Arylsilylation of Electron-Deficient Alkenes via Cooperative Photoredox and Nickel Catalysis

Zhikun Zhang and Xile Hu*

Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), ISIC-LSCI, Lausanne 1015, Switzerland

ABSTRACT: Carbosilylation of alkenes can be an efficient approach to the synthesis of organosilicon compounds. However, few general methods of carbosilylation are known. Here we introduce a strategy for arylsilylation of electron-deficient terminal alkenes by combining photoredox-catalyzed silyl radical generation, innate reactivity of silyl radical with alkene, and Ni-catalyzed aryl-alkyl cross-coupling. This cooperative photoredox and nickel catalysis operates under mild conditions. It employs readily available alkenes, aryl bromides, and silane as reagents, and produces useful synthetic building blocks in a modular manner.

KEYWORDS: nickel catalysis • arylsilylation • photoredox catalysis • cooperative catalysis • organosilicon
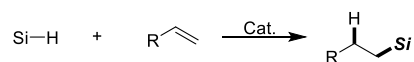
INTRODUCTION

Silicon-containing compounds have very wide applications in organic synthesis, medicinal chemistry and material science.[1] Hydrosilylation is a widely used method to synthesize organosilicon compounds from readily available alkenes (Scheme 1a).[2] However, hydrosilylation introduces only one functional (silyl) group. Carbosilylation of alkenes, on the other hand, can introduce simultaneously two functional groups, providing rapid access to functionalized organosilicon compounds. Despite progress in difunctionlization of alkenes,[3] carbosilylation remains under-developed.[4] In earlier examples, only dienes and allenes were suitable substrates.[4b-d, 4f] Kambe and co-workers then reported Cp_2TiCl_2-catalyzed carbosilylation of alkenes through silylation of an *in-situ* generated alkyl Grignard reagent (Scheme1b)[4e]. The latter intermediate, however, limited the functional group compatibility. Engle and co-workers recently reported Pd-catalyzed, 8-aminoquinoline (AQ) directed aryl/alkenylsilylation of alkenes (Scheme1b)[4h]. The reaction occurred via quenching of an organopalladium intermediate with $PhMe_2Si$-Bpin, which nonetheless generated some 1, 2-carboborylation byproduct. Additionally, the AQ directing group limited the scope of alkenes. In the above two examples, silylation was achieved by reaction of a silicon reagent on an organometallic intermediate. We wondered whether carbosilylation via silyl radicals would become a complementary approach to overcome some of the limitations of previous methods.

Silyl radicals are well known intermediates in organic synthesis.[5] Traditionally, silyl radicals are generated by oxidation of silanes with radical initiators (e.g., azobisisobutyronitrile (AIBN), peroxides.) under thermal conditions.[6] Recently, photoredox catalysis was developed to generate silyl radicals under much milder conditions.[7] We thought that if a silyl radical could be generated by photoredox-oxidation of a silane, it could be trapped by an alkene to give a β-silyl alkyl radical
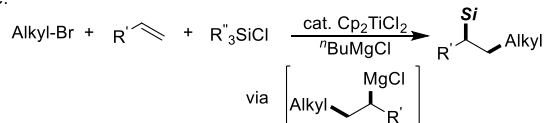
(Scheme 1c). This radical could be further trapped by a Ni(II) aryl Br intermediate generated from oxidation addition of an aryl bromide to a Ni(0) species (Scheme 1c).[8-9] Reductive elimination of the resulting Ni(III) alkyl aryl intermediate would yield the arylsilylation product together with a Ni(I) species which could be transformed into the original Ni(0) catalyst by the reduced photoredox catalyst. Although transformations of β-silyl alkyl radical intermediates were previously applied for carbosilylation of alkenes, those transformations were based on further oxidation followed by reactions with nucleophiles (Scheme 1b),[4k] further reduction followed by reactions with electrophiles,[4l] or intramolecular addition to arenes[4i, 4j, 4m, 4n]. A general, cross-coupling type carbosilylation remained elusive. In view of this state of the art, our strategy appeared attractive.
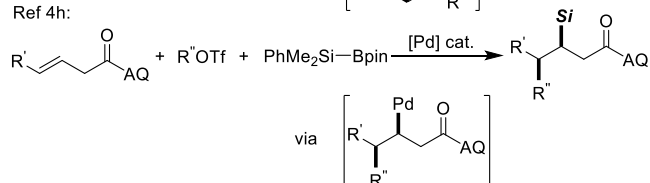
a) A general scheme for hydrosilylation of alkenes

Si—H + R⟍ →(Cat.) H / R–CH$_2$–Si

b) Selected prior examples of carbosilylation of alkenes

Ref 4e:

Alkyl-Br + R'⟍ + R''$_3$SiCl →(cat. Cp$_2$TiCl$_2$ / ^{n}BuMgCl) R'–Si–Alkyl

via [Alkyl–⟍–R' MgCl]

Ref 4h:

R'–CH=CH–CH$_2$–C(O)–AQ + R''OTf + PhMe$_2$Si—Bpin →([Pd] cat.) R'–(Si)–CH(R'')–CH$_2$–C(O)–AQ

via [R'–(Pd)–CH(R'')–CH$_2$–C(O)–AQ]

Ref 4k:

R^{2}R^{1}C=CH(R^3)(H) + Si—H + Nu—H →(cat. FeCl$_2$ / DTBP) Nu–Si / R^{2}R^{1}R^3

[⊕ Si / R^2 R^1 R^3]

c) Our design strategy for arylsilylation of alkenes via cooperative photoredox and nickel catalysis.

Si—H + R⟍ + Ar-X →(PC/Ni / Light) Ar / R–Si

Ar—Ni^{III} / R–Si

Ni^I

P

$\overrightarrow{PC}$

PC

R⟍ + Si—H →(PC*) R·–Si →(→PC)

Ar—Ni^{II}—Br

Ni^0

ArBr

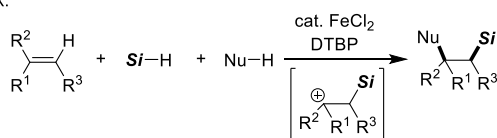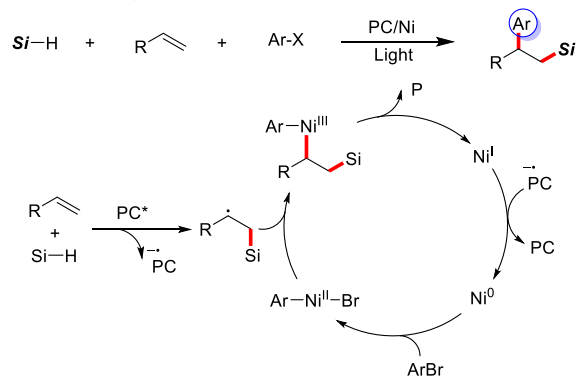Scheme 1. (a) A general scheme for hydrosilylation of alkenes; (b) Selected prior examples of carbosilylation of alkenes; (c) Our design strategy for arylsilylation of alkenes via cooperative photoredox and nickel catalysis.

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RESULTS AND DISCUSSION

Following this design, we explored conditions for arylsilylation of methyl acrylate (**1a**), which is a good radical acceptor. We chose TMS_3SiH (**2a**) as the silane due to its weak Si-H bond,[6d, 6e] prone to formation of a silyl radical. We chose bromobenzene (**3a**) as an archetypical aryl halide. We first applied [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF$_6$ (**PC1**) as the photocatalyst,[7b] NiBr$_2$·DME as the Ni source, and 4,4′-di-tert-butyl-2,2′-dipyridyl as ligand (for Ni). An encouraging yield of 15% of the desired product **4a** was obtained upon illumination with blue LED in DME at room temperature after 12 h, when 2.0 equiv of Na_2CO_3 was used as base (Table 1, entry 1). Other ligands and bases were used, but the yields were lower (Tables S1 and S2, SI). The solvents had a strong influence on the yields of the reaction (Table S3, SI). 1,4-dioxane was the best solvent, giving a yield of 54% for **4a** (Table 1, entry 2). A slight modification on the substrate ratio improved the yield to 60% (Table 1, entry 3). Other Ni salts were screened as the Ni sources (Table S4, SI), and Ni(COD)$_2$ was found to be the best, probably by facilitating the oxidative addition of phenyl bromide (Table 1, entry 4). We then screened other photocatalysts. [Ir(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$ (**PC2**) improved the yield to 76% (Table 1, entry 5), while [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (**PC3**) and 4CzIPN (**PC4**) were not efficient at all (Table 1, entry 6,7). The performance of the photocatalysts **PC1-3** correlated with their excited-state oxidation potentials (see below for details). A further tuning of substrate ratio (Table S5, SI) led to the optimized conditions, under which **4a** could be obtained in 88% yield. (Table 1, entry 8). Control experiments showed that the nickel catalyst, photocatalyst, and light are all necessary for the reaction (Table S6, SI). Chlorobenzene and iodobenzene were not suitable substrates (Table S6, SI). Without base, the yield decreased sharply (Table S6, SI), probably due to the decomposition of catalysts under acidic conditions.

Table 1. Summary of key reaction parameters.[a]
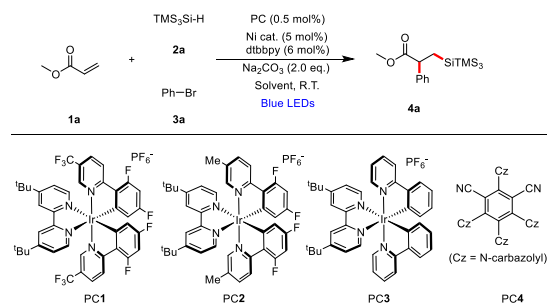
Entry	1a : 2a : 3a	Ni salt	PC	Solvent	Yields (%)[b]
1	1.5 : 1.0 : 1.5	NiBr$_2$·DME	PC1	DME	15
2	1.5 : 1.0 : 1.5	NiBr$_2$·DME	PC1	1,4-Dioxane	54
3	1.5 : 1.5 : 1.0	NiBr$_2$·DME	PC1	1,4-Dioxane	60
4	1.5 : 1.5 : 1.0	Ni(COD)$_2$	PC1	1,4-Dioxane	65
5	1.5 : 1.5 : 1.0	Ni(COD)$_2$	PC2	1,4-Dioxane	76
6	1.5 : 1.5 : 1.0	Ni(COD)$_2$	PC3	1,4-Dioxane	<5%
7	1.5 : 1.5 : 1.0	Ni(COD)$_2$	PC4	1,4-Dioxane	<5%
8	1.0 : 1.5 : 2.0	Ni(COD)$_2$	PC2	1,4-Dioxane	88 (80)

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2.0 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. Additional details can be found in the SI. [b] Yields were determined by GC-FID analysis with dodecane as internal standard; the yield in parentheses for entry 8 is isolated yield. TMS = trimethylsilyl, DME = dimethoxyethane, COD = 1, 5-cyclooctadiene, dtbbpy = 4, 4′-di-tert-butyl-2, 2′-dipyridyl, LED = light emitting diode, PC = photoredox catalyst.

We then explored the scope of this arylsilylation using the optimized conditions (Table 2). A large number of aryl bromides (**3a-3aa**) could be coupled. Reactions of 4-substituted aryl bromides typically gave high yields of arylsilylation (**4a-4d**, **4f**, **4g-4o**). The substituents could be electron rich (**4b**, **4c**, **4f**), neutral (**4a**), or poor (**4g-4o**). 3-Substituted aryl bromides were coupled in reasonable yields as well (**4q-4s**). A crystal structure of **4p** was determined (for details, see section 6 in SI). The reactions tolerated potentially coordinating functional groups such as ester, amide, aldehyde, and nitrile. Moreover, groups potentially reactive in cross-coupling such as boryl (**4t**)

and aryl-bromide (**4w**) were also tolerated. But styrene (**4u**) and alkynyl (**4v**) groups posed a problem and the yields were low. While 2-bromonaphthalene was easily coupled (**4e**), 1-bromonaphthalene (**3aj**) was not a viable substrate, likely due to steric hindrance. Likewise, 2-methyl phenyl bromide (**3ak**) could not be coupled. These results might be rationalized by the difficulty in trapping of an alkyl group with a large tri(trimethylsilyl)silyl group at the α-position by a nickel intermediate with a hindered aryl group. Unhindered, disubstituted aryl bromides could be coupled to give good yields (**4w-4y**). Coupling of aryl bromides conjugated to a heteroaryl group was achieved as well (**4z** and **4aa**), despite potential addition of the silyl radical to the heterocycle via Minisci-type reaction.[10]

The arylsilylation also worked with heteroaryl bromides such as 3- and 4-bromo pyridines (**4ab-4ai**), although the yields were more modest compared to those of coupling with aryl bromides. A gram-scale reaction was conducted for the synthesis of **4l**, and the product was obtained in 73% yield, demonstrating the robustness of the reaction for scale-up.

We then probed the scope of alkenes using methyl 4-bromobenzoate (**1k**) as the arylation reagent. Different alkyl acrylates including phenol, benzyl alcohol, 3-oxobutanol, *N*-boc-4-hydroxypiperidine and ethyl 6-hydroxyhexanoate derived acrylates were viable alkene partners (**4aj-4an**). Reaction with acrylonitrile also gave a high yield (**4ao**). Vinyl acetate could be used, but the yield was low (**4ap**). Arylsilylation of styrenes (**1i**), alkyl alkenes (**1j**), and multi-substituted methyl acrylates (**1k**), however, were unsuccessful.

The synthetic utility of arylsilylation products was demonstrated by several further transformations of compound **4a** (Scheme 2). The ester group in **4a** could be reduced to an alcohol group by LiAlH₄ (Scheme 2a). The tri(trimethylsilyl)silyl group in the resulting compound **6** could then be oxidized to a second alcohol group, yielding 2-phenyl-1,3- propanediol (**7**). The

tri(trimethylsilyl)silyl group in **4a** could also be converted to a disilane group (as in **8**). Oxidation of the disilane group gave a siloxane **9**. Both propanediol and siloxane are useful building blocks in organic and polymer synthesis.

Table 2. Scope of arylsilylation of alkenes. [a, b]
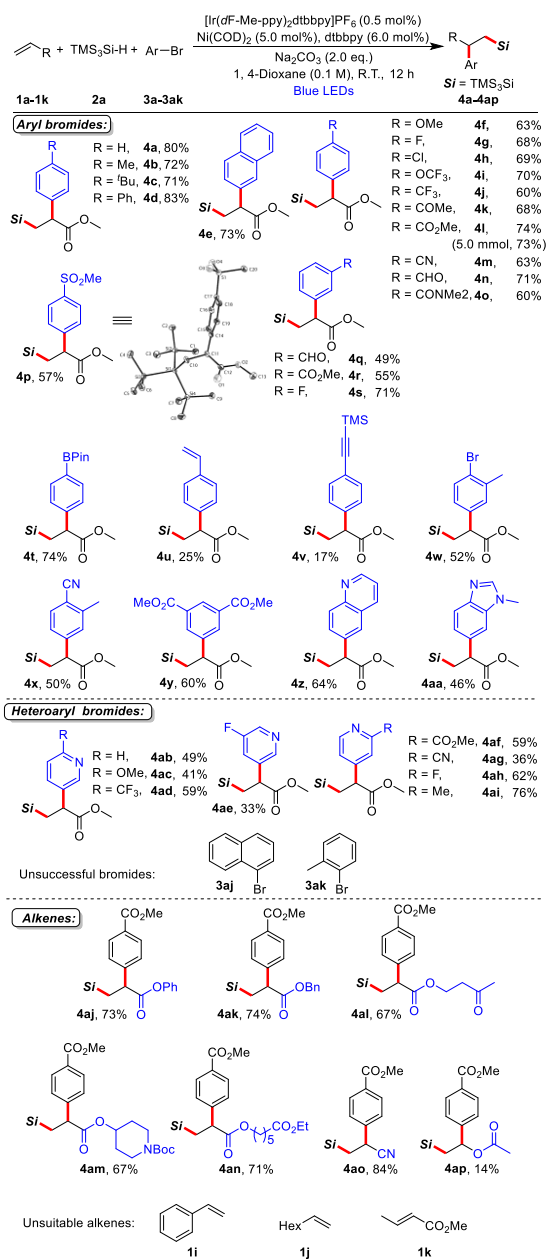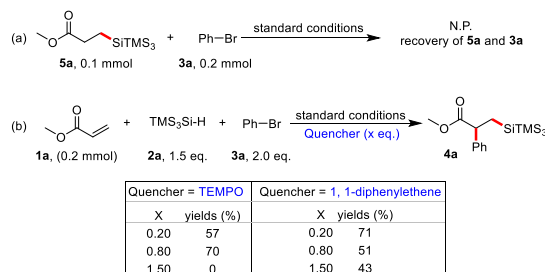

[a] Conditions same as entry 8 in Table 1. [b] Yields of isolated products. TMS = trimethylsilyl

In the test arylsilylation reaction (Table 1), the major side product (ca. 10%) was methyl β-TMS$_3$Si-propionate (**5a**), originated from hydrosilylation of methyl acrylate (**1a**) with silane (**2a**). When **5a** was treated with bromobenzene (**3a**) under conditions of arylsilylation, no reaction occurred (Fig. 1a). This result excluded the possibility that arylsilylation proceeded first by hydrosilylation followed by α-arylation. When the reaction was conducted in the presence of radical scavengers such as (2, 2, 6, 6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 1,1-diphenylethane, the yields decreased (Fig. 1b). However, a significant amount of TEMPO (1.5 equiv) was needed to completely quench the reaction. The silylated TEMPO was not observed in GC-MS, probably due to its instability, but 1, 1-diphenyl-2-(TMS)$_3$Si-ethane was observed. Light–dark interval experiments showed that the product was formed only under light (Fig. S1, SI). The quantum yield was 0.93 (for details, see section 5 in SI). These results suggest that arylsilylation is mostly a non-chain radical process. Fluorescence quenching experiments were conducted on PC**2** using all possible quenchers in the reaction mixture, including **1a**, **2a**, **3a** and [(dtbbpy)Ni(Ph)(Br)] (**10**), *in-situ* prepared from reaction of Ni(COD)$_2$, dtbbpy, and PhBr (for details, see section 5 in SI). No significant quenching was observed with **1a**, **2a**, or **3a** (Fig. S2, SI). However, **10** efficiently quenched the excited state of PC**2** (Fig. 1c), following a linear Stern-Volmer plot (Fig. 1d). Additionally, strong quenching was observed using ^{n}Bu$_4$NBr, a soluble source of Br$^-$, as the quencher (Fig. S3, SI). These results suggest quenching of excited PC**2** by **10** leads to oxidation of its Br$^-$ ligand to a Br. Similar photoredox generation of Br· from Br$^-$ was previously reported.[7b] Addition of extra ^{n}Bu$_4$NBr during the reaction slightly decreased the yield due to an increase of side product **5a** (Table S6, SI). This mode of initiation is consistent with the performance of different catalysts. Both PC**1** ($E_{1/2}^{red}$ [Ir(III)*/Ir(II)] = +1.21 V vs saturated calomel electrode (SCE) in CH$_3$CN)[11] and PC**2** ($E_{1/2}^{red}$ [Ir(III)*/Ir(II)] = 0.97 V vs saturated calomel

electrode (SCE) in CH$_3$CN)[11] could oxidize Br$^-$ (($E_{1/2}^{red}$ = +0.80 V vs SCE in dimethoxyethane (DME))[7b] upon illumination, initiating the arylsilylaiton catalytic cycle. The excited state of PC**3** ($E_{1/2}^{red}$ [Ir(III)*/Ir(II)] = 0.66 V vs saturated calomel electrode (SCE) in CH$_3$CN)[11], however, is not oxidizing enough for oxidation of Br$^-$, which explains why PC**3** is not a viable photocatalyst. For PC**4**, the excited-state oxidation potential is sufficient to oxidize Br$^-$ anion, but the catalyst might be too unstable for this reaction. The higher catalytic efficiency of PC**2** compared to PC**1** might also be related to their excited state oxidation potentials. The higher oxidation power for PC**1*** induced more side reactions (according to GC-MS analysis). The involvement of Br· also explains the inactivity of PhCl and PhI as substrates. Cl$^-$ is more difficult than Br$^-$ to oxidize. Although I$^-$ is expected to be oxidized to I· under the photocatalytic conditions, the latter has a too low oxidation power to abstract an H atom from a silane.
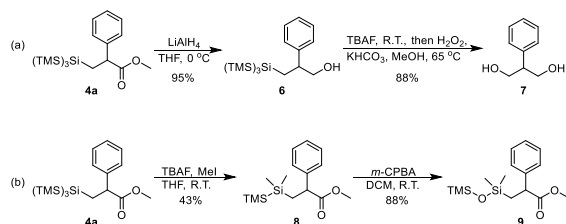
Scheme 2. Further transformations of an arylsilylation product **4a**. (a) Synthesis of 2-phenyl-1, 3-propanediol (**7**); (b) Synthesis of a disilane (**8**) and a siloxane (**9**).
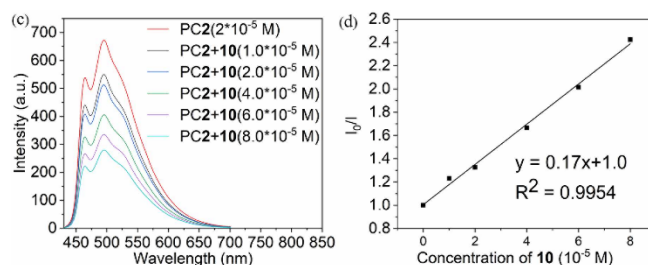

Quencher = TEMPO		Quencher = 1, 1-diphenylethene	
X	yields (%)	X	yields (%)
0.20	57	0.20	71
0.80	70	0.80	51
1.50	0	1.50	43

Figure 1. Mechanistic investigations. (a) Reaction of **5a** with PhBr under standard arylsilylation conditions. (b) Arylsilylation in the presence of radical scavengers. For experimental details, see the Supporting Information. (c) Quenching of excited Ir* (III) photocatalyst PC**2** with **10** (**10** = [(dtbbpy) Ni(Ph)(Br)]); (d) Stern-Vomer linear fitting of the quenching in (c).

Based on the above results and literature,[7b] we proposed a mechanism for the arylsilylation (Fig. 2). Oxidative addition bromobenzene (**3a**) to a Ni (0) catalyst (**A**) gives a Ni(II)(Ph)(Br) intermediate (**B**). Meanwhile, the Ir^{III} photocatalyst is excited by blue LED light. The excited-state is then reductively quenched by Br to give Ir^{II} and a Br·. The latter abstracts a hydrogen atom from silane (**2a**) to give a silyl radical (**E**). Addition of **E** to methyl acrylate (**1a**) generates a β-silyl alkyl radical (**F**), which is trapped by nickel species **B** to give a Ni(III) intermediate (**C**). C-C reductive elimination from **C** yields the arylsilylation **4a** and a Ni(I) species (**D**), which is reduced by Ir(II) to regenerate both the Ir(III) photocatalyst and the Ni(0) catalyst.
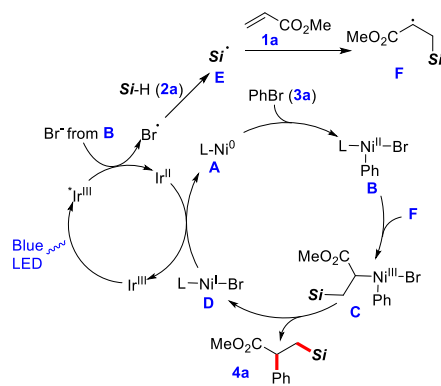

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Figure 2. A proposed mechanism for arylsilylation of alkenes via cooperative photoredox and nickel catalysis.

CONCLUSIONS

In summary, by combing photoredox and nickel catalysis, we achieved arylsilylation of electron-deficient terminal alkenes using aryl bromides and TMS_3SiH as reaction partners. The silylation involved a photo-generated silyl radical intermediate, whereas the arylation proceeded via Ni-catalyzed cross coupling. The reactions could be conducted under mild conditions, exhibiting broad scope and high functional group tolerance. The products are useful synthetic intermediates.

ASSOCIATED CONTENT

AUTHOR INFORMATION

Corresponding Author

*E-mail: xile.hu@epfl.ch

ORCID

Zhikun Zhang: 0000-0002-0591-3680

Xile Hu: 0000-0001-8335-1196

Author Contributions

The authors declare no competing financial interests.

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, catalyst and compounds characterization (PDF)

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Table of Contents Graphic

$Ar-Br$ +

TMS_3Si-H

$R\diagup\!\!\!=$

$[Ir(dF-Me-ppy)_2dtbbpy]PF_6$
$Ni(COD)_2/dtbbpy$
Na_2CO_3, Dioxane, R.T., 12 h
Blue LEDs

via

$Ar{-}Ni$
R
Si

Ar
R
Si

42 examples
up to 84% yield