Supporting Information

for

Synthesis of indole–cycloalkyl[b]pyridine hybrids via a four-component six-step tandem process

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Experimental procedure, compound characterization data and copies of NMR spectra
**Experimental section**

**General**

Melting point of the indole–cycloalkyl[b]pyridine-3-carbonitrile hybrids were measured in open capillary tubes using a Sigma melting point apparatus, Sl. No. 71281, watts-250, volts-230 AC and are uncorrected. The $^1$H, $^{13}$C, DEPT, H,H-COSY, C,H-COSY and HMBC spectra were recorded on a Bruker 300 MHz NMR instrument using TMS as internal standard and CDCl$_3$ and/or DMSO-d$_6$ as solvents. Standard Bruker software was used throughout the spectral analysis. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental CHNS analyzer. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60–80 °C) and ethyl acetate as the eluent. All the chemicals were purchased from Sigma-Aldrich, Alfa-Aesar or Merck and used without further purification. The single crystal X-ray data set was collected on Bruker AXS KAPPA APEX-2 diffractometer equipped with graphite monochromator. The structure was solved by direct methods and refined by full-matrix least squares calculations using SHELXL-2014.

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General procedure for the synthesis of indole–cycloalkyl[b] pyridine-3-carbonitriles 7, 12 and 14–18

A mixture of 3-(1H-indol-3-yl)-3-oxopropanenitrile 3 (0.1 g, 0.543 mmol), aromatic aldehyde 4 (0.543 mmol), cycloalkanone 5 (0.543 mmol) and ammonium acetate (6, 0.1 g, 1.1 mmol) was dissolved in ethanol (10 mL) and heated to reflux on a heating mantle for 2 h. After completion of the reaction as evident from TLC, the reaction mixture was set aside at ambient temperature for 6–7 h. The precipitate formed was filtered and dried to get the pure indole–cycloalkyl[b]pyridine-3-carbonitriles. The unaromatized product was obtained in the cases where the product was precipitated within 2 h.

Compounds characterization data

2-(1H-Indol-3-yl)-4-phenyl-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]pyridine-3-carbonitrile (7a)

Obtained as pale yellow solid (211.9 mg, 0.488 mmol, 90%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.18–1.75 (m, 14H), 2.06–2.20 (m, 2H), 2.59 (t, $J$=7.5 Hz, 2H), 3.02 (t, $J$=7.5 Hz, 2H), 7.25–7.38 (m, 4H), 7.40–7.47 (m, 1H), 7.48–7.54 (m, 3H), 8.18 (d, $J$=3.0 Hz, 1H), 8.51–8.54 (m, 1H), 8.57 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 22.8, 23.3, 25.9, 26.5, 26.8, 26.9, 27.3, 27.7, 28.6, 33.1, 103.5, 111.3, 114.1, 121.2, 122.2, 122.9, 126.4, 126.8, 128.3, 128.5, 128.6, 130.7, 136.2, 137.2, 153.7, 155.0, 165.0 ppm; Anal. Calcd. for C$_{30}$H$_{31}$N$_3$: C, 83.10; H, 7.21; N, 9.69; found: C 83.19, H 7.02, N 9.52.
2-(1H-Indol-3-yl)-4-(p-tolyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]pyridine-3-carbonitrile (7b)

Obtained as white solid (226.0 mg, 0.505 mmol, 93%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 1.19–1.88 (m, 14H), 2.01–2.25 (m, 2H), 2.45 (s, 3H), 2.61 (t, \(J=7.8\) Hz, 2H), 3.03 (t, \(J=7.8\) Hz, 2H), 7.18–7.36 (m, 7H), 8.15 (s, 1H), 8.47–8.56 (m, 1H), 8.72–8.78 (m, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 18.3, 21.4, 22.8, 23.3, 25.9, 26.5, 26.9, 27.3, 27.6, 28.6, 33.0, 28.3, 103.6, 111.4, 121.0, 122.1, 122.7, 126.4, 126.8, 128.2, 129.2, 130.8, 134.2, 136.2, 138.3, 153.8, 155.2, 164.8 ppm; Anal. Calcd. for C\(_{31}\)H\(_{33}\)N\(_3\): C, 83.18; H, 7.43; N, 9.39; found: C 83.28, H 7.58, N 9.26.

2-(1H-Indol-3-yl)-4-(4-methoxyphenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]-pyridine-3-carbonitrile (7c)

Obtained as pale yellow solid (213.5 mg, 0.461 mmol, 85%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 1.22–1.76 (m, 14H), 2.04–2.22 (m, 2H), 2.62 (t, \(J=7.5\) Hz, 2H), 3.02 (t, \(J=7.5\) Hz, 2H), 3.88 (s, 3H), 7.04 (d, \(J=8.7\) Hz, 2H), 7.24–7.30 (m, 4H), 7.35–7.39 (m, 1H), 8.16 (d, \(J=2.7\) Hz, 1H), 8.49–8.55 (m, 1H), 8.67 (br s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 22.3, 23.3, 25.9, 26.5, 26.9, 27.3, 27.7, 28.5, 33.1, 55.2, 103.9, 111.3, 114.0, 114.1, 118.9, 121.1, 122.2, 122.9, 126.4, 126.7, 129.4, 129.6, 131.1, 136.2, 153.7, 154.9, 159.6, 164.9 ppm; Anal. Calcd. for C\(_{31}\)H\(_{33}\)N\(_3\)O: C, 80.31; H, 7.17; N, 9.06; found: C, 81.18; H, 7.05; N, 9.16.

2-(1H-Indol-3-yl)-4-(4-isopropylphenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]-pyridine-3-carbonitrile (7d)

Obtained as white solid (234.9 mg, 0.494 mmol, 91%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 1.35 (d, \(J=6.9\)Hz, 6H), 1.39–1.72 (m, 14H), 2.08–2.22 (m, 2H), 2.63 (t, \(J=7.2\)Hz, 2H),
2.96–3.11 (m, 3H), 7.21–7.36 (m, 7H), 8.12 (d, $J=3.0$ Hz, 1H), 8.47–8.50 (m, 1H), 8.70 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ$_C$: 23.0, 23.5, 23.9, 25.9, 26.6, 27.0, 27.3, 27.7, 28.7, 33.1, 33.9, 103.7, 111.3, 114.2, 121.1, 122.3, 122.8, 126.5, 126.6, 126.8, 128.3, 130.9, 134.6, 136.3, 149.2, 153.8, 155.3, 164.8 ppm; Anal. Calcd. for C$_{33}$H$_{37}$N$_3$: C, 83.33; H, 7.84; N, 8.83; found: C 83.20, H 7.76, N 8.92.

4-(4-Fluorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]-pyridine-3-carbonitrile (7e)

Obtained as pale yellow solid (225.6 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$) δ$_H$: 1.19–1.79 (m, 14H), 2.03–2.21 (m, 2H), 2.52–2.68 (m, 2H), 2.95–3.11 (m, 2H), 7.18–7.41 (m, 7H), 8.14–8.22 (m, 1H), 8.47–8.55 (m, 1H), 8.59 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ$_C$: 22.8, 23.3, 25.9, 26.5, 26.9, 27.3, 27.7, 28.6, 33.1, 103.6, 111.4, 115.6, 115.9, 121.2, 122.2, 122.9, 126.4, 126.8, 130.2, 136.2, 153.8, 154.0, 165.2 ppm; Anal. Calcd. for C$_{30}$H$_{30}$FN$_3$: C, 79.79; H, 6.70; N, 9.31; found: C 71.62, H 6.81, N 9.28.

4-(4-Chlorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]-pyridine-3-carbonitrile (7f)

Obtained as pale yellow solid (236.3 mg, 0.505 mmol, 93%). $^1$H NMR (300 MHz, CDCl$_3$) δ$_H$: 1.27–1.58 (m, 14H), 2.03–2.18 (m, 2H), 2.56 (t, $J=7.5$ Hz, 2H), 3.01 (t, $J=7.8$ Hz, 2H), 7.26 (d, $J=8.1$ Hz, 4H), 7.33–7.41 (m, 1H), 7.49 (d, $J=8.4$ Hz, 2H), 8.16 (d, $J=3.0$ Hz, 1H), 8.45–8.53 (m, 1H), 8.58 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ$_C$: 22.8, 23.3, 25.9, 26.5, 26.9, 27.3, 27.7, 28.6, 33.1, 103.2, 111.4, 113.9, 118.5, 121.2, 122.2, 122.9, 126.4, 126.8, 128.9, 129.8, 130.6, 134.8, 135.6, 136.2, 153.7, 153.9, 165.2
ppm; Anal. Calcd. for C_{30}H_{30}ClN_3: C, 76.99; H, 6.46; N, 8.98; found: C 76.87, H 6.59, N 8.91.

4-(4-Cyanophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]-pyridine-3-carbonitrile (7h)

Obtained as white solid (212.0 mg, 0.462 mmol, 85%). $^1$H-NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.15–1.95 (m, 14H), 2.01–2.28 (m, 2H), 2.45–2.66 (m, 2H), 3.03 (t, $J$=7.5 Hz, 2H), 7.26–7.31 (m, 2H), 7.42–7.48 (m, 3H), 7.82 (d, $J$=8.1 Hz, 2H), 8.21 (d, $J$=3.0 Hz, 1H), 8.51–8.54 (m, 1H), 8.58 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO-d$_6$) $\delta_C$: 21.9, 22.4, 24.9, 25.5, 25.9, 26.0, 26.3, 26.7, 27.7, 32.1, 101.1, 111.0, 111.7, 112.1, 117.5, 120.0, 121.3, 121.6, 125.5, 126.8, 128.7, 131.6, 135.8, 141.2, 151.9, 153.3, 164.4 ppm; Anal. Calcd. for C$_{31}$H$_{30}$N$_4$: C, 81.19; H, 6.59; N, 12.22; found: C 81.25, H 6.44, N 12.08.

2-(1H-Indol-3-yl)-4-(4-nitrophenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[b]-pyridine-3-carbonitrile (7i)

Obtained as pale yellow solid (246.9 mg, 0.515 mmol, 95%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.17–1.90 (m, 14H), 2.01–2.22 (m, 2H), 2.56 (t, $J$=7.5 Hz, 2H), 3.04 (t, $J$=7.5 Hz, 2H), 7.30 (q, $J$= 3Hz, 2H), 7.39–7.47 (m, 1H), 7.54 (d, $J$=8.4 Hz, 2H), 8.23 (d, $J$=3.0 Hz, 1H), 8.40 (d, $J$=8.7 Hz, 2H), 8.53–8.63 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta_C$: 22.9, 23.4, 25.9, 26.4, 26.9, 27.1, 27.3, 27.7, 28.7, 33.2, 102.4, 111.4, 121.5, 122.4, 123.2, 123.9, 126.4, 126.9, 129.8, 129.9, 136.3, 143.9, 148.1, 152.6, 154.0, 165.6 ppm; Anal. Calcd. for C$_{30}$H$_{30}$N$_4$O$_2$: C, 75.29; H, 6.32; N, 11.71; found: C 75.19, H 6.23, N 11.59.
2-(1H-Indol-3-yl)-4-(o-tolyl)-5,6,7,8,9,10,11,12,13,14-decahydrocycloclodeca[b]pyridine-3-carbonitrile (7j)

Obtained as pale yellow solid (228.2 mg, 0.510 mmol, 94%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\)H: 1.18–1.82 (m, 16H), 2.15 (s, 3H), 2.33–2.43 (m, 1H), 2.57–2.71 (m, 1H), 2.92–3.02 (m, 1H), 3.07–3.16 (m, 1H), 7.19 (d, \(J=7.2\) Hz, 1H), 7.25–7.30 (m, 3H), 7.34–7.40 (m, 3H), 8.18 (d, \(J=2.7\) Hz, 1H), 8.57–8.60 (m, 1H), 8.68 (br s, 1H) ppm; \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\)C: 19.8, 22.7, 23.3, 25.9, 26.6, 26.9, 27.0, 27.4, 27.7, 28.2, 33.1, 103.3, 111.3, 114.1, 118.4, 121.2, 122.3, 122.9, 126.0, 126.4, 126.8, 128.5, 128.9, 130.4, 130.6, 135.1, 136.2, 136.6, 153.9, 154.8, 165.2 ppm; Anal. Calcd. for C\(_{31}\)H\(_{33}\)N\(_3\): C, 83.18; H, 7.43; N, 9.39; found: C, 83.31; H, 7.53; N, 9.48.

4-(2-Bromophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocycloclodeca[b]pyridine-3-carbonitrile (7l)

Obtained as pale yellow solid (255.7 mg, 0.499 mmol, 92%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\)H: 1.15–1.85 (m, 14H), 1.98–2.26 (m, 2H), 2.37–2.46 (m, 1H), 2.61–2.71 (m, 1H), 2.91–3.01 (m, 1H), 3.06–3.16 (m, 1H), 7.26–7.49 (m, 7H), 7.76 (d, \(J=6.9\) Hz, 1H), 8.23 (d, \(J=2.7\) Hz, 1H), 8.55 (br s, 1H) ppm; \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\)C: 22.7, 23.3, 25.8, 26.7, 26.9, 27.2, 27.4, 27.7, 28.2, 33.1, 103.3, 111.3, 121.3, 122.4, 122.7, 123.0, 126.4, 126.9, 127.6, 130.3, 130.4, 130.6, 133.1, 136.3, 153.7, 153.9, 165.5 ppm; Anal. Calcd. for C\(_{30}\)H\(_{30}\)BrN\(_3\): C, 70.31; H, 5.90; N, 8.20; found: C 70.46, H 5.83, N 8.15.

2-(1H-Indol-3-yl)-4-(3-nitrophenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocycloclodeca[b]pyridine-3-carbonitrile (7m)

Obtained as pale yellow solid (244.0 mg, 0.510 mmol, 94%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\)H: 1.14–1.92 (m, 14H), 2.01–2.27 (m, 2H), 2.57 (t, \(J=6.9\) Hz, 2H), 2.92–3.18 (m,
2H), 7.25–7.38 (m, 3H), 7.68–7.73 (m, 2H), 8.17 (d, J=2.7 Hz, 1H), 8.23–8.28 (m, 1H), 8.34–8.41 (m, 1H), 8.51–8.55 (m, 1H), 8.66 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ$_C$: 22.8, 23.3, 25.8, 26.4, 26.8, 26.9, 27.3, 27.7, 28.6, 33.1, 102.8, 111.4, 121.4, 122.3, 123.1, 123.6, 123.8, 126.9, 129.9, 130.3, 134.7, 136.2, 148.2, 152.2, 154.1, 165.7 ppm; Anal. Calcd. for C$_{30}$H$_{30}$N$_4$O$_2$: C, 75.29; H, 6.32; N, 11.71; found: C 75.40, H 6.39, N 7.83.

4-(2,4-Dichlorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocycloclododeca[b]-pyridine-3-carbonitrile (7n)

Obtained as white solid (253.7 mg, 0.505 mmol, 93%). $^1$H NMR (300 MHz, CDCl$_3$) δ$_H$: 1.18–1.88 (m, 12H), 1.98–2.27 (m, 3H), 2.37–2.47 (m, 1H), 2.60–2.69 (m, 1H), 2.93–3.15 (m, 3H), 7.23–7.30 (m, 2H), 7.40–7.45 (m, 3H), 7.58 (d, J=2.1 Hz, 1H), 8.23 (d, J=2.7 Hz, 1H), 8.53–8.56 (m, 2H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ$_C$: 22.9, 23.4, 25.9, 26.6, 27.3, 27.4, 27.7, 28.3, 33.3, 102.1, 111.3, 121.4, 122.5, 123.2, 126.9, 127.6, 130.0, 130.8, 131.2, 133.8, 135.7, 136.3, 151.1, 154.1, 165.6 ppm.; Anal. Calcd. For C$_{30}$H$_{29}$N$_3$: C, 71.71; H, 5.82; N, 8.36; found: C 71.64, H 5.71, N 8.20.

4-(3,4-Dimethoxyphenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocycloclododeca[b]pyridine-3-carbonitrile (7s)

Obtained as pale yellow solid (243.8 mg, 0.494 mmol, 91%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δ$_H$: 1.06–1.67 (m, 16H), 1.93–2.14 (m, 2H), 2.43–2.68 (m, 2H), 3.83 (s, 3H), 3.87 (s, 3H), 6.77–6.83 (m, 2H), 6.94 (d, J=9.0 Hz, 1H), 7.09–7.15 (m, 2H), 7.38 (t, J=3.0 Hz, 1H), 8.15 (d, J=2.7 Hz, 1H), 8.42 (t, J=3.6 Hz, 1H), 10.8 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) δ$_C$: 22.1, 22.6, 25.2, 25.8, 26.3, 26.6, 27.0, 28.1, 32.4, 55.2, 55.3, 102.6, 110.4, 111.0, 112.7, 118.3, 120.0, 120.4, 121.6, 121.7, 125.9, 126.7,
129.1, 129.9, 136.0, 148.0, 148.3, 153.3, 154.0, 164.1 ppm; Anal. Calcd. for C\textsubscript{32}H\textsubscript{35}N\textsubscript{3}O\textsubscript{2}: C, 77.86; H, 7.15; N, 8.51; found: C, 77.97; H, 7.25; N, 8.39.

2-(1H-Indol-3-yl)-4-(3,4,5-trimethoxyphenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclodeca[b]pyridine-3-carbonitrile (7t)

Obtained as white solid (261.6 mg, 0.499 mmol, 92%). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) δ\textsubscript{H}: 1.27–1.87 (m, 12H), 2.01–2.28 (m, 2H), 2.53–2.76 (m, 2H), 2.93–3.16 (m, 2H), 3.77 (s, 2H), 3.88 (s, 6H), 3.95 (s, 3H), 6.51 (s, 2H), 7.26–7.44 (m, 3H), 8.21 (s, 1H), 8.46–8.56 (m, 1H), 8.68 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\textsubscript{3}) δ\textsubscript{C}: 22.8, 23.3, 25.9, 26.6, 27.1, 27.2, 27.4, 27.7, 29.1, 33.1, 56.1, 25.2, 61.0, 103.5, 105.8, 106.2, 111.4, 113.9, 118.6, 121.2, 122.1, 122.9, 126.4, 126.8, 130.8, 132.6, 136.3, 137.9, 153.2, 153.8, 154.8, 165.1 ppm. Anal. Calcd. For C\textsubscript{33}H\textsubscript{37}N\textsubscript{3}O\textsubscript{3}: C, 75.69; H, 7.12; N, 8.02; found: C, 75.74; H, 7.02; N, 8.14.

2-(1H-Indol-3-yl)-4-(thiophen-2-yl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclodeca[b]pyridine-3-carbonitrile (7u)

Obtained as brown solid; Yield (214.8 mg, 0.489 mmol, 90%). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) δ\textsubscript{H}: 1.24–1.82 (m, 14H), 2.01–2.24 (m, 2H), 2.62–2.81 (m, 2H), 2.91–3.15 (m, 2H), 7.15–7.55 (m, 6H), 8.20 (s, 1H), 8.42–8.67 (m, 2H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\textsubscript{3}) δ\textsubscript{C}: 23.0, 23.5, 25.9, 26.7, 27.1, 27.3, 27.5, 27.7, 29.3, 33.2, 104.8, 111.3, 114.2, 118.4, 121.3, 122.4, 123.1, 126.5, 126.9, 127.2, 127.3, 128.9, 132.5, 136.3, 136.5, 147.8, 153.9, 165.1 ppm; Anal. Calcd. for C\textsubscript{28}H\textsubscript{29}N\textsubscript{3}S: C, 76.50; H, 6.65; N, 9.56; found: C 76.64, H 6.57, N 9.53.
2-(5-Bromo-1H-indol-3-yl)-4-(p-tolyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclooctodeca[b]-pyridine-3-carbonitrile (14b)

Obtained as white solid (184.0 mg, 0.349 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δ$_H$: 1.06–1.61 (m, 14H), 1.91–2.06 (m, 2H), 2.30 (s, 3H), 2.39–2.51 (m, 2H), 2.80–2.95 (m, 2H), 7.05 (d, $J$=8.1 Hz, 2H), 7.15–7.22 (m, 4H), 8.09 (d, $J$=3.0 Hz, 1H), 8.56 (s, 1H), 10.71 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) δ$_C$: 19.9, 21.5, 21.9, 24.3, 24.8, 25.3, 25.6, 26.1, 27.0, 31.5, 101.5, 111.5, 112.1, 112.2, 123.4, 123.5, 126.8, 127.1, 127.8, 129.3, 132.8, 133.9, 136.7, 151.7, 153.5, 163.1 ppm; Anal. Calcd. for C$_{31}$H$_{32}$BrN$_3$: C, 70.72; H, 6.13; N, 7.98; found: C 70.63, H 6.29, N 7.85.

2-(5-Bromo-1H-indol-3-yl)-4-(4-isopropylphenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclooctodeca[b]pyridine-3-carbonitrile (4d)

Obtained as white solid (189.7 mg, 0.342 mmol, 90%). $^1$H NMR (300 MHz, CDCl$_3$) δ$_H$: 1.33 (d, $J$=6.9Hz, 6H), 1.37–1.76 (m, 14H), 2.06–2.22 (m, 2H), 2.54–2.67 (m, 2H), 2.92–3.11 (m, 3H), 7.23 (d, $J$=8.1 Hz, 3H), 7.36 (d, $J$=8.1 Hz, 3H), 8.17 (s, 1H), 8.65 (br s, 1H), 8.70 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) δ$_C$: 22.1, 22.6, 23.0, 24.9, 25.5, 25.9, 26.2, 26.6, 27.7, 32.1, 33.9, 102.2, 112.2, 112.4, 112.9, 117.7, 124.1, 125.6, 127.4, 127.5, 130.0, 133.6, 134.4, 148.1, 152.4, 154.2, 163.8 ppm; Anal. Calcd. for C$_{33}$H$_{36}$BrN$_3$: C, 71.47; H, 6.54; N, 7.58; found: C 71.55, H 5.47, N 7.65.

2-(5-Bromo-1H-indol-3-yl)-4-(4-chlorophenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclooctodeca[b]pyridine-3-carbonitrile (14f)

Obtained as white solid (197.4 mg, 0.361 mmol, 95%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δ$_H$: 1.10–1.73 (m, 16H), 1.91–2.14 (m, 2H), 2.82–3.05 (m, 2H), 7.22–7.38 (m, 4H), 7.48 (d, $J$=8.1 Hz, 2H), 8.19 (s, 1H), 8.61 (s, 1H), 11.63 (s, 1H) ppm; $^{13}$C
NMR (75 MHz, CDCl₃+DMSO–d₆) δC: 21.2, 21.6, 23.9, 24.4, 24.9, 25.2, 25.7, 26.6, 31.2, 100.8, 110.9, 111.9, 116.5, 123.2, 126.4, 126.9, 127.1, 128.5, 128.6, 132.5, 133.6, 134.1, 151.5, 151.7, 163.0 ppm; Anal. Calcd. for C₃₀H₂₉BrClN₃: C, 65.88; H, 5.34; N, 7.68; found: C 65.80, H 5.22, N 7.77.

2-(5-Bromo-1H-indol-3-yl)-4-(4-bromophenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclo-
dodeca[b]pyridine-3-carbonitrile (14g)

Obtained as pale yellow solid (206.7 mg, 0.349 mmol, 92%). ¹H NMR (300 MHz, CDCl₃+DMSO–d₆) δH: 1.08–1.73 (m, 16H), 1.91–2.15 (m, 2H), 2.84–3.04 (m, 2H), 7.29 (d, J=8.1 Hz, 3H), 7.42 (d, J=8.7 Hz, 1H), 7.68 (d, J=8.1 Hz, 2H), 8.23 (s, 1H), 8.61 (s, 1H), 11.71 (s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃+DMSO–d₆) δC: 2.08, 21.2, 23.5, 24.0, 24.5, 24.9, 25.4, 26.2, 30.7, 100.5, 110.5, 111.5, 111.9, 120.5, 122.7, 122.9, 126.1, 126.9, 128.3, 128.6, 129.7, 133.2, 134.2, 151.1, 151.5, 162.6 ppm; Anal. Calcd. for C₃₀H₂₉BrClN₃: C, 60.93; H, 4.94; N, 7.11; found: C 60.81, H 5.02, N 7.25.

2-(5-Bromo-1H-indol-3-yl)-4-(3-nitrophenyl)-5,6,7,8,9,10,11,12,13,14-decahydrocyclo-
deca[b]pyridine-3-carbonitrile (14m)

Obtained as pale yellow solid (201.2 mg, 0.361 mmol, 95%). ¹H NMR (300 MHz, CDCl₃+DMSO–d₆) δH: 0.97–1.69 (m, 14H), 2.09–2.30 (m, 2H), 2.31–2.43 (m, 2H), 2.44–2.59 (m, 2H), 7.18 (d, J=8.7 Hz, 1H), 7.31 (d, J=8.7 Hz, 1H), 7.45–7.57 (m, 2H), 7.60–7.72 (m, 1H), 7.97–8.10 (m, 2H), 8.27 (s, 1H), 11.48 (s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃+DMSO–d₆) δC: 22.7, 22.9, 23.1, 24.7, 25.0, 25.1, 25.4, 25.6, 26.5, 26.7, 108.9, 110.2, 113.5, 114.3, 122.5, 123.2, 125.2, 128.9, 130.2, 134.3, 145.1, 148.9, 149.1 ppm; Anal. Calcd. for C₃₀H₂₉BrN₄O₂: C, 64.63; H, 5.24; N, 10.05; found: C 64.56, H 5.39, N 10.14.
2-(5-Bromo-1H-indol-3-yl)-4-(4-chloro-2-fluorophenyl)-5,6,7,8,9, 10,11,12,13,14-decahydro-
cyclododeca[b]pyridine-3-carbonitrile (14p)

Obtained as pale yellow solid (191.0 mg, 0.338 mmol, 89%). $^1$H NMR (300 MHz, 
CDCl$_3$+DMSO–d$_6$) $\delta$: 0.58–1.35 (m, 16H), 1.44–1.77 (m, 2H), 1.88–2.21 (br s, 2H), 
6.77–6.85 (m, 5H), 7.72 (s, 1H), 8.18 (s, 1H), 10.78 (s, 1H) ppm; $^{13}$C NMR (75 MHz, 
CDCl$_3$+DMSO–d$_6$) $\delta$: 22.3, 22.7, 25.0, 25.5, 25.9, 26.4, 26.8, 27.5, 32.4, 102.2, 112.1, 
112.6, 113.4, 116.1, 124.4, 124.5, 127.5, 127.9, 130.4, 130.8, 134.7, 147.0, 152.9, 156.5, 
159.8, 164.6 ppm; Anal. Calcd. for C$_{30}$H$_{28}$BrClF$_3$: C, 63.78; H, 5.00; N, 7.44; found: C 
63.91, H 5.09, N 7.54.

2-(5-Bromo-1H-indol-3-yl)-4-(3,4-dimethoxyphenyl)-5,6,7,8,9,10,11,12,13,14-decahydro-
cyclododeca[b]pyridine-3-carbonitrile (14s)

Obtained as pale yellow solid (195.8 mg, 0.342 mmol, 90%). $^1$H NMR (300 MHz, 
CDCl$_3$+DMSO–d$_6$) $\delta$: 1.08–1.72 (m, 16H), 1.90–2.14 (m, 2H), 2.80–3.03 (m, 2H), 3.79 
(s, 3H), 3.85 (s, 3H), 6.73–6.92 (m, 2H), 6.94–7.08 (m, 1H), 7.18–7.30 (m, 1H), 7.33– 
7.44 (m, 1H), 8.21 (d, $J$=3.0 Hz, 1H), 8.62 (s, 1H), 11.64 (s, 1H) ppm. $^{13}$C NMR (75 MHz, 
CDCl$_3$+DMSO–d$_6$) $\delta$: 21.4, 21.8, 24.2, 24.7, 25.3, 25.5, 26.0, 27.0, 31.4, 54.3, 54.5, 101.7, 110.1, 110.8, 112.0, 112.1, 119.6, 123.3, 123.4, 126.7, 127.0, 129.3, 133.7, 
147.3, 147.6, 151.6, 153.1, 162.9 Anal. Calcd. for C$_{32}$H$_{34}$BrF$_3$N$_2$: C, 67.13; H, 5.99; N, 
7.34; found: C 67.21, H 5.91, N 7.39.

2-(5-Bromo-1H-indol-3-yl)-4-(3,4,5-trimethoxyphenyl)-5,6,7,8,9,10,11,12,13,14-decahydro-
cyclododeca[b]pyridine-3-carbonitrile (14t)

Obtained as white solid (215.2 mg, 0.357 mmol, 94%). $^1$H NMR (300 MHz, 
CDCl$_3$+DMSO–d$_6$) $\delta$: 1.13–1.75 (m, 14H), 1.91–2.16 (m, 2H), 2.53–2.68 (m, 2H), 2.86–
3.02 (m, 2H), 3.73–3.85 (m, 9H), 6.61 (s, 2H), 7.21–7.29 (m, 1H), 7.37–7.44 (m, Hz, 1H), 8.25 (s, 1H), 8.62 (s, 1H), 11.71 (s, 1H) ppm; \[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\): 21.0, 21.4, 23.8, 24.3, 24.9, 25.0, 25.1, 25.5, 26.8, 30.9, 54.4, 58.5, 101.0, 104.4, 110.8, 111.6, 116.4, 122.9, 126.3, 126.8, 128.7, 130.5, 133.3, 136.0, 151.1, 151.2, 152.8, 162.5 ppm; Anal. Calcd. for C\(_{33}\)H\(_{36}\)BrN\(_3\)O\(_3\): C, 65.78; H, 6.02; N, 6.97; found: C 65.90, H 6.09, N 7.05.

4-(4-Bromophenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10,11,12,13,14-dodecahydrocyclododeca-
[b]pyridine-3-carbonitrile (12g)

Obtained as white solid (248.5 mg, 0.483 mmol, 89%). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\): 1.05–1.75 (m, 16H), 1.99–2.30 (m, 2H), 2.49–2.61 (m, 2H), 4.18 (s, 1H), 7.05–7.14 (m, 2H), 7.22 (d, \(J=9.0\) Hz, 2H), 7.33–7.44 (m, 3H), 7.46–7.52 (m, 1H), 7.54–7.62 (m, 2H), 11.09 (s, 1H) ppm; \[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\): 21.1, 21.5, 23.0, 23.3, 23.8, 24.0, 24.9, 25.0, 43.0, 75.4, 107.9, 109.2, 111.1, 118.9, 119.1, 119.2, 121.1, 122.3, 124.3, 125.9, 128.4, 130.4, 130.7, 135.3, 143.7, 144.5 ppm; Anal. Calcd. for C\(_{30}\)H\(_{32}\)BrN\(_3\): C, 70.03; H, 6.27; N, 8.17; found: C, 70.15; H, 6.37; N, 8.25.

4-(2-Chlorophenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10,11,12,13,14-dodecahydrocyclododeca-
[b]pyridine-3-carbonitrile (12k)

Obtained as white solid (242.5 mg, 0.516 mmol, 95%). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \(\delta\): 1.21–1.89 (m, 16H), 1.95–2.13 (m, 1H), 2.15–2.34 (m, 1H), 2.54–2.72 (m, 1H), 5.04 (s, 1H), 5.89 (s, 1H), 7.10–7.22 (m, 3H), 7.23–7.33 (m, 3H), 7.34–7.44 (m, 2H), 7.50–7.57 (m, 1H), 7.60–7.65 (m, 1H), 9.22 (s, 1H) ppm; \[^{13}\text{C}\] NMR (75 MHz, CDCl\(_3\)) \(\delta\): 22.3, 24.3, 24.4, 24.7, 24.8, 24.9, 25.6, 26.2, 26.3, 40.2, 76.7, 108.8, 111.6, 112.4, 118.9, 120.8, 122.7, 123.3, 124.7, 126.7, 127.6, 128.0, 129.3, 130.6, 130.8, 132.3, 136.1, 143.8, 145.1
ppm; Anal. Calcd. for C$_{30}$H$_{32}$ClN$_3$: C, 76.66; H, 6.86; N, 8.94; found: C, 76.80; H, 6.90; N, 8.79.

4-(2-Chloro-3-methoxyphenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10,11,12,13,14-dodecahydrocyclododeca[b] pyridine-3-carbonitrile (12o)

Obtained as white solid (249.8 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_H$: 1.18–1.92 (m, 17H), 2.02–2.14 (m, 1H), 2.16–2.23 (m, 1H), 2.48–2.64 (m, 1H), 3.90 (s, 3H), 5.01 (s, 1H), 6.84 (dd, $J=7.5$ Hz, 1H), 7.10–7.25 (m, 5H), 7.42 (d, $J=7.2$ Hz, 1H), 7.56 (d, $J=2.7$ Hz, 1H), 7.62 (d, $J=7.2$ Hz, 1H), 11.0 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_C$: 27.5, 27.7, 29.6, 29.9, 30.2, 30.3, 31.0, 31.4, 31.5, 45.7, 81.7, 114.2, 115.3, 116.2, 117.4, 125.0, 125.4, 125.7, 127.4, 127.7, 128.1, 130.5, 132.0, 132.8, 136.7, 141.6, 150.4, 151.1, 159.7 ppm; Anal. Calcd. for C$_{31}$H$_{34}$ClN$_3$O: C, 74.46; H, 6.85; N, 8.40; found: C, 74.59; H, 6.94; N, 8.49.

4-(4-Chloro-2-fluorophenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10,11,12,13,14-dodecahydrocyclododeca[b] pyridine-3-carbonitrile (12p)

Obtained as white solid (230.3 mg, 0.472 mmol, 87%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.16–1.86 (m, 16H), 1.94–2.10 (m, 1H), 2.17–2.33 (m, 1H), 2.53–2.71 (m, 1H), 4.73 (s, 1H), 5.87 (s, 1H), 7.08–7.13 (m, 2H), 7.16–7.23 (m, 2H), 7.31–7.37 (m, 2H), 7.53 (d, $J=2.4$ Hz, 1H), 7.61–7.67 (m, 1H), 9.08 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta_C$: 22.8, 22.9, 24.7, 25.0, 25.2, 25.3, 26.0, 26.6, 26.9, 37.2, 76.6, 109.5, 110.7, 112.7, 116.3, 116.7, 119.3, 121.4, 123.2, 123.3, 125.2, 125.4, 125.5, 127.0, 131.4, 131.4, 131.5, 131.6, 131.8, 133.5, 133.6, 136.6, 145.7, 158.4, 161.6 ppm; Anal. Calcd. for C$_{30}$H$_{31}$ClFNN$_3$: C, 73.83; H, 6.40; N, 8.61; found: C, 73.78; H, 6.51; N, 8.70.
4-(2,5-Dimethoxyphenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10,11,12,13,14-dodecahydrocyclo-
dodeca[b]pyridine-3-carbonitrile (12q)

Obtained as white solid (228.9 mg, 0.462 mmol, 85%). \(^1\)H NMR (300 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\)H: 1.14–1.88 (m, 17H), 2.05–2.60 (m, 2H), 2.39–2.58 (m, 1H), 3.64 (s, 3H), 3.77 (s, 3H), 4.67 (s, 1H), 6.66 (dd, \(J=9.0\) Hz, 1H), 6.79 (d, \(J=7.5\) Hz, 1H), 6.90 (d, \(J=3.0\) Hz, 1H), 7.03–7.13 (m, 2H), 7.38 (d, \(J=7.8\) Hz, 1H), 7.51 (d, \(J=2.4\) Hz, 1H), 7.55 (d, \(J=7.5\) Hz, 1H), 7.75 (s, 1H), 11.24 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\)C: 20.7, 21.1, 22.7, 23.4, 24.5, 24.6, 24.7, 34.4, 53.9, 55.1, 74.7, 107.8, 109.8, 110.1, 110.3, 110.6, 114.3, 118.5, 118.7, 120.6, 122.0, 124.0, 125.4, 130.1, 134.9, 135.3, 143.8, 149.0, 152.7 ppm; Anal. Calcd. for C\(_{32}\)H\(_{37}\)N\(_3\)O\(_2\): C, 77.54; H, 7.52; N, 8.48; found: C, 77.45; H, 7.48; N, 8.55.

4-(2,6-Difluorophenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10,11,12,13,14-dodecahydrocyclo-
deca[b]pyridine-3-carbonitrile (12r)

Obtained as white solid (227.8 mg, 0.483 mmol, 89%). \(^1\)H NMR (300 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\)H: 1.11–1.79 (br s, 17H), 1.88–2.05 (m, 1H), 2.09–2.26 (m, 1H), 2.33–2.46 (m, 1H), 4.87 (s, 1H), 6.83 (t, \(J=8.4\) Hz, 2H), 7.02–7.18 (m, 3H), 7.35 (d, \(J=7.5\) Hz, 1H), 7.50 (d, \(J=2.7\) Hz, 1H), 7.56 (d, \(J=6.0\) Hz, 1H), 7.61 (s, 1H), 11.09 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\)C: 27.5, 27.7, 29.6, 29.8, 30.0, 30.2, 30.3, 30.9, 31.3, 31.4, 39.2, 78.2, 112.4, 114.3, 116.5, 116.9, 117.3, 125.2, 125.3, 125.5, 125.7, 125.9, 127.3, 128.3, 130.6, 130.8, 133.4, 133.6, 133.7, 137.3, 141.6, 151.5, 165.3, 165.4, 168.6, 168.7 ppm; Anal. Calcd. for C\(_{30}\)H\(_{31}\)F\(_2\)N\(_3\): C, 76.41; H, 6.63; N, 8.91; found: C, 76.55; H, 6.77; N, 8.99.
2-(1H-Indol-3-yl)-4-phenyl-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15a)

Obtained as white solid (188.9 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.33–1.70 (m, 6H), 1.90–2.06 (m, 2H), 2.60–2.80 (m, 2H), 3.11–3.33 (m, 2H), 7.17–7.66 (m, 8H), 8.19 (s, 1H), 8.47–8.71 (m, 2H), ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 25.7, 26.5, 27.4, 30.8, 31.0, 36.1, 103.7, 111.3, 114.0, 121.2, 122.3, 122.9, 126.5, 126.7, 128.2, 128.6, 128.7, 130.3, 136.2, 154.1, 154.2, 165.6 ppm; Anal. Calcd. for C$_{26}$H$_{23}$N$_3$: C, 82.73; H, 6.14; N, 11.13; found: C 82.65, H 6.07, N 11.19.

2-(1H-Indol-3-yl)-4-(p-tolyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile(15b)

Obtained as white solid (197.7 mg, 0.505 mmol, 93%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.32–1.61 (m, 6H), 1.88–2.06 (m, 2H), 2.44 (s, 3H), 2.60–2.74 (m, 2H), 3.11–3.25 (m, 2H), 7.19–7.39 (m, 7H), 8.17 (d, $J$=3.0 Hz, 1H), 8.48–8.56 (m, 1H), 8.61 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 21.4, 25.7, 26.5, 27.3, 30.7, 31.0, 36.1, 1039, 111.3, 121.1, 122.2, 122.9, 126.4, 126.7, 128.1, 129.3, 130.5, 134.0, 136.2, 138.4, 154.2, 154.3, 165.5 ppm; Anal. Calcd. for C$_{27}$H$_{25}$N$_3$: C, 82.83; H, 6.44; N, 10.73; found: C 82.94, H 6.54, N 10.81.

2-(1H-Indol-3-yl)-4-(4-isopropylphenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15d)

Obtained as white solid (209.6 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.33 (d, $J$=6.9 Hz, 6H), 1.37–1.59 (m, 6H), 1.90–2.05 (m, 2H), 2.62–2.74 (m, 2H), 2.92–3.07 (m, 1H), 3.13–3.25 (m, 2H), 7.22–7.29 (m, 4H), 7.36 (d, $J$=7.8 Hz, 3H), 8.14–8.21 (m, 1H), 8.47–8.56 (m, 1H), 8.60 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 23.8, 25.7, 26.5, 27.3, 30.7, 31.1, 33.8, 36.0, 103.9, 111.3, 121.0, 122.1, 122.7, 126.4, 126.6, 126.7,
128.1, 130.5, 134.2, 136.2, 149.1, 154.2, 154.3, 165.5 ppm; Anal. Calcd. for C_{29}H_{29}N_{3}: C, 83.02; H, 6.97; N, 10.02; found: C, 83.19; H, 6.89; N 10.18.

4-(4-Fluorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15e)

Obtained as yellow solid (201.6 mg, 0.510 mmol, 94%). \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta_H \): 1.30–1.67 (m, 6H), 1.84–2.06 (m, 2H), 2.56–2.78 (m, 2H), 3.09–3.31 (m, 2H), 7.20–7.38 (m, 7H), 8.15 (d, \( J=2.7 \) Hz, 1H), 8.49–8.58 (m, 1H), 8.70 (s, 1H) ppm; \( ^{13}C \) NMR (75 MHz, CDCl\(_3\)) \( \delta_C \): 25.7, 26.5, 27.3, 30.7, 30.9, 36.0, 103.7, 111.4, 113.8, 115.6, 115.9, 121.2, 122.2, 122.9, 126.7, 130.1, 130.2, 130.4, 136.3, 153.1, 154.3, 161.2, 164.4, 165.7 ppm; Anal. Calcd. for C_{26}H_{22}FN_{3}; C, 78.96; H, 5.61; N, 10.63; found: C 78.83, H 5.70, N 10.52.

4-(4-Chlorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15f)

Obtained as yellow solid (201.3 mg, 0.489 mmol, 90%). \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta_H \): 1.32–1.66 (m, 6H), 1.88–2.09 (s, 2H), 2.65 (t, \( J=6.0 \) Hz, 2H), 3.18 (t, \( J=6.0 \) Hz, 2H), 7.18–7.43 (m, 5H), 7.49 (d, \( J=8.4 \) Hz, 2H), 8.15 (d, \( J=2.7 \) Hz, 1H), 8.47–8.60 (m, 1H), 8.66 (br s, 1H) ppm; \( ^{13}C \) NMR (75 MHz, CDCl\(_3\)) \( \delta_C \): 25.7, 26.5, 27.4, 30.7, 31.0, 36.1, 103.5, 111.3, 113.9, 121.3, 122.3, 123.1, 126.4, 126.8, 129.0, 129.7, 130.3, 134.9, 135.4, 136.3, 152.9, 154.3, 165.8 ppm; Anal. Calcd. for C_{26}H_{22}ClN_{3}: C, 75.81; H, 5.38; N, 10.20; found: C 75.96, H 5.46, N 10.28.
4-(4-Bromophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15g)

Obtained as yellow solid (225.5 mg, 0.494 mmol, 91%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.30–1.71 (m, 6H), 1.86–2.14 (m, 2H), 2.53–2.81 (m, 2H), 3.05–3.33 (m, 2H), 7.20 (d, $J=6.0$ Hz, 2H), 7.24–7.35 (m, 2H), 7.37–7.51 (m, 1H), 7.66 (d, $J=8.1$ Hz, 2H), 8.22 (s, 1H), 8.56 (s, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta_C$: 25.7, 26.5, 27.4, 30.7, 31.0, 36.1, 103.5, 111.3, 113.9, 121.3, 122.3, 123.1, 126.4, 126.8, 129.0, 129.7, 130.3, 134.9, 135.4, 136.3, 152.9, 154.3, 165.8 ppm; Anal. Calcd. for C$_{26}$H$_{22}$BrN$_3$: C, 68.43; H, 4.86; N, 9.21; found: C, 68.60; H, 4.77; N, 9.09.

4-(4-Cyanophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15h)

Obtained as white solid (179.1 mg, 0.445 mmol, 82%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.31–1.57 (m, 6H), 1.88–2.10 (m, 2H), 2.52–2.75 (m, 2H), 3.08–3.32 (t, 2H), 7.27–7.31 (m, 2H), 7.42–7.52 (m, 3H), 7.83 (d, $J=7.5$ Hz, 2H), 8.19–8.25 (m, 1H), 8.50–8.63 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta_C$: 25.6, 26.4, 27.4, 30.7, 30.9, 36.1, 102.6, 111.4, 112.9, 118.3, 121.4, 122.4, 123.2, 126.8, 129.3, 129.6, 132.5, 136.2, 141.7, 151.9, 154.2, 166.2 ppm; Anal. Calcd. for C$_{27}$H$_{22}$N$_4$: C, 80.57; H, 5.51; N, 13.92; found: C 80.49, H 5.46, N 13.90.

2-(1H-indol-3-yl)-4-(4-nitrophenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15i)

Obtained as pale yellow solid (211.0 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.30–1.62 (m, 6H), 1.88–2.08 (m, 2H), 2.51–2.73 (m, 2H), 3.10–3.31 (m, 2H), 7.26–7.40 (m, 2H), 7.36–7.44 (m, 1H), 7.52 (d, $J=8.1$ Hz, 2H), 8.21 (d, $J=2.7$ Hz, 1H),
8.39 (d, J=8.4 Hz, 2H), 8.54–8.59 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δC: 25.6, 26.4, 27.4, 30.7, 30.9, 36.1, 102.5, 111.4, 121.4, 122.3, 123.2, 124.0, 126.3, 126.8, 129.5, 129.6, 136.2, 143.6, 148.0, 151.6, 154.4, 166.3 ppm; Anal. Calcd. for C$_{26}$H$_{22}$N$_4$O$_2$: C, 73.92; H, 5.25; N, 13.26; found: C 73.80, H 5.39, N 13.35.

2-(1H-indol-3-yl)-4-(o-tolyl)-1,4,5,6,7,8,9,10-octahydrocycloocta[b]pyridine-3-carbonitrile (15j)

 Obtained as pale yellow solid (194.4 mg, 0.494 mmol, 91%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δH: 1.15–1.86 (m, 9H), 1.90–2.07 (m, 1H), 2.17–2.39 (m, 2H), 2.44 (s, 3H), 4.60 (s, 1H), 7.10–7.22 (m, 5H), 7.40–7.50 (m, 3H), 7.51 (d, J=2.4 Hz, 1H), 7.57–7.62 (m, 1H), 11.02 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) δC: 18.8, 25.3, 25.7, 27.8, 28.0, 28.3, 40.8, 108.2, 109.1, 111.1, 119.1, 121.2, 122.6, 124.5, 125.4, 125.5, 125.6, 129.1, 129.2, 130.1, 133.9, 135.3, 144.0, 144.5 ppm; Anal. Calcd. for C$_{27}$H$_{27}$N$_3$: C, 82.41; H, 6.92; N, 10.68; found: C, 82.57; H, 6.82; N, 10.80.

4-(2-Bromophenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10-octahydrocycloocta[b]pyridine-3-carbonitrile (15l)

 Obtained as pale yellow solid (233.8 mg, 0.510 mmol, 94%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δH: 1.12–2.45 (m, 12H), 4.89 (s, 1H), 7.02–7.15 (m, 3H), 7.30 (t, J=7.5 Hz, 1H), 7.38 (d, J=8.1 Hz, 1H), 7.44 (d, J=8.1 Hz, 1H), 7.53 (d, J=2.7 Hz, 1H), 7.58–7.62 (m, 3H), 11.02 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) δC: 25.3, 25.6, 27.6, 27.8, 28.0, 28.3, 43.5, 75.9, 108.0, 108.9, 111.1, 119.1, 121.2, 121.3, 122.0, 124.5, 125.7, 127.3, 130.5, 130.9, 131.1, 135.3, 144.6, 145.5 ppm; Anal. Calcd. for C$_{26}$H$_{24}$BrN$_3$: C, 68.12; H, 5.28; N, 9.17; found: C, 68.26; H, 5.34; N, 9.27.
2-(1H-indol-3-yl)-4-(3-nitrophenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15m)

Obtained as pale yellow solid (211.0 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$H: 1.31–1.67 (m, 6H), 1.89–2.05 (m, 2H), 2.55–2.73 (m, 2H), 3.21 (t, $J$=6.3 Hz, 2H), 7.26–7.32 (m, 2H), 7.41–7.44 (m, 1H), 7.66–7.75 (m, 2H), 8.21–8.24 (m, 2H), 8.35–8.57 (m, 1H), 8.49–8.57 (m, 1H), 8.61 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$C: 25.6, 26.4, 27.4, 30.7, 30.9, 36.1, 102.9, 111.4, 121.4, 122.3, 123.1, 123.5, 123.8, 126.3, 126.9, 129.9, 134.6, 136.2, 138.5, 148.2, 151.2, 154.5, 166.3 ppm; Anal. Calcd. for C$_{26}$H$_{22}$N$_4$O$_2$: C, 73.92; H, 5.25; N, 13.26; found: C, 73.82; H, 5.09; N, 13.18.

4-(2,4-Dichlorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15n)

Obtained as white solid (206.0 mg, 0.461 mmol, 85%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$H: 1.28–1.67 (m, 6H), 1.85–2.08 (m, 2H), 2.44–2.80 (m, 2H), 3.08–3.36 (m, 2H), 7.26–7.42 (m, 5H), 7.59 (s, 1H), 8.14 (s, 1H), 8.47–8.61 (m, 1H), 8.70 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$C: 25.7, 26.4, 27.6, 30.2, 30.7, 36.1, 103.3, 111.4, 121.3, 122.3, 123.1, 126.8, 127.6, 130.0, 130.3, 130.9, 133.7, 135.7, 136.2, 150.1, 154.5, 166.3 ppm; Anal. Calcd. for C$_{26}$H$_{21}$Cl$_2$N$_3$: C, 69.96; H, 4.74; N, 9.41; found: C 69.85, H 4.66, N 9.53.

4-(4-Chloro-2-fluorophenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15p)

Obtained as white solid (219.2 mg, 0.510 mmol, 94%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$H: 1.28–1.72 (m, 6H), 1.87–2.12 (m, 2H), 2.54–2.85 (m, 2H), 3.21 (t, $J$=6.3 Hz, 2H), 7.21–7.42 (m, 6H), 8.20 (d, $J$=3.0 Hz, 1H), 8.52–8.57 (m, 1H), 8.60 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$C: 25.6, 26.4, 27.7, 30.5, 30.7, 36.1, 103.7, 111.4, 113.8, 118.2, 121.3,
122.2, 123.0, 126.3, 126.8, 130.9, 136.2, 146.8, 154.5, 157.2, 160.5, 166.1 ppm; Anal. Calcd. for C_{26}H_{21}ClFN_{3}: C, 72.64; H, 4.92; N, 9.77; found: C, 72.73; H, 4.80; N, 9.63.

4-(2,6-Difluorophenyl)-2-(1H-indol-3-yl)-1,4,5,6,7,8,9,10-octahydrocycloocta[b]pyridine-3-carbonitrile (15r)

Obtained as white solid (207.5 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δ$_H$: 1.07–1.268 (m, 1H), 1.41–1.87 (m, 7H), 2.05 (t, J=6.3 Hz, 2H), 2.13–2.42 (m, 2H), 4.96 (s, 1H), 5.84 (s, 1H), 6.91 (t, J=8.4 Hz, 2H), 7.14–7.41 (m, 4H), 7.56 (d, J=2.7 Hz, 1H), 7.65–7.75 (m, 1H), 9.00 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) δ$_C$: 25.8, 27.8, 28.0, 28.3, 28.5, 43.8, 76.1, 108.3, 109.1, 111.4, 119.3, 121.4, 121.6, 122.3, 124.7, 125.9, 127.6, 130.8, 131.1, 131.3, 135.6, 144.9, 145.7 ppm; Anal. Calcd. for C$_{26}$H$_{23}$F$_2$N$_3$: C, 75.16; H, 5.58; N, 10.11; found: C, 75.29; H, 5.64; N, 10.04.

4-(3,4-Dimethoxyphenyl)-2-(1H-indol-3-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15s)

Obtained as white solid (218.5 mg, 0.499 mmol, 92%). $^1$H NMR (300 MHz, CDCl$_3$) δ$_H$: 1.30–1.68 (m, 6H), 1.87–2.14 (m, 2H), 2.59–2.85 (m, 2H), 3.06–3.37 (m, 2H), 3.90 (s, 3H), 3.94 (s, 3H), 6.81 (s, 1H), 6.87 (d, J=8.1 Hz, 1H), 6.99 (d, J=8.1 Hz, 1H), 7.20–7.31 (m, 2H), 7.31–7.40 (m, 1H), 8.11–8.21 (m, 1H), 8.45–8.60 (m, 1H), 8.81 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ$_C$: 25.8, 26.5, 27.4, 30.7, 31.3, 36.0, 55.8, 56.0, 104.0, 111.1, 111.3, 111.5, 121.0, 121.1, 122.2, 122.9, 126.7, 129.4, 130.7, 136.2, 148.8, 149.1, 153.9, 154.2, 165.5 ppm; Anal. Calcd. for C$_{28}$H$_{27}$N$_3$O$_2$: C, 76.86; H, 6.22; N, 9.60; found: C, 76.98; H, 6.31; N, 9.71.
2-(1H-Indol-3-yl)-4-(3,4,5-trimethoxyphenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15t)

Obtained as white solid (241.1 mg, 0.515 mmol, 95%). $^1$H NMR (300 MHz, CDCl$_3$) δ: 1.35–1.69 (m, 6H), 1.90–2.07 (m, 2H), 2.62–2.79 (m, 2H), 3.09–3.26 (m, 2H), 3.88 (s, 6H), 3.94 (s, 3H), 6.43–6.56 (m, 2H), 7.19–7.32 (m, 2H), 7.34–7.46 (m, 1H), 8.16–8.25 (m, 1H), 8.46–8.58 (m, 1H), 8.68 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 25.9, 26.4, 27.6, 30.7, 31.6, 35.9, 56.3, 62.0, 103.6, 105.7, 111.3, 113.9, 118.6, 121.2, 122.2, 122.9, 126.4, 126.7, 130.4, 132.4, 136.3, 138.0, 153.2, 153.9, 154.2, 165.6 ppm; Anal. Calcd. for C$_{29}$H$_{29}$N$_3$O$_3$: C, 74.50; H, 6.25; N, 8.99; found: C, 74.59, H, 6.36, N, 8.85.

2-(1H-Indol-3-yl)-4-(thiophen-2-yl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (15u)

Obtained as pale yellow solid (195.6 mg, 0.510 mmol, 94%). $^1$H NMR (300 MHz, CDCl$_3$) δ: 1.33–1.80 (m, 6H), 1.87–2.09 (m, 2H), 2.79 (t, J=6.0 Hz, 2H), 3.20 (t, J=6.0 Hz, 2H), 7.14–7.21 (m, 2H), 7.26–7.30 (m, 2H), 7.36–7.40 (m, 1H), 7.53 (dd, J=5.1 Hz, 1H), 8.19 (d, J=2.7 Hz, 1H), 8.46–8.55 (m, 1H), 8.67 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 25.8, 25.9, 26.4, 27.9, 30.7, 31.8, 35.9, 105.0, 111.3, 113.9, 118.4, 121.2, 122.3, 122.9, 126.4, 126.8, 127.2, 127.3, 128.5, 128.9, 132.2, 136.2, 136.3, 146.8, 154.4, 165.6 ppm; Anal. Calcd. for C$_{24}$H$_{21}$N$_3$S: C, 75.16; H, 5.52; N, 10.96; found: C, 75.11; H, 5.43; N, 10.94.

2-(5-Bromo-1H-indol-3-yl)-4-phenyl-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (16a)

Obtained as pale yellow solid (152.6 mg, 0.334 mmol, 88%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) δ: 1.20–1.62 (m, 6H), 1.76–1.99 (m, 2H), 2.44–2.67 (m, 2H), 2.95–
3.25 (m, 2H), 7.15–7.62 (m, 7H), 8.24 (s, 1H), 8.62 (s, 1H), 11.71 (br s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta\)\(_{C}\): 23.8, 24.4, 25.3, 28.8, 28.9, 34.0, 101.1, 110.8, 111.7, 111.9, 116.5, 123.0, 123.1, 126.4, 126.8, 128.2, 133.5, 135.1, 151.7, 152.0, 163.4 ppm; Anal. Calcd. for C\(_{26}\)H\(_{22}\)BrN\(_3\): C, 68.43; H, 4.86; N, 9.21; Found: C, 68.58; H, 4.75; N, 9.30.

**2-(5-Bromo-1H-indol-3-yl)-4-(p-tolyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (16b)**

Obtained as white solid (159.1 mg, 0.338 mmol, 89%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\)\(_{H}\): 1.34–1.61 (m, 6H), 1.89–2.06 (m, 2H), 2.45 (s, 3H), 2.62–2.76 (m, 2H), 3.13–3.27 (m, 2H), 7.18–7.31 (m, 6H), 8.14 (d, \(J=3.0\) Hz, 1H), 8.65 (s, 1H), 8.83 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\)\(_{C}\): 21.4, 25.7, 26.4, 27.3, 30.7, 31.0, 36.0, 104.0, 112.8, 113.4, 114.5, 124.8, 125.7, 127.5, 128.0, 129.3, 131.0, 133.8, 134.8, 138.5, 153.6, 154.4, 165.7 ppm; Anal. Calcd. for C\(_{27}\)H\(_{24}\)BrN\(_3\): C, 68.94; H, 5.14; N, 8.93; Found: C, 68.82; H, 5.26; N, 8.80.

**2-(5-Bromo-1H-indol-3-yl)-4-(4-methoxyphenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (16c)**

Obtained as white solid (164.5 mg, 0.338 mmol, 89%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\)\(_{H}\): 1.33–1.63 (m, 6H), 1.89–2.07 (m, 2H), 2.61–2.77 (m, 2H), 3.10–3.28 (m, 2H), 3.87 (s, 3H), 7.04 (d, \(J=8.7\) Hz, 2H), 7.18–7.34 (m, 4H), 8.11 (d, \(J=3.0\) Hz, 1H), 8.65 (s, 1H), 8.96 (br s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\)\(_{C}\): 25.7, 26.4, 27.3, 30.7, 30.9, 36.0, 55.2, 104.1, 112.8, 113.3, 114.0, 114.4, 118.7, 124.7, 125.6, 127.5, 128.0, 128.8, 129.4, 131.2, 134.8, 153.6, 154.0, 159.7, 165.7 ppm; Anal. Calcd. for C\(_{27}\)H\(_{24}\)BrN\(_3\)O: C, 66.67; H, 4.97; N, 8.64; found: C, 66.58; H, 4.86; N, 8.70.
2-(5-Bromo-1H-indol-3-yl)-4-(4-isopropylphenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]-pyridine-3-carbonitrile (16d)

Obtained as white solid (170.5 mg, 0.342 mmol, 90%). \(^1\)H NMR (300 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta_H\): 1.27 (d, \(J=6.9\), 6H), 1.30–1.51 (m, 6H), 1.79–2.02 (m, 2H), 2.50–2.69 (m, 2H), 2.87–3.00 (m, 1H), 3.03–3.21 (m, 2H), 7.18 (d, \(J=8.1\) Hz, 2H), 7.25–7.40 (m, 5H), 8.20–8.27 (m, 1H), 8.66 (s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \(\delta_C\): 22.3, 24.0, 24.7, 25.5, 29.0, 29.3, 32.0, 34.3, 101.5, 111.2, 112.1, 116.9, 123.3, 124.9, 126.6, 126.7, 126.9, 128.7, 132.6, 133.7, 147.2, 152.0, 152.4, 163.5 ppm; Anal. Calcd. for C\(_{29}\)H\(_{28}\)BrN\(_3\): C, 69.88; H, 5.66; N, 8.43; found: C, 69.95; H, 5.59; N, 8.56.

2-(5-Bromo-1H-indol-3-yl)-4-(4-fluorophenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (16e)

Obtained as pale yellow solid (165.8 mg, 0.349 mmol, 92%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_H\): 1.35–1.59 (m, 6H), 1.89–2.06 (m, 2H), 2.59–2.73 (m, 2H), 3.12–3.27 (m, 2H), 7.15–7.42 (m, 6H), 8.22 (d, \(J=2.1\) Hz, 1H), 8.58–8.73 (m, 2H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_C\): 24.7, 25.5, 26.3, 29.7, 29.9, 35.1, 102.3, 111.9, 112.4, 113.0, 114.6, 114.9, 117.5, 124.1, 124.2, 127.3, 127.5, 129.3, 129.4, 132.0, 134.4, 152.0, 152.9, 160.1, 163.4, 164.7 ppm; Anal. Calcd. for C\(_{26}\)H\(_{21}\)BrFN\(_3\): C, 65.83; H, 4.46; N, 8.86; found: C, 65.76; H, 4.51; N, 8.81.

2-(5-Bromo-1H-indol-3-yl)-4-(4-chlorophenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (16f)

Obtained as white solid (169.7 mg, 0.345 mmol, 91%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_H\): 1.31–1.65 (m, 6H), 1.88–2.07 (m, 2H), 2.55–2.75 (m, 2H), 3.08–3.30 (m, 2H), 7.20–7.34 (m, 4H), 7.51 (d, \(J=7.5\) Hz, 2H), 8.07–8.16 (m, 1H), 8.67 (s, 1H), 8.85 (br s, 1H) ppm;
\( ^{13} \text{C} \) NMR (75 MHz, CDCl\(_3\)) \( \delta \): 25.7, 26.5, 27.4, 30.7, 31.0, 36.1, 103.5, 112.7, 113.6, 114.7, 125.1, 126.0, 127.5, 128.1, 129.0, 129.7, 130.7, 134.9, 135.0, 135.2, 152.9, 153.7, 166.1 ppm; Anal. Calcd. for C\(_{26}\)H\(_{21}\)BrClN\(_3\): C, 63.62; H, 4.31; N, 8.56; found: C, 63.53; H, 4.21; N, 8.69.

2-(5-Bromo-1H-indol-3-yl)-4-(4-bromophenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridine-3-carbonitrile (16g)

Obtained as pale yellow solid (193.2 mg, 0.361 mmol, 95%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 1.28–1.63 (m, 6H), 1.86–2.10 (m, 2H), 2.55–2.81 (m, 2H), 7.18–7.35 (m, 4H), 7.66 (d, \( J=8.1 \) Hz, 2H), 8.17 (s, 1H), 8.67 (s, 1H), 8.76 (br s, 1H) ppm; \(^{13} \text{C} \) NMR (75 MHz, CDCl\(_3\)) \( \delta \): 25.7, 26.5, 27.4, 30.7, 31.0, 36.1, 103.4, 112.7, 114.7, 123.2, 125.0, 126.0, 127.5, 128.1, 129.9, 130.6, 132.0, 134.8, 135.7, 152.9, 153.6, 166.1 ppm; Anal. Calcd. for C\(_{26}\)H\(_{21}\)Br\(_2\)N\(_3\): C, 58.34; H, 3.95; N, 7.85; found: C, 58.48; H, 3.81; N, 7.75.

2-(5-Bromo-1H-indol-3-yl)-4-(2-chloro-3-methoxy phenyl)-1,4,5,6,7,8,9,10-octahydrocycloocta[b]pyridine-3-carbonitrile (16o)

Obtained as pale yellow solid (178.8 mg, 0.342 mmol, 90%). \(^1\)H NMR (300 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \( \delta \): 1.07–2.15 (m, 10H), 2.22–2.44 (m, 2H), 3.86 (s, 3H), 4.97 (s, 1H), 6.83–6.88 (m, 1H), 7.21–7.34 (m, 4H), 7.44–7.50 (m, 1H), 7.71 (s, 1H), 7.91–8.18 (m, 1H), 11.45 (d, \( J=16.2 \) Hz, 1H) ppm; \(^{13} \text{C} \) NMR (75 MHz, CDCl\(_3\)+DMSO–d\(_6\)) \( \delta \): 24.8, 25.2, 26.9, 27.3, 27.7, 39.1, 54.7, 107.4, 108.0, 108.8, 111.4, 112.3, 119.0, 121.2, 121.3, 121.7, 123.2, 125.8, 126.2, 126.5, 130.3, 133.5, 143.6, 144.5, 152.9 ppm; Anal. Calcd. for C\(_{27}\)H\(_{23}\)BrClN\(_3\)O: C, 62.02; H, 4.82; N, 8.04; found: C, 62.16; H, 4.96; N, 8.11.
2-(5-Bromo-1H-indol-3-yl)-4-(4-chloro-2-fluorophenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]-pyridine-3-carbonitrile (16p)

Obtained as pale yellow solid (174.7 mg, 0.342 mmol, 90%) $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_H$: 1.21–1.59 (m, 6H), 1.78–2.02 (m, 2H), 2.41–2.74 (m, 2H), 2.99–3.25 (m, 2H), 7.25–7.41 (m, 5H), 8.26 (d, $J$=2.7 Hz, 1H), 8.65 (s, 1H), 11.68 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_C$: 23.8, 24.4, 25.8, 28.6, 29.0, 34.2, 101.3, 110.7, 112.0, 112.1, 123.2, 123.4, 123.5, 126.4, 127.0, 129.0, 129.9, 133.6, 144.9, 152.1, 155.3, 158.7, 164.1 ppm; Anal. Calcd. for C$_{26}$H$_{20}$BrClFN$_3$: C, 61.37; H, 3.96; N, 8.26; found: C, 61.45; H, 3.86; N, 8.14.

2-(5-Bromo-1H-indol-3-yl)-4-(3,4,5-trimethoxyphenyl)-5,6,7,8,9,10-hexahydrocycloocta[b]-pyridine-3-carbonitrile (16t)

Obtained as pale yellow solid (198.0 mg, 0.361 mmol, 95%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_H$: 1.29–1.66 (m, 6H), 1.78–2.02 (m, 2H), 2.55–2.76 (m, 2H), 3.00–3.18 (m, 2H), 3.81 (s, 9H), 6.43–6.62 (m, 2H), 7.23–7.37 (m, 2H), 8.15–8.25 (m, 1H), 8.57 (s, 1H), 11.54 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_C$: 24.3, 24.7, 26.0, 29.1, 29.9, 34.2, 54.7, 59.0, 101.6, 104.2, 111.1, 112.0, 112.1, 116.8, 123.3, 123.4, 126.7, 127.0, 128.8, 130.8, 133.8, 136.4, 151.6, 152.0, 152.2, 163.7 ppm; Anal. Calcd. for C$_{29}$H$_{28}$BrClFN$_3$: C, 61.37; H, 3.96; N, 8.26; found: C, 61.45; H, 3.86; N, 8.14.

2-(5-Bromo-1H-indol-3-yl)-4-(p-tolyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine-3-carbonitrile (17b)

Obtained as white solid (163.9 mg, 0.434 mmol, 80%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$: 1.51–2.01 (m, 6H), 2.45 (s, 3H), 2.59–2.74 (m, 2H), 3.20–3.35 (m, 2H), 7.21–7.40 (m, 7H), 8.14 (d, $J$=3.0 Hz, 1H), 8.43–8.54 (m, 1H), 8.66 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) $\delta_C$: 24.3, 24.7, 26.0, 29.1, 29.9, 34.2, 54.7, 59.0, 101.6, 104.2, 111.1, 112.0, 112.1, 116.8, 123.3, 123.4, 126.7, 127.0, 128.8, 130.8, 133.8, 136.4, 151.6, 152.0, 152.2, 163.7 ppm; Anal. Calcd. for C$_{29}$H$_{28}$BrClFN$_3$: C, 63.74; H, 5.16; N, 7.69; found: C, 63.88; H, 5.21; N, 7.75.
CDCl$_3$ $\delta$C: 21.4, 26.4, 27.7, 29.8, 32.1, 40.1, 103.5, 111.3, 121.2, 122.3, 122.9, 126.5, 126.7, 128.5, 129.4, 132.6, 134.0, 136.3, 138.5, 153.3, 153.8, 167.3 ppm; Anal. Calcd. for C$_{26}$H$_{23}$N$_3$: C, 82.73; H, 6.14; N, 11.13; found: C, 82.79; H, 6.26; N, 11.20.

4-(4-Chlorophenyl)-2-(1H-indol-3-yl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine-3-carbonitrile (17f)

Obtained as white solid (177.1 mg, 0.445 mmol, 82%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$H: 1.72–2.04 (m, 6H), 2.48–2.75 (m, 2H), 3.15–3.41 (m, 2H), 7.25–7.30 (m, 4H), 7.32–7.40 (m, 1H), 7.51 (d, $J$=8.4 Hz, 2H), 8.15 (d, $J$=2.7 Hz, 1H), 8.45–8.53 (m, 1H), 8.69 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$C: 26.2, 27.6, 29.7, 32.0, 40.0, 102.9, 111.4, 113.7, 121.2, 122.0, 122.9, 126.2, 126.8, 129.0, 130.0, 134.9, 135.2, 136.2, 151.8, 153.9, 167.6 ppm; Anal. Calcd. for C$_{25}$H$_{20}$ClN$_3$: C, 75.46; H, 5.07; N, 10.56; found: C, 75.51; H, 5.16; N, 10.42.

4-(2-Bromophenyl)-2-(1H-indol-3-yl)-4,5,6,7,8,9-hexahydro-1H-cyclohepta[b]pyridine-3-carbonitrile (17l)

Obtained as yellow solid (214.7 mg, 0.483 mmol, 89%). $^1$H NMR (300 MHz, CDCl$_3$+DMSO–d$_6$) $\delta$H: 0.96–1.19 (m, 1H), 1.33–2.14(m, 7H), 2.19–2.44 (m, 2H), 4.84 (s, 1H), 7.03–7.14 (m, 3H), 7.30–7.38 (m, 2H), 7.46 (d, $J$=8.1 Hz, 1H), 7.51 (s, 1H), 7.59 (t, $J$=9.0 Hz, 3H), 11.08 (br s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO–d$_6$) $\delta$C: 24.7, 25.8, 30.2, 30.7, 30.8, 45.9, 76.0, 107.9, 110.6, 110.9, 118.9, 119.1, 120.9, 121.2, 121.6, 124.3, 125.3, 127.1, 127.2, 133.7, 135.1, 143.9, 144.6 ppm; Anal. Calcd. for C$_{25}$H$_{22}$BrN$_3$: C, 67.57; H, 4.99; N, 9.46; found: C, 67.64; H, 5.10; N, 9.36.
2-(1H-Indol-3-yl)-4-(4-(methylthio)phenyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine-3-carbonitrile (17v)

Obtained as yellow solid (186.7 mg, 0.456 mmol, 84%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_H\): 1.70–2.03 (m, 6H), 2.55 (s, 3H), 2.57–2.72 (m, 2H), 3.19–3.35 (m, 2H), 7.22–7.41 (m, 7H), 8.09–8.22 (m, 1H), 8.41–8.54 (m, 1H), 8.60–8.72 (br s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_C\): 15.3, 26.3, 27.7, 29.7, 32.1, 40.0, 103.3, 111.3, 113.9, 121.2, 122.9, 126.1, 126.3, 126.8, 129.0, 132.7, 133.2, 136.2, 152.6, 153.8, 167.4 ppm; Anal. Calcd. for C\(_{26}\)H\(_{23}\)N\(_3\)S; C, 76.25; H, 5.66; N, 10.26; found: C, 76.33; H, 5.70; N, 10.20.

2-(1H-Indol-3-yl)-4-phenyl-5,6,7,8-tetrahydroquinoline-3-carbonitrile (18a)

Obtained as yellow solid (153.6 mg, 0.439 mmol, 81%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_H\): 1.66–1.84 (m, 2H), 1.87–2.07 (m, 2H), 2.50 (t, \(J=6.3\) Hz, 2H), 3.18 (t, \(J=6.3\) Hz, 2H), 7.25–7.38 (m, 2H), 7.30–7.38 (m, 3H), 7.50–7.59 (m, 3H), 8.13 (d, \(J=2.7\) Hz, 1H), 8.42–8.52 (m, 1H), 8.72 (br s, 1H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_C\): 23.0, 23.1, 27.5, 34.1, 103.7, 111.7, 121.6, 122.5, 123.4, 127.2, 127.5, 128.6, 129.2, 136.7, 154.4, 155.0, 161.8 ppm; Anal. Calcd. for C\(_{24}\)H\(_{19}\)N\(_3\): C, 82.49; H, 5.48; N, 12.03; found: C, 82.56; H, 5.42; N, 12.05.

2-(1H-Indol-3-yl)-4-(p-tolyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile (18b)

Obtained as pale yellow solid (157.8 mg, 0.434 mmol, 80%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta_H\): 1.73–1.84 (m, 2H), 2.40 (s, 2H), 2.45 (s, 3H), 2.61 (t, \(J=6.0\) Hz, 2H), 2.96 (t, \(J=6.0\) Hz, 2H), 7.23–7.48 (m, 6H), 8.24 (d, \(J=2.7\) Hz, 1H), 8.39 (br s, 1H), 8.52–8.62 (m, 2H) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta_C\): 21.8, 21.9, 22.9, 28.2, 28.4, 103.9, 111.7, 121.7, 122.5, 123.4, 127.3, 128.7, 128.7, 129.4, 129.9, 130.3, 131.6, 135.0, 136.6, 154.1,
159.4, 156.0 ppm; Anal. Calcd. for C_{25}H_{21}N_3: C, 82.61; H, 5.82; N, 11.56; found: C, 82.76; H, 5.90; N, 11.60.

4-(4-Chlorophenyl)-2-(1H-indol-3-yl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile (18f)

Obtained as white solid (166.7 mg, 0.434 mmol, 80%). ¹H NMR (300 MHz, CDCl₃) δH: 1.74–1.85 (m, 2H), 1.88–2.02 (m, 2H), 2.47 (t, J=6.3 Hz, 2H), 3.16 (t, J=6.3 Hz, 2H), 7.26–7.43 (m, 5H), 7.51 (d, J=8.4 Hz, 2H), 8.15 (d, J=3.0 Hz, 1H), 8.43–8.52 (m, 1H), 8.66 (br s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δC: 22.5, 22.7, 27.1, 33.7, 102.9, 111.3, 114.1, 121.3, 122.3, 123.1, 126.7, 129.2, 129.3, 129.7, 134.7, 135.1, 136.3, 153.2, 161.7 ppm; Anal. Calcd. for C_{24}H_{18}ClN_3: C, 75.09; H, 4.73; N, 10.95; found: C, 75.15; H, 4.77; N, 10.98.

2-(1H-Indol-3-yl)-4-(4-(methylthio)phenyl)-5,6,7,8-tetrahydro-quinoline-3-carbonitrile(18v)

Obtained as yellow solid (182.5 mg, 0.461 mmol, 85%). ¹H NMR (300 MHz, CDCl₃) δH: 1.67–2.05 (m, 4H), 2.41–2.67 (m, 5H), 3.07–3.28 (m, 2H), 7.15–7.49 (m, 6H), 7.67 (d, J=7.8 Hz, 1H), 8.16 (s, 1H), 8.46 (s, 1H), 8.69 (s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δC: 15.3, 22.5, 22.7, 27.1, 33.6, 103.1, 111.3, 121.2, 122.0, 122.9, 126.0, 126.1, 126.3, 126.7, 126.8, 128.7, 129.9, 132.1, 136.2, 153.9, 154.0, 161.5 ppm; Anal. Calcd. for C_{25}H_{21}N_3S: C, 75.92; H, 5.35; N, 10.62; found: C, 75.81; H, 5.28; N, 10.60.
Copies of NMR spectra

Figure 1: $^1$H and $^{13}$C NMR spectra of 7a
**Figure 2:** $^1$H and $^{13}$C NMR spectra of 7b
Figure 3: $^1$H and $^{13}$C NMR spectra of 7c
Figure 4: $^1$H and $^{13}$C NMR spectra of 7d
Figure 5: $^1$H and $^{13}$C NMR spectra of 7e
Figure 6: $^1$H and $^{13}$C NMR spectra of 7f
Figure 7: $^1$H and $^{13}$C NMR spectra of 7h
Figure 8: $^1$H and $^{13}$C NMR spectra of 7i
Figure 9: $^1$H and $^{13}$C NMR spectra of 7j
Figure 10: $^1$H and $^{13}$C NMR spectra of 71
Figure 11: $^1$H and $^{13}$C NMR spectra of 7m
Figure 12: $^1$H and $^{13}$C NMR spectra of 7n
Figure 13: $^1$H and $^{13}$C NMR spectra of 7s
Figure 14: $^1$H and $^{13}$C NMR spectra of 7t
Figure 15: $^1$H and $^{13}$C NMR spectra of 7u
Figure 16: $^1$H and $^{13}$C NMR spectra of 14b
Figure 17: $^1$H and $^{13}$C NMR spectra of 14d
Figure 18: $^1$H and $^{13}$C NMR spectra of 14f
Figure 19: $^1$H and $^{13}$C NMR spectra of 14g
Figure 20: $^1$H and $^{13}$C NMR spectra of 14m
Figure 21: $^1$H and $^{13}$C NMR spectra of 14p
Figure 22: $^1$H and $^{13}$C NMR spectra of 14s
Figure 23: $^1$H and $^{13}$C NMR spectra of 14t
Figure 24: $^1$H and $^{13}$C NMR spectra of 12g
Figure 25: $^1$H and $^{13}$C NMR spectra of 12k
Figure 26: $^1$H and $^{13}$C NMR spectra of 12o
Figure 27: \(^1\)H and \(^{13}\)C NMR spectra of 12p
Figure 28: $^1$H and $^{13}$C NMR spectra of 12q
Figure 29: $^1$H and $^{13}$C NMR spectra of 12r
Figure 30: $^1$H and $^{13}$C NMR spectra of 15a
Figure 31: $^1$H and $^{13}$C NMR spectra of 15b
**Figure 32:** $^1$H and $^{13}$C NMR spectra of 15d
Figure 33: $^1$H and $^{13}$C NMR spectra of 15e
Figure 34: $^1$H and $^{13}$C NMR spectra of 15f
Figure 35: $^1$H and $^{13}$C NMR spectra of 15g
Figure 36: $^1$H and $^{13}$C NMR spectra of 15h
Figure 37: $^1$H and $^{13}$C NMR spectra of 15i
Figure 38: $^1$H and $^{13}$C NMR spectra of 15j
Figure 39: $^1$H and $^{13}$C NMR spectra of 15l
Figure 40: $^1$H and $^{13}$C NMR spectra of 15m
Figure 41: $^1$H and $^{13}$C NMR spectra of 15n
Figure 42: $^1$H and $^{13}$C NMR spectra of 15p
Figure 43: $^1$H and $^{13}$C NMR spectra of 15r
Figure 44: $^1$H and $^{13}$C NMR spectra of 15s
Figure 45: $^1$H and $^{13}$C NMR spectra of 15t
Figure 46: $^1$H and $^{13}$C NMR spectra of 15u
Figure 47: $^1$H and $^{13}$C NMR spectra of 16a
Figure 48: $^1$H and $^{13}$C NMR spectra of 16b
Figure 49: $^1$H and $^{13}$C NMR spectra of 16c
Figure 50: $^1$H and $^{13}$C NMR spectra of 16d
Figure 51: $^1$H and $^{13}$C NMR spectra of 16e
Figure 52: $^1$H and $^{13}$C NMR spectra of 16f
Figure 53: $^1$H and $^{13}$C NMR spectra of 16g
Figure 54: $^1$H and $^{13}$C NMR spectra of 16o
Figure 55: $^1$H and $^{13}$C NMR spectra of 16p
Figure 56: $^1$H and $^{13}$C NMR spectra of 16t
Figure 57: $^1$H and $^{13}$C NMR spectra of 17b
Figure 58: $^1$H and $^{13}$C NMR spectra of 17f
Figure 59: $^1$H and $^{13}$C NMR spectra of 171
Figure 60: $^1$H and $^{13}$C NMR spectra of 17v
Figure 61: $^1$H and $^{13}$C NMR spectra of 18a
Figure 62: $^1$H and $^{13}$C NMR spectra of 18b
Figure 63: $^1$H and $^{13}$C NMR spectra of 18f
Figure 64: $^1$H and $^{13}$C NMR spectra of 18v
X-ray structure determination and refinement

X-ray diffraction intensity data were collected for compounds 12r and 16f on a Bruker Smart Apex II single crystal X-ray diffractometer equipped with graphite mono-chromated MoKα (λ=0.7103 Å) radiation and CCD detector. Crystals were cut to suitable size and mounted on a glass fiber using cyanoacrylate adhesive. The unit cell parameters were determined from 36 frames (0.5° ω and φ scans) from three different crystallographic zones and using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolutions of 0.75 Å. The intensity data collection, frames integration, Lorentz and polarization correction and decay correction were done using SAINT. Empirical absorption correction multi-scan was performed using SADABS program. The accuracy of the crystal structures was evidenced from the final residual R- and wR- factors and other parameters including estimated standard deviations in the values of bond length and bond angles, ‘data-to-parameter’ ratio, etc. Details of the crystal data, data collection and refinement of 12r and 16f are given in Tables S1 and S2, respectively.
**Table S1.** Crystal data and structure refinement parameters of 12r

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<th>Parameter</th>
<th>Value</th>
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<td><strong>Empirical formula</strong></td>
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<td><strong>Wavelength</strong></td>
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<tr>
<td><strong>Space group</strong></td>
<td>P 21/n</td>
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| **Unit cell dimensions**           | \[
| a = 11.5752(7) Å                  | \alpha = \gamma = 90°                     |
| b = 7.8182(4) Å                   | \beta = 101.362(2)°                       |
| c = 28.9629(17) Å                 |                                            |
| **Volume**                         | 2569.7(3) Å                               |
| **Z**                              | 4                                          |
| **Density (calculated)**           | 1.219 Mg/m\textsuperscript{3}              |
| **Absorption coefficient**         | 0.082 mm\textsuperscript{-1}              |
| **F(000)**                         | 1000                                       |
| **Crystal size**                   | 0.250 x 0.200 x 0.150 mm\textsuperscript{3} |
| **Theta range for data collection**| 3.1 to 28.7°.                             |
| **Index ranges**                   | -15<=h<=15, -10<=k<=10, -39<=l<=39         |
| **Reflections collected**          | 53269                                      |
| **Independent reflections**        | 6872 [R(int) = 0.0697]                     |
| **Completeness to theta = 25.242°**| 99.2 %                                     |
| **Refinement method**              | Full-matrix least-squares on F\textsuperscript{2} |
| **Data / restraints / parameters** | 6872 / 3 / 317                            |
| **Goodness-of-fit on F\textsuperscript{2}** | 1.328                                      |
| **Final R indices [I>2\sigma(I)]** | R1 = 0.0735, wR2 = 0.1617                 |
| **R indices (all data)**           | R1 = 0.1440, wR2 = 0.1911                 |
| **Largest diff. peak and hole**    | 0.356 and -0.254 e.Å\textsuperscript{-3}  |
Table S2. Crystal data and structure refinement parameters of 16f

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<td>Wavelength</td>
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<td>Unit cell dimensions</td>
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<tr>
<td>Temperature</td>
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<tr>
<td>Space group</td>
<td>P 21/n</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td>Theta range for data collection</td>
<td>3 to 25°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13&lt;=h&lt;=13, -13&lt;=k&lt;=13, -22&lt;=l&lt;=22</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>40938</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>40938 [R(int) = 0.0404]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / parameters</td>
<td>40938 / 280</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.008</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0432, wR2 = 0.1200</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0685, wR2 = 0.1416</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.524 and -0.686 e.Å⁻³</td>
</tr>
</tbody>
</table>