Electronic Supplementary Information

Design, synthesis and SAR study of novel sulfonylureas containing an alkenyl moiety

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General Synthetic Procedure for compounds 2a-c

0.1 mol of 4-methylbenzoic acid (1a) was slowly added to 40 ml CISO,H, and the mixture was heated to 120°C for 8 hours, the HCl gas released from the reaction system was absorbed by aqueous NaOH. After the mixture was cooled to room temperature, it was carefully poured on to sufficient crushed ice. Collect the white solid by suction filtration and wash the solid with cold water. Then dissolve the white solid with THF and add this solution to 50 ml ammonium hydroxide at 0°C. The reaction mixture was heated to 50°C for 30 min and THF was removed in vacuo. Adjust the acidity to pH 1 with hydrochloric acid and collect the precipitated white solid to obtain 4-methyl-3-sulfamoylbenzoic acid (2a), yield 85.1%, white solid, m.p. 221-222°C. 1H NMR (400 MHz, DMSO-d6) δ 8.43 (d, J = 1.8 Hz, 1H, Ph-H), 8.01 (dd, J = 7.8, 1.9 Hz, 1H, Ph-H), 7.56 (s, 2H, SO₂NH₂), 7.52 (d, J = 8.0 Hz, 1H, Ph-H), 2.65 (s, 3H, CH₃). 2b and 2c were synthesized by similar procedure except that the reaction temperature was 140°C.

4-chloro-3-sulfamoylbenzoic acid (2b), yield 83.0%, white solid, m.p. 254-256°C, 1H NMR (400 MHz, DMSO-d6) δ 13.60 (s, 1H, COOH), 8.51 (d, J = 2.0 Hz, 1H, Ph-H), 8.10 (dd, J = 8.2, 2.1 Hz, 1H, Ph-H), 7.82 (d, J = 7.0 Hz, 1H, Ph-H), 7.79 (d, J = 8.3 Hz, 1H, Ph-H).

4-bromo-3-sulfamoylbenzoic acid (2c), yield 81.2%, white solid, m.p. 258-259°C, 1H NMR (400 MHz, DMSO-d6) δ 13.59 (s, 1H, COOH), 8.53 (d, J = 1.5 Hz, 1H, Ph-H), 8.02 – 7.95 (m, 2H, Ph-H), 7.78 (s, 2H, SO₂NH₂).

General Procedure for Preparation of the compound 3a-c

To a solution of 100 mmol 4-methyl-3-sulfamoylbenzoic acid (2a) in THF was added 200 mmol NaBH₄ and the mixture was stirred until the gas evolution ceased. And then 266 mmol BF₃·Et₂O was added dropwise at room temperature and stirring was continued for additional 1 hour. 1M HCl was added carefully to quench the reaction. THF was then removed in vacuo. The aqueous phase was extracted with ethyl acetate for 3 times. The combined organic phase was washed with saturated NaHCO₃ solution, brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was washed with small amount of ethyl acetate to give 5-(hydroxymethyl)-2-methylbenzenesulfonamide (3a), yield 82.4%, white crystals, m.p. 105-106°C, 1H NMR (400 MHz, DMSO-d6) δ 7.84 (s, 1H, Ph-H), 7.39 (d, J = 7.8 Hz, 1H, Ph-H), 7.34 (s, 2H, SO₂NH₂), 7.31 (d, J = 7.7 Hz, 1H, Ph-H), 4.51 (s, 2H, CH₂), 2.56 (s, 3H, CH₃). 3b was purified by column chromatography (petroleum ether/acetone 4:1-1:1) and 3c was synthesized by similar procedures with 3a.

5-(hydroxymethyl)-2-chlorobenzensulfonamide (3b), yield 75.0%, white crystals, m.p. 149-150°C, 1H NMR (400 MHz, DMSO-d6) δ 7.97 (s, 1H, Ph-H), 7.58 (d, J = 5.9 Hz, 3H, Ph-H, SO₂NH₂), 7.51 (d, J = 8.0 Hz, 1H, Ph-H), 5.49 (s, 1H, OH), 4.55 (s, 2H, CH₂).

5-(hydroxymethyl)-2-bromobenzensulfonamide (3c), yield 90.0%, white crystals, m.p. 160-161°C, 1H NMR (400 MHz, DMSO-d6) δ 8.01 (d, J = 2.1 Hz, 1H, Ph-H), 7.73 (d, J = 8.1 Hz, 1H, Ph-H), 7.55 (d, J = 8.1 Hz, 1H, Ph-H), 5.49 (s, J = 5.6 Hz, 1H, OH), 4.53 (s, J = 5.6 Hz, 2H, CH₂).

General Procedure for Preparation of the compound 4a-c

A mixture of 10 mmol 5-(hydroxymethyl)-2-methylbenzenesulfonamide (3a) and 100 mmol MnO₂ were stirred in ethyl acetate at room temperature for 4 hours. Remove the MnO₂ by suction filtration through a celite pad and wash the solid with ethyl acetate for several times. The filtrates were concentrated at reduced pressure to provide 5-formyl-2-methylbenzenesulfonamide (4a) in 91.1% yield, white solid, m.p. 95-96°C, 1H NMR (400 MHz, CDCl₃) δ 10.02 (s, 1H, CHO), 8.50 (s, 1H, Ph-H), 7.99 (d, J = 7.7 Hz, 1H, Ph-H), 7.52 (d, J = 7.8 Hz, 1H, Ph-H), 4.99 (s,
2H, SO₂NH₂), 2.79 (s, 3H, CH₃), 4b and 4c were synthesized by similar procedures.

5-formyl-2-chlorobenzenesulfonamide (4b), yield 89.5%, white solid, m.p. 128-129°C, ¹H NMR (400 MHz, DMSO) δ 10.08 (s, 1H, CHO), 8.46 (d, J = 2.0 Hz, 1H, Ph-H), 8.13 (dd, J = 8.1, 2.0 Hz, 1H, Ph-H), 7.91 (d, J = 8.1 Hz, 1H, Ph-H), 7.84 (s, 2H, SO₂NH₂).

5-formyl-2-bromobenzenesulfonamide (4c), yield 95.0%, white solid, m.p. 135-136°C, ¹H NMR (400 MHz, CDCl₃) δ 10.07 (s, 1H, CHO), 8.64 (d, J = 1.5 Hz, 1H, Ph-H), 7.98 – 7.95 (m, 2H, Ph-H), 5.25 (s, 2H, SO₂NH₂).

2. Herbicidal activities of compounds 9 at 375g/hm²

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3. $^1$H NMR and $^{13}$C NMR spectra of title compounds

$^1$H NMR spectra of intermediate 7a-m

$^1$H NMR (300 MHz, CDCl$_3$) spectrum of 7a

$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 7b
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 7c

$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 7d
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7e

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7f
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7g

$^1$H NMR (400 MHz, DMSO-d$_6$) spectrum of 7h
^1H NMR (400 MHz, acetone-^d_6) spectrum of 7i

^1H NMR (400 MHz, DMSO-^d_6) spectrum of 7j
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7k

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 7l
$^1$H NMR (400 MHz, DMSO-d$_6$) spectrum of 7m
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9a
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9b
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9c
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9d
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9e
$^1$H NMR (400MHz, CDCl$_3$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9f
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9g
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9h
$^1$H NMR (400MHz, CDCl$_3$) and $^{13}$C NMR (100MHz, CDCl$_3$) spectra of 9i
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9j
$^{1}$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9k
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, CDCl$_3$) spectra of 9l
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9m
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$^1$H NMR (400MHz, DMSO-$d_6$) and $^{13}$C NMR (100MHz, DMSO-$d_6$) spectra of 9r
$^1$H NMR (400MHz, CDCl$_3$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9s
$^1$H NMR (400MHz, acetone-$d_6$) and $^{13}$C NMR (100MHz, acetone-$d_6$) spectra of 9t
$^{1}$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9u
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9v
$^1$H NMR (400MHz, DMSO-$d_6$) and $^{13}$C NMR (100MHz, DMSO-$d_6$) spectra of 9w
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, DMSO-d$_6$) spectra of 9x
$^1$H NMR (400MHz, DMSO-d$_6$) and $^{13}$C NMR (100MHz, CDCl$_3$) spectra of 9y
$^1$H NMR (400MHz, DMSO-$d_6$) and $^{13}$C NMR (100MHz, acetone-$d_6$) spectra of 9z
$^1$H NMR (400MHz, acetone-$d_6$) and $^{13}$C NMR (100MHz, DMSO-$d_6$) spectra of 9aa