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Photocatalysis

Formal β-C–H Arylation of Aldehydes and Ketones by Cooperative Nickel and Photoredox Catalysis

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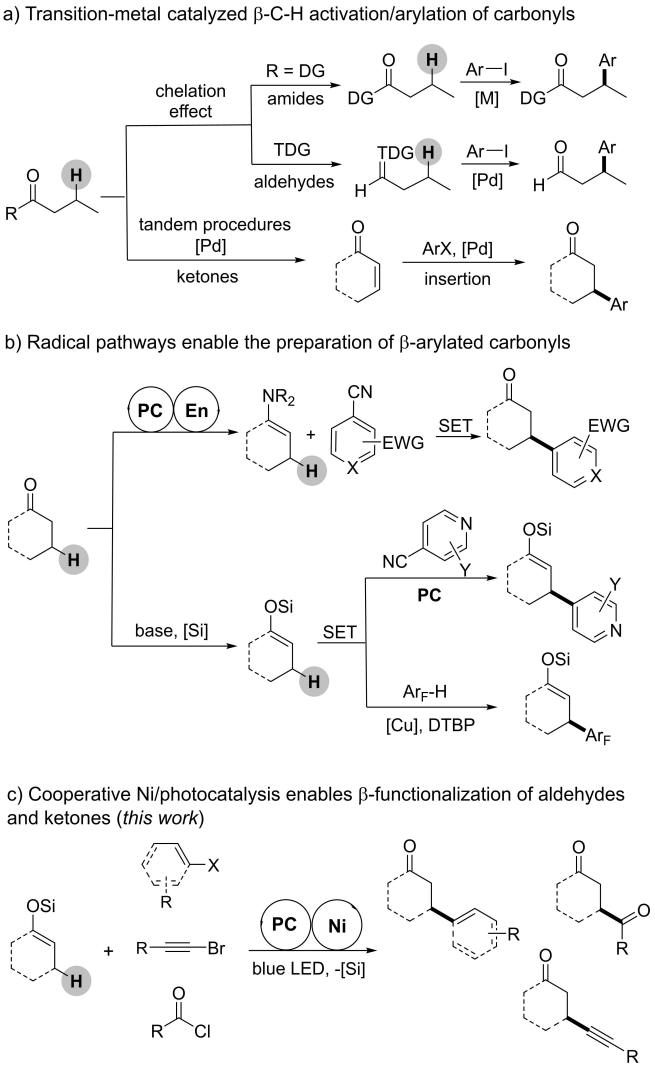
Abstract: α-C–H-functionalization of ketones and aldehydes has been intensively explored in organic synthesis. The functionalization of unactivated β-C–H bonds in such carbonyl compounds is less well investigated and developing a general method for their β-C–H arylation remains challenging. Herein we report a method that uses cooperative nickel and photoredox catalysis for the formal β-C–H arylation of aldehydes and ketones with (hetero)aryl bromides. The method features mild conditions, remarkable scope and wide functional group tolerance. Importantly, the introduced synthetic strategy also allows the β-alkenylation, β-alkynylation and β-acylation of aldehydes under similar conditions. Mechanistic studies revealed that this transformation proceeds through a single electron oxidation/Ni-mediated coupling/reductive elimination cascade.

Due to the ubiquity of C–H bonds in organic compounds, developing novel and efficient methods for site selective functionalization of C(sp^3)–H bonds is important in synthetic chemistry.[1] The conversion of inert C–H bonds into C–C bonds leads to value-added compounds.[2] For example, the direct C–H arylation at the β-position or at remote C–H bonds in ketones or aldehydes will provide intermediates for preparing biologically important natural and pharmaceutical products.[3] Compared to the well-established methods for the synthesis of α-aryl carbonyl systems,[4] the direct arylation for unactivated β-C–H bonds is more challenging and only a few approaches have been reported.[5] For instance, directing-group mediated β-C–H functionalization of amides with aryl iodides using transition-metal catalysis has been intensively investigated (Scheme 1a).[6] To circumvent additional costs for installing and removing a directing group, Yu and Ge introduced amino-acid based transient directing groups (TDG) to realize Pd-catalyzed β-C–H arylation of aldehydes.[7] Along with directing group strategies, Baudoin and Dong achieved β-C–H arylation of ketones via Pd-catalyzed tandem processes, where Pd-catalysis allows for initial α,β-dehydrogenation and also for subsequent β-arylation.[8] As drawbacks of these elegant methods, the high cost of the noble metal catalyst, the need for stoichiometric additives like silver salts and limited examples for heteroarylation have to be mentioned.



Scheme 1. Different strategies for β-C–H arylation of carbonyls.

Radical chemistry has gained great attention recently, mainly driven by the developments in the fields of photoredox catalysis and electrochemistry.[9] Along these lines, β-C–H arylation of carbonyls has been achieved using the radical approach (Scheme 1b). For example, MacMillan and

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co-workers developed cooperative enamine/photoredox catalysis using electron-deficient cyanoarenes as coupling partners.[10] Moreover, Ooi and Chang independently reported β-C–H arylation of aldehydes and ketones via single-electron transfer (SET) of preformed silyl enol ethers and subsequent (hetero)arylation.[11]

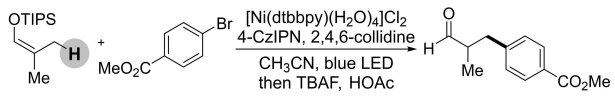
Although powerful, the limited scope with respect to β-heteroarylation and insufficient functional group tolerance have hampered wider applications of these elegant methods. Given the importance of such privileged scaffolds, developing more general and environmentally benign synthetic methods for ketone and aldehyde β-arylation are still highly desirable.

Palladium catalysis has occupied a dominant role for β-C–H arylation of carbonyls, whereas cheap nickel salts have rarely been used in such transformations to date.[12] Recently, dual photoredox and transition metal catalysis have emerged as a powerful tool in organic synthesis.[13] Motivated by these findings,[14] we assumed that cooperative nickel and photocatalysis should allow for the β-C–H functionalization of carbonyls via their readily prepared silyl enol ethers with (hetero)aryl bromides, bromoalkynes or acyl chlorides as coupling partners (Scheme 1c).

We commenced our studies with triisopropyl silyl enol ether **1a** and methyl 4-bromobenzoate **2a** as model substrates. After extensive optimization we found that the combination of $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (10 mol %), 4-CzIPN (2.5 mol %) and 2,4,6-collidine (1.5 equiv) under blue light irradiation in MeCN successfully afforded after silyl enol ether hydrolysis the targeted β-arylated aldehyde **3a** in 86 % yield (Table 1, entry 1). Control experiments showed that the reaction did not proceed in the absence of Ni- or photocatalyst (Table 1, entry 2). Replacing 4-CzIPN with other photocatalysts like PC2 and PC4 led to worse results, while PC3 afforded a similar yield (Table 1, entries 3–5). A survey of nickel catalysts revealed that the combination of $NiCl_2$ and dtbbpy showed a lower yield as compared to the yield obtained with its preformed nickel complex. Other nickel salts such as $Ni(OTf)_2$ and $Ni(OAc)_2{\cdot}4H_2O$ also catalyzed this reaction, albeit with much lower efficiency (Table 1, entries 6–8). However, Cu-catalysis did not work (entry 9). Screening the bases showed that inorganic bases like Cs_2CO_3 and K_3PO_4 were not suitable for this reaction. Using DMF or DMSO as the solvent instead of MeCN turned out to be worse and a low yield was noted with DCE (entries 11 and 12).

With the optimized conditions in hand, we then started to evaluate the substrate scope. First, the scope of aryl bromides was explored with **1a** as the coupling partner (Scheme 2). Aryl bromides bearing electron-withdrawing groups including ester, acyl and formyl groups delivered the β-arylated aldehydes **3a**–**3c** in high yields (82–86 %). Additional functional groups like chloride, alkene, furan, thiophene and amino acid moieties were all well tolerated (**3d**–**3h**). Cyclic ketones are also eligible substrates (**3i**). Notably, bromobenzenes bearing additional chloro- and boronic ester-substituents reacted with complete chemoselectivity (**3k** and **3l**). Aryl bromides bearing electron-donating substituents such as *tert*-butyl, methoxy and amidyl

Table 1: Reaction optimization.[a]

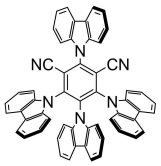


1a **2a** **3a**

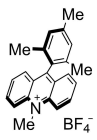
Entry	Variation from the standard conditions	Yield [%][b]
1	none	86
2	without PC or nickel catalysis	n.d.
3	PC2 instead of PC1	69
4	PC3 instead of PC1	84
5	PC4 instead of PC1	n.d.
6	$NiCl_2$/L1 instead of $[Ni(dtbbpy)(H_2O)_4]Cl_2$	68
7	$Ni(OTf)_2$/L1 instead of $[Ni(dtbbpy)(H_2O)_4]Cl_2$	39
8	$Ni(OAc)_2{\cdot}4H_2O$/L1 instead of $[Ni(dtbbpy)(H_2O)_4]Cl_2$	27
9	$CuBr{\bullet}Me_2S$/L2 instead of $[Ni(dtbbpy)(H_2O)_4]Cl_2$	n.d.
10	Cs_2CO_3 or K_3PO_4 instead of 2,4,6-collidine	n.d.
11	DMF or DMSO as solvent	n.d.
12	DCE as solvent	23

PC1 : 4-CzIPN PC2: $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

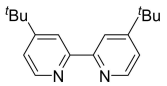
PC3: $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ PC4: Acr-$Mes^+ClO_4^-$

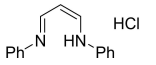


4-CzIPN



Acr-$Mes^+ClO_4^-$

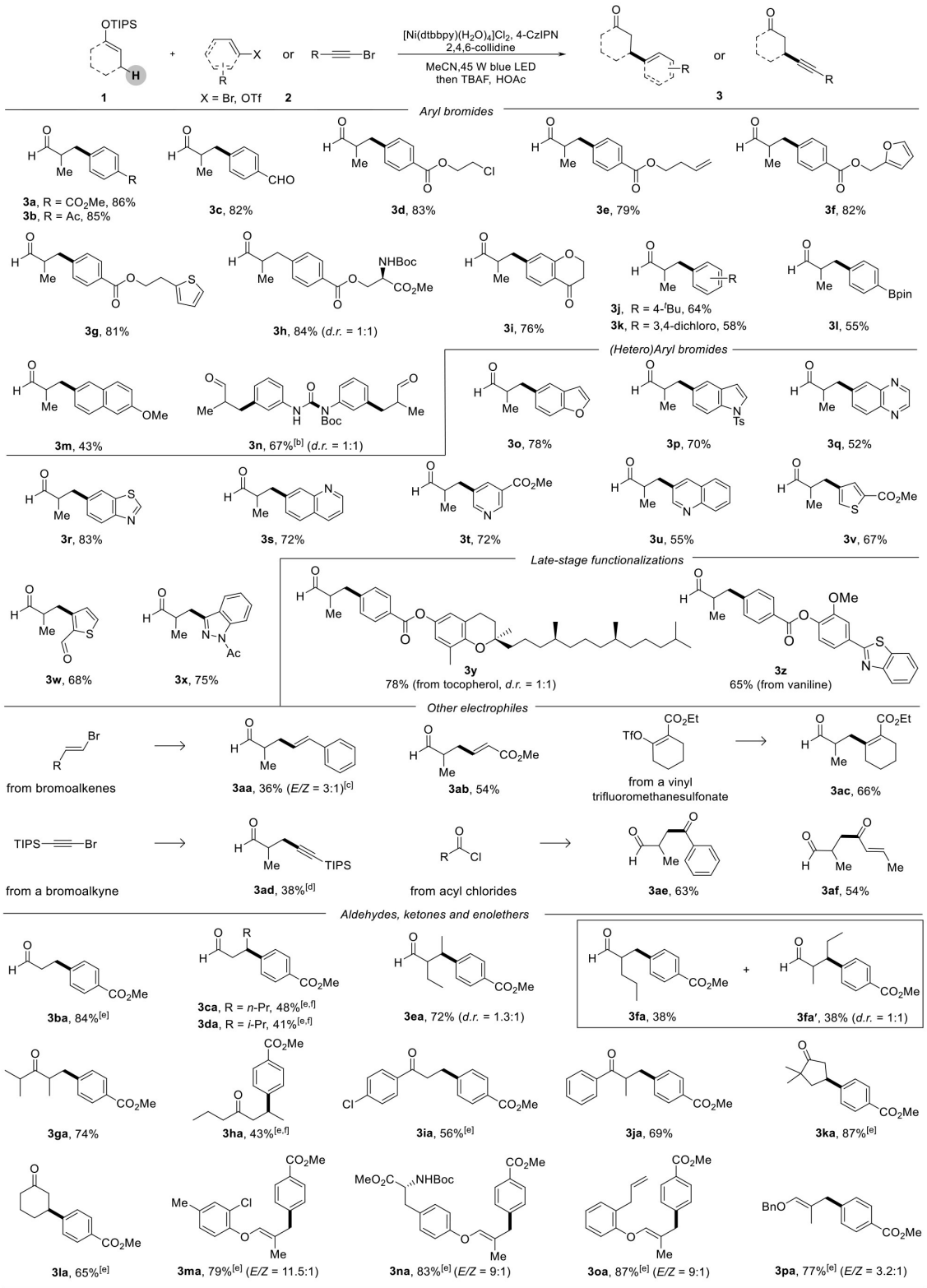
L1: 

L2: 

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (10 mol %), 4-CzIPN (2.5 mol %), 2,4,6-collidine (0.15 mmol) in CH_3CN (1 mL) at rt under irradiation of 45 W Kessil blue LED (λ_{max} = 456 nm) for 24 h. [b] Isolated yields. TIPS = triisopropylsilyl. n.d. = not detected.

also afforded the targeted products in moderate to good yields (**3j**, **3m** and **3n**). The generality of this strategy for preparing β-heteroaryl-substituted aldehydes was convincingly documented by the direct installation of a wide range of heteroaryl moieties including benzofuran, indole, quinoxaline, benzothiazole, quinolone, pyridine, thiophene and indazol (**3o**–**3x**). Furthermore, the late-stage functionalization of more complicated compounds like tocopherol and vaniline also worked well (**3y** and **3z**). Importantly, our method goes beyond the β-(hetero)arylation, as electrophiles like bromoalkynes, bromoalkenes, vinyl trifluoromethanesulfonates and acyl chlorides also engaged in this transformation to provide the corresponding β-functionalized products in moderate to good yields (**3aa**–**3af**). These results show that our approach provides a rather general solution for the β-functionalization of aldehydes.

Next, we started to explore the scope with respect to the carbonyl component using **2a** as the coupling partner. The triisopropylsilyl enol ether derived from propionaldehyde

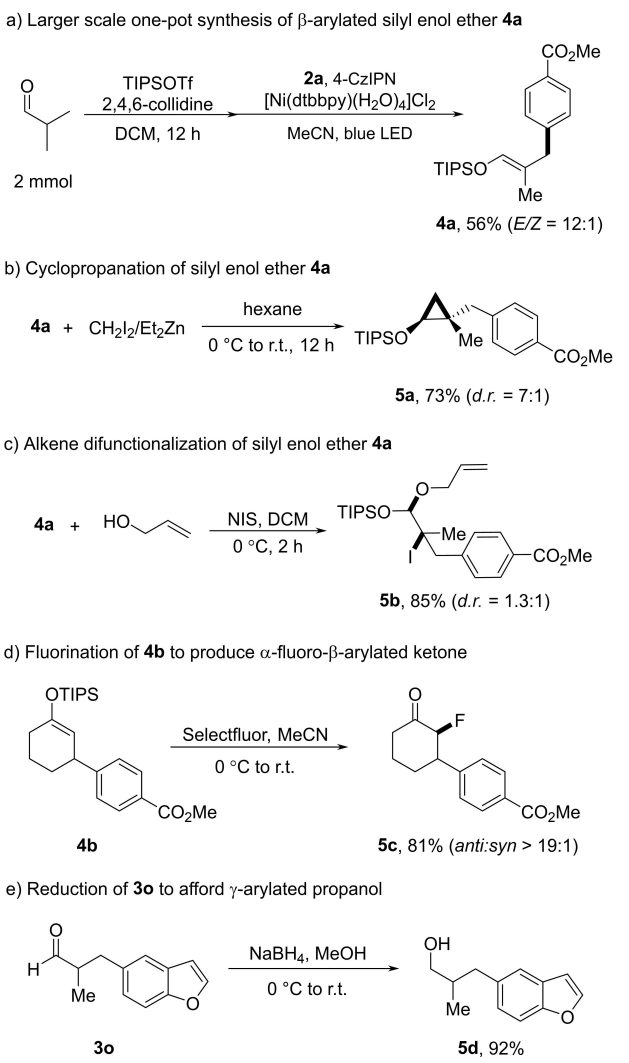


Scheme 2. Substrate scope. Reactions were conducted using **1** (0.2 mmol), **2** (0.1 mmol), $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (10 mol%), 4-CzIPN (2.5 mol%), 2,4,6-collidine (0.15 mmol) in CH_3CN (1 mL) at rt under irradiation with a 45 W Kessil blue LED for 24 h. [b] *tert*-Butyl (3-bromophenyl)carbamate was the starting material. Intermolecular amination occurred between NHBoc moieties during desilylation. [c] β-Bromostyrene was used as a 6:1 *E*/*Z*-mixture. [d] Using $NiBr_2{\cdot}3H_2O$ (10 mol%) and bathocuproine (12 mol%) to replace $[Ni(dtbbpy)(H_2O)_4]Cl_2$. [e] $Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (3 mol%) as photocatalyst instead of 4-CzIPN. [f] Reactions performed with 3.0 equiv of silyl enol ether.

could be β-functionalized to afford after desilylation the 3-arylated propionaldehyde **3ba** in 84 % yield.

Longer chain aliphatic aldehydes including γ-branched congeners provided β-arylated products with moderate yields (**3ca** and **3da**). The reaction of 2-ethylbutyraldehyde with **2a** gave **3ea** as a mixture of diastereomers in 72 % yield with low diastereoselectivity. 2-Methylpentanal bearing a β-CH_3 and a β-CH_2 entity reacted without any regioselectivity (**3fa**). Pleasingly, acyclic ketones also engaged in this reaction. Thus, the O-silyl enol ethers derived from 2,4-dimethyl-3-pentanone and 4-heptanone were successfully β-arylated to provide **3ga** (74 %) and **3ha** (43 %). Alkyl aryl ketones are also eligible substrates, as shown by the preparation of **3ia** and **3ja** in good yields. Moreover, this protocol could also be applied to the β-C–H functionalization of cyclic ketones. Cyclohexanone and 2,2-dimethylcyclopentanone reacted via their O-silyl enol ethers with **2a** to give the arylated ketones in good yields (**3ka** and **3la**). In addition to the silyl enol ethers, benzyl and aryl enol ethers could be used as substrates for the C–H arylation. We were pleased to find that the arylation occurred with high yields and moderate to high *E*-stereoselectivity (**3ma**–**3pa**).

To document the robustness of this transformation, larger scale one-pot synthesis of **4a** was achieved in 56 % yield with high *E*-selectivity (Scheme 3). This offers additional opportunities for the follow-up chemistry. Hence, rather than hydrolyzing the silyl enol ether, this valuable functional entity can be used for further manipulations. For example, cyclopropanation of **4a** gave **5a** upon reaction with CH_2I_2/Et_2Zn in 73 % yield with a slight loss in stereoselectivity. Iodoetherification of **4a** with NIS and allyl alcohol afforded the mixed O,O-acetal **5b** (85 %). Moreover, treatment of **4b** with Selectfluor gave the α-fluoro-β-arylated ketone **5c** in high yield and excellent diastereoselectivity.[15a] Finally, simple reduction of **3o** afforded the γ-arylated alcohol **5d** in high yield.

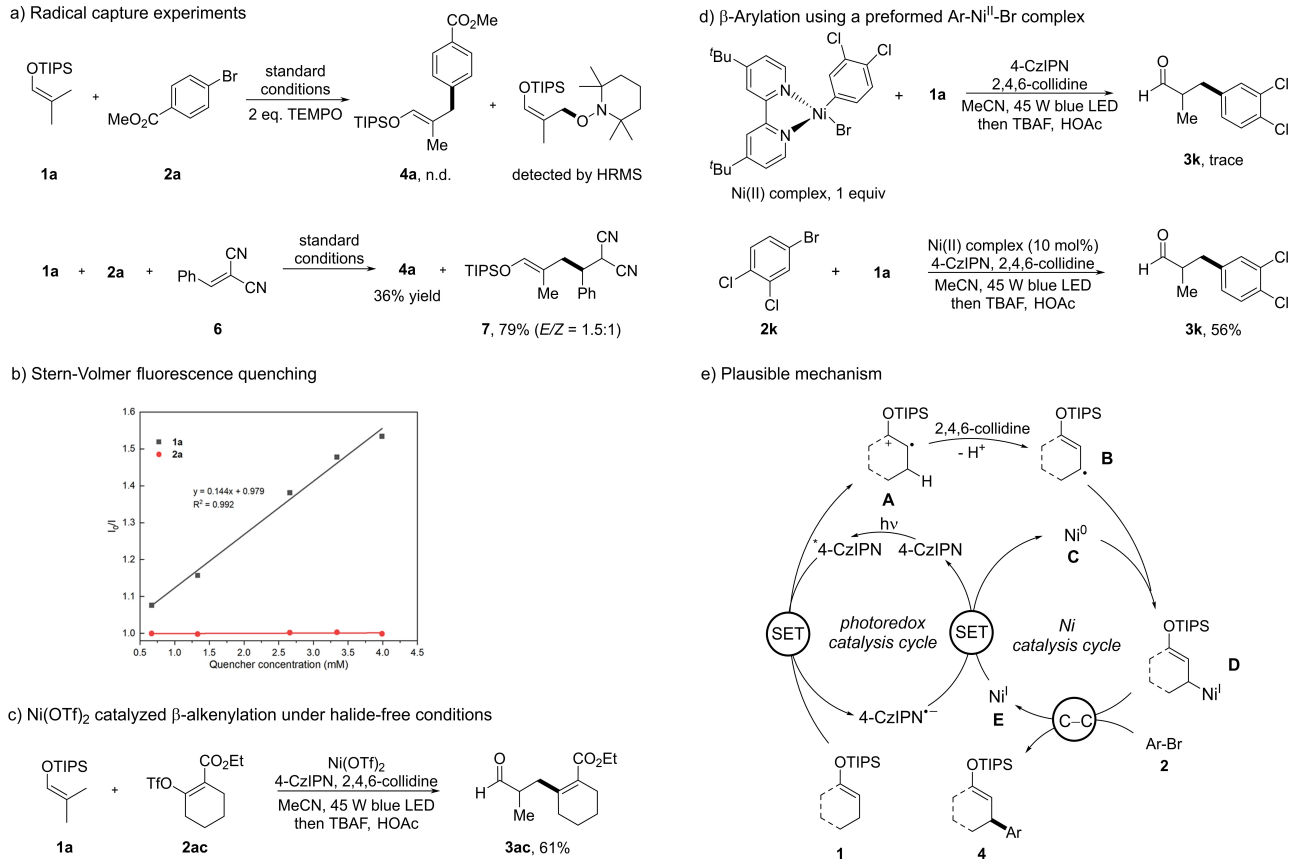


Scheme 3. Larger scale experiment and follow-up transformations.

Regarding the mechanism, radical capture experiments were conducted first. Adding TEMPO (2 equiv) fully suppressed the coupling of **1a** with **2a**, and the TEMPO adduct derived from **1a** could be detected by HRMS (Scheme 4a). Conducting the model reaction in the presence of the electron-deficient alkene **6** (1 equiv) afforded the Giese-type addition product **7** (79 %) along with product **4a** (36 %). These experiments show that an allyl radical derived from the silyl enol ether **1a** is generated under the applied conditions. Stern–Volmer fluorescence quenching experiments revealed that only **1a** could quench the excited state of 4-CzIPN (Scheme 4b). The results for light on–off experiments and a quantum yield of 0.0014 ruled out a photoredox catalyst-initiated chain mechanism (see Supporting Information). In addition, $Ni(OTf)_2$ catalyzed β-alkenylation of **1a** with **2ac** afforded the product **3ac** in 61 % yield under halide-free conditions, which further confirmed that the SET between 4-CzIPN and **1a** was feasible, although we could not fully rule out the possibility of hydrogen atom abstraction by halide radical under the applied reaction conditions (Scheme 4c).[14f] Moreover, stoichiometric reaction of the pre-synthesized Ar-Ni^{II}-Br complex with **1a** only afforded trace amount of the desired product. If the nickel complex was used in catalytic amount, product **3k** was formed in 56 % yield (Scheme 4d). These results indicated that Ar–Ni^{II} complex might not be a competent intermediate in this reaction.

Based on these experiments and literature precedence,[11] the following mechanism is proposed for this transformation (Scheme 4e). The excited 4-CzIPN first oxidizes the silyl enol ether **1** via SET to generate a radical cation **A**.[15] Upon deprotonation with 2,4,6-collidine, the allylic radical **B** is formed, which is then intercepted by Ni^0 to form the Ni^I complex **D**. Next, oxidative addition of **D** with an aryl bromide **2** affords a Ni^{III} complex and subsequent reductive elimination eventually delivers the arylated silyl enol ether **4** along with a Ni^I complex **E**. Ni^0 is then regenerated by SET reduction of **E** with the reduced photocatalyst, closing the photoredox catalysis cycle.[16,17]

In summary, the intermolecular formal β-C–H arylation of aldehydes and ketones via their readily prepared silyl enol ethers has been achieved by cooperative nickel and photoredox catalysis. The introduced method features broad



Scheme 4. Mechanistic studies and proposed mechanism.

scope for both coupling partners and excellent functional group tolerance. Notably, the generality of this method could be expanded to the β-alkenylation, β-alkynylation and β-acylation. The C–H functionalized silyl enol ethers can be hydrolyzed to the carbonyls or be isolated and further chemically modified. Alkyl and aryl enol ethers also serve as substrates for C–H functionalization. The reported β-C–H functionalization is robust and should be of interest to chemists in academia and also in industry.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Allylic Radicals · C–H Activation · Carbonyls · Dual Catalysis · Silyl Enol Ethers

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