A novel one-pot synthesis of some new interesting pyrrole derivatives

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Experimental Section:

Melting points were measured on the Electrothermal 9100 apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-470 Spectrophotometer. ^1H NMR and ^{13}C NMR spectra were determined on a Bruker 500 and 300 DRX AVNCE instrument at 500 or 300 and 125 or 75 MHz, respectively. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer. Microwave irradiation were carried out in a National oven, model 5250, at 2450 MHz.

General procedure for preparation of **3a-c** and **5a-5d**:

Montmorillonite K10 (0.5 g) was placed in a mortar followed by addition of 11*H*-indeno[1,2-*b*]quinoxalin-11-ones **1a-c** or isatin derivatives **4a-d** (1 mmol) and 4-hydroxy proline **2** (0.131g, 1 mmol) to which was added five drop of DMSO as a wet solvent. These materials were then mixed using a pestle for ca. 5min. The homogenized mixture was placed in a pyrex test tube and then loaded into the microwave oven and irradiated for 2 min with a power of 900w. The contents were cooled to room temperature and mixed thoroughly with 10 mL acetone. The solid inorganic material was filtered off. After separation of montmorillonite K10, water added to the mixture and the separated solid was filtered off and dried under high vacuum and recrystallised in ethanol to give a pure crystalline products.

Spectral data for Products **3a-c** and **5a-d**:

11-(1*H*-pyrrol-1-yl)-11*H*-indeno[1,2-*b*]quinoxaline **3a**: mp: 180-181 °C, IR (KBr) (ν_{max} , cm^{-1}): 3095, 2920, 1478; ^1H NMR (CDCl_3 , 500 MHz) δ_{H} : 6.21(1H, s, CH), 6.23 (2H, t, $J=2.10$ Hz, $\text{CH}_{\text{pyrrole}}$), 6.74 (2H, t, $J=2.09$ Hz, $\text{CH}_{\text{pyrrole}}$), 7.58-8.29 (8H, m, Arom); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} : 61.63 (CH), 109.30, 120.40 ($2\text{CH}_{\text{pyrrole}}$), 122.78, 125.99, 128.99, 129.36, 129.81, 130.34, 130.38, 132.19, 137.19, 141.67, 142.59, 143.80, 153.17, 158.16 (arom). MS (m/z , %):

283 (M^+ , 100), 217 (85), 190 (60), 141 (15), 114 (15), 89 (45), 63 (16), 39 (50). Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.54; H, 4.62; N, 14.83. Found: C, 80.58; H, 4.63; N, 14.81.

8-methyl-11-(1*H*-pyrrol-1-yl)-11*H*-indeno[1,2-*b*]quinoxaline **3b**: mp: 192-193 °C, IR (KBr) ($\nu_{\max}$, cm^{-1}): 3098, 2918, 1483; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} : 2.66 (3H, s, CH_3), 6.25 (1H, s, CH), 6.27 (2H, bs, $\text{CH}_{\text{pyrrole}}$), 6.74 (2H, t, $J=1.80$ Hz, $\text{CH}_{\text{pyrrole}}$), 7.62-8.23 (7H, m, Arom); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} : 22.08 (CH_3), 62.13 (CH), 109.55, 120.44 ($2\text{CH}_{\text{pyrrole}}$), 122.58, 124.70, 128.69, 130.45, 131.13, 132.55, 136.70, 141.14, 141.38, 142.88, 143.88, 148.42, 153.17, 158.16 (arom). MS (m/z , %): 297 (M^+ , 30), 246 (100), 231 (55), 218 (60), 190 (15), 130 (15), 89 (30). Anal. Calcd for $C_{20}H_{15}N_3$: C, 80.78; H, 5.08; N, 14.13. Found: C, 80.77; H, 5.05; N, 14.11.

7,8-dimethyl-11-(1*H*-pyrrol-1-yl)-11*H*-indeno[1,2-*b*]quinoxaline **3c**: mp: 231-232 °C, IR (KBr) ($\nu_{\max}$, cm^{-1}): 3120, 2915, 1486, 1329; ^1H NMR (CDCl_3 , 500 MHz) δ_{H} : 2.44 and 2.47 (6H, 2s, 2CH_3), 6.12 (1H, s, CH), 6.23 (2H, t, $J=1.26$ Hz, $\text{CH}_{\text{pyrrole}}$), 6.73 (2H, t, $J=1.33$ Hz, $\text{CH}_{\text{pyrrole}}$), 7.50-8.19 (6H, m, Arom); ^{13}C NMR (CDCl_3 , 125 MHz) δ_{C} : 20.23 and 20.35 (2CH_3), 61.66 (CH), 109.17, 120.37 ($2\text{CH}_{\text{pyrrole}}$), 122.29, 125.83, 128.33, 129.00, 130.16, 131.54, 137.67, 139.72, 140.50, 140.65, 141.60, 143.56, 152.37, 157.14 (arom). MS (m/z , %): 311 (M^+ , 100), 245 (90), 229 (30), 103 (15), 77 (15), 39 (45). Anal. Calcd for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.49. Found: C, 79.88; H, 5.55; N, 13.51.

3-(1*H*-pyrrol-1-yl)indolin-2-one **5a**: mp: 143-144 °C, IR (KBr) ($\nu_{\max}$, cm^{-1}): 3295, 3190, 1711, 1614, 1482; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} : 6.51 (1H, s, CH), 6.25 (2H, bs, $\text{CH}_{\text{pyrrole}}$), 6.70 (2H, bs, $\text{CH}_{\text{pyrrole}}$), 6.85-7.34 (4H, m, Arom), 8.87 (1H, bs, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} : 60.85 (CH), 109.54, 110.76 ($2\text{CH}_{\text{pyrrole}}$), 120.33, 123.30, 125.10, 125.53, 130.21, 141.31 (arom), 175.16 (C=O). MS (m/z , %): 198 (M^+ , 100), 169 (85), 132 (90), 104 (10), 39 (10). Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13; O, 8.07. Found: C, 72.73; H, 5.09; N, 14.12.

1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one **5b**: mp: 133-134 °C, IR (KBr) (ν_{max} , cm^{-1}): 1712, 1606, 1486; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} : 3.23 (3H, s, CH_3), 5.48 (1H, s, CH), 6.22 (2H, bs, $\text{CH}_{\text{pyrrole}}$), 6.68 (2H, bs, $\text{CH}_{\text{pyrrole}}$), 6.89-7.42 (4H, m, Arom); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} : 26.42 (CH_3), 60.29 (CH), 108.65, 109.36 ($2\text{CH}_{\text{pyrrole}}$), 120.21, 123.23, 124.53, 125.31, 130.20, 144.17 (arom), 172.45 (C=O). MS (m/z , %): 198 (M^+ , 100), 169 (85), 132 (90), 104 (10), 39 (10). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$: C, 73.56; H, 5.70; N, 13.20; O, 7.54. Found: C, 73.54; H, 5.72; N, 13.18.

1-benzyl-3-(1*H*-pyrrol-1-yl)indolin-2-one **5c**: mp: 126-127 °C, IR (KBr) (ν_{max} , cm^{-1}): 1713, 1609, 1485; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} : 4.93 (2H, d, $^2J=7.00$ Hz, CH_2), 5.58 (1H, s, CH), 6.25 (2H, t, $J=1.84$ Hz, $\text{CH}_{\text{pyrrole}}$), 6.71 (2H, t, $J=1.86$ Hz, $\text{CH}_{\text{pyrrole}}$), 6.79-7.31 (9H, m, Arom); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} : 44.12 (CH_2), 60.40 (CH), 109.56, 109.78 ($2\text{CH}_{\text{pyrrole}}$), 120.30, 123.34, 124.66, 125.45, 127.41, 127.91, 128.95, 130.16, 135.35, 143.31 (arom), 172.68 (C=O). MS (m/z , %): 288 (M^+ , 65), 222 (100), 197 (10), 91 (90), 65 (10). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$: C, 73.56; H, 5.70; N, 13.20; O, 7.54. Found: C, 73.53; H, 5.77; N, 13.30.

5-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one **5d**: mp: 163-164 °C, IR (KBr) (ν_{max} , cm^{-1}): 3200, 1708, 1619, 1487; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} : 4.93 (3H, s, CH_3), 5.58 (1H, s, CH), 6.25 (2H, t, $J=1.96$ Hz, $\text{CH}_{\text{pyrrole}}$), 6.71 (2H, t, $J=2.01$ Hz, $\text{CH}_{\text{pyrrole}}$), 6.79-7.31 (4H, m, Arom), 9.09 (1H, bs, NH); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} : 44.12 (CH_3), 60.40 (CH), 109.54, 110.76 ($2\text{CH}_{\text{pyrrole}}$), 120.33, 123.30, 125.10, 125.53, 130.21, 141.31 (arom), 175.16 (C=O). MS (m/z , %): 288 (M^+ , 65), 222 (100), 197 (10), 91 (90), 65 (10). Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}$: C, 79.14; H, 5.59; N, 9.72; O, 5.55. Found: C, 79.15; H, 5.60; N, 9.77.

5-bromo-3-(1*H*-pyrrol-1-yl)indolin-2-one **5e**: mp: 171-172 °C, IR (KBr) (ν_{max} , cm^{-1}): 3240, 1714, 1610, 1487; ^1H NMR (CDCl_3 , 300 MHz) δ_{H} : 5.50 (1H, s, CH), 6.26 (2H, s, $\text{CH}_{\text{pyrrole}}$), 6.67 (2H,

s, CH_{pyrrole}), 6.78-7.45 (3H, m, Arom), 9.07 (1H, bs, NH); ¹³C NMR (CDCl₃, 75 MHz) δ_C: 60.75 (CH), 109.90, 112.43 (2CH_{pyrrole}), 115.95, 120.33, 127.12, 128.49, 133.16, 140.26 (arom), 174.96 (C=O). MS (m/z, %): 278 (M⁺+2, 80), 276 (M⁺, 80), 249 (15), 247 (15), 212 (95), 210 (100), 168 (20), 103 (30), 67 (85), 39 (50). Anal. Calcd for C₁₂H₉BrN₂O: C, 52.01; H, 3.27; Br, 28.83; N, 10.11; O, 5.77. Found: C, 52.08; H, 3.28; Br, 28.81; N, 10.12.

DI/KAZEMIZADE-R2/83.03.09

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DI/KAZEMIZADEH-R4/83.03.09

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DI/KAZEMIZADEH-R11/83.03.24

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C13

R4

S10

S15

S11

S16

S12

S17

S13

S18