Supplementary Material

Synthesis and insecticidal activity of novel benzothiazole derivatives containing the coumarin moiety

Wei-Jie Si, Min Chen, Xue-Lun Wang, Meng-Qi Wang, Jian Jiao, Xin-Can Fu, and Chun-Long Yang

a Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing 210 095, China
b Jiangsu Key Laboratory of Pesticide Science, Nanjing Agricultural University, Nanjing 210 095, China
c Key Laboratory of Monitoring and Management of Crop Diseases and Insect Pests, Ministry of Agriculture, Nanjing Agricultural University, Nanjing 210 095, China

Email: ycl@njau.edu.cn

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I. Data of key intermediates

7-Hydroxy-2H-chromen-2-one(2a)

White power; yield 74.2%; mp 233–235 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 10.59 (s, 1H,OH), 7.94 (d, J 9.5 Hz, 1H, Coumarin-4-H), 7.53 (d, J 8.5 Hz, 1H, Coumarin-5-H), 6.80 (dd, J 8.5, 2.3 Hz, 1H, Coumarin-6-H), 6.72 (d, J 2.2 Hz, 1H, Coumarin-8-H), 6.21 (d, J 9.5 Hz, 1H, Coumarin-3-H); EI-MS, \(m/z\): 162 [M]+; Anal Calcd. for C\(_9\)H\(_8\)O\(_3\) (162.03).

7-Hydroxy-4-methyl-2H-chromen-2-one(2b)

Light yellow powder; yield 87.6%; mp 187–188 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 10.54 (s, 1H,OH), 7.59 (t, J 8.4 Hz, 1H, Coumarin-4-H), 6.81 (dd, J 8.7, 2.3 Hz, 1H, Coumarin-6-H), 6.71 (d, J 2.3 Hz, 1H, Coumarin-8-H), 6.13 (s, 1H, Coumarin-3-H), 2.37 (s, 3H,CH\(_3\)); EI-MS, \(m/z\): 176 [M]+; Anal Calcd. for C\(_{10}\)H\(_{12}\)O\(_2\) (176.05).

4-(Benzothiazole-2-yl)phenol(4a)

White power; yield 67.1%; mp 223–225 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 10.24 (s, 1H,OH), 8.12–8.06 (m, 1H, Benzothiazole-4-H), 8.01–7.91 (m, 3H, Benzothiazole-5,6,7-3H), 7.54–7.48 (m, 1H, Benzothiazol-2-phenyl-2-H), 7.44–7.37 (m, 1H, Benzothiazol-2-phenyl-6-H), 6.97–6.90 (m, 2H, Benzothiazol-2-phenyl-3,5-2H); EI-MS, \(m/z\): 227 [M]+; Anal Calcd. for C\(_{13}\)H\(_{15}\)O (227.04).

4-(Benzothiazol-2-yl)-2-methoxyphenol(4b)

White power; yield 73.4%; mp 172–174 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 9.87 (s, 1H,OH), 8.09 (d, J 7.8 Hz, 1H, Benzothiazole-4-H), 8.00 (d, J 8.0 Hz, 1H, Benzothiazole-7-H), 7.64 (d, J 2.0 Hz, 1H, Benzothiazole-5-H), 7.55–7.47 (m, 2H, Benzothiazole-6-H, Benzothiazol-2-phenyl-6-H), 7.45–7.37 (m, 1H, Benzothiazol-2-phenyl-2-H), 6.95 (d, J 8.2 Hz, 1H, Benzothiazol-2-phenyl-5-H), 3.91 (s, 3H,CH\(_3\)); EI-MS, \(m/z\): 257 [M]+; Anal Calcd. for C\(_{14}\)H\(_{11}\)NO\(_2\)S (257.05).

3-(Benzothiazol-2-yl)phenol(4c)

White power; yield 60.2%; mp 165–167 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 9.92 (s, 1H,OH), 8.14 (d, J 7.8 Hz, 1H, Benzothiazole-4-H), 8.06 (d, J 8.0 Hz, 1H, Benzothiazole-7-H), 7.51 (dq, J 15.1, 7.2 Hz, 4H, Benzothiazole-5,6-2H, Benzothiazol-2-phenyl-5,6-2H), 7.38 (dd, J 10.6, 5.6 Hz, 1H, Benzothiazol-2-phenyl-2-H), 7.01–6.94 (m, 1H, Benzothiazol-2-phenyl-4-H); EI-MS, \(m/z\): 227 [M]+; Anal Calcd. for C\(_{13}\)H\(_{9}\)NOS (227.04).

2-(4-(2-Bromoethoxy)phenyl)benzothiazole(5a)

White powder; yield 71.5%; mp 131–133 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 8.12 (d, J 7.9 Hz, 1H, Benzothiazole-4-H), 8.09–8.00 (m, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.53 (t, J 7.6 Hz, 1H, Benzothiazole-5-H), 7.44 (t, J 7.5 Hz, 1H, Benzothiazole-6-H), 7.16 (d, J 8.7 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.44 (t, J 10.4 Hz, 2H,CH\(_2\)), 3.86 (t, J 10.4 Hz, 2H,CH\(_2\)-Br).

2-(4-(3-Bromopropoxy)phenyl)benzothiazole(5b)

White powder; yield 74.2%; mp 115–116 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 8.12 (d, J 7.8 Hz, 1H, Benzothiazole-4-H), 8.03 (dd, J 11.2, 8.4 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.53 (t, J 7.2 Hz, 1H, Benzothiazole-5-H), 7.44 (t, J 7.2 Hz, 1H, Benzothiazole-6-H), 7.15 (d, J 8.8 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.20 (t, J 6.0 Hz, 2H,CH\(_2\)), 3.70 (t, J 6.5 Hz, 2H,CH\(_2\)-Br), 2.33–2.27 (m, 2H, CH\(_2\)).

2-(4-(4-Bromobutoxy)phenyl)benzothiazole(5c)

Yellow-white powder; yield 78.3%; mp 112–114 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 8.15–8.08 (m, 1H, Benzothiazole-4-H), 8.03 (t, J 8.3 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.57–7.49 (m, 1H, Benzothiazole-5-H), 7.46–7.39 (m, 1H, Benzothiazole-6-H), 7.13 (d, J 8.9 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.12 (t, J 6.2 Hz, 2H, CH\(_2\)), 3.64 (t, J 6.6 Hz, 2H,CH\(_2\)-Br), 2.04–1.94 (m, 2H, CH\(_2\)), 1.95–1.83 (m, 2H, CH\(_2\)).

2-(4-(5-Bromopentyl)oxy)phenyl)benzothiazole(5d)

Off-white powder; yield 80.8%; mp 109–111 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 8.10 (t, J 6.6 Hz, 1H, Benzothiazole-4-H), 8.02 (dd, J 8.2, 6.3 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.52 (dd, J
11.3, 4.1 Hz, 1H, Benzothiazole-5-H), 7.42 (dd, J 11.1, 4.0 Hz, 1H, Benzothiazole-6-H), 7.14–7.07 (m, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.09 (dd, J 13.1, 6.7 Hz, 2H, CH₂), 3.57 (q, J 7.0 Hz, 2H, CH₂-Br), 1.94–1.83 (m, 2H, CH₂), 1.83–1.72 (m, 2H, CH₂), 1.55 (dq, J 14.7, 7.8 Hz, 2H, CH₂), 1.94–1.83 (m, 2H, CH₂), 1.83–1.72 (m, 2H, CH₂), 1.55 (dq, J 14.7, 7.8 Hz, 2H, CH₂).

2-(4-((6-Bromohexyl)oxy)phenyl)benzothiazole(5e)

Grey Powder; yield 85.2%; mp 95–96 °C; ¹H NMR (400 MHz, DMSO-d₆) δ: 8.11 (d, J 7.9 Hz, 1H, Benzothiazole-4-H), 8.02 (dd, J 8.3, 6.5 Hz, 3H, Benzothiazole-7-H, Benzothiazol-2-phenyl-2,6-2H), 7.56–7.49 (m, 1H, Benzothiazole-5-H), 7.46–7.40 (m, 1H, Benzothiazole-6-H), 7.11 (d, J 8.8 Hz, 2H, Benzothiazol-2-phenyl-3,5-2H), 4.07 (t, J 6.4 Hz, 2H, CH₂), 3.55 (t, J 6.7 Hz, 2H, CH₂-Br), 1.90–1.66 (m, 4H, 2xCH₂), 1.53–1.30 (m, 4H, 2xCH₂).

II. Crystallographic data of compound 6v

Table 1. Crystallographic data of compound 6v

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<td>Min. and Max. Resd. Dens [e Å⁻³]</td>
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Spectrograms of key intermediates and all title compounds
$^1$H NMR, and MS spectra of the compound 2a

$^1$H NMR, and MS spectra of the compound 2b
$^1$H NMR, and MS spectra of the compound 4a
$^1$H NMR, and MS spectra of the compound 4b
$^1$H NMR, and MS spectra of the compound 4c
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6a
1H NMR, 13C NMR and HRMS spectra of the compound 6b
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6c
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6d
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6e
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6f
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6g
\(^1\)H NMR, \(^{13}\)C NMR and HRMS spectra of the compound 6h
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6i
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6j
H NMR, C NMR and HRMS spectra of the compound 6k
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6l
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6m
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6n
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6o
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6p
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6q
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6r
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound $6s$
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6t
$^{1}H$ NMR, $^{13}C$ NMR and HRMS spectra of the compound 6u
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6v
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6w
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6x
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6y
$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6z
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$^1$H NMR, $^{13}$C NMR and HRMS spectra of the compound 6dd