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$n\text{Bu}_4\text{Ni}$ -catalyzed direct amination of benzoxazoles with tertiary amines using TBHP as oxidant under microwave irradiation

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Abstract: A facile, efficient, and practical method for $n\text{Bu}_4\text{Ni}$ -catalyzed direct C–H amination of benzoxazoles with tertiary amines has been developed. The system could be performed in the absence of metal catalyst and only requires *tert*-butyl hydroperoxide as oxidant under microwave irradiation. A variety of substituted benzoxazol-2-amines were synthesized with moderate to good yield.

Keywords: benzoxazole; microwave irradiation; $n\text{Bu}_4\text{Ni}$ catalysis; tertiary amine.

1 Introduction

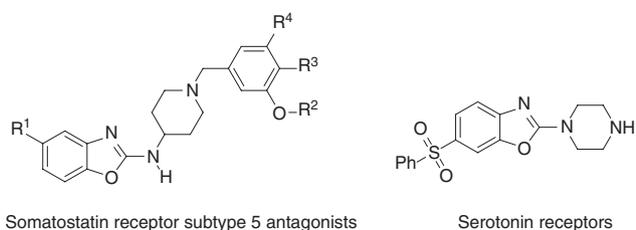
Oxazoles are extremely important structural motifs that are featured prominently in pharmaceuticals and organic materials [1, 2]. Among them, 2-aminobenzoxazoles display high activity, and some drug targets have been addressed by 2-aminated benzoxazoles (Scheme 1), such as small-molecule somatostatin receptor subtype 5 antagonists [3], and as partial antagonists for serotonin (5-hydroxytryptamine) receptors, which are promising targets for the treatment of Alzheimer disease and schizophrenia [4]. Therefore, the development of efficient methods for their preparation is highly important. Transition-metal-catalyzed C–H bond activation of heteroarenes are important in synthetic organic chemistry [5–7], which have been widely used in the synthesis of organic compounds and natural products. Generally, 2-aminobenzoxazole derivatives are synthesized by transition metal-catalyzed amination with *N*-chloroamines, amines, and amides or with *O*-acylated hydroxylamines

and others [8–11]. As a complementary methodology of the above methods, transition metal-catalyzed (including Pd [12], Ni [13], Cu [14–20], Fe [21, 22], Ag [23], Co, Mn [24]) C–H direct amination has become the main strategy to construct 2-aminobenzoxazoles. Although significant advances have been achieved, some disadvantages remain, such as high temperature, long reaction time, poisonous ligands, strong acid or base, and non-economic effects. Additionally, heavy metal impurities in drug intermediates and harsh reaction conditions have limited the utility of such methods. Hence, the development of environmentally benign procedures based on transition metal-free catalysis to synthesize such compounds is highly desirable.

Recently, Studer et al. [25] have developed a metal-free protocol for the highly efficient direct amination of non-activated benzoxazoles and 1,3,4-oxadiazoles with secondary amines using catalytic amounts of triflic acid and 2,2,6,6-tetramethylpiperidine-*N*-oxoammonium tetrafluoroborate ($\text{TEMPO}^+\text{BF}_4^-$) as an organic oxidant. Bhanage et al. [26] and Sun et al. [27] have synthesized substituted benzoxazol-2-amines using benzoxazoles with aliphatic secondary amines through the ring-opening step and further oxidative cyclization, and 2-iodoxybenzoic acid and *N*-bromosuccinimide were used as an oxidant, respectively. Lamani and Prabhu [28] and Nachtsheim et al. [29] have also reported a metal-free route of oxidative amination of benzoxazole with secondary or primary amines in the presence of catalytic iodine or tetrabutylammonium iodide (TBAI) using aqueous *tert*-butyl hydroperoxide (TBHP) as the oxidant. Subsequently, Wang et al. [30] have described an efficient TBAI/TBHP-mediated method for benzoxazoles amination under transition metal-free conditions using formamides as nitrogen sources [30]. Moreover, the direct amination of benzoxazoles with secondary amines using a catalytic amount of *N*-iodosuccinimide and aqueous H_2O_2 as an oxidant or using lithium *tert*-butoxide and iodine as the medium has also been reported [31, 32]. Despite the remarkable success achieved, a direct transition metal-free-catalyzed amination of benzoxazoles was rarely reported with tertiary amines as amino group sources. Given that tertiary amines are widely found in natural products and more

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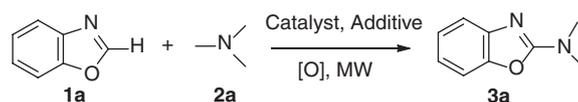
**Scheme 1:** Two bioactive 2-aminobenzoxazole derivatives.

easily available than primary or secondary amines in the laboratories, the synthesis of benzoxazol-2-amines from tertiary amines is more expected. Moreover, in view of the increasing attention to design environmentally benign and metal-free methods for the formation of C–N bonds

and continuation of our research on green chemistry [33, 34], herein we report a facile, efficient, and practical method for $n\text{Bu}_4\text{NI}$ -catalyzed direct amination of benzoxazoles with tertiary amines as nitrogen sources and a catalytic amount of TBAI/TBHP as the oxidant in acetic acid under microwave irradiation.

2 Results and discussion

We began our investigation with the reaction of benzoxazole (**1a**) with trimethylamine (**2a**) as a model reaction. As seen in Table 1, a variety of reaction conditions were employed to achieve the optimal conditions. Initial

Table 1: Optimization of reaction conditions.

Entry	Catalyst (mol%)	[O] (equiv)	Additive (equiv)	Solvent	Temperature (°C)	Yield ^a (%)
1	TBAI (5)	TBHP ^b (2)	AcOH (2)	THF	100	Trace
2	TBAI (5)	TBHP (2)	AcOH (2)	PhCl	100	Trace
3	TBAI (5)	TBHP (2)	AcOH (2)	DCE	100	Trace
4	TBAI (5)	TBHP (2)	AcOH (2)	Dioxane	100	30
5	TBAI (5)	TBHP (2)	AcOH (2)	DMSO	100	28
6	TBAI (5)	TBHP (2)	AcOH (2)	CH ₃ CN	100	57
7	TBAI (5)	H ₂ O ₂ (2)	AcOH (2)	CH ₃ CN	100	<10
8	TBAI (5)	DTBP (2)	AcOH (2)	CH ₃ CN	100	Trace
9	TBAI (5)	AIBN (2)	AcOH (2)	CH ₃ CN	100	<5
10	TBAI (5)	K ₂ S ₂ O ₈ (2)	AcOH (2)	CH ₃ CN	100	Trace
11	TBAI (5)	(NH ₄) ₂ S ₂ O ₈ (2)	AcOH (2)	CH ₃ CN	100	<5
12	KI (5)	TBHP (2)	AcOH (2)	CH ₃ CN	100	54
13	I ₂ (5)	TBHP (2)	AcOH (2)	CH ₃ CN	100	53
14	TBAI (10)	TBHP (2)	AcOH (2)	CH ₃ CN	100	65
15	TBAI (15)	TBHP (2)	AcOH (2)	CH ₃ CN	100	50
16	TBAI (10)	TBHP (1:1.5:2.5:3)	AcOH (2)	CH ₃ CN	100	43:53:52:51 ^c
17	TBAI (10)	TBHP (2)	TFA (2)	CH ₃ CN	100	Trace
18	TBAI (10)	TBHP (2)	PhCO ₂ H (2)	CH ₃ CN	100	56
19	TBAI (10)	TBHP (2)	HCl (2)	CH ₃ CN	100	<10
20	TBAI (10)	TBHP (2)	None	CH ₃ CN	100	Trace
21	TBAI (10)	TBHP (2)	AcOH (1:1.5:2.5:3)	CH ₃ CN	100	46:52:56:53 ^d
22	TBAI (10)	TBHP (2)	AcOH (2)	CH ₃ CN	20	<5
23	TBAI (10)	TBHP (2)	AcOH (2)	CH ₃ CN	60	22
24	TBAI (10)	TBHP (2)	AcOH (2)	CH ₃ CN	80	53
25	TBAI (10)	TBHP (2)	AcOH (2)	CH ₃ CN	120	45
26	TBAI (10)	None	AcOH (2)	CH ₃ CN	100	nr ^e
27	None	TBHP (2)	AcOH (2)	CH ₃ CN	100	nr ^e
28	TBAI (10)	TBHP (2)	AcOH (2)	CH ₃ CN	100	50 ^f

Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), catalyst, oxidant, and acid additive was stirred in solvent (1.5 mL) for 20 min under microwave irradiation. The given equivalents (equiv) and mol% are related to **1a**.

^aIsolated yields. ^b70 % TBHP aqueous solution. ^cWhen 1.0, 1.5, 2.5, and 3.0 equiv TBHP were added, the yields of product were 43, 53, 52, and 51 %, respectively. ^dWhen 1.0, 1.5, 2.5, and 3.0 equiv AcOH were added, the yields of product were 46, 52, 56, and 53 %, respectively.

^enr = no reaction. ^fNo microwave irradiation; reaction time is 12 h.

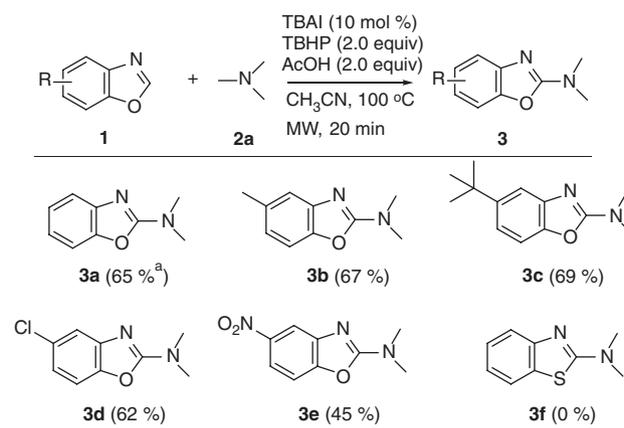
screening of the solvents revealed that the solvents such as THF, PhCl, and 1,2-dichloroethane (DCE) are not suitable for this reaction (Table 1, entries 1–3). Further investigation has shown that the reaction proceeds well in acetonitrile in the presence of AcOH (2.0 equiv) using catalytic amounts of TBAI (5 mol%) and TBHP (2.0 equiv) as the oxidant (Table 1, entries 4–6). Unfortunately, replacement of TBHP with H₂O₂, di-*tert*-butylperoxide (DTBP), AIBN, K₂S₂O₈, or (NH₄)₂S₂O₈ proved to be ineffective, which led to a dramatically decreased yield or no product at all (Table 1, entries 7–11). When potassium iodide or iodine was employed instead of TBAI, the corresponding reaction also proceeded smoothly, presumably due to their similar capability to promote the reaction with TBAI (Table 1, entries 12 and 13). Gratifyingly, increasing the amount of TBAI (10 mol%) resulted in high yields, indicating the significance of a catalyst in the reaction (Table 1, entries 14 and 15). The screening of the amount of TBHP showed that a good yield (65 %) of the product **3a** was obtained when 2.0 equiv of TBHP was employed, and excessive or less amounts of the oxidant caused decreased conversion (Table 1, entries 14 and 16). Furthermore, various additives were investigated, which, compared to AcOH, PhCO₂H, and hydrochloric acid, were less effective, whereas a strong acid, such as trifluoroacetic acid (TFA), was a completely ineffective additive (Table 1, entries 17–19). The reaction of benzoxazole **1a** and trimethylamine **2a** in the absence of AcOH resulted in a trace amount of **3a**, indicating the significance of the acid additive in the reaction (Table 1, entry 20). Notably, excessive or less amounts of additive would lead to a slight decreased yield, and 2.0 equiv of additive AcOH was the optimized choice (Table 1, entries 14 and 21). In addition, increasing the temperature from 20 to 120 °C could enhance the reaction efficacy, and a good yield of 65 % could be obtained at 100 °C (Table 1, entries 14 and 22–25). Amination of benzoxazole **1a** was not observed in the absence of either TBHP or TBAI, indicating that the TBAI/TBHP combination is crucial for the reaction (Table 1, entries 26 and 27). When the microwave irradiation was not used, only a 50 % yield was obtained after 12 h (Table 1, entry 28). Microwave-assisted direct amination of benzoxazoles was an effective technique, which led to shorter reaction time and increased yield, matched with green chemistry protocols.

Under the optimized conditions, the scope of this oxidative C–H amination reaction was investigated with respect to azole under the same conditions (Table 1, entry 14). Regarding the benzoxazole moiety, several functional groups including electron-donating (methyl, *tert*-butyl) and electron-withdrawing (chloro, nitro) substituents were tolerated well (Table 2). Notably, the electronic

nature of the substituents on the phenyl ring of benzoxazoles affected the reaction yield, such as 5-methylbenzoxazole and 5-*tert*-butylbenzoxazole, containing the electron-donating substituents, increased the yields of products (Table 2, **3b** and **3c**); the effect is the reverse with electron-withdrawing substituents (Table 2, **3d** and **3e**). A reaction with 5-nitrobenzoxazole afforded the corresponding product with a sharply lower yield (45 %). It is noteworthy that a chloro substituent was compatible under standard conditions to give the corresponding functionalized amine products such as **3d** in good yield. Unfortunately, benzothiazole did not afford the desired products **3f**. The lower reactivity of the substrate observed here is probably due to their weaker acidity.

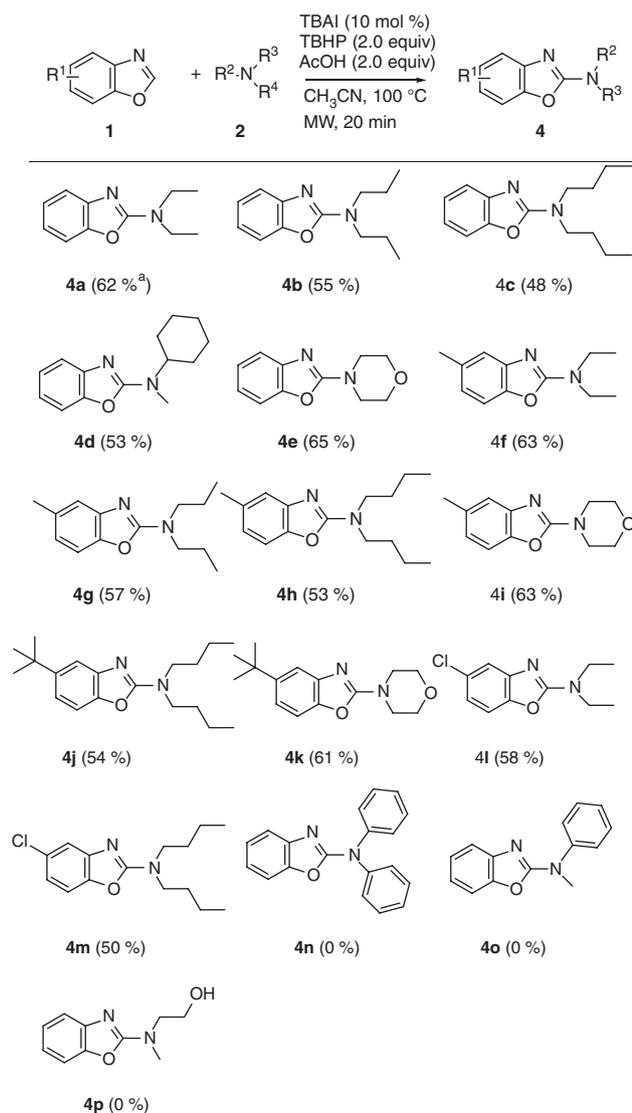
Next, the scope of this reaction with a variety of tertiary amines was investigated. As shown in Table 3, almost all linear alkyl tertiary amines with linear alkyl substituents, bearing α -H adjacent to the nitrogen atom, provided the desired products **4a–4d**, **4f–4h**, **4j**, **4l**, and **4m** in 48–63 % yield. Furthermore, with the carbon chain of acyclic tertiary amines increasing, the yield of products decreased from 65 to 48 % (Table 2, **3a**, and Table 3, **4a–4c**). This might be attributed to the steric hindrance of tertiary amines. In addition to acyclic tertiary amines, cyclic amines could be used in this transformation. It was gratifying to find that *N*-methyl morpholine reacted exclusively at the exocyclic C–N bond to give cyclic amines **4e**, **4i**, and **4k** in 61–65 % yield. Unfortunately, no product **4n** formation was observed with triphenylamine as an amino group source, in which no C–H bond in the α -position of the nitrogen atom is contained, thus suggesting that α -H

Table 2: Synthesis of *N,N*-dimethyl azole-2-amines from substituted benzoxazoles and trimethylamine.



Reaction conditions: **1** (0.25 mmol), trimethylamine **2a** (0.75 mmol), TBAI (10 mol%), TBHP (2.0 equiv), and AcOH (2.0 equiv) in 1.5 mL CH₃CN solvent at 100 °C under microwave irradiation for 20 min.

^aIsolated yields.

Table 3: Synthesis of benzoxazol-2-amine derivatives from benzoxazoles and tertiary amines.

Reaction conditions: **1** (0.25 mmol), tertiary amine **2** (0.75 mmol), TBAI (10 mol%), TBHP (2.0 equiv), and AcOH (2.0 equiv) in 1.5 mL of CH₃CN at 100 °C under microwave irradiation for 20 min.

^aIsolated yields.

is essential for the C–H amination under these conditions. However, when *N,N*-dimethylaniline as an amino source was employed, no product **4o** was obtained. Moreover, 2-(dimethylamino)ethanol with an unprotected hydroxyl group was not tolerated under the standard oxidizing reaction condition, no product **4p** was produced.

The bulky *N,N*-dimethyl-1-phenylmethanamine containing two kinds of α -H afforded two types of products (Table 4), **5** and **3**, with an almost 4:3 ratio, which indicated that the C–N bond of **II** position is broken more easily than that of **I** position. This might be attributed

to the fact that a sterically less hindered methyl group is much more facile for cleavage.

To gain an insight into the reaction mechanism, the following control experiments were performed under the standard reaction conditions. First, benzoxazole reacted with dimethylamine under the standard reaction conditions, and *N,N*-dimethyl-benzoxazol-2-amine **3a** was produced successfully, which indicated that dimethylamine was an important intermediate for the reaction of benzoxazole with trimethylamine. Meanwhile, when the radical scavenger TEMPO (2,2,6,6-tetramethylpiperidin-*N*-oxyl) was added to the reaction system, the reaction was inhibited (Scheme 2, Eq. b), which implies that the reaction presumably proceeds *via* a radical intermediate.

On the basis of the above results and previous reports [35–37], a plausible mechanism for this reaction is illustrated in Scheme 3. Initially, the *tert*-butoxyl and *tert*-butylperoxyl radicals were formed by the promotion of TBAI through I₂-I⁻ redox process. The generated *tert*-butoxy radical abstracts an α -H adjacent to the nitrogen atom of trimethylamine to afford radical **I**, followed by a single electron transfer oxidation to give an iminium intermediate **II**. Subsequently, the secondary amine **IV** is generated by hydrolysis of **II** through **III**. In the presence of AcOH, benzoxazole is protonated to form the reactive intermediate **V**. Then, the secondary amine **IV** immediately combines with the reactive intermediate **V**, leading to the intermediate **VI**. Finally, the desired amide product is produced through an oxidation process of the intermediate **VI**.

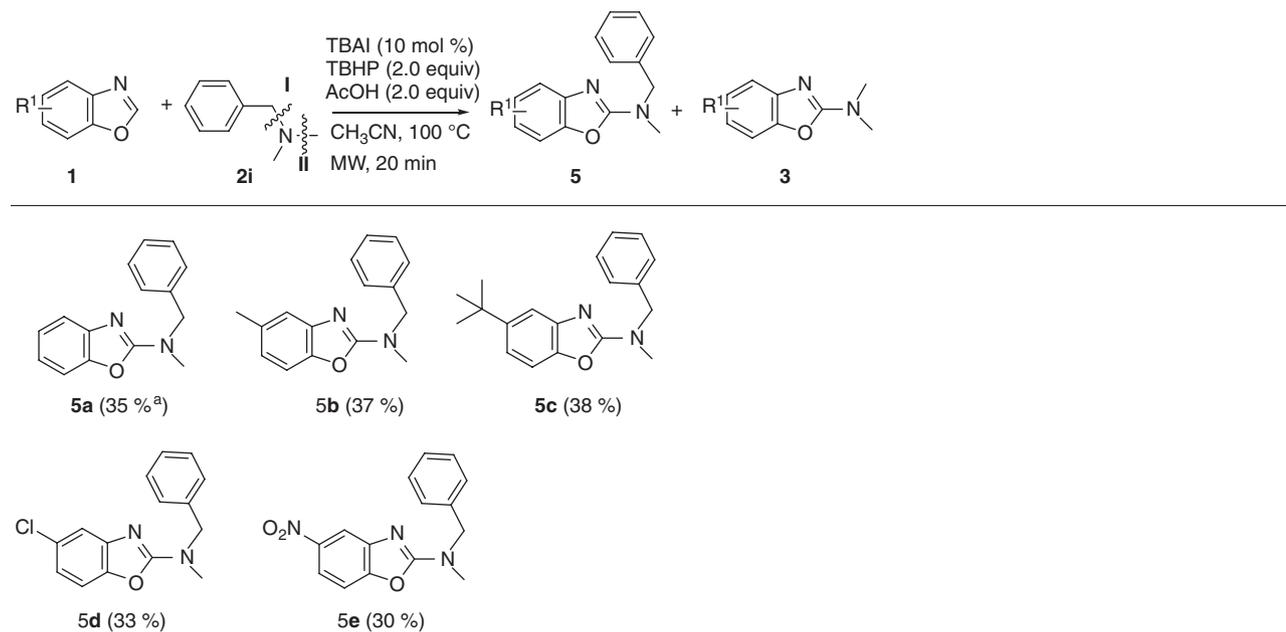
3 Conclusion

We have developed a mild, efficient, and green ⁿBu₄NI-catalyzed direct oxidative amination of benzoxazole with tertiary amines to form a 2-aminobenzoxazole derivative under microwave radiation. A wide range of benzoxazole derivatives containing electron-donating and electron-withdrawing groups were coupled with various tertiary amines, which included linear and cyclic amines. The present method constitutes a user-friendly and environmentally benign reaction for C–N bond formation of benzoxazoles.

4 Experimental section

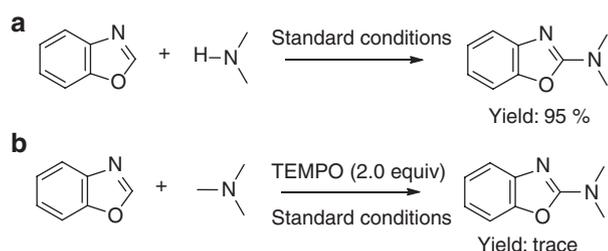
4.1 General

Anhydrous solvents were obtained by standard procedure. All substrates were purchased from J & K

Table 4: Direct amination of benzoxazole with *N,N*-dimethyl-1-phenylmethanamine.

Reaction conditions: **1** (0.25 mmol), *N,N*-dimethyl-1-phenylmethanamine **2i** (0.75 mmol), TBAI (10 mol%), TBHP (2.0 equiv), and AcOH (2.0 equiv) in 1.5 mL of CH_3CN solvent at 100 °C under microwave irradiation for 20 min.

^aIsolated yields.

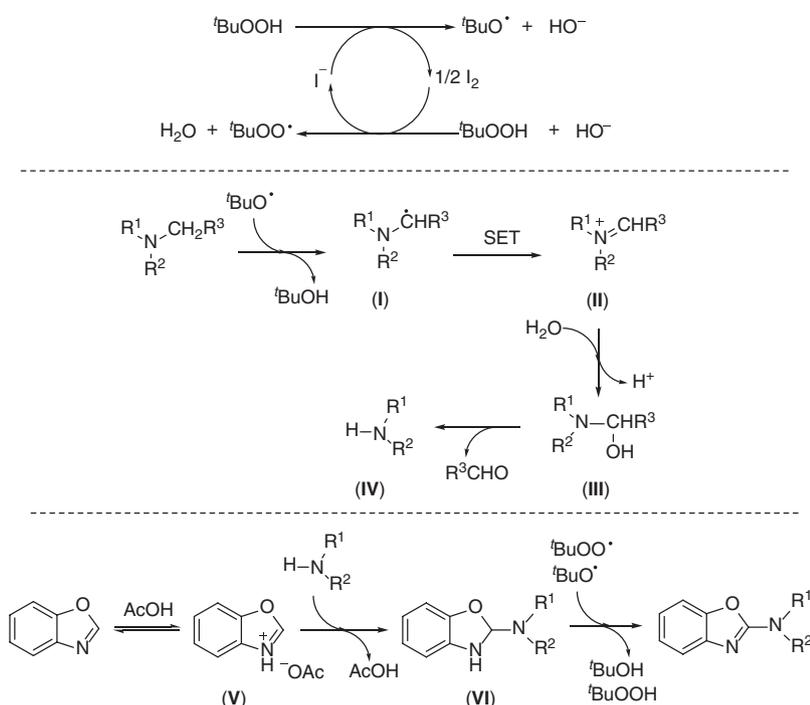
**Scheme 2:** Investigation of the reaction mechanism.

Scientific Ltd. and were used without further purification. Column chromatography was performed using 200–300 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 or 365 nm). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 400-MHz spectrometer. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad), coupling constants in hertz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. High-resolution mass spectra

(HRMS) were obtained on a Q-TOF instrument using the ESI technique. IR spectra were recorded on a Shimadzu IR-408 Fourier transform infrared spectrophotometer using a thin film supported on KBr pellets. Melting points were measured on an XT4A microscopic apparatus and are uncorrected.

4.2 General procedure for the synthesis of benzoxazol-2-amine derivatives

Benzoxazole **1** (0.25 mmol), tertiary amines **2** (0.75 mmol), TBAI (0.025 mmol, 10 mg), TBHP (70 % aqueous solution, 0.5 mmol), and AcOH (0.5 mmol, 30 mg) in CH_3CN (1.5 mL) were added to a 5-mL microwave reaction tube. The reaction mixture was put into a microwave reactor at 100 °C for 20 min. After completion of the reaction, the mixture was quenched by addition of a saturated solution of sodium disulfite (1.0 mL) and a saturated solution of sodium hydrogen carbonate (2.0 mL). Then the mixture was extracted with ethyl acetate (3×5 mL), combined organic phases were dried over anhydrous Na_2SO_4 , and the organic solvent was removed under vacuum. The crude residue was purified by chromatography on a silica gel column using ethyl acetate-petroleum ether (1:5 to 2:1) as eluant to obtain the desired product.



Scheme 3: Proposed mechanism for the amination reaction of benzoxazole.

4.2.1 *N,N*-dimethylbenzo[*d*]oxazol-2-amine (3a)

Orange solid; m.p. 83–84 °C (from chloroform; lit. [23]: 80–82 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.35 (dd, *J* = 7.8 Hz, *J* = 0.7 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.14 (td, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 6.98 (td, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 3.17 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.1, 149.1, 143.6, 123.8 (CH), 120.2 (CH), 115.9 (CH), 108.6 (CH), 37.7 (CH₃). – MS ((+)-ESI): *m/z* = 163.3 (calcd. 163.1 for C₉H₁₁N₂O, [M+H]⁺).

4.2.2 *N,N*,5-trimethylbenzo[*d*]oxazol-2-amine (3b)

Light orange solid; m.p. 70–71 °C (from chloroform; lit. [23]: 68–70 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.15 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.78 (dd, *J* = 8.1 Hz, *J* = 0.8 Hz, 1H), 3.16 (s, 6H), 2.37 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.2, 147.2, 143.7, 133.5, 120.8 (CH), 116.4 (CH), 107.9 (CH), 37.6 (CH₃), 21.5 (CH₃). – MS ((+)-ESI): *m/z* = 177.2 (calcd. 177.1 for C₁₀H₁₃N₂O, [M+H]⁺).

4.2.3 5-(*tert*-Butyl)-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3c)

Colorless solid; m.p. 68–69 °C (from chloroform; lit. [20]: 70–72 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.42

(d, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H), 3.16 (s, 6H), 1.33 (s, 9H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.3, 147.3, 147.0, 143.3, 117.3 (CH), 113.2 (CH), 107.6 (CH), 37.6 (CH₃), 34.7, 31.8 (CH₃). – MS ((+)-ESI): *m/z* = 219.3 (calcd. 219.1 for C₁₃H₁₉N₂O, [M+H]⁺).

4.2.4 5-Chloro-*N,N*-dimethylbenzo[*d*]oxazol-2-amine (3d)

White solid; m.p. 84–85 °C (from chloroform; lit. [23]: 83–85 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.29 (d, *J* = 2.1 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* = 8.4, *J* = 2.1 Hz, 1H), 3.18 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.7, 147.7, 145.0, 129.1, 119.9 (CH), 116.0 (CH), 109.0 (CH), 37.6 (CH₃). – MS ((+)-ESI): *m/z* = 197.2 (calcd. 197.0 for C₉H₁₀ClN₂O, [M+H]⁺).

4.2.5 *N,N*-dimethyl-5-nitrobenzo[*d*]oxazol-2-amine (3e)

Yellow solid; m.p. 168–170 °C (from chloroform; lit. [23]: 166–168 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 8.12 (d, *J* = 2.3 Hz, 1H), 7.95 (dd, *J* = 8.4 Hz, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 3.23 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 164.4, 153.0, 145.0, 144.5, 116.7 (CH), 111.3 (CH), 109.0 (CH), 37.6 (CH₃). – MS ((+)-ESI): *m/z* = 208.2 (calcd. 208.1 for C₉H₁₀N₃O₃, [M+H]⁺).

4.2.6 *N,N*-diethylbenzo[*d*]oxazol-2-amine (4a) [13]

Colorless liquid. – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.35$ (dd, $J = 7.8$ Hz, $J = 0.6$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.14 (td, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H), 6.98 (td, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H), 3.58 (q, $J = 7.1$ Hz, 4H), 1.28 (t, $J = 7.1$ Hz, 6H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.2$, 148.8, 143.6, 123.8 (CH), 119.9 (CH), 115.8 (CH), 108.5 (CH), 42.9 (CH_2), 13.5 (CH_3). – MS ((+)-ESI): $m/z = 191.3$ (calcd. 191.1 for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.7 *N,N*-dipropylbenzo[*d*]oxazol-2-amine (4b) [13]

Light yellow liquid. – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.34$ (d, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.13 (td, $J = 7.8$ Hz, $J = 1.0$ Hz, 1H), 6.97 (td, $J = 7.8$ Hz, $J = 1.0$ Hz, 1H), 3.48 (t, $J = 7.6$ Hz, 4H), 1.71 (m, 4H), 0.96 (t, $J = 7.6$ Hz, 6H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.7$, 148.7, 143.7, 123.7 (CH), 119.9 (CH), 115.8 (CH), 108.5 (CH), 50.3 (CH_2), 21.2 (CH_2), 11.2 (CH_3). – MS ((+)-ESI): $m/z = 219.3$ (calcd. 219.1 for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.8 *N,N*-dibutylbenzo[*d*]oxazol-2-amine (4c) [13]

Light yellow liquid. – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.34$ (dd, $J = 7.8$ Hz, $J = 0.6$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.13 (td, $J = 7.8$ Hz, $J = 1.1$ Hz, 1H), 6.97 (td, $J = 7.8$ Hz, $J = 1.1$ Hz, 1H), 3.50 (t, $J = 7.5$ Hz, 4H), 1.66 (m, 4H), 1.37 (m, 4H), 0.96 (t, $J = 7.5$ Hz, 6H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.7$, 148.7, 143.7, 123.7 (CH), 119.8 (CH), 115.8 (CH), 108.5 (CH), 48.3 (CH_2), 30.1 (CH_2), 20.0 (CH_2), 13.9 (CH_3). – MS ((+)-ESI): $m/z = 247.1$ (calcd. 247.2 for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.9 *N*-cyclohexyl-*N*-methylbenzo[*d*]oxazol-2-amine (4d) [38]

Yellow viscous liquid. – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.34$ (d, $J = 7.8$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.13 (td, $J = 7.8$ Hz, $J = 0.9$ Hz, 1H), 6.97 (td, $J = 7.8$ Hz, $J = 0.9$ Hz, 1H), 4.17–4.09 (m, 1H), 3.06 (s, 3H), 1.87–1.82 (m, 4H), 1.70 (d, $J = 13.0$ Hz, 1H), 1.68–1.42 (m, 4H), 1.18–1.13 (m, 1H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.7$, 148.7, 143.6, 123.8 (CH), 119.9 (CH), 115.8 (CH), 108.5 (CH), 56.7 (CH), 29.9 (CH_2), 29.5 (CH), 25.6 (CH_2), 25.5 (CH_2). – MS ((+)-ESI): $m/z = 231.2$ (calcd. 231.1 for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.10 2-Morpholinobenzo[*d*]oxazole (4e)

Pale yellow solid; m.p. 91–92 °C (from chloroform; lit. [28]): 90–94 °C). – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.37$ (dd, $J = 7.8$ Hz, $J = 0.6$ Hz, 1H), 7.27 (d, $J = 6.4$ Hz, 1H), 7.18 (td, $J = 7.8$ Hz, $J = 1.0$ Hz, 1H), 7.04 (td, $J = 7.8$ Hz, $J = 1.0$ Hz, 1H), 3.83–3.81 (m, 4H), 3.70–3.68 (m, 4H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.1$, 148.7, 142.8, 124.0 (CH), 120.9 (CH), 116.5 (CH), 108.8 (CH), 66.2 (CH_2), 45.7 (CH_2). – MS ((+)-ESI): $m/z = 205.2$ (calcd. 205.0 for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$, $[\text{M}+\text{H}]^+$).

4.2.11 *N,N*-diethyl-5-methylbenzo[*d*]oxazol-2-amine (4f) [20]

Yellow viscous liquid. – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.15$ (s, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.78 (dd, $J = 8.0$ Hz, $J = 0.9$ Hz, 1H), 3.57 (q, $J = 7.1$ Hz, 4H), 2.38 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 4H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.4$, 146.9, 143.7, 133.4, 120.5 (CH), 116.2 (CH), 107.8 (CH), 42.9 (CH_2), 21.5 (CH_3), 13.5 (CH_3). – MS ((+)-ESI): $m/z = 205.2$ (calcd. 205.1 for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.12 5-Methyl-*N,N*-dipropylbenzo[*d*]oxazol-2-amine (4g)

Colorless solid; m.p. 39–40 °C (from chloroform; lit. [13]: 38–40 °C). – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.15$ (s, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.77 (d, $J = 8.1$ Hz, 1H), 3.46 (t, $J = 7.4$ Hz, 4H), 2.38 (s, 6H), 1.75–1.65 (m, 4H), 0.95 (t, $J = 7.4$ Hz, 6H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.9$, 146.9, 143.9, 133.4, 120.5 (CH), 116.2 (CH), 107.8 (CH), 50.3 (CH_2), 21.5 (CH_3), 21.2 (CH_2), 11.2 (CH_3). – MS ((+)-ESI): $m/z = 233.3$ (calcd. 233.1 for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.13 *N,N*-dibutyl-5-methylbenzo[*d*]oxazol-2-amine (4h)

Colorless solid; m.p. 60–61 °C (from chloroform; lit. [13]: 58–60 °C). – ^1H NMR (400.13 MHz, CDCl_3): $\delta = 7.14$ (s, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 3.48 (t, $J = 7.6$ Hz, 4H), 2.37 (s, 3H), 1.68–1.60 (m, 4H), 1.42–1.32 (m, 4H), 0.95 (t, $J = 7.6$ Hz, 6H). – ^{13}C NMR (100.61 MHz, CDCl_3): $\delta = 162.8$, 146.9, 143.8, 133.3, 120.4 (CH), 116.2 (CH), 107.8 (CH), 48.3 (CH_2), 30.2 (CH_2), 21.5 (CH_3), 20.0 (CH_2), 13.9 (CH_3). – MS ((+)-ESI): $m/z = 261.3$ (calcd. 261.1 for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.14 5-Methyl-2-morpholinobenzo[d]oxazole (4i)

White solid; m.p. 120–121 °C (from chloroform; lit. [24]: 119–122 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.16 (s, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.82–3.80 (m, 4H), 3.68–3.66 (m, 4H), 2.39 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 162.2, 146.9, 142.9, 133.7, 121.6 (CH), 116.8 (CH), 108.1 (CH), 66.2 (CH₂), 45.7 (CH₂), 21.5 (CH₃). – MS ((+)-ESI): *m/z* = 219.3 (calcd. 219.1 for C₁₂H₁₅N₂O₂, [M+H]⁺).

4.2.15 5-(*tert*-Butyl)-*N,N*-dibutylbenzo[d]oxazol-2-amine (4j) [13]

Colorless viscous liquid. – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.42 (d, *J* = 1.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 3.49 (t, *J* = 7.5 Hz, 4H), 1.68–1.61 (m, 4H), 1.41–1.36 (m, 4H), 1.33 (s, 9H), 0.95 (t, *J* = 7.5 Hz, 6H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 162.9, 147.1, 146.7, 143.5, 116.9 (CH), 112.9 (CH), 107.5 (CH), 48.3 (CH₂), 34.7, 31.8 (CH₃), 30.1 (CH₂), 20.0 (CH₂), 13.9 (CH₃). – MS ((+)-ESI): *m/z* = 303.3 (calcd. 303.2 for C₁₉H₃₁N₂O, [M+H]⁺).

4.2.16 5-(*tert*-Butyl)-2-morpholinobenzo[d]oxazole (4k) [39]

Colorless solid. – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.43 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 3.81 (t, *J* = 4.6 Hz, 4H), 3.67 (t, *J* = 4.6 Hz, 4H), 1.34 (s, 9H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 162.3, 147.5, 146.7, 142.6, 118.1 (CH), 113.6 (CH), 107.9 (CH), 66.2 (CH₂), 45.8 (CH₂), 34.8, 31.7 (CH₃). – MS ((+)-ESI): *m/z* = 261.3 (calcd. 261.2 for C₁₅H₂₁N₂O₂, [M+H]⁺).

4.2.17 5-Chloro-*N,N*-diethylbenzo[d]oxazol-2-amine (4l) [24]

Yellow liquid. – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.29 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 3.57 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 162.9, 147.5, 145.0, 129.1, 119.7 (CH), 115.9 (CH), 108.9 (CH), 43.0 (CH₂), 13.4 (CH₃). – MS ((+)-ESI): *m/z* = 225.2 (calcd. 225.1 for C₁₁H₁₄ClN₂O, [M+H]⁺).

4.2.18 *N,N*-dibutyl-5-chlorobenzo[d]oxazol-2-amine (4m)

White solid; m.p. 63–65 °C (from chloroform; lit. [13]: 60–61 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.29 (d, *J* =

2.0 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 3.49 (t, *J* = 7.5 Hz, 4H), 1.69–1.61 (m, 4H), 1.42–1.33 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 6H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.3, 147.4, 129.0, 119.6 (CH), 115.8 (CH), 108.9 (CH), 48.4 (CH₂), 30.0 (CH₂), 19.9 (CH₂), 13.9 (CH₃). – MS ((+)-ESI): *m/z* = 281.2 (calcd. for C₁₅H₂₂N₂O, [M+H]⁺).

4.2.19 *N*-benzyl-*N*-methylbenzo[d]oxazol-2-amine (5a)

White solid; m.p. 52–53 °C (from chloroform; lit. [28]: 50–54 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.45 (d, *J* = 7.8 Hz, 1H), 7.39–7.29 (m, 6H), 7.21 (td, *J* = 7.8 Hz, *J* = 1.1 Hz, 1H), 7.05 (td, *J* = 7.8 Hz, *J* = 1.1 Hz, 1H), 4.77 (s, 2H), 3.15 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.0, 149.0, 143.5, 136.5, 128.8 (CH), 127.8 (CH), 127.7 (CH), 124.0 (CH), 120.4 (CH), 116.2 (CH), 108.8 (CH), 53.9 (CH₂), 35.2 (CH₃). – MS ((+)-ESI): *m/z* = 239.3 (calcd. 239.1 for C₁₅H₁₅N₂O, [M+H]⁺).

4.2.20 *N*-benzyl-*N*,5-dimethylbenzo[d]oxazol-2-amine (5b)

White solid; m.p. 51–52 °C (from chloroform; lit. [13]: 50–51 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.39–7.31 (m, 5H), 7.21 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 4.77 (s, 2H), 3.15 (s, 3H), 2.43 (s, 3H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.2, 147.2, 143.6, 136.5, 133.6, 128.7 (CH), 127.7 (CH), 127.6 (CH), 121.0 (CH), 116.5 (CH), 108.1 (CH), 53.8 (CH₂), 35.2 (CH₃), 21.6 (CH₃). – MS ((+)-ESI): *m/z* = 253.3 (calcd. 253.1 for C₁₆H₁₇N₂O, [M+H]⁺).

4.2.21 *N*-benzyl-5-(*tert*-butyl)-*N*-methylbenzo[d]oxazol-2-amine (5c)

Colorless solid. – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.55 (s, 1H), 7.38–7.31 (m, 5H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.11 (dd, *J* = 8.4 Hz, *J* = 2.3 Hz, 1H), 4.77 (s, 2H), 3.14 (s, 3H), 1.41 (s, 9H). – ¹³C NMR (100.61 MHz, CDCl₃): δ = 163.2, 147.4, 147.0, 143.4, 136.5, 128.7 (CH), 127.7 (CH), 127.6 (CH), 117.6 (CH), 113.3 (CH), 107.8 (CH), 53.8 (CH₂), 35.1 (CH₃), 34.8, 31.9 (CH₃). – HRMS ((+)-ESI): *m/z* = 295.1807 (calcd. 295.1805 for C₁₉H₂₃N₂O, [M+H]⁺).

4.2.22 *N*-benzyl-5-chloro-*N*-methylbenzo[d]oxazol-2-amine (5d)

Pale brown solid, mp 71–72 °C (from chloroform; lit. [40]: 69–70 °C). – ¹H NMR (400.13 MHz, CDCl₃): δ = 7.35–7.25 (m, 6H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.95 (dd, *J* = 8.4 Hz, *J* = 2.5

Hz, 1H), 4.74 (s, 2H), 3.12 (s, 3H). – ^{13}C NMR (100.61 MHz, CDCl_3): δ = 163.7, 147.6, 144.9, 136.1, 129.3, 128.8 (CH), 127.8 (CH), 127.6 (CH), 120.1 (CH), 116.2 (CH), 109.1 (CH), 53.8 (CH_2), 35.2 (CH_3). – MS ((+)-ESI): m/z = 273.3 (calcd. 273.1 for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{O}$, $[\text{M}+\text{H}]^+$).

4.2.23 *N*-benzyl-*N*-methyl-5-nitrobenzo[d]oxazol-2-amine (5e)

Colorless solid. – ^1H NMR (400.13 MHz, CDCl_3): δ = 8.19 (d, J = 2.2 Hz, 1H), 8.00 (dd, J = 8.7 Hz, J = 2.2 Hz, 1H), 7.39–7.26 (m, 6H), 4.78 (s, 2H), 3.17 (s, 3H). – ^{13}C NMR (100.61 MHz, CDCl_3): δ = 164.5, 152.9, 145.2, 144.5, 135.6, 128.9 (CH), 128.1 (CH), 127.7 (CH), 116.9 (CH), 111.6 (CH), 108.3 (CH), 54.0 (CH_2), 35.2 (CH_3). – HRMS ((+)-ESI): m/z = 284.1032 (calcd. 284.1030 for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_3$, $[\text{M}+\text{H}]^+$).

5 Supporting information

^1H NMR and ^{13}C NMR spectra of **3a–3e**, **4a–4m**, and **5a–5e** are given as supporting information available online (DOI: 10.1515/znb-2015-0212).

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