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Base-Catalyzed Borylation/B−O Elimination of Propynols and B_2pin_2 Delivering Tetrasubstituted Alkenylboronates

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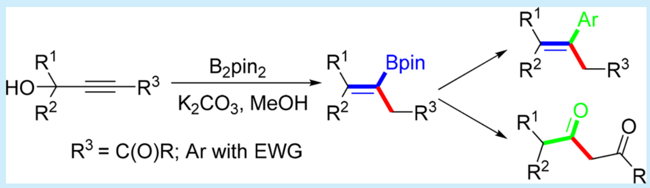
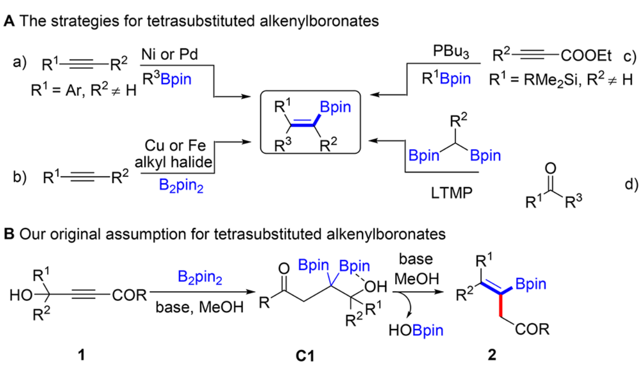
Supporting Information

ABSTRACT: An efficient approach to tetrasubstituted alkenylboronates via a cascade borylation/B−O elimination of propynols and B_2pin_2 was disclosed. A series of tetrasubstituted alkenylboronates were readily furnished with this strategy in good yields, with further transformations leading to tetrasubstituted alkenes and β-diketones demonstrating the synthetic potential of the alkenylboronates constructed by this strategy as versatile intermediates in organic synthesis.



Organoboron compounds are not only indispensable partners in Suzuki coupling[1,2] but also key structural motifs which are encountered in materials science,[3] chemosensor development,[4] as well as many bioactive natural compounds.[5] Among all types of organoboron compounds, alkenylboronates are synthetically versatile and important building blocks;[6,7] for example, β-aryl alkenylboronates are key intermediates for the synthesis of stilbenoid compounds,[7c] and tetrasubstituted alkenylboronates are the key precursors for the construction of tetrasubstituted alkenes,[8] given that they are frequently found in a myriad of critical bioactive compounds and pharmaceuticals.[9] However, to our knowledge, the known methods for the synthesis of tetrasubstituted alkenylboronates[10] are relatively rare, and they are mainly limited to transition-metal-catalyzed carboboration of alkynes. Suginome and co-workers reported a series of elegant examples about palladium or nickel-catalyzed carboboration of alkyne (Scheme 1A, a) via intramolecular[8] or intermolecular[11] pathways. Soon after, Cu-catalyzed[10,12] or Fe-catalyzed[13] carboboration of internal alkynes through three-component coupling with B_2pin_2 and halohydrocarbons became an efficient approach for fabricating tetrasubstituted alkenylboronates (Scheme 1A, b). Copper-catalyzed borylation of propargylic substrates or (α-alkoxy) allenes could also give the tetrasubstituted allenylboronates[12h,14a] or 2-boryl-1,3-butadienes.[14b] Recently, Sawamura and Ohmiya's group reported an antiselective vicinal silaboration[15c] (Scheme 1A, c) of alkynoates through phosphine organocatalysis,[15] which provides an efficient and green method for the synthesis of tetrasubstituted alkenylboronates. Shibata's group[16a] and Fernández's group[16b] reported stereoselective synthesis of tetrasubstituted alkenylboronates via the nucleophilic addition of 1,1-diboronates to carbonyl compounds with lithium 2,2,6,6-tetramethylpiperidide (LTMP)[16] (Scheme 1A, d). Despite significant advances toward the synthesis of tetrasubstituted alkenylboronates, there are several restrictions in the current methods: (1) most of the metal-catalyzed addition reactions are limited to aryl alkynes; (2) the boron sources are usually difficult to handle in the palladium- or nickel-catalyzed carboboration reactions;[10] (3) a strictly anhydrous condition was required.[15,16] Given the high demands on environmentally benign synthesis, an operational simple, effective, and highly selective synthesis of tetrasubstituted alkenylboronates which has no requirement on transition-metal involvement becomes a big challenge.

Scheme 1. Synthesis of Tetrasubstituted Alkenylboronates



Herein, we addressed the gap and designed an efficient and green approach to tetrasubstituted alkenylboronates through a K_2CO_3-catalyzed reaction between propynols and B_2pin_2 (Scheme 1B). Inspired by our previous works[17a−c] on the domino-borylation−protodeboronation (DBP) strategy and

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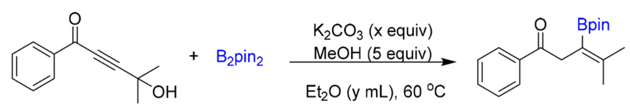
base-promoted B−B bond activation and C−B bond formation,[17a−c,18] we envisaged that when ynone (**1**) was subjected to the system of B_2pin_2, MeOH and base, *geminal*-diboronates (**C1**) would be obtained (Scheme 1B).[17d,e] However, this reaction did not stop at this stage; the hydroxyl group which was adjacent to the two Bpin moieties had a strong propensity to attach to the B atom, and therefore, one molecule of HO-Bpin would eventually be eliminated,[16,18f,19] resulting in the tetrasubstituted alkenylboronates **2** (Scheme 1A, d). It is of note that this strategy is very different from the metal-free *trans*-diboration of propargylic alcohols with a stoichiometric amount of ^{n}BuLi, in which a pseudo-intramolecular strategy[20] was involved that significantly lowered the activation barrier of addition of boryl anion to the triple bond.

In order to validate our hypothesis, 4-hydroxy-4-methyl-1-phenylpent-2-yn-1-one (**1a**) was chosen as the model substrate and subjected to various conditions in the presence of B_2pin_2, bases (for more details about the examination of base, see the Supporting Information) and MeOH; to our delight, the desired tetrasubstituted alkenylboronate (**2a**) was indeed obtained in 30% yield with K_2CO_3 as base (Table 1, entry 1). This result encouraged us, and a careful survey on different parameters was subsequently carried out. It was of note that both the concentration and the amount of base have significant effects on the reactions (Table 1, entries 1−4 and entries 4−7). Eventually, condition screening suggested that 0.3 equiv of K_2CO_3 as the catalyst with 2 equiv of B_2pin_2 in Et_2O at 60 °C for 6 h were the optimal conditions (Table 1, entry 8). It is worth mentioning that prolonged time was not helpful in increasing the yield of **2a** (Table 1, entries 9−11); instead, it became very harmful, especially in air (Table 1, entry 12).

Table 1. Optimization of Tetrasubstituted Alkenylboronate 2a



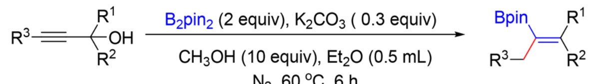
1a, 0.2 mmol   2.0 equiv   **2a**

entry	K_2CO_3 (equiv)	Et_2O (mL)	time (h)	yield[a] (%)
1	1.5	2.0	12	30
2	1.5	1.0	12	45
3	0.7	1.0	12	42
4	0.7	0.5	12	56
5	0.5	0.5	12	46
6	0.3	0.5	12	65
7	0.1	0.5	12	48
8	**0.3**	**0.5**	**6**	**72 (80)**[b]
9	0.3	0.2	12	55
10	0.3	0.5	18	61
11	0.3	0.5	24	63
12[c]	0.3	0.5	24	33

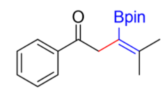
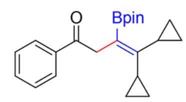
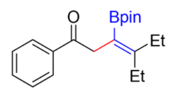
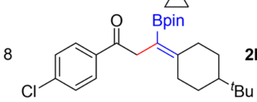
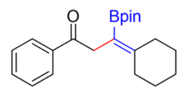
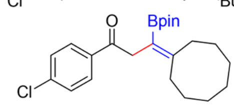
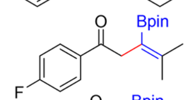
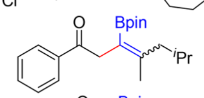
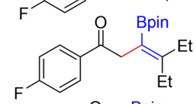
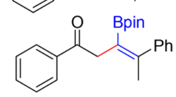
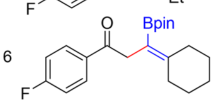
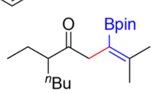
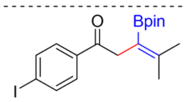
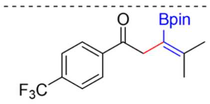
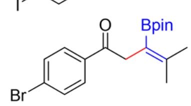
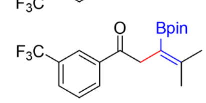
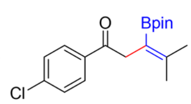
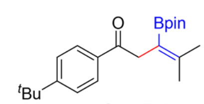
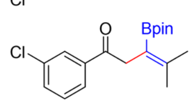
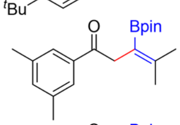
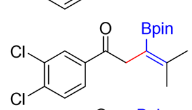
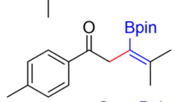
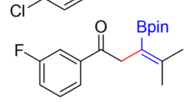
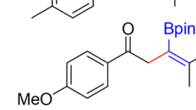
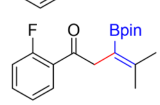
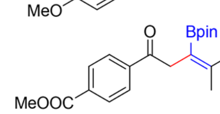
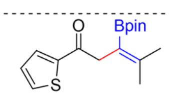
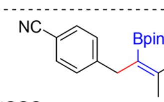
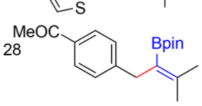
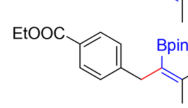
[a]Isolated yield. [b]When MeOH (10 equiv) was used, the yield was 80% . [c]Under air.

With the optimal conditions in hand (Table 1, entry 8), the substrate scope of propynols was investigated, and the results are shown in Table 2. First, we explored the effect of the substituents which are bound to the same carbon atom as the hydroxyl group in the transformation (**2a−c**, **2d−f**, and **2g−k**). Gratifyingly, Me, Et, ^{i}Pr, cyclopropyl, cyclohexyl, as well as cyclooctyl were all well tolerated under the standard conditions, and the corresponding tetrasubstituted alkenylboronates were furnished with moderate to good yields (65%−80%). It is worth noting that when the substituent groups adjacent to the hydroxyl group were not identical, a mixture of *cis*- and *trans*-isomerism of tetrasubstituted alkenylboronate

Table 2. Synthesis of Tetrasubstituted Alkenylboronates



1, 0.2 mmol   **2**, isolated yield

entry	product		yield (%)	entry	product		yield (%)
1		**2a**	80	7		**2g**	71
2		**2b**	65	8		**2h**	65
3		**2c**	72	9		**2i**	70
4		**2d**	75 (72)[a]	10		**2j** *E*/*Z* 1:1	70
5		**2e**	68	11		(*E*)-**2k**	25
6		**2f**	74	12		**2l**	56
13		**2m**	58	20		**2t**	68
14		**2n**	70	21		**2u**	62
15		**2o**	78	22		**2v**	72
16		**2p**	73	23		**2w**	77
17		**2q**	60	24		**2x**	75
18		**2r**	72	25		**2y**	85
19		**2s**	68	26		**2z**	50
27		**2aa**	82	29		**2ac**	48
28		**2ab**	45	30		**2ad**	38

[a]Reaction of 1.0 mmol of substrate with B_2pin_2 (2.2 equiv) for 12 h.

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with a rate of ~1:1 was obtained (**2j**), and the yield was 70%. When the substituents were very different (e.g., alkyl/aryl, **2k**), only the *E* (confirmed by NOE) form product was obtained with a low yield of 25%. Remarkably, when we extended the substrates from aryl ynone to alkyl ynone, to our delight, the corresponding long-chain vinylboronic esters **2l** was obtained albeit with a relatively low yield (56%). Next, we applied the optimal conditions to the ynones (**1**) with various substituents on the aromatic rings; gratifyingly, both electron-deficient groups (F, Cl, Br, I, CF_3, and COOMe) (**2m−u**, **2z**) and electron-rich groups (^{t}Bu, Me, and MeO) (**2v−y**) were compatible in this transformation. Notably, the iodo group, which usually was sensitive to transition-metal-catalyzed reactions, was also well tolerated in our strategy (**2m**), making the further structural elaborations feasible on the final products. Heterocyclic substrates and alkyne aromatics with strong electron-withdrawing groups (such as C(O)Me, CN, EtO(O)C) could also convert well under the standard conditions, giving the tetrasubstituted alkenylboronates (**2aa−ad**) in moderate yields.

Gratifyingly, when we created the tetrasubstituted alkenylboronate **2d** at the conditions screening stage, the unexpected compound 1-(4-fluorophenyl)-4-hydroxy-4- methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-one (**3d**) was distinctly observed and isolated sequentially. In view of this, we speculated that the compound **3d** may be the key intermediate for this conversion. Therefore, we decided to monitor the reaction process (Figure1) by NMR studies; as we can see,

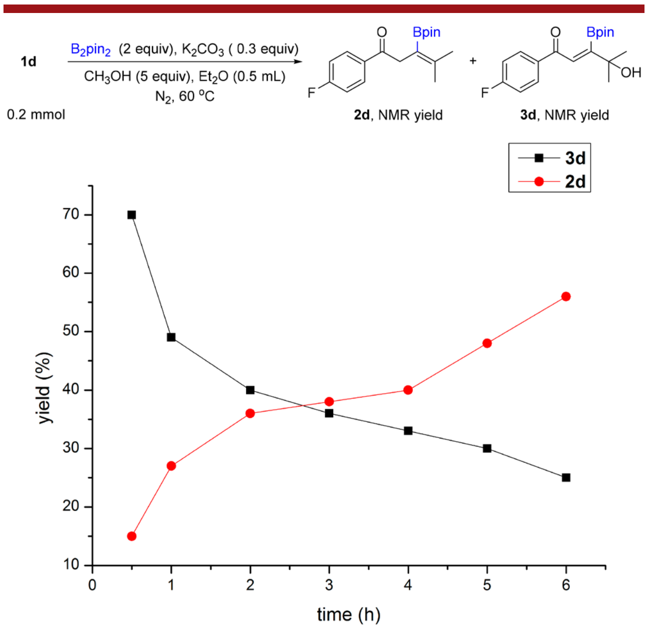
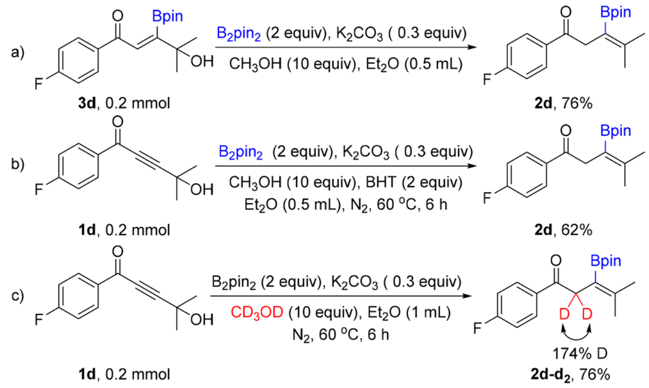


Figure 1. Process monitoring.

initially **3d** was formed dramatically, and as time goes on, compound **3d** was gradually converted into compound **2d**. To further prove this, we synthesized compound **3d** and subjected it to our optimized conditions; this compound stood well under the standard conditions, giving **2d** with an isolated yield of 76% (Scheme 2a). This result clearly indicates that compound **3d** might be the key intermediate for our transformation. With plenty of research coverage on boryl radicals, we conjectured if this conversion underwent a free-radical process as well, but we soon ruled out the possibility of a free-radical course due to the negative result on the radical-

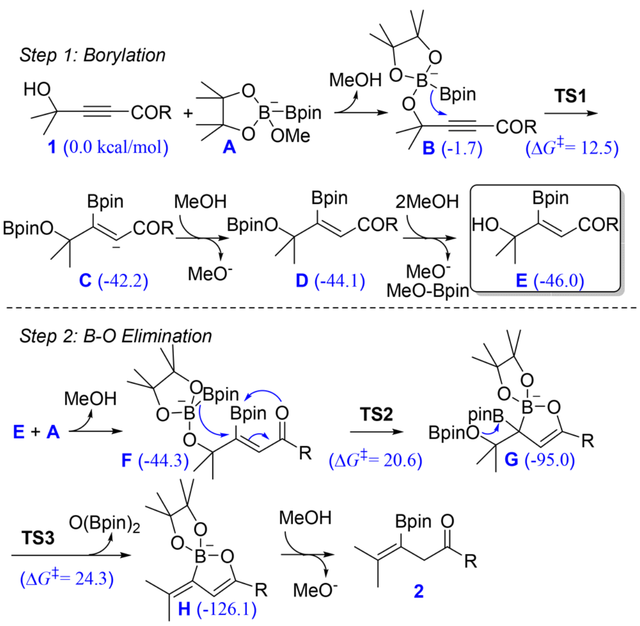
Scheme 2. Control Experiments



trapping experiment (Scheme 2b). We also performed the reaction with CD_3OD instead of MeOH under the standard conditions, and the highly di-*D*-substituted alkenylboronate (**2d**-d_2) was obtained with a yield of 76% and a rate of 87% D (Scheme 2c), which suggested that the proton source was derived from methanol.

Based on our DBP study[17a−c] and previous reports,[18] we proposed a cascade pathway involving borylation and B−O elimination steps through an alkenylboronate intermediate **E** for this transformation depicted in Scheme 3, which is

Scheme 3. Proposed Mechanism[a]



[a]The values given in parentheses are the relative Gibbs free energies calculated by M11 density functional in diethyl ether solvent. R group is phenyl in our calculations. The energies are reported in kcal/mol.

preliminarily studied by density functional theory (DFT) calculations. In the presence of base, the formation of methoxyborate **A** could be formed by the bonding of methoxide to B_2pin_2 with 18.3 kcal/mol exergonic. The alkoxy exchange between **A** and reactant **1** could form a propargoxyborate **B** reversibly. The cleavage of B−B bond leading to a nucleophilic attack with a C−C triple bond could take place via transition state **TS1** with a free energy barrier of only 12.5 kcal/mol. The followed protonation and alcoholysis

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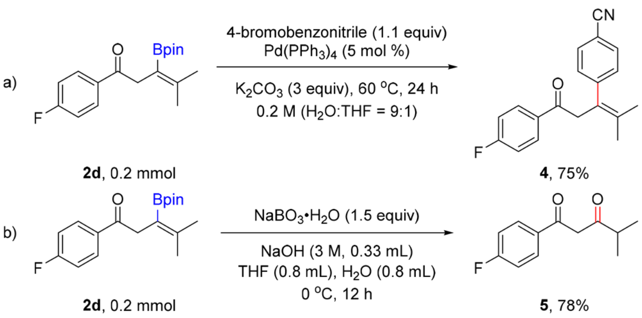
by methanol forms alkenylboronate intermediate **E** irreversibly. In the second step, alkoxy exchange takes place between intermediate **E** and methoxyborate **A** to form complex **F** reversibly. Correspondingly, another nucleophilic addition also could take place via transition state **TS2** with a free energy barrier of 20.6 kcal/mol with the activation of boryl group to form a boraspiro intermediate **G**. The followed B−O bond elimination could take place via transition state **TS3** with a free energy barrier of 24.3 kcal/mol to form an alkenylborate intermediate **H**, which could be protonated to yield product **2**. Further computational and experimental studies for the detailed mechanism of this transformation are underway.

The tetrasubstituted alkenylboronates are very important synthetic intermediates; therefore, further transformation of **2d** was applied (Scheme 4). The Suzuki coupling of alkenylboronates (**2d**) with 4-bromobenzonitrile easily afforded the tetrasubstituted alkene[21] **4** with a cyano group on the ring in good yield (Scheme 4a). 1,3-Diketones[22] are important raw materials for chemical synthesis and widely used in organic chemistry as well as in pharmaceutical industry. To our delight, alkenylboronate (**2d**) was readily oxidized into to β-diketones with sodium perborate as mild oxidant, rendering the product **5** in 78% (Scheme 4b).

Scheme 4. Synthetic Application of Alkenylboronates



In summary, we have developed an efficient strategy to access tetrasubstituted alkenylboronates via borylation/B−O elimination of propynols and B_2pin_2 with DBP strategy. Through this strategy, a series of tetrasubstituted alkenylboronates were afforded in good yields. Tetrasubstituted alkenes and β-diketones were further accordingly obtained from tetrasubstituted alkenylboronates, indicating the synthetic potential of the alkenylboronates as versatile intermediates in organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02077.

Experimental details, characterization data, DFT calculations, and ^{1}H, ^{13}C, and ^{11}B NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Suzuki, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6722. (b) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. *Chem. Rev.* **2016**, *116*, 9091. (c) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E. *Chem. Soc. Rev.* **2017**, *46*, 415.

(2) (a) Zhou, Y. Y.; You, W.; Smith, K. B.; Brown, M. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 3475. (b) Pirnot, M. T.; Wang, Y. M.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 48. (c) Kuang, Z.; Li, B.; Song, Q. *Chem. Commun.* **2018**, *54*, 34.

(3) Brooks, W. L. A.; Sumerlin, B. S. *Chem. Rev.* **2016**, *116*, 1375.

(4) Bull, S. D.; Davidson, M. G.; van den Elsen, J. M. H.; Fossey, J. S.; Jenkins, A. T. A.; Jiang, Y.-B.; Kubo, Y.; Marken, F.; Sakurai, K.; Zhao, J.; James, T. D. *Acc. Chem. Res.* **2013**, *46*, 312.

(5) (a) Roupe, K. A.; Remsberg, C. M.; Yanez, J. A.; Davies, N. M. *Curr. Clin. Pharmacol.* **2006**, *1*, 81. (b) Trippier, P. C.; McGuigan, C. *MedChemComm* **2010**, *1*, 183.

(6) (a) Wang, C.; Wu, C.; Ge, S. *ACS Catal.* **2016**, *6*, 7585. (b) Shade, R. E.; Hyde, A. M.; Olsen, J.-C.; Merlic, C. A. *J. Am. Chem. Soc.* **2010**, *132*, 1202.

(7) (a) Liu, S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2008**, *130*, 6918. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. (c) Paramore, A.; Frantz, S. *Nat. Rev. Drug Discovery* **2003**, *2*, 611.

(8) (a) Suginome, M.; Yamamoto, A.; Murakami, M. *J. Am. Chem. Soc.* **2003**, *125*, 6358. (b) Yamamoto, A.; Suginome, M. *J. Am. Chem. Soc.* **2005**, *127*, 15706. (c) Daini, M.; Yamamoto, A.; Suginome, M. *J. Am. Chem. Soc.* **2008**, *130*, 2918.

(9) (a) Negishi, E.; Wang, G.; Rao, H.; Xu, Z. *J. Org. Chem.* **2010**, *75*, 3151. (b) Epothilone A: Höfle, G.; Bedorf, N.; Steinmetz, H.; Schomburg, D.; Gerth, K.; Reichenbach, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1567. (c) Calyculin A: Suganuma, M.; Fujiki, H.; Furaya-Suguri, H.; Yoshizawa, S.; Yasumoto, S.; Kato, Y.; Fusetani, N.; Sugimura, T. *Cancer Res.* **1990**, *50*, 3521.

(10) (a) Alfaro, R.; Parra, A.; Aleman, J.; Garcia Ruano, J. L.; Tortosa, M. *J. Am. Chem. Soc.* **2012**, *134*, 15165. (b) Itoh, T.; Shimizu, Y.; Kanai, M. *J. Am. Chem. Soc.* **2016**, *138*, 7528. (c) Bin, H.-Y.; Wei, X.; Zi, J.; Zuo, Y.- J.; Wang, T.- C.; Zhong, C. *ACS Catal.* **2015**, *5*, 6670. (d) Han, J. T.; Yun, J. *Org. Lett.* **2018**, *20*, 2104.

(11) (a) Suginome, M.; Yamamoto, A.; Murakami, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2380. (b) Suginome, M.; Shirakura, M.; Yamamoto, A. *J. Am. Chem. Soc.* **2006**, *128*, 14438. (c) Daini, M.; Suginome, M. *Chem. Commun.* **2008**, *44*, 5224. (d) Mannathan, S.; Jeganmohan, M.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2009**, *48*, 2192. (e) Yoshida, H. *ACS Catal.* **2016**, *6*, 1799.

(12) (a) Yoshida, H.; Kageyuki, I.; Takaki, K. *Org. Lett.* **2013**, *15*, 952. (b) Zhou, Y.; You, W.; Smith, K. B.; Brown, M. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 3475. (c) Zhang, L.; Cheng, J.; Carry, B.; Hou, Z. *J. Am. Chem. Soc.* **2012**, *134*, 14314. (d) Kubota, K.; Iwamoto, H.; Yamamoto, E.; Ito, H. *Org. Lett.* **2015**, *17*, 620. (e) Liu, P.; Fukui, Y.;

DOI: 10.1021/acs.orglett.8b02077
Org. Lett. XXXX, XXX, XXX−XXX

Tian, P.; He, Z.-T.; Sun, C.-Y.; Wu, N.-Y.; Lin, G.-Q. *J. Am. Chem. Soc.* **2013**, *135*, 11700. (f) Takemoto, Y.; Yoshida, H.; Takaki, K. *Chem. - Eur. J.* **2012**, *18*, 14841. (g) Yoshida, H.; Takemoto, Y.; Takaki, K. *Chem. Commun.* **2015**, *51*, 6297. (h) Ito, H.; Sasaki, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 15774.

(13) Nakagawa, N.; Hatakeyama, T.; Nakamura, M. *Chem. - Eur. J.* **2015**, *21*, 4257.

(14) (a) Zhao, T. S.; Yang, Y.; Lessing, T.; Szabo, K. J. *J. Am. Chem. Soc.* **2014**, *136*, 7563. (b) Semba, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 12400.

(15) (a) Wakamatsu, T.; Nagao, K.; Ohmiya, H.; Sawamura, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 11620. (b) Nagao, K.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2014**, *136*, 10605. (c) Nagao, K.; Ohmiya, H.; Sawamura, M. *Org. Lett.* **2015**, *17*, 1304. (d) Yamazaki, A.; Nagao, K.; Iwai, T.; Ohmiya, H.; Sawamura, M. *Angew. Chem., Int. Ed.* **2018**, *57*, 3196.

(16) (a) Endo, K.; Hirokami, M.; Shibata, T. *J. Org. Chem.* **2010**, *75*, 3469. (b) La Cascia, E.; Cuenca, A. B.; Fernández, E. *Chem. - Eur. J.* **2016**, *22*, 18737. (c) Coombs, J. R.; Zhang, L.; Morken, J. P. *Org. Lett.* **2015**, *17*, 1708.

(17) (a) Yang, K.; Song, Q. *Green Chem.* **2016**, *18*, 932. (b) Gao, G.; Yan, J.; Yang, K.; Chen, F.; Song, Q. *Green Chem.* **2017**, *19*, 3997. (c) Ding, W.; Song, Q. *Org. Chem. Front.* **2016**, *3*, 14. (d) Gao, M.; Thorpe, S. B.; Santos, W. L. *Org. Lett.* **2009**, *11*, 3478. (e) Netsu, Y.; Tsukada, N. *Lett. Org. Chem.* **2017**, *14*, 243.

(18) (a) Bonet, A.; Pubill-Ulldemolins, C.; Bo, C.; Gulyás, H.; Fernández, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7158. (b) Miralles, N.; Cid, J.; Cuenca, A. B.; Carbó, J. J.; Fernández, E. *Chem. Commun.* **2015**, *51*, 1693. (c) Cuenca, A. B.; Zigon, N.; Duplan, V.; Hoshino, M.; Fujita, M.; Fernández, E. *Chem. - Eur. J.* **2016**, *22*, 4723. (d) Bonet, A.; Solé, C.; Gulyás, H.; Fernández, E. *Org. Biomol. Chem.* **2012**, *10*, 6621. (e) Morinaga, A.; Nagao, K.; Ohmiya, H.; Sawamura, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 15859. (f) Miralles, N.; Alan, R.; Szabó, K.; Fernández, E. *Angew. Chem., Int. Ed.* **2016**, *55*, 4303.

(19) (a) Miralles, N.; Maza, R. J.; Fernández, E. *Adv. Synth. Catal.* **2018**, *360*, 1306. (b) Nallagonda, R.; Padala, K.; Masarwa, A. *Org. Biomol. Chem.* **2018**, *16*, 1050. (c) Matteson, D. S.; Moody, R. J. *Organometallics* **1982**, *1*, 20. (d) Cuenca, A. B.; Cid, J.; Garcia-Lopez, D.; Carbo, J. J.; Fernandez, E. *Org. Biomol. Chem.* **2015**, *13*, 9659. (e) Sun, W.; Wang, L.; Xia, C.; Liu, C. *Angew. Chem., Int. Ed.* **2018**, *57*, 5501. (f) Iacono, C. E.; Stephens, T. C.; Rajan, T. S.; Pattison, G. *J. Am. Chem. Soc.* **2018**, *140*, 2036.

(20) Nagashima, Y.; Hirano, K.; Takita, R.; Uchiyama, M. *J. Am. Chem. Soc.* **2014**, *136*, 8532.

(21) Flynn, A. B.; Ogilvie, W. W. *Chem. Rev.* **2007**, *107*, 4698.

(22) (a) Sada, M.; Matsubara, S. *J. Am. Chem. Soc.* **2010**, *132*, 432. (b) Mitsudome, T.; Yoshida, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 5961.

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