

## An Efficient Solid-phase Parallel Synthesis of 2-Amino and 2-Amidobenzo[*d*]oxazole Derivatives *via* Cyclization Reactions of 2-Hydroxyphenylthiourea Resin

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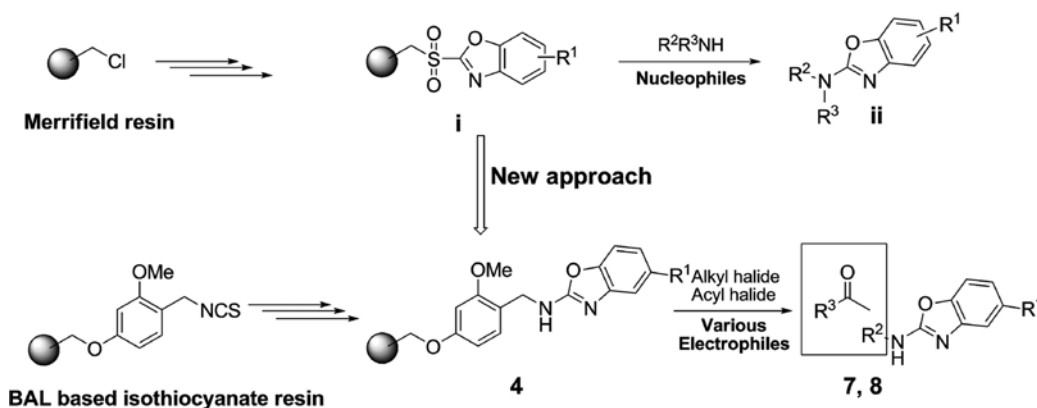
An efficient solid-phase methodology has been developed for the synthesis of 2-amino and 2-amidobenzo[*d*]oxazole derivatives. The key step in this procedure involves the preparation of polymer-bound 2-aminobenzo[*d*]oxazole resins **4** by cyclization reaction of 2-hydroxyphenylthiourea resin **3**. The resin-bound 2-hydroxyphenylthiourea **3** is produced by the addition of 2-aminophenol to the isothiocyanate-terminated resin **2** and serve as a key intermediate for the linker resin. This core skeleton 2-aminobenzo[*d*]oxazole resin **4** undergoes functionalization reaction with various electrophiles, such as alkylhalides and acid chlorides to generate 2-amino and 2-amidobenzo[*d*]oxazole resins **5** and **6** respectively. Finally, 2-amino and 2-amidobenzo[*d*]oxazole derivatives **7** and **8** are then generated in good yields and purities by cleavage of the respective resins **5** and **6** under trifluoroacetic acid (TFA) in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>).

**Key Words** : Solid-phase parallel synthesis, Heterocycles, Benzo[*d*]oxazole, 2-Hydroxyphenylthiourea linker, BOMBA resin

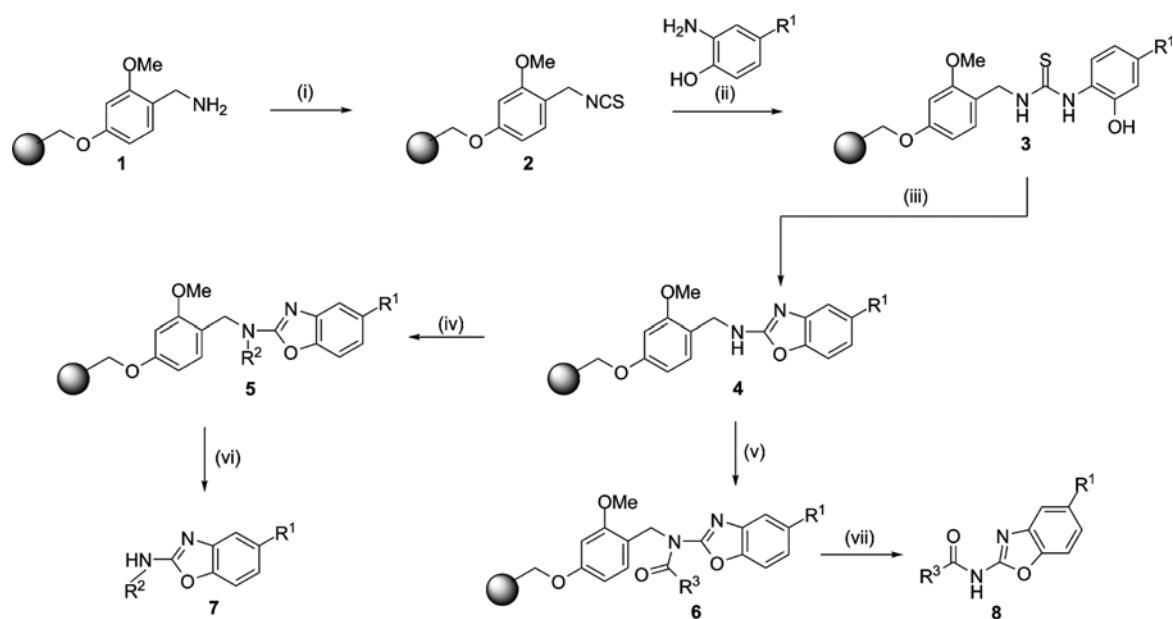
### Introduction

Heterocyclic compounds serve as ideal scaffolds on which pharmacophores can be appended to yield potent and selective drugs.<sup>1</sup> This is especially true for five-member ring heterocyclic compounds, which are core components of a large number of substances that possess a wide range of interesting biological activities. In this respect, the potential of the benzo[*d*]oxazole scaffold to serve as a privileged structure for the generation of drug-like libraries in drug-discovery programs has been plentifully demonstrated in medicinal chemistry.<sup>2</sup> As part of a recent drug discovery effort, we explored target libraries that are based on the five-membered heterocyclic privileged structures.<sup>3</sup> Even though, benzo[*d*]oxazole derivatives are of particular interest in medicinal chemistry and, consequently, have been targets of a number of solution- and solid-phase synthetic studies,<sup>4</sup> the methods developed to date for the preparation of benzo-

[*d*]oxazole libraries do not have sufficiently high levels of diversity. Therefore, we have previously concentrated our efforts on describing a facile and rapid solid-phase strategy for the preparation of a small molecule library based on the benzo[*d*]oxazole scaffold. And, we reported a useful method for the solid-phase synthesis of 2-aminobenzo[*d*]oxazole derivatives using thioether linkage as the safety-catch linker.<sup>5</sup> In the processes, the choice of the linker that serves to attach the library scaffold to the polymer support is critical. Thus, a variety of elegant linking methods have been developed (*i.e.*, safety-catch linkers<sup>6</sup>) that enable additional diversity to be introduced into the products during the cleavage reactions. The sulfone linker is an example of a safety-catch linker that can be cleaved from resins by using nucleophilic substitution reactions with amines.<sup>7</sup> We have utilized this general methodology to produce amine-functionalized 2-aminobenzo[*d*]oxazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole, and thiazole libraries through consecutive oxidation and amine-promoted



**Scheme 1.** Strategy used to make various 2-amino and 2-amidobenzo[*d*]oxazole libraries *via* thiourea linker.



**Scheme 2.** Solid-phase synthesis route to the various 2-amino and 2-amidobenzo[*d*]oxazole derivatives.

*Reagents and conditions:* i) CS<sub>2</sub>, Et<sub>3</sub>N, *p*-TsCl, THF, 0 °C to rt, 18 h; ii) 2-Aminophenol, Et<sub>3</sub>N, 1,4-dioxane, 80 °C, 12 h; iii) HgO, 1,4-dioxane, 80 °C, 24 h; iv) Alkyl halides, *t*-BuOK, *N*-methylpyrrolidone (NMP), 60 °C, 24 h; v) Acyl halides, LiHMDS, THF, 60 °C, 12 h; vi) TFA:CH<sub>2</sub>Cl<sub>2</sub> (1:4), 40 °C, 12 h; and vii) TFA:CH<sub>2</sub>Cl<sub>2</sub> (1:4), rt, 3 h.

cleavage of thiourea linkages produced in carbon disulfide mediated reactions of the Merrifield resin.<sup>5,8</sup> However, our developed method suffered a limitation in that we couldn't efficiently introduce various substituents such as amine and amides on the 2-position of the benzo[*d*]oxazole core skeleton by nucleophilic substitution reaction at the last cleavage step as shown Scheme 1 (resin **i** → compound **ii**). Moreover the nucleophile substitution reaction of the last cleavage step could only progress with various amine nucleophiles, except for alcohols and thiols. As a result of these limitations, we undertook an investigation aimed at developing efficient and simple parallel synthesis methods to produce various 2-amino and 2-amidobenzo[*d*]oxazole derivatives by a new type of solid-phase linker which can be used to introduce various substituents on the 2-position of benzo[*d*]oxazole at the last cleavage step. Herein we report our recent progress on this project which includes the first solid-phase synthesis protocol for 2-amino and 2-amidobenzo[*d*]oxazole derivatives **7** and **8** (Scheme 1; resin **4** → compound **7**).

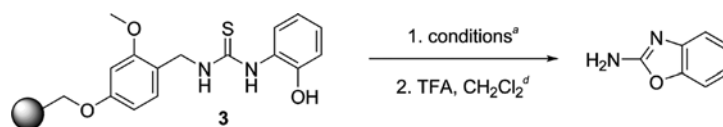
## Results and Discussion

The overall synthesis strategy used to prepare the target 2-amino and 2-amidobenzo[*d*]oxazole analogues **7** and **8** is outlined in Scheme 2. The initial solid phase synthesis route that we developed to prepare for substances containing the benzo[*d*]oxazole scaffold involved the formation of the intermediate 2-aminobenzo[*d*]oxazole resin **4** from solid-supported 2-hydroxyphenylthiourea linker **3**, which is derived from the isothiocyanate-terminated resin **2**. Next cyclization of thiourea resin **3** in the presence of HgO produced the compound **4** as the key intermediate resin. Subsequently, *N*-

alkylation and *N*-acylation reactions respectively furnished a variety of resins **5** and **6**. Finally, the desired 2-amino and 2-amido substituted benzo[*d*]oxazole derivatives **7** and **8** were smoothly obtained by cleavage of linker from the 2-*N*-substituted resins **5** and **6**, respectively under the condition of dilute TFA in good yields and purities (Scheme 2).

For the solid-phase parallel synthesis methodology, we selected the backbone amide linker (BAL) resin **1**, because we have previously developed a facile and very useful method for synthesizing the isothiocyanate-terminated resin **2** using BAL resin **1**. Even though we have previously reported the synthesis of isothiocyanate-terminated resin **2** by reaction with thiophosgene (CSCl<sub>2</sub>) in the presence of triethylamine in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C to room temperature in high yield,<sup>10</sup> the starting reagent of CSCl<sub>2</sub> was very difficult to purchase from commercial chemical companies since it was designated a ban material of air-transport. Therefore, the effort was focused on the development of more efficient and convenient method for synthesizing the isothiocyanate-terminated resin **2**. In our results, we achieved a much higher yield and easier synthesis condition of the isothiocyanate-terminated resin **2** compared to the CSCl<sub>2</sub> reagent method by reaction with amine resin **1** and carbon disulfide (CS<sub>2</sub>) in the presence of triethylamine (Et<sub>3</sub>N) in tetrahydrofuran (THF) at 0 °C to room temperature, based on Wong's solution-phase synthesis.<sup>9</sup> The formation of resin **2** was confirmed by inspection of its attenuated total reflection (ATR) single bead Fourier transform infrared (FTIR) spectrum, which showed the presence of the typical isothiocyanate band at 2071 cm<sup>-1</sup>.

This kind of resin-bound isothiocyanate **2** reacts with 2-aminophenol in the presence of Et<sub>3</sub>N in 1,4-dioxane solvent at 80 °C to give 2-hydroxyphenyl thiourea **3** as the key



**Table 1.** Results from an investigation of conditions to promote cyclization of 2-hydroxyphenylthiourea resin **3** to 2-aminobenzo[d]oxazole resin **4**

Entry	Reagent <sup>a</sup>	Solvent	Yield <sup>b,c</sup> (%)	Entry	Reagent <sup>a</sup>	Solvent	Yield <sup>b,c</sup> (%)
<b>1</b>	FeCl <sub>3</sub>	THF	9	<b>5</b>	EDC	THF	20
<b>2</b>	CuCl/DIPEA	Toluene:CH <sub>3</sub> CN	5	<b>6</b>	HgO	CH <sub>3</sub> CN	34
<b>3</b>	DIB/Et <sub>3</sub> N	CH <sub>3</sub> CN	19	<b>7</b>	HgO	1,4-Dioxane	71
<b>4</b>	<i>p</i> -TsCl/NaOH	THF	20				

<sup>a</sup>5.0 equiv are used. <sup>b</sup>Four-step overall yields from BAL resin **1** (loading capacity of resin **1** is 1.1 mmolg<sup>-1</sup>) <sup>c</sup>Yield determined by LC/MS. <sup>d</sup>TFA:CH<sub>2</sub>Cl<sub>2</sub> (1:1), 40 °C, 12 h.

intermediate linker resin, signaled by the absence of the isothiocyanate band at 2071 cm<sup>-1</sup> and by the appearance of the thiourea peak at 1649 and 1585 cm<sup>-1</sup> (Figure 1, 3(c)). We made many attempts to find the suitable solid-phase cyclodesulfurization reaction conditions based on the known benzo[d]oxazole cyclization condition, such as FeCl<sub>3</sub>,<sup>12</sup> CuCl,<sup>13</sup> DIB,<sup>14</sup> *p*-TsCl,<sup>15</sup> EDC<sup>16</sup> and HgO<sup>11</sup> as shown in Table



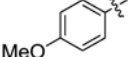
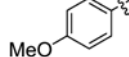

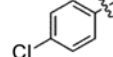
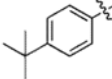

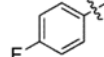

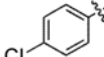


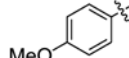

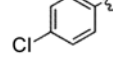
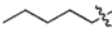


1. Our results show that 2-aminobenzo[d]oxazole resin **4** can be efficiently generated by cyclization of 2-hydroxyphenylthiourea resin **3** in the presence of HgO in 1,4-dioxane at 80 °C for 24 h.<sup>11</sup> (Table 1, entry 7). This effort demonstrated that the proposed procedure is one of the best methods in the solid-phase synthesis of 2-aminobenzo[d]oxazole derivatives *via* cyclodesulfurization in the presence of HgO in 1,4-

**Table 2.** Yields and purities of the *N*-alkylaminobenzo[d]oxazole derivatives **7**

Code	R <sup>1</sup>	R <sup>2</sup>	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>	Code	R <sup>1</sup>	R <sup>2</sup>	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>
<b>7a</b>	H		30	99	<b>7k</b>	MeO		25	94
<b>7b</b>	H		23	96	<b>7l</b>	MeO		20	99
<b>7c</b>	H		29	99	<b>7m</b>	MeO		35	93
<b>7d</b>	H		25	99	<b>7n</b>	MeO		35	97
<b>7e</b>	H		24	>99	<b>7o</b>	MeO		31	>99
<b>7f</b>	H		28	95	<b>7p</b>	Cl		38	99
<b>7g</b>	H		31	96	<b>7q</b>	Cl		32	98
<b>7h</b>	H		29	98	<b>7r</b>	Cl		33	99
<b>7i</b>	H		30	>99	<b>7s</b>	Cl		26	>99
<b>7j</b>	H	Me	20	99	<b>7t</b>	Cl		35	98

<sup>a</sup>Five-step overall yields from BAL resin **1** (loading capacity of resin **1** is 1.1 mmol/g). <sup>b</sup>All of the purified products were checked by LC/MS.

**Table 3.** Yields and purities of the *N*-(benzo[*d*]oxazol-2-yl)amide derivatives **8**

Code	R <sup>1</sup>	R <sup>2</sup>	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>	Code	R <sup>1</sup>	R <sup>2</sup>	Yield (%) <sup>a</sup>	Purity (%) <sup>b</sup>
<b>8a</b>	H		33	>99	<b>8k</b>	MeO		32	98
<b>8b</b>	H		27	>99	<b>8l</b>	MeO		45	98
<b>8c</b>	H		29	98	<b>8m</b>	MeO		24	99
<b>8d</b>	H		25	>99	<b>8n</b>	MeO		24	99
<b>8e</b>	H		29	>99	<b>8o</b>	MeO		16	99
<b>8f</b>	H		19	96	<b>8p</b>	Cl		43	96
<b>8g</b>	H		28	97	<b>8q</b>	Cl		46	98
<b>8h</b>	H		31	98	<b>8r</b>	Cl		31	98
<b>8i</b>	H		23	>99	<b>8s</b>	Cl		31	99
<b>8j</b>	H	Me	42	>99	<b>8t</b>	Cl		26	97

<sup>a</sup>Five-step overall yields from BAL resin **1** (loading capacity of resin **1** is 1.1 mmol/g). <sup>b</sup>All of the purified products were checked by LC/MS.

dioxane at 80 °C.

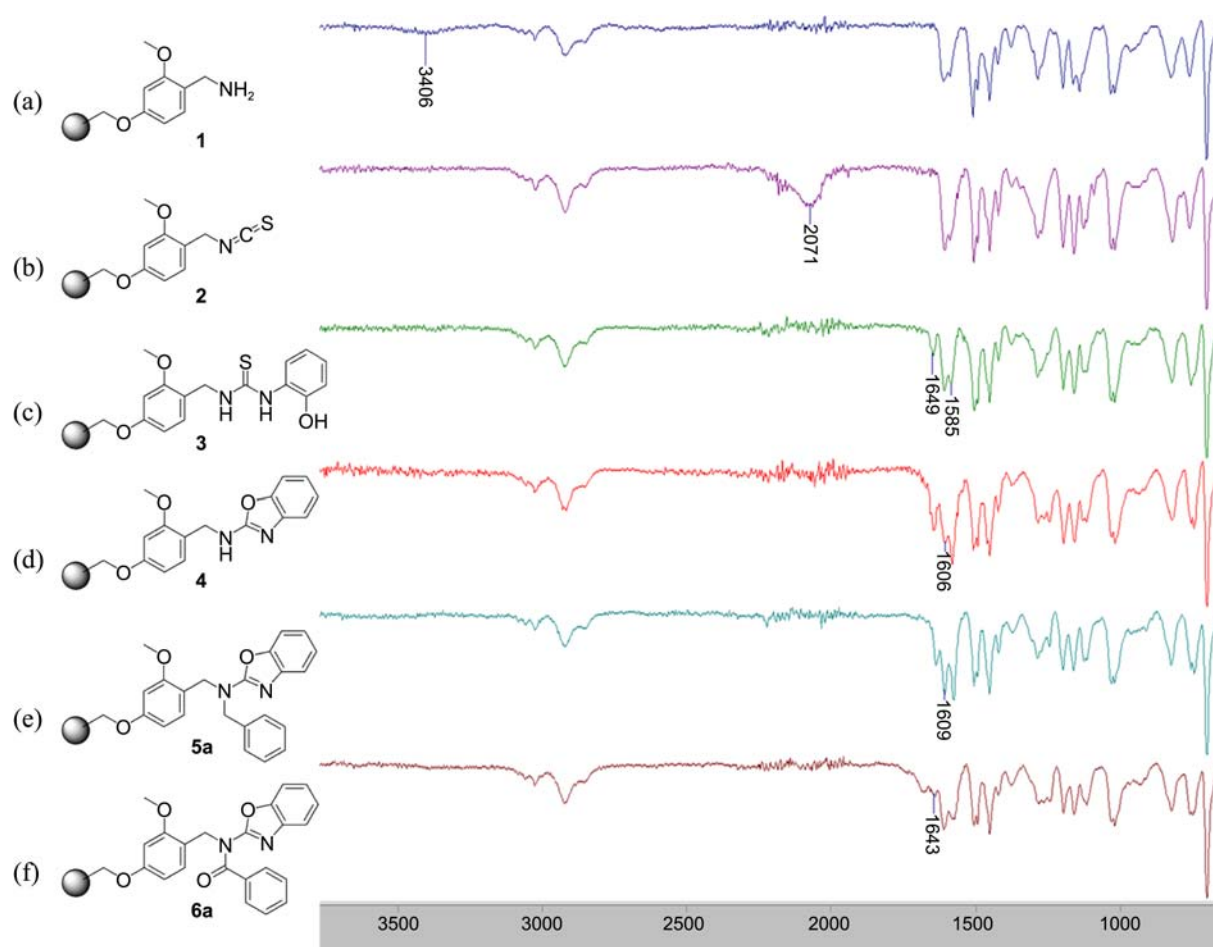
This process led to the formation of the 2-aminobenzo[*d*]oxazole resin **4**, whose single bead FTIR spectrum contained imine stretching bands at 1606 cm<sup>-1</sup> (Figure 1, **4(d)**). With the resin **4** in hand, we next turn our attention to the introduction of various alkyl and acyl substitution at the 2-*N* position on 2-aminobenzo[*d*]oxazole core skeleton resin **4**. Alkylation of 2-aminobenzo[*d*]oxazole resin **4** proceeded smoothly to give the desired *N*-alkylamino benzo[*d*]oxazole resin **5** when the resin was reacted with the various alkyl halide in the presence of *t*-BuOK in 1,4-dioxane solvent at 60 °C for 24 h. In this step, the progress of this reaction (R<sup>2</sup> = Bn) was monitored by ATR-FTIR spectroscopy, which have revealed the growth of the band intensity of the C-N bond at 1609 cm<sup>-1</sup> (Figure 1, **5a(e)**). Final cleavage of linker from the resin **5** was accomplished by treatment of TFA in CH<sub>2</sub>Cl<sub>2</sub> to give various *N*-alkylaminobenzo[*d*]oxazole derivatives. <sup>1</sup>H NMR spectroscopic properties of **7a**, following purified by passing through a short plug of silica, were identical to the corresponding substances produced by using solution-phase synthesis routes.

As shown by the data given in Table 2, the various desired *N*-substituted alkylamino benzo[*d*]oxazole derivatives **7** can be produced by this five-step route in high overall yields and

purities. It was possible to introduce various alkyl building blocks on the 2-amino groups of the benzo[*d*]oxazole core skeleton ring (**7a-7t**).

Next, the acylation reaction of 2-aminobenzo[*d*]oxazole resin **4** produced *N*-substituted amidobenzoxazole resin **6** with various acid chlorides in the condition of LiHMDS in THF solvent at 60 °C for 12 h. This progress of reaction (R<sup>3</sup> = Ph) was also monitored by ATR-FTIR spectroscopy, which revealed the appearance of an amide band at 1643 cm<sup>-1</sup> (Figure 1, **6a(f)**). This 2-amidobenzo[*d*]oxazole resin **6** could easily be converted to the *N*-substituted amidobenzoxazole derivatives **8** by treatment TFA in CH<sub>2</sub>Cl<sub>2</sub>. As shown by the data given in Table 2, various *N*-substituted amidobenzoxazole derivatives **8** (**8a-8t**) could be produced by this five-step route in high overall yields and purities.

In this research, an efficient solid-phase methodology has been developed for the synthesis of 2-aminobenzo[*d*]oxazole-based libraries. This solid-phase synthesis route proved much more efficient for generating various 2-aminobenzo[*d*]oxazole-based libraries **7** and **8** than our previously developed solid-phase synthesis method. The key diversification commences with a 2-aminobenzo[*d*]oxazole core skeleton resin **4** and relies on the alkylation or acylation of the 2-*N* position on the 2-aminobenzo[*d*]oxazole ring. This strategy, based on



**Figure 1.** ATR-FTIR spectra on single beads of 2-aminobenzo[d]oxazole resins **1** (a), **2** (b), **3**(c), **4** (d), **5a** (e), and **6a** (f).

an efficient solid-phase sequence, enables the construction of a large library and is potentially applicable for the preparation of other drug-like 2-aminobenzo[d]oxazole ring systems. Finally, the calculated physicochemical properties of members of the library constructed by using this approach are well distributed within reasonable, orally acceptable, drug-like ranges. Further studies in this area are underway, the results of which will be reported in due course.

### Experimental Section

**General Procedure for Synthesis.** All chemicals were reagent grade and used as purchased. Reactions were monitored by thin layer chromatography (TLC) analysis using Merck silica gel 60 F-254 thin layer plates or ATR-FTIR analysis using ATR-FTIR spectrometer (Smiths Detection). Flash column chromatography was carried out on Merck silica gel 60 (230-400 mesh). The crude products were purified by parallel chromatography using Isorea One (Biotage).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{d}$  units relative to deuterated solvent as an internal reference using a Bruker 400 MHz NMR instrument. Liquid chromatography-mass spectrometry (LC-MS/Agilent 6400) analysis was performed on an electrospray ionization (ESI) mass spectrometer with Diode-array detector (DAD) detection. LC-MS area

percentage purities of all products were determined by LC peak area analysis (Poroshell 120 EC- $\text{C}_{18}$  column, 4.6 mm  $\times$  100 mm; PDA detector at 254 nm; 70/30:  $\text{CH}_3\text{CN}/5$  mM  $\text{NH}_4\text{HCO}_2$ ). High-resolution mass spectrometry fast-atom bombardment (HRMS-FAB) spectra were obtained using API 4000Q TRAP LC/MS/MS system (Applied Biosystems).

**Representative Procedure for the Preparation of Isothiocyanate-terminated Resin (2).** To a mixture of BOMBA resin **1** (5.00 g, 5.5 mmol) in THF (80 mL) was added  $\text{Et}_3\text{N}$  (7.67 mL, 55.0 mmol) and  $\text{CS}_2$  (1.98 mL, 33.0 mmol) at 0  $^\circ\text{C}$ . The mixture was stirred at room temperature for 3 h, *p*-TsCl (5.24 g, 27.5 mmol) was added at 0  $^\circ\text{C}$ , and the mixture was stirred at rt for 15 h. The precipitate obtained by filtration of the mixture was washed with THF,  $\text{H}_2\text{O}$ , MeOH and  $\text{CH}_2\text{Cl}_2$  and dried in a vacuum oven. This process gave resin **2** (5.02 g) as a dark yellow solid. Single-Bead ATR-FTIR: 2071 ( $\text{N}=\text{C}=\text{S}$ ), 1607, 1505, 1492, 1450, 1420, 1374, 1284, 1195, 1158, 1125, 1089  $\text{cm}^{-1}$ .

**Representative Procedure for the Preparation of 2-Hydroxyphenylthiourea Resin (3a).** A mixture of isothiocyanate resin **2** (5.02 g, 5.5 mmol), 2-aminophenol (2.40 g, 22.0 mmol) and  $\text{Et}_3\text{N}$  (3.83 mL, 27.5 mmol) in 1,4-dioxane (80 mL) was stirred at 80  $^\circ\text{C}$  for 12 h. The resin was filtered and washed several times with  $\text{H}_2\text{O}$ , MeOH and  $\text{CH}_2\text{Cl}_2$  and then dried in a vacuum oven. Resin **3** was obtained as a light

brown solid (5.29 g). Single-Bead ATR-FTIR: 1649 (C=S), 1607, 1584 (C=S), 1503, 1492, 1450  $\text{cm}^{-1}$ .

**Representative Procedure for the Preparation of 2-Aminobenzo[d]xazole Resin (4a).** A mixture of 2-hydroxyphenylthiourea resin **3** (5.29 g, 5.5 mmol) and HgO (5.96 g, 27.5 mmol) in 1,4-dioxane (80 mL) was stirred at 80 °C for 24 h. The resin was filtered and excess HgO was dissolved with 10% HCl. The resin was washed in H<sub>2</sub>O the several times with MeOH and CH<sub>2</sub>Cl<sub>2</sub>, followed by washing with 10% triethylamine in CH<sub>2</sub>Cl<sub>2</sub> to neutralize the amine. Following the final wash with MeOH, the resin was dried in a vacuum oven. Resin **4** was black in color (5.20 g). Single-Bead ATR-FTIR: 1643, 1606 (C=N), 1579, 1506, 1491, 1450  $\text{cm}^{-1}$ .

**Representative Procedure for the Preparation of N-Benzylaminobenzo[d]xazole Resin (5a).** To a mixture of 2-aminobenzo[d]xazole resin **4** (150 mg, 0.15 mmol) in NMP (4 mL) was added *t*-BuOK (168 mg, 1.5 mmol) at room temperature. The resulting mixture was stirred for 1 h. Benzyl chloride (86.5  $\mu\text{L}$ , 0.75 mmol) was added, and the resulting mixture was stirred at 60 °C for 24 h. The resin was filtered and washed several times with H<sub>2</sub>O, MeOH and CH<sub>2</sub>Cl<sub>2</sub>, and then the resin was dried in a vacuum oven. Resin **5a** was obtained as a black solid (155 mg). Single-Bead ATR-FTIR: 1635, 1609 (C-N), 1575, 1504, 1493, 1451  $\text{cm}^{-1}$ .

**Representative Procedure for the Preparation of N-(benzo[d]oxazol-2-yl)benzamide Resin (6a).** To a mixture of 2-aminobenzo[d]oxazole resin **4** (150 mg, 0.15 mmol) in anhydrous THF (4 mL) was added lithium bis(trimethylsilyl)amides (LiHMDS) (126 mg, 0.75 mmol) at room temperature. The resulting mixture was stirred for 1 h. Benzoyl chloride (87.1  $\mu\text{L}$ , 0.75 mmol) was added, and the resulting mixture was stirred at 60 °C for 12 h. The resin was filtered and washed several times with H<sub>2</sub>O, MeOH and CH<sub>2</sub>Cl<sub>2</sub>, and then dried in a vacuum oven. Resin **6a** was obtained as a black solid (160 mg). Single-Bead ATR-FTIR: 3027, 2923, 1643 (C=O), 1609, 1577, 1571, 1504, 1492, 1450  $\text{cm}^{-1}$ .

**Representative Procedure for the First Generation Alkylation Reaction Step v, Preparation of N-Benzylbenzo[d]oxazol-2-amine (7a) from Resin (5a).** A mixture of *N*-benzylaminobenzo[d]xazole resin **5a** (155 mg, 0.15 mmol) and 2 mL of cleavage cocktail (TFA-CH<sub>2</sub>Cl<sub>2</sub> = 1:4, v/v) was shaken at 40 °C for 8 h. Filtration followed by washing the precipitate with CH<sub>2</sub>Cl<sub>2</sub> afforded a filtrate that was neutralized by saturated K<sub>2</sub>CO<sub>3</sub> solution. The filtrate was washed with water and dried over MgSO<sub>4</sub>. The solution was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/EtOAc, 3:1) to afford *N*-benzylbenzo[d]oxazol-2-amine **7a**. Yield (10 mg, 30%, five-step overall yield from BAL resin, loading capacity 1.1 mmol/g) as a white solid. mp 116.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46-7.27 (m, 6H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (td, *J* = 7.7, 0.8 Hz, 1H), 7.04 (td, *J* = 7.8, 1.0 Hz, 1H), 5.59 (s, 1H), 4.68 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.98, 148.62, 142.93, 137.71, 128.84, 127.86, 127.62, 123.96, 120.97, 116.51, 108.81, 47.16  $\text{cm}^{-1}$ ; LC-MS (ESI): *m/z* = 225 [M+1]<sup>+</sup>; HRMS (EI): *m/z* = [M + 1]<sup>+</sup> calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O: 225.2658; found: 225.096.

**N-(4-methoxybenzyl)benzo[d]oxazol-2-amine (7b):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 9.3 Hz, 1H), 7.17 (td, *J* = 7.7, 1.0 Hz, 1H), 7.04 (td, *J* = 7.9, 1.1 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.32 (bs, 1H), 4.60 (s, 2H), 3.80 (s, *J* = 5.9 Hz, 3H); LC-MS (ESI): *m/z* = 255 [M+1]<sup>+</sup>.

**N-(4-methylbenzyl)benzo[d]oxazol-2-amine (7c):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 13.3, 8.4 Hz, 3H), 7.20-7.13 (m, 3H), 7.04 (td, *J* = 7.8, 1.1 Hz, 1H), 5.23 (bs, 1H), 4.64 (s, 2H), 2.35 (s, 3H), 1.61 (s, 3H); LC-MS (ESI): *m/z* = 239 [M+1]<sup>+</sup>.

**N-(4-fluorobenzyl)benzo[d]oxazol-2-amine (7d):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40-7.32 (m, 3H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.17 (td, *J* = 7.7, 0.9 Hz, 1H), 7.09-7.00 (m, 3H), 5.45 (s, 1H), 4.65 (s, 2H); LC-MS (ESI): *m/z* = 243 [M+1]<sup>+</sup>.

**N-(4-chlorobenzyl)benzo[d]oxazol-2-amine (7e):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39-7.30 (m, 5H), 7.28-7.23 (m, 2H), 7.18 (td, *J* = 7.7, 1.1 Hz, 1H), 7.05 (td, *J* = 7.8, 1.2 Hz, 1H), 5.42 (s, 1H), 4.65 (s, 2H); LC-MS (ESI): *m/z* = 259 [M+1]<sup>+</sup>.

**N-(4-(trifluoromethyl)benzyl)benzo[d]oxazol-2-amine (7f):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd, *J* = 40.9, 8.1 Hz, 4H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 5.7 Hz, 1H), 7.18 (td, *J* = 7.7, 1.0 Hz, 1H), 7.06 (td, *J* = 7.9, 1.1 Hz, 1H), 5.65-5.48 (bs, 1H), 4.75 (s, 2H); LC-MS (ESI): *m/z* = 293 [M+1]<sup>+</sup>.

**N-(3-phenylpropyl)benzo[d]oxazol-2-amine (7g):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, *J* = 7.7 Hz, 1H), 7.32-7.24 (m, 3H), 7.23-7.13 (m, 4H), 7.03 (dd, *J* = 11.2, 4.3 Hz, 1H), 5.08 (s, 1H), 3.52 (t, *J* = 6.9 Hz, 2H), 2.83-2.65 (m, 2H), 2.09-1.97 (m, 2H); LC-MS (ESI): *m/z* = 253 [M+1]<sup>+</sup>.

**N-(cyclopropylmethyl)benzo[d]oxazol-2-amine (7h):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.16 (td, *J* = 7.7, 1.0 Hz, 1H), 7.03 (td, *J* = 7.8, 1.1 Hz, 1H), 5.08 (s, 1H), 3.35 (dd, *J* = 6.7, 5.0 Hz, 2H), 1.23-1.08 (m, 1H), 0.67-0.47 (m, 2H), 0.39-0.22 (m, 2H); LC-MS (ESI): *m/z* = 189 [M+1]<sup>+</sup>.

**N-(cyclohexylmethyl)benzo[d]oxazol-2-amine (7i):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 5.27 (s, 1H), 3.33 (d, *J* = 2.9 Hz, 2H), 1.87-1.57 (m, 5H), 1.35-1.11 (m, 3H), 1.08-0.78 (m, 2H); LC-MS (ESI): *m/z* = 231 [M+1]<sup>+</sup>.

**N-methylbenzo[d]oxazol-2-amine (7j):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.20-7.13 (m, 1H), 7.03 (td, *J* = 7.9, 0.9 Hz, 1H), 4.98 (s, 1H), 3.13 (s, 3H); LC-MS (ESI): *m/z* = 149 [M+1]<sup>+</sup>.

**N-benzyl-5-methoxybenzo[d]oxazol-2-amine (7k):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.25 (m, 5H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.60 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.47 (s, 1H), 4.66 (s, 2H), 3.81 (d, *J* = 5.4 Hz, 3H); LC-MS (ESI): *m/z* = 255 [M+1]<sup>+</sup>.

**5-Methoxy-N-(4-methoxybenzyl)benzo[d]oxazol-2-amine (7l):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.91-6.86 (m, 2H), 6.60 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.21 (s, 1H), 4.58 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H); LC-MS (ESI): *m/z* = 285 [M+1]<sup>+</sup>.

**5-Methoxy-N-(4-(trifluoromethyl)benzyl)benzo[d]oxazol-2-amine (7m):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (dd,

$J = 42.8, 8.1$  Hz, 4H), 7.13 (d,  $J = 8.7$  Hz, 1H), 6.90 (d,  $J = 2.5$  Hz, 1H), 6.62 (dd,  $J = 8.7, 2.5$  Hz, 1H), 5.66 (s, 1H), 4.73 (s, 2H), 3.80 (s, 3H); LC-MS (ESI):  $m/z = 323$  [M+1]<sup>+</sup>.

**5-Methoxy-*N*-(3-phenylpropyl)benzo[d]oxazol-2-amine (7n):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32-7.26 (m, 2H), 7.23-7.16 (m, 3H), 7.10 (d,  $J = 8.7$  Hz, 1H), 6.93 (d,  $J = 2.5$  Hz, 1H), 6.59 (dd,  $J = 8.7, 2.6$  Hz, 1H), 4.96 (s, 1H), 3.80 (s, 3H), 3.55-3.46 (m, 2H), 2.74 (m, 2H), 2.07-1.96 (m, 2H); LC-MS (ESI):  $m/z = 283$  [M+1]<sup>+</sup>.

***N*-(cyclohexylmethyl)-5-methoxybenzo[d]oxazol-2-amine (7o):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.10 (d,  $J = 8.7$  Hz, 1H), 6.93 (d,  $J = 2.5$  Hz, 1H), 6.58 (dd,  $J = 8.7, 2.6$  Hz, 1H), 5.01 (s, 1H), 3.80 (s, 3H), 3.31 (t,  $J = 6.4$  Hz, 2H), 1.87-1.56 (m, 6H), 1.33-1.10 (m, 3H), 1.00 (qd,  $J = 12.0, 2.9$  Hz, 2H); LC-MS (ESI):  $m/z = 261$  [M+1]<sup>+</sup>.

***N*-benzyl-5-chlorobenzo[d]oxazol-2-amine (7p):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.29 (m, 5H), 7.22 (d,  $J = 2.1$  Hz, 1H), 7.14 (d,  $J = 8.4$  Hz, 1H), 6.99 (dd,  $J = 8.5, 2.1$  Hz, 1H), 5.75 (s, 1H), 4.66 (d,  $J = 3.3$  Hz, 2H); LC-MS (ESI):  $m/z = 259$  [M+1]<sup>+</sup>.

**5-Chloro-*N*-(4-methoxybenzyl)benzo[d]oxazol-2-amine (7q):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34-7.28 (m, 2H), 7.14 (d,  $J = 8.7$  Hz, 1H), 6.99 (dd,  $J = 8.4, 2.1$  Hz, 1H), 6.93-6.85 (m, 2H), 5.48 (s, 1H), 4.59 (d,  $J = 5.2$  Hz, 2H), 3.81 (s, 3H); LC-MS (ESI):  $m/z = 289$  [M+1]<sup>+</sup>.

**5-Chloro-*N*-(4-(trifluoromethyl)benzyl)benzo[d]oxazol-2-amine (7r):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d,  $J = 8.1$  Hz, 2H), 7.51 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 2.0$  Hz, 1H), 7.16 (d,  $J = 8.5$  Hz, 1H), 7.02 (dd,  $J = 8.5, 2.1$  Hz, 1H), 5.61 (s, 1H), 4.74 (s, 2H); LC-MS (ESI):  $m/z = 327$  [M+1]<sup>+</sup>.

**5-Chloro-*N*-(3-phenylpropyl)benzo[d]oxazol-2-amine (7s):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.27 (m, 3H), 7.24-7.16 (m, 3H), 7.12 (d,  $J = 8.3$  Hz, 1H), 6.99 (dd,  $J = 8.4, 2.1$  Hz, 1H), 5.04 (s, 1H), 3.50 (dt,  $J = 7.0, 5.9$  Hz, 2H), 2.74 (m, 2H), 2.12-1.94 (m, 2H); LC-MS (ESI):  $m/z = 287$  [M+1]<sup>+</sup>.

**5-Chloro-*N*-(cyclohexylmethyl)benzo[d]oxazol-2-amine (7t):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 (d,  $J = 2.0$  Hz, 1H), 7.12 (d,  $J = 8.3$  Hz, 1H), 6.98 (dd,  $J = 8.4, 2.1$  Hz, 1H), 5.17 (s, 1H), 3.32 (t,  $J = 6.4$  Hz, 2H), 1.87-1.54 (m, 6H), 1.34-1.11 (m, 3H), 1.06-0.94 (m, 2H); LC-MS (ESI):  $m/z = 265$  [M+1]<sup>+</sup>.

**Representative Procedure for the Second-generation Acylation Reaction Step vi, the Preparation of *N*-(benzo[d]oxazol-2-yl)benzamide (8a) from Resin (6a).** Resin **6a** (160 mg) was treated with a mixture of (TFA-CH<sub>2</sub>Cl<sub>2</sub> = 1:4, v/v) for 3 h at room temperature, and then, washed with CH<sub>2</sub>Cl<sub>2</sub> several times. The organic filtrates were neutralized by saturated K<sub>2</sub>CO<sub>3</sub> solution. The filtrate was washed with water and dried over MgSO<sub>4</sub>. The solution was concentrated under reduced pressure and the residue was washed with diethyl ether to afford *N*-(benzo[d]oxazol-2-yl)benzamide **8a** (12 mg, 33%, five-step overall yield from BAL resin, loading capacity 1.1 mmol/g) as a white solid. mp 327.8 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.78 (s, 1H), 6.65 (d,  $J = 7.5$  Hz, 2H), 6.28-6.21 (m, 2H), 6.19 (d,  $J = 7.1$  Hz, 1H), 6.14 (t,  $J = 7.6$  Hz, 2H), 5.97-5.85 (m, 2H); LC-MS (ESI):  $m/z = 239$  [M+1]<sup>+</sup>; HRMS (EI):  $m/z = [M + 1]^+$  calcd for

C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>: 239.0821; found: 239.126.

***N*-(benzo[d]oxazol-2-yl)-4-methoxybenzamide (8b):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26-8.04 (m, 2H), 7.47 (d,  $J = 7.0$  Hz, 1H), 7.39-7.20 (m, 4H), 6.95 (d,  $J = 8.7$  Hz, 2H), 3.87 (s, 3H); LC-MS (ESI):  $m/z = 269$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)-4-methylbenzamide (8c):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (s, 2H), 7.53-7.44 (m, 1H), 7.38-7.22 (m, 5H), 2.42 (s, 3H); LC-MS (ESI):  $m/z = 253$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)-4-tert-butylbenzamide (8d):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 2H), 7.49 (d,  $J = 8.3$  Hz, 3H), 7.34-7.20 (m, 3H), 1.35 (s, 9H); LC-MS (ESI):  $m/z = 295$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)-4-fluorobenzamide (8e):** <sup>1</sup>H NMR (400 MHz, DMSO) δ 12.42 (s, 1H), 8.15 (dd,  $J = 8.5, 5.7$  Hz, 2H), 7.64 (d,  $J = 7.8$  Hz, 1H), 7.58 (d,  $J = 7.3$  Hz, 1H), 7.46-7.24 (m, 4H); LC-MS (ESI):  $m/z = 257$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)-4-chlorobenzamide (8f):** <sup>1</sup>H NMR (400 MHz, DMSO) δ 12.45 (s, 1H), 8.09 (d,  $J = 8.5$  Hz, 2H), 7.69-7.54 (m, 4H), 7.40-7.26 (m, 2H); LC-MS (ESI):  $m/z = 273$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)thiophene-2-carboxamide (8g):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d,  $J = 3.1$  Hz, 1H), 7.57 (d,  $J = 4.2$  Hz, 1H), 7.48-7.41 (m, 1H), 7.37-7.24 (m, 3H), 7.13 (dd,  $J = 4.8, 3.9$  Hz, 1H); LC-MS (ESI):  $m/z = 245$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)cyclopropanecarboxamide (8h):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.22 (s, 1H), 7.56 (d,  $J = 7.6$  Hz, 1H), 7.51 (d,  $J = 7.6$  Hz, 1H), 7.36-7.22 (m, 2H), 2.40-2.15 (m, 1H), 1.31-1.19 (m, 2H), 1.09-0.97 (m, 2H); LC-MS (ESI):  $m/z = 203$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)hexanamide (8i):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.32-9.03 (m, 1H), 7.78-7.54 (m, 1H), 7.48 (d,  $J = 7.9$  Hz, 1H), 7.34-7.23 (m, 1H), 2.83-2.58 (m, 2H), 1.85-1.70 (m, 2H), 1.47-1.29 (m, 4H), 0.93 (d,  $J = 7.0$  Hz, 3H); LC-MS (ESI):  $m/z = 233$  [M+1]<sup>+</sup>.

***N*-(benzo[d]oxazol-2-yl)acetamide (8j):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.94 (s, 1H), 7.62 (d,  $J = 7.7$  Hz, 1H), 7.51 (d,  $J = 7.9$  Hz, 1H), 7.40-7.23 (m, 2H), 2.52 (s, 3H); LC-MS (ESI):  $m/z = 177$  [M+1]<sup>+</sup>.

***N*-(5-methoxybenzo[d]oxazol-2-yl)benzamide (8k):** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.01 (s, 1H), 8.04 (s, 2H), 7.65 (s, 2H), 7.61-7.47 (m, 3H), 7.20 (s, 1H), 6.88 (dd,  $J = 8.8, 2.1$  Hz, 1H), 3.81 (s, 3H); LC-MS (ESI):  $m/z = 269$  [M+1]<sup>+</sup>.

**4-Methoxy-*N*-(5-methoxybenzo[d]oxazol-2-yl)benzamide (8l):** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.91 (d,  $J = 8.5$  Hz, 3H), 6.96 (d,  $J = 8.6$  Hz, 3H), 3.80 (s,  $J = 10.0$  Hz, 6H); LC-MS (ESI):  $m/z = 299$  [M+1]<sup>+</sup>.

**4-Chloro-*N*-(5-methoxybenzo[d]oxazol-2-yl)benzamide (8m):** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.39 (s, 1H), 8.08 (d,  $J = 8.3$  Hz, 2H), 7.61 (d,  $J = 8.5$  Hz, 2H), 7.54 (d,  $J = 8.9$  Hz, 1H), 7.14 (s, 1H), 6.88 (dd,  $J = 8.9, 2.6$  Hz, 1H), 3.80 (s, 3H); LC-MS (ESI):  $m/z = 303$  [M+1]<sup>+</sup>.

***N*-(5-methoxybenzo[d]oxazol-2-yl)cyclopropanecarboxamide (8n):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.53 (s, 1H), 7.36 (d,  $J = 8.9$  Hz, 1H), 7.07 (s, 1H), 6.83 (dd,  $J = 8.9, 2.5$  Hz, 1H), 3.84 (s, 3H), 2.36-2.12 (m, 1H), 1.28-1.20 (m, 2H), 1.03 (td,  $J = 7.2, 3.9$  Hz, 2H); LC-MS (ESI):  $m/z = 233$

[M+1]<sup>+</sup>.

**N-(5-methoxybenzo[d]oxazol-2-yl)hexanamide (8o):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.46 (s, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.10 (s, 1H), 6.83 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.85 (s, 3H), 2.81-2.63 (m, 2H), 1.84-1.72 (m, 2H), 1.48-1.28 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H); LC-MS (ESI): *m/z* = 263 [M+1]<sup>+</sup>.

**N-(5-chlorobenzo[d]oxazol-2-yl)benzamide (8p):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (s, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.24 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.14 (s, 1H); LC-MS (ESI): *m/z* = 273 [M+1]<sup>+</sup>.

**N-(5-chlorobenzo[d]oxazol-2-yl)-4-methoxybenzamide (8q):** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.02 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.34 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); LC-MS (ESI): *m/z* = 303 [M+1]<sup>+</sup>.

**4-Chloro-N-(5-chlorobenzo[d]oxazol-2-yl)benzamide (8r):** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.27 (s, 1H), 8.05 (s, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 8.6, 2.2 Hz, 1H); LC-MS (ESI): *m/z* = 307 [M+1]<sup>+</sup>.

**N-(5-chlorobenzo[d]oxazol-2-yl)cyclopropanecarboxamide (8s):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.98 (s, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.24 (dd, *J* = 8.6, 2.1 Hz, 1H), 2.74 (s, 2H), 1.85-1.72 (m, 2H), 1.45-1.33 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H); LC-MS (ESI): *m/z* = 237 [M+1]<sup>+</sup>.

**N-(5-chlorobenzo[d]oxazol-2-yl)hexanamide (8t):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.45 (s, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.23 (dd, *J* = 8.6, 2.1 Hz, 1H), 2.29 (s, 1H), 1.31-1.20 (m, 2H), 1.10-1.00 (m, 2H); LC-MS (ESI): *m/z* = 267 [M+1]<sup>+</sup>.

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**Supporting Information Available.** Full analytical data of compounds, copies of <sup>1</sup>H NMR, <sup>13</sup>C NMR, LC-MS, and High Resolution-MS spectra of compounds **7a** and **8a** and the <sup>1</sup>H NMR, and MS spectra of compounds **7b-7t** and **8b-8t**.

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