Organic LETTERS

Letter

pubs.acs.org/OrgLett

Coumarin to Isocoumarin: One-Pot Synthesis of 3-Substituted Isocoumarins from 4-Hydroxycoumarins and Benzyne Precursors

Kashmiri Neog,[†] Dhiraj Dutta,[†] Babulal Das,[‡] and Pranjal Gogoi*[,†]

[†]Applied Organic Chemistry Group, Chemical Science and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, India

[‡]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

Supporting Information

ABSTRACT: A novel transition-metal-free direct synthesis of 3-substituted isocoumarin from 4-hydroxycoumarin and a benzyne precursor is developed. This synthetic strategy proceeds via C−O and C−C bond cleavage as well as C−O and C−C bond formations in a single reaction vessel by simple treatment with CsF in the absence of catalyst. This methodology affords moderate to good yields of 3-substituted isocoumarins and is tolerant of a variety of functional groups including halide.

Lactones and their derivatives are of growing importance as targets for synthesis, largely because of their presence in numerous compounds of biological interest and their importance as drugs and biological agents.[1] Among them, six-membered lactone derivatives, particularly isocoumarins, represent an important class of naturally occurring lactones that exhibit a wide range of pharmacological properties.[2] In fact, a large number of isocoumarins have been isolated from plant sources and explored for their potential therapeutic applications, which include antifungal,[3] antimicrobial,[4] anticancer,[5] antiallergic,[6] anti-inflammatory,[7] anti-HIV,[8] and anticoagulant[9] activities. Among the variety of substituted isocoumarins, the 3-substituted variants are significant because of their biological activities. Typical examples of such biologically active isocoumarins are shown in Figure 1. Among these, capillarin and artemidin have

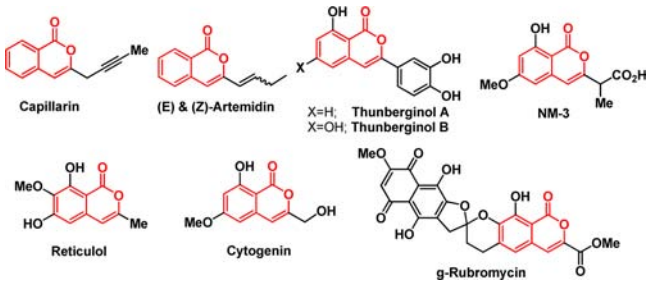


Figure 1. Representative biologically active 3-substituted isocoumarins.

demonstrated potent antifungal activity.[3a,10] Thunberginol A and B are known for their antiallergic and antimicrobial activities.[11] Reticulol and cytogenin are known as antitumor agents.[12] Moreover, synthetic isocoumarin NM-3 is highly effective in the treatment of solid tumors and has entered clinical trials.[13] In addition, γ-rubromycin has been synthesized as a potential drug for inhibition of HIV reverse transcriptase and human telomerase.[14] On the other hand, 3-substituted isocoumarins are also used as intermediates for the synthesis of various natural products, such as canesin, 3-alkylisocoumarin, as well as some alkaloids.[15] The broad spectrum of pharmacological and physiological activities has led to continued interest in the synthesis of 3-substituted isocoumarins. In this regard, various synthetic methods have been developed for the synthesis of these molecules and comprehensively reviewed by Barry in 1964, Napolitano in 1997, and Pal in 2011.[2a,16] The classical methods for the synthesis of these molecules have involved multiple steps and harsh reaction conditions. To overcome these limitations and to achieve structurally diverse isocoumarins, palladium-mediated annulations of 2-alkenyl or 2-allylbenzoic acids have been developed.[17] These methods still suffer from either multistep reactions or the use of toxic organothallium and organonickel reagents. In the late of 20th century, 2-halocarboxylic acid was recognized as a coupling partner using palladium as a catalyst for the synthesis of isocoumarins.[18] Later, this substrate was also used as a starting material for the synthesis of isocoumarins in an improved way with respect to catalyst and reaction conditions.[19] 2-Alkynylcarboxylic acids and their derivatives have also been explored as efficient synthons for the same purpose.[20] In addition to these, anhydride,[21] *o*-allylbenzaldehyde,[22] 2-formylbenzoic acid,[23] 1-(2-halophenyl)-1,3-dione,[24] and 2,3-allenoates[25] have also been reported as important starting materials for the synthesis of isocoumarins. Recently, a C−H activation strategy involving benzoic acids and peresters in the presence of a ruthenium or rhodium catalyst provided atom-economical methods for the synthesis of 3,4-disubstituted isocoumarins.[26] While there are presently a number

Received: January 7, 2017
Published: January 17, 2017

DOI: 10.1021/acs.orglett.7b00027
Org. Lett. 2017, 19, 730−733

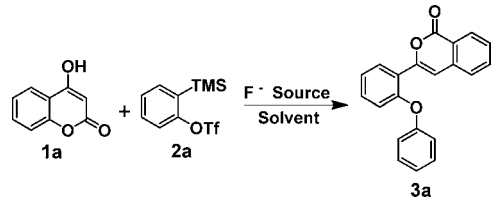
of efficient synthetic procedures to prepare these compounds, there remain several limitations, as well. Thus, most of the reported procedures involve multiple steps, use a transition-metal as catalyst, and require expensive reagents/catalysts and harsh reaction conditions. In view of these limitations, the development of an efficient strategy for the synthesis of 3-substituted isocoumarins is highly desirable.

4-Hydroxycoumarins are very important precursors in the realm of organic synthesis.[27] They not only are significant in synthetic end points but also constitute the structural nucleus of many natural products. They have been used as raw materials for the synthesis of various heterocycles, biologically active molecules, and natural products. On the other hand, arynes have been successfully used as versatile reactive intermediates for the synthesis of various synthetic compounds and natural products.[28] Recently, these reactive intermediates have been extensively used for the atom-economic synthesis of valuable products as they avoid transition metals and harsh reaction conditions.[29] Kobayashi and his group have used arynes as coupling partners for the synthesis of 3-substituted isocoumarins.[30] However, use of a NHC−copper complex and formation of phthalides as side products demerits the method. In continuation of our research on 4-hydroxycoumarin and aryne chemistry for the synthesis of fused pyridines and coumestans,[31] we envisaged here a transition-metal-free synthesis of 3-substituted isocoumarins from 4-hydroxycoumarins and arynes.

To achieve this challenging transformation, we optimized our reaction conditions employing 4-hydroxycoumarin **1a** and benzyne precursor **2a** as the model substrates to examine the reaction. Our investigation began with the reaction of compounds **1a** (1 mmol) and **2a** (2.5 mmol) in the presence of CsF (3 mmol) as the fluoride source in acetonitrile at room temperature. Under these reaction conditions, the desired product **3a** was obtained in 39% yield after 24 h stirring. Interestingly, when the reaction temperature was increased to 80 °C, product **3a** was obtained in 77% yield (Table 1, entry 2). In addition, when 18-crown-6 was used as an additive, the yield of our reaction improved under the same reaction conditions, but it gave almost an identical result (Table 1, entries 4 and 7). As shown in Table 1, several other fluoride sources such as KF and TBAF were also examined for our reaction (Table 1, entries 5 and 8). However, they afforded a low yield of product **3a**. The effect of solvent was also investigated. The use of THF as the reaction medium gave a trace (~10%) amount of product **3a** under the same reaction conditions. On the other hand, desired product **3a** was not observed when DCE, dioxane, and DMF were used as solvents (Table 1, entries 10−12). As a control experiment, the reaction was performed in the absence of fluoride source, and no desired product **3a** was observed (Table 1, entry 13). Product **3a** was initially characterized by NMR, and finally the constitution and configuration of the product was confirmed by X-ray crystal structure analysis (see Supporting Information).

After the optimization process for the reaction conditions, various 3-substituted isocoumarins were synthesized and are presented in Table 2. As shown in Table 2, *o*-silyl aryl triflate **2a** was treated with a variety of 4-hydroxycoumarins bearing fluoro, chloro, bromo, methyl, and methoxy substituents, leading to our desired 3-substituted isocoumarins in moderate to good yields (Table 2; **3a**−**3j**). Both electron-rich and electron-deficient 4-hydroxycoumarins efficiently participated in our one-pot reaction with benzyne precursors, and the desired products (**3b**−**3j**) were obtained in good yields. It is noteworthy that some

Table 1. Optimization Studies[a]



entry	solvent	F^- source	additive (1 mmol)	temp (°C)	yield **3a** (%)[b]
1	CH_3CN	CsF		rt	39
2	CH_3CN	CsF		80	77
3	CH_3CN	CsF		80	29[c]
4	CH_3CN	CsF	18-crown-6	80	75
5	CH_3CN	KF		80	27
6	CH_3CN	KF	18-crown-6	80	30
7	THF	KF	18-crown-6	60	69
8	CH_3CN	TBAF		80	32
9	THF	CsF		60	trace
10	DCE	CsF		80	ND
11	dioxane	CsF		80	ND
12	DMF	CsF		80	ND
13	CH_3CN			80	ND

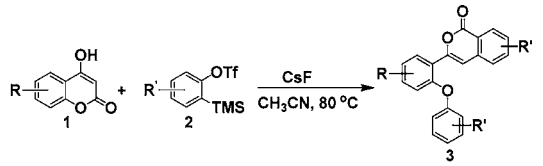
[a]Conditions: 4-Hydroxycoumarin (1.0 mmol), *o*-silyl aryl triflate (2.5 mmol), fluoride source (3 mmol); solvent (7 mL) stirred at 80 °C. [b]Isolated yield. ND: Not detected. [c]*o*-Silyl aryl triflate (1 mmol), fluoride source (1.5 mmol).

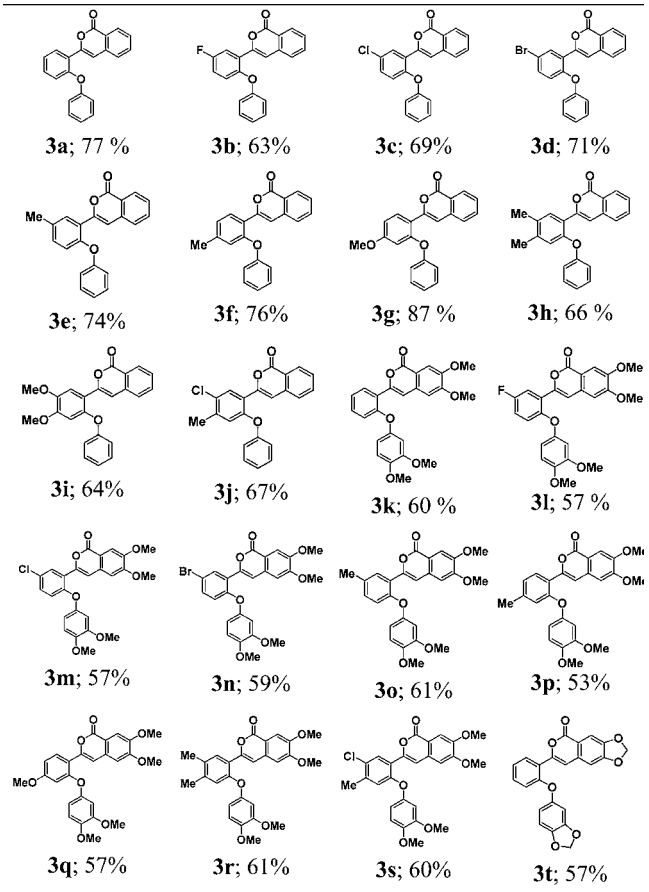
sensitive functional groups, like chloro and bromo, were compatible with the reaction conditions, which could be used for further functionalization of our synthesized 3-substituted isocoumarins (Table 2; **3c**, **3d**, **3j**, **3m**, **3n**, and **3s**). Moreover, 6,7-disubstituted 4-hydroxycoumarins also smoothly participated in our reaction, leading to the expected products **3h**, **3i**, and **3j** in good yields. Other symmetrical silyl triflates such as 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2b** and 5-(trimethylsilyl)benzo[*d*][1,3]dioxol-6-yl trifluoromethanesulfonate **2c**[32] were also examined as benzyne precursors for our one-pot strategy. In this regard, silyl triflate **2b** was treated with a variety of 4-hydroxycoumarins for the synthesis of various 3-substituted isocoumarins in moderate yields with excellent regioselectivity (Table 2; **3k**−**3s**). Silyl triflate **2c** was also treated with 4-hydroxycoumarin for the synthesis of isocoumarin **3t** in good yield.

Silyl triflates with symmetrical substituents afforded yields of isocoumarins relatively lower than those of unsubstituted silyl triflate. Additionally, unsymmetrical benzyne precursor (i.e., 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d**) was also used for the synthesis of various isocoumarins. Benzyne precursor **2d** was treated with 4-hydroxycoumarin and 7-chloro-4-hydroxycoumarin to provide 3-substituted isocoumarins **3ux** and **3vx**, respectively, as complex mixtures of their regioisomers under the optimized reaction conditions (Scheme 1). The regioisomers are not separated, and they are represented as mixtures (see Supporting Information). Unsymmetrical benzyne precursor 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2e** was also used for the synthesis of isocoumarin. Under the optimized reaction conditions, benzyne precursor **2e** was treated with 7-bromo-4-hydroxycoumarin, and the desired isocoumarin **3w** was obtained in 22% yield with excellent regioselectivity (Scheme 2).

DOI: 10.1021/acs.orglett.7b00027
Org. Lett. 2017, 19, 730−733

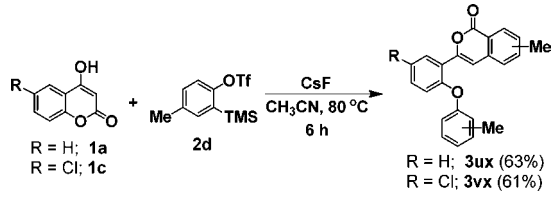
Table 2. One-Pot Synthesis of Isocoumarins from 4-Hydroxycoumarins and Benzyne Precursors[a]



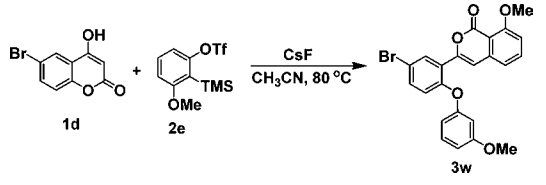


[a]Conditions: 4-Hydroxycoumarin (1.0 mmol), *o*-silyl aryl triflate (2.5 mmol), CsF (3 mmol), CH_3CN (7 mL) stirred at 80 °C for 6 h.

Scheme 1. Synthesis of Isocoumarins from Unsymmetrical Benzyne Precursors 2d

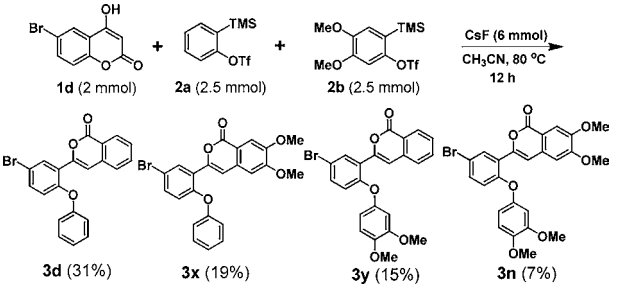


Scheme 2. Synthesis of Isocoumarin 3w from Unsymmetrical Benzyne Precursors 2e



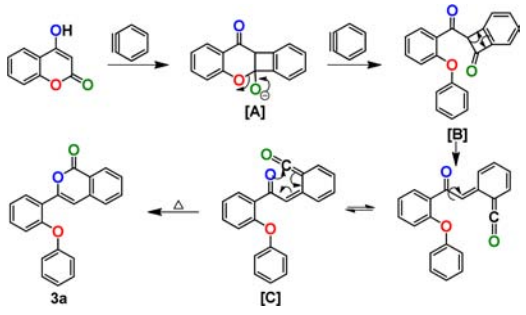
To further explore our synthetic strategy, two different benzyne precursors were used in a single transformation. In this protocol, 7-bromo-4-hydroxycoumarin **1d** (2 mmol) was treated with benzyne precursors **2a** (2.5 mmol) and **2b** (2.5 mmol) in the presence of CsF (6 mmol) in acetonitrile at 80 °C. The desired isocoumarins, **3d** and **3n**, along with two other hybrid isocoumarins, **3x** and **3y**, were also obtained in a single transformation (Scheme 3).

Scheme 3. One-Pot Synthesis of Isocoumarins Using Two Different Benzyne Precursors



A plausible reaction mechanism for the synthesis of isocoumarin is shown in Scheme 4, based on our experiments

Scheme 4. Plausible Reaction Mechanism for the Synthesis of Isocoumarin



and reported mechanisms.[24,33] We assume that in the presence of CsF, 4-hydroxycoumarin reacts with two molecules of benzyne, which leads to the four-membered ring intermediate **B** via anion intermediate **A**. Intermediate **B** undergoes rapid rearrangement to the corresponding ketene intermediate **C**,[24] which might be due to ring strain. Finally, the ketene intermediate **C** undergoes ring closure to the desired six-membered isocoumarin **3a**.

In summary, we have developed a novel transition-metal-free synthetic protocol for the direct synthesis of 3-substituted isocoumarins from 4-hydroxycoumarins by simple treatment with CsF. A series of isocoumarins have been synthesized using this one-pot synthetic strategy in good yields with excellent functional group tolerance that includes halide. One of the isocoumarin structures has been unambiguously established by single-crystal XRD study. Importantly, this reaction strategy was accomplished through C−O and C−C bond cleavage as well as new C−O and C−C bond formations in a single reaction vessel. This efficient and convenient strategy opens a new avenue for the rapid synthesis of 3-substituted isocoumarins from readily available materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00027.

DOI: 10.1021/acs.orglett.7b00027
Org. Lett. 2017, 19, 730−733

Experimental details, characterization data, copies of NMR spectra, and single-crystal X-ray analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: gogoipranj@yahoo.co.uk.

ORCID

Pranjal Gogoi: 0000-0003-0711-0328

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the CSIR, New Delhi, for financial support under CSIR-ORIGIN (CSC-0108) project. We are grateful to the Director, CSIR-NEIST, Jorhat, India, for the interest in this work.

REFERENCES

(1) (a) Janecki, T. *Natural Lactones and Lactams: Synthesis, Occurrence and Biological Activity*; Wiley-VCH: Weinheim, Germany, 2013. (b) Horikawa, M.; Inai, M.; Oguri, Y.; Kuroda, E.; Tanaka, M.; Suzuki, S.; Ito, T.; Takahashi, S.; Kaku, H.; Tsunoda, T. *J. Nat. Prod.* **2014**, *77*, 2459.

(2) (a) Barry, R. D. *Chem. Rev.* **1964**, *64*, 229. (b) Hill, R. A. *Progress in the Chemistry of Organic Natural Products*; Springer: Berlin, 1986; Vol. *49*, pp 1−78.

(3) (a) Engelmeier, D.; Hadacek, F.; Hofer, O.; Lutz-Kutschera, G.; Nagl, M.; Wurz, G.; Greger, H. *J. Nat. Prod.* **2004**, *67*, 19. (b) Rukachaisirikul, V.; Rodglin, A.; Sukpondma, Y.; Phongpaichit, S.; Buatong, J.; Sakayaroj, J. *J. Nat. Prod.* **2012**, *75*, 853.

(4) (a) Yoshikawa, M.; Harada, E.; Naitoh, Y.; Inoue, K.; Matsuda, H.; Shimoda, H.; Yamahara, J.; Murakami, N. *Chem. Pharm. Bull.* **1994**, *42*, 2225. (b) Kornsakulkarn, J.; Thongpanchang, C.; Lapanun, S.; Srichomthong, K. *J. Nat. Prod.* **2009**, *72*, 1341.

(5) (a) Kawano, T.; Agata, N.; Kharbanda, S.; Avigan, D.; Kufe, D. *Cancer Chemother. Pharmacol.* **2007**, *59*, 329. (b) Riveiro, M. E.; Moglioni, A.; Vazquez, R.; Gomez, N.; Facorro, G.; Piehl, L.; De Celis, E. R.; Shayo, C.; Davio, C. *Bioorg. Med. Chem.* **2008**, *16*, 2665.

(6) Yoshikawa, M.; Harada, E.; Naitoh, Y.; Inoue, K.; Matsuda, H.; Shimoda, H.; Yamahara, J.; Murakami, N. *Chem. Pharm. Bull.* **1994**, *42*, 2225.

(7) Furuta, T.; Fukuyama, Y.; Asakawa, Y. *Phytochemistry* **1986**, *25*, 517.

(8) (a) Shikishima, Y.; Takaishi, Y.; Honda, G.; Ito, M.; Takeda, Y.; Kodzhimatov, O. K.; Ashurmetov, O.; Lee, K. H. *Chem. Pharm. Bull.* **2001**, *49*, 877. (b) Goldman, M. E.; Salituro, G. S.; Bowen, J. A.; Williamson, J. M.; Zink, L.; Schleif, W. A.; Emini, E. A. *Mol. Pharmacol.* **1990**, *38*, 20.

(9) Gage, B. F. *Hematology* **2006**, *2006*, 467.

(10) Meepagala, K. M.; Sturtz, G.; Wedge, D. E. *J. Agric. Food Chem.* **2002**, *50*, 6989.

(11) (a) Kurume, A.; Kamata, Y.; Yamashita, M.; Wang, Q.; Matsuda, H.; Yoshikawa, M.; Kawasaki, I.; Ohta, S. *Chem. Pharm. Bull.* **2008**, *56*, 1264. (b) Matsuda, H.; Wang, Q.; Matsuhira, K.; Nakamura, S.; Yuan, D.; Yoshikawa, M. *Phytomedicine* **2008**, *15*, 177. (c) Yoshikawa, M.; Harada, E.; Naitoh, Y.; Inoue, K.; Matsuda, H.; Shimoda, H.; Yamahara, J.; Murakami, N. *Chem. Pharm. Bull.* **1994**, *42*, 2225.

(12) Lim, D.-S.; Kwak, Y.-S.; Kim, J.-H.; Ko, S.-H.; Yoon, W.- H.; Kim, C.-H. *Chemotherapy* **2003**, *49*, 146.

(13) (a) Kawano, T.; Agata, N.; Kharbanda, S.; Avigan, D.; Kufe, D. *Cancer Chemother. Pharmacol.* **2007**, *59*, 329. (b) Agata, N.; Nogi, H.; Milhollen, M.; Kharbanda, S.; Kufe, D. *Cancer Res.* **2004**, *64*, 8512.

(14) Rathwell, D. C. K.; Yang, S.-H.; Tsang, K. Y.; Brimble, M. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 7996.

(15) (a) Hauser, F. M.; Rhee, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 4533. (b) Barber, J.; Carter, R. H.; Garson, R. J.; Staunton, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2577. (c) Jones, J. B.; Pinder, A. R. *J. Chem. Soc.* **1958**, 2612. (d) Cai, S.; Wang, F.; Xi, C. *J. Org. Chem.* **2012**, *77*, 2331.

(16) (a) Napolitano, E. *Org. Prep. Proced. Int.* **1997**, *29*, 631. (b) Pal, S.; Chatare, V.; Pal, M. *Curr. Org. Chem.* **2011**, *15*, 782.

(17) (a) Larock, R. C.; Yum, E. K.; Doty, M. J.; Sham, K. K. C. *J. Org. Chem.* **1995**, *60*, 3270. (b) Larock, R. C.; Varaprath, S.; Lau, H. H.; Fellows, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 5274. (c) Korte, D. E.; Hegedus, L. S.; Wirth, R. K. *J. Org. Chem.* **1977**, *42*, 1329.

(18) (a) Cherry, K.; Parrain, J.-L.; Thibonnet, J.; Duchene, A.; Abarbri, M. *J. Org. Chem.* **2005**, *70*, 6669. (b) Subramanian, V.; Batchu, V. R.; Barange, D.; Pal, M. *J. Org. Chem.* **2005**, *70*, 4778. (c) Roy, S.; Roy, S.; Neuenswander, B.; Hill, D.; Larock, R. C. *J. Comb. Chem.* **2009**, *11*, 1128 and refs cited therein.

(19) (a) Guo, X.-X. *J. Org. Chem.* **2013**, *78*, 1660. (b) Cai, S.; Wang, F.; Xi, C. *J. Org. Chem.* **2012**, *77*, 2331.

(20) (a) Yao, T.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 5936. (b) Kavala, V.; Wang, C.-C.; Barange, D. K.; Kuo, C. − W.; Lei, P. − M.; Yao, C. − F. *J. Org. Chem.* **2012**, *77*, 5022. (c) Speranca, A.; Godoi, B.; Pinton, S.; Back, D. F.; Menezes, P. H.; Zeni, G. *J. Org. Chem.* **2011**, *76*, 6789. (d) Uchiyama, M.; Ozawa, H.; Takuma, K.; Matsumoto, Y.; Yonehara, M.; Hiroya, K.; Sakamoto, T. *Org. Lett.* **2006**, *8*, 5517.

(21) (a) Kajita, Y.; Kurahashi, T.; Matsubara, S. *J. Am. Chem. Soc.* **2008**, *130*, 17226. (b) Xie, H.; Sun, Q.; Ren, G.; Cao, Z. *J. Org. Chem.* **2014**, *79*, 11911.

(22) Chen, P. − Y.; Huang, K. − S.; Tsai, C. − C.; Wang, T. − P.; Wang, E. − C. *Org. Lett.* **2012**, *14*, 4930.

(23) Faggi, C.; Garcia-Valverde, M.; Marcaccini, S.; Menchi, G. *Org. Lett.* **2010**, *12*, 788.

(24) Ge, Z. − Y.; Fei, X. − D.; Tang, T.; Zhu, Y. − M.; Shen, J. − K. *J. Org. Chem.* **2012**, *77*, 5736.

(25) Chen, B.; Ma, S. *Org. Lett.* **2013**, *15*, 3884.

(26) (a) Ackermann, L.; Pospech, J.; Graczyk, K.; Rauch, K. *Org. Lett.* **2012**, *14*, 930. (b) Mo, J.; Wang, L.; Cui, X. *Org. Lett.* **2015**, *17*, 4960. (c) Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362. (d) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2007**, *9*, 1407.

(27) (a) Eisenhauer, H. R.; Link, K. P. *J. Am. Chem. Soc.* **1953**, *75*, 2046. (b) Wolf, F. F.; Klare, H.; Goldfuss, B. *J. Org. Chem.* **2016**, *81*, 1762. (c) Lin, Y.; Shen, X.; Yuan, Q.; Yan, Y. *Nat. Commun.* **2013**, *4*, 3603.

(28) (a) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* **2012**, *41*, 3140. (b) Tadross, P. M.; Stoltz, B. M. *Chem. Rev.* **2012**, *112*, 3550 and refs cited therein.

(29) (a) Bhojgude, S. S.; Roy, T.; Gonnade, R. G.; Biju, A. T. *Org. Lett.* **2016**, *18*, 5424. (b) Roy, T.; Thangaraj, M.; Kaicharla, T.; Kamath, R. V.; Gonnade, R. G.; Biju, A. T. *Org. Lett.* **2016**, *18*, 5428. (c) Zhang, J.; Chen, Z.-X.; Du, T.; Li, B.; Gu, Y.; Tian, S.-K. *Org. Lett.* **2016**, *18*, 4872. (d) Reddy, R. S.; Lagishetti, C.; Chen, S.; Kiran, I. N. C.; He, Y. *Org. Lett.* **2016**, *18*, 4546. (e) Shu, W.-M.; Zheng, K.-L.; Ma, J.-R.; Wu, A.-X. *Org. Lett.* **2016**, *18*, 3762.

(30) Yoo, W.-J.; Nguyen, T. V. Q.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 10213.

(31) (a) Goswami, L.; Gogoi, S.; Gogoi, J.; Boruah, R. K.; Boruah, R. C.; Gogoi, P. *ACS Comb. Sci.* **2016**, *18*, 253. (b) Neog, K.; Borah, A.; Gogoi, P. *J. Org. Chem.* **2016**, *81*, 11971.

(32) Ueta, Y.; Mikami, K.; Ito, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 7525.

(33) Tambar, U.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 5340.

DOI: 10.1021/acs.orglett.7b00027
Org. Lett. 2017, 19, 730−733