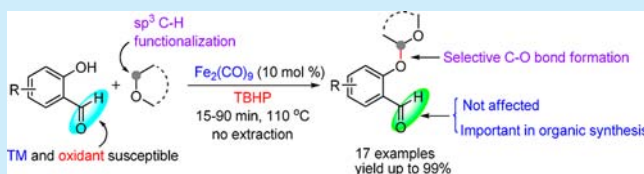


Iron-Catalyzed Oxidative Direct  $\alpha$ -C–H Bond Functionalization of Cyclic Ethers: Selective C–O Bond Formation in the Presence of a Labile Aldehyde GroupBalaji D. Barve,<sup>†,‡</sup> Yang-Chang Wu,<sup>†,§</sup> Mohamed El-Shazly,<sup>†,||</sup> Michal Korinek,<sup>†</sup> Yuan-Bin Cheng,<sup>†</sup> Jeh-Jeng Wang,<sup>\*,‡</sup> and Fang-Rong Chang<sup>\*,†,⊥</sup><sup>†</sup>Graduate Institute of Natural Products, College of Pharmacy, Kaohsiung Medical University, Kaohsiung 807, Taiwan<sup>‡</sup>Department of Medicinal and Applied Chemistry, College of Life Sciences, Kaohsiung Medical University, Kaohsiung 807, Taiwan<sup>§</sup>School of Pharmacy, College of Pharmacy, China Medical University, Taichung 404, Taiwan<sup>||</sup>Department of Pharmacognosy and Natural Products Chemistry, Faculty of Pharmacy, Ain-Shams University, Organization of African Unity Street 11566, Abassia, Cairo, Egypt<sup>⊥</sup>Translational Research Center and Cancer Center, Kaohsiung Medical University Hospital, Kaohsiung 807, Taiwan

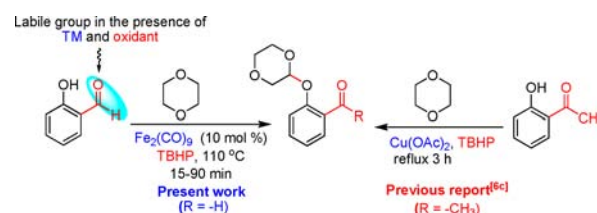
## S Supporting Information

**ABSTRACT:** Iron catalyzed oxidative coupling of salicylaldehydes with cyclic ethers proceeded through the direct  $\alpha$ -C–H functionalization of ethers, forming the corresponding acetals in moderate to excellent yields. This is the first example of iron catalyzed selective C–O bond formation in the presence of a sensitive aldehyde moiety.



Metal catalyzed coupling reactions have become an important tool in organic chemistry for carbon–carbon and carbon–heteroatom bond formation.<sup>1</sup> Pharmaceutical drugs and complex natural products were successfully synthesized utilizing these reactions.<sup>2</sup> Due to the abundant existence of C–H bonds in organic molecules, the functionalization of these stable bonds is always a stimulating task. Metal catalyzed direct C–H bond activation/functionalization has emerged as a useful strategy to tackle this task.<sup>2a,b,3</sup> Transition metal catalyzed direct  $\alpha$ -C(sp<sup>3</sup>)–H bond functionalization of ethers is one such reaction which has recently attracted more attention.<sup>4</sup>

In the past few years, different Cross-Dehydrogenative-Coupling (CDC) reactions were employed for the formation of C–C bonds via  $\alpha$ -C–H bond functionalization of heteroatoms.<sup>5</sup> However, reports on the formation of the C–O bond via  $\alpha$ -C–H bond activation/functionalization of ethers are scarce.<sup>6</sup> In a recent successful attempt, Reddy et al. reported a copper catalyzed construction of the C–O bond through reacting  $\beta$ -ketoesters or 2-keto-substituted phenols with ethers.<sup>6c</sup> The Phan group investigated the use of a heterogeneous copper catalyst in promoting the reaction between ethers and 2-carbonyl-substituted phenols.<sup>6a</sup> The 2-keto-substituted phenols (ketone group) used in these protocols are known to be more stable in the presence of an oxidant and a transition metal (TM) compared with the labile 2-formyl-substituted phenols (aldehyde group). Therefore the selective C–O bond formation in the presence of an *ortho*-formyl group under oxidative conditions is still a challenging goal (Scheme 1).

Scheme 1. Reported Method for C–O Bond Formation via  $\alpha$ -C–H Bond Functionalization of Ethers

Free intact formyl functionality can be easily converted to various functional groups and holds enormous potential applications in organic synthesis.<sup>7</sup> Just recently the Patel group reported an efficient protocol for copper catalyzed *O*-arylation of phenols under oxidative conditions without affecting the formyl moiety.<sup>8</sup>

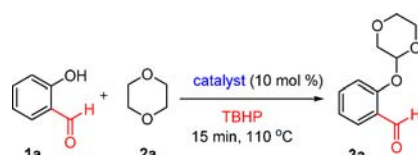
Inspired by the unique approaches of Reddy, Phan, and Patel along with our continuing efforts to explore new avenues in metal catalyzed reactions,<sup>9</sup> we report here a novel iron catalyzed direct  $\alpha$ -C–H bond functionalization of ethers for the formation of C–O bonds under oxidative conditions while selectively saving the labile formyl functionality.<sup>10</sup> According to our knowledge this is the first report on iron catalyzed formation of a C–O bond via  $\alpha$ -C–H bond functionalization of cyclic ethers.<sup>10</sup>

Iron catalysts play an important role in organic synthesis because they are relatively safe, inexpensive, stable, and less

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hazardous to the environment when compared to other transition metal catalysts.<sup>4a,c,d,5e,10</sup> Recently, pioneering work by Zhiping Li successfully demonstrated the applications of iron catalysts in several cross dehydrogenative coupling reactions including phenolic substrates.<sup>10a,d</sup> We started our investigation through checking the reaction between salicylaldehyde (**1a**), *tert*-butyl hydroperoxide (TBHP, 70 wt % in water, 6.0 equiv), and 1,4-dioxane (**2a**) in the presence of iron oxide (10 mol %). Based on previous reports we assumed that the formyl moiety in **1a** will be oxidized or may undergo subsequent reactions.<sup>11,12</sup> However, the reaction did not proceed (Table 1, entry 1). Fortunately, we tested another


Table 1. Catalyst Optimization<sup>a</sup>


entry	catalyst	yield (%) <sup>b</sup>
1	Fe <sub>2</sub> O <sub>3</sub>	NR <sup>c</sup>
2	FeBr <sub>2</sub>	42 <sup>d</sup>
3	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	NR
4	FeCl <sub>3</sub>	ND <sup>d,e</sup>
5	Fe(powder)	NR
6	FeCl <sub>3</sub> ·6H <sub>2</sub> O	ND <sup>d</sup>
7	Fe <sub>2</sub> (CO) <sub>9</sub>	69
8	FeSO <sub>4</sub> ·7H <sub>2</sub> O	NR
9	Fe(acac) <sub>3</sub>	40 <sup>d</sup>
10	—	NR

<sup>a</sup>Reaction conditions: **1a** (1.0 equiv), 1,4-dioxane (2 mL), catalyst (10 mol %), TBHP (70 wt % in water, 6.0 equiv), 110 °C, 15 min. <sup>b</sup>Isolated yields. <sup>c</sup>No reaction. <sup>d</sup>Trace amount of salicylic acid was formed. <sup>e</sup>Not detected.

iron salt and the target acetal was formed in the presence of FeBr<sub>2</sub> in a moderate yield along with traces of salicylic acid (Table 1, entry 2).

Encouraged by these results, we screened different iron catalysts aiming to improve the reaction yield (Table 1). In the presence of FeCl<sub>3</sub> or FeCl<sub>3</sub>·6H<sub>2</sub>O, traces of salicylic acid were detected (Table 1, entries 4, 6). Gratifyingly, the use of Fe<sub>2</sub>(CO)<sub>9</sub> as a catalyst offered the target acetal in 69% yield (Table 1, entry 7), making it the most optimum catalyst which was utilized for further investigation. Due to the reported sensitivity of the aldehyde group toward different oxidants, we also screened several oxidants to check the reaction outcome (Table 2).<sup>11</sup> The use of aqueous TBHP (70 wt % in water, 6.0 equiv) as an oxidant resulted in the formation of 69% of the target product (Table 2, entry 13). Replacing the aqueous TBHP with TBHP in decane (5–6 M) resulted in a significant increase in the product yield (85%) (Table 2, entry 14). We also evaluated the effect of temperature, catalyst loading, oxidant equivalent, and solvent type on the reaction yield. Running the reaction at lower temperature, lowering the catalyst loading, or decreasing the oxidant equivalent resulted in a lower reaction yield (<65%). Different solvents such as water<sup>11b,12a</sup> and 1,1,2-trichloroethane<sup>11c</sup> in 1:1 ratio (with 1,4-dioxane) did not provide the product, while in the presence of acetonitrile<sup>11e–g</sup> and methanol<sup>11j</sup> (with 1,4-dioxane) the target product was formed in lower yields (<40%) along with traces of salicylic acid. The reaction did not proceed without a metal

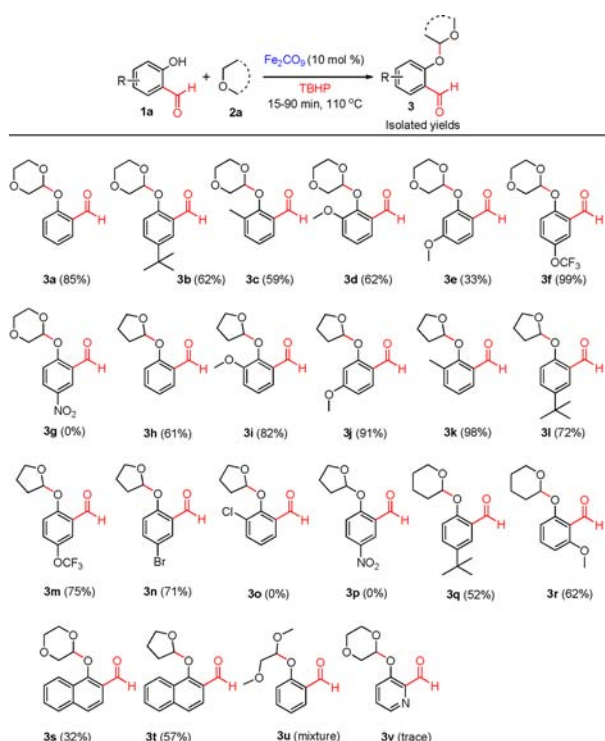
Table 2. Oxidant Optimization<sup>a</sup>


entry	oxidant	yield (%) <sup>b</sup>
1	—	NR <sup>c</sup>
2	DDQ	NR
3	PIFA	ND <sup>d,e</sup>
4	NaIO <sub>4</sub>	NR
6	H <sub>2</sub> O <sub>2</sub>	trace
7	benzoquinone	trace
8	Mg(ClO <sub>4</sub> ) <sub>2</sub>	NR <sup>e</sup>
9	Oxone	NR <sup>e</sup>
10	MnO <sub>2</sub>	NR
11	MCPBA	NR
12	di- <i>tert</i> -butyl peroxide	20%
13	TBHP (H <sub>2</sub> O)	69%
14	TBHP (decane)	86%
15	<i>m</i> -CPBA	NR
16	sodium chlorite	NR

<sup>a</sup>Reaction conditions: **1a** (1.0 equiv), 1,4-dioxane (2.0 mL), Fe<sub>2</sub>(CO)<sub>9</sub> (10 mol %), oxidant (6.0 equiv), 110 °C, 15 min. <sup>b</sup>Isolated yields. <sup>c</sup>No reaction. <sup>d</sup>Not detected. <sup>e</sup>3.0 equiv of oxidant were used.

catalyst or an oxidant suggesting their crucial importance for this type of transformation (Table 1, entry 10; Table 2, entry 1).

The aforementioned optimization results suggested that the highest yield of the target acetal (**3a**) (85%) can be obtained by reacting **1a** with 1,4-dioxane (**2a**) using Fe<sub>2</sub>(CO)<sub>9</sub> (10 mol %) as the catalyst and TBHP (6.0 equiv, 5–6 M in decane) as the oxidant at 110 °C for 15 min. With the optimized conditions in hand, we next explored the substrate scope of this reaction using several ethers and different substituted salicylaldehydes (Scheme 2). The reaction of salicylaldehydes carrying electron-donating groups with 1,4-dioxane offered the desired acetals in good yields (Scheme 2, **3b–3d**). However, 4-methoxy substituted salicylaldehyde yielded the corresponding acetal in a lower yield (Scheme 2, **3e**). Salicylaldehydes with electron-withdrawing groups such as –OCF<sub>3</sub> reacted smoothly forming the target product in an excellent yield (Scheme 2, **3f**). But this protocol failed to deliver the corresponding acetal when the 5-nitro-salicylaldehyde was used as the starting material (Scheme 2, **3g**). Interestingly, the reaction of tetrahydrofuran (THF) with different salicylaldehydes carrying electron-donating and -withdrawing as well as bromo groups provided the corresponding acetals in good to excellent yields (Scheme 2, **3h–3n**). However, salicylaldehydes with 3-chloro or 5-nitro substituents did not react with THF (Scheme 2, **3o** and **3p**). This result may be due to the presence of electron-withdrawing groups (NO<sub>2</sub> and Cl) at meta position to the formyl group reducing its ability to form a complex with Fe. Moreover, the six-membered cyclic ether, tetrahydropyran, reacted smoothly rendering the target acetals in good yields (Scheme 2, **3q** and **3r**). The developed methodology proved useful with other aromatic aldehydes such as naphthaldehydes which furnished the corresponding products in moderate to good yields (Scheme 2, **3s** and **3t**). Unfortunately, the protocol was not applicable to aliphatic ethers forming a complex mixture (**3u**), which may be attributed to the competitive reaction between

Scheme 2. Substrate Scope for the  $\alpha$ -C–H Bond Functionalization of Ethers<sup>a</sup>

<sup>a</sup>Reaction conditions: **1** (1.0 equiv), ether (2.0 mL),  $\text{Fe}_2(\text{CO})_9$  (10 mol %), TBHP (6.0 equiv 5–6 M, in decane), 110 °C, 15–90 min.

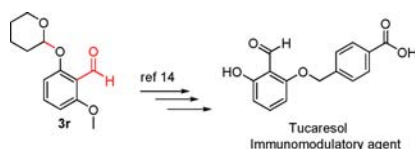
the terminal methyl and the internal methylene groups. Also heterocyclic aldehydes such as 3-hydroxy-2-pyridinecarbaldehyde provided traces of the target product (**3v**).

Notably in all successful substrates, the use of an oxidant and a transition metal led to the selective formation of a C–O bond without affecting the sensitive formyl moiety. Moreover, no further extraction (workup) was required for product purification. This protocol also offers an efficient and alternative route for the protection of the phenolic hydroxyl group as an acetal by overcoming several drawbacks of known protection methods.<sup>13</sup>

Using this methodology we successfully synthesized an important pharmaceutical intermediate (**3r**) in a single step by avoiding the tedious protocols which utilize resorcinol as the starting material.<sup>14</sup> This compound is the intermediate in the preparation of the immunomodulatory drug, tucaresol, and its related analogues.<sup>14</sup> Thus, the developed protocol represents an attractive and alternative route for the preparation of an important intermediate in tucaresol synthesis (Scheme 3).

The reaction mechanism was investigated by running different control experiments. Simple phenol did not react with 1,4-dioxane suggesting the crucial importance of the *ortho*-formyl group. The addition of a radical scavenger such as

Scheme 3. Potential Application of Methodology



TEMPO to the reaction medium prevented any product formation suggesting a radical pathway. It is proposed that the salicylaldehyde may form a coordination complex with iron.<sup>10,15b</sup> This complex can react with the dioxane radical (formed following H-abstraction by a *tert*-butoxyl radical of TBHP)<sup>4a,5b,6d,15a</sup> furnishing the corresponding acetal.

In summary, we developed a simple, efficient, and novel iron catalyzed protocol for selective C–O bond formation without affecting the sensitive aldehyde group in the presence of a transition metal and an oxidant. This approach can be used for the selective protection of hydroxyl groups by ethers. Importantly, the products with intact aldehyde groups can be utilized in several organic transformations. Further studies to reveal the reaction mechanism and extend the applications of this methodology are currently underway in our laboratory.

## ■ ASSOCIATED CONTENT

### § Supporting Information

Experimental procedure, characterization data of new products, <sup>1</sup>H and <sup>13</sup>C NMR copies of all the compounds are available in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [aaronfrc@kmu.edu.tw](mailto:aaronfrc@kmu.edu.tw).

\*E-mail: [jjwang@kmu.edu.tw](mailto:jjwang@kmu.edu.tw).

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Modha, S. G.; Mehta, V. P.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2013**, *42*, 5042. (b) Han, F. S. *Chem. Soc. Rev.* **2013**, *42*, 5270. (c) Wegner, H. A.; Auzias, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8236. (d) Chinchilla, R.; Najera, C. *Chem. Soc. Rev.* **2011**, *40*, 5084. (e) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (f) Shi, W.; Liu, C.; Lei, A. *Chem. Soc. Rev.* **2011**, *40*, 2761.
- (2) (a) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (b) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (c) Evano, G.; Blanchard, N.; Toum, M. *Chem. Rev.* **2008**, *108*, 3054.
- (3) (a) Li, B.; Dixneuf, P. H. *Chem. Soc. Rev.* **2013**, *42*, 5744. (b) Shang, X.; Liu, Z. Q. *Chem. Soc. Rev.* **2013**, *42*, 3253. (c) Arockiam, P.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (d) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (e) Kuhl, N.; Hopkinson, M. N.; Delord, J. W.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (f) Dyker, G. *Handbook of C–H Transformations. Applications in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2005.
- (4) (a) Wei, W. T.; Zhou, M. B.; Fan, J. H.; Liu, W.; Song, R. J.; Liu, Y.; Hu, M.; Xie, P.; Li, J. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 3638. (b) Liu, D.; Liu, C.; Li, H.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 4453. (c) Singh, P. P.; Gudup, S.; Aruri, H.; Singh, U.; Ambala, S.; Yadav, M.; Sawant, S. D.; Vishwakarma, R. A. *Org. Biomol. Chem.* **2012**,



10, 1587. (d) Singh, P. P.; Gudup, S.; Ambala, S.; Singh, U.; Dadhwal, S.; Singh, B.; Sawant, S. D.; Vishwakarma, R. A. *Chem. Commun.* **2011**, 47, 5852.

(5) (a) Xie, Z.; Cai, Y.; Hu, H.; Lin, C.; Jiang, J.; Chen, Z.; Wang, L.; Pan, Y. *Org. Lett.* **2013**, 15, 4600. (b) Huang, X. F.; Zhu, Z. Q.; Huang, Z. Z. *Tetrahedron* **2013**, 69, 8579. (c) Xie, J.; Li, H.; Zhou, J.; Cheng, Y.; Zhu, C. *Angew. Chem., Int. Ed.* **2012**, 51, 1252. (d) Park, S. J.; Price, J. R.; Todd, M. H. *J. Org. Chem.* **2012**, 77, 949. (e) Li, Z.; Yu, R.; Li, H. *Angew. Chem., Int. Ed.* **2008**, 47, 7497. (f) Li, Z.; Bohle, D. S.; Li, C. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 8928. (g) Li, Z.; Li, C. J. *J. Am. Chem. Soc.* **2005**, 127, 6968. (h) Murahashi, S. I.; Komiya, N.; Terai, H. *Angew. Chem., Int. Ed.* **2005**, 44, 6931.

(6) (a) Phan, N. T. S.; Vu, P. H. L.; Nguyen, T. T. *J. Catal.* **2013**, 306, 38. (b) Zhang, S.; Guo, L. N.; Wang, H.; Duan, X. H. *Org. Biomol. Chem.* **2013**, 11, 4308. (c) Kumar, G. S.; Pieber, B.; Reddy, K. R.; Kappe, C. O. *Chem.—Eur. J.* **2012**, 18, 6124. (d) Chen, L.; Shi, E.; Liu, Z.; Chen, S.; Wei, W.; Li, H.; Xu, K.; Wan, X. *Chem.—Eur. J.* **2011**, 17, 4085.

(7) (a) Hashimoto, T.; Takiguchi, Y.; Keiji, M. *J. Am. Chem. Soc.* **2013**, 135, 11473. (b) Matcha, K.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2013**, 52, 2082. (c) Aakeroy, C. B.; Sinha, A. S.; Epa, K. N.; Spartz, C. L.; Desper, J. *Chem. Commun.* **2012**, 48, 11289. (d) Wu, C. Y.; Hu, M.; Liu, Y.; Song, R. J.; Lei, Y.; Tang, B. X.; Li, R. J.; Li, J. H. *Chem. Commun.* **2012**, 48, 3197. (e) Saxin, M. F.; Seifert, T.; Landergren, M. R.; Suuronen, T.; Kakkonen, M. L.; Jarho, E. M.; Luthman, K. *J. Med. Chem.* **2012**, 55, 7104. (f) Barancelli, D. A.; Salles, A. G., Jr.; Taylor, J. G.; Correia, C. R. D. *Org. Lett.* **2012**, 14, 6036.

(8) Rout, S. K.; Guin, S.; Banerjee, A.; Khatun, N.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2013**, 15, 4106.

(9) (a) While revising this manuscript our group also reported the selective formation of carbamates in the presence of a sensitive aldehyde group; please see: Barve, B. D.; Wu, Y. C.; El-Shazly, M.; Chuang, D. W.; Cheng, Y. B.; Wang, J. J.; Chang, F. R. *J. Org. Chem.* **2014**, DOI: 10.1021/jo402798k. (b) Chuang, D. W.; El-Shazly, M.; Chen, C. C.; Barve, B. D.; Wu, M. J.; Chang, F. R.; Wu, Y. C. *Tetrahedron Lett.* **2013**, 54, 5162. (c) Barve, B. D.; Wu, Y. C.; El-Shazly, M.; Chuang, D. W.; Tsai, Y. H.; Wu, S. F.; Korinek, M.; Du, Y. C.; Hsieh, C. T.; Wang, J. J.; Chang, F. R. *Eur. J. Org. Chem.* **2012**, 6760. (d) Chuang, D. W.; El-Shazly, M.; Barve, B. D.; Chung, Y. M.; Chang, F. R.; Wu, Y. C. *Eur. J. Org. Chem.* **2012**, 4533.

(10) (a) Fan, J.; Li, Z. *Org. Chem. Front.* **2014**, 1, 194. and references therein (b) Parnes, R.; Kshirsagar, U. A.; Werbeloff, A.; Regev, C.; Pappo, D. *Org. Lett.* **2012**, 14, 3324. (c) Sun, C. L.; Li, B. J.; Shi, Z. J. *Chem. Rev.* **2011**, 111, 1293. (d) Guo, X.; Li, W.; Li, Z. *Eur. J. Org. Chem.* **2010**, 5787. (e) Czaplik, W. M.; Mayer, M.; Cvengros, J.; von Wangelin, A. J. *ChemSusChem* **2009**, 2, 396.

(11) (a) Rout, S. K.; Guin, S.; Ghara, K. K.; Banerjee, A.; Patel, B. K. *Org. Lett.* **2012**, 14, 3982. (b) Sodhi, R. K.; Paul, S.; Clark, J. H. *Green Chem.* **2012**, 14, 1649. (c) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2012**, 51, 3231. (d) Xu, K.; Hu, Y.; Zhang, S.; Zha, Z.; Wang, Z. *Chem.—Eur. J.* **2012**, 18, 9793. (e) Das, R.; Chakraborty, D. *Appl. Organometal. Chem.* **2011**, 25, 437. (f) Chakraborty, D.; Gowda, R. R.; Malik, P. *Tetrahedron Lett.* **2009**, 50, 6553. (g) Mannam, S.; Sekar, G. *Tetrahedron Lett.* **2008**, 49, 1083. (h) Grill, J. M.; Ogle, J. W.; Miller, S. A. *J. Org. Chem.* **2006**, 71, 9291. (i) Abaee, M. S.; Sharifi, R.; Mojtahedi, M. M. *Org. Lett.* **2005**, 26, 5893. (j) Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, 5, 1031. (k) Heaney, H.; Newbold, A. J. *Tetrahedron Lett.* **2001**, 42, 6607. (l) Webb, K. S.; Ruskay, S. J. *Tetrahedron* **1998**, 54, 401.

(12) (a) Shapiro, N.; Vigalok, A. *Angew. Chem., Int. Ed.* **2008**, 47, 2849. (b) Vanoye, L.; Reguillon, A. F.; Aloui, A.; Philippea, R.; de Bellefon, C. *RSC Adv.* **2013**, 3, 18931.

(13) Greene, T. W.; Wuts, P. G. M. *Protective Group in Organic Synthesis*, 4th ed.; John Wiley and Sons, Inc.: New York, 2007, p 370.

(14) Zacharie, B.; Attardo, G.; Barriault, N.; Penney, C. J. *Chem. Soc., Perkin Trans. 1* **1997**, 2925.

(15) (a) Guo, S. R.; Yuan, Y. Q.; Xiang, J. N. *Org. Lett.* **2013**, 15, 4654. (b) Li, Z.; Cao, L.; Li, C. J. *Angew. Chem., Int. Ed.* **2007**, 46, 6505.