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Note

Tandem C-O and C-N bonds Formation Through O-Arylation and [3,3]-Rearrangement by Diaryliodonium Salts: Synthesis of N-Aryl Benzo[1,2,3]triazin-4(1H)-one Derivatives

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Tandem C−O and C−N bonds Formation Through *O*-Arylation and [3,3]-Rearrangement by Diaryliodonium Salts: Synthesis of *N*-Aryl Benzo[1,2,3]triazin-4(1H)-one Derivatives

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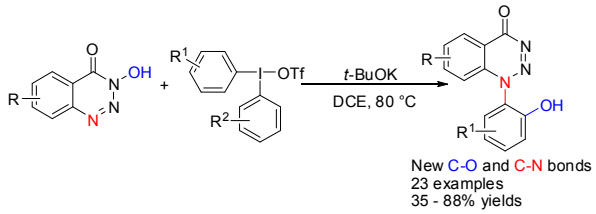


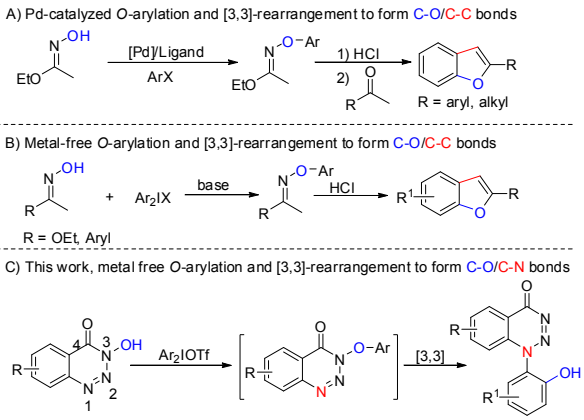
ABSTRACT: Metal-free *O*-arylation and [3, 3]-rearrangement have been showed as an efficient strategy to construct new C−O and C−N bonds in one-pot reaction. The method was used to prepare *N*-aryl benzo[1,2,3]triazin-4(1H)-one derivatives in good yields from *N*-hydroxy benzo[1,2,3]triazin-4(3H)-one and diaryliodonium salts. The reaction was tolerated a variety of sensitive functional groups such as iodine, nitro, ester, and aldehyde groups. A rational mechanism was proposed based on the experimental results and the reaction was easily up to gram scale.

[3,3]-Rearrangement reactions, as features in the chemistry field which could build surprising and unexpected structures, have attracted much attentions for chemists.[1] Many compounds that are difficult to synthesize by traditional methods could be obtained easily by [3,3]-rearrangement.[2] The rearrangement of N−O bond compounds

was one of the most important strategies to construct C−C or C−heteroatom bonds in organic synthesis due to its efficient access to diverse scaffolds,[3] such as 2-amino-2'-hydroxy-1,1'-biaryl derivatives,[4] polysubstituted furans,[5] pyrroles,[6] isoxazolines,[7] or related functional compounds.[8] In recent years, arylation of N−O bond combined with [3,3]-rearrangement have been demonstrated useful strategy in organic synthesis because its fast construction of complex molecules.[9] In 2010, Buchwald developed a Pd-catalyzed *O*-arylation of ethyl acetohydroximate with aryl chlorides, bromides, and iodides to prepare *O*-arylhydroxyamines and further condensation with ketones to construct benzofurans by [3,3]-rearrangement (Scheme 1A).[9a] To overcome the shortcomings by transition metal catalysis, such as harsh conditions, requirement of complicated ligands, and tolerance of sensitive functional groups, the metal-free strategy has been paid much attentions in the arylation process.[10, 11] Diaryliodonium salts have been utilized extensively as versatile arylation agents for a variety of nucleophiles in transition-metal free conditions due to its easy preparation, high reactivity and selectivity.[12, 13] Very recently, Kürti and Olofsson independently developed metal-free *O*-arylation of oximes by diaryliodonium salts as accesses to *O*-arylhydroxylamines and synthesis of benzofuran scaffolds *via* further sequence of [3,3]-rearrangement (Scheme 1B).[11] Although the metal-free *O*-arylation of N−O bond to proceed [3,3]-rearrangement have been studied, as we known, only new C−O and C−C bond was formed in the process. We envisioned that *O*-arylation of *N*-hydroxybenzo[1,2,3]triazin-4(3H)-one with diaryliodonium salts and sequence of [3,3]-rearrangement on the *N*-atom would produce new C−O and C−N bonds in

one-pot reaction and provide the *N*-aryl benzo[1,2,3]triazin-4(1H)-one easily (Scheme 1C).[14]

Benzo[1,2,3]triazin-4-one derivatives are not only as important heterocyclic scaffolds in pharmaceutical and medicinal chemistry,[15] but also served as important organic intermediate.[16] However, *N*-aryl benzo[1,2,3]triazin-4(1H)-one derivatives were rarely studied before due to its synthetic challenge.[17] Herein, we report a simple and mild method to construct C−O/C−N bonds in one-pot reaction of *O*-arylation and [3,3]-rearrangement. It would allow more facile to study the reactivities and applications of these compounds.

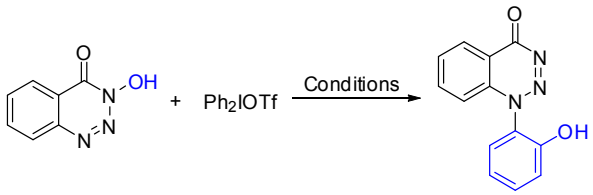


Scheme 1. Strategies of *O*-arylation and [3,3]-rearrangement process.

Initially, we ran the reaction of *N*-hydroxybenzo[1,2,3]triazin-4(3H)-one **1a** and diphenyliodonium triflate **2a** with *t*-BuOK in DMSO at 80 ˚C for 18 h. To our surprise, no *O*-arylation product was observed and only *N*-aryl benzo[1,2,3]triazin-4(1H)-one **3a** was observed in 38% yield (Table 1, entry 1). From product **3a**, it showed that new C-O bond and C-N bond were formed in the process. This observation inspired us to develop an efficient method to construct new C−O and C−N bond to prepare *N*-aryl benzo[1,2,3]triazin-4(1H)-one. As illustrated in Table 1, the screening of solvents

showed that DCE (1, 2-dichloroethane) was the best solvent for this transformation (Table 1, entries 1-8). The choice of base had great effect on the reaction (Table 1, entries 8-12). Interestingly, product **3a** was obtained in high yield with pyridine (Table 1, entry 13). The yield of product **3a** decreased obviously either the temperature was lower or higher (Table 1, entry 8 *vs* entries 14-17). No desired product **3a** was observed and only substrate **1a** was recovered in the absence of base (Table 1, entry 18). Product **3a** was very stable and not discomposed even at 140 ˚C for 24 h.[18]

Table 1. Optimization of reaction [a]



1a **2a** **3a**

entry	base	solvent	T (˚C)	**3a** %[b]
1	*t*-BuOK	DMSO	80	38
2	*t*-BuOK	DMF	80	56
3	*t*-BuOK	MeCN	80	76
4	*t*-BuOK	MeOH	80	27
5	*t*-BuOK	THF	80	59
6	*t*-BuOK	Dioxane	80	78
7	*t*-BuOK	Toluene	80	75
8	*t*-BuOK	DCE	80	88
9	*t*-BuONa	DCE	80	26
10	NaH	DCE	80	82
11	KOH	DCE	80	55
12	Cs_2CO_3	DCE	80	50
13	Pyridine	DCE	80	85
14	*t*-BuOK	DCE	25	0[c]
15	*t*-BuOK	DCE	50	20
16	*t*-BuOK	DCE	100	71
17	*t*-BuOK	DCE	120	67

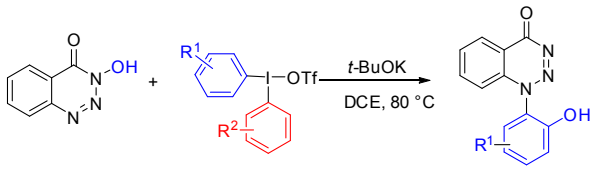
18	-	DCE	80	0

[a] Reaction conditions: **1a** (0.5 mmol), Ph_2IOTf (0.75 mmol, 1.5 equiv), base (0.75 mmol, 1.5 equiv), solvent (5 mL), 18-24 h; [b] Isolated yield; [c] *O*-arylation product **4a** was isolated in 25% yield.

To examine the scope of present protocols, a variety of diaryliodonium salts **2** were subjected to the optimal conditions. As shown in Table 2, a series of desired product **3** were obtained from moderate to good yields. This method was suitable for both electron-rich and electron-deficient diaryliodonium salts **2**, either *para*-, *meta*-, or *ortho*-substituents on the iodonium salts. However, the *meta*-, or *ortho*-substituted diaryliodonium salts gave lower yields (Table 2, entries 7, 8 and 14) might due to the steric hindrance. To our delight, the regioselectivity of product **3g** and **3m** was high with only one isomer when the *meta*-substituted diaryliodonium salts **2g** and **2m** were used (Table 2, entries 7 and 14). When unsymmetric diaryliodonium salts were used, the reaction proceeded with high chemoselectivity and the more electron-deficient aryl moieties could be transferred to the desired products (Table 2, entries 9-16).[19] However, when the aryl moieties was presented with electron-withdrawing group, the reaction needed to run at 100 ˚C in order to get high yields (Table 2, entries, 7, 15 and 16). In particular, for diaryliodonium salt **2i**, the 4-PhO substituted aryl group was transferred to product **3i** as major isomer and 4-MeO substituted aryl moiety product **3b** was isolated in 10% yield only (Table 2, entry 10). This method was compatible with some important functional groups on the phenyl ring of the diaryliodonium salts, such as fluorine, chlorine, bromine, methoxy, nitro, ester, and aldehyde substituents,

which could be applied to further synthetic transformations easily.

Table 2. The Scope of diaryliodonium salts.[a]

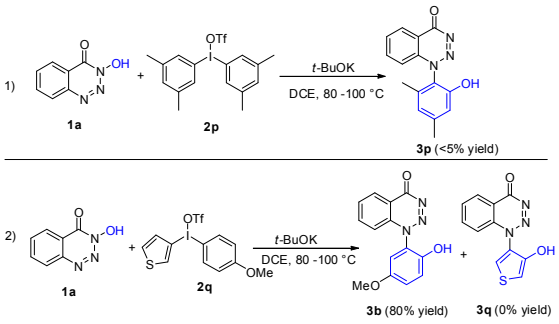


1a **2** **3**

entry	**2**	R^1	R^2	**3**	yield%[b]
1	**2a**	H	H	**3a**	88
2	**2b**	4-MeO	4-MeO	**3b**	84
3	**2c**	4-Me	4-Me	**3c**	86
4	**2d**	4-*t*-Bu	4-*t*-Bu	**3d**	78
5	**2e**	4-Cl	4-Cl	**3e**	85
6	**2f**	4-F	4-F	**3f**	85
7	**2g**	3-NO_2	3-NO_2	**3g**	59[c,d]
8	**2h**	2-Me	2-Me	**3h**	42
9	**2aa**	H	4-MeO	**3a**	78
10	**2i**	4-PhO	4-MeO	**3i**	75[e]
11	**2j**	4-Ph	4-MeO	**3j**	85
12	**3k**	4-*i*-Pr	4-MeO	**3k**	78
13	**3l**	4-Br	4-MeO	**3l**	68
14	**3m**	3-Br	4-MeO	**3m**	63[c]
15	**3n**	4-CO_2Me	H	**3n**	74[d]
16	**3o**	4-CHO	H	**3o**	46[d]

[a] Reaction conditions: **1a** (0.5 mmol), iodonium salts **2** (0.75 mmol, 1.5 equiv), *t*-BuOK (0.75 mmol, 1.5 equiv), DCE (5 mL), 80 ˚C, 18-24 h; [b] Isolated yield; [c] regioselectivity for [3,3]-rearrangement step, > 20:1, only one isomer; [d] ran at 100 ˚C; [e] Product **3b** was also isolated in 10% yield.

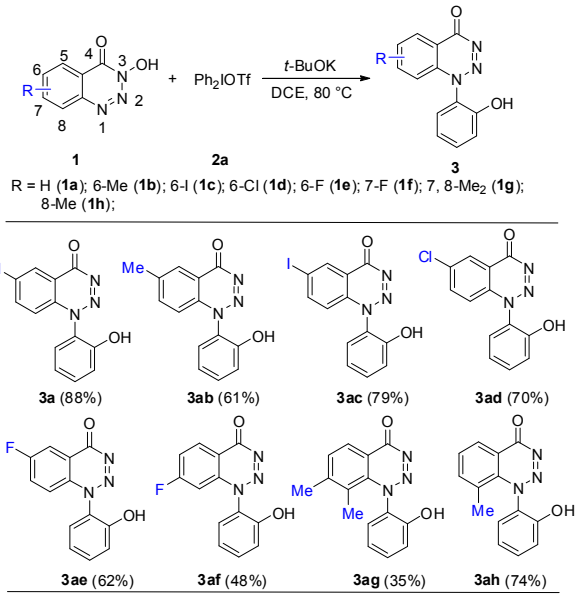
When substrate **1a** reacted with diaryliodonium salts **2p**, only <5% yield of product **3p** was observed perhaps due to steric hindrance (Scheme 2-1). While substrate **1a** was treated with diaryliodonium salts **2q**, product **3b** was obtained in 80% yield and no product **3q** was observed (Scheme 2-2).



Scheme 2. No desired products for two diaryliodonium salts **2p** and **2q.**

Subsequently, the scope of 3-hydroxy benzo[1,2,3]triazin-4(3H)-one **1** was tested to examine its effect on the formation of desired products **3**. As shown in Table 3, various of 3-hydroxy benzo[1,2,3]triazin-4(3H)-ones **1** was tolerated different substituted groups either 6, 7, or 8-position on the aryl ring, such as methyl, fluorine, chlorine and iodine (**3ab-3ah**). Product **3** was obtained from moderate to good yields. However, when the substituted groups were presented in 7-position of aryl ring, the yields decreased obviously (**3af** and **3ag**).

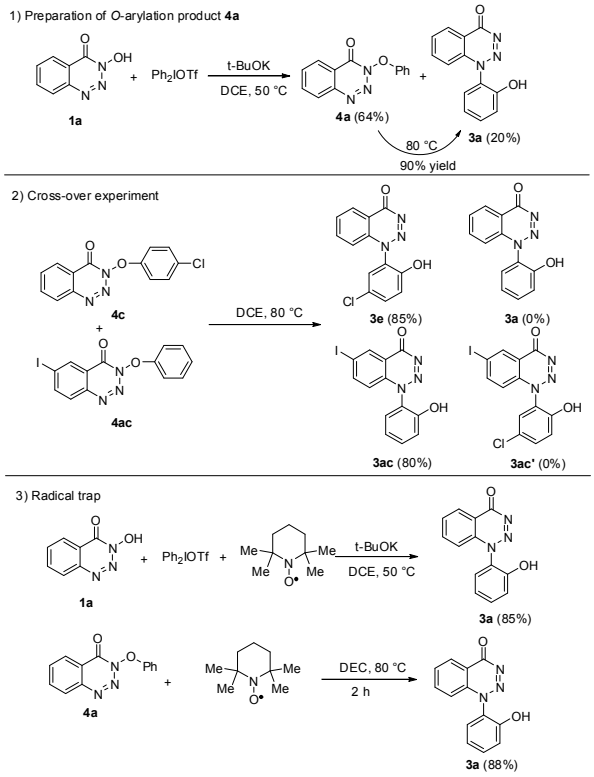
Table 3. The scope of 3-hydroxybenzo[1,2,3]triazin-4(3H)-one[a,b]



[a] Reaction conditions: **1** (0.5 mmol), Ph_2IOTf (0.75 mmol, 1.5 equiv), *t*-BuOK (0.75

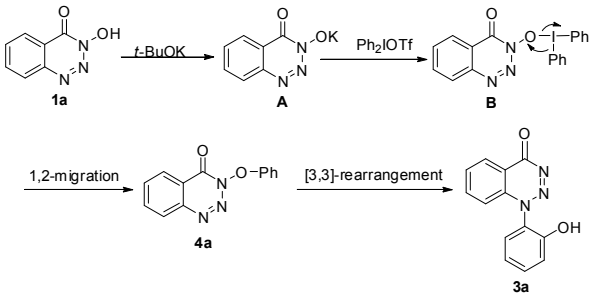
mmol, 1.5 equiv), DCE (5 mL), 80 ˚C, 18-24 h; [b] Isolated yield.

The *O*-arylation intermediate **4a** was isolated when the reaction was run at 50 ˚C. Intermediate **4a** could be converted into **3a** in 90% yield at 80 ˚C for 2 h, as illustrated in Scheme 3-1. To have a better understanding of the [3,3]-rearrangement steps, we tested two other product-based mechanistic experiments. As shown in Scheme 3-2, no crossover products were observed when the mixture of **4c** and **4ac** was run at 80 ˚C for 3 h. This result suggests that the [3,3]-rearrangement might be an intramolecular process. When radical trap TEMPO (2.0 equiv) was added in the optimal condition or heated with *O*-arylation intermediate **4a**, analogue yield of **3a** was obtained (Scheme 3-3), which demonstrates that the N-O bond cleavage might not proceed in radical process.



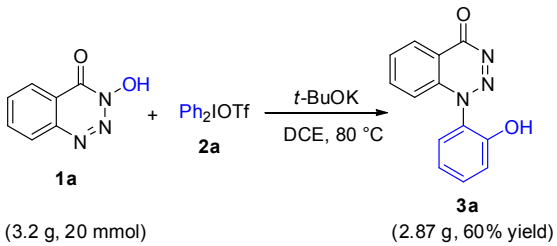
Scheme 3. Mechanism studies

Based on the above experimental results, a proposed mechanism for synthesis of product **3a** from substrate **1a** with diaryliodonium **s**alt **2a** is illustrated in Scheme 4. Deprotonation of substrate **1a** gives intermediate **A**.[20] Int-**A** goes through a substitution to form iodonium salt **B** which proceeds a 1,2-phenyl migration to provide *O*-arylation product **4a**,[19,21] then **4a** undergoes [3,3]-rearrangement and hydrogen migration to give product **3a**. [22]



Scheme 4 Proposed mechanism

In order to show the usefulness of this new transformation, gram scale reaction was performed in the optimal condition (Scheme 5). When 3.2 g (20 mmol) of substrate **1a** reacted with diphenyliodonium salt **2a**, product **3a** was obtained with 2.87 g in 60% yield, which would allow these compounds to be studied more easily for their reactivity and further applications.



Scheme 5. Gram scale reaction**.**

In summary, we have shown that *N*-aryl benzo[1,2,3]triazin-4(1H)-one derivatives can be prepared in good yields *via* a simple and mild one-pot reaction of *O*-arylation

of 3-hydroxy benzo[1,2,3]triazin-4(3H)-one with diaryliodonium salts and sequence of [3,3]-rearrangement. The reaction was tolerated not only a variety of electron-rich or electron-deficient substituents on diaryliodonium salts but also sensitive functional groups such as halides, nitro, ester, aldehyde. The mechanism studies showed that the cleavage of N−O bond might be an intramolecular process *via* [3,3]-rearrangement. The reaction was easily up to gram scale. The feature of present protocol was that new C−O and C−N bonds were formed by *O*-arylation and [3,3]-rearrangement in one-pot reaction under metal-free, mild and simple conditions.

EXPERIMENTAL SECTION

General Methods. All reactions were performed under an atmosphere of air. Commercially available reagents were used without further purification. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on 400, 500, or 600 MHz instrument with TMS as the internal standard. NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz (Hz), and integration. IR spectra were recorded on FT-IR spectrometer, and only major peaks are reported in cm^{-1}. HRMS were measured in ESI mode and the mass analyzer of the HRMS was TOF. Flash column chromatography was performed on silica gel (300-400 mesh).

General procedure for preparing *N*-aryl benzo[1,2,3]triazin-4(1H)-ones 3: A Schlenk tube, open to air, was charged with **1** (0.5 mmol), and DCE (5 mL). *t*-BuOK (0.75 mmol, 1.5 equiv) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 5 min. Then, diaryliodonium salts **2**

(0.75 mmol, 1.5 equiv) was added in one portion. The reaction was stirred at 80 ˚C or 100 ˚C and monitored by TLC until **1** was consumed completely (18-24 h). At this time, the DCE was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel) using gradient eluent (ethyl acetate/petroleum ether = 1/10 to 1/1) to provide product **3** as brown solid.

1-(2-Hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3a), 0.105 g, 88% yield, brown solid, mp: 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.30 (s, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.98 (t, J = 7.2 Hz, 1H), 7.90 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 153.5, 145.1, 135.0, 134.2, 134.0, 129.4, 127.0, 125.7, 123.1, 120.4, 120.0, 118.5; IR (thin film) 3425, 3064, 1673, 1606, 1473, 1259, 754, 671 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{10}N_3O_2$ $(M+H)^+$ 240.0773, found 240.0768.

1-(2-Hydroxy-5-methoxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3b), 0.113 g, 84% yield, brown solid, mp: 120-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.94 (s, 1H), 8.40 (d, J = 7.5 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.97−7.94 (m, 2H), 7.89 (t, J = 7.5 Hz, 1H), 7.12 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 152.9, 148.1, 145.2, 135.0, 133.9, 128.9, 126.8, 125.8, 122.8, 121.3, 118.5, 105.8, 56.1; IR (thin film) 3559, 3069, 2931, 1662, 1632, 1498, 1261, 771 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}N_3O_3$ $(M-H)^-$ 268.0722, found 268.0716.

1-(2-Hydroxy-5-methylphenyl)benzo[1,2,3]triazin-4(1H)-one (3c), 0.108 g, 86%

yield, brown solid, mp: 144-145 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.04 (s, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.97−7.94 (m, 1H), 7.89 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 151.4, 145.2, 135.3, 134.9, 133.8, 129.7, 129.1, 126.8, 125.8, 122.8, 120.2, 118.5, 20.5; IR (thin film) 3440, 3074, 2919, 1663, 1596, 1500, 1267, 780 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}N_3O_2$ $(M-H)^-$ 252.0773, found 252.0767.

1-(5-tert-Butyl-2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3d), 0.115 g, 78% yield, brown solid, mp: 164-165 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.06 (s, 1H), 8.44 (d, J = 1.8 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.97 (t, J = 7.2 Hz, 1H), 7.88 (t, J = 7.2 Hz, 1H), 7.54 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 151.3, 145.3, 143.4, 135.0, 133.9, 131.9, 128.9, 127.0, 125.8, 120.1, 119.4, 118.5, 34.4, 31.3; IR (thin film) 3442, 3069, 2962, 1670, 1505, 1462, 1266, 774 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}N_3O_2$ $(M-H)^-$ 294.1243, found 294.1236.

1-(5-Chloro-2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3e), 0.116 g, 85% yield, brown solid, mp: 189-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.37 (s, 1H), 8.52 (d, J = 2.0 Hz, 1H), 8.41 (d, J = 7.6 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.02−7.98 (m, 1H), 7.94−7.90 (m, 1H), 7.46 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 152.3, 145.0, 135.3, 134.5, 134.2, 129.3, 127.2, 125.9, 124.9, 122.6, 121.9, 118.7; IR (thin film) 3439, 3064, 1644, 1606, 1475, 1243, 773, 679 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_9N_3O_2Cl$ $(M+H)^+$ 274.0383,

found 274.0380.

1-(5-Fluoro-2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3f), 0.109 g, 85% yield, brown solid, mp: 173-174 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.17 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.26 (dd, J = 9.5 Hz, 2.5 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 8.00−7.97 (m, 1H), 7.93 (t, J = 7.5 Hz, 1H), 7.24−7.23 (m, 1H), 7.19−7.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8, 156.4 (d, J = 239.0 Hz), 150.1, 145.1, 135.2, 134.4, 127.1, 125.9, 122.0 (d, J = 24.0 Hz), 121.7, 121.6, 118.7, 109.5 (d, J = 28.0 Hz); IR (thin film) 3429, 3080, 1679, 1598, 1498, 1247, 771, 676 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_9N_3O_2F$ $(M+H)^+$ 258.0679, found 258.0670.

1-(2-Hydroxy-4-nitrophenyl)benzo[1,2,3]triazin-4(1H)-one (3g), 0.083 g, 59% yield, brown solid, mp: 248-249 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.69 (s, 1H), 8.72 (d, J = 9.6 Hz, 1H), 8.44 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.06−8.03 (m, 2H), 7.99 (t, J = 7.2 Hz, 1H), 7.88 (dd, J = 9.0 Hz, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 154.1, 150.6, 145.0, 135.6, 135.3, 132.9, 127.5, 126.1, 124.7, 119.0, 116.3, 114.2; IR (thin film) 3430, 3066, 1646, 1573, 1524, 1464, 1248, 775 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_4O_4$ $(M-H)^-$ 283.0468, found 283.0467.

1-(2-Hydroxy-3-methylphenyl)benzo[1,2,3]triazin-4(1H)-one (3h), 0.053 g, 42% yield, brown solid, mp: 159-160 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.54 (s, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.95−7.93 (m, 1H), 7.87 (t, J = 7.2 Hz, 1H), 7.34 (d, J = 6.6 Hz, 1H), 6.92−6.90 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 152.0, 145.3, 135.0, 134.9, 133.9, 129.7, 129.3, 126.9, 125.8, 120.8, 119.1, 118.5, 16.4; IR (thin film) 3428, 3075, 2923, 1682,

1599, 1467, 1254, 770 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}N_3O_2$ $(M-H)^-$ 252.0773, found 252.0767.

1-(2-Hydroxy-5-phenoxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3i), 0.124 g, 75% yield, brown solid, mp: 162-163 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 12.18 (s, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 2.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.95 (t, J = 7.2 Hz, 1H), 7.89 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.8 Hz, 2H), 7.22−7.17 (m, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.0, 157.6, 150.0, 149.3, 145.1, 135.1, 134.2, 129.9, 129.8, 127.2, 126.5, 125.8, 123.3, 121.6, 118.6, 117.8, 113.7; IR (thin film) 3432, 3061, 1734, 1596, 1484, 1210, 771, 680 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{12}N_3O_3$ $(M-H)^-$ 330.0879, found 330.0871.

1-(4-Hydroxybiphenyl-3-yl)benzo[1,2,3]triazin-4(1H)-one (3j), 0.134 g, 85% yield, brown solid, mp: 194-195 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 12.32 (s, 1H), 8.67 (d, J = 1.8 Hz, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.97−7.94 (m, 1H), 7.88−7.86 (m, 1H), 7.71 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 152.9, 145.2, 139.2, 135.1, 134.1, 133.5, 133.0, 129.5, 128.9, 127.5, 127.1, 126.7, 125.8, 121.3, 121.0, 118.6; IR (thin film) 3434, 3035, 1673, 1600, 1480, 1294, 761 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{12}N_3O_2$ $(M-H)^-$ 314.0930, found 314.0916.

1-(2-Hydroxy-5-isopropylphenyl)benzo[1,2,3]triazin-4(1H)-one (3k), 0.109 g, 78% yield, brown solid, mp: 170-171 °C. ^1H NMR (600 MHz, DMSO-d_6): δ 10.43 (s, 1H),

8.23 (d, J = 8.4 Hz, 1H), 8.10−8.05 (m, 2H), 8.00−7.98 (m, 1H), 7.61 (d, J = 1.8 Hz, 1H), 7.36−7.35 (m, 1H), 7.07 (d, J = 8.4 Hz, 1H), 2.93−2.89 (m, 1H), 1.22 (d, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.9, 148.8, 146.5, 139.9, 135.5, 135.1, 134.6, 130.3, 127.2, 125.1, 123.2, 118.2, 117.8, 32.9, 24.3; IR (thin film) 3433, 3043, 2956, 2868, 1674, 1571, 1460, 1266, 774 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}N_3O_2$ $(M-H)^-$ 280.1086, found 280.1080.

1-(5-Bromo-2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3l), 0.108 g, 68% yield, brown solid, mp: 201-202 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.37 (s, 1H), 8.66 (d, J = 2.0 Hz, 1H), 8.42 (d, J = 7.5 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 8.01 (t, J = 7.5 Hz, 1H), 7.93−7.90 (m, 1H), 7.58 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 7.11 (d, J = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8, 152.8, 145.1, 137.0, 135.2, 134.5, 129.8, 127.2, 125.9, 125.6, 122.3, 118.8, 111.6; IR (thin film) 3430, 3071, 1681, 1599, 1474, 1294, 772, 678 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2Br$ $(M-H)^-$ 315.9722, found 315.9713.

1-(4-Bromo-2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3m), 0.099 g, 63% yield, brown solid, mp: 166-167 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.49 (s, 1H), 8.39−8.35 (m, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.99−7.96 (m, 1H), 7.91 (t, J = 7.0 Hz, 1H), 7.37 (s, 1H), 7.17 (d, J = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8, 154.1, 145.1, 135.2, 134.3, 128.5, 128.4, 127.0, 125.9, 124.2, 123.5, 123.4, 118.7; IR (thin film) 3429, 3061, 1647, 1600, 1569, 1465, 1236, 766 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2Br$ $(M-H)^-$ 315.9722, found 315.9713.

Methyl 4-hydroxy-3-(4-oxobenzo[1,2,3]triazin-1(4H)-yl)benzoate (3n), 0.109 g, 74%

yield, brown solid, mp: 159-160 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.87 (s, 1H), 9.17 (d, J = 1.2 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 2H), 8.01 (t, J = 7.8 Hz, 1H), 7.93 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.4, 164.6, 157.1, 145.0, 135.2, 134.7, 134.5, 128.8, 127.3, 125.7, 125.4, 122.2, 120.6, 118.7, 52.3; IR (thin film) 3416, 3070, 2966, 1732, 1685, 1613, 1431, 293, 765 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{10}N_3O_4$ $(M-H)^-$ 296.0671, found 296.0675.

4-Hydroxy-3-(4-oxobenzo[1,2,3]triazin-1(4H)-yl)benzaldehyde (3o), 0.061 g, 46% yield, brown solid, mp: 183-184 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.12 (s, 1H), 9.99 (s, 1H), 9.05 (d, J = 1.2 Hz, 1H), 8.41 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.04−8.01 (m, 2H), 7.96 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 189.3, 164.5, 158.4, 144.9, 135.4, 134.7, 134.0, 129.3, 129.1, 127.3, 126.2, 125.9, 121.5, 118.8; IR (thin film) 3428, 3063, 2808, 2720, 1692, 1642, 1603, 1572, 1252, 771 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_8N_3O_3$ $(M-H)^-$ 266.0566, found 266.0556.

1-(2-Hydroxyphenyl)-6-methylbenzo[1,2,3]triazin-4(1H)-one (3ab), 0.077 g, 61% yield, brown solid, mp: 188-189 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.71 (s, 1H), 8.02 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 2.58 (s ,3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.6, 151.0, 146.0, 144.7, 136.9, 135.3, 132.3, 127.2, 125.8, 124.3, 119.6, 118.3, 117.8, 22.2; IR (thin film) 3427, 3031, 2871, 1665, 1609, 1482, 1293, 1256, 758 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}N_3O_2$

$(M-H)^-$ 252.0773, found 252.0767.

1-(2-Hydroxyphenyl)-6-iodobenzo[1,2,3]triazin-4(1H)-one (3ac), 0.144 g, 79% yield, brown solid, mp: 203-204 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.66 (s, 1H), 8.50 (d, J = 1.0 Hz, 1H), 8.37 (dd, J = 8.5 Hz, 1.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.48−7.45 (m, 1H), 7.13 (d, J = 8.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.4, 150.9, 145.6, 144.1, 135.5, 133.6, 132.5, 128.8, 125.8, 119.6, 118.8, 118.4, 102.4; IR (thin film) 3421, 3066, 1655, 1609, 1583, 1478, 1248, 756 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2I$ $(M-H)^-$ 363.9583, found 363.9575.

6-Chloro-1-(2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3ad), 0.095 g, 70% yield, brown solid, mp: 190-191 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.12 (s, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 1.2 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.89 (dd, J = 9.0 Hz, 1.8 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.9, 153.6, 143.6, 140.5, 135.9, 134.4, 129.4, 128.6, 125.3, 123.1, 120.6, 120.2, 119.4; IR (thin film) 3422, 3067, 1648, 1606, 1575, 1480, 1241, 759 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2Cl$ $(M-H)^-$ 272.0227, found 272.0221.

6-Fluoro-1-(2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3ae), 0.079 g, 62% yield, brown solid, mp: 153-154 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.14 (s, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.10 (dd, J = 8.4 Hz, 4.8 Hz, 1H), 8.01 (dd, J = 7.8 Hz, 2.4 Hz, 1H), 7.70−7.67 (m, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.04 (t, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2 (d, J = 259.0 Hz), 164.4 (d, J

= 3.3 Hz), 153.4, 142.0, 134.2, 130.4 (d, J = 8.8 Hz), 129.3, 124.5 (d, J = 25.0 Hz), 123.0, 120.5, 120.1, 111.0, 110.9; IR (thin film) 3428, 3050, 1654, 1612, 1575, 1477, 1246, 762 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2F$ $(M-H)^-$ 256.0523, found 256.0517.

7-Fluoro-1-(2-hydroxyphenyl)benzo[1,2,3]triazin-4(1H)-one (3af), 0.061 g, 48% yield, brown solid, mp: 182-183 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 12.15 (s, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.42−8.39 (m, 1H), 7.65-7.64 (m, 1H), 7.60−7.57 (m, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H). 7.05 (t, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1 (d, J = 255.0 Hz), 164.3, 153.7, 147.0 (d, J = 13.0 Hz), 134.6, 129.4, 128.9 (d, J = 9.9 Hz), 123.2, 123.1 (d, J = 24.0 Hz), 120.6, 120.2, 115.2, 111.8 (d, J = 22.9 Hz); IR (thin film) 3430, 3063, 1646, 1611, 1584, 1479, 1246, 763 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_9N_3O_2F$ $(M+H)^+$ 258.0679, found 258.0675.

1-(2-Hydroxyphenyl)-7,8-dimethylbenzo[1,2,3]triazin-4(1H)-one (3ag), 0.046 g, 35% yield, brown solid, mp: 193-194 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 12.42 (s, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 2.67 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.5, 153.5, 144.4, 143.7, 136.3, 134.7, 133.9, 129.8, 123.0, 122.6, 120.5, 120.0, 116.9, 20.7, 13.2; IR (thin film) 3433, 3035, 2924, 1659, 1602, 1479, 1286, 775 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}N_3O_2$ $(M-H)^-$ 266.0930, found 266.0923.

1-(2-Hydroxyphenyl)-8-methylbenzo[1,2,3]triazin-4(1H)-one (3ah), 0.093 g, 74% yield, brown solid, mp: 195-196°C. ^1H NMR (600 MHz, $CDCl_3$): δ 12.34 (s, 1H),

8.44 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.75−7.71 (m, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.4, 153.5, 143.9, 136.9, 135.7, 134.0, 133.8, 129.7, 123.3, 123.1, 120.5, 120.0, 118.8, 17.1; IR (thin film) 3427, 3058, 2923, 1660, 1591, 1478, 1291, 763 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}N_3O_2$ $(M-H)^-$ 252.0773, found 252.0765.

General procedure for Synthesis of *O*-arylation product 4: A Schlenk tube was charged with **1** (0.5 mmol) and DCE (5 mL). *t*-BuOK (0.75 mmol, 1.5 equiv) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 5 min. Then, diaryliodonium salts **2** (0.75 mmol, 1.5 equiv.) was added in one portion. The reaction was stirred at room temperature for 18-24 h. At this time, the DCE was removed under reduced pressure and crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel) using gradient eluents (ethyl acetate/petroleum ether 1/10 to 1/6) to provide product **4** as yellow solid.

3-Phenoxybenzo[1,2,3]triazin-4(3H)-one (4a), 0.076 g, 64% yield, yellow solid, mp: 114-115 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.34 (d, J = 8.0 Hz, 2H), 8.18 (t, J = 8.0 Hz, 1H), 8.01 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.21−7.17 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.9, 151.0, 144.3, 136.3, 133.7, 130.5, 129.2, 125.7, 124.9, 122.9, 114.2; IR (thin film) 3068, 1715, 1585, 1483, 1183, 1160, 751 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_8O_2N_3$ $(M-H)^-$ 238.0617, found 238.0609.

3-(4-Chlorophenoxy)benzo[1,2,3]triazin-4(3H)-one (4c), 0.069 g, 50% yield,

yellow solid, mp: 120-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.41 (d, J = 7.8 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.04 (t, J = 7.8 Hz, 1H), 7.87 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 9.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.3, 150.7, 144.2, 135.5, 132.8, 130.5, 129.8, 129.1, 125.8, 122.5, 117.1; IR (thin film) 3104, 1722, 1584, 1483, 1187, 1163, 772 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2Cl$ $(M-H)^-$ 272.0227, found 272.0222.

6-Iodo-3-phenoxybenzo[1,2,3]triazin-4(3H)-one (4ac), 0.049 g, 27% yield, yellow solid, mp: 145-146 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 149.3, 144.5, 143.3, 134.8, 130.2, 129.9, 125.3, 123.6, 115.3, 99.6; IR (thin film) 3054, 1716, 1586, 1487, 1185, 1163, 751 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_7N_3O_2I$ $(M-H)^-$ 363.9583, found 363.9575.

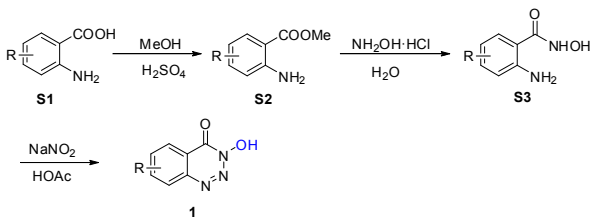
Thermal rearrangement of 4a to 3a: In Schlenk tube was charged with **4a** (0.060 g, 0.25 mmol) and DCE (2.5 mL). The mixture was stirred vigorously at 80 ˚C for 3 h. At this time, the DCE was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel) using gradient eluent (ethyl acetate/petroleum ether 1/10 to 1/2) to provide product **3a** as brown solid (0.054 mg, 90% yield). The ^{1}H and ^{13}C NMR spectra of **3a** were consistent with the data described above.

Cross-over experiment of mixture 4c and 4ac: In Schlenk tube was charged with **4c** (0.027 g, 0.10 mmol) and **4ac** (0.036 mg, 0.10 mmol), dissolved in DCE (2.5 mL).

The mixture was stirred vigorously at 80 ˚C for 3 h. At this time, the DCE was removed under reduced pressure and the crude product was obtained as brown solid (60 mg). ^{1}H and ^{13}C NMR spectra of the **3e** and **3ac** in the crude mixture was determined by contrast with pure **3e** and **3ac** which have been characterized above. The yields were determined by the ratio of **3e** (85% yield) and **3ac** (80% yield) from the spectrum. And no cross-over products **3a** and **3ac'** were observed in the crude NMR.

Gram scale reaction: In 250 mL one-neck round bottle flask was charged with **1a** (3.2 g, 20 mmol) and DCE (200 mL). *t*-BuOK (30 mmol, 1.5 equiv) was added in portions at room temperature. The mixture was stirred vigorously at room temperature for 5 min. Then, diaryliodonium salts **2a** (30 mmol, 1.5 equiv) was also added in portions. The reaction was stirred at 80˚C and monitored by TLC until **1a** was consumed completely (18 h). At this time, the DCE was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel) using gradient eluent (ethyl acetate/petroleum ether 1/10 to 1:1) to provide product **3a** as brown solid (2.87g, 60% yield). The ^{1}H and ^{13}C NMR spectra of **3a** were consistent with the data described above.

General procedure for synthesis of *N*-hydroxyl benzo[1,2,3]triazin-4(3H)-ones 1:



A mixture of *ortho*-amino benzoic acids **S1** (20 mmol), absolute methanol (20

mL), and concentrated H_2SO_4 (6 mL) was refluxed for 48 h. After cooling, the mixture was concentrated to about 10 mL and poured into 15 g of ice. The mixture was basified with concentrated aqueous ammonia to pH 8-9 with cooling in an ice bath, and white precipitate was collected by filtration. The filtrate was extracted with ether (4 × 50 mL) and the combined ether layer was washed with brine and dried with Na_2SO_4. Evaporation of the ether afforded a solid which was recrystallized from hexane to give **S2** as white solid and used directly into the next step.

Hydroxylamine hydrochloride (10 mmol) was added slowly with stirring and cooling to aqueous NaOH (10 mL, 1.0 M) solution. To the solution was added **S1** (10 mmol) in portions followed by MeOH (10 mL), and the mixture was stirred for 48 h. The solution was concentrated under reduced pressure and acidified with cooling to pH 5-6 with 25% of HCl. The white precipitate was filtered, washed with a small amount of cold water, and dried in vaccuo to give **S2** as a white solid which was pure enough to the next step.

To a suspension of **S2** in water (10 mL) was added concentrated HCl (4 mL) with stirring. While the mixture cooled in an ice bath, a cold solution of $NaNO_2$ (1.38 g, 20 mmol) in water was added dropwise and the temperature was maintained below 0 °C. The mixture was further stirring in the ice bath for another 30 min, and the solid was filtered, washed with a small amount of cold water, and dried to give *N*-hydroxyl benzo[1,2,3]triazin-4(3H)-one **1** as a light brown solid.

The substrates **1a-c** have been reported before and their spectra data matched literature values: **1a-c** [23]

3-Hydroxy-6-methylbenzo[1,2,3]triazin-4(3H)-one (1b), 2.86 g, 80% yield, brown solid, mp: 215-216 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.07 (s, 1H), 7.99 (s, 1H), 7.83 (s, 1H) (N-OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, DMSO-d_6): δ 151.5, 143.9, 142.7, 136.9, 128.5, 124.3, 121.6, 21.8; IR (thin film) 3394, 3069, 2963, 1669, 1644, 1480, 1223, 840, 698 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_8H_6N_3O_2$ $(M-H)^-$ 176.0460, found 176.0461.

3-Hydroxy-6-iodobenzo[1,2,3]triazin-4(3H)-one (1c), 4.32 g, 75% yield, brown solid, mp: 194-195 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.55 (s, 1H), 8.37 (d, J = 4.5 Hz, 1H), 7.96 (d, J = 5.0 Hz, 1H) (N-OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, DMSO-d_6): δ 150.0, 144.0, 143.3, 133.4, 130.1, 123.0, 100.4; IR (thin film) 3637, 3079, 1679, 1504, 1454, 1269, 837, 691 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_7H_3IN_3O_2$ $(M-H)^-$ 287.9270, found 287.9273.

6-Chloro-3-hydroxybenzo[1,2,3]triazin-4(3H)-one (1d), 1.1 g, 56% yield, brown solid, mp: > 300 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.22 (s, 2H), 8.09 (s, 1H) (N-OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, DMSO-d_6): δ 150.5, 142.9, 137.3, 135.6, 130.8, 124.2, 123.1; IR (thin film) 3409, 3094, 1714, 1637, 1563, 1459, 1189, 841, 609 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_7H_3ClN_3O_2$ $(M-H)^-$ 195.9914, found 195.9912.

6-Fluoro-3-hydroxybenzo[d][1,2,3]triazin-4(3H)-one (1e), 1.92 g, 53% yield, brown solid, mp: 196-197 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.33 (s, 1H), 7.98 (s, 2H) (N-OH resonance was too broad to be observed); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.6 (d, J = 252.4 Hz), 150.8, 141.6, 132.3 (d, J = 10.0 Hz), 124.3 (d, J

= 24.5 Hz), 124.0 (d, *J* = 10.0 Hz), 110.3 (d, *J* = 24.5 Hz); IR (thin film) 3647, 3091, 1676, 1650, 1579, 1480, 1236, 835, 732 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_7H_3FN_3O_2$ $(M-H)^-$ 180.0209, found 180.0208.

7-Fluoro-3-hydroxybenzo[1,2,3]triazin-4(3H)-one (1f), 0.959 g, 53% yield, brown solid, m.p: > 300 °C. ^1H NMR (600 MHz, DMSO-d_6): δ 13.04 (s, 1H), 8.34 (s, 1H), 8.07 (s, 1H), 7.80 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 166.6 (d, *J* = 252.0 Hz), 150.9, 146.1 (d, *J* = 12.0 Hz), 128.7 (d, *J* = 9.7 Hz), 121.8 (d, *J* = 22.9 Hz), 118.8, 113.7 (d, *J* = 22.9 Hz); IR (thin film) 3466, 3085, 1637, 1595, 1486, 1250, 828, 754 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_7H_3FN_3O_2$ $(M-H)^-$ 180.0209, found 180.0210.

3-Hydroxy-7,8-dimethylbenzo[1,2,3]triazin-4(3H)-one (1g), 1.1 g, 57% yield, brown solid, mp: 205-206 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 12.81 (s, 1H), 7.98 (s, 1H), 7.02 (s, 1H), 2.67 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 151.4, 144.5, 142.4, 135.8, 134.6, 121.9, 119.6, 20.5, 13.1; IR (thin film) 3434, 3077, 2926, 1638, 1561, 1442, 1251, 1080, 702 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_9H_8N_3O_2$ $(M-H)^-$190.0617, found 190.0608.

3-Hydroxy-8-methylbenzo[1,2,3]triazin-4(3H)-one (1h), 0.461 g, 26% yield, brown solid, mp: 250-251 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 12.89 (s, 1H), 8.06 (s, 1H), 7.86 (s, 1H), 7.64 (s, 1H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 151.4, 142.5, 137.7, 136.0, 132.6, 122.8, 121.7, 17.2; IR (thin film) 3416, 3079, 2996, 1666, 1641, 1468, 1239, 766 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_8H_6N_3O_2$ $(M-H)^-$ 176.0460, found 176.0451.

General procedure for synthesis of diaryliodonium salts 2

Aryl boronic acid (10 mmol, 1.0 equiv) and CH_2Cl_2 (40 mL) were combined in a dried round-bottom flask. The mixture was cooled to 0 °C for 5 min, BF_3•OEt_2 (1.12 mL, 1.10 equiv) was added, and the mixture was stirred for 10 min. A solution of 2-(diacetoxyiodo)arene (1.05 equiv) in CH_2Cl_2 (20 mL) was added slowly for 10-15 min and stirred for additional 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 °C again and TfOH (1.67 mL, 1.1 equiv) was dropped into the mixture. Then, the mixture was stirred for 10 min at 0 °C and warmed to room temperature for additional 10 min. At this time, the solvent was removed under reduced pressure and the residual ran through a short silica gel column (about 5 cm) with 5% of MeOH in CH_2Cl_2 quickly. The mixture was concentrated under vacuum and Et_2O (100 mL) was added to the residual to form a white solid. Filtrated and obtained the diaryliodonium salts **2** as white solid.

Some diaryliodonium salts are reported before and their spectra data matched literature values: **2a**, **c, o**[24], **2b**, **2d-f** and **2h**[25], **2g**[26], **2j**[27], **2l**[28], **2m** and **2o**[29], **2p**[30].

(4-Methoxyphenyl)(4-phenoxyphenyl)iodonium triflate (2i), 3.2 g, 58% yield, white solid, mp: 120-121 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.18 (d, J = 8.5 Hz, 2H), 8.16 (d, J = 8.5 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.5 Hz, 1H), 7.09−7.04 (m, 6H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.4, 160.6, 155.1, 137.6, 137.5, 130.9, 125.5, 122.4 (q, J = 319.7 Hz), 120.8, 120.5, 117.9, 108.9, 106.2, 56.1; IR (thin film) 3083,2945, 2842, 1575, 1485, 1251, 1168, 829, 638 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{16}IO_2$ $(M-OTf)^+$ 403.0195, found 403.0194.

(4-Isopropylphenyl)(4-methoxyphenyl)iodonium triflate (2k), 2.1 g, 42% yield, white solid, mp: 164-165 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.17 (d, J = 9.0 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 3.79 (s, 3H), 2.92−2.90 (m, 1H), 1.16 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.4, 153.3, 137.6, 135.3, 130.2, 122.4 (q, J = 315.1 Hz), 117.9, 114.0, 105.8, 56.1, 33.7, 23.9; IR (thin film) 3086, 2966, 2847, 1577, 1486, 1250, 1167, 830, 639 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}OI$ $(M-OTf)^+$ 353.0402, found 353.0387.

(4-Methoxyphenyl)(thiophen-3-yl)iodonium triflate (2q), 2.7 g, 59% yield, white solid, mp: 125-126 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.57 (d, J = 6.5 Hz, 1H), 8.15 (d, J = 9.0 Hz, 2H), 7.79−7.77 (m, 1H), 7.67 (d, J = 4.5 Hz, 1H), 7.08 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.8, 136.9, 135.3, 131.4, 130.6, 121.9 (q, J = 320.6 Hz), 117.3, 106.2, 101.5, 55.6; IR (thin film) 3452, 3097, 2970, 2841, 1578, 1488, 1256, 823 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{11}H_{10}IOS$ $(M-OTf)^+$ 316.9497, found 316.9486.

ASSOCIATED CONTENT

Supporting Information

Spectra of compounds **3a-3o, 3ab-3ah, 4a, 4c, 4ac**, **1d-h**, **2i**, **2k**, and **2q**, this material is available free of charge via the Internet at http://pubs.acs.org.

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