Organic LETTERS

Letter

pubs.acs.org/OrgLett

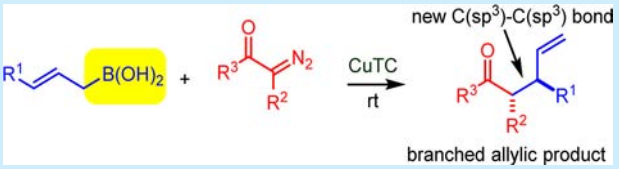
Copper-Catalyzed Cross-Coupling of Allylboronic Acids with α-Diazoketones

Arindam Das, Dong Wang,‡ Marie-Charlotte Belhomme,‡ and Kálmán J. Szabó*

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691 Stockholm, Sweden

Supporting Information

ABSTRACT: Copper-catalyzed cross-coupling of substituted allylboronic acids with α-diazoketones was studied. This allylation reaction is highly regioselective, providing the branched allylic product. The process involves creation of a new C(sp^3)−C(sp^3) bond by retaining the keto functional group of the α-diazoketone precursor.

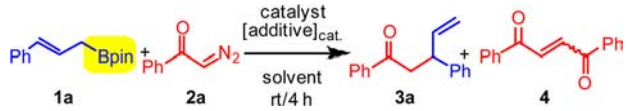


Allylboration is a very powerful method in selective organic synthesis.[1] The most widely used application is allylboration of carbonyl compounds[2] and imines,[1a,2a,g,3] to obtain homoallylic alcohols and amines. A new emerging area involves transition metal catalyzed cross-coupling reactions involving allylboron species. The research group of Miyaura[4] and our group[5] published independently cross-coupling reactions employing alkyl−allyl and crotyl boronates with aryl halides. Both studies pointed out that the cross-coupling reactions selectively gave the branched allylic product using appropriate ligands. This is surprising, since palladium-catalyzed allylic substitutions usually provide the corresponding linear allylic isomer.[6] Recently, the groups of Buchwald[7] and Organ[8] have studied the regioselectivity of the process with particular attention on the prenylation reactions. These authors found that the regioselectivity can be efficiently controlled by choice of the ligands and the additives of the reaction. In a very recent study the groups of Crudden[9] and Aggarwal[9b] studied the regio- and stereochemistry of this interesting reaction using chiral allylboronate substrates. In addition Morken and co-workers published useful palladium-catalyzed allyl−allyl cross-coupling reactions[10] and nickel-catalyzed conjugate addition to enones[11] based on allylboronates.

As a part of our research program on studying the synthesis and application of allylboronates,[2a−c,5,12] we decided to extend the synthetic scope of the cross-coupling reactions of allylboron species. Considering the above successful Suzuki−Miyaura and allyl−allyl coupling reactions, we focused our attention on other types of C−C bond-forming cross-couplings involving organoboronates. Inspired by the seminal cross-coupling reactions of aryl- and vinyl boronates with α-diazoketones by Barluenga[13] and Wang,[14] we chose to investigate the coupling of allylboronic acid derivatives.

Initially, we attempted a coupling reaction of the readily available cinnamyl boronate[12b,15] **1a** and α-diazoketone **2a** under mild conditions in CH_2Cl_2. The reaction without any catalyst or using Pd-catalyst did not result in any product (Table 1, entries 1−2). However, when we employed CuI or CuTC catalysts, traces of the branched coupling product **3a** were formed (entries 3−4). The major product arose from dimerization of **2a**, affording **4**. Heating the reaction to 50 °C or changing the solvent to toluene did not alter the results (entries 5−6). Application of acid catalysis,[2a,16] which is usually suitable for activation of allyl-Bpin compounds, did not increase the amount of the coupling product **3a** (entries 7−8). Addition of base was not efficient either (entry 9). These studies suggested that cinnamyl-Bpin **1a** is not reactive enough for synthetically useful cross-coupling with diazoketones. Our recent studies indicated that allylboronic acids are much more reactive in allylboration of ketones and imines than allyl-Bpin compounds.[2b,c,12d,e] Therefore, we decided to employ cinnamylboronic acid **1b** instead of **1a** in the cross-coupling reaction (eqs 1−4). When the reaction was performed with cinnamylboronic acid **1b** under the above mild conditions

Table 1. Attempted Coupling of Cinnamyl-Bpin 1a with α-Diazoketone 2a[a]

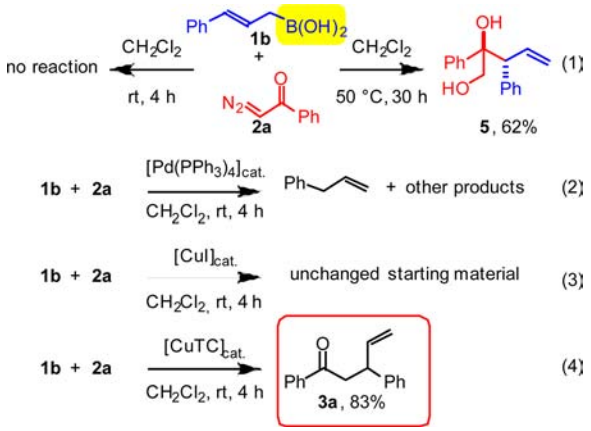


entry	solvent	catalyst	additive	**3a** (%)[b]	**4** (%)[b]
1	CH_2Cl_2	–	–	0	0
2	CH_2Cl_2	$Pd(PP_3)_4$	–	0	0
3	CH_2Cl_2	CuI	–	<5	74
4	CH_2Cl_2	CuTC	–	<5	69
5[c]	CH_2Cl_2	CuTC	–	<5	64
6	toluene	CuTC	–	<5	61
7	CH_2Cl_2	CuTC	$BF_3{\cdot}Et_2O$	<5	24
8	CH_2Cl_2	CuTC	PhCOOH	<5	82
9	CH_2Cl_2	CuTC	NaOMe	<5	0

[a]Unless otherwise stated a mixture of **1a** (0.12 mmol), **2a** (0.1 mmol), catalyst (10 mol %), and the additive (10 mol %) in CH_2Cl_2 (0.5 mL) was stirred at rt for 4 h. [b]The yield was determined by ^{1}H NMR using naphthalene as an internal standard. [c]The reaction was performed at 50 °C.

Received: August 6, 2015
Published: September 16, 2015

DOI: 10.1021/acs.orglett.5b02285
Org. Lett. 2015, 17, 4754−4757



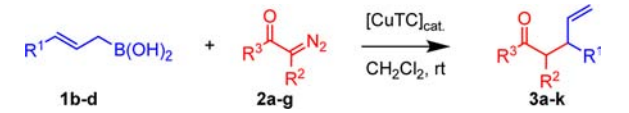
(rt, 4 h in CH_2Cl_2) in the absence of catalyst, no reaction was observed (eq 1). However, at 50 °C we obtained homoallyl alcohol derivative **5**, which was certainly formed by allylboration of the keto group[2b,c] followed by hydrolysis of the terminal diazo functional group by residual water. Using a Pd-catalyst under mild conditions mainly led to protodeborylation of **1b** and formation of several other products, except cross-coupling product **3a** (eq 2). We could not observe any reaction in the presence of CuI (eq 3).

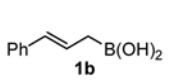
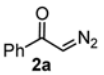
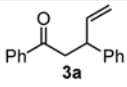
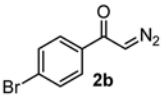
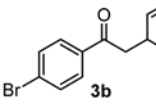
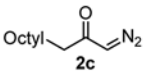
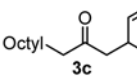
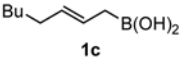
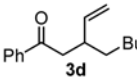
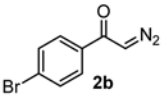
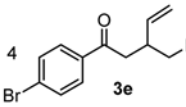
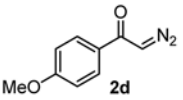
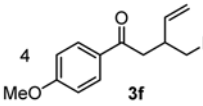
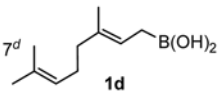
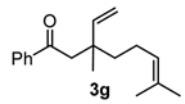
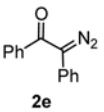
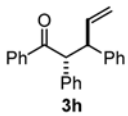
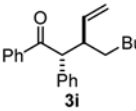
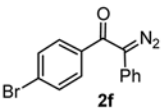
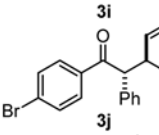
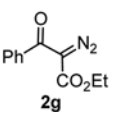
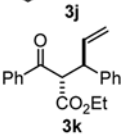
We found that the desired coupling can be achieved with a high yield using cinnamylboronic acid **1b** and α-diazoketone **2a** in the presence of CuTC as a catalyst at room temperature (eq 4). The process is highly regioselective, as only the branched regioisomer **3a** was formed. Thus, the regioslectivity is the same as that in the analogous Suzuki–Miyaura coupling of allylboronic acids[5] and, interestingly, the same as usually found in the reaction of allylboronates with carbonyl compounds[1b,2b,c] and with imines.[12d,e]

The above experiments (Table 1 and eqs 1–4) suggest that allylboronic acids (such as **1b**) are more reactive than allyl-Bpin compounds (such as **1a**) for cross-coupling with α-diazoketones. In the presence of CuTC catalyst, cinnamylboronic acid **1b** reacted under mild conditions without additives and without formation of dimerization product **4**. Thus, in further studies we employed allylboronic acids **1b–d** with various α-diazocarbonyl compounds to explore the synthetic scope of the reaction (Table 2). The functional group tolerance of the reaction is remarkable. Despite the high electrophilicity of the allylboronic acids,[12d,e] the keto group in all products remained unchanged. The reaction proceeds smoothly in the presence of aromatic bromo (**2b**) and methoxy (**2d**) substituents in the diazoketones (entries 2, 5–6). We were able to employ even a diazoketone with an aliphatic substituent (**2c**, entry 3). In this case the reaction was conducted at lower temperature (−20 °C → 0 °C) than the above processes to avoid formation of side products.

The successful cross-coupling of **1b** with **2c**, resulting in **3c**, is a remarkable reaction. This process is both acid sensitive (decomposition of the diazo compound), base sensitive (decomposition of the allylboronic acid and aldol condensation of **2c**), and oxidation sensitive (oxidation of the allylboronic acid). The successful accomplishment of this cross-coupling was probably due to the fact that, with the exception of CuTC, the reaction does not require additives, such as a Lewis base/acid activator and an oxidant for regeneration of the catalyst. Similarly to cinnamylboronic acid **1b**, octyl boronic acid **1c** also reacted with high branched selectivity with α-diazoketones **2a**, **2b**, and **2d** (entries 4–6). The reactions resulted in **3d–f** with high yields without allylation of the keto functional group. Geraniol boronic acid **1d** also reacted readily with **2a**, affording **3g** (entry 7), which is impressive, as this process involves formation of a quaternary center. Formation of the linear isomer (product with α-selectivity, which does not have a quaternary center) could not be observed in the crude reaction mixture.

Table 2. Cross-Coupling of Allylboronic Acids with α-Diazoketones[a]



entry	boronic acid	α-diazoketone	time (h)	product	yield (%)[b]
1	 **1b**	 **2a**	4	 **3a**	83
2	**1b**	 **2b**	4	 **3b**	86
3[c]	**1b**	 **2c**	1	 **3c**	57
4	 **1c**	**2a**	6	 **3d**	87
5	**1c**	 **2b**	4	 **3e**	83
6	**1c**	 **2d**	4	 **3f**	81
7[d]	 **1d**	**2a**	6	 **3g**	34
8[e]	**1b**	 **2e**	2	 **3h**	77 (9.1:1)[f]
9[e,g]	**1c**	**2e**	6.5	 **3i**	65 (3:1)[f]
10[e]	**1b**	 **2f**	2	 **3j**	81 (4:1)[f]
11[h]	**1b**	 **2g**	12	 **3k**	78 (1.2:1)[f]

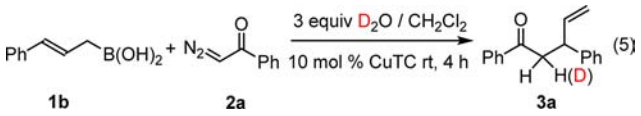
[a]Unless otherwise stated a mixture of **1b–d** (0.12 mmol), **2a–g** (0.1 mmol), and CuTC (10 mol %) was stirred in CH_2Cl_2 (0.5 mL) at rt. [b]Isolated yields. [c]The reaction mixture of **1b** (0.2 mmol), **2c** (0.1 mmol), and CuTC (20 mol %) was stirred at −20 °C for 3 h and then at 0 °C for 1 h at rt. [d]**1d** (0.2 mmol), **2a** (0.1 mmol), and CuTC (10 mol %) were used. [e]The reaction was performed at 0 °C. [f]The ratio of the diastereomers was determined from the crude product by ^{1}H NMR. [g]**1c** (0.05 mmol), **2e** (0.1 mmol), and CuTC (10 mol %) were used. [h]The reaction was performed at 45 °C.

DOI: 10.1021/acs.orglett.5b02285
Org. Lett. 2015, 17, 4754–4757

We have briefly investigated the stereoselectivity of the process using disubstituted diazoketones **2e–g** (entries 8–11). Most of the reactions (entries 8–10) were conducted at 0 °C to increase the diastereoselectivity. The reaction of cinnamylboronic acid **1b** and **2e** proceeded with high diastereoselectivity, as the ratio of the stereoisomers (determined by ^{1}H NMR) was 9:1. The stereoselectivity was assigned on the basis of the published structure[17] of the major diastereomer **3h**. This indicates a trans stereoselectivity for the cross-coupling reaction. The same stereoselectivity was observed for the allylboration of aldehydes,[2a] ketones,[2b,c] and imines[12d] with allylboronic acids. The stereoselectivity of the reaction is lower with **1c** than with cinnamyl boronic acid **1b**, as the ratio of the stereoisomers was 3:1 (entry 9). An obvious explanation is that the pentyl moiety in **1c** exerts a weaker stereoinduction effect than the phenyl group in **1b**. The bromo-analog of **2e** reacted also with trans selectivity with cinnamylboronic acid **1b** (entry 10). However, the diastereoselectivity of the reaction with **2f** was somewhat lower than that with **2e**. α-Keto diazoester **2g** reacted sluggishly with cinnamylboronic acid **1b**. The reaction was very slow at 0 °C or at rt; therefore, the reaction was conducted at an elevated temperature (45 °C). Possibly because of the elevated temperature, the stereoselectivity of the process is poor. Yet, the regioselectivity and the yield of the reaction are high.

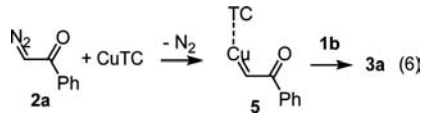
Currently the detailed mechanism of the cross-coupling reaction of allylboronic acids with diazoketones is unclear and requires further investigation and modeling studies. The mechanism is probably very different from the Pd-catalyzed cross-coupling of vinyl- and arylboronic acid with diazo compounds,[14] as the above process (eq 4 and Table 2) does not require an external oxidant, indicating that the process is redox neutral.

In the cross-coupling reaction of **1b** and **2** an additional hydrogen is also added to the product (**3**). We attempted to explore the source of this hydrogen by a deuterium labeling experiment (eq 5). When 3 equiv of D_2O were added to the



reaction mixture of **1b** and **3a** under the usual reaction conditions (Table 2, entry 1), we observed about 20% deuterium uptake at the $COCH_2$ group of **3a** (eq 5). This indicates that the reaction involves a protonation step. The reaction is carried out under dry/inert conditions. Formation of boroxin from **1b** under dry conditions is well documented.[2b] Thus, a possible proton source under the cross-coupling reaction is water produced by the boroxin formation. We could not observe any deuterium uptake, when the solvent was changed from CH_2Cl_2 to CD_2Cl_2 under the usual reaction conditions (Table 2, entry 1).

CuTC has been used as an efficient catalyst in coupling reactions of α-diazoketones. Lacour and co-workers[18] have shown that CuTC is a particularly effective catalyst for decomposition of diazo reagents. It is well established that copper reagents readily form copper carbenes from diazo compounds.[19] Some of the copper carbenes formed in these processes have been isolated and fully characterized.[20] It was shown that α-diazocarbonyl compounds particularly easily undergo copper carbene formation, as the loss of N_2 is facilitated by chelation control.[19,21] Therefore, we suggest that the first step of the cross-coupling is formation of copper carbene (such as **5**) from α-diazoketone (such as **2a**) and CuTC (eq 6). Formation of dimeric product **4** (Table 1) in the nonproductive reactions in the presence of **1a** also suggests an initial Cu-carbene formation.



The reaction may also involve formation of Cu(I)-allyl species before or after the formation of Cu-carbenes. Formation of Cu(I)-allyl species has also been suggested[22] or observed[23] from suitable Cu-sources and metal-allyl reagents. However, the origin of the high branched selectivity of the process is still unclear.

In summary, we have presented the first catalytic cross-coupling of allylboronic species with α-diazoketones. The presented CuTC catalyzed process leads to formation of a new $C(sp^3)–C(sp^3)$ bond with clean γ-selectivity. The reaction exclusively gives the branched allylic isomer, and using geraniol boronic acid, a quaternary carbon center can be selectively formed. The reaction has a remarkable tolerance toward the carbonyl group of the α-diazoketone. Because of the mild, neutral, and nonoxidative reaction conditions, both aromatic and aliphatic diazoketones and allylboronic acids can be employed. The stereoselectivity of the reaction is dependent on the substrates. The reaction of cinnamyl boronic acid **1b** and **2e** proceeds with excellent trans stereoselectivity. The presented reaction will extend the synthetic scope of the application of allylboron species.[10,24] It also provides a new complementary method for $C(sp^3)–C(sp^3)$ bond formation for synthesis of branched homoallyl carbonyl compounds.[25]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02285.

Detailed experimental procedures and compound characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kalman@organ.su.se.

Author Contributions

‡D.W. and M.-C.B. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the financial support of the Swedish Research Council (VR) and the Knut och Alice Wallenbergs Foundation.

■ REFERENCES

(1) (a) Hall, D. G. *Boronic Acids*; Wiley: Weinheim, 2011. (b) Hall, D. G.; Lachance, H. *Allylboration of Carbonyl Compounds*; Wiley: Hoboken, NJ, 2012.

(2) (a) Selander, N.; Kipke, A.; Sebelius, S.; Szabó, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 13723. (b) Raducan, M.; Alam, R.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 13050. (c) Alam, R.; Raducan, M.; Eriksson,

DOI: 10.1021/acs.orglett.5b02285
Org. Lett. 2015, 17, 4754–4757

L.; Szabó, K. J. *Org. Lett.* **2013**, *15*, 2546. (d) Zhao, T. S. N.; Zhao, J.; Szabó, K. J. *Org. Lett.* **2015**, *17*, 2290. (e) Ding, J. Y.; Hall, D. G. *Angew. Chem., Int. Ed.* **2013**, *52*, 8069. (f) Carosi, L.; Hall, D. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5913. (g) Hesse, M.; Essafi, S.; Watson, C.; Harvey, J.; Hirst, D.; Willis, C.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 6145. (h) Chen, J. L. Y.; Scott, H. K.; Hesse, M. J.; Willis, C. L.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2013**, *135*, 5316. (i) Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 560. (j) Böse, D.; Niesobski, P.; Lübcke, M.; Pietruszka, J. *J. Org. Chem.* **2014**, *79*, 4699.

(3) (a) Kobayashi, S.; Mori, Y.; Fossey, J. S.; Salter, M. M. *Chem. Rev.* **2011**, *111*, 2626. (b) Kobayashi, S.; Sugiura, M.; Ogawa, C. *Adv. Synth. Catal.* **2004**, *346*, 1023. (c) Friestad, G. K. *Eur. J. Org. Chem.* **2005**, *2005*, 3157. (d) Wada, R.; Shibuguchi, T.; Makino, S.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 7687. (e) Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2007**, *129*, 15398. (f) Silverio, D. L.; Torker, S.; Pilyugina, T.; Vieira, E. M.; Snapper, M. L.; Haeffner, F.; Hoveyda, A. H. *Nature* **2013**, *494*, 216. (g) Kliman, L. T.; Mlynarski, S. N.; Ferris, G. E.; Morken, J. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 521. (h) Chen, M.; Roush, W. R. *J. Org. Chem.* **2013**, *78*, 3. (i) Nowrouzi, F.; Batey, R. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 892. (j) Dhudshia, B.; Tiburcio, J.; Thadani, A. N. *Chem. Commun.* **2005**, 5551.

(4) (a) Yamamoto, Y.; Takada, S.; Miyaura, N. *Chem. Lett.* **2006**, *35*, 704. (b) Yamamoto, Y.; Takada, S.; Miyaura, N. *Chem. Lett.* **2006**, *35*, 1368.

(5) Sebelius, S.; Olsson, V. J.; Wallner, O. A.; Szabó, K. J. *J. Am. Chem. Soc.* **2006**, *128*, 8150.

(6) (a) Tsuji, J. *Palladium Reagents and Catalysts. New Perspectives for the 21st Century*; Wiley: Chichester, U.K., 2004. (b) Szabó, K. J. *Chem. Soc. Rev.* **2001**, *30*, 136.

(7) Yang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2013**, *135*, 10642.

(8) Farmer, J. L.; Hunter, H. N.; Organ, M. G. *J. Am. Chem. Soc.* **2012**, *134*, 17470.

(9) (a) Glasspoole, B. W.; Ghozati, K.; Moir, J. W.; Crudden, C. M. *Chem. Commun.* **2012**, *48*, 1230. (b) Chausset-Boissarie, L.; Ghozati, K.; LaBine, E.; Chen, J. L. Y.; Aggarwal, V. K.; Crudden, C. M. *Chem. - Eur. J.* **2013**, *19*, 17698.

(10) Brozek, L. A.; Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 16778.

(11) (a) Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978. (b) Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.

(12) (a) Dutheuil, G.; Selander, N.; Szabó, K. J.; Aggarwal, V. K. *Synthesis* **2008**, *2008*, 2293. (b) Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409. (c) Larsson, J. M.; Szabó, K. J. *J. Am. Chem. Soc.* **2013**, *135*, 443. (d) Alam, R.; Das, A.; Huang, G.; Eriksson, L.; Himo, F.; Szabó, K. J. *Chem. Sci.* **2014**, *5*, 2732. (e) Das, A.; Alam, R.; Eriksson, L.; Szabó, K. J. *Org. Lett.* **2014**, *16*, 3808. (f) Zhao, T. S. N.; Yang, Y.; Lessing, T.; Szabó, K. J. *J. Am. Chem. Soc.* **2014**, *136*, 7563.

(13) (a) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486. (b) Barluenga, J.; Tomás-Gamasa, M.; Aznar, F.; Valdés, C. *Nat. Chem.* **2009**, *1*, 494.

(14) (a) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236. (b) Peng, C.; Wang, Y.; Wang, J. *J. Am. Chem. Soc.* **2008**, *130*, 1566. (c) Zhao, X.; Jing, J.; Lu, K.; Zhang, Y.; Wang, J. *Chem. Commun.* **2010**, *46*, 1724. (d) Xia, Y.; Xia, Y.; Liu, Z.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2014**, *79*, 7711.

(15) Zhang, P.; Roundtree, I. A.; Morken, J. P. *Org. Lett.* **2012**, *14*, 1416.

(16) (a) Kennedy, J. W.; Hall, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 11586. (b) Lachance, H.; Lu, X.; Gravel, M.; Hall, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 10160. (c) Elford, T. G.; Arimura, Y.; Yu, S. H.; Hall, D. G. *J. Org. Chem.* **2007**, *72*, 1276.

(17) Ketcham, J. M.; Biannic, B.; Aponick, A. *Chem. Commun.* **2013**, *49*, 4157.

(18) Sharma, A.; Besnard, C.; Guenee, L.; Lacour, J. *Org. Biomol. Chem.* **2012**, *10*, 966.

(19) Kirmse, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1088.

(20) (a) Straub, B. F.; Hofmann, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1288. (b) Hofmann, P.; Shishkov, I. V.; Rominger, F. *Inorg. Chem.* **2008**, *47*, 11755. (c) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085.

(21) Fraile, J. M.; García, J. I.; Martínez-Merino, V.; Mayoral, J. A.; Salvatella, L. *J. Am. Chem. Soc.* **2001**, *123*, 7616.

(22) Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8910.

(23) (a) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H.; Smith, R. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 4404. (b) Russo, V.; Herron, J. R.; Ball, Z. T. *Org. Lett.* **2010**, *12*, 220.

(24) (a) Leonori, D.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 1082. (b) Lu, Z.; Wilsily, A.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8154. (c) Lu, Z.; Fu, G. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 6676. (d) Xu, H.; Zhao, C.; Qian, Q.; Deng, W.; Gong, H. *Chem. Sci.* **2013**, *4*, 4022. (e) Yang, C.-T.; Zhang, Z.-Q.; Liu, Y.-C.; Liu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 3904. (f) Ding, J.; Rybak, T.; Hall, D. G. *Nat. Commun.* **2014**, *5*, 5474.

(25) (a) Krautwald, S.; Sarlah, D.; Schafroth, M. A.; Carreira, E. M. *Science* **2013**, *340*, 1065. (b) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2003**, *125*, 8974.

DOI: 10.1021/acs.orglett.5b02285
Org. Lett. 2015, 17, 4754−4757