Supporting information

for

**Iodine mediated intramolecular C2-amidative cyclization of indoles: A facile access to indole fused tetracycles**

Sindhura Badigenchala, V. Rajeshkumar and G. Sekar*

*Department of Chemistry, Indian Institute of Technology Madras, Chennai, Tamilnadu-600 036. India

gsekar@iitm.ac.in

Table of contents

1. General considerations 2
2. Experimental conditions and spectral data of compounds 2
3. Crystal data of compound 7a 31
4. References 53
1. General considerations

All reactions were carried out in reaction tubes closed with stoppers and in LR grade solvents. All the solvents used for the reactions were obtained from Fischer Scientific, India Pvt. Ltd. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra synthesis Pvt. Ltd. India and used for column chromatography using hexanes and ethyl acetate mixture as eluent. Cs_{2}CO_{3} was purchased from Sigma-Aldrich Company. Other reagents such as indole, iodine were purchased from Spectrochem India Pvt. Ltd., 2-fluoro nitrobenzene and 2-bromo nitrobenzene were obtained from Avra synthesis Pvt. Ltd. India. Various substituted indoles were obtained from Spectrochem India Pvt. Ltd and Alfa Aesar Company. All the reactions were carried out in temperature controlled IKA magnetic stirrers. \(^{1}\)H and \(^{13}\)C NMR spectra were recorded on a Bruker 400 instrument. \(^{1}\)H NMR spectra were reported relative to Me_{4}Si (δ 0.0 ppm) or residual CDCl\(_{3}\) (δ 7.26 ppm). \(^{13}\)C NMR were reported relative to CDCl\(_{3}\) (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and were reported in frequency of absorption (cm\(^{-1}\)). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. Melting points were measured either on a Toshniwal melting point apparatus or on a Kofler-Heizitschmikroskop apparatus. The melting points were uncorrected.

2. Experimental conditions

**General Procedure for the preparation of compounds 8a-f, 8i and 8k**

\[
R \begin{array}{c} \text{NH}+ \text{F} \text{NO}_2 \\ \text{NaH (1.5 equiv)} \\ \text{THF, rt to reflux, 16 h} \\ \text{8a-i} \end{array}
\]

To a well stirred solution of indole (5 mmol) in dry THF maintained in ice bath, NaH (7.5 mmol) was added portion wise and is stirred at room temperature for 0.5 h. This was cooled using ice bath and 1-fluoro-2-nitrobenzene (6.5 mmol) was added slowly. The resulting reaction mixture was warmed to room temperature and was refluxed until the reaction was completed by TLC analysis. THF was removed by using rotary evaporator. Then the crude reaction was washed with water (2\( \times \)15 mL) and extracted with ethyl acetate. Combined organic layers were dried over Na_{2}SO_{4}, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to afford pure compound 8a-i.
General Procedure for the preparation of compounds 8g and 8h

8k (1 mmol) was taken into a clean dry round bottomed flask, and ArB(OH)$_2$ (1.5 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.1 mmol), K$_2$CO$_3$ (3 mmol) and 4 mL of DMF:H$_2$O (2:1) were added successively and the resulting reaction mixture was stirred at 80 °C. After the completion of reaction as monitored by TLC, reaction mixture was washed with water (2×15 mL) and extracted with ethyl acetate. Combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to afford pure compound 8g-h.

Spectral data for compounds 5a-i and 5k

1-(2-Nitrophenyl)-1H-indole (8a): Orange solid, mp 86-87 °C [lit. 85 °C]$^{1}$; R$_f$ 0.46 (10% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz, ppm) δ 6.74 (dd, $J$=3.2, 0.8Hz, 1H), 7.12-7.22 (m, 4H), 7.55-7.62 (m, 2H), 7.67-7.71 (m, 1H), 7.74 (dt, $J$=7.8, 1.2Hz, 1H), 8.04 (dd, $J$=8.2,1.2Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 105.2, 109.6, 121.1, 121.5, 123.1, 125.6, 128.1, 128.5, 129.1, 129.9, 133.0, 133.8, 136.8, 146.5; FTIR (KBr) 3057, 1604, 1493, 1455, 1351 cm$^{-1}$.

5-Methoxy-1-(2-nitrophenyl)-1H-indole (8b): Yellow solid, mp 75-77 °C; R$_f$ 0.51 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 3.86 (s, 3H), 6.66 (d, $J$=7.6 Hz, 1H), 7.04 (s, 2H), 7.47 (s, 1H), 7.53-7.60 (m, 2H), 7.73 (dt, $J$=7.6, 1.6 Hz, 1H), 8.02 (dd, $J$=8, 1.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 56.0, 103.3, 104.9, 110.4, 113.1, 125.6, 128.2, 128.6, 129.6, 129.7, 132.0, 133.1, 133.7, 146.3, 155.1; FTIR (KBr) 3110, 2938, 2834, 1607, 1528, 1492, 1447 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{15}$H$_{13}$N$_2$O$_3$: 269.0926; found: 269.0924.

5-Methyl-1-(2-nitrophenyl)-1H-indole (8c): Yellow solid, mp 78-80 °C; R$_f$ 0.45 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.46 (s, 3H), 6.66 (d, $J$=7.6 Hz, 1H), 7.04 (s, 2H), 7.47 (s, 1H), 7.53-7.60 (m, 2H), 7.73 (dt, $J$=7.6, 1.6 Hz, 1H), 8.02 (dd, $J$=8, 1.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 21.5,
104.8, 109.3, 121.2, 124.7, 125.6, 128.1, 128.2, 129.4, 129.7, 130.4, 133.2, 133.7, 135.2; FTIR (KBr) 3104, 2919, 2863, 1605, 1529, 1495, 1468, 133.2, 133.7, 135.2.

5-Fluoro-1-(2-nitrophenyl)-1H-indole (8d): Sticky orange solid, Rf 0.57 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 6.69 (d, J=3.2 Hz, 1H), 6.94 (dt, J=9, 2.4 Hz, 1H), 7.01-7.06 (m, 1H), 7.20 (d, J=3.6 Hz, 1H), 7.32 (dd, J=9.2, 2.4 Hz, 1H), 7.56-7.62 m, 2H), 7.76 (dt, J=7.6, 1.6 Hz, 1H), 8.04 (dd, J=8, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 105.0, 105.1, 106.3, 106.5, 110.3, 110.4, 111.3, 111.5, 125.7, 128.8, 129.7, 129.9, 132.8, 133.9, 159.8; 19F NMR (C6F6, 500 MHz) δ -126.68; FTIR (KBr) 3108, 1606, 1586, 1529, 1495, 1451, 1350 cm⁻¹.

3-Methyl-1-(2-nitrophenyl)-1H-indole (8e): Dark orange sticky solid, Rf 0.45 (10% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.39 (d, J=1.2 Hz, 3H), 6.94 (d, J=1.2 Hz, 1H), 7.12-7.15 (m, 1H), 7.19-7.23 (m, 2H), 7.52 (dt, J=7.8, 1.6 Hz, 1H), 7.57 (dd, J=8, 1.2 Hz, 1H), 7.61-7.65 (m, 1H), 7.71 (dt, J=7.6, 1.6 Hz, 1H), 8.01 (dd, J=8.2, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 9.7, 109.5, 114.6, 119.6, 120.6, 123.1, 125.4, 125.6, 127.9, 129.8, 133.2, 133.6, 136.9, 146.2; FTIR (KBr) 3054, 2919, 2861, 1604, 1529, 1494, 1455, 1350 cm⁻¹.

1-(2-Nitrophenyl)-1H-pyrrolo[2,3-b]pyridine (8f): Yellow solid, mp 86-88 °C [lit. 159 °C]; Rf 0.45 (30% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 6.70 (d, J=3.6 Hz, 1H), 7.12 (dd, J=7.6, 8 Hz, 1H), 7.36 (d, J=3.6 Hz, 1H), 7.59 (dd, J=8, 1.2 Hz, 1H), 7.52-7.58 (m, 1H), 7.74 (dt, J=7.6, 1.6 Hz), 7.96 (dd, J=12, 1.6 Hz, 1H), 8.09 (dd, J=8.2, 1.2 Hz, 1H), 8.27 (dd, J=4.8, 1.6 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 103.3, 115.9, 117.4, 121.2, 125.8, 127.7, 128.2, 129.3, 129.5, 131.7, 133.9, 144.1, 147.9; FTIR (KBr) 3053, 1600, 1423, 1355, 1279, 1156 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C13H10N3O2: 240.0773; found: 240.0777.

5-Phenyl-1-(2-nitrophenyl)-1H-indole (8g): Brown solid, mp 105-107 °C; Rf 0.52 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 6.79 (dd, J=3.2, 0.8 Hz, 1H), 7.18-7.22 (m, 2H), 7.33 (tt, J=7.2, 1.2 Hz, 1H), 7.41-7.49 (m, 3H), 8.06 (dd, J=8.2, 1.2 Hz, 1H), 7.57-7.68 (m, 4H), 7.76 (dt, J=7.6, 1.2 Hz, 1H), 7.89 (d, J=1.6 Hz, 1H), 8.06 (dd, J=8.2, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 105.5, 109.9, 120.0, 123.0, 125.7, 126.7, 127.6, 128.5, 128.7, 128.8, 129.6, 129.8, 133.0, 133.8, 134.7, 136.3, 142.2, 146.4; FTIR (KBr) 2918, 1604, 1529, 1462, 1346 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C20H15N5O2: 315.1134; found: 315.1138.
5-(4-Methyl phenyl)-1-(2-nitrophenyl)-1H-indole (8h): Brown solid, mp 108-110 °C; R_f 0.52 (20% ethyl acetate in hexanes); ^1H NMR (CDCl_3, 400 MHz) δ 2.41 (s, 3H), 6.78 (dd, J=3.4, 0.8 Hz, 1H), 7.17-7.21 (m, 2H), 7.26 (d, J=7.6 Hz, 2H), 7.44 (dd, J=8.4, 1.6 Hz, 1H), 7.54 (d, J=8 Hz, 2H), 7.56-7.65 (m, 2H), 7.76 (dt, J=7.6, 1.2 Hz, 1H), 7.87 (d, J=1.6 Hz, 1H), 8.06 (dd, J=8.2, 1.2 Hz, 1H); ^13C NMR (CDCl_3, 100 MHz) δ 21.2, 105.5, 109.8, 119.8, 122.9, 125.7, 127.4, 128.5, 128.7, 129.5, 129.6, 129.8, 133.0, 133.9, 134.7, 136.4, 139.4, 146.3; FTIR (KBr) 2922, 2857, 1605, 1528, 1493, 1465, 1347, 1178 cm^-1; HRMS (m/z): [M+H]^+ calcd. for C_{21}H_{17}N_2O_2: 329.1290; found: 329.1215.

5-Cyano-1-(2-nitrophenyl)-1H-indole (8i): Yellow solid, mp 178-180 °C [lit. 186 °C]²; R_f 0.45 (40% ethyl acetate in hexanes); ^1H NMR (CDCl_3, 400 MHz) δ 6.80 (dd, J=3.2, 0.8 Hz, 1H), 7.14 (d, J=8.4 Hz, 1H), 7.29 (d, J=3.2 Hz, 1H), 7.43 (d, J=8.4, 0.8 Hz, 1H), 7.58 (dd, J=8, 2 Hz, 1H), 7.68 (dt, J=7.8, 0.8 Hz, 1H), 7.81 (dd, J=8.2, 1.2 Hz, 1H), 8.04 (dd, J=1.4, 0.8 Hz, 1H); ^13C NMR (CDCl_3, 100 MHz) δ 104.4, 105.5, 110.6, 120.3, 125.9, 126.0, 126.9, 128.8, 129.8, 130.1, 130.6, 131.8, 134.2, 138.6, 146.5; FTIR (KBr) 2221, 1604, 1529, 1490, 1344 cm^-1.

5-Bromo-1-(2-nitrophenyl)-1H-indole (8k): Orange solid, mp 148-150 °C; R_f 0.52 (20% ethyl acetate in hexanes); ^1H NMR (CDCl_3, 400 MHz) δ 6.67 (dd, J=3.2, 0.8 Hz, 1H), 6.98 (d, J=8.8 Hz, 1H), 7.16 (d, J=3.2 Hz, 1H), 7.28 (dd, J=8.8, 2 Hz, 1H), 7.57 (dd, J=7.8, 1.6 Hz, 1H), 7.61 (dd, J=8, 1.6 Hz, 1H), 7.76 (dt, J=7.8, 1.6 Hz, 1H), 7.81 (d, J=1.6 Hz, 1H), 8.05 (dd, J=8.2, 1.6 Hz, 1H); ^13C NMR (CDCl_3, 100 MHz) δ 104.6, 111.1, 114.3, 124.0, 125.8, 126.0, 129.0, 129.4, 130.0, 130.8, 132.5, 133.9, 135.7; FTIR (KBr) 3099, 1606, 1528, 1495, 1452, 1349, 1283 cm^-1; HRMS (m/z): [M+H]^+ calcd. for C_{14}H_{10}N_2O_2Br: 316.9926; found: 316.9935 (HRMS data for 79Br isotope).

General Procedure for the preparation of compounds 9a-i

To a solution of compound 8 (4 mmol) in ethanol (8 mL), was added Pd/C (0.4 mmol). The resulting suspension was stirred under hydrogen pressure using hydrogen balloon until the completion of reaction.
The reaction mixture was filtered over celite and rinsed with DCM. The solvents were removed under vacuum and crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to obtain pure product 9.

**Spectral data for compounds 6a-i**

1-(2-Aminophenyl)-1H-indole\(^9\) (9a): Orange viscous liquid, R\(_f\) 0.50 (10% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.53 (bs, 2H), 6.60 (d, \(J=3.2\) Hz, 1H), 6.75-6.81 (m, 2H), 7.04-7.19 (m, 6H), 7.58-7.62 (m, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 103.4, 110.9, 116.6, 119.0, 120.3, 121.1, 122.4, 125.3, 128.7, 128.8, 129.3, 136.6, 142.8; FTIR (KBr) 3463, 3372, 3050, 1617, 1508, 1460, 1261, 746 cm\(^{-1}\); HRMS (m/z): [M+H]\(^+\) calcd. for C\(_{21}\)H\(_{13}\)N\(_2\): 209.1079; found: 209.1072.

5-Methoxy-1-(2-aminophenyl)-1H-indole\(^9\) (9b): White solid, mp 68-70 °C [lit. 66 °C]\(^9\); R\(_f\) 0.50 (15% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.37 (bs, 2H), 3.78 (s, 3H), 6.52 (d, \(J=2.4\) Hz, 1H), 6.74-6.83 (m, 3H), 6.96 (d, \(J=9.2\) Hz, 1H), 7.05-7.12 (m, 3H), 7.13-7.18 (m, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 56.0, 102.8, 103.1, 111.6, 112.6, 116.7, 119.1, 125.5, 128.7, 129.2, 129.2, 129.3, 131.9, 142.7, 154.7; FTIR (KBr) 3464, 3370, 2995, 2941, 2831, 1617, 1583, 1506, 1472, 1451, 1340 cm\(^{-1}\); HRMS (m/z): [M+H]\(^+\) calcd. for C\(_{15}\)H\(_{15}\)N\(_2\)O: 239.1184; found: 239.1172.

5-Methyl-1-(2-aminophenyl)-1H-indole\(^9\) (9c): Brown viscous liquid, R\(_f\) 0.43 (10% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.47 (s, 3H), 3.68 (bs, 2H), 6.61 (dd, \(J=3.2, 0.8\) Hz, 1H), 6.90 (dt, \(J=7.6, 1.6\) Hz, 1H), 6.94 (dd, \(J=8, 1.2\) Hz, 1H), 7.01-7.08 (m, 2H), 7.19 (d, \(J=3.2\) Hz, 1H), 7.21 (dd, \(J=7.6, 1.6\) Hz, 1H), 7.24-7.29 (m, 1H), 7.48 (s, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.5, 103.0, 110.5, 117.1, 119.5, 120.8, 124.0, 125.9, 128.7, 128.8, 129.0, 129.2, 129.6, 135.0, 142.0; FTIR (KBr) 3464, 3373, 3030, 2919, 2859, 1618, 1508, 1470, 1369, 754 cm\(^{-1}\).

5-Fluoro-1-(2-aminophenyl)-1H-indole (9d): Brown viscous liquid, R\(_f\) 0.43 (10% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.62 (bs, 2H), 6.66 (dd, \(J=3, 0.8\) Hz, 1H), 6.88-6.97 (m, 3H), 7.07 (1:1q, \(J=4.4\) Hz, 1H), 7.21 (dd, \(J=7.8, 1.6\) Hz, 1H), 7.25-7.31 (m, 2H), 7.34 (dd, \(J=9.6, 2.4\) Hz, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 103.4, 105.7, 106.0, 110.6, 110.9, 111.5, 111.6, 117.0, 119.4, 125.3, 128.7, 129.5, 130.3, 133.2, 142.3, 157.2, 159.6; \(^1\)F NMR (C\(_6\)F\(_6\), 500 MHz) \(\delta\) -127.78; FTIR (KBr) 3472, 3380, 3101, 1619, 1584, 1508, 1470, 1370, 1276 cm\(^{-1}\).
3-Methyl-1-(2-aminophenyl)-1H-indole (9e): Pale brown solid, mp 44-46 °C [lit. 43 °C]; Rf 0.53 (10% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.29 (d, J=1.2 Hz, 3H), 3.41 (bs, 2H), 6.71-6.77 (m, 2H), 6.88 (d, J=1.2 Hz, 1H), 7.00-7.14 (m, 5H), 7.52-7.55 (m, 1H); 13C NMR (CDCl3, 100 MHz) δ 9.7, 110.7, 112.5, 116.5, 118.8, 119.1, 119.6, 122.3, 125.4, 126.2, 128.7, 129.0, 129.1, 136.8, 142.9; FTIR (KBr) 3468, 3375, 3048, 2922, 2858, 1617, 1506, 1457, 1367, 1262 cm⁻¹.

2-(1H-pyrrolo[2,3-b]pyridin-1-yl)aniline (9f): White solid, mp 104-106 °C; Rf 0.45 (30% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 3.74 (bs, 2H), 6.66 (d, J=3.6 Hz, 1H), 6.90 (dt, J=7.6, 1.6 Hz, 1H), 6.95 (dd, J=8, 1.2 Hz, 1H), 7.13 (dd, J=7.6 Hz, 1H), 7.18-7.25 (m, 2H), 7.34 (d, J=3.6 Hz, 1H), 8.00 (dd, J=7.6, 1.6 Hz, 1H), 8.34 (dd, J=4.8, 1.6 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 101.9, 116.5, 117.8, 119.5, 121.2, 125.3, 128.4, 129.2, 129.6, 129.7, 142.4, 143.7, 147.7; FTIR (KBr) 3329, 3216, 1624, 1510, 1423, 1319 cm⁻¹.

5-Phenyl-1-(2-aminophenyl)-1H-indole (9g): White solid, mp 92-94 °C [lit. 92 °C]; Rf 0.43 (15% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 3.21 (bs, 2H), 6.64 (d, J=3.8 Hz, 1H), 6.74-6.81 (m, 2H), 7.08-7.25 (m, 5H), 7.31-7.37 (m, 3H), 7.53-7.58 (m, 2H), 7.81 (s, 1H); 13C NMR (CDCl3, 100 MHz) δ 103.8, 111.1, 116.6, 118.9, 119.6, 122.2, 125.0, 126.5, 127.5, 128.7, 128.8, 129.2, 129.4, 133.9, 136.0, 142.5, 143.0; FTIR (KBr) 3470, 3378, 3033, 1617, 1507, 1466, 1368, 1228 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C20H17N2: 285.1392; found: 285.1398.

5-(4-Methyl phenyl)-1-(2-aminophenyl)-1H-indole (9h): Brown solid, mp 112-114 °C; Rf 0.43 (15% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.41 (s, 3H), 2.82 (bs, 2H), 6.87-6.95 (m, 2H), 7.19-7.30 (m, 6H), 7.44 (dd, J=8.4, 1.6 Hz, 1H), 7.56 (d, J=8 Hz, 2H), 7.89 (d, J=1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.2, 103.8, 111.1, 116.6, 118.9, 119.6, 122.2, 125.0, 126.5, 127.5, 128.7, 128.8, 129.2, 129.4, 133.9, 136.0, 142.5, 143.0; FTIR (KBr) 3467, 3376, 3026, 2921, 2855, 1617, 1507, 1467, 1369, 1227 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C21H19N2: 299.1548; found: 299.1551.

5-Cyano-1-(2-aminophenyl)-1H-indole (9i): Yellow solid, mp 126-128 °C; Rf 0.45 (30% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 3.50 (bs, 2H), 6.77 (d, J=4, 0.8 Hz, 1H), 6.86-6.93 (m, 2H), 7.15-7.21 (m, 2H), 7.28-7.33 (m, 1H), 7.35 (d, J=3.2 Hz, 1H), 7.40 (dd, J=8.4, 0.8 Hz, 1H), 8.03 (d, J=0.8 Hz, 1H);
$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 103.5, 104.2, 111.8, 116.9, 119.2, 120.7, 123.9, 125.3, 126.7, 128.4, 128.5, 130.1, 131.1, 138.2, 142.7; FTIR (KBr) 3464, 3368, 3105, 3060, 2221, 1619, 1507, 1469, 1330 cm$^{-1}$.

**General Procedure for the preparation of compounds 1a-i**[2]

To a solution of compound 9 (3.5 mmol) in 3 mL pyridine maintained at 0°C was added $p$-toluenesulfonyl chloride (4.6 mmol) and was stirred at room temperature for 4-5 h. Then the reaction mixture was washed with 10% HCl solution (2×15 mL) and extracted with ethyl acetate. Then the organic layer was washed with water (1×10 mL). Combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to afford pure compound 1.

**General Procedure for the preparation of compound 1j**[3]

To a solution of compound 9a (3.5 mmol) in 3 mL pyridine maintained at 0°C was added $p$-bromobenzenesulfonyl chloride (4.6 mmol) and was stirred at room temperature for 4-5 h. Then the reaction mixture is washed with 10% HCl solution (2×15 mL) and extracted with ethyl acetate. Then the organic layer was washed with water (1×10 mL). Combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to afford pure compound 1j.

**Spectral data for nitro compounds 1a-j**

$N$-(2-(1H-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (1a): Pale brown solid, mp 112-114 °C; R$_f$ 0.46 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.39 (s, 3H), 6.31 (s, 1H), 6.62-6.68 (m, 3H), 7.09 (dt, $J$=7.2, 1.2 Hz, 1H), 7.12 (m, 5H), 7.12-7.22 (m, 3H), 7.88 (dd, $J$=8, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 27.1, 104.7, 109.9, 121.0, 121.4, 121.9, 123.1, 125.6, 127.3, 128.0, 128.7, 128.9, 129.6, 129.8, 129.8, 134.0, 135.8, 136.9, 144.3; FTIR (KBr) 3352, 2923, 2856, 1595, 1505, 1458, 1340, 1162, 747 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{21}$H$_{19}$N$_2$O$_2$S: 363.1167; found: 363.1154.
**N-(2-(5-methoxy-1H-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (1b):**
Light brown solid, mp 128-130 °C; $R_f$ 0.48 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.39 (s, 3H), 3.88 (s, 3H), 6.34 (s, 1H), 6.52 (d, $J$=8.8 Hz), 6.57 (dd, $J$=3.2, 0.8 Hz, 1H), 6.63 (d, $J$=3.2 Hz, 1H), 6.73 (dd, $J$=12, 2.4 Hz, 1H), 6.81 (d, $J$=3 Hz, 1H), 6.93 (dd, $J$=9.2, 8.8 Hz, 1H), 6.96-6.98 (m, 3H), 7.07-7.12 (m, 1H), 7.13-7.23 (m, 3H), 7.38-7.45 (m, 3H), 7.61 (td, $J$=7.6, 0.4 Hz, 1H), 7.87 (dd, $J$=8, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 21.7, 56.0, 102.9, 104.4, 110.7, 113.3, 121.7, 125.5, 127.3, 128.6, 128.8, 129.2, 129.5, 129.8, 129.9, 132.1, 133.9, 135.7, 144.3 155.1; FTIR (KBr) 3331, 2929, 2836, 1595, 1503, 1160 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{22}$H$_{21}$N$_2$O$_3$: 393.1273; found: 393.1273.

**N-(2-(5-methyl-1H-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (1c):**
Pale brown gum, $R_f$ 0.55 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.39 (s, 3H), 2.47 (s, 3H), 6.35 (s, 1H), 6.54-6.60 (m, 3H), 6.93 (dd, $J$=8.4, 1.6 Hz, 1H), 7.12-7.17 (m, 3H), 7.20 (dt, $J$=7.2, 1.6 Hz, 1H), 7.39-7.47 (m, 4H), 7.85 (dd, $J$=8, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 21.5, 21.7, 104.2, 109.6, 121.1, 121.9, 124.7, 125.6, 127.3, 128.1, 128.8, 129.0, 129.4, 129.7, 130.0, 130.3, 133.9, 135.3, 135.8, 144.2; FTIR (KBr) 3333, 3026, 2921, 2861, 1595, 1505, 121.1, 121.9, 124.7, 125.6, 127.3, 128.1, 128.8, 129.0, 129.4, 129.7, 130.0, 130.3, 133.9, 135.3, 135.8, 144.2; FTIR (KBr) 3333, 3026, 2921, 2861, 1595, 1505, 1467, 1370 cm$^{-1}$.

**N-(2-(5-fluoro-1H-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (1d):**
White solid, mp 126-128 °C; $R_f$ 0.48 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.39 (s, 3H), 6.27 (s, 1H), 6.53 (dd, $J$=9.2, 8.8 Hz, 1H), 6.61 (d, $J$=3 Hz, 1H), 6.71 (d, $J$=3.2 Hz, 1H), 6.81 (d, $J$=8, 2.4 Hz, 1H), 7.12-7.18 (m, 3H), 7.22 (dt, $J$=7.4, 1.2 Hz, 1H), 7.31 (dd, $J$=9.2, 2.4 Hz, 1H), 7.42 (d, $J$=8.4 Hz, 2H), 7.44-7.48 (m, 1H), 7.81 (dd, $J$=8.4, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 21.7, 104.6, 104.7, 106.1, 106.4, 110.7, 110.8, 111.3, 111.6, 122.0, 125.6, 127.3, 128.9, 129.6, 129.8, 130.0, 130.0, 133.9, 135.3, 135.8, 144.2; $^{19}$F NMR (C$_6$F$_6$, 500 MHz) δ -126.71; FTIR (KBr) 3337, 3066, 2924, 2859, 1593, 1503, 1468, 1357 cm$^{-1}$.

**4-Methyl-N-(2-(3-methyl-1H-indol-1-yl)phenyl)benzenesulfonamide (1e):**
White solid, mp 136-138 °C; $R_f$ 0.42 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.32 (d, $J$=1.2 Hz, 1H), 2.41 (s, 3H), 6.31 (d, $J$=1.2 Hz, 1H), 6.35 (s, 1H), 7.07-7.12 (m, 1H), 7.13-7.23 (m, 5H), 7.38-7.45 (m, 3H), 7.61 (td, $J$=7.6, 0.4 Hz, 1H), 7.87 (dd, $J$=8, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 9.7, 21.7, 109.7, 113.9, 119.5, 120.3, 122.2, 123.0, 125.6, 127.3, 128.8, 129.2, 129.3, 129.7, 130.1, 133.9, 135.9, 137.2, 144.2; FTIR (KBr) 3328, 3049, 2922, 2867, 1596, 1503, 1455, 1341, 1164, 745 cm$^{-1}$. 
N-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)-4-methylbenzenesulfonamide (1f):
Pale brown solid, mp 80-82 °C; Rf 0.48 (30% ethyl acetate in hexanes); 'H NMR (CDCl₃, 500 MHz) δ 2.23 (s, 3H), 6.39 (s, 1H), 6.62 (s, 1H), 6.81 (d, J=6.5 Hz, 2H), 6.90 (d, J=7 Hz, 2H), 7.05 (d, J=6.5 Hz, 1H), 7.14 (s, 1H), 7.25 (s, 1H), 7.35 (s, 1H), 7.69 (d, J=6.5 Hz, 1H), 7.93 (d, J=6 Hz, 1H), 8.31 (s, 1H), 9.20 (s, 1H); 'C NMR (CDCl₃, 125 MHz) δ 21.5, 102.9, 117.0, 121.9, 126.2, 127.9, 128.4, 129.2, 129.3, 130.1, 130.6, 131.6, 134.0, 137.0, 142.9, 143.3, 146.6; FTIR (KBr) 3058, 2924, 2863, 1592, 1510, 1423, 1333, 1270 cm⁻¹; HRMS (m/z): [M+H]^+ calcd. for C₂₀H₁₈N₃O₂S: 364.1120; found: 364.1106.

4-Methyl-N-(2-(5-phenyl-1H-indol-1-yl)phenyl)benzenesulfonamide (1g):
Pale brown solid, mp 150-152 °C; Rf 0.55 (20% ethyl acetate in hexanes); 'H NMR (CDCl₃, 400 MHz) δ 2.29 (s, 3H), 6.27 (s, 1H), 6.57-6.62 (m, 2H), 6.65 (d, J=8.4 Hz, 1H), 7.06 (d, J=8 Hz, 2H), 7.09-7.18 (m, 2H), 7.19-7.29 (m, 2H), 7.32-7.42 (m, 5H), 7.56 (d, J=8 Hz, 2H), 7.77-7.84 (m, 2H); 'C NMR (CDCl₃, 100 MHz) δ 21.7, 105.1, 110.1, 110.1, 119.1, 122.1, 122.9, 125.6, 126.8, 127.3, 127.5, 128.7, 128.9, 129.3, 129.7, 129.8, 129.8, 133.9, 134.7, 135.8, 136.4, 142.2, 144.3; FTIR (KBr) 3333, 3056, 2923, 2852, 1596, 1504, 1464, 1402, 1337 cm⁻¹; HRMS (m/z): [M+H]^+ calcd. for C₂₇H₂₃N₂O₂S: 439.1480; found: 439.1467.

4-methyl-N-(2-(5-(p-tolyl)-1H-indol-1-yl)phenyl)benzenesulfonamide (1h):
Pale brown solid, mp 194-196 °C; Rf 0.52 (20% ethyl acetate in hexanes); 'H NMR (CDCl₃, 400 MHz) δ 2.39 (s, 3H), 2.42 (s, 3H), 6.39 (s, 1H), 6.66-6.70 (m, 2H), 6.72 (d, J=8.4 Hz, 1H), 7.15 (d, J=8 Hz, 2H), 7.18-7.25 (m, 2H), 7.28 (d, J=7.6 Hz, 2H), 7.32 (dd, J=8.4, 1.2 Hz, 1H), 7.43-7.46 (m, 3H), 7.55 (td, J=8.4, 2 Hz, 2H), 7.86 (dd, J=1.6, 0.4 Hz, 1H), 7.89 (dd, J=8.2, 1.2, 1H); 'C NMR (CDCl₃, 100 MHz) δ 21.2, 21.7, 105.0, 110.1, 119.7, 122.0, 122.8, 125.6, 127.3, 127.4, 128.6, 128.9, 129.2, 129.6, 129.8, 129.8, 133.9, 134.6, 135.8, 136.3, 136.4, 139.3, 144.3; FTIR (KBr) 3361, 2923, 2858, 1598, 1502, 1468, 1335, 1242 cm⁻¹; HRMS (m/z): [M+H]^+ calcd. for C₂₈H₂₅N₂O₂S: 453.1637; found: 453.1628.

N-(2-(5-cyano-1H-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (1i):
White solid, mp 144-146 °C; Rf 0.40 (40% ethyl acetate in hexanes); 'H NMR (CDCl₃, 400 MHz) δ 2.40 (s, 3H), 6.20 (s, 1H), 6.67 (d, J=8.4 Hz, 1H), 6.74 (d, J=3.4 Hz, 1H), 6.84 (d, J=3.2 Hz, 1H), 7.12-7.19 (m, 3H), 7.42 (d, J=8.4 Hz, 2H), 7.49 (dt, J=8.2, 1.6 Hz, 1H), 7.86 (dd, J=8.4, 1.2 Hz, 1H), 8.01 (d, J=0.8 Hz, 1H); 'C NMR (CDCl₃, 100 MHz) δ 21.7, 104.3, 105.3, 111.0, 120.3, 122.6, 125.9, 125.9, 126.9, 127.2, 128.4, 128.8,
N-(2-(1H-indol-1-yl)phenyl)-4-bromobenzenesulfonamide (1j): Pale brown solid, mp 126-128 °C; Rf 0.45 (15% ethyl acetate in hexanes); 1H NMR (CDCl₃, 400 MHz) δ 6.27 (s, 1H), 6.52 (d, J=8.4 Hz, 1H), 6.60 (dd, J=11.2, 3.2 Hz, 2H), 7.04 (t, J=8 Hz, 1H), 7.08-7.15 (m, 2H), 7.16-7.24 (m, 3H), 7.31-7.42 (m, 3H), 7.60 (d, J=8 Hz, 1H), 7.79 (d, J=8 Hz, 1H); 13C NMR (CDCl₃, 100 MHz) δ 105.0, 109.6, 121.1, 121.5, 122.8, 123.4, 126.3, 127.7, 128.5, 128.6, 129.0, 129.7, 130.4, 132.4, 133.3, 136.8, 137.6; FTIR (KBr) 3397, 2925, 2857, 2221, 1597, 1500, 1467, 1357 cm⁻¹; HRMS (m/z): [M+H]⁺ calcd. for C₂₀H₁₆N₂O₂SBr: 427.0116; found: 427.0113 (HRMS data for ⁷⁹Br isotope).

General procedure for iodine mediated intramolecular C2 amidative cyclization of compounds 1a-j

1 (0.5 mmol) was taken in a clean, dry reaction tube. To this iodine (0.3 mmol), Cs₂CO₃ (1.0 mmol) and acetonitrile (2 mL) were added. Reaction tube was stoppered and the resulting reaction mixture was stirred at 60 °C. After 4 h the second portion of iodine (0.3 mmol) was added and reaction was allowed to stir at 60 °C. Upon completion of reaction was monitored by TLC, then the solvent was removed under vacuum in rotary evaporator and DCM was added. The crude reaction mixture was washed with Na₂S₂O₃ solution (2 × 10 mL) and extracted with DCM. The organic layer was washed water (1 × 10 mL). Combined organic layers were concentrated using rotary evaporator and residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent to afford pure product 2.

Spectral data of compounds 2a-j

10-Tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2a): White solid, mp 148-150 °C; Rf 0.50 (15% ethyl acetate in hexanes); 1H NMR (CDCl₃, 400 MHz) δ 2.28 (s, 3H), 6.57 (d, J=0.4 Hz, 1H), 7.22 (m, 3H), 7.33 (dt, J=8, 1.2 Hz, 1H), 7.59 (dd, J=1.0, 0.4 Hz, 1H), 7.68-7.72 (m, 2H), 7.79 (d, J=8.4 Hz, 2H), 8.04 (dd, J=8, 0.4 Hz, 1H); 13C NMR (CDCl₃, 100 MHz) δ 21.7, 82.1, 110.5, 110.7, 115.1, 120.7, 121.2, 121.7, 123.1, 125.1, 127.0, 127.1,
129.8, 130.0, 132.5, 133.6, 138.9, 145.7; FTIR (KBr) 2922, 2856, 1578, 1492, 1377, 1177, 1019 cm⁻¹; HRMS (m/z): [M+H]^+ calcd. for C_{21}H_{17}N_{2}O_{2}S: 361.1011; found: 361.0999.

2-Methoxy-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2b): Pale brown solid, mp 142-144 °C; R_f 0.51 (20% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.28 (s, 3H), 3.89 (s, 3H), 6.49 (s, 1H), 6.87 (dd, \(J=8.8\) Hz, 1H), 7.13 (d, \(J=8\) Hz, 2H), 7.17 (d, \(J=2.4\) Hz, 1H), 7.22 (dt, \(J=8, 1.2\) Hz, 1H), 7.31 (dt, \(J=7.6, 1.2\) Hz, 1H), 7.52 (d, \(J=8\) Hz, 1H), 7.56 (d, \(J=8.8\) Hz, 1H), 7.79 (d, \(J=8.4\) Hz, 2H), 8.02 (dd, \(J=8, 0.8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.7, 56.0, 103.7, 110.0, 110.1, 111.3, 115.0, 122.1, 122.7, 125.1, 127.1, 128.3, 130.0, 133.3, 133.4, 133.7, 139.4, 145.7, 155.5; FTIR (KBr) 3065, 2924, 2854, 1598, 1577, 1490 cm⁻¹; HRMS (m/z): [M+H]^+ calcd. for C_{22}H_{19}N_{2}O_{3}S: 391.1116; found: 391.1102.

2-Methyl-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2c): White solid, mp 155-158 °C; R_f 0.52 (15% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.27 (s, 3H), 2.49 (s, 3H), 6.48 (s, 1H), 7.06 (dd, \(J=8.4\), 1.2 Hz, 1H), 7.12 (d, \(J=8\) Hz, 2H), 7.22 (dt, \(J=8, 1.2\) Hz, 1H), 7.31 (dt, \(J=7.8, 1.2\) Hz, 1H), 7.49 (s, 1H), 7.53-7.58 (m, 2H), 7.78 (d, \(J=8.4\) Hz, 2H), 8.02 (d, \(J=8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.7, 21.8, 81.7, 110.3, 115.1, 121.0, 122.1, 122.8, 125.1, 125.3, 127.1, 128.3, 129.9, 129.9, 131.2, 132.8, 133.5, 133.6, 139.0, 145.6; FTIR (KBr) 3061, 2923, 2858, 1600, 1575, 1495, 1457, 1377 cm⁻¹.

2-Fluoro-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2d): Pale yellow solid, mp 162-165 °C; R_f 0.50 (15% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.29 (s, 3H), 6.53 (s, 1H), 6.97 (dt, \(J=9.2, 2.4\) Hz, 1H), 7.15 (q, \(J=8.8\) Hz, 3H), 7.31-7.37 (m, 2H), 7.56 (d, \(J=7.8\) Hz, 1H), 7.59 (dd, \(J=8.8, 8.4\) Hz, 1H), 7.80 (d, \(J=8\) Hz, 1H), 7.82 (d, \(J=8\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.7, 82.1, 106.4, 106.6, 108.5, 108.8, 110.2, 111.2, 111.3, 115.1, 123.2, 125.1, 125.8, 127.8, 128.3, 129.5, 130.0, 133.3, 145.9; \(^{19}\)F NMR (C\(_6\)F\(_6\), 500 MHz) \(\delta\) -124.47; FTIR (KBr) 2923, 2855, 1568, 1489, 1466, 1458 cm⁻¹.

11-Methyl-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2e): White solid, mp 158-160 °C; R_f 0.45 (10% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.14 (s, 3H), 2.60 (s, 3H), 6.93 (d, \(J=8\) Hz, 2H), 7.10 (dt, \(J=8, 1.2\) Hz, 1H), 7.16-7.24 (m, 3H), 7.35-7.42 (m, 3H), 7.49-7.55 (m, 1H), 7.57-7.62 (m, 1H), 8.01 (dd, \(J=8, 0.4\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 9.3, 21.6, 94.8, 109.8, 110.4, 117.6, 119.6, 121.1, 121.4, 122.5, 125.9, 126.8, 127.3, 129.7, 130.6, 133.6, 135.0, 145.1; FTIR (KBr) 3057, 2923, 2859, 1603, 1499, 1365, 1242, 1176 cm⁻¹; HRMS (m/z): [M+H]^+ calcd. for C_{22}H_{19}N_{2}O_{3}S: 375.1167; found: 375.1176.
**6-Tosyl-6H-benzo[4',5']imidazo[1',2':1,5]pyrrolo[2,3-b]pyridine (2f):** White solid, mp 140-142 °C; Rf 0.48 (20% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 2.29 (s, 3H), 6.51 (s, 1H), 7.15 (d, \(J=8\) Hz, 2H), 7.21 (dd, \(J=8\) Hz, 1H), 7.29 (dt, \(J=8\), 1.5 Hz, 1H), 7.36 (dt, \(J=5\), 1 Hz, 1H), 7.79 (d, \(J=8.5\) Hz, 2H), 7.98 (dd, \(J=8\), 1.5 Hz, 1H), 8.02 (d, \(J=7.5\) Hz, 1H), 8.12 (d, \(J=8\) Hz, 1H), 8.32 (dd, \(J=4.5\), 1.5 Hz, 1H); \(^1\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 21.7, 112.8, 114.8, 117.7, 124.0, 125.5, 127.1, 128.6, 128.8, 130.0, 133.4, 133.5, 139.0, 140.9, 146.0; FTIR (KBr) 3060, 2923, 2851, 1599, 1553, 1496, 1428 cm\(^{-1}\); HRMS (m/z): [M+H]\(^+\) calcd. for C\(_{20}\)H\(_{16}\)N\(_3\)O\(_2\)S: 362.0963; found: 362.0975.

**2-Phenyl-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2g):** White solid, mp 173-175 °C; Rf 0.41 (15% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.19, (s, 3H), 6.52 (s, 1H), 7.05 (d, \(J=8\) Hz, 2H), 7.14-7.19 (m, 1H), 7.22-7.28 (m, 2H), 7.35-7.41 (m, 3H), 7.51 (d, \(J=8\) Hz, 1H), 7.56-7.60 (m, 2H), 7.64 (d, \(J=8.4\) Hz, 1H), 7.72 (d, \(J=8.4\) Hz, 2H), 7.81 (d, \(J=1.2\) Hz, 1H), 7.96 (d, \(J=8\) Hz, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.7, 110.5, 110.9, 115.1, 119.7, 120.4, 123.1, 125.2, 126.4, 126.8, 127.1, 127.6, 128.9, 129.7, 130.0, 133.1, 133.6, 135.3, 139.4, 142.3; FTIR (KBr) 3059, 2923, 2856, 1602, 1574, 1489, 1468 cm\(^{-1}\); HRMS (m/z): [M+H]\(^+\) calcd. for C\(_{27}\)H\(_{21}\)N\(_2\)O\(_2\)S: 437.1324; found: 437.1340.

**2-((p-Tolyl)-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (2h):** Light brown solid, mp 165-167 °C; Rf 0.43 (15% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.19 (s, 3H), 2.33 (s, 3H), 6.51 (s, 1H), 7.05 (d, \(J=8.4\) Hz, 2H), 7.15-7.21 (m, 3H), 7.24 (dt, \(J=7.6\), 1.2 Hz, 1H), 7.37 (dd, \(J=8.4\), 2.0 Hz, 1H), 7.45-7.55 (m, 3H), 7.63 (d, \(J=8.4\) Hz, 1H), 7.71 (d, \(J=8.4\) Hz, 2H), 7.79 (d, \(J=1.2\) Hz, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.2, 21.7, 82.3, 110.5, 110.8, 115.1, 119.7, 120.3, 123.1, 125.2, 126.3, 127.1, 127.4, 129.6, 129.7, 130.0, 133.0, 133.5, 133.5, 135.2, 136.5, 139.3, 145.7; FTIR (KBr) 3029, 2921, 2856, 1602, 1575, 1490, 1458, 1375, 1317 cm\(^{-1}\); HRMS (m/z): [M+H]\(^+\) calcd. for C\(_{28}\)H\(_{23}\)N\(_2\)O\(_2\)S: 451.1480; found: 451.1461.

**10-Tosyl-10H-benzo[4,5]imidazo[1,2-a]indole-2-carbonitrile (2i):** Pale brown solid, mp 220-222 °C; Rf 0.50 (50% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.30 (s, 3H), 6.61 (s, 1H), 7.17 (d, \(J=8.4\) Hz, 2H), 7.31-7.40 (m, 2H), 7.47 (dd, \(J=8.2\), 1.2 Hz, 1H), 7.61-7.65 (m, 1H), 7.74 (d, \(J=8.4\) Hz, 1H), 7.80 (d, \(J=8.4\) Hz, 2H), 8.01 (d, \(J=1.2\) Hz, 1H), 8.04-8.09 (m, 1H); \(^1\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 21.7, 82.1, 104.9, 111.1, 111.4, 115.2, 120.4, 123.6, 124.4, 125.3, 126.0, 127.1, 128.2, 128.7, 130.1, 132.2, 133.4, 133.6, 140.4, 146.2; FTIR (KBr) 2922, 2854, 2221, 1603, 1566, 1490, 1375 cm\(^{-1}\).
**10-((4-Bromophenyl)sulfonyl)-10H-benzo[4,5]imidazo[1,2-a]indole (2j):** Pale green solid, mp 148-150 °C; Rf 0.46 (10% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 6.48 (s, 1H), 7.15-7.21 (m, 3H), 7.26 (dt, J=8, 0.8 Hz, 1H), 7.39 (d, J=8.8 Hz, 2H), 7.52 (d, J=8 Hz), 7.60-7.64 (m, 2H), 7.66 (d, J=8.8 Hz, 2H), 7.93 (d, J=8 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.7, 82.1, 110.5, 110.7, 115.1, 120.7, 121.2, 121.7, 123.1, 125.1, 127.0, 127.1, 129.8, 130.0, 132.5, 133.6, 138.9, 145.7; FTIR (KBr) 3062, 1605, 1572, 1494, 1457, 1385 cm⁻¹; HRMS (m/z): [M+H]⁺ calcd. for C20H14N2O2SBr: 424.9959; found:424.9980 (HRMS data for 79Br isotope).

3. General procedure for the preparation of compounds 3a-h

**General procedure for the preparation of compounds 10a-h**

\[ \text{N-alkylated indole (4 mmol), Pd(OAc)}_2 (0.4 \text{ mmol), PPh}_3 (0.3 \text{mmol), K}_2 \text{CO}_3 (12 \text{ mmol) and TBAB (0.8 mmol) were taken into an oven dried 50 mL round bottom flask.} \]

The flask was closed with septum, evacuated and back filled with N₂. To this dry DMF, 2-bromo-1-nitrobenzene was added under inert atmosphere at room temperature. The resulting reaction mixture was heated at 115 °C under N₂ atmosphere. After the completion of reaction, the reaction mixture was washed with water (2×15 mL) and extracted with ethyl acetate. Combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to afford pure compound 10a-h.

**Spectral data for 3-aryl nitro compounds 10a-h**

**1-Methyl-3-(2-nitrophenyl)-1H-indole (10a):** Yellow solid, mp 106-108 °C; Rf 0.43 (15% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 3.43 (s, 3H), 6.39 (s, 1H), 7.04 (dt, J=7.6, 0.8 Hz, 1H), 7.16 (t, J=7.2 Hz, 1H), 7.24 (d, J=8 Hz, 1H), 7.39 (d, J=7.6 Hz, 1H), 7.45 (dt, J=7.4, 1.2 Hz, 1H), 7.52 (d, J=8 Hz, 2H), 7.90 (d, J=8Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 30.7, 102.5, 109.6, 119.0, 120.5, 120.9, 122.3, 124.3, 126.9, 129.7, 132.7, 133.6, 135.8, 137.9, 149.8; FTIR (KBr) 3057, 2926, 2856, 1611, 1527, 1466, 1435, 1348 cm⁻¹.
**1-Ethyl-3-(2-nitrophenyl)-1H-indole (10b):** Yellow solid, $R_f$ 0.46 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.43 (t, $J$=7.2 Hz, 3H), 4.13 (q, $J$=7.2 Hz, 2H), 7.03-7.10 (m, 1H), 7.16-7.22 (m, 2H), 7.29-7.34 (m, 2H), 7.44 (d, $J$=8 Hz, 1H), 7.51 (dt, $J$=7.6, 1.2 Hz, 1H), 7.58 (dd, $J$=7.8, 1.2 Hz, 1H), 7.72 (dd, $J$=8, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 15.5, 41.3, 109.9, 111.0, 119.2, 120.0, 122.4, 124.1, 126.5, 126.9, 129.4, 129.7, 131.9, 132.6, 136.1; FTIR (KBr) 3057, 2928, 2878, 1609, 1525, 1464, 1352 cm$^{-1}$.

**1-Isopropyl-3-(2-nitrophenyl)-1H-indole (10c):** Yellow semi solid; $R_f$ 0.43 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.58 (d, $J$=6.8 Hz, 6H), 4.72 (septet, $J$=6.8 Hz, 1H), 7.15 (dt, $J$=7.8, 1.2 Hz, 1H), 7.27 (dt, $J$=7.4, 1.2 Hz, 1H), 7.39 (s, 1H), 7.40-7.46 (m, 2H), 7.53 (td, $J$=7.6, 1.2 Hz, 1H), 7.60 (dt, $J$=7.6, 1.2 Hz, 1H), 7.67 (dd, $J$=7.6, 1.2 Hz, 1H), 7.81 (dd, $J$=12.2, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 22.9, 47.5, 110.1, 111.0, 119.2, 120.4, 122.2, 123.3, 124.2, 126.8, 126.9, 129.6, 132.0, 132.6, 135.9, 149.8; FTIR (KBr) 3050, 2973, 2927, 1608, 1523, 1461, 1403, 1361 cm$^{-1}$.

**3-(2-nitrophenyl)-1-propyl-1H-indole (10d):** Orange semi solid; $R_f$ 0.45 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.88 (t, $J$=7.2 Hz, 3H), 1.83 (sextet, $J$=7.2 Hz, 2H), 4.05 (t, $J$=7.2 Hz, 2H), 7.07 (dt, $J$=7.4, 1.2 Hz, 1H), 7.16-7.21 (m, 2H), 7.29-7.35 (m, 2H), 7.45 (s, $J$=8.0 Hz, 1H), 7.52 (s, $J$=8.0, 1.2 Hz, 1H), 7.59 (dd, $J$=7.8, 1.2 Hz, 1H), 7.73 (dd, $J$=8.4, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 11.6, 23.5, 48.4, 110.1, 110.7, 119.2, 120.3, 122.3, 124.1, 126.9, 127.3, 129.3, 131.9, 132.5, 133.6, 136.3, 149.9; FTIR (KBr) 3058, 2965, 2931, 2877, 1608, 1527, 1465, 1436 cm$^{-1}$.

**1-butyl-3-(2-nitrophenyl)-1H-indole (10e):** Orange semi solid, $R_f$ 0.46 (15% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.96 (t, $J$=7.6 Hz, 3H), 1.38 (sextet, $J$=7.2 Hz, 2H), 4.16 (t, $J$=7.6 Hz, 2H), 7.15 (t, $J$=8.0 Hz, 1H), 7.24-7.29 (m, 2H), 7.38-7.43 (m, 2H), 7.53 (d, $J$=8.0 Hz, 1H), 7.60 (dt, $J$=7.6, 1.2 Hz, 1H), 7.67 (dd, $J$=7.8, 1.2 Hz, 1H), 7.81 (dd, $J$=8.0, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 13.8, 20.3, 32.3, 46.5, 110.1, 110.7, 119.2, 120.4, 122.3, 124.1, 126.9, 127.3, 128.0, 129.3, 132.0, 132.5, 136.3, 149.9; FTIR (KBr) 3058, 2958, 2869, 1609, 1527, 1465, 1357 cm$^{-1}$. 

1Et NO$_2$

1iPr NO$_2$

1nPr NO$_2$

1nBu NO$_2$
5-Methoxy-1-methyl-3-(2-nitrophenyl)-1H-indole (10f): Yellow solid, R<sub>f</sub> 0.43 (20% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 3.69 (s, 3H), 3.71 (s, 3H), 6.81-6.86 (m, 2H), 7.07 (s, 1H), 7.15 (d, J=9.6 Hz, 1H), 7.30 (dt, J=7.2, 1.6 Hz, 1H), 7.43-7.53 (m, 2H), 7.71 (dd, J=8, 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 33.2, 55.1, 100.8, 110.7, 112.9, 124.1, 124.9, 126.8, 128.5, 129.2, 131.0, 132.0, 132.4, 133.5, 149.8, 155.0; FTIR (KBr) 3067, 2928, 2857, 1612, 1572, 1525, 1489, 1457, 1428, 1350, 1261 cm<sup>-1</sup>.

1-Methyl-3-(2-nitrophenyl)-1H-pyrrolo[2,3-b]pyridine (10g): Yellow solid, R<sub>f</sub> 0.43 (30% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 4.02 (s, 3H), 7.15 (dd, J=8.0, 7.6 Hz, 1H), 7.38 (s, 1H), 7.47-7.50 (m, 1H), 7.55-7.59 (m, 1H), 7.61-7.64 (m, 1H), 7.83-7.89 (m, 2H), 8.40 (dd, J=4.8, 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 32.0, 110.1, 116.5, 119.8, 124.4, 125.8, 127.7, 127.8, 128.2, 128.4, 132.3, 132.5, 143.0, 149.8; FTIR (KBr) 3061, 2924, 2857, 1607, 1525, 1453, 1407, 1351 cm<sup>-1</sup>.

1-Methyl-3-(2-nitrophenyl)-1H-indole-5-carbonitrile (10h): Yellow solid, mp 144-146 °C; R<sub>f</sub> 0.45 (30% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 3.88 (s, 3H), 7.31 (s, 1H), 7.42 (d, J=8.8 Hz, 1H), 7.48-7.52 (m, 2H), 7.57 (dd, J=7.8, 1.6 Hz, 1H), 7.65 (dd, J=7.4, 1.6 Hz, 1H), 7.84 (d, J=1.4 Hz, 1H), 7.86 (dd, J=8, 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 33.4, 103.7, 110.8, 112.1, 120.5, 124.3, 124.9, 125.4, 126.9, 128.1, 130.2, 130.6, 132.4, 132.6, 133.6, 138.4; FTIR (KBr) 2925, 2859, 2220, 1613, 1526, 1484, 1351 cm<sup>-1</sup>.

**General procedure for the preparation of compounds 11a-h**

To a solution of compound 10 (3 mmol) in ethanol (6 mL), was added Pd/C (0.3 mmol). The resulting suspension was stirred under hydrogen pressure using hydrogen balloon until the completion of reaction. The reaction mixture was filtered over celite and rinsed with DCM. The solvent was removed under vacuum and crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to obtain pure product 11.
Spectral data for 3-aryl amino compounds 11a-h

2-(1-Methyl-1H-indol-3-yl)aniline (11a): Brown solid, mp 138-140 °C; R$_f$ 0.46 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 3.91 (s, 3H), 3.71 (bs, 2H), 6.87-7.32 (m, 3H), 7.34-7.44 (m, 2H), 7.48 (d, J=8 Hz, 1H), 7.74 (td, J=8, 0.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 32.9, 109.5, 113.3, 115.4, 118.4, 119.6, 120.5, 120.7, 122.1, 127.0, 127.7, 127.8, 131.3, 137.1, 144.7; FTIR (KBr) 3458, 3370, 3048, 2931, 2821, 1612, 1547, 1482, 1375, 746 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{15}$H$_{15}$N$_2$: 223.1235; found: 223.1240.

2-(1-Ethyl-1H-indol-3-yl)aniline (11b): Brown sticky solid, R$_f$ 0.50 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.44 (t, J=7.2 Hz, 3H), 3.08(bs, 2H), 4.15 (q, J=7.2 Hz, 2H), 6.76 (t, J=7.6 Hz, 2H), 7.07 (q, J=8 Hz, 2H), 7.18 (s, 2H), 7.23 (d, J=7.6 Hz, 1H), 7.33 (d, J=8.4 Hz, 1H), 7.55 (d, J=8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 15.6, 41.2, 109.6, 113.4, 115.7, 118.7, 119.7, 120.7, 121.1, 122.0, 126.0, 127.2, 127.9, 131.4, 136.3, 144.4; FTIR (KBr) 3459, 3371, 3050, 2975, 2931, 2880, 1612, 1546, 1458, 1365 cm$^{-1}$.

2-(1-Isopropyl-1H-indol-3-yl)aniline (11c): Colourless semi solid; R$_f$ 0.45 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.58 (d, J=6.8 Hz, 6H), 4.75 (septet, J=6.8 Hz, 1H), 6.82-6.87 (m, 2H), 7.16 (dq, J=7.6, 1.2 Hz, 2H), 7.27 (dt, J=7.8, 1.2 Hz, 1H), 7.31-7.34 (m, 1H), 7.45 (d, J=8.4 Hz, 1H), 7.64 (d, J=8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 23.0, 47.3, 109.8, 113.5, 115.4, 118.5, 119.6, 120.6, 121.0, 121.8, 122.7, 127.0, 127.8, 131.3, 136.0, 144.7; FTIR (KBr) 3463, 3370, 3050, 2973, 2927, 1612, 1546, 1461, 1365, 1249 cm$^{-1}$.

2-(1-Propyl-1H-indol-3-yl)aniline (11d): Pale Brown semi solid; R$_f$ 0.46 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 0.89 (t, J=7.2 Hz, 3H), 1.84 (sextet, J=7.2 Hz, 2H), 3.69-3.92 (bs, 2H), 4.05 (t, J=7.2 Hz, 2H), 6.71-6.79 (m, 2H), 7.07 (dq, J=8.0, 1.2 Hz, 2H), 7.15-7.21 (m, 2H), 7.23 (dd, J=7.6, 1.6 Hz, 1H), 7.32 (d, J=8 Hz, 1H), 7.55 (d, J=8.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 11.8, 23.7, 48.2, 109.8, 113.1, 115.5, 118.4, 119.6, 120.6, 120.8, 121.9, 126.9, 127.0, 127.8, 131.3, 136.4, 144.7; FTIR (KBr) 3459, 3370, 3050, 2962, 2873, 1612, 1546, 1461 cm$^{-1}$.
2-(1-butyl-1H-indol-3-yl)aniline (11e): Pale Brown semi solid; R<sub>r</sub> 0.44 (20% ethyl acetate in hexanes)<sup>a</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.88 (t, <i>J</i>=7.6 Hz, 3H), 1.31 (sextet, <i>J</i>=7.6 Hz, 2H), 1.73-1.84 (m, 2H), 3.77 (bs, 2H), 4.09 (t, <i>J</i>=7.2 Hz, 2H), 6.76 (dt, <i>J</i>=8.0, 1.2 Hz, 2H), 7.04-7.11 (m, 2H), 7.15-7.21 (m, 2H), 7.23 (dd, <i>J</i>=7.4, 1.2 Hz, 1H), 7.33 (d, <i>J</i>=8.0 Hz, 1H), 7.55 (d, <i>J</i>=8.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 13.9, 20.4, 32.4, 46.3, 109.8, 113.1, 115.5, 118.4, 119.5, 120.6, 121.9, 126.8, 127.0, 127.8, 131.3, 136.4, 144.7; FTIR (KBr) 3459, 3370, 3050, 2954, 2869, 1612, 1546, 1461 cm<sup>-1</sup>.

2-(5-Methoxy-1-methyl-1H-indol-3-yl)aniline (11f): Brown solid, mp 118-120 °C; R<sub>r</sub> 0.50 (25% ethyl acetate in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 3.93 (s, 6H), 3.37 (bs, 2H), 6.96 (t, <i>J</i>=8 Hz, 2H), 7.06 (dd, <i>J</i>=7, 2 Hz, 1H), 7.17 (d, <i>J</i>=2.5 Hz, 1H), 7.23-7.33 (m, 2H), 7.36-7.43 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 33.1, 56.1, 101.9, 110.4, 112.6, 112.8, 115.5, 118.5, 120.9, 127.8, 128.3, 128.9, 131.2, 132.5, 144.7, 154.4; FTIR (KBr) 3456, 3370, 3053, 2926, 2836, 1613, 1488, 1452, 1368, 753 cm<sup>-1</sup>.

2-(1-Methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)aniline (11g): Pale brown solid, mp 136-138 °C; R<sub>r</sub> 0.45 (40% ethyl acetate in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 3.49 (bs, 2H), 3.97 (s, 3H), 6.81-6.87 (m, 2H), 7.10 (dd, <i>J</i>=7, 2 Hz, 1H), 7.17 (d, <i>J</i>=2.5 Hz, 1H), 7.26 (dd, <i>J</i>=7.6, 1.6 Hz, 1 H), 7.33 (s, H), 7.97 (d, <i>J</i>=8 Hz, 1H), 8.38 (dd, <i>J</i>=4.6, 1.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 31.5, 112.0, 115.6, 115.8, 118.6, 119.5, 119.9, 127.6, 128.2, 129.0, 131.1, 143.3, 144.7, 147.9; FTIR (KBr) 3419, 3303, 2924, 1622, 1490, 1459, 1345 cm<sup>-1</sup>.

3-(2-Aminophenyl)-1-methyl-1H-indole-5-carbonitrile (11h): Brown solid, mp 166-168 °C; R<sub>r</sub> 0.45 (40% ethyl acetate in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 3.43 (bs, 2H), 3.88 (s, 3H), 6.86 (t, <i>J</i>=8 Hz, 2H), 7.21 (q, <i>J</i>=7.6 Hz, 2H), 7.30 (s, 1H), 7.41 (d, <i>J</i>=8.4 Hz, 1H), 7.49 (d, <i>J</i>=8.8 Hz, 1H), 7.98 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 33.3, 102.9, 110.5, 114.6, 115.9, 118.9, 119.1, 120.8, 125.0, 126.4, 126.9, 128.6, 129.8, 131.3, 138.6; FTIR (KBr) 3421, 3367, 3063, 2923, 2217, 1616, 1487, 1449, 1379 cm<sup>-1</sup>.
General Procedure for the preparation of compounds 3a-h

To a solution of compound 11 (2.5 mmol) in 3 mL pyridine maintained at 0 °C was added p-toluenesulfonyl chloride (3.3 mmol) and was stirred at room temperature for 4-5 h. Then the reaction mixture was washed with 10% HCl solution (2×15 mL) and extracted with ethyl acetate. Then the organic layer was washed with water (1×10 mL). Combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as eluent to afford pure compound 3.

Spectral data for compounds 3a-h

**4-methyl-N-(2-(1-methyl-1H-indol-3-yl)phenyl)benzenesulfonamide (3a):** White solid, mp 148-150 °C; R$_f$ 0.43 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.29 (s, 3H), 3.72 (s, 3H), 6.59 (s, 1H), 6.84 (s, 1H), 6.97-7.07 (m, 5H), 7.14-7.25 (m, 3H), 7.37 (d, $J$=8.4 Hz, 2H), 7.63 (dd, $J$=8.2, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 21.7, 33.1, 109.7, 110.9, 119.4, 120.3, 120.4, 122.7, 124.6, 126.1, 127.0, 127.3, 127.5, 128.2, 129.5, 131.7, 135.3, 136.5, 137.1, 143.7; FTIR (KBr) 3057, 2926, 2856, 1611, 1527, 1466, 1435, 1348 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{22}$H$_{21}$N$_2$O$_2$S: 377.1324; found: 377.1326.

**4-Methyl-N-(2-(1-ethyl-1H-indol-3-yl)phenyl)benzenesulfonamide (3b):** White solid, mp 92-94 °C; R$_f$ 0.43 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.51 (t, $J$=7.2 Hz, 3H), 2.37 (s, 3H), 4.19 (q, $J$=7.2 Hz, 2H), 6.75 (s, 1H), 6.91 (s, 1H), 7.05-7.10 (m, 1H), 7.10-7.16 (m, 4H), 7.22-7.35 (m, 3H), 7.47 (td, $J$=8.4, 2 Hz, 2H), 7.50 (d, $J$=8 Hz, 1H), 7.72 (dd, $J$=8.2, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 15.7, 21.8, 41.3, 109.9, 111.0, 119.6, 120.4, 120.5, 122.7, 124.7, 125.8, 126.3, 127.2, 128.2, 129.7, 131.8, 135.3, 136.3, 136.5, 143.8; FTIR (KBr) 3455, 2926, 2856, 1611, 1527, 1466, 1435, 1348 cm$^{-1}$. 
N-(2-(1-isopropyl-1H-indol-3-yl)phenyl)-4-methylbenzenesulfonamide (3c): White solid, mp 120-122 °C; Rf 0.45 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 1.55 (d, J=6.8 Hz, 6H), 2.38 (s, 3H), 4.71 (septet, J=6.8 Hz, 1H), 6.86 (s, 1H), 6.89 (s, 1H), 7.07 (dt, J=7.2, 0.8 Hz, 1H), 7.11-7.17 (m, 4H), 7.24-7.29 (m, 2H), 7.32 (dt, J=7.6, 1.6 Hz, 1H), 7.43 (d, J=8.4 Hz, 1H), 7.49 (td, J=8.0, 1.6, Hz, 2H), 7.75 (dd, J=8.4, 0.8 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.7, 23.0, 47.4, 110.0, 111.0, 119.5, 120.2, 120.3, 122.4, 122.5, 124.6, 126.3, 127.1, 127.3, 128.1, 129.6, 131.7, 135.2, 135.9, 136.4, 143.8; FTIR (KBr) 3316, 3054, 2977, 2927, 1600, 1546, 1461, 1160 cm⁻¹;

4-methyl-N-(2-(1-propyl-1H-indol-3-yl)phenyl)benzenesulfonamide (3d): Pale brown semi solid; Rf 0.43 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 0.98 (t, J=7.2 Hz, 3H), 1.90 (sextet, J=7.2 Hz, 2H), 2.37 (s, 3H), 4.09 (t, J=7.2 Hz, 2H), 6.72(s, 1H), 6.92 (s, 1H), 7.07 (dt, J=7.4, 1.2 Hz, 1H), 7.11-7.17 (m, 4H), 7.24-7.34 (m, 3H), 7.39 (d, J=8.4 Hz, 1H), 7.47 (d, J=8.4 Hz, 2H), 7.73 (dd, J=8.2, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 11.8, 21.7, 23.6, 48.3, 110.0, 110.7, 119.5, 120.2, 120.3, 122.5, 124.6, 126.1, 126.6, 127.1, 127.3, 128.1, 129.6, 131.7, 135.2, 136.4, 136.4, 143.8; FTIR (KBr) 3320, 3054, 2965, 2877, 1600, 1550, 1465, 1334, 1160 cm⁻¹;

N-(2-(1-butyl-1H-indol-3-yl)phenyl)-4-methylbenzenesulfonamide (3e): colourless semi solid; Rf 0.45 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 0.99 (t, J=7.6 Hz, 3H), 1.39 (sextet, J=7.6 Hz, 2H), 1.85 (quintet, J=7.6 Hz, 2H), 2.37 (s, 3H), 4.12 (t, J=7.2 Hz, 2H), 6.71(s, 1H), 6.92 (s, 1H), 7.07 (dt, J=6.8, 0.8 Hz, 1H), 7.10-7.17 (m, 4H), 7.24-7.31 (m, 3H), 7.39 (d, J=8.4 Hz, 1H), 7.47 (d, J=8.0 Hz, 2H), 7.73 (dd, J=8.2, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 13.9, 20.4, 21.7, 32.3, 46.4, 109.9, 110.7, 119.5, 120.2, 120.3, 122.5, 124.6, 126.1, 126.5, 127.0, 127.3, 128.1, 129.6, 131.7, 135.2, 136.4, 143.8; FTIR (KBr) 3320, 3054, 2958, 2869, 1600, 1550, 1465, 1334, 1160 cm⁻¹;

N-(2-(5-Methoxy-1-methyl-1H-indol-3-yl)phenyl)-4-methylbenzenesulfonamide (3f): Pale brown solid, mp 144-146 °C; Rf 0.55 (30% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.37 (s, 3H), 3.76 (s, 3H), 3.78 (s, 3H), 6.60-6.63 (m, 2H), 6.92-6.97 (m, 2H), 7.10-7.16 (m, 3H), 7.22-7.29 (m, 3H), 7.60 (dd, J=8.4 Hz, 2H), 7.67 (dd, J=8.2, 0.8 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.7, 33.3, 56.1, 100.9, 110.4, 110.7, 113.3, 120.6, 124.8, 126.4, 127.4, 128.0, 128.2, 129.6, 130.1, 131.6, 132.5, 135.3, 136.6, 143.8, 155.0; FTIR (KBr) 3315, 3060, 2926, 2838, 1608, 1548, 1487, 1334 cm⁻¹.
4-Methyl-N-(2-(1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)phenyl)benzenesulfonamide (3g): Pale yellow solid, mp 182-184 °C; Rf 0.50 (50% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.37 (s, 3H), 3.94 (s, 3H), 6.86 (s, 2H), 7.02-7.10 (m, 1H), 7.13 (d, J=8 Hz, 1H), 7.17 (d, J=7.2 Hz, 1H), 7.22 (dd, J=7.6, 1.6 Hz, 1H), 7.33 (t, J=7.6 Hz, 1H), 7.44-7.55 (m, 3H), 7.68 (d, J=8.4 Hz, 1H), 8.39 (d, J=4.8 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.7, 31.9, 116.2, 121.4, 125.0, 125.5, 127.2, 127.3, 128.0, 128.5, 128.6, 131.5, 135.7, 136.6, 143.2, 143.9; FTIR (KBr) 3326, 3060, 2925, 2856, 1599, 1491, 1461, 1342, 1161 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C21H21N3O2S: 378.1276; found: 378.1276.

N-(2-(5-cyano-1-methyl-1H-indol-3-yl)phenyl)-4-methylbenzenesulfonamide (3h): Pale brown solid, mp 186-188 °C; Rf 0.47 (40% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.40 (s, 3H), 3.87 (s, 3H), 6.78 (s, 1H), 6.96 (s, 1H), 7.12-7.18 (m, 4H), 7.24 (d, J=0.8Hz, 1H), 7.33-7.38 (m, 1H), 7.39-7.46 (m, 3H), 7.48 (dd, J=8.4, 1.6 Hz, 1H), 7.74 (d, J=8Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.7, 33.4, 103.4, 110.7, 112.0, 120.4, 120.7, 124.4, 124.9, 125.1, 125.5, 127.2, 127.2, 129.0, 129.7, 130.0, 131.7, 135.3, 136.0, 138.5, 144.4; FTIR (KBr) 3328, 2925, 2219, 1610, 1486, 1395, 1333 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C23H20N3O2S: 402.1276; found: 402.1283.

General Procedure for the preparation of compounds 3i-m[5]

To the solution of N-methyl indole (5 mmol) in DCE was added 2-aminobenzyl alcohol (7.5 mmol) and TFA (1.5 mmol) at room temperature. The resulting reaction mixture was stirred at 50 °C. After the completion of the reaction, the reaction was quenched with the NaHCO3 and extracted with DCM. This was washed with brine solution and organic layers were dried over Na2SO4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as an eluent to afford pure compound 12.
Spectral data for compounds 12i-m

2-((1-Methyl-1H-indol-3-yl)methyl)aniline (12i): Light brown sticky solid, \( R_f \) 0.43 (20% ethyl acetate in hexanes); 
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 3.41 (bs, 2H), 3.55 (s, 3H), 3.89 (s, 3H), 6.54-6.58 (m, 2H), 6.66 (dt, \( J=7.6 \), 1.2 Hz, 1H), 6.96-7.02 (m, 2H), 7.06 (dd, \( J=7.6 \), 1.2 Hz, 1H), 7.12 (dd, \( J=8 \), 1.2 Hz, 1H), 7.16-7.19 (m, 1H), 7.47 (td, \( J=7.6 \), 1.2 Hz, 1H); 
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 28.1, 32.7, 109.3, 112.2, 115.9, 11.8, 119.0, 119., 121.8, 125.6, 127.1, 127.4, 127.9, 130.5, 137.4, 144.8; FTIR (KBr) 3443, 3057, 2962, 1621, 1483, 1370 cm\(^{-1}\).

2-((5-bromo-1-methyl-1H-indol-3-yl)methyl)aniline (12j): white solid, mp 118-120 °C \( R_f \) 0.53 (20% ethyl acetate in hexanes); 
\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm) \( \delta \) 3.57 (s, 3H), 3.90 (s, 2H), 6.59 (s, 1H), 6.74 (q, \( J=8 \) Hz, 2H), 7.00-7.08 (m, 3H), 7.16-7.22 (m, 1H), 7.60 (s, 1H); 
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm) \( \delta \) 27.7, 32.9, 110.8, 111.4, 112.5, 118.4, 121.8, 122.0, 124.6, 127.7, 128.0, 128.7, 129.5, 130.5, 136.0, 140.1; FTIR (KBr) 3441, 3371, 3060, 2920, 2851, 1619, 1585, 1493, 1476, 1456, 1375, 1247 cm\(^{-1}\); HRMS (\( m/z \)): [M+H]\(^+\) calcd. for C\(_{16}\)H\(_{16}\)N\(_2\)Br: 315.0497; found: 315.0523 (HRMS data for \(^{79}\)Br isotope).

2-((5-Methoxy-1-methyl-1H-indol-3-yl)methyl)aniline (12k): brown oil, \( R_f \) 0.43 (25% ethyl acetate in hexanes); 
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 3.66 (s, 3H), 3.82 (s, 3H), 4.01 (s, 2H), 6.66 (s, 1H), 6.81 (q, \( J=8.4 \) Hz, 2H), 6.88 (dd, \( J=8.8 \), 2.4 Hz, 1H), 6.99 (d, \( J=2 \) Hz, 1H), 7.1 (dt, \( J=7.6 \), 1.2 Hz, 1H), 7.15-7.21 (m, 2H); 
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 28.2, 32.9, 56.0, 101.0, 111.3, 112.1, 116.9, 120.0, 126.7, 127.5, 127.9, 128.1, 130.5, 132.8, 143.2, 153.9; FTIR (KBr) 3443, 3365, 3051, 2924, 2832, 1620, 1580, 1491, 1455, 1428, 1262 cm\(^{-1}\).

2-((1-ethyl-1H-indol-3-yl)methyl)aniline (12l): Light brown oil, \( R_f \) 0.52 (20% ethyl acetate in hexanes); 
\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm) \( \delta \) 1.28 (t, \( J=7.2 \) Hz, 3H), 3.63 (bs, 2H), 3.92 (s, 2H), 3.96 (q, \( J=7.2 \) Hz, 2H), 6.60 (d, \( J=8.0 \) Hz, 1H), 6.65 (s, 1H), 6.68 (dt, \( J=7.2 \), 1.2 Hz, 1H), 6.94-7.02 (m, 2H), 7.04-7.14 (m, 2H), 7.21 (d, \( J=8.4 \) Hz, 1H), 7.47 (d, \( J=8.0 \) Hz, 1H); 
\(^{13}\)C NMR (CDCl\(_3\), 100 MHz, ppm) \( \delta \) 15.5, 28.2, 40.8, 109.4, 112.2, 115.9, 118.8, 118.9, 119.3, 121.6, 125.4, 125.6,
127.4, 128.0, 130.5, 136.4, 144.7; FTIR (KBr) 3444, 3366, 3048, 2975, 2930, 2882, 1619, 1583, 1494, 1459, 1334, 1277 cm⁻¹;

**2-((1-isopropyl-1H-indol-3-yl)methyl)aniline (12m):** Light brown semi solid, Rf 0.48 (20% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 1.48 (6H, d, J = 6.83 Hz), 3.42-3.43 (br s, 2H), 4.64 (sep, J = 6.8 Hz, 1H), 6.69 (dd, J = 7.8, 1.2 Hz, 1H), 6.78 (dt, J = 7.8, 1.2 Hz, 1H), 6.90 (s, 1H), 7.07-7.14 (m, 2H), 7.16-7.25 (m, 2H), 7.37 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 22.9, 28.5, 47.1, 109.6, 112.2, 115.9, 118.7, 119.0, 119.4, 121.6, 121.9, 125.6, 127.4, 128.0, 130.6, 136.2, 145.0; FTIR (KBr) 3444, 3367, 3043, 2969, 2923, 1616, 1416, 1357 cm⁻¹.

**General Procedure for the preparation of compounds 3i-m:**

To a solution of compound 12 (2.5 mmol) in 3 mL pyridine maintained at 0 °C was added p-toluenesulfonyl chloride (3.3 mmol) and was stirred at room temperature for 4-5 h. Then the reaction mixture is washed with 10% HCl solution (2×15 mL) and extracted with ethyl acetate. Then the organic layer was washed with water (1×10 mL). Combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using hexanes/ethyl acetate as an eluent to afford pure compound 3i-m.

**Spectral data for compounds 3i-m**

**4-Methyl-N-(2-((1-methyl-1H-indol-3-yl)methyl)phenyl)benzenesulfonamide (3i):** Pale yellow solid, mp 198-200 °C [lit. 203 °C]⁵; Rf 0.50 (25% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 2.40 (s, 3H), 3.67 (s, 2H), 3.72 (s, 3H), 6.58-6.63 (m, 2H), 7.04 (dt, J = 7.4, 1.2 Hz, 1H), 7.11-7.18 (m, 3H), 7.20-7.27 (m, 4H), 7.28-7.32 (m, 1H), 7.43-7.49 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 28.6, 32.9, 109.6, 110.6, 112.2, 119.1, 119.4, 122.3, 124.3, 124.3, 126.1, 127.0, 127.2, 127.4, 127.7, 126.7, 130.7, 133.1, 135.4, 136.9, 137.7 cm⁻¹; FTIR (KBr) 3431, 2923, 1636, 1480, 1378 cm⁻¹; HRMS (m/z): [M+H]⁺ calcd. for C₂₃H₂₃N₂O₂S: 391.1480; found: 391.1480.
N-(2-((5-bromo-1-methyl-1H-indol-3-yl)methyl)phenyl)-4-methylbenzenesulfonamide (3j): white solid, mp 158-160°C [lit. 157°C]; Rf 0.52 (30% ethyl acetate in hexanes); 1H NMR (CDCl₃, 400 MHz, ppm) δ 2.42 (s, 3H), 3.59 (s, 2H), 3.68 (s, 3H), 6.49 (bs, 1H), 6.58 (s, 1H), 7.13-7.18 (m, 3H), 7.20 (d, J=8.0 Hz, 2H), 7.22-7.27 (m, 1H), 7.28-7.32 (m, 2H), 7.47 (d, J=8 Hz, 1H); 13C NMR (CDCl₃, 100 MHz, ppm) δ 21.7, 28.1, 33.0, 111.1, 111.1, 112.7, 121.7, 124.9, 125.1, 126.4, 127.1, 127.9, 128.2, 129.0, 130.6, 132.9, 135.2, 136.2, 136.9, 144.0; FTIR (KBr) 3282, 3064, 2921, 1598, 1491, 1476, 1455, 1377, 1291, 1120 cm⁻¹; HRMS (m/z): [M+H]⁺ calcd. for C₂₃H₂₁N₂O₂NaSBr: 491.0405; found: 491.0427 (HRMS data for 79Br isotope).

N-(2-((5-Methoxy-1-methyl-1H-indol-3-yl)methyl)phenyl)-4-methylbenzenesulfonamide (3k): Pale pink solid, mp 120-122°C [lit. 123°C]; Rf 0.41 (20% ethyl acetate in hexanes); 1H NMR (CDCl₃, 400 MHz) δ 2.28 (s, 3H), 3.56 (s, 5H), 3.64 (s, 3H), 6.48 (s, 1H), 6.57 (d, J=2.4 Hz, 1H), 6.61 (s, 1H), 7.01-7.15 (m, 6H), 7.32-7.37 (m, 3H); 13C NMR (CDCl₃, 100 MHz, ppm) δ 21.6, 28.6, 33.0, 56.0, 101.1, 110.3, 110.5, 112.3, 1240, 125.9, 127.1, 127.6, 127.6, 127.6, 130.0, 130.6, 133.0, 133.0, 133.4, 136.8, 143.7, 154.0; FTIR (KBr) 3285, 3068, 2926, 2836, 1491, 1455, 1375, 1329, 1159 cm⁻¹.

4-methyl-N-(2-((1-ethyl-1H-indol-3-yl)methyl)phenyl)benzenesulfonamide (3l): White solid, mp 192-194°C; Rf 0.46 (15% ethyl acetate in hexanes); 1H NMR (CDCl₃, 400 MHz, ppm) δ 1.42 (t, J=7.2 Hz, 3H), 2.39 (s, 3H), 3.68 (s, 2H), 4.11 (q, J=7.2 Hz, 2H), 6.66 (bs, 1H), 6.71 (s, 1H), 7.02 (t, J= 7.2 Hz, 1H), 7.14 (d, J= 8.8 Hz, 3H), 7.19-7.25 (m, 4H), 7.33 (d, J=8.4 Hz, 1H), 7.41 (d, J=8.4 Hz, 2H), 7.45 (d, J=8.0 Hz, 1H); 13C NMR (CDCl₃, 100 MHz, ppm) δ 15.6, 21.7, 28.8, 41.1, 109.7, 111.4, 119.3, 122.2, 123.9, 125.3, 125.9, 127.1, 127.1, 127.5, 127.7, 129.7, 130.7, 132.7, 135.5, 136.7, 136.8, 143.8; FTIR (KBr) 3266, 2925, 2855, 1597, 1577, 1483, 1459, 1375, 1329, 1159 cm⁻¹;
NMR (CDCl$_3$, 100 MHz) $\delta$ 21.7, 22.9, 29.1, 47.2, 109.9, 111.3, 119.3, 119.4, 121.9, 122.1, 123.5, 125.7, 127.1, 127.4, 127.7, 129.6, 130.7, 132.4, 135.6, 136.5, 136.7, 143.7; FTIR (KBr) 3274, 3050, 2973, 1596, 1465, 1334 cm$^{-1}$.

General procedure for iodine mediated intramolecular C2 amidative cyclization of compounds 3a-h

3 (0.5 mmol) was taken in a clean and dry reaction tube. To this iodine (0.6 mmol), Cs$_2$CO$_3$ (1.0 mmol) and acetonitrile (2 mL) was added. Reaction tube is stoppered and the resulting reaction mixture was stirred at 60 °C. After 4 h the second portion of iodine (0.3 mmol) was added and reaction was allowed to stir at 60 °C. Upon completion of reaction as monitored by TLC, solvent was removed under vacuum in rotary evaporator and DCM was added. The crude reaction mixture was washed with saturated Na$_2$S$_2$O$_3$ solution (2 × 10 mL) and extracted with DCM. The organic layer was washed water (1 × 10 mL). Combined organic layers were concentrated using rotary evaporator and residue is purified by column chromatography on silica gel using hexanes/ethyl acetate as an eluent to afford pure product 4.

Spectral data for compounds 4a-j

5-Methyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole (4a)$^{10}$: White solid, mp 164-166 °C [lit. 162 °C]$^{10}$; R$_f$ 0.56 (10% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.11 (s, 3H), 4.13 (s, 3H), 6.86 (d, $J$=8.4 Hz, 2H), 7.11 (dt, $J$=7.6, 1.2 Hz, 1H), 7.15-7.30 (m, 5H), 7.41 (d, $J$=8 Hz, 1H), 7.50 (dd, $J$=7.6, 0.8 Hz, 1H), 7.71 (d, $J$=7.6 Hz, 1H), 8.07 (dd, $J$=8.4, 0.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 21.6, 34.0, 111.0, 118.0, 118.5, 119.5, 120.5, 121.0, 122.3, 122.4, 125.6, 127.0, 129.4, 132.5, 140.7, 141.7, 143.0, 145.0; FTIR (KBr) 3057, 2923, 2853, 1600, 1528, 1505, 1436, 1396, 1368, 1175 cm$^{-1}$; HRMS (m/z): [M+H]$^+$ calcd. for C$_{22}$H$_{19}$N$_2$O$_2$: 375.1167; found: 375.1166.

5-Ethyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole (4b): Pale brown solid, mp 156-158 °C; R$_f$ 0.55 (10% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.48 (t, $J$=7.2 Hz, 3H), 2.11 (s, 3H), 4.70 (q, $J$=7.2 Hz, 2H), 6.86 (d, $J$=8.4 Hz, 2H), 7.11 (dt, $J$=7.6, 1.2 Hz, 1H), 7.15-7.21 (m, 2H), 7.21-7.29 (m, 3H), 7.45 (d, $J$=8 Hz, 1H), 7.49 (td, $J$=7.6, 0.8 Hz, 1H), 7.72dd, $J$=7.4, 0.8 Hz, 1H), 8.07 (dd, $J$=8.2, 0.8 Hz, 1H); $^{13}$C
NMR (CDCl₃, 100 MHz) δ 15.0, 21.6, 41.8, 109.6, 111.3, 117.9, 118.4, 119.6, 120.9, 122.3, 125.6, 127.0, 127.3, 129.4, 132.5, 140.8, 141.0, 142.5, 144.9; FTIR (KBr) 3056, 2926, 2859, 1604, 1515, 1453, 1370, 1251, 1176 cm⁻¹; HRMS (m/z): [M+H]⁺ calcd. for C₂₃H₂₁N₂O₂S: 389.1324; found: 389.1313.

5-Isopropyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole (4c): White solid, mp 148-150 °C; Rₛ 0.53 (10% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 1.74 (d, J=7.2 Hz, 6H), 2.17 (s, 3H), 5.64 (septet, J=7.2 Hz, 1H), 6.88 (s, 1H), 6.89 (d, J=8 Hz 2H), 7.15-7.22 (m, 3H), 7.23-7.29 (m, 3H), 7.49 (dd, J=7.6, 0.8 Hz, 1H), 7.73-7.79 (m, 2H), 8.11 (d, J=8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.6, 51.8, 114.5, 118.3, 118.8, 120.0, 120.7, 121.6, 122.1, 122.3, 125.9, 127.2, 128.1, 131.3, 139.4, 141.4, 143.7, 144.8; FTIR (KBr) 3058, 2973, 2927, 2854, 1604, 1531, 1504, 1457, 1172 cm⁻¹;

5-propyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole (4d): Pale brown semi solid; Rₛ 0.55 (10% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 0.94 (t, J=7.6 Hz, 3H), 2.01 (sextet, J=7.6 Hz, 2H), 2.19 (s, 3H), 4.69 (t, J=7.6 Hz, 2H), 6.93 (d, J=8.0 Hz 2H), 7.19 (dt, J=8.4, 1.2 Hz, 1H), 7.21-7.29 (m, 2H), 7.30-7.35 (m, 3H), 7.52 (d, J=8.0 Hz, 1H), 7.58 (dd, J=3.6, 0.8 Hz, 1H), 7.80 (d, J=7.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 11.4, 21.6, 22.9, 48.2, 109.5, 111.4, 117.9, 118.4, 119.5, 120.6, 120.8, 122.1, 122.4, 125.5, 126.9, 127.3, 129.3, 132.3, 140.7, 141.2, 142.5, 144.9; FTIR (KBr) 3058, 2965, 2927, 2865, 1604, 1511, 1454, 1176 cm⁻¹;

5-butyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole (4e): White solid, mp 137-139 °C; Rₛ 0.52 (10% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 0.96 (t, J=7.6 Hz, 3H), 1.35 (sextet, J=7.6 Hz, 2H), 1.94 (quintet, J=7.6 Hz, 2H) 2.19 (s, 3H), 4.74 (t, J=7.6 Hz, 2H), 7.32 (d, J=8.4 Hz, 3H), 7.52 (d, J=8.4 Hz, 1H), 7.58 (d, J=7.6 Hz, 1H), 8.16 (d, J=8.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 11.4, 21.6, 22.9, 48.2, 109.5, 111.4, 117.9, 118.4, 119.5, 120.6, 120.8, 122.1, 122.4, 125.5, 126.9, 127.3, 129.3, 132.3, 140.7, 141.2, 142.5, 144.9; FTIR (KBr) 3058, 2965, 2927, 2865, 1604, 1511, 1454, 1176 cm⁻¹;

2-Methoxy-5-methyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole (4f): Pale green solid, mp 162-164 °C; Rₛ 0.43 (15% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 2.11 (s, 3H), 3.82 (s, 3H), 4.08 (s, 3H), 6.83-6.92 (m, 3H), 7.10 (dt, J=8.4, 1.2 Hz, 1H), 7.15-7.21 (m, 2H), 7.23 (d, J=8.4 Hz, 2H), 7.28 (d, J=8.8 Hz, 1H), 7.47 (d, J=7.4 Hz, 1H), 8.05 (d, J=8.4 Hz, 1H); ¹³C NMR (CDCl₃, 100
10-Methyl-9-tosyl-9,10-dihydropyrido[3',2':4,5]pyrrolo[2,3-b]indole (4g): White solid, mp 160-162 °C; Rf 0.46 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.21 (s, 3H), 4.33 (s, 3H), 6.98 (d, J=8.4 Hz, 2H), 7.20 (dd, J=7.6 Hz, 1H), 7.22-7.27 (m, 1H), 7.31 (t, J=8.4 Hz, 1H), 7.39 (d, J=8.4 Hz, 2H), 7.58 (d, J=7.6 Hz, 1H), 8.05 (dd, J=7.6, 0.8 Hz, 1H), 8.22 (d, J=8.4 Hz, 1H), 8.40 (dd, J=4.8, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.6, 32.5, 106.1, 113.9, 117.0, 117.6, 118.5, 122.9, 125.6, 126.6, 126.9, 127.0, 129.6, 132.9, 139.9, 142.4, 145.2, 151.5; FTIR (KBr) 3056, 2926, 1609, 1514, 1435 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C21H21N2O3S: 376.1120; found: 376.1131.

5-Methyl-6-tosyl-5,6-dihydroindolo[2,3-b]indole-2-carbonitrile (4h): White solid, mp 223-225 °C; Rf 0.43 (20% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz ppm) δ 2.13 (s, 3H), 4.16 (s, 3H), 6.89 (d, J=8 Hz, 2H), 7.15-7.28 (m, 4H), 7.42-7.52 (m, 3H), 8.00 (s, 1H), 8.08 (d, J=8 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.7, 34.4, 104.2, 109.2, 111.7, 118.0, 118.9, 120.2, 120.5, 124.5, 126.0, 126.2, 127.0, 129.6, 132.4, 140.8, 143.0, 144.2, 145.5; FTIR (KBr) 2923, 2855, 2217, 1614, 1515, 1466, 1439, 1169 cm⁻¹.

6-Methyl-5-tosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline (4i): Pale red solid, mp 97-99 °C; Rf 0.46 (10% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz) δ 2.21 (d, J=18.6 Hz, 1H), 2.27 (s, 3H), 3.41 (d, J=18.6 Hz, 1H), 3.86 (s, 3H), 6.89 (s, 3H), 6.93 (d, J=8.4 Hz, 1H), 7.03 (dt, J=7.2, 0.8 Hz, 1H), 7.11 (dt, J=7.6, 1.2 Hz, 1H), 7.15-7.25 (m, 2H), 7.28 (d, J=8.4 Hz, 1H), 7.32 (dd, J=7.6, 0.8 Hz, 1H), 7.77 (dd, J=8, 1.2 Hz, 1H); 13C NMR (CDCl3, 100 MHz) δ 21.8, 25.3, 30.8, 106.2, 110.0, 118.2, 119.6, 122.1, 124.1, 126.6, 127.3, 128.2, 128.7, 128.9, 129.1, 131.7, 133.5, 136.3, 136.4, 138.2, 144.8; FTIR (KBr) 3054, 2925, 2855, 1636, 1608, 1516, 1483, 1428 cm⁻¹; HRMS (m/z): [M+H]+ calcd. for C23H21N2O2S: 389.1324; found: 389.1327.

9-bromo-6-methyl-5-tosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline (4j): White solid, mp 154-156 °C; Rf 0.52 (10% ethyl acetate in hexanes); 1H NMR (CDCl3, 400 MHz, ppm) δ 2.23 (d, J=18.4 Hz, 1H), 2.38 (s, 3H), 3.44 (d, J=18.4 Hz, 1H), 3.93 (s, 3H), 6.93 (d, J=8.4 Hz, 2H), 7.02 (d, J=8.0 Hz, 3H), 7.21-7.26 (m, 2H), 7.30-7.36 (m, 2H), 7.53 (d, J=0.8 Hz, 1H), 7.85 (dd, J=8, 0.8 Hz, 1H)
Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz, ppm) δ 21.8, 25.1, 31.0, 105.8, 111.6, 112.9, 120.8, 124.9, 125.6, 126.3, 126.8, 127.5, 128.2, 128.7, 128.8, 129.3, 131.5, 135.0, 135.9, 138.0, 145.1; FTIR (KBr) 3060, 2953, 2853, 1606, 1596, 1567, 1491, 1468, 1362, 1280 cm$^{-1}$; HRMS (m/z): [M+Na]$^{+}$ calcd. for C$_{23}$H$_{19}$N$_2$O$_2$NaSBr: 489.0248; found: 489.0219 (HRMS data for $^{79}$Br isotope).

General procedure for iodine mediated intramolecular domino cyclization-detosylation-aromatization reaction of compounds 3i-m

3 (0.5 mmol) was taken in a clean and dry reaction tube. To this iodine (0.6 mmol), Cs$_2$CO$_3$ (1.0 mmol) and acetonitrile (2 mL) were added. The reaction tube was stoppered and the resulting reaction mixture was stirred at 60 °C. After 4 h the second portion of iodine (0.3 mmol) was added and reaction is allowed to stir at 60 °C. Upon completion of reaction as monitored by TLC, solvent was removed under vacuum in rotary evaporator and DCM was added. The crude reaction mixture was washed with saturated Na$_2$S$_2$O$_3$ solution (2 × 10 mL) and extracted with DCM. The organic layer was washed with water (1 × 10 mL). Combined organic layers were concentrated using rotary evaporator and residue is purified by column chromatography on silica gel using hexanes/ethyl acetate as an eluent to afford pure product 5.

6-Methyl-6H-indolo[2,3-b]quinoline (5a): Pale yellow solid, mp 83-87 °C; R$_f$ 0.42 (10% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 500 MHz) δ 4.02 (s, 3H), 7.32 (d, J=7.2 Hz, 1H), 7.41 (d, J=8 Hz, 1H), 7.47 (dt, J=7, 1 Hz, 1H), 7.57-7.62 (m, 1H), 7.71-7.76 (m, 1H), 8.00 (d, J=8.5 Hz, 1H), 8.22 (d, J=8.5 Hz, 1H), 8.70 (s, 1H) ; $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 28.2, 109.0, 118.6, 120.4, 120.4, 121.6, 123.3, 124.0, 127.0, 128.1, 128.4, 128.7, 129.4, 142.9, 146.0, 152.3; FTIR (KBr) 3053, 2928, 1607, 1579, 1483, 1430 cm$^{-1}$.

9-bromo-6-methyl-6H-indolo[2,3-b]quinoline (5b): Yellow solid, mp 132-134 °C; R$_f$ 0.46 (20% ethyl acetate in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz, ppm) δ 3.86 (s, 3H), 7.07 (1:1 q, J=7.2 Hz, 1H), 7.14-7.19 (m, 1H), 7.39 (t, J= 7.2 Hz, 1H), 7.56 (dd, J= 8.4, 2.4 Hz, 1H), 7.65 (dt, J= 8.4, 2.4 Hz, 1H), 7.70 (d, J= 8.4 Hz, 1H), 7.75 (t, J= 7.2 Hz, 1H), 8.00 (d, J= 8.4 Hz, 1H), 8.14 (d, J= 8.5 Hz, 1H), 8.22 (d, J= 8.5 Hz, 1H), 8.70 (s, 1H) ; $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 28.2, 109.0, 118.6, 120.4, 120.4, 121.6, 123.3, 124.0, 127.0, 128.1, 128.4, 128.7, 129.4, 142.9, 146.0, 152.3; FTIR (KBr) 3053, 2928, 1607, 1579, 1483, 1430 cm$^{-1}$. 

28
7.6, 1.2 Hz, 1H), 7.89 (d, J= 8.0 Hz, 1H), 8.07 (d, J=8.8 Hz, 1H), 8.11 (s, 1H), 8.52 (s, 1H); δ 28.1, 110.3, 112.9, 117.2, 122.2, 123.5, 124.1, 124.3, 127.4, 127.8, 128.2, 128.4, 128.8, 129.6, 130.9, 141.5; FTIR (KBr) 2923, 2852, 1603, 1572, 1477, 1458, 1325, 1254 cm^{-1}; HRMS (m/z): [M+H]^+ calcd. For C_{16}H_{12}N_{2}Br: 311.0184; found: 311.0172 (HRMS data for {^79}Br isotope).

9-Methoxy-6-methyl-6H-indolo[2,3-b]quinoline (5c): Yellow solid, mp 110-112 °C; R_f 0.46 (20% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) δ 3.95 (s, 3H), 3.96 (s, 3H), 7.20 (dd, \(J=8.6\), 2.4 Hz, 1H), 7.31 (d, \(J=8.8\) Hz, 1H), 7.44 (dd, \(J=7.4\), 1.2 Hz, 1H), 7.66 (d, \(J=2.4\) Hz, 1H), 7.71 (dt, \(J=7.6\), 1.6 Hz, 1H), 7.98 (dd, \(J=8.4\), 1.2 Hz, 1H), 8.15 (d, \(J=8.4\) Hz, 1H), 8.66 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) δ 28.0, 56.3, 105.7, 109.5, 116.3, 118.5, 120.9, 122.9, 123.9, 127.7, 127.8, 128.3, 128.7, 129.1, 137.7, 154.5; FTIR (KBr) 3055, 2927, 2855, 1615, 1576, 1392, 1285 cm\(^{-1}\).

6-ethyl-6H-indolo[2,3-b]quiniline (5d): White solid, mp 93-95 °C; R_f 0.56 (10% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 1.52 (t, \(J=7.2\) Hz, 3H), 4.61 (q, \(J=7.2\) Hz, 2H), 7.30 (dt, \(J=7.2\), 0.8 Hz, 1H), 7.42-7.49 (m, 2H), 7.58 (dt, \(J=7.6\), 1.2 Hz, 1H), 7.73 (dt, \(J=7.6\), 1.6 Hz, 1H), 8.00 (dd, \(J=8.2\), 1.6 Hz, 1H), 8.17 (t, \(J=8.4\) Hz, 2H), 8.71 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) δ 13.8, 36.4, 109.0, 118.5, 120.0, 120.7, 121.7, 123.0, 124.2, 127.5, 127.8, 128.2, 128.6, 129.0, 142.0, 146.7, 152.1; FTIR (KBr) 3055, 2926, 2853, 1605, 1571, 1481, 1450, 1349, 1229 cm\(^{-1}\);

6-Isopropyl-6H-indolo[2,3-b]quinoline (5e): Pale orange solid, mp 98-100 °C; R_f 0.54 (10% ethyl acetate in hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 1.66 (d, \(J=7.0\) Hz, 6H), 5.56 (septet, \(J=7.0\) Hz, 1H), 7.17 (t, \(J=7.5\) Hz, 1H), 7.34 (t, \(J=8\) Hz, 1H), 7.43 (t, \(J=7.5\) Hz, 1H), 7.49 (d, \(J=8.5\) Hz, 1H), 7.60 (t, \(J=7.5\) Hz, 1H), 7.88 (d, \(J=8.5\) Hz, 1H), 8.02 (d, \(J=8.5\) Hz, 1H), 8.59 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) δ 21.0, 44.9, 110.7, 118.3, 119.5, 121.1, 121.5, 122.7, 124.1, 127.0, 127.2, 127.6, 128.3, 128.7, 141.3, 146.8, 152.3; FTIR (KBr) 3058, 2969, 2854, 1604, 1569, 1461, 1365, 1234 cm\(^{-1}\).

**General procedure for iodine mediated intramolecular competitive experiment:**

6a (0.5 mmol) was taken in a clean and dry reaction tube. To this iodine (0.6 mmol), Cs\(_2\)CO\(_3\) (1.0 mmol) and acetonitrile (2 mL) were added. The reaction tube was stoppered and the resulting reaction
mixture was stirred at 60 °C. After 4 h the second portion of iodine (0.3 mmol) was added and reaction is allowed to stir at 60 °C. Upon completion of reaction as monitored by TLC, solvent was removed under vacuum in rotary evaporator and DCM was added. The crude reaction mixture was washed with saturated Na₂S₂O₃ solution (2 × 10 mL) and extracted with DCM. The organic layer was washed with water (1 × 10 mL). Combined organic layers were concentrated using rotary evaporator and residue is purified by column chromatography on silica gel using hexanes/ethyl acetate as an eluent to afford pure products 7a and 7b.

**14,15-ditosyl-15H-benzo[4,5]imidazo[1,2-a]indolo[2,3-b]indol-(14H)-ol (7a):** White solid, mp 198-200 °C; Rf 0.41 (20% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 500 MHz, ppm) δ 2.21 (s, 3H), 2.45 (s, 3H), 6.61 (d, J=7.6 Hz, 1H), 6.93 (d, J=8 Hz, 2H), 6.96 (dd, J=7.4, 1.2 Hz, 1H), 7.02 (dt, J=7.6, 1.6 Hz, 1H), 7.07-7.10 (m, 2H), 7.27 (d, J=8.0 Hz, 3H), 7.39 (d, J=8 Hz, 4H), 7.71 (dd, J=8, 1.6 Hz, 1H), 7.77 (dd, J=7.6, 1.2 Hz, 1H), 7.83 (d, J=8.0 Hz, 1H), 7.87 (d, J=8.8 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 21.4, 21.9, 87.5, 110.8, 111.9, 113.6, 113.7, 123.2, 123.4, 123.7, 124.6, 125.1, 125.3, 126.1, 128.0, 129.0, 129.8, 129.9, 132.6, 132.8, 134.4, 135.3, 138.9, 141.3, 143.5, 144.4, 145.2; FTIR (KBr) 3061, 2923, 2857, 1597, 1487, 1169 cm⁻¹;  

**2-(6-tosylindolo[2,3-b]indol-5(6H)-yl)aniline (7b):** Pale yellow solid, mp 105-107 °C; Rf 0.56 (20% ethyl acetate in hexanes); ¹H NMR (CDCl₃, 500 MHz, ppm) δ 2.24 (s, 3H), 6.89 (t, J=7.6 Hz, 1H), 7.12-7.20 (m, 2H), 7.23-7.27 (m, 1H), 7.28-7.32 (m, 2H), 7.33-7.40 (m, 2H), 7.46 (d, J=8.4 Hz, 2H), 7.76 (d, J=7.2 Hz, 1H), 7.89 (d, J=7.6 Hz, 1H), 8.21 (d, J=8.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 21.6, 112.4, 116.8, 116.9, 118.8, 118.9, 119.3, 120.9, 121.9, 122.8, 122.8, 125.1, 126.0, 127.1, 129.1, 129.5, 129.8, 134.0, 139.9, 141.6, 141.7, 143.9, 144.9; FTIR (KBr) 3472, 3382, 3056, 2925, 2857, 1615, 1509, 1456, 1375, 1262 cm⁻¹;
Crystal data for compound 7a

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>7a</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C35 H28 Cl3 N3 O5 S2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>741.07</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.1831(2) Å, alpha = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 17.6304(4) Å, beta = 92.2453(11) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 18.6382(5) Å, gamma = 90 deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>3343.59(13) Å^3</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.472 Mg/m^3</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.447 mm^-1</td>
</tr>
<tr>
<td>F(000)</td>
<td>1528</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.350 x 0.250 x 0.250 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.590 to 25.000 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-12&lt;=h&lt;=12, -20&lt;=k&lt;=18, -22&lt;=l&lt;=22</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>26328 / 5880 [R(int) = 0.0276]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>25.000 100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5880 / 0 / 436</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.023</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0495, wR2 = 0.1330</td>
</tr>
</tbody>
</table>
R indices (all data) \hspace{1cm} R₁ = 0.0715, \, \text{wR}^2 = 0.1514

Extinction coefficient \hspace{2cm} n/a

Largest diff. peak and hole \hspace{1cm} 0.495 and -0.485 e.A⁻³

**Table 2.** Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 7a.

U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>2960(3)</td>
<td>3370(2)</td>
<td>10259(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>3468(4)</td>
<td>4066(3)</td>
<td>10038(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>2769(4)</td>
<td>4557(2)</td>
<td>9599(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>1523(4)</td>
<td>4366(2)</td>
<td>9352(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>1006(3)</td>
<td>3675(2)</td>
<td>9548(2)</td>
</tr>
<tr>
<td>C(6)</td>
<td>-315(3)</td>
<td>3348(2)</td>
<td>9332(2)</td>
</tr>
<tr>
<td>C(7)</td>
<td>-418(3)</td>
<td>2619(2)</td>
<td>9828(2)</td>
</tr>
<tr>
<td>C(8)</td>
<td>1705(3)</td>
<td>3185(2)</td>
<td>9998(2)</td>
</tr>
<tr>
<td>C(9)</td>
<td>-366(3)</td>
<td>2989(2)</td>
<td>8598(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>-250(3)</td>
<td>3336(2)</td>
<td>7941(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>-393(3)</td>
<td>2903(2)</td>
<td>7324(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>-598(3)</td>
<td>2132(2)</td>
<td>7371(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C(13)</td>
<td>-709(3)</td>
<td>1772</td>
<td>8028(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>-623(3)</td>
<td>2223(2)</td>
<td>8638(2)</td>
</tr>
<tr>
<td>C(15)</td>
<td>-1886(3)</td>
<td>1611(2)</td>
<td>9603(2)</td>
</tr>
<tr>
<td>C(16)</td>
<td>-2530(4)</td>
<td>976(2)</td>
<td>9336(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>-3624(4)</td>
<td>729(3)</td>
<td>9695(3)</td>
</tr>
<tr>
<td>C(18)</td>
<td>-4035(4)</td>
<td>1098(3)</td>
<td>10295(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>-3390(3)</td>
<td>1726(2)</td>
<td>10563(2)</td>
</tr>
<tr>
<td>C(20)</td>
<td>-2307(3)</td>
<td>1975(2)</td>
<td>10214(2)</td>
</tr>
<tr>
<td>C(21)</td>
<td>-964(3)</td>
<td>2763(2)</td>
<td>11806(2)</td>
</tr>
<tr>
<td>C(22)</td>
<td>-1804(3)</td>
<td>2431(2)</td>
<td>12280(2)</td>
</tr>
<tr>
<td>C(23)</td>
<td>-1309(3)</td>
<td>2145(2)</td>
<td>12922(2)</td>
</tr>
<tr>
<td>C(24)</td>
<td>19(3)</td>
<td>2201(2)</td>
<td>13112(2)</td>
</tr>
<tr>
<td>C(25)</td>
<td>839(3)</td>
<td>2516(2)</td>
<td>12616(2)</td>
</tr>
<tr>
<td>C(26)</td>
<td>365(3)</td>
<td>2792(2)</td>
<td>11972(2)</td>
</tr>
<tr>
<td>C(27)</td>
<td>560(4)</td>
<td>1957(3)</td>
<td>13838(2)</td>
</tr>
<tr>
<td>C(28)</td>
<td>1909(3)</td>
<td>1206(2)</td>
<td>9608(2)</td>
</tr>
<tr>
<td>C(29)</td>
<td>1179(3)</td>
<td>591(2)</td>
<td>9364(2)</td>
</tr>
<tr>
<td>C(30)</td>
<td>1549(4)</td>
<td>199(2)</td>
<td>8760(2)</td>
</tr>
<tr>
<td>C(31)</td>
<td>2616(4)</td>
<td>418(2)</td>
<td>8391(2)</td>
</tr>
<tr>
<td>C(32)</td>
<td>3326(4)</td>
<td>1030(2)</td>
<td>8633(2)</td>
</tr>
<tr>
<td>C(33)</td>
<td>2992(4)</td>
<td>1426(2)</td>
<td>9238(2)</td>
</tr>
<tr>
<td>C(34)</td>
<td>3004(5)</td>
<td>-13(3)</td>
<td>7726(3)</td>
</tr>
<tr>
<td>C(35)</td>
<td>2951(4)</td>
<td>5262(2)</td>
<td>2013(2)</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>1795(1)</td>
<td>4553(1)</td>
<td>1919(1)</td>
</tr>
<tr>
<td>Cl(2)</td>
<td>3098(2)</td>
<td>5614(1)</td>
<td>2872(1)</td>
</tr>
<tr>
<td></td>
<td>Cl(3)</td>
<td>4498(1)</td>
<td>4916(1)</td>
</tr>
<tr>
<td>---</td>
<td>--------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td></td>
<td>N(1)</td>
<td>-763(2)</td>
<td>1986(1)</td>
</tr>
<tr>
<td></td>
<td>N(2)</td>
<td>-1469(2)</td>
<td>2608(1)</td>
</tr>
<tr>
<td></td>
<td>N(3)</td>
<td>918(2)</td>
<td>2541(1)</td>
</tr>
<tr>
<td></td>
<td>O(1)</td>
<td>-1382(2)</td>
<td>3878(1)</td>
</tr>
<tr>
<td></td>
<td>O(2)</td>
<td>-728(3)</td>
<td>3813(1)</td>
</tr>
<tr>
<td></td>
<td>O(3)</td>
<td>-2951(2)</td>
<td>3343(2)</td>
</tr>
<tr>
<td></td>
<td>O(4)</td>
<td>2675(2)</td>
<td>1823(2)</td>
</tr>
<tr>
<td></td>
<td>O(5)</td>
<td>424(2)</td>
<td>1297(1)</td>
</tr>
<tr>
<td></td>
<td>S(1)</td>
<td>-1590(1)</td>
<td>3203(1)</td>
</tr>
<tr>
<td></td>
<td>S(2)</td>
<td>1493(1)</td>
<td>1688(1)</td>
</tr>
</tbody>
</table>

**Table 3.** Bond lengths [Å] and angles [deg] for 7a.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-C(8)</td>
<td>1.388(4)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.400(6)</td>
</tr>
<tr>
<td>C(1)-H(1)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.371(6)</td>
</tr>
<tr>
<td>C(2)-H(2)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.375(5)</td>
</tr>
<tr>
<td>C(3)-H(3)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.381(5)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.9300</td>
</tr>
</tbody>
</table>
C(5)-C(8)  1.383(5)
C(5)-C(6)  1.504(4)
C(6)-O(1)  1.436(4)
C(6)-C(9)  1.507(4)
C(6)-C(7)  1.590(4)
C(7)-N(1)  1.452(4)
C(7)-N(2)  1.472(4)
C(7)-N(3)  1.485(4)
C(8)-N(3)  1.432(4)
C(9)-C(14) 1.377(4)
C(9)-C(10) 1.378(4)
C(10)-C(11) 1.383(5)
C(10)-H(10) 0.9300
C(11)-C(12) 1.378(5)
C(11)-H(11) 0.9300
C(12)-C(13) 1.389(5)
C(12)-H(12) 0.9300
C(13)-C(14) 1.388(4)
C(13)-H(13) 0.9300
C(14)-N(1)  1.418(4)
C(15)-C(16) 1.379(5)
C(15)-C(20) 1.389(4)
C(15)-N(1)  1.412(4)
C(16)-C(17) 1.391(5)
C(16)-H(16) 0.9300
<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(17)-C(18)</td>
<td>1.373(6)</td>
</tr>
<tr>
<td>C(17)-H(17)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(18)-C(19)</td>
<td>1.371(5)</td>
</tr>
<tr>
<td>C(18)-H(18)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.374(4)</td>
</tr>
<tr>
<td>C(19)-H(19)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(20)-N(2)</td>
<td>1.421(4)</td>
</tr>
<tr>
<td>C(21)-C(26)</td>
<td>1.377(4)</td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td>1.384(4)</td>
</tr>
<tr>
<td>C(21)-S(1)</td>
<td>1.756(3)</td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td>1.376(5)</td>
</tr>
<tr>
<td>C(22)-H(22)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(23)-C(24)</td>
<td>1.388(5)</td>
</tr>
<tr>
<td>C(23)-H(23)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(24)-C(25)</td>
<td>1.386(5)</td>
</tr>
<tr>
<td>C(24)-C(27)</td>
<td>1.504(5)</td>
</tr>
<tr>
<td>C(25)-C(26)</td>
<td>1.366(5)</td>
</tr>
<tr>
<td>C(25)-H(25)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(26)-H(26)</td>
<td>0.9300</td>
</tr>
<tr>
<td>C(27)-H(27A)</td>
<td>0.9600</td>
</tr>
<tr>
<td>C(27)-H(27B)</td>
<td>0.9600</td>
</tr>
<tr>
<td>C(27)-H(27C)</td>
<td>0.9600</td>
</tr>
<tr>
<td>C(28)-C(33)</td>
<td>1.378(4)</td>
</tr>
<tr>
<td>C(28)-C(29)</td>
<td>1.382(5)</td>
</tr>
<tr>
<td>C(28)-S(2)</td>
<td>1.758(3)</td>
</tr>
</tbody>
</table>
C(29)-C(30)  1.384(5)  
C(29)-H(29)  0.9300  
C(30)-C(31)  1.365(5)  
C(30)-H(30)  0.9300  
C(31)-C(32)  1.366(6)  
C(31)-C(34)  1.518(6)  
C(32)-C(33)  1.381(5)  
C(32)-H(32)  0.9300  
C(33)-H(33)  0.9300  
C(34)-H(34A)  0.9600  
C(34)-H(34B)  0.9600  
C(34)-H(34C)  0.9600  
C(35)-Cl(2)  1.719(4)  
C(35)-Cl(1)  1.721(4)  
C(35)-Cl(3)  1.770(5)  
C(35)-H(35)  0.9800  
N(2)-S(1)  1.644(3)  
N(3)-S(2)  1.662(3)  
O(1)-H(1A)  0.8200  
O(2)-S(1)  1.428(2)  
O(3)-S(1)  1.422(2)  
O(4)-S(2)  1.422(2)  
O(5)-S(2)  1.425(2)  
C(8)-C(1)-C(2)  116.7(4)
C(8)-C(1)-H(1)        121.7
C(2)-C(1)-H(1)        121.7
C(3)-C(2)-C(1)        122.7(4)
C(3)-C(2)-H(2)        118.7
C(1)-C(2)-H(2)        118.7
C(2)-C(3)-C(4)        119.7(4)
C(2)-C(3)-H(2)        118.7
C(3)-C(4)-C(5)        118.9(4)
C(3)-C(4)-H(3)        120.2
C(4)-C(3)-H(3)        120.2
C(3)-C(4)-C(5)        118.9(4)
C(3)-C(4)-H(4)        120.5
C(5)-C(4)-H(4)        120.5
C(4)-C(5)-C(8)        121.3(3)
C(4)-C(5)-C(6)        127.8(3)
C(8)-C(5)-C(6)        110.9(3)
O(1)-C(6)-C(5)        114.2(2)
O(1)-C(6)-C(9)        108.4(2)
C(5)-C(6)-C(9)        113.7(2)
O(1)-C(6)-C(7)        115.6(2)
C(5)-C(6)-C(7)        103.5(2)
C(9)-C(6)-C(7)        100.7(2)
N(1)-C(7)-N(2)        102.8(2)
N(1)-C(7)-N(3)        112.5(2)
N(2)-C(7)-N(3)        113.3(2)
N(1)-C(7)-C(6)        107.0(2)
N(2)-C(7)-C(6)        117.3(2)
<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)-C(7)-C(6)</td>
<td>104.1(2)</td>
</tr>
<tr>
<td>C(5)-C(8)-C(1)</td>
<td>120.7(3)</td>
</tr>
<tr>
<td>C(5)-C(8)-N(3)</td>
<td>110.5(3)</td>
</tr>
<tr>
<td>C(1)-C(8)-N(3)</td>
<td>128.6(3)</td>
</tr>
<tr>
<td>C(14)-C(9)-C(10)</td>
<td>120.5(3)</td>
</tr>
<tr>
<td>C(14)-C(9)-C(6)</td>
<td>111.3(3)</td>
</tr>
<tr>
<td>C(10)-C(9)-C(6)</td>
<td>128.2(3)</td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)</td>
<td>118.9(3)</td>
</tr>
<tr>
<td>C(10)-C(9)-C(6)</td>
<td>120.5</td>
</tr>
<tr>
<td>C(11)-C(10)-H(10)</td>
<td>120.5</td>
</tr>
<tr>
<td>C(9)-C(14)-C(13)</td>
<td>121.5(3)</td>
</tr>
<tr>
<td>C(9)-C(14)-N(1)</td>
<td>111.5(2)</td>
</tr>
<tr>
<td>C(16)-C(15)-C(20)</td>
<td>120.9(3)</td>
</tr>
<tr>
<td>C(16)-C(15)-N(1)</td>
<td>130.0(3)</td>
</tr>
<tr>
<td>C(20)-C(15)-N(1)</td>
<td>109.2(3)</td>
</tr>
</tbody>
</table>
C(15)-C(16)-C(17)  117.3(4)
C(15)-C(16)-H(16)  121.4
C(17)-C(16)-H(16)  121.4
C(18)-C(17)-C(16)  121.3(4)
C(18)-C(17)-H(17)  119.4
C(16)-C(17)-H(17)  119.4
C(19)-C(18)-C(17)  121.4(4)
C(19)-C(18)-H(18)  119.3
C(17)-C(18)-H(18)  119.3
C(18)-C(19)-C(20)  117.9(4)
C(18)-C(19)-H(19)  121.1
C(20)-C(19)-H(19)  121.1
C(19)-C(20)-C(15)  121.3(3)
C(19)-C(20)-N(2)   131.0(3)
C(15)-C(20)-N(2)   107.7(2)
C(26)-C(21)-C(22)  120.0(3)
C(26)-C(21)-S(1)   119.5(2)
C(22)-C(21)-S(1)   119.5(2)
C(22)-C(23)-C(24)  117.8(3)
<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(25)-C(24)-C(27)</td>
<td>120.3(3)</td>
</tr>
<tr>
<td>C(23)-C(24)-C(27)</td>
<td>121.9(3)</td>
</tr>
<tr>
<td>C(26)-C(25)-C(24)</td>
<td>121.8(3)</td>
</tr>
<tr>
<td>C(26)-C(25)-H(25)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(24)-C(25)-H(25)</td>
<td>119.1</td>
</tr>
<tr>
<td>C(25)-C(26)-C(21)</td>
<td>119.6(3)</td>
</tr>
<tr>
<td>C(25)-C(26)-H(26)</td>
<td>120.2</td>
</tr>
<tr>
<td>C(21)-C(26)-H(26)</td>
<td>120.2</td>
</tr>
<tr>
<td>C(24)-C(27)-H(27A)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(24)-C(27)-H(27B)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(27A)-C(27)-H(27B)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(24)-C(27)-H(27C)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(27A)-C(27)-H(27C)</td>
<td>109.5</td>
</tr>
<tr>
<td>H(27B)-C(27)-H(27C)</td>
<td>109.5</td>
</tr>
<tr>
<td>C(33)-C(28)-C(29)</td>
<td>119.1(3)</td>
</tr>
<tr>
<td>C(33)-C(28)-S(2)</td>
<td>120.2(3)</td>
</tr>
<tr>
<td>C(29)-C(28)-S(2)</td>
<td>120.6(3)</td>
</tr>
<tr>
<td>C(28)-C(29)-C(30)</td>
<td>119.9(3)</td>
</tr>
<tr>
<td>C(28)-C(29)-H(29)</td>
<td>120.0</td>
</tr>
<tr>
<td>C(30)-C(29)-H(29)</td>
<td>120.0</td>
</tr>
<tr>
<td>C(31)-C(30)-C(29)</td>
<td>121.1(4)</td>
</tr>
<tr>
<td>C(31)-C(30)-H(30)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(29)-C(30)-H(30)</td>
<td>119.4</td>
</tr>
<tr>
<td>C(30)-C(31)-C(32)</td>
<td>118.5(4)</td>
</tr>
<tr>
<td>C(30)-C(31)-C(34)</td>
<td>120.6(4)</td>
</tr>
</tbody>
</table>
C(32)-C(31)-C(34)  120.9(4)
C(31)-C(32)-C(33)  121.7(4)
C(31)-C(32)-H(32)  119.2
C(33)-C(32)-H(32)  119.2
C(28)-C(33)-C(32)  119.6(4)
C(28)-C(33)-H(33)  120.2
C(32)-C(33)-H(33)  120.2
C(31)-C(34)-H(34A)  109.5
C(31)-C(34)-H(34B)  109.5
H(34A)-C(34)-H(34B)  109.5
C(31)-C(34)-H(34C)  109.5
H(34A)-C(34)-H(34C)  109.5
H(34B)-C(34)-H(34C)  109.5
Cl(2)-C(35)-Cl(1)  113.1(3)
Cl(2)-C(35)-Cl(3)  108.9(2)
Cl(1)-C(35)-Cl(3)  109.6(2)
Cl(2)-C(35)-H(35)  108.4
Cl(1)-C(35)-H(35)  108.4
Cl(3)-C(35)-H(35)  108.4
C(15)-N(1)-C(14)  123.8(2)
C(15)-N(1)-C(7)  110.2(2)
C(14)-N(1)-C(7)  108.2(2)
C(20)-N(2)-C(7)  110.0(2)
C(20)-N(2)-S(1)  124.9(2)
C(7)-N(2)-S(1)  124.91(19)
Table 4. Anisotropic displacement parameters (Å² x 10³) for 7a.

The anisotropic displacement factor exponent takes the form:

\[-2 \pi^2 \left( h^2 a^*^2 U_{11} + \ldots + 2 h k a^* b^* U_{12} \right)\]

Symmetry transformations used to generate equivalent atoms:
<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>51(2)</td>
<td>83(3)</td>
<td>52(2)</td>
<td>-14(2)</td>
<td>0(2)</td>
<td>-14(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>58(2)</td>
<td>89(3)</td>
<td>79(3)</td>
<td>-31(2)</td>
<td>14(2)</td>
<td>-37(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>78(3)</td>
<td>64(3)</td>
<td>79(3)</td>
<td>-11(2)</td>
<td>21(2)</td>
<td>-29(2)</td>
</tr>
<tr>
<td>C(4)</td>
<td>68(2)</td>
<td>52(2)</td>
<td>64(2)</td>
<td>-4(2)</td>
<td>15(2)</td>
<td>-17(2)</td>
</tr>
<tr>
<td>C(5)</td>
<td>50(2)</td>
<td>49(2)</td>
<td>41(2)</td>
<td>-6(1)</td>
<td>8(1)</td>
<td>-12(2)</td>
</tr>
<tr>
<td>C(6)</td>
<td>43(2)</td>
<td>44(2)</td>
<td>39(2)</td>
<td>2(1)</td>
<td>4(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>40(2)</td>
<td>42(2)</td>
<td>32(1)</td>
<td>-1(1)</td>
<td>3(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>42(2)</td>
<td>55(2)</td>
<td>39(2)</td>
<td>-9(1)</td>
<td>6(1)</td>
<td>-12(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>38(2)</td>
<td>50(2)</td>
<td>35(2)</td>
<td>2(1)</td>
<td>2(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>51(2)</td>
<td>61(2)</td>
<td>44(2)</td>
<td>11(2)</td>
<td>9(1)</td>
<td>-2(2)</td>
</tr>
<tr>
<td>C(11)</td>
<td>49(2)</td>
<td>90(3)</td>
<td>35(2)</td>
<td>9(2)</td>
<td>9(1)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(12)</td>
<td>53(2)</td>
<td>86(3)</td>
<td>37(2)</td>
<td>-11(2)</td>
<td>1(1)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C(13)</td>
<td>51(2)</td>
<td>59(2)</td>
<td>41(2)</td>
<td>-9(2)</td>
<td>-1(1)</td>
<td>3(2)</td>
</tr>
<tr>
<td>C(14)</td>
<td>35(1)</td>
<td>51(2)</td>
<td>34(2)</td>
<td>0(1)</td>
<td>-1(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>43(2)</td>
<td>43(2)</td>
<td>46(2)</td>
<td>5(1)</td>
<td>-3(1)</td>
<td>-7(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>67(2)</td>
<td>57(2)</td>
<td>63(2)</td>
<td>-6(2)</td>
<td>-3(2)</td>
<td>-16(2)</td>
</tr>
<tr>
<td>C(17)</td>
<td>70(2)</td>
<td>74(3)</td>
<td>96(3)</td>
<td>1(2)</td>
<td>-3(2)</td>
<td>-39(2)</td>
</tr>
<tr>
<td>C(18)</td>
<td>62(2)</td>
<td>91(3)</td>
<td>84(3)</td>
<td>3(2)</td>
<td>12(2)</td>
<td>-33(2)</td>
</tr>
<tr>
<td>C(19)</td>
<td>54(2)</td>
<td>79(3)</td>
<td>59(2)</td>
<td>2(2)</td>
<td>13(2)</td>
<td>-16(2)</td>
</tr>
<tr>
<td>C(20)</td>
<td>42(2)</td>
<td>50(2)</td>
<td>44(2)</td>
<td>3(1)</td>
<td>2(1)</td>
<td>-7(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>45(2)</td>
<td>59(2)</td>
<td>39(2)</td>
<td>-8(2)</td>
<td>7(1)</td>
<td>-7(2)</td>
</tr>
</tbody>
</table>
C(22)  42(2)  92(3)  52(2)  2(2)  7(2)  -14(2)
C(23)  58(2)  85(3)  48(2)  7(2)  10(2)  -15(2)
C(24)  55(2)  57(2)  49(2)  -8(2)  7(2)  1(2)
C(25)  41(2)  79(3)  57(2)  -13(2)  6(2)  -4(2)
C(26)  48(2)  73(2)  45(2)  -10(2)  13(2)  -14(2)
C(27)  71(2)  91(3)  58(2)  2(2)  -2(2)  9(2)
C(28)  44(2)  49(2)  49(2)  11(2)  0(1)  4(1)
C(29)  57(2)  51(2)  80(3)  11(2)  9(2)  -7(2)
C(30)  69(2)  51(2)  93(3)  -14(2)  3(2)  -1(2)
C(31)  64(2)  58(2)  78(3)  -5(2)  7(2)  9(2)
C(32)  70(2)  76(3)  86(3)  -8(2)  30(2)  -11(2)
C(33)  60(2)  65(2)  79(3)  -7(2)  15(2)  -17(2)
C(34)  108(4)  105(4)  116(4)  -44(3)  30(3)  10(3)
C(35)  91(3)  63(2)  70(3)  12(2)  -15(2)  -9(2)
Cl(1)  97(1)  79(1)  177(2)  -19(1)  -3(1)  -24(1)
Cl(2)  171(1)  86(1)  73(1)  -13(1)  -16(1)  9(1)
Cl(3)  97(1)  118(1)  105(1)  3(1)  5(1)  -3(1)
N(1)   41(1)  41(1)  33(1)  -1(1)  1(1)  -5(1)
N(2)   46(1)  49(2)  38(1)  -4(1)  8(1)  -9(1)
N(3)   40(1)  50(2)  37(1)  0(1)  -2(1)  -6(1)
O(1)   54(1)  53(1)  47(1)  4(1)  2(1)  4(1)
O(2)   88(2)  49(1)  52(1)  -8(1)  14(1)  -11(1)
O(3)   60(1)  86(2)  59(2)  -4(1)  13(1)  17(1)
O(4)   60(1)  96(2)  54(2)  10(1)  -22(1)  1(1)
O(5)   65(1)  72(2)  49(1)  24(1)  6(1)  -4(1)
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 7a.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>3439</td>
<td>3047</td>
<td>10564</td>
<td>75</td>
</tr>
<tr>
<td>H(2)</td>
<td>4313</td>
<td>4201</td>
<td>10196</td>
<td>90</td>
</tr>
<tr>
<td>H(3)</td>
<td>3137</td>
<td>5018</td>
<td>9469</td>
<td>88</td>
</tr>
<tr>
<td>H(4)</td>
<td>1036</td>
<td>4696</td>
<td>9057</td>
<td>73</td>
</tr>
<tr>
<td>H(10)</td>
<td>-77</td>
<td>3853</td>
<td>7913</td>
<td>62</td>
</tr>
<tr>
<td>H(11)</td>
<td>-352</td>
<td>3133</td>
<td>6876</td>
<td>69</td>
</tr>
<tr>
<td>H(12)</td>
<td>-663</td>
<td>1846</td>
<td>6952</td>
<td>70</td>
</tr>
<tr>
<td>H(13)</td>
<td>-836</td>
<td>1250</td>
<td>8058</td>
<td>60</td>
</tr>
<tr>
<td>H(16)</td>
<td>-2245</td>
<td>724</td>
<td>8933</td>
<td>75</td>
</tr>
<tr>
<td>H(17)</td>
<td>-4085</td>
<td>306</td>
<td>9526</td>
<td>96</td>
</tr>
<tr>
<td>H(18)</td>
<td>-4767</td>
<td>918</td>
<td>10525</td>
<td>94</td>
</tr>
<tr>
<td>H(19)</td>
<td>-3677</td>
<td>1976</td>
<td>10968</td>
<td>76</td>
</tr>
<tr>
<td>H(22)</td>
<td>-2700</td>
<td>2401</td>
<td>12165</td>
<td>74</td>
</tr>
</tbody>
</table>
Table 6. Torsion angles [deg] for 7a.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(8)-C(1)-C(2)-C(3)</td>
<td></td>
<td></td>
<td></td>
<td>1.3(6)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)-C(4)</td>
<td></td>
<td></td>
<td></td>
<td>-0.8(6)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)-C(5)</td>
<td></td>
<td></td>
<td></td>
<td>-0.6(6)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)-C(8)</td>
<td></td>
<td></td>
<td></td>
<td>1.5(5)</td>
</tr>
<tr>
<td>C(3)-C(4)-C(5)-C(6)</td>
<td></td>
<td></td>
<td></td>
<td>-179.0(3)</td>
</tr>
</tbody>
</table>

H(23)       -1873          1910         13234          76
H(25)        1737          2541         12726          71
H(26)         937          2997         11647          66
H(27A)        376          2340         14186         110
H(27B)       1494          1888         13820         110
H(27C)        157          1489         13971         110
H(29)         440           440          9605          75
H(30)        1062          -220          8604          85
H(32)        4054          1184          8384          92
H(33)        3494          1839          9396          82
H(34A)       2693          -526          7752         164
H(34B)       3944           14          7700         164
H(34C)       2621           228          7306         164
H(35)        2692          5678          1689          90
H(1A)       -1256          4158          9715          77
<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(4)-C(5)-C(6)-O(1)</td>
<td>-44.4(4)</td>
</tr>
<tr>
<td>C(8)-C(5)-C(6)-O(1)</td>
<td>135.2(3)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)-C(9)</td>
<td>80.8(4)</td>
</tr>
<tr>
<td>C(8)-C(5)-C(6)-C(9)</td>
<td>-99.6(3)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)-C(7)</td>
<td>-170.9(3)</td>
</tr>
<tr>
<td>C(8)-C(5)-C(6)-C(7)</td>
<td>8.7(3)</td>
</tr>
<tr>
<td>O(1)-C(6)-C(7)-N(1)</td>
<td>105.8(3)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)-N(1)</td>
<td>-128.6(2)</td>
</tr>
<tr>
<td>C(9)-C(6)-C(7)-N(1)</td>
<td>-10.8(3)</td>
</tr>
<tr>
<td>O(1)-C(6)-C(7)-N(2)</td>
<td>-8.9(4)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)-N(2)</td>
<td>116.7(3)</td>
</tr>
<tr>
<td>C(9)-C(6)-C(7)-N(2)</td>
<td>-125.5(2)</td>
</tr>
<tr>
<td>O(1)-C(6)-C(9)-C(14)</td>
<td>-115.0(3)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(9)-C(14)</td>
<td>116.8(3)</td>
</tr>
<tr>
<td>C(7)-C(6)-C(9)-C(14)</td>
<td>6.7(3)</td>
</tr>
<tr>
<td>O(1)-C(6)-C(9)-C(10)</td>
<td>61.9(4)</td>
</tr>
<tr>
<td>Bond Sequence</td>
<td>Angle (deg)</td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
</tr>
<tr>
<td>C(5)-C(6)-C(9)-C(10)</td>
<td>-66.3(4)</td>
</tr>
<tr>
<td>C(7)-C(6)-C(9)-C(10)</td>
<td>-176.3(3)</td>
</tr>
<tr>
<td>C(14)-C(9)-C(10)-C(11)</td>
<td>0.0(4)</td>
</tr>
<tr>
<td>C(6)-C(9)-C(10)-C(11)</td>
<td>-176.7(3)</td>
</tr>
<tr>
<td>C(14)-C(9)-C(10)-C(11)</td>
<td>0.0(4)</td>
</tr>
<tr>
<td>C(10)-C(11)-C(12)-C(13)</td>
<td>2.1(5)</td>
</tr>
<tr>
<td>C(11)-C(12)-C(13)-C(14)</td>
<td>0.8(5)</td>
</tr>
<tr>
<td>C(10)-C(9)-C(14)-C(13)</td>
<td>3.1(4)</td>
</tr>
<tr>
<td>C(6)-C(9)-C(14)-C(13)</td>
<td>-179.7(3)</td>
</tr>
<tr>
<td>C(10)-C(9)-C(14)-N(1)</td>
<td>-177.4(3)</td>
</tr>
<tr>
<td>C(6)-C(9)-C(14)-N(1)</td>
<td>-0.2(3)</td>
</tr>
<tr>
<td>C(12)-C(13)-C(14)-C(9)</td>
<td>-3.5(4)</td>
</tr>
<tr>
<td>C(12)-C(13)-C(14)-N(1)</td>
<td>177.1(3)</td>
</tr>
<tr>
<td>C(20)-C(15)-C(16)-C(17)</td>
<td>1.2(5)</td>
</tr>
<tr>
<td>N(1)-C(15)-C(16)-C(17)</td>
<td>179.7(3)</td>
</tr>
<tr>
<td>C(15)-C(16)-C(17)-C(18)</td>
<td>-0.7(6)</td>
</tr>
<tr>
<td>C(16)-C(17)-C(18)-C(19)</td>
<td>0.3(7)</td>
</tr>
<tr>
<td>C(17)-C(18)-C(19)-C(20)</td>
<td>-0.5(6)</td>
</tr>
<tr>
<td>C(18)-C(19)-C(20)-C(15)</td>
<td>1.0(5)</td>
</tr>
<tr>
<td>C(18)-C(19)-C(20)-N(2)</td>
<td>178.1(4)</td>
</tr>
<tr>
<td>C(16)-C(15)-C(20)-C(19)</td>
<td>-1.4(5)</td>
</tr>
<tr>
<td>N(1)-C(15)-C(20)-C(19)</td>
<td>179.8(3)</td>
</tr>
<tr>
<td>C(16)-C(15)-C(20)-N(2)</td>
<td>-179.1(3)</td>
</tr>
<tr>
<td>N(1)-C(15)-C(20)-N(2)</td>
<td>2.1(3)</td>
</tr>
<tr>
<td>C(26)-C(21)-C(22)-C(23)</td>
<td>1.4(6)</td>
</tr>
</tbody>
</table>
S(1)-C(21)-C(22)-C(23)  -174.6(3)
C(21)-C(22)-C(23)-C(24)  1.7(6)
C(22)-C(23)-C(24)-C(25)  -3.5(6)
C(22)-C(23)-C(24)-C(27)  174.2(4)
C(23)-C(24)-C(25)-C(26)  2.4(5)
C(27)-C(24)-C(25)-C(26)  -175.4(4)
C(24)-C(25)-C(26)-C(21)  0.5(5)
C(22)-C(21)-C(26)-C(25)  -2.4(5)
S(1)-C(21)-C(26)-C(25)  173.5(3)
C(33)-C(28)-C(29)-C(30)  0.7(5)
S(2)-C(28)-C(29)-C(30)  -177.5(3)
C(28)-C(29)-C(30)-C(31)  -1.1(6)
C(29)-C(30)-C(31)-C(32)  0.6(6)
C(29)-C(30)-C(31)-C(34)  -179.5(4)
C(30)-C(31)-C(32)-C(33)  0.2(7)
C(34)-C(31)-C(32)-C(33)  -179.7(5)
C(29)-C(28)-C(33)-C(32)  0.1(6)
S(2)-C(28)-C(33)-C(32)  178.3(3)
C(31)-C(32)-C(33)-C(28)  -0.6(7)
C(16)-C(15)-N(1)-C(14)  51.5(5)
C(20)-C(15)-N(1)-C(14)  -129.8(3)
C(16)-C(15)-N(1)-C(7)  -178.1(3)
C(20)-C(15)-N(1)-C(7)  0.5(3)
C(9)-C(14)-N(1)-C(15)  123.8(3)
C(13)-C(14)-N(1)-C(15)  -56.7(4)
C(9)-C(14)-N(1)-C(7)  -7.3(3)
C(13)-C(14)-N(1)-C(7)  172.1(3)
N(2)-C(7)-N(1)-C(15)  -2.7(3)
N(3)-C(7)-N(1)-C(15)  119.5(2)
C(6)-C(7)-N(1)-C(15)  -126.9(2)
N(2)-C(7)-N(1)-C(14)  135.4(2)
N(3)-C(7)-N(1)-C(14)  -102.3(3)
C(6)-C(7)-N(1)-C(14)  11.3(3)
C(19)-C(20)-N(2)-C(7)  178.7(3)
C(15)-C(20)-N(2)-C(7)  -3.9(3)
C(19)-C(20)-N(2)-S(1)  3.0(5)
C(15)-C(20)-N(2)-S(1)  -179.6(2)
N(1)-C(7)-N(2)-C(20)  4.0(3)
N(3)-C(7)-N(2)-C(20)  -117.6(3)
C(6)-C(7)-N(2)-C(20)  121.0(3)
N(1)-C(7)-N(2)-S(1)  179.7(2)
N(3)-C(7)-N(2)-S(1)  58.0(3)
C(6)-C(7)-N(2)-S(1)  -63.3(3)
C(5)-C(8)-N(3)-C(7)  -2.1(3)
C(1)-C(8)-N(3)-C(7)  173.5(3)
C(5)-C(8)-N(3)-S(2)  153.6(2)
C(1)-C(8)-N(3)-S(2)  -30.8(4)
N(1)-C(7)-N(3)-C(8)  122.7(2)
N(2)-C(7)-N(3)-C(8)  -121.2(3)
C(6)-C(7)-N(3)-C(8)  7.3(3)
N(1)-C(7)-N(3)-S(2)  -34.5(3)
N(2)-C(7)-N(3)-S(2)  81.6(3)
C(6)-C(7)-N(3)-S(2)  -149.92(19)
C(20)-N(2)-S(1)-O(3) -40.5(3)
C(7)-N(2)-S(1)-O(3)  144.5(2)
C(20)-N(2)-S(1)-O(2) -169.2(3)
C(7)-N(2)-S(1)-O(2)  15.8(3)
C(20)-N(2)-S(1)-C(21) 76.0(3)
C(7)-N(2)-S(1)-C(21) -99.0(3)
C(26)-C(21)-S(1)-O(3) -158.5(3)
C(22)-C(21)-S(1)-O(3) 17.5(3)
C(26)-C(21)-S(1)-O(2) -27.3(3)
C(22)-C(21)-S(1)-O(2) 148.7(3)
C(26)-C(21)-S(1)-N(2) 85.5(3)
C(22)-C(21)-S(1)-N(2) -98.6(3)
C(8)-N(3)-S(2)-O(4)  35.9(3)
C(7)-N(3)-S(2)-O(4) -170.6(2)
C(8)-N(3)-S(2)-O(5)  164.7(2)
C(7)-N(3)-S(2)-O(5) -41.7(2)
C(8)-N(3)-S(2)-C(28) -79.4(3)
C(7)-N(3)-S(2)-C(28)  74.1(2)
C(33)-C(28)-S(2)-O(4) -42.4(3)
C(29)-C(28)-S(2)-O(4) 135.8(3)
C(33)-C(28)-S(2)-O(5) -174.3(3)
C(29)-C(28)-S(2)-O(5)  3.9(3)
C(33)-C(28)-S(2)-N(3) 71.4(3)
C(29)-C(28)-S(2)-N(3) -110.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 7a [Å and deg.].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
</table>

References: