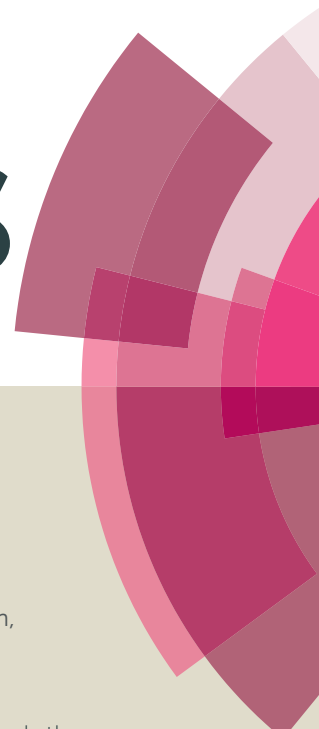


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Research on Controllable Degradation of Sulfonylurea Herbicides

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In order to seek ecologically safer and environmentally benign sulfonylurea herbicides (SU), an insight of structure / bioassay / soil degradation tri-factor relationship was firstly established. With the introduction of various groups (alkyl, nitro, halogen, cyano etc) at the 5th position of its benzene ring, a structural derivation of Chlorsulfuron was designed, synthesized, and evaluated for their herbicidal activity. The title compounds were confirmed by infrared spectroscopy, ultraviolet spectra, ¹H and ¹³C NMR, mass spectra, elemental analysis and X-ray diffraction. Bioassay results confirmed that most derivatives retained their superior herbicidal activities in comparison with Chlorsulfuron. After investigating soil degradation behavior of each molecule under set conditions, it was found that electron-withdrawing substituents at 5th position of benzene ring remained their long degradation half-lives, yet introduction of electron-donating substituents accelerated their degradation rates. These results will provide a valuable clue to further explore the potential controllable degradation of SU and other herbicides, and to discover novel herbicides which are favorable for environmentally and ecologically sustainable development.

Introduction

In the past two decades, an important class of herbicides sulfonylureas (SU), has been developed. These structures interfere with an unique enzyme existing only in plants, acetolactate synthase (ALS),^{1, 2} which results in blocking of the biosynthesis of three branched-chain amino acids which have brought outstanding properties such as ultra-low application rate, good selectivity and negligible mammalian toxicity.^{3, 4}

In recent years, with large scale application of sulfonylurea herbicides, sometimes the residues have showed up certain phytotoxicity in crop rotation which are not conducive to environmental protection and ecologically sustainable development.^{5, 6} Experiments,⁷ as well as evidence from farmers in China and Australia, have suggested that under certain conditions, a few sulfonylurea herbicides persist long enough to affect the growth of sensitive crops such as grain legumes, field peas and sunflower in the following season.^{8, 9} In 2013, three sulfonylurea herbicides, Chlorsulfuron, Metsulfuron-methyl, and Ethametsulfuron (**Fig. 1**), have been prohibited in China due to their persistent existence in soil which is harmful to the next rotation crop. Due to the huge

population and comparatively rather limited arable land in China, a traditional intensive cultivation practice has been undertaken to rear 2-3 different crops annually on the same piece of land,¹⁰ which requires that herbicides used should degrade efficiently in soil during different period of this particular crop rotation system. Sulfonylurea herbicides if degrade too slow than expected, there will pose a phytotoxicity problem to the next crop. In summary, our cultivation system (various crops per land per year) requires a special approach to integrate sulfonylurea herbicides into our plant protection practices. During our innovation program, it is anticipated that "green herbicides" should be highly active as well as to possess a suitable degradation rate in which residues will not persist in soil to hurt the next crop seedlings.

The researches about the relationship of degradation behaviors and structural modification can contribute to development of environment-friendly pesticides which are favorable for ecological protection. Recently, several reports mentioned that by introducing a special moiety onto the 5th position of its classical benzene ring, the revised sulfonylurea structure could exert influence on its degradation rate, *i.e.* Iodosulfuron-methyl-sodium, Foramsulfuron, and Flupyr-sulfuron-methyl-sodium (**Fig. 1**).^{10, 11} It inspired us to further explore the relationship about degradation behaviors and structural modification of SU molecules. Based on our previous experience, the introduction of a few substituents at 5th position of the benzene ring in sulfonylurea structures was favorable to remain the herbicidal activity, on the other hand, can accelerate their hydrolysis in water with different pH values.^{10, 12} To our knowledge, the current researches about the degradation on sulfonylurea herbicides mostly focused individually on soil degradation, hydrolysis or photodegradation under different

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†Electronic Supplementary Information (ESI) available: Containing the crystal data for compound **1-12**, soil degradation curves and structure spectra of all target compounds, including ¹H and ¹³C NMR, IR, UV and MS. See DOI: 10.1039/x0xx00000x

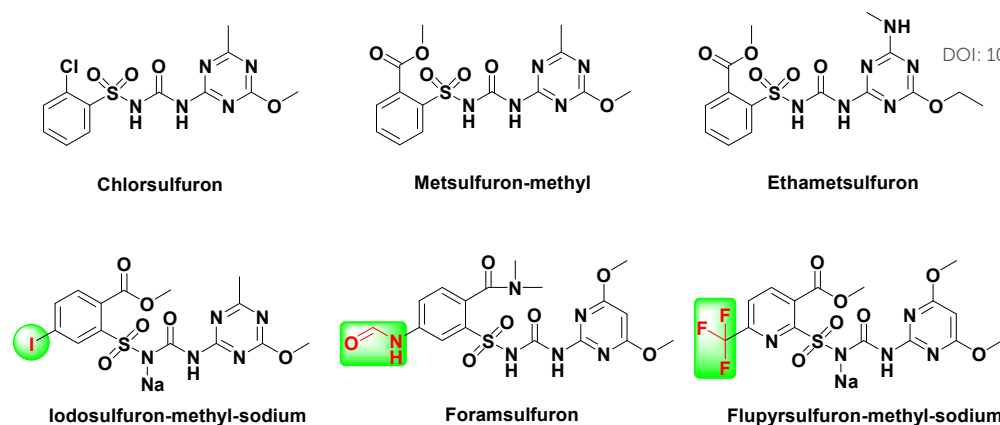
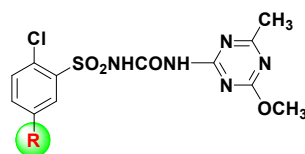


Figure 1 Several structures of sulfonylurea herbicides



R = H (Chlorsulfuron), CH₃, C₂H₅, i-C₃H₇, N(CH₃)₂, NO₂, F, Cl, Br, I, CN, CF₃

Figure 2 Design strategy of target compounds

conditions,¹³⁻¹⁶ such as pH values, temperature, light, sterile or non-sterile, and organic amendments. However, there are no reports available about the systemic relationship between the soil degradation and structural modification of sulfonylurea herbicides by introducing different substituents onto the 5th position of their benzene ring. Therefore, this relationship should be studied to guide the search for ecologically safer and environmentally benign sulfonylureas.

The classical Chlorsulfuron had been considered once to be a popular sulfonylurea herbicide widely applied in grain fields in China. In this study, a series of Chlorsulfuron derivatives were designed and synthesized with introducing various groups (alkyl, nitro, halogen, cyano *etc*) onto the 5th position of its benzene ring (Fig. 2). The corresponding synthetic routes towards intermediates II-1 ~ II-12 and target compounds I-1 ~ I-12 were designed and carried out according to Scheme 1 and Scheme 2 respectively. Followed by evaluation of herbicidal activity and investigation of soil degradation under set conditions, an insight of structure / bioassay / soil degradation tri-factor relationship was firstly established, which will provide us important information on environment and ecological impact during future SU global application.

Materials and methods

Soil

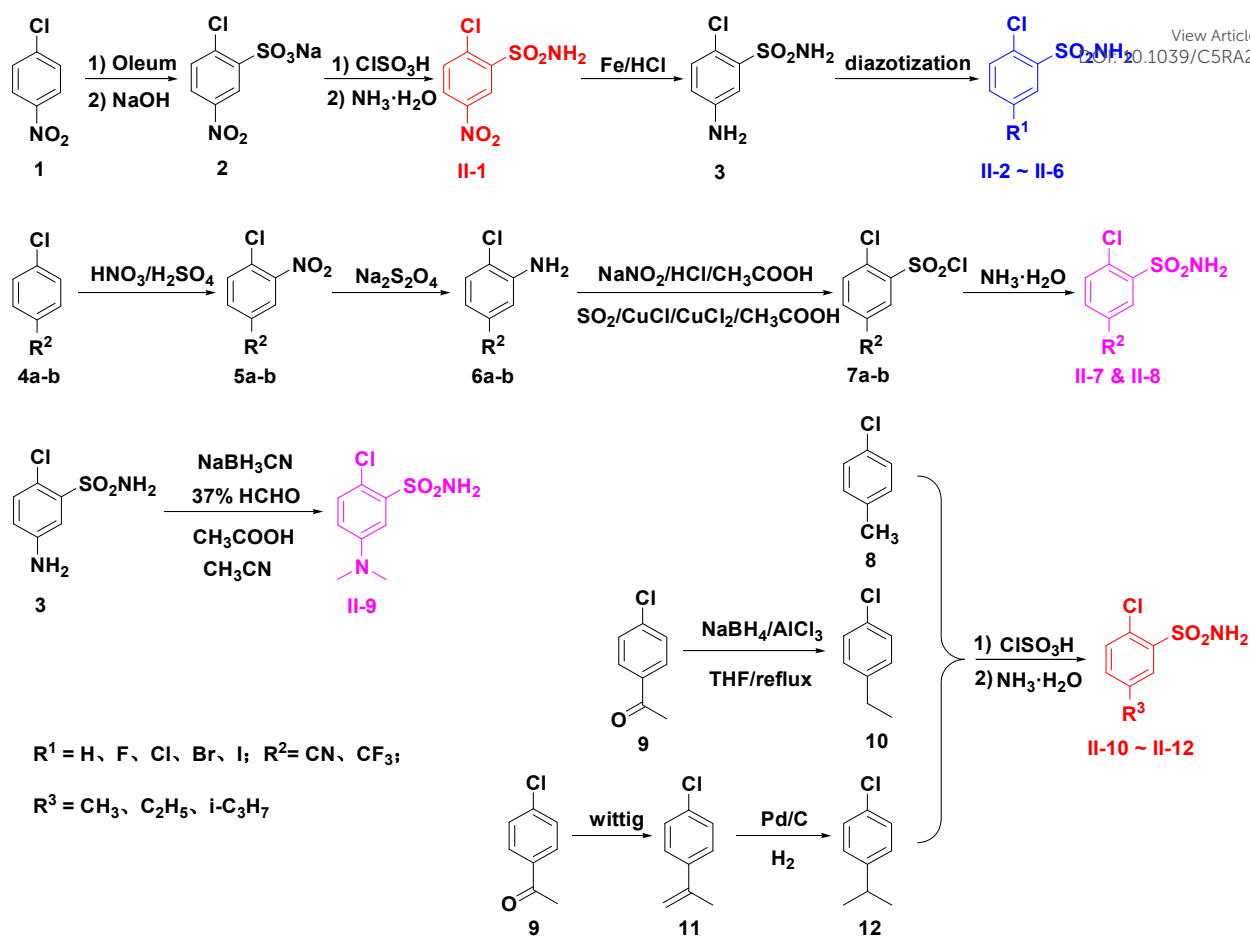
A soil from the plain of Ji'an city (Jiangxi Province, China) was sampled from the upper layer (0-25 cm), air-dried in the shade and passed through a 2 mm sieve. It is a red acid soil, with pH 5.41 (soil/water ratio 1:5), soil organic matter content 6.85 g/kg and 25% water-holding capacity (WHC).

Reagents and Instruments

All reaction reagents were analytical grade, while all analytical reagents for high performance liquid chromatograph (HPLC) were HPLC grade, including methanol, acetonitrile *etc*. Melting points of all compounds were determined on an X-4 binocular microscope (Gongyi Tech. Instrument Co., Henan, China), and the temperatures were uncorrected. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AV-400 spectrometer (400 MHz), and chemical-shift values (δ) were reported as parts per million (ppm) with tetramethylsilane as the internal standard. Elemental analyses (EA) were measured on a vario EL CUBE elemental analyzer. Infrared (IR) spectra were recorded on a Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer using KBr pellets. Ultraviolet (UV) spectra were performed on a TU-1810 ultraviolet-visible spectrophotometer. Mass spectra were recorded on a Thermo-Finnigan LCQ-Advantage LC/mass detector instrument. HPLC data were obtained on a SHIMADZU LC-20AT. Column chromatography purification was carried out using silica gel (200–300 mesh).

General synthetic procedure for title compounds I-1 ~ I-12

1-(2-Chloro-5-nitrophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-1) was prepared as follows. To a mixture of intermediate II-1 (1.15g, 4.8 mmol) and a catalytic amount of triethylenediamine (0.06 g, 0.5 mmol) in anhydrous toluene (50 mL) was added dropwise oxalyl chloride (3.05 g, 24 mmol) at room temperature. The solution was heated to 60 °C and stirred for 8h, then heated up to 100 °C to continue reacting for another 12 h. The excess oxalyl chloride and a little toluene was distilled to remove, followed by the addition of 4-methoxy-6-methyl-1,3,5-triazin-2-amine. The mixture was stirred for 8h at 70 °C, and then concentrated to be purified through chromatograph on silica gel using dichloromethane /



Compounds	5-substituted group	Compounds	5-substituted group	Compounds	5-substituted group
II-1	NO ₂	II-5	Br	II-9	N(CH ₃) ₂
II-2	H	II-6	I	II-10	CH ₃
II-3	F	II-7	CN	II-11	C ₂ H ₅
II-4	Cl	II-8	CF ₃	II-12	<i>i</i> -C ₃ H ₇

Scheme 1 Synthesis of intermediates II

ethyl acetate (v/v 5:1) as eluent to give white solid **I-1**. Compounds **I-2 ~ I-12** were synthesized similarly.

1-(2-Chloro-5-nitrophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-1)

White granular, yield 53%, *mp* 144-146 °C. Found: C, 35.7; H, 2.7; N, 20.8. Calc. for C₁₂H₁₁ClN₆O₆S: C, 35.7; H, 2.75; N, 20.8%. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 235. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1728 (C=O), 1354 and 1173 (SO₂). δH (400 MHz; (CD₃)CO) 2.40 (3H, s, CH₃), 3.90 (3H, s, OCH₃), 7.88 (1H, d, J 8.7, Ph-H), 8.45 (1H, d, J 8.6, Ph-H), 8.83 (1H, s, Ph-H), 9.81 (1H, s, NH), 13.15 (1H, s, NH). δC (101 MHz; (CD₃)CO) 25.5, 55.9, 128.4, 130.3, 134.5, 138.6, 139.0, 147.4, 149.1, 165.1, 171.8, 179.8. *m/z* (ESI) [M-H]⁻ Found: 400.9. Calc. for C₁₂H₁₀ClN₆O₆S⁻: 401.0.

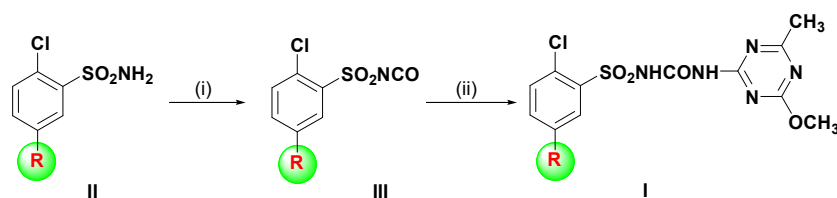
1-(2-Chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-2)

White granular, yield 58%, *mp* 163-165 °C. Found: C, 40.3; H, 3.4; N, 19.5. Calc. for C₁₂H₁₂ClN₅O₄S: C, 40.3; H, 3.4; N, 19.6%. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 234. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1716 (C=O),

1350 and 1165 (SO₂). δH (400 MHz; (CD₃)CO) 2.53 (3H, s, CH₃), 4.04 (3H, s, OCH₃), 7.62 – 7.69 (2H, m, Ph-H), 7.75 (1H, t, J 7.6, Ph-H), 8.26 (1H, d, J 7.9, Ph-H), 9.77 (1H, s, NH), 12.96 (1H, s, NH). δC (101 MHz; (CD₃)CO) 24.6, 55.0, 127.5, 131.4, 131.8, 132.7, 135.2, 136.5, 148.2, 164.3, 170.8, 178.9. *m/z* (ESI) [M-H]⁻ Found: 355.9. Calc. for C₁₂H₁₁ClN₅O₄S⁻: 356.0.

1-(2-Chloro-5-fluorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-3)

White granular, yield 59%, *mp* 165-166 °C. Found: C, 38.6; H, 3.0; N, 18.5. Calc. for C₁₂H₁₁ClFNO₄S: C, 38.4; H, 2.95; N, 18.6%. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 233. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1716 (C=O), 1362 and 1166 (SO₂). δH (400 MHz; (CD₃)CO) 2.52 (3H, s, CH₃), 4.03 (3H, s, OCH₃), 7.44 – 7.61 (1H, m, Ph-H), 7.67 – 7.76 (1H, m, Ph-H), 7.81 – 8.01 (1H, m, Ph-H), 9.81 (1H, s, NH), 13.03 (1H, s, NH). δC (101 MHz; (CD₃)CO) 24.6, 55.0, 119.7 (d, J 26.7), 122.3 (d, J 23.2), 126.8 (d, J 3.6), 133.8 (d, J 7.8), 138.1 (d, J 7.4), 148.2, 160.5 (d, J 249.2), 164.2, 170.8,

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Products	R	Products	R	Products	R
I-1	NO ₂	I-5	Br	I-9	N(CH ₃) ₂
I-2	H (Chlorsulfuron)	I-6	I	I-10	CH ₃
I-3	F	I-7	CN	I-11	C ₂ H ₅
I-4	Cl	I-8	CF ₃	I-12	<i>i</i> -C ₃ H ₇

Scheme 2 Synthesis of target compounds. Reagents and conditions: (i) (COCl)₂, DABCO, anhydrous toluene, 60 °C, 8h; 60 – 100 °C; 100 °C, 12h; (ii) 4-methoxy-6-methyl-1,3,5-triazin-2-amine, anhydrous toluene, 70 °C, 8h.

178.9. δ F (376 MHz, (CD₃)CO) -114.1. m/z (ESI) [M-H]⁻ Found: 373.9. Calc. for C₁₂H₁₀ClFN₅O₄S⁻: 374.0.

1-(2, 5-Dichlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-4)

White granular, yield 62%, *mp* 164-165 °C. Found: C, 36.95; H, 3.1; N, 17.5. Calc. for C₁₂H₁₁Cl₂N₅O₄S: C, 36.75; H, 2.8; N, 17.8 %. λ_{max} (CH₂Cl₂)/nm 233. ν_{max} (KBr)/cm⁻¹ 1716 (C=O), 1368 and 1171 (SO₂). δ H (400 MHz; (CD₃)CO) 2.53 (3H, s, CH₃), 4.04 (3H, s, OCH₃), 7.73 (1H, d, J 8.6, Ph-H), 7.80 (1H, dd, J 8.6, 2.5, Ph-H), 8.19 (1H, d, J 2.5, Ph-H), 9.88 (1H, s, NH), 13.13 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 24.6, 55.0, 130.1, 132.1, 132.7, 133.4, 134.9, 138.0, 148.3, 164.2, 170.8, 178.8. m/z (ESI) [M-H]⁻ Found: 389.9. Calc. for C₁₂H₁₀Cl₂N₅O₄S⁻: 390.0.

1-(2-Chloro-5-bromophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-5)

White granular, yield 65%, *mp* 165-167 °C. Found: C, 33.4; H, 2.8; N, 15.85. Calc. for C₁₂H₁₁BrClN₅O₄S: C, 33.0; H, 2.5; N, 16.0 %. λ_{max} (CH₂Cl₂)/nm 235 nm. ν_{max} (KBr)/cm⁻¹ 1715 (C=O), 1369 and 1169 (SO₂). δ H (400 MHz; (CD₃)CO) 2.52 (3H, s, CH₃), 4.03 (3H, s, OCH₃), 7.64 (1H, d, J 8.5, Ph-H), 7.92 (1H, d, J 8.5, Ph-H), 8.32 (1H, s, Ph-H), 9.86 (1H, s, NH), 13.10 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 24.6, 55.0, 120.1, 130.8, 133.6, 134.9, 137.9, 138.1, 148.3, 164.2, 170.8, 178.8. m/z (ESI) [M-H]⁻ Found: 433.8. Calc. for C₁₂H₁₀BrClN₅O₄S⁻: 433.9.

1-(2-Chloro-5-iodophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-6)

White granular, yield 57%, *mp* 179-181 °C. Found: C, 29.9; H, 2.4; N, 14.5. Calc. for C₁₂H₁₁ClIN₅O₄S: C, 29.8; H, 2.3; N, 14.5 %. λ_{max} (CH₂Cl₂)/nm 234. ν_{max} (KBr)/cm⁻¹ 1728 (C=O), 1358 and 1170 (SO₂). δ H (400 MHz; (CD₃)CO) 2.51 (3H, s, CH₃), 4.02 (3H, s, OCH₃), 7.47 (1H, d, J 8.3, Ph-H), 8.08 (1H, d, J 8.1, Ph-H), 8.48 (1H, d, J 1.8, Ph-H), 9.67 (1H, s, NH), 13.02 (1H, s, NH). m/z (ESI) [M-H]⁻ Found: 481.8. Calc. for C₁₂H₁₀ClIN₅O₄S⁻: 481.9.

1-(2-Chloro-5-cyanophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-7)

White granular, yield 58%, *mp* 176-178 °C. Found: C, 40.9; H, 3.4; N, 21.6. Calc. for C₁₃H₁₁ClN₆O₄S: C, 40.8; H, 2.9; N, 22.0 %. λ_{max} (CH₂Cl₂)/nm 234. ν_{max} (KBr)/cm⁻¹ 1710 (C=O), 1356 and 1166 (SO₂). δ H (400 MHz; (CD₃)CO) 2.54 (3H, s, CH₃), 4.05 (3H, s, OCH₃), 7.95 (1H, d, J 8.3, Ph-H), 8.18 (1H, dd, J 1.9, 8.3, Ph-H), 8.56 (1H, d, J 1.9, Ph-H), 9.86 (1H, s, NH), 13.21 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 24.6, 55.0, 111.6, 116.4, 133.2, 136.0, 136.5, 138.0, 148.6, 164.3, 170.8, 178.8. m/z (ESI) [M-H]⁻ Found: 380.9. Calc. for C₁₃H₁₀ClN₆O₄S⁻: 381.0.

1-(2-Chloro-5-trifluoromethylphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-8)

White granular, yield 57%, *mp* 136-138 °C. Found: C, 36.7; H, 2.7; N, 16.4. Calc. for C₁₃H₁₁ClF₃N₅O₄S: C, 36.7; H, 2.6; N, 16.45 %. λ_{max} (CH₂Cl₂)/nm 233. ν_{max} (KBr)/cm⁻¹ 1716 (C=O), 1361 and 1177 (SO₂). δ H (400 MHz; (CD₃)CO) 2.54 (3H, s, CH₃), 4.05 (3H, s, OCH₃), 7.97 (1H, d, J 8.4, Ph-H), 8.13 (1H, ddd, J 0.5, 2.2, 8.4, Ph-H), 8.49 (1H, d, J 2.1, Ph-H), 9.89 (1H, s, NH), 13.21 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 24.6, 55.0, 123.2 (q, J 273.2), 129.0 (q, J 34.1), 129.5 (q, J 3.9), 131.8 (q, J 3.4), 133.3, 135.9, 137.6, 148.3, 164.2, 170.8, 178.9. δ F (376 MHz, (CD₃)CO) -63.32. m/z (ESI) [M-H]⁻ Found: 424.0. Calc. for C₁₃H₁₀ClF₃N₅O₄S⁻: 424.0.

1-(2-Chloro-5-dimethylaminophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-9)

White granular, yield 60%, *mp* 172-174 °C. Found: C, 41.6; H, 4.4; N, 20.5. Calc. for C₁₄H₁₇ClN₆O₄S: C, 41.95; H, 4.3; N, 20.9 %. λ_{max} (CH₂Cl₂)/nm 234. ν_{max} (KBr)/cm⁻¹ 1713 (C=O), 1355 and 1164 (SO₂). δ H (400 MHz; (CD₃)CO) 2.52 (3H, s, CH₃), 3.05 (6H, s, N(CH₃)₂), 4.04 (3H, s, OCH₃), 6.98 (1H, d, J 8.9, Ph-H), 7.38 (1H, d, J 8.9, Ph-H), 7.49 (1H, s, Ph-H), 9.74 (1H, s, NH), 12.84 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 24.6, 39.5, 54.9, 115.0, 116.3, 117.4, 131.9, 136.5, 148.1, 149.1, 164.2, 170.8, 178.8. m/z (ESI) [M-H]⁻ Found: 399.0. Calc. for C₁₄H₁₆ClN₆O₄S⁻: 399.1.

1-(2-Chloro-5-methylphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-10)

White granular, yield 61%, *mp* 187-188 °C. Found: C, 42.0; H, 3.7; N, 18.8. Calc. for C₁₃H₁₄ClN₅O₄S: C, 42.0; H, 3.8; N,

18.8 %. λ_{max} (CH₂Cl₂)/nm 235. ν_{max} (KBr)/cm⁻¹ 1711 (C=O), 1353 and 1165 (SO₂). δ H (400 MHz; (CD₃)CO) 2.33 (3H, s, Ph-CH₃), 2.38 (3H, s, CH₃), 3.90 (3H, s, OCH₃), 7.40 (2H, s, Ph-H), 7.90 (1H, s, Ph-H), 9.64 (1H, s, NH), 12.80 (1H, s, NH). δ C NMR (101 MHz; (CD₃)CO) 20.7, 25.5, 55.8, 129.2, 132.4, 133.7, 136.6, 137.0, 138.9, 149.0, 165.2, 171.7, 179.7. m/z (ESI) [M-H]⁻ Found: 369.9. Calc. for C₁₃H₁₃ClN₅O₄S⁻: 370.0.

1-(2-Chloro-5-ethylphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-11)

White granular, yield 66%, mp 151-153 °C. Found: C, 43.75; H, 4.1; N, 18.0. Calc. for C₁₄H₁₆ClN₅O₄S: C, 43.6; H, 4.2; N, 18.15 %. λ_{max} (CH₂Cl₂)/nm 234. ν_{max} (KBr)/cm⁻¹ 1714 (C=O), 1354 and 1168 (SO₂). δ H (400 MHz; (CD₃)CO) 1.27 (3H, t, J 7.6, CH₂CH₃), 2.52 (3H, s, CH₃), 2.78 (2H, q, J 7.6, CH₂CH₃), 4.03 (3H, s, OCH₃), 7.56 (1H, d, J 8.2, Ph-H), 7.59 (1H, dd, J 1.9, 8.2, Ph-H), 8.06 (1H, d, J 1.7, Ph-H), 9.76 (1H, s, NH), 12.91 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 14.7, 24.6, 27.7, 55.0, 128.4, 131.7, 131.8, 134.6, 136.2, 144.1, 148.2, 164.2, 170.8, 178.8. m/z (ESI) [M-H]⁻ Found: 384.0. Calc. for C₁₄H₁₅ClN₅O₄S⁻: 384.0.

1-(2-Chloro-5-isopropylphenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (I-12)

White granular, yield 59%, mp 137-138 °C. Found: C, 45.1; H, 4.5; N, 17.4. Calc. for C₁₅H₁₈ClN₅O₄S: C, 45.1; H, 4.5; N, 17.5 %. λ_{max} (CH₂Cl₂)/nm 234. ν_{max} (KBr)/cm⁻¹ 1715 (C=O), 1357 and 1164 (SO₂). δ H (400 MHz; (CD₃)CO) 1.29 (6H, d, J 6.9, CH(CH₃)₂), 2.52 (3H, s, CH₃), 3.01 – 3.19 (1H, m, CH), 4.03 (3H, s, OCH₃), 7.57 (1H, d, J 8.2, Ph-H), 7.63 (1H, dd, J 2.1, 8.2, Ph-H), 8.09 (1H, d, J 2.1, Ph-H), 9.80 (1H, s, NH), 12.97 (1H, s, NH). δ C (101 MHz; (CD₃)CO) 23.0, 24.6, 33.4, 55.0, 128.5, 130.6, 131.7, 133.1, 136.2, 148.2, 148.5, 164.3, 170.8, 178.8. m/z (ESI) [M-H]⁻ Found: 398.0. Calc. for C₁₅H₁₇ClN₅O₄S⁻: 398.1.

X-ray Diffraction Analysis

The target compound **I-12** was recrystallized by slow evaporation from a mixture of ethyl acetate and n-hexane to afford a colourless single crystal with dimensions of 0.20 × 0.18 × 0.12 mm, which was mounted on a glass fiber for X-ray diffraction analysis. The data were collected at 113(2) K on a Rigaku Saturn 724 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å), $\theta_{max} = 27.91^\circ$. The molecular formula is C₁₅H₁₈ClN₅O₄S and the formula weight is 399.85. The crystal was a monoclinic system, space group *P2(1)/n*, with unit cell parameters: a = 9.4336 (19) Å; b = 11.524 (2) Å; c = 16.608 (3) Å, V = 1773.1 (6) Å³, Z = 4, density (calculated) = 1.498 g/cm³, and linear absorption coefficient 0.366 mm⁻¹. In total, 17,832 integrated reflections were collected, reducing to a data set of 4,240 unique with $R_{int} = 0.0549$, and completeness of data (to $\theta = 27.91^\circ$) of 99.7%. Data were collected and processed using Crystal Clear (Rigaku). An empirical absorption correction was applied using CrystalClear (Rigaku). The structure was solved by direct methods with the SHELXS-97 program.¹⁷ Full-matrix least-squares refinement based on F^2 using the weight of $1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.3384P]$ gave final values of $R = 0.0439$,

$wR = 0.1090$. Hydrogen atoms were observed and refined with a fixed value of their isotropic displacement parameter. The correction for absorption was multi-scan, $T_{min} = 0.9304$, $T_{max} = 0.9574$.

Herbicidal Activity Screening

Herbicidal activities were tested in greenhouse (25 ± 2 °C) according to the following method.¹¹ The emulsions of purified compounds (10.0 mg) were respectively prepared by dissolving them in *N,N*-dimethylformamide (1 mL) with the addition of a certain amount of Tween 80 (1.0 g) in distilled water (1000 mL). The mixture of the same amount of *N,N*-dimethylformamide, Tween 80, and distilled water was used as a negative control and Chlorsulfuron was employed as a positive control. Each experiment was performed in triplicate. The solutions of tested compounds were sprayed with a laboratory belt sprayer delivering a 750 L/ha (1 ha=10000 m²) spray volume.

Soil treatment: sandy clay (100.0 g) in a plastic box (11.0 cm×7.5 cm×6.0 cm) was wetted with distilled water. Fifteen sprouting seeds of the test weeds were planted in the fine earth (0.6 cm depth) in the glasshouse and sprayed with the test compound solution. After spraying for 28 days, the ground fresh weight was measured and compared to the negative group to calculate the inhibition percent of fresh weight. The test weed involves *Brassica campestris*, *Amaranthus tricolor*, *Echinochloa crusgalli* and *Digitaria adscendens*.

Foliage spray: seedlings (one leaf and one stem) of the test weeds were sprayed with the test compound solution at the same rate as used for the soil treatment test. The calculated method and test materials were as same as soil treatment.

Soil Degradation Investigating

The soil degradation of Chlorsulfuron derivatives were investigated in acid soil (pH 5.41) with the initial additive concentration of 5 mg a.i./kg under laboratory conditions at 25 °C and a moisture content corresponding to 70% field capacity.

The samples were analysed by a high-performance liquid chromatograph (HPLC) technique. The methods employed a Shimadzu HPLC (series LC-20AT), equipped with a binary pump (Shimadzu, LC-20AT), an UV/VIS detector (Shimadzu, SPD-20A), an auto sampler (Shimadzu, SIL-20A), a Shimadzu shim-pack VP-ODS column (5 μ m, 250 mm × 4.6 mm) connected to a Shimadzu shim-pack GVP-ODS (10 mm × 4.6 mm) precolumn, and a computer (model Dell) for carrying out the analysis. The mobile phases consisted of methanol (A) and phosphoric acid solution in double distilled water (B) (pH = 3.00) with a flow rate of 0.8 ~ 1.0 mL/min. The injection volume was set at 10 μ L, and the detector wavelength was adjusted at 235 nm according to the UV spectra of the target compounds. The specific HPLC analytical conditions, which could ensure good separation between soil contaminants and standard samples, were listed in **Table 1**. From the results, the HPLC analytical methods were adjusted according to the different molecular characteristics. Therefore, the Log *P* values for target compounds were calculated with Prediction System of Log *P* (CISOC-Log *P*) as previously reported,¹⁸ and

Table 1 Analytical conditions for the soil degradation of target compounds

Compounds	R	HPLC analysis conditions (wavelength, flow rate, mobile phase (v/v))	Extraction solvents (v/v)	View Article Online DOI: 10.1039/C5RA25765D		
				Adding mass fraction (mg/kg)	Average recovery rate/%	Coefficient of Variation/%
I-1	NO ₂	235 nm, 1.0 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 60/40	acetone/DCM/Phosphoric acid solution (pH 2.0) = 40/5/5	5	86.71	1.34
				2	83.56	1.89
				0.5	79.43	4.14
I-2	H	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 60/40	acetone/THF/DCM = 30/5/5	5	81.81	1.30
				2	82.35	4.04
				0.5	80.23	1.55
I-3	F	235 nm, 1.0 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 60/40	acetone/DCM/Phosphoric acid solution (pH 2.0) = 40/5/5	5	86.40	1.44
				2	82.79	1.60
				0.5	75.57	2.55
I-4	Cl	235 nm, 1.0 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 65/35	acetone/THF/DCM = 30/10/10	5	84.51	2.77
				2	81.75	1.40
				0.5	72.08	1.64
I-5	Br	235 nm, 1.0 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 65/35	acetone/THF/DCM = 30/10/10	5	75.50	3.84
				2	73.80	3.27
				0.5	72.26	1.84
I-6	I	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 70/30	acetone/THF/DCM = 30/5/5	5	84.09	1.80
				2	82.07	1.46
				0.5	83.58	2.47
I-7	CN	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 60/40	acetone/THF/DCM/Phosphoric acid solution (pH 2.0) = 30/10/10/10	5	91.06	1.03
				2	87.79	4.03
				0.5	73.44	4.22
I-8	CF ₃	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 70/30	acetone/THF/DCM = 30/20/10	5	81.25	1.84
				2	83.41	3.43
				0.5	88.05	3.41
I-9	N(CH ₃) ₂	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 65/35	acetone/THF/DCM = 30/10/10	5	74.53	1.67
				2	72.91	1.31
				0.5	72.80	2.59
I-10	CH ₃	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 65/35	acetone/THF/DCM = 30/10/10	5	83.90	4.41
				2	84.59	1.20
				0.5	88.69	1.32
I-11	C ₂ H ₅	235 nm, 1.0 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 65/35	acetone/THF/DCM = 30/5/5	5	84.95	4.35
				2	83.66	1.50
				0.5	75.10	2.35
I-12	i-C ₃ H ₇	235 nm, 0.8 mL/min, CH ₃ OH/H ₂ O (pH 3.0) = 70/30	acetone/THF/DCM = 30/5/5	5	93.52	1.10
				2	91.40	1.62
				0.5	91.31	3.63

Note: Compound I-2 represent Chlorsulfuron, and the determination of soil recovery rates was performed in quintuplet at each adding mass fraction to calculate the average recovery rate and coefficient of variation.

displayed in Fig. 3. Then the appropriate extraction solvent was selected in accordance with Log *P* values by measuring soil recovery rates and coefficients of variation (Table 1). When all the analytical methods were ready, the soil degradation behaviors were investigated under set conditions.

Testing soil (20.00 g, air-dry weight) passed through 2 mm sieve was weighed into six groups of 150 mL Erlenmeyer flasks, three in each group respectively, and added standard solutions at a concentration of 5 mg a.i./kg. Followed the solvent volatilizing completely under a fume hood, the soil was thoroughly mixed, and an appropriate volume of distilled water

was added to adjust the soil moisture content to approximately 70% field capacity. The bottles were then stoppered with a cotton plug and put into an ecological incubator (temperature 25 ± 1 °C, humidity 80%) to incubate in the dark prior to treatment. In the cultivating process, the moisture content in Erlenmeyer flask was adjusted regularly to maintain the original water-holding state. The samples were taken periodically and added the extraction solvent for extraction. The mixture was shaken for 2h at 200 r/min with an oscillator, and then centrifuged for 2 min at 6500 r/min with a Thermo Scientific Legend Mach 1.6 R centrifuge to obtain supernatant

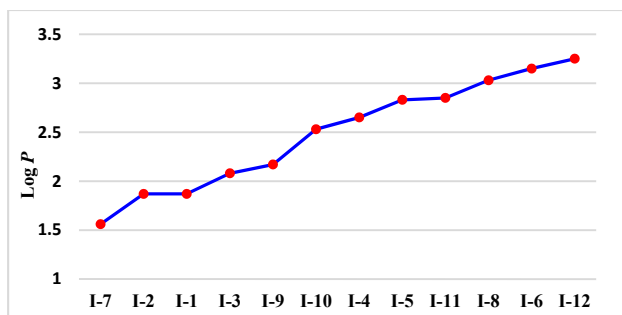


Figure 3 The relationship of structures and calculated Log P values for target compounds

which was concentrated later in vacuum at room temperature. After the residue was extracted by dichloromethane (30 mL \times 2), the combined organic layer was dried by anhydrous sodium sulfate, filtered and concentrated up to dryness. The product was dissolved in acetonitrile (10 mL), and filtered through a filter membrane (0.22 μ m) to HPLC analysis. Each sample was taken six times for drawing first-order kinetic curves, and every time was performed in triplet for statistical analysis.

Results and discussion

Synthetic chemistry

Herein, the important intermediates **II** were designed and synthesized according to the methods in **Scheme 1**. Firstly, intermediate **II-1** was prepared from *1-chloro-4-nitrobenzene* **1** through sulfonation and nucleophilic substitution reactions as previously reported,¹⁹ and then reduced to provide *2-chloro-4-aminobenzenesulfonamide* **3** with Fe/HCl in ethanol which was diazotized to get intermediates **II-2** ~ **II-6** with different diazo reagents as reported literatures.²⁰⁻²⁴ Compound **II-7** (or **II-8**) was synthesized by a process starting from nitration of material **4a** (or **4b**) with fuming nitric acid/concentrated sulfuric acid,^{25, 26} followed by reduction of nitro group with Na₂S₂O₄, diazotization of amino group²⁷ and then nucleophilic substitution reaction. Compound **3** was transformed to intermediate **II-9** by reaction with NaBH₄CN, formalin, CH₃COOH in acetonitrile.²⁸ *4'-Chloroacetophenone* **9** was reduced to produce *1-chloro-4-ethylbenzene* **10** with NaBH₄/AlCl₃ in tetrahydrofuran.²⁹ Synthesis of *1-chloro-4-isopropylbenzene* **12** from material **9** usually involves Wittig reaction, reduction of olefin group with Pd/C/H₂ in methanol. Intermediate **II-10** was synthesized by reaction of *1-chloro-4-methylbenzene* **8** with chlorosulfonic acid,^{30, 31} ammonium hydroxide, and compounds **II-11**, **II-12** were prepared as the same manner, which all the structures were also confirmed by ¹³C-HMBC. The synthetic route towards the target compounds was summarized in **Scheme 2**. Subsequently, twelve molecules were synthesized from intermediates **II**. Compounds **III** were prepared by reaction of materials **II** with oxalyl chloride and a catalytic amount of triethylenediamine (DABCO), and converted to products **I** through reaction with *4-methoxy-6-methyl-1,3,5-triazin-2-amine* in anhydrous toluene. All target compounds were purified by chromatography on silica gel using dichloromethane/ethyl acetate as eluent. The synthesized compounds were identified and characterized by infrared spectroscopy (IR), ultraviolet (UV) spectra, ¹H NMR, ¹³C NMR, mass spectra and

elemental analysis (EA). Several unique structural characteristics were also revealed via the crystal structure of compound **I-12** (**Fig. 4**).

Crystal structure analysis

Several molecular characteristics were apparently presented upon crystal structure analysis of compound **I-12** (CCDC No. 1426721). From the data, the bond angles of O(1) – S(1) – C(1), O(2) – S(1) – C(1), and N(1) – S(1) – C(1) were 107.86(8)°, 109.27(8)°, and 106.65(8)° respectively, indicating the sp³ hybridization state of the S(1) atom. The sum of O(3) – C(10) – N(1), O(3) – C(10) – N(2), and N(1) – C(10) – N(2) angles was 359.99°, indicating the sp² hybridization state of the C(10) atom. The torsion angle of O(3) – C(10) – N(2) – H(2) was 0.083(14)°, while 176.539(16)° for O(3) – C(10) – N(1) – H(1). The dihedral angle between two planes containing N(1) – C(10) – O(3) – N(2) and C(11) – N(3) – C(12) – N(4) – C(13) – N(5) was 13.379(70)°, which showed both planes were non-planar. In the meantime, the dihedral angle between the benzene ring and the triazine ring was 66.914(52)°, demonstrating their non-plane.

Biological assay

The herbicidal activities of target compounds, with Chlorsulfuron as a positive control, against four weeds representing monocotyledonous and dicotyledonous plants at 150 g/ha and 30 g/ha respectively, were shown in **Table 2** and comprehensively evaluated. From the data, in a given category, no matter soil treatment or foliage spray, the herbicidal activities of the title compounds against dicotyledonous plants were higher than those against monocotyledons, including positive control Chlorsulfuron (compound **I-2**). In addition, no compounds displayed good inhibition rate against *Digitaria sanguinalis* regardless of which spraying methods adopted whereas, on the other hand, almost all of the target compounds exhibited excellent herbicidal activity against *Amaranthus tricolor* at 30 g/ha. Interestingly, the structure **I-9** containing dimethylamino group at 5th position exhibited superior herbicidal activities under soil treatment at 150 g/ha against *Brassica campestris*, *Amaranthus tricolor*, *Echinochloa crusgalli*, and *Digitaria sanguinalis* with the inhibition percent of 100, 98.5, 92.6, and 91.3% respectively. In the meantime, the introduction of halo, nitro, dimethylamino, and methyl groups at 5th position was favorable to remain or improve the herbicidal activities of the target compounds, while ethyl, isopropyl, cyano, and trifluoromethyl substituents decreased the inhibition rates. For example, the

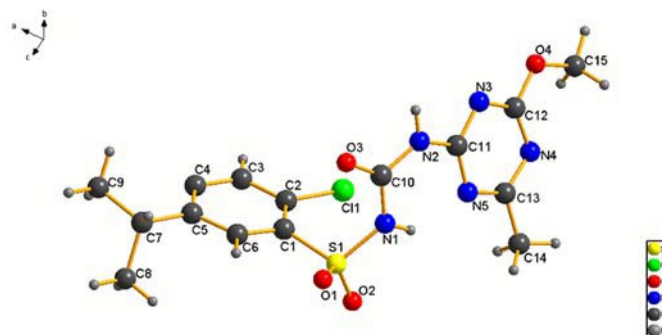


Figure 4 The crystal structure of compound **I-12**

Table 2 Herbicidal activity of the target compounds

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Compo unds	R	Concentra tion (g a.i./ha)	Herbicidal activity (inhibition percent)/%							
			Soil treatment				Foliage spray			
			<i>Brassica campest -ris</i>	<i>Amaran -thus tricolor</i>	<i>Echinoc -hloa crusgall -i</i>	<i>Digitar -ia sangui -nalis</i>	<i>Brassica campestri -s</i>	<i>Amaran -thus tricolor</i>	<i>Echinoc -hloa crusgall -i</i>	<i>Digitar -ia sangui -nalis</i>
I-1	NO ₂	30	84.0	60.6	65.4	6.8	100	98.3	74.9	0
		150	98.1	98.5	86.2	12.6	100	100	85.1	0
I-2	H	30	100	99.2	67.9	14.6	100	100	79.2	0
		150	100	100	88.0	69.9	100	100	84.7	0
I-3	F	30	97.5	99.2	78.6	20.4	86.8	100	64.8	16.7
		150	99.7	99.8	81.1	72.8	100	100	89.8	29.7
I-4	Cl	30	96.2	99.2	41.6	16.5	100	100	59.3	0
		150	99.7	100	62.1	59.2	100	100	66.7	12.4
I-5	Br	30	80.8	99.2	18.5	3.9	87.2	100	45.2	0
		150	99.1	100	49.8	33.0	100	100	64.0	0
I-6	I	30	100	100	57.2	1.0	100	100	59.7	3.8
		150	100	100	72.8	8.7	100	100	64.4	8.1
I-7	CN	30	17.6	84.8	40.7	0	44.9	100	35.8	9.6
		150	32.7	88.6	50.6	10.7	62.1	100	47.5	13.9
I-8	CF ₃	30	61.0	88.6	1.2	16.5	100	78.8	22.5	8.1
		150	95.6	98.5	25.1	20.4	100	100	38.1	27.5
I-9	N(CH ₃) ₂	30	93.7	69.7	38.3	38.8	100	100	69.8	16.7
		150	100	98.5	92.6	91.3	100	100	88.3	38.3
I-10	CH ₃	30	95.6	100	19.3	29.1	100	100	36.9	0
		150	97.5	100	59.7	39.8	100	100	55.7	16.7
I-11	C ₂ H ₅	30	64.2	82.6	20.2	0	100	99.2	15.4	9.6
		150	87.7	97.0	33.3	36.9	100	100	33.8	39.7
I-12	i-C ₃ H ₇	30	54.1	52.3	8.6	14.6	58.6	100	11.1	0
		150	95.6	80.3	29.2	30.1	75.8	100	18.1	16.7

Note: Compound **I-2** represent Chlorsulfuron.

herbicidal activities of compounds **I-1** (5-nitro), **I-3** (5-fluoro), **I-4** (5-chloro), **I-5** (5-bromo), **I-6** (5-iodo), **I-9** (5-dimethylamino), and **I-10** (5-methyl) were similar to the positive control Chlorsulfuron (**I-2**), however, the products **I-7** (5-cyano), **I-8** (5-trifluoromethyl), **I-11** (5-ethyl), and **I-12** (5-isopropyl) displayed relatively weak herbicidal activities when compared with Chlorsulfuron. From the above results, it was concluded that most compounds in general showed good herbicidal activities in comparison with Chlorsulfuron except structures **I-7** and **I-12**.

Soil Degradation

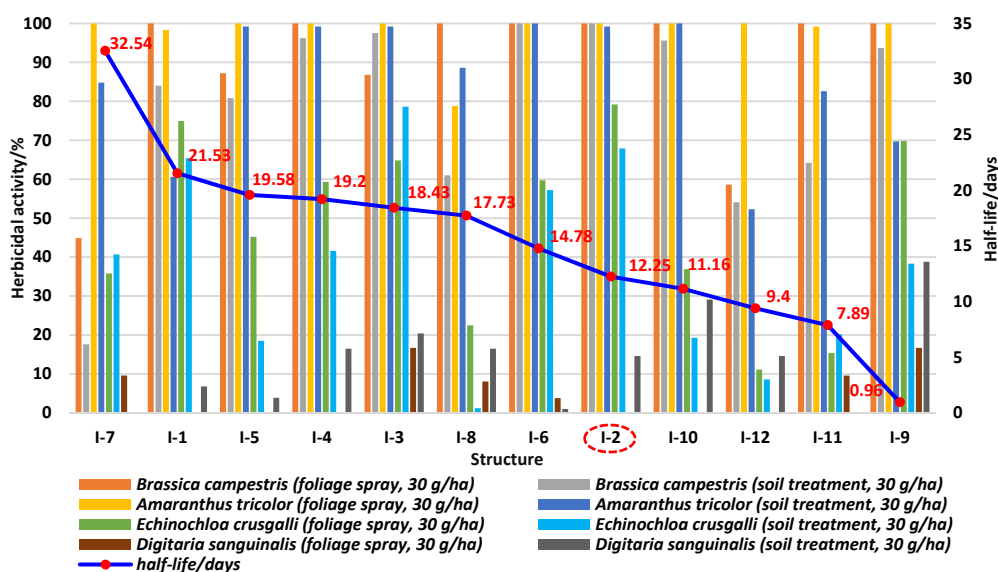
The soil degradation for target compounds was investigated under set conditions, and should follow first-order kinetic equation. The appropriate HPLC analytical conditions were confirmed through comparing HPLC analyses of blank soil, test soil and standard samples. In the process of extraction solvent selection, methanol, acetonitrile, acetone, tetrahydrofuran (THF), dichloromethane (DCM) and mixed solutions, like acetone / dichloromethane, acetone / tetrahydrofuran, and acetone / tetrahydrofuran / dichloromethane

were chosen to measure the soil recovery rates respectively. Interestingly, a ternary mixed system, acetone / tetrahydrofuran / dichloromethane, was found to be favorable to extract the standard samples. At last, the disappearance of SU was reported by plotting the concentration as a function of the degradation time. Each experiment was performed in triplicate to measure the standard deviation. The corresponding first-order kinetic equations and half-life ($t_{1/2}$) periods were shown in **Table 3** respectively. From the data, it was concluded that the introduction of electron-donating substituents at 5th position of the benzene ring inclined to accelerate the degradation rates, while with the electron-withdrawing groups to prolong the half-life periods of target compounds in comparison with Chlorsulfuron (**I-2**). For example, the half-life data of **I-9** (5-dimethylamino), **I-11** (5-ethyl), **I-12** (5-isopropyl), and **I-10** (5-methyl) were 0.96, 7.89, 9.4, and 11.16 days respectively, which were shorter than that of Chlorsulfuron ($t_{1/2} = 12.25$ days), however, those of compounds **I-6** (5-iodo), **I-8** (5-trifluoromethyl), **I-3** (5-fluoro), **I-4** (5-chloro), **I-5** (5-bromo), **I-1** (5-nitro), and **I-7** (5-cyano) were 14.78, 17.73, 18.43, 19.2, 19.58, 21.53, and 32.54 days

Table 3 Kinetic parameters for the soil degradation

Compounds	R	First-order kinetic equation	Correlation coefficient / R^2	Half-life $t_{1/2}$ /days
I-7	CN	$C_t = 4.698e^{-0.0213t}$	0.9978	32.54
I-1	NO ₂	$C_t = 4.445e^{-0.0322t}$	0.9958	21.53
I-5	Br	$C_t = 3.842e^{-0.0354t}$	0.9983	19.58
I-4	Cl	$C_t = 3.845e^{-0.0361t}$	0.9982	19.20
I-3	F	$C_t = 4.542e^{-0.0376t}$	0.9998	18.43
I-8	CF ₃	$C_t = 3.911e^{-0.0391t}$	0.9944	17.73
I-6	I	$C_t = 3.824e^{-0.0469t}$	0.9989	14.78
I-2	H	$C_t = 3.914e^{-0.0566t}$	0.9979	12.25
I-10	CH ₃	$C_t = 4.284e^{-0.0621t}$	0.9978	11.16
I-12	i-C ₃ H ₇	$C_t = 4.392e^{-0.0737t}$	0.9973	9.40
I-11	C ₂ H ₅	$C_t = 4.466e^{-0.0878t}$	0.9975	7.89
I-9	N(CH ₃) ₂	$C_t = 3.982e^{-0.725t}$	0.9945	0.96

Note: Compound I-2 represent Chlorsulfuron.

**Figure 5** The relationship of structures, herbicidal activity and half-life

respectively. Surprisingly, the half-life of compound I-9 was less than one day. Furthermore, the degradation rates among the target compounds introduced halo groups at 5th position had no significant difference. For instance, the degradation half-life data of compounds I-6, I-3, I-4, and I-5 were 14.78, 18.43, 19.2, and 19.58 days respectively. From the above experimental results, it was confirmed that the introduction of different substituents at 5th position do influence the soil degradation rates of target compounds, which could provide valuable information to explore potential controllable degradation of other herbicides.

Conclusions

In summary, a structural derivation of Chlorsulfuron was designed and synthesized by introducing various groups (alkyl, nitro, halogen, cyano *etc*) onto the 5th position of its benzene ring. Identities of the target compounds were confirmed by IR, UV, ¹H and ¹³C NMR, MS, EA and X-ray diffraction. Bioassay results indicated that most of synthesized sulfonylureas showed superior herbicidal activities when compared with Chlorsulfuron. After their soil degradation behaviors were investigated, an insight of structure / bioassay / soil degradation tri-factor relationship was firstly established and summarized in Fig. 5. As observed from the figure, the introduction of various substituents at 5th position of the benzene ring can remain or vary the herbicidal activities, such as nitro, halo, methyl, and dimethylamino *etc*, on the other hand, can influence the soil degradation rates where

electron-donating groups are favorable, especially dimethylamino group. These results will provide a valuable clue to further explore the potential controllable degradation of SU and other herbicides to seek ecologically safer and environmentally benign herbicides. It will also provide us a new strategy to decrease the relevant impact on our environment and ecology during future herbicides research program.

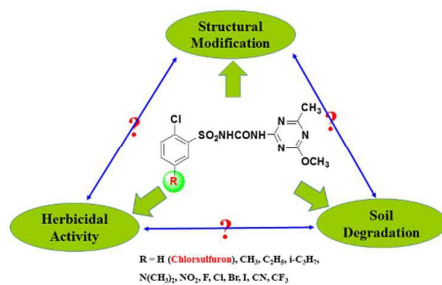
Acknowledgements

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Notes and references

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Graphic for table of contents



Through studying structure, bioassay and soil degradation tri-factor relationship, potential controllable degradation of SU was firstly explored and summarized.