Organic & Biomolecular Chemistry

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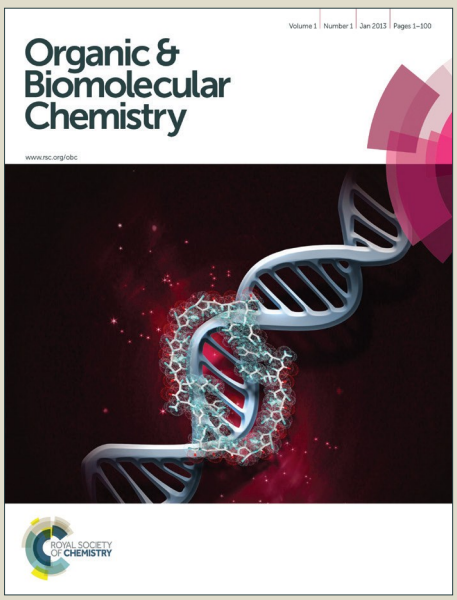

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ARTICLE

Synthesis of Polysubstituted 1,2-Dihydroquinolines and Indoles *via* Cascade Reactions of Arylamines and Propargylic Alcohols Catalyzed by $FeCl_3·6H_2O$

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Min Shao,[a] Yunjun Wu,[a] Zhijun Feng,[a] Xiaoxia Gu[a] and Shaoyin Wang*[a,b]

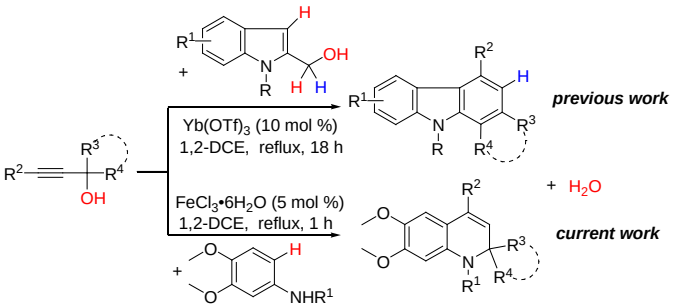
An efficient, environmentally friendly and high-yielding route from inexpensive starting materials to 1,2-dihydroquinolines has been developed. This procedure proceeded *via* a cascade Friedel-Crafts-type reaction and 6-*endo-trig* hydroamination under the catalysis of $FeCl_3·6H_2O$, involving the formation of two new σ (C–C and C–N) bonds in a single operation for the construction of 1,2-dihydroquinoline skeleton in good to excellent yields.

Introduction

1,2-Dihydroquinolines represent an important structural motif embedded both in many naturally occurring alkaloids.[1] and synthetic drug candidates with important pharmacological properties, such as antibacterial,[2] anti-inflammatory,[3] antimalarial,[4] anti-allergic,[5] and progesterone receptor agonists.[6] In addition they can be easily transformed into corresponding 1,2,3,4-tetrahydroquinoline and quinolone derivatives.[7]

Consequently, numerous synthetic strategies have been developed for their construction. For example, Brønsted and Lewis acid-catalyzed tandem reactions of anilines with α-ketoesters,[8] Michael-aldol reactions,[9] transition metal-catalyzed tandem reactions of anilines with propargylic alcohols,[10] reactions of aromatic amines with alkynes,[11] olefin metathesis reactions,[12] and intramolecular allylic amination[13] and many others have been reported.[14] Despite these advances, these methods more or less have suffered from drawbacks such as high reaction temperature, long reaction times and unsatisfactory yields. Therefore, the development of an efficient, operationally simple, eco-friendly and practical method for the synthesis of 1,2-dihydroquinolines under mild reaction conditions is in high demand.

Iron salt catalysts have received much attention because of their low costs, abundance, and environmentally benign properties.[15] In particular, $FeCl_3$ has been widely applied as a Lewis acid catalyst for the catalytic synthesis of various heterocyclic compounds.[15b, 16] Recently, our group has been interested in the development of cascade processes using simple propargylic alcohols as a versatile three-carbon synthon for the construction of useful cyclic structures, such as carbazoles and naphthalenes.[17] As part of our continued efforts devoted to the exploitation of propargylic alcohols in organic synthesis, herein, we report a novel $FeCl_3·6H_2O$-catalyzed domino Friedel-Crafts reaction-intramolecular hydroamination process of them with aryl amines, leading to 1,2-dihydroquinoline and indole derivatives in good to excellent yields under mild conditions (Scheme 1).



Scheme 1. Lewis acid-catalyzed dehydrative [3+3]-annulation way to useful heterocycles

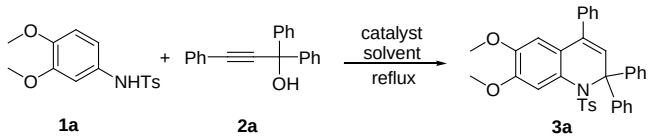
Results and discussion

The reaction of arylamine **1a** and propargylic alcohol **2a** was selected as a model reaction for optimization of reaction conditions (Table 1). Using 1,2-DCE (1,2-dichloroethane) as solvent, different metal triflates and metal halides were screened and $FeCl_3·6H_2O$ was found to be the most efficient catalyst for this reaction (Table 1, entries 2-9). No reaction occurred in the absence of the catalyst (Table 1, entry 1). Performing the reaction at a lowered temperature (25°C) or in

[a] Department of Chemistry, Wannan Medical College, Wuhu, Anhui 241002, China. E-mail: wsychem@163.com
[b] Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China.

†Electronic Supplementary Information (ESI) available: Copies of ^1H and ^{13}C NMR spectra for newly synthesized compounds, CIF for compounds **3g**, **5**, **6**, **7**. See DOI: 10.1039/ x0xx00000x

Table 1. Screening for the reaction conditions[a]



1a 2a 3a

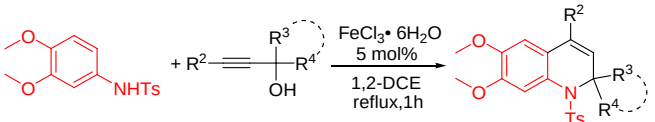
entry	catalyst (mol %)	solvent	time (h)	yield (%)[b]
1	No catalyst	1,2-DCE	6	0
2	$Sc(OTf)_3$ (10%)	1,2-DCE	1	71
3	$Y(OTf)_3$ (10%)	1,2-DCE	1	68
4	$Yb(OTf)_3$ (10%)	1,2-DCE	1	50
5	$Cu(OTf)_2$ (10%)	1,2-DCE	0.5	60
6	$CuBr_2$(10%)	1,2-DCE	1	54
7	CuCl (10%)	1,2-DCE	1	63
8	$FeCl_3$ (10%)	1,2-DCE	0.5	81
9[c]	$FeCl_3·6H_2O$ (10%)	1,2-DCE	6	40
10	$FeCl_3·6H_2O$ (10%)	1,2-DCE	1	82
11[d]	$FeCl_3·6H_2O$ (10%)	Toluene	1	55
12[d]	$FeCl_3·6H_2O$ (10%)	DMF	1	0
13[d]	$FeCl_3·6H_2O$ (10%)	DMSO	1	44
14	$FeCl_3·6H_2O$ (10%)	THF	1	50
15	$FeCl_3·6H_2O$ (5%)	1,2-DCE	1	84
16	$FeCl_3·6H_2O$ (2%)	1,2-DCE	1	70

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (5 mL). [b]Yield of the isolated pure product. [c]Reaction was run at 25°C. [d]Reaction was run at 90 °C.

other solvents such toluene, DMF, DMSO or THF all gave inferior results (Table 1, entries 10-14). Further screen of catalyst loading amount revealed that 5 mol % was optimal for the reaction, while lower (2 mol %) led to reduced yields (Table 1, entries 15-16). It is worth mentioning that the reaction is tolerant of moisture and air, which could be performed in unpurified commercial solvents under open air.

With the optimized reaction conditions in hand, the scope of the reaction was then examined with a series of arylamines **1** and propargylic alcohols **2** (Table 2). First, a series of substituted **2** were reacted with **1a** to examine the substituent effect (Table 2, entries 1-18). In general, propargylic alcohols **2** bearing electron-donating substituents on the aryl groups R^2 provided higher yields than those with electron-withdrawing ones (Table 2, entries 1-5). And propargylic alcohols **2** bearing electron-donating substituents on either of the two aryl groups (R^3, R^4) also provided higher yields than those with electron-withdrawing ones (Table 2, entries 6-9). Such a phenomenon suggests the intermediacy of carbocation species in this reaction. When R^3 is methyl group or H, the target products can also be produced smoothly (Table 2, entries 10-15). Moreover, when 9-fluorenyl-substituted substrates **2p-2r** were subjected to the reaction conditions, spiro-compounds **3p-3r** could be formed in 43-59% yields (Table 2, entry 16-18). Differently substituted arylamines **1** were then examined in the reaction and the target products were obtained in good yields (Scheme 2). The structures of the product **3g** (Figure 1) was additionally confirmed by X-ray crystallographic analysis (See Supporting Information for details).

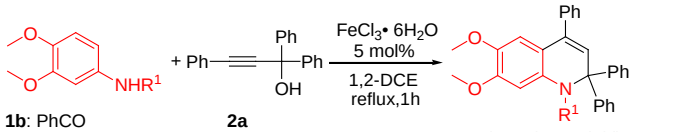
Table 2. Scope study with different arylamines **1a** and propargylic alcohols **2**[a]



1a 2 3

Entry	$R^2/R^3/R^4$	Product	Yield[b]
1	$C_6H_5/C_6H_5/C_6H_5$ (**2a**)	**3a**	84
2	4-$MeC_6H_4/C_6H_5/C_6H_5$ (**2b**)	**3b**	87
3	2-$ClC_6H_4/C_6H_5/C_6H_5$ (**2c**)	**3c**	59
4	3-$ClC_6H_4/C_6H_5/C_6H_5$ (**2d**)	**3d**	68
5	4-$ClC_6H_4/C_6H_5/C_6H_5$ (**2e**)	**3e**	75
6	C_6H_5/4-MeC_6H_4/4-MeC_6H_4 (**2f**)	**3f**	86
7	C_6H_5/4-ClC_6H_4/4-ClC_6H_4 (**2g**)	**3g** (X-ray)	43
8	C_6H_5/C_6H_5/4-$MeOC_6H_4$ (**2h**)	**3h**	86
9	C_6H_5/C_6H_5/4-ClC_6H_4 (**2i**)	**3i**	80
10	C_6H_5/Me/C_6H_5 (**2j**)	**3j**	72
11	C_6H_5/Me/4-$MeOC_6H_4$ (**2k**)	**3k**	79
12	C_6H_5/Me/4-BrC_6H_4 (**2l**)	**3l**	69
13	C_6H_5/H/4-$MeOC_6H_4$ (**2m**)	**3m**	55
14	C_6H_5/H/4-ClC_6H_4 (**2n**)	**3n**	53
15	C_6H_5/H/2-furyl (**2o**)	**3o**	61
16	C_6H_5/9-fluorenyl (**2p**)	**3p**	55
17	4-MeC_6H_4/9-fluorenyl (**2q**)	**3q**	43
18	4-ClC_6H_4/9-fluorenyl (**2r**)	**3r**	59

[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), $FeCl_3·6H_2O$ (0.025 mmol), 1,2-DCE (5 mL), 1 h. [b]Yield of the isolated product.



1b: PhCO
1c: 4-MeC_6H_4CO

2a

3s: PhCO (87% yield)
3t: 4-MeC_6H_4CO (88% yield)

Scheme 2. Scope Study with Different Arylamines **1** and Propargylic Alcohol **2a**

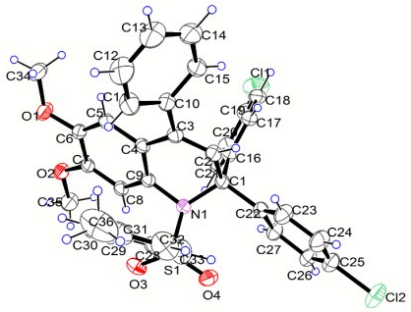
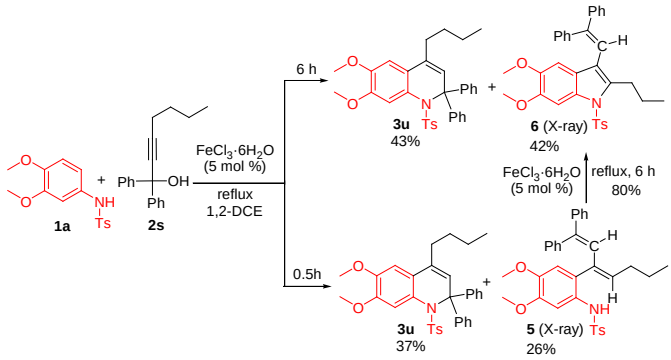
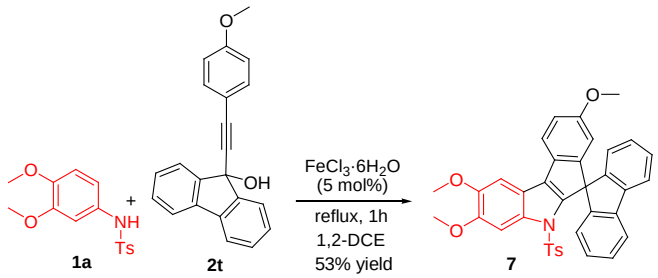


Figure 1. Crystal structure of compound **3g**

When propargylic alcohol **2s** bearing an alkyl group (R^2) was used in the reaction, in addition to the 1,2-dihydroquinoline product **3u**, a indole product **6** was also isolated in a comparable yield (Scheme 3). Control experiment on the reaction terminated at 0.5 hour suggested diene compound **5** as the intermediate to the indole product, which could be transformed into **6** in a yield of 80% under the typical reaction conditions. Interestingly, when R^2 is an aryl group with a strongly electron-donating substituent such as 4-MeO in



Scheme 3. Reaction of arylamine **1a** with propargylic alcohol **2s**



Equation 1. The synthesis of indole product

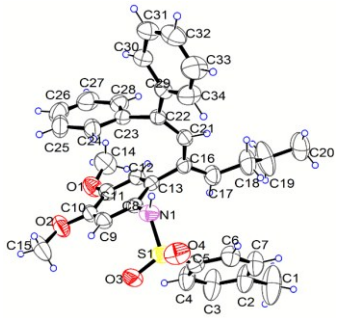
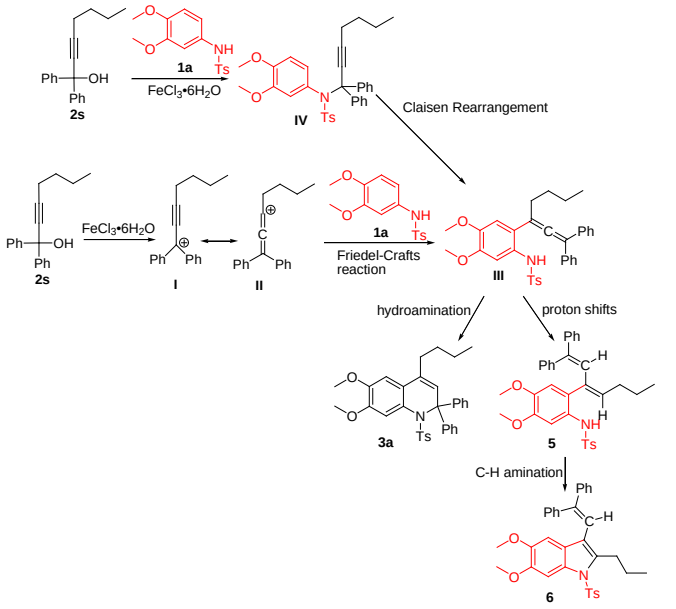


Figure 2. Crystal structure of compound **5**

propargylic alcohol **2t**, the corresponding indole product **7** became the sole product isolated (Eq 1). The structures of the intermediate **5** (Figure 2) products **6** and **7** were additionally confirmed by X-ray crystallographic analysis (See Supporting Information for details).

Based on the above experimental results, a plausible mechanism for the reaction was proposed using the formation of 1,2-dihydroquinoline **3u** and indole **6** as example (Scheme 4). First, propargylic alcohol **2s** is converted to the allenic carbocation **II** *via* Meyer-Schuster rearrangement,[18] which would then undergo Friedel-Crafts-type reaction with **1a** to form the allene intermediate **III**. Then allene intermediate **III** is converted to the 1,2-dihydroquinoline **3a** by 6-*endo*-*trig* hydroamination. Alternately, intermediate **III** can also be transformed into 1,3-diene **5** by tandem proton shifts, and the latter may undergo an intramolecular oxidative C(sp^2)-H amination to provide the indole product **6**.[19] Another pathway to the allene intermediate **III** involves the formation of intermediate propargylic amine **IV**, which can also be converted to the allene intermediate **III** by Claisen rearrangement.[10]



Scheme 4. A Possible mechanism for the synthesis of 1,2-dihydroquinoline **3a** and indole **6**

Conclusions

In summary, we have developed an efficient approach to 1,2-dihydroquinolines *via* $FeCl_3·6H_2O$ catalyzed cascade reactions of propargylic alcohols and arylamines. Through the adjustment of the substituent of the propargylic alcohols, corresponding indole products were also obtainable by this method. Efforts toward a deeper understanding of the reaction mechanism and the application of this methodology to synthesize other useful heterocycles from propargylic alcohols are ongoing in our laboratories.

Acknowledgements

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Experimental

General methods

Flash column chromatography was performed using silica gel (200–400 mesh). For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light. ^{1}H NMR spectra were recorded on 300 MHz or 500 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported relative to internal standard TMS (0). The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants are reported in Hertz (Hz). ^{13}C NMR were recorded on 75 or 125 MHz and referenced to the internal solvent signals (central peak is 77.00 in $CDCl_3$). Data are reported as

follows: chemical shift, multiplicity, coupling constants and integration. Melting points were uncorrected. IR spectra were reported in frequency of absorption (cm^{-1}). High resolution mass spectral (HRMS) data were obtained with an ionization mode of ESI and a TOF analyzer. The propargylic alcohols **2** were prepared from phenylacetylene and ketone or aldehydes according to the published methods.[20] All commercially available reagents and solvents were used without further purification unless noted otherwise.

General Procedure for the Synthesis of 3

A solution of arylamines **1** (0.5 mmol), propargylic alcohols **2** (0.5 mmol) and $FeCl_3·6H_2O$ (0.025 mmol) in 1,2-DCE (5 mL) was stirred under air at reflux for 1 h. After being cooled down to room temperature, the solvent was evaporated and the crude product was purified by silica gel column chromatography with hexane-EtOAc (3:1, v/v).

Procedure for the Synthesis of 7

A solution of anilines **1a** (0.5 mmol), propargyl alcohols **2t** (0.5 mmol) and $FeCl_3·6H_2O$ (0.025 mmol) in 1,2-DCE (5 mL) was stirred under air at reflux for 1 h. After being cooled down to room temperature, the solvent was evaporated and the crude product was purified by silica gel column chromatography with hexane-EtOAc (3:1, v/v).

Characterization Data of Products

6,7-Dimethoxy-2,2,4-triphenyl-1-tosyl-1,2-dihydroquinoline (3a). White solid (241 mg, 84%); M.p. 207-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (d, *J* = 7.0 Hz, 4H), 7.40 – 7.29 (m, 3H), 7.28 – 7.10 (m, 8H), 7.08 – 6.94 (m, 4H), 6.84 (s, 1H), 6.25 (s, 1H), 4.04 (s, 3H), 3.56 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.30, 147.17, 142.98, 138.76, 138.14, 137.30, 130.90, 128.80, 128.65, 128.06, 128.00, 127.37, 127.04, 124.09, 113.75, 107.87, 68.63, 56.36, 55.61, 21.36; IR (KBr) *v* 3006, 2933, 1600, 1506, 1401, 1104, 703 , 569 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{32}NO_4S+H]^+$): 574.2047; found: 574.2047.

6,7-Dimethoxy-2,2-diphenyl-4-p-tolyl-1-tosyl-1,2-dihydroquinoline (3b). White solid (256 mg, 87%); M.p. 209-210 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (d, *J* = 6.8 Hz, 4H), 7.29 – 7.08 (m, 10H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 6.26 (s, 1H), 4.04 (s, 3H), 3.58 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.19, 147.12, 142.93, 138.64, 137.71, 137.30, 135.21, 130.84, 128.76, 128.61, 128.53, 128.37, 127.98, 127.35, 127.00, 124.22, 113.71, 107.88, 68.63, 56.34, 55.61, 21.38, 21.18; IR (KBr) *v* 3024, 2966, 1618, 1513, 1415, 1169, 707 , 573 cm^{-1}; HRMS: m/z calcd for ($[C_{37}H_{34}NO_4S+H]^+$): 588.2203; found: 588.2205.

4-(2-Chlorophenyl)-6,7-dimethoxy-2,2-diphenyl-1-tosyl-1,2-dihydroquinoline (3c). White solid (179 mg, 59%); M.p. 207-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.53 – 7.33 (m, 5H), 7.33 – 7.15 (m, 8H), 7.15 – 7.03 (m, 5H), 6.82 (s, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.04 (s, 1H), 4.02 (s, 3H), 3.57 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.28, 147.20, 142.88, 138.67, 136.79, 136.24, 133.85, 132.99, 131.54, 130.00, 129.89, 129.54, 129.28, 128.90, 127.86, 127.45, 127.08, 126.52, 123.06, 113.63, 107.61, 69.22, 56.37, 55.72, 21.46; IR (KBr) *v* 3132, 2828, 1509, 1404, 1350, 1169, 707 , 573 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{31}ClNO_4S+H]^+$): 608.1657; found: 608.1657.

4-(3-Chlorophenyl)-6,7-dimethoxy-2,2-diphenyl-1-tosyl-1,2-dihydroquinoline (3d). White solid (207 mg, 68%); M.p. 208-209 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.51 (d, *J* = 7.0 Hz, 4H), 7.37 – 7.10 (m, 10H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.98 – 6.90 (m, 1H), 6.90 – 6.83 (m, 2H), 6.19 (s, 1H), 4.05 (s, 3H), 3.59 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.19, 147.12, 142.93, 138.64, 137.71, 137.30, 135.21, 130.84, 128.76, 128.61, 128.53, 128.37, 127.98, 127.35, 127.00, 124.22, 113.71, 107.88, 68.63, 56.34, 55.61, 21.38, 21.18; IR (KBr) *v* 3006, 2930, 1509, 1404, 1350, 1162 , 707 , 577 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{31}ClNO_4S+H]^+$): 608.1657; found: 608.1657.

4-(4-Chlorophenyl)-6,7-dimethoxy-2,2-diphenyl-1-tosyl-1,2-dihydroquinoline (3e). White solid (228 mg, 75%); M.p. 211-212 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (d, *J* = 7.0 Hz, 4H), 7.34 – 7.26 (m, 2H), 7.25 – 7.08 (m, 8H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 6.19 (s, 1H), 4.04 (s, 3H), 3.58 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.28, 147.20, 142.88, 138.67, 136.79, 136.24, 133.85, 132.99, 131.54, 130.00, 129.89, 129.28, 128.90, 127.86, 127.45, 127.08, 126.52, 123.06, 113.63, 107.61, 69.22, 56.37, 55.72, 21.46; IR (KBr) *v* 2991, 2930, 1513, 1401, 1166, 703 , 573 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{31}ClNO_4S+H]^+$): 608.1657; found: 608.1657.

6,7-Dimethoxy-4-phenyl-2,2-dip-tolyl-1-tosyl-1,2-dihydroquinoline (3f). White solid (259mg, 86%); M.p. 183-184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 – 7.28 (m, 7H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.06 – 6.93 (m, 8H), 6.80 (s, 1H), 6.25 (s, 1H), 4.04 (s, 3H), 3.58 (s, 3H), 2.30 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.23, 147.14, 142.87, 138.54, 138.31, 137.49, 136.59, 130.99, 129.33, 128.69, 128.59, 128.12, 128.06, 128.02, 127.87, 124.18, 113.88, 107.91, 68.42, 56.37, 55.64, 21.37, 20.98; IR (KBr) *v* 3006, 2926, 1509, 1401, 1169, 703 , 566 cm^{-1}; HRMS: m/z calcd for ($[C_{38}H_{36}NO_4S+H]^+$): 602.2360; found: 602.2361.

2,2-Bis(4-chlorophenyl)-6,7-dimethoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (3g). White solid (138 mg, 43%); M.p. 218-219 °C; 1H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 4H), 7.37-7.28 (m, 3H), 7.21 – 7.08 (m, 6H), 7.06 – 6.91 (m, 4H), 6.70 (s, 1H), 6.26 (s, 1H), 4.05 (s, 3H), 3.60 (s, 3H), 2.31 (s, 3H), 1.58 (s, 1H), 0.00 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.66, 147.44, 143.36, 139.55, 137.78, 136.97, 133.14, 130.59, 128.80, 128.62, 128.21, 128.17, 127.97, 127.73, 127.35, 123.94, 113.47, 108.11, 67.77, 56.42, 55.71, 21.40; IR (KBr) *v* 3006, 2832, 1607, 1404, 1162, 703 , 573 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{30}Cl_2NO_4S+H]^+$): 642.1267; found: 642.1266.

6,7-Dimethoxy-2-(4-methoxyphenyl)-2,4-diphenyl-1-tosyl-1,2-dihydroquinoline (3h). White solid (260 mg, 86%); M.p. 230-231 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.49 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.29 (m, 5H), 7.23 – 7.10 (m, 5H), 7.07 – 6.98 (m, 4H), 6.78 (s, 1H), 6.71 (d, *J* = 9.1 Hz, 2H), 6.27 (s, 1H), 4.04 (s, 3H), 3.73 (s, 3H), 3.58 (s, 3H), 2.29 (s, 3H);^{13}C NMR (75 MHz, DMSO) δ 158.43, 148.21, 147.10, 142.90, 138.65, 138.19, 137.52, 130.87, 129.35, 128.63, 128.08, 127.89, 127.34, 126.84, 124.01, 113.76, 112.63, 107.82, 68.32, 56.35, 55.61, 55.00, 21.37; IR (KBr) *v* 3016, 2933, 2832, 1607, 1513, 1404, 1162, 707 , 566 cm^{-1}; HRMS: m/z calcd for ($[C_{37}H_{34}NO_5S+H]^+$): 604.2152; found: 604.2152.

2-(4-Chlorophenyl)-6,7-dimethoxy-2,4-diphenyl-1-tosyl-1,2-dihydroquinoline (3i). Yellow solid (243 mg, 80%); M.p. 148-149 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.53 – 7.38 (m, 4H), 7.38 – 7.30 (m, 3H), 7.25 – 7.10 (m, 7H), 7.07 – 6.93 (m, 4H), 6.77 (s, 1H), 6.26 (s, 1H), 4.04 (s, 3H), 3.58 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.45, 147.29, 143.18, 139.16, 137.94, 137.10, 132.89, 130.72, 128.72, 128.64, 128.11, 128.08, 128.03, 127.98, 127.54, 127.24, 124.01, 113.58, 107.95, 68.17, 56.39, 55.66, 21.39 ; IR (KBr) *v* 3009, 2933, 2832, 1737, 1607, 1513, 11401, 1166, 703 , 566 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{31}ClNO_4S+H]^+$): 608.1657; found: 608.1659.

6,7-Dimethoxy-2-methyl-2,4-diphenyl-1-tosyl-1,2-dihydroquinoline (3j). Yellow solid (184 mg, 72%); M.p. 100-101 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.40 – 7.27 (m, 5H), 7.23 (s, 1H), 7.19 – 6.97 (m, 7H), 6.30 (s, 1H), 5.73 (s, 1H), 3.90 (s, 3H), 3.57 (s, 3H), 2.24 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.98, 147.00, 142.98, 138.65, 137.62, 137.40, 130.74, 129.73, 129.04, 128.49, 127.96, 127.90, 127.82, 127.52, 126.97, 125.34, 124.28, 113.37, 107.47, 63.73, 56.12, 55.62, 31.11, 21.30; IR (KBr) *v* 2955, 2832, 1607, 1509, 1404, 1166, 700 , 577 cm^{-1}; HRMS: m/z calcd for ($[C_{31}H_{30}NO_4S+H]^+$): 512.1890; found: 512.1890.

6,7-Dimethoxy-2-(4-methoxyphenyl)-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (3k). White solid (214 mg, 79%); M.p. 233-234 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.40 – 7.27 (m, 5H), 7.24 (s, 1H), 7.19 – 6.97 (m, 7H), 6.30 (s, 1H), 5.73 (s, 1H), 3.90 (s, 3H), 3.57 (s, 3H), 2.24 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 158.30, 147.96, 146.96, 142.93, 138.74, 138.56, 137.65, 137.43, 130.74, 129.86, 129.02, 128.46, 127.95, 127.87, 127.51, 126.49, 124.30, 113.39, 113.11, 107.44, 63.39, 56.10, 55.63, 55.00, 31.12, 21.28;IR (KBr) *v* 3006, 2933, 2836, 1607, 1509, 1408, 1177, 707 , 577 cm^{-1}; HRMS: m/z calcd for ($[C_{32}H_{32}NO_5S+H]^+$): 542.1996; found: 542.1996.

2-(4-Bromophenyl)-6,7-dimethoxy-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (3l). White solid (204 mg, 69%); M.p. 227-228 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 3H), 7.34 – 7.21 (m, 7H), 7.06 – 6.96 (m, 4H), 6.30 (s, 1H), 5.67 (s, 1H), 3.92 (s, 3H), 3.60 (s, 3H), 2.23 (s, 3H), 2.05 (s, 3H) ;^{13}C NMR (75 MHz, DMSO) δ 148.21, 147.16, 146.31, 143.15, 139.07, 137.39, 137.16, 130.97, 130.59, 129.10, 128.92, 128.46, 128.05, 128.01, 127.52, 127.18, 124.14, 120.78, 113.23, 107.58, 63.40, 56.17, 55.68, 30.96, 21.31; IR (KBr) *v* 3024, 2948, 2828, 1600, 1509, 1404, 1162, 707 , 577 cm^{-1}; HRMS: m/z calcd for ($[C_{31}H_{29}BrNO_4S+H]^+$): 590.0995; found: 590.0995.

6,7-Bimethoxy-2-(4-methoxyphenyl)-4-phenyl-1-tosyl-1,2-dihydroquinoline (3m). White solid (145 mg, 55%); M.p. 213-214 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.34 – 7.19 (m, 7H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.78 (m, 2H), 6.35 (s, 1H), 6.13 (d, *J* = 6.3 Hz, 1H), 5.75 (d, *J* = 6.3 Hz, 1H), 3.92 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H), 1.60 (s, 1H); ^{13}C NMR (75 MHz, DMSO) δ 159.25, 148.55, 147.10, 143.33, 138.22, 138.00, 135.51, 130.05, 128.98, 128.93, 128.43, 128.03, 127.74, 127.51, 126.57, 123.24, 122.08, 113.76, 111.86, 108.10, 56.24, 56.10, 55.78, 55.16, 21.34; IR (KBr) *v* 3414, 3136, 2832, 1618, 1513, 1401, 1173, 696 , 573 cm^{-1}; HRMS: m/z calcd for ($[C_{31}H_{30}NO_5S+H]^+$): 528.1839; found: 528.1839.

2-(4-Chlorophenyl)-6,7-dimethoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (3n). White solid (141 mg, 53%); M.p. 262-263 ^{o}C;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 3H), 7.33 – 7.20 (m, 7H), 7.10 – 7.01 (m, 2H), 6.88 – 6.79 (m, 2H), 6.35 (s, 1H), 6.08 (d, *J* = 6.4 Hz, 1H), 5.71 (d, *J* = 6.3 Hz, 1H), 3.93 (s, 3H), 3.62 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.71, 147.21, 143.51, 138.61, 137.92, 136.90, 135.26, 133.65, 129.02, 128.94, 128.52, 128.36, 128.05, 127.88, 127.48, 126.42, 122.99, 121.05, 111.61, 108.20, 56.10, 55.87, 55.76, 21.32; IR (KBr) *v* 2955, 2828, 1607, 1513, 1401, 1166, 710 , 580 cm^{-1}; HRMS: m/z calcd for ($[C_{30}H_{27}ClNO_4S+H]^+$): 532.1344; found: 532.1345.

2-(Furan-2-yl)-6,7-dimethoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (3o). White solid (149 mg, 61%); M.p. 242-243 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.34 – 7.19 (m, 7H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.78 (m, 2H), 6.35 (s, 1H), 6.13 (d, *J* = 6.3 Hz, 1H), 5.75 (d, *J* = 6.3 Hz, 1H), 3.92 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H), 2.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.61, 147.14, 143.41, 138.34, 138.23, 138.19, 135.48, 129.02, 128.45, 128.39, 128.05, 127.87, 127.78, 127.59, 127.55, 126.67, 123.22, 121.82, 111.80, 108.18, 56.59, 56.14, 55.79, 21.36; IR (KBr) *v* 2936, 1587, 1513, 1401, 1166, 710 , 588 cm^{-1}; HRMS: m/z calcd for ($[C_{28}H_{26}NO_5S+H]^+$): 488.1526; found: 488.1526.

6',7'-Dimethoxy-4'-phenyl-1'-tosyl-1'*H*-spiro[fluorene-9,2'-quinoline] (3p). White solid (157 mg, 55%); M.p. 223-225 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.74 – 7.65 (m, 4H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.28 (m, 10H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.87 (s, 1H), 5.43 – 5.37 (m, 1H), 3.81 (s, 3H), 3.58 (s, 3H), 2.36 (s, 3H), 1.57 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.01, 148.42, 143.43, 142.58, 140.78, 139.84, 138.86, 138.11, 136.57, 129.16, 129.01, 128.84, 128.39, 128.23, 127.74, 126.94, 126.23, 125.19, 120.11, 118.90, 117.74, 116.48, 66.47, 61.27, 57.08, 21.54; IR (KBr) *v* 2951, 1618, 1516, 1404, 1166, 775, 707 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{30}NO_4S+H]^+$): 572.1890; found: 572.1890.

6',7'-Dimethoxy-4'-(p-tolyl)-1'-tosyl-1'*H*-spiro[fluorene-9,2'-quinoline] (3q). White solid (126 mg, 43%); M.p. 209-210 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H), 7.42 – 7.28 (m, 5H), 7.25 – 7.15 (m, 4H), 7.15 – 7.01 (m, 6H), 6.73 (s, 1H), 5.65 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.14, 146.31, 146.07, 142.84, 139.66, 139.11, 138.54, 137.86, 135.09, 130.86, 129.16, 129.12, 128.98, 128.31, 128.05, 127.20, 126.98, 126.32, 122.62, 119.60, 111.67, 108.78, 77.42, 77.00, 76.58, 70.59, 56.16, 56.04, 21.44, 21.20; IR (KBr) *v* 3025, 1600, 1509, 1404, 1162, 746, 663 cm^{-1}; HRMS: m/z calcd for ($[C_{37}H_{32}NO_4S+H]^+$): 586.2047; found: 586.2049.

4'-(4-Chlorophenyl)-6',7'-dimethoxy-1'-tosyl-1'*H*-spiro-[fluorene-9,2'-quinoline] (3r). White solid (179 mg, 59%); M.p. 163-164 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.29 (m, 7H), 7.29 – 7.24 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.12 – 7.06 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 5.65 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.44, 146.37, 145.92, 142.93, 139.65, 138.84, 137.53, 136.54, 133.92, 130.83, 129.80, 129.25, 128.98, 128.89, 128.66, 127.28, 126.98, 126.29, 121.93, 119.65, 111.57, 108.55, 70.56, 56.18, 56.08, 21.41; IR (KBr) *v* 3060, 1618, 1513, 1404,

1166, 739, 620 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{29}ClNO_4S+H]^+$): 606.1500; found: 606.1500.

(6,7-Dimethoxy-2,2,4-triphenylquinolin-1(2*H*)-yl)(phenyl)-methanone (3s). Yellow solid (227 mg, 87%); M.p. 243-244 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.58 – 7.35 (m, 9H), 7.35 – 7.18 (m, 9H), 6.52 (s, 1H), 6.35 (s, 1H), 6.05 (s, 1H), 3.58 (s, 3H), 3.30 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.32, 147.78, 144.96, 138.26, 137.30, 134.73, 132.73, 132.06, 130.93, 129.77, 128.66, 128.49, 128.41, 128.05, 127.86, 127.09, 119.08, 110.78, 108.68, 69.43, 55.76, 55.74; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.32, 147.78, 144.96, 138.26, 137.30, 134.73, 132.73, 132.06, 130.93, 129.77, 128.66, 128.49, 128.41, 128.05, 127.86, 127.09, 119.08, 110.78, 108.68, 69.43, 55.76, 55.74; IR (KBr) *v* 2951, 2832, 1668, 1509, 1401, 1130, 703, 631 cm^{-1}; HRMS: m/z calcd for ($[C_{36}H_{30}NO_3+H]^+$): 524.2220; found: 524.2222.

(6,7-Dimethoxy-2,2,4-triphenylquinolin-1(2*H*)-yl)(*p*-tolyl)-methanone (3t). Yellow solid (236 mg, 88%); M.p. 277-278 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 6H), 7.50 – 7.34 (m, 5H), 7.33 – 7.17 (m, 6H), 7.11 (s, 1H), 7.09 (s, 1H), 6.51 (s, 1H), 6.34 (s, 1H), 6.07 (s, 1H), 3.59 (s, 3H), 3.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.38, 147.72, 144.79, 141.38, 138.31, 134.71, 134.46, 132.73, 132.37, 129.87, 129.06, 128.66, 128.48, 128.02, 127.82, 127.03, 118.94, 110.59, 108.54, 69.33, 55.73, 55.72, 21.42; IR (KBr) *v* 3048, 2930, 2836, 1661, 1516, 1401, 1267, 700 , 573 cm^{-1}; HRMS: m/z calcd for ($[C_{37}H_{32}NO_3+H]^+$): 538.2377; found: 538.2378.

4-Butyl-6,7-dimethoxy-2,2-diphenyl-1-tosyl-1,2-dihydroquinoline (3u). Yellow solid (119 mg, 43%); M.p. 223-224 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.40 (m, 4H), 7.21 – 7.11 (m, 6H), 7.08 – 6.98 (m, 4H), 6.56 (s, 1H), 6.51 (s, 1H), 4.02 (s, 3H), 3.81 (s, 3H), 2.36 (s, 3H), 2.19 – 2.05 (m, 2H), 1.41 – 1.19 (m, 4H), 0.95 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.76, 147.45, 143.80, 142.70, 137.66, 136.11, 130.23, 128.85, 128.48, 127.90, 127.22, 126.95, 126.88, 124.72, 113.94, 105.00, 68.36, 56.31, 55.77, 31.32, 30.01, 22.80, 21.45, 14.12; IR (KBr) *v* 2946, 2827, 1600, 1511, 1401, 1166, 713 , 583 cm^{-1};; HRMS: m/z calcd for ($[C_{34}H_{36}NO_4S+H]^+$): 554.2360; found: 554.2360.

(E)-N-(2-(1,1-diphenylhepta-1,3-dien-3-yl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (5). White solid (72 mg, 26%); M.p. 191-193 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.38 – 7.31 (m, 3H), 7.28 – 7.23 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.06 – 6.96 (m, 3H), 6.82 (s, 2H), 6.80 – 6.74 (m, 2H), 6.56 (s, 1H), 6.09 (s, 1H), 4.95 – 4.83 (m, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.37 (s, 3H), 2.13 – 2.00 (m, 2H), 1.44 – 1.27 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 147.66, 145.87, 145.64, 143.38, 142.23, 139.10, 138.27, 136.43, 134.34, 129.65, 129.30, 128.38, 128.32, 127.98, 127.70, 127.42, 127.22, 127.14, 125.73, 123.88, 113.36, 106.78, 56.00, 55.78, 31.18, 22.48, 21.48, 14.07; IR (KBr) *v* 3332, 2950, 2828, 1599, 1513, 1401, 1169, 715 , 580 cm^{-1}; HRMS: m/z calcd for ($[C_{34}H_{36}NO_4S+H]^+$): 554.2360; found: 554.2360.

3-(2,2-Diphenylvinyl)-5,6-dimethoxy-2-propyl-1-tosyl-1*H*-indole (6). Brown solid (116 mg, 42%); M.p. 161-163 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.53 – 7.45 (m, 2H), 7.40 – 7.31 (m, 5H), 7.23 – 7.14 (m, 2H), 7.13 – 7.03 (m, 1H), 7.02 – 6.92 (m, 4H), 6.75 (s, 1H), 6.17 (s, 1H), 3.92 (s, 3H), 3.50 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.83 – 1.64 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.81, 146.49, 144.79, 144.32, 143.37, 140.28, 138.94, 135.72, 130.82, 130.18, 129.56, 128.50, 128.15, 127.89, 127.74, 127.42, 126.13, 121.86, 120.65, 119.31, 101.76, 98.98, 56.13, 55.65, 29.33, 23.76, 21.56, 13.96; IR (KBr) *v* 2936, 2825, 1598, 1513, 1401, 1160, 709 , 578 cm^{-1}; HRMS: m/z calcd for ($[C_{34}H_{34}NO_4S+H]^+$): 552.2203; found: 552.2203.

2',3',8'-Trimethoxy-5'-tosyl-5'*H*-spiro[fluorene-9,6'-indeno-[2,1-b]indole] (7). Brown solid (159 mg, 53%); M.p. 293-295 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.77 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.30 (s, 1H), 7.13 – 7.03 (m, 2H), 7.02 – 6.90 (m, 4H), 6.79 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 2H), 6.05 (d, *J* = 2.4 Hz, 1H), 4.05 (s, 3H), 3.99 (s, 3H), 3.58 (s, 3H), 2.27 (s, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 158.11, 153.22, 147.83, 147.23, 145.98, 144.25, 142.89, 142.58, 135.41, 134.93, 129.79, 129.33, 129.06, 127.87, 127.44, 126.68, 123.51, 120.18, 119.51, 116.84, 111.76, 110.31, 101.32, 98.98, 63.21, 56.36, 56.32, 55.32, 21.45; IR (KBr) *v* 2959, 2836, 1621, 1401, 1281, 743, 674 cm^{-1}; HRMS: m/z calcd for ($[C_{37}H_{30}NO_5S+H]^+$): 600.1839; found: 600.1841.

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