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Photo-Induced N–N Coupling of *o*-Nitrobenzyl Alcohols and Indolines To Give *N*-Aryl-1-amino Indoles

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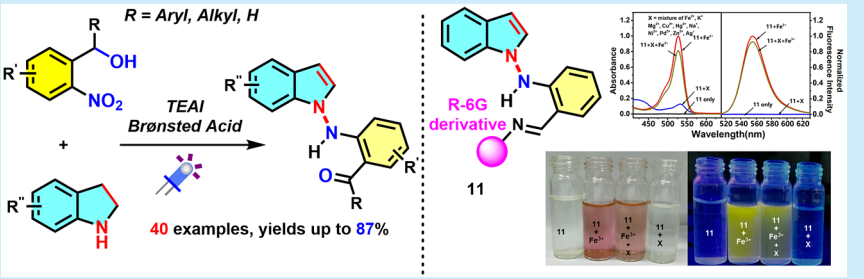


ABSTRACT: A novel method to synthesize *N*-aryl-1-amino indoles was established by the photoinduced N–N coupling reaction. This protocol is by treatment of *o*-nitrobenzyl alcohols and indolines in the presence of TEAI and acetic acid with a 24 W ultraviolet (UV) light-emitting diode (LED) (385–405 nm) irradiation. The products bearing an aldehyde group can be further transformed to fluorescent probes based on Rhodamine 6G derivative **11**, which shows a high specificity and sensitivity for Fe^{3+}.

Indole derivatives are important bioactive substances that exist widely in many bioactive molecules, drugs, agricultural chemicals.[1] In addition, their application as fluorescent probes has also been widely reported.[2] *N*-substituted-1-amino indoles as one of the typical indoles are known for their excellent activities against the symptoms of Alzheimer's disease, Chagas disease, and depression (Figure 1),[3] but there is no report on fluorescent probes.

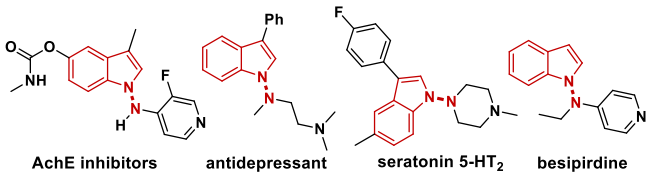
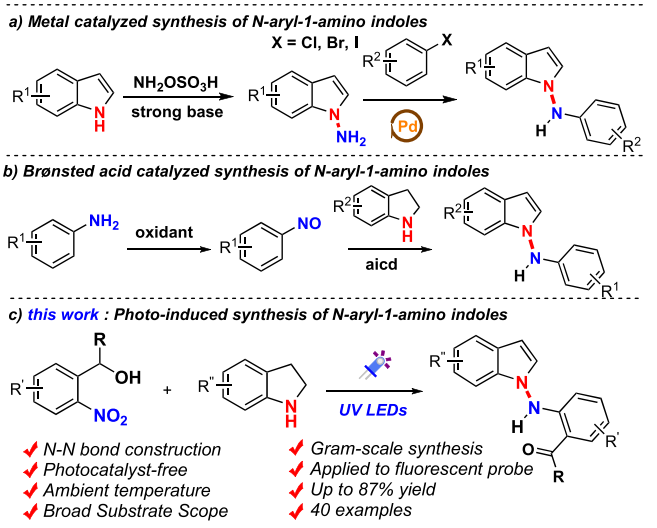


Figure 1. Representative bioactive *N*-substituted-1-amino indoles.

Although the synthesis of *N*-alky and *N*-heterocycle indoles has been well-established in organic synthesis,[4] the synthesis of *N*-amino indoles is still remaining a challenge issue. It can be due to the high electronegativity of nitrogen[5] and cumbersome procedures. Three pioneering groups have tried two methods to construct *N*-aryl-1-amino indoles (Scheme 1). The first protocol is starting from indole, which can generate 1-amino indole with hydroxylamine-*O*-sulfonic acid and strong bases, and followed by a Pd-catalyzed C–N cross-coupling reaction with relative halide (Scheme 1a).[6] Tunge et al.[7] developed another efficient route using inexpensive Brønsted acid catalysts to promote a redox amination process, which could efficiently realize the

Scheme 1. Intermolecular N–N Coupling to Synthesize *N*-aryl-1-amino Indoles



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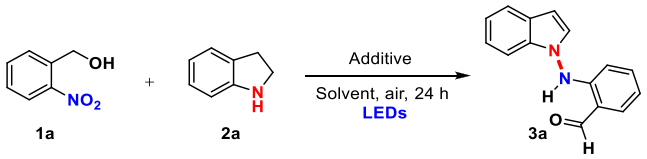
multistep coupling of anilines and indolines to synthesize *N*-aryl-1-amino indoles (Scheme 1b).[8] Inspiring by these ideas and our previous finding about *o*-nitrobenzyl alcohols,[9] herein, we disclosed a protocol which realize the construction of *N*-aryl-1-amino indoles in one-pot by a redox coupling process (Scheme 1c). The inexpensive *o*-nitrobenzyl alcohols could produce the oxidized intermediates via a photoinduced method, which can construct *N*−*N* bonds with indolines. These products bearing an aldehyde or ketone group, can be further transformed into useful functional molecules, such as fluorescent probes.

We initiated our studies with *o*-nitrobenzyl alcohol **1a** and indoline **2a** as model substrates to screen the reaction conditions (Table 1). At the outset, we obtained 30% yield with no

Table 1. Optimization of Reaction Conditions[a]



entry	1a:2a	additive (equiv)	base/acid (equiv)	solvent (mL)	yield (%)
1[b]	1:1	–	–	MeCN (2.0)	30
2[b]	1:1	–	K_2HPO_3 (2.0)	MeCN (2.0)	32
3[b]	1:1	–	K_2HPO_3 (2.0)	DCM (2.0)	42
4[b]	1:1	–	K_2HPO_3 (2.0)	DMF (2.0)	trace
5[b]	1:1	–	K_2HPO_3 (2.0)	toluene (2.0)	trace
6[b]	1:1	–	HCOOK (2.0)	DCM (2.0)	38
7[b]	3:1	–	–	DCM (2.0)	51
8[c]	3:1	–	–	DCM (2.0)	12
9[d]	3:1	–	–	DCM (2.0)	n.r.
10	3:1	–	–	DCM (2.0)	56
11	3:1	$PhI(OAc)_2$ (0.5)	–	DCM (2.0)	61
12	3:1	TBHP (0.5)	–	DCM (2.0)	52
13	3:1	TEAI (0.5)	–	DCM (2.0)	63
14	3:1	TEAI (0.5)	–	DCM (4.0)	68
15	3:1	TEAI (0.5)	$PhCO_2H$ (0.5)	DCM (4.0)	74
16	3:1	TEAI (0.5)	AcOH (0.5)	DCM (4.0)	81
17	2:1	TEAI (0.5)	AcOH (0.5)	DCM (4.0)	79
18	2:1	***TEAI (1.0)***	***AcOH (1.0)***	***DCM (4.0)***	***86 (93)***[e]
19	2:1	TEAI (2.0)	AcOH (2.0)	DCM (4.0)	77
20	2:1	TEAI (1.0)	AcOH (1.0)	DCM (4.0)	88[f]

[a]Reaction conditions: **1a** (0.4 mmol) **2a** (0.2 mmol, 1.0 equiv), TEAI (0.2 mmol), AcOH (0.2 mmol), solvent (4.0 mL), 24 h, room temperature, with a 24 W UV LEDs (385−405 nm) irradiation under air. Isolated yields. [b]With UV light (350−380 nm) irradiation. [c]With blue light (440−460 nm) irradiation. [d]No light. [e]Yields determined by GC-MS. [f]N_2.

additives (Table 1, entry 1), and the weak base K_2HPO_3 might promote the reaction (Table 1, entry 2). Then the solvents and bases were screened, the bases helped little, and the DCM was the superior solvent (Table 1, entries 3−6). We adjusted the ratio to 3:1 (**1a**:**2a**) because of the ordinary conversion of **1a**, and the yield reached 51% yield simultaneously (Table 1, entry 7). Subsequently, the light source was screened, and the UV light (385−405 nm) achieved the highest yield in 56%. Meanwhile, the reaction did not start with no light irradiation (Table 1, entries 8−10). Some additives were added and oxidants did not seem to work, but the tetraethylammonium iodide (TEAI) could better reduce the production of byproduct indole to promote the process, achieved in 66% yield (Table 1, entries 11−13). The amount of solvent was increased and the self-coupling products of *o*-nitrobenzyl alcohol reduced obviously (Table 1, entry 14). After screening the acids, the combination of acetic acid and TEAI could greatly improve the reaction yield to 81% (Table 1, entries 15 and 16). In the end, we screened the equiv of acetic acid and TEAI, isolated in 86% yield when the acetic acid and TEAI achieved at 1 equiv (Table 1, entries 17−19). By the way, we also conducted this reaction under N_2 atmosphere and achieved 88% yield.

With the optimized reaction conditions in hand, we investigated the substrate scope of *o*-nitrobenzyl alcohols **1** with **2a** (Scheme 2). The *o*-nitrobenzyl alcohol starting materials (A−J) were prepared by the reductive coupling of *o*-nitrobenzaldehyde and phenylboronic acid (see more details in the Supporting Information). At the outset, we investigated the effect of methyl groups at different sites on the reaction. The 5-methyl (**3b**) delivered the highest yield (87%), oppositely, the 2-methyl (**3c**) and 3-methyl (**3d**) delivered the unsatisfactory yield (39% and 59%, respectively) because of the steric demands of reactive intermediate. In the same 5-position, electron-withdrawing groups (**3e**−**3f**) also achieved nice yields in 81% and 77%, and electron-donating groups (**3g**) achieved moderate yield in 58%. Subsequently, the groups with different steric hindrances at the 4-position (**3h**−**3l**) were investigated and achieved moderate to good yields (59%−72%). In addition, the absolute configuration of **3e** was unambiguously confirmed by the single-crystal X-ray diffraction.

Next, we further studied the effect of the substituent at the benzylic position (R) on the reaction. Product **3m** with alkyl group achieved in 62% yield, and the effect that different sites and various groups on the benzene ring (R) contributes to the reaction was explored (**3n**-**3r**). The *m*-substituted and *p*-substituted substrates had a better reaction effect than the *o*-substituted, and both electron withdrawing and electron-donating groups showed good yields (61%−77%). Products **3s**-**3t** with aryl and heterocycle groups also achieved in 72% and 60%, respectively. We explored the combined effects of the two substitution sites (**3u**−**3v**). They afforded good yields, and the strong electron-withdrawing group (*p*-NO_2) had a poorer yield (61%). Finally, the *o*-nitropyridine alcohols could also be compatible with the reaction and obtained the **3w** in 70% yield.

Ultimately, the generality of the indoline framework was also examined (Scheme 3). Products **4a**−**4p** with various groups were achieved in moderate to good yields (37%−85%). The reaction was compatible with indolines that bearing electron-withdrawing or electron-donating groups, but the 5-I (**4g**) achieved an unsatisfactory yield, because of the dehalogenation. The strong electron-withdrawing groups, such as 5-CN (**4l**) and 5-NO_2 (**4m**) afforded the desired products in 61% and 41%, respectively. Notably, compared with 5-Cl (**4e**) and 6-Cl (**4o**) products, the 7-Cl (**4p**) had a poorer yield, which could be explained as a steric effect. Finally, the heterocyclic indoline was explored, and the product **4q** was obtained in good yield (64%).

With the completion of the substrate expansion, we began to excavate the potential of this skeleton and performed some functionalized applications. We used *p*-toluenesulfonyl hydrazide **5** to react with **3a** to obtain **6** in excellent yield (91%), which can be used as an intermediate to participate in various cyclization reactions (Scheme 4a).[10] On the other hand, we used 2-bromobenzyl bromide **7** to react with **3a** under strong alkaline conditions to obtain **8**. Then, the palladium catalyst, ligand, and strong base were utilized as partners in an intramolecular

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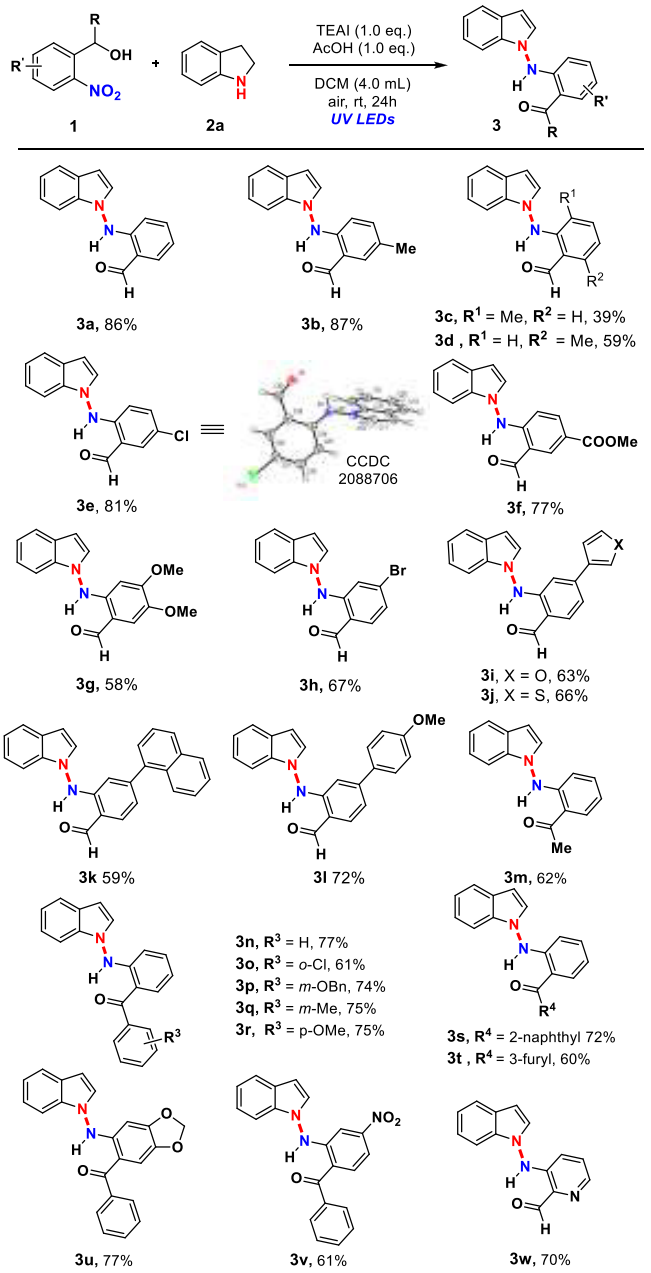
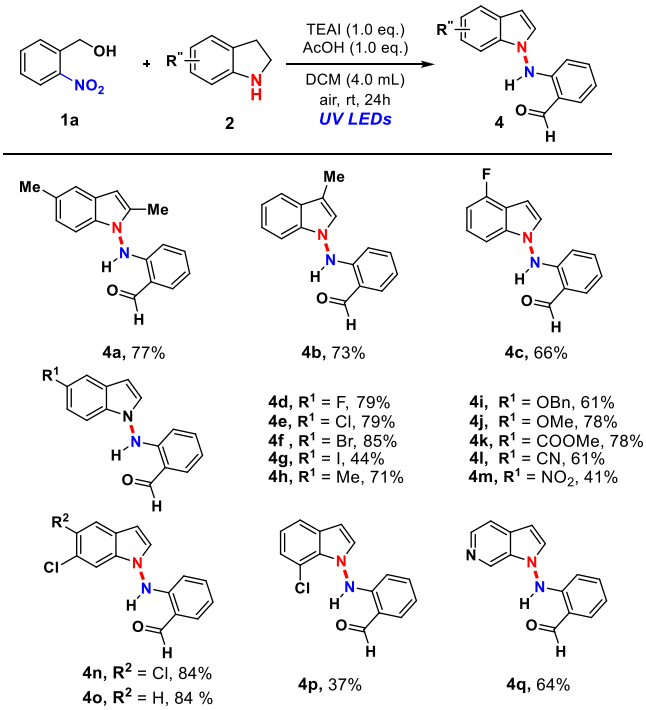
Scheme 2. Substrate Scope of *o*-Nitrobenzyl Alcohols[a]



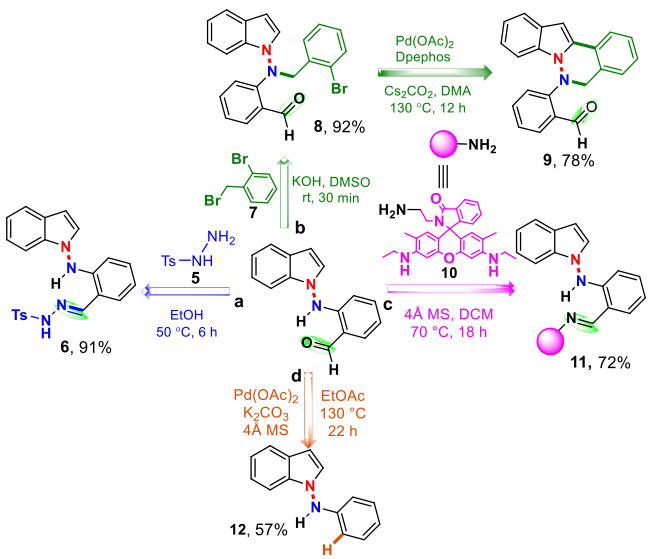
[a]Reaction conditions: **1** (0.4 mmol), **2a** (0.2 mmol, 1.0 equiv), TEAI (0.2 mmol), AcOH (0.2 mmol), DCM (4.0 mL), 24 h, room temperature, with a 24 W UV LEDs (385−405 nm) irradiation under air. Isolated yields.

Scheme 3. Substrate Scope of Indolines[a]



[a]Reaction conditions: **1** (0.4 mmol), **2a** (0.2 mmol, 1.0 equiv), TEAI (0.2 mmol), AcOH (0.2 mmol), DCM (4.0 mL), 24 h, room temperature, with a 24 W UV LEDs (385−405 nm) irradiation under air. Isolated yields.

Scheme 4. Synthetic Applications



cyclization method to synthesize **9** whose analogues had nice antiproliferative activity (Scheme 4b).[6a,11] A cyclic derivative of Rhodamine 6G **10** could react with **3a** to form an imine compound **11**, which may be used for detecting metal ions (Scheme 4c).[12] By the way, the aldehyde group could be removed by palladium catalysts, and obtained the desired product **12** in 57% yield.[13]

In order to verify the advantages of **11** as a fluorescent probe, we used common metal cations to explore its sensitivity and specificity for Fe^{3+}. As shown in Figure 2, the color changes (Figure 2A) were from colorless to pink and fluorescence changes (Figure 2B) were from colorless to yellow. Variations of UV−vis (Figure 2C) and fluorescence spectra (Figure 2D) of **11** (20 μM) caused by Fe^{3+} and other mixed metal cations were recorded in Figure 2. Obviously, after adding Fe^{3+}, the solution which only contained **11** or contained **11** and other mixed-metal cations (including Fe^{2+}, K^+, Mg^{2+}, Cu^{2+}, Hg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Ag^+, 50 μM, respectively) both had strong absorption at 527 nm and strong emission at 555 nm. Compared with other fluorescent probes which could respond to both Fe^{3+} and Hg^{2+},[14] our fluorescent probe **11** could specifically recognize Fe^{3+} in complicated environments, which can be explained as the coordination of Fe^{3+} and *N*-aryl-1-amino indole formed a large

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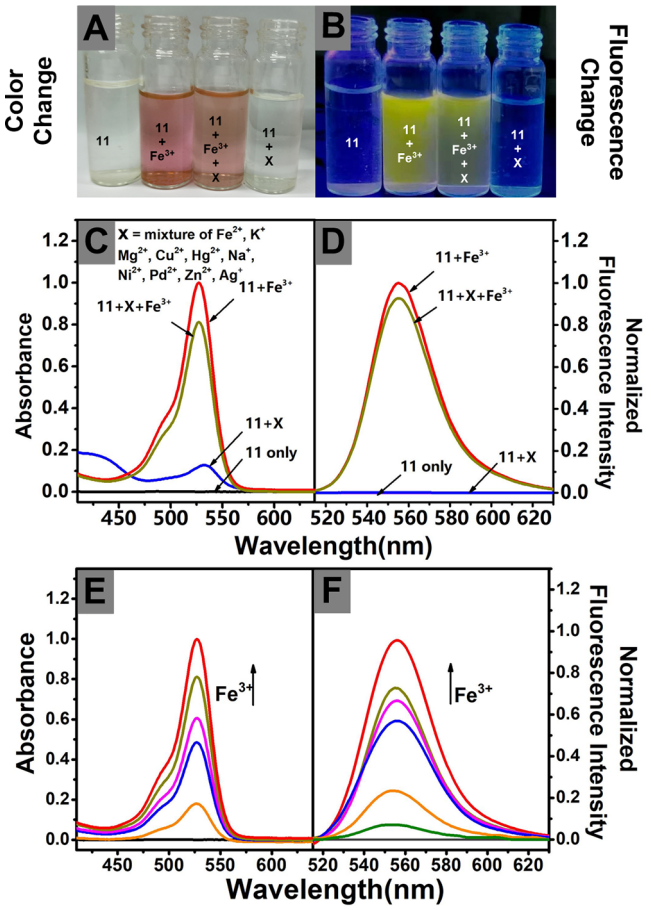
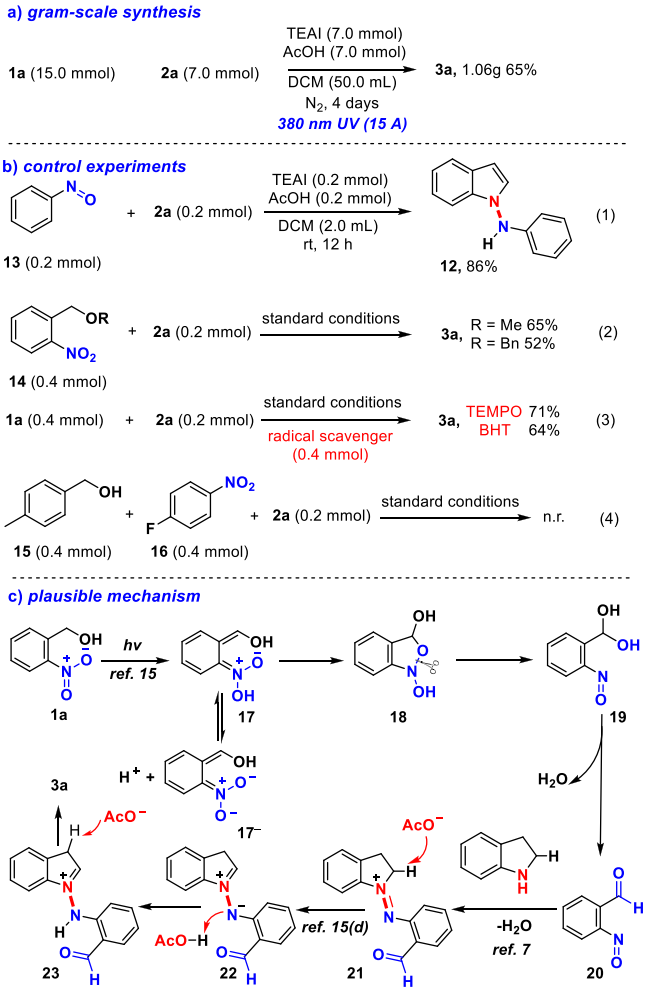


Figure 2. (A) Color changes (X = Fe^{2+}, K^+, Mg^{2+}, Cu^{2+}, Hg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Ag^+); (B) fluorescence changes; (C) UV-vis spectra of **11** (X and Fe^{3+} are 50 μM, respectively); (D) fluorescence spectra of **11**. (E) UV-vis spectra of **11** (Fe^{3+} concentrations of 0, 10, 20, 30, 40, 50 μM); (F) fluorescence spectra of **11** (Fe^{3+} concentrations of 0, 2.5, 5, 10, 20, 30, 40, 50 μM). See Figures S6 and S7 in the Supporting Information) for the full-size panels.

steric hindrance structure (for changes of chemical shifts in ^{1}H NMR chart, see Figure S8 in the Supporting Information). A spectral variation of **11** upon the gradual addition of Fe^{3+} (0−2.5 equiv) was shown in Figure 2 with a standard solution. Obviously, the absorption spectra (Figure 2E) and emission bands (Figure 2F) were gradually enhanced with an increasing concentration of Fe^{3+} ions. Based on the above experimental results, we have proven that **11** had high selectivity and sensitivity for Fe^{3+} ions as a novel fluorescent probe.

To show the practicability of this protocol, we used a high-power argon lamp as the light source to conduct a gram-scale reaction (Scheme 5a). The nitrogen environment was used to prevent the rapid oxidation of indoline at high concentrations. After stirring for 4 days, the product **3a** (1.06 g) was obtained with 75% yield. To gain mechanistic insights into these processes, the following control experiments were conducted. At first, nitrosobenzene **13** could react with indoline in the presence of TEAI and acetic acid, which afforded the desired product **12** in 86% yield (Scheme 5b (1)). On the basis of redox amination, we hypothesized that the indoline and nitrosobenzene **13** combined into an azo ion intermediate, then experienced a series of proton transfer to construct **12**. This experiment demonstrated that nitrosobenzene derivative were the key intermediates. Next, we conducted **14** with indoline

Scheme 5. Gram-Scale Synthesis and Mechanistic Studies



under the standard conditions, obtained **3a** in 65% and 52% when alkoxyl groups were methyl and benzyl, respectively (Scheme 5b (2)). It revealed that there may be some oxygen transfer and alkoxy group departure routes in these processes. Two equivalents of radical scavengers were added to the reaction to investigate whether there were other types of free radicals in the system (Scheme 5b (3)). We did not detect any other trapped radicals via GC-MS, which revealed that the reaction route is redox coupling of nitrosobenzene intermediates and indolines. We used intermolecular benzyl alcohol and nitrobenzene compounds to conduct with indoline under standard conditions (Scheme 5b (4)), and no reaction was observed. This experiment revealed that the intramolecular *o*-nitrobenzyl alcohol was necessary for the reaction. We also used some other secondary amines such as *N*-ethylaniline, 1,2,3,4-tetrahydro quinoline and tetrahydro pyrrole, etc. to react with **1a** under the standard conditions, but no desired products were detected (Figure S4 in the Supporting Information). Then we conducted a light on−off experiment, which revealed that light was indispensable to promote the reaction (Figure S5(a) in the Supporting Information). In order to verify the promotion effect of TEAI, we conducted a monitoring control experiment under standard conditions, and found that TEAI could inhibit the production of byproduct indole (see Figure S5(b) in the Supporting Information).

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Based on the above experiments and previous literature reports,[7,15] we have proposed a plausible reaction mechanism. At first, *o*-nitrobenzyl alcohol **1a** transforms to intermediate **17** under the irradiation of UV light quickly. The intermediate **17** can transform to its conjugate base $\mathbf{17}^-$ spontaneously under alkaline conditions. By the ring fragmentation, intermediate **18** transforms to transient hemiketal species **19**, then loses 1 equiv of water to afford *o*-nitrosobenzaldehyde **20**. Because of the high activity of **20** and the reducibility of indoline,[7] they combine with each other to generate intermediate **21**. In this process, we used TEAI to inhibit the production of byproduct indole. Then,[15d] the azo ion **21** may experience a deprotonation process to form azomethine ylide **22**, which could transform to a new iminium ion **23**, because of the reprotonation of the dipolar intermediate. Finally, the π-bond hyperconjugation effect and proton loss lead to the aromatization and formation of **3a**.

In conclusion, we have developed a new method for the synthesis of *N*-aryl-1-amino indoles by UV light-induced reductive amination coupling reaction. As active intermediates of the redox coupling process, nitrosobenzene species could react with reductive indolines, which were facilitated by mild Brønsted acid and TEAI catalysts. Based on the molecular skeleton, we have developed a new Rhodamine-based fluorescent probe, which showed "turn-on" fluorescent and real-time colorimetric responses to Fe^{3+} in a mixed-metal-cations environment with high selectivity and sensitivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02227.

Detailed experimental procedures, characterization data, spectra data of the ^1H, ^{13}C, and ^{19}F NMR for raw materials and obtained products (PDF)

HRMS data (ZIP)

FAIR data, including the primary NMR FID files, for compounds **3a−w**, **4a−q**, **A-J**, **6**, **8**, **9**, **11**, **12** (ZIP)

Accession Codes

CCDC 2088706 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or 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.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Mizoguchi, H.; Oikawa, H.; Oguri, H. Biogenetically inspired synthesis and skeletal diversification of indole alkaloids. *Nat. Chem.* **2014**, *6*, 57. (b) Gordon, C. P.; Venn-Brown, B.; Robertson, M. J.; Young, K. A.; Chau, N.; Mariana, A.; Whiting, A.; Chircop, M.; Robinson, P. J.; McCluskey, A. Development of Second-Generation Indole-Based Dynamin GTPase Inhibitors. *J. Med. Chem.* **2013**, *56*, 46.

(2) (a) Mahapatra, A. K.; Maiti, K.; Maji, R.; Manna, S. K.; Mondal, S.; Ali, S. S.; Manna, S. Ratiometric fluorescent and chromogenic chemodosimeter for cyanide detection in water and its application in bioimaging. *RSC Adv.* **2015**, *5*, 24274. (b) Zhao, C.; Zhou, Y.; Lin, Q.; Zhu, L.; Feng, P.; Zhang, Y.; Cao, J. Development of an Indole-Based Boron-Dipyrromethene Fluorescent Probe for Benzenethiols. *J. Phys. Chem. B* **2011**, *115*, 642.

(3) (a) Chi, J.; Hang, C.; Zhu, Y.; Katayama, H. Synthesis of Indolo [1, 2-*b*] indazole Derivatives via Copper (I)-Catalyzed Intramolecular Amination Reaction. *Synth. Commun.* **2010**, *40*, 1123. (b) Chaudhaery, S. S.; Roy, K. K.; Shakya, N.; Saxena, G.; Sammi, S. R.; Nazir, A.; Nath, C.; Saxena, A. K. Novel Carbamates as Orally Active Acetylcholinesterase Inhibitors Found to Improve Scopolamine-Induced Cognition Impairment: Pharmacophore-Based Virtual Screening, Synthesis, and Pharmacology. *J. Med. Chem.* **2010**, *53*, 6490. (c) Frontana-Uribe, B. A.; Moinet, C.; Toupet, L. N-Substituted 1-Aminoindoles from Electrogenerated N-Substituted 2-(ortho-Nitrosophenyl)ethylamines. *Eur. J. Org. Chem.* **1999**, *1999*, 419. (d) Klein, J. T.; Davis, L.; Olsen, G. E.; Wong, G. S.; Huger, F. P.; Smith, C. P.; Petko, W. W.; Cornfeldt, M.; Wilker, J. C.; Blitzer, R.; et al. Synthesis and Structure−Activity Relationships of N-Propyl-N-(4-pyridinyl)-1 H-indol-1-amine (Besi-

pirdine) and Related Analogs as Potential Therapeutic Agents for Alzheimer's Disease. *J. Med. Chem.* **1996**, *39*, 570.
(4) (a) Bhattacharjee, P.; Bora, U. Organocatalytic dimensions to the C−H functionalization of the carbocyclic core in indoles: a review update. *Org. Chem. Front.* **2021**, *8*, 2343. (b) Ge, Y.; Wang, H.; Wang, H.-N.; Yu, S.-S.; Yang, R.; Chen, X.; Zhao, Q.; Chen, G. Biomimetic Total Syntheses of Ergot Alkaloids via Decarboxylative Giese Coupling. *Org. Lett.* **2021**, *23*, 370. (c) Song, C.; Liu, K.; Jiang, X.; Dong, X.; Weng, Y.; Chiang, C.-W.; Lei, A. Electrooxidation Enables Selective Dehydrogenative [4 + 2] Annulation between Indole Derivatives. *Angew. Chem., Int. Ed.* **2020**, *59*, 7193. (d) Zhu, M.; Zheng, C.; Zhang, X.; You, S.-L. Synthesis of Cyclobutane-Fused Angular Tetracyclic Spiroindolines via Visible-Light-Promoted Intramolecular Dearomatization of Indole Derivatives. *J. Am. Chem. Soc.* **2019**, *141*, 2636.
(5) (a) Wang, H.; Jung, H.; Song, F.; Zhu, S.; Bai, Z.; Chen, D.; He, G.; Chang, S.; Chen, G. Nitrene-mediated intermolecular N−N coupling for efficient synthesis of hydrazides. *Nat. Chem.* **2021**, *13*, 378. (b) Vemuri, P. Y.; Patureau, F. W. Cross-Dehydrogenative N−N Coupling of Aromatic and Aliphatic Methoxyamides with Benzotriazoles. *Org. Lett.* **2021**, *23*, 3902. (c) Li, G.; Yang, L.; Liu, J.-J.; Zhang, W.; Cao, R.; Wang, C.; Zhang, Z.; Xiao, J.; Xue, D. Light-Promoted C−N Coupling of Aryl Halides with Nitroarenes. *Angew. Chem., Int. Ed.* **2021**, *60*, 5230.
(6) (a) Luong, T. T. H.; Brion, J.-D.; Alami, M.; Messaoudi, S. Synthesis of Fused 1-Aminoindole Polycycles by a Sequence of Palladium-Catalyzed N−H and C (sp^2)−H Arylations. *J. Org. Chem.* **2015**, *80*, 751. (b) Brachet, E.; Messaoudi, S.; Peyrat, J.-F.; Brion, J.-D.; Alami, M. Palladium-Catalyzed Cross-Coupling of 1-Aminoazoles with Aryl Chlorides: Application to the Synthesis of Unsymmetrical *N,N′*-Diaryl-1-aminoindoles. *Adv. Synth. Catal.* **2012**, *354*, 2829. (c) Messaoudi, S.; Brion, J.-D.; Alami, M. Palladium-catalyzed selective *N*-(hetero)arylation or *N,N′*-di(hetero)arylation of 1-amino indoles. *Tetrahedron Lett.* **2011**, *52*, 2687.
(7) Ramakumar, K.; Tunge, J. A. Synthesis of *N*-aryl-1-aminoindoles via intermolecular redox amination. *Chem. Commun.* **2014**, *50*, 13056.
(8) (a) Chen, X.; Yang, Z.; Chen, X.; Liang, W.; Zhu, Z.; Xie, F.; Li, Y. Hydrogen-Transfer-Mediated *N*-Arylation of Naphthols Using Indolines as Hydrogen Donors. *J. Org. Chem.* **2020**, *85*, 508. (b) Karjee, P.; Sarkar, T.; Kar, S.; Punniyamurthy, T. Transition-Metal-Free Stereospecific Oxidative Annulative Coupling of Indolines with Aziridines. *J. Org. Chem.* **2020**, *85*, 8261.
(9) Yang, T.; Lu, H.; Qiu, R.; Hong, L.; Yin, S.-F.; Kambe, N. Photocatalyst-free Synthesis of Indazolones under CO2 atm. *Chem. - Asian J.* **2019**, *14*, 1436.
(10) Wang, G.; Sun, J.; Wang, K.; Han, J.; Li, H.; Duan, G.; You, G.; Li, F.; Xia, C. Palladium-catalyzed direct C−H nitration and intramolecular C−H functionalization for the synthesis of 3-nitro-1-(phenylsulfonyl)-1*H*-indazole derivatives. *Org. Chem. Front.* **2019**, *6*, 1608.
(11) Zhu, Y.-m.; Kiryu, Y.; Katayama, H. Intramolecular aromatic amination by a hydrazino group for the synthesis of indolo [1, 2-*b*] indazole derivatives. *Tetrahedron Lett.* **2002**, *43*, 3577.
(12) (a) Ji, S.; Meng, X.; Ye, W.; Feng, Y.; Sheng, H.; Cai, Y.; Liu, J.; Zhu, X.; Guo, Q. A rhodamine-based ″turn-on″ fluorescent probe for Fe^{3+} in aqueous solution. *Dalton Trans* **2014**, *43*, 1583. (b) Lee, M. H.; Giap, T. V.; Kim, S. H.; Lee, Y. H.; Kang, C.; Kim, J. S. A novel strategy to selectively detect Fe(iii) in aqueous media driven by hydrolysis of a rhodamine 6G Schiff base. *Chem. Commun.* **2010**, *46*, 1407. (c) Wu, J.-S.; Hwang, I.-C.; Kim, K. S.; Kim, J. S. Rhodamine-Based Hg^{2+}-Selective Chemodosimeter in Aqueous Solution: Fluorescent OFF−ON. *Org. Lett.* **2007**, *9*, 907.
(13) Akanksha; Maiti, D. Microwave-assisted palladium mediated decarbonylation reaction: synthesis of eulatachromene. *Green Chem.* **2012**, *14*, 2314.
(14) Lee, M. H.; Lee, H.; Chang, M. J.; Kim, H. S.; Kang, C.; Kim, J. S. A fluorescent probe for the Fe^{3+} ion pool in endoplasmic reticulum in liver cells. *Dyes Pigm.* **2016**, *130*, 245.
(15) (a) Kraemer, N.; Li, C. J.; Zhu, J. S.; Larach, J. M.; Tsui, K. Y.; Tantillo, D. J.; Haddadin, M. J.; Kurth, M. J. Davis−Beirut Reaction: A Photochemical Brønsted Acid Catalyzed Route to *N*-Aryl 2*H*-Indazoles. *Org. Lett.* **2019**, *21*, 6058. (b) Zhu, J. S.; Kraemer, N.; Li, C. J.; Haddadin, M. J.; Kurth, M. J. Photochemical Preparation of 1,2-Dihydro-3*H*-indazol-3-ones in Aqueous Solvent at Room Temperature. *J. Org. Chem.* **2018**, *83*, 15493. (c) Klán, P.; Šolomek, T. s.; Bochet, C. G.; Blanc, A.; Givens, R.; Rubina, M.; Popik, V.; Kostikov, A.; Wirz, J. Photoremovable protecting groups in chemistry and biology: reaction mechanisms and efficacy. *Chem. Rev.* **2013**, *113*, 119. (d) Deb, I.; Das, D.; Seidel, D. Redox Isomerization via Azomethine Ylide Intermediates: N-Alkyl Indoles from Indolines and Aldehydes. *Org. Lett.* **2011**, *13*, 812.

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