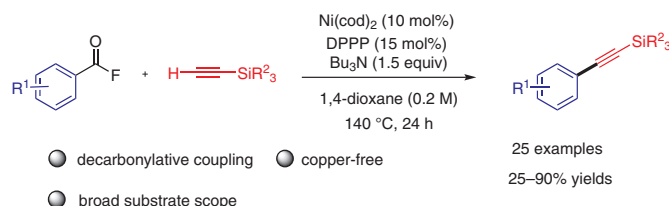Cluster

Nickel-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 method has a wide 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 products were effectively suppressed.
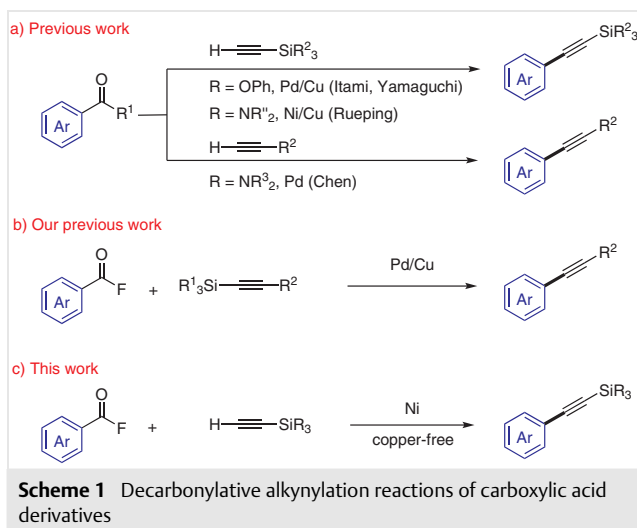
Over the past few decades, the Sonogashira–Hagihara (S–H) reaction,[1] the Pd/Cu-co-catalyzed coupling of terminal alkynes with aryl (pseudo)halides, has resulted in significant progress in the construction of C(sp^2)–C(sp) bonds.[2] Further explorations of this reaction have involved optimizing the reaction conditions to avoid the formation of homocoupled byproducts through the use of copper-free reactions[3] or sila-S–H reactions,[4,5] and the development of more economical catalyst systems 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 in which nickel or other metals have been used as catalysts.

Finding a naturally abundant coupling partner is another approach to optimizing the S–H reaction. Sodium sulfonates,[9] arylhydrazines,[10] and arylsulfonyl hydrazides[11] have been employed as coupling partners instead of the commonly used aryl or vinyl (pseudo)halides, but there is still 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] The group of Itami and Yamaguchi developed the

first example of a Pd/Cu-co-catalyzed alkynylation of aromatic esters in a decarbonylative manner.[12] Meanwhile, Rueping and co-workers developed an effective Ni/Cu co-catalyst for the deamidative cross-coupling of silylated terminal alkynes with amides under base-free conditions, which permitted the direct conversion of amides into alkynes.[13] An example in which copper is not used as a co-catalyst is the Pd-catalyzed decarbonylative alkynylation of amides with terminal alkynes, a reaction that can be applied to various alkynes bearing aryl, alkyl, or silyl substituents.[14]

Acyl fluorides, which can be prepared from the corresponding carboxylic acids, have been widely used in carbon−carbon and carbon−heteroatom bond-formation reactions[15] as ‘RCO’ (carbonyl-retentive)[16] or ‘R’ (decarbonylative)[17–21] sources, due to their unique stability and reactivity. In the decarbonylation reaction, since the first examples of decarbonylative transformations of acid fluorides were disclosed,[17] acyl fluorides have been used as coupling partners in reduction,[18] Suzuki–Miyaura-type arylation,[19] and direct C–H arylation reactions.[20] As an extension of our research on various decarbonylative reactions of acyl fluorides,[21] we recently succeeded in developing a Pd/Cu-co-catalyzed decarbonylative sila-S–H alkynylation of acyl fluorides with silylated internal alkynes (Scheme 1b).[22] The reaction proceeds through cleavage of the C–Si bond, so that no silicon is present in the product. On the other hand, because silylated terminal alkynes can be subjected to further conversions, more-direct methods for reacting silylated terminal alkynes with acyl fluorides, especially by using cheaper catalyst systems, are still highly desirable. Here, we report a nickel-catalyzed decarbonylative alkynylation of acyl fluorides with silylated alkynes under copper-free condition, which provides a direct method for converting acyl fluorides into the corresponding internal silylalkynes (Scheme 1c).

Scheme 1 Decarbonylative alkynylation reactions of carboxylic acid derivatives

Table 1 Optimization of the Reaction Conditions[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[c]	DPPP	1,4-dioxane	68
7[c,d]	DPPP	1,4-dioxane	65
8[c,d,e]	**DPPP**	**1,4-dioxane**	**73**
9[c,f]	DPPP	1,4-dioxane	58
10[c,g]	DPPP	1,4-dioxane	13
11[c,h]	DPPP	1,4-dioxane	33
12[c,i]	DPPP	1,4-dioxane	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Ni(cod)$_2$ (0.02 mmol), ligand (0.04 mmol), Et$_3$N (1.5 equiv), solvent (1 mL), 140 °C, 24 h.
[b] GC yields with dodecane as an internal standard.
[c] **2a** (2.0 equiv).
[d] DPPP (15 mol%).
[e] Bu$_3$N instead of Et$_3$N.
[f] No base.
[g] With CuI (10 mol %).
[h] 2-Naphthoyl chloride instead of **1a**.
[i] Without Ni(cod)$_2$.

To optimize the reaction conditions, we initially conducted the reaction by employing 2-naphthoyl fluoride (**1a**) and ethynyl(triisopropyl)silane (**2a**) as coupling partners and Ni(cod)$_2$ as the catalyst in 1,4-dioxane (Table 1). The nature of the phosphine ligands had a significant effect on the outcome of the reaction (Table 1, 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 given by 1,2-bis(diphenylphosphino)ethane (DPPE). Other bidentate or monodentate phosphine ligands gave much lower yields [see Supporting Information (SI), Table S2]. Subsequently, toluene, DMF, and DMI were tested as solvents instead of 1,4-dioxane, but all of these gave poor yields of **3aa** (entries 4 and 5 and SI, Table S3). To our delight, reducing the amount of **2a** to two equivalents afforded **3aa** in 68% yield (entry 6). However, when the amount of **2a** was further reduced to one equivalent, only 42% of **3aa** was obtained (SI, Table S4). Furthermore, lowering the amount of DPPP to 15 mol% gave **3aa** in 65% yield (entry 7). After screening a series of inorganic and organic bases, we found that when Bu$_3$N was employed instead of Et$_3$N, the yield of **3aa** was improved to 73% (entry 8). Compound **1a** was converted to **3aa** in 58% yield in the absence of 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), implying that the acyl fluoride has unique properties in the decarbonylative alkynylation reaction. This reaction did not proceed at all in the absence of the Ni catalyst (entry 12).

With the optimized reaction conditions in hand [Ni(cod)$_2$ (10 mol %), DPPP (15 mol %), Bu$_3$N (1.5 equiv), 140 °C], we investigated the substrate scope of acyl fluorides (Scheme 2). Naphthoyl fluorides **1a** and **1b** and benzoyl fluoride (**1c**) were smoothly converted into the corresponding products **3aa–ca** in good yields. Acyl fluorides with electron-donating methyl (**1d**), *tert*-butyl (**1e**), or phenyl (**1f**) groups in the *para*-position were efficiently converted into the corresponding alkynylsilanes **3da–fa** in yields of 76–90%. Although it is known that carbon–OMe bonds are cleaved in the presence of nickel catalysts,[23] substrate **1g** bearing a methoxy group nevertheless gave **3ga** in 81% yield. Substrate **1h** bearing an acetal functional group was also tolerated in this reaction, giving product **3ha** in 90% yield. Alkynylsilanes **3ia–ma** bearing electron-withdrawing groups in the *para*-position were also obtained in moderate to good yields. Unlike the previously reported coupling of aryl esters,[12] this reaction tolerates both methyl and phenyl esters. Moreover, acyl fluoride **1n** functionalized with a fluoro group was also tolerated.[24] Next, the steric effects of *ortho*-substituents on the acyl fluoride were evaluated. Acyl fluoride **1o** with an *ortho*-Me group reacted smoothly, yielding **3oa** in 81% yield. However, when the Me group was replaced by a bulkier Ph group, the yield of **3pa** decreased
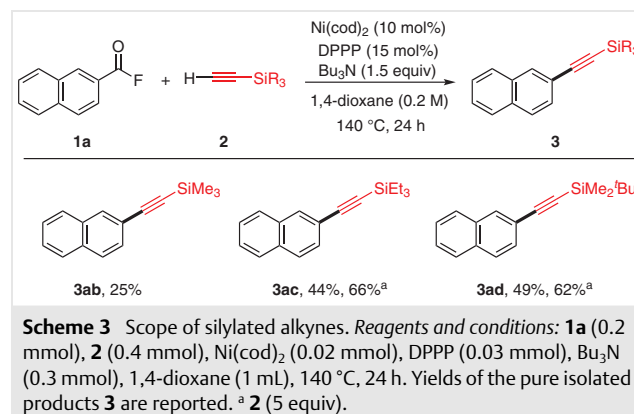
to 58%, and only 53% of product **3qa** was obtained from 2,4,6-trimethylbenzoyl fluoride (**1q**), which has a higher steric hindrance. Heterocyclic acyl fluorides **1r–t** were also suitable substrates, giving products **3ra–ta** in moderate yields. The reaction of **1u**, derived from commercially available probenecid, afforded **3ua** in 78% yield. We also synthesized the conjugated enyne **3va** in 76% yield as a 1:1 mixture of (*E*)- and (*Z*)-isomers.
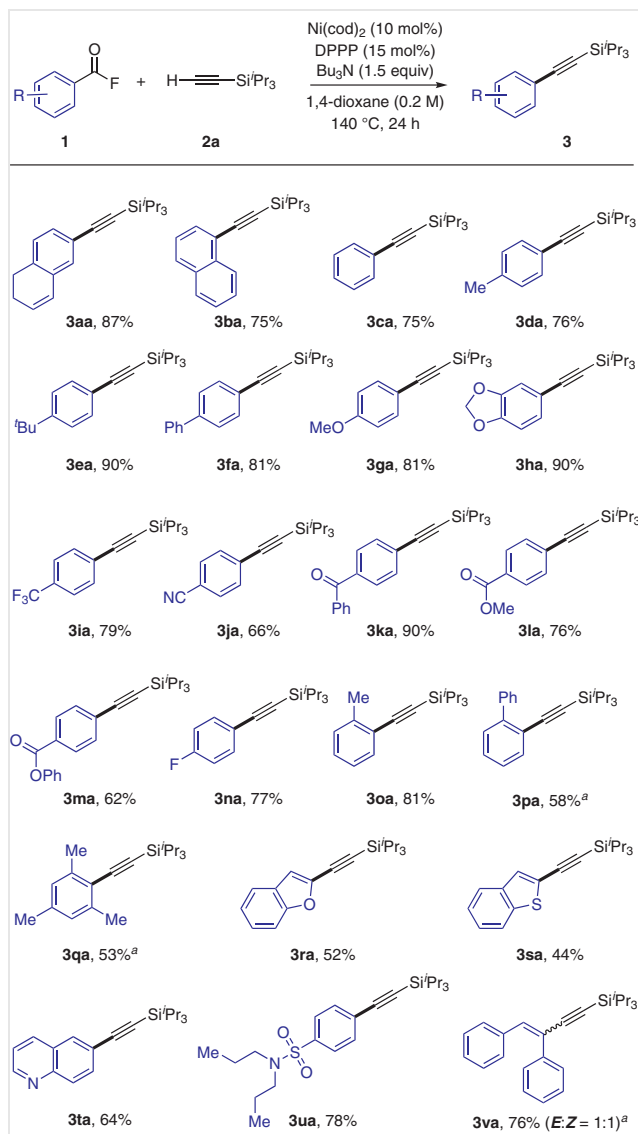

Scheme 2 Scope of acyl fluorides: *Reagents and conditions*: **1** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)$_2$ (0.02 mmol), DPPP (0.03 mmol), Bu$_3$N (0.3 mmol), 1,4-dioxane (1 mL), 140 °C, 24 h. Yields of the pure isolated products **3** are reported. [a] **1** (0.3 mmol), **2a** (0.2 mmol), 48 h.

Next, the effect of the silyl group on the alkyne **2** was investigated (Scheme 3). Regardless of whether steric hindrance by the silyl group was increased or reduced, the

yield of the desired product decreased, with **3ab**, **3ac**, and **3ad** being obtained in yields of 25, 44, and 49%, respectively. To our delight, however, when we increased the amount of **2** to five equivalents, **3ac** and **3ad** were obtained in yields of 66 and 62%, respectively. Attempts were also made to extend the range of substrate to include terminal alkynes with aryl or alkyl groups. However, when ethynylbenzene or oct-1-yne was used as a coupling partner, the desired product was not obtained (see SI for details), probably due to trimerization or polymerization of the aromatic or aliphatic terminal alkyne by the Ni catalyst.

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. Yields of the pure isolated products **3** are reported. [a] **2** (5 equiv).

By combining the reaction mechanism proposed in previous reports[2,25] with our experimental results described above, we developed a plausible catalytic cycle for this reaction, shown in Scheme 4. First, oxidative addition of the acyl fluoride to Ni(0) proceeds through C–F bond cleavage to give complex **A**. This reacts with silyl alkyne **2** under basic conditions to give complex **B**, as proposed for a reported copper-free palladium-catalyzed S–H reaction.[26] Subsequent decarbonylation gives intermediate **C**, and further CO extrusion gives intermediate **D**, from which reductive elimination yields the cross-coupled product **3** with regeneration of the initial Ni(0) catalyst. Because few aryl alkynyl ketones were generally produced, CO extrusion might occur before reductive elimination and might constitute 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 a second molecule of **2** to give **4** through homohydroalkynylation.[27] Another possibility for the formation of intermediate **B** without copper salt assistance is as follows. As shown in Table 1, entry 9, the fact that the coupled products **3** can be obtained 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 a competing oxidative addition of acyl fluoride **1** or silylated alkyne **2** to the Ni(0) catalyst.

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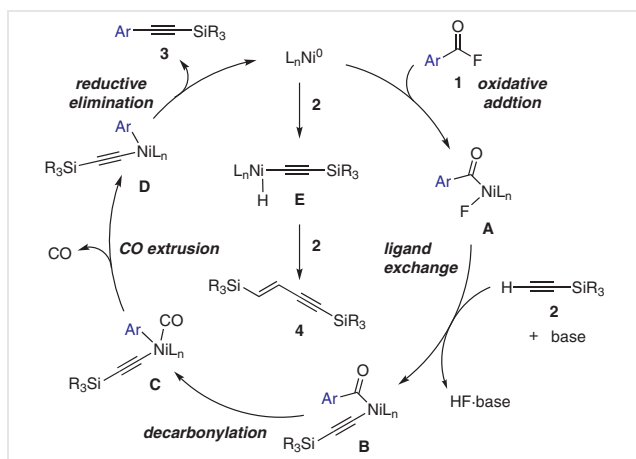
Scheme 4 Proposed mechanism

In summary, we have developed a nickel-catalyzed, copper-free S–H reaction that proceeds by a decarbonylative pathway with acyl fluorides as coupling partners and shows a broad substrate scope.[28] Detailed density functional theory calculations are currently being performed to elucidate the sequence of transmetalation and decarbonylation in the catalytic cycle.

Acknowledgment

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1705954.

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(28) **Silylated Internal Alkynes 3**: **General Procedure**
An oven-dried 20 mL Schlenk tube containing a magnetic stir-ring 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 N$_2$, and the mixture was stirred for 30 s at r.t. The appropriate acyl fluoride **1** (0.2 mmol), silyl alkyne **2** (0.4 mmol), and Bu$_3$N (0.3 mmol) were added, and the mixture was heated at 140 °C in a heating block with stirring for 24 h, then cooled to r.t. The reaction was quenched with sat. aq NH$_4$Cl, and the mixture was extracted with Et$_2$O. The combined organic phase was dried (MgSO$_4$) and concentrated under vacuum, and the residue was purified by column chromatography (silica gel, EtOAc–hexane).

Triisopropyl(2-naphthylethynyl)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, 21 H), 7.48–7.50 (m, 2 H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.76–7.82 (m, 3 H), 8.02 (s, 1 H). ^{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.