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Syntheses and Herbicidal Activities of Novel Triazolinone Derivatives

YAN-PING LUO, LI-LI JIANG, GUO-DONG WANG, QIONG CHEN, AND GUANG-FU YANG*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

Protoporphyrinogen oxidase (Protox, EC 1.3.3.4) has been identified as one of the most important action targets of herbicides. To search for novel Protox inhibitors, a series of title compounds **1**, **2**, and **3** were designed and synthesized by introducing three types of pharmacophores, cyclic imide, phenylurea, and (*E*)-methyl 2-methoxyimino-2-*o*-tolylacetate, into the scaffold of triazolinone. The bioassay results indicated that the resulting cyclic imide-type triazolinones **1** displayed much better herbicidal activities than phenylurea-type triazolinones **2**. Most fortunately, compound **3**, methyl 2-[3-methyl-(2-fluoro-4-chloro-5-ethylsulfonamidephenyl)-4,5-dihydro-5-oxo-1*H*-1,2,4-triazol-4-yl]methyl-enephenyl-2-(*E*)-methoxyiminoacetate, was found to be the most promising candidate due to its comparable herbicidal activity at 75−150 g of active ingredient/ha with the commercial product sulfentrazone. On the basis of test results of herbicidal spectrum and crop selectivity, compound **3** could be developed as a postemergent herbicide used for the control of broadleaf weeds in rice fields.

KEYWORDS: Protoporphyrinogen oxidase; triazolinone; herbicide; crop selectivity

INTRODUCTION

Since the 1990s, phenyl triazolinone derivatives with herbicidal activities, known as inhibitors of protoporphyrinogen oxidase (Protox, EC 1.3.3.4), which is an enzyme in the chlorophyll biosynthetic pathway (*1, 2*), have attracted considerable attention from the field of pesticide chemistry (*3–6*). To date, several phenyl triazolinone derivatives have been commercially available. As shown in **Figure 1**, for example, sulfentrazone, the first herbicide of this class to be commercialized, was put on the market for weed control in soybean by FMC Corp. in the 1990s (*7*). Carfentrazone-ethyl and azafenidin were subsequently developed as commercial products by FMC (*8*) and DuPont (*9*), respectively. The action mode of sulfentrazone, carfentrazone-ethyl, and azafenidin is the inhibition of Protox, which causes the accumulation of protoporphyrin IX (Proto IX), which is involved in the light-dependent formation of singlet oxygen responsible for membrane peroxidation (**Figure 2**).

These triazolinone-type herbicides possess a common structural feature: a 2,4,5-trisubstituted phenyl group. Of the phenyl substitution patterns investigated, the ones that led to the most active compounds were F or Cl at C-2 and Cl at C-4, whereas a variety of groups were found to be acceptable at C-5 (*5, 10*). The derivatives of cyclic imide and phenyl urea always showed highly effective herbicidal activities (*11, 12*); if the phenylimide or phenylurea group is introduced into the C-5 position, the resulting compounds **1** and **2** might display interesting biological activities (**Scheme 1**). Additionally, of the substituents at N-4 investigated, the CHF_2 group always gave the highest herbicidal activity. However, the success of azafenidin indicated that a suitable group rather than only CHF_2 is also acceptable at N-4. Then, the pharmacophore of (*E*)-methyl 2-methoxyimino-2-*o*-tolylacetate, which was found to display a variety of biological activities (*13–15*), was introduced into the N-4 position to afford the designed compound **3** as shown in **Scheme 1**. Herein, we report the detailed syntheses and herbicidal activities of compounds **1**−**3**, and the results indicate that compound **3** displayed promising herbicidal activity with good crop safety.

MATERIALS AND METHODS

All chemical reagents were commercially available and treated with standard methods before use. Solvents were dried in a routine way and redistilled. ^{1}H NMR spectra was recorded on a Mercury-Plus 400 spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the internal reference. MS spectra were determined using a Finnigan Trace MS organic mass spectrometry, and signals were given in *m/z*. Elementary analyses were performed on a Vario EL III elementary analysis instrument. Melting points were taken on a Buchi B-545 melting point apparatus and uncorrected. 1-Substituted phenyl-3-methyl-4*H*-1,2,4-triazol-5-ones **4** were prepared according to the existing methods (*4*).

4a: (X = F, Y = Br, R = H); yield, 88%; mp 204–206 °C [lit. (*4*), 201–203 °C]; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.28 (s, 3H, CH_3), 7.22–7.44 (m, 3H, ArH), 11.72 (s, 1H, NH); EI MS, *m/z* (%) 272 (M^+, 49), 271 (15), 188 (54), 107 (100).

* Author to whom correspondence should be addressed (telephone +86-27-67867800; fax +86-27-67867141; e-mail gfyang@mail.ccnu.edu.cn).

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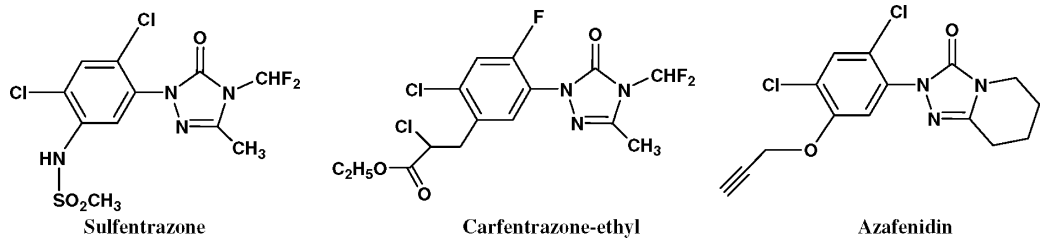


Figure 1. Structures of some commercial Protox inhibitors.

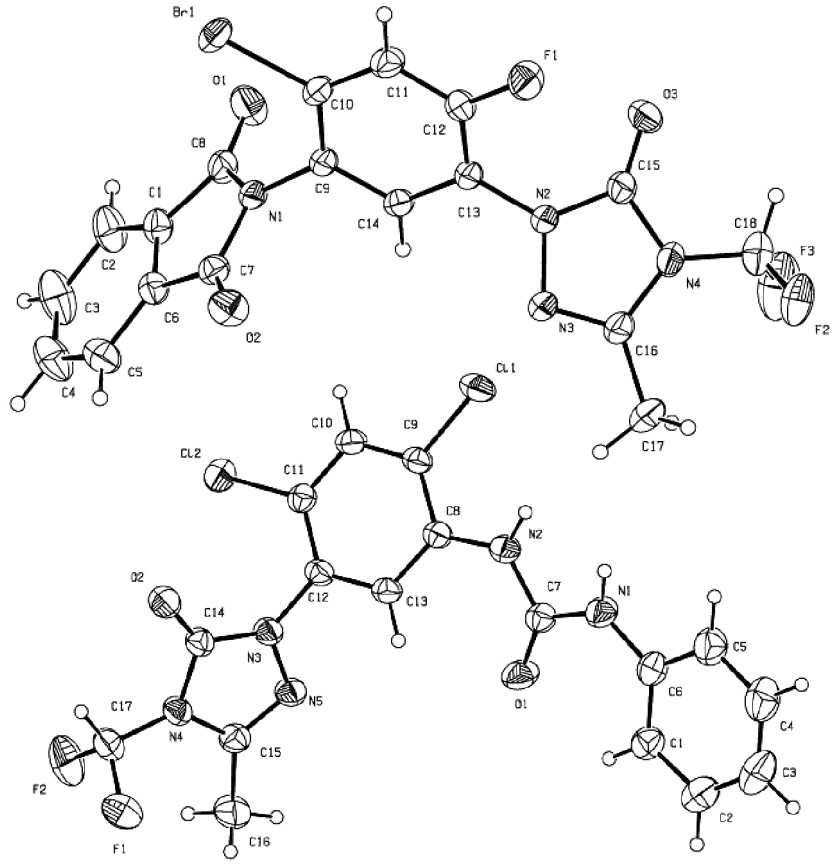


Figure 2. Crystal structures of compounds **1a** and **2g**.

4b: (X = Cl, Y = Cl, R = H); yield, 92%; mp 189–191 °C [lit. (*4*), 174–175 °C]; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.27 (s, 3H, CH_3), 7.19–7.56 (m, 3H, ArH), 11.85 (s, 1H, NH).

4c: (X = Br, Y = F, R = H); yield, 85%; mp 179–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.28 (s, 3H, CH_3), 7.13–7.48 (m, 3H, ArH), 11.70 (s, 1H, NH); EI MS, *m*/*z* (%) 272 (M^+, 32), 271 (33), 191 (100), 107 (67).

4d: (X = Cl, Y = H, R = NO_2); yield, 61%; mp 232–234 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.32 (s, 3H, CH_3), 7.72–8.40 (m, 3H, ArH), 11.52 (s, 1H, NH).

4e: (X = F, Y = Cl, R = $C_2H_5SO_2NH$); yield, 79%; mp 216–218 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 1.27 (t, 3H, J = 7.2 Hz, CH_3), 2.16 (s, 3H, CH_3), 3.14 (q, 2H, J = 7.2 Hz, CH_2), 7.58–7.75 (m, 2H, ArH), 9.65 (s, 1H, $C_2H_5SO_2N\underline{H}$), 11.82 (s, 1H, NH).

Preparation of 1,4-Disubstituted 3-Methyl-4-difluoromethyl-1,2,4-triazol-5-one (5). To a stirred solution of 0.12 mol of 1-substituted phenyl-3-methyl-4*H*-1,2,4-triazol-5-ones **4** were added 13.5 g (0.24 mol) of powdered potassium hydroxide and 3.9 g (0.012 mol) of tetrabutylammonium bromide in 500 mL of THF, and CHF_2Cl was bubbled into the reaction mixture. After 12 h, an additional 6.7 g (0.12 mol) of powdered potassium hydroxide was added to the reaction mixture, and CHF_2Cl continued to bubble into the reaction mixture. Upon completion of addition to the reaction mixture according to thin layer chromatographic (TLC) analysis, the mixture was concentrated under reduced pressure to a residue. The residue was extracted with methylene chloride, and the combined extracts were washed with water; the organic layer was dried with sodium sulfate, filtered, and concentrated under reduced pressure to a residue. The residue was purified by column chromatography on silica gel using 20:1 petroleum ether/acetone as an eluent. The appropriate fractions were combined and concentrated under reduced pressure to yield intermediates **5**.

5a: (X = F, Y = Br, R = H); yield, 91%; mp 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H, CH_3), 7.05 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CH), 7.38–7.44 (m, 3H, ArH).

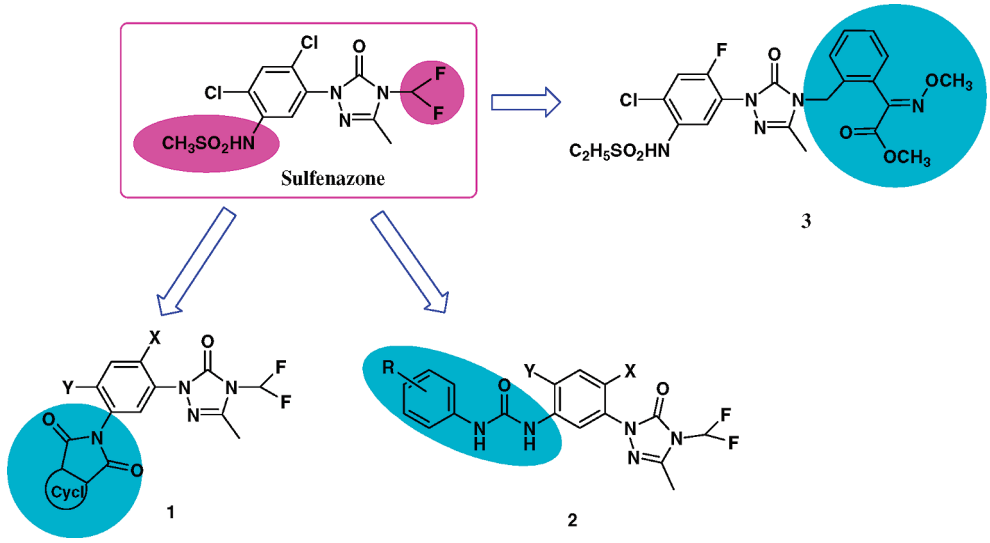
5b: (X = Cl, Y = Cl, R = H); yield, 83%; mp 111–113 °C [lit. (*4*), 108–110 °C]; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H, CH_3), 7.05 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CH), 7.26–7.55 (m, 3H, ArH); EI MS, *m*/*z* (%) 294 (M^+, 25), 257 (54), 160 (64), 158 (100), 122 (40).

5c (X = Br, Y = F, R = H); yield, 75%; mp 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H, CH_3), 7.07 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CH), 7.14–7.47 (m, 3H, ArH).

5d (X = Cl, Y = H, R = NO_2); yield, 78%; mp 141–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.51 (s, 3H, CH_3), 7.07 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CH), 7.71–8.38 (m, 3H, ArH); EI MS, *m*/*z* (%) 305 (M^+, 100), 269 (59), 172 (47), 140 (61), 123 (87).

Preparation of 1-(5-Amino-2,4-disubstituted-phenyl)-3-methyl-4-difluoromethane-1,2,4-triazol-5-one (6). To a stirred solution of 0.04 mol of intermediate **5** in 20 mL of concentrated sulfuric acid was slowly added 3.8 g of 68% nitric acid; the reaction mixture temperature was maintained at 25 °C for 30 min, and then the mixture was poured into ice–water. The resultant solid was collected by filtration and recrystallized from ethanol to afford 2-(5-nitro-2,4-disubstituted-phenyl)-3-

Scheme 1. Molecular Design of the Title Compounds **1**−**3**



methyl-4-substituent-1,2,4-triazol-5-one, which was not identified and was used in next step. To a stirred solution of 0.01 mol of the above nitro-intermediate, 0.54 g (0.01 mol) of ammonium chloride in 50 mL of ethanol, and 5 mL of water was added portionwise 2.24 g (0.04 mol) of powered iron (*16*). Upon completion of addition, the reaction mixture was refluxed for 4 h and filtered through diatomaceous earth, and the filtrate was concentrated under reduced pressure to a residue. The residue was recrystallized from ethanol to yield compounds **6**.

6a: (X = F, Y = Br); yield, 79%; mp 121–123 °C [lit. (*4*), 117–119 °C].

6b: (X = Cl, Y = Cl); yield, 94%; mp 137–139 °C [lit. (*4*), 133–135 °C].

6c: (X = Br, Y = F); yield, 70%; mp 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H, CH_3), 4.16 (s, 2H, NH_2), 7.06 (t, 1H, J = 58 Hz, CHF_2), 6.82–7.40 (m, 2H, ArH).

6d (X = Cl, Y = H); yield, 66%; mp 131–133 °C; EI MS, *m/z* (%) 274 (M^+, 91), 238 (100), 196 (30), 138 (32).

General Procedure for the Synthesis of the Title Compounds 1. To a stirred solution of 1 mmol of intermediate **6** was added 1.1 mmol of cyclic anhydrate in 10 mL of acetic acid with refluxing. Upon completion of addition, the reaction mixture was refluxed for 8 h. The reaction mixture was diluted with water; the resultant solid was collected by filtration and recrystallized from ethanol to yield the title compounds **1**.

1a: yield, 67%; mp 197–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.47 (s, 3H, CH_3), 7.05 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.62 (dd, 2H, ^3J = 8.8 Hz, ^4J = 6.8 Hz, ArH), 7.82–7.99 (m, 4H, ArH); EI MS, *m/z* (%) 468 ([M + 1]$^+$, 12), 466 ([M − 1]$^+$, 11), 387 (100), 252 (24), 130 (15), 126 (14), 104 (28), 76 (25). Anal. Calcd for $C_{18}H_{10}BrF_3N_4O_3$: C, 46.27; H, 2.16; N, 11.99. Found: C, 46.57; H, 1.91; N, 12.10.

1b: yield, 70%; mp 164–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.47 (s, 3H, CH_3), 7.05 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.62–7.64 (m, 2H, ArH), 7.82–7.99 (m, 4H, ArH); EI MS, *m/z* (%) 440 ([M + 1]$^+$, 28), 438 ([M − 1]$^+$, 36), 405 (37), 403 (100), 269 (27), 104 (26). Anal. Calcd for $C_{18}H_{10}Cl_2F_2N_4O_3$: C, 49.22; H, 2.29; N, 12.76. Found: C, 49.33; H, 2.25; N, 12.49.

1c: yield, 70%; mp 199–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.48 (s, 3H, CH_3), 7.06 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.59 (dd, 2H, ^3J = 8.8 Hz, ^4J = 6.8 Hz, ArH), 7.82–7.99 (m, 4H, ArH); EI MS, *m/z* (%) 468 ([M + 1]$^+$, 33), 466 ([M − 1]$^+$, 29), 387 (100), 346 (26), 296 (37), 253 (59), 196 (12), 130 (10), 104 (26), 76 (15). Anal. Calcd for $C_{18}H_{10}BrF_3N_4O_3$: C, 46.27; H, 2.16; N, 11.99. Found: C, 46.50; H, 1.91; N, 12.09.

1d: yield, 61%; mp 200–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 2.49 (s, 3H, CH_3), 7.07 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.61–7.72 (m, 3H, ArH), 7.81–7.98 (m, 4H, ArH); EI MS, *m/z* (%) 406 ([M + 1]$^+$, 22), 404 ([M − 1]$^+$, 100), 369 (59), 278 (18), 270 (21), 235 (67), 207 (18), 179 (23), 130 (23), 104 (92). Anal. Calcd for $C_{18}H_{11}ClF_2N_4O_3$: C, 53.41; H, 2.74; N, 13.84. Found: C, 53.27; H, 2.53; N, 13.72.

1e: yield, 58%; mp 173–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.83 (s, 4H, 2 × CH_2), 2.44 (s, 4H, 2 × CH_2), 2.46 (s, 3H, CH_3), 7.04 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.53 (dd, 2H, ^{3}J = 8.8 Hz, ^{4}J = 6.8 Hz, ArH). EI MS: m/z (%) 472 ([M+1]$^+$, 15), 470 ([M-1]$^+$, 13), 391 (100), 363 (51), 335 (19), 257 (12), 195 (15), 149 (23), 128 (12), 114 (12), 80 (22). Anal. Calcd for $C_{18}H_{14}BrF_3N_4O_3$: C, 45.88; H, 2.99; N, 11.89. Found: C, 46.18; H, 2.64; N, 11.95.

1f: yield, 56%; mp 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.83 (s, 4H, 2 × CH_2), 2.36–2.44 (m, 4H, 2 × CH_2), 2.46 (s, 3H, CH_3), 7.04 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.39–7.70 (m, 2H, ArH); EI MS, *m/z* (%) 444 ([M + 1]$^+$, 18), 442 ([M − 1]$^+$, 49), 407 (100), 379 (12), 280 (13), 236 (18), 79 (26). Anal. Calcd for $C_{18}H_{14}Cl_2F_2N_4O_3$: C, 48.78; H, 3.18; N, 12.64. Found: C, 48.55; H, 2.88; N, 12.29.

1g: yield, 59%; mp 175–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.83 (s, 4H, 2 × CH_2), 2.43 (s, 4H, 2 × CH_2), 2.47 (s, 3H, CH_3), 7.05 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.50 (dd, 2H, ^3J = 8.8 Hz, ^4J = 6.8 Hz, ArH); EI MS, *m/z* (%) 472 ([M + 1]$^+$, 29), 470 ([M − 1]$^+$, 27), 391 (100), 350 (25), 306 (13), 242 (12), 108 (21), 107 (28), 80 (24). Anal. Calcd for $C_{18}H_{14}BrF_3N_4O_3$: C, 45.88; H, 2.99; N, 11.89. Found: C, 45.81; H, 2.61; N, 11.96.

1h: yield, 62%; mp 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.82 (s, 4H, 2 × CH_2), 2.42 (s, 4H, CH_3), 2.48 (s, 3H, CH_3), 7.06 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.49–7.62 (m, 3H, ArH); EI MS, *m/z* (%) 410 ([M + 1]$^+$, 10), 408 ([M − 1]$^+$, 43), 373 (100), 332 (17), 282 (17), 248 (16), 246 (54), 217 (14), 107 (18), 77 (28). Anal. Calcd for $C_{18}H_{15}ClF_2N_4O_3$: C, 52.89; H, 3.70; N, 13.71. Found: C, 52.88; H, 3.68; N, 13.75.

1i: yield, 48%; mp 167–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.53–2.04 (m, 8H, 4 × CH_2), 2.46 (s, 3H, CH_3), 3.04–3.13 (m, 2H, 2 × CH), 7.03 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.52 (dd, 2H, ^3J = 8.8 Hz, ^4J = 6.8 Hz, ArH); EI MS, *m/z* (%) 474 ([M + 1]$^+$, 10), 472 ([M − 1]$^+$, 8), 393 (100), 365 (82), 311 (32), 285 (50), 230 (18), 149 (43), 121 (12). Anal. Calcd for $C_{18}H_{16}BrF_3N_4O_3$: C, 45.68; H, 3.41; N, 11.84. Found: C, 45.59; H, 3.29; N, 11.60.

1j: yield, 42%; mp 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.54–1.96 (m, 8H, 4 × CH_2), 2.46 (s, 3H, CH_3), 3.05–3.13 (m, 2H, 2 × CH), 7.04 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.35–7.71 (m, 2H, ArH); EI MS, *m/z* (%) 446 ([M + 1]$^+$, 15), 444 ([M − 1]$^+$, 39), 409 (90), 381 (85), 299 (26), 200 (41), 165 (60), 81 (100). Anal. Calcd for $C_{18}H_{16}Cl_2F_2N_4O_3$: C, 48.56; H, 3.62; N, 12.58. Found: C, 48.81; H, 3.38; N, 12.63.

1k: yield, 44%; mp 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.51–1.92 (m, 8H, 4 × CH_2), 2.47 (s, 3H, CH_3), 3.07–3.09 (m, 2H, 2 × CH), 7.04 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.49 (dd, 2H, ^3J = 8.8 Hz,

^4J = 6.8 Hz, ArH); EI MS, *m/z* (%) 473 (M^+, 11), 393 (100), 283 (18), 282 (25), 242 (18), 191 (14), 149 (28). Anal. Calcd for $C_{18}H_{16}BrF_3N_4O_3$: C, 45.68; H, 3.41; N, 11.84. Found: C, 45.36; H, 3.23; N, 12.04.

1l: yield, 51%; mp 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.51 (br, 4H, 2 × CH_2), 1.88–1.93 (m, 4H, 2 × CH_2), 2.48 (s, 3H, CH_3), 3.03–3.05 (m, 2H, 2 × CH), 7.05 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.20–7.64 (m, 3H, ArH); EI MS, *m/z* (%) 411 (M^+, 12), 410 ([M − 1]$^+$, 78), 375 (100), 325 (18), 265 (16). Anal. Calcd for $C_{18}H_{17}ClF_2N_4O_3$: C, 52.63; H, 4.17; N, 13.64. Found: C, 52.71; H, 4.31; N, 13.57.

General Procedure for the Synthesis of the Title Compounds 2. To a stirred solution of 1 mmol of intermediates **6** was added 1.1 mmol of aryl isocyanate in 10 mL of dichloromethane with refluxing. Upon completion of addition, the reaction mixture was concentrated under pressure to remove solvent and then was diluted with water; the resultant solid was collected by filtration and recrystallized from ethanol to yield the title compounds **2**.

2a: white solid; yield, 79%; mp 213–215 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.48 (s, 3H, CH_3), 7.54 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 6.86–7.70 (m, 8H, ArH, 2 × NH); EI MS, *m/z* (%) 393 ([M − 1]$^+$, 29), 274 (57), 265 (26), 239 (99), 166 (12), 140 (14), 119 (20), 93 (100). Anal. Calcd for $C_{17}H_{14}ClF_2N_5O_2$: C, 51.85; H, 3.58; N, 17.79. Found: C, 51.70; H, 3.70; N, 17.60.

2b: white solid; yield, 86%; mp 250–251 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.41 (s, 3H, CH_3), 7.33–7.67 (m, 7H, ArH), 7.55 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 8.95 (s, 1H, NHAr), 9.09 (s, 1H, NHArCl); EI MS, *m/z* (%) 428 (M^+, 5), 429 ([M + 1]$^+$, 20), 427 ([M − 1]$^+$, 31), 300 (11), 274 (60), 265 (35), 239 (99), 166 (11), 153 (22), 140 (12), 129 (31), 127 (100), 113 (12), 105 (117). Anal. Calcd for $C_{17}H_{13}Cl_2F_2N_5O_2$: C, 47.68; H, 3.06; N, 16.35. Found: C, 47.60; H, 2.90; N, 16.28.

2c: white solid; yield, 95%; mp 229–231 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.41 (s, 3H, CH_3), 6.99–7.47 (m, 5H, Ar), 7.51 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.89 (d, 1H, *J* = 9.6 Hz, ArH), 8.29 (s, 1H, NH), 8.30 (d, 1H, *J* = 7.6 Hz, ArH), 9.52 (s, 1H, NHAr); EI MS, *m/z* (%) 455 ([M − 1]$^+$, 17), 457 ([M + 1]$^+$, 18), 376 (100), 338 (73), 204 (14), 202 (16), 149 (13), 123 (37), 119 (11). Anal. Calcd for $C_{17}H_{13}BrF_3N_5O_2$: C, 44.76; H, 2.87; N, 15.35. Found: C, 44.55; H, 2.86; N, 15.26.

2d: white solid; yield, 96%; mp 217–218 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.41 (s, 3H, CH_3), 7.42 (dd, 4H, *J* = 8.8 Hz, 4-ClArH), 7.51 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.89 (d, 1H, *J* = 10 Hz, ArH), 8.28 (d, 1H, *J* = 7.6 Hz, ArH), 8.31 (s, 1H, NHAr), 9.63 (s, 1H, NHArCl); EI MS, *m/z* (%) 491 (M^+, 20), 410 (97), 338 (78), 336 (69), 202 (19), 127 (100). Anal. Calcd for $C_{17}H_{12}BrClF_3N_5O_2$: C, 41.61; H, 2.47; N, 14.27. Found: C, 41.56; H, 2.40; N, 14.06.

2e: white solid; yield, 90%; mp 199–201 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.33 (s, 3H, CH_3), 7.01–7.68 (m, 5H, Ar), 7.30 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.84–8.42 (dd, 2H, *J* = 10 Hz, 7.6 Hz, Ar), 8.88 (s, 1H, NHAr), 9.15 (s, 1H, NHPh); EI MS, *m/z* (%) 457 ([M + 1]$^+$, 20), 455 ([M − 1]$^+$, 18), 338 (31), 336 (29), 257 (100), 216 (17), 166 (15), 123 (22), 119 (15). Anal. Calcd for $C_{17}H_{13}BrF_3N_5O_2$: C, 44.76; H, 2.87; N, 15.35. Found: C, 44.58; H, 2.72; N, 15.39.

2f: white solid; yield, 90%; mp 260–262 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.40 (s, 3H, CH_3), 7.42 (dd, 4H, *J* = 8.8 Hz, ArCl), 7.48 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.85 (d, 1H, *J* = 10.8 Hz, ArH), 8.39 (d, 1H, *J* = 7.6 Hz, ArH), 8.89 (s, 1H, NHAr), 9.27 (s, 1H, NHArCl); EI MS, *m/z* (%) 491 ([M + 1]$^+$, 22), 283 (23), 257 (99), 216 (32), 203 (13), 166 (32), 154 (36), 149 (31), 127 (100), 123 (72), 108 (12). Anal. Calcd for $C_{17}H_{12}BrClF_3N_5O_2$: C, 41.61; H, 2.47; N, 14.27. Found: C, 41.59; H, 2.34; N, 14.28.

2g: white solid; yield, 91%; mp 231–233 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.41 (s, 3H, CH_3), 7.25 (m, 5H, Ar), 7.52 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.91–8.47 (m, 2H, ArH), 8.58 (s, 1H, ArNH), 9.54 (s, 1H, PhNH); EI MS, *m/z* (%) 428 (M^+, 6), 429 ([M + 1]$^+$, 33), 427 ([M − 1]$^+$, 48), 394 (21), 392 (64), 310 (42), 308 (69), 273 (83), 174 (34), 165 (31), 158 (10), 146 (21), 139 (76), 120 (47), 93 (100). Anal. Calcd for $C_{17}H_{13}Cl_2F_2N_5O_2$: C, 47.68; H, 3.06; N, 16.35. Found: C, 47.51; H, 2.91; N, 16.21.

2h: white solid; yield, 95%; mp 258–259 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 2.41 (s, 3H, CH_3), 7.40 (dd, 4H, *J* = 8.8 Hz, ArCl), 7.50 (t, 1H, $^2J_{H\text{-}F}$ = 58 Hz, CHF_2), 7.91–8.44 (m, 2H, Ar), 8.59 (s, 1H, ArNH), 9.65 (s, 1H, NHArCl); EI MS, *m/z* (%) 463 (M^+, 23), 428 (17), 426 (25), 310 (55), 299 (22), 273 (100), 174 (24), 165 (19), 153 (45), 139 (54), 127 (99). Anal. Calcd for $C_{17}H_{12}Cl_3F_2N_5O_2$: C, 44.13; H, 2.61; N, 15.14. Found: C, 44.41; H, 2.59; N, 14.98.

Preparation of 1,4-Disubstituted 1,2,4-Triazol-5-one (3). A mixture of 0.33 g (1 mmol) of 1-(4- chloro-2-fluoro-5-(mercaptoethynylperoxyamino)phenyl)-3-methyl-1*H*-1,2,4-triazol-5(4*H*)-one **4e**, 0.21 g (1.5 mmol) of anhydrous potassium carbonated, and 0.31 g (1.1 mmol) of (*E*)-methyl 2-(2-bromomethyl)phenyl-2-methoxyiminoacetate in DMF (8 mL) was stirred for 17 h at 50 °C, according to thin layer chromatographic (TLC) analysis. Then ice–water was added to the reaction mixture to form a precipitate, which was purified by column chromatography on silica gel using 6:1 petroleum ether/acetone as an eluent. The appropriate fractions were combined and concentrated under reduced pressure to yield the title compound **3**: yield, 57%; mp 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.40 (t, 3H, *J* = 7.2 Hz, CH_3), 2.00 (s, 3H, CH_3), 3.19 (q, 2H, *J* = 7.2 Hz, CH_2), 3.88 (s, 3H, OCH_3), 4.07 (s, 3H, $NOCH_3$), 4.77 (s, 2H, CH_2), 6.74 (s, 1H, $C_2H_5SO_2N\underline{H}$), 7.17–7.95 (m, 6H, ArH); EI MS, *m/z* (%) 540 (M^+, 22), 477 (100), 451 (47), 383 (6), 116 (37). Anal. Calcd for $C_{22}H_{23}ClFN_5O_6S$: C, 48.94; H, 4.29; N, 12.97. Found: C, 49.27; H, 4.33; N, 13.20.

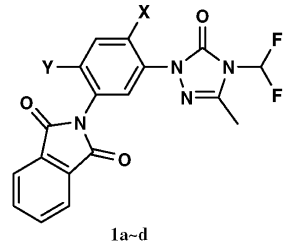
X-ray Diffractions. Data collection was measured at 298 ± 2 K on a Bruker SMART CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (λ) 0.71073 Å: SMART (*17*); cell refinement, SAINT (*17*); data reduction, SAINT; program(s) used to solve structure, SHELXS97 (*18*); program(s) used to refine structure, SHELXL97 (*18*); molecular graphics, SHELXTL (*18*); software used to prepare material for publication, SHELXTL (*18*). Hydrogen atoms were observed and refined with a fixed value of their isotropic displacement parameter.

Crystal data for **1a** (0.30 mm × 0.20 mm × 0.20 mm): θ_{max} = 27.00; 10706 measured reflections; 4079 independent reflections (R_{int} = 0.0270) of which 3114 had $|F_o| > 2|F_o|$. Data were corrected for Lorentz and polarization effects and for absorption (T_{min} = 0.5529; T_{max} = 0.6628). Full-matrix least-squares refinement based on F^2 using the weight of $1/[\sigma^2(F_o^2) + (0.0777P)^2 + 0.0996P]$ gave final values of R = 0.0411, ωR = 0.1125, and GOF(F) = 1.062 for 263 variables and 4079 contributing reflections. Maximum shift/error was 0.001, and maximum/minimum residual electron density = 0.634/−0.446 e Å^{-3}.

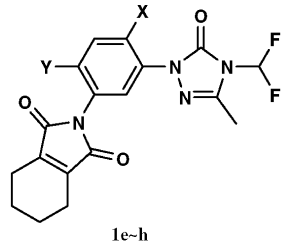
Crystal Data for **2g** (0.20 mm × 0.20 mm × 0.10 mm): θ_{max} = 27.00; 15943 measured reflections; 4148 independent reflections (R_{int} = 0.0417) of which 3174 had $|F_o| > 2|F_o|$. Data were corrected for Lorentz and polarization effects and for absorption (T_{min} = 0.9270; T_{max} = 0.9625). Full-matrix least-squares refinement based on F^2 using the weight of $1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.0000P]$ gave final values of R = 0.0462, ωR = 0.1198, and GOF(F) = 1.008 for 260 variables and 4148 contributing reflections. Maximum shift/error was 0.002, and maximum/minimum residual electron density = 0.312/−0.230 e Å^{-3}.

Herbicidal Activities. The herbicidal activities of compounds **1**−**3** against *Echinochloa crusgalli* (EC), *Digiatra sanguinalis* (DS), *Setaria viridis* (SV), *Brassica juncea* (BJ), *Amaranthus retroflexus* (AR), and *Chenopodium album* (CA) were evaluated according to a previously reported procedure (*19*); sulfentrazone was selected as a control. All test compounds were formulated as 100 g/L emulsified concentrates by using DMF as solvent and TW-80 as emulsification reagent. The concentrates were diluted with water to the required concentration and applied to pot-grown plants in a greenhouse. The soil used was a clay soil, pH 6.5, 1.6% organic matter, 37.3% clay particles, and CEC = 12.1 mol/kg. The rate of application [grams of active ingredient (ai) per hectare] was calculated by the total amount of active ingredient in the formulation divided by the surface area of the pot. Plastic pots with a diameter of 9.5 cm were filled with soil to a depth of 8 cm. Approximately 20 seeds of *E. crusgalli*, *D. sanguinalis*, *S. viridis*, *B. juncea*, *A. retroflexus*, and *C. album* were sown in the soil at the depth of 1−3 cm and grown at 15–30 °C in a greenhouse. The diluted formulation solutions were applied for postemergence treatment, dicotyledon weeds were treated at the two-leaf stage, and monocoty-

Table 1. Postemergence Herbicidal Activity of Compounds **1**−**3** (150 g of ai/ha)



1a~d



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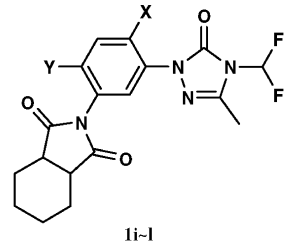
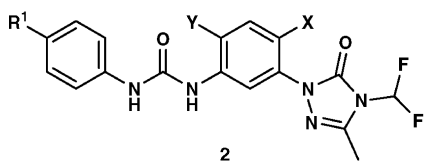
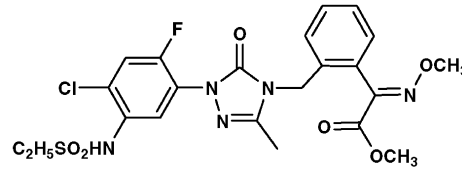


1i~l



2



3

no.	X	Y	R^1	EC[a]	DS	SV	BJ	AR	CA
1a	F	Br	/	+[b]	++	++	++	+++	++
1b	Cl	Cl	/	+	+	+	−	+++	+++
1c	Br	F	/	−	−	−	−	−	−
1d	Cl	H	/	−	−	−	−	−	−
1e	F	Br	/	+	+	+	−	+++	+++
1f	Cl	Cl	/	+	+	+	−	+++	+++
1g	Br	F	/	−	−	−	+	+	−
1h	Cl	H	/	−	−	−	−	−	−
1i	F	Br	/	+	+	+	+	+++	+++
1j	Cl	Cl	/	−	−	−	−	+++	++
1k	Bt	F	/	−	−	−	+	−	+
1l	Cl	H	/	−	−	−	−	−	−
2a	Cl	H	H	−	−	−	−	−	−
2b	Cl	H	Cl	−	−	−	−	−	−
2c	F	Br	H	−	−	−	−	−	−
2d	F	Br	Cl	−	−	−	−	−	−
2e	Br	F	H	−	−	−	−	−	−
2f	Br	F	Cl	−	−	−	−	−	−
2g	Cl	Cl	H	−	−	−	−	−	−
2h	Cl	Cl	Cl	−	−	−	−	−	−
3	/	/	/	+	+	+	++	+++	++
sulfentrazone	/	/	/	−	−	++	+++	+++	+++

[a] EC, *Echinochloa crusgalli*; DS, *Digitaria sanguinalis*; SV, *Setaria viridis*; BJ, *Brassica juncea*; AR, *Amaranthus retroflexus*; CA, *Chenopodium album.* [b] Rating system for the growth inhibition percentage: +++, 100%; ++, >80%; +, 50–80%; −, <50%.

ledon weeds were treated at the 1-leaf stage, respectively. The postemergence application rate was 150 g of ai/ha. Untreated seedlings were used as the control group, and the solvent (DMF)-treated seedlings were used as the solvent control group. Herbicidal activity was evaluated visually 15 days post-treatment. The results of herbicidal activities are shown in **Table 1**. Ten kinds of weeds, such as *C. album*, *Cassia tora* (CT), *B. juncea*, *A. retroflexus*, *Eclipta prostrate* (EP), *Cerastium arvense* (CAR), *Portulaca oleracea* (PO), *E. crusgalli*, *D. sanguinalis*, and *S. viridis*, were used for the test of the herbicidal spectrum of compound **3**.

*Crop Selectivity (**20**).* The conventional rice, soybean, cotton, wheat, rape, and maize were respectively planted in plots (diameter = 12 cm) containing test soil and grown in a greenhouse at 20−25 °C. After the plants had reached the four-leaf stage, the spraying treatment was conducted at different dosages by diluting the formulation of compound **3** with water. The visual injury and growth state of the individual plants were observed at regular intervals. The final evaluation for crop safety of compound **3** was conducted by visual observation in 30 days after treatment on a 0−100 scale.

RESULTS AND DISCUSSION

Synthetic Chemistry of the Title Compounds. As shown in **Scheme 1**, first, according to the reported method (*4*), the starting material, 1-aryltriazolinone **4**, was prepared by a two-step procedure, diazotization and Curtis rearrangement of the corresponding anilines. Then, 1-aryltriazolinones **4a**−**d** were converted easily to the corresponding intermediates **5a**−**d** by nucleophilic substitution with CHF_2Cl. Intermediates **6a**−**d** can be prepared in yields of 66−94% by nitration and subsequent reduction of compounds **5a**−**d**. Subsequently, intermediates **6a**−**d** reacted with cyclic anhydride in the refluxing AcOH solution to yield the title compounds **1a**−**l**, whereas the addition reaction of intermediates **6a**−**d** with aryl isocyanates in the refluxing dichloromethane solution afforded the title compounds **2a**−**h** in yields of 79−96% (**Scheme 2**). Additionally, compound **4e** reacted with (*E*)-methyl 2-(2-bromomethyl)phenyl-2-methoxyiminoacetate to give the title compound **3** in a yield of 57%. The structures of all intermediates and title compounds were confirmed by elemental analyses, ^{1}H NMR, and EI-MS spectral data. In addition, the crystal structures of **1a** and **2g** were determined by X-ray diffraction analyses. As shown in **Figure 2**, the indoline-1,3-dione ring of **1a** adopted a planar conformation, and the dihedral angel between the indoline-1,3-dione and phenyl ring is 74.42°. In addition, some intramolecular and intermolecular hydrogen bonds could be observed, such as C(18)−H(18)···O(3) (2.86 Å, 104.7°), C(4)−H(4)···O(2) (3.43 Å, 151.2°), C(3)−H(3)···O(1) (3.24 Å, 142.9°), and C(14)−H(14)···O(3) (3.18 Å, 148.0°) in crystal **1a** and C(13)−H(13)···O(1) (2.86 Å, 119.8°), C(1)−H(1)···O(1) (2.91 Å, 121.6°), N(2)−H(2A)···O(2) (3.02 Å, 148.0°), and N(1)−H(1A)···O(2) (2.93 Å, 168.0°) in crystal **2g**.

Scheme 2

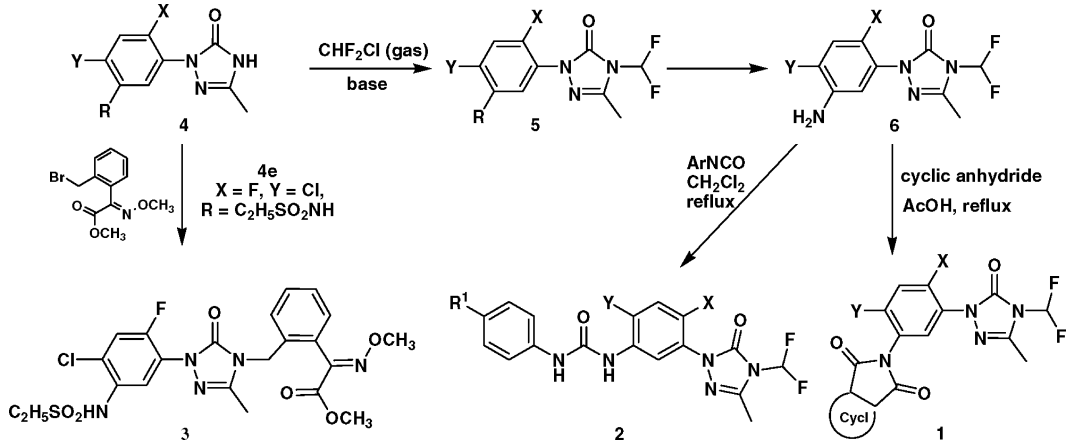


Table 2. Further Herbicidal Spectrum Test of Compound **3** (Postemergence)

compound	dosage (g of ai/ha)	CA[a]	CT	BJ	AR	EP	CAR	PO	EC	DS	SV
3	37.5	+[b]	+	++	++	++	++	+++	−	+	−
	75	++	++	++	++	++	+++	+++	+	+	−
	150	++	+++	++	+++	+++	+++	+++	+	+	+
sulfentrazone	37.5	+++	++	++	+++	+++	++	+++	+	+	−
	75	+++	++	+++	+++	+++	+++	+++	+	+	+
	150	+++	++	+++	+++	+++	+++	+++	+	+	+

[a] CA, *Chenopodium album*; CT, *Cassia tora*; BJ, *Brassica juncea*; AR, *Amaranthus retroflexus*; EP, *Eclipta prostrate*; CAR, *Cerastium arvense*; PO, *Portulaca oleracea*; EC, *Echinochloa crusgalli*; DS, *Digitaria sanguinalis*; SV, *Setaria viridis*. [b] Rating system for the growth inhibition percentage: +++, 100%; ++, >80%; +, 50–80%; −, <50%.

Herbicidal Activities and Structure–Activity Relationships. The postemergence herbicidal activity of compounds **1**−**3** was tested in a greenhouse at the concentration of 150 g of ai/ha; a triazolinone-type commercial product, sulfentrazone, was selected as a control. As shown in **Table 1**, some of compounds (**1a**, **1b**, **1e**, **1f**, **1i**, and **3**) were found to display promising and broad-spectrum herbicidal activities; unfortunately, compounds **2a**−**h** did not display obvious herbicidal activities against the test weeds. For example, compound **1a** displayed >80% inhibition activities against *D. sanguinalis*, *S. viridis*, *B. juncea*, *A. retroflexus*, and *C. album* and also displayed moderate herbicidal activity against *E. crusgalli*. On the contrary, sulfentrazone did not display obvious herbicidal activity against *E. crusgalli* and *D. sanguinalis*. Additionally, compounds **1b**, **1e**, **1f**, **1i**, and **1j** showed high herbicidal activities (>80% inhibition) against *A. retroflexus* and *C. album*.

Structure–activity relationship analysis indicated that of the substitution patterns at the C-5 position investigated herein, an imine group rather than a phenylurea group was found to be acceptable. Substitution patterns at C-2 and C-4 have important influence on the herbicidal activity of compound **1**. F or Cl substitution at C-2 always led to active compounds, whereas Br substitution at C-2 always led to an inactive one. Meanwhile, F, Cl, and Br substitution at C-4 did not show any different influence on the herbicidal activity. For example, compounds **1a** (X = F, Y = Br), **1e** (X = F, Y = Br), and **1i** (X = F, Y = Br) displayed broad-spectrum herbicidal activities, whereas **1c** (X = Br, Y = F), **1g** (X = Br, Y = F), and **1k** (X = Br, Y = F) did not display herbicidal activities. In addition, compounds **1d** and **1h** displayed no herbicidal activity, which revealed that derivatives without substitution at C-4 are not acceptable.

Herbicidal Spectrum and Crop Selectivity of Compound 3. The derivatives containing the pharmacophore of (*E*)-methyl 2-methoxyimino-2-*o*-tolylacetate have been proved to display broad-spectrum biological activity; however, there is no report about the synthesis and herbicidal activity of triazolinone derivatives bearing this pharmacophore. Then, compound **3** was selected as an interesting lead for further tests. As shown in **Table 2**, overall, compound **3** displayed comparable herbicidal activities with sulfentrazone at the dosage of 37.5−150 g of ai/ha. Broadleaf weeds, such as *C. album*, *B. juncea*, *A. retroflexus*, and *E. prostrate*, are generally more sensitive to compound **3** than monocot weeds, such as *E. crusgalli*, *D. sanguinalis*, and *S. viridis*. Most interestingly, some broadleaf weeds such as *B. juncea*, *A. retroflexus*, *E. prostrate*, *C. arvense*, and *P. oleracea* are highly sensitive to compound **3** even at dosages as low as 37.5 g of ai/ha, whereas *C. album* and *C. tora* are slightly less sensitive.

Table 3. Activities of Compound **3** against Different Crops

dosage (g of ai/ha)	rice	cotton	soybean	maize	rape	wheat
75	0	60	60	40	80	40
150	0	/	/	/	/	/
300	0	/	/	/	/	/
450	10	/	/	/	/	/

Among tested crops, only rice exhibited high tolerance to compound **3** by postemergence application at dosages of 75−300 g of ai/ha, whereas cotton, rape, soybean, maize, and wheat are susceptible even at dosages as low as 75 g. of ai/ha (**Table 3**). At the dosage of 450 g of ai/ha, rice still exhibited tolerance to compound **3**, which indicated that compound **3** might be developed as a potential herbicide used for weed control in rice fields.

Conclusion. In summary, a series of 1,2,4-triazolin-5(1*H*)-ones were designed and synthesized by introducing the pharmacophore of cyclic imide, phenylurea, and (*E*)-methyl 2-methoxyimino-2-*o*-tolylacetate into the scaffold of triazolinone. The results of herbicidal activity and crop selectivity indicated that compound **3**, methyl 2-[3-methyl-(2-fluoro-4-chloro-5-ethyl-

sulfonamidephenyl)-4,5-dihydro-5-oxo-1*H*-1,2,4-triazol-4-yl]methylenephenyl-2-(*E*)-methoxyiminoacetate, could be developed as a postemergence herbicide with a high level of selectivity in rice. It has a low application dosage and a broad weed control spectrum. Further field trials and structural modification are under way.

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