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Synthesis of Benzimidazolones via One-Pot Reaction of Hydroxylamines, Aldehydes, and Trimethylsilyl Cyanide Promoted by Diacetoxyiodobenzene

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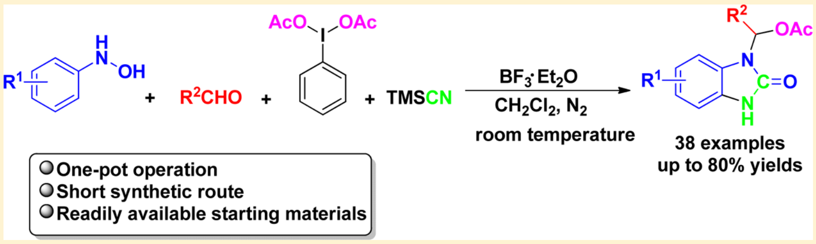
Ⓢ *Supporting Information*



ABSTRACT: A novel and efficient $PhI(OAc)_2$-promoted one-pot reaction of aromatic hydroxylamines, aldehydes, and TMSCN in the presence of $BF_3{\cdot}Et_2O$ is described. A wide variety of *N*-substituted benzimidazolones are obtained with satisfactory yields under mild reaction conditions. The method was proven to be efficient for the synthesis of benzimidazolone derivatives from readily available starting materials.

■ INTRODUCTION

Benzimidazolones, important derivatives of benzimidazoles, were found to exhibit a wide range of biological activities such as antidiabetic,[1] antiulcer,[2] anti-infective,[3] and analgesic agents.[4] Many benzimidazolone-containing organic molecules, such as oxatomide, droperidol, and others, have been successfully developed as clinical drugs (Figure 1).[5−8] Furthermore, benzimidazolones have also been widely used in material science.[9−13] For instance, Pigment Yellow 151, a greenish shade of yellow pigment,[14] is widely applied in plastics, inks, and industrial paint because of its high color strength, excellent heat stability, warping resistance, and good fastness.

Thus, considerable attention has been paid to the development of methods for the construction of benzimidazolone-containing organic compounds.[15−17] Until now, many synthetic approaches have been developed for the synthesis of benzimidazolone and its derivatives (Scheme 1, a−d). The conventional methods are based on phosgenation of *o*-phenylenediamine[18] and are being gradually discarded since phosgene is highly toxic. Recently, several nonphosgene approaches have been reported, including condensation of *o*-phenylenediamines or 2-nitroaniline with urea,[19] dimethyl carbonate,[20] carbon dioxide,[21] or carbon monoxide.[22] Benzimidazolones can also be generated by the reaction of 2-aminobenzamide with iodosylbenzene,[23] ionic-liquid-catalyzed carbonylation of *o*-phenylenediamines with CO_2,[21] and cascade C−N coupling of monosubstituted ureas.[24] Although much progress has been made toward the synthesis of benzimidazolones, it is still necessary to develop more effective methods for the synthesis of benzimidazolone and its derivatives.

On the other hand, diacetoxyiodobenzene ($PhI(OAc)_2$), one of the most popular hypervalent iodine reagents, is widely used in organic synthesis due to their low toxicity, high stability, ease of handling, and commercial availability. Except for its traditional application as oxidative reagent in organic synthesis, $PhI(OAc)_2$ has also been applied in other transformations,[25] including α-functionalization of carbonyl compounds,[26] C−C bond forming reactions,[27] C−O bond forming reactions,[28] cyclizations,[29] etc. In this paper, we report the first example of $PhI(OAc)_2$-promoted one-pot reaction of hydroxylamines, aldehydes, and trimethylsilyl cyanide in the presence of Lewis acids to afford the biologically interesting *N*-monosubstituted benzimidazolones in good yields (Scheme 1, e).

■ RESULTS AND DISCUSSION

We initiated our study with *N*-phenylhydroxylamine **1a** and benzaldehyde **2a** as subsatrates, 1 equiv of $PhI(OAc)_2$ **3a** as oxidant, 3 equiv of TMSCN **4** as N-source, and 4 equiv of $BF_3{\cdot}Et_2O$ **5a** as Lewis acid. The reaction was carried out in dry CH_2Cl_2 under nitrogen atmosphere at room temperature. The desired product **6a** was obtained with 30% yield. Next, the reaction conditions were examined in detail in order to improve the yield, and the results are summarized in Table 1. When the molar ratio of *N*-phenylhydroxylamine **1a** and benzaldehyde **2a**

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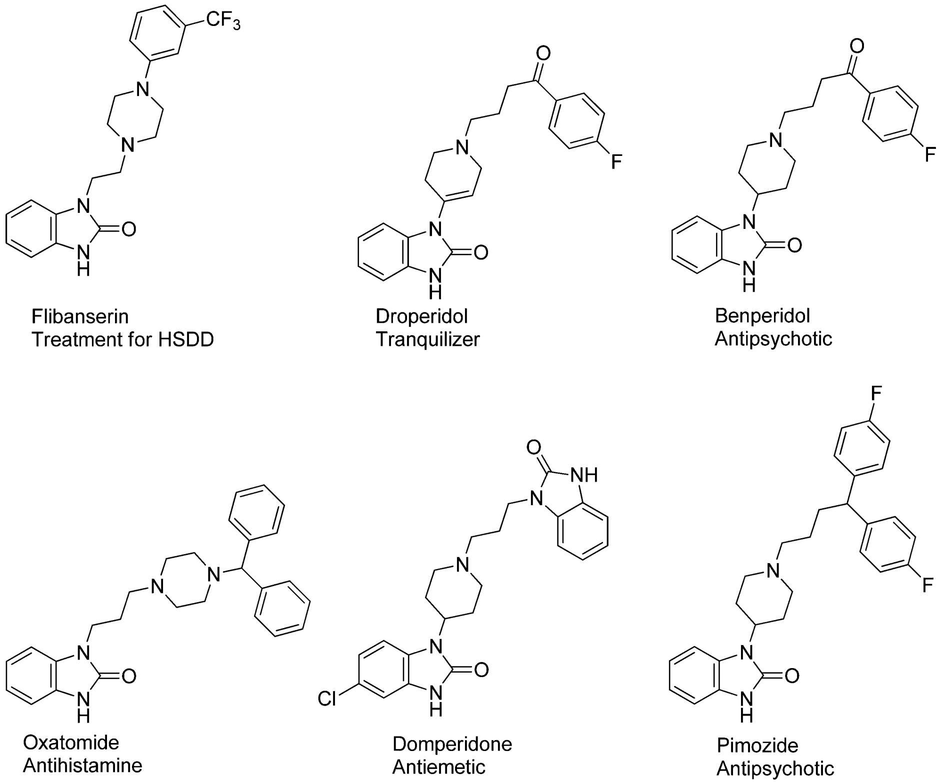


Figure 1. Representative clinical drugs containing benzimidazolones.

Scheme 1. Preparation of Benzimidazolones

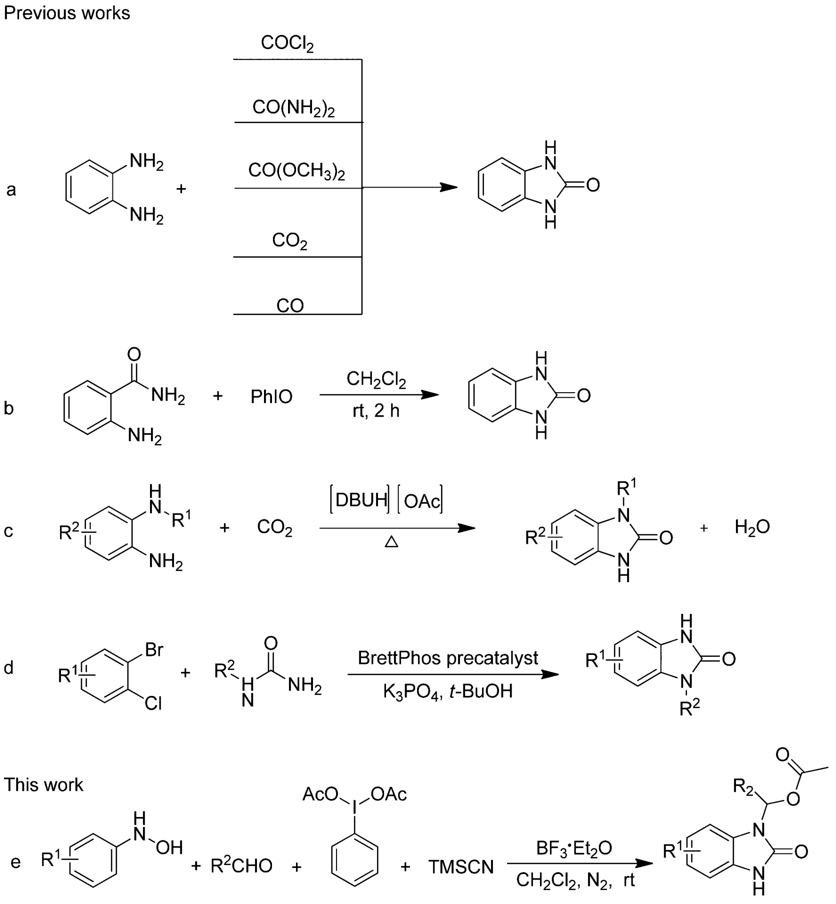
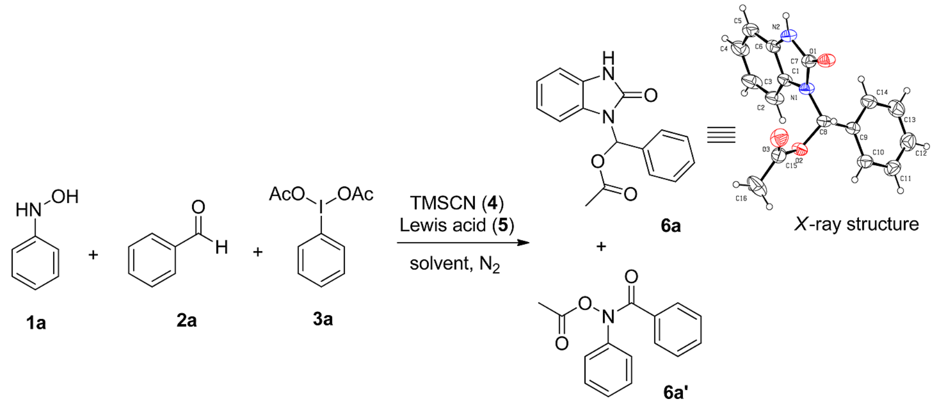


Table 1. Optimization of the Reaction Conditions[a]



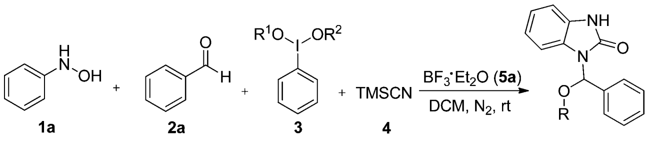
entry	1a/2a/3a/4/5 molar ratio	Lewis acid	solvent	products[b] (%) 6a	products[b] (%) 6a′
1	1:1:1:3:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	30	0
2	1:1:1.5:3:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	41	0
3	1:1:2:3:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	61	0
4	1:1:3:3:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	49	0
5	1:1:2:2:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	44	0
6	1:1:2:4:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	48	0
7	1:1:2:3:3	$BF_3 \cdot Et_2O$	CH_2Cl_2	46	0
8	1:1:2:3:5	$BF_3 \cdot Et_2O$	CH_2Cl_2	50	0
9	1:1:2:3:0	$BF_3 \cdot Et_2O$	CH_2Cl_2	0	0
10	1:1:2:3:4	$BF_3 \cdot Et_2O$	THF	35	0
11	1:1:2:3:4	$BF_3 \cdot Et_2O$	DMF	24	0
12	1:1:2:3:4	$BF_3 \cdot Et_2O$	PhMe	31	0
13	1:1:2:3:4	$BF_3 \cdot Et_2O$	MeCN	45	0
14	1:1:2:3:4	$BF_3 \cdot Et_2O$	$CHCl_3$	49	0
15	1:1:2:3:4	$BF_3 \cdot Et_2O$	$MeNO_2$	48	0
16	1:1:2:3:4	$ZnCl_2$	CH_2Cl_2	10	35
17	1:1:2:3:4	$FeCl_3$	CH_2Cl_2	0	0
18	1:1:2:3:4	$AlCl_3$	CH_2Cl_2	5	30
19	1:1:2:3:4	$SnCl_4$	CH_2Cl_2	0	0
20	1:1:2:3:4	$Mg(ClO_4)_2$	CH_2Cl_2	0	13
21	1:1:2:3:4	$Cu\ (AcO)_2$	CH_2Cl_2	0	36
22[c]	1:1:2:3:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	24	0
23[d]	1:1:2:3:4	$BF_3 \cdot Et_2O$	CH_2Cl_2	41	0

[a] Reactions were carried out on a scale of **1a** (0.46 mmol) and **2a** (0.46 mmol) in DCM (5 mL). Nitrone formed from **1a** and **2a** was added under nitrogen atmosphere into a mixture of **3a** (0.92 mmol), **4** (1.38 mmol), and **5** (1.84 mmol), which was stirred in new solvent (5 mL) for 30 min beforehand. [b] Isolated yields. [c] The reaction was conducted at 0 °C. [d] The reaction was conducted under reflux.

was fixed to 1:1,[30] the molar ratio of the substrates **3a**, **4**, and **5a** was examined (Table 1, entries 1−9). It was found that the yield of **6a** increased from 30% to 61% when the molar ratio of $PhI(OAc)_2$ increased from 1 to 2 equiv (Table 1, entries 1−3). Continuing to increase the ratio of $PhI(OAc)_2$ did not lead to an increase of the yield of **6a** (Table 1, entry 4). The molar ratio of TMSCN and $BF_3 \cdot Et_2O$ was also examined. When the amount of TMSCN decreased from 3 to 2 equiv, the yield of **6a** dropped from 61% to 44%, but increasing of its amount to 4 equiv did not influence the result too much (Table 1, entries 3, 5, and 6). Moreover, when $BF_3 \cdot Et_2O$ was used above 4 equiv, the yield of **6a** did not increase (Table 1, entries 3, 7, and 8). In particular, the reaction could not occur in the absence of $BF_3 \cdot Et_2O$, which shows that $BF_3 \cdot Et_2O$ plays an important role in initiating the reaction (Table 1, entry 9). Thus, the best molar ratio of *N*-phenylhydroxylamine/PhCHO/$PhI(OAc)_2$/TMSCN/$BF_3 \cdot Et_2O$ was determined to be 1:1:2:3:4. Afterward, different solvents were screened (Table 1, entries 10−15). The reaction could occur in dichloromethane, acetonitrile, chloroform, and nitromethane, but the yields of **6a** in THF, DMF, and toluene were lower. Consequently, CH_2Cl_2 was chosen as the solvent in the following studies. In order to improve the product yield further, the reactions were carried out in the presence of Lewis acid such as $ZnCl_2$, $FeCl_3$, $AlCl_3$, $SnCl_4$, $Mg(ClO_4)_2$, and $Cu(AcO)_2$ (Table 1, entries 16−21). The results revealed that the use of Lewis acid led to the formation of **6a′** in reaction in addition to **6a**. In particular, when $Mg(ClO_4)_2$ or $Cu(AcO)_2$ was used, **6a′** became the sole product (Table 1, entries 20 and 21). We envisioned that the formation of **6a′** was due to the oxidative rearrangement reaction. Finally, the investigation of temperature on the reaction showed that the yield of **6a** at 0 °C or reflux was lower than that at room temperature (Table 1, entries 22 and 23).

Next, different hypervalent iodine reagents such as [bis(trifluoroacetoxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene were investigated in the reactions (Table 2).

Table 2. Screening of Hypervalent Iodine Reagents[a]



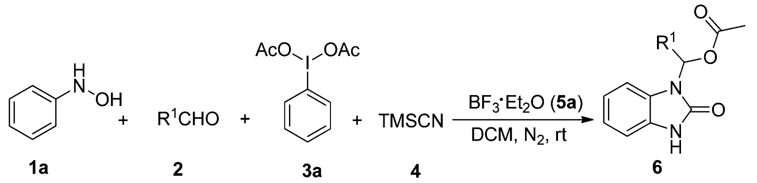
	products	yield[b] (%)
3a: $R^1 = R^2 = Ac$	**6a**: R = Ac	61
3b: $R^1 = R^2 = COCF_3$	**7**: R = $COCF_3$	0
3c: $R^1 = R^2$ = 4-methoxycinnamoyl	**8**: R = 4-methoxycinnamoyl	0
3d: R^1 = H; R^2 = Ts	**9**: R = H	0
3d: R^1 = H; R^2 = Ts	**9′**: R = Ts	0

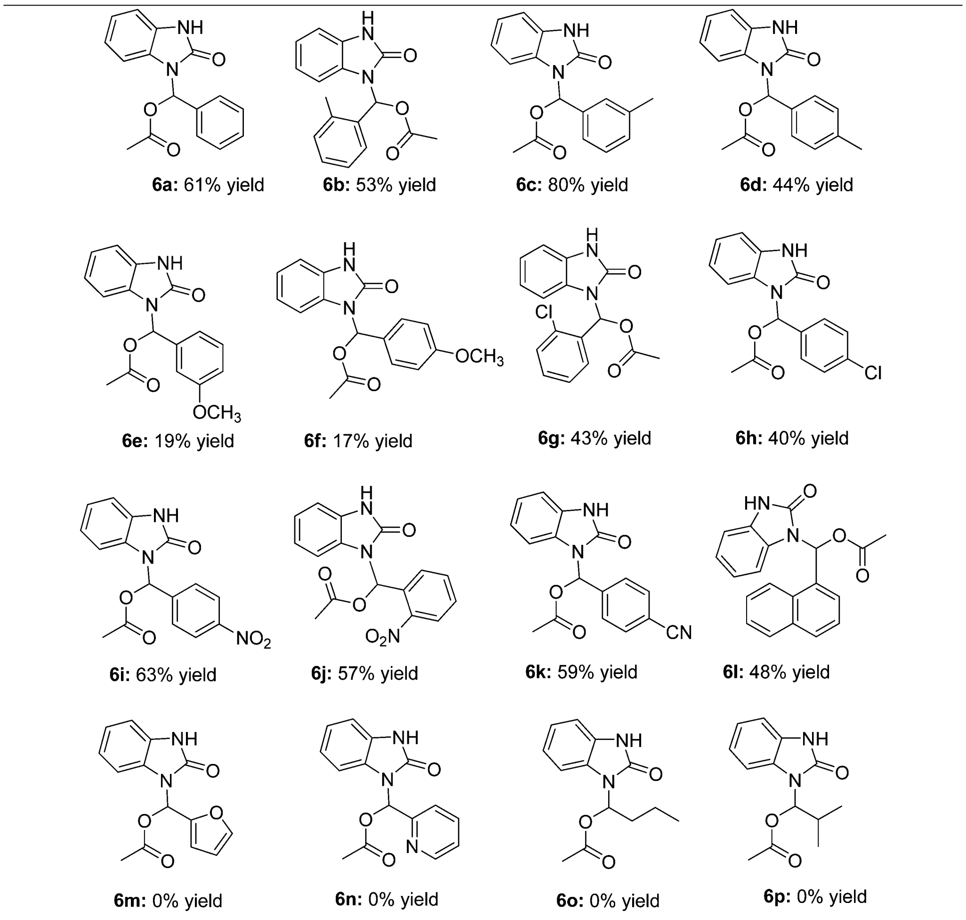
[a] Reactions were carried out on a scale of **1a** (0.46 mmol) and **2a** (0.46 mmol) in DCM (5 mL). Nitrone formed from **1a** and **2a** was added into a mixture of **3** (0.92 mmol), **4** (1.38 mmol), and **5a** (1.84 mmol), which was stirred in DCM for 30 min beforehand. [b] Isolated yields.

Unfortunately, the corresponding benzimidazolones could not be obtained when the other hypervalent iodine reagents were used instead of $PhI(OAc)_2$. Thus, the best reaction conditions were treatment of *N*-phenylhydroxylamine with 1 equiv of benzaldehyde in CH_2Cl_2 at room temperature overnight. The reaction mixture was then added into another mixture of 2 equiv of $PhI(OAc)_2$, 3 equiv of TMSCN, and 4 equiv of $BF_3 \cdot Et_2O$ to give the target product.

Under the optimized reaction conditions, the generality of aldehydes was first checked. As shown in Table 3, most of the aromatic aldehydes gave the corresponding benzimidazolones in reasonable to good yields. The aromatic aldehydes with electron-withdrawing groups on the phenyl rings usually gave the products in higher yields than those with electron-donating groups on the phenyl rings. For instance, when *p*-nitro or *p*-nitrile benzaldehyde was used, the corresponding products could be obtained in 63% and 59% yields (Table 3, **6i** and **6k**), but *p*-methoxybenzaldehyde gave the corresponding product in only 17% yield.

Table 3. Reactions of Different Aldehydes for the Synthesis of Benzimidazolones[a]





6a: 61% yield
6b: 53% yield
6c: 80% yield
6d: 44% yield
6e: 19% yield
6f: 17% yield
6g: 43% yield
6h: 40% yield
6i: 63% yield
6j: 57% yield
6k: 59% yield
6l: 48% yield
6m: 0% yield
6n: 0% yield
6o: 0% yield
6p: 0% yield

[a] Reactions were carried out on a scale of **1a** (0.46 mmol) and **2** (0.46 mmol) in DCM (5 mL). Nitrones formed from **1a** and **2** were added into a mixture of **3a** (0.92 mmol), **4** (1.38 mmol), and **5a** (1.84 mmol), which was stirred in DCM for 30 min beforehand. Isolated yields.

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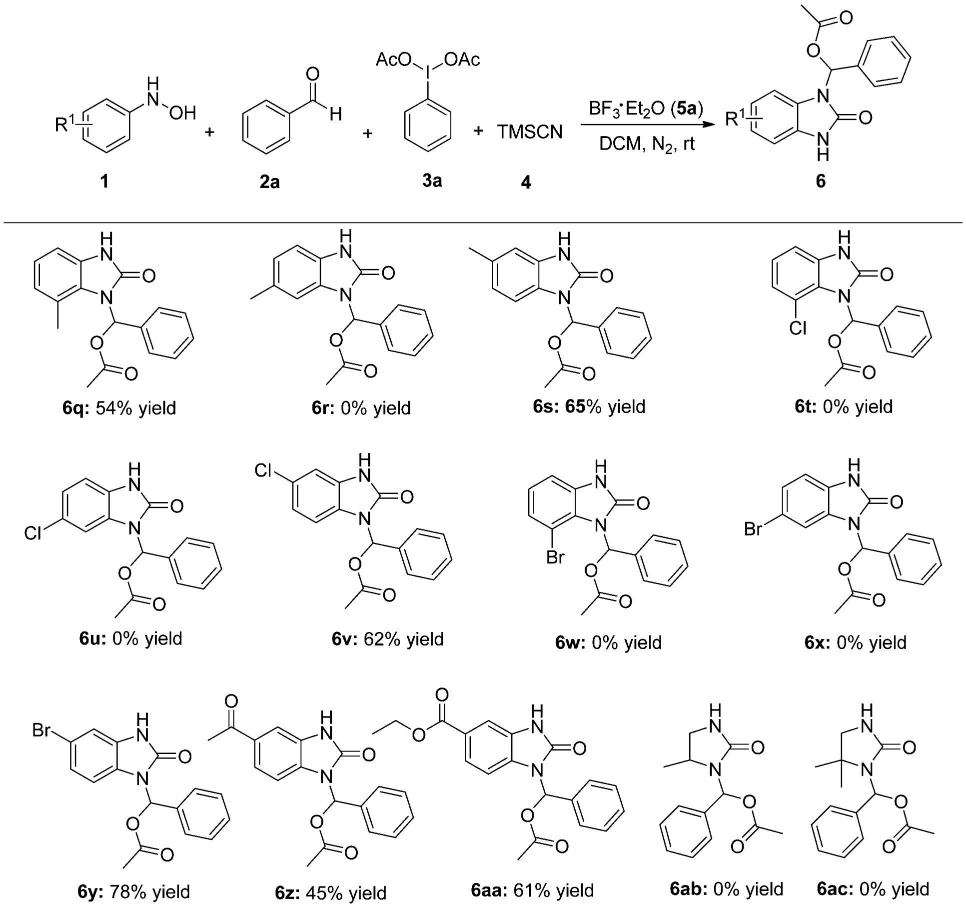
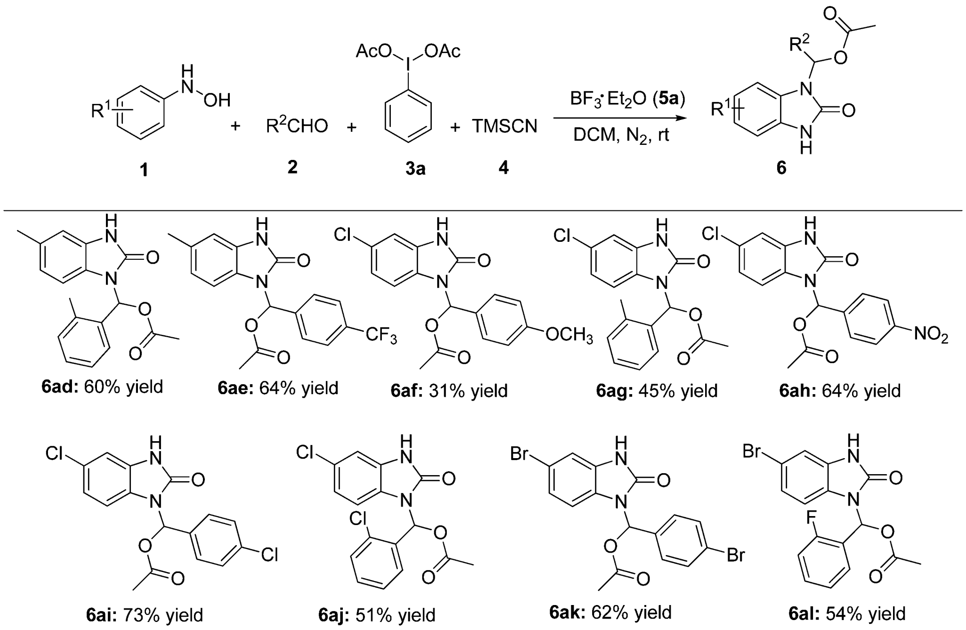
Table 4. Reactions of Different Hydroxylamines for the Synthesis of Benzimidazolones[a]



6q: 54% yield
6r: 0% yield
6s: 65% yield
6t: 0% yield
6u: 0% yield
6v: 62% yield
6w: 0% yield
6x: 0% yield
6y: 78% yield
6z: 45% yield
6aa: 61% yield
6ab: 0% yield
6ac: 0% yield

[a] Reactions were carried out on a scale of **1** (0.46 mmol) and **2a** (0.46 mmol) in DCM (5 mL). Nitrones formed from **1** and **2a** were added into a mixture of **3a** (0.92 mmol), **4** (1.38 mmol), and **5a** (1.84 mmol), which was stirred in DCM for 30 min beforehand. Isolated yields.

Table 5. Reactions of Different Aldehydes with Different Hydroxylamines for the Synthesis of Benzimidazolones[a]



6ad: 60% yield
6ae: 64% yield
6af: 31% yield
6ag: 45% yield
6ah: 64% yield
6ai: 73% yield
6aj: 51% yield
6ak: 62% yield
6al: 54% yield

[a] Reactions were carried out on a scale of **1** (0.46 mmol) and **2** (0.46 mmol) in DCM (5 mL). Nitrones formed from **1** and **2** were added into a mixture of **3a** (0.92 mmol), **4** (1.38 mmol), and **5a** (1.84 mmol), which was stirred in DCM for 30 min beforehand. Isolated yields.

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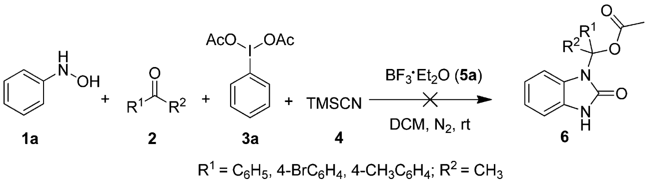
Scheme 2. Diacetoxyiodobenzene-Promoted Reactions of Hydroxylamine, Ketones, and Trimethylsilyl Cyanide



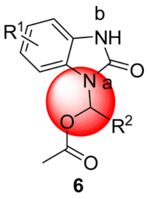


Figure 2. Different properties of nitrogen atoms at positions a and b.

The positions of the substituents on the phenyl rings of aldehydes had little influence on the product yields. For instance, the yield of the product from *o*-nitrobenzaldehyde was slightly lower than that from *p*-nitrobenzaldehyde (Table 3, **6j** and **6i**). Unfortunately, heterocyclic aromatic aldehydes such as furan-2-carbaldehyde or picolinaldehyde and aliphatic aldehyde such as *n*-butylaldehyde or isobutyl aldehydes could not afford the desired products (Table 3, **6m−p**).

Next, various aromatic and aliphatic hydroxylamines were reacted with benzaldehyde **2a** to examine the generality of the reaction (Table 4). The hydroxylamines bearing an electron-withdrawing group on their phenyl rings usually gave the corresponding products in yields higher than those with electron-donating groups. The reason was that the electron-withdrawing groups on the phenyl rings of aromatic hydroxylamines could increase the electrophilicity of in situ formed nitrone by an inductive effect. The positions of substituents on the phenyl rings of aromatic hydroxylamines greatly influenced the reaction results. The *para*-substituted aromatic hydroxylamines usually gave the corresponding products in good yields whether the substituents were electron-donating or electron-withdrawing groups (Table 4, **6s**, **6v**, and **6y−aa**). However, if the *meta*-substituted hydroxylamines were used, no product could be obtained (Table 4, **6r**, **6u**, and **6x**). Unfortunately, aliphatic hydroxylamines did not afford the products (Table 4, **6ab** and **6ac**).

Further investigation for generality of substrates was conducted between various benzaldehydes and various hydroxylamines. As shown in Table 5, the reaction could smoothly occur to afford the corresponding products when different aromatic aldehydes reacted with different aromatic hydroxylamines. When ketones were used as substrates instead of aldehydes, the reactions did not occur (Scheme 2).

Finally, the application of products **6** in organic synthesis was briefly investigated. As shown in Figure 2, nitrogen at position a in the products is protected by a hemiaminal group, and nitrogen at position b is a free amino group. Thus, the hemiaminal group could be hydrolyzed to release the amino group to give benzimidazolones. In addition, nitrogen at position b could be manipulated first, and then the nitrogen at position a was released. For instance, when product **6a** was exposed to concentrated HCl, benzimidazolone **10** could be obtained in 76% yield (Scheme 3, a). The product **6a** could react at first with benzyl bromide in the presence of potassium carbonate to afford compound **11**, which was then hydrolyzed to product **12** in 80% yield (Scheme 3, b). Furthermore, the acetoxy group in the product **6c** could be exchanged to more stable ethoxy groups to give compound **13** in 82% yield (Scheme 3, c).

To investigate the mechanism, some nitrones were prepared first and then reacted with PhI(OAc)$_2$ and TMSCN in the presence of BF$_3$·Et$_2$O. It was found that the desired products were also obtained (Table 6), which confirmed that nitrones were first formed at the beginning of the reaction. On the basis of the literature[31−33] and experimental results, a possible

Scheme 3. Synthetic Applications of 6

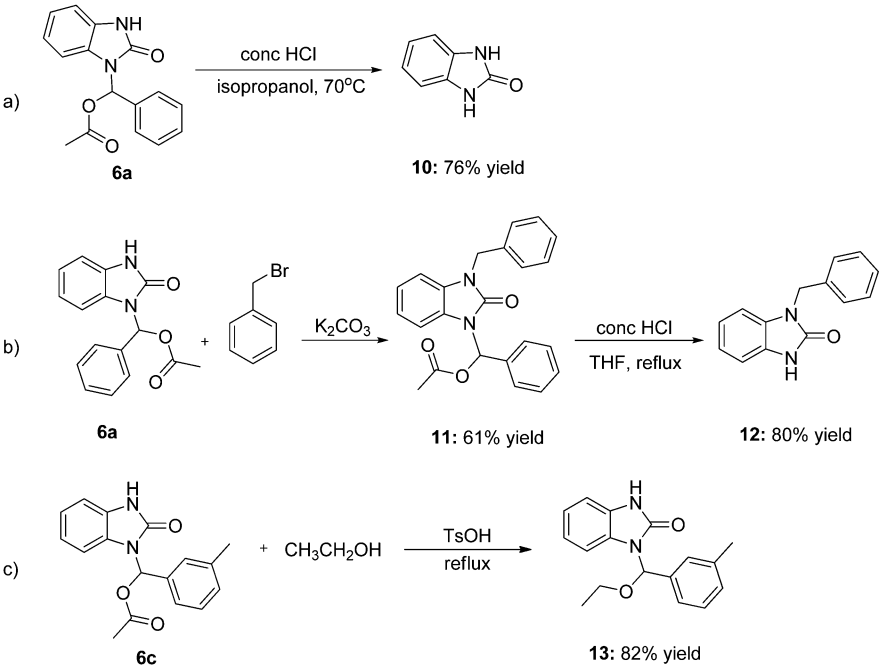


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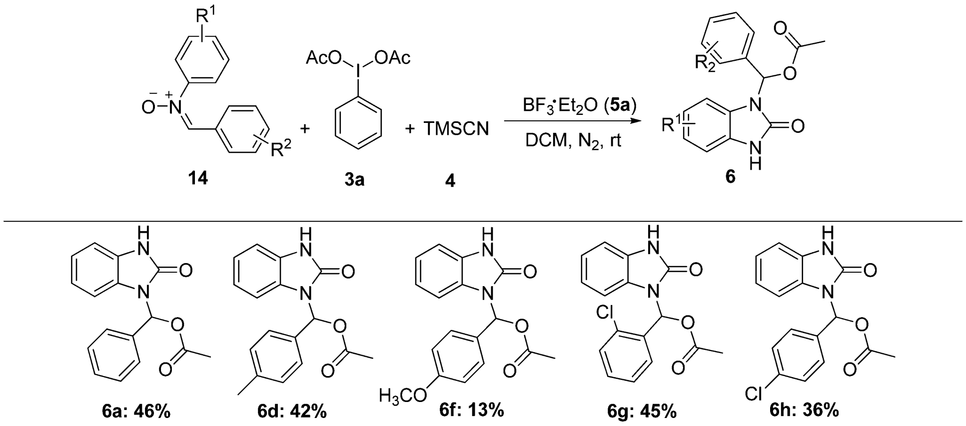
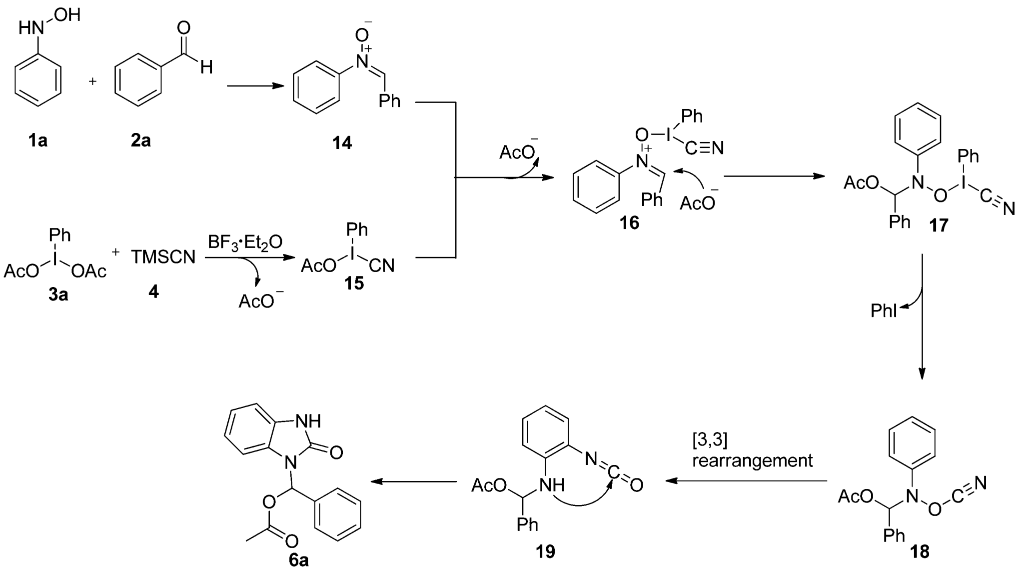
Table 6. Diacetoxyiodobenzene-Promoted Reactions of Nitrones and Trimethylsilyl Cyanide[a]



[a]Reactions were carried out on a scale of **3a** (0.92 mmol), **4** (1.38 mmol), and **5a** (1.84 mmol) in DCM (5 mL); after the mixture was stirred for 30 min under nitrogen atmosphere, **14** (0.46 mmol) was added. Isolated yields.

Scheme 4. Plausible Mechanism



mechanism was proposed in Scheme 4. First, *N*-phenylhydroxylamine **1a** reacted with benzaldehyde **2a** to give nitrone **14**. $PhI(OAc)_2$ was activated by $BF_3 \cdot Et_2O$ through coordination to the oxygen atoms of the ligands on iodine,[32] and then ligand exchange between $PhI(OAc)_2$ and TMSCN afforded intermediate **15**. A second ligand exchange between **14** and **15** produced intermediate **16**, which was attached by AcO^- anion to afford intermediate **17**. Decomposition of intermediate **17** gave the intermediate **18**, which conducted [3,3] rearrangement to afford isocyanate **19**. Intramolecular addition and proton migration produced final product **6a**.

■ CONCLUSIONS

In summary, we have developed the first $PhI(OAc)_2$-promoted one-pot reaction of aromatic hydroxylamines, aldehydes, and TMSCN to give benzimidazolones in the presence of $BF_3 \cdot Et_2O$. Under the reaction conditions, aromatic aldehydes bearing different functional groups on their phenyl rings could be easily converted into the corresponding products with satisfactory yields, while heterocylic aldehydes, aliphatic aldehydes, and ketones did not work. This novel protocol provided an efficient method for the construction of benzimidazolones.

■ EXPERIMENTAL SECTION

General Methods. All isolated new compounds were characterized on the basis of ^1H NMR and ^{13}C NMR spectroscopic data and HRMS data. ^1H NMR and ^{13}C NMR chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard.

General Procedure for the Synthesis of Compounds 6 from 1, 2, 3a, 4, and 5a. *N*-Phenylhydroxylamines **1** (0.46 mmol, 1 equiv) and aldehydes **2** (0.46 mmol, 1 equiv) were mixed in DCM (5 mL) at room temperature and stirred overnight for the formation of nitrone. This nitrone-containing mixture was added into another mixture of $PhI(OAc)_2$ **3a** (0.92 mmol, 2 equiv), TMSCN **4** (1.38 mmol, 3 equiv), and $BF_3 \cdot Et_2O$ **5a** (1.84 mmol, 4 equiv) in DCM, which was stirred for 30 min in another round-bottom flask beforehand under nitrogen atmosphere. After the reaction was completed, saturated $NaHCO_3$ solution (10 mL) was added to the reaction mixture followed by stirring for 10 min. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Purification of the residue by silica gel column chromatography using PE/EA (4:1) as the eluent afforded the products **6**.

General Procedure for the Synthesis of Compounds 6 from 14, 3a, 4, and 5a. A mixture of $PhI(OAc)_2$ **3a** (0.92 mmol, 2 equiv), TMSCN **4** (1.38 mmol, 3 equiv), and $BF_3 \cdot Et_2O$ **5a** (1.84 mmol, 4 equiv) was stirred in DCM (5 mL) for 30 min under nitrogen atmosphere, and then nitrones **14** (0.46 mmol, 1 equiv) were added. After the reaction was completed, saturated $NaHCO_3$ solution (10 mL) was added to the reaction mixture followed by stirring for 10 min. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Purification of the residue by silica gel column chromatography using PE/EA (4:1) as the eluent afforded the products **6**.

*(2-Oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)methyl acetate (**6a**):* white solid; mp 165−166 °C; yield 79.1 mg (61%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.07 (s, 1H), 7.43−7.36 (m, 5H), 7.13 (d, J = 7.8 Hz, 1H), 7.04 (td, J = 7.8, 1.2 Hz, 1H), 6.92−6.89 (m, 1H), 6.82 (d, J = 7.8 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 154.9, 134.9, 133.7, 129.0, 128.4, 127.4, 127.1, 122.5, 121.4, 110.6, 110.3, 75.2, 20.7; HRMS (ESI) calcd for $C_{16}H_{14}N_2O_3Na$ [M + Na]$^+$ 305.0897, found 305.0894.

*N-Acetoxy-N-phenylbenzamide (**6a'**):*[34] white solid; mp 53−54 °C; yield 41.1 mg (35%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.53−7.52 (m, 2H), 7.38−7.35 (m, 1H), 7.33−7.25 (m, 7H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 166.8, 140.6, 133.2, 131.0, 129.2, 128.8, 128.4, 128.1, 126.9, 18.4; HRMS (ESI) calcd for $C_{15}H_{14}NO_3$ [M + H]$^+$ 256.0968, found 256.0970

*(2-Oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(o-tolyl)methyl acetate (**6b**):* white solid; mp 144−145 °C; yield 72.2 mg (53%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.08 (s, 1H), 7.65−7.64 (m, 1H), 7.30−7.28 (m, 2H), 7.18−7.14 (m, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.87 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 154.8, 136.4, 132.8, 131.4, 129.1, 128.4, 127.8, 125.9, 125.8, 122.2, 121.3, 110.5, 110.2, 74.9, 20.7, 19.1; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3Na$ [M + Na]$^+$ 319.1053, found 319.1058.

*(2-Oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(m-tolyl)methyl acetate (**6c**):* white solid; mp 154−155 °C; yield 108.9 mg (80%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.63 (br, 1H), 8.05 (s, 1H), 7.28−7.21 (m, 3H), 7.15 (d, J = 7.8 Hz, 2H), 7.03 (t, J = 7.8, 1H), 6.90 (t, J = 7.8, 1H), 6.85 (d, J = 7.8 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 155.1, 138.5, 135.0, 129.6, 128.6, 128.4, 127.5, 126.5, 122.9, 122.2, 121.3, 110.8, 110.1, 75.7, 21.5, 20.7; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3Na$ [M + Na]$^+$ 319.1053, found 319.1057.

*(2-Oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(p-tolyl)methyl acetate (**6d**):* white solid; mp 191−192 °C; yield 59.9 mg (44%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.08 (s, 1H), 7.32 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.8 Hz, 1H), 6.91 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 155.1, 138.6, 132.1, 129.3, 128.4, 127.5, 125.8, 122.2, 121.2, 110.8, 110.2, 75.7, 21.1, 20.7; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3Na$ [M + Na]$^+$ 319.1053, found 319.1059.

*(3-Methoxyphenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6e**):* white solid; mp 143−144 °C; yield 27.3 mg (19%). ^1H NMR (600 MHz, $CDCl_3$) δ 10.88 (s, 1H), 8.07 (s, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.04−6.98 (m, 3H), 6.91−6.86 (m, 3H), 3.76 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 159.8, 155.0, 136.6, 129.8, 128.4, 127.3, 122.2, 121.2, 118.1, 113.8, 112.0, 110.6, 110.2, 75.4, 55.2, 20.6; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_4Na$ [M + Na]$^+$ 335.1002, found 335.1007.

*(4-Methoxyphenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6f**):* white solid; yellow oil; yield 24.4 mg (17%). ^1H NMR (600 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.00 (s, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.93−6.89 (m, 3H), 6.85 (d, J = 7.8 Hz, 1H), 3.80 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 159.9, 154.8, 128.3, 127.5, 127.2, 127.0, 122.2, 121.3, 114.1, 110.9, 110.0, 75.7, 55.3, 20.7; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_4Na$ [M + Na]$^+$ 335.1002, found 335.1006.

*(2-Chlorophenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6g**):* white solid; mp 202−204 °C; yield 62.6 mg (43%). ^1H NMR (600 MHz, $CDCl_3$) δ 10.44 (br, 1H), 8.08 (s, 1H), 7.70−7.68 (m, 1H), 7.40−7.38 (m, 1H), 7.36−7.32 (m, 2H), 7.13 (d, J = 7.2, 1H), 7.05 (t, J = 7.2, 1H), 6.94−6.89 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 154.6, 133.3, 132.4, 130.5, 128.4, 128.1, 128.0, 126.6, 122.3, 121.3, 110.2, 110.1, 74.5, 20.6; HRMS (ESI) calcd for $C_{16}H_{13}ClN_2O_3Na$ [M + Na]$^+$ 339.0507, found 339.0511.

*(4-Chlorophenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6h**):* white solid; mp 198−199 °C; yield 58.3 mg (40%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.67 (s, 1H), 8.03 (s, 1H), 7.36 (s, 4H), 7.15 (d, J = 7.8 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.92 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 154.9, 134.9, 133.7, 129.0, 128.4, 127.4, 127.1, 122.5, 121.4, 110.6, 110.3, 75.2, 20.7; HRMS (ESI) calcd for $C_{16}H_{13}ClN_2O_3Na$ [M + Na]$^+$ 339.0507, found 339.0512.

*(4-Nitrophenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6i**):* white solid; mp 233−234 °C; yield 94.8 mg (63%); ^1H NMR (600 MHz, DMSO-d_6) δ 11.21 (s, 1H), 8.26 (d, J = 9.0 Hz, 2H), 7.84 (s, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.03−6.98 (m, 2H), 6.87 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.0, 153.1, 147.8, 142.5, 128.7, 127.4, 127.0, 123.9, 122.1, 120.9, 109.7, 109.5, 74.5, 20.4; HRMS (ESI) calcd for $C_{16}H_{13}N_3O_5Na$ [M + Na]$^+$ 350.0747, found 350.0750.

*(2-Nitrophenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6j**):* white solid; mp 235−237 °C; yield 85.7 mg (57%); ^1H NMR (600 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.16 (s, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.2 Hz, 1H), 7.75 (t, J = 7.8 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.06−7.02 (m, 2H), 6.89 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 152.9, 147.9, 133.6, 131.0, 128.7, 128.5, 128.2, 127.3, 125.4, 122.2, 121.0, 109.6, 109.4, 73.1, 19.9; HRMS (ESI) calcd for $C_{16}H_{13}N_3O_5Na$ [M + Na]$^+$ 350.0747, found 350.0744.

*(4-Cyanophenyl)(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6k**):* white solid; mp 217−218 °C; yield 83.3 mg (59%). ^1H NMR (600 MHz, $CDCl_3$) δ 10.57 (s, 1H), 8.08 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.8 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 6.95 (t, J = 7.8 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 154.7, 140.3, 132.6, 128.3, 126.9, 126.8, 122.7, 121.6, 118.1, 113.0, 110.4, 110.3, 74.8, 20.6; HRMS (ESI) calcd for $C_{17}H_{13}N_3O_3Na$ [M + Na]$^+$ 330.0849, found 330.0845.

*Naphthalen-1-yl(2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)-methyl acetate (**6l**):* white solid; mp 223−224 °C; yield 73.3 mg (48%); ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.65 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.94−7.84 (m, 3H), 7.56−7.44 (m, 3H), 7.13 (d, J = 7.6 Hz, 1H), 7.01−6.97 (m, 2H), 6.88−6.84 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 154.7, 133.9, 130.4, 130.2, 130.1, 128.8, 128.4, 128.0, 127.2, 126.2, 124.5, 124.3, 123.0, 122.2, 121.3, 110.8, 110.1, 74.6, 20.8; HRMS (ESI) calcd for $C_{20}H_{16}N_2O_3Na$ [M + Na]$^+$ 355.1053, found 355.1049.

*(7-Methyl-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)-methyl acetate (**6q**):* white solid; mp 264−265 °C; yield 73.5 mg (54%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.07 (s, 1H), 7.42−7.35 (m, 5H), 6.86 (d, J = 7.8 Hz, 1H), 6.82 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 2.41 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 155.2, 135.2, 128.8, 128.7, 127.5, 127.1, 125.9, 123.4, 121.2, 120.0, 108.3, 75.8, 20.7, 16.2; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3Na$ [M + Na]$^+$ 319.1053, found 319.1059.

*(5-Methyl-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)-methyl acetate (**6s**):* white solid; mp 208−209 °C; yield 88.5 mg (65%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.06 (s, 1H), 7.42−7.34 (m, 5H), 6.99 (s, 1H), 6.71−6.67 (m, 2H), 2.31 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 155.2, 135.1, 132.1, 128.8, 128.7, 128.6, 125.9, 125.2, 121.9, 110.8, 110.4, 75.7, 21.2, 20.7; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3Na$ [M + Na]$^+$ 319.1053, found 319.1058.

*(5-Chloro-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)-methyl acetate (**6v**):* white solid; mp 198−199 °C; yield 90.3 mg (62%); ^1H NMR (600 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.04 (s, 1H), 7.40−7.37 (m, 5H), 7.17 (d, J = 1.8 Hz, 1H), 6.88−6.86 (m, 1H), 6.72 (d, J = 8.4 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 155.1, 134.6, 129.3, 129.0, 128.8, 128.0, 126.0, 125.8, 121.4, 111.4, 110.6, 75.6, 20.7; HRMS (ESI) calcd for $C_{16}H_{13}ClN_2O_3Na$ [M + Na]$^+$ 339.0507, found339.0510.

*(5-Bromo-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)-methyl acetate (**6y**):* white solid; mp 202−203 °C; yield 129.5 mg

(78%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.83 (s, 1H), 8.03(s, 1H), 7.40−7.36 (m, 5H), 7.31 (d, J = 1.8 Hz, 1H), 7.02 (dd, J = 8.4, 1.8 Hz, 1H), 6.68 (d, J = 9.0 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 169.1, 155.1, 134.8, 129.8, 129.2, 129.0, 126.6, 125.9, 124.4, 115.3, 113.5, 112.0, 75.7, 20.8; HRMS (ESI) calcd for $C_{16}H_{13}BrN_2O_3Na$ [M + Na]$^+$ 383.0002, found 382.9999.

*(5-Acetyl-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)-methyl acetate (**6z**):* white solid; mp 210−211 °C; yield 67.1 mg (45%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.87 (s, 1H), 8.09 (s, 1H), 7.81 (d, J = 1.2 Hz, 1H), 7.61 (dd, J = 8.4, 1.8 Hz, 1H), 7.45−7.37 (m, 5H), 6.90 (d, J = 8.4 Hz, 1H), 2.56 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 197.0, 168.9, 155.1, 134.5, 131.9, 131.3, 129.1, 128.8, 128.5, 125.8, 122.8, 110.2, 110.1, 75.6, 26.5, 20.6; HRMS (ESI) calcd for $C_{18}H_{16}N_2O_4Na$ [M + Na]$^+$ 347.1002, found 347.1000.

*Ethyl 1-(acetoxy(phenyl)methyl)-2-oxo-2,3-dihydro-1H-benz[d]-imidazole-5-carboxylate (**6aa**):* white solid; mp 195−196 °C; yield 99.3 mg (61%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.93 (s, 1H), 8.09 (s, 1H), 7.88 (s, 1H), 7.70 (dd, J = 8.4, 1.2 Hz, 1H), 7.44−7.38 (m, 5H), 6.89 (d, J = 8.4 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.24 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.9, 166.3, 155.2, 134.6, 131.0, 129.0, 128.8, 128.2, 125.7, 124.7, 123.7, 111.3, 110.1, 75.6, 60.9, 20.6, 14.2; HRMS (ESI) calcd for $C_{19}H_{18}N_2O_5Na$ [M + Na]$^+$ 377.1108, found 377.1110.

*(5-Methyl-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(o-tolyl)-methyl acetate (**6ad**):* white solid; mp 191−193 °C; yield 85.6 mg (60%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.76 (s, 1H), 8.05 (s, 1H), 7.64−7.63 (m, 1H), 7.29−7.27 (m, 2H), 7.17−7.16 (m, 1H), 6.99 (s, 1H), 6.67 (s, 2H), 2.30 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.8, 155.0, 136.3, 132.9, 132.1, 131.3, 129.1, 128.5, 125.9, 125.8, 125.6, 121.9, 110.7, 110.2, 74.9, 21.2, 20.7, 19.1; HRMS (ESI) calcd for $C_{18}H_{18}N_2O_3Na$ [M + Na]$^+$ 333.1210, found 333.1208.

*(5-Methyl-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(4-(trifluoromethyl)phenyl)methyl acetate (**6ae**):* white solid; mp 206−208 °C; yield 107.2 mg (64%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.73 (s, 1H), 8.09 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.00 (s, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 2.32 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.9, 155.1, 139.2, 132.6, 131.1 (q, J_{C-F} = 31.5 Hz), 128.6, 126.5, 125.7 (q, J_{C-F} = 4.5 Hz), 124.8, 122.8 (q, J_{C-F} = 270 Hz), 122.1, 111.0, 110.1, 75.1, 21.2, 20.6; HRMS (ESI) calcd for $C_{18}H_{15}F_3N_2O_3Na$ [M + Na]$^+$ 387.0927, found 387.0930.

*(5-Chloro-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(4-methoxyphenyl)methyl acetate (**6af**):* yellow oil; yield 49.5 mg (31%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.32 (s, 1H), 7.94 (s, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 1.8 Hz, 1H), 6.91−6.88 (m, 3H), 6.74 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.9, 160.1, 154.3, 128.9, 127.9, 127.2, 126.6, 126.2, 121.6, 114.2, 111.6, 110.2, 75.7, 55.3, 20.7; HRMS (ESI) calcd for $C_{17}H_{15}ClN_2O_4Na$ [M + Na]$^+$ 369.0613, found 369.0610.

*(5-Chloro-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(o-tolyl)-methyl acetate (**6ag**):* white solid; mp 201−202 °C; yield 68.5 mg (45%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.81 (s, 1H), 8.03 (s, 1H), 7.62 (d, J = 6.6 Hz, 1H), 7.33−7.28 (m, 2H), 7.20−7.17 (m, 2H), 6.86 (dd, J = 9.0, 2.4 Hz, 1H), 6.71 (d, J = 9.0 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.7, 154.8, 136.3, 132.4, 131.5, 129.3, 129.2, 127.9, 126.4, 125.9, 125.8, 121.4, 111.2, 110.6, 74.7, 20.7, 19.1; HRMS (ESI) calcd for $C_{17}H_{15}ClN_2O_3Na$ [M + Na]$^+$ 353.0663, found 353.0668.

*(5-Chloro-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(4-nitrophenyl)methyl acetate (**6ah**):* white solid; mp 194−195 °C; yield 106.6 mg (64%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.56 (s, 1H), 8.26 (d, J = 9.0 Hz, 2H), 8.05 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 1.8 Hz, 1H), 6.92 (dd, J = 8.4, 1.8 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.7, 154.7, 148.3, 141.6, 129.2, 128.5, 127.1, 125.4, 124.1, 121.8, 111.0, 110.9, 74.7, 20.6; HRMS (ESI) calcd for $C_{16}H_{12}ClN_3O_5Na$ [M + Na]$^+$ 384.0358, found 384.0363.

*(5-Chloro-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(4-chlorophenyl)methyl acetate (**6ai**):* white solid; mp 174−175 °C; yield 117.9 mg (73%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 10.69 (s, 1H), 7.97 (s, 1H), 7.37 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 7.16 (d, J = 2.4 Hz, 1H), 6.90 (dd, J = 8.4, 2.4 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.8, 154.9, 135.1, 133.2, 129.3, 129.1, 128.2, 127.3, 125.7, 121.6, 111.3, 110.7, 75.1, 20.6; HRMS (ESI) calcd for $C_{16}H_{12}Cl_2N_2O_3Na$ [M + Na]$^+$ 373.0117, found 373.0125.

*(5-Chloro-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(2-chlorophenyl)methyl acetate (**6aj**):* white solid; mp 217−218 °C; yield 82.3 mg (51%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.34 (s, 1H), 8.02 (s, 1H), 7.70−7.67 (m, 1H), 7.42−7.35 (m, 3H), 7.14 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.6, 154.5, 133.2, 132.0, 130.6, 130.5, 129.2, 128.1, 128.0, 126.7, 121.4, 110.9, 110.5, 74.4, 20.6; HRMS (ESI) calcd for $C_{16}H_{12}Cl_2N_2O_3Na$ [M + Na]$^+$ 373.0117, found 373.0124.

*(5-Bromo-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(4-bromophenyl)methyl acetate (**6ak**):* white solid; mp 223−224 °C; yield 125.5 mg (62%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.58 (s, 1H), 7.94 (s, 1H), 7.53 (d, J = 6.4 Hz, 2H), 7.31−7.26 (m, 3H), 7.05 (dd, J = 8.0, 1.6 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.8, 154.7, 133.8, 132.0, 129.5, 127.6, 126.1, 124.4, 123.3, 115.4, 113.5, 111.7, 75.1, 20.6; HRMS (ESI) calcd for $C_{16}H_{12}Br_2N_2O_3Na$ [M + Na]$^+$ 460.9107, found 460.9111.

*(5-Bromo-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(2-fluorophenyl)methyl acetate (**6al**):* white solid; mp 245−246 °C; yield 94.1 mg (54%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.86 (s, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.50−45 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.25−7.20 (m, 1H), 7.15 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.4, 1.6 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 159.3 (d, J_{C-F} = 369.0 Hz), 152.4, 131.5 (d, J_{C-F} = 13.5 Hz), 130.1, 127.9 (d, J_{C-F} = 3.0 Hz), 126.7, 124.6 (d, J_{C-F} = 6.0 Hz), 123.4, 122.0 (d, J_{C-F} = 16.5 Hz), 116.1 (d, J_{C-F} = 31.5 Hz), 113.8, 112.0, 110.9, 71.5, 20.3; HRMS (ESI) calcd for $C_{16}H_{12}BrFN_2O_3Na$ [M + Na]$^+$ 400.9908 found 400.9913.

General Procedure for the Synthesis of Compound 10. Compound **6a** (0.18 mmol, 1 equiv) was dissolved in 2-propanol (5 mL), and then concentrated hydrochloric acid (0.72 mmol, 4 equiv) was added. The reaction mixture was stirred at 70 °C for 1 h and then cooled to room temperature. Ethyl acetate (5 mL) and aqueous sodium hydroxide solution were added, and the mixture was stirred for another 30 min. The organic layer was separated, dried, and evaporated under reduced pressure. Pure compound **10** as a white solid was produced via recrystallization in 2-propanol (5 mL).

*1H-Benz[d]imidazol-2(3H)-one (**10**):*[35] white solid; >312 °C; yield 18.3 mg (76%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.56 (s, 2H), 6.90 (s, 4H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.7, 130.1, 120.8, 108.9.

General Procedure for the Synthesis of Compound 11. A mixture of **6a** (0.32 mmol, 1 equiv), benzyl bromide (0.48 mmol, 1.5 equiv), potassium carbonate (0.26 mmol, 0.8 equiv), and DMF (6 mL) was stirred at room temperature overnight. Water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 6 mL). The organic layer was dried (MgSO$_4$) and concentrated. Purification of the residue by silica gel column chromatography using PE/EA (6:1) as the eluent afforded the product **11**.

*(3-Benzyl-2-oxo-2,3-dihydro-1H-benz[d]imidazol-1-yl)(phenyl)-methyl acetate (**11**):* white solid; mp 141−142 °C; yield 72.6 mg (61%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (s, 1H), 7.43−7.25 (m, 10H), 6.96 (td, J = 7.6, 1.2 Hz, 1H), 6.90−6.81 (m, 3H), 5.10 (d, J = 2.0 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 168.8, 153.5, 136.0, 135.2, 129.6, 128.8, 128.7, 128.6, 127.7, 127.5, 126.7, 125.9, 121.9, 121.4, 110.6, 108.5, 76.3, 45.0, 20.7; HRMS (ESI) calcd for $C_{23}H_{20}N_2O_3Na$ [M + Na]$^+$ 395.1366, found 395.1362.

General Procedure for the Synthesis of Compound 12. Compound **11** (0.13 mmol, 1 equiv) was dissolved in THF (5 mL), and concentrated hydrochloric acid (2.5 mL) was added. The reaction mixture was stirred at 70 °C for 1 h. After the solution was cooled, ethyl acetate (5 mL) and aqueous sodium hydroxide solution were added, and the mixture was stirred for 30 min. The organic layer was dried (MgSO$_4$) and concentrated. Purification of the residue by silica gel column chromatography using PE/EA (1.5:1) as the eluent afforded the product **12**.

*1-Benzyl-1H-benz[d]imidazol-2(3H)-one (**12**):*[36] white solid; mp 211−213 °C; yield 23.3 mg (80%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 7.34−7.31 (m, 4H), 7.27−7.24 (m, 1H), 7.02−6.93 (m, 4H), 5.00 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.6, 142.4, 135.2, 133.8, 133.5, 132.5, 126.2, 125.7, 114.0, 113.3, 48.4; HRMS (ESI) calcd for $C_{14}H_{12}N_2ONa$ [M + Na]$^+$ 247.0842, found 247.0838.

General Procedure for the Synthesis of Compound 13. Compound **6c** (0.17 mmol, 1 equiv) and *p*-toluenesulfonic acid (0.20 mmol, 1.2 equiv) were added into EtOH (5 mL). The reaction mixture was stirred at reflux temperature for 1 h. After the solution was cooled, the residue was purified by silica gel column chromatography using PE/EA (15:1) as eluent to give the product **13**.

*1-(Ethoxy(m-tolyl)methyl)-1H-benz[d]imidazol-2(3H)-one (**13**):* white solid; mp 120−121 °C; yield 39.3 mg (82%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.33−7.30 (m, 2H), 7.25−7.21 (m, 1H), 7.13−7.10 (m, 2H), 7.03−7.00 (m, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.89 (t, J = 7.8 Hz, 1H), 6.76 (s, 1H), 3.76−3.71 (m, 1H), 3.68−3.63 (m, 1H), 2.33 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 138.1, 137.5, 129.1, 128.3, 128.1, 127.7, 126.8, 123.2, 121.8, 121.3, 111.6, 109.6, 82.4, 64.2, 21.5, 14.8; HRMS (ESI) calcd for $C_{17}H_{18}N_2O_2Na$ [M + Na]$^+$ 305.1260, found 305.1258.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02781.

^{1}H NMR, ^{13}C NMR, and HRMS spectra of **6** and **10−13** and crystallographic data for **6a** (PDF)
Crystallographic data for **6a** (CIF)

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Notes

The authors declare no competing financial interest.

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