Tetrahedron Letters 54 (2013) 2579–2582

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Effective and one-step stereo-controlled synthesis of benzyloxylated-diiodopentanes for the synthesis of five-membered imino-sugars

Lina Guo [a], Yonghui Liu [a], Yue Wan [a], Peng George Wang [a,b], Wei Zhao [a,*]

[a] College of Pharmacy, State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, PR China
[b] The Department of Chemistry, Georgia State University, Atlanta, GA 30302, USA

ARTICLE INFO

Article history:
Received 25 November 2012
Revised 2 February 2013
Accepted 22 February 2013
Available online 21 March 2013

Keywords:
Carbohydrate mimetics
Benzyloxylated-diiodopentanes
Stereo-controlled synthesis
Ring-closure
Remote group participation

ABSTRACT

An effective and stereo-controlled synthesis of 1,3,4-tris(benzyloxy)-2,5-diiodopentane starting from 2,3,5-tris(benzyloxy)pentane-1,4-diol was reported. Synthesis was improved to get the diiodide compound instead of forming the ring-closure product (benzyloxylated tetrahydrofuran). From the diiodide intermediate, the five-membered aza-sugar was synthesized with high yield.

Carbohydrate mimetics in which the endocyclic oxygen is replaced by sulfur, nitrogen, and other heteroatoms (Fig. 1a) have been found to possess a range of biological activities against HIV, Gaucher's disease, hepatitis, cancer, diabetes, and other diseases.[1] The five-membered sugar mimetics (**1** and **3**), core structures of many azasugar- and thiosugar-nucleosides, have emerged as promising synthetic drugs as inhibitors of DNA- or RNA-related enzymes[2] and glycosidases (Fig. 1).[3] The C-nucleoside hydrochloride D-ImmH (**2**), now 'Fodosine™', is in phase II clinical trials as an anti-T-cell leukemia agent.[4] A new class of naturally occurring glycosidase inhibitors (**4**) was isolated by Yoshikawa et al.[5] from *Salacia reticulata* Wight (known as 'kothala himbutu' in Singhalese), used in Ayurveda medicine for the treatment of Type II diabetes mellitus, and the core structure was thiosugar (**3**). In this regard, the development of reaction methodologies, which provides a simple and economically favorable synthesis of such carbohydrate mimetics, is very necessary.

To date, a number of synthetic strategies for the total synthesis of these challenging imino-, thio-, and seleno-sugar mimetics have been demonstrated, starting from amino acids[6] or carbohydrates as well as by asymmetric[7] or enzymatic synthesis.[8] Previous studies show that a simple and convenient strategy was to introduce two leaving groups via one step and close the sugar ring by a nucleophile reactant (Scheme 1a). For example, Fleet has demonstrated the efficient assembly of azetidines with poly-hydroxyl and poly-chiral centers via a ring closure reaction from sugar ditriflate.[9] Satoh has investigated the synthesis of thiosugar via ring open sugar by the reduction reaction.[10] However, these methods suffered from the drawback of the carbon chiral centers of C5 which were reversed by the S_N2 nucleophilic reaction. Recently, Kumar et al.[11] and Zhang et al.[12] synthesized a series of imino-sugar derivatives by inversion of the configuration of C5 by the Mitsunobu reaction followed by the second S_N2 substitution reaction

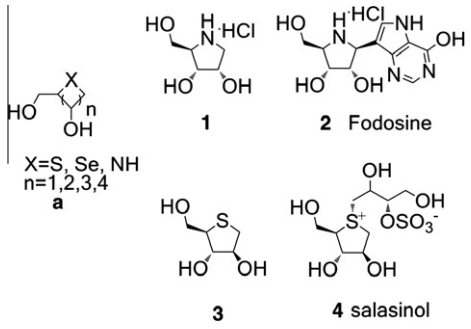
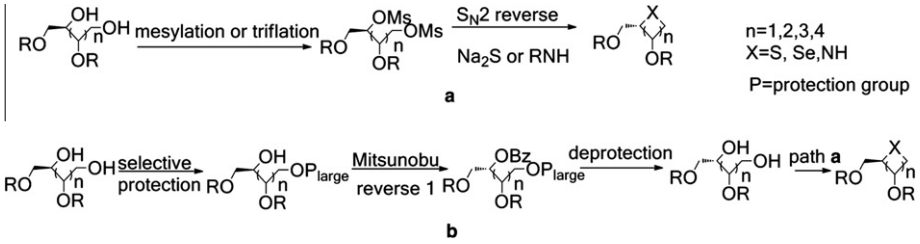


Figure 1. Carbohydrate derivatives with O atom substituted by other heteroatoms (S, N, and Se).

* Corresponding author. Tel./fax: +86 022 2350 7760.
E-mail address: wzhao@nankai.edu.cn (W. Zhao).

0040-4039/$ - see front matter
http://dx.doi.org/10.1016/j.tetlet.2013.02.115



Scheme 1. Reported strategies for the ring-closure reaction.

(Scheme 1b). Although this strategy can synthesize target products in a good yield, the synthetic routes are time-consuming because of the protection and deprotection steps. Protection group-free synthesis of aza-sugars from carbohydrates was also reported,[13] but only 2,3-*cis*-pyrrolidine products could be obtained. In continuation of our studies on glycosidase inhibitors,[14] we herein report a more concise and practical synthesis of imino-sugar derivatives from stereo-controlled benzyloxylated-diiodopentane intermediate via stereochemistry.

Skrydstrup and co-workers[17] reported the transformation of two hydroxyl groups into iodic groups simultaneously from methyl 2,4-di-*O*-benzyl-D-mannopyranoside. The alkene product, but not the C3-nitrile compound was isolated due to the trans-β-elimination reaction of the C4-proton. Also, only the 3,6-anhydro product was observed from corresponding ditriflate sugars. In our approach, diol compound **5**, easily prepared from D-ribose through four steps,[10] was treated with PPh_3/I_2 to afford the key intermediate **6**[15] as depicted in Scheme 2. Subjection of the diiodide derivative **6** to excess sodium azide in DMF led to the mono-substituted compound **8**[16] selectively. Subsequent treatment of **8** with PPh_3/THF/H_2O and ring-closure simultaneously, afforded the protected 1,4-imino D-ribitol. After deprotection using Pd/C, the final compound (+)-1,4-dideoxy-1,4-imino D-ribitol **1**,[7] which is consistent with that reported in literatures,[7] was obtained.

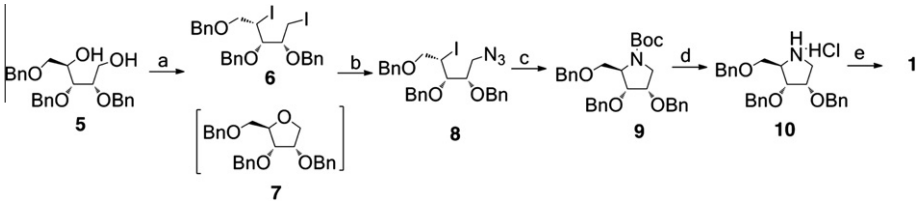
Unfortunately, at room temperature or at higher temperature, the yield of diiodide compound **6** from diol compound **5** was very low (only 5%). It was assumed that this was due to the lower reactivity of the secondary hydroxyl group[18]and the mono-substituted intermediate (Scheme 3a) was produced predominantly. With the nucleophilic group and the leaving group existing in one linear structure, the intramolecular nucleophilic reaction happened easily to obtain the 2,5-anhydro products **7**[19] (Scheme 3a). To avoid the intramolecular nucleophilic reaction and the formation of 2,5-anhydro products, lower temperature was applied for the synthesis of the di-phosphide intermediate (Scheme 3b). The lower temperature reaction was conducted using diethyl ether–acetonitrile (1:1, v/v) or DCM as solvent which, among many other solvents screened, such as THF and toluene, was found to be best in terms of suspension and reaction yield. An effort to prevent the formation of 2,5-anhydro product **7** by lowering the temperature and prolonging the reaction time led to maximized yield of diiodide compound **6**. As shown in Scheme 4, the ratio and the yield of compounds **6** and **7** varied, as the reaction time was prolonged at the same temperature. After stirring at −30 °C for 48 h and a subsequent reaction time of 2 h in refluxing toluene, diiodide compound **6** was obtained in 90% yield.

With the key diiodide compound **6** in hand, azido-iodide compound **8**,[16] instead of diazido compound, was synthesized selectively and conveniently using sodium azide in DMF under 50 °C for 3 h. After reduction and ring-closure simultaneously, the secondary amine was protected by Boc for purification. Deprotection of Boc by AcCl/MeOH and subsequent debenzylation using Pd/C under hydrogen atmosphere afforded compound **1**[20] in nearly quantitative yield.

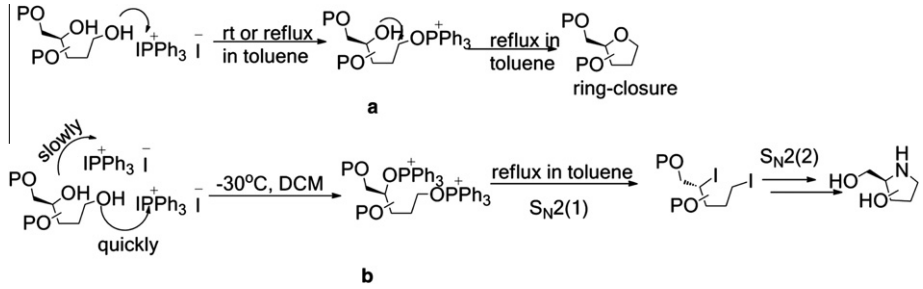
Afterward, the diiodide product **12**[21] (P/E = 10:1, R_f = 0.8) was synthesized from arabinose with high yield and simple operation to further demonstrate the efficiency of this general application (Scheme 5). As an important intermediate for the synthesis of salasinol, the corresponding thiosugar **13**[22] was prepared with an overall yield of 92%.

To test the feasibility of this approach, the developed protocol was further applied to the six-membered aza-sugars' synthesis. However, a complex mixture of elimination products was obtained with no trace of the corresponding diiodide and the major product **14** was separated and characterized. The spectroscopic data were consistent with the compound reported in the literature.[23] The remote group participation of methyloxyl and benzyloxyl groups has been disclosed in previous synthesis.[24] It was hypothesized that intramolecular participation of the 4-*O*-benzyl group led to the formation of oxonium ion intermediate (Scheme 6), which was attacked by the iodide ion to form **14** and benzyl iodide. The spectroscopic data of the benzyl iodide product supported this hypothesis.

In summary, we have developed a novel and efficient synthesis of stereo-controlled benzyloxylated-diiopentane which was the key intermediate of carbohydrate mimetics' synthesis. The most important feature of this system was to simultaneously convert two hydroxyl groups into iodic groups as leaving ligands and reverse the stereochemistry of the 4-OH with high yield. This method is practical for the large scale synthesis of poly-benzylated-diiopentanes and imino-sugar derivatives available to the carbohydrate mimetics research.



Scheme 2. Reagents and conditions: (a) PPh_3/I_2, 90% for **6** and **7** (Scheme 4); (b) NaN_3, 90%; (c) (i) PPh_3/H_2O, THF, (ii) Boc_2O/NaOH, 82%, (d) AcCl/MeOH (100%); (e) Pd/C, H_2 (97%).

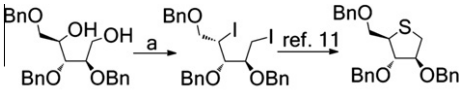


Scheme 3. (a) The pathway of ring closure; (b) the pathway of diiodide reaction.

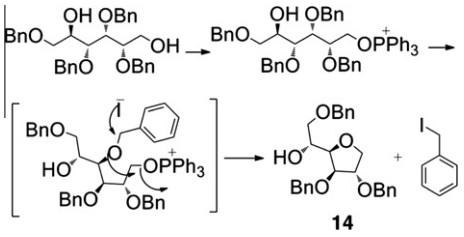
time[a]:	4h	24h	36h	48h
6	10.3[b]	43.8	69.7	89.7
7	72.1	51.3	20.4	hence
ratio	1:7	1:1	3.5:1	

a. the reaction kept under -30 °C.
b. % yield of ioslation

Scheme 4. The varied yield of diiodide compound.



Scheme 5. The synthesis of diiodide compound **12** from arabinose.



Scheme 6. Proposed mechanism for remote group participation reaction.

Acknowledgments

We thank the National High Technology Research and Development Program of China (863 Program 2012AA021505) and the Natural Science Foundation of Tianjin (Grant No. 12JCYBJC18600) for financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.02.115. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Horne, G.; Wilson, F. X.; Tinsley, J.; Williams, D. H.; Storer, R. *Drug Discov. Today* **2011**, *16*, 107–118; (b) Compain, P.; Chagnault, V.; Martin, O. R. *Tetrahedron: Asymmetry* **2009**, *20*, 672–711; (c) Afarinkia, K.; Bahar, A. *Tetrahedron: Asymmetry* **2005**, *16*, 1239–1287; (d) Pearson, M. S. M.; Mathé-Allainmat, M.; Fargeas, V.; Lebreton, J. *Eur. J. Org. Chem.* **2005**, 2159–2191; (e) Lillelund, V. H.; Jensen, H. H.; Liang, X. F.; Bols, M. *Chem. Rev.* **2002**, *102*, 515–553; (f) Asano, N.; Nash, R. J.; Molyneux, R. J.; Fleet, G. W. J. *Tetrahedron: Asymmetry* **2000**, *11*, 1645–1680.
2. (a) Balakrishnan, K.; Nimmanapalli, R.; Ravandi, F.; Keating, M. J.; Gandhi, V. *Blood* **2006**, *108*, 2392–2398; (b) Fandy, Tamer E. *Curr. Med. Chem.* **2009**, *16*, 2075–2085; (c) Jeong, L. S.; Choe, S. A.; Gunaga, P.; Kim, H. O.; Lee, H. W.; Lee, S. K.; Tosh, D. K.; Patel, A.; Palaniappan, K. K.; Gao, Z.-G.; Jacobson, K. A.; Moon, H. R. *J. Med. Chem.* **2007**, *50*, 3159–3162; (d) Satoh, H.; Yoshimura, Y.; Sakata, S.; Miura, S.; Machida, H. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 989–992.
3. (a) Wang, G.-N.; Xiong, Y. L.; Ye, J.; Zhang, L.-H.; Ye, X.-S. *ACS Med. Chem. Lett.* **2011**, *2*, 682–686; (b) Ganesan, M.; Madhukarrao, R. V.; Ramesh, N. G. *Org. Biomol. Chem.* **2010**, *8*, 1527–1530; (c) Mercer, T. B.; Jenkinson, S. F.; Bartholomew, B.; Nash, R. J.; Miyauchi, S.; Kato, A.; Fleet, G. W. J. *Tetrahedron: Asymmetry* **2009**, *20*, 2368–2373; (d) Ganesan, M.; lundt, I. *Tetrahedron Lett.* **1998**, *39*, 5841–5844.
4. Clinch, K.; Evans, G. B.; Fleet, G. W. J.; Furneaux, R. H.; Johnson, S. W.; Lenz, D. H.; Mee, S. P. H.; Rands, P. R.; Schramm, V. L.; Ringia, E. A. T.; Tyler, P. C. *Org. Biomol. Chem.* **2006**, *4*, 1131–1139.
5. (a) Yoshikawa, M.; Murakami, T.; Shimada, H.; Matsuda, H.; Yamahara, J.; Tanabe, G.; Muraoka, O. *Tetrahedron Lett.* **1997**, *38*, 8367–8370; (b) Yoshikawa, M.; Murakami, T.; Yashiro, K.; Matsuda, H. *Chem. Pharm. Bull.* **1998**, *46*, 1339–1340; (c) Yoshikawa, M.; Morikawa, T.; Matsuda, H.; Tanabe, G.; Muraoka, O. *Bioorg. Med. Chem.* **2002**, *10*, 1547–1554; (d) Tanabe, G.; Yoshikai, K.; Hatanaka, T.; Yamamoto, M.; Shao, Y.; Minematsu, T.; Muraoka, O.; Wang, T.; Matsudab, H.; Yoshikawa, M. *Bioorg. Med. Chem.* **2007**, 3926–3937.
6. Chiacchio, U.; Borrello, L.; Crispino, L.; Rescifina, A.; Merino, P.; Macchi, B.; Balestrieri, E.; Mastino, A.; Piperno, A.; Romeo, G. *J. Med. Chem.* **2009**, *52*, 4054–4057.
7. Kumareswaran, R.; Hassner, A. *Tetrahedron: Asymmetry* **2001**, *12*, 3409–3415. we reported the spectroscopic data for **1** in MeOD: (+)-1,4-dideoxy-1,4-imino D-ribitol hydrochloride ^{1}H NMR (MeOD, 400 MHz) δ 4.23 (m, C_2H), 4.09 (dd, C_3H, J = 8, 4 Hz), 3.88 (dd, C_5H, J = 12, 3.2 Hz), 3.73 (dd, C_5H, J = 12, 5.8 Hz), 3.52 (m, C_4H), 3.35 (dd, C_1H, J = 12.4, 3.6 Hz), 3.23 (d, C_1H, J = 12.4 Hz); ^{13}C NMR (MeOD, 100 MHz) δ 73.00, 71.16, 63.97, 59.46, 51.14.
8. (a) Kajimoto, T.; Liu, K. K.-C.; Pederson, R. L.; Zhong, Z. Y.; Ichikawa, Y.; John, A.; Porco, Jr.; Wong, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6187–6196; (b) Gijsen, H. J. M.; Qiao, L.; Fitz, W.; Wong, C.-H. *Chem. Rev.* **1996**, *96*, 443–473.
9. (a) Lenagh-Snow, G. M. J.; Araujo, N.; Jenkinson, S. F.; Rutherford, C.; Nakagawa, S.; Kato, A.; Yu, C.-Y.; Weymouth Wilson, A. C.; Fleet, W. J. *Org. Lett.* **2011**, *13*, 5834–5837; (b) Araújo, N.; Jenkinson, S. F.; Martínez, R. F.; Glawar, A. F. G.; Wormald, M. R.; Butters, T. D.; Nakagawa, S.; Adachi, I.; Kato, A.; Yoshihara, A.; Akimitsu, K.; Izumori, K.; Fleet, G. W. J. *Org. Lett.* **2012**, 4174–4177.
10. Satoh, H.; Yoshimura, Y.; Sakata, S.; Miura, S.; Machida, H.; Matsuda, A. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 989–992.
11. Kumar, N. S.; Pinto, B. M. *Carbohydr. Res.* **2005**, *340*, 2612–2619.
12. Zhang, Z. X.; Wu, B. L.; Wang, B.; Li, T. H.; Zhang, P. F.; Guo, L. N.; Wang, W. J.; Zhao, W.; Wang, P. G. *Tetrahedron Lett.* **2011**, *52*, 3802–3804.
13. Dangerfield, E. M.; Timmer, M. S. M.; Stocker, B. L. *Org. Lett.* **2009**, *11*, 535–538.
14. Li, T. H.; Guo, L. N.; Zhang, Y.; Lin, J. P.; Wang, J. J.; Zhang, Z. X.; Li, J.; Zhang, W. P.; Zhao, W.; Wang, P. G. *Bioorg. Med. Chem.* **2011**, *19*, 2136–2144.
15. *Spectroscopic data for* ***6****:* (2*S*,3*S*,4*R*)-1,3,4-tribenzyloxy-2,5-diiodopentane ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.26 (m, 15H), 4.85 (d, J = 12.6 Hz, 1H), 4.79 (dd, J = 7.2, 8.8 Hz, 1H), 4.75–4.69 (m, 2H), 4.56 (t, J = 12.6 Hz, 1H), 4.48 (t, J = 10.8 Hz, 2H), 3.87–3.78 (m, 2H), 3.60–3.54 (m, 2H), 3.32 (d, J = 8.4 Hz, 1H), 3.22 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.98, 137.52, 137.21, 128.47, 128.44, 128.20, 128.04, 127.89, 127.86, 127.77, 127.58, 79.36, 78.06, 74.96, 72.73, 72.67,71.78, 35.82, 9.06. HRMS Calcd for $C_{26}H_{32}I_2NO_3$ m/z: 660.0472 (M+NH_4)$^+$. Found: 660.0446.
16. *Spectroscopic data for* ***8****:* (2*S*,3*S*,4*S*)-5-azido-1,3,4-tri (benzyloxy)-2-iodopentane ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.25 (m, 15H), 4.76–4.73 (m, 2H), 4.69–4.61 (m, 3H), 4.52 (d, J = 12.0 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 3.86–3.78 (m, 2H), 3.72 (dd, J = 2.8, 5.6 Hz, 1H), 3.65 (dd, J = 2.4, 13.2 Hz, 1H), 3.36 (d, J = 8.4 Hz, 1H), 3.29 (dd, J = 2.4, 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.05, 137.62, 137.54, 128.69, 128.65, 128.60, 128.54, 128.47, 128.30, 128.22, 128.13, 128.05, 127.91, 127.77, 81.73, 75.78, 74.64, 73.02, 72.95, 72.76, 49.78, 35.54. HRMS Calcd for $C_{26}H_{32}IN_4O_3$ m/z: 575.1519 (M+NH_4)$^+$, Found: 575.1511.
17. Mikkelsen, L. M.; Krintel, S. L.; Jiménez-Barbero, J.; Skrydstrup, T. *J. Org. Chem.* **2002**, *67*, 6297–6308.
18. Minakawa, N.; Kaga, D.; Kato, Y.; Endo, K.; Tanak, M.; Sasaki, T.; Matsuda, A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2182–2189.

19. Yamazaki, O.; Togo, H.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2891–2896.
20. *Spectroscopic data for* ***10****:* (2*R*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl) pyrrolidine hydrochloride ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.32 (br, 2H), 7.34–7.21 (m, 15H), 4.66 (dd, *J* = 6.4, 12 Hz, 2H), 4.52 (d, *J* = 12 Hz, 1H), 4.46 (d, *J* = 11.2 Hz, 1H), 4.42 (t, *J* = 12.4 Hz, 2H), 4.00 (br, 1H), 3.95–3.92 (m, 2H), 3.77 (d, *J* = 9.6 Hz, 1H), 3.73(dd, *J* = 4, 10.8 Hz, 1H), 3.50 (d, *J* = 11.2 Hz, 1H), 3.32 (dd, *J* = 3.2, 12 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.57, 137.21, 137.09, 128.51, 128.42, 128.12, 128.00, 127.95, 127.80, 77.97, 74.07, 73.30, 72.30, 71.63, 66.55, 59.84, 47.06. HRMS Calcd for $C_{26}H_{30}NO_3$ *m*/*z*: 404.5213 $(M+H)^+$, Found: 404.5211.
21. *Spectroscopic data for* ***12****:* (2*S*,3*S*,4*S*)-1,3,4-tribenzyloxy-2,5-diiodopentane ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.30(m, 15H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.61 (d, *J* = 11.2 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.29 (ddd, *J* = 2.8, 5.6, 8.4 Hz, 1H), 3.81 (dd, *J* = 8.4, 10.4 Hz, 1H), 3.70 (dd, *J* = 5.6, 10.4 Hz, 1H), 3.58 (dd, *J* = 4.6, 10.6 Hz, 1H), 3.50 (dd, *J* = 2.8, 6.4 Hz, 1H), 3.40 (dd, *J* = 4, 11.2 Hz,1H), 3.26 (dd, *J* = 4.8, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.27, 137.65, 137.64, 128.41, 128.32, 128.11, 127.87, 127.77, 127.72, 127.68, 127.61, 82.06, 79.18, 74.73, 73.03, 72.69,72.58, 31.97, 5.92. HRMS Calcd for $C_{26}H_{32}I_2NO_3$ *m*/*z*: 660.0472 $(M+NH_4)^+$. Found: 660.0459.
22. Ghavami, A.; Johnston, B. D.; Pinto, B. M. *J. Org. Chem.* **2001**, *66*, 2312.
23. Jiang, Y.-H.; Fang, Z.-J.; Zheng, B.-H.; Feng, W.-W. *Hecheng Huaxue* **2011**, *19*, 24–27. The structure of this compound was characterized in this Letter by ^{1}H NMR, ^{13}C NMR, HSQC and NOESY. *Spectroscopic data for* ***14****:* (*R*)-2-(benzyloxy)-1-((2*R*,3*R*,4*S*)-3,4-bis(benzyloxy)tetrahydrofuran-2-yl)ethanol ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34–7.27 (m, 15H), 4.59 (dd, *J* = 3.6, 12 Hz, 2H), 4.57 (dd, *J* = 3.6, 12 Hz, 2H), 4.48 (d, *J* = 12 Hz, 1H), 4.45 (d, *J* = 12 Hz, 1H), 4.17–4.08 (m, 3H), 4.06 (d, *J* = 4.0 Hz, 1H), 3.97 (dd, *J* = 4.0, 8.4 Hz, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.74 (dd, *J* = 2.8, 10.0 Hz, 1H), 3.61 (dd, *J* = 6.4, 9.6 Hz, 1H), 2.73 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.21, 137.76, 128.66, 128.62, 128.52, 128.10, 128.01, 127.96, 127.82, 127.74, 82.15, 82.02, 80.43, 73.62, 72.41,72.38, 71.98, 71.50, 68.70. HRMS Calcd for $C_{27}H_{31}O_5$ *m*/*z*: 435.2171 $(M+H)^+$, Found: 435.2173.
24. (a) Winstein, S.; Allred, E. L.; Heck, R.; Glick, R. *Tetrahedron* **1958**, *3*, 1; (b) Allred, E. L.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 3991; (c) Mootoo, D. R.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1986**, 1570; (d) Liu, Z.; Byun, H.-S.; Bittman, R. *J. Org. Chem.* **2011**, *76*, 8588–8598.