JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Subscriber access provided by FLORIDA ATLANTIC UNIV

Article

Kresoxim-methyl Derivatives: Synthesis and Herbicidal activities of (Pyridinylphenoxymethylene)phenyl Methoxyiminoacetates

Yang-Yang Cao, Da-Jie Mao, Wei-Wei Wang, and Xiao-Hua Du

J. Agric. Food Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.jafc.7b02710 • Publication Date (Web): 07 Jul 2017

Downloaded from http://pubs.acs.org on July 18, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

Journal of Agricultural and Food Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Kresoxim-methyl Derivatives: Synthesis and Herbicidal Activities of (Pyridinylphenoxymethylene)phenyl Methoxyiminoacetates

Yang-yang Cao,[†] Da-jie Mao,[†,‡] Wei-wei Wang,[†] and Xiao-hua Du[*,†]

[†]*Catalytic Hydrogenation Research Center, Zhejiang University of Technology, Zhejiang Key Laboratory of Green Pesticides and Cleaner Production Technology, Zhejiang Green Pesticide Collaborative Innovation Center, Hangzhou 310014, PR China*

[‡]*Ninhua Co. Ltd., Ningbo 315000, PR China*

---

[*] Corresponding author (Tel: +86-571-88320430; Fax: +86-571-88320066; E-mail: *duxiaohua@zjut.edu.cn*).

Abstract

A series of new kresoxim-methyl derivatives, (pyridinylphenoxymethylene)phenyl methoxyiminoacetates, were synthesized and their structures were confirmed by NMR and HRMS. Although derived from a fungicide, the bioassays indicated that several new compounds had good herbicidal activities. At 37.5 g a.i./ha, compound **5c** showed 100% inhibition against *Abutilon theophrasti*, *Amaranthus retroflexus* and *Eclipta prostrata*, which was better than mesotrione. Compound **5e** had a broad herbicidal spectrum against broadleaf weeds. The present work indicates that **5c** and **5e** may serve as new candidates for potential herbicides.

Keywords: Pyridinylphenyl, Methoxyiminoacetate, Synthesis, Herbicidal activity

Introduction

Strobilurins, an important family of fungicides, have been widely identified as one of the most promising lead compounds for the development of a new generation of industrial fungicides for crop protection.[1-6] Since the successful development of kresoxim-methyl and azoxystrobin, many chemists have studied strobilurins. At present, the modification of these new compounds is mainly concentrated in the side chain,[7-11] including the structure of benzothiazole,[12,13] chalcone,[14] *N*-acetyl pyrazoline,[15] pyrazole,[16] and quinoxaline[17] structures. Some new strobilurin derivatives which were introduced of pyridine structure in the side chain showed excellent biological activities,[18-20] however, few of them with good herbicidal activity have been reported.

Substituted phenylpyridines described by Schaefer et al.[21,22] showed good herbicidal activity. Liu et al.[23] also reported that some substituted benzenesulfonamides with phenylpyridine moieties showed better herbicidal activities than mesotrione.

In our research on the fungicidal activities of kresoxim-methyl derivatives,[24] some serious phytotoxities by several methoxyiminoacetate compounds containing phenylpyridine moieties were found, which raised our interest in the study of herbicidal activity of this kind of compounds. Herein, a series of new structural kresoxim-methyl derivatives were obtained by splicing the phenylpyridine structure with the active structure of kresoxim-methyl. These newly synthesized compounds were characterized by ^1H NMR, ^{13}C NMR, and HRMS. Furthermore, the herbicidal activities were investigated with in vitro, glasshouse and field tests.

Materials and methods

Synthesis. All starting materials and reagents were commercially available and used without further purification except as indicated. Solvents, such as dichloromethane, dimethylformamide, isopropanol, ethyl acetate, petroleum ether, and acetone were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Chemical reagents, such as 4-hydroxyphenylboronic acid, 2,3-Dichloro-5-(trifluoromethyl)pyridine, and 2-Bromo-3,5-dichloropyridine were purchased from Shanghai Shaoyuan Co. Ltd. (Shanghai, China). ^{1}H NMR and ^{13}C NMR spectra were recorded on an AVANCE III spectrometer (Bruker, Hangzhou, China) at 500 and 125 MHz NMR, respectively. High resolution mass spectrometry (HRMS) were recorded on a model 6545 Q-TOF LCMS spectrometer equipped with an ESI source and controlled by MassHunter software (Agilent, Hangzhou, China). Melting points were taken on a B-545 melting point apparatus (Buchi, Hangzhou, China) and were uncorrected.

An overview synthesis of (pyridinylphenoxymethylene)phenyl methoxyiminoacetates is shown in Figure 1.

Synthesis of Intermediates A (3a-3p). 4-(3-Chloro-5-trifluoromethylpyridin-2-yl) phenol, **3c**, as an example. 2,3-Dichloro-5-trifluoromethylpyridine (5 mmol, 1.08 g), 4-hydroxybenzeneboronic acid (5.5 mmol, 0.76 g), potassium phosphate tribasic (10 mmol, 4.25 g) and bis(triphenylphosphine)palladium(II) chloride (0.5 mol%, 0.056 g) in a mixture of 10 mL of isopropanol and 10 mL of water were stirred at 60 °C for 3 h in a nitrogen atmosphere. Thereafter, the reaction solution was poured into water, followed by extraction with ethyl acetate three times. The organic layers were combined, washed with an aqueous saturated sodium chloride solution, dried with anhydrous sodium sulfate, and concentrated. The residue was subjected to recrystallization using ethanol and water at the temperature of 70 °C to obtain 1.15 g white solid of intermediate **3c**.

The other intermediates were synthesized by the same method.

Synthesis of Intermediate B (4). Methyl (2-chloromethyl)-α-methyloximinobenzene acetate was synthesized according to the previously reported route,[25,26] which is shown in Figure 2.

Synthesis of Kresoxim-methyl Derivatives. Methyl (*E*)-α-(methoxyimino)-2-((4-(3-chloro-5-trifluoromethylpyridin-2-yl)phenoxy)methyl)benzene acetate is described as an example. **3c** (3 mmol, 0.87 g), 10 mL of dimethylformamide (DMF) and sodium hydride (4.5 mmol, 0.18 g) were stirred at room temperature for 30 min. Then, **4** (3.6 mmol, 0.89 g) was added and the reaction was stirred at 60 °C for 10 h. Thereafter, the reaction solution was poured into water, followed by extraction with ethyl acetate three times. The organic layers were combined, washed with an aqueous saturated sodium chloride solution, dried with anhydrous sodium sulfate, and concentrated. The residue was subjected to silica gel column chromatography using petroleum ether/dichloromethane/acetone (10:1:1, v/v/v) to obtain **5c** as a white solid, **m.p.** 97.2-98.7 °C.

The remaining compounds were synthesized using the synthetic method of **5c**.

5a. Yield: 78.7%. Yellow solid. M.p. 89.8-91.6 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.86 (d, *J*=1.1Hz, 1H), 8.02 (d, *J*=1.6Hz, 1H), 7.41-7.34 (m, 5H), 7.16-7.14 (m, 1H), 7.10 (td, *J*=7.5, 1.0Hz, 1H), 6.93 (d, *J*=8.5, 1H), 4.98 (s, 2H), 4.04 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.18, 159.48 (d, *J*=1.25Hz), 155.71, 149.01, 143.92 (q, *J*=3.75Hz), 135.23, 134.02 (q, *J*=3.75Hz), 132.44, 130.92, 130.24, 129.63, 127.72 (q, *J*=78.75Hz), 126.68, 126.43, 126.16, 125.81, 123.92, 121.75, 121.20, 112.84, 68.19, 63.86, 53.04. HR-MS: $(M+Na)^+$, $C_{23}H_{18}ClF_3N_2O_4Na$, calculated: 501.0799, found: 501.0804.

5b. Yield: 80.2%. White solid. M.p. 88.3-89.9 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 9.04 (d, *J*=1.0Hz, 1H), 8.59 (d, *J*=1.5Hz, 1H), 7.56 (d, *J*=7.4Hz, 1H), 7.47-7.39 (m, 3H), 7.29 (d, *J*=7.65Hz, 1H), 7.24 (dd, *J*=7.5, 1.25Hz, 1H), 7.21-7.20 (m, 1H), 7.07-7.05 (m, 1H), 4.98 (s, 2H), 3.89 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.26, 159.63, 158.21, 149.43, 144.12 (q, *J*=3.75Hz), 138.18, 135.30 (q, *J*=3.75Hz), 135.02, 130.26, 129.60, 129.39, 129.31, 128.61, 127.83 (d, *J*=1.25Hz), 126.13 (q, *J*=32.5Hz), 123.80, 122.17, 121.63, 116.31, 115.74, 68.53, 63.81, 52.95. HR-MS: $(M+Na)^+$, $C_{23}H_{18}ClF_3N_2O_4Na$, calculated: 501.0799, found: 501.0801.

5c. Yield: 85.5%. White solid. M.p. 97.2-98.7 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.82 (d, *J*=0.9Hz, 1H), 8.02 (d, *J*=1.5Hz, 1H), 7.78-7.75 (m, 2H), 7.57 (d, *J*=7.5Hz, 1H), 7.49-7.41 (m, 2H), 7.24 (d, *J*=7.5, 1.2Hz, 1H), 7.02-7.00 (m, 2H), 5.04 (s, 2H), 4.05 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.18, 159.54, 159.20, 149.35, 144.05 (q, *J*=3.8Hz), 135.22 (q, *J*=3.3Hz), 134.80, 130.97, 129.67 (d, *J*=5Hz), 129.53, 129.37, 128.56, 127.77 (d, *J*=13.2Hz), 125.35 (q, *J*=33.75Hz), 122.74 (q, *J*=271.25Hz), 114.34, 77.28, 77.03, 76.78, 68.37, 63.74, 52.87, 43.79. HR-MS: $(M+Na)^+$, $C_{23}H_{18}ClF_3N_2O_4Na$, calculated: 501.0799, found: 501.0799.

5d. Yield: 80.6%. Yellow solid. M.p. 95.0-96.7 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.55 (d, *J*=2.1Hz, 1H), 7.81 (d, *J*=2.1Hz, 1H), 7.56 (d, *J*=7.4Hz, 1H), 7.45-7.30 (m, 5H), 7.23 (dd, *J*=7.5, 1.2Hz, 1H), 7.00-6.99 (m, 1H), 5.03 (s, 2H), 4.01 (s, 3H), 3.82 (s, 3H). ^{13}H NMR (125MHz, $CDCl_3$) δ: 163.24, 158.15, 154.39, 149.42, 146.39, 138.37, 137.43, 135.09, 130.52, 130.18, 129.56, 129.36, 129.18, 128.56, 127.81, 127.77, 122.11, 115.76, 115.64, 68.45, 63.79, 52.94. HR-MS: $(M+Na)^+$, $C_{22}H_{18}Cl_2N_2O_4Na$, calculated: 467.0536, found: 467.0536.

5e. Yield: 78.9%. White solid. M.p. 107.5-110.6 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.53 (d, *J*=2.15Hz, 1H), 7.81 (d, *J*=2.15Hz, 1H), 7.70-7.67 (m, 2H), 7.57 (d, *J*=7.6Hz, 1H), 7.48-7.40 (m, 2H), 7.23 (dd, *J*=7.53, 1.2Hz, 1H), 6.70-6.98 (m, 2H), 5.02 (s, 2H), 4.05 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.27, 159.17, 154.20, 149.44, 146.38, 137.45, 135.00, 130.77, 129.95, 129.94, 129.88, 129.85, 129.60, 129.41, 128.60, 127.85, 127.79, 114.37, 114.36, 68.41, 63.83, 52.97. HR-MS: $(M+Na)^+$, $C_{22}H_{18}Cl_2N_2O_4Na$, calculated: 467.0536, found: 467.0535.

5f. Yield: 77.8%. Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.50 (d, *J*=0.5Hz, 1H), 7.58-7.53 (m, 4H), 7.47-7.37 (m, 3H), 7.24-7.22 (m, 1H), 6.99 (dd, *J*=7.9, 2.4Hz, 1H), 5.03 (s, 2H), 4.03 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.31, 158.63, 149.50, 144.30, 144.26, 135.73, 135.11, 129.58, 129.53, 128.61, 127.98, 127.87, 124.49, 124.30, 121.54, 121.49, 116.12, 114.93, 114.89, 68.53, 63.84, 52.98. HR-MS: $(M+Na)^+$, $C_{22}H_{18}ClFN_2O_4Na$, calculated: 451.0831, found: 451.0831.

5g. Yield: 75.7%. White solid. M.p. 129.0-131.8 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.47 (d, *J*=0.5Hz, 1H), 7.91 (dd, *J*=8.8, 1.5Hz, 2H), 7.57 (d, *J*=7.4Hz, 1H), 7.52 (dd, *J*=10.55, 2.0Hz, 1H), 7.48-7.40 (m, 2H), 7.23 (dd, *J*=7.5, 1.2Hz, 1H), 7.02-6.99 (m, 2H), 5.03 (s, 2H), 4.04 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.28, 158.43 (d, *J*=261.25Hz), 155.28, 149.42, 144.13 (d, *J*=6.25Hz), 144.03, 134.95, 130.04, 129.99, 129.61, 129.54 (d, *J*=3.75Hz), 129.41, 128.61, 127.88, 127.80, 127.35 (d, *J*=5Hz), 124.20 (d, *J*=23.75Hz), 114.80, 114.79, 68.39, 63.84, 52.99. HR-MS: $(M+Na)^+$, $C_{22}H_{18}ClFN_2O_4Na$, calculated: 451.0831, found: 451.0831.

5h. Yield: 70.8%. Colorless oil. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.37 (s, 1H), 7.56 (d, *J*=7.55Hz, 1H), 7.46-7.38 (m, 3H), 7.34 (t, *J*=7.9, 7.9Hz, 1H), 7.21 (d, *J*=7.35Hz, 1H), 7.10 (d, *J*=7.55Hz, 1H), 7.04 (s, 1H), 6.94 (dd, *J*=8.23, 2.33Hz, 1H), 5.01 (s, 2H), 4.00 (s, 3H), 3.82 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.21, 158.13, 155.64, 149.42, 147.22, 141.89, 139.08, 135.32, 131.53, 130.18, 129.51, 129.27, 129.11, 128.46, 127.70, 127.61, 121.82, 115.17, 114.50, 68.23, 63.75, 52.88, 19.69, 17.90. HR-MS: $(M+H)^+$, $C_{24}H_{25}N_2O_4$, calculated: 405.1809, found: 405.1809.

5i. Yield: 74.3%. Cream yellow solid. M.p. 107.4-108.9 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.35 (d, *J*=1.25Hz, 1H), 7.58 (d, *J*=7.5Hz, 1H), 7.47-7.39 (m, 5H), 7.23 (dd, *J*=7.55, 1.2Hz, 1H), 6.98-6.95 (m, 2H), 5.00 (s, 2H), 4.05 (s, 3H), 3.86 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.30, 158.12, 155.43, 149.49, 147.22, 139.26, 135.24, 133.41, 131.17, 130.24, 130.18, 130.08, 129.58, 129.39, 128.53, 127.84, 127.76, 115.40, 114.38, 68.37, 63.83, 52.97, 20.04, 17.91. HR-MS: $(M+H)^+$, $C_{24}H_{25}N_2O_4$, calculated: 405.1809, found: 405.1809.

5j. Yield: 68.9%. Yellow solid. M.p. 104.7-105.9 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.45-8.44 (m, 1H), 7.83-7.82 (m, 1H), 7.59-7.57 (m, 1H), 7.47-7.33 (m, 3H), 7.27-7.20 (m, 3H), 6.97-6.94 (m, 1H), 5.01 (s, 2H), 4.02 (s, 3H), 3.83 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.24, 158.00, 154.98, 149.43, 148.46, 141.59, 140.71, 135.24, 133.46, 129.54, 129.31, 128.99, 128.49, 127.80, 127.67, 122.17, 119.22, 115.58, 115.29, 68.35, 63.80, 52.93, 17.57. HR-MS: $(M+Na)^+$, $C_{23}H_{21}BrN_2O_4Na$, calculated: 491.0577, found: 491.0577.

5k. Yield: 65.3%. Yellow solid. M.p. 142.1-143.6 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.43-8.42 (m, 1H), 7.81-7.80 (m, 1H), 7.63-7.61 (m, 2H), 7.58-7.57 (m, 1H), 7.48-7.39 (m, 2H), 7.23 (dd, *J*=7.53, 1.23Hz, 1H), 6.98-6.96 (m, 2H), 5.02 (s, 2H), 4.05 (s, 3H), 3.86 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.26, 158.68, 154.71, 149.43, 148.41, 141.73, 135.11, 132.95, 132.20, 130.71, 129.57, 129.36, 128.53, 127.79, 127.77, 125.77, 122.06, 119.13, 114.13, 68.33, 63.83, 52.96, 17.52. HR-MS: $(M+Na)^+$, $C_{23}H_{21}BrN_2O_4Na$, calculated: 491.0577, found: 491.0577.

5l. Yield: 60.6%. Colorless oil. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.51 (d, *J*=1.95Hz, 1H), 7.58 (d, *J*=1.2Hz, 1H), 7.35-7.32 (m, 5H), 7.15-7.13 (m, 1H), 7.08 (t, *J*=7.35, 7Hz, 1H), 6.92 (d, *J*=8.2Hz, 1H), 4.92 (s, 2H), 4.03 (s, 3H), 3.85 (s, 3H), 2.19 (s, 3H). ^{13}C NMR

(125MHz, $CDCl_3$) δ: 163.17, 155.50, 155.12, 149.02, 145.25, 136.88, 135.29, 134.26, 130.56, 130.35, 129.81, 129.60, 129.38, 128.25, 127.99, 127.34, 126.66, 121.47, 113.06, 68.20, 63.84, 53.03, 18.97. HR-MS: $(M+H)^+$, $C_{23}H_{22}ClN_2O_4$, calculated: 425.1263, found: 425.1263.

5m. Yield: 62.8%. Brown oil. ^1H NMR (500MHz, $CDCl_3$) δ: 8.54 (d, *J*=1.65Hz, 1H), 7.68 (s, 1H), 7.56 (d, *J*=7.4Hz, 1H), 7.46-7.36 (m, 3H), 7.21 (dd, *J*=7.55, 1.2Hz, 1H), 7.11 (d, *J*=7.5Hz, 1H), 7.03 (s, 1H), 6.98 (dd, *J*=8.2, 2.15Hz, 1H), 5.02 (s, 2H), 4.00 (s, 3H), 3.83 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.17, 158.16, 156.53, 149.36, 145.48, 140.69, 137.84, 135.14, 132.30, 130.21, 129.50, 129.28, 128.50, 127.66, 125.77, 121.64, 115.14, 114.94, 68.28, 63.73, 53.38, 52.87, 19.72. HR-MS: $(M+H)^+$, $C_{23}H_{22}ClN_2O_4$, calculated: 425.1263, found: 425.1263.

5n. Yield: 61.9%. Brown oil. ^1H NMR (500MHz, $CDCl_3$) δ: 8.47 (s, 1H), 7.58-7.40 (m, 6H), 7.23 (d, *J*=7.25Hz, 1H), 6.98 (s, 2H), 5.01 (s, 2H), 4.05 (s, 3H), 3.87 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.26, 158.47, 156.39, 149.44, 145.57, 145.56, 137.90, 135.06, 132.32, 132.02, 130.21, 130.20, 129.76, 129.58, 129.39, 128.54, 127.80, 114.49, 114.48, 68.38, 63.82, 52.96, 20.13. HR-MS: $(M+Na)^+$, $C_{23}H_{21}ClN_2O_4Na$, calculated: 447.1082, found: 447.1082.

5o. Yield: 55.5%. White solid. M.p. 123.0-125.2 °C. ^1H NMR (500MHz, $CDCl_3$) δ: 8.59 (d, *J*=1.95Hz, 1H), 7.76 (d, *J*=1.65Hz, 1H), 7.56 (d, *J*=7.45Hz, 1H), 7.46-7.34 (m, 3H), 7.21 (dd, *J*=7.4, 1.1Hz, 1H), 7.08 (d, *J*=7.6Hz, 1H), 7.02-7.01 (m, 1H), 6.96 (dd, *J*=8.2, 2.1Hz, 1H), 5.01 (s, 2H), 4.00 (s, 3H), 3.83 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.24, 158.23, 156.80, 149.41, 147.57, 140.89, 140.48, 135.18, 132.97, 129.57, 129.38, 129.31, 128.55, 127.73, 127.71, 121.64, 119.01, 115.13, 115.12, 68.35, 63.80, 52.94, 19.75. HR-MS: $(M+H)^+$, $C_{23}H_{22}BrN_2O_4$, calculated: 469.0757, found: 469.0756.

5p. Yield: 58.7%. White solid. M.p. 107.4-110.2 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ: 8.58 (d, *J*=1.9Hz, 1H), 7.76 (d, *J*=1.55, 1H), 7.57 (d, *J*=7.55Hz, 1H), 7.47-7.42 (m, 4H), 7.23 (dd, *J*=7.55, 1.15Hz, 1H), 7.00-6.97 (m, 2H), 5.01 (s, 2H), 4.05 (s, 3H), 3.86 (s，3H), 2.38 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 163.27, 158.53, 156.67, 149.43, 147.68, 140.80, 135.05, 132.60, 132.18, 130.20, 130.19, 129.58, 129.39, 128.55, 127.81, 127.80, 118.47, 114.53, 114.52, 68.39, 63.83, 52.97, 20.12. HR-MS: $(M+Na)^+$, $C_{23}H_{21}BrN_2O_4Na$, calculated: 491.0577, found: 491.0577.

Herbicidal Activities Assay in Petri Dish Tests. Wheat, sorghum, barnyard grass, cucumber, rape and radish seeds were selected as the test targets. The germinated seeds were placed in the 9 cm inner diameter petri dish respectively with two layers of filter papers and 9 mL of each new compound solutions at 100 mg/L were added into the petri dish. Afterwards, the petri dish were placed in an artificial climate chamber at a temperature of 28 °C, light intensity of 300 Lux, and relative humidity of 75%. The root and stem inhibition rate of all the test targets were investigated after 7 d. The results are showed in Table 1.

Herbicidal Activities Assay in Glasshouse Tests. All plant materials were obtained from the Bioassay Testing and Safety Assessment Center in Zhejiang Research Institute of Chemical Industry. The herbicidal activities of all target compounds against monocotyledon weeds such as *Digitaria sanguinalis*, *Echinochloa crusgalli*, *Setaria viridis*, *Alopecurus aequalis*, *Polypogon fugax*, and *Poa annua* and dicotyledon weeds such as *Abutilon theophrasti*, *Amaranthus retroflexus*, *Eclipta prostrata*, *Brassica juncea*, *Chenopodium serotinum*, and *Stellaria media* were evaluated according to a previously reported procedure.[27-29] Mesotrione and pyribambenz-isopropyl were selected as controls. All test compounds were formulated as a 100 g/L emulsified concentrates by using DMF as solvent and Tween-80 as emulsification reagent. The concentrates were diluted with water to obtain the required concentration and applied to pot-grown plants in a greenhouse. Plastic pots with a diameter of 7.5 cm were filled with soil to a depth of 5.6 cm containing 33.3% garden soil and 66.7% nursery substrates. The seeds of the test plants were sown separately according to species. Approximately 12 seeds of the tested weeds were sown in the soil at the depth of 0.2 cm and grown at 15-30 °C in a greenhouse. The diluted formulation solutions were applied for pre-emergence treatment 24 h after the weeds were sown. For post-emergence treatment, all weeds were treated at the 3-leaf stage. The pre- and post-emergence application rates were estimated as 150 g a.i./ha. Untreated seedlings were used as the control group, and the solvent (DMF+Tween-80) treated seedlings were used as the solvent control group. Herbicidal activity was evaluated visually 15-20 d post-treatment. The DMF+Tween-80 control displayed no herbicidal activity, and the results are reported in Tables 2 and 3.

Evaluation was on a scale from 0 to 100, where 0 means no damage or normal growth and 100 means no emergence of the plants or complete destruction of at least the above-ground parts.

Herbicidal Activities Assay in Field Tests. The field tests were performed on the basis of field efficacy trials of Chinese pesticide standards (GB/T17980.40-2000) in Hangzhou, China. The test weeds in the maize field were at 3-4 leaf stage and the maize were at 4-5 leaf stage. The controlling weeds comprised the following species: *Eclipta prostrate*, *Amaranthus retroflexus*, *Portulaca oleracea*, *Digitaria sanguinalis*, *Eleusine indica*, and *Cyperus iria* in Hangzhou, China. The application rate for treatment was 18.75, 37.5, 75, 150 and 300 g a.i./ha (**5c** or **5e** 5% EC (emulsifiable concentrate)). The application rate for treatment of mesotrione which was used as the control was 75 and 150 g a.i./ha (mesotrione

9% SC (suspension concentrate)). Formulas used in these tests are as follows: Control effect (%) = (the number of live weeds in the control area − the number of live weeds in the treated area) / the number of live weeds in the control area × 100%. The results are reported in Tables 4 and 5.

Herbicidal Spectrum Test. The herbicidal activities of the compounds **5c** and **5e** against about 22 broadleaf weeds were evaluated according to the same procedure in a glasshouse. Nicosulfuron was selected as a control. The post-emergence application rates was estimated as 18.75 g a.i./ha. The results are reported in Table 6.

Crop Selectivity. The conventional three varieties of wheat and three varieties of maize were planted separately in pots (6.5 cm diameter) containing test soil with *Amaranthus retroflexus* distributed evenly in it and grown in a greenhouse. After the plants reached the 3- or 4-leaf stage, the spraying treatment was conducted at different dosages. The visual injury and growth state of the individual plants were observed at regular intervals. After 30 d, the herbicidal activity was visually investigated and the fresh weight inhibition rate was determined. The ED_{10} values of the crops and the ED_{90} values of the weeds were calculated using DPS statistical software to obtain the selectivity coefficient between the crops and the weeds. Formulas used in these tests are as follows: selectivity coefficient = the ED_{10} values of the crops / the ED_{90} values of the weeds. The results are reported in Table 7.

Results and discussion

Synthetic Chemistry of the Title Compounds. As shown in Figures 2 and 3, all target compounds were prepared by a multistep synthetic route using substituted pyridines and phthalide as the starting materials. The reactions of the intermediates A and B, respectively, via nucleophilic substitution using DMF as the solvent afforded a range of novel compounds in considerable yields. The target compounds were characterized by NMR and

HRMS. All spectral and analytical data were consistent with the assigned structures.

Herbicidal Activity. As shown in Table 1, herbicidal activities assay in petri dish tests indicate that some new compounds integrating a phenylpyridine moiety with methoxyiminoacetate had a very good inhibitory activity on the growth of targets. Furthermore, the kresoxim-methyl unit was necessary to maintain herbicidal activity. Thus, a series of target compounds were synthesized and evaluated for their herbicidal ability to control the harmful weeds using pre- and post-emergence treatment in the glasshouse and the field tests. For pre-emergence treatment in the glasshouse, some designed kresoxim-methyl derivatives were compared to the commercial herbicide pyribambenz isopropyl. The post-emergence herbicidal activities of the rest compounds were tested in a greenhouse against harmful weeds. The commercial herbicide mesotrione were selected as the control. As shown in Table 2, at 150 g a.i./ha, compounds **5b**, **5c** and **5e** showed 100% inhibition against *Abutilon theophrasti*, *Amaranthus retroflexus* and *Eclipta prostrata* for post-emergence treatment, and compounds **5n** and **5p** also showed greater than 80% inhibition against these three broadleaf weeds. Furthermore, **5c** exhibited excellent herbicidal activity against all target weeds. The other compounds exhibited general herbicidal activity. Compounds **5b** and **5e** showed favourable herbicidal activity against the other five target weeds except *Echinochloa crusgalli* for pre-emergence treatment.

According to further test results as shown in Table 3, at 37.5 g a.i./ha, the activity of **5c** showed nearly 100% inhibition against *Abutilon theophrasti*, *Amaranthus retroflexus* and *Eclipta prostrata*, which was slightly better than the activity of mesotrione at 150 g a.i./ha for post-emergence treatment. Similarly, **5e** also showed good herbicidal activity at 37.5 g a.i./ha for post-emergence treatment.

Based on the structural analysis of all new compounds, it was found that the herbicidal activity of the compound was significantly improved when the benzene ring was attached to the 2-position of the pyridine ring. Furthermore, the compounds showed excellent herbicidal activity when substituted pyridine and active structure of trifloxystrobin were in the *para*-position of the benzene ring. Additionally, containing chloride or trifluoromethyl groups at the 3-position and 5-position on pyridine ring was essential for high herbicidal activity.

Herbicidal activity results in field test (Tables 4 and 5) showed that the herbicidal activity of **5c** and **5e** at 18.75-300 g a.i./ha against broadleaf weeds (*Amaranthus retroflexus*, *Eclipta prostrata*， and *Portulaca oleracea*) proved roughly equivalent to the control of 9% mesotrione SC at 75-150 g a.i./ha. However, the two test compounds had poor or no obvious control effect against Gramineae and Cyperaceae weeds, which were significantly lower than that of mesotrione at the same concentration.

Herbicidal Spectrum. 22 broadleaf weeds were selected for herbicidal test of **5c** and **5e**. Table 6 generally showed that the control effect of **5e** was better than that of **5c** at the dosage of 18.75 g a.i./ha, and they were all better than that of nicosulfuron. **5e** had an excellent broad herbicidal spectrum against broadleaf weeds.

Crop Selectivity. Compounds **5c** and **5e** with promising herbicidal activity were chosen as representatives for further crop selectivity studies. As shown in Table 7, **5c** and **5e** had a certain selectivity between wheat/maize and *Amaranthus retroflexus*, which were better than nicosulfuron in the wheat field, but slightly lower than nicosulfuron in the maize field. There were also some differences among different wheat/maize varieties. Crop selectivity studies indicated that **5c** and **5e** might be developed as a potential herbicide for wheat and maize fields.

In summary, a series of new (pyridinylphenoxymethylene)phenyl methoxyiminoacetates were designed and synthesized as potential herbicides. The result of in greenhouse and field tests indicated that some newly synthesized compounds had good herbicidal activities at the dosage of 37.5 g a.i./ha. Most interestingly, the activity of **5c** and **5e** against broadleaf weeds proved slightly better than mesotrione at 37.5 g a.i./ha. The herbicidal assay in field tests in Hangzhou indicated that **5c** and **5e** had excellent herbicidal activities. Our results suggest that **5c** and **5e** may be new candidates as potential herbicides.

Acknowledgments

This work was financially supported by the National Key Research and Development Plan (2016YFD0300708).

The herbicidal activities assay of this work was completed by the Bioassay Testing and Safety Assessment Center in Zhejiang Research Institute of Chemical Industry.

References

1. Sauter, H; Steglich, W; Anke, T. Strobilurins: evolution of a new class of active substances. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1329-1349.

2. Bartlett, D. W.; Clough, J. M.; Godwin, J. R.; Hall, A. A.; Hamer, M.; Parr-Dobrzanski, B. The strobilurin fungicides. *Pest Manage. Sci.* **2002**, *58*, 649-662.

3. Fisher, N.; Meunier, B. Re-examination of inhibitor resistance conferred by Q_0-site mutations in cytochrome b using yeast as a model system. *Pest Manage. Sci.* **2005**, *61*, 973-978.

4. Gisi, U.; Sierotzki, H.; Cook, A.; McCaffery, A. Mechanisms influencing the evolution of resistance to Q_0 inhibitor fungicides. *Pest Manage. Sci.* **2002**, *58*, 859-867.

5. Sierotzki, H.; Parisi, S.; Steinfeld, U.; Tenzer, I.; Poirey, S.; Gisi, U. Mode of resistance to respiration inhibitors at the cytochrome bc_1 complex of *Mycosphaerella fijiensis*. *Pest Manage. Sci.* **2000**, *56*, 833-841.

6. Beautement, K.; Clough, J. M.; De Fraine, P. J.; Godfrey, C. R. A. Fungicidal *β*-methoxyacrylates: From natural products to novel synthetic agricultural fungicides. *Pestic. Sci.* **1991**, *31*, 499-519.

7. Jeschke, P. The unque role of fluorine in the design of active ingredients for modern crop protection. *ChemBioChem* **2004**, *5*, 570-589.

8. Sauter, H.; Steglich, W.; Anke, T. Strobilurins: evolution of a new class of active substrances. *Angew. Chem. Int. Ed.* **1999**, *38*, 1329-1349.

9. Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. D.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. Use of lanthanid (III) ions as catalysts for the reactions of amine with nitriles. *J. Org. Chem.* **1987**, *52*, 1017-1021.

10. De Fraine, P. J.; Snell, B. K.; Clough, J. M.; Anthony, V. M.; Beautement, K.

Heterocyclic compounds as fungicides. EP 206523, 1986.

11. Gayer, H.; Gerdes, P.; Kuhnt, D.; Dutzmann, S.; Dehne, H. W.; Haenssler, G. Preparation of pesticidal 2-(oximino)-2-(thienyl)acetic acid derivatives. WO 9501973, 1995.

12. Huang, W.; Zhao, P. L.; Liu, C. L.; Chen, Q.; Liu, Z. M.; Yang, G. F. Design, synthesis, and fungicidal activities of new strobilurin derivatives. *J. Agric. Food Chem.* **2007**, *55*, 3004-3010.

13. Hao, G. F.; Yang, S. G.; Huang, W.; Wang, L.; Shen, Y. Q.; Tu, W. L.; Li, H.; Huang, L. S.; Wu, J. W.; Edward, A. B.; Yang, G. F. Rational design of highly potent and slow-binding cytochrome bc_1 inhibitor as fungicide by computational substitution optimization. *Sci. Rep.* **2015**, *5*, 13471.

14. Zhao, P. L.; Liu, C. L.; Huang, W.; Wang, Y. Z.; Yang, G. F. Synthesis and fungicidal evaluation of novel chalcone-based strobilurin analogues. *J. Agric. Food Chem.* **2007**, *55*, 5697-5700.

15. Zhao, P. L.; Wang, F.; Zhang, M. Z.; Liu, Z. M.; Huang, W.; Yang, G. F. Synthesis, fungicidal, and insecticidal activities of *β*-methoxyacrylate-containing *N*-acetyl pyrazoline derivatives. *J. Agric. Food Chem.* **2008**, *56*, 10767-10773.

16. Zhao, P. L.; Wang, L.; Zhu, X. L.; Huang, X. Q.; Zhan, C. G.; Wu, J. W.; Yang, G. F. Subnanomolar inhibitor of cytochrome bc_1 complex designed by optimizing interaction with conformationally flexible residues. *J. Am. Chem. Soc.* **2010**, *132*, 185-194.

17. Hao, G. F.; Wang, F.; Li, H.; Zhu, X. L.; Yang, W. C.; Huang, L. S.; Wu, J. W.; Edward, A. B.; Yang, G. F. Computational discovery of picomolar Q_0 site inhibitors of cytochrome bc_1 complex. *J. Am. Chem. Soc.* **2012**, *134*, 11168-11176.

18. Ziegler, H.; Neff, D.; Stutz, W. Preparation of 2-aryl-2-(methoxyimino)acetate esters via palladium-catalyzed cross-coupling reaction of aryl boronic acid and 2-(methoxyimino)acetate esters. WO 9520569, 1995.

19. Wassilios, G.; Albrecht, H.; Hubert, S.; Beate, H.; Reinhard, D.; Eberhard, A.; Gisela, L. Preparation of [(2-alkoximinoalkyl) phenyl] glyoxylate oximes and analogs as agrochemical fungicides. EP 499823, 1992.

20. Wenderoth, B.; Brand, S.; Schuetz, F.; Kuekenhoehner, T.; Roehl, F.; Ammermann, E.; Lorenz, G. Preparation of (pyridinyloxy) phenylglyoxylate *O*-methyl oximes as agrochemical fungicides. DE 3835028, 1990.

21. Schaefer, P.; Hamprecht, G.; Puhl, M.; Westphalen, K. O.; Zagar, C. Synthesis and herbicidal activity of phenylpyridines-a new lead. *Chimia* **2003**, *57*, 715-719.

22. Schaefer, P.; Hamprecht, G.; Heistracher, E.; Koenig, H.; Klintz, R.; Muenster, P.; Rang, H.; Westphalen, K. O.; Gerber, M.; Walter, H. Preparation of substituted 2-phenylpyridine herbicides. DE 4323916, 1995.

23. Xie, Y.; Chi, H. W.; Guan, A. Y., Liu, C. L.; Ma, H. J.; Cui, D. L. Design, synthesis, and herbicidal activity of novel substituted 3-(pyridin-2-yl) benzenesulfonamide derivatives. *J. Agric. Food Chem.* **2014**, *62*, 12491-12496.

24. Mao, D. J.; Hu, C. B.; Liu, J. H.; Du, X. H.; Xu, Z. Y. Synthesis and fungicidal activity of novel methoximinoacetates containing phenylpyridine moieties. *Chin. J. Pestic. Sci.* **2014**, *16*, 406-413.

25. Wang, W. W.; Liu, Z. F.; Du, X. H. Synthesis of 2-methyl chloride-α-methoxyl and amino benzene methyl acetate. *Agrochemicals* **2015**, *54*, 180-182.

26. Lu, C. J.; Liu, J. H.; Du, X. H. Synthesis of trifloxystrobin. *Agrochemicals* **2011**, *50*, 187-191, 212.

27. Chen, C. N.; Chen, Q.; Liu, Y. C.; Zhu, X. L.; Niu, C. W.; Xi, Z.; Yang, G. F. Syntheses and herbicidal activity of new triazolopyrimidine-2-sulfonamides as acetohydroxyacid synthase inhibitors. *Bioorg. Med. Chem.* **2010**, *18*, 4897-4904.

28. Chen, C. N.; Lv, L. L.; Ji, F. Q.; Chen, Q.; Xu, H.; Niu, C. W.; Xi, Z.; Yang, G. F. Design and synthesis of *N*-2,6-difluorophenyl-5-methoxyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide as acetohydroxyacid synthase inhibitor. *Bioorg. Med. Chem.* **2009**, *17*, 3011-3017.

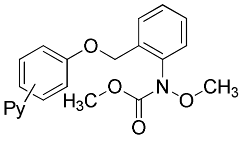
29. Li, Y. X.; Luo, Y. P.; Xi, Z.; Niu, C. W.; He, Y. Z.; Yang, G. F. Design and syntheses of novel phthalazin-1(2*H*)-one derivatives as acetohydroxyacid synthase inhibitors. *J. Agric. Food Chem.* **2006**, *54*, 9135-9139.

Figure Captions

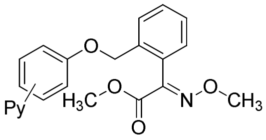
Figure 1. Overview Synthetic Methods of Kresoxim-methyl Derivatives.

Figure 2. Synthetic Methods of Intermediate B.

Table 1. Chemical Structures and Herbicidal Activity Assay in Petri Dish Tests at the Concentration of 100 mg/L.



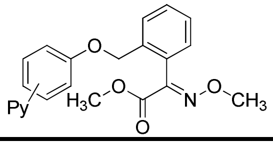
I



II

No.	Py	wheat		sorghum		barnyard grass		cucumber		rape		radish	
		root	stem	root	stem	root	stem	root	stem	root	stem	root	stem
I-1	3-(3-F-pyridin-2-yl)	0	0	0	0	0	0	0	0	30	30	0	0
II-1	3-(3-F-pyridin-2-yl)	0	0	80	80	80	80	50	50	0	0	50	0
I-2	3-(3-CF_3-pyridin-2-yl)	0	0	50	0	0	0	0	0	0	0	0	0
II-2	3-(3-CF_3-pyridin-2-yl)	50	50	80	50	80	80	30	0	80	40	80	50
I-3	4-(3-CF_3-pyridin-2-yl)	0	0	0	0	0	0	0	0	0	0	0	0
II-3	4-(3-CF_3-pyridin-2-yl)	0	0	0	0	0	0	0	0	80	80	80	50
I-4	3-(3-Cl-5-CF_3-pyridin-2-yl)	0	0	0	0	30	30	30	0	0	0	0	0
II-4	3-(3-Cl-5-CF_3-pyridin-2-yl)	50	20	100	100	100	95	95	95	100	100	100	100
I-5	4-(3,5-Cl_2-pyridin-2-yl)	0	0	0	0	30	30	30	0	30	0	0	0
II-5	4-(3,5-Cl_2-pyridin-2-yl)	50	0	100	100	100	100	100	100	100	100	100	100

Table 2. Chemical Structures and Herbicidal Activity of Kresoxim-methyl Derivatives by Pre- and Post-emergence Treatment in Glasshouse Tests at the Dosage of 150 g a.i./ha.



No.	Py	*Abutilon theophrasti*	*Amaranthus retroflexus*	*Eclipta prostrata*	*Digitaria sanguinalis*	*Echinochloa crusgalli*	*Setaria viridis*
Post-emergence Treatment							
5a	2-(3-Cl-5-CF_3-pyridin-2-yl)	0	0	30	0	0	0
5b	3-(3-Cl-5-CF_3-pyridin-2-yl)	100	100	100	0	0	0
5c	4-(3-Cl-5-CF_3-pyridin-2-yl)	100	100	100	95	100	90
5d	3-(3,5-Cl_2-pyridin-2-yl)	0	90	90	30	30	30
5e	4-(3,5-Cl_2-pyridin-2-yl)	100	100	100	0	0	0
5f	3-(5-Cl-3-F-pyridin-2-yl)	0	90	80	30	30	30
5g	4-(5-Cl-3-F-pyridin-2-yl)	0	100	90	0	30	30
5h	3-(3,5-Me_2-pyridin-2-yl)	0	0	30	0	0	0
5i	4-(3,5-Me_2-pyridin-2-yl)	0	50	30	0	0	0
5j	3-(3-Br-5-Me-pyridin-2-yl)	0	30	30	0	30	30
5k	4-(3-Br-5-Me-pyridin-2-yl)	0	50	0	0	0	0
5l	2-(5-Cl-3-Me-pyridin-2-yl)	0	0	0	0	0	0
5m	3-(5-Cl-3-Me-pyridin-2-yl)	0	30	30	0	0	0
5n	4-(5-Cl-3-Me-pyridin-2-yl)	80	100	90	30	30	30
5o	3-(5-Br-3-Me-pyridin-2-yl)	0	30	30	0	0	0
5p	4-(5-Br-3-Me-pyridin-2-yl)	100	100	90	30	30	30
	Mesotrione	95	100	100	80	85	80
Pre-emergence Treatment							
5a	2-(3-Cl-5-CF_3-pyridin-2-yl)	0	0	0	0	0	0
5b	3-(3-Cl-5-CF_3-pyridin-2-yl)	100	100	85	80	0	50
5c	4-(3-Cl-5-CF_3-pyridin-2-yl)	0	50	0	0	30	0
5d	3-(3,5-Cl_2-pyridin-2-yl)	0	0	0	0	0	0
5e	4-(3,5-Cl_2-pyridin-2-yl)	100	100	100	50	0	50
5f	3-(5-Cl-3-F-pyridin-2-yl)	0	100	0	0	0	0
5g	4-(5-Cl-3-F-pyridin-2-yl)	0	0	0	0	0	0
5h	3-(3,5-Me_2-pyridin-2-yl)	0	90	0	0	0	0
5i	4-(3,5-Me_2-pyridin-2-yl)	0	0	0	0	0	0
5j	3-(3-Br-5-Me-pyridin-2-yl)	0	0	0	0	0	0
5k	4-(3-Br-5-Me-pyridin-2-yl)	0	0	0	0	0	0
5l	2-(5-Cl-3-Me-pyridin-2-yl)	0	0	0	0	0	0
5m	3-(5-Cl-3-Me-pyridin-2-yl)	0	90	0	0	0	0
5n	4-(5-Cl-3-Me-pyridin-2-yl)	0	0	0	0	0	0
5o	3-(5-Br-3-Me-pyridin-2-yl)	0	80	0	0	0	0
5p	4-(5-Br-3-Me-pyridin-2-yl)	0	100	90	50	50	50
	Pyribambenz isopropyl	100	95	75	97.5	97.5	97.5

Table 3. Herbicidal Activity of the Selected Compounds by Pre- and Post-emergence Treatment in Glasshouse Tests.

No.	Dosage g a.i./ha	*Abutilon theophrasti*	*Amaranthus retroflexus*	*Eclipta prostrata*	*Digitaria sanguinalis*	*Echinochloa crusgalli*	*Setaria viridis*
Post-emergence Treatment							
5b	37.5	30	100	97.5	0	0	0
	75	60	100	100	0	0	0
	150	100	100	100	0	0	0
5c	37.5	100	100	100	50	50	50
	75	100	100	100	60	60	50
	150	100	100	100	95	100	90
5e	37.5	100	100	97.5	0	0	0
	75	100	100	100	0	0	0
	150	100	100	100	0	0	0
5n	37.5	30	70	40	30	20	20
	75	50	90	50	40	30	30
	150	80	100	90	50	40	40
5p	37.5	50	60	40	20	20	20
	75	60	70	50	30	30	30
	150	100	100	90	30	30	30
Mesotrione	150	95	100	100	80	85	80
Pre-emergence Treatment							
5b	37.5	0	0	0	0	0	0
	75	0	15	0	0	0	0
	150	100	100	85	80	0	50
5e	37.5	0	20	0	0	0	0
	75	0	30	0	0	0	0
	150	100	100	100	50	0	50
Pyribambenz isopropyl	150	100	95	75	97.5	97.5	97.5

Table 4. Herbicidal Activity of **5c** and **5e** in Maize Field Tests (after 20 d).

Management	Dosage g a.i./ha	*Amaranthus retroflexus*	*Eclipta prostrata*	*Portulaca oleracea*	*Digitaria sanguinalis*	*Eleusine indica*	*Cyperus iria*	Total
5c (5% EC)	18.75	74.3	73.4	75.0	13.2	8.0	6.6	39.9
	37.5	84.2	81.3	82.7	17.6	14.0	13.2	47.1
	75	89.1	87.5	88.5	22.1	20.0	17.4	52.2
	150	94.1	93.8	94.2	35.3	32.0	27.3	60.7
	300	98.0	96.9	98.1	48.5	42.0	38.0	68.4
5e (5% EC)	18.75	73.3	71.9	73.1	1.5	0.0	-2.5	34.2
	37.5	80.2	78.1	80.8	2.9	2.0	-1.7	38.2
	75	83.2	81.3	88.5	7.4	4.0	0.8	41.7
	150	90.1	87.5	92.3	10.3	6.0	1.7	45.4
	300	93.1	90.6	96.2	13.2	8.0	2.5	47.8
Mesotrione (9% SC)	75	97.0	95.3	96.2	67.6	62.0	39.7	73.2
	150	100.0	100.0	100.0	82.4	78.0	54.5	82.9

Table 5. Herbicidal Activity of **5c** and **5e** in Maize Field Tests (after 30 d).

Management	Dosage g a.i./ha	*Amaranthus retroflexus*	*Eclipta prostrata*	*Portulaca oleracea*	*Digitaria sanguinalis*	*Eleusine indica*	*Cyperus iria*	Total
5c (5% EC)	18.75	75.1	74.1	78.3	11.6	7.7	6.7	39.1
	37.5	83.5	81.7	85.0	16.4	12.4	13.0	45.6
	75	89.6	86.9	90.3	19.1	18.1	17.3	50.7
	150	93.9	93.4	94.9	30.0	32.6	27.1	58.7
	300	99.2	97.0	98.2	43.7	42.8	37.3	66.9
5e (5% EC)	18.75	72.1	70.9	72.9	-0.4	-1.5	-4.3	31.5
	37.5	78.9	77.1	79.8	-0.7	-2.3	-2.9	34.8
	75	82.7	82.0	88.5	0.9	-1.9	-1.6	37.9
	150	89.9	86.3	91.9	1.6	0.0	-1.0	41.0
	300	93.1	91.7	95.9	3.9	1.5	-0.1	43.5
Mesotrione (9% SC)	75	98.3	98.1	96.9	68.2	62.5	39.4	72.9
	150	100.0	100.0	100.0	81.6	77.9	54.6	81.9

Table 6. Herbicidal Spectrum Test of **5c** and **5e** at the Concentration of 18.75 g a.i./ha.

Weeds	**5c**	**5e**	Nicosulfuron
Pharbitis nil	80	50	50
Cassia tora	90	80	50
Commelina bengalensis	82.5	80	50
Bidens pilosa	100	75	70
Abutilon theophrasti	90	100	40
Eclipta prostrata	100	100	80
Xanthium sibiricum	90	100	80
Phytolacca americana	90	95	80
Bidens tripartita	70	90	80
Nicandra physaloides	90	100	80
Solanum nigrum	40	100	100
Amaranthus spinosus	40	85	30
Amaranthus retroflexus	80	85	80
Portulaca oleracea	100	100	30
Clinopodium chinense	70	70	60
Boehmeria nivea	40	50	70
Sonchus asper	90	100	50
Carpesium abrotanoides	70	80	60
Monochoria vaginalis	30	70	30
Ammannia baccifera	50	80	30
Ammannia arenaria	50	80	30
Aster tataricus	40	85	30

Table 7. Crop Selectivity between Wheat/Maize and *Amaranthus retroflexus*.

No.	target	correlation coefficient/R	ED_{90} g a.i./ha	ED_{10} g a.i./ha	selectivity coefficient
5c	*Amaranthus retroflexus*	0.9806	14.3	-	-
	Wheat 1 (Jimai 22)	0.9872	-	79.4	5.6
	Wheat 2 (Yangmai 158)	0.9447	-	151.5	10.6
	Wheat 3 (Tainong 18)	0.9939	-	86.9	6.1
	Maize 1 (Huyunuo 3)	0.9915	-	104.7	7.3
	Maize 2 (Nongda 108)	0.9880	-	148.8	10.4
	Maize 3 (Chaotian 3)	0.9613	-	120.8	8.5
5e	*Amaranthus retroflexus*	0.9797	12.9	-	-
	Wheat 1 (Jimai 22)	0.9813	-	106.0	8.2
	Wheat 2 (Yangmai 158)	0.9175	-	207.4	16.0
	Wheat 3 (Tainong 18)	0.9904	-	92.4	7.1
	Maize 1 (Huyunuo 3)	0.9971	-	102.5	7.9
	Maize 2 (Nongda 108)	0.9843	-	148.3	11.5
	Maize 3 (Chaotian 3)	0.9729	-	139.7	10.8
Nicosulfuron	*Amaranthus retroflexus*	0.9896	23.7	-	-
	Wheat 1 (Jimai 22)	0.9908	-	16.3	0.7
	Wheat 2 (Yangmai 158)	0.9906	-	97.5	4.1
	Wheat 3 (Tainong 18)	0.9979	-	45.7	1.9
	Maize 1 (Huyunuo 3)	0.9747	-	347.1	14.6
	Maize 2 (Nongda 108)	0.6699	-	975.4	41.1
	Maize 3 (Chaotian 3)	0.8504	-	467.5	19.7

Figure 1.

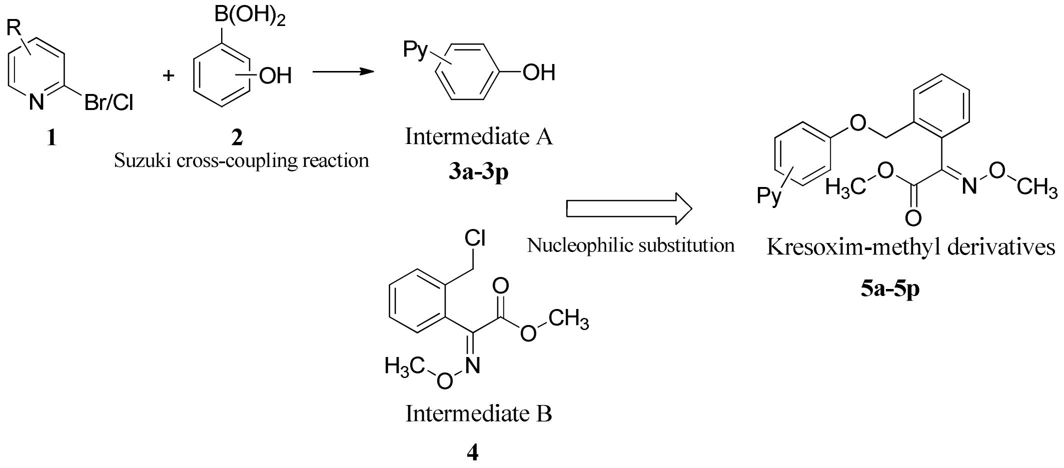

R
Br/Cl
N
1
B(OH)2
OH
2
Suzuki cross-coupling reaction
Py
OH
Intermediate A
3a-3p
Cl
O
CH3
H3C
O
N
Intermediate B
4
Nucleophilic substitution
O
Py
H3C
O
N
O
CH3
O
Kresoxim-methyl derivatives
5a-5p

Figure 2.

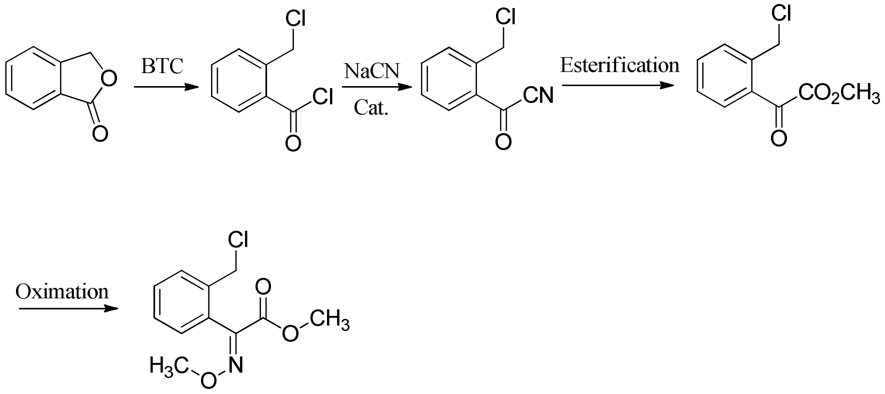

O
O
BTC
Cl
Cl
O
NaCN
Cat.
Cl
CN
O
Esterification
Cl
CO2CH3
O
Oximation
Cl
O
O
CH3
H3C
O
N

Table of Contents Graphic