



SUPPLEMENTARY MATERIAL TO
Spectral characterization and antimicrobial activity studies of 5,6-dichloro-1*H*-benzimidazol-2-yl-(4'/5'/6'-substituted)-phenols (HL₁ – HL₂₀) and Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes of HL₁

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EXPERIMENTAL

Chemistry and apparatus

All chemicals and solvents were of reagent grade and they were used without further purification.

Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyzer. Melting points were determined using a Buchi M-560 melting-point apparatus. Molar conductivity of the complexes was measured on a WTW Cond315i conductivity meter in DMF at 25 °C. Magnetic measurements: MK1 Sherwood Scientific apparatus (at room temperature by Gouy's method). NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer. FT-IR spectra were recorded on a Bruker Optics Vertex 70 spectrometer using Attenuated Total Reflection (ATR) techniques between 400 and 4000 cm⁻¹. The Electron Spray Ionization-Mass Spectrometry (ESI-MS) analysis was carried out in positive ion modes using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS. Fluorescence spectra were performed on a Shimadzu RF-5301 PC Spectrofluorophotometer in EtOH ($c = \sim 1 \times 10^{-4}$ mol L⁻¹).

2-(5,6-Dichloro-1*H*-benzimidazol-2-yl)phenol (HL₁): Yield: 80 %. Slightly yellow solid. Decomposition point (Dec. p.): 331 °C. (+)ESI-MS (m/z): calculated for [C₁₃H₈Cl₂N₂O]⁺ 279.1, observed 279.3 (100 %) and 281.3 for [C₁₃H₈Cl₂N₂O + 2H]⁺ (73.9 %). Combustion analysis for C₁₃H₈Cl₂N₂O: Calculated. C 55.94, H 2.89, N 10.04; found C 56.15, H 3.03, N 9.97. IR (ATR): 3333m ν(NH+OH), 3101m ν(CH)_{ar}, 1639m ν(C=N), 1600m ν(C=C), 1578m, 1487s, 1370m, 1256m ν(C–O), 1136m, 1106m, 960m, 865m δ(CH)_{ar}, 739s ν(C–Cl), 678m, 580m, 553m, 422m, cm⁻¹. ¹H-NMR (500 MHz, DMSO-*d*₆, δ): 13.30 (*s*, 1H, NH), 12.42 (*s*, 1H, OH), 8.08 (*dd*, 1H, *J*₁ = 7.9, *J*₂ = 1.6, H3'), 8.00 (*brs*, 1H, H4), 7.84 (*brs*, 1H, H7), 7.41 (*dt*, 1H, *J*₁ =

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1.6, $J_2 = 7.2$, $J_3 = 8.4$, H5'), 7.06 (*dd*, 1H, $J_1 = 8.3$, $J_2 = 1.0$, H6'), 7.03 (*dt*, 1H, $J_1 = 7.6$, $J_2 = 1.1$, H4'). Fluorescence spectra ($\lambda_{\max}$ / nm): 394w, 466s.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-4-fluorophenol (HL₂): Yield: 71 %. Light yellow solid. Dec. p.: 352 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_7Cl_2FN_2O]^+$ 297.1, observed 297.3 (100 %) and 299.3 for $[(C_{13}H_7Cl_2FN_2O + 2H)]^+$ (66.0 %). Combustion analysis for $C_{13}H_7Cl_2FN_2O$: Calculated. C 52.55, H 2.37, N 9.43; found C 52.71, H 2.53, N 9.27. IR (ATR, cm^{-1}): 3341m $\nu(NH+OH)$, 3078m $\nu(CH)_{ar.}$, 1650m $\nu(C=N)$, 1600m $\nu(C=C)$, 1583m, 1498m, 1448m, 1304m, 1255m $\nu(C-O)$, 1168m, 1096m, 976m, 859m, 814s $\delta(CH)_{ar.}$, 780m, 743m $\nu(C-Cl)$, 665m, 561s, 470m, 443m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.27 (*s*, 1H, NH), 12.21 (*s*, 1H, OH), 8.02 (*brs*, 1H, H4), 7.93 (*d*, 1H, $J = 3.1$, H3'), 7.91 (*brs*, 1H, H7), 7.28 (*dd*, 1H, $J_1 = 9.0$, $J_2 = 3.1$, H5'), 7.08 (*d*, 1H, $J = 9.1$, H6'). Fluorescence spectra ($\lambda_{\max}$ / nm): 393w, 480s.

4-Bromo-2-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (HL₃): Yield: 85 %. Yellowish grey solid. Dec. p.: 220 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_7BrCl_2N_2O + H]^+$ 359.0, observed 359.3 (100 %) and 357.3 for $[(C_{13}H_7BrCl_2N_2O - H)]^+$ (53.3 %). Combustion analysis for $C_{13}H_7BrCl_2N_2O$: Calculated. C 43.61, H 1.97, N 7.82; found C 43.45, H 1.91, N 7.74. IR (ATR, cm^{-1}): 3341m $\nu(NH+OH)$, 3075m $\nu(CH)_{ar.}$, 2960m,br, 1719m $\nu(C=O)$, 1620m $\nu(C=N)$, 1609m $\nu(C=C)$, 1482m, 1372m, 1249s $\nu(C-O)$, 1136m, 965m, 866m, 801s $\delta(CH)_{ar.}$, 739m $\nu(C-Cl)$, 632m, 565m $\nu(C-Br)$, 487m, 420m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.31 (*brs*, 1H, NH), 12.51 (*brs*, 1H, OH), 8.16 (*d*, 1H, $J = 2.4$, H3'), 7.92 (*brs*, 2H, H4+H7), 7.43 (*dd*, 1H, $J_1 = 8.8$, $J_2 = 2.4$, H5'), 7.10 (*d*, 1H, $J = 8.8$, H6'). Fluorescence spectra ($\lambda_{\max}$ / nm): 393w, 474s.

4-Chloro-2-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (HL₄): Yield: 81 %. Yellowish grey solid. Dec. p.: 221 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_7Cl_3N_2O]^+$ 313.5, observed 313.2 (100 %) and 315.2 for $[(C_{13}H_7Cl_3N_2O + 2H)]^+$ (90.1 %). Combustion analysis for $C_{13}H_7Cl_3N_2O$: Calculated. C 49.79, H 2.25, N 8.93; found: C 49.64, H 2.16, N 8.80. IR (cm^{-1}): 3338m $\nu(NH+OH)$, 3077m $\nu(CH)_{ar.}$, 2960m,br, 1723m $\nu(C=O)$, 1621m $\nu(C=N)$, 1602m $\nu(C=C)$, 1576m, 1474m, 1444m, 1355m, 1278m, 1249m $\nu(C-O)$, 1136m, 1095m, 965m, 866m, 800m $\delta(CH)_{ar.}$, 745m $\nu(C-Cl)$, 720m $\nu(C-Cl)$, 648m, 564m, 543m, 490m, 420m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.32 (*brs*, 1H, NH), 12.52 (*brs*, 1H, OH), 8.29 (*d*, 1H, $J = 2.4$, H3'), 8.01 (*brs*, 1H, H4), 7.88 (*brs*, 1H, H7), 7.54 (*dd*, 1H, $J_1 = 8.8$, $J_2 = 2.4$, H5'), 7.03 (*d*, 1H, $J = 8.8$, H6'). Fluorescence spectroscopy ($\lambda_{\max}/nm$): 394w, 475m.

2-(5,6-dichloro-1H-benzimidazol-2-yl)-4-iodophenol (HL₅): Yield: 65 %. Light orange solid. Dec. p.: 231 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_7Cl_2IN_2O]^+$ 405.1, observed 405.1 (100 %) and 407.1 for $[(C_{13}H_7Cl_2IN_2O + 2H)]^+$ (73.9 %). Combustion analysis for $C_{13}H_7Cl_2IN_2O$: Calculated. C 38.55, H 1.74, N 6.92; found: C 38.41, H 1.63, N 6.84. IR (cm^{-1}): 3351m $\nu(NH+OH)$, 3094m $\nu(CH)_{ar.}$, 2930m,br, 1656m $\nu(C=N)$, 1605m $\nu(C=C)$, 1565m, 1466s, 1366m, 1273m $\nu(C-O)$, 1181m, 1128m, 1095m, 961m, 865m, 814s $\delta(CH)_{ar.}$, 760m $\nu(C-Cl)$, 678m, 564m, 540m $\nu(C-I)$, 508m, 419m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.22 (*s*, 1H, NH), 12.51 (*s*, 1H, OH), 8.38 (*d*, 1H, $J = 2.0$, H3'), 8.00 (*brs*, 1H, H4), 7.84 (*brs*, 1H, H7), 7.64 (*dd*, 1H, $J_1 = 8.7$, $J_2 = 2.0$, H5'), 6.87 (*d*, 1H, $J = 8.7$, H6'). Fluorescence spectroscopy ($\lambda_{\max}/nm$): 393w, 476m.

2-Chloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (HL₆): Yield: 80 %. Matte yellow solid. Dec. p.: 373 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_7Cl_3N_2O]^+$ 313.5, observed 313.2 (100 %), 315.2 $[(C_{13}H_7Cl_3N_2O + 2H)]^+$ (100 %) and 317.2 for $[(C_{13}H_7Cl_3N_2O + 4H)]^+$ (47.6 %). Combustion analysis for $C_{13}H_7Cl_3N_2O$: Calculated. C 49.79, H 2.25, N 8.93; found: C 49.63, H 2.33, N 8.77. IR (cm^{-1}): 3336m,br $\nu(NH+OH)$, 3075w $\nu(CH)_{ar.}$, 1624m $\nu(C=N)$, 1601m $\nu(C=C)$,

1464m, 1441m, 1373m, 1252m $\nu(\text{C}-\text{O})$, 1094m, 968m, 860m $\delta(\text{CH})_{\text{ar.}}$, 785m, 747m $\nu(\text{C}-\text{Cl})$, 736m $\nu(\text{C}-\text{Cl})$, 665m, 611m, 571s, 427m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ): 13.72 (*brs*, 1H, NH), 13.38 (*s*, 1H, OH1'), 8.08 (*brs*, 1H, H4), 8.02 (*dd*, 1H, $J_1 = 7.9$, $J_2 = 1.5$, H3'), 7.87 (*brs*, 1H, H7), 7.59 (*dd*, 1H, $J_1 = 7.9$, $J_2 = 1.5$, H5'), 7.06 (*t*, 1H, $J_1 = J_2 = 7.9$, H4'). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 394w,br, 463m,br.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-6-methoxyphenol (**HL7**): Yield: 90 %. Creamy colored solid. Dec. p.: 343 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2]^+$ 309.0, observed 309.1 (100 %), 311.1 ($[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2 + 2\text{H}]^+$ (69.7 %). Combustion analysis for $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2$: Calculated. C 54.39, H 3.26, N 9.06; found: C 54.25, H 3.37, N 8.95. IR (cm^{-1}): 3294m,br $\nu(\text{NH}+\text{OH})$, 3058w $\nu(\text{CH})_{\text{ar.}}$, 2943m $\nu(\text{CH})_{\text{al.}}$, 1623m $\nu(\text{C}=\text{N})$, 1591m $\nu(\text{C}=\text{C})$, 1476m, 1420m, 1372m, 1249s $\nu(\text{C}-\text{O})$, 1182m $\nu(\text{C}-\text{O})$, 1095m, 1056m, 967m, 857m $\delta(\text{CH})_{\text{ar.}}$, 776m $\nu(\text{C}-\text{Cl})$, 731m, 603m, 545m, 425m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ): 13.33 (*brs*, 1H, NH), 12.50 (*brs*, 1H, OH'), 7.92 (*brs*, 2H, H4+H3'), 7.63 (*d*, 1H, $J = 2.9$, H7), 7.12 (*dd*, 1H, $J_1 = 8.0$, $J_2 = 1.1$, H5'), 6.97 (*t*, 1H, $J_1 = J_2 = 8.0$, H4'), 3.84 (*s*, 3H, OCH₃). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 394w,br, 481s.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-5-methoxyphenol (**HL8**): Yield: 80 %. Slightly yellow solid. Dec. p.: 292 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2]^+$ 309.0, observed 309.3 (100 %), 311.2 ($[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2 + 2\text{H}]^+$ (64.7 %). Combustion analysis for $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2$: Calculated. C 54.39, H 3.26, N 9.06; found: C 54.24, H 3.41, N 8.94. IR (cm^{-1}): 3344m,br $\nu(\text{NH}+\text{OH})$, 3102m $\nu(\text{CH})_{\text{ar.}}$, 2971m $\nu(\text{CH})_{\text{al.}}$, 1640m $\nu(\text{C}=\text{N})$, 1600m $\nu(\text{C}=\text{C})$, 1453m, 1388s, 1267m $\nu(\text{C}-\text{O})$, 1200m $\nu(\text{C}-\text{O})$, 1134m, 1026m, 951m, 865m, 817m $\delta(\text{CH})_{\text{ar.}}$, 796m $\nu(\text{C}-\text{Cl})$, 672m, 568m, 548m, 475m, 425m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ): 13.17 (*s*, 1H, NH), 12.68 (*s*, 1H, OH), 7.96 (*d*, 1H, $J = 8.8$, H3'), 7.94 (*s*, 1H, H4), 7.77 (*s*, 1H, H7), 6.64 (*dd*, 1H, $J_1 = 8.8$, $J_2 = 2.5$, H4'), 6.59 (*d*, 1H, $J = 2.4$, H6'), 3.81 (*s*, 3H, OCH₃). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 394w,br, 452m.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-4-methoxyphenol (**HL9**): Yield: 71 %. Slightly yellow solid. Dec. p.: 352 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2]^+$ 309.0, observed 309.2 (100 %), 311.2 ($[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2 + 2\text{H}]^+$ (59.9 %). Combustion analysis for $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2$: Calculated. C 54.39, H 3.26, N 9.06; found: C 54.25, H 3.43, N 8.95. IR (cm^{-1}): 3306m $\nu(\text{NH}+\text{OH})$, 3076m $\nu(\text{CH})_{\text{ar.}}$, 2974m $\nu(\text{CH})_{\text{al.}}$, 1619m $\nu(\text{C}=\text{N})$, 1598m $\nu(\text{C}=\text{C})$, 1493m, 1450m, 1370m, 1273m $\nu(\text{C}-\text{O})$, 1214m $\nu(\text{C}-\text{O})$, 1171m, 1042m, 968m, 866m, 809m $\delta(\text{CH})_{\text{ar.}}$, 758m $\nu(\text{C}-\text{Cl})$, 726m, 673m, 573m, 512m, 438m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ): 13.24 (*s*, 1H, NH), 11.92 (*s*, 1H, OH), 8.01 (*brs*, 1H, H4), 7.85 (*brs*, 1H, H7), 7.66 (*d*, 1H, $J = 2.4$, H3'), 7.03 (*dd*, 1H, $J_1 = 8.9$, $J_2 = 2.6$, H5'), 6.99 (*d*, 1H, $J_1 = 8.9$, $J_2 = 7.9$, H6'), 3.80 (*s*, 3H, OCH₃). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 389s,br, 508m,br.

2-(5,6-dichloro-1H-benzimidazol-2-yl)-4-methylphenol (**HL10**): Yield: 72 %. Slightly yellow solid. Dec. p.: 326 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}]^+$ 293.0, observed 293.2 (69.9 %), 295.2 ($[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O} + 2\text{H}]^+$ (100 %). Combustion analysis for $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}$: Calculated. C 57.36, H 3.44, N 9.56; found: C 57.47, H 3.30, N 9.49. FT-IR (cm^{-1}): 3467m $\nu(\text{OH})$, 3376m $\nu(\text{NH})$, 3062m $\nu(\text{CH})_{\text{ar.}}$, 2925m $\nu(\text{CH})_{\text{al.}}$, 1614m $\nu(\text{C}=\text{N})$, 1584m $\nu(\text{C}=\text{C})$, 1485s, 1354m, 1284m $\nu(\text{C}-\text{O})$, 1257m, 1134m, 962m, 855m, 812s $\delta(\text{CH})_{\text{ar.}}$, 780m $\nu(\text{C}-\text{Cl})$, 685m, 554m, 476m, 442m, 421m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO- d_6 , δ): 13.20 (*brs*, 1H, NH), 12.16 (*brs*, 1H, OH), 7.95 (*brs*, 1H, H4), 7.89 (*d*, 1H, $J = 1.7$, H3'), 7.84 (*brs*, 1H, H7), 7.21 (*dd*, 1H, $J_1 = 8.3$, $J_2 = 1.8$, H5'), 6.95 (*d*, 1H, $J = 8.3$, H6'), 2.32 (*s*, 3H, CH₃). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 375w,br, 394w,br, 482m.

2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-methylphenol (**HL11**): Yield: 94 %. Slightly bright yellow solid. Dec. p.: 357 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}]^+$ 293.0,

observed 293.3 (100 %), 295.2 ($[\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O} + 2\text{H}]^+$ (92.7 %). Combustion analysis for $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}$: Calculated. C 57.36, H 3.44, N 9.56; found: C 57.50, H 3.55, N 9.42. IR (cm^{-1}): 3323m,br $\nu(\text{NH}+\text{OH})$, 3054m $\nu(\text{CH})_{\text{ar.}}$, 2951m $\nu(\text{CH})_{\text{al.}}$, 1628m $\nu(\text{C}=\text{N})$, 1601m $\nu(\text{C}=\text{C})$, 1475m, 1445m, 1415m, 1370m, 1300m, 1252m $\nu(\text{C}-\text{O})$, 1094m, 1013m, 966m, 886m, 863m $\delta(\text{CH})_{\text{ar.}}$, 786s $\nu(\text{C}-\text{Cl})$, 665m, 573s, 518m, 428m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO-d_6 , δ): 13.52 (s, 1H, NH), 13.01 (s, 1H, OH), 8.03 (s, 1H, H4), 7.87 d (1H, $J = 7.6$, H3'), 7.81 s (1H, H7), 7.31 d (1H, $J = 7.3$, H5'), 6.95 dd (1H, $J_1 = 7.5$, $J_2 = 7.6$, H4'), 2.26 (s, 3H, CH_3). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 379w,br, 473s.

2-Bromo-4-chloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (HL12): Yield: 82 %. Mate light yellow solid. Dec. p.: 228 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{13}\text{H}_6\text{BrCl}_3\text{N}_2\text{O} + \text{H}]^+$ 393.5, observed 393.1 (100 %), 395.1 ($[\text{C}_{13}\text{H}_6\text{BrCl}_3\text{N}_2\text{O} + 3\text{H}]^+$ (64.5 %), 391.1 ($[\text{C}_{13}\text{H}_6\text{BrCl}_3\text{N}_2\text{O} - \text{H}]^+$ (55.7 %). Combustion analysis for $\text{C}_{13}\text{H}_6\text{BrCl}_3\text{N}_2\text{O}$: Calculated. C 39.78, H 1.54, N 7.14; found: C 39.75, H 1.66, N 7.01. IR (cm^{-1}): 3403m $\nu(\text{NH}+\text{OH})$, 3085m $\nu(\text{CH})_{\text{ar.}}$, 1669s $\nu(\text{C}=\text{O})$, 1624m $\nu(\text{C}=\text{N})$, 1601m $\nu(\text{C}=\text{C})$, 1448m, 1373m, 1256m $\nu(\text{C}-\text{O})$, 1096m, 970m, 853m $\delta(\text{CH})_{\text{ar.}}$, 754m $\nu(\text{C}-\text{Cl})$, 722m $\nu(\text{C}-\text{Cl})$, 669m, 610m, 554m $\nu(\text{C}-\text{Br})$, 498m, 423m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO-d_6 , δ): 13.80 (brs, 1H, NH), 13.44 (s, 1H, OH), 8.18 (brs, 1H, H4), 8.05 (brs, 1H, H7), 7.95 (s, 1H, H3'), 7.84 (brs, 1H, H5'). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 393w,br, 479s,br.

4-Bromo-2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-fluorophenol (HL13): Yield: 74 %. Dirty yellow solid. Dec. p.: 284 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{13}\text{H}_6\text{BrCl}_2\text{FN}_2\text{O} + \text{H}]^+$ 376.0, observed 377.2 (100 %), 375.1 ($[\text{C}_{13}\text{H}_6\text{BrCl}_2\text{FN}_2\text{O} - \text{H}]^+$ (65.6 %). Combustion analysis for $\text{C}_{13}\text{H}_6\text{BrCl}_2\text{FN}_2\text{O}$: Calculated. C 41.53, H 1.61, N 7.45; found: C 41.43, H 1.73, N 7.27. IR (cm^{-1}): 3398m $\nu(\text{NH}+\text{OH})$, 3084m $\nu(\text{CH})_{\text{ar.}}$, 2872m,br, 1662s $\nu(\text{C}=\text{O})$, 1614m $\nu(\text{C}=\text{N})$, 1577m $\nu(\text{C}=\text{C})$, 1489s, 1374m, 1265s $\nu(\text{C}-\text{O})$, 1233m, 1095m, 972m, 916m, 855s $\delta(\text{CH})_{\text{ar.}}$, 807m, 754m $\nu(\text{C}-\text{Cl})$, 666m, 553m $\nu(\text{C}-\text{Br})$, 427m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO-d_6 , δ): 13.58 (brs, 1H, NH), 13.15 (brs, 1H, OH), 8.10 (d, 1H, $J = 2.3$, H5'), 7.96 (brs, 1H, H4), 7.94 (brs, 1H, H7), 7.66 (d, 1H, $J = 2.4$, H3'). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 393w,br, 418sh, 469s.

2-Chloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)-4-fluorophenol (HL14): Yield: 89 %. Slightly yellow solid. Dec. p.: 341 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{13}\text{H}_6\text{Cl}_3\text{FN}_2\text{O}]^+$ 331.5, observed 331.3 (100 %), 333.3 ($[\text{C}_{13}\text{H}_6\text{Cl}_3\text{FN}_2\text{O} + 2\text{H}]^+$ (73.9 %). Combustion analysis for $\text{C}_{13}\text{H}_6\text{Cl}_3\text{FN}_2\text{O}$: Calculated. C 47.09, H 1.82, N 8.45; found: C 47.21, H 1.96, N 8.27. IR (cm^{-1}): 3420m $\nu(\text{NH}+\text{OH})$, 3089m $\nu(\text{CH})_{\text{ar.}}$, 1662m $\nu(\text{C}=\text{O})$, 1622m $\nu(\text{C}=\text{N})$, 1577m $\nu(\text{C}=\text{C})$, 1466m, 1444s, 1370m, 1264m $\nu(\text{C}-\text{O})$, 1209m, 1100m, 999m, 867s $\delta(\text{CH})_{\text{ar.}}$, 793m $\nu(\text{C}-\text{Cl})$, 741m $\nu(\text{C}-\text{Cl})$, 666m, 573m, 507m, 425m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO-d_6 , δ): 13.69 (brs, 1H, NH), 13.48 (brs, 1H, OH), 8.06 (brs, 1H, H5'), 7.92 (d, 1H, $J = 3.0$, H4), 7.90 (d, 1H, $J = 3.0$, H7), 7.61 (d, 1H, $J = 3.0$, H3'). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 394w,br, 482m,br.

2,4-Dichloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (HL15): Yield: 86 %. Mate yellow solid. Dec. p.: 344 °C. (+)ESI-MS (m/z): calculated for $[\text{C}_{13}\text{H}_6\text{Cl}_4\text{N}_2\text{O} + \text{H}]^+$ 349.0, observed 349.3 (100 %), 347.3 ($[\text{C}_{13}\text{H}_6\text{Cl}_4\text{N}_2\text{O} - \text{H}]^+$ (64.2 %), 351.3 ($[\text{C}_{13}\text{H}_6\text{Cl}_4\text{N}_2\text{O} + 3\text{H}]^+$ (54.8 %). Combustion analysis for $\text{C}_{13}\text{H}_6\text{Cl}_4\text{N}_2\text{O}$: Calculated C 44.87, H 1.74, N 8.05; found: C 44.71, H 1.87, N 8.16. IR (cm^{-1}): 3408m $\nu(\text{NH}+\text{OH})$, 3078m $\nu(\text{CH})_{\text{ar.}}$, 1722m $\nu(\text{C}=\text{O})$, 1657m $\nu(\text{C}=\text{N})$, 1623m $\nu(\text{C}=\text{C})$, 1576m, 1477m, 1442s, 1365m, 1259m $\nu(\text{C}-\text{O})$, 1187m, 1099m, 974m, 869m, 817m $\delta(\text{CH})_{\text{ar.}}$, 766m $\nu(\text{C}-\text{Cl})$, 728m $\nu(\text{C}-\text{Cl})$, 667m, 614m, 558m, 501m, 427m, cm^{-1} . $^1\text{H-NMR}$ (500 MHz, DMSO-d_6 , δ): 13.78 (brs, 2H, NH+OH), 8.15 (d, 1H, $J = 2.5$, H3'), 8.07 (brs, 1H, H4), 8.03 (brs, 1H, H7), 7.73 (d, 1H, $J = 2.5$, H5'). Fluorescence spectroscopy ($\lambda_{\text{max}}/\text{nm}$): 393w,br, 478m,br.

2,4-Dibromo-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (HL16): Yield: 75 %. Orange yellow solid. Dec. p.: 275 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_6Br_2Cl_2N_2O]^+$ 437.0, observed 437.3 (100 %), 439.3 ($[C_{13}H_6Br_2Cl_2N_2O + 2H]^+$ (98.9 %), 435.3 ($[C_{13}H_6Br_2Cl_2N_2O - H]^+$ (41.6 %). Combustion analysis for $C_{13}H_6Br_2Cl_2N_2O$: Calculated. C 35.74, H 1.38, N 6.41; found: C 35.65, H 1.47, N 6.55. IR (cm^{-1}): 3354w $\nu(NH)$, 3313w $\nu(OH)$, 3069m $\nu(CH)_{ar.}$, 1637m $\nu(C=N)$, 1604m $\nu(C=C)$, 1558m, 1458s, 1445s, 1364m, 1259m $\nu(C-O)$, 1097m, 973m, 855s, 836m $\delta(CH)_{ar.}$, 733m $\nu(C-Cl)$, 684m, 599m, 550m $\nu(C-Br)$, 447m, 420m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.88 (*brs*, 1H, NH), 13.82 (*brs*, 1H, OH), 8.32 (*s*, 1H, J = 2.2, H3'), 8.08 (*brs*, 1H, H4), 8.03 (*brs*, 1H, H7), 7.94 (*d*, 1H, J = 2.1, H5'). Fluorescence spectroscopy (λ_{max}/nm): 479s.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-4,6-diiodophenol (HL17): Yield: 76 %. Yellowish orange solid. Dec. p.: 203 °C. (+)ESI-MS (m/z): calculated for $[C_{13}H_6Cl_2I_2N_2O]^+$ 531.0, observed 531.3 (100 %), 533.2 ($[C_{13}H_6Cl_2I_2N_2O + 2H]^+$ (64.1 %). Combustion analysis for $C_{13}H_6Cl_2I_2N_2O$: Calculated. C 29.41, H 1.14, N 5.28; found: C 29.57, H 1.07, N 5.37. IR (cm^{-1}): 3472m $\nu(NH)$, 3375m $\nu(OH)$, 3059m $\nu(CH)_{ar.}$, 1665m $\nu(C=O)$, 1622m $\nu(C=N)$, 1594m $\nu(C=C)$, 1440s, 1356m, 1257m $\nu(C-O)$, 1136m, 1093m, 965m, 860s, 825m $\delta(CH)_{ar.}$, 736m $\nu(C-Cl)$, 662m, 595m, 541m $\nu(C-I)$, 426m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.73 (*brs*, 1H, NH), 12.64 (*s*, 1H, OH), 8.39 (*d*, 1H, J = 2.0, H5'), 8.13 (*s*, 1H, H4), 7.99 (*d*, 1H, J = 2.0, H3'), 7.95 (*s*, 1H, H7). Fluorescence spectroscopy (λ_{max}/nm): 393w, br 486s.

4-Chloro-2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-methoxyphenol (HL18): Yield: 85 %. Matte yellow solid. Dec. p.: 274 °C. (+)ESI-MS (m/z): calculated for $[C_{14}H_9Cl_3N_2O_2]^+$ 343.5, observed 343.2 (100 %), 345.2 ($[C_{14}H_9Cl_3N_2O_2 + 2H]^+$ (92.9 %). Combustion analysis for $C_{14}H_9Cl_3N_2O_2$: Calculated. C 48.94, H 2.64, N 8.15; found: C 48.79, H 2.80, N 8.00. IR (cm^{-1}): 3359m $\nu(NH+OH)$, 3102m $\nu(CH)_{ar.}$, 2951m $\nu(CH)_{al.}$, 2858m, br, 1665m $\nu(C=N)$, 1614m $\nu(C=C)$, 1579m, 1488m, 1442s, 1405m, 1315m, 1249s $\nu(C-O)$, 1095m, 1051m, 974m, 836m, 807m $\delta(CH)_{ar.}$, 730m $\nu(C-Cl)$, 725m $\nu(C-Cl)$, 621m, 552m, 433m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.40 (*s*, 1H, NH), 12.62 (*s*, 1H, OH), 7.98 (*brs*, 1H, H4), 7.89 (*brs*, 1H, H7), 7.73 (*d*, 1H, J = 2.4, H3'), 7.18 (*d*, 1H, J = 2.0, H5'), 3.87 (*s*, 3H, OCH₃). Fluorescence spectroscopy (λ_{max}/nm): 393w, 482s.

4-Bromo-2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-methoxyphenol (HL19): Yield: 75 %. Skin color solid. Dec. p.: 229 °C. (+)ESI-MS (m/z): calculated for $[C_{14}H_9BrCl_2N_2O_2 + H]^+$ 389.0, observed 389.1 (100 %), 387.1 ($[C_{14}H_9BrCl_2N_2O_2 - H]^+$ (61.2 %). Combustion analysis for $C_{14}H_9BrCl_2N_2O_2$: Calculated. C 43.33, H 2.34, N 7.22; found: C 43.51, H 2.23, N 7.03. IR (cm^{-1}): 3356m $\nu(NH)$, 3279m $\nu(OH)$, 3083m $\nu(CH)_{ar.}$, 2852w, br, 1675m $\nu(C=O)$, 1621m $\nu(C=N)$, 1602m $\nu(C=C)$, 1440m, 1372m, 1254s $\nu(C-O)$, 1238m $\nu(C-O)$, 1093m, 1058m, 972m, 838m, 806m $\delta(CH)_{ar.}$, 710m $\nu(C-Cl)$, 640m, 551m $\nu(C-Br)$, 487m, 428m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.42 (*s*, 1H, NH), 12.66 (*s*, 1H, OH), 8.04 (*s*, 1H, H4), 7.87 (*s*, 1H, H7), 7.86 (*d*, 1H, J = 2.2, H5'), 7.25 (*d*, 1H, J = 2.2, H3'), 3.87 (*s*, 3H, OCH₃). Fluorescence spectra (λ_{max}/nm): 393w, 486s.

2,4-Dibromo-6-(5,6-dichloro-1H-benzimidazol-2-yl)-3-methoxyphenol (HL20): Yield: 88 %. Yellowish orange solid. Dec. p.: 234 °C. (+)ESI-MS (m/z): calculated for $[C_{14}H_8Br_2Cl_2N_2O_2]^+$ 467.0, observed 467.1 (100 %), 469.1 ($[C_{14}H_8Br_2Cl_2N_2O_2 + 2H]^+$ (83.2 %). Combustion analysis for $C_{14}H_8Br_2Cl_2N_2O_2$: Calculated. C 36.01, H 1.73, N 6.00; found: C 36.35, H 1.93, N 5.87. IR (ATR, cm^{-1}): 3367w $\nu(OH)$, 3126m $\nu(NH)$, 3088m $\nu(CH)_{ar.}$, 2938m $\nu(CH)_{al.}$, 1665m $\nu(C=O)$, 1632m $\nu(C=N)$, 1600m, $\nu(C=C)$, 1564m, 1429m, 1372s, 1260m $\nu(C-O)$, 1230m $\nu(C-O)$, 1096m, 1061m, 970m, 863m $\delta(CH)_{ar.}$, 774m, 753m $\nu(C-Cl)$, 664m, 627m, 551m $\nu(C-Br)$, 460m, 412m, cm^{-1} . 1H -NMR (500 MHz, DMSO- d_6 , δ): 13.76 (*brs*, 2H,

NH+OH), 8.38 (*s*, 1H, H3'), 7.97 (*s*, 1H, H4), 7.95 (*s*, 1H, H7), 3.86 (*s*, 3H, OCH₃).
 Fluorescence spectra (λ_{max} / nm): 393w,br, 467m,br.

TABLE SI. Selected bond distances and angles for **HL18** (Å, °)

C7—N1	1.367(3)	C7—N2	1.323(3)
C2—C11	1.739(3)	C3—C12	1.740(3)
C1—C2	1.377(4)	C2—C3	1.401(4)
C7—C8	1.461(3)	C9—O1	1.353(3)
C10—O2	1.368(3)	C14—O2	1.428(3)
C12—C13	1.740(3)	C9—C10	1.402(4)
C10—C11	1.376(4)	C11—C12	1.391(4)
C9—O1—H1A	109.5	N2—C7—N1	111.8(2)
N1—C5—C6	105.4(2)	C1—C2—C11	119.3(2)
C3—C2—C11	119.6(2)	C2—C3—C12	119.9(2)
C4—C3—C12	118.2(2)	N1—C5—C6	105.4(2)
N2—C7—N1	111.8(2)	C10—O2—C14	116.1(2)
C11—C12—C13	117.8(2)	C13—C12—C13	120.6(2)

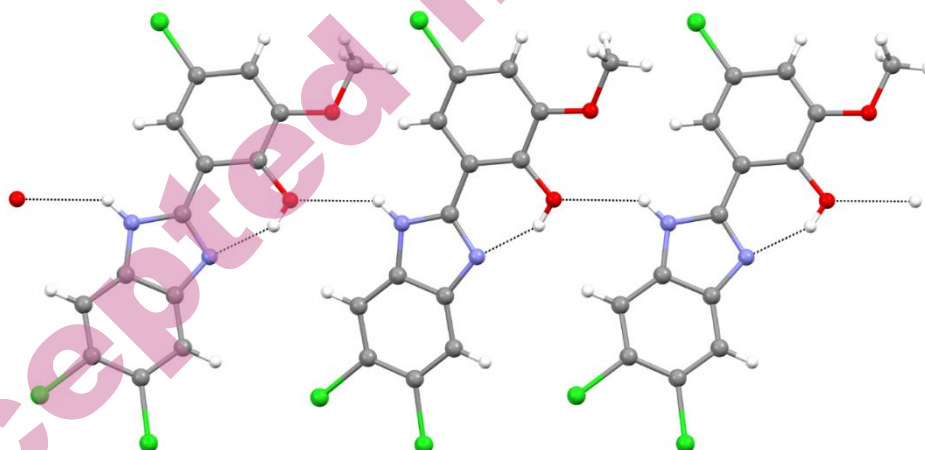


Fig. S1. Part of the crystal structure of **HL18**, showing the formation of C(6) chain.