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Letter

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Coupling Reaction of Cu-Based Carbene and Nitroso Radical: A Tandem Reaction To Construct Isoxazolines

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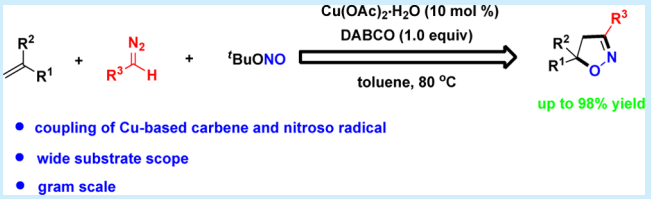
Supporting Information

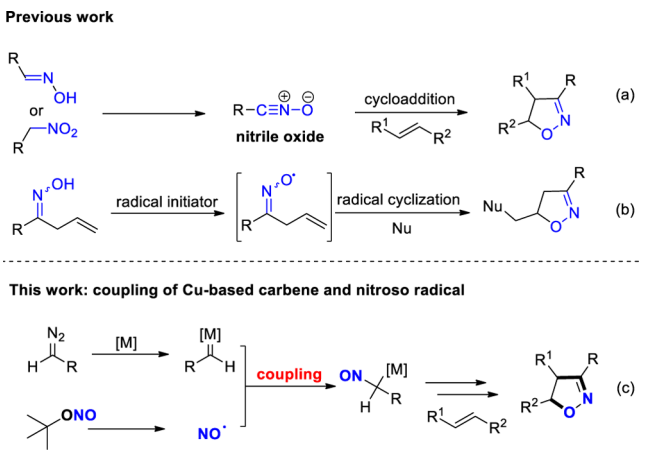
ABSTRACT: In this letter, an unprecedented cross-coupling reaction between copper carbene and nitroso radical has been developed. This radical-carbene coupling reaction (RCC reaction) offers a novel approach for the preparation of various isoxazolines, which features the construction of C−C, C−O, and C═N bonds in a one-pot process. The synthetic utility of our method is further enhanced by its mild reaction conditions, wide substrate scope, and simple procedures.



Transition-metal-catalyzed reactions of diazo compounds that produce active metal carbene species have greatly enriched synthetic chemistry.[1] In this regard, a variety of transition metals, including copper, rhodium, iridium, ruthenium, palladium, and gold, have demonstrated excellent catalytic properties in numerous carbene-based transformations. On the other hand, free radical intermediates have played pivotal roles in modern organic synthesis, enabling access to a wide range of functionalized molecules.[2] Therefore, it came as a natural surprise that there were few reported studies on the direct coupling between radical and carbene intermediates.[3] This, we speculate, could have been caused by the extreme reactivity of both types of species, making their concentrations too low for efficient cross-coupling. Thus, the development of an effective radical-carbene coupling reaction (RCC reaction) would not only provide a new synthetic strategy for preparing polyfunctionalized molecules but also, quite possibly, enhance our understanding of the underlying mechanism of the direct coupling reaction between radical and carbene.

Isoxazolines are important heterocylic structural motifs that are widely present in biologically active natural products and pharmaceutical molecules.[4] The preparation of isoxazolines is of particular interest to organic chemists due to their use as key intermediates in reactions to construct various synthetic structures[5] and as chiral ligands for asymmetric catalysis.[6] Current methods to construct isoxazoline structures usually involve the cycloaddition of nitrile oxide intermediates to 1,2-dipoles (Scheme 1a)[7] or intramolecular free radical cyclization (Scheme 1b).[8] Our laboratory recently reported several RCC reactions that can be used to furnish a wide variety of compounds, such as β-ester-γ-amino ketones,[9a,c] γ-peroxy esters,[9b] β-carbonyl sulfones[9d] and indoles,[9e] with high chemoselectivity. In addition, we argue that *tert*-butyl nitrite (^{t}BuONO) can be exploited as a potential source of the nitroso radical when heated.[10] Based on these considerations, we herein report the development of a novel and efficient method for preparing isoxazolines through the cross-coupling of transition metal based carbene with the nitroso radical generated in situ from ^{t}BuONO (Scheme 1c). This novel radical-carbene coupling reaction (RCC reaction) provides a novel strategy to deliver isoxazolines with wide scopes under mild conditions.

Scheme 1. Strategies for the Synthesis of Isoxazolines



Our model reaction to generate isoxazolines included 1-(*tert*-butyl)-4-vinylbenzene (**1a**), ^{t}BuONO (**2**), and ethyl diazoacetate (**3a**) as the alkene substrate, radical source, and carbene progenitor, respectively. The choice of a suitable catalytic system was critical to tilt the reaction toward RCC in preference to the classical interception of the metal−carbene complex by an alkene,[1] the latter of which would yield a substituted cyclopropane byproduct. We first evaluated the suitability of $Mn(OAc)_2{\cdot}4H_2O$ as the metal catalyst based on our recent development of a Mn-catalyzed RCC reaction for indole synthesis.[9e] Unfortunately, no appreciable formation of

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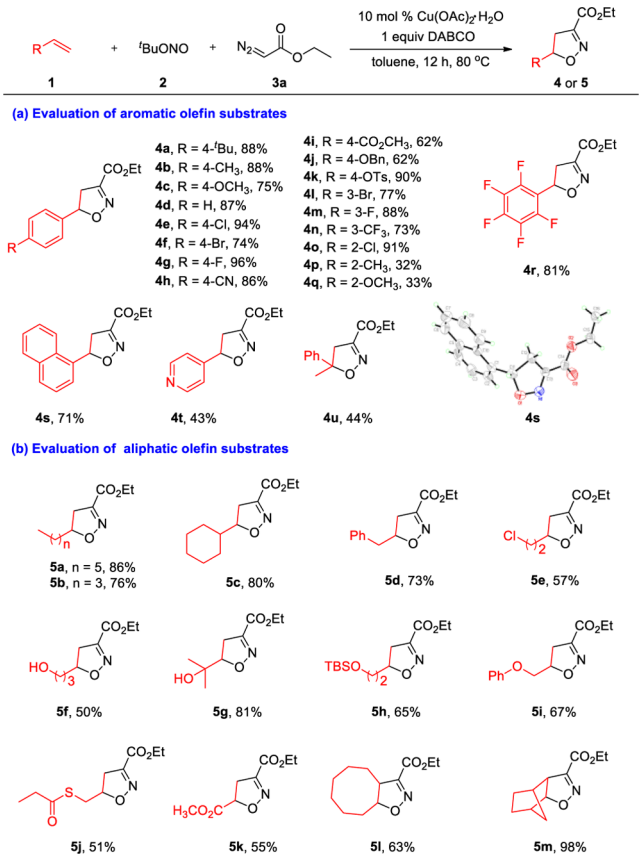
the target isoxazoline product **4a** was detected in the reaction mixture (Table S1, entry 1; see Supporting Information). Subsequent screening of a large panel of transition-metal catalysts (entries 2−10) found the use of $Cu(OAc)_2·H_2O$ in conjunction with DABCO resulted in the generation of **4a** in 88% yield (entry 10). Additional screening indicated that DABCO was essential for the success of the reaction, as switching to a different base was shown to be highly deleterious (entries 11−15). Furthermore, the replacement of toluene by other solvents also significantly hampered product formation (entries 18−21). Notably, we demonstrated that the cross-coupling reaction could be performed on a gram scale by successfully reacting 10 mmol of **1a** in one pot to obtain **4a** in 80% yield (entry 22).

We next assessed the substrate scope of the coupling reaction under the optimized conditions (Scheme 2a). The results

Scheme 2. Scope of Olefins[a]



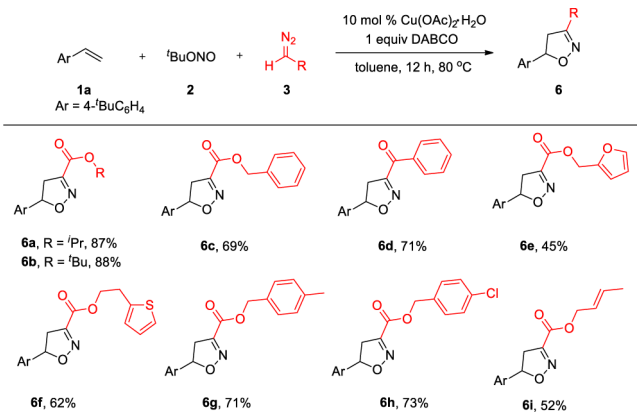
[a]Reaction conditions: **1** (0.5 mmol, 1.0 equiv), **2** (1.0 mmol, 2.0 equiv), **3a** (1.0 mmol, 2.0 equiv), $Cu(OAc)_2·H_2O$ (0.05 mmol, 10 mol %), DABCO (0.5 mmol, 1.0 equiv), and toluene (2.0 mL) at 80 °C for 12 h in a sealed tube.

showed that both electron-donating and electron-withdrawing groups on the aryl ring are compatible with the reaction (**4b**−**4q**). Moreover, the use of a polyfluoro-substituted styrene was well tolerated (**4r**). Meanwhile, 1-vinylnaphthalene (**1s**) also exhibited excellent reactivity, in which the corresponding isoxazoline product **4s** was isolated in 71% yield and structurally confirmed by X-ray single-crystal diffraction (see Supporting Information). Both 4-vinylpyridine (**1t**) and the 1,1-disubstituted styrene prop-1-en-2-ylbenzene (**1u**) were shown to be slightly less efficient yet nonetheless suitable substrates, furnishing **4t** and **4u** in moderate yields, respectively.

We further tested whether the more challenging aliphatic olefins could be employed. As shown in Scheme 2b, unsubstituted terminal alkenes (**5a**−**5d**) and those carrying functional groups such as chlorine, hydroxy, and ether (**5e**−**5j**) were all shown to be well-suited substrates. In particular, the use of electron-deficient olefins such as acrylate did not significantly inhibit the formation of the isoxazoline product (**5k**). Cyclic alkenes, including cyclooctene and norbornylene, also demonstrated satisfactory compatibility with the coupling reaction (**5l** and **5m**).

In order to demonstrate the broad applicability of our synthetic method, we then examined the use of different diazo reagents. As listed in Scheme 3, various ester groups in the *α*-

Scheme 3. Scope of Diazo Compounds[a]



[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv), **2** (1.0 mmol, 2.0 equiv), **3** (1.0 mmol, 2.0 equiv), $Cu(OAc)_2·H_2O$ (0.05 mmol, 10 mol %), DABCO (0.5 mmol, 1.0 equiv), and toluene (2.0 mL) at 80 °C for 12 h in a sealed tube.

diazo compounds, including, in particular, those that contained an allylic moeity (**6i**), were all well tolerated. Diazoketone also reacted efficiently and furnished the corresponding product **6d** in 71% yield. Furthermore, the presence of a heterocycle displayed no obvious detrimental effect on the reaction efficiency (**6e**, **6f**).

To explore the mechanism of this transformation, we analyzed the reaction mixture by GC-MS and detected a trace amount of cyclopropanation product. On the other hand, no formation of **4a** was observed in the absence of $Cu(OAc)_2·H_2O$ (Table S1, entry 16). Taken together, these findings suggested the involvement of a copper−carbene intermediate. On the other hand, since nitro compounds could undergo classical dipole cycloaddition with olefins to produce isoxazolines,[7a] we thus suspected the in situ generation of a nitro-bearing intermediate. However, this was contradicted by the failure to detect ethyl nitroacetate following the treatment of *tert*-butyl nitrite with ethyl diazoacetate under the standard reaction conditions (Scheme 4a). It is worth noting that the formation of **4a** was indeed observed after **1a** was reacted with ethyl nitroacetate (Scheme 4b). However, kinetic studies revealed that this reaction was significantly slower than the model reaction in which ^tBuONO and ethyl diazoacetate were used (Figure 1). These results served as further evidence against the in situ formation of a nitro compound and subsequent participation in this isoxazoline formation reaction.

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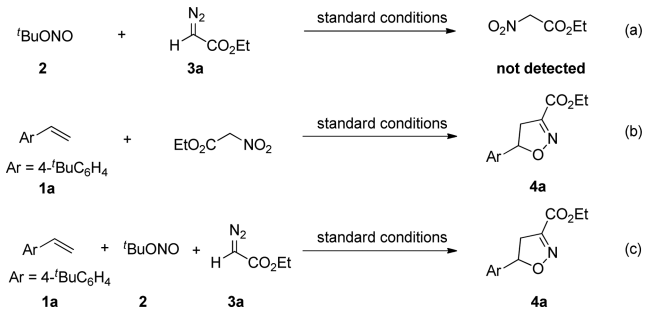
Scheme 4. Preliminary Mechanism Research



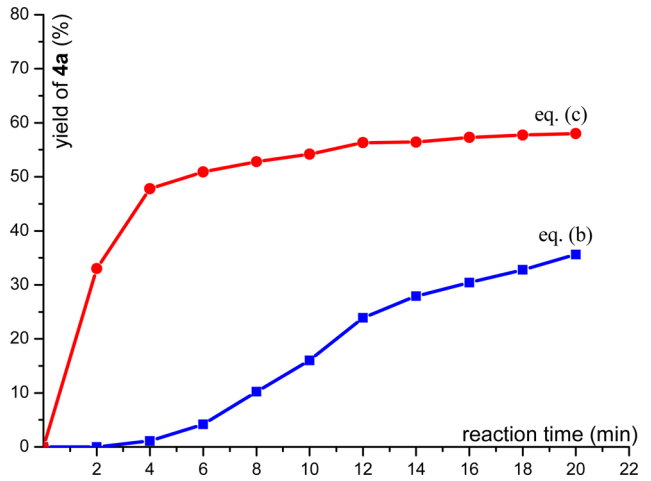
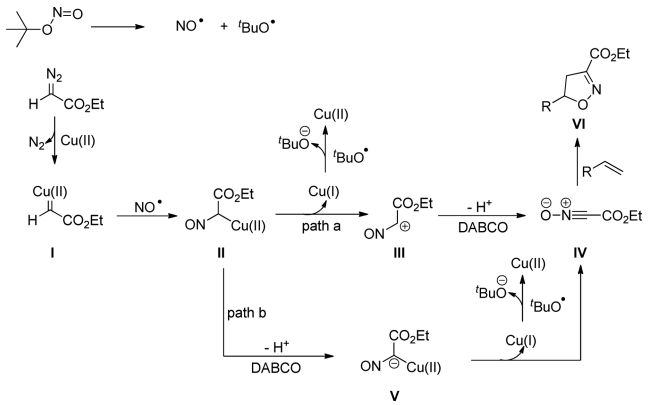


Figure 1. Kinetics of eq (b) and eq (c) monitored by GC.

We also investigated the possible involvement of other reactive species, including the cyclopropane intermediate **7**, pyrazole **8**, the nitrification intermediate **9**, and oxime **10**. As depicted, no product formation of **4a** was observed when we reacted **7** or **8** with ^{t}BuONO (Scheme S1a, S1b in Supporting Information), **9** with **3a** (Scheme S1c), or **10** with **1a** (Scheme S1d), which excluded the possibility of them as intermediates in this transformation.

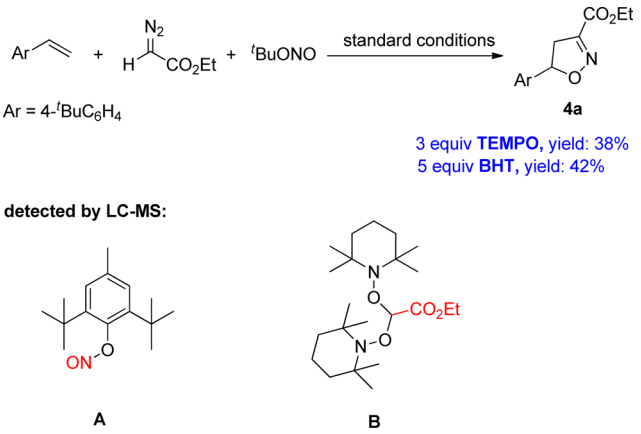
Based on the above-mentioned results and earlier literature reports, we formulated a plausible mechanism of the RCC reaction leading to isoxazolines as depicted in Scheme 5. First, *tert*-butyl nitrite undergoes homolytic cleavage to form both a nitroso radical and a *tert*-butoxy radical when heated. Meanwhile, the interaction of the diazo compound with the Cu catalyst gives rise to the Cu-based carbene intermediate **I**, which is immediately intercepted by the nitroso radical to afford the organocopper intermediate **II**. Subsequently, heterolytic bond cleavage with the electrons going to copper generate nitrile oxide intermediate **IV** after deprotonation.[11] At the same time, Cu(I) was quickly oxidized into Cu(II) by the *tert*-butoxyl radical to participate in the catalytic cycle (path a). At present, another pathway could not be excluded. Loss of a proton from intermediate **II** took place to generate intermediate **V**, which then underwent heterolytic bond cleavage to form intermediate **IV** (path b). Finally, intermediate **IV** would furnish the desired isoxazolines **VI** through 1,3-dipolar cycloaddition.[7]

Scheme 5. Proposed Mechanism



To experimentally verify our proposed mechanism, we added radical scavengers such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) to the model reaction (Scheme 6). In both cases, the product yield was significantly reduced, lending support to the presence of a key radical intermediate. More importantly, we observed the formation of adducts resulting from the sequestration of the nitroso radical by BHT (**A**) and that of the reactive carbene species by TEMPO (**B**).

Scheme 6. Trapping of Radicals by TEMPO/BHT



In conclusion, we have developed a novel radical−carbene coupling reaction (RCC reaction) that allows efficient synthesis of diverse isoxazoline derivatives. During this tandem process, one C−C bond, one C−O bond, and one C═N bond are constructed in a one-pot reaction from readily available starting reagents. Simple and commercially available *tert*-butyl nitrite plays the role as a source of nitroso radical. Further mechanistic investigations and the development of other RCC reactions are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02885.

X-ray data for **4s** (CIF)

Experimental procedure, characterization data, copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For selected reviews on carbene chemistry, see: (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (b) Hodgson, D. M.; Pierard, F. Y. T. M.; Stupple, P. A. *Chem. Soc. Rev.* **2001**, *30*, 50. (c) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861. (d) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183. (e) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417. (f) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704. (g) Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40*, 1857. (h) Zhu, S.-F.; Zhou, Q.-L. *Acc. Chem. Res.* **2012**, *45*, 1365. (i) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236. (j) Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. *Chem. Rev.* **2015**, *115*, 9981. (k) Candeias, N. R.; Paterna, R.; Gois, P. M. P. *Chem. Rev.* **2016**, *116*, 2937. (l) DeAngelis, A.; Panish, R.; Fox, J. M. *Acc. Chem. Res.* **2016**, *49*, 115.

(2) For selected reviews on radical chemistry: (a) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237. (b) Renaud, P.; Sibi, M. P. *Radicals in Organic Synthesis*; Wiley−VCH: Weinheim, 2001. (c) Studer, A. *Chem. - Eur. J.* **2001**, *7*, 1159. (d) Zard, S. Z. *Radical Reactions in Organic Synthesis*; Oxford University Press: 2003. (e) Studer, A. *Chem. Soc. Rev.* **2004**, *33*, 267. (f) Gansäuer, A. *Radicals in Synthesis*; Springer: Heidelberg, 2006. (g) Yan, M.; Lo, J. C.; Edwards, J. T.; Baran, P. S. *J. Am. Chem. Soc.* **2016**, *138*, 12692.

(3) For metal carbene insertion into C−H bonds, selected examples, see: (a) Nakamura, E.; Yoshikai, N.; Yamanaka, M. *J. Am. Chem. Soc.* **2002**, *124*, 7181. (b) Thu, H.-Y.; Tong, G. S.-M.; Huang, J.-S.; Chan, S. L.-F.; Deng, Q.-H.; Che, C.-M. *Angew. Chem., Int. Ed.* **2008**, *47*, 9747. (c) Suematsu, H.; Katsuki, T. *J. Am. Chem. Soc.* **2009**, *131*, 14218. (d) Chuprakov, S.; Malik, J. A.; Zibinsky, M.; Fokin, V. V. *J. Am. Chem. Soc.* **2011**, *133*, 10352. (e) Lo, V. K.-Y.; Guo, Z.; Choi, M. K.-W.; Yu, W.-Y.; Huang, J.-S.; Che, C.-M. *J. Am. Chem. Soc.* **2012**, *134*, 7588. (f) Qin, C.; Davies, H. M. L. *J. Am. Chem. Soc.* **2014**, *136*, 9792. (g) He, J.; Hamann, L. G.; Davies, H. M. L.; Beckwith, R. E. J. *Nat. Commun.* **2015**, *6*, 5943. (h) Guptill, D. M.; Davies, H. M. L. *J. Am. Chem. Soc.* **2014**, *136*, 17718. (i) Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L. *Nature* **2016**, *533*, 230. For Co(III)-based carbene radicals, see: (j) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2010**, *132*, 10891. (k) Xu, X.; Lu, H.; Ruppel, J. V.; Cui, X.; Lopez de Mesa, S.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 15292. (l) Lu, H.; Dzik, W. I.; Xu, X.; Wojtas, L.; de Bruin, B.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 8518. (m) Xu, X.; Zhu, S.; Cui, X.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 11857. (n) Das, B. G.; Chirila, A.; Tromp, M.; Reek, J. N. H.; Bruin, B. d. *J. Am. Chem. Soc.* **2016**, *138*, 8968. (o) Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2017**, *139*, 1049.

(4) (a) Schaller, C.; Demange, R.; Picasso, S.; Vogel, P. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 277. (b) Tangallapally, R. P.; Sun, D.; Rakesh; Budha, N.; Lee, R. E. B.; Lenaerts, A. J. M.; Meibohm, B.; Lee, R. E. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6638. (c) Varshney, V.; Mishra, N. N.; Shukla, P. K.; Sahu, D. P. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3573.

(5) (a) Kozikowski, A. P.; Stein, P. D. *J. Am. Chem. Soc.* **1982**, *104*, 4023. (b) Curran, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 5826. (c) Bode, J. W.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 1587. (d) Minter, A. R.; Fuller, A. A.; Mapp, A. K. *J. Am. Chem. Soc.* **2003**, *125*, 6846. (e) Fuller, A. A.; Chen, B.; Minter, A. R.; Mapp, A. K. *J. Am. Chem. Soc.* **2005**, *127*, 5376. (f) Jiang, D.; Peng, J.; Chen, Y. *Org. Lett.* **2008**, *10*, 1695. (g) Tang, S.; He, J.; Sun, Y.; He, L.; She, X. *J. Org. Chem.* **2010**, *75*, 1961.

(6) (a) Reference 5a. (b) Arai, M. A.; Kuraishi, M.; Arai, T.; Sasai, H. *J. Am. Chem. Soc.* **2001**, *123*, 2907. (c) Marotta, E.; Micheloni, L. M.; Scardovi, N.; Righi, P. *Org. Lett.* **2001**, *3*, 727. (d) Arai, M. A.; Arai, T.; Sasai, H. *Org. Lett.* **1999**, *1*, 1795. (e) Zhu, M.-K.; Zhao, J.-F.; Loh, T.-P. *J. Am. Chem. Soc.* **2010**, *132*, 6284. (f) Minakata, S.; Okumura, S.; Nagamachi, T.; Takeda, Y. *Org. Lett.* **2011**, *13*, 2966. (g) Han, B.; Yang, X.-L.; Fang, R.; Yu, W.; Wang, C.; Duan, X.-Y.; Liu, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 8816.

(7) Selected examples: (a) Vaughan, W. R.; Spencer, J. L. *J. Org. Chem.* **1960**, *25*, 1160. (b) Cecchi, L.; De Sarlo, F.; Machetti, F. *Eur. J. Org. Chem.* **2006**, 4852. (c) Cecchi, L.; De Sarlo, F.; Machetti, F. *Chem. - Eur. J.* **2008**, *14*, 7903. (d) Mendelsohn, B. A.; Lee, S.; Kim, S.; Teyssier, F.; Aulakh, V. S.; Ciufolini, M. A. *Org. Lett.* **2009**, *11*, 1539. (e) Jen, T.; Mendelsohn, B. A.; Ciufolini, M. A. *J. Org. Chem.* **2011**, *76*, 728. (f) Minakata, S.; Okumura, S.; Nagamachi, T.; Takeda, Y. *Org. Lett.* **2011**, *13*, 2966. (g) Yoshimura, A.; Middleton, K. R.; Todora, A. D.; Kastern, B. J.; Koski, S. R.; Maskaev, A. V.; Zhdankin, V. V. *Org. Lett.* **2013**, *15*, 4010. (h) Li, C.; Deng, H.; Li, C.; Jia, X.; Li, J. *Org. Lett.* **2015**, *17*, 5718. (i) Wang, G.-W.; Cheng, M.-X.; Ma, R.-S.; Yang, S.-D. *Chem. Commun.* **2015**, *51*, 6308. (j) Gao, M.; Li, Y.; Gan, Y.; Xu, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 8795. (k) Kesornpun, C.; Aree, T.; Mahidol, C.; Ruchirawat, S.; Kittakoop, P. *Angew. Chem., Int. Ed.* **2016**, *55*, 3997.

(8) Selected examples: (a) Reference 6g. (b) Zhu, L.; Yu, H.; Xu, Z.; Jiang, X.; Lin, L.; Wang, R. *Org. Lett.* **2014**, *16*, 1562. (c) Zhu, L.; Wang, G.; Guo, Q.; Xu, Z.; Zhang, D.; Wang, R. *Org. Lett.* **2014**, *16*, 5390. (d) Yang, X.-L.; Chen, F.; Zhou, N.-N.; Yu, W.; Han, B. *Org. Lett.* **2014**, *16*, 6476. (e) Dong, K.-Y.; Qin, H.-T.; Liu, F.; Zhu, C. *Eur. J. Org. Chem.* **2015**, 1419. (f) Zhang, X.-W.; Xiao, Z.-F.; Zhuang, Y.-J.; Wang, M.-M.; Kang, Y.-B. *Adv. Synth. Catal.* **2016**, *358*, 1942. (g) Chen, F.; Yang, X.-L.; Wu, Z.-W.; Han, B. *J. Org. Chem.* **2016**, *81*, 3042.

(9) (a) Zhang, J.; Jiang, J.; Xu, D.; Luo, Q.; Wang, H.; Chen, J.; Li, H.; Wang, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 1231. (b) Jiang, J.; Liu, J.; Yang, L.; Shao, Y.; Cheng, J.; Bao, X.; Wan, X. *Chem. Commun.* **2015**, *51*, 14728. (c) Ling, J.; Zhang, J.; Zhao, Y.; Xu, Y.; Wang, H.; Lv, Y.; Ji, M.; Ma, L.; Ma, M.; Wan, X. *Org. Biomol. Chem.* **2016**, *14*, 5310. (d) Wang, Y.; Ma, L.; Ma, M.; Zheng, H.; Shao, Y.; Wan, X. *Org. Lett.* **2016**, *18*, 5082. (e) Li, H.; Zhao, Y.; Ma, L.; Ma, M.; Jiang, J.; Wan, X. *Chem. Commun.* **2017**, *53*, 5993.

(10) Selected examples on ^{t}BuONO: (a) Taniguchi, T.; Yajima, A.; Ishibashi, H. *Adv. Synth. Catal.* **2011**, *353*, 2643. (b) Gao, P.; Li, H.-X.; Hao, X.-H.; Jin, D.-P.; Chen, D.-Q.; Yan, X.-B.; Wu, X.-X.; Song, X.-R.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2014**, *16*, 6298. (c) Hu, M.; Song, R.-J.; Li, J.-H. *Angew. Chem., Int. Ed.* **2015**, *54*, 608. (d) Chaudhary, P.; Gupta, S.; Muniyappan, N.; Sabiah, S.; Kandasamy, J. *Green Chem.* **2016**, *18*, 2323. (e) Miao, C.-X.; Yu, B.; He, L.-N. *Green Chem.* **2011**, *13*, 541. (f) Maity, S.; Naveen, T.; Sharma, U.; Maiti, D. *Org. Lett.* **2013**, *15*, 3384. (g) Shu, Z.; Ye, Y.; Deng, Y.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 10573. (h) Chen, F.; Huang, X.; Li, X.; Shen, T.; Zou, M.; Jiao, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 10495. (i) Dutta, U.; Maity, S.; Kancherla, R.; Maiti, D. *Org. Lett.* **2014**, *16*, 6302. (j) Liang, Y.-F.; Li, X.; Wang, X.; Yan, Y.; Feng, P.; Jiao, N. *ACS Catal.* **2015**, *5*, 1956. (k) Yan, H.; Mao, J.; Rong, G.; Liu, D.; Zheng, Y.; He, Y. *Green Chem.* **2015**, *17*, 2723. (l) Dutta, U.; Lupton, D. W.; Maiti, D. *Org. Lett.* **2016**, *18*, 860. (m) Liu, J.; Zheng, H.-X.; Yao, C.-Z.; Sun, B.-F.; Kang, Y.-B. *J. Am. Chem. Soc.* **2016**, *138*, 3294. (n) Yang, J.; Liu, Y.-Y.; Song, R.-J.; Peng, Z.-H.; Li, J.-H. *Adv. Synth. Catal.* **2016**, *358*, 2286. (o) Yang, X.-H.; Song, R.-J.; Li, J.-H. *Adv. Synth. Catal.* **2015**, *357*, 3849. (p) Hu, M.; Liu, B.; Ouyang, X.-H.; Song, R.-J.; Li, J.-H. *Adv. Synth. Catal.* **2015**, *357*, 3332. (q) Yang, X.-H.; Ouyang, X.-H.; Wei, W.-T.; Song, R.-J.; Li, J.-H. *Adv. Synth. Catal.* **2015**, *357*, 1161.

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