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. ¹H NMR (400 MHz, CDCl₃): δ = 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). ¹³C NMR (100 MHz, CDCl₃): δ = 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. ¹H NMR (500 MHz, CDCl₃): δ = 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). ¹³C NMR (125 MHz, CDCl₃): δ = 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. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 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). ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 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

(100), 111 (71), 75 (37) , 55 (9). Anal. calcd. for $C_{11}H_{10}BrClN_2OS$: C, 39.60; H, 3.02; N, 8.40. Found: C, 39.59; H, 2.95; N, 8.46.

***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, $CDCl_3$): 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). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{11}H_{10}BrFN_2OS$: 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, $DMSO-d_6$): 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). ^{13}C NMR (125 MHz, $DMSO-d_6$): 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 $C_{11}H_{10}BrN_3O_3S$: 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, $DMSO-d_6$): 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). ^{13}C NMR (125 MHz, $DMSO-d_6$): δ = 35.8, 45.9, 48.6, 123.5, 130.1, 141.9, 149.3,

170.6, 173.7. Anal. calcd. for $C_{11}H_{10}BrN_3O_3S$: C, 38.39; H, 2.93; N, 12.21. Found: C, 38.22; H, 2.76; N, 12.00.

^1H -NMR spectra of compound **4a** (400 MHz, CDCl_3)

^{13}C -NMR spectra of compound **4a** (100 MHz, CDCl_3)

^1H -NMR spectra of compound **4b** (500 MHz, DMSO)

^{13}C -NMR spectra of compound **4b** (125 MHz, DMSO)

¹H-NMR spectra of compound **4c** (500 MHz, CDCl₃)

GM7

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PROCNO 224

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DE 6.50 usec
TE 673.2 K
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TD0 1

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PL1 -1.00 dB
SFO1 499.9999662 MHz

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SSB 0
LB 0.00 Hz
GB 0
PC 2.00

^{13}C -NMR spectra of compound **4c** (125 MHz, CDCl_3)

GM 7

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167.02

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139.08
131.63
130.32
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Current Data Parameters
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PROCNO 144

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FIDRES 0.438846 Kz
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RG 362
DW 8.000 usec
DE 6.00 usec
TE 673.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999999 sec
TD0 1

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PL1 2.50 dB
SFO1 125.7369253 MHz

CHANNEL f2
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PL13 18.50 dB
PL2 -1.00 dB
SFO2 499.9999670 MHz

F2 - Processing parameters
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SSB 0
LB 3.00 Hz
GB 0
AC 1.40

¹H-NMR spectra of compound **4d** (500 MHz, DMSO)

^{13}C -NMR spectra of compound **4d** (125 MHz, DMSO)

^1H -NMR spectra of compound **4e** (500 MHz, CDCl_3)

^{13}C -NMR spectra of compound **4e** (125 MHz, CDCl_3)

^1H -NMR spectra of compound **4f** (500 MHz, DMSO)

^{13}C -NMR spectra of compound **4f** (125 MHz, DMSO)

^1H -NMR spectra of compound **4g** (500 MHz, DMSO)

^{13}C -NMR spectra of compound **4g** (125 MHz, DMSO)