Phenyliodine Bis(trifluoroacetate) Mediated Intramolecular Oxidative Coupling of Electron-Rich *N*-Phenyl Benzamides

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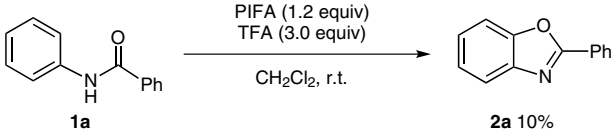
Abstract: The intramolecular oxidative C–O coupling of *N*-(4-alkoxy-phenyl) and *N*-(4-acetamido-phenyl) benzamides was achieved under metal-free conditions by using phenyliodine bis(trifluoroacetate) as oxidant and TMSOTf as catalyst. The reactions afford benzoxazole products in high yields.

Key words: hypervalent iodine, *N*-phenyl benzamides, cyclization, oxidative coupling, benzoxazoles

$PhI(OAc)_2$ (PIDA) and $PhI(OCOCF_3)_2$ (PIFA) are versatile organic hypervalent iodine reagents which have found wide applications in organic synthesis.[1] One characteristic property of PIDA and PIFA is that they are capable of promoting the oxidative couplings involving electron-rich aromatic compounds: for instances, the intra- and intermolecular biaryl coupling,[2,3] the C–C bond formation between aryl rings and other groups,[4] and the functionalization of aromatic rings.[5] It is also possible to apply the reactions to the synthesis of aromatic heterocycles via intramoleluar C_{Ar}–H/X (X = N, O, S, etc.) coupling,[6–8] but studies toward this end are not fully explored.

Benzoxazoles have long been of interest to synthetic organic chemists due to their important applications in medicinal chemistry.[9] Recently, Ueda and Nagasawa reported a very efficient synthesis of benzoxazoles from anilides via $Cu(OTf)_2$-catalyzed intramolecular oxidative C–O coupling.[10] We anticipated that this transformation might also be achieved under metal-free conditions by using PIDA or PIFA as oxidant. However, the reactions of anilides with hypervalent iodine(III) reagents were investigated before, but no benzoxazole products have been reported in these works so far to our knowledge. In an early study, Barlin and Riggs found that acetanilides having electron-donating substituents at the *para* position reacted with PIDA to afford *meta*-acetoxy-substituted products in high yields.[11] The reaction was later demonstrated to proceed via an ionic pathway by Nair et al.[12] Recently, Gu reported that the reaction between anilides and PIFA led to the direct *para* acetoxylation and etherification of anilides.[13] Kikugawa et al. investigated the reaction between *N*-arylamides and PIFA, and found that the composition of the products depended on the electronic nature of anilides and reaction conditions.[14] The reaction of electron-rich anilides in TFA (10 equiv)–$CHCl_3$ led to the trifluoroacetoxylation at the *para* position of the *N*-phenyl ring, while the electron-withdrawing group substituted counterparts were converted into N-iodophenylation products in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP)–TFA (10:1). On the other hand, it was reported that when *N*-(3,4-dimethoxyphenyl)benzamide was subjected to PIFA in CH_2Cl_2, the intermolecular C–C oxidative coupling took place, giving rise to the dimerization product. The reaction proceeded probably via a single-electron-transfer mechanism.[15] These studies indicate that the reactions of *N*-arylamides with hypervalent iodine reagents are largely influenced by the reaction conditions, the structural features of the substrates and hypervalent iodine reagents. We hoped that by choosing reaction conditions and substrates, the hypervalent iodine reagent promoted transformation from *N*-arylamides to benzoxazoles could be realized. Herein we wish to report our preliminary study toward this goal.

Our investigation was initiated by treating *N*-phenyl benzamide **1a** with PIFA in several non-nucleophilic solvents such as CH_2Cl_2, trifluoroethanol (TFE), HFIP, and MeCN. When CH_2Cl_2 was used as solvent, the reaction did not take place, with the starting material being recovered. Using Lewis acids such as $BF_3{\cdot}OEt_2$ and TMSOTf as catalyst resulted in the decomposition of **1a**. When 3.0 equivalents of trifluoroacetic acid (TFA) were used in combination with PIFA, the benzoxazole product **2a** was generated in 10% yield (Scheme 1). No improvement was made when the reaction was performed in other solvents. PIDA was ineffective to promote the desired reaction either under various conditions.



1a **2a** 10%

Scheme 1

We speculated that the disappointing results with **1a** might be due to the lack of substituents to stabilize the cation species that was expected to generate during the reaction. Therefore, *N*-(4-ethoxyphenyl)benzamide (**1b**) was chosen next as the substrate and was subjected to the reaction conditions previously used upon **1a**. The results are shown in Table 1.

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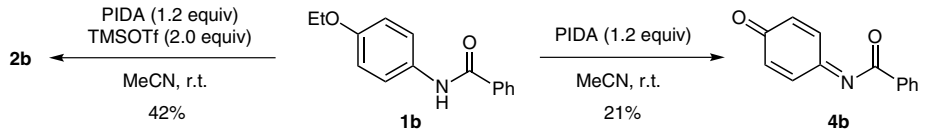


Scheme 2

When the reaction was carried out in CH_2Cl_2 with PIFA as oxidant in the absence of Lewis acid, benzoxazole **2b** was generated in only trace amount, and the major product was found to be compound **3b** (Table 1, entry 1). Using MeCN as solvent raised the yield of **3b** (81%, Table 1, entry 2). On the other hand, the reaction in TFE resulted in the decomposition of **1b** (Table 1, entry 3). The desired **2b** was formed in 12% yield when the reaction was conducted in HFIP (Table 1, entry 4). In contrast to these results, when TMSOTf was used in combination with PIFA, the expected reaction took place in CH_2Cl_2, MeCN, and TFE at room temperature, giving rise to compound **2b** in varying yields. Using 2.0 equivalents of TMSOTf guaranteed a complete conversion in five minutes. MeCN performed the best among these three solvents (Table 1, entry 12). The reaction also took place at low temperature (Table 1, entry 8). Similar results were obtained with $BF_3{\cdot}OEt_2$ as the catalyst except in TFE (Table 1, entry 13). However, when THF was used as solvent, the reaction proceeded poorly, with **1b** mostly decomposed (Table 1, entry 15).

N-(4-Ethoxyphenyl)benzamide (**1b**) can also react with PIDA to afford **2b** with the assistance of TMSOTf or $BF_3{\cdot}OEt_2$, but the yield was considerably lower (Scheme 2). In the absence of Lewis acid, on the other hand, the reaction generated unexpectedly compound **4b** in low yield.

To further improve the yield of the benzoxazole product, we performed the reaction in dilute solution (with concentration of **1b** at 0.01 M) under the conditions otherwise the same as shown in Table 1, entry 12. As expected, the yield of **2b** was raised to 96%. These conditions were then applied to a variety of substituted anilides, and the results are summarized in Table 2. The reaction proceeded very fast for *N*-(4-alkyloxy-phenyl) benzamides, and the corresponding benzoxazoles were generated in high yields (Table 2, entries 1–9). Compound **1k** and **1l** were transformed smoothly to **2k** and **2l** too in good yields (Table 2, entries 10 and 11). However, the expected reaction failed to take place for compounds **1m**–**p** (Table 2, entries 11–14).

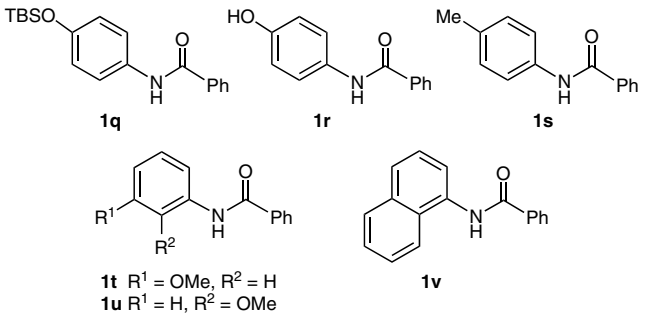


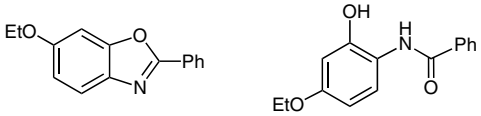
Figure 1 Compounds decomposed mostly under the reaction conditions

Compounds shown in Figure 1 decomposed mostly under the reaction conditions.

Two different mechanisms might account for the formation of benzoxazole products (Scheme 3). One involves the electrophilic activation of the *N*-phenyl ring in the form of nitrenium ion, which is generated from the attack of PIFA on the amide moiety [Scheme 3, path (a)].[14] In this mechanism, compound **1b** firstly reacts with PIFA to generate intermediate **A**, which is converted into the nitrenium ion **B** by cleavage of the N–I bond. The formation of **B** is largely favored by the presence of *para* alkoxy group. In the next step, a nucleophilic attack at the phenyl ring by

Table 1 Screening of the Conditions for the Reaction of **1b** with PIFA[a]

Entry	Solvent	Additive (equiv)	Reaction time (min)	Product	Yield (%)[b]
1	CH_2Cl_2	none	120	**2b** **3b**	trace 47
2	MeCN	none	120	**2b** **3b**	trace 81
3	TFE	none	10	–[c]	
4	HFIP	none	10	**2b**	12
5	CH_2Cl_2	TMSOTf (1.0)	5	**2b**	30
6	CH_2Cl_2	TMSOTf (2.0)	5	**2b**	58
7	CH_2Cl_2	$BF_3{\cdot}OEt_2$ (2.0)	5	**2b**	53
8	CH_2Cl_2	TMSOTf (2.0)	5	**2b**	50[d]
9	CH_2Cl_2	$BF_3{\cdot}OEt_2$ (2.0)	5	**2b**	55[d]
10	MeCN	$BF_3{\cdot}OEt_2$ (1.0)	5	**2b**	30
11	MeCN	$BF_3{\cdot}OEt_2$ (2.0)	5	**2b**	74
12	MeCN	TMSOTf (2.0)	5	**2b**	78
13	TFE	$BF_3{\cdot}OEt_2$ (2.0)	5	–[c]	
14	TFE	TMSOTf (2.0)	5	**2b**	41
15	THF	TMSOTf (2.0)	5	**2b**	5



[a] The reaction was carried out on 0.2 mmol scale in 2 mL solvent at r.t. unless otherwise specified.
[b] Isolated yield.
[c] The substrate decomposed under the conditions.
[d] The reaction was performed at –40 °C.

the carbonyl oxygen generates cyclization product **C**, from which **2b** is formed after deprotonation. The other possible mechanism involves the single electron transfer (SET) from **1b** to PIFA [Scheme 3, path (b)]. This mechanism has been employed generally to rationalize the intra- and intermolecular oxidative coupling of electron-rich aromatic compounds.[2,3] Both mechanisms are consistent with the fact that only electron-rich 4-alkoxy-substituted substrates were suitable for the reaction. For compounds less electronically rich and with higher oxidation potentials, such as **1a** and **1s**, other competitive pathways would dominate. Compounds **1q**, **1r**, and **1u**, despite being electronically rich, were labile to decompose under the reaction conditions. The failure of compounds **1m–p** suggests that the nucleophilicity of the amido oxygen atom also has a large influence on the reaction.

Table 2 The Reactions of *N*-Phenyl Anilides with PIFA[a,16,17]

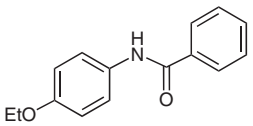
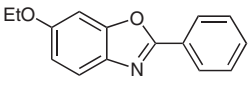
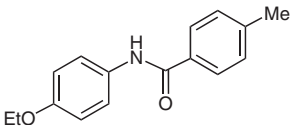
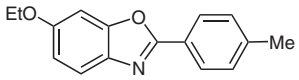
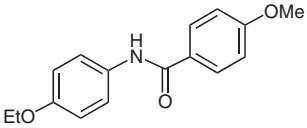
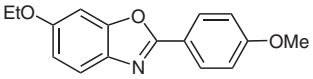
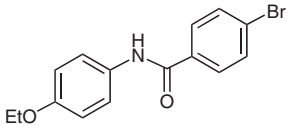
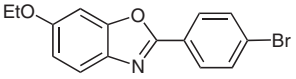
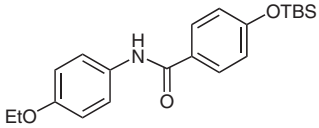
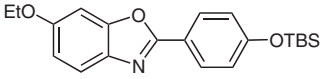
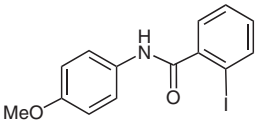
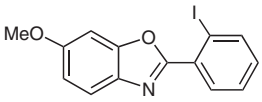
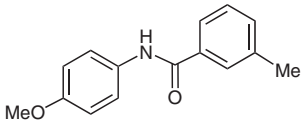
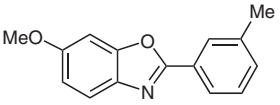
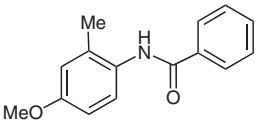
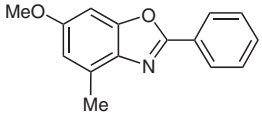
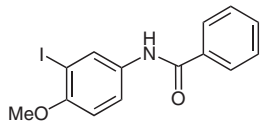
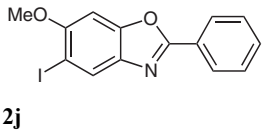
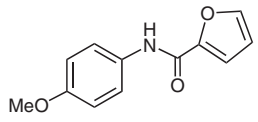
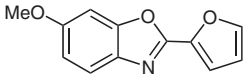
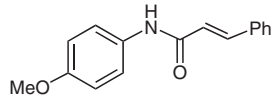
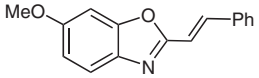
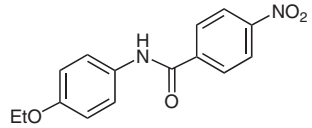
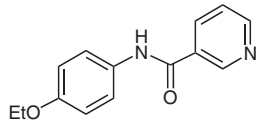
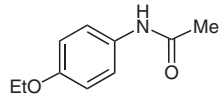
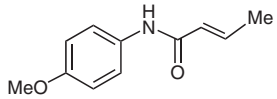
Entry	Substrate	Product	Yield (%)[b]
1	 **1b**	 **2b**	96
2	 **1c**	 **2c**	97
3	 **1d**	 **2d**	98
4	 **1e**	 **2e**	93
5	 **1f**	 **2f**	90
6	 **1g**	 **2g**	72
7	 **1h**	 **2h**	96
8	 **1i**	 **2i**	99

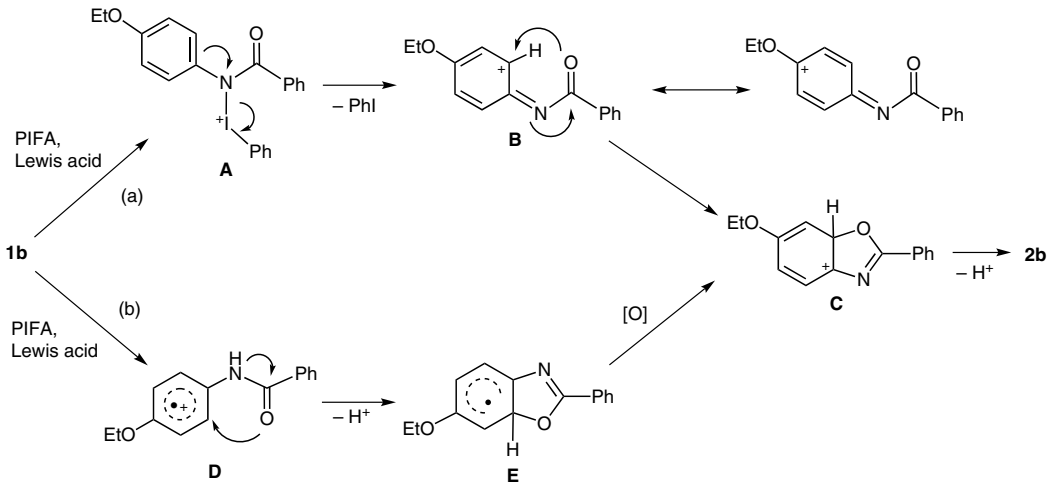
Table 2 The Reactions of *N*-Phenyl Anilides with PIFA[a,16,17] (continued)

Entry	Substrate	Product	Yield (%)[b]
9	 **1j**	 **2j**	88
10	 **1k**	 **2k**	74
11	 **1l**	 **2l**	76
12	 **1m**	n.r.[c]	–
13	 **1n**	decomp.[d]	–
14	 **1o**	n.r.[c]	–
15	 **1p**	decomp.[d]	–

[a] The reaction was performed at 0.01 M in MeCN.
[b] Isolated yield.
[c] No reaction took place after prolonged reaction time.
[d] The starting material decomposed.

As shown in Table 1, Lewis acids $BF_3{\cdot}OEt_2$ and TMSOTf played a critical role in determining the reaction course. In the absence of $BF_3{\cdot}OEt_2$ or TMSOTf, compound **3b** was obtained after workup when the reaction was carried out in MeCN and CH_2Cl_2 (Table 1, entries 1 and 2), whereas in the presence of these Lewis acids, the intramolecular C–O coupling took place readily. It is well-known that acids can promote the hypervalent iodine reagent mediated electron transfer process as well as the geneation of intermediates like **B**.[2,3,14] As a result, the formation of benzoxazoles was facilitated by $BF_3{\cdot}OEt_2$ or TMSOTf according to the mechanisms shown in Scheme 3.

The unreactiveness of *N*-(4-ethoxy-phenyl) acetanilide (**1o**) towards PIFA suggested that if the acetamido group, an electron-donating group too, was attached to the *para* position of the *N*-phenyl ring of benzamide, selective C–O coupling would be observed for the benzamido group. Indeed, when compounds **5a–f** were treated with PIFA in the presence of TMSOTf, **6a–f** were obtained, respectively, in satisfactory yields (Table 3, entries 1–6). In the case of **5c**, deprotection product **6c′** was generated along with **6c**. Compound **5g** can be converted into the symmetrical benzodioxazole **6g** if excessive amount of PIFA and TMSOTf were used (Table 3, entry 7). It is worthy of note that while TMSOTf was effective to catalyze the reactions, using $BF_3{\cdot}OEt_2$ as catalyst failed to convert **5a** into



Scheme 3

6a. On the other hand, the results were unsatisfactory when the substrate was compound **5h** or **5i**. The majority of these two compounds decomposed under these reaction conditions (Table 3, entries 8 and 9).

In summary, we found that PIFA could promote the intramolecular oxidative coupling of electron-rich *N*-phenyl benzamides to generate benzoxazole products. The use of Lewis acid such as $BF_3{\cdot}OEt_2$ and TMSOTf was critical for the reaction to proceed. The reaction was very sensitive to the structure features of the substrates. While *N*-(4-alkoxy-phenyl)benzamides could be converted into corresponding benzoxazoles in high yields, *N*-(4-alkoxy-phenyl)acetanilde was unreactive under the same conditions. Consequently, selective C–O coupling can be achieved for *N*-(4-acetamido-phenyl)benzamides.

Table 3 The Selective C–O Coupling for Compounds **5**[a,16,17]

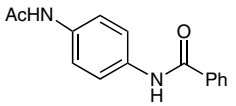
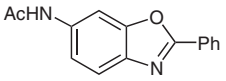
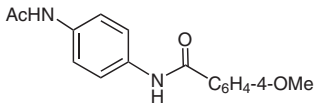
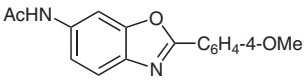
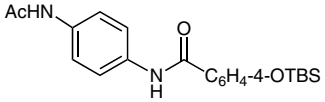
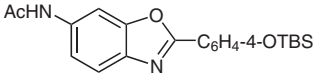
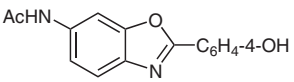
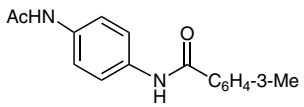
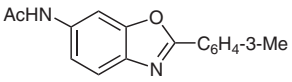
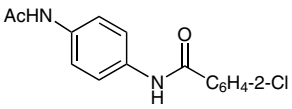
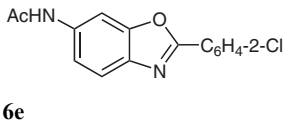
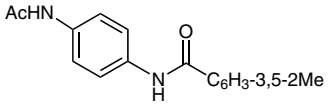
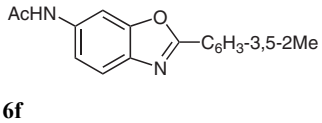
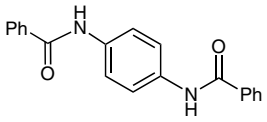
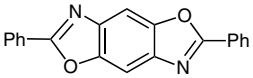
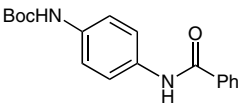
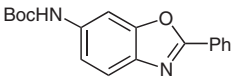
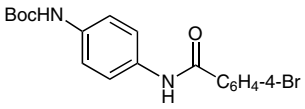
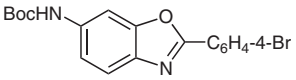
Entry	Substrate	Product (s)	Yield (%)[b]
1	 **5a**	 **6a**	86
2	 **5b**	 **6b**	96
3	 **5c**	 **6c**  **6c′**	**6c** 55 **6c′** 23
4	 **5d**	 **6d**	90

Table 3 The Selective C–O Coupling for Compounds **5**[a,16,17] (continued)

Entry	Substrate	Product (s)	Yield (%)[b]
5	 **5e**	 **6e**	75
6	 **5f**	 **6f**	99
7	 **5g**	 **6g**	82[c]
8	 **5h**	 **6h**	37[d]
9	 **5i**	 **6i**	27[d]

[a] Conditions: 1.2 equiv of PIFA and 2.0 equiv of TMSOTf were used unless otherwise specified. The reaction time was 5 min at r.t.
[b] Isolated yield.
[c] Conditions: 3.0 equiv of PIFA and 4.0 equiv of TMSOTf were used.
[d] Conditions: 1.2 equiv of $BF_3{\cdot}OEt_2$ was used as Lewis acid. Using TMSOTf resulted in lower yield of the desired product.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(16) **General Procedure for the Reactions of 1 (or 5)**
To a stirred MeCN solution (40 mL) containing **1** (or **5**, 0.5 mmol) and TMSOTf (1.0 mmol) was added dropwise PIFA (0.6 mmol) in MeCN (10 mL). The stirring was continued at r.t. for another 5 min. The mixture was then poured into a sat. $NaHCO_3$ solution (100 mL), and the product was extracted with EtOAc (2 × 100 mL). The combined organic phase was washed with brine, and then dried with anhyd $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure, and the residual was treated with flash column chromatography to give **2** (or **6**).

(17) **Typical Spectroscopic Data for the Products**
6-Ethoxy-2-(4-bromophenyl)benzo[*d*]oxazole (2e)
White solid; mp 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (t, 3 H, *J* = 7.2 Hz, CH_3CH_2), 4.08 (q, 2 H, *J* = 7.2 Hz, OCH_2), 6.95 (dd, 1 H, *J* = 8.8, 2.4 Hz, C_5-H), 7.06 (d, 1 H, *J* = 2.4 Hz, C_7-H), 7.61 (d, 1 H, *J* = 8.8 Hz, C_4-H), 7.62 (d, 2 H, *J* = 8.4 Hz, 4-BrPhH), 8.04 (d, 2 H, *J* = 8.4 Hz, 4-BrPhH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 64.2, 96.0, 113.5, 120.0, 125.6, 126.3, 128.5, 132.1, 135.6, 151.6, 157.8, 161.2. MS (EI): *m/z* (rel. int., %) = 317 (71) [M^+], 262 (7), 210 (10), 183 (21), 79 (54), 51 (100). ESI-HRMS: *m/z* calcd for $C_{15}H_{12}BrNO_2$ + H: 318.0124; found: 318.0134
***N*-{2-Phenylbenzo[*d*]oxazol-6-yl}acetamide (6a)**
Light yellow solid; mp 176–177 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ = 2.13 (s, 3 H, CH_3CO), 7.38 (dd, 1 H, *J* = 8.8, 1.6 Hz, C_5-H), 7.59–7.61 (m, 3 H, PhH), 7.64 (d, 1 H, *J* = 8.8 Hz, C_4-H), 8.21–8.24 (m, 2 H, PhH), 8.39 (d, 1 H, *J* = 1.6 Hz, C_7-H), 9.50 (br s, 1 H, NH). ^{13}C NMR (100 MHz, acetone-d_6): δ = 24.4, 102.3, 117.2, 120.5, 128.1, 128.2, 130.0, 132.3, 138.6, 138.7, 152.0, 163.3, 169.2. MS (EI): *m/z* (rel. int., %) = 252 (39) [M^+], 210 (100), 149 (6). ESI-HRMS: *m/z* calcd for $C_{15}H_{12}N_2O_2$ + H: 253.0972; found: 253.0973
***N*-{2-(4-Methoxyphenyl)benzo[*d*]oxazol-6-yl}acetamide (6b)**
Light yellow solid; mp 187–189 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.09 (s, 3 H, CH_3CO), 3.85 (s, 3 H, OCH_3), 7.13 (d, 2 H, *J* = 8.4 Hz, 4-MeOPhH), 7.37 (d, 1 H, *J* = 8.4 Hz, C_5-H), 7.65 (d, 1 H, *J* = 8.8 Hz, C_4-H), 8.09 (d, 2 H, *J* = 8.8 Hz, 4-MeOPhH), 8.22 (s, 1 H, C_7-H), 10.22 (br s, 1 H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 24.0, 55.5, 101.1, 114.7, 116.2, 118.9, 119.1, 128.8, 136.9, 137.1, 150.2, 161.9, 162.0, 168.4. MS (EI): *m/z* (rel. int., %) = 282 (15) [M^+], 240 (18), 225 (10), 178 (12), 149 (100). ESI-HRMS: *m/z* calcd for $C_{16}H_{14}N_2O_3$ + H: 283.1077; found: 283.1080.

