

Supplementary Material

An expedient synthesis of novel 2-substituted thiazolo[4,5-*f*]isoquinolines/quinolines and benzo[1,2-*d*:4,3-*d'*]bisthiazoles and their potential as inhibitors of COX-1 and COX-2

Manas Chakrabarty,^{a*} Ajanta Mukherji,^a Sulakshana Karmakar,^a Ratna Mukherjee,^a
Kenichiro Nagai,^b Athina Geronikaki,^c and Pitta Eleni^c

^aDepartment of Chemistry, Bose Institute, 93/1, A. P. C. Road, Kolkata – 700009, India

^bSchool of Pharmacy, Kitasato University, Minato-ku, Tokyo 108-8641, Japan

^cDepartment of Pharmaceutical Chemistry, School of Pharmacy, Aristotle University of
Thessaloniki, Thessaloniki 54124, Greece

E-mail: chakmanas09@gmail.com

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5-(*N'*-Ethylthioureido)isoquinoline (2b). Yield 0.213 g (92%); grey crystals (from PE/EA); mp 170 °C (lit.²⁹ mp 158–160 °C); IR 3235, 3163, 1588, 1551, 1529, 1382, 1324, 1260, 1218, 1056, 818, 798, 766 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 1.09 (t, *J*=7 Hz, 3H), 3.47 (dq, *J*_I=7 Hz, *J*₂=5.5 Hz, 2H), 7.67 (t, *J*=7.5 Hz, 1H), 7.69 (d, *J*=6 Hz, 1H), 7.71–7.79 (m, 1H), 7.75 (t, *J*=5.5 Hz, 1H), 8.01 (d, *J*=8.5 Hz, 1H), 8.52 (d, *J*=6 Hz, 1H), 9.32 (d, *J*=0.5 Hz, 1H), 9.60 (br s, 1H); ¹³C NMR δ 15.1 (CH₃), 39.8 (CH₂), 116.7, 126.7, 128.1, 129.5, 143.8, 153.4 (all Ar-CH), 129.9, 133.1, 134.7, 182.4 (all Ar-C); LR EI-MS *m/z* (%) 231 (M⁺), 197, 187, 186 (100), 169, 161, 159, 144, 128, 117, 101.

5-(*N'*-*n*-Propylthioureido)isoquinoline (2c). Yield 0.219 g (89%); grey crystals (from PE/DCM); mp 153–154 °C (dec.); IR 3238, 3137, 1587, 1549, 1518, 1382, 1322, 1273, 1213, 1076, 817, 760 cm⁻¹; ¹H NMR (CDCl₃) δ 0.81 (t, *J*=7.5 Hz, 3H), 1.51 (sextet, *J*=7 Hz, 2H), 3.54 (apparent q, *J*≈6.5 Hz, 2H), 5.82 (br s, 1H), 7.66 (t, *J*=7.5 Hz, 1H), 7.69 (d, *J*=7.5 Hz, 1H), 7.81 (d, *J*=6 Hz, 1H), 7.98 (d, *J*=8 Hz, 1H), 8.55 (d, *J*=6 Hz, 1H), 8.60 (br, 1H), 9.26 (s, 1H); ¹³C NMR δ 11.6 (CH₃), 22.6, 47.5 (both CH₂), 115.9, 127.8, 128.5, 129.7, 144.6, 153.1 (all Ar-CH), 129.9, 133.2 (2×), 182.0 (all Ar-C); LR EI-MS *m/z* (%) 245 (M⁺), 186, 169, 161, 144 (100), 117, 43, 41; HR EI-MS *m/z* calcd for C₁₃H₁₅N₃S (M⁺), 245.0987; found 245.0986.

5-(*N'*-Benzylthioureido)isoquinoline (2d). Yield 0.275 g (94%); white needles (from PE/DCM); mp 181–182 °C; IR 3132, 1587, 1544, 1518, 1385, 1345, 1275, 1209, 1193, 1032, 949, 821, 758 cm⁻¹; ¹H NMR (CDCl₃) δ 4.83 (d, *J*=5.5 Hz, 2H), 5.97 (br s, 1H), 7.19 (d, *J*=7 Hz, 2H), 7.22–7.27 (m, 1H), 7.24 (t, *J*=7 Hz, 2H), 7.62 (t, *J*=7.5 Hz, 1H), 7.68 (d, *J*=7.5 Hz, 1H), 7.79 (br, 1H), 7.97 (d, *J*=8 Hz, 1H), 8.19 (br s, 1H), 8.57 (d, *J*=6 Hz, 1H), 9.27 (s, 1H); ¹³C NMR δ 49.9 (CH₂), 115.6, 127.7, 128.0 (2×), 128.2, 128.8, 129.1 (2×), 129.7, 144.8, 153.3 (all Ar-CH), 129.9, 133.1, 134.7, 182.4 (all Ar-C); LR EI-MS *m/z* (%) 293 (M⁺), 259, 186, 144, 106, 91 (100); HR EI-MS *m/z* calcd for C₁₇H₁₅N₃S (M⁺), 293.0987; found 293.0989.

5-(*N'*-Ethylthioureido)quinoline (7b). Yield 0.198 g (86%); off-white shining globules (from MeOH); mp 222 °C (dec.); IR (nujol) 3142, 1613, 1600, 1546, 1515, 1321, 1261, 1235, 1155, 1096, 1062, 890, 798, 731 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 1.06 (t, *J*=6.5 Hz, 3H), *ca.* 3.46 (quintet, *J*=*ca.* 6.5 Hz, 2H), 7.52 (d, *J*=7.5 Hz, 1H), 7.55 (dd, *J*_I=8.5 Hz, *J*₂=4 Hz, 1H), 7.66 (br, 1H), 7.74 (t, *J*=8 Hz, 1H), 7.93 (d, *J*=8.5 Hz, 1H), 8.23 (d, *J*=8 Hz, 1H), 8.90 (dd, *J*_I=4 Hz, *J*₂=1.5 Hz, 1H), 9.61 (br s, 1H); ¹³C NMR δ 15.1 (CH₃), 39.9 (CH₂), 122.1, 126.01, 128.4, 130.0, 132.4, 151.4 (all Ar-CH), 126.05, 135.8, 149.3, 182.4 (all Ar-C); LR EI-MS *m/z* (%) 231 (M⁺), 197, 169, 161, 144 (100), 128, 117, 116, 101; HR EI-MS *m/z* calcd for C₁₂H₁₃N₃S, 231.0831; found 231.0820.

5-(*N'*-*n*-Propylthioureido)quinoline (7c). Yield 0.196 g (80%); light cream coloured needles (from MeOH); mp 188–190 °C; IR (nujol) 3135, 1587, 1573, 1538, 1507, 1381, 1261, 1216, 1142, 1082, 890, 797, 738 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 0.83 (t, *J*=6.5 Hz, 3H), *ca.* 1.51 and 3.39 (m, 2H each), 7.54 (d, *J*=7.5 Hz, 1H), 7.55 (dd, *J*_I=8.5 Hz, *J*₂=4.5 Hz, 1H), 7.68 (br s, 1H), 7.74 (dd, *J*_I=8.5 Hz, *J*₂=7.5 Hz, 1H), 7.93 (d, *J*=8.5 Hz, 1H), 8.23 (d, *J*=8 Hz, 1H), 8.90 (dd, *J*_I=4.5 Hz, *J*₂=1.5 Hz, 1H), 9.61 (s, 1H); ¹³C NMR δ 12.1 (CH₃), 22.7, 46.8 (both CH₂), 122.1, 125.9, 128.4, 130.0, 132.4, 151.3 (all Ar-CH), 124.0, 135.7, 149.2, 182.8 (all Ar-C); LR EI-MS *m/z* (%)

245 (M^+), 212, 211, 170, 169, 161, 144 (100), 128, 43; HR EI-MS m/z calcd for $C_{13}H_{15}N_3S$, 245.0986; found 245.0991.

5-(*N'*-Benzylthioureido)quinoline (7d). Yield 0.293 g (100%); white shining globules (from MeOH); mp 219–220 °C; IR (nujol) 3164, 1593, 1546, 1513, 1348, 1314, 1275, 1215, 1195, 963, 890, 804, 751, 731, 704 cm^{-1} ; 1H NMR (DMSO- d_6) δ 4.71 (d, $J=6$ Hz, 2H), 7.23 (t, $J=6$ Hz, 1H), 7.26–7.36 (m, 4H), 7.56 (t, $J=7$ Hz, 2H), 7.75 (t, $J=8$ Hz, 1H), 7.94 (d, $J=8.5$ Hz, 1H), 8.13 and 8.25 (br, 1H each), 8.90 (ill-split d, 1H), 9.79 (br s, 1H); ^{13}C NMR δ 48.4 (CH_2), 122.2, 126.3, 127.6, 128.1 (2 $\times$), 128.6, 129.0 (2 $\times$), 130.0, 132.4, 151.4 (all Ar-CH), 126.2, 135.6, 140.0, 149.3, 183.3 (all Ar-C); LR EI-MS m/z (%) 293 (M^+), 259, 161, 144, 91 (100); HR EI-MS m/z calcd for $C_{17}H_{15}N_3S$, 293.0986; found 293.0995.

6-(*N'*-Ethylthioureido)benzothiazole (8b). Yield 0.2 g (85%); off-white needles (from MeOH); mp 180–182 °C; IR (nujol) 3246, 3170, 1540, 1239, 1155, 923, 857, 724 cm^{-1} ; 1H NMR (DMSO- d_6) δ 1.10 (t, $J=6$ Hz, 3H, CH_3CH_2), 3.48 (quintet, $J=6$ Hz, 2H, $CH_2CH_2CH_2$), 7.44 (dd, $J_1=9$ Hz, $J_2=2$ Hz, 1H, H-5), 7.82 (br s, 1H, $CH_2NHCH=S$), 7.99 (d, $J=9$ Hz, 1H, H-4), 8.22 (d, $J=2$ Hz, 1H, H-7), 9.28 (s, 1H, H-2), 9.62 (s, 1H, ArNHC=S); ^{13}C NMR δ 15.0 (CH_3), 39.6 (CH_2), 117.2 (CH-7), 123.5 (2 $\times$; CH-4,5), 134.7 (C-7a), 137.7 (C-6), 150.8 (C-3a), 156.1 (CH-2), 181.2 (C=S); LR EI-MS m/z (%) 237 (M^+), 204, 203, 192, 175, 150 (100), 134; HR EI-MS m/z calcd. for $C_{10}H_{11}N_3S_2$, 237.0394; found 237.0395.

6-(*N'*-*n*-Propylthioureido)benzothiazole (8c). Yield 0.213 g (85%); off-white prisms (from MeOH); mp 218–220 °C; IR (nujol) 3265, 3148, 1530, 1375, 1237, 1203, 1079, 857 cm^{-1} ; 1H NMR (DMSO- d_6) δ 0.88 (t, $J=7$ Hz, 3H), 1.55 (sextet, $J=7$ Hz, 2H), 3.42 (br s, 2H), 7.46 (d, $J=8$ Hz, 1H), 7.84 (br s, 1H), 7.99 (d, $J=8.5$ Hz, 1H), 8.25, 9.28 and 9.63 (s, 1H each); ^{13}C NMR δ 12.2 (CH_3), 22.6, 46.5 (both CH_2), 117.0, 123.5 (2 $\times$), 156.1 (all Ar-CH), 134.7, 137.8, 150.7, 181.4 (all Ar-C); LR EI-MS m/z (%) 251 (M^+), 218, 217, 192, 176, 175, 150 (100), 134; HR EI-MS m/z calcd for $C_{11}H_{13}N_3S_2$, 251.0551; found 251.0553.

6-(*N'*-Benzylthioureido)benzothiazole (8d). Yield 0.263 g (88%); white needles (from MeOH); mp 190 °C; IR (nujol) 3230, 3138, 1546, 1520, 1314, 1280, 1175, 963, 923, 844, 744 cm^{-1} ; 1H NMR (DMSO- d_6) δ 4.75 (d, $J=5$ Hz, 2H), 7.24 (tt, $J_1=6$ Hz, $J_2=2.5$ Hz, 1H), 7.32–7.35 (m, 4H), 7.49 (dd, $J_1=9$ Hz, $J_2=2$ Hz, 1H), 8.01 (d, $J=9$ Hz, 1H), 8.27 (br s, 1H), 8.28 (d, $J=2$ Hz, 1H), 9.30 and 9.80 (s, 1H each); ^{13}C NMR δ 48.1 (CH_2), 117.6, 123.6, 124.0, 127.7, 128.3 (2 $\times$), 129.1 (2 $\times$), 156.3 (all Ar-CH), 134.7, 137.6, 139.8, 150.9, 182.0 (all Ar-C); LR EI-MS m/z (%) 299 (M^+), 265, 192, 150, 106, 91 (100); HR EI-MS m/z calcd for $C_{15}H_{13}N_3S_2$, 299.0551; found 299.0550.

2-Alkylaminothiazolo[4,5-*f*]isoquinolines (3b-d), -thiazolo[4,5-*f*]quinolines (9b-d) and -benzo-[1,2-*d*:4,3-*d'*]bisthiazoles (10b-d)

2-Ethylaminothiazolo[4,5-*f*]isoquinoline (3b). Yield 0.226 g (98%); light yellow crystals (from DCM); mp 156–158 °C (dec.); IR 3188, 1621, 1591, 1554, 1486, 1467, 1373, 1344, 1282, 1032, 828, 796, 772 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.36 (t, $J=7$ Hz, 3H), 3.51 (dq, $J_1=7$ Hz, $J_2=4$ Hz, 2H), 6.03 (br s, 1H), 7.64 and 7.79 (d, $J=8.5$ Hz, 1H each), 8.26 and 8.59 (d, $J=5.5$ Hz, 1H each), 9.25

(s, 1H); ^{13}C NMR δ 15.1 (CH_3), 41.0 (CH_2), 117.1, 120.6, 120.8, 143.5, 152.4 (all Ar-CH), 127.7, 129.4, 129.8, 147.4, 169.1 (all Ar-C); LR EI-MS m/z (%) 229 (M^+ ; 100), 214, 201, 187, 186, 156; HR EI-MS m/z calcd for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{S}$ (M^+), 229.0673; found 229.0664.

2-*n*-Propylaminothiazolo[4,5-*f*]isoquinoline (3c). Yield 0.24 g (98%); dark brown needles (from PE/DCM); mp 160–161 °C (dec.); IR 3182, 3150, 1619, 1597, 1551, 1467, 1364, 1288, 1034, 914, 891, 829, 761cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 0.96 (t, $J=7.5$ Hz, 3H), 1.65 (sextet, $J=7.5$ Hz, 2H), 3.39 (apparent q, $J=6.5$ Hz, 2H), 7.70 and 7.97 (d, $J=8.5$ Hz, 1H each), 8.13 (d, $J=6$ Hz, 1H), 8.32 (t, $J=5$ Hz, 1H), 8.50 (br d, $J=5$ Hz, 1H), 9.26 (s, 1H); ^{13}C NMR δ 12.3 (CH_3), 22.8, 47.0 (both CH_2), 117.1, 120.4, 121.7, 143.6, 152.8 (all Ar-CH), 127.8, 128.5, 129.8, 147.5, 168.9 (all Ar-C); LR EI-MS m/z (%) 243 (M^+ ; 100), 214, 201, 200, 187; HR EI-MS m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{S}$ (M^+), 243.0830; found 243.0833.

2-Benzylaminothiazolo[4,5-*f*]isoquinoline (3d). Yield 0.27 g (92%); brown crystals (from PE/DCM); mp 167–168 °C (dec.); IR 3207, 1617, 1577, 1538, 1489, 1371, 1241, 1220, 1197, 1029, 830, 798, 738cm^{-1} ; ^1H NMR (CDCl_3) δ 4.69 (s, 2H), 6.43 (s, 1H), 7.30 (tt, $J_1=7$ Hz, $J_2=1.5$ Hz, 1H), 7.34 (tt, $J_1=7$ Hz, $J_2=1.5$ Hz, 2H), 7.41 (dd, $J_1=7$ Hz, $J_2=1$ Hz, 2H), 7.64 and 7.77 (d, $J=8.5$ Hz, 1H each), 8.26 (d, $J=5.5$ Hz, 1H), 8.56 and 9.24 (br s, 1H each); ^{13}C NMR δ 50.0 (CH_2), 117.2, 120.6, 121.1, 128.1 (2 $\times$), 128.3, 129.2 (2 $\times$), 143.6, 152.4 (all Ar-CH), 128.3, 129.5, 130.0, 137.6, 147.2, 168.9 (all Ar-C); LR EI-MS m/z (%) 291 (M^+), 187, 91 (100), 65; HR ESI-MS m/z calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{S}$ ($\text{M}+\text{H}$) $^+$, 292.0903; found 292.0904.

2-Ethylaminothiazolo[4,5-*f*]quinoline (9b). Eluted with PE/EA (3:1); yield 0.194 g (85%); light brown tiny needles (from PE/EA/MeOH); mp 172–175 °C; IR (nujol) 3198, 1588, 1556, 1401, 1357, 1344, 1295, 1169, 1076, 917, 830, 804cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 1.24 (t, $J=7$ Hz, 3H), 3.45 (quintet, $J=7$ Hz, 2H), 7.50 (dd, $J_1=8.5$ Hz, $J_2=4$ Hz, 1H), 7.64 and 8.03 (d, $J=9$ Hz, 1H each), 8.25 (t, $J=4.5$ Hz, 1H), 8.71 (d, $J=8$ Hz, 1H), 8.83 (ill-split d, 1H); ^{13}C NMR δ 15.2 (CH_3), 39.9 (CH_2), 121.67, 122.1, 123.4, 132.5, 150.1 (all Ar-CH), 121.61, 125.4, 147.7, 148.9, 169.1 (all Ar-C); LR EI-MS m/z (%) 229 (M^+ ; 100), 214, 201, 187, 186; HR EI-MS m/z calcd for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{S}$, 229.0674; found 229.0667.

2-*n*-Propylaminothiazolo[4,5-*f*]quinoline (9c). Eluted with PE/EA (3:1); yield 0.236 g (97%); pale yellow leaflets (from PE/EA/MeOH); mp 104–106 °C; IR (nujol) 3224, 1586, 1560, 1354, 1142, 1069, 830, 804cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 0.95 (t, $J=7$ Hz, 3H), 1.65 (sextet, $J=7$ Hz, 2H), 3.39 (dt, $J_1=7$ Hz, $J_2=5$ Hz, 2H), 7.50 (dd, $J_1=8.5$ Hz, $J_2=4$ Hz, 1H), 7.64 and 8.03 (d, $J=8.5$ Hz, 1H each), 8.27 (t, $J=5$ Hz, 1H), 8.71 (dd, $J_1=8.5$ Hz, $J_2=1$ Hz, 1H), 8.83 (dd, $J_1=4$ Hz, $J_2=1.5$ Hz, 1H); ^{13}C NMR δ 12.3 (CH_3), 22.8, 47.0 (both CH_2), 121.6, 122.1, 123.4, 132.5, 150.1 (all Ar-CH), 121.5, 125.4, 147.7, 148.8, 169.4 (all Ar-C); LR EI-MS m/z (%) 243 (M^+ ; 100), 215, 214, 201, 200, 187; HR EI-MS m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{S}$, 243.0830; found 243.0826.

2-Benzylaminothiazolo[4,5-*f*]quinoline (9d). Eluted with PE/EA (4:1); yield 0.25 g (86%); orange yellow needles (from PE/EA/MeOH); mp 168–171 °C (dec.); IR (nujol) 3199, 1608, 1586, 1534, 1357, 1346, 1278, 1219, 1195, 1076, 903, 804, 721, 703cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 4.67 (d, $J=5.5$ Hz, 2H), 7.26 (t, $J=7.5$ Hz, 1H), 7.35 (t, $J=7.5$ Hz, 2H), 7.45 (d, $J=7.5$ Hz, 2H),

7.52 (dd, $J_1=8.5$ Hz, $J_2=4$ Hz, 1H), 7.66 and 8.04 (d, $J=9$ Hz, 1H each), 8.72 (d, $J=8$ Hz, 1H), 8.78 (t, $J=5.5$ Hz, 1H), 8.84 (dd, $J_1=4$ Hz, $J_2=1.5$ Hz, 1H); ^{13}C NMR δ 48.4 (CH_2), 121.7, 122.4, 123.4, 128.0, 128.5 (2 $\times$), 129.2 (2 $\times$), 132.5, 150.2 (all Ar-CH), 121.6, 125.7, 139.6, 147.7, 148.6, 169.3 (all Ar-C); LR EI-MS m/z (%) 291 (M^+), 289, 187, 91 (100); HR EI-MS m/z calcd for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{S}$, 291.0830; found 291.0830.

2-Ethylaminobenzo[1,2-*d*:4,3-*d'*]bisthiazole (10b). Yield 0.195 g (83%); off-white needles (from PE/DCM); mp 132–133 °C; IR (nujol) 3217, 1613, 1573, 1540, 1414, 1261, 1149, 1056, 983, 824 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.36 (t, $J=7.5$ Hz, 3H, CH_3CH_2), 3.50 (q, $J=7.5$ Hz, 2H, CH_3CH_2), 6.11 (s, 1H, Ar-NH), 7.67 and 8.03 (d, $J=8.5$ Hz, 1H each, H-4 and H-5, respectively), 8.84 (s, 1H, H-7); ^{13}C NMR δ 15.2 (CH_3), 41.0 (CH_2), 118.2 (CH-4), 121.6 (CH-5), 122.1 (C-8b), 126.8 (C-8a), 149.7 (C-5a), 150.8 (CH-7), 151.3 (C-3a), 167.8 (C-2); LR EI-MS m/z (%) 235 (M^+ ; 100), 220, 207, 193, 192; HR EI-MS m/z calcd for $\text{C}_{10}\text{H}_9\text{N}_3\text{S}_2$, 235.0238; found 235.0234.

2-*n*-Propylaminobenzo[1,2-*d*:4,3-*d'*]bisthiazole (10c). Yield 0.204 g (82%); white needles (from PE/DCM); mp 176–177 °C; IR (nujol) 3212, 1622, 1580, 1540, 1462, 1377, 1281, 1235, 1069, 930, 817 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.03 (t, $J=7$ Hz, 3H), 1.75 (sextet, $J=7$ Hz, 2H), 3.41 (t, $J=7$ Hz, 2H), 6.23 (br s, 1H), 7.66 and 8.03 (d, $J=8.5$ Hz, 1H each), 8.84 (s, 1H); ^{13}C NMR δ 11.8 (CH_3), 23.2, 48.0 (both CH_2), 118.2, 121.6, 150.8 (all Ar-CH), 122.1, 126.8, 149.7, 151.3, 168.1 (all Ar-C); LR EI-MS m/z (%) 249 (M^+), 220, 207 (100), 193, 180; HR EI-MS m/z calcd for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{S}_2$, 249.0394; found 249.0394.

2-Benzylaminobenzo[1,2-*d*:4,3-*d'*]bisthiazole (10d). Yield 0.258 g (87%); light yellow needles (from PE/DCM); mp 169–170 °C; IR (nujol) 3211, 1615, 1580, 1540, 1275, 1129, 976, 930, 824 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.65 (s, 2H), 7.01 (br s, 1H), 7.31 (t, $J=7$ Hz, 1H), 7.35 (t, $J=7$ Hz, 2H), 7.42 (d, $J=7$ Hz, 2H), 7.50 and 7.97 (d, $J=9$ Hz, 1H each), 8.80 (s, 1H); ^{13}C NMR δ 50.0 (CH_2), 118.2, 121.7, 128.1 (2 $\times$), 128.4, 129.3 (2 $\times$), 150.9 (all Ar-CH), 122.2, 126.8, 137.5, 149.8, 151.0, 168.0 (all Ar-C); LR EI-MS m/z (%) 297 (M^+), 296, 193, 106, 91 (100); HR EI-MS m/z calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{S}_2$, 297.0394; found 297.0399.

Ethyl *N*-(5-isoquinolinyl/quinolinyl)dithiocarbamates (12b, 13b) and ethyl *N*-(6-benzothiazolyl)dithiocarbamate (14b)

Ethyl *N*-(5-isoquinolinyl)dithiocarbamate (12b). Eluted with PE/EA (83:17); yield 0.153 g (62%); white crystals (from PE/EA); mp 132–133 °C; IR 3113, 1627, 1593, 1542, 1493, 1373, 1341, 1319, 1277, 981, 822, 757, 700 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 1.24 (ill-split singlet, 3H), 3.21 (q, $J=6.5$ Hz, 2H), 7.60 (d, $J=5.5$ Hz, 1H), 7.72 (t, $J=7.5$ Hz, 1H), 7.76 (dd, $J_1=7.5$ Hz, $J_2=1.0$ Hz, 1H), 8.14 (d, $J=8.0$ Hz, 1H), 8.55 (d, $J=6.0$ Hz, 1H), 9.38 (s, 1H), 11.85 (br s, 1H); ^{13}C NMR δ 14.8 (CH_3), 30.1 (CH_2), 116.5, 128.1 (2 $\times$), 130.6, 144.3, 153.6 (all Ar-CH), 128.5, 129.7, 132.7, 201.1 (all Ar-C); LR EI-MS m/z (%) 248 (M^+), 187, 186 (100), 159, 101; HR EI-MS m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}_2$ (M^+), 248.0442; found 248.0441.

Ethyl *N*-(5-quinolinyl)dithiocarbamate (13b). Yield 0.186 g (75%); brownish yellow globules (from EA/MeOH); mp 120–122 °C (dec.); IR 3432, 3101, 1615, 1593, 1574, 1538, 1500, 1469, 1395, 1367, 1329, 1314, 1245, 1206, 1164, 1082, 1024, 986, 978, 882, 803, 743, 728, 710 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 1.25 (t, *J*=7.5 Hz, 3H), 3.21 (q, *J*=7.5 Hz, 2H), *ca.* 7.58 (m, 2H), 7.79 (t, *J*=8 Hz, 1H), 8.04 (d, *J*=8 Hz, 1H), 8.14 (d, *J*=8.5 Hz, 1H), 8.93 (ill-split d, *J*=3 Hz, 1H), 11.85 (br s, 1H); ¹³C NMR δ 14.8 (CH₃), 30.1 (CH₂), 122.7, 129.9, 132.2, 151.8 (all Ar-CH), 125.4, 126.6, 149.0, 199.4 (all Ar-C); GC-EI MS (RT=14.49 min) *m/z* (%) 187, 186 (100), 128. Anal. Calcd for C₁₂H₁₂N₂S₂: C, 58.06; H, 4.84; N, 11.29. Found: C, 58.02; H, 4.86; N, 11.27.

Ethyl *N*-(6-benzothiazolyl)dithiocarbamate (14b). Eluted with PE/EA (17:3); yield 0.19 g (75%); greenish needles (from EA/MeOH); mp 198–200 °C (dec.); IR 3106, 1589, 1495, 1398, 1316, 1290, 1051, 1013, 964, 920, 853, 741 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 1.26 (t, *J*=7 Hz, 3H), 3.22 (q, *J*=7 Hz, 2H), 7.64 (br s, 1H), 8.07 (d, *J*=9 Hz, 1H), 8.48 (br s, 1H), 9.37 and 11.80 (s, 1H each); ¹³C NMR δ 14.9 (CH₃), 29.8 (CH₂), 118.6, 123.6, 124.2, 157.5 (all Ar-CH), 134.6, 137.8, 151.9, 198.6 (all Ar-C); LR ESI-MS 255 *m/z* (M+H)⁺, 277 (M+Na)⁺; GC-EI MS (RT=14.85 min) *m/z* (%) 192 (100), 134. Anal. Calcd for C₁₀H₁₀N₂S₃: C, 47.24; H, 3.93; N, 11.02. Found: C, 47.29; H, 3.90; N, 11.04.

2-Ethylthiothiazolo[4,5-*f*]isoquinoline (15b), -thiazolo[4,5-*f*]quinoline (16a) and -benzo[1,2-*d*:4,3-*d'*]bisthiazole (17a)

2-Ethylthiothiazolo[4,5-*f*]isoquinoline (15b). Eluted with PE/EA (22:3); yield 0.209 g (85%); white flakes (from PE/DCM); mp 70–71 °C; IR 1618, 1551, 1486, 1446, 1369, 1286, 1060, 1014, 906, 834, 802, 771 cm⁻¹; ¹H NMR (CDCl₃) δ 1.56 (t, *J*=7.5 Hz, 3H), 3.45 (q, *J*=7.5 Hz, 2H), 7.81 and 7.90 (d, *J*=8.5 Hz, 1H each), 8.45 and 8.69 (d, *J*=5.5 Hz, 1H each), 9.30 (s, 1H); ¹³C NMR δ 14.9 (CH₃), 28.8 (CH₂), 117.1, 120.3, 123.9, 144.7, 152.3 (all Ar-CH), 127.3, 130.7, 136.1, 148.4, 167.8 (all Ar-C); LR EI-MS *m/z* (%) 246 (M⁺; 100), 218, 213, 173, 159; HR EI-MS *m/z* calcd for C₁₂H₁₀N₂S₂ (M⁺), 246.0286; found 246.0287.

2-Ethylthiothiazolo[4,5-*f*]quinoline (16b). Yield 0.224 g (91%); pale yellow needles (from EtOH/H₂O); mp 52–55 °C; IR 1599, 1492, 1447, 1387, 1361, 1260, 1189, 1073, 1030, 1011, 902, 831, 805, 780, 756 cm⁻¹; ¹H NMR (CDCl₃) δ 1.55 (t, *J*=7.5 Hz, 3H, SCH₂CH₃), 3.43 (q, *J*=7.5 Hz, 2H, SCH₂CH₃), 7.53 (dd, *J*₁=8.5 Hz, *J*₂=4 Hz, 1H, H-5), 7.99 (d, *J*=9.5 Hz, 1H, H-9), 8.0 (d, *J*=9.5 Hz, 1H, H-8), 8.96 (dd, *J*₁=4 Hz, *J*₂=1.5 Hz, 1H, H-6), 9.01 (dd, *J*₁=8.5 Hz, *J*₂=1.5 Hz, 1H, H-4); ¹³C NMR δ 15.0 (CH₃), 28.8 (SCH₂), 122.0 (CH-8), 122.1 (CH-5), 123.3 (C-3b), 126.2 (CH-9), 132.2 (C-9a), 132.6 (CH-4), 147.6 (C-7a), 149.5 (C-3a), 150.3 (CH-6), 168.0 (C-2); GC-EI MS (RT=19.39 min) *m/z* (%) 246 (M⁺; 100), 218, 217, 214, 213, 173, 160. Anal. Calcd for C₁₂H₁₀N₂S₂: C, 58.53; H, 4.06; N, 11.38. Found: C, 58.60; H, 4.07; N, 11.35.

2-Ethylthiobenzo[1,2-*d*:4,3-*d'*]bisthiazole (17b). Yield 0.214 g (85%); off-white prisms (from PE/DCM); mp 149–150 °C; IR 1576, 1466, 1445, 1397, 1330, 1279, 1258, 1016, 928, 833, 798 cm⁻¹; ¹H NMR (CDCl₃) δ 1.52 (t, *J*=7.5 Hz, 3H, SCH₂CH₃), 3.39 (q, *J*=7.5 Hz, 2H, SCH₂CH₃),

7.98 and 8.13 (d, $J=9$ Hz, 1H each, H-4 and H-5, respectively), 8.97 (s, 1H); ^{13}C NMR δ 14.9 (CH₃), 28.7 (CH₂), 120.5 (CH-4), 122.0 (CH-5), 126.5 (C-8a), 128.1 (C-8b), 151.2 (C-5a), 152.2 (C-3a), 152.7 (CH-7), 166.9 (C-2); GC-EI MS (RT=19.10 min) m/z (%) 252 (M^+ ; 100), 224, 219, 166. Anal. Calcd for C₁₀H₈N₂S₃: C, 47.61; H, 3.17; N, 11.11. Found: C, 47.50; H, 3.16; N, 11.18.

***N*-(5-isoquinolinyl/quinolinyl)amides (21, 22b,c) and *N*-(6-benzothiazolyl)amide (23b)**

5-Propionamidoisoquinoline (21b). Eluted with PE/EA (1:1); yield 0.191 g (95%); white needles (from EA); mp 164–166 °C; IR 3270, 1656, 1535, 1459, 1387, 1325, 1281, 1258, 1218, 822, 808, 755, 713 cm⁻¹; ^1H NMR (CDCl₃ + DMSO-*d*₆) δ 1.28 (t, $J=7.5$ Hz, 3H), 2.54 (q, $J\approx 7.5$ Hz, 2H), 7.55 (t, $J=8$ Hz, 1H), 7.75 (d, $J=8$ Hz, 1H), 7.81 (d, $J=6$ Hz, 1H), 8.02 (d, $J=7.5$ Hz, 1H), 8.47 (d, $J=6$ Hz, 1H), 9.19 (s, 1H), 9.26 (br s, 1H); ^{13}C NMR δ 10.2 (CH₃), 30.2 (CH₂), 115.6, 124.9, 125.5, 127.4, 142.9, 152.9 (all Ar-CH), 129.3, 130.6, 133.0, 173.9 (all Ar-C); GC EI-MS (RT=17.01 min) m/z (%) 200 (M^+), 145, 144 (100), 117. Anal. Calcd for C₁₂H₁₂N₂O: C, 72.00; H, 6.00; N, 14.00. Found: C, 72.08; H, 5.99; N, 14.03.

5-*i*-Butyramidoisoquinoline (21c). Yield 0.2 g (93%); white needles (from PE/EA); mp 147–148 °C; IR 3262, 1655, 1527, 1458, 1382, 1324, 1278, 1253, 1209, 1102, 822, 763, 702 cm⁻¹; ^1H NMR (CDCl₃ + DMSO-*d*₆) δ 1.29 (d, $J=6.5$ Hz, 6H), 2.83 (septet, $J=6.5$ Hz, 1H), 7.57 (t, $J=7.5$ Hz, 1H), 7.78 (d, $J=8$ Hz, 1H), 7.85 (d, $J=6$ Hz, 1H), 8.02 (d, $J=7.5$ Hz, 1H), 8.46 (d, $J=6$ Hz, 1H), 9.21 (s, 1H), 9.32 (br s, 1H); ^{13}C NMR δ 20.0 (2×CH₃), 35.8 (aliphatic CH), 116.1, 125.1, 126.2, 127.7, 142.0, 152.3 (all Ar-CH), 129.2, 131.0, 133.1, 177.2 (all Ar-C); GC EI-MS (RT=17.22 min) m/z (%) 214 (M^+), 145, 144 (100), 117, 116, 41. Anal. Calcd for C₁₃H₁₄N₂O: C, 72.89; H, 6.54; N, 13.08. Found: C, 72.94; H, 6.55; N, 13.04.

5-Propionamidoquinoline (22b). Yield 0.188 g (94%); pale cream-coloured needles (from PE/C₆H₆); mp 164–166 °C; IR (nujol) 3264, 1659, 1540, 1493, 1321, 1268, 804, 724 cm⁻¹; ^1H NMR (DMSO-*d*₆) δ 1.15 (t, $J=7.5$ Hz, 3H), 2.49 (q, $J=7.5$ Hz, 2H), 7.54 (dd, $J_1=8.5$ Hz, $J_2=4$ Hz, 1H), 7.71 (t, $J=8$ Hz, 1H), 7.77 (d, $J=7.5$ Hz, 1H), 7.84 (d, $J=8$ Hz, 1H), 8.46 (d, $J=8.5$ Hz, further ill-split, 1H), 8.90 (dd, $J_1=4$ Hz, $J_2=1.5$ Hz, 1H), 9.96 (s, 1H); ^{13}C NMR δ 10.6 (CH₃), 29.9 (CH₂), 121.7, 122.3, 126.7, 129.9, 132.3, 151.2 (all Ar-CH), 123.6, 134.9, 149.0, 173.6 (all Ar-C); GC-EI MS (RT=16.97 min) m/z (%) 200 (M^+), 144 (100), 117. Anal. Calcd for C₁₂H₁₂N₂O: C, 72.00; H, 6.00; N, 14.00. Found: C, 72.09; H, 6.02; N, 13.98.

5-*n*-Butyramidoquinoline (22c). Yield 0.193 g (90%); milky white needles (from PE/C₆H₆); mp 118–120 °C; IR 3266, 1659, 1535, 1494, 1321, 1265, 1208, 969, 796, 727 cm⁻¹; ^1H NMR (CDCl₃) δ 0.99 (t, $J=7$ Hz, 3H), 1.75 (sextet, $J=7$ Hz, 2H), 2.39 (t, $J=7$ Hz, 2H), *ca.* 7.26 (m, 1H), 7.56 (t, $J=7.5$ Hz, 1H), 7.61 (d, $J=7$ Hz, 1H), 7.88 and 8.08 (d, $J=8$ Hz, 1H each), 8.09 (s, 1H), 8.83 (ill-split s, 1H); ^{13}C NMR δ 14.1 (CH₃), 19.6, 39.3 (both CH₂), 121.1, 122.8, 127.8, 129.4, 130.7, 150.6 (all Ar-CH), 123.7, 132.9, 148.8, 172.9 (all Ar-C); GC-EI MS (RT=17.75 min) m/z (%) 214 (M^+), 144 (100), 117. Anal. Calcd for C₁₃H₁₄N₂O: C, 72.89; H, 6.54; N, 13.08. Found: C, 72.82; H, 6.52; N, 13.11.

6-Propionamidobenzothiazole (23b). Yield 0.206 g (100%); white needles (from PE/EA); mp 150–151 °C; IR 3280, 1684, 1662, 1535, 1471, 1399, 1315, 1284, 1242, 1196, 1076, 907, 839, 811, 791 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 1.09 (t, $J=7.5$ Hz, 3H), 2.35 (q, $J=7.5$ Hz, 2H), 7.57 (dd, $J_1=9$ Hz, $J_2=2$ Hz, 1H), 7.98 (d, $J=9$ Hz, 1H), 8.53 (d, $J=1.5$ Hz, 1H), 9.22 and 10.11 (s, 1H each); ^{13}C NMR δ 10.5 (CH_3), 30.4 (CH_2), 112.2, 119.5, 123.7, 155.2 (all Ar-CH), 135.0, 138.0, 149.7, 173.1 (all Ar-C); GC-EI MS (RT=17.55 min) m/z (%) 206 (M^+), 150 (100). Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{OS}$: C, 58.25; H, 4.85; N, 13.59. Found: C, 58.30; H, 4.86; N, 13.62.

5-Benzamidoisoquinoline (21d)/-quinoline (22d)/6-Benzamidobenzothiazole (23c)

5-Benzamidoisoquinoline (21d). Eluted with PE/EA (2:3); yield 0.224 g (90%); white flakes (from PE/EA); mp 157–158 °C (dec.) (lit.^{8a} mp 158–159 °C); IR 3273, 1647, 1610, 1517, 1486, 1425, 1345, 1284, 830, 756, 711 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 7.57 (t, $J=7.5$ Hz, 2H), 7.64 (t, $J=7.5$ Hz, 1H), 8.04 (t, $J=8$ Hz, 1H), 8.15 (dd, $J_1=8$ Hz, $J_2=1$ Hz, 2H), 8.26 (d, $J=7.5$ Hz, 1H), 8.41 (d, $J=6.5$ Hz, 1H), 8.44 (d, $J=8$ Hz, 1H), 8.65 (d, $J=6.5$ Hz, 1H), 9.95 and 11.02 (s, 1H each); ^{13}C NMR δ 122.1, 128.9 (2 $\times$), 129.1, 129.3 (2 $\times$), 131.2, 132.90, 132.99, 133.4, 148.5 (all Ar-CH), 128.7, 134.5, 134.7, 135.0, 167.3 (all Ar-C); GC EI-MS (RT=21.72 min) m/z (%) 248 (M^+), 105 (100), 78, 77, 51.

5-Benzamidoquinoline (22d). Yield 0.248 g (100%); pale cream-coloured, shining needles (from PE/EA/MeOH); mp 188–191 °C; IR (nujol) 3191, 1719, 1646, 1513, 1308, 804 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 7.54 (dd, $J_1=8.5$ Hz, $J_2=4$ Hz, 1H), 7.57 (t, $J=7.5$ Hz, 2H), 7.63 (tt, $J_1=7.5$ Hz, $J_2=1.5$ Hz, 1H), 7.71 (d, $J=7.5$ Hz, 1H), *ca.* 7.79 (t, $J=8$ Hz, 1H), 7.96 (d, $J=8$ Hz, 1H), 8.09 (d, $J=8.5$ Hz, further ill-split, 2H), 8.39 (d, $J=8.5$ Hz, further ill-split, 1H), 8.93 (dd, $J_1=4.5$ Hz, $J_2=1.5$ Hz, 1H), 10.54 (s, 1H); ^{13}C NMR δ 121.9, 124.6, 128.0, 128.7 (2 $\times$), 129.3 (2 $\times$), 129.8, 132.6, 133.0, 151.4 (all Ar-CH), 125.1, 135.0, 135.1, 149.0, 167.2 (all Ar-C); GC-EI MS (RT=21.74 min) m/z (%) 248 (M^+), 105 (100), 77, 51. Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$: C, 77.42; H, 4.84; N, 11.29. Found: C, 77.37; H, 4.85; N, 11.31.

6-Benzamidobenzothiazole (23c). Yield 0.254 g (100%); white needles (from PE/EA); mp 189–190 °C; IR (nujol) 3277, 1646, 1563, 1513, 1281, 897, 866, 824, 791 cm^{-1} ; ^1H NMR (DMSO- d_6) δ 7.54 (t, $J=7$ Hz, 2H), 7.59 (dt, $J_1=7$ Hz, $J_2=1.5$ Hz, 1H), 7.83 (dd, $J_1=9$ Hz, $J_2=2$ Hz, 1H), 7.99 (d, $J=7$ Hz, 2H), 8.06 (d, $J=8.5$ Hz, 1H), 8.70 (d, $J=2$ Hz, 1H), 9.28 and 10.51 (s, 1H each); ^{13}C NMR δ 113.8, 120.8, 123.7, 128.6 (2 $\times$), 129.3 (2 $\times$), 132.5, 155.7 (all Ar-CH), 134.9, 135.7, 137.8, 150.3, 166.6 (all Ar-C); GC-EI MS (RT=22.29 min) m/z (%) 254 (M^+), 105 (100), 77, 51. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}$: C, 66.14; H, 3.93; N, 11.02. Found: C, 66.24; H, 3.94; N, 11.06.

***N*-(5-isoquinolinyl/quinolinyl)thioamides (24b-d, 25b-d) and *N*-(6-benzothiazolyl)thioamides (26b,c)**

5-(Thiopropionamido)isoquinoline (24b). Eluted with PE/EA (83:17); yield 0.196 g (90%); light brown crystals (from EA/MeOH); mp 157–158 °C (dec.); IR 3145, 1624, 1595, 1541, 1401,

1371, 1280, 1174, 1152, 1031, 829, 755, 714 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 1.38 (t, $J=7.5$ Hz, 3H), 2.91 (q, $J=7.5$ Hz, 2H), 7.64 (d, further ill-split, $J=6$ Hz, 1H), 7.72 (t, $J=7.5$ Hz, 1H), 7.77 (d, $J=7.5$ Hz, 1H), 8.10 (d, $J=8$ Hz, 1H), 8.52 (d, $J=6$ Hz, 1H), 9.37 (d, $J=1$ Hz, 1H), 11.69 (s, 1H); ^{13}C NMR δ 15.0 (CH_3), 39.5 (CH_2), 116.7, 128.02, 128.05, 130.0, 143.9, 153.6 (all Ar-CH), 129.7, 132.2, 135.8, 209.9 (all Ar-C); GC EI-MS (RT=18.53 min) m/z (%) 216 (M^+), 183, 161 (100), 144, 117. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$: C, 66.66; H, 5.55; N, 12.96. Found: C, 66.61; H, 5.53; N, 12.99.

5-(Thio-*i*-butyramido)isoquinoline (24c). Eluted with PE/EA (7:3); yield 0.225 g (98%); light brown crystals (from PE/EA); mp 181–182 $^{\circ}\text{C}$; IR 3132, 1625, 1594, 1543, 1494, 1407, 1376, 1300, 1242, 1021, 821, 755, 707 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.47 (d, $J=6.5$ Hz, 6H), 3.21 (septet, $J=6.5$ Hz, 1H), 7.56 (d, $J=5.5$ Hz, 1H), 7.63 (t, $J=8$ Hz, 1H), 7.85 (d, $J=7$ Hz, 1H), 7.94 (d, $J=7.5$ Hz, 1H), 8.49 (d, $J=5.5$ Hz, 1H), 9.25 (s, 1H), 9.33 (br s, 1H); ^{13}C NMR δ 23.4 ($2\times\text{CH}_3$), 45.3 (aliphatic-CH), 115.6, 127.4, 128.2, 129.8, 143.8, 153.3 (all Ar-CH), 129.6, 132.4, 134.4, 214.8 (all Ar-C); GC EI-MS (RT=18.71 min) m/z (%) 230 (M^+), 229, 197, 161 (100), 155, 144, 117. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{S}$: C, 67.82; H, 6.08; N, 12.17; found: C, 67.84; H, 6.09; N, 12.14.

5-(Thiobenzamido)isoquinoline (24d). Eluted with PE/EA (7:3); yield 0.255 g (96%); yellow prisms (from PE/EA); mp 205–206 $^{\circ}\text{C}$ (dec.); IR 3140, 1594, 1558, 1443, 1389, 1352, 1255, 1238, 1049, 984, 882, 820, 766, 715 cm^{-1} ; ^1H NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$) δ 7.47 (t, $J=7$ Hz, 2H), 7.54 (t, $J=7$ Hz, 1H), 7.69 (t, $J=7.5$ Hz, 1H), 7.73 (d, $J=5.5$ Hz, 1H), 7.89 (d, $J=7$ Hz, 1H), 7.99 (d, $J=8$ Hz, 1H), 8.07 (d, $J=7$ Hz, 2H), 8.50 (d, $J=6$ Hz, 1H), 9.28 and 11.12 (s, 1H each); ^{13}C NMR δ 116.3, 127.4, 127.9 ($3\times$), 128.6 ($2\times$), 129.7, 131.7, 143.7, 153.2 (all Ar-CH), 129.6, 132.4, 135.9, 142.0 (all Ar-C), 201.8 ($\text{C}=\text{S}$); GC EI-MS (RT=22.88 min) m/z (%) 264 (M^+), 231, 161 (100), 121, 77, 51. Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}$: C, 72.72; H, 4.54; N, 10.60; found: C, 72.78; H, 4.55; N, 10.63.

5-(Thiopropionamido)quinoline (25b). Yield 0.179 g (83%); light brown prisms (from PE/EA/MeOH); mp 121–122 $^{\circ}\text{C}$ (dec.); IR (nujol) 3118, 1614, 1595, 1574, 1540, 1500, 1462, 1397, 1374, 1306, 1177, 1152, 1141, 1087, 1052, 1017, 976, 804, 718 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$) δ 1.38 (t, $J=7.5$ Hz, 3H), 2.90 (q, $J=7.5$ Hz, 2H), 7.55 (dd, $J_1=8$ Hz, $J_2=4.5$ Hz, 1H), 7.56 (d, $J=7.5$ Hz, 1H), 7.79 (t, $J=8$ Hz, 1H), 8.0 and 8.18 (d, $J=8$ Hz, 1H each), 8.92 (dd, $J_1=4.5$ Hz, $J_2=1.5$ Hz), 11.69 (br s, 1H); ^{13}C NMR δ 15.0 (CH_3), 39.5 (CH_2), 122.3, 126.1, 129.3, 129.8, 132.5, 151.6 (all Ar-CH), 125.0, 136.9, 149.0, 209.9 (all Ar-C); GC-EI MS (RT=18.30 min) m/z (%) 216 (M^+), 183, 161 (100), 144, 128, 117. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$: C, 66.67; H, 5.56; N, 12.96. Found: C, 66.72; H, 5.55; N, 12.94.

5-(Thio-*n*-butyramido)quinoline (25c). Yield 0.202 g (88%); pale brown flakes (from PE/EA/MeOH); mp 112–114 $^{\circ}\text{C}$ (dec.); IR 3114, 1618, 1594, 1575, 1533, 1501, 1470, 1429, 1388, 1316, 1203, 1180, 1147, 1056, 805, 734, 718 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.07 (t, $J=7.5$ Hz, 3H), 1.97 (sextet, $J=7.5$ Hz, 2H), 2.91 (t, $J=7.5$ Hz, 2H), 7.37 (dd, $J_1=8.5$ Hz, $J_2=4$ Hz, 1H), 7.53 (d, $J=7.5$ Hz, 1H), 7.67 (t, $J=8$ Hz, 1H), 8.03 and 8.10 (d, $J=8.5$ Hz, 1H each), 8.86 (dd, $J_1=4$ Hz, $J_2=1.5$ Hz, 1H), 9.49 (s, 1H); ^{13}C NMR δ 13.9 (CH_3), 23.6, 49.6 (both CH_2), 121.8, 126.0, 129.4,

130.1, 131.7, 151.0 (all Ar-CH), 125.0, 135.4, 148.9, 209.0 (all Ar-C); GC-EI MS (RT=18.99 min) m/z (%) 230 (M^+), 197, 161 (100), 144, 128, 117. Anal. Calcd for $C_{13}H_{14}N_2S$: C, 67.83; H, 6.09; N, 12.17. Found: C, 67.91; H, 6.10; N, 12.15.

5-(Thiobenzamido)quinoline (25d). Yield 0.245 g (93%); chrome yellow needles (from PE/EA/MeOH); mp 110–112 °C (dec.); IR (nujol) 3131, 1593, 1533, 1228, 1029, 983, 804, 724 cm^{-1} ; 1H NMR (DMSO- d_6) δ 7.52 (t, $J=7.5$ Hz, 2H), 7.56 (dd, $J_I=8.5$ Hz, $J_2=4.5$ Hz, 1H), 7.59 (t, $J=7.5$ Hz, further ill-split, 1H), 7.65 (dd, $J_I=7.5$ Hz, $J_2=0.5$ Hz, 1H), 7.84 (dd, $J_I=8.5$ Hz, $J_2=7.5$ Hz, 1H), 8.04 (dd, $J_I=7.5$ Hz, $J_2=1$ Hz, 2H), 8.05 (d, $J=8.5$ Hz, 1H), 8.25 (d, $J=8$ Hz, 1H), 8.94 (dd, $J_I=4.5$ Hz, $J_2=1.5$ Hz, 1H), 11.99 (s, 1H); ^{13}C NMR δ 122.5, 126.4, 128.5 (2 $\times$), 129.0 (2 $\times$), 129.6, 130.0, 132.1, 132.7, 151.6 (all Ar-CH), 125.1, 137.6, 141.9, 149.1, 201.4 (all Ar-C); LR EI-MS m/z (%) 264 (M^+), 263, 231, 161, 128, 121 (100), 77, 51; HR EI-MS m/z calcd for $C_{16}H_{12}N_2S$, 264.0721; found 264.0717.

6-(Thiopropionamido)benzothiazole (26b). Eluted with PE/EA (4:1); yield 0.157 g (71%); yellow leaflets (from EA/MeOH); mp 210–212 °C; IR 3230, 1581, 1537, 1477, 1388, 1299, 1248, 1218, 1153, 1127, 1070, 917, 869, 831, 740 cm^{-1} ; 1H NMR (DMSO- d_6) δ 1.28 (t, $J=7.5$ Hz, 3H), 2.77 (q, $J=7.5$ Hz, 2H), 7.74 (dd, $J_I=8.5$ Hz, $J_2=2$ Hz, 1H), 8.08 (d, $J=8.5$ Hz, 1H), 8.76 (d, $J=2$ Hz, 1H), 9.36 and 11.70 (s, 1H each); ^{13}C NMR δ 14.9 (CH_3), 40.8 (CH_2), 114.2, 117.5, 123.5, 157.3 (all Ar-CH), 134.4, 137.9, 151.7, 206.8 (all Ar-C); LR EI-MS m/z (%) 222 (M^+ ; 100), 221, 193, 189, 167, 150, 134, 73; HR EI-MS m/z calcd for $C_{10}H_{10}N_2S_2$, 222.0286; found 222.0284.

6-(Thiobenzamido)benzothiazole (26c). Eluted with PE/EA (17:3); yield 0.2 g (74%); yellow needles (from EA/MeOH); mp 148–150 °C; IR 3298, 3048, 1595, 1500, 1445, 1353, 1250, 1119, 1028, 999, 828, 771, 743, 715 cm^{-1} ; 1H NMR (DMSO- d_6) δ 7.47 (t, $J=7.5$ Hz, 2H), 7.53 (t, $J=7.5$ Hz, 1H), 7.84–7.87 (m, 1H), 7.86 (d, $J=7.5$ Hz, 1H), 8.13 (d, $J=9$ Hz, 1H), 8.71, 9.39 and 11.95 (s, 1H each); ^{13}C NMR δ 118.6, 123.6, 124.5, 128.3 (2 $\times$), 128.9 (2 $\times$), 131.7, 157.5 (all Ar-CH), 134.4, 138.4, 143.3, 151.9, 199.0 (all Ar-C); LR EI-MS m/z (%) 270 (M^+), 269, 237, 167, 121 (100), 77, 51; HR EI-MS m/z calcd for $C_{14}H_{10}N_2S_2$, 270.0285; found 270.0284.

2-Alkyl/phenylthiazolo[4,5-*f*]isoquinolines (27b-d), -thiazolo[4,5-*f*]quinolines (28b-d) and benzo [1,2-*d*:4,3-*d'*]bisthiazoles (29b,c)

2-Ethylthiazolo[4,5-*f*]isoquinoline (27b). Yield 0.21 g (98%); cream coloured crystals (from PE/DCM); mp 70–71 °C; IR 1614, 1550, 1500, 1425, 1372, 1317, 1177, 1146, 1030, 959, 904, 831, 809, 772 cm^{-1} ; 1H NMR (CDCl $_3$) δ 1.54 (t, $J=7.5$ Hz, 3H), 3.27 (q, $J=7.5$ Hz, 2H), 7.85 (dd, $J_I=8.5$ Hz, $J_2=0.5$ Hz, 1H), 7.97 (d, $J=8.5$ Hz, 1H), 8.50 (dt, $J_I=6$ Hz, $J_2=1$ Hz, 1H), 8.71 (d, $J=5.5$ Hz, 1H), 9.32 (d, $J=1$ Hz, 1H); ^{13}C NMR δ 14.4 (CH_3), 28.2 (Ar- CH_2), 117.0, 120.9, 124.3, 144.8, 152.3 (all Ar-CH), 127.3, 131.6, 136.1, 148.2, 174.3 (all Ar-C); LR EI-MS m/z (%) 214 (M^+ ; 100), 213, 199; HR EI-MS m/z calcd for $C_{12}H_{10}N_2S$ (M^+), 214.0564; found 214.0567.

2-*i*-Propylthiazolo[4,5-*f*]isoquinoline (27c). Eluted with PE/EA (9:1); yield 0.206 g (90%); colourless liquid; IR (neat) 1618, 1552, 1504, 1462, 1371, 1305, 1194, 1031, 911, 836, 806, 774

cm^{-1} ; ^1H NMR (CDCl_3) δ 1.55 (d, $J=7$ Hz, 6H), 3.55 (septet, $J=7$ Hz, 1H), 7.85 and 7.99 (d, $J=8.5$ Hz, 1H each), 8.52 and 8.71 (d, $J=5.5$ Hz, 1H each), 9.32 (s, 1H); ^{13}C NMR δ 23.5 ($2\times\text{CH}_3$), 34.6 (CH), 117.1, 121.0, 124.3, 144.6, 152.2 (all Ar-CH), 127.3, 131.7, 135.8, 148.1, 179.4 (all Ar-C); GC EI-MS (RT=17.38 min) m/z (%) 228 (M^+), 213 (100), 160. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$: C, 68.42; H, 5.26; N, 12.28. Found: C, 68.47; H, 5.24; N, 12.24.

2-Phenylthiazolo[4,5-*f*]isoquinoline (27d). Yield 0.25 g (95%); cream coloured crystals (from PE/EA); mp 140 °C; IR 1618, 1550, 1472, 1444, 1369, 1252, 1030, 979, 910, 873, 833, 804, 759 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.48-7.55 (m, 3H), 7.88 and 8.02 (d, $J=8.5$ Hz, 1H each), 8.14-8.20 (m, 2H), 8.61 and 8.74 (d, $J=5.5$ Hz, 1H each), 9.33 (s, 1H); ^{13}C NMR δ 117.2, 120.9, 124.9, 127.8 ($2\times$), 129.5 ($2\times$), 131.4, 145.0, 152.3 (all Ar-CH), 127.5, 132.0, 133.8, 136.2, 149.2, 168.7 (all Ar-C); GC EI-MS (RT=22.52 min) m/z (%) 262 (M^+ ; 100). Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}$: C, 73.28; H, 3.81; N, 10.68. Found: C, 73.32; H, 3.80; N, 10.71.

2-Ethylthiazolo[4,5-*f*]quinoline (28b). Yield 0.186 g (87%); cream coloured prisms (from PE/EA); mp 76–78 °C (dec.); IR 1605, 1557, 1502, 1382, 1361, 1307, 1184, 1177, 1150, 1054, 956, 900, 839, 819, 809, 763 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.53 (t, $J=7.5$ Hz, 3H, CH_2CH_3), 3.25 (q, $J=7.5$ Hz, 2H, CH_2CH_3), 7.54 (dd, $J_1=8$ Hz, $J_2=4$ Hz, 1H, H-5), 8.03 (d, further ill-split, $J=9$ Hz, 1H, H-8), 8.07 (d, $J=9$ Hz, 1H, H-9), 8.96 (dd, $J_1=4$ Hz, $J_2=1.5$ Hz, H-6), 9.05 (ddd, $J_1=8.5$ Hz, $J_2=1.5$ Hz, $J_3=0.5$ Hz, 1H, H-4); ^{13}C NMR δ 14.5 (CH_3), 28.2 (CH_2), 121.9 (CH-5), 122.6 (CH-9), 124.0 (C-3b), 126.8 (CH-8), 132.1 (C-9a), 132.4 (CH-4), 147.7 (C-7a), 149.3 (C-3a), 150.2 (CH-6), 174.6 (C-2); GC-EI MS (RT=16.60 min) m/z (%) 214 (M^+ ; 100), 213, 199, 155. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}$: C, 67.29; H, 4.67; N, 13.08. Found: C, 67.21; H, 4.68; N, 13.10.

2-*n*-Propylthiazolo[4,5-*f*]quinoline (28c). Yield 0.221 g (97%); cream coloured needles (from PE/EA); mp 85–87 °C; IR 1605, 1558, 1501, 1359, 1185, 1173, 1152, 1068, 906, 833, 818, 769 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.10 (t, $J=7.5$ Hz, 3H), 1.97 (sextet, $J=7.5$ Hz, 2H), 3.19 (t, $J=7.5$ Hz, 2H), 7.55 (dd, $J_1=8.5$ Hz, $J_2=4.5$ Hz, 1H), 8.03 and 8.08 (d, $J=9$ Hz, 1H each), 8.96 (dd, $J_1=4.5$ Hz, $J_2=1.5$ Hz, 1H), 9.06 (dd, $J_1=8.5$ Hz, $J_2=1$ Hz, 1H); ^{13}C NMR δ 14.1 (CH_3), 23.7, 36.7 (both CH_2), 121.9, 122.6, 126.8, 132.5, 150.2 (all Ar-CH), 124.0, 132.2, 147.7, 149.3, 173.2 (all Ar-C); GC-EI MS (RT=17.38 min) m/z (%) 228 (M^+), 213, 201, 200 (100), 199. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$: C, 68.42; H, 5.26; N, 12.28. Found: C, 68.51; H, 5.25; N, 12.31.

2-Phenylthiazolo[4,5-*f*]quinoline (28d). Yield 0.233 g (89%); white globules (from PE/EA); mp 138–140 °C; IR (nujol) 1607, 1559, 1069, 973, 908, 825, 809, 759 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.47-7.53 (m, 3H), 7.56 (dd, $J_1=8$ Hz, $J_2=4$ Hz, 1H), 8.05 (dd, $J_1=9$ Hz, $J_2=0.5$ Hz, 1H), 8.11 (d, $J=9$ Hz, 1H), 8.13-8.18 (m, 2H), 8.98 (dd, $J_1=4$ Hz, $J_2=1.5$ Hz, 1H), 9.15 (ddd, $J_1=8$ Hz, $J_2=1.5$ Hz, $J_3=0.5$ Hz, 1H); ^{13}C NMR δ 122.1, 122.6, 127.4, 127.7 ($2\times$), 129.5 ($2\times$), 131.3, 132.7, 150.46 (all Ar-CH), 124.4, 132.3, 134.0, 148.0, 150.42, 168.9 (all Ar-C); LR EI-MS m/z (%) 262 (M^+ ; 100), 159; HR EI-MS m/z calcd for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}$, 262.0565; found 262.0571.

2-Ethylbenzo[1,2-*d*:4,3-*d'*]bisthiazole (29b). Yield 0.21 g (95%); white needles (from PE/DCM); mp 133–135 °C; IR 1582, 1500, 1454, 1398, 1386, 1286, 1176, 1097, 976, 834, 818,

781, 740 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.51 (t, $J=7.5$ Hz, 3H, CH_2CH_3), 3.20 (q, $J=7.5$ Hz, 2H, CH_2CH_3), 8.07 and 8.17 (d, $J=8.5$ Hz, 1H each, H-4 and H-5, respectively), 8.99 (s, 1H, H-7); ^{13}C NMR δ 14.2 (CH_3), 28.1 (CH_2), 121.4 (CH-4), 121.9 (CH-5), 127.0 (C-8a), 128.1 (C-8b), 151.6 (C-5a), 152.0 (C-3a), 152.8 (CH-7), 173.4 (C-2); LR EI-MS m/z (%) 220 (M^+ ; 100), 219, 205; HR EI-MS m/z calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{S}_2$, 220.0129; found 220.0125.

2-Phenylbenzo[1,2-*d*:4,3-*d'*]bisthiazole (29c). Yield 0.25 g (93%); yellow needles (from PE/DCM); mp 158–160 $^\circ\text{C}$; IR 1576, 1513, 1479, 1402, 1334, 1286, 837, 825, 752 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.48–7.50 (m, 3H), 8.06–8.08 (m, 2H), 8.15 and 8.19 (d, $J=9$ Hz, 1H each), 8.99 (s, 1H); ^{13}C NMR δ 122.0, 122.4, 127.9 (2 $\times$), 129.5 (2 $\times$), 131.5, 153.1 (all Ar-CH), 127.0, 128.2, 133.6, 151.9, 152.9, 168.0 (all Ar-C); LR EI-MS m/z (%) 268 (M^+ ; 100); HR EI-MS m/z calcd for $\text{C}_{14}\text{H}_8\text{N}_2\text{S}_2$, 268.0129; found 268.0124.

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