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Trifluoromethylation

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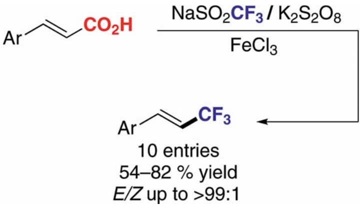

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Iron-Mediated Decarboxylative Trifluoromethylation of α,β-Unsaturated Carboxylic Acids with Trifluoromethanesulfinate

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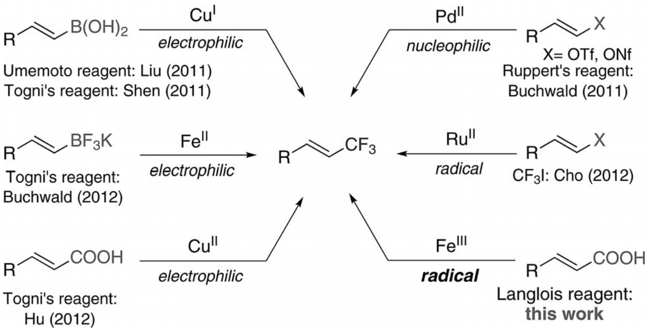
A sustainable $FeCl_3$-mediated method has been developed for the decarboxylative trifluoromethylation of α,β-unsaturated carboxylic acids by using $NaSO_2CF_3$ as an economic and stable CF_3 source. The reaction proceeds under mild condition and tolerates various functional groups. Advantageously, this method does not require an inert atmosphere and proceeds well in air at ambient temperature.

Introduction

The introduction of fluoroalkyl groups and particularly the trifluoromethyl (CF_3) group in pharmaceuticals and drug candidates can improve their physical, chemical, and biological properties because of the electronic properties, special size, lipophilicity, and metabolic stability of the trifluoromethyl group.[1] The importance of CF_3-containing molecules provides a continuing driving force for the development of more efficient and versatile trifluoromethylation methods.[1,2] Although a variety of processes for the construction of C_{sp^3}–CF_3 bonds have been developed over the last few years,[3] fewer reports are available for the construction of C_{sp^2}–CF_3 bonds.[4] Recently, rapid advances in palladium-[5] and copper-mediated[2b,3a,3d,4d,6,7] trifluoromethylation for the construction of C_{aryl}–CF_3 bonds have been observed. In comparison, transition-metal-mediated trifluoromethylation to construct C_{vinyl}–CF_3 bonds has not been well developed. Liu[8] and Shen[6d] reported the Cu^I-catalyzed electrophilic trifluoromethylation of vinylic boronic acids,[9] whereas Buchwald[10] and Cho[11] reported the nucleophilic and radical trifluoromethylation of vinyl triflates and aliphatic alkene, respectively (Scheme 1). Later, vinyl trifluoroborates[12] and vinyl carboxylic acids[13] were used for electrophilic trifluoromethylation. However, the processes of Liu and Shen suffer from lack of stereoselectivity, whereas Buchwald's procedure requires an expensive palladium catalyst. In addition, most of these methodologies rely on boronic acids or esters or a costly, relatively unstable, electrophilic trifluoromethyl source. Therefore, the development of an economic, efficient, and environmentally benign method for this transformation is highly desirable. In this respect, iron-based methods are attractive owing to the abundance and lower toxicity of iron. Thus, there is a strong incentive to develop a sustainable iron-based method for the construction of C_{vinyl}–CF_3 bonds.



Scheme 1. Metal-mediated methods for vinylic trifluoromethylation.

Consequently, we thought to develop an iron-based decarboxylative trifluoromethylation reaction to synthesize C_{vinyl}–CF_3 compounds by employing α,β-unsaturated carboxylic acids. Over the past several years, a series of decarboxylative coupling reactions have been developed by Goossen,[14] Myers,[15] Liu,[16] and others by employing carboxylic acids as stable, abundant, economic, and easily available coupling partners.[17] In this communication, we report our initial results on the $FeCl_3$-mediated decarboxylative trifluoromethylation of α,β-unsaturated carboxylic acids by employing stable and inexpensive sodium trifluoromethanesulfinate ($NaSO_2CF_3$, sodium triflinate, Langlois reagent) as a CF_3 source. The Langlois reagent has found importance in radical trifluoromethylation reactions as an economic and bench-top-stable CF_3 source.[18] The

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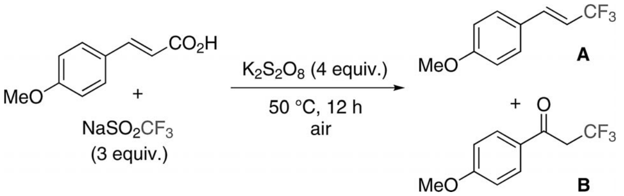
Baran[19] and Sanford[6f] groups have also utilized $NaSO_2CF_3$ for the efficient trifluoromethylation of heterocycles and aryl boronic acids.[20]

Results and Discussion

Initially decarboxylative trifluoromethylation of 4-methoxycinnamic acid was carried out by using different combinations of the radical initiator, iron source, and solvent to optimize the reaction conditions (Table 1, see also the Supporting Information). Under metal-free conditions, the best yield of (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**A**, 51%) was observed with $K_2S_2O_8$ (4 equiv.) as the radical initiator in $MeCN/H_2O$ (1:0.5 mL), and 1-(4-methoxyphenyl)-3,3,3-trifluoropropan-1-one (**B**) was obtained as a side product in 23% yield (Table 1, entry 1). With the use of di-*tert*-butyl peroxide (DTBP) as the radical initiator and other solvent combinations with water, side product **B** was not observed, but the yield of **A** decreased drastically (Table 1, entries 2, 3, 5, and 6).

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



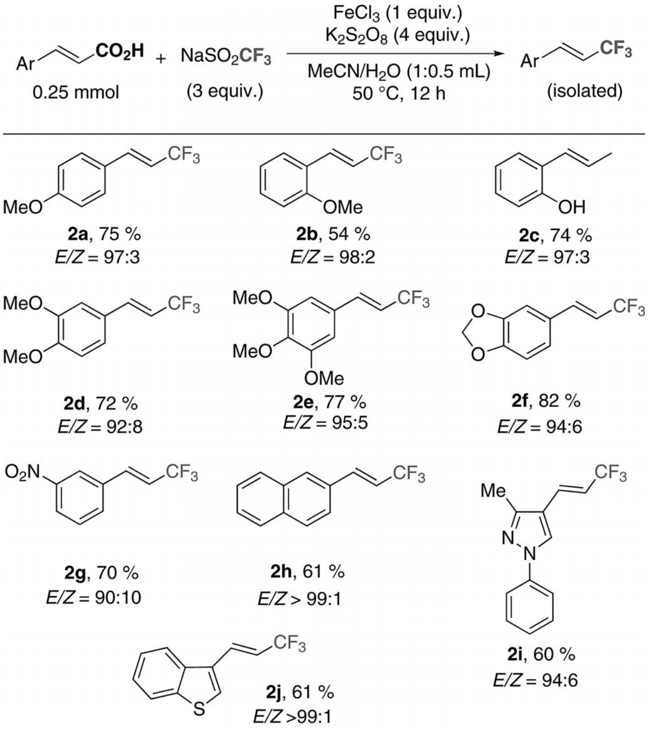
Entry	Metal source (equiv.)	Solvent	GC Yield of **A** (**B**) [%]
1	–	$MeCN/H_2O$	51 (23)
2	–	DCE/H_2O	12
3	–	DMF/H_2O	7
4	–	CH_2Cl_2/H_2O	23 (4)
5	–	TFT/H_2O	10
6	–	$MeCN/H_2O$	9[b]
7	–	$MeCN/H_2O$	12 (4)[c]
8	–	$MeCN/H_2O$	23 (6)[d]
9	$FeCl_3$ (0.2)	$MeCN/H_2O$	61 (2)
10	$FeCl_2$ (0.2)	$MeCN/H_2O$	54 (<1)
11	$FeCl_3$ (1)	$MeCN/H_2O$	76 (3)
12	$FeCl_2$ (1)	$MeCN/H_2O$	67 (4)
13	$FeSO_4\cdot 6H_2O$ (1)	$MeCN/H_2O$	13
14	$Fe(OAc)_2$ (1)	$MeCN/H_2O$	7
15	$FeBr_3$ (1)	$MeCN/H_2O$	21 (3)
16	$Fe(ClO_4)_2$ (1)	$MeCN/H_2O$	13
17	$FeCl_3$ (2)	$MeCN/H_2O$	73 (5)
18	$FeCl_2$ (2)	$MeCN/H_2O$	68 (2)
19	$FeCl_3$ (1)	$MeCN/H_2O$	63[e]
20	$FeCl_3$ (1)	$MeCN/H_2O$	52 (12)[f]
21	CuI (0.2)	$MeCN/H_2O$	28(3)
22	$CuCl_2$ (0.2)	$MeCN/H_2O$	31(2)
23	$NiCl_2$ (0.2)	$MeCN/H_2O$	29(4)

[a] Reaction conditions: 4-methoxycinnamic acid (0.2 mmol), $NaSO_2CF_3$ (0.6 mmol), $K_2S_2O_8$ (0.8 mmol), $MeCN/H_2O$ (1:0.5 mL) at 50 °C for 12 h. DCE = 1,2-dichloroethane, TFT = trifluorotoluene [b] DTBP. [c] TBHP. [d] H_2O_2 was used instead of $K_2S_2O_8$. [e] 40 °C. [f] 70 °C.

Other radical initiators including *tert*-butyl hydroperoxide (TBHP) and H_2O_2 afforded desired product **A** in much lower yield relative to that obtained with $K_2S_2O_8$ and side product **B** was also observed (Table 1, entries 7 and 8). Compound **A** was formed preferentially by using 20 mol-% of either $FeCl_3$ (reagent grade, 97%) or $FeCl_2$ (Table 1, entries 9 and 10). Finally, a stoichiometric amount of $FeCl_3$ or $FeCl_2$ further increased the yield of desired product **A** (Table 1, entries 11 and 12). A further increase in the amount of $FeCl_3$ or $FeCl_2$ had no observable effect on the yield (Table 1, entries 17 and 18).

The scope of this decarboxylative trifluoromethylation was explored with structurally diverse cinnamic acids (Table 2). Both electron-rich (i.e., **2a**–**c**,**e**,**f**) and electron-poor (i.e., **2g**,**h**) cinnamic acids were successfully trifluoromethylated, and good yields of the corresponding decarboxylative trifluoromethylated products were obtained with excellent stereoselectivity. A decrease in the yield was observed for the substrate bearing the *o*-OCH_3 substituent (i.e., product **2b**) relative to the yield obtained for the substrate bearing a *p*-OCH_3 substituent (i.e., product **2a**). The reaction proceeded with equal ease for di- and trisubstituted cinnamic acid derivatives (i.e., products **2d** and **2e**, respectively). Notably, an earlier reported iron-catalyzed reaction failed with a trisubstituted substrate.[12] Desired CF_3-containing product **2c** was obtained in good yield with an unprotected Ar–OH group, which can be useful for C–O

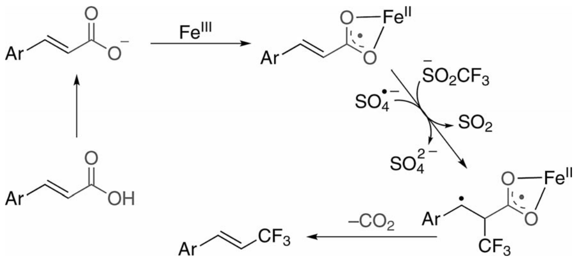
Table 2. Trifluoromethylation of α,β-unsaturated carboxylic acids.[a,b]



[a] Reaction conditions: 4-methoxycinnamic acid (0.25 mmol), $NaSO_2CF_3$ (0.75 mmol), $K_2S_2O_8$ (1 mmol), $FeCl_3$ (0.25 mmol), $MeCN/H_2O$ (1.2:0.6 mL) at 50 °C for 12 h. [b] *E*/*Z* ratios were calculated on the basis of ^{19}F NMR spectroscopy.

cross-couplings and related transformations. Further, nitrogen- and sulfur-containing heterocyclic analogues gave desired products **2i** and **2j**, respectively, in preparatively useful yields.

Presumably, the reaction starts with the generation of iron carboxylate followed by attack of the trifluoromethyl radical (Scheme 2). Finally, facile removal of CO_2 leads to the desired decarboxylative trifluoromethylated product. $FeCl_3$ is likely to assist in the elimination of CO_2.



Scheme 2. Proposed mechanism for vinylic trifluoromethylation.

Conclusions

In summary, an iron-based efficient and practical method has been developed for the decarboxylative trifluoromethylation of α,β-unsaturated carboxylic acids by using the Langlois reagent, $NaSO_2CF_3$. This reaction proceeds well for a number of substrates including heteroarylcinnamic acids and tolerates several electron-donating as well as electron-withdrawing functional groups under mild reaction conditions. A detailed study is currently ongoing in our laboratory and will be reported in due course.

Experimental Section

General Procedure for the Trifluoromethylation of α,β-Unsaturated Carboxylic Acids: The carboxylic acid (0.25 mmol), $K_2S_2O_8$ (1.0 mmol), and sodium triflinate (0.75 mmol) were placed in an oven-dried, screw cap reaction tube. A solution of $FeCl_3$ (97%, reagent grade, 0.42 M in H_2O, 0.6 mL) and MeCN (1.2 mL) were then added. The reaction tube was placed in a preheated oil bath at 50 °C and stirred vigorously for 12 h. Upon completion of the reaction, the reaction tube was allowed to reach room temperature. Diethyl ether (10 mL) and a saturated aqueous solution of NaCl (3 mL) were added, the contents were shaken vigorously, and the organic layer was separated. The aqueous layer was extracted one more time with ethyl ether (10 mL). The combined organic layer was dried with Na_2SO_4, filtered through Celite, and concentrated. The product was purified by column chromatography (EtOAc/petroleum ether).

Supporting Information (see footnote on the first page of this article): Experimental procedures; product characterization; and copies of the ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra.

Acknowledgments

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[1] a) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, Germany, **2004**; b) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, U.K., **2006**; c) K. Muller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; d) T. Furuya, A. S. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470–477; e) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; f) O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, *111*, 4475–4521; g) K. L. Kirk, *J. Fluorine Chem.* **2006**, *127*, 1013–1029; h) W. K. Hagmann, *J. Med. Chem.* **2008**, *51*, 4359–4369; i) C. Isanbor, D. O'Hagan, *J. Fluorine Chem.* **2006**, *127*, 303–319; j) K. L. Kirk, *Org. Process Res. Dev.* **2008**, *12*, 305–321; k) X. F. Wu, H. Neumann, M. Beller, *Chem. Asian J.* **2012**, *7*, 1744–1754.

[2] a) G. K. S. Prakash, J. Hu, *Acc. Chem. Res.* **2007**, *40*, 921–930; b) L. Chu, F.-L. Qing, *J. Am. Chem. Soc.* **2010**, *132*, 7262–7263; c) T. Liu, Q. Shen, *Eur. J. Org. Chem.* **2012**, 6679–6687; d) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, DOI: 10.1021/cr300503r.

[3] a) X. Wang, Y. Ye, S. Zhang, J. Feng, Y. Xu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 16410–16413; b) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem.* **2011**, *123*, 6243–6246; *Angew. Chem. Int. Ed.* **2011**, *50*, 6119–6122; c) A. D. Dilman, V. V. Levin, *Eur. J. Org. Chem.* **2011**, 831–841; d) Y. Ye, M. S. Sanford, *J. Am. Chem. Soc.* **2012**, *134*, 9034–9037; e) A. Studer, *Angew. Chem.* **2012**, *124*, 9082–9090; *Angew. Chem. Int. Ed.* **2012**, *51*, 8950–8958; f) S. Mizuta, S. Verhoog, K. M. Engle, T. Khotavivattana, M. O'Duill, K. Wheelhouse, G. Rassias, M. Médebielle, V. Gouverneur, *J. Am. Chem. Soc.* **2013**, *135*, 2505–2508.

[4] a) R. J. Lundgren, M. Stradiotto, *Angew. Chem.* **2010**, *122*, 9510–9512; *Angew. Chem. Int. Ed.* **2010**, *49*, 9322–9324; b) C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao, *Angew. Chem.* **2011**, *123*, 1936–1940; *Angew. Chem. Int. Ed.* **2011**, *50*, 1896–1900; c) Y. Ye, S. H. Lee, M. S. Sanford, *Org. Lett.* **2011**, *13*, 5464–5467; d) L. Chu, F.-L. Qing, *J. Am. Chem. Soc.* **2012**, *134*, 1298–1304; e) A. Hafner, S. Bräse, *Angew. Chem.* **2012**, *124*, 3773–3775; *Angew. Chem. Int. Ed.* **2012**, *51*, 3713–3715.

[5] a) E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson, S. L. Buchwald, *Science* **2010**, *328*, 1679–1681; b) R. N. Loy, M. S. Sanford, *Org. Lett.* **2011**, *13*, 2548–2551; c) N. D. Ball, J. B. Gary, Y. Ye, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 7577–7584; d) Y. Ye, N. D. Ball, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2010**, *132*, 14682–14687; e) X.-G. Zhang, H.-X. Dai, M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 11948–11951; f) Y. C. Zhao, J. B. Hu, *Angew. Chem.* **2012**, *124*, 1057–1060; *Angew. Chem. Int. Ed.* **2012**, *51*, 1033–1036; g) L.-S. Zhang, K. Chen, G. Chen, B.-J. Li, S. Luo, Q.-Y. Guo, J.-B. Wei, Z.-J. Shi, *Org. Lett.* **2013**, *15*, 10–13.

[6] a) R. Shimizu, H. Egami, Y. Hamashima, M. Sodeoka, *Angew. Chem.* **2012**, *124*, 4655–4658; *Angew. Chem. Int. Ed.* **2012**, *51*, 4577–4580; b) M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **2009**, 1909–1911; c) T. Knauber, F. Arikan, G.-V. Röschenthaler, L. J. Gooßen, *Chem. Eur. J.* **2011**, *17*, 2689–2697; d) T. Liu, Q. Shen, *Org. Lett.* **2011**, *13*, 2342–2345; e) X. Jiang, L. Chu, F.-L. Qing, *J. Org. Chem.* **2012**, *77*, 1251–1257; f) Y. Ye, S. A. Kunzi, M. S. Sanford, *Org. Lett.* **2012**, *14*, 4979–4981; g) H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig, *Angew. Chem.* **2011**, *123*, 3877–3882; *Angew. Chem. Int. Ed.* **2011**, *50*, 3793–3798; h) Q. Qi, Q. Shen, L. Lu, *J. Am. Chem. Soc.* **2012**, *134*, 6548–6551; i) G. G. Dubinina, H. Furutachi, D. A. Vicic, *J. Am. Chem. Soc.* **2008**, *130*, 8600–8601; j) C. P. Zhang, Z. L. Wang, Q. Y. Chen, C. T. Zhang, Y. C. Gu, J. C. Xiao, *An-*

gew. Chem. **2011**, *123*, 1936–1940; *Angew. Chem. Int. Ed.* **2011**, *50*, 1896–1900; k) P. Novák, A. Lishchynskyi, V. V. Grushin, *Angew. Chem.* **2012**, *124*, 7887–7890; *Angew. Chem. Int. Ed.* **2012**, *51*, 7767–7770; l) O. A. Tomashenko, E. C. Escudero-Adán, M. Martínez Belmonte, V. V. Grushin, *Angew. Chem.* **2011**, *123*, 7797–7801; *Angew. Chem. Int. Ed.* **2011**, *50*, 7655–7659; m) A. Zanardi, M. A. Novikov, E. Martin, J. Benet-Buchholz, V. V. Grushin, *J. Am. Chem. Soc.* **2011**, *133*, 20901–20913.

[7] a) 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*, 15300–15303; b) Y. Miyake, S.-i. Ota, Y. Nishibayashi, *Chem. Eur. J.* **2012**, *18*, 13255–13258; c) L. Chu, F.-L. Qing, *Org. Lett.* **2012**, *14*, 2106–2109; d) A. T. Parsons, S. L. Buchwald, *Angew. Chem.* **2011**, *123*, 9286–9289; *Angew. Chem. Int. Ed.* **2011**, *50*, 9120–9123; e) P. Novák, A. Lishchynskyi, V. V. Grushin, *J. Am. Chem. Soc.* **2012**, *134*, 16167–16170; f) J. Xu, B. Xiao, C.-Q. Xie, D.-F. Luo, L. Liu, Y. Fu, *Angew. Chem.* **2012**, *124*, 12719–12722; *Angew. Chem. Int. Ed.* **2012**, *51*, 12551–12554; g) M. Hu, C. Ni, J. Hu, *J. Am. Chem. Soc.* **2012**, *134*, 15257–15260; h) S. Mizuta, O. Galicia-López, K. M. Engle, S. Verhoog, K. Wheelhouse, G. Rassias, V. Gouverneur, *Chem. Eur. J.* **2012**, *18*, 8583–8587; i) H. Kawai, T. Furukawa, Y. Nomura, E. Tokunaga, N. Shibata, *Org. Lett.* **2011**, *13*, 3596–3599.

[8] J. Xu, D.-F. Luo, B. Xiao, Z.-J. Liu, T.-J. Gong, Y. Fu, L. Liu, *Chem. Commun.* **2011**, *47*, 4300–4302.

[9] Y. Li, L. Wu, H. Neumann, M. Beller, *Chem. Commun.* **2013**, *49*, 2628–2630.

[10] E. J. Cho, S. L. Buchwald, *Org. Lett.* **2011**, *13*, 6552–6555.

[11] N. Iqbal, S. Choi, E. Kim, E. J. Cho, *J. Org. Chem.* **2012**, *77*, 11383–11387.

[12] A. T. Parsons, T. D. Senecal, S. L. Buchwald, *Angew. Chem.* **2012**, *124*, 3001–3004; *Angew. Chem. Int. Ed.* **2012**, *51*, 2947–2950.

[13] Z. He, T. Luo, M. Hu, Y. Cao, J. Hu, *Angew. Chem.* **2012**, *124*, 4010–4013; *Angew. Chem. Int. Ed.* **2012**, *51*, 3944–3947.

[14] a) L. J. Goossen, G. Deng, L. M. Levy, *Science* **2006**, *313*, 662–664; b) L. J. Goossen, K. Goossen, N. Rodriguez, M. Blanchot, C. Linder, B. Zimmermann, *Pure Appl. Chem.* **2008**, *80*, 1725–1733; c) N. Rodriguez, L. J. Goossen, *Chem. Soc. Rev.* **2011**, *40*, 5030–5048; d) S. Bhadra, W. I. Dzik, L. J. Goossen, *J. Am. Chem. Soc.* **2012**, *134*, 9938–9941.

[15] a) A. G. Myers, D. Tanaka, M. R. Mannion, *J. Am. Chem. Soc.* **2002**, *124*, 11250–11251; b) D. Tanaka, A. G. Myers, *Org. Lett.* **2004**, *6*, 433–436.

[16] a) S.-L. Zhang, Y. Fu, R. Shang, Q.-X. Guo, L. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 638–646; b) R. Shang, D.-S. Ji, L. Chu, Y. Fu, L. Liu, *Angew. Chem.* **2011**, *123*, 4562–4566; *Angew. Chem. Int. Ed.* **2011**, *50*, 4470–4474.

[17] a) F. Zhang, M. F. Greaney, *Angew. Chem.* **2010**, *122*, 2828–2831; *Angew. Chem. Int. Ed.* **2010**, *49*, 2768–2771; b) P. Fang, M. Li, H. Ge, *J. Am. Chem. Soc.* **2010**, *132*, 11898–11899; c) R. R. P. Torregrosa, Y. Ariyarathna, K. Chattopadhyay, J. A. Tunge, *J. Am. Chem. Soc.* **2010**, *132*, 9280–9282; d) P. Hu, Y. Shang, W. Su, *Angew. Chem.* **2012**, *124*, 6047–6051; *Angew. Chem. Int. Ed.* **2012**, *51*, 5945–5949; e) Y. Zhang, S. Patel, N. Mainolfi, *Chem. Sci.* **2012**, *3*, 3196–3199.

[18] a) Z. J. Li, Z. L. Cui, Z. Q. Liu, *Org. Lett.* **2013**, *15*, 406–409; b) Y. D. Ye, S. A. Kuenzi, M. S. Sanford, *Org. Lett.* **2012**, *14*, 4979–4981; c) B. R. Langlois, E. Laurent, N. Roidot, *Tetrahedron Lett.* **1991**, *32*, 7525–7528; d) B. R. Langlois, E. Laurent, N. Roidot, *Tetrahedron Lett.* **1992**, *33*, 1291–1294.

[19] Y. N. 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*, 14411–14415.

[20] Recently, a copper-catalyzed decarboxylative trifluoromethylation was reported, see: Z. Li, Z. Cui, Z.-Q. Liu, *Org. Lett.* **2013**, *15*, 406–409.

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