Brønsted acid-promoted multicomponent reaction for the
construction of pyrrolocoumarin derivatives

Zhiwei Chen*, Sunjia Ye, and Xiongfei Zhang

Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou, 310014, P. R. China; E-mail: chenzhiwei@zjut.edu.cn

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General information

All reagents were obtained from commercial sources (purity >99%) and used without further purification, unless otherwise indicated. Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Ltd. Reactions were stirred using Teflon-coated magnetic stir bars. Thin-layer chromatography (TLC).

Melting points were determined using a Büchi B-540 capillary melting point apparatus. IR spectra were recorded with a Thermo Nicolet AVATAR 370 spectrophotometer in KBr. 1H NMR and 13C NMR were recorded with Varian instrument at 600 and 150 MHz, respectively, and TMS was used as internal standard. Mass spectra were measured with Thermo Finnigan LCQ-Advantage. High resolution mass spectral (HRMS) analyze were measured on a Bruker micrOTOF-Q II instrument using ESI techniques.

General procedure for the synthesis of indole-containing pyrrolocoumarin derivatives:
In a 10 mL reaction tube, 4-aminocoumarins 1 (1 mmol), arylglyoxal monohydrates 2 (1.1 mmol) and indoles 3 (1.1 mmol), p-TSA (34 mg, 0.2 mmol), and EtOH (3 mL) were mixed and then capped. The mixture was heated for 3 h at 100 °C (oil bath). Upon completion of the reaction, monitored by TLC, the reaction solution was transferred to a 100 mL single-necked flask. Water (30 mL) was added to it. After being stirred for 3 h, the solution was filtered. The residue was purified by column chromatography (CH₂Cl₂/MeOH, 180:1 v/v) to afford target product 4.
3-(2-Methyl-1H-indol-3-yl)-2-phenylchromeno[4,3-b]pyrrol-4(1H)-one (4a): Pale yellow powder (289 mg, 74%); mp 189-191 °C. IR (KBr): 3421, 1695, 1507 cm⁻¹. 

¹H NMR (600 MHz, DMSO-d₆): δ = 12.74 (s, 1H), 11.00 (s, 1H), 8.34 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.41 (m, 4H), 7.33–7.25 (m, 3H), 7.22 (t, J = 7.2 Hz, 1H), 6.97 (t, J = 8.4 Hz, 2H), 6.79 (t, J = 7.2 Hz, 1H), 2.09 (s, 3H).


2-Phenyl-3-(2-phenyl-1H-indol-3-yl)chromeno[4,3-b]pyrrol-4(1H)-one (4b): Light green powder (230 mg, 51%); mp >300 °C. IR (KBr): 3361, 1660, 1505 cm⁻¹. 

¹H NMR (600 MHz, DMSO-d₆): δ = 12.77 (s, 1H), 11.51 (s, 1H), 8.36 (dd, J = 7.8, 1.4 Hz, 1H), 7.53–7.47 (m, 3H), 7.46–7.35 (m, 5H), 7.25 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.16 (dt, J = 8.4, 3.2 Hz, 2H), 7.12–7.08 (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.88 (t, J = 7.2 Hz, 1H). 


3-(1H-indol-3-yl)-2-phenylchromeno[4,3-b]pyrrol-4(1H)-one (4c): Brown-red powder (214 mg, 57%); mp 291-293 °C. IR (KBr): 3422, 1687, 1505 cm⁻¹. 

¹H NMR (600 MHz, DMSO-d₆): δ = 12.74 (s, 1H), 11.18 (s, 1H), 8.33 (d, J = 7.2 Hz, 1H), 7.50–7.37 (m, 7H), 7.29 (t, J = 7.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.79 (t, J = 7.2 Hz, 1H). 

¹³C NMR (150 MHz, DMSO-d₆): δ = 157.9, 151.8, 136.5, 135.9, 134.0, 132.4,
129.17, 128.8, 128.1, 127.8, 127.3, 126.3, 124.4, 122.2, 121.2, 120.0, 119.0, 117.1, 114.3, 114.2, 111.9, 108.5, 107.0. MS (ESI): \( m/z = 377 \) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{25}\)H\(_{18}\)N\(_2\)NaO\(_2\) [M + Na]\(^+\): 399.1109; found 399.1114.

3-(5-Methyl-1H-indol-3-yl)-2-phenylchromeno[4,3-b]pyrrol-4(1H)-one (4d): Light yellow powder (222 mg, 57%); mp 281-283 °C. IR (KBr): 3408, 1695, 1506 cm\(^{-1}\). \(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \( \delta = 12.73 \) (s, 1H), 11.01 (s, 1H), 8.30 (d, \( J = 7.8 \) Hz, 1H), 7.51–7.36 (m, 5H), 7.34–7.21 (m, 5H), 6.86 (d, \( J = 8.4 \) Hz, 1H), 6.77 (s, 1H), 2.17 (s, 3H). \(^1\)C NMR (150 MHz, DMSO-\(d_6\)): \( \delta = 157.9, 151.7, 135.8, 134.8, 134.1, 132.4, 129.2, 128.7, 128.1, 127.8, 127.3, 126.1, 124.4, 122.8, 122.1, 119.7, 117.1, 114.5, 114.2, 111.5, 108.6, 106.5, 21.6. MS (ESI): \( m/z = 391 \) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{26}\)H\(_{18}\)N\(_2\)NaO\(_2\) [M + Na]\(^+\): 413.1266; found 413.1259.

3-(5-Bromo-1H-indol-3-yl)-2-phenylchromeno[4,3-b]pyrrol-4(1H)-one (4e): Off-white powder (264 mg, 58%); mp 272-274 °C. IR (KBr): 3439, 1667, 1507 cm\(^{-1}\). \(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \( \delta = 12.80 \) (s, 1H), 11.41 (d, \( J = 1.8 \) Hz, 1H), 8.33 (dd, \( J = 7.8, 1.4 \) Hz, 1H), 7.51–7.38 (m, 7H), 7.36–7.31 (m, 2H), 7.31–7.27 (m, 1H), 7.16 (dd, \( J = 8.4, 1.8 \) Hz, 1H), 7.12 (d, \( J = 1.8 \) Hz, 1H). \(^1\)C NMR (150 MHz, DMSO-\(d_6\)): \( \delta = 157.9, 151.8, 136.0, 135.1, 134.2, 132.2, 129.3, 129.2, 128.9, 128.3, 128.0, 127.9, 124.5, 123.7, 122.3, 117.1, 114.2, 113.9, 113.4, 111.7, 108.5, 106.9. MS (ESI): \( m/z = 455 \) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{26}\)H\(_{15}\)BrN\(_2\)NaO\(_2\) [M + Na]\(^+\): 477.0215; found 477.0213.

3-(1-Benzyl-1H-indol-3-yl)-2-phenylchromeno[4,3-b]pyrrol-4(1H)-one (4f): Brown powder (219 mg, 47%); mp 159-161 °C. IR (KBr): 3424, 1691, 1507 cm\(^{-1}\). \(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \( \delta = 12.78 \) (s, 1H), 8.33 (d, \( J = 7.8 \) Hz, 1H), 7.53 (s, 1H), 7.50–7.47 (m, 3H), 7.41 (dd, \( J = 16.8, 8.4 \) Hz, 3H), 7.31 (q, \( J = 7.2 \) Hz, 4H), 7.28–7.19 (m, 4H), 7.09 (d, \( J = 7.8 \) Hz, 1H), 7.05 (t, \( J = 7.8 \) Hz, 1H), 6.86 (t, \( J = 7.2 \) Hz, 1H).
Hz, 1H), 5.47 (s, 2H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 157.8, 151.8, 138.8, 136.3, 135.9, 134.3, 132.2, 130.0, 129.2, 128.9, 128.8, 128.4, 128.2, 127.9, 127.7, 127.3, 124.5, 122.2, 121.5, 120.5, 119.4, 117.1, 114.2, 113.7, 110.6, 108.7, 107.0, 49.5. MS (ESI): $m/z = 467$ [M + H]$^+$. HRMS-ESI: calcd for C$_{32}$H$_{22}$N$_2$NaO$_2$ [M + Na]$^+$: 489.1579; found 489.1595.

2-(2-Chlorophenyl)-3-(2-methyl-1H-indol-3-yl)chrome no[4,3-b]pyrrol-4(1H)-one (4g): Pale yellow powder (264 mg, 58%); mp 280-282 °C. IR (KBr): 3423, 1677, 1505 cm$^{-1}$. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 12.96$ (s, 1H), 10.92 (s, 1H), 8.19 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.51–7.46 (m, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.35–7.30 (m, 1H), 7.23 (m, 3H), 7.06 (d, $J = 7.8$ Hz, 1H), 6.92 (t, $J = 7.2$ Hz, 1H), 6.77 (t, $J = 7.2$ Hz, 1H), 2.12 (s, 3H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 157.7, 151.8, 135.9, 135.6, 134.6, 133.7, 133.2, 132.1, 131.9, 130.5, 130.1, 129.3, 129.0, 127.5, 124.5, 121.8, 120.2, 118.8, 118.7, 117.2, 115.9, 114.3, 110.7, 108.1, 104.0, 12.5. MS (ESI): $m/z = 425$ [M + H]$^+$. HRMS-ESI: calcd for C$_{26}$H$_{17}$ClN$_2$NaO$_2$ [M + Na]$^+$: 447.0876; found 447.0886.

2-(3-Chlorophenyl)-3-(2-methyl-1H-indol-3-yl)chrome no[4,3-b]pyrrol-4(1H)-one (4h): Pale yellow powder (314 mg, 74%); mp 199-201 °C. IR (KBr): 3423, 1671, 1506 cm$^{-1}$. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 12.80$ (s, 1H), 11.08 (s, 1H), 8.34 (d, $J = 7.8$ Hz, 1H), 8.34 (d, $J = 7.8$ Hz, 1H), 7.57 (s, 1H), 7.51–7.47 (m, 1H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.29–7.21 (m, 3H), 7.02–6.94 (m, 2H), 6.81 (t, $J = 7.8$ Hz, 1H), 2.14 (s, 3H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 157.6, 151.9, 136.4, 136.0, 134.5, 134.4, 133.6, 132.4, 130.7, 129.4, 128.5, 127.4, 126.7, 125.7, 124.5, 122.3, 120.5, 119.0, 118.9, 117.1, 114.9, 114.1, 111.0, 109.3, 104.2, 12.7. MS (ESI): $m/z = 425$ [M + H]$^+$. HRMS-ESI: calcd for C$_{26}$H$_{17}$ClN$_2$NaO$_2$ [M + Na]$^+$: 447.0876; found 447.0882.
2-(4-Chlorophenyl)-3-(2-methyl-1H-indol-3-yl)chrome
no[4,3-b]pyrrol-4(1H)-one (4i): Light yellow powder (348 mg, 82%); mp >300 °C. IR (KBr): 3373, 1662, 1471 cm⁻¹. ¹H NMR (600 MHz, DMSO-d₆): δ = 12.79 (s, 1H), 11.06 (s, 1H), 8.33 (d, J = 7.8 Hz, 1H), 7.52–7.47 (m, 1H), 7.45–7.40 (m, 4H), 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H), 2.13 (s, 3H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 157.6, 151.9, 136.2, 135.9, 134.5, 132.9, 132.2, 131.3, 129.3, 129.0, 128.9, 128.5, 124.5, 122.2, 120.5, 118.9, 117.1, 114.4, 114.2, 111.0, 109.2, 104.2, 12.7. MS (ESI): m/z = 425 [M + H]⁺. HRMS-ESI: calcd for C₂₆H₁₇ClN₂NaO₂ [M + Na]⁺: 447.0876; found 447.0878.

2-(4-Fluorophenyl)-3-(2-methyl-1H-indol-3-yl)chrome
no[4,3-b]pyrrol-4(1H)-one (4j): Pale yellow powder (330 mg, 81%); mp 257-259 °C. IR (KBr): 3379, 1664, 1504 cm⁻¹. ¹H NMR (600 MHz, DMSO-d₆): δ = 12.78 (s, 1H), 11.05 (s, 1H), 8.34 (dd, J = 7.8, 1.0 Hz, 1H), 7.51–7.39 (m, 5H), 7.32 (d, J = 8.4 Hz, 1H), 7.16 (t, J = 8.4 Hz, 2H), 6.99 (q, J = 7.2 Hz, 2H), 6.81 (t, J = 7.2 Hz, 1H), 2.14 (s, 3H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 161.7 (d, J_CF = 245.0 Hz), 157.7, 151.8, 136.0, 135.9, 134.4, 133.3, 129.5, 129.1, 129.0, 128.7, 124.4, 122.1, 120.4, 119.0, 118.9, 117.1, 115.9, 115.8, 114.2, 113.7, 110.9, 109.1, 104.3, 12.7. MS (ESI): m/z = 409 [M + H]⁺. HRMS-ESI: calcd for C₂₆H₁₇FN₂NaO₂ [M + Na]⁺: 431.1172; found 447.1179.

2-(4-Bromophenyl)-3-(2-methyl-1H-indol-3-yl)chrome
no[4,3-b]pyrrol-4(1H)-one (4k): Yellow powder (388 mg, 83%); mp >300 °C. IR (KBr): 3394, 1691, 1507 cm⁻¹. ¹H NMR (600 MHz, DMSO-d₆): δ = 12.77 (s, 1H), 11.04 (s, 1H), 8.33 (d, J = 7.2 Hz, 1H), 7.56–7.27 (m, 8H), 6.98 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H), 2.12 (s, 2H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 157.9, 151.8, 135.8, 134.8, 134.1, 132.4, 129.1, 128.7, 128.2, 127.8, 127.8, 127.3, 126.2, 124.4, 122.8, 122.2, 119.8, 117.1, 114.5,
114.2, 111.5, 108.7, 106.6, 21.7. MS (ESI): \( m/z = 469 \) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{26}\)H\(_{13}\)BrN\(_3\)NaO\(_2\) [M + Na]\(^+\): 491.0371; found 491.0365.

3-(2-Methyl-1H-indol-3-yl)-2-(4-nitrophenyl)chromeno[4,3-b]pyrrol-4(1H)-one (4l): Tan powder (352 mg, 81%); mp > 300 °C. IR (KBr): 3450, 1694, 1515, 1340 cm\(^{-1}\). \(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \( \delta = 12.98\) (s, 1H), 11.17 (s, 1H), 8.38 (d, \( J = 7.2\) Hz, 1H), 8.15 (d, \( J = 8.4\) Hz, 1H), 7.67 (d, \( J = 8.4\) Hz, 2H), 7.56–7.51 (m, 1H), 7.45 (t, \( J = 7.2\) Hz, 2H), 7.34 (d, \( J = 7.8\) Hz, 1H), 7.00 (t, \( J = 7.2\) Hz, 1H), 6.93 (d, \( J = 7.8\) Hz, 1H), 6.81 (t, \( J = 7.2\) Hz, 1H), 2.17 (s, 3H). \(^13\)C NMR (150 MHz, DMSO-\(d_6\)): \( \delta = 157.4, 152.1, 146.0, 138.9, 137.4, 136.0, 134.8, 131.7, 129.8, 128.2, 127.7, 124.6, 124.2, 122.5, 120.7, 119.1, 118.8, 117.2, 117.1, 113.9, 111.1, 109.5, 103.9, 12.7. MS (ESI): \( m/z = 436 \) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{26}\)H\(_{13}\)N\(_3\)NaO\(_2\) [M + Na]\(^+\): 458.1117; found 458.1110.

4-(3-(2-Methyl-1H-indol-3-yl)-4-oxo-1,4-dihydrochromeno[4,3-b]pyrrol-2-yl)benzonitrile (4m): Light yellow powder (344 mg, 83%); mp >300 °C. IR (KBr): 3397, 2224, 1692, 1507 cm\(^{-1}\). \(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \( \delta = 12.90\) (s, 1H), 11.14 (s, 1H), 8.36 (dd, \( J = 7.8, 1.2\) Hz, 1H), 7.76 (d, \( J = 8.4\) Hz, 2H), 7.59 (d, \( J = 8.4\) Hz, 2H), 7.55–7.50 (m, 1H), 7.44 (dd, \( J = 7.8, 6.0\) Hz, 2H), 7.33 (d, \( J = 7.8\) Hz, 1H), 7.00 (t, \( J = 7.2\) Hz, 1H), 6.92 (d, \( J = 7.8\) Hz, 1H), 6.81 (t, \( J = 7.2\) Hz, 1H), 2.15 (s, 3H). \(^13\)C NMR (150 MHz, DMSO-\(d_6\)): \( \delta = 157.4, 152.0, 137.1, 136.9, 136.019, 134.7, 132.8, 132.1, 129.7, 128.2, 127.5, 124.5, 122.4, 120.6, 119.3, 119.1, 118.8, 117.2, 116.3, 1140, 111.1, 109.5, 109.4, 104.0, 12.7. MS (ESI): \( m/z = 416 \) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{27}\)H\(_{17}\)N\(_3\)NaO\(_2\) [M + Na]\(^+\): 438.1218; found 438.1210.

3-(2-Methyl-1H-indol-3-yl)-2-(o-tolyl)chromeno[4,3-b]pyrrol-4(1H)-one (4n): Pale yellow powder (263 mg, 65%); mp >300 °C. IR (KBr): 3419, 1687, 1505 cm\(^{-1}\). \(^1\)H
NMR (600 MHz, DMSO-d6): δ = 12.79 (s, 1H), 10.88 (s, 1H), 8.19 (dd, J = 7.8, 1.2 Hz, 1H), 7.49–7.41 (m, 2H), 7.40–7.36 (m, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.25–7.15 (m, 4H), 7.04 (d, J = 7.8 Hz, 1H), 6.93 (t, J = 7.8 Hz, 1H), 6.78 (t, J = 7.2 Hz, 1H), 2.05 (s, 3H), 2.05 (s, 3H). 13C NMR (150 MHz, DMSO-d6): δ = 157.8, 151.8, 137.4, 135.6, 135.6, 134.7, 134.2, 132.7, 131.3, 130.6, 129.0, 128.6, 126.1, 124.4, 121.8, 120.2, 119.0, 118.7, 117.1, 114.9, 114.4, 110.7, 108.2, 104.7, 20.2, 12.6. MS (ESI): m/z = 405 [M + H]+. HRMS-ESI: calcd for C27H20N2NaO2 [M + Na]+: 427.1422; found 427.1430.

3-(2-Methyl-1H-indol-3-yl)-2-(m-tolyl)chromeno[4,3-b]pyrrol-4(1H)-one (4o): Yellow powder (291 mg, 72%); mp >300 °C. IR (KBr): 3360, 1665, 1506 cm⁻¹. 1H NMR (600 MHz, DMSO-d6): δ = 12.72 (s, 1H), 11.01 (s, 1H), 8.37 (dd, J = 7.8, 1.2 Hz, 1H), 7.51–7.45 (m, 1H), 7.41 (dd, J = 15.6, 8.4 Hz, 3H), 7.32 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 4.8 Hz, 2H), 7.06–7.03 (m, 1H), 7.01–6.95 (m, 2H), 6.81 (t, J = 7.2 Hz, 1H), 2.24 (s, 3H), 2.12 (s, 3H). 13C NMR (150 MHz, DMSO-d6): δ = 157.7, 151.8, 137.8, 135.9, 134.4, 134.3, 132.4, 129.1, 128.9, 128.7, 128.3, 127.9, 124.6, 124.4, 122.2, 120.3, 119.1, 118.8, 117.1, 114.3, 113.7, 110.8, 109.2, 104.7, 21.6, 12.7. MS (ESI): m/z = 405 [M + H]+. HRMS-ESI: calcd for C27H20N2NaO2 [M + Na]+: 427.1422; found 427.1431.

3-(2-Methyl-1H-indol-3-yl)-2-(p-tolyl)chromeno[4,3-b]pyrrol-4(1H)-one (4p): Yellow powder (287 mg, 71%); mp 290-292 °C. IR (KBr): 3397, 1664, 1506 cm⁻¹. 1H NMR (600 MHz, DMSO-d6): δ = 12.68 (s, 1H), 10.99 (s, 1H), 8.35 (d, J = 7.8 Hz, 1H), 7.49–7.44 (m, 1H), 7.43–7.38 (m, 2H), 7.31 (t, J = 7.2 Hz, 3H), 7.08 (d, J = 7.8 Hz, 2H), 7.00–6.94 (m, 2H), 6.80 (t, J = 7.2 Hz, 1H), 2.24 (s, 3H), 2.10 (s, 3H). 13C NMR (150 MHz, DMSO-d6): δ = 157.7, 151.8, 137.0, 135.9, 135.8, 134.4, 134.3, 129.6, 129.4, 129.0, 128.9, 127.2, 124.4, 122.2, 120.3, 119.1, 118.8, 117.0, 114.3, 113.3, 110.8, 109.2, 104.7, 21.2, 12.7. MS (ESI): m/z = 405 [M + H]+. HRMS-ESI: calcd for C27H20N2NaO2 [M + Na]+: 427.1422; found 427.1416.
2-(4-Methoxyphenyl)-3-(2-methyl-1H-indol-3-yl)chromeno[4,3-b]pyrrol-4(1H)-one (4q): Brown yellow powder (286 mg, 68%); mp 214-216 °C. IR (KBr): 3383, 1690, 1504 cm⁻¹. ¹H NMR (600 MHz, DMSO-d₆): δ = 12.65 (s, 1H), 10.99 (s, 1H), 8.33 (dd, J = 7.8, 1.2 Hz, 1H), 7.48–7.45 (m, 1H), 7.43–7.38 (m, 2H), 7.37–7.34 (m, 2H), 7.30 (d, J = 8.4 Hz, 1H), 6.99–6.97 (m, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.82–6.79 (m, 1H), 3.72 (s, 3H), 2.11 (s, 3H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 158.9, 157.7, 151.7, 135.9, 135.5, 135.0, 134.3, 128.9, 128.7, 124.9, 124.4, 122.07, 120.3, 119.1, 118.81, 117.0, 114.3, 112.6, 110.9, 109.2, 104.7, 55.5, 12.7. MS (ESI): m/z = 421 [M + H]⁺. HRMS-ESI: calcd for C₂₉H₂₀N₂NaO₃ [M + Na]⁺: 443.1372; found 443.1379.

2-(4-Hydroxyphenyl)-3-(2-methyl-1H-indol-3-yl)chromeno[4,3-b]pyrrol-4(1H)-one (4r): Brown yellow powder (267 mg, 66%); mp 220-222 °C. IR (KBr): 3398, 1695, 1504 cm⁻¹. ¹H NMR (600 MHz, DMSO-d₆): δ = 10.97 (s, 1H), 9.55 (s, 1H), 8.32 (dd, J = 7.8, 1.2 Hz, 1H), 7.48–7.43 (m, 1H), 7.42–7.37 (m, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.01–6.93 (m, 2H), 6.83–6.76 (m, 1H), 6.67 (d, J = 8.4 Hz, 2H), 2.11 (s, 3H). ¹³C NMR (150 MHz, DMSO-d₆): δ = 162.5, 161.9, 156.4, 140.6, 140.1, 139.6, 139.0, 133.7, 133.7, 133.6, 129.1, 128.1, 126.7, 125.0, 123.9, 123.5, 121.7, 120.4, 119.1, 117.0, 115.6, 115.5, 113.8, 109.6, 17.4. MS (ESI): m/z = 407 [M + H]⁺. HRMS-ESI: calcd for C₂₇H₁₈N₂NaO₃ [M + Na]⁺: 429.1215; found 429.1210.

2-(Benzod[d][1,3]dioxol-5-yl)-3-(2-methyl-1H-indol-3-yl)chromeno[4,3-b]pyrrol-4(1H)-one (4s): Light yellow powder (299 mg, 69%); mp 224-226 °C. IR (KBr): 3413, 1682, 1503 cm⁻¹. ¹H NMR (600 MHz, DMSO-d₆): δ = 12.63 (s, 1H), 11.02 (s, 1H), 8.35–8.28 (m, 1H), 7.49–7.43 (m, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 7.02–6.93 (m, 3H), 6.90 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 5.98 (d, J = 2.4 Hz, 2H), 2.14 (s, 3H). ¹³C NMR (150 MHz,
DMSO-$d_6$): $\delta = 157.7, 151.8, 147.6, 146.9, 135.9, 135.6, 134.4, 134.1, 129.0, 128.9, 126.3, 124.4, 122.1, 121.3, 120.4, 119.0, 118.9, 117.0, 114.3, 113.0, 110.9, 109.2, 108.9, 107.6, 104.6, 101.5, 12.7. MS (ESI): $m/z = 435$ [M + H]$^+$. HRMS-ESI: calcld for C$_{27}$H$_{18}$N$_2$NaO$_4$ [M + Na]$^+$: 457.1164; found 457.1168.

3-(2-Methyl-1H-indol-3-yl)-2-(naphthalen-1-yl)chrome no[4,3-b]pyrrol-4(1H)-one (4t): Light yellow powder (295 mg, 67%); mp >300 ºC. IR (KBr): 3420, 1692, 1506 cm$^{-1}$. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 1$H NMR (600 MHz, DMSO) $\delta 13.05$ (s, 1H), 10.80 (s, 1H), 8.22 (d, $J = 7.6$ Hz, 1H), 7.97–7.83 (m, 3H), 7.57–7.32 (m, 7H), 7.22–6.56 (m, 4H), 2.06 (s, 3H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 157.9, 151.9, 136.0, 135.5, 133.7, 133.7, 132.0, 130.56, 129.2, 129.1, 129.0, 128.6, 126.8, 126.5, 126.1, 125.8, 124.5, 121.9, 120.1, 118.6, 117.1, 115.8, 114.5, 110.6, 108.5, 104.6, 12.7. MS (ESI): $m/z = 441$ [M + H]$^+$. HRMS-ESI: calcld for C$_{30}$H$_{20}$N$_2$NaO$_4$ [M + Na]$^+$: 463.1422; found 463.1427.

3-(2-Methyl-1H-indol-3-yl)-2-(thiophen-2-yl)chromeno [4,3-b]pyrrol-4(1H)-one (4u): Light green powder (295 mg, 64%); mp >300 ºC. IR (KBr): 3418, 1687, 1506 cm$^{-1}$. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 12.73$ (s, 1H), 11.14 (s, 1H), 8.35 (d, $J = 7.2$ Hz, 1H), 7.60–7.29 (m, 6H), 7.11–6.97 (m, 3H), 6.85 (t, $J = 6.6$ Hz, 1H), 2.19 (s, 3H). $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta = 157.5, 151.9, 136.2, 135.9, 135.2, 133.6, 130.0, 129.3, 129.0, 127.0, 126.7, 124.9, 124.5, 122.2, 120.5, 119.0, 118.9, 117.1, 114.1, 113.6, 110.9, 109.4, 104.0, 12.7. MS (ESI): $m/z = 397$ [M + H]$^+$. HRMS-ESI: calcld for C$_{24}$H$_{16}$N$_2$NaO$_2$S [M + Na]$^+$: 419.0830; found 419.0841.

8-Chloro-3-(2-methyl-1H-indol-3-yl)-2-phenylchrome no[4,3-b]pyrrol-4(1H)-one (4v): Brown yellow powder (305 mg, 72%); mp 259–291 ºC. IR (KBr): 3401, 1697, 1508 cm$^{-1}$. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 12.77$ (s, 1H), 11.02 (s, 1H), 8.47 (s, 1H), 7.53–7.37 (m, 4H), 7.34–7.20 (m, 4H), 6.97 (q, $J = 7.8$ Hz, 2H), 6.79 (t, $J = 7.2$ Hz, 1H), 2.06 (s, 3H).
11 Hz, 1H), 2.10 (s, 3H). \textsuperscript{13}C NMR (150 MHz, DMSO-\textit{d}_6): \(\delta = 157.2, 150.4, 135.9, 134.7, 134.6, 134.4, 132.2, 128.9, 128.7, 128.6, 128.4, 127.9, 127.2, 121.6, 120.4, 119.0, 118.9, 115.7, 114.0, 110.9, 109.6, 104.3, 12.63. MS (ESI): \(m/z = 426\) [M + H]\(^+\).


\[\text{8-(Tert-butyl)-3-(2-methyl-1H-indol-3-yl)-2-phenylchromeno[4,3-b]pyrrol-4(1H)-one (4w):}\]

Light yellow powder (343 mg, 77%); mp \(>300\) °C.

IR (KBr): 3456, 1694, 1523 cm\(^{-1}\). \(\textsuperscript{1}H\) NMR (600 MHz, DMSO-\textit{d}_6): \(\delta = 11.00 (s, 1H), 8.41 (s, 1H), 7.49 (d, \(J = 8.4\) Hz, 1H), 7.42 (d, \(J = 7.8\) Hz, 2H), 7.35–7.26 (m, 4H), 7.22 (t, \(J = 7.2\) Hz, 1H), 2.10 (s, 3H), 1.40 (s, 9H). \(\textsuperscript{13}C\) NMR (150 MHz, DMSO-\textit{d}_6): \(\delta = 157.9, 149.9, 147.0, 136.4, 135.9, 134.3, 134.2, 132.6, 128.8, 127.7, 127.4, 126.4, 120.4, 119.1, 118.8, 116.5, 113.7, 113.6, 110.9, 109.1, 104.6, 35.1, 31.8, 12.6. MS (ESI): \(m/z = 447\) [M + H]\(^+\). HRMS-ESI: calcd for C\(_{24}\)H\(_{16}\)N\(_2\)NaO\(_2\)S [M + Na]\(^+\): 469.1892; found 469.1882.

\[\text{2,2-Bis(2-methyl-1H-indol-3-yl)-1-phenylethanone (5):}\]

Brown powder; mp 201-203 °C. \(\textsuperscript{1}H\) NMR (600 MHz, DMSO-\textit{d}_6): \(\delta = 10.86 (s, 1H), 8.05 (d, \(J = 7.8\) Hz, 1H), 7.53 (t, \(J = 7.2\) Hz, 1H), 7.43 (t, \(J = 7.8\) Hz, 1H), 7.22 (d, \(J = 8.4\) Hz, 1H), 7.15 (d, \(J = 7.8\) Hz, 1H), 6.93 (t, \(J = 7.8\) Hz, 1H), 6.78 (t, \(J = 7.8\) Hz, 1H), 6.44 (s, 1H), 2.16 (s, 3H). HRMS-ESI: calcd for C\(_{26}\)H\(_{22}\)N\(_2\)O [M + Na]\(^+\): 401.1630; found 401.1642.

\[\text{2-Hydroxy-2-(2-methyl-1H-indol-3-yl)-1-phenylethanone (A):}\]

White powder; mp 156-158 °C. \(\textsuperscript{1}H\) NMR (600 MHz, DMSO-\textit{d}_6): \(\delta = 10.96 (s, 1H), 7.88 (d, \(J = 7.2\) Hz, 2H), 7.49 (m, 2H), 7.38 (t, \(J = 7.8\) Hz, 2H), 7.20 (d, \(J = 7.8\) Hz, 1H), 6.94 (m, 2H), 5.32 (d, \(J = 4.2\) Hz, 1H), 2.43 (s, 3H). HRMS-ESI: calcd for C\(_{17}\)H\(_{16}\)NO\(_2\) [M + H]\(^+\): 266.1181; found 266.1162.
\(^1\)H NMR spectra of compound 4a

\(^{13}\)C NMR spectra of compound 4a
$^1$H NMR spectra of compound 4b

$^{13}$C NMR spectra of compound 4b
$^1$H NMR spectra of compound 4c

$^{13}$C NMR spectra of compound 4c
$^1$H NMR spectra of compound 4d

$^{13}$C NMR spectra of compound 4d
$^1$H NMR spectra of compound 4e

$^{13}$C NMR spectra of compound 4e
$^1$H NMR spectra of compound 4f
$^1$H NMR spectra of compound 4g

$^{13}$C NMR spectra of compound 4g
$^1$H NMR spectra of compound $4h$

$^{13}$C NMR spectra of compound $4h$
$^1$H NMR spectra of compound 4i

$^{13}$C NMR spectra of compound 4i
$^1$H NMR spectra of compound 4j

$^{13}$C NMR spectra of compound 4j
$^1$H NMR spectra of compound 4k

$^{13}$C NMR spectra of compound 4k
$^1$H NMR spectra of compound 4I

$^{13}$C NMR spectra of compound 4I
$^1$H NMR spectra of compound 4m

$^{13}$C NMR spectra of compound 4m
$^1$H NMR spectra of compound 4n

$^{13}$C NMR spectra of compound 4n
$^1$H NMR spectra of compound 4o

$^{13}$C NMR spectra of compound 4o
$^{1}$H NMR spectra of compound 4p

$^{13}$C NMR spectra of compound 4p
$^1$H NMR spectra of compound 4q

$^{13}$C NMR spectra of compound 4q
$^1$H NMR spectra of compound 4r

$^{13}$C NMR spectra of compound 4r
$^1$H NMR spectra of compound 4s

$^{13}$C NMR spectra of compound 4s
$^1$H NMR spectra of compound 4t

$^{13}$C NMR spectra of compound 4t
$^1$H NMR spectra of compound 4u

$^{13}$C NMR spectra of compound 4u
$^1$H NMR spectra of compound 4v

$^{13}$C NMR spectra of compound 4v
$^{1}$H NMR spectra of compound 4w

$^{13}$C NMR spectra of compound 4w
$^1$H NMR spectra of compound 5

$^1$H NMR spectra of compound A