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Trialkylborane-Mediated Multicomponent Reaction for the Diastereoselective Synthesis of *Anti-δ,δ*-Disubstituted Homoallylic Alcohols

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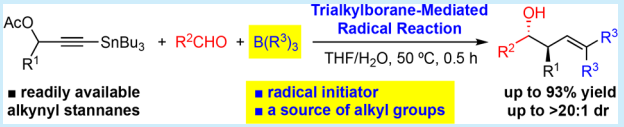
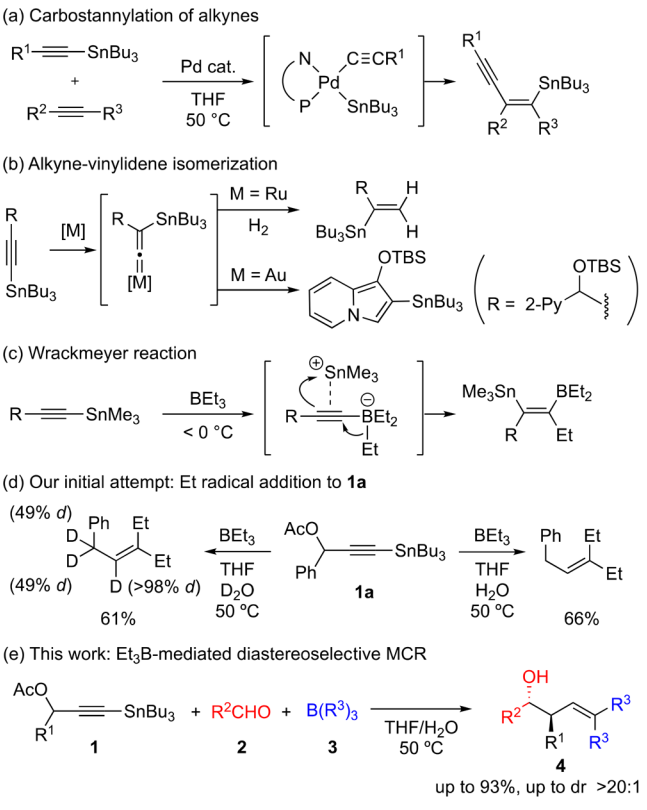
Supporting Information

ABSTRACT: The trialkylborane/O_2-mediated reaction of propargyl acetates having a tributylstannyl group at an alkyne terminus with aldehydes in a THF−H_2O solvent system gave *anti-δ,δ*-disubstituted homoallylic alcohols with good to high diastereoselectivity. Intriguingly, two alkyl groups derived from trialkylborane were embedded into the reaction product. The trialkylborane plays a key role not only as a radical initiator but also as a source of alkyl radicals.



Devising elaborate synthetic strategies for the ever-increasing complexity of organic molecules from simple precursors is an important subject in organic synthesis.[1] Alkynyl-metalloid/metal compounds, such as alkynylboronates and alkynylstannanes, serve as versatile building blocks for such purposes because sequential stereospecific carbon−carbon and carbon−heteroatom bond formation can be achieved.[2,3] Among these important classes of reagents, alkynylstannanes are particularly attractive because practical and functional-group-tolerant synthesis of alkynylstannanes has been established.[4,5] Moreover, these compounds exhibit distinct reactivity that can lead to several synthetically useful intermediates depending on the choice of reaction conditions. For example, the Migita−Kosugi−Stille coupling reaction using alkynylstannanes is still a powerful tool for the construction of C(sp)−C(sp2) and C(sp)−C(sp) bonds.[6] In addition, palladium-catalyzed carbostannylation of alkynes has demonstrated the significant synthetic potential of this reaction to provide 1-stannylated-1,3-enynes regio- and stereoselectively (Scheme 1a).[7] Furthermore, the stannyl group can undergo 1,2-migration upon alkyne−vinylidene isomerization of alkynylstannanes (Scheme 1b).[8,9] Interestingly, trialkylboranes readily react with alkynylstannanes by cleavage of the Sn−C bond in inert solvent to give vinylstannanes containing a vicinal boryl group (Wrackmeyer reaction) (Scheme 1c).[10] However, to the best of our knowledge, no examples of the addition of alkyl radical to alkynylstannanes have ever been reported.[11] In addition, the reactivities of alkynylstannanes possessing a leaving group at the propargylic position remain largely unexplored, even though these reagents offer a great degree of synthetic flexibility. After many screenings of free-radical reactions using 1-phenyl-3-(tributylstannyl)propargyl acetates (**1a**), we found that the reaction of **1a** and triethylborane in the THF/H_2O solvent system gave the unexpected formation of 1-phenyl-3-ethylpent-2-ene, where two ethyl groups derived from triethylborane were incorporated in the product (Scheme 1d, right). Inspired by this interesting transformation, we carried out the reaction in the presence of deuterium oxide instead of H_2O (Scheme 1d, left). As a result, deuterium was

Scheme 1. Diverse Reactivities of Alkynylstannanes



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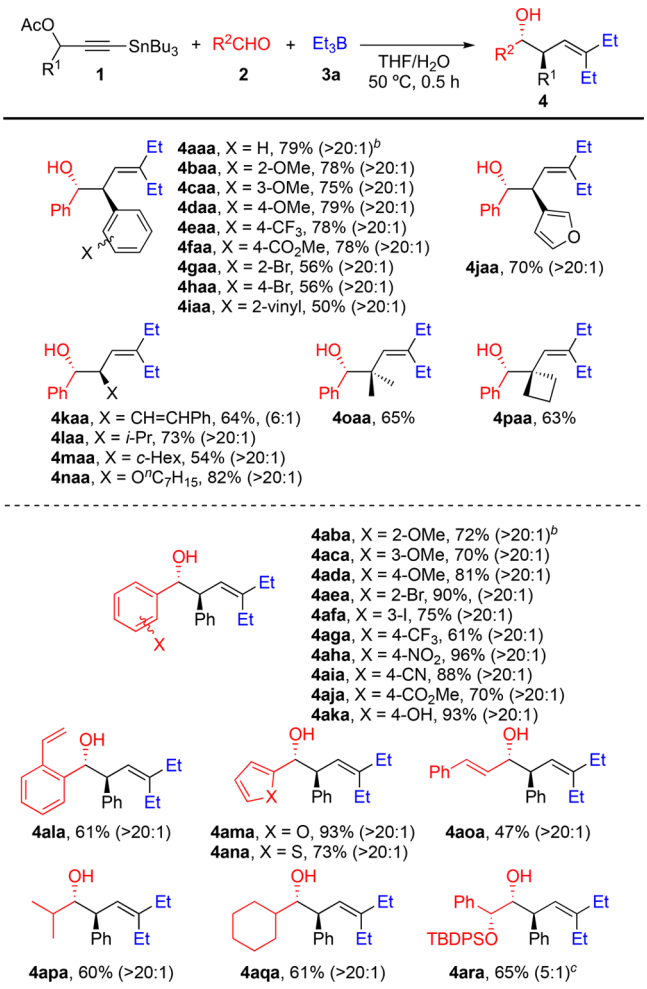
incorporated exclusively at two specific positions. We hypothesized that such formation might involve both vinyl radical and allylstannane intermediates. We were pleased to find that *anti*-δ,δ-disubstituted homoallylic alcohol **4aaa** was obtained in 79% with excellent diastereoselectivity if the reaction of **1a** and triethylborane (**3a**) was performed in the presence of benzaldehyde (**2a**) (Scheme 2). Trialkylboranes

Scheme 2. Scope of the Et_3B-Mediated MCR[a]



[a]Unless noted otherwise, the reaction of **1** (0.5 mmol) with **2** (1.2 mmol) and **3a** (1 M in hexane, 0.6 mmol) was carried out in THF/H_2O (2.5 mL, 4/1) at 50 °C under Ar. [b]The ratio of *anti*:*syn* determined by ^1H NMR analysis of the crude reaction mixture. [c](1*R*,2*R*,3*S*)-**4ara**:(1*R*,2*S*,3*R*)-**4ara** = 5:1. TBDPS = *tert*-butyldiphenylsilyl.

generally participate in free-radical reactions as an initiator only;[11] little is known about the use of these compounds as both radical initiators and sources of alkyl radicals.[12] In general, diastereoselectivity in free-radical reactions can be controlled by several strategies, namely, substrate-controlled, Lewis acid controlled, and chiral auxiliary-controlled strategies.[13] Therefore, the development of a new strategy for diastereoselective multicomponent reactions (MCRs) based on a R_3B/O_2-mediated radical chain process is challenging and an important subject in synthetic organic chemistry.[14] Herein, we report a diastereoselective free-radical-mediated three-component assembly reaction with an Et_3B/O_2 system that provides access to a diverse range of *anti*-δ,δ-disubstituted homoallylic alcohols **4** from readily available 3-(tributylstannyl)propargyl acetates **1**,[5] aldehydes **2**, and trialkylboranes **3** (Scheme 1e). The diastereoselective synthesis of functional group tolerated δ,δ-disubstituted homoallylic alcohols remains a formidable challenge.[15]

With optimal conditions in hand,[16] we first sought to explore the substrate scope with regard to 3-(tributylstannyl)propargyl acetates **1** by carrying out reactions with benzaldehyde (**2a**) and triethylborane (**3a**) (Scheme 2). We found that various 1-aryl- and 1-heteroaryl-substituted 3-(tributylstannyl)propargyl acetates **1a**–**j** afforded the desired homoallylic alcohols **4aaa**–**jaa** in good yields with excellent *anti*-selectivities. The stereochemistry of **4aaa** was carefully confirmed by its derivatization to a known compound.[16] In contrast, the reaction of β-styryl-substituted propargyl acetate **1k** gave the desired product **4kaa** in 64% yield with a diastereoselectivity of 6:1. We also found that alkyl- and alkoxy-substituted substrates were compatible under these conditions, enabling the preparation of homoallylic alcohols **4laa**–**paa** in moderate to good yields with excellent diastereoselectivities. Next, we investigated the generality of aldehyde scope. We were pleased to find that the MCR displayed wide functional-group compatibility. For example, the reactions proceeded cleanly regardless of the electronic nature of the substituents on aromatic aldehydes. Thus, a diverse range of homoallylic alcohols **4aba**–**ala** were prepared from the corresponding aromatic aldehydes with either an electron-donating or an electron-withdrawing group on each position of the aromatic ring. To our delight, without the prior protection of the hydroxyl group, 4-hydroxybenzaldehyde was smoothly engaged in the reaction to furnish **4aka** in an excellent yield of 93%. Furthermore, heterocyclic aldehydes such as furfural and 2-thiophenecarboxaldehyde could be effectively transformed into the desired homoallylic alcohols **4ama** and **4ana** in 93% and 73% yields, respectively, with excellent diastereoselectivity. An α,β-unsaturated aldehyde also participated in the current MCR, providing a homoallylic alcohol **4aoa** as a sole product in 47%, which indicates that a competing reaction pathway of the conjugate addition of ethyl radical to the aldehyde is efficiently suppressed.[11,17] Several substantially less reactive aliphatic aldehydes also took part in the reaction to provide access to both **4apa** and **4aqa** in good yields. The present MCR with α-chiral alkoxy-substituted aldehydes proceeded with a good level of diastereoselectivity to give **4ara**, as in the case of Pd-catalyzed umpolung allylation,[18] which provides a different diastereoselectivity from that obtained in the crotylation of α-chiral alkoxy-substituted aldehydes with (*E*)-crotylboronates.[19]

Finally, we explored the scope of this MCR with other organoboranes (Scheme 3). We observed that the rate of a reaction decreased as the size of the alkyl substituent on the borane was increased.[20] Commercially available tri-*n*-butylborane took part in this reaction to furnish **4aab** in 70% yield. The practicality of the present method was demonstrated by a scale-up experiment at a gram scale of **1a**, where **4aab** was produced in 66% yield. Additionally, it was found that unpurified trialkylboranes derived from the hydroboration of alkenes could be used. For example, reactions with several functionalized organoboranes prepared from TBS-protected allylic and homoallylic alcohols with borane dimethyl sulfide complex also gave the desired products **4aac** and **4aad**, respectively, with excellent diastereoselectivity, and two alkyl groups derived from a trialkylborane were nicely incorporated

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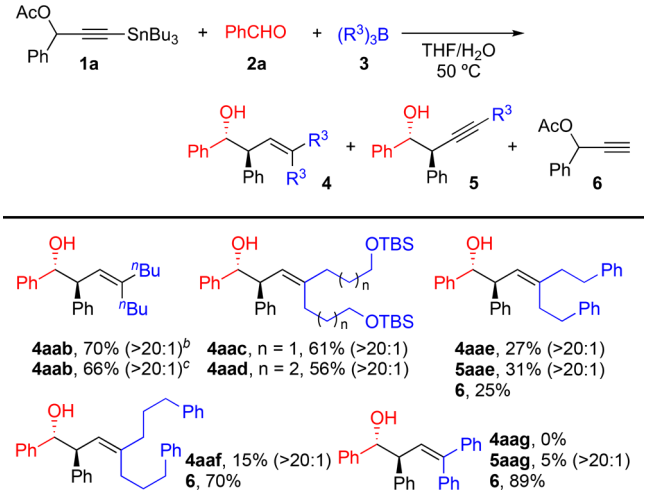
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 3. Scope with Respect to Triorganoboranes[a]

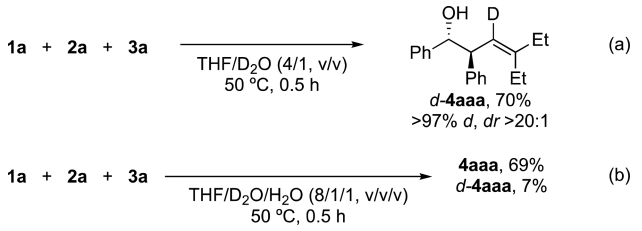


[a]Reaction conditions identical to those in Scheme 2. [b]The ratio of *anti*/*syn* determined by ^{1}H NMR analysis of the crude reaction mixture. [c]3 mmol scale reaction. TBS = *tert*-butyldimethylsilyl.

at the germinal position. In reactions with trialkylboranes possessing benzylic protons, in contrast with the above results, the efficiency decreased, resulting in the corresponding alcohols **4aae** and **4aaf** in diminished yields, but high levels of stereoselectivity persisted. In both cases, a significant amount of propargyl acetate **6** was isolated, presumably via protodestannylation of **1a** under the reaction conditions. In these examinations, homopropargyl alcohols **5aae** and **5aag** were also observed. Further attempts to use triphenylborane or *sec*-trialkylboranes resulted in no conversion into the desired products (e.g., **4aag**).

To gain insight into the mechanism of the present MCR, the reaction of **1a**, **2a**, and **3a** was conducted in THF/D_2O as a solvent (Scheme 4). Interestingly, the reaction afforded *d*-**4aaa**

Scheme 4. Kinetic Deuterium Isotope Effect

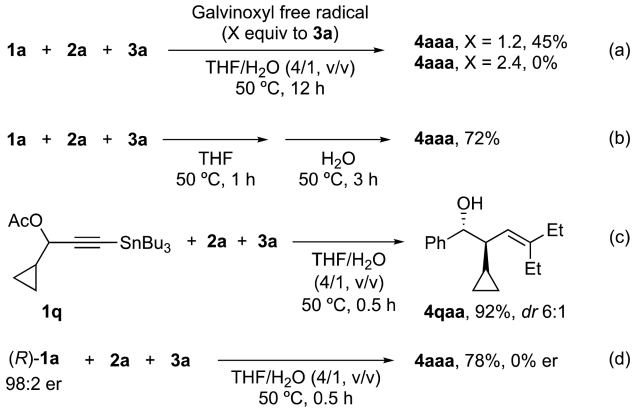


with almost complete deuterium incorporation exclusively at a specific position (Scheme 4a). In addition, a large kinetic deuterium isotope effect for the overall reaction (k_H/k_D = 9.9) was observed using THF/D_2O/H_2O as a solvent, suggesting that O−H bond homolysis of the $Et_3B{\cdot}OH_2$ complex is the rate-limiting step (Scheme 4b).[21]

Next, we performed further mechanistic studies (Scheme 5). Conducting the reaction in the presence of galvinoxyl free radical[22] (2.4 equiv to Et_3B) as a radical scavenger led to no reaction, suggesting that the present reaction proceeds through a free-radical mechanism (Scheme 5a). Although no reaction was observed in dry THF, subsequent addition of H_2O promoted the reaction to give **4aaa** in 72% yield (Scheme 5b).

Interestingly, radical clock experiments[23] using substrate **1q**, which contained a cyclopropyl ring, did not undergo

Scheme 5. Mechanistic Studies



rearrangement, affording **4qaa** in 92% yield with good diastereoselectivity (Scheme 5c). This represents the rare example of diastereoselective carbonyl α-(cyclopropyl)-allylation.[24] In addition, an attempt to use chiral substrate (*R*)-**1a** gave a racemic form of **4aaa** (Scheme 5d).

To further clarify the reaction mechanism, a control experiment using **5aaa** instead of **1a** was examined. However, **5aaa** was recovered quantitatively, suggesting that **5aaa** can be ruled out as an intermediate of the reaction. In this context, while MCR occurred only with tributylstannyl-substituted propargyl carboxylates such as acetate, pivalate, and carbonate as a substrate,[16] performing the reaction using **7**−**11** as a substrate resulted in no reaction (Figure 1).

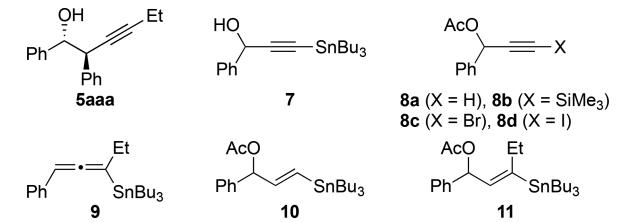


Figure 1. Unsuccessful substrates.

On the basis of the above results, a preliminary reaction mechanism is described in Figure 2. Initially, Et_3B reacts with residual O_2 in H_2O by bimolecular homolytic substitution reaction (S_H2) to produce an ethyl radical ($Et^•$) and a diethylborylperoxy radical.[11,25] Addition of $Et^•$ to **1** produces vinyl radical **I**, which successively reacts with $Et_3B{\cdot}OH_2$ complex to lead to **II**.[21] A severe 1,3-allylic strain of **II** would facilitate the addition of $Et^•$ to generate (*E*)-allylstannane **III** along with EtB(OH)OAc and $Et^•$. Given the poor ability of acetoxy radical as a leaving group, the organoborane presumably plays a crucial role as a Lewis acid in this step. In addition, the observed difference in reactivity between **11** and **II** might be explained by the greater 1,3-allylic strain of the latter. Subsequently, the addition of allylstannane **III** to an aldehyde proceeds via a chairlike cyclic transition state **IV** to give the product **4** with *anti*-diastereoselectivity.[26] In this context, the thermally promoted allylation of aldehydes with α-alkoxyallylstannanes and α-alkylallylstannanes is known to occur at 130−150 °C.[27] In addition, allylation of aldehydes with allylstannanes can take place at room temperature under neutral conditions by using a high-pressure technique.[28] In sharp contrast to these reports, the developed reaction

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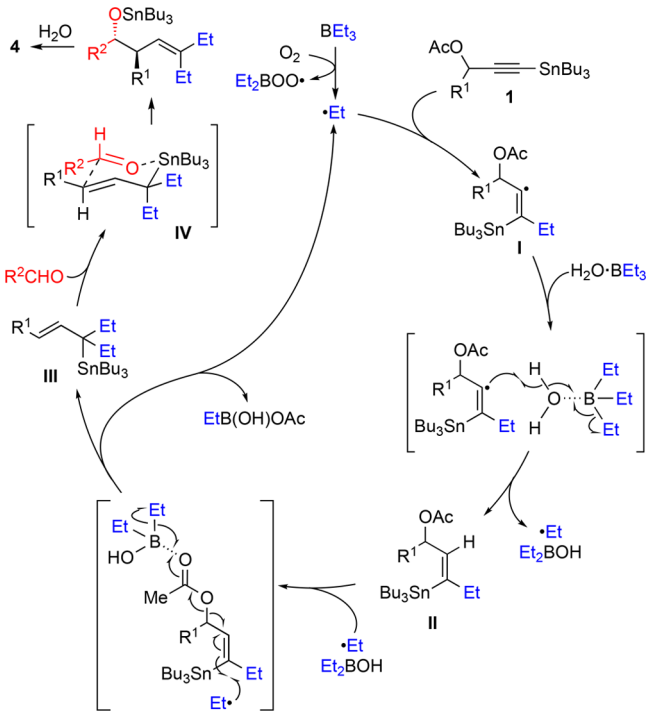

Figure 2. Plausible reaction mechanism.

proceeds under very mild conditions, presumably due to the increased ionic character of the Sn−C bond of the allylstannane **III** possessing two additional ethyl substituents.[29] The radical clock experiment as described above also supports the present reaction mechanism.

In summary, we have developed a mild and general free-radical-mediated MCR of propargyl acetates possessing a tributylstannyl group at an alkyne terminus, aldehydes, and trialkylboranes initiated by a trialkylborane/O_2 system. This process tolerates a broad spectrum of functionalized propargylic acetates and aldehydes, providing rapid access to *anti*-*δ*,*δ*-disubstituted homoallylic alcohols with good to excellent diastereoselectivities. The present free-radical-mediated MCR can become an attractive tool in organic synthesis. Further studies on the reaction mechanism and scope of the reactivity of organostannyl-substituted propargyl acetates are underway in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03761.

Experimental procedures, analytical data, and copies of ^{1}H and ^{13}C NMR spectra of all newly synthesized products (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hudlicky, T.; Natchus, M. G. In *Organic Synthesis: Theory and Applications*; JAI Press: London, 1993; Vol. 2, p 1.

(2) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon Press: New York, 1991; Vol. 4, Chapter 4.4, pp 865−911.

(3) For Sn: C−S bond formation: (a) Ichinose, Y.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1988**, *17*, 669. (b) Labadie, S. S. *J. Org. Chem.* **1989**, *54*, 2496. (c) Neumann, W. P.; Wicenec, C. *Chem. Ber.* **1993**, *126*, 763. C−P bond formation: Li, Y.; Chakrabarty, S.; Mück-Lichtenfeld, C.; Studer, A. *Angew. Chem., Int. Ed.* **2016**, *55*, 802. For B: C−O bond formation: (d) Chan, D. M. T.; Monaco, K. L.; Wang, R.-P.; Winters, M. P. *Tetrahedron Lett.* **1998**, *39*, 2933. (e) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937. C−N bond formation: (f) Antilla, J. C.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 2077. (g) Rucker, R. P.; Whittaker, A. M.; Dang, H.; Lalic, G. *J. Am. Chem. Soc.* **2012**, *134*, 6571. C−S bond formation: (h) Herradura, P. S.; Pendola, K. A.; Guy, R. K. *Org. Lett.* **2000**, *2*, 2019.

(4) (a) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295. (b) Neumann, W. P.; Kleiner, F. G. *Tetrahedron Lett.* **1964**, *5*, 3779. (c) Davies, A. G.; Kleinschmidt, D. C.; Palan, P. R.; Vasishtha, S. C. *J. Chem. Soc. C* **1971**, 3972. (d) Kleiner, F. G.; Neumann, W. P. *Justus Liebigs Ann. Chem.* **1968**, *716*, 19.

(5) (a) Kiyokawa, K.; Tachikake, N.; Yasuda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10393. (b) Forster, F.; Rendón López, V. M.; Oestreich, M. *J. Am. Chem. Soc.* **2018**, *140*, 1259.

(6) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138. (c) Wright, M. E.; Porsch, M. J.; Buckley, C.; Cochran, B. B. *J. Am. Chem. Soc.* **1997**, *119*, 8393. (d) Cordovilla, C.; Bartolomé, C.; Martínez-Ilarduya, J. M.; Espinet, P. *ACS Catal.* **2015**, *5*, 3040. (e) Meng, L.; Fujikawa, T.; Kuwayama, M.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2016**, *138*, 10351. (f) Moreno, J.; Schweighöfer, F.; Wachtveitl, J.; Hecht, S. *Chem. - Eur. J.* **2016**, *22*, 1070. (g) Schaubach, S.; Michigami, K.; Fürstner, A. *Synthesis* **2016**, *49*, 202. (h) Kawashima, H.; Hiroto, S.; Shinokubo, H. *J. Org. Chem.* **2017**, *82*, 10425. (i) Levashov, A. S.; Buryi, D. S.; Goncharova, O. V.; Konshin, V. V.; Dotsenko, V. V.; Andreev, A. A. *New J. Chem.* **2017**, *41*, 2910. (j) Levashov, A. S.; Aksenov, N. A.; Aksenova, I. V.; Konshin, V. V. *New J. Chem.* **2017**, *41*, 8297. (k) Akram, M. O.; Shinde, P. S.; Chintawar, C. C.; Patil, N. T. *Org. Biomol. Chem.* **2018**, *16*, 2865. (l) Pu, M.; Sanhueza, I. A.; Senol, E.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2018**, *57*, 15081.

(7) (a) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975. (b) Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 10221. (c) Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *Org. Lett.* **2000**, *2*, 2209. (d) Yoshida, H.; Shirakawa, E.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *Organometallics* **2000**, *19*, 5671. (e) Yoshida, H.; Shirakawa, E.; Nakao, Y.; Honda, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 637. (f) Shimizu, M.; Jiang, G.; Murai, M.; Takeda, Y.; Nakao, Y.; Hiyama, T.; Shirakawa, E. *Chem. Lett.* **2005**, *34*, 1700. (g) Shi, Y.; Peterson, S. M.; Haberaecker, W. W.; Blum, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 2168. (h) Kinashi, N.; Sakaguchi, K.; Katsumura, S.; Shinada, T. *Tetrahedron Lett.* **2016**, *57*, 129.

DOI: 10.1021/acs.orglett.8b03761
Org. Lett. XXXX, XXX, XXX−XXX

(8) Shirakawa, E.; Morita, R.; Tsuchimoto, T.; Kawakami, Y. *J. Am. Chem. Soc.* **2004**, *126*, 13614.
(9) (a) Seregin, I. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 12050. (b) Seregin, I. V.; Schammel, A. W.; Gevorgyan, V. *Tetrahedron* **2008**, *64*, 6876.
(10) For a review of the advanced Wrackmeyer reaction, see: (a) Wrackmeyer, B. *Coord. Chem. Rev.* **1995**, *145*, 125. (b) Kehr, G.; Erker, G. *Chem. Sci.* **2016**, *7*, 56.
(11) For reviews of radical reactions, see: (a) Yorimitsu, H.; Oshima, K. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. *1*, pp 11−27. (b) Subramanian, H.; Landais, Y.; Sibi, M. P. *Comprehensive Organic Synthesis*, 2nd ed.; Knochel, P., Molander, G. A., Eds.; Elsevier, 2014; Vol. *2*, Chapter 4.12. (c) Wille, U. *Chem. Rev.* **2013**, *113*, 813. (d) *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgilialoglu, C., Studer, A., Eds.; John Wiley and Sons: Chichester, U.K., 2012. (e) Rowlands, G. J. *Tetrahedron* **2010**, *66*, 1593. (f) Rowlands, G. J. *Tetrahedron* **2009**, *65*, 8603. (g) Zimmerman, J.; Sibi, M. P. *Top. Curr. Chem.* **2006**, *263*, 71. (h) Srikanth, G. S. C.; Castle, S. L. *Tetrahedron* **2005**, *61*, 10377. (i) Bar, G.; Parsons, A. F. *Chem. Soc. Rev.* **2003**, *32*, 251. (j) Sibi, M. P.; Manyem, S.; Zimmerman, J. *Chem. Rev.* **2003**, *103*, 3263. (k) Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415. (l) Renaud, P.; Gerster, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2562. (m) Fallis, A. G.; Brinza, I. M. *Tetrahedron* **1997**, *53*, 17543. (n) Albert, M.; Fensterbank, L.; Lacôte, E.; Malacria, M. *Top. Curr. Chem.* **2006**, *264*, 1. (o) Denes, F.; Pichowicz, M.; Povie, G.; Renaud, P. *Chem. Rev.* **2014**, *114*, 2587.
(12) (a) Yoshimitsu, T.; Arano, Y.; Nagaoka, H. *J. Org. Chem.* **2005**, *70*, 2342. (b) Valpuesta, M.; Muñoz, C.; Díaz, A.; Torres, G.; Suau, R. *Eur. J. Org. Chem.* **2010**, *2010*, 1934.
(13) Bar, G.; Parsons, A. F. *Chem. Soc. Rev.* **2003**, *32*, 251.
(14) A three-component reaction by a hybrid-type of radical/anionic reactions exhibits good to high levels of diastereoselectivity; see: (a) Takai, K.; Matsukawa, N.; Takahashi, A.; Fujii, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 152. (b) Barluenga, J.; Rodríguez, F.; Fañanás, F. J.; Rubio, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 3084.
(15) Hesse, M. J.; Essafi, S.; Watson, C. G.; Harvey, J. N.; Hirst, D.; Willis, C. L.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 6145−6149.
(16) See the Supporting Information.
(17) (a) Suzuki, A.; Arase, A.; Matsumoto, H.; Itoh, M.; Brown, H. C.; Rogic, M. M.; Rathke, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 5708. (b) Brown, H. C.; Rogić, M. M.; Rathke, M. W.; Kabalka, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 5709.
(18) Vogt, M.; Ceylan, S.; Kirschning, A. *Tetrahedron* **2010**, *66*, 6450.
(19) (a) Hoffmann, R. W.; Weidmann, U. *Chem. Ber.* **1985**, *118*, 3966. (b) Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.
(20) (a) Curran, D. P.; McFadden, T. R. *J. Am. Chem. Soc.* **2016**, *138*, 7741. (b) Darmency, V.; Renaud, P. In *Radicals Synthesis I*; Springer-Verlag, Berlin, 2006; pp 71−106.
(21) (a) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 12513. (b) Medeiros, M. R.; Schacherer, L. N.; Spiegel, D. A.; Wood, J. L. *Org. Lett.* **2007**, *9*, 4427.
(22) Coppinger, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 501.
(23) (a) Newcomb, M.; Toy, P. H. *Acc. Chem. Res.* **2000**, *33*, 449. (b) Baldwin, J. E. *Chem. Rev.* **2003**, *103*, 1197.
(24) (a) Tsutsumi, R.; Hong, S.; Krische, M. J. *Chem. - Eur. J.* **2015**, *21*, 12903. (b) Fleury, L. M.; Ashfeld, B. L. *Org. Lett.* **2009**, *11*, 5670. (c) Fleury, L. M.; Kosal, A. D.; Masters, J. T.; Ashfeld, B. L. *J. Org. Chem.* **2013**, *78*, 253.
(25) Soulard, V.; Villa, G.; Vollmar, D. P.; Renaud, P. *J. Am. Chem. Soc.* **2018**, *140*, 155.
(26) Denmark, S.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, 2008; pp 299−401.
(27) (a) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1984**, 800. (b) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1529. (c) Schmidtmann, E. S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4634.
(28) (a) Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 489.
(29) Koreeda, M.; Tanaka, Y. *Chem. Lett.* **1982**, *11*, 1299.

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