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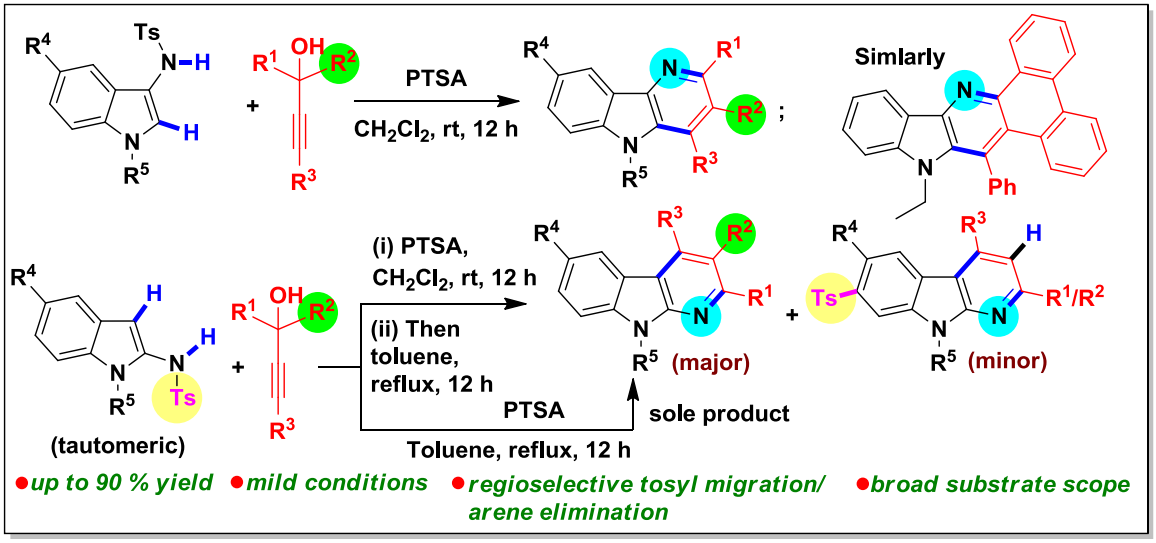
Transition Metal-free, Brønsted Acid Mediated Cascade Sequence in the Reaction of Propargyl Alcohols with Sulfonamido-indoles/-indolines: Highly Substituted δ- and α-Carbolines

*Karuppu Selvaraj and K. C. Kumara Swamy**

School of Chemistry, University of Hyderabad, Hyderabad -500046, Telangana, India

ABSTRACT: Brønsted acid mediated, transition metal free, reaction of propargyl alcohols with sulfonamido-indoles/-indolines under mild conditions affords highly substituted δ- or α-carbolines in good to excellent yields. This protocol involves cascade reaction sequences of Friedel-Crafts alkylation/ [1,5]-hydrogen shift/ electrocyclization/ elimination/ [1,2]-aryl migration followed by aromatization. An unexpected regioselective tosyl group migration from indole 2- to 6-position and arene elimination leading to α-carbolines has also been discovered.



INTRODUCTION

Carboline motif is found in a multitude of natural alkaloids and pharmaceutically active compounds.[1,2] Although β- and γ-carbolines are relatively well studied, there has also been a significant interest in the α- and δ-carbolines. Benzo-fused α- and δ-carbolines are active as antiviral, antitumor, antimalarial, antiproliferative, antifungal, antibacterial, central nervous system stimulating and antiplasmodial agents.[3] In particular, δ-carbolines are potential cancer therapeutics (e.g., SYUIQ-5)[4] and α-carboline mescengricin[5] is a potential neural protective agent (cf. Figure 1). A Pd-catalyzed Ullmann cross-coupling/reductive cyclization route by Banwell and coworkers and a rhodium catalyzed syntheses via aryl azides by Driver and coworkers for such isomeric carbolines are known.[6] Otherwise, only a limited number of methods are available for the synthesis of α- and δ-carbolines.[7] Some recently reported methods for the latter class of compounds include (i) DDQ mediated regioselective switching approach of indolylchalcone oxime esters,[8] (ii) Ni-catalyzed [2+2+2] cycloaddition of ynamide-nitriles or alkyne cyanamides with alkynes,[9] (iii) Suzuki-Miyaura reactions of 1-chloro-2-bromopyridine or 2,3-dibromopyridine with 2-bromophenylboronic acid,[10] (iv) reaction using indolylchalcone oxime esters,[11] (v) Pd-catalyzed sequential reaction of 2-iodoanilines with *N*-tosyl-enynamines,[12] (vi) decarboxylative nitrile insertion of indole-2-carboxylic acids[13] and (vii) thermal rearrangement of indolylchalcone oxime esters.[14] Important methods for syntheses of α-carbolines include annulation reaction of azaindoles, intramolecular Diels-Alder reaction, Graebe-Ullmann reaction of triazoles, and palladium catalyzed arylamination followed by intramolecular coupling reactions.[15] Indoloquinazolines also contain nitrogen atoms at 1,3-positions but form another interesting class of fused hetereocycles.[16] Many of these methods involve multi-steps, harsh reaction conditions, and use of expensive metal catalysts. In continuation of our studies on the chemistry of propargylic alcohols,[17] we herein describe a transition metal-free cascade approach for the

syntheses of highly substituted δ- and α-carbolines *via* Brønsted acid mediated [1,2]-aryl migration of propargyl alcohols with sulfonamido-indoles/-indolines. In addition, a unique tosyl group migration with concomitant arene elimination is also highlighted.

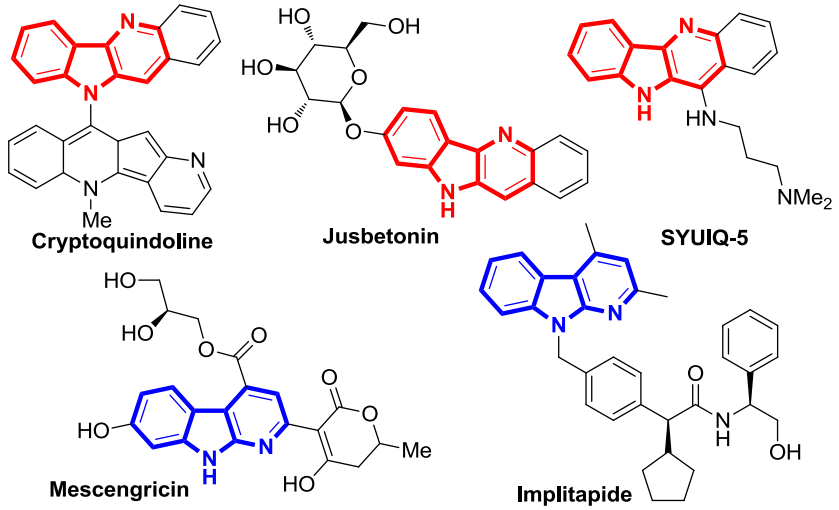
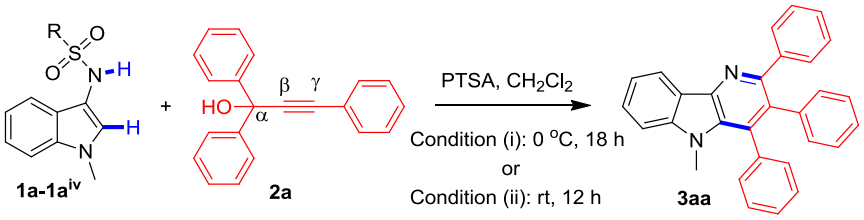


Figure 1. Examples of biologically active δ- and α-carbolines

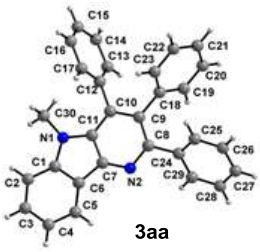
RESULTS AND DISCUSSION

To begin with, from the reaction between 3-sulfonamidoindole **1a** and propargylic alcohol **2a** using an equiv amount of *p*-toluenesulfonic acid (PTSA) at 0 °C for 18 h in dichloromethane (DCM), surprisingly, we isolated the δ-carboline **3aa** [cf. condition (i) in Scheme 1, and Figure S1 (X-ray) SI] in 52% yield *via* [1,2]-aryl migration. Subsequently, we evaluated the influence of R group on sulfonyl moiety of sulfonamidoindoles **1a**$^{i\text{-}iv}$ and found that tosyl group still was the best choice [under condition (ii)] for reactions shown in Scheme 1.

Scheme 1. Formation of α-Carboline 3aa from Brønsted Acid Mediated [1,2]-Aryl Migration/Cyclization of Propargyl Alcohol 2a with Sulfonamidoindoles 1



Precursor	Yield of **3aa**
1a: R = Tol	52% [condition (i)]
	82% [condition (ii)]
1a^{i}: R = Ph	70% [condition (ii)]
1a^{ii} : R = *p*-ClC$_6$H$_4$	65% [condition (ii)]
1a^{iii}: R = 2-naphthyl	73% [condition (ii)]
1a^{iv}: R = Me	55% [condition (ii)]



Based on the first reaction (Table 1, entries 1-2), we screened the reaction conditions by changing the catalyst,[18] solvent, temperature, time etc. The reaction time could be significantly shortened by performing the reaction using 1.5 equiv (instead of 1 equiv) of PTSA at rt (25 ^{o}C) to obtain the highest yield of **3aa** (Table 1, entry 3). The reaction conducted in dichloromethane (DCM) at 40 °C led to lower yield (entry 4). The effectiveness of a few other acid catalysts such as $FeCl_3$, $AlCl_3$, I_2 and, $BF_3.OEt_2$ was also checked, and it was found that product **3aa** was obtained in lower yields (entries 5-8). The best solvent was dichloromethane (DCM, entry 3) which provided a higher yield than other solvents such as dichloroethane (DCE), acetonitrile (CH_3CN), tetrahydrofuran (THF), toluene (PhMe), dimethyl sulfoxide (DMSO), or 1,4-dioxane (entries 9-14). Transition metal compounds like $Sc(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$ and $InCl_3$ were not useful for this transformation (entries 15-18). No reaction occurred in the absence of the catalyst (entry 19). Increasing the catalyst amount and reaction timing did not improve yield of the reaction (entries 20-21). Brønsted acids such as TfOH, MsOH and AcOH were also checked for their efficiency. While TfOH and MsOH gave slightly lower yields of the product **3aa** (entries 22-23) compared to PTSA

(entry 3), no reaction is occurred when AcOH was used (entry 24). Thus PTSA in DCM at rt (entry 3) was the best for this transformation.

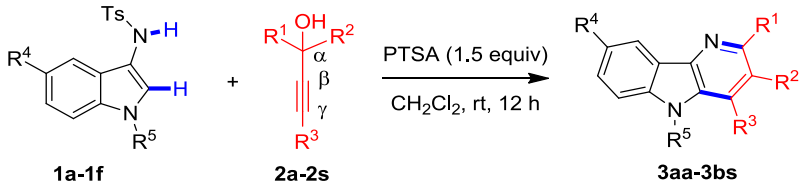
Table 1. Screening of reaction conditions[a]

entry	catalyst (equiv.)	solvent	temp (°C)	time (h)	yield (%)[b] **3aa**
1	PTSA (1.0)	DCM	0	18	52
2	PTSA (1.0)	DCM	rt	12	82
3	PTSA (1.5)	DCM	rt	12	90
4	PTSA (1.5)	DCM	40	12	75
5	$FeCl_3$ (1.5)	DCM	rt	12	60
6	$AlCl_3$ (1.5)	DCM	rt	12	55
7	I_2 (1.5)	DCM	rt	12	34
8	$BF_3.OEt_2$ (1.5)	DCM	rt	12	20
9	PTSA (1.5)	DCE	rt	12	46
10	PTSA (1.5)	CH_3CN	rt	12	55
11	PTSA (1.5)	THF	rt	12	20
12	PTSA (1.5)	toluene	rt	12	42
13	PTSA (1.5)	DMSO	rt	12	trace
14	PTSA (1.5)	1,4-dioxane	rt	12	trace
15	$Sc(OTf)_3$ (1.5)	DCM	rt	12	nr[c]
16	$Yb(OTf)_3$ (1.5)	DCM	rt	12	nr
17	$In(OTf)_3$ (1.5)	DCM	rt	12	nr
18	$InCl_3$ (1.5)	DCM	rt	12	nr
19	no catalyst	DCM	rt	12	nr
20	PTSA (2.0)	DCM	rt	24	88
21	PTSA (2.5)	DCM	rt	24	89
22	TfOH	DCM	rt	12	80
23	MsOH	DCM	rt	12	76
24	AcOH	DCM	rt	12	nr

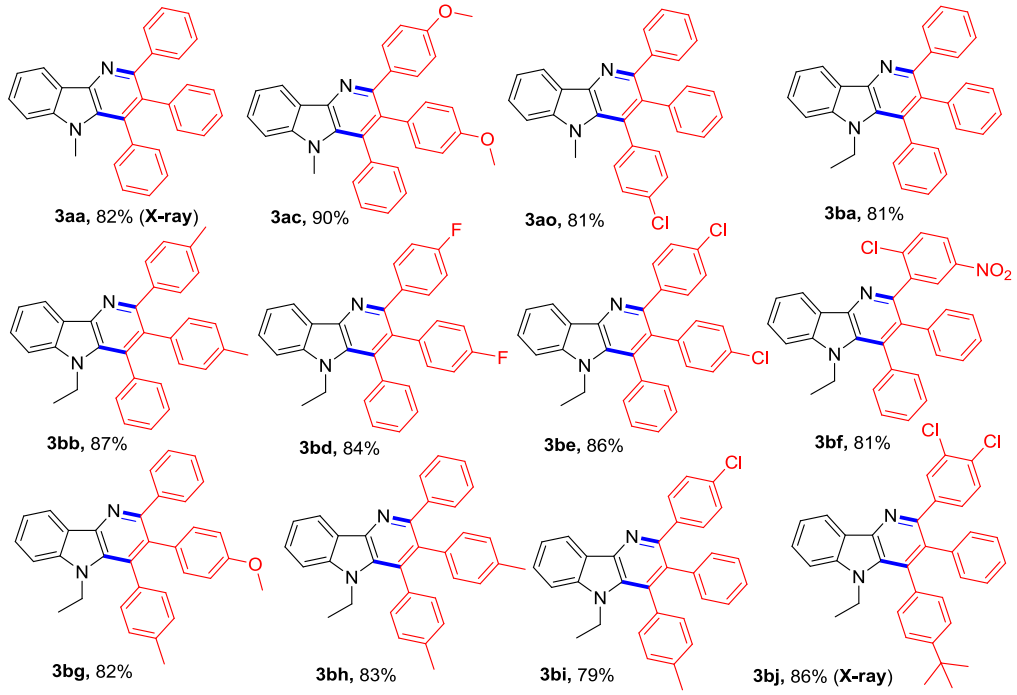
[a]Reaction conditions: **1a** (0.100 g, 0.33 mmol), **2a** (0.113 g, 0.40 mmol), solvent (5 mL). [b]Yield after isolation is based on **1a**. [c]nr = no reaction.

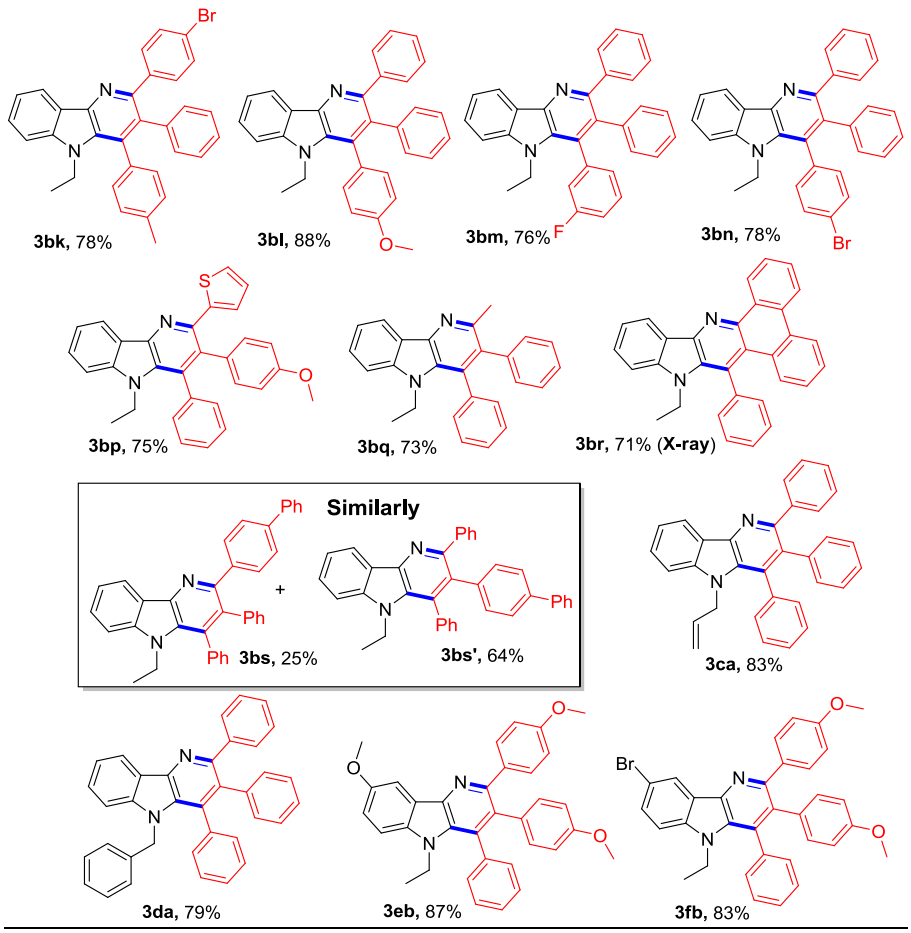
Next, we synthesized highly substituted δ-carbolines **3aa-3fb** *via* [1,2]-aryl migration by varying 3-sulfonamidoindoles **1a-fa** and propargylic alcohols **2a-s**. The substituent on the *N*-position (R^5) of the 3-sulfonamidoindoles **1** could be methyl, ethyl, allyl, or benzyl, providing the δ-carbolines **3aa-3da** in 79-83% yield. The 3-toluenesulfonamidoindole with -OMe or -Br substituent at the 5-position (R^4) also led to the products **3eb** and **3fb** in excellent yields. A variety of α-substituted propargyl alcohols **2** readily afforded the products **3ac-3be** (Table 2). Electron-donating substituent (OMe, Me; **3ac-3bb**) at the *para*-position ($R^1 = R^2$) provided higher yields than those with electron-withdrawing substituent (F, Cl; **3bd-3be**), suggesting the intermediacy of a carbocation in this reaction. When propargylic alcohols **2f-2k** with two different α-aryl groups (electron-rich and electron-poor) were employed, the electron-rich aryl group migrated preferentially to yield the products **3bf-3bk** (X-ray for **3bj** in Figure S2, SI).[19] Electron-donating substituent (R^3) at *para*-position of the phenyl ring gave higher yield (e.g., **3bl**) than an electron-withdrawing group at *meta*- or *para*-position (**3bm-3bn, 3ao**). This reaction also worked well when R^2 was methyl or thiophene (**2p**-**2q**) giving the products **3bp-3bq** in moderate yields. The reaction failed when R^3 = *n*-butyl or cyclopropyl. With 9-fluorenyl-substituted propargyl alcohol **2r**; the benzo-annulated quinoline **3br** (X-ray, Figure S3, SI) was obtained as a single product in 71% yield. Interestingly, the propargylic alcohol **2s** with different aryl groups (R^1 = Ph; R^2 = biphenyl) gave both [1,2]-phenyl migrated δ-carboline **3bs** and [1,2]-biphenyl migrated δ-carboline **3bs'** in 25% and 64% yields, respectively (Table 2).

Table 2. Scope of the reaction of 3-sulfonamidoindole **1** with propargylic alcohols **2**[a,b]



1a-1f **2a-2s** **3aa-3bs**



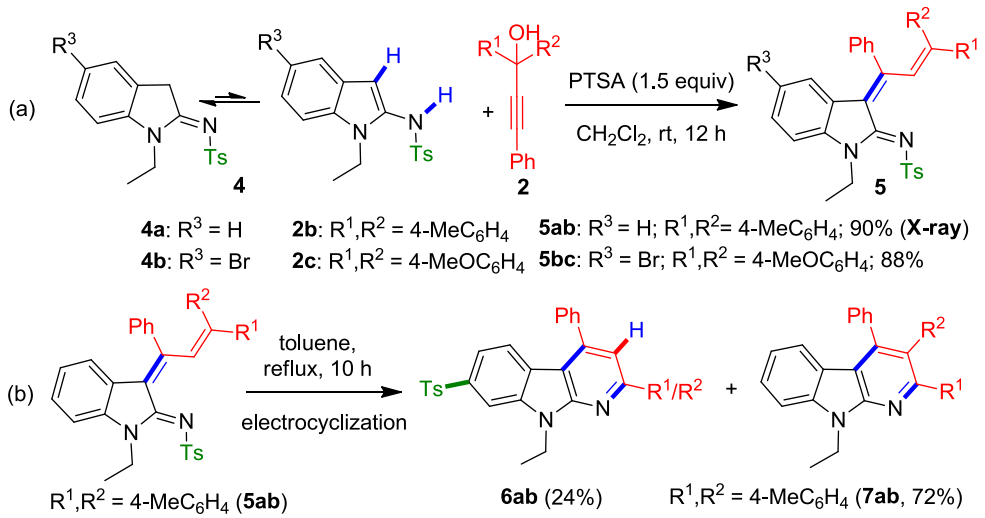


[a]Reaction conditions: 3-sulfonamidoindoles **1** (1.0 equiv), propargylic alcohols **2** (1.2 equiv), solvent (DCM, 5 mL), 12 h, 25 °C. [b]Yield after isolation.

Next, we turned our attention to α-carbolines. Towards this, 2-sulfonamidoindolines **4a-b** and propargylic alcohols **2b-c** were tested as substrates (Scheme 2) under the above optimized conditions, but cyclized products were not observed. The conjugated sulfonamidoindolines **5ab** (X-ray, Figure S4, SI) and **5bc** were formed as the only isolable compounds. We believe that under these conditions, the highly activated propargyl alcohols **2b-2c** undergo Friedel-Crafts reaction with sulfonamidoindolines followed by [1,5]-hydride shift (Scheme 2a). Compound **5ab** upon heating in toluene (reflux, 18 h) underwent 6π-electrocyclization to afford the rather unexpected 6-sulfonyl substituted α-carboline **6ab** via regioselective migration of sulfonyl group and α-carboline **7ab** in 24% and 72% yields, respectively

(Scheme 2b). The cross-over experiment between equiv amounts of compound **5ab** and $PhSO_2Na$ did not lead to the incorporation of $PhSO_2$ moiety at the 6-position. Also, by the use of an equiv amount of PTSA in toluene under reflux conditions, compound **5ab** afforded higher yield of α-carboline **7ab** and lower yield of tosyl migrated product **6ab**. The reaction took place equally well under nitrogen atmosphere also indicating that it is most likely not an oxidative elimination reaction. Based on these observations we opine that the tosyl group has migrated from indole substrate only, although a detailed pathway could not be ascertained.

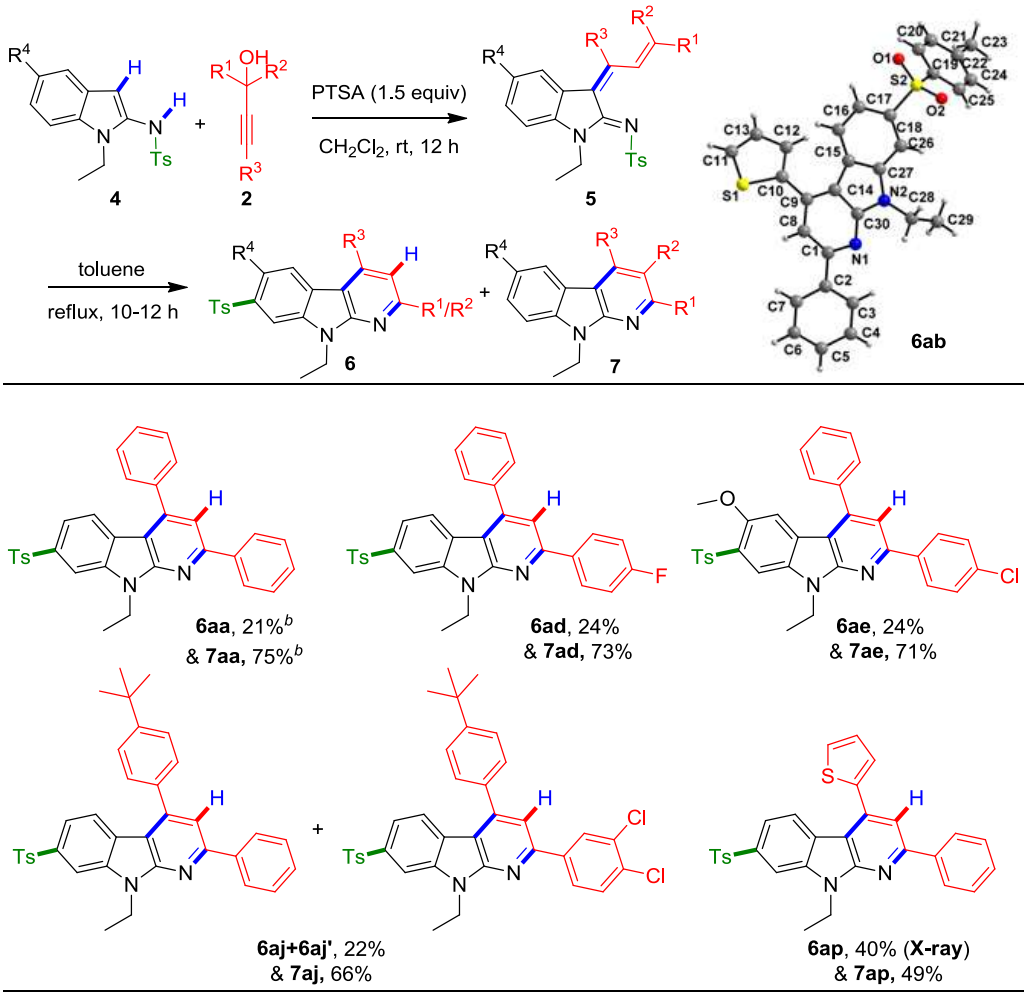
Scheme 2. Reaction of 2-Sulfonamidoindolines 4 with Propargylic Alcohols 2



Although the yield of **6ab** is moderate, this tosyl migration is interesting because it takes place without the intervention of a base or a metal catalyst or a Lewis acid.[20] Thus we have been successful in isolating 6-sulfonyl substituted α-carbolines **6** also readily (X-ray for **6ap** in Figure S5, SI). The unsymmetrical propargyl alcohol **2j** gave the tosyl migrated products **6aj+6aj'** and the α-carboline **7aj** (Table 3). To the best of our knowledge, this is the first report to directly introduce sulfonyl group on C-6 position of indole without the use of a catalyst. Further, to check the elimination of alkyl group (R^1 or R^2) on tosyl migration product **6**, we treated the propargyl alcohol **2t** (R^1 = CH_3 and R^2 = Me_2CHCH_2) with 2-

sulfonamidoindoline **4a** under optimized conditions, but the reaction did not occur; both starting materials were recovered.

Table 3. Scope of tosyl migration in the reaction of 2-sulfonamidoindolines **4** and propargylic alcohols **2**[a]

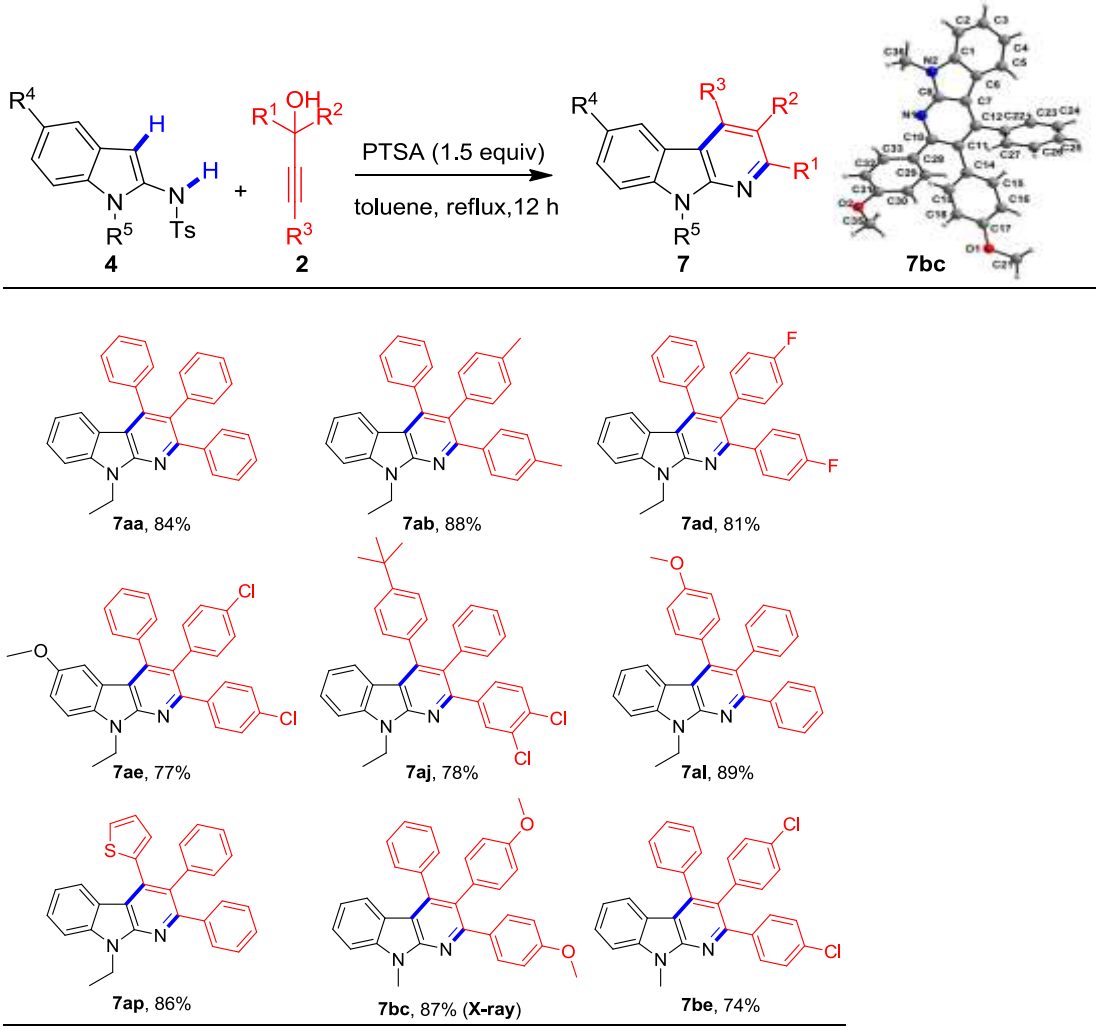


[a]Reaction conditions: 2-sulfonamidoindolines **4** (1.0 equiv), propargylic alcohol **2** (1.2 equiv), (i) solvent DCM (5 mL), 12 h, (ii) solvent toluene (5 mL), 12 h. [b]Yields of the isolated products.

In the next step, we found that the α-carboline **7aa** is the only product if the reaction of **4a** with **2a** is conducted in the presence of equiv amount of PTSA in refluxing toluene for 12 h.

By this minor modification, we were able to obtain an easier route to the α-carbolines **7aa-7be** (X-ray for **7bc** in Figure S6, SI) exclusively in one pot as shown in Scheme 3. Use of 2-sulfonamido-indoline **4e** (R^4 = R^5 = H) and the propargyl alcohol $(4\text{-MeOC}_6H_4)_2$ (HO)C≡CPh (**2b**) under the conditions employed here afforded the α,β-unsaturated ketone $(4\text{-MeOC}_6H_4)_2$C=CHC(O)Ph (major product, ca 85%; ^{1}H NMR, HRMS) and the butadiene substituted isomeric N-((*E*)-3-(3,3-bis(4-methoxyphenyl)-1-phenylallylidene)indolin-2-ylidene)-4-methylbenzenesulfonamide **5** (minor product, ca 15%; ^{1}H NMR, HRMS).

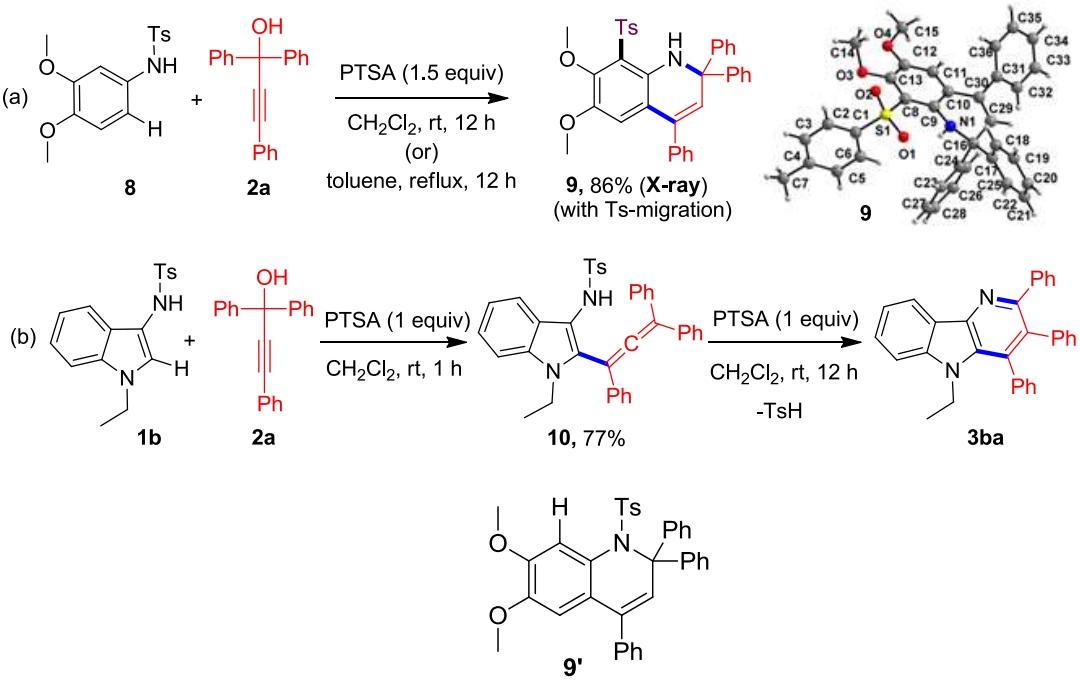
Scheme 3. One Pot Synthesis of α-Carbolines 7aa-7be[a,b]



[a]Reaction conditions: 2-sulfonamidoindoles **4** (1.0 equiv), propargylic alcohols **2** (1.2 equiv), solvent (Toluene, 5 mL), 12 h, 110 °C. [b]Yield after isolation.

In order to explore the reaction pathway, we treated benzenesulfonamide **8** with **2a** in the presence of PTSA and found that 8-tosyl-1,2-dihydroquinoline **9** is the sole product, via tosyl migration instead of aryl migration (Scheme 4a). An isomeric compound **9'** without tosyl migration was reported earlier.[21] Thus our result shows that indole moiety is necessary for the [1,2]-aryl migration. We then reasoned that the reaction could go through an allenic intermediate and indeed were able to isolate the allene **10** from the reaction of 3-sulfonamidoindoles **1b** with propargyl alcohol **2a** by slightly altering the reaction conditions as shown in Scheme 4b.

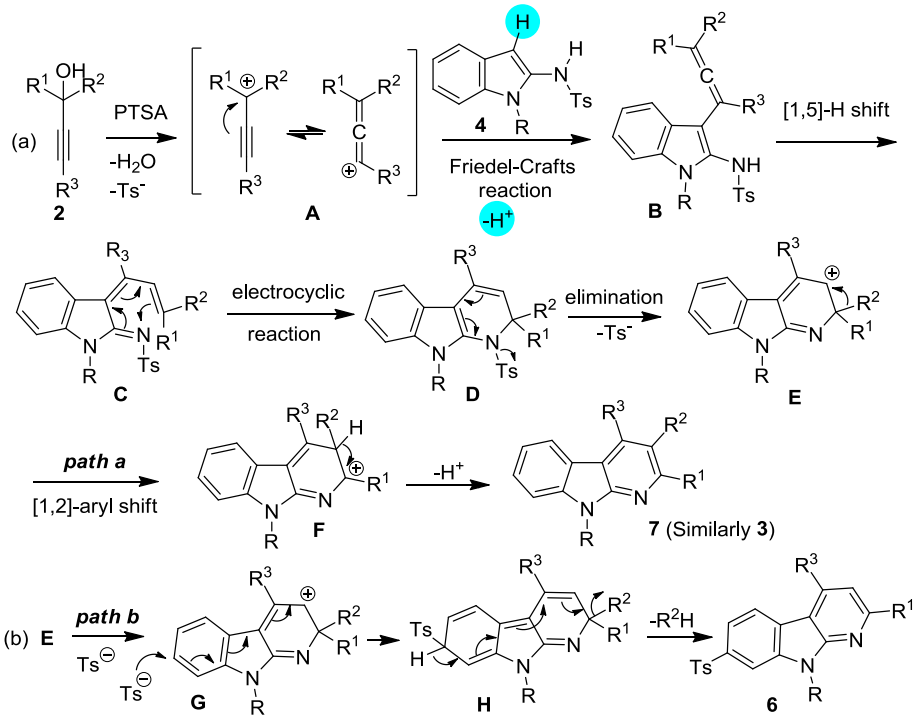
Scheme 4. Additional Reactions to Explore the Reaction Pathway



A possible pathway for the formation of 6-sulfonyl substituted α-carbolines **6** and α-carbolines **7** is shown in Scheme 5. Some of the steps observed here are similar to that recently observed in transition metal catalyzed carbazole synthesis.[19] First, propargylic alcohol **2** is converted to the allenic carbocation **A** in the presence of PTSA *via* Meyer-

Schuster rearrangement,[22] which would then undergo Friedel-Crafts-type reaction with **4** to form the allene intermediate **B**, as supported by the isolation of compound **10** (cf. Scheme 4b). Then intermediate **B** would be transformed to imine **C** *via* [1,5]-hydride shift. This step supported by the isolation of the compound **5** (cf. Scheme 2). Then species **C** undergoes cascade reaction of 6π-electrocylization (**D**) and elimination of *p*-toluenesulfonyl anion to give **E**. Intermediate **E** may follow two pathways. In *path a,* it undergoes [1,2]-aryl shift to afford **F** and subsequent aromatization to deliver the δ-carboline **7**. In path *b,* intermediate **E** undergoes migration of *p*-toluenesulfonyl anion to the indole C-6 position to give **G** followed by elimination of aromatic group[23] to lead to 6-sulfonyl substituted α-carboline **6** *via* **H**. It is possible that the [1,2]-aryl migration (*path a*) from **E** is faster than tosyl migration (*path b*) in the presence of *p*TSA. This may be the reason for selective formation of **7** (cf. Scheme 3). Since the reaction was conducted in toluene, we had difficulty in identifying traces of liberated arene arising from tosyl migration/arene expulsion. The δ-carbolines **3** are formed in a manner similar to **7**.

Scheme 5. Possible Pathway for the Formation of 6-Sulfonyl Substituted α-Carbolines 6 and α-Carbolines 7 (or 3)



CONCLUSIONS

In summary, we have demonstrated a transition metal-free method for the synthesis of highly substituted δ- and α-carbolines via Brønsted acid mediated reaction of propargyl alcohols with sulfonamido-indoles/-indolines. The reaction involves a cascade sequence of Friedel-Crafts/ [1,5]-hydride shift/ electrocyclization/ elimination/ [1,2]-aryl migration and aromatization leading to δ- and α- carbolines in good to excellent yields. A novel route for the synthesis of 6-sulfonyl substituted α-carbolines *via* unexpected tosyl group migration/ arene elimination has been developed.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in air, unless otherwise specified. All Chemicals were procured from Aldrich or local manufacturers and used as purchased without further purification, unless noted. Sulfonamido-indoles/-indolines and propargyl alcohols were prepared using known literature methods.[24-25] Melting points were determined using a

SUPERFIT hot stage apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using 5 mm tubes on a Bruker 400 and 500 MHz NMR spectrometer [field strengths: 400/ 100 or 500/ 125 MHz respectively] in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to TMS (^{1}H, ^{13}C: = 0). All *J* values are in Hz. Infrared spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment. Crystallographic data were collected at 293 K on an X-ray diffractometer system using Mo-Kα radiation (λ = 0.71073 Å) or Cu-K_α (λ = 1.54184 Å) radiation. Structures were solved and refined using standard methods.[26] Thin-layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh)/neutral alumina, for column elution process hexane-EtOAc mixture was used as the eluent unless otherwise stated.

(i) General procedure for the synthesis of sulfonamido-indoles/-indolines 1a-f and 4a-e.[24]

An oven dried 25 mL round-bottomed flask was charged with 1-methyl indole (0.5 g, 3.8 mmol) and *p*-toluenesulfonyl azide (1.05 g, 5.3 mmol) in 5 mL of dry 1,4-dioxane under nitrogen atmosphere. The mixture was stirred with heating (oil bath temperature at 75-80 °C) for 18-24 h, and cooled. Addition of ethanol (25 mL) resulted in most of 2-sulfonamidoindoline **4** to crystallize/precipitate from the solution. The solvent was removed from the mother liquor and the residue purified by column chromatography on silica gel using hexane/ethyl acetate (70:30) to obtain the 3-sulfonamidoindole **1** (lower R_f than compound **4**). Compounds **1b-f** and **4b-e** were prepared from the appropriate *N*-substituted indole and *p*-toluenesulfonyl azide by using the same procedure using same molar quantities. Among these, **1a**, **4d**, and **4e** are known;[24] compounds **1b**, **1c**, **1d**, **1e**, **1f**, **4a**, **4b**, and **4c** are new.

*N-(1-Ethyl-1H-indol-3-yl)-4-methylbenzenesulfonamide (**1b**).* White solid, yield 0.350 g (32%); mp 146-148 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 1H), 7.19-7.13 (m, 4H), 7.08 (s, 1H), 6.98 (dd→t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 4.12 (qrt, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.43 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.4, 136.8, 134.3, 129.4, 127.4, 124.6, 124.4, 122.0, 119.7, 117.8, 110.8, 109.4, 41.0, 21.5, 15.4; IR (neat): ν_{max} 3261, 3062, 2976, 1471, 1447, 1337, 1302, 1235, 1160, 1135, 1093, 813, 742, 663 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{18}N_2O_2SNa$ (M^+ + Na): *m/z* 337.0987. Found: 337.0988.

*N-(1-Allyl-1H-indol-3-yl)-4-methylbenzenesulfonamide (**1c**).* White solid, yield 0.315 g (30%); mp 123-125 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.64 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.18-7.15 (m, 4H), 7.06 (s, 1H), 6.99 (td, *J* = 7.0, 1.0 Hz, 1H), 6.33 (s, 1H), 5.99-5.91 (m, 1H), 5.21 (dd, *J* = 10.5, 1.0 Hz, 1H), 5.02 (dd, *J* = 17.0, 1.0 Hz, 1H), 4.67 (~dt, *J* = 5.0, 1.0 Hz, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.4, 136.6, 134.7, 132.9, 129.4, 127.4, 125.0, 124.6, 122.3, 119.9, 117.8, 117.5, 111.2, 109.8, 48.8, 21.5; IR (neat): ν_{max} 3264, 3049, 2923, 1597, 1464, 1370, 1335, 1303, 1285, 1149, 1087, 946, 895, 809, 733, 663 cm^{-1}; HRMS (ESI): Calcd. for $C_{18}H_{18}N_2O_2SNa$ (M^+ + Na): *m/z* 349.0987. Found: 349.0986.

*N-(1-Benzyl-1H-indol-3-yl)-4-methylbenzenesulfonamide (**1d**).* White solid, yield 0.323 g (35%); mp 142-144 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.65 (m, 2H), 7.33-7.23 (m, 5H), 7.17-7.13 (m, 3H), 7.06-7.01 (m, 4H), 6.44 (s, 1H), 5.25 (s, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.5, 136.5, 136.4, 134.9, 129.4, 128.8, 127.8, 127.5, 126.7, 125.2, 124.7, 122.5, 120.1, 117.9, 111.5, 109.9, 50.1, 21.5; IR (neat): ν_{max} 3248, 3056, 1593, 1493,

1462, 1347, 1297, 1253, 1207, 1153, 1089, 1032, 887, 814, 753, 704 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{21}N_2O_2S$ (M^+ + H): *m/z* 377.1324. Found: 377.1322.

N-(1-Ethyl-5-methoxy-1H-indol-3-yl)-4-methylbenzenesulfonamide ***(1e)***. White solid, yield 0.291 g (29%); mp 165-167 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.21-7.16 (m, 3H), 7.01 (s, 1H), 6.81 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.23 (s, 1H), 4.08 (qrt, *J* = 7.5 Hz, 2H), 3.66 (s, 3H), 2.40 (s, 3H), 1.42 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.3, 143.3, 137.0, 129.6, 129.4, 127.6, 125.4, 125.2, 112.9, 110.4, 110.3, 98.9, 55.5, 41.2, 21.5, 15.4; IR (neat): ν_{max} 3256, 2941, 1597, 1483, 1448, 1323, 1299, 1211, 1155, 1091, 1010, 916, 814, 798, 658 cm^{-1}; HRMS (ESI): Calcd. for $C_{18}H_{21}N_2O_3S$ (M^+ + H): *m/z* 345.1273. Found: 345.1275.

N-(5-Bromo-1-ethyl-1H-indol-3-yl)-4-methylbenzenesulfonamide ***(1f)***. White solid, yield 0.248 g (28%); mp 213-215 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.23-7.21 (m, 3H), 7.15 (t, *J* = 8.5 Hz, 1H), 7.12 (s, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 6.10 (s, 1H), 4.12 (qrt, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.9, 136.6, 133.0, 129.5, 127.5, 126.6, 126.4, 124.9, 120.3, 113.3, 111.0, 110.1, 41.3, 21.5, 15.2; IR (neat): ν_{max} 3257, 3129, 2923, 1562, 1456, 1404, 1326, 1275, 1161, 1091, 1049, 884, 862, 810, 791, 694 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{18}BrN_2O_2S$ (M^+ + H): *m/z* 393.0272. Found: 393.0272.

(Z)-N-(1-Ethylindolin-2-ylidene)-4-methylbenzenesulfonamide ***(4a)***. Pale yellow solid, yield 0.520 g (48%); mp 164-166 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.35-7.29 (m, 4H), 7.12 (td, *J* = 8.0, 0.4 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 4.20 (s, 2H), 3.94 (qrt, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.2, 143.0, 142.7, 139.5, 129.5, 128.1, 126.6_3, 126.5_7, 124.6, 123.6, 109.3, 37.0, 36.2, 21.5, 12.1;

IR (neat): ν_{max} 3063, 2978, 2935, 1557, 1455, 1364, 1351, 1276, 1179, 1083, 993, 851, 815, 746, 677 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{19}N_2O_2S$ (M^+ + H): *m/z* 315.1167. Found: 315.1168.

*(Z)-N-(5-Bromo-1-ethylindolin-2-ylidene)-4-methylbenzenesulfonamide (**4b**)*. White solid, yield 0.520 g (59%); mp 221-223 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.88 (m, 2H), 7.47-7.44 (m, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 1H), 4.22 (s, 2H), 3.91 (qrt, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 142.9, 142.2, 139.2, 131.0, 129.4, 128.6, 127.8, 126.4, 116.3, 110.5, 37.1, 36.0, 21.5, 11.9; IR (neat): ν_{max} 3066, 2973, 2925, 1560, 1476, 1365, 1348, 1272, 1142, 1082, 1054, 987, 810, 764, 691 cm^{-1}; HRMS (ESI): Calcd. for $C_{17}H_{18}BrN_2O_2S$ (M^+ + H): *m/z* 393.0272. Found: 393.0275.

*(Z)-N-(1-Ethyl-5-methoxyindolin-2-ylidene)-4-methylbenzenesulfonamide (**4c**)*. Pale yellow solid, yield 0.623 g (63%); mp 176-178 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.31-7.28 (m, 2H), 6.96-6.94 (m, 1H), 6.88-6.83 (m, 2H), 4.17 (s, 2H), 3.92 (qrt, *J* = 7.5 Hz, 2H), 3.81 (s, 3H), 2.42 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.6, 156.7, 142.6, 139.7, 136.4, 129.3, 127.9, 126.6, 112.6, 111.5, 109.7, 55.8, 37.0, 36.4, 21.5, 12.0; IR (neat): ν_{max} 2975, 1555, 1489, 1458, 1438, 1270, 1143, 1077, 986, 913, 808, 766, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{18}H_{21}N_2O_3S$ (M^+ + H): *m/z* 345.1273. Found: 345.1275.

(ii) General procedure for synthesis of propargyl alcohols 2a-t. A literature procedure was followed.[25a] To a THF solution (10 mL) of phenylacetylene (1.12 g, 10.9 mmol) was added *n*-BuLi (8.5 mmol, 1.6 M in hexane) drop-wise over a period of 5 min at -78 °C under nitrogen

atmosphere. The solution was allowed to warm to 0 °C over 1 h and held at 0 °C for an additional 30 min. The solution was then recooled to -78 °C and benzophenone (1.00 g, 5.4 mmol) was added in one portion. The solution was allowed to warm to 25 ^{o}C over 1 h and held at this temperature for an additional 3 h. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ethyl acetate (3 x 25 mL). The organic layer was washed with water (2 x 25 mL) and brine solution (25 mL). This was then dried over anh. Na_2SO_4, filtered, and concentrated. The crude material thus obtained was purified by column chromatography on silica gel using hexane/ethyl acetate (95:5) to obtain the pure propargylic alcohol **2a**. Compounds **2b-t** were prepared from appropriate acetylene and ketone by using the same procedure. Among these, **2a**,[25a] **2b**, **2d**, **2e**, **2l**, **2n**, **2o**, **2q**,[25b] **2p**,[25c] **2c**, **2m**,[25d] **2h**, **2k**, **2s**,[25e] **2r**,[25f] and **2t**[25g] are known compounds and **2f**, **2g**, **2i**, and **2j** are new.

*1-(2-Chloro-5-nitrophenyl)-1,3-diphenylprop-2-yn-1-ol (**2f**).* White solid, yield 1.28 g (92%); mp 109-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (d, *J* = 3.0 Hz, 1H), 8.18 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.62-7.60 (m, 2H), 7.55-7.52 (m, 3H), 7.42-7.35 (m, 7H), 3.16 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.5, 143.2, 141.9, 139.7, 132.2, 131.8, 129.1, 128.7, 128.6, 128.5, 126.9, 124.0, 122.9, 121.9, 88.1, 88.0, 73.3; IR (neat): ν_{max} 3350, 3085, 1606, 1517, 1490, 1342, 1297, 1245, 1166, 1048, 944, 772, 742, 755, 699 cm^{-1}; HRMS (ESI): Calcd. for $C_{21}H_{14}ClNO_3Na$ (M^+ + Na): *m/z* 386.0560. Found: 386.0561.

*1-(4-Methoxyphenyl)-1-phenyl-3-(p-tolyl)prop-2-yn-1-ol (**2g**).* Colourless liquid, yield 1.30 g (84%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.0 Hz, 2H), 7.62-7.59 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39-7.36 (m, 2H), 7.31-7.29 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.91-6.88 (m, 2H), 3.82 (s, 3H), 2.85 (s, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.1,

145.5, 138.8, 137.6, 131.7, 129.1, 128.3, 127.6, 127.5, 126.1, 119.5, 113.6, 91.4, 87.2, 74.6, 55.3, 21.5; IR (neat): ν_{max} 3547, 3493, 3031, 1605, 1506, 1449, 1242, 1168, 1046, 988, 815, 724 cm^{-1}; HRMS (ESI): Calcd. for $C_{23}H_{20}O_2Na$ (M^+ + Na): *m/z* 351.1361. Found: 351.1360.

1-(4-Chlorophenyl)-1-phenyl-3-(p-tolyl)prop-2-yn-1-ol ***(2i)***. White solid, yield 1.38 g (90%); mp 71-73 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.64-7.61 (m, 2H), 7.43-7.36 (m, 4H), 7.34-7.29 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 2.89 (s, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 143.8, 139.1, 133.6, 131.8, 129.2, 128.5_0, 128.4_7, 128.0, 127.6, 126.1, 119.1, 90.6, 87.8, 74.5, 21.6; IR (neat): ν_{max} 3341, 3056, 3025, 2360, 2221, 1509, 1484, 1447, 1174, 1090, 1041, 1013, 990, 895, 817, 747, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{22}H_{17}ClONa$ (M^+ + Na): *m/z* 355.0866. Found: 355.0866.

3-(4-(Tert-butyl)phenyl)-1-(3,4-dichlorophenyl)-1-phenylprop-2-yn-1-ol ***(2j)***. Colourless liquid, yield 1.53 g (94%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.0 Hz, 1H), 7.69-7.66 (m, 2H), 7.50-7.46 (m, 3H), 7.42-7.37 (m, 5H), 7.33 (tt, *J* = 7.5, 1.0 Hz, 1H), 2.92 (s, 1H), 1.43 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 152.5, 145.5, 144.3, 132.4, 131.8, 131.7, 130.3, 128.6, 128.2_2, 128.1_8, 126.0, 125.7, 125.5, 118.9, 90.1, 88.2, 74.1, 34.9, 31.2; IR (neat): ν_{max} 3341, 3056, 3025, 2360, 2221, 1509, 1484, 1447, 1403, 1174, 1090, 1013, 990, 816, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{25}H_{22}Cl_2ONa$ (M^+ + Na): *m/z* 431.0945. Found: 431.0946.

(iii) General procedure for the synthesis of δ-carbolines 3aa-3fb, 5ab, and 5bc. An oven dried 25 mL round-bottomed flask was charged with 3-sulfonamidoindole **1a** (0.100 g, 0.33 mmol), propargyl alcohol **2a** (0.113 g, 0.40 mmol) and PTSA (1.5 equiv) in dichloromethane (10 mL). The mixture was stirred at room temperature (25 ^oC) in open air for 12 hours and

monitored by TLC for the disappearance of starting materials. After the appropriate period, the reaction mixture was treated with dichloromethane (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with dichloromethane (10 mL). The combined organic part was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired product **3aa** as a white solid. Compounds **3ac-3fb, 5ab** and **5bc** were prepared from appropriate 3-sulfonamidoindole and propargyl alcohol by using the same procedure.

*5-Methyl-2,3,4-triphenyl-5H-pyrido[3,2-b]indole (**3aa**).* White solid, yield 0.112 g (82%); mp 163-165 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56-8.54 (m, 1H), 7.61-7.57 (m, 1H), 7.43-7.34 (m, 4H), 7.30-7.18 (m, 8H), 7.03-6.99 (m, 3H), 6.96-6.93 (m, 2H), 3.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.6, 143.3, 141.8, 141.3, 138.6, 136.4, 132.9, 132.4, 131.7, 131.3, 130.8, 130.4, 127.7, 127.5_8, 127.5_5, 127.5, 127.2, 126.7, 126.1, 122.1, 121.2, 119.9, 109.0, 31.7; IR (neat): ν_{max} 3056, 2926, 2853, 1618, 1542, 1491, 1442, 1385, 1213, 1154, 912, 748, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{23}N_2$ (M^+ + H): *m/z* 411.1861. Found: 411.1853.

*2,3-Bis(4-methoxyphenyl)-5-methyl-4-phenyl-5H-pyrido[3,2-b]indole (**3ac**).* White solid, yield 0.141 g (90%); mp 209-211 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 7.5 Hz, 1H), 7.59-7.56 (m, 1H), 7.39-7.32 (m, 4H), 7.30-7.29 (m, 3H), 7.24-7.21 (m, 2H), 6.85-6.82 (m, 2H), 6.78-6.75 (m, 2H), 6.59-6.56 (m, 2H), 3.79 (s, 3H), 3.71 (s, 3H), 3.23 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.4, 157.7, 150.5, 143.2, 141.1, 136.6, 134.7, 132.7, 132.6, 132.3, 131.6, 131.2, 131.1, 130.8, 127.6_1, 127.5_6, 127.4, 122.2, 121.1, 119.8, 113.1, 112.8, 108.9, 55.2, 55.0, 31.6; IR (neat): ν_{max} 3055, 2932, 2838, 1611, 1513, 1448, 1384, 1331,

1289, 1246, 1177, 1032, 835, 745, 704 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N_2O_2$ (M^+ + H): *m/z* 471.2072. Found: 471.2078.

*2-(4-Chlorophenyl)-5-methyl-3,4-diphenyl-5H-pyrido[3,2-b]indole (**3ao**)*. White solid, yield 0.121 g (81%); mp 208-210 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 7.5 Hz, 1H), 7.61-7.58 (m, 1H), 7.41-7.35 (m, 4H), 7.30-7.28 (m, 3H), 7.24-7.22 (m, 2H), 7.20-7.18 (m, 2H), 7.05-7.04 (m, 3H), 6.94-6.93 (m, 2H), 3.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.1, 143.4, 141.4, 140.3, 138.3, 136.1, 132.8_1, 132.7_8, 132.5, 131.7, 131.6, 131.3, 130.7, 127.9, 127.7, 127.6, 127.4, 127.3, 122.0, 121.1, 120.0, 109.0, 31.7; IR (neat): ν_{max} 3058, 2926, 2854, 1619, 1490, 1442, 1386, 1331, 1214, 1155, 1091, 838, 747, 704 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{22}ClN_2$ (M^+ + H): *m/z* 445.1471. Found: 445.1476.

*5-Ethyl-2,3,4-triphenyl-5H-pyrido[3,2-b]indole (**3ba**)*. White solid, yield 0.110 g (81%); mp 204-206 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.2 Hz, 1H), 7.61-7.57 (m, 1H), 7.45-7.42 (m, 3H), 7.38-7.34 (m, 1H), 7.30-7.26 (m, 5H), 7.24-7.18 (m, 3H), 7.02-6.99 (m, 3H), 6.97-6.95 (m, 2H), 3.78 (qrt, *J* = 7.0 Hz, 2H), 1.02 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 142.3, 141.9, 141.6, 138.7, 136.6, 133.0, 132.3, 131.8, 130.4, 130.3_1, 130.2_6, 127.7_4, 127.7_0, 127.6_6, 127.5, 127.1, 126.7, 126.0, 122.6, 121.4, 119.9, 109.3, 38.6, 14.3; IR (neat): ν_{max} 3056, 2974, 2925, 2856, 1616, 1542, 1466, 1385, 1338, 1205, 917, 752, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N_2$ (M^+ + H): *m/z* 425.2017. Found: 425.2012.

*5-Ethyl-2,3-bis(4-methylphenyl)-4-phenyl-5H-pyrido[3,2-b]indole (**3bb**)*. White solid, yield 0.125 g (87%); mp 207-209 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.36-7.32 (m, 3H), 7.30-7.24 (m, 5H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.84-6.80 (m, 4H), 3.74 (qrt, *J* = 7.0 Hz, 2H), 2.31 (s, 3H), 2.20 (s, 3H), 0.99 (t, *J* =

7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 150.7, 142.2, 141.5, 139.2, 136.8, 136.1, 135.8, 135.3, 132.9, 132.4, 131.5, 130.2_9, 130.2_6, 128.3, 127.9, 127.7, 127.6, 127.5, 122.7, 121.3, 119.8, 109.2, 38.5, 21.3, 21.2, 14.2; IR (neat): ν_{max} 3027, 2972, 2924, 2858, 1618, 1515, 1465, 1385, 1340, 1203, 824, 744, 706 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2$ (M^+ + H): *m/z* 453.2330. Found: 453.2332.

*2,3-Bis(4-fluorophenyl)-5-methyl-4-phenyl-5H-pyrido[3,2-b]indole (**3bd**)*. White solid, yield 0.181 g (84%); mp 232-234 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.39-7.35 (m, 3H), 7.33-7.30 (m, 3H), 7.26-7.23 (m, 2H), 6.94-6.87 (m, 4H), 6.75-6.71 (m, 2H), 3.77 (qrt, *J* = 7.0 Hz, 2H), 1.01 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.7 Hz), 161.2 (d, *J* = 244.4 Hz), 149.5, 142.3, 141.8, 137.8 (d, *J* = 3.5 Hz), 136.3, 134.6 (d, *J* = 3.5 Hz), 133.1 (d, *J* = 7.9 Hz), 132.5, 132.0 (d, *J* = 7.9 Hz), 131.8, 130.3, 130.1, 127.9_4, 127.8_7, 127.8, 122.4, 121.3, 120.1, 114.5 (d, *J* = 24.3 Hz), 114.4 (d, *J* = 24.3 Hz), 109.3, 38.6, 14.2; IR (neat): ν_{max} 3058, 2978, 2928, 1607, 1510, 1466, 1387, 1338, 1215, 1155, 838, 745 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}F_2N_2$ (M^+ + H): *m/z* 461.1829. Found: 461.1831.

*2,3-Bis(4-chlorophenyl)-5-ethyl-4-phenyl-5H-pyrido[3,2-b]indole (**3be**)*. White solid, yield 0.133g (86%); mp 236-238 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.38-7.30 (m, 6H), 7.25-7.20 (m, 4H), 7.02-7.00 (m, 2H), 6.88-6.85 (m, 2H), 3.77 (qrt, *J* = 7.0 Hz, 2H), 1.01 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 148.9, 142.4, 142.0, 140.1, 137.1, 136.0, 133.0, 132.9, 132.3_3, 132.3_2, 131.7, 131.5, 130.3, 130.1, 128.1, 128.0, 127.9_5, 127.9_0, 127.6, 122.3, 121.3, 120.2, 109.4, 38.6, 14.2; IR (neat): ν_{max} 3058, 2976, 2928, 1618, 1491, 1387, 1341, 1205, 1090, 1015, 833, 744 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}Cl_2N_2$ (M^+ + H): *m/z* 493.1238. Found: 493.1252.

2-(2-Chloro-5-nitrophenyl)-5-ethyl-3,4-diphenyl-5H-pyrido[3,2-b]indole ***(3bf)***. White solid, yield 0.136 g (81%); mp 197-199 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 3.0 Hz, 1H), 8.50 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.29 (s, 5H), 6.96 (s, 5H), 3.82 (qrt, *J* = 7.0 Hz, 2H), 1.05 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.4, 145.7, 142.4, 142.2, 141.6, 140.9, 137.1, 135.8, 133.8, 132.2, 130.8, 130.1_4, 130.0_8, 128.2, 127.9, 127.8, 127.3, 127.1, 126.6, 123.3, 122.0, 121.3, 120.3, 109.4, 38.7, 14.2; IR (neat): ν_{max} 3059, 2976, 2926, 2857, 1526, 1385, 1343, 1208, 1108, 905, 830, 744, 704 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}ClN_3O_2$ (M^+ + H): *m/z* 504.1479. Found: 504.1481.

5-Ethyl-3-(4-methoxyphenyl)-4-(4-methylphenyl)-2-phenyl-5H-pyrido[3,2-b]indole ***(3bg)***. White solid, yield 0.123 g (82%); mp 181-183 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.6 Hz, 1H), 7.59-7.55 (m, 1H), 7.45-7.41 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.25-7.17 (m, 3H), 7.15-7.09 (m, 4H), 6.86-6.83 (m, 2H), 6.58-6.54 (m, 2H), 3.78 (qrt, *J* = 6.8 Hz, 2H), 3.70 (s, 3H), 2.37 (s, 3H), 1.01 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.7, 150.9, 142.2_4, 142.1_5, 141.4, 137.2, 133.6, 132.8_2, 132.7_6, 131.1, 130.6, 130.4, 130.1, 128.5, 127.6, 127.5, 126.6, 122.6, 121.3, 119.8, 112.6, 109.3, 55.0, 38.5, 21.4, 14.3; IR (neat): ν_{max} 3049, 2970, 2927, 1614, 1513, 1463, 1384, 1337, 1245, 1204, 1030, 745, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2O$ (M^+ + H): *m/z* 469.2280. Found: 469.2286.

5-Ethyl-3,4-bis(4-methylphenyl)-2-phenyl-5H-pyrido[3,2-b]indole ***(3bh)***. White solid, yield 0.119 g (83%); mp 196-198 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.6 Hz, 1H), 7.59-7.54 (m, 1H), 7.43-7.40 (m, 3H), 7.36-7.32 (m, 1H), 7.23-7.17 (m, 3H), 7.16-7.08 (m, 4H), 6.81 (s, 4H), 3.76 (qrt, *J* = 6.8 Hz, 2H), 2.37 (s, 3H), 2.20 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.7, 142.2, 142.1, 141.4, 137.1, 135.7, 135.3, 133.5, 133.1, 132.6, 131.5, 130.6, 130.4, 130.0, 128.4, 127.8, 127.5, 127.4, 126.5, 122.6, 121.3, 119.2, 109.3, 38.5, 21.4, 21.2, 14.2; IR (neat): ν_{max} 3048, 2975, 2924, 1618, 1511, 1464, 1384, 1339, 1204, 1023, 823, 744, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2$ (M^+ + H): *m/z* 453.2331. Found: 453.2332.

2-(4-Chlorophenyl)-5-ethyl-4-(4-methylphenyl)-3-phenyl-5H-pyrido[3,2-b]indole ***(3bi)***. White solid, yield 0.119 g (79%); mp 254-256 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.5 Hz, 1H), 7.60-7.56 (m, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.37-7.34 (m, 3H), 7.18-7.16 (m, 2H), 7.13-7.07 (m, 4H), 7.05-7.02 (m, 3H), 6.94-6.92 (m, 2H), 3.78 (qrt, *J* = 7.0 Hz, 2H), 2.35 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 149.1, 142.3, 141.7, 140.4, 138.6, 137.3, 133.2, 133.1, 132.7, 132.6, 131.7_0, 131.6_7, 130.6, 130.0, 128.4, 127.8, 127.7, 127.3, 126.1, 122.4, 121.2, 120.0, 109.3, 38.5, 21.3, 14.2; IR (neat): ν_{max} 3053, 2975, 2926, 1617, 1494, 1386, 1340, 1205, 1090, 1016, 829, 745, 703 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}ClN_2$ (M^+ + H): *m/z* 473.1784. Found: 473.1789.

4-(4-Tert-butylphenyl)-2-(2,3-dichlorophenyl)-5-ethyl-3-phenyl-5H-pyrido[3,2-b]indole ***(3bj)***. White solid, yield 0.150 g (86%); mp 241-243 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.0 Hz, 1H), 7.69-7.68 (m, 1H), 7.61-7.58 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.31-7.28 (m, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.17-7.15 (m, 3H), 7.07-7.04 (m, 3H), 6.95-6.93 (m, 2H), 3.79 (qrt, *J* = 7.0 Hz, 2H), 1.33 (s, 9H), 1.01 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 150.9, 147.6, 142.4, 142.0, 141.7, 138.2, 133.1, 132.9, 132.7, 132.4, 131.7, 131.6, 130.8_0, 130.7_6, 129.8, 129.7, 129.2, 127.9, 127.4, 126.4, 124.5, 122.4, 121.3, 120.1, 109.3, 38.6, 34.6, 31.3, 14.2; IR (neat): ν_{max} 3057, 2963, 2869, 1618,

1469, 1386, 1344, 1205, 1136, 1028, 888, 748, 704 cm^{-1}; HRMS (ESI): Calcd. for $C_{35}H_{31}Cl_2N_2$ (M^+ + H): *m/z* 549.1864. Found: 549.1868.

2-(4-Bromophenyl)-5-ethyl-4-(4-methylphenyl)-3-phenyl-5H-pyrido[3,2-b]indole ***(3bk)***. White solid, yield 0.129 g (78%); mp 250-252 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.37-7.28 (m, 5H), 7.14-7.08 (m, 4H), 7.05-7.04 (m, 3H), 6.95-6.93 (m, 2H), 3.79 (qrt, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.1, 142.3, 141.7, 140.9, 138.6, 137.3, 133.2, 133.0, 132.6, 132.1, 131.7, 130.6, 130.0, 128.4, 127.8, 127.3, 126.2, 122.5, 121.3, 121.1, 120.0, 109.3, 38.6, 21.4, 14.2; IR (neat): ν_{max} 3053, 2973, 2925, 1617, 1475, 1386, 1340, 1205, 1076, 1013, 828, 746, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}BrN_2$ (M^+ + H): *m/z* 517.1279. Found: 517.1280.

5-Ethyl-4-(4-methoxyphenyl)-2,3-diphenyl-5H-pyrido[3,2-b]indole ***(3bl)***. White solid, yield 0.128 g (88%); mp 209-211 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.5 Hz, 1H), 7.59-7.56 (m, 1H), 7.45-7.41 (m, 3H), 7.37-7.34 (m, 1H), 7.32-7.19 (m, 8H), 6.86-6.83 (m, 2H), 6.57-6.54 (m, 2H), 3.76 (qrt, *J* = 7.0 Hz, 2H), 3.69 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.7, 150.8, 142.2, 142.1, 141.5, 136.7, 132.7, 132.6_2, 132.5_8, 131.0, 130.4, 130.2, 127.7, 127.6_3, 127.5_9, 127.5_6, 126.5, 122.6, 121.3, 119.9, 112.6, 109.2, 55.0, 38.5, 14.2; IR (neat): ν_{max} 3054, 2968, 2926, 1613, 1513, 1461, 1384, 1335, 1245, 1202, 1030, 744, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N_2O$ (M^+ + H): *m/z* 455.2123. Found: 455.2124.

5-Ethyl-4-(3-fluorophenyl)-2,3-diphenyl-5H-pyrido[3,2-b]indole ***(3bm)***. White solid, yield 0.107 g (76%); mp 176-178 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.5 Hz, 1H), 7.61-

7.58 (m, 1H), 7.45-7.42 (m, 3H), 7.39-7.36 (m, 1H), 7.28-7.19 (m, 4H), 7.08-6.94 (m, 8H), 3.81 (qrt, J = 7.5 Hz, 2H), 1.06 (t, J = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 162.0 (d, J = 245.8 Hz), 150.6, 142.3, 141.8, 141.6, 138.8 (d, J = 7.7 Hz), 138.4, 132.8, 131.6 (d, J = 7.1 Hz), 130.8, 130.7, 130.4, 130.0, 129.4 (d, J = 8.3 Hz), 127.9, 127.5, 127.3, 127.2, 126.8, 126.2_7, 126.2_6, 122.5, 121.4, 120.1, 117.4 (d, J = 21.3 Hz), 114.7 (d, J = 21.8 Hz), 109.3, 38.6, 14.2; IR (neat): ν_{max} 3057, 2975, 2927, 1614, 1583, 1483, 1386, 1339, 1206, 1146, 782, 744, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}FN_2$ (M^+ + H): *m/z* 443.1924. Found: 443.1923.

4-(4-Bromophenyl)-5-ethyl-2,3-diphenyl-5H-pyrido[3,2-b]indole (***3bn***). White solid, yield 0.125 g (78%); mp 225-227 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 8.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.39-7.25 (m, 10H), 7.06-7.03 (m, 3H), 6.96-6.94 (m, 2H), 3.78 (qrt, J = 7.0 Hz, 2H), 1.02 (t, J = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 149.1, 142.3, 141.8, 140.8, 138.4, 136.3, 132.9, 132.4, 132.1, 130.6, 130.4, 130.2, 127.9, 127.7, 127.3, 126.3, 122.4, 121.3, 121.1, 120.1, 109.3, 38.6, 14.2; IR (neat): ν_{max} 3056, 2976, 2929, 1617, 1542, 1385, 1337, 1203, 1074, 1010, 832, 740, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{24}BrN_2$ (M^+ + H): *m/z* 503.1123. Found: 503.1124.

5-Ethyl-3-(4-methoxyphenyl)-4-phenyl-2-(thiophen-2-yl)-5H-pyrido[3,2-b]indole (***3bp***). White solid, yield 0.110 g (75%); mp 252-254 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, J = 7.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.39-7.34 (m, 2H), 7.28-7.27 (m, 3H), 7.23-7.20 (m, 3H), 7.00 (d, J = 8.5 Hz, 2H), 6.82-6.81 (m, 1H), 6.73 (d, J = 8.5 Hz, 2H), 6.45-6.44 (m, 1H), 3.78 (s, 3H), 3.68 (qrt, J = 7.0 Hz, 2H), 0.98 (t, J = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 158.6, 146.5, 143.8, 142.3, 141.4, 136.4, 132.9, 131.3, 130.8, 130.2, 130.1, 127.8, 127.7, 127.5, 127.1, 126.6, 126.2, 122.5, 121.4, 119.9, 113.4, 109.2, 55.1, 38.5, 14.1; IR (neat): ν_{max}

3056, 2969, 2928, 1612, 1513, 1457, 1387, 1324, 1240, 1195, 1030, 836, 744, 703 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{25}N_2OS$ (M^+ + H): *m/z* 461.1688. Found: 461.1689.

*5-Ethyl-2-methyl-3,4-diphenyl-5H-pyrido[3,2-b]indole (**3bq**)*. White solid, yield 0.085 g (73%); mp 215-217 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 7.5 Hz, 0.5 Hz, 1H), 7.57-7.53 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35-7.32 (m, 1H), 7.26-7.19 (m, 7H), 7.17-7.14 (m, 1H), 7.08-7.06 (m, 2H), 3.72 (qrt, *J* = 7.0 Hz, 2H), 2.53 (s, 3H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.4, 141.8, 140.9, 139.2, 136.5, 133.7, 132.0, 130.3, 129.9, 129.7, 127.7, 127.6, 127.5, 127.3, 126.4, 122.2, 120.8, 119.7, 109.2, 38.4, 24.3, 14.1; IR (neat): ν_{max} 3056, 2975, 2925, 1616, 1548, 1457, 1386, 1338, 1212, 1128, 744, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{26}H_{23}N_2$ (M^+ + H): *m/z* 363.1861. Found: 363.1867.

*14-Ethyl-15-phenyl-14H-dibenzo[f,h]indolo[3,2-b]Quinoline (**3br**)*. White solid, yield 0.096 g (71%); mp 227-229 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.69 (d, *J* = 7.6 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 7.79 (td, *J* = 7.2, 1.2 Hz, 1H), 7.74-7.60 (m, 8H), 7.51-7.47 (m, 1H), 7.44-7.40 (m, 2H), 7.08-7.04 (m, 1H), 3.65 (qrt, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.2, 142.8, 141.8, 139.5, 132.3, 131.9, 131.2, 130.5, 130.4, 130.2, 129.5, 129.1_2, 129.0_6, 128.7, 128.6, 127.8, 127.4, 126.3, 125.9, 125.2, 123.3, 122.5, 122.2, 121.6, 121.2, 120.0, 109.5, 39.0, 14.2; IR (neat): ν_{max} 3053, 2976, 2928, 1615, 1486, 1385, 1338, 1203, 1149, 915, 743, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}N_2$ (M^+ + H): *m/z* 423.1861. Found: 423.1870.

*3-([1,1'-Biphenyl]-4-yl)-5-ethyl-2,4-diphenyl-5H-pyrido[3,2-b]indole (**3bs**)*. White solid, yield 0.040 g (25%); mp 228-230 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.5 Hz, 1H), 7.61-7.57 (m, 3H), 7.52-7.51 (m, 2H), 7.47-7.41 (m, 5H), 7.38-7.27 (m, 8H), 7.04-7.01 (m,

3H), 7.00-6.98 (m, 2H), 3.78 (qrt, J = 7.0 Hz, 2H), 1.02 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 150.1, 142.3, 141.7, 141.1, 140.9, 139.3, 138.7, 136.5, 133.0, 132.4, 131.8, 130.8, 130.3_1, 130.2_7, 128.7, 127.7_3, 127.6_7, 127.6_3, 127.2, 127.1, 127.0, 126.3, 126.1, 122.6, 121.3, 119.9, 109.2, 38.6, 14.2; IR (neat): ν_{max} 3055, 2971, 2924, 1616, 1485, 1387, 1339, 1205, 846, 751, 703 cm^{-1}; HRMS (ESI): Calcd. for $C_{37}H_{29}N_2$ (M^+ + H): *m/z* 501.2331. Found: 501.2338.

2-([1,1'-Biphenyl]-4-yl)-5-ethyl-3,4-diphenyl-5H-pyrido[3,2-b]indole (***3bs'***). White solid, yield 0.101 g (64%); mp 222-224 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 8.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.54-7.52 (m, 2H), 7.49-7.46 (m, 2H), 7.44-7.35 (m, 4H), 7.33-7.27 (m, 8H), 7.24-7.17 (m, 3H), 7.02-7.00 (m, 2H), 3.79 (qrt, J = 7.0 Hz, 2H), 1.02 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 150.6, 142.3, 141.9, 141.8, 140.6, 138.3, 137.9, 136.6, 132.6, 132.4, 132.2, 130.5, 130.4, 130.3, 128.7, 127.8, 127.7, 127.6, 127.1, 126.7_9, 126.7_5, 125.6, 122.6, 121.4, 120.0, 109.3, 38.6, 14.2; IR (neat): ν_{max} 3053, 2976, 2928, 1615, 1486, 1385, 1338, 1203, 1149, 915, 743, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{37}H_{29}N_2$ (M^+ + H): *m/z* 501.2331. Found: 501.2341.

2,3,4-Triphenyl-5-(prop-2-en-1-yl)-5H-pyrido[3,2-b]indole (***3ca***). White solid, yield 0.111 g (83%); mp 205-207 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.57-8.54 (m, 1H), 7.58-7.54 (m, 1H), 7.44-7.41 (m, 2H), 7.38-7.34 (m, 2H), 7.28-7.18 (m, 8H), 7.01-6.98 (m, 3H), 6.94-6.92 (m, 2H), 5.61-5.52 (m, 1H), 5.00 (dd, J = 10.4, 1.0 Hz, 1H), 4.65 (dd, J = 17.2, 1.0 Hz, 1H), 4.33-4.31 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.8, 142.8, 141.8, 141.5, 138.6, 136.1, 133.1, 132.9, 132.5, 131.7, 130.6, 130.4_5, 130.3_9, 127.8, 127.7, 127.6, 127.5, 127.1, 126.8, 126.0, 122.4, 121.2, 120.2, 116.0, 109.8. 46.1; IR (neat): ν_{max} 3056, 2923, 2858, 1616, 1490,

1447, 1385, 1332, 1198, 921, 747, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{25}N_2$ (M^+ + H): *m/z* 437.2017. Found: 437.2023.

*5-Benzyl-2,3,4-triphenyl-5H-pyrido[3,2-b]indole (**3da**)*. White solid, yield 0.102 g (79%); mp 196-198 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.40-7.36 (m, 1H), 7.29 (d, *J* = 9.2 Hz, 1H), 7.24-7.12 (m, 7H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.97-6.93 (m, 5H), 6.90-6.88 (m, 2H), 5.02 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.9, 143.1, 141.7, 141.5, 138.5, 137.4, 135.6, 133.3, 132.8, 131.7, 130.6, 130.4, 130.3, 128.3, 128.0, 127.5, 127.4, 127.0, 126.8$_7$, 126.7$_8$, 126.0, 125.5, 121.3, 120.3, 109.6, 47.3; IR (neat): ν_{max} 3059, 2924, 2854, 1692, 1545, 1493, 1449, 1388, 1318, 1197, 1148, 1027, 764, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{36}H_{27}N_2$ (M^+ + H): *m/z* 487.2174. Found: 487.2166.

*5-Ethyl-8-methoxy-2,3-bis(4-methoxyphenyl)-4-phenyl-5H-pyrido[3,2-b]indole (**3eb**)*. White solid, yield 0.130 g (87%); mp 241-243 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.36 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.32-7.27 (m, 4H), 7.25-7.19 (m, 3H), 6.84-6.83 (m, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 3.99 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H), 3.70 (qrt, *J* = 7.0 Hz, 2H), 0.97 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 157.6, 154.2, 150.2, 141.1, 137.2, 136.8, 134.7, 132.7, 132.3, 131.5, 131.2, 130.7, 130.2, 127.7, 127.5, 122.8, 117.9, 113.1, 112.7, 110.2, 102.5, 56.1, 55.2, 55.0, 38.6, 14.3; IR (neat): ν_{max} 2927, 2844, 1609, 1509, 1448, 1283, 1246, 1186, 1034, 835, 741, 705 cm^{-1}; HRMS (ESI): Calcd. for $C_{34}H_{31}N_2O_3$ (M^+ + H): *m/z* 515.2335. Found: 515.2335.

*8-Bromo-5-ethyl-2,3-bis(4-methoxyphenyl)-4-phenyl-5H-pyrido[3,2-b]indole (**3fb**)*. White solid, yield 0.120 g (83%); mp 235-237 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 4H), 7.25-7.22 (m,

2H), 6.84-6.81 (m, 2H), 6.78-6.75 (m, 2H), 6.58-6.55 (m, 2H), 3.79 (s, 3H), 3.70 (qrt, J = 7.2 Hz, 2H), 3.70 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 158.5, 157.7, 151.1, 140.7, 140.2, 136.4, 134.4, 133.1, 133.0, 132.6, 131.4, 130.9, 130.6, 130.1_4, 130.1_1, 127.8, 127.7, 124.3, 123.9, 113.1, 112.8, 110.8, 55.2, 55.0, 38.7, 14.2; IR (neat): ν_{max} 2927, 2840, 1609, 1514, 1457, 1376, 1296, 1248, 1180, 1033, 834, 801 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{28}BrN_2O_2$ (M^+ + H): *m/z* 563.1334. Found: 563.1334.

*(Z)-N-((E)-1-Ethyl-3-(1-phenyl-3,3-di-p-tolylallylidene)indolin-2-ylidene)-4-methylbenzenesulfonamide (**5ab**)*. Dark red solid, yield 0.175 g (90%); mp 170-172 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.66 (s, 1H), 7.18 (td, J = 8.0, 1.0 Hz, 1H), 7.12-7.07 (m, 1H), 7.03-6.95 (m, 7H), 6.86-6.85 (m, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.66 (td, J = 8.0, 1.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 6.58 (d, J = 8.0 Hz, 2H), 6.03 (d, J = 7.5 Hz, 1H), 4.65 (qrt, J = 7.0 Hz, 2H), 2.40 (s, 3H), 2.24 (s, 3H), 2.07 (s, 3H), 1.62 (t, J = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.3, 154.6, 152.6, 142.5, 141.5, 141.3, 140.9, 140.4, 138.7, 138.4, 138.2, 137.6, 137.3, 130.9, 130.5, 129.7, 128.6, 128.4_1, 128.3_6, 128.1, 127.9_3, 127.8_7, 127.8, 127.6, 125.5, 124.6, 122.9, 122.6, 109.6, 40.2, 21.3, 21.2, 21.1, 13.0; IR (neat): ν_{max} 3029, 2924, 1581, 1539, 1470, 1362, 1278, 1143, 1085, 1014, 821, 774, 750, 705 cm^{-1}; Calcd. for $C_{40}H_{37}N_2O_2S$ (M^+ + H): *m/z* 609.2576. Found: 609.2585.

*(Z)-N-((E)-3-(3,3-Bis(4-methoxyphenyl)-1-phenylallylidene)-5-bromo-1-ethylindolin-2-ylidene)-4-methylbenzenesulfonamide (**5bc**)*. Dark red solid, yield 0.160 g (88%); mp 159-161 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.61 (s, 1H), 7.26 (dd, J = 8.5, 2.0 Hz, 1H), 7.15-7.12 (m, 1H), 7.06-7.01 (m, 4H), 6.89-6.87 (m, 3H), 6.74 (d, J = 9.0 Hz, 2H), 6.68-6.64 (m, 4H), 6.51 (d, J = 9.0 Hz, 2H), 6.00 (d, J = 2.0 Hz, 1H), 4.61 (qrt, J = 7.0 Hz, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.09 (s, 3H), 1.58 (t, J = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR

(125 MHz, $CDCl_3$) δ 160.3, 159.6, 157.4, 154.2, 153.9, 141.2, 141.1, 141.0, 139.8, 134.2, 132.9, 132.0, 130.0_9, 130.0_6, 129.6, 129.5, 128.4, 127.9, 126.6, 125.9, 125.8, 125.5, 115.6, 113.4, 113.1, 110.8, 55.3, 40.3, 21.2, 13.0; IR (neat): ν_{max} 2927, 2842, 1579, 1512, 1466, 1350, 1250, 1178, 1142, 1084, 1030, 828, 770 cm^{-1}; HRMS (ESI): Calcd. for $C_{40}H_{36}BrN_2O_4S$ ($M^+ + H$): *m/z* 719.1579. Found: 719.1587.

(iv) Procedure for the synthesis of compounds 6ab and 7ab. An oven dried 25 mL round-bottomed flask was charged with compound **5ab** (0.100 g, 0.16 mmol) in toluene (10 mL). The mixture was stirred at 110 ºC in open air for 10 h and monitored by TLC until the disappearance of starting materials. After the appropriate period, the solvent was removed under reduced pressure to afford the crude product. Purification by column chromatography (ethyl acetate: hexane; 1:9) afforded the desired products **6ab** and **7ab** (higher R_f).

*9-Ethyl-4-phenyl-2-(p-tolyl)-7-tosyl-9H-pyrido[2,3-b]indole (**6ab**).* White solid, yield 0.020 g (24%); mp 214-216 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.16-8.14 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.50 Hz, 1H), 7.68-7.66 (m, 2H), 7.61-7.53 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.74 (qrt, *J* = 7.0 Hz, 2H), 2.46 (s, 3H), 2.40 (s, 3H), 1.58 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.6, 152.8, 146.8, 143.9, 139.3_3, 139.3_0, 138.9, 138.8, 138.5, 136.7, 129.9, 129.5, 128.8_9, 128.8_6, 128.6, 127.6, 127.2, 124.1, 123.0, 118.1, 114.0, 110.8, 108.4, 36.7, 21.5, 21.4, 14.2; IR (neat): ν_{max} 3058, 2977, 2927, 1565, 1444, 1408, 1308, 1148, 1092, 820, 731, 673 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2O_2S$ ($M^+ + H$): *m/z* 517.1950. Found: 517.1950.

*9-Ethyl-4-phenyl-2,3-di-p-tolyl-9H-pyrido[2,3-b]indole (**7ab**).* White solid, yield 0.054 g (72%); mp 209-211 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H), 7.45-7.42 (m, 1H),

7.37-7.34 (m, 5H), 7.27-7.24 (m, 2H), 7.04 (d, J = 7.5 Hz, 2H), 7.01-6.95 (m, 2H), 6.84 (s, 4H), 4.67 (qrt, J = 7.5 Hz, 2H), 2.33 (s, 3H), 2.23 (s, 3H), 1.56 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.6, 150.2, 144.8, 140.0, 139.1, 138.5, 136.7, 135.8, 135.2, 131.9, 130.3, 129.4, 128.2, 128.1, 128.0, 127.2_2, 127.1_8, 126.0, 122.6, 120.8, 119.2, 112.8, 108.8, 36.1, 21.2, 21.1, 14.1; IR (neat): ν_{max} 2972, 2920, 2861, 1564, 1462, 1400, 1353, 1213, 1021, 822, 740 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{29}N_2$ (M^+ + H): *m/z* 453.2331. Found: 453.2325.

(v) General procedure for synthesis of compounds 6aa-6ap. An oven dried 25 mL round-bottomed flask was charged with 2-sulfonamidoindoline **4a** (0.100 g, 31 mmol), propargyl alcohol **2a** (0.108 g, 0.38 mmol) and PTSA (1.5 equiv) in dichloromethane (10 mL). The mixture was stirred at 25 ^oC in open air for 12 h and monitored by TLC until the disappearance of starting materials. After the appropriate period, the reaction mixture was treated with dichloromethane (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with dichloromethane (10 mL). The combined organic part was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product **5**. The crude compound **5** was dissolved in toluene (10 mL), stirred at 110 ºC in open air for 12 h and monitored by TLC until the disappearance of starting materials. After the appropriate period, the solvent was removed under reduced pressure to obtain the two products **6** and **7**. Purification by column chromatography (ethyl acetate: hexane; 1:9) afforded the desired products **6aa** and **7aa** (higher R_f). Compounds **6ad-6ap** were prepared from appropriate 2-sulfonamidoindoline and propargyl alcohol by using the same procedure.

*9-Ethyl-2,4-diphenyl-7-tosyl-9H-pyrido[2,3-b]indole (**6aa**)*. White solid, yield 0.035 g (21%); mp 253-255 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.36-

7.33 (m, 3H), 7.25-7.19 (m, 6H), 7.15-7.08 (m, 5H), 6.97-6.93 (m, 4H), 6.85-6.82 (m, 2H), 4.64 (qrt, J = 7.2 Hz, 2H), 2.30 (s, 3H), 1.49 (t, J = 5.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.6, 150.2, 144.9, 142.8, 140.2, 138.2, 138.1, 137.7, 137.1, 136.5, 131.0, 129.4, 128.8, 128.1, 127.3_4, 127.2_6, 126.7, 126.6, 126.5, 126.3, 125.1, 123.4, 122.1, 117.2, 111.0, 107.3, 35.6, 20.5, 13.2; IR (neat): ν_{max} 3055, 2976, 2929, 1567, 1475, 1403, 1351, 1301, 1238, 1145, 1024, 748, 701 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N_2O_2S$ (M^+ + H): *m/z* 503.1793. Found: 503.1790.

*9-Ethyl-2-(4-fluorophenyl)-4-phenyl-7-tosyl-9H-pyrido[2,3-b]indole (**6ad**).* White solid, yield 0.041 g (24%); mp 266-268 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25-8.22 (m, 2H), 8.16 (d, J = 1.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 1H), 7.67-7.65 (m, 2H), 7.60-7.57 (m, 3H), 7.55 (dd, J = 8.5, 1.5 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.24-7.20 (m, 2H), 4.74 (qrt, J = 7.0 Hz, 2H), 2.40 (s, 3H), 1.59 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.6 (d, J = 247.3 Hz), 153.3, 151.6, 145.8, 142.7, 138.1, 137.8, 137.6, 137.4, 134.4 (d, J = 3.1 Hz), 128.7, 128.0 (d, J = 8.2 Hz), 127.7, 127.4, 126.4, 122.8, 122.0, 117.1, 114.5 (d, J = 21.3 Hz), 14.4, 112.7, 109.8, 107.3, 35.5, 20.4, 13.0; IR (neat): ν_{max} 3062, 2975, 2928, 1566, 1445, 1408, 1311, 1224, 1151, 1093, 836, 727, 673 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{26}FN_2O_2S$ (M^+ + H): *m/z* 521.1699. Found: 521.1699.

*2-(4-Chlorophenyl)-9-ethyl-6-methoxy-4-phenyl-7-tosyl-9H-pyrido[2,3-b]indole (**6ae**).* White solid, yield 0.060 g (24%); mp 254-256 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.89-7.87 (m, 2H), 7.49-7.34 (m, 5H), 7.28-7.23 (m, 5H), 7.19-7.17 (m, 2H), 7.06-7.03 (m, 2H), 6.90-6.87 (m, 2H), 6.39 (s, 1H), 4.71 (qrt, J = 7.0 Hz, 2H), 3.41 (s, 3H), 2.41 (s, 3H), 1.59 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.2, 150.3, 149.7, 144.8, 142.6, 138.5, 137.7, 136.1, 135.5, 132.9, 132.5, 132.1, 131.5, 130.7, 128.0_9, 128.0_4, 127.4_4, 127.3_9,

127.2, 126.9$_5$, 126.8$_9$, 125.1, 124.5, 111.2, 109.4, 105.2, 55.0, 35.6, 20.5, 13.3; IR (neat): ν_{max} 3059, 2975, 2933, 1569, 1468, 1428, 1308, 1220, 1147, 1090, 1015, 835, 732, 696 cm^{-1}; HRMS (ESI): Calcd. for $C_{33}H_{28}ClN_2O_3S$ (M^+ + H): *m/z* 567.1509. Found: 567.1509.

Compounds ***6aj***+***6aj'*** *(mixture).* White solid, yield 0.090 g (22%); ^{1}H NMR (500 MHz, $CDCl_3$) 8.35 (d, *J* = 2.0 Hz, 1H), 8.16 (dd, *J* = 5.5, 1.5 Hz, 2H), 8.06 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.90-7.82 (m, 5H), 7.64-7.56 (m, 8H), 7.47 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.34-7.29 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.11-7.05 (m, 5H), 6.92-6.90 (m, 2H), 4.76-4.90 (m, 4H), 2.40 (s, 6H), 1.60-1.57 (m, 6H), 1.45 (s, 9H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.6, 151.7$_3$, 151.6$_6$, 151.4, 150.1, 150.0, 146.2, 145.5, 142.9, 140.3, 138.5, 138.3, 138.2, 138.$_{12}$, 138.0$_9$, 138.0$_6$, 136.6, 134.3, 132.9, 132.2, 132.0, 131.4, 130.8$_2$, 130.7$_6$, 130.7, 129.6, 128.8, 128.7, 128.3, 128.1, 127.7, 127.4, 127.3, 127.2, 126.6$_3$, 126.6$_1$, 126.3, 125.5, 125.3, 124.8, 124.7, 124.1, 123.3, 122.9, 122.4$_2$, 122.3$_8$, 117.4, 113.1, 111.7, 110.7, 107.5, 107.4, 35.7, 35.6, 33.9, 33.6, 30.4, 30.3, 20.5, 13.2, 13.1; HRMS (ESI) **6aj**: Calcd. for $C_{36}H_{35}N_2O_2S$ (M^+ + H): *m/z* 559.2419. Found: 559.2420. HRMS (ESI) **6aj'**: Calcd. for $C_{36}H_{33}Cl_2N_2O_2S$ (M^+ + H): *m/z* 627.1640. Found: 627.1638.

9-Ethyl-2-phenyl-4-(thiophen-2-yl)-7-tosyl-9H-pyrido[2,3-b]indole ***(6ap).*** White solid, yield 0.068 g (40%); mp 268-270 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.23 (m, 2H), 8.17 (d, *J* = 1.2 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.62 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.58-7.52 (m, 4H), 7.49-7.46 (m, 1H), 7.32-7.27 (m, 4H), 4.74 (qrt, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.58 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.5, 153.0, 143.9, 139.6, 139.4, 139.2$_4$, 139.2$_2$, 139.0, 138.9, 129.9, 129.3, 128.8, 127.8, 127.7, 127.6, 127.4, 127.3, 123.9, 123.1, 118.3, 115.0, 111.1, 108.5, 36.7, 21.5, 14.1; IR (neat): ν_{max}

3062, 2973, 2926, 1566, 1442, 1407, 1308, 1222, 1149, 1090, 813, 729, 679 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{25}N_2O_2S_2$ (M^+ + H): *m/z* 509.1357. Found: 509.1352.

(vi) Procedure for one spot synthesis of α-carbolines 7aa-7be. An oven dried 25 mL round-bottomed flask was charged with 2-sulfonamidoindoline **4a** (0.100 g, 0.31 mmol), propargyl alcohol **2a** (0.119 g, 0.38 mmol) and PTSA (1.5 equiv) in toluene (10 mL). The mixture was stirred at 110 ºC in open air for 12 h and monitored by TLC until the starting materials disappeared. After the appropriate period, the solvent was removed under reduced pressure. Further, the reaction mixture was treated with dichloromethane (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with dichloromethane (10 mL). The combined organic portion was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by column chromatography (ethyl acetate: hexane; 1:9) afforded the desired product **7aa** as a white solid. Compounds **7ab-7be** were prepared from appropriate 2-sulfonamidoindoline and propargyl alcohol by using the same procedure.

*9-Ethyl-2,3,4-triphenyl-9H-pyrido[2,3-b]indole (**7aa**).* White solid, yield 0.114 g (84%); mp 211-213 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.44 (m, 4H), 7.37-7.32 (m, 3H), 7.27-7.22 (m, 5H), 7.05-6.96 (m, 7H), 4.69 (qrt, *J* = 7.0 Hz, 2H), 1.57 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.6, 150.3, 144.7, 141.8, 140.1, 138.8, 138.2, 132.2, 130.5, 129.4, 128.1, 127.4_3, 127.3_9, 127.3, 127.2, 127.1, 126.2, 125.8, 122.7, 120.8, 119.3, 112.9, 108.9, 36.2, 14.1; IR (neat): ν_{max} 3056, 2977, 2931, 1567, 1475, 1403, 1351, 1301, 1238, 1145, 1024, 744, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{25}N_2$ (M^+ + H): *m/z* 425.2018. Found: 425.2020.

*9-Ethyl-2,3-bis(4-fluorophenyl)-4-phenyl-9H-pyrido[2,3-b]indole (**7ad**)*. White solid, yield 0.122 g (81%); mp 239-241 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.46-7.41 (m, 2H), 7.40-7.36 (m, 3H), 7.28-7.23 (m, 2H), 7.03-6.89 (m, 6H), 6.80-6.74 (m, 2H), 4.69 (qrt, *J* = 7.2 Hz, 2H), 1.58 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.6 Hz), 161.7 (d, *J* = 244.3 Hz), 153.5, 150.3, 144.9, 140.1, 137.9, 137.7 (d, *J* = 3.1 Hz), 134.6 (d, *J* = 3.2 Hz), 133.5 (d, *J* = 7.8 Hz), 132.1 (d, *J* = 8.0 Hz), 129.3, 128.3, 127.6, 126.4, 126.1, 122.7, 120.6, 119.5, 114.5_2 (d, *J* = 21.4 Hz), 114.4_7 (d, *J* = 21.0 Hz), 113.1, 109.0, 36.2, 14.1; IR (neat): ν_{max} 3061, 2977, 2928, 1570, 1507, 1464, 1401, 1354, 1299, 1215, 1148, 1091, 840, 742, 702 cm^{-1}; HRMS (ESI): Calcd. for $C_{31}H_{23}F_2N_2$ (M^+ + H): *m/z* 461.1829. Found: 461.1831.

*2,3-Bis(4-chlorophenyl)-9-ethyl-6-methoxy-4-phenyl-9H-pyrido[2,3-b]indole (**7ae**)*. White solid, yield 0.118 g (77%); mp 242-244 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (m, 6H), 7.25-7.22 (m, 4H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.05-7.03 (m, 2H), 6.91-6.88 (m, 2H), 6.47 (d, *J* = 2.4 Hz, 1H), 4.63 (qrt, *J* = 7.2 Hz, 2H), 3.58 (s, 3H), 1.54 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.6, 152.0, 149.5, 143.7, 138.9, 136.6, 136.1, 133.9, 132.4, 132.3, 131.1, 130.7, 128.3, 127.3, 126.8, 126.7, 126..6, 124.3, 119.8, 114.5, 112.1, 108.6, 104.6, 54.4, 35.2, 13.2; IR (neat): ν_{max} 2924, 2855, 1740, 1569, 1478, 1271, 1216, 1175, 1137, 1087, 840, 800, 738, 700 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{25}Cl_2N_2O$ (M^+ + H): *m/z* 523.1344. Found: 523.1344.

*4-(4-(Tert-butyl)phenyl)-2-(2,3-dichlorophenyl)-9-ethyl-3-phenyl-9H-pyrido[2,3-b]indole (**7aj**)*. White solid, yield 0.121 g (78%); mp 248-250 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) 7.68-7.67 (m, 1H), 7.51-7.46 (m, 2H), 7.36-7.34 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.17-7.14 (m, 3H), 7.11-7.06 (m, 4H), 7.03-7.00 (m, 1H), 6.95-6.93 (m, 2H), 4.67 (qrt, *J* = 7.0 Hz, 2H),

1.58 (t, J = 7.0 Hz, 3H), 1.37 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 151.6, 150.6, 150.3, 145.2, 141.9, 140.2, 138.3, 134.6, 132.4, 132.0, 131.6, 131.2, 129.8, 129.2, 129.0, 127.5, 126.5, 126.2, 124.9, 122.9, 120.7, 119.5, 113.7, 108.9, 36.2, 34.6, 31.4, 14.1; IR (neat): ν_{max} 3057, 2962, 2869, 1569, 1470, 1403, 1350, 1302, 1236, 1133, 1025, 809, 742, 705 cm^{-1}; HRMS (ESI): Calcd. for $C_{35}H_{31}Cl_2N_2$ (M^+ + H): *m/z* 549.1864. Found: 549.1865.

*9-Ethyl-2,3-diiphenyl-4-(4-methoxyphenyl)-9H-pyrido[2,3-b]indole (**7al**).* White solid, yield 0.130 g (89%); mp 245-247 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.43 (m, 4H), 7.39-7.35 (m, 3H), 7.28-7.22 (m, 5H), 7.04-6.96 (m, 2H), 6.87-6.84 (m, 2H), 6.60-6.57 (m, 2H), 4.68 (qrt, J = 7.2 Hz, 2H), 3.72 (s, 3H), 1.57 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.6, 154.7, 150.2, 144.2, 141.9, 140.0, 138.4, 133.1, 131.0, 130.5, 129.4, 128.2, 127.5, 127.3, 127.0, 126.9, 126.2, 122.7, 120.8, 119.3, 113.0, 112.8, 108.9, 55.0, 36.1, 14.2; IR (neat): ν_{max} 2965, 1606, 1554, 1489, 1469, 1446, 1290, 1240, 1207, 1035, 799, 769 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N_2O$ (M^+ + H): *m/z* 455.2123. Found: 455.2124.

*9-Ethyl-2,3-diphenyl-4-(thiophen-2-yl)-9H-pyrido[2,3-b]indole (**7ap**).* White solid, yield 0.118 g (86%); mp 261-263 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.47-7.43 (m, 2H), 7.38 (dd, J = 5.2, 1.6 Hz, 1H), 7.27-7.21 (m, 4H), 7.12-7.04 (m, 8H), 4.68 (qrt, J = 7.2 Hz, 2H), 1.56 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 154.4, 150.2, 141.6, 140.1, 138.7, 138.4, 137.4, 131.8, 130.4, 128.7, 127.9, 127.4, 127.3, 127.2, 126.7, 126.6, 126.5, 126.2, 122.7, 120.5, 119.5, 114.1, 109.0, 36.2, 14.1; IR (neat): ν_{max} 3053, 2964, 2926, 2858, 1563, 1467, 1438, 1395, 1340, 1267, 1083, 1022, 798, 745, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{29}H_{23}N_2S$ (M^+ + H): *m/z* 431.1582. Found: 431.1583.

*2,3-Bis(4-methoxyphenyl)-9-methyl-4-phenyl-9H-pyrido[2,3-b]indole (**7bc**).* White solid, yield 0.136 g (87%); mp 269-271 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 4H), 7.36-7.31 (m, 3H), 7.23-7.20 (m, 2H), 7.00-6.94 (m, 2H), 6.86-6.82 (m, 2H), 6.78-6.74 (m, 2H), 6.60-6.56 (m, 2H), 4.04 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.8, 157.7, 154.4, 150.8, 145.0, 141.0, 138.4, 134.4, 133.1, 131.7, 131.2, 129.2, 128.1, 127.3, 126.7, 126.1, 122.4, 120.7, 119.4, 113.1, 112.9, 112.7, 108.7, 55.2, 55.0, 27.7; IR (neat): ν_{max} 2925, 2849, 1609, 1568, 1514, 1467, 1295, 1247, 1177, 1032, 837, 747, 705 cm^{-1}; HRMS (ESI): Calcd. for $C_{32}H_{27}N_2O_2$ (M^+ + H): *m/z* 471.2073. Found: 471.2079.

*2,3-Bis(4-chlorophenyl)-9-methyl-4-phenyl-9H-pyrido[2,3-b]indole (**7be**).* White solid, yield 0.118 g (74%); mp 261-263 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.39-7.38 (m, 5H), 7.25-7.22 (m, 4H), 7.05-7.02 (m, 4H), 6.89-6.87 (m, 2H), 4.07 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.1, 149.9, 143.8, 140.1, 138.8, 136.6, 136.0, 132.4, 132.3, 131.1, 130.7, 128.2, 127.3, 126.9, 126.7_2, 126.6_8, 125.6, 124.9, 121.5, 119.3, 118.7, 112.3, 107.8, 26.7; IR (neat): ν_{max} 2923, 2855, 1568, 1489, 1395, 1340, 1302, 1262, 1210, 1156, 1088, 1016, 838, 744 cm^{-1}; HRMS (ESI): Calcd. for $C_{30}H_{21}Cl_2N_2$ (M^+ + H): *m/z* 479.1082. Found: 479.1082.

(vii) Synthesis of 6,7-Dimethoxy-2,2,4-triphenyl-8-tosyl-1,2-dihydroquinoline (9). An oven dried 25 mL round-bottomed flask was charged with benzenesulfonamide **8** (0.100 g, 0.32 mmol), propargyl alcohol **2a** (0.111 g, 0.39 mmol) and PTSA (1.5 equiv) in dichloromethane (10 mL) at 25 ^{o}C (or in toluene at reflux). The mixture was stirred in open air for 12 h and monitored by TLC for the disappearance of starting materials. Then dichloromethane (10 mL) and water (15 mL) were added. The organic phase was separated and the aqueous layer washed with dichloromethane (10 mL). The combined organic part was

dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by column chromatography (ethyl acetate: hexane 2:8) afforded the desired product **9**. White solid, yield 0.160 g (86%); mp 206-208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.44-7.38 (m, 8H), 7.32-7.28 (m, 2H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.80 (s, 1H), 6.00 (d, *J* = 1.5 Hz, 1H), 3.75 (s, 3H), 3.53 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.8, 147.5, 143.3, 142.7, 141.0, 139.1, 138.9, 135.7, 129.0, 128.9, 128.5, 128.4, 128.3, 127.9, 127.2, 127.0, 126.9, 119.1, 118.0, 116.4, 63.5, 61.1, 57.0, 21.5; IR (neat): ν_{max} 3337, 2934, 1463, 1140, 1423, 1274, 1131, 1046, 958, 799, 703, 622 cm^{-1}; HRMS (ESI): Calcd. for $C_{36}H_{32}NO_4S$ (M^+ + H): *m/z* 574.2052. Found: 574.2052.

(viii) Synthesis of *N*-(1-Ethyl-2-(1,3,3-triphenylpropa-1,2-dien-1-yl)-1H-indol-3-yl)-4-methylbenzenesulfonamide (10). An oven dried 25 mL round-bottomed flask was charged with 3-sulfonamidoindole **4a** (0.100 g, 31 mmol), propargyl alcohol **2a** (0.108 g, 0.38 mmol) and PTSA (1.0 equiv) in dichloromethane (10 mL). The mixture was stirred at 25 ^{o}C in open air for 1 h and monitored by TLC until the starting materials disappeared. After the appropriate period, the solvent was removed under reduced pressure. Further, the reaction mixture was treated with dichloromethane (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with dichloromethane (10 mL). The combined organic portion was dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to afford the crude product. Purification by column chromatography (ethyl acetate: hexane; 1:9) afforded the desired product **10.** White solid, yield 0.142 g (77%); mp 158-160 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.48-7.39 (m, 10H), 7.33-7.17 (m, 8H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.99 (s, 1H), 3.92 (qrt, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 208.1, 142.9,

136.4, 135.1, 135.0, 134.3, 129.1, 129.0$_3$, 129.0$_1$, 128.6, 128.4, 127.5, 127.4, 126.4, 125.6, 122.7, 120.4, 120.2, 113.1, 111.0, 109.6, 101.4, 39.5, 21.5, 15.0; IR (neat): ν_{max} 3335, 3057, 2975, 2925, 1598, 1490, 1454, 1347, 1229, 1163, 1091, 756, 698 cm^{-1}; HRMS (ESI): Calcd. for $C_{38}H_{33}N_2O_2S$ (M^+ + H): *m/z* 581.2263. Found: 581.2267.

(ix) X-ray data of 3aa, **3bj, 3br**, **5ab**, **6ap**, **7bc and 9.**

Compound 3aa: $C_{30}H_{22}N_2$, *M* = 410.50, Triclinic, Space group *P-1*, *a* = 9.625(2), *b* = 11.220(3), *c* = 12.370(3)Å, *V* = 1103.2(5)Å^3, α = 105.068(10) ^{o}, β = 103.743(9) ^{o}, γ = 112.523(9) ^{o}, *Z* = 2, μ = 0.072 mm^{-1}, data/restraints/parameters: 3872/0/290, R indices (I> 2\s(I)): R1 = 0.0413, *w*R2 (all data) = 0.1067. CCDC No: 1859542.

Compound 3bj: $C_{35}H_{29}Cl_2N_2$, *M* = 548.50, Triclinic, Space group *P-1*, *a* = 10.0035(6), *b* = 13.0323(9), *c* = 13.1608(8)Å, *V* = 1481.36(16)Å^3, α = 108.315(2)^o, β = 107.297(2)^o, γ = 100.516(2)^o, *Z* = 2, μ = 0.245 mm^{-1}, data/restraints/parameters: 5192/0/362, R indices (2sigma(I)): R1 = 0.0853, *w*R2 (all data) = 0.2383. CCDC No: 1859543.

Compound 3br: $C_{31}H_{22}N_2$, *M* = 422.51, Monoclinic, Space group *P21/c*, *a* = 21.1443(9), *b* = 14.1022(6), *c* = 15.9946(7)Å, *V* = 4473.9(3) Å^3, β = 110.2700(10)^o, *Z* = 8, μ = 0.073 mm^{-1}, data/restraints/parameters: 7975/0/595, R indices (I> 2\s(I)): R1 = 0.0553, *w*R2 (all data) = 0.1982. CCDC No: 1859544.

Compound 5ab: $C_{40}H_{36}N_2O_2S$, *M* = 609.78, Monoclinic, Space group *P21/c*, *a* = 15.9963(8), *b* = 15.7038(10), *c* = 13.4664(6) Å, *V* = 3356.2(3) Å^3, β = 97.196(5)^o, *Z* = 4, μ = 1.137 mm^{-1}, data/restraints/parameters: 6456/0/410, R indices (I> 2\s(I)): R1 = 0.0567, *w*R2 (all data) = 0.1606. CCDC No: 1859545.

Compound 6ap: $C_{30}H_{24}N_2O_2S_2$, *M* = 508.63, Triclinic, Space group *P-1*, *a* = 8.7173(4), *b* = 11.0589(5), *c* = 13.3630(6) Å, *V* = 1255.12(10) Å^3, α = 84.1090(10)^o, β = 86.375(2)^o, γ = 78.6410(10)^o, *Z* = 2, μ = 0.243 mm^{-1}, data/restraints/parameters: 5776/0/325, R indices (I> 2\s(I)): R1 = 0.0630, *w*R2 (all data) = 0.1898. CCDC No: 1859547.

Compound 7bc: $C_{32}H_{26}N_2O_2$, M = 470.55, Triclinic, Space group *P-1*, a = 10.7608(15), b = 11.6326(16), c = 11.9031(16) Å, V = 1243.8(3) Å^3, α = 83.679(11)^o, β = 67.103(13)^o, γ = 65.229(14)^o, Z = 2, μ = 0.619 mm^{-1}, data/restraints/parameters: 4744/0/328, R indices (I> 2\s(I)): R1 = 0.0673, *w*R2 (all data) = 0.1796. CCDC No: 1859546.

Compound 9: $C_{36}H_{31}NO_4S$, M = 573.68, Monoclinic, Space group *P 21/n*, a = 14.5928(11), b = 8.4320(5), c = 25.9668(19) Å, V = 3118.9(4) Å^3, β = 102.539(2)^o, Z = 4, μ = 0.143 mm^{-1}, data/restraints/parameters: 5475/0/386, R indices (2sigma(I)): R1 = 0.0712, *w*R2 (all data) = 0.1456. Although the structure could be refined well, the reflections were rather weak. CCDC No: 1876877.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data (cif files), ORTEPs of compounds **3aa, 3bj, 3br, 5ab, 6ap, 7bc** and **9** (Figures S1-S7; CCDC 1859542-1859547 and 1876877), and ^{1}H/ ^{13}C{H} NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author

*E-mail: kckssc@uohyd.ac.in; kckssc@yahoo.com

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