# Iron(0)-Catalyzed Transfer Hydrogenative Condensation of Nitroarenes with Alcohols: A Straightforward Approach to Benzoxazoles, Benzothiazoles, and Benzimidazoles

Ramachandra Reddy Putta, Simin Chun, Seung Hyun Choi, Seok Beom Lee, Dong-Chan Oh, and Suckchang Hong*

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**ABSTRACT:** The iron-catalyzed hydrogen transfer strategy has been applied to the redox condensation of *o*-hydroxynitrobenzene with alcohol, leading to the formation of benzoxazole derivatives. A wide range of 2-substituted benzoxazoles were synthesized in good to excellent yields without the addition of an external redox agent. A series of control experiments provided a plausible mechanism. Furthermore, the reaction system was successfully extended to the synthesis of benzothiazoles and benzimidazoles.
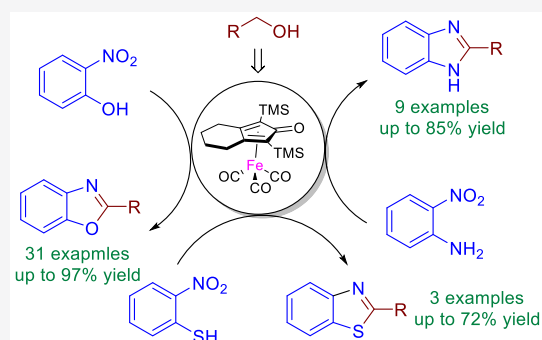
## INTRODUCTION

Benzazoles (benzoxazoles, benzothiazoles, and benzimidazoles) are common structures in many natural products and synthetic drugs. In particular, 2-substituted benzoxazoles are considered a core moiety in drug discovery because of their wide range of biological activities.[1] In addition to biological applications, these compounds have been applied in fluorescent chemosensors[2] and other functional materials.[3] Because of the important pharmaceutical and industrial applications, many synthetic protocols for benzazole derivatives have been developed. The most straightforward approach involves condensation of *o*-hydroxy/mercapto/amino anilines with carbonyl compounds, in particular, an aldehyde.[4] Compared with labile aldehydes, low-oxidation-level substrates, such as alcohol and amine, are readily available and usually supplied as feedstock. Based on these advantages, low-oxidation-level substrates have been employed in the synthesis of benzazoles via oxidative annulation, which is initiated by in situ formation of aldehyde or imine intermediate.[5] Moreover, metal-catalyzed cyclization of *o*-haloanilides was also reported for the synthesis of benzazoles.[6]

In recent years, redox condensation of nitroarenes with low-oxidation-level substrates has attracted much attention of organic chemists. Nitroarenes are usually considered a precursor of aniline, and they can be reduced to aniline by a redox process with a low-oxidation-level partner. Redox condensation provides an efficient synthetic approach to benzazole motifs from readily available starting materials through a one-pot reaction. Nguyen et al. developed a Fe/S-catalyzed cyclization of *o*-substituted nitrobenzenes with 4-picoline, alkyl amines, and aryl acetic acids to form 2-aryl benzazoles.[7] Inspired by that report, Gan et al. extended similar Fe/S redox systems to benzyl chlorides and disulfides.[8] Pd-catalyzed carbonylative coupling of *o*-substituted nitrobenzenes with aryl halides has also been reported; however, stoichiometric Fe(CO)$_5$ was used as a carbonyl source and reducing reagent.[9] Alcohols have received more attention as reducing partners because of their availability in a wide range of structures. Indeed, alcohols have been widely applied in redox condensations with *o*-nitrophenols and *o*-nitroaniline, leading to the corresponding benzazoles.[10] These reactions usually proceed using a specific metal catalyst or heterogeneous catalyst. However, the formation of organic waste and the use of excess alcohols are often major concerns. Therefore, an efficient synthetic method for these benzazoles from simple and readily available starting materials is still desirable.

Tricarbonyl ($\eta^4$-cyclopentadienone) iron(0) complexes have been extensively applied to construct C−N, C−C, and C−O bonds through a hydrogen-borrowing strategy.[11] In this strategy, alcohol can be applied as both a coupling partner and a reductant. Using this iron complex, we recently reported

**Scheme 1. Synthesis of Benzazoles from Nitroarene through a Redox Strategy**
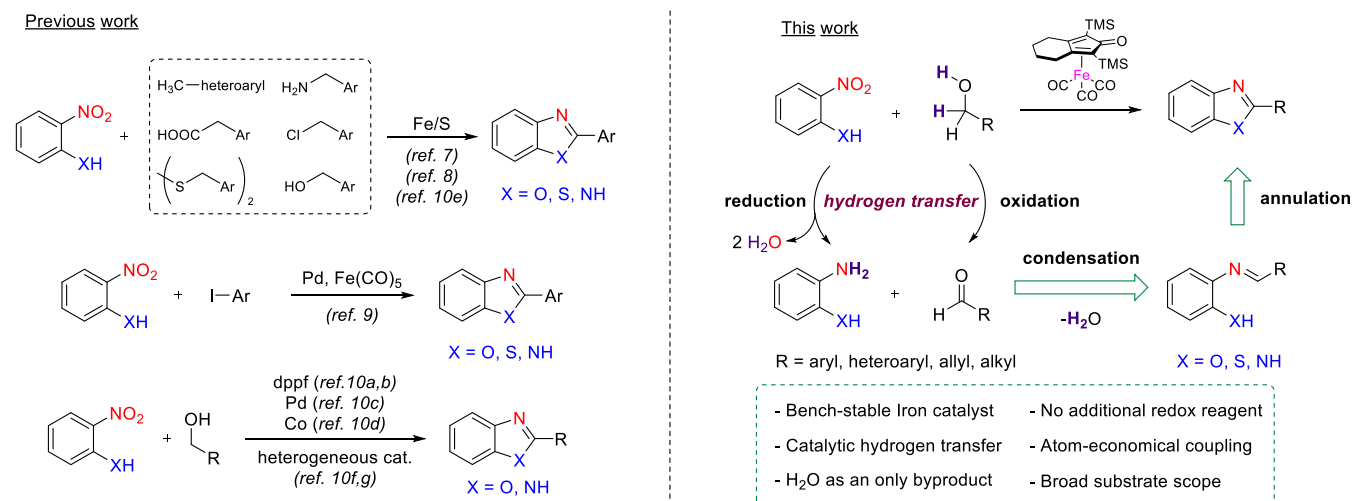


the synthesis of benzimidazoles via acceptorless dehydrogenative coupling of alcohols with 1,2-diaminobenzene.[12] Based on our previous work, we envisioned that nitroarenes could be applied as a hydrogen acceptor to balance the transfer of hydrogen. Even if the hydrogenation of C=O, C=N, and C=C bonds has been reported using this iron complex, a reduction of nitro group via hydrogen transfer has rarely been investigated to date. Herein, we report a facile synthesis of 2-substituted benzazoles by iron-catalyzed transfer hydrogenative annulation of o-nitrophenol/thiophenol/aniline with alcohols (Scheme 1). No additional redox reagents were needed, and only water was generated as a byproduct in this transformation.

## ■ RESULTS AND DISCUSSION

We began the optimization study for the transfer hydrogenative condensation of o-nitrophenol **1a** using benzyl alcohol **2a** as a reducing partner (Table 1). The preliminary reaction was

carried out using **Fe 1** as a catalyst (3 mol %), and the expected 2-phenylbenzoxazole **3aa** was isolated in 51% yield along with 2-(benzylamino) phenol **3aa′** (entry 1). We supposed that the catalyst could mediate imine reduction competitively with the annulation process. To suppress the formation of **3aa′**, catalyst loading was reduced to 2 mol % and the formation of **3aa′** was significantly decreased (entry 2). Moreover, o-xylene and cyclopentyl methyl ether (CPME) afford benzoxazole **3aa** more selectively than toluene (entries 3 and 4). When alcohol **2a** was decreased from 2.0 to 1.5 equiv, an excellent yield of **3aa** was achieved without side product **3aa′** (entries 5 and 6). Further decreasing the quantities of catalyst or alcohol gave a negative result on the reaction (entries 7 and 8). In addition, various iron complexes, including commercially available $FeCl_3 \cdot 6H_2O$ and $Fe_2(CO)_9$, were screened to determine the best catalyst in the reaction condition. Among these complexes, **Fe 1** showed the highest activity in transfer hydrogenative condensation (see details in the Supporting Information). All reactions were carried out under pressure in a sealed tube to enhance the efficiency of hydrogen transfer, especially for the reduction of nitro group.

With the optimized conditions, we investigated the substrate scope for transfer hydrogenative condensation between o-nitrophenol **1** and alcohol **2** (Table 2). Various benzyl alcohols afforded the desired benzoxazole products **3ab–al** in high yields (70−97%). In the case of alcohols with strong electron-withdrawing groups such as $CO_2Me$ and CN, benzoxazole products were obtained in lower yields (**3al−an**). Generally, an alcohol with a para-substituent provided the desired products in a slightly higher yield than that of an alcohol with meta- and ortho-substituents (**3ab−ag**). A series of alcohols containing heterocycles (furan, thiophene, and pyridine) also gave the corresponding products (**3aq−as**). In addition to benzylic alcohols, allyl and alkyl alcohols were explored. Although the yields were lower than those achieved by benzylic alcohols, the allyl and alkyl alcohols could afford the desired products (**3at**, **3au**). It is important to note that a small amount of o-aminophenol, which might be generated in situ by hydrogenation of **1a**, was observed in some cases.

Next, variously substituted o-nitrophenols **1** were used for transfer hydrogenative condensation with benzyl alcohol **2a**. Electron-rich nitrophenols tend to afford products in higher yields than electron-deficient nitrophenols (**3ba−ea**). In

**Table 1. Optimization of the synthesis of 2-phenylbenzoxazole**[a]



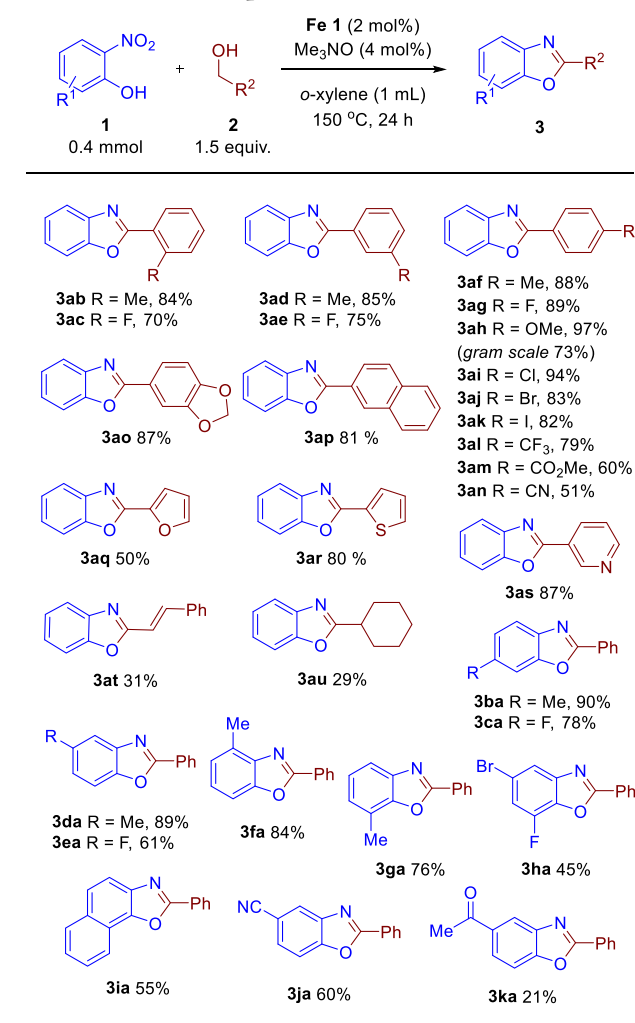| entry | 2a (equiv) | solvent | yield (%)[b] | |
| | | | 3aa | 3aa′ |
|---|---|---|---|---|
| 1[c] | 2.0 | toluene | 51 | 48 |
| 2 | 2.0 | toluene | 58 | 25 |
| 3 | 2.0 | o-xylene | 77 | 11 |
| 4 | 2.0 | CPME | 74 | 10 |
| 5 | 1.5 | CPME | 87 | |
| **6** | **1.5** | **o-xylene** | **89** | |
| 7[d] | 1.5 | o-xylene | 67 | |
| 8 | 1.0 | o-xylene | 51 | |

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.4−0.8 mmol), **Fe 1** (2 mol %), $Me_3NO$ (4 mol %), and solvent (1 mL) in a sealed tube at 150 °C for 24 h. [b]Isolated yield. [c]**Fe 1** (3 mol %), $Me_3NO$ (6 mol %). [d]**Fe 1** (1.5 mol %), $Me_3NO$ (3 mol %).

## Table 2. Reaction Scope for Benzoxazoles



dimerized disulfide product. When we added 1 equiv of
$^t$BuONa to suppress the dimerization of **4a**, the yield of **5aa** was
significantly increased to 71% (Scheme 2). 3-Pyridine and 1-
naphthalene were also successfully substituted on the 2-position
of benzothiazole with good yields (**5as**, **5av**).

## Scheme 2. Synthesis of Benzothiazoles
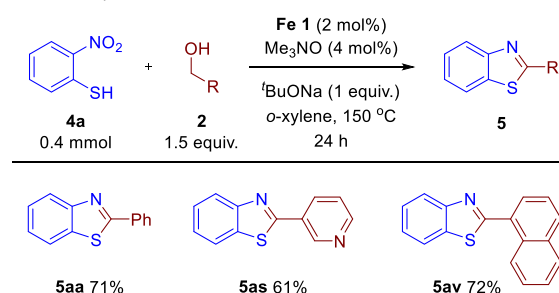


To further extend the reaction system, we employed *o*-
nitroaniline **6a** as a substrate to explore the possibility of
benzimidazole formation (Table 3). While no annulated

## Table 3. Optimization Studies for the Synthesis of 2-Phenylbenzimidazole[a]



| entry | $^t$BuONa (equiv) | solvent | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 | | *o*-xylene | 24 | |
| 2 | 1.0 | *o*-xylene | 24 | 19 |
| 3 | 1.0 | toluene | 24 | 15 |
| 4 | 1.0 | CPME | 24 | 45 |
| 5 | 1.0 | 1,4-dioxane | 24 | 18 |
| 6 | 1.0 | chlorobenzene | 24 | 62 |
| 7 | 1.0 | chlorobenzene | 42 | 75 |
| 8[c] | 1.0 | chlorobenzene | 42 | 70 |
| **9** | **1.5** | **chlorobenzene** | **42** | **80** |

[a]Reaction conditions: **6a** (0.4 mmol), **2a** (0.6 mmol), **Fe 1** (2 mol
%), Me$_3$NO (4 mol %), $^t$BuONa (0.4−0.8 mmol), and solvent (1
mL) in a sealed tube at 150 °C. [b]Isolated yield. [c]160 °C.

particular, CN- and COCH$_3$-substituted **1** gave the desired
products in low yields (**3ja**, **3ka**). Although we could not
observe any reduced products, a trace amount of aldol
condensation product was observed in the reaction for **3ka**.
These results indicate that the nitrophenol **1** bearing electron-
rich substituents facilitate the transfer hydrogenative annulation
higher than those of electron-withdrawing substituents. If there
was a substituent at the *ortho*-position to the OH group in
nitrophenol, benzoxazole products were obtained in lower
yields (**3ga−ia**). No hydrogenated or reduced products were
observed in the reaction containing substituents that could be
affected by hydrogenation, such as halogen, ester, and nitrile.
The tolerance of various functional groups opens the pathway
for further modifications of the benzoxazole products.
Furthermore, the practical utility of the developed method
was demonstrated by the gram-scale reaction of **3ah** (73%).

After the successful synthesis of benzoxazoles from *o*-
nitrophenol, we envisioned that benzothiazole and benzimida-
zoles could also be synthesized by replacing *o*-nitrophenol with
*o*-nitrothiophenol/aniline. First, we explored the feasibility of
benzothiazole formation between *o*-nitrothiophenol **4a** and
benzyl alcohol **2a** using the above reaction conditions. Freshly
prepared *o*-nitrothiophenol **4a** was used in the reaction since **4a**
is unstable and easily undergoes dimerization to 2,2′-
dinitrodiphenyl disulfide itself. However, a low yield of the
desired benzothiazole **5aa** was obtained (30%) along with the

products could be detected under the standard conditions,
significant amounts of 1,2-diamonobenzene and benzaldehyde,
which can be generated through hydrogen transfer, were
observed (entry 1). Based on our experience and previous
reports,[10d,g,12] we expected that a stoichiometric base is
required for the formation of benzimidazole. The screening of
bases was followed, and $^t$BuONa was found to be the most
appropriate one (entry 2), whereas other bases ($^t$BuOK, KOH,
and K$_2$CO$_3$) gave only trace amounts of benzimidazole **7aa**
(results are not shown). Considering the more polar character
of benzimidazole than benzoxazoles and benzothiazoles, we
assumed that solvent may be a crucial factor in the
benzimidazole synthesis. Thus, we examined the solvent effect
and revealed that chlorobenzene is the best solvent (entries 2−
6). A longer reaction time afforded **7aa** in higher yield (entry
7), and a slightly diminished yield was observed at a higher
temperature (entry 8). The highest yield of **7aa** was obtained by
increasing the quantity of base to 1.5 equiv (entry 9, 80%).

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With the optimal conditions in hand, the scope of alcohol substrates was investigated for the synthesis of benzimidazole (Table 4). Similar to benzoxazole, benzyl alcohols with

**Table 4. Scope of Alcohols for the Synthesis of Benzimidazoles**



7af R = Me, 80%
7ah R = OMe, 85%
7ag R = F, 79%
7aj R = Br, 63%

7ao 71%

7av 77 %

7ar 59 %

7as 63%
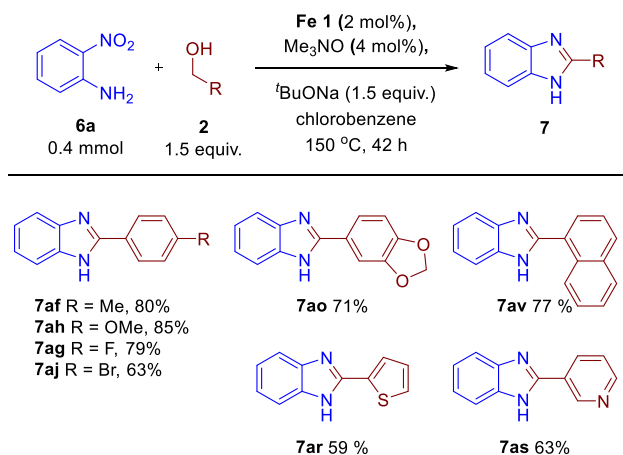
electron-donating groups (7af, 7ah) are more favorable than those having electron-withdrawing groups (7ag, 7aj). Hetero-aryl-substituted alcohols also afforded the desired products 7ar and 7as in satisfactory yields. Notably, any 1,2-disubstituted benzimidazole products were not observed in the reaction, which is often problematic in the selective synthesis of benzimidazole.

Several control experiments were performed to investigate the reaction mechanism (Scheme 3). When the reaction was

**Scheme 3. Mechanism Studies**
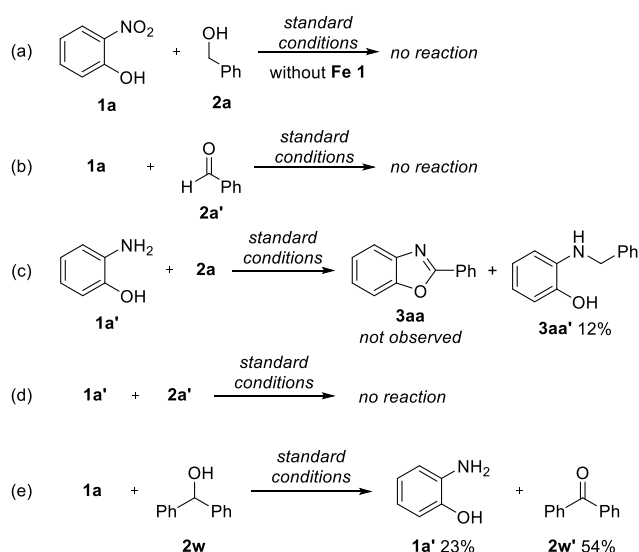


carried out in the absence of a catalyst, any products were not observed (Scheme 3a). This result indicates the vital role of iron catalyst in the hydrogen transfer. As shown in Scheme 3b, benzaldehyde 2a′ was applied directly in the reaction instead of 2a. However, nitro reduction of 1a did not occur and no products were observed. If o-aminophenol 1a′ was treated with 2a, no desired product was detected, and a small amount of 3aa′ was observed (Scheme 3c). N-Benzyl product 3aa′ could

be formed via the C−N bond formation by transfer hydrogenation between amine 1a′ and alcohol 2a. These experiments revealed that both hydrogen acceptors and hydrogen donors are required for iron-catalyzed hydrogen transfer. Furthermore, the reaction of prereduced 1a′ with preoxidized 2a′ could not produce the desired product 3aa, and most of starting materials remained (Scheme 3d). We speculated that imine formation and cyclization between 1a′ and 2a′ are reversible until the final oxidative aromatization. Therefore, the iron complex was determined not only to serve as a hydrogen mediator between the nitro and alcohol groups but also to be involved in the final oxidative aromatization to form the desired product 3aa. To determine the key redox intermediates, secondary alcohol 2w was applied in the reaction as a reducing partner (Scheme 3e). Although annulation did not occur, both o-aminophenol 1a′ and ketone 2w′ were directly obtained. This result confirmed that the alcohol is oxidized into the corresponding carbonyl intermediate and that the nitro group is reduced to an amino group in situ by iron-catalyzed hydrogen transfer process.

Based on the above-described experiments, a plausible mechanism of the transfer hydrogenative condensation for benzoxazole was proposed, as depicted in Scheme 4. First, the

**Scheme 4. Proposed Mechanism for the Synthesis of Benzoxazole**
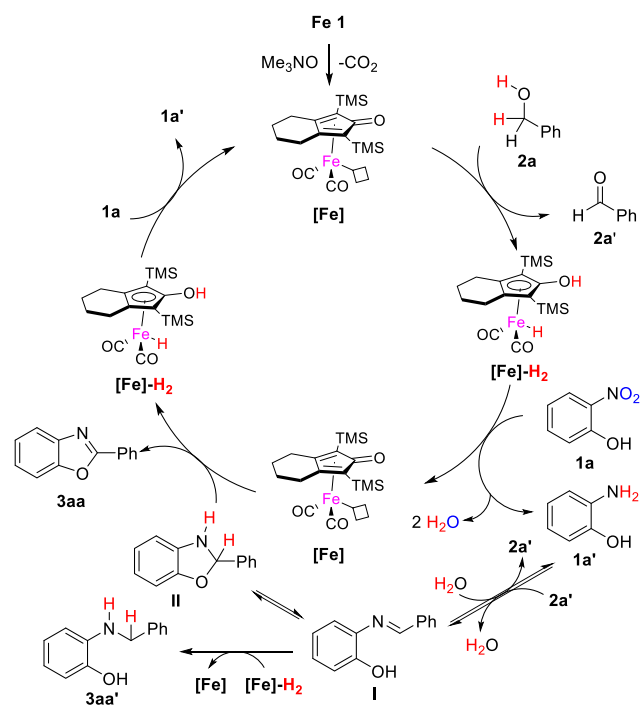


iron catalyst Fe 1 is activated by Me₃NO to form 16-electron iron species [Fe]. [Fe] mediates the oxidation of alcohol 2a and generates [Fe]-H₂, which reduces nitrophenol 1a to amino-phenol 1a′. Condensation of the oxidized aldehyde 2a′ with 1a′ produces imine intermediate I, followed by cyclization to form intermediate II. All steps from 1a′ and 2a′ to intermediate II are reversible; thus, [Fe]-mediated oxidative aromatization of II leads to completion of benzoxazole 3aa. In the case of benzimidazole synthesis, the oxidative aromatization did not occur with [Fe] alone, and the base helps to complete the benzimidazole synthesis at this step. As mentioned above, we

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also identified **3aa′** as a side product, which might be generated from imine **I** by [**Fe**]-**H₂** mediated hydrogenation.

## CONCLUSIONS

In conclusion, we have described the iron-catalyzed transfer hydrogenative condensation of nitroarenes with alcohol for the synthesis of benzazoles. Tricarbonyl ($\eta^4$-cyclopentadienone) iron(0) complexes have been applied in a hydrogen transfer strategy between nitro and alcohol functionalities. This is a pioneering work on the reduction of nitro group via hydrogen transfer using this type of iron complex. A wide range of benzoxazole derivatives were synthesized in good to excellent yields. A plausible mechanism for benzoxazole formation was presented based on the control experiments. The main advantages of the developed method are that no additional oxidants or reductants were required, and only water was generated as a stoichiometric byproduct. Moreover, the reaction system was successfully extended to the synthesis of benzothiazoles and benzimidazoles. Therefore, this methodology provides an efficient alternative for the synthesis of benzazole derivatives. Further extension to access other types of *N*-heterocycles using an iron-catalyzed hydrogen transfer strategy is under investigation in our research group.

## EXPERIMENTAL SECTION

**General Information.** All catalytic reactions were carried out under an argon atmosphere using a sealed tube. Iron complexes **Fe 1–5** and **Fe 6** were prepared according to the literature.[13,14] All commercially available reagents and solvents (purchased from Sigma-Aldrich, TCI, Alfa Aesar, and Acros Organics) were used without further purification unless otherwise noted. Reactions were monitored by thin-layer chromatography on a silica gel 60 F254 plate using UV illumination at 254 nm. Column chromatography was performed on silica gel (230–400 mesh) using a mixture of *n*-hexane/ethyl acetate or dichloromethane (DCM)/methanol as eluents. Nuclear magnetic resonance ($^1$H NMR, $^{13}$C NMR, $^{19}$F NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz ($^1$H), 100 MHz ($^{13}$C), 376 MHz ($^{19}$F)] using CDCl₃ or DMSO-$d_6$ as solvent. The chemical shifts are given in parts per million (ppm) on the delta ($\delta$) scale. The solvent peak was used as a reference value, for $^1$H NMR: CDCl₃ = 7.26 ppm, DMSO-$d_6$ = 2.50 ppm; for $^{13}$C{$^1$H} NMR: CDCl₃ = 77.16 ppm, DMSO-$d_6$ = 39.52 ppm. Coupling constants ($J$) are expressed in hertz (Hz). IR spectra were recorded on a JASCO, FT/IR-4200 infrared spectrophotometer and are reported in cm$^{-1}$. All high-resolution mass spectra (HRMS) were acquired under fast atom bombardment (FAB) mode on a JMS-700 MStation mass spectrometer using a double-focusing magnetic sector. Melting points were measured on a Büchi B-540 melting point apparatus and were not corrected.

**Synthesis of Benzoxazoles.** *General Procedure A.* A mixture of *o*-nitrophenol (0.4 mmol, 1.0 equiv), alcohol (0.6 mmol, 1.5 equiv), **Fe 1** (3.35 mg, 0.008 mmol), and Me₃NO (1.2 mg, 0.016 mmol) was placed in a dried 10 mL sealed tube. The tube was degassed and backfilled with argon three times; then, *o*-xylene (1 mL) was added using a syringe under argon flow. The reaction tube was capped, and then the mixture was stirred and heated at 150 °C in an oil bath for 24 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate as an eluent to afford the desired benzoxazole derivatives **3**.

*2-Phenylbenzo[d]oxazole (3aa).* Following the general procedure **A** with **1a** (55.6 mg) and **2a** (62 μL), **3aa** was obtained as a white solid (69.5 mg, 89% yield). Mp 103−105 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.26−8.28 (m, 2H), 7.79 (q, $J$ = 3.0 Hz, 1H), 7.60 (q, $J$ = 3.0 Hz, 1H), 7.52−7.55 (m, 3H), 7.35−7.38 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 163.2, 150.9, 142.2, 131.7, 129.0, 127.8, 127.3, 125.2, 124.7, 120.1, 110.7. HRMS (FAB$^+$) *m/z* calcd for C₁₃H₁₀NO [M + H]$^+$: 196.0762, found: 196.0759.

*2-(Benzylamino)phenol (3aa′).* Following the general procedure **A** with **1a** (55.6 mg) and **2a** (0.8 mmol, 83 μL), **3aa′** was obtained as colorless oil (8.8 mg, 11% yield). Eluent: *n*-hexane/ethyl acetate (90/10). $^1$H NMR (400 MHz, CDCl₃) δ 7.34−7.41 (m, 4H), 7.26−7.30 (m, 1H), 6.84 (t, $J$ = 7.4 Hz, 1H), 6.62−6.73 (m, 3H), 4.63 (s, 1H), 4.36 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 143.5, 139.5, 137.1, 128.713, 127.7, 127.3, 121.9, 117.9, 114.4, 112.6, 48.7. HRMS (FAB$^+$) *m/z* calcd for C₁₃H₁₃NO [M + H]$^+$: 199.0997, found: 199.0993.

*2-(o-Tolyl)benzo[d]oxazole (3ab).* Following the general procedure **A** with **1a** (55.6 mg) and **2b** (73.3 mg), **3ab** was obtained as a white solid (70 mg, 84% yield). Mp 69−71 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.17−8.19 (m, 1H), 7.81 (dd, $J$ = 5.7, 3.4 Hz, 1H), 7.60 (q, $J$ = 3.1 Hz, 1H), 7.35−7.42 (m, 5H), 2.82 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 163.5, 150.4, 142.2, 139.0, 131.9, 131.0, 130.1, 126.3, 126.2, 125.1, 124.5, 120.2, 110.6, 22.4. HRMS (FAB$^+$) *m/z* calcd for C₁₄H₁₂NO [M + H]$^+$: 210.0919, found: 210.0912.

*2-(2-Fluorophenyl)benzo[d]oxazole (3ac).* Following the general procedure **A** with **1a** (55.6 mg) and **2c** (65 μL), **3ac** was obtained as a white solid (59.9 mg, 70% yield). Mp 97−99 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.25 (td, $J$ = 7.5, 1.7 Hz, 1H), 7.83−7.85 (m, 1H), 7.61−7.64 (m, 1H), 7.51−7.54 (m, 1H), 7.38−7.41 (m, 2H), 7.30−7.34 (m, 1H), 7.26−7.28 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 160.9 (d, $J$ = 256.8 Hz), 159.5 (d, $J$ = 4.8 Hz), 150.6, 141.9, 133.2 (d, $J$ = 8.7 Hz), 130.6, 125.6, 124.6 (d, $J$ = 2.9 Hz), 124.6, 120.5, 117.2 (d, $J$ = 21.1 Hz), 115.6 (d, $J$ = 10.5 Hz), 110.81. $^{19}$F NMR (376 MHz, CDCl₃) δ −110.0. HRMS (FAB$^+$) *m/z* calcd for C₁₃H₉FNO [M + H]$^+$: 214.0668, found: 214.0664.

*2-(m-Tolyl)benzo[d]oxazole (3ad).* Following the general procedure **A** with **1a** (55.6 mg) and **2d** (73.3 mg), **3ad** was obtained as a white solid (71.2 mg, 85% yield). Mp 81−83 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 8.06 (d, $J$ = 7.8 Hz, 1H), 7.77−7.79 (m, 1H), 7.57−7.60 (m, 1H), 7.42 (t, $J$ = 7.5 Hz, 1H), 7.35 (dt, $J$ = 9.5, 3.7 Hz, 3H), 2.46 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 163.4, 150.9, 142.2, 138.9, 132.5, 129.0, 128.3, 127.1, 125.2, 124.9, 124.7, 120.1, 110.7, 21.5. HRMS (FAB$^+$) *m/z* calcd for C₁₄H₁₂NO [M + H]$^+$: 210.0919, found: 210.0915.

*2-(3-Fluorophenyl)benzo[d]oxazole (3ae).* Following the general procedure **A** with **1a** (55.6 mg) and **2e** (65 μL), **3ae** was obtained as a white solid (64.0 mg, 75% yield). Mp 91−93 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.05−8.07 (m, 1H), 7.94−7.98 (m, 1H), 7.78−7.80 (m, 1H), 7.59−7.61 (m, 1H), 7.51 (td, $J$ = 8.0, 5.6 Hz, 1H), 7.37−7.41 (m, 2H), 7.25 (dt, $J$ = 9.1, 1.6 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 163.0 (d, $J$ = 245.3 Hz), 161.9 (d, $J$ = 3.8 Hz), 150.9, 142.0, 130.8 (d, $J$ = 7.7 Hz), 129.3 (d, $J$ = 8.6 Hz), 125.6, 124.9, 123.4 (d, $J$ = 2.9 Hz), 120.3, 118.6 (d, $J$ = 21.0 Hz), 114.7 (d, $J$ = 24.0 Hz), 110.8. $^{19}$F NMR (376 MHz, CDCl₃) δ −111.7. HRMS (FAB$^+$) *m/z* calcd for C₁₃H₉FNO [M + H]$^+$: 214.0668, found: 214.0672.

*2-(p-Tolyl)benzo[d]oxazole (3af).* Following the general procedure **A** with **1a** (55.6 mg) and **2f** (73.3 mg), **3af** was obtained as a white solid (73.5 mg, 88% yield). Mp 115−117 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.15 (d, $J$ = 8.3 Hz, 2H), 7.75−7.77 (m, 1H), 7.56−7.58 (m, 1H), 7.32−7.36 (m, 4H), 2.45 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 163.4, 150.8, 142.3, 142.2, 129.8, 127.7, 125.0, 124.6, 124.5, 120.0, 110.6, 21.8. HRMS (FAB$^+$) *m/z* calcd for C₁₄H₁₂NO [M + H]$^+$: 210.0919, found: 210.0914.

*2-(4-Fluorophenyl)benzo[d]oxazole (3ag).* Following the general procedure **A** with **1a** (55.6 mg) and **2g** (65 μL), **3ag** was obtained as a white solid (76.1 mg, 89% yield). Mp 97−99 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl₃) δ 8.25−8.28 (m, 2H), 7.76−7.78 (m, 1H), 7.57−7.59 (m, 1H), 7.35−7.38 (m, 2H), 7.20−7.24 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl₃) δ 164.9 (d, $J$ = 250.1 Hz), 162.3, 150.9, 142.2, 129.9 (d, $J$ = 9.5 Hz), 125.3, 124.8, 123.6 (d, $J$ = 3.9 Hz), 120.1, 116.3 (d, $J$ = 22.0 Hz), 110.7. $^{19}$F NMR (376 MHz, CDCl₃) δ −107.4. HRMS (FAB$^+$) *m/z* calcd for C₁₃H₉FNO [M + H]$^+$: 214.0668, found: 214.0660.

*2-(4-Methoxyphenyl)benzo[d]oxazole (3ah).* Following the general procedure **A** with **1a** (55.6 mg) and **2h** (82.9 mg), **3ah** was obtained as a white solid (87 mg, 97% yield). Mp 102−104 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (dd, *J* = 7.1, 2.1 Hz, 2H), 7.73−7.75 (m, 1H), 7.55−7.57 (m, 1H), 7.31−7.34 (m, 2H), 7.04 (dd, *J* = 6.9, 1.8 Hz, 2H), 3.90 (s, 3H) $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 163.3, 162.4, 150.8, 142.4, 129.5, 124.7, 124.5, 119.8, 119.7, 114.5, 110.5, 55.6. HRMS (FAB$^+$) *m/z* calcd for C$_{14}$H$_{12}$NO$_2$ [M + H]$^+$: 226.0868, found: 226.0864.

*Procedure for the Gram-Scale Synthesis of 3ah.* A mixture of *o*-nitrophenol **1a** (1.0 g, 7.19 mmol), 4-methoxy benzyl alcohol **2h** (1.49 g, 10.79 mmol), **Fe 1** (60.17 mg, 2 mol %), and Me$_3$NO (21.60 mg, 4 mol %) was placed in a dried 100 mL sealed tube. The tube was degassed and backfilled with argon three times; then, *o*-xylene (18 mL) was added using a syringe under argon flow. The reaction tube was capped, and then the mixture was stirred and heated at 150 °C in an oil bath for 24 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (97/3) as an eluent to afford the corresponding benzoxazole **3ah** (1.18 g, 73% yield) (1.25 g, 77% for 42 h).

*2-(4-Chlorophenyl)benzo[d]oxazole (3ai).* Following the general procedure **A** with **1a** (55.6 mg) and **2i** (85.5 mg), **3ai** was obtained as a white solid (86.1 mg, 94% yield). Mp 150−152 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.76−7.79 (m, 1H), 7.58−7.60 (m, 1H), 7.51 (dt, *J* = 9.0, 2.3 Hz, 2H), 7.36−7.39 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 150.9, 142.2, 137.9, 129.4, 129.0, 125.8, 125.5, 124.9, 120.2, 110.8. HRMS (FAB$^+$) *m/z* calcd for C$_{13}$H$_9$ClNO [M + H]$^+$: 230.0373, found: 230.0372.

*2-(4-Bromophenyl)benzo[d]oxazole (3aj).* Following the general procedure **A** with **1a** (55.6 mg) and **2j** (112.3 mg), **3aj** was obtained as a white solid (91.1 mg, 83% yield). Mp 156−158 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, *J* = 8.7 Hz, 2H), 7.76−7.79 (m, 1H), 7.68 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.58−7.60 (m, 1H), 7.37 (td, *J* = 3.3, 2.1 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.3, 150.9, 142.1, 132.4, 129.2, 126.4, 126.2, 125.5, 124.9, 120.3, 110.8. HRMS (FAB$^+$) *m/z* calcd for C$_{13}$H$_9$BrNO [M + H]$^+$: 273.9868, found: 273.9858.

*2-(4-Iodophenyl)benzo[d]oxazole (3ak).* Following the general procedure **A** with **1a** (55.6 mg) and **2k** (140.5 mg), **3ak** was obtained as a white solid (105.2 mg, 82% yield). Mp 168−170 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96−7.99 (m, 1H), 7.87−7.90 (m, 1H), 7.76−7.78 (m, 1H), 7.57−7.59 (m, 1H), 7.37 (td, *J* = 3.4, 1.8 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.5, 150.9, 142.1, 138.4, 129.1, 126.8, 125.6, 124.9, 120.3, 110.8, 98.6. HRMS (FAB$^+$) *m/z* calcd for C$_{13}$H$_9$INO [M + H]$^+$: 321.9729, found: 321.9728.

*2-(4-(Trifluoromethyl)phenyl)benzo[d]oxazole (3al).* Following the general procedure **A** with **1a** (55.6 mg) and **2l** (82 µL), **3al** was obtained as a white solid (83.1 mg, 79% yield). Mp 142−144 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38 (d, *J* = 8.2 Hz, 3H), 7.79−7.82 (m, 5H), 7.62 (td, *J* = 3.7, 1.7 Hz, 2H), 7.39−7.42 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 161.6, 151.0, 142.0, 133.1 (q, *J* = 32.5 Hz), 130.6, 128.0, 126.1 (q, *J* =3.8 Hz), 125.9, 125.2−119.8 (q, *J* =270.2), 120.5, 110.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −62.9. HRMS (FAB$^+$) *m/z* calcd for C$_{14}$H$_9$F$_3$NO [M + H]$^+$: 264.0636, found: 264.0631.

*Methyl 4-(Benzo[d]oxazol-2-yl)benzoate (3am).* Following the general procedure **A** with **1a** (55.6 mg) and **2m** (99.7 mg), **3am** was obtained as a white solid (61.0 mg, 60% yield). Mp 193−195 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33−8.35 (m, 2H), 8.20 (d, *J* = 8.7 Hz, 2H), 7.80−7.82 (m, 1H), 7.61−7.63 (m, 1H), 7.40 (dd, *J* = 6.1, 2.6 Hz, 2H), 3.97 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 166.5, 162.1, 151.0, 142.1, 132.7, 131.8, 130.3, 127.6, 125.9, 125.0, 120.5, 110.9, 52.6. IR (neat) $v$ 3072, 1718, 1540, 1456, 1260, 1108 cm$^{-1}$. HRMS (FAB$^+$) *m/z* calcd for C$_{15}$H$_{12}$NO$_3$ [M + H]$^+$: 254.0814, found: 254.0817.

*4-(Benzo[d]oxazol-2-yl)benzonitrile (3an).* Following the general procedure **A** with **1a** (55.6 mg) and **2n** (79.9 mg), **3an** was obtained as

a white solid (45.1 mg, 51% yield). Mp 203−205 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.34 (dd, *J* = 6.9, 1.8 Hz, 2H), 7.79−7.81 (m, 3H), 7.60 (q, *J* = 3.1 Hz, 1H), 7.39−7.43 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 151.0, 142.0, 132.8, 131.2, 128.0, 126.3, 125.2, 120.7, 118.3, 114.8, 111.0. IR (neat) $v$ 3065, 2308, 1652, 1507, 1216, 750, 689, 669 cm$^{-1}$. HRMS (FAB$^+$) *m/z* calcd for C$_{14}$H$_9$N$_2$O [M + H]$^+$: 221.0715, found: 221.0716.

*2-(Benzo[d][1,3]dioxol-5-yl)benzo[d]oxazole (3ao).* Following the general procedure **A** with **1a** (55.6 mg) and **2o** (91.3 mg), **3ao** was obtained as a white solid (83.1 mg, 87% yield). Mp 150−152 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.72−7.74 (m, 1H), 7.70 (d, *J* = 1.4 Hz, 1H), 7.54−7.56 (m, 1H), 7.32−7.34 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.07 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 163.0, 150.8, 150.7, 148.4, 142.3, 124.9, 124.7, 123.0, 121.3, 119.9, 110.6, 108.9, 107.8, 101.9. HRMS (FAB$^+$) *m/z* calcd for C$_{14}$H$_{10}$NO$_3$ [M + H]$^+$: 240.0661, found: 240.0658.

*2-(Naphthalen-2-yl)benzo[d]oxazole (3ap).* Following the general procedure **A** with **1a** (55.6 mg) and **2p** (94.9 mg), **3ap** was obtained as a white solid (79.3 mg, 81% yield). Mp 111−113 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.79 (s, 1H), 8.33 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.99 (q, *J* = 4.3 Hz, 2H), 7.91 (q, *J* = 3.0 Hz, 1H), 7.82 (q, *J* = 3.0 Hz, 1H), 7.57−7.65 (m, 3H), 7.39 (q, *J* = 3.2 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 163.4, 151.0, 142.4, 134.9, 133.1, 129.1, 128.9, 128.3, 128.7, 128.0, 127.7, 125.3, 124.8, 124.5, 124.1, 120.2, 110.8. HRMS (FAB$^+$) *m/z* calcd for C$_{17}$H$_{12}$NO [M + H]$^+$: 246.0919, found: 246.0916.

*2-(Furan-2-yl)benzo[d]oxazole (3aq).* Following the general procedure **A** with **1a** (55. 6 mg) and **2q** (52 µL), **3aq** was obtained as a white solid (37.2 mg, 50% yield). Mp 87−89 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75−7.77 (m, 1H), 7.67 (s, 1H), 7.55−7.57 (m, 1H), 7.36 (dt, *J* = 7.0, 2.2 Hz, 2H), 7.28 (t, *J* = 2.5 Hz, 1H), 7.26 (*J* = 2.3 Hz, 1H), 6.61−6.63 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 155.4, 150.3, 145.9, 142.7, 141.8, 125.4, 125.0, 120.3, 114.4, 112.4, 110.7. HRMS (FAB$^+$) *m/z* calcd for C$_{11}$H$_8$NO$_2$ [M + H]$^+$: 186.0555, found: 186.0561.

*2-(Thiophen-2-yl)benzo[d]oxazole (3ar).* Following the general procedure **A** with **1a** (55.6 mg) and **2r** (57 µL), **3ar** was obtained as a white solid (64.2 mg, 80% yield). Mp 104−106 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (q, *J* = 1.7 Hz, 1H), 7.73−7.75 (m, 1H), 7.54−7.57 (m, 2H), 7.33−7.36 (m, 2H), 7.20 (dd, *J* = 4.8, 3.9 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 159.2, 150.6, 142.1, 130.4, 130.1, 129.8, 128.4, 125.2, 124.9, 119.9, 110.6. HRMS (FAB$^+$) *m/z* calcd for C$_{11}$H$_8$NOS [M + H]$^+$: 202.0327, found: 202.0326.

*2-(Pyridin-3-yl)benzo[d]oxazole (3as).* Following the general procedure **A** with **1a** (55.6 mg) and **2s** (58 µL), **3as** was obtained as a white solid (68.2 mg, 87% yield). Mp 112−114 °C. Eluent: *n*-hexane/ethyl acetate (90/10). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.48 (d, *J* = 0.9 Hz, 1H), 8.77 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.52 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.80−7.82 (m, 1H), 7.61−7.64 (m, 1H), 7.48 (ddd, *J* = 8.0, 4.8, 0.9 Hz, 1H), 7.39−7.43 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 160.8, 152.2, 150.8, 148.9, 141.9, 134.8, 125.8, 125.0, 123.8, 123.6, 120.4, 110.9. HRMS (FAB$^+$) *m/z* calcd for C$_{12}$H$_9$N$_2$O [M + H]$^+$: 197.0715, found: 197.0716.

*2-Styrylbenzo[d]oxazole (3at).* Following the general procedure **A** with **1a** (55.6 mg) and **2t** (80.5 mg), **3at** was obtained as a white solid (27.8 mg, 31% yield). Mp 83−85 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, *J* = 16.5 Hz, 1H), 7.72 (q, *J* = 3.1 Hz, 1H), 7.60−7.62 (m, 2H), 7.52−7.55 (m, 1H), 7.38−7.45 (m, 3H), 7.34 (td, *J* = 3.5, 1.8 Hz, 2H), 7.09 (d, *J* = 16.5 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 150.6, 142.3, 139.6, 135.3, 129.9, 129.1, 127.7, 125.4, 124.7, 120.0, 114.1, 110.5. HRMS (FAB$^+$) *m/z* calcd for C$_{15}$H$_{12}$NO [M + H]$^+$: 222.0919, found: 222.0924.

*2-Cyclohexylbenzo[d]oxazole (3au).* Following the general procedure **A** with **1a** (55.6 mg) and **2u** (74 µL), **3au** was obtained as a white solid (23.2 mg, 29% yield). Mp 37−39 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67−7.69 (m, 1H), 7.46−7.49 (m, 1H), 7.26−7.31 (m, 2H), 2.95 (qd, *J* =

7.5, 3.8 Hz, 1H), 2.15–2.19 (m, 2H), 1.87 (dt, $J$ = 12.7, 3.6 Hz, 2H), 1.67–1.76 (m, 3H), 1.25–1.49 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.6, 150.7, 141.4, 124.5, 124.1, 119.8, 110.4, 38.1, 30.6, 25.9, 25.8. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_{16}$NO [M + H]$^+$: 202.1232, found: 202.1235.

*6-Methyl-2-phenylbenzo[d]oxazole (3ba).* Following the general procedure A with **1b** (61.3 mg) and **2a** (62 µL), **3ba** was obtained as a white solid (75.3 mg, 90% yield). Mp 93–95 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (td, $J$ = 4.0, 1.6 Hz, 2H), 7.64 (d, $J$ = 7.9 Hz, 1H), 7.51 (q, $J$ = 3.3 Hz, 3H), 7.38 (s, 1H), 7.15–7.18 (m, 1H), 2.50 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.7, 151.2, 140.0, 135.7, 131.4, 129.0, 127.6, 127.5, 125.9, 119.5, 110.9, 21.9. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{12}$NO [M + H]$^+$: 210.0919, found: 210.0920.

*6-Fluoro-2-phenylbenzo[d]oxazole (3ca).* Following the general procedure A with **1c** (62.8 mg) and **2a** (62 µL), **3ca** was obtained as a white solid (66.7 mg, 78% yield). m.p 109–111 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21–8.24 (m, 2H), 7.70 (q, $J$ = 4.6 Hz, 1H), 7.52–7.56 (m, 3H), 7.32 (dd, $J$ = 7.8, 2.3 Hz, 1H), 7.08–7.14 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 163.6 (d, $J$ = 2.9 Hz), 160.8 (d, $J$ = 242.5 Hz), 150.8 (d, $J$ = 14.3 Hz), 138.6, 131.8, 129.1, 127.6, 127.0, 120.4 (d, $J$ = 9.5 Hz), 112.7 (d, $J$ = 24.8 Hz), 98.8 (d, $J$ = 27.7 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −115.0. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_9$FNO [M + H]$^+$: 214.0668, found: 214.0670.

*5-Methyl-2-phenylbenzo[d]oxazole (3da).* Following the general procedure A with **1d** (61.3 mg) and **2a** (62 µL), **3da** was obtained as a white solid (74.6 mg, 89% yield). Mp 101–103 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23–8.26 (m, 2H), 7.56 (s, 1H), 7.50–7.53 (m, 3H), 7.45 (d, $J$ = 7.9 Hz, 1H), 7.16 (dd, $J$ = 8.6, 1.2 Hz, 1H), 2.49 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 163.2, 149.1, 142.4, 134.5, 131.5, 129.0, 127.7, 127.5, 126.3, 120.0, 110.0, 21.6. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{12}$NO [M + H]$^+$: 210.0919, found: 210.0918.

*5-Fluoro-2-phenylbenzo[d]oxazole (3ea).* Following the general procedure A with **1e** (62.8 mg) and **2a** (62 µL), **3ea** was obtained as a white solid (51.8 mg, 61% yield). m.p 104–106 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (dd, $J$ = 7.6, 2.1 Hz, 2H), 7.50–7.56 (m, 4H), 7.45 (dd, $J$ = 8.6, 2.4 Hz, 1H), 7.09 (td, $J$ = 9.2, 2.4 Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 164.9, 160.3 (d, $J$ = 237.7 Hz), 147.2, 143.1 (d, $J$ = 13.4 Hz), 132.0, 129.1, 127.8, 127.1 (d, $J$ = 12.4 Hz), 112.9 (d, $J$ = 25.8 Hz), 111.0 (d, $J$ = 10.5 Hz), 106.6 (d, $J$ = 24.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −117.6. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_9$FNO [M + H]$^+$: 214.0668, found: 214.0667.

*4-Methyl-2-phenylbenzo[d]oxazole (3fa).* Following the general procedure A with **1f** (61.3 mg) and **2a** (62 µL), **3fa** was obtained as a white solid (70.3 mg, 84% yield). Mp 90–92 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.29–8.31 (m, 2H), 7.53–7.56 (m, 3H), 7.43 (d, $J$ = 7.9 Hz, 1H), 7.26 (t, $J$ = 7.6 Hz, 1H), 7.17 (d, $J$ = 8.6 Hz, 1H), 2.71 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.4, 150.7, 141.6, 131.4, 130.741, 128.944, 127.741, 127.6, 125.2, 124.9, 108.0, 16.7. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{12}$NO [M + H]$^+$: 210.0919, found: 210.0922.

*7-Methyl-2-phenylbenzo[d]oxazole (3ga).* Following the general procedure A with **1g** (61.3 mg) and **2a** (62 µL), **3ga** was obtained as a yellow solid (63.4 mg, 76% yield). Mp 88–90 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27–8.29 (m, 2H), 7.60 (d, $J$ = 7.9 Hz, 1H), 7.54 (q, $J$ = 2.4 Hz, 3H), 7.24–7.27 (m, 2H), 7.15 (d, $J$ = 7.3 Hz, 1H), 2.60 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 150.2, 141.8, 131.6, 129.0, 127.7, 127.5, 126.3, 124.6, 121.3, 117.5, 15.4. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{12}$NO [M + H]$^+$: 210.0919, found: 210.0922.

*5-Bromo-7-fluoro-2-phenylbenzo[d]oxazole (3ha).* Following the general procedure A with **1h** (94.4 mg) and **2a** (62 µL), **3ha** was obtained as a white solid (52.4 mg, 45% yield). m.p 157–159 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J$ = 6.7 Hz, 2H), 7.71 (s, 1H), 7.53–7.59 (m, 3H), 7.27–7.30 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 164.8, 148.0, 145.9 (d, $J$ = 104.4 Hz), 137.4, 132.5, 129.2, 128.2, 126.2, 119.2 (d, $J$ = 11.0 Hz),

116.7 (d, $J$ = 6.7 Hz), 115.8 (d, $J$ = 19.1 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −131.6. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_8$BrFNO [M + H]$^+$: 291.9773, found: 291.9777.

*2-Phenylnaphtho[2,1-d]oxazole (3ia).* Following the general procedure A with **1i** (75.7 mg) and **2a** (62 µL), **3ia** was obtained as a white solid (53.9 mg, 55% yield). m.p 122–124 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31–8.36 (m, 3H), 7.99 (d, $J$ = 8.6 Hz, 1H), 7.86 (d, $J$ = 8.6 Hz, 1H), 7.80 (d, $J$ = 8.6 Hz, 1H), 7.66 (t, $J$ = 7.4 Hz, 1H), 7.53–7.58 (m, 4H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.6, 146.6, 138.8, 131.9, 131.3, 129.1, 128.9, 127.6, 127.5, 127.0, 125.8, 125.6, 120.5, 120.3, 118.8. HRMS (FAB$^+$) $m/z$ calcd for C$_{17}$H$_{12}$NO [M + H]$^+$: 246.0919, found: 246.0915.

*2-Phenylbenzo[d]oxazole-5-carbonitrile (3ja).* Following the general procedure A with **1j** (65.7 mg) and **2a** (62 µL), **3ja** was obtained as a white solid (52.7 mg, 60% yield). m.p 196–198 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25–8.27 (m, 2H), 8.08 (s, 1H), 7.66–7.69 (m, 1H), 7.54–7.61 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 165.2, 153.2, 142.7, 132.6, 129.2, 129.2, 128.1, 126.1, 124.6, 118.9, 111.9, 108.6. IR (neat) $\upsilon$ 3062, 2224, 1619, 1551, 1261, 788, 705, 689 cm$^{-1}$. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_9$N$_2$O [M + H]$^+$: 221.0715, found: 221.0713.

*1-(2-Phenylbenzo[d]oxazol-5-yl)ethan-1-one (3ka).* Following the general procedure A with **1k** (72.5 mg) and **2a** (62 µL), **3ka** was obtained as a white solid (19.7 mg, 21% yield). Mp 145–147 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J$ = 0.9 Hz, 1H), 8.27 (dd, $J$ = 7.8, 1.8 Hz, 2H), 8.06 (dd, $J$ = 8.7, 1.8 Hz, 1H), 7.64 (d, $J$ = 8.7 Hz, 1H), 7.55–7.57 (m, 3H), 2.70 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 197.3, 164.7, 153.9, 142.5, 134.6, 132.2, 129.2, 128.0, 126.7, 126.0, 121.1, 110.8, 26.9. IR (neat) $\upsilon$ 3067, 2920, 1675, 814, 722, 688 cm$^{-1}$. HRMS (FAB$^+$) $m/z$ calcd for C$_{15}$H$_{12}$NO$_2$ [M + H]$^+$: 238.0868, found: 238.0861.

**Synthesis of Benzothiazoles.** *Preparation of o-Nitrothiophenol 4a.*[15] To a suspension of *o*-nitrophenyl disulfide (1 g, 3.25 mmol) in 25 mL of dry tetrahydrofuran (THF), PPh$_3$ (1.28 g, 4.88 mmol), 2-mercaptoethanol (0.23 mL, 3.25 mmol), and H$_2$O (0.6 mL, 32.5 mmol) were added. The solution was stirred at 50 °C for 8 h, then cooled to rt. The mixture was concentrated, redissolved in dichloromethane (DCM), washed with brine, dried over Na$_2$SO$_4$, and evaporated. The resulting orange oil was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (90/10) as an eluent to afford the bright-yellow solid **4a** (834 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J$ = 8.2 Hz, 1H), 7.44 (dd, $J$ = 4.8, 1.1 Hz, 2H), 7.27–7.31 (m, 1H), 4.02 (s, 1H).

*General Procedure B.* To a predried 10 mL sealed tube, *o*-nitrothiophenol **4a** (0.4 mmol, 1.0 equiv), alcohol **2** (0.6 mmol, 1.5 equiv), Fe **1** (3.35 mg, 0.008 mmol), Me$_3$NO (1.2 mg, 0.016 mmol), and $^t$BuONa (38.50 mg, 0.4 mmol, 1.0 equiv) were added. The tube was degassed and backfilled with argon three times; then, *o*-xylene (1 mL) was added using a syringe under argon flow. The reaction tube was capped, and then the mixture was stirred and heated at 150 °C in an oil bath for 24 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate as an eluent to afford the desired benzothiazole derivatives **5**.

*2-Phenylbenzo[d]thiazole (5aa).* Following the general procedure B with **4a** (62.1 mg) and **2a** (62 µL), **5aa** was obtained as a white solid (60.2 mg, 71% yield). Mp 114–116 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07–8.12 (m, 3H), 7.91–7.93 (m, 1H), 7.48–7.52 (m, 4H), 7.37–7.42 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 168.2, 154.3, 135.2, 133.7, 131.1, 129.1, 127.8, 126.4, 125.3, 123.4, 121.7. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_{10}$NS [M + H]$^+$: 212.0534, found: 212.0538.

*2-(Pyridin-3-yl)benzo[d]thiazole (5as).* Following the general procedure B with **4a** (62.1 mg) and **2s** (58 µL), **5as** was obtained as a white solid (52.1 mg, 61% yield). Mp 129–131 °C. Eluent: *n*-hexane/ethyl acetate (90/10). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.30 (d, $J$ = 1.8 Hz, 1H), 8.73 (q, $J$ = 2.0 Hz, 1H), 8.40 (td, $J$ = 5.1, 2.7 Hz, 1H), 8.11 (d, $J$ = 8.6 Hz, 1H), 7.95 (d, $J$ = 8.0 Hz, 1H), 7.52–7.56 (m, 1H),

7.42−7.47 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 164.7, 154.1, 151.8, 148.8, 135.1, 134.7, 129.8, 126.8, 125.9, 123.9, 123.6, 121.9. HRMS (FAB$^+$) $m/z$ calcd for C$_{12}$H$_9$N$_2$S [M + H]$^+$: 213.0486, found: 213.0490.

*2-(Naphthalen-1-yl)benzo[d]thiazole (5av).* Following the general procedure **B** with **4a** (62.1 mg) and **2v** (94.9 mg), **5av** was obtained as a white solid (75.0 mg, 72% yield). Mp 126−128 °C. Eluent: *n*-hexane/ethyl acetate (97/3). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.93 (d, $J$ = 8.6 Hz, 1H), 8.20 (d, $J$ = 8.0 Hz, 1H), 7.93−8.01 (m, 4H), 7.54−7.65 (m, 4H), 7.44−7.48 (m, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 167.8, 154.3, 135.6, 134.2, 131.2, 131.0, 130.8, 129.5, 128.6, 127.8, 126.7, 126.4, 126.0, 125.4, 125.1, 123.7, 121.6. HRMS (FAB$^+$) $m/z$ calcd for C$_{17}$H$_{12}$NS [M + H]$^+$: 262.0690, found: 262.0692.

**Synthesis of Benzimidazoles.** *General Procedure C.* A 10 mL sealed tube was charged with *o*-nitroaniline **6a** (0.4 mmol, 1.0 equiv), alcohol **2** (0.6 mmol, 1.5 equiv), **Fe 1** (3.35 mg, 0.008 mmol), Me$_3$NO (1.2 mg, 0.016 mmol), and $^t$BuONa (57.66 mg, 0.6 mmol, 1.5 equiv). The tube was degassed and backfilled with argon three times; then, chlorobenzene (1 mL) was added using a syringe under argon flow. The reaction tube was capped, and then the mixture was stirred and heated at 150 °C in an oil bath for 42 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The resulting residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate or dichloromethane/methanol as an eluent to provide the desired benzimidazoles **7**.

*2-Phenyl-1H-benzo[d]imidazole (7aa).* Following the general procedure **C** with **6a** (55.3 mg) and **2a** (62 $\mu$L), **7aa** was obtained as a white solid (62.4 mg, 80% yield). Mp 291−293 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.90 (s, 1H), 8.17 (d, $J$ = 6.9 Hz, 2H), 7.47−7.59 (m, 5H), 7.20 (td, $J$ = 6.5, 3.8 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 151.2, 130.2, 129.8, 129.0, 126.5, 122.1. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_{11}$N$_2$ [M + H]$^+$: 195.0922, found: 195.0924.

*2-(p-Tolyl)-1H-benzo[d]imidazole (7af).* Following the general procedure **C** with **6a** (55.3 mg) and **2f** (73.3 mg), **7af** was obtained as a white solid (66.5 mg, 80% yield). Mp 265−267 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.82 (s, 1H), 8.07 (d, $J$ = 7.9 Hz, 2H), 7.64 (d, $J$ = 7.3 Hz, 1H), 7.51 (d, $J$ = 7.3 Hz, 1H), 7.36 (d, $J$ = 7.9 Hz, 2H), 7.19 (dd, $J$ = 8.7, 6.0 Hz, 2H), 2.38 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 151.4, 143.8, 139.6, 135.0, 129.5, 127.5, 126.4, 122.4, 121.6, 118.7, 111.2, 21.0. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{13}$N$_2$ [M + H]$^+$: 209.1079, found: 209.1076.

*2-(4-Fluorophenyl)-1H-benzo[d]imidazole (7ag).* Following the general procedure **C** with **6a** (55.3 mg) and **2g** (65 $\mu$L), **7ag** was obtained as a white solid (67.4 mg, 79% yield). Mp 250−252 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.90 (s, 1H), 8.22 (td, $J$ = 6.1, 2.2 Hz, 2H), 7.65 (d, $J$ = 7.4 Hz, 1H), 7.52 (d, $J$ = 7.4 Hz, 1H), 7.37−7.42 (m, 2H), 7.20 (dd, $J$ = 8.4, 6.3 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 163.2 (d, $J$ = 246.3 Hz), 150.6, 128.8 (d, $J$ = 8.6 Hz), 126.8 (d, $J$ = 2.9 Hz), 122.4, 116.2 (d, $J$ = 22.3 Hz). $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ −111.1. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_{10}$N$_2$F [M + H]$^+$: 213.0828, found: 213.0828.

*2-(4-Methoxyphenyl)-1H-benzo[d]imidazole (7ah).* Following the general procedure **C** with **6a** (55.3 mg) and **2h** (82.9 mg), **7ah** was obtained as a white solid (76.1 mg, 85% yield). Mp 225−227 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.75 (s, 1H), 8.12 (d, $J$ = 8.6 Hz, 2H), 7.62 (d, $J$ = 6.7 Hz, 1H), 7.49 (d, $J$ = 6.7 Hz, 1H), 7.17 (d, $J$ = 4.9 Hz, 2H), 7.11 (d, $J$ = 8.6 Hz, 2H), 3.84 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 160.6, 151.4, 143.940, 135.0, 128.0, 122.7, 122.1, 121.5, 118.5, 114.4, 111.1, 55.4. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{13}$N$_2$O[M + H]$^+$: 225.1028, found: 225.1027.

*2-(4-Bromophenyl)-1H-benzo[d]imidazole (7aj).* Following the general procedure **C** with **6a** (55.3 mg) and **2j** (112.3 mg), **7aj** was obtained as a white solid (69.2 mg, 63% yield). Mp 277−279 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.99 (s, 1H), 8.12 (dt, $J$ = 9.0, 2.1 Hz, 2H), 7.76−7.79 (m, 2H),

7.60 (s, 2H), 7.22 (td, $J$ = 6.4, 3.5 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 150.2, 132.0, 129.4, 128.4, 123.3, 122.5. HRMS (FAB$^+$) $m/z$ calcd for C$_{13}$H$_{10}$BrN$_2$ [M + H]$^+$: 273.0027, found: 273.0024.

*2-(Benzo[d][1,3]dioxol-5-yl)-1H-benzo[d]imidazole (7ao).* Following the general procedure **C** with **6a** (55.3 mg) and **2o** (91.3 mg), **7ao** was obtained as a white solid (67.6 mg, 71% yield). Mp 250−252 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.73 (s, 1H), 7.71 (td, $J$ = 8.9, 1.4 Hz, 2H), 7.62 (d, $J$ = 6.7 Hz, 1H), 7.49 (d, $J$ = 6.7 Hz, 1H), 7.18 (q, $J$ = 4.5 Hz, 2H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.12 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 151.1, 148.7, 147.9, 143.7, 134.9, 124.3, 122.3, 121.56, 120.9, 118.6, 111.1, 108.8, 106.5, 101.6. HRMS (FAB$^+$) $m/z$ calcd for C$_{14}$H$_{11}$N$_2$O$_2$ [M + H]$^+$: 239.0821, found: 239.0815.

*2-(Thiophen-2-yl)-1H-benzo[d]imidazole (7ar).* Following the general procedure **C** with **6a** (55.3 mg) and **2r** (57 $\mu$L), **7ar** was obtained as a white solid (47.3 mg, 59% yield). Mp 280−282 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.93 (s, 1H), 7.83 (d, $J$ = 3.7 Hz, 1H), 7.72 (d, $J$ = 4.3 Hz, 1H), 7.54 (s, 2H), 7.19−7.24 (m, 3H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 147.0, 133.7, 128.8, 128.3, 126.7, 122.6, 121.8, 118.5, 111.1. HRMS (FAB$^+$) $m/z$ calcd for C$_{11}$H$_9$N$_2$S [M + H]$^+$: 201.0486, found: 201.0484.

*2-(Pyridin-3-yl)-1H-benzo[d]imidazole (7as).* Following the general procedure **C** with **6a** (55.3 mg) and **2s** (58 $\mu$L), **7as** was obtained as a white solid (49.4 mg, 63% yield). Mp 254−256 °C. Eluent: dichloromethane/methanol (98/2). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.10 (s, 1H), 9.35 (d, $J$ = 1.8 Hz, 1H), 8.67 (dd, $J$ = 4.9, 1.2 Hz, 1H), 8.49 (dt, $J$ = 7.9, 1.8 Hz, 1H), 7.57−7.72 (m, 3H), 7.24 (d, $J$ = 4.3 Hz, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 150.5, 148.9, 147.5, 143.7, 135.0, 133.8, 126.2, 124.0, 123.0, 122.0, 119.1, 111.512. HRMS (FAB$^+$) $m/z$ calcd for C$_{12}$H$_{10}$N$_3$ [M + H]$^+$: 196.0875, found: 196.0874.

*2-(Naphthalen-1-yl)-1H-benzo[d]imidazole (7av).* Following the general procedure **C** with **6a** (55.3 mg) and **2v** (94.9 mg), **7av** was obtained as a white solid (75.1 mg, 77% yield). Mp 254−256 °C. Eluent: *n*-hexane/ethyl acetate (4/1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.94 (s, 1H), 9.11 (d, $J$ = 8.6 Hz, 1H), 8.01−8.11 (m, 3H), 7.79 (d, $J$ = 6.7 Hz, 1H), 7.58−7.71 (m, 4H), 7.27 (s, 2H). $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$) $\delta$ 151.4, 143.940, 134.5, 133.6, 130.5, 130.2, 128.4, 127.9, 127.5, 127.1, 126.4, 125.3, 122.7, 121.6, 119.1, 111.4. HRMS (FAB$^+$) $m/z$ calcd for C$_{17}$H$_{13}$N$_2$ [M + H]$^+$: 245.1079, found: 245.1081.

*Experimental Procedure for the Reaction of Secondary Alcohol 2w with 1a.* A mixture of *o*-nitrophenol **1a** (55.6 mg, 0.4 mmol), benzhydrol **2w** (110.5 mg, 0.6 mmol), **Fe 1** (3.35 mg, 0.008 mmol), and Me$_3$NO (1.20 mg, 0.016 mmol) was placed in a dried 10 mL sealed tube. The tube was degassed and backfilled with argon three times; then, *o*-xylene (1.0 mL) was added using a syringe under argon flow. The reaction tube was capped, and then the mixture was stirred and heated at 150 °C in an oil bath for 24 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (5−25%) as an eluent to afford *o*-aminophenol **1a′** (10.0 mg, 23% yield based on **1a**) and benzophenone **2w′** (59.1 mg, 54% yield based on **2w**).

*2-Aminophenol (1a′).*[16] Brown solid. Eluent: *n*-hexane/ethyl acetate (75/25). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.90 (s, 1H), 6.62 (d, $J$ = 8.0 Hz, 1H), 6.50−6.58 (m, 2H), 6.37 (td, $J$ = 7.4, 1.2 Hz, 1H), 4.44 (s, 2H).

*Benzophenone (2w′).*[17] White solid. Eluent: *n*-hexane/ethyl acetate (95/5). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80−7.82 (m, 4H), 7.57−7.61 (m, 2H), 7.49 (t, $J$ = 7.6 Hz, 4H).

## ■ ASSOCIATED CONTENT

**ⓈI** **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02191.

$^1$H and $^{13}$C NMR spectra and results of catalyst screening (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

**Suckchang Hong** − *Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea;* ⊙ orcid.org/0000-0003-4975-9192; Email: schong17@snu.ac.kr

### Authors

**Ramachandra Reddy Putta** − *BK 21 Plus Project, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea*

**Simin Chun** − *Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea*

**Seung Hyun Choi** − *Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea*

**Seok Beom Lee** − *Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea*

**Dong-Chan Oh** − *Natural Products Research Institute, College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea;* ⊙ orcid.org/0000-0001-6405-5535

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.joc.0c02191

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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