SUPPORTING INFORMATION

A Straightforward Approach Toward Dihydrothiazoles via Intramolecular Bromocyclization

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**N-(5-(bromomethyl)-4,5-dihydrothiazol-2-yl)benzamide (4a)**

Yield: 0.22 g (73%); white powder; mp 193-195°C. IR (KBr): 3314, 1685, 1614, 1406, 1238, 1057, 756, 682 cm⁻¹. 

$^1$H NMR (400 MHz, CDCl₃): $\delta = 3.45$ (t, $J = 10.4$ Hz, 1H), 3.58 (dd, $J = 4.4, 10.4$ Hz, 1H), 3.70 (dd, $J = 7.2, 12.8$ Hz, 1H), 3.79 (dd, $J = 2.2, 12.6$ Hz, 1H), 3.89-3.95 (m, 1H), 7.47 (t, $J = 7.1$ Hz, 1H), 7.56 (t, $J = 7.2$ Hz, 2H), 8.07 (d, $J = 7.5$ Hz, 2H), 9.60 (brs, 1H).

$^{13}$C NMR (100 MHz, CDCl₃): $\delta = 33.7, 46.7, 51.4, 127.4, 128.9, 132.5, 135.0, 170.8, 173.3$.

Anal. calcd. for C₁₁H₁₁BrN₂OS: C, 44.16; H, 3.71; N, 9.36. Found: C, 44.09; H, 3.61; N, 9.42.

**N-(5-(bromomethyl)-4,5-dihydrothiazol-2-yl)-3-chlorobenzamide (4c)**

Yield: 0.26 g (77%); white powder; mp 117-118°C. IR (KBr): 3307, 1703, 1622, 1460, 1240, 1090, 873, 769, 694 cm⁻¹. 

$^1$H NMR (500 MHz, CDCl₃): $\delta = 3.60$ (dd, $J = 3.5, 12.5$ Hz, 2H), 3.68 (t, $J = 9.5$ Hz, 2H), 4.22-4.31 (m, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.60 (dd, $J = 1.0, 8.0$ Hz, 1H), 7.99 (d, $J = 7.5$ Hz, 1H), 8.06 (s, 1H), 9.19 (s, 1H). 

$^{13}$C NMR (125 MHz, CDCl₃): $\delta = 35.8, 45.9, 47.5, 127.3, 128.7, 130.3, 131.6, 133.1, 138.4, 167.0, 173.0$. MS: m/z (%) = 333 (8) [M+2]$^+$, 331 (7) [M]$^+$, 340 (84), 253 (24), 139 (100), 111 UPPO(40), 75 (16), 41 (6). Anal. calcd. for C₁₁H₁₀BrClN₂OS: C, 39.60; H, 3.02; N, 8.40. Found: C, 39.67; H, 3.01; N, 8.42.

**N-(5-(bromomethyl)-4,5-dihydrothiazol-2-yl)-4-chlorobenzamide (4d)**

Yield: 0.22 g (65%); white powder; mp 232-233°C. IR (KBr): 3300, 1703, 1610, 1435, 1258, 1095, 844 cm⁻¹. 

$^1$H NMR (500 MHz, DMSO-d₆): $\delta = 3.72-3.76$ (m, 2H), 3.80 (dd, $J = 5.4, 10.1$ Hz, 1H), 3.88 (dd, $J = 8.2, 12.3$ Hz, 1H), 4.19-4.20 (m, 1H), 7.59 (d, $J = 8.5$ Hz, 2H), 8.05 (d, $J = 8.5$ Hz, 2H), 9.83 (s, 1H). 

$^{13}$C NMR (125 MHz, DMSO-d₆): $\delta = 35.7, 46.1, 49.0, 128.6, 130.7, 133.2, 137.6, 170.6, 172.0$. MS: m/z (%) = 333 (7) [M+2]$^+$, 331 (4) [M]$^+$, 305 (8), 253 (76), 139
N-(5-(bromomethyl)-4,5-dihydrothiazol-2-yl)-2-fluorobenzamide (4e)

Yield: 0.16 g (50%); white powder; mp 193°C. IR (KBr): 3314, 1687, 1625, 1409, 1263, 1088, 755 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 3.65-3.69 (m, 2H), 3.74-3.78 (m, 2H), 4.22 (m, 1H), 7.20-7.25 (m, 2H), 7.68 (m, 1H), 7.82-7.84 (m, 1H), 9.83 (brs, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 35.8, 46.0, 49.5, 116.5 (d, J_C-F = 22 Hz), 128.4, 130.7, 131.6, 135.1, 159.5 (d, J_C-F = 253 Hz), 169.7, 171.2. Anal. calcd. for C₁₁H₁₀BrFN₂OS: C, 41.66; H, 3.18; N, 8.83. Found: C, 41.69; H, 3.20; N, 8.77.

N-(5-(bromomethyl)-4,5-dihydrothiazol-2-yl)-3-nitrobenzamide (4f)

Yield: 0.23 g (68%); white powder; mp 210-212°C. IR (KBr): 3305, 1712, 1615, 1444, 1261, 1087, 840, 784, 671 cm⁻¹. ¹H NMR (500 MHz, DMSO-ᵈₛ): δ = 3.69-3.76 (m, 2H), 3.80 (dd, J = 5.4, 9.9 Hz, 1H), 3.85-3.89 (m, 1H), 4.19 (m, 1H), 7.80 (t, J = 7.9 Hz, 1H), 8.41 (t, 2H), 8.82 (s, 1H), 9.37 (brs, 1H). ¹³C NMR (125 MHz, DMSO-ᵈₛ): δ = 35.8, 46.1, 48.3, 123.4, 126.8, 130.3, 135.0, 136.8, 147.8, 170.6, 173.3. MS: m/z (%) = 344 (2) [M+2]⁺, 342 (2) [M⁺], 264 (82), 221 (9), 150 (100), 104 (39), 76 (52), 50 (22). Anal. calcd. for C₁₁H₁₀BrN₃O₃S: C, 38.39; H, 2.93; N, 12.21. Found: C, 38.25; H, 3.03; N, 12.13.

N-(5-(bromomethyl)-4,5-dihydrothiazol-2-yl)-4-nitrobenzamide (4g)

Yield: 0.25 g (74%); white powder; mp 233-234°C. IR (KBr): 3301, 1702, 1608, 1420, 1253, 1083, 823 cm⁻¹. ¹H NMR (500 MHz, DMSO-ᵈₛ): δ = 3.60-3.62 (d, J = 11.9 Hz, 1H), 3.70 (t, J = 9.4 Hz, 1H), 3.77 (m, 2H), 4.11 (m, 1H), 8.26 (d, J = 8.6 Hz, 2H), 8.31 (d, J = 8.6 Hz, 2H), 9.83 (brs, 1H). ¹³C NMR (125 MHz, DMSO-ᵈₛ): δ = 35.8, 45.9, 48.6, 123.5, 130.1, 141.9, 149.3,
170.6, 173.7. Anal. calcd. for C$_{11}$H$_{10}$BrN$_3$O$_3$S: C, 38.39; H, 2.93; N, 12.21. Found: C, 38.22; H, 2.76; N, 12.00.
$^1$H-NMR spectra of compound 4a (400 MHz, CDCl$_3$)
$^{13}$C-NMR spectra of compound 4a (100 MHz, CDCl$_3$)
$^1$H-NMR spectra of compound $4b$ (500 MHz, DMSO)
$^{13}$C-NMR spectra of compound 4b (125 MHz, DMSO)
$^1$H-NMR spectra of compound 4c (500 MHz, CDCl$_3$)
$^{13}$C-NMR spectra of compound 4c (125 MHz, CDCl$_3$)
$^1$H-NMR spectra of compound 4d (500 MHz, DMSO)
$^{13}$C-NMR spectra of compound 4d (125 MHz, DMSO)
$^1$H-NMR spectra of compound 4e (500 MHz, CDCl$_3$)
$^{13}$C-NMR spectra of compound 4e (125 MHz, CDCl$_3$)
$^{1}$H-NMR spectra of compound 4f (500 MHz, DMSO)
\[ ^{13}C\text{-NMR spectra of compound 4f (125 MHz, DMSO)} \]
$^1$H-NMR spectra of compound 4g (500 MHz, DMSO)
$^{13}$C-NMR spectra of compound 4g (125 MHz, DMSO)