An Efficient Synthetic Protocol for Quinoxalinones, Benzoxazinones, and Benzothiazinones from 2-Oxo-2-aryl-acetyl Bromide Precursors

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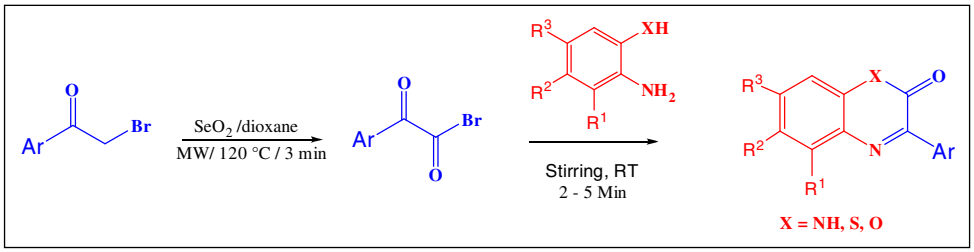

α-Bromoketones undergo selenium dioxide oxidation to yield reactive 2-oxo-2-arylacetyl bromides that are trapped by aryl-1,2-diamines, 1,2-aminophenol or 1,2-aminothiophenol to give quinoxalinones, benzoxazinones, and benzothiazinones, respectively, in good yield.

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INTRODUCTION

Quinoxalinone core is commonly found in compounds displaying a variety of medicinal properties, such as antimicrobial, anticancer, anxiolytic, analgesic, antispastic, antiallergic, and antithrombotic activities [1]. Quinoxalinones have been shown to exhibit the anxiolytic [2] and neuroprotective activities [3] in human clinical testing. Polymerase inhibitor **A** [4] has quinoxalinone entity, and compound **B** [5,6] is used as a drug for cardiovascular diseases (Fig. 1). Despite broad physiological significance of this moiety, there are only few synthetic routes available to this class of heterocycles [7]. Recently, quinoxalinones have been synthesized by palladium-catalyzed intramolecular N-arylations [8a], intramolecular copper-catalyzed Ullmann-type reaction [8b], and Hinsberg reaction of α-keto ester with aromatic 1,2-diamines [8c].

The related heterocyclic moieties having wide scope in the area of photochemistry and photobiology are benz [1,4]oxazin-2-ones and benz[1,4]thiazin-2-ones. Benzoxazinone derivatives are a class of compounds exhibiting spectral and photophysical properties of great interest [9]. Benzothiazinone derivative **C** exhibits bacteriostatic activity with respect to strains *Staphylococcus aureus* P-209 and *Escherichia coli* M17 [10], and the derivative **D** is effective as an antitumour agent [11]. Because of their intense fluorescence characteristics both in organic solutions and crystalline state, the benzoxazinone derivatives are employed as singlet oxygen sensitizers [12]. Previously, these oxazinone/thiazinone moieties have been synthesized by the condensation of 2-aminophenol/2-aminothiophenol with glyoxal/benzil/benzoyl formate [13]/1-phenyl propane-1,2-dione [14]/phenacyl bromide followed by oxidation with m-CPBA [15]. This article describes a simple protocol for the synthesis of these classes of compounds.

RESULTS AND DISCUSSION

All the synthetic routes reported for the synthesis of quinoxalinones [16], benzoxazinones, and benzothiazinones require longer reaction time, harsh conditions, metal catalyst, and tedious work-up process. Realizing these difficulties, a simple and efficient route to synthesize these moieties in good yield from a novel precursor, arylacetyl bromide **2**, is envisaged.

Substituted phenacyl bromides **1** have been taken as the precursors for the sequence of the reactions described in this work. It can be pointed out that phenacyl bromide reacted with 2-aminothiophenol to give 2*H*-benzothiazine that was subsequently oxidized to give benzothiazinone [15]. In the present investigation, we intend to use the dicarbonyl compound ArCOCOBr, generated from phenacyl bromide, as the starting material to construct benzohetroazinone system. A survey on the reactions of phenacyl bromide with oxidizing agents indicates that there is only one report wherein 2-β-naphthyl acetyl bromide has been subjected to selenium dioxide oxidation yielding, probably, the diketo compound. But the oxidized acetyl bromide has not been isolated, only the respective ester has been isolated and characterized [17]. No other method of generating ArCOCOBr could be traced. Realizing the longer reaction time reported for the reaction of $ArCOCH_2Br$ with

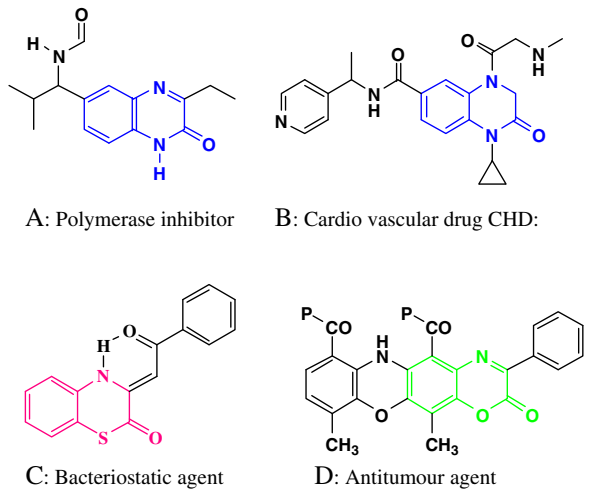
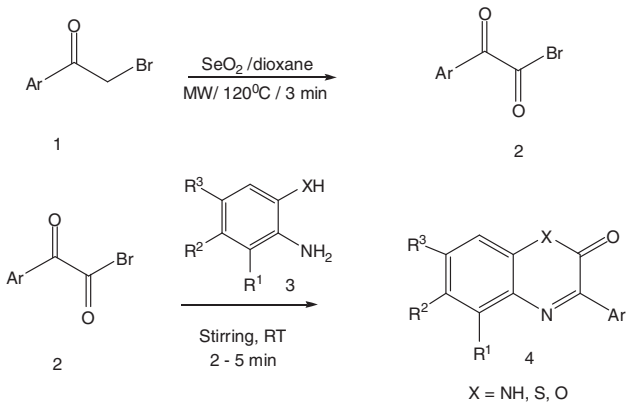


Figure 1. Some important heterocycles of biological significance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

selenium dioxide [17], we carried out the oxidation of phenacyl bromide and its analogies **1** by selenium dioxide in 1,4-dioxane under microwave irradiation at 120°C for 3 min to get 2-oxo-2-arylacetyl bromides **2** in good yield. The compounds **2** are highly lachrymatory, and isolation and characterization have been found difficult.

Nevertheless, the viscous 2-oxo-2-phenylacetyl bromide (**2**, Ar═Ph) has been isolated and characterized by ^{1}H and ^{13}C NMR spectra. In all other cases, **2** has not been isolated and used as such for subsequent transformation. To the solution of dioxane containing the intermediate 2-oxo-2-arylacetyl bromide **2**, 1,2-phenylenediamine/2-aminothiophenol/2-aminophenol (**3**) was added and stirred well at room temperature for a few minutes (Scheme 1). Solid quinoxalinone/benzoxazinone /benzothiazinone (**4**) was thrown out of the reaction medium, which was purified by column chromatography. Eight 1,2-diketones have been

Scheme 1



generated assisted by microwaves, and they have all been allowed to react with different 1,2-difunctional aromatic compounds to obtain a range of widely substituted quinoxalinones, benzoxazinones, and benzothiazinones (**4**).

Although it cannot be claimed as a one-pot reaction, the whole reaction sequence is very simple and gets completed within 10 min, giving excellent yield of **4** (Table 1). The compounds are all adequately characterized (see Supporting Information). The structure of **4k** has been unambiguously confirmed by single crystal X-ray analysis (Fig.2) [18].

When 3,5-dimethylphenylenediamine is allowed to react with 2-oxo-2-phenylacetyl bromide **2** (Ar═phenyl) or 2-oxo-2-(4-methylphenyl)acetyl bromide **2** (Ar═4-methylphenyl), a mixture of regioisomeric **4** was obtained in almost equal amount of the individual regiomers (Table 1, **4h** and **4i**) as evident from the NMR spectra of these compounds. Unfortunately, it was not possible to separate these two isomers in these two cases.

An attempted one-pot reaction involving 1,2-phenylenediamine, phenacyl bromide, and selenium dioxide in the expectation of getting the target heterocycle **4** was not successful as 1,2-diamine immediately reacts with selenium dioxide yielding benzo[*c*][1,2,5]selenadiazole **5** (Scheme 2) [19].

Thus, the synthesis of a set of novel quinoxalinones, benzoxazinones, and benzothiazinones has been achieved from a potential precursor, 2-oxo-2-arylacetyl bromide, which was obtained from substituted phenacyl bromide by oxidation. The protocol is simple and less time-consuming, resulting in very good yield of the target heterocycles.

EXPERIMENTAL

All melting points were recorded in open capillaries and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer (Bruker, Fallanden, Switzerland) in $CDCl_3$/DMSO-d_6 using TMS as internal standard. The chemical shifts are presented in δ-scale. Elemental analyses were performed on a Perkin Elmer 2400 series II Elemental CHNS analyzer (Perkin Elmer, Lv Venlo, The Netherlands). Microwave syntheses were carried out in CEM-DISCOVER model no. 908010 (CEM Corporation, Matthews, NC, USA). All chromatographic separations were performed on a 60–120 mesh silica gel using petroleum ether–ethyl acetate as eluent.

General procedure for the preparation of 2-oxo-2-phenyl acetyl bromide (2a). Selenium dioxide 0.55 g (0.005 mol) was dissolved in dioxane (3.0 mL) taken in a 10-mL microwave vial. To this, phenacyl bromide 1.0 g (0.005 mol) was added, and the reaction mixture was subjected to microwave irradiation (CEM-DISCOVER model no. 908010) at 120°C for 3 min in 150 watts microwave power. Completion of the reaction was confirmed by TLC. Data for **2a**: This compound was obtained as viscous oil; yield above 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.66 (m, 3H), 8.16 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.8, 130.5, 131.9, 135.2, 163.7, 185.6.

General procedure for preparation of quinoxalinone/benzoxazinone/benzothiazinone (4). The generated 2-oxo-2-phenyl

Table 1

Synthesis of quinoxalinones, benzoxazinones, and benzothiazinones from 2-oxo-2-aryl acetyl bromides **2**.

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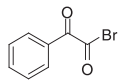
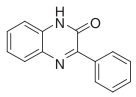
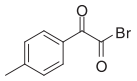
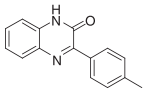
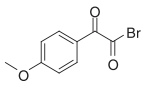
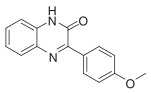
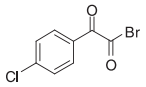
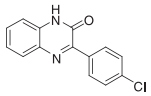
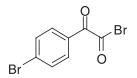
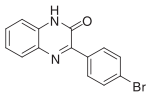
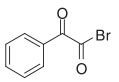
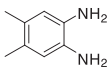
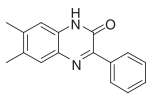
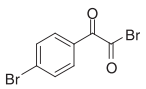
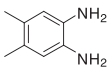
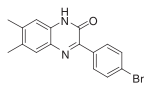
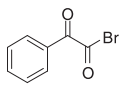
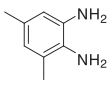
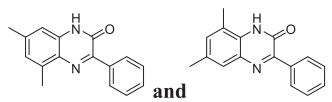
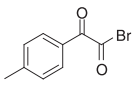
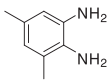
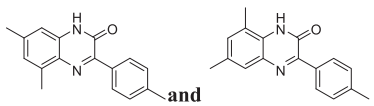
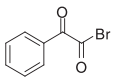
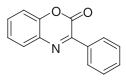
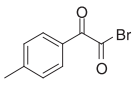
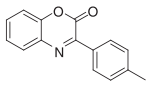
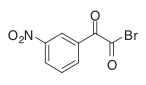
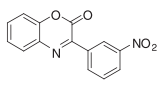
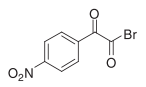
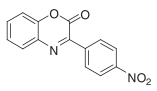
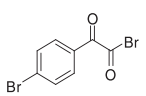
4a				89
4b				87
4c				84
4d				87
4e				89
4f				79
4g				81
4h[a]				82
4i[a]				78
4j				79
4k				81
4l				80
4m				81
4n				82
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Table 1 *(Continued)*

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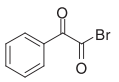
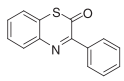
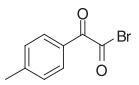
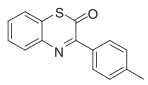
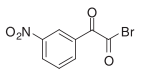
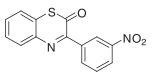
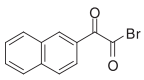
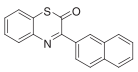
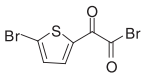
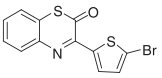
4q				82
4r				81
4s				87
4t				86
4u				82

[a]Mixture of isomers was obtained.

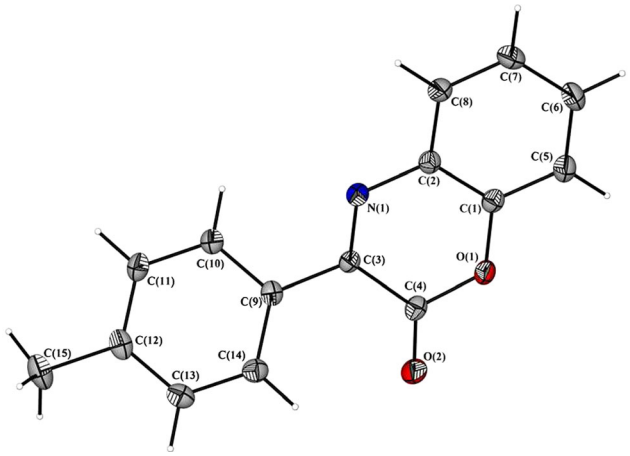
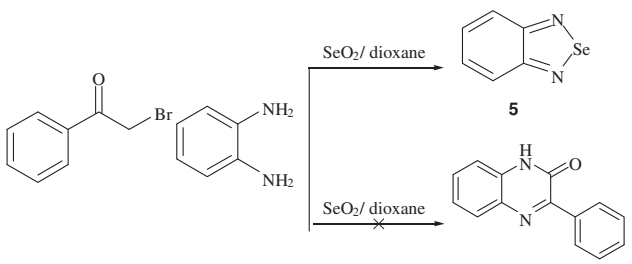


Figure 2. ORTEP diagram of compound **4k**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2



acetyl bromide 2 in dioxane was stirred with equimolar amount of *o*-phenylenediamine/2-aminophenol/2-aminothiophenol for 2–5 min. The isolated solid quinoxalinone/benzoxazinone/benzothiazinone was purified by column chromatography from petroleum ether and ethyl acetate mixture (98:2).

3-Phenylquinoxalin-2(1H)-one (4a). This compound was obtained as straw yellow color solid; mp > 250°C (Lit. mp 237–239°C [8*c*]); IR: NH 3095, CO 1665 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.29 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.43–7.52 (m, 4H), 7.85 (d, *J* = 7.5 Hz, 1H), 8.33 (d, J = 7.8 Hz, 2H), 12.4 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 113.7, 121.8, 126.3, 127.3, 128.6, 129.3, 130.6, 130.7, 132.8, 134.1, 151.2, 153.3; *Anal*. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.60. Found: C, 75.45; H, 4.61; N, 12.43.

3-(4-Methylphenyl)quinoxalin-2(1H)-one (4b). This compound was obtained as straw yellow color solid; mp > 250°C; IR: NH 3112, CO 1668 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 2.30 (s, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 2H), 12.4 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 18.6, 111.8, 113.7, 121.8, 127.2, 128.0,* 129.7, 130.5, 131.1, 138.8, 149.9, 153.8; *Anal*. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.08; H, 4.99; N, 11.92. * Two carbons merged together.

3-(4-Methoxyphenyl)quinoxalin-2(1H)-one (4c). This compound was obtained as straw yellow color solid; mp > 250°C; IR: NH 3117, CO 1667 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 3.86 (s, 3H), 6.97 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H),

7.33 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 8.41 (d, J = 8.1 Hz, 2H), 12.4 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 53.8, 111.8, 113.7, 121.8, 127.2, 128.0,* 129.7, 130.5, 131.1, 152.0, 153.8, 159.8; *Anal*. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10. Found: C, 71.28; H, 4.65; N, 10.95. * Two carbons merged together.

3-(4-Chlorophenyl)quinoxalin-2(1H)-one (4d). This compound was obtained as straw yellow color solid; mp > 250°C; IR: NH 3103, CO 1668 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.30 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.43–7.50 (m, 3H), 7.80 (d, J = 7.5 Hz, 1H), 8.41 (d, J = 8.4 Hz, 2H), 12.62 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 113.7, 121.8, 126.3, 127.3, 128.6, 129.3, 130.6, 130.7, 132.8, 134.1, 151.2, 153.3; *Anal*. Calcd for $C_{14}H_9ClN_2O$: C, 65.51; H, 3.53; N, 10.91. Found: C, 65.38; H, 3.65; N, 10.82.

3-(4-Bromophenyl)quinoxalin-2(1H)-one (4e). This compound was obtained as straw yellow color solid; mp > 250°C; IR: NH 3083, CO 1662 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.30 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 6.9 Hz, 2H), 7.82 (d, J = 7.5 Hz, 1H), 8.32 (d, J = 6.9 Hz, 2H), 12.51 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 113.8, 121.9, 122.8, 128.9, 129.3, 129.6, 130.6, 130.8, 133.3, 134.1, 151.4, 153.4; *Anal*. Calcd for $C_{14}H_9BrN_2O$: C, 55.84; H, 3.01; N, 9.30. Found: C, 55.69; H, 3.14; N, 9.16.

6,7-Dimethyl-3-phenylquinoxalin-2(1H)-one (4f). This compound was obtained as straw yellow color solid; mp > 250°C; IR: NH 3102, CO 1660 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.32 (s, 3H), 2.34 (s, 3H), 7.10 (s, 1H), 7.21–7.28 (m, 3H), 8.25 (d, J = 8.4 Hz, 2H), 12.34 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 17.3, 18.2, 113.8, 121.9, 122.8, 128.9, 129.3, 129.6, 130.6, 130.8, 133.3, 134.1, 151.4, 153.4; *Anal*. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.64; H, 5.53; N, 11.23.

3-(4-Bromophenyl)-6,7-dimethylquinoxalin-2(1H)-one (4g). This compound was obtained as straw yellow color solid; mp > 250°C; IR: NH 3123, CO 1669 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.31 (s,3H), 2.33 (s, 3H), 7.09 (s, 1H), 7.54 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 8.4 Hz, 2H), 12.46 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 17.7, 18.6, 113.9, 122.4, 127.2, 128.8, 129.3, 129.5, 130.7, 130.8, 133.6, 138.8, 149.9, 153.4; MS: *m/z* 328.9 (M^+); *Anal.* Calcd for $C_{16}H_{13}BrN_2O$: C, 58.38; H, 3.98; N, 8.51. Found: C, 58.46; H, 4.02; N, 8.62.

3-Phenyl-2H-benzo[b][1,4]oxazin-2-one (4j). This compound was obtained as colorless solid; mp 124–126°C; IR: CO 1741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.35 (td, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.44–7.54 (m, 4H), 7.81 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H), 8.31 (d, J = 5.7 Hz, J = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.0, 125.4, 128.3, 129.3,* 131.0, 131.3, 131.5, 134.0, 146.3, 150.7, 152.1; MS: *m/z* 224.0 (M^+); *Anal*. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.25; H, 4.11; N, 6.30.* Two carbons merged here.

3-(4-Methylphenyl)-2H-benzo[b][1,4]oxazin-2-one (4k). This compound was obtained as colorless solid; mp 110–112°C; IR: CO 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.25–7.34 (m, 3H), 7.38 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.48 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.81 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 8.24 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 116.0, 125.4, 129.1, 129.3, 129.4, 130.7, 131.4, 131.7, 141.9, 146.3, 150.6, 152.3; *Anal*. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.85; H, 4.61; N, 5.82.

3-(3-Nitrophenyl)-2H-benzo[b][1,4]oxazin-2-one (4l). This compound was obtained as colorless solid; mp 165–167°C; IR: CO 1746, NO_2 1691, 1397 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.69 (t, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 8.38 (d, J = 8.1 Hz, 1H) 8.78 (d, J = 7.8 Hz, 1H), 9.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.3, 124.4, 125.6, 125.9, 129.4, 129.8, 131.3, 132.2, 135.1, 135.5, 146.6, 148.1, 148.4, 151.9; *Anal*. Calcd for $C_{14}H_8N_2O_4$: C, 62.29; H, 3.01; N, 10.44. Found: C, 62.18; H, 2.92; N, 10.51.

3-(4-Nitrophenyl)-2H-benzo[b][1,4]oxazin-2-one (4m). This compound was obtained as colorless solid; mp 182–184°C; IR: CO 1746, NO_2 1695, 1393 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (dd, J = 8.1 Hz, 1.2 Hz, 1H), 7.45 (td, J = 8.1 Hz, 1.2 Hz, 1H), 7.61 (td, J = 8.1 Hz, 1.2 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 9.0 Hz, 2H) 8.56 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.3, 123.3, 125.9, 129.2, 129.9, 131.4, 132.4, 139.5, 146.5, 148.3, 149.2, 151.8; *Anal*. Calcd for $C_{14}H_8N_2O_4$: C, 62.29; H, 3.01; N, 10.44. Found: C, 62.14; H, 2.88; N, 10.38.

3-(4-Bromophenyl)-2H-benzo[b][1,4]oxazin-2-one (4n). This compound was obtained as colorless solid; mp 160–162°C; IR: CO 1749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, J = 7.8 Hz, 1H), 7.40 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.53 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.61 (d, J = 8.7 Hz, 2H), 7.83 (dd, J = 7.8 Hz, 1.5 Hz, 1H), 8.25 (d, J = 8.7 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.2, 125.6, 129.5, 130.9, 131.4, 131.5, 131.6, 131.9, 132.9, 146.5, 149.5, 152.0; *Anal*. Calcd for $C_{14}H_8BrNO_2$: C, 55.66; H, 2.67; N, 4.64. Found: C, 55.42; H, 2.54; N, 4.49.

3-(Naphthalen-2-yl)-2H-benzo[b][1,4]oxazin-2-one (4o). This compound was obtained as colorless solid; mp 127–129°C; IR: CO 1747 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (td, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.39 (dd, J = 7.5 Hz, J = 1.2 Hz, 1H), 7.47–7.57 (m, 3H), 7.84–7.92 (m, 3H), 7.97 (d, J = 7.5 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 9.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.1, 125.3, 125.5, 126.4, 127.5, 127.9, 128.0, 129.4, 129.6, 131.0, 131.1, 131.4, 131.8, 132.8, 134.6, 146.4, 150.1, 152.3; *Anal*. Calcd for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.22; H, 4.09; N, 5.06.

3-(5-Bromothiophen-2-yl)-2H-benzo[b][1,4]oxazin-2-one (4p). This compound was obtained as colorless solid; mp 90–92°C; IR: CO 1749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, J = 4.2 Hz, 1H) 7.26 (d, J = 8.1 Hz, 1H), 7.36 (td, J = 8.1 Hz, J = 1.5 Hz, 1H), 7.49 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.2, 121.1, 125.7, 128.8, 130.6, 131.4, 131.5, 133.3, 139.8, 144.4, 145.8, 151.2; *Anal.* Calcd for $C_{12}H_6BrNO_2S$: C, 46.77; H, 1.96; N, 4.55; S, 10.41. Found: C, 46.59; H, 2.03; N, 4.62; S, 10.34.

3-Phenyl-2H-benzo[b][1,4]thiazin-2-one (4q). This compound was obtained as colorless solid; mp 109–111°C; IR: CO 1637 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (t, J = 7.8 Hz, 1H), 7.46–7.54 (m, 4H), 7.87 (d, J = 7.8 Hz, 1H), 8.06–8.09 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.6, 123.2, 125.1, 126.2, 127.5, 128.9, 130.9, 131.3, 133.6, 135.0, 154.1, 168.0; *Anal*. Calcd for $C_{14}H_9NOS$: C, 70.27; H, 3.79; N, 5.85; S, 13.40. Found: C, 70.16; H, 3.84; N, 5.78; S, 13.32.

3-(4-Methylphenyl)-2H-benzo[b][1,4]thiazin-2-one (4r). This compound was obtained as colorless solid; mp 110–112°C; IR: CO 1639 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 7.25 (d, J = 8.1 Hz, 2H), 7.35 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.45 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 21.4, 121.4, 122.9, 124.9, 126.1,* 127.4, 129.6, 130.9, 134.9, 141.3, 154.1, 168.1; MS: *m/z* 254.2 (M^+); *Anal*. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.66. Found: C, 70.23; H, 4.25; N, 5.48; S, 12.59; * Two carbons merged here.

3-(3-Nitrophenyl)-2H-benzo[b][1,4]thiazin-2-one (4s). This compound was obtained as colorless solid; mp 157–159°C; IR: CO 1633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 7.56 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 7.67 (t, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.33 (dd, *J* = 8.1 Hz, *J* = 0.9 Hz, 1H), 8.40 (dd, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 9.24 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.8, 122.3, 122.8, 123.7, 125.1, 126.0, 126.8, 130.0, 132.9, 135.2, 135.3, 148.8, 153.9, 164.8; *Anal*. Calcd for $C_{14}H_8N_2O_3S$: C, 59.15; H, 2.84; N, 9.85; S, 11.28. Found: C, 59.06; H, 2.92; N, 9.73; S, 11.19.

3-(Naphthalen-2-yl)-2H-benzo[b][1,4]thiazin-2-one (4t). This compound was obtained as colorless solid; mp 165–167°C; IR: CO 1641 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39 (td, *J* = 7.5 Hz, *J* = 1.8 Hz, 1H), 7.47–7.55 (m, 3H), 7.85–7.97 (m, 4H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H), 8.55 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.6, 123.5, 124.4, 125.2, 126.3, 126.8, 127.4, 127.6, 127.8,* 128.8, 131.0, 133.2, 134.6, 135.2,154.3, 168.1; *Anal*. Calcd for $C_{18}H_{11}NOS$: C, 74.72; H, 3.83; N, 4.84; S, 11.08. Found: C, 74.68; H, 3.79; N, 4.79; S, 10.97.

3-(5-Bromothiophen-2-yl)-2H-benzo[b][1,4]thiazin-2-one (4u). This compound was obtained as colorless solid; mp 89–91°C; IR: CO 1642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 5.2 Hz, 1H) 7.50–7.61 (m, 2H), 7.98 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.37 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.2, 125.5, 126.4, 127.7, 131.3, 131.5, 134.9, 137.8, 140.3, 153.5, 165.9, 175.4; *Anal*. Calcd for $C_{12}H_6BrNOS_2$: C, 44.45; H, 1.87; N, 4.32; S, 19.78. Found: C, 44.59; H, 1.78; N, 4.28; S, 19.82.

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