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Visible Light Photoredox Catalysis: Synthesis of Indazolo[2,3-*a*]quinolines from 2-(2-Nitrophenyl)-1,2,3,4-tetrahydroquinolines

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ABSTRACT

The synthesis of indazolo[2,3-*a*]quinoline derivatives in moderate to good yields from 2-(2-nitrophenyl)-1,2,3,4-tetrahydroquinolines via visible light photoredox catalysis is reported. The reaction involves a novel ruthenium-catalyzed intramolecular formation of the N−N bond of the indazole ring.

Indazoles and related derivatives[1] have received considerable attention in the past decades due to their diverse biological activities[2] which include analgesic,[3] antipyretic,[4] antiangiogenic,[5] antiviral,[6] anticancer,[7] and anti-inflammatory.[8] These broad bioactivities have prompted chemists to develop novel routes for the preparation of the functionalized indazole ring systems for small molecular screening in drug discovery. While existing indazole synthetic strategies mainly involve metal halide catalyzed[9] or base-mediated 2-nitrobenzylamines,[10] base-promoted cyclizations of arylamino oximes,[11] microwave-enhanced cyclization of nitrenes,[12] aryne [3 + 2] cycloadditions,[13] coupling of organometallic reagents with aryldiazonium salts,[14] cyclization of 2-azidobenzylidene Schiff bases,[15] and metal-catalyzed C−H functionalization,[16]

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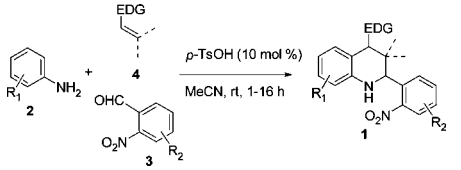
utilization of visible light photoredox catalysis (VLPC) for the preparation of indazole derivatives has never been reported. VLPC has recently developed into an essential branch of photochemical catalysis that provides widely applicable methods for organic synthesis.[17] For instance, VLPC-mediated transformations have been successfully applied in functional group conversions,[18] intramolecular cyclizations,[19] cycloadditions,[20] atom transfer radical additions,[21] C−C and N−N bond cleavage,[22] and C−H functionalization reactions.[23] In our efforts toward the development of a greener and more atom-economical synthetic approach to diversify the indazole scaffold, here we report the preparation of indazolo[2,3-*a*]quinoline derivatives from 2-(2-nitrophenyl)-1,2,3,4-tetrahydroquinolines via visible-light-mediated photocatalysis. The scope of this synthetic methodology is investigated, and a possible mechanism for the visible-light-promoted indazole formation is also proposed.

Three-component synthesis of the precursors 2-(2-nitrophenyl)-1,2,3,4-tetrahydroquinolines **1** by the Povarov reaction[24] is shown at the top of Table 1. They can be readily accessed by reacting aromatic amine **2**, 2-nitro substituted aromatic aldehyde **3**, and the electron-donating group (EDG) substituted alkene **4** in acetonitrile at rt in the presence of a catalytic amount of *p*-toluenesulfonic acid.

Table 1 lists the yields, reaction times, and isomeric ratios of this reaction. The molecular structures of the major product of **1a**, **1h**, **1k**, and **1l** were characterized by the X-ray crystallography (see the Supporting Information).[25]

Table 1. List of the 2-Nitrophenylquinolines Prepared by Three-Component Povarov Reaction



entry	R_1	R_2	4[c]	1	time (h)	yield (%)[d]	ratio (*cis*/*trans*)[e]
1	4-OMe	4-H	**4a**	**1a**	1	86	71:29
2	4-OMe	4-NO_2	**4a**	**1b**	2	68	58:42
3	**2a**[a]	4-H	**4a**	**1c**	2	70	39:61
4	4-OMe	4-H	**4b**	**1d**	8	65	15:85
5	4-OMe	4-NO_2	**4b**	**1e**	12	68	23:77
6	**2a**	4-H	**4b**	**1f**	12	83	16:84
7	4-F	4-H	**4b**	**1g**	16	55	19:81
8	4-OMe	4-H	**4c**	**1h**	2	85	38:62
9	4-OMe	4-NO_2	**4c**	**1i**	4	75	67:33
10	**2a**	4-H	**4c**	**1j**	2	84	47:53
11	4-H	4-H	**4c**	**1k**	6	69	21:79
12	4-OMe	4-H	**4d**	**1l**	12	93	>98:2
13	4-OMe	**3a**[b]	**4d**	**1m**	12	67	>98:2
14	4-H	4-H	**4d**	**1n**	12	83	>98:2
15	4-F	4-H	**4d**	**1o**	16	53	63:37
16	4-OMe	4-H	**4e**	**1p**	3	78	86:14
17	4-OMe	4-NO_2	**4e**	**1q**	6	74	88:12
18	4-H	4-H	**4e**	**1r**	6	64	71:29

[a] **2a**: naphthalen-2-amine. [b] **3a**: 1-nitro-2-naphthaldehyde. [c] **4a**: 2,3-dihydrofuran. **4b**: isobutyraldehyde. **4c**: 3,4-dihydro-2*H*-pyran. **4d**: 1-vinylpyrrolidin-2-one. **4e**: 1-vinylcarbazole. [d] Yield of isolated products. [e] *Cis*/*trans* ratio determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixtures.

With compounds **1a**−**r** in hand, their photochemical properties were then investigated. We found that 2-nitrophenylquinoline **1a** can be converted to the corresponding fused indazole **5a** via visible light irradiation (a 23 W household fluorescent bulb) in the presence of substoichiometric quantities of photoredox catalyst $Ru(bpy)_3Cl_2$. Table 2 summarizes the catalyst loading and solvent screen for the synthesis of **5a** from **1a** under VLPC. No cyclization was observed when either catalyst or light was excluded from this protocol (entries 1 and 2), indicating that both

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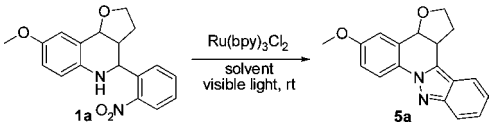
(25) Crystallographic data (excluding structure factors) for **1a**, **1h**, **1k**, **1l**, **5a**, **5d**, **5f**, **5i**, **5l**, and **5p** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-917665, -951462, -951463, -951464, -917660, -917659, -917661, -917664, -917662, and -917663, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

metal catalyst and light are crucial for this reaction. While increasing catalytic amounts of the Ru catalyst (entries 3–6) led to a noticeable improvement in both yield and reaction time, a 1.0 mol % catalyst concentration was chosen as the economic conditions for further investigation. Among the solvents examined, acetonitrile was found to be the most effective one. More polar solvents such as $MeNO_2$, THF, and EtOH generally gave slightly lower yields. A prolonged reaction time did not increase the yields accordingly (entries 7–9). Additionally, to probe the role played by oxygen in this annulation, the reaction conditions under a nitrogen or an argon atmosphere were also studied. The results indicated that this reaction is insensitive to oxygen in the air (entries 10 and 11). Finally, we observed slightly diminished reactivity when the ruthenium was replaced with the organic photosensitizer Eosin Y (5.0 mol %) (entry 12).[26] Thus, it appears that 1.0 mol % $Ru(bpy)_3Cl_2$ catalyst in MeCN under atmospheric conditions is the optimal catalyst–solvent combination, which was employed subsequently for all further reactions.

Table 2. Catalyst Loading and Solvent Screen for the Synthesis of **5a** from **1a** under VLPC[a]



entry	mol % $Ru(bpy)_3Cl_2$	solvent	condition	time (h)	yield (%)[b]
1	none	MeCN	air	24	0
2	1.0	MeCN	air	24	0[c]
3	0.1	MeCN	air	7	88
4	0.5	MeCN	air	5	93
5	**1.0**	**MeCN**	**air**	**3.5**	**95**
6	5.0	MeCN	air	2	98
7	1.0	EtOH	air	8	75
8	1.0	$MeNO_2$	air	8	81
9	1.0	THF	air	10	66
10	1.0	MeCN	N_2	3.5	95
11	1.0	MeCN	Ar	3.5	94
12	Eosin Y[d]	MeCN	air	12	80

[a] Reactions were conducted with 2.5×10^{-2} M (10 mL) reactant in a 25 mL round-bottom flask. [b] Yield of isolated products. [c] The reaction was run in the dark. [d] 5.0 mol %.

Figure 1 lists the structure, yield, and reaction time of the indazolo[2,3-*a*]quinoline derivatives **5a**–**r** prepared from **1a**–**r** by VLPC. A total of 18 examples were given with the isolated yields ranging from 66 to 96%. The molecular structures of the prepared compounds were fully elucidated by spectroscopic data. In the ^1H NMR spectra, a characteristic doublet absorption peak at the chemical shift between 7.87 and 8.98 ppm, which was assigned to the hydrogen adjacent to the N-atom in the indazole ring, was observed for all prepared compounds. Some of the heterocyclic structures (**5a**, **5d**, **5f**, **5i**, **5l**, and **5p**) were further characterized by the X-ray crystal analysis as shown in Figure 2.[25] Note that further aromatization of some quinoline products was also detected, but the yield was low.

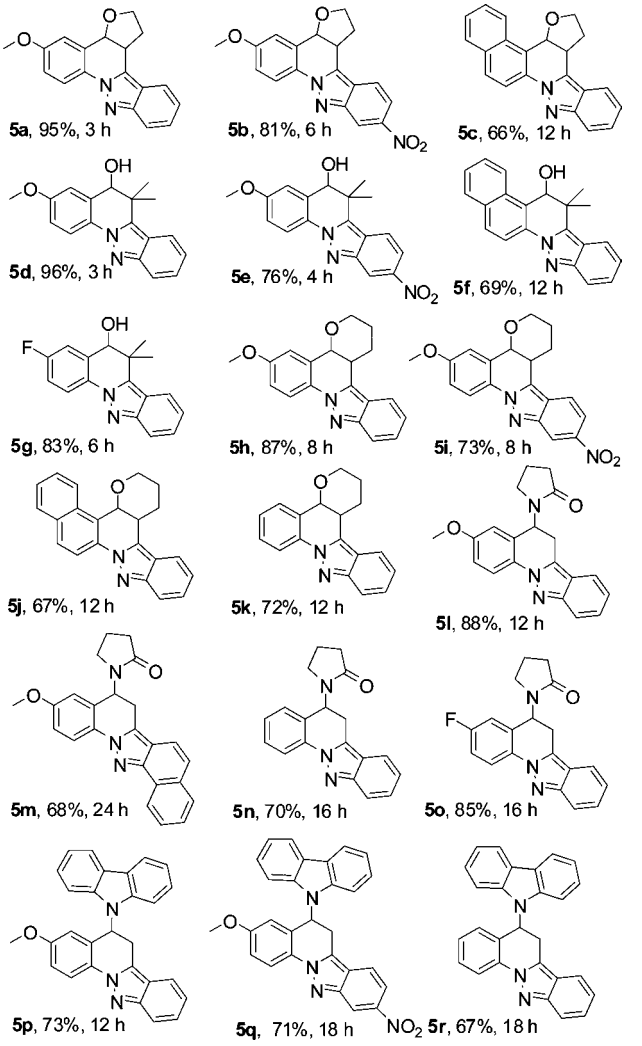


Figure 1. Structures of the prepared compounds **5a**–**r**.

Since both Povarov and the subsequent VLPC reactions were performed in the same solvent (acetonitrile), compounds **5a**–**r** were also prepared via a one-pot tandem reaction by sequentially adding the two catalysts (5 mol % of *p*-TsOH and 1 mol % of $Ru(bpy)_3Cl_2$) into the mixture of aromatic amine **2**, 2-nitro substituted aromatic aldehyde **3**, and alkene **4** in acetonitrile under visible light irradiation conditions. Table 3 lists the reaction times and overall yields of the one-pot multicomponent reactions. Most reactions gave moderate to good yields (61–92%) except for **5m**–**r** (44–58%), which are prone to undergo further elimination to afford the aromatized products due to the presence of a bulky lactam or carbazole moiety.

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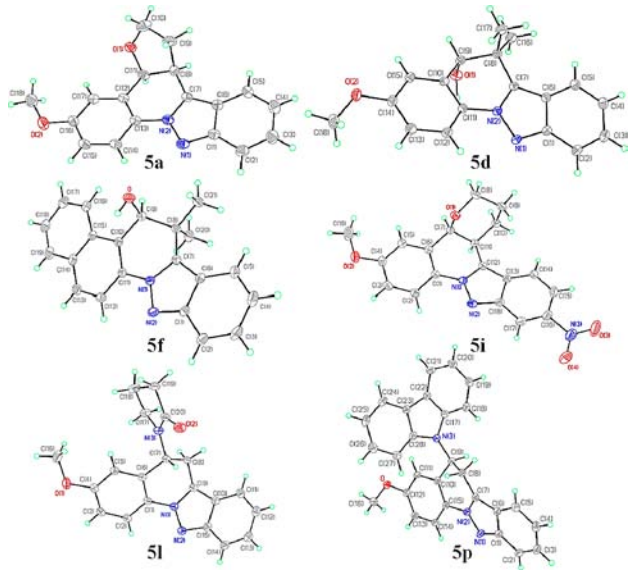


Figure 2. ORTEP diagrams of **5a**, **5d**, **5f**, **5i**, **5l**, and **5p**.

Table 3. Preparation of **5a**–**r** via the One-Pot Tandem Reaction from **2**, **3**, and **4**[a]

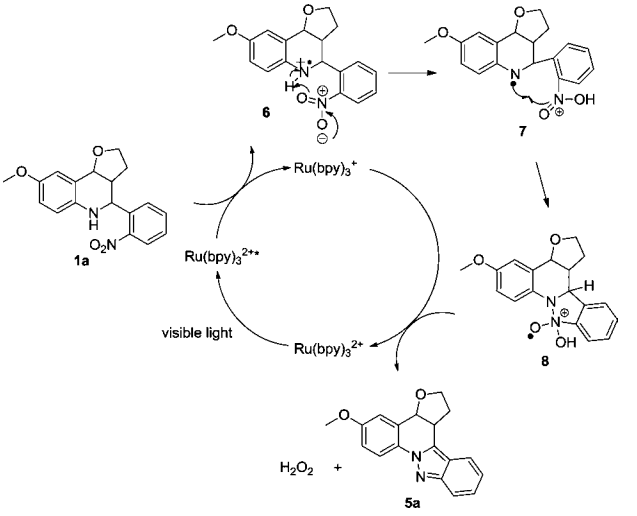
2 + **3** + **4** $\xrightarrow[\text{MeCN, rt, overnight}]{p\text{-TsOH (5 mol \%)}}$ $\xrightarrow[\text{MeCN, visiblelight}]{Ru(bpy)_3Cl_2 \text{ (1 mol \%)}}$ **5**

entry	product	time (h)	yield (%)[b]	entry	product	time (h)	yield (%)[b]
1	**5a**	6	92	10	**5j**	24	69
2	**5b**	12	82	11	**5k**	24	65
3	**5c**	24	74	12	**5l**	16	62
4	**5d**	8	83	13	**5m**	24	54
5	**5e**	10	61	14	**5n**	18	51
6	**5f**	18	73	15	**5o**	24	50
7	**5g**	18	66	16	**5p**	12	58
8	**5h**	8	88	17	**5q**	24	46
9	**5i**	12	76	18	**5r**	24	44

[a] Reactions were conducted with 2.5×10^{-2} M (10 mL) reactant in a 25 mL round-bottom flask. [b] Yield of isolated products.

Scheme 1 depicts a plausible mechanism for the formation of indazolo[2,3-*a*]quinoline **5a** from **1a** via VLPC. Presumably, it begins with single-electron transfer (SET) to the visible-light-excited $Ru(bpy)_3^{2+}$* from **1a** to provide the strong reductant $Ru(bpy)_3^{+}$ and radical cation **6**. The latter further undergoes intramolecular proton transfer from the amine H-atom to the adjacent *ortho* nitro oxygen to give the nitrene **7**. The subsequent N–N bond formation

Scheme 1. Plausible Mechanism for the Formation of **5a** from **1a**



between the nitrene nitrogen and nitrogen atom of the protonated nitro group of **7** furnishes the radical cation **8**. Finally, the reductive quenching cycle is completed by back electron transfer (BET) from $Ru(bpy)_3^{+}$ to the radical cation **8** to afford the target compound **5a** and byproduct hydrogen peroxide, along with the regenerated $Ru(bpy)_3^{2+}$ catalyst. The bond formation during the construction of the indazole skeleton is atom-economical, with a total mass loss of only 34 g/mol, that is, equivalent to the release of one molecule of water and half a molecule of oxygen. To the best our knowledge, this synthetic strategy represents the first reported indazole ring preparation that utilizes visible light photoredox catalysis in the reaction conditions.

In summary, we have developed an efficient synthesis of indazolo[2,3-*a*]quinoline derivatives from 2-(2-nitrophenyl)-1,2,3,4-tetrahydroquinolines via visible-light-mediated photocatalysis. This synthetic approach involves a ruthenium-catalyzed intramolecular formation of the N–N bond of the indazole ring, which can provide an alternate access to the highly important heterocyclic indazole derivatives.

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Supporting Information Available. Synthetic procedures for **1a**–**1r** and **5a**–**5r**; ORTEP of **1a**, **1h**, **1k**, **1l**; and ^1H and ^{13}C NMR spectra of all compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.