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Chemoselective Cu-catalyzed acylsilylation of vinyl arenes using silylboronates and acyl fluorides

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We report the chemoselective copper-catalyzed acylsilylation of vinyl arenes using bench-stable silylboronates and acyl fluorides, which enables efficient access to β-silyl ketones under mild conditions. The reaction proceeds without the need for photochemical activation and exhibits a broad substrate scope, tolerating a wide range of electron-deficient and heteroaromatic vinyl arenes, as well as electronically diverse acyl fluorides, including drug-derived motifs. A key to this success is the LUMO-lowering effect of the electron-withdrawing substituents on the aryl ring, which enhances nucleophilic attack by a silylcopper(I) species. Mechanistically, the transformation proceeds *via* a PCy_3-ligated copper catalyst, mediating Si–B σ-bond transmetalation, alkene insertion, and nucleophilic substitution with acyl fluoride. Notably, acyl fluorides outperform commonly used acid chlorides and acyl imidazoles, offering both improved reactivity and catalyst turnover through the formation of a reactive Cu–F intermediate, which regenerates the active silylcopper species with the concomitant formation of F–Bpin. It is worth noting that this system enables clear discrimination between electronically similar vinyl arenes. The method should be a promising platform for site-selective and chemoselective alkene functionalization in complex settings.

Introduction

Organosilicon compounds are indispensable in modern chemical science, with applications ranging from advanced materials such as elastomers to pharmaceuticals and agrochemicals.[1] Their value stems in part from the unique physicochemical properties of the silicon–carbon (C–Si) bond, which can modulate molecular lipophilicity, metabolic stability, and stereochemistry. As a result, the development of efficient synthetic methodologies to form C–Si bonds remains an area of intense interest.[2] Among these, three-component alkene difunctionalization has emerged as a particularly powerful strategy.[3] This approach enables the simultaneous installation of a silyl group and a carbon-based fragment across an olefin, rapidly increasing molecular complexity from simple precursors. In this context, silylboronic esters ($R_3SiBpin$)[4] have proven particularly valuable because of their stability, ease of handling, and reactivity in both two- and three-component C–Si bond-forming transformations.

In 2021, our group demonstrated that silylboronates could engage aryl and alkyl fluorides in a catalyst-free defluorinative carbosilylation of vinyl arenes, revealing that even the typically inert C–F bond can cleave to function as a traceless leaving group in alkene functionalization.[5] In this process, fluoride is efficiently sequestered as potassium fluoride (KF), enabling clean and selective transformations of readily available organic fluorides[6] *via* C–F bond activation[7] (Fig. 1a). In the same year, Brown and co-workers developed a Ni-catalyzed silylacylation of alkenes using preformed silylzinc reagents and acid chlorides, furnishing β-silyl ketones *via* a nucleophilic [Ni]–SiR_3 intermediate that undergoes alkene insertion and acyl trapping (Fig. 1b).[8] More recently, Ohmiya *et al.* reported a visible-light-mediated acylsilylation using $R_3SiBpin$ as a radical precursor in combination with *N*-heterocyclic carbene (NHC) catalysis, achieving acylsilylation under mild conditions (Fig. 1c).[9] Despite these notable advances, existing methods still face limitations, including: (i) the need for air- and moisture-sensitive silylzinc reagents; (ii) the use of corrosive and unstable acid chlorides; and (iii) photochemical activation requiring specialized catalyst systems and light sources. Although acyl imidazoles are known to be effective acylating agents, their synthetic accessibility is limited.[10] To overcome these challenges, we turned our attention to acyl fluorides,[11] bench-stable electrophiles that are readily accessible *via* deoxyfluorination or oxidative fluorination.[12] Although the C–F bond in acyl fluorides is typically inert under the standard conditions, it can be selectively activated by π-acidic late transition metals, particularly copper (Cu), which is capable of engaging in oxidative addition to polarized C–F bonds. This makes acyl fluorides attractive partners for catalytic processes that aim for both efficiency and environmental sustainability. Recently, our

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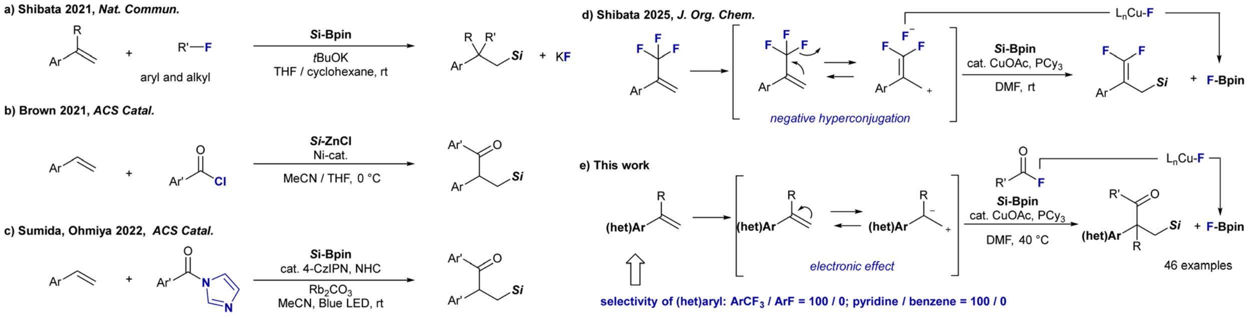

a) Shibata 2021, Nat. Commun.
aryl and alkyl
Si-Bpin
tBuOK
THF / cyclohexane, rt
+ KF
b) Brown 2021, ACS Catal.
Si-ZnCl
Ni-cat.
MeCN / THF, 0 °C
c) Sumida, Ohmiya 2022, ACS Catal.
Si-Bpin
cat. 4-CzIPN, NHC
Rb2CO3
MeCN, Blue LED, rt
d) Shibata 2025, J. Org. Chem.
negative hyperconjugation
Si-Bpin
cat. CuOAc, PCy3
DMF, rt
LnCu-F
+ F-Bpin
e) This work
(het)Ar
electronic effect
Si-Bpin
cat. CuOAc, PCy3
DMF, 40 °C
LnCu-F
+ F-Bpin
46 examples
selectivity of (het)aryl: ArCF3 / ArF = 100 / 0; pyridine / benzene = 100 / 0

Fig. 1 Background and motivation of this work. (a–d) Previous works. (e) Chemoselective acylsilylation of vinyl arenes (this work).

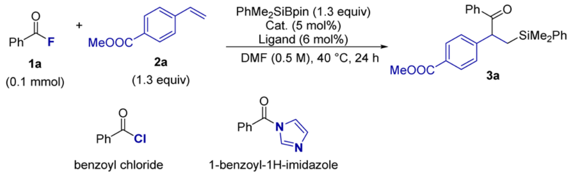
group reported the Cu-catalyzed defluorosilylation of trifluoromethylalkenes, in which trifluoromethyl (CF_3) moiety plays a dual mechanistic role: its electron-withdrawing nature and negative hyperconjugation activate the alkene toward nucleophilic attack by the silylcopper species, whereas selective C–F bond cleavage enables C–Si bond formation, accompanied by the generation of a stable F–Bpin byproduct *via* a Cu–F intermediate (Fig. 1d).[13]

Building on this mechanistic foundation, we now report an chemoselective Cu-catalyzed acylsilylation of vinyl arenes using readily available silylboronates and acyl fluorides. This transformation proceeds smoothly at 40 °C under photochemical-free conditions and exhibits broad compatibility with electron-deficient and heteroaromatic vinyl arenes, as well as a diverse range of acyl fluorides, including those derived from drug-like molecules. The reaction delivers β-silyl ketones in up to 99% isolated yield, with excellent chemoselectivity and functional group tolerance. A critical factor for the success of this transformation is the polarization of the alkene moiety in the vinyl arenes with electron-deficient substituents, which lowers the LUMO energy of the alkene and thereby facilitates nucleophilic attack by the silylcopper species. Mechanistically, the reaction is promoted by a PCy_3-ligated copper catalyst that mediates a sequence of key steps: Si–B σ-bond transmetalation, migratory insertion into the alkene, and nucleophilic substitution with acyl fluoride. The resulting fluoride byproduct is efficiently captured as F–Bpin, formed through a Cu–F intermediate. It is worth noting that this system enables clear discrimination between electronically similar vinyl arenes, such as CF_3-substituted vinylbenzene *vs. para*-fluorostyrene, and 4-vinylpyridine *vs.* styrene. This level of selectivity highlights the potential of the methodology as a promising platform for site-selective and chemoselective alkene functionalization in complex molecular settings (Fig. 1e).

Results and discussion

Based on our previous findings on Cu-catalyzed defluorosilylation of trifluoromethylalkenes,[13] we hypothesized that the alkene component in this three-component coupling should be electronically polarized to enable an efficient reaction. Thus, methyl 4-vinylbenzoate (**1a**) was selected as a model substrate for optimization, in combination with benzoyl fluoride (**2a**) and silylboronate, $PhMe_2SiBpin$, under copper catalysis (Table 1). Initial experiments were performed under our previously established conditions:[13] CuOAc (5 mol%) and PCy_3 (6 mol%) in DMF at room temperature (entry 1). While the reaction proceeded cleanly by TLC monitoring, the conversion was incomplete, and the desired β-silyl ketone **3aa** was isolated in 91% yield, with a little amount of unreacted **1a** and **2a** remaining. Increasing the temperature to 40 °C led to quantitative formation of **3aa** (99%), establishing this as the optimal temperature (entry 2). To examine the influence of the copper source,

Table 1 Optimization of the reaction conditions[a]


1a
(0.1 mmol)
2a
(1.3 equiv)
PhMe2SiBpin (1.3 equiv)
Cat. (5 mol%)
Ligand (6 mol%)
DMF (0.5 M), 40 °C, 24 h
3a
benzoyl chloride
1-benzoyl-1H-imidazole

Entry	Cat.	Ligand	Yield[b] of **3aa**
1[c]	CuOAc	PCy_3	91%
2	CuOAc	PCy_3	99% (96%)[d]
3	CuCl	PCy_3	NR
4	CuBr	PCy_3	NR
5	CuF_2	PCy_3	32%
6	$Cu(OAc)_2$	PCy_3	74%
7	$[(MeCN)_4Cu]PF_6$	PCy_3	36%
8	$Cu(CF_3COO)_2\cdot H_2O$	PCy_3	49%
9	$Fe(OAc)_2$	PCy_3	NR
10	$Pd(OAc)_2$	PCy_3	NR
11	CuOAc	PPh_3	35%
12	CuOAc	P^tBu_3	33%
13	CuOAc	XPhos	NR
14	CuOAc	DCPE	29%
15	—	PCy_3	NR
16	CuOAc	—	NR
17[e]	CuOAc	PCy_3	0
18[f]	CuOAc	PCy_3	68%

[a] $PhMe_2SiBpin$ (1.3 equiv), **2a** (1.3 equiv), and **1a** (0.1 mmol) in DMF, 40 °C for 24 h. [b] Determined by trimethyl orthoformate (11.0 μL) as internal standard. [c] The reaction was performed at room temperature. [d] Isolated yield. [e] Reaction was performed using benzoyl chloride (PhCOCl) instead of **1a**. [f] Reaction was performed using 1-benzoyl-1*H*-imidazole instead of **1a**.

a variety of copper(I) and copper(II) salts were tested. Both CuCl and CuBr were catalytically inactive, affording no detectable product (entries 3 and 4). Other copper salts such as CuF_2, $Cu(OAc)_2$, $[(MeCN)_4Cu]PF_6$, and $Cu(CF_3COO)_2\cdot H_2O$ gave diminished yields ranging from 32% to 74% (entries 5–8), indicating that CuOAc is uniquely suited for this transformation. To probe metal specificity, $Fe(OAc)_2$ and $Pd(OAc)_2$ were also examined, but failed to catalyze the reaction (entries 9 and 10), emphasizing the reactivity of copper in this system. Next, we evaluated the effect of various phosphine ligands (entries 11–14). PPh_3 and P^tBu_3 gave moderate yields (35% and 33%, respectively), whereas XPhos (dicyclohexyl[2′,4′,6′-tris(propan-2-yl)[1,1′-biphenyl]-2-yl]phosphane) was entirely ineffective (0%) and DCPE (1,2-bis(dicyclohexylphosphino)ethane) provided only 29% of the product. Finally, control experiments confirmed that both CuOAc and PCy_3 are essential for the reaction; omitting either component resulted in no product formation, confirming their cooperative role in catalysis (entries 15 and 16).

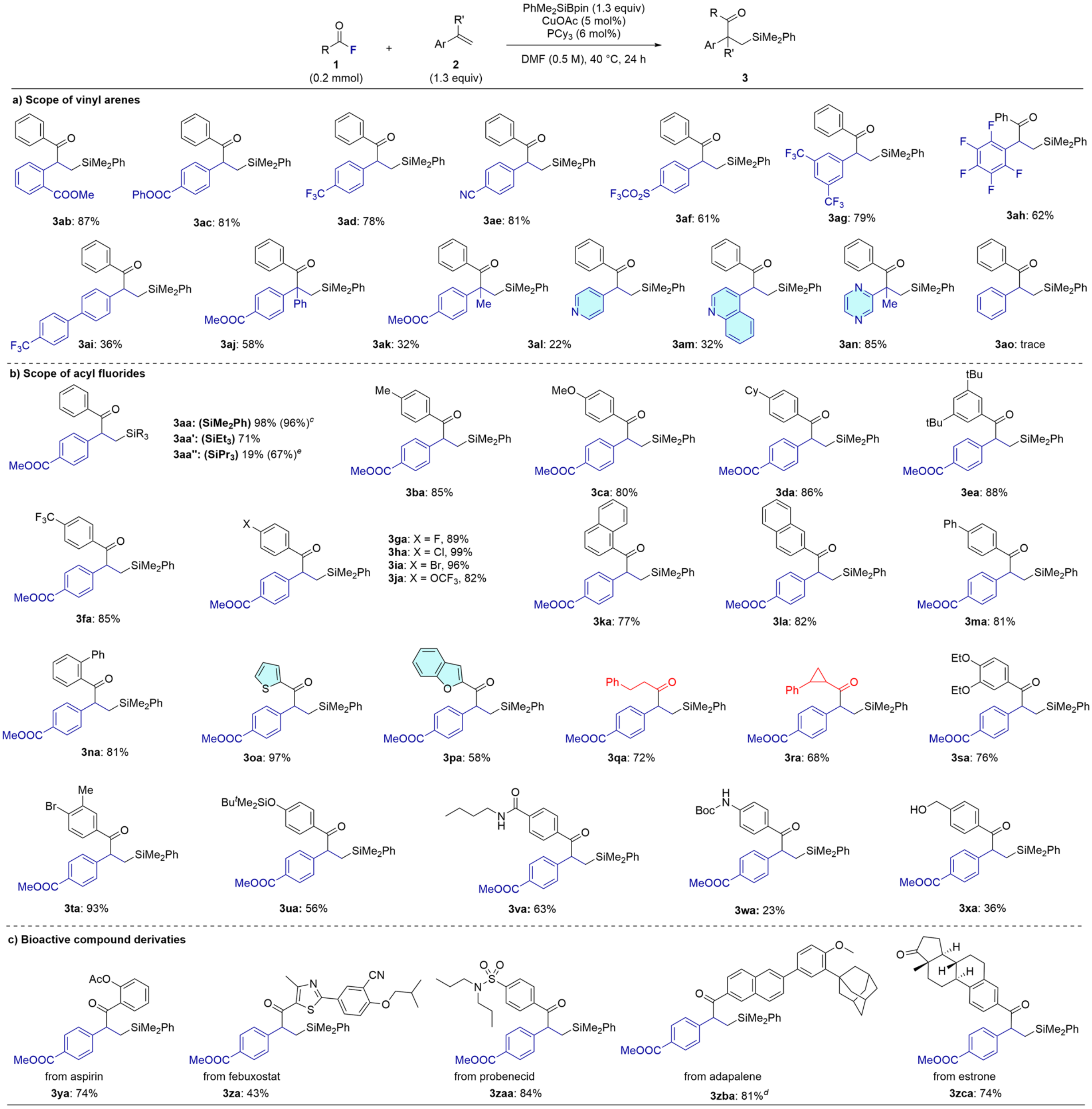
To elucidate the unique role of acyl fluoride (**1a**) in this transformation, we compared its reactivity with other common acyl electrophiles under optimized Cu-catalyzed conditions. Benzoyl chloride, which was previously used in the Ni/Zn system (by Brown, Fig. 1b),[8] was completely unreactive, affording 0% of the acylsilylation product (entry 17). In contrast, benzoyl imidazole, the electrophile employed by Sumida and Ohmiya under photoredox/NHC conditions (Fig. 1c),[9] gave a moderate 68% yield (entry 18). These results suggest that, despite its strong bond, the C–F moiety in acyl fluorides serves as the most compatible leaving group in the current copper system.

With the optimized reaction conditions established, we explored the substrate scope of the acylsilylation reaction. First, to confirm the hypothesis of the polarization of the alkene moiety in vinyl arenes with substituents, we evaluated various electron-deficient vinyl arenes (**2**) under optimized conditions (Scheme 1a). Methyl 2-vinylbenzoate (**2b**) underwent smooth acylsilylation with **1a** and $PhMe_2SiBpin$, affording **3ab** in 87% yield. Phenyl 4-vinylbenzoate (**2c**) also provided acylsilylation product **3ac** in 81% yield. Vinyl arenes bearing CF_3 (**2d**, **2g**), cyano (**2e**), and trifluoromethanesulfonyl (**2f**) groups afforded desired products **3ad**–**3ag** in 61–81% yields. Also, 1,2,3,4,5-pentafluoro-6-vinylbenzene **2h** furnished the desired product **3ah** in good yield of 62%. Interestingly, even vinyl biphenyl (**2i**) bearing a remotely positioned CF_3 group afforded product **3ai** in 36% yield, suggesting that electron-withdrawing effects at a distance can still promote the reaction, albeit with reduced efficiency in extended aryl systems. Disubstituted vinyl arenes (**2j** and **2k**) were also examined, delivering **3aj** and **3ak** in 58% and 32% yields, respectively. Notably, 4-vinylpyridine (**2l**) underwent the transformation to give **3al** in 22% yield, demonstrating the applicability of the protocol to heteroaromatic alkenes. We then tried 2 more *N*-heteroaromatic alkenes, including quinoline and pyrazine, corresponding products obtained with 32% (**3am**) and 85% (**3an**), respectively. On the other hand, styrene (**2o**) showed little to no reactivity under the standard conditions resulting in a trace amount of **3ao** detected, importance the critical role of electronic situation on the aromatic ring in facilitating the reaction.

Next, we investigated a range of acyl fluorides (**1**) in combination with the vinyl arenes derivative **2a** to evaluate the generality of the protocol (Scheme 1b). Acyl fluorides bearing electron-donating groups such as methyl (**1b**), methoxy (**1c**), and cyclohexyl (**1d**) at the *para* position of the aryl ring afforded the desired products **3ba**–**3da** in good yields (80–86%). A bulky 3,5-di-*tert*-butyl-substituted acyl fluoride (**1e**) also performed well, delivering **3ea** in 88% yield. Next, we examined substrates bearing electron-withdrawing and halogen substituents including CF_3 (**1f**), fluoro (**1g**), chloro (**1h**), bromo (**1i**), and trifluoromethoxy (**1j**). These gave excellent results with $PhMe_2SiBpin$ and **2a**, affording **3fa**–**3ja** in 82–99% yields. Extended π-systems such as naphthyl and biphenyl derivatives (**1k**–**1m**) also participated efficiently, delivering **3ka**–**3ma** in 77–82% yields. Notably, a sterically hindered *ortho*-phenyl-substituted acyl fluoride (**1n**) gave **3na** in 81% yield, suggesting that steric effects are minimal under the optimized conditions. Heteroaryl acyl fluorides, including thiophene (**1o**) and benzofuran (**1p**) derivatives, were also compatible, affording **3oa** and **3pa** in 97% and 58% yields, respectively. Furthermore, aliphatic acyl fluorides (**1q** and **1r**) delivered the corresponding products **3qa** and **3ra** in 72% and 68% yields, highlighting the versatility of this method. Moreover, disubstituted aryl fluorides (**1s** and **1t**) furnished the desired β-silyl ketones **3sa** and **3ta** in 76% and 93% yields, respectively. In addition, we examined the reactivity of several challenging substrates. *tert*-Butyldimethylsilyl-protected derivative (**1u**) afforded the desired product **3ua** in a moderate yield of 56%. Substrates bearing functional groups with relatively acidic protons, such as a secondary amide (**1v**), a secondary amine (**1w**), and a benzyl alcohol (**1x**), were also investigated. Among these, substrate **1v** furnished the corresponding product in good yield (**3va**: 63%), whereas **1w** and **1x** delivered only modest yields (**3wa**: 23%, **3xa**: 36%). We next evaluated alternative silylboranes by replacing $PhMe_2SiBpin$ with $Et_3SiBpin$ and $^nPr_3SiBpin$. Both reagents proved suitable for the transformation. The use of $Et_3SiBpin$ furnished the desired product in good yield (**3aa′**: 71%), whereas $^nPr_3SiBpin$ afforded the corresponding product (**3aa″**) in 67% yield, albeit requiring an elevated reaction temperature. The reaction between **1a** and **2a** was successfully scaled up from 0.2 mmol to 2 mmol, affording **3aa** in 96% yield without any loss in efficiency, thereby demonstrating the practicality and scalability of the method.

Synthetic application I

To demonstrate the synthetic utility of this Cu-catalyzed acylsilylation protocol, we investigated its application in the late-stage functionalization of various pharmaceutical derivatives bearing carbonyl fluoride moiety in the presence of vinyl arene **2a** and $PhMe_2SiBpin$ (Scheme 1c). Structurally simple aspirin-derived acyl fluoride (**1y**) underwent smooth conversion to the corresponding β-silyl ketone **3ya** in 74% yield. In contrast, the more structurally complex febuxostat derivative (**1z**) afforded a moderate 43% yield of product **3za**, likely due to steric or electronic interference. Encouragingly, several other drug-

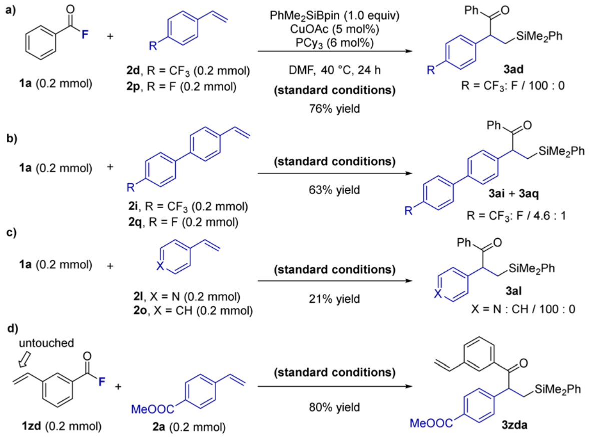

PhMe2SiBpin (1.3 equiv)
CuOAc (5 mol%)
PCy3 (6 mol%)
DMF (0.5 M), 40 °C, 24 h
1 (0.2 mmol)
2 (1.3 equiv)
3
a) Scope of vinyl arenes
3ab: 87%
3ac: 81%
3ad: 78%
3ae: 81%
3af: 61%
3ag: 79%
3ah: 62%
3ai: 36%
3aj: 58%
3ak: 32%
3al: 22%
3am: 32%
3an: 85%
3ao: trace
b) Scope of acyl fluorides
3aa: (SiMe2Ph) 98% (96%)c
3aa': (SiEt3) 71%
3aa'': (SiPr3) 19% (67%)e
3ba: 85%
3ca: 80%
3da: 86%
3ea: 88%
3fa: 85%
3ga: X = F, 89%
3ha: X = Cl, 99%
3ia: X = Br, 96%
3ja: X = OCF3, 82%
3ka: 77%
3la: 82%
3ma: 81%
3na: 81%
3oa: 97%
3pa: 58%
3qa: 72%
3ra: 68%
3sa: 76%
3ta: 93%
3ua: 56%
3va: 63%
3wa: 23%
3xa: 36%
c) Bioactive compound derivaties
from aspirin
3ya: 74%
from febuxostat
3za: 43%
from probenecid
3zaa: 84%
from adapalene
3zba: 81%d
from estrone
3zca: 74%

Scheme 1 Scope of substrates.[a] Yields of isolated products;[b] unless otherwise noted, the reaction was conducted with CuOAc (5 mol%), PCy_3 (6 mol%), $PhMe_2SiBpin$ (1.3 equiv), **2** (1.3 equiv), and **1** (0.2 mmol) in DMF (0.5 M), 40 °C for 24 h;[c] the reaction was performed with 2.0 mmol scale;[d] the reaction was performed at 100 °C;[e] the reaction was performed at 80 °C.

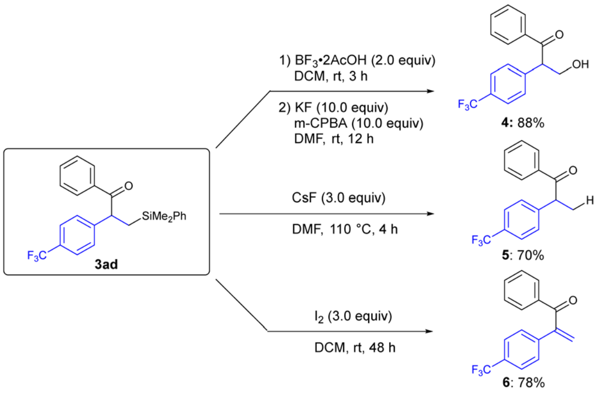
derived acyl fluorides were well tolerated under the reaction conditions. Derivatives of probenecid (**1za**), adapalene (**1zb**), and estrone (**1zc**) furnished the corresponding products **3zaa**, **3zba**, and **3zca** in 84%, 81%, and 74% yields, respectively, indicating broad functional group tolerance and suitability for late-stage diversification of bioactive molecules.

Synthetic application II

Encouraged by the unique reactivity profile of this chemoselective Cu-catalyzed acylsilylation, particularly its high sensitivity to the electronic nature of the arene moiety as exemplified by the low reactivity of styrene **2o** (see Scheme 1), we explored the potential for chemoselective transformation in mixtures of electronically distinct two vinyl arenes **2**. We first investigated the competitive chemoselective acylsilylation of *p*-CF_3 vinyl benzene (**2d**) and *p*-fluoro vinyl benzene (**2p**) using benzoyl fluoride (**1a**) under the standard conditions. Remarkably, only **2d** reacted to afford the desired product **3ad** in 76% yield, with exclusive selectivity ($CF_3 : F = 100 : 0$) (Scheme 2a). This high discrimination suggests that the stronger electron-withdrawing CF_3 group more effectively activates the alkene for nucleophilic attack by the silylcopper species. This selectivity also extended to biphenyl derivatives bearing remote CF_3 and F groups. In


a)
1a (0.2 mmol)
2d, R = CF3 (0.2 mmol)
2p, R = F (0.2 mmol)
PhMe2SiBpin (1.0 equiv)
CuOAc (5 mol%)
PCy3 (6 mol%)
DMF, 40 °C, 24 h
(standard conditions)
76% yield
3ad
R = CF3 : F / 100 : 0
b)
1a (0.2 mmol)
2i, R = CF3 (0.2 mmol)
2q, R = F (0.2 mmol)
(standard conditions)
63% yield
3ai + 3aq
R = CF3 : F / 4.6 : 1
c)
1a (0.2 mmol)
2l, X = N (0.2 mmol)
2o, X = CH (0.2 mmol)
(standard conditions)
21% yield
3al
X = N : CH / 100 : 0
d)
untouched
1zd (0.2 mmol)
MeOOC
2a (0.2 mmol)
(standard conditions)
80% yield
3zda
SiMe2Ph

Scheme 2 Competitive experiments.[a] Yields of isolated products.


3ad
F3C
SiMe2Ph
1) BF3•2AcOH (2.0 equiv)
DCM, rt, 3 h
2) KF (10.0 equiv)
m-CPBA (10.0 equiv)
DMF, rt, 12 h
OH
4: 88%
CsF (3.0 equiv)
DMF, 110 °C, 4 h
H
5: 70%
I2 (3.0 equiv)
DCM, rt, 48 h
6: 78%

Scheme 3 Representative transformations of **3ad**[a].[a] Yields of isolated products.

a competitive experiment, the acylsilylation product **3ai** derived from the CF_3-substituted substrate **2i** was obtained in 63% yield with notable chemoselectivity ($CF_3 : F = 4.6 : 1$), highlighting the ability to distinguish subtle electronic differences at distant positions (Scheme 2b). Next, we examined heteroarene discrimination. A mixture of 4-vinylpyridine (**2l**) and styrene (**2o**) was subjected to the standard reaction with **1a**. In this case, only **2l** reacted to deliver **3al** in 21% yield, with complete selectivity (pyridine : benzene = 100 : 0) (Scheme 2c). This result highlights the high reactivity of heteroarenes in this system. Finally, to test site-selectivity within a single molecule, we subjected acyl fluoride bearing a vinyl arene group (compound **1zd**) to acylsilylation conditions in the presence of 4-methoxycarbonyl vinyl benzene (**2a**). The reaction exclusively furnished product **3zda** in 80% yield, with the vinyl group in **1zd** remaining untouched (Scheme 2d). These results collectively demonstrate the distinctive electronic discrimination achievable in this system, making it a promising platform for site-selective and chemoselective alkene functionalization in complex settings.

Synthetic application III

Representative transformations of β-silyl ketone were performed at the C–Si bond while retaining the ketone functionality (Scheme 3). Fleming–Tamao oxidation of **3ad** with $BF_3 \cdot AcOH$ and *m*-CPBA afforded β-hydroxy ketone **4** in 88% yield. Desilylation of **3ad** with CsF gave product **5** in 70% yield, and iodine-mediated olefination of **3ad** furnished α,β-unsaturated ketone **6** in 78% yield.

Reaction mechanism

A plausible catalytic cycle, consistent with these observations, is shown in Fig. 2. The reaction begins with σ-bond metathesis between CuOAc/PCy_3 and $PhMe_2SiBpin$, generating silylcopper(I) species **I** and releasing AcO–Bpin. Next, migratory insertion of an electron-deficient vinyl arene into the Cu–Si bond affords the corresponding alkyl–copper(I) intermediate **II**. This intermediate then undergoes nucleophilic acyl substitution with the acyl fluoride. The intrinsic affinity of Cu for fluorine facilitates C–F bond cleavage, forming a putative acyl–copper(I) intermediate **III**. The strong σ-donating PCy_3 ligand stabilizes this high-valent species and promotes the substitution event. Subsequently, β-fluoride elimination from **III** delivers the β-silyl ketone **3** and a Cu(I)–F complex **IV**. Finally, regeneration of active silylcopper(I) species **I** occurs *via* a second σ-bond metathesis between **IV** and $PhMe_2SiBpin$, liberating F–Bpin as the byproduct. The formation of F–Bpin was confirmed by ^{19}F NMR spectroscopy, supporting the proposed fluoride-transfer pathway.

The superior performance of acyl fluorides in this transformation can be rationalized by two synergistic effects. First, the polarized C–F bond in acyl fluorides undergoes more facile oxidative addition or nucleophilic substitution by copper than the more covalent C–Cl bond in acyl chlorides (see entry 17, Table 1). Second, with respect to catalyst turnover, the resulting Cu–F species **IV** is readily reactivated by Si–Bpin to regenerate the silylcopper complex, whereas the analogous Cu–Cl species is less reactive in σ-bond metathesis, thereby impeding the catalytic cycle. Together, these mechanistic insights explain the

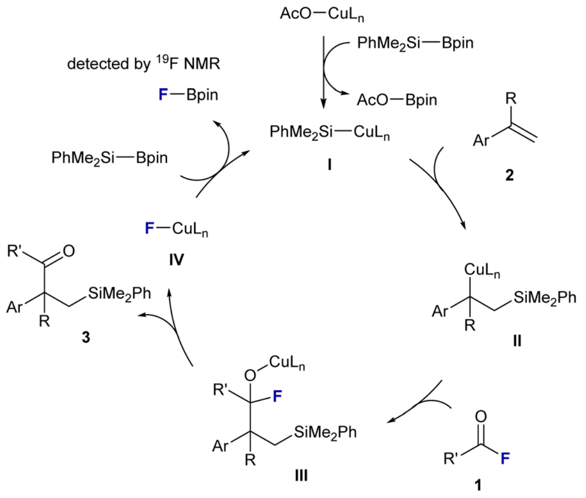

AcO—CuLn
PhMe2Si—Bpin
AcO—Bpin
detected by 19F NMR
F—Bpin
PhMe2Si—Bpin
PhMe2Si—CuLn
I
Ar
R
2
F—CuLn
IV
R'
O
Ar
R
SiMe2Ph
3
CuLn
SiMe2Ph
II
O
CuLn
R'
F
SiMe2Ph
III
O
R'
F
1

Fig. 2 Proposed reaction mechanism.

high efficiency of acyl fluorides over acyl chlorides and acyl imidazoles (entries 17 and 18, Table 1) in the present Cu/PCy_3 system, and emphasize the strategic utility of carbonyl fluorides as ideal electrophiles in copper-catalyzed alkene difunctionalization chemistry.

Limitations of the study

We explored the applicability of this acylsilylation protocol to alkyl-substituted alkenes beyond the scope of vinyl arenes **2**. However, no reaction was observed, highlighting a key limitation of the method. The starting alkenes remained unconsumed, suggesting that the aryl moiety in vinyl arenes **2** is critical for reactivity, particularly in the initial step involving insertion of the Cu–Si species (intermediate **I**). Without the conjugated aryl group, the alkene likely lacks sufficient electronic activation to undergo migratory insertion, preventing formation of the key alkyl–Cu intermediate (**II**) (Fig. 2).

Conclusions

In summary, we have developed a chemoselective copper-catalyzed acylsilylation of electron-deficient vinyl arenes including heteroaromatics using readily available acyl fluorides and silylboronates under mild and operationally simple conditions. This method provides efficient access to a broad range of β-silyl ketones with high chemoselectivity and excellent functional group tolerance, including halogens, nitriles, esters, heterocycles, and pharmaceutically relevant motifs. Even reactive functional groups such amine, amide, and alcohol are compatible with this reaction system. The reaction proceeds *via* a well-defined catalytic cycle involving silylcopper(I) species, migratory alkene insertion, and nucleophilic substitution with the acyl fluoride, followed by β-fluoride elimination. Mechanistic studies highlight the strategic advantage of using acyl fluorides over acyl chlorides and acyl imidazoles, with both improved reactivity and more efficient catalyst turnover. The formation of F–Bpin as the terminal byproduct further supports the proposed fluoride-transfer pathway. The utility of this protocol was demonstrated through the late-stage functionalization of complex pharmaceutical derivatives. The ability to distinguish between electronically similar alkenes—such as CF_3- *vs.* fluoro-substituted styrenes, or 4-vinylpyridine *vs.* styrene—highlights the potential of this method for precise chemoselective alkene functionalization.

Author contributions

ZZ, JZ, SO and SI performed the experiments and analyzed the data. ZZ, SO and NS wrote the manuscript. NS supervised the project. All authors contributed to the manuscript and have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available within the article and the SI.

Supplementary information: Materials and methods, experimental procedures, characterization data, and NMR spectral. See DOI: https://doi.org/10.1039/d5sc05220c.

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