Heterocycle Synthesis

Deutsche Ausgabe: DOI: 10.1002/ange.201603352
Internationale Ausgabe: DOI: 10.1002/anie.201603352

Selective Oxytrifluoromethylation of Allylamines with CO_2

*Jian-Heng Ye, Lei Song, Wen-Jun Zhou, Tao Ju, Zhu-Bao Yin, Si-Shun Yan, Zhen Zhang, Jing Li, and Da-Gang Yu**

In memory of Wei-Yuan Huang

Abstract: *Reported is the first oxy-trifluoromethylation of allylamines with carbon dioxide (CO_2) using copper catalysis, thus leading to important CF_3-containing 2-oxazolidones. It is also the first time CO_2, a nontoxic and easily available greenhouse gas, has been used to tune the difunctionalization of alkenes from amino- to oxy-trifluoromethylation. Of particular note, this multicomponent reaction is highly chemo-, regio-, and diastereoselective under redox-neutral and mild reaction conditions. Moreover, these reactions feature good functional-group tolerance, broad substrate scope, easy scalability and facile product diversification. The important products could also be formed with either spirocycles or two adjacent tetrasubstituted carbon centers.*

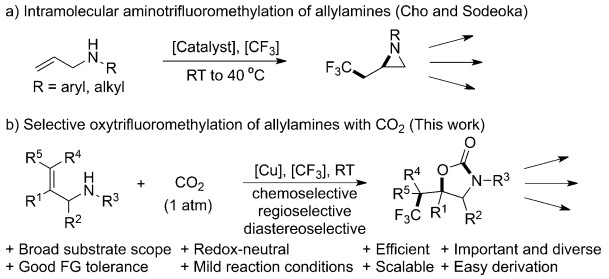


Figure 1. Amino- and oxy-trifluoromethylation of alkenes. FG = functional group.

The trifluoromethyl group (CF_3) is a very important motif in agrochemicals, functional materials, and pharmaceuticals, because of its unique lipophilicity, metabolic stability, and electronegativity.[1] Accordingly, different kinds of trifluoromethylation methods,[2] especially for the construction of $C(sp^3)$–CF_3 bonds,[3–7] have been reported. Methods for the difunctionalizing trifluoromethylation of alkenes, including carbo-,[4] halo-,[5] oxy-,[6] and amino-trifluoromethylation,[6i,7] have developed rapidly with significant improvement in accessible molecular complexity. Notably, the trifluoromethylation of allylamines has attracted much attention because of its high importance. For example, both the groups of Cho[6i] and Sodeoka[7a,e] independently realized the photoredox and copper-catalyzed aminotrifluoromethylation of allylamine to give CF_3-containing aziridines, which could undergo diverse N-migratory functionalizations with various kinds of nucleophiles[7a] (Figure 1a). These methods are efficient under mild reaction conditions, thus indicating the high reactivity and low-energy barrier of such aminotrifluoromethylations.

Carbon dioxide (CO_2) is not only a greenhouse gas but also a nontoxic, abundant, and recyclable building block in organic synthesis.[8] Although it is challenging to utilize it under mild reaction conditions because of its thermodynamic stability and kinetic inertness, many kinds of transformations have been developed with huge effort and various strategies. Notably, the application of CO_2 in the construction of important heterocycles,[8,9] which is the subject of long-standing interest in pharmaceutical discovery and organic synthesis, is highly attractive as it avoids the use of toxic CO or phosgene. However, the challenging of utilization of CO_2 to generate important heterocycles with concomitant incorporation of CF_3 has not been reported yet.

2-Oxazolidones are important heterocycles which serve as useful intermediates in organic synthesis, and because of their unique properties they exist widely in drugs, semiconductor devices, and chiral auxiliaries.[10] Although many synthetic methods have been reported,[11] to the best of our knowledge, there is no general method to construct important CF_3-containing 2-oxazolidones from reagents which are readily available and easy to handle. Inspired by the above-mentioned successes,[6–8] we envisioned that the reaction mode of allylamines could be tuned from amino- to oxy-trifluoromethylation by incorporation of the entire "CO_2" moiety. This designed reaction might not only afford important CF_3-containing 2-oxazolidones from simple starting materials, but it could also open a direct and important route to productively sequester the greenhouse gas. With continuous interest in CO_2 utilization,[9b] we herein report the first copper-catalyzed highly selective oxytrifluoromethylation of diverse allylamines with CO_2 to synthesize important CF_3-containing 2-oxazolidones under redox-neutral and mild reaction conditions (Figure 1b).

Although multicomponent reactions (MCRs) can generate diverse complex products expediently from simple substrates with low cost, high efficiency, and pot-economy,

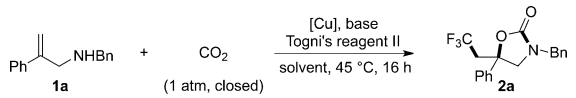
[*] J.-H. Ye, L. Song, Prof. Dr. W.-J. Zhou, T. Ju, Z.-B. Yin, S.-S. Yan, Z. Zhang, Dr. J. Li, Prof. Dr. D.-G. Yu
Key Laboratory of Green Chemistry & Technology
of Ministry of Education, College of Chemistry, Sichuan University
29 Wangjiang Road, Chengdu 610064 (P.R. China)
E-mail: dgyu@scu.edu.cn
Homepage: http://chem.scu.edu.cn/en/DaGangYu
Prof. Dr. W.-J. Zhou
College of Chemistry and Chemical Engineering
Neijiang Normal University, Neijiang 641112 (P.R. China)
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201603352.

in designing this procedure, we identified four main challenges that needed to be addressed: 1) Chemoselectivity between N–CF_3 and C–CF_3 bond formation. The side reaction of direct nucleophilic attack of amines to electrophilic trifluoromethylation reagents is one key challenge in such a multicomponent reaction.[12] 2) Chemoselectivity between amino- and oxy-trifluoromethylation. Efficient generation of a carbamic acid intermediate with subsequent C–O formation should be preferred to the C–N bond formation, which is vital to the designed reaction. However, because of the thermodynamic stability and general inertness, CO_2 tends to react with strong nucleophiles only under harsh reaction conditions, thus making it challenging to compete with the facile aminotrifluoromethylation (Figure 1a). 3) Regioselectivity between *endo* and *exo* cyclization. Besides the chemoselectivity, the cyclization step must be regioselective so as to give one heterocycle in good yield. 4) Decomposition of the products in the presence of base. The proton α to the CF_3 group is quite acidic, and might result in facile decomposition of the 2-oxazolidones by elimination.

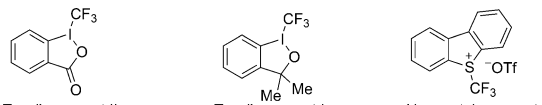
With these challenges in mind, we selected *N*-benzyl-2-phenylprop-2-en-1-amine (**1a**) as our initial starting material because of its availability and facile derivatization of the desired product **2a** (Table 1). We first examined the reaction between **1a** and Togni's reagent II, which is easy to handle and readily prepared from inexpensive 2-iodobenzoic acid in three steps without chromatography,[13] in the presence of stable $[Cu(MeCN)_4PF_6]$ as a catalyst and 1 atm of CO_2 in acetonitrile (entry 1). Unfortunately, only the aminotrifluoromethylation product was observed in this case. We thought that addition of a base might enhance the nucleophilicity of an amine or activate CO_2. Among the various kinds of bases tested (entries 2–5), we were delighted to identify DBU as the best choice, thus providing **2a** in 70% yield (GC). The yield was increased to 88% (GC) when 2.0 equivalents of DBU were used (entry 6). Several other copper catalysts (entries 7–9) and solvents (entries 10–12) were explored, but they all gave **2a** in lower yields. Importantly, the reaction also proceeded smoothly and with better yield at room temperature (entry 13). Alternative CF_3 sources, such as Togni's reagent I and Umemoto's reagent, were also effective in this reaction (entries 14 and 15). The transformation neither proceed without a copper catalyst nor in the presence of just $In(OTf)_3$ or $Yb(OTf)_3$ (entries 16–18), thus suggesting that the copper catalyst is vital to this transformation but does not act as a Lewis acid.

With the standard reaction conditions (Table 1, entry 13) in hand, we investigated the effect of substituents on the amine nitrogen (Table 2). Both primary and secondary alkyl-

Table 1: Optimization of the reaction conditions.[a]

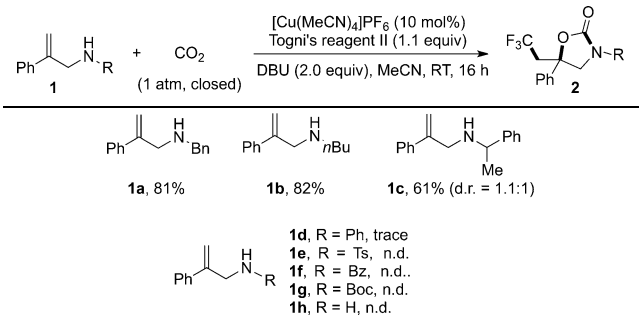


Entry	Catalyst	Base	Solvent	Yield [%][b]
1	$[Cu(MeCN)_4]PF_6$	–	MeCN	n.d.
2[c]	$[Cu(MeCN)_4]PF_6$	K_2CO_3	MeCN	< 5
3[c]	$[Cu(MeCN)_4]PF_6$	Cs_2CO_3	MeCN	25
4[c]	$[Cu(MeCN)_4]PF_6$	NaO*t*Bu	MeCN	20
5[c]	$[Cu(MeCN)_4]PF_6$	DBU	MeCN	70
6	$[Cu(MeCN)_4]PF_6$	DBU	MeCN	88
7	CuCl	DBU	MeCN	82
8	CuBr	DBU	MeCN	74
9	$Cu(acac)_2$	DBU	MeCN	34
10	$[Cu(MeCN)_4]PF_6$	DBU	DCM	57
11	$[Cu(MeCN)_4]PF_6$	DBU	THF	38
12	$[Cu(MeCN)_4]PF_6$	DBU	DMF	84
13[d]	$[Cu(MeCN)_4]PF_6$	DBU	MeCN	90 (81)
14[d,e]	$[Cu(MeCN)_4]PF_6$	DBU	MeCN	87
15[d,f]	$[Cu(MeCN)_4]PF_6$	DBU	MeCN	77
16[d]	–	DBU	MeCN	n.d.
17[d]	$In(OTf)_3$	DBU	MeCN	n.d.
18[d]	$Yb(OTf)_3$	DBU	MeCN	n.d.



[a] Reaction conditions: **1a** (0.4 mmol), 1 atm of CO_2, Togni's reagent II (0.44 mmol), base (0.8 mmol), catalyst (0.04 mmol), solvent (4 mL), 45 °C, 16 hours. [b] GC yields are given with dodecane as an internal standard and the isolated yields are given in parentheses. [c] Base (0.6 mmol). [d] Room temperature (RT). [e] Togni's reagent I was used. [f] Umemoto's reagent was used. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DCM = dichloromethane, DMF = *N*,*N*-dimethylformamide, n.d. = not detected, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

Table 2: Test of different substituents on the amine nitrogen.[a]

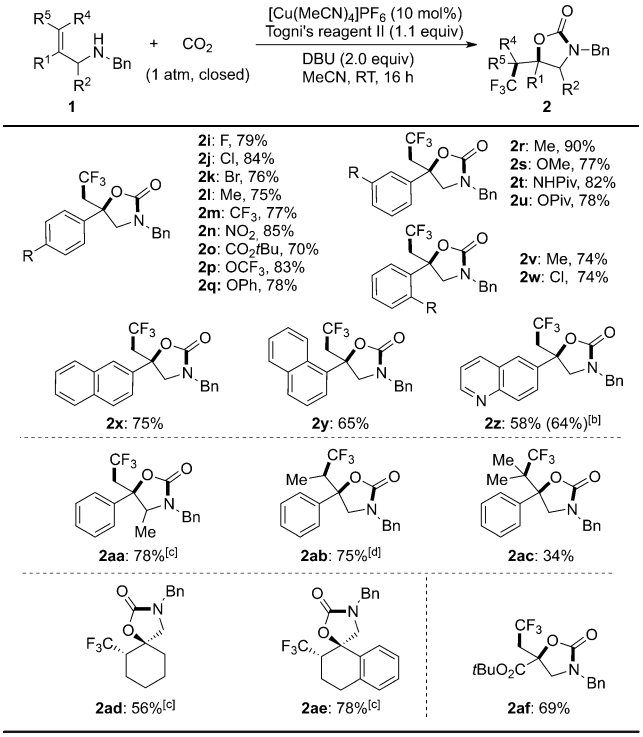


[a] The standard reaction conditions. Yields are those of the isolated products. Boc = *tert*-butoxycarbonyl, Bz = benzoyl, Ts = 4-toluenesulfonyl.

substituted substrates, **1a**, **1b**, and **1c**, gave products in moderate to good yields, while the aryl-substituted substrate **1d** only gave trace amounts of product. Neither strongly electron-withdrawing substituents (**1e**–**g**) nor the free amine **1h** generated the desired products. These results indicate that the nucleophilicity of the nitrogen atom is very important to this transformation.

Based on these results, we next explored the substrate scope of the reaction (Table 3). We found that various allylamines can be transformed into the desired 2-oxoazolidone products in moderate to good yields. Both electron-donating and electron-withdrawing groups on the vinylic aromatic substituent were compatible. This reaction tolerated many kinds of functional groups, including fluoro (**2i**), chloro

Table 3: Substrate scope of allylamines.[a]



[a] The standard reaction conditions.Yields are those of the isolated products. [b] 30 h. [c] No diastereoisomer is detected. [d] d.r. > 16:1. See the Supporting Information for details. Piv = pivaloyl.

(**2j** and **2w**), bromo (**2k**), ether (**2p**, **2q** and **2s**), nitro (**2n**), ester (**2o** and **2u**), and amide (**2t**) groups, which may be beneficial for subsequent transformations.[14] The substituents at either the *meta* (**2r**–**u**) or *ortho* position (**2v** and **2w**) of the vinylic aromatic ring did not hamper the reactions. While incomplete conversion and a diminished yield were observed for the reaction of the 1-naphthyl **1y**, the 2-naphthyl-substituted analogue **1x** reacted smoothly. The heteroaromatic substrate **1z** underwent clean reaction to give the product **2z** selectively and in moderate yield without detection of any arene trifluoromethylation.[15]

Besides different (hetero)arene derivatives, we further tested the allylamines with other substituents (Table 3). For example, the substrate **1aa**, having a methyl group α to the amine, showed good reactivity in this reaction. Although the trifluoromethylation of internal alkenes at the position with increased steric hindrance is highly challenging, the allylamines **1ab** and **1ac** underwent reactions to give the desired products in moderate to good yields. The facile generation of **2ac**, in which a quaternary carbon atom and an adjacent tetrasubstituted carbon atom are both established, is particularly noteworthy. Considering the wide existence and high importance of spiro-heterocycles, we further tested the reactions of allylamines bearing cyclic alkenes to give **2ad** and **2ae** in moderate to high efficiency. Importantly, the products **2aa**, **2ab**, **2ad**, and **2ae** were all obtained with high diastereoselectivity. The two-dimensional NMR spectrum and single-crystal X-ray structure (see below) showed the *anti* relationship between the generated C–O and C–CF_3 bonds in **2ae** (see the Supporting Information for details). Moreover, to our delight, acrylate derivatives, such as **1af**, could also react efficiently to provide a new class of useful products, thus demonstrating the broad substrate scope of our system.

To gain more insight into this reaction, mechanistic studies were conducted (see the Supporting Information). When radical scavengers, either 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) or 2,6-di-tert-butyl-4-methyl-phenol (BHT) or 1,1-diphenylethylene, were added under the standard reaction conditions, the reaction was significantly inhibited. Meanwhile, the radical coupling adducts TEMPO–CF_3 and BHT–CF_3 were detected, and indicate that the reaction might involve the $^{\bullet}CF_3$ radical.

Based on these mechanistic studies and the observed high diastereoselectivity, we propose a possible reaction mechanism using **1ae** as an example substrate (Figure 2). A single-

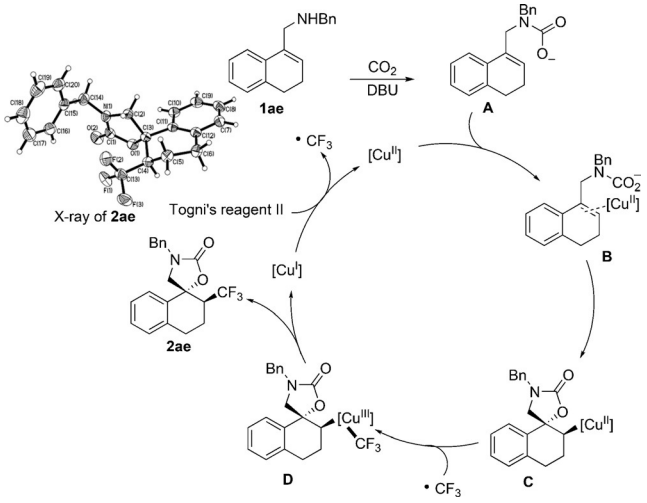
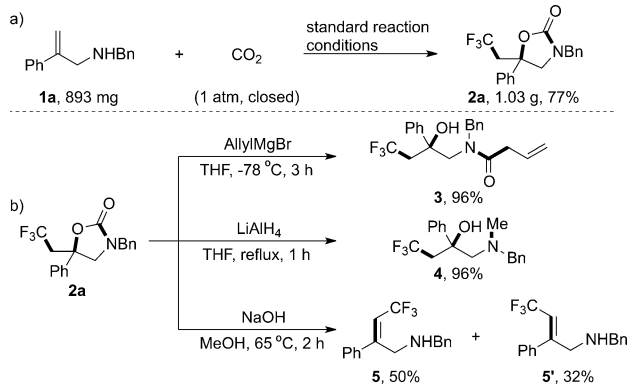


Figure 2. Proposed mechanism and X-ray structure of **2ae**.[16]

electron transfer (SET) occurs between the Cu^{I} complex and Togni's reagent II to generate a $^{\bullet}CF_3$ radical and a Cu^{II} complex. Meanwhile, the reaction of **1ae** with CO_2 and DBU generates the carbamate **A**, which further coordinates to the Cu^{II} complex to form **B**. Then the key cyclization reaction occurs with both C–O and C–Cu^{II} bond generation, with *anti* diastereoselectivity, to form the cyclic carbamate intermediate **C**. Combination of the $^{\bullet}CF_3$ radical with **C** generates a highly reactive Cu^{III} complex (**D**), which undergoes reductive elimination to afford **2ae** along with regeneration of the Cu^{I} catalyst. Given the complicated pathways, a Cu^{III} complex[6h] might be generated directly from Cu^{I} and Togni's reagent II and then react with **A** to generate **D**. Moreover, the reaction of a $^{\bullet}CF_3$ radical with the alkene to generate a new carbon radical or cation, which is then trapped by the carbamate, cannot be excluded at this time.

While 2-oxazolidones are valuable in their own right, Scheme 1 details their role as a starting material for several notable transformations. Firstly, the conversion of **1a** under our reaction conditions is amenable to scale-up to gram quantities with comparable yield and efficiency (Scheme 1a).



Scheme 1. Gram-scale synthesis and transformations of **2a**. See the Supporting Information for details.

Secondly, the reaction of **2a** with an allyl Grignard reagent afforded the amide **3** in high yield, while reaction with $LiAlH_4$ provided the privileged amino alcohol **4**. Moreover, the reaction with NaOH gave the CF_3-containing allylamines **5** and **5′**, most likely by elimination/decarboxylation, in good yield and as a mixture of alkene isomers.

In summary, we have developed a novel, versatile, and straightforward copper-catalyzed difunctionalization of allylamines to generate important CF_3-containing 2-oxazolidones. CO_2 plays a vital role in tuning the reaction from amino- to oxy-trifluoromethylation with excellent chemoselectivity, regioselectivity, and diastereoselectivity. This multicomponent reaction is scalable and shows broad substrate scope and functional-group compatibility under redox-neutral and mild reaction conditions. Important products could also be formed with either spirocycles or two adjacent tetrasubstituted carbon centers. Facile product diversification and the generation of $^{\bullet}CF_3$ radical in the reaction have been demonstrated.

Acknowledgments

We thank the "1000-Youth Talents Plan", a Start-up Grant from Sichuan University, the "973" Project from the MOST of China (2015CB856600), and the National Natural Science Foundation of China (21502124) for financial support. We thank Prof. Jason J. Chruma (Sichuan University) for helpful manuscript revisions. We also thank the comprehensive training platform of the Specialized Laboratory in the College of Chemistry at Sichuan University for compound testing.

Keywords: carbon dioxide · copper · fluorine · heterocycles · reaction mechanisms

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10022–10026
Angew. Chem. **2016**, *128*, 10176–10180

[1] a) P. Jeschke, *ChemBioChem* **2004**, *5*, 570; b) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881; c) W. K. Hagmann, *J. Med. Chem.* **2008**, *51*, 4359; d) S. Swallow, *Prog. Med. Chem.* **2015**, *54*, 65.

[2] For recent reviews, see: a) O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, *111*, 4475; b) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470; c) H. Amii, *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 752; d) A. Studer, *Angew. Chem. Int. Ed.* **2012**, *51*, 8950; *Angew. Chem.* **2012**, *124*, 9082; e) X.-F. Wu, H. Neumann, M. Beller, *Chem. Asian J.* **2012**, *7*, 1744; f) Y. Ye, M. S. Sanford, *Synlett* **2012**, 2005; g) P. Chen, G. Liu, *Synthesis* **2013**, 2919; h) L. Chu, F.-L. Qing, *Acc. Chem. Res.* **2014**, *47*, 1513; i) H. Egami, M. Sodeoka, *Angew. Chem. Int. Ed.* **2014**, *53*, 8294; *Angew. Chem.* **2014**, *126*, 8434; j) J. Charpentier, N. Früh, A. Togni, *Chem. Rev.* **2015**, *115*, 650; k) C. Alonso, E. M. de Marigorta, G. Rubiales, F. Palacios, *Chem. Rev.* **2015**, *115*, 1847.

[3] For recent examples, see: a) D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 10875; b) A. T. Parsons, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 9120; *Angew. Chem.* **2011**, *123*, 9286; c) J. Xu, Y. Fu, D.-F. Luo, Y.-Y. Jiang, B. Xiao, Z.-J. Liu, T.-J. Gong, L. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 15300; d) X. Wang, Y. Ye, S. Zhang, J. Feng, Y. Xu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 16410; e) X. Jiang, L. Chu, F.-L. Qing, *Org. Lett.* **2012**, *14*, 2870; f) A. T. Herrmann, L. L. Smith, A. Zakarian, *J. Am. Chem. Soc.* **2012**, *134*, 6976; g) Q.-H. Deng, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2012**, *134*, 10769; h) G. K. S. Prakash, P. V. Jog, P. T. D. Batamack, G. A. Olah, *Science* **2012**, *338*, 1324; i) F. Wang, X. Qi, Z. Liang, P. Chen, G. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 1881; *Angew. Chem.* **2014**, *126*, 1912.

[4] For selected examples, see: a) X. Mu, T. Wu, H.-Y. Wang, Y.-L. Guo, G. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 878; b) H. Egami, R. Shimizu, S. Kawamura, M. Sodeoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 4000; *Angew. Chem.* **2013**, *125*, 4092; c) X. Liu, F. Xiong, X. Huang, L. Xu, P. Li, X. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 6962; *Angew. Chem.* **2013**, *125*, 7100; d) H. Egami, R. Shimizu, Y. Usui, M. Sodeoka, *Chem. Commun.* **2013**, *49*, 7346; e) Z.-M. Chen, W. Bai, S.-H. Wang, B.-M. Yang, Y.-Q. Tu, F.-M. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 9781; *Angew. Chem.* **2013**, *125*, 9963; f) P. Xu, J. Xie, Q. Xue, C. Pan, Y. Cheng, C. Zhu, *Chem. Eur. J.* **2013**, *19*, 14039; g) W. Kong, M. Casimiro, E. Merino, C. Nevado, *J. Am. Chem. Soc.* **2013**, *135*, 14480; h) F. Wang, D. Wang, X. Mu, P. Chen, G. Liu, *J. Am. Chem. Soc.* **2014**, *136*, 10202; i) F. Yang, P. Klumphu, Y.-M. Liang, B. H. Lipshutz, *Chem. Commun.* **2014**, *50*, 936; j) B. Sahoo, J.-L. Li, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 11577; *Angew. Chem.* **2015**, *127*, 11740.

[5] a) W. An, N. Ha, H. M. Lee, Y. R. Malpani, D.-H. Lee, Y.-S. Jung, S. B. Han, *Adv. Synth. Catal.* **2015**, *357*, 3949; b) M. Fu, L. Chen, Y. Jiang, Z.-X. Jiang, Z. Yang, *Org. Lett.* **2016**, *18*, 348.

[6] a) Y. Li, A. Studer, *Angew. Chem. Int. Ed.* **2012**, *51*, 8221; *Angew. Chem.* **2012**, *124*, 8345; b) H. Egami, R. Shimizu, M. Sodeoka, *Tetrahedron Lett.* **2012**, *53*, 5503; c) R. Zhu, S. L. Buchwald, *J. Am. Chem. Soc.* **2012**, *134*, 12462; d) Y. Yasu, T. Koike, M. Akita, *Angew. Chem. Int. Ed.* **2012**, *51*, 9567; *Angew. Chem.* **2012**, *124*, 9705; e) C. Feng, T.-P. Loh, *Chem. Sci.* **2012**, *3*, 3458; f) P. G. Janson, I. Ghoneim, N. O. Ilchenko, K. J. Szabó, *Org. Lett.* **2012**, *14*, 2882; g) R. Zhu, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2013**, *52*, 12655; *Angew. Chem.* **2013**, *125*, 12887; h) D.-F. Lu, C.-L. Zhu, H. Xu, *Chem. Sci.* **2013**, *4*, 2478; i) E. Kim, S. Choi, H. Kim, E. J. Cho, *Chem. Eur. J.* **2013**, *19*, 6209; j) Y.-T. He, L.-H. Li, Y.-F. Yang, Y.-Q. Wang, J.-Y. Luo, X.-Y. Liu, Y.-M. Liang, *Chem. Commun.* **2013**, *49*, 5687; k) Q. Yu, S. Ma, *Chem. Eur. J.* **2013**, *19*, 13304; l) X.-Y. Jiang, F.-L. Qing, *Angew. Chem. Int. Ed.* **2013**, *52*, 14177; *Angew. Chem.* **2013**, *125*, 14427; m) H. Egami, R. Shimizu, Y. Usui, M. Sodeoka, *J. Fluorine Chem.* **2014**, *167*, 172.

[7] a) H. Egami, S. Kawamura, A. Miyazaki, M. Sodeoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 7841; *Angew. Chem.* **2013**, *125*, 7995; b) Y. Yasu, T. Koike, M. Akita, *Org. Lett.* **2013**, *15*, 2136; c) J.-S. Lin, Y.-P. Xiong, C.-L. Ma, L.-J. Zhao, B. Tan, X.-Y. Liu, *Chem. Eur. J.* **2014**, *20*, 1332; d) J.-S. Lin, X.-G. Liu, X.-L. Zhu, B. Tan,

X.-Y. Liu, *J. Org. Chem.* **2014**, *79*, 7084; e) S. Kawamura, H. Egami, M. Sodeoka, *J. Am. Chem. Soc.* **2015**, *137*, 4865; f) K. Shen, Q. Wang, *Org. Chem. Front.* **2016**, *3*, 222.

[8] a) T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365; b) D. M. D′Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058; *Angew. Chem.* **2010**, *122*, 6194; c) K. Huang, C.-L. Sun, Z.-J. Shi, *Chem. Soc. Rev.* **2011**, *40*, 2435; d) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510; *Angew. Chem.* **2011**, *123*, 8662; e) Z.-Z. Yang, Y.-N. Zhao, L.-N. He, *RSC Adv.* **2011**, *1*, 545; f) X. Han, M. Poliakoff, *Chem. Soc. Rev.* **2012**, *41*, 1428; g) L. Zhang, Z. Hou, *Pure Appl. Chem.* **2012**, *84*, 1705; h) L. Zhang, Z. Hou, *Chem. Sci.* **2013**, *4*, 3395;i) N. Kielland, C. J. Whiteoak, A. W. Kleij, *Adv. Synth. Catal.* **2013**, *355*, 2115; j) M. He, Y. Sun, B. Han, *Angew. Chem. Int. Ed.* **2013**, *52*, 9620; *Angew. Chem.* **2013**, *125*, 9798; k) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709; l) C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482; m) D. Yu, S. P. Teong, Y. Zhang, *Coord. Chem. Rev.* **2015**, *293 – 294*, 279; n) B. Yu, L.-N. He, *ChemSusChem* **2015**, *8*, 52; o) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353; p) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933.

[9] a) K. Sasano, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2013**, *135*, 10954; b) Z. Zhang, L.-L. Liao, S.-S. Yan, L. Wang, Y.-Q. He, J.-H. Ye, J. Li, Y.-G. Zhi, D.-G. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 7068; *Angew. Chem.* **2016**, *128*, 7184.

[10] *Oxazolidinones—Advances in Research and Application* (Ed.: Q. A. Acton), Scholarly Editions, Atlanta, **2012**.

[11] For reviews, see: a) *Oxazoles*: *Synthesis Reactions, and Spectroscopy* (Ed.: D. C. Palmer), Wiley, Hoboken, **2003**; b) Z.-Z. Yang, L.-N. He, J. Gao, A.-H. Liu, B. Yu, *Energy Environ. Sci.* **2012**, *5*, 6602; For selected examples, see: c) T. Toda, Y. Kitagawa, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 334; *Angew. Chem.* **1987**, *99*, 366; d) S. Pulla, C. M. Felton, P. Ramidi, Y. Gartia, N. Ali, U. B. Nasini, A. Ghosh, *J. CO_2 Util.* **2013**, *2*, 49; e) K. Yamashita, S. Hase, Y. Kayaki, T. Ikariya, *Org. Lett.* **2015**, *17*, 2334; f) J. R. Khusnutdinova, J. A. Garg, D. Milstein, *ACS Catal.* **2015**, *5*, 2416.

[12] C. Pooput, W. R. Dolbier, M. Médebielle, *J. Org. Chem.* **2006**, *71*, 3564.

[13] V. Matousek, E. Pietrasiak, R. Schwenk, A. Togni, *J. Org. Chem.* **2013**, *78*, 6763, and references therein.

[14] a) R. C. Larock, *Comprehensive Organic Transformations*: *A Guide to Functional Group Preparations*, VCH, New York, **1989**; b) *Metal-Catalyzed Cross-Coupling Reactions and More* (Eds.: A. de Meijere, S. Bräse, M. Oestreich), Wiley-VCH, Weinheim, **2014**.

[15] Y. Ji, T. Brueckl, R. D. Baxter, Y. Fujiwara, I. B. Seiple, S. Su, D. G. Blackmond, P. S. Baran, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 14411.

[16] CCDC 1478850 (**2ae**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: April 6, 2016
Published online: July 14, 2016

