Supporting Information

A facile synthesis of some 3-(benzimidazol-2-yl)- and 3,6-di(benzimidazol-2-yl)-9-ethyl-9H-carbazoles

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1. General Information, experimental procedure and characterization data

General Information

All reagents and solvents were obtained from commercial sources and appropriately purified, if necessary. The deuterated solvent (DMSO) for NMR spectroscopy was obtained from Merck. Following chemicals were obtained from Sigma Aldrich Melting points were measured using a Mel-Temp melting point apparatus and are uncorrected. Measurements IR spectra were recorded between 4000 and 650 cm⁻¹ using a Perkin Elmer Spectrum 100 FT-IR spectrometer ¹H and ¹³C NMR spectra were recorded in DMSO solution on a Varian 500 MHz spectrophotometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS)

measurements were performed on a Bruker Daltonics microTOF. High resolution mass spectra (HRMS) reported to 4 decimal places were recorded on a Agilent G6530B Accurate-Mass Q-TOF LC/MS.

Experimental procedure and characterization data

General Procedure for the preparation of mono-benzimidazoles (4-8).

A mixture of 3-carbaldehyde **2** and *o*-phenyldiamine derivatives (1:1 eq) was heated at 100 °C in DMF (4 mL) for 8 h. The reaction mixture was poured into ice-water and the resulting precipitate was filtered, washed with water and dried. The crude product was purified by flash column chromatography using dichloromethane/ethyl acetate (9:1) as eluent to afford the mono-benzimidazoles.

3-(1H-benzo[d]imidazol-2-yl)-9-ethyl-9H-carbazole (4).

This compound was obtained as a white solid; yield: 94%; m.p: 255-257 °C; IR (KBr): $\nu_{\max}$ 3648, 3049, 2977, 1628, 1599, 1488, 1470, 1439, 1403, 1374, 1346, 1328, 1150, 744 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 1.54 (s, 3H, CH_3), 4.68 (s, 2H, CH_2), 7.38 (s, 2H, aryl H), 7.47 (s, H, aryl H), 7.71 and 7.97 (m, 5H, aryl H), 8.43 (s, H, aryl H), 8.50 (s, H, aryl H), 9.18 (s, H aryl H), 13.05 (s, H, benzimidazole NH); ^{13}C NMR (DMSO): δ 13.8 (CH_3), 37.3 (CH_2), 119.0, 119.1, 120.0, 121.1, 121.9, 121.9, 122, 124.7, 126.4, 140.3, 140.6, 152.8 (aryl C and CH); Maldi (TOF); m/z 312 $[\text{M}]^+$; HRMS (ESI): Found m/z 312.1501 $[\text{M}]^+$; calculated for $\text{C}_{21}\text{H}_{17}\text{N}_3$ 312.1510.

9-ethyl-3-(6-methyl-1H-benzo[d]imidazol-2-yl)-9H-carbazole (5).

This compound was obtained as a yellow solid; yield: 90%; m.p: 286-288 °C; IR (KBr): $\nu_{\max}$ 3410, 3328, 3049, 2961, 2922, 2852, 1628, 1599, 1445, 1345, 1288, 1231, 1155, 797, 749 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 1.35 (t, 3H, $J=7.07$ Hz, CH_3), 2.44 (s, 3H, CH_3), 4.51 (q, 2H, $J=6.95$ Hz, CH_2), 7.02 (d, H, $J=7.46$ Hz, aryl H), 7.28 (t, 2H, $J=7.39$ Hz, aryl H), 7.51 (t, 2H,

$J=7.37$ Hz, aryl H), 7.65 (d, H, $J=8.18$ Hz, aryl H), 7.78 (d, H, $J=8.60$ Hz, aryl H), 8.24 (d, H, $J=7.65$ Hz, aryl H), 8.29 (dd, H, $J=1.24$ Hz, aryl H), 8.95 (s, H, aryl H), 12.6 (s, H, benzimidazole H); ^{13}C NMR (DMSO): δ 14.2, 21.8 (CH_3), 37.6 (CH_2), 109.9, 119.0, 119.1, 119.8, 120.8, 121.6, 122.6, 122.8, 124.8, 126.7, 124.8, 126.7, 140.5, 140.7 (aryl C and CH); Maldi (TOF); m/z 326 $[\text{M}]^+$; HRMS (ESI): Found m/z 326.1669 $[\text{M}]^+$; calculated for $\text{C}_{22}\text{H}_{19}\text{N}_3$ 326.1657.

9-ethyl-3-(6-methoxy-1H-benzo[d]imidazol-2-yl)-9H-carbazole (6).

This compound was obtained as a yellow solid; yield: 73%; m.p: 260-262 °C; IR (KBr): ν_{max} 3054, 2966, 2925, 1630, 1597, 1449, 1436, 1392, 1351, 1328, 1279, 1230, 1155, 1033, 796 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 1.54 (s, 3H, CH_3), 4.02 (s, 3H, OCH_3), 4.69 (s, 2H, CH_2), 7.02 (d, H, $J=0.84$ Hz, aryl H), 7.48 (d, 2H, $J=5.23$ Hz, aryl H), 7.70 (s, 2H, aryl H), 7.85 (s, H, aryl H) 7.96 (s, H, aryl H), 8.44 (t, 2H, $J=8.64$ Hz aryl H), 9.12 (s, H, aryl H), 12.5 (s, H, benzimidazole H); ^{13}C NMR (DMSO): δ 18.9 (CH_3), 37.3 (CH_2), 60.6 (OCH_3), 109.9, 114.6, 114.7, 123.5, 123.7, 124.5, 126.4, 127.4, 129.4, 131.4, 145.3, 160.7 (aryl C and CH); Maldi (TOF); m/z 342 $[\text{M}]^+$; HRMS (ESI): Found m/z 342.1623 $[\text{M}]^+$; calculated for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}$ 342.1606.

3-(6-chloro-1H-benzo[d]imidazol-2-yl)-9-ethyl-9H-carbazole (7).

This compound was obtained as a yellow solid; yield: 89%; m.p: 280-282 °C; IR (KBr): ν_{max} 3367, 3054, 2981, 2925, 2851 1628, 1599, 1492, 1467, 1449, 1343, 1328, 1230, 908, 803, 747 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 1.36 (t, 3H, $J=7.10$ Hz CH_3), 4.51 (q, 2H, $J=7.03$ Hz CH_2), 7.20 (d, H, $J=8.00$ Hz, aryl H), 7.30 (t, H, $J=7.44$ Hz, aryl H), 7.52 (t, 2H, $J=7.65$ Hz aryl H), 7.66 (t, 2H, $J=8.23$ Hz, aryl H), 7.78 (d, H, $J=8.23$ Hz, aryl H), 8.25 (d, H, $J=7.67$ Hz, aryl H), 8.30 (dd, H, $J=1.46$ Hz, aryl H), 8.97 (s, H, aryl H), 13.0 (s, H, benzimidazole H); ^{13}C NMR

(DMSO): δ 14.2 (CH₃), 37.6 (CH₂), 110.0, 119.4, 119.9, 120.9, 122.6, 122.8, 124.9, 126.8, 140.6, 141.0 (aryl C and CH); Maldi (TOF); m/z 346 [M]⁺; HRMS (ESI): Found m/z 346.1111 [M]⁺; calculated for C₂₁H₁₆ClN₃ 346.1116.

9-ethyl-3-(6-nitro-1H-benzo[d]imidazol-2-yl)-9H-carbazole (8).

This compound was obtained as a yellow solid; yield: 78%; m.p: 175-177 °C; IR (KBr): $\nu_{\max}$ 3493, 3367, 3235, 2977, 1630, 1596, 1522, 1496, 1471, 1448, 1424, 1375, 1320, 1236, 1155, 1125, 1059, 730 cm⁻¹; ¹H NMR (500 MHz, DMSO): δ 1.35 (t, 3H, J =7.06 Hz CH₃), 4.49 (q, 2H, J =6.92 Hz CH₂), 7.27 (t, H, J =7.38 Hz, aryl H), 7.52 (t, H, J =7.47 Hz, aryl H), 7.66 and 7.82 (m, 3H, aryl H), 7.81 (dd, H, J =1.82 Hz, aryl H), 8.25 and 8.43 (m, 3H, aryl H), 9.01 (s, H, aryl H); ¹³C NMR (DMSO): δ 14.2 (CH₃), 37.7 (CH₂), 109.9, 110.1, 118.1, 120.0, 120.1, 120.1, 120.9, 122.6, 122.9, 125.2, 126.9, 140.6, 141.4 (aryl C and CH); Maldi (TOF); m/z 357 [M]⁺; HRMS (ESI): Found m/z 357.1359 [M]⁺; calculated for C₂₁H₁₆N₄O₂ 357.1352.

General Procedure for the preparation of bis-benzimidazoles (9-12)

A mixture of 3,6-dicarbaldehyde **3** (1 eq) and *o*-phenyldiamine derivative (2 eq) was heated at 120 °C in DMSO (5 mL) for 24 h. The reaction mixture was poured into ice-water and the resulting precipitate was filtered, washed with water and dried. The crude product was purified by flash column chromatography using dichloromethane/ethyl acetate (5:5) as eluent to afford the bis-benzimidazoles.

3,6-di(1H-benzo[d]imidazol-2-yl)-9-ethyl-9H-carbazole (9).

This compound was obtained as a brown solid; yield: 63%; m.p: >320 °C (lit.^[33] m.p: >300 °C); IR (KBr): $\nu_{\max}$ 3638, 3052, 2971, 2925, 1602, 1485, 1437, 1400, 1364, 1276, 1230, 1147, 804, 734 cm⁻¹; ¹H NMR (500 MHz, DMSO): δ 1.41 (t, 3H, J =7.10 Hz, CH₃), 4.55 (q, 2H, J =7.03 Hz,

CH₂), 7.21 (s, 4H, aryl H), 7.62(s, 4H, aryl H), 7.83 (d, 2H, *J*=8.54 Hz, aryl H), 8.37 (d, 2H, *J*=8.36 Hz, aryl H), 9.14 (s, 2H, aryl H), 12.9 (s, 2H, 2x benzimidazole H); ¹³C NMR (DMSO): δ 14.3 (CH₃), 37.9 (CH₂), 110.4, 119.3, 122.1, 122.2, 122.9, 125.2, 141.4, 152.8 (aryl C and CH); Maldi (TOF); *m/z* 428 [M]⁺; HRMS (ESI): Found *m/z* 428.1878 [M]⁺; calculated for C₂₈H₂₁N₅ 428.1875.

9-ethyl-3,6-bis(5-methyl-1H-benzo[d]imidazol-2-yl)-9H-carbazole (10).

This compound was obtained as a brown solid; yield: 51%; m.p: >320 °C; IR (KBr): $\nu_{\max}$ 3638, 2922, 2852, 1628, 1604, 1483, 1440, 1380, 1343, 1300, 1276, 1232, 1150, 1129, 798 cm⁻¹; ¹H NMR (500 MHz, DMSO): δ 1.41 (t, 3H, *J*=7.10 Hz, CH₃), 2.45 (s, 6H, 2xCH₃), 4.54 (q, 2H, *J*=7.03 Hz, CH₂), 7.01 (d, 2H, *J*=7.86 Hz aryl H), 7.40 and 7.49 (m, 4H, aryl H), 7.83 (d, 2H, *J*=8.50 Hz, aryl H), 8.33 (d, 2H, *J*=7.06 Hz, aryl H), 9.10 (s, 2H, aryl H), 12.7 (s, 2H, 2x benzimidazole H); ¹³C NMR (DMSO): δ 14.3, 21.8 (CH₃), 37.9 (CH₂), 110.4, 119.1, 122.2, 122.9, 123.5, 123.6, 125.1, 141.3, 152.5 (aryl C and CH); Maldi (TOF); *m/z* 456 [M]⁺; HRMS (ESI): Found *m/z* 456.2197 [M]⁺; calculated for C₃₀H₂₅N₅ 456.2188.

9-ethyl-3,6-bis(5-methoxy-1H-benzo[d]imidazol-2-yl)-9H-carbazole (11).

This compound was obtained as a yellow solid; yield: 46%; m.p: >320 °C; IR (KBr): $\nu_{\max}$ 3188, 2931, 2837, 1631, 1602, 1449, 1429, 1395, 1349, 1269, 1239, 1157, 1026, 804 cm⁻¹; ¹H NMR (500 MHz, DMSO): δ 1.38 (s, 3H, CH₃), 3.82 (s, 6H, 2xOCH₃) 4.53 (s, 2H, CH₂), 6.83 (s, 2H, aryl H), 7.09 (s, 2H, aryl H), 7.49 (s, 2H, aryl H), 7.80 (s, 2H, aryl H), 8.30 (s, 2H, aryl H), 9.05 (s, 2H, aryl H); ¹³C NMR (DMSO): δ 14.3 (CH₃), 30.0 (CH₂), 55.9 (OCH₃), 109.9, 110.0, 110.4, 111.5, 118.9, 122.2, 122.9, 125.0, 141.2, 156.0 (aryl C and CH); Maldi (TOF); *m/z* 488 [M]⁺; HRMS (ESI): Found *m/z* 488.2088 [M]⁺; calculated for C₃₀H₂₅N₅O₂ 488.2087.

3,6-bis(5-chloro-1H-benzo[d]imidazol-2-yl)-9-ethyl-9H-carbazole (12).

This compound was obtained as a brown solid; yield: 42%; m.p: >320 °C; IR (KBr): $\nu_{\max}$ 3643, 3065, 2975, 2928, 1602, 1431, 1385, 1344, 1233, 1152, 1124, 1056, 925, 801 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 1.41 (t, 3H, $J=7.06$ Hz, CH_3), 4.54 (q, 2H, $J=7.07$ Hz CH_2), 7.21 (d, 2H, $J=7.96$ Hz, aryl H), 7.59 and 7.69 (m, 4H, aryl H), 7.84 (d, 2H, $J=8.58$ Hz, aryl H), 8.35 (d, 2H, $J=8.43$ Hz, aryl H), 9.11 (s, 2H, aryl H), 13.08 (s, 2H, 2x benzimidazole H); ^{13}C NMR (DMSO): δ 14.3 (CH_3), 37.9 (CH_2), 109.9, 110.5, 116.8, 119.5, 121.6, 122.9, 125.4, 141.6 (aryl C and CH); Maldi (TOF); m/z 496 $[\text{M}]^+$; HRMS (ESI): Found m/z 496.1088 $[\text{M}]^+$; calculated for $\text{C}_{28}\text{H}_{19}\text{Cl}_2\text{N}_5$ 496.1096.

2. Copies of ^1H NMR, ^{13}C NMR, Mass spectra

Figure 1. ^1H NMR, ^{13}C NMR, and mass spectra of compound **4**

Figure 2. ^1H NMR, ^{13}C NMR, and mass spectra of compound **5**

Figure 3. ^1H NMR, ^{13}C NMR, and mass spectra of compound **6**

Figure 4. ^1H NMR, ^{13}C NMR, and mass spectra of compound **7**

Figure 5. ^1H NMR, ^{13}C NMR, and mass spectra of compound **8**

Figure 6. ^1H NMR, ^{13}C NMR, and mass spectra of compound **9**

Figure 7. ^1H NMR, ^{13}C NMR, and mass spectra of compound **10**

Figure 8. ^1H NMR, ^{13}C NMR, and mass spectra of compound **11**

Figure 9. ^1H NMR, ^{13}C NMR, and mass spectra of compound **12**

Figure 1. ¹H NMR (DMSO-d₆) spectra of compound 4

Figure 1. ^{13}C NMR (DMSO- d_6) spectra of compound 4

Figure 1. Mass spectra of compound 4

Figure 2. ¹H NMR (DMSO-d₆) spectra of compound **5**

Figure 2. ^{13}C NMR (DMSO-d_6) spectra of compound **5**

Figure 2. Mass spectra of compound **5**

Figure 3. ¹H NMR (DMSO-d₆) spectra of compound **6**

Figure 3. ¹³C NMR (DMSO-d₆) spectra of compound 6

Figure 3. Mass spectra of compound 6

Figure 4. ¹H NMR (DMSO-d₆) spectra of compound 7

Figure 4. ¹³C NMR (DMSO-d₆) spectra of compound 7

Figure 4. Mass spectra of compound 7

Figure 5. ¹³C NMR (DMSO-d₆) spectra of compound 8

Figure 5. Mass spectra of compound 8

Figure 6. ¹H NMR (DMSO-d₆) spectra of compound **9**

Figure 6. ¹³C NMR (DMSO-d₆) spectra of compound **9**

Figure 6. Mass spectra of compound **9**

Figure 7. ¹H NMR (DMSO-d₆) spectra of compound **10**

Figure 7. ¹³C NMR (DMSO-d₆) spectra of compound **10**

Figure 7. Mass spectra of compound **10**

Figure 8. ¹H NMR (DMSO-d₆) spectra of compound 11

Figure 8. ¹³C NMR (DMSO-d₆) spectra of compound **11**

Figure 8. Mass spectra of compound **11**

Figure 9. ¹H NMR (DMSO-d₆) spectra of compound **12**

Figure 9. ¹³C NMR (DMSO-d₆) spectra of compound 12

Figure 9. Mass spectra of compound 12