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Palladium Catalyzed Vinyltrifluoromethylation of Aryl Halides through Decarboxylative Cross-Coupling with 2-(Trifluoromethyl)acrylic Acid

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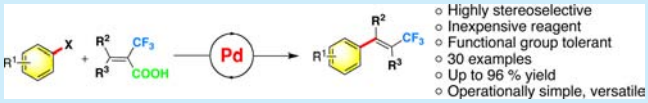
Supporting Information

ABSTRACT: An efficient Pd-catalyzed stereoselective vinyltrifluoromethylation of aryl halides, through decarboxylative cross-coupling with 2-(trifluoromethyl)acrylic acid is described. The ready availability of the starting materials, the high level of functional group tolerance, and excellent *E*/*Z* selectivity make this protocol a safe and operationally convenient strategy for efficient synthesis of vinyltrifluoromethyl derivatives.



The increase in prevalence of the trifluoromethyl (CF_3) functionality in pharmaceuticals, agrochemicals, paints, liquid crystal displays (LCDs), and polymers can be attributed to its unique physicochemical properties.[1] For example, in medicinal chemistry, the trifluoromethyl group is introduced into organic scaffolds in attempts to improve the properties of bioactive molecules such as metabolic stability, liphophilicity, and selectivity. Accordingly, selective synthetic methods for the preparation of trifluoromethylated intermediates or building blocks are of great importance.[2] Most of the current methodologies for the introduction of the trifluoromethyl group entail either costly reagents for innate substitution or preactivated substrates containing directing groups.[3] Despite their practical importance, these strategies require prefunctionalized substrates, the preparation of which can often call for tedious functional group interconversions and often lead to undesired waste formation. Several new methods for the direct formation of alkynyl $C(sp)-CF_3$, aromatic $C(sp^2)-CF_3$, and aliphatic compounds with $C(sp^3)-CF_3$ have been reported recently, highlighting the importance of this particular transformation.[4−6]

Despite significant advancements in this area, there is no general method for the production of the CF_3 group containing functionalized alkenes. Selective trifluoromethylation of alkenes through transition metal catalysis is rare (Figure 1). Buchwald and co-workers reported the synthesis of β-trifluoromethylstyrenes through iron catalyzed trifluoromethylation of prefunctionalized vinylboron derivatives with Togni's reagent.[7] Furthermore, Feng et al. found that reaction of an enamide with Cu^I/Togni's reagent could provide trifluoromethyl substituted olefin derivatives,[8] and photoredox catalysis with a ruthenium complex for the construction of trifluoromethylated alkenes with CF_3I was also reported.[9] While some current methodologies are limited to specific substrate classes such as heterocycles, electron-deficient arenes, and phenols,[10] others require the use of hazardous reagents that are mostly available in the gaseous form and which have corrosive properties.[11] The cost and limited availability of these reagents combined with poor functional group tolerance have prompted our interest in developing alternative, more general, and more sustainable catalytic strategies.[12]

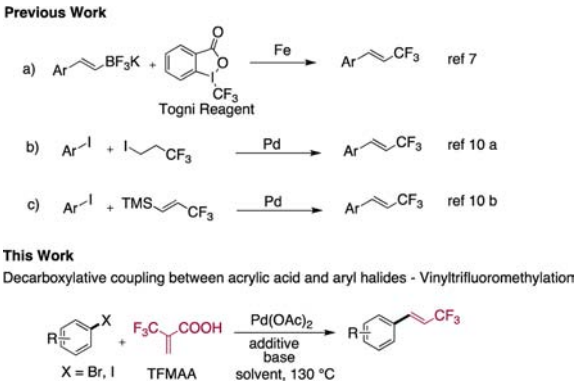


Figure 1. β-Trifluoromethylation reactions (TFMAA = 2-(trifluoromethyl)acrylic acid, **2**).

Herein we report a Pd-catalyzed decarboxylative cross-coupling between aryl halides and 2-(trifluoromethyl)acrylic acid (TFMAA, **2**) for the highly selective direct synthesis of diverse olefins.[13] To the best of our knowledge, there exists no example of decarboxylative coupling between acrylic acid and aryl halides for aryl vinyltrifluoromethylation. The performance of the present catalytic system allowed us to extend this methodology to various heterocyclic systems.

Initial experiments were carried out using bromobenzene (**1**) as a model substrate, 2-(trifluoromethyl)acrylic acid (**2**), and 10 mol % of $Pd(OAc)_2$ as a catalyst. Optimization with respect to bases, solvents, and several additives was explored under these reaction conditions (Table 1). Initial studies in the presence of

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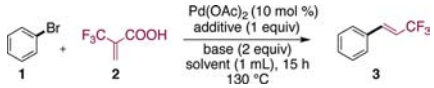
Table 1. Pd-Catalyzed Decarboxylative Reaction of Acrylic Acid and Aryl Halides: Variation of Reaction Conditions[a]



entry	solvent	base	additive	(*E*/*Z*)	yield (%)[b]
1	DMF	K_2CO_3	$Cu(OAc)_2$	–	0
2	DMSO	K_2CO_3	$Cu(OAc)_2$	–	5
3	PhMe	K_2CO_3	$Cu(OAc)_2$	–	9
4	xylene	K_2CO_3	$Cu(OAc)_2$	–	NR
5	1,2-DCB	K_2CO_3	$Cu(OAc)_2$	–	8
6	mesitylene	K_2CO_3	$Cu(OAc)_2$	–	0
7	*p*-cymene	K_2CO_3	$Cu(OAc)_2$	–	0
8	NMP	K_2CO_3	$Cu(OAc)_2$	95/5	55
9	NMP	K_2CO_3	$Cu(OPiv)_2$	90/10	50
10	NMP	K_2CO_3	$Cu(SO_3CF_3)_2$	–	0
11[c]	NMP	K_2CO_3	CuO	≥95:5	92 (89)
12	NMP	K_2CO_3	–	–	trace
13[d]	NMP	K_2CO_3	CuO	≥95:5	89
14[e]	NMP	K_2CO_3	CuO	≥95:5	75
15	NMP	K_2CO_3	AgO	50/50	48
16	NMP	K_2CO_3	AgOAc	60/40	35
17	NMP	K_2CO_3	AgF	–	28
18	NMP	K_2CO_3	$AgCO_3$	–	18
19	NMP	Cs_2CO_3	CuO	–	4
20	NMP	Na_2CO_3	CuO	–	6
21	NMP	NaOAc	CuO	–	0
22	NMP	KOAc	CuO	–	0
23	NMP	NaOH	CuO	–	0
24	NMP	KOH	CuO	–	0
25[f]	NMP	K_2CO_3	CuO	–	0
26[g]	NMP	K_2CO_3	CuO	–	93 (90)

[a]Reactions were performed with 1 mmol of TFMAA (**2**), 2 mmol of bromobenzene, 0.1 equiv of $Pd(OAc)_2$, 1 equiv of additive, 2 equiv of base, 1 mL of solvent at 130 °C for 15 h. [b]Yields were determined by ^1H NMR using CH_2Cl_2 as the internal standard. Isolated yields shown in parentheses. [c]The reaction was performed under N_2. [d]The reaction was performed under air. [e]The reaction was performed at 105 °C for 48 h. [f]In the absence of $Pd(OAc)_2$. [g]The reaction was conducted on a 0.5 mmol scale with $Pd(OAc)_2$ (5 mol %) and additive (0.5 equiv), in NMP (1 mL). DMF = dimethylformamide, DMSO = dimethyl sulfoxide, 1,2-DCB = 1,2-dichlorobenzene, NMP = 1-methyl-2-pyrrolidinone.

potassium carbonate (2 equiv) and copper acetate (0.2 equiv) (entries 1–8) showed that *N*-methyl pyrrolidine (NMP) effectively facilitated the reaction and 55% of the desired product was obtained. This improvement is in agreement with the positive effect of NMP observed in a number of organic reactions.[14] Interestingly, none of the other high boiling point solvents examined afforded the product in significant yield. It is important to note that the reaction is highly selective toward the linear vinyltrifluoromethylation product, as no traces of the branched isomer formation were detected under these reaction conditions.

Next, we examined the influence of different additives on the reaction (Table 1, entries 9–16). It should be noted that $Cu(OPiv)_2$ and $Cu(OTf)_2$ were less effective than $Cu(OAc)_2$ for this reaction (Table 1, entries 9–10). Among the oxidants tested, CuO was the most effective affording the cross-coupled product in 92% yield (entry 11). The vinyl trifluoromethylation of the substrate was completely inhibited in the absence of an additive (entry 12). Interestingly, we found that the reaction can be carried out under an air atmosphere (entry 13) and afforded the vinyl-CF_3 product in comparable yield to when performed under nitrogen (entry 11), highlighting a practical advantage of the method. Subsequent attempts at lower temperature showed that an excellent yield can be achieved at 105 °C, although a longer reaction time was required (entry 14). The screening of silver-based additives, such as silver oxide, silver acetate, silver fluoride, and silver carbonate, gave modest yields (Table 1, entries 15–18). Finally, the influence of a base was studied (entries 19–24). K_2CO_3 proved superior, though cesium carbonate and sodium carbonate afforded low yields of the coupled adducts (Table 1, entries 19 and 20). Reactions with sodium acetate, potassium acetate, sodium hydroxide, and potassium hydroxide afforded only trace amounts of products (Table 1, entries 21–24). The loading of the catalyst could be decreased to 5 mol %; thus, the optimized conditions can be summarized as $Pd(OAc)_2$ as the catalyst (5 mol %), additive CuO (1 equiv), bromobenzene (**1**) as the substrate (2 equiv), 2-(trifluoromethyl)acrylic acid (**2**) (0.5 equiv), and K_2CO_3 (1 equiv) as the base (Table 1, entry 26).

With the best optimized reaction conditions in hand ($Pd(OAc)_2$/CuO/K_2CO_3), we turned our attention to the evaluation of the substrate scope of the decarboxylative Pd-catalyzed vinyltrifluoromethylation of aryl halides by Heck type reaction with acrylic acid (Table 2). Excellent *E*/*Z* product ratios were observed in most cases. Using aryl bromides with either electron-donating (Table 2, entries 2–3) or electron-withdrawing groups (Table 2, entries 4–10) at the *para*-position led to the formation of the corresponding vinyl-CF_3 derivatives in good to moderate yields in all the cases. Remarkably, a number of synthetically useful functionalities, including aryl chloride, bromide, nitrile, aldehyde, and ester groups, were tolerated under the reaction conditions. Interestingly, aryl bromide substituted with an *N*,*N*-dimethylamino substituent at the *para*-position furnished exclusively the *E*-product (Table 2, entry 8). In the case of an aryl bromide substituted with an acetyl group at the *para*-position the resultant alkene stereoisomers are inseparable by column chromatography (Table 2, entry 11). When the 4-bromobiphenyl was used, we were able to isolate both the pure and mixture of stereoisomers in good yields (Table 2, entry 12). Gratifyingly, this reaction could also be applied to the synthesis of ethers **3m**, albeit in moderate yield (Table 2, entry 13). Next this reaction was extended with 2-bromonaphthalene and found to produce the corresponding vinyl-CF_3 derivative in good yield (Table 2, entry 14). In contrast, the 1-bromonaphthalene was much less reactive under these conditions (Table 2, entry 15). Although the electrophile scope was broad, we found that substrates with *meta*-functionalization furnished vinyl-CF_3 products in high yields, and with good to moderate *E*/*Z* selectivity (Table 2, entries 16–19). We were pleased to observe that 3,5-dimethyl-1-iodo benzene (**1t**) could be utilized, providing similar reaction rates and excellent *E*/*Z* selectivity (Table 2, entry 20). It is significant to note that this method tolerates substituents at the *ortho*-position, as demonstrated by the vinyltrifluoromethylations of **1u**–**1v**, which furnished the corresponding products with excellent *E*/*Z*-selectivities (Table 2, entries 21–22).

After having observed the general reactivity with aryl bromides, we turned our attention to the reactivity of different heterocycles to vinyltrifluoromethylation (Table 3). To our delight, the coupling reaction with both thiophene and pyridine proceeded in good yield (Table 3, entries 1–2). The reaction was stereoselective, predominantly affording the *E*-product of the corresponding vinyl-CF_3. When 6-bromoquinoline was reacted,

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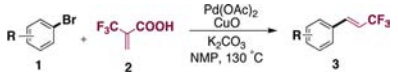
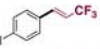
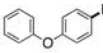
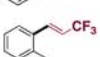
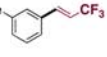
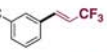
Table 2. Scope of Aryl Bromides with 2-(Trifluoromethyl)acrylic Acid[a]



Entry	Aryl bromide		Product		(E/Z)	Yield (%)[b]
1		1a		3a	≥ 95:5	92
2		1b		3b	≥ 95:5	90
3		1c		3c	≥ 95:5	95
4		1d		3d	≥ 95:5	72
5		1e		3e	≥ 95:5	75
6		1f		3f	≥ 95:5	70
7		1g		3g	≥ 95:5	35
8		1h		3h	≥ 95:5	69
9		1i		3i	≥ 95:5	59
10		1j		3j	≥ 95:5	71
11		1k		3k	≥ 90:10	65
12		1l		3l	≥ 95:5	56
13		1m		3m	≥ 95:5	85
14		1n		3n	≥ 95:5	90
15		1o		3o	≥ 95:5	58
16		1p		3p	≥ 95:5	74
17		1q		3q	≥ 95:5	70
18		1r		3r	≥ 50:50	81
19		1s		3s	≥ 85:15	80
20		1t		3t	≥ 95:5	82
21		1u		3u	≥ 95:5	75
22		1v		3v	≥ 95:5	69

[a]Reactions were performed with **1** (2 equiv), TFMAA (**2**) (1 equiv), $Pd(OAc)_2$ (5 mol %), CuO (0.5 equiv), K_2CO_3 (1 equiv), NMP (1 mL) at 130 °C for 15 h. [b]Isolated yields.

the corresponding product was obtained with moderate *E*/*Z*-selectivity (Table 3, entry 3). Quinolines containing substituents at both the 2- and 6-positions also underwent the reaction with excellent stereoselectivity (Table 3, entry 4). Furthermore, the reaction of 5-bromoisoquinoline afforded good selectivity and a high yield (Table 3, entry 5). Finally, the vinyltrifluoromethylation of 8-bromo-3-methoxyisoquinoline was achieved with a 96% isolated yield, though, surprisingly, with an *E*/*Z*-selectivity of 90:10 (Table 3, entry 6).

Table 3. Scope of Heterocyclic Bromides with 2-(Trifluoromethyl)acrylic Acid[a]

Entry	Aryl(Hetero) bromide		Product		(E/Z)	Yield (%)[b]
1		4a		5a	≥95:5	85
2		4b		5b	≥95:5	96
3		4c		5c	≥95:5	96
4		4d		5d	≥95:5	96
5		4e		5e	≥95:5	96
6		4f		5f + 5f′	90:10	96

[a]Reactions were performed with **4** (1 equiv), TFMAA (**2**) (2 equiv), $Pd(OAc)_2$ (5 mol %), CuO (0.5 equiv), K_2CO_3 (1 equiv), NMP (1 mL) at 130 °C for 15 h. [b]Isolated yields.

To gain mechanistic insights, additional experiments were performed. When the reaction was conducted in the presence of a radical scavenger, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT), none of the decarboxylative vinyl-TEMPO or vinyl-BHT products were observed (Scheme 1a). These results excluded the possibility of vinyl radical formation through decarboxylation and confirmed the transmetalation of *in situ* generated vinyl-CF_3 and subsequent reductive elimination. We also found this reaction was stereoconvergent, as the *cis* and *trans* mixture of 4,4,4-trifluorocrotonic acid (**6**) yielded the *E*-isomer as the major product (Scheme 1b).

Scheme 1. Mechanistic Investigations of the Vinyltrifluoromethylation

Based on the experimental findings presented above we proposed a mechanism for the aryl vinyltrifluoromethylation (Scheme 2). After initial formation of organometallic complex **B** via oxidative addition, the subsquent entropically favorable decarboxylation of acrylic acid generates the Pd(II) complex **C**.[15] Finally, reductive elimination affords the product **7** and regenerates the active catalyst via Cu(II) reoxidation. An alternative mechanism could involve the direct carbometalation of 2-(trifluoromethyl)acrylic acid **D** followed by decarboxylation

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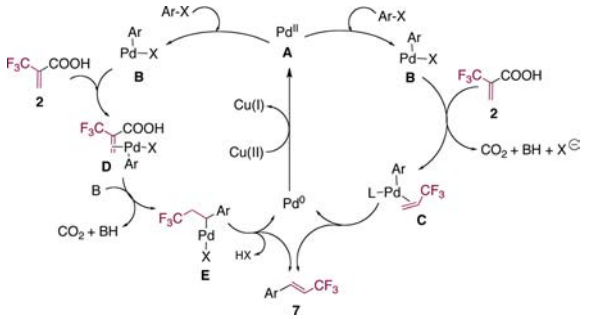
Scheme 2. Proposed Catalytic Cycle for Aryl Vinyltrifluoromethylation (Ar = aryl; X = Br, I; B = base; L = solvent)



and stereoselective β-hydride elimination of **E** to afford the product **7**.[16]

In conclusion, we have shown that decarboxylative cross-coupling of 2-(trifluoromethyl)acrylic acid with various aryl halides provides a new, steroeselective strategy for the incorporation of the vinyltrifluoromethyl functionality into aryl bromide containing structures. From a synthetic standpoint, this transformation is an extremely simple and efficient method for incorporating the versatile vinyltrifluoromethyl moiety into target structures, a task that can otherwise require costly reagents and more difficult handling processes. Unlike some current methodologies that are limited to specific substrate classes, our method is amenable to a broad range of functionalities, e.g. chlorides, esters, ethers, aldehydes, acetyl and nitriles, and even heterocycles. Importantly, the demonstration of the stereoselective nature of the reaction suggests opportunities for further utilization. Moreover, this new and unusually simple strategy for the simultaneous incorporation of vinyl and CF_3 functionalities is also of importance due to increasing interest in fluoroorganic compounds and trifluoromethylating reagents. More detailed mechanistic studies shall be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectroscopic data (copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{13}C-APT). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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