

Highly efficient regioselective synthesis of pyrroles *via* a tandem enamine formation-Michael addition-cyclization sequence under catalyst- and solvent-free conditions

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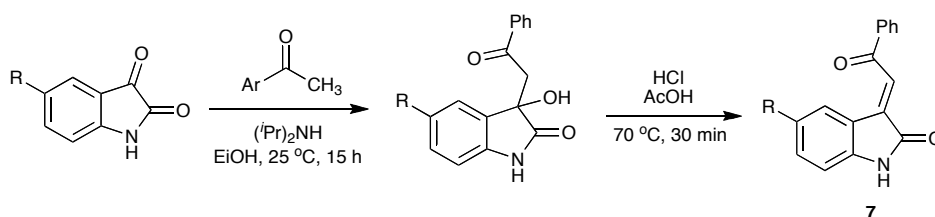
Supporting Information

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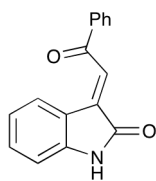
1. Synthesis of compounds 7

The compounds **7** were prepared from isatin derivatives and aryl methyl ketones using literature procedure¹



2. Characterization data of compounds 7

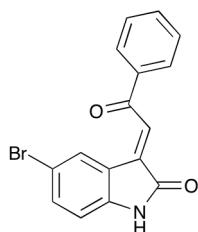
(*E*)-3-(2-Oxo-2-phenylethylidene)indolin-2-one (**7a**):



7a

Orange solid, mp. 189-191 °C; ¹H NMR (DMSO-d₆, 300 MHz) δ 6.88 (d, *J* = 8.1 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.69-7.72 (m, 2H), 8.06-8.09 (m, 3H), 10.78 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 110.3, 119.9, 121.7, 125.8, 126.7, 128.5, 129.1, 132.9, 134.0, 136.4, 137.0, 144.9, 168.2, 191.7.

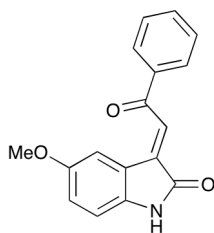
(*E*)-5-Bromo-3-(2-oxo-2-phenylethylidene)indolin-2-one (**7b**):



7b

Red solid, mp. 213-215 °C; ¹H NMR (DMSO-d₆, 300 MHz) δ 6.80 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.54-7.58 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.85 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 2H), 8.47 (d, *J* = 1.8 Hz, 1H), 10.54 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 112.2, 113.2, 121.8, 126.7, 128.6, 129.1, 129.2, 134.1, 135.2, 135.8, 137.0, 144.2, 167.7, 190.7.

(*E*)-5-Methoxy-3-(2-oxo-2-phenylethylidene)indolin-2-one (**7c**):

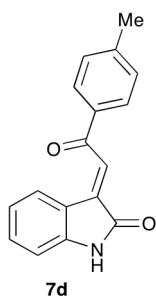


7c

Red solid, mp. 172-174 °C; ¹H NMR (CDCl₃, 300 MHz) δ 3.81 (s, 3H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.86 (s, 1H), 8.00 (d, *J* = 2.1 Hz, 1H), 8.12 (d, *J* = 7.5 Hz, 2H), 8.20 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 55.3, 110.4, 112.9, 118.3, 120.6, 124.7, 128.2, 128.5, 133.4, 137.2, 137.8, 138.6, 154.4, 168.6, 190.5.

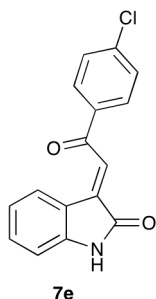
¹ (a) F. Braude and H. G. Lindwall, *J. Am. Chem. Soc.*, 1933, **55**, 325; (b) S. J. Edeson, J. Jiang, S. Swanson, P. A. Procopiu, H. Adams, A. J. H. M. Meijer and J. P. A. Harrity, *Org. Biomol. Chem.*, 2014, **12**, 3201.

(E)-3-(2-Oxo-2-*p*-tolylethylidene)indolin-2-one (7d):



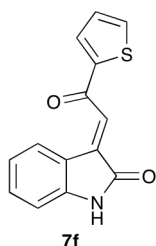
Orange solid, mp.163-165 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) δ 2.41 (s, 3H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 7.34 (td, *J* = 7.5, 0.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.70 (s, 1H), 7.96-7.99 (m, 3H), 10.82 (s, 1H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 21.2, 110.3, 119.3, 121.7, 126.1, 126.6, 128.6, 129.6, 132.7, 134.5, 136.1, 144.7, 144.8, 168.2, 190.7.

(E)-3-(2-(4-Chlorophenyl)-2-oxoethylidene)indolin-2-one (7e):



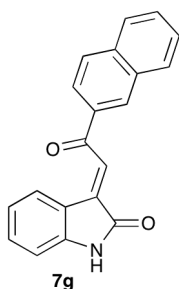
Red solid, mp.197-199 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) δ 6.89 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.69 (s, 1H), 8.04-8.10 (m, 3H), 10.83 (s, 1H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 110.3, 199.9, 121.7, 125.0, 126.9, 129.1, 130.4, 133.1, 135.7, 136.9, 138.9, 145.0, 168.1, 189.8.

(E)-3-(2-Oxo-2-(thiophen-2-yl)ethylidene)indolin-2-one (7f):



Red solid, mp.188-192 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) δ 6.89 (d, *J* = 7.8 Hz, 1H), 7.0 (td, *J* = 7.5, 0.9 Hz, 1H), 7.30-7.40 (m, 2H), 7.65 (s, 1H), 8.12-8.17 (m, 2H), 8.32 (d, *J* = 7.5 Hz, 1H), 10.84 (s, 1H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 110.3, 120.0, 121.8, 124.3, 127.7, 129.4, 133.3, 134.4, 136.8, 137.1, 145.1, 145.2, 168.2, 182.56.

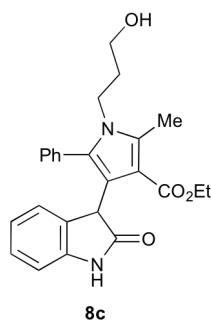
(E)-3-(2-(Naphthalen-2-yl)-2-oxoethylidene)indolin-2-one (7g):



Orange solid, mp.219 -221 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) δ 6.90 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.62-7.74 (m, 2H), 7.90 (s, 1H), 8.02-8.11 (m, 4H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.80 (s, 1H), 10.96 (s, 1H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 110.34, 120.0, 121.7, 123.5, 126.1, 126.8, 127.1, 127.7, 128.8, 129.2, 129.9, 131.0, 132.2, 132.9, 134.4, 135.3, 136.4, 144.9, 168.3, 191.0.

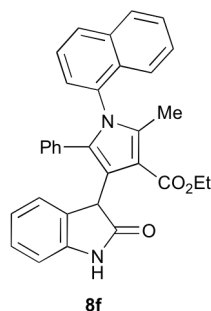
3. Characterization data for compounds 8

Ethyl 1-(3-hydroxypropyl)-2-methyl-4-(2-oxoindolin-3-yl)-5-phenyl-1H-pyrrole-3-carboxylate (8c).



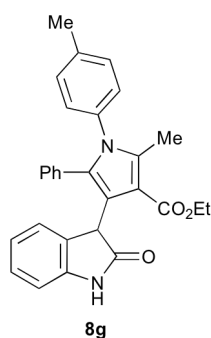
Pale brown solid, mp. 130-132 °C; IR (Neat): 3496, 3143, 3087, 1695, 1669, 1618, 1527, 1469, 1270, 1189, 1123 cm^{-1} ; ^1H NMR (DMSO- d_6 , 300 MHz) δ 0.81 (t, J = 7.2 Hz, 3H), 1.52-1.65 (m, 2H), 2.51 (s, 3H), 3.22-3.27 (m, 2H), 3.70-3.75 (m, 2H), 3.89 (t, J = 7.5 Hz, 2H), 4.10 (s, 1H), 4.55 (t, J = 4.8 Hz, 1H), 6.77-6.82 (m, 3H), 7.07-7.13 (m, 1H), 7.48-7.51 (m, 5H), 10.3 (s, 1H); ^{13}C NMR (DMSO- d_6 , 75 MHz)* δ 16.5, 19.1, 38.4, 50.3, 63.0, 63.1, 113.9, 114.0, 120.1, 126.0, 127.7, 132.2, 133.7, 133.9, 136.0, 136.1, 136.6, 140.0, 141.7, 147.9, 169.2, 183.6. Anal Calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_4$: C, 71.75; H, 6.26; N, 6.69. Found: C, 71.40; H, 6.34; N, 6.53. *one sp^2 carbon merged with others.

Ethyl 2-methyl-1-(naphthalen-1-yl)-4-(2-oxoindolin-3-yl)-5-phenyl-1H-pyrrole-3-carboxylate (8f).



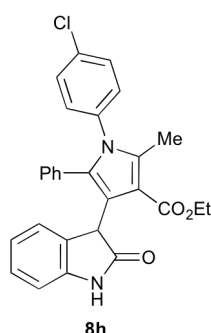
Off-white solid, mp. 254-256 °C; IR (Neat): 3146, 3083, 1688, 1616, 1530, 1468, 1262, 1113 cm^{-1} ; ^1H NMR (DMSO- d_6 , 300 MHz) δ 0.88 (t, J = 6.3 Hz, 3H), 2.11 (s, 3H), 3.82 (q, J = 6.3 Hz, 2H), 4.35 (s, 1H), 6.85-6.98 (m, 2H), 7.12-7.24 (m, 8H), 7.58-7.67 (m, 4H), 8.02 (d, J = 7.8 Hz, 2H), 10.39 (s, 1H); ^{13}C NMR (DMSO- d_6 , 75 MHz)* δ 9.7, 11.6, 42.9, 56.0, 106.5, 107.6, 112.9, 118.7, 119.7, 120.3, 123.1, 124.5, 124.9, 125.2, 125.7, 126.0, 127.0, 127.8, 128.0, 128.3, 129.1, 131.2, 134.4, 135.9, 140.6, 161.6, 175.9. Anal Calcd for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}_3$: C, 78.99; H, 5.39; N, 5.76. Found: C, 78.64; H, 5.37; N, 5.86. *three sp^2 carbons merged with others.

Ethyl 2-methyl-4-(2-oxoindolin-3-yl)-5-phenyl-1-*p*-tolyl-1H-pyrrole-3-carboxylate (8g).



Off-white solid, mp. 164-166 °C; IR (Neat): 3148, 3084, 2974, 1691, 1618, 1513, 1468, 1263, 1139, 1088 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.66 (t, J = 6.9 Hz, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 3.58 (q, J = 6.9 Hz, 2H), 4.10 (s, 1H), 6.62-6.69 (m, 2H), 6.76 (d, J = 7.2 Hz, 1H), 6.92-7.06 (m, 10H), 10.17 (s, 1H); ^{13}C NMR (CDCl_3 , 75 MHz)* δ 17.7, 19.1, 25.8, 50.3, 63.4, 114.0, 115.0, 120.3, 126.1, 127.8, 132.3, 133.0, 133.4, 134.8, 135.9, 136.5, 139.8, 140.8, 142.6, 142.9, 148.0, 169.1, 183.6. Anal Calcd for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}_3$: C, 77.31; H, 5.82; N, 6.22. Found: C, 76.97; H, 5.80; N, 6.22. *two sp^2 carbons merged with others.

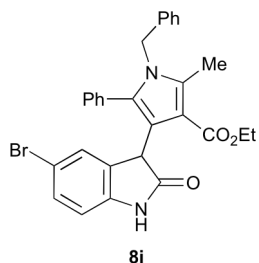
Ethyl 1-(4-chlorophenyl)-2-methyl-4-(2-oxoindolin-3-yl)-5-phenyl-1H-pyrrole-3-carboxylate (8h).



Off-white solid, mp. 232-235 °C; IR (Neat): 3141, 3075, 1693, 1618, 1530, 1492, 1366, 1262, 1085 cm^{-1} ; ^1H NMR (DMSO- d_6 , 300 MHz) δ 0.84 (t, J = 6.9 Hz, 3H), 2.29 (s, 3H), 3.77 (q, J = 6.9 Hz, 2H), 4.30 (s, 1H), 6.81-6.88 (m, 2H), 6.96 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.26-7.32 (m, 7H), 7.47 (d, J = 8.1 Hz, 2H), 10.38 (s, 1H); ^{13}C NMR (DMSO- d_6 , 75 MHz)* δ 12.4,

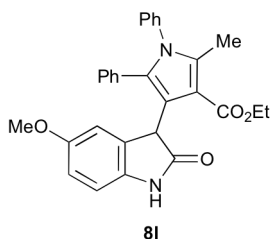
13.8, 45.0, 58.2, 108.7, 110.2, 115.4, 120.8, 122.6, 127.1, 127.9, 128.3, 129.1, 130.3, 130.6, 131.1, 132.9, 135.5, 136.1, 137.3, 142.7, 163.8, 178.2. Anal Calcd for C₂₈H₂₃ClN₂O₃: C, 71.41; H, 4.92; N, 5.95. Found: C, 71.18; H, 4.95; N, 5.98. *one sp² carbon merged with others.

Ethyl 1-benzyl-4-(5-bromo-2-oxindolin-3-yl)-2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (8j).



Off-white solid, mp. 216-219 °C; IR (Neat): 3284, 2924, 1721, 1694, 1684, 1522, 1472, 1435, 1272, 1199 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.87 (t, *J* = 6.9 Hz, 3H), 2.38 (s, 3H), 3.78 (q, *J* = 6.9 Hz, 2H), 4.25 (s, 1H), 5.13 (s, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.90-6.98 (m, 3H), 7.23-7.43 (m, 9H), 10.51 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* 11.5, 13.9, 45.2, 47.2, 58.2, 109.3, 110.6, 112.5, 114.3, 125.0, 125.6, 127.2, 128.7, 129.7, 130.2, 130.8, 133.9, 135.8, 136.8, 137.4, 142.1, 163.8, 177.8. Anal Calcd for C₂₉H₂₅BrN₂O₃: C, 65.79; H, 4.76; N, 5.29. Found: C, 65.47; H, 4.71; N, 5.39. Two sp² carbons merged with others.

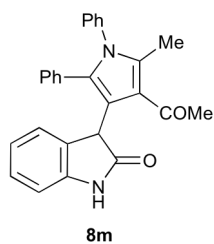
Ethyl 4-(5-methoxy-2-oxindolin-3-yl)-2-methyl-1,5-diphenyl-1H-pyrrole-3-carboxylate (8l).



Off-white solid, mp. 224-227 °C; IR (Neat): 3165, 2929, 1694, 1604, 1489, 1262, 1172, 1087 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 2.29 (s, 3H), 3.66 (s, 3H), 3.74 (q, *J* = 6.9 Hz, 2H), 4.28 (s, 1H), 6.56-6.72 (m, 3H), 7.25-7.41 (m, 10H), 10.20 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 12.4, 13.9, 45.5, 55.4, 58.2, 108.9, 109.9, 110.3, 111.1, 115.1, 127.7, 128.1, 128.3, 128.5, 129.0, 130.5, 130.6, 132.7, 135.6, 136.2, 137.2, 154.5, 163.9, 178.0. Anal Calcd for C₂₉H₂₆N₂O₄: C, 74.66; H, 5.62; N, 6.00. Found: C, 74.35; H, 5.51; N, 6.02. *one sp² carbon merged

with others.

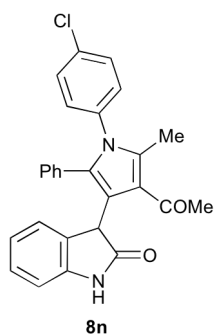
3-(4-Acetyl-5-methyl-1,2-diphenyl-1H-pyrrol-3-yl)indolin-2-one (8m).



Pale brown solid, mp. 232-235 °C; IR (Neat): 3313, 3055, 1713, 1645, 1619, 1486, 1423, 1206, 1066 cm⁻¹. ¹H NMR (DMSO-d₆, 300 MHz) δ 2.20 (s, 3H), 2.33 (s, 3H), 4.22 (s, 1H), 6.80-6.88 (m, 4H), 7.07-7.40 (m, 10H), 10.29 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 15.9, 32.4, 47.2, 110.8, 117.7, 120.0, 122.7, 124.4, 129.1, 129.8, 130.2, 130.5, 130.9, 131.2, 132.7, 137.7, 138.0, 139.3, 145.3, 180.0, 194.6. Anal Calcd for C₂₇H₂₂N₂O₂: C, 79.78; H, 5.46; N, 6.89. Found: C, 79.44; H, 5.35; N, 6.81. *two sp² carbons

merged with others.

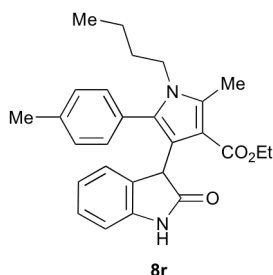
3-(4-Acetyl-1-(4-chlorophenyl)-5-methyl-2-phenyl-1H-pyrrol-3-yl)indolin-2-one (8n).



Pale brown solid, mp. 260-262 °C; IR (Neat): 3336, 3040, 1720, 1647, 1495, 1208, 1092 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 2.19 (s, 3H), 2.32 (s, 3H), 4.20 (s, 1H), 6.81-7.48 (m, 13H), 10.29 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 13.7, 30.3, 45.0, 108.7, 115.8, 120.6, 122.3, 127.0, 127.9, 128.2, 129.1, 130.3, 130.6, 132.9, 135.6, 136.1, 143.2, 177.8, 192.5. Anal Calcd for C₂₇H₂₁Cl

N₂O₂: C, 79.78; H, 5.46; N, 6.89. Found: C, 79.49; H, 5.39; N, 6.80. *four sp² carbons merged with others.

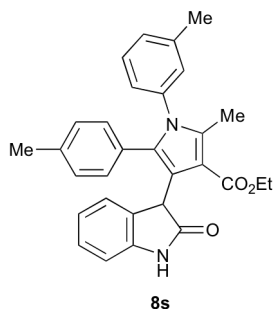
Ethyl 1-butyl-2-methyl-4-(2-oxoindolin-3-yl)-5-*p*-tolyl-1*H*-pyrrole-3-carboxylate (8r).



Off-white solid, mp. 142-144 °C; IR (Neat): 3177, 3032, 2923, 1698, 1619, 1499, 1265, 1099 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.50 (t, *J* = 7.5 Hz, 3H), 0.57 (t, *J* = 7.2 Hz, 3H), 0.83-0.91 (m, 2H), 1.19-1.22 (m, 2H), 2.12 (s, 3H), 2.28 (s, 3H), 3.53 (q, *J* = 7.2 Hz, 2H), 3.58 (t, *J* = 7.5 Hz, 2H), 3.87 (s, 1H), 6.53-6.61 (m, 3H), 6.84-6.88 (m, 1H), 7.08-7.10 (m, 4H), 10.05 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 11.2, 13.2, 13.8, 19.1, 20.8, 31.9, 43.4, 45.1, 57.8, 108.6, 108.8, 114.7, 120.7, 122.3, 126.8, 127.9, 129.2, 130.8, 131.4, 134.8, 136.0, 137.9, 142.7, 163.9, 178.4. Anal Calcd for C₂₇H₃₀N₂O₃: C, 75.32; H, 7.02; N, 6.51. Found. C, 75.02;

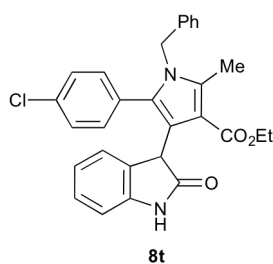
H, 6.93; N, 6.55.

Ethyl 2-methyl-4-(2-oxoindolin-3-yl)-1-*m*-tolyl-5-*p*-tolyl-1*H*-pyrrole-3-carboxylate (8s).



Off-white solid, mp. 238-240 °C; IR (Neat): 3246, 3056, 2959, 1695, 1619, 1470, 1266, 1105 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.84 (t, *J* = 6.9 Hz, 3H), 2.21 (s, 3H), 2.26 (s, 3H), 2.26 (s, 3H), 3.74-3.83 (m, 2H), 4.27 (s, 1H), 6.80-6.91 (m, 3H), 7.05-7.18 (m, 8H), 7.27 (t, *J* = 7.8 Hz, 1H), 10.35 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 12.4, 13.8, 20.6, 45.1, 58.1, 108.7, 109.8, 115.0, 120.8, 122.5, 125.5, 127.0, 127.7, 128.7, 128.9, 130.5, 131.3, 135.5, 137.1, 137.2, 138.6, 142.7, 163.9, 178.4. Anal Calcd for C₃₀H₂₈N₂O₃: C, 77.56; H, 6.08; N, 6.03. Found: C, 77.29; H, 6.00; N, 5.93. *one sp³ and two sp² carbons merged with others

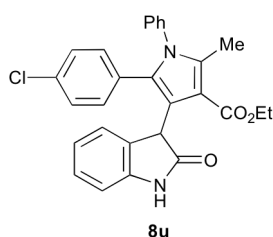
Ethyl 1-benzyl-5-(4-chlorophenyl)-2-methyl-4-(2-oxoindolin-3-yl)-1*H*-pyrrole-3-carboxylate (8t).



Off-white solid, mp. 176-178 °C; IR (Neat): 3181, 2976, 1709, 1618, 1470, 1271, 1118, 1015 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.82 (t, *J* = 6.9 Hz, 3H), 2.37 (s, 3H), 3.69-3.78 (m, 2H), 4.18 (s, 1H), 5.13 (s, 2H), 6.79-6.89 (m, 5H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.23-7.42 (m, 5H), 7.50 (d, *J* = 8.1 Hz, 2H), 10.35 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 11.3, 13.8, 45.1, 47.2, 58.1, 108.7, 109.7, 115.5, 120.8, 122.4, 125.5, 127.0, 127.2, 128.7, 129.2, 131.2, 132.5, 133.5, 134.2, 137.0, 137.4, 142.7, 163.8, 178.2. Anal Calcd for C₂₉H₂₅ClN₂O₃: C, 71.82; H, 5.20; N, 5.78. Found: C,

71.70; H, 5.13; N, 5.77. *one sp² carbon merged with others

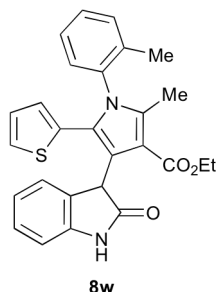
Ethyl 5-(4-chlorophenyl)-2-methyl-4-(2-oxoindolin-3-yl)-1-phenyl-1*H*-pyrrole-3-carboxylate (8u).



Off-white solid, mp. 257-259 °C; IR (Neat): 3176, 3036, 2924, 1707, 1619, 1472, 1268, 1139, 1085 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.65 (t, *J* = 6.9 Hz, 3H), 2.1 (s, 3H), 3.50-3.63 (m, 2H), 4.10 (s, 1H), 6.61-6.76 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 7.03-7.21 (m, 9H), 10.20 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 10.1, 11.6, 42.7, 56.0, 106.5, 107.9, 113.4, 118.6, 120.4, 124.8,

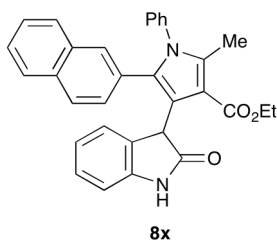
126.0, 126.2, 126.9, 127.2, 128.9, 130.1, 130.4, 132.0, 134.7, 135.3, 140.5, 161.6, 175.9. Anal Calcd for C₂₈H₂₃ClN₂O₃: C, 71.41; H, 4.92; N, 5.95. Found: C, 71.18; H, 4.87; N, 5.90. *one sp² carbon merged with others.

Ethyl 2-methyl-4-(2-oxoindolin-3-yl)-5-(thiophen-2-yl)-1-*o*-tolyl-1H-pyrrole-3-carboxylate (8w).



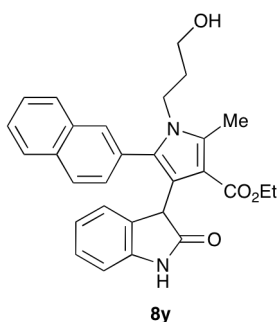
Off-white solid, mp. 160-162 °C; IR (Neat): 3252, 3086, 2979, 1696, 1619, 1470, 1266, 1119 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.88 (t, *J* = 5.4 Hz, 3H), 1.92 (s, 3H), 2.16 (s, 3H), 3.82 (q, *J* = 5.4 Hz, 2H), 4.50 (s, 1H), 6.83-7.01 (m, 4H), 7.14-7.14 (m, 2H), 7.35-7.38 (m, 4H), 7.48 (d, *J* = 4.2 Hz, 1H), 10.39 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 12.0, 13.8, 16.7, 45.3, 58.3, 108.8, 109.9, 117.4, 121.0, 122.4, 126.8, 127.0, 127.1, 127.7, 128.2, 129.1, 129.3, 129.4, 130.5, 130.8, 131.2, 135.9, 136.3, 137.9, 142.9, 163.6, 177.9. Anal Calcd for C₂₇H₂₄N₂O₃S: C, 71.03; H, 5.30; N, 6.14; S, 7.02. Found: C, 70.73; H, 5.23; N, 6.04; S, 6.95.

Ethyl 2-methyl-5-(naphthalen-1-yl)-4-(2-oxoindolin-3-yl)-1-phenyl-1H-pyrrole-3-carboxylate (8x).



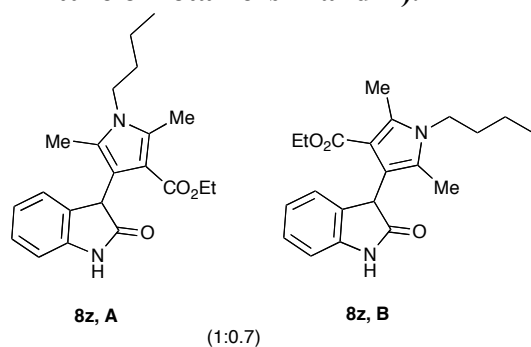
Off-white solid, mp. 118-120 °C; IR (Neat): 3252, 3056, 2926, 1701, 1619, 1470, 1265, 1086 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.87 (t, *J* = 6.9 Hz, 3H), 2.32 (s, 3H), 3.80 (q, *J* = 6.9 Hz, 2H), 4.40 (s, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.28-7.49 (m, 7H), 7.75-7.87 (m, 5H), 10.38 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz)* δ 12.5, 13.8, 45.1, 58.2, 108.7, 110.1, 115.7, 120.6, 122.6, 126.4, 126.5, 127.1, 127.4, 127.5, 127.9, 128.2, 128.2, 128.5, 129.1, 129.7, 131.2, 132.0, 132.3, 135.4, 137.2, 137.4, 142.8, 163.9, 178.3. Anal Calcd for C₃₂H₂₆N₂O₃: C, 78.99; H, 5.39; N, 5.76. Found: C, 78.66; H, 5.27; N, 5.71. *one sp² carbon merged with others.

Ethyl 1-(3-hydroxypropyl)-2-methyl-5-(naphthalen-1-yl)-4-(2-oxoindolin-3-yl)-1H-pyrrole-3-carboxylate (8y).



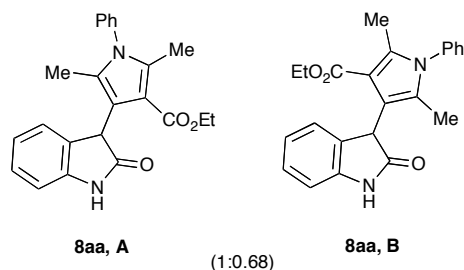
Off-white solid, mp. 108-110 °C; IR (Neat): 3450, 3272, 2953, 1698, 1470, 1267, 1121, 1088 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 0.61 (t, *J* = 7.2 Hz, 3H), 1.20-1.34 (m, 2H), 2.20 (s, 3H), 3.02 (m, 2H), 3.53 (t, *J* = 6.9 Hz, 2H), 3.74 (m, 2H), 3.95 (s, 1H), 4.28 (s, 1H), 6.53-6.62 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 7.34-7.37 (m, 3H), 7.75-7.84 (m, 4H), 10.07 (s, 1H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 11.3, 13.8, 33.3, 41.5, 45.2, 57.7, 57.9, 108.6, 109.0, 115.3, 120.8, 122.4, 126.6, 126.7, 126.9, 127.6, 128.1, 128.2, 128.4, 128.5, 130.0, 131.4, 132.5, 132.7, 134.6, 136.6, 142.7, 164.0, 178.4. Anal Calcd for C₂₉H₂₈N₂O₃: C, 74.34; H, 6.02; N, 5.98. Found: C, 74.01; H, 5.95; N, 5.91.

Ethyl 1-butyl-2,5-dimethyl-4(2-oxoindolin-3-yl)-1H-pyrrole-3-carboxylate (8z, 1:0.7 mixture of rotamers A and B).



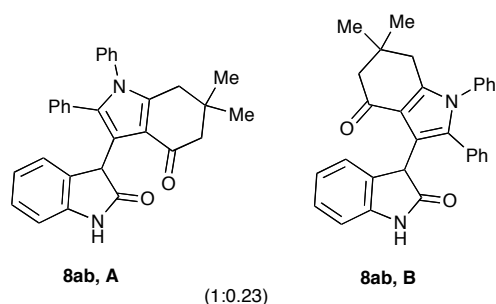
Off white solid, mp. 168-170 °C; IR (Neat): 3172, 3075, 2959, 1697, 1676, 1616, 1471, 1287, 1226 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.89-1.02 (m, 12H, **A** & **B**), 1.29-1.41 (m, 4H, **A** & **B**), 1.44-1.53 (m, 2H, **A**), 1.55-1.61 (m, 2H, **B**), 1.69 (s, 3H, **B**), 2.33 (s, 3H, **A**), 2.53 (s, 3H, **B**), 3.68 (t, $J = 7.8$ Hz, 2H, **B**), 3.79-3.91 (m, 4H, **A**), 4.29-4.33 (m, 2H, **B**), 4.61 (s, 1H, **A**), 5.86 (s, 1H, **B**), 6.84-6.99 (m, 5H, **A** & **B**), 7.08-7.20 (m, 3H, **A** & **B**), 8.28 (s, 1H, **A**), 8.42 (s, 1H, **B**); ^{13}C NMR (CDCl_3 , 75 MHz) δ 10.1, 10.2, 11.6, 12.1, 13.7, 13.8, 14.1, 14.5, 20.1, 20.2, 32.6, 32.7, 43.4, 43.9, 44.4, 45.6, 58.6, 59.3, 108.9, 109.4, 109.7, 110.8, 112.3, 114.1, 121.8, 122.4, 123.0, 124.5, 125.4, 127.2, 128.3, 131.3, 131.5, 134.6, 136.3, 141.0, 141.7, 164.9, 166.2, 180.6, 181.1. Anal calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_3$: C, 71.16; H, 7.39; N, 7.90. Found C, 70.84; H, 7.22; N, 7.79.

Ethyl 2,5-dimethyl-4-(2-oxoindolin-3-yl)-1-phenyl-1H-pyrrole-3-carboxylate (8aa, 1:0.68 mixture of rotamers A and B).



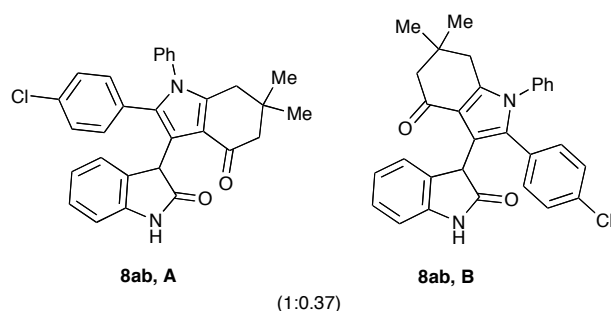
Pale yellow solid, mp. 266-268 °C; IR (Neat): 3195, 3088, 2986, 1691, 1608, 1488, 1260, 1213 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.98 (t, $J = 7.2$ Hz, 3H, **A**), 1.36 (t, $J = 6.9$ Hz, 3H, **B**), 1.47 (s, 3H, **B**), 2.11 (s, 3H, **A**), 2.25 (s, 3H, **A**), 2.29 (s, 3H, **B**), 3.93 (q, $J = 6.9$ Hz, 2H, **A**), 4.34-4.37 (m, 2H, **B**), 4.67 (s, 1H, **A**), 5.95 (s, 1H, **B**), 6.90-7.10 (m, 6H, **A** & **B**), 7.18-7.28 (m, 6H, **A** & **B**), 7.44-7.53 (m, 6H, **A** & **B**), 8.49 (s, 1H, **A**), 8.56 (s, 1H, **B**); ^{13}C NMR (CDCl_3 , 75 MHz) δ 11.7, 13.7, 14.2, 15.0, 15.4, 45.3, 46.6, 59.7, 60.4, 110.4, 110.5, 110.6, 112.3, 113.7, 115.3, 122.8, 123.3, 124.0, 125.3, 125.6, 127.7, 128.2, 129.2, 129.4, 129.5, 129.6, 129.9, 130.3, 130.4, 130.6, 132.0, 132.1, 136.8, 138.4, 138.6, 141.9, 142.7, 165.8, 167.1, 181.3, 181.9. Anal calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_3$: C, 73.78; H, 5.92; N, 7.48. Found C, 73.45; H, 5.75; N, 7.26.

3-(4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-1,2-diphenyl-1H-indol-3-yl)indolin-2-one (8ab, 1:0.23 mixture of rotamers A and B): Data for major rotamer A.



Pale yellow solid, mp. 178-180 °C; IR (Neat): 3180, 2955, 2871, 1721, 1642, 1491, 1460, 1326, 1262, 1208 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz) δ 1.00 (s, 3H), 1.06 (s, 3H), 2.20 (d, $J = 16.2$ Hz, 1H), 2.29 (d, $J = 16.2$ Hz, 1H), 2.53 (s, 2H), 4.66 (s, 1H), 6.91-7.01 (m, 4H), 7.13-7.28 (m, 8H), 7.35-7.38 (m, 2H), 7.89 (s, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 28.4, 28.9, 35.3, 37.1, 44.7, 51.9, 109.4, 114.1, 117.1, 121.6, 123.0, 127.4, 127.6, 127.8, 127.9, 128.3, 129.1, 130.2, 130.6, 130.7, 137.1, 137.3, 142.5, 144.0, 170.2, 193.0. Anal calcd for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_2$; C, 80.69; H, 5.87; N, 6.27. Found C, 80.39; H, 5.78; N, 6.13.

3-(2-(4-chlorophenyl)-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-1-phenyl-1H-indol-3-yl)indolin-2-one (8ac, 1:0.37 mixture of rotamers A and B): Data for major rotamer A.



Pale yellow solid, mp. 160-162 °C; IR (Neat): 3193, 2988, 1724, 1652, 1477, 1356, 1244, 1211 cm^{-1} ; ^1H NMR (CDCl_3 , 300MHz) δ 1.00 (s, 3H), 1.05 (s, 3H), 2.19 (d, $J = 16.2$ Hz, 1H), 2.25 (d, $J = 16.2$ Hz, 1H), 2.52 (s, 2H), 4.60 (s, 1H), 6.88-7.02 (m, 3H), 7.12-7.40 (m, 10H), 7.86 (s, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 28.4, 28.8, 35.3, 37.1, 44.7, 51.9, 109.5, 114.6, 117.1, 121.6, 122.9, 127.7, 128.3, 128.6, 129.1, 130.3, 131.9, 134.0, 135.8, 137.0, 142.6, 144.3, 179.1, 193.0. Anal calcd for $\text{C}_{30}\text{H}_{25}\text{ClN}_2\text{O}_2$; C, 74.91; H, 5.24; N, 5.82. Found C, 74.68; H, 5.08; N, 5.67.

4. ^1H and ^{13}C NMR Spectra of compounds 8

