DOI:10.1021/jf903855y

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

# Synthesis of 1-Acyl-3-isopropenylbenzimidazolone Derivatives and Their Activity against *Botrytis cinerea*†

Sheng-Kun Li,§ Zhi-Qin Ji,§ Ji-Wen Zhang,§ Zheng-Yan Guo,§ and Wen-Jun Wu*,§,#

§Institute of Pesticide Science, Northwest Agricultural and Forestry University, Yangling, Shaanxi 712100, China, and #State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China

A series of 1-acyl-3-isopropenylbenzimidazolone derivatives were synthesized, and their structures were characterized by $^{1}H$ and $^{13}C$ NMR and elemental analysis. Their fungicidal activities against *Botrytis cinerea* were also evaluated by spore germination assay. The acrylic acid, methacrylic acid, 4-chlorophenyl acetic acid, and 2-chlorobenzoic acid derivatives exhibited strong fungicidal activity. This implied that benzimidazolones might be potential fungicide leading compounds.

**KEYWORDS: Benzimidazolone derivatives; synthesis; fungicidal activities**

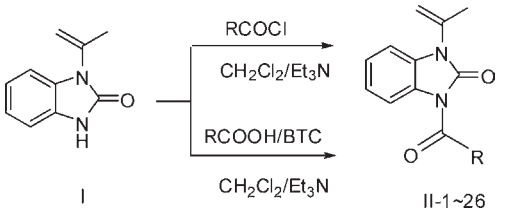
## INTRODUCTION

Gray mold, which is caused by *Botrytis cinerea*, is one of the most common diseases on vegetable and fruit crops (*1*). Its development is dependent upon favorable climatic conditions, and it has been a serious threat in greenhouses when humidity is high and temperature is moderate. Protecting crops against *B. cinerea* requires multiple applications of fungicides, during the whole period from bud burst until ripening. However, with the extensive use of synthetic fungicides, *B. cinerea* has developed resistance to many commercialized products (*2*, *3*).

Benzimidazolone derivatives have been found to exhibit anti-HIV (*4*), antitrichinellosis (*5*), antinociceptive (*6*), antitumor activities (*7*), and other pharmacological activities (*8*−*11*), whereas only a few of them exhibit antimicrobial activities. For example, the benzimidazolone derivative bearing a sugar residue on the aromatic nitrogen effectively inhibits the growth of bacteria such as *Bacillus cereus*, *Streptomyces chartreusis*, and *Escherichia coli* (*12*). However, to the best of our knowledge, there has been no report on the fungicidal activity of benzimidazolones against plant pathogens.

1-Isopropenylbenzimidazolone (**Scheme 1**, compound **I**), which could be prepared by the condensation of *o*-phenylenediamine with acetoacetic ester (*13*), is often used as the intermediate to synthesize other benzimidazolones (*7*, *14*, *15*). In most cases, isopropenyl, playing the role of amine protecting group, was removed or substituted by other groups in the succeeding procedures. In other cases, substituents were introduced to the other nitrogen atom of 1-isopropenylbenzimidazolone. In a recent paper, five sulfonamide derivatives of isopropenylbenzimidazolone were synthesized and their cytotoxicities against several strains of cancer cell evaluated (*7*). In general, the bioactivities of isopropenylbenzimidazolone derivatives were still not thoroughly investigated.

**Scheme 1**




In this paper, we prepared a series of isopropenylbenzimidazolone derivatives; herein the alkyl carbonyl or aromatic carbonyl was introduced to the nitrogen atom by amide bond (**Scheme 1**, compounds **II-1**−**II-26**). Their fungicidal activities against *B. cinerea* were evaluated by the method of spore germination, and several compounds exhibited strong inhibition. Here we report the exciting results. The structure−activity relationship of these benzimidazolone derivatives is also discussed.

## MATERIALS AND METHODS

**Instruments.** The melting points of the products were determined on an X-4 apparatus (Beijing Tech Instrument Co., Beijing, China) and are uncorrected. $^{1}H$ and $^{13}C$ NMR spectra were taken on a Bruker Avance 600 MHz (600 MHz for $^{1}H$ and 150 MHz for $^{13}C$, respectively) spectrometer in $CDCl_3$ solution with TMS as an internal standard. Elemental analyses were carried out on an Elementar Vairo EL analyzer.

*Synthetic Procedures.* Isopropenyl benzimidazolone (**I**) (Zhengzhou Sigma Chemical Co., Henan, China), bis(trichloromethyl)carbonate (GL Biochem Co., Shanghai, China), carboxylic acids, dichloromethane, and triethylamine were commercial reagents (Sinopharm Chemical Reagent Co., Shanghai, China). Target compounds (**II-1**−**II-n**) were synthesized by the acylations of **I** with corresponding carboxylic acid or acyl chloride (*7*) (**Scheme 1**; **Table 1**).

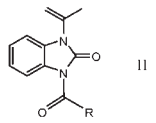
*Method A. General Synthetic Procedures for* ***II-1***− ***II-19***. With nitrogen protection, to a solution of **I** (0.174 g, 1 mmol) in dichloromethane (10 mL)

†Part of the ECUST-Qian Pesticide Cluster.

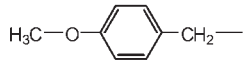
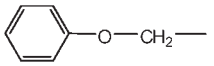
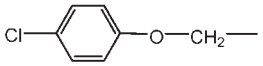
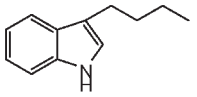
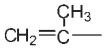
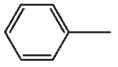
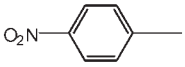
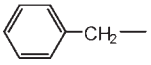
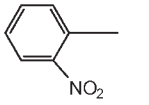
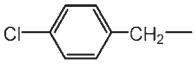
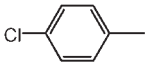
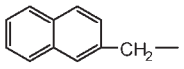
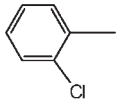
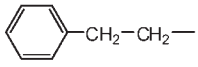
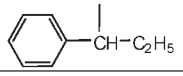
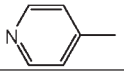
*Address correspondence to this author at the Institute of Pesticide Science, Northwest Agricultural and Forestry University, No. 3 Taicheng Road, Yangling, Shaanxi 712100, China (telephone +86-29-87093987; fax +86-29-87093987; e-mail wenjun_wu@263.net).

 Published on Web 01/26/2010 

**Table 1.** Title Compounds and Inhibition of Spore Germination against *B. cinerea*



II

| No. | R | $IC_{50}$, μg/ml (±SD) | No. | R | $IC_{50}$, μg/ml (±SD) |
|---|---|---|---|---|---|
| II-1 | $H_3C$— | >500 | II-14 |  | 118.08±1.26 |
| II-2 | $C_2H_5$— | >500 | II-15 |  | 303.04±0.90 |
| II-3 | $C_3H_7$— | >500 | II-16 |  | 108.12±3.46 |
| II-4 | $CH_3(CH_2)_2CH_2$— | 254.27±1.05 | II-17 |  | 301.63±2.27 |
| II-5 | $CH_3(CH_2)_3CH_2$— | 129.29±0.94 | II-18 | $CH_2$=CH— | 32.16±0.35 |
| II-6 | $(CH_3)_2CH$— | 133.99±0.67 | II-19 |  | 64.04±1.36 |
| II-7 | $(C_2H_5)_2CH$— | 276.60±0.62 | II-20 |  | 81.94±0.73 |
| II-8 | $(CH_3)_2CHCH_2CH_2$— | 334.60±2.78 | II-21 |  | 93.32±1.22 |
| II-9 |  | 168.42±0.16 | II-22 |  | 441.73±1.17 |
| II-10 |  | 17.27±0.45 | II-23 |  | 66.85±0.80 |
| II-11 |  | >500 | II-24 |  | 17.17±0.34 |
| II-12 |  | 125.76±0.72 | II-25 |  | 103.71±1.84 |
| II-13 |  | 185.83±0.51 | II-26 |  | 151.98±1.07 |
| | Pyrimethanil | 209.46±0.76 | | | |

were added triethylamine (0.3 mL, 2.1 mmol) and carboxylic acid (1 mmol). After the mixture had been stirred for 5 min in an ice−water bath, bis(trichloromethyl) carbonate (BTC, 40 mg, 1 mmol) in dichloromethane (2 mL) was added, and the mixture was stirred overnight at room temperature. Saturated $NaHCO_3$ solution (20 mL) was added to the mixture, and the mixture was extracted by dichloromethane (3 × 15 mL). The organic extracts were combined, washed with water and saturated NaCl solution in that order, dried over $Na_2SO_4$, and finally concentrated under vacuum. The concentrated mixture was subjected to a silica gel column, and eluted by the mixture of petroleum ether and ethyl acetate (5:1, v/v) to give target compounds.

*Method B. General Synthetic Procedures for* ***II-20*****−*****II-26***. With nitrogen protection, to a solution of **I** (0.174 g, 1 mmol) in dichloromethane (10 mL) was added triethylamine (0.3 mL, 2.1 mmol). Carboxylic chloride (1 mmol) in dichloromethane (2 mL) was added in an ice−water bath, and the mixture was stirred for 5 h at room temperature. After the solvent had been evaporated, saturated $NH_4Cl$ solution (10 mL) was added, and the mixture was extracted by dichloromethane (3 × 15 mL). The organic extracts were combined, washed with water and saturated NaCl solution in that order, dried over $Na_2SO_4$, and finally concentrated under vacuum. After purification with a silica gel column as described above, target compounds were obtained.

*1-Acetyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-1***). Yield, 60.1%; mp, 102−104 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.20 (s, 3H, $CH_3$ of isopropenyl), 2.77 (s, 3H, $CH_3$ of acetyl), 5.26 (s, 1H, C=$CH_2$), 5.47 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.27 (m, 2H, Ph), 8.22 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8 ($CH_3$ of isopropenyl), 25.8 ($CH_3$ of acetyl), 105.6, 115.1, 115.9, 122.9, 124.6, 126.4, 129.3, 137.0, 150.8 (CO), 170.6 (CO of acetyl). Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.82; H, 5.65; N, 12.82.

*1-(Prop-1-en-2-yl)-3-propionyl-1H-benzo[d]imidazol-2(3H)-one* (***II-2***). Yield, 65.8%; mp, 126−128 °C; $^1$H NMR ($CDCl_3$), $\delta$ 1.26 (t, $J$ = 7.5 Hz, 3H, $CH_3$ of propionyl), 2.19 (s, 3H, $CH_3$ of isopropenyl), 3.19 (q, $J$ = 7.5 Hz, 2H, $CH_2$ of propionyl), 5.25 (s, 1H, C=$CH_2$), 5.47 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.27 (m, 2H, Ph), 8.24 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 8.2 ($CH_3$ of propionyl), 19.8 ($CH_3$ of isopropenyl), 31.0 ($CH_2$ of propionyl), 108.6, 115.4, 115.9, 122.9, 124.4, 126.6, 129.4, 137.1, 150.7 (CO), 174.6 (CO of propionyl). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.96; H, 6.19; N, 12.09.

*1-Butyryl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-3***). Yield, 90.0%; mp, 104−106 °C; $^1$H NMR ($CDCl_3$), $\delta$ 1.05 (t, $J$ = 7.5 Hz, 3H, $CH_3$ of butyryl), 1.81 (m, 2H, $CH_2$ of butyryl), 2.19 (s, 3H, $CH_3$ of isopropenyl), 3.15 (t, $J$ = 7.5 Hz, 2H, $CH_2$ of butyryl), 5.25 (s, 1H, C=$CH_2$), 5.47 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.16−7.27 (m, 2H, Ph), 8.24 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 13.7 ($CH_3$ of butyryl), 17.6 ($CH_2$ of butyryl), 19.8 ($CH_3$ of isopropenyl), 39.3 ($CH_2$ of butyryl), 108.6, 115.4, 115.9, 122.9, 124.4, 126.6, 129.4, 137.1, 150.7 (CO), 173.7 (CO of butyryl). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.92; H, 6.65; N, 11.37.

*1-Pentanoyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-4***). Yield, 88.4%; mp, 114−116 °C; $^1$H NMR ($CDCl_3$), $\delta$ 0.97 (t, $J$ = 7.8 Hz, 3H, $CH_3$ of pentanoyl), 1.42−1.46 (m, 2H, $CH_2$ of pentanoyl), 1.76 (m, 2H, $CH_2$ of pentanoyl), 2.19 (s, 3H, $CH_3$), 3.11 (t, $J$ = 7.4 Hz, 2H, $CH_2$ of pentanoyl), 5.26 (s, 1H, C=$CH_2$), 5.47 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.27 (m, 2H, Ph), 8.24 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 13.9 ($CH_3$ of pentanoyl), 19.8, 22.3($CH_2$ of pentanoyl), 26.2($CH_2$ of pentanoyl), 37.2 ($CH_2$ of pentanoyl), 108.6, 115.4, 115.9, 122.9, 124.4, 126.6, 129.4, 137.0, 150.7 (CO), 174.0 (CO of pentanoyl). Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.95; H, 7.24; N, 10.65.

*1-Hexanoyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-5***). Yield, 90.1%; mp, 42−44 °C; $^1$H NMR ($CDCl_3$), $\delta$ 0.92 (t, $J$ = 7.8 Hz, 3H, $CH_3$ of hexanoyl), 1.36−1.43 (m, 4H, 2 × $CH_2$ of hexanoyl), 1.78 (t, $J$ = 7.8 Hz, 2H, $CH_2$ of hexanoyl), 2.19 (s, 3H, $CH_3$), 3.16(t, $J$ = 7.8 Hz, 2H, $CH_2$ of hexanoyl), 5.27 (s, 1H, C = $CH_2$), 5.47 (s, 1H, C = $CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.23 (m, 2H, Ph), 8.24 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 13.9 ($CH_3$ of hexanoyl), 19.8, 22.5 ($CH_2$ of hexanoyl), 23.8 ($CH_2$ of hexanoyl), 31.3 ($CH_2$ of hexanoyl), 37.4 ($CH_2$ of hexanoyl), 108.6, 115.4, 115.9, 122.9, 124.4, 126.6, 129.4, 137.1, 150.7 (CO), 173.9 (CO of hexanoyl). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.68; H, 7.52; N, 10.15.

*1-Isobutyryl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-6***). Yield, 89.7%; mp, 88−90 °C; $^1$H NMR ($CDCl_3$), $\delta$ 1.26 (d, $J$ = 7.4 Hz, 3H, $CH_3$ of isobutyryl), 1.30 (d, $J$ = 7.4 Hz, 3H, $CH_3$ of isobutyryl), 2.22 (s, 3H, $CH_3$ of isopropenyl), 4.02−4.06(m, 1H, CH of isobutyryl), 5.26 (s, 1H, C=$CH_2$), 5.47 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.27 (m, 2H, Ph), 8.23 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 18.9 (2 × $CH_3$ of isobutyryl), 19.8 ($CH_3$ of isopropenyl), 34.3 (CH of isobutyryl), 108.6, 115.4, 116.1, 122.9, 124.4, 126.9, 129.5, 137.1, 150.4 (CO), 178.3 (CO of isobutyryl). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.95; H, 6.65; N, 11.35.

*1-(2-Ethylbutanoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-7***). Yield, 91.0%; mp, 118−120 °C; $^1$H NMR ($CDCl_3$), $\delta$ 0.97 (t, $J$ = 7.0 Hz, 6H, 2 × $CH_3$ of 2-ethylbutanoyl), 1.66 (m, 4H, 2 × $CH_2$ of 2-ethylbutanoyl), 2.20 (s, 3H, $CH_3$), 2.30−2.32 (m, 1H, CH of 2-ethylbutanoyl), 5.27 (s, 1H, C=$CH_2$), 5.48 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.16−7.26 (m, 2H, Ph), 8.26 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 11.6 (2 × $CH_3$ of 2-ethylbutanoyl), 19.7, 24.3 (2 × $CH_2$ of 2-ethylbutanoyl), 47.4 (CH of 2-ethylbutanoyl), 105.8, 114.9, 114.7, 122.6, 124.2, 126.0, 129.3, 137.1, 151.0 (CO), 170.4 (CO of 2-ethylbutanoyl). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.72; H, 7.48; N, 10.15.

*1-(4-Methylpentanoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-8***). Yield, 81.1%; mp, 70−72 °C; $^1$H NMR ($CDCl_3$), $\delta$ 0.96 (d, $J$ = 7.6 Hz, 6H, 2 × $CH_3$ of 4-methylpentanoyl), 1.66−1.69 (m, 2H, $CH_2$ of 4-methylpentanoyl), 1.66−1.69 (m, 1H, CH of 4-methylpentanoyl), 2.20 (s, 3H, $CH_3$), 3.18 (t, $J$ = 7.6, 2H, $CH_2$ of 4-methylpentanoyl), 5.26 (s, 1H, C=$CH_2$), 5.47 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.16−7.26 (m, 2H, Ph), 8.23(d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 22.4 (2 × $CH_3$ of 4-methylpentanoyl), 27.7 ($CH_2$ of 4-methylpentanoyl), 32.9 (CH of 4-methylpentanoyl), 35.5 ($CH_2$ of 4-methylpentanoyl), 108.6, 115.5, 115.9, 122.9, 124.4, 126.6, 129.4, 137.1, 150.7 (CO), 174.2 (CO of 4-methylpentanoyl). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.75; H, 7.49; N, 10.12.

*1-(2-Phenylacetyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-9***). Yield, 59.2%; mp, 124−126 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.20 (s, 3H, $CH_3$), 4.54 (s, 2H, $CH_2$ of 2-phenylacetyl), 5.27 (s, 1H, C=$CH_2$), 5.49 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.12−7.38 (m, 7H, Ph), 8.21 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 43.5 ($CH_2$ of 2-phenylacetyl), 108.6, 115.7, 116.0, 123.0, 124.7, 126.5, 127.1, 128.5, 129.4, 129.9, 133.5, 136.9, 150.4 (CO), 171.7 (CO of 2-phenylacetyl). Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.12; H, 5.60; N, 9.46.

*1-(2-(4-Chlorophenyl)acetyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-10***). Yield, 73.6%; mp, 90−92 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.20 (s, 3H, $CH_3$), 4.51 (s, 2H, $CH_2$ of (4-chlorophenyl)acetyl), 5.27 (s, 1H, C=$CH_2$), 5.49 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.12−7.38 (m, 6H, Ph), 8.20 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 42.8 ($CH_2$ of (4-chlorophenyl)acetyl), 108.7, 115.7, 116.0, 123.1, 124.8, 126.5, 128.7, 129.5, 131.3, 132.0, 133.1, 136.9, 150.6 (CO), 171.2 (CO of (4-chlorophenyl)acetyl). Anal. Calcd for $C_{18}H_{15}N_2O_2Cl$: C, 66.16; H, 4.63; N, 8.57. Found: C, 66.38; H, 4.69; N, 8.45.

*1-(2-(Naphthalen-2-yl)acetyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-11***). Yield, 72.5%; mp, 128−130 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.25 (s, 3H, $CH_3$), 4.99 (s, 2H, $CH_2$ of 2-(naphthalen-2-yl)acetyl), 5.32 (s, 1H, C=$CH_2$), 5.51 (s, 1H, C=$CH_2$), 7.08−7.14 (m, 2H, Ph), 7.20−7.25 (m, 1H, Ph), 7.46−7.53 (m, 4H, Ph), 7.83−7.94 (m, 4H, Ph), 8.16 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.9, 41.4 ($CH_2$ of 2-(naphthalen-2-yl)acetyl), 108.7. 115.7, 116.1, 123.0, 123.9, 124.7, 125.4, 125.7, 126.3, 126.6, 128.2, 128.3, 128.8, 129.5, 130.3, 132.4, 133.8, 137.0, 150.9 (CO), 171.4 (CO of 2-(naphthalen-2-yl)acetyl). Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.35; H, 5.39; N, 8.09.

*1-(3-Phenylpropanoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-12***). Yield, 51.2%; mp, 78−80 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.18 (s, 3H, $CH_3$), 3.11 (t, $J$ = 7.0 Hz, 2H, $CH_2$ of 2-phenylacetyl), 3.50 (t, $J$ = 7.0 Hz, 2H, $CH_2$ of 2-phenylacetyl), 5.24 (s, 1H, C=$CH_2$), 5.46 (s, 1H, C=$CH_2$), 7.05 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.27 (m, 7H, Ph), 8.24 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 30.1 ($CH_2$ of 2-phenylacetyl), 39.0 ($CH_2$ of 2-phenylacetyl), 108.6, 115.4, 115.9, 122.9, 124.6, 126.1, 126.5, 128.4, 128.6, 129.4, 137.0, 140.6, 150.4 (CO), 172.9 (CO of 2-phenylacetyl). Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.65; H, 6.03; N, 8.95.

*1-(2-Phenylbutanoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-13***). Yield, 65.1%; mp, 48−50 °C; $^1$H NMR ($CDCl_3$), $\delta$ 0.92 (t, $J$ = 7.8 Hz, 3H, $CH_3$ of 2-phenylbutanoyl), 1.91, 2.26 (m, 2H, $CH_2$ of 2-phenylbutanoyl), 2.14 (s, 3H, $CH_3$), 5.20 (s, 1H, C=$CH_2$), 5.44 (s, 1H, C=$CH_2$), 5.26 (m, 1H, CH of 2-phenylbutanoyl), 6.99 (d, $J$ = 7.0 Hz, 1H, Ph), 7.10−7.33 (m, 5H, Ph), 7.48 (d, $J$ = 7.0, 2H, Ph), 8.25 (d, $J$ = 8.0, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 12.1 ($CH_3$ of 2-phenylbutanoyl), 19.7, 27.4 ($CH_2$ of 2-phenylbutanoyl), 52.0 (CH of 2-phenylbutanoyl), 108.4, 115.6, 116.0, 122.8, 124.5, 126.8, 127.1, 128.4, 128.8, 129.3, 136.9, 138.5, 150.3 (CO), 174.5 (CO of 2-phenylbutanoyl). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 75.16; H, 6.38; N, 8.46.

*1-(2-(4-Methoxyphenyl)acetyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-14***). Yield, 80.1%; mp, 118−120 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.20 (s, 3H, $CH_3$), 3.80 (s, 3H, $CH_3$ of 2-(4-methoxyphenyl)acetyl), 4.48 (s, 2H, $CH_2$ of 2-(4-methoxyphenyl)acetyl), 5.26 (s, 1H, C=$CH_2$), 5.48 (s, 1H, C=$CH_2$), 6.89 (d, $J$ = 7.8 Hz, 2H, Ph), 7.05 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.22 (m, 2H, Ph), 7.30 (d, $J$ = 7.8 Hz, 2H, Ph), 8.21 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 42.6 ($CH_2$ of 2-(4-methoxyphenyl)-acetyl), 55.2 ($CH_3$ of 2-(4-methoxyphenyl)acetyl), 108.6, 113.9, 115.6, 116.0, 122.9, 124.6, 125.6, 126.7, 129.5, 130.9, 137.0, 150.7 (CO), 158.7, 172.1 (CONH). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.93; H, 5.72; N, 8.50.

*1-(2-Phenoxyacetyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-15***). Yield, 46.4%; mp, 118−120 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.22 (s, 3H, $CH_3$), 5.29 (s, 1H, C=$CH_2$), 5.50 (s, 1H, C=$CH_2$), 5.43 (s, 2H, $CH_2$ of 2-phenoxyacetyl), 6.99−7.03 (m, 4H, Ph), 7.17−7.32 (m, 4H, Ph), 8.25 (d, $J$ = 7.8 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 68.3 ($CH_2$ of 2-phenoxyacetyl), 108.9, 114.8, 115.6, 115.8, 121.6, 123.3, 125.1, 125.9, 129.5, 130.0, 136.8, 150.6 (CO), 157.9, 168.6 (CO of 2-phenoxyacetyl). Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.34; H, 5.30; N, 8.89.

*1-(2-(4-Chlorophenoxy)acetyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-16***). Yield, 77.5%; mp, 136−138 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.22 (s, 3H, $CH_3$), 5.29 (s, 1H, C = $CH_2$), 5.50 (s, 1H, C=$CH_2$), 5.40 (s, 2H, $CH_2$ of 2-(4-chlorophenoxy)acetyl), 6.93−6.96 (m, 2H, Ph), 7.09 (d, $J$ = 8.0 Hz, 1H, Ph), 7.19−7.27 (m, 4H, Ph), 8.23 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 68.5 ($CH_2$ of 2-(4-chlorophenoxy)acetyl), 109.0,

115.8, 116.1, 123.4, 124.6, 125.2, 125.6, 126.6, 129.4, 130.0, 136.7, 150.5 (CO), 156.4, 168.2 (CO of 2-(4-chlorophenoxy)acetyl). Anal. Calcd for $C_{18}H_{15}ClN_2O_3$: C, 63.07; H, 4.41; N, 8.17. Found: C, 63.22; H, 4.49; N, 8.00.

*1-(4-(1H-Indol-3-yl)butanoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-17***). Yield, 65.4%; mp, 176−178 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.18 (s, 3H, $CH_3$), 2.22 (m, 2H, $CH_2$ of 4-(indol-3-yl)butanoyl), 2.92 (m, 2H, $CH_2$ of 4-(indol-3-yl)butanoyl), 3.27 (m, 2H, $CH_2$ of 4-(indol-3-yl)butanoyl), 5.24 (s, 1H, C=$CH_2$), 5.46 (s, 1H, C=$CH_2$), 7.03−7.22 (m, 5H, Ph or heterocycle), 7.25 (s, 1H, heterocycle), 7.33 (d, $J$ = 7.5 Hz, 1H, Ph), 7.65 (d, $J$ = 7.5 Hz, 1H, Ph), 7.99 (s, 1H, NH), 8.23 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 24.4 ($CH_2$ of 4-(indol-3-yl)butanoyl), 24.5 ($CH_2$ of 4-(indol-3-yl)butanoyl), 37.2 ($CH_2$ of 4-(indol-3-yl)butanoyl), 108.5, 111.0, 115.5, 115.7, 115.9, 118.9, 119.1, 121.5, 121.8, 122.8, 124.4, 126.6, 127.4, 129.4, 136.3, 137.0, 150.1 (CO), 173.4 (CO of 4-(indol-3-yl)butanoyl). Anal. Calcd for $C_{22}H_{21}N_3O_2$: C, 73.52; H, 5.89; N, 11.69. Found: C, 73.69; H, 5.98; N, 11.52.

*1-Acryloyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-18***). Yield, 77.1%; mp, 108−110 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.20 (s, 3H, $CH_3$ of isopropenyl), 5.27 (s, 1H, C=$CH_2$), 5.48 (s, 1H, C=$CH_2$), 5.99 (d, $J$ = 16.2 Hz, 1H, $CH_2$ of acryloyl), 6.68 (d, $J$ = 12.8 Hz, 1H, $CH_2$ of acryloyl), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.15−7.27 (m, 2H, Ph), 7.74 (dd, $J$ = 16.2, 12.8 Hz, 1H, CH of acryloyl), 8.23 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 108.7, 115.5, 116.5, 123.0, 124.7, 126.6, 129.1 ($CH_2$ of acryloyl), 129.7, 132.1 (CH of acryloyl), 137.0, 150.7 (CO), 165.3 (CO of acryloyl). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.60; H, 5.36; N, 12.15.

*1-Methacryloyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-19***). Yield, 45.2%; mp, 124−126 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.17 (s, 3H, $CH_3$ of methacryloyl), 2.21 (s, 3H, $CH_3$), 5.25 (s, 1H, C=$CH_2$), 5.44 (s, 1H, C=$CH_2$), 5.41, 5.61 (s, 2H, $CH_2$ of methacryloyl), 7.08 (d, $J$ = 8.0 Hz, 1H, Ph), 7.14−7.26 (m, 2H, Ph), 7.98 (d, $J$ = 8.0 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.7, 20.1 ($CH_3$ of methacryloyl), 108.9, 110.0 ($CH_2$ of methacryloyl), 114.8, 114.9, 122.8, 124.4, 126.6, 129.6, 137.5, 140.5 (C of methacryloyl), 154.8 (CO), 170.3 (CO of methacryloyl). Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.72; H, 5.95; N, 11.26.

*1-Benzoyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-20***). Yield, 86.3%; mp, 118−120 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.16 (s, 3H, $CH_3$), 5.26 (s, 1H, C=$CH_2$), 5.42 (s, 1H, C=$CH_2$), 7.12 (d, $J$ = 8.4 Hz, 1H, Ph), 7.18−7.26 (m, 2H, Ph), 7.49 (t, $J$ = 7.4, 2H, Ph), 7.60 (t, $J$ = 7.4 Hz, 1H, Ph), 7.80 (d, $J$ = 7.4 Hz, 2H, Ph), 7.97 (d, $J$ = 8.4, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.7, 109.0, 114.7, 114.9, 122.8, 124.5, 127.0. 128.0, 129.3, 129.9, 132.8, 133.6, 137.1, 150.2 (CO), 168.5 (CO of benzoyl). Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.56; H, 5.18; N, 9.86.

*1-(4-Nitrobenzoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-21***). Yield, 46.1%; mp, 142−144 °C; $^1$H NMR ($CDCl_3$), $\delta$2.14 (s, 3H, $CH_3$), 5.26 (s, 1H, C=$CH_2$), 5.44 (s, 1H, C=$CH_2$), 7.14 (d, $J$ = 7.8 Hz, 1H, Ph), 7.23−7.30 (m, 2H, Ph), 7.88 (d, $J$ = 9.0 Hz, 2H, Ph), 8.10 (d, $J$ = 7.8 Hz, 1H, Ph), 8.20 (d, $J$ = 9.0 Hz, 2H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.7, 109.3, 115.2, 115.3, 123.2, 123.3, 125.3, 126.3, 129.7, 130.0, 136.8, 139.7, 149.6, 150.0 (CO), 167.1 (CO of 4-nitrobenzoy). Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.42; H, 4.15; N, 12.80.

*1-(2-Nitrobenzoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-22***). Yield, 90.1%; mp, 146−148 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.07 (s, 3H, $CH_3$), 5.21 (s, 1H, C=$CH_2$), 5.39 (s, 1H, C=$CH_2$), 7.06 (d, $J$ = 8.0 Hz, 1H, Ph), 7.24−7.31 (m, 2H, Ph), 7.52 (d, $J$ = 8.2 Hz, 1H, Ph), 7.66 (t, $J$ = 8.2, 1H, Ph), 7.80 (t, $J$ = 8.2, 1H, Ph), 8.25 (d, $J$ = 8.0 Hz, 1H, Ph), 8.37 (d, $J$ = 8.2, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.6, 109.0, 115.5, 115.7, 123.3, 124.1, 125.2, 126.1, 127.8, 129.8, 130.4, 132.3, 134.6, 136.6, 145.0, 150.0 (CO), 165.6 (CO of 2-nitrobenzoyl). Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.32; H, 4.18; N, 12.75.

*1-(4-Chlorobenzoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-23***). Yield, 65.0%; mp, 138−140 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.16 (s, 3H, $CH_3$), 5.26 (s, 1H, C=$CH_2$), 5.43 (s, 1H, C=$CH_2$), 7.12 (d, $J$ = 7.8 Hz, 1H, Ph), 7.19−7.26 (m, 2H, Ph), 7.45 (d, $J$ = 8.0, 2H, Ph), 7.74(d, $J$ = 8.0 Hz, 2H, Ph), 7.96 (d, $J$ = 7.8 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.7, 109.1, 114.8, 115.0, 122.9, 124.7, 126.8, 128.9, 129.9, 130.8, 131.9, 137.1, 139.1, 150.3 (CO), 167.9 (CO of 4-chlorobenzoyl). Anal. Calcd for $C_{17}H_{13}N_2O_2Cl$: C, 65.29; H, 4.19; N, 8.96. Found: C, 65.45; H, 4.25; N, 8.75.

*1-(2-Chlorobenzoyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-24***). Yield, 96.4%; mp, 82−86 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.12(s, 3H, $CH_3$), 5.23 (s, 1H, C=$CH_2$), 5.39 (s, 1H, C=$CH_2$), 7.09 (d, $J$ = 7.8 Hz, 1H, Ph), 7.21−7.47 (m, 6H, Ph), 8.27 (d, $J$ = 7.8 Hz, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.6, 108.9, 115.0, 115.5, 123.1, 124.8, 126.1, 126.7, 128.1, 129.2, 129.9, 130.7, 131.5, 135.1, 136.8, 149.6 (CO), 166.3 (CO of 2-chlorobenzoyl). Anal. Calcd for $C_{17}H_{13}N_2O_2Cl$: C, 65.29; H, 4.19; N, 8.96. Found: C, 65.40; H, 4.29; N, 8.78.

*1-(Furan-2-carbonyl)-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-25***). Yield, 64.2%; mp, 104−106 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.19 (s, 3H, $CH_3$), 5.29 (s, 1H, C=$CH_2$), 5.46 (s, 1H, C=$CH_2$), 6.61 (dd, $J$ = 3.6, 1.2 Hz, 1H, CH of furan-2-carbonyl), 7.09 (d, $J$ = 7.8 Hz, 1H, Ph), 7.16−7.26 (m, 2H, Ph), 7.54 (d, $J$ = 3.6 Hz, 1H, CH of furan-2-carbonyl), 7.70 (d, $J$ = 1.2 Hz, 1H, CH of furan-2-carbonyl), 7.84 (d, $J$ = 7.8, 1H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.8, 109.0, 112.3 (CH of furan-2-carbonyl), 114.3, 115.1, 121.6 (CH of furan-2-carbonyl), 122.7, 124.3, 126.9, 129.8, 137.2, 146.1 (CH of furan-2-carbonyl), 147.4 (C of furan-2-carbonyl), 149.9 (CO), 157.0 (CO of furan-2-carbonyl). Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.42; H, 4.62; N, 10.26.

*1-Isonicotinoyl-3-(prop-1-en-2-yl)-1H-benzo[d]imidazol-2(3H)-one* (***II-26***). Yield, 81.0%; mp, 132−134 °C; $^1$H NMR ($CDCl_3$), $\delta$ 2.15 (s, 3H, $CH_3$), 5.26 (s, 1H, C=$CH_2$), 5.44 (s, 1H, C=$CH_2$), 7.12 (d, $J$ = 8.4 Hz, 1H, Ph), 7.22−7.30 (m, 2H, Ph), 7.55 (d, $J$ = 7.8, 2H, Ph), 8.10 (d, $J$ = 8.4 Hz, 1H, Ph), 8.79 (d, $J$ = 7.8, 2H, Ph); $^{13}$C NMR ($CDCl_3$), $\delta$ 19.7, 109.2, 115.3, 115.4, 121.9, 123.2, 125.2, 126.3, 130.0, 136.8, 141.5, 150.0 (CO), 167.2 (CO of isonicotinoyl). Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05. Found: C, 69.03; H, 4.75; N, 14.86.

**Microorganism and Preparation of Spore Suspension.** The tested fungal pathogen, *B. cinerea*, was provided by the Institute of Plant Disease, Northwest A&F University. The strain was retrieved from the storage tube and cultured for 2 weeks at 20 °C on potato dextrose agar (PDA, Difco). Plates were then flooded with sterile distilled water, and conidia were scraped with a glass stick. Mycelial debris was removed by filtration through double-layer cheesecloth, and the spores were harvested and suspended in sterile distilled water containing 0.1% (v/v) Tween 20. Spores were counted using a hemocytometer and adjusted to $1.0 \times 10^6$ spores/mL (*16*).

**Spore Germination Assay.** The tested samples (10 mg) dissolved in methanol (0.1 mL) were diluted with sterile distilled water to prepare 10 mL stock solution, which was further diluted to prepare test solutions in which the final concentration of methanol was < 1% (v/v). A series of concentrations of tested samples and one control (1% methanol with sterile distilled water) were separately tested for spore germination of *B. cinerea*. The samples were inoculated with spore suspension of *B. cinerea* containing $1.0 \times 10^6$ spores/mL. Aliquots of 10 $\mu$L of prepared spore suspension were placed on separate glass slides in triplicate. Slides containing the spores were incubated in a moisture chamber at 25 °C for 6 h. Each slide was then observed under the microscope for spore germination. The spore-generated germ tubes were enumerated, and percentage of spore germination was calculated. Pyrimethanil was preferred as the positive control.

**Statistical Analysis.** The experimental data of the fungicidal activities were analyzed using SPSS 13.0 for Windows.

## RESULTS AND DISCUSSION

**Synthesis.** *N*-Acyl derivatives of isopropenyl benzimidazolone could be readily synthesized by the acylation of **I** with corresponding carboxylic acid or acyl chloride in good yields. **II-1** had been reported to be synthesized using the same procedure (*13*), and it could also be prepared from 4-methyl-2,3-dihydro-1*H*-1,5-benzodiazepin-2-one by acetylation in pyridine (*17*). In a program of screening antitumor compounds, **II-20** was once obtained by reaction of benzoyl chloride with **I** (*7*), but the fungicidal activity of these two compounds was not mentioned in the references.

The title compounds, including **II-1** and **II-20**, were characterized with $^1$H NMR, $^{13}$C NMR, and elemental analysis.

**Fungicidal Acitivity.** The fungicidal activities of the title compounds against *B. cinerea* were evaluated by spore germination assay, and the results are listed in **Table 1**. The fungicidal activity was strongly influenced by the acyl group on the nitrogen atom. Among the saturated aliphatic acid derivatives (**II-1**−**II-5**), the activities became higher with extension of the carbon chain. When a side chain was introduced to the main carbon chain, a methyl or an ethyl at the α-position (**II-6** and **II-7**) helped with their activities, because their activities were much higher than those of **II-2** and **II-3**. However, compound **II-8**, with a methyl group at the γ-position of pentanoyl, gave a little lower activity than corresponding compound **II-4**. Similarly, **II-17**, with a bulky indole ring at the γ-position of butanoyl, also exhibited lower activity.

The introduction of a hydrophobic benzene ring to the alkyl chain increased the fungicidal activities to a large extent. Phenylethylcarbonyl derivative **II-12** and benzylcarbonyl derivatives (**II-9**, **II-10**, and **II-13**) showed much higher activities than corresponding alkyl derivatives **II-1**−**II-3**. Among them, 4-clorobenzylcarbonyl compound **II-10** exhibited uncommon activity, with a median inhibitory concentration ($IC_{50}$) value of 17.27 μg/mL. Phenoxyacetyl compound **II-15** and 4-chlorophenoxyacetyl compound **II-16** also gave moderate activities with **II-16** higher than **II-15**, which also indicates that a chloro atom at the para-position of the benzene ring could increase the activity. Compound **II-11**, bearing a bulky phenanthryl, gave very low activity.

Compared to most of the alkyl acyl derivatives and control compound pyrimethanil, acrylamide compounds **II-18** and **II-19** showed higher activities, as their median inhibitory concentration ($IC_{50}$) values were only 32.42 and 63.45 μg/mL, respectively. This implied that α,β-unsaturated carbonyl might play an important role in their fungicidal activity.

Substituted benzoyl (**II-20**, **II-21**, **II-23**, and **II-24**) and other aromatic carbonyl derivatives (**II-25** and **II-26**) of isopropenyl benzimidazolone also exhibited stronger inhibiting activity than alkyl acyl derivatives and pyrimethanil. The type and position of the substituted group introduced to the benzene ring could obviously affect the bioactivity. When chloro was introduced to the ortho- or para-position of benzoyl, their activities were much higher than corresponding nitro derivatives. Of all the compounds, **II-24** exhibited the highest inhibiting activity, with $IC_{50}$ = 17.17 μg/mL.

In conclusion, 1-acyl-3-isopropenylbenzimidazolone derivatives were prepared and their fungicidal activities against *B. cinerea* evaluated. Although some derivatives of acrylamide, phenylacetamide, and benzamides exhibited good fungicidal activity, there is no obvious structure−activity relationship tendency in general. Indeed, the experiment mentioned above is only a preliminary investigation, and there are more works to be carried out. Nevertheless, because the core skeleton of benzimidazolone possesses great potential in structure modification, it deserves further investigation. The progress will be reported in the future.

## LITERATURE CITED


(1) Fokkema, N. J. Biological control of fungal plant diseases. *BioControl* **1996**, *41*, 333–342.

(2) Elad, Y.; Gullino, M. L.; Shtienberg, D.; Aloi, C. Managing *Botrytis cinerea* on the tomatoes in greenhouses in the Mediterranean. *Crop Prot*. **1995**, *14*, 105–109.

(3) Elad, Y.; Yunis, H.; Katan, T. Multiple fungicide resistance to benzimidazoles, dicarboximides and diethofencarb in field isolates of *Botrytis cinerea* in Israel. *Plant Pathol*. **1992**, *41*, 41–46.

(4) Barreca, M. L.; Rao, A.; Luca, L. D.; Iraci, N.; Monforte, A. M.; Maga, G.; Clercq, E. D.; Pannecouque, C.; Balzarini, J.; Chimirri, A. Discovery of novel benzimidazolones as potent non-nucleoside reverse transcriptase inhibitors active against wild-type and mutant HIV-1 strains. *Bioorg. Med. Chem. Lett*. **2007**, *17*, 1956–1960.

(5) Mavrova, A. T.; Anichina, K. K.; Vuchev, D. I.; Tsenov, J. A.; Kondeva, M. S.; Micheva, M. K. Synthesis and antitrichinellosis activity of some 2-substituted-[1,3]thiazolo[3,2-α]benzimidazol-3(2*H*)-ones. *Bioorg. Med. Chem*. **2005**, *13*, 5550–5559.

(6) Nacak, S.; Dogruer, D. S.; Sahin, M. F. Synthesis and antinociceptive activity of (1-benzyl-2(3*H*)-benzimidazolon-3-yl) acetic acid derivatives. *Farmaco* **1999**, *54*, 768–772.

(7) Khodarahmi, G. A.; Chen, C. S.; Hakimelahi, G. H.; Tseng, C. T.; Chern, J. W. Design, synthesis, and cytotoxicity of 4-sulfonamide substituted benzamidobenzimidazolones and an acyl benzimidazolone. *J. Iran. Chem. Soc*. **2005**, *2*, 124–134.

(8) Badarau, E.; Suzenet, F.; Bojarski, A. J.; Finaru, A. L.; Guillaumet, G. Benzimidazolone-based serotonin 5-$HT_{1A}$ or 5-$HT_7$R ligands: synthesis and biological evaluation. *Bioorg. Med. Chem. Lett*. **2009**, *19*, 1600–1603.

(9) Omura, H.; Kawai, M.; Shima, A.; Iwata, Y.; Ito, F.; Masuda, T.; Ohta, A.; Makita, N.; Omoto, K.; Sugimoto, H.; Kikuchi, A.; Iwata, H.; Ando, K. The SAR studies of novel CB2 selective agonists, benzimidazolone derivatives. *Bioorg. Med. Chem. Lett*. **2008**, *18*, 3310–3314.

(10) Baragatti, B.; Biagi, G.; Calderone, V.; Giorgi, I.; Livi, O.; Martinotti, E.; Scartoni, V. Triazolyl-benzimidazolones and triazolyl-benzotriazoles: new potential potassium channel activators.II. *Eur. J. Med. Chem*. **2000**, *35*, 949–955.

(11) Singh, S.; Syme, C. A.; Singh, A. K.; Devor, D. C.; Bridges, R. J. Benzimidazolone activators of chloride secretion: potential therapeutics for cystic fibrosis and chronic obstructive pulmonary disease. *J. Pharmacol. Exp. Ther*. **2001**, *296*, 600–611.

(12) Messaoudi, S.; Sancelme, M.; Polard-Housset, V.; Aboab, B.; Moreau, P.; Prudhomme, M. Synthesis and biological evaluation of oxindoles and benzimidazolinones derivatives. *Eur. J. Med. Chem*. **2004**, *39*, 453–458.

(13) Davoll, J.; Laney, D. H. Some N-substituted 2-oxobenzimidazolines. *J. Chem. Soc*. **1960**, 314–318.

(14) Ayupova, A. T.; Kadyrov, Ch.Sh.; Seitanidi, K. Synthesis of substituted 1-isopropenyl-and 1-alkylbenzimidazolones. *Chem. Heterocycl. Compd*. **1972**, *10*, 207–209.

(15) Lakhrissi, B.; Benksim, A.; Massoui, M.; Essassi E1, M.; Lequart, V.; Joly, N.; Beaupère, D.; Wadouachi, A.; Martin, P. Towards the synthesis of new benzimidazolone derivatives with surfactant properties. *Carbohydr. Res*. **2008**, *343*, 421–433.

(16) Lee, S. K.; Sohn, H. B.; Kim, G. G.; Chung, Y. R. Enhancement of biological control of *Botrytis cinerea* on cucumber by foliar sprays and bed potting mixes of *Trichoderma harzianum* YC459 and its application on tomato in the greenhouse. *Plant Pathol*. **2006**, *22*, 283–288.

(17) Puodzhyunaite, B. A.; Yanchene, R. A.; Terent'ev, P. B. Transformation of dihydro-1,5- benzodiazepin-2-ones under the influence of acetic anhydride. *Chem. Heterocycl. Compd*. **1988**, *2004*, 311–317.


**Received for review July 31, 2009. Revised manuscript received January 13, 2010. Accepted January 15, 2010. This work was funded by grants from the National Key Project for Basic Research (No. 2010CB126100), the National Natural Science Foundation of China (No. 20672087 and 30971935), and the Province Key Technologies R&D Program of Shaanxi, China (2009K02-04).**