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Transition-Metal-Free β-C−H Bond Carbonylation of Enamides or Amides with a Trifluoromethyl Group as CO Surrogate for the Synthesis of 1,3-Oxazin-6-ones

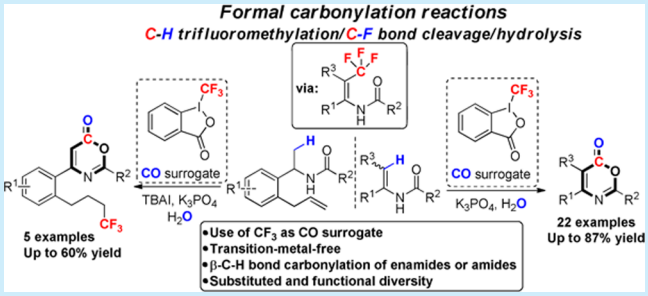
Ping Song,[†,‡,§] Peng Yu,[‡,§] Jin-Shun Lin,[‡] Yiqun Li,[*,†] Ning-Yuan Yang,[‡] and Xin-Yuan Liu[*,‡]

[†]Department of Chemistry, Jinan University, Guangzhou, Guangdong 510632, P. R. China

[‡]Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, China

Supporting Information

ABSTRACT: A cascade β-C−H bond trifluoromethylation/C(sp^3)−F bond activation/hydrolysis reaction of enamides with Togni's reagent has been disclosed. This formal C−H bond carbonylation reaction utilizes the CF_3 group as a CO surrogate to provide an efficient approach to 1,3-oxazin-6-ones in satisfactory yields. Furthermore, CF_3-containing 1,3-oxazin-6-ones could also be accessed using this method by using alkenyl *N*-ethylamides involving the functionalization of one C_{sp2}−H, one C_{sp3}−H, one C_{sp2}−H, and three C_{sp3}−F bonds. The broad substrate scope of this method enables access to synthetically or pharmaceutically important compounds, which are difficult to access by known methods.



The 1,3-oxazin-6-one frameworks have been recognized as important building blocks in a number of pharmaceuticals and biologically active molecules,[1] as exemplified by the novel lipase inhibitor cetilistat (ATL-962),[1d] salinazinone A,[1e,f] and salinazinone B[1e,f] (Figure 1). Toward this end, much attention

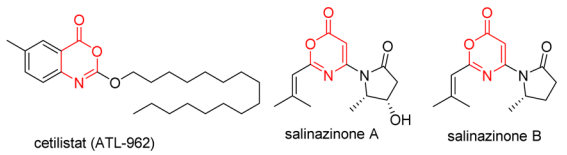
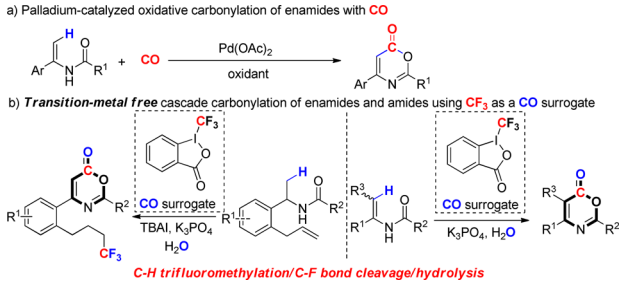


Figure 1. Representative natural products or biologically active molecules bearing a 1,3-oxazin-6-one motif.

has been recently paid to the development of new methods for their syntheses.[1c,2] One of the straightforward approaches to this structure is transition-metal-catalyzed carbonylation[3] via β-C−H bond activation of amides with carbon monoxide (CO).[2c,3d,4] In this context, Guan and co-workers have developed an elegant palladium-catalyzed oxidative carbonylation of enamides with a stoichiometric amount of $Cu(OAc)_2$ as the oxidant (Scheme 1a).[5a] Very recently, Lei and co-workers achieved a significant breakthrough by merging palladium with photoredox catalysis to enable aerobic oxidative carbonylation of enamides (Scheme 1a).[5b] Despite these advances, some crucial and challenging issues have been far from being fully addressed, such as the limited product scope with regard to only products bearing α-substituted aryl groups and the use of expensive and complex transition-metal catalysts including use of a stoichiometric amount of $Cu(OAc)_2$ as the oxidant.[5a,b] Most importantly,

Scheme 1. Carbonylation of Enamides or Amides



although carbon monoxide (CO) is well-known as one of the cheapest and most abundant C1 building blocks, its toxicity and the need for high-pressure equipment for its manipulation limited the synthetic applications of carbonylation reactions.[3] To address these challenges and circumvent the safety issue, the development of a new efficient protocol, which streamlines the access to 1,3-oxazin-6-one motifs with a wider substrate scope under mild transition-metal-free conditions using new and benign CO surrogates[6] for carbonylation reactions, would still be of meaningful importance in development of both synthetic organic and pharmaceutical chemistry.

The selective incorporation of a CF_3 group into drug molecules may give rise to significant improvement in the drug's pharmacokinetic properties, binding selectivity, and metabolic stability.[7] Among the most direct approaches for the

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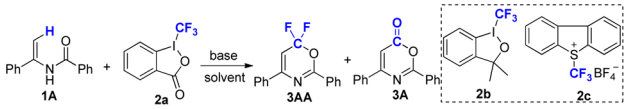
construction of C−CF_3 bonds is the direct radical C−H trifluoromethylation of various types of organic molecules by using Togni's reagent as the CF_3 radical source.[8] Contrary to the C−F or C−CF_3 bond formations, the development of novel synthetic methods for the activation or cleavage of C−F bonds has also received much attention owing to the importance of the resulting more valuable partially fluorinated or nonfluorinated organic compounds from readily available per- or oligofluorinated starting materials.[9] However, the elegant combination of direct radical C−H trifluoromethylation and selective cleavage of C−F bonds for the construction of functionally diverse heterocycles, to the best of our knowledge, still remain elusive. Encouraged by our recent success in the direct radical trifluoromethylation of β-C−H of α,β-unsaturated amides and β-C_{sp3}−H bond of amides[10] and inspired by base-mediated C−F bond activation and cleavage,[11] we became particularly interested in the development of a new and efficient protocol using Togni's reagent as a CO surrogate for carbonylation reactions. On the basis of our continuous interest in the radical-initiated chemistry,[10a,b,12] we report herein the discovery of commercially available Togni's reagent as the CO surrogate for highly efficient construction of skeletally and functionally diverse 1,3-oxazin-6-one motifs via selective β−C-H bond trifluoromethylation of enamides or amides and C(sp^3)−F bond activation/hydrolysis cascade processes under mild transition-metal-free conditions (Scheme 1b).

We began our investigation by reacting *N*-(1-phenylvinyl)-benzamide **1A** with commercially available Togni's reagent **2a**[13] in the presence of K_3PO_4 as the base, considering the fact that both the fluorine and potassium can associate strongly according to Pearson's HSAB[14] (hard and soft acids and bases) principle (Scheme 2 and Table S1). To our delight, K_3PO_4 (2.0 equiv)

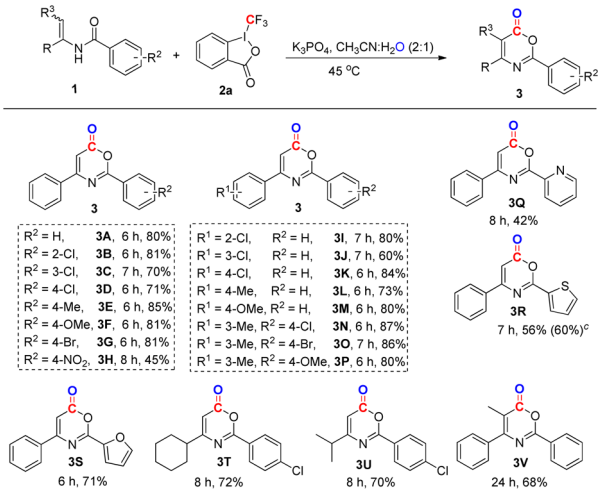
Scheme 2. Model Reaction



could activate this reaction in dichloromethane (DCM) at 80 °C to provide the corresponding difluoro-1,3-oxazine product **3AA**, albeit with 29% yield (Table S1, entry 1). Encouraged by this result, we also screened different bases (entries 2−4) and organic solvents (entries 5−9) and found that K_3PO_4 as the base in polar, nonprotic solvent CH_3CN gave the best result with 93% yield. To our disappointment, when the CF_3 reagent was changed from **2a** to **2b** or Umemoto's reagent (**2c**), no desired product was detected (entries 10 and 11). To our surprise, the difluoro-1,3-oxazine product **3AA** was partially hydrolyzed to the corresponding 1,3-oxazin-6-one **3A** during the reaction system when 5.0 equiv of water was used (entry 12). To further improve the yield of 1,3-oxazin-6-one **3A**, various reaction conditions were re-examined. Upon optimization of the conditions through variation of the K_3PO_4 loading, solvent, and reaction time (entries 13−17), the optimal reaction conditions were determined to be 5.0 equiv of K_3PO_4 with **2a** as the CF_3 source in CH_3CN/H_2O (2:1) at 45 °C for 6 h, giving 1,3-oxazin-6-one **3A** in 85% yield in a one-pot fashion (entry 14).

With the optimized conditions in hand, the substrate scope of enamides **1** with diverse substituents was next investigated. As shown in Scheme 3, the cascade reaction proceeded smoothly, irrespective of the position and electronic nature of the

Scheme 3. Substrate Scope of *N*-(1-Arylvinyl)benzamides[a,b]



[a]Reaction conditions: **1** (0.2 mmol, 1.0 equiv), Togni's reagent **2a** (1.2 equiv), K_3PO_4 (5.0 equiv), CH_3CN/H_2O (2.0 mL/1.0 mL) at 45 °C under argon. [b]Yield of the isolated product based on **1**. [c]The reaction was carried out on a 1.0 mmol scale.

substituents (R^2) on the aryl ring at the α position of the amide group, to afford the desired products in moderate to high yields. For example, various enamides, bearing either electron-donating groups (R^2 = OMe, Me) or electron-withdrawing groups (R^2 = Cl, Br, NO_2) at different positions (*ortho*, *meta* or *para*) on the aryl ring, consistently afforded the corresponding products **3A−H** in 45−85% yields. In addition, aryl enamides with chloro, methyl, and methoxyl groups on the aromatic ring at the different positions were compatible to afford **3I−P** in 60−87% yields. The structure of **3B** was determined by X-ray crystallographic analysis (Figure S1). It is encouraging to note that products that are difficult to prepare via palladium-catalyzed oxidative carbonylation of enamides,[5] such as 1,3-oxazin-6-ones containing heteroaromatic (pyridine (**3Q**), thiophene (**3R**), or furan (**3S**)) groups, can also be accessed using this method. We next turned to the very challenging aliphatic enamides to further probe the scope of the reaction. Indeed, under the current reaction system, the use of cyclohexylvinyl or isopropylvinyl substrate was compatible to form **3T** or **3U** in 72 and 70% yields, respectively. Most importantly, the α,β-disubstituted enamides **1V** also underwent this reaction to furnish the desired trisubstituted product **3V** in 68% yield. The reaction yield of **1R** was not changed when the reaction was carried out on a 1.0 mmol scale to evaluate the practicality of such process.

To expand the synthetic utility of this methodology, we next focused our attention on more challenging β-C_{sp3}−H bond functionalization-initiated formal carbonylation reaction of amides with CF_3 group as the CO surrogate. Encouraged by our recent success in phosphine-catalyzed remote β-C_{sp3}−H trifluoromethylation of amides triggered by radical trifluoromethylation of alkenes with Togni's reagent,[10b] we envisaged that such alkenyl *N*-ethylamide **4** could be used as the substrate to achieve the remote β-C_{sp3}−H bond formal carbonylation reaction of amides via a cascade sequence under the based-mediated reaction conditions. To our disappointment, treatment of *N*-(1-(2-allylphenyl)ethyl)benzamide **4A** with Togni's reagent **2a** in the presence of either K_3PO_4 or organic phosphines under otherwise identical conditions gave a low product yield (Table S2). Therefore, we surmised that the combination of organic

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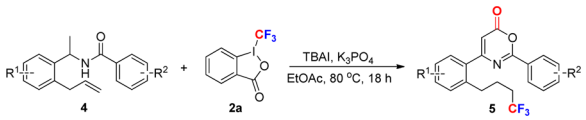
base or other single-electron-transfer (SET) reagent with inorganic base may be a suitable reaction system for the development of such a reaction. As expected, we were delighted to find that the desired product **5A** was obtained in 51% isolated yield in the presence of 20 mol % of TBAI[10a] and 4 equiv of K_3PO_4 in EtOAc after the reaction conditions were optimized through variation of the organic base or other SET reagent, inorganic base, and solvent (Table S2). The structure of **5A** was determined by X-ray crystallographic analysis (Figure S1). The electronic effect of the substituents on the phenyl ring was investigated, and the result showed that substrates bearing both electron-withdrawing and electron-donating groups afforded the CF_3-containing 1,3-oxazin-6-ones **5A**–**E** in moderate yields (49–60%) (Table 1). It is encouraging to note that the present process is a rather general protocol for the one-pot synthesis of the CF_3-containing 1,3-oxazin-6-ones from simple alkenyl *N*-ethylamides through simultaneous functionalization of one C_{sp2}–H, one C_{sp3}–H, one C_{sp2}–H, and three C_{sp3}–F bonds and selective installation of different functional groups with remarkable precision under transition-metal-free conditions.

Table 1. Reaction Scope for *N*-(1-(2-Allylphenyl)ethyl)benzamide[a]



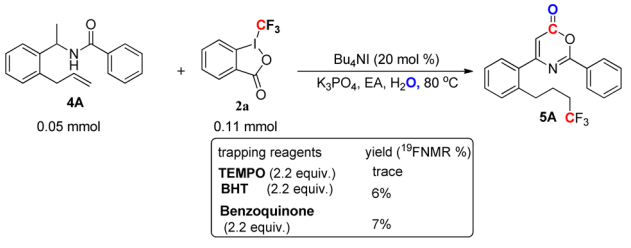
4 2a 5

entry	R^1	R^2	5	time (h)	yield[b] (%)
1	H	H	**5A**	18	51
2	H	4-Br	**5B**	18	58
3	5-Me	H	**5C**	18	60
4	4-Me	H	**5D**	18	57
5	4-Cl	H	**5E**	18	49

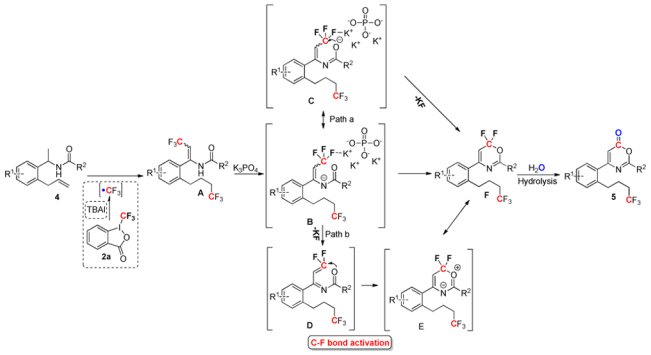
[a]Reaction conditions: **4** (0.2 mmol, 1.0 equiv), Togni's reagent **2a** (0.44 mmol, 2.2 equiv), TBAI (20 mol %), K_3PO_4 (4.0 equiv), EtOAc (3.0 mL) at 80 °C under argon. [b]Yield of the isolated product based on **4**. TBAI = tetra-*n*-butylammonium iodide.

To obtain insight into the reaction mechanism, radical-trapping experiments of **4A** were conducted by employing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), and benzoquinone under the standard conditions, respectively (Scheme 4). The reactions were found to be remarkably inhibited by these reagents, together with previous studies on radical trifluoromethylation of alkenes with Togni's reagent by organic bases,[10b,12c] suggesting that the CF_3 radical is likely involved as the reactive species under the current reaction conditions. A tentative mechanism for the reaction of alkenyl *N*-ethylamide **4** is proposed as depicted in Scheme 5. Initially, the CF_3 radical species, in situ generated from

Scheme 4. Control Experiments



Scheme 5. Mechanistic Proposal



the reaction of Togni's reagent **2a** with TBAI via a SET, attacks the alkene to afford a nascent α-CF_3-alkyl radical intermediate, followed by 1,5-H radical shift/generation of enamide/addition of CF_3 radical species to enamide to afford bistrifluoromethylated enamide **A**.[10b] For the substrate *N*-(1-arylvinyl)benzamides **1**, deprotonation of **1** in the present of K_3PO_4 could attack Togni's reagent **2a** through a Friedel–Crafts reaction to produce **A**.[10f] Then, C–F activation through the trifluoromethyl group activated by potassium ions in the presence of K_3PO_4 resulting from a beneficial C–F–K interaction[11] would generate cyclic difluoro species **F** through nucleophilic attack of the oxygen atom[11] via keto–enol tautomerization (**B** to **C**, path a), and the formation of potassium fluoride as the byproduct acts as the driving force of this reaction. Another alternative pathway (path b) was shown as follows: Intermediate **B** can be readily defluorinated to generate *gem*-difluoroalkene **D** through S_N2' reaction by amide anion. The resulting difluoroalkene **D** is then attacked by amide carbonyl group to generate a cyclic intermediate **E**, which tautomerizes to produce **F**. Hydrolysis of the CF_2 to a carbonyl group could furnish the desired 1,3-oxazin-6-one **5**.

In summary, we have successfully realized the formal carbonylation reaction of enamides with Togni's reagent as the CO surrogate via selective β-C–H bond trifluoromethylation/$C(sp^3)$–F bond activation/hydrolysis cascade processes. The overall process serves as a novel and efficient approach to 1,3-oxazin-6-one motifs in satisfactory yields, featuring a broad substrate scope with a high degree of skeletal and functional diversity. Furthermore, the newly developed one-pot protocol from alkenyl *N*-ethylamides by simultaneous functionalization of one C_{sp2}–H, one C_{sp3}–H, one C_{sp2}–H, and three C_{sp3}–F bonds provides a facile and step-economical access to valuable CF_3-containing 1,3-oxazin-6-ones.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00178.

Experimental procedures, characterization of all new compounds, Tables S1 and S2, and Figure S1 (PDF)
Crystallographic data for **3B** (CIF)
Crystallographic data for **5A** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: tlyq@jnu.edu.cn.
*E-mail: liuxy3@sustc.edu.cn.

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ORCID

Yiqun Li: 0000-0002-3303-1730
Xin-Yuan Liu: 0000-0002-6978-6465

Author Contributions

[§]P.S. and P.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Jarvest, R. L.; Parratt, M. J.; Debouck, C. M.; Gorniak, J. G.; Jennings, L. J.; Serafinowska, H. T.; Strickler, J. E. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2463. (b) Gütschow, M.; Neumann, U. *Bioorg. Med. Chem.* **1997**, *5*, 1935. (c) Neumann, U.; Schechter, N. M.; Gütschow, M. *Bioorg. Med. Chem.* **2001**, *9*, 947. (d) Kopelman, P.; Bryson, A.; Hickling, R.; Rissanen, A.; Rossner, S.; Toubro, S.; Valensi, P. *Int. J. Obes.* **2007**, *31*, 494. (e) Kim, M. C.; Lee, J. H.; Shin, B.; Subedi, L.; Cha, J. W.; Park, J.-S.; Oh, D.-C.; Kim, S. Y.; Kwon, H. C. *Org. Lett.* **2015**, *17*, 5024. (f) Fu, P.; La, S.; MacMillan, J. B. *J. Nat. Prod.* **2016**, *79*, 455.

(2) (a) Alajarín, M.; Vidal, A.; Sánchez-Andrada, P.; Tovar, F.; Ochoa, G. *Org. Lett.* **2000**, *2*, 965. (b) George, L.; Veedu, R. N.; Sheibani, H.; Taherpour, A. A.; Flammang, R.; Wentrup, C. *J. Org. Chem.* **2007**, *72*, 1399. (c) Giri, R.; Lam, J. K.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 686. (d) Houlden, C. E.; Hutchby, M.; Bailey, C. D.; Ford, J. G.; Tyler, S. N.; Gagne, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Angew. Chem., Int. Ed.* **2009**, *48*, 1830. (e) Liu, Q.; Chen, P.; Liu, G. *ACS Catal.* **2013**, *3*, 178. (f) Ge, Z.-Y.; Xu, Q.-M.; Fei, X.-D.; Tang, T.; Zhu, Y.-M.; Ji, S.-J. *J. Org. Chem.* **2013**, *78*, 4524. (g) Wu, X.-F.; Sharif, M.; Shoaib, K.; Neumann, H.; Pews-Davtyan, A.; Langer, P.; Beller, M. *Chem. - Eur. J.* **2013**, *19*, 6230. (h) Li, W.; Wu, X.-F. *J. Org. Chem.* **2014**, *79*, 10410. (i) Karad, S. N.; Chung, W.-K.; Liu, R.-S. *Chem. Sci.* **2015**, *6*, 5964.

(3) (a) Schiesser, C. H.; Wille, U.; Matsubara, H.; Ryu, I. *Acc. Chem. Res.* **2007**, *40*, 303. (b) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114. (c) Liu, Q.; Zhang, H.; Lei, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10788. (d) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986. (e) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1. (f) Wu, X.-F.; Neumann, H.; Beller, M. *ChemSusChem* **2013**, *6*, 229. (g) Sumino, S.; Fusano, A.; Fukuyama, T.; Ryu, I. *Acc. Chem. Res.* **2014**, *47*, 1563.

(4) (a) Cernak, T. A.; Lambert, T. H. *J. Am. Chem. Soc.* **2009**, *131*, 3124. (b) Li, W.; Liu, C.; Zhang, H.; Ye, K.; Zhang, G.; Zhang, W.; Duan, Z.; You, S.; Lei, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 2443. (c) Li, H.; Dong, K.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 10239. (d) Schranck, J.; Wu, X.-F.; Tlili, A.; Neumann, H.; Beller, M. *Chem. - Eur. J.* **2013**, *19*, 12959. (e) Luo, S.; Luo, F.-X.; Zhang, X.-S.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2013**, *52*, 10598. (f) Shi, R.; Lu, L.; Zhang, H.; Chen, B.; Sha, Y.; Liu, C.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 10582. (g) Yasuhara, S.; Sasa, M.; Kusakabe, T.; Takayama, H.; Kimura, M.; Mochida, T.; Kato, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3912. (h) Guan, Z.-H.; Chen, M.; Ren, Z.-H. *J. Am. Chem. Soc.* **2012**, *134*, 17490. (i) Xing, Q.; Li, F. *Topics in Heterocyclic Chemistry*; Springer: Germany, 2015.

(5) (a) Chen, M.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Angew. Chem., Int. Ed.* **2013**, *52*, 14196. (b) Liu, K.; Zou, M.; Lei, A. *J. Org. Chem.* **2016**, *81*, 7088.

(6) (a) Friis, S. D.; Lindhardt, A. T.; Skrydstrup, T. *Acc. Chem. Res.* **2016**, *49*, 594. (b) Wu, L.; Liu, Q.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 6310. (c) Li, W.; Wu, X.-F. *Adv. Synth. Catal.* **2015**, *357*, 3393. (d) Shibata, T.; Toshida, N.; Takagi, K. *J. Org. Chem.* **2002**, *67*, 7446. (e) Gehrtz, P. H.; Hirschbeck, V.; Fleischer, I. *Chem. Commun.* **2015**, *51*, 12574. (f) Gockel, S. N.; Hull, K. L. *Org. Lett.* **2015**, *17*, 3236.

(7) For selected reviews, see: (a) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (b) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (c) Nie, J.; Guo, H.-C.; Cahard, D.; Ma, J.-A. *Chem. Rev.* **2011**, *111*, 455. (d) Furuya, T.; Kamlet, A. S.; Ritter, T. *Nature* **2011**, *473*, 470. (e) Yang, X.; Wu, T.; Phipps, R. J.; Toste, F. D. *Chem. Rev.* **2015**, *115*, 826.

(8) For selected reviews on trifluoromethylation of organic compounds, see: (a) Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8950. (b) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214. (c) Chen, P.; Liu, G. *Synthesis* **2013**, *45*, 2919. (d) Studer, A.; Curran, D. P. *Nat. Chem.* **2014**, *6*, 765. (e) Chu, L.; Qing, F.-L. *Acc. Chem. Res.* **2014**, *47*, 1513. (f) Merino, E.; Nevado, C. *Chem. Soc. Rev.* **2014**, *43*, 6598. (g) Egami, H.; Sodeoka, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 8294. (h) Barata-Vallejo, S.; Lantano, B.; Postigo, A. *Chem. - Eur. J.* **2014**, *20*, 16806. (i) Charpentier, J.; Fruh, N.; Togni, A. *Chem. Rev.* **2015**, *115*, 650. (j) Gao, P.; Song, X.-R.; Liu, X.-Y.; Liang, Y.-M. *Chem. - Eur. J.* **2015**, *21*, 7648. (k) Liu, X.; Xu, C.; Wang, M.; Liu, Q. *Chem. Rev.* **2015**, *115*, 683. (l) Ni, C.; Hu, M.; Hu, J. *Chem. Rev.* **2015**, *115*, 765.

(9) (a) Stahl, T.; Klare, H. F. T.; Oestreich, M. *ACS Catal.* **2013**, *3*, 1578. (b) Kuehnel, M. F.; Lentz, D.; Braun, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 3328. (c) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119.

(10) (a) Li, L.; Guo, J.-Y.; Liu, X.-G.; Chen, S.; Wang, Y.; Tan, B.; Liu, X.-Y. *Org. Lett.* **2014**, *16*, 6032. (b) Yu, P.; Zheng, S.-C.; Yang, N.-Y.; Tan, B.; Liu, X.-Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 4041. For the other research groups for the similar works, see: (c) Feng, C.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2013**, *52*, 12414. (d) Besset, T.; Cahard, D.; Pannecoucke, X. *J. Org. Chem.* **2014**, *79*, 413. (e) Fang, Z.; Ning, Y.; Mi, P.; Liao, P.; Bi, X. *Org. Lett.* **2014**, *16*, 1522. (f) Feng, C.; Loh, T.-P. *Chem. Sci.* **2012**, *3*, 3458.

(11) (a) Ichikawa, J.; Wada, Y.; Miyazaki, H.; Mori, T.; Kuroki, H. *Org. Lett.* **2003**, *5*, 1455. (b) Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 1434. (c) Fuchibe, K.; Takahashi, M.; Ichikawa, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 12059. (d) Haufe, G.; Suzuki, S.; Yasui, H.; Terada, C.; Kitayama, T.; Shiro, M.; Shibata, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 12275. (e) Hammann, J. M.; Unzner, T. A.; Magauer, T. *Chem. - Eur. J.* **2014**, *20*, 6733. (f) Xiong, Y.; Zhang, X.; Huang, T.; Cao, S. *J. Org. Chem.* **2014**, *79*, 6395. (g) Yang, J.; Mao, A.; Yue, Z.; Zhu, W.; Luo, X.; Zhu, C.; Xiao, Y.; Zhang, J. *Chem. Commun.* **2015**, *51*, 8326. (h) Zhang, Z.; Zhou, Q.; Yu, W.; Li, T.; Wu, G.; Zhang, Y.; Wang, J. *Org. Lett.* **2015**, *17*, 2474. (i) Li, X.; Peng, S.; Li, L.; Huang, Y. *Nat. Commun.* **2015**, *6*, 6913. (j) Zhu, J.; Pérez, M.; Caputo, C. B.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2014**, *55*, 1417. (k) Dryzhakov, M.; Moran, J. *ACS Catal.* **2016**, *6*, 3670. (l) Yoshida, S.; Shimomori, K.; Kim, Y.; Hosoya, T. *Angew. Chem., Int. Ed.* **2016**, *55*, 10406.

(12) (a) Huang, L.; Lin, J.-S.; Tan, B.; Liu, X.-Y. *ACS Catal.* **2015**, *5*, 2826. (b) Yu, P.; Lin, J.-S.; Li, L.; Zheng, S.-C.; Xiong, Y.-P.; Zhao, L.-J.; Tan, B.; Liu, X.-Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 11890. (c) Yang, N.-Y.; Li, Z.-L.; Ye, L.; Tan, B.; Liu, X.-Y. *Chem. Commun.* **2016**, *52*, 9052. (d) Lin, J.-S.; Dong, X.-Y.; Li, T.-T.; Jiang, N.-C.; Tan, B.; Liu, X.-Y. *J. Am. Chem. Soc.* **2016**, *138*, 9357.

(13) Synthesis of Togni's reagent: Eisenberger, P.; Gischig, S.; Togni, A. *Chem. - Eur. J.* **2006**, *12*, 2579.

(14) Pearson, R. G. *Chemical Hardness:Applications from Molecules to Solids*; Wiley-VCH: Weinheim, 1997.

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