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A One-Pot MCR-Oxidation Approach towards Indole-fused Heteroacenes

P. V. Santhini,[a,b] Akhil Krishnan R.,[a] Sheba Ann Babu,[a] Betna Shamlin Simethy,[a] Gourab Das,[b,c] Vakayil K. Praveen,[b,c] Sunil Varughese[a,b] and Jubi John*[a,b]

[a] Organic Chemistry Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram-695019, India
E-mail: jubijohn@niist.res.in

[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-NIIST Campus, Thiruvananthapuram-695019, India

[c] Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram-695019, India

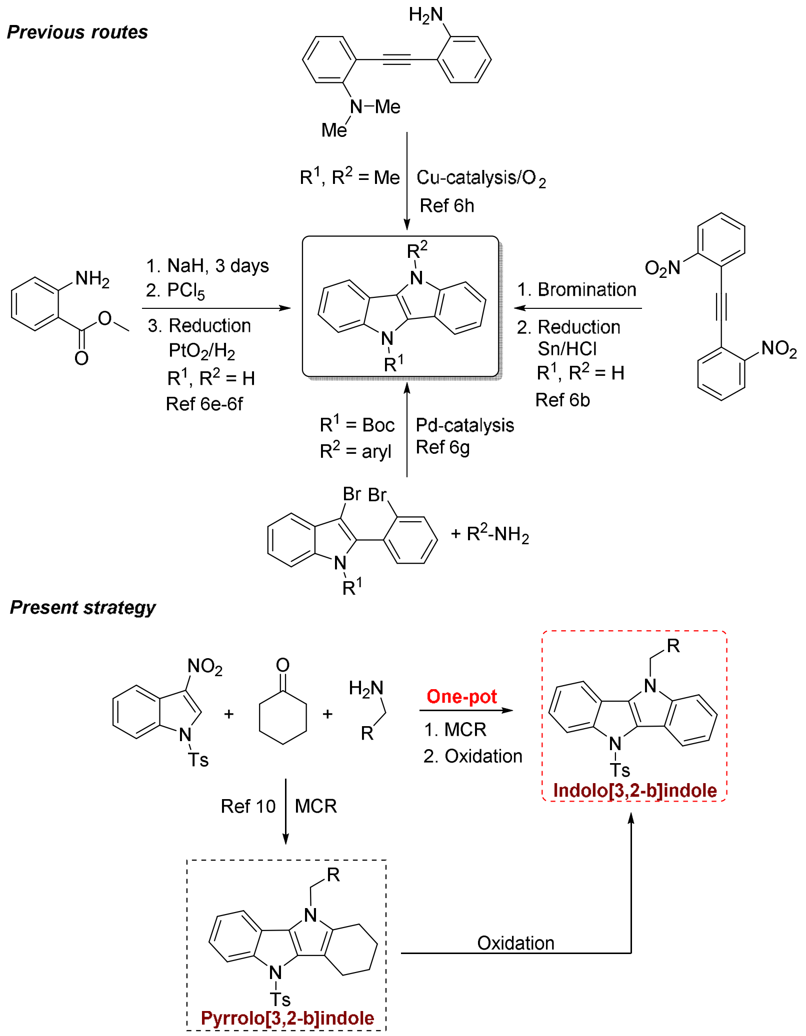
Abstract

A straightforward synthetic route towards indole-fused heteroacenes was developed. The strategy comprises of a one-pot process starting with a multicomponent reaction of cyclohexanone, primary amine and *N*-tosyl-3-nitroindole followed by an oxidation step. The one-pot approach was found to be general affording both symmetric and non-symmetric indolo[3,2-b]indoles in good yields. The strategy was also utilized for accessing 5-ring fused benzo[g]indolo[3,2-b]indole. We could extend the methodology for the synthesis of benzothieno[3,2-b]indoles starting from 3-nitro-benzothiophene. The importance of the developed method was exemplified by performing the reaction sequence in gram scale and also by the synthetic transformations of indolo[3,2-b]indoles. In addition, the change in photophysical properties with extension of conjugation of the synthesized heteroacenes was studied.

Introduction

The past decades have witnessed intensive research for the development of polycyclic aromatic hydrocarbons/acenes due to its intriguing electronic and luminescent properties.[1] These features of polycondensed acenes have made them interesting candidates for applications in organic semiconductors, light-emitting diodes, field-effect transistors and photovoltaics.[1] Recently, *N*-heteroacenes have emerged as excellent additions to the family of polycyclic aromatic compounds which exhibit analogues properties required for applications as functional materials.[2] These characteristics have fuelled the research for the development of facile synthetic routes toward extended π-conjugated *N*-heteroacenes.[3] In the present report, we disclose a practical one-pot transition metal-free approach towards indolo-fused heteroacenes.

Indolo[3,2-b]indole moieties are known to be excellent electron donors with better charge mobility.[4] These indole fused heteroacenes were made use for developing high spin organic polymers,[5a] as core donor in heterojunction solar cell,[5b] in organic field-effect transistors[5c] and organic photovoltaics.[5d-f] Despite of these interesting properties, the wide application of these heteroacenes are limited due to the lack of short and efficient synthetic routes.[6] The existing methods for the synthesis of indolo[3,2-b]indole involve multiple steps and majority of them require metal catalysed reduction as the final step (Scheme 1). One of the first reports for the synthesis of this heteroacene involved the bromination of o,o'-dinitrotolan followed by reduction of the intermediate dibromostyrene with Sn/HCl.[6b] A reductive ring closure route was recently described which involves an intermolecular cyclization of o-aminobenzoic acid ester followed by chlorination and finally reductive ring closure of the diimidoyl chloride.[6e-f] Indolo[3,2-b]indole was also synthesized by metal catalyzed routes, the first one being a Pd-catalysed double *N*-arylation of anilines with the dihalobiaryls.[6g] Soon after, a copper-catalysed intramolecular oxidative diamination of bis(2-aminophenyl)acetylene was reported for accessing these heteroacenes.[6h]

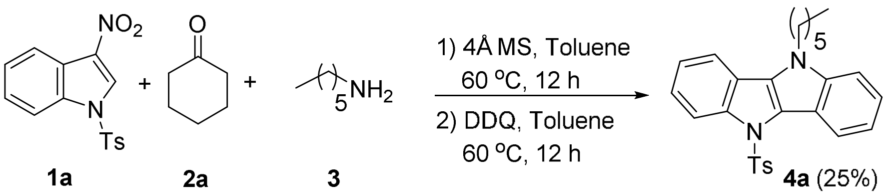


Scheme 1. Synthetic routes towards indolo[3,2-b]indole.

The chemistry of electrophilic indoles[7] were thoroughly studied by different groups for functionalization and annulation of indole moiety.[8] Different *N*-heterocycles were synthesized from enamines derived from enoloisable ketones and primary amines.[9] Based on these literature precedents, recently we have unraveled a general multicomponent reaction involving an enolizable ketone, a 1° amine and *N*-tosyl-3-nitroindole for the syntheses of pyrrolo[3,2-b]indole heterocycles.[10] The multicomponent reaction proceeds *via* the formation of enamine from the condensation of the enolizable ketone and primary amine. The enamine then adds to 3-nitroindole and subsequently pyrrole-annulation occurs by the elimination of hyponitrous acid and water. We envisaged that indolo[3,2-b]indoles could be synthesized in 'one-pot' by starting with cyclohexanone as the enolizable ketone in the multicomponent reaction followed by an oxidation step (Scheme 1) and in our initial communication we showed that pyrrolo[3,2-b]indole could be easily oxidized to indolo[3,2-b]indole. In this article we report our entire efforts in developing a general one-pot strategy toward indolo[3,2-b]indoles and benzothieno[3,2-b]indole.

Results and Discussion

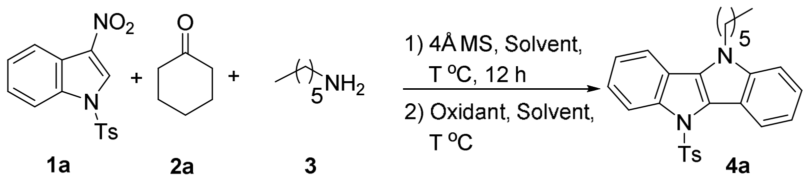
We initiated our studies with *N*-tosyl-3-nitroindole **1a**, cyclohexanone **2a** and *n*-hexylamine as substrates. After completion of the MCR for the synthesis of the intermediate pyrrolo[3,2-b]indole, DDQ was added and the reaction was left at 60 °C for 12 h. As expected, indolo[3,2-b]indole **4a** was obtained in 25% yield (Scheme 2).



Scheme 2. One-pot approach towards indolo[3,2-b]indole **4a**.

The optimal conditions for the 'one-pot' fused heteroacene synthesis were identified with 3-nitroindole **1a**, cyclohexanone **2a** and *n*-hexyl amine as substrates (Table 1). The initial reaction at 60 °C afforded the product in 25% yield (Table 1, Entry 1). By increasing the temperature to 80 °C, the yield of **4a** rose to 45% (Table 1, Entries 1-2). Changing the oxidant to chloranil improved the yield to 63% at 80 °C (Table 1, Entries 3-4). Screening of various solvents such as CH_3CN, DCM, DCE showed that toluene was the most suitable medium for this reaction (Table 1, Entry 4-7). The best yield of 72% was obtained for **4a** from the reaction at 100 °C (Table 1, Entry 8). Further increase in the temperature diminished the yield of the indoloindole **4a** (Table 1, Entry 9).

Table 1. Optimization studies[a]

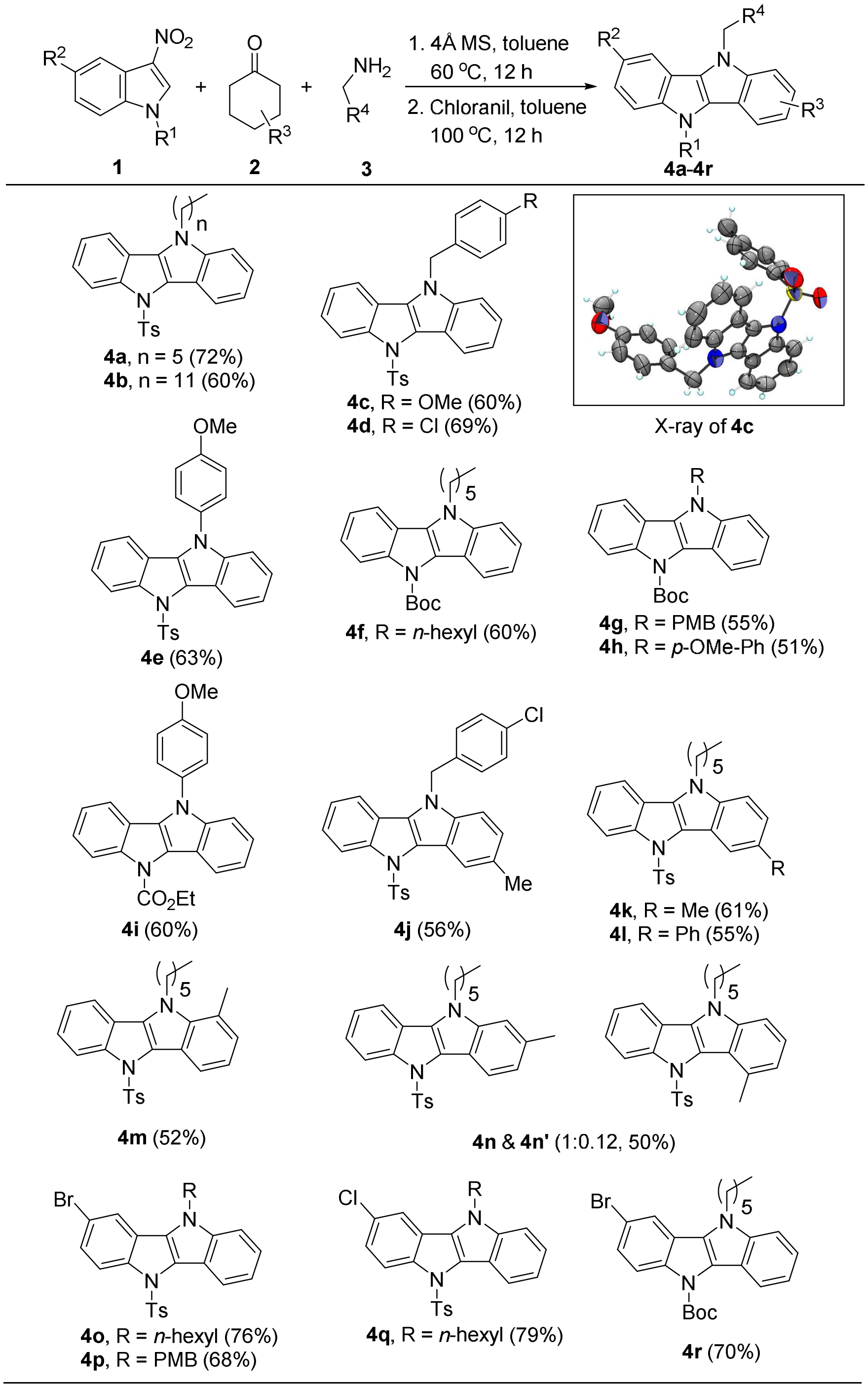


Entry	Oxidant	Solvent	Temp (°C)	Yield (%)
1	DDQ	toluene	60	25
2	DDQ	toluene	80	45
3	Chloranil	toluene	60	55
4	Chloranil	toluene	80	63
5	Chloranil	CH_3CN	60	40
6	Chloranil	DCM	45	40
7	Chloranil	DCE	80	32
8	**Chloranil**	**toluene**	**100**	**72**
9	Chloranil	toluene	120	62

[a] Reaction conditions: 1) **1a** (1.0 equiv., 0.16 mmol), **2a** (2.0 equiv.), **3** (2.0 equiv.), 4Å MS (50 mg), solvent, 60 °C, 12 h. 2) Oxidant (3.0 equiv.), solvent, T °C, 12 h. Isolated yield

Table 2 depicts the results of the detailed studies on the scope of indolo[3,2-b]indole synthesis. Straight chain amines, benzylamines and *p*-anisidine underwent the MCR-oxidation sequence with *N*-tosyl-3-nitro-indole **1a** and cyclohexanone **2a** to furnish the expected products **4a** to **4e** in good yields. The structure of the fused indole was confirmed from X-ray crystal data of **4c**. Indoloindoles **4f** to **4h** were obtained in moderate to good yields with different amines when the *N*-protection was changed to 'Boc' group. Again, **4i** was obtained in 60% yield from 3-nitroindole with carboethoxy group protecting the indole *N*-atom. Our next task was to study the reactivity of different substituted cyclohexanones which would enable the synthesis of unsymmetrical indolo[3,2-b]indoles (with respect to substituents on the aryl ring), the synthesis of which was not possible/tedious with reported procedures.[6] To our delight, 4-methyl-, 4-phenyl- & 2-methyl cyclohexanones reacted well under the 'one-pot' reaction conditions affording the corresponding unsymmetrical indoloindoles **4j** to **4m** in moderate to good yields (Table 2). The one-pot process with 3-methylcyclohexanone afforded a 1:0.12 mixture of regioisomers **4n** and **4n'** in 50% yield. The investigations on the generality of the methodology were concluded with the reactions of halogen (Br&Cl) substituted 3-nitroindoles from which the expected products **4o** to **4r** were isolated in good yields. The value of the developed methodology escalates due to the possibility of synthesizing halogen substituted indolo[3,2-b]indole moieties which can be further functionalized for material applications.

Table 2. Generality of indolo[3,2-b]indole synthesis[a]



4a, n = 5 (72%)
4b, n = 11 (60%)

4c, R = OMe (60%)
4d, R = Cl (69%)

4e (63%)

4f, R = *n*-hexyl (60%)

4g, R = PMB (55%)
4h, R = *p*-OMe-Ph (51%)

4i (60%)

4j (56%)

4k, R = Me (61%)
4l, R = Ph (55%)

4m (52%)

4n & **4n'** (1:0.12, 50%)

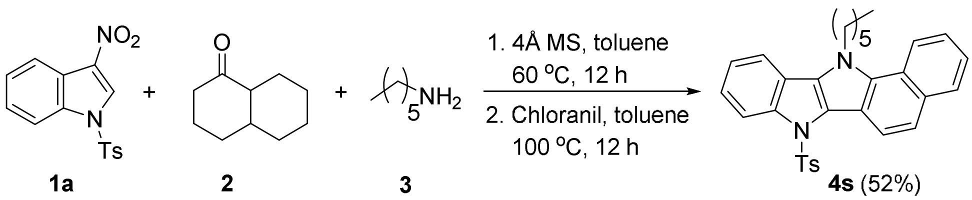
4o, R = *n*-hexyl (76%)
4p, R = PMB (68%)

4q, R = *n*-hexyl (79%)

4r (70%)

[a] Reaction conditions: (i) **1** (50 mg), **2** (2.0 equiv.), **3** (2.0 equiv.), 4 Å MS (50 mg), toluene (0.3 mL), 60 °C, 12 h. (ii) Chloranil (3.0 equiv.), toluene (0.7 mL), 100 °C, 12 h.

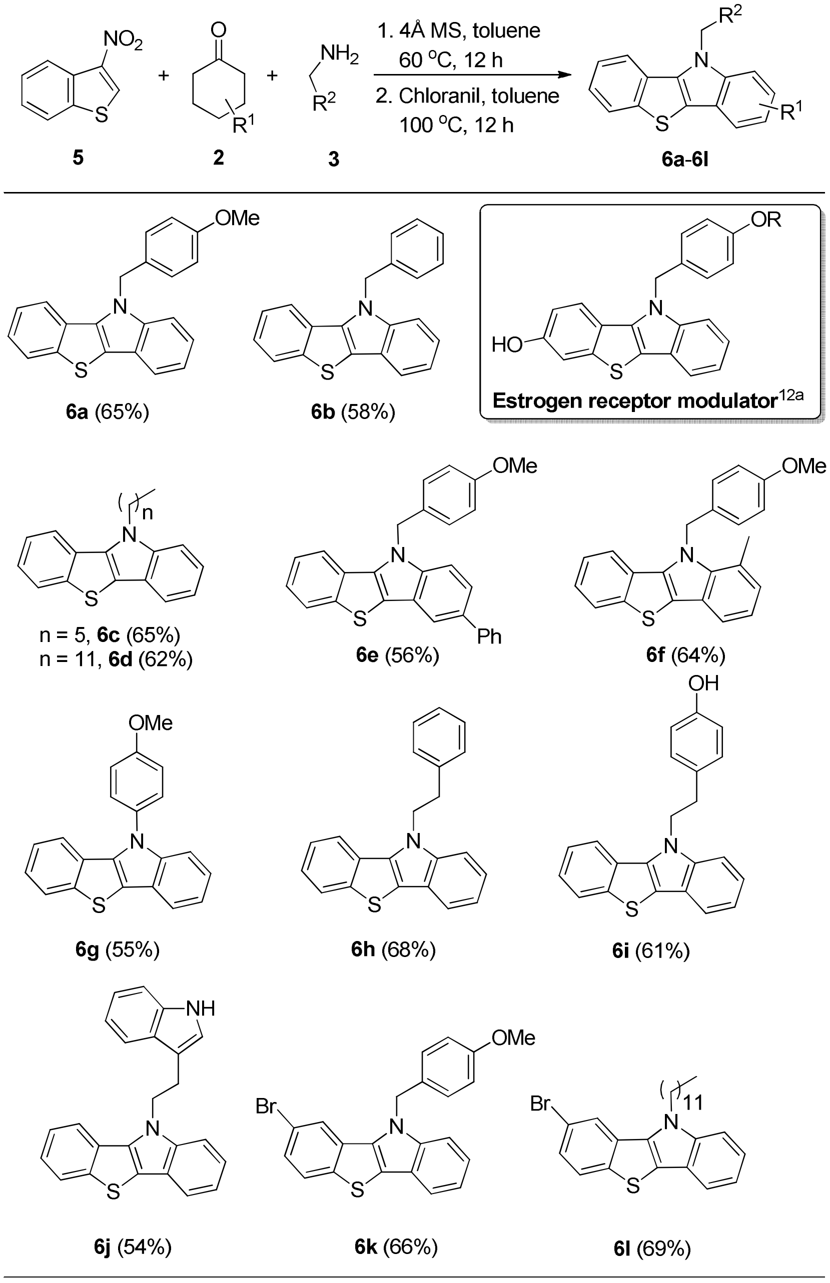
Having developed a general and efficient methodology for accessing indolo[3,2-b]indoles, we were motivated to extent the strategy for the synthesis of a pentacyclic *N*-heteroacene. The obvious choice towards this goal would be to start with α-tetralone as the enolizable ketone for the MCR. But, we have already reported that α-tetralone failed to react due to electronic reasons.[10] Hence we chose to proceed with 1-decalone (mixture of *cis* and *trans* isomers) as the ketone moiety in the sequential MCR-oxidation protocol (Scheme 3). To our joy and as expected, the corresponding benzo[g]indolo[3,2-b]indole **4s** was obtained in 52% yield.



Scheme 3. One-pot approach towards benzo[g]indolo[3,2-b]indole **4s**.

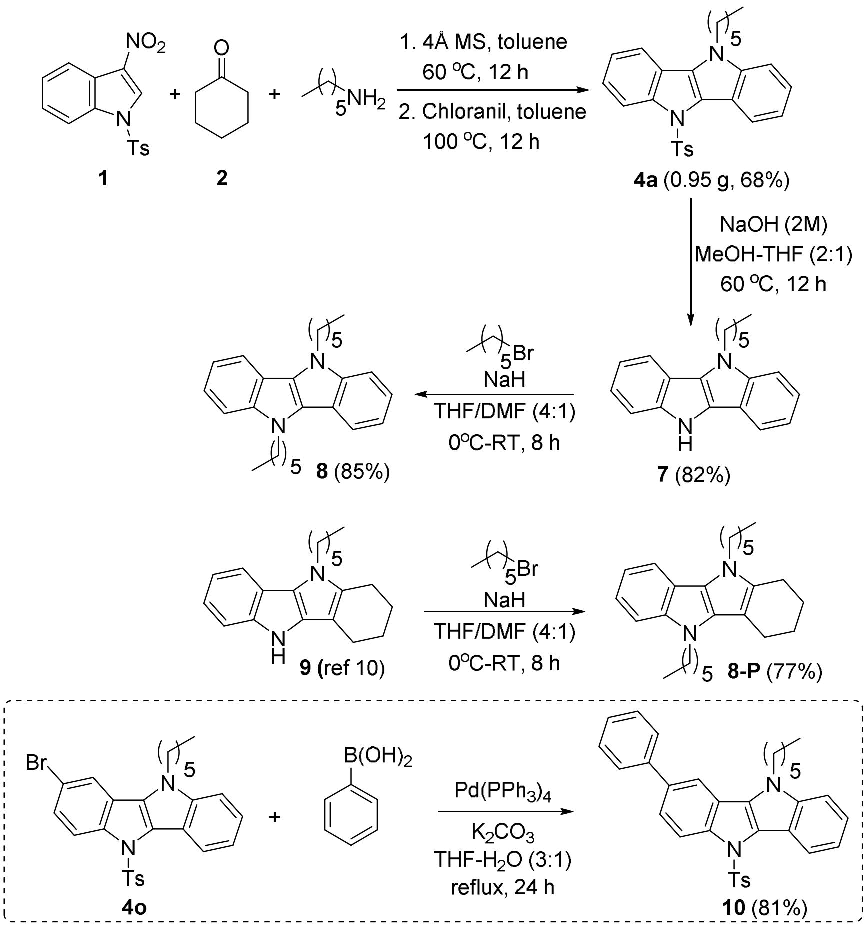
Our success in the heteroannulation of indole prompted us to investigate the reactivity of 3-nitro-benzothiophene under the same one-pot heteroannulation protocol. The MCR-oxidation reaction sequence with 3-nitrobenzothiophene **5**, cyclohexanone and 4-methoxy benzylamine afforded the expected benzothieno[3,2-b]indole **6a** in 65% yield (Table 3). Analogues of benzothieno[3,2-b]indole[11] are used for material applications and also have shown promising biological activity.[12] Majority of the reported procedures for the synthesis of these heteroacenes involves the use of transition metal catalysts.[11] A metal-free route involving multiple steps was reported for the synthesis of the estrogen receptor modulator starting from benzenethiol (Figure shown in Table 3).[12a] Our one-pot process worked well with *n*-hexyl and decyl amines affording the corresponding products **6c** and **6d** in good yields. Substituted cyclohexanones also furnished the expected benzothienoindoles **6e** and **6f** in good yields. 4-methoxyaniline was also compatible with the developed conditions affording the product **6g** in 55% yield. Benzothienoindole **6h** was obtained in good yield starting with 2-phenylethylamine as the amine moiety. Next, we were interested in checking the reactivity of naturally available amines towards the annulation reaction with the aim for synthesizing benzothienoindoles with potential bioactivities. Both tyramine and tryptamine participated in the one-pot MCR-oxidation reaction sequence affording products **6i** and **6j** respectively in good yields. Finally, the methodology also worked perfectly with 5-bromo-3-nitrobenzo[b]thiophene yielding the corresponding products **6k** and **6l** in good yields.

Table 3. Generality of benzothieno[3,2-b]indole synthesis[a]



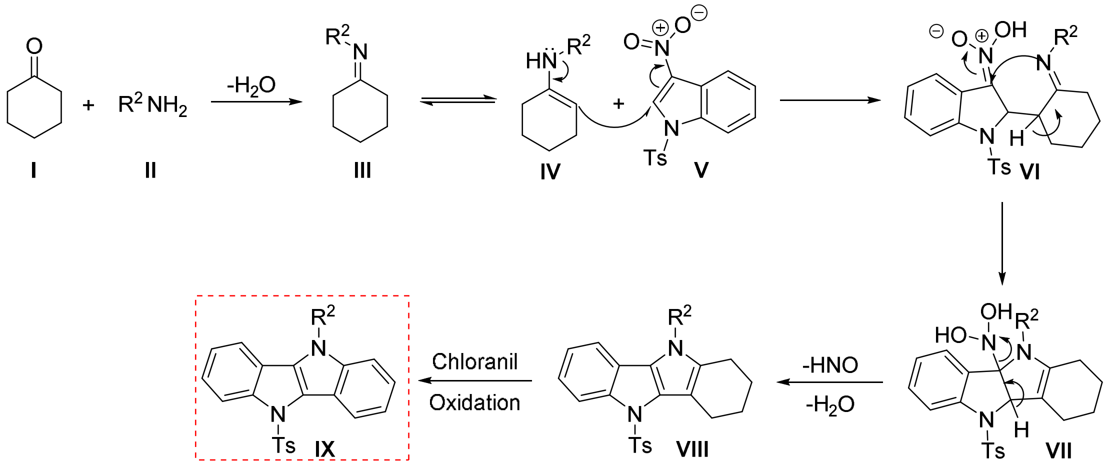
[a]Reaction conditions: (i) **5** (50 mg), **2** (2.0 equiv.), **3** (2.0 equiv.), 4 Å MS (50 mg), toluene (0.3 mL), 60 °C, 12 h. (ii) Chloranil (3.0 equiv.), toluene (0.7 mL), 100 °C, 12 h.

To further highlight the synthetic utility of the developed heteroannulation process, we attempted the gram scale synthesis of indolo[3,2-b]indole. Starting from one gram of *N*-tosyl-3-nitroindole **1a**, we obtained the corresponding product **4a** in 68% yield (Scheme 4). The tosyl-group on the *N*-atom of the indolo[3,2-b]indole **4a** could be directly removed by treatment with NaOH.[13] The deprotected compound **7** was easily *N*-alkylated by treating with bromohexane under baisic conditions to afford 5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole **8** in 85% yield. It is noteworthy to mention that indolo[3,2-b]indoles can be synthesized with different groups on both *N*-atoms, depending on the application. 10-hexyl-pyrrolo[3,2-b]indole **9** was also *N*-alkylated towards dihexyl-pyrrolo[3,2-b]indole **8-P** following the above mentioned alkylation procedure. These dihexyl pyrroloindole **8-P** and indoloindole **8** were syntheized to study and compare their basic photophysical properties. Finally, we did a Suzuki reaction of indoloindole **4o** with phenyl boronic acid, hence proving that the compounds synthesized with our strategy can be easily functionalized at multiple centers.



Scheme 4. Scale-up and synthetic transformations of indoloindoles.

The initial stage of the mechanism for this one-pot reaction is the MCR to furnish the intermediate pyrrolo[3,2-b]indole (Scheme 5). The mechanism of the MCR is the same as was described in our communication.[10] The reaction commences with the condensation of cyclohexanone **I** and amine **II** to furnish the imine **III**. The enamine form **IV** which is in equilibrium with the imine then participates in a Michael addition to the C-2 position of 3-nitro-*N*-Tosyl indole to form the intermediate **VI**. The pyrroline intermediate **VII** is generated by the attack of the enamine to the C-3 carbon of the nitronate in **VI**. The pyrroloindole **VIII** is then formed by the elimination of hyponitrous acid and water from the intermediate **VII**. Finally, the oxidation of pyrroloindole with chloranil affords the corresponding indolo[3,2-b]indole **IX**.



Scheme 5. Mechanism of indoloindole formation.

In order to understand the impact of oxidation induced aromatization of pyrrolo[3,2-b]indole and benzothieno[3,2-b]pyrrole, we have compared the photophysical properties of compounds **8-P**, **8**, **6c-P** and **6c**. Due to the solubility reason, we have selected acetonitrile as the solvent for conducting the photophysical studies where the compounds were found to exist as molecularly dissolved species (1 x 10^{-5} M). The results of the photophysical properties have been summarized in Figure 1, 2 and Table 4. Pyrrolo[3,2-b]indole **8-P** showed two well distinct absorption maxima at 258 (ε = 2.35 x 10^4 L mol^{-1} cm^{-1}) and 318 nm (ε = 1.05 x 10^4 L mol^{-1} cm^{-1}) and a broad emission profile with maximum at 389 nm (Φ_F = 0.31, τ = 7.18 ns). The lowest energy absorption centered at 318 nm can be assigned to $S_0 \rightarrow S_1$ transition and the intense absorption band at 258 nm is most likely originated from the higher energy electronic transiton.[6f,6g] In the case of indolo[3,2-b]indole **8** the absorption maxima was found to be slightly red shifted (λ_{max} = 261 nm, ε = 6.74 x 10^4 L mol^{-1} cm^{-1}; λ_{max} = 323 nm, ε = 2.37 x 10^4 L mol^{-1} cm^{-1}) along with the formation of a new shoulder band at 353 nm (ε = 0.86 x 10^4 L mol^{-1} cm^{-1}). The long-wavelength absorption band at 353 nm involve electronic transition from S_0 ground state to relatively low-lying S_1 excited state.[6f,6g] The absorption maximum at 323 nm with a weak shoulder can be assigned to $S_0 \rightarrow S_2$ transition and the higher energy absorption band ($S_0 \rightarrow S_5$) is centered at 261 nm. Interestingly, the emission spectrum of **8** was found to be shifted towards longer wavelength region with maximum at 407 nm (Φ_F = 0.46, τ = 6.12 ns) with a shoulder band at 388 nm. This observation implies that the indolo[3,2-b]indole **8** is having improved photophysical features (molar extinction coefficient, ε and fluorescence quantum yield, Φ_F) than that of the parent pyrrolo[3,2-b]indole **8-P** (Figure 1).

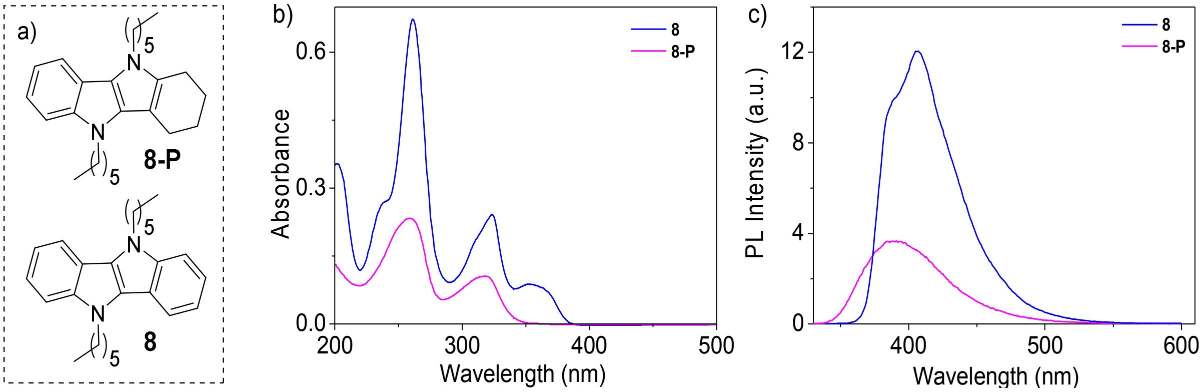


Figure 1. a) Molecular structure of pyrrolo[3,2-b]indole **8-P** and indolo[3,2-b]indole **8**. b) UV-Vis absorption and c) fluorescence spectra of **8-P** and **8** in acetonitrile (1 x 10^{-5} M), λ_{ex} = 318 (**8-P**) and 323 nm (**8**).

We then extended similar kind of studies to compare the properties of benzothieno[3,2-b]indole **6c** with its parent benzothieno[3,2-b]pyrrole molecule **6c-P** (Figure 2). In the case of **6c-P**, a broad absorption spectrum was obtained with maxima at 259 (ε = 1.20 x 10^4 L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$), 274 (ε = 1.13 x 10^4 L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$) and 297 nm (ε = 1.26 x 10^4 L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$). Furthermore, the molecule **6c-P** was found to be non-emissive. On contrary, **6c** displayed a well-resolved absorption spectrum with maxima at 252 nm (ε = 2.31 x 10^4 L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$), 308 (ε =1.83 x 10^4 L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$) and 342 nm (ε = 0.71 x 10^4 L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$). This molecule also showed weak emission feature with maximum centered at 375 nm (Φ_{F} = 0.04, τ = 0.36 ns) along with a weak vibronic shoulder band at 360 nm. Similar to previous case, here also we have observed that oxidation of the parent benzothieno[3,2-b]pyrrole **6c-P** leads to improved photophysical properties.

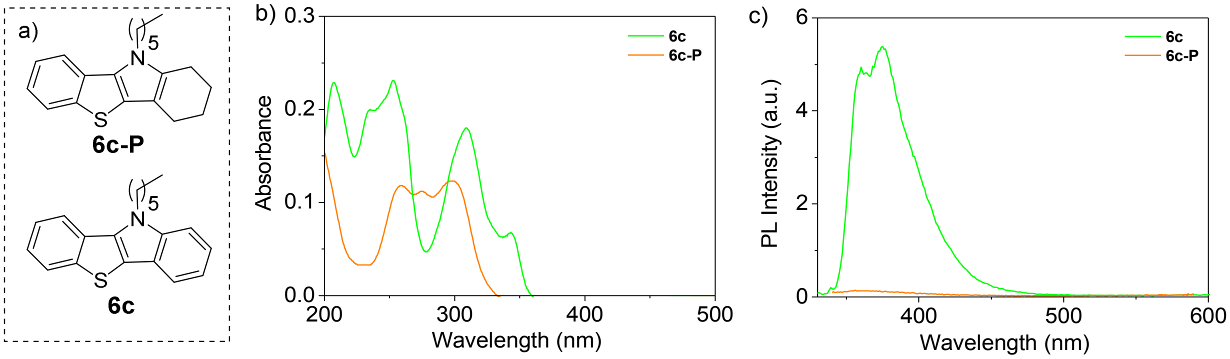


Figure 2. a) Molecular structure of benzothieno[3,2-b]pyrrole **6c-P** and benzothieno[3,2-b]indole **6c**. b) UV-Vis absorption and c) fluorescence spectra of **6c-P** and **6c** in acetonitrile (1 x 10^{-5} M), λ_{ex} = 297 (**6c-P**) and 308 nm (**6c**).

Table 4. Photophysical properties of compound **8-P**, **8**, **6c-P** and **6c** in acetonitrile (1 x 10^{-5} M)

Compound	λ_{abs} (nm)	ε (10^4 L mol^{-1} cm^{-1})	$\lambda_{\text{em}}{}^{a}$ (nm)	$\Phi_{\text{F}}{}^{b}$	τ^{c} (ns)
8-P	258, 318	2.35, 1.05	389	0.31	7.18
8	261, 323, 353	6.74, 2.37, 0.86	388, 407	0.46	6.12
6c-P	259, 274, 297	1.2, 1.13, 1.26	-	-	-
6c	252, 308, 342	2.31, 1.83, 0.71	360, 375	0.04	0.36

[a] Excitation wavelength, λ_{ex} = 318 (**8-P**), 323 (**8**), and 308 nm (**6c**). [b] Fluorescence quantum yields were determined using quinine sulphate as the standard (Φ_{F} = 0.546 in 0.1 N H_2SO_4). [c] λ_{ex} = 330 nm is used for fluorescence lifetime (τ) measurements.

Conclusion

In conclusion, we have developed a simple, metal-free and one-pot method for the synthesis of indolo[3,2-b]indole, the most general and applicable route reported to-date. We could demonstrate the applicability of the sequential MCR-oxidation strategy for the generation of symmetrical and unsymmetrical indolo[3,2-b]indoles; highly relevant for material applications and which was not probable with existing methods. In addition, by selecting an appropriate enolizable ketone, we were able to synthesize 5-ring fused benzo[g]indolo[3,2-b]indole. We could also extend the strategy for accessing benzothieno[3,2-b]indole, another moiety of medicinal and material interest. The importance of the one-pot heteroannulation process was demonstrated by synthesizing indoloindole in gram-scale and also by synthetic modification of fused-indole moieties. Finally, we have also evaluated and compared the basic photophysical properties of the synthesized *N*-heteroacenes.

Experimental Section

General experimental methods: All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulfate binder. Gravity column chromatography was performed using neutral alumina and mixtures of hexane-ethyl acetate were used for elution. Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ and CD_3CN as solvents). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.25ppm) CD_3CN (1.94 ppm). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quadret); dd (double doublet); m (multiplet). Coupling constants are reported as J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03 ppm) CD_3CN (1.32 ppm),. In some of the cases, the ^{13}C of compound were recorded in a 7:3 mixture of $CDCl_3$ and CCl_4. In those ^{13}C a spectrum, the peak seen at δ 96.0 ppm corresponds to the carbon of CCl_4. Mass spectra were recorded under ESI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer with orbitrap analyzer. IR spectra were recorded on Bruker FT-IR spectrometer. The 1-tosyl-3-nitroindoles were prepared by following literature report.[14] Pyrrolo[3,2-b]indole **8-P** and benzothieno[3,2-b]pyrrole **6c-P** were synthesized following our initial communication.[10] The electronic absorption spectra were recorded on a Shimadzu spectrophotometer UV-2100. The fluorescence spectra were recorded on a SPEX-Fluorolog-3 FL3-221 spectrofluorimeter. Optical studies in solution-state were carried out in a 1 cm quartz cuvette. Relative quantum yield measurements were carried out using quinine sulphate in 0.1 N H_2SO_4 as the standard which has a reported quantum yield of Φ_F = 0.546.[15,16] Fluorescence lifetime measurements were carried out using IBH (model 5000 DPS) time-correlated single photon counting system. The lifetime values were obtained using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as χ^2 (< 1.1) as well as the visual inspection of the residuals.

Synthetic procedure for the Multicomponent Reaction toward Indole-fused Heteroacenes

Genral procedure for the synthesis of indolo[3,2-b]indole (4a-4s): The enolizable ketone, cyclohexanone (31 mg, 0.32 mmol) and primary amine, *n*-hexylamine (32 mg, 0.32 mmol) were weighed into a dry reaction tube. Dry toluene (0.3 mL) along with 4 Å MS (50 mg) was added and allowed to stir at 60 °C for 1 hour, after which 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol) was added into it and again kept it for stirring at the same temperature for 11 hours. After the complete consumption of 3-nitro-*N*-tosyl indole, Chloranil (117 mg, 0.47 mmol) along with toluene (0.7 mL) was added and kept at 100 °C for 10 hours. The solvent was evaporated in vacuo and the residue on activated neutral alumina column chromatography yielded indolo[3,2-b]indole with hexanes and ethyl acetate as eluent.

Synthesis and characterization of indolo[3,2-b]indole (4a-4s)

5-Hexyl-10-tosyl-5,10-dihydroindolo[3,2-b]indole (4a): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), *n*-hexylamine (32 mg, 0.32 mmol), cyclohexanone (31 mg, 0.32 mmol), and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as a colourless viscous liquid (51 mg, 72%). **Analytical Data of 4a**: TLC (SiO_2): Rf; 0.43 (7% ethyl acetate in hexane). IR (neat) ν_{max}: 2919, 2849, 1911, 1879, 1796, 1675, 1603, 1507, 1383, 1353, 1246, 1167, 1029, 947 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.53 (d, *J* = 7.5 Hz, 1H), 8.35 (d, *J* = 8 Hz, 1H), 7.62-7.58 (m, 2H), 7.41-7.28 (m, 3H), 7.23-7.22 (m, 1H), 7.16-7.14 (m, 2H), 6.99 (d, *J* = 8Hz, 2H), 4.39 (t, *J* = 7Hz, 2H), 2.22 (s, 3H),1.88-1.84 (m, 2H), 1.29-1.21(m, 6H), 0.81 (t, *J* = 7Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 140.7, 140.5, 134.3, 130.2, 129.4, 126.8, 124.4, 123.9, 122.6, 120.7, 120.1, 117.5, 116.4, 109.6, 45.0, 31.5, 30.2, 26.6, 22.5, 21.4, 13.9. HRMS (ESI-Orbitrap) m/z: (M+Na)$^+$ calcd for $C_{27}H_{28}N_2O_2SNa$ 467.1763; Found: 467.1763.

5-Dodecyl-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4b**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), dodecylamine (59 mg, 0.32 mmol) and cyclohexanone (31 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as a colourless viscous liquid (50 mg, 60%). **Analytical Data of 4b**: TLC (SiO_2): Rf; 0.41 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.55 (d, *J* = 8 Hz, 1H), 8.36 (d, *J* = 8 Hz, 1H), 7.65-7.58 (m, 3H), 7.44-7.42 (m, 1H), 7.38-7.29 (m, 4H), 7.02-6.99 (m, 2H), 4.39 (t, *J* = 7 Hz, 2H), 2.21 (s, 3H), 1.87- 1.85 (m, 2H), 1.25-1.11 (m, 18H) 0.87 (t, *J* = 7Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 140.7, 140.5, 134.2, 130.3, 129.4, 126.8, 124.5, 123.9, 122.6, 120.7, 120.0, 117.7, 116.4, 109.7, 45.1, 31.9, 30.2, 29.6, 29.5, 29.3, 27.0, 22.7, 21.4, 14.1. HRMS (ESI-Orbitrap) m/z: (M+H)$^+$ calcd for $C_{33}H_{41}N_2O_2S$ 529.2883; Found: 529.2875.

5-(4-Methoxybenzyl)-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4c**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), 4-methoxybenzylamine (44 mg, 0.32 mmol) and cyclohexanone (31 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (7% ethyl acetate in hexane) to afford the desired product as a white solid (46 mg, 60%). **Analytical Data of 4c**: Mp; 195-197 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.56-8.54 (m, 1H), 8.33 (d, *J* = 8.5Hz, 1H), 7.60-7.58 (m, 2H), 7.46-7.45 (m, 1H), 7.38-7.28 (m, 4H), 7.22-7.20 (m, 1H), 7.02-6.96 (m, 4H), 6.73-6.72 (m, 2H), 5.55 (s, 2H), 3.71 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 144.0, 140.9, 140.7, 134.4, 130.5, 129.5, 129.4, 129.0, 127.4, 126.6, 124.5, 123.9, 123.0, 122.4, 120.8, 120.5, 120.2, 117.7, 116.7, 116.4, 114.3, 114.0, 109.9, 55.1, 47.9, 21.5. HRMS (ESI-Orbitrap) m/z: (M+Na)$^+$ calcd for $C_{29}H_{24}N_2O_3SNa$ 503.1399; Found: 503.1406.

5-(4-Chlorobenzyl)-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4d**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), 4-chlorobenzylamine (45 mg, 0.32 mmol) and cyclohexanone (31 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (7% ethyl acetate in hexane) to afford the desired product as a white solid (53 mg, 69%). **Analytical Data of 4d**: Mp; 195-197 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.58-8.56 (m, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 7.60-7.59 (m, 2H), 7.33-7.32 (m, 4H), 7.19-7.17 (m, 4H), 7.02-6.94 (m, 2H), 6.95 (d, *J* = 8.5 Hz, 2H) 5.57 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 140.8, 140.7, 135.6, 134.2, 133.6, 129.6, 129.4, 129.1, 128.8, 127.5, 127.3, 127.1, 126.8, 124.7, 124.0, 123.2, 120.8, 120.7, 120.0, 117.5, 116.5, 109.8, 47.8, 21.5. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{28}H_{22}ClN_2O_2S$ 485.1085; Found: 485.1088.

5-(4-Methoxyphenyl)-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4e**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), 4-methoxyaniline (39 mg, 0.32 mmol) and cyclohexanone (31 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (7% ethyl acetate in hexane) to afford the desired product as a white solid (47 mg, 63%). **Analytical Data of 4e**: Mp; 195-200 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.59-8.58 (m, 1H), 8.34 (d, *J* = 8.5Hz, 1H), 7.68-7.65 (m, 2H), 7.46 -7.44 (m, 2H), 7.39 -7.37 (m, 1H), 7.34 -7.29 (m, 3H), 7.18 -7.11 (m, 2H), 7.08-7.04 (m , 4H), 3.92 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 144.4, 141.8, 140.8, 134.8, 130.6, 129.7, 128.1, 127.1, 124.9, 123.8, 123.4, 121.2, 120.9, 120.1, 118.4, 116.3, 115.0, 110.9, 55.7, 21.7. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{28}H_{22}N_2O_3SNa$ 489.1243; Found: 489.1239.

***tert*-Butyl 10-hexylindolo[3,2-b]indole-5(10H)-carboxylate** (**4f**): The reaction was performed according to general procedure with 3-nitro-*N*-Boc indole (50 mg, 0.19 mmol), *n*-hexylamine (38 mg, 0.38 mmol) and cyclohexanone (37 mg, 0.38 mmol) and chloranil (140 mg, 0.57 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a viscous liquid (45 mg, 60%). **Analytical Data of 4f**: TLC (SiO_2): Rf; 0.65 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): 1H NMR (500MHz,CDCl3,TMS): δ 8.49 (d, *J* = 8 Hz, 1H), 8.31 (brs, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8 Hz, 1H), 7.35-7.27 (m, 3H), 7.19 (t, *J* = 8 Hz, 1H), 4.46 (t, *J* = 7 Hz, 2H), 1.95-1.90 (m, 2H), 1.80 (s, 9H), 1.40-1.24 (m, 6H), 0.84 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 140.4, 123.9, 122.6, 122.2, 118.9, 117.4, 116.9, 116.3, 109.4, 83.8, 45.0, 31.6, 30.4, 28.6, 26.7, 22.5, 14.0. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{25}H_{30}N_2O_2Na$ 413.2199; Found: 413.2205.

***tert*-Butyl 10-(4-methoxybenzyl)indolo[3,2-b]indole-5(10H)-carboxylate** (**4g**): The reaction was performed according to general procedure with 3-nitro-*N*-Boc indole (50 mg, 0.19 mmol), 4-methoxy benzylamine (52 mg, 0.38 mmol) and cyclohexanone (37mg, 0.38 mmol) and chloranil (140 mg, 0.57 mmol). The crude product was purified by activated neutral alumina column chromatography (5% ethyl acetate in hexane) to afford the desired product as a white solid (45 mg, 55%). **Analytical Data of 4g**: Mp; 155-157 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.52 (d, *J* = 7.5 Hz, 1H), 8.29 (brs, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H), 7.32-7.27 (m, 2H), 7.23-7.21 (m, 2H), 7.09 (d, *J* = 9 Hz, 2H), 6.78-6.76 (m, 2H), 5.63 (s, 2H), 3.72 (s, 3H), 1.81 (s, 9H). ^{13}C

NMR (125 MHz, $CDCl_3$): δ 159.0, 150.8, 140.7, 129.5, 127.5, 124.0, 122.6, 119.4, 118.8, 117.5, 116.9, 116.6, 114.2, 109.6, 84.0, 55.2, 47.9, 28.6. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{27}H_{26}N_2O_3Na$ 449.1835; Found: 449.1852.

***tert*-Butyl 10-(4-methoxyphenyl)indolo[3,2-b]indole-5(10H)-carboxylate** (**4h**): The reaction was performed according to general procedure with 3-nitro-*N*-Boc indole (50 mg, 0.19 mmol), 4-methoxy aniline (47 mg, 0.38 mmol) and cyclohexanone (37mg, 0.38 mmol) and chloranil (140 mg, 0.57 mmol). The crude product was purified by activated neutral alumina column chromatography (5% ethyl acetate in hexane) to afford the desired product as a white solid (40 mg, 51%). **Analytical Data of 4h**: Mp; 160-162 ^oC. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.54-8.53 (m, 1H), 8.30-8.28 (m, 1H), 7.54-7.52 (m, 2H), 7.41- 7.39 (m, 1H), 7.33-7.30 (m, 3H), 7.25-7.23 (m, 1H), 7.17-7.12 (m, 3H), 3.94 (s, 3H), 1.82 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 150.8, 141.4, 130.8, 128.0, 124.2, 122.8, 122.4, 121.7, 120.0, 117.9, 116.8, 114.8, 110.4, 84.1, 55.6, 28.6. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{26}H_{24}N_2O_3Na$ 435.1679; Found: 435.1689.

Ethyl 10-(4-methoxyphenyl)indolo[3,2-b]indole-5(10H)-carboxylate (**4i**): The reaction was performed according to general procedure with ethyl 3-nitro-1H-indole-1-carboxylate (50 mg, 0.21 mmol), 4-methoxy aniline (52 mg, 0.42 mmol) and cyclohexanone (41mg, 0.42 mmol) and chloranil (155 mg, 0.63 mmol). The crude product was purified by activated neutral alumina column chromatography (5% ethyl acetate in hexane) to afford the desired product as a white solid (49 mg, 60%). **Analytical Data of 4i**: Mp; 120-125 ^oC. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.35-8.21 (m, 2H), 7.52-7.46 (m, 2H), 7.39-7.34 (m, 3H), 7.24-7.15 (m, 3H), 7.12-7.09 (m, 2H), 4.72-4.65 (m, 2H), 3.92(s, 3H), 1.65-1.60 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 141.6, 130.7, 130.1, 128.8, 127.9, 124.7, 122.9, 120.8, 120.2, 118.6, 117.9, 116.9, 115.0, 114.8, 110.5, 63.2, 55.5, 14.8. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{24}H_{20}N_2O_3$ 384.1468; Found: 384.1479.

10-(4-Chlorobenzyl)-3-methyl-5-tosyl-5,10-dihydroindolo[3,2-b]indole (**4j**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), 4-chlorobenzylamine (45 mg, 0.32 mmol) and 4-methyl cyclohexanone (36 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (7% ethyl acetate in hexane) to afford the desired product as a white solid (43 mg, 56%). **Analytical Data of 4j**: Mp; 185-190 ^oC. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.36-8.32 (m, 2H), 7.61-7.58 (m, 3H), 7.40-7.39 (m, 1H), 7.33-7.31 (m, 1H), 7.23-7.14 (m, 4H), 7.04- 7.01 (m, 2H), 6.95- 6.90 (m, 2H), 5.54 (s, 2H), 2.58 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 140.7, 139.4, 135.7, 134.1, 133.5, 131.4, 130.6, 130.2, 129.6, 129.4, 129.0, 128.8, 127.5, 127.2, 127.1, 126.8, 124.8, 124.6, 124.0, 120.4, 120.1, 117.5, 116.5, 109.5, 47.8, 21.7, 21.5. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{29}H_{23}ClN_2O_2SNa$ 521.1061; Found: 521.1065.

10-Hexyl-4-methyl-5-tosyl-5,10-dihydroindolo[3,2-b]indole (**4k**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), n-hexylamine (32 mg, 0.32 mmol), 4-methyl cyclohexanone (36 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a colourless viscous liquid (44 mg, 61%). **Analytical Data of 4k**: TLC (SiO_2): R_f; 0.43 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.33 -8.30 (m, 2H), 7.60 -7.56 (m, 3H), 7.35 -7.27 (m, 3H), 7.15 -7.14 (m, 1H), 6.98 (d, *J* = 8 Hz, 2H), 4.35 (t, *J* = 7 Hz, 2H), 2.58 (s, 3H), 2.21 (s, 3H), 1.85 -1.81 (m, 2H), 1.29 - 120 (s, 6H), 0.80 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 140.7, 139.0, 134.3, 130.4, 129.3, 126.8, 124.3, 123.8, 121.6, 120.4, 120.3, 117.5, 116.6, 116.5, 109.6, 45.0, 31.5, 30.2, 26.6, 22.4, 21.8, 21.5, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{28}H_{30}N_2O_2SNa$ 481.1920; Found: 481.1924.

10-Hexyl-3-phenyl-5-tosyl-5,10-dihydroindolo[3,2-b]indole (**4l**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), n-hexylamine (32 mg, 0.32 mmol), 4-phenyl cyclohexanone (56 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a colourless viscous liquid (45 mg, 55%). **Analytical Data of 4l**: TLC (SiO_2): R_f; 0.37 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.78 (s, 1H), 8.36 (d, *J* = 8 Hz, 1H), 7.79- 7.77 (m, 2H), 7.63- 7.58 (m, 4H), 7.49-7.44 (m, 2H), 7.38- 7.29 (m, 4H), 6.99 (d, *J* = 8 Hz, 2H), 4.40 (t, *J* = 7.5 Hz, 2H), 2.21 (s, 3H), 1.90-1.87 (m, 2H), 1.34-1.18 (m, 6H), 0.82 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 142.2, 140.8, 140.0, 133.5, 130.8, 129.4, 128.7, 128.6, 127.4, 126.8, 126.4, 124.6, 123.9, 122.3, 120.2, 119.0, 117.6, 116.5, 109.9, 45.2, 31.5, 30.3, 26.7, 22.5, 21.5, 14.0. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{33}H_{32}N_2O_2SNa$ 543.2076; Found: 543.2076.

10-Hexyl-1-methyl-5-tosyl-5,10-dihydroindolo[3,2-b]indole (**4m**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), *n*-hexylamine (32 mg, 0.32 mmol), 2-methyl cyclohexanone (36 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a colourless viscous liquid (38 mg, 52%). **Analytical Data of 4m**: TLC (SiO_2): R_f; 0.41 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.46 (d, *J* = 7 Hz, 1H), 8.38 (d, *J* = 7 Hz, 1H), 7.63-7.56 (m, 3H), 7.38-7.35 (m, 2H), 7.19-7.16 (m, 1H), 7.07-6.98 (m, 3H), 4.59 (t, *J* = 7.5 Hz, 2H), 2.79 (s, 3H), 2.21 (s, 3H), 1.80-1.77 (m, 2H), 1.28-1.19 (m, 6H), 0.83 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 140.9, 134.1, 129.4, 126.8, 124.4, 123.9, 122.3, 121.2, 120.6, 120.3, 118.9, 117.7, 117.5, 116.6, 47.4, 32.0, 31.5, 26.3, 22.5, 21.5, 20.4, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{28}H_{30}N_2O_2SNa$ 481.1920; Found: 481.1932.

10-Hexyl-2-methyl-5-tosyl-5,10-dihydroindolo[3,2-b]indole (**4n**) & **10-hexyl-4-methyl-5-tosyl-5,10-dihydroindolo[3,2-b]indole** (**4n'**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), n-hexylamine (32 mg, 0.32 mmol), 3-methyl cyclohexanone (36 mg, 0.32 mmol) and chloranil (117 mg, 0.47 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a 1:0.12 mixture of regioisomers (from 1H NMR analysis) and appeared as a colourless viscous liquid (36 mg, 50%). **Analytical Data of 4n&4n'**: TLC (SiO_2): R_f; 0.41 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): 8.40 (d, *J* = 8.5 Hz, 1H), 8.33 (d, *J* = 8 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, .12H) 7.61-7.58 (m, 3H), 7.35-7.29 (m, 2.25H), 7.24-7.23 (m, .33 H), 7.20 (s, 1H), 7.12 (d, J = 8 Hz, 1H), 6.99 (d, *J* = 8 Hz, 2H), 6.96-6.94 (m, .35H), 6.75 (d, *J* = 8 Hz, .3H), 4.35 (t, *J* = 7.5 Hz, 2H), 4.28 (t, *J* = 7.5 Hz, .25H), 2.98 (s, 0.32 H), 2.57 (s, 3H), 2.20 (s, 3H), 2.15 (s, 0.48H), 1.86-1.83 (m, 2H), 1.31-1.22 (m, 9H), 0.82-0.79 (m, 3.23H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 140.9, 140.4, 134.2, 132.7, 129.8, 129.4, 126.8, 124.1, 123.8, 121.8, 120.5, 120.3, 117.4, 116.3, 114.3, 109.8, 45.0, 31.5, 30.2, 26.6, 22.5, 22.1, 21.4, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{28}H_{31}N_2O_2S$ 459.2100; Found: 459.2115.

3-Bromo-5-hexyl-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4o**): The reaction was performed according to general procedure with 5-bromo-3-nitro-*N*-tosyl indole (50 mg, 0.13 mmol), n-hexylamine (26 mg, 0.26 mmol) and cyclohexanone (26mg, 0.26 mmol) and chloranil (96 mg, 0.39 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a pale yellow viscous liquid (50 mg, 76%). **Analytical Data of 4o**: TLC (SiO_2): R_f; 0.41 (7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.52 (d, *J* = 8 Hz, 1H), 8.22 (d, *J* = 9 Hz, 1H), 7.70 (s, 1H), 7.57-7.54 (m, 2H), 7.45-7.27 (m, 4H), 7.03-7.00 (m, 2H), 4.35 (t, *J* = 7 Hz, 2H), 2.23 (s, 3H), 1.88-1.82 (m, 2H), 1.28-1.19 (m, 6H), 0.82 (t, *J* = 7Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 140.8, 139.3, 134.0, 129.5, 127.1, 126.8, 123.3, 121.7, 120.9, 120.3, 117.7, 117.3, 116.1, 109.9, 45.0, 31.4, 30.2, 26.6, 22.4, 21.5, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{27}H_{27}BrN_2O_2SNa$ 545.0868; Found: 545.0874.

3-Bromo-5-(4-methoxybenzyl)-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4p**): The reaction was performed according to general procedure with 5-bromo-3-nitro-*N*-tosyl indole (50 mg, 0.13 mmol), 4-methoxy benzylamine (36 mg, 0.26 mmol) and cyclohexanone (26mg, 0.26 mmol) and chloranil (96 mg, 0.39 mmol). The crude product was purified by activated neutral alumina column chromatography (5% ethyl acetate in hexane) to afford the desired product as a white solid (49 mg, 68%). **Analytical Data of 4p**: Mp; 175-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.55-8.53 (m, 1H), 8.21-8.19 (m, 1H), 7.57 (d, *J* = 8 Hz, 2H), 7.41-7.36 (m, 2H), 7.32-7.30 (m, 2H), 7.26-7.24 (m, 1H), 7.02 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 9 Hz, 2H), 6.75-6.74 (m, 2H), 5.49 (s, 2H), 3.73 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 144.6, 141.2, 139.2, 134.6, 133.9, 130.2, 129.6, 127.5, 126.9, 126.8, 123.6, 121.6, 120.9, 120.7, 120.5, 117.6, 117.4, 116.4, 114.4, 110.2, 108.3, 55.2, 48.0, 21.5. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{29}H_{23}BrN_2O_3SNa$ 581.0505; Found: 581.0509.

3-Chloro-5-hexyl-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**4q**): The reaction was performed according to general procedure with 5-chloro-3-nitro-*N*-tosyl indole (50 mg, 0.14 mmol), n-hexylamine (28 mg, 0.28 mmol) and cyclohexanone (27mg, 0.28 mmol) and chloranil (103 mg, 0.39 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a white solid (54 mg, 79%). **Analytical Data of 4q**: Mp; 135-140 ^oC. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.54 (d, *J* = 8 Hz, 1H), 8.28 (d, *J* = 9 Hz, 1H), 7.58-7.56 (m, 3H), 7.44-7.30 (m, 4H), 7.02-7.01 (m, 2H), 4.36 (t, *J* = 7 Hz, 2H), 2.22 (s, 3H), 1.88-1.82 (m, 2H), 1.27-1.22 (m, 6H), 0.81 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.6, 140.8, 138.9, 133.9, 129.7, 129.5, 126.8, 124.4, 123.3, 121.3, 120.8, 120.3, 117.3, 116.1, 109.9, 45.1, 31.4, 30.2, 26.6, 22.4, 21.5, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{27}H_{27}ClN_2O_2SNa$ 501.1374; Found: 501.1385.

***tert*-Butyl 8-bromo-10-hexylindolo[3,2-b]indole-5(10H)-carboxylate** (**4r**): The reaction was performed according to general procedure with 5-bromo-3-nitro-*N*-Boc indole (50 mg, 0.15 mmol), n-hexylamine (30 mg, 0.30 mmol) and cyclohexanone (29 mg, 0.30 mmol) and chloranil (111 mg, 0.45 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a pale yellow viscous liquid (48 mg, 70%). **Analytical Data of 4r**: TLC (SiO_2):R_f; 0.71 (7% ethyl acetate in hexane). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.44-8.43 (m, 1H), 8.14-8.13 (m, 1H), 7.78 (s, 1H), 7.41-7.35 (m, 2H), 7.29-7.26 (m, 1H), 7.16 (t, *J* = 8 Hz, 1H), 4.38 (t, *J* = 8 Hz, 2H), 1.92-1.86 (m, 2H), 1.79 (s, 9H), 1.38-1.25 (m, 6H), 0.85 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 144.6, 141.2, 139.2, 134.6, 133.9, 130.2, 129.6, 127.5, 126.9, 126.8, 123.6, 121.6, 120.9, 120.7, 120.5, 117.6, 117.4, 116.4, 114.4, 110.2, 108.3, 55.2, 48.0, 21.5. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{25}H_{29}BrN_2O_2Na$ 491.1304; Found: 491.1325.

12-hexyl-7-tosyl-7,12-dihydrobenzo[g]indolo[3,2-b]indole (**4s**): The reaction was performed according to general procedure with 3-nitro-*N*-tosyl indole (50 mg, 0.16 mmol), n-hexylamine (32 mg, 0.32 mmol) and 1-decalone (48 mg, 0.32 mmol) and chloranil (194 mg, 0.80 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a pale yellow viscous liquid (41 mg, 52%). **Analytical Data of 4s**: TLC (SiO_2): R_f; 0.61 (7% ethyl acetate in hexane). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.43-8.36 (m, 2H), 8.04 (s, 1H), 7.71-7.68 (m, 2H), 7.59-7.50 (m, 4H), 7.38 – 7.35 (m, 2H), 6.96 (d, *J* = 8 Hz, 2H), 4.87-4.84(m, 2H), 2.19 (s, 3H), 2.08-2.07 (m, 2H), 1.42-1.30 (m, 6H), 0.85-0.82 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 141.1, 133.9, 133.7, 131.7, 130.5, 129.5, 129.4, 126.8, 125.6, 124.3, 124.1, 123.9, 123.2, 122.8, 121.9, 120.8, 120.2, 117.2, 116.8, 113.7, 48.8, 31.4, 26.4, 22.5, 21.4, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{31}H_{30}N_2O_2SNa$ 517.1920; Found: 517.1932.

General procedure for the synthesis of benzothieno[3,2-b]indoles (6a – 6l): The enolizable ketone, cyclohexanone (55 mg, 0.56 mmol) and primary amine, *n*-hexylamine (56 mg, 0.56 mmol) were weighed into a dry reaction tube. Dry toluene (0.3 mL) along with 4 Å MS (50 mg) was added and allowed to stir at 60 °C for 1 hour, after which 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol) was added into it and again kept it for stirring at the same temperature for 11 hours. After the complete consumption of 3-nitro-benzo[b]thiophene, Chloranil (206 mg, 0.84 mmol) along with toluene (0.7 mL) was added and kept at 100 °C for 12 h. The solvent was evaporated in vacuo and the residue on activated neutral alumina column chromatography yielded benzothieno[3,2-b]indoles with hexanes and ethyl acetate as eluent.

Synthesis and Characerisation of benzothieno[3,2-b]indoles (6a – 6l)

10-(4-methoxybenzyl)-10H-benzo[4,5]thieno[3,2-b]indole (**6a**)**:** The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), 4-methoxy benzylamine (77 mg, 0.56 mmol) and cyclohexanone (55 mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as white solid (62 mg, 65%). **Analytical Data of 6a**: Mp; 135-148 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.91-7.89 (m, 1H), 7.85-7.81 (m, 2H), 7.45 (d, *J* = 8 Hz, 1H), 7.35-7.31 (m, 3H), 7.24-7.20 (m, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.83-6.79 (m, 2H), 5.76 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 143.2, 141.8, 137.7, 129.4, 127.3, 127.2, 126.9, 124.5, 124.3, 123.9, 123.2, 121.9, 120.0, 119.8, 119.5, 115.8, 114.3, 110.2, 55.3, 47.9. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{22}H_{18}NOS$ 344.1103; Found: 344.1102.

10-(benzyl)-10H-benzo[4,5]thieno[3,2-b]indole (**6b**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), benzylamine (60 mg, 0.56 mmol) and cyclohexanone (55 mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as white solid (51 mg, 58%). **Analytical Data of 6b**: Mp; 132-135 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.91-7.90 (m, 1H), 7.83-7.81 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.34-7.31 (m, 4H), 7.28-7.26 (m, 1H), 7.25-7.23 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 5.83 (s, 2H). ^{13}C NMR (125 MHz, CDCl3): δ 143.2, 141.9, 137.4, 129.0, 127.7, 126.1, 124.5, 124.3, 123.9, 123.2, 120.0, 119.9, 119.5, 110.1, 48.4. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{21}H_{16}NS$ 314.0998; Found: 314.0986.

10-Hexyl-10H-benzo[4,5]thieno[3,2-b]indole (**6c**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), *n*-hexylamine (56 mg, 0.56 mmol) and cyclohexanone (55 mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a pale yellow viscous liquid (56 mg, 65%). **Analytical Data of 6c**: TLC (SiO_2): R_f; 0.72 (5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl3, TMS): δ 7.99 (d, *J* = 8 Hz, 1H), 7.92 (d, *J* = 8 Hz, 1H), 7.78 (d, *J* = 8 Hz, 1H), 7.49-7.44 (m, 2H), 7.37-7.33 (m, 2H), 7.23-7.20 (m, 1H), 4.57 (t, *J* = 7.5 Hz, 2H), 1.99-1.93 (m, 2H), 1.48 -1.45 (m, 2H), 1.34-1.25 (m, 4H), 0.87 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 141.5, 127.0, 124.6, 124.2, 123.8, 122.8, 120.0, 119.4, 115.3, 109.9, 45.1, 31.6, 30.5, 26.7, 22.5, 14.0. HRMS (ESI-HRMS) (m/z): Calcd for $C_{20}H_{21}NS$, $(M)^+$: 307.13947; Found: 307.13926. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{20}H_{22}NS$ 308.1467; Found: 308.1473.

10-dodecyl-10H-benzo[4,5]thieno[3,2-b]indole (**6d**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), *n*-dodecylamine (104 mg, 0.56 mmol) and cyclohexanone (55 mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (2% ethyl acetate in hexane) to afford the desired product as a pale yellow viscous liquid (68 mg, 62%). **Analytical Data of 6d**: TLC (SiO_2): R_f; 0.75 (5% ethyl acetate in hexane). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.98 (d, *J* = 8 Hz, 1H), 7.91 (d, *J* = 8 Hz, 1H), 7.77 (d, *J* = 8 Hz, 1H), 7.48-7.43 (m, 2H), 7.36-7.32 (m, 2H), 7.22-7.19 (m, 1H), 4.56 (t, *J* = 7.5 Hz, 2H), 1.98-1.92 (m, 2H), 1.46 -1.43 (m, 2H), 1.33-1.23 (m, 16H), 0.87 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 141.5, 137.4, 127.0, 124.6, 124.3, 123.8, 122.8, 121.6, 119.9, 119.4, 115.3, 109.9, 45.1, 31.9, 30.5, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{26}H_{33}NS$ 391.2328; Found: 391.2336.

10-(4-Methoxybenzyl)-3-phenyl-10H-benzo[4,5]thieno[3,2-b]indole (**6e**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), 4-methoxy benzylamine (77 mg, 0.56 mmol) and 4-phenyl cyclohexanone (98 mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as a White solid (65 mg, 56%). **Analytical Data of 6e**: Mp; 152-155 ^{o}C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.90-7.88 (m, 1H), 7.83-7.81 (m, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.56-7.53 (m, 1H), 7.46-7.43 (m, 3H), 7.34-7.29 (m, 3H), 7.09 (d, *J* = 9 Hz, 2H), 6.78 (d, J = 9 Hz, 2H), 5.71 (s, 2H), 3.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 143.3, 142.0, 141.3, 138.2, 133.4, 129.3, 128.8, 127.4, 127.3, 126.6, 124.6, 124.4, 124.0, 122.9, 122.3, 120.1, 117.9, 116.0, 114.4, 110.4, 55.3, 48.0. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{28}H_{21}NOSNa$ 442.1236; Found: 442.1234.

10-(4-Methoxybenzyl)-1-methyl-10H-benzo[4,5]thieno[3,2-b]indole (**6f**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), 4-methoxy benzylamine (77 mg, 0.56 mmol) and 2-methyl cyclohexanone (63 mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as a whit solid (64 mg, 64%). **Analytical Data of 6f**: Mp; 135-138 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.89-7.87 (m, 1H), 7.73-7.21 (m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.28-7.27 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.05-7.02 (m, 3H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.99 (s, 2H), 3.74 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 143.2, 138.5, 130.9, 127.1, 126.6, 126.5, 124.5, 124.2, 123.7, 122.7, 121.9, 120.1, 117.6, 114.4, 55.2, 49.7, 19.8. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{23}H_{19}NOSNa$ 380.1079; Found: 380.1083.

10-(4-methoxyphenyl)-10H-benzo[4,5]thieno[3,2-b]indole (**6g**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), 4-methoxy aniline (69 mg, 0.56 mmol) and cyclohexanone (55mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as white solid (51 mg, 55%). **Analytical Data of 6g**: Mp; 125-128 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.89 (d, *J* = 8 Hz, 1H), 7.83-7.81 (m, 1H), 7.50-7.49 (m, 2H), 7.33-7.27 (m, 4H), 7.25-7.24 (m, 1H), 7.23-7.19 (m, 1H), 7.15-7.13 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 154.5, 142.9, 129.0, 124.3, 124.0, 123.9, 123.3, 122.5, 120.4, 120.2, 119.3, 114.9, 111.0, 55.6. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{21}H_{16}NOS$ 330.0947; Found: 330.0950.

10-phenethyl-10H-benzo[4,5]thieno[3,2-b]indole (**6h**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), 2-phenylethylamine (67 mg, 0.56 mmol) and cyclohexanone (55mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as an amorphous solid (62 mg, 68%). **Analytical Data of 6h**: Mp; 98-100 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.00 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.78 (d, *J* = 8 Hz, 1H), 7.47-7.44 (m, 1H), 7.38-7.35 (m, 1H), 7.32-7.27 (m, 4H), 7.23-7.19 (m, 4H), 4.79 (t, *J* = 8 Hz, 2H), 3.21 (t, *J* = 8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 141.3, 138.1, 137.2, 128.8, 126.8, 124.6, 124.3, 123.8, 123.0, 121.7, 119.7, 119.6, 119.4, 109.8, 46.7, 36.8. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{22}H_{18}NS$ 328.1154; Found: 328.1161.

4-(2-(10H-benzo[4,5]thieno[3,2-b]indol-10-yl)ethyl)phenol (**6i**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), tyramine (77 mg, 0.56 mmol) and cyclohexanone (55mg, 0.56 mmol) and chloranil (206 mg, 0.84 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as an amorphous solid (62 mg, 61%). **Analytical Data of 6i:** TLC (SiO_2): R_f; 0.51 (30% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.98 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8 Hz, 1H), 7.47-7.43 (m, 1H) 7.37-7.34 (m, 2H), 7.31-7.28 (m, 1H), 7.22-7.19 (m, 1H), 7.05 (d, *J* = 8 Hz, 2H), 6.74-6.72 (m, 2H), 4.75 (t, *J* = 8 Hz, 2H), 3.14 (t, *J* = 8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 141.3, 130.4, 130.0, 126.9, 124.6, 124.3, 123.8, 122.9, 121.7, 120.2, 119.7, 119.5, 119.4, 115.6, 109.9, 46.9, 35.9. HRMS (ESI-Orbitrap) m/z: $(M+Na)^+$ calcd for $C_{22}H_{17}NOSNa$ 366.0923; Found: 366.0917.

10-(2-(1H-indol-3-yl)ethyl)-10H-benzo[4,5]thieno[3,2-b]indole (**6j**): The reaction was performed according to general procedure with 3-nitro-benzo[b]thiophene (50 mg, 0.28 mmol), tryptamine (89 mg, 0.56 mmol) and cyclohexanone (55mg, 0.56 mmol) and chloranil (206 mg, 0.45 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as an amorphous solid (110 mg, 54%). **Analytical Data of 6j**: TLC (SiO_2): R_f; 0.54 (20% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.93–7.90 (m, 2H), 7.78 (d, *J* = 8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.37–7.33 (m, 4H), 7.29-7.27 (m, 1H), 7.24–7.18 (m, 3H), 6.86 (s, 1H), 4.87 (t, *J* = 8 Hz, 2H), 3.39 (t, *J* = 7.5 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$): δ 143.2, 141.4, 136.3, 124.5, 123.8, 122.9, 122.3, 119.8, 119.7, 119.5, 119.4, 118.4, 111.3, 109.9, 45.7, 29.7. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{24}H_{19}N_2S$ 367.1263; Found: 367.1267.

8-bromo-10-(4-methoxybenzyl)-10H-benzo[4,5]thieno[3,2-b]indole (**6k**): The reaction was performed according to general procedure with 5-bromo 3-nitro-benzo[b]thiophene (50 mg, 0.19 mmol), 4-methoxybenzylamine (53 mg, 0.38 mmol) and cyclohexanone (37 mg, 0.38 mmol) and chloranil (140 mg, 0.57 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as white solid (53 mg, 66%). **Analytical Data of 6k**: Mp; 118-120 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.95 (s, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.41-7.39 (m, 1H), 7.34 (t, *J* = 8 Hz, 1H), 7.25-7.23 (m, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.71 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 142.0, 141.7, 136.5, 129.0, 128.3, 127.3, 127.2, 126.7, 125.6, 123.8, 122.8, 121.6, 120.1, 119.6, 118.1, 114.5, 110.3, 55.3, 48.0. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{22}H_{16}BrNOS$ 421.0130; Found: 421.0130.

8-bromo-10-dodecyl-10H-benzo[4,5]thieno[3,2-b]indole (**6l**): The reaction was performed according to general procedure with 5-bromo 3-nitro-benzo[b]thiophene (50 mg, 0.19 mmol), 1-dodecylamine (70 mg, 0.38 mmol) and cyclohexanone (37 mg, 0.38 mmol) and chloranil (140 mg, 0.57 mmol). The crude product was purified by activated neutral alumina column chromatography (3% ethyl acetate in hexane) to afford the desired product as viscous liquid (62 mg, 69%). **Analytical Data of 6l**: TLC (SiO_2): R_f; 0.75 (7% ethyl acetate in hexane). ^{1}H NMR (500

MHz, $CDCl_3$, TMS): δ 8.09 (s, 1H), 7.78-7.76 (m, 2H), 7.49 (d, *J* = 8 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.38-7.36 (m, 1H), 7.24-7.21(m, 1H), 4.54 (t, *J* = 7.5 Hz, 2H), 1.96-1.93 (m, 2H), 1.47-1.43 (m, 2H), 1.37-1.34 (m, 2H), 1.29-1.24 (m, 14H), 0.87 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7, 136.2, 128.5, 126.5, 125.7, 123.4, 122.6, 121.3, 119.6, 118.1, 116.8, 110.1, 45.1, 30.4, 29.6, 29.5, 29.4, 29.3, 27.0, 22.7, 14.1. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{26}H_{32}BrNS$ 469.1433; Found: 469.1435.

Procedure for Scale up Synthesis of 4a: The enolizable ketone, cyclohexanone (621 mg, 6.33 mmol) and primary amine, *n*-hexylamine (640 mg, 6.33 mmol) were weighed into a dry reaction tube. Dry toluene (6 mL) along with 4 Å MS (1 g) was added and allowed to stir at 60 °C for 1 hour, after which 3-nitro-*N*-tosyl indole (1g, 3.16 mmol) was added into it and again kept for stirring for 11 hours at the same temperature. After the complete consumption of 3-nitro-*N*-tosyl indole, Chloranil (2.3 g, 9.48 mmol) along with toluene (14 mL) was added and kept for stirring for 10 hours at 100 °C. The solvent was evaporated in vacuo and the residue on activated neutral alumina column chromatography yielded indolo[3,2-b]indole with mixtures of hexane and ethyl acetate as eluent (956 mg, 68%).

Synthesis and characterization of 5-hexyl-5,10-dihydroindolo[3,2-b]indole (**7**): A solution of NaOH (2.0 M, 2.0 mL) in MeOH was added to a stirring solution of of indoloindole **4a** (100 mg, 0.226 mmol) in dry THF (1.0 mL) and the resulting mixture was refluxed under nitrogen for overnight. Upon completion, the reaction mixture was concentrated under reduced pressure and water was added and extracted with EtOAc. The organic layer washed successively with brine and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and the residue on activated neutral alumina column chromatography (5% ethyl acetate in hexane) yielded the deprotected compound **7** as white solid (54 mg, 82%). **Analytical Data of 7**: Mp; 145-148 °C. ^1H NMR (500MHz, CD_3CN,TMS): δ 9.41 (brs, 1H), 7.90-7.79 (m, 2H), 7.57-7.54 (m, 2H), 7.30-7.24 (m, 2H), 7.19-7.13 (m, 2H), 4.55 (t, *J* = 7 Hz, 2H), 1.95-1.92 (m, 2H), 1.31-1.22 (m, 6H), 0.82 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, CD_3CN): ^{13}C NMR (125 MHz, CD_3CN): δ 141.8, 141.6, 122.9, 122.7, 119.7, 118.3, 113.3, 110.9, 45.8, 32.3, 27.3, 23.2, 14.2. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{20}H_{22}N_2$ 290.1777; Found: 290.1780.

Synthesis and characterization of 5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole (**8**): To a stirred solution of **7** (100 mg, 0.34 mmol) in a mixture of THF:DMF (4:1, 5 mL), NaH (12 mg, 0.51 mmol) was added portion wise under nitrogen atmosphere at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 minutes. The reaction mixture was cooled again to 0 °C and 1-bromohexane (67 mg, 0.41 mmol) was added dropwise and stirred at room temperature for 8 hours. Upon completion, water was added and then extracted with EtOAc. The organic layer washed successively with brine and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and the residue on activated neutral alumina column chromatography (2% ethyl acetate in hexane) yielded the deprotected compound **8** as a white solid (108 mg, 85%). **Analytical Data of 8**: Mp; 68 °C. ^{1}H NMR (500MHz, $CDCl_3$,TMS): δ 7.84-7.83 (m, 2H), 7.47-7.46 (m, 2H), 7.29-7.25 (m, 2H), 7.18-7.12 (m, 2H), 4.48 (s, 4H), 1.97-1.96 (m, 4H), 4.48 (brs, 4H), 1.30-1.26 (m, 8H), 0.84 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): ^{13}C NMR (125 MHz, CD_3CN): δ 140.6, 125.9, 121.5, 117.9, 117.7, 114.6, 109.7, 45.3, 31.6, 30.3, 26.8, 22.5, 14.0. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{26}H_{34}N_2$ 374.2716; Found: 374.2736.

Synthesis and characterization of 10-hexyl-1,2,3,4,5,10-hexahydroindolo[3,2-b]indole (**9**)[10]: A solution of NaOH (2.0 M, 2.0 mL) in MeOH was added to a stirring solution of 10-hexyl-5-tosyl-1,2,3,4,5,10-hexahydroindolo[3,2-b]indole (100 mg, 0.22 mmol) in dry THF (1 mL) and the resulting mixture was refluxed under nitrogen for overnight. Upon completion, the reaction mixture was concentrated under reduced pressure and water was added and then extracted with EtOAc. The organic layer washed successively with brine and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and the residue on activated neutral alumina column chromatography (5% ethyl acetate in hexane) yielded the deprotected compound **9** as an amorphous pale yellow solid (56 mg, 85%). **Analytical Data of 9*:*** TLC (SiO_2): Rf; 0.33 (7% ethyl acetate in hexane). ^{1}H NMR (500MHz, CD_3CN,TMS): δ 8.56 (brs, 1H), 7.56-7.54 (m, 1H), 7.32-7.31 (m, 1H), 6.99-6.98 (m, 2H), 4.08 (t, *J* = 7 Hz, 2H), 2.71 (t, *J* = 6 Hz, 2H), 2.63(t, *J* = 6 Hz, 2H), 1.93-1.87 (m, 2H), 1.84-1.73 (m, 4H) 1.31-1.25 (m, 6H), 0.84 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, CD_3CN): δ 140.6, 133.0, 131.5, 120.3, 119.7, 118.5, 116.0, 111.9, 100.5, 45.2, 31.9, 31.5, 26.8, 23.8, 23.7, 23.0, 22.9, 21.9, 13.8. HRMS (ESI-Orbitrap) m/z: $(M-H)^+$ calcd for $C_{20}H_{25}N_2$ 293.2012; Found: 293.2017.

Synthesis and characterization of 5,10-dihexyl-1,2,3,4,5,10-hexahydroindolo[3,2-b]indole (8-P): To a stirred solution of **9** (100 mg, 0.34 mmol) in a mixture of THF:DMF (4:1, 5 mL), NaH (12 mg, 0.51 mmol) was added portion wise under nitrogen atmosphere at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 minutes. The reaction mixture was cooled again to 0 °C and 1-bromohexane (67 mg, 0.41 mmol) was added dropwise and stirred at room temperature for 8 hours. Upon completion, the reaction mixture was concentrated under reduced pressure and water was added, and then extracted with EtOAc. The organic layer washed successively with brine and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and the residue on activated neutral alumina column chromatography (2% ethyl acetate in hexane) yielded the deprotected compound **8-P** as a white solid (99 mg, 77%). **Analytical Data of 8-P**: Mp; 58-60 °C. ^{1}H NMR (500MHz, $CDCl_3$,TMS): δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 8 Hz, 1H), 7.09 (t, *J* = 8 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.18 (t, *J* = 7.5 Hz, 2H), 4.08 (t, *J* = 7.5 Hz, 2H), 2.84 (t, *J* = 6 Hz, 2H), 2.74 (t, *J* = 6 Hz, 2H), 1.92 – 1.79 (m, 8H), 1.42 – 1.25 (m, 12H), 0.89-0.85 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): ^{13}C NMR (125 MHz, CD_3CN): δ 139.8, 132.2, 132.1, 119.2, 118.9, 117.2, 115.7, 115.7, 108.8, 99.6, 45.2, 44.9, 31.7, 31.1, 30.8, 26.9, 26.7, 23.5, 23.2, 22.8, 22.6, 22.0, 14.0. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{26}H_{39}N_2$ 379.3107; Found: 379.3114.

Synthesis and characterization of 5-hexyl-3-phenyl-10-tosyl-5,10-dihydroindolo[3,2-b]indole (**10**): A mixture of indoloindole **4o** (100 mg, 0.192 mmol), phenyl boronicacid (35 mg, 0.288 mmol), $Pd(PPh_3)_4$ (21 mg, 0.019 mmol), K_2CO_3 (130 mg, 0.960 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Dry THF (1.5 mL) and water (0.5 mL) was added then, the reaction mixture was purged with argon and allowed to stir at 65 ^oC for 24 hours. The solvent was evaporated in vacuum and the residue on activated neutral alumina column chromatography (3% ethyl acetate in hexane) yielded the product as a white amorphous solid (81 mg, 81%). **Analytical Data of 10**: TLC (SiO_2): R_f; 0.37 (7% ethyl acetate in hexane). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 8.56 (d, *J* = 8 Hz, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 1H), 7.65-7.45 (m, 4H), 7.60 (s, 1H), 7.49-7.45 (m, 3H), 7.39-7.30 (m, 3H), 7.02 (d, *J* = 8 Hz, 2H), 4.44 (t, *J* = 7 Hz, 2H), 2.21 (s, 3H), 1.91-1.88 (m, 2H), 1.27-1.19 (m, 6H), 0.80 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 141.1, 140.6, 140.0, 137.3, 134.2, 130.2, 129.5, 128.9, 127.3, 127.3, 126.8, 123.9, 122.8, 120.8, 120.6, 116.1, 45.1, 31.5, 30.2, 29.7, 26.6, 22.5, 21.5, 13.9. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{33}H_{33}N_2O_2S$ 521.2257; Found: 521.2259.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Copies of ^1H and ^{13}C NMR spectra of all newly synthesized compounds (PDF) and crystallographic data for **4c**.

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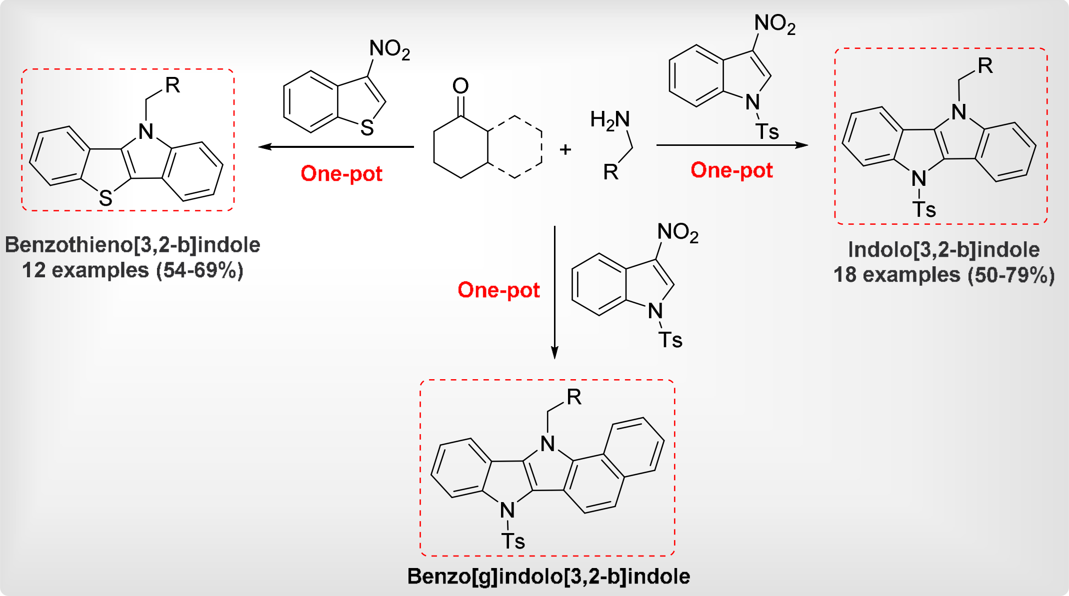
NO$_2$
S
O
H$_2$N
R
+
NO$_2$
N
Ts
One-pot
One-pot
One-pot
N
R
S
Benzothieno[3,2-b]indole
12 examples (54-69%)
N
R
N
Ts
Indolo[3,2-b]indole
18 examples (50-79%)
NO$_2$
N
Ts
R
N
N
Ts
Benzo[g]indolo[3,2-b]indole