Supporting Information for

Three-Component, Four-Molecule Ru-Catalyzed Cascade Reactions of Indoles, Alkyl Bromides, and Sodium Nitrite

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1. General Methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^1H and ^{13}C NMR spectra. CDCl_3 or $\text{DMSO}-d_6$ was used as the NMR solvent. HRFABMS spectra were recorded on a FTMS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

Materials

Commercially available starting materials and solvents were used as supplied, without further purification.

2. General Procedure for the Preparation of 4.

To a solution of indole (0.50 mmol), alkyl bromide (0.7 mmol) and NaNO_2 (1.0 mmol) in DMF (1 mL) was added $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.075 mmol) under atmosphere and the mixture was stirred at 40 °C for 8-26 h (monitored by TLC). The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product.

Spectroscopic Data of the Products 4.

(*E*)-2,3'-Bi(3*H*-indol)-3-one *O*-benzyl oxime (**4aa**)

Red solid, mp: 201-203 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max} : 3453, 3206, 1542, 1437, 1131. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 11.91 (s, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 2.7 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.46-7.39 (m, 4H), 7.36 (t, J = 7.2 Hz, 1H), 7.25-7.18 (m, 2H), 7.17-7.12 (m, 1H), 5.59 (s, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 162.0, 157.7, 155.1, 137.3, 137.0, 133.2, 132.6, 129.1, 129.0, 128.8, 127.5, 126.4, 126.0, 123.3, 122.9, 121.7, 121.4, 120.2, 112.6, 108.7, 78.6. HRESIMS calcd for $[\text{C}_{23}\text{H}_{17}\text{N}_3\text{O} + \text{H}]^+$ 352.1450 (100%), found 352.1439 (100%).

(*E*)-5,5'-Difluoro-2,3'-bi(3*H*-indol)-3-one *O*-benzyl oxime (**4ba**)

Red-brown solid, mp: 250-252 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3410, 2928, 1552, 1468, 1132. ^1H NMR (400 MHz, DMSO-*d*₆): δ 11.98 (s, 1H), 8.37 (d, J = 3.0 Hz, 1H), 8.14 (dd, J = 10.1, 2.6 Hz, 1H), 7.65 (dd, J = 8.0, 2.6 Hz, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.50 (dd, J = 8.9, 4.6 Hz, 1H), 7.48–7.41 (m, 3H), 7.40–7.36 (m, 1H), 7.26 (dt, J = 2.6, 8.9 Hz, 1H), 7.08 (dt, J = 2.6, 8.9 Hz, 1H), 5.60 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*₆): δ 161.8 (d, J = 3.2 Hz), 160.5 (d, J = 250.8 Hz), 158.7 (d, J = 234.0 Hz), 154.4, 153.8, 137.1, 133.9, 133.6, 129.1 (d, J = 2.6 Hz), 128.9, 126.8 (d, J = 11.0 Hz), 122.1 (d, J = 9.9 Hz), 121.2 (d, J = 8.4 Hz), 119.1 (d, J = 23.5 Hz), 114.6 (d, J = 26.4 Hz), 113.8 (d, J = 9.9 Hz), 111.4 (d, J = 26.4 Hz), 108.7 (d, J = 4.4 Hz), 107.7, 107.4, 78.9. HRESIMS calcd for $[\text{C}_{23}\text{H}_{15}\text{F}_2\text{N}_3\text{O} + \text{H}]^+$ 388.1261 (100%), found 388.1250 (100%).

(*E*)-3-(Benzyloxyimino)-2,3'-bi(3*H*-indol)-5,5'-dicarbonitrile (**4ca**)

Red solid, mp: 298-300 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3432, 2923, 1543, 1449, 1128. ^1H NMR (400 MHz, DMSO-*d*₆): δ 12.59 (s, 1H), 8.89 (s, 1H), 8.62 (s, 1H), 8.29 (s, 1H), 7.98 (dd, J = 8.0, 1.6 Hz, 1H), 7.74 (dd, J = 10.9, 8.3 Hz, 2H), 7.68 (dd, J = 8.5, 1.6 Hz, 1H), 7.66–7.61 (m, 2H), 7.52–7.46 (m, 2H), 7.46–7.42 (m, 1H), 5.72 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*₆): δ 164.0, 160.4, 153.3, 139.0, 137.8, 137.0, 136.0, 130.3, 129.3, 129.2, 129.1, 129.0, 127.7, 126.5, 126.1, 121.7, 121.3, 120.7, 119.3, 114.4, 108.8, 108.3, 104.3, 79.4. HRESIMS calcd for $[\text{C}_{25}\text{H}_{15}\text{N}_5\text{O} + \text{H}]^+$ 402.1355 (100%), found 402.1346 (100%).

(*E*)-6,6'-Difluoro-2,3'-bi(3*H*-indol)-3-one *O*-benzyl oxime (**4da**)

Orange solid, mp: 202-203 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3443, 3204, 2926, 1548, 1463, 1130. ^1H NMR (400 MHz, DMSO-*d*₆): δ 12.07 (s, 1H), 8.48 (dd, J = 8.8, 5.8 Hz, 1H), 8.44 (d, J = 2.9 Hz, 1H), 7.96 (dd, J = 8.2, 5.8 Hz, 1H), 7.61–7.55 (m, 2H), 7.51–7.45 (m, 2H), 7.45–7.40 (m, 1H), 7.35 (dd, J = 6.3, 2.3 Hz, 1H), 7.33 (dd, J = 6.3, 2.3 Hz, 1H), 7.12 (dt, J = 2.3, 9.6 Hz, 1H), 7.03 (dq, J = 2.3, 9.6 Hz, 1H), 5.64 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*₆): δ 165.4 (d, J = 248.5 Hz), 163.6, 160.0 (d, J = 236.6 Hz), 159.9 (d, J = 7.9 Hz), 153.8, 137.2, 133.9, 129.1, 129.0, 128.9, 128.8, 128.7 (d, J = 10.3 Hz), 123.9 (d, J = 9.9 Hz), 123.0, 118.0, 112.2 (d, J = 23.1 Hz), 110.1 (d, J = 23.8 Hz), 108.6, 108.2 (d, J = 24.6 Hz), 99.0 (d, J = 25.7 Hz), 78.8. HRESIMS calcd for $[\text{C}_{23}\text{H}_{15}\text{F}_2\text{N}_3\text{O} + \text{H}]^+$ 388.1261 (100%), found 388.1253 (100%).

(*E*)-2,3'-Bi(3*H*-indol)-3-one *O*-(4-methylbenzyl) oxime (**4ab**)

Red solid, mp: 193-195 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3411, 2925, 1542, 1441, 1133. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.91 (s, 1H), 8.49 (dd, J = 8.5, 1.6 Hz, 1H), 8.38 (d, J = 2.9 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H), 7.50 (dd, J = 7.4, 1.6 Hz, 1H), 7.43 (d, J = 7.7 Hz, 2H), 7.41 (d, J = 3.6 Hz, 2H), 7.25–7.17 (m, 4H), 7.17–7.12 (m, 1H), 5.53 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.0, 157.7, 155.0, 138.2, 137.0, 134.2, 133.1, 132.5, 129.6, 129.2, 127.4, 126.4, 126.0, 123.3, 122.9, 121.7, 121.4, 120.1, 112.6, 108.7, 78.6, 21.3. HRESIMS calcd for $[\text{C}_{24}\text{H}_{19}\text{N}_3\text{O} + \text{H}]^+$ 366.1606 (100%), found 366.1594 (100%).

(*E*)-5,5'-Difluoro-2,3'-bi(3*H*-indol)-3-one *O*-(4-methylbenzyl) oxime (**4bb**)

Red solid, mp: 246-248 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3404, 2922, 1548, 1460, 1128. ^1H NMR (400 MHz, DMSO-*d*6): δ 12.01 (s, 1H), 8.39 (d, J = 3.0 Hz, 1H), 8.14 (dd, J = 9.8, 2.6 Hz, 1H), 7.63 (dd, J = 8.0, 2.6 Hz, 1H), 7.51 (dd, J = 8.8, 4.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.28 (dt, J = 2.6, 9.8 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.08 (dt, J = 2.6, 8.8 Hz, 1H), 5.55 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 161.8 (d, J = 2.2 Hz), 160.6 (d, J = 248.7 Hz), 158.7 (d, J = 234.0 Hz), 154.3 (d, J = 2.4 Hz), 153.7 (d, J = 2.1 Hz), 138.4, 134.0, 133.9, 133.6, 129.7, 129.3, 126.8 (d, J = 10.9 Hz), 122.1 (d, J = 10.0 Hz), 121.2 (d, J = 8.8 Hz), 119.1 (d, J = 23.1 Hz), 114.6 (d, J = 25.7 Hz), 113.9 (d, J = 9.9 Hz), 111.5 (d, J = 25.7 Hz), 108.7 (d, J = 4.5 Hz), 107.6 (d, J = 25.3 Hz), 78.9, 21.3. HRESIMS calcd for $[\text{C}_{24}\text{H}_{17}\text{F}_2\text{N}_3\text{O} + \text{H}]^+$ 402.1418 (100%), found 402.1407 (100%).

(*E*)-5,5'-Dibromo-2,3'-bi(3*H*-indol)-3-one *O*-(4-methylbenzyl) oxime (**4eb**)

Red-brown solid, mp: 195-197 °C (from EtOAc/PE = 1:8). IR (KBr) ν_{max} : 3417, 3249, 2925, 1548, 1438, 1133. ^1H NMR (400 MHz, DMSO-*d*6): δ 12.14 (d, J = 2.3 Hz, 1H), 8.60 (d, J = 2.0 Hz, 1H), 8.39 (d, J = 3.0 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 7.62 (dd, J = 8.2, 2.0 Hz, 1H), 7.47 (t, J = 8.5 Hz, 2H), 7.44 (dd, J = 8.2, 2.0 Hz, 2H), 7.36 (dd, J = 8.5, 2.0 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 5.57 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 161.8, 156.4, 153.8, 138.4, 135.8, 135.5, 134.1, 131.4, 129.7, 129.3, 128.0, 126.0, 124.8, 123.0, 122.1, 118.0, 114.8, 114.6, 108.0, 100.0, 79.0, 21.3. HRESIMS calcd for $[\text{C}_{24}\text{H}_{17}\text{Br}_2\text{N}_3\text{O} - \text{H}]^+$ 519.9660 (50%), 521.9640 (100%), found 519.9669 (50%), 521.9648 (100%).

(*E*)-2,3'-Bi(3*H*-indol)-3-one *O*-(4-fluorobenzyl) oxime (**4ac**)

Red solid, mp: 169-171 °C (from EtOAc/PE = 1:8). IR (KBr) ν_{max} : 3412, 3144, 2924, 1544, 1440, 1219. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.92 (d, J = 2.0 Hz, 1H), 8.50 (dd, J = 6.7, 1.8 Hz, 1H), 8.38 (d, J = 3.1 Hz, 1H), 7.91 (d, J = 7.3 Hz, 1H), 7.64–7.59 (m, 2H), 7.51 (dd, J = 6.7, 1.8 Hz, 1H), 7.43 (dd, J = 4.7, 1.1 Hz, 2H), 7.29–7.21 (m, 4H), 7.18–7.13 (m, 1H), 5.59 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.6 (d, J = 244.3 Hz), 162.0, 157.7, 155.1, 137.0, 133.6 (d, J = 2.9 Hz), 133.2, 132.5, 131.3 (d, J = 8.4 Hz), 127.5, 126.4, 126.0, 123.3, 122.9, 121.7, 121.4, 120.2, 115.9 (d, J = 21.3 Hz), 112.6, 108.7, 77.8. HRESIMS calcd for $[\text{C}_{23}\text{H}_{16}\text{FN}_3\text{O} + \text{H}]^+$ 370.1356 (100%), found 370.1347 (100%).

(*E*)-Bi(3*H*-indol)-3-one *O*-(4-(trifluoromethyl)benzyl) oxime (**4ad**)

Red solid, mp: 214-216 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3419, 3216, 2925, 1547, 1328, 1122. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.90 (d, J = 2.0 Hz, 1H), 8.50 (dd, J = 6.8, 2.0 Hz, 1H), 8.36 (d, J = 2.9 Hz, 1H), 7.97 (d, J = 7.3 Hz, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 6.8, 2.0 Hz, 1H), 7.46–7.42 (m, 2H), 7.25–7.16 (m, 3H), 5.72 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 161.9, 157.8, 151.5, 142.3, 137.0, 133.3, 132.6, 129.3 (q, J = 31.9 Hz), 129.2, 129.1, 127.7, 126.4, 126.1, 126.0 (q, J = 3.6 Hz), 123.3, 122.9, 121.7, 121.4, 120.2, 112.6, 108.7, 77.5. HRESIMS calcd for $[\text{C}_{24}\text{H}_{16}\text{F}_3\text{N}_3\text{O} + \text{H}]^+$ 420.1324 (100%), found 420.1314 (100%).
(*E*)-5,5'-Dibromo-bi(3*H*-indol)-3-one *O*-(4-(trifluoromethyl)benzyl) oxime (**4ed**)

(*E*)-5,5'-Dibromo-bi(3*H*-indol)-3-one *O*-(4-(trifluoromethyl)benzyl) oxime (**4ed**). Red solid, mp: 235-237 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3423, 3205, 2927, 1548, 1436, 1117. ^1H NMR (400 MHz, DMSO-*d*6): δ 12.08 (s, 1H), 8.59 (d, J = 2.0 Hz, 1H), 8.31 (s, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.75 (q, J = 8.4 Hz, 4H), 7.60 (dd, J = 8.4, 2.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 8.4, 2.0 Hz, 1H), 5.71 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 161.7, 156.5, 154.4, 142.1, 135.8, 135.6, 134.0, 129.8, 129.4, 129.3, 129.2 (q, J = 31.6 Hz), 128.0, 126.0, 125.9 (q, J = 3.8 Hz), 124.8, 123.0, 122.1, 118.1, 114.7, 114.6, 108.0, 77.8. HRESIMS calcd for $[\text{C}_{24}\text{H}_{14}\text{Br}_2\text{F}_3\text{N}_3\text{O} - \text{H}]^+$ 573.9377 (50%), 575.9357 (100%), 577.9377 (50%), found 573.9386 (50%), 575.9366 (100%), 577.9345 (50%).

(*E*)-7,7'-Dimethyl-bi(3*H*-indol)-3-one *O*-(3-fluorobenzyl) oxime (**4fe**)

Brown solid, mp: 134-135 °C (from EtOAc/PE = 1:4). IR (KBr) $\nu_{\max}$: 3431, 2925, 1550, 1447, 1132. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.87 (d, J = 2.0 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.29 (d, J = 2.9 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.48 (q, J = 7.8 Hz, 1H), 7.40–7.33 (m, 2H), 7.26 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 8.3 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 5.59 (s, 2H), 2.52 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.6 (d, J = 243.9 Hz), 160.8, 155.9, 140.4 (d, J = 7.3 Hz), 136.4, 134.5, 131.7, 131.1 (d, J = 8.4 Hz), 129.2, 126.2, 125.9, 125.3, 124.8, 124.7, 123.9, 121.9, 121.7, 121.1, 120.6, 115.6 (d, J = 11.0 Hz), 115.4 (d, J = 11.4 Hz), 109.3, 77.4, 17.2, 16.3. HRESIMS calcd for $[\text{C}_{25}\text{H}_{20}\text{FN}_3\text{O} + \text{H}]^+$ 398.1669 (100%), found 398.1659 (100%).

(*E*)-5,5'-Dibromo-bi(3*H*-indol)-3-one *O*-(3-chlorobenzyl) oxime (**4ef**)

Red solid, mp: 234-235 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max} : 3431, 2927, 1541, 1435, 1133. ^1H NMR (400 MHz, DMSO-*d*6): δ 12.15 (d, J = 2.4 Hz, 1H), 8.61 (d, J = 2.0 Hz, 1H), 8.37 (d, J = 3.1 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.65–7.61 (m, 2H), 7.55–7.51 (m, 1H), 7.50–7.43 (m, 4H), 7.37 (dd, J = 8.5, 2.0 Hz, 1H), 5.63 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 161.7, 156.5, 154.2, 139.7, 135.8, 135.7, 135.6, 134.0, 133.7, 131.0, 129.8, 128.8, 128.0, 127.6, 126.0, 124.8, 123.0, 122.1, 118.1, 114.8, 114.6, 108.0, 77.9. HRESIMS calcd for $[\text{C}_{23}\text{H}_{14}\text{Br}_2\text{ClN}_3\text{O} - \text{H}]^+$ 539.9114 (50%), 541.9093 (100%), 543.9073 (50%), found 539.9127 (50%), 541.9103 (100%), 543.9081 (50%).

(*E*)-7,7'-Dimethyl-bi(3*H*-indol)-3-one *O*-(3-chlorobenzyl) oxime (**4ff**)

Red solid, mp: 225-227 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max} : 3415, 2924, 1552, 1434, 1129. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.85 (s, 1H), 8.38 (d, J = 7.9 Hz, 1H), 8.28 (d, J = 3.1 Hz, 1H), 7.78 (d, J = 7.0 Hz, 1H), 7.60 (s, 1H), 7.53–7.44 (m, 3H), 7.28 (d, J = 7.7 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.0 Hz, 1H), 5.60 (s, 2H), 2.52 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 160.8, 155.9, 155.9, 140.0, 136.4, 134.6, 133.7, 131.7, 131.0, 129.3, 128.7, 128.6, 127.4, 126.2, 125.9, 125.3, 123.9, 121.9, 121.7, 121.1, 120.6, 109.3, 77.4, 17.2, 16.3. HRESIMS calcd for $[\text{C}_{25}\text{H}_{20}\text{ClN}_3\text{O} + \text{H}]^+$ 414.1373 (100%), 416.1344 (32%), found 414.1364 (100%), 416.1328 (32%).

(*E*)-Bi(3*H*-indol)-3-one *O*-(2-chloro-4-fluorobenzyl) oxime (**4ag**)

Red solid, mp: 232-234 °C (from EtOAc/PE = 1:8). IR (KBr) $\nu_{\max}$: 3409, 3204, 2923, 1543, 1441, 1130. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.93 (s, 1H), 8.49 (d, J = 7.3 Hz, 1H), 8.38 (d, J = 2.3 Hz, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.75 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.47–7.42 (m, 2H), 7.29 (t, J = 8.5 Hz, 1H), 7.21 (d, J = 6.6 Hz, 2H), 7.18–7.12 (m, 1H), 5.65 (s, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.5 (d, J = 248.2 Hz), 161.8, 157.7, 155.5, 137.0, 134.9 (d, J = 10.8 Hz), 133.5 (d, J = 9.2 Hz), 133.3, 132.7, 131.4 (d, J = 3.5 Hz), 127.6, 126.4, 126.1, 123.3, 122.9, 121.7, 121.4, 120.2, 117.4 (d, J = 25.2 Hz), 115.1 (d, J = 21.1 Hz), 112.6, 108.6, 75.2. HRESIMS calcd for $[\text{C}_{23}\text{H}_{15}\text{ClFN}_3\text{O} + \text{H}]^+$ 404.0966 (100%), 406.0936 (32%), found 404.0953 (100%), 406.0917 (32%).

(*E*)-5,5'-Dimethoxy-2,3'-bi(3*H*-indol)-3-one *O*-(2-chloro-4-fluorobenzyl) oxime (**4gg**)

Brown solid, mp: 164-165 °C (from EtOAc/PE = 1:8). IR (KBr) $\nu_{\max}$: 3323, 2865, 1503, 1383. ^1H NMR (400 MHz, DMSO-*d*6): δ 8.52 (s, 1H), 8.26 (d, J = 2.8 Hz, 1H), 7.99 (d, J = 2.1 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.29 (t, J = 6.7 Hz, 1H), 7.00 (dd, J = 8.4, 2.1 Hz, 1H), 6.86 (dd, J = 8.4, 2.1 Hz, 1H), 5.60 (s, 2H), 3.96 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.5 (d, J = 248.8 Hz), 160.4, 157.9, 155.7, 155.4, 151.2, 134.9 (d, J = 10.8 Hz), 133.5 (d, J = 9.2 Hz), 132.1, 131.9, 131.4 (d, J = 3.4 Hz), 127.0, 122.3, 120.5, 117.5 (d, J = 25.2 Hz), 117.0, 115.1 (d, J = 21.1 Hz), 114.6, 113.1, 112.7, 108.5, 105.2, 75.2, 56.0, 55.9. HRESIMS calcd for $[\text{C}_{25}\text{H}_{19}\text{ClFN}_3\text{O}_3 + \text{H}]^+$ 464.1177 (100%), 466.1148 (32%), found 464.1167 (100%), 466.1133 (32%).

(*E*)-2,3'-Bi(3*H*-indol)-3-one *O*-allyl oxime (**4ah**)

Red solid, mp: 122-123 °C (from EtOAc/PE = 1:8). IR (KBr) $\nu_{\max}$: 3371, 2921, 1549, 1431. ^1H NMR (400 MHz, DMSO-*d*6): δ 11.91 (s, 1H), 8.51 (d, J = 7.0 Hz, 1H), 8.40 (d, J = 2.9 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H), 7.51 (dd, J = 7.0, 1.5 Hz, 1H), 7.49–7.41 (m, 2H), 7.31–7.13 (m, 3H), 6.26–6.15 (m, 1H), 5.50 (dd, J = 17.3, 1.5 Hz, 1H), 5.37 (d, J = 10.4 Hz, 1H), 5.06 (d, J = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.0, 157.7, 155.0, 137.0, 134.2, 133.1, 132.5, 127.5, 126.4, 126.0, 123.3, 122.9, 121.7, 121.4, 120.2, 119.3, 112.6, 108.7, 77.6. HRAPCIMS calcd for $[\text{C}_{19}\text{H}_{15}\text{N}_3\text{O} + \text{H}]^+$ 302.1293 (100%), found 302.1284 (100%).

(*E*)-7,7'-Dimethyl-2,3'-bi(3*H*-indol)-3-one *O*-allyl oxime (**4fh**)

Red solid, mp: 168-169 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max} : 3394, 2923, 1554, 1434, 1124. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (d, J = 8.0 Hz, 1H), 8.42 (s, 1H), 8.32 (d, J = 2.4 Hz, 1H), 7.85 (d, J = 6.8 Hz, 1H), 7.27–7.21 (m, 2H), 7.10 (d, J = 7.2 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.24–6.12 (m, 1H), 5.47 (dq, J = 17.3, 1.5 Hz, 1H), 5.36 (dq, J = 1.2, 10.5 Hz, 1H), 4.98 (dt, J = 1.2, 5.8 Hz, 2H), 2.63 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.0, 155.8, 155.7, 135.7, 133.8, 133.6, 129.9, 129.7, 126.1, 125.4, 124.9, 124.0, 122.0, 121.4, 121.0, 120.1, 118.5, 111.0, 77.3, 16.5, 16.2. HRESIMS calcd for $[\text{C}_{21}\text{H}_{19}\text{N}_3\text{O} + \text{H}]^+$ 330.1606 (100%), found 330.1596 (100%).

(*E*)-2,3'-Bi(3*H*-indol)-3-one *O*-butyl oxime (**4ai**)

Red solid, mp: 191-193 °C (from EtOAc/PE = 1:8). IR (KBr) ν_{max} : 3363, 2910, 1540, 1421. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 11.89 (s, 1H), 8.52 (dd, J = 6.7, 2.2 Hz, 1H), 8.41 (d, J = 2.9 Hz, 1H), 7.93 (d, J = 7.2 Hz, 1H), 7.52 (dd, J = 6.7, 2.2 Hz, 1H), 7.47–7.41 (m, 2H), 7.28–7.21 (m, 2H), 7.20–7.14 (m, 1H), 4.53 (t, J = 6.5 Hz, 2H), 1.86–1.77 (m, 2H), 1.52–1.43 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 162.0, 157.6, 154.7, 137.0, 133.0, 132.5, 127.3, 126.4, 126.0, 123.3, 122.9, 121.6, 121.5, 120.1, 112.6, 108.8, 76.8, 31.3, 19.1, 14.2. HRESIMS calcd for $[\text{C}_{20}\text{H}_{19}\text{N}_3\text{O} + \text{H}]^+$ 318.1606 (100%), found 318.1592 (100%).

(*E*)-2,3'-Bi(3*H*-indol)-3-one *O*-cyclopropylmethyl oxime (**4aj**)

Red solid, mp: 183-185 °C (from EtOAc/PE = 1:8). IR (KBr) ν_{max} : 3461, 3215, 1551, 1443, 1139. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 11.86 (s, 1H), 8.52 (dd, J = 6.5, 2.1 Hz, 1H), 8.40 (d, J = 2.9 Hz, 1H), 7.95 (d, J = 7.3 Hz, 1H), 7.51 (dd, J = 7.0, 1.3 Hz, 1H), 7.43 (d, J = 3.8 Hz, 2H), 7.26–7.14 (m, 3H), 4.36 (d, J = 7.3 Hz, 2H), 1.39–1.30 (m, 1H), 0.66–0.58 (m, 2H), 0.46–0.40 (m,

2H). ^{13}C NMR (100 MHz, DMSO-*d*6): δ 162.0, 157.6, 154.6, 137.0, 132.9, 132.5, 127.4, 126.4, 125.9, 123.2, 122.9, 121.6, 121.5, 120.1, 112.6, 108.8, 81.5, 10.8, 3.5. HRAPCIMS calcd for $[\text{C}_{20}\text{H}_{17}\text{N}_3\text{O} + \text{H}]^+$ 316.1450 (100%), found 316.1436 (100%).

3. Copies of ^1H , ^{13}C Spectra

4. Copies of high resolution mass spectra of compounds

T: FTMS + p ESI sid=20.00 Full ms [300.00-550.00]

T: FTMS + p ESI Full ms [280.00-500.00]

T: FTMS + p ESI Full ms [300.00-550.00]

T: FTMS - p ESI Full ms [450.00-600.00]

T: FTMS - p ESI Full ms [520.00-650.00]

T: FTMS + p ESI Full ms [200.00-600.00]

T: FTMS + p ESI Full ms [280.00-500.00]

T: FTMS + p ESI sid=20.00 Full ms [350.00-550.00]

T: FTMS + p APCI corona Full ms [280.00-400.00]

T: FTMS + p ESI Full ms [325.00-400.00]

T: FTMS + p APCI corona Full ms [250.00-400.00]

T: FTMS + p APCI corona Full ms [250.00-400.00]

5. X-ray Data of Compound 4aa

Figure 1. ORTEP representation of the molecular structure of **4aa**.