Supporting Information

Synthesis of 1,4-dithiins from pentathiepins

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Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Specord M-80 instrument in KBr pellets. ¹H NMR were recorded on a Bruker WM 250 spectrometer (250 MHz) and ¹³C NMR spectra were recorded on a Bruker AM 300 (75.5 MHz) in CDCl₃ solution. J-values are given in Hz. Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument using electron impact ionisation.

General procedure for the preparation of 1,4-dithiins. A solution of triphenylphosphine (4 mmol) in dichloromethane (3 ml) was added dropwise to a stirred solution of appropriate pentathiepin (1 mmol) and appropriate alkyne (3 mmol) in dichloromethane (10 ml) at room temperature. The reaction mixture was stirred for 1 h, solvent was evaporated under reduced pressure, and the corresponding dithiin was separated by column chromatography (Silica gel Merck 60).

Dimethyl 5-methyl-5H-[1,4]dithiino[2,3-*b*]pyrrole-2,3-dicarboxylate 4 Yield 83%. Orange crystals, mp 60-62 °C. Found (%): C, 46.18; H, 3.95; N, 4.73. Calc. for C₁₁H₁₁NO₄S₂ (%): C, 46.30; H, 3.89; N, 4.91. Found M⁺, 285.0130; C₁₁H₁₁NO₄S₂ requires M, 285.0123. ¹H NMR (CDCl₃) δ: 3.81 (6H, s, 2CH₃), 3.82 (3H, s, CH₃), 6.00 (1H, d, CH, J 2.8), 6.79 (1H, d, CH, J 2.8). ¹³C NMR (CDCl₃) δ: 34.7 (CH₃), 52.6 (CH₃), 53.2 (CH₃), 107.8 and 127.4 (2 CH), 111.0, 118.4, 131.3 and 140.3 (4 sp² tertiary C), 164.1 and 165.3 (C=O). IR, (KBr) ν/cm⁻¹: 3212, 3096, 3016, 2984, 2376, 1732, 1568, 1488, 1312, 1296, 1204, 1044, 1008, 904, 848, 808, 760, 736, 720, 696, 652. MS, m/z (%): 285 (M⁺, 100), 270 (25), 254 (40), 226 (70), 168 (40), 155(50).

Dimethyl thieno[2,3-*b*][1,4]dithiin-2,3-dicarboxylate 6 Yield 88%. Orange oil. Found

(%): C, 41.44; H, 2.72. Calc. $C_{10}H_8O_4S_3$ for (%): C, 41.65; H, 2.80. Found M^+ , 287.9587; $C_{10}H_8O_4S_3$ requires M , 287.9585. 1H NMR ($CDCl_3$) δ : 3.83 (3H, s, CH_3), 3.84 (3H, s, CH_3), 6.83 (1H, d, CH, J 5.2), 7.40 (1H, d, CH, J 5.2). ^{13}C NMR ($CDCl_3$) δ : 53.4 (CH_3), 126.3 and 130.1 (2 CH), 127.8, 130.4, 133.4 and 137.7 (4 sp^2 tertiary C), 162.4 and 163.3 (2 C=O). IR, (KBr) ν/cm^{-1} : 3096, 3048, 3008, 2984, 1724, 1572, 1496, 1416, 1252, 1088, 1072, 1008, 888, 760, 752, 732, 720, 672, 664. MS, m/z (%): 288 (M^+ , 100), 257 (35), 229 (33), 199 (50), 171 (30), 158(40).

Dimethyl 5,7-dichloro-6-methyl-6H-[1,4]dithiino[2,3-c]pyrrole-2,3-dicarboxylate 8a

Yield 85%. Yellow crystals, mp 113-116 °C. Found (%): C, 37.17; H, 2.46; N, 3.74. Calc. for $C_{11}H_9Cl_2NO_4S_2$ (%): C, 37.30; H, 2.56; N, 3.95. Found M^+ , 352.9359; $C_{11}H_9Cl_2NO_4S_2$ requires M , 352.9350. 1H NMR ($CDCl_3$) δ : 3.49 (3H, s, CH_3), 3.82 (6H, s, 2 CH_3). ^{13}C NMR ($CDCl_3$) δ : 32.0 (CH_3), 53.3 (CH_3), 106.4, 112.9 and 133.3 (3 sp^2 tertiary C), 163.3 (C=O). IR, (KBr) ν/cm^{-1} : 2952, 1724, 1608, 1532, 1460, 1308, 1248, 1156, 1052, 1012, 992, 904, 752, 704, 652. MS, m/z (%): 357 ($M^+ + 4$, 10), 355 ($M^+ + 2$, 40), 353 (M^+ , 65), 318 (100), 294 (35), 277 (43), 168 (40), 183(46).

Dimethyl 5,7-dichloro-6-isopropyl-6H-[1,4]dithiino[2,3-c]pyrrole-2,3-dicarboxylate 8b

Yield 92%. Yellow oil. Found (%): C, 40.65; H, 3.34; N, 3.85. Calc. for $C_{13}H_{13}Cl_2NO_4S_2$ (%): C, 40.84; H, 3.43; N, 3.66. Found M^+ , 380.9663; $C_{13}H_{13}Cl_2NO_4S_2$ requires M , 380.9663. 1H NMR ($CDCl_3$) δ : 1.53 (6H, d, CH_3 , J 6.9), 3.82 (6H, s, 2 CH_3), 4.66 (1H, sept, CH, J 6.9). ^{13}C NMR ($CDCl_3$) δ : 21.1 (CH_3), 50.7 (CH), 53.3 (CH_3), 106.9, 111.9 and 131.3 (4 sp^2 tertiary C), 163.4 (C=O). IR, (KBr) ν/cm^{-1} : 2992, 2968, 1740, 1556, 1460, 1256, 1104, 1072, 1012, 908, 760, 736, 720, 660. MS, m/z (%): 385 ($M^+ + 4$, 10), 383 ($M^+ + 2$, 60), 381 (M^+ , 65), 339 (40), 304 (38), 274 (45), 272 (100).

Dimethyl 5-methyl-5H-[1,4]dithiino[2,3-b]indole-2,3-dicarboxylate 10

Yield 89%. Red crystals, mp 124-126 °C. Found (%): C, 53.54; H, 3.80; N, 4.46. Calc. for $C_{15}H_{13}NO_4S_2$ (%): C, 53.72; H, 3.91; N, 4.18. Found M^+ , 335.0286; $C_{15}H_{13}NO_4S_2$ requires M , 335.0286. 1H NMR ($CDCl_3$) δ : 3.72 (3H, s, CH_3), 3.85 (3H, s, CH_3), 3.87 (3H, s, CH_3), 7.17 (1H, d J 7.9, Ar), 7.25 (2H, dd J 7.9 and 3.3, Ar), 7.46 (1H, d J 7.9, Ar). ^{13}C NMR ($CDCl_3$) δ : 30.7 (CH_3), 53.3 (2 CH_3); 109.8, 117.6, 120.7 and 122.7 (4 CH); 102.4, 124.8, 128.0, 130.1, 140.5 and 140.6 (6 sp^2 tertiary C); 162.4 and 163.9 (C=O). IR, (KBr) ν/cm^{-1} : 3412, 3012, 2956, 1740, 1716, 1568, 1464, 1436, 1324, 1260, 1240, 1236, 1072, 1000, 984, 968, 900, 752, 740, 680. MS, m/z (%): 335 (M^+ , 85), 276 (100), 248 (10), 218 (15), 205 (40).

Tetramethyl 5-isopropyl-5H-bis[1,4]dithiino[2,3-b:2',3'-d]pyrrole-2,3,7,8-

tetracarboxylate 12 Yield 78%. Red crystals, mp 92-93 °C. Found (%): C, 44.34; H, 3.82; N,

2.49. Calc. for $C_{19}H_{19}NO_8S_4$ (%): C, 44.09; H, 3.70; N, 2.71. Found M^+ , 516.9970; $C_{19}H_{19}NO_8S_4$ requires M , 516.9993. 1H NMR ($CDCl_3$) δ : 1.57 (6H, d, 2 CH_3 , J 7.2), 3.92 (12H, s, 4 CH_3), 4.51 (1H, sept, CH, J 7.2). ^{13}C NMR ($CDCl_3$) δ : 21.2 (CH_3), 50.3 (CH), 53.2

(CH₃), 112.3, 118.2, 133.8 and 142.9 (4 sp² tertiary C), 162.4 and 165.6 (C=O). IR, (KBr) ν/cm^{-1} : 2980, 2970, 1730, 1580, 1480, 1320, 1300, 1220, 1050, 1000, 900, 850, 810, 760, 730, 710, 650. MS, m/z (%): 517 (M⁺, 16), 474 (15), 348 (30), 316 (20), 285 (100).

Dimethyl 1,4-benzodithiin-2,3-dicarboxylate 14 Yield 83%. Yellow oil. Found (%): C, 50.84; H, 3.78. Calc. for C₁₂H₁₀O₄S₂ (%): C, 51.05; H, 3.57. Found M⁺, 282.0027; C₁₂H₁₀O₄S₂ requires M, 282.0021. ¹H NMR (CDCl₃) δ : 3.67 (6H, s, 2CH₃), 7.11 (2H, m, Ar), 7.22 (2H, m, Ar). ¹³C NMR (CDCl₃) δ : 53.2 (2CH₃); 128.7, 128.7 (2 CH); 133.2 and 135.4 (2 sp² tertiary C); 163.0 (C=O). IR, (KBr) ν/cm^{-1} : 3056, 3000, 2952, 2928, 2848, 1736, 1728, 1720, 1580, 1556, 1452, 1432, 1256, 1080, 1008, 904, 752, 688. MS, m/z (%): 282 (M⁺, 100), 251 (30), 193 (60), 152 (70).

(3-Benzoyl-thieno[2,3-*b*][1,4]dithiin-2-yl)-phenyl-methanone 16 Yield 64%. Yellow crystals, mp 128-130 °C. Found (%): C, 62.98; H, 3.30. Calc. C₂₀H₁₂O₂S₃ for (%): C, 63.13; H, 3.18. Found M⁺, 379.9989; C₂₀H₁₂O₂S₃ requires M, 379.9999. ¹H NMR (CDCl₃) δ : 6.93 (1H, d, J 5.3 CH), 7.36 (4H, m, Ar, J 7.2), 7.48 (1H, d, J 5.3 CH), 7.53 (2H, t, Ar, J 7.2), 7.68 (4H, t, Ar, J 7.2). ¹³C NMR (CDCl₃) δ : 126.3, 128.4, 129.3, 130.1 and 133.7 (5 CH); 128.2, 131.4, 132.9, 135.2, 140.9 and 144.0 (6 sp² tertiary C), 189.0 and 189.8 (C=O). IR, (KBr) ν/cm^{-1} : 2924, 2856, 1664, 1656, 1552, 1448, 1252, 1084, 960, 796, 716, 684. MS, m/z (%): 380 (M⁺, 70), 275 (15), 105 (100), 77(50).

(3-Benzoyl-5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrol-2-yl)-phenyl-methanone 17 Yield 77%. Yellow crystals, mp 193-196 °C. Found (%): C, 56.33; H, 2.85; N, 3.37. Calc. for C₂₁H₁₃Cl₂NO₂S₂ (%): C, 56.51; H, 2.94; N, 3.14. Found M⁺, 444.9763; C₂₁H₁₃Cl₂NO₂S₂ requires M, 444.9765. ¹H NMR (CDCl₃) δ : 3.57 (3H, s, CH₃), 7.36 (4H, dd, Ar, J 7.9 and 7.2), 7.52 (2H, t, Ar, J 7.9), 7.71 (4H, d, Ar, J 7.2). ¹³C NMR (CDCl₃) δ : 32.2 (CH₃); 128.5, 129.6 and 133.74 (CH); 108.8, 135.7, 140.2 and 157.7 (4 sp² tertiary C), 190.6 (C=O). IR, (KBr) ν/cm^{-1} : 2920, 2852, 1672, 1660, 1596, 1536, 1476, 1448, 1240, 1120, 1096, 808, 752, 692, 660, 644. MS, m/z (%): 449 (M⁺ + 4, 2), 447 (M⁺ + 2, 12), 445 (M⁺, 20), 105(100), 77 (85).

(2-Benzoyl-9-methyl-9*H*-1,4-dithia-9-aza-fluoren-3-yl)-phenyl-methanone 18 Yield 93%. Red crystals, mp 191-193 °C. Found (%): C, 70.05; H, 3.88; N, 3.47. Calc. for C₂₅H₁₇NO₂S₂ (%): C, 70.23; H, 4.01; N, 3.28. Found M⁺, 427.0713; C₂₅H₁₇NO₂S₂ requires M, 427.0701. ¹H NMR (CDCl₃) δ : 3.78 (3H, s, CH₃), 7.20 (1H, m, Ar), 7.34 (6H, m, Ar), 7.53 (3H, m, Ar), 7.69 (4H, m, Ar). ¹³C NMR (CDCl₃) δ : 30.8 (CH₃); 109.9, 117.8, 120.7, 122.8, 128.4, 129.3 and 133.8 (7 CH); 105.2, 124.9, 130.0, 135.2, 135.5, 138.2, 140.5 and 146.6 (8 sp² tertiary C); 190.2 and 190.5 (C=O). IR, (KBr) ν/cm^{-1} : 3112, 3090, 2940, 2356, 1668, 1656, 1596, 1556, 1460, 1448, 1340, 1316, 1240, 1180, 1012, 800, 748, 720, 692, 648. MS, m/z (%): 427 (M⁺, 10), 322 (10), 105 (100), 77 (50).

(3-Benzoyl-benzo[1,4]dithiin-2-yl)-phenyl-methanone 19 Yield 88%. Yellow crystals,

mp 157-159 °C. Found (%): C, 70.39; H, 3.65. Calc. for $C_{22}H_{14}O_2S_2$ (%): C, 70.56; H, 3.77. Found M^+ , 374.0420; $C_{22}H_{14}O_2S_2$ requires M , 374.0435. 1H NMR ($CDCl_3$) δ : 7.37 (4H, m, Ar), 7.50 (6H, m, Ar), 7.69 (4H, m, Ar). ^{13}C NMR ($CDCl_3$) δ : 128.6, 128.9, 129.5, 132.3 and 133.8 (5 CH); 132.4, 134.4 and 142.5 (3 sp^2 tertiary C); 190.3 (C=O). IR, (KBr) ν/cm^{-1} : 3056, 3004, 2960, 2928, 2856, 2324, 1732, 1660, 1532, 1448, 1436, 1304, 1284, 1244, 1100, 1020, 804, 760, 692, 660. MS, m/z (%): 374 (M^+ , 24), 269 (10), 105 (100), 77 (80).

Methyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate 20 Yield 50%. Yellow oil. Found (%): C, 47.34; H, 3.82, N, 6.45. Calc. for $C_9H_9NO_2S_2$ (%): C, 47.56; H, 3.99, N, 6.16. 1H NMR ($CDCl_3$) δ : 3.51 (3H, s, CH_3), 3.80 (3H, s, CH_3), 5.92 (H, d, $J = 2.9$, CH), 6.71 (H, d, $J = 2.9$, CH), 7.34 (1H, s, CH). ^{13}C NMR ($CDCl_3$) δ : 30.3 (CH_3), 53.5 (CH_3), 108.4, 126.7 and 132.0 (3 CH), 109.8, 115.0 and 129.5 (3 sp^2 tertiary C), 163.0 (C=O). IR, (KBr) ν/cm^{-1} : 3030, 2950, 2930, 1720, 1560, 1500, 1440, 1310, 1280, 1230, 1050, 910, 820, 730, 720. MS, m/z (%): 227 (M^+ , 100), 212 (18), 195 (20), 183 (46).

Methyl 6-chloro-5-ethyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate 22 Yield 36%. Yellow oil. Found (%): C, 43.45; H, 3.87, N, 5.33. Calc. for $C_{10}H_{10}ClNO_2S_2$ (%): C, 43.55; H, 3.65, N, 5.08. 1H NMR ($CDCl_3$) δ : 1.29 (3H, t, $J = 7.2$, CH_3), 3.80 (3H, s, CH_3), 3.89 (2H, q, $J = 7.2$, CH_2), 5.92 (1H, s, CH), 7.40 (1H, s, CH). ^{13}C NMR ($CDCl_3$) δ : 15.7 (CH_3), 40.3 (CH_2), 52.7 (CH_3), 106.4 and 131.5 (2 CH), 112.8, 118.7, 129.0 and 130.7 (4 sp^2 tertiary C), 162.0 (C=O). IR, (KBr) ν/cm^{-1} : 3040, 2960, 2940, 1720, 1560, 1510, 1470, 1440, 1310, 1240, 1050, 910, 730. MS, m/z (%): 275 (M^+ , 100), 240 (37), 216 (62), 188 (25), 167 (20), 149 (42).

Methyl 5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2-carboxylate 23 Yield 40%. Yellow oil. Found (%): C, 36.22; H, 2.17, N, 5.03. Calc. for $C_9H_7Cl_2NO_2S_2$ (%): C, 36.49; H, 2.38, N, 4.73. 1H NMR ($CDCl_3$) δ : 3.44 (3H, s, CH_3), 3.81 (3H, s, CH_3), 7.36 (1H, s, CH). ^{13}C NMR ($CDCl_3$) δ : 29.6 (CH_3), 52.6 (CH_3), 128.1 (CH), 102.0, 104.7, 112.6, 120.1 and 129.4 (5 sp^2 tertiary C), 162.2 (C=O). IR, (KBr) ν/cm^{-1} : 2920, 2850, 1720, 1680, 1540, 1430, 1370, 1320, 1240, 1180, 1100, 980, 790. MS, m/z (%): 295 (M^+ , 100), 260 (98), 236 (38), 219 (56), 103 (72).

Figure S1. ^1H NMR spectrum of dimethyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2,3-dicarboxylate **4** (CDCl_3).

Figure S2. ^{13}C NMR spectrum of dimethyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2,3-dicarboxylate **4** (CDCl_3).

Figure S3. ^1H NMR spectrum of dimethyl thieno[2,3-*b*][1,4]dithiin-2,3-dicarboxylate **6** (CDCl_3).

Figure S4. ^{13}C NMR spectrum of dimethyl thieno[2,3-*b*][1,4]dithiin-2,3-dicarboxylate **6** (CDCl_3).

Figure S5. ^1H NMR spectrum of dimethyl 5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2,3-dicarboxylate **8a** (CDCl_3).

Figure S6. ^{13}C NMR spectrum of dimethyl 5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2,3-dicarboxylate **8a** (CDCl_3).

Figure S7. ^1H NMR spectrum of dimethyl 5,7-dichloro-6-ethyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2,3-dicarboxylate **8b** (CDCl_3).

Figure S8. ^{13}C NMR spectrum of dimethyl 5,7-dichloro-6-ethyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2,3-dicarboxylate **8b** (CDCl_3).

Figure S9. ^1H NMR spectrum of dimethyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]indole-2,3-dicarboxylate **10** (CDCl_3).

Figure S10. ^{13}C NMR spectrum of dimethyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]indole-2,3-dicarboxylate **10** (CDCl_3).

Figure S11. ^1H NMR spectrum of tetramethyl 5-isopropyl-5*H*-bis[1,4]dithiino[2,3-*b*:2',3'-*d*]pyrrole-2,3,7,8-tetracarboxylate **12** (CDCl_3).

Figure S12. ^{13}C NMR spectrum of tetramethyl 5-isopropyl-5*H*-bis[1,4]dithiino[2,3-*b*:2',3'-*d*]pyrrole-2,3,7,8-tetracarboxylate **12** (CDCl_3).

Figure S13. ^1H NMR spectrum of dimethyl 1,4-benzodithiine-2,3-dicarboxylate **14** (CDCl_3).

Figure S14. ^{13}C NMR spectrum of dimethyl 1,4-benzodithiine-2,3-dicarboxylate **14** (CDCl_3).

Figure S15. ^1H NMR spectrum of (3-benzoyl-thieno[2,3-*b*][1,4]dithiin-2-yl)-phenyl-methanone **16** (CDCl_3).

Figure S16. ^{13}C NMR spectrum of (3-benzoyl-thieno[2,3-*b*][1,4]dithiin-2-yl)-phenyl-methanone **16** (CDCl_3).

Figure S17. ^1H NMR spectrum of (3-benzoyl-5,7-dichloro-6-methyl-6H-[1,4]dithiino[2,3-*c*]pyrrol-2-yl)-phenyl-methanone **17** (CDCl_3).

Figure S18. ^{13}C NMR spectrum of (3-benzoyl-5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrol-2-yl)-phenyl-methanone **17** (CDCl_3).

Figure S19. ^1H NMR spectrum of (2-benzoyl-9-methyl-9H-1,4-dithia-9-aza-fluoren-3-yl)-phenyl-methanone **18** (CDCl_3).

Figure S20. ^{13}C NMR spectrum of (2-benzoyl-9-methyl-9H-1,4-dithia-9-aza-fluoren-3-yl)-phenyl-methanone **18** (CDCl_3).

Figure S21. ^1H NMR spectrum of (3-benzoyl-benzo[1,4]dithiin-2-yl)-phenyl-methanone **19** (CDCl_3).

Figure S22. ^{13}C NMR spectrum of (3-benzoyl-benzo[1,4]dithiin-2-yl)-phenyl-methanone **19** (CDCl_3).

Figure S23. ^1H NMR spectrum of methyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate **20** (CDCl_3).

Figure S24. ^{13}C NMR spectrum of methyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate **20** (CDCl_3).

Figure S25. HMBC spectrum of methyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate **20** (CDCl₃).

Figure S26. ^1H NMR spectrum of methyl 6-chloro-5-ethyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate **22** (CDCl_3).

Figure S27. ^{13}C NMR spectrum of methyl 6-chloro-5-ethyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate **22** (CDCl_3).

Figure S28. HMBC spectrum of methyl 6-chloro-5-ethyl-5*H*-[1,4]dithiino[2,3-*b*]pyrrole-2-carboxylate **22** (CDCl₃).

Figure S29. ^1H NMR spectrum of methyl 5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2-carboxylate **23** (CDCl_3).

Figure S30. ^{13}C NMR spectrum of methyl 5,7-dichloro-6-methyl-6*H*-[1,4]dithiino[2,3-*c*]pyrrole-2-carboxylate **23** (CDCl_3).