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Diaryliodonium Salt-Mediated Intramolecular C–N Bond Formation Using Boron-Masking *N*-Hydroxyamides

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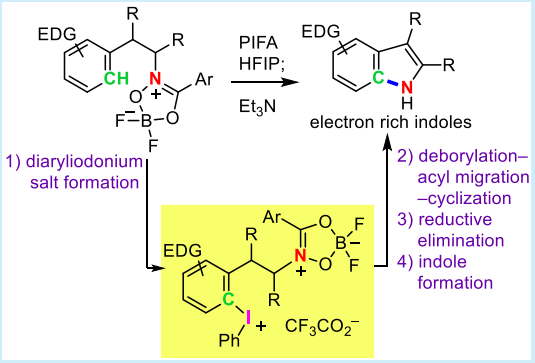
Supporting Information

ABSTRACT: Intramolecular aromatic C–N bond formation reactions using electron-rich aromatic tethered boron-masking *N*-hydroxyamide as substrate were realized. These new C–N bond formation reactions involve the in situ generation of a diaryliodonium salt by treatment with hypervalent iodine, deborylation by base treatment, spontaneous N → O acyl migration, cyclization, reductive elimination, elimination of benzoic acid, and tautomerization to indole formation. Hereby, we obtained highly functionalized electron-rich indoles and quinoline in practical yields.

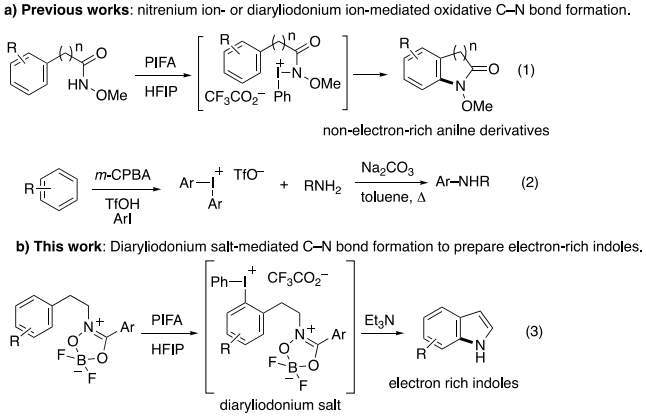


The discovery of new C–N bond formation reactions is an important topic in current organic chemistry, particularly because these methods provide a new synthetic strategy for the development of new organic materials, drugs, and agricultural chemicals. For example, Buchwald–Hartwig C–N bond formation reactions were a breakthrough in the evolution of retrosynthetic analysis.[1] To date, aromatic C–N bond formation using hypervalent iodine as the oxidant has been reported by several groups.[2,3] The unique amino cation or its equivalents via hypervalent iodine oxidation of amide nitrogen are reported to afford nonelectron-rich anilines, lactams, or carbazoles (Scheme 1a, eq 1). Recently, Olofsson and co-workers reported direct C–N bond formation, using an in situ generated diaryliodonium salt (Scheme 1a, eq 2).[4] However, when applying the reported methodology, the synthesis of election-rich anilines or their equivalents is not easily accomplished. This is because of an overoxidation reaction by hypervalent iodine of in situ generated electron-rich anilines.

Herein, we describe intramolecular aromatic C–N bond formation by a stepwise protocol using boron-masking *N*-hydroxyamide as the substrate to form electron-rich indoles and quinoline in a one-pot operation (Scheme 1b, eq 3). In the reaction, an in situ generated, highly reactive diaryliodonium salt was detected as a key intermediate. This is the first example of a reaction in which an acyl migration pathway of *N*-hydroxyamide is employed in an oxidative C–N bond forming reaction.

It is difficult to employ primary or secondary nitrosoalkanes as electrophiles because they quickly convert to stabilized *cis* and *trans* dimers or easily tautomerize to thermodynamically stable oximes.[5] After recognizing the challenge presented when using such an unstable species in nucleophilic C–N bond formation, we then considered that the generation of a primary nitrosoalkane from *N*-hydroxyamide via hypervalent iodine oxidation, followed by Friedel–Crafts-type cyclization, could be used to prepare electron-rich indoles (Scheme 2). Thus, the hypervalent iodine complex **2**, prepared from *N*-hydroxyamide **1** and [bis(trifluoroacetoxy)iodo]benzene (PIFA), should undergo oxidative cleavage to afford primary nitrosoalkane **4**.

Scheme 1. Oxidative C–N Bond Formation Using Hypervalent Iodine



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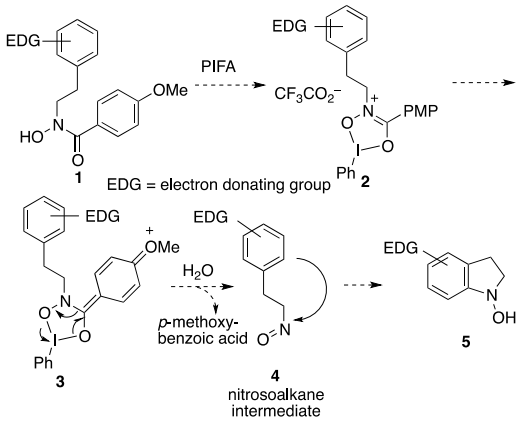
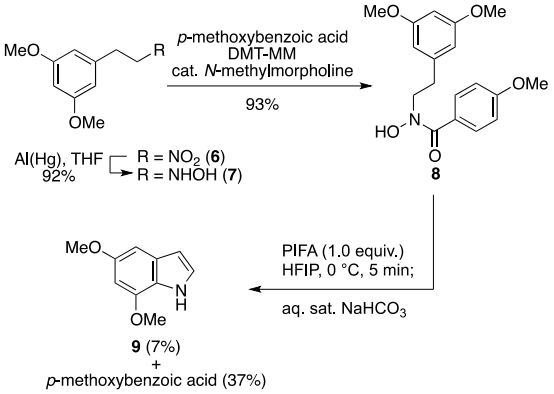
Scheme 2. Our Initial Hypothesis: In Situ Generation of Nitrosoalkane Followed by the Friedel–Crafts-Type C–N Bond Formation Reaction



The generated primary nitroso moiety would be immediately trapped by an electron-rich aromatic group tethered to nitrogen via a Friedel–Crafts-type C–N bond formation to afford cyclic product **5** along with hydrolyzed *p*-methoxybenzoic acid. Finally, **5** could be easily converted to the corresponding indoles via dehydration and tautomerization.

In our preliminary investigations (first attempt), we selected *N*-hydroxyamide **8**, which contains a 1,3-dimethoxybenzene moiety, as the substrate (Scheme 3). The coupling precursor **7** was prepared by the reduction of known nitro compound **6** with Al(Hg)[6,7] (excess Al(Hg), THF, 23 °C). To prepare *N*-hydroxyamide **8**, the amino group on a hydroxylamine moiety had to condense with *p*-methoxybenzoic acid, selectively. Initially, *p*-methoxybenzoyl chloride was employed in a condensation reaction with hydroxylamine to obtain **8**. However, we were unable to achieve reproducibility; the amine and hydroxyl groups often reacted to afford an amide/ester mixture. Thereafter, 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM), developed by Kunishima et al., was selected as the coupling reagent to prepare *N*-hydroxyamide. DMT-MM is reported to be an amide-selective coupling reagent in the presence of an hydroxyl group.[8] Thus, the treatment of hydroxylamine **7** and *p*-methoxybenzoic acid (1 equiv) with DMT-MM (1.2 equiv) in the presence of 10 mol % *N*-methyl morpholine afforded the desired *N*-hydroxyamide **8** in excellent yield and with good selectively (CH_3CN, −20 °C, 15 h, 93%). This protocol that we discovered is the first example that includes the use of DMT-MM in *N*-hydroxyamide synthesis.

Scheme 3. Indole Synthesis: First Attempt

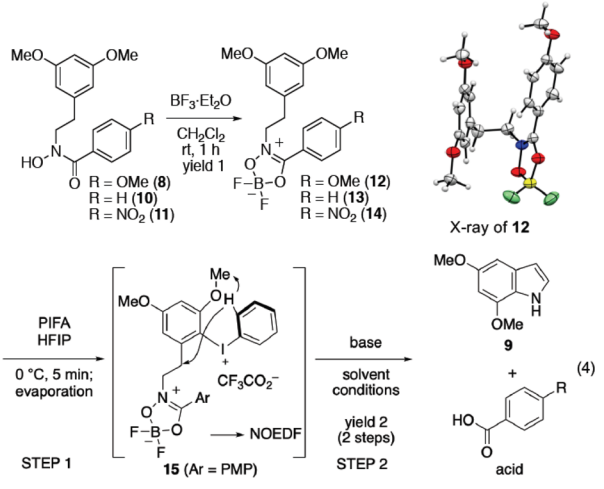


With a suitable precursor now in hand, we next examined the proposed indole synthesis. When 1 equiv of PIFA was added to a solution of **8** in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) at 0 °C (5 min), followed by the addition of aqueous saturated $NaHCO_3$, the compound 5,7-dimethoxyindole (**9**) was obtained in 7% yield, along with 37% of hydrolyzed *p*-methoxybenzoic acid.

After several attempts to achieve optimization, we noticed that the *N*-hydroxyamide moiety was very unstable; it formed a complex mixture under the reaction conditions. On the other hand, we considered that indole formation took place after the formation of a diaryliodonium salt on an electron-rich aromatic group via nucleophilic addition to hypervalent iodine. Therefore, the *N*-hydroxyamide moiety was masked as a boron salt[9] before PIFA treatment. Thus, *N*-hydroxyamide **8** was treated with 2 equiv of boron trifluoride–ether complex in CH_2Cl_2 to afford the aromatic tethered boron-masking *N*-hydroxyamide **12** in quantitative yield (23 °C, 1 h; Table 1). A single crystal of **12** was obtained and used to confirm the structure by X-ray analysis (CCDC 1963790).

With the boron-masking *N*-hydroxyamide **12** now in hand, we re-examined the indole synthesis. When **12** was treated with 1 equiv of PIFA in HFIP at 0 °C, the starting material was immediately consumed, according to TLC analysis. After the addition of aqueous saturated $NaHCO_3$ solution to the reaction mixture, our desired product 5,7-dimethoxyindole

Table 1. Optimization of Indole Synthesis[a]



entry	R	yield 1[b]	base (equiv)	conditions	yield 2[b] 9 (%)	yield 2[b] acid
1	OMe	quant	aqueous sat $NaHCO_3$	0 °C, 15 min	77	quant
2	OMe	quant	Et_3N (10)	THF, 0 °C, 2 h	98	quant
3	H	97%	Et_3N (10)	THF, 0 °C, 1.5 h	97	quant
4	NO_2	quant	Et_3N (10)	THF, 0 °C, 10 min	87	quant

[a]Reaction conditions. Step 1: a reaction mixture of **12**–**14** (0.0528 mmol) and PIFA (0.0528 mmol) in HFIP (3.6 mL) was stirred for 5 min at 0 °C, followed by evaporation to remove all HFIP. Step 2: base was added to the crude mixture of products of step 1 in solvent (3.6 mL) at 0 °C. [b]Isolated yield.

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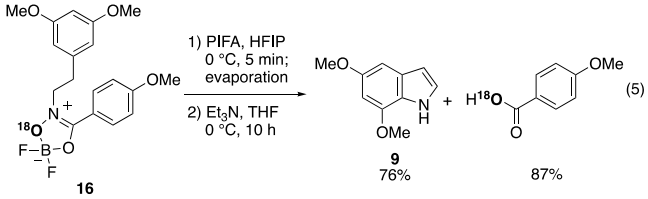
(**9**) was obtained in 77% yield, along with *p*-methoxybenzoic acid in quantitative yield (Table 1, entry 1). To understand the reaction mechanism (the first PIFA treatment), NMR analysis in deuterated HFIP was carried out. Hypervalent iodine reacted on the 1,3-dimethoxybenzene moiety in almost full conversion.[3j,10] The reaction site and the structure of iodonium salt **15** were confirmed by 2D NMR, NOE, and MS (Figure S1). Thus, a single diaryliodonium salt was generated in situ via regioselective nucleophilic addition in the first step.

Further improvement in the reaction yield was achieved when Et_3N was used as the base instead of $NaHCO_3$. Thus, after evaporation of the diaryliodonium salt mixture, anhydrous Et_3N in THF solution was added in a one-pot operation (10 equiv of Et_3N, 0 °C, 2 h; Table 1, entry 2). The product **9** was obtained in almost quantitative yield (98%). It emerged that the *p*-methoxy group on the benzoic acid moiety was not required, although it was an essential functional group in our initial hypothesis. Thus, when the simple benzoyl-substituted substrate **13** was employed, the reaction proceeded smoothly and the desired indole **9** was obtained in excellent yield (1.5 h; Table 1, entry 3). Furthermore, a *p*-nitrobenzoyl-substituted substrate **14** was also a suitable substrate; it promoted indole formation. Of importance is that the reaction time in the second step was only 10 min, although here, the reaction yield was slightly decreased (Table 1, entry 4). We recognized that the electron-withdrawing group at the benzoyl group would strongly accelerate C−N bond formation.

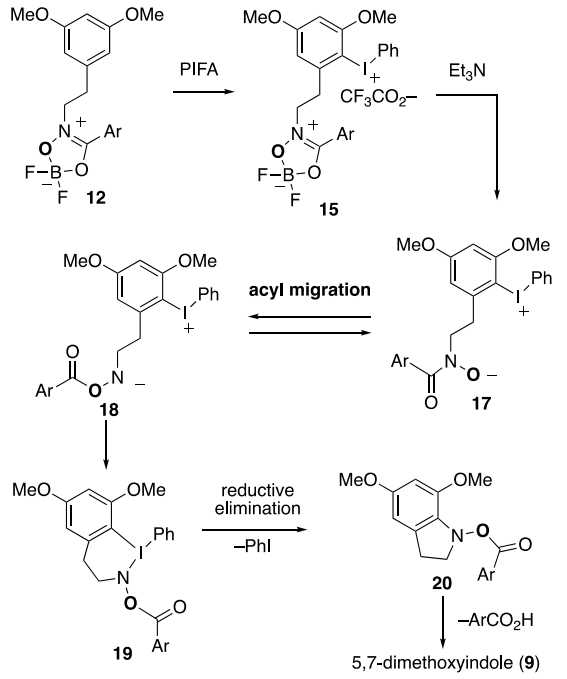
Next, our interest moved to the origin of the oxygen of the recovered benzoic acid. The ^{18}O isotope derivative **16**, labeled on the *N*-hydroxy amine moiety, was prepared from $NaN^{18}O_2$ (eq 5, below). When the ^{18}O-labeled cyclic boron compound **16** was employed under optimized reaction conditions, ^{18}O-labeled *p*-methoxybenzoic acid was obtained in 87% yield along with indole **9** (see the details in the Supporting Information). In 1984, Nikishin et al. reported an N → O acyl migration reaction from *N*-hydroxy amide to *O*-acylhydroxylamine.[11] We propose that the recovered benzoic acid was generated via an acyl migration pathway.



Next, a kinetic study of the second step was performed. Thus, the in situ generated diaryliodonium salt **15**, in the presence of Et_3N in THF-d_8, was monitored by NMR (Figure S2). The diaryliodonium salt **15** reacted to form three products, specifically, indole **9**, *p*-methoxybenzoic, and iodobenzene, with no reaction intermediates. (**15** was fully consumed.) In addition, when the reaction was carried out in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a radical scavenger, our desired indole was produced smoothly without any side products. We therefore excluded the radical mechanism via single electron transfer (SET).

Our proposed reaction mechanism derived from the above experiments is shown in Scheme 4. The cyclic boron compound **12** is converted to diaryliodonium salt **15** by PIFA treatment in non-nucleophilic HFIP. The treatment of the iodonium salt **15** with Et_3N results in nucleophilic deborylation to afford the oxoanion **17**. This deborylation step is the rate-limiting step estimated by the above kinetic

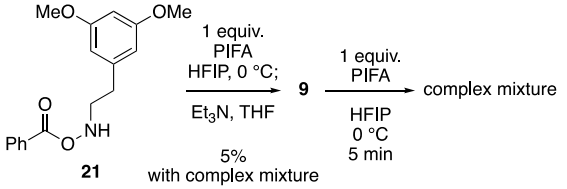
Scheme 4. Proposed Reaction Mechanism



study. It is further supported by the effect of an electron-withdrawing group on benzoic acid (Table 1, entries 2 and 4). Next, an N → O acyl migration reaction takes place to afford an *O*-acyl intermediate **18**. It is conceivable that an equilibrium state exists between compounds **17** and **18**. We speculated that the intramolecular cyclization of **18** affords the six-membered heterocyclic compound **19**. Following a reductive elimination process[4] to form a C−N bond, the indole precursor **20** is generated. Finally, desorption of *p*-methoxybenzoic acid followed by tautomerization affords 5,7-dimethoxyindole (**9**).

After consideration of the reaction mechanism, *O*-benzoylhydroxylamine **21**,[12] an acyl migration intermediate in our proposed mechanism, was exposed to PIFA oxidation (Scheme 5). However, when **21** was treated with 1 equiv of

Scheme 5. Indole Synthesis Using *O*-Benzoylhydroxylamine 21



PIFA in HFIP followed by Et_3N treatment, our desired indole **9** was obtained in only 5% yield, along with an inseparable complex mixture. We subsequently determined that the electron-rich indole that we obtained, **9**, was highly reactive toward PIFA oxidation. When indole **9** was treated with 1 equiv of PIFA in HFIP at 0 °C, **9** was immediately oxidized and a complex mixture was obtained. Thus, the stepwise C−N bond formation process that we discovered here is essential for the synthesis of electron-rich indoles. In particular, the usage of boron-masking *N*-hydroxyamide as the substrate and acyl migration after the preparation of diaryliodonium salts are the keys to success.

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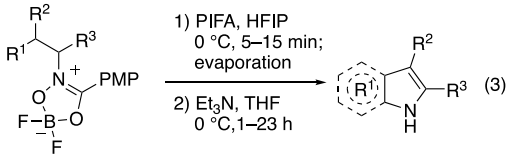
Org. Lett. XXXX, XXX, XXX−XXX

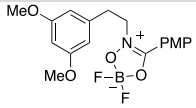
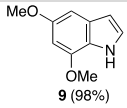
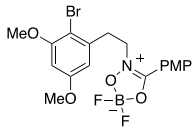
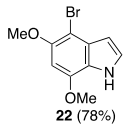
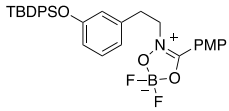
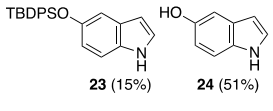
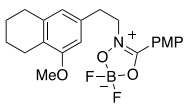
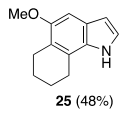
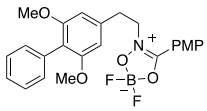
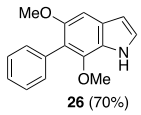
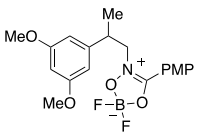
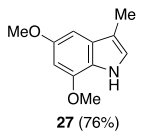
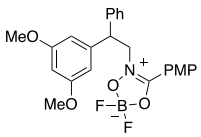
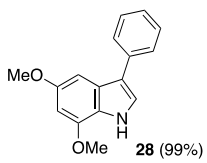
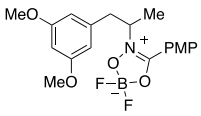
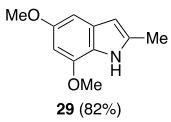
Having established fully optimized conditions, we next examined the substrate scope of the reaction we developed. When brominated **12** was employed, 4-bromo-5,7-dimethoxy indole (**22**) was obtained in 78% yield (Table 2, entry 2). In the case of the substrate having a monosiloxyphenyl group, the indole synthesis proceeded in good conversion to afford the corresponding indoles; the silyl group was mainly eliminated [Table 2, entry 3; total indole 66% (**23**, 15%; **24**, 51%)]. From this result, we recognized that one hydroxy moiety on an aromatic group was sufficient to promote the newly discovered C−N bond formation reaction. Furthermore, dialkyl-substituted monomethoxy substrates are also suitable substrates to promote the indole formation. The three-membered ring indole **25** was obtained in 48% yield (Table 2, entry 4). The unique biphenyl indole **26** was also successfully prepared through our newly discovered methodology (70%; Table 2, entry 5). C3-substituted indoles were also obtained. When substrates with methyl or phenyl group substituents on tether were employed in the reaction, the desired C3-substituted indoles **27** and **28** were obtained in high yields (**27**, 76%; **28**, 99%; Table 2, entries 6 and 7). A C2-methyl-substituted indole **29** was also obtained in excellent yield (82%; Table 2, entry 8).

Next, the one-carbon-elongated substrate **30** was employed to prepare hydroquinoline **31** or its double bond isomers (Scheme 6). When **30** was treated with PIFA followed by Et_3N treatment, the unexpected 6,8-dimethoxyquinoline (**32**) and 6,8-dimethoxy-1,2,3,4-tetrahydroquinoline (**33**) were obtained in 43% and 31% yields, respectively. These results indicated that a redox disproportionation reaction of the generated **31** took place after the desired intramolecular C−N bond formation reaction. Therefore, additional PIFA oxidation to quinoline **32** from tetrahydroquinoline **33** was carried out in a one-pot operation. After removal of the Et_3N and solvent from the reaction mixture, PIFA in HFIP was directly added to the reaction vessel, once again. As a result, quinoline **32** was obtained as the sole product in 71% yield. Thus, our methodology was expanded to include the synthesis of quinoline.

In conclusion, we have discovered a new stepwise and oxidative intramolecular C−N bond formation reaction, which uses a boron-masking *N*-hydroxyamide. The reaction commenced with the generation of a diaryliodonium salt by treatment with hypervalent iodine, deborylation by base treatment, spontaneous N → O acyl migration, cyclization, reductive elimination, elimination of benzoic acid, and tautomerization to afford multisubstituted indoles or quinoline. The six-step transformation proceeded in one pot, following a simple protocol. The methods described here are useful for the efficient synthesis of electron-rich indoles, which are usually difficult to synthesis by oxidation. Unprotected electron-rich

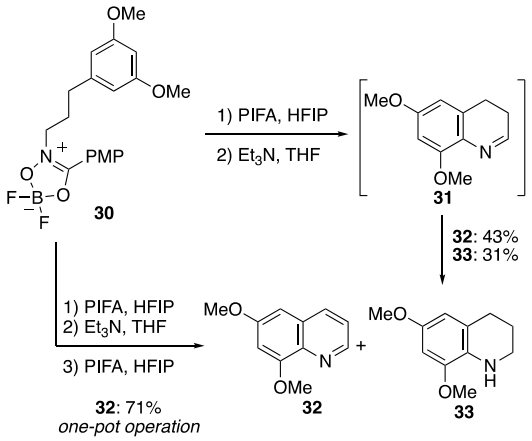
Table 2. Substrate Scope[a]



entry	Substrates	Products (yield[b])
1		 **9** (98%)
2		 **22** (78%)
3		 **23** (15%) **24** (51%)
4[c]		 **25** (48%)
5		 **26** (70%)
6		 **27** (76%)
7		 **28** (99%)
8		 **29** (82%)

[a]Reaction conditions. Step 1: a reaction mixture of the boron complex (0.0528 mmol) and PIFA (0.0528 mmol) in HFIP (3.6 mL) was stirred at 0 °C, followed by evaporation to remove all HFIP. Step 2: Et_3N (0.528 mmol) was added to the crude mixture of the products of step 1 in THF (3.6 mL) at 0 °C. [b]Isolated yield. [c]Excess aqueous saturated $NaHCO_3$ was employed in step 2 (see the details in the Supporting Information).

Scheme 6. Synthesis of 6,8-Dimethoxyquinoline



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indoles are usually highly sensitive toward oxidants. Thus, in this stepwise protocol, the usage of boron-masking *N*-hydroxyamide as the substrate and acyl migration after the preparation of diaryliodonium salts are the keys to success. This method may also be referred to as aromatic C−H amination. The reaction proceeds very efficiently to afford highly functionalized indoles and quinoline. Further developments related to the reaction with this unique mechanism are currently underway in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04076.

^{1}H-NMR data; kinetic study; experimental details and characterization data for all new compounds (PDF)

Accession Codes

CCDC 1963790 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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