

Benzimidazolinone synthesis through hypervalent iodine-mediated cycloaddition between aryl isocyanates and *O*-substituted hydroxylamines

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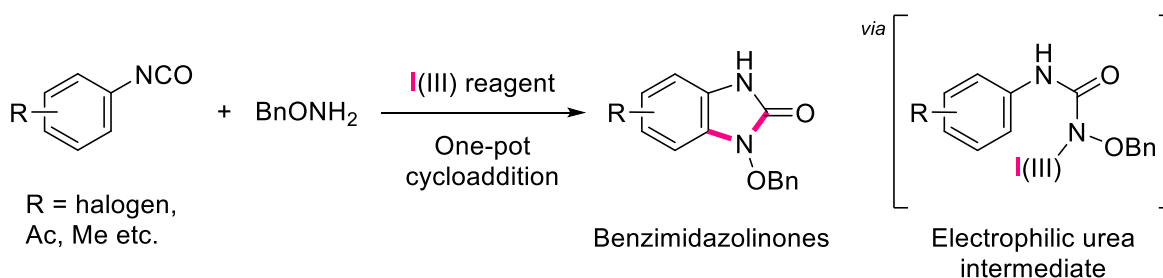
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Abstract

We developed a one-pot cycloaddition methodology for the synthesis of benzimidazolinones, which involves the formation of arylureas using *O*-benzyl hydroxylamine as a specific nitrogen source, followed by oxidative aromatic C–H amination promoted by hypervalent iodine reagent and catalyst. Our protocol utilized readily available starting materials, thereby enabling rapid access to the target benzimidazolinones. Additionally, the product from this one-pot process was further derivatized to produce an *N,N'*-disubstituted benzimidazolinone.

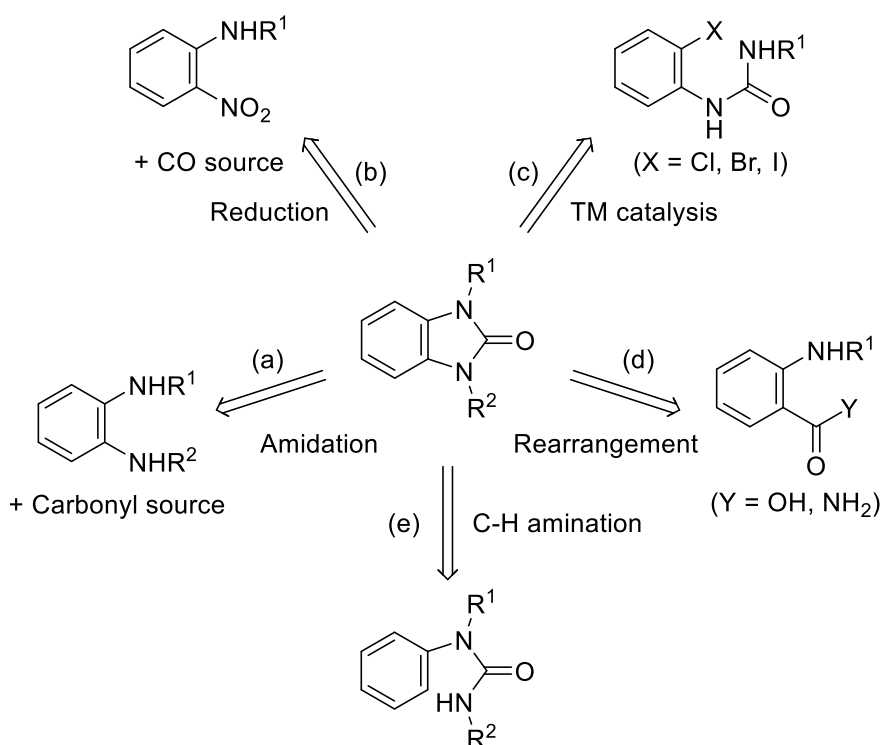


Keywords: Hypervalent iodine, cycloaddition, C–H amination, one-pot synthesis, benzimidazolinones

Introduction

Benzimidazolinones, a class of benzo-fused cyclic ureas, are instrumental in the discovery of biologically active compounds. Numerous molecules incorporating benzimidazolinone motifs have been synthesized and evaluated. These molecules exhibit diverse biological activities, including antitumor activity,¹ modulation of peroxisome proliferator-activated receptors,² inhibition of amino acid oxidase,³ and deregulation of B-cell lymphoma 6 protein.⁴ Consequently, benzimidazolinone structures serve as important scaffolds for the identification of bioactive compounds.

Numerous synthetic methodologies have been developed for the production of benzimidazolinones. A common method involves the amidation of 1,2-diaminobenzenes with an appropriate carbonyl source (Scheme 1a).⁵⁻¹² Another synthetic approach involves a reductive carbonylation reaction in which 2-nitroanilines are activated in the presence of a reduction catalyst and carbon monoxide sources (Scheme 1b).¹³⁻¹⁶ Transition-metal-catalyzed intramolecular C–N coupling reactions have also been employed for the synthesis of benzimidazolinones (Scheme 1c).¹⁷⁻²⁶ Furthermore, the synthesis of benzimidazolinones was accomplished through cascade reactions in which 2-aminobenzoic acid derivatives were converted into the corresponding isocyanates, followed by successive intramolecular attacks by amino groups to furnish the benzimidazolinone structures (Scheme 1d).²⁷⁻³¹ Currently, various techniques are used to produce benzimidazolinones.



Scheme 1. Representative synthetic methodologies for accessing benzimidazolinones.

C–H amination has emerged as an effective strategy for benzimidazolinone production. Unlike conventional methods, which depend on preinstalled functional groups on the aromatic rings, C–H amination reactions enable the direct transformation of omnipresent aromatic C–H bonds into C–N bonds (Scheme 1e), thereby offering streamlined access to benzimidazolinones from readily available precursors. Over the past few

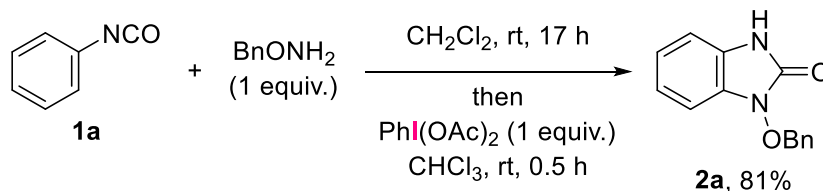
decades, various C–H amination reactions specifically dedicated to the synthesis of benzimidazolinones have been developed, utilizing common starting materials, such as arylureas,^{32–34} anilines,³⁵ and anilides.³⁶ Although these pioneering methodologies require harsh reaction conditions, toxic reagents, and specialized equipment, C–H amination reactions have demonstrated their efficacy as systems for the synthesis of benzimidazolinones.

Hypervalent iodine reagents, recognized for their low toxicity, safety, and environmental compatibility, serve as potent organic oxidants for the synthesis of benzimidazolinones. These reagents facilitate C–H amination reactions under mild conditions using a standard laboratory apparatus, enabling the one-step synthesis of structurally diverse benzimidazolinones from easily accessible aryl urea.^{37,38} In addition to their stoichiometric applications, significant advancements have been made in the catalytic use of hypervalent iodine reagents over the past two decades.³⁹ Recently, catalytic methodologies have been successfully employed in the synthesis of benzimidazolinones, thereby minimizing the consumption of expensive hypervalent iodine reagents.^{40,41}

We anticipate that the practical synthesis of benzimidazolinones can be achieved using hypervalent iodine reagents. Recently, Youn et al. demonstrated a transition-metal-catalyzed C–H amination protocol that facilitated the one-pot formation of benzimidazolinones from aryl isocyanates and amines.⁴² However, this method requires stringent conditions to efficiently promote the reaction. Given the reactivity of hypervalent iodine reagents under mild conditions, it was hypothesized that hypervalent iodine-mediated C–H amination reactions could enhance the existing cycloaddition procedure. In this study, we investigated the one-pot cycloaddition synthesis of benzimidazolinones, starting from aryl isocyanate amines and hydroxyl amines via a C–H amination reaction facilitated by a hypervalent iodine reagent.

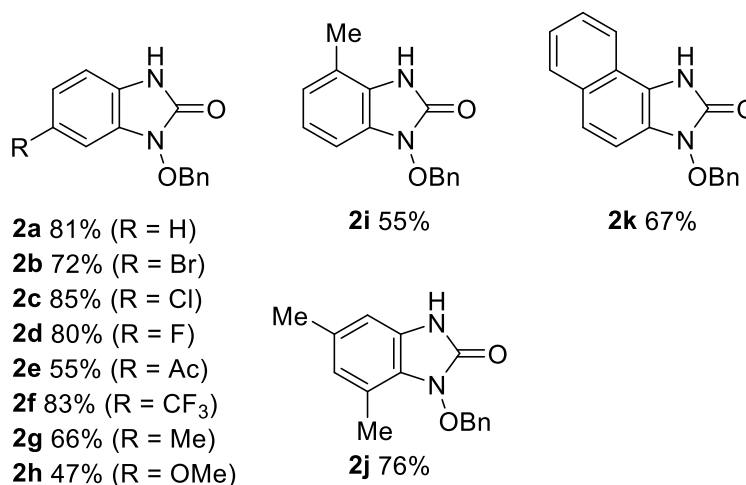
Results and Discussion

Initially, we conducted a preliminary study to determine the optimal reaction conditions for cycloaddition synthesis. Drawing on our previous findings, *N*-alkoxy-*N'*-arylureas, synthesized via an addition reaction between aryl isocyanates and *O*-alkoxyamines, were selected as pivotal intermediates. Systematic evaluation of the reaction conditions led to the determination of an effective reagent combination, as illustrated in Scheme 2. Gratefully, the residue from the reaction between phenyl isocyanate **1a** (0.3 mmol) and commercially available *O*-benzyloxyamine was treated with phenyliodine(III) diacetate to obtain benzimidazolinone **2a** in an 81% yield. This was achieved after the dichloromethane solvent was removed under reduced pressure and replaced with chloroform (Scheme 2). A scale-up experiment using 1.0 g of **1a** afforded **2a** in 75% yield, which was comparable to the result obtained on the 0.3 mmol scale experiment. Condition-screening experiments revealed that no benzimidazolinone formation occurred when *O*-benzyloxyamine was replaced with other amines, such as *N*-aminophthalimide, *O*-(tetrahydropyran-2-yl)hydroxylamine, and *p*-nitrobenzyloxycarbonyl-protected hydroxylamine. Furthermore, the use of *O*-benzyloxyamine hydrochloride reduced the yield of **2a** (66%), likely because of the diminished nucleophilicity of the amine salt. However, the addition of Hünig's base to release free *O*-methoxyamine from the hydrochloride failed to promote the cycloaddition reaction, resulting in the absence of **2a**. A slight decrease in the yield of **2a** (69%) was observed when the C–H amination reaction was performed in dichloromethane, indicating that chloroform was a more effective solvent.



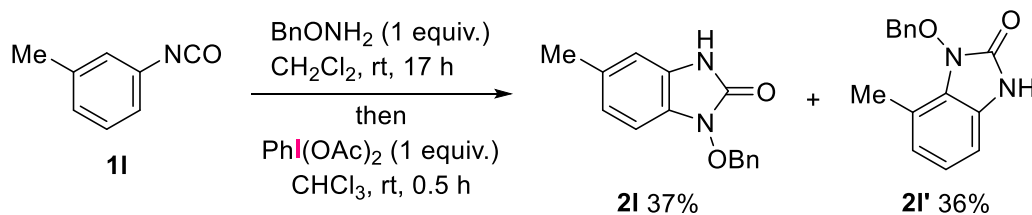
Scheme 2. Initial trial of the one-pot cycloaddition.

The substrate scope of the cycloaddition reaction was investigated (Scheme 3). Halogen-substituted isocyanates **1b–d** exhibited comparable reactivities, giving benzimidazolinones **2b–d** in yields ranging from 72% to 85%. Isocyanates containing electron-withdrawing groups **1e** and **1f** produced cyclized products **2e** and **2f** in 60% and 83% yields, respectively. Electron-rich isocyanates **1g** and **1h** were tolerant of the reaction conditions, providing benzimidazolinones **2g** and **2h** in 66% and 47% yields, respectively. The reactions of *ortho*-substituted isocyanates **1i** and disubstituted isocyanate **1j** under the reaction conditions resulted in the formation of benzimidazolinones **2i** and **2j** in moderate yields. Furthermore, naphthalene-containing isocyanate **1k** was compatible with iodine-mediated oxidation, yielding the corresponding product **2k** in a 67% yield.



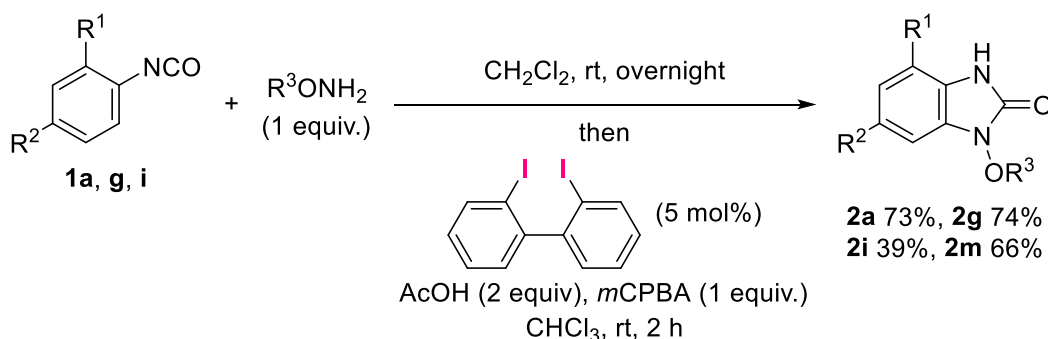
Scheme 3. Substrate scope. Reaction conditions: **1a–k** (0.30 mmol), *O*-benzylhydroxyamine (0.30–0.40 mmol) in dichloromethane (1 mL) at room temperature for 17 h and then iodobenzene diacetate (0.30 mmol) in chloroform (1.5 mL) at room temperature for 0.5 h.

Meta-substituted isocyanate **1l** yielded a regioisomeric mixture of benzimidazolinones **2l** and **2l'** (Scheme 4). ¹H NMR spectroscopy analysis of the product mixture indicated that **2l** and **2l'** were produced in an approximately 1:1 ratio.



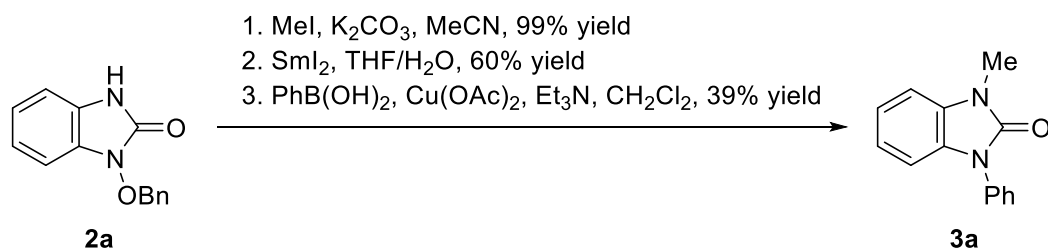
Scheme 4. Reaction of *meta*-substituted isocyanate **1l**.

Hypervalent iodine catalysis was applied in the C–H amination step of the one-pot synthesis to develop a more efficient cycloaddition procedure (Scheme 5). Drawing upon our previous work,⁴¹ 2,2'-diiodobiphenyl was selected as a precursor of highly reactive hypervalent iodine catalyst. Subsequent to the formation of the arylurea intermediate from isocyanate **1a**, an *in situ* generated iodine catalyst facilitated the C–H amination reaction, affording benzimidazolone **2a** in a 73% yield in the presence of *m*-chloroperbenzoic acid (*m*CPBA) and acetic acid. Under the catalytic reaction conditions, *p*-methyl substituted isocyanate **1g** afforded the cyclized product **2g** in a 74% yield, whereas *o*-methyl isocyanate **1i** produced the corresponding product **2i** in a 39% yield. In addition, *O*-(4-nitrobenzyl)hydroxyamine hydrochloride was a viable amine source, providing benzimidazolone **2m** in a 66% yield.



Scheme 5. Synthesis of benzimidazolones via hypervalent iodine catalysis. Products: **2a** (R¹ = R² = H, R³ = Bn), **2g** (R¹ = H, R² = Me, R³ = Bn), **2i** (R¹ = Me, R² = H, R³ = Bn), **2m** (R¹ = R² = H, R³ = 4-nitrobenzyl).

Benzimidazolone product **2a** was further derivatized to synthesize **3a**, featuring different substituents on each nitrogen atom (Scheme 6). *N*-methylation of **2a** was achieved using iodomethane under basic conditions. Subsequently, samarium-mediated reductive N–O bond cleavage resulted in the formation of *N*-methyl-2-benzimidazolone, which underwent *N*-phenylation⁴³ to yield *N*-methyl-*N'*-phenyl benzimidazolone **3a**.



Scheme 6. Derivatization of the cycloaddition reaction product.

Conclusions

We developed a mild, metal-free, synthetic approach for the production of benzimidazolinones utilizing hypervalent iodine reagent and catalyst. The key to this method is the use of *O*-benzyl hydroxylamine as an external nitrogen source, which allows base-free synthesis of arylurea intermediates. Subsequent C–H amination reactions were facilitated by a hypervalent iodine reagent, providing various benzimidazolinones with efficiencies reaching up to an 85% yield. An additional experiment demonstrated the applicability of hypervalent iodine catalysis in the cycloaddition process. The product of the cycloaddition reaction was further derivatized to obtain asymmetric benzimidazolinones with different substituents on each nitrogen atom.

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-AL400 spectrometer (^1H NMR: 400 MHz, ^{19}F NMR: 376 MHz, and ^{13}C NMR: 100 MHz at 25 °C. The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. The chemical shifts in the ^1H NMR spectra were recorded relative to the residual solvent peaks (CDCl_3 : δ 7.26, $\text{DMSO}-d_6$: δ 2.50). The chemical shifts in the ^{13}C NMR spectrum were also recorded relative to the residual solvent peaks (CDCl_3 : δ 77.0, $\text{DMSO}-d_6$: δ 39.5). The chemical shifts in ^{19}F NMR spectrum were recorded relative to residual solvent peaks (PhCF_3 : δ -63.7). Melting points were measured using a Büchi B 545 apparatus and uncorrected. High-resolution mass spectra obtained using a direct analysis method in real time (DART) were recorded using a Thermo Scientific Exactive Plus Orbitrap (Thermo Fisher Scientific, Inc., Waltham, MA, USA). Flash column chromatography and analytical TLC were performed using Merck Silica gel 60 (230–400 mesh) and Merck Silica gel F254 plates (0.25 mm), respectively. Spots and bands were detected via ultraviolet irradiation (254 and 365 nm) or by staining with 5% phosphomolybdic acid, followed by heating.

General procedure for the one-pot synthesis of benzimidazolinones 2. Arylisocyanate **1** (0.3 mmol) and *O*-benzyloxylamine (0.3–0.4 mmol) were dissolved in CH_2Cl_2 (1.0 mL) in a sealed tube. After stirring at room temperature for 17 h, the reaction mixture was concentrated under reduced pressure. CHCl_3 (1.5 mL) and iodobenzene diacetate (0.3 mmol) were added to the resulting residue, and the mixture was stirred at room temperature for 0.5 h. The resulting mixture was treated with saturated aqueous solutions of NaHCO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ and then extracted with CH_2Cl_2 (5 mL \times 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4 . After filtering, the solution was concentrated and purified using flash column chromatography to obtain desired product **2**, which was triturated if necessary.

1-(Benzyloxy)-1,3-dihydro-2H-benzo[d]imidazol-2-one (2a). Following the general procedure, **1a** (36.8 mg, 0.3 mmol) and *O*-benzyloxylamine (42.3 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (67.4 mg, 81% yield); ^1H NMR (400 MHz, CDCl_3): δ 10.70 (s, 1H), 7.50 (dd, J = 6.3 Hz, 2.9 Hz, 2H), 7.37–7.35 (m, 3H), 7.13–7.11 (m, 1H), 7.04–6.97 (m, 2H), 6.82 (d, J = 7.3 Hz, 1H), 5.27 (s, 2H).; ^{13}C NMR (100 MHz, CDCl_3): δ 153.0, 134.3, 130.1, 129.4, 128.8, 127.9, 124.3, 122.1, 121.7, 110.4, 107.3, 79.4.

Spectrum data of **2a** were matched with the product reported in literature.³

1-(Benzyloxy)-6-bromo-1,3-dihydro-2H-benzo[d]imidazol-2-one (2b). Following the general procedure, **1b** (60.3 mg, 0.3 mmol) and *O*-benzyloxylamine (36.7 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (68.2 mg, 72% yield); ¹H NMR (400 MHz, CDCl₃): δ 9.38 (s, 1H), 7.50-7.48 (m, 2H), 7.42-7.38 (m, 3H), 7.14 (dd, *J* = 8.3 Hz, 2.0 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 1.0 Hz, 1H), 5.25 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 152.7, 133.9, 130.2, 129.8, 129.0, 128.9, 125.0, 123.2, 114.6, 111.6, 110.6, 79.7.

1-(Benzyloxy)-6-chloro-1,3-dihydro-2H-benzo[d]imidazol-2-one (2c). Following the general procedure, **1c** (46.5 mg, 0.3 mmol) and *O*-benzyloxylamine (39.8 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (70.5 mg, 85% yield); ¹H NMR (400 MHz, CDCl₃): δ 10.55 (s, 1H), 7.51-7.47 (m, 2H), 7.41-7.38 (m, 3H), 7.01-7.00 (m, 2H), 6.75 (d, *J* = 1.5 Hz, 1H), 5.26 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 152.9, 133.9, 130.2, 129.7, 128.9, 128.7, 127.5, 122.7, 122.2, 111.2, 107.8, 79.7.

Spectrum data of **2c** were matched with the product reported in literature.³

1-(Benzyloxy)-6-fluoro-1,3-dihydro-2H-benzo[d]imidazol-2-one (2d). Following the general procedure, **1d** (44.7 mg, 0.3 mmol) and *O*-benzyloxylamine (36.4 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (60.9 mg, 80% yield); ¹H NMR (400 MHz, CDCl₃): δ 10.66 (s, 1H), 7.49-7.48 (m, 2H), 7.39-7.38 (m, 3H), 7.02 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 6.73 (td, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.50 (dd, *J* = 8.0 Hz, 1.7 Hz, 1H), 5.27 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 158.8 (d, *J* = 239.2 Hz), 153.5, 134.0, 130.2, 129.7, 128.9, 128.5 (d, *J* = 12.4 Hz), 120.2 (d, *J* = 1.7 Hz), 110.9 (d, *J* = 9.1 Hz), 108.8 (d, *J* = 24.0 Hz), 95.7 (d, *J* = 29.8 Hz), 79.6; ¹⁹F NMR (376 MHz, CDCl₃): δ -121.1.

Spectrum data of **2d** were matched with the product reported in literature.³

6-Acetyl-1-(benzyloxy)-1,3-dihydro-2H-benzo[d]imidazol-2-one (2e). Following the general procedure, **1e** (48.9 mg, 0.3 mmol) and *O*-benzyloxylamine (45.5 mg, 0.4 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 1:1), the title compound was obtained as a white amorphous solid (51.6 mg, 60% yield); ¹H NMR (400 MHz, CDCl₃): δ 9.73 (s, 1H), 7.71 (dd, *J* = 8.3 Hz, 2.0 Hz, 1H), 7.53-7.51 (m, 2H), 7.40-7.38 (m, 3H), 7.30 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.30 (d, *J* = 2.9 Hz, 2H), 2.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 196.9, 153.2, 134.1, 131.6, 130.3, 129.7, 128.9, 128.2, 128.1, 123.8, 109.9, 107.6, 79.9, 26.6; HRMS *m/z* calcd for [M]⁺ 282.1004, found 282.0998.

1-(Benzyloxy)-6-(trifluoromethyl)-1,3-dihydro-2H-benzo[d]imidazol-2-one (2f). Following the general procedure, **1f** (58.0 mg, 0.3 mmol) and *O*-benzyloxylamine (36.5 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (70.6 mg, 83% yield); ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.53 (s, 1H), 7.52 (d, *J* = 2.4 Hz, 2H), 7.37-7.36 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 5.22 (s, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 151.1, 134.5, 130.2, 129.2, 128.5, 128.0, 127.5, 124.6 (q, *J* = 271.5 Hz), 121.7 (q, *J* = 32.3 Hz), 118.74 (q, *J* = 4.1 Hz), 109.6, 103.4 (q, *J* = 4.1 Hz), 78.8; ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ -62.0; HRMS *m/z* calcd for [M]⁺ 308.0773, found 308.0769.

1-(Benzyloxy)-6-methyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2g). Following the general procedure, **1g** (40.7 mg, 0.3 mmol) and *O*-benzyloxylamine (35.6 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1) and subsequent trituration with *n*-hexane from CH₂Cl₂ solution, the title compound was obtained as a white amorphous solid (48.3 mg, 66% yield); ¹H NMR (400 MHz, CDCl₃): δ 9.83 (bs, 1H), 7.53-7.52 (m, 2H), 7.39-7.38 (m, 3H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.62 (s, 1H), 5.26 (s, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 152.9, 134.4, 131.7, 130.1, 129.4, 128.8, 128.1, 122.7, 122.0, 110.0, 107.9, 79.4, 21.5.

Spectrum data of **2g** were matched with the product reported in literature.³

1-(Benzyloxy)-6-methoxy-1,3-dihydro-2H-benzo[d]imidazol-2-one (2h). Following the general procedure, **1h** (53.4 mg, 0.3 mmol) and *O*-benzyloxylamine (36.6 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1) and subsequent trituration with *n*-hexane from CH₂Cl₂ solution, the title compound was obtained as a white amorphous solid (37.5 mg, 47% yield); ¹H NMR (400 MHz, CDCl₃): δ 10.29 (s, 1H), 7.52-7.49 (m, 2H), 7.38-7.37 (m, 3H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.58 (dd, *J* = 8.5 Hz, 1.2 Hz, 1H), 6.30 (s, 1H), 5.26 (s, 2H), 3.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 155.7, 153.3, 134.5, 130.3, 129.5, 128.9, 128.9, 117.9, 110.8, 108.4, 93.9, 79.5, 55.9.

1-(Benzyloxy)-4-methyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2i). Following the general procedure, **1i** (41.4 mg, 0.3 mmol) and *O*-benzyloxylamine (36.6 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (41.3 mg, 55% yield); ¹H NMR (400 MHz, CDCl₃): δ 10.07 (s, 0.3H), 7.51-7.50 (m, 2H), 7.38-7.36 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.3 Hz, 1H), 5.25 (s, 2H), 2.38 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 151.4, 134.5, 129.9, 129.1, 128.5, 127.4, 123.3, 122.7, 121.0, 119.2, 104.2, 78.2, 15.8.

Spectrum data of **2i** were matched with the product reported in literature.³

1-(Benzyloxy)-5,7-dimethyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2j). Following the general procedure, **1j** (50.0 mg, 0.3 mmol) and *O*-benzyloxylamine (37.2 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a white amorphous solid (61.8 mg, 76% yield); ¹H NMR (400 MHz, CDCl₃): δ 10.30 (s, 1H), 7.57-7.55 (m, 2H), 7.42-7.40 (m, 3H), 6.82 (s, 1H), 6.68 (s, 1H), 5.27 (s, 2H), 2.49 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 153.3, 133.9, 132.1, 129.8, 129.3, 128.8, 125.2, 125.0, 123.7, 119.1, 108.7, 79.7, 21.3, 16.6.

3-(Benzyloxy)-1,3-dihydro-2H-naphtho[1,2-*d*]imidazol-2-one (2k). Following the general procedure, **1k** (55.8 mg, 0.3 mmol) and *O*-benzyloxylamine (36.3 mg, 0.3 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 2:1), the title compound was obtained as a pale green amorphous solid (57.5 mg, 67% yield); ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.90 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.56-7.51 (m, 4H), 7.40-7.36 (m, 4H), 7.18 (d, *J* = 8.3 Hz, 1H), 5.26 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 152.8, 134.2, 130.1, 129.7, 129.4, 128.7, 126.6, 124.2, 123.5, 122.1, 120.5, 119.9, 118.1, 108.3, 79.7.

Spectrum data of **2k** were matched with the product reported in literature.³²

1-(Benzyloxy)-5-methyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2l) and 1-(Benzyloxy)-7-methyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2l') (mixture). Following the general procedure, **1l** (55.8 mg, 0.3 mmol) and *O*-benzyloxylamine (36.3 mg, 0.3 mmol) were used. After purification via column chromatography (*n*-hexane/ethyl acetate = 2:1), a mixture of the title compounds was obtained as a pale brown amorphous solid (57.2 mg). ¹H NMR spectroscopy analysis of the resulting mixture revealed that **2l** and **2l'** were afforded in 37% and 36%, respectively; ¹H NMR (400 MHz, CDCl₃): δ 10.55 (s, 1H), 10.47 (s, 1H), 7.58-7.55 (m, 2H), 7.53-7.51 (m, 2H), 7.42-7.41 (m, 3H), 7.39-7.37 (m, 3H), 7.00-6.99 (m, 2H), 6.95 (s, 1H), 6.87 (d, *J* = 6.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.30 (s, 2H), 5.27 (s, 2H), 2.54 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 153.0, 134.2, 133.6, 131.8, 129.9, 129.7, 129.2, 129.2, 128.6, 125.7, 125.7, 124.6, 124.4, 124.3, 122.2, 122.1, 119.2, 110.8, 108.1, 107.0, 79.7, 79.2, 21.3, 16.5.

Spectrum data of **2l** and **2l'** were matched with the products reported in literature.³

General procedure for the catalytic one-pot synthesis of benzimidazolinones 2. Aryl isocyanate (1.0 mmol) was added to a solution of *O*-benzyloxylamine (1.0 mmol) in CH₂Cl₂ (1 mL). After stirring overnight at room temperature, the reaction mixture was concentrated under reduced pressure. CHCl₃ (5 mL), 2,2'-diiodobiphenyl (0.05 mmol), acetic acid (2.0 mmol), and *m*-chloroperoxybenzoic acid (1.0 mmol) were added to the resulting residue. The mixture was stirred at room temperature for 2 h, diluted with ethyl acetate, and

transferred to a separate funnel. The organic layer was washed with saturated aqueous solutions of NaHCO₃, Na₂S₂O₃, and brine and dried over Na₂SO₄. After filtration, the solution was concentrated and purified using flash column chromatography to obtain the desired product, **2**.

1-((4-Nitrobenzyl)oxy)-1,3-dihydro-2H-benzo[d]imidazol-2-one (2m). Following the general procedure, **1a** (0.11 mL, 1.0 mmol) and *O*-(4-nitrobenzyl)hydroxylamine hydrochloride (208.7 mg, 1.0 mmol) were used. After purification by column chromatography (*n*-hexane/ethyl acetate = 1:1), the title compound was obtained as a beige solid (232.8 mg, 66% yield); ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.07 (s, 1H), 8.26 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.00 (s, 4H), 5.35 (s, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 151.0, 147.7, 142.0, 130.7, 127.5, 124.6, 123.5, 121.7, 121.1, 109.5, 106.7, 76.9; HRMS *m/z* calcd for [M]⁺ 285.0750, found 285.0747.

Procedure for N-methylation of 2a. K₂CO₃ (0.554 g, 4.01 mmol) and iodomethane (187 μL, 3.00 mmol) were added to a solution of **2a** (0.477 g, 2.00 mmol) in MeCN (25 mL). The reaction mixture was stirred at room temperature for 24 h. An aqueous NH₃ solution was added to the reaction mixture. The resulting mixture was poured into a separating funnel with ethyl acetate and water. The organic layer was partitioned, and the aqueous layer was extracted with EtOAc. After drying and concentrating the mixture, chromatography (*n*-hexane/ethyl acetate = 1:1) of the crude material yielded **2a'** (0.500 g, 99% yield).

1-(Benzyloxy)-3-methyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2a'). ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.50 (m, 2H), 7.38-7.37 (m, 3H), 7.07-6.93 (m, 3H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 2H), 3.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 134.3, 129.9, 129.2, 128.6, 127.1, 126.4, 121.6, 121.5, 107.6, 107.0, 79.1, 27.1.

Spectrum data of **2a'** were matched with the product reported in literature.³

Procedure for reductive N–O bond cleavage of 2a'. SmI₂ (0.1 M in THF, 20 mL, 10.0 equiv.) was added to a solution of **2a'** (51.1 mg, 0.2 mmol) in dry THF (2 mL) and deoxygenated water (0.1 mL) at 0 °C. At the same temperature, the mixture was stirred for 3 h, diluted with ethyl acetate, washed with saturated NaHCO₃, saturated Na₂S₂O₃, and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified using column chromatography (*n*-hexane/ethyl acetate = 1:1) to obtain **2a''** (17.8 mg, 60%).

1-Methyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2a''). ¹H NMR (400 MHz, CDCl₃): δ 10.46 (s, 1H), 7.14-7.12 (m, 1H), 7.10-7.08 (m, 2H), 6.99-6.98 (m, 1H), 3.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.2, 131.0, 128.1, 121.7, 121.4, 109.8, 107.8, 27.0.

Spectrum data of **2a''** were matched with the product reported in literature.⁴⁴

Procedure for N-phenylation of 2a. A slurry of **2a''** (7.47 mg, 0.05 mmol), phenylboronic acid (12.68 mg, 0.1 mmol), anhydrous Cu(OAc)₂ (10.17 mg, 0.05 mmol), and triethylamine (14 μL, 0.1 mmol) in dichloromethane (2 mL) were stirred at room temperature for 56 h. The progress of the reaction was monitored using TLC. The mixture was then concentrated under reduced pressure. The residue was purified using column chromatography (*n*-hexane/ethyl acetate = 4:1) to yield **3a** (4.4 mg, 39%).

1-Methyl-3-phenyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (3a). ¹H NMR (400 MHz, CDCl₃): δ 7.54-7.53 (m, 4H), 7.43-7.37 (m, 1H), 7.18-7.12 (m, 1H), 7.09-7.05 (m, 3H), 3.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 153.7, 134.9, 130.3, 129.6, 129.5, 127.7, 126.1, 122.1, 121.6, 108.8, 107.8, 27.4.

Spectrum data of **3a** were matched with the product reported in literature.³³

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Supplementary Material

Supplementary data associated with this article is available in the Supplementary Material.

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