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Nickel/copper-cocatalyzed decarbonylative silylation of acyl fluorides

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Ni/Cu-cocatalyzed decarbonylative silylation of acyl fluorides with silylboranes has been developed to afford various arylsilanes with high efficiency and good functional-group compatibility via carbonfluorine bond cleavage and carbon-silicon bond formation. Such transformation can not only extend the functionalization type of acyl fluorides but complement the synthetic route for arylsilanes.

Since organosilicon compounds are of a great importance in organic synthesis,1 drug discovery2 and materials science,3 various synthetic strategies have been established by constructing the C-Si bond. Traditional synthetic methods of arylsilanes involves the reactions of Grignard or organolithium reagent with silyl electrophiles, 1a,4 in which ester and ketone functional groups cannot be incorporated. Alternatively, transition-metal-catalyzed silvlation of aryl halides has been developed for the preparation of arylsilanes.⁵ Although defluorosilylation of fluoroarenes via C-F bond activation has been reported recently, the synthesis of the starting materials requires multi-step reactions.⁶ In addition, a direct C-H silylation of unreactive aromatic compounds with hydrosilanes were also investigated to obtain arylsilanes.⁷ Furthermore, silvlation of nitriles with disilanes via C-CN bond cleavage⁸ and of pivalates or anisoles with silvlboranes via C-O bond cleavage⁹ provided a new access to arylsilanes (Scheme 1a).

Utilizing decarboxylation/decarbonylation, transformations of carboxylic acid and their derivatives into valuable compounds under transition metal catalysis have drawn much attention owing to their natural abundance and easy availability.¹⁰ Among them, early study found that palladium-catalyzed silylation of acyl chlorides bearing strong electron-withdrawing groups with hexamethyldisilanes gave a mixture of acylsilane and arylsilane, in which the selective

decarbonylative silylation of acyl chlorides was observed with chlorinated disilanes.¹¹ Rueping¹² and Shi¹³ independently succeeded in nickel/copper-cocatalyzed decarbonylative silylation of phenolic esters via C–O bond cleavage. Building up on the previous work, Reuping expanded the decarbonylation silylation strategy for arylamides via C–N bond cleavage (Scheme 1b).¹⁴ However, phenolic esters and arylamides are generally prepared from the corresponding carboxylic acids via acyl chlorides in two steps, and a large waste derived from phenols and amines are generated after the reaction.^{12,14}

On the other hand, acyl fluorides display many superiorities than the corresponding carboxylic derivatives, showing great stability and high reactivity.¹⁵ Moreover, acyl fluorides acting as the acyl fragment without a CO loss in transition-metalcatalyzed have been witnessed in cross-couplings of Negishi,16 Hiyama,¹⁷ Suzuki-Miyaura,¹⁸ and other reactions such as reductive coupling with vinyl triflates, 19 reduction, 20 boroacylation of allenes,²¹ and C-H coupling with azoles²² to give the corresponding ketones or aldehydes. Recently, reactions of acyl fluorides serving as an arylation moiety via decarbonylative process for C-C bond formation have been extensively investigated, including trifluoromethylation,23 reduction,^{20b} Suzuki-Miyaura type-arylation,²⁴ and direct C-H arylation.²⁵ We have also reported the Ni(cod)₂/DPPE catalytic system for decarbonylative alkylation of acyl fluorides.²⁶ The outcome suggested that utilization of acyl fluoride is the key to this transformation and other acyl halides cannot be participated.

Due to the indispensable and versatile main group elements, namely, boron, silicon, and tin in cross-coupling chemistry,²⁷ carbon-heteroatom bond-forming reactions of acyl fluorides are highly desired. Encouraged by a unique nature of acyl fluorides in various decarbonylative C–C bond-forming reactions and our continuous interest of acyl halides in crosscoupling reactions,^{26,28} we have developed nickel-catalyzed borylation²⁹ and stannylation³⁰ of acyl fluorides with diborons and silylstannanes, respectively, in a decarbonylation manner. Herein, we report our new approach to the synthesis of

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 $^{^+}$ Electronic Supplementary Information (ESI) available: experimental procedures, spectroscopic data and copies of $^1H,\ ^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra. See DOI: 10.1039/x0xx00000x

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arylsilanes by nickel/copper-cocatalyzed decarbonylative silylation of acyl fluorides with silylboranes (Scheme 1c).

(a) Transition-metal-catalyzed silvlative couplings

$$Ar - x + R_3Si - R' \xrightarrow{[TM]} Ar - SiR_3$$

X = halides (R' = SiMe₂OEt, H, SiMe₃, Bpin) $\mathsf{X}=\mathsf{H}\;(\mathsf{R'}=\mathsf{H});\,\mathsf{X}=\mathsf{CN}\;(\mathsf{R'}=\mathsf{SiMe}_3),\,\mathsf{X}=\mathsf{OMe}\;\mathsf{or}\;\mathsf{OPiv}\;(\mathsf{R'}=\mathsf{Bpin})$

(b) Decarbonylative silvlation of carbonyl compounds

$$Ar \xrightarrow{V} X + R_3Si - Bpin \xrightarrow{[Ni]/[Cu]} Ar - SiR_3$$

 $X = OPh \text{ or } NR'_2$

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(c) Decarbonylative silylation of acyl fluorides (This work)

Initially, we chose the reaction of 2-naphthoyl fluoride (1a) with silylborane 2a under basic conditions as the model reaction. An inexpensive PPh₃ ligand was preferable due to its excellent performance in nickel-catalyzed decarbonylative borylation.²⁹ However, only 5% of silvlated product 3a was detected, along with a large amount of 2a unconsumed (Table 1, entry 1), where 22% of naphthalene from decarbonylative reduction and 58% of

2,2'-binaphthalene derived from decarbonylative homocoupling were observed. This outcome revealed that nickel/PPh₃ catalytic system cannot efficiently activate 2a to promote transmetalation of the oxidative adduct. Thus, CuOAc

Table 1 Optimization of the reaction conditions ^a				
O F + Et ₃ Si-Bpin Ni(cod) ₂ (10 mol %) [Cu] (30 mol %) Ligand (40 mol %) Base (3 equiv) toluene 140 °C, 24 h			SiEt ₃	
1a 2a				3a
Entry	[Cu]	Ligand	Base	3 a (%) ^b
1	-	PPh₃	KF	5
2	CuOAc	PPh₃	KF	85
3	CuOAc	PCy ₃	KF	50
4	CuOAc	P ⁿ Bu₃	KF	32
5	CuOAc	P(OPh)₃	KF	11
6	CuOAc	PPh₃	CsF	18
7	CuOAc	PPh₃	NaF	49
8	CuOAc	PPh₃	LiF	45
9	CuOAc	PPh₃	KOAc	71
10	Cu(OAc) ₂	PPh₃	KF	31
11	CuCl ₂	PPh₃	KF	0
12	CuF ₂	PPh₃	KF	77
13 ^c	CuF ₂	PPh₃	KF	89 (85)
14 ^d	CuF ₂	PPh₃	KF	0
15	CuF ₂	-	KF	<1
16	CuF ₂	PPh₃	-	46
17 ^e	CuF ₂	PPh₃	KF	0

^a 1a (0.2 mmol), 2a (0.4 mmol), Ni(cod)₂ (0.02 mmol) in toluene (1.0 mL) at 140 °C for 24

h. ^b Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal

standard. An isolated yield is given in parentheses. ^c 150 °C. ^d Without, Ni(rod) anline DOI: 10.1039/C9CC05325E Naphthovl chloride instead of 1a.

was added because of the reported profound effect of copper salts in activation of the Si-B bond.³¹ As expected, 85% of **3a** was obtained, along with 10% of naphthalene as a by-product (entry 2). Notably, cooperation of the copper salt suppressed the competitive decarbonylative homocoupling and reduction. Other monodentate phosphine ligands such as PCy₃, PⁿBu₃, and P(OPh)₃ showed moderate to poor activities in this transformation (entries 3-5). Although acyl fluorides could act as a mild base in some cases,²⁴ exogenous base is still required in the present silulation reaction. Among the bases used, KF gave the best result (entry 2 and entries 6-9). Various cuprous and cupric salts were also examined (entries 10-13 and Table S5), and CuF₂ showed the superior result with the target product 3a in 89% yield (entry 13). Screening of the reaction temperatures demonstrated that the higher reaction temperature greatly increased the conversion of 1a to the decarbonylative silylation product 3a, suppressing the formation of homocoupled product (Table S6). Control experiments shown in entries 14-15 confirmed the crucial factors of Ni(cod)₂ and PPh₃ to succeed in this transformation; no or trace of 3a was observed. In the absence of KF, only 46% formation of 3a was detected (entry 16). In a sharp contrast, employing 2-naphthoyl chloride instead of 1a under the optimized reaction conditions, 2a remained unreacted and no silylation product 3a was formed (entry 17). We reasoned that the oxidative adduct NiAr(Cl)(PPh₃)₂ cannot undergo ligand exchange with silylboranes.²⁴ This different reactivity demonstrated the unique nature of acyl fluorides in the present silylation. It is noteworthy that no acylsilane in a retentive fashion was detected in all cases, suggesting that PPh₃ with a weak coordinating ability favors easily dissociation from a nickel center, which is favorable for facile CO migration and extrusion.

With the optimized reaction conditions in hand, a wide range of acyl fluorides were investigated as shown in Table 2. The π -extended aromatic acyl fluorides could be accommodated, providing naphthylsilanes 3a and 3b in 85% and 82% yields, respectively. The benzoyl fluoride substituted by a methyl group in the para-position was well tolerated in this reaction, affording the target product 3c in 85% yield. A steric effect was illustrated by the phenyl-substituted substrates in the ortho-, meta-, and para-positions; p-phenylbenzoyl fluoride (1d) gained superiority than *m*-phenyl-(1e) and *o*-phenyl (1f) counterparts. Other electron-rich alkoxy groups such as p-methoxy (3g), 3,4,5-trimethoxy (3h) and p-butoxy (3i) were also well tolerated during the reaction, although the Ni-catalyzed silvlation via C-O bond cleavage has been reported at lower temperature.⁹ This protocol was also featured by acyl fluorides bearing functional groups at the para-position, including amine, fluoride, ketone, and methyl ester, resulting in the formation of the desired products 3j-3m in 50-66% yields. In particular, phenolic ester skeleton (3n) was reported as a reactive electrophile under the nickel/copper cocatalysis in a decarbonylative silylation.^{12,13} Therefore, our method could be a useful complement to other silulation processes that are inaccessible for compatibility of alkoxy and phenolic ester groups. Furthermore, the reaction could be extended to heteroatom-containing acyl fluorides, affording arylsilanes 30 and 3p in 71% and 65% yields, respectively. Unfortunately, other surrogate alkenyl and aliphatic acyl fluorides failed to participate in this transformation. For

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example, only a trace amount of the decarbonylative silulation product was detected when dodecanoyl fluoride was employed as the coupling partner (Scheme S1).



 o Reaction conditions: 1 (0.2 mmol), 2a (0.4 mmol), Ni(cod)₂ (0.02 mmol), CuF₂ (0.06 mmol), PPh₃ (0.08 mmol), KF (0.6 mmol), toluene (1 mL), 150 °C, 24 h. b Isolated yields.



Different silyl groups in organosilicon compounds can control the reactivity in Hiyama reaction to construct the new C–C bonds,³² and in halogenation to provide new building blocks for further transformations.^{6a,9b,33} Thus, electronic and steric effects of the silicon moiety on the present decarbonylative silylation were tested by using four types of silylboranes under the standard reaction conditions (Scheme 2). All of silylboranes are proved to be good coupling partners using 2-naphthoyl fluoride (**1a**), yielding the corresponding arylsilanes **3q-3t** in 63-96% yields. It is noteworthy that "Pr₃Si-Bpin could be converted into the desired product **3q** in 64% with our method, whereas phenyl 2-naphthoate gave only 31% of **3q** with Rueping's protocol,¹² which further demonstrated the efficiency of our method.

Carboxylic acid-containing drug-probenecid, primarily used to treat gout and hyperuricemia³⁴ was also viable in nickel/coppercatalyzed decarbonylative silylation reaction. Deoxyfluorination of probenecid by conventional method,³⁵ followed decarbonylative silylation process furnished the target product **3u** in 72% yield (Scheme 3a), whereas the attempt of one-pot synthesis of **3u** without isolation of acyl fluoride (**1u**) provided an unsatisfactory result with the formation of **3u** in 28% yield (Scheme S2). Besides, late-stage decarbonylative silylation of estrone derivative owas conducted as shown in Scheme 3b, the ether Reation of estrone with methyl 4-(bromomethyl)benzoate (4), followed by hydrolysis afforded carboxylic acid 6. Finally, compound 6 was subjected to the two-step deoxyfluorination/decarbonylative silylation to provide **3v** in 75% yield.





^a Reaction conditions for deoxyfluorination of carboxylic acid: carboxylic acid (3 mmol), Deoxo-Fluor[®] reagent (3.3 mmol), CH₂Cl₂ (15 mL), 0 °C, 30 min. ^b Reaction conditions for decarbonylative silylation: **1** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)₂ (0.02 mmol), CuF₂ (0.06 mmol), PPh₃ (0.08 mmol), KF (0.6 mmol), toluene (1 mL), 150 °C, 24 h.

Scheme 3 Synthetic applications.

Considering related references and our previous work, a plausible mechanism is shown in Scheme 4. Oxidative addition of acyl fluorides **1** to the nickel(0) catalyst **A** yields acylnickel(II) complex **B**. Subsequently, decarbonylation of complex **B** gave the arylnickel species **C**.^{24,29} In the copper catalytic cycle, the formation of active Cu-Si species from silylboranes **2** can be accounted for a larger electronegativity of B (2.051) than Si (1.916),³⁶ as well as bond dissociation energy of diatomic B–F (732 kJ mol⁻¹) and Si–F (576 kJ mol⁻¹).³⁷ Therefore, a fluoride ion activates silylborane by a construction of the more stronger B–F bond to generate silylcopper species **D**.³¹ Transmetalation between aryl(fluoro)nickel(II) complex **C** and silylcopper species **D** afforded complex **E**, the subsequent reductive elimination of **E** yields the desired arylsilanes **3**, regenerating nickel(0) species **A**.

In summary, we have developed the nickel/copper co-catalyst system for decarbonylative silylation reaction of acyl fluorides to synthesize a wide range of aryl and heteroarylsilanes, in which an inexpensive and stable PPh_3 is indispensable. This study can expand the chemistry of acyl fluorides in terms of carbon-heteroatom bond formations, as well as a useful complement to other silylation processes.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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A transformation of aroyl fluorides with silylboron via nickel/coppercocatalysed carbon-fluorine bond cleavage and a sequential decarbonylation, which provides an efficient protocol to functionalize arylsilanes, has been disclosed.

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