Synthesis and Biological Activities of Novel 1,3-bis[substituted-pyridyl(thiazolyl)methyl]-2-substitutedmethylideneimidazolidines

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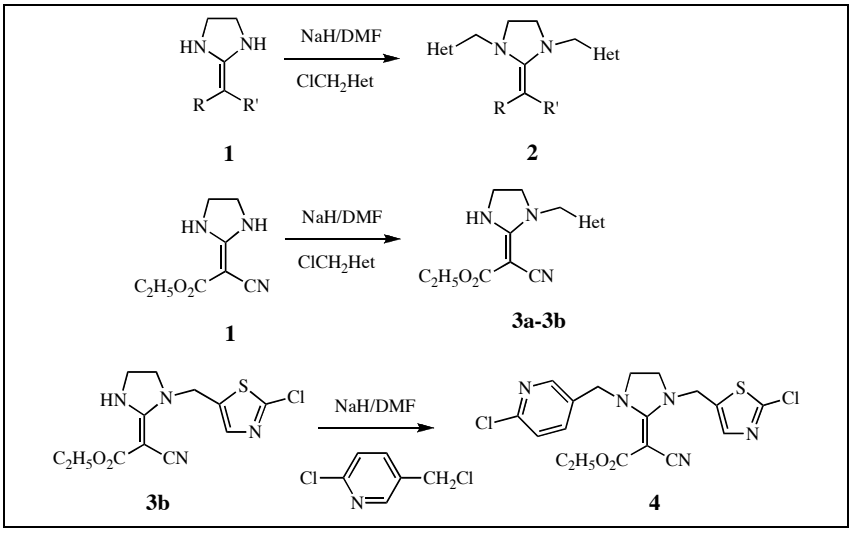

A series of novel 1,3-dissubstitutedpyridyl(thiazolyl)methyl-2-substituted-methylideneimidazolidine derivatives **2** and **4** were designed and synthesized *via* the *N*-alkylation of the disubstituted heterocyclic ketene aminal derivative **1**. When **1** (R = CN, R' = $COOC_2H_5$) was used as the starting materials, mono *N*-alkylated reaction can take place in good yields owing to the presence of the intramolecular hydrogen bond. However, as for **1** (R = R' = CN), it is difficult to obtain pure mono *N*-alkylated product. The structures of the target compounds were confirmed by IR, ^{1}H NMR, EI-MS and elemental analyses, and, in the case of **2c**, by single crystal X-ray diffraction. The preliminary bioassay indicated that some of the title compounds possess moderate fungicidal and insecticidal activity.

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INTRODUCTION

The latest class of chemical insecticides with outstanding economical impact on the agrochemical industry comprises the neonicotinoid insecticides, which act agonistically and show high selectivity to insect nicotinic acetylcholine receptor. Imidacloprid [1-(6-chloro-3-pyridyl)methyl-*N*-nitro imidazolidinimine, see Figure 1] is the first commercially and widely used neonicotinoid insecticide with relatively low human toxicity [1,2], and thiamethoxam (see Figure 1) is a second generation neonicotinoid insecticide with more active insecticidal activity. It was found that most of the biologically active neonicotinic compounds contain the aminomethylpyridine or aminomethylthiazole moiety [3,4]. Moreover, in the study of pharmaceuticals and agrochemicals, the introduction of pyridine or thiazole ring into parent compounds may improve the properties and biological activities of compounds, and many pyridyl and 1,3-thiazolyl-containing compounds are also known to possess a wide range of biological and pharmacological activities [5-8], as well as low toxicity toward mammals. Some mono *N*-substituted heterocyclic ketene aminal derivatives have also been reported [9-11]. However, there are only a few reports on the synthesis and biological activities of 1,3-bis substituted imidazolidine derivatives. As a continuation of our search for new biologically active compounds [12-13], we designed and synthesized a series of novel 1,3-bis substituted pyridyl (thiazolyl)methyl-2-substituted-methylidene imidazolidine derivatives *via* the *N*-alkylation of the disubstituted heterocyclic ketene aminal derivative **1** in mild condition, which is similar to imidacloprid in the chemical structure.

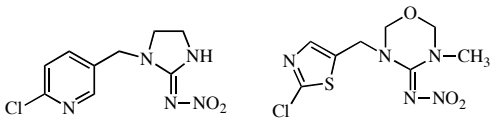
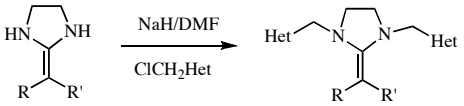


Figure 1

RESULTS AND DISCUSSION

Various disubstituted heterocyclic ketene aminal **1** reacted with 2-chloro-5-(chloromethyl)pyridine or 2-chloro-5-(chloromethy)thiazole to give 1,3-bis *N*-alkylated products **2** in satisfactory yields in the presence of NaH/DMF system. However, when excess anhydrous K_2CO_3 was used, the reaction takes place very slowly, and the higher reaction temperature required results in many by-products and difficult purification (Scheme 1).

Scheme 1



1 **2**

R, R' = CN, $CO_2C_2H_5$, *O*,*O*-diethylphosphonyl
Het = 6-chloropyridin-3-yl, 2-chlorothiazol-5-yl

The disubstituted heterocyclic ketene aminal **1** (When R = CN, $COOC_2H_5$) reacts with 2-chloro-5-(chloromethyl)thiazole, or 3-(chloromethyl)pyridine under basic reaction condition (NaH/DMF) to give the mono *N*-alkylated product **3**. The alkylation reaction between compound **1** and chloromethylpyridine (thiazole) takes place on the N atom at the opposite position of ester group under the reaction condition, compounds **3** all have *E*-configuration, which is due to the presence of an intra molecular hydrogen bond between the N-H and the ester group as indicated by the downfield shift of the N-H signal to 8.75 ppm in the ^{1}H NMR spectra and bathochromic shift of the carbonyl absorption (1680-1660 cm^{-1}) in the IR spectra, which is consistent to the reference [11]. It is noteworthy that even when excess 3-(chloromethyl)pyridine (2 equimolecular) was used as the alkylation agent, no double only mono substituted product was obtained; as for 2-chloro-5-(chloromethyl)thiazole, in order to obtain the pure mono substituted derivative, the molecular ratio of **1** and alkyl halide has to be 1:1, otherwise, the mixtures of the mono and double substituted imidazolidines were formed, which are very difficult to purify due to their similar polarity. On the other hand, for **1** (R = R' = CN), it is difficult to obtain pure mono alkylated derivatives even in excess **1** due to the absence of an intra molecular hydrogen bond between N-H and CN group.

(*E*) 1-(2-Chlorothiazol-5-yl)methyl-2-[(cyano)(ethoxycarbonyl)methylidene] imidazolidine (**3b**) can easily react with 2-chloro-5-(chloromethyl)pyridine to provide asymmetric double substituted imidazolidine derivative **4**. (Scheme 2). The reaction condition is listed in Table 1.

All products were fully characterized by IR, ^{1}H NMR, EI-MS and elemental analysis. All the spectral data were

Scheme 2

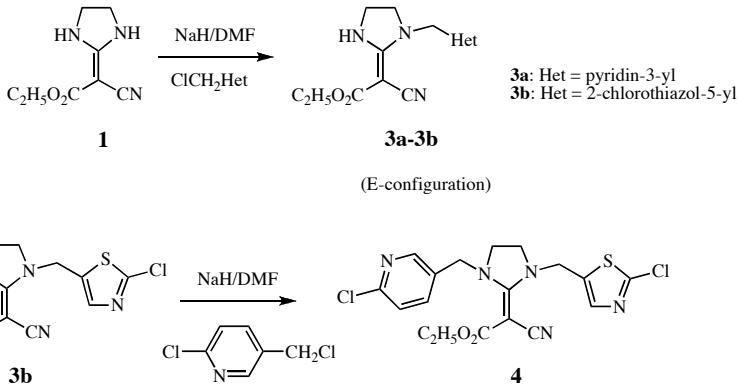


Table 1 Reaction conditions of the target compounds

Compd.	R	R'	Het	Condition	Yield (%)*
2a	CN	CN	6-chloro-pyridin-3-yl	r.t./5 hr	86
2b	CN	CN	2-chloro-thiazol-5-yl	r.t./6 hr	75
2c	COOEt	CN	6-chloro-pyridin-3-yl	r.t./6 hr	78
2d	COOEt	CN	2-chloro-thiazol-5-yl	r.t./6 hr	66
2e	CN	*O*,*O*-diethylphosphonyl	6-chloro-pyridin-3-yl	r.t./6 hr	77
2f	COOEt	*O*,*O*-diethylphosphonyl	6-chloro-pyridin-3-yl	r.t./5 hr	72
3a	COOEt	CN	pyridin-3-yl	r.t./5 hr	87
3b	COOEt	CN	2-chloro-thiazol-5-yl	r.t./5 hr	69
4	COOEt	CN		r.t./5 hr	70

Yields of isolated products based on 2-substituted-methylene imidazolidine **1** or **3b**

in accordance with the anticipated structures. In the ^{1}H NMR spectra of **2**, the CH_2CH_2 fragment in the imidazolidine moiety displayed a singlet with a chemical shifts of 3.5, while the protons of the CH_2 linking with the pyridine or thiazole ring is shifted downfield to 4.7. However, for compounds **3** and **4**, the CH_2CH_2 fragment in the imidazolidine moiety displayed two resonances with different chemical shifts as a result of their different chemical environments. In order to confirm their molecular structure absolutely, a single crystal of **2c** was obtained from absolute ethanol and the molecular structure was determined by X-ray diffraction [14].

Compounds **2**, **3**, **4** were tested for insecticidal activities against aphides at the concentration of 250 mg/L according to a previously reported method [15]. The result is listed in Table 2, which indicated that some of the title compounds possess moderate insecticidal activity.

Table 2 Insecticidal activity of compound **2**, **3** and **4** against aphides:

(250 mg/L, inhibitory rate %)

Compd.	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**3a**	**3b**	**4**
Inhibitory rate	17.2	56.0	8.4	28.5	42.4	39.3	36.0	11.0	45.1

The fungicidal activities of the target compounds **2**, **3**, **4** were tested at a concentration of 50 mg/L. The five fungi used, *Fusarium oxysporium, Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Colletotrichum gossypii*, belong to the group of field fungi and were isolated from corresponding crops. The activity data were listed in Table 3. The preliminary bioassay indicated that some of the title compounds possess moderate fungicidal activity, for example, compounds **2c** and **3b** show 72.5% and 67.6% inhibitory activity against *Botrytis cinereapers* fungus, respectively.

Table 3 The fungicidal activity of compounds **2, 3** and **4** (50 mg/L, inhibitory rate %)

Compd.	*Fusarium oxysporium*	*Rhizoctonia solani*	*Botrytis cinereapers*	*Gibberella zeae*	*Colletotrichum gossypii*
2a	11.8	2.1	21.9	15.6	21.4
2b	35.0	8.6	11.8	38.8	15.79
2c	11.8	13.7	72.5	25.0	17.9
2d	23.5	28.6	41.6	19.2	21.2
2e	-17.7	23.3	46.9	40.6	7.1
2f	5.9	12.6	56.3	31.2	25.0
3a	0	29.0	32.1	57.9	36.5
3b	11.4	40.9	67.6	42.8	24.5
4	25.0	30.1	23.5	23.1	15.8

In conclusion, we designed and synthesized a series of novel 1,3-bis substituted pyridyl(thiazolyl)methyl-2-substituted-methylideneimidazolidine derivatives including two mono substituted derivatives. The results of the preliminary bioassays indicated that some of the title compounds possess moderate fungicidal and insecticidal activity.

EXPERIMENTAL

Melting points were determined with a WRS-1B digital melting point apparatus and are uncorrected. ^{1}H NMR spectra was recorded with a Varian MERCURY-PLUS400 spectrometer with TMS as the internal reference and $CDCl_3$ as the solvent, while mass spectra were obtained with a Finnigan TRACEMS2000 spectrometer using the EI method. IR spectra were measured by a Nicolet NEXUS470 spectrometer. Elemental analyses were performed with an Elementar Vario ELIII CHNSO elementary analyzer. All of the solvents and materials were reagent grade and purified as required. 2-Substituted methylidene imidazolidines (**1**) were synthesized according to the reported methods [16-19].

General Procedure for the Preparation of 1,3-disubstitutedpyridyl(thiazolyl)methyl-2-substitued-methylidene-imidazolidines (2). Under N_2 atmosphere, the solution of of 2-substituted methylidene imidazolidine (**1**) (0.01 mol) dissovled in DMF (5 mL) was added dropwise to a mixture of NaH (0.02 mol) and anhydrous DMF (10 mL) at 0~5 °C for 0.5 h until no more bubble was evolved. The solution of 2-chloro-5-(chloromethyl)-pyridine or 2-chloro-5-(chloromethyl)-thiazole (0.02 mol) in DMF (5 mL) was added dropwise to the flask while cooling in an ice-bath. After the addition was complete, the mixture was stirred at room temperature until the reaction completed (monitored by TLC). The solution was concentrated under vacuum. The residue was washed with brine, extracted with $CHCl_3$ (3×30 mL) and dried over anhydrous $MgSO_4$, respectively. The filtrate was evaporated and the residue was

purified by flash column chromatography on silica gel (CH_2Cl_2:CH_3OH (*v*/*v*) =15~10:1), giving the corresponding **2** in 66~86% yields.

1,3-Bis-(6-chloropyridin-3-ylmethyl)-2-(bis-cyanomethylidene)imidazolidine (2a). White crystals, mp 187-188°; ir: CN 2202, 2171, CO 1710 cm^{-1}; ^1H nmr: δ 3.67 (s, 4H, CH_2CH_2), 4.84 (s, 4H, CH_2N), 7.42 (d, J = 7.6 Hz, 2H, H-C(5) of pyridine), 7.74 (d, J = 6.8 Hz, 2H, H-C(4) of pyridine), 8.36 (s, 2H, H-C(2) of pyridine); ms: m/z 386 (36), 384 (M+, 66), 258 (62), 232 (22), 126 (100), 98 (21), 90 (26), 62 (10). *Anal.* Calcd. for $C_{18}H_{14}Cl_2N_6$: C, 56.12; H, 3.66; N, 21.81. Found: C, 55.96; H, 3.58; N, 21.57.

1,3-Bis-(2-chlorothiazol-5-ylmethyl)-2-(bis-cyanomethylidene)imidazolidine (2b). White crystals, mp 197-198°; ir: CN 2190, 2175 cm^{-1}; ^1H nmr: δ 3.62 (s, 4H, CH_2CH_2), 4.89 (s, 4H, $2CH_2N$), 7.73 (s, 2H, thiazole-H). ms: m/z 398 (28), 396 (M^+, 73), 237(65), 211 (34), 132 (100), 98 (21), 62 (15). *Anal.* Calcd. for $C_{14}H_{10}Cl_2N_6S_2$: C, 42.32; H, 2.54; N, 21.15. Found: C, 42.28; H, 2.61; N, 21.37.

1,3-Bis-(6-chloropyridin-3-ylmethyl)-2-[(cyano)(ethoxycarbonyl)methylidene]imidazolidine (2c). White crystals, mp 172-174°; ir: CN 2182, CO 1692, 1678, 1540 cm^{-1}; ^1H nmr: δ 1.29 (t, 3H, CH_3), 3.49 (s, 4H, CH_2CH_2), 4.17 (q, 2H, CH_2CH_3), 4.67 (s, 4H, CH_2N), 7.39 (d, J = 8.0 Hz, 2H, H-C(5) of pyridine), 7.82 (d, J = 6.8 Hz, 2H, H-C(4) of pyridine), 8.36 (s, 2H, H-C(2) of pyridine). *Anal.* Calcd. for $C_{20}H_{19}Cl_2N_5O_2$: C, 55.57; H, 4.43; N, 16.20. Found: C, 55.76; H, 4.18; N, 15.97.

1,3-Bis-(2-chlorothiazol-5-ylmethyl)-2-[(cyano)(ethoxycarbonyl)methylidene] imidazolidine (2d). yellow viscous solid; ir: CN 2190, CO 1725 cm^{-1}; ^1H nmr: δ 1.18 (t, 3H, CH_3), 3.58 (s, 4H, CH_2CH_2), 4.06 (q, 2H, CH_2CH_3), 4.74 (s, 4H, CH_2N), 7.70 (s, 2H, thiazole-H); ms: m/z 445 (30), 443 (M^+, 72), 284 (64), 258 (22), 211(18), 132 (100), 109 (10). *Anal.* Calcd. for $C_{16}H_{15}Cl_2N_5O_2S_2$: C, 43.25; H, 3.40; N, 15.76. Found: C, 43.48; H, 3.31; N, 15.64.

1,3-Bis-(6-chloropyridin-3-ylmethyl)-2-[(cyano)(*O*,*O*-diethylphosphonyl)methylidene]imidazolidine (2e). white crystals, mp 117-118°; ir: CN 2164, P=O 1248, P-O-C 1103 cm^{-1}; ^1H nmr: δ 1.33 (t, 6H, CH_2CH_3), 3.43 (s, 4H, CH_2CH_2), 4.11 (q, 4H, CH_2CH_3), 4.81 (s, 4H, CH_2N), 7.37 (d, J = 7.6 Hz, 2H, H-C(5) of pyridine), 7.92 (d, J = 6.8 Hz, 2H, H-C(4) of pyridine), 8.34 (s, 2H, H-C(2) of pyridine). *Anal.* Calcd. for $C_{21}H_{24}Cl_2N_5O_3P$: C, 50.82; H, 4.87; N, 14.11. Found: C, 50.69; H, 4.80; N, 13.99.

1,3-Bis-(6-chloropyridin-3-ylmethyl)-2-[(ethoxycarbonyl)-(*O*,*O*-diethylphosphonyl)methylidene]imidazolidine (2f). white crystals, mp 143-145°; ir: CO 1720, P=O 1277, P-O-C) 1220, 1107 cm^{-1}; ^1H nmr: δ 1.20-1.25 (m, 9H, CH_3), 3.47 (s, 4H, CH_2CH_2), 4.05-4.13 (m, 6H, CH_2CH_3), 4.70 (s, 4H, CH_2N), 7.36 (d, J = 7.6 Hz, 2H, H-C(5) of pyridine), 7.92 (d, J = 7.2 Hz, 2H, H-C(4) of pyridine), 8.32 (s, 2H, H-C(2) of pyridine). *Anal.* Calcd. for $C_{23}H_{29}Cl_2N_4O_5P$: C, 50.84; H, 5.38; N, 10.31. Found: C, 50.96; H, 5.63; N, 10.25.

Preparation of (*E*) 1-substitued-2-[(ethoxycarbonyl)-(cyano)methylidene]-3*H*-imidazolines 3. To a mixture of NaH (0.012 mol) and unhydrous DMF (10 mL) in 50 mL three-necked flask, was added dropwise the solution of 2-substitutedmethylidene imidazolidine (2) (0.012 mol) in DMF (5 mL) under N_2 at 0-5 °C. After no more bubble was evolved, the solution of 2-chloro-5-(chloromethyl)-thiazole or 3-(chloromethyl)-pyridine (0.01 mol) in DMF (5 mL) was added dropwise to the above solution while cooling in an ice-bath. After the addition complete, the mixture was stirred at room temperature until the reaction finished (monitored by TLC) and the mixture was concentrated under vacuum. The residue was washed with brine, extracted with $CHCl_3$ (3×30 mL) and dried over anhydrous $MgSO_4$, respectively. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (CH_2Cl_2:CH_3OH (*v*/*v*) =15~10:1), giving the corresponding imidazolines 3a-3b in 69-87% yields.

(*E*) 1-(pyridin-3-ylmethyl)-2-[(ethoxycarbonyl)(cyano)-methylidene]-3*H*-imidazoline (3a). white crystals, mp 126-128°; ir: N-H 3250, CN 2195, CO 1665 cm^{-1}; ^1H nmr: δ 1.32 (t, 3H, CH_3), 3.55-3.57 (m, 2H, CH_2CH_2), 3.63-3.65 (m, 2H, CH_2CH_2), 4.21 (q, 2H, CH_2CH_3), 5.00 (s, 2H, NCH_2), 7.38 (s, 1H, H-C(2) of pyridine), 7.81 (d, 1H, H-C(5) of pyridine), 8.58 (d, J = 7.6Hz, 1H, H-C(4) of pyridine), 8.75(s, 1H, H-C(6) of pyridine), 8.75 (s, 1H, NH); ms: m/z 274 (13), 272 (M^+, 77), 227 (49), 197 (62), 159 (76), 133 (28), 92 (100), 65 (28). *Anal.* Calcd. for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.67; H, 5.81; N, 20.69.

(*E*) 1-(2-Chlorothiazol-5-ylmethyl)-2-[(ethoxycarbonyl)-(cyano)methylidene]-3*H*-imidazoline (3b). white crystals, mp 119-121°; ir: N-H 3302, CN 2180, CO 1680 cm^{-1}; ^1H nmr: δ 1.30 (t, 3H, CH_3), 3.61-3.72 (m, 2H, CH_2CH_2), 3.74-3.81 (m, 2H, CH_2CH_2), 4.16-4.23 (m, 2H, CH_2CH_3), 5.06 (s, 2H, NCH_2), 7.53 (s, 1H, thiazole-H), 8.72 (s, 1H, NH). *Anal.* Calcd. for $C_{12}H_{13}ClN_4O_2S$: C, 46.08; H, 4.19; N, 17.91. Found: C, 45.91; H, 4.08; N, 17.84.

Preparation of 1-(6-chloropyridin-3-ylmethyl)-3-(2-chlorothiazol-5-ylmethyl)-2-[(ethoxycarbonyl)(cyano)methylidene]-imidazolidine (4). The solution of **3b** (0.012 mol) in DMF (5mL) was added dropwise to a mixture of NaH (0.012 mol) and anhydrous DMF (10 mL) under N_2 at 0~5 °C. After no more bubble was evolved, the solution of 2-chloro-5-(chloromethyl)-pyridine (0.01 mol) in DMF (5mL) was added dropwise to the above solution while cooling in an ice-bath. After the addition complete, the mixture was stirred at room temperature until the reaction finished (monitored by TLC). The mixture was concentrated under vacuum, washed with brine, extracted with $CHCl_3$ (3×30 mL) and dried over anhydrous $MgSO_4$, respectively. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether:acetone (*v*/*v*) = 2:1), giving the corresponding asymmetrical disubstituted imidazoline **4** in 70% yield. white viscous solid; ir: CN 2190, CO 1728 cm^{-1}; ^1H nmr: δ 1.26-1.34 (m, 3H, CH_3), 3.45-3.53 (m, 2H, CH_2CH_2), 3.55-3.60 (m, 2H, CH_2CH_2), 4.17-4.23 (m, 2H, CH_2CH_3), 4.68 (s, 2H, NCH_2), 4.76 (s, 2H, NCH_2), 7.38 (d, J = 8.0 Hz, 1H, H-C(5) of pyridine); 7.49 (s, 1H, H-C(2) of pyridine); 7.80 (d, J = 7.2 Hz, 1H, H-C(3) of pyridine), 8.32 (s, 1H, thiazole-H); ms: m/z 440 (16), 438 (M^+, 38), 312 (24), 306(18), 126 (100), 90 (70). *Anal.* Calcd. for $C_{18}H_{17}Cl_2N_5O_2S$: C, 49.32; H, 3.91; N, 15.98. Found: C, 49.27; H, 3.76; N, 15.75.

Fungicidal activity testing. The fungicidal activity measurement method was adapted from the one described by Molina Torres *et al.* [20]. The synthesized target compounds were dissolved in 0.5-1.0 mL of DMF to the concentration of 500 mg/L. The solutions (1 mL) were mixed rapidly with thawed potato glucose agar culture medium (9 mL) under 50 ℃. The mixtures were poured into Petri dishes. After the dished were cooled, the solidified plates were incubated with 4 mm mycelium disk, inverted, and incubated at 28 ℃ for 48 h. Distilled water was used as the blank control. Three replicates of each test were carried out. The mycelial elongation radius (mm) of fungi settlements was

measured after 48 h of culture. The growth inhibitory rates were calculated with the following equation: $I = [(C\text{-}T)/C] \times 100\%$. Here, I is the growth inhibitory rate (%), T is the treatment group fungi settlement radius (mm) and C is the radius of the blank control. The results are listed in Table 3.

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