Feng Cheng and De-Qing Shi*

Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, Hubei, People's Republic of China
*E-mail: chshidq@mail.ccnu.edu.cn

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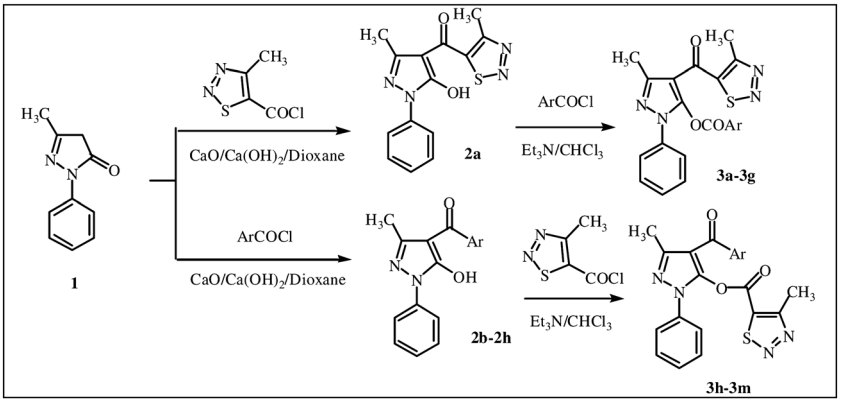

A series of novel acylpyrazole derivatives containing 1,2,3-thiadiazole ring **3a**–**3m** were synthesized by the condensations of 1-phenyl-3-methyl-4-(substituted benzal or 4-methyl-1,2,3-thiadiazole-5-carbonyl)-5-hydroxypyrazole **2** with 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride or substituted benzoyl chloride. Their structures were confirmed by IR, ^{1}H-NMR, mass spectroscopy, and elemental analyses. The results of preliminary bioassays showed that some of the title compounds **3** exhibited moderate to good herbicidal activities against dicotyledonous plants (*Brassica campestris* L.) at the concentration of 100 mg/L. For example, compounds **3e**, **3f**, **3g**, and **3k** possessed 74.6%, 72.2%, 70.3%, and 84.5% inhibition against *B. campestris* L., respectively, whereas commercially available herbicide Sulcotrione showed only 35.0% inhibition at the same concentration. Moreover, these compounds displayed higher herbicidal activity against *B. campestris* L. than *Echinochloa crus-galli*. However, these compounds showed weak activities at the concentration of 10 mg/L.

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INTRODUCTION

(4-Hydroxyphenyl)pyruvate dioxygenase (HPPD, EC 1.13.11.27) is a nonheme Fe(II)-dependent enzyme that catalyzes the conversion of (4-hydroxyphenyl)pyruvate (HPP) to homogentisate in the tyrosine catabolism pathway. Continued scientific interest in HPPD has arisen due to the importance of this enzyme in the treatment of type 1 tyrosinemia and alkaptonuria and its use as a target for the development of herbicides [1–4]. The benzoylpyrazole derivatives represent a relatively new class of highly active, bleaching herbicides, which are a subset of a larger class of "diketone" herbicides [5,6]. For example, pyrazolate [7] and pyrazoxyfen (Fig. 1) [8], as two commercial rice herbicides, acted as prodrugs for HPPD inhibitors. So, the benzoylpyrazole area chemistry attracted more and more attention. Recently, 1,2,3-thiadiazole derivatives as one kind of nitrogen heterocyclic compounds with a wide spectrum of remarkable biological activities are widely used as agrochemicals [9–11]. For example, acibenzolar-*S*-methyl and tiadinil were developed and used as plant activators, which induces fungicide resistance in rice plants; however, thidiazuron was used as plant growth regulator (Fig. 1). To find novel HPPD inhibitor lead compounds with high activity and low toxicity, based on the commercial HPPD herbicides, pyrazolate and pyrazoxyfen as lead compounds, we designed and synthesized a series of novel acylpyrazole derivatives containing 1,2,3-thiadiazole ring **3**. Herein, we would like to report the synthesis and herbicidal activities of the title compounds **3** in this article (Scheme 1).

RESULTS AND DISCUSSION

1-Phenyl-3-methyl-4-(substituted benzal or 4-methyl-1,2,3-thiadiazole-5-carbonyl)-5-hydroxypyrazole **2** were synthesized *via* the Scotton–Baumann reaction of pyrazolone **1** and substituted benzoyl chlorides or 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride, followed by the Fries rearrangement in the presence of calcium hydroxide as the catalyst [12,13]. On one hand, calcium hydroxide

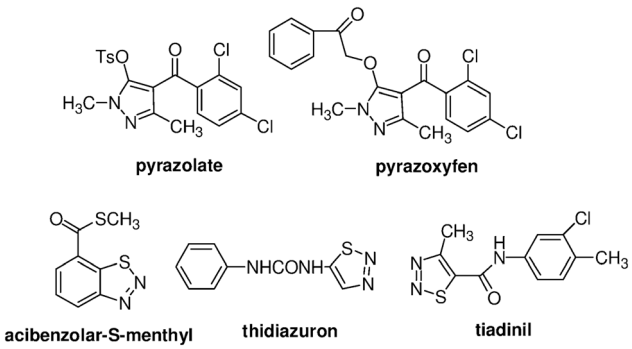


Figure 1. Some commercial pyrazole and 1,2,3-thiadiazole pesticides.

can remove hydrochloride formed in the Scotton–Baumann reaction; so it can improve the yields of the Scotton–Baumann reaction. On the other hand, calcium ion can form the complex with the benzoyl hydroxypyrazole **2** and prevent the multiacylation reaction of pyrazolone. Finally, **2** reacted with substituted benzoyl chloride or 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride in the presence of triethylamine in chloroform with an ice-bath cooling to get the title compounds **3** in moderate to excellent yields.

The structures of compounds **3** were deduced from their spectral data (IR, ^{1}H-NMR, and EI-MS or ESI-MS) and elemental analyses, which were listed in the Experimental section. In the ^{1}H-NMR spectra of compounds **3h**–**3m**, the two methyl protons with attached pyrazole and thiadiazole rings were displayed as two singlets with chemical shift δ *ca*. 2.5 and 2.8, respectively; the aromatic protons were exhibited as multiple peaks with chemical shifts δ *ca*. 7.4–8.6. IR spectra of compounds **3** showed normal stretching absorption bands, indicating the existence Ar—H (∼3050 cm^{-1}), C=O (∼1760, ∼1650 cm^{-1}), Ar (1580, 1510, 1480 cm^{-1}), C—O—C (∼1240, ∼1060 cm^{-1}). The EI or ESI mass spectra of compounds **3** revealed the existence of the molecular ion peaks or strong M + K − 1 or M + Na peaks, which were in good accordance with the given structures of products.

Herbicidal activity. The preliminary herbicidal activity (*in vitro*) of the title compounds **3** against *Brassica campestris* L. (rape) and *Echinochloa crus-galli* (barnyard grass) has been investigated at the dosages of 100 and 10 mg/L and compared with the commercially available herbicide, Sulcotrione, according to the method described in Experimental section and are listed in Table 1. The results of preliminary bioassays showed that some of the title compounds **3** exhibited moderate to good herbicidal activities against dicotyledonous plants (*B. campestris* L.) at the concentration of 100 mg/L. For example, compounds **3e**, **3f**, **3g**, and **3k** possessed 74.6%, 72.2%, 70.3%, and 84.5% inhibition against *B. campestris* L., respectively, whereas commercially available herbicide Sulcotrione showed only 35.0% inhibition at the same concentration. For the preliminary structure–activity relationships, as the data shown in Table 1, we noticed that the different substituents in benzene ring have some influence on the herbicidal activity. For compounds **3a**–**3g**, the compounds with an electron-releasing group in the benzene ring displayed better herbicidal activity against *B. campestris* L. than those with electron-donating one; so compound **3d** (R = *p*-CH$_3$) showed the weakest herbicidal activity. This result can be explained by the fact that those compounds with an electron-releasing group in the benzene ring are more easily hydrolyzed to 5-hydroxy acylpyrazole than those with an electron-donating one; hence 5-hydroxy acylpyrazole can combine with Fe(II) ion and exhibit better HPPD inhibitory activity. As for compounds **3h**–**3m**, compound **3k** (R = *p*-CH$_3$) displayed the best herbicidal activity against *B. campestris* L., whereas compounds **3l** (R = 4-F) and **3m** (R = 2-NO$_2$) showed the weakest herbicidal activity; however, the reason is not very clear.

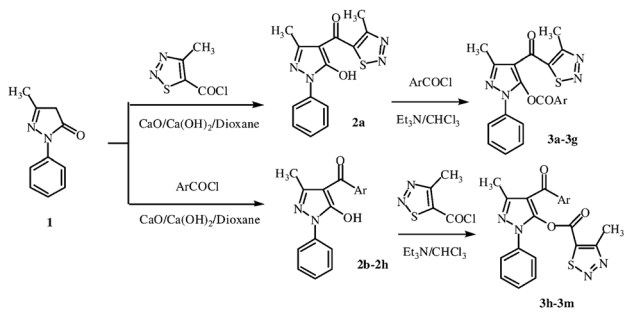
Moreover, these compounds displayed higher herbicidal activity against dicotyledonous plant (*B. campestris* L.)

Table 1

The herbicidal activities of compounds **3a**–**3m** (*in vitro*, percent inhibition).

	B. campestris root test		*E. crus-galli* cup test	
Compound	100 mg/L	10 mg/L	100 mg/L	10 mg/L
3a	64.5	0	10.0	5.0
3b	68.3	0	20.0	0
3c	68.5	0	5.0	0
3d	12.4	0	10.0	0
3e	74.6	0	10.0	0
3f	72.2	0	20.0	15.0
3g	70.3	0	30.0	15.0
3h	64.9	0	30.0	10.0
3i	54.6	0	30.0	15.0
3j	63.5	3.0	0	0
3k	84.5	37.2	5.0	0
3l	41.3	0	20.0	15.0
3m	31.0	0	25.0	0
Sulcotrione	35.0	0	35.0	30.0

Scheme 1. Synthetic route to compounds **3a–3m**.



than monocotyledonous one (*E. crus-galli*). However, these compounds showed weak herbicidal activities at the concentration of 10 mg/L. Further evaluation of biological activity and investigation of their structure–activity relationship are on the way.

In conclusion, a series of novel acylpyrazole derivatives containing 1,2,3-thiadiazole ring **3a**–**3m** were designed and synthesized. The results of preliminary bioassays showed that some of the title compounds **3** exhibited moderate to good herbicidal activities at the concentration of 100 mg/L. Moreover, these compounds displayed higher herbicidal activity against dicotyledonous plants (*B. campestris* L.) than monocotyledonous one (*E. crus-galli*). However, the target compounds **3** showed weak activities at the concentration of 10 mg/L.

EXPERIMENTAL

Melting points were determined with a WRS-1B digital melting point apparatus and were uncorrected. ^{1}H-NMR spectra were recorded with a Varian Mercury PLUS 600 (600 MHz) 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 or an Applied Biosystems API 2000 LC/MS/MS (ESI-MS) spectrometer. IR spectra were measured by a Nicolet NEXUS470 spectrometer. Elemental analyses were performed with an Elementar Vario ELIII CHNSO elemental analyzer. 5-Methyl-2-phenyl-2,4-dihydropyrazol-3-one **1** was obtained by the reaction of ethyl acetylacetate with phenylhydrazine [14], and 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride was synthesized according to the reported methods [15]. All of the solvents and materials were reagent grade and purified as required.

General procedure for the synthesis of 1-phenyl-3-methyl-4-(substituted benzal or 4-methyl-1,2,3-thiadiazole-5-carbonyl)-5-hydroxypyrazole 2. To the stirred solution of 5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one **1** (0.52 g, 3 mmol) in anhydrous dioxane (10 mL), the powders of $Ca(OH)_2$ (0.36 g, 4.8 mmol) and CaO (0.07 g, 1.2 mmol) were added at 80°C. After the addition was completed, the solution was stirred under reflux for 20 min. Substituted benzoyl chloride (3 mmol) or 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride (0.49 g, 3 mmol) in anhydrous dioxane (5 mL) was added dropwise with strong stirring. The mixture was stirred under reflux till the reaction was complete (monitored by TLC). After the mixture was cooled to room temperature, dilute hydrochloric acid (2 mol/L, 7.5 mL) was added; the mixture was allowed to stir for 30 min, and water (20 mL) was added. The solid was collected by filtration and recrystallized from the mixture of methanol and water (v/v, 1:1) to get **2** in 75–86% yields.

1-Phenyl-3-methyl-4-(4-methyl-1,2,3-thiadiazole-5-carbonyl)-5-hydroxypyrazole (2a). Light brown solid, yield: 76%, mp 93–95°C; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 1.96 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 7.36 (t, *J* = 6.6 Hz, 1H, Ar—H), 7.50 (t, *J* = 8.4 Hz, 2H, Ar—H), 7.82 (s, 2H, Ar—H), 15.84 (s, 1H, OH). Anal. Calcd for $C_{14}H_{12}N_4O_2S$: C, 55.99; H, 4.03; N, 18.65. Found: C, 55.83; H, 4.15; N, 18.71.

1-Phenyl-3-methyl-4-(benzal)-5-hydroxypyrazole (2b). Light yellow solid, yield: 83%, mp 89–90°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 7.31–7.38 (m, 4H, ArH), 7.44 (t, *J* = 7.8 Hz, 2H, ArH), 7.52 (d, *J* = 7.8 Hz, 2H, ArH), 7.65 (d, *J* = 7.2 Hz, 2H, ArH), 15.56 (s, 1H, OH). Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.18; H, 4.93; N, 10.20.

1-Phenyl-3-methyl-4-(4-chlorobenzal)-5-hydroxypyrazole (2c). White solid, yield: 86%, mp 105–107°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.35 (d, *J* = 7.8 Hz, 2H, ArH), 7.42 (t, *J* = 7.8 Hz, 1H, ArH), 7.48 (t, *J* = 7.2 Hz, 2H, ArH), 7.53 (d, *J* = 7.2 Hz, 2H, ArH), 7.62 (d, *J* = 7.8 Hz, 2H, ArH), 15.73 (s, 1H, OH). Anal. Calcd for $C_{17}H_{13}ClN_2O_2$: C, 65.29; H, 4.19; N, 8.96. Found: C, 65.37; H, 4.30; N, 9.05.

1-Phenyl-3-methyl-4-(4-nitrobenzal)-5-hydroxypyrazole (2d). White solid, yield: 75%, mp 190–192°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 7.42 (t, *J* = 7.2 Hz, 1H, ArH), 7.47 (t, *J* = 7.8 Hz, 2H, ArH), 7.53 (d, *J* = 7.8 Hz, 2H, ArH), 7.90 (d, *J* = 8.4 Hz, 2H, ArH), 8.26 (d, *J* = 9.0 Hz, 2H, ArH), 15.89 (s, 1H, OH). Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.04; H, 4.16; N, 12.86.

1-Phenyl-3-methyl-4-(2-methylbenzal)-5-hydroxypyrazole (2e). Light yellow solid, yield: 84%, mp 105–106°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.29 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.14 (d, *J* = 7.2 Hz, 2H, ArH), 7.40 (t, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.8 Hz, 2H, ArH), 7.53 (d, *J* = 7.2 Hz, 2H, ArH), 7.61 (d, *J* = 7.8 Hz, 2H, ArH), 15.90 (s, 1H, OH). Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.74; H, 5.57; N, 9.73.

1-Phenyl-3-methyl-4-(4-fluorobenzal)-5-hydroxypyrazole (2f). Colorless solid, yield: 81%, mp 132–133°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_3), 7.07 (t, *J* = 7.8 Hz, 2H, ArH), 7.43 (d, *J* = 7.2 Hz, 1H, ArH), 7.51 (t, *J* = 7.2 Hz, 2H, ArH), 7.56 (d, *J* = 7.8 Hz, 2H, ArH), 7.81 (dd, *J* = 5.4 Hz, *J* = 7.8 Hz, 2H, ArH), 15.97 (s, 1H, OH). Anal. Calcd for $C_{17}H_{13}FN_2O_2$: C, 68.91; H, 4.42; N, 9.45. Found: C, 68.70; H, 4.56; N, 9.28.

1-Phenyl-3-methyl-4-(2-nitrobenzal)-5-hydroxypyrazole (2g). Light brown solid, yield: 80%, mp 160–162°C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 7.45 (d, *J* = 7.8 Hz, 1H, ArH), 7.51 (t, *J* = 7.2 Hz, 2H, ArH), 7.56 (t, *J* = 7.2 Hz, 2H, ArH), 7.62 (t, *J* = 7.8 Hz, 1H, ArH), 8.09 (d, *J* = 7.8 Hz, 1H, ArH), 8.31 (d, *J* = 7.8 Hz, 1H, ArH), 8.54 (s, 1H, ArH), 15.99 (s, 1H, OH). Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.41; H, 3.88; N, 12.92.

General procedure for the synthesis of pyrazole derivatives containing 1,2,3-thiadiazole ring 3. Compound **2** (2.0 mmol), triethylamine (0.22 g, 2.2 mmol), and anhydrous chloroform (10 mL) were added to a three-necked flask; a solution of 4-methyl-1,2,3-thiadiazole-5-carbonyl chloride (0.32 g, 2.0 mmol) or substituted benzoyl chloride (2.0 mmol) in anhydrous chloroform (5 mL) was added dropwise slowly with an ice-bath cooling. After the addition was completed, the mixture was stirred at room temperature for 4–8 h till the reaction was complete (monitored by TLC). The work-up involved washing with 5% hydrochloric acid, 5% $NaHCO_3$, and brine, respectively. After phase separation, drying over anhydrous sodium sulfate, filtration and evaporation, the crude product was recrystallized from the mixture of petroleum ether and ethyl acetate to give the target compounds **3** in 63–85% yields.

Data for 3a (Ar = C_6H_5). White solid, yield: 84%, mp 93–94°C; IR: Ar—H 3086, C=O 1751, 1687, Ar 1515, 1478, 1450, C—O—C 1262, 1204 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.52 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 7.37 (t, *J* = 7.2 Hz, 1H, Ar—H),

7.42–7.45 (m, 4H, Ar—H), 7.55 (q, *J* = 7.8 Hz, 2H, Ar—H), 7.61–7.64 (m, 1H, Ar—H), 7.77 (q, *J* = 8.4 Hz, 2H, Ar—H); ESI-MS: *m/z* 426 (M + Na − 1, 100), 404 (M, 65). Anal. Calcd for $C_{21}H_{16}N_4O_3S$: C, 62.36; H, 3.99; N, 13.85. Found: C, 62.15; H, 3.71; N, 13.64.

Data for 3b (Ar = 4-FC$_6$H$_4$). Orange crystals, yield: 63%, mp 107–108°C; IR: Ph—H 2984, C=O 1764, 1651, Ph 1557, 1502, 1475, C—O—C 1236, 1195 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.50 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 7.11 (t, *J* = 8.4 Hz, 2H, ArH), 7.37–7.44 (m, 3H, ArH), 7.53 (d, *J* = 8.4 Hz, 2H, ArH), 7.80 (dd, *J* = 4.8 Hz, *J* = 8.4 Hz, 2H, ArH); ESI-MS: *m/z* 460 (M + K − 1, 45), 444 (M + Na − 1, 83), 422 (M, 100). Anal. Calcd for $C_{21}H_{15}FN_4O_3S$: C, 59.71; H, 3.58; N, 13.26. Found: C, 59.87; H, 3.32; N, 13.05.

Data for 3c (Ar = 2-FC$_6$H$_4$). Colorless solid, yield: 82%, mp 103–104°C; IR: Ph—H 3077, 2927, C=O 1772, 1650, Ph 1612, 1550, 1465, 1450, C—O—C 1229, 1062 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.50 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 7.15 (t *J* = 9.6 Hz, 1H, ArH), 7.20 (t, *J* = 8.4 Hz, 1H, ArH), 7.39 (d, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.2 Hz, 2H, ArH), 7.58–7.62 (m, 3H, ArH), 7.67 (t, *J* = 7.2 Hz, 1H, ArH); EI-MS: *m/z* 422 (M$^+$, 4.6), 272 (100), 244 (35), 201 (42), 160 (48), 128 (41), 91 (39.5), 77 (85), 71 (38). Anal. Calcd for $C_{21}H_{15}FN_4O_3S$: C, 59.71; H, 3.58; N, 13.26. Found: C, 59.53; H, 3.66; N, 13.31.

Data for 3d (Ar = 4-CH$_3$C$_6$H$_4$). Colorless solid, yield: 79%, mp 117–118°C; IR: Ph—H 2931, C=O 1755, 1642, Ph 1529, 1467, 1446, C—O—C 1241, 1063 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 7.21 (d, *J* = 7.2 Hz, 2H, ArH), 7.35 (t, *J* = 7.2 Hz, 1H, ArH), 7.42 (t, *J* = 7.2 Hz, 2H, ArH), 7.54 (d, *J* = 7.8 Hz, 2H, ArH), 7.64 (d, *J* = 7.8 Hz, 2H, ArH); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 12.99, 14.85, 21.87, 111.43, 122.79, 123.31, 128.66, 129.40, 129.69, 130.13, 136.46, 145.78, 146.61, 147.15, 151.16, 158.31, 162.00, 179.40; ESI-MS (70 eV): *m/z* 418 (M$^+$, 6.7), 272 (100), 244 (34), 201 (40), 160 (43), 141 (12), 113 (15), 91 (18), 77 (45), 51 (10). Anal. Calcd for $C_{22}H_{18}N_4O_3S$: C, 63.14; H, 4.34; N, 13.39. Found: C, 63.04; H, 4.40; N, 13.13.

Data for 3e (Ar = 2-ClC$_6$H$_4$). White solid, yield: 73%, mp 86–87°C; IR: Ph—H 2947, C=O 1762, 1651, Ph 1536, 1462, 1440, C—O—C 1243, 1065 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.47 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 7.31 (t, *J* = 7.8 Hz, 1H, ArH), 7.41 (d, *J* = 7.2 Hz, 1H, ArH), 7.45–7.48 (m, 3H, ArH), 7.49 (t, *J* = 7.2 Hz, 1H, ArH), 7.56 (d, *J* = 7.8 Hz, 2H, ArH), 7.61 (d, *J* = 7.8 Hz, 1H, ArH); ESI-MS: *m/z* 460 (M+Na-1, 48), 440 (62), 438 (M, 100). Anal. Calcd for $C_{21}H_{15}ClN_4O_3S$: C, 57.47; H, 3.44; N, 12.77. Found: C, 57.61; H, 3.50; N, 12.85.

Data for 3f (Ar = 4-ClC$_6$H$_4$). White solid, yield: 75%, mp 107–109°C; IR: Ph—H 3102, 2930, C=O 1760, 1638, Ph 1527, 1487, 1446, 1400, C—O—C 1240, 1064 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.49 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 7.37 (t, *J* = 7.2 Hz, 1H, ArH), 7.40–7.44 (m, 4H, ArH), 7.52 (d, *J* = 7.8 Hz, 2H, ArH), 7.71 (d, *J* = 7.8 Hz, 2H, ArH); ESI-MS (70 eV): *m/z* 438 (M$^+$, 2.7), 271 (6), 207 (5), 139 (100), 111 (18), 77 (7.6). Anal. Calcd for $C_{21}H_{15}ClN_4O_3S$: C, 57.47; H, 3.44; N, 12.77. Found: C, 57.56; H, 3.37; N, 12.62.

Data for 3g (Ar = 4-NO$_2$C$_6$H$_4$). Light yellow solid, yield: 78%, mp 136–138°C; IR: Ph—H 3005, 2962, C=O 1741, 1643, Ph 1535, 1485, 1446, C—O—C 1257, 1069, cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 7.41 (t, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.2 Hz, 2H, ArH), 7.53 (d, *J* = 7.2 Hz, 2H, ArH), 8.00 (d, *J* = 8.4 Hz, 2H, ArH), 8.29 (d, *J* = 8.4 Hz, 2H, ArH); ESI-MS: *m/z* 472 (M + Na, 36), 449 (M+, 100). Anal. Calcd for $C_{21}H_{15}N_5O_5S$: C, 56.12; H, 3.36; N, 15.58. Found: C, 56.34; H, 3.40; N, 15.31.

Data for 3h (Ar = C$_6$H$_5$). White solid, yield: 85%, mp 137–138°C; IR: Ph—H 2929, C=O 1766, 1648, Ph 1552, 1505, 1471, 1448, C—O—C 1198, 1064 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 7.35–7.41 (m, 4H, ArH), 7.46 (t, *J* = 7.8 Hz, 2H, ArH), 7.54 (d, *J* = 7.8 Hz, 2H, ArH), 7.68 (d, *J* = 7.2 Hz, 2H, ArH); EI-MS (70 eV): *m/z* 404 (M$^+$, 3.6), 278 (95), 200 (58), 132 (23), 105 (100), 91 (44), 77 (97). Anal. Calcd for $C_{21}H_{16}N_4O_3S$: C, 62.36; H, 3.99; N, 13.85. Found: C, 62.41; H, 3.75; N, 13.92.

Data for 3i (Ar = 4-ClC$_6$H$_4$). White solid, yield: 76%, mp 95–96 °C; IR: Ph—H 2930, C=O 1770, 1641, Ph 1559, 1509, 1470, 1442, C—O—C 1195, 1061 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_3), 2.83 (s, 3H, CH_3), 7.37 (d, *J* = 8.4 Hz, 2H, ArH), 7.46 (t, *J* = 7.8 Hz, 1H, ArH), 7.47 (t, *J* = 7.2 Hz, 2H, ArH), 7.54 (d, *J* = 7.2 Hz, 2H, ArH), 7.66 (d, *J* = 8.4 Hz, 2H, ArH); EI-MS (70 eV): *m/z* 438 (M$^+$, 2.1), 312 (43), 278 (25), 200 (100), 139 (65), 111 (34), 91 (48), 77 (33). Anal. Calcd for $C_{21}H_{15}ClN_4O_3S$: C, 57.47; H, 3.44; N, 12.77. Found: C, 57.29; H, 3.48; N, 12.60.

Data for 3j (Ar = 4-NO$_2$C$_6$H$_4$). Light brown solid, yield: 78%, mp 140–142°C; IR: Ph—H 2934, C=O 1768, 1645, Ph 1552, 1502, 1474, 1445, C—O—C 1196, 1066 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 7.45 (t, *J* = 7.2 Hz, 1H, ArH), 7.49 (t, *J* = 7.8 Hz, 2H, ArH), 7.55 (d, *J* = 7.8 Hz, 2H, ArH), 7.87 (d, *J* = 8.4 Hz, 2H, ArH), 8.28 (d, *J* = 9.0 Hz, 2H, ArH); ESI-MS: *m/z* 477 (M + K − 1, 78), 472 (M + Na, 100), 449 (M+, 52). Anal. Calcd for $C_{21}H_{15}N_5O_5S$: C, 56.12; H, 3.36; N, 15.58. Found: C, 56.06; H, 3.44; N, 15.67.

Data for 3k (Ar = 4-CH$_3$C$_6$H$_4$). Colorless solid, yield: 73%, mp 148–149°C; IR: Ph—H 2936, C=O 1762, 1648, Ph 1545, 1506, 1480, 1441, C—O—C 1204, 1065 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.27 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 7.15 (d, *J* = 7.8 Hz, 2H, ArH), 7.41 (t, *J* = 7.2 Hz, 1H, ArH), 7.47 (t, *J* = 7.8 Hz, 2H, ArH), 7.55 (d, *J* = 7.2 Hz, 2H, ArH), 7.60 (d, *J* = 7.8 Hz, 2H, ArH); ESI-MS: *m/z* 456 (M+K-1, 45), 440 (M + Na − 1, 78), 418 (M+, 100). Anal. Calcd for $C_{22}H_{18}N_4O_3S$: C, 63.14; H, 4.34; N, 13.39. Found: C, 63.37; H, 4.61; N, 13.10.

Data for 3l (Ar = 4-FC$_6$H$_4$). Colorless solid, yield: 76%, mp 133–135°C; IR: Ph—H 3063, 2930, C=O 1766, 1648, Ph 1597, 1553, 1504, 1472, C—O—C 1197, 1063 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 2.83 (s, 3H, CH_3), 7.09 (t, *J* = 8.4 Hz, 2H, ArH), 7.41 (d, *J* = 7.2 Hz, 1H, ArH), 7.48 (t, *J* = 7.2 Hz, 2H, ArH), 7.55 (d, *J* = 7.8 Hz, 2H, ArH), 7.77 (dd, *J* = 5.4 Hz, *J* = 7.8 Hz, 2H, ArH); ESI-MS: *m/z* 444 (M + Na − 1, 67), 422 (M+, 100). Anal. Calcd for $C_{21}H_{15}FN_4O_3S$: C, 59.71; H, 3.58; N, 13.26. Found: C, 59.55; H, 3.77; N, 13.03.

Data for 3m (Ar = 2-NO$_2$C$_6$H$_4$). White solid, yield: 68%, mp 140–141°C; IR: Ph—H 3012, 2966, C=O 1745, 1647, Ph 1537, 1482, 1445, C—O—C 1252, 1055, cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.39 (s, 3H, CH_3), 2.82 (s, 3H, CH_3), 7.43 (d, *J* = 7.8 Hz, 1H, ArH), 7.49 (t, *J* = 7.2 Hz, 2H, ArH), 7.56 (t, *J* = 7.8 Hz, 2H, ArH), 7.63 (t, *J* = 8.4 Hz, 1H, ArH), 8.07 (d, *J* = 7.8 Hz, 1H, ArH), 8.30 (d, *J* = 9.0 Hz, 1H, ArH), 8.56 (s, 1H, ArH); ESI-MS: *m/z* 487 (M + K − 1, 75), 471 (M + Na − 1, 100), 449 (M+, 42). Anal. Calcd for $C_{21}H_{15}N_5O_5S$: C, 56.12; H, 3.36; N, 15.58. Found: C, 56.01; H, 3.14; N, 15.77.

Herbicidal Activity (*in vitro*). The herbicidal evaluation of compounds **3** was carried out in the laboratory of biological activities test, State Key Laboratory of Elemento-organic Chemistry, Nankai University, China. Compounds **3** were determined with *B. campestris* L. and *E. crus-galli* as samples of annual dicotyledonous and monocotyledonous plants, respectively, using a previously reported procedure [16]. For all of the bioassay tests, each treatment was repeated twice.

Treatment. The emulsions of purified compounds were prepared by dissolving them in *N*,*N*-dimethylformamide (100 μL) with the addition of Tween 20 (2 μL). The mixture of the same amount of water, *N*,*N*-dimethylformamide, and Tween 20 was used as control. The commercially available herbicide, Sulcotrione was used as a compared sample to evaluate the herbicidal activity.

Inhibition of the root growth of rape (*B. campestris* L.). Rape seeds were soaked in distilled water for 4 h before being placed on a filter paper in a 6 cm Petri plate, to which 2 mL of inhibitor solution had been added in advance. Usually, 10 seeds were used on each plate. The plate was placed in a dark room and allowed to germinate for 72 h at 28 ± 1 °C. The lengths of 10 rape roots selected from each plate were measured, and the means were calculated. The percentage inhibition was used to describe the control efficiency of the compounds. The herbicidal activity is listed in Table 1.

Inhibition of the Seedling Growth of Barnyard Grass (*E. crus-galli*). Ten *E. crus-galli* seeds were placed into a 50 mL cup covered with a layer of glass beads and a piece of filter paper at the bottom, to which 6 mL of inhibitor solution had been added in advance. The cup was placed in a bright room, and the seeds were allowed to germinate for 72 h at 28 ± 1°C. The heights of the above-ground parts of the seedlings in each cup were measured, and the means were calculated. The percentage inhibition was used to describe the control efficiency of the compounds. The herbicidal activity is also listed in Table 1.

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