Received: 1 October 2017 | Revised: 26 December 2017 | Accepted: 26 December 2017

DOI: 10.1002/aoc.4284

FULL PAPER

WILEY Applied Organometallic Chemistry

Highly efficient $AgNO_3$-catalyzed approach to 2-(benzo[*d*]azol-2-yl)phenols from salicylaldehydes with 2-aminothiophenol, 2-aminophenol and benzene-1,2-diamine

Xinwei He | Yuhao Wu | Wenjing Jin | Xiaoshun Wang | Cong Wu | Yongjia Shang

Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials (State Key Laboratory Cultivation Base), College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, People's Republic of China

Correspondence
Xinwei He, Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, People's Republic of China.
Email: xinweihe@mail.ahnu.edu.cn

Funding information
Doctoral Scientific Research Foundation of Anhui Normal University, Grant/Award Number: 2016XJJ110; Natural Science Foundation of Education Administration of Anhui Province, Grant/Award Number: KJ2016A267; National Natural Science Foundation of China, Grant/Award Number: 21372008, 21772001

A new, convenient and efficient $AgNO_3$-catalyzed strategy for the preparation of 2-(benzo[*d*]azol-2-yl)phenol derivatives in good to excellent yields (63–98%) is described. The reaction proceeds via condensation/intramolecular nucleophilic addition/oxidation process between substituted salicylaldehydes and 2-aminothiophenol, 2-aminophenol or benzene-1,2-diamine under mild reaction conditions. Notably, this reaction utilizes cheap $AgNO_3$ as a readily available and low-cost benign oxidant at low catalyst loadings with excellent functional group tolerance.

KEYWORDS
condensation, oxidation, phenols, salicylaldehydes, silver nitrate

1 | INTRODUCTION

Phenol and its derivatives are important compounds, which not only are widely present in various bioactive natural products, pharmaceuticals and many newly developed functional materials[1] but also are used as fundamental raw materials in Ullman coupling, Suzuki coupling (aryl triflates, pivalates, carbamates, etc., instead of aryl halides) and other organic reactions for the synthesis of various functional molecules.[2] Phenols bearing benzothiazole, benzoxazole and benzimidazole groups are fluorescent compounds that are widely studied for their fundamental photophysics and as optical probes due to their dual emission via excited-state intramolecular proton transfer.[3] In particular, boron complexes of 2-(benzo[*d*]azol-2-yl)phenols have been extensively explored for various applications.[4] Therefore, the synthesis of functionalized phenol derivatives has attracted much attention in recent years.

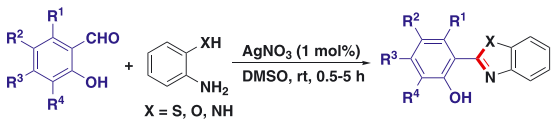
Over the past decade, silver salt catalysts have significantly emerged to promote a broad range of organic transformations, such as cyclization,[5] cycloaddition,[6] allylation,[7] tandem reactions,[8] decarboxylation[9] and other reactions[10] owing to their efficiency, abundance, affordability and simple operation. Very recently, silver nitrate ($AgNO_3$) has attracted much attention as a promising alternative to traditional transition metal catalysts and has also been employed for organic reactions, such as phosphorylation,[11] radical reactions,[12] addition,[13] domino reactions[14] and others.[15]

As part of our program on the study of transition metal-catalyzed reactions for the synthesis of heterocyclic compounds,[16] we herein report a convenient and efficient method for the synthesis of 2-(benzo[*d*]azol-2-yl)phenol derivatives via a $AgNO_3$-catalyzed condensation/intramolecular nucleophilic addition/oxidation process with salicylaldehydes and 2-aminothiophenol, 2-aminophenol or benzene-1,2-diamine (Scheme 1).

2 | RESULTS AND DISCUSSION

As a model system, salicylaldehyde **1a** and 2-aminobenzenethiol **2a** were chosen as substrates for an initial study, as summarized in Table 1. First, several transition metal catalysts, namely $FeCl_3$, $Sc(OTf)_3$, $Cu(OAc)_2$, $NiCl_2{\cdot}6H_2O$, $Hg(OAc)_2$, $Zn(OTf)_2$ and $AgNO_3$, were investigated (Table 1, entries 1–7). Of these, $AgNO_3$ was found to be the best catalyst, giving the desired product **5a** in 78% yield (Table 1, entry 7). Other silver salts, namely AgOAc, $AgSbF_6$, AgOTf and $AgBF_4$, were also screened, identifying all of these silver salts as being effective for this transformation (Table 1, entries 8–11). Then, screening the reaction solvent revealed that dimethylsulfoxide (DMSO) was the solvent of choice and that the yield of **5a** could be improved to 87% (Table 1, entry 15). Various reaction temperatures and reaction times were attempted (Table 1, entries 21–26). It was found that the highest yield (91%) of the desired product **5a** was obtained at room temperature in a time of 1 h (Table 1, entry 25). Additionally, altering the amount of $AgNO_3$ gave no significant difference in reaction yield (Table 1, entries 27–30). However, the product yield dropped to 62% in the absence of the catalyst after a prolonged reaction time of 5 h (Table 1, entry 31). Therefore, this reaction could be best performed with 1 mol% of $AgNO_3$ as catalyst in DMSO at room temperature for 1 h (Table 1, entry 30).

With the optimum reaction conditions in hand, we first investigated the scope of substrates for the synthesis of 2-(benzo[*d*]thiazol-2-yl)phenol derivatives (**5**). As evident from Table 2, the tested substrates afforded good to excellent yields (72–97%). Functional groups such as halogen (fluoro, chloro, bromo), methyl, methoxyl, hydroxyl, nitro, *tert*-butyl and diethylamino on the phenyl ring of the salicylaldehyde were tolerated well, and all *para*-, *meta*- and *ortho*-substituted salicylaldehydes were easily converted into the desired products. It should be noted that steric hindrance had an obvious effect on the reaction. The substituted salicylaldehydes bearing bulky *tert*-butyl and bromo groups at the *ortho* and *para* positions (**1 h**) of the hydroxyl could give lower yields (Table 2, entries 8 and 14). The structure of the product **5a** was unambiguously confirmed by X-ray crystallographic analysis (Figure 1).



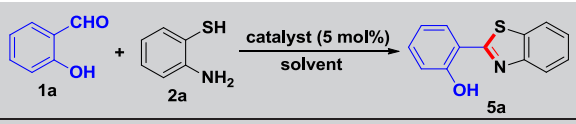
SCHEME 1 $AgNO_3$-catalyzed condensation/oxidation for the synthesis of 2-(benzo[*d*]azol-2-yl)phenol derivatives

We next set out to explore the scope of salicylaldehydes and 2-aminophenols under the standard conditions (Table 3). The results demonstrated that the optimal conditions were compatible with various salicylaldehydes having substituents, such as halogen groups (fluoro, chloro, bromo), methyl, methoxyl, *tert*-butyl and diethylamino, on the aryl ring. Moreover, *tert*-butyl group at the 3,5-position of salicylaldehydes participated successfully in this reaction, and the corresponding product **6 g** was obtained in 68% yield (Table 3, entry 7). For 2-aminophenols, substrates with a moderately electron-donating R^5 group (e.g. CH_3; Table 3, entries 11–15) or a moderately electron-withdrawing R^5 group (e.g. Cl; Table 3, entries 17–21) gave the desired products in good to excellent yields (83–90%). To our delight, product **6p** was obtained in 63% yield (Table 3, entry 16) with 2-aminophenol bearing a bulky *tert*-butyl group at the *para* position of the hydroxyl (**3c**).

Furthermore, to expand the scope of the present approach, we next subjected benzene-1,2-diamine (**4a**) to the otherwise identical reaction conditions as described above (Table 4). Pleasingly, the corresponding products 2-(1*H*-benzo[*d*]imidazol-2-yl)phenols were obtained in 65–92% yields, and the results are summarized in Table 4. Likewise, various moderately electron-withdrawing or electron-donating groups on the benzene ring of salicylaldehydes, such as Cl, Br and CH_3, are well tolerated in the reaction to afford the desired products in high yields (Table 4, entries 2, 6–8). Notably, as in the case of substrates 2-aminobenzenethiol **2a** and 2-aminophenols **3**, substrates with a strongly electron-donating group (e.g. OCH_3, NEt_2; Table 4, entries 3 and 4) or a bulky *tert*-butyl group (Table 4, entry 5) were also tolerated in the reaction to give the corresponding products in 90, 89 and 65% yields, respectively.

Additionally, we carried out a gram-scale reaction of 2-aminobenzenethiol (**2a**; 10 mmol) with 2-hydroxy-5-methylbenzaldehyde (**1b**; 10 mmol) or 2-hydroxy-5-nitrobenzaldehyde (**1 l**; 10 mmol) under the standard conditions, and the products **5b** and **5 l** were isolated in 94% (2.26 g) and 86% (2.34 g) yield, respectively (Scheme 2), which showed promise for this synthetic method as a useful tool in practical synthetic contexts.

TABLE 1 Optimization of reaction conditions[a]



Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	$FeCl_3$	EtOH	70	7	54
2	$Sc(OTf)_3$	EtOH	70	7	42
3	$Cu(OAc)_2$	EtOH	70	7	33
4	$NiCl_2{\cdot}6H_2O$	EtOH	70	7	50
5	$Hg(OAc)_2$	EtOH	70	7	57
6	$Zn(OTf)_2$	EtOH	70	7	48
7	$AgNO_3$	EtOH	70	7	78
8	AgOAc	EtOH	70	7	76
9	$AgSbF_6$	EtOH	70	7	72
10	AgOTf	EtOH	70	7	74
11	$AgBF_4$	EtOH	70	7	75
12	$AgNO_3$	DMF	70	7	71
13	$AgNO_3$	THF	70	7	15
14	$AgNO_3$	Toluene	70	7	Trace
15	$AgNO_3$	DMSO	70	7	87
16	$AgNO_3$	CH_3CN	70	7	20
17	$AgNO_3$	H_2O	70	7	70
18	$AgNO_3$	1,4-Dioxane	70	7	62
19	$AgNO_3$	Acetone	70	7	58
20	$AgNO_3$	Cyclohexane	70	7	35
21	$AgNO_3$	DMSO	50	7	87
22	$AgNO_3$	DMSO	RT	7	89
23	$AgNO_3$	DMSO	RT	5	91
24	$AgNO_3$	DMSO	RT	2	91
25	$AgNO_3$	DMSO	RT	1	91
26	$AgNO_3$	DMSO	RT	0.5	79
27[c]	$AgNO_3$	DMSO	RT	1	91
28[d]	$AgNO_3$	DMSO	RT	1	91
29[e]	$AgNO_3$	DMSO	RT	1	92
30[f]	$AgNO_3$	DMSO	RT	1	90
31	—	DMSO	RT	5	62

[a]Reaction conditions: salicylaldehyde **1a** (1 mmol), 2-aminobenzenethiol **2a** (1 mmol), solvent (3 ml), catalyst (10 mol%).

[b]Isolated yield.

[c]15 mol% of catalyst was used.

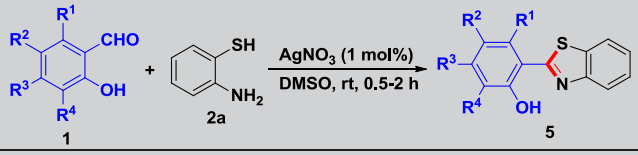
[d]10 mol% of catalyst was used.

[e]3 mol% of catalyst was used.

[f]1 mol% of catalyst was used.

To gain insight into the possible mechanism of this reaction, a few control experiments were carried out (Scheme 3). When salicylaldehyde **1a** reacted with 2-aminobenzenethiol **2a** under optimized reaction conditions, in the absence of catalyst, the corresponding product **5a** was obtained in 56% yield. We next treated this

TABLE 2 $AgNO_3$-catalyzed synthesis of 2-(benzo[*d*]thiazol-2-yl)phenols[a]



Entry	R^1, R^2, R^3, R^4	Product 5	Yield (%)[b]
1	**1a** (H, H, H, H)	**5a**	90
2	**1b** (H, CH_3, H, H)	**5b**	98
3	**1c** (H, H, CH_3, H)	**5c**	92
4	**1d** (H, H, CH_3O, H)	**5d**	93
5	**1e** (H, H, NEt_2, H)	**5e**	93
6	**1f** (H, H, H, CH_3)	**5f**	88
7	**1 g** (H, H, H, OCH_3)	**5 g**	89
8	**1 h** ($C(CH_3)_3$, H, $C(CH_3)_3$, H)	**5 h**	75
9	**1i** (H, F, H, H)	**5i**	91
10	**1j** (H, Cl, H, H)	**5j**	95
11	**1 k** (H, Br, H, H)	**5 k**	97
12	**1 l** (H, NO_2, H, H)	**5 l**	92
13	**1 m** (H, Cl, H, Cl)	**5 m**	88
14	**1n** (H, Br, H, Br)	**5n**	72
15	**1o** (H, OH, H, H)	**5o**	87
16	**1p** (H, H, OH, H)	**5p**	85
17	**1q** (—CH=CHCH=CH—, H, H, H)	**5q**	90

[a]Reaction conditions: salicylaldehydes **1** (1 mmol), 2-aminobenzenethiol **2a** (1 mmol), DMSO (3 ml), $AgNO_3$ (1 mol%) at room temperature.

[b]Isolated yield.

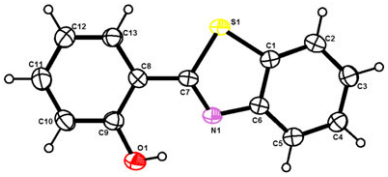


FIGURE 1 X-ray crystal structure of compound **5a**

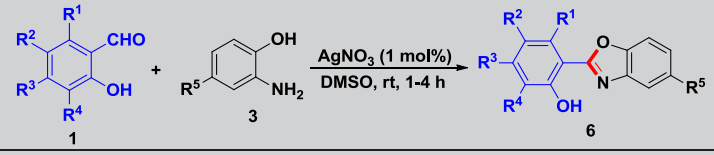
reaction with $AgNO_3$ (1 equiv.) as catalyst under nitrogen atmosphere, and the desired product **5a** was obtained in 88% yield. These results indicated that the oxidation process possibly proceeded with $AgNO_3$ as oxidant.

On the basis of the results discussed above and previous reports,[17] a tentative mechanism to account for this transformation is illustrated in Scheme 4. Firstly, intermediate **A** is generated from the condensation of salicylaldehydes with 2-substituted anilines (**2a**, **3a** or **4a**), which rapidly reaches equilibrium with another cyclic intermediate dihydrobenzoazole **B** via intramolecular nucleophilic addition. Finally, the oxidation of intermediate **B** affords the desired products and Ag(0) in the presence of $AgNO_3$ as oxidant. The Ag(I) species is regenerated by oxidation of Ag(0) via the second oxidative process with the assistance of DMSO/air.

3 | CONCLUSIONS

We have described a successful strategy for the efficient and convenient preparation of functionalized 2-(benzo[*d*]azol-2-yl)phenol derivatives in good to excellent yields under mild conditions. The reaction proceeds via condensation/intramolecular nucleophilic addition/oxidation process between substituted salicylaldehydes and 2-aminothiophenol, 2-aminophenol or benzene-1, 2-diamine in the presence of $AgNO_3$, which could be employed as low-cost and moderate inorganic oxidant in this reaction. The current strategy offers several advantages such as excellent yields of products, simple starting materials, low catalyst loadings, excellent functional group tolerance and mild reaction conditions, hence opening new avenues for its application in medicinal and dye chemistry.

TABLE 3 $AgNO_3$-catalyzed synthesis of 2-(benzo[*d*]oxazol-2-yl)phenols[a]



Entry	R^1, R^2, R^3, R^4	R^5	Product 6	Yield (%)[b]
1	**1a** (H, H, H, H)	H (**3a**)	**6a**	91
2	**1b** (H, CH_3, H, H)	H (**3a**)	**6b**	92
3	**1c** (H, H, CH_3, H)	H (**3a**)	**6c**	89
4	**1d** (H, H, CH_3O, H)	H (**3a**)	**6d**	87
5	**1e** (H, H, NEt_2, H)	H (**3a**)	**6e**	82
6	**1 g** (H, H, H, CH_3O)	H (**3a**)	**6f**	73
7	**1 h** ($C(CH_3)_3$, H, $C(CH_3)_3$, H)	H (**3a**)	**6 g**	68
8	**1j** (H, Cl, H, H)	H (**3a**)	**6 h**	92
9	**1 k** (H, Br, H, H)	H (**3a**)	**6i**	91
10	**1q** (—CH=CHCH=CH—, H, H, H)	H (**3a**)	**6j**	89
11	**1a** (H, H, H, H)	CH_3 (**3b**)	**6 k**	83
12	**1b** (H, CH_3, H, H)	CH_3 (**3b**)	**6 l**	90
13	**1i** (H, F, H, H)	CH_3 (**3b**)	**6 m**	89
14	**1j** (H, Cl, H, H)	CH_3 (**3b**)	**6n**	88
15	**1 k** (H, Br, H, H)	CH_3 (**3b**)	**6o**	85
16	**1j** (H, Cl, H, H)	^{t}Bu (**3c**)	**6p**	63
17	**1a** (H, H, H, H)	Cl (**3d**)	**6q**	89
18	**1i** (H, F, H, H)	Cl (**3d**)	**6r**	88
19	**1j** (H, Cl, H, H)	Cl (**3d**)	**6 s**	89
20	**1 k** (H, Br, H, H)	Cl (**3d**)	**6 t**	89
21	**1 l** (H, NO_2, H, H)	Cl (**3d**)	**6u**	87

[a]Reaction conditions: salicylaldehydes **1** (1 mmol), 2-aminophenols **3** (1 mmol), DMSO (3 ml), $AgNO_3$ (1 mol%) at room temperature.

[b]Isolated yield.

4 | EXPERIMENTAL

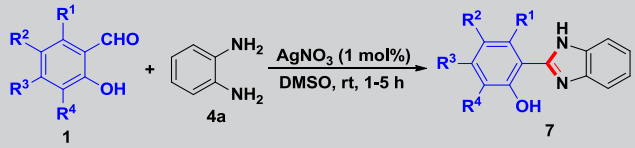
4.1 | General

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received, and the solvents were purified and dried using standard procedures. The chromatography solvents were of technical grade and distilled prior to use. Flash chromatography was performed using 200–300 mesh silica gel with the indicated solvent system according to standard techniques. The ^{1}H NMR and ^{13}C NMR spectra were recorded using 300 MHz spectrometers unless otherwise specified. The chemical shifts (δ) in parts per million are reported relative to the residual signals of chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C), and all ^{13}C NMR spectra that were recorded with broadband proton decoupling are denoted ^{13}C{^{1}H}NMR. The multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet), and the coupling constants (J) are reported in hertz. The HRMS analyses with a quadrupole time-of-flight mass spectrometer yielded ion mass/charge (m/z) ratios in atomic mass units.

4.2 | General Procedure for Synthesis of 2-(Benzo[*d*]thiazol-2-yl)phenols (3)

To a solution of salicylaldehydes (**1**; 1 mmol), 2-aminobenzenethiol (**2a**; 1 mmol) and $AgNO_3$ (0.01 mmol) in DMSO (3 ml) were added and the resulting mixture was stirred at room temperature. Upon the completion of this reaction (monitored by TLC), the mixture was diluted with CH_2Cl_2 (3 × 10 ml), and washed with brine. Organic layers were combined, dried over Na_2SO_4, filtered and evaporated in a vacuum. The residue was further purified by

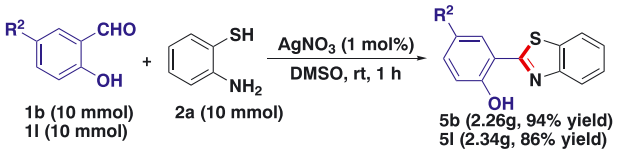
TABLE 4 $AgNO_3$-catalyzed synthesis of 2-(1*H*-benzo[*d*]imidazol-2-yl)phenols[a]



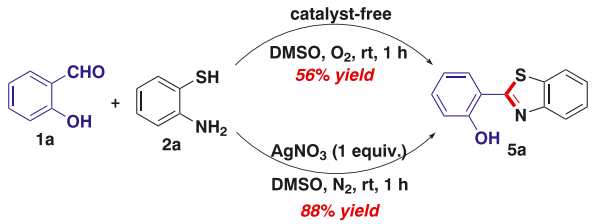
Entry	R^1, R^2, R^3, R^4	Product 7	Yield (%)[b]
1	**1a** (H, H, H, H)	**7a**	90
2	**1b** (H, CH_3, H, H)	**7b**	82
3	**1d** (H, H, CH_3O, H)	**7c**	90
4	**1e** (H, H, NEt_2, H)	**7d**	89
5	**1 h** ($C(CH_3)_3$, H, $C(CH_3)_3$, H)	**7e**	65
6	**1i** (H, F, H, H)	**7f**	88
7	**1j** (H, Cl, H, H)	**7 g**	87
8	**1 k** (H, Br, H, H)	**7 h**	88
9	**1q** (—CH=CHCH=CH—, H, H, H)	**7i**	92

[a]Reaction conditions: salicylaldehydes **1** (1 mmol), benzene-1,2-diamine **4a** (1 mmol), DMSO (3 ml), $AgNO_3$ (1 mol%) at room temperature.

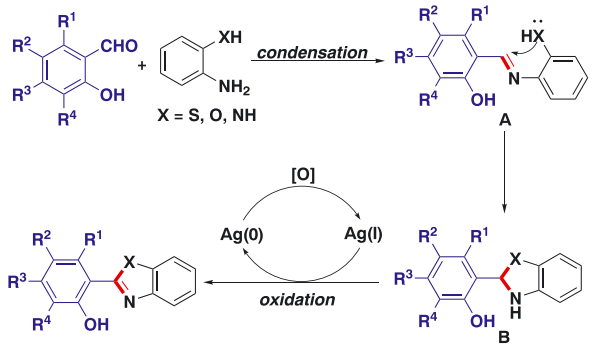
[b]Isolated yield.



SCHEME 2 Gram-scale synthesis



SCHEME 3 Control experiments



SCHEME 4 Proposed reaction mechanism

flash column chromatography on silica gel (200–300 mesh) with petroleum ether and ethyl acetate (6:1–8:1, v/v) as eluting solvent to give the desired products (**5**).

2-(Benzo[*d*]thiazol-2-yl)phenol (**5a**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.55 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.36–7.43 (m, 2H), 7.13 (d, J = 8.1 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 169.7, 158.3, 152.2, 133.1, 133.0, 128.8, 127.1, 125.9, 122.5, 121.9, 119.9, 118.2, 117.1. HRMS (APCI) calcd for $[C_{13}H_9NOS + H]^+$ 228.0483, found 228.0483.

2-(Benzo[*d*]thiazol-2-yl)-4-methylphenol (**5b**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.32 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 169.8, 156.2, 152.3, 134.1, 133.0, 129.0, 128.7, 127.0, 125.8, 122.5, 121.8, 118.0, 116.7, 20.8. HRMS (APCI) calcd for $[C_{14}H_{11}NOS + H]^+$ 242.0639, found 242.0640.

2-(Benzo[*d*]thiazol-2-yl)-5-methylphenol (**5c**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.03 (s, 1H, OH), 8.62 (s, 1H, C_6H_4), 7.67 (d, J = 7.2 Hz, 1H, C_6H_4), 7.14–7.29 (m, 4H, C_6H_4), 6.87 (t, J = 7.5 Hz, 1H, C_6H_4), 2.34(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 163.4, 159.8, 146.8, 135.0, 132.0, 130.7, 127.9, 127.4, 126.9, 119.1, 118.8, 118.0, 16.0. HRMS (APCI) calcd for $[C_{14}H_{11}NOS + H]^+$ 242.0639, found 242.0640.

2-(Benzo[*d*]thiazol-2-yl)-5-methoxyphenol (**5d**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.77 (s, 1H), 7.94

(d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 6.60 (s, 1H), 6.55 (d, J = 8.7 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 169.6, 163.8, 160.3, 152.2, 132.5, 130.0, 126.9, 125.3, 122.0, 121.7, 110.7, 108.0, 101.7, 55.8. HRMS (APCI) calcd for $[C_{14}H_{11}NO_2S + H]^+$ 258.0589, found 258.0589.

2-(Benzo[*d*]thiazol-2-yl)-5-(diethylamino)phenol (**5e**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.58 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.40–7.48 (m, 2H), 7.30 (t, J = 7.5 Hz, 1H), 6.29 (d, J = 6.0 Hz, 2H), 3.42 (q, J = 6.9 Hz, 4H), 1.22 (t, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 170.0, 160.2, 152.6, 151.7, 132.3, 130.2, 126.6, 124.5, 121.6, 121.4, 106.2, 104.5, 104.5, 98.2, 44.9, 13.1. HRMS (APCI) calcd for $[C_{17}H_{18}N_2OS + H]^+$ 299.1218, found 299.1219.

2-(Benzo[*d*]thiazol-2-yl)-6-methylphenol (**5f**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.77 (s, 1H, OH), 7.98 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.47–7.57 (m, 2H), 7.39 (t, J = 7.5 Hz, 1H), 6.86 (t, J = 7.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 170.2, 156.6, 152.2, 134.0, 133.1, 127.3, 127.0, 126.4, 125.8, 122.4, 121.8, 119.3, 116.4, 16.4. HRMS (APCI) calcd for $[C_{14}H_{11}NOS + H]^+$ 242.0639, found 242.0640.

2-(Benzo[*d*]thiazol-2-yl)-6-methoxyphenol (**5 g**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.74 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 6.97 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 169.3, 151.7, 148.9, 148.2, 132.6, 126.6, 125.5, 122.2, 121.4, 119.9, 119.1, 116.7, 114.0, 56.2. HRMS (APCI) calcd for $[C_{14}H_{11}NO_2S + H]^+$ 258.0589, found 258.0589.

2-(Benzo[*d*]thiazol-2-yl)-4,6-di-*tert*-butylphenol (**5 h**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 13.22 (s, 1H), 8.67 (s, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.51 (s, 1H), 7.16–7.26 (m, 3H), 1.51 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 164.4, 158.8, 147.0, 141.1, 137.6, 132.0, 129.0, 127.8, 127.5, 127.2, 118.7, 118.1, 35.5, 34.6, 31.8, 29.8. HRMS (APCI) calcd for $[C_{21}H_{25}NOS + H]^+$ 340.1735, found 340.1733.

2-(Benzo[*d*]thiazol-2-yl)-4-fluorophenol (**5i**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.31 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 8.7 Hz, 1H), 7.02–7.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 167.1, 156.1, 153.1($^1J_{CF}$ = 9.3 Hz), 150.6, 131.6, 125.8 ($^1J_{CF}$ = 75.8 Hz), 121.3, 120.5, 118.9 ($^1J_{CF}$ = 23.1 Hz), 118.0 ($^1J_{CF}$ = 7.7 Hz), 115.5 ($^1J_{CF}$ = 7.7 Hz), 112.7 ($^1J_{CF}$ = 24.5 Hz). HRMS (APCI) calcd for $[C_{13}H_8FNOS + H]^+$ 246.0389, found 246.0391.

2-(Benzo[*d*]thiazol-2-yl)-4-chlorophenol (**5j**). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 12.53 (s, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.64 (s, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 168.2, 156.9, 152.0, 133.0, 132.9, 127.9, 127.3, 126.3, 124.5, 122.7, 122.0, 119.8, 118.0. HRMS (APCI) calcd for $[C_{13}H_8ClNOS + H]^+$ 262.0093, found 262.0093.

2-(Benzo[*d*]thiazol-2-yl)-4-bromophenol (**5 k**). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 12.57 (s, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 6.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.43–7.46 (m, 2H), 7.01 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 168.1, 157.4, 152.0, 135.7, 133.0, 130.8, 127.3, 126.3, 122.7, 122.0, 120.2, 118.7, 111.4. HRMS (APCI) calcd for $[C_{13}H_8BrNOS + H]^+$ 305.9588, found 305.9588.

2-(Benzo[*d*]thiazol-2-yl)-4-nitrophenol (**5 l**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 13.53 (s, 1H), 8.64 (s, 1H), 8.28 (d, J = 9.3 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.48–7.60 (m, 2H), 7.21 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 167.6, 163.5, 151.5, 140.6, 133.0, 128.1, 127.6, 126.9, 124.9, 122.9, 119.0, 116.8. HRMS (APCI) calcd for $[C_{13}H_8N_2O_3S + H]^+$ 273.0334, found 273.0334.

2-(Benzo[*d*]thiazol-2-yl)-4,6-dichlorophenol (**5 m**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 13.30 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.42–7.53 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 167.2, 152.7, 151.2, 132.7, 132.2, 127.2, 126.3, 125.9, 123.8, 123.6, 122.5, 121.7, 118.2. HRMS (APCI) calcd for $[C_{13}H_7Cl_2NOS + H]^+$ 295.9704, found 295.9704.

2-(Benzo[*d*]thiazol-2-yl)-4,6-dibromophenol (**5n**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 13.53 (s, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.78 (s, 1H), 7.49–7.59 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 167.3, 154.4, 151.5, 138.1, 133.1, 130.0, 127.6, 126.7, 122.9, 122.1, 119.1, 113.2, 111.2. HRMS (APCI) calcd for $[C_{13}H_7Br_2NOS + H]^+$ 385.8673, found 385.8673.

2-(Benzo[*d*]thiazol-2-yl)benzene-1,4-diol (**5o**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.09 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.17 (s, 1H), 7.01 (d, J = 8.7 Hz, 1H), 6.92 (d, J = 9.0 Hz, 1H), 4.72 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 164.0, 152.3, 148.0, 126.7, 125.6, 122.2, 121.5, 120.8, 118.7, 113.7. HRMS (APCI) calcd for $[C_{13}H_9NO_2S + H]^+$ 244.0432, found 244.0433.

4-(Benzo[*d*]thiazol-2-yl)benzene-1,3-diol (**5p**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.10 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.17 (s, 1H), 7.01 (d, J = 9.0 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 4.73 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 169.2, 152.6, 148.5, 133.1, 127.1, 126.0, 122.6, 121.9, 121.2, 119.1, 117.0, 114.1. HRMS (APCI) calcd for $[C_{13}H_9NO_2S + H]^+$ 244.0432, found 244.0433.

1-(Benzo[*d*]thiazol-2-yl)naphthalen-2-ol (**5q**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 14.24 (s, 1H), 8.82 (d, J = 8.7 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.2 Hz, 1H), 7.84–7.88 (m, 2H), 7.65 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.41-7.47 (m, 2H), 7.35 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 167.0, 159.4, 149.9, 134.2, 133.2, 131.5, 129.9, 128.9, 128.5, 127.1, 125.7, 124.0, 122.9, 122.0, 121.5, 121.4, 120.2, 109.9. HRMS (APCI) calcd for $[C_{17}H_{11}NOS + H]^+$ 278.0640, found 278.0640.

2-(Benzo[*d*]oxazol-2-yl)phenol (**6a**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.28 (s, 1H), 8.67 (s, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.94–7.05 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 164.3, 160.9, 150.2, 136.2, 134.1, 133.1, 129.1, 121.4, 119.9, 118.7, 117.6, 116.2. HRMS (APCI) calcd for $[C_{13}H_9NO_2 + H]^+$ 212.0712, found 212.0712.

2-(Benzo[*d*]oxazol-2-yl)-4-methylphenol (**6b**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.07 (s, 1H), 8.62 (s, 1H), 7.18–7.23 (m, 2H), 7.13 (d, J = 7.8 Hz, 1H), 6.92–7.03 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 164.0, 158.3, 149.9, 136.0, 134.7, 132.7, 128.7, 121.0, 118.9, 118.3, 117.0, 115.8, 20.3. HRMS (APCI) calcd for $[C_{14}H_{11}NO_2 + H]^+$ 226.0868, found 226.0867.

2-(Benzo[*d*]oxazol-2-yl)-5-methylphenol (**6c**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.17 (s, 1H), 8.63 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 6.92–7.02 (m, 1H), 6.85 (s, 1H), 6.80 (d, J = 8.1 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 164.0, 158.3, 149.9, 136.0, 134.7, 132.7, 128.7, 121.0, 118.9, 118.3, 117.0, 115.8, 20.3. HRMS (APCI) calcd for $[C_{14}H_{11}NO_2 + H]^+$ 226.0868, found 226.0867.

2-(Benzo[*d*]oxazol-2-yl)-5-methoxyphenol (**6d**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.66 (s, 1H), 8.56 (s, 1H), 7.31 (d, J = 8.7 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 6.51–6.54 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 163.0, 149.6, 134.0, 128.1, 121.5, 120.9, 119.5, 118.2, 115.6, 115.1, 107.6, 101.0, 55.5. HRMS (APCI) calcd for $[C_{14}H_{11}NO_3 + H]^+$ 242.0817, found 242.0817.

2-(Benzo[*d*]oxazol-2-yl)-5-(diethylamino)phenol (**6e**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.41 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 6.9 Hz, 2H), 7.00 (d, J = 8.1 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 6.28 (d, J = 8.7 Hz, 1H), 6.18 (s, 1H), 3.41 (q, J = 6.9 Hz, 4H), 1.20 (t, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 161.7, 152.2, 149.6, 134.4, 127.0, 120.7, 117.8, 115.3, 104.1, 97.5, 44.6, 12.6. HRMS (APCI) calcd for $[C_{17}H_{18}N_2O_2 + H]^+$ 283.1447, found 283.1447.

2-(Benzo[*d*]oxazol-2-yl)-6-methoxyphenol (**6f**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.51 (s, 1H), 8.69 (s, 1H), 7.15–7.21 (m, 2H), 6.88–7.07 (m, 5H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 163.2, 150.8, 150.2, 148.4, 135.4, 128.8, 123.9, 120.9, 119.3, 119.1, 118.1, 116.0, 115.2, 56.2. HRMS (APCI) calcd for $[C_{14}H_{11}NO_3 + H]^+$ 242.0817, found 242.0815.

2-(Benzo[*d*]oxazol-2-yl)-4,6-di-tert-butylphenol (**6 g**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.70 (s, 1H), 7.49 (s, 1H), 7.14–7.20 (m, 2H), 6.93–7.04 (m, 2H), 5.89 (s, 1H), 1.47 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 165.2, 157.7, 149.8, 141.2, 137.1, 135.9, 128.7, 128.4, 127.2, 120.9, 118.4, 118.2, 115.6, 35.1, 34.2, 31.4, 29.4. HRMS (APCI) calcd for $[C_{21}H_{25}NO_2 + H]^+$ 324.1964, found 324.1964.

2-(Benzo[*d*]oxazol-2-yl)-4-chlorophenol (**6 h**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.34 (s, 1H), 8.61 (s, 1H), 7.32–7.39 (m, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 6.97–7.03 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 162.7, 159.5, 150.3, 135.6, 133.8, 131.9, 129.6, 124.6, 121.6, 120.4, 119.2, 118.7, 117.6, 116.5. HRMS (APCI) calcd for $[C_{13}H_8ClNO_2 + H]^+$ 246.0322, found 246.0324.

2-(Benzo[*d*]oxazol-2-yl)-4-bromophenol (**6i**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.37 (s, 1H), 8.60 (s, 1H), 7.54 (s, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.20–7.23 (m, 1H), 7.14 (d, J = 7.8 Hz, 1H), 6.99–7.03 (m, 1H), 6.97 (d, J = 6.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 162.6, 159.9, 150.3, 136.6, 135.6, 135.0, 129.6, 121.6, 121.0, 119.6, 118.8, 116.5, 111.4. HRMS (APCI) calcd for $[C_{13}H_8BrNO_2 + H]^+$ 289.9817, found 289.9817.

1-(Benzo[*d*]oxazol-2-yl)naphthalen-2-ol (**6j**). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 10.31 (s, 1H), 9.48 (d, J = 10.0 Hz, 1H), 8.36 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 9.5 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 6.76 (d, J = 9.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 178.5, 150.1, 149.2, 138.7, 134.7, 129.8, 129.3, 128.9, 127.5, 126.6, 125.9, 123.8, 120.6,120.5, 118.4, 116.7, 108.5. HRMS (APCI) calcd for $[C_{17}H_{11}NO_2 + H]^+$ 262.0868, found 262.0868.

2-(5-Methylbenzo[*d*]oxazol-2-yl)phenol (**6 k**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.29 (s, 1H), 8.66 (s, 1H), 7.40 (d, J = 7.8 Hz, 1H), 6.94–7.07 (m, 3H), 6.84 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 163.2, 160.8, 150.1, 139.7, 133.9, 133.5, 132.9, 122.1, 119.9, 119.7, 118.1, 117.5, 116.8, 21.6. HRMS (APCI) calcd for $[C_{14}H_{11}NO_2 + H]^+$ 226.0868, found 226.0868.

4-Methyl-2-(5-methylbenzo[*d*]oxazol-2-yl)phenol (**6 l**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.14 (s, 1H), 8.60 (s, 1H), 7.21 (d, J = 6.9 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H),

6.94 (d, J = 8.7 Hz, 1H), 6.84 (s, 1H), 6.78 (d, J = 7.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 162.8, 158.2, 149.7, 139.1, 134.3, 133.3, 132.5, 128.6, 121.7, 119.0, 117.7, 116.9, 116.4, 21.2, 20.3. HRMS (APCI) calcd for $[C_{15}H_{13}NO_2 + H]^+$ 240.1025, found 240.1025.

4-Fluoro-2-(5-methylbenzo[*d*]oxazol-2-yl)phenol (**6 m**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.41 (s, 1H), 8.60 (s, 1H), 7.54 (s, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 6.85 (s, 1H), 6.79 (d, J = 8.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 161.0, 159.5, 149.7, 139.8, 135.9, 134.4, 132.6, 121.9, 120.8, 119.2, 117.8, 116.6, 111.0, 21.3. HRMS (APCI) calcd for $[C_{14}H_{10}FNO_2 + H]^+$ 244.0774, found 244.0774.

4-Chloro-2-(5-methylbenzo[*d*]oxazol-2-yl)phenol (**6n**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.36 (s, 1H), 8.60 (s, 1H), 7.39 (s, 1H), 7.34 (d, J = 8.7 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 6.84 (s, 1H), 6.79 (d, J = 8.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 161.5, 159.4, 150.1, 140.2, 133.5, 133.0, 131.8, 124.6, 122.3, 119.1, 118.2, 117.0, 21.6. HRMS (APCI) calcd for $[C_{14}H_{10}ClNO_2 + H]^+$ 260.0478, found 260.0475.

4-Bromo-2-(5-methylbenzo[*d*]oxazol-2-yl)phenol (**6o**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 12.45 (s, 1H), 8.60 (s, 1H), 7.53 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.84 (s, 1H), 6.79 (d, J = 7.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 160.4, 159.0, 151.7, 138.8, 135.2, 134.1, 132.1, 132.0, 129.1, 121.8, 120.8, 119.6, 119.4, 117.5, 21.3. HRMS (APCI) calcd for $[C_{14}H_{10}BrNO_2 + H]^+$ 303.9973, found 303.9975.

2-(5-(*tert*-Butyl)benzo[*d*]oxazol-2-yl)-4-chlorophenol (**6p**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.90 (s, 1H), 9.57 (s, 1H), 8.98 (s, 1H), 7.73 (s, 1H), 7.39 (d, J = 9.0 Hz, 1H), 7.33 (s, 1H), 7.17 (s, J = 8.4 Hz, 1H), 6.95 (d, J = 9.3 Hz, 1H), 6.88 (d, J = 8.7 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 160.3, 149.3, 142.5, 135.4, 134.4, 130.1, 125.7, 121.7, 119.6, 116.5, 31.7, 29.4. HRMS (APCI) calcd for $[C_{17}H_{16}ClNO_2 + H]^+$ 302.0948, found 302.0946.

2-(5-Chlorobenzo[*d*]oxazol-2-yl)phenol (**6q**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.50 (s, 1H), 10.24 (s, 1H), 8.94 (s, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 6.91–6.97 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 162.8, 161.0, 152.5, 134.8, 133.5, 132.8, 131.8, 121.3, 119.9, 119.3, 117.1, 116.5. HRMS (APCI) calcd for $[C_{13}H_8ClNO_2 + H]^+$ 246.0322, found 246.0324.

2-(5-Chlorobenzo[*d*]oxazol-2-yl)-4-fluorophenol (**6r**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.09 (s, 1H), 10.24 (s, 1H), 8.92 (s, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.24 (t, J = 8.7 Hz, 1H), 6.90–6.97 (m, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 161.2, 157.1, 153.8, 152.6, 134.6, 132.2, 121.3, 120.5 ($^1J_{CF}$ = 91.8 Hz), 119.9, 118.5 ($^1J_{CF}$ = 29.7 Hz), 117.4 ($^1J_{CF}$ = 92.4 Hz), 116.6. HRMS (APCI) calcd for $[C_{13}H_7ClFNO_2 + H]^+$ 264.0228, found 264.0228.

4-Chloro-2-(5-chlorobenzo[*d*]oxazol-2-yl)phenol (**6 s**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.46 (s, 1H), 10.29 (s, 1H), 8.93 (s, 1H), 7.71 (s, 1H), 7.34–7.41 (m, 1H), 6.91-6.98 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 161.0, 159.7, 152.6, 133.0, 131.3, 121.2, 121.1, 119.9, 119.1, 116.6. HRMS (APCI) calcd for $[C_{13}H_7Cl_2NO_2 + H]^+$ 279.9932, found 279.9931.

4-Bromo-2-(5-chlorobenzo[*d*]oxazol-2-yl)phenol (**6 t**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.47 (s, 1H), 10.27 (s, 1H), 8.93 (s, 1H), 7.84 (s, 1H), 7.33–7.52 (m, 1H), 6.88–6.96 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 160.9, 160.1, 152.6, 135.7, 134.4, 132.3, 121.8, 121.2, 119.9, 119.6, 116.6, 110.0. HRMS (APCI) calcd for $[C_{13}H_7BrClNO_2 + H]^+$ 323.9427, found 323.9427.

2-(5-Chlorobenzo[*d*]oxazol-2-yl)-4-nitrophenol (**6u**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 15.26 (s, 1H), 10.70 (s, 1H), 9.23 (s, 1H), 8.61 (s, 1H), 8.21 (d, J = 9.0 Hz, 1H), 7.54 (d, J = 9.0 Hz, 1H), 6.99 (d, J = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 170.3, 160.4, 152.2, 138.3, 133.0, 131.2, 129.9, 129.0, 120.9, 120.1, 119.9, 117.9, 116.7. HRMS (APCI) calcd for $[C_{13}H_7ClN_2O_4 + H]^+$ 291.0173, found 291.0173.

2-(1*H*-Benzo[*d*]imidazol-2-yl)phenol (**7a**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.16 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.27–7.39 (m, 3H), 7.01 (t, J = 9.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 158.8, 152.5, 141.5, 134.0, 132.5, 127.0, 124.1, 123.3, 119.9, 118.9, 118.0, 113.4, 112.3. HRMS (APCI) calcd for $[C_{13}H_{10}N_2O + H]^+$ 211.0871, found 211.0871.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-4-methylphenol (**7b**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.90 (s, 1H), 7.85 (s, 1H), 7.62 (s, 2H), 7.13–7.24 (m, 2H), 6.92 (t, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 156.3, 152.2, 141.4, 132.8, 128.1, 126.6, 123.5, 122.8, 118.3, 117.4, 112.6, 111.9, 20.6. HRMS (APCI) calcd for $[C_{14}H_{12}N_2O + H]^+$ 225.1028, found 225.1026.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-5-methoxyphenol (**7c**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.36 (s, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.63 (s, 1H), 7.54 (s, 1H), 7.22 (s, 2H), 6.59 (t, J = 8.7 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 162.6, 160.4, 152.5, 141.2, 133.4, 127.7, 123.2, 122.6, 117.9, 111.6, 107.0, 106.1, 101.9, 55.7. HRMS (APCI) calcd for $[C_{14}H_{12}N_2O_2 + H]^+$ 241.0977, found 241.0978.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-5-(diethylamino)phenol (**7d**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 7.53 (s, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.20–7.23 (m, 2H), 6.30 (s, 1H),

6.25 (d, J = 7.5 Hz, 1H), 3.36 (q, J = 6.9 Hz, 4H), 1.16 (t, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 160.7, 153.8, 151.1, 128.0, 122.8, 104.4, 101.1, 98.6, 44.5, 13.4. HRMS (APCI) calcd for $[C_{17}H_{19}N_3O + H]^+$ 282.1606, found 282.1606.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-4,6-di-*tert*-butylphenol (**7e**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.49 (s, 2H), 7.73 (s, 1H), 7.41–7.47 (m, 3H), 7.27–7.30 (m, 2H), 1.50 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 156.0, 152.5, 140.5, 137.8, 126.9, 124.5, 123.4, 122.8, 118.6, 111.1, 110.4, 35.3, 34.4, 31.6, 29.5. HRMS (APCI) calcd for $[C_{21}H_{26}N_2O + H]^+$ 323.2123, found 323.2124.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-4-fluorophenol (**7f**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.16 (s, 1H), 7.88 (d, J = 9.6 Hz, 1H), 7.68 (s, 1H), 7.58 (s, 1H), 7.02–7.19 (m, 3H), 6.99 (d, J = 8.7 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 157.0, 154.7, 153.9, 151.1, 141.2, 133.5, 123.9 ($^1J_{CF}$ = 184.8 Hz), 118.9 ($^1J_{CF}$ = 15.9 Hz), 118.7 ($^1J_{CF}$ = 41.7 Hz), 118.5, 113.3, 112.4, 112.1 ($^1J_{CF}$ = 41.7 Hz). HRMS (APCI) calcd for $[C_{13}H_9FN_2O + H]^+$ 229.0777, found 229.0779.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-4-chlorophenol (**7 g**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.27 (s, 1H), 8.16 (s, 1H), 7.71 (s, 1H), 7.62 (s, 1H), 7.28–7.42 (m, 3H), 7.08 (d, J = 8.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 157.5, 151.2, 141.4, 134.3, 132.0, 126.4, 124.4, 123.6, 119.8, 118.9, 114.9, 112.5. HRMS (APCI) calcd for $[C_{13}H_9ClN_2O + H]^+$ 245.0482, found 245.0483.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-4-bromophenol (**7 h**). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.29 (s, 1H), 8.28 (s, 1H), 7.71 (s, 1H), 7.62 (s, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.29 (s, 2H), 7.02 (d, J = 8.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 157.9, 151.1, 141.5, 134.8, 129.2, 124.4, 123.4, 120.3, 118.9, 115.5, 112.5, 111.0. HRMS (APCI) calcd for $[C_{13}H_9BrN_2O + H]^+$ 288.9977, found 288.9977.

1-(1*H*-Benzo[*d*]imidazol-2-yl)naphthalen-2-ol (**7i**). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 15.23 (s, 1H), 9.44 (s, 1H), 8.10–8.18 (m, 1H), 7.70–7.86 (m, 2H), 7.50–7.56 (m, 1H), 7.34–7.40 (m, 1H), 7.10–7.19 (m, 2H), 6.81–6.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 165.5, 157.0, 140.3, 136.7, 135.6, 129.3, 128.0, 122.1, 120.5, 119.3, 119.1, 119.0, 118.8, 116.0. HRMS (APCI) calcd for $[C_{17}H_{12}N_2O + H]^+$ 261.1028, found 261.1028.

ACKNOWLEDGMENTS

This work was partially supported by the National Natural Science Foundation of China (nos. 21372008, 21772001), the Natural Science Foundation of Education Administration of Anhui Province (no. KJ2016A267), the Special and Excellent Research Fund of Anhui Normal University, and the Doctoral Scientific Research Foundation of Anhui Normal University (no. 2016XJJ110).

ORCID

Xinwei He http://orcid.org/0000-0002-1974-2464
Yongjia Shang http://orcid.org/0000-0001-9873-9150

REFERENCES

[1] a) J. H. P. Tyman (Ed), *Synthetic and Natural Phenols*, Elsevier, New York **1996**; b) G. Li, P. Gao, X. Lv, C. Qu, Q. Yan, Y. Wang, S. Yang, J. Wang, *Org. Lett.* **2017**, *19*, 2682.

[2] Selected cross-coupling reactions involving phenols and their derivatives: a)W. Song, L. Ackermann, *Angew. Chem. Int. Ed.* **2012**, *51*, 8251; b) X.-Q. Hao, L.-J. Chen, B. Ren, L.-Y. Li, X.-Y. Yang, J.-F. Gong, J.-L. Niu, M.-P. Song, *Org. Lett.* **2014**, *16*, 1104; c) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu, J. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 6904; d) R. Zhu, J. Wei, Z. Shi, *Chem. Sci.* **2013**, *4*, 3706; e) U. Sharma, T. Naveen, A. Maji, S. Manna, D. Maiti, *Angew. Chem. Int. Ed.* **2013**, *52*, 12669; f) R. Takise, K. Muto, J. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2014**, *53*, 6791; g) A. Correa, R. Martin, *J. Am. Chem. Soc.* **2014**, *136*, 7253; h) P. Sang, M. Yu, H. Tu, J. Zou, Y. Zhang, *Chem. Commun.* **2013**, *49*, 701; i) Y.-Z. Chen, Y.-X. Zhou, H. Wang, J. Lu, T. Uchida, Q. Xu, S.-H. Yu, H.-L. Jiang, *ACS Catal.* **2015**, *5*, 2062.

[3] a) D. L. Williams, A. Heller, *J. Phys. Chem.* **1970**, *74*, 4473; b) K. Anthony, R. G. Brown, J. D. Hepworth, K. W. Hodson, B. May, M. A. West, *J. Chem. Soc. Perkin. Trans. II* **1984**, 2111; c) T. Chen, T. Wei, Z. Zhang, Y. Chen, J. Qiang, F. Wang, X. Chen, *Dyes Pigm.* **2017**, *140*, 392; d) Z. Chen, X. Zhong, W. Qu, T. Shi, H. Liu, H. He, X. Zhang, S. Wang, *Tetrahedron Lett.* **2017**, *58*, 2596; e) E. Soleimani, M. M. Khodaei, H. Yazdani, P. Saei, J. Z. Reza, *J. Iran. Chem. Soc.* **2015**, *12*, 1281.

[4] a) M. J. Kwak, Y. Kim, *Bull. Korean Chem. Soc.* **2009**, *30*, 2865; b) J. Massue, D. Frath, P. Retailleau, G. Ulrich, R. Ziessel, *Chem. – Eur. J.* **2013**, *19*, 5375; c) J. Massue, D. Frath, G. Ulrich, P. Retailleau, R. Ziessel, *Org. Lett.* **2012**, *14*, 230; d) M. Santra, H. Moon, M.-H. Park, T.-W. Lee, Y. K. Kim, K. H. Ahn, *Chem. – Eur. J.* **2012**, *18*, 9886; e) D. Li, H. Zhang, C. Wang, S. Huang, J. Guo, Y. Wang, *J. Mater. Chem.* **2012**, *22*, 4319; f) D. Frath, J. Massue, G. Ulrich, R. Ziessel, *Angew. Chem. Int. Ed.* **2014**, *53*, 2290.

[5] a) L. Gao, S. Ye, Q. Ding, Z. Chen, J. Wu, *Tetrahedron* **2012**, *68*, 2765; b) S. P. Shukla, R. Tiwari, A. K. Verma, *Tetrahedron* **2012**, *68*, 9035; c) Q. Xiao, D. Zheng, Q. Ding, J. Wu, *Tetrahedron* **2013**, *69*, 5119; d) J. Yang, Q. Xiao, J. Sheng, J. Wu, *Tetrahedron* **2014**, *70*, 30; e) R. K. Saunthwal, A. K. Danodia, K. M. Saini, A. K. Verma, *Org. Biomol. Chem.* **2017**, *15*, 6934.

[6] a) Z. Hu, J. Dong, Y. Men, Z. Lin, J. Cai, X. Xu, *Angew. Chem. Int. Ed.* **2017**, *56*, 1805; b) X. Zhang, X. Wang, Y. Gao, X. Xu, *Chem. Commun.* **2017**, *53*, 2427.

[7] S.-C. Lu, H.-S. Li, S. Xu, G.-Y. Duan, *Org. Biomol. Chem.* **2017**, *15*, 324.

[8] a) Y. Ning, N. Wu, H. Yu, P. Liao, X. Li, X. Bi, *Org. Lett.* **2015**, *17*, 2198; b) X. Wang, Z. Wang, *Tetrahedron* **2014**, *70*, 5720. c) W. Hao, T. Zhang, M. Cai, *Tetrahedron* **2013**, *69*, 9219; d) J.-J. Cao, T.-H. Zhu, Z.-Y. Gu, W.-J. Hao, S.-Y. Wang, S.-J. Ji, *Tetrahedron* **2014**, *70*, 6985; e) T. Arto, P. Fernández, F. J. Fañanás, F. Rodríguez, *Chem. Commun.* **2016**, *52*, 13405; f) P. Sharma, N. P. Kumar, N. H. Krishna, D. Prasanna, B. Sridhar, N. Shankaraiah, *Org. Chem. Front.* **2016**, *3*, 1503.

[9] a) F. Jafarpour, N. Jalalimanesh, M. B. A. Olia, A. O. Kashani, *Tetrahedron* **2010**, *66*, 9508; b) X.-L. Xu, W.-T. Xu, J.-W. Wu, J.-B. He, H.-J. Xu, *Org. Biomol. Chem.* **2016**, *14*, 9970.

[10] a) X.-C. Tan, Y. Liang, F.-P. Bao, H.-S. Wang, Y.-M. Pan, *Tetrahedron* **2014**, *70*, 6717; b) M. Sun, S. Sun, H. Qiao, F. Yang, Y. Zhu, J. Kang, Y. Wu, Y. Wu, *Org. Chem. Front.* **2016**, *3*, 1646; c) L. Zhang, P. Xiao, X. Guan, Z. Huang, J. Zhang, X. Bi, *Org. Biomol. Chem.* **2017**, *15*, 1580; d) J. Li, G. Qin, H. Huang, *Org. Biomol. Chem.* **2016**, *14*, 10572; e) G. Deng, J. Luo, *Tetrahedron* **2013**, *69*, 5937.

[11] H.-J. Zhang, W. Lin, Z. Wu, W. Ruan, T.-B. Wen, *Chem. Commun.* **2015**, *51*, 3450.

[12] a) H. Chen, L. Zhu, C. Li, *Org. Chem. Front.* **2017**, *4*, 565; b) K. Yan, D. Yang, W. Wei, F. Wang, Y. Shuai, Q. Li, H. Wang, *J. Org. Chem.* **2015**, *80*, 1550; c) Q. Tian, B. Chen, G. Zhang, *Green Chem.* **2016**, *18*, 6236.

[13] J. Yin, Y. Bai, M. Mao, G. Zhu, *J. Org. Chem.* **2014**, *79*, 9179.

[14] a) A. K. Verma, D. Choudhary, R. K. Saunthwal, V. Rustagi, M. Patel, R. K. Tiwari, *J. Org. Chem.* **2013**, *78*, 6657; b) X. Zhou, C. Huang, Y. Zeng, J. Xiong, Y. Xiao, J. Zhang, *Chem. Commun.* **2017**, *53*, 1084; c) M. Bhanuchandra, M. R. Kuram, A. K. Sahoo, *J. Org. Chem.* **2013**, *78*, 11824.

[15] a) N. R. Patel, R. A. Flowers II, *J. Org. Chem.* **2015**, *80*, 5834; b) H.-J. Zhang, W. Lin, Z. Wu, W. Ruan, T.-B. Wen, *Chem. Commun.* **2015**, *51*, 3450.

[16] a) X.-W. He, Y.-J. Shang, Z.-Y. Yu, M. Fang, Y. Zhou, G. Han, F.-L. Wu, *J. Org. Chem.* **2014**, *79*, 8882; b) X.-W. He, Y.-J. Shang, Y. Zhou, Z.-Y. Yu, G. Han, W.-J. Jin, J.-J. Chen, *Tetrahedron* **2015**, *71*, 863; c) X.-W. He, Z.-L. Yan, X.-Q. Hu, Y. Zuo, C. Jiang, L. Jin, Y.-J. Shang, *Synth. Commun.* **2014**, *44*, 1507; d) Y.-J. Shang, X.-Q. Hu, X.-W. He, J.-J. Tao, G. Han, F.-L. Wu, J. Wang, *J. Org. Chem.* **2015**, *80*, 4760; e) X.-W. He, J.-J. Tao, X.-Q. Hu, H. Wang, Y.-J. Shang, *J. Org. Chem.* **2016**, *81*, 2062.

[17] a) G. Zhang, P. Wang, F. Yang, Y. Wu, *Tetrahedron* **2015**, *71*, 57; b) M. Chhabra, S. Sinha, S. Banerjee, P. Paira, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 213; c) K. Bahrami, M. M. Khodaei, F. Naali, *J. Org. Chem.* **2008**, *73*, 6835.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: He X, Wu Y, Jin W, Wang X, Wu C, Shang Y. Highly efficient $AgNO_3$-catalyzed approach to 2-(benzo[*d*]azol-2-yl)phenols from salicylaldehydes with 2-aminothiophenol, 2-aminophenol and benzene-1,2-diamine. *Appl Organometal Chem*. 2018;e4284. https://doi.org/10.1002/aoc.4284