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A new synthetic route for the synthesis of enantioenriched 1,2,3,4-tetrahydronaphthalene-derived 1,3-diols

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ABSTRACT

In this report, we presented a new approach to access a (1,3-butadiene-2-yl)carbinol, (1*R*,2*R*)- and (1*S*,2*S*)-1-(hydroxymethyl)-1-vinyl-1,2,3,4-tetrahydronaphthalene-2-ols. Starting from commercially available 1,4-diol-2-butyne, a six-step synthesis involving dibromination, Zn-mediated addition reaction of phenylpropyl aldehyde, epoxidation, epoxy–arene cyclization, and resolution with *D*(+)-Camphor afforded the title compounds.

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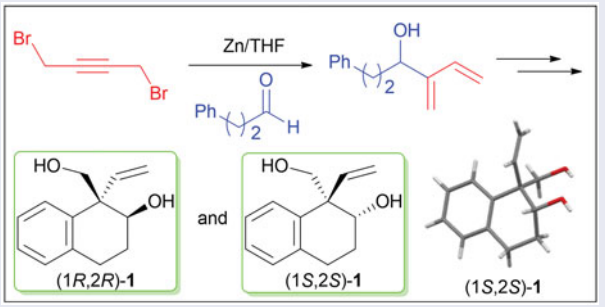
KEYWORDS
Asymmetric synthesis; 1,3-diene; 1,3-diol; oxetane

GRAPHICAL ABSTRACT



We herein presented a new approach to access a (1,3-butandien-2-yl)carbinol, (1R,2R)- and (1S,2S)-1-(hydroxymethyl)-1-vinyl-1,2,3,4-tetrahydronaphthalen-2-ols.

Introduction

Chiral 1,3-diol motif exists extensively in a variety of pharmaceutical and biologically active molecules.[1] It has been widely reported that chiral 1,3-diols, the same as 1,2- and 1,4-diols, play an important role in organic synthesis:[2] (1) working as synthons to construct complex compounds; (2) acting as chiral ligands or catalysts in asymmetric

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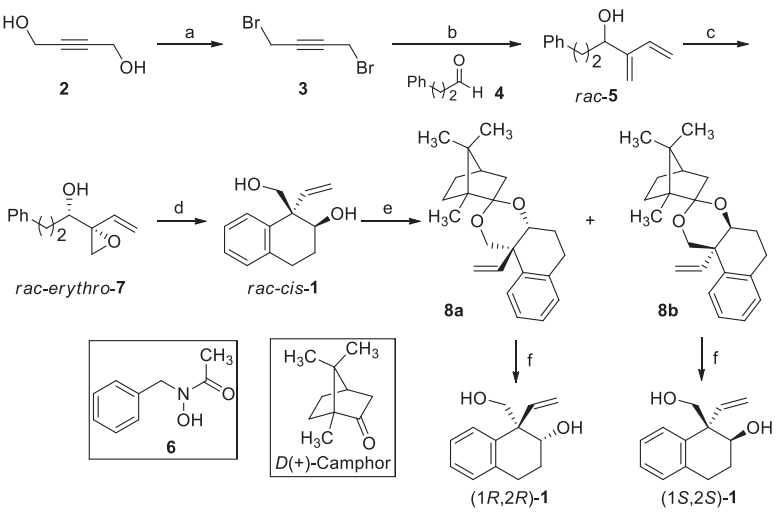
synthesis;[3] (3) using as chiral resolving agents to separate racemic compounds. Therefore, the synthesis of novel chiral 1,3-diol compounds represents an important task for organic chemists. Thus far, a lot of synthetic methods have been documented including enantioselective reductions of β-hydroxyl ketones[4] and 1,3-diketones,[5] cascade reactions initiated from asymmetric aldol reactions,[6] and so on.[7]

In 2015, a chiral 1,3-diol (1*S*,2*S*)-**1** featuring a tetrahydronaphthalene backbone was serendipitously obtained from a chiral 1,3-butadienyl-2-carbinol by our group.[8] We envisaged that the 1,3-diol would be potentially used as a chiral ligand, catalyst, or synthetic precursor. However, the previous synthetic route reported by us has several synthetic limitations: (1) the use of chiral phosphoric acid and anhydrous *t*-butyl hydroperoxide (TBHP) is cost-consuming; (2) 93% *ee* of (1*S*,2*S*)-**1** is not satisfactory for being a chiral ligand or catalyst. Toward addressing these issues and creating a reliable and practical synthetic method to generate chiral (1*S*,2*S*)-**1** and (1*R*,2*R*)-**1** in a large-scale manner, we started to launch this project and reported the details herein.

Discussion

In order to establish an economical, efficient, and easily-handled synthetic route to get both (1*R*,2*R*)-**1** and (1*S*,2*S*)-**1**, a six-step synthesis starting from 2-butyne-1,4-diol **2** was designed (Scheme 1). The first task was to seek for a useful way to get (1,3-butadiene-2-yl)carbinol *rac*-**5**, which is an important type of building block in total synthesis.[9] They could be generally accessed through the addition reaction of aldehydes with various unsaturated reagents.[10] For instance, the pioneering work of creating a protocol of using 1-trimethylsilyl-2,3-butadiene reagent in the presence of $TiCl_4$-catalyst was reported by Hatakeyama,[10a] as well as Brown et al. established the non-catalytic addition reaction between aldehydes and homoallenylated boronates.[10b] In 1999, the



Scheme 1. Synthetic route to (1*R*,2*R*)-1 and (1*S*,2*S*)-1. Reagents and conditions: (a) PBr_3, pyridine, Et_2O, 0–40 °C, 89%. (b) Zinc, THF, r.t., 52%. (c) $VO(O^iPr)_3$, **6**, TBHP (70% aq.), CH_2Cl_2, r.t., 60%. (d) $Zn(NTf_2)_2$, CH_2Cl_2, r.t., 75%. (e) *p*-TsOH, D(+)-Camphor, benzene, reflux, 100% conversion. (f) *p*-TsOH, CH_2Cl_2/H_2O, 85–87%.

catalytic asymmetric dienylation of aldehydes using buta-2,3-dienylstannane was developed by Hatakeyama and Yu independently.[10c,d] The enantioselective synthesis of (1,3-diene-2-yl)carbinols by employing homoallenylbromide with a chiral Cr^{III}-catalyst was achieved by Yamamoto et al.[10e] Miscellaneous other synthetic methods including using 1,3-butadiene-2-yl organometallic reagents,[11] ethylene-alkyne cross-metathesis with propargyl alcohols,[12] tandem alkylbromide-epoxide vinylations using dimethylsulfonium methylide,[13] and cascade allenylation/desilylation/isomerization[14] were also illustrated. In view of easy availability of starting materials and large-scale synthesis of (1,3-butandien-2-yl)carbinol products, Chan's method involving using 1,4-dibromo-2-butyne reagent and aldehydes was considered to be more promising than the above-listed methods.[15] However, the key issue of Chan's work is the use of stoichiometric amount of expensive In(0) metal. Considering cheap Zn(0) metal bearing similar chemical property to In(0) metal in Barbier-type reaction, we hoped Zn(0) could replace In(0) to mediate the 1,3-butadiene-2-ylation of aldehydes. The optimization of the reaction condition was shown in Table 1. Compound **3** was easily accessible through the dibromination of commercially available 1,4-diol-2-butyne. According to Chan's method,[15a] the transformation of compound **3** and phenylpropyl aldehyde **4** in aqueous media proceeded in only 25% yield (entry 1, Table 1). The replacement of In(0) to Zn(0) could not deliver any desired product (entry 2). The use of organic solvents, such as DMF, Et_2O, and THF (entries 3–5), was essential for the reaction mediated by Zn(0), and up to 36% yield was obtained in THF at 25 °C. Anhydrous THF improved the yield to 52%, which could be understood in the plausible mechanism (Figure 1). In the presence of trace amount of water, hydrolysis of organozinc intermediate **I** may occur to lead to undesired reaction pathway. The addition of propargyl intermediate **I** to aldehyde **4** provides allenyl intermediate **II**, which undergoes the second oxidative insertion of Zn(0) to afford homoallenyl organozinc intermediate **III**. After the reaction, workup of the reaction mixture with saturated aqueous NH_4Cl gave the desired (1,3-butadiene-2-yl)carbinol *rac*-**5**.

Table 1. Optimization of reaction conditions for 3 and 4.

Entry	Metal[a]	T/°C	Solvent	Yield/%
1	In	25	H_2O	25
2	Zn	25	H_2O	Trace
3	Zn	25	DMF	20
4	Zn	25	Et_2O	13
5	Zn	25	THF	36
6[b]	Zn	25	THF	52
7[b]	Zn	50	THF	15

[a]Zn was activated with diluted HCl (aq.). [b]Anhydrous THF was used.

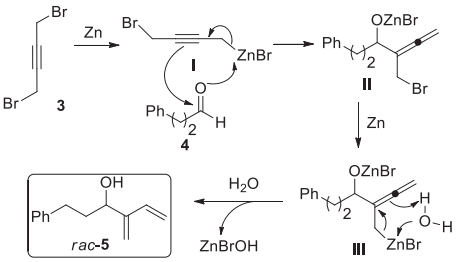
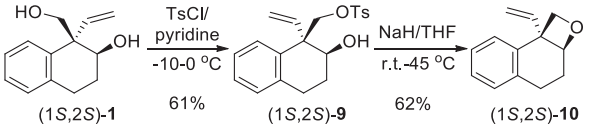


Figure 1. Plausible reaction mechanism for the transformation of **3** to *rac*-**5**.



Scheme 2. Synthetic utility of chiral 1,3-diol (*S,S*)-**1**.

With *rac*-**5** in hand, we continued to study the epoxidation of the allylic alcohol at low cost. Expensive anhydrous TBHP reagent was usually utilized as an oxidizing reagent in Sharpless-epoxidation reactions.[16] The Yamamoto group paved the way to employ cheap aqueous TBHP reagent.[17] Inspired by this work, we carried out the non-asymmetric variant by using easily-prepared hydroxamic acid **6** as a racemic ligand. As expected, *rac-erythro*-**7** was readily obtained in 60% yield when injecting 70% aq. TBHP reagent, which facilitated the 6-*exo-tet* epoxy–arene cyclization to provide *rac-cis*-**1** according to our previously identified procedure.[8]

The final task was how to resolve 1,3-diol *rac-cis*-**1**. Initial attempts of using various common chiral resolving reagents via non-covalent interactions, such as *L*-Proline, (+)-1-benzylcinchonanium chloride and (*R*)-(+)-1-phenylethylamine, were failed even by changing a wide array of solvents. To our delight, two ketal diastereoisomers **8a** and **8b** formed from *rac-cis*-**1** and *D*(+)-Camphor were successfully separated by using silica-gel column chromatography. Consequently, **8a** and **8b** were hydrolyzed to give both target enantiomers (1*R*,2*R*)-**1** and (1*S*,2*S*)-**1** with 95% *ee*, which was recrystallized once in petroleum ether/ethyl ether to give two enantiomers with 99% *ee* (85–87% yields). The absolute configuration of (*R,R*)-**1** was well determined by single crystal X-ray diffraction (see SI; CCDC 1552373 ((R,R)-1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre).

The synthetic utility of (1*S*,2*S*)-**1** was demonstrated in Scheme 2. Selective tosylation of the primary alcohol for (1*S*,2*S*)-**9** was achieved based on the reactivity difference between the two hydroxyl groups. Under basic condition, 1,2,3,4-tetrahydronaphthalene-derived oxetane (1*S*,2*S*)-**10** was successfully built in 62% yield, which is regularly embedded as a key motif in natural products, such as paclitaxel.[18]

In this report, we mainly focused on the updated synthesis of a (1,3-butadiene-2-yl)carbinol and both enantiomers of 1-(hydroxymethyl)-1-vinyl-1,2,3,4-tetrahydronaphthalene-2-ols. The reaction mechanism of the Zn-mediated reaction of phenylpropyl aldehyde and 1,4-dibromo-2-butyne to form (1,3-butadiene-2-yl)carbinol was proposed. The synthetically useful pathway features cost-effective and practical. The asymmetric synthesis of an enantioenriched 1,2,3,4-tetrahydronaphthalene-derived oxetane was facilitated by the chiral 1,3-diol. Further, synthetic application of the chiral 1,3-diols in novel chiral ligands and catalysts synthesis are ongoing in our lab.

Experimental sections

Chiral resolution of rac-cis-*1*

rac-cis-**1** (1.0 g, 5.0 mmol), *D*(+)-Camphor (2.28 g, 15.0 mmol) and *p*-TsOH·H_2O (19 mg, 0.02 mmol) were refluxed in 30 mL benzene with azeotropic removal of water.

After *rac-cis*-**1** was fully consumed, anhydrous potassium carbonate was added. The reaction mixture was allowed to stir for 5 min before filtration. The filtrate was concentrated under vacuum and the residue was separated on a column of silica gel (pure petroleum ether, Rf = 0.2) to give pure white solid **8a** (0.3798 g, 23%) and **8b** (0.3614 g, 22%) at the first time. The residue of ketal diastereoisomers was again separated, and the total yields of **8a** and **8b** were 45% and 44%, respectively. The ketals **8a** and **8b** were readily hydrolyzed in the presence of *p*-TsOH·H_2O to give two enantiomers (1*R*,2*R*)-**1** ($[\alpha]_D^{20} = -5.4$ (c = 1.0, $CHCl_3$)) and (1*S*,2*S*)-**1** ($[\alpha]_D^{20} = +5.6$ (c = 1.0, $CHCl_3$))[8].

8a, 45%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 1H), 7.22–7.11 (m, 3H), 5.76 (dd, 17.5 Hz, 10.5 Hz, 1H), 5.14 (d, 11.0 Hz, 1H), 4.67 (d, 17.5 Hz, 1H), 4.29 (d, 12.0 Hz, 1H), 4.07 (d, 2.5 Hz, 1H), 3.94 (d, 11.5 Hz, 1H), 3.17–3.09 (m, 1H), 2.61 (dd, 16.5 Hz, 6.0 Hz, 1H), 2.22–2.17 (m, 2H), 2.02–1.95 (m, 1H), 1.86–1.78 (m, 3H), 1.70–1.64 (m, 1H), 1.19–1.09 (m, 2H), 1.00 (s, 3H), 0.82 (s, 3H), 0.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.99, 137.94, 136.31, 128.62, 128.16, 125.73, 125.38, 117.56, 106.88, 71.74, 66.78, 53.44, 47.48, 45.38, 44.10, 38.79, 28.78, 27.13, 24.86, 24.18, 20.79, 20.67, 9.53. mp =64–65 °C. IR (KBr): 3066.3, 2942.8, 2871.5, 1862.9, 1635.3, 1471.4, 1450.2, 1371.1, 1315.2, 1267.0, 1232.3, 1203.4, 1176.4, 1122.4, 1045.3, 993.2, 929.5, 757.9. HRMS calcd. for $[M]^+$: 338.2246; found: 338.2236. $[\alpha]_D^{20} = -73.4$ (c = 0.5, $CHCl_3$).

8b, 44%: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 1H), 7.20–7.12 (m, 3H), 5.75 (dd, 17.5 Hz, 11.0 Hz, 1H), 5.13 (d, 11.0 Hz, 1H), 4.67 (d, 17.0 Hz, 1H), 4.17 (d, 12.0 Hz, 1H), 4.02–4.01 (m, 1H), 3.93 (d, 12.0 Hz, 1H), 3.16–3.10 (m, 1H), 2.60 (dd, 16.5 Hz, 6.0 Hz, 1H), 2.17–2.14 (m, 1H), 2.02–1.94 (m, 2H), 1.89–1.85 (m, 1H), 1.79–1.77 (m, 1H), 1.70–1.66 (m, 1H), 1.62–1.57 (m, 1H), 1.20–1.11 (m, 2H), 0.94 (s, 3H), 0.81 (s, 3H), 0.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.02, 137.97, 136.23, 128.71, 128.07, 125.77, 125.50, 117.67, 106.90, 69.29, 53.49, 47.84, 45.23, 44.05, 38.55, 28.36, 27.22, 24.97, 24.31, 20.84, 20.77, 9.39. mp =83–84 °C. IR (KBr): 3060.5, 2925.5, 2865.7, 1857.1, 1591.0, 1479.1, 1450.2, 1380.8, 1317.1, 1263.1, 1197.6, 1122.4, 1047.2, 977.7, 925.7, 757.9. HRMS calcd. for $[M]^+$: 338.2246; found: 338.2236. $[\alpha]_D^{20} = +23.4$ (c = 1.0, $CHCl_3$).

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References

[1] (a) Norcross, R. D.; Paterson, I. *Chem. Rev.* **1995**, *95*, 2041. DOI: 10.1021/cr00038a012. (b) Liu, G.-L.; Chi, Z.; Wang, G.-Y.; Wang, Z.-P.; Li, Y.; Chi, Z.-M. *Crit. Rev. Biotechnol.* **2015**, *35*, 222. DOI: 10.3109/07388551.2013.833582. (c) Shibata, H.; Tsuchikawa, H.; Hayashi, T.; Matsumori, N.; Murata, M.; Usui, T.; *Chem. Asian J.* **2015**, *10*, 915. DOI: 10.1021/cr00038a012.

[2] Bhowmick, K. C.; Joshi, N. N. *Tetrahedron Asymmetry*. **2006**, *17*, 1901. DOI: 10.1016/j.tetasy.2006.06.023.

[3] (a) Fukuzawa, S.; Komuro, Y.; Nakano, N.; Obara, S. *Tetrahedron Lett*. **2003**, *44*, 3671. DOI: 10.1016/S0040-4039(03)00674-9. (b) Zeng, Q.-L.; Tang, H.-Y.; Zhang, S.; Liu, J.-C. *Chin. J. Chem*. **2008**, *26*, 1435. DOI: 10.1002/cjoc.200890261. (c) Gogoi, P.; Kotipalli, T.; Indukuri, K.; Bondalapati, S.; Saha, P.; Saikia, A. K. *Tetrahedron Lett*. **2012**, *53*, 2726. DOI: 10.1016/j.tetlet.2012.03.077. (d) Jiang, B.; Chen, Z.; Tang, X. *Org. Lett*. **2002**, *4*, 3451. DOI: 10.1021/ol026544i. (e) Jiang, B.; Chen, Z.-L.; Xiong, W.-N. *Chem. Commun*. **2002**, 1524. DOI: 10.1039/b203984b. (f) Zavesky, B. P.; Johnson, J. S. *Angew. Chem. Int. Ed*. **2017**, *56*, 8805. DOI: 10.1016/S0040-4039(03)00674-9.

[4] (a) Labeeuw, O.; Roche, C.; Phansavath, P.; Genêt, J.-P. *Org. Lett*. **2007**, *9*, 105. DOI: 10.1021/ol062631p. (b) Carlone, A.; Bartoli, G.; Bosco, M.; Pesciaioli, F.; Ricci, P.; Sambri, L.; Melchiorre, P. *Eur. J. Org. Chem*. **2007**, *2007*, 5492. DOI: 10.1021/ol062631p.

[5] (a) Yildiz, T.; Yusufoglu, A. *Monatsh. Chem*. **2013**, *144*, 183. DOI: 10.1007/s00706-012-0792-7. (b) Ohtsuka, Y.; Kubota, T.; Ikeno, T.; Nagata T.; Yamada, T. *Synlett*. **2000**, 535. DOI: 10.1055/s-2000-6584. (c) Xu, F.; Zacuto, M. J.; Kohmura, Y.; Rosen, J.; Gibb, A.; Alam, M.; Scott, J.; Tschaen, D.; *Org. Lett*. **2014**, *16*, 5422. DOI: 10.1021/ol502661g. (d) Cheng, T.; Ye, Q.; Zhao, Q.; Liu, G.; *Org. Lett*. **2015**, *17*, 4972. DOI: 10.1021/acs.orglett.5b02394. (e) Ke, Z.; Tan, C. K.; Chen, F.; Yeung, Y. Y. *J. Am. Chem. Soc*. **2014**, *136*, 5627. DOI: 10.1021/ja5029155. (f) Son, S.-M.; Lee, H.-K.; *J. Org. Chem*. **2014**, *79*, 2666. DOI: 10.1021/jo500148j. (g) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc*. **1988**, *110*, 629. DOI: 10.1021/ja00210a070. (h) Fan, Q. H.; Yeung, C. H.; Chan, A. S. C. *Tetrahedron: Asymmetry* **1997**, *8*, 4041. (i) Cotman, A. E.; Cahard, D.; Mohar, B. *Angew. Chem. Int. Ed*. **2016**, *55*, 5294. DOI: 10.1007/s00706-012-0792-7.

[6] (a) Gnanadesikan, V.; Horiuchi, Y.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc*. **2004**, *126*, 7782. DOI: 10.1021/ja047906f. (b) Mlynarski, J.; Mitura, M. *Tetrahedron Lett*. **2004**, *45*, 7549. DOI: 10.1016/j.tetlet.2004.08.134. (c) Nakajima, M.; Ichibakase, T. *Synthesis* **2012**, *44*, 3145. DOI: 10.1055/s-0031-1291138. (d) Hayashi, Y.; Itoh, T.; Aratake, S.; Ishikawa, H. *Angew. Chem. Int. Ed*. **2008**, *47*, 2082. DOI: 10.1002/anie.200704870. (e) Qiao, Y. P.; Chen, Q. K.; Lin, S. R.; Ni, B. K.; Headley, A. D. *J. Org. Chem*. **2013**, *78*, 2693. DOI: 10.1021/ja047906f.

[7] (a) Bode, S. E.; Wolberg, M.; Müller, M. *Synthesis* **2006**, 557. DOI: 10.1055/s-2006-926315. (b) Gupta, P.; Mahajan, N.; Taneja, S. C. *Catal. Sci. Technol*. **2013**, *3*, 2462. DOI: 10.1039/c3cy00125c.

[8] Huang, Y.-Y.; Yang, X.; Lv, Z.-C.; Cai, C.; Kai, C.; Pei, Y.; Feng, Y. *Angew. Chem. Int. Ed*. **2015**, *54*, 7299. DOI: 10.1002/anie.201501832.

[9] (a) Yanagimoto, D.; Kawano, K.; Takahashi, K.; Ishihara J.; Hatakeyama, S. *Heterocycles* **2009**, *77*, 249. DOI: 10.3987/COM-08-S(F)58. (b) Hatakeyama, S. *J. Syn. Org. Chem. Jpn*. **1997**, *55*, 793. DOI: 10.5059/yukigoseikyokaishi.55.793. (c) Xiang, A. X.; Watson, D. A.; Ling, T.; Theodorakis, E. A. *J. Org. Chem*. **1998**, *63*, 6774. DOI: 10.1021/jo981331l. (d) Hatakeyama, S.; Yoshida, M.; Esumi, T.; Iwabuchi, Y.; Irie, H.; Kawamoto, T.; Yamada, H.; Nishizawa, M. *Tetrahedron Lett*. **1997**, *38*, 7887. DOI: 10.1016/S0040-4039(97)10077-6.

[10] (a) Hatakeyama, S.; Sugawara, K.; Kawamura, M.; Takano, S. *Tetrahedron Lett*. **1991**, *32*, 4509. DOI: 10.1016/0040-4039(91)80026-3. (b) Soundararajan, R.; Li, G.-S.; Brown, H. C. *J. Org. Chem*. **1996**, *61*, 100. DOI: 10.1021/jo9513976. (c) Luo, M.; Iwabuchi, Y.; Hatakeyama, S. *Chem. Commun*. **1999**, 267. DOI: 10.1039/a809081e. (d) Yu, C.-M.; Lee, S.-J.; Jeon, M. *J. Chem. Soc. Perkin Trans.1* **1999**, 3557. DOI: 10.1039/a908119d. (e) Naodovic, M.; Xia, G.-Y.; Yamamoto, H. *Org. Lett*. **2008**, *10*, 4053. DOI: 10.1016/0040-4039(91)80026-3.

[11] (a) Tsuge, O.; Kanemasa, S.; Takenaka, S. *B. Chem. Soc. Jpn*. **1986**, *17*, 3137. DOI: 10.1246/bcsj.58.3137. (b) Bloch, R.; Chaptal-Gradoz, N. *J. Org. Chem*. **1994**, *59*, 4162. DOI: 10.1021/jo00094a029. (c) Brown, P. A.; Jenkins, P. R. *J. Chem. Soc. Perkin Trans. 1* **1986**, *5*, 1129. DOI: 10.1039/P19860001129.

[12] Smulik, J. A.; Diver, S. T. *Org. Lett*. **2000**, *2*, 2271. DOI: 10.1021/ol006035l.

[13] Alcaraz, L.; Cox, K.; Cridland, A. P.; Kinchin, E.; Morris, J.; Thompson, S. P. *Org. Lett.* **2005**, *7*, 1399. DOI: 10.1021/ol0502329.

[14] Durán-Galván, M.; Connell, B. T. *Eur. J. Org. Chem.* **2010**, *2010*, 2445. DOI: 10.1002/ejoc.201000199.

[15] (a) Lu, W.; Ma, J.; Yang, Y.; Chan, T. H. *Org. Lett.* **2000**, *2*, 3469. DOI: 10.1021/ol000239k. (b) Alcaide, B.; Almendros, P.; Rodríguez-Acebes, R. *J. Org. Chem.* **2005**, *70*, 3198. DOI: 10.1021/jo050130w. (c) Alcaide, B.; Almendros, P.; Rodríguez-Acebes, R. *J. Org. Chem.* **2002**, *67*, 1925. DOI: 10.1021/ol000239k.

[16] Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. DOI: 10.1021/ja00253a032.

[17] Zhang, W.; Basak, A.; Kosugi, Y.; Hoshino, Y.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 4389. DOI: 10.1002/anie.200500938.

[18] (a) Bull, J. A.; Croft, R. A.; Davis, O. A.; Doran, R.; Morgan, K. F. *Chem. Rev.* **2016**, *116*, 12150. DOI: 10.1021/acs.chemrev.6b00274. (b) Vitale, P.; Perna, F. M.; Agrimi, G.; Scilimati, A.; Salomone, A.; Cardellicchioe, C.; Capriati, V. *Org. Biomol. Chem.* **2016**, *14*, 11438. DOI: 10.1021/acs.chemrev.6b00274.