Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 19 (2008) 598–602

Organometallation of (*R*)-2,3-cyclohexylideneglyceraldehyde derived ketones: a simple and stereoselective strategy for the synthesis of (+)-tanikolide

Prasad Vichare and Angshuman Chattopadhyay*

Bio-organic Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received 26 December 2007; accepted 25 January 2008
Available online 4 March 2008

Abstract—Several metal mediated allylations and Grignard additions to ketones **3** and **5**, both derived from (*R*)-2,3-cylcohexylideneglyceraldehyde, took place with very high diastereoselectivity producing the same tertiary carbinol **4b** as the major product. Subsequently, **4b** was exploited to synthesize (+)-tanikolide efficiently through a series of simple reactions employing an RCM strategy.

1. Introduction

(+)-Tanikolide **I** is a brine-shrimp toxic and antifungal marine metabolite, isolated from the lipid extract of a blue green algae, cyanobacterium, *Lyngbia majuscula*, from a species collected on the Tanikely island, Madagascar. When tested for toxicity, this compound displayed an LD_{50} of 3.6 μg/ mL against brine-shrimp and 9.0 μg/ mL against the snail.[1] The striking structural feature of **1** is the presence of a stereogenic quaternary carbon center in a δ-lactone framework, in association with a hydroxymethyl group. Interestingly, all these functional units are individually prevalent in many other classes of biologically relevant molecules.[2] As a result of this unique structural feature, (+)-tanikolide has become an attractive target for organic synthesis.[3–5] In this regard, all these previous syntheses emphasized on the stereoselective generation of the desired quaternary carbon center through varied strategies viz Sharpless asymmetric dihydroxylation/epoxidation of an allylic alcohol,[3] exploitation of templates D-erythrulose,[4a] D-erythrose,[4b] insertion of the dichlorocarbene into a chiral 2°-alcohol,[5a] asymmetric α-alkylation of a β-keto ester followed by Baeyer–Villiger oxidation,[5b] etc. Among them, we were especially attracted by the work of Carda et al.,[4a] who accomplished the synthesis of **I** through a stereoselective construction of the relevant tertiary carbinol via allylation of D-erythrulose derived ketones.[6a]

During our ongoing program on the synthesis of bioactive molecules, we have exploited (*R*)-2,3-cyclohexylideneglyceraldehyde **1**[7a] to construct various structural units viz., alkanetriols,[7a–d] ribofuranoses,[7c,e–g] γ-lactones,[7h] δ-lactones,[7i] 2,5-disubstituted tetrahydrofurans,[7j] etc., which are widely prevalent in bioactive natural products. Herein, we report the potential of **1** in comparison with erythrulose[4a,6a] to produce tertiary carbinols relevant to the synthesis of **I**. From this viewpoint, the present work predominantly focused on our endeavor to exploit **1** for the stereoselective synthesis of homoallylic tertiary carbinol **4** through several alkylmetallations of ketones **3** and **5** originally from **1**. In this context, it should be mentioned that the preparation of tertiary alcohols by stereoselective alkylations of prochiral ketones[6] has drawn considerable attention in organic synthesis.

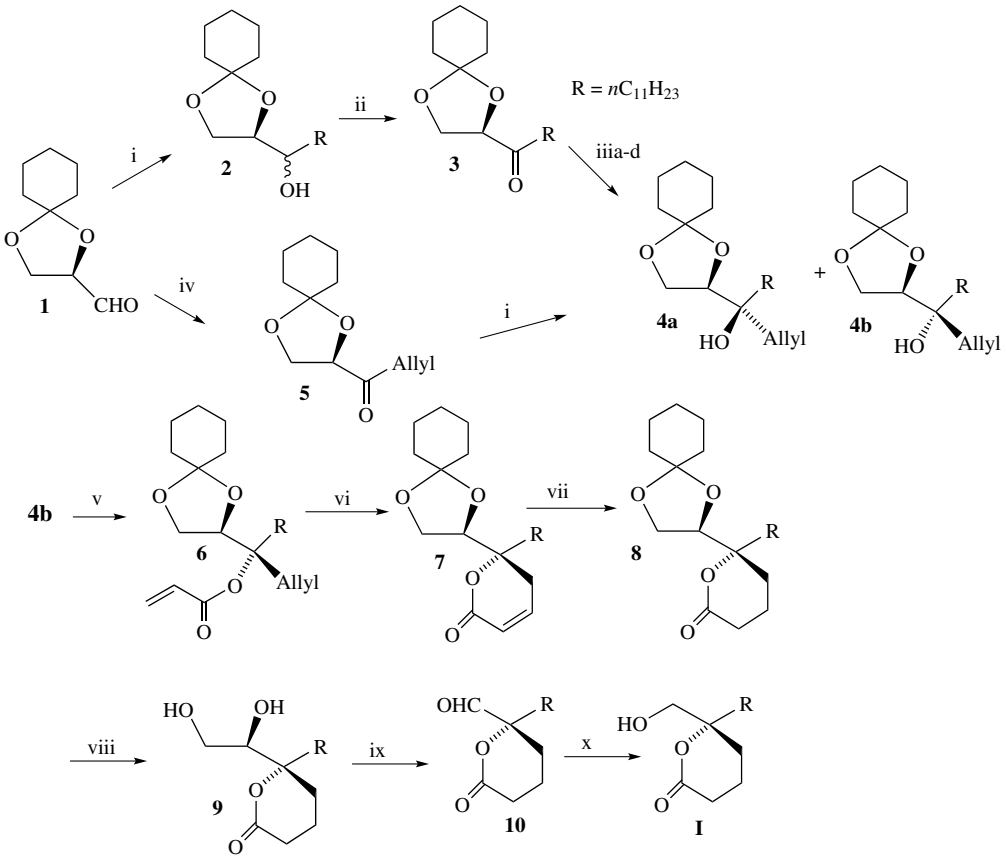
2. Results and discussion

To start with (Scheme 1), **1** was treated with undecylmagnesiumbromide and product **2** was oxidized with PCC to produce ketone **3** in good yield. Next, **3** was subjected to allylation following three different procedures with a view to make a comparative survey about their efficacies and stereoselectivities for this substrate, viz.

(i) Mediated with zinc following Luche's procedure[8] (Table 1, entry a), (ii) mediated with low valent cobalt, copper, and iron (Table 1, entries b–d) in distilled THF,[9] which

* Corresponding author. Tel.: +91 22 25595422; fax: +91 22 25505151; e-mail: achat@apsara.barc.ernet.in

0957-4166/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2008.01.034



Scheme 1. Reagents and conditions: (i) $nC_{11}H_{23}MgBr$, THF, −30 °C; (ii) PCC, CH_2Cl_2, rt; (iii) (a) allylBr Zn, aq NH_4Cl, THF; (b) allylBr, $CoCl_2{\cdot}8H_2O$, Zn, THF, rt; (c) allylBr, $CuCl_2{\cdot}2H_2O$, Zn, THF, rt; (d) allylBr, $FeCl_3$, Zn, THF, rt; (iv) Ref. 7e; (v) EtMgBr, CH_2=CHCOCl, THF, rt; (vi) $PhCH{=}RuCl_2(PCy_3)_2$, DCM, reflux; (vii) H_2, 5% Pd/C, EtOH; (viii) CF_3CO_2H, H_2O, 0 °C; (ix) $NaIO_4$, CH_3CN/H_2O (6:4), rt; (x) K-Selectride, THF, −78 °C.

Table 1. Organometallations of ketones **3** and **5**

Entry	Ketone	RBr	Source of M of RM/solvent	Ketone/RBr/Zn/metal salt	Rxn time	Product ratio **4a**:**4b**	Overall yield (%)
a	**3**	allylBr	Zn, aq NH_4Cl/dist THF	1:3.5:3.0:—	3 h	6.6:93.4	77.5
b	**3**	allylBr	Zn, $CoCl_2{\cdot}8H_2O$/dist THF	1:4.5:4.5:4.5	48 h	2.5:97.5	22.5
c	**3**	allylBr	Zn, $CuCl_2{\cdot}2H_2O$/dist THF	1:3.5:3.5:3.5	20 h	1.5:98.5	72.5
d	**3**	allylBr	Zn, $FeCl_3$/dist THF	1:3.0:2.5:2.5	40 min	7.9:92.1	83.5
e	**3**	allylBr	Grignard/dry Et_2O			11.8:88.2	79.1
f	**5**	$nC_{11}H_{23}Br$	Grignard/dry THF			2.0:98.0	78.2

were prepared in situ following a bimetal redox strategy,[7f,10] and (iii) through allyl Grignard addition in anhydrous conditions at −30 °C (Table 1, entry e).

For both Luche's and Fe-mediated additions (Table 1, entries a and d), the reactions took place with comparable efficiency giving good yields of product **4**. The Fe-mediated reaction proceeded at a faster rate. In contrast, as in previous occasions,[7f] the progress of Co and Cu mediated allylations (Table 1, entries b and c) was quite sluggish. The Cu mediated reactions proceeded with reasonably good yield of the product after stirring the mixture for longer reaction time (20 h). However, Co mediated reactions progressed disappointingly, even after stirring the reaction mixture for 48 hrs despite using an excess amount of reagents. Evidently, all these allylations of **3** (Table 1, entries a–e) predominantly produced **4b** with very high selectivity and producing small amounts of **4a**. Both the diastereoisomers were easily separable from each other by column chromatography. Among all these allylations (Table 1, entries a–e), the selectivity of the Cu mediated reaction (Table 1, entry c) was found to be the highest. Interestingly, for all these allylations [both in anhydrous (Table 1, entry e) and hydrous (Table 1, entries a–d) conditions], the approach of an allyl nucleophile to the carbonyl of **3** took place via a rigid α-chelate transition state (Fig. 1) as was reflected with the predominant formation of **4b**. This is in contrast with all our organometallations of **1**,[7a–c,f,i] carbonyls originating from **1**,[7e,g,h] and allylmetallations of other α-hydroxyketones,[6a] which preferably took place via a Felkin–Anh transition state. Notably, the stereoselectivities of the present allylations of **3** were in contrast with those

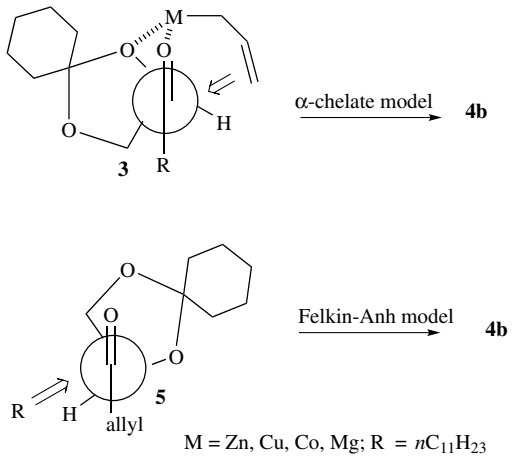


Figure 1.

reported for allyl indium addition under aqueous condition to the corresponding isopropylidene derivative of **1**.[4a]

Next, the preparation of **4** was attempted following an alternate route, which involved the addition of undecylmagnesiumbromide to homoallylic ketone **5**,[7e] derived from **1**. Interestingly, this reaction also produced the same isomer **4b** with very high selectivity (Table 1, entry f) suggesting that unlike the allylations of **3**, the addition of undecylGrignard to **5** under anhydrous conditions (entry f) took place via a Felkin–Anh transition state (Fig. 1).

Hence, all these organometallations of both carbonyls **3** and **5** derived from **1** stereoselectively yielded the same tertiary carbinol **4b**, the desired isomer to synthesize (+)-tanikolide. Next, the Grignard mediated acrolylation of **4b** afforded **6**, which was then subjected to a Grubbs RCM reaction[11] to afford hexenolide **7** in good overall yield (86%). This was hydrogenated to produce **8** and then deketalized under acidic conditions to afford 1,2-diol **9** in good yield. The $NaIO_4$ cleavage of **9** afforded aldehyde **10**, which was unstable and so was not purified further. As a result, it was subjected to reduction with K-Selectride to directly produce the target compound **I** whose spectral and optical data were in agreement with the reported ones.[3a,4a]

3. Conclusion

In conclusion, similarly to (*R*)-erythrulose, compound **1** has also been efficiently exploited as a good substrate to prepare (*R*)-+-tanikolide employing various alkylmetallations of carbonyls **3** and **5**, followed by an RCM reaction. The efficacy of this approach is due to the ready availability of **1**, its highly stable ketal functionality that enables to carry out several inexpensive allylation reactions easily,[9] and importantly high stereoselective formation of tertiary alcohol **4b**. It is worth noting that contrary to the Felkin–Anh attack for many literature precedent allylations of α-hydroxycarbonyls,[4a,6a,7] all the allylations of **3** both under wet and anhydrous conditions took place through an α-chelate transition state, whereas the Grignard addition to homoallylic ketone **5** predictably took place with Felkin–Anh attack. The presence of two functionalities such as 1,2-cyclohexylidenediol and an olefin in **4b**, which can be selectively exploited, should allow this molecule to be transformed into other tertiary carbinols relevant to various other synthetic objectives.

4. Experimental

Chemicals used as starting materials are commercially available and were used without further purification. All solvents used for the extraction and chromatography were distilled twice at atmospheric pressure prior to use. The ^1H and ^{13}C NMR spectra were scanned with a Brucker Ac-200 (200 MHz) instrument in $CDCl_3$. The organic extracts were desiccated over dry Na_2SO_4.

4.1. (2*R*)-1,2-*O*-Cyclohexylidene-1,2-dihydroxytetradeca-3-one 3

Following a standard procedure, a solution of **1** (5.1 g, 30 mmol) in THF (60 mL) was added to a suspension of Grignard reagent prepared from 1-bromoundecane (17.6 g, 75 mmol) and Mg (1.92 g, 80 mmol) in THF (100 mL). The crude product **2**, obtained after the usual workup, was taken in CH_2Cl_2 (60 mL) and added to a stirred suspension of PCC (9.7 g, 45 mmol) in CH_2Cl_2 (80 mL) at 0 °C. After stirring the mixture for 3 h, when the reaction was complete (TLC), dry ether (100 mL) was added to the mixture. The supernatant was filtered through a pad of silica gel, which was subsequently eluted with ether. The combined extracts were concentrated in vacuo and the residue was chromatographed (silica gel, 0–10% EtOAc/hexane) to obtain pure **3** (6.86 g, 70.5% from **1**); $[\alpha]_D^{22} = +22.5$ (*c* 0.12, $CHCl_3$); IR: 2923, 1715, 1466, 1369, 1162, 1101 cm^{-1}; ^1H NMR: δ 0.92 (t, $J = 6.5$ Hz, 3H), 1.30 (m. 18H), 1.4–1.6 (m. 10H), 2.65 (t, $J = 7.5$ Hz, 2H), 4.00 (dd, $J = 8.4$, 5.6 Hz, 1H), 4.22 (t, $J = 7.9$ Hz, 1H), 4.46 (dd, $J = 7.7$, 5.7 Hz, 1H). Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.03; H, 11.80. Found: C, 73.88; H, 11.55.

4.2. General procedure of low valent metal mediated allylations of 3 (Table 1, entries b, c, and d)

To a well-stirred mixture of **3** (3.24 g, 0.01 mol), allyl bromide (0.02 mol), and metal salt [$CoCl_2 \cdot 6H_2O$ (8.4 g, 0.035 mol) or $CuCl_2 \cdot 2H_2O$ (6.0 g, 0.035 mol) or $FeCl_3$ (4.9 g, 0.03 mol)] in THF (70 mL) was added Zn dust (2.25 g, 0.035 mol for Co and Cu; 1.95 g, 0.03 mol for Fe) in portions over a period of 15 min. The mixture was stirred at ambient temperature for the period as shown in the table. The reaction mixture was then treated successively with water (50 mL) and EtOAc (100 mL), stirred for an additional 10 min and then filtered. The filtrate was treated with 2% aqueous HCl to dissolve a small amount of the suspended particles. The organic layer was then separated. The aqueous layer was extracted with EtOAc. The combined organic layer was washed with water, brine, and then dried. Solvent removal and column chromatography of the residue (silica gel, 0–15% EtOAc in petroleum ether)

afforded **4a** and **4b** in pure form whose overall yields and proportions are shown in Table 1.

Other allylations of **3** (Table 1, entries a and e): following the same procedures as carried out with **1**,[7a,b] Luche's and Grignard allylation were performed with **3**. The overall yields and proportions are shown in Table 1.

An alternate preparation of **4a** and **4b** (Table 1 entry f): to a cooled (0 °C) suspension of Grignard reagent prepared from 1-bromoundecane (17.6 g, 75 mmol) and Mg (1.92 g, 80 mmol) in THF (100 mL) as carried out as above was added a solution of ketone **5** (14.7 g, 70 mmol) in THF (30 mL) over a period of 1 h. The mixture was stirred for an additional 2 h at room temperature and then treated with saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with water, brine, and then dried. Solvent removal under reduced pressure and column chromatography of the residue (silica gel, 0–15% EtOAc in petroleum ether) afforded **4a** and **4b** in pure forms, whose overall yields and proportions are shown in Table 1.

4.3. (2*R*,3*R*)-1,2-*O*-Cyclohexylidene-3-undecyl-hex-5-en-1,2,3-triol 4a

R_f: 0.73 (10% EtOAc in hexane); $[\alpha]_D^{25} = +11.6$ (*c* 0.8, $CHCl_3$); ^{1}H NMR: δ 0.84 (br t, 3H), 1.24–1.36 (m, 22H), 1.60 (m, 8H), 2.06 (m, 1H, overlapped with a br s, 1H), 2.33 (m, 1H), 3.7–4.0 (m, 3H), 5.0–5.1 (m, 2H), 5.6–5.9 (m, 1H). ^{13}C NMR: δ 14.06, 22.64, 22.87, 23.80, 23.94, 25.14, 29.29, 29.58, 30.17, 31.87, 34.64, 35.02, 36.01, 41.72, 64.20, 72.88, 79.22, 109.27, 118.16, 133.71. Anal. Calcd for $C_{23}H_{42}O_3$: C, 75.36; H, 11.55. Found: C, 75.62; H, 11.32.

4.4. (2*R*,3*S*)-1,2-*O*–Cyclohexylidene-3-undecyl-hex-5-en-1,2,3-triol 4b

R_f: 0.66 (10% EtOAc in hexane); $[\alpha]_D^{25} = -5.3$ (*c* 0.9, $CHCl_3$); ^{1}H NMR: δ 0.86 (br t, 3H), 1.24–1.37 (m, 22H), 1.60 (m, 8H), 1.91 (br s, 1H), 2.02 (dd, $J = 14.0$, 8.2 Hz, 1H), 2.28 (dd, $J = 14.0$, 6.4 Hz, 1H), 3.8–4.0 (m, 3H), 5.0–5.1 (m, 2H), 5.6–5.8 (m, 1H). ^{13}C NMR: δ 14.03, 22.62, 23.07, 23.75, 23.90, 25.13, 29.29, 29.57, 30.10, 31.85, 34.96, 35.94, 37.21, 39.29, 64.15, 72.98, 79.54, 109.15, 118.11, 133.07. Anal. Calcd for $C_{23}H_{42}O_3$: C, 75.36; H, 11.55. Found: C, 75.55; H, 11.62.

4.5. (5*R*)-5[(2′*R*)-1′,2′-*O*-Cyclohexylidenedihydroxyethyl]hexadec-2-en-5-olide 7

To a stirred 1 M suspension of ethylmagnesiumbromide (3.4 mL, 3.4 mmol, prepared from EtBr and Mg in THF following the usual procedure) was added a solution of **4b** (1.2 g, 3.3 mmol) in THF (30 mL) over a period of 30 min at room temperature. The mixture was refluxed for 30 min at room temperature and then cooled to 0 °C. Acryloyl chloride (0.618 mL, 3.2 mmol) was added to it over a period of 10 min. The mixture was stirred at room temperature for an additional 30 min and treated with water. This was extracted with EtOAc. The combined organic extract was washed with water, brine, and dried. Solvent removal under reduced pressure and column chromatography of the residue (silica gel, 0–15% EtOAc in petroleum ether) afforded **6** (1.1 g, 81%) in pure form. A fraction of **6** (420 mg, 1 mmol) was taken in CH_2Cl_2 (50 mL). Grubb's catalyst [$PhCH{=}RuCl_2$-$(PCy_3)_2$] (41 mg, 5 mol %) was added in one portion to a stirred solution of **6**. The mixture was heated at reflux for 14 h (monitored with TLC). Solvent was removed under reduced pressure and the residue was chromatographed on silica gel (0–15% EtOAc in petroleum ether) to afford **7** (370 mg, 94.3%) in pure form. $[\alpha]_D^{25} = +2.7$ (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 0.85 (br t, 3H), 1.24–1.37 (m, 22H), 1.5–1.6 (m, 8H), 2.44 (br d, $J = 19.0$ Hz, 1H), 2.63 (br d, $J = 19.2$ Hz, 1H), 3.84–4.03 (m, 2H), 4.33 (t, $J = 6.4$ Hz, 1H), 5.98 (d, $J = 9.8$ Hz, 1H), 6.75 (m, 1H). ^{13}C NMR: δ 14.05, 22.60, 23.38, 23.58, 23.87, 25.05, 27.82, 29.25, 29.44, 29.51, 29.90, 31.82, 33.94, 34.55, 35.68, 64.21, 77.61, 83.75, 110.4, 120.36, 143.59, 162.97. Anal. Calcd for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27. Found: C, 73.68; H, 10.52.

4.6. (5*R*)-5[(2′*R*)-Dihydroxyethyl]-5-hexadecaolide 9

In a hydrogenation flask, 5% Pd in charcoal (60 mg) was suspended in EtOH (15 mL) and stirred for 10 min under an H_2 atmosphere. To this solution of **7** (370 mg, 0.0943 mmol) in EtOH (20 mL) was added through a syringe. The reaction mixture was stirred for 10 h at room temperature and filtered through Celite. The Celite pad was thoroughly washed with EtOH. The organic layer was concentrated under reduced pressure, and the residue was chromatographed on silica gel (0–15% EtOAc in petroleum ether) to afford pure **8** (316 mg, 85%). This was taken in CH_2Cl_2 (20 mL) and cooled to (0 °C). To this was added 90% aqueous trifluoroacetic acid (5 mL). The mixture was stirred for about 1 h until the starting material disappeared (TLC) and then extracted with $CHCl_3$. The combined organic extract was washed with water, brine, and dried. After solvent removal under reduced pressure, the residue was purified by passing through a short pad of silica gel eluting with MeOH in $CHCl_3$ (5%, v/v) to afford pure diol **9** (180 mg, 71.7%). $[\alpha]_D^{25} = -12.1$ (*c* 1.1, $CHCl_3$); ^{1}H NMR: δ 0.86 (br t, 3H), 1.2–1.7 (m, 22H), 1.75–2.0 (m, 2H), 2.38 (m, 2H), 3.48 (m, 1H), 3.70 (m, 2H, overlapped with a br s, 2H). ^{13}C NMR: δ 14.07, 16.82, 22.63, 22.94, 25.89, 29.30, 29.59, 29.82, 30.04, 31.85, 37.12, 62.04, 75.51, 87.35, 173.15. Anal. Calcd for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90. Found: C, 68.96; H, 10.66.

4.7. Tanikolide I

A solution of **9** (180 mg, 0.57 mmol) in 60% aqueous CH_3CN (30 mL) was treated with $NaIO_4$ (214 mg, 1.0 mmol) and the mixture was stirred at room temperature for 1 h until the starting material had disappeared (TLC). It was filtered and thoroughly washed with EtOAc. The combined organic extract was washed with water, brine, and dried. After solvent removal under reduced pressure, the residue was purified by passing through a short pad of silica gel eluting with EtOAc in hexane (15%) to afford aldehyde **10** (135 mg). This was taken in THF (30 mL) and the solution was cooled to −78 °C. To this was added

K-Selectride (3 mL of 1 M THF solution) over a period of 30 min. The mixture was stirred for an additional 30 min and quenched with water and extracted with EtOAc. The combined organic extract was washed with water, brine, and dried. After solvent removal under reduced pressure, the residue was purified by passing through a short pad of silica gel eluting with EtOAc in hexane (15%, v/v) to afford **I** (80 mg, 59.2%). $[\alpha]_D^{25} = +2.1$ (*c* 1.0, $CHCl_3$); lit.[3a] $[\alpha]_D^{22} = +1.9$ (*c* 1.0, $CHCl_3$); ^1H NMR: δ 0.86 (br t, 3H), 1.2–1.4 (m, 18H), 1.55–1.76 (m, 4H), 1.8–2.0 (m, 2H), 2.32–2.44 (m, 2H), 3.19 (br s, 1H), 3.51 (d, $J = 12$ Hz, 1H), 3.64 (d, $J = 12$ Hz, 1H). ^{13}C NMR: δ 14.06, 16.63, 22.63, 23.39, 26.59, 29.28, 29.43, 29.55, 29.73, 29.98, 31.85, 36.71, 67.41, 86.61, 172.03.

References

1. Singh, I. P.; Milligan, K. E.; Gerwick, W. H. *J. Nat. Prod.* **1999**, *62*, 1333.
2. (a) Mori, K. *Tetrahedron* **1989**, *45*, 3233; (b) Doan, H. D.; Gallon, J.; Piou, A.; Vatele, J.-M. *Synlett* **2007**, 983; (c) Hanessian, S. *Total Synthesis of Natural Products: The Chiron approach*; Pergamon Press: Oxford, 1983; (d) Goldstein, J. L.; Brown, M. S. *Nature* **1990**, *343*, 425.
3. (a) Ohgiya, T.; Nakamura, K.; Nishiyama, S. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1549; (b) Mizutani, H.; Watanabe, M.; Honda, T. *Tetrahedron* **2002**, *58*, 8929; (c) Schomaker, J. M.; Boran, B. *Org. Biol. Chem.* **2004**, *2*, 621; (d) Kita, Y.; Matsuda, S.; Fujii, E.; Horai, M.; Hata, K.; Fujioka, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5857.
4. (a) Carda, M.; Rodriguez, S.; Castillo, E.; Bellido, A.; Diazoltra, S.; Marco, J. A. *Tetrahedron* **2003**, *59*, 857; (b) Koumbis, A. E.; Dieti, K. M.; Vikentiou, M. G.; Gallos, J. K. *Tetrahedron Lett.* **2003**, *44*, 2513.
5. (a) Arasaki, H.; Iwata, M.; Makida, M.; Masaki, Y. *Chem. Pharm. Bull.* **2004**, *52*, 848; (b) Wu, F.; Hong, R.; Khan, J.; Liu, X.; Deng, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 4301.
6. (a) Carda, M.; Castillo, E.; Rodriguez, S.; Gonzalez, F.; Marco, J. A. *Tetrahedron: Asymmetry* **2001**, *12*, 1417; (b) Nakamura, M.; Hirai, A.; Sogi, M.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 5846; (c) Evans, D. A.; Tregay, S. W.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T. *J. Am. Chem. Soc.* **2000**, *122*, 7936; (d) Jiang, B.; Tang, X. *Org. Lett.* **2002**, *4*, 3451; (e) Garcia, C.; Walsh, P. *Org. Lett.* **2003**, *5*, 3641; (f) Ojida, A.; Yamano, T.; Taya, N.; Tasaka, A. *Org. Lett.* **2002**, *4*, 3051; (g) Ramon, D.; Yus, M. *Tetrahedron Lett.* **1998**, *39*, 1239; (h) Weber, B.; Seebach, D. *Tetrahedron* **1994**, *50*, 6117.
7. (a) Chattopadhyay, A.; Mamdapur, V. R. *J. Org. Chem.* **1995**, *60*, 585; (b) Chattopadhyay, A. *J. Org. Chem.* **1996**, *61*, 6104; (c) Chattopadhyay, A.; Dhotare, B.; Hassarajani, S. A. *J. Org. Chem.* **1999**, *64*, 6874; (d) Dhotare, B.; Salaskar, A.; Chattopadhyay, A. *Synthesis* **2003**, 2571; (e) Dhotare, B.; Chattopadhyay, A. *Synthesis* **2001**, 1337; (f) Chattopadhyay, A.; Goswami, D.; Dhotare, B. *Tetrahedron Lett.* **2006**, *47*, 4701; (g) Chattopadhyay, A. *Tetrahedron: Asymmetry* **1997**, *8*, 2727; (h) Dhotare, B.; Chattopadhyay, A. *Tetrahedron Lett.* **2005**, *46*, 3103; (i) Dhotare, B.; Goswami, D.; Chattopadhyay, A. *Tetrahedron Lett.* **2005**, *46*, 6219; (j) Chattopadhyay, A.; Vichare, P.; Dhotare, B. *Tetrahedron Lett.* **2007**, *48*, 2871.
8. (a) Petrier, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 910; (b) Einhorn, C.; Luche, J. L. *J. Organomet. Chem.* **1987**, *322*, 177; (c) Petrier, C.; Einhorn, J.; Luche, J. L. *Tetrahedron Lett.* **1985**, *26*, 1449.
9. As explained earlier,[7f] distilled THF always contains some amount of moisture which plays a significant role in facilitating bimetal redox reactions and subsequent allylation reactions.
10. Chattopadhyay, A.; Dubey, A. *J. Org. Chem.* **2007**, *72*, 9357.
11. Trnaka, T.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.