Supplementary Information

Synthetic chemistry experimental

**Ethyl N-(2-cyanophenyl)carbamate (S1)**

![Chemical structure of S1](image)

2-Aminobenzonitrile (6.28 g, 53 mmol) and ethyl chloroformate (26 ml, 273 mmol) were mixed and heated to reflux for 6 hours. Excess solvent was evaporated in vacuo then 16 ml of toluene were added and then the reaction mixture was cooled to approximately 80 °C and then 38 ml of cyclohexane were added to induce crystallisation. The product was recrystallised from cyclohexane and dried under vacuum to obtain the product (S1) as pale yellowish crystals (7.26 g, 38.1 mmol, 95%).

Melting point 104-105 °C (Lit. 103-104 °C) (Gelotte et al., 1990).

1H NMR (400MHz, chloroform-d3) δ 8.24 (d, J = 8.4 Hz, 1H, H-6), 7.53 - 7.61 (m, 2H, Ar-H), 7.15 (br, s, 1H, NH), 7.09 - 7.14 (m, 1H, Ar-H), 4.27 (q, J = 7.1 Hz, 2H, CH2), 1.35 (t, J = 7.1 Hz, 3H, CH3).

13C NMR (101 MHz, chloroform-d3) δ ppm 152.9 (C=O), 141.0 (C-1), 134.2 (C≡N), 132.3 (C-Ar), 123.1 (C-Ar), 119.3 (C-Ar), 116.4 (C-Ar), 100.9 (C-Ar), 62.0 (CH2), 14.4 (CH3).

GC-MS m/z (relative intensity, %) 190 (20) (M+), 144 (100)

IR  cm⁻¹ 3300 (NH stretch), 2221 (CN stretch), 1705 (C=O stretch).

**3-Amino-N-2-(7-nitrobenzoyl) indoline-1-carboxylate (S2)**

![Chemical structure of S2](image)

Ethyl (2-cyanophenyl) carbamate (S1) (2.01 g, 13.8 mmol) was added to a solution of potassium carbonate (4.21 g, 30.46 mmol) in dimethyl-formamide (21 ml). The solution was stirred at room temperature for 45 minutes. A solution of 2-bromo-2' nitro acetophenone (3.05 g, 12.40 mmol) in DMF (10 ml) was added drop wise (over 5 min) to the reaction mixture and stirring was continued for 2.5 hours. Then the reaction mixture was slowly poured into 200 ml of distilled water and a yellow precipitate formed which was allowed to settle for 18 hours, which was then collected by filtration and dried in vacuo. Recrystallisation was carried out twice from methylated spirits and shiny yellow crystals of (S2) were obtained (2.18 g, 50%).

Melting point 204-205 °C

1H NMR (400MHz, chloroform-d3) δ ppm 8.13 (dd, J = 0.7 Hz, J = 7.7Hz, 1H), 7.93 - 7.99 (m, 1H), 7.52 - 7.65 (m, 5H, Ar-H), 7.31 - 7.38 (m, 1H, H-6), 6.32 (br, s, 2H, NH2), 3.90 (q, J = 7.1 Hz, 2H, CH2), 1.00 (t, J = 7.1 Hz, 3H, CH3).

13C NMR (101MHz, chloroform-d3) δ ppm 182.1 (C-1'), 151.4 (C-8), 147.4 (C-7'), 146.5 (C-Ar), 138.6 (C-7a), 136.5 (C-4a), 132.1 (C-3), 130.5 (C-7'), 129.8 (C-Ar), 128.0 (C-Ar), 124.0 (C-Ar), 123.1 (C-Ar), 121.3 (C-Ar), 119.6 (C-Ar), 116.3 (C-Ar), 114.6 (C-Ar), 62.6 (C-9), 13.4 (C-10).

ESI-MS M/z (relative intensity %) 354 (12) (M+), 376 (100) (M+Na)

IR cm⁻¹ 3461 (NH stretch), 3333 (CN stretch), 1705 (C=O stretch).

**5,10-dihydroindolo[3,2-b]quinolin-11-one (S3)**

![Chemical structure of S3](image)
To a solution of 3-amino-N-2-(7-nitrobenzoyl) indoline-1-carboxylate (S2) (0.77 g, 2.18 mmol) in THF (10ml), sodium hydride (0.20 g, 8.30 mmol) (60% w/v NaH in mineral oil) was added under dry conditions and the mixture was stirred for 1.75 hours. The reaction mixture was poured into 75 ml of distilled water then acidified by dropwise addition of concentrated acetic acid. A yellow-brown colour precipitate was collected by filtration which was then washed twice with water and dried in vacuo.

To the solid, 10 ml of ethanol were added with stirring to form a solution. Then aqueous sodium hydroxide solution (1.5 g in 10 ml) was added and the mixture was heated to reflux for 30 minutes. The reaction mixture was evaporated and the remaining residue was gently triturated with distilled water (25 ml). The solid was dried and recrystallised twice from ethanol to form yellow-brown crystals of 5,10-dihydroindolo[3,2-b]quinolin-11-one (S3) (230 mg, 69%).

**Melting point > 300 oC.**

**1H NMR (400 MHz, DMSO- d6)** \( \delta \) ppm 12.18 - 12.61 (s, 1 H), 11.57 - 11.75 (m, 1 H), 8.36 (dd, \( J =8.13, 1.14 \) Hz, 1 H), 8.19 (d, \( J =7.92 \) Hz, 1 H), 7.62 - 7.78 (m, 1 H), 7.42 - 7.55 (m, 1 H), 7.16 - 7.24 (m, 1 H)

**13C NMR (101 MHz, DMSO-d6)** \( \delta \) ppm 167.2 (C=O), 138.8 (C-4a), 138.4 (C-9a), 130.5 (C-5a), 128.7 (C-Ar), 127.2 (C-Ar), 125.0 (C-Ar), 122.9 (C-Ar), 122.7 (C-Ar), 120.6 (C-Ar), 120.2 (C-Ar), 117.6 (C-Ar), 115.7 (C-Ar), 112.4 (C-Ar).

**ESI-MS m/z (relative intensity, %)** 234 (13) (M+) 233 (100).

**IR cm**-1 3158 (NH stretch), 2953 (NH stretch), 1632 (C=O stretch), 1547.

**11-Bromo-10H-indolo[3,2-b]quinolone (S4)**

To 5,10-dihydroindolo[3,2-b]quinolin-11-one (S3) (0.20 g, 0.85 mmol), phosphorous oxybromide (0.2 g, 0.69 mmol) and phosphorous tri-bromide (2.5 ml, 26.32 mmol) were added. The mixture was heated to reflux for 16 hours. The reaction mixture was basified by using potassium hydrogen carbonate (10% aqueous solution) and extracted with chloroform (4 X 100 ml) and the organic phases were collected, combined and dried with magne-sium sulfate. The solvent was evaporated in vacuo to give a yellow solid (180 mg) was obtained which was purified by using column chromatography on silica gel (eluent 1:4 diethyl ether in hexane) to give a bright yellow coloured solid (S4) (92 mg, 36%).

**Melting point 117-118 oC**

**1H NMR (400 MHz, DMSO- d6)** \( \delta \) ppm 11.66 (br.s, 1H, NH), 8.37 (m, 1, H), 8.26 (m, 2H), 7.64 - 7.79 (m, 4H, Ar-H), 7.33 - 7.38 (m, 1H).

**13C NMR (101 MHz, DMSO-d6)** \( \delta \) ppm 145.7 (C-5a), 144.1 (C-9a), 143.9 (C-4a), 132.5 (C-10a), 130.5 (C-Ar), 129.4 (C-Ar), 127.0 (C-Ar), 126.7 (C-Ar), 125.1 (C-Ar), 124.7 (C-Ar), 121.9 (C-Ar), 121.1 (C-Ar), 121.4 (C-5b), 120.4(C-Ar), 112.3 (C-Ar), 109.6(C-Ar).

**ESI-MS m/z (relative intensity, %)** 295(100) (M-1) 297 (99) (M+) (bromine iso-topes).

**11-Bromo-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4a)**
Under dry conditions, 11-Bromo-10H-indolo[3,2-b]quinoline (51) (Figure 4.4) (0.40 g, 1.35 mmol) and methyltriflate (0.26 ml, 2.38 mmol) were stirred in 12 ml of toluene for 24 hours at room temperature. The reaction mixture was poured into diethyl ether (150 ml) and the yellow precipitate was collected by filtration and dried in vacuo. Aqueous ammonia solution (3.3% v/v, 10 ml) was added to the solid which was stirred to convert the product to its free base form and then the mixture was extracted using chloroform (4 x 75ml). The collected organic layers were combined and were evaporated in vacuo to give the crude product which was then purified by column chromatography on silica gel by using DCM: methanol: NH4OH (5:1:0.1) as the eluent. Finally the free base was converted to its hydrochloride salt by neutralising with 0.1 M methanolic hydrochloric acid (5 ml) and the solution was evaporated in vacuo to give 11-Bromo-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride, a bright yellow coloured solid (38) (Figure 4.5) (45 mg, 11%).

Melting point 120-122 oC

1H NMR (400 MHz, methanol -d4) δ ppm 9.14 - 9.17 (s, 1 H, NH), 8.75 - 8.80 (m, 1 H), 8.65 - 8.71 (m, 1 H), 8.47 - 8.53 (m, 1 H), 8.16 - 8.23 (m, 1 H), 7.92 - 8.00 (m, 1 H), 7.82 - 7.87 (m, 1 H), 7.54 - 7.61 (m, 1 H), 5.13 (s, 3 H, CH3)

13C NMR (101 MHz, methanol-d4) δ ppm 147.31 (C-9a), 145.2 (C-10a), 143.31 (C-5a), 130.40 (C-4a), 130.29 (C-Ar), 129.32 (C-Ar), 127.81 (C-Ar), 126.03 (C-11) (C-Ar), 124.10 (C-11a), 122.64 (C-Ar), 122.54 (C-Ar), 120.96 (C-Ar), 119.54 (C-Ar), 111.10 (C-5b), 111.24 (C-Ar), 29.73.12 (N-CH3)

ESI-MS m/z (relative intensity, %) 312 (3) [M+2], 310 (3) [M+], (bromine iso-topes), 232 (100).

IR cm⁻¹ 3556 (NH stretch), 1684 (C=N conjugated system)

10H-indolo[3,2-b]quinoline-11-carboxylic acid (55)

Isatin (4.25 g, 28.89 mmol) in aqueous sodium hydroxide solution (25.75 g in 115 ml of water) was added to indoxyl acetate (5.00 g, 28.54 mmol) and the mixture was stirred for 10 days under nitrogen. Water (50 ml) was added to the mixture and air was passed through the solution slowly to allow excess indoxyl acetate to oxidise, then the solution was heated to boiling and filtered to collect the hot filtrate. Concentrated hydrochloric acid (36% v/v aqueous) was added drop wise to the filtrate with vigorous stirring until a slight permanent precipitate was formed then 0.5 g of activated charcoal was added and the mixture was filtered. The filtrate was added to the same volume of ethanol with stirring then the solution was acidified using concentrated hydrochloric acid, to form a precipitate which was collected by filtration and dried in vacuo to give quindoline-11-carboxylic acid (Figure 4.6) a bright yellow coloured solid (55) (5.38 g, 72%).

1H NMR (400 MHz, DMSO-d6) δ ppm 11.46 (br. s, NH), 9.03 - 9.17 (m, 1 H, H-1), 8.43 (d, 1 H, J=7.79 Hz, H-4), 8.25 - 8.37 (m, 1 H, H-9), 7.61 - 7.85 (m, 4 H), 7.27 - 7.41 (t, 1 H, J=8). 13C NMR (101 MHz, DMSO-d6) δ ppm 168.14 (C=O), 147.2 (C-9a), 145.3 (C-4a), 143.1 (C-Ar), 138.6 (C-Ar), 132.9 (C-Ar), 131.2 (C-Ar), 129.3 (C-Ar), 127.4 (C-Ar), 126.8 (C-Ar), 125.6 (C-Ar), 124.2 (C-Ar), 122.2(C-Ar), 120.9(C-Ar), 120.5(C-Ar), 113.2(C-Ar), 112.5(C-Ar).

IR cm⁻¹ 1705 (C=O stretch), 3343 (amine NH stretch)

ESI-MS m/z (relative intensity, %) 262(100) (M+)
To 5,10-dihydroindolo[3,2-b]quinolin-11-one (S3) (0.50 g, 2.13 mmol), phosphorous oxychloride (0.50 g, 3.26 mmol) and phosphorous pentachloride (0.5 g, 2.13 mmol) were added then the mixture was heated to re-flux for 4 hours. Then the reaction mixture was basified using aqueous sodium hydroxide solution (10% w/v, cooled to 0 oC) and extracted with ethyl acetate (4 X 100 ml). The organic phases were dried with magnesium sulfate then the solvent was evaporated in vacuo. A yellow coloured solid (180 mg) was obtained which was purified by using column chromatography on silica gel (eluent 1:5 diethyl ether in hexane) to give a pale-brown coloured solid (S6) (0.29 g, 53.8%). 1H NMR (400 MHz, DMSO-d6) δ ppm 11.89 (1H, NH), 8.37 (d, J=7.7 Hz, 1H), 8.30 (m, 2H), 7.76 (m, 2H), 7.68 (dd, J = 6.9, 8Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.35 (dd, J = 7.3, 7.7 Hz, 1H).

13C NMR (101 MHz, DMSO-d6) δ ppm 146.34 (C-4a), 145.31 (C-5a), 143.28 (C-9a), 130.87, 130.15 (C-11), 129.34 (C-9), 127.00 (C-Ar), 125.26 (C-Ar), 123.18 (C-Ar), 121.41 (C-Ar), 121.27 (C-Ar), 121.13 (C-Ar), 120.71 (C-Ar), 118.43 (C-Ar), 112.51 (C-Ar)

ESI-MS M/z (relative intensity, %) 253 (20) [M+], 255 (100) [M+2] (chlorine isotopes)

IR cm⁻¹ 3164 (N-H stretch), 2851 (C-H aromatic stretch)

According to general procedure B, 4.8 11-chloro-10H-indolo[3,2-b]quinoline (S6) ((0.09 g, 0.4 mmol) and methyl iodide (0.057 g, 0.4 mmol) were used to give 11-Chloro-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4c) as a yellow coloured solid (0.068 g, 56.1 %)

1H NMR (400 MHz, DMSO-d6) δ ppm 13.4 (s, NH), 8.84 (m, 2 H), 8.66 (d, J=8.28 Hz, 1 H), 8.26 (dd, J = 9.4, 7.7 Hz, 1H), 8.05 - 8.14 (m, 1 H), 7.93 - 8.01 (m, 1 H), 7.85 - 7.92 (m, 1 H), 7.55 (dd, J=8.9, 7.7 Hz, 1 H), 5.03 (s, 3 H, CH3).

13C NMR (101 MHz, DMSO-d6) δ ppm 146.4(C9a), 139.2 (C-5a), 136.2(C-4a), 135.0 (C-Ar), 133.3 (C-11), 132.2 (C-10a), 129.4 (C-11), 128.9 (C-Ar), 127.1 (C-Ar), 125.1 (C-Ar), 123.8 (C-Ar), 122.5 (C-Ar), 119.2 (C-Ar), 114.9 (C-Ar), 113.0 (C-9), 39.9 (N-CH3)

ESI-MS M/z (relative intensity, %) 269 (32.4) [M+2], 267 (100.0) [M+] (chlorine isotopes)

IR cm⁻¹ 3164 (N-H stretch), 1624(Conjugated cyclic C=N bend)
To 10H-indolo[3,2-b]quinoline-11-carboxylic acid (S5) (Figure 4.6) (1.80 g, 6.83 mmol) diphenyl ether (20 ml) was added and the mixture was heated to reflux for 6 hours. It was then cooled and petroleum ether (35ml) was added with stirring then the resulting crystals were collected by filtration and washed with excess petroleum ether and dried in vacuo to give pale green crystals of 10H-indolo[3,2-b]quinoline (S7) (Figure 4.9) (1.28 g, 85%)

Melting point 249-251 °C

1H NMR (400 MHz, DMSO-d6) δ ppm 11.4 (s, 1H, NH), 8.37 (d, J = 8.0, 1H), 8.29 (m, 1H), 8.20 (d, J=8.01, 1H), 8.11 (d, J=7.36 1H), 7.66 (m, 1H), 7.64 (m, 1H), 7.58 (d, J=7.26, 1H), 7.56 (m, 1H), 7.28 (m, 1H)

13C NMR (101 MHz, DMSO-d6) δ 146.2 (C-5a), 144.5 (C-9a), 143.9 (C-4a), 133.0 (C-10a), 130.2 (C-Ar), 129.2 (C-Ar) 128.0 (C-Ar), 127.2 (C-Ar), 126.5 (C-Ar), 125.3 (C-Ar), 121.5 (C-Ar), 119.8 (C-Ar), 113.5 (C-11), 112.0 (C-9).

ESI-MS M/z (relative intensity, %) 217 (100) [M+]

IR cm-1 3329 (NH stretch) and absence of carbonyl group

5-Methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (1)

According to the general procedure B, methyl iodide (1.28 g, 9.01 mmol) and 10H-indolo[3,2-b]quinoline (S7) (1.20 g, 5.864 mmol) were used to give cryp-tolepine (Figure 4.10) as a yellow coloured solid (1) (104 mg, 8%).

Melting point 280 - 282 °C

1H NMR (400 MHz, DMSO-d6) δ ppm 12.78 (s, NH), 9.28 (s, 1H), 8.81(d, 1H, J=8.5 Hz), 8.76 (d, 1H, J=9.1 Hz), 8.59 (dd, 1H, J=7.4, 1.0 Hz), 8.17 (ddd, 1H, J=8.0, 8.0, 1.4 Hz), 7.95 (dd, 1H, J=8.1, 8.1 Hz), 7.92 (dd, 1H, J=7.2, 7.2 Hz), 7.85 (d, 1H,J=8.3 Hz), 7.51 (ddd, 1H, J=7.7, 7.7, 1.0 Hz), 5.04 (s, 3H, N-CH3).

13C NMR (101 MHz, DMSO-d6) δ ppm 145.4 (C-9a) 139.7 (C-5a), 137 (C-4a) 135.2 (C-8), 133.7 (C-3), 132.5 (C-1), 130.6 (C-2), 127.6 (C-11a), 127.2 (C-10a), 126.9 (C-6), 125.1 (C-11), 121.8 (C-7), 117.9 (C-4), 114.8 (C-5b), 39.9 (CH3-N)

IR cm-1 (KBr): 3432 (NH stretch) 1626 (C-H Aromatic stretch)

ESI-MS M/z (relative intensity, %) 233 (100, M-Cl) 139 (11)

11-Iodo-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4b)
According to the general procedure B, Methyl iodide (0.2 ml, 5.25 mmol) and 11-bromo-10H-indolo[3,2-b]quinoline (S4) (Figure 4.4) (0.0265 g, 0.09 mmol) were used to give hydrochloride salt of 4.14 11-Iodo-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4b) as a bright yellow coloured solid (0.015 g, 43%)

\[ \delta \text{ppm 8.71 - 8.79 (m, 1 H), 8.64 (s, 2 H), 8.17 - 8.26 (m, 1 H), 7.94 - 8.04 (m, 2 H), 7.91 (s, 1 H), 7.53 - 7.63 (m, 1 H), 4.86 (s, 3 H, N-CH}_3 \]

\[ \delta \text{ppm = 143.32 (C-9a), 140.37 (C-5a), 135.7 (C-10a), 134.3 (C-4a), 134.1(C-3), 129.9 (C-Ar), 128.4 (C-Ar), 127.7 (C-Ar), 127.2 (C-Ar), 124.4 (C-Ar), 123.6 (C-7), 119.7 (C-Ar), 119.1 (C-Ar), 114.6 (C-Ar), 110.7 (C-Ar), 28.73 (N-CH}_3 \]

MS M/z (relative intensity, %) 359 (100, M - Cl), 360 (29)

IR cm⁻¹ 3322 (N-H stretch), 1613 (Conjugated cyclic C=N bend).

N-isopropyl-10H-indolo[3,2-b]quinoline-11-carboxamide (S8)

Using 10H-indolo[3,2-b]quinoline-11-carboxylic acid (S5) (0.5 g, 1.9 mmol) and isopropylamine (0.14ml, 1.9 mmol), general procedure C was followed to give N-isopropyl-10H-indolo[3,2-b]quinoline-11-carboxamide (Figure 4.12) as a yellow colour solid (S8) (0.77 g, 83.4%)

Melting point 263-265 oC

1H NMR (400 MHz, methanol-d4) \[ \delta \text{ppm 11.76 (s, N H), 7.63 (s, H) 7.42 (m, 1H), 7.81 (m, 1H), 7.91 (m, 2H), 8.2 (m, 1H), 8.3 (m, 2H) 8.6 (m, 1H) 3.77 (m, 1H) 1.04 (d, 6H) \]

13C NMR (101 MHz, methanol-d4) \[ \delta \text{ppm = 166.7 (C-12), 148.34 (C-5a), 145.2 (C- 9a) 143.42 (C-4a), 137.4 (C-10a), 134.0 (C-11), 129.2 (C-Ar), 128.6 (C-Ar), 127.7 (C-Ar), 127.1 (C-Ar), 125.0 (C-Ar), 123.4 (C-Ar), 123.0 (C-Ar), 118.9 (C-Ar), 117.2 (C-Ar), 114.5 (C-9), 41.1 (C-14), 22.5 (C -15, C-16) \]

ESI-MS: M/z (relative intensity, %) 303 (100, M+), 244 (80) 216 (85)

IR cm⁻¹ 1646 (amide C=O stretch) 3169 (NH stretch)

N-butyl-10H-indolo[3,2-b]quinoline-11-carboxamide (S9)

Using 10H-indolo[3,2-b]quinoline-11-carboxylic acid (S5) (0.5 g, 1.9 mmol) and isopropylamine (0.14ml, 1.9 mmol), general procedure C was followed to give N-isopropyl-10H-indolo[3,2-b]quinoline-11-carboxamide (Figure 4.12) as a yellow colour solid (S8) (0.77 g, 83.4%)
Using 10H-indolo[3,2-b]quinoline-11-carboxylic acid (S5) (Figure 4.6) (0.5 g, 1.9 mmol) and and butylamine (0.18 ml, 1.9 mmol), general procedure C was followed to give N-butyl-10H-indolo[3,2-b]quinoline-11-carboxamide (Figure 4.13) as a yellow colour solid (S9) (0.514 g, 91%)
Melting point 270-272 oC

1H NMR (400 MHz, DMSO- d6) δ ppm 11.42 (s, 1 H), 8.97 (t, J=5.40 Hz, 1 H), 8.41 (d, J=7.78 Hz, 1 H), 8.30 (d, J=7.78 Hz, 1 H), 8.09 - 8.18 (m, 1 H), 7.60 - 7.80 (m, 4 H), 7.30 - 7.40 (m, 1 H), 3.49 - 3.61 (m, 2 H), 1.71 (m, J=14.81, 7.36 Hz, 2 H), 1.03 (t, J=7.40 Hz, 3 H)
13C NMR (400 MHz, DMSO-d6) δ ppm 165.4 (C-12), 146.7 (C-5a), 144.9 (C-9a), 143.7 (C-4a), 130.5 (C-11), 129.6 (C-10a), 129.2 (C-Ar), 126.6 (C-Ar), 126.1 (C-Ar), 124.8 (C-Ar), 123.2 (C-Ar), 121.8 (C-Ar), 121.5 (C-Ar), 121.2 (C-Ar), 120.2 (C-Ar), 112.3 (C-9), 41.6 (C-14), 29.5 (C-15), 20.3 (C-16), 14.2 (C-17).

IR cm⁻¹ 1646 (amide C=O stretch)
ESI-MS: M/z (relative intensity, %) 317 (100, M) 244 (85), 216(79) 190 (50)

N-[2-(2-hydroxyethylamino)ethyl]-10H-indolo[3,2-b]quinoline-11-carboxamide (S10)

Using 10H-indolo[3,2-b]quinoline-11-carboxylic acid (S5) (Figure 4.6) (0.5 g, 1.9 mmol) and 2-(2 aminoethylamino)ethanol (0.14 ml, 1.9 mmol), general procedure C was followed to give N-[2-(2-hydroxyethylamino)ethyl]-10H-indolo[3,2-b]quinoline-11-carboxamide (S10) as a brownish yellow colour solid (0.078 g, 12%)

1H NMR (400 MHz, methanol-d4) δ ppm 8.36 (d, J=7.78 Hz, 1 H), 8.10 (dd, J=8.16, 4.39 Hz, 2 H), 7.43 - 7.64 (m, 4 H), 7.25 (t, J=7.40 Hz, 1 H), 3.69 - 3.84 (m, 4 H), 3.54 - 3.63 (m, 2 H), 3.35 (s, 2 H), 1.23 (br. s., 1 H)
13C NMR (101 MHz, methanol-d4) δ 166.3 (C-12), 147.6 (C-5a), 145.9 (C-9a), 144.1 (C-4a), 131.6 (C-11), 130.8 (C-Ar), 129.0 (C-Ar), 127.7 (C-Ar), 127.1 (C-Ar), 125.3 (C-Ar), 124.0 (C-Ar), 122.7 (C-Ar), 121.5 (C-Ar), 121.4 (C-Ar), 121.2 (C-7) (C-1), 112.7 (C-9), 60.9 (C-18), 51.6 (C-17), 40.07 (C-15), 38.6 (C-14)
ESI-MS: M/z (relative intensity, %) 347 (100, M+), 313 (49)
N-isopropyl-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-carboxamide hydrochloride (5a)

According to the general procedure A, N-isopropyl-10H-indolo[3,2-b]quinoline-11-carboxamide (S8) (0.2 g, 0.7 mmol) (Figure 4.12) and methyltriflate were used to give N-isopropyl-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-carboxamide hydrochloride (Figure 4.15) as yellow solid (5a) (0.037 g, 17%).

1H NMR (400 MHz, methanol-d4) δ ppm 8.75 (dd, \( J = 16.44, 8.91 \) Hz, 2 H), 8.40 (d, \( J = 8.53 \) Hz, 1 H), 8.22 (t, \( J = 7.78 \) Hz, 1 H), 7.91 - 8.09 (m, 2 H), 7.85 (d, \( J = 8.28 \) Hz, 1 H), 7.60 (t, \( J = 7.78 \) Hz, 1 H), 5.14 (s, 3 H), 4.46 - 4.57 (m, 1 H), 1.44 (d, \( J = 6.53 \) Hz, 6 H)

13C NMR (101 MHz, methanol-d4) δ 168.4 (C-12), 147.6 (C-9a) 139.14 (C-5a) 136.3 (C-Ar) 134.6 (C-Ar), 132.5 (C-Ar), 127.9 (C-Ar), 126.2 (C-Ar), 125.6 (C-Ar), 124.6 (C-Ar), 122.0 (C-Ar), 121.5 (C-Ar), 117.5 (C-Ar), 115.9 (C-Ar), 114.1 (C-Ar), 113.0 (C-9), 44.2 (C-14), 41.2 (N5-CH3), 22.92 (C-15, 16)

ESI-MS: M/z (relative intensity, %) 318 (100, M), 319 (20, M+1) HIRES-MS (ESI): calculated for [M - Cl] (C20H20N3OCl) required m/z 318.1606, found 318.1615

N-butyl-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-carboxamide chloride (5b)

According to the general procedure A, N-butyl-10H-indolo[3,2-b]quinoline-11-carboxamide (S9) (0.2 g, 0.6 mmol) and methyltriflate were used to give N-butyl-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-carboxamide chloride (5b) as yellow solid (0.048 g, 23%)

1H NMR (400 MHz, methanol-d4) δ ppm 12.66 (s, NH), 8.74 (dd, \( J = 15.43, 8.78 \) Hz, 2 H), 8.39 (dd, \( J = 8.47, 1.07 \) Hz, 1 H), 8.20 (d, \( J = 1.38 \) Hz, 1 H), 7.91 - 8.03 (m, 2 H), 7.82 (d, \( J = 8.41 \) Hz, 1 H), 7.58 (s, 1 H), 5.13 (s, 3 H), 3.70 (t, \( J = 7.28 \) Hz, 2 H), 1.78 (t, \( J = 7.34 \) Hz, 2 H), 1.48 - 1.61 (m, 2 H), 1.05 (t, \( J = 7.34 \) Hz, 3 H)

13C NMR (101 MHz, methanol-d4) δ 163.4 (C-12), 146.8 (C-9a), 139.7 (C-5a), 136.0(C-Ar), 134.6(C-Ar), 132.5 (C-Ar), 130.8(C-Ar), 130.3(C-Ar), 127.8(C-Ar), 126.3(C-Ar), 125.6(C-Ar), 123.0(C-Ar), 122.0(C-Ar), 117.4(C-Ar), 114.1 (C-Ar), 113.0(C-9), 39.7(53b-CH3), 30.9 (C-15), 20.0 (C-16), 12.4 (C-17) ESI-MS: M/z (relative intensity, %): 332 (100, M+), 333 (20, M+1) HIRES-MS (ESI): calculated for [M - Cl] - (C21H22N3OCl) required m/z 332.1763, found 332.1769
N-[2-(2-hydroxyethylamino)ethyl]-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-carboxamide chloride (5c)

According to the general procedure A, N-[2-(2-hydroxyethylamino)ethyl]-10H-indolo[3,2-b]quinoline-11-carboxamide (S10) (Figure 4.14) (0.2 g, 0.6 mmol) and methyltriflate were used to give N-[2-(2-hydroxyethylamino)ethyl]-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-carboxamide chloride (Figure 4.17) as orange-yellow solid (5c) (0.01 g, 4.39%).

1H NMR (400 MHz, methanol-d4) δ ppm 8.65 - 8.80 (m, 2 H), 8.41 - 8.53 (m, 1 H), 8.12 - 8.24 (m, 1 H), 7.89 - 8.01 (m, 2 H), 7.50 - 7.61 (m, 1 H), 5.12 (s, 3 H), 4.00 - 4.09 (m, 2 H), 3.87 - 3.98 (m, 2 H), 3.55 (m, 2 H)

13C NMR (101 MHz, methanol-d4) δ ppm 166.3 (C-12), 147.6 (C-9a), 145.9 (C-5a), 144.1 (C-4a), 131.6 (C-Ar), 130.8 (C-Ar), 129.0 (C-Ar), 127.7 (C-Ar), 127.1 (C-Ar), 125.3 (C-Ar), 124.0 (C-Ar), 122.7 (C-Ar), 121.5 (C-Ar), 121.4 (C-Ar), 121.2 (C-Ar), 112.7 (C-Ar), 57.6 (C-18), 51.6 (C-17), 48.4 (C-15), 39.7 (N-CH3), 37.5 (C-14)

ESI-MS M/z (relative intensity, %): 363 (100, M+Cl), 364 (60, M+1)
HIRES-MS (ESI): calculated for [M - Cl]- (C21H23N4O2Cl) required m/z 363.1821, found m/z 363.1828

N-isopropyl-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-amine hydrochloride (3a)

Using 11-Chloro-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4c) (Figure 4.8) (0.1 g, 0.3 mmol) and isopropylamine (0.05 ml, 0.6 mmol), gene-ral procedure D was followed to give N-isopropyl-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-amine hydrochloride (Figure 4.18) as yellow colour crys-tals (3a) (0.12 g, 61%).

Melting point 283-285 oC

1H NMR (400 MHz, methanol-d4) δ ppm 8.64 (d, J=8.53 Hz, 1 H), 8.54 (d, J=8.53 Hz, 1 H), 8.28 (d, J=8.78 Hz, 1 H), 7.98 - 8.09 (m, 1 H), 7.84 (d, J=8.28 Hz, 1 H), 7.67 - 7.79 (m, 1 H), 7.38 - 7.48 (m, 1 H), 4.68 (s, 3 H), 4.23 (m, 1H), 1.57 (d, J=6.27 Hz, 6 H)

13C NMR (101 MHz, DMSO) δ ppm 144.6 (C-Ar), 143.7 (C-9a), 137.5 (C-4a), 135.8 (C-5a), 131.9 (C-Ar), 127.8 (C-Ar), 127.6 (C-Ar), 125.9 (C-Ar), 124.5 (C-Ar), 123.1 (C-Ar), 121.44 (C-Ar), 119.8 (C-Ar), 116.5 (C-Ar), 112 (C-9), 53.94 (C-13), 39.65 (N-CH3), 22.9 (C-14, 15)

ESI-MS M/z (relative intensity, %) 290 (100, M+)
According to the general procedure D, 11-Chloro-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4c) (0.1 g, 0.3 mmol) and butylamine (0.06 ml, 0.6 mmol) were used to give N-buty1-5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-amine hydrochloride (Figure 4.19) as yellow crystals (3b) (0.07 g, 68%)

Melting point >300 oC

1H NMR (400 MHz, methanol-d4) δ ppm 8.47 - 8.65 (m, 2 H), 8.27 (d, J=8.78 Hz, 1 H), 8.02 (t, J=7.78 Hz, 1 H), 7.78 - 7.86 (m, 1 H), 7.72 (dt, J=14.43, 7.34 Hz, 2 H), 7.42 (t, J=7.65 Hz, 1 H), 4.67 (s, 3 H), 4.10 - 4.22 (m, 2 H), 1.84 - 1.96 (m, 2 H), 1.43 (d, J=7.53 Hz, 2 H), 0.88 (s, 3 H)

13C NMR (101 MHz, methanol-d4) δ ppm 144.2 (C-11), 142.1 (C-Ar), 137.5 (C-Ar), 133.83 (C-Ar), 131.95 (C-Ar), 127.84 (C-Ar), 127.65 (C-Ar), 125.93 (C-Ar), 124 (C-Ar), 123 (C-Ar), 121.44 (C-Ar), 119.8 (C-Ar), 116.5 (C-Ar), 112 (C-9), 56.41 (C-13), 38.65 (N5-CH3), 33.2 (C-14), 21.07 (C-15), 13.76 (C-16).

ESI-MS M/z (relative intensity, %)304 (100, M+)

HIRES-MS (ESI): calculated for [M - Cl]- (C20H22N3Cl) required m/z 304.1814, found 304.1810
According to the general procedure D, 11-Chloro-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4c) (Figure 4.8) (0.5 g, 1.6 mmol) and 2-(2-aminoethylamino)ethanol (0.162 ml, 1.6 mmol) were used to give 2-[2-([5-methyl-10H-indolo[3,2-b]quinolin-5-ium-11-yl)amino]ethylamino]ethanol chloride (3d) (0.1364 g, 23%).

Melting point >300 oC
1H NMR (400 MHz, DMSO- d6) δ ppm 11.58 (s, 1H, NH), 8.85 - 8.91 (m, 1H), 8.54 - 8.61 (m, 1H), 8.35 - 8.41 (m, 1H), 7.96 - 8.06 (m, 2H), 7.67 - 7.76 (m, 2H), 7.33 - 7.42 (m, 1H), 4.65 (s, 3H), 3.57 - 3.70 (m, 2H), 2.83 - 2.92 (m, 2H), 2.66 - 2.71 (m, 2H), 2.56 - 2.65 (m, 2H)
13C NMR (101 MHz, DMSO- d6) δ ppm 145.9 (C-11), 139.3 (C-9a), 137.4 (C-4a), 133.43 (C-Ar), 131.95 (C-Ar), 127.84 (C-Ar), 127.65 (C-Ar), 125.93 (C-Ar), 124 (C-Ar), 123 (C-Ar), 121.4 (C-Ar), 119.8 (C-Ar), 116.5 (C-Ar), 114.6 (C-Ar), 112.7 (C-9), 57.51 (C-17), 57.03 (C-13), 52.4 (C-16), 49.6 (C-14), 38.4 (N5-CH3)
ESI-MS M/z (relative intensity, %) 335 (100, M) 336 (35, M+1)
HIRES-MS (ESI): calculated for [M - Cl]- (C20H23N4OCl) required m/z 335.1872, found 335.1875
According to the general procedure A, 11-chloro-10H-indolo[3,2-b]quinoline (S6) (0.2 g, 0.8 mmol) and ethyl triflate (0.15 g, 0.8 mmol) were used to give 11-chloro-5-ethyl-10H-indolo[3,2-b]quinolin-5-ium chloride as brownish yellow solid (4d) (0.142 g, 56%).

**1H NMR (400 MHz, DMSO- d6)** \( \delta \) ppm 12.82 (s, NH), 8.49 (m, 1H), 8.24 (m, 1H) 8.16 (m, 1H) 8.09 (m, 1H), 7.68 (m, 1H), 7.64 (m, 1H), 7.24 (m, 1H), 5.2 (q, \( J = 6.80 \) Hz, 2H, CH2), 1.80 (t, \( J = 6.80 \) Hz, 3H, CH3).

**13C NMR (101 MHz, DMSO- d6)** \( \delta \) ppm 147.5 (C-9a), 139.7 (C-5a), 138.1 (C-4a), 138.70 (C-Ar) 136.75 (C-Ar), 135.4 (C-Ar), 133.02 (C-Ar), 128.23 (C-Ar), 126.9 (C-Ar), 125 (C-Ar), 124.5 (C-Ar), 123 (C-Ar), 119.42 (C-Ar), 115.4 (C-5b), 114.1(C-9), 47.8 (N5-CH2), 13.8 (N5-CH3)

**ESI-MS M/z (relative intensity, %)** 281 (100, M+) 263 (31)

**HIRES-MS (ESI)**: calculated for [M - Cl]- (C17H14N2Cl2) required m/z 281.0846, found 281.0842

**N-butyl-5-chloro-5-ethyl-10H-indolo[3,2-b]quinolin-11- amine (3e)**

According to the general procedure D, 11-chloro-5-ethyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4d) (0.10 g, 0.3 mmol) and butylamine (0.044 g, 0.3 mmol) were used to give N-butyl-5-chloro-5-ethyl-10H-indolo[3,2-b]quinolin-11-ammine (Figure 4.22) as yellow colour crystals (3e) (0.037 g, 35%).

**Melting point** 296-298 °C

**1H NMR (400 MHz, methanol-d4)** \( \delta \) ppm 8.65 (d, \( J = 8.53 \) Hz, 1H), 8.30 - 8.47 (m, 2H), 8.07 (t, \( J = 7.78 \) Hz, 1H), 7.83 - 7.93 (m, 1H), 7.67 - 7.82 (m, 2H), 7.49 (t, \( J = 7.65 \) Hz, 1H), 5.24 (q, \( J = 7.28 \) Hz, 2H, N-Ch2), 4.22 (t, \( J = 7.03 \) Hz, 2H), 2.85 - 3.01 (m, 3H), 1.94 (quin, \( J = 7.28 \) Hz, 2H), 1.81 (t, \( J = 7.15 \) Hz, 3H), 1.53 - 1.72 (m, 2H), 1.46 (sxt, \( J = 7.43 \) Hz, 2H), 1.03 (t, \( J = 7.22 \), Hz, 3H)

**13C NMR (101 MHz, methanol-d4)** \( \delta \) ppm 144.08 (C-11), 143.73 (C-9a), 143.02(C-4a), 137.5,133.83, 131.95, 127.84, 125.93(C-Ar), 124.52 (C-Ar), 123.04 (C-Ar), 121.44 (C-Ar), 119.8 (C-Ar), 116.5 (C-Ar), 112.3 (C-4), 112 (C-9), 49.2 (C-13) 43.14 (N5-CH2), 33.2 (C-14), 21.07 (C-15), 13.76 (N5-CH3), 12.98 (C-C16)

**ESI-MS M/z (relative intensity, %)** 318 (100, M+) 319 (20, M+1)

**HIRES-MS (ESI)**: calculated for [M - Cl]- (C21H14N2Cl2) required m/z 318.1970, found 318.1961
5-methyl-N-pentyl-10H-indolo[3,2-b]quinolin-5-ium-11-amine chloride (3c)

According to the general procedure D, 11-Chloro-5-methyl-10H-indolo[3,2-b]quinolin-5-ium chloride (4c) (0.1 g, 0.3 mmol) and pentylamine (0.523 g, 0.6 mmol) were used to give 5-methyl-N-pentyl-10H-indolo[3,2-b]quinolin-5-ium-11-amine chloride (3c) (Figure 4.23) as yellow crystals (0.06 g, 67%).

Melting point 303-305 oC

1H NMR (400 MHz, DMSO-d6) δ ppm 8.79 (d, J = 8.28 Hz, 1H), 8.58 (d, J = 8.53 Hz, 1H), 8.36 (d, J = 8.78 Hz, 1H), 8.03 (t, J = 7.53 Hz, 1H), 7.90 (d, J = 8.28 Hz, 1H), 7.66 - 7.77 (m, 2H), 7.39 (t, J = 7.65 Hz, 1H), 4.63 (s, 3H), 4.17 (t, J = 7.03 Hz, 2H), 1.21 - 1.5 (m, 6H), 0.88 (m, J = 2.76, 6.90 Hz, 3H)

13C NMR (101 MHz, DMSO-d6) δ ppm 144.09 (C-11), 143.63 (C-9a), 137.5 (C-4a), 133.83 (C-Ar), 131.95 (C-Ar), 127.84 (C-Ar), 127.65 (C-Ar), 125.93 (C-Ar), 124 (C-Ar), 123 (C-Ar), 121.44 (C-Ar), 119.8 (C-Ar), 116.5 (C-Ar), 113.1 (C-4), 112 (C-9), 47.92 (C-13) 38.22 (N5-CH3), 32.4 (C-14), 28.34 (C-15), 22.31(C-16), 14 (C-17).

ESI-MS M/z (relative intensity, %) 318 (100, M+) 319 (20, M+1)