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Organophotoredox-Catalyzed Direct C−H Amination of 2*H*-Indazoles with Amines

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01973 Read Online

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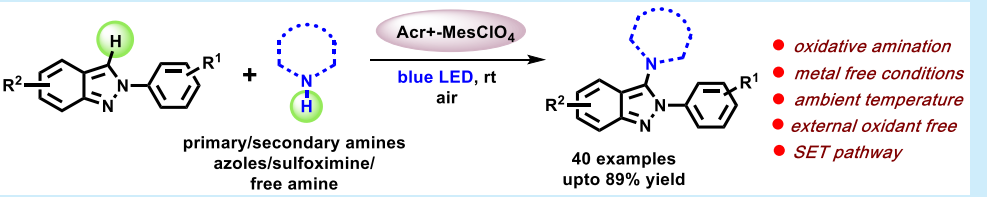

ABSTRACT: A general and practical method for the direct C−H amination of 2*H*-indazoles with a series of amines including aliphatic primary amines, secondary amines, azoles, and sulfoximines via organophotoredox-catalyzed oxidative coupling has been disclosed at room temperature under ambient air conditions. Additionally, this protocol is used for free aminated 2*H*-indazole synthesis. A mechanistic study revealed that a single electron transfer (SET) pathway might be involved in this reaction.

The development of a practical method to build up the C−N bond is highly demanding in organic synthesis due to the extensive manifestation of nitrogen-containing molecules in natural products, pharmaceuticals, agrochemicals, and polymer sciences.[1] Transition-metal-catalyzed Buchwald−Hartwig, Ullmann−Goldberg, and Chan−Lam cross couplings are great achievements in this field.[2] In addition, the photochemical and thermal decomposition of the N−X bond (X = N, O, S, halogen) into a N-centered radical offers a concise route for oxidative C−H amination of various arenes.[3,4] Classical methods on radical amination of arenes with *N*-chloroamines under strong acidic conditions were reported by Minisci,[5a] Chow,[5b] and Kompa.[5c] Harsh reaction conditions, limited substrate scope, and tedious synthetic steps to preincorporate the functional groups in the substrate sometimes diminish the synthetic utility of these methodologies. As an alternative, C−H/N−H oxidative cross-coupling reactions have recently acquired much attention because of their straightforwardness and high atom economy.[6] Normally, transition-metal catalysts along with terminal oxidants are used for such a C−N bond formation.[7] In some cases, a stoichiometric amount of hypervalent iodine reagents is extensively utilized for amination reactions.[8] Recently, photocatalytic C−H amination has gained considerable attention.[9,10] For example, Nicewicz et al. reported a breakthrough work for the direct C−H amination of activated arenes with azoles and primary aliphatic amines.[9] Similarly, a dual catalytic system was also introduced by Lei[10a] and König[10b] for the generation and utilization of various N-centered radicals.

Indazoles as a privileged skeleton of nitrogen-containing fused heterocycles are widely used in the field of medicinal chemistry and material sciences.[11] In particular, anti-inflammatory, antitumor, antimicrobial, HIV-protease inhibition, anticancer, antiplatelet, antidepressant drugs, etc. are shown by indazole. Some marketed drugs like bendazac (nonsteroidal anti-inflammatory drug), pazopanib or votrient (tyrosine kinase inhibitor), MK-4827 (anticancer agent), etc. contain an indazole skeleton.[11,12] Importantly, indazole derivatives have elite photophysical properties and are used as fluorescent probes.[13] On the other hand, aliphatic amines and azoles are important structural features, present in natural products and pharmaceuticals.[14] Therefore, the development of a practical methodology for the synthesis of amino-substituted 2*H*-indazoles is highly desirable.

In recent times, visible-light-mediated photoredox-catalyzed reactions offer an intriguing opportunity to explore modern organic transformations.[15] Organic redox-active molecules are employed as superior alternatives to their metal counterparts due to their nontoxicity, synthetic usefulness, and better environmental perspective.[16] However, to the best of our knowledge, C−H amination reaction of 2*H*-indazoles is not yet established in the current literature.[17] With our continuous efforts on photochemical C−H functionalization of heterocycles,[18] herein we wish to report a strategy of organophotoredox-catalyzed direct C−H amination of 2*H*-indazoles

Received: June 12, 2020

https://dx.doi.org/10.1021/acs.orglett.0c01973
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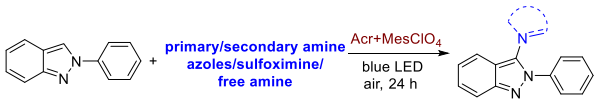
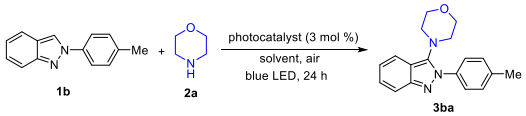
with primary and secondary amines, azoles, and sulfoximine (Scheme 1).

Scheme 1. C−H Amination Reactions of 2*H*-Indazoles



We commenced our study by taking 2-(*p*-tolyl)-2*H*-indazole (**1b**) and morpholine (**2a**) as model substrates (Table 1).

Table 1. Optimization of the Reaction Conditions[a]



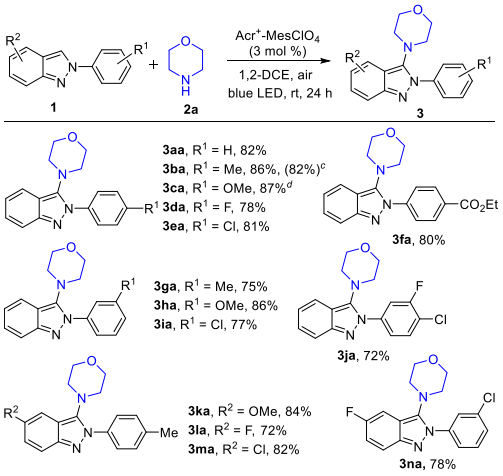
entry	photocatalyst	solvent	yields (%)
1	Acr^+-$MesClO_4$	CH_3CN	65
2	Acr^+-$MesClO_4$	THF	48
3	Acr^+-$MesClO_4$	toluene	55
4	Acr^+-$MesClO_4$	DCM	68
5	Acr^+-$MesClO_4$	1,2-DCE	86
6	Acr^+-$MesClO_4$	1,4-dioxane	trace
7	Acr^+-$MesClO_4$	DMSO	21
8	Acr^+-$MesClO_4$	DMF	nr
9	Acr^+-$MesClO_4$	H_2O	nr
10	TPPT	1,2-DCE	27
11	eosin Y	1,2-DCE	nr
12	rhodamin 6G	1,2-DCE	nr
13	rose bengal	1,2-DCE	nr
14	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	1,2-DCE	nr
15	-	1,2-DCE	nr
16	Acr^+-$MesClO_4$	1,2-DCE	nr[b]
17	Acr^+-$MesClO_4$	1,2-DCE	nr[c]

[a]Reaction conditions: **1b** (0.2 mmol), **2a** (0.6 mmol), photocatalyst (3 mol %), solvent (2 mL), 34 W blue LED. [b]In the dark. [c]Under argon atmosphere. nr = no reaction.

Initially, the reaction was carried out using 3 equiv of morpholine and 3 mol % of Acr^+-$MesClO_4$ (9-mesityl-10-methylacridinium ion) as photocatalyst in CH_3CN under ambient air and blue LED irradiation. Pleasingly, the desired coupling product **3ba** was obtained in 65% yield after 24 h (Table 1, entry 1). Being motivated by this initial result, various common solvents were screened including THF, toluene, DCM, 1,2-DCE, 1,4-dioxane, DMSO, DMF, and H_2O (Table 1, entries 2−9). Among these, 1,2-DCE was proved to be the best choice, and the product was obtained in 86% yield (Table 1, entry 5). Further optimization was performed with various photocatalysts like TPPT (2,4,6-triphenylpyrylium tetrafluoroborate), eosin Y, rhodamine 6G, rose bengal, and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (Table 1, entries 10−14). However, they were less effective than Acr^+-$MesClO_4$. Moreover, no formation of product was observed in the absence of any photocatalyst as well as under dark conditions and an argon atmosphere (Table 1, entries 15−17). Finally, the optimal reaction conditions were attained using 3 mol % of Acr^+-$MesClO_4$ in 1,2-DCE under ambient air and blue LED irradiation at room temperature for 24 h (Table 1, entry 5).

With the optimized protocol for amination reaction, the scope of this methodology was investigated, and the results are depicted in Scheme 2. At first, the effect of different substituent on the phenyl ring of 2*H*-indazole derivatives was examined. In

Scheme 2. Scope of 2*H*-Indazoles[a,b]



[a]Reaction conditions: 0.2 mmol of **1**, 0.6 mmol of **2a** in the presence of 3 mol % of Acr^+-$MesClO_4$ in 2 mL of 1,2-DCE at room temperature under blue LED. [b]Isolated yields. [c]5 mmol scale. [d]Reaction time 10 h.

this case, a series of 3-amino 2*H*-indazole derivatives were achieved in good to excellent yields (**3aa**−**3na**). 2*H*-Indazole derivatives bearing −Me, −OMe, and halogen like −F and −Cl substituents at the *para* position afforded the corresponding products in moderate to good yields (**3aa**−**3ea**). Interestingly $-CO_2Et$-substituted indazole also reacted well with **2a** to give **3fa** in 80% yield. Gratifyingly, *meta*-substituted 2*H*-indazole derivatives effectively provided the desired aminated products in synthetically useful yields (**3ga**−**3ia**). Moreover, some disubstituted indazoles were compatible under the present reaction conditions (**3ja**−**3na**). The gram-scale synthesis was also executed taking 2-(*p*-tolyl)-2*H*-indazole (**1b**) and morpholine (**2a**). The yield of coupling product **3ba** did not decrease significantly, which suggests the scalability and practicality of the present protocol.

To acquire the generality of the current reaction, a variety of amines were scrutinized as shown in Scheme 3.

Different secondary amines like piperidine, 2,6-dimethylmorpholine, and thiomorpholine underwent the amination smoothly to afford the desired coupling products in moderate to good yields (**3bb**−**3gd**). In addition, a variety of primary amines gave the anticipated product in good yields (**3be**−**3aj**). However, some other amines, such as aniline, dibenzylamine, and diphenylamine, failed to produce the desired products under these optimized conditions.

Similarly, a series of 3-sulfoximino-2*H*-indazole derivatives were obtained by the reaction between different substituted 2*H*-indazoles and sulfoximine (Scheme 4). Interestingly $-CF_3$- and NO_2-substituted indazoles were also compatible with the present protocol in producing the products in good yields (**3pk** and **3qk**).

The present protocol was successfully applied to the coupling of 2*H*-indazoles with other aromatic heterocycles including pyrazole, imidazole, benzimidazole, and triazole derivatives (Scheme 5). In all the cases, it afforded the desired product in excellent yields (**3bl**−**3bp**). Pleasingly, free aminated product was also obtained under the present reaction

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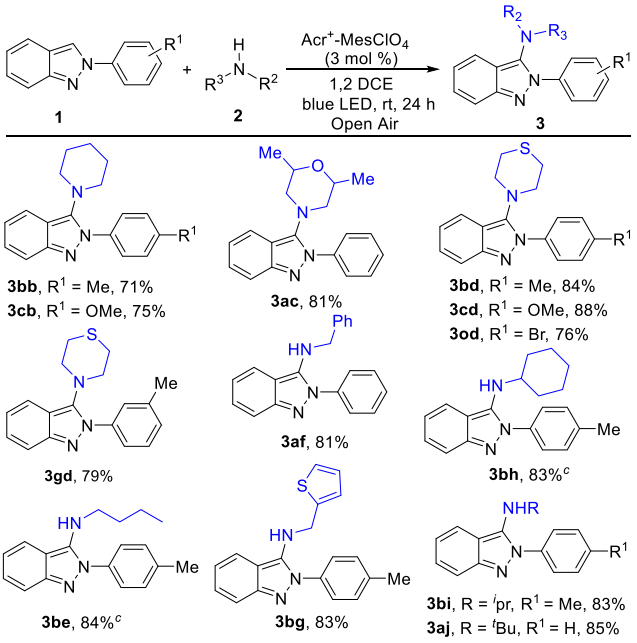
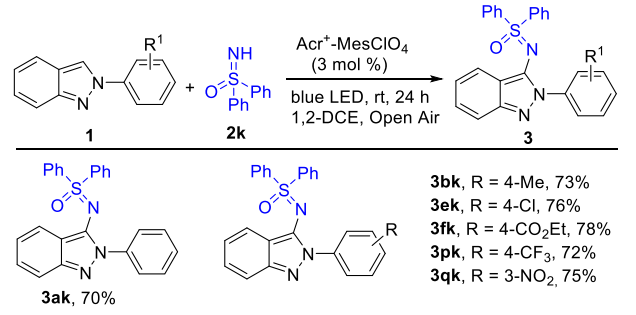
Scheme 3. Substrate Scope with Variation of Amines[a,b]



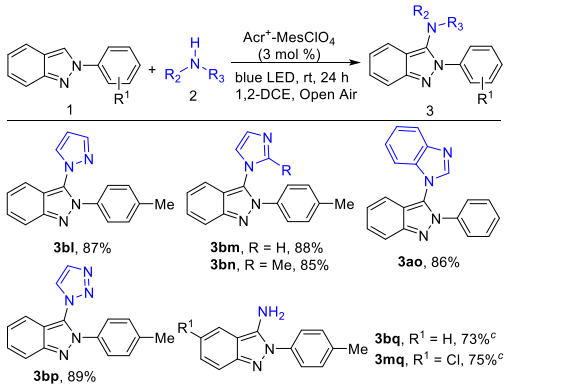
[a]Reaction conditions: 0.2 mmol of **1**, 0.6 mmol of **2** in the presence of 3 mol % of Acr^+-$MesClO_4$ in 2 mL of 1,2-DCE at room temperature under blue LED. [b]Isolated yields. [c]Reaction time 28 h.

Scheme 4. Scope of 2*H*-Indazoles with Sulfoximine[a]



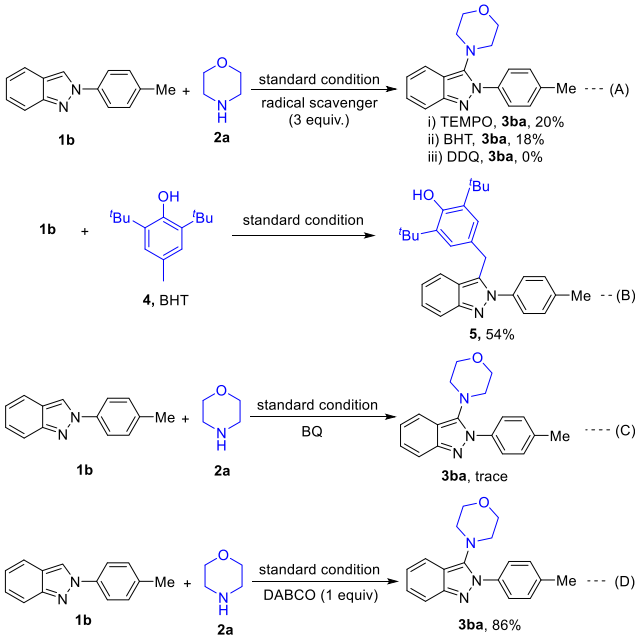
[a]Reaction conditions: 0.2 mmol of **1**, 0.6 mmol of **2k** in the presence of 3 mol % of Acr^+-$MesClO_4$ in 2 mL of 1,2-DCE at room temperature under a blue LED.

Scheme 5. Substrate Scope of Heteroaromatic Amines[a,b]



[a]Reaction conditions: 0.2 mmol of **1**, 0.6 mmol of **2** in the presence of 3 mol % of Acr^+-$MesClO_4$ in 2 mL of 1,2-DCE at room temperature under blue LED. [b]Isolated yields. [c]$NH_4^+CO_2NH_2^-$ is used as the amine source.

Scheme 6. Control Experiments



conditions using ammonium carbamate as the amine source (**3bq** and **3mq**).

To find out more about the reaction mechanism, a few control experiments were carried out (Scheme 6). The yield of the reaction was decreased in the presence of radical scavengers like 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2,6-di-*tert*-butyl-4-methyl phenol (BHT), and 2,3-dichloro-5,6-dicyano-1,*p*-benzoquinone (DDQ) (Scheme 6, eq A). However, 2-(*p*-tolyl)-2*H*-indazole (**1b**) reacted well with BHT (**4**) to produce the radical adduct 2,6-di-*tert*-butyl-4-((2-(*p*-tolyl)-2*H*-indazol-3-yl)methyl)phenol (**5**) in 54% yield (Scheme 6, eq B).

These observations indicate that the radical process might be involved in this reaction. In addition, when benzoquinone (BQ), a superoxide quencher,[19] was employed in the reaction, only a trace amount of product was achieved (Scheme 6, eq C). The present reaction was not inhibited by the addition of a singlet oxygen quencher like 1,4-diazabicyclo[2.2.2]octane (DABCO)[20] which suggests that singlet oxygen is not necessary for this cross-coupling reaction (Scheme 6, eq D).

The redox potentials of **1b**, **2a**, **2f**, **2k**, and Acr^+-$MesClO_4$ were evaluated by cyclic voltammetry (see SI), and $E_{1/2(PC^+*/PC\bullet)}$ was also calculated (see SI). The fluorescence quenching experiment of the photocatalyst in the presence of various quenchers was also performed. Based upon the above experimental outcome and literature reports,[9] a plausible mechanistic proposal is described in Scheme 7. A single electron transfer (SET) from 2*H*-indazole to the excited state of Acr^+-$MesClO_4$ (Acr^+*) provided the radical cation intermediate (**A**) and photocatalyst radical $Acr^\bullet$ (for details see the SI). Although amines (**2a**, **2f**, and **2k**) hold similar oxidation potentials to those of the indazole (**1b**), the formation of an amine cation radical could also be possible.[9] However, a fluorescence quenching study shows that indazole has an almost double S−V quenching constant value compared to amines, and thereby indazole participates in the SET process with the photocatalyst (see SI). The photoredox cycle is

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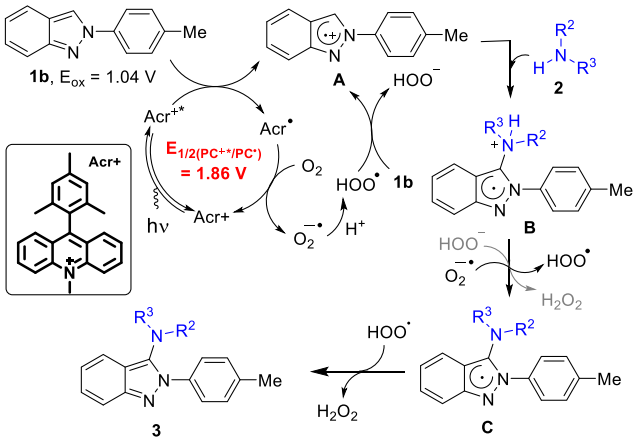
Scheme 7. Plausible Mechanistic Pathway



completed by O_2 through superoxide radical anion ($O_2^{\bullet-}$) formation. Consequently, addition of amine (**2**) to the 2-(*p*-toly)-2*H*-indazole radical cation (**A**) affords intermediate **B**. Then, $O_2^{\bullet-}$ abstracts a proton from **B** to produce **C** and $HO_2^{\bullet}$. Here we could not rule out the possibility of radical-chain propagation as we were unable to perform the quantum yield calculation in our system. Therefore, it is plausible that transfer of an electron from 2*H*-indazole (**1b**) to $HO_2^{\bullet}$ initiates the radical chain process.[15g] Finally, $HO_2^{\bullet}$ abstracts a hydrogen from intermediate **C** to afford the coupling product **3** together with H_2O_2. The detection of H_2O_2 is performed by a starch–iodine experiment (see SI).

In conclusion, we have established an efficient organo-photoredox-catalyzed strategy for the direct C–H amination of 2*H*-indazoles using a series of primary and secondary aliphatic amines, azoles, and sulfoximines under ambient air in high yields. Broad functional group tolerance, scalability, metal- and oxidant-free reaction conditions, and step- and atom-economical routes associated with this C–N bond formation imply its great potential for widespread applications in organic synthesis and pharmaceutical research. As far as we know, this is the first report for the synthesis of 3-amino-substituted 2*H*-indazoles. We believe this visible-light-induced metal- and oxidant-free C–H amination strategy makes this reaction more suitable for further synthetic applications in both academic institutes and industries.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01973.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.H. acknowledges the financial support from CSIR, New Delhi (Grant no. 02(0307)/17/EMR-II). S.N. and A.K.G. thank CSIR for their fellowship.

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https://dx.doi.org/10.1021/acs.orglett.0c01973
Org. Lett. XXXX, XXX, XXX−XXX