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Synthesis and fungicidal activity of novel 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-ones

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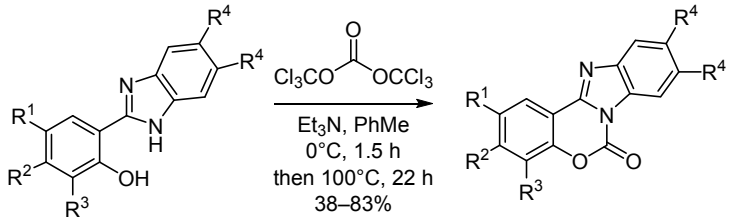

R^1–R^4 = H, Me, OMe, Br

A series of 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one derivatives were synthesized in moderate to good yield by reaction of 2-(1*H*-benzimidazol-2-yl)phenols with triphosgene, and the structures of the target compounds were characterized by NMR, IR, and HRMS methods. The fungicidal activity of the compounds was evaluated at 50 μg/ml concentration, and unsubstituted 6*H*-benzimidazo-[1,2-*c*][1,3]benzoxazin-6-one showed 75.1% activity against *Sclerotinia sclerotium*, which was higher than that of chlorothalonil.

Keywords: 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-ones, substituted 2-(1*H*-benzimidazol-2-yl)phenols, fungicidal activity, synthesis.

1,3-Benzoxazinone derivatives have received much attention in the research fields of pharmaceuticals and pesticides because of their broad pharmacological and biological activities such as antibacterial and antifungal,[1–3] peroxisome proliferator activated receptor (PPAR) agonistic, antidiabetic, antihyperlipidaemic,[4] DNA-PK enzyme inhibiting,[5,6] anticancer.[7,8] 1,3-Benzoxazinone derivatives also possess photochromic properties.[9,10] Therefore, the studies on 1,3-benzoxazinones raised great interest of chemists. On the other hand, benzimidazoles also have unique activities like insecticidal,[11,12] antibacterial and antifungal,[13–15] herbicidal,[16] and antiviral.[17] Benzimidazole derivative carbendazim (methyl benzimidazol-2-ylcarbamate) is extensively used as anthelmintic, antiprotozoal agent, and post-harvest fungicide on fruits and vegetables.[18] Thiabendazole serves as a common post-harvest pesticide to control the diseases of citrus fruits caused by fungi.[19]

Recently, we reported series of substituted 1,3-benzoxazines which showed good fungicidal activities.[20–22] However, to our knowledge, there are few reports on compounds containing both 1,3-benzoxazinone and benzimidazole moieties. Therefore, we designed a new class of 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one derivatives **4** by the fusion of 1,3-benzoxazinone moiety and benzimidazole structure in order to obtain highly active compounds as our continuous projects aimed at the discovery of new active fungicidies.[20–23] The synthetic route to the target compounds **4a**–**p** is shown in Scheme 1.

The intermediate 2-(1*H*-benzimidazol-2-yl)phenols **3a**–**p** were synthesized in 38–78% yields (Table 1) by the reaction of substituted salicylaldehydes **1a**–**h** with benzene-1,2-diamine derivatives **2a**,**b** in the presence of $NaHSO_3$ in EtOH[24] (Scheme 1). Afterward, to prepare substituted 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-ones **4a**–**p**, we initially screened the reaction conditions using the reaction of 2-(1*H*-benzimidazol-2-yl)phenol (**3a**) with triphosgene[25] as a model reaction (Table 2). It was found that in the absence of a base the reaction gave the desired product **4a** in only 8% yield (Table 2, entry 1). In the search of an appropriate base (Table 2, entries 2–6), Et_3N was found to be the most suitable for the reaction as shown by yield of 75% (Table 2, entry 7). Then, we investigated the effect of the ratio of reactants, temperature, and reaction time on the yield of the reaction (Table 2, entries 8–18, 20) and

Scheme 1. Synthesis of 2-(1*H*-benzimidazol-2-yl)phenols **3a–p** and 6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-ones **4a–p**

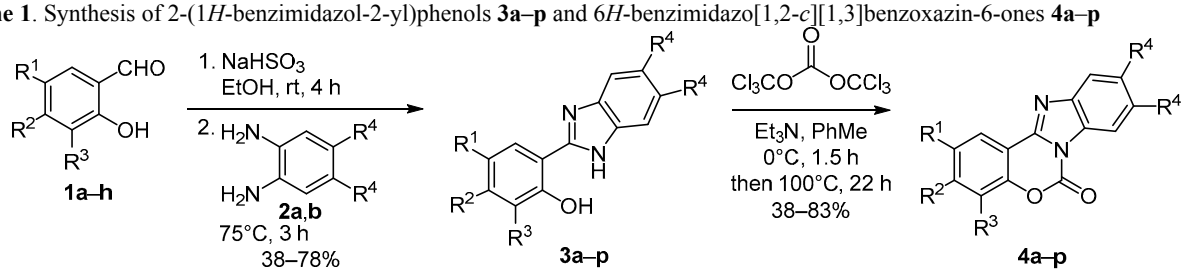

Table 1. Yields of compounds **3**, **4 a–p**

Entry	R^1	R^2	R^3	R^4	Compound **3** (yield, %)	Compound **4** (yield, %)*
1	H	H	H	H	**3a** (77)	**4a**** (83)
2	H	H	Me	H	**3b** (62)	**4b**** (68)
3	H	Me	H	H	**3c** (70)	**4c**** (72)
4	Me	H	H	H	**3d** (73)	**4d**** (76)
5	H	H	OMe	H	**3e** (73)	**4e**** (70)
6	H	OMe	H	H	**3f** (77)	**4f** (79)
7	OMe	H	H	H	**3g** (78)	**4g** (83)
8	Br	H	H	H	**3h** (40)	**4h**** (50)
9	H	H	H	Me	**3i** (74)	**4i** (78)
10	H	H	Me	Me	**3j** (61)	**4j** (63)
11	H	Me	H	Me	**3k** (68)	**4k** (68)
12	Me	H	H	Me	**3l** (71)	**4l** (71)
13	H	H	OMe	Me	**3m** (69)	**4m** (66)
14	H	OMe	H	Me	**3n** (73)	**4n** (69)
15	OMe	H	H	Me	**3o** (76)	**4o** (79)
16	Br	H	H	Me	**3p** (38)	**4p** (38)

* Reaction conditions: compound **3** : triphosgene : Et_3N = 1:0.65:2, solvent PhMe, 100°C, 22 h.
** Compounds described earlier.[26]

Table 2. Optimization of the reaction conditions for the synthesis of compound **4a** (solvent PhMe)

Entry	Compound **3a**: triphosgene	Time, h	Temperature, °C	Base (equiv)	Yield, %
1	1:0.65	18	100	–	8
2	1:0.65	18	100	DMF (2)	29
3	1:0.65	18	100	*N*-Ethylethylenediamine (2)	38
4	1:0.65	18	100	Pyridine (2)	51
5	1:0.65	18	100	DMAP (2)	70
6	1:0.65	18	100	Triethylenediamine (2)	63
7	1:0.65	18	100	Et_3N (2)	75
8	1:0.65	18	100	Et_3N (1)	63
10	1:0.65	18	100	Et_3N (3)	74
11	1:0.65	18	100	Et_3N (4)	67
12	1:0.55	18	100	Et_3N (2)	67
13	1:0.75	18	100	Et_3N (2)	75
14	1:0.85	18	100	Et_3N (2)	61
15	1:0.65	18	90	Et_3N (2)	56
16	1:0.65	18	100	Et_3N (2)	78
17	1:0.65	18	110	Et_3N (2)	58
18	1:0.65	20	100	Et_3N (2)	78
19	**1:0.65**	**22**	**100**	**Et_3N (2)**	**83**
20	1:0.65	24	100	Et_3N (2)	70

obtained the optimized reaction conditions: the molar ratio of compound **3a** : triphosgene : Et_3N = 1:0.65:2, temperature 100°C, time 22 h, in which the desired product **4a** was produced in 83% yield (Table 2, entry 19).

Under the optimized reaction conditions 6*H*-benzimidazo-[1,2-*c*][1,3]benzoxazin-6-ones **4a–p** were prepared in 38–83% yields (Table 1). It can be seen that the yield of compound **4a** without the substituents in 1,3-benzoxazinone and benzimidazole is higher than the yields of compounds with any R = Me (Table 1, entries 1–4). Moreover, the position of methyl or methoxy group on the phenyl ring has influence on the reaction yield following the order of position 6 > position 7 > position 8 regardless of the nature of the substituent.

The structures of compounds **4a–p** were characterized by IR, ^1H and ^{13}C NMR spectra, and HRMS. This can be illustrated with compound **4b**. In ^1H NMR spectrum, signals at 8.26–7.30 ppm correspond to the protons of the phenyl group, and the single peak at 2.48 ppm – to the protons of the methyl group. In ^{13}C NMR spectrum, the peak at 149.4 ppm belongs to the carbonyl carbon, the signals at 146.1–111.9 ppm correspond to the carbons of the phenyl group. The signal at 143.7 ppm corresponds to carbon atom linked to the N=C double bond, and signal at 15.6 ppm – to the methyl carbon.

According to the standard method NY/T1156.5-2006,[20–22] the *in vitro* fungicidal activity of compounds **4a–p** against *Sclerotinia sclerotium*, *Phytophthora capsici*, *Botrytis cinerea*, *Rhizoctonia solani*, *Gibberella zeae*, and *Magnaporthe oryzae* was evaluated at the 50 μg/ml concentration, employing the mycelium growth rate test method with chlorothalonil as the reference compound. As shown in Table 3, compounds **4a–p** exhibited moderate to good fungicidal activity against the tested fungi. In general, the fungicidal activity against *Sclerotinia sclerotium* was the best, and the activities of compounds **4a**,**c**,**h**,**n** were 75.1, 63.6, 56.9, and 58.8%, respectively, which are all higher than that of chlorothalonil. For *Gibberella zeae*, *Phytophthora capsici*, *Sclerotinia sclerotium*, and *Magnaporth oryzae*, compound **4a** without substituents on the phenyl ring demonstrated higher activity than those with substituents. For *Rhizoctonia solani*, compounds **4h**,**p** with electron-withdrawing group (R^1 = Br) showed higher activity than those with electron-donating group or hydrogen. For *Gibberella zeae*, compounds with methyl group as a substituent exhibited higher activity than those

Table 3. Fungicidal activity of compounds **4a**–**p** (inhibition rate, %)

Compound	R^1	R^2	R^3	R^4	Fungi					
					Gibberella zeae	*Phytophthora capsici*	*Sclerotinia sclerotium*	*Botrytis cinerea*	*Rhizoctonia solani*	*Magnaporthe oryzae*
4a	H	H	H	H	51.7	35.7	75.1	9.1	41.5	44.4
4b	H	H	Me	H	45.2	13.3	35.7	41.9	38.9	12.5
4c	H	Me	H	H	29.0	20.0	63.6	9.7	11.1	25.0
4d	Me	H	H	H	48.4	3.3	17.9	9.7	8.3	10.0
4e	H	H	OMe	H	12.5	16.7	29.4	7.7	28.8	33.3
4f	H	OMe	H	H	9.7	3.3	32.1	32.3	13.9	10.0
4g	OMe	H	H	H	41.7	3.3	37.3	15.4	36.4	16.7
4h	Br	H	H	H	37.5	3.3	56.9	12.8	48.5	33.3
4i	H	H	H	Me	12.5	6.7	37.3	7.7	6.1	16.7
4j	H	H	Me	Me	29.2	6.7	49.0	17.9	6.1	16.7
4k	H	Me	H	Me	25.0	10.0	5.9	17.9	21.2	16.7
4l	Me	H	H	Me	8.3	6.7	9.8	10.3	22.7	16.7
4m	H	H	OMe	Me	20.8	10.0	9.8	15.4	27.3	25.0
4n	H	OMe	H	Me	33.3	10.0	58.8	7.7	6.1	33.3
4o	OMe	H	H	Me	12.5	10.0	9.8	7.7	15.2	16.7
4p	Br	H	H	Me	29.2	6.7	5.9	7.7	30.3	16.7
Chlorothalonil					73.1	89.3	53.8	96.2	94.2	92.6

with methoxy group regardless of the position of these groups, and for *Botrytis cinerea*, when any R = Me, the fungicidal activity of compounds abided the same rule.

In conclusion, we have prepared a variety of substituted 1,3-benzoxazinobenzimidazoles in moderate to good yields, and the fungicidal activity of the compounds was evaluated. 6*H*-Benzimidazo[1,2-*c*][1,3]benzoxazin-6-one showed 75.1% activity against *Sclerotinia sclerotium*, which was higher than that of the reference compound chlorothalonil.

Experimental

IR spectra of compounds were recorded for samples in KBr pellets on a Nicolet 6700 FT-IR instrument. ^{1}H and ^{13}C NMR spectra (500 and 125 MHz, respectively) were recorded on a Bruker Avance spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as internal standard. HRMS were recorded on a Waters UPLC/XevoQTof LC/MS instrument (ESI). Melting points were determined on a WRS-1B digital melting point apparatus and were uncorrected. Column chromatography was carried out using silica gel (200–300 mesh).

Reagents were purchased from Meryer Chemical Technology Co., Ltd. and Energy & Chemicals Company (China) of analytical grades and used without further purification. All anhydrous solvents were dried by standard procedures.

Synthesis of substituted 2-(1*H*-benzimidazol-2-yl)-phenols 3a–p[24] (General method). Salicylaldehyde **1a**–**h** (10 mmol) and $NaHSO_3$ (1.56 g, 15 mmol) were added into a 100-ml round-bottomed flask containing EtOH (30 ml), and the mixture was stirred at room temperature for 4 h. Then the corresponding benzene-1,2-diamine **2a**,**b** (10 mmol) was added and the solution was heated at 75°C for 3 h (checked by TLC). After the reaction was completed, the reaction solution was poured into cold H_2O (100 ml), and a large amount of precipitate formed. After standing, the solid was filtered off, washed with EtOAc, and the obtained crude product was purified by column chromatography, eluent EtOAc – petroleum ether, 1:4.

2-(1*H*-Benzimidazol-2-yl)phenol (3a). Yield 1.618 g (77%), white solid, mp 251–252°C. IR spectrum, ν, cm^{-1}: 3325 (NH), 1632 (C=N), 1594 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.13 (2H, s, OH, NH); 8.02 (1H, dd, *J* = 7.8, *J* = 1.4, H Ar); 7.67 (1H, d, *J* = 6.7, H Ar); 7.57 (1H, s, H Ar); 7.34 (1H, s, H Ar); 7.24 (2H, s, H Ar); 7.01–6.98 (2H, m, H Ar). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 158.0 (C–OH); 151.7 (C=N); 140.9; 133.2; 131.7; 126.2; 123.3; 122.4; 119.1; 117.9; 117.2; 112.6; 111.5. Found, *m*/*z*: 210.0798 $[M+H]^+$. $C_{13}H_{10}N_2O$. Calculated, *m*/*z*: 210.0793.

2-(1*H*-Benzimidazol-2-yl)-6-methylphenol (3b). Yield 1.390 g (62%), yellow solid, mp 218–220°C. IR spectrum, ν, cm^{-1}: 3239 (NH), 1626 (C=N), 1596 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.55 (1H, s, NH); 13.27 (1H, s, OH); 7.92 (1H, d, *J* = 7.8, H Ar); 7.75 (1H, d, *J* = 7.8, H Ar); 7.63 (1H, d, *J* = 7.8, H Ar); 7.34–7.29 (3H, m, H Ar); 6.95 (1H, s, H Ar); 2.29 (3H, s, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 156.5 (C–OH); 152.2 (C=N); 140.8; 133.2; 132.6; 125.8; 123.7; 123.4; 122.5; 118.6; 117.9; 111.6; 111.5; 15.9 (CH_3). Found, *m*/*z*: 224.0955 $[M+H]^+$. $C_{14}H_{12}N_2O$. Calculated, *m*/*z*: 224.0950.

2-(1*H*-Benzimidazol-2-yl)-5-methylphenol (3c). Yield 1.570 g (70%), yellow solid, mp 237–239°C. IR spectrum, ν, cm^{-1}: 3254 (NH), 1634 (C=N), 1587 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.13 (2H, s, OH, NH); 7.97 (1H, d, *J* = 8.0, H Ar); 7.68 (2H, d, *J* = 3.3,

H Ar); 7.30–7.29 (2H, m, H Ar); 6.90 (1H, s, H Ar); 6.87 (1H, d, J = 8.0, H Ar); 2.35 (3H, s, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 158.0 (C–OH); 151.9 (C=N); 142.0; 126.0 (2C); 122.5; 120.1 (2C); 117.8; 117.4 (2C); 111.4; 110.0; 21.1 (CH_3). Found, *m*/*z*: 224.0944 $[M+H]^+$. $C_{14}H_{12}N_2O$. Calculated, *m*/*z*: 224.0950.

2-(1*H*-Benzimidazol-2-yl)-4-methylphenol (3d). Yield 1.637 g (73%), yellow solid, mp 247–248°C. IR spectrum, ν, cm^{-1}: 3289 (NH), 1637 (C=N), 1586 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.16 (1H, s, NH); 12.94 (1H, s, OH); 7.91 (1H, s, H Ar); 7.72 (1H, s, H Ar); 7.64 (1H, s, H Ar); 7.29 (2H, s, H Ar); 7.20 (1H, d, J = 8.3, H Ar); 6.97 (1H, d, J = 8.3, H Ar); 2.35 (3H, s, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 155.9 (C–OH); 151.8 (C=N); 141.0; 133.2; 132.4; 127.6; 126.2; 123.1; 122.3; 117.9; 117.0; 112.2; 111.5; 20.2 (CH_3). Found, *m*/*z*: 224.0942 $[M+H]^+$. $C_{14}H_{12}N_2O$. Calculated, *m*/*z*: 224.0950.

2-(1*H*-Benzimidazol-2-yl)-6-methoxyphenol (3e). Yield 1.754 g (73%), white solid, mp 217–218°C. IR spectrum, ν, cm^{-1}: 3335 (NH), 1626 (C=N), 1593 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.28 (2H, s, OH, NH); 7.76–7.69 (3H, m, H Ar); 7.32 (2H, s, H Ar); 7.09 (1H, d, J = 7.9, H Ar); 6.98 (1H, t, J = 8.0, H Ar); 3.87 (3H, s, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 152.0 (C–OH); 148.6 (C=N); 148.4; 140.8; 133.1; 123.3; 122.5; 118.7; 118.0; 117.6; 113.9; 112.6; 111.6; 55.7 (OCH_3). Found, *m*/*z*: 240.0895 $[M+H]^+$. $C_{14}H_{12}N_2O_2$. Calculated, *m*/*z*: 240.0899.

2-(1*H*-Benzimidazol-2-yl)-5-methoxyphenol (3f). Yield 1.850 g (77%), white solid, mp 238–239°C. IR spectrum, ν, cm^{-1}: 3347 (NH), 1619 (C=N), 1590 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.46 (1H, s, NH); 13.08 (1H, s, OH); 8.02 (1H, d, J = 8.6, H Ar); 7.70 (1H, s, H Ar); 7.62 (1H, s, H Ar); 7.28 (2H, d, J = 4.3, H Ar); 6.67 (2H, dt, J = 6.3, J = 2.4, H Ar); 3.84 (3H, s, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 162.2 (C–OH); 160.0 (C=N); 152.1; 140.8; 127.3; 122.8; 122.2; 117.5 (2C); 111.2; 106.5; 105.7; 101.5; 55.3 (OCH_3). Found, *m*/*z*: 240.0899 $[M+H]^+$. $C_{14}H_{12}N_2O_2$. Calculated, *m*/*z*: 240.2573.

2-(1*H*-Benzimidazol-2-yl)-4-methoxyphenol (3g). Yield 1.874 g (78%), white solid, mp 283–284°C. IR spectrum, ν, cm^{-1}: 3314 (NH), 1612 (C=N), 1590 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.14 (1H, s, NH); 12.77 (1H, s, OH); 7.71 (3H, d, J = 1.7, H Ar); 7.32–7.30 (2H, m, H Ar); 7.04–7.00 (2H, m, H Ar); 3.84 (3H, s, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 152.0 |(C–OH); 151.9 (C=N); 150.8; 139.6; 132.1; 131.6; 130.9; 118.3; 118.0; 117.8; 112.5; 111.4; 109.7; 55.7 (OCH_3). Found, *m*/*z*: 240.0899 $[M+H]^+$. $C_{14}H_{12}N_2O_2$. Calculated, *m*/*z*: 240.2573.

2-(1*H*-Benzimidazol-2-yl)-4-bromophenol (3h). Yield 1.157 g (40%), white solid, mp 220–221°C. IR spectrum, ν, cm^{-1}: 3346 (NH), 1636 (C=N), 1582 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.29 (2H, s, OH, NH); 8.29 (1H, s, H Ar); 7.70 (1H, s, H Ar); 7.64 (1H, s, H Ar); 7.51 (1H, d, J = 8.4, H Ar); 7.29 (2H, s, H Ar); 7.01 (1H, d, J = 8.7, H Ar). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 157.2 (C–OH, C=N); 150.3 (2C); 133.9 (2C); 128.4 (2C); 123.1; 119.4 (2C); 114.6; 110.1. Found, *m*/*z*: 287.9891 $[M+H]^+$. $C_{13}H_9BrN_2O$. Calculated, *m*/*z*: 287.9898.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)phenol (3i). Yield 1.763 g (74%), white solid, mp 238–239°C. IR spectrum, ν, cm^{-1}: 3256 (NH), 1636 (C=N), 1590 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.24 (1H, s, NH); 12.94 (1H, s, OH); 8.00 (1H, d, J = 7.6, H Ar); 7.46 (1H, s, H Ar); 7.34 (2H, t, J = 7.7, H Ar); 6.99 (2H, m, H Ar); 2.33 (6H, s, $2CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 157.9 (C–OH); 150.8 (C=N); 131.3 (2C); 125.9 (2C); 119.0 (2C); 117.9; 117.1 (2C); 112.8; 111.5; 20.0 ($2CH_3$). Found, *m*/*z*: 238.1101 $[M+H]^+$. $C_{15}H_{14}N_2O$. Calculated, *m*/*z*: 238.1106.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)-6-methylphenol (3j). Yield 1.539 g (61%), yellow solid, mp 297–298°C. IR spectrum, ν, cm^{-1}: 3342 (NH), 1632 (C=N), 1601 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.64 (1H, s, NH); 13.00 (1H, s, OH); 7.91 (1H, d, J = 7.6, H Ar); 7.55 (1H, s, H Ar); 7.42 (1H, s, H Ar); 7.30 (1H, d, J = 7.2, H Ar); 6.96 (1H, t, J = 7.6, H Ar); 2.42 (3H, s, CH_3); 2.40 (3H, s, CH_3); 2.32 (3H, s, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 156.2 (C–OH); 151.2 (C=N); 139.3; 132.1; 132.0; 131.6; 130.8; 125.5; 123.3; 118.4; 117.9; 111.8; 111.4; 20.0 (CH_3); 19.9 (CH_3); 15.8 (CH_3). Found, *m*/*z*: 252.1257 $[M+H]^+$. $C_{16}H_{16}N_2O$. Calculated, *m*/*z*: 252.1263.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)-5-methylphenol (3k). Yield 1.716 g (68%), yellow solid, mp 238–239°C. IR spectrum, ν, cm^{-1}: 3235 (NH), 1648 (C=N), 1585 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.24 (1H, s, NH); 12.91 (1H, s, OH); 7.95 (1H, d, J = 7.0, H Ar); 7.56–7.42 (2H, m, H Ar); 6.97–6.81 (2H, m, H Ar); 2.39 (6H, s, $2CH_3$); 2.38 (3H, s, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 157.8 (C–OH); 151.1 (C=N); 141.5; 139.4; 131.8; 131.5; 130.7; 125.7; 120.0; 117.8; 117.3; 111.3; 110.2; 21.1 (CH_3); 20.0 (CH_3); 19.9 (CH_3). Found, *m*/*z*: 252.1256 $[M+H]^+$. $C_{16}H_{16}N_2O$. Calculated, *m*/*z*: 252.1263.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)-4-methylphenol (3l). Yield 1.791 g (71%), yellow solid, mp 244–246°C. IR spectrum, ν, cm^{-1}: 3278 (NH), 1637 (C=N), 1581 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.03 (1H, s, NH); 12.91 (1H, s, OH); 7.86 (1H, s, H Ar); 7.48 (1H, s, H Ar); 7.38 (1H, s, H Ar); 7.17 (1H, d, J = 7.6, H Ar); 6.94 (1H, d, J = 8.0, H Ar); 2.34 (9H, s, $3CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 155.8 (C–OH); 150.9 (C=N); 132.0 (2C); 127.5 (2C); 125.8 (2C); 117.9; 116.8 (2C); 112.4; 111.4; 20.2 (CH_3); 19.9 ($2CH_3$). Found, *m*/*z*: 252.1268 $[M+H]^+$. $C_{16}H_{16}N_2O$. Calculated, *m*/*z*: 252.1263.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)-6-methoxyphenol (3m). Yield 1.851 g (69%), yellow solid, mp 239–241°C. IR spectrum, ν, cm^{-1}: 3318 (NH), 1637 (C=N), 1592 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.47 (1H, s, NH); 13.00 (1H, s, OH); 7.67 (1H, d, J = 7.9, H Ar); 7.56 (1H, s, H Ar); 7.42 (1H, s, H Ar); 7.11 (1H, d, J = 7.8, H Ar); 6.99 (1H, t, J = 8.0, H Ar); 3.90 (3H, s, OCH_3); 2.40 (6H, s, $2CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 151.1 (C–OH); 148.6 (C=N); 148.2; 139.3; 132.1; 131.5; 130.9; 118.5; 117.9; 117.4; 113.6; 112.7; 111.4; 55.7 (OCH_3); 19.9 ($2CH_3$). Found, *m*/*z*: 268.1207 $[M+H]^+$. $C_{16}H_{16}N_2O_2$. Calculated, *m*/*z*: 268.1212.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)-5-methoxyphenol (3n). Yield 1.958 g (73%), yellow solid, mp 294–295°C.

IR spectrum, ν, cm^{-1}: 3257 (NH), 1616 (C=N), 1591 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.44 (1H, s, NH); 12.80 (1H, s, OH); 7.91 (1H, d, *J* = 8.7, H Ar); 7.36 (2H, s, H Ar); 6.60–6.56 (2H, m, H Ar); 3.78 (3H, s, OCH_3); 2.30 (6H, s, $2CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 161.9 (2C); 159.8 (2C); 151.3 (2C); 126.9; 106.3 (2C); 106.0 (2C); 101.5 (2C); 55.3 (OCH_3); 20.0 ($2CH_3$). Found, *m*/*z*: 268.1206 $[M+H]^+$. $C_{16}H_{16}N_2O_2$. Calculated, *m*/*z*: 268.1212.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)-4-methoxyphenol (3o). Yield 2.039 g (76%), yellow solid, mp 292–294°C. IR spectrum, ν, cm^{-1}: 3259 (NH), 1639 (C=N), 1581 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 12.87 (1H, s, NH); 12.78 (1H, s, OH); 7.61 (1H, s, H Ar); 7.43 (1H, s, H Ar); 7.38 (1H, s, H Ar); 6.94 (2H, s, H Ar); 3.79 (3H, s, OCH_3); 2.32 (6H, s, $2CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 152.0 (C–OH); 151.9 (C=N); 150.8; 139.6; 118.2 (2C); 117.8 (2C); 112.5; 111.4; 111.3; 109.7 (2C); 55.7 (OCH_3); 19.9 ($2CH_3$). Found, *m*/*z*: 268.1218 $[M+H]^+$. $C_{16}H_{16}N_2O_2$. Calculated, *m*/*z*: 268.1212.

4-Bromo-2-(5,6-dimethyl-1*H*-benzimidazol-2-yl)phenol (3p). Yield 1.205 g (38%), yellow solid, mp 200–202°C. IR spectrum, ν, cm^{-1}: 3281 (NH), 1633 (C=N), 1580 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 13.40 (1H, s, NH); 13.02 (1H, s, OH); 8.23 (1H, s, H Ar); 7.45 (3H, m, H Ar); 6.98 (1H, d, *J* = 8.7, H Ar); 2.32 (6H, s, $2CH_3$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 157.0 (2C, C–OH, C=N); 149.3; 133.5 (2C); 128.0 (2C); 119.3 (2C); 118.0; 114.8; 111.6; 110.0; 19.9 ($2CH_3$). Found, *m*/*z*: 316.0205 $[M+H]^+$. $C_{15}H_{13}BrN_2O$. Calculated, *m*/*z*: 316.0211.

Synthesis of substituted 6*H*-benzimidazo[1,2-*c*][1,3]-benzoxazin-6-ones 4a–p (General method). A mixture of substituted 2-(benzimidazolyl)phenol **3a**–**p** (2 mmol) and Et_3N (0.405g, 4 mmol) was added into a 100-ml three-necked round-bottom flask containing PhMe (30 ml), then PhMe solution of triphosgene (0.386g, 1.3 mmol) was slowly added. The formed reaction mixture was stirred at 0°C for 1.5 h. Then, the mixture was heated at 100°C for 22 h under nitrogen atmosphere. After the reaction was completed (TLC control), the reaction mixture was diluted with EtOAc (30 ml), filtered, and concentrated under the reduced pressure. The crude product was purified by column chromatography (eluent EtOAc – petroleum ether, 1:6), affording the desired products as white solids.

6*H*-Benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4a). Yield 0.392 g (83%), mp 200–202°C. IR spectrum, ν, cm^{-1}: 1771 (C=O), 1628 (C=N), 1588 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.37 (1H, d, *J* = 7.8, H Ar); 8.31 (1H, d, *J* = 7.4, H Ar); 7.89–7.88 (1H, m, H Ar); 7.65 (1H, d, *J* = 7.3, H Ar); 7.53–7.44 (4H, m, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.4 (C=O); 146.2; 144.0 (C=N); 143.3; 133.5; 130.7; 126.6; 126.4; 125.9; 125.3; 120.3; 117.3; 115.2; 112.6. Found, *m*/*z*: 237.0657 $[M+H]^+$. $C_{14}H_9N_2O_2$. Calculated, *m*/*z*: 237.0664.

4-Methyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4b). Yield 0.340 g (68%), mp 191–193°C. IR spectrum, ν, cm^{-1}: 1765 (C=O), 1630 (C=N), 1608 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.26 (1H, d, *J* = 7.4, H Ar); 8.12 (1H, d, *J* = 7.7, H Ar); 7.82 (1H, d, *J* = 7.8, H Ar); 7.50–7.45 (2H, m, H Ar); 7.44–7.40 (1H, m, H Ar); 7.30 (1H, t, *J* = 7.6, H Ar); 2.48 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$); δ, ppm: 149.4 (C=O); 146.1; 143.7 (C=N); 142.9; 134.4; 130.2; 126.6; 126.2; 125.5; 125.3; 122.4; 119.8; 114.7; 111.9; 15.6 (CH_3). Found, *m*/*z*: 251.0828 $[M+H]^+$. $C_{15}H_{11}N_2O_2$. Calculated, *m*/*z*: 251.0821.

3-Methyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4c). Yield 0.360 g (72%), mp 214–216°C. IR spectrum, ν, cm^{-1}: 1766 (C=O), 1629 (C=N), 1576 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 7.5, H Ar); 8.14 (1H, d, *J* = 8.0, H Ar); 7.80 (1H, d, *J* = 7.8, H Ar); 7.46 (2H, t, *J* = 7.7, H Ar); 7.21 (1H, d, *J* = 8.0, H Ar); 7.16 (1H, s, H Ar); 2.45 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.1 (C=O); 146.0; 144.6 (C=N); 143.7; 143.0; 130.3; 127.2; 126.2; 125.2; 124.5; 119.8; 116.9; 114.7; 109.5; 21.8 (CH_3). Found, *m*/*z*: 251.0815 $[M+H]^+$. $C_{15}H_{11}N_2O_2$. Calculated, *m*/*z*: 251.0821.

2-Methyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4d). Yield 0.380 g (76%), mp 186–188°C. IR spectrum, ν, cm^{-1}: 1780 (C=O), 1627 (C=N), 1594 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 7.5, H Ar); 8.05 (1H, s, H Ar); 7.80 (1H, d, *J* = 7.4, H Ar); 7.46 (2H, t, *J* = 6.8, H Ar); 7.36 (1H, d, *J* = 8.4, H Ar); 7.24 (1H, d, *J* = 8.5, H Ar); 2.42 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 149.1 (C=O); 145.8; 143.6 (C=N); 142.9; 136.1; 134.0; 130.3; 126.1; 125.4; 124.5; 119.9; 116.5; 114.7; 111.7; 20.7 (CH_3). Found, *m*/*z*: 251.0817 $[M+H]^+$. $C_{15}H_{11}N_2O_2$. Calculated, *m*/*z*: 251.0821.

4-Methoxy-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4e). Yield 0.373 g (70%), mp 231–232°C. IR spectrum, ν, cm^{-1}: 1766 (C=O), 1630 (C=N), 1592 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 8.15 (1H, s, H Ar); 7.85 (1H, s, H Ar); 7.76 (1H, s, H Ar); 7.51 (2H, s, H Ar); 7.42–7.39 (2H, m, H Ar); 3.95 (3H, s, OCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 147.0 (C=O); 146.6; 143.4 (C=N); 142.8; 140.6; 130.4; 126.0; 125.8; 125.0; 119.7; 115.4; 115.2; 114.3; 113.2; 56.3 (OCH_3). Found, *m*/*z*: 267.0776 $[M+H]^+$. $C_{15}H_{11}N_2O_3$. Calculated, *m*/*z*: 267.0770.

3-Methoxy-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4f). Yield 0.421 g (79%), mp 188–190°C. IR spectrum, ν, cm^{-1}: 1770 (C=O), 1632 (C=N), 1580 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.18 (1H, d, *J* = 7.5, H Ar); 8.12 (1H, d, *J* = 8.6, H Ar); 7.75 (1H, d, *J* = 7.5, H Ar); 7.45–7.38 (2H, m, H Ar); 6.91 (1H, d, *J* = 8.2, H Ar); 6.79 (1H, s, H Ar); 3.85 (3H, s, OCH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 163.9 (C=O); 152.9; 146.3 (C=N); 144.0; 143.3; 130.4; 126.4; 126.2; 125.2; 119.8; 114.8; 114.0; 105.2; 101.3; 56.1 (OCH_3). Found, *m*/*z*: 267.0765 $[M+H]^+$. $C_{15}H_{11}N_2O_3$. Calculated, *m*/*z*: 267.0770.

2-Methoxy-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4g). Yield 0.442 g (83%), mp 191–192°C. IR spectrum, ν, cm^{-1}: 1772 (C=O), 1625 (C=N), 1580 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.32–8.27 (1H, m, H Ar); 8.14 (1H, s, H Ar); 7.86 (1H, d, *J* = 7.0, H Ar); 7.53–7.46 (2H, m, H Ar); 7.42 (1H, dd, *J* = 8.5, *J* =1.8, H Ar); 7.31 (1H, d, *J* = 8.5, H Ar); 2.47 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 157.5 (C=O); 146.2; 145.6 (C=N); 143.9; 143.3; 130.7; 126.5; 125.8; 122.0; 120.2; 118.5;

115.1; 112.8; 106.1; 56.3 (OCH_3). Found, *m*/*z*: 267.0763 $[M+H]^+$. $C_{15}H_{11}N_2O_3$. Calculated, *m*/*z*: 267.0770.

2-Bromo-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4h). Yield 0.315 g (50%), mp 259–261°C. IR spectrum, ν, cm^{-1}: 1781 (C=O), 1626 (C=N), 1584 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 8.36 (1H, d, *J* = 2.3, H Ar); 8.20–8.18 (1H, m, H Ar); 7.93–7.90 (2H, m, H Ar); 7.60–7.54 (3H, m, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 150.4 (C=O); 145.4; 143.3 (C=N); 142.7; 135.7; 130.4; 126.3; 126.0; 125.4; 119.9; 119.3; 117.6; 114.7; 114.3. Found, *m*/*z*: 314.9762 $[M+H]^+$. $C_{14}H_8BrN_2O_3$. Calculated, *m*/*z*: 314.9769.

9,10-Dimethyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4i). Yield 0.412 g (78%), mp 262–263°C. IR spectrum, ν, cm^{-1}: 1768 (C=O), 1622 (C=N), 1589 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 8.24 (1H, d, *J* = 7.4, H Ar); 7.95 (1H, s, H Ar); 7.71 (1H, t, *J* = 7.7, H Ar); 7.64 (1H, s, H Ar); 7.55 (1H, d, *J* = 8.1, H Ar); 7.51 (1H, t, *J* = 7.5, H Ar); 2.40 (3H, s, CH_3); 2.38 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.0 (C=O); 145.1; 143.1 (C=N); 142.1; 135.6; 135.2; 132.8; 128.7; 126.0; 124.9; 120.1; 116.9; 115.0; 112.5; 20.5 (CH_3); 20.5 (CH_3). Found, *m*/*z*: 265.0972 $[M+H]^+$. $C_{16}H_{13}N_2O_2$. Calculated, *m*/*z*: 265.0977.

4,9,10-Trimethyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4j). Yield 0.351 g (63%), mp 257–258°C. IR spectrum, ν, cm^{-1}: 1768 (C=O), 1625 (C=N), 1563 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.10 (1H, s, H Ar); 8.02 (1H, s, H Ar); 7.57 (1H, s, H Ar); 7.39 (1H, dd, *J* = 8.5, 1.6, H Ar); 7.29–7.27 (1H, m, H Ar); 2.46 (3H, s, CH_3); 2.42 (3H, s, CH_3); 2.40 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 149.1 (C=O); 145.2; 143.2 (C=N); 142.1; 136.0; 135.4; 135.0; 133.7; 128.7; 124.5; 120.0; 116.6; 114.9; 112.1; 20.8 (CH_3); 20.5 ($2CH_3$). Found, *m*/*z*: 279.1128 $[M+H]^+$. $C_{17}H_{15}N_2O_2$. Calculated, *m*/*z*: 279.1134.

3,9,10-Trimethyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4k). Yield 0.379 g (68%), mp 234–235°C. IR spectrum, ν, cm^{-1}: 1766 (C=O), 1627 (C=N), 1586 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.20 (1H, d, *J* = 7.9, H Ar); 8.05 (1H, s, H Ar); 7.60 (1H, s, H Ar); 7.26 (1H, d, *J* = 4.6, H Ar); 7.22 (1H, s, H Ar); 2.50 (3H, s, CH_3); 2.44 (3H, s, CH_3); 2.42 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 151.1 (C=O); 145.4; 144.2 (C=N); 143.3; 142.3; 135.4; 134.9; 128.7; 127.2; 124.5; 120.0; 117.0; 115.0; 109.9; 29.7 (CH_3); 21.9 (CH_3); 20.5 (CH_3). Found, *m*/*z*: 279.1140 $[M+H]^+$. $C_{17}H_{15}N_2O_2$. Calculated, *m*/*z*: 279.1134.

2,9,10-Trimethyl-6*H*-benzimidazo[1,2-*c*][1,3]benzoxazin-6-one (4l). Yield 0.395 g (71%), mp 260–261°C. IR spectrum, ν, cm^{-1}: 1764 (C=O), 1627 (C=N), 1598 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.15 (1H, d, *J* = 7.3, H Ar); 8.03 (1H, s, H Ar); 7.58 (1H, s, H Ar); 7.44 (1H, d, *J* = 7.0, H Ar); 7.34–7.30 (1H, m, H Ar); 2.52 (3H, s, CH_3); 2.43 (3H, s, CH_3); 2.41 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 149.4 (C=O); 145.5; 143.1 (C=N); 142.2; 135.5; 135.0; 134.1; 128.6; 126.6; 125.5; 122.4; 120.0; 114.9; 112.3; 20.5 (CH_3); 20.5 (CH_3); 15.7 (CH_3). Found, *m*/*z*: 279.1129 $[M+H]^+$. $C_{17}H_{15}N_2O_2$. Calculated, *m*/*z*: 279.1134.

4-Methoxy-9,10-dimethyl-6*H*-benzimidazo[1,2-*c*][1,3]-benzoxazin-6-one (4m). Yield 0.388 g (66%), mp 278–279°C. IR spectrum, ν, cm^{-1}: 1764 (C=O), 1615 (C=N), 1587 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.10 (1H, s, H Ar); 7.92 (1H, dd, *J* = 7.9, *J* = 1.0, H Ar); 7.63 (1H, s, H Ar); 7.39 (1H, t, *J* = 8.1, H Ar); 7.18–7.16 (1H, m, H Ar); 4.02 (3H, s, OCH_3); 2.45 (3H, s, CH_3); 2.43 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 147.6 (C=O); 145.2; 142.7 (C=N); 142.1; 140.7; 135.6; 135.2; 128.7; 126.1; 120.1; 115.8; 115.0; 114.5; 113.4; 56.4 (OCH_3); 29.7 (CH_3); 20.5 (CH_3). Found, *m*/*z*: 295.1077 $[M+H]^+$. $C_{17}H_{15}N_2O_2$. Calculated, *m*/*z*: 295.1083.

3-Methoxy-9,10-dimethyl-6*H*-benzimidazo[1,2-*c*][1,3]-benzoxazin-6-one (4n). Yield 0.406 g (69%), mp 227–228°C. IR spectrum, ν, cm^{-1}: 1766 (C=O), 1623 (C=N), 1585 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.23 (1H, d, *J* = 8.7, H Ar); 8.02 (1H, s, H Ar); 7.57 (1H, s, H Ar); 7.02 (1H, d, *J* = 8.4, H Ar); 6.90 (1H, s, H Ar); 3.96 (3H, d, *J* = 8.4, OCH_3); 2.46 (3H, s, CH_3); 2.43 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 163.4 (C=O); 152.5; 145.3 (C=N); 143.2; 142.1; 135.3; 134.5; 128.4; 125.9; 119.7; 114.8; 113.7; 105.2; 101.1; 55.9 (OCH_3); 29.7 (CH_3); 20.4 (CH_3). Found, *m*/*z*: 295.1088 $[M+H]^+$. $C_{17}H_{15}N_2O_3$. Calculated, *m*/*z*: 295.1083.

2-Methoxy-9,10-dimethyl-6*H*-benzimidazo[1,2-*c*][1,3]-benzoxazin-6-one (4o). Yield 0.465 g (79%), mp 247–248°C. IR spectrum, ν, cm^{-1}: 1758 (C=O), 1623 (C=N), 1601 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.04 (1H, s, H Ar); 7.69 (1H, d, *J* = 3.0, H Ar); 7.58 (1H, s, H Ar); 7.32 (1H, d, *J* = 9.1, H Ar); 7.15 (1H, dd, *J* = 9.1, *J* = 3.0, H Ar); 3.92 (3H, s, OCH_3); 2.43 (3H, s, CH_3); 2.41 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 157.3 (C=O); 145.2; 145.2 (C=N); 143.2; 142.1; 135.5; 135.1; 128.7; 121.3; 120.0; 118.2; 115.0; 112.8; 105.7; 56.1 (OCH_3); 20.5 ($2CH_3$). Found, *m*/*z*: 295.1075 $[M+H]^+$. $C_{17}H_{15}N_2O_3$. Calculated, *m*/*z*: 295.1083.

2-Bromo-9,10-dimethyl-6*H*-benzimidazo[1,2-*c*][1,3]-benzoxazin-6-one (4p). Yield 0.261 g (38%), mp 282–283°C. IR spectrum, ν, cm^{-1}: 1777 (C=O), 1626 (C=N), 1588 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.33 (1H, s, H Ar); 8.05 (1H, s, H Ar); 7.61 (2H, s, H Ar); 7.44 (1H, d, *J* = 6.0, H Ar); 2.44 (3H, s, CH_3); 2.42 (3H, s, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 149.8 (C=O); 143.7; 142.6 (C=N); 142.1; 135.9; 135.8; 135.5; 128.7; 127.4; 120.3; 119.0; 118.7; 115.0; 114.2; 20.6 (CH_3); 20.5 (CH_3). Found, *m*/*z*: 343.0076 $[M+H]^+$. $C_{16}H_{11}BrN_2O_2$ Calculated, *m*/*z*: 343.0082.

***In vitro* fungicidal activity of compounds 4a–p** was tested according to the standard method NY/T1156.5-2006.[20–22] The *in vitro* inhibition of mycelium growth in the agriculture medium caused by the title compounds against six strains of phytopathogenic fungi was performed. Referencing standard method NY/T1156.5-2006, antifungal activity assays adopted drug-containing medium method. Stock solution of every test compound was prepared in Me_2CO and then diluted to the required test concentration (500 μg/ml) with sorporl-144 (concentration 200 μg/ml). Solutions of the test compounds (1 ml) were added to potato dextrose agar (PDA) medium (9 ml, 45°C) to provide the final

concentration of 50 μg/ml. The mixed medium without sample was used as the blank control. The inocula, 4 mm in diameter, were removed from the margins of actively growing colonies of mycelium and placed in the centers of the above plates. 4 Replicates per treatment were performed. Percentages of growth inhibition were calculated by comparing the mean value of the diameters of the mycelia in the test plates after placing in 24°C biochemical incubator thermostat for 3 days.

Supplementary information file containing ^{1}H and ^{13}C NMR spectra of the synthesized compounds **4a**–**p** is available at the journal website at http://link.springer.com/journal/10593.

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