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Nickel-Catalyzed Reductive Cross-Coupling of (Hetero)Aryl Iodides with Fluorinated Secondary Alkyl Bromides

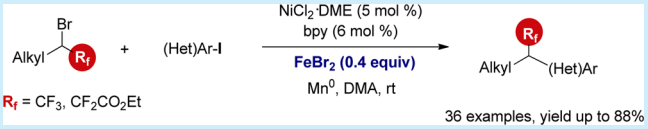
Xuefei Li,[†] Zhang Feng,[‡] Zhong-Xing Jiang,*[,†] and Xingang Zhang*[,‡]

[†]School of Pharmaceutical Sciences, Wuhan University, 189 Donghu Lu, Wuhan 430071, China

[‡]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Supporting Information

ABSTRACT: A mild and efficient nickel-catalyzed reductive cross-coupling between fluorinated secondary alkyl bromides and (hetero)aryl iodides is described. The use of $FeBr_2$ as an additive successfully overcomes the hydrodebromination and β-fluorine elimination of fluorinated substrates and allows the efficient synthesis of a wide range of trifluoromethyl and difluoroalkyl containing aliphatic compounds with a fluoroalkyl substituted tertiary carbon center. The notable features of this protocol are the synthetic and operational simplicity without preparation of moisture sensitive organometallic reagents and excellent functional group compatibility, even toward active proton containing substrates.



Transition-metal-catalyzed cross-couplings represent one of the fundamental transformations in C−C bond formation.[1] Efficient catalytic systems for a wide range of substrates are widely utilized in the production of pharmaceuticals, fine chemicals, and functional materials. Recently, nickel-catalyzed reductive cross-couplings between two electrophiles have emerged as direct methods for the construction of $C(sp^2)$−$C(sp^3)$[2] and $C(sp^3)$−$C(sp^3)$[3] bonds because such a strategy omits the preparation of air- and moisture-sensitive organometallics from the corresponding organic halides.[4] Although important progress in this field has been made, the use of fluorinated secondary alkyl halides [R_f(Alkyl)CHX, R_f = fluoroalkyl, X = halides] as a coupling partner has not been reported thus far; this still poses a synthesis challenge due to the difficulties in suppressing the hydrodehalogenation and β-fluorine elimination of fluorinated substrates.[5]

The trifluoromethyl group (CF_3) is of paramount importance in the discovery of new bioactive molecules and advanced functional materials owning to its strong electron-withdrawing ability, high lipophilicity, bulky steric effect, etc.[6] Over the past few years, great endeavors have been devoted to the synthesis of trifluoromethylated aromatic compounds.[7] In contrast, less attention has been paid to the development of efficient and general methods for trifluoromethylated aliphatic compounds with a CF_3 substituted tertiary carbon center.[7b,e,8] Therefore, it is of great interest to develop general and efficient strategies for such compounds. During our manuscript preparation, an efficient nickel catalyzed Negishi cross-coupling between fluorinated secondary alkyl electrophiles with aryl- and alkylzincs were reported.[9] Despite the importance of this method in trifluoromethylated aliphatic compounds, the use of organozinc reagents less sensitive to moisture is accompanied by extra synthetic steps and special operations. As part of our systematic study on transition-metal-catalyzed reactions for the efficient synthesis of fluorinated compounds,[10] we herein describe an efficient and mild nickel-catalyzed reductive cross-coupling between (hetero)aryl iodides and readily available trifluoromethylated secondary alkyl bromides [CF_3(Alkyl)CHBr].[11]

Our initial studies focused on the nickel-catalyzed reductive cross-coupling between trifluoromethylated secondary alkyl bromide **1a** with phenyl iodide **2a** (Table 1). However, no desired product **3a** was observed when the reaction was carried out with **1a** (1.0 equiv), **2a** (1.1 equiv), $NiCl_2$·DME (10 mol %), bpy (12 mol %), and Mn^0 (3.0 equiv) in DMF at room temperature. A higher reaction temperature promoted the reaction and led to **3a** in a 19% yield (entry 1). However, both hydrodebrominated and β-fluorine eliminated byproducts **5a** and **6a** were produced in 36% and 7% yield, respectively. Further optimization of the reaction conditions by examining a range of bipyridine-based ligands and nickel catalysts showed the combination of bpy and $NiCl_2$·DME was still the best choice (entries 2−4, for details; see the Supporting Information). No improvement in the reaction efficiency was observed by adding iodide ion (i.e., Bu_4NI, NaI) or acids (i.e., Et_3N·HCl, CF_3CO_2H) to activate the reaction medium[12,13] (entries 5−8). It has been demonstrated that, for the nickel-catalyzed reductive cross-coupling, a radical pathway is involved in the oxidative addition of alkyl halides to the nickel(I) complex.[14] We reasoned that the formation of byproducts **5a** and **6a** is probably because an active trifluoromethyl containing alkyl radical species was generated in the reaction process, which results in a series of byproducts.

Accordingly, iron salts were examined to improve the yield of **3a** (entries 9−13), as low valent iron species could be produced by the reduction of manganese metal with Fe^{II} or Fe^{III}, which may have a beneficial effect on the catalytic cycle.[15] To our delight, a

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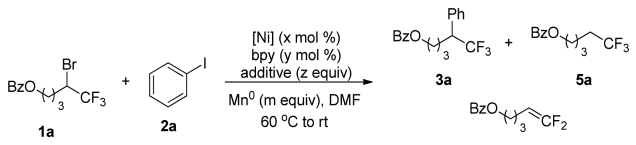
Table 1. Representative Results for Optimization of Ni-Catalyzed Reductive Cross-Coupling between 1a and 2a[a]



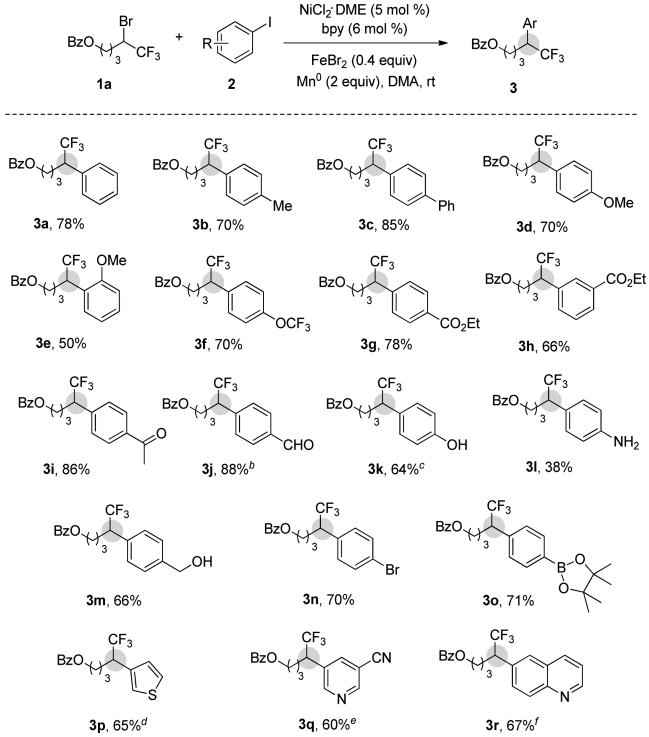
entry	[Ni] (x)	bpy (y)	additive (z)	Mn^0 (m)	yield (%)[b] 3a/5a/6a
1	$NiCl_2$·DME (10)	12	–	3	19/36/7
2	$NiBr_2$·DME (10)	12	–	3	0/0/0
3	$NiCl_2(PPh_3)_2$ (10)	12	–	3	0/27/13
4	$Ni(COD)_2$ (10)	12	–	3	0/0/0
5	$NiCl_2$·DME (10)	12	Bu_4NI (0.5)	3	13/24/9
6	$NiCl_2$·DME (10)	12	NaI (0.5)	3	0/2/0
7	$NiCl_2$·DME (10)	12	Et_3N·HCl (0.5)	3	15/34/4
8	$NiCl_2$·DME (10)	12	CF_3CO_2H(0.5)	3	18/28/10
9	$NiCl_2$·DME (10)	12	$FeBr_2$ (0.5)	3	43/13/6
10	$NiCl_2$·DME (10)	12	$FeBr_3$ (0.5)	3	41/5/7
11	$NiCl_2$·DME (10)	12	$FeCl_2$ (0.5)	3	37/13/8
12	$NiCl_2$·DME (10)	12	$FeCl_3$ (0.5)	3	32/11/8
13[c]	$NiCl_2$·DME (5)	6	$FeBr_2$ (0.4)	2	86(78)/1/10
14[c]	$NiCl_2$ (5)	6	$FeBr_2$ (0.4)	2	18/16/18
15[c]	–	6	$FeBr_2$ (0.4)	2	nd/7/6
16[c]	–	6	$FeBr_2$ (0.05)	2	nd/5/2
17[c]	–	–	$FeBr_2$ (0.4)	2	nd/4/6
18[c]	$NiCl_2$·DME (5)	6	–	2	3/9/0
19[c]	$NiCl_2$·DME (5)	–	$FeBr_2$ (0.4)	2	0/4/3

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2a** (1.1 equiv), DMF (2 mL), 60 °C, 6 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard, and number in parentheses is isolated yield. [c]**1a** (1.0 equiv), **2a** (1.3 equiv), DMA (2 mL), rt, 24 h.

43% yield of **3a** was afforded, albeit with some byproducts, when $FeBr_2$ (0.5 equiv) was used (entry 9). Other iron salts also benefited the reaction, but showed less activity (entries 10−12). However, the exact role of iron species remains elusive at this stage and will be addressed in the future. Finally, the optimized reaction conditions were identified by evaluation of the solvents, reaction temperature, and the loading amount of nickel catalyst and additive, providing **3a** in 78% yield upon isolation (entry 13). It is noteworthy that under the optimized reactions only 5 mol % of $NiCl_2$·DME was used and the reaction can be conducted at room temperature (entry 13). A high concentration of Ni catalyst and iron species still provided comparable yields of **3a**, but increased homocoupling of **2a** was observed when a high loading of Ni catalyst was used[16] (for details, see the Supporting Information). However, the use of $NiCl_2$ led to a poor yield of **3a** (entry 14). Either no or a trace amount of product was observed in the absence of nickel catalyst, bipyridine ligand, or iron species, thus demonstrating the essential role of these three factors in the reaction (entries 15−19).

Upon the establishment of viable reaction conditions, a wide range of aryl iodides were employed as substrates in this transformation (Scheme 1). Overall, good to high yields of **3** were obtained, and the electronic nature of the substituents on aryl iodides showed no bias toward the reaction efficiency. A variety of versatile functional groups, including base or organometallic reagent-sensitive functionalities, such as ester, enolizable ketone, formyl, and nitrile were quite well-tolerated (**3g**−**3j** and **3q**). Remarkably, the free proton containing substrates, such as phenol, aniline, and alcohol underwent the reaction smoothly and provided **3k**−**3m** in moderate to good yields. This is in sharp contrast to the previous results,[9] in which the organozinc reagents are very sensitive to such functional groups, as a result of additional protection and deprotection steps were required. Thus, the current reaction features the advantage of synthetic and operational simplicity. Most importantly, the aryl bromide and aryl boronic ester showed good tolerance (**3n** and **3o**), which provided good opportunities for the synthesis of complex molecules. This is distinct from the classic transition-metal-catalyzed cross-coupling, in which aryl bromides and aryl boronic esters are good coupling partners. Heteroaromatics are a prominent moiety found in numerous pharmaceuticals and agrochemicals. Synthesis of fluorinated compounds bearing heteroaromatic rings is highly relevant for drug discovery and development. To our delight, thiophene, pyridine, and quinoline containing substrates are competent coupling partners and

Scheme 1. Ni-Catalyzed Reductive Cross-Coupling between 1a and a Variety of Aryl Iodides 2[a]



[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2** (1.3 equiv), DMA (4 mL), 24 h. All reported yields are isolated yields. [b]Reaction ran at 50 °C for 48 h. [c]Aryl iodide (2.0 equiv), 36 h. [d]$NiCl_2$·DME (8 mol %), bpy (9.6 mol %). [e]5-Bromonicotinonitrile was used. [f]Reaction ran for 36 h.

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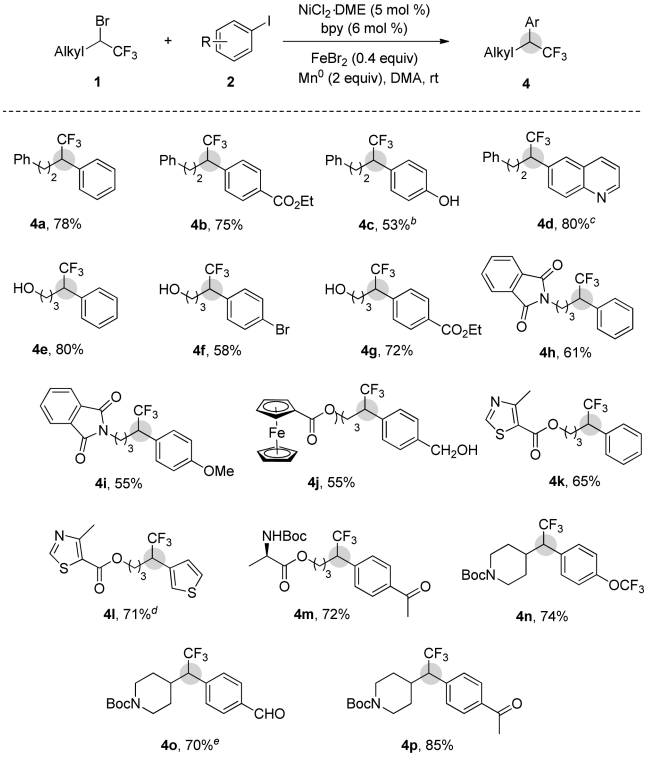
provided **3p**−**3r** in good yields, thus highlighting the generality of the current process.

In addition to demonstrating the scope of this reaction, a variety of trifluoromethylated secondary alkyl bromides were examined (Scheme 2). Generally, good to high yields of **4** were

Scheme 2. Ni-Catalyzed Reductive Cross-Coupling between 1 and 2[a]

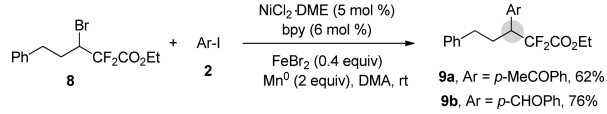


[a]Reaction conditions (unless otherwise specified): **1** (0.4 mmol, 1.0 equiv), **2** (1.3 equiv), DMA (4 mL), 24 h. All reported yields are isolated yields. [b]Aryl iodide (2.0 equiv), 36 h. [c]Reaction ran for 36 h. [d]$NiCl_2$·DME (8 mol %), bpy (9.6 mol %). [e]Reaction ran at 50 °C for 48 h.

also obtained. Again, excellent functional group compatibility were observed for the current reaction. In particular, *N*-heteroaromatics and nucleophile-sensitive phenols, alcohols, and active proton-containing amides still furnished the corresponding products with high efficiency (**4c**−**4g**, **4j** and **4m**). Importantly, thiazole, an important structural motif in natural products and biologically active molecules, underwent the reaction smoothly (**4k**). An even higher yield of **4l** was obtained when the thiazole containing alkyl bromide was treated with 3-iodothiophene. The ferrocenyl group also showed good tolerance, leading to **4j** in moderate yield. Moreover, the amino acid containing alkyl bromide did not affect the reaction efficiency and provide **4m** in 72% yield. This is noteworthy, as the fluorinated amino acids and their derivatives have important applications in the design of biologically active peptides and protein engineering.[17] Remarkably, the sterically hindered piperidine containing alkyl bromide was a competent coupling partner and afforded **4n**−**4p** with high efficiency, thus further demonstrating the broad substrate of this method. The trifluoromethylated tertiary alkyl bromides were not applicable to the current reaction.[18]

Notably, the reaction can also be extended to difluoroacetylated secondary alkyl bromide **8**. As shown in Scheme 3,

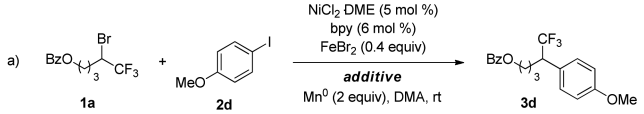
Scheme 3. Ni-Catalyzed Reductive Cross-Coupling between Two Electrophiles



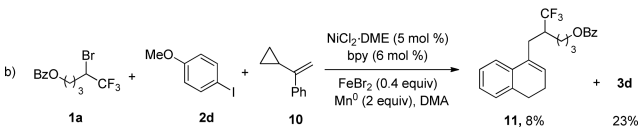
treatment of **8** with aryl iodides **2** still afforded the corresponding products **9** with high efficiency.[19] Previous work required aryl magnesium reagents as a coupling partner, which are incompatible with enolizable ketone and formyl group, thus further demonstrating the advantages of the current method.[5d]

To probe whether an alkyl radical existed in the reaction, radical inhibition experiments were conducted (Scheme 4a).

Scheme 4. Radical Inhibition and Radical-Clock Experiments



additive	**3d**, yield (%)
none	70
1,4-dinitrobenzene (0.05 equiv)	22
1,4-dinitrobenzene (0.2 equiv)	0
hydroquinone (1.0 equiv)	35
hydroquinone (1.5 equiv)	0



Dramatically decreased yields of **3d** were observed with the addition of an ET scavenger 1,4-dinitrobenzene[20] or a radical inhibitor hydroquinone to the reaction of **1a** with **2d** in the presence of $NiCl_2$·DME (5 mol %), bpy (6 mol %), $FeBr_2$ (0.4 equiv), and Mn^0 (2.0 equiv) in DMA. Thus, these results suggest an alkyl radical may be involved in the catalytic cycle. To confirm that a free alkyl radical was generated during the reaction, a radical-clock experiment was conducted (Scheme 4b). When compound **10**[21] was treated with **1a** in the presence of aryl iodide **2d** under standard reaction conditions, a ring-expanded product **11** was generated (8% yield, determined by ^{19}F NMR) along with a 23% yield of **3d**. This finding demonstrates that a free radical is generated in the reaction process.

In conclusion, we have demonstrated a mild and efficient nickel-catalyzed reductive cross-coupling between fluorinated secondary alkyl bromides and (hetero)aryl iodides. The additive $FeBr_2$ plays an essential role in the promotion of the reaction and allows a broad substrate scope with high efficiency under mild reaction conditions. A deep understanding of the exact role of iron species in the current process would be a subject for future work. The significant features of this protocol are the use of bench stable and abundant organic halides without preparation of moisture-sensitive organometallic reagents and excellent functional group compatibility, even toward free proton-

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containing substrates and heteroaromatics. Thus, this method provides facile access to fluoroalkyl containing aliphatic compounds for drug discovery and development.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02716.

Detailed experimental procedures, and characterization data for new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zxjiang@whu.edu.cn.
*E-mail: xgzhang@mail.sioc.ac.cn.

Notes

The authors declare no competing financial interest.

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(11) The trifluoromethylated secondary alkyl bromides [CF_3(Alkyl)CHBr] can be easily synthesized from $TMSCF_3$ and aldehydes; see Supporting Information p S13.

(12) I^- is known to accelerate the reduction of Ni(II) salts to an active catalyst in the reductive reactions, probably through acceleration of electron transfer between Mn and Ni or through *in situ* generation of alkyl iodides; see: (a) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627. (b) Prinsell, M. R.; Everson, D. A.; Weix, D. J. *Chem. Commun.* **2010**, *46*, 5743.

(13) TFA is known to activate the Mn^0 surface.

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(16) No homocoupling of **1a** was observed when the loading amount of $NiCl_2$·DME or $FeBr_2$ was increased. The formation of homocoupling of **2a** does not depend on the concentration of $FeBr_2$, as no increased homocoupling of **2a** was observed when the loading amount of $FeBr_2$ was increased.

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(18) When CF_3CH_2Cl was employed as a coupling partner to react with **2a**, only a poor yield of corresponding product was obtained.

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