OL Organic Letters

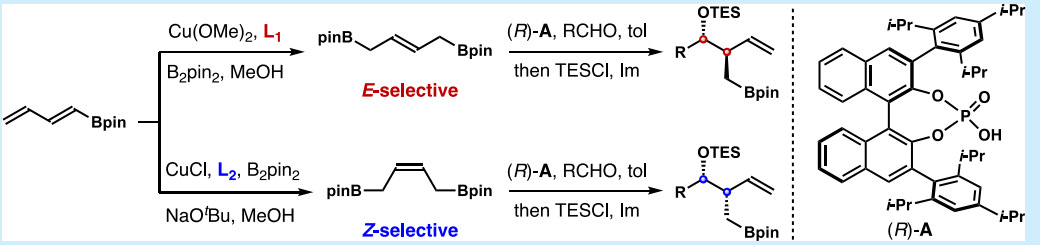
pubs.acs.org/OrgLett Letter

Enantioselective *anti*- and *syn*-(Borylmethyl)allylation of Aldehydes via Brønsted Acid Catalysis

Jiaming Liu and Ming Chen*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c03366 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: The enantioselective *anti*- and *syn*-(borylmethyl)allylation of aldehydes via phosphoric acid catalysis is reported. Both (*E*)- and (*Z*)-γ-borylmethyl allylboronate reagents were prepared via the Cu-catalyzed highly stereoselective protoboration of 1,3-dienylboronate. Chiral phosphoric acid-catalyzed aldehyde allylation with either the (*E*)- or (*Z*)-allylboron reagent provided 1,2-*anti*- or 1,2-*syn*-adducts in good yields with high enantioselectivities. The application to the synthesis of morinol D was accomplished.

Chiral nonracemic 1,2-*anti*- and 1,2-*syn*-2-hydroxymethyl-3-ene-1-ols (highlighted in blue in Figure 1) are key

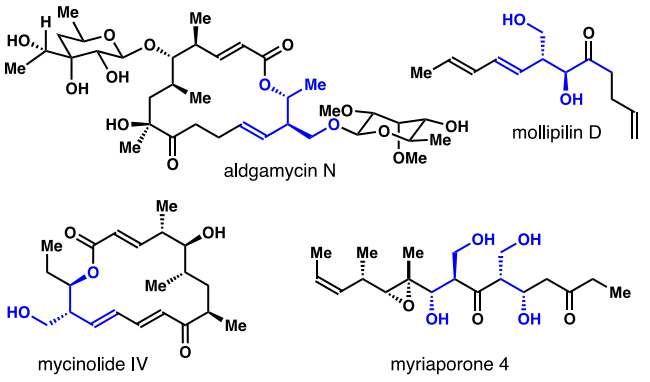


Figure 1. Selected natural products containing 1,2-*syn*- or *anti*-hydroxymethyl-1,3-diols.

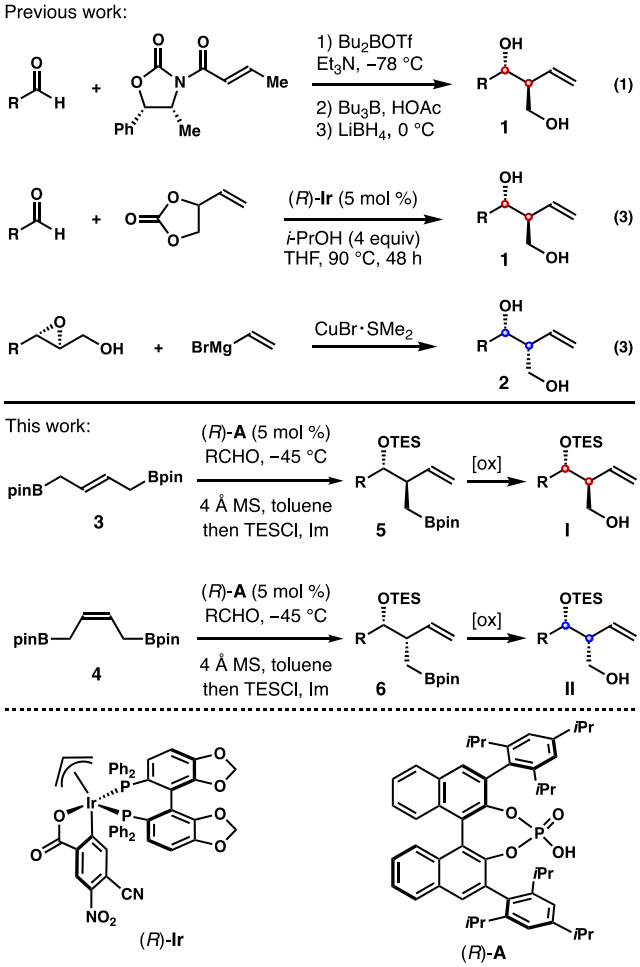
structural motifs in numerous biologically active natural products.[1−3] The diastereo- and enantioselective synthesis of these structural entities is therefore an important objective in organic synthesis. Several approaches are available to generate these molecules in a racemic form with good *anti*- or *syn*-selectivities.[4] However, methods that allow for their enantioselective syntheses are underdeveloped. As shown in Scheme 1, Evans reported a chiral auxiliary-based aldol addition/reduction reaction sequence to generate enantioenriched 1,2-*anti*-isomer **1** (eq 1, Scheme 1).[5a] This method has been widely adopted in the syntheses of natural products that contain such a structural motif.[5] More recently, a catalytic variant of this method was disclosed by the Shibasaki group.[6] Using a cyclic carbonate as the allyl donor, Krische and coworkers reported an elegant Ir-catalyzed *anti*-(hydroxymethyl)-allylation strategy to access enantioenriched diol **1** (eq 2, Scheme 1).[7] By contrast, asymmetric synthesis of 1,2-*syn*-isomer **2** mainly relies on vinyl Grignard addition to enantioenriched epoxy alcohols (eq 3, Scheme 1).[8] The development of catalytic methods that allow for the access to enantioenriched *syn*-isomer **2** would be desirable.

Pioneered by the Antilla group, chiral phosphoric acid-catalyzed enantioselective aldehyde addition with unsaturated organoboron compounds has emerged as a powerful method to access enantioenriched homoallylic, allenic, and homopropargylic alcohols.[9−12] Inspired by prior studies, we envisioned a chiral phosphoric acid-catalyzed asymmetric aldehyde allylboration strategy to synthesize both 1,2-*anti*- and 1,2-*syn*-2-hydroxymethyl-3-ene-1-ols, **1** and **2**, respectively. As shown in Scheme 1, on the basis of the well-established chairlike transition state typically involved in allylboration chemistry,[13] we anticipate that chiral phosphoric acid (*R*)-**A**-catalyzed aldehyde addition with (*E*)-γ-borylmethyl allylboronate **3** should provide 1,2-*anti* adduct **5** with high diastereo- and enantioselectivity. Similarly, the reaction with (*Z*)-reagent **4** should generate 1,2-*syn* adduct **6** selectively. Subsequent

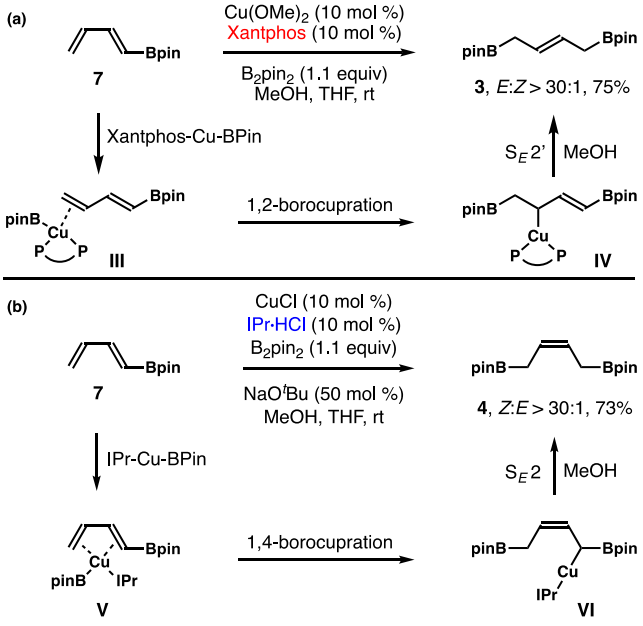
Received: October 8, 2020

https://dx.doi.org/10.1021/acs.orglett.0c03366
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 1. Approaches for Enantioselective Syntheses of 1,2-*anti*- and 1,2-*syn*-2-Hydroxymethyl-3-ene-1-ols



Scheme 2. Stereoselective Syntheses of (*E*)- and (*Z*)-γ-Borylmethyl Allylboronates 3 and 4



oxidation of the Bpin group in **5** and **6** will produce enantioenriched and monoprotected 1,2-*anti*- and 1,2-*syn*-2-hydroxymethyl-3-ene-1-ols (**I** and **II**, Scheme 1). Moreover, the Bpin group in intermediates **5** and **6** should be amenable to a variety of transformations in addition to oxidation.[14,15] With our continuing interests in carbonyl allylation chemistry,[16] we report herein enantioselective aldehyde addition with (*E*)- or (*Z*)-γ-borylmethyl allylboronate, **3** or **4**, to provide 1,2-*anti*- or 1,2-*syn* adducts in good yields with high enantioselectivities. The method was successfully applied to the synthesis of natural product morinol D.

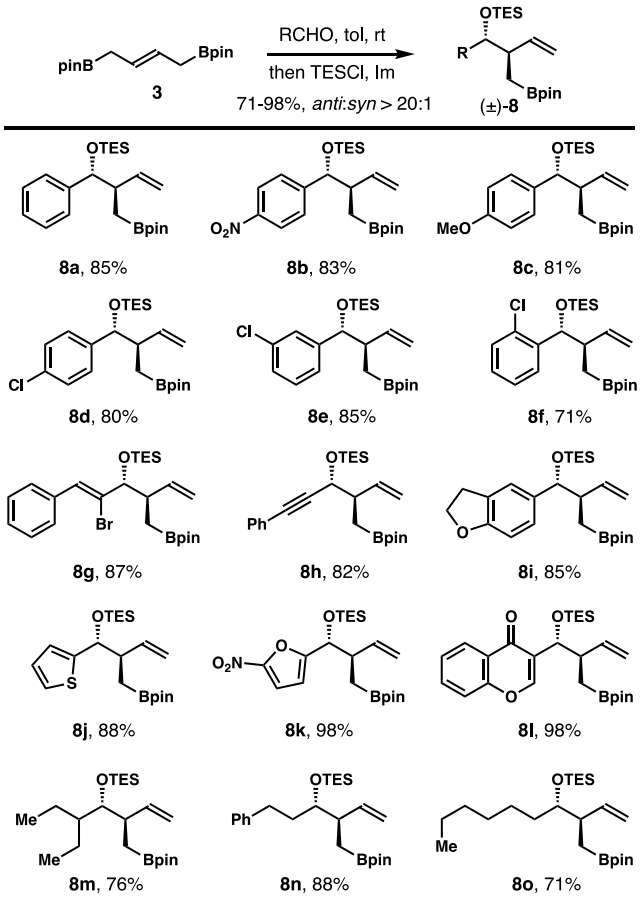
We began our studies by developing suitable methods for stereoselective syntheses of (*E*)- and (*Z*)-γ-borylmethyl allylboronate reagents **3** and **4**.[17] After initial experimentations, a Cu-catalyzed diene protoboration approach was identified for stereoselective syntheses of **3** and **4**.[18] We discovered that, in the presence of a bidentate phosphine ligand Xantphos, the $Cu(OMe)_2$-catalyzed protoboration of 1,3-dienylboronate **7** gave (*E*)-γ-borylmethyl allylboronate **3** in a 75% yield with a >30:1 (*E*)-selectivity (Scheme 2a). The (*Z*)-isomer **4** was also synthesized with high (*Z*)-selectivity from 1,3-dienylboronate **7** simply by replacing Xantphos with a monodentate NHC ligand. (*Z*)-γ-Borylmethyl allylboronate **4** was obtained in a 73% yield with a >30:1 (*Z*)-selectivity (Scheme 2b). The rationale for (*E*)- or (*Z*)-selective protoboration is shown in Scheme 2. We propose that the Xantphos-ligated Cu-Bpin complex coordinates to one alkene unit of diene **7** to form Cu-complex **III**, which undergoes 1,2-borocupration to give allylcopper intermediate **IV**. Subsequent protonation of allylcopper **IV** with MeOH proceeds via an S_E2' pathway to give (*E*)-γ-borylmethyl allylboronate **3** with high (*E*)-selectivity. On the other hand, IPr-ligated Cu-Bpin forms complex **V** with diene **7**. Then, a 1,4-borocupration occurs to give (*Z*)-allylcopper species **VI**. Direct S_E2 protonation of allylcopper **VI** produces (*Z*)-γ-borylmethyl allylboronate **4** selectively. Experimental evidence to support the formation of (*Z*)-allylcopper **VI** and the S_E2 protonation pathway was obtained from the stoichiometric reaction of the preformed IPrCuCl complex, B_2pin_2, and NaO^{t}Bu with diene **7** and subsequent protonation with MeOH. The coupling constant of two olefinic protons of intermediate **VI** is 10.6 Hz, which is consistent with a (*Z*)-alkene geometry. Protonation of (*Z*)-allylcopper **VI** with MeOH gave allylboronate **4** (Supporting Information).

After obtaining reagents **3** and **4**, aldehyde allylation studies with (*E*)-reagent **3** were conducted first. As shown in Scheme 3, a broad scope of aldehydes participated in reactions with **3** to give *anti*-products **8** in good yields with excellent diastereoselectivities after *in situ* protection of the secondary alcohol group as a TES-ether. Aromatic aldehydes with an electron-donating or electron-withdrawing group at the *para*-position reacted with **3** to afford *anti*-adducts **8a−c** in 81−85% yields. Reactions with aromatic aldehydes substituted with chlorine at the *para*-, *meta*-, or *ortho*-position proceeded smoothly to give products **8d−f** in 71−85% yields. Similar results were obtained from reactions with α,β-unsaturated aldehydes, and *anti*-adducts **8g,h** were obtained in 82−87% yields. Aldehydes that contain a heterocycle are suitable substrates for the allylation, and products **8i−l** were isolated in 85−98% yields. Several representative aliphatic aldehydes also reacted with **3** to deliver *anti*-products **8m−o** in 71−88% yields.

Next, we explored the scope of aldehydes that participated in the *syn*-(borylmethyl)allylation reaction with (*Z*)-allylboronate

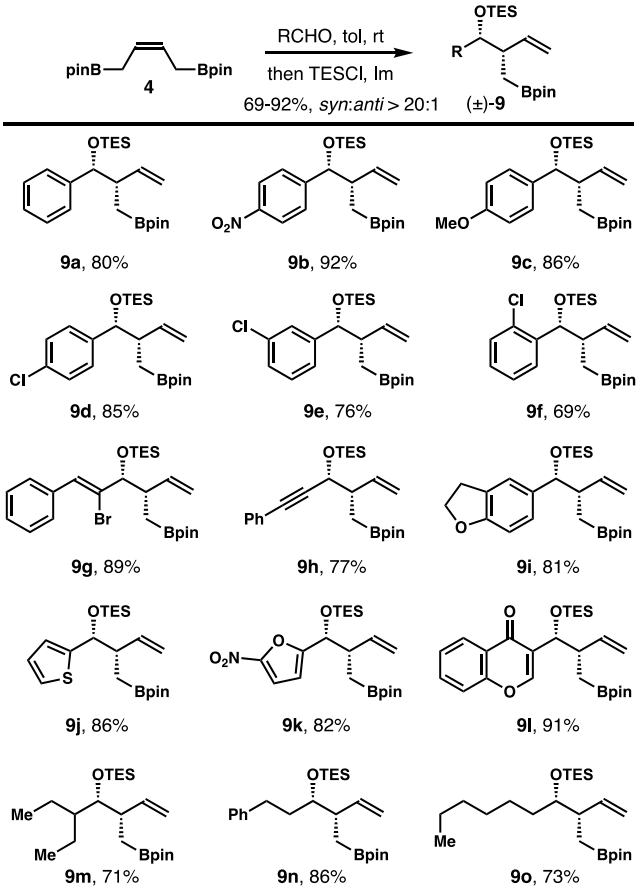
https://dx.doi.org/10.1021/acs.orglett.0c03366
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 3. Aldehyde Scope for *anti*-(Borylmethyl)allylation[a]



[a]Reaction conditions are as follows: allylboronate **3** (0.13 mmol, 1.3 equiv), aldehyde (0.1 mmol, 1.0 equiv), and toluene (0.3 mL) at rt, then TESCl (1.5 equiv), imidazole (2.0 equiv), and DMF (0.2 mL) at rt. Yields of isolated products are listed.

Scheme 4. Aldehyde Scope for *syn*-(Borylmethyl)allylation[a]



[a]Reaction conditions are as follows: allylboronate **4** (0.13 mmol, 1.3 equiv), aldehyde (0.1 mmol, 1.0 equiv), and toluene (0.3 mL) at rt, then TESCl (1.5 equiv), imidazole (2.0 equiv), and DMF (0.2 mL) at rt. Yields of isolated products are listed.

4, and the results are summarized in Scheme 4. The allylation tolerates a variety of aldehydes, including aromatic aldehydes with different substitution patterns, α,β-unsaturated aldehydes, aldehydes with a heterocycle, and aliphatic aldehydes. In all cases, 1,2-*syn* adducts **9** were formed as a single diastereomer in 69−92% yields.

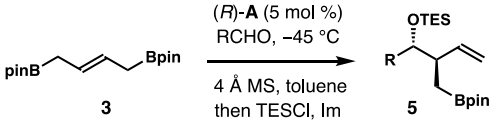
To access enantioenriched 1,2-*anti* or 1,2-*syn* products, **5** or **6**, asymmetric allylations with boronate **3** or **4** were conducted in the presence of chiral phosphoric acid (*R*)-**A**. As shown in Scheme 5, the reaction between benzaldehyde and (*E*)-allylboronate **3** with 5 mol % acid (*R*)-**A** as the catalyst occurred at −45 °C in toluene. After *in situ* protection of the secondary alcohol group, *anti*-adduct **5a** was obtained in 84% yield with 99% ee. Using this protocol, a collection of aldehydes, *ortho*-substituted aromatic aldehydes and aliphatic aldehydes in particular, reacted with allylboronate **3** to give *anti*-products **5b−i** in 71−98% yields with 90−99% ee.[19]

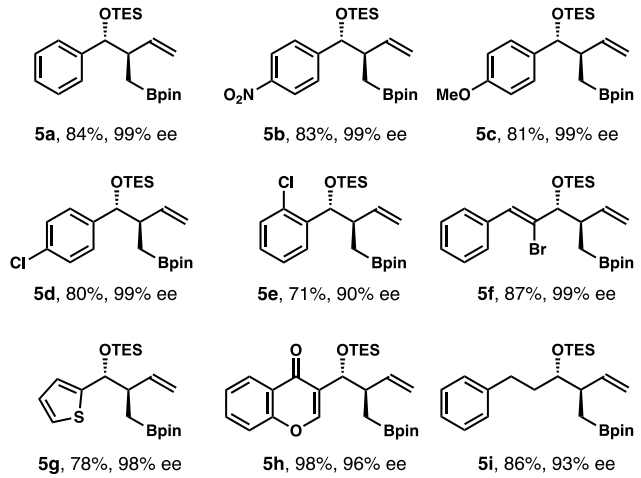
Asymmetric aldehyde allylation with (*Z*)-reagent **4** turned out to be more challenging. We noticed that (*Z*)-allylboronate **4** was much less reactive than (*E*)-isomer **3** toward aldehyde addition. Additionally, the enantioselectivities of *syn*-adducts **6** are generally lower than the optical purities of *anti*-adducts **5**, presumably owing to the uncatalyzed background reactions. Nevertheless, reactions of **4** with representative aldehydes occurred to give *syn*-adducts **6a−g** in 62−88% yields with 81−91% ee, as summarized in Scheme 6. Reactions with 2-thiophene carboxaldehyde and hydrocinnamaldehyde gave products **6h,i**, respectively, in 79−86% yields with moderate enantioselectivities (70−74% ee). The *anti*- and *syn*-relative configurations of **5** and **6** were assigned by the coupling constant analyses of the corresponding acetonides (Supporting Information).

To demonstrate the synthetic utility of this method, the total synthesis of natural product morinol D was conducted.[20] As shown in Scheme 7, the asymmetric allylation of veratraldehyde (**10**) with (*E*)-allylboronate **3**, followed by oxidative workup, gave *anti*-hydroxymethyl-1,3-diol **11** in a 73% yield with 94% ee. Protection of the alcohol groups in **11** with excess TIPSCl only occurred at the primary alcohol group. The secondary OH group of **11** was converted to a TES ether by adding TESCl to the reaction mixture, affording product **12** in an 85% yield. The hydroboration−oxidation of **12** with 9-BBN produced alcohol **13** in a 97% yield, which underwent Dess-Marin oxidation to give **14** in an 86% yield. Aldehyde **14** was transformed to vinyl boronate **16** in a 65% yield and >30:1 (*E*)-selectivity by using the olefination protocol developed by the Morken group.[21] The Pd-catalyzed Suzuki coupling of **16** with 4-iodoanisole (**17**), followed by deprotection of the silyl ethers with TBAF, gave morinol D (**18**) in a 65% yield over two steps.

https://dx.doi.org/10.1021/acs.orglett.0c03366
Org. Lett. XXXX, XXX, XXX−XXX

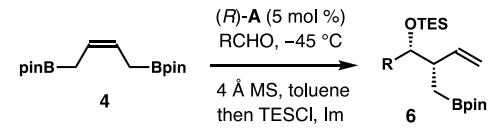
Scheme 5. Enantioselective *anti*-(Borylmethyl)allylation of Aldehydes with (*E*)-Allylboronate 3[a,b,c]

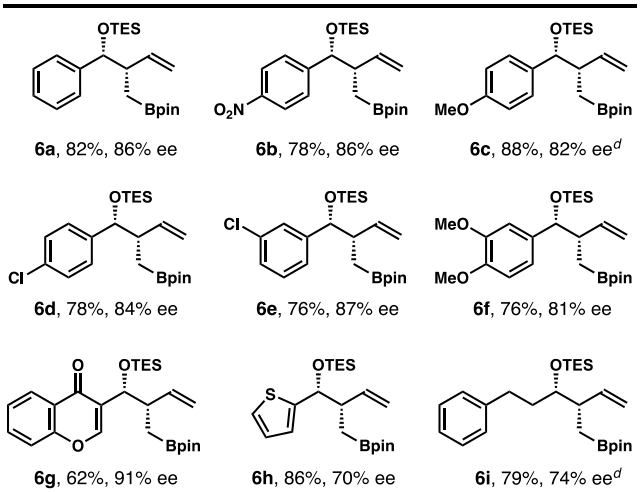




[a]Reaction conditions are as follows: allylboronate **3** (0.1 mmol, 1.0 equiv), aldehyde (0.2 mmol, 2.0 equiv), phosphoric acid (*R*)-**A** (5 mol %), 4 Å molecular sieves (25 mg), and toluene (0.3 mL) at − 45 °C, then TESCl (1.5 equiv), imidazole (2.0 equiv), and DMF (0.2 mL) at rt. [b]Enantioselectivities were determined by HPLC analysis using a chiral stationary phase. [c]Yields of isolated products are listed.

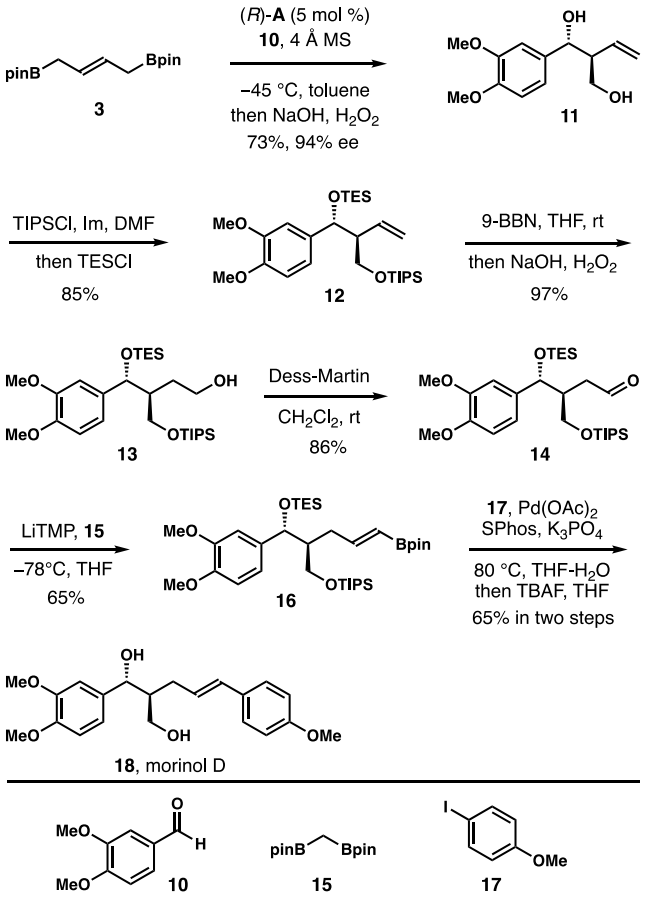
Scheme 6. Enantioselective *syn*-(Borylmethyl)allylation of Aldehydes with (*Z*)-Allylboronate 4[a,b,c]





[a]Reaction conditions are as follows: allylboronate **4** (0.1 mmol, 1.0 equiv), aldehyde (0.2 mmol, 2.0 equiv), phosphoric acid (*R*)-**A** (5 mol %), 4 Å molecular sieves (25 mg), and toluene (0.3 mL) at − 45 °C, then TESCl (1.5 equiv), imidazole (2.0 equiv), and DMF (0.2 mL) at rt. [b]Enantioselectivities were determined by HPLC analysis using a chiral stationary phase. [c]Yields of isolated products are listed. [d]The reaction was conducted with 10 mol % acid (*R*)-**A**.

Scheme 7. Enantioselective Synthesis of Morinol D



In summary, we developed a chiral phosphoric acid-catalyzed enantioselective *anti*- and *syn*-(borylmethyl)allylation of aldehydes with (*E*)- and (*Z*)-γ-borylmethyl allylboronate reagents **3** and **4**, respectively. Reagents **3** and **4** were synthesized via a Cu-catalyzed stereoselective protoboration of 1,3-dienylboronate **7** with either a bidentate phosphine ligand or a monodentate NHC ligand. In the presence of a catalytic amount of chiral phosphoric acid (*R*)-**A**, asymmetric aldehyde allylation with (*E*)-reagent **3** gave *anti*-adducts **5** in good yields with excellent enantioselectivities. Allylation reactions with (*Z*)-reagent **4** also proceeded to deliver *syn*-adducts **6** in good yields and enantioselectivities. The synthetic utility of the method was demonstrated by the total synthesis of morinol D.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03366.

^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Ming Chen − *Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849, United States;* orcid.org/0000-0002-9841-8274; Email: mzc0102@auburn.edu

https://dx.doi.org/10.1021/acs.orglett.0c03366
Org. Lett. XXXX, XXX, XXX−XXX

Author

Jiaming Liu − *Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c03366

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support provided by Auburn University is gratefully acknowledged.

■ REFERENCES

(1) (a) Schmitz, F. J.; Gunasekera, S. P.; Yalamanchili, G.; Hossain, M. B.; van der Helm, D. *J. Am. Chem. Soc.* **1984**, *106*, 7251. (b) Fusetani, N.; Sugawara, T.; Matsunaga, S.; Hirota, H. *J. Org. Chem.* **1991**, *56*, 4971. (c) Yamauchi, S.; Uno, H. *Org. Biomol. Chem.* **2003**, *1*, 1323. (d) Zhu, Y.; Lv, Z.-P.; Xue, C.-B.; Wu, W.-S. *Helv. Chim. Acta* **2009**, *92*, 536. (e) Rateb, M. E.; Houssen, W. E.; Arnold, M.; Abdelrahman, M. H.; Deng, H.; Harrison, W. T. A.; Okoro, C. K.; Asenjo, J. A.; Andrews, B. A.; Ferguson, G.; Bull, A. T.; Goodfellow, M.; Ebel, R.; Jaspars, M. *J. Nat. Prod.* **2011**, *74*, 1491. (f) Asai, T.; Morita, S.; Shirata, N.; Taniguchi, T.; Monde, K.; Sakurai, H.; Ozeki, T.; Oshima, Y. *Org. Lett.* **2012**, *14*, 5456. (g) Takahashi, M.; Suzuki, N.; Ishikawa, T.; Huang, H.-Y.; Chang, H.-S.; Chen, I.-S. *J. Nat. Prod.* **2014**, *77*, 2585. (h) Wang, C.-X.; Ding, R.; Jiang, S.-T.; Tang, J.-S.; Hu, D.; Chen, G.-D.; Lin, F.; Hong, K.; Yao, X.-S.; Gao, H. *J. Nat. Prod.* **2016**, *79*, 2446.

(2) For selected syntheses of tylonolide, see: (a) Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1982**, *104*, 2027. (b) Masamune, S.; Lu, L. D. L.; Jackson, W. P.; Kaiho, T.; Toyoda, T. *J. Am. Chem. Soc.* **1982**, *104*, 5523. (c) Grieco, P. A.; Inanaga, J.; Lin, N. H.; Yanami, T. *J. Am. Chem. Soc.* **1982**, *104*, 5781. For mycinolide, see: (d) Suzuki, K.; Matsumoto, T.; Tomooka, K.; Matsumoto, K.; Tsuchihashi, G.-i. *Chem. Lett.* **1987**, *16*, 113. (e) Matsumoto, T.; Maeta, H.; Suzuki, K.; Tsuchihashi, G.-i. *Tetrahedron Lett.* **1988**, *29*, 3575. For selected syntheses of myriaporones, see: (f) Pérez, M.; del Pozo, C.; Reyes, F.; Rodríguez, A.; Francesch, A.; Echavarren, A. M.; Cuevas, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 1724. (g) Fleming, K. N.; Taylor, R. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 1728. For selected syntheses of tedanolide and 13-deoxytedanolide, see: (h) Julian, L. D.; Newcom, J. S.; Roush, W. R. *J. Am. Chem. Soc.* **2005**, *127*, 6186. (i) Ehrlich, G.; Hassfeld, J.; Eggert, U.; Kalesse, M. *J. Am. Chem. Soc.* **2006**, *128*, 14038. (j) Smith, A. B., III; Lee, D. *J. Am. Chem. Soc.* **2007**, *129*, 10957. (k) Dunetz, J. R.; Julian, L. D.; Newcom, J. S.; Roush, W. R. *J. Am. Chem. Soc.* **2008**, *130*, 16407.

(3) (a) Yamada, K.; Tatematsu, H.; Unno, R.; Hirata, Y.; Hirono, I. *Tetrahedron Lett.* **1978**, *19* (46), 4543. (b) Mohanraj, S.; Kulanthaivel, P.; Subramanian, P.; Herz, W. *Phytochemistry* **1981**, *20*, 1991. (c) Shi, B.-J.; Xiong, A.-Z.; Zheng, S.-S.; Chou, G.-X.; Wang, Z.-T. *Nat. Prod. Res.* **2010**, *24*, 1897. For selected syntheses, see: (d) Tatsuta, K.; Takahashi, H.; Amemiya, Y.; Kinoshita, M. *J. Am. Chem. Soc.* **1983**, *105*, 4096. (e) Ito, H.; Ikeuchi, Y.; Taguchi, T.; Hanzawa, Y.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 5469. (f) Denmark, S. E.; Thorarensen, A.; Middleton, D. S. *J. Am. Chem. Soc.* **1996**, *118*, 8266.

(4) (a) Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4473. (b) Fujimura, O.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1705. (c) Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577. (d) Nakajima, M.; Saito, M.; Hashimoto, S. *Chem. Pharm. Bull.* **2000**, *48* (2), 306. (e) Araki, S.; Kameda, K.; Tanaka, J.; Hirashita, T.; Yamamura, H.; Kawai, M. *J. Org. Chem.* **2001**, *66*, 7919. (f) Bandini, M.; Cozzi, P. G.; Licciulli, S.; Umani-Ronchi, A. *Synthesis* **2004**, 409. (g) Gagliardo, M.; Selander, N.; Mehendale, N. C.; van Koten, G.; Klein Gebbink, R. J. M.; Szabó, K. J. *Chem. - Eur. J.* **2008**, *14*, 4800. (h) Fujioka, K.; Yokoe, H.; Inoue, A.; Soga, K.; Tsubuki, M.; Shishido, K. *J. Org. Chem.* **2014**, *79*, 7512. (i) López-Martínez, J. L.; Torres-García, I.; Rodríguez-García, I.; Muñoz-Dorado, M.; Álvarez-Corral, M. *J. Org. Chem.* **2019**, *84*, 806.

(5) (a) Evans, D. A.; Sjogren, E. B.; Bartroli, J.; Dow, R. L. *Tetrahedron Lett.* **1986**, *27*, 4957. (b) Chiang, Y. C. P.; Yang, S. S.; Heck, J. V.; Chabala, J. C.; Chang, M. N. *J. Org. Chem.* **1989**, *54*, 5708. (c) Evans, D. A.; Dow, R. L.; Shih, T. L.; Takacs, J. M.; Zahler, R. *J. Am. Chem. Soc.* **1990**, *112*, 5290. (d) Roush, W. R.; Bannister, T. D.; Wendt, M. D.; Jablonowski, J. A.; Scheidt, K. A. *J. Org. Chem.* **2002**, *67*, 4275. (e) Reynolds, A. J.; Scott, A. J.; Turner, C. I.; Sherburn, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 12108. (f) Hamel, C.; Prusov, E. V.; Gertsch, J.; Schweizer, W. B.; Altmann, K.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 10081. (g) Kister, J.; Ess, D. H.; Roush, W. R. *Org. Lett.* **2013**, *15*, 5436.

(6) (a) Cui, J.; Ohtsuki, A.; Watanabe, T.; Kumagai, N.; Shibasaki, M. *Chem. - Eur. J.* **2018**, *24*, 2598. (b) Takeuchi, T.; Kumagai, N.; Shibasaki, M. *J. Org. Chem.* **2018**, *83*, 5851.

(7) Zhang, Y. J.; Yang, J. H.; Kim, S. H.; Krische, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 4562.

(8) (a) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339. (b) Horita, K.; Tanaka, K.; Yonemitsu, O. *Chem. Pharm. Bull.* **1993**, *41*, 2044. (c) Richardson, T. I.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1997**, *119*, 12360. (d) Hanazawa, T.; Koiwa, M.; Hareau, G. P.-J.; Sato, F. *Tetrahedron Lett.* **2000**, *41*, 2659. (e) Iwata, Y.; Tanino, K.; Miyashita, M. *Org. Lett.* **2005**, *7*, 2341.

(9) (a) Akiyama, T.; Itoh, J.; Yokota, D.; Fuchibe, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1566. (b) Uraguchi, D.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 5356. For selected reviews, see: (c) Akiyama, T. *Chem. Rev.* **2007**, *107*, 5744. (d) Terada, M. *Chem. Commun.* **2008**, 4097. (e) Akiyama, T.; Mori, K. *Chem. Rev.* **2015**, *115*, 9277.

(10) (a) Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884. (b) Miura, T.; Nishida, Y.; Morimoto, M.; Murakami, M. *J. Am. Chem. Soc.* **2013**, *135*, 11497. (c) Incerti-Pradillos, C. A.; Kabeshov, M. A.; Malkov, A. V. *Angew. Chem., Int. Ed.* **2013**, *52* (20), 5338. (d) Huang, Y.; Yang, X.; Lv, Z.; Cai, C.; Kai, C.; Pei, Y.; Feng, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 7299. (e) Barrio, P.; Rodríguez, E.; Saito, K.; Fustero, S.; Akiyama, T. *Chem. Commun.* **2015**, *51*, 5246. (f) Clot-Almenara, L.; Rodríguez-Escrich, C.; Osorio-Planes, L.; Pericàs, M. A. *ACS Catal.* **2016**, *6*, 7647. (g) Miura, T.; Nakahashi, J.; Murakami, M. *Angew. Chem., Int. Ed.* **2017**, *56*, 6989. (h) Miura, T.; Nakahashi, J.; Zhou, W.; Shiratori, Y.; Stewart, S. G.; Murakami, M. *J. Am. Chem. Soc.* **2017**, *139*, 10903. (i) Gao, S.; Chen, M. *Org. Lett.* **2018**, *20*, 6174. (j) Miura, T.; Oku, N.; Murakami, M. *Angew. Chem., Int. Ed.* **2019**, *58*, 14620. (k) Gao, S.; Chen, M. *Org. Lett.* **2020**, *22*, 400. (l) Gao, S.; Duan, M.; Houk, K. N.; Chen, M. *Angew. Chem., Int. Ed.* **2020**, *59*, 10540. (m) Chen, J.; Chen, M. *Org. Lett.* **2020**, *22*, 7321. (n) Gao, S.; Duan, M.; Shao, Q.; Houk, K. N.; Chen, M. *J. Am. Chem. Soc.* **2020**, *142*, 18355. (o) Liu, Y.; Mazet, C. A. *J. Org. Chem.* **2020**, *85*, 5638. (p) Yuan, J.; Jain, P.; Antilla, J. C. *J. Org. Chem.* **2020**, *85*, 12988.

(11) (a) Jain, P.; Wang, H.; Houk, K. N.; Antilla, J. C. *Angew. Chem., Int. Ed.* **2012**, *51*, 1391. (b) Chen, M.; Roush, W. R. *J. Am. Chem. Soc.* **2012**, *134*, 10947. (c) Reddy, L. R. *Org. Lett.* **2012**, *14*, 1142. (d) Tsai, A. S.; Chen, M.; Roush, W. R. *Org. Lett.* **2013**, *15*, 1568. (e) Wang, M.; Khan, S.; Miliordos, E.; Chen, M. *Org. Lett.* **2018**, *20*, 3810.

(12) (a) Reddy, L. R. *Chem. Commun.* **2012**, *48*, 9189. (b) Wang, M.; Khan, S.; Miliordos, E.; Chen, M. *Adv. Synth. Catal.* **2018**, *360*, 4634.

(13) (a) Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (c) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763. (d) Lachance, H.; Hall, D. G. *Org. React.* **2009**, *73*, 1. (e) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2011**, *111*, 7774. (f) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2013**, *113*, 5595.

(14) (a) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687. (b) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535.

(15) Collins, B. S. L.; Wilson, C. M.; Myers, E. L.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2017**, *56*, 11700.
(16) (a) Gao, S.; Chen, J.; Chen, M. *Chem. Sci.* **2019**, *10*, 3637. (b) Gao, S.; Chen, M. *Chem. Sci.* **2019**, *10*, 7554. (c) Wang, M.; Gao, S.; Chen, M. *Org. Lett.* **2019**, *21*, 2151. (d) Chen, J.; Gao, S.; Gorden, J. D.; Chen, M. *Org. Lett.* **2019**, *21* (12), 4638. (e) Chen, J.; Gao, S.; Chen, M. *Org. Lett.* **2019**, *21*, 8800. (f) Chen, J.; Gao, S.; Chen, M. *Org. Lett.* **2019**, *21*, 9893. (g) Liu, J.; Gao, S.; Chen, M. *Tetrahedron* **2019**, *75*, 4110. (h) Gao, S.; Chen, M. *Chem. Commun.* **2019**, *55*, 11199. (i) Liu, J.; Gao, S.; Chen, M. *Org. Process Res. Dev.* **2019**, *23*, 1659. (j) Chen, J.; Gao, S.; Chen, M. *Chem. Sci.* **2019**, *10*, 10601. (k) Liu, J.; Tong, X.; Chen, M. *J. Org. Chem.* **2020**, *85*, 5193. (l) Chen, J.; Miliordos, E.; Chen, M. *Angew. Chem.* **2020**, No. 06420, DOI: 10.1002/ange.202006420.
(17) (a) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, 2073. (b) Goldberg, S. D.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 807. (c) Yamamoto, Y.; Takahashi, M.; Miyaura, N. *Synlett* **2002**, *2002* (01), 0128. (d) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630. (e) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780. (f) Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9686. (g) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693. (h) Occhipinti, G.; Törnroos, K. W.; Jensen, V. R. *Organometallics* **2017**, *36*, 3284. (i) Li, C.; Yang, Z.; Wang, L.; Guo, Y.; Huang, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2020**, *59*, 6278.
(18) (a) Sasaki, Y.; Zhong, C.; Sawamura, M.; Ito, H. *J. Am. Chem. Soc.* **2010**, *132*, 1226. (b) Semba, K.; Shinomiya, M.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. - Eur. J.* **2013**, *19*, 7125. (c) Gao, S.; Wang, M.; Chen, M. *Org. Lett.* **2018**, *20*, 7921. (d) Perry, G. J. P.; Jia, T.; Procter, D. *ACS Catal.* **2020**, *10*, 1485.
(19) For chiral phosphoric acid-catalyzed allylboration with *ortho*-substituted aromatic aldehydes and aliphatic aldehydes, the enantioselectivities are moderate in general; see: (a) Xing, C.-H.; Liao, Y.-X.; Zhang, Y.; Sabarova, D.; Bassous, M.; Hu, Q.-S. *Eur. J. Org. Chem.* **2012**, *2012*, 1115. (b) Hessler, F.; Betík, R.; Kadlčíková, A.; Belle, R.; Kotora, M. *Eur. J. Org. Chem.* **2014**, *2014*, 7245. (c) Rodríguez, E.; Grayson, M. N.; Asensio, A.; Barrio, P.; Houk, K. N.; Fustero, S. *ACS Catal.* **2016**, *6*, 2506.
(20) (a) Su, B.-N.; Takaishi, Y.; Kusumi, T. *Tetrahedron* **1999**, *55*, 14571. (b) Yamauchi, S.; Uno, H. *Org. Biomol. Chem.* **2003**, *1*, 1323.
(21) Coombs, J. R.; Zhang, L.; Morken, J. P. *Org. Lett.* **2015**, *17*, 1708.

https://dx.doi.org/10.1021/acs.orglett.0c03366
Org. Lett. XXXX, XXX, XXX−XXX