

# METAL-FREE SP<sup>3</sup> C-H BOND OXIDATION AND FUNCTIONALIZATION OF $\alpha$ -BROMOKETONES TO QUINOXALINONE, BENZOXAZINONE, AND BENZOTHIAZINONE HETEROCYCLIC COMPOUNDS

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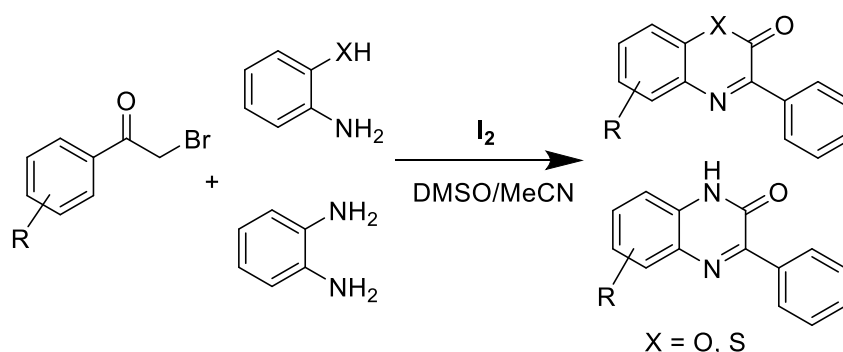
**Abstract** – A series of heterocyclic compounds (benzothiazinones, benzoxazinones and quinoxalinones) were efficiently synthesized in excellent yields via  $\alpha$ -bromoketones with *o*-substituted aniline (2-aminothiophenol, aryl-1,2-diamines and 2-aminophenol). This protocol accomplishes sp<sup>3</sup> C-H bond oxidation and functionalization in one-pot without any metal catalyst.

## INTRODUCTION

Heterocyclic derivatives are all important units which are frequently found in pharmaceuticals and other biologically active products,<sup>1</sup> among all the heterocyclic compounds, benzothiazinone, benzoxazinone and quinoxalinone compounds generally are used as antimicrobial, antithrombotic activities, antihistaminics, antipsychotics, antiemetics,<sup>2-7</sup> and as raw materials to synthesis enantiomerically pure heterocyclic compounds.<sup>8</sup> Benzothiazinone compounds are used as promising anticarcinogen.<sup>9</sup> Benzoxazinone derivatives are employed as singlet oxygen sensitizers duo to their intense fluorescence characteristics both in organic solutions and crystalline state.<sup>10</sup> Despite wide applications of this heterocycles, the synthetic routes have been rarely reported. Previously, the synthetic procedures for the preparation of oxazinone/thiazinone moieties employed the condensation of 2-aminophenol/2-aminothiophenol with glyoxal/benzil/benzoyl formate/1-phenylpropane-1,2-dione/phenacyl bromide using *m*-CPBA as oxidizing agent.<sup>11</sup> Recently, a new procedure was reported to gain quinoxalinone, benzoxazinone, and benzothiazinone heterocyclic compounds through two steps, first 2-oxo-2-arylacetyl bromides were synthesized by selenium dioxide

oxidation of  $\alpha$ -bromoketones, then 2-oxo-2-arylacetyl bromides react with aryl-1,2-diamines, 2-aminophenol or 2-aminothiophenol to give corresponding heterocyclic compounds.<sup>12</sup> Although various methods have been reported for constructing the heterocycles, metal oxides, microwave irradiation, and peroxide were needed and accompanied complex operations.

Herein, we report a convenient and efficient procedure for the synthesis of benzothiazinone, benzoxazinone and quinoxalinone heterocyclic compounds through oxidation and functionalization of  $\alpha$ -bromoketones with *o*-substituted aniline using I<sub>2</sub>/DMSO as oxidant. Compared with the conventional methods, this procedure is accomplished sp<sup>3</sup> C-H bond oxidation and functionalization in one-pot without using any metal catalyst (Scheme 1). Metal-free sp<sup>3</sup> C-H bond oxidation of  $\alpha$ -bromoketones and conversion was exhibited,<sup>13</sup> however sp<sup>3</sup> C-H bond oxidation of  $\alpha$ -bromoketones and subsequent reaction with *o*-substituted aniline to benzothiazinones, benzoxazinones and quinoxalinones has never been reported.



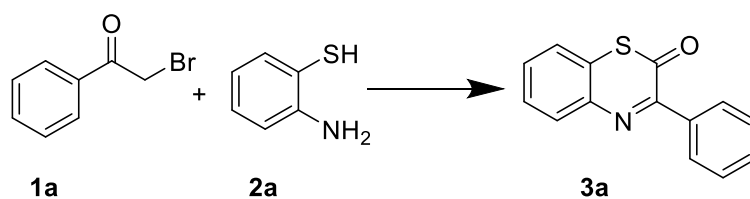
**Scheme 1.** Synthesis routes of heterocyclic compounds

## RESULTS AND DISCUSSION

2-Bromoacetophenone **1a** and 2-aminobenzenethiol **2a** are selected as template substrates to optimize the present sp<sup>3</sup> C-H bond oxidation and functionalization to construct 3-phenyl-2H-benzo[*b*][1,4]thiazin-2-one compound **3a**, and the results are compiled in Table 1. First, various additives such as the TBHP, *m*-CPBA, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, PhI(OAc)<sub>2</sub>, CuO and I<sub>2</sub> are screened under 120 °C (Table 1, entries 1-6). Preliminary screening shows that TBHP, *m*-CPBA, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, PhI(OAc)<sub>2</sub>, CuO cannot mediate the present reaction (Table 1, entries 1-5), and I<sub>2</sub> shows the highest efficiency among the examined additives. The reaction takes place smoothly to produce the corresponding compound **3a** in a 55% yield (Table 1, entry 6). The reaction is found to be sensitive to solvent (Table 1, entries 7-9), e.g. only trace **3a** is detected in DMF. To improve the yield of the reaction, the mixed solvents are used, and the compound **3a** is obtained in 78% yield in DMSO/DCE (Table 1, entry 10). Other mixed solvents are screened, and

DMSO/MeCN serve as the good solvents, 90% yield of **3a** is obtained (Table 1, entry 12). This transformation also depends on the reaction temperature, and the yield of **3a** dramatically decreases to 72% at 90 °C (Table 1, entry 13). Further increase the reaction temperature to 130 °C leads to no evident improvement in the yield (Table 1, entry 14). Thus, the optimal reaction conditions are emerged as described in Table 1, entry 12.

**Table 1.** Optimization of the reaction conditions<sup>a</sup>



Entry	Solvent	Additive	Yield of <b>3a</b> <sup>b</sup>
1	DMSO	TBHP	--
2	DMSO	<i>m</i> -CPMA	--
3	DMSO	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	--
4	DMSO	PhI(OAc) <sub>2</sub>	trace
5	DMSO	CuO	trace
6	DMSO	I <sub>2</sub>	55%
7	MeCN	I <sub>2</sub>	38%
8	DCE	I <sub>2</sub>	31%
9	DMF	I <sub>2</sub>	trace
10	DMSO/DCE	I <sub>2</sub>	78%
11	DMSO/DMF	I <sub>2</sub>	66%
12	DMSO/MeCN	I <sub>2</sub>	90%
13 <sup>c</sup>	DMSO/MeCN	I <sub>2</sub>	72%
14 <sup>d</sup>	DMSO/MeCN	I <sub>2</sub>	92%

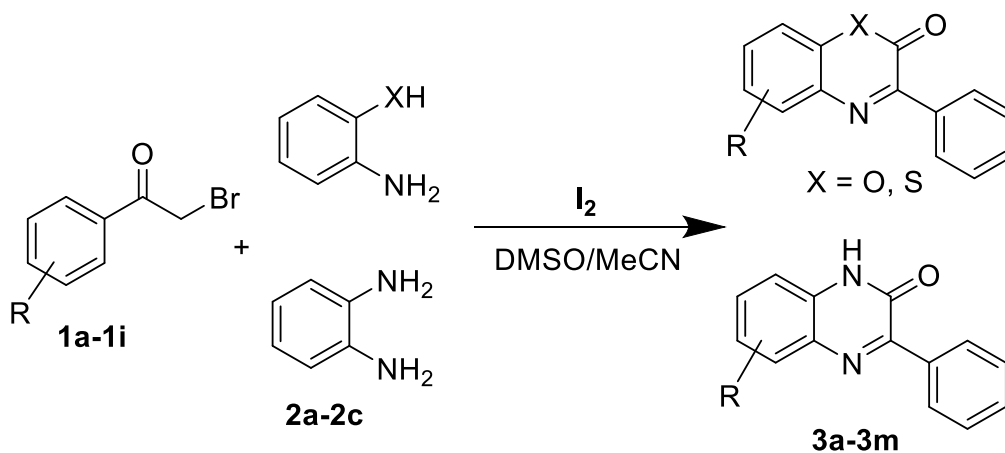
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.25 mmol), additive (0.4 mmol), solvent (2 mL) and mixed solvents (1:1) in a sealed glass tube (10 mL) at 120 °C, 12 h. <sup>b</sup>The separated yield. <sup>c</sup>90 °C. <sup>d</sup>130 °C.

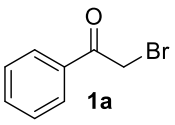
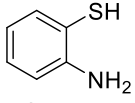
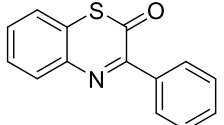
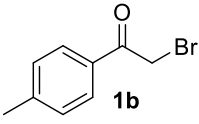
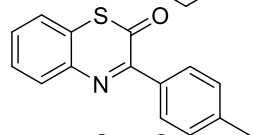
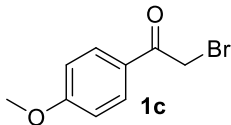
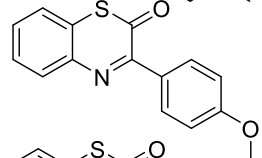
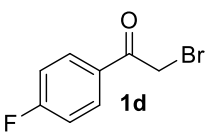
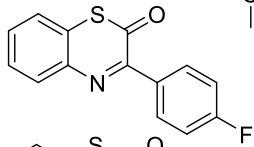
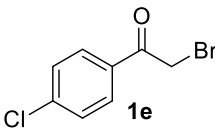
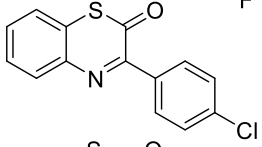
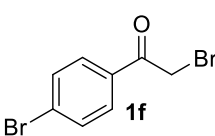
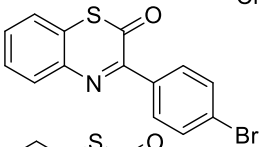
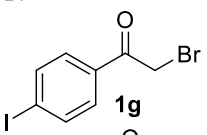
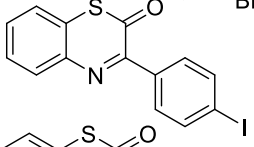
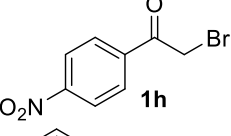
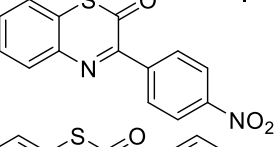
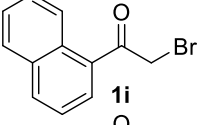
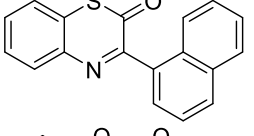
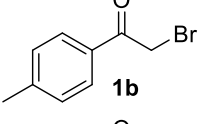
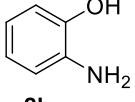
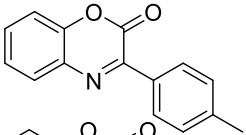
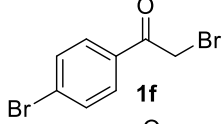
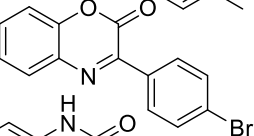
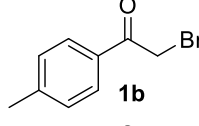
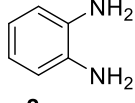
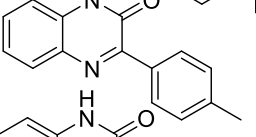
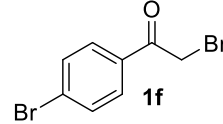
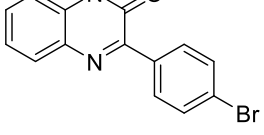
With optimized reaction conditions in hand, we investigated the generality of the oxidation and functionalization of sp<sup>3</sup> C-H bond to other substrates, and the results showed that the reaction is a general method for the preparation of benzothiazinones, benzoxazinones and quinoxalinones heterocyclic compounds (Table 2). 2-Aminobenzenethiol **2a** reacts readily with different kinds of 2-bromoacetophenone, bearing both electron-donating groups and electron-withdrawing groups on the

aromatic rings to give the corresponding benzothiazinone compounds (Table 2, entries 1-9). The results showed that the electronic and steric nature of the aromatic ketones was shown to have little influence on the reaction efficiency. 2-Aminobenzenethiol **2a** and electron-donating groups substituted 2-bromoacetophenone such as 2-bromo-1-(*p*-tolyl)ethan-1-one **1b** and 2-bromo-1-(4-methoxyphenyl)ethan-1-one **1c** were employed in this reaction to synthesize heterocycles derivatives **3b** and **3c** in excellent yields (Table 2, entries 2-3). The reaction shows wide functional-group tolerance, functional groups such as F (Table 2, entry 4), Cl (Table 2, entry 5), Br (Table 2, entry 6), I (Table 2, entry 7), NO<sub>2</sub> (Table 2, entry 8) are all compatible, and the corresponding heterocycles derivatives **3d-3h** are produced in good to excellent yields. 2-Bromo-1-(naphthalen-2-yl)ethan-1-one **1i** also undergo the present oxidation and functionalization reactions with **2a**, and the corresponding products **3i** is afforded in 79% yield.

In addition to 2-aminobenzenethiol, *o*-substituted anilines such as 2-aminophenol **2b** and *o*-phenylenediamine **2c**, also serve as efficient substrates under the current conditions and converted to the corresponding benzoxazinones and quinoxalinones heterocyclic compounds in 80%-88% yields (Table 2, entries 10-13). Electron-donating group methyl **1b** and electron-withdrawing group bromine **1f** attached to the  $\alpha$ -bromoketones react with 2-aminophenol **2b** to give the corresponding benzoxazinones **3j** and **3k** in 88% and 86% yields respectively (Table 2, entries 10-11). To our delight, quinoxalinone heterocyclic compounds are also efficiently synthesized under the present condition, the reaction of methyl or bromine substituted  $\alpha$ -bromoketones with *o*-phenylenediamine **2c** proceed smoothly to give the quinoxalinones heterocyclic compounds in 85% and 80% yields (Table 2, entries 12-13).

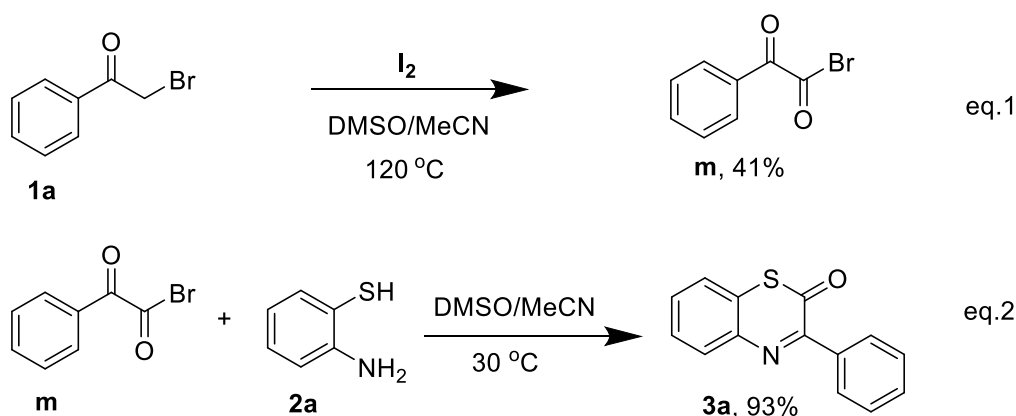
**Table 2.** Metal-free oxidation and functionalization of  $\alpha$ -bromoketones with *o*-substituted anilines for the synthesis of heterocycle compounds<sup>a</sup>



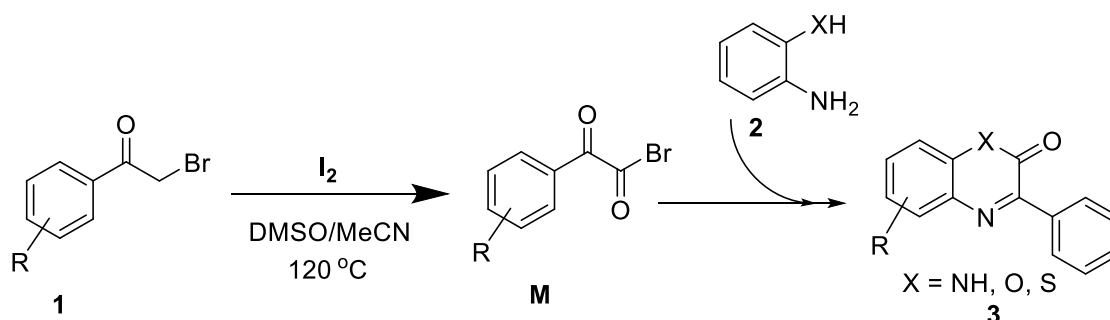
Entry	Substrate 1	Substrate 2	Product and Yield <sup>b</sup>
1	 <b>1a</b>	 <b>2a</b>	 <b>3a</b> , 88%
2	 <b>1b</b>	<b>2a</b>	 <b>3b</b> , 90%
3	 <b>1c</b>	<b>2a</b>	 <b>3c</b> , 85%
4	 <b>1d</b>	<b>2a</b>	 <b>3d</b> , 84%
5	 <b>1e</b>	<b>2a</b>	 <b>3e</b> , 92%
6	 <b>1f</b>	<b>2a</b>	 <b>3f</b> , 90%
7	 <b>1g</b>	<b>2a</b>	 <b>3g</b> , 80%
8	 <b>1h</b>	<b>2a</b>	 <b>3h</b> , 80%
9	 <b>1i</b>	<b>2a</b>	 <b>3i</b> , 79%
10	 <b>1b</b>	 <b>2b</b>	 <b>3j</b> , 88%
11	 <b>1f</b>	<b>2b</b>	 <b>3k</b> , 86%
12	 <b>1b</b>	 <b>2c</b>	 <b>3l</b> , 85%
13	 <b>1f</b>	<b>2c</b>	 <b>3m</b> , 80%

<sup>a</sup>Reaction conditions: **1a-1i** (0.2 mmol), **2a-2c** (0.25 mmol), I<sub>2</sub> (0.4 mmol), DMSO/MeCN (2 mL) in a sealed glass tube (25 mL) at 120 °C, 12 h. <sup>b</sup>Isolated yields.

The oxidation and functionalization of  $sp^3$  C-H bond reaction mechanism was also investigated. 2-Bromoacetophenone **1a** and 2 equivalents  $I_2$  were heated in DMSO/MeCN at 120 °C for 12 h, the corresponding 2-oxo-2-phenylacetyl bromide **m** was obtained in 41% yield (eq 1). When 2-oxo-2-phenylacetyl bromide **m** was used as a substrate, the product **3a** was obtained in 93% yield at 30 °C without any additive (eq. 2). Therefore, it is speculated that 2-oxo-2-phenylacetyl bromide **m** probably serves as efficient intermediate in the current oxidation and functionalization of  $sp^3$  C-H bond reaction system.



Based on our experimental results described above and the literatures,<sup>12-13</sup> a plausible reaction process for the present oxidation and functionalization of  $sp^3$  C-H bond is proposed, as shown in Scheme 2. In the  $I_2$ /DMSO system, the C-H bonds of  $\alpha$ -bromoketone **1** is first oxidized to form 2-oxo-2-phenylacetyl bromide **M**. Subsequently, the resulting 2-oxo-2-phenylacetyl bromide **M** is captured by *o*-substituted anilines **2** and undergoes dehydration and dehydrobromination reaction to produce heterocyclic compounds **3**.



**Scheme 2.** Plausible mechanism for  $sp^3$  C-H oxidative and functionalization to heterocyclic compounds

In summary, we have demonstrated an efficient metal-free oxidation and functionalization  $sp^3$  C-H bonds strategy to construct benzothiazinones, benzoxazinones and quinoxalinones heterocycle compounds via  $\alpha$ -bromoketones with *o*-substituted anilines. In the present system, metal-free  $sp^3$  C-H bond oxidation and

functionalization are achieved in one pot under the mild reaction conditions. This oxidation cyclization reaction provides an environmentally friendly protocol to heterocyclic compounds.

## EXPERIMENTAL

### General

All reagents were used without further purification. The reactions were monitored by GC and GC-MS. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz and 100 MHz respectively. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS result was recorded on GC-MS QP2010, and GC analysis was performed on GC 2010 plus. Melting point of compound was measured by digital display micromelting point meter (Gongyi Yuhua X-4). HRMS was tested at Hunan University (MAT95XP). 2-Bromoacetophenone **1** (0.2 mmol), *o*-substituted anilines **2** and solvents were purchased from Energy Chemical, Alfa, Aladdin.

### General procedure for the synthesis of heterocyclic compounds

2-Bromoacetophenone **1** (0.2 mmol), *o*-substituted anilines **2** (0.25 mmol), and iodine (0.4 mmol) were placed in a Schlenk tube (25 mL), and the mixture was stirred at 120 °C for 12 h, the reactions were monitored by GC and TLC. Then, the mixture was cooled to room temperature, washed with saturated NaCl solution. The crude product was extracted with EtOAc three times. The organic layer was dried over anhydrous  $\text{MgSO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with petroleum to afford the analytically pure products.

### 3-Phenyl-2*H*-benzo[*b*][1,4]thiazin-2-one (**3a**)<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (20:1) to afford the desired product in 88%, white solid, mp 110-112 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57 (q,  $J = 4.2$  Hz, 2H), 8.24 (d,  $J = 6.8$  Hz, 1H), 8.02 (d,  $J = 8.0$  Hz, 1H), 7.58-7.68 (m, 1H), 7.55-7.57 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ . 185.4, 167.1, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.6, 126.9, 125.8, 122.2. MS (EI),  $m/z = 239$ .

### 3-(*p*-Tolyl)-2*H*-benzo[*b*][1,4]thiazin-2-one (**3b**)<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (20:1) to afford the desired product in 90%, white solid, mp 109-111 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (d,  $J = 8.0$  Hz, 2H), 8.00 (d,  $J = 7.2$  Hz, 1H), 7.57 (d,  $J = 6.0$  Hz, 1H), 7.52-7.56 (m, 2H), 7.34 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ . 184.9, 167.5, 153.9, 145.1, 137.0, 132.4, 131.4, 129.3, 127.5, 126.9, 125.7, 122.2, 21.9. MS (EI),  $m/z = 253$ .

### **3-(4-Methoxyphenyl)-2H-benzo[*b*][1,4]thiazin-2-one (3c)<sup>12</sup>**

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 85%, white solid, mp 115-117 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.46 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 6.0 Hz, 1H), 7.52-7.56 (m, 2H), 7.34 (m, *J* = 8.0 Hz, 2H), 3.93 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ. 183.5, 167.9, 164.4, 153.9, 136.9, 133.9, 127.8, 127.4, 126.8, 125.6, 122.2, 113.9, 55.6. MS (EI), *m/z* = 269.

### **3-(4-Fluorophenyl)-2H-benzo[*b*][1,4]thiazin-2-one (3d)**

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 84%, white solid, mp 102-104 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.46 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.56-7.60 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ. 185.0, 167.3 (d, *J* = 16 Hz), 154.5, 137.7, 134.3, 132.6, 130.2, 128.5, 127.8, 126.5, 122.9. MS (EI), *m/z* = 257, HRMS (EI): calcd for C<sub>14</sub>H<sub>8</sub>FNOS: 257.0311, found: 257.0332.

### **3-(4-Chlorophenyl)-2H-benzo[*b*][1,4]thiazin-2-one (3e)**

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 92%, faint yellow solid, mp 112-114 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.57 (q, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.52-7.62 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ. 184.3, 166.8, 153.8, 137.1, 133.7, 132.8, 131.9, 129.6, 127.9, 127.1, 125.8, 122.2. MS (EI), *m/z* = 273, HRMS (EI): calcd for C<sub>14</sub>H<sub>8</sub>ClNOS: 273.0015, found: 273.0034.

### **3-(4-Bromophenyl)-2H-benzo[*b*][1,4]thiazin-2-one (3f)**

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 90%, faint yellow solid, mp 121-123 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.46 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.56-7.61 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 183.9, 166.8, 153.8, 140.6, 137.0, 133.2, 132.7, 128.9, 127.8, 127.1, 125.8, 122.2. MS (EI), *m/z* = 316, HRMS (EI): calcd for C<sub>14</sub>H<sub>8</sub>BrNOS: 316.9150, found: 316.9169.

### **3-(4-Iodophenyl)-2H-benzo[*b*][1,4]thiazin-2-one (3g)**

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 80%, faint yellow solid, mp 129-131 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.49 (d, *J* = 8.8 Hz, 2H), 8.26 (t, *J* = 8.8 Hz, 1H), 8.05 (q, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.59-7.75 (m, 2H); <sup>13</sup>C NMR (100



MHz, CDCl<sub>3</sub>):  $\delta$  184.3, 166.8, 153.8, 137.1, 133.7, 132.8, 131.9, 129.6, 127.9, 127.1, 125.8, 122.2. MS (EI),  $m/z$  = 364, HRMS (EI): calcd for C<sub>14</sub>H<sub>8</sub>INOS: 364.9371, found: 364.9390.

### **3-(4-Nitrophenyl)-2H-benzo[*b*][1,4]thiazin-2-one (3h)**<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 80%, white solid, mp 171-173 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.93 (d,  $J$  = 8.0 Hz, 2H), 8.27 (d,  $J$  = 7.6 Hz, 1H), 8.03 (q,  $J$  = 7.2 Hz, 1H), 7.57-7.62 (m, 2H), 7.79 (d,  $J$  = 8.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  184.4, 166.9, 153.9, 137.2, 133.8, 132.9, 132.0, 129.7, 127.9, 127.2, 125.9, 122.4. MS (EI),  $m/z$  = 284.

### **3-(Naphthalen-1-yl)-2H-benzo[*b*][1,4]thiazin-2-one (3i)**<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 79%, white solid, mp 162-165 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.26 (s,  $J$  = 8.0 Hz, 1H), 8.31-8.36 (m, 3H), 8.19 (d,  $J$  = 8.0 Hz, 1H), 8.12 (d,  $J$  = 8.0 Hz, 1H), 8.06 (d,  $J$  = 8.0 Hz, 1H), 7.68-7.76 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  185.3, 167.3, 153.8, 136.7, 135.8, 134.1, 132.3, 130.5, 129.9, 128.8, 128.6, 128.2, 127.9, 127.7, 126.0, 123.4. MS (EI),  $m/z$  = 289.

### **3-(*p*-Tolyl)-2H-benzo[*b*][1,4]oxazin-2-one (3j)**<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 88%, white solid, mp 113-115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (d,  $J$  = 8.4 Hz, 2H), 8.23 (t,  $J$  = 6.8 Hz, 1H), 8.02 (t,  $J$  = 7.2 Hz, 1H), 7.70 (d,  $J$  = 8.8 Hz, 2H), 7.56-7.61 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  184.2, 167.0, 154.0, 140.8, 137.3, 133.5, 132.9, 129.1, 128.0, 127.3, 126.0, 122.4. MS (EI),  $m/z$  = 237.

### **3-(4-Bromophenyl)-2H-benzo[*b*][1,4]oxazin-2-one (3k)**<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 86%, white solid, mp 158-160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.54 (d,  $J$  = 8.4 Hz, 2H), 8.08 (d,  $J$  = 8.8 Hz, 1H), 8.07 (t,  $J$  = 3.8 Hz, 1H), 7.59-7.64 (m, 2H), 7.34 (d,  $J$  = 8.0 Hz, 2H), 2.53 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  185.0, 167.6, 154.0, 145.2, 137.1, 132.5, 131.6, 129.4, 127.6, 127.0, 125.8, 122.3, 22.0. MS (EI),  $m/z$  = 300.

### **3-(*p*-Tolyl)quinoxalin-2(1H)-one (3l)**<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 85%, white solid, mp > 250 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  11.53 (s, 1H), 8.38 (d,  $J$  = 8.0 Hz, 2H),

8.15 (d,  $J = 7.2$  Hz, 1H), 7.90 (t,  $J = 7.6$  Hz, 1H), 7.43-7.50 (m, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.6, 168.1, 154.5, 145.7, 137.6, 133.0, 132.1, 129.9, 128.1, 127.5, 126.3, 122.822.5. MS (EI),  $m/z = 236$ .

### 3-(4-Bromophenyl)quinoxalin-2(1H)-one (3m)<sup>12</sup>

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/EtOAc (10:1) to afford the desired product in 80%, white solid, mp > 250 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.89 (s, 1H), 8.39 (d,  $J = 8.8$  Hz, 2H), 8.16 (d,  $J = 8.8$  Hz, 1H), 7.95 (d,  $J = 8.0$  Hz, 1H), 7.63 (d,  $J = 8.8$  Hz, 2H), 7.49-7.53 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  184.6, 167.0, 154.1, 137.3, 133.9, 133.1, 132.2, 129.8, 128.1, 127.4, 126.1, 122.5. MS (EI),  $m/z = 299$ .

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