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Nickel(II)-Catalyzed Site-Selective C−H Bond Trifluoromethylation of Arylamine in Water through a Coordinating Activation Strategy

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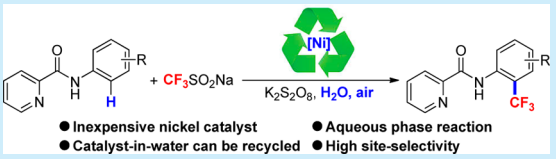
Supporting Information

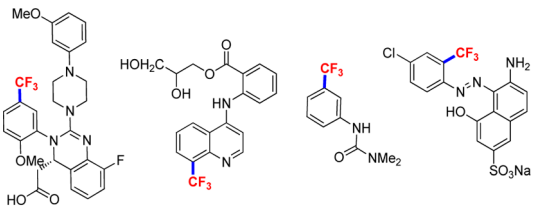
ABSTRACT: The first example of nickel(II)-catalyzed site-selective C−H bond trifluoromethylation of arylamine in water is established. In this transformation, a coordinating activation strategy is performed by the utilization of picolinamide as a directing group, and target products are obtained in moderate to good yields. In addition, the catalyst-in-water system can be reutilized eight times with a slight loss of catalytic activity and applied in the green, concise synthesis of acid red 266. Furthermore, a series of control experiments verify that a single-electron transfer mechanism is responsible for this reaction.



Transition-metal-catalyzed trifluoromethylation has emerged as a dramatic tactic for the trifluoromethylation of organic molecules.[1] Previous works[1a−j] from many groups are focused on the formation of trifluoromethylated compounds from arylboronic acids, aryl acid, arylamine, and aryl halides, while more recent efforts have led to fast development of C−H trifluoromethylation.[1k−t]

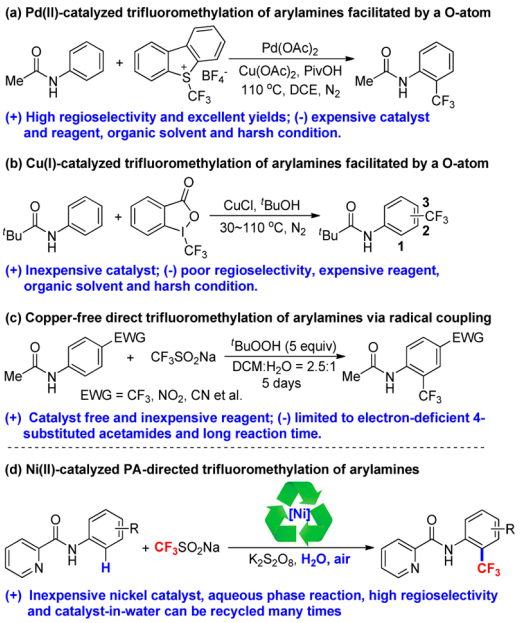
Trifluoromethylaniline, as an important kind of organic intermediate, is extensively utilized in the production of pharmaceuticals, agrochemicals, and dyes (Scheme 1).[2]

Scheme 1. Application of Trifluoromethylated Arylamines



Recently, transition-metal-catalyzed C−H trifluoromethylation of arylamine derivatives has received considerable attention. The palladium-catalyzed trifluoromethylation of acetamide was developed by Shi's group through the mechanism of oxidative addition/reductive elimination facilitated by a O atom of amide (Scheme 2a).[1s] Shortly after Shi's report, Xi et al. demonstrated CuCl-catalyzed *ortho*-trifluoromethylation of arylamine. Unfortunately, this system showed poor regioselectivity, because of the involvement of radical intermediates and the lack of a stable auxiliary (Scheme 2b).[1t] For these two transformations above, expensive catalyst or trifluoromethylating reagents, organic solvents, relatively high temperatures, as well as an inert atmosphere were indispensable, making these methods inadaptable to large-scale synthesis. In 2014, Cao et al. demonstrated copper-free direct C−H trifluoromethylation of acetanilides with Langlois' reagent via radical pathway (Scheme 2c).[3] However,

Scheme 2. C−H Trifluoromethylation of Arylamine



because of the substituent effect, the substrates were confined to electron-deficient 4-substituted acetamides. Furthermore, 5 days were needed for this transformation. Indeed, these protocols represent great infusive advances, but some important aspects still need continuous improvement.

In 2005, Daugulis and co-workers exploited the picolinamide (PA) moiety as a bidentate directing group, for use in palladium-catalyzed C−H functionalization reactions.[4] Since then, new PA-directed C−H functionalization reactions have been successfully achieved using copper instead of noble metal palladium in catalytic reaction.[5] Recently, the groups of Nakamura[6a] and

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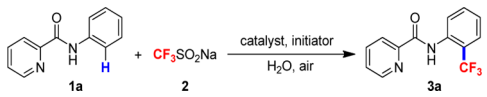
You[6b] reported an iron-catalyzed directed C(sp^2)−H and C(sp^3)−H functionalization assisted by the PA-directing group, respectively.[6] In contrast, nickel-catalyzed PA-directed C−H functionalization is rarely established.

Owing to the characteristics of abundance, low price, and unique reactivity, nickel is widely employed as a prevalent catalyst in many organic reactions.[7] Recently, nickel-catalyzed C−H functionalization has also received considerable attention. Preeminent advances have been demonstrated by many groups.[8] However, nickel-catalyzed trifluoromethylation is seldom reported. In that context, we report a nickel(II)-catalyzed trifluoromethylation of arylamine derivatives at the *ortho* position in water through a coordinating activation strategy (Scheme 2d).

We initially studied the trifluoromethylation of *N*-phenylpicolinamide by using cobalt chloride ($CoCl_2$) as catalyst, Langlois' reagent (CF_3SO_2Na) as CF_3 source, potassium persulfate ($K_2S_2O_8$) as initiator, and water (H_2O) as solvent at 50 °C under air atmosphere. The unexpected product was successfully isolated in 29% yield (Table 1, entry 1). Accordingly,

Table 1. Optimization of Reaction Conditions[a,b]



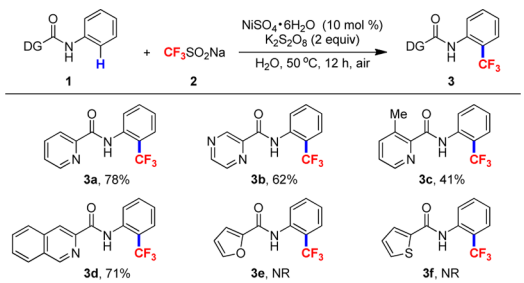
entry	catalyst	initiator	yield[b] (%)
1	$CoCl_2$	$K_2S_2O_8$	29
2	$Co(OAc)_2·4H_2O$	$K_2S_2O_8$	33
3	CoF_2	$K_2S_2O_8$	41
4	$Fe(OTf)_3$	$K_2S_2O_8$	trace
5	$Cu(OAc)_2$	$K_2S_2O_8$	trace
6	$MnBr_2$	$K_2S_2O_8$	22
7	$NiCl_2$	$K_2S_2O_8$	59
8	$Ni(OTf)_2$	$K_2S_2O_8$	44
9	$Ni(acac)_2$	$K_2S_2O_8$	53
10	**$NiSO_4·6H_2O$**	**$K_2S_2O_8$**	**78**
11		$K_2S_2O_8$	0
12	$NiSO_4·6H_2O$	TBHP	23
13	$NiSO_4·6H_2O$	DTBP	20
14	$NiSO_4·6H_2O$	DCP	trace
15	$NiSO_4·6H_2O$	CH_3CO_3H	trace
16	$NiSO_4·6H_2O$	H_2O_2	trace
17	$NiSO_4·6H_2O$	$Na_2S_2O_8$	65
18	$NiSO_4·6H_2O$	$(NH_4)_2S_2O_8$	72
19	$NiSO_4·6H_2O$		0
20[c]	$NiSO_4·6H_2O$	$K_2S_2O_8$	trace
21[d]	$NiSO_4·6H_2O$	$K_2S_2O_8$	76
22[e]	$NiSO_4·6H_2O$	$K_2S_2O_8$	78

[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), catalyst (10 mol %), initiator (2 equiv), H_2O (4 mL), stirred at 50 °C, under air, for 12 h. [b]Isolated yields. [c]Stirred at rt. [d]Stirred at 100 °C. [e]Under N_2.

several kinds of metal catalysts including cobalt(II), iron(III), copper(II), manganese(II), and nickel(II) salts were investigated (Table 1, entries 2−10), and a better yield of 78% was obtained by using $NiSO_4·6H_2O$ as catalyst. As expected, no desired product was detected in the absence of any metal catalysts (Table 1, entry 11). This result revealed that metal catalyst played a crucial role in this transformation. Further screening in initiators, temperature, as well as atmosphere did nothing to enhance the product yield (Table 1, entries 12−22).

Subsequently, an investigation of various kinds of directing groups was performed (Scheme 3). The trifluoromethylation of

Scheme 3. Influence of Directing Group[a,b]

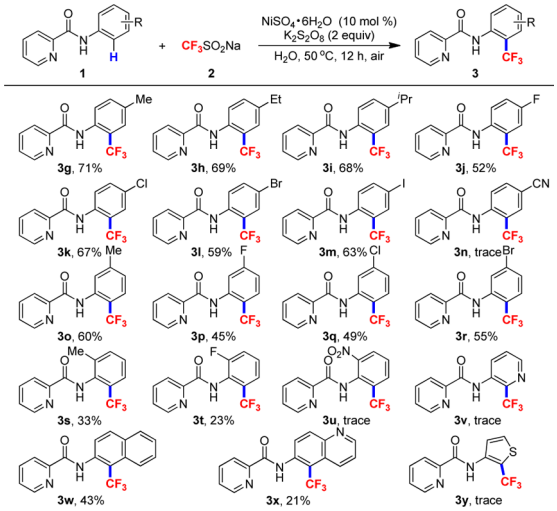


[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $NiSO_4·6H_2O$ (10 mol %), $K_2S_2O_8$ (2 equiv), H_2O (4 mL), stirred at 50 °C, under air, for 12 h. [b]Isolated yields.

arylamine derivative **1a** did furnish the *ortho*-trifluoromethylated product **3a** in 78% yield. Others bearing *N*-containing bidentate directing groups reacted with a low yield (**3b**−**d**), and products **3e** and **3f** were not gained. These results indicated the crucial role of both heterocyclic nitrogen and amide, most likely as bidentate binding site for a metal atom.[5c]

After obtaining the reliable direct C−H bond trifluoromethylation protocol, we then surveyed the substrate scope of arylamines (Scheme 4). Pleasingly, most substrates could react

Scheme 4. Substrate Scope of Arylamines[a,b]



[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $NiSO_4·6H_2O$ (10 mol %), $K_2S_2O_8$ (2 equiv), H_2O (4 mL), stirred at 50 °C, under air, for 12 h. [b]Isolated yields.

smoothly. Overall, arylamine derivatives with various alkyl and halogen groups at *para* position revealed better activities, and the corresponding products (**3g**−**m**) were isolated in 52−71% yield. Transformation of *meta*-substituted arylamines with Langlois' reagent (CF_3SO_2Na) delivered the *ortho*-trifluoromethylated products (**3o**−**r**) in 45−60% yield. Substrates bearing *ortho*-substituted groups transformed into products with a low yield of 33% and 23% (**3s**, **3t**). Interestingly, bulky arylamines such as naphthylamine and quinolylamine also furnished the corresponding products **3w** and **3x** in 43% and 21% yields, respectively. Electron-withdrawing substituent-bearing aryl-

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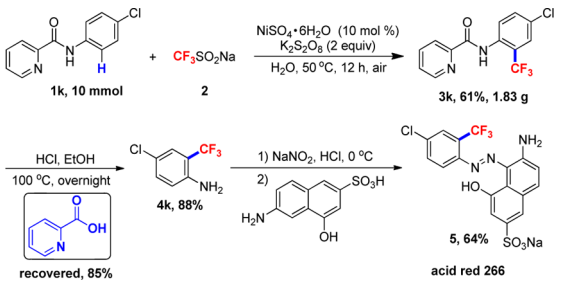
amines and heteroarylamines are strong electron-deficient substrates, which are not conducive to this reaction, so substrates (**3n**, **3u**, **3v**, and **3y**) did not undergo the C−H bond trifluoromethylation.

With the effective method of trifluoromethylation in hand, we next inspected the applicability of this method to prepare acid red 266 which has been widely used in the dye industry (Scheme 5).

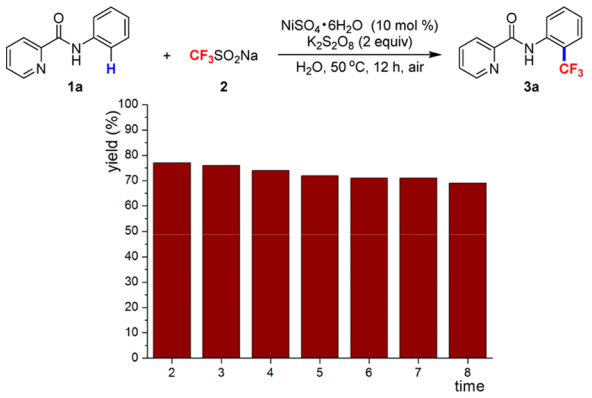
Scheme 5. Application of Trifluoromethylation



First, gram-scale synthesis of compound **3k** was successful proceed under optimum conditions, and the target product was acquired in 61% yield. Second, the hydrolysis reaction was carried out in the presence of hydrochloric acid, and 4-chloro-2-(trifluoromethyl)aniline was obtained in 88% yield and 2-picolinic acid was recovered in 85% yield. Finally, successive diazotization, C−N coupling, and salt-forming reactions gave rise to the desired product **5** in 64% yield, thus providing a feasible pathway to the green, concise synthesis of acid red 266.

Since it was our intention to design a green environmental protection method for the trifluoromethylation of arylamine derivatives, a recycling experiment of the catalyst-in-water was performed (Scheme 6). According to the difference in the

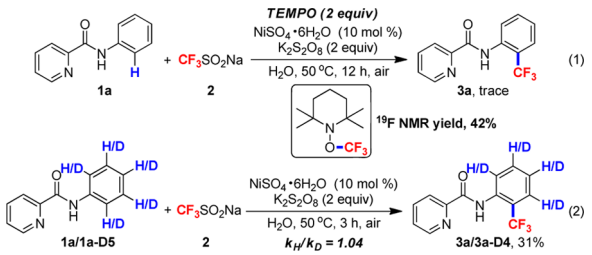
Scheme 6. Recycling Catalyst-in-Water System



solubility of nickel(II) salt and organic product in water and ethyl acetate, catalyst-in-water could be retrieved by an easy phase separation from the organic layer. The retrieved catalyst-in-water (containing sulfates) could be reutilized in the next round. The catalytic activity of nickel(II) catalyst remained stable after eight rounds, affording the target product in 69% yield.

In order to gain more insights into the mechanism of nickel(II)-catalyzed site-selective C−H bond trifluoromethylation, a series of control experiments were conducted, such as structure effect of substrates, radical inhibition, proton exchange, and kinetic isotope effect experiments. First, specific substrates (**1w**−**y**) failed to afford the corresponding product, these results showed that the N atom of pyridine and amide group with a free NH were very considerable for this reaction (see the Supporting Information). Furthermore, because substrate **1w** could not be converted into any product, we could also eliminate the mechanism of aryl electrophilic substitution.[5c] In addition, when the two *ortho* positions of arylamine were substituted by methyl (**1z**), the substrate lost reactivity, suggesting that the trifluoromethylation only happened at the *ortho* position of arylamine. Second, the reaction was completely suppressed when 2 equiv of TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl) was added and 42% yield of TEMPO−CF_3 adduct was detected by ^{19}F NMR, implying that a radical reaction pathway might be involved in the transformation (Scheme 7, eq 1). To explore the

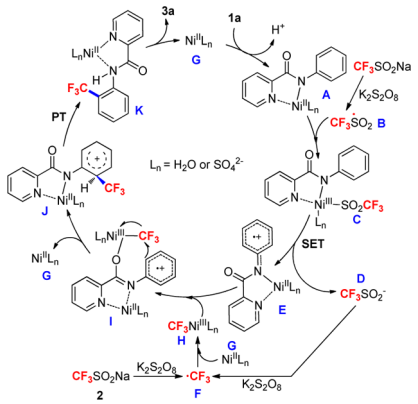
Scheme 7. Control Experiments



C−H activation step, further exploration about kinetic isotope effects (KIE) was performed through the intermolecular competition. When equal amounts of **1a** and **1a-D5** were treated with Langlois' reagent (CF_3SO_2Na) together under standard conditions for 3 h, the mixed products **3a**/**3a-D4** were obtained in 31% yield, giving a low ratio (k = 1.04), indicating that the rate-determining step does not involve C−H cleavage (Scheme 7, eq 2).[9] In addition, an irreversible C−H cleavage also can be approved for the reaction because no compound **1a-D** was detected in the proton-exchange experiment (see the SI).

We considered that a single-electron transfer (SET) mechanism could be involved on the grounds of experimental results and previous reports (Scheme 8).[8a−c,10] Initially, $Ni^{II}L_n$

Scheme 8. Plausible Mechanism



was combined with substrate **1a** to generate intermediate **A**. In the meantime, radical **B** was provided from Langlois' reagent (CF_3SO_2Na) by oxidation of potassium persulfate ($K_2S_2O_8$). Subsequently, complex **A** turned into compound **C** through radical **B** addition. Then, complex **E** and anion **D** were generated via a SET process. Meanwhile, anion **D** and CF_3SO_2Na transformed into trifluoromethyl radical **F** by oxidation of potassium persulfate ($K_2S_2O_8$). Followed by the combination of

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trifluoromethyl radical **F** and $Ni^{II}L_n$, a $CF_3Ni^{III}L_n$ species (**H**) was formed.[11] Then the weak coordination of $CF_3Ni^{III}L_n$ species with the oxygen atom of amide group produced complex **I**.[5b] Next, complex **I** underwent intramolecular trifluoromethylation to give cationic complex **J**. Eventually, after the generation of complex **K** through a proton-transfer (**PT**) process, desired product **3a** was gained via a metal dissociation process.

In conclusion, we have reported the first example of nickel(II)-catalyzed and picolinamide-assisted site-selective C−H bond trifluoromethylation of arylamine in water. Furthermore, this transformation has been successfully applied to the efficient synthesis of acid red 266. Of importance, the catalyst-in-water system could be reutilized eight times with a slight loss of catalytic activity. Finally, control experiments verified that a SET mechanism was responsible for this reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02823.

Experimental procedures, characterization data, and ^1H, ^{13}C and ^{19}F NMR spectra for the synthesized compounds (PDF)

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Notes

The authors declare no competing financial interest.

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