K_2CO_3/H_2O in [omim][BF_4] Ionic Liquid: A Green Medium for Efficient Room-Temperature Synthesis of *N*-Substituted 1,4-Benzoxazin-3-ones

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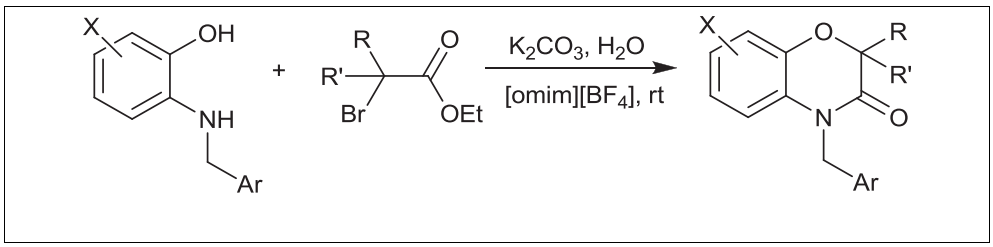

A medium consisting of K_2CO_3 and H_2O in [omim][BF_4] ionic liquid (IL) was used to synthesize *N*-substituted 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one derivatives from their corresponding *o*-aminophenols and 2-bromoalkanoates. As a result, chemoselective formation of benzoxazinones in high yields has been observed at room temperature. After the reactions and separation of the products, the IL was recovered and successfully reused in subsequent reactions without significant loss of activity.

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INTRODUCTION

In line with recent environmental mandates to minimize the use of toxic organic solvents or replace them with safer alternatives, ionic liquids (ILs) have emerged as a new class of stable, nonvolatile, and inert media for various organic transformations [1]. More importantly, in many instances, their use has been accompanied with dramatic rate and selectivity enhancements [2]. In this regard, a particular application has been the use of potassium carbonate (K_2CO_3) to boost the synthetic transformations that require the removal of acidic hydrogens in their initial steps [3].

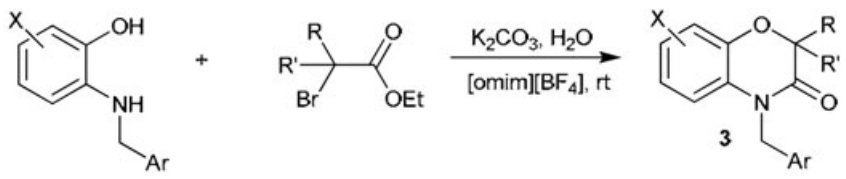
Extensive investigations have been carried out in recent years on 2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one scaffold (e.g., compound **3**). These types of structures are very important in synthetic [4] and medicinal organic chemistry [5] and contribute to the structure of many biologically active synthetic and natural products [6]. In the majority of the available methods, condensation of *o*-aminophenols or *o*-nitrophenols with α-substituted carbonyl derivatives or their synthetic equivalents has been used as the main pathway for the synthesis of **3** [7]. However, *o*-aminophenols have usually been the preferred starting materials as in their ring closure, the extra steps of *O*-alkylation and nitro group reduction associated with the use of *o*-nitrophenols are skipped [8]. Nevertheless, in the majority of the available methods for the synthesis of 1,4-benzoxazin-3-ones either high-temperature treatment is required, more than one-step reaction is involved, an external stimulant such as microwave irradiation is used, or limited range of substrates is used.

In the framework of our studies on heterocyclic systems [9], and in continuation of our previous investigations on the development of environmentally friendly procedures [10], we recently communicated our preliminary results on IL-mediated synthesis of **3** using 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) where mainly unsubstituted *o*-aminophenols underwent room-temperature annulation with 2-bromoalkanoates [11]. In continuation, we now wish to report the extension of the methodology in cyclization of *N*-substituted substrates (Scheme 1) that are known to annulate under relatively harsh conditions [7(a)]. In the current work, reactions occurred at room temperature using K_2CO_3 and water, the conditions were noticeably mild, and the IL medium was efficiently recycled into the subsequent reactions.

RESULTS AND DISCUSSIONS

First, we obtained the optimized conditions using the reaction of 2-(benzylamino)phenol (**1a**) with ethyl 2-bromopropionate (**2b**) as shown in Table 1. KF, NaOEt, and Et_3N in [omim][BF_4] were used as the IL induced no significant reaction (entries 1–3). Among carbonate bases (entries 4–6), only K_2CO_3 caused slight conversion of the reactants to product **3ab** (entry 6). Addition of a few drops of water

Scheme 1



1a: X=H, Ar=C_6H_5
1b: X=H, Ar=(4-MeO)C_6H_4
1c: X=H, Ar=(4-Cl)C_6H_4
1d: X=H, Ar=furan-2-yl
1e: X=5-Me, Ar=furan-2-yl
1f: X=4-Cl, Ar=furan-2-yl

2a: R=R'=H
2b: R=H, R'=Me
2c: R=H, R'=Et
2d: R=R'=Me

to the mixtures improved the yield of all reactions (entries 7–11). Consequently, in the presence of the IL and water, again K_2CO_3 showed the best performance leading to nearly quantitative formation of **3ab** in much shorter time period (entry 12). In the absence of the IL, the yield dropped dramatically illustrating the crucial role of [omim][BF_4] in the progress of the reaction (entry 13). Alteration of the cationic or anionic components of the IL also led to lower yields of the product (entries 14–20).

The optimized conditions ([omim][BF_4]/K_2CO_3/H_2O) were then used to evaluate the generality of the method (Table 2). Reactions of **1a–c** with **2a** rapidly gave single products **3aa**, **3ba**, and **3ca**, respectively (entries 1–3). Similarly, reactions with secondary 2-bromoalkanoate (**2c**) led to high-yield formation of products **3ac**, **3bc**, and **3cc** (entries 4–6). Interestingly, reactions of **2d**, a bromoalkanoate with tertiary carbon at its α position, proceeded efficiently (entries 7–9) giving the respective products but in longer times. Because of high-steric bulks, synthesis of these compounds is not very facile, with few low-yielding procedures for their synthesis available in the literature [12].

To further illustrate the generality of the procedure, various *N*-furanylmethyl-substituted *o*-aminophenols were also subjected to the optimized annulation conditions. As summarized in Table 3, 2-((furan-2-ylmethyl)amino) phenol (**1d**) reacted efficiently with **2a** (entry 1), **2b** (entry 2), and **2d** (entry 3) to produce the expected products in high yields. Similar results were also observed for the reactions of electron-releasing (entries 4 and 5) and electron-withdrawing-substituted substrates (entries 6 and 7), **1e** and **1f**, respectively.

In the majority of the examples, single products formed rapidly at room temperature and easily separated from the reaction mixtures by a simple ethereal extraction allowing efficient recovery of the IL and its reuse in subsequent reactions without significant loss of activity. This was shown by conducting five reactions of **1a** with **2b** in a row, while each time the recovered IL was reused in the next reaction. As a result, 95, 94, 92, 89, and 89% of **3ab** was obtained, respectively, illustrating the efficiency of the recovered IL.

A mechanism is proposed for the process based on the observed results, as shown in Scheme 2. Initially, K_2CO_3 could deprotonate the hydroxy group of the *o*-aminophenol to produce the corresponding phenolate to attack compound **2**. The intramolecular annulation of the ethyl aminophenoxyalkanoate intermediate would then give the product. This was supported by low-temperature separation of the more sluggish intermediate **3a′d** for the reaction of **1a** with **2d**.

In summary, the versatility and efficiency of the current method could be easily concluded by the comparison of the results with previous related investigations [13]. The present work shows the first general methodology for the facile room-temperature annulation of *N*-substituted *o*-aminophenols with various types of 2-bromoalkanoates.

Table 1

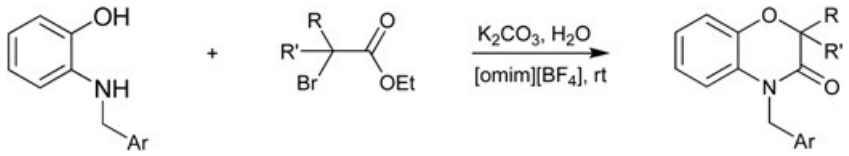
Optimization of the reaction conditions.

Entry	Conditions	Time (h)	Yield (%)[a]
1	[omim][BF_4]/KF	24	0
2	[omim][BF_4]/NaOEt	24	<5
3	[omim][BF_4]/NEt_3	24	<5
4	[omim][BF_4]/Na_2CO_3	24	0
5	[omim][BF_4]/$NaHCO_3$	24	0
6	[omim][BF_4]/K_2CO_3	24	10
7	[omim][BF_4]/KF/H_2O	24	5
8	[omim][BF_4]/NaOEt/H_2O	24	5
9	[omim][BF_4]/NEt_3/H_2O	24	<5
10	[omim][BF_4]/Na_2CO_3/H_2O	24	15
11	[omim][BF_4]/$NaHCO_3$/H_2O	24	5
12	[omim][BF_4]/K_2CO_3/H_2O	2	95
13	K_2CO_3/H_2O	24	<5
14	[bmim][BF_4]/K_2CO_3/H_2O	2	91
15	[omim]Cl/K_2CO_3/H_2O	2	50
16	[omim][NO_3]/K_2CO_3/H_2O	2	26
17	[opy][BF_4]/K_2CO_3/H_2O	2	81
18	[bpy][BF_4]/K_2CO_3/H_2O	2	68
19	[omim][PF_6]/K_2CO_3/H_2O	2	18
20	[bmim][PF_6]/K_2CO_3/H_2O	2	9

[a]Isolated yields.

Table 2

IL-mediated synthesis of *N*-substituted benzoxazinones.



Entry	*o*-Aminophenols	2-Bromoalkanoate	Product	Time (h)	Yield (%)[a]
1	**1a**	**2a**	**3aa**	2	82
2	**1b**	**2a**	**3ba**	2	86
3	**1c**	**2a**	**3ca**	4	78
4	**1a**	**2c**	**3ac**	3	98
5	**1b**	**2c**	**3bc**	4	95
6	**1c**	**2c**	**3cc**	8	94
7	**1a**	**2d**	**3ad**	24	88
8	**1b**	**2d**	**3bd**	24	86
9	**1c**	**2d**	**3cd**	48	85

[a]Isolated yields.

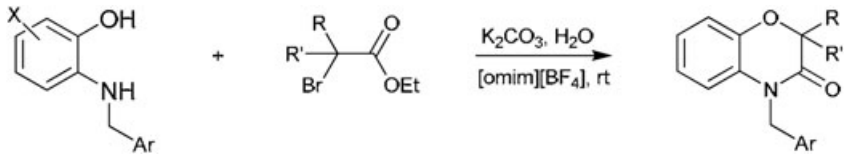
High yields of the products, chemoselectivity of the reaction, efficient recovery of the IL, and successful engagement of tertiary 2-bromoalkanoates in the reaction are the main advantages of the methodology. Application of the procedure in annulation of *o*-aminothiophenols and phenylenediamines with various α-substituted carbonyl compounds is currently under study and will be reported in due course.

EXPERIMENTAL

General. Melting points are uncorrected. IR spectra were recorded using KBr disks on a Shimadzu IRPrestige-21 infrared spectrometer. NMR spectra were obtained on a FT-NMR Bruker Ultra Shield™ (500 MHz) as $CDCl_3$ solutions using TMS as an internal standard reference. Elemental analyses were performed using a Thermo Finnigan Flash EA 1112 instrument. Mass spectra were obtained on a Fisons Trio 1000 instrument at ionization potential of 70 eV. Thin-layer chromatography (TLC) experiments were carried out on precoated silicagel plates using EtOAc/hexane (1:4) as the eluent. Solvents and reagents were purchased from commercial sources. ILs, 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF_4]), 1-buyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), *N*-octylpyridinium tetrafluoroborate ([opy][BF_4]), *N*-butylpyridinium tetrafluoroborate ([bpy][BF_4]), 1-octyl-3-methylimidazolium chloride ([omim]Cl), 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]), 1-buyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), and 1-octyl-3-methylimidazolium nitrate ([omim][NO_3]), were prepared using known procedures [14]. Products **3aa** [11], **3ab**

Table 3

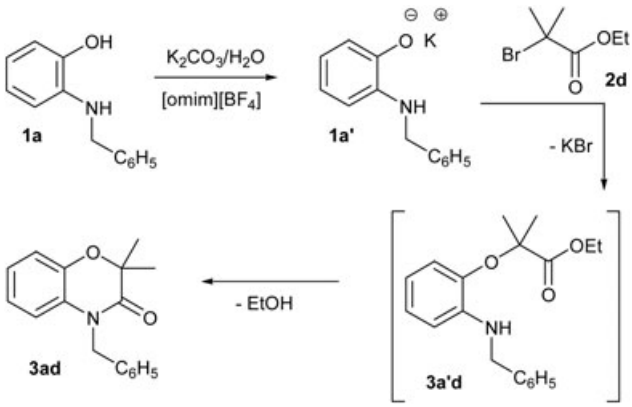
IL-mediated synthesis of *N*-furanylmethyl benzoxazinones.



Entry	*o*-Aminophenols	2-Bromoalkanoate	Product	Time (h)	Yield (%)[a]
1	**1d**	**2a**	**3da**	1.5	96
2	**1d**	**2b**	**3db**	1.5	85
3	**1d**	**2d**	**3dd**	24	92
4	**1e**	**2a**	**3ea**	1	98
5	**1e**	**2b**	**3eb**	1	80
6	**1f**	**2a**	**3fa**	6	95
7	**1f**	**2b**	**3fb**	6	85

[a]Isolated yields.

Scheme 2. The proposed mechanism.



[11], **3ad** [11], **3da** [7(a)], **3ea** [7(a)], **3eb** [7(a)], **3fa** [7(a)], and **3fb** [7(a)] were known and their identity was confirmed by comparison of their spectroscopic data with the available literature. All other products were new and were characterized based on their ^{1}H NMR, ^{13}C NMR, IR, and mass spectra and elemental analyses.

Typical experimental procedure. A mixture of **1a** (200 mg, 1 mmol), water (0.1 mL), and K_2CO_3 (166 mg, 1.2 mmol) was added to [omim][BF_4] (0.78 mL, 3 mmol). After 5 min stirring, **2b** (217 mg, 1.2 mmol) was added to the mixture and stirring continued at room temperature. The progress of the reaction was monitored by TLC. After 2 h, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic phase was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The product was obtained by column chromatography of the solid residue using silica gel and EtOAc/hexanes (1:4) as the eluent. The IL was dissolved in CH_2Cl_2 and filtered to remove any residual of K_2CO_3. The volatile content of the IL was removed using a rotary evaporator. Product **3ab** was obtained in 95% (242 mg) yield.

Spectral data. ***4-Benzyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3aa).*** White solid; mp 66–68°C; IR (KBr) 1680, 1595, 1498, 1394, 1321 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34–7.31 (m, 2H), 7.27–7.23 (m, 3H), 7.01–6.95 (m, 2H), 6.92–6.88 (m, 2H), 5.17 (s, 2H), 4.73 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.2, 145.8, 136.5, 129.4, 129.3, 128.0, 127.1, 124.5, 123.3, 117.5, 116.2, 68.2, 45.5; MS 239, 148, 120, 91; Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 76.36; H, 5.58; N, 5.32%.

4-Benzyl-2-methyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3ab). Light yellow solid; mp 53–55°C; IR (KBr) 3030, 2933, 1689, 1604, 1500, 1394, 1251 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34–7.31 (m, 2H), 7.27–7.24 (m, 3H), 7.01 (dd, *J* = 2, 7.5 Hz, 1H), 6.97 (ddd, *J* = 2, 7, 7.5 Hz, 1H), 6.92 (ddd, *J* = 2, 7, 7.5 Hz, 1H), 6.89 (dd, *J* = 2, 7 Hz, 1H), 5.18 (d, *J* = 16 Hz, 1H), 5.12 (d, *J* = 16 Hz, 1H), 4.78 (q, *J* = 6.8 Hz, 1H), 1.65 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.3, 144.7, 136.5, 129.3, 129.1, 127.6, 126.7, 124.2, 122.8, 117.5, 115.7, 73.8, 45.5, 16.7; MS 253, 196, 120, 91; Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.89; H, 5.98; N, 5.18%.

4-(4-Methoxybenzyl)-2H-benzo[b][1,4]oxazin-3(4H)-one (3ba). White solid; mp 88–91°C; IR (KBr) 3064, 2951, 2897, 1687, 1608, 1498, 1402, 1251 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.20 (d, *J* = 8, 2H), 7.00–6.92 (m, 4H), 6.85 (d, *J* = 8, 2H), 5.10 (s, 2H), 4.71 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.9, 159.2, 145.5, 129.0, 128.3, 128.2, 124.1, 122.9, 117.1, 115.9, 114.5, 67.9, 55.5, 44.6; MS 269, 121; Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.42; H, 5.61; N, 4.91%.

4-(4-Chlorobenzyl)-2H-benzo[b][1,4]oxazin-3(4H)-one (3ca). Light yellow solid; mp 82–84°C; IR (KBr) 3043, 2927, 2848, 1681, 1595, 1494, 1396, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.01–6.96 (m, 2H), 6.91 (ddd, *J* = 1.5, 7, 8 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.12 (s, 2H), 4.71 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.2, 145.9, 135.0, 133.9, 129.6, 129.0, 128.6, 124.7, 123.3, 117.6, 116.0, 68.2, 44.9; MS 273, 127, 125; Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.80; H, 4.55; N, 5.01%.

4-Benzyl-2-ethyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3ac). Light yellow solid; mp 52–54°C; IR (KBr) 3034, 2968, 1672, 1597, 1498, 1458, 1398 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34–7.31 (m, 2H), 7.27–7.24 (m, 3H), 7.02 (dd, *J* = 8, 1.5 Hz, 1H), 6.98 (ddd, *J* = 1.5, 6.5, 7 Hz, 1H), 6.90 (ddd, *J* = 1.5, 7, 8 Hz, 1H), 6.87 (dd, *J* = 1.5, 8 Hz, 1H), 5.24 (d, *J* = 16 Hz, 1H), 5.07 (d, *J* = 16 Hz, 1H), 4.63 (dd, *J* = 8.5, 5 Hz, 1H), 2.03–1.94 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.0, 144.4, 136.6, 129.3, 129.2, 127.7, 126.8, 124.3, 122.8, 117.7, 115.5, 78.7, 45.4, 24.2, 9.8; MS 267, 196, 120, 91; Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.01; H, 6.41; N, 4.98%.

2-Ethyl-4-(4-methoxybenzyl)-2H-benzo[b][1,4]oxazin-3 (4H)-one (3bc). White solid; mp 61–63°C; IR (KBr) 3026, 2968, 2929, 2845, 1674, 1598, 1502, 1396, 1309 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 7 Hz, 1H), 6.97–6.93 (m, 1H), 6.89–6.87 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.16 (d, *J* = 16 Hz, 1H), 5.00 (d, *J* = 16 Hz, 1H), 4.58 (dd, *J* = 4.5, 8.5 Hz, 1H), 3.77 (s, 3H), 2.02–1.89 (m, 2H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.0, 161.3, 146.5, 131.3, 130.7, 130.3, 126.3, 124.8, 119.8, 117.8, 116.7, 80.8, 57.7, 47.0, 26.3, 12.0; MS 297, 121; Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.69; H, 6.44; N, 4.43%.

4-(4-Chlorobenzyl)-2-ethyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3cc). Light yellow solid; mp 67–69°C; IR (KBr) 3057, 2970, 2927, 2864, 1685, 1595, 1496, 1450, 1396 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.02 (dd, *J* = 1.5, 8 Hz, 1H), 6.98 (ddd, *J* = 1.5, 7.5, 7.5 Hz, 1H), 6.91 (ddd, *J* = 1.5, 7.5, 8 Hz, 1H), 6.81 (dd, *J* = 1.5, 7 Hz, 1H), 5.17 (dd, *J* = 16 Hz, 1H), 5.04 (dd, *J* = 16 Hz, 1H), 4.60 (dd, *J* = 4.5, 8.5 Hz, 1H), 2.03–1.89 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.1, 144.6, 135.2, 133.7, 129.5, 129.1, 128.4, 124.5, 122.9, 117.9, 115.5, 78.7, 44.9, 24.2, 9.9; MS 301, 127, 125; Anal. Calcd for $C_{17}H_{16}ClNO_2$: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.47; H, 5.31; N, 4.10%.

4-Benzyl-2,2-dimethyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3ad). Light yellow solid; mp 67–69°C; IR (KBr) 3034, 2972, 2933, 1680, 1598, 1496, 1456, 1390, 1253 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34–7.31 (m, 2H), 7.26–7.23 (m, 3H), 6.98–6.96 (m, 2H), 6.89 (ddd, *J* = 2, 7, 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 5.14 (s, 2H), 1.60 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.3, 143.7, 136.7, 129.4, 129.1, 127.6, 126.6, 124.1, 122.5, 117.9, 115.3, 78.1, 45.7,

24.1; MS 267, 196, 134, 91; Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.03; H, 6.42; N, 4.85%.

4-(4-Methoxybenzyl)-2,2-dimethyl-2H-benzo[b][1,4]oxazin-3 (4H)-one (3bd). Light yellow solid; mp 65–67°C; IR (KBr) 3066, 2972, 2931, 2837, 1672, 1610, 1506, 1392, 1253, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.17 (d, *J* = 8.5 Hz, 2H), 6.96–6.94 (m, 2H), 6.90–6.87 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.07 (s, 2H), 3.77 (s, 3H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.5, 159.4, 143.9, 129.7, 129.0, 128.3, 124.3, 122.7, 118.1, 115.5, 114.8, 78.3, 55.7, 45.4, 24.4; MS 297, 134, 121; Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.57; H, 6.44; N, 4.48%.

4-(4-Chlorobenzyl)-2,2-dimethyl-2H-benzo[b][1,4]oxazin-3 (4H)-one (3cd). Light yellow solid; mp 97–99°C; IR (KBr) 3061, 2976, 2929, 2864, 1668, 1600, 1496, 1392, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 4.1 Hz, 2H), 6.90–6.87 (m, 1H), 6.78 (d, *J* = 8 Hz, 1H), 5.09 (s, 2H), 1.57 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.6, 144.0, 135.5, 133.7, 129.5, 129.4, 128.4, 124.6, 122.9, 118.3, 115.3, 78.4, 45.3, 24.3; MS 301, 127, 125; Anal. Calcd for $C_{17}H_{16}ClNO_2$: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.50; H, 5.33; N, 4.49%.

4-(Furan-2-ylmethyl)-2-methyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3db). Yellow solid; mp 82–84°C; IR (KBr) 3115, 2987, 2864, 1680, 1600, 1502, 1394, 1273 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.35 (dd, *J* = 1, 2 Hz, 1H), 7.21–7.19 (m, 1H), 7.03–6.99 (m, 3H), 6.32–6.29 (m, 2H), 5.16 (d, *J* = 16 Hz, 1H), 4.99 (d, *J* = 16 Hz, 1H), 4.64 (q, *J* = 7 Hz, 1H), 1.58 (d, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.1, 150.2, 145.0, 142.6, 129.5, 124.4, 123.1, 117.7, 115.7, 111.0, 108.9, 73.9, 39.2, 16.7; MS 243, 134, 120, 81; Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.75; H, 5.40; N, 4.93%.

4-(Furan-2-ylmethyl)-2,2-dimethyl-2H-benzo[b][1,4]oxazin-3(4H)-one (3dd). Light yellow solid; mp 47–49°C; IR (KBr) 3115, 2983, 2929, 1680, 1597, 1502, 1463, 1390, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.34 (dd, *J* = 1, 1.5 Hz, 1H), 7.14–7.11 (m, 1H), 7.01–6.95 (m, 3H), 6.31 (dd, *J* = 2, 3 Hz, 1H), 6.25 (d, *J* = 3 Hz, 1H), 5.08 (s, 2H), 1.51 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.1, 150.4, 143.8, 142.5, 129.5, 124.4, 122.7, 118.1, 115.2, 111.0, 108.5, 78.2, 39.3, 24.1; MS 257, 134, 120, 81; Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.02; H, 5.87; N, 5.07%.

Ethyl 2-(2-(benzylamino)phenoxy)-2-methylpropanoate (3a′d). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.42–7.40 (m, 2H), 7.37–7.34 (m, 3H), 7.01–6.98 (m, 1H), 6.94–6.89 (m, 1H), 6.88–6.87 (m, 1H), 6.79 (dd, *J* = 1, 8 Hz, 1H), 5.17 (s, 1H), 4.41 (s, 2H), 4.26 (q, *J* = 7 Hz, 2H), 1.62 (s, 6H), 1.29 (t, *J* = 7 Hz, 3H); MS 313, 267, 198, 134, 91.

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