



# Stereoselective synthesis of the C14–C23 fragment of biselyngbyolide A and B enabled by transition metal catalysis

Rakesh G. Thorat, Bailey A. Brooks, Brandon Nichols, Andrew M. Harned\*

Texas Tech University, Department of Chemistry & Biochemistry, 1204 Boston Ave., Lubbock, TX, 79409-1061, USA

## ARTICLE INFO

### Article history:

Received 17 September 2018

Received in revised form

15 October 2018

Accepted 24 October 2018

Available online 2 November 2018

### Keywords:

Stille reaction

Oxidation

Allylation

Stereoselectivity

Catalysis

## ABSTRACT

Transition metal catalysis has enabled the highly stereoselective and protecting group-free synthesis of the C14–C23 fragment of the apoptosis-inducing natural products biselyngbyolide A and B. A Pd-catalyzed Stille reaction between a vinyl stannane and a crotyl carbonate formed the skipped diene with complete control of the trisubstituted bond and excellent control over the branched/linear products. A Cu-catalyzed Stahl oxidation was used to form the requisite aldehyde needed for a Ag-catalyzed asymmetric allylation. The latter provided the final fragment with excellent stereochemical control.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Between 2009 and 2015, Suenaga and co-workers reported the isolation of a small family of polyketide natural products from the marine cyanobacterium *Lyngbya* sp [1]. Glycosylated members of this family were christened as biselyngbyasides, while the aglycone macrolides were called biselyngbyolides (Fig. 1). Initial biological screening revealed that compounds **1–4** have significant anticancer activity against a number of cell lines. These compounds were also found to induce apoptosis in cancerous cells as well as mature osteoclasts [2]. More recently, compounds **1**, **2**, and **4** were found to be potent inhibitors of sarco/endoplasmic reticulum  $\text{Ca}^{2+}$ -ATPase (SERCA) [3], a membrane-bound protein that plays a key role in stress response within the cell and the caspase signaling pathway [4]. X-ray crystallography revealed the binding site of these compounds to be distinct from other known SERCA inhibitors [3].

Owing to their interesting biological activity, these compounds have drawn the attention of the synthetic community. Completed syntheses of biselyngbyolide A [5], biselyngbyolide B [6–8], and biselyngbyaside [9] have already appeared in the literature [10] but most suffer from deficiencies on a number of fronts. Many involve numerous protecting group manipulations and oxidation state

changes that drive up the step count. Others rely on stoichiometric chiral reagents or auxiliaries to set the absolute configuration of the different stereocenters.

From the outset, our approach to the biselyngbyolides has been to target a common intermediate, that would allow for introduction of the C5 hydroxyl group at a late stage, if so desired. In this manner one could access either structural series depending on needs. The macrocycle of this intermediate can be formed through a Pd-catalyzed coupling reaction [5–9], after joining two smaller fragments. Our group recently reported a nine step synthesis of the C1–C13 fragment of biselyngbyolide B [11]. The efficiency of this route was realized by relying on organocatalytic and transition metal-catalyzed reactions for C–C bond formation and for generating the C7 and C10 stereocenters. A photocatalytic cyanomethylation reaction [12] was used to form the C10 stereocenter. The C7 stereocenter was formed using an iridium-catalyzed allylation reaction [13]. Finally, a cross metathesis was used to forge the C4–C5 alkene. Relying on these robust catalytic reactions allowed us to minimize the use of protecting groups and oxidation state changes. With this same goal in place, we then set out to address the construction of the C14–C23 fragment.

The stereoselective construction of the trisubstituted C18–C19 alkene is a key challenge of the targeted fragment. Not only is this a trisubstituted double bond, but it is also part of a skipped diene. Consequently, any C–C bond forming reactions must be mild enough to prevent conjugation of the diene. Previous attempts at

\* Corresponding author.

E-mail address: [andrew.harned@ttu.edu](mailto:andrew.harned@ttu.edu) (A.M. Harned).

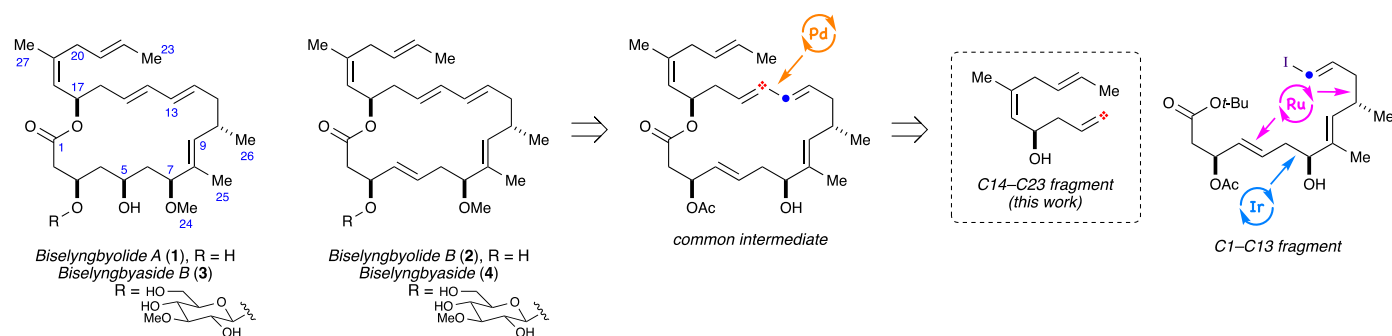
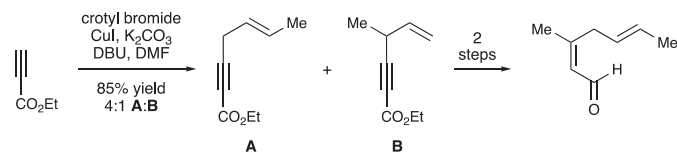


Fig. 1. Structures of the biselyngbyaside family of natural products and our synthetic approach.

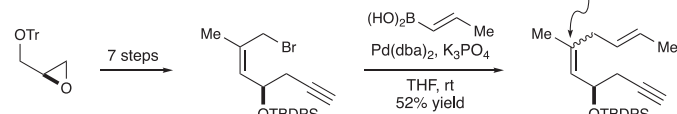
forming the C19–C20 bond are summarized in Scheme 1. Most suffer from either poor regioselectivity [7,10a] (A vs. B and C vs. D) or poor control of *Z/E* selectivity [5,6]. These problems are exacerbated by the fact that these product mixtures must be carried through several steps before the isomers can be separated. While our work was underway, Maier reported a solution to both of these problems, but had to introduce an ester group that then needed to be converted into a CH<sub>3</sub> over three steps [8].

In addition to identifying conditions for a more efficient construction of the C19–C20 bond, it would also be beneficial if

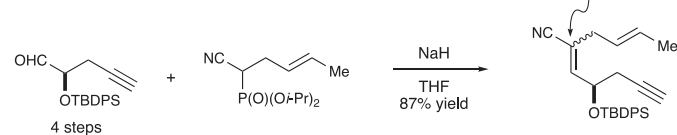
Chandrasekhar – 2013



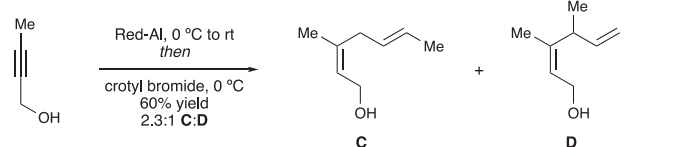
Suenaga – 2014



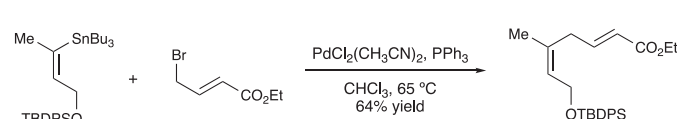
Suenaga – 2016



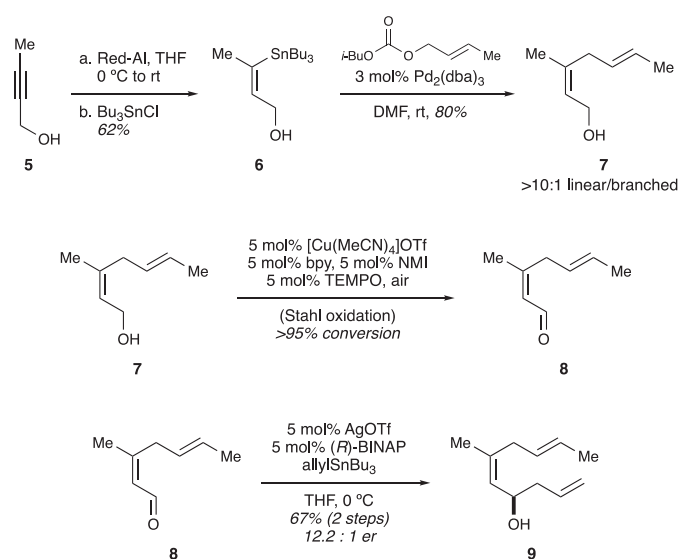
Goswami – 2016



Maier – 2018



Scheme 1. Previous routes used to construct the C19–C20 bond.



Scheme 2.

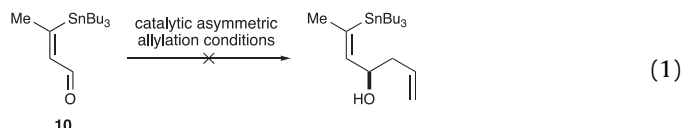
formation of the C17 stereocenter could be achieved using catalyst control. Existing routes rely on a commercial source that must then heavily modified for this application [5,6], or use a chiral reagent [7,8] or auxiliary [10a] to introduce asymmetry. Herein we report our efforts on both of these fronts.

## 2. Results and discussion

Using a known procedure [14], we first prepared stannyl alcohol **6** from 2-butyl-1-ol (**5**, Scheme 2). The alkenyl stannane was then transformed into skipped diene **7** using the indicated crotyl carbonate. This was accomplished using the “ligand-free” Pd-catalyzed coupling conditions first reported by Echavarren [15,16]. These conditions were attractive due to their mild nature and their ability to deliver skipped dienes with high yield and regioselectivity. In this case, the C19–C20 bond was formed with complete *Z/E* selectivity for the trisubstituted alkene and excellent (>10:1) branched/linear selectivity. Copper-catalyzed Stahl oxidation [17] of alcohol **7** was then used to prepare aldehyde **8**. These conditions were chosen over more traditional oxidations (e.g., PCC, MnO<sub>2</sub>, Dess–Martin, Swern) owing to their environmentally friendly nature (air is terminal oxidant and water is only stoichiometric byproduct). Finally, the C17 stereocenter was generated using a Yamamoto allylation [18] of aldehyde (*R*)-**8**. Chiral GC analysis revealed alcohol **9** was formed with 12.2:1 er.

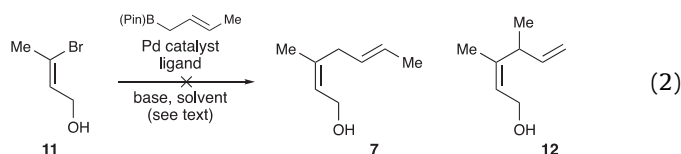
We attempted to prepare alcohol **9** by performing a Krische

allylation [13] on primary alcohol **7**. Unfortunately, the formation of alcohol **9** was accompanied by significant amounts of another compound that was tentatively assigned to be a conjugated diene. Unambiguous assignment was complicated by the inseparable nature of the product mixture. We also made several attempts at performing an asymmetric allylation on known [14] enal **10** (eqn. (1)). Unfortunately, we were unable to adapt existing catalytic asymmetric allylation conditions to this substrate. We attribute this problem to the large size of the  $\text{SnBu}_3$  and, possibly, the reactivity of the vinyl stannane.

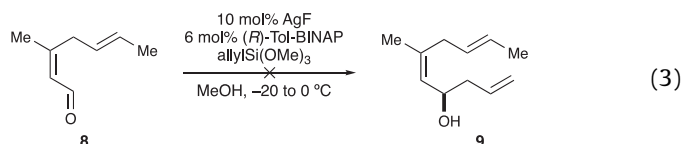


Our route to C14–C23 fragment **9** addresses the branched/linear problems experienced Chandrasekhar [10a] and Goswami [7], as well as the problems of *Z/E* mixtures faced by Suenaga [5,6]. We have also shown that catalytic conditions can be used to generate the C17 stereocenter. That said, the route as a whole could be improved by avoiding the use of organotin reagents. In principle, we could avoid the use of allyltributylstannane by using Yamamoto's modified Ag-catalyzed asymmetric allylation that employs allyltrimethoxysilane as the nucleophile [19,20]. However, avoiding the Stille reaction used to prepare **7** was expected to be more troublesome as there are no established alternative methods that can construct a skipped diene as efficiently and effectively as Echavarren's method. Fortunately, Buchwald has shown that the regioselectivity of Suzuki reactions between  $\gamma$ -substituted allylboronates and aryl halides can be controlled by ligand choice [21].

Several attempts at coupling known [22] alkenyl bromide **11** to the indicated commercially available crotyl pinacol boronate were made (eqn. (2)). These included standard Suzuki conditions ( $\text{Pd}(\text{PPh}_3)_4$ , aq. NaOH, THF) as well as conditions similar to those reported by Buchwald [21] ( $\text{Pd}(\text{OAc})_2$ , S-Phos or X-Phos,  $\text{Cs}_2\text{CO}_3$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ), but all either failed to provide any coupling products or provided low yields (<20%) of branched product **12**.



Several attempts were also made at using Yamamoto's modified conditions for the asymmetric allylation of aldehyde **8** (eqn. (3)) [19]. Unfortunately, very poor conversion was observed even after extended reaction times (3 days). The steric crowding around aldehyde **8**, together with the diminished nucleophilicity of allyltrimethoxysilane, are likely responsible for the poor performance of this reaction.



### 3. Conclusion

We have developed a highly stereoselective synthesis of the C14–C23 fragment common to the biselyngbyolide and biselyngbyaside natural products. By relying on mild transition metal-catalyzed reactions we were able to address many of the pitfalls

faced in previous routes to the same intermediate. We have also been able to avoid the use of protecting groups. Future work aimed at joining this fragment with our previously synthesized C1–C13 fragment [11] will be reported in due course.

## 4. Experimental section

### 4.1. Materials and methods

Unless otherwise stated, reactions were performed in flame- or oven-dried glassware under an argon atmosphere using anhydrous solvents. Tetrahydrofuran, dichloromethane, diethyl ether, toluene, acetonitrile, and dimethyl formamide were dried by passage through a column of activated molecular sieves. The Stahl Aerobic Oxidation TEMPO solution [0.2 M solution of 1-methylimidazole (NMI), 2,2'-bipyridyl (bpy), and TEMPO in acetonitrile], tetrakisacetonitrile copper(I) triflate, and (*E*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased from Sigma Aldrich. All other chemicals were purchased from commercial sources and used as received. Reactions were monitored using thin-layer chromatography (TLC) using glass plates precoated with silica gel XHL w/UV254 (250 mm) purchased from SILICYCLE® and visualized by UV light or  $\text{KMnO}_4$ , phosphomolybdic acid, anisaldehyde, or 2,4-DNP stains; followed by heating. Silica gel (particle size 32–63 mm) purchased from SILICYCLE® was used for flash column chromatography.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are reported relative to the residual solvent peak ( $\delta$  7.26 and  $\delta$  77.0 for  $^1\text{H}$  and  $^{13}\text{C}$  in  $\text{CDCl}_3$ ), or tetramethylsilane ( $\delta$  0.00 for  $^1\text{H}$ ) when the residual solvent peak is obscured. Data for  $^1\text{H}$  NMR spectra are reported as follows: (instrument field strength, solvent)  $\delta$  chemical shift (ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, app = apparent. Data for  $^{13}\text{C}$  NMR spectra are reported in terms of chemical shift ( $\delta$  ppm).

### 4.2. (*Z*)-3-(tributylstannyl)but-2-en-1-ol (**6**)

To a solution of but-2-yn-1-ol (0.940 g, 13.4 mmol, 1 equiv.) in THF (20 mL) at 0 °C was added a solution of Red-Al (4.8 mL, 60% w/v solution in toluene, 14.17 mmol, 1.06 equiv.). The reaction mixture was stirred at 0 °C for 30 min and then warmed to ambient temperature for 2 h. After cooling to 0 °C,  $\text{Bu}_3\text{SnCl}$  (7.25 g, 26.74 mmol, 2 equiv.) was added by syringe. After stirring at ambient temperature for 4 h, a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  was added. The mixture was extracted with EtOAc (3  $\times$  15 mL). The combined organic layer was washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated in vacuo. The residue was purified by flash chromatography (9:1 hexane:EtOAc) to provide the title compound (**6**) as a colorless oil (3.00 g, 62%). The spectral data was in agreement with the literature [14].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.27 (tdd,  $J$  = 4.9, 3.3, 1.6 Hz, 1H), 4.02 (t,  $J$  = 5.9 Hz, 2H), 1.95 (d,  $J$  = 0.8 Hz, 3H), 1.52–1.45 (m, 7H), 1.36–1.27 (m, 6H), 0.96–0.92 (m, 6H), 0.89 (t,  $J$  = 7.3 Hz, 9H) [1].  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 138.8, 65.0, 29.2, 27.3, 26.9, 13.7, 10.2.

### 4.3. (2*Z*,5*E*)-3-methylhepta-2,5-dien-1-ol (**7**)

A round bottom flask was charged with (*Z*)-3-(tributylstannyl)but-2-en-1-ol (**6**, 310.0 mg, 0.86 mmol, 1 equiv.) and (*E*)-but-2-en-1-yl isobutyl carbonate (185.0 mg, 1.07 mmol, 1.25 equiv.). The flask was evacuated and filled with argon three times before adding DMF (2 mL). To this solution was added  $\text{Pd}_2(\text{dba})_3$  (15.7 mg, 0.017 mmol,

0.02 equiv.). The reaction was stirred at room temperature for 3 h (monitored by TLC). Water (5 mL) was added and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The organic layer was filtered through small plug of silica and concentrated in vacuo. The residue was purified by flash chromatography (4:1 hexane:EtOAc) to provide the title compound (**7**) as a colorless oil (95 mg, 80%). The spectral data was in agreement with the literature [7].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.50–5.43 (m, 2H), 5.40–5.33 (m, 1H), 4.14 (dd,  $J = 7.0, 0.8$  Hz, 2H), 2.75 (dd,  $J = 6.4, 0.9$  Hz, 2H), 1.73 (dd,  $J = 2.1, 1.0$  Hz, 3H), 1.66 (dq,  $J = 6.3, 1.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.0, 128.2, 126.2, 124.1, 59.0, 35.2, 23.5, 17.8. HRMS (ESI+) 109.1012 calc'd for  $\text{C}_8\text{H}_{13}$  [M - OH] $^+$ , 109.0978 found.

#### 4.4. (4*R*,5*Z*,8*E*)-6-methyldeca-1,5,8-trien-4-ol (**9**)

To a solution of (2*Z*,5*E*)-3-methylhepta-2,5-dien-1-ol (**7**, 252.4 mg, 2.00 mmol, 1 equiv.) in  $\text{CH}_3\text{CN}$  (1 mL) was added tetrakisacetonitrile copper(I) triflate (38.7 mg, 0.103 mmol, 0.05 equiv.) followed by Stahl Aerobic Oxidation TEMPO solution (500  $\mu\text{L}$ , 250  $\mu\text{L}$  per mmol) without exclusion of air. The reaction was stirred until the solution changed color to dark blue/green. The mixture was filtered through small plug of silica gel, which was washed with EtOAc ( $3 \times 5$  mL). The filtrate was concentrated to provide crude (2*Z*,5*E*)-3-methylhepta-2,5-dienal (**8**), which was used in the next step without purification.

A flask covered with aluminum foil was charged with silver(I) triflate (26.7 mg, 0.104 mmol, 0.052 equiv.) and (*R*)-BINAP (67.3 mg, 0.104 mmol, 0.054 equiv.). After flushing with argon, THF (3 mL) was added and the mixture stirred for 15 min at room temperature. To the resulting solution was added a solution of aldehyde **8** (248.4 mg, 2.00 mmol, 1 equiv.) in THF (1 mL). The reaction was cooled to  $-20^\circ\text{C}$  and allyltributylstannane (326  $\mu\text{L}$ , 2.02 mmol, 1.01 equiv.) was added dropwise by syringe. The reaction was stirred at  $-20^\circ\text{C}$  for 72 h (with exclusion of direct light). Saturated aqueous  $\text{NaHCO}_3$  (2–3 mL) was added and the mixture stirred for 30 min. The mixture was filtered through a pad of Celite. After washing the Celite with EtOAc ( $3 \times 5$  mL), the filtrate was dried and concentrated in vacuo. The residue was purified by flash chromatography (4:1 hexane:EtOAc) to provide the title compound (**9**) as a colorless oil (222.0 mg, 67%). The spectral data was in agreement with the literature [7].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.87–5.76 (m, 1H), 5.50–5.43 (m, 1H), 5.40–5.33 (m, 1H), 5.23 (dd,  $J = 7.8, 7.2$  Hz, 1H), 5.16–5.10 (m, 2H), 4.42 (dd,  $J = 14.3, 7.2$  Hz, 1H), 2.76 (dd,  $J = 10.6, 4.1$  Hz, 2H), 2.28 (t,  $J = 6.6$  Hz, 2H), 1.71 (d,  $J = 1.4$  Hz, 3H), 1.65 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 134.5, 128.3, 127.8, 126.3, 117.8, 67.4, 42.2, 35.6, 23.4, 17.8. HRMS (ESI+) 149.1325 calc'd for  $\text{C}_{11}\text{H}_{17}$  [M - OH] $^+$ , 149.1318 found.

Analytical chiral GC was performed using an Agilent 6890 Series Gas Chromatograph equipped with an Astec CHIRALDEX G-TA (30 m  $\times$  0.25 mm  $\times$  0.12  $\mu\text{m}$ ) column. Helium was used as the carrier gas (1 mL/min). A temperature ramp from  $40^\circ\text{C}$  to  $120^\circ\text{C}$  ( $3^\circ\text{C}/\text{min}$  ramp) was used for the separation. Retention time, major isomer = 23.079; minor isomer = 23.224 min.

#### 4.5. (2*Z*)-3,4-dimethylhexa-2,5-dien-1-ol (**12**)

To a solution of (*Z*)-3-bromobut-2-en-1-ol (**11**, 80 mg, 0.53 mmol, 1 equiv.) in 3:2  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  (5 mL, degassed with argon) was added  $\text{Pd}(\text{OAc})_2$  (2.4 mg, 0.011 mmol, 0.02 equiv.), S-Phos (8.7 mg, 0.022 mmol, 0.04 equiv.), (*E*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.16 mL, 0.79 mmol, 1.5 equiv.), and  $\text{Cs}_2\text{CO}_3$  (517.9 mg, 1.59 mmol, 3 equiv.). The reaction was heated at reflux for 24 h. After cooling to room temperature, water was added to the reaction and the mixture extracted with EtOAc ( $4 \times 5$  mL). The combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ) and

concentrated in vacuo. The residue was purified by flash chromatography on silica gel (9:1 hexane:EtOAc) to provide the title compound (**12**) as a colorless oil (13 mg, 19%). The spectral data was in agreement with the minor peaks present in a literature report [7].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.87–5.74 (m, 1H), 5.44 (t,  $J = 7.0$  Hz, 1H), 5.05–4.96 (m, 2H), 4.16 (t,  $J = 8.4$  Hz, 2H), 3.43–3.33 (m, 1H), 1.64 (d,  $J = 7.7$  Hz, 3H), 1.14–1.07 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.00 (C), 141.9 (CH), 124.8 (CH), 114.0 ( $\text{CH}_2$ ), 59.0 ( $\text{CH}_2$ ), 38.5 (CH), 19.5 ( $\text{CH}_3$ ), 18.1 ( $\text{CH}_3$ ). HRMS (ESI+) 109.1012 calc'd for  $\text{C}_8\text{H}_{13}$  [M - OH] $^+$ , 109.0979 found.

#### Acknowledgments

Financial support for this project provided by Texas Tech University. B.N. was supported by Plains Bridges to the Baccalaureate Program (NIH 5R25GM83730-2) awarded to Jaclyn Cañas-Carrell (TTU). NMR data was collected using instruments supported by the National Science Foundation CRIF Program (CHE-1048553). We thank Prof. Daniel Armstrong (UT Arlington) for analytical assistance. We are very appreciative of Prof. Jeremy May for giving us the opportunity to contribute to this special issue.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tet.2018.10.066>.

#### References

- [1] (a) T. Teruya, H. Sasaki, K. Kitamura, T. Nakayama, K. Suenaga, *Org. Lett.* 11 (2009) 2421; (b) M. Morita, O. Ohno, K. Suenaga, *Chem. Lett.* 41 (2012) 165; (c) M. Morita, O. Ohno, T. Teruya, T. Yamori, T. Inuzuka, K. Suenaga, *Tetrahedron* 68 (2012) 5984; (d) O. Ohno, A. Watanabe, M. Morita, K. Suenaga, *Chem. Lett.* 43 (2014) 287; (e) A. Watanabe, O. Ohno, M. Morita, T. Inuzuka, K. Suenaga, *Bull. Chem. Soc. Jpn.* 88 (2015) 1256.
- [2] T. Yonezawa, N. Mase, H. Sasaki, T. Teruya, S.-i. Hasegawa, B.-Y. Cha, K. Yagasaki, K. Suenaga, K. Nagai, J.-T. Woo, *J. Cell. Biochem.* 113 (2012) 440.
- [3] M. Morita, H. Ogawa, O. Ohno, T. Yamori, K. Suenaga, C. Toyoshima, *FEBS Lett.* 589 (2015) 1406.
- [4] (a) H. Liu, R.C. Bowes III, B. van de Water, C. Sillence, J.F. Nagelkerke, J.L. Stevens, *J. Biol. Chem.* 272 (1997) 21751; (b) C. Caspersen, P.S. Pedersen, M. Treiman, *J. Biol. Chem.* 275 (2000) 22363.
- [5] T. Tanabe, E. Sato, N. Nakajima, A. Ohkubo, O. Ohno, K. Suenaga, *Org. Lett.* 16 (2014) 2858.
- [6] E. Sato, Y. Tanabe, N. Nakajima, A. Ohkubo, K. Suenaga, *Org. Lett.* 18 (2016) 2047.
- [7] S. Das, D. Paul, R.K. Goswami, *Org. Lett.* 18 (2016) 1908.
- [8] L. Kämmler, M.E. Maier, *J. Org. Chem.* 83 (2018) 4554.
- [9] E. Sato, M. Sato, Y. Tanabe, N. Nakajima, A. Ohkubo, K. Suenaga, *J. Org. Chem.* 82 (2017) 6770.
- [10] For synthesis of fragments, see: (a) S. Chandrasekhar, G. Rajesh, T. Naresh, *Tetrahedron Lett.* 54 (2013) 252; (b) P. Sawant, M.E. Maier, *Synlett* (2011) 3002.
- [11] R.G. Thorat, A.M. Harned, *Chem. Commun.* 54 (2018) 241.
- [12] E.R. Welin, A.A. Warkentin, J.C. Conrad, D.W.C. MacMillan, *Angew. Chem. Int. Ed.* 54 (2015) 9668.
- [13] I.S. Kim, M.-Y. Ngai, M.J. Krische, *J. Am. Chem. Soc.* 130 (2008) 14891.
- [14] B.H. Lipshutz, G.C. Closoki, W. Chrisman, D.W. Chung, D.B. Ball, J. Howell, *Org. Lett.* 7 (2005) 4561.
- [15] A.M. Castaño, A.M. Echavarren, *Tetrahedron Lett.* 37 (1996) 6587.
- [16] (a) J. Justica, J.E. Oltra, J.M. Cuerva, *J. Org. Chem.* 69 (2004) 5803–5806; (b) I. Paterson, E.A. Anderson, S.M. Dalby, J.H. Lim, P. Maltas, *Org. Biomol. Chem.* 10 (2012) 5873; (c) T. Suto, Y. Yanagita, Y. Nagashima, S. Takikawa, Y. Kurosu, N. Matsuo, T. Sato, N. Chida, *J. Am. Chem. Soc.* 139 (2017) 2952.
- [17] (a) J.M. Hoover, S.S. Stahl, *J. Am. Chem. Soc.* 133 (2011) 16901; (b) J.E. Steves, S.S. Stahl, *J. Org. Chem.* 80 (2015) 11184.
- [18] A. Yanagisawa, H. Nakashima, A. Ishiba, H. Yamamoto, *J. Am. Chem. Soc.* 118 (1996) 4723.
- [19] (a) A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto, H. Yamamoto, *Angew. Chem. Int. Ed.* 38 (1999) 3701; (b) H. Yamamoto, M. Wadamoto, *Chem. Asian J.* 2 (2007) 692.
- [20] (a) K. Fujii, K. Maki, M. Kanai, M. Shibasaki, *Org. Lett.* 5 (2003) 733; (b) K. Maki, R. Motoki, K. Fujii, M. Kanai, T. Kobayashi, S. Tamura, M. Shibasaki,

- J. Am. Chem. Soc. 127 (2005) 17111;  
(c) M. Hangyou, H. Ishiyama, Y. Takahashi, T. Kubota, J. Kobayashi, Tetrahedron Lett. 50 (2009) 1475;  
(d) S.M. Sarkar, E.N. Wanzala, S. Shibahara, K. Takahashi, J. Ishihara, S. Hatakeyama, Chem. Commun. (2009) 5907.
- [21] Y. Yang, S.L. Buchwald, J. Am. Chem. Soc. 135 (2013) 10642.  
[22] R.J. Armstrong, C. García-Ruiz, E.L. Myers, V.K. Aggarwal, Angew. Chem. Int. Ed. 56 (2017) 786.