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One-Pot Synthesis of 2-Arylbenzoxazinones from 2-Arylindoles with (Diacetoxyiodo)benzene as the Sole Oxidant

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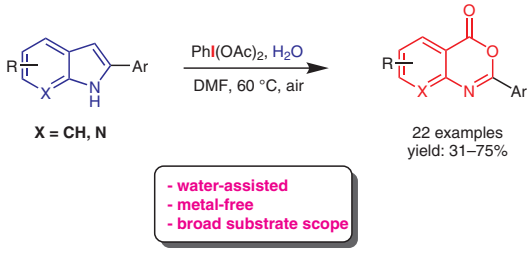

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Abstract A series of synthetically interesting 2-arylbenzoxazinones was prepared from 2-arylindoles by an efficient oxidative reaction mediated by (diacetoxyiodo)benzene [PhI(OAc)$_2$] and assisted by water. PhI(OAc)$_2$ was used as the sole oxidant and water was a crucial additive. Our preliminary mechanistic investigations suggest that a water-involved, iodine(III)-promoted sequential oxidation of 2-arylindoles, which was terminated by an interesting Grob-type fragmentation of a fused tricyclic precursor, might be the main components of this one-pot transformation.

Key words benzoxazinones, hypervalent iodine, indoles, oxidation, water-assisted

The 4*H*-3,1-benzoxazin-4-one core is an important structural skeleton found in many bioactive compounds and pharmaceutical drugs (Figure 1). For example, **I** has the ability to lower the level of plasma cholesterol and triglycerides,[1] **II** and **III** show good cytotoxicity against P338 cells,[2] and **IV** acts as a serine hydrolase inhibitor.[3] Importantly, 2-substituted 4*H*-3,1-benzoxazin-4-ones are also versatile building blocks for the synthesis of pharmaceutically active compounds. An example is compound **V**, an anticonvulsant agent, which can be synthesized from 2-phenyl-4*H*-3,1-benzoxazin-4-one (**2a**) in two steps (Scheme 1).[4] Due to its synthetic importance, the development of approaches toward the preparation of 4*H*-3,1-benzoxazin-4-one derivatives has received considerable attention in organic synthesis.

The traditional synthesis of benzoxazinones is by cyclization of substituted anthranilic acids, for which corrosive and toxic acyl chlorides are inevitably required.[4] More recently, transition-metal-catalyzed carbonylation of *o*-haloanilines,[5] benzanilides,[6] and aryl urea derivatives[7] has been reported to give benzoxazinones, in which carbon monoxide is used as the carbonyl source. Additionally, palladium-catalyzed cleavage of the C–C triple bond in 2-azidoalkynylbenzenes was found to be an alternative route for the synthesis of benzoxazinones.[8] Copper-catalyzed cyclization of *N*-acyl-2-halobenzamides was also disclosed to yield a variety of benzoxazinones.[9] Recently, oxidative

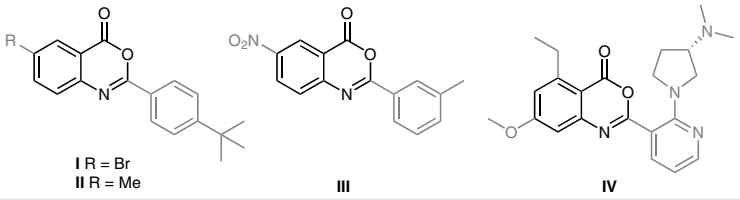
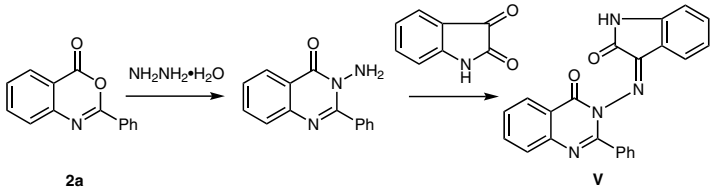


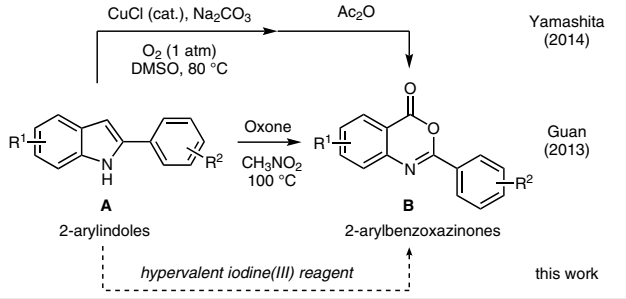
Figure 1 Some bioactive molecules with the 4*H*-3,1-benzoxazin-4-one core



Scheme 1 Using benzoxazinone in the synthesis of the anticonvulsant quinazolinone **V**

tandem cyclization of *N*-TFA-protected 2-alkynylanilines was revealed to afford 2-arylbenzoxazinones.[10]

In addition to the above-mentioned 1,2-disubstituted benzene derivatives as substrates, interestingly, substituted indoles **A** as starting materials were also investigated in the synthesis of benzoxazinones **B**. As shown in Scheme 2, the synthesis of 2-arylbenzoxazinones could be alternatively accessed from 2-arylindoles by Oxone-mediated oxidation[11] or a copper-catalyzed aerobic oxidative tandem reaction.[12] It has also been reported that visible-light photocatalytic aerobic oxygenation of indoles could afford a few examples of benzoxazinones.[13] To the best of our knowledge, however, the one-pot synthesis of 2-arylbenzoxazinones by a hypervalent iodine(III)-mediated oxidative reaction of 2-arylindoles has not yet been reported (Scheme 2).

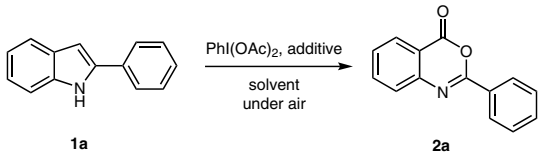


Scheme 2 Synthesis of 2-arylbenzoxazinones from 2-arylindoles

The chemistry of hypervalent iodine compounds has experienced an unprecedented, explosive development in the past decades.[14] The oxidation properties of hypervalent iodine(III) compounds resemble those of heavy metal species [e.g., Hg(III), Tl(III), Pb(IV)], but without the accompanying toxicity and environmental problems. Generally, hypervalent organic iodine reagents have mild and highly selective oxidizing properties. Notably, the commercially available $PhI(OAc)_2$, as one of the most widely used trivalent iodine reagents, has been used in various kinds of oxidation reactions, such as the oxidation of alcohols or phenols,[15] the oxidative functionalization of carbonyl compounds and olefins,[16] oxidative rearrangement and fragmentation reactions,[17] free-radical cyclization reactions,[18] and oxidative coupling of electron-rich aromatics.[19] In connection to our interest in hypervalent iodine chemistry, we recently developed a novel method for the straightforward synthesis of 2-arylbenzoxazinone derivatives from 2-arylindoles by using $PhI(OAc)_2$ as the sole oxidant. Herein, we report our preliminary results.

Initially, the hypervalent iodine mediated oxidative reaction was investigated in DMF under air at 100 °C by using 2-arylindole **1a** as substrate and $PhI(OAc)_2$ as oxidant, and the desired benzoxazinone product **2a** could be obtained, but in a low yield of 13% (Table 1, entry 1). By varying the reaction temperature from 40 °C to 100 °C (entries 1–5), the reaction yield could be slightly improved at 60 °C (entry 3). The amount of $PhI(OAc)_2$ as oxidant was also examined in this model (entries 6–8), and it was found that at least four equivalents of $PhI(OAc)_2$ were required for a better conversion of **1a** to **2a** (entry 7). Additionally, some basic and acidic additives (entries 9, 10) were also added to the current model reaction, but no positive results were observed. Interestingly, a significant improvement of reaction yield was achieved when three equivalents of H_2O were added to the model reaction (entry 11). Following further examination on the quantities of H_2O (entries 12–14), an optimal yield of 71% could be obtained with 10 to 15 equivalents of H_2O (entries 13, 14). Compared with DMF as

Table 1 Optimization of Reaction Conditions[a]



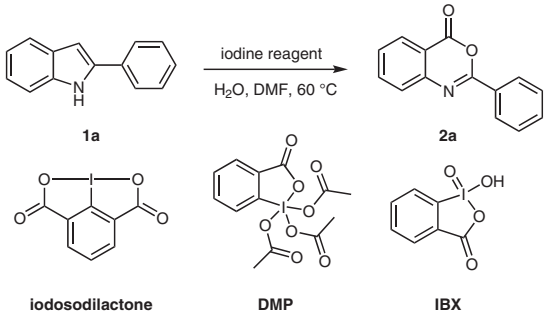
Entry	Equiv of PhI $(OAc)_2$	Solvent	Additive (equiv)	Temp (°C)	Yield[b] (%)
1	3	DMF[c]	–	100	13
2	3	DMF[c]	–	80	15
3	3	DMF[c]	–	60	19
4	3	DMF[c]	–	40	16
5	3	DMF[c]	–	0	trace[d]
6	2	DMF[c]	–	60	10
7	4	DMF[c]	–	60	20
8	5	DMF[c]	–	60	20
9	4	DMF	base[e] (3)	60	0
10	4	DMF	acid[f] (3)	60	0–14
11	4	DMF	H_2O (3)	60	57
12	4	DMF	H_2O (6)	60	68
13	4	DMF	H_2O (10)	60	71
14	4	DMF	H_2O (15)	60	71
15	4	DMA	H_2O (10)	60	52
16	4	DMSO	H_2O (10)	60	0
17	4	MeCN	H_2O (10)	60	9
18	4	THF	H_2O (10)	60	42
19	4	EtOAc	H_2O (10)	60	33
20	4	toluene	H_2O (10)	60	20

[a] Reaction conditions: **1a** (1.0 mmol), $PhI(OAc)_2$, additive, solvent (10 mL), under air, 24 h.
[b] Isolated yield.
[c] This reaction was conducted under air, and therefore introducing some water to the reaction system could not be avoided as DMF is moisture-sensitive in air.
[d] The oxidative side product, 2-phenyl-3*H*-indol-3-one (**3a**), was isolated in 8% yield.
[e] No desired product could be isolated when a base (e.g., Na_2CO_3, $NaHCO_3$, NaOH, Et_3N, pyridine, DMAP) was used as additive.
[f] The following acids were investigated (product yield given in parentheses): TFA (5%), AcOH (14%), $TsOH·H_2O$ (0%).

solvent (entry 13), a further screening of a series of solvents was also conducted (entries 15–20), but solvents other than DMF gave inferior results in terms of chemical yield.

Considering the different oxidation properties of hypervalent iodine reagents, a variety of iodine(III) oxidants with different oxy ligands [e.g., $PhI(OCOCF_3)_2$, $PhI(OPiv)_2$, $PhI(OCOPh)_2$, PhIO, PhI(OH)OTs, iodosodilactone[20]] were used instead of $PhI(OAc)_2$ (Table 2, entries 1–6), but a negative influence on the reaction yield was observed in these cases.

Table 2 Optimization of the Iodine Reagent[a]

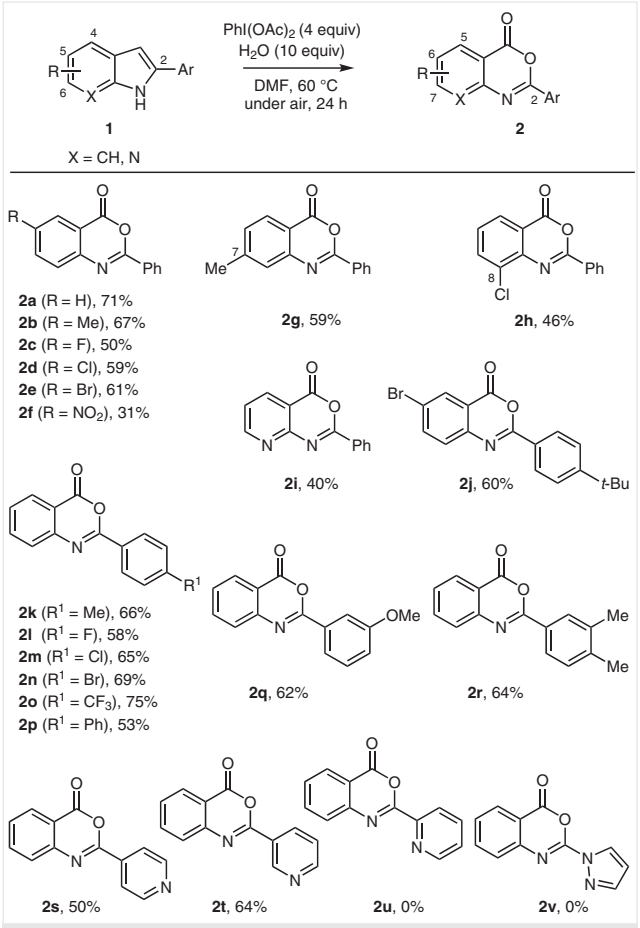


Entry	Iodine reagent	Yield[b] (%)
1	$PhI(OCOCF_3)_2$	11
2	$PhI(OPiv)_2$	21
3	$PhI(OCOPh)_2$	26
4	PhIO	38
5	PhI(OH)OTs	0
6	iodosodilactone	23
7	$4\text{-}FC_6H_4I(OAc)_2$	64
8	$4\text{-}MeOC_6H_4I(OAc)_2$	63
9	IBX	0
10	DMP	0

[a] Reaction conditions: **1a** (1.0 mmol), iodine reagent (4 equiv), H_2O (10 equiv), DMF (10 mL), 60 °C, under air, 24 h.
[b] Isolated yield.

To probe the electronic effect of the aryl substituent in the analogues of $PhI(OAc)_2$, 4-(diacetoxyiodo)fluorobenzene (Table 2, entry 7) and 4-(diacetoxyiodo)anisole[17] (entry 8) were then tested, showing positive reactivity with slightly reduced yields. Two iodine(V) reagents, IBX and DMP (entries 9 and 10), were also examined as oxidants, but the expected 2-arylbenzoxazinone **2a** was not isolated.

After the above optimization of the reaction conditions, the scope and generality of this reaction were then investigated (Scheme 3). A series of 2-phenylindoles **1a–f** with electronically different substituents (R = H, Me, F, Cl, Br, NO_2) were firstly used as substrates, and the desired 2-phenylbenzoxazinones **2a–f** could be achieved in reasonable to moderate yields. It should be noted that 6-nitro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (**2f**), obtained in 31% yield by our protocol, could only be afforded in a trace amount by Yamashita's method.[12] Both the 7- and 8-substituted indoles **1g**,**h** showed similar reactivity to that of the aforementioned 6-substituted indoles. In addition, 2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (**1i**) was also tested under the optimized conditions, giving the expected 2-phenyl-4*H*-pyrido[2,3-*d*][1,3]oxazin-4-one (**2i**) in moderate yield. Importantly, functionalized benzoxazinone **2j**, a biologically interesting substance,[1] could be readily obtained in 60% yield.



Scheme 3 Oxidation of 2-arylindoles **1** for the synthesis of 2-arylbenzoxazinones **2** by using $PhI(OAc)_2$. *Reagents and conditions*: **1** (1.0 mmol), $PhI(OAc)_2$ (4.0 equiv), H_2O (10 equiv), DMF (10 mL), 60 °C, 24 h, under air; isolated yields are given.

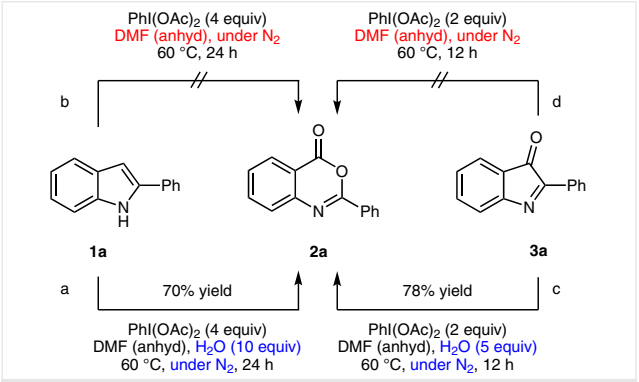
Subsequently, the influence of the C-2 aryl group in indoles **1** was then examined. As shown in Scheme 3, various 2-arylindoles **1k–r** bearing electron-donating and electron-withdrawing groups on the C-2 aryl ring were employed under the developed reaction conditions, and the corresponding benzoxazinones **2k–r** could be obtained smoothly in moderate yields. Additionally, two examples using **1s**,**t** with C-2 heteroaromatic substituents were also investigat-

ed, successfully giving the corresponding pyridyl-containing products **2s** and **2t**. However, from 2-(2-pyridyl)-1*H*-indole (**1u**) and 2-(1*H*-pyrazol-1-yl)-1*H*-indole (**1v**) as substrates under the present oxidation reaction conditions, surprisingly no desired products could be isolated, showing the negative influence of *ortho* heteroaryl substituents on the formation of the desired benzoxazinones.

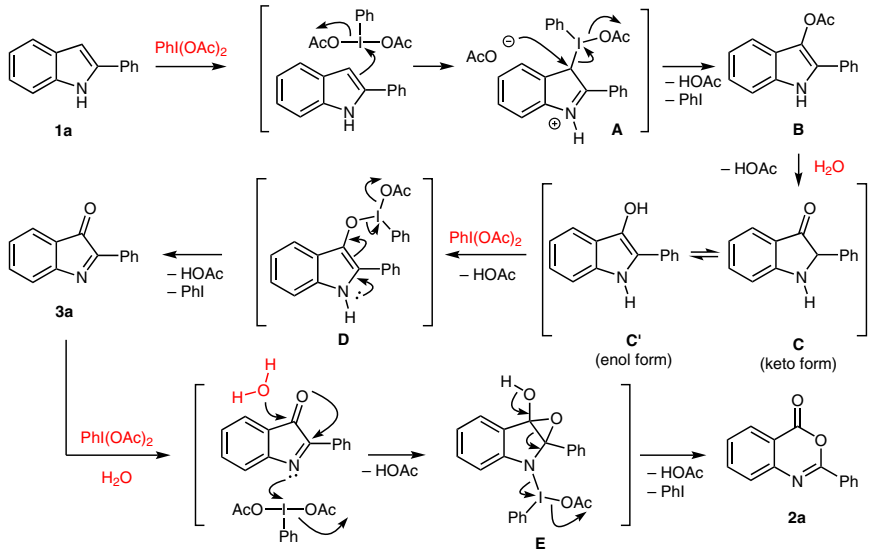
Several control experiments were conducted in order to develop a plausible mechanism for this reaction (Scheme 4). Compared with the results when using **1a** under our standard conditions (Table 1, entry 13, 71% yield), a similar reaction efficiency for **2a** (70% yield) could also be obtained in the presence of water under nitrogen instead of air (Scheme 4, a). However, the absence of water in absolute anhydrous DMF under nitrogen did not result in the formation of the desired benzoxazinone product **2a** (Scheme 4, b), indicating the essential assisting role of water in the current iodine(III)-mediated oxidative transformation. Since 2-phenyl-3*H*-indol-3-one (**3a**) was obtained as an oxidative side product in 8% yield during optimization of the reaction conditions (Table 1, entry 5), one additional experiment using **3a** was then conducted in the $PhI(OAc)_2$-mediated oxidation in the presence of water in DMF under nitrogen (Scheme 4, c). In contrast to the formation of no product from **3a** in the absence of water in anhydrous DMF under nitrogen (Scheme 4, d), the desired product **2a** was obtained in 78% yield in this case (Scheme 4, c), indicating that **3a** might be involved as an intermediate in this iodine(III)-mediated oxidation reaction.

On the basis of the above studies, a plausible mechanism for this reaction is proposed in Scheme 5, as exemplified by the transformation of **1a** to **2a**. Initially, electrophilic attack of $PhI(OAc)_2$ at the C-3 position of indole **1a** gave 3-acetoxy-substituted indole **B**[21] via intermediate **A**. Subsequently, hydrolysis of the enol ester group in **B** gave 2-phenyl-3-oxindole **C** and its enol tautomer **C′**,[22] which could be further oxidized via the iodine(III) species **D** to afford 2-phenyl-3*H*-indol-3-one (**3a**). After nucleophilic attack of water on the carbonyl group in **3a** and ligand exchange of $PhI(OAc)_2$ with the imino group in **3a**, a novel Grob-type fragmentation,[23] chemically initiated by the higher oxidation state of the iodine center in **E**, furnished the final benzoxazinone product **2a** with the release of PhI and HOAc.

In summary, a novel water-assisted, $PhI(OAc)_2$-mediated oxidative reaction has been developed, providing an alternative method for the one-pot synthesis of various 2-arylbenzoxazinones starting from readily available 2-arylindoles. This reaction has a wide functional group tolerance, and is characterized by the employment of $PhI(OAc)_2$ as the sole oxidant and the presence of water as a crucial additive. Preliminary mechanistic investigations suggest that a water-involved, iodine(III)-promoted sequential oxidation of 2-arylindoles, terminated by an interesting Grob-type frag-



Scheme 4 Control experiments for preliminary mechanistic studies



Scheme 5 Proposed mechanism for the water-assisted, $PhI(OAc)_2$-mediated oxidative reaction

mentation of a fused tricyclic precursor, might be involved in this reaction. The current water-assisted, iodine(III)-mediated oxidative reaction not only expands the application of hypervalent iodine chemistry, but also enriches the synthetic chemistry of the 4*H*-3,1-benzoxazin-4-one core structure based on the oxidation chemistry of indoles.

Chemicals and reagents were purchased from commercial suppliers and used as received. ^{1}H NMR spectra (400 MHz) were obtained from samples in $CDCl_3$, unless noted otherwise. The chemical shift values are given relative to internal TMS. Unless noted otherwise, the purification was performed by using column chromatography on silica gel.

4*H*-Benzo[*d*][1,3]oxazin-4-ones 2; General Procedure

A mixture of **1** (1.0 mmol), $PhI(OAc)_2$ (1.288 g, 4.0 mmol), and H_2O (180 µL, 10 mmol) in DMF (10 mL) was stirred at 60 °C under air for 24 h, and then the mixture was cooled to r.t. The mixture was quenched with H_2O (30 mL) and extracted with EtOAc. The organic extracts were washed with brine, dried over Na_2SO_4, and then concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE–EtOAc) to give the corresponding product **2**.

2-Phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2a)[11]

Yield: 158 mg (71%); colorless needles; mp 113–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.0 Hz, 2 H), 8.25 (d, *J* = 8.0 Hz, 1 H), 7.84–7.80 (t, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.52–7.49 (m, 4 H).

ESI-MS: *m*/*z* for $C_{14}H_9NO_2$: 224.06; found: 224.06.

6-Methyl-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2b)[11]

Yield: 159 mg (67%); colorless needles; mp 139–140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.6 Hz, 2 H), 8.01 (s, 1 H), 7.62–7.46 (m, 5 H), 2.47 (s, 3 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}NO_2$: 238.08; found: 238.10.

6-Fluoro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2c)[11]

Yield: 120 mg (50%); colorless needles; mp 131–132 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.2 Hz, 2 H), 7.88–7.85 (m, 1 H), 7.69–7.67 (m, 1 H), 7.56–7.48 (m, 4 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8FNO_2$: 242.05; found: 242.10.

6-Chloro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2d)[11]

Yield: 152 mg (59%); colorless needles; mp 188–189 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.2 Hz, 2 H), 8.17 (s, 1 H), 7.76–7.48 (m, 4 H), 7.52 (t, *J* = 8.0 Hz, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8ClNO_2$: 258.02; found: 258.10.

6-Bromo-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2e)[11]

Yield: 184 mg (61%); colorless needles; mp 189–190 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 8.28 (d, *J* = 7.2 Hz, 2 H), 7.90 (d, *J* = 8.2 Hz, 1 H), 7.57–7.47 (m, 4 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8BrNO_2$: 301.97; found: 302.00.

6-Nitro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2f)[8]

Yield: 120 mg (31%); yellow needles; mp 157–158 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.17 (s, 1 H), 8.33 (d, *J* = 8.0 Hz, 2 H), 8.21–8.18 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.91 (d, *J* = 9.6 Hz, 1 H), 7.74–7.71 (t, *J* = 7.2 Hz, 1 H), 7.63–7.59 (t, *J* = 8.0 Hz, 2 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8N_2O_4$: 269.05; found: 269.11.

7-Methyl-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2g)[11]

Yield: 140 mg (59%); colorless needles; mp 159–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.6 Hz, 2 H), 8.11 (d, *J* = 8.0 Hz, 1 H), 7.57–7.47 (m, 4 H), 7.31 (d, *J* = 8 Hz, 1 H), 2.49 (s, 3 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}NO_2$: 238.08; found: 238.10.

8-Chloro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (2h)[11]

Yield: 118 mg (46%); colorless needles; mp 172–173 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.0 Hz, 2 H), 8.15 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.60–7.56 (t, *J* = 7.2 Hz, 1 H), 7.52–7.49 (m, 2 H), 7.43–7.39 (m, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8ClNO_2$: 258.02; found: 258.06.

2-Phenyl-4*H*-pyrido[2,3-*d*][1,3]oxazin-4-one (2i)[24]

Yield: 89 mg (40%); yellow needles; mp 130–131 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.53 (d, *J* = 8.04 Hz, 1 H), 8.32 (d, *J* = 7.6 Hz, 2 H), 7.71–7.67 (t, *J* = 7.2 Hz, 1 H), 7.60–7.56 (t, *J* = 7.6 Hz, 2 H), 7.27–7.24 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.0 (CH), 165.5 (C), 161.9 (C), 158.6 (C), 135.2 (CH), 134.4 (CH), 131.4 (C), 130.3 (CH), 128.9 (CH), 132.8 (CH), 114.8 (C).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_8N_2O_2$: 225.06; found: 225.1.

6-Bromo-2-(4-*tert*-butylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2j)[1]

Yield: 215 mg (60%); colorless needles; mp 131–133 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 2 H), 7.88 (dd, *J* = 8.4 Hz, 1 H), 7.55–7.49 (m, 3 H), 1.35 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4 (C), 157.6 (C), 156.8 (C), 146.1 (C), 139.6 (CH), 131.0 (CH), 128.8 (CH), 128.2 (CH), 127.0 (CH), 125.8 (CH), 121.1 (CH), 118.3 (CH), 35.2 (CH), 31.1 (CH_3).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}BrNO_2$: 358.04; found: 358.4.

2-(*p*-Tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2k)[10]

Yield: 156 mg (66%); colorless needles; mp 144–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22–8.17 (m, 3 H), 8.81–8.77 (t, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 8 Hz, 1 H), 7.49–7.46 (t, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 2.42 (s, 3 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}NO_2$: 238.08; found: 238.12.

2-(4-Fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2l)[11]

Yield: 140 mg (58%); colorless needles; mp 124–125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32–8.28 (m, 2 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 7.82–7.79 (t, *J* = 8.0 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.51–7.48 (t, *J* = 7.6 Hz, 1 H), 7.19–7.15 (t, *J* = 8.4 Hz, 2 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8FNO_2$: 242.05; found: 242.08.

2-(4-Chlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2m)[11]

Yield: 167 mg (65%); colorless needles; mp 181–182 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.21 (m, 3 H), 7.83–7.79 (m, 1 H), 7.67 (d, *J* = 8.0Hz, 1 H), 7.53–7.45 (m, 3 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8ClNO_2$: 258.02; found: 258.05.

2-(4-Bromophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2n)[11]

Yield: 208 mg (69%); colorless needles; mp 179–180 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 7.6 Hz, 1 H), 8.16 (d, *J* = 8.0 Hz, 2 H), 7.83–7.19 (t, *J* = 6.8 Hz, 1 H), 7.67–7.62 (m, 3 H), 7.53–7.49 (t, *J* = 7.2 Hz, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_8BrNO_2$: 301.97; found: 302.00.

2-[4-(Trifluoromethyl)phenyl]-4*H*-benzo[*d*][1,3]oxazin-4-one (2o)[8]

Yield: 218 mg (75%); colorless needles; mp 90–91 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.4 Hz, 2 H), 8.25 (d, *J* = 8.0 Hz, 1 H), 7.86–7.82 (t, *J* = 8 Hz, 1 H), 7.76 (d, *J* = 8.4, 2 H), 7.71 (d, *J* = 8 Hz, 1 H), 7.56–7.53 (t, *J* = 7.6 Hz, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_8F_3NO_2$: 292.05; found: 292.09.

2-(1,1′-Biphenyl-4-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2p)[11]

Yield: 158 mg (53%); colorless needles; mp 138–139 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.4 Hz, 2 H), 8.23 (d, *J* = 7.6 Hz, 1 H), 7.84–7.80 (t, *J* = 8.0 Hz, 1 H), 7.73–7.64 (m, 5 H), 7.52–7.37 (m, 4 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{13}NO_2$: 300.09; found: 300.16.

2-(3-Methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2q)[11]

Yield: 157 mg (62%); colorless needles; mp 117–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.0 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 7.83–7.80 (m, 2 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.52–7.48 (t, *J* = 7.6 Hz, 1 H), 7.41–7.37 (t, *J* = 8.0 Hz, 1 H), 7.11–7.09 (dd, *J* = 0.2, 6.4 Hz, 1 H), 3.89 (s, 3 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}NO_3$: 254.07; found: 254.09.

2-(3,4-Dimethylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2r)[11]

Yield: 161 mg (64%); colorless needles; mp 144–145 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.12 (d, *J* = 7.6 Hz, 1 H), 7.94–7.88 (m, 3 H), 7.68 (d, *J* = 8 Hz, 1 H), 7.60–7.56 (t, *J* = 7.6 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 1 H), 2.30 (s, 3 H), 2.29 (s, 3 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{13}NO_2$: 252.09; found: 252.11.

2-(4-Pyridyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2s)[11]

Yield: 112 mg (50%); white solid; mp 161–162 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 5.2 Hz, 2 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 8.11 (d, *J* = 5.6 Hz, 2 H), 7.87–7.83 (m, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.59–7.55 (t, *J* = 7.6 Hz, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_8N_2O_2$: 225.06; found: 225.1.

2-(3-Pyridyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (2t)[25]

Yield: 143 mg (64%); white solid; mp 129–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (s, 1 H), 8.77 (d, *J* = 7.6 Hz, 1 H), 8.53 (d, *J* = 7.6 Hz, 1 H), 8.24 (d, *J* = 8.0 Hz, 1 H), 7.85–7.81 (t, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.55–7.51 (t, *J* = 7.6 Hz, 1 H), 7.45–7.42 (dd, *J* = 8.0, 4.8 Hz, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_8N_2O_2$: 225.06; found: 225.09.

2-Phenyl-3*H*-indol-3-one (3a)[11]

Yield: 17 mg (8%); red solid; mp 96–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 7.6 Hz, 2 H), 7.54–7.45 (m, 5 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.26 (t, *J* = 7.6 Hz, 1 H).

ESI-MS: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_9NO$: 208.07; found: 208.05.

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Supporting Information

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