

The Dual Role of Benzophenone in Visible-Light/Nickel Photoredox Catalyzed C-H Arylations: Hydrogen Atom Transfer and Energy Transfer

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Abstract: A dual catalytic protocol for the direct arylation of non-activated C(sp³)-H bonds was developed. Upon photochemical excitation, the excited triplet state of a diaryl ketone photosensitizer abstracts a hydrogen atom from an aliphatic C-H bond. This inherent reactivity was exploited for the generation of benzylic radicals which subsequently enter a nickel catalytic cycle, accomplishing the benzylic arylation.

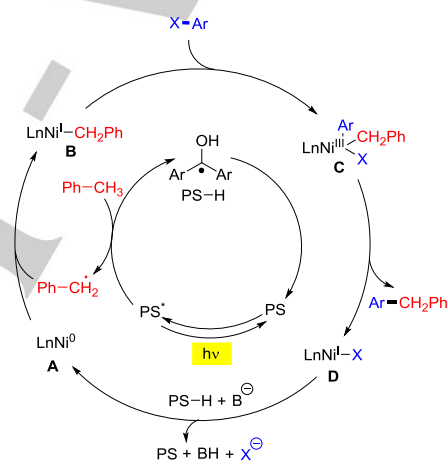
The direct functionalization of inert C-H bonds facilitates the access to complex molecular structures in organic synthesis. Hence, the direct modification of C-H bonds has been extensively investigated in the last two decades. Whereas transition-metal-catalyzed processes with the assistance of directing groups have been widely used for the activation of C(sp²)-H bonds,^[1] applying this strategy to C(sp³)-H bonds is more challenging.^[2] Nevertheless, organic free radical chemistry has been utilized as an alternative tool for the functionalization of inert aliphatic C-H bonds.^[3]

Conventionally, harsh reaction conditions employing the use of strong acids, peroxides or high energy UV light, are necessary for the generation of C(sp³) radicals. The recent progress in the field of visible light mediated photoredox catalyzed reactions allows milder access to C(sp³) centered radical intermediates and their subsequent functionalization.^[4] Furthermore, the combination of photocatalysis and nickel catalysis has emerged as an elegant approach for the direct arylation of unactivated C(sp³)-H bonds.^[5] For example, MacMillan and co-workers reported a protocol for the α -arylation of cyclic and acyclic amines, lactams and ureas.^[5a] The groups of Doyle^[5b] and Molander^[5c] described the α -arylation of ethers. Recently, our group has successfully achieved the arylation of allylic C(sp³)-H bonds.^[5g]

The H-atom abstraction agent, in these reports has been a transient radical species generated either through electron transfer or via energy transfer by the photocatalyst. We considered simplifying this step by using the excited state of a photosensitizer itself for the H-atom abstraction. Organic compounds^[4a,6] as well as inorganic complex structures^[4d,5f,7] are known for their ability to abstract H-atoms upon photochemical excitation. Among the organic compounds applied, diaryl ketones have long served this purpose owing to their accessible

triplet excited states. Therefore, we decided to engage this class of compounds in catalytic amounts as organic photosensitizers (PS) for the C(sp³)-H arylation.^[8]

Diarylmethane moieties are important structural motifs in bio-active compounds, drug molecules and organic materials.^[9] Hence, methods for their facile synthesis are of great demand. We therefore aimed at developing a general protocol for the benzylic arylation using visible-light-catalysis and at the same time expanding the application of diaryl ketones in dual photoredox/transition-metal catalysis.^[10,11] Our mechanistic hypothesis is depicted in Scheme 1.



Scheme 1. Mechanistic hypothesis.

The triplet PS*, formed upon photochemical excitation of the ground state PS, initiates the reaction via H-atom abstraction from toluene. The resulting benzyl radical is trapped by an *in situ* generated Ni(0) species **A** to form **B**. The Ni(I) species **B** adds oxidatively to the haloarene substrate and the resulting Ni(III) complex **C** produces subsequently the desired coupling product via reductive elimination. This step leads also to the formation of **D** which, upon base-assisted reduction by the reduced PS (PS-H), gives **A**, closing the catalytic cycle ($E_{\text{red}}[\text{Ni}^{\text{I}}/\text{Ni}^{\text{0}}] = -1.10\text{V}$ vs Ag/AgCl in DMF;^[12] $E_{1/2}^{\text{red}}[\text{PhCOPh}] = -2.20\text{V}$ vs Ag/AgNO₃ in MeCN^[13]). An alternative mechanism in which the oxidative addition of Ni(0) species to the aryl halide precedes the radical trapping step might also be operating.^[14]

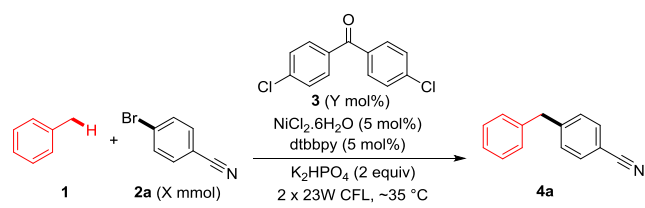
For the initial experiments, we selected 4,4'-dichlorobenzophenone (**3**) ($E_{1/2}^{\text{red}}[\mathbf{3}] = -2.09\text{V}$ vs Ag/AgNO₃ in MeCN, $\lambda_{\text{max}} = 344\text{ nm}$) (see SI) as photosensitizer, as it was recently successfully used by Guin and co-workers in combination with household CFL lamps in the C(sp³)-H alkenylation/alkynylation reaction.^[6h] Initially we irradiated 4-bromobenzonitrile (**2a**) in the presence of **3** (25 mol%), NiCl₂·6H₂O (5 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbbpy) as ligand (5 mol%) and K₂HPO₄ as base (2 equiv) with two 23W

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CFL lamps for 18 hours, in toluene as solvent. The reaction setup was cooled with a fan from the top to keep the reaction temperature constant at $\sim 35^\circ\text{C}$ (see SI). Pleasingly, the desired coupling product **4a** was formed in 51% NMR yield (Table 1, entry 1). The reaction reached full conversion with further dilution of the reaction mixture from 0.35 M to 0.2 M and gave **4a** in 94% yield after purification (entry 2). Furthermore, 20 mol% of **3** was also sufficient to achieve full reaction efficiency (entry 3). Further decrease in the amount of photosensitizer led to diminished yields (entries 4 and 5).

Table 1. Optimization of the reaction conditions.^[a]



Entry	2a (X mmol)	3 (Y mol%)	Conc. (M)	Yield (%) ^[b]
1	0.35	25	0.12	51
2	0.2	25	0.05	94 ^[c]
3	0.2	20	0.05	100
4	0.2	10	0.05	48
5	0.2	5	0.05	37

[a] The reaction mixture in toluene was irradiated with two household CFL lamps from two sides for 18 h under Ar. [b] NMR yield was calculated with CH_2Br_2 as internal standard. [c] Yield after purification.

Control experiments proved that all reagents as well as light-irradiation are indispensable for the reaction to proceed (see SI). In addition, a wide range of diarylketones and similar compounds were evaluated as photosensitizers (see SI). Interestingly, among the diaryl ketones tested, **3** turned out to be the most efficient candidate for our reaction (see SI).

With the optimized conditions in hand, we proceeded to explore the scope of the reaction. First, we tested the reactivity of different bromoarenes in the reaction with toluene (Figure 1). Aryl bromides bearing electron withdrawing groups (CF_3 , Ac, CO_2Me) in the *para* position reacted efficiently to give the corresponding desired products **4b-4d** in good yields (53-79%). Notably, chemoselectivity was achieved in the case of 4-chlorobromobenzene as the reaction took place only at the C-Br bond (**4e**, 62%). Fluorine as substituent was as well tolerated and the corresponding product **4f** was isolated in 71% yield. However, the yield dropped to 41% when the substituent at the *para* position was changed to a phenyl group (**4g**). To our delight, electron-rich substrates were also suitable for our reaction. 4-Bromotoluene gave the desired product **4h** as an inseparable mixture with trace amount of bibenzyl which was formed as a result of the homocoupling of the benzyl radicals (see Scheme 2b). 1-Bromo-4-(*tert*-butyl)benzene as substrate showed similar reactivity (68%, **4i**). Compound **4j** was obtained in excellent yield (92%) when 4-bromoanisole reacted with toluene. The reaction between bromobenzene and toluene furnished diphenylmethane (**4k**) in 55% yield. Pleasingly,

increased steric hindrance posed by *meta* and *ortho* substituents did not inhibit the reaction (**4l-4n**). To be noted, the radical species was never formed at the benzylic position of the bromotoluenes (**2h**, **2l**, **2n**). This chemoselectivity can be attributed to the statistical leverage of **1** over the limiting reagents.

Substrates **2p-2r** with fused rings were also tolerated and the products **4p-4r** were obtained in good to excellent yields. Furthermore, a heteroaromatic bromide substrate, 2-bromo-6-cyanopyridine, furnished the product in almost quantitative yield (99%).

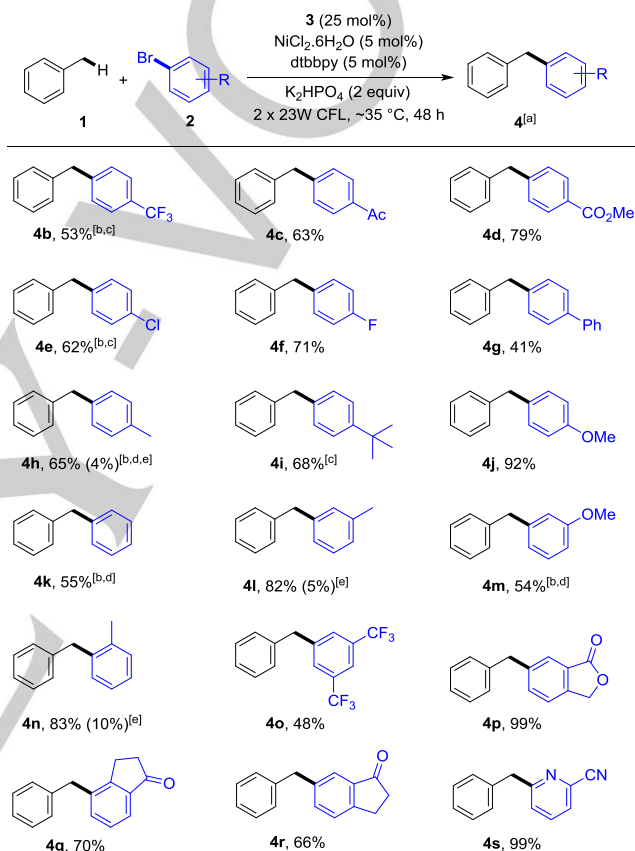


Figure 1. Substrate scope of aryl bromides. [a] Reaction conditions: **2** (0.2 mmol), **3** (0.05 mmol, 0.25 equiv), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 0.05 equiv), dtbbpy (0.01 mmol, 0.05 equiv), K_2HPO_4 (0.4 mmol, 2.0 equiv), **1** (6 mL), under irradiation with two 23W CFL lamps, under Ar, 48 h; yields after purification. [b] 4 mL of toluene was used. [c] 18 h. [d] 24 h. [e] Amount of inseparable bibenzyl impurity is given in parenthesis.

After exploring the scope of the reaction with respect to the structure of the bromo containing substrates, we turned our attention to the iodo and chloro analogous (Figure 2). Unexpectedly, 4-iodobenzonitrile (**5a**) exhibited much lower reactivity (39% NMR yield) compared to its bromo analogue **2a**. This was surprising because the aryl-I bond should be more reactive towards oxidative addition compared to the aryl-Br bond.^[15] This observation led us to consider an underlying parallel propagation mechanism where **3** acts as a triplet sensitizer (see Scheme 2c).^[16]

Recently, our and Molander group proposed an energy transfer from the photocatalyst to a Ni(II) species leading to an excited Ni(II) species which undergoes subsequent homolysis to give Ni(I) and a halide radical.^[5c,g] The halide radical can then abstract a H-atom from the H-donor. To find support for our hypothesis and in pursuit of an improved scope of iodoarenes, we conducted the reaction between **5a** and toluene (**1**) in the presence of 1 equiv of tetrabutyl ammonium bromide (TBAB) as additive. In line with our assumption, the yield of **4a** increased to 72%. The same strategy was applied to other iodoarenes **5** and all of them worked quite well, furnishing the desired products in good yields.

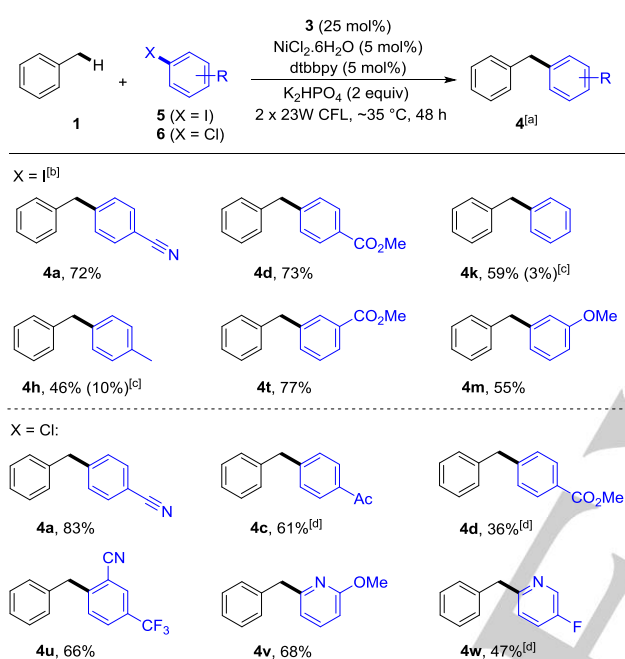


Figure 2. Substrate scope of aryl iodides and chlorides. [a] Reaction conditions: **5/6** (0.2 mmol), **3** (0.05 mmol, 0.25 equiv), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 0.05 equiv), dtbbpy (0.01 mmol, 0.05 equiv), K_2HPO_4 (0.4 mmol, 2.0 equiv), **1** (6 mL), under irradiation with two 23W CFL lamps, under Ar, 48 h; yields after purification. [b] In the case of aryl iodides TBAB (0.2 mmol, 1.0 equiv) was added. [c] Amount of inseparable bibenzyl impurity in parenthesis. [d] NMR yield calculated with CH_2Br_2 as internal standard is given in parenthesis.

When 4-chlorobenzonitrile was reacted with toluene for 48 hours, the desired product was isolated in 83% yield. However, substrates bearing acyl and carboxymethyl groups showed moderate reactivity affording the products **4c** and **4d** with 61% and 36% NMR yield, respectively. A di-substituted aryl chloride was also tested and gave the corresponding product **4u** in 66% yield. Similar efficiency (68%) was observed when 2-chloro-6-methoxypyridine was reacted with toluene under the standard conditions. Finally, 2-chloro-5-fluoropyridine also reacted in moderate yield. It is worth mentioning that during exploring the chloro substrate scope, sometimes the photosensitizer **3** was also partially benzylated at the C-Cl bond leading to a mixture of monobenzyl and dibenzyl benzophenones. We conducted a control experiment replacing **3** with 4-chloro-4'-benzyl benzophenone which gave decreased yield of 57% (entry 15,

Table S1). This observation provides a rationale for diminished yields in case of chloroarenes. Next, we explored other C-H bond donating coupling partners in reaction with bromo derivative **2a** (Figure 3). *Para*-xylene reacted smoothly to produce diarylmethane **12a** in 89% yield in 24 hours. *Meta* and *ortho* isomers of xylene gave similar yields as well (82% and 87%, respectively). Following the same trend, mesitylene showed excellent reactivity with 85% yield for product **12d**. Additionally, **12e** was formed in good yield (67%) within 20 hours when relatively electron-deficient 4-chlorotoluene was reacted with **2a**.

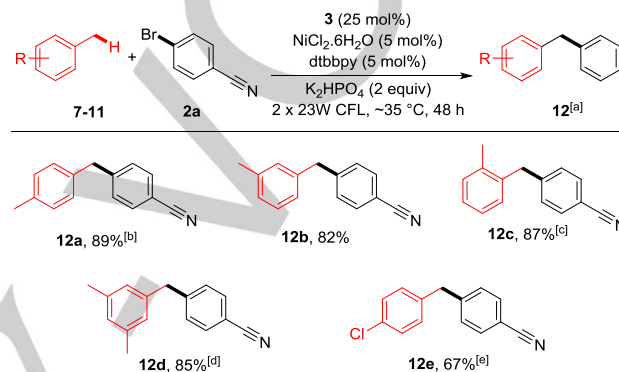
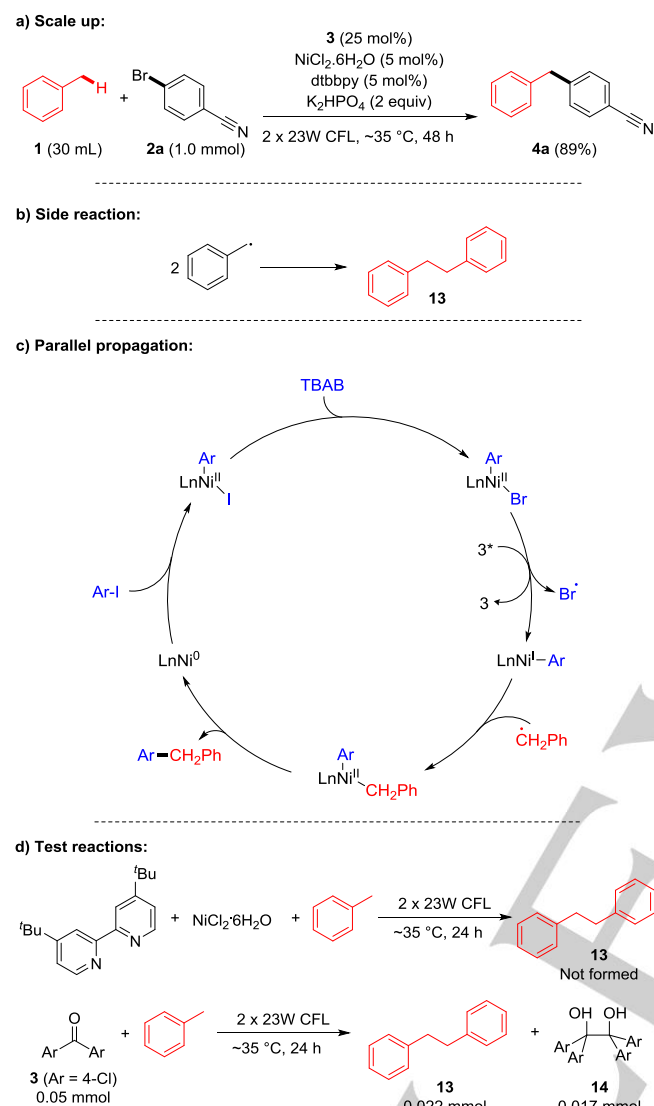


Figure 3. C-H bond donating coupling partners. [a] Reaction conditions: **2a** (0.2 mmol), **3** (0.05 mmol, 0.25 equiv), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 0.05 equiv), dtbbpy (0.01 mmol, 0.05 equiv), K_2HPO_4 (0.4 mmol, 2.0 equiv), **7-11** (6 mL) under irradiation with two 23W CFL lamps, under Ar, 48 h; yields after purification. [b] 24 h. [c] *o*-Xylene (4 mL) was used. [d] Mesitylene (5 mL) and benzene as co-solvent (1 mL) were used. [e] **3** (20 mol%), 4-chlorotoluene (4 mL), 20 h.

In order to examine the scalability of the reaction we performed the transformation with substrate **2a** on larger scale (1.0 mmol) with the same reaction setup (Scheme 2a). Pleasingly, the yield of **4a** did not decrease significantly with the scale-up. It is noteworthy that a flow-reactor which is often used for scaling up photoredox catalyzed transformations was not necessary in this case. Finally, additional experiments were performed in order to gain a deeper insight into the mechanism. The involvement of the benzyl radical in the reaction was confirmed by the formation of bibenzyl (**13**) as side-product. Regarding the generation of the benzyl radicals, this process can be accomplished either by the photocatalyst with the formation of PS-H (Scheme 1) which is subsequently involved in the generation of Ni(0) or by a chlorine radical which results from the homolysis of the excited form of the ligated NiCl_2 complex by the light-source.^[17]

To address these questions, we irradiated an equimolar mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and dtbbpy (0.05 mmol) in toluene (6 mL) for 24 hours (Scheme 2d). Formation of bibenzyl was not detected in the NMR spectra after reaction. When the same experiment was performed with **3**, 0.022 mmol of bibenzyl (arising from the homocoupling of benzyl radicals) and 0.017 mmol of benzopinacol **14** were detected by NMR spectroscopy after reaction. Therefore, we conclude that diaryl ketone **3** serves as initiator for this reaction. This, together with the improved yields for iodoarenes after the addition of TBAB, leads to the

conclusion that **3** acts as both: HAT agent and energy-transfer agent.



Scheme 2. Scale up and mechanistic insight.

In summary, we developed a protocol for the benzylic arylation with aryl halides as arylating agents using a dual metal / photocatalytic system. Benzophenone was applied as photocatalyst, serving both purposes of atom transfer and electron transfer agent. Furthermore, mechanistic experiments indicate that the photocatalyst plays an additional role of energy transfer agent. The newly designed transformation tolerates a broad range of aryl halides and different arenes containing methyl groups, leading to diarylmethanes in good yields. Notably, the reaction could be scaled up with ease without the need of specialized equipment.

Acknowledgements

P.E.K. thanks the Deutsche Bundesstiftung Umwelt for financial support. We thank Marc Jentsch for helping us with CV measurements. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement no. 617044 (SunCatChem).

Keywords: Atom transfer • Energy transfer • Benzophenone • C-H functionalization • Metallaphotoredox

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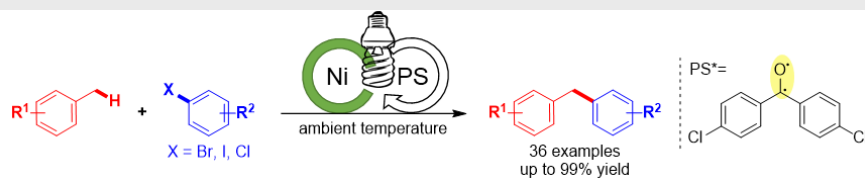
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Entry for the Table of Contents

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Text for Table of Contents