Ni-Catalyzed Decarbonylative Alkynylation of Acyl Fluorides with Terminal Alkynes under Copper-Free Conditions
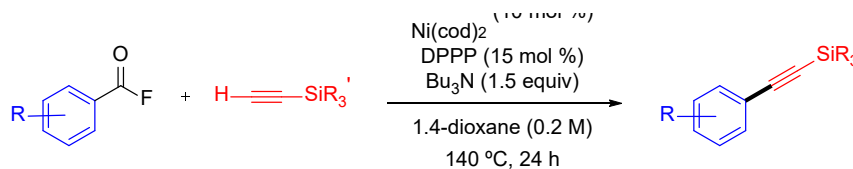
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- decarbonylative coupling
- copper-free
- broad substrate scope

25 examples
25-90% yields

Abstract Nickel-catalyzed decarbonylative alkynylation of acyl fluorides with terminal silylethynes under copper-free conditions is described. This newly developed methodology can exhibit a wide range of substrate scope, affording internal silylethynes in moderate to high yields. The formation of 1,3-diynes as homocoupled products and conjugate enones as carbonyl-retentive reaction was effectively suppressed.

Key words nickel, copper-free, decarbonylative transformation, alkynylation, acyl fluorides

Over the past few decades, Sonogashira–Hagihara (S–H) reaction,[1] the Pd/Cu-cocatalyzed coupling reaction of terminal alkynes with aryl (pseudo)halides, has made a significant progress in the construction of C(sp^2)–C(sp) bonds.[2] The further exploration of this reaction remain in optimizing the reaction conditions to avoid the formation of a homocoupled byproduct by means of the copper-free reactions[3] and "sila"-S–H reactions[4,5], or in finding more economical catalyst system to replace expensive Pd with Ni/Cu,[6] Ni,[7] or Cu.[8] However, in most cases, palladium is still used as the primary catalyst for the S-H reaction, and only a few examples have been reported under conditions where nickel or other metals have been used as catalysts.

Finding a naturally abundant coupling partner is another approach to optimizing the S-H reaction. Instead of the common aryl and vinyl (pseudo)halides, sodium sulfonates,[9] arylhydrazines,[10] and arylsulfonyl hydrazides[11] have been employed as coupling partners, but there is a need to develop other coupling partners that can be obtained from naturally abundant starting materials. Recently, esters and amides derived from carboxylic acids have been applied as coupling partners in S-H reactions (Scheme 1a).[12-14] Itami and Yamaguchi *et al.* developed the first example of Pd/Cu-cocatalyzed alkynylation of aromatic esters in a decarbonylative manner.[12] Meanwhile, On the other hand, Rueping developed an effective Ni/Cu cocatalyst for the deamidative cross-coupling reaction of silylated terminal

alkynes with amides under base-free conditions, which allowed direct conversion of amides to alkynes.[13] An example of not using copper as a co-catalyst is the Pd-catalyzed decarbonylative alkynylation of amides with terminal alkynes, in which various alkynes bearing aryl, alkyl, and silyl substituents were applicable.[14]
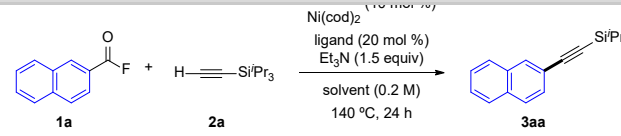
On the other hand, acyl fluorides also can be prepared from corresponding carboxylic acids and have been widely applied in carbon–carbon and carbon–heteroatom bond formation[15] as "RCO" (carbonyl-retentive)[16] or "R" (decarbonylative)[17-21] source due to their unique stability and reactivity. Particularly in the decarbonylation reaction, since the first example of decarbonylative transformations of acid fluorides has been disclosed,[17] acyl fluorides have been utilized as coupling partners in reduction,[18] Suzuki–Miyaura-type arylation,[19] and direct C–H arylation.[20] As an extension of our research on various decarbonylative reactions of acyl fluorides,[21] very recently we have also succeeded in the Pd/Cu-cocatalyzed decarbonylative "sila"-S–H-type alkynylation of acyl fluorides
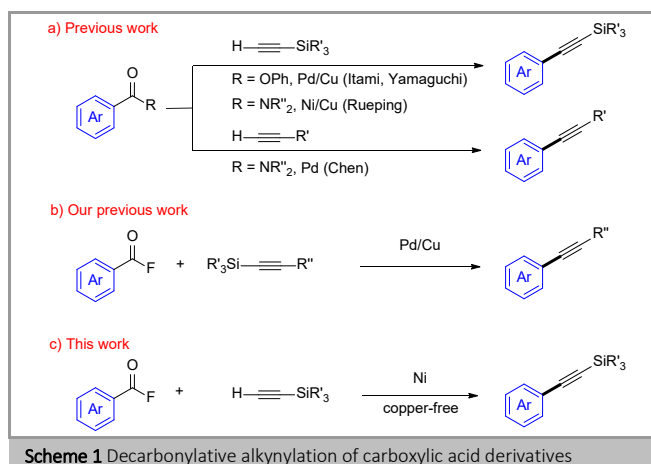
Scheme 1 Decarbonylative alkynylation of carboxylic acid derivatives

with silylated internal alkynes (Scheme 1b).[22] The reaction proceeds via cleavage of the carbon-silicon bond, so that no silicon is present in the product. On the other hand, since silylated terminal alkynes allow for further conversions, more direct methods for reacting silylated terminal alkynes with acyl fluoride, especially using cheaper catalyst systems, are still highly desirable. We herein report nickel-catalyzed decarbonylative alkynylation of acyl fluorides with silylated alkynes under copper-free condition, which offers a direct way to convert acyl fluorides to corresponding internal silylethynes (Scheme 1c).

Table 1 Optimize Reaction Condition [a]

Entry	Ligand (20 mol %)	Solvent	Yield (%)[b]
1	DPPE	1.4-dioxane	32
2	DPPP	1.4-dioxane	64
3	DCYPE	1.4-dioxane	5
4	DPPP	toluene	51
5	DPPP	DMF	18
6	DPPP	1.4-dioxane	68[c]
7	DPPP	1.4-dioxane	65[c,d]
8	**DPPP**	**1.4-dioxane**	**73[c,d,e]**
9	DPPP	1.4-dioxane	58[c,f]
10	DPPP	1.4-dioxane	13[c,g]
11	DPPP	1.4-dioxane	33[c,h]
12	DPPP	1.4-dioxane	0[c,i]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), Ni(cod)$_2$ (0.02 mmol), ligand (0.04 mmol), solvent (1 mL), 140 ºC, 24 h.
[b] GC yields using n-dodecane as an internal standard.
[c] **2a**, 2.0 equiv.
[d] DPPP, 15 mol %.
[e] Bu$_3$N instead of Et$_3$N.
[f] Without base.
[g] With CuI (10 mol %).
[h] 2-Naphthoyl chloride instead of **1a**.
[i] Without Ni(cod)$_2$.

Initially, we conducted the reaction by employing 2-naphthoyl fluoride (**1a**) and (triisopropylsilyl)acetylene (**2a**) as coupling partners and Ni(cod)$_2$ as the catalyst in 1,4-dioxane to optimize the reaction condition, and the results are summarized in Table 1. The nature of the phosphine ligands had a significant effect on the outcome of the reaction (entries 1-3). When 1,3-bis(diphenylphosphino)propane (DPPP) was used as a ligand, the desired product was obtained in 64% GC yield, twice that of 1,2-bis(diphenylphosphino)ethane (DPPE). The other bidentate or monodentate phosphine ligands gave much lower yields (Table S2, ESI†). Subsequently, toluene, DMF, and DMI were tested as solvents instead of 1,4-dioxane, but all of which resulted in poor yields of **3aa** (entries 4 and 5, Table S3, ESI†). To our delight, reducing the amount of **2a** to 2 equiv afforded **3aa** in 68% yield (entry 6). However, when **2a** was further reduced to 1 equiv, only 42% of **3aa** was obtained (Table S4, ESI†). Furthermore, lowering the amount of DPPP to 15 mol % also could gave a comparable yield of **3aa** (entry 7). After screening a series of inorganic or organic bases, when Bu$_3$N was employed instead of Et$_3$N, the yield of **3aa** was improved to 73% yield (entry 8). Compound **1a** was converted to **3aa** in 58% yield, even without the base (entry 9). Interestingly, the addition of CuI, which is generally required for S-H reactions, dramatically reduced the yield of the target product (entry 10). The activity of

2-naphthoyl chloride was lower than that of 2-naphthoyl fluoride, yielding only 33% of **3aa** (entry 11), implies that the acryl fluoride has unique properties for decarbonylative alkynylation reactions. This reaction did not proceed at all without the addition of a Ni catalyst (entry 12).
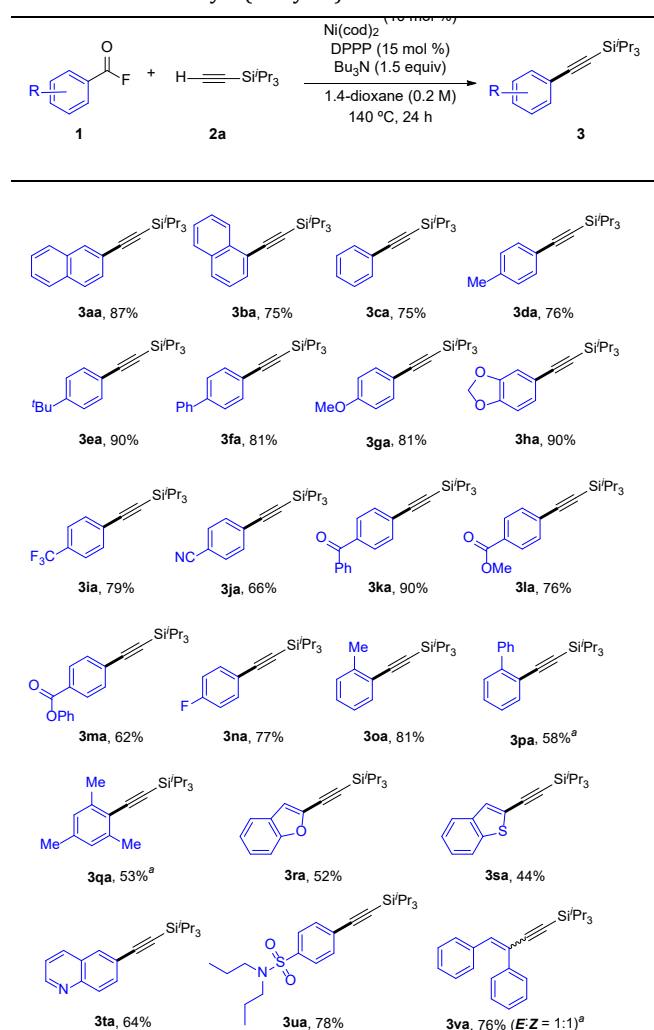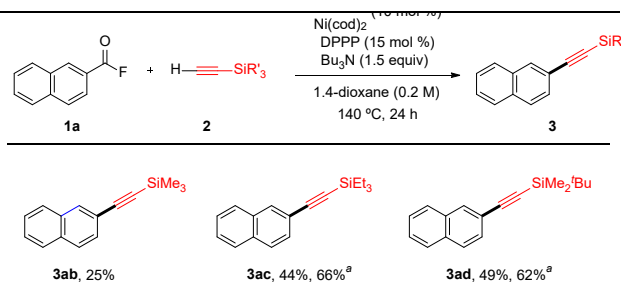

Scheme 2 Scope of acyl fluorides: *Reagents and conditions:* **1** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), DPPP (0.03 mmol), Bu$_3$N (0.3 mmol), 1,4-dioxane (1 mL), 140 °C, 24 h. Yield of the pure isolated products **3**. [a] **1** (0.3 mmol), **2a** (0.2 mmol), 48 h.

With the optimized reaction conditions in hand, *i.e.,* Ni(cod)$_2$ (10 mol %), DPPP (15 mol %), Bu$_3$N (1.5 equiv), 140 ºC, we investigated the substrate scope of acyl fluorides and the results are summarized in Scheme 2. Polycyclic acyl fluorides and benzoyl fluoride can smoothly convert to **3aa-3ca** in good yields. And, acyl fluorides with electron-donating groups at *para*-position, for example, Me (**1d**), *t*Bu (**1e**), and Ph (**1f**) groups, could be converted to the corresponding alkynylsilanes **3da-3fa** effectively (76-90%). Although it is known that the carbon-OMe bond is cleaved in the presence of a nickel catalyst,[23] the substrate bearing an OMe group also afforded **3ga** in 81% yield. An acetal functional group was also tolerated in this reaction, giving the product **3ha** in 90% yield. In addition, alkynylsilanes **3ia-3ma** bearing electron-withdrawing groups at *para*-position were obtained in moderate to good yields. Unlike the previously reported coupling with aryl esters,[12] this reaction allows for both methyl and phenyl esters to be well tolerated. Besides, acyl fluoride functionalized with fluoride group (**1n**) also could be

tolerated in this reaction.[24] Accordingly, the steric effect at *ortho*-position of acyl fluorides was evaluated. In this reaction, the acyl fluoride with a Me group reacted smoothly, yielding **3oa** in 81% yield. However, when the Me group was replaced by an even bulkier Ph group, the yield of **3pa** decreased to 58%. Furthermore, only 53% of **3qa** was obtained from 2,4,6-trimethylbenzoyl fluoride, which has a higher steric hindrance. Heterocyclic acyl fluorides **1r-1t** were also applicable substrates, giving **3ra-3ta** in moderate yields. Besides, the reaction of **1u**, derived from commercially available probenecid, afforded **3ua** in 78% yield. We also synthesized conjugated enynes **3va** in 76% yield as the 1:1 mixture of stereoisomers.

Next, the effect of the silyl group on the alkynes was investigated and the results are shown in Scheme 3. Regardless of reducing or increasing the steric hindrance of the silyl group, the yields of the desired products decreased, with **3ab**, **3ac**, and **3ad** being obtained in 25%, 44%, and 49% yields, respectively. To our delight, when we increased the amount of **2** to 5 equiv, **3ac** and **3ad** could be obtained in 66% and 62% yields, respectively. Attempts were also made to extend the range of substrate to terminal alkynes with aryl and alkyl groups. However, when phenylacetylene and 1-octyne were used as coupling partners, the desired product was not obtained at all (see ESI† for details). The reason for this result is probably due to the trimerization or polymerization of aromatic and aliphatic terminal alkynes under Ni catalysis.

Scheme 3 Scope of silylated alkynes. Reagents and conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), DPPP (0.03 mmol), Bu$_3$N (0.3 mmol), 1,4-dioxane (1 mL), 140 °C, 24 h. Yield of the pure isolated product **3**. *a* **2** (5 equiv).

By combining the reaction mechanism proposed in the previous reports[2,25] and our experimental results described above, a plausible catalytic cycle for this reaction is shown in Scheme 4. First, oxidative addition of the acyl fluoride to Ni(0) proceeds via C–F bond cleavage to give complex **A**. Complex **A** reacts with silyl alkynes **2** under basic conditions to give complex **B**, which is the reaction mechanism proposed for the reported copper-free palladium-catalyzed S-H reaction.[26] Subsequently, a sequential reaction occurs in which decarbonylation gives intermediate **C** and further CO extrusion gives intermediate **D**, from which reductive elimination yields cross-coupled products **3**, and the initial Ni(0) catalyst is regenerated. The result that, in most cases, few aryl alkynyl ketones were produced indicates that CO extrusion might occur prior to reductive elimination and not a rate-limiting step. Considering the formation of enyne **4** as a by-product, oxidative addition of silylated alkynes **2** to Ni(0) results in the formation of complex **E**, which further reacts with the second molecule of **2** to give **4** through homo-hydroalkynylation.[27] Another possibility for the formation of intermediate **B** without copper salt assistance is as follows. Alternatively, as shown in entry 9 of Table 1, the fact that the coupled products **3** can be obtained even in the absence of a base suggests that this reaction may proceed by ligand exchange

between complex **A** and complex **E**, resulting in the formation of complex **B** along with the hydrido(fluoro)nickel complex. Thus, the yield of the desired product **3** might be affected by the competing oxidative addition between acyl fluorides **1** and silylated alkynes **2** to the Ni(0) catalyst.
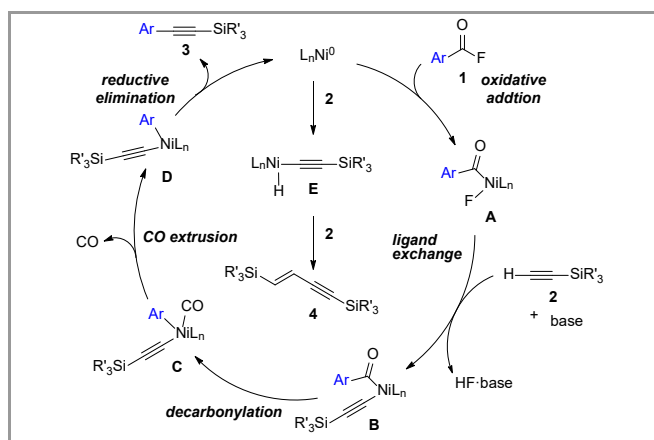
Scheme 4 Proposed mechanism

In summary, we have developed a nickel-catalyzed, copper-free S-H reaction, which proceeds via a decarbonylation pathway using acyl fluorides as coupling partners and shows a wide range of substrates.[28] Detailed DFT calculations are currently being performed to elucidate the sequence of transmetallation and decarbonylation in the catalytic cycle.

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Notes

The authors declare no competing financial interest.

Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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(28) **General Procedure for the Synthesis of Silylated Internal Alkynes 3**: An oven-dried 20 mL of Schlenk tube containing a magnetic stirring bar was charged with Ni(cod)$_2$ (5.5 mg, 0.02 mmol, 10 mol %), DPPP (12.4 mg, 0.03 mmol, 15 mol %), 1,4-dioxane (1 mL) under dry nitrogen, which was stirred for 30 seconds at room temperature. Then, acyl fluorides **1** (0.2 mmol) silyl alkynes **2** (0.4 mmol) and Bu$_3$N (0.3 mmol) were added. The mixture was heated at 140 ºC in a heating block with stirring for 24 h. After being at room temperature, the mixture was quenched with saturated NH$_4$Cl and then aqueous solution was extracted with diethyl ether. The combined organic phase was dried over anhydrous MgSO$_4$, and evaporated under vacuum to remove the volatiles. The residue was purified by column chromatography (EtOAc/hexane) on silica gel to afford the corresponding products **3**.

Characterization Data of Representative Silylated Internal Alkynes 3 Triisopropyl(naphthalen-2-ylethynyl)silane (3aa)[13]
Yellow oil, yield 53.6 mg (87%). R_f = 0.54 (hexane). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.19 (s, 21H), 7.48-7.50 (m, 2H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.76-7.82 (m, 3H), 8.02 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 11.5, 18.9,

91.1, 107.6, 121.0, 126.6, 126.8, 127.85, 127.87, 128.0, 129.0, 132.0, 133.0, 133.1.