DOI: 10.1002/ejoc.201000596

# Water-Accelerated Cationic π-(7-*endo*) Cyclisation: Application to Indole-Based Peri-Annulated Polyheterocycles[‡]

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**Keywords:** Nitrogen heterocycles / Medicinal chemistry / Cyclization / Cations

An efficient and versatile method for the synthesis of indole-based polycyclic indolo-benzazepine and its derivatives through water-accelerated cationic π-cyclisation is described. The strategy involves condensation of arylamine moieties linked to C-4 in indole/azaindole systems with arylaldehydes in water containing catalytic amount of Brønsted acids. The C–C bond formation in water is complete within 10–30 min, furnishing the title compounds in excellent yields and purities, whereas in organic solvents 10–12 h are required. Furthermore, aldehydes both with electron-donating and-withdrawing substituents facilitate the π-cyclisation equally.

## Introduction

Indole-based fused heterocycles belong to the most widely distributed naturally occurring compounds, isolated from plants, fungi and marine organisms.[1] The range of applications for these therapeutically relevant compounds includes as protein kinase C inhibitors, as 5-HT agonists, as melatonin agonists and as glucocorticoid receptor modulators, displaying cytotoxic, antiviral, antimicrobial, antiparasitic, antiinflammatory, antiserotonin, Ca2þ, calmodulin-antagonistic and antitopoisomerase-I activities.[2] These polyheterocycles frequently feature structurally diverse

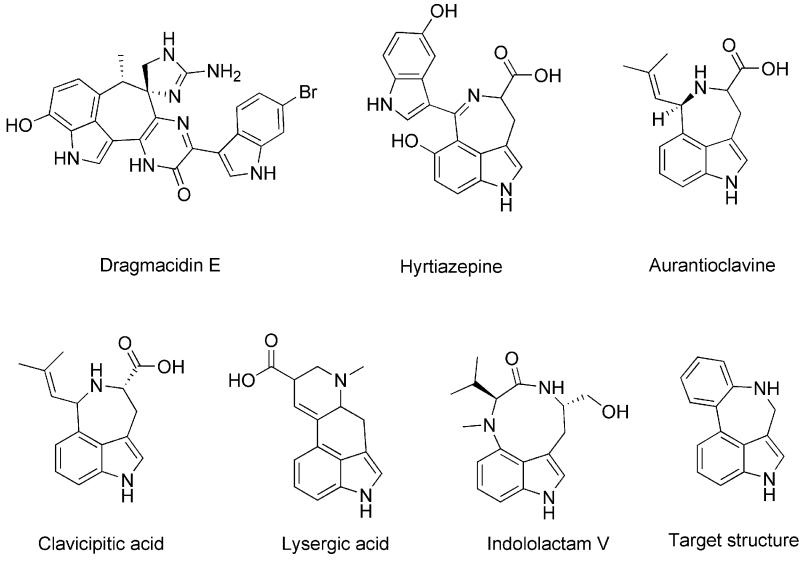


Figure 1. Structures of naturally occurring indole-based peri-annulated frameworks and the target molecule.

novel frameworks and remain a source of new natural-product-inspired[3] chemical entities for chemical biology-research.

Of the myriad reactions devoted to the synthesis of indole-based polyheterocycles, π-cyclisation reactions have remained a method of choice, and chemists continue to develop efficient and practical variants of these reactions to

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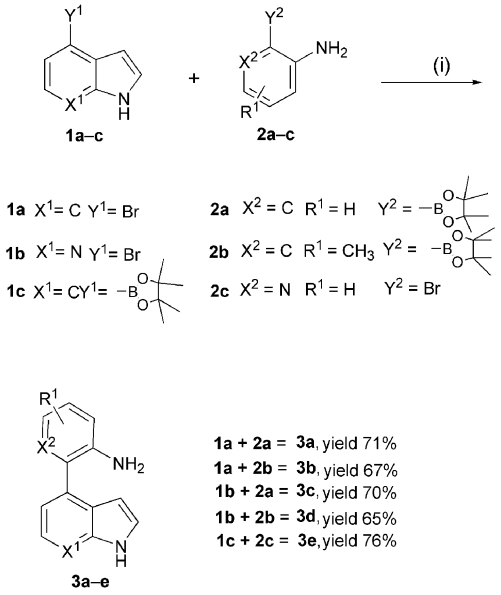
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000596.

make use of mild reaction conditions, substrate manipulation, and environmentally friendly catalysts/conditions.[4] In continuation of our ongoing studies relating to the synthesis of indole-based polyheterocycles indolo-quinolines[5] and azepino-indoles[6] through π-cyclisations, coupled with our interest in carrying out organic reactions in water,[7] we were prompted to use π-cyclisation reactions in aqueous media for the generation of indole-based polyheterocycles. In recent years, water has been demonstrated as an ideal medium for many organic transformations even if the starting materials and products appear to be insoluble.[8] In fact, ever since the application of water as a solvent in organic chemistry was rediscovered by Breslow,[9] a variety of organic reactions, including allylation, the Diels–Alder reaction,[10] the Wittig reaction,[11] the aldol reaction,[12] Mannich-type reactions,[13] the Michael reaction,[14] the Claisen rearrangement,[15] Sonogashira coupling,[16] Tsuji–Trost-type reactions,[17] the Heck reaction[18] and even dehydration reactions,[19] have been achieved in water with significant enhancements of the reaction rates.[20] This has been attributed to hydrophobic packing,[9] solvent polarity,[21] hydration[22] and hydrogen bonding.[23] Here we describe the water-accelerated synthesis of indolo[3,4-*cd*][1]benzazepine and its derivatives through π-cyclisation reactions.

For our studies involving π-cyclisation reactions in aqueous media, the target structure indolo[3,4-*cd*][1]benzazepine (Figure 1) was inspired by several naturally occurring indole-based peri-fused frameworks in which the indole rings are fused through C-3 and C-4 to six-, seven- and eight-membered rings.[24] To the best of our knowledge this is the first report dealing with the cationic π-(7-*endo*-*trig*) cyclisation in water. Literature reports dealing with the synthesis of peri-fused indoles are scarce and have been predominantly reported in organic solvents.[25]

## Results and Discussion

The synthetic strategy for the indolo-benzazepines involved the preparation of a key intermediate of type **3** (Scheme 1) in which an arylamine is tethered to the indole at C-4. We envisaged that condensation of intermediates of type **3** with aldehydes might facilitate cationic π-cyclisation in the resulting aldimines to furnish indole-annulated seven-membered rings through the involvement of the nucleophilic indole C-3, which is in the "*meta*" position relative to C-4. The substrates of type **3** differ from our previous indole-based arylamine substrates[4] with respect to the location of the arylamine, which is generally "*ortho*"-oriented instead of "*meta*" with respect to the nucleophilic carbon (C-2/C-3). Our studies commenced with the synthesis of the substrate **3a** (Scheme 1), required as a key intermediate for the Pictet–Spengler reaction, which was carried out by means of a Suzuki coupling reaction between 4-bromoindole (**1a**) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylamine (**2a**, Scheme 1). In order to increase the diversity in compounds **3**, the strategy was then successfully also applied to the synthesis of substrates **3b**–**d**. Compound **3e**, however, was synthesised through the coupling of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**1c**) with 2-bromopyridin-3-amine.




Scheme 1. Reagents and conditions: i) $PdCl_2(PPh_3)_2$, $Na_2CO_3$, 80 °C, DMF, 4 h.

The boronates were in general prepared by treatment of bromo compounds with bis[pinacolato]diboron by the procedure published elsewhere[26] and were used in situ for the Suzuki coupling. Similarly, 4-bromo-7-azaindole, required for the synthesis of substrates **3c** and **3d**, was obtained by treatment of 7-azaindole with *m*CPBA in ethyl acetate to give the *N*-oxide, which was then treated with methanesulfonic anhydride and tetramethylammonium bromide in DMF at room temp. to give the desired product.[27]

Once we had the desired substrates **3a**–**e** to hand, we next investigated their abilities to undergo cationic π-(7-*endo*) cyclisation when condensed with aldehydes both in water and in organic solvent. Because Pictet–Spengler reactions are in general more favoured with aldehydes bearing electron-withdrawing groups as substituents than with aldehydes bearing electron-donating groups, we initially examined the capability of the substrate **3a** to undergo 7-*endo* cyclisation (Table 1) with aldehydes bearing either an electron-donating or an electron-withdrawing substituent. Interestingly, the cationic π-cyclisation occurred both in organic and in aqueous media through the attack of the electron-rich C-3 nucleophile of the indole ring on the iminium ion, thereby resulting in a seven-membered ring annulated to the indole ring. The final compound after crystallisation was characterised by NMR and ESMS as the indolo-benzazepine **4b**. Interestingly, out of the different acidic protocols (Table 1) used, the best results were obtained when the substrate **3a** was treated with 4-nitrobenzaldehyde in TFA in water (5%) at room temp. for 10 min, which effected complete conversion of **3a** and afforded **4b** with >95% purity based on HPLC and in >90% isolated yield. Out of the

Table 1. Optimisation of reaction conditions for the conversion of **3a** into **4b** and **4f**.

| Entry | Reaction conditions | Temp (°C) | Time | 4-Nitrobenzaldehyde | 4-Ethoxybenzaldehyde |
|---|---|---|---|---|---|
| 1 | TFA in $CH_3CN$ (2%) | r.t. | 24 h | 46 | 41 |
| 2 | $Yb(OTf)_3$ in $CH_3CN$ | r.t. | 24 h | 35 | 30 |
| 3 | *p*-TsOH in $CH_3CN$ (1%) | r.t. | 24 h | 36 | 28 |
| 4 | triflic acid in DMF (1%) | r.t. | 24 h | 36 | 29 |
| 5 | TFA in DCM (2%) | r.t. | 12 h | 90 | 83 |
| 6 | TFA in water (5%) | r.t. | 10 min | 94 | 87 |
| 7 | $Yb(OTf)_3$ in water | r.t. | 12 h | n.r.[a] | n.r. |

[a] n.r. = no reaction.

Table 2. Optimisation of reaction conditions for the conversion of **3c** into **6c** and **6e**.

| Entry | Reaction conditions | Temp. [°C] | Time | 4-Nitrobenzaldehyde | 3,4-Dimethoxybenzaldehyde |
|---|---|---|---|---|---|
| 1 | TFA in water (1%) | room temp. | 30 min | 33 | 21 |
| 2 | TFA in water (2%) | room temp. | 30 min | 42 | 29 |
| 3 | TFA in water (5%) | room temp. | 30 min | 93 | 37 |
| 4 | TFA in water (5%) | 80 °C | 30 min | 90 | 82 |
| 5 | TFA in water (10%) | 80 °C | 30 min | 94 | 85 |

organic solvents studied, TFA in dry DCM (2%) at room temp. for 12 h effected complete conversion of **3a** into **4b**. The use of water as a reaction medium had thus significantly enhanced the rate of cationic π-cyclisation relative to the organic solvent protocol.

Similarly, condensation of 4-ethoxybenzaldehyde with the substrate **3a** furnished the peri-fused product **4f** in the presence of TFA in water (5%) at room temp. in 10 min (Method A) whereas in organic solvents such as TFA in dry DCM (2%) at room temp. it took 12 h for completion of the reaction. The use of other acid/Lewis acid catalysts traditionally used under Pictet–Spengler protocols, such as *p*TsOH and $Yb(OTf)_3$ either at room temp. or in the complete absence of an acid catalyst, failed to produce *endo*-cyclised products both in the organic solvent and in water.

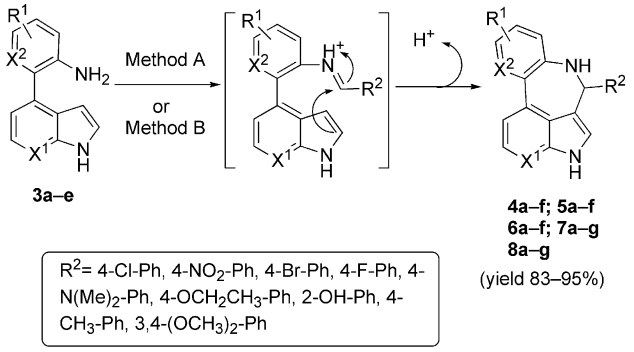
We next examined the efficacy of the 7-azaindole-based substrate **3c** in undergoing π-cyclisation under aqueous conditions. Surprisingly, treatment of **3c** with 4-nitrobenzaldehyde or with 3,4-dimethoxybenzaldehyde in TFA in water (5%) at room temp. failed to result in complete cyclisation, furnishing the desired products **6c** and **6e** only in poor yield. This prompted us to optimise the reaction conditions through variation of the concentration of TFA and of the temperature (Table 2). The best results were obtained when condensation of **3c** with the aldehydes bearing electron-donating or electron-withdrawing groups was carried out in the presence of TFA in water (10%) at 80 °C for 30 min (Method B).

After successfully optimizing the reaction conditions for the indole- and 7-azaindole-based substrates **3**, we examined the scope and limitations of the strategy by treating the substrates **3a**–**e** with 11 different arylaldehydes and aliphatic aldehydes. In all cases, the substrates efficiently underwent π-cyclisation when condensed with aromatic aldehydes to yield 34 compounds (**4a**–**g**, **5a**–**i**, **6a**–**f**, **7a**–**f** and **8a**–**j**) in excellent yields (Table 3, Scheme 2). In general, the reactions were not sensitive to the electronic properties of the substituent on the phenyl ring, with both electron-donating groups and electron-withdrawing groups being successfully employable with equal ease. The isolated yields of the final compounds varied from 83–95%.

Table 3. Synthesis of indolo-benzazepines **4**, **5**, **8** and benzoazulenes **6**, **7**.

| Entry | Substrate | $R^2$ | Product | Yield [%] |
|---|---|---|---|---|
| 1 | **3a** | 4-Cl-$C_6H_4$ | **4a** | 93 |
| 2 | **3a** | 4-$NO_2$-$C_6H_4$ | **4b** | 94 |
| 3 | **3a** | 4-Br-$C_6H_4$ | **4c** | 91 |
| 4 | **3a** | 4-F-$C_6H_4$ | **4d** | 89 |
| 5 | **3a** | 4-$CH_3$-$C_6H_4$ | **4e** | 86 |
| 6 | **3a** | 4-$C_2H_5O$-$C_6H_4$ | **4f** | 87 |
| 7 | **3a** | 2-OH-$C_6H_4$ | **4g** | 85 |
| 8 | **3b** | 4-Cl-$C_6H_4$ | **5a** | 90 |
| 9 | **3b** | 4-$NO_2$-$C_6H_4$ | **5b** | 92 |
| 10 | **3b** | 4-Br-$C_6H_4$ | **5c** | 88 |
| 11 | **3b** | 4-F-$C_6H_4$ | **5d** | 87 |
| 12 | **3b** | 4-$CH_3$-$C_6H_4$ | **5e** | 84 |
| 13 | **3b** | 4-$C_2H_5O$-$C_6H_4$ | **5f** | 86 |
| 14 | **3b** | 4-$N(CH_3)_2$-$C_6H_4$ | **5g** | 83 |
| 15 | **3b** | $CH_3CH_2$ | **5h** | 45 |
| 16 | **3b** | $(CH_3)_3C$ | **5i** | 54 |
| 17 | **3c** | 4-Cl-$C_6H_4$ | **6a** | 90 |
| 18 | **3c** | 4-Br-$C_6H_4$ | **6b** | 91 |
| 19 | **3c** | 4-$NO_2$-$C_6H_4$ | **6c** | 94 |
| 20 | **3c** | 2-OH-$C_6H_4$ | **6d** | 86 |
| 21 | **3c** | 3,4-di-$OCH_3$-$C_6H_3$ | **6e** | 85 |
| 22 | **3c** | 4-F-$C_6H_4$ | **6f** | 88 |
| 23 | **3d** | 4-Cl-$C_6H_4$ | **7a** | 89 |
| 24 | **3d** | 4-Br-$C_6H_4$ | **7b** | 87 |
| 25 | **3d** | 4-$NO_2$-$C_6H_4$ | **7c** | 90 |
| 26 | **3d** | 4-F-$C_6H_4$ | **7d** | 88 |
| 27 | **3d** | 4-$C_2H_5O$-$C_6H_4$ | **7e** | 86 |
| 28 | **3d** | 4-$CH_3$-$C_6H_4$ | **7f** | 85 |
| 29 | **3e** | 4-Cl-$C_6H_4$ | **8a** | 91 |
| 30 | **3e** | 4-Br-$C_6H_4$ | **8b** | 93 |
| 31 | **3e** | 4-$NO_2$-$C_6H_4$ | **8c** | 95 |
| 32 | **3e** | 4-F-$C_6H_4$ | **8d** | 90 |
| 33 | **3e** | 4-$C_2H_5O$-$C_6H_4$ | **8e** | 88 |
| 34 | **3e** | 4-$CH_3$-$C_6H_4$ | **8f** | 86 |
| 35 | **3e** | 2-OH-$C_6H_4$ | **8g** | 85 |
| 36 | **3e** | 3,4-di-$OCH_3$-$C_6H_3$ | **8h** | 87 |
| 37 | **3e** | $CH_3$ $CH_2$ | **8i** | 51 |
| 38 | **3e** | $(CH_3)_3C$ | **8j** | 63 |




Scheme 2. Reagents and conditions, Method A: $R^2CHO$, TFA in $H_2O$ (5%) at room temp., 10 min; Method B: $R^2CHO$, TFA in $H_2O$ (10%) at 80 °C, 30 min.

Condensation of the substrates **3b** and **3e** with aliphatic aldehydes (Entries 15, 16, 37 and 38) furnished the endo cyclised products in moderate yields (45–63%). Ketones failed to undergo cationic π-(7-*endo*) cyclisation generally, with ketimines remaining the only products isolated even after three days of heating. This may be attributed to the lower electrophilicities of ketimines than their aldimine counterparts,[28] because the electrophilicities of imines have been documented as the driving force for cationic π-cyclisation.[29]

## Conclusions

We have developed a mild and efficient method for the synthesis of indole-based perifused polycycles through water-accelerated cationic π-cyclisation in water. The workup procedure was effortless and purification of the products did not require column chromatography, which proved to be an additional advantage for the synthesis of indolo-benzazepine and benzoazulene motifs.

## Experimental Section

**General:** All solvents were commercially available and were used without purification. All products were characterised by $^1$H NMR, $^{13}$C NMR, ESMS, HRMS, IR and HPLC. Analytical TLC was performed with 2.5 × 5 cm plates coated (0.25 mm) with silica gel 60F-254 and visualisation was accomplished with UV light and iodine. Column chromatography was performed with silica gel (100–200 mesh). $^1$H NMR spectra (300 MHz and 200 MHz) are reported as follows: chemical shifts in ppm downfield from TMS as internal standard ($\delta$ scale), multiplicity [br. s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, o = overlapped, integration and coupling constant (Hz)]. All $^{13}$C NMR spectra (75 MHz and 50 MHz) were determined with complete proton decoupling and are reported in ppm. Analytical HPLC was performed with a reversed-phase C-18 column (250 mm × 4.6 mm). Retention time on HPLC (C18 reversed-phase column; 150 × 4.6 mm; 5 μm) with a linear gradient of 10–100% $CH_3CN$ in water over 30 min, flow rate of 1.0 mL min$^{-1}$ and UV detection at 220/254 nm. Mass spectra were recorded with a electron-spray mass spectrometer.

**General Procedure for the Synthesis of Substrates 3a–e by Suzuki Coupling:** A solution of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylamine (**2a**, 1.00 g, 4.56 mmol) and 4-bromo-1*H*-indole (**1a**, 0.89 g, 4.56 mmol) in DMF (5 mL) was degassed with nitrogen for 15 min, followed by addition of $Na_2CO_3$ (1.45 g, 2 M in water) under a continuous flow of nitrogen. $PdCl_2(PPh_3)_2$ (0.32 g, 0.45 mmol) was added under nitrogen and the reaction mixture was stirred at 80 °C for 4 h. The solution was diluted with $H_2O$ (5 mL) and the product was extracted three times with EtOAc (10 mL). The combined organic layer was dried with $Na_2SO_4$ and the solvent was removed in vacuo. The crude product was purified with a silica gel column and with hexane/ethyl acetate (90:10, v/v) as eluent to afford 2-(1*H*-indol-4-yl)aniline (**3a**) in 71% yield.

**General Procedure for the Synthesis of 2-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenylamine (2a):** A solution of bis[pinacolato]diboron (3.24 g, 12.78 mmol), 2-bromoaniline (2.0 g, 11.62 mmol), tricyclohexylphosphane (0.39 g, 1.39 mmol) and potassium acetate (1.7 g, 17.43 mmol) in dry dioxane (15 mL) was purged with nitrogen for 15 min, followed by the addition of tris[dibenzylideneacetone]dipalladium(0) (0.53 g, 0.58 mmol). The reaction mixture was heated at 80 °C for 16 h, filtered through celite, washed with ethyl acetate and concentrated to provide the product, which was used without further purification.

**General Procedure for the Pictet–Spengler Reaction Leading to the Synthesis of the Indolo-benzazepine and Benzoazulene Derivatives 4, 5, 6, 7 and 8:** A solution of a compound **3** (1 equiv.) and a corresponding aldehyde $\mathbf{R^2}$ (1.1. equiv.) was treated with a solution of trifluoroacetic acid in $H_2O$ (5%, 5 mL). The reaction mixture was stirred at room temp. for 10 min. After completion of the reaction, $NaHCO_3$ solution was added and the product was extracted three times with EtOAc (5 mL). The combined organic layer was dried with $Na_2SO_4$ and the solvent was removed in vacuo. The crude product was purified by trituration with $Et_2O$ in hexane, (5%) to afford the pure compound.

**2-(1*H*-Indol-4-yl)phenylamine (3a):** Yield 1.51 g (71%), light yellow solid, m.p. 135–136 °C, $R_f$ = 0.83 (EtOAc/hexane, 1:1). $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.17 (br. s, 1 H, ArNH), 7.39 (d, $J$ = 8.1 Hz, 1 H, ArH), 7.35–7.33 (m, 1 H, ArH), 7.16 (t, $J$ = 7.3 Hz, 1 H, ArH), 7.10–7.04 (m, 2 H, ArH), 6.95 (d, $J$ = 7.1 Hz, 1 H, ArH), 6.80–6.77 (m, 1 H, ArH), 6.68–6.63 (m, 1 H, ArH), 6.18–6.17 (m, 1 H, ArH), 4.57 (br. s, 2 H, $NH_2$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 145.1, 136.1, 131.2, 130.3, 126.7, 125.5, 125.3, 125.2, 110.5, 110.3, 100.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3393, 1603, 1481 cm$^{-1}$. MS (ES$^+$): $m/z$ = 209.3 [M + 1]$^+$. $C_{14}H_{12}N_2$ (208.26): calcd. C 80.74, H 5.81, N 13.45; found C 80.65, H 5.92, N 13.51.

**2-(1*H*-Indol-4-yl)-4-methylphenylamine (3b):** Yield 1.52 g (67%), brown liquid, $R_f$ = 0.78 (EtOAc/hexane, 1:1). $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.18 (br. s, 1 H, ArNH), 7.37 (d, $J$ = 8.8 Hz, 2 H, ArH), 7.14 (t, $J$ = 7.7 Hz, 1 H, ArH), 6.94–6.90 (m, 3 H, ArH), 6.71 (t, $J$ = 6.8 Hz, 1 H, ArH), 6.17 (s, 1 H, ArH), 4.38 (br. s, 2 H, $NH_2$), 2.19 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 142.6, 136.1, 131.4, 130.7, 128.3, 126.2, 125.4, 125.3, 124.6, 121.2, 119.3, 115.2, 110.4, 100.7, 24.9 ppm. IR (neat): $\tilde{\nu}_{max}$ = 3382, 1614, 1494 cm$^{-1}$. MS (ES$^+$): $m/z$ = 223.2 [M + 1]$^+$. $C_{15}H_{14}N_2$ (222.29): calcd. C 81.05, H 6.35, N 12.60; found C 81.10, H 6.29, N 12.57.

**2-(1*H*-Pyrrolo[2,3-*b*]pyridin-4-yl)phenylamine (3c):** Yield 1.49 g (70%), yellow solid, m.p. 159–163 °C, $R_f$ = 0.16 (EtOAc/hexane, 1:1). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 10.70 (br. s, 1 H, ArNH), 8.40 (d, $J$ = 4.5 Hz, 1 H, ArH), 7.39–7.16 (m, 4 H, ArH), 6.91–6.82 (m, 2 H, ArH), 6.47 (s, 1 H, ArH), 3.83 (br. s, 2 H, $NH_2$) ppm.

$^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 148.9, 145.2, 142.8, 139.5, 130.1, 128.9, 125.9, 122.5, 118.2, 116.4, 115.5, 115.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3454, 3379, 2365, 1608 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 210.4 [M + 1]$^+$. $C_{13}H_{11}N_3$ (209.25): calcd. C 74.62, H 5.30, N 20.08; found C 74.56, H 5.38, N 20.05.

**4-Methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-4-yl)phenylamine (3d):** Yield 1.48 g (65%), pale yellow solid, m.p. 196–198 °C, $R_f$ = 0.13 (EtOAc/hexane, 1:1). $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.69 (br. s, 1 H, ArNH), 8.31–8.22 (m, 1 H, ArH), 7.46 (s, 1 H, ArH), 7.04–6.95 (m, 3 H, ArH), 6.73 (d, *J* = 8.5 Hz, 1 H, ArH), 6.26 (s, 1 H, ArH), 4.59 (br. s, 2 H, NH$_2$), 2.19 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 148.9, 142.8, 142.7, 139.6, 130.4, 129.5, 125.9, 124.8, 122.7, 118.2, 115.7, 115.6, 99.6, 20.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3357, 3141, 2916, 1602 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 224.3 [M + 1]$^+$. $C_{14}H_{13}N_3$ (223.28): calcd. C 75.31, H 5.87, N 18.82; found C 75.25, H 5.90, N 18.75.

**2-(1*H*-Indol-4-yl)pyridin-3-amine (3e):** Yield 1.62 g (76%), light brown solid, m.p. 167–169 °C, $R_f$ = 0.22 (EtOAc/hexane, 1:1). $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.21 (br. s, 1 H, ArNH), 7.93 (dd, *J* = 4.3, 1.7 Hz, 1 H, ArH), 7.44 (d, *J* = 7.4 Hz, 1 H, ArH), 7.35 (t, *J* = 2.8 Hz, 1 H, ArH), 7.23–7.05 (m, 4 H, ArH), 6.27–6.25 (m, 1 H, ArH), 3.39 (br. s, 2 H, NH$_2$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 143.8, 141.7, 137.3, 136.3, 130.6, 125.9, 125.5, 122.7, 121.5, 120.9, 119.3, 111.2, 101.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3453, 3151, 1610 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 210.4 [M + 1]$^+$. $C_{13}H_{11}N_3$ (209.25): calcd. C 74.62, H 5.30, N 20.08; found C 74.56, H 5.34, N 20.12.

**6-(4-Chlorophenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (4a):** Yield 0.148 g (93%), dark brown solid, m.p. 136–138 °C, $R_f$ = 0.20 (EtOAc/hexane, 1:4), $t_R$ = 15.76 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.96 (s, 1 H, ArNH), 7.78 (d, *J* = 7.5 Hz, 1 H, ArH), 7.39–7.18 (m, 7 H, ArH), 7.02–6.81 (m, 4 H, ArH), 5.96 (d, *J* = 2.8 Hz, 1 H, NH), 5.52 (d, *J* = 2.4 Hz, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 147.8, 143.0, 136.7, 131.1, 130.6, 129.6, 129.1, 128.2, 127.8, 127.3, 125.5, 123.4, 121.9, 121.4, 120.8, 58.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3159, 1596, 1468 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 331.2 [M + 1]$^+$. $C_{21}H_{15}ClN_2$ (330.82): calcd. C 76.24, H 4.57, N 8.47; found C 76.21, H 4.58, N 8.49.

**6-(4-Nitrophenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (4b):** Yield 0.154 g (94%), green solid, m.p. 231–233 °C, $R_f$ = 0.63 (EtOAc/hexane, 1:1), $t_R$ = 15.23 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 11.04 (s, 1 H, ArNH), 8.06 (d, *J* = 8.7 Hz, 2 H, ArH), 7.78 (d, *J* = 7.4 Hz, 1 H, ArH), 7.42–7.39 (m, 3 H, ArH), 7.35 (d, *J* = 7.7 Hz, 1 H, ArH), 7.22 (t, *J* = 7.7 Hz, 1 H, ArH), 7.00–6.95 (m, 2 H, ArH), 6.91–6.87 (m, 2 H, ArH), 6.22 (d, *J* = 4.1 Hz, 1 H, NH), 5.71 (d, *J* = 3.8 Hz, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]-DMSO): $\delta$ = 151.9, 147.1, 146.0, 136.7, 130.4, 129.2, 128.9, 128.3, 127.3, 125.5, 124.2, 123.4, 123.0, 121.9, 121.6, 121.2, 117.3, 117.0, 110.0, 58.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3399, 1602, 1516 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 342.3 [M + 1]$^+$. $C_{21}H_{15}N_3O_2$ (341.37): calcd. C 73.89, H 4.43, N 12.31; found C 73.87, H 4.45, N 12.31.

**6-(4-Bromophenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (4c):** Yield 0.164 g (91%), grey solid, m.p. 139–140 °C, $R_f$ = 0.80 (EtOAc/hexane, 1:1), $t_R$ = 14.21 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 10.99 (s, 1 H, ArNH), 7.78 (d, *J* = 7.8 Hz, 1 H, ArH), 7.42–7.31 (m, 4 H, ArH), 7.20 (d, *J* = 7.7 Hz, 1 H, ArH), 7.13 (d, *J* = 8.3 Hz, 2 H, ArH), 7.01 (d, *J* = 7.0 Hz, 1 H, ArH), 6.93–6.87 (m, 2 H, ArH), 6.80 (d, *J* = 2.0 Hz, 1 H, ArH), 6.00 (d, *J* = 3.3 Hz, 1 H, NH), 5.50 (d, *J* = 3.0 Hz, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]-DMSO): $\delta$ = 147.7, 143.4, 136.7, 132.3, 130.7, 130.6, 129.9, 129.1, 128.2, 127.2, 125.5, 123.4, 121.8, 121.4, 120.8, 119.7, 118.1, 117.1, 109.9, 58.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3422, 3159, 1653, 1466 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 375.2 [M + 1]$^+$. $C_{21}H_{15}BrN_2$ (375.27): calcd. C 67.21, H 4.03, N 7.47; found C 67.20, H 4.07, N 7.46.

**6-(4-Fluorophenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (4d):** Yield 0.134 g (89%), purple solid, m.p. 155–157 °C, $R_f$ = 0.20 (EtOAc/hexane, 1:4), $t_R$ = 12.98 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 10.96 (s, 1 H, ArNH), 7.79 (d, *J* = 7.5 Hz, 1 H, ArH), 7.38 (d, *J* = 7.5 Hz, 1 H, ArH), 7.33 (d, *J* = 7.8 Hz, 1 H, ArH), 7.26–7.17 (m, 3 H, ArH), 7.08–6.88 (m, 5 H, ArH), 6.76 (s, 1 H, ArH), 5.90 (s, 1 H, NH), 5.50 (s, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 147.9, 140.1, 136.7, 130.6, 129.7, 129.6, 129.1, 128.2, 127.2, 125.5, 123.3, 121.8, 121.4, 120.7, 118.9, 117.1, 114.8, 114.3, 109.9, 58.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3405, 1605, 1467 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 315.3 [M + 1]$^+$. $C_{21}H_{15}FN_2$ (314.36): calcd. C 80.24, H 4.81, N 8.91; found C 80.23, H 4.80, N 8.90.

**6-(4-Methylphenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (4e):** Yield 0.128 g (86%), brown solid, m.p. 133–134 °C, $R_f$ = 0.82 (EtOAc/hexane, 1:1), $t_R$ = 13.45 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 10.91 (s, 1 H, ArNH), 7.79 (d, *J* = 7.4 Hz, 1 H, ArH), 7.38–7.30 (m, 2 H, ArH), 7.21–7.16 (m, 1 H, ArH), 7.12–7.03 (m, 4 H, ArH), 7.00–6.87 (m, 3 H, ArH), 6.67 (d, *J* = 1.9 Hz, 1 H, ArH), 5.79 (s, 1 H, NH), 5.41 (s, 1 H, CH), 2.23 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 141.0, 138.5, 136.7, 136.5, 130.7, 129.8, 129.6, 128.8, 128.7, 128.5, 128.4, 127.7, 127.2, 125.6, 125.3, 123.3, 121.7, 117.1, 116.9, 109.8, 59.5, 20.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3422, 2922, 1637, 1450 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 311.2 [M + 1]$^+$. $C_{22}H_{18}N_2$ (310.40): calcd. C 85.13, H 5.85, N 9.03; found C 85.10, H 5.90, N 9.09.

**6-(4-Ethoxyphenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (4f):** Yield 0.142 g (87%), grey solid, m.p. 229–231 °C, $R_f$ = 0.83 (EtOAc/hexane, 1:1), $t_R$ = 15.60 min. $^1$H NMR (200 MHz, [D$_6$]-DMSO): $\delta$ = 10.89 (s, 1 H, ArNH), 7.79 (d, *J* = 7.5 Hz, 1 H, ArH), 7.38–7.29 (m, 2 H, ArH), 7.22–7.11 (m, 3 H, ArH), 7.05–6.86 (m, 3 H, ArH), 6.79 (d, *J* = 8.6 Hz, 2 H, ArH), 6.66 (d, *J* = 2.1 Hz, 1 H, ArH), 5.73 (d, *J* = 2.6 Hz, 1 H, NH), 5.41 (d, *J* = 2.1 Hz, 1 H, CH), 3.93 (q, *J* = 6.9 Hz, 2 H, CH$_2$), 1.28 (t, *J* = 6.9 Hz, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 157.3, 148.5, 136.7, 136.0, 130.7, 128.9, 128.3, 127.3, 125.6, 123.3, 121.8, 121.2, 120.6, 119.7, 117.1, 113.8, 109.8, 62.8, 59.2, 14.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3177, 1617, 1439 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 341.3 [M + 1]$^+$. $C_{23}H_{20}N_2O$ (340.42): calcd. C 81.15, H 5.92, N 8.23; found C 81.01, H 5.98, N 8.23.

**2-(6,7-Dihydro-4*H*-indolo[3,4-*cd*][1]benzazepin-6-yl)phenol (4g):** Yield 0.128 g (85%), green solid, m.p. 180–181 °C, $R_f$ = 0.80 (EtOAc/hexane, 1:1), $t_R$ = 12.55 min. $^1$H NMR (200 MHz, [D$_6$]-DMSO): $\delta$ = 10.92 (s, 1 H, ArNH), 9.65 (br. s, 1 H, OH), 7.78 (d, *J* = 7.1 Hz, 1 H, ArH), 7.35 (t, *J* = 8.1 Hz, 2 H, ArH), 7.02–6.80 (m, 5 H, ArH), 6.75–6.65 (m, 2 H, ArH), 6.54 (t, *J* = 7.4 Hz, 2 H, ArH), 5.74 (br. s, 1 H, NH), 5.40 (s, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 154.4, 148.3, 136.7, 130.7, 130.0, 129.1, 128.4, 128.3, 127.8, 127.2, 126.0, 123.1, 121.7, 121.5, 120.6, 118.7, 118.4, 117.1, 114.8, 109.9, 54.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3368, 1611, 1467 cm$^{-1}$. MS (ES$^+$): *m*/*z* = 313.2 [M + 1]$^+$. $C_{21}H_{16}N_2O$ (312.37): calcd. C 80.75, H 5.16, N 8.97; found C 80.73, H 5.17, N 8.95.

**6-(4-Chlorophenyl)-10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5a):** Yield 0.139 g (90%), off-white solid, m.p. 150–152 °C, $R_f$ = 0.76 (EtOAc/hexane, 1:1), $t_R$ = 21.35 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 10.90 (s, 1 H, ArNH), 7.58 (s, 1 H, ArH), 7.40–7.15 (m, 7 H, ArH), 6.81 (s, 3 H, ArH), 5.86 (s, 1 H, NH), 5.48 (s, 1 H, CH), 2.24 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 145.2, 143.2, 136.8, 131.2, 131.1, 130.7, 129.9, 129.6, 129.4, 129.0, 128.7, 128.1, 127.8, 125.6, 123.5, 121.9, 120.8, 118.5, 117.1, 109.9, 58.8, 20.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3430,

3171, 1649 cm$^{-1}$. MS (ES$^+$): $m/z$ = 345.2 [M + 1]$^+$. $C_{22}H_{17}ClN_2$ (344.84): calcd. C 76.63, H 4.97, N 8.12; found C 76.50, H 5.01, N 8.00.

**10-Methyl-6-(4-nitrophenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5b):** Yield 0.147 g (92%), yellow solid, m.p. >250 °C, $R_f$ = 0.74 (EtOAc/hexane, 1:1), $t_R$ = 20.56 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.06 (d, $J$ = 1.6 Hz, 1 H, ArNH), 8.18–8.15 (m, 1 H, ArH), 8.07 (d, $J$ = 8.7 Hz, 2 H, ArH), 7.58 (d, $J$ = 4.0 Hz, 1 H, ArH), 7.41–7.36 (m, 3 H, ArH), 7.33 (s, 1 H, ArH), 7.26–7.19 (m, 1 H, ArH), 6.96 (d, $J$ = 2.1 Hz, 1 H, ArH), 6.78 (s, 1 H, ArH), 6.12 (d, $J$ = 3.9 Hz, 1 H, NH), 5.67 (d, $J$ = 3.7 Hz, 1 H, CH), 2.22 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 145.3, 143.6, 136.8, 132.3, 131.3, 130.8, 130.0, 129.8, 129.0, 128.7, 128.1, 125.6, 123.5, 121.9, 120.8, 119.7, 118.3, 117.1, 109.9, 58.8, 20.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3434, 3188, 1704, 1610, 1517 cm$^{-1}$. MS (ES$^+$): $m/z$ = 356.2 [M + 1]$^+$. $C_{22}H_{17}N_3O_2$ (355.40): calcd. C 74.35, H 4.82, N 11.82; found C 74.01, H 5.00, N 11.50.

**6-(4-Bromophenyl)-10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5c):** Yield 0.153 g (88%), white solid, m.p. 225–226 °C, $R_f$ = 0.83 (EtOAc/hexane, 1:1), $t_R$ = 21.78 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.98 (d, $J$ = 1.9 Hz, 1 H, ArNH), 7.84 (s, 1 H, ArH), 7.58 (s, 1 H, ArH), 7.41–7.36 (m, 3 H, ArH), 7.31 (d, $J$ = 7.8 Hz, 1 H, ArH), 7.19 (t, $J$ = 7.8 Hz, 1 H, ArH), 7.12 (d, $J$ = 8.4 Hz, 2 H, ArH), 6.80 (s, 2 H, ArH), 5.87 (d, $J$ = 3.4 Hz, 1 H, NH), 5.46 (d, $J$ = 3.2 Hz, 1 H, CH), 2.24 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 152.2, 146.1, 144.6, 136.8, 130.7, 130.6, 130.0, 129.2, 128.9, 128.7, 128.2, 125.6, 124.3, 123.1, 121.9, 121.2, 117.3, 117.2, 110.0, 58.6, 20.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3422, 3174, 1579 cm$^{-1}$. MS (ES$^+$): $m/z$ = 389.2 [M + 1]$^+$. $C_{22}H_{17}BrN_2$ (389.29): calcd. C 67.88, H 4.40, N 7.20; found C 67.50, H 4.81, N 6.88.

**6-(4-Fluorophenyl)-10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5d):** Yield 0.128 g (87%), light blue solid, m.p. 144–146 °C, $R_f$ = 0.20 (1:4 EtOAc/hexane), $t_R$ = 19.90 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.91 (s, 1 H, ArNH), 7.59 (s, 1 H, ArH), 7.38 (d, $J$ = 7.4 Hz, 1 H, ArH), 7.31 (d, $J$ = 7.8 Hz, 1 H, ArH), 7.24–7.16 (m, 3 H, ArH), 7.04 (t, $J$ = 8.8 Hz, 2 H, ArH), 6.85–6.79 (m, 2 H, ArH), 6.73 (d, $J$ = 1.8 Hz, 1 H, ArH), 5.71 (d, $J$ = 2.8 Hz, 1 H, NH), 5.45 (d, $J$ = 2.4 Hz, 1 H, CH), 2.25 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 145.6, 140.4, 140.3, 136.7, 130.7, 129.8, 129.6, 129.0, 128.7, 128.1, 125.6, 123.4, 121.8, 120.75, 119.0, 117.1, 114.8, 114.4, 109.9, 58.9, 20.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3172, 1606, 1501 cm$^{-1}$. MS (ES$^+$): $m/z$ = 329.2 [M + 1]$^+$. $C_{22}H_{17}FN_2$ (328.39): calcd. C 80.47, H 5.22, N 8.53; found C 80.50, H 5.12, N 8.61.

**10-Methyl-6-(4-methylphenyl)-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5e):** Yield 0.122 g (84%), brown solid, m.p. 140–142 °C, $R_f$ = 0.80 (EtOAc/hexane, 1:1), $t_R$ = 20.56 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.86 (s, 1 H, ArNH), 7.60 (s, 1 H, ArH), 7.39–7.29 (m, 2 H, ArH), 7.21–7.03 (m, 5 H, ArH), 6.87–6.82 (m, 2 H, ArH), 6.65 (s, 1 H, ArH), 5.59 (s, 1 H, NH), 5.36 (s, 1 H, CH), 2.25 (s, 3 H, CH$_3$), 2.24 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 145.9, 141.1, 136.7, 135.7, 130.8, 129.6, 128.9, 128.6, 128.0, 127.8, 125.6, 123.4, 121.7, 120.6, 119.5, 117.0, 109.8, 59.6, 20.7, 20.5 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3428, 2930, 2359, 1657 cm$^{-1}$. MS (ES$^+$): $m/z$ = 325.3 [M + 1]$^+$. $C_{23}H_{20}N_2$ (324.42): calcd. C 85.15, H 6.21, N 8.63; found C 85.10, H 6.27, N 8.50.

**6-(4-Ethoxyphenyl)-10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5f):** Yield 0.137 g (86%), brown solid, m.p. 182–183 °C, $R_f$ = 0.73 (EtOAc/hexane, 1:1), $t_R$ = 22.27 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.83 (d, $J$ = 1.9 Hz, 1 H, ArNH), 7.58 (s, 1 H, ArH), 7.36 (d, $J$ = 7.4 Hz, 1 H, ArH), 7.30 (d, $J$ = 7.7 Hz, 1 H, ArH), 7.18 (t, $J$ = 7.7 Hz, 1 H, ArH), 7.09 (d, $J$ = 8.5 Hz, 2 H, ArH), 6.81 (s, 2 H, ArH), 6.76 (d, $J$ = 8.6 Hz, 2 H, ArH), 6.64 (d, $J$ = 2.0 Hz, 1 H, ArH), 5.50 (d, $J$ = 2.0 Hz, 1 H, NH), 5.34 (s, 1 H, CH), 3.93 (q, $J$ = 6.9 Hz, 2 H, CH$_2$), 2.23 (s, 3 H, CH$_3$), 1.26 (t, $J$ = 6.9 Hz, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 157.5, 146.0, 136.9, 136.3, 131.0, 130.0, 129.1, 128.9, 128.4, 125.9, 123.6, 122.0, 120.8, 119.9, 117.3, 114.0, 110.1, 63.1, 59.5, 20.7, 14.9 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3183, 1610, 1460 cm$^{-1}$. MS (ES$^+$): $m/z$ = 355.3 [M + 1]$^+$. $C_{24}H_{22}N_2O$ (354.45): calcd. C 81.33, H 6.26, N 7.90; found C 81.37, H 6.21, N 7.85.

***N*,*N*-Dimethyl-4-(10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepin-6-yl)aniline (5g):** Yield 0.132 g (83%), orange yellow solid, m.p. 197–199 °C, $R_f$ = 0.60 (EtOAc/hexane, 1:1), $t_R$ = 21.13 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.83 (s, 1 H, ArNH), 7.61 (s, 1 H, ArH), 7.37 (d, $J$ = 7.3 Hz, 1 H, ArH), 7.29 (d, $J$ = 7.8 Hz, 1 H, ArH), 7.17 (t, $J$ = 7.7 Hz, 1 H, ArH), 7.07 (d, $J$ = 8.6 Hz, 2 H, ArH), 6.91–6.82 (m, 2 H, ArH), 6.63 (d, $J$ = 8.7 Hz, 2 H, ArH), 6.58 (s, 1 H, ArH), 5.40 (s, 1 H, NH), 5.23 (s, 1 H, CH), 2.84 [s, 6 H, N(CH$_3$)$_2$], 2.26 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]-DMSO): $\delta$ = 145.5, 143.9, 136.9, 130.6, 130.0, 128.8, 127.2, 124.9, 123.6, 122.8, 119.1, 117.7, 113.9, 112.9, 112.7, 111.1, 58.6, 20.8, 20.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3435, 2844, 1672, 1604 cm$^{-1}$. MS (ES$^+$): $m/z$ = 354.3 [M + 1]$^+$. $C_{24}H_{23}N_3$ (353.47): calcd. C 81.55, H 6.56, N 11.89; found C 81.49, H 6.62, N 11.85.

**6-Ethyl-10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5h):** Yield 0.053 g (45%), yellow liquid, $R_f$ = 0.38 (EtOAc/hexane, 2:8), $t_R$ = 20.03 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.84 (s, 1 H, ArNH), 7.63 (s, 1 H, ArH), 7.34 (d, $J$ = 4.7 Hz, 1 H, ArH), 7.27 (d, $J$ = 7.5 Hz, 1 H, ArH), 7.18–7.15 (m, 1 H, ArH), 7.09 (d, $J$ = 2.0 Hz, 1 H, ArH), 6.98–6.91 (m, 2 H, ArH), 5.44 (s, 1 H, NH), 4.13 (t, $J$ = 4.8 Hz, 1 H, CH), 2.30 (s, 3 H, CH$_3$), 1.62–1.53 (m, 2 H, CH$_2$), 0.97 (t, $J$ = 7.2 Hz, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 145.3, 136.6, 130.7, 129.2, 128.9, 128.5, 128.0, 125.4, 123.0, 121.5, 119.8, 119.0, 116.7, 109.5, 56.9, 29.2, 20.4, 10.9 ppm. IR (neat): $\tilde{\nu}_{max}$ = 3423, 2930, 1649 cm$^{-1}$. MS (ES$^+$): $m/z$ = 263.3 [M + 1]$^+$. $C_{18}H_{18}N_2$ (262.35): calcd. C 82.41, H 6.92, N 10.68; found C 81.03, H 6.30, N 11.00.

**6-*tert*-Butyl-10-methyl-6,7-dihydro-4*H*-indolo[3,4-*cd*][1]benzazepine (5i):** Yield 0.070 g (54%), brown solid, m.p. 112–113 °C, $R_f$ = 0.38 (EtOAc/hexane, 2:8), $t_R$ = 19.23 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 10.90 (s, 1 H, ArNH), 7.57 (s, 1 H, ArH), 7.34–7.24 (m, 2 H, ArH), 7.15–7.06 (m, 2 H, ArH), 6.91 (s, 2 H, ArH), 5.74 (d, $J$ = 4.2 Hz, 1 H, NH), 4.05 (s, 1 H, CH), 2.28 (s, 3 H, CH$_3$), 0.77 [s, 9 H, (CH$_3$)$_3$] ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 145.4, 136.4, 130.7, 128.6, 128.4, 128.3, 126.6, 122.5, 121.5, 121.2, 116.7, 115.8, 109.4, 64.6, 27.7, 20.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3407, 2949, 1618, 1479 cm$^{-1}$. MS (ES$^+$): $m/z$ = 291.3 [M + 1]$^+$. $C_{20}H_{22}N_2$ (290.41): calcd. C 82.72, H 7.64, N 9.65; found C 83.01, H 6.50, N 8.75.

**6-(4-Chlorophenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo[*cd*,*f*]azulene (6a):** Yield 0.142 g (90%), pale yellow solid, m.p. >250 °C, $R_f$ = 0.13 (EtOAc/hexane, 1:1), $t_R$ = 14.26 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.50 (d, $J$ = 1.5 Hz, 1 H, ArNH), 8.26 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.91 (d, $J$ = 7.4 Hz, 1 H, ArH), 7.40 (d, $J$ = 5.4 Hz, 1 H, ArH), 7.27 (d, $J$ = 8.5 Hz, 2 H, ArH), 7.17 (d, $J$ = 8.4 Hz, 2 H, ArH), 7.14–7.09 (m, 1 H, ArH), 7.00–6.91 (m, 3 H, ArH), 6.33 (d, $J$ = 3.7 Hz, 1 H, NH), 5.57 (d, $J$ = 3.4 Hz, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 149.3, 148.8, 143.2, 142.5, 137.9, 131.2, 129.5, 129.3, 128.2, 128.0, 126.0, 123.7, 121.1, 120.4, 117.8, 116.8, 111.8, 58.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2867, 1598, 1461 cm$^{-1}$. MS (ES$^+$): $m/z$ = 332.3 [M + 1]$^+$. $C_{20}H_{14}ClN_3$

(331.80): calcd. C 72.40, H 4.25, N 12.66; found C 71.10, H 4.50, N 12.80.

**6-(4-Bromophenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo[*cd*,*f*]azulene (6b):** Yield 0.163 g (91%), yellow solid, m.p. >250 °C, $R_f$ = 0.16 (EtOAc/hexane, 1:1), $t_R$ = 13.49 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 11.49 (s, 1 H, ArNH), 8.26 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.91 (d, $J$ = 7.5 Hz, 1 H, ArH), 7.42–7.39 (m, 3 H, ArH), 7.11 (d, $J$ = 8.3 Hz, 3 H, ArH), 6.99–6.91 (m, 3 H, ArH), 6.32 (d, $J$ = 3.6 Hz, 1 H, NH), 5.55 (d, $J$ = 3.4 Hz, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 149.4, 148.8, 143.3, 142.9, 137.9, 130.9, 129.9, 129.4, 128.3, 126.0, 123.8, 121.3, 120.5, 119.9, 117.8, 116.7, 111.9, 58.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3438, 3100, 2867, 1593, 1465 cm$^{-1}$. MS (ES$^+$): $m/z$ = 376.3 [M + 1]$^+$. $C_{20}H_{14}BrN_3$ (376.25): calcd. C 63.84, H 3.75, N 11.17; found C 64.40, H 3.95, N 12.20.

**6-(4-Nitrophenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo[*cd*,*f*]azulene (6c):** Yield 0.154 g (94%), yellow solid, m.p. >250 °C, $R_f$ = 0.12 (EtOAc/hexane, 1:1), $t_R$ = 12.98 min. $^1$H NMR (200 MHz, [D$_6$]-DMSO): $\delta$ = 11.56 (br. s, 1 H, ArNH), 8.27 (d, $J$ = 4.0 Hz, 1 H, ArH), 8.06 (d, $J$ = 7.1 Hz, 2 H, ArH), 7.90 (d, $J$ = 7.7 Hz, 1 H, ArH), 7.38 (d, $J$ = 8.0 Hz, 3 H, ArH), 7.10 (s, 2 H, ArH), 6.94 (d, $J$ = 7.1 Hz, 2 H, ArH), 6.53 (s, 1 H, NH), 5.74 (s, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 151.3, 149.5, 148.2, 146.2, 143.4, 137.8, 129.5, 128.9, 128.3, 126.2, 123.7, 123.2, 121.5, 120.9, 117.8, 115.7, 111.9, 58.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3343, 3102, 1595, 1510 cm$^{-1}$. MS (ES$^+$): $m/z$ = 343.3 [M + 1]$^+$. $C_{20}H_{14}N_4O_2$ (342.36): calcd. C 70.17, H 4.12, N 16.37; found C 71.10, H 3.98, N 18.12.

**2-(6,7-Dihydro-4*H*-3,4,7-triazadibenzo[*cd*,*f*]azulen-6-yl)phenol (6d):** Yield 0.129 g (86%), light pink solid, m.p. 235–238 °C, $R_f$ = 0.10 (EtOAc/hexane, 1:1), $t_R$ = 11.20 min. $^1$H NMR (300 MHz, [D$_6$]-DMSO): $\delta$ = 11.42 (s, 1 H, ArNH), 9.73 (s, 1 H, OH), 8.26 (s, 1 H, ArH), 7.92 (d, $J$ = 7.4 Hz, 1 H, ArH), 7.41 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.12–6.83 (m, 6 H, ArH), 6.63–6.52 (m, 2 H, ArH), 5.79 (d, $J$ = 2.1 Hz, 1 H, NH), 5.69 (s, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 154.5, 149.3, 143.1, 137.9, 129.5, 129.2, 128.2, 128.0, 126.0, 123.5, 121.3, 120.1, 118.7, 117.0, 114.9, 53.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3042, 1592 cm$^{-1}$. MS (ES$^+$): $m/z$ = 314.3 [M + 1]$^+$. $C_{20}H_{15}N_3O$ (313.36): calcd. C 76.66, H 4.82, N 13.41; found C 76.68, H 4.83, N 13.39.

**6-(3,4-Dimethoxyphenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo[*cd*,*f*]-azulene (6e):** Yield 0.133 g (85%), yellow solid, m.p. 150–152 °C, $R_f$ = 0.13 (EtOAc/hexane, 1:1), $t_R$ = 11.87 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.42 (s, 1 H, ArNH), 8.24 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.92 (d, $J$ = 7.8 Hz, 1 H, ArH), 7.39 (d, $J$ = 5.4 Hz, 1 H, ArH), 7.16–7.05 (m, 2 H, ArH), 6.99–6.92 (m, 2 H, ArH), 6.88 (d, $J$ = 1.9 Hz, 1 H, ArH), 6.71 (d, $J$ = 8.2 Hz, 1 H, ArH), 6.59–6.56 (m, 1 H, ArH), 6.12 (d, $J$ = 2.8 Hz, 1 H, NH), 5.44 (d, $J$ = 2.3 Hz, 1 H, CH), 3.34 (s, 6 H, 2 × OCH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]-DMSO): $\delta$ = 156.7, 149.3, 146.2, 140.0, 142.5, 136.9, 133.3, 130.5, 125.6, 124.0, 120.9, 117.9, 116.4, 113.3, 112.0, 111.6, 59.5, 55.9 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3117, 2834, 1594 cm$^{-1}$. MS (ES$^+$): $m/z$ = 358.3 [M + 1]$^+$. $C_{22}H_{19}N_3O_2$ (357.41): calcd. C 73.93, H 5.36, N 11.76; found C 73.93, H 5.36, N 11.76.

**6-(4-Fluorophenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo[*cd*,*f*]azulene (6f):** Yield 0.145 g (88%), yellow solid, m.p. >250 °C, $R_f$ = 0.14 (EtOAc/hexane, 1:1), $t_R$ = 13.15 min. $^1$H NMR (200 MHz, [D$_6$]-DMSO): $\delta$ = 11.47 (br. s, 1 H, ArNH), 8.25 (d, $J$ = 5.3 Hz, 1 H, ArH), 7.91 (d, $J$ = 7.8 Hz, 1 H, ArH), 7.40 (d, $J$ = 5.5 Hz, 1 H, ArH), 7.25–7.16 (m, 2 H, ArH), 7.12–6.97 (m, 4 H, ArH), 6.92–6.91 (m, 2 H, ArH), 6.25 (d, $J$ = 3.5 Hz, 1 H, NH), 5.55 (d, $J$ = 3.0 Hz, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 149.4, 149.0, 143.2, 139.7, 137.9, 129.6, 129.5, 129.3, 128.2, 125.9, 123.6, 121.2, 120.3, 117.8, 117.3, 114.8, 114.5, 111.7, 58.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3125, 2875, 1595 cm$^{-1}$. MS (ES$^+$): $m/z$ = 316.4 [M + 1]$^+$. $C_{20}H_{14}FN_3$ (315.35): calcd. C 76.18, H 4.47, N 13.33; found C 76.23, H 4.38, N 13.35.

**6-(4-Chlorophenyl)-10-methyl-6,7-dihydro-4*H*-3,4,7-triazadibenzo-[*cd*,*f*]azulene (7a):** Yield 0.137 g (89%), brown solid, m.p. >250 °C, $R_f$ = 0.16 (EtOAc/hexane, 1:1), $t_R$ = 15.14 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.44 (s, 1 H, ArNH), 8.25 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.71 (s, 1 H, ArH), 7.40 (d, $J$ = 5.4 Hz, 1 H, ArH), 7.27 (d, $J$ = 8.4 Hz, 2 H, ArH), 7.16 (d, $J$ = 8.4 Hz, 2 H, ArH), 6.98–6.86 (m, 3 H, ArH), 6.14 (d, $J$ = 3.7 Hz, 1 H, NH), 5.52 (d, $J$ = 3.4 Hz, 1 H, CH), 2.25 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 149.4, 146.2, 143.1, 142.6, 137.9, 131.2, 130.2, 129.7, 129.5, 128.4, 127.9, 125.9, 123.7, 120.3, 117.8, 116.9, 111.7, 58.1, 20.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3141, 2861, 1590, 1466 cm$^{-1}$. MS (ES$^+$): $m/z$ = 346.3 [M + 1]$^+$. $C_{21}H_{16}ClN_3$ (345.83): calcd. C 72.93, H 4.66, N 12.15; found C 72.93, H 4.66, N 12.15.

**6-(4-Bromophenyl)-10-methyl-6,7-dihydro-4*H*-3,4,7-triazadibenzo-[*cd*,*f*]azulene (7b):** Yield 0.152 g (87%), white solid, m.p. >250 °C, $R_f$ = 0.16 (EtOAc/hexane, 1:1), $t_R$ = 14.21 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.45 (s, 1 H, ArNH), 8.25 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.71 (s, 1 H, ArH), 7.41–7.38 (m, 3 H, ArH), 7.10 (d, $J$ = 8.3 Hz, 2 H, ArH), 6.97–6.85 (m, 3 H, ArH), 6.15 (d, $J$ = 3.3 Hz, 1 H, NH), 5.51 (d, $J$ = 3.2 Hz, 1 H, CH), 2.25 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 149.4, 146.2, 143.1, 143.0, 137.9, 130.8, 130.2, 129.9, 129.8, 128.4, 125.9, 123.7, 120.3, 119.8, 117.8, 116.7, 111.7, 58.1, 20.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3141, 2864, 1583, 1468 cm$^{-1}$. MS (ES$^+$): $m/z$ = 390.3 [M + 1]$^+$. $C_{21}H_{16}BrN_3$ (390.28): calcd. C 64.63, H 4.13, N 10.77; found C 64.70, H 4.08, N 10.74.

**10-Methyl-6-(4-nitrophenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo-[*cd*,*f*]azulene (7c):** Yield 0.144 g (90%), yellow solid, m.p. >250 °C, $R_f$ = 0.12 (EtOAc/hexane, 1:1), $t_R$ = 15.35 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.54 (s, 1 H, ArNH), 8.28–8.24 (m, 1 H, ArH), 8.07 (d, $J$ = 8.6 Hz, 2 H, ArH), 7.71 (s, 1 H, ArH), 7.44–7.36 (m, 3 H, ArH), 7.10 (d, $J$ = 2.0 Hz, 1 H, ArH), 6.92 (d, $J$ = 8.1 Hz, 1 H, ArH), 6.84 (d, $J$ = 8.0 Hz, 1 H, ArH), 6.38 (d, $J$ = 4.2 Hz, 1 H, NH), 5.70 (d, $J$ = 3.8 Hz, 1 H, CH), 2.23 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 151.6, 149.5, 146.4, 145.8, 143.5, 138.1, 130.8, 130.5, 130.3, 128.9, 128.7, 126.3, 124.4, 124.0, 123.9, 123.3, 120.9, 117.9, 115.9, 58.2, 20.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2862, 2361, 1590, 1510 cm$^{-1}$. MS (ES$^+$): $m/z$ = 357.3 [M + 1]$^+$. $C_{21}H_{16}N_4O_2$ (356.38): calcd. C 70.77, H 4.53, N 15.72; found C 70.74, H 4.58, N 15.74.

**6-(4-Fluorophenyl)-10-methyl-6,7-dihydro-4*H*-3,4,7-triazadibenzo-[*cd*,*f*]azulene (7d):** Yield 0.130 g (88%), brown solid, m.p. >250 °C, $R_f$ = 0.16 (EtOAc/hexane, 1:1), $t_R$ = 14.98 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.47 (s, 1 H, ArNH), 8.25 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.71 (s, 1 H, ArH), 7.40 (d, $J$ = 5.5 Hz, 1 H, ArH), 7.25–7.19 (m, 2 H, ArH), 7.04 (t, $J$ = 8.9 Hz, 2 H, ArH), 6.91 (m, 3 H, ArH), 6.12 (d, $J$ = 3.8 Hz, 1 H, NH), 5.51 (d, $J$ = 3.0 Hz, 1 H, CH), 2.25 (s, 3 H, CH$_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 149.4, 146.5, 143.1, 139.8, 137.8, 130.1, 129.7, 129.6, 129.5, 128.4, 125.9, 123.7, 120.2, 117.8, 117.4, 114.8, 114.5, 111.7, 58.3, 20.2 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3141, 2873, 1639, 1441 cm$^{-1}$. MS (ES$^+$): $m/z$ = 330.4 [M + 1]$^+$. $C_{21}H_{16}FN_3$ (329.38): calcd. C 76.58, H 4.90, N 12.76; found C 76.60, H 4.83, N 12.71.

**6-(4-Ethoxyphenyl)-10-methyl-6,7-dihydro-4*H*-3,4,7-triazadibenzo-[*cd*,*f*]azulene (7e):** Yield 0.137 g (86%), pale yellow solid, m.p. >250 °C, $R_f$ = 0.16 (EtOAc/hexane, 1:1), $t_R$ = 13.57 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.39 (s, 1 H, ArNH), 8.24 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.71 (s, 1 H, ArH), 7.39 (d, $J$ = 5.4 Hz, 1 H, ArH), 7.09 (d, $J$ = 8.6 Hz, 2 H, ArH), 6.93 (s, 2 H, ArH), 6.82–

6.75 (m, 3 H, ArH), 5.95 (d, $J$ = 2.6 Hz, 1 H, NH), 5.40 (d, $J$ = 2.2 Hz, 1 H, CH), 3.93 (q, $J$ = 6.9 Hz, 2 H, $CH_2$), 2.26 (s, 3 H, $CH_3$), 1.27 (t, $J$ = 6.9 Hz, 3 H, $CH_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 157.3, 149.4, 146.9, 143.0, 138.0, 135.5, 130.1, 129.6, 128.8, 128.4, 125.8, 123.7, 120.0, 118.1, 117.9, 113.8, 111.7, 62.8, 58.6, 20.3, 14.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3133, 2900, 1593, 1465 cm$^{-1}$. MS (ES$^+$): $m/z$ = 356.3 [M + 1]$^+$. $C_{23}H_{21}N_3O$ (355.44): calcd. C 77.72, H 5.96, N 11.82; found C 77.69, H 5.94, N 11.88.

**10-Methyl-6-(4-methylphenyl)-6,7-dihydro-4*H*-3,4,7-triazadibenzo-[*cd*,*f*]azulene (7f):** Yield 0.124 g (85%), yellow solid, m.p. >250 °C, $R_f$ = 0.29 (EtOAc/hexane, 1:1), $t_R$ = 14.53 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.40 (s, 1 H, ArNH), 8.24 (d, $J$ = 5.2 Hz, 1 H, ArH), 7.71 (s, 1 H, ArH), 7.39 (d, $J$ = 5.4 Hz, 1 H, ArH), 7.10–7.00 (m, 4 H, ArH), 6.92 (s, 2 H, ArH), 6.84 (d, $J$ = 2.2 Hz, 1 H, ArH), 6.00 (d, $J$ = 3.3 Hz, 1 H, NH), 5.43 (d, $J$ = 3.0 Hz, 1 H, CH), 2.25 (s, 3 H, $CH_3$), 2.22 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 149.4, 146.8, 143.0, 140.6, 138.0, 135.8, 130.1, 129.6, 128.6, 128.4, 127.6, 125.8, 123.7, 120.0, 117.8, 111.6, 58.8, 20.6, 20.3 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3117, 2900, 1588, 1464 cm$^{-1}$. MS (ES$^+$): $m/z$ = 326.3 [M + 1]$^+$. $C_{22}H_{19}N_3$ (325.41): calcd. C 81.20, H 5.89, N 12.91; found C 81.25, H 5.83, N 12.87.

**6-(4-Chlorophenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indole (8a):** Yield 0.144 g (91%), light yellow solid, m.p. 180–181 °C, $R_f$ = 0.60 (EtOAc/hexane, 1:1), $t_R$ = 14.87 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.07 (d, $J$ = 1.6 Hz, 1 H, ArNH), 8.15–8.05 (m, 1 H, ArH), 8.06 (d, $J$ = 7.6 Hz, 1 H, ArH), 7.40 (d, $J$ = 7.4 Hz, 1 H, ArH), 7.30–7.20 (m, 4 H, ArH), 7.15 (d, $J$ = 8.4 Hz, 2 H, ArH), 7.03–6.99 (m, 1 H, ArH), 6.96 (d, $J$ = 2.2 Hz, 1 H, ArH), 6.30 (d, $J$ = 3.7 Hz, 1 H, NH), 5.60 (d, $J$ = 3.5 Hz, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 143.8, 143.0, 141.4, 136.8, 131.6, 131.5, 131.3, 129.9, 129.5, 128.9, 128.7, 128.0, 125.4, 122.0, 121.5, 118.7, 117.3, 111.0, 57.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3250, 2930, 1598, 1423 cm$^{-1}$. MS (ES$^+$): $m/z$ = 332.3 [M + 1]$^+$. $C_{20}H_{14}ClN_3$ (331.80): calcd. C 72.40, H 4.25, N 12.66; found C 72.43, H 4.21, N 12.65.

**6-(4-Bromophenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indole (8b):** Yield 0.167 g (93%), orange solid, m.p. 135–137 °C, $R_f$ = 0.77 (EtOAc/hexane, 1:1), $t_R$ = 15.45 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.07 (d, $J$ = 2.0 Hz, 1 H, ArNH), 8.14 (dd, $J$ = 4.3, 1.4 Hz, 1 H, ArH), 8.06 (dd, $J$ = 7.4, 0.6 Hz, 1 H, ArH), 7.42–7.38 (m, 3 H, ArH), 7.28 (dd, $J$ = 8.0, 1.4 Hz, 1 H, ArH), 7.23 (d, $J$ = 7.8 Hz, 1 H, ArH), 7.10 (d, $J$ = 8.4 Hz, 2 H, ArH), 7.04–6.99 (m, 1 H, ArH), 6.95 (d, $J$ = 2.3 Hz, 1 H, ArH), 6.31 (d, $J$ = 3.8 Hz, 1 H, NH), 5.58 (d, $J$ = 3.7 Hz, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 145.2, 143.8, 143.4, 141.3, 136.8, 131.6, 131.4, 130.9, 129.8, 128.8, 128.6, 125.3, 122.0, 121.5, 121.3, 119.8, 118.6, 117.2, 111.0, 57.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3254, 2930, 1585, 1423 cm$^{-1}$. MS (ES$^+$): $m/z$ = 376.4 [M + 1]$^+$. $C_{20}H_{14}BrN_3$ (376.25): calcd. C 63.84, H 3.75, N 11.17; found C 63.81, H 3.76, N 11.13.

**6-(4-Nitrophenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indole (8c):** Yield 0.155 g (95%), brown solid, m.p. 206–209 °C, $R_f$ = 0.43 (EtOAc/hexane, 1:1), $t_R$ = 15.89 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.16 (s, 1 H, ArNH), 8.31 (s, 1 H, ArH), 8.10–8.06 (m, 3 H, ArH), 7.44–7.35 (m, 3 H, ArH), 7.24 (t, $J$ = 7.7 Hz, 2 H, ArH), 7.07–6.97 (m, 2 H, ArH), 6.52 (d, $J$ = 4.3 Hz, 1 H, NH), 5.78 (d, $J$ = 4.1 Hz, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 151.8, 146.2, 145.4, 143.3, 141.5, 136.8, 131.5, 131.4, 130.2, 129.9, 128.8, 125.3, 123.3, 122.1, 121.7, 121.6, 118.3, 116.2, 111.2, 57.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3163, 1676, 1591, 1510 cm$^{-1}$. MS (ES$^+$): $m/z$ = 343.3 [M + 1]$^+$. $C_{20}H_{14}N_4O_2$ (342.36): calcd. C 70.17, H 4.12, N 16.37; found C 70.15, H 4.13, N 16.35.

**6-(4-Fluorophenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indole (8d):** Yield 0.135 g (90%), brown solid, m.p. 185–186 °C, $R_f$ = 0.40 (EtOAc/hexane, 1:1), $t_R$ = 17.07 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 11.02 (s, 1 H, ArNH), 8.15 (dd, $J$ = 4.3, 1.3 Hz, 1 H, ArH), 8.07 (d, $J$ = 7.7 Hz, 1 H, ArH), 7.39 (d, $J$ = 7.4 Hz, 1 H, ArH), 7.18 (dd, $J$ = 8.0, 1.4 Hz, 1 H, ArH), 7.25–7.18 (m, 3 H, ArH), 7.07–6.99 (m, 3 H, ArH), 6.88 (d, $J$ = 1.9 Hz, 1 H, ArH), 6.20 (d, $J$ = 3.3 Hz, 1 H, NH), 5.58 (d, $J$ = 2.9 Hz, 1 H, CH) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 145.2, 143.9, 141.3, 136.8, 131.4, 130.4, 129.9, 129.6, 128.8, 125.4, 121.9, 121.5, 121.2, 118.6, 117.8, 114.8, 114.6, 111.0, 57.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2925, 2363, 1647, 1609, 1435 cm$^{-1}$. MS (ES$^+$): $m/z$ = 316.4 [M + 1]$^+$. $C_{20}H_{14}FN_3$ (315.35): calcd. C 76.18, H 4.47, N 13.33; found C 76.19, H 4.43, N 13.30.

**6-(4-Ethoxyphenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indole (8e):** Yield 0.128 g (88%), orange solid, m.p. 235–236 °C, $R_f$ = 0.12 (EtOAc/hexane, 1:9), $t_R$ = 14.26 min. $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 10.98 (s, 1 H, ArNH), 8.15 (dd, $J$ = 4.3, 1.4 Hz, 1 H, ArH), 8.06 (dd, $J$ = 7.6, 0.8 Hz, 1 H, ArH), 7.40–7.34 (m, 2 H, ArH), 7.22 (t, $J$ = 7.8 Hz, 1 H, ArH), 7.10 (d, $J$ = 8.6 Hz, 2 H, ArH), 7.05–7.01 (m, 1 H, ArH), 6.82–6.76 (m, 3 H, ArH), 6.11 (s, 1 H, NH), 5.49 (s, 1 H, CH), 3.94 (q, $J$ = 6.9 Hz, 2 H, $CH_2$), 1.28 (t, $J$ = 6.9 Hz, 3 H, $CH_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 157.4, 145.0, 144.4, 141.0, 136.8, 135.8, 130.3, 130.0, 128.8, 125.4, 122.0, 121.4, 121.1, 118.6, 118.4, 113.8, 111.0, 62.8, 58.0, 14.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3145, 1611, 1403 cm$^{-1}$. MS (ES$^+$): $m/z$ = 342.3 [M + 1]$^+$. $C_{22}H_{19}N_3O$ (341.41): calcd. C 77.40, H 5.61, N 12.31; found C 77.43, H 5.62, N 12.33.

**6-(4-Methylphenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indole (8f):** Yield 0.144 g (86%), brown solid, m.p. 195–196 °C, $R_f$ = 0.63 (EtOAc/hexane, 1:1), $t_R$ = 17.53 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.01 (s, 1 H, ArNH), 8.12–8.04 (m, 2 H, ArH), 7.40–7.17 (m, 3 H, ArH), 7.04 (s, 5 H, ArH), 6.84 (s, 1 H, ArH), 617 (s, 1 H, NH), 5.51 (s, 1 H, CH), 2.21 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 144.3, 140.9, 136.8, 135.8, 130.5, 129.9, 128.6, 127.6, 125.5, 121.9, 121.4, 121.1, 118.6, 118.1, 110.9, 58.3, 20.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3414, 3258, 1579 cm$^{-1}$. MS (ES$^+$): $m/z$ = 312.4 [M + 1]$^+$. $C_{21}H_{17}N_3$ (311.39): calcd. C 81.00, H 5.50, N 13.49; found C 81.03, H 5.52, N 13.45.

**2-(6,7-Dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-*cd*]indol-6-yl)-phenol (8g):** Yield 0.127 g (85%), brown solid, m.p. 220–222 °C, $R_f$ = 0.50 (EtOAc/hexane, 1:1), $t_R$ = 13.85 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.01 (d, $J$ = 1.4 Hz, 1 H, ArNH), 9.76 (br. s, 1 H, OH), 8.14 (dd, $J$ = 4.3, 1.4 Hz, 1 H, ArH), 8.08–8.04 (m, 1 H, ArH), 7.41–7.37 (m, 1 H, ArH), 7.29–7.19 (m, 2 H, ArH), 7.02–6.94 (m, 2 H, ArH), 6.87–6.81 (m, 2 H, ArH), 6.59–6.51 (m, 2 H, ArH), 5.81 (d, $J$ = 2.9 Hz, 1 H, NH), 5.69 (d, $J$ = 3.4 Hz, 1 H, CH) ppm. $^{13}$C NMR (50 MHz, [D$_6$]DMSO): $\delta$ = 154.4, 145.3, 144.3, 141.4, 136.8, 130.5, 129.8, 128.1, 127.8, 125.9, 121.9, 121.4, 120.9, 118.6, 117.5, 114.9, 111.0, 53.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3155, 2938, 1625, 1410 cm$^{-1}$. MS (ES$^+$): $m/z$ = 314.4 [M + 1]$^+$. $C_{20}H_{15}N_3O$ (313.36): calcd. C 76.66, H 4.82, N 13.41; found C 76.67, H 4.81, N 13.43.

**6-(3,4-Dimethoxyphenyl)-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino-[3,4,5-*cd*]indole (8h):** Yield 0.148 g (87%), white solid, m.p. 236–238 °C, $R_f$ = 0.38 (EtOAc/hexane, 1:1), $t_R$ = 15.01 min. $^1$H NMR (200 MHz, [D$_6$]DMSO): $\delta$ = 11.01 (s, 1 H, ArNH), 8.16–8.03 (m, 2 H, ArH), 7.38 (d, $J$ = 7.6 Hz, 2 H, ArH), 7.21 (t, $J$ = 7.8 Hz, 1 H, ArH), 7.06–7.01 (m, 2 H, ArH), 6.85 (s, 1 H, ArH), 6.75 (d, $J$ = 8.1 Hz, 1 H, ArH), 6.53 (d, $J$ = 8.4 Hz, 1 H, ArH), 6.14 (s, 1 H, NH), 5.47 (d, $J$ = 1.6 Hz, 1 H, CH), 3.66 (s, 6 H, 2 × $OCH_3$) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 148.5, 147.7, 145.2, 144.3,

141.1, 136.8, 136.3, 130.5, 129.8, 125.4, 121.9, 121.3, 121.1, 119.7, 118.5, 118.3, 111.7, 111.1, 110.9, 58.4, 55.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3180, 1594, 1419 $cm^{-1}$. MS ($ES^+$): *m*/*z* = 358.3 $[M + 1]^+$. $C_{22}H_{19}N_3O_2$ (357.41): calcd. C 73.93, H 5.36, N 11.76; found C 73.95, H 5.33, N 11.72.

**6-Ethyl-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-cd]indole (8i):** Yield 0.060 g (51%), brown solid, m.p. 148–149 °C, $R_f$ = 0.38 (EtOAc/hexane, 2:8), $t_R$ = 15.32 min. $^1H$ NMR (300 MHz, $[D_6]$-DMSO): $\delta$ = 10.91 (s, 1 H, ArNH), 8.18 (s, 1 H, ArH), 8.04–8.01 (m, 1 H, ArH), 7.41–7.31 (m, 2 H, ArH), 7.17–7.10 (m, 3 H, ArH), 5.90 (s, 1 H, NH), 4.23 (s, 1 H, CH), 1.62–1.52 (m, 2 H, ArH), 0.92 (d, *J* = 3.3 Hz, 3 H, NH) ppm. $^{13}C$ NMR (75 MHz, $[D_6]$DMSO): $\delta$ = 145.1, 143.8, 140.8, 136.8, 130.4, 129.5, 125.0, 122.0, 121.2, 119.7, 118.7, 118.3, 110.7, 56.0, 29.7, 10.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3300, 2930, 2367, 1641, 1429 $cm^{-1}$. MS ($ES^+$): *m*/*z* = 250.3 $[M + 1]^+$. $C_{16}H_{15}N_3$ (249.31): calcd. C 77.08, H 6.06, N 16.85; found C 76.50, H 6.70, N 16.10.

**6-*tert*-Butyl-6,7-dihydro-4*H*-pyrido[2′,3′:6,7]azepino[3,4,5-cd]indole (8j):** Yield 0.083 g (63%), light green solid, m.p. 174–176 °C, $R_f$ = 0.40 (EtOAc/hexane, 2:8), $t_R$ = 14.03 min. $^1H$ NMR (300 MHz, $[D_6]$DMSO): $\delta$ = 11.00 (s, 1 H, ArNH), 8.11–8.05 (m, 2 H, ArH), 7.35–7.31 (m, 2 H, ArH), 7.18–7.06 (m, 3 H, ArH), 6.09 (d, *J* = 5.0 Hz, 1 H, NH), 4.13 (d, *J* = 5.0 Hz, 1 H, CH), 0.77 [s, 9 H, $(CH_3)_3$] ppm. $^{13}C$ NMR (75 MHz, $[D_6]$DMSO): $\delta$ = 144.4, 144.4, 139.5, 136.4, 130.4, 128.2, 126.3, 122.1, 121.9, 120.8, 118.2, 114.8, 110.5, 63.8, 27.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3407, 2930, 2375, 1649 $cm^{-1}$. MS ($ES^+$): *m*/*z* = 278.3 $[M + 1]^+$. $C_{18}H_{19}N_3$ (277.37): calcd. C 77.95, H 6.90, N 15.15; found C 77.43, H 6.23, N 15.20.

**Supporting Information** (see also the footnote on the first page of this article): $^1H$- and $^{13}C$-NMR spectra of compounds **4a**–**f**, **5a**–**d**, **5h**, **6a**–**c**,**7a**–**c**, **7e**–**f**, **8b**, **8e**, **8g**–**h**, **8j**.

## Acknowledgments

The authors are grateful to SAIF, CDRI, Lucknow for supplying spectroscopic data. M. S., P. K. A., S. K. S., A. K. M. and S. G. are grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi, for fellowships.

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Received: April 29, 2010
Published Online: July 20, 2010

  