Research Article

Dual N-Heterocyclic Carbene/Photoredox-Catalyzed Coupling of Acyl Fluorides and Alkyl Silanes

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ABSTRACT: The combination of N-heterocyclic carbene (NHC) organo-catalysis with photochemical activation is becoming increasingly established as an approach for conducting radical organic reactions under mild and practical conditions. As comparatively easy to prepare and handle organic compounds, alkyl silanes are attractive substrates for radical chemistry as desilylative mesolysis of the corresponding radical cations is known to be rapid. Here, we report the successful application of benzyl silane derivatives as source of alkyl radicals in dual NHC/ photoredox-catalyzed radical−radical coupling reactions with acyl fluorides. Relatively electron-rich benzyl silanes reacted smoothly to afford the corresponding ketones in generally good yields, while optimization of the NHC and photocatalyst allowed for a wider scope including primary benzyl substrates. Furthermore, initial experiments revealed that organosilanes bearing N-, O- and S-heteroatoms can also serve as alkyl radical sources under these conditions.

KEYWORDS: *N-heterocyclic carbenes, silanes, photoredox catalysis, ketones, radicals*
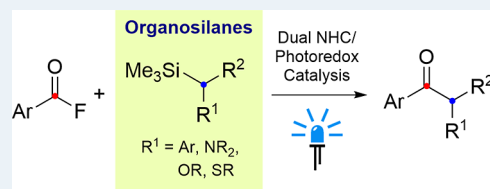
INTRODUCTION

Over the last few decades, organocatalysis using N-heterocyclic carbenes (NHCs) has emerged as a powerful approach to prepare organic molecules. Umpolung processes where NHCs transiently invert the inherent polarity of aldehyde substrates are the most widely developed reaction class.[1] In recent years, considerable research effort has been devoted to expanding the scope of transformations achievable through NHC organo-catalysis.[2] Some of the most intriguing advances have been made by combining NHCs with light irradiation.[3] As demonstrated by our group in 2020,[4] upon addition/ elimination to a suitable acyl electrophile, an NHC can influence the absorption characteristics and subsequent photochemical reactivity of a neighboring carbonyl group (Figure 1a, Path 1). Using this Photo-NHC concept, ketone-like reactivity could be accessed with otherwise unsuitable acyl fluoride substrates in a novel photoenolization/Diels−Alder (PEDA) process.[5,6]

The NHC moiety in an organocatalytic intermediate can also have a decisive influence on its redox properties. Since the pioneering work of DiRocco and Rovis, who first reported a dual NHC/[Ru(bpy)₃]Cl₂ (bpy = 2,2′-bipyridine) catalyzed umpolung reaction of aldehydes with tertiary amines under visible light irradiation in 2012,[7] several groups have explored the combination of NHC organocatalysis with photoredox activation.[3] Upon reaction with aldehyde substrates, the resulting Breslow intermediate **A** features an electron-rich enamine motif, which can be readily oxidized under photo-redox conditions (Figure 1a, Path 2). Similarly, acyl azolium species **B** generated upon addition/elimination of an NHC

onto an activated carboxylic acid derivative are rendered significantly more susceptible to single electron reduction due to the neighboring cationic azolium fragment (Figure 1a, Path 3). In each case, radical species **C** are generated, which benefit from enhanced stability by virtue of spin delocalization onto the NHC moiety.[8] A focus of research conducted in the past few years has been the exploration of suitable alkyl radical precursors for engaging with species **C** through radical−radical coupling. When starting from aldehydes, precursors that generate radicals upon single electron reduction are required and significant success has been achieved employing benzyl bromides and iodides.[9] With carbonyl substrates at the carboxylic acid oxidation level, alkyl radicals must instead be generated upon single electron oxidation of an appropriate precursor compound. The first successful application of this approach was achieved by Scheidt and co-workers in 2020 employing 4-benzyl-substituted Hantzsch esters as sources of benzyl radicals.[10] Since then, a number of alternative radical precursors have been reported for NHC/photoredox-catalyzed benzylation of carboxyl substrates including carboxylic acids[11] and organoboron species,[12] while benzyl radicals have also been generated from *in situ*-generated benzyl xanthate species[13] or even hydrogen atom abstraction from electron-
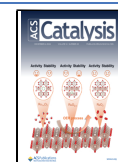
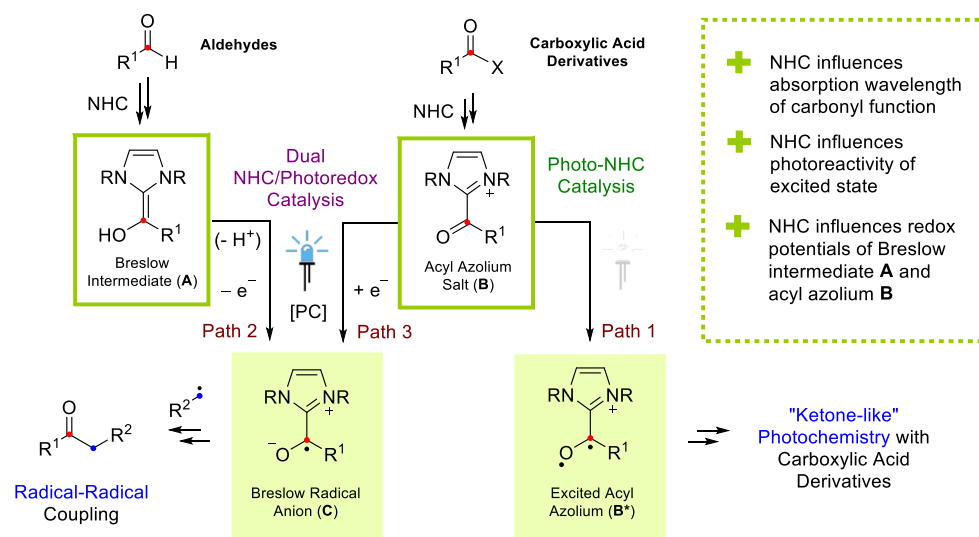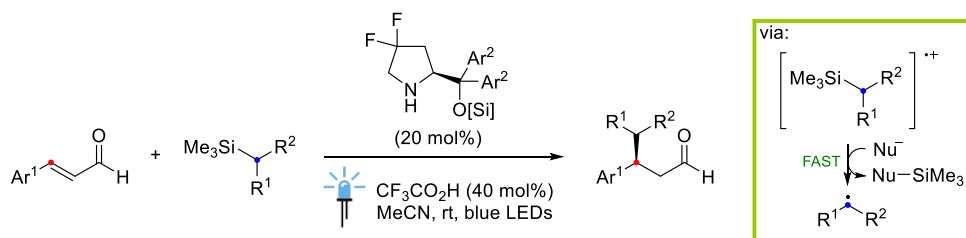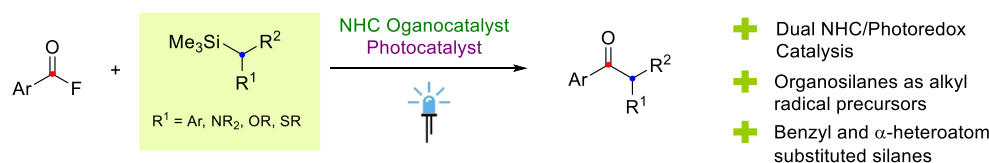**Figure 1.** Light-mediated NHC organocatalysis. (a) Activation pathways of Breslow intermediates **A** and acyl azolium salts **B**: direct irradiation (Photo-NHC catalysis, Path 1) and photoredox reduction (Path 3) of **B** and oxidation of **A** (Path 2). (b) Light-mediated organocatalyzed coupling of benzyl silanes with enal substrates $(Ar^2 = (3,5\text{-di-}(i\text{-}C_3F_7)C_6H_3); [Si] = Si(t\text{-}C_6H_{13})Me_2)$. (c) This work: dual NHC/photoredox-catalyzed alkylation of acyl fluorides with organosilanes.

rich alkyl benzenes.[14,15] Coupling of benzyl radicals formed upon addition of various radicals to styrene derivatives has also been extensively reported.[16,17]

Comparatively straightforward to synthesize and easy to store and handle, organosilanes possess a number of features that make them attractive reagents for organic synthesis, including in radical chemistry. As demonstrated by the groups of Alyev et al.[18] and Yoshida et al.,[19] organosilanes featuring π-systems adjacent to the silicon, such as benzyl(trimethyl)silane, undergo efficient desilylation upon single electron oxidation. Indeed, the rate of mesolytic C−Si bond cleavage in benzyl silyl radical cations is extremely fast, making an oxidation/desilylation sequence a highly attractive approach for the selective generation of benzyl radicals.[20] The combination of this concept with organocatalysis was demonstrated by Melchiorre and co-workers in 2017 (Figure 1b).[21] Using a proline derivative as catalyst, an efficient asymmetric benzylation of enal substrates was achieved with benzyl-(trimethyl)silanes generating benzyl radicals upon single

electron oxidation by photoexcited iminium ion intermediates. Moreover, negatively charged benzyl (biscatecholo)silicates[10c] and an electron-rich α-carbazolyl silane species[12a] have been previously employed in dual NHC/photoredox coupling reactions.[22] Inspired by these reports, we considered whether benzyl silanes could serve as useful general precursors of benzyl radicals in NHC-catalyzed coupling reactions. Here we report the successful validation of this approach in a dual NHC/photoredox benzylation of acyl fluoride substrates. Moreover, exploration of different organosilane derivatives allowed for the extension of the methodology beyond benzylation (Figure 1c).

■ METHODS

At the start of the study, we sought to investigate the key mechanistic steps of our reaction design using a stoichiometric acyl azolium salt. Imidazolium species **1a** was synthesized as a model substrate and reacted in the presence of (4-methoxy)-benzyl(trimethyl)silane **2a** (1.1 equiv) in degassed anhydrous MeCN. As the prior report from Melchiorre and co-workers

Scheme 1. Initial Investigations Employing Stoichiometric Acyl Azolium Salt 1[a]

Entry	[M]F	^{1}H NMR Yield
1	TBAF	38% (40%)
2	CsF	39%
3	AgF	2%

4
(CCDC: 2356113)
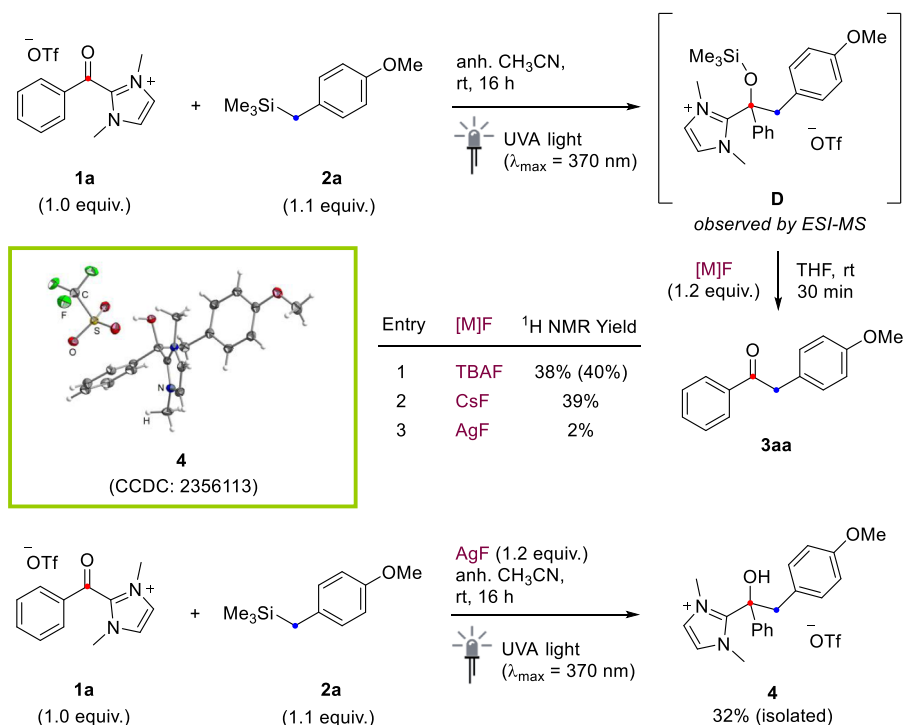
[a]Initial conditions: Benzoyl imidazolium salt (**1a**, 0.20 mmol, 1.0 equiv), benzyl silane (**2a**, 0.22 mmol, 1.1 equiv) in degassed anhydrous MeCN (2.0 mL) irradiated with light from UVA LEDs (λ_{max} = 370 nm) for 16 h at rt. Crude residue redissolved in THF (3.0 mL), stirred with [M]F salt (1.2 equiv) for 30 min at rt. ^{1}H NMR yields using CH$_2$Br$_2$ as an internal standard. Isolated yields in parentheses.

Table 1. Optimization of the Dual NHC/Photoredox-Catalyzed Benzylation Reaction of Acyl Fluoride 5a with Benzyl Silanes
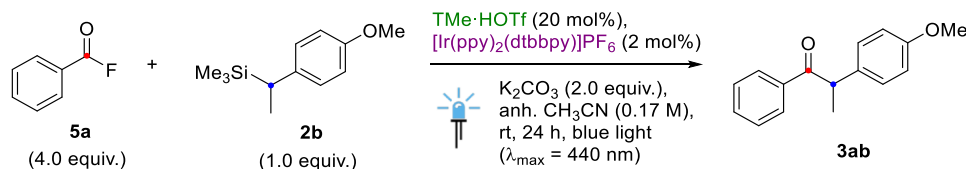
entry[a]	variation from standard conditions	^{1}H NMR Yield[b]
1	**2a** (1.0 equiv) in place of **2b**	33%
2	none	65%
3	[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %) as photocatalyst	47%
4	4CzIPN (2 mol %) as photocatalyst	53%
5	TMes HBF$_4$ as NHC precursor	54%
6	IMes HCl as NHC precursor	2%
7	thiazolium(dipp) HClO$_4$ as NHC precursor	31%
8	Cs$_2$CO$_3$ (1.0 equiv) as base	74%
9	Cs$_2$CO$_3$ (1.0 equiv), CH$_2$Cl$_2$ as solvent	73%
10	Cs$_2$CO$_3$ (1.0 equiv), 1,2-DCE as solvent	53%
11	Cs$_2$CO$_3$ (1.0 equiv), DMF as solvent	40%
12	Cs$_2$CO$_3$ (1.0 equiv), THF as solvent	33%
13	Cs$_2$CO$_3$ (1.0 equiv), **5a** (2.0 equiv)	76%
14	Cs$_2$CO$_3$ (1.0 equiv), **5a** (2.0 equiv), no degassing	76% (76%)
15	Cs$_2$CO$_3$ (1.0 equiv), **5a** (2.0 equiv), no light	traces
16	Cs$_2$CO$_3$ (1.0 equiv), **5a** (2.0 equiv), no NHC precursor	
17	**5a** (2.0 equiv), no Cs$_2$CO$_3$	2%
18	Cs$_2$CO$_3$ (1.0 equiv), **5a** (2.0 equiv), no photocatalyst	8%

[a]Conditions: benzoyl fluoride (**5a**), benzyl silane (**2a** or **2b**), NHC precursor, photocatalyst and base in degassed solvent irradiated with light from blue LEDs (λ_{max} = 440 nm) for 24 h at rt. [b]^{1}H NMR yields using CH$_2$Br$_2$ as an internal standard. Isolated yields in parentheses. TMe·HCl = 1,4-dimethyl-4H-1,2,4-triazol-1-ium chloride; TMes·HBF$_4$ = 2-mesityl-2,5,6,7-tetrahydropyrrolo[2,1-c][1,2,4] triazol-4-ium tetrafluoroborate; ppy = 2-phenylpyridine; dtbbpy = 4,4′-di-tert-butyl-2,2′-bypyridine; dF(CF$_3$)ppy = 3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-N]phenyl; 4CzIPN = 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene.

Scheme 2. Scope and Limitations of the Dual NHC/Photoredox-Catalyzed Coupling of Acyl Fluorides 5 with Secondary Benzyl Silane 2b[a]
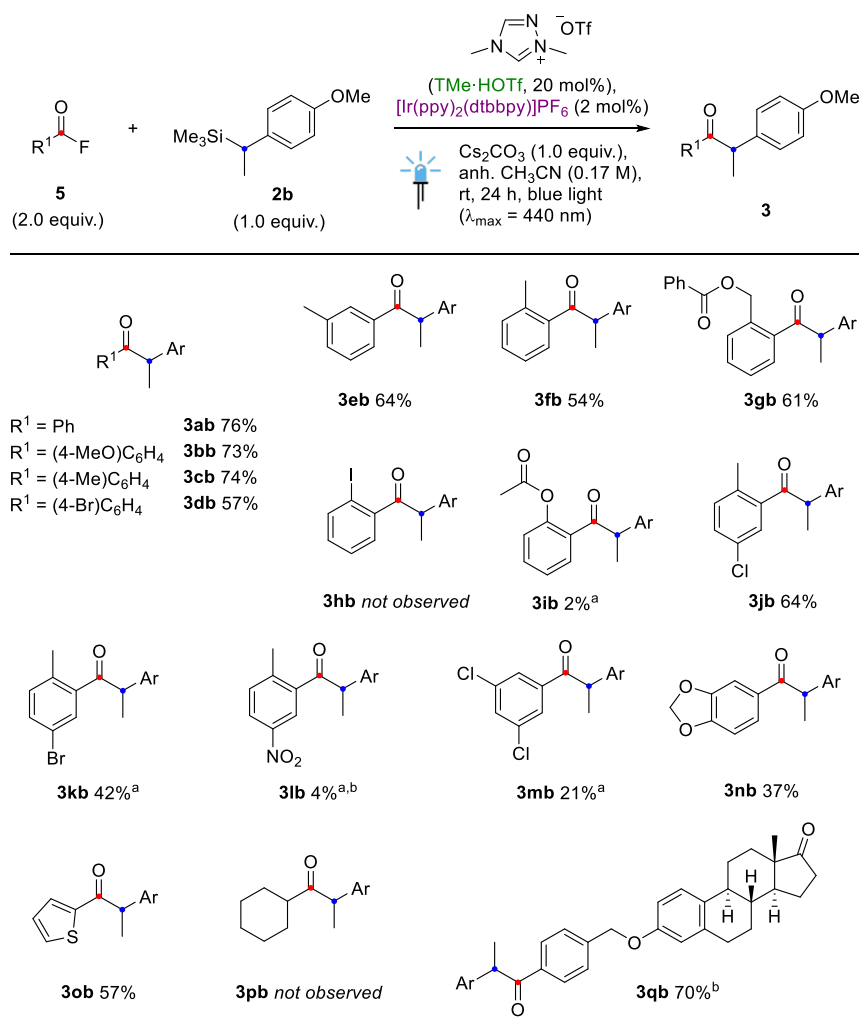
employing benzyl silane substrates under proline organo-catalysis had been successful using light irradiation without an additional photocatalyst,[21a] the reaction mixture was simply irradiated with UVA light (λ_{max} = 370 nm) for 16 h. The crude ^{1}H NMR spectrum was complex with no peaks consistent with the formation of the desired ketone product **3aa**. Nevertheless, conversion of both starting materials had occurred while ESI mass spectrometry suggested the presence of an adduct containing all the constituent atoms of both the acyl azolium cation and benzyl silane **2a**. Hypothesizing that this species could be the silylated tetrahedral intermediate compound **D** (Scheme 1), the reaction mixture was subsequently redissolved in THF and tetra-*n*-butylammonium fluoride (TBAF, 1.2 equiv) was added. Under these conditions, intermediate **D**, which feasibly results from silylation of the initially formed alkoxide species following radical–radical coupling, would be expected to undergo desilylation with subsequent elimination of the NHC delivering the ketone product. Indeed, after 30 min at rt, peaks consistent with **3aa** were observed in the crude ^{1}H NMR spectrum while isolation by column chromatography

provided the pure ketone in 40% yield. The successful formation of **3aa** validates the proposed radical benzylation process and demonstrates that benzyl silane species such as **2a** can undergo light-induced conversion into benzyl radicals in the presence of NHC-derived acyl azolium salts. Conducting the same two-stage process with azolium **1a** and benzyl silane **2a** but with CsF instead of TBAF led to an almost identical yield of **3aa** (39%, ^{1}H NMR yield), however, performing the same sequence with AgF provided only 2% of the ketone. Irradiating **1a** and **2a** in the presence of AgF (1.2 equiv) directly in a single step also did not lead to appreciable formation of **3aa**, however efficient conversion into the alcohol species **4** was observed. Under these conditions, final elimination of the NHC is seemingly unfavored and **4** could be isolated in 32% yield after column chromatography while X-ray diffraction analysis of a single crystal allowed for unambiguous assignment of the structure (Scheme 1).

With the reactivity validated using a stoichiometric acyl azolium salt, we next turned our attention to the development of a catalytic benzylation process.[23] As acyl fluorides had

Scheme 3. Scope and Limitations of the Dual NHC/Photoredox-Catalyzed Coupling of Acyl Fluoride 5a with Different Benzyl Silanes 2[a]
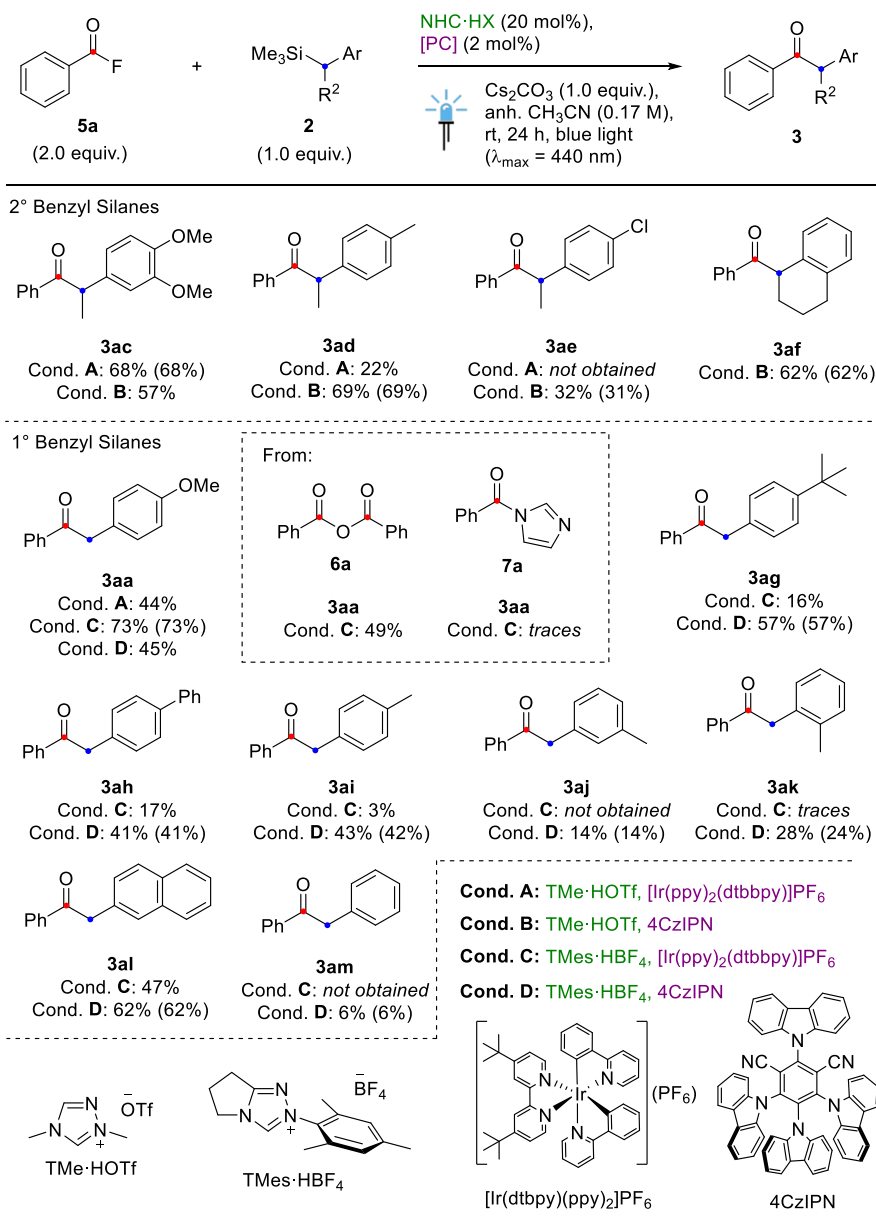
[a]Conditions: Acyl fluoride (**5a**, 0.60 mmol, 2.0 equiv), benzyl silane (**2**, 0.30 mmol, 1.0 equiv), TMe·HOTf or TMes·HBF$_4$ (20 mol %), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ or 4CzIPN (2 mol %) and Cs$_2$CO$_3$ (0.30 mmol, 1.0 equiv) in anhydrous MeCN (1.8 mL) irradiated with light from blue LEDs (λ_{max} = 440 nm) for 24 h at rt. ^{1}H NMR yields calculated from reactions on a 0.1 mmol scale using CH$_2$Br$_2$ as an internal standard, isolated yields in parentheses.

proved to be effective carboxylic acid derivative starting materials in our previous work on a Photo−NHC−catalyzed PEDA reaction,[4] benzoyl fluoride **5a** was selected as substrate. Significant success has been achieved conducting NHC organocatalysis in the presence of an additional photocatalyst[3] and with the aim of employing lower energy and thus more functional group tolerant visible light, we decided to explore performing the benzylation process under dual NHC/photoredox catalysis conditions rather than under direct UVA irradiation. Such processes have proven most successful using triazolylidene NHCs and the simple methyl derivative 1,4-dimethyl-1,2,4-triazolium triflate (TMe·HOTf, 20 mol %) was selected as catalyst in the presence of K$_2$CO$_3$ (2.0 equiv) as base. Thus, the NHC catalyst and base were reacted together

with acyl fluoride **5a** (4.0 equiv) and (4-methoxy)benzyl-(trimethyl)silane **2a** (1.0 equiv) under blue light irradiation (λ_{max} = 440 nm) in degassed MeCN with additional [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %) as photocatalyst. After 24 h at rt, analysis of the crude reaction mixture revealed the formation of the desired ketone **3aa**, albeit in a low yield of only 33% (^{1}H NMR yield, internal standard = CH$_2$Br$_2$, Table 1, entry 1). At this stage, we considered whether switching to a secondary benzyl silane substrate would allow for an improvement in the reaction efficiency. Replacing **2a** with silane **2b**, which should provide a better stabilized secondary benzyl radical upon single electron oxidation and desilylation, delivered the corresponding ketone **3ab** in a markedly higher

^{1}H NMR yield of 65% (entry 2). Changing to other visible light photocatalysts such as $[Ir(dF(CF_3)ppy)(dtbbpy)]PF_6$ or 4CzIPN did not lead to an improvement in efficiency (entries 3−4) while switching to a variety of different NHC organocatalysts was similarly ineffective (entries 5−7). A notable increase in the yield was observed, however, upon using Cs_2CO_3 (1.0 equiv) as the base with **3ab** being delivered in 74% ^{1}H NMR yield (entry 8). A survey of different reaction solvents confirmed the superiority of MeCN, however decent conversion was nevertheless observed in a range of different media with CH_2Cl_2 being almost as efficient (entries 9−12). Reducing the equivalents of the acyl fluoride substrate to 2.0 equiv. did not lead to a drop in the amount of **3ab** formed with the ketone in fact being obtained in a slightly higher ^{1}H NMR yield of 76%, while degassing of the reaction mixture was found to be unnecessary (entries 13−14, isolated yield after column chromatography = 76%). Finally, control reactions performed in the absence of the NHC catalyst, base or light confirmed the requirement for each component while removing the photocatalyst resulted in a significant drop in efficiency with **3ab** being formed in only 8% ^{1}H NMR yield (entries 15−18).

With an established set of catalytic conditions for the benzylation process, the scope and limitations of the methodology were investigated (Scheme 2). First, a selection of acyl fluorides **5** were tested using secondary substrate **2b** as a representative benzyl silane. When reacted under the optimized conditions from Table 1 (Scheme 2), a selection of 4-substituted aroyl fluorides including the methoxy and methyl-containing compounds **5b** and **5c** could be smoothly converted into the corresponding ketones **3bb** and **3cb** in good yields. The successful conversion of the 4-bromo-substituted compound **5d** is noteworthy as the ketone product **3db** is feasibly amenable to further functionalization through cross-coupling methodologies. Substitution at the 3- and 2-positions was well tolerated as demonstrated for the methyl-bearing aroyl fluorides **5e** and **5f** (yields = **3eb**: 64%; **3fb**: 55%). The aroyl fluoride **5g**, which features the sterically more demanding CH_2OBz group at the 2-position could be similarly converted into the corresponding ketone **3gb** in a good yield of 61%; however, 2-iodo and 2-acetyl substituted substrates led to either no product or only trace amounts, respectively. A selection of disubstituted aromatic substrates were also investigated. The 2-methyl-5-halogenyl-substituted derivatives **5j** (halogen = Cl) and **5k** (halogen = Br) reacted smoothly to afford ketones **3jb** and **3kb** in 64% and 42% yield, respectively. Aroyl fluoride **5l**, however, which features a photochemically noninnocent nitro-group, afforded only a trace amount of the corresponding ketone product. The 3,5-(dichloro)aroyl ketone **3mb** and the cyclic acetal derivative **3nb** could be obtained in moderate yields, while subjecting 2-thiophenoyl fluoride **5o** to the standard conditions revealed that the dual NHC/photoredox benzylation method can proceed successfully with heteroaromatic carboxylic acid derivatives with ketone **3ob** being isolated in 57% yield after column chromatography. A test reaction with cyclohexanoyl fluoride **5p** was unsuccessful suggesting aliphatic derivatives are not suitable substrates.[24] Finally, to evaluate the efficiency of the process with more complex substrates, an acyl fluoride derived from the steroid estrone was prepared and subjected to the standard conditions. Pleasingly the corresponding coupled product was formed successfully with purification by column chromatography providing **3qb** in 70% yield.
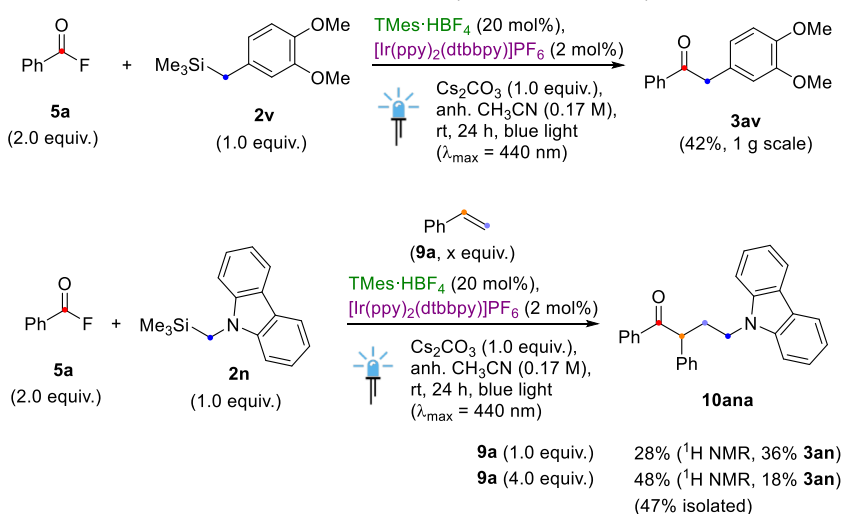
We next turned our attention to an evaluation of the scope and limitations of the process with different benzyl silanes **2**. Starting with secondary derivatives, the electron-rich 3,4-dimethoxy-substituted compound **2c** was subjected to the standard conditions with **5a** as a representative acyl fluoride. After 24 h at rt, smooth conversion into the corresponding ketone was observed with **3ac** being isolated in 68% after column chromatography. A test reaction with the 4-methyl-containing secondary benzyl fluoride **2d**, however, was less successful. Under the standard conditions with TMe·HOTf and $[Ir(ppy)_2(dtbbpy)]PF_6$, a low conversion to the desired ketone **3ad** was obtained (22% ^{1}H NMR yield). As a result, a further round of optimization was performed with the aim of increasing the efficiency of the benzylation process with less electron-rich secondary organosilanes.[23] Although proving less efficient with the electron-rich substrates **2b** and **2c**, changing the photocatalyst from the iridium complex to the organic species 4CzIPN led to a notable improvement with silane **2d**. Under these conditions, ketone **3ad** could be isolated in a good yield of 69% after column chromatography. A similar effect was observed with the 4-chloro-substituted benzyl silane **2e**. With the iridium catalyst (Conditions A), the desired benzylation did not proceed, however switching to 4CzIPN (Conditions B) resulted in significant conversion to the ketone **3ae**, which could be isolated in a moderate yield of 31%. Pleasingly, these conditions were also successful with the 1,2,3,4-tetrahydro-naphthalene-derived silane **2f** with ketone **3af** being furnished in 62% yield after column chromatography.

At this stage, the efficiency of the coupling process with primary benzyl silane substrates was investigated (Scheme 3).[25] As observed during the initial optimization studies, 4-(methoxy)benzyl silane **2a** was found to be less reactive than the corresponding secondary species **2b** with ketone **3aa** being delivered in only 44% ^{1}H NMR yield under the standard conditions with $[Ir(ppy)_2(dtbbpy)]PF_6$ (Conditions A, cf. 76% ^{1}H NMR yield of **3ab**). After a further short round of optimization,[23] the isolated yield of **3aa** could be increased significantly to 73% upon changing the NHC precatalyst to the *N*-mesityl-substituted triazolium salt TMes·HBF$_4$ (Conditions C). A survey of alternative carboxylic acid derivative substrates for the benzylation process with silane **2a** under these conditions was also conducted. While acyl fluoride **5a** remained the most effective benzoyl source, benzoic anhydride **6a** could also be successfully converted (^{1}H NMR yield of **3aa** = 49%), however *N*-benzoyl imidazole **7a**, which has been previously employed in dual NHC/photoredox-catalyzed coupling reactions, led only to trace amounts of the product. The conditions with TMes·HBF$_4$ were then tested with the 4-*tert*-butyl-substituted primary benzyl silane **2g**. Disappointingly, however, sluggish conversion was observed with ketone **3ag** being delivered in only 16% ^{1}H NMR yield. As 4CzIPN had proven more successful than $[Ir(ppy)_2(dtbbpy)]PF_6$ with less electron rich secondary benzyl silane substrates, the reaction with **2g** was repeated using this photocatalyst together with TMes·HBF$_4$ (Conditions D). To our delight, the ketone product was formed smoothly under these conditions with isolation by column chromatography delivering **3ag** in a much improved 57% yield. With the exception of the comparatively electron rich 4-methoxy-substituted silane **2a**, the combination of TMes·HBF$_4$ and 4CzIPN led to higher yields for all the primary benzyl silanes tested. The 4-phenyl and 4-methyl-substituted derivatives **2h** and **2i** could be converted into the corresponding ketones **3ah** and **3ai** in moderate yields of 41%

Scheme 4. Scope and Limitations of the Dual NHC/Photoredox-Catalyzed Coupling of Acyl Fluoride 5a with Different α-Heteroatom-Substituted Silanes 2[a]

X = NR₂

3an
Cond. **C**: 60% (60%)
Cond. **D**: 37%

3ao
Cond. **C**: 14%
Cond. **D**: 35% (34%)

3ap
Cond. **C**: 18%
Cond. **D**: 35% (35%)

X = OR

3aq
Cond. **C**: 10%
Cond. **D**: 15%

3ar
Cond. **C**: 16%
Cond. **D**: 20%

3as
Cond. **C**: *not obtained*
Cond. **D**: 24% (24%)

8
(By-product)

X = SR

3at
Cond. **C**: 19% (9%)
Cond. **D**: 18%

3au
Cond. **C**: 12%
Cond. **D**: 19% (19%)
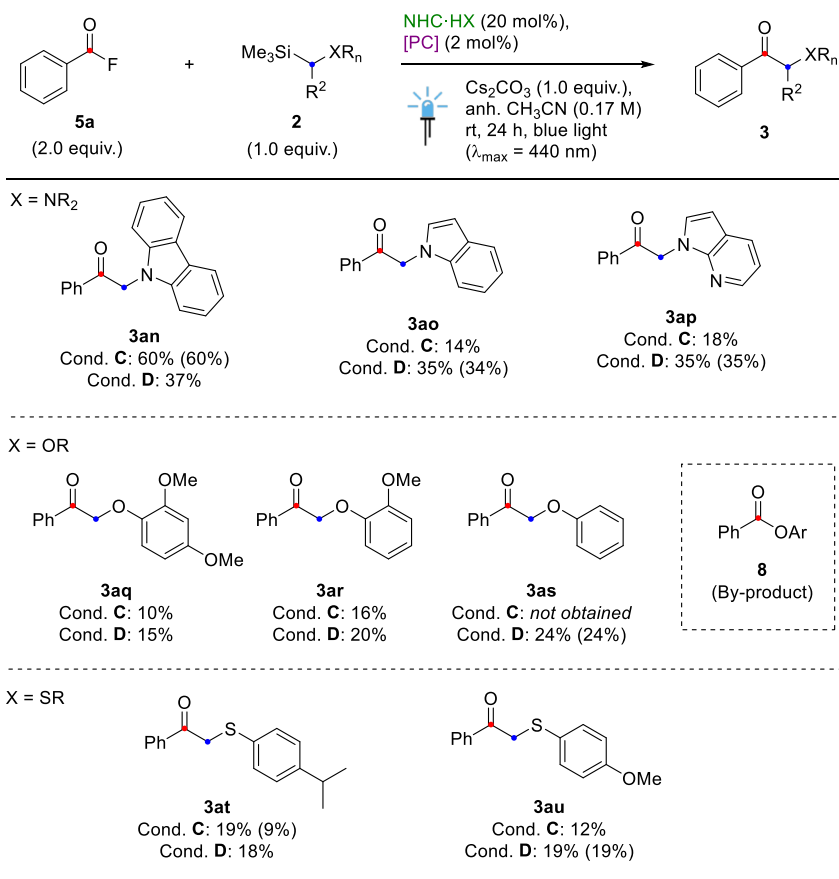
[a]Conditions: Acyl fluoride (**5a**, 0.60 mmol, 2.0 equiv), α-heteroatom-substituted silane (**2**, 0.30 mmol, 1.0 equiv), TMe·HOTf or TMes·HBF₄ (20 mol %), [Ir(ppy)₂(dtbbpy)]PF₆ or 4CzIPN (2 mol %) and Cs₂CO₃ (0.30 mmol, 1.0 equiv) in anhydrous MeCN (1.8 mL) irradiated with light from blue LEDs (λ_max = 440 nm) for 24 h at rt. See Scheme 3 for catalysts used under Conditions **A−D**. ¹H NMR yields calculated from reactions on a 0.1 mmol scale using CH₂Br₂ as an internal standard, isolated yields in parentheses.

Scheme 5. Gram Scale Reaction and Extension to a Radical Relay Process with Styrene

3av
(42%, 1 g scale)

10ana
9a (1.0 equiv.)   28% (¹H NMR, 36% **3an**)
9a (4.0 equiv.)   48% (¹H NMR, 18% **3an**)
(47% isolated)

and 42%, respectively, although methyl substituents at the 2- or 3-positions were less well tolerated (yields = **3aj**: 24%; **3ak**: 14%). The 2-naphthyl-derived silane **2l** was converted efficiently, delivering ketone **3al** in 62% isolated yield; however, the analogous benzene derivative **2m** was not a

suitable substrate, providing ketone **3am** in only 6% isolated yield.

Finally, having established the feasibility of the coupling process using benzyl silanes, we considered whether alternative organosilane structures could also serve as effective precursors

Scheme 6. Plausible Reaction Mechanism for the Dual NHC/Photoredox-Catalyzed Coupling of Acyl Fluorides 5 and Organosilanes 2[a]
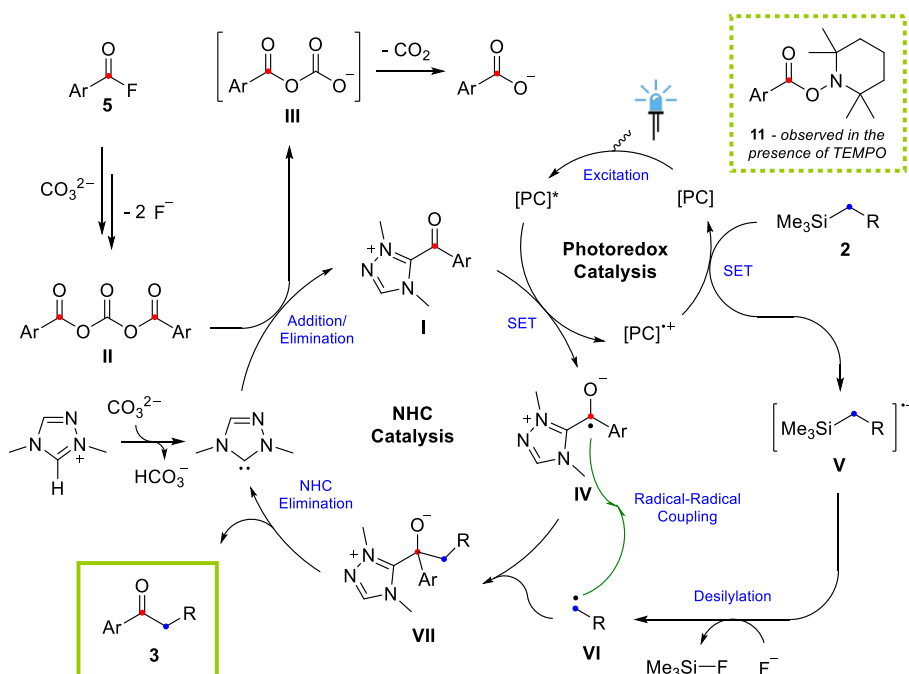
[a]R = Ar, OR, NR₂, SR.

to a wider range of alkyl radicals under dual NHC/photoredox catalysis conditions.[26] As comparatively electron rich derivatives, organosilanes featuring an α-heteroatom are susceptible to single electron oxidation with subsequent desilylation providing alkyl radicals stabilized by the adjacent lone pairs (Scheme 4). The feasibility of dual NHC/photoredox-catalyzed coupling with the carbazole-substituted silane 2n has been demonstrated previously by the group of Li[12a] and we initially tested this substrate under the optimized conditions with TMes·HBF₄ and [Ir(ppy)₂(dtbbpy)]PF₆ (Conditions C). To our delight, smooth conversion to the desired α-carbazolyl ketone was observed and product 3an could be isolated in 60% yield after column chromatography. The related indole derivative 2o also reacted, however, only 14% ¹H NMR yield of the corresponding ketone 3ao was obtained. Upon performing the reaction with 4CzIPN as photocatalyst (Conditions D), a marked improvement was observed with 3ao being isolated in 34% yield. Similarly, the 7-azaindole derivative 2p could be converted to ketone 3ap in 35% isolated yield under the same conditions. We next turned our attention to organosilane substrates featuring oxygen and sulfur heteroatoms α to the silicon. With the phenol derivative substrates 2q, 2r and 2s, Conditions D with TMes·HBF₄ and 4CzIPN again proved most effective, although the yields of the corresponding ketones were comparatively low in each case (<25%). In these reactions, esters 8 resulting from dealkylation of the phenolic starting materials followed by benzoylation with the acyl fluoride 3a were observed as significant side-products. Finally, similarly low conversions were observed with the thiophenol derivative substrates 2t and 2u using Conditions C or D with the corresponding ketones 3at and 3au being isolated in only 9% (Conditions C) and 19% (Conditions D) yields, respectively.

To further evaluate the synthetic utility of the method, a gram−scale reaction between acyl fluoride 5a and the (3,4-dimethoxyl)benzyl silane 2v was carried out under the standard conditions with TMes·HBF₄ and [Ir(ppy)₂(dtbbpy)]-PF₆ (Scheme 5). To our delight, the corresponding product 3av could be isolated in a good yield of 42%. Furthermore, inspired by reports of dual NHC/photoredox-catalyzed radical relay reactions with alternative alkyl radical sources, the prospect of incorporating alkene coupling partners into the reactions with alkyl silanes was investigated. Although benzyl derivatives were not suitable in such processes, when the reaction with α-heteroatom-substituted silane 2n and acyl fluoride 5a was conducted in the presence of styrene 9a (1.0 equiv), the radical relay product 10ana resulting from initial addition of the α-amino-radical to the alkene followed by radical−radical coupling was formed in 28% ¹H NMR yield alongside 36% of the direct coupling product 3an. Pleasingly, increasing the equivalents of styrene led to a higher selectivity for the radical relay process with 10ana being isolated in 47% yield using 4.0 equiv of styrene (¹H NMR yield = 48%, ¹H NMR yield of 3an = 18%).

Having established the scope of the process, our attention turned to an investigation of the reaction mechanism. As outlined in the introduction above, our reaction design involved the intermediacy of a key acyl azolium species I (Scheme 6). Indeed, stoichiometric studies had shown that independently synthesized benzoyl imidazolium species 1a is successfully converted into the product 3aa (Scheme 1). Such a species could feasibly be generated upon addition/elimination of the NHC catalyst to an acyl fluoride 5. In order to get more insight into this step, density functional theory calculations were carried out to calculate free enthalpies at the ωB97M-V/def2-QZVP//PBEh-3c level of theory including an explicit solvation enthalpy by COSMO-RS BP-TZVPD-FINE.[27] While addition of the triazolylidene NHC TMe, generated upon deprotonation of the corresponding triazolium salt, TMe·HOTf, to 5a was facile (barrier: 64.2 kJ

mol^{-1}), the subsequent elimination of the fluoride ion affording acyl azolium **I** was calculated to be highly endergonic (ΔG = 290.1 kJ mol^{-1}). While this value is likely an upper bound, the high energy cost nevertheless suggests that acyl fluoride **5a** may not be the active electrophile in the system.[28] Indeed, mixing TMe, preformed by deprotonation of TMe·HOTf with sodium hydride, with acyl fluoride **5a** in an NMR tube (solvent: CD$_3$CN) did not lead to discernible formation of the corresponding acyl azolium species. Studer and co-workers have recently suggested bis(acyl) carbonate species derived from a reaction between the carbonate base and acyl fluorides may act as electrophiles for NHC organocatalysis. To test whether such species may be involved in this process, addition/elimination of TMe to the representative species **II** (Ar = Ph) was calculated. In this case, exergonic formation of the acyl azolium species **I** was observed, with benzoyl carbonate present as a contact ion pair (ΔG = −35.9 kJ mol^{-1}). We therefore tentatively propose that the active electrophile in this process could be the (bis)acyl carbonate **II**. Notably, this scenario is consistent with the greater efficiency observed with more than one equivalent of the acyl fluoride **5a** and when using stoichiometric amounts of the base, which not only functions to deprotonate the NHC precatalyst but also plays an integral role in generating the active electrophile.[29]

According to our reaction design, the presence of the cationic triazolium fragment in acyl azolium species **I** leads to a lowering of the carbonyl reduction potential allowing for single electron reduction to zwitterionic radical **IV**. To gain further experimental evidence of this step, Stern Volmer luminescence quenching experiments were carried out using [Ir-(ppy)$_2$(dtbbpy)]PF$_6$ as photocatalyst. While no appreciable quenching of the photocatalyst luminescence was observed in the presence of either the acyl fluoride **5a** or benzyl silane **2b**, concentration dependent quenching occurred with benzoyl triazolium **1b**, indicating species of general structure **I** can be directly reduced by the photocatalyst excited state.[23] Performing the standard reaction between acyl fluoride **5a** and silane **2b** in the presence of TEMPO (1.0 equiv) led both to a considerable reduction in the yield of **3ab** obtained (22% ^{1}H NMR yield cf. 76% without TEMPO) and the formation of the TEMPO ester **11**. This species would be formed upon radical–radical coupling of TEMPO and zwitterionic radical **IV** followed by NHC elimination. To complete the photocatalytic cycle, the alkyl silane species **2** would then react with the oxidized photocatalyst ([PC]$^{\bullet+}$ in Scheme 6), regenerating the ground state photocatalyst and forming the silane radical cation **V**. As previously established,[20] desilylation of radical cations **V** affording an alkyl radical **VI** is very fast and aided by activation by an adventitious nucleophile in the reaction medium. DFT calculations on this step for benzyl trimethylsilane (R = Ph) indicated assistance by the acetonitrile solvent affording [(MeCN)SiMe$_3$]$^+$ as a byproduct is exergonic by 53.4 kJ mol^{-1}. The further trapping of this species by a fluoride ion (or direct nucleophilic attack of F$^-$ to **V**) would provide FSiMe$_3$, which represents an energetic sink for the reaction. Radical–radical coupling between the azolium radical **IV** and alkyl radical **VI** generating zwitterionic species **VII** is calculated to be exergonic by 68.3 kJ mol^{-1}, with final elimination of the NHC organocatalyst proceeding readily with a barrier of 20.7 kJ mol^{-1} to deliver the final ketone product **3**.[30]

CONCLUSIONS

In summary, a dual NHC/photoredox-catalyzed radical coupling method has been developed employing organosilanes as sources of alkyl radicals. Using acyl fluorides as coupling partners, benzyl silanes underwent single electron oxidation and desilylation under photoredox catalysis conditions, eventually affording ketone products. Comparatively electron-rich silane species reacted most efficiently, however, switching the NHC and photocatalyst allowed for less activated derivatives including primary benzyl substrates to be coupled successfully. Moreover, while generally lower yielding, organo-silanes bearing N-, O- and S-heteroatoms could also be converted. In establishing diverse organosilanes as suitable substrates for coupling reactions, this work further demonstrates the growing potential of dual NHC/photoredox catalysis and further studies are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.4c03103.

Experimental procedures, analytical data, NMR spectra of novel compounds (PDF)
(CIF)

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Notes

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■ REFERENCES

(1) Selected reviews: (a) Enders, D.; Niemeier, O.; Henseler, A. Organocatalysis by N-Heterocyclic Carbenes. *Chem. Rev.* **2007**, *107*, 5606−5655. (b) Izquierdo, J.; Hutson, G. E.; Cohen, D. T.; Scheidt, K. A. A Continuum of Progress: Applications of N-Heterocyclic Carbene Catalysis in Total Synthesis. *Angew. Chem., Int. Ed.* **2012**, *51*, 11686−11698. (c) Bugaut, X.; Glorius, F. Organocatalytic Umpolung: N-Heterocyclic Carbenes and Beyond. *Chem. Soc. Rev.* **2012**, *41*, 3511−3522. (d) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An Overview of N-Heterocyclic Carbenes. *Nature* **2014**, *510*, 485−496. (e) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. Organocatalytic Reactions Enabled by N-Heterocyclic Carbenes. *Chem. Rev.* **2015**, *115*, 9307−9387. (f) Menon, R. S.; Biju, A. T.; Nair, V. Recent Advances in Employing Homoenolates Generated by N-Heterocyclic Carbene (NHC) Catalysis in Carbon−Carbon Bond-Forming Reactions. *Chem. Soc. Rev.* **2015**, *44*, 5040−5052. (g) Zhang, C.; Hooper, J. F.; Lupton, D. W. N-Heterocyclic Carbene Catalysis via the α,β-Unsaturated Acyl Azolium. *ACS Catal.* **2017**, *7*, 2583−2596. (h) Chen, X.-Y.; Liu, Q.; Chauhan, P.; Enders, D. N.-. N-Heterocyclic Carbene Catalysis via Azolium Dienolates: An Efficient Strategy for Remote Enantioselective Functionalizations. *Angew. Chem., Int. Ed.* **2018**, *57*, 3862−3873. (i) Chen, X.; Wang, H.; Jin, Z.; Chi, Y. R. N Carbene Organocatalysis: Activation Modes and Typical Reactive Intermediates. *Chin. J. Chem.* **2020**, *38*, 1167−1202. (j) Bellotti, P.; Koy, M.; Hopkinson, M. N.; Glorius, F. Recent Advances in the Chemistry and Applications of N-Heterocyclic Carbenes. *Nat. Rev. Chem* **2021**, *5*, 711−725. (k) Pareek, M.; Reddi, Y.; Sunoj, R. B. Tale of the Breslow Intermediate, a Central Player in N-Heterocyclic Carbene Organocatalysis: Then and Now. *Chem. Sci.* **2021**, *12*, 7973−7992. (l) Song, R.; Xie, Y.; Jin, Z.; Chi, Y. R. Carbene-Catalyzed Asymmetric Construction of Atropisomers. *Angew. Chem., Int. Ed.* **2021**, *60*, 26026−26037.

(2) Selected reviews: (a) Vora, H. U.; Wheeler, P.; Rovis, T. Exploiting Acyl and Enol Azolium Intermediates via N-Heterocyclic Carbene-Catalyzed Reactions of α-Reducible Aldehydes. *Adv. Synth. Catal.* **2012**, *354*, 1617−1639. (b) Ryan, S. J.; Candish, L.; Lupton, D. W. Acyl anion free N-heterocyclic carbene organocatalysis. *Chem. Soc. Rev.* **2013**, *42*, 4906−4917. (c) Zhang, C.; Hooper, J. F.; Lupton, D. W. N-Heterocyclic Carbene Catalysis via the α,β-Unsaturated Acyl Azolium. *ACS Catal.* **2017**, *7*, 2583−2596. (d) Chen, X.; Wang, H.; Jin, Z.; Chi, Y. R. N Carbene Organocatalysis: Activation Modes and Typical Reactive Intermediates. *Chin. J. Chem.* **2020**, *38*, 1167−1202. (e) Zhao, C.; Blaszczyk, S. A.; Wang, J. Asymmetric reactions of N-heterocyclic carbene (NHC)-based chiral acyl azoliums and azolium enolates. *Green Synth. Catal.* **2021**, *2*, 198−215. (f) Huang, Y.; Peng, X.; Li, T. Recent Advances in NHC-Catalyzed Chemoselective Activation of Carbonyl Compounds. *Chem.—Asian J.* **2024**, *19*, No. e202400097.

(3) Selected reviews (a) Ishii, T.; Nagao, K.; Ohmiya, H. Recent advances in N-heterocyclic carbene-based radical catalysis. *Chem. Sci.* **2020**, *11*, 5630−5636. (b) Ohmiya, H. N-Heterocyclic Carbene-Based Catalysis Enabling Cross-Coupling Reactions. *ACS Catal.* **2020**, *10*, 6862−6869. (c) Mavroskoufis, A.; Jakob, M.; Hopkinson, M. N. Light-Promoted Organocatalysis with N-Heterocyclic Carbenes. *ChemPhotoChem* **2020**, *4*, 5147−5153. (d) Liu, Q.; Chen, X.-Y. Dual N-Heterocyclic Carbene/Photocatalysis: A New Strategy for

Radical Processes. *Org. Chem. Front.* **2020**, *7*, 2082−2087. (e) Liu, J.; Xing, X.-N.; Huang, J.-H.; Lu, L.-Q.; Xiao, W.-J. Light Opens a New Window for N-Heterocyclic Carbene Catalysis. *Chem. Sci.* **2020**, *11*, 10605−10613. (f) Marzo, L. Recent Advances in Organic Synthesis Using Light-Mediated N-Heterocyclic Carbene Catalysis. *Eur. J. Org Chem.* **2021**, *2021*, 4603−4610. (g) Liu, K.; Schwenzer, M.; Studer, A. Radical NHC Catalysis. *ACS Catal.* **2022**, *12*, 11984−11999. (h) Tang, Q.; Du, D.; Gao, J. Radical Acylation of Alkenes by NHC-Organocatalysis. *Eur. J. Org Chem.* **2023**, *26*, No. e202300832. (i) Wang, X.; Wu, S.; Yang, R.; Song, H.; Liu, Y.; Wang, Q. Recent advances in combining photo- and N-heterocyclic carbene catalysis. *Chem. Sci.* **2023**, *14*, 13367−13383. (j) Cai, H.; Yang, X.; Ren, S.-C.; Chi, Y. R. Radical Reactions with N-Heterocyclic Carbene (NHC)-Derived Acyl Azoliums for Access to Multifunctionalized Ketones. *ACS Catal.* **2024**, *14*, 8270−8293.

(4) Mavroskoufis, A.; Rajes, K.; Golz, P.; Agrawal, A.; Ruß, V.; Götze, J. P.; Hopkinson, M. N-Heterocyclic Carbene Catalyzed Photoenolization/Diels−Alder Reaction of Acid Fluorides. *Angew. Chem., Int. Ed.* **2020**, *59*, 3190−3194.

(5) (a) Highlight: Hopkinson, M. N.; Mavroskoufis, A. Photo-NHC Catalysis: Accessing Ketone Photochemistry with Carboxylic Acid Derivatives. *Synlett* **2021**, *32*, 95−101. (b) Mechanistic study: Mavroskoufis, A.; Lohani, M.; Weber, M.; Hopkinson, M. N.; Götze, J. P. A (TD-)DFT Study on Photo-NHC-Catalysis: Photoenolization/Diels-Alder Reaction of Acid Fluorides Catalyzed by N-Heterocyclic Carbenes. *Chem. Sci.* **2023**, *14*, 4027−4037.

(6) Related stoichiometric process with alkyl-substituted acyl azolium salts Mavroskoufis, A.; Rieck, A.; Hopkinson, M. N. Norrish Type II Reactions of Acyl Azolium Salts. *Tetrahedron* **2021**, *100*, 132497.

(7) DiRocco, D. A.; Rovis, T. Catalytic Asymmetric α-Acylation of Tertiary Amines Mediated by a Dual Catalysis Mode: N-Heterocyclic Carbene and Photoredox Catalysis. *J. Am. Chem. Soc.* **2012**, *134*, 8094−8097.

(8) Review Martin, C. D.; Soleilhavoup, M.; Bertrand, G. Carbene-stabilized main group radicals and radical ions. *Chem. Sci.* **2013**, *4*, 3020−3030.

(9) (a) Dai, L.; Xia, Z.-H.; Gao, Y.-Y.; Gao, Z.-H.; Ye, S. Visible-Light-Driven N-Heterocyclic Carbene Catalyzed γ- and ε-Alkylation with Alkyl Radicals. *Angew. Chem., Int. Ed.* **2019**, *58*, 18124−18130. (b) Dai, L.; Ye, S. Photo/N-Heterocyclic Carbene Co-catalyzed Ring Opening and γ-Alkylation of Cyclopropane Enal. *Org. Lett.* **2020**, *22*, 986−990. (c) Xu, Y.-Y.; Dai, L.; Gao, Z.-H.; Ye, S. ε-Benzylation via Cooperative Photoredox and N-Heterocyclic Carbene Catalysis. *J. Org. Chem.* **2022**, *87*, 14970−14974.

(10) (a) Bay, A. V.; Fitzpatrick, K. P.; Betori, R. C.; Scheidt, K. A. Combined Photoredox and Carbene Catalysis for the Synthesis of Ketones from Carboxylic Acids. *Angew. Chem., Int. Ed.* **2020**, *59*, 9143−9148. (b) Ren, S.-C.; Lv, W.-X.; Yang, X.; Yan, J.-L.; Xu, J.; Wang, F.-X.; Hao, L.; Chai, H.; Jin, Z.; Chi, Y. R. Carbene-Catalyzed Alkylation of Carboxylic Esters via Direct Photoexcitation of Acyl Azolium Intermediates. *ACS Catal.* **2021**, *11*, 2925−2934. (c) Bay, A. V.; Fitzpatrick, K. P.; González-Montiel, G. A.; Farah, A. O.; Cheong, P. H. Y.; Scheidt, K. A. Light-Driven Carbene Catalysis for the Synthesis of Aliphatic and α-Amino Ketones. *Angew. Chem., Int. Ed.* **2021**, *60*, 17925−17931. (d) Bay, A. V.; Farnam, E. J.; Scheidt, K. A. Synthesis of Cyclohexanones by a Tandem Photocatalyzed Annulation. *J. Am. Chem. Soc.* **2022**, *144*, 7030−7037. (e) Wang, X.; Tang, Y.; Ye, S.; Zhang, J.; Kuang, Y.; Wu, J. Access to Sulfoxides under NHC/Photocatalysis via a Radical Pathway. *Org. Lett.* **2022**, *24*, 2059−2063. (f) Byun, S.; Hwang, M. U.; Wise, H. R.; Bay, A. V.; Cheong, P. H. Y.; Scheidt, K. A. Light-Driven Enantioselective Carbene- Catalyzed Radical-Radical Coupling. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202312829.

(11) Ren, S.-C.; Yang, X.; Mondal, B.; Mou, C.; Tian, W.; Jin, Z.; Chi, Y. R. Carbene and photocatalyst-catalyzed decarboxylative radical coupling of carboxylic acids and acyl imidazoles to form ketones. *Nat. Commun.* **2022**, *13*, 2846.

(12) (a) Huang, H.; Dai, Q.-S.; Leng, H.-J.; Li, Q.-Z.; Yang, S.-L.; Tao, Y.-M.; Zhang, X.; Qi, T.; Li, J.-L. Suzuki-type cross-coupling of alkyl trifluoroborates with acid fluoride enabled by NHC/photoredox dual catalysis. *Chem. Sci.* **2022**, *13*, 2584−2590. (b) Process with stoichiometric acyl azolium salts Zhu, J. L.; Scheidt, K. A. Photocatalytic acyl azolium-promoted alkoxycarbonylation of trifluoroborates. *Tetrahedron* **2021**, *92*, 132288.

(13) Tan, C. Y.; Kim, M.; Hong, S. Photoinduced Electron Transfer from Xanthates to Acyl Azoliums: Divergent Ketone Synthesis via N-Heterocyclic Carbene Catalysis. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202306191.

(14) (a) Meng, Q.-Y.; Lezius, L.; Studer, A. Benzylic C−H acylation by cooperative NHC and photoredox catalysis. *Nat. Commun.* **2021**, *12*, 2068. (b) Wang, X.; Yang, R.; Zhu, B.; Liu, Y.; Song, H.; Dong, J.; Wang, Q. Direct allylic acylation via cross-coupling involving cooperative N-heterocyclic carbene, hydrogen atom transfer, and photoredox catalysis. *Nat. Commun.* **2023**, *14*, 2951. (c) With cocatalysis by CeCl₃ Rourke, M. J.; Wang, C. T.; Schull, C. R.; Scheidt, K. A. Acyl Azolium−Photoredox-Enabled Synthesis of β-Keto Sulfides. *ACS Catal.* **2023**, *13*, 7987−7994. (d) With cocatalysis by thiols Wang, X.; Yang, R.; Zhu, B.; Liu, Y.; Song, H.; Dong, J.; Wang, Q. Direct allylic acylation via cross-coupling involving cooperative N-heterocyclic carbene, hydrogen atom transfer, and photoredox catalysis. *Nat. Commun.* **2023**, *14*, 2951. (e) Very recent report employing dihydroquinazolinones obtained from benzyl ketones Li, Q.-Z.; He, M.-H.; Zeng, R.; Lei, Y.-Y.; Yu, Z.-Y.; Jiang, M.; Zhang, X.; Li, J.-L. Molecular Editing of Ketones through N-Heterocyclic Carbene and Photo Dual Catalysis. *J. Am. Chem. Soc.* **2024**, *146*, 22829−22839.

(15) Selected photochemical NHC-catalyzed coupling reactions of carboxylic acid derivatives with alkyl radicals bearing α-heteroatoms: (a) Wang, X.; Zhu, B.; Liu, Y.; Wang, Q. Combined Photoredox and Carbene Catalysis for the Synthesis of α-Amino Ketones from Carboxylic Acids. *ACS Catal.* **2022**, *12*, 2522−2531. (b) Zhu, J. L.; Schull, C. R.; Tam, A. T.; Rentería-Gómez, Á.; Gogoi, A. R.; Gutierrez, O.; Scheidt, K. A. Photoinduced Acylations Via Azolium-Promoted Intermolecular Hydrogen Atom Transfer. *J. Am. Chem. Soc.* **2023**, *145*, 1535−1541. (c) With stoichiometric acyl azolium salts Rourke, M. J.; Wang, C. T.; Schull, C. R.; Scheidt, K. A. Acyl Azolium−Photoredox-Enabled Synthesis of β-Keto Sulfides. *ACS Catal.* **2023**, *13*, 7987−7994.

(16) Selected examples (from carboxylic acid derivative substrates): (a) Meng, Q.-Y.; Döben, N.; Studer, A. Cooperative NHC and Photoredox Catalysis for the Synthesis of β-Trifluoromethylated Alkyl Aryl Ketones. *Angew. Chem., Int. Ed.* **2020**, *59*, 19956−19960. (b) Sato, Y.; Goto, Y.; Nakamura, K.; Miyamoto, Y.; Sumida, Y.; Ohmiya, H. Light-Driven N-Heterocyclic Carbene Catalysis Using Alkylborates. *ACS Catal.* **2021**, *11*, 12886−12892. (c) Takemura, N.; Sumida, Y.; Ohmiya, H. Organic Photoredox-Catalyzed Silyl Radical Generation from Silylboronate. *ACS Catal.* **2022**, *12*, 7804−7810. (d) Wang, L.; Sun, J.; Xia, J.; Li, M.; Zhang, L.; Ma, R.; Zheng, G.; Zhang, Q. Visible light-mediated NHCs and photoredox co-catalyzed radical 1,2-dicarbonylation of alkenes for 1,4-diketones. *Sci. China: Chem.* **2022**, *65*, 1938−1944. (e) Döben, N.; Reimler, J.; Studer, A. Cooperative NHC/Photoredox Catalysis: Three Component Radical Coupling of Aroyl Fluorides, Styrenes and Alcohols. *Adv. Synth. Catal.* **2022**, *364*, 3348−3353. (f) Wang, P.; Fitzpatrick, K. P.; Scheidt, K. A. Combined Photoredox and Carbene Catalysis for the Synthesis of γ-Aryloxy Ketones. *Adv. Synth. Catal.* **2022**, *364*, 518−524. (g) Tao, X.; Wang, Q.; Kong, L.; Ni, S.; Pan, Y.; Wang, Y. Branched-Selective Hydroacylation of Alkenes via Photoredox Cobalt and N-Heterocyclic Carbene Cooperative Triple Catalysis. *ACS Catal.* **2022**, *12*, 15241−15248. (h) Li, S.; Shu, H.; Wang, S.; Yang, W.; Tang, F.; Li, X.-X.; Fan, S.; Feng, Y.-S. Cooperative NHC and Photoredox Catalysis for the Synthesis of 1,4-Dicarbonyl Compounds via Diacylation of Alkenes. *Org. Lett.* **2022**, *24*, 5710−5714. (i) Li, S.; Zheng, C.; Wang, S.; Li, X.-X.; Zhang, Q.; Fan, S.; Feng, Y.-S. Ketone Synthesis via Irradiation-Induced Generation of a Persistent Ketyl Radical from Acyl Azolium Salts. *Org. Lett.* **2023**, *25*, 6522−6527. (j) Wang, Z.; Li,

X.; Li, W.; Cao, Y.; Li, H. Metal-free reductive acyldifluoroalkylation of alkenes through cooperative NHC and organophotocatalysis. *Org. Chem. Front.* **2023**, *10*, 4250−4255. (k) Dong, Y.-X.; Zhang, C.-L.; Gao, Z.-H.; Ye, S. Iminoacylation of Alkenes via Photoredox N-Heterocyclic Carbene Catalysis. *Org. Lett.* **2023**, *25*, 855−860. (l) Tanaka, N.; Zhu, J. L.; Valencia, O. L.; Schull, C. R.; Scheidt, K. A. Cooperative Carbene Photocatalysis for β-Amino Ester Synthesis. *J. Am. Chem. Soc.* **2023**, *145*, 24486−24492. (m) Sato, Y.; Miyamoto, Y.; Matsui, T.; Sumida, Y.; Ohmiya, H. Diastereoselective congested β-amido ketone synthesis via NHC-catalyzed radical-radical coupling. *Chem Catal.* **2023**, *3*, 100736. (n) Liu, W.-C.; Zhang, X.; Chen, L.; Zeng, R.; Tian, Y.-H.; Ma, E.-D.; Wang, Y.-P.; Zhang, B.; Li, J.-L. Energy-Transfer-Enabled Radical Acylation Using Free Alkyl Boronic Acids through Photo and NHC Dual Catalysis. *ACS Catal.* **2024**, *14*, 3181−3190. (o) Lezius, L.; Reimler, J.; Studer, A.; Döben, N.; Hamm, M.; Daniliuc, C. G. Aminoacylation of Alkenes by Cooperative NHC and Photoredox Catalysis. *Synlett* **2024**, *35*, 445−450. (p) Benzyl radical generation through oxidation of benzofurans Yu, X.; Meng, Q.-Y.; Daniliuc, C. G.; Studer, A. Aroyl Fluorides as Bifunctional Reagents for Dearomatizing Fluoroaroylation of Benzofurans. *J. Am. Chem. Soc.* **2022**, *144*, 7072−7079. (q) Benzyl radical generation through fluoride trapping of oxidized *gem*-difluorostyrenes Yu, X.; Maity, A.; Studer, A. Cooperative Photoredox and N-Heterocyclic Carbene Catalyzed Fluoroaroylation for the Synthesis of α-Trifluoromethyl-Substituted Ketones. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202310288. (r) Huang, T.; Yin, H.; Li, T.; Yu, C.; Zhang, K.; Yao, C. NHC catalyzed radical tandem cyclization: an efficient synthesis of α,α-difluoro-γ-lactam derivatives. *Org. Biomol. Chem.* **2024**, *22*, 6988−6998. (s) Jialingbieke, A.; Hu, X.; Liu, Z.; Lin, X.; Yin, Y.; Li, J.; Huang, Y.; Du, D. Organocatalytic radical aminoacylation of alkenes for β-aminoketone synthesis. *Sci. China: Chem.* **2024**, *67*..

(17) With benzyl radicals generated upon radical addition to aryl cyclopropanes Zuo, Z.; Daniliuc, C. G.; Studer, A. Cooperative NHC/Photoredox Catalyzed Ring-Opening of Aryl Cyclopropanes to 1-Aroyloxylated-3-Acylated Alkanes. *Angew. Chem., Int. Ed.* **2021**, *60*, 25252−25257.

(18) Alyev, I. Y.; Rozhkov, I. N.; Knunyants, I. L. Anode chemistry of organosilanes. Oxidative replacement of alkyl group by fluoride ion. *Tetrahedron Lett.* **1976**, *17*, 2469−2470.

(19) Yoshida, J.-i.; Murata, T.; Isoe, S. Electrochemical oxidation of organosilicon compounds I. Oxidative cleavage of carbon-silicon bond in allylsilanes and benzylsilanes. *Tetrahedron Lett.* **1986**, *27*, 3373−3376.

(20) (a) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. Nucleophile-assisted cleavage of silane cation radicals. *J. Am. Chem. Soc.* **1989**, *111*, 8973−8975. (b) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. Nucleophile-Assisted Cleavage of Benzyltrialkylsilane Cation Radicals. *J. Am. Chem. Soc.* **1997**, *119*, 1876−1883.

(21) (a) Silvi, M.; Verrier, C.; Rey, Y. P.; Buzzetti, L.; Melchiorre, P. Visible-light excitation of iminium ions enables the enantioselective catalytic β-alkylation of enals. *Nat. Chem.* **2017**, *9*, 868−873. (b) Recent review of applications of organosilanes in asymmetric catalysis Hou, L.; Cao, W.; Feng, X. Applications of Organosilanes in Visible Light-induced Catalytic Asymmetric Reactions. *ChemCatChem* **2024**, *16*, No. e202400385.

(22) An amino silane has also been studied as a mechanistic probe for dual NHC/photoredox catalyzed coupling with Hantzsch esters (see ref 10b).

(23) For more information, see the Supporting Information.

(24) Aliphatic acyl electrophiles are often challenging substrates in NHC organocatalysis that may undergo a range of undesired side-reactions (e.g., aldol-type processes). See ref 1.

(25) Attempts to synthesize a tertiary benzyl silane substrate to test in this process proved unsuccessful. Tertiary benzyl silanes are scarce in the literature.

(26) Simple alkyl silanes without an α-aryl group or α-heteroatom are likely too challenging to oxidize to be effective alkyl radical sources under these conditions.

(27) (a) Neese, F. Software Update: The ORCA Program System-Version 5.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2022**, *12*, No. e1606. (b) Klamt, A. Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena. *J. Phys. Chem.* **1995**, *99*, 2224−2235. (c) Mardirossian, N.; Head-Gordon, M. ωB97M-V: A Combinatorially Optimized, Range-Separated Hybrid, Meta-GGA Density Functional with VV10 Nonlocal Correlation. *J. Chem. Phys.* **2016**, *144*, 214110. (d) Grimme, S.; Brandenburg, J. G.; Bannwarth, C.; Hansen, A. Consistent Structures and Interactions by Density Functional Theory with Small Atomic Orbital Basis Sets. *J. Chem. Phys.* **2015**, *143*, 054107. (e) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(28) Given the presence of diverse cationic and other potentially Lewis acidic species, including silicon derivatives, in the reaction mixture, assisted elimination of the fluoride ion can nevertheless not be definitively ruled out.

(29) A further possible candidate as active electrophile is the corresponding anhydride species, which could feasibly be formed in the reaction mixture. Notably benzoyl anhydride **6a** was found to be a competent substrate in the reaction albeit with lower efficiency than acyl fluoride **5a**.

(30) The successful reaction on stoichiometric benzoyl imidazolium salt **1** under UVA irradiation likely proceeds through direct excitation and subsequent electron transfer from the benzyl silane. This mechanism is shown in Scheme S4 in the Supporting Information.

(31) Bennett, L.; Melchers, B.; Proppe, B. *Curta: A General-Purpose High-Performance Computer at ZEDAT*; Freie Universität Berlin, 2020.