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Formation of Amidinyl Radicals via Visible-Light-Promoted Reduction of *N*-Phenyl Amidoxime Esters and Application to the Synthesis of 2-Substituted Benzimidazoles

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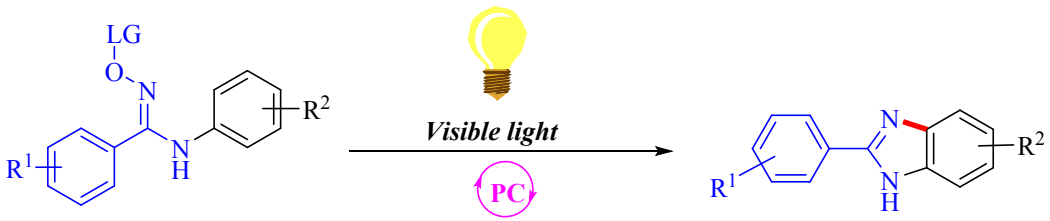


ABSTRACT. We have developed a new method for the synthesis of 2-substituted benzimidazoles via amidinyl radicals generated by visible-light-promoted reduction of *N*-phenyl amidoxime esters in the presence of an iridium photocatalyst. This is the first report of the use of *N*-phenyl amidoxime esters as amidinyl radical precursors, and the first use of substituted benzene rings as amidinyl radical acceptors. This method widens the application range of substrates and overcomes the shortcomings of the traditional methods for synthesis of 2-substituted benzimidazoles, which require harsh reaction conditions, involve difficult-to-prepare substituted *o*-phenylenediamine substrates, and produce acidic waste.

INTRODUCTION

Benzimidazole is a privileged structural motif because of its various biological activities, including anticancer,[1] antimicrobial,[2] antiviral,[3] and antidiabetes activities.[4] The motif is found in many pharmaceutical and agrochemical products, such as the fungicides thiabendazole and carbendazim, the anthelmintics albendazole and mebendazole, and the proton pump inhibitor omeprazole (Figure 1).[5] Therefore, numerous methods for synthesis of the benzimidazole scaffold have been established. The conventional methods, which involve condensation of substituted o-phenylenediamines with carboxylic acids and their derivatives[6] or condensation via

oxidative cyclization of o-phenylenediamines with appropriate aldehydes (Figure 2, path a),[7] usually require strongly acidic conditions, high temperatures, or stoichiometric oxidants. Furthermore, the necessary substituted o-phenylenediamines are often difficult to prepare. An alternative method involving oxidative cyclocondensation of o-phenylenediamines with primary amines,[8] alcohols,[9] halides,[10] and even methylarenes[11] was recently reported, but this method also requires harsh reaction conditions. Thus, a mild, environmentally friendly method for synthesizing benzimidazoles remains to be developed.

Figure 1. Chemical structures of thiabendazole, carbendazim, albendazole, mebendazole, and omeprazole.

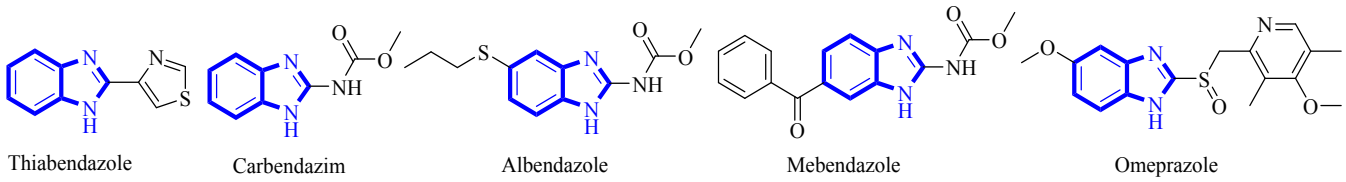
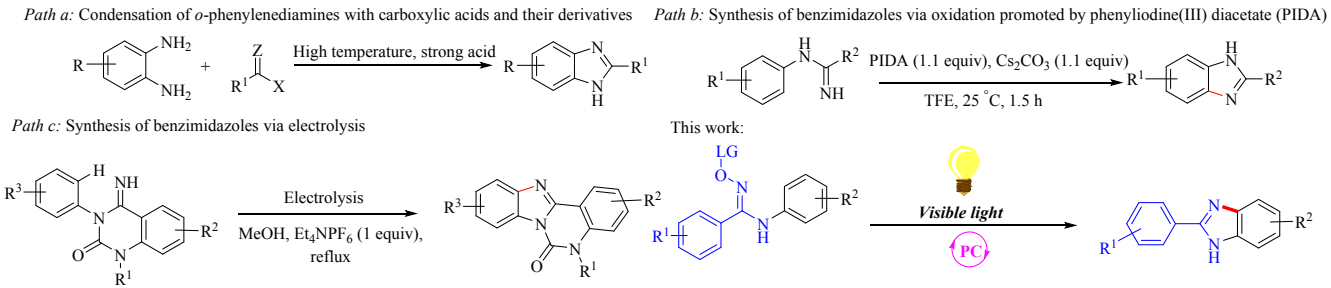


Figure 2. Synthesis strategy of benzimidazole.



One possibility that has been explored is the use of nitrogen-centered radicals, such as iminyl and amidinyl radicals. During recent decades, iminyl radicals have frequently been utilized to synthesize azaheterocycles because the cyclizations of these radicals are intrinsically faster, and their reductions slower, than those of aminyl radicals.[12] Methods for producing iminyl radicals include direct cleavage of N–X, N–N, N–O, N–S, and even N–H bonds, and indirect generation by the addition of other radical species to cyano groups.[13] In particular, oxime derivatives (e.g., oxime esters and oxime ethers), which have comparatively weak N–O bonds, have been widely used as precursors of iminyl radicals.[14] Recently, the research groups of Leonori,[15] Yu,[16] Loh,[17] and Studer[18] carried out pioneering work on visible-light-promoted electron-transfer reactions that produce iminyl radicals from oxime derivatives and can be used to construct nitrogen-containing heterocycles in an efficient and environmentally friendly manner.

Amidinyl radicals, which are analogous to iminyl radicals, are useful intermediates for the synthesis of imidazolines and imidazoles, as reported by Zard.[19] However, to generate amidinyl radicals from amidoxime benzoates, these investigators employed a hazardous stannane–diazo initiator. Subsequently, Selander carried out a series of transition-metal-catalyzed cascade reactions involving

intramolecular cyclization/functionalization reactions between amidinyl radicals and C–C double bonds to synthesize functionalized imidazolines.[20] There have been a few reports of the use of amidinyl radicals to synthesize benzimidazoles. For instance, Zhu reported that benzimidazoles can be synthesized by means of direct C(sp^2)–H imidation of *N*-arylamidines promoted by phenyliodine(III) diacetate (Figure 2, path b), and these investigators proposed a pathway involving an amidinyl radical intermediate.[21a] However, electron-rich groups that are easily oxidized are not suitable for their systems. Punniyamurthy reported the synthesis of benzimidazoles via iodobenzene catalyzed C-H amination of *N*-substituted amidines using *m*-chloroperbenzoic acid.[21b] This method can only be used to synthesize *N*-sulfonyl or *N*-aryl substituted benzimidazoles and it can't contain nitro group. Finally, Xu obtained functionalized tetracyclic benzimidazoles by means of efficient, straightforward electrolytic cleavage of N–H bonds via amidinyl radical intermediates (Figure 2, path c).[22] A specific 1-benzyl-4-imino-3-phenyl-3,4-dihydroquinazolin-2(1*H*)-one structure was used for their electrochemical reaction system. When the substrate was changed into 2-fluoro-*N*-methyl-*N*-phenylbenzimidamide, the yield decreased significantly.

However, there are only a few methods for generating amidinyl radicals, and new methods are urgently needed if the their reactions are to be explored further. In light of the above-described previous work, we hypothesized that visible-light-promoted electron-transfer

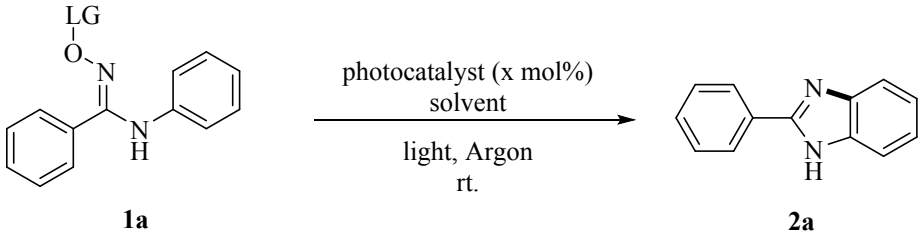
might be an effective strategy for reducing the N–O bonds of *N*-phenyl amidoxime esters to provide amidinyl radicals, which could then undergo intramolecular homolytic aromatic substitution, oxidation, and deprotonation to afford benzimidazoles. In fact, this strategy proved feasible and afforded 2-substituted benzimidazoles. To our knowledge, the generation of amidinyl radicals via visible-light-promoted reduction of amidoxime esters has not previously been reported.

RESULTS AND DISCUSSION

We chose *N*-phenyl-*N*′-((4-(trifluoromethyl)benzoyl)oxy) benzimidamide (**1a**, for the preparation scheme see Supporting Information) as a model substrate for experiments aimed at optimizing the reaction conditions (Table 1). To our delight, we found that target product **2a** could be obtained in 45% yield by irradiation of **1a** with a 13 W white LED light for 12 h at room temperature in DMF in the presence of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2%) as a photocatalyst (entry 1). None of the other photocatalysts that we evaluated gave better results (entrys 2–5). When the amount of photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was decreased, the substrate was completely consumed; a photocatalyst loading of 1% was sufficient, although the yield was somewhat lower (entry 6). We next screened a variety of solvents. Polar aprotic solvents (DMSO and CH_3CN, entries 7 and 8) and the polar protonic solvent

$(CF_3)_2CHOH$ (entry 9) decreased the yield, and the chlorinated solvent 1,2-dichloroethane did not improve the yield (entry 10). To our surprise, changing the solvent to methyl *tert*-butyl ether dramatically increased the yield (to 68%, entry 11) and was more suitable than other ethers (dimethoxyethane, THF, and 1,4-dioxane; entries 12–14). All attempts to improve the yield further by varying the light source (entries 15–17), increasing the photocatalyst loading (entry 18), or decreasing the substrate concentration (entry 19) failed. Finally, in the absence of a photocatalyst or light (entries 20 and 21), no reaction occurred, which indicates that both the photocatalyst and light were indispensable. As a control, we also tried the reaction conditions of Zhu[21a] and Punniyamurthy[21b] (entries 22 and 23). Compound 1A was decomposed under the above conditions. Using the optimized reaction conditions (entry 11), we evaluated other *O*-acyl amidoxime substrates as potential amidinyl radical precursors (Table 2) and found that the *p*-trifluoromethylbenzoate acyl group gave the best yield, which confirmed the wisdom of our choice of *p*-trifluoromethylbenzoate as a leaving group. The reaction of **1a** is easy to upscale to gram scale, with **2a** isolated in 61% yield on a 6 mmol scale under the optimized reaction conditions (Table 1, entry 11).

Table 1. Optimization of conditions for the synthesis of 2-substituted benzimidazoles via amidinyl radicals.[a]



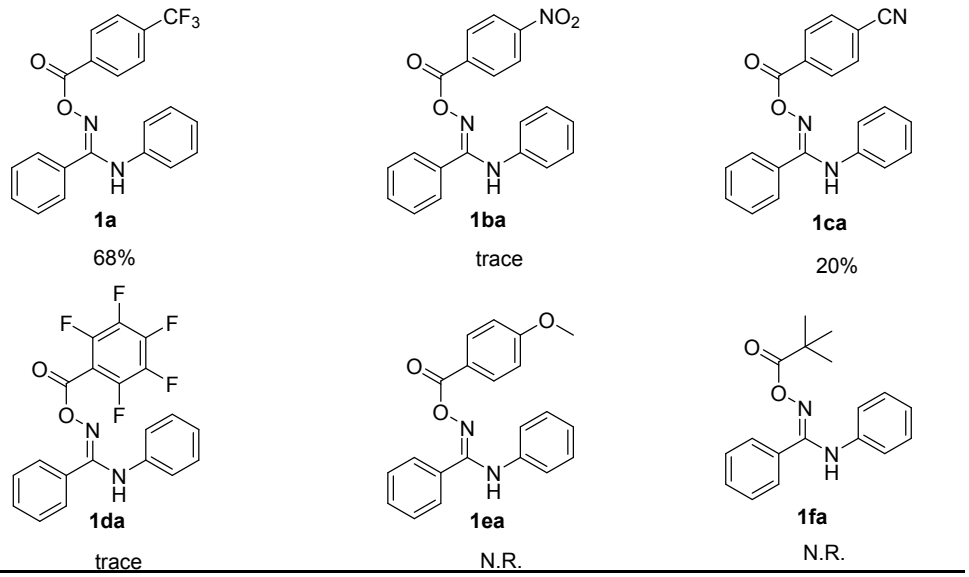
1a **2a**

Entry	Photocatalyst	Solvent	Light	Time (h)	Yield (%)[b]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(2%)	DMF	13 W white LED	12	45
2	$Ru(bpy)_3(PF_6)_2$(2%)	DMF	13 W white LED	20	N.R. [c]
3	$Ir(ppy)_3$(2%)	DMF	13 W white LED	20	N.P.[d]
4	$Ir(ppy)_2(dtbbpy)PF_6$(2%)	DMF	13 W white LED	20	N.R.
5	Eosin Y(2%)	DMF	13 W white LED	20	N.R.
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	DMF	13 W white LED	12	31
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	DMSO	13 W white LED	36	13
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	CH_3CN	13 W white LED	36	21
9	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	$(CF_3)_2CHOH$	13 W white LED	36	trace
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	DCE	13 W white LED	36	26
11	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	MTBE	13 W white LED	36	68
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	DME	13 W white LED	36	31

13	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	THF	13 W white LED	36	31
14	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	dioxane	13 W white LED	36	58
15	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	MTBE	5 W blue LED	36	63
16	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	MTBE	5 W green LED	36	N.R.
17	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	MTBE	23 W white CFL	36	56
18	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(2%)	MTBE	13 W white LED	36	55
19[e]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(2%)	MTBE	13 W white LED	36	66
20	/	MTBE	13 W white LED	36	N.R.
21	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$(1%)	MTBE	/	36	N.R.
22[f]	PIDA	TFE	/	1.5	N.P.
23[g]	*m*CPBA	HFIP	/	12	N.P.

[a] Reaction conditions, unless otherwise noted: **1a** (0.2 mmol, 1 equiv), 1 mL DMF, Ar atmosphere, 13 W white LED, rt, LG = 4-(trifluoromethyl)benzoyl. Abbreviations: DME, dimethoxyethane; HFIP, $(CF_3)_2CHOH$; MTBE, methyl *tert*-butyl ether. [b] Isolated yields are provided. N.R. = no reaction. [c] 2 mL of MTBE was used. [d] N.P. = No Product. [e] 2 mL MTBE. [f] **1a** (0.2 mmol), PIDA (1.1 equiv), Cs_2CO_3 (1.1 equiv), in TFE (1 mL), at 0 °C under air for 1.5 h.[21a] [g] **Ia** (0.5 mmol), iodobenzene (20 mol %), *m*CPBA (1.5 equiv), HFIP (1 mL), rt.[21b]

Table 2. Screening of Acyl Groups[a]

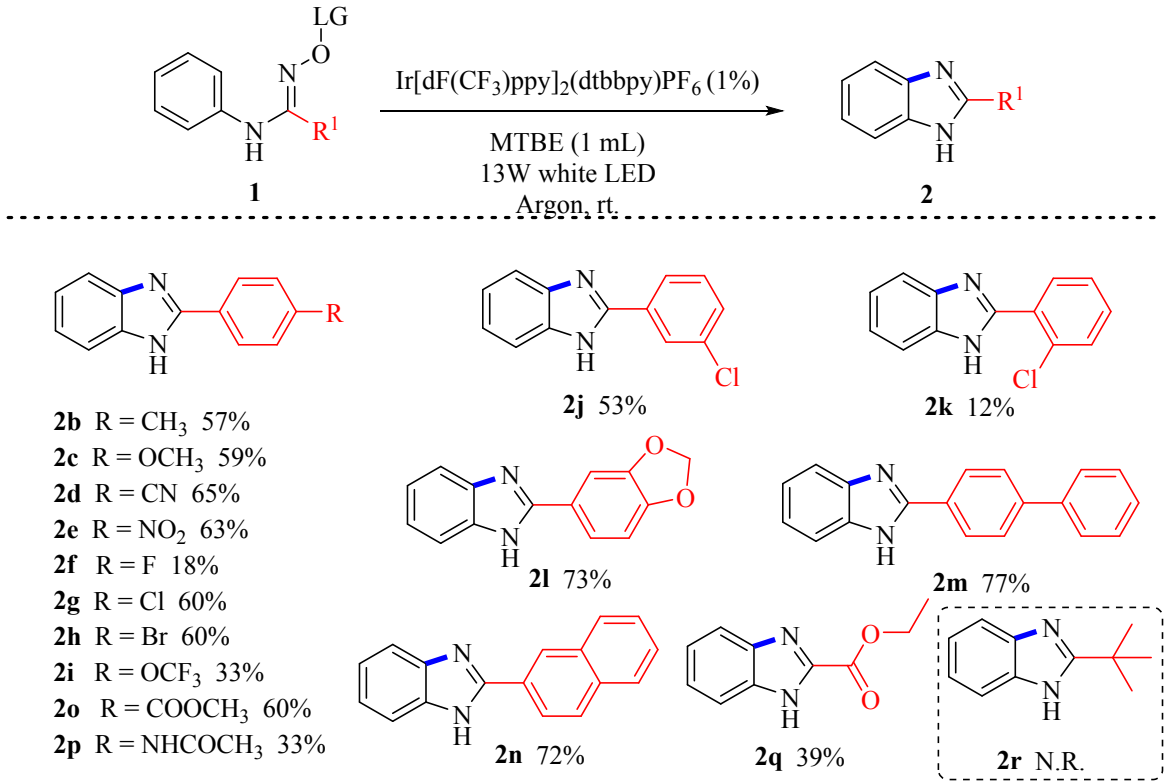


[a] Conditions: **1** (0.2 mmol, 1 equiv), 1 mL MTBE, Argon atmosphere, 13 W white LED, at room temperature for 36 h, the yields given in the table are all separation yields.

Next, we investigated the substrate scope of the reaction (Scheme 1) by subjecting various *N*-phenyl-*N'*-((4-(trifluoromethyl)benzoyl)oxy) imidamides to the optimized reaction conditions (Table 1, entry 11). Substrates bearing a variety of *para*-substituted phenyl groups at R^1 (e.g., alkyl, alkoxyl, cyano, nitro, halogen) were satisfactory (**2b**–**2k**). Substrates with electron-donating *para* substituents (**2b** and **2c**) gave yields comparable to those obtained with most of the substrates bearing electron-withdrawing groups (**2d**, **2e**, **2g**, **2h**, and **2j** but not **2f** and **2i**), which suggests that the electronic nature of the substituent had no obvious effect on the reaction. The nitro group (**2e**) and amido group (**2p**) are also tolerated. The location of the substituent on the

phenyl ring had a noticeable effect on reactivity. For instance, an *ortho*-chloro substrate gave a lower yield (**2k**, 12%) than the corresponding *para*- and *meta*-chloro substrates (**2g**, 60%; **2j**, 53% , respectively). When R^1 was a ring-fused phenyl group or some other aryl group, the corresponding 2-substituted benzimidazoles were obtained in good yields (**2n**–**2o**). Furthermore, R^1 could be an electron-withdrawing group such as an ester (**2q**), although the yield was only moderate. However, when R^1 was an alkyl group (**2r**), none of the desired product was obtained, perhaps because the oxidation–reduction potential of the substrate was incompatible with the excited-state potential of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ ($E_{1/2}^{IV/*III}$ = −0.96 V vs. SCE).

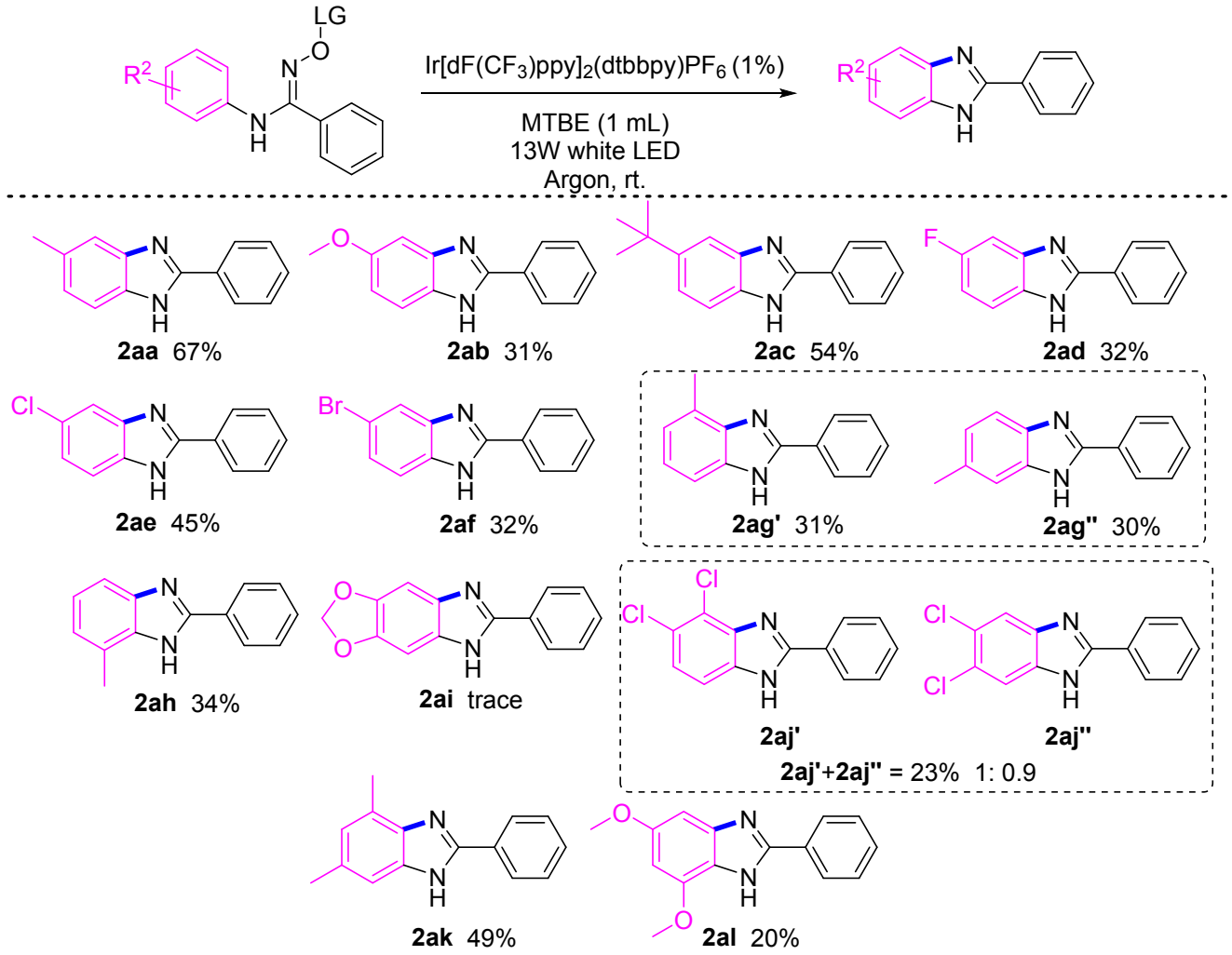
Scheme 1. Scope of the reaction with respect to the R^1 group of the substrate.



We also evaluated the effects of substituents R^2 on the benzene ring of the radical acceptor moiety of the substrate (Scheme 2). The weak electron-donating *para*-alkyl substituents (**2aa** and **2ac**) gave better yields than halogens (**2ad**, **2ae** and **2af**) or an electron-donating heteroatom (**2ab**). The results showed that the *para*-alkyl substituents were beneficial to the reaction. A substrate with a *meta*-methyl group gave an approximately 1:1 mixture of two substituted benzimidazole products (**2ag′** and **2ag″**). The *ortho*-methyl-substituted substrate gave **2ah** as the sole product (34%). Substrates with 3,4-dichloro-, 3,5-dimethyl-, and 2,4-dimethoxy-substituted

benzene rings afforded moderate yields of the desired products, but substrate with a 3,4-dioxamethylene-substituted benzene ring gave only a trace of desired product **2ai**. Due to the influence of ring tension, the power supply capability of oxygen atom decreases greatly. The results for the lack of **2ai** may be attributed to the effect of electronic effect on benzene ring. The 3,4-dichloro-substituted substrate gave two different benzimidazole products (**2aj**′ and **2aj**″) in a 1:0.9 ratio.

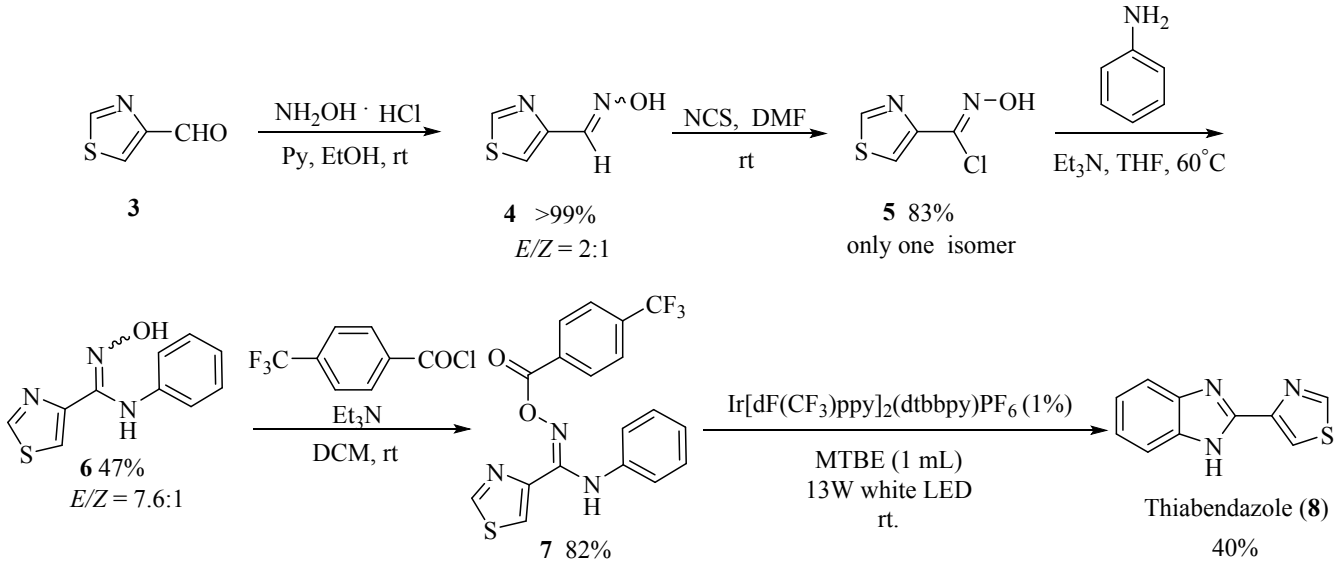
Scheme 2. Scope of the reaction with respect to the radical acceptor benzene ring.



Finally, we evaluated the utility of this new method by applying it to the synthesis of the fungicide thiabendazole (**8**, Scheme 3). Specifically, thiazole-4-formaldehyde oxime (**4**) was obtained quantitatively by condensation of thiazole-4-formaldehyde (**3**) with hydroxylamine hydrochloride. Intermediate **4** was chlorinated with *N*-chlorosuccinimide to afford intermediate **5** (83%), which reacted

with aniline to give compound **6** in 47% yield. Acylation of **6** with 4-trifluoromethyl benzoyl chloride gave key intermediate **7** (82%). Subjecting **7** to the optimized reaction conditions gave thiabendazole (**8**) in 40% yield. Current work provides a reference for the development of the clean production of thiabendazole.

Scheme 3. Synthesis of the fungicide thiabendazole.



Having explored the substrate scope and utility of the reaction, we turned our attention to the mechanism (Scheme 4). To confirm that the reaction involved an amidinyl radical, we carried out free-radical-trapping experiments with **1a** under the optimal conditions for 36 h. When TEMPO (either 2 or 0.5 equiv) was added to the system, the formation of product **2a** was not detected by TLC,

indicating that the reaction did not occur in the presence of the radical trap. When BHT was used as a free-radical scavenger, the reaction did occur, but the yield was markedly reduced. To eliminate the possibility that the process involved chain reactions of free radicals, we carried out a light/dark experiment with substrate **1i**, using trifluorotoluene as an internal standard and ^{19}F NMR to track product formation. The reaction was carried out under the standard conditions except that the light was turned on or off every 2 h. A plot of the product yield versus time showed that the reaction proceeded when the light was on but stopped when it was off. This result indicates that the reaction was a single-electron-transfer process catalyzed by visible light and that it did not involve chain reactions of free radicals.

Scheme 4. Mechanistic experiments.

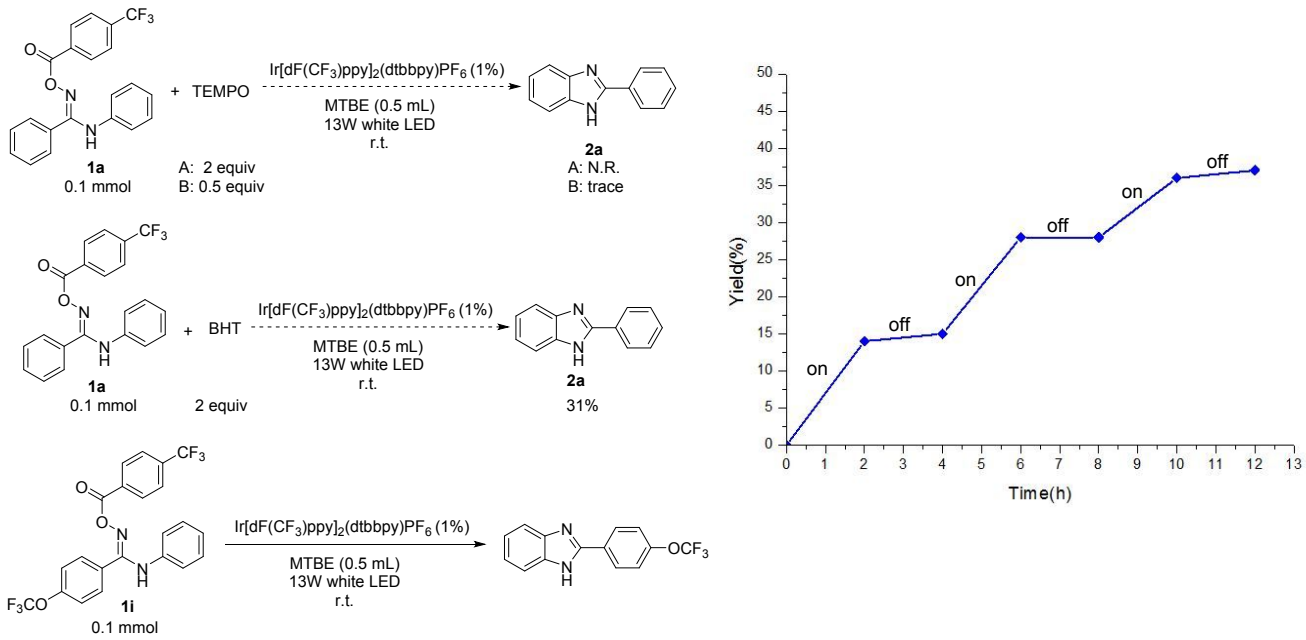
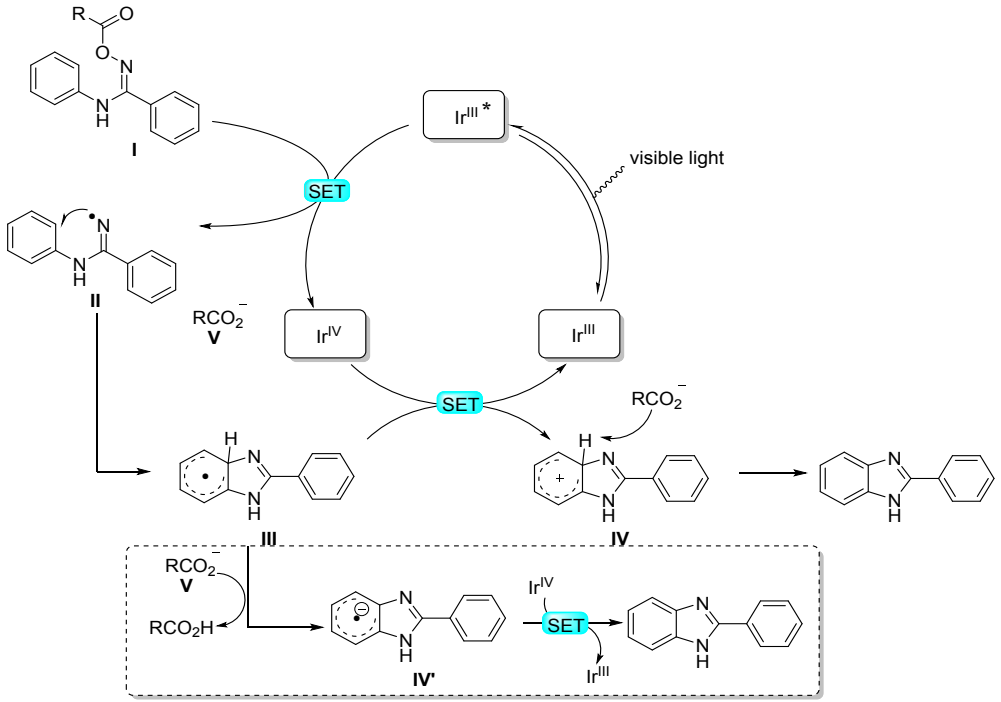


Figure 3. Possible mechanisms.



On the basis of the above-described experiments, we propose the possible reaction mechanisms shown in Figure 3. First, visible-light irradiation converts the photocatalyst to an excited-state (Ir^{III*}) species. Then the excited-state photocatalyst transfers an electron to substrate **I**, which undergoes N–O bond cleavage to form amidinyl radical intermediate **II** and carboxylate ion **V**. The *N*-centered radical **II** reacts with the adjacent benzene ring to form intermediate **III**. The electron-deficient photocatalyst, which is strongly oxidizing, extracts an electron from **III** to generate cationic intermediate **IV**. This single-electron transfer restores the photocatalyst to the ground state, completing the photocatalytic cycle. The benzimidazole product is generated by aromatization of intermediate **IV**

accompanied by extraction of a proton by carboxylate ion **V**. Of course, we cannot rule out the possibility that intermediate **III** loses a proton to carboxylate anion **V** and is then oxidized by the photocatalyst to give the benzimidazole.

CONCLUSION

In conclusion, we have developed a new method for the synthesis of 2-substituted benzimidazoles from *N*-phenyl amidoxime esters via amidinyl radicals generated by visible-light irradiation in the presence of an Ir catalyst. This is the first report of the use of *N*-aniline oxime esters as amidinyl radical precursors and the use of substituted benzene rings as amidinyl radical acceptors. The electron-rich groups that are easily oxidized and nitro group, which are intolerable by reported methods,[21] also can give designed products with good yield. The method described herein does not suffer from the shortcomings of traditional methods for synthesis of 2-substituted benzimidazoles, which include harsh reaction conditions, the difficulty of preparing the necessary substituted *o*-phenylenediamine substrates, and production of acidic waste.

EXPERIMENTAL SECTION

General Methods and Materials. Reagents were purchased from commercial sources and were used as received. The melting points of the products were determined on an X-4 binocular microscope (Gongyi Yuhua Instrument Co., China) and the thermometer was not corrected. NMR

spectra were acquired with a Bruker 400 MHz (100 MHz for ^{13}C $\{^1H\}$) instrument at room temperature. Chemical shifts were measured relative to residual solvent peaks of $CDCl_3$ (^1H: δ = 7.26 ppm; ^{13}C $\{^1H\}$: δ = 77.0 ppm) with tetramethylsilane as internal standards. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, and bs = broad singlet. All first-order splitting patterns were assigned on the basis of multiplet appearance. Splitting patterns that could not be easily interpreted were designated multiplet (m) or broad (br). HRMS data were obtained with an FT-ICR MS spectrometer (Ionspec, 7.0 T). Analytical TLC was performed on silica gel GF 254. Column chromatographic purification was performed using silica gel. White LED (13 W), blue LED (5 W, λ_{max} = 470 nm), green LED (5 W, λ_{max} = 550 nm) and white CFL (5 W) were purchased from JIADENG (LS) and used for light irradiation.

The structures of S-I, S-II and S-III and detailed preparation route of intermediates S-II and S-III can be seen in Support Information.

Preparation of Chloraldoxime S-II.

Method 1: To the solution of aldoxime **S-I** (10 mmol) in dichloromethane and isopropanol (v/v 4:1) 50 mL was added dropwise *tert*-butyl hypochlorite (15 mmol) at -10 ^oC. The reaction mixture was stirred for 3 h to give the solution of **S-II**, which was directly used to the next step without further purification.

Method 2: To the solution of NCS (11 mmol) in DMF (5 mL) was added dropwise the solution of aldoxime (10 mmol) in DMF. And the solution was heated with oil bath to 50 ^oC and stirred for 1 h. Then the solution was concentrated. The residue was taken into water (50 mL) and extracted with ethyl acetate (70 mL × 3). The combined organic layer was washed with H_2O (25 mL×2), brine (25 mL×2), dried with anhydrous Na_2SO_4, and concentrated. The residue was directly used to the next step without further purification.

Preparation of Aminoximes S-III.[23]

To the solution of chloraldoxime **S-II** (10 mmol) in THF (50 mL) was added dropwise corresponding amines and triethylamine. The mixture was heated with oil bath to 60 °C and stirred at for 12 h, cooled to room temperature, and filtered. The filtrate was concentrated and purified by flash column chromatography to afford aminoximes **S-III**.

(*E*)-*N*'-Hydroxy-*N*-phenylbenzimidamide (S-IIIa)

Chromatography (Petroleum ether:EtOAc 20:1 to 12:1), white solid, 0.95 g, yield 45%, mp. 136−137 ℃ (lit. [23a]: mp. 132−134 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.2 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 139.7, 131.1, 129.7, 128.8, 128.4, 128.4, 122.7, 121.3.

(*E*)-*N*'-Hydroxy-4-methyl-*N*-phenylbenzimidamide (S-IIIb)

Chromatography (Petroleum ether:EtOAc 20:1 to 12:1), white solid, 0.86 g, yield 38%, mp. 124−125 ℃ (lit. [23a]: mp. 119−120 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.14 – 7.06 (m, 4H), 6.92 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 139.9, 139.7, 129.2, 128.7, 128.3, 128.0, 122.7, 121.4, 21.4. HR-MS (ESI): Calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1179, found 227.1180.

(*E*)-*N*'-Hydroxy-4-methoxy-*N*-phenylbenzimidamide (S-IIIc)

Chromatography (Petroleum ether:EtOAc 20:1 to 12:1), white solid, 1.04 g, yield 43%, mp. 120−121 ℃ (lit. [23a]: mp. 102−104 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 7.6 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.0 Hz, 2H), 3.80

(s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7, 151.7, 139.9, 129.8, 128.7, 123.4, 122.6, 121.3, 113.8, 55.3. HR-MS (ESI): Calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1128, found 243.1129.

(*E*)-4-Cyano-*N′*-hydroxy-*N*-phenylbenzimidamide (S-IIId)

Chromatography (Petroleum ether:EtOAc 10:1 to 6:1), white solid, 1.26 g, yield 53%, mp. 144−145 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.27 (br, 1H), 7.15 (t, J = 7.6 Hz, 2H), 6.99 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.7, 139.0, 135.7, 132.2, 129.1, 128.9, 123.6, 121.7, 118.3, 113.3. HR-MS (ESI): Calcd for $C_{14}H_{12}N_3O$ $[M+H]^+$ 238.0975, found 238.0975.

(*E*)-*N′*-Hydroxy-4-nitro-*N*-phenylbenzimidamide (S-IIIe)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), yellow solid, 0.98 g, 38%, mp. 174−176 ℃ (lit. [23a]: mp. 166−170 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.28 (s, 1H, N**H**), 7.15 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.68 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.5, 148.4, 138.9, 137.5, 129.2, 129.2, 123.7, 123.7, 121.8. HR-MS (ESI): Calcd for $C_{13}H_{12}N_3O_3$ $[M+H]^+$ 258.0873, found 258.0874.

(*E*)-4-Fluoro-*N′*-hydroxy-*N*-phenylbenzimidamide (S-IIIf)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.15 g, yield 50%, mp. 135−136 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.33 (br, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.08 – 6.94 (m, 3H), 6.70 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.6 (d, J = 248.2 Hz), 151.2, 139.5, 130.4 (d, J = 8.3 Hz), 128.9, 127.1 (d, J = 3.0 Hz), 123.0, 121.6, 115.6 (d, J = 21.7 Hz). HR-MS (ESI): Calcd for $C_{13}H_{12}FN_2O$ $[M+H]^+$ 231.0928, found 231.0930.

(*E*)-4-Chloro-*N′*-hydroxy-*N*-phenylbenzimidamide (S-IIIg)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.11 g, yield 45%, mp. 133−135 ℃ (lit. [23a]: mp. 132−133 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.15 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 6.72 – 6.65 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.2, 139.4, 135.8, 129.7, 129.6, 128.9, 128.8, 123.1, 121.6. HR-MS (ESI): Calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$ 247.0633, found 247.0635.

(*E*)-4-Bromo-*N′*-hydroxy-*N*-phenylbenzimidamide (S-IIIh)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.37 g, yield 47%, mp. 167−168 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.2, 139.4, 131.7, 130.1, 129.9, 128.9, 124.1, 123.1, 121.6. HR-MS (ESI): Calcd for $C_{13}H_{12}BrN_2O$ $[M+H]^+$ 291.0128, found 291.0124.

(*E*)-*N′*-Hydroxy-*N*-phenyl-4-(trifluoromethoxy)benzimidamide (S-IIIi)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), yellow solid, 0.80 g, yield 27%, mp. 99−100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.32 (s, 1H), 7.15 – 7.10 (m, 4H), 6.95 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.0, 150.2, 139.3, 130.0, 129.6, 128.9, 123.2, 121.6, 120.7. HR-MS (ESI): Calcd for $C_{14}H_{12}F_3N_2O_2$ $[M+H]^+$ 297.0845, found 297.0846.

(*E*)-3-Chloro-*N′*-hydroxy-*N*-phenylbenzimidamide (S-IIIj)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.31 g, yield 53%, mp. 131−132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 1.6 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 7.14 (t, J = 7.6 Hz, 2H), 6.97 (d, J = 7.6 Hz, 1H), 6.71 – 6.65 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.0, 139.3, 134.4, 133.0, 129.8, 129.6, 128.9, 128.4, 126.7, 123.3, 121.5. HR-MS (ESI): Calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$ 247.0633, found 247.0634.

(*E*)-2-Chloro-*N*′-hydroxy-*N*-phenylbenzimidamide (S-IIIk)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.28 g, yield 52%, mp. 124−125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 1H), 7.44 (s, 1H), 7.37 – 7.26 (m, 3H), 7.06 (t, J = 7.6 Hz, 2H), 6.91 (t, J = 7.6 Hz, 1H), 6.65 – 6.59 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.0, 138.8, 133.9, 131.8, 131.0, 130.5, 130.0, 128.8, 126.9, 123.1, 120.8. HR-MS (ESI): Calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$ 247.0633, found 247.0634.

(*E*)-*N*′-Hydroxy-*N*-phenylbenzo[*d*][1,3]dioxole-5-carboximidamide (S-IIIl)

Chromatography (Petroleum ether:EtOAc 8:1 to 5:1), white solid, 0.90 g, yield 35%, mp. 151−152 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 8.4, 7.6 Hz, 2H), 6.98 – 6.91 (m, 2H), 6.90 (d, J = 1.6 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.72 – 6.67 (m, 2H), 5.96 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.7, 148.9, 147.6, 139.8, 128.8, 124.9, 122.8, 122.7, 121.2, 108.7, 108.4, 101.4. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2O_3$ $[M+H]^+$ 257.0921, found 257.0923.

(*E*)-*N*′-Hydroxy-*N*-phenyl-[1,1'-biphenyl]-4-carboximidamide (S-IIIm)

Chromatography (Petroleum ether:EtOAc 15:1 to 10:1), yellow solid, 1.32 g, yield 46%, mp. 174−175 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 6H), 7.47 – 7.31 (m, 4H), 7.12 (t, J = 7.6 Hz, 2H), 6.94 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.9, 142.5, 140.2, 139.6, 129.6, 128.9, 128.8, 127.7, 127.1, 127.1, 122.9, 121.5. HR-MS (ESI): Calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$ 289.1335, found 289.1335.

(*E*)-*N*′-hydroxy-*N*-phenyl-2-naphthimidamide (S-IIIn)

Chromatography (Petroleum ether:EtOAc 25:1 to 10:1), yellow solid, 0.71 g, yield 27%, mp. 182−184 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.68 (s, 1H), 8.42 (s, 1H), 7.99 (s, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.03 (t, J = 8.0 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 149.6, 142.0, 133.5, 133.0, 131.0, 128.9, 128.7, 128.2, 128.0, 127.4, 127.1, 126.9, 125.7, 121.0, 120.1. HR-MS (ESI): Calcd for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1183.

Methyl (*E*)-4-(*N′*-hydroxy-*N*-phenylcarbamimidoyl)benzoate (S-IIIo)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.27 g, yield 47%, mp. 149−150 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.32 (s, 1H), 7.10 (t, J = 7.6 Hz, 2H), 6.94 (t, J = 7.6 Hz, 1H), 65 6. (d, J = 7.6 Hz, 2H), 3.90 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 151.3, 139.3, 135.5, 131.1, 129.7, 128.9, 128.4, 123.2, 121.6, 52.3. HR-MS (ESI): Calcd for $C_{15}H_{15}N_2O_3$ $[M+H]^+$ 271.1077, found 271.1079.

(*E*)-*N*-(4-(*N′*-Hydroxy-*N*-phenylcarbamimidoyl)phenyl)acetamide (S-IIIp)

Chromatography (Petroleum ether:EtOAc 10:1 to 4:1), white solid, 0.97 g, yield 36%, mp. 103−104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.34 (br, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 6.90 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 7.6 Hz, 2H), 2.09 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.6, 151.7, 139.6, 139.3, 129.1, 128.8, 126.6, 122.8, 121.4, 119.3, 24.6. HR-MS (ESI): Calcd for $C_{15}H_{16}N_3O_2$ $[M+H]^+$ 270.1237, found 270.1238.

Ethyl (*E*)-2-(hydroxyimino)-2-(phenylamino)acetate (S-IIIq)

Chromatography (Petroleum ether:EtOAc 10:1 to 6:1), yellow solid, 1.1 g, yield 53%, mp. 107−109 ℃ (lit. [23b]: 106−108 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.95 (s, 1H), 6.92 (d, J = 7.6 Hz, 2H), 4.25 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz,

3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.8, 143.3, 139.1, 128.9, 124.0, 121.1, 62.4, 13.8. HR-MS (ESI): Calcd for $C_{10}H_{13}N_2O_3$ $[M+H]^+$ 209.0921, found 209.0922.

(*E*)-*N′*-Hydroxy-*N*-phenylpivalimidamide (S-IIIr)

Chromatography (Petroleum ether:EtOAc 30:1 to 15:1), white solid, 0.73 g, yield 38%, mp. 118−119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.26 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 5.91 (s, 1H), 1.20 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 141.2, 128.4, 122.8, 121.6, 36.6, 28.2. HR-MS (ESI): Calcd for $C_{11}H_{17}N_2O$ $[M+H]^+$ 193.1335, found 193.1335.

(*E*)-*N′*-Hydroxy-*N*-(*p*-tolyl)benzimidamide (S-IIIaa)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 1.4 g, yield 62%, mp. 165−166 ℃ (lit. [23c]: 161.5−163 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 137.1, 132.4, 131.2, 129.6, 129.3, 128.5, 128.4, 121.7, 20.7. HR-MS (ESI): Calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1179, found 227.1181.

(*E*)-*N′*-Hydroxy-*N*-(4-methoxyphenyl)benzimidamide (S-IIIab)

Chromatography (Petroleum ether:EtOAc 20:1 to 8:1), yellow solid, 1.23 g, yield 51%, mp. 129−130 ℃ (lit. [23c]: 154.4−157.2 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 –7.39 (m, 2H), 7.35 – 7.30 (m, 1H), 7.30 – 7.24 (m, 2H), 6.65 (s, 4H), 3.70 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.7, 152.6, 132.8, 131.2, 129.5, 128.6, 128.3, 123.9, 114.0, 55.4. HR-MS (ESI): Calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1128, found 243.1128.

(*E*)-*N*-(4-(*tert*-Butyl)phenyl)-*N′*-hydroxybenzimidamide (S-IIIac)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 1.26 g, yield 47%, mp. 172−173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.28 (m, 3H), 7.11 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 1.23 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 145.5, 137.1, 131.3, 129.6, 128.5, 128.4, 125.6, 120.9, 34.2, 31.4. HR-MS (ESI): Calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ 269.1648, found 269.1652.

(*E*)-*N*-(4-Fluorophenyl)-*N′*-hydroxybenzimidamide (S-IIIad)

Chromatography (Petroleum ether:EtOAc 20:1 to 8:1), white solid, 0.69 g, yield 30%, mp. 147−148 ℃ (lit. [23c]: 147.5−149 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 –7.36 (m, 3H), 7.36 – 7.29 (m, 2H), 6.88 – 6.78 (m, 2H), 6.71 – 6.63 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.88 (d, J = 242.3 Hz), 152.1, 135.7 (d, J = 2.6 Hz), 130.8, 129.8, 128.5, 123.4 (d, J = 8.0 Hz), 115.50 (d, J = 22.5 Hz). HR-MS (ESI): Calcd for $C_{13}H_{12}FN_2O$ $[M+H]^+$ 231.0928, found 231.0928.

(*E*)-*N*-(4-Chlorophenyl)-*N′*-hydroxybenzimidamide (S-IIIae)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.89 g, yield 36%, mp. 187−188 ℃ (lit. [23c]: 182.5−183.6 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (br, 1H, 7.48 – 7.29 (m, 5H), 7.06 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.6, 138.3, 130.7, 130.0, 128.8, 128.6, 128.3, 128.0, 122.4. HR-MS (ESI): Calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$ 247.0633, found 247.0633.

(*E*)-*N*-(4-Bromophenyl)-*N′*-hydroxybenzimidamide (S-IIIaf)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), yellow solid, 0.52 g, yield 18%, mp. 198−200 ℃ (lit. [23c]: 192−193.5 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 3H), 7.35 – 7.30 (m, 2H), 7.20 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.5, 138.8, 131.8, 130.6, 130.0, 128.6, 128.3, 122.7, 115.5. HR-MS (ESI): Calcd for $C_{13}H_{12}BrN_2O$ $[M+H]^+$ 291.0128, found 291.0119.

(*E*)-*N′*-Hydroxy-*N*-(*m*-tolyl)benzimidamide (S-IIIag)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 0.77 g, yield 34%, mp. 136−137 ℃ (lit. [23d]: 133.2−133.7 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.39 – 7.27 (m, 3H), 7.23 (br, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.54 (s, 1H), 6.41 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 2.18 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 139.6, 138.7, 131.2, 129.6, 128.5, 128.4, 123.5, 121.9, 118.4, 21.3. HR-MS (ESI): Calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1179, found 227.1183.

(*E*)-*N'*-Hydroxy-*N*-(*o*-tolyl)benzimidamide (S-IIIah)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), yellow solid, 0.5 g, yield 22%, mp. 147−148 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.24 (m, 3H), 7.14 (d, J = 7.2 Hz, 1H), 6.99 (s, 1H), 6.93 –6.81 (m, 1H), 6.45 (dd, J = 7.6, 1.1 Hz, 1H), 2.36 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7, 138.1, 131.33, 130.5, 129.8, 129.6, 128.3, 128.2, 126.1, 123.7, 123.5, 18.0. HR-MS (ESI): Calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1179, found 227.1181.

(*E*)-*N*-(Benzo[*d*][1,3]dioxol-5-yl)-*N'*-hydroxybenzimidamide (S-IIIai)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), brown solid, 1.13 g, yield 44%, mp. 201−203 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.13 (s, 1H), 7.38 – 7.28 (m, 5H), 6.61 (d, J = 8.4 Hz, 1H), 6.34 (d, J = 2.0 Hz, 1H), 6.07 (dd, J = 8.4, 2.0 Hz, 1H), 5.88 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 150.2, 147.4, 142.2, 136.4, 133.3, 129.3, 128.6, 128.3, 113.9, 108.1, 103.3, 101.2. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2O_3$ $[M+H]^+$ 257.0921, found 257.0921.

(*E*)-*N*-(3,4-Dichlorophenyl)-*N'*-hydroxybenzimidamide (S-IIIaj)

Chromatography (Petroleum ether:EtOAc 20:1 to 10:1), white solid, 0.39 g, yield 14%, mp. 170−172 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.40 – 7.34 (m, 2H), 7.14 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 2.8 Hz, 1H), 6.44 (dd, J = 8.8, 2.8 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz,

$CDCl_3$) δ 151.1, 139.3, 132.5, 130.3, 130.2, 130.2, 128.8, 128.2, 126.0, 122.4, 120.3. HR-MS (ESI): Calcd for $C_{13}H_{11}C_{l2}N_2O$ $[M+H]^+$ 281.0243, found 281.0245.

(*E*)-*N*-(3,5-Dimethylphenyl)-*N′*-hydroxybenzimidamide (S-IIIak)

Chromatography (Petroleum ether:EtOAc 20:1 to 12:1), white solid, 1.13 g, yield 47%, mp. 143−144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.39 – 7.27 (m, 3H), 7.22 (br, 1H), 6.56 (s, 1H), 6.27 (s, 2H), 2.11 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 139.6, 138.3, 131.3, 129.6, 128.4, 128.3, 124.4, 119.1, 21.2. HR-MS (ESI): Calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$ 241.1335, found 241.1333.

(*E*)-*N*-(2,4-Dimethoxyphenyl)-*N′*-hydroxybenzimidamide (S-IIIal)

Chromatography (Petroleum ether:EtOAc 15:1 to 8:1), white solid, 1.25 g, yield 46%, mp. 137−139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.37 – 7.26 (m, 3H), 7.13 (s, 1H), 6.42 (d, J = 2.4 Hz, 1H), 6.32 (d, J = 8.8 Hz, 1H), 6.13 (dd, J = 8.8, 2.4 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.2, 152.4, 151.7, 131.6, 129.4, 128.4, 128.2, 122.9, 122.4, 103.3, 99.0, 55.6, 55.4. HR-MS (ESI): Calcd for $C_{15}H_{17}N_2O_3$ $[M+H]^+$ 273.1234, found 273.1233.

Preparation of Substrates 1. To the solution of amidoximes **S-III** (1 mmol) and triethylamine (1.2 mmol) in dichloromethane (10 mL) was added dropwise the solution of corresponding benzoyl chlorides (1.1 mmol) in dichloromethane (5 mL). The mixture was stirred at 0 ^{o}C for 1 h, added saturated sodium bicarbonate solution (25 mL), and separated. The water phase was extracted with dichloromethane (40 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography to afford substrates **1**.

(*E*)-*N*-Phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1a)

Chromatography (Petroleum ether:EtOAc 20:1), yellow solid, 0.3 g, yield 80%, mp. 68−70 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.17 (s, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 157.0, 138.7, 134.5 (q, J = 32.7 Hz), 132.7, 130.8, 130.0, 129.6, 129.4, 129.0, 128.5, 125.5 (J = 3.2 Hz), 124.5, 123.6 (q, J = 270.9 Hz), 123.1. HR-MS (ESI): Calcd for $C_{21}H_{16}F_3N_2O_2$ $[M+H]^+$ 385.1158, found 385.1159.

(*E*)-4-Methyl-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1b)

Chromatography (Petroleum ether:EtOAc 20:1), white solid, 0.34 g, yield 85%, mp. 141−143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.21 – 6.98 (m, 5H), 6.83 (d, J = 7.6 Hz, 2H), 2.33 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 157.1, 141.1, 138.8, 134.5 (q, J = 32.6 Hz), 132.8, 130.0, 129.3, 129.2, 129.0, 126.6, 125.5 (q, J = 3.3 Hz), 124.4, 123.6 (q, J = 271.1 Hz), 123.0, 21.5. HR-MS (ESI): Calcd for $C_{22}H_{18}F_3N_2O_2$ $[M+H]^+$ 399.1315, found 399.1318.

(*E*)-4-Methoxy-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1c)

Chromatography (Petroleum ether:EtOAc 25:1 to 15:1), white solid, 0.35 g, yield 85%, mp. 137−138 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.20 – 7.15 (m, 3H), 7.03 (t, J = 7.2 Hz, 1H), 6.83 (t, J = 9.2 Hz, 4H), 3.79 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 161.6, 156.8, 138.9, 134.5 (q, J = 32.4 Hz), 132.8, 130.9, 129.9, 129.0, 125.5 (q, J = 3.7 Hz), 124.3, 123.6 (q, J = 271.0 Hz), 122.9, 121.6, 113.9, 55.3. HR-MS (ESI): Calcd for $C_{22}H_{18}F_3N_2O_3$ $[M+H]^+$ 415.1264, found 415.1263.

(*E*)-4-Cyano-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1d)

Chromatography (Petroleum ether:EtOAc 25:1 to 20:1), white solid, 0.25 g, yield 61%, mp. 99−101 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.53 (s, 1H), 8.26 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 8.0 Hz, 2H), 7.04 (d, J =

7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.9, 155.9, 139.7, 136.0, 133.1, 133.0 (q, *J* = 31.8 Hz), 132.8, 130.93, 130.6, 129.2, 126.0 (q, *J* = 3.7 Hz), 124.6, 124.2, 124.2 (q, *J* = 271.7 Hz), 118.7, 113.4. HR-MS (ESI): Calcd for $C_{22}H_{15}F_3N_3O_2$ $[M+H]^+$ 410.1111, found 410.1113.

(*E*)-4-Nitro-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1e)

Chromatography (Petroleum ether:EtOAc 25:1 to 15:1), yellow solid, 0.32 g, yield 75%, mp. 143−144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 8.16(d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.6, 155.3, 149.0, 137.7, 136.0, 134.9 (q, *J* = 32.7 Hz), 132.2, 130.5, 130.0, 129.4, 125.7 (q, *J* = 3.5 Hz), 125.5, 123.6, 123.6, 123.5 (q, *J* = 271.1 Hz). HR-MS (ESI): Calcd for $C_{21}H_{15}F_3N_3O_4$ $[M+H]^+$ 430.1009, found 430.1013.

(*E*)-4-Fluoro-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1f)

Chromatography (Petroleum ether:EtOAc 25:1 to 15:1), white solid, 0.31 g, yield 77%, mp. 74−76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.44 (m, 2H), 7.29 (s, 1H), 7.23 – 6.95 (m, 5H), 6.83 (d, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2 (d, *J* = 249.9 Hz), 162.8, 156.2, 138.4, 134.6 (q, *J* = 32.7 Hz), 132.5, 131.5 (d, *J* = 8.7 Hz), 130.0, 129.1, 125.6 (q, *J* = 3.5 Hz), 124.8, 123.5 (q, *J* = 271.2 Hz), 123.2, 115.7 (d, *J* = 21.9 Hz). HR-MS (ESI): Calcd for $C_{21}H_{15}F_4N_2O_2$ $[M+H]^+$ 403.1064, found 403.1068.

(*E*)-4-Chloro-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1g)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.32 g, yield 77%, mp. 113−114 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.4, 155.7, 139.5, 135.2, 132.8 (q, *J* = 31.8 Hz), 132.8, 131.0,

130.37, 129.6, 128.6, 128.5, 125.5 (q, J = 3.6 Hz), 123.8, 123.7 (q, J = 271.3 Hz), 123.4. HR-MS (ESI): Calcd for $C_{21}H_{15}ClF_3N_2O_2$ $[M+H]^+$ 419.0769, found 419.0771.

(*E*)-4-Bromo-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1h)

Chromatography (Petroleum ether:EtOAc 20:1), white solid, 0.37 g, yield 80%, mp. 129−130 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.17 (s, 1H), 7.09 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 156.2, 138.2, 134.7 (q, J = 32.5 Hz), 132.5, 131.8, 130.9, 130.0, 129.2, 128.5, 125.6 (q, J = 3.7 Hz), 125.4, 124.9, 123.5 (q, J = 271.0 Hz), 123.2. HR-MS (ESI): Calcd for $C_{21}H_{15}BrF_3N_2O_2$ $[M+H]^+$ 463.0264, found 463.0262.

(*E*)-*N*-Phenyl-4-(trifluoromethoxy)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1i)

Chromatography (Petroleum ether:EtOAc 25:1 to 20:1), white solid, 0.45 g, yield 96%, mp. 127−129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.24 – 7.03 (m, 5H), 6.84 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 155.9, 150.9, 138.2, 134.7 (q, J = 32.5 Hz), 132.5, 131.1, 130.0, 129.2, 128.1, 125.6 (q, J = 3.7 Hz), 125.0, 123.5 (q, J = 271.0 Hz), 123.3, 120.7, 120.3 (q, J = 256.8 Hz). HR-MS (ESI): Calcd for $C_{22}H_{15}F_6N_2O_3$ $[M+H]^+$ 469.0981, found 469.0984.

(*E*)-3-Chloro-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1j)

Chromatography (Petroleum ether:EtOAc 20:1), white solid, 0.34 g, yield 81%, mp. 113−114 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.58 (s, 1H), 7.41 – 7.15 (m, 6H), 7.07 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 155.8, 138.2, 134.7 (q, J = 32.7 Hz), 134.6, 132.4, 131.4, 130.9, 130.0, 129.7, 129.4, 129.2, 127.6, 125.6 (q, J = 3.6 Hz), 125.0, 123.5 (q, J = 271.2 Hz), 123.2. HR-MS (ESI): Calcd for $C_{21}H_{15}ClF_3N_2O_2$ $[M+H]^+$ 419.0769, found 419.0771.

(*E*)/(*Z*)-2-Chloro-*N*-phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1k)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.38 g, yield 91%, *E/Z* isomers, *E:Z* = 1 : 0.74, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H+0.74H), 7.64 – 7.53 (m, 1.5H+1.5H), 7.51 – 7.28 (m, 3.5H+3H), 7.21 – 7.02 (m, 2H+1.74), 6.85 (d, *J* = 8.0 Hz, 2H). *E:* ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.54, 155.43, 137.39, 134.7 (q, *J* = 32.8 Hz), 133.8, 132.4, 131.8, 130.1, 130.0, 130.90, 129.6, 128.9, 127.0, 125.6 (q, *J* = 3.7 Hz), 125.3, 123.6 (q, *J* = 271.4 Hz), 123.2. HR-MS (ESI): Calcd for $C_{21}H_{15}ClF_3N_2O_2$ $[M+H]^+$ 419.0769, found 419.0773.

(*E*)-*N*-Phenyl-*N'*-((4-(trifluoromethyl)benzoyl)oxy)benzo[*d*][1,3]dioxole-5-carboximidamide (1l)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.35 g, yield 82%, mp. 153−154 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.13 – 7.04 (m, 3H), 7.00 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 156.6, 149.8, 147.7, 138.8, 134.5 (q, *J* = 32.5 Hz), 132.6, 129.9, 129.0, 125.5 (q, *J* = 3.7 Hz), 124.4, 124.2, 123.5 (q, *J* = 271.0 Hz), 123.1, 122.8, 109.5, 108.4, 101.6. HR-MS (ESI): Calcd for $C_{22}H_{16}F_3N_2O_4$ $[M+H]^+$ 429.1057, found 429.1060.

(*E*)-*N*-Phenyl-*N'*-((4-(trifluoromethyl)benzoyl)oxy)-[1,1'-biphenyl]-4-carboximidamide (1m)

Chromatography (Petroleum ether:EtOAc 25:1 to 20:1), white solid, 0.36 g, yield 78%, mp. 155−156 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.62–7.48 (m, 6H), 7.44 – 7.28 (m, 4H), 7.22 – 6.80 (m, 5H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 156.8, 143.4, 140.0, 138.8, 134.6 (q, *J* = 32.5 Hz), 132.7, 130.0, 129.8, 129.0, 128.9, 128.5, 127.9, 127.1, 125.5 (q, *J* = 3.4 Hz), 124.5, 123.6 (q, *J* = 271.0 Hz), 123.0. HR-MS (ESI): Calcd for $C_{27}H_{20}F_3N_2O_2$ $[M+H]^+$ 461.1471, found 461.1472.

(*E*)-*N*-Phenyl-*N'*-((4-(trifluoromethyl)benzoyl)oxy)-2-naphthimidamide (1n)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.32 g, yield 74%, mp. 163−165 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.15 (d, J = 7.6 Hz, 2H), 7.86–7.64 (m, 5H), 7.56–7.45 (m, 2H), 7.42–7.28 (m, 2H), 7.13 (t, J = 7.2 Hz, 2H), 7.00 (t, J = 6.8 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 157.1, 138.6, 134.6 (q, J = 32.5 Hz), 134.3, 132.8, 132.7, 130.0, 129.9, 129.1, 128.8, 128.2, 127.7, 127.5, 127.0, 126.6, 125.6 (q, J = 3.5 Hz), 125.6, 124.5, 123.6 (q, J = 271.1 Hz), 123.0. HR-MS (ESI): Calcd for $C_{25}H_{18}F_3N_2O_2$ $[M+H]^+$ 435.1315, found 435.1312.

Methyl(*E*)-4-(*N*-Phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)carbamimidoyl)benzoate (1o)

Chromatography (Petroleum ether:EtOAc 25:1 to 20:1), white solid, 0.31 g, yield 70%, mp. 90−91 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.33 (s, 1H), 7.24 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 2H), 3.97 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 162.7, 156.3, 138.2, 134.7 (q, J = 32.5 Hz), 134.0, 132.4, 132.0, 130.0, 129.7, 129.5, 129.2, 125.6 (q, J = 3.5 Hz), 125.0, 123.5 (q, J = 271.0 Hz), 123.3, 52.4. HR-MS (ESI): Calcd for $C_{23}H_{18}F_3N_2O_4$ $[M+H]^+$ 443.1213, found 443.1217.

(*E*)-*N*-(4-(*N*-Phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)carbamimidoyl)phenyl)acetamide (1p)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.3 g, yield 68%, mp. > 300 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 9.30 (s, 1H), 8.20 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 2.06 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 169.2, 163.0, 156.7, 141.8, 140.4, 133.4, 133.1 (q, J = 31.6 Hz), 130.8, 130.3, 129.0, 126.0 (q, J = 3.7 Hz), 125.2, 124.2 (q, J = 271.2 Hz), 123.8, 123.4, 118.8, 24.6. HR-MS (ESI): Calcd for $C_{23}H_{19}F_3N_3O_3$ $[M+H]^+$ 442.1373, found 442.1368.

Ethyl (*E*)-2-(phenylamino)-2-(((4-(trifluoromethyl)benzoyl)oxy)imino)acetate (1q)

Chromatography (Petroleum ether:EtOAc 15:1), white solid, 0.27 g, yield 71%, mp. 109−110 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.40 (s, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 161.4, 145.1, 138.3, 134.6 (q, J = 32.7 Hz), 131.6, 129.9, 129.1, 126.0, 125.2 (q, J = 3.7 Hz), 124.0, 123.5 (q, J = 272.8 Hz), 63.9, 14.0. HR-MS (ESI): Calcd for $C_{18}H_{16}F_3N_2O_4$ $[M+H]^+$ 381.1057, found 381.1056.

(*E*)-*N*-Phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)pivalimidamide (1r)

Chromatography (Petroleum ether:EtOAc 25:1 to 20:1), white solid, 0.23 g, yield 62%, mp. 131−133 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.27 – 7.12 (m, 4H), 6.97 (t, J = 8.4 Hz, 3H), 1.34 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 161.9, 161.6, 141.9, 132.7, 132.3 (q, J = 31.9 Hz), 129.2, 128.3, 125.0 (q, J = 3.7 Hz), 123.6 (q, J = 270.6 Hz), 123.1, 122.3, 36.9, 27.6. HR-MS (ESI): Calcd for $C_{19}H_{20}F_3N_2O_2$ $[M+H]^+$ 365.1471, found 365.1472.

(*E*)-*N*-(*p*-Tolyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1aa)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.34 g, yield 85%, mp. 134−135 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 8.25 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.47 – 7.36 (m, 5H), 6.97 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 2.17 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.1, 157.3, 137.6, 133.4, 133.3, 132.8 (q, J = 31.3 Hz), 131.3, 130.9, 130.8, 129.7, 129.5, 128.8, 125.9 (q, J = 3.6 Hz), 124.2 (q, J = 270.9 Hz), 124.1, 20.7. HR-MS (ESI): Calcd for $C_{22}H_{18}F_3N_2O_2$ $[M+H]^+$ 399.1315, found 399.1319.

(*E*)-*N*-(4-Methoxyphenyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ab)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.35 g, yield 85%, mp. 116−117 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 8.30 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.49 –7.34 (m, 5H), 6.85 (d, J = 9.2 Hz, 2H), 6.75 (d, J = 9.2 Hz, 2H), 3.65 (s, 3H). ^{13}C

{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.1, 157.6, 156.5, 133.5, 133.1 (q, J = 31.9 Hz), 132.9, 131.3, 130.9, 130.6, 129.7, 128.7, 126.3, 125.9 (q, J = 3.8 Hz), 124.3 (q, J = 270.9 Hz), 114.2, 55.6. HR-MS (ESI): Calcd for $C_{22}H_{18}F_3N_2O_3$ $[M+H]^+$ 415.1264, found 415.1267.

(*E*)-*N*-(4-(*tert*-Butyl)phenyl)-*N*′-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ac)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.32 g, yield 73%, mp. 161−162 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 1H), 8.11 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.59 – 7.36 (m, 5H), 7.18 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 1.16 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.4, 156.4, 145.9, 137.4, 132.9, 132.6 (q, J = 31.7 Hz), 131.0, 130.6, 130.2, 129.1, 128.4, 125.4 (q, J = 3.6 Hz), 125.2, 123.7 (q, J = 271.1 Hz), 122.6, 33.9, 31.0. HR-MS (ESI): Calcd for $C_{25}H_{24}F_3N_2O_2$ $[M+H]^+$ 441.1784, found 441.1789.

(*E*)-*N*-(4-Fluorophenyl)-*N*′-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ad)

Chromatography (Petroleum ether:EtOAc 25:1 to 15:1), white solid, 0.37 g, yield 92%, mp. 116−117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.54 –7.28 (m, 5H), 7.15 (s, 1H), 6.94 – 6.76 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 159.9 (d, J = 245.4 Hz), 157.3, 134.5, 132.6, 130.8, 130.0, 129.4, 129.2, 128.6, 125.6 (q, J = 3.3 Hz), 125.3 (d, J = 8.3 Hz), 123.5 (q, J = 271.2 Hz), 115.8 (d, J = 23.0 Hz). HR-MS (ESI): Calcd for $C_{21}H_{15}F_4N_2O_2$ $[M+H]^+$ 403.1064, found 403.1070.

(*E*)-*N*-(4-Chlorophenyl)-*N*′-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ae)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.27 g, yield 65%, mp. 122−123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.52 – 7.27 (m, 6H), 7.10 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 156.8, 137.2, 134.7 (q, J = 32.8 Hz), 132.5, 130.9, 130.0, 129.4, 129.2, 129.0, 128.7, 125.6 (q, J = 3.4 Hz), 124.2, 123.5 (q, J = 271.0 Hz). HR-MS (ESI): Calcd for $C_{21}H_{15}ClF_3N_2O_2$ $[M+H]^+$ 419.0769, found 419.0768.

(*E*)-*N*-(4-Bromophenyl)-*N*′-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1af)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.34 g, yield 73%, mp. 93−94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.54 – 7.33 (m, 5H), 7.29 (d, J = 8.8 Hz, 2H), 7.11 (s, 1H), 6.70 (d, J = 8.8 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 156.7, 137.7, 134.6 (q, J = 32.6 Hz), 132.4, 132.0, 131.0, 130.0, 129.3, 129.1, 128.7, 125.6 (q, J = 3.8 Hz), 124.5, 123.5 (q, J = 271.4 Hz), 117.5. HR-MS (ESI): Calcd for $C_{21}H_{15}BrF_3N_2O_2$ $[M+H]^+$ 463.0264, found 463.0267.

(*E*)-*N*-(*m*-Tolyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ag)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.33 g, yield 83%, mp. 127−128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.23 (s, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 6.57 (d, J = 8.0 Hz, 1H), 2.20 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 157.1, 139.0, 138.5, 134.5 (q, J = 32.9 Hz), 132.7, 130.7, 130.0, 129.7, 129.4, 128.7, 128.5, 125.5 (q, J = 3.5 Hz), 125.3, 123.6, 123.6 (q, J = 271.3 Hz), 120.2, 21.2. HR-MS (ESI): Calcd for $C_{22}H_{18}F_3N_2O_2$ $[M+H]^+$ 399.1315, found 399.1320.

(*E*)-*N*-(*o*-Tolyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ah)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.3 g, yield 75%, mp. 148−150 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.55 – 7.27 (m, 5H), 7.17 (d, J = 7.6 Hz, 1H), 7.06 – 6.93 (m, 2H), 6.87 (s, 1H), 6.73 (d, J = 7.6 Hz, 1H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 157.5, 137.2, 134.5 (q, J = 32.5 Hz), 132.7, 131.7, 130.8, 130.8, 129.9, 129.1, 128.4, 127.6, 126.5, 125.6, 125.6, 125.5 (q, J = 3.7 Hz), 123.6 (q, J = 271.1 Hz), 18.1. HR-MS (ESI): Calcd for $C_{22}H_{18}F_3N_2O_2$ $[M+H]^+$ 399.1315, found 399.1316.

(*E*)-*N*-(Benzo[*d*][1,3]dioxol-5-yl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ai)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), yellow solid, 0.35 g, yield 82%, mp. 136 −137 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.51 – 7.27 (m, 5H), 7.19 (s, 1H), 6.57 (d, J = 8.0 Hz, 1H), 6.39 (s, 1H), 6.35 (d, J = 8.0 Hz, 1H), 5.88 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.9, 157.6, 147.9, 145.0, 134.5 (q, J = 32.6 Hz), 132.7, 132.6, 130.6, 130.0, 129.5, 129.4, 128.4, 125.5 (q, J = 3.6 Hz), 123.6 (q, J = 271.0 Hz), 117.5, 108.0, 106.0, 101.5. HR-MS (ESI): Calcd for $C_{22}H_{16}F_3N_2O_4$ $[M+H]^+$ 429.1057, found 429.1060.

(*E*)-*N*-(3,4-Dichlorophenyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1aj)

Chromatography (Petroleum ether:EtOAc 25:1 to 15:1), white solid, 0.37 g, yield 81%, mp. 157−159 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.49 – 7.29 (m, 6H), 7.15 (d, J = 8.8 Hz, 1H), 6.97 (d, J = 2.4 Hz, 1H), 6.55 (dd, J = 8.8, 2.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 156.3, 138.2, 134.8 (q, J = 32.9 Hz), 132.7, 132.3, 131.2, 130.4, 130.0, 129.2, 128.8, 128.0, 125.6 (q, J = 3.6 Hz), 124.2, 123.5 (q, J = 270.9 Hz), 122.1. HR-MS (ESI): Calcd for $C_{21}H_{14}Cl_2F_3N_2O_2$ $[M+H]^+$ 453.0379, found 453.0377.

(*E*)-*N*-(3,5-Dimethylphenyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1ak)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.39 g, yield 95%, mp. 142−143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.11 (s, 1H), 6.67 (s, 1H), 6.44 (s, 2H), 2.14 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.8, 157.1, 138.7, 138.4, 134.5 (q, J = 32.6 Hz), 132.8, 130.7, 129.9, 129.8, 129.3, 128.4, 126.2, 125.5 (q, J = 3.6 Hz), 123.6 (q, J = 271.1 Hz), 120.8, 21.1. HR-MS (ESI): Calcd for $C_{23}H_{20}F_3N_2O_2$ $[M+H]^+$ 413.1471, found 413.1475.

(*E*)-*N*-(2,4-Dimethoxyphenyl)-*N′*-((4-(trifluoromethyl)benzoyl)oxy)benzimidamide (1al)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.27 g, yield 60%, mp. 138−139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.53 – 7.29 (m, 5H), 7.02 (s, 1H), 6.52 (d, J = 8.8 Hz, 1H), 6.42 (d, J = 2.8 Hz, 1H), 6.19 (dd, J = 8.8, 2.8 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 157.9, 152.7, 134.5 (q, J = 32.6 Hz), 132.9, 130.5, 130.0, 129.8, 129.2, 128.3, 125.5 (q, J = 3.6 Hz), 125.1, 123.6 (q, J = 270.8 Hz), 120.7, 103.7, 99.0, 55.6, 55.5. HR-MS (ESI): Calcd for $C_{23}H_{20}F_3N_2O_4$ $[M+H]^+$ 445.1370, found 445.1371.

(*E*)-*N*′-((4-Nitrobenzoyl)oxy)-*N*-phenylbenzimidamide (1ba)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), yellow solid, 0.24 g, yield 66%, mp. 97−99 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 8.0 Hz, 2H), 7.12 (s, 1H), 7.07 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.1, 157.1, 150.6, 138.4, 134.9, 130.0, 130.7, 129.4, 129.4, 129.1, 128.6, 124.8, 123.7, 123.1. HR-MS (ESI): Calcd for $C_{20}H_{16}N_3O_4$ $[M+H]^+$ 362.1135, found 362.1138.

(*E*)-*N*′-((4-Cyanobenzoyl)oxy)-*N*-phenylbenzimidamide (1ca)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.19 g, yield 56%, mp. 132−134 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.06 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4, 157.1, 138.4, 133.3, 132.4, 130.9, 130.1, 129.4, 129.4, 129.1, 128.6, 124.7, 123.1, 117.9, 116.6. HR-MS (ESI): Calcd for $C_{21}H_{16}N_3O_2$ $[M+H]^+$ 342.1237, found 342.1241.

(*E*)-*N*′-((Perfluorobenzoyl)oxy)-*N*-phenylbenzimidamide (1da)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.24 g, yield 60%, mp. 120−121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.26 (s, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 7.6

Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 138.0, 130.9, 129.4, 129.0, 128.7, 128.6, 124.8, 123.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.88 (d, J = 18.1 Hz), -147.18 (t, J = 20.5 Hz), -159.27 (t, J = 19.5 Hz). HR-MS (ESI): Calcd for $C_{20}H_{12}F_5N_2O_2$ $[M+H]^+$ 407.0813, found 407.0814.

(*E*)-*N'*-((4-Methoxybenzoyl)oxy)-*N*-phenylbenzimidamide (1ea)

Chromatography (Petroleum ether:EtOAc 20:1 to 15:1), white solid, 0.3 g, yield 87%, mp. 193−195 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.2 Hz, 2H), 7.28 (s, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 7.6 Hz, 2H), 3.87 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.6, 156.6, 138.7, 131.7, 130.6, 129.7, 129.4, 129.0, 128.4, 124.3, 122.9, 121.5, 113.8, 55.5. HR-MS (ESI): Calcd for $C_{21}H_{19}N_2O_3$ $[M+H]^+$ 347.1390, found 347.1390.

(*E*)-*N*-Phenyl-*N'*-(pivaloyloxy)benzimidamide (1fa)

Chromatography (Petroleum ether:EtOAc 20:1), white solid, 0.27 g, yield 91%, mp. 119−121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 8.0 Hz, 2H), 7.02 (t, J = 7.6, 1H), 7.00 (s, 1H), 6.76 (d, J = 7.6 Hz, 2H), 1.35 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.6, 156.2, 138.7, 130.5, 129.8, 129.3, 129.0, 128.4, 124.2, 122.7, 39.0, 27.5. HR-MS (ESI): Calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$ 297.1598, found 297.1602.

Synthesis of Products 2. To a Schlenk tube (25 mL) was added substrates (0.2 mmol) and 1% photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$. The tube was sealed and replaced gas with argon three to four times, then methyl *tert*-butyl ether (1 mL) was injected. The mixture was stirred at room temperature for 36 h under illumination (approximately 2 cm away from the light source). Then the reaction mixture was taken into ethyl acetate (15 mL), and washed with saturated sodium carbonate solution (10 mL). The water phase was extracted with ethyl acetate (20 mL × 2). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography to afford benzimidazoles **2**.

2-Phenyl-1*H*-benzo[*d*]imidazole (2a)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 26.4 mg, yield 68%, mp. 292−294 ℃ (lit. [7e]: 297−299 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.91 (s, 1H), 8.18 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 6.8 Hz, 1H), 7.59 – 7.46 (m, 4H), 7.21 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 151.2, 143.8, 135.0, 130.1, 129.8, 128.9, 126.4, 122.5, 121.6, 118.8, 111.3. HR-MS (ESI): Calcd for $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0917, found 195.0919.

2-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole (2b)

Chromatography (Petroleum ether:EtOAc 16:1 to 8:1), white solid, 23.7 mg, yield 57%, mp. 280−281 ℃ (lit. [7e]: 270−271 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, J = 8.0 Hz, 2H), 7.60 (dd, J = 5.6, 3.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.20 (dd, J = 5.6, 3.2 Hz, 2H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 151.3, 139.5, 129.5, 127.4, 126.4, 121.9, 20.9. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1076.

2-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (2c)

Chromatography (Petroleum ether:EtOAc 8:1 to 6:1), white solid, 26.4 mg, yield 59%, mp. 230−231 ℃ (lit. [7e]: 233−234 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.76 (s, 1H), 8.12 (d, J = 8.8 Hz, 2H),7.61 – 7.50 (m, 2H), 7.17 (d, J = 4.0 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 161.0, 151.8, 128.4, 123.1, 118.9, 114.8, 111.5, 55.8. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1022, found 225.1025.

4-(1*H*-Benzo[*d*]imidazol-2-yl)benzonitrile (2d)

Chromatography (Petroleum ether:EtOAc 10:1 to 6:1), white solid, 28.5 mg, yield 65%, mp. 266−267 ℃ (lit. [7f]: 264−266 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.22 (s, 1H), 8.36 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.36 – 7.14

(m, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 149.3, 143.7, 135.1, 134.2, 133.0, 126.9, 123.4, 122.2, 119.3, 118.6, 111.8, 111.7. HR-MS (ESI): Calcd for $C_{14}H_{10}N_3$ $[M+H]^+$ 220.0869, found 220.0871.

2-(4-Nitrophenyl)-1*H*-benzo[*d*]imidazole (2e)

Chromatography (Petroleum ether:EtOAc 8:1 to 6:1), yellow solid, 30.1 mg, yield 63%, mp. >300 ℃ (lit. [7e]: >300 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.31 (s, 1H), 8.52 – 8.31 (m, 4H), 7.83 – 7.53 (m, 2H), 7.29 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 149.0, 147.7, 143.8, 136.0, 135.2, 127.3, 124.2, 123.5, 122.3, 119.4, 111.8. HR-MS (ESI): Calcd for $C_{13}H_{10}N_3O_2$ $[M+H]^+$ 240.0768, found 240.0769.

2-(4-Fluorophenyl)-1*H*-benzo[*d*]imidazole (2f)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 7.6 mg, yield 18%, mp. 180−181 ℃ (lit. [7f]: 181−182 ℃). ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.17 – 8.07 (m, 2H), 7.60 (dd, J = 6.0, 3.2 Hz, 2H), 7.37 – 7.17 (m, 4H). ^{13}C {^{1}H} NMR (100 MHz, CD_3OD-d_4) δ 164.0 (d, J = 249.5 Hz),151.1, 128.7 (d, J = 8.6 Hz), 126.1 (d, J = 3.1 Hz), 122.6, 115.7 (d, J = 22.3 Hz), 114.5. HR-MS (ESI): Calcd for $C_{13}H_{10}FN_2$ $[M+H]^+$ 213.0823, found 213.0826.

2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole (2g)

Chromatography (Petroleum ether:EtOAc 12:1 to 8:1), white solid, 27.4 mg, yield 60%, mp. 298−299 ℃ (lit. [7f]: 288−290 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.21 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 7.2 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 150.1, 143.7, 135.0, 134.5, 129.0, 128.1, 122.8, 121.8, 118.9, 111.4. HR-MS (ESI): Calcd for $C_{13}H_{10}ClN_2$ $[M+H]^+$ 229.0527, found 229.0528.

2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole (2h)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), yellow solid, 32.8 mg, yield 60%, mp. 295−297 ℃ (lit. [7g]: 282−284 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.12 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.30 – 7.12 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 150.2, 143.8, 135.1, 132.0, 129.4, 128.3, 123.2, 122.7, 122.0, 118.9, 111.4. HR-MS (ESI): Calcd for $C_{13}H_{10}BrN_2$ $[M+H]^+$ 273.0022, found 273.0023.

2-(4-(Trifluoromethoxy)phenyl)-1*H*-benzo[*d*]imidazole (2i)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 18.3 mg, yield 33%, mp. 229–230 ℃ (lit. [7h]: 222 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.04 (s, 1H), 8.31 (d, J = 8.8 Hz, 2H), 7.63 (s, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.23 (dd, J = 6.0, 3.2 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 149.9, 149.2, 149.2, 129.4, 128.4, 122.3, 121.4, 120.0 (q, J = 256.8 Hz), 111.5. HR-MS (ESI): Calcd for $C_{14}H_{10}F_3N_2O$ $[M+H]^+$ 279.0740, found 279.0742.

2-(3-Chlorophenyl)-1*H*-benzo[*d*]imidazole (2j)

Chromatography (Petroleum ether:EtOAc 9:1), white solid, 24.2 mg, yield 53%, mp. 223−225 ℃ (lit. [7g]: 227−229 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.24 (s, 1H), 8.16 (d, J = 6.4 Hz, 1H), 7.69 (d, J = 6.4 Hz, 1H), 7.64 – 7.48 (m, 3H), 7.26 – 7.15 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 150.2, 144.1, 135.4, 134.2, 132.6, 131.4, 130.0, 126.5, 125.5, 123.4, 122.4, 119.6, 112.0. HR-MS (ESI): Calcd for $C_{13}H_{10}ClN_2$ $[M+H]^+$ 229.0527, found 229.0527.

2-(2-Chlorophenyl)-1*H*-benzo[*d*]imidazole (2k)

Chromatography (Petroleum ether:EtOAc 15:1 to 10:1), white solid, 5.5 mg, yield 12%, mp. 232–233 ℃ (lit. [7e]: 237−238 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.73 (s, 1H), 7.91 (dd, J = 6.8, 2.0 Hz, 1H), 7.70 (s, 1H), 7.66(dd, J = 6.8, 2.0 Hz, 2H), 7.62 – 7.48 (m, 3H), 7.25 (s, 2H). ^{13}C

{^{1}H} NMR (100 MHz, DMSO-d_6) δ 149.1, 143.2, 134.6, 132.1, 131.6, 131.2, 130.3, 129.9, 127.4, 122.7, 121.7, 119.1, 111.7. HR-MS (ESI): Calcd for $C_{13}H_{10}ClN_2$ $[M+H]^+$ 229.0527, found 229.0529.

2-(Benzo[*d*][1,3]dioxol-5-yl)-1*H*-benzo[*d*]imidazole (2l)

Chromatography (Petroleum ether:EtOAc 8:1 to 6:1), white solid, 33.4 mg, yield 73%, mp. 252−254 ℃ (lit. [7h]: 246 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.75 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.56 (s, 2H), 7.25 – 7.14 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 6.13 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 151.6, 149.2, 148.3, 124.7, 122.4, 121.3, 109.2, 106.9, 102.0. HR-MS (ESI): Calcd for $C_{14}H_{11}N_2O_2$ $[M+H]^+$ 239.0815, found 239.0814.

2-([1,1'-Biphenyl]-4-yl)-1*H*-benzo[*d*]imidazole (2m)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 41.6 mg, yield 77%, mp. >300 ℃ (lit. [8]: 290−292 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.30 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 7.2 Hz, 2H), 7.74 – 7.36 (m, 5H), 7.24 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 150.9, 144.0, 141.3, 139.2, 135.0, 129.1, 129.0, 127.9, 127.1, 127.0, 126.7, 122.6, 121.8, 118.9, 111.3. HR-MS (ESI): Calcd for $C_{19}H_{15}N_2$ $[M+H]^+$ 271.1230, found 271.1228.

2-(Naphthalen-2-yl)-1*H*-benzo[*d*]imidazole (2n)

Chromatography (Petroleum ether:EtOAc 8:1), white solid, 35.2 mg, yield 72%, mp. 218−219 ℃ (lit. [7e]: 220−222 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.12 (s, 1H), 8.77 (s, 1H), 8.34 (s, 1H), 8.21 – 7.90 (m, 3H), 7.62 (s, 4H), 7.25 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 151.2, 133.4, 132.8, 128.5, 128.4, 127.8, 127.6, 127.1, 126.9, 125.8, 123.9, 122.1. HR-MS (ESI): Calcd for $C_{17}H_{13}N_2$ $[M+H]^+$ 245.1073, found 245.1075.

Methyl 4-(1*H*-benzo[*d*]imidazol-2-yl)benzoate (2o)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 30.3 mg, yield 60%, mp. 236–237 ℃ (lit. [7e]: 232−234 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.15 (s, 1H), 8.33 (d, J = 8.4 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.32 – 7.17 (m, 2H), 3.90 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.8, 150.0, 143.8, 135.1, 134.3, 130.3, 129.8, 126.6, 123.1, 122.0, 119.2, 111.6, 52.3. HR-MS (ESI): Calcd for $C_{15}H_{13}N_2O_2$ $[M+H]^+$ 253.0972, found 253.0973.

_N_-(4-(1_H_-Benzo[_d_]imidazol-2-yl)phenyl)acetamide (2p)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 16.6 mg, yield 33%, mp. >300 ℃ (lit. [6c]: 314 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.83 (s, 1H), 10.19 (s, 1H), 8.10 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.57 (dd, J = 6.0, 3.2 Hz, 2H), 7.18 (dd, J = 6.0, 3.2 Hz, 2H), 2.10 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 168.6, 151.2, 140.8, 127.1, 124.6, 121.9, 118.9, 24.1. HR-MS (ESI): Calcd for $C_{15}H_{14}N_3O$ $[M+H]^+$ 252.1131, found 252.1131.

Ethyl 1_H_-benzo[_d_]imidazole-2-carboxylate (2q)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 14.8 mg, yield 39%, mp. 222–224 ℃ (lit. [6d]: 222−223 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.47 (s, 1H), 7.68 (s, 2H), 7.35 (s, 2H), 4.43 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.3, 141.7, 61.6, 14.1. HR-MS (ESI): Calcd for $C_{10}H_{11}N_2O_2$ $[M+H]^+$ 191.0815, found 191.0809.

5-Methyl-2-phenyl-1_H_-benzo[_d_]imidazole (2aa)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 27.9 mg, yield 67%, mp. 249–250 ℃ (lit. [7e]: 245−249 ℃). (tautomeric isomer): ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.76 (s, 1H), 8.17 (d, J = 6.0 Hz, 2H), 7.65 – 7.27 (m, 5H), 7.04 (s, 1H), 2.45 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 151.6, 151.2, 144.6, 142.4, 135.7, 133.5, 132.3, 130.8, 130.1, 129.4, 126.7, 124.4, 123.7, 119.1, 118.9, 111.5, 111.3, 21.8, 21.8. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1075.

5-Methoxy-2-phenyl-1*H*-benzo[*d*]imidazole (2ab)[7i]

Chromatography (Petroleum ether:EtOAc 8:1 to 6:1), white solid, 13.9 mg, yield 31%, mp. 148–150 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.98 (m, 2H), 7.52 (d, J = 8.8 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.09 (d, J = 2.0 Hz, 1H), 6.91 (dd, J = 8.8, 2.0 Hz, 1H), 3.84 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.7, 151.5, 130.0, 129.9, 129.1, 126.4, 112.6, 55.8. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1022, found 225.1026.

(*tert*-Butyl)-2-phenyl-1*H*-benzo[*d*]imidazole (2ac)

Chromatography (Petroleum ether:EtOAc 10:1), white solid, 27.0 mg, yield 54%, mp. 176–178 ℃ (lit. [8b]: 171−172 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.26 – 8.18 (m, 2H), 7.52 (s, 1H), 7.51(d, J = 8.4 Hz, 1H), 7.36 – 7.20 (m, 4H), 1.27 (d, J = 7.6 Hz, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.6, 146.4, 138.8, 137.4, 130.0, 130.0, 129.1, 127.1, 121.0, 114.8, 111.2, 34.8, 31.8. HR-MS (ESI): Calcd for $C_{17}H_{19}N_2$ $[M+H]^+$ 251.1543, found 251.1545.

5-Fluoro-2-phenyl-1*H*-benzo[*d*]imidazole (2ad)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 13.6 mg, yield 32%, mp. 242–244 ℃ (lit. [8b]: 240−242 ℃). (tautomeric isomer): ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.05 (s, 1H), 8.17 (d, J = 7.2 Hz, 2H), 7.67 – 7.28 (m, 5H), 7.07 (t, J = 8.8 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 153.4, 152.7, 144.6, 140.9, 132.1, 130.6, 130.4, 130.4, 130.3, 129.5, 126.9, 126.8, 120.3, 120.2, 112.4, 112.4, 111.2, 110.9, 110.4, 110.2, 104.9, 104.7, 98.3, 98.0. HR-MS (ESI): Calcd for $C_{13}H_{10}FN_2$ $[M+H]^+$ 213.0823, found 213.0824.

5-Chloro-2-phenyl-1*H*-benzo[*d*]imidazole (2ae)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 20.6 mg, yield 45%, mp. 211–213 ℃ (lit. [8b]: 207−208 ℃). (tautomeric isomer): ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.16+13.14 (s, 1H), 8.19 (d, J = 7.2 Hz, 2H), 7.74 (s, 0.5H), 7.69 (d, J = 8.4 Hz, 0.5H), 7.64 – 7.47 (m, 4H), 7.29 – 7.18 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 152.8, 152.4, 144.7, 142.6, 135.7, 133.8, 130.2, 130.2, 129.7, 129.0, 126.8, 126.6, 126.0, 122.6, 122.0, 120.1, 118.2, 112.6, 111.0. HR-MS (ESI): Calcd for $C_{13}H_{10}ClN_2$ $[M+H]^+$ 229.0527, found 229.0528.

5-Bromo-2-phenyl-1*H*-benzo[*d*]imidazole (2af)

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), yellow solid, 17.5 mg, yield 32%, mp. 201–203 ℃ (lit. [8b]: 200−202 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 4.4 Hz, 2H), 7.71 (s, 1H), 7.45 (s, 4H), 7.35 (d, J = 8.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.9, 130.6, 129.3, 129.2, 126.8, 126.2, 116.0. HR-MS (ESI): Calcd for $C_{13}H_{10}BrN_2$ $[M+H]^+$ 273.0022, found 273.0020.

4-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole (2ag')[7i]

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 12.9 mg, yield 31%, mp. 260–261 ℃. ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.12 (d, J = 8.0Hz, 2H), 7.58 – 7.47 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 2.62 (s, 3H). ^{13}C {^{1}H} NMR (100MHz, CD_3OD-d_4) δ 153.2, 131.3, 131.2, 130.1, 128.0, 124.4, 123.9, 17.2. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1074.

6-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole(2ag'')

Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 12.5 mg, yield 30%, mp. 250–251 ℃ (lit. [7e]: 245−249 ℃). ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.08 – 8.04 (m, 2H), 7.56 – 7.45 (m, 4H), 7.39 (s, 1H), 7.09 (dd, J = 8.4, 1.2 Hz, 1H), 2.46 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CD_3OD-d_4) δ 153.1, 134.0, 131.2, 131.2, 130.1, 127.7, 125.5, 115.5, 21.8. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1075.

7-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole(2ah)[7i]

Chromatography (Petroleum ether:EtOAc 10:1), white solid, 14.2 mg, yield 34%, mp. 259–260 ℃. ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.16 – 8.08 (m, 2H), 7.58 – 7.46 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 2.62 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CD_3OD-d_4) δ 153.2, 131.3, 131.2, 130.1, 128.0, 124.5, 123.9, 17.2. HR-MS (ESI): Calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1074.

4,5-Dichloro-2-phenyl-1*H*-benzo[*d*]imidazole (2aj') and 5,6-dichloro-2-phenyl-1*H*-benzo[*d*]imidazole (2aj'')[9e]

Chromatography (Petroleum ether:EtOAc 8:1), yellow solid, 12.1 mg, yield 23%. **2aj**': ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.11 (dd, J = 6.4, 2.8 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.49 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H). **2aj**'': ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.05 (dd, J = 6.4, 2.8 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.74 (s, 2H). **2aj**'+ **2aj**'': ^{13}C {^{1}H} NMR (100 MHz, MeOD-d_4) δ 155.5, 155.4, 139.8, 138.8, 138.2, 132.5, 132.2, 130.4, 130.2, 129.9, 129.4, 128.4, 128.2, 127.6, 125.8, 120.2, 117.1, 114.4. HR-MS (ESI): Calcd for $C_{13}H_9Cl_2N_2$ $[M+H]^+$ 263.0137, found 263.0140.

4,6-Dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (2ak)

Chromatography (Petroleum ether:EtOAc 8:1 to 6:1), white solid, 21.8 mg, yield 49%, mp. 196–197 ℃ (lit. [21]: 204−206 ℃). ^{1}H NMR (400 MHz, CD_3OD-d_4) δ 8.14 – 8.08 (m, 2H), 7.58 – 7.46 (m, 3H), 7.23 (s, 1H), 6.89 (s, 1H), 2.59 (s, 3H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, CD_3OD-d_4) δ 151.4, 132.4, 130.0, 129.6, 128.6, 126.5, 124.7, 20.3, 15.7. HR-MS (ESI): Calcd for $C_{15}H_{15}N_2$ $[M+H]^+$ 223.1230, found 223.1233.

5,7-Dimethoxy-2-phenyl-1*H*-benzo[*d*]imidazole (2al)

Chromatography (Petroleum ether:EtOAc 10:1), white solid, 10.2 mg, yield 20%, mp. 209–211 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.74 (s, 1H), 8.46 – 7.95 (m, 2H), 7.65 – 7.33 (m, 3H), 6.62 (s, 1H), 6.38 (s, 1H), 3.94 (s, 3H), 3.81 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 157.0, 151.3, 148.6, 136.6, 130.4, 129.2, 128.8, 125.9, 94.1, 86.6, 55.5, 55.4. HR-MS (ESI): Calcd for $C_{15}H_{15}N_2O_2$ $[M+H]^+$ 255.1128, found 255.1133.

Gram-scale Reaction

To a Schlenk tube was added substrate **1a** (6 mmol) and 1% photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$. The tube was sealed and replaced gas with argon three to four times. Then methyl *tert*-butyl ether (30 mL) was injected, and the mixture was stirred at room temperature for 36 h under illumination (approximately 2 cm away from the light source). Then the reaction mixture was taken into ethyl acetate (300 mL), and washed with saturated sodium carbonate solution (200 mL). The water phase was extracted with ethyl acetate (100 mL × 2). The combined organic phase was washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (Petroleum ether:EtOAc 10:1 to 8:1) to afford benzimidazole **2a** 0.71 g, yield 61%.

Preparation of Thiazole-4-carbaldehyde Oxime (4).

The mixture of thiazole-4-carbaldehyde (2.26 g, 20 mmol), hydroxylamine hydrochloride (1.47 g, 21 mmol) and pyridine (1.67 g, 21 mmol) in ethanol (40 mL) was stirred at room temperature for 16 h, and concentrated. The residue was taken into ethyl acetate (50 mL), and washed with saturated sodium carbonate solution (50 mL). The water phase was extracted with ethyl acetate (50 mL × 2). The combined organic phase was washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated to give compound **4** (2,6 g, 99% yield) as a yellow solid, mp. 122–124 ℃ (lit. [24a]: 115−122 ℃). *E*/*Z* = 2:1. *E*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (brs, 1H), 8.86 (d, *J* = 2.0 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 7.91 (s, 1H). *Z*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.0 Hz, 1H), 8.37 (s, 1H), 7.65 (d, *J* = 2.0 Hz, 1H).

Preparation of (*Z*)-*N*-Hydroxythiazole-4-carbimidoyl Chloride (5).

To the solution of thiazole-4-carbaldehyde oxime (**4**) (0.52 g, 4.1 mmol) in DMF (4.1 mL) was added dropwise NCS (0.58 g, 4.36 mmol) at 0 °C. Then the reaction solution stirred at 0 °C for 1 h and at room temperature for 2 h, then added water (14 mL). The mixture was filtered to afford compound **5** (0.55 g, 83% yield) as a white solid, mp. 154–156 ℃ (lit. [24]: >175 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 9.19 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.4, 148.3, 130.9, 121.0.

Preparation of *N*′-Hydroxy-*N*-phenylthiazole-4-carboximidamide (6).

To the solution of chloraldoxime **5** (0.54 g, 3.3 mmol) in THF (50 mL) was added dropwise aniline (0.325 g, 3.3 mmol) and triethylamine (0.68 g, 6.6 mmol). The mixture was heated with oil bath to 60 °C and stirred for 12 h, cooled to room temperature, and filtered. The filtrate was concentrated and purified by flash column chromatography (CH_2Cl_2:CH_3OH 100:1 to 50:1) to afford aminoxime **6** (0.34 g, 47% yield) as a yellow solid, mp. 215–216 ℃. *E/Z* = 7.6:1, *E*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.58 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.0, 147.5, 146.8, 139.6, 128.8, 123.2, 121.3, 120.1. HR-MS (ESI): Calcd for Chemical Formula: $C_{10}H_{10}N_3O_S$ $[M+H]^+$ 220.0539, found 220.0542.

Preparation of (*E*)-*N*-Phenyl-*N′*-((4-(trifluoromethyl)benzoyl)oxy)thiazole-4-carboximidamide (7).

The procedures for preparation of **1** was used. Chromatography (Petroleum ether:EtOAc 10:1 to 8:1), white solid, 0.32 g, yield 82%, mp. 150–151 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 7.84 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.10 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.6, 152.8, 149.0, 147.0, 139.5, 134.3 (q, *J* = 32.5 Hz), 132.2, 129.8, 128.9, 125.2, 125.1 (q, *J* = 3.5 Hz), 123.8, 123.6 (q, *J* = 271.1 Hz), 120.9. HR-MS (ESI): Calcd for $C_{18}H_{13}F_3N_3O_2S$ $[M+H]^+$ 392.0675, found 392.0677.

Preparation of 4-(1*H*-Benzo[d]imidazol-2-yl)thiazole (Thiabendazole 8).

The procedures for preparation of **2** was used. Chromatography (Petroleum ether:EtOAc 8:1), white solid, 16.1 g, yield 40%, mp. 297–298 ℃ (lit.[24b]: 115−122 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.97 (s, 1H), 9.34 (d, *J* = 1.8 Hz, 1H), 8.45 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.16 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 156.1, 147.6, 147.5, 144.2, 134.8, 123.1, 122.2, 119.9, 119.2, 112.2. HR-MS (ESI): Calcd for $C_{10}H_8N_3S$ $[M+H]^+$ 202.0433, found 202.0434.

ASSOCIATED CONTENT

Supporting Information

Scheme for the preparation of substrates **1**. Copies of ^{1}H NMR and ^{13}C NMR spectra for the compounds. This information is free of charge from the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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