

Visible-Light-Catalyzed Direct Benzylic C(sp³)-H Amination Reaction by Cross-Dehydrogenative Coupling

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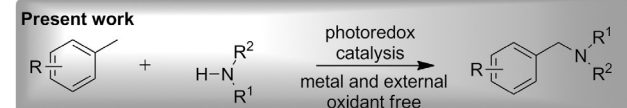
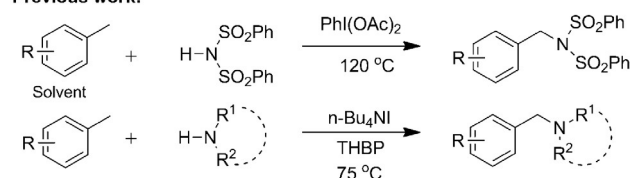
Abstract: A conceptually new and synthetically valuable cross-dehydrogenative benzylic C(sp³)-H amination reaction is reported by visible-light photoredox catalysis. This protocol employs DCA (9,10-dicyanoanthracene) as a visible-light-absorbing photoredox catalyst and an amide as the nitrogen source without the need of either a transition metal or an external oxidant.

Direct amination of a saturated C-H bond is emerging as an important methodology for C-N bond formation.^[1] The nitrogen source in the majority of these reactions is a metal-catalyzed nitrenoid that inserts into the C(sp³)-H bond using either organic azides,^[2] iminoiodanes^[3] or haloamine derivatives (ZNNaX)^[4] as nitrene precursors. While non-selectivity, low yield, and employment of a highly electrophilic nitrene source typically marked the former processes, use of hypervalent iodine reagents and the generation of a stoichiometric amount of environmentally non-benign iodobenzene remains a major drawback of the later approaches. Although, an alternative approach of generating nitrene and its insertion into the C-H bond by rhodium-catalyzed decomposition of *N*-tosyloxycarbamates^[5] overcomes some of these problems, the high costs of the rhodium metal and its non-recyclability limit its use. Furthermore, hypervalent *N*-trifluoromethylsulfonylimino-λ³-bromane^[6] has also been used as an active organo nitrenoid species for the C-H amination reaction but this strategy produces a stoichiometric amount of trifluoromethylbromobenzene as a by-product. A divergent regioselectivity of intramolecular C-H amination has also been reported by generating nitrenoid species from two differently engineered variants of P450BM3 where one is favoring amination of benzylic C-H bonds and the other is favoring homo-benzylic C-H bonds,^[7] but this approach is highly substrate specific. Apart from using metal/organo nitrenoids, another interesting methodology in this area is reported by directed metal-catalyzed inter- and intramolecular amination of C-H bonds.^[8] However, use of a directing group as an appendage limits its scope. Efforts have also been directed to replace costly transition metals in C-H amination reactions by developing catalytic cross-dehydrogenative couplings

(CDC) using more environmental friendly metal salts^[9,10] or metal-free conditions,^[11] but these strategies require strong oxidizing agents. Radical-based cross-coupling reactions^[12] are also reported in this area but selectivity remains the main issue in these approaches. Sarpong and co-workers have reported an interesting strategy for intramolecular nitrogen incorporation by oxidation of a benzylic C,N-di-anion using iodine as an oxidant^[13] but the major constraint of this strategy remains functional group tolerance owing to the use of an excess of strong base.

It becomes apparent from the above introduction that during the last decade several fundamental reactions have been discovered for direct C-H amination but the majority of them either uses costly and toxic transition-metal catalysts or requires strong oxidizing agents and the majority of them also suffers from regio- and chemoselectivity issues. Therefore, it was felt necessary that there is an urgent requirement of developing an entirely new chemistry for the C-H amination reaction which should overcome all the problems associated with earlier methods and would also address environmental issues (see Scheme 1). In the context of fulfilling this

Previous work: [11a], [11h]



Scheme 1. Inter-molecular cross-dehydrogenative benzylic C(sp³)-H amination reactions.

challenge, our attention was drawn towards one of our own recent reports wherein a benzylic C-H bond was functionalized for C-O bond formation by photoredox catalysis.^[14] However, when the same protocol was attempted for C-N bond formation, the reaction failed due to competitive electron-transfer processes between amine and alkyl aryl groups.

Therefore, we envisioned an entirely new strategy to generate first the benzylic radical **6** by H abstraction from a captodative aminyl radical **5**,^[15] which was perceived to be generated by a one-electron photoredox oxidation of **2a** using a singlet excited state of 9,10-dicyanoanthracene (DCA) as an electron acceptor^[16] followed by one electron oxidation of **6**

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by DCA to form the benzylic cation **7**. Reaction of this cation **7** with **2a** was envisaged to give the C–H aminated product **3** directly by following the catalytic cycle as shown in Figure 1. Towards accomplishing our proposed goal, a mixture of alkyl

intermediate, **2a** (2 mmol) was photolyzed in the presence of DCA (3×10^{-4} mol dm $^{-3}$, 0.75 mol %) alone, under identical reaction conditions as described above, which gave **2aa** exclusively (Scheme 3 A).

Compound **8a** is likely to have formed either by the reaction of benzylic radical **6** with atmospheric oxygen or by further oxidation of the corresponding alcohol 1-phenylethanol. However, our attempt to detect 1-phenylethanol in the above reaction has so far been in vain. The formation of the benzylic radical intermediate was confirmed by trapping with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO; Scheme 3 D).^[19] Evidence for the involvement of benzylic carbocation for the formation of **3a** is obtained by carrying out an identical photolysis experiment in a mixture of acetic acid: acetonitrile (1:9) which produced **3a** along with **9a** (Scheme 3 B). Further support for the involvement of carbocationic species in the amination reaction was obtained by isolating **10** and **3a'** by exposing isochroman **1a'** under the identical reaction conditions

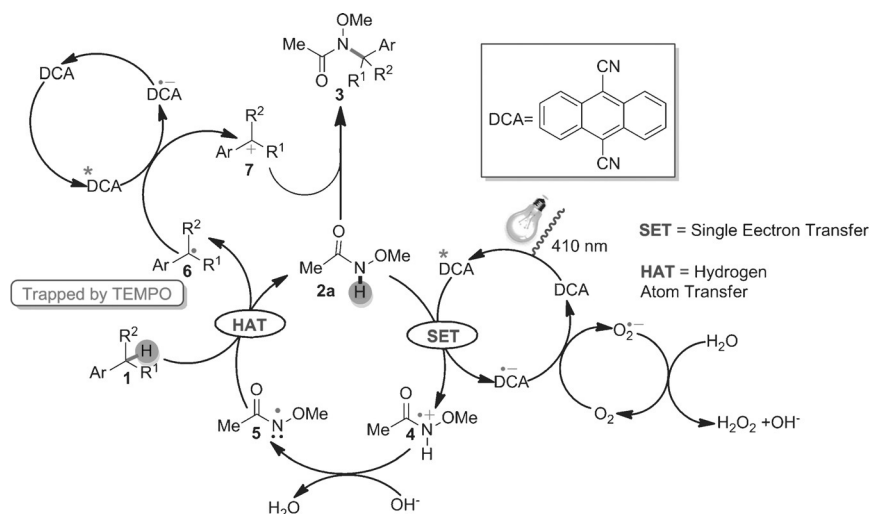
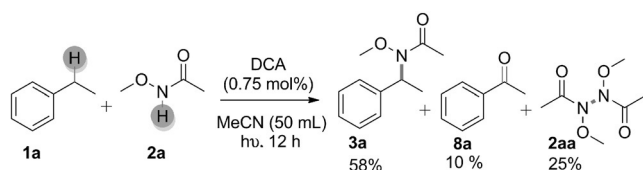


Figure 1. Concept of cross-dehydrogenative benzylic C(sp 3)–H amination reaction by photoredox catalysis.

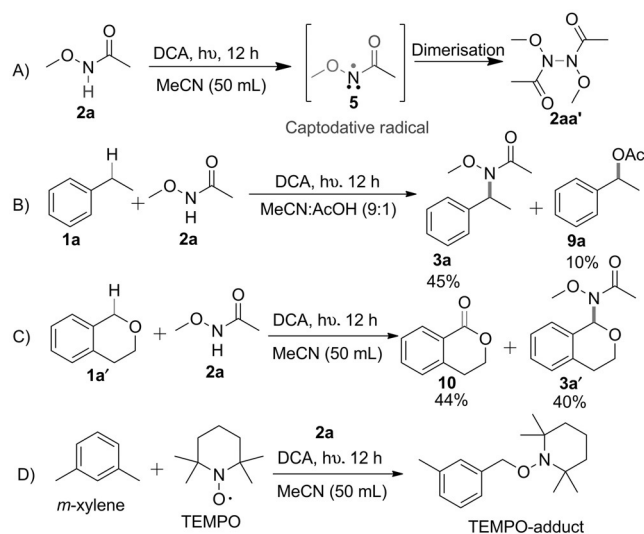
aryl **1a** (2 mmol), amine **2a** (3 mmol), and DCA (3×10^{-4} mol dm $^{-3}$) in 50 mL (0.75 mol %) acetonitrile (MeCN) was photolyzed using a visible-light (410 nm) source. Visible light (410 nm) was obtained by using a combination of Pyrex and a CuSO $_4$:NH $_3$ solution filter^[17] from a 450-W Hanovia medium pressure lamp.^[18] Care was taken that all the light was absorbed by DCA only in the present experimental setup. Consumption of **1a** was monitored by GC. No significant loss in the concentration of DCA was noticed by GC even after 12–15 h of photolysis.

The reaction mixture was concentrated and purified by column chromatography to produce **3a** in 58% yield (the yield is based on the consumption of **1a**) along with **8a** (10%) and **2aa** (25%; Scheme 2). Some amount of amide was always recovered from our reaction mixture as expected from the proposed mechanistic cycle (Figure 1). The optimized study showed that this is the best reaction condition for this reaction.^[19]

No further improvement in product formation was observed even after prolonged irradiation. Formation of **2aa** in this reaction suggests the involvement of a radical intermediate **5**. In order to support the formation of **5** as an



Scheme 2. Cross-dehydrogenative benzylic C(sp 3)–H amination reaction.



Scheme 3. Dimerization of the amine by radical formation and support for the involvement of benzylic carbocation and radical in the amination reaction.

as described above for **1a** (Scheme 3 C). To better understand the mechanism of this benzylic C(sp 3)–H amination, DFT calculations were performed for the reaction of **2a** with **7** ($\Delta H^\ddagger = 10.7$ kcal mol $^{-1}$ and $\Delta G^\ddagger = 24.5$ kcal mol $^{-1}$) compared with the reaction of **5** with **6** ($\Delta H^\ddagger = 25.5$ kcal mol $^{-1}$ and $\Delta G^\ddagger = 39.2$ kcal mol $^{-1}$). The value for the reaction **2a** with **7** was found less. The calculated reaction Gibbs free-energies ($\Delta_r G$) for the cation and free radical pathways are -28.5 kcal mol $^{-1}$ and -64.1 kcal mol $^{-1}$, respectively.^[19]

To optimize this C–H amination reaction, several amides (**2a–e**) were evaluated along with ethyl benzene (**1a**) and results are summarized in Table 1.

From the above results, it can be noted that anomeric amides only produced C–H aminated products and non-anomeric amides such as **2d** and **2e** were recovered as such

Table 1: Optimization of the amination reaction using different amines.^[a,b,c]

| Amine | Product | Yield ^[b] |
|---------------|---------------|----------------------|
| | | |
| 2a | 3a | 58% (75%) |
| 2b | 3b | 56% (70%) |
| 2c | 3c | 52% (72%) |
| 2d | 3d | 0 |
| 2e | 3e | 0 |

[a] Reaction conditions: **1a** (2 mmol), **2** (3 mmol), DCA (0.75 mol %) in acetonitrile 50 mL. [b] Isolated yields based on the consumption of **1a**. Conversion of the reaction based on **1a** given in parentheses.

from the reaction mixture and no isolable amounts of any product were formed. Since **2a** was found to be relatively better in initiating cross-dehydrogenative coupling with aryl alkyls, it was used for studying the generality of the reaction with several alkyl aryls and results are given in Table 2. From the above results, it is interesting to note that alkyl aryls having both electron-withdrawing and donating substituents on the aromatic ring reacted equally well. Reaction with various *p*-halotoluenes suggested a reactivity order as $F > Cl > Br$ (Table 2, entries **3s–u**). Furthermore, reaction with differently substituted benzylic substrates were also studied and the reactivity order was found to be $2^\circ > 1^\circ = 3^\circ$ (Table 2, entries **3f–i**). When the industrial raw material *p*- and *m*-xylenes were studied, exclusively mono-aminated products **3j** and **3k** were obtained in good yields (72% and 70%, respectively).

In this series, mesitylene, indane, and tetralene also provided only mono-aminated products **3l**, **3m** and **3n**, respectively, in good yields. This method was also found to be quite wide-ranging with other aromatics such as methyl-naphthalene, fluorene, 4-methyl-biphenyl producing corresponding aminated products **3o–r**, respectively, (Table 2). Protected phenol gave corresponding aminated product **3v** in comparable yield. Reaction with allylbenzene was also quite successful in generating the corresponding allyl-aminated product **3x** (Table 2), though, in moderate yield (50%). It may be interesting to mention that the Pd-catalyzed allylic amination reaction is reported to form a rearranged product.^[20]

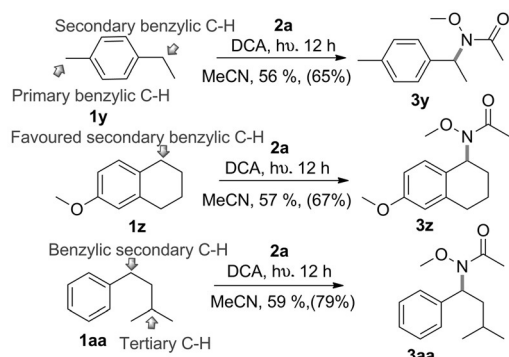
These interesting results prompted us to explore further the regioselectivity of this reaction as well. Towards this end, reaction of 4-ethyl toluene (**1y**) was studied in detail which gave **3y** (56%) exclusively. Formation of exclusive **3y** is explained by considering the stability of the corresponding secondary benzylic radical in comparison to the primary benzylic radical by at least 3.87 kcal mol^{−1}. Similar calcula-

Table 2: Study of substrates scope.^[a,b]

| | | <ul style="list-style-type: none"> • Metal and oxidant-free • Ambient temperature • Regioselectivity | |
|-------------|-----------|---|----------------|
| Substrate 1 | Product 3 | Yield (%) | Conversion (%) |
| | | 55% | (70%) |
| | | 58% | (75%) |
| | | 64% | (74%) |
| | | 50% | (70%) |
| | | 72% | (84%) |
| | | 70% | (82%) |
| | | 75% | (82%) |
| | | 60% | (62%) |
| | | 58% | (66%) |
| | | 55% | (73%) |
| | | 57% | (72%) |
| | | 70% | (78%) |
| | | 68% | (82%) |
| | | 67% | (72%) |
| | | 59% | (71%) |
| | | 52% | (68%) |
| | | 57% | (76%) |
| | | 60% | (77%) |
| | | 50% | (60%) |
| | | 53% | (71%) |
| | | 55% | (72%) |
| | | 56% | (72%) |

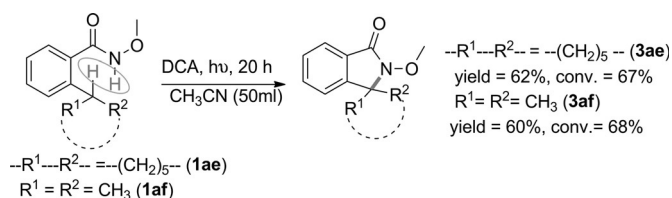
[a] Reaction conditions: **1** (2 mmol), **2** (3 mmol), DCA (0.75 mol %) in acetonitrile 50 mL. [b] Isolated yields based on consumption of **1**. [c] Conversion of the reaction based on **1**.

tions for relative stability of corresponding radicals from **1z** and **1aa** responsible for the formation of **3z** and **3aa** were also carried out and results indicated that corresponding radicals responsible for the formation of these products were found stable by 0.71 kcal mol⁻¹ and 7.08 kcal mol⁻¹, respectively (Scheme 4).^[19]



Scheme 4. Regioselective dehydrogenative benzylic C–H amination

The application of this CDC coupling reaction was further extended for the synthesis of amino acid derivatives from direct benzylic C–H amination of corresponding phenyl alkanolic acids. Different types of α -, β -, and γ -amino acid derivatives **3ab–3ad** (Table 2) were synthesized by carrying out identical irradiation as mentioned earlier for **1a**. This strategy was also found successful for intramolecular benzylic C(sp³)–H amination^[21] of **1ae** and **1af** to give **3ae** and **3af**, respectively (Scheme 5).



Scheme 5. Intramolecular cross-dehydrogenative benzylic C(sp³)–H amination reaction by photoredox catalysis.

In conclusion, we have developed a conceptually new metal-free and external oxidant-free protocol for selective incorporation of nitrogen into a benzylic C(sp³)–H bond by an atom-economic cross-dehydrogenative coupling initiated by visible-light photoredox catalysis. This protocol has a broad substrate scope and regioselectivity. This method can possibly be useful to transform industrial raw materials, such as toluene, xylene and mesitylene into value-added corresponding monoaminated products.

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Keywords: amination · C–H functionalization · cross-coupling · photoredox catalysis · synthetic methods

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