J.; Witty, D. R. *Tetrahedron: Asymmetry* **1990**, *1*, 119. (b) Hosaka, A.; Ichikawa, S.; Shindo, H.; Sato, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 797. (c) Mulzer, J.; Becker, R.; Brunner, E. *J. Am. Chem. Soc.* **1989**, *111*, 7500. (d) Abiko, A.; Roberts, J. C.; Takemasa, T.; Masamune, S. *Tetrahedron Lett.* **1986**, *27*, 4536. (e) Zanardi, F.; Battistini, L.; Nespi, M.; Rassu, G.; Spanu, P.; Cornia, M.; Casiraghi, G. *Tetrahedron: Asymmetry* **1996**, *7*, 1167. (f) Fleet, G. W. J.; Son, J. C. *Tetrahedron* **1988**, *44*, 2637. (g) Weir, C. A.; Taylor, C. M. *J. Org. Chem.* **1999**, *64*, 1554. (h) Chen, S. Y.; Joullie, M. M. *Tetrahedron Lett.* **1983**, *24*, 5027. (i) Bols, M.; Lundt, I. *Acta Chem. Scand.* **1992**, *46*, 298. (j) Kim, H. J.; Lee, W. S.; Yang, M. S.; Lee, S. G.; Park, K. H. *Synlett* **1999**, 614. (k) Kim, I. S.; Zee, O. P.; Jung, Y. H. *Org. Lett.* **2006**, *8*, 4101.
(10) (a) Karl, J.-U.; Wieland, T. *Liebigs Ann. Chem.* **1981**, 1445. (b) Durand, J.-O.; Larchevêque, M.; Petit, Y. *Tetrahedron Lett.* **1998**, *39*, 5743. (c) Arakawa, Y.; Yoshifuji, S. *Chem. Pharm. Bull.* **1991**, *39*, 2219. (d) Humphrey, A. J.; Parsons, S. F.; Smith, M. E. B.; Turner, N. J. *Tetrahedron Lett.* **2000**, *41*, 4481. (e) Hulme, A. N.; Montgomery, C. H.; Henderson, D. K. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1837. (f) Huwe, C. M.; Blechert, S. *Synthesis* **1997**, 61. (g) Goli, D. M.; Cheesman, B. V.; Hassan, M. E.; Lodaya, R.; Slama, J. T. *Carbohydr. Res.* **1994**, *259*, 219. (h) Ribes, C.; Falomir, E.; Carda, M.; Marco, J. A. *J. Org. Chem.* **2008**, *73*, 7779; and references cited therein.
(11) (a) Jones, D. W. C.; Nash, R. J.; Bell, E. A.; Williams, J. M. *Tetrahedron Lett.* **1985**, *26*, 3125. (b) Dhavale, D. D.; Kumar, K. S. A.; Chaudhari, V. D.; Sharma, T.; Sabharwal, S. G.; Reddy, J. P. *Org. Biomol. Chem.* **2005**, *3*, 3720. (c) Sugiyama, M.; Hong, Z.; Liang, P.-H.; Dean, S. M.; Whalen, L. J.; Greenberg, W. A.; Wong, C.-H. *J. Am. Chem. Soc.* **2007**, *129*, 14811. (d) Huang, Y.; Dalton, D. R. *J. Org. Chem.* **1997**, *62*, 372. (e) Zhou, X.; Liu, W.-H.; Ye, J.-L.; Huang, P.-Q. *Tetrahedron* **2007**, *63*, 6364. (f) Lombardo, M.; Fabbroni, S.; Trombini, C. *J. Org. Chem.* **2001**, *66*, 1264.
(12) (a) Pandey, S. K.; Kumar, P. *Synlett* **2007**, 2894. (b) Pandey, S. K.; Kumar, P. *Tetrahedron Lett.* **2005**, *46*, 4091. (c) Cherian, S. K.; Kumar, P. *Tetrahedron: Asymmetry* **2007**, *18*, 982. (d) Kandula, S. V.; Kumar, P. *Tetrahedron* **2006**, *62*, 9942. (e) Kumar, P.; Bodas, M. S. *J. Org. Chem.* **2005**, *70*, 360. (f) Bodas, M. S.; Upadhyay, P. K.; Kumar, P. *Tetrahedron Lett.* **2004**, *45*, 987. (g) Upadhyay, P. K.; Prasad, R.; Pandey, M.; Kumar, P. *Tetrahedron Lett.* **2009**, *50*, 2440.
(13) (a) Garner, P.; Park, J. M. *J. Org. Chem.* **1987**, *52*, 2361. (b) Garner, P.; Park, J. M. *Org. Synth.* **1991**, *70*, 18. (c) Garner, P.; Ramakanth, S. *J. Org. Chem.* **1986**, *51*, 2609. (d) Garner, P.; Park, J. M.; Mallecki, E. *J. Org. Chem.* **1988**, *53*, 4395.
(14) (a) Kolb, H. C.; VanNiewenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (b) Becker, H.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 448.
(15) Dondoni, A.; Merino, P.; Perrone, D. *Tetrahedron* **1993**, *49*, 2939.