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Pd-Catalyzed Diastereoselective Trifluoromethylthiolation of Functionalized Acrylamides

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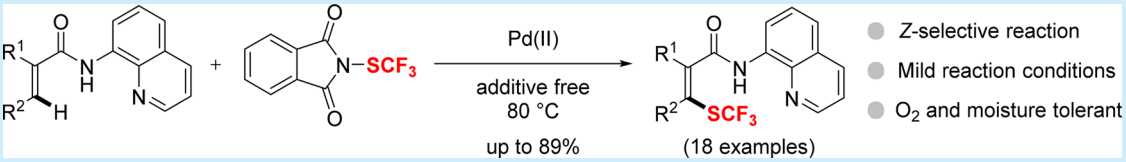
Supporting Information



ABSTRACT: The Pd-catalyzed diastereoselective trifluoromethylthiolation of acrylamides was developed to allow the formation of the *Z*-isomer as a single product. Using a C−H bond functionalization strategy, the method was applied to a broad range of *α*-aryl, *α*-alkyl, and *α*,*β*-disubstituted acrylamides bearing the amide derived from the 8-aminoquinoline as a directing group. Mechanistic studies as well as postfunctionalization of the products were performed. This approach opens new routes to unprecedented SCF_3-containing scaffolds.

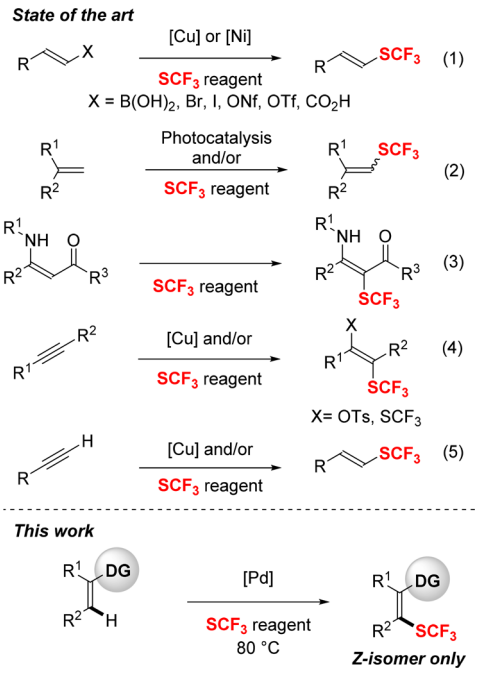
Organofluorine chemistry currently appears to be an essential research field from both an academic and industrial point of view.[1] The unique features of the fluorine atom and its ability to modulate the properties of the molecules make this atom and more generally the fluorinated groups highly attractive.[2] Consequently, the quest for efficient methodologies for their incorporation, the discovery of new fluorinated groups, and the will to tackle original synthetic challenges are desirable and inspire the scientific community to develop new tools.[3]

Over the years, special interest was focused toward the emergent SCF_3 group.[4] Indeed, this motif showcased interesting properties such as its high electron-withdrawing character[5] as well as a particular and unique Hansch hydrophobic parameter (π = 1.44).[6] These features afforded specific biological activities to the molecules bearing this motif as illustrated with Fipronil, Toltrazuril, and Tiflorex, for instance. Therefore, the interest to develop efficient synthetic methodologies to introduce this motif rapidly increased over the past five years.[7] Although most of the reported methods relied on the functionalization of aromatic derivatives, the access to trifluoromethylthiolated olefinic derivatives remains scarce.

From pioneering work by Harris in 1972,[8] various strategies were recently developed to synthesize vinyl trifluoromethylthioethers. The copper-catalyzed or -mediated trifluoromethylthiolation of vinyl boronic acids,[9] vinyl halides,[10] and pseudo halides[11] using either a nucleophilic or an electrophilic SCF_3 reagent was depicted by several research groups such as Vicic, Shibata, Billard, Lu and Shen, Rueping and Weng, among others (Scheme 1, eq 1). In these cases, the stereochemistry of the products resulted from the stereochemistry of the starting material. Recently, a decarboxylative trifluoromethylthiolation of cinnamic acids mediated by copper and using $AgSCF_3$ as the SCF_3 source was reported leading mainly to the *E*-isomer.[12]

To avoid the use of functionalized substrates, Glorius reported a photocatalyzed trifluoromethylthiolation of terminal alkenes

Scheme 1. State of the Art and Present Work



using the Munavalli reagent with moderate to high selectivity toward the *E*-isomer (Scheme 1, eq 2).[13a] The same year, the group of Shen developed a trifluoromethylthiolation of styrenes using the *N*-trifluoromethylthiodibenzenesulfonimide as the electrophilic SCF_3 source (Scheme 1, eq 2).[13b] Alternatively, SCF_3-containing olefins were also prepared from enamines[14]

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Org. Lett. XXXX, XXX, XXX−XXX

(Scheme 1, eq 3) and also alkynes,[15] albeit limited to a few reports. In the last case, the difunctionalization of internal alkynes was independently developed by the group of Billard[15a] and Qing[15b] (Scheme 1, eq 4), and more recently, Cao[15c] reported the hydrotrifluoromethylthiolation of terminal alkynes (Scheme 1, eq 5). Quite surprisingly, no method for the selective formation of the *Z*-trifluoromethylthiolated alkenes was reported to date.

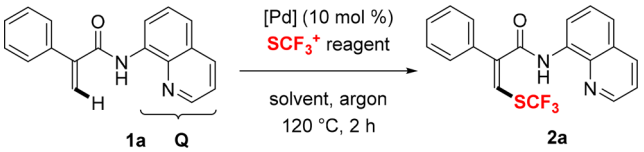
Over the past decade, the transition metal catalyzed C−H bond functionalization appeared to be a powerful tool in performing selective and atom economical transformations.[16] Among the targeted substrates, versatile olefins are challenging compounds for C−H bond activation.[16g] Indeed, olefins are prompt to undergo polymerization and required specific conditions to be functionalized according to a C−H bond activation event. When taking into account these considerations, the direct introduction of the SCF_3 moiety through a transition metal catalyzed direct $C(sp^2)$−H functionalization would be highly valuable in offering an access to the difficult-to-synthesize *Z*-olefins, which still represents a synthetic challenge.

In recent years, our group focused on merging transition metal catalyzed C−H bond activation and organofluorine chemistry to build original fluorinated scaffolds.[17] Hence, we anticipated that the use of a suitable directing group (DG) would allow the selective formation of the challenging *Z*-SCF_3-containing olefins. Herein, we report the first Pd-catalyzed direct *β*-trifluoromethylthiolation of *α*- and *α,β*-functionalized acrylamides by C−H bond functionalization.

At the outset of this study, the trifluoromethylthiolation reaction was conducted with the acrylamide **1a** derived from the 8-aminoquinoline and an equimolar amount of the Munavalli reagent **I** as the electrophilic SCF_3 source (Table 1). When the reaction was carried out using 10 mol % of $PdCl_2$ as a catalyst in DCE at 120 °C, no expected product was detected (Table 1, entry 1). To our delight, the replacement of DCE by DMF led to a complete conversion of **1a** and the expected product **2a** was obtained as a single *Z*-isomer in an almost quantitative NMR yield and 74% isolated yield (Table 1, entry 2). Remarkably, the transformation was fully selective toward the formation of the *Z*-isomer as confirmed by 2D NMR experiments.[18] Note that other solvents such as toluene and 1,4-dioxane were inefficient, as no trace of **2a** was found (Table 1, entries 3 and 4). Moreover, the reaction was not sensitive to water, since its use as cosolvent with DMF (1:9 ratio) allowed the formation of **2a** in 60% NMR yield (Table 1, entry 5). Then, various Pd-catalysts were evaluated. A total shut down of the reaction was generally observed (Table 1, entries 6−8), except in the case of $PdBr_2$ (Table 1, entry 9), which afforded **2a** in 93% NMR yield. Interestingly, other electrophilic sources were also suitable such as the Haas (**II**) and the Billard (**III**) reagents,[4d] furnishing the expected product **2a**, albeit in lower NMR yields (Table 1, entries 10 and 11). Finally, the reaction temperature was investigated. Pleasingly, the transformation proceeded smoothly at 80 °C for 14 h under air, giving a robust and straightforward access to **2a** under mild conditions in 99% NMR yield and 78% isolated yield (Table 1, entry 12). Note that all the other directing groups tested within the course of this optimization led to no reaction.[18]

With the best conditions in hand, the scope of the reaction was investigated (Scheme 2). A panel of various *α*-aryl-substituted acrylamides was functionalized in good to high yields. In all cases, the monotrifluoromethylthiolation reaction on the olefin occurred and no product resulting from the side functionalization of the quinoline part at the C5 position has been detected.

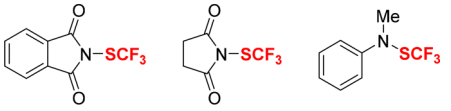
Table 1. Optimization of the Reaction Conditions[a]



1a Q 2a

entry	[Pd]	SCF_3^+ reagent	solvent	yield (%)[b]
1	$PdCl_2$	**I**	DCE	NR
2	$PdCl_2$	**I**	DMF	99 (74)[c]
3	$PdCl_2$	**I**	toluene	NR
4	$PdCl_2$	**I**	1,4-dioxane	NR
5[d]	$PdCl_2$	**I**	DMF/H_2O	60
6	$Pd(OAc)_2$	**I**	DMF	NR
7	$Pd(TFA)_2$	**I**	DMF	NR
8	$Pd(acac)_2$	**I**	DMF	NR
9	$PdBr_2$	**I**	DMF	93
10	$PdCl_2$	**II**	DMF	91
11	$PdCl_2$	**III**	DMF	70
12[e]	**$PdCl_2$**	**I**	**DMF**	**99 (78)**[c]

[a]Reaction conditions: **1a** (0.1 mmol), SCF_3^+ reagent (0.1 mmol), [Pd] (10 mol %), solvent (1 mL), 120 °C, 2 h, argon. [b]Yields were determined by ^{19}F NMR using *α,α,α*-trifluoroacetophenone as an internal standard. [c]Reaction run on 0.2 mmol; isolated yield. [d]DMF/H_2O (9:1) was used as a solvent. [e]Reaction was carried out at 80 °C under air for 14 h. NR: no reaction.



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In addition, the scale of the reaction was increased to 2 mmol, demonstrating the synthetic utility of the process. The reaction was tolerant to aromatic rings substituted with electron-donating (OMe, *t*Bu, and Ph) (**2b−d**, **2h**, and **2k**) and electron-withdrawing groups (CF_3) (**2i**). Note that, in the case of compound **2c**, the stereochemistry of the olefin was unambiguously ascertained through X-ray crystallographic analysis.[18] Interestingly, olefins bearing a halogen on the aromatic ring (Cl, Br, and I) were suitable substrates (**1e−g**, **1j**, **1l**), with the halogen being intact at the end of the transformation allowing further functionalization by cross-coupling reactions, for instance. The substitution patterns on the aromatic ring did not affect the outcome of the reaction as demonstrated for instance in the case of an aromatic bearing a methoxy group (**2b**, **2h**, and **2k**) or a chlorine atom (**2e**, **2j**, and **2l**). The scope of this transformation was extended to the *α*-naphtyl-substituted olefin, and the desired product **2m** was obtained in an excellent 85% yield. Then, acrylamides bearing a disubstituted aromatic motif at the *α*-position were tested. Dichloride and dioxolane derivatives **1n** and **1o** furnished the corresponding products **2n** and **2o** in 77% and 62% yields, respectively. Due to the high interest of pyridine derivatives in medicinal and agrochemistry, **1p** was reacted under our standard conditions. Pleasingly, the reaction afforded the SCF_3-containing olefin **2p** in a moderate 49% yield.

Finally, the functionalization of an acrylamide bearing a methyl at the *α*-position was investigated. To our delight, using 30 mol % of $PdCl_2$ and 2 equiv of **I**, the expected product **2q** was isolated in 30% yield, without isomerization of the double bond. This approach was also extended to the more challenging *α,β*-disubstituted olefin **1r**. The corresponding tetrasubstituted acrylamide **2r** was successfully functionalized, albeit in a low

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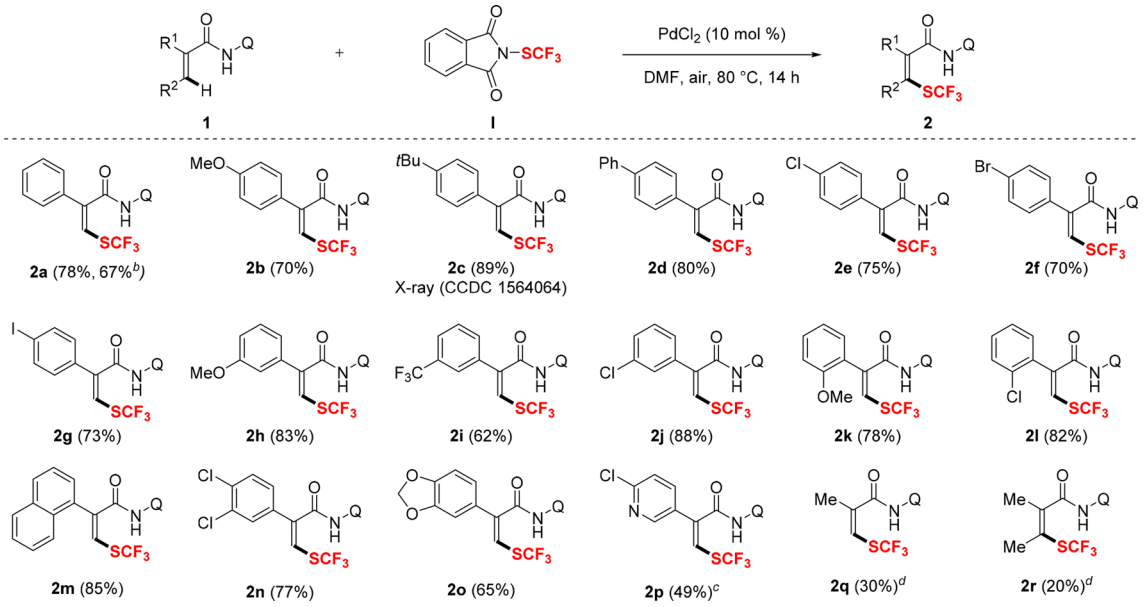
Scheme 2. Substrate Scope[a]

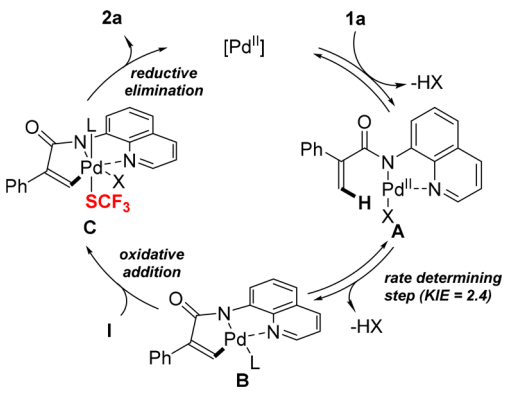


[a]**1** (0.2 mmol), **I** (0.2 mmol), $PdCl_2$ (0.02 mmol), DMF (2 mL), 80 °C, 14 h; isolated yields were given. [b]Reaction was performed on a 2 mmol scale. [c]Reaction was carried out with 20 mol % of $PdCl_2$ and 2 equiv of **I** for 36 h. [d]30 mol % of $PdCl_2$ and 2 equiv of **I** were used. Q = 8-quinolyl.

yield, showcasing the potential of this approach toward the synthesis of fully decorated trifluoromethylthiolated alkenes with complete control of the geometry.

To gain a better understanding of the reaction mechanism, additional experiments with isotopically labeled olefins were performed.[18] Scrambling experiments revealed a H/D exchange suggesting that the C−H bond activation step is reversible. Therefore, a kinetic isotopic effect (KIE) experiment was performed using **1a** and [D]-**1a** in parallel reactions.[18] A KIE value of 2.4 was determined, indicating that the C−H bond activation event was the rate-determining step. In light of these results and the literature data,[16] a plausible mechanistic pathway has been proposed (Scheme 3). First, intermediate **A** resulted

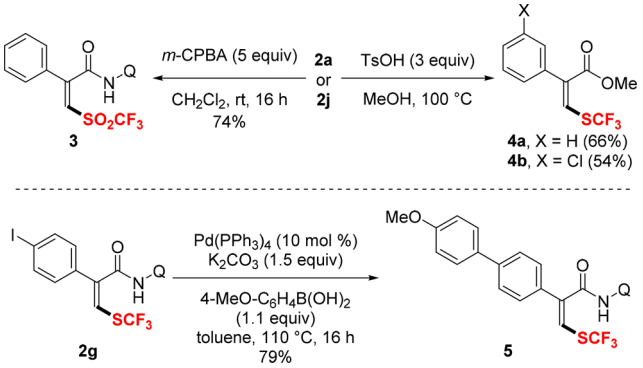
Scheme 3. Proposed Catalytic Cycle



from the coordination of the catalyst to the bidentate directing group from **1a**. Then, the formation of the metallacycle occurred in a reversible fashion leading to the intermediate **B**. Subsequently, it underwent an oxidative addition with the electrophilic SCF_3-source **I** to afford a putative Pd(IV) species **C**. Finally, a reductive elimination regenerated the catalyst and furnished the product **2a**.

Then, the synthetic value of the approach was further demonstrated by offering an efficient access to another high-value added fluorinated group, the SO_2CF_3 residue (Scheme 4).

Scheme 4. Post-functionalization Reactions



In the presence of *m*-CPBA, the SCF_3 group was selectively oxidized into the corresponding sulfone **3** in a good yield (74%). Moreover, the removal of the 8-aminoquinoline group on **2a** and **2j** was realized in the presence of *para*-toluenesulfonic acid in methanol leading to the corresponding esters **4a** and **4b** in 66% yield and 54% yield, respectively (Scheme 4). Finally, when **2g** was engaged in a Suzuki cross-coupling reaction with the *para*-methoxy phenyl boronic acid, **5** was selectively obtained in a high yield, without any alteration of the olefinic part.

In conclusion, we have developed a novel synthetic approach for the synthesis of trifluoromethylthiolated olefins with complete control of the selectivity. The *Z*-isomers were obtained in good to excellent yields under mild conditions. The depicted process is robust, straightforward, operationally simple, and air and moisture tolerant. An array of functionalized acrylamides featuring different substitution patterns (α-substituted and α,β-disubstituted olefins) as well as various functional groups was efficiently trifluoromethylthiolated by a Pd-catalyzed directed C−

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H bond functionalization. A plausible Pd(II)/Pd(IV) reaction mechanism was suggested. This transformation provided an access to new fluorinated building blocks, inaccessible to this point.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02384.

Procedures, characterization data, ^{1}H, ^{13}C, and ^{19}F NMR spectra, and characterization data for the X-ray crystal structure of **2c** (CCDC 1564064) (PDF)

Crystallographic data for **2c** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. *Chem. Rev.* **2014**, *114*, 2432. (b) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (c) Gillis, E. P.; Eastman, K. J.; Hill, M. D.; Donnelly, D. J.; Meanwell, N. A. *J. Med. Chem.* **2015**, *58*, 8315. (d) Ilardi, E. A.; Vitaku, E.; Njardarson, J. T. *J. Med. Chem.* **2014**, *57*, 2832.

(2) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308.

(3) (a) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214. (b) Ni, C.; Hu, J. *Chem. Soc. Rev.* **2016**, *45*, 5441. (c) Landelle, G.; Panossian, A.; Leroux, F. *Curr. Top. Med. Chem.* **2014**, *14*, 941. (d) Landelle, G.; Panossian, A.; Pazenok, S.; Vors, J.-P.; Leroux, F. R. *Beilstein J. Org. Chem.* **2013**, *9*, 2476. (e) Champagne, P. A.; Desroches, J.; Hamel, J.-D.; Vandamme, M.; Paquin, J.-F. *Chem. Rev.* **2015**, *115*, 9073. (f) Merino, E.; Nevado, C. *Chem. Soc. Rev.* **2014**, *43*, 6598. (g) Egami, H.; Sodeoka, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 8294. (h) Belhomme, M.-C.; Besset, T.; Poisson, T.; Pannecoucke, X. *Chem. - Eur. J.* **2015**, *21*, 12836. (i) Besset, T.; Poisson, T.; Pannecoucke, X. *Chem. - Eur. J.* **2014**, *20*, 16830.

(4) (a) Toulgoat, F.; Alazet, S.; Billard, T. *Eur. J. Org. Chem.* **2014**, *2014*, 2415. (b) Xu, X.-H.; Matsuzaki, K.; Shibata, N. *Chem. Rev.* **2015**, *115*, 731. (c) Barata-Vallejo, S.; Bonesi, S.; Postigo, A. *Org. Biomol. Chem.* **2016**, *14*, 7150. (d) Li, M.; Guo, J.; Xue, X.-S.; Cheng, J.-P. *Org. Lett.* **2016**, *18*, 264.

(5) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(6) Hansch, C.; Leo, A.; Unger, S. H.; Kim, K. H.; Nikaitani, D.; Lien, E. J. *J. Med. Chem.* **1973**, *16*, 1207.

(7) For selected examples, see: (a) Alazet, S.; Zimmer, L.; Billard, T. *Chem. - Eur. J.* **2014**, *20*, 8589. (b) Exner, B.; Bayarmagnai, B.; Jia, F.; Goossen, L. J. *Chem. - Eur. J.* **2015**, *21*, 17220. (c) Hu, M.; Rong, J.; Miao, W.; Ni, C.; Han, Y.; Hu, J. *Org. Lett.* **2014**, *16*, 2030. (d) Hu, F.; Shao, X.-X.; Zhu, D.-H.; Lu, L.; Shen, Q. *Angew. Chem., Int. Ed.* **2014**, *53*, 6105. (e) Liu, J.-B.; Xu, X.-H.; Chen, Z.-H.; Qing, F.-L. *Angew. Chem., Int. Ed.* **2015**, *54*, 897. (f) Yang, T.; Lu, L.; Shen, Q. *Chem. Commun.* **2015**, *51*, 5479. (g) Ye, K.-Y.; Zhang, X.; Dai, L.-X.; You, S.-L. *J. Org. Chem.* **2014**, *79*, 12106. (h) Huang, Z.; Yang, Y.-D.; Tokunaga, E.; Shibata, N. *Org. Lett.* **2015**, *17*, 1094. (i) Danoun, G.; Bayarmagnai, B.; Gruenberg, M. F.; Goossen, L. J. *Chem. Sci.* **2014**, *5*, 1312. (j) Zhang, K.; Liu, J.-B.; Qing, F.-L. *Chem. Commun.* **2014**, *50*, 14157. (k) Jiang, L.; Qian, J.; Yi, W.; Lu, G.; Cai, C.; Zhang, W. *Angew. Chem., Int. Ed.* **2015**, *54*, 14965. (l) Yang, Y.; Xu, L.; Yu, S.; Liu, X.; Zhang, Y.; Vicic, D. A. *Chem. - Eur. J.* **2016**, *22*, 858. (m) Candish, L.; Pitzer, L.; Gomez-Suarez, A.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 4753. (n) Tran, L. D.; Popov, I.; Daugulis, O. *J. Am. Chem. Soc.* **2012**, *134*, 18237. (o) Xu, C.; Shen, Q. *Org. Lett.* **2014**, *16*, 2046. (p) Chen, C.; Xu, X.-H.; Yang, B.; Qing, F.-L. *Org. Lett.* **2014**, *16*, 3372. (q) Yin, W.; Wang, Z.; Huang, Y. *Adv. Synth. Catal.* **2014**, *356*, 2998. (r) Wang, Q.; Xie, F.; Li, X. *J. Org. Chem.* **2015**, *80*, 8361. (s) Liu, X.-G.; Li, Q.; Wang, H. *Adv. Synth. Catal.* **2017**, *359*, 1942. (t) Guo, S.; Zhang, X.; Tang, P. *Angew. Chem., Int. Ed.* **2015**, *54*, 4065. (u) Wu, H.; Xiao, Z.; Wu, J.; Guo, Y.; Xiao, J.-C.; Liu, C.; Chen, Q.-Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 4070. (v) Bu, M.; Lu, G.; Cai, C. *Org. Chem. Front.* **2017**, *4*, 266.

(8) Harris, J. F., Jr. *J. Org. Chem.* **1972**, *37*, 1340.

(9) (a) Zhang, C.-P.; Vicic, D. A. *Chem. - Asian J.* **2012**, *7*, 1756. (b) Shao, X.; Wang, X.; Yang, T.; Lu, L.; Shen, Q. *Angew. Chem., Int. Ed.* **2013**, *52*, 3457. (c) Pluta, R.; Nikolaienko, P.; Rueping, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 1650. (d) Kang, K.; Xu, C.; Shen, Q. *Org. Chem. Front.* **2014**, *1*, 294. (e) Arimori, S.; Takada, M.; Shibata, N. *Dalton Trans.* **2015**, *44*, 19456. (f) Glenadel, Q.; Alazet, S.; Tlili, A.; Billard, T. *Chem. - Eur. J.* **2015**, *21*, 14694.

(10) (a) Rueping, M.; Tolstoluzhsky, N.; Nikolaienko, P. *Chem. - Eur. J.* **2013**, *19*, 14043. (b) Zhu, P.; He, X.; Chen, X.; You, Y.; Yuan, Y.; Weng, Z. *Tetrahedron* **2014**, *70*, 672. (c) Huang, Y.; Ding, J.; Wu, C.; Zheng, H.; Weng, Z. *J. Org. Chem.* **2015**, *80*, 2912. (d) Hou, C.; Lin, X.; Huang, Y.; Chen, Z.; Weng, Z. *Synthesis* **2015**, *47*, 969.

(11) Dürr, A. B.; Yin, G.; Kalvet, I.; Napoly, F.; Schoenebeck, F. *Chem. Sci.* **2016**, *7*, 1076.

(12) Pan, S.; Huang, Y.; Qing, F.-L. *Chem. - Asian J.* **2016**, *11*, 2854.

(13) (a) Honeker, R.; Garza-Sanchez, R. A.; Hopkinson, M. N.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 4395. (b) Zhang, P.; Li, M.; Xue, X.-S.; Xu, C.; Zhao, Q.; Liu, Y.; Wang, H.; Guo, Y.; Lu, L.; Shen, Q. *J. Org. Chem.* **2016**, *81*, 7486.

(14) (a) Bu, M.-J.; Lu, G.-P.; Cai, C. *Org. Chem. Front.* **2017**, *4*, 266. (b) Yang, Y.-D.; Azuma, A.; Tokunaga, E.; Yamasaki, M.; Shiro, M.; Shibata, N. *J. Am. Chem. Soc.* **2013**, *135*, 8782.

(15) (a) Ferry, A.; Billard, T.; Langlois, B. R.; Bacqué, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8551. (b) Pan, S.; Li, H.; Huang, Y.; Xu, X.-H.; Qing, F.-L. *Org. Lett.* **2017**, *19*, 3247. (c) Wu, W.; Dai, W.; Ji, X.; Cao, S. *Org. Lett.* **2016**, *18*, 2918.

(16) For reviews, see: (a) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (b) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem. - Eur. J.* **2010**, *16*, 2654. (c) Cernak, T.; Dykstra, K. D.; Tyagarajan, S.; Vachal, P.; Krska, S. W. *Chem. Soc. Rev.* **2016**, *45*, 546. (d) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front.* **2015**, *2*, 1107. (e) Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. *Chem. Soc. Rev.* **2016**, *45*, 2900. For an issue on C−H bond activation, see: (f) Crabtree, R. H.; Lei, A. *Chem. Rev.* **2017**, *117*, 8481−9520. (g) Wang, K.; Hu, F.; Zhang, Y.; Wang, J. *Sci. China: Chem.* **2015**, *58*, 1252.

(17) (a) Xiong, H.-Y.; Besset, T.; Cahard, D.; Pannecoucke, X. *J. Org. Chem.* **2015**, *80*, 4204. (b) Besset, T.; Cahard, D.; Pannecoucke, X. *J. Org. Chem.* **2014**, *79*, 413. (c) Zhao, Q.; Tognetti, V.; Joubert, L.; Besset, T.; Pannecoucke, X.; Bouillon, J.-P.; Poisson, T. *Org. Lett.* **2017**, *19*, 2106. (d) Zhao, Q.; Besset, T.; Poisson, T.; Bouillon, J.-P.; Pannecoucke, X. *Eur. J. Org. Chem.* **2016**, *2016*, 76. (e) Belhomme, M.-C.; Bayle, A.; Poisson, T.; Pannecoucke, X. *Eur. J. Org. Chem.* **2015**, *2015*, 1719. (f) Belhomme, M.-C.; Poisson, T.; Pannecoucke, X. *J. Org. Chem.* **2014**, *79*, 7205. (g) Belhomme, M.-C.; Dru, D.; Xiong, H.-Y.; Cahard, D.; Besset, T.; Poisson, T.; Pannecoucke, X. *Synthesis* **2014**, *46*, 1859. (h) Belhomme, M.-C.; Poisson, T.; Pannecoucke, X. *Org. Lett.* **2013**, *15*, 3428.

(18) See the Supporting Information for details.

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