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Synthesis of Tetrahydro-1*H*-indeno[1,2-*b*]pyridine *via* Cascade Cyclization and Friedel-Crafts Reaction

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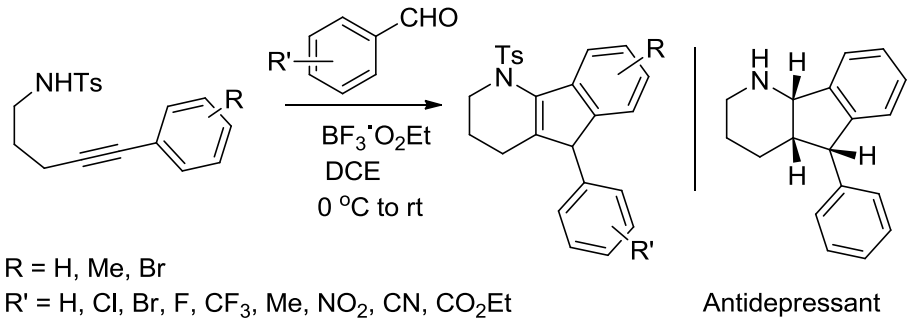


ABSTRACT: A convenient protocol has been established for the synthesis of 1-tosyl-2,3,4,5-tetrahydro-1*H*-indeno[1,2-*b*]pyridine *via* cascade cyclization and Friedel-Crafts reaction of 4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamides and aldehydes in good yields. The methodology has been used for the total synthesis of antidepressant agent (±)-5-phenyl-2,3,4,4*a*,5,9*b*-hexahydro-1*H*-indeno[1,2-*b*]pyridine.

INTRODUCTION

The tetrahydro-1*H*-indeno[1,2-*b*]pyridines are class of nitrogen heterocycles containing piperidine ring fused to 2,3-dihydro-1*H*-indene. Many molecules of these possess biological

activity like other nitrogen containing alkaloids. As for example, hexahydroindenopyridine (HHIP) **1** is a new class of compounds known for their antidepressant,[1] and inhibition of 11β-hydroxysteroid dehydrogenase enzyme 1 (11β-HSD1).[2] On the other hand, 2,4*a*,9,9*a*-tetrahydro-1*H*-indeno[2,1-*b*]pyridine ring system is found in natural products such as haouamines A (**2**) and B (**3**), two metabolites, isolated from the ascidian *Aplidium haouarianum* (Figure 1).[3] There are only a few methods for the synthesis of 1*H*-indeno[1,2-*b*]pyridines[1b,4]. The major drawback of these methods is the requirement of multistep procedures.[1b,4] Therefore, the development of highly efficient methods for the synthesis of 1*H*-indeno[1,2-*b*]pyridines are still in demand.

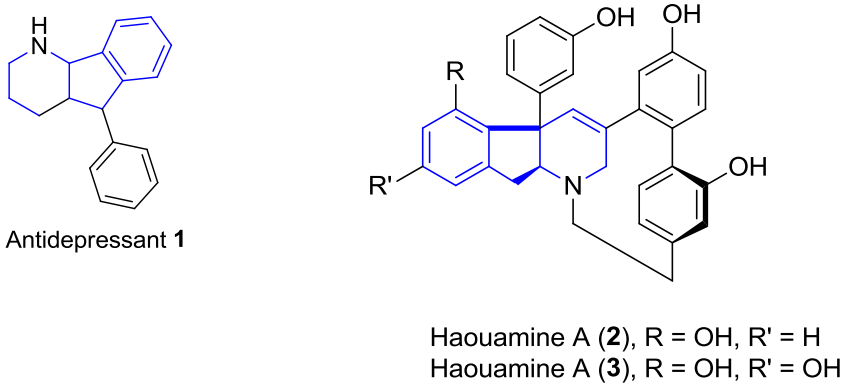
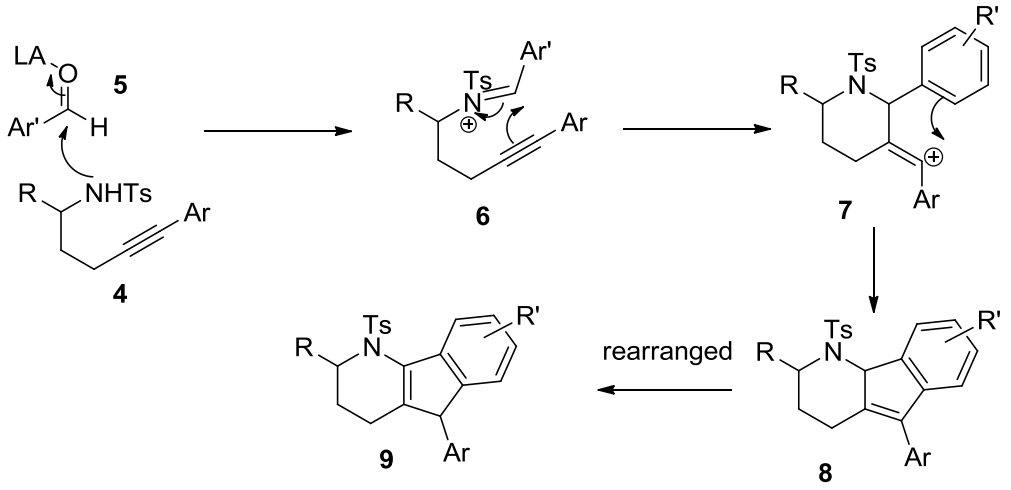


Figure 1. Biologically important indeno[1,2-*b*]pyridine

Cascade reactions are gaining importance in organic synthesis due to its ability to form complex molecular framework.[5] Similarly, Friedel-Crafts reaction is one of the important reaction in organic synthesis for C-C bond formation.[4d,6] On the other hand, tandem Prins- and Friedel-Crafts[7] and aza-Prins-Friedel-Crafts[8] reactions are considered as an efficient methodology for the synthesis of variously substituted heterocyclic compounds. Jin and coworkers have reported the triflic acid catalyzed cascade cyclization of arenyl enynes *via* acetylene-cation cyclization and Fridel-Crafts type reaction.[9] On the basis of these facts, we envisioned that the reaction of α-sulfonamido-alkynes **4** with aldehydes **5** under Lewis acidic

conditions would provide intermediate **6** (Scheme 1). Tandem aza-Prins cyclization and Friedel-Crafts type reaction may provide product **8**. The product **8** may rearrange to give more stable enamide **9**.



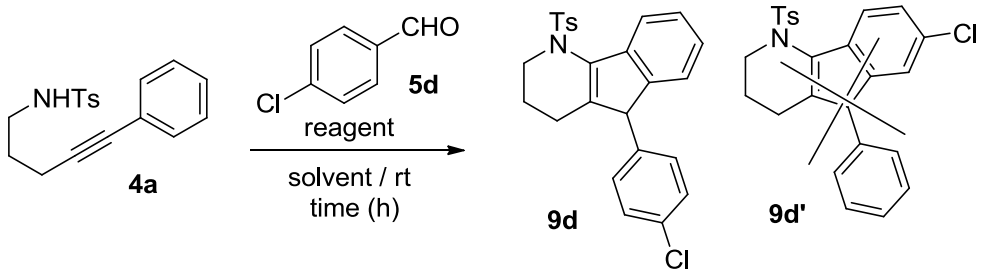
Scheme 1 Possible reaction pathways

RESULTS AND DISCUSSION

In continuation of our interest in the synthesis of nitrogen heterocycles we were in search of a methodology for the synthesis of these nitrogen heterocycles.[10] In this article we now present a simple method for the synthesis of tetrahydro-1*H*-indeno[1,2-*b*]pyridine framework from the reaction of 4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamides and aldehydes. To start with, 4-methyl-*N*-(5-phenylpent-4-yn-1-yl)benzenesulfonamide was reacted with parachlorobenzaldehyde in dichloromethane with two equivalents of boron trifluoride etherate and 5-(4-chlorophenyl)-1-tosyl-2,3,4,5-tetrahydro-1*H*-indeno[1,2-b]pyridine **9d** was obtained in 45 % yield in 12h, instead of proposed product 7-chloro-5- phenyl-1-tosyl-2,3,4,5-tetrahydro-1*H*-indeno[1,2-*b*]pyridine **9d'**. The structure of the compound **9d** was determined from NMR and X-ray crystallographic analysis (see SI).[11] To optimize the reaction conditions, different reagents and solvents were screened and the results are summerized in Table 1. The reaction with one equivalent of $BF_3{\cdot}OEt_2$ gave 38% yield. The

same reaction with two equivalents of $BF_3{\cdot}OEt_2$ in 1,2-dichloroethane (DCE) gave 70% yield, but in toluene it produced only 30% yield. The reaction was also performed in different Lewis and Brønsted acidic conditions. Metal triflates such as zinc, copper, indium and silver triflates were also screened for the reaction. Out of these, only zinc, copper and indium triflates gave 13%, 9% and 25% yields, respectively. In the case of AgOTf, starting material was recovered in 98% yield. Similarly, metal salts $InCl_3$ and $FeCl_3$ gave 18 and 20% yields, respectively. Brønsted acids such as camphor sulfonic acid (CSA) failed to give the desired product but starting material was recovered in 96% yield. On the other hand, triflic acid (TfOH) gave 20% yield.

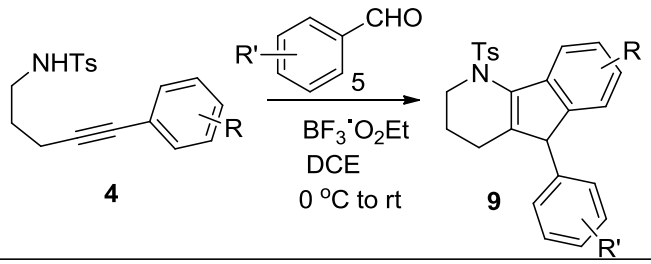
Table 1. Optimization of the reaction condition

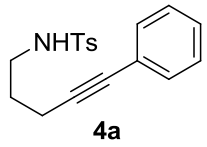
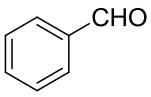
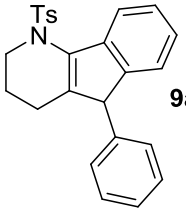
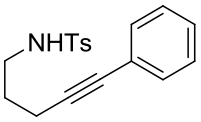
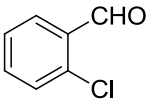
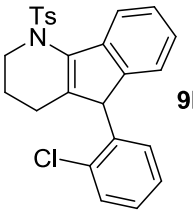
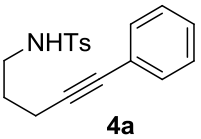
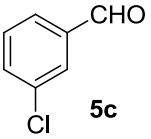
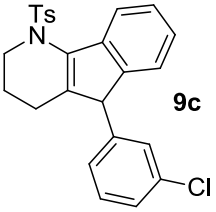
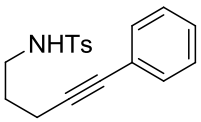
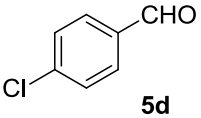
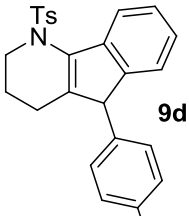
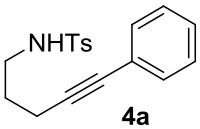
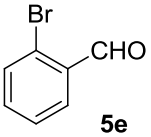
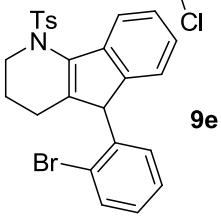
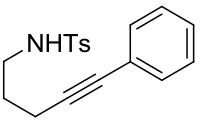
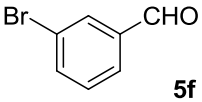
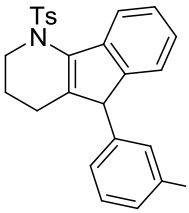
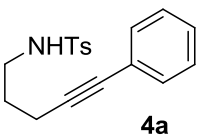
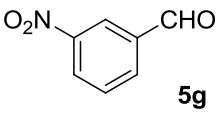
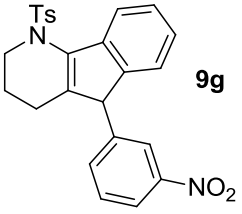


entry	reagent (mmol)	solvent	time/h	yield (%)[a]
1	$BF_3{\cdot}OEt_2$ (2)	CH_2Cl_2	12	45
2	$BF_3{\cdot}OEt_2$ (1)	CH_2Cl_2	12	38
3	$BF_3{\cdot}OEt_2$ (2)	DCE	12	70
4	$BF_3{\cdot}OEt_2$ (2)	toluene	12	30
5	$Zn(OTf)_2$ (1)	CH_2Cl_2	24	13
6	$Cu(OTf)_2$ (1)	CH_2Cl_2	24	9
7	$In(OTf)_3$ (1)	CH_2Cl_2	24	25
8	Ag(OTf) (1)	CH_2Cl_2	24	--[b]
9	$InCl_3$ (1)	CH_2Cl_2	24	18
10	$FeCl_3$ (1.2)	CH_2Cl_2	24	20
11	CSA (1.2)	CH_2Cl_2	24	--[b]
12	TfOH (1.2)	CH_2Cl_2	24	20

[a]Yield refers to isolated yield. Compounds are characterised by ^1H, ^{13}C NMR, IR and Mass spectrometry. [b]No reaction, starting material was recovered.

Table 2. Synthesis of tetrahydro-1*H*-indeno[1,2-*b*]pyridine



Sl.No.	amide **4**	aldehyde **5**	product **9**	yield (%)[a]
1	 **4a**	 **5a**	 **9a**	57
2	 **4a**	 **5b**	 **9b**	62
3	 **4a**	 **5c**	 **9c**	65
4	 **4a**	 **5d**	 **9d**	70
5	 **4a**	 **5e**	 **9e**	53
6	 **4a**	 **5f**	 **9f**	59
7	 **4a**	 **5g**	 **9g**	54

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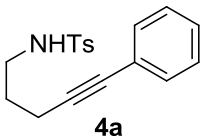
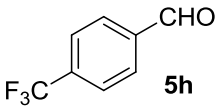
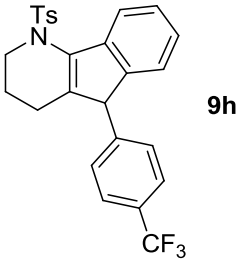
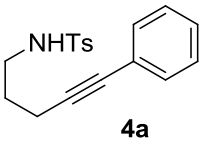
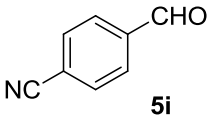
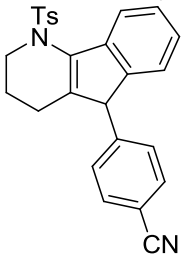
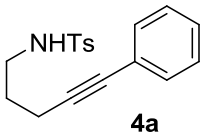
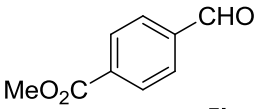
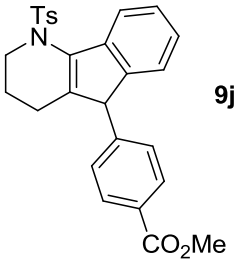
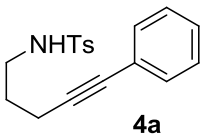
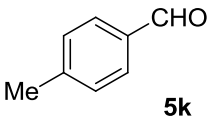
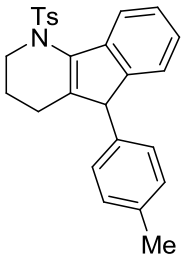
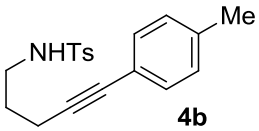
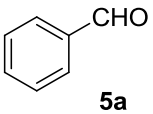
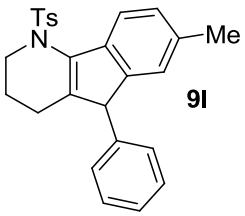
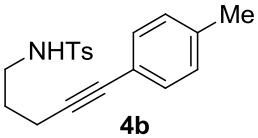
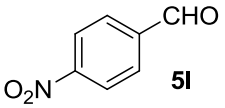
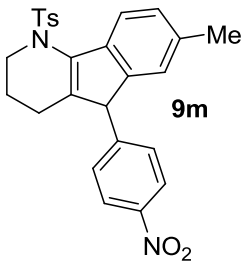
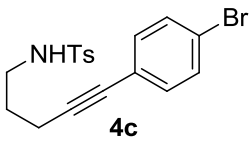
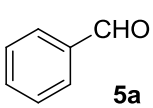
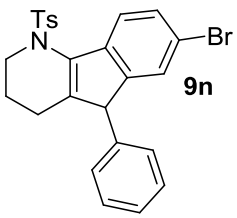
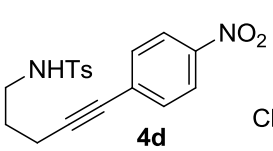
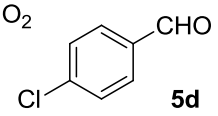
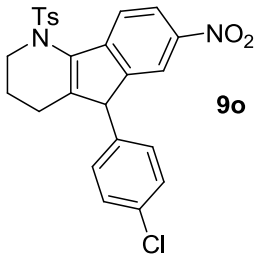
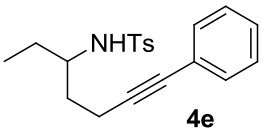
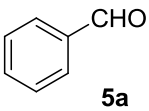
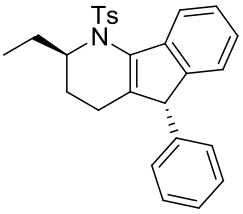
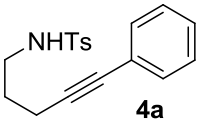
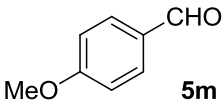
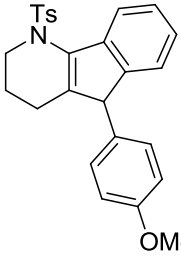
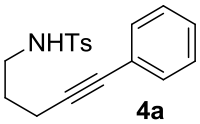
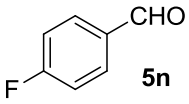
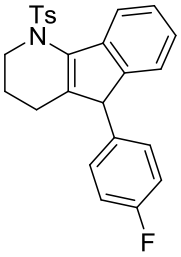
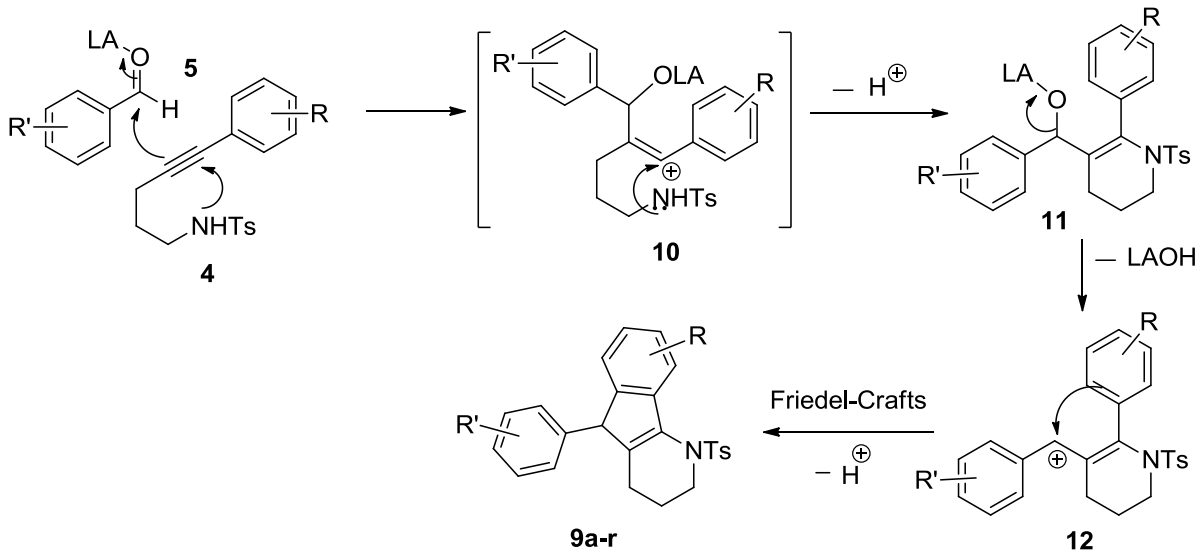
8	 **4a**	 **5h**	 **9h**	61
9	 **4a**	 **5i**	 **9i**	78
10	 **4a**	 **5j**	 **9j**	75
11	 **4a**	 **5k**	 **9k**	87
12	 **4b**	 **5a**	 **9l**	57
13	 **4b**	 **5l**	 **9m**	56
14	 **4c**	 **5a**	 **9n**	52

SL No.	amide **4**	aldehyde **5**	product **9**	yield (%)[a]
15	 **4d**	 **5d**	 **9o**	0
16	 **4e**	 **5a**	 **9p**	81
17	 **4a**	 **5m**	 **9q**	0
18	 **4a**	 **5n**	 **9r**	52

[a]Yields refer to isolated yield. Compounds are characterized by ^{1}H, ^{13}C NMR, IR and mass spectrometry.

With this optimized conditions in hand, we further examined the scope of the reaction with variety of substrates (Table 2). It was observed from the Table 2 that alkynes having aryl substituents (entries 1-14, 16 and 18) gave the desired product in good yields. Both electron-withdrawing and electron-donating groups in the aromatic ring of the aldehydes gave moderate to high yields. However, aldehyde having highly electron donating methoxy group on the aromatic ring (entry 17) decomposed under these reaction conditions. Similarly, methyl and bromide substituted aryl groups (entries 12-14) in the alkyne side chain gave moderate yields. In this case, mixture of unidentified by-products were observed. On the contrary, substrate (entry 15) having electron withdrawing nitro group on the aromatic ring failed to give product. This is due to the destabilization of carbocation **10** formed during the

reaction (Scheme 2). The structure of the products was determined by ^{1}H, ^{13}C NMR and X-ray crystallographic analysis of **9d**, **9e, 9k** and **9n** (see SI).[11] The sharp down field shift of C-5H proton of compounds **9b** and **9e** (δ 5.04 ppm) is due to the electron withdrawing effect of ortho substituted chloride and bromide groups on the aromatic ring. Ethyl substituted alkyne (entry 16) gave *trans* product **9p** with respect to ethyl and phenyl at 2 and 5 positions, the stereochemistry of which was determined by X-ray crystallographic analysis (see SI).[11] The structure of the products in Table 2 is in contrast to the proposed structure in which aromatic ring of aldehyde is taking part in Friedel-Crafts reaction (Scheme 1). But in reality aromatic ring of the alkyne side chain is taking part in Friedel-Crafts reaction. Therefore, a mechanism of the reaction is proposed as shown in Scheme 2. The boron trifluoride etherate activates the carbonyl group of the aldehyde for the nucleophilic attack by alkyne group which is subsequently attacked by tosylamide group to form intermediate **11**, which after decomposition generates carbocation **12**. The carbocation **12** is attacked by aryl group to give the Friedel-Crafts product **9a-r**.

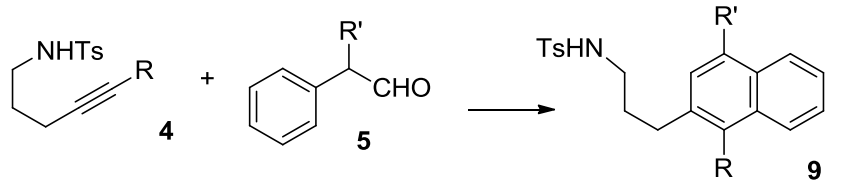


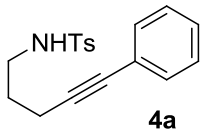
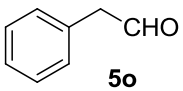
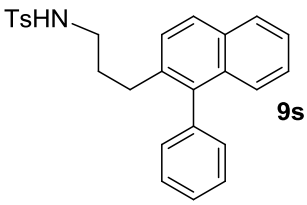
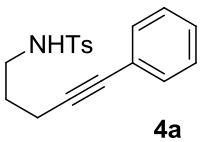
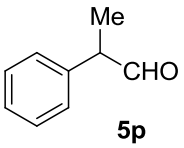
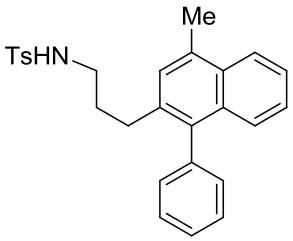
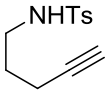
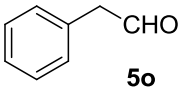
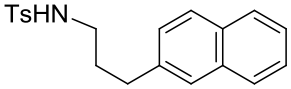
Scheme 2. Mechanism for the formation of tetrahydro-1*H*-indeno[1,2-*b*]pyridine

There is an unexpected result in the reaction of alkyne **4a** with phenylacetaldehyde **5o** and 2-phenylpropanal **5p** (entries 19 and 20) where sulphonamide substituted aromatized products

9s and **9t** were obtained in 71 and 74% yields, respectively (Table 3). The structure of compounds **9s** and **9t** was determined from ^{1}H, ^{13}C NMR, COSEY and HMQC analysis of compound **9s** (see SI). Compound **9s** shows broad singlet at δ 4.44 ppm in ^{1}H NMR and eighteen signals in the aromatic region of ^{13}C NMR. Moreover, proton at δ 4.44 ppm do not correlate with carbon in HMQC analysis (see SI). This indicates that this peak belong to the

Table 3. Formation of naphthalene derivative

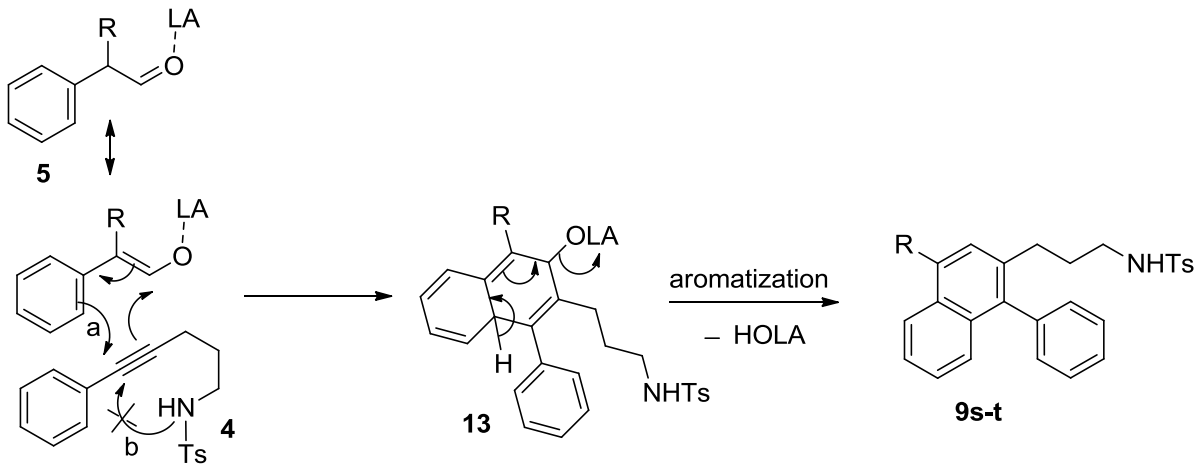


SL No.	amide **4**	aldehyde **5**	product **9**	yield (%)[a]
19	 **4a**	 **5o**	 **9s**	71
20	 **4a**	 **5p**	 **9t**	74
21	 **4f**	 **5o**	 **9u**	0

[a]Yields refer to isolated yield. Compounds are characterized by ^{1}H, ^{13}C NMR, IR and mass spectrometry.

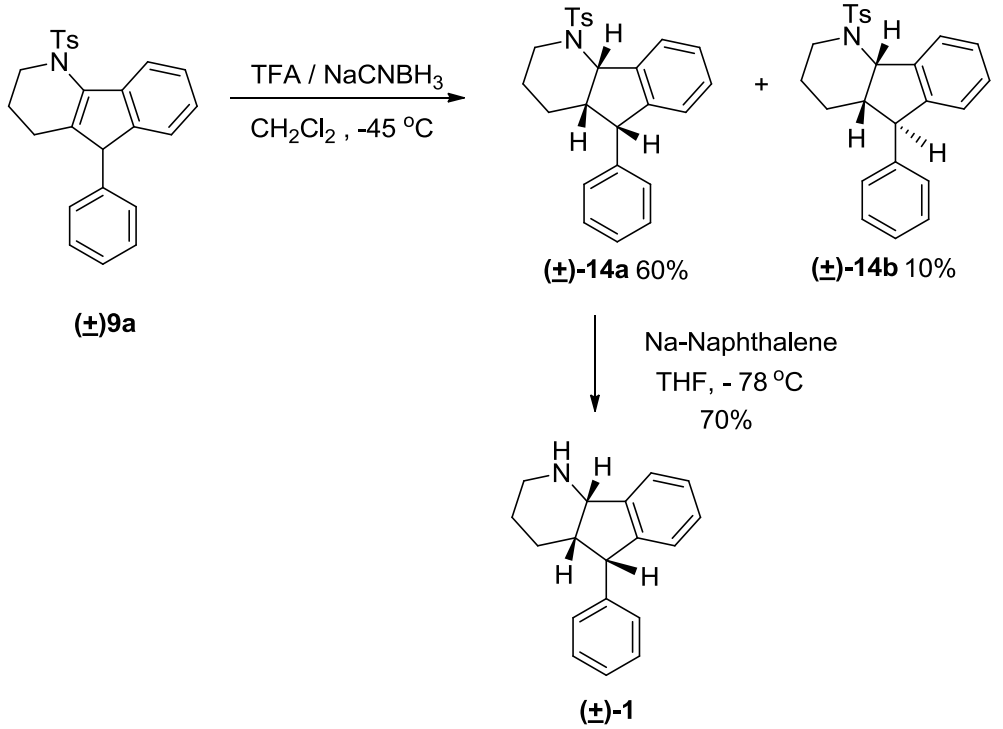
–NH- proton of –NHTs group. It was observed from the Table 3 that alkynes having aryl substituents (entries 19 and 20) gave the desired product but terminal alkyne **4f** (entry 21) failed to produce the same.

The formation of **9s** and **9t** is shown in Scheme 3. In this case, aldehyde **5** enolized under Lewis acidic conditions, which subsequently reacts with alkyne **4** to form Diels-Alder adduct **13**, which after aromatization gives naphthalene derivatives **9s-t**.[12]



Scheme 3. Mechanism for the formation of naphthalene derivatives

The former strategy is successfully applied for the synthesis of (±)-5-phenyl-2,3,4,4*a*,5,9*b*-hexahydro-1*H*-indeno[1,2-*b*]pyridine (**1**). The compound **1** is considered as antidepressant agent.[1a] The synthesis started with the reduction of (±)-**9a** with sodium cyanoborohydride and trifluoroacetic acid in dichloromethane to give diastereomeric mixtures *cis*-(±)-**14a** and



Scheme 4. Total synthesis of (±)-5-phenyl-2,3,4,4*a*,5,9*b*-hexahydro-1*H*-indeno[1,2-*b*]pyridine.

trans-(±)-**14b**, in 60% and 10% yields, respectively (Scheme **4**). The compound (±)-**14a** after deprotection of tosyl group with sodium naphthalide gave final product (±)-**1**.[1a] The *cis* and *trans* stereochemistry of compounds (±)-**14a** and (±)-**14b** were determined by coupling constants and NOE experiments.[1a] The vicinal coupling constant of proton C-9bH of (±)-**14a**, resonating at 5.47 ppm, was found to be 5.6 Hz. Similarly, the vicinal coupling constant of proton C-9bH of (±)-**14b**, resonating at 5.10 ppm, was also found to be 5.6 Hz. This indicates that in both the compounds the configuration of ring junction is same. As seen from the

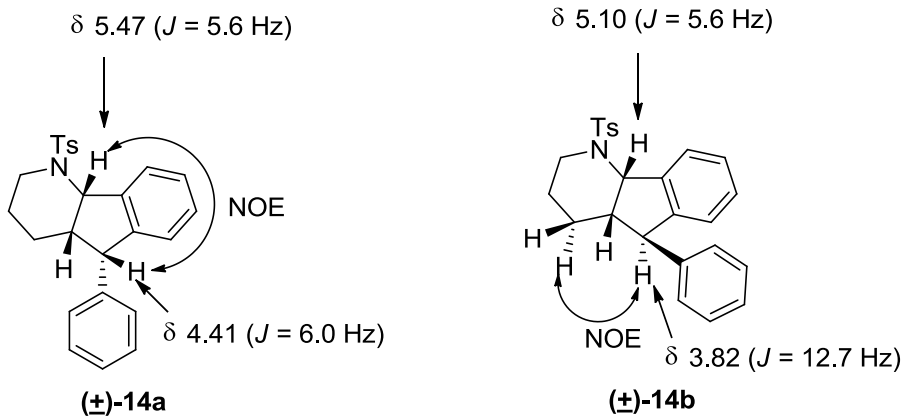
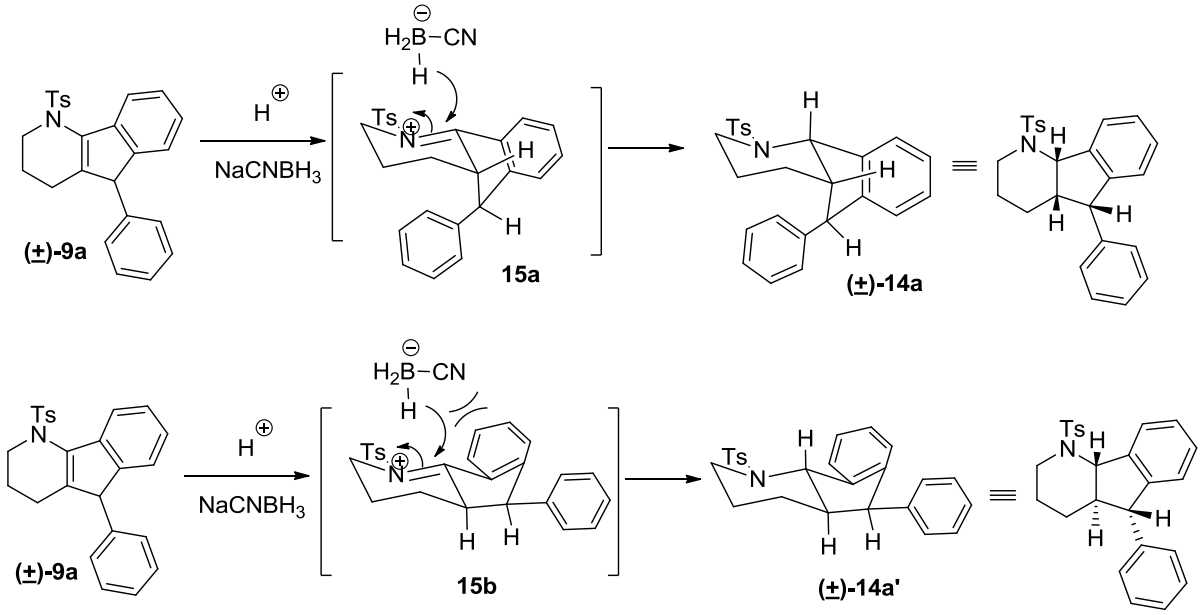


Figure 2. Coupling constants and NOE of compounds (±)-**14a** and (±)-**14b**

mechanism of formation of (±)**14a** and (±)**14b** from (±)-**9a** after protonation and subsequent addition of hydride, the stereochemistry of ring junction should be *cis* (Scheme 5). Out of the two possible transition states **15a** and **15b**, in their chair conformation, transition state **15a** is more favoured than **15b** due to the repulsion between the phenyl group and incoming cyanoborohydride in the latter. On the other hand, the vicinal coupling constants of proton C-5H of (±)-**14a**, resonating at 4.41 ppm, and (±)-**14b**, resonating at 3.82 ppm, were found to be 6.0 and 12.7 Hz, respectively. The compound (±)-**14a** showed a clear characteristic NOE correlation between the hydrogens C-9bH and C-5H, which clearly indicates that the two hydrogens are *cis* to each other (Figure 2). Whereas, there was no such NOE correlation

between the hydrogens C-9bH and C-5H in compound (±)-**14b**. Therefore, the configuration of C-9bH and C-5H protons of compound (±)-**14b** is *trans*.



Scheme 5. Mechanism of formation of hexahydro-1*H*-indeno[1,2-*b*]pyridine

CONCLUSIONS

In conclusion, we have developed a mild and efficient method for the synthesis of tetrahydro-1*H*-indeno[1,2-*b*]pyridine via cascade cyclization of alkyne tosylamides and aryl aldehydes in good yields. The reaction is compatible with a wide range of functional groups such as ester, nitro, nitrile and halides. The methodology is used for the synthesis of biologically active molecule (±)-5-Phenyl-2,3,4,4*a*,5,9*b*-hexahydro-1*H*-indeno[1,2-*b*]pyridine.

EXPERIMENTAL SECTION

General Information: All the reagents were of reagent grade (AR grade) and were used as purchased without further purification. Melting points were recorded in an open capillary tube and are uncorrected. Fourier transform-infra red (FT-IR) spectra were recorded as neat

liquid or KBr pellets. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (600 MHz, 400 MHz) or ^{13}C (150 MHz, 100 MHz) NMR. Chemical shifts (δ) are reported in ppm and spin-spin coupling constants (J) are given in Hz. HRMS spectra were recorded using Q-TOF mass spectrometer.

Synthesis of sulfonamide: The starting materials 4-methyl-*N*-(pent-4-yn-1-yl)benzene-sulfonamide (**4a-f**) derivatives were prepared from the literature procedure.[13] Compounds **4a** and **4f** are known and their spectroscopic data agreed well with the reported data.[13]

***General Procedure for Formation of Indenopyridine*:**

To a solution of *N*-tosylated alkyne amine (100 mg, 0.3 mmol) in dry 1,2-dichloroethane (2 mL) was added benzaldehyde (35 mg, 0.33 mmol) at 0 ºC, followed by $BF_3{\cdot}OEt_2$ (84 mg, 0.6 mmol). The reaction mixture was brought to room temperature and kept for 12 h. After completion of the reaction, as determined by TLC, dichloroethane was added to the reaction mixture, washed with saturated sodium bicarbonate and brine solutions, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by column chromatography using ethyl acetate and hexane as eluents.

*4-Methyl-N-(5-(p-tolyl)pent-4-yn-1-yl)benzenesulfonamide (**4b**):*

Colorless solid; mp 99-101 ºC; R_f (hexane/ EtOAc 4:2) 0.58; yield 229 mg, 70% ^1H NMR (600 MHz, $CDCl_3$) δ 1.72-1.77 (m, 2 H), 2.33 (s, 3 H), 2.39 (s, 3 H), 2.41 (t, *J* = 7.2 Hz, 2 H), 3.10-3.12 (m, 2 H), 5.01 (brs, 1 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.9, 21.6, 21.7, 28.5, 42.5, 81.9, 87.7, 127.3, 128.3, 129.1, 129.9, 131.5, 137.0, 138.0, 143.5; IR (KBr, neat) 3276, 3052, 2925, 2851, 1912, 1892, 1599, 1429, 1326, 1159, 1093, 958, 815, 665 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{22}NO_2S$ $(M + H)^+$ 328.1366, found 328.1384.

*N-(5-(4-Bromophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide (**4c**):*

Colorless solid; mp 114-116 ºC; R_f (hexane/ EtOAc 4:2) 0.6; yield 262, mg, 67% ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73-1.80 (m, 2 H), 2.41 (s, 3 H), 2.43 (t, *J* = 7.2 Hz, 2 H), 3.09-3.14 (m, 2 H), 4.78 (brs, 1 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9, 21.8, 28.4, 42.4, 80.9, 89.8, 122.1, 122.6, 127.3, 129.9, 131.6, 133.2, 137.0, 143.7; IR (KBr, neat) 3275, 3059, 2927, 2855, 1644, 1583, 1487, 1325, 1160, 1071, 1010, 817, 737, 663 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{19}BrNO_2S$ $(M + H)^+$ 394.0294, found 394.0313.

*4-Methyl-N-(5-(4-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide (**4d**):*

Colorless solid; mp 126-128; R_f (hexane/ EtOAc 2:1) 0.33; yield 250 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77-1.85 (m, 2 H), 2.42 (s, 3 H), 2.51 (t, *J* = 6.8 Hz, 2 H), 3.11-3.16 (m, 2 H), 4.52 (brs, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H), 8.15 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.9, 21.7, 28.3, 42.3, 80.3, 94.8, 123.6, 127.2, 129.9, 130.8, 132.4, 136.9, 143.7, 146.9; IR (KBr, neat) 3298, 2925, 2228, 1593, 1515, 1342, 1158, 1094, 854, 750, 688 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{19}N_2O_4S$ $(M + H)^+$ 359.1060, found 359.1086.

*4-Methyl-N-(7-phenylhept-6-yn-3-yl)benzenesulfonamide (**4e**):*

Colorless solid; mp 65-67; R_f (hexane/ EtOAc 9:1) 0.33; yield 249 mg, 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3 H), 1.38-1.47 (m, 1 H), 1.49-1.57 (m, 1 H), 1.58-1.66 (m, 1 H), 1.69-1.74 (m, 1 H), 2.30-2.36 (m, 2 H), 2.38 (s, 3 H), 3.30-3.39 (m, 1 H), 4.83 (brs, 1 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.28-7.30 (m, 3 H), 7.35-7.38 (m, 2 H), 7.78 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 16.0, 21.6, 27.8, 33.4, 54.8, 81.3, 89.3, 123.8, 127.1, 127.8, 128.3, 129.7, 131.6, 138.2, 143.3; IR (KBr, neat) 3282, 3059, 2966, 2876, 2236, 1953, 1599, 1491, 1307, 1161, 1093, 1008, 912, 758, 664 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{24}NO_2S$ $(M + H)^+$ 342.1522, found 342.1530.

*5-Phenyl-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9a**):*

Colorless solid; mp 150-152 °C; R_f (hexane/ EtOAc 9:1) 0.49; yield 73 mg, 57%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.21-1.27 (m, 1 H), 1.37-1.41 (m, 1 H), 1.87 (dt, *J* = 18.6 and 6.6 Hz, 1 H), 2.08 (dt, *J* = 18.6 and 7.2 Hz, 1 H), 2.41 (s, 3 H), 3.54 (ddd, *J* = 12.6, 7.2 and 3.0 Hz, 1 H), 3.81 (ddd, *J* = 14.4, 6.6 and 3.0 Hz, 1 H), 4.29 (s, 1 H), 6.95 (d, *J* = 7.2 Hz, 2 H), 7.13-7.16 (m, 2 H), 7.21-7.28 (m, 5 H), 7.31-7.34 (m, 1 H), 7.66 (d, *J* = 7.8 Hz, 2 H), 8.01 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.8, 22.1, 47.9, 55.9, 122.5, 123.7, 125.6, 127.0, 127.2, 128.1, 128.3, 128.9, 129.8, 136.1, 136.7, 138.8, 139.8, 141.1, 144.1, 146.6; IR (KBr, neat) 3060, 2926, 2856, 1600, 1493, 1454, 1353, 1166, 1092, 985, 811, 662 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{24}NO_2S$ $(M + H)^+$ 402.1522, found 402.1521.

*5-(2-Chlorophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9b**):*

Colorless solid; mp 162-164 °C; R_f (hexane/ EtOAc 9:1) 0.53; yield 86 mg, 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.29 (m, 1 H), 1.37-1.41 (m, 1 H), 1.85 (ddd, *J* = 10.8, 6.6 and 4.2 Hz, 1 H), 2.18 (ddd, *J* = 18.0, 11.4 and 6.6 Hz, 1 H), 2.41 (s, 3 H), 3.55 (ddd, *J* = 13.8, 9.6 and 4.2 Hz, 1 H), 3.81 (ddd, *J* = 15.0, 9.6 and 5.4 Hz, 1 H), 5.04 (s, 1 H), 6.47 (d, *J* = 7.6 Hz, 1 H), 7.04 (t, *J* = 9.6 Hz, 1 H), 7.16 (t, *J* = 7.6 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.21 (s, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 8.01 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.8, 22.0, 47.9, 51.4, 122.7, 123.7, 125.7, 127.2, 127.4, 128.1, 128.4, 128.5, 129.9, 135.2, 136.1, 137.1, 137.8, 141.2, 144.1, 146.1; IR (KBr, neat) 3063, 2928, 2855, 1597, 1490, 1456, 1354, 1164, 1091, 986, 813, 740 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}ClNO_2S$ $(M + H)^+$ 436.1133, found 436.1118.

*5-(3-Chlorophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9c**):*

Colorless solid; mp 156-158 °C; R_f (hexane/ EtOAc 9:1) 0.48; yield 90 mg, 65%; ^{1}H NMR (600MHz, $CDCl_3$) δ 1.17-1.21 (m, 1 H), 1.39-1.43 (m, 1 H), 1.85 (ddd, *J* = 18.6, 6.6 and 4.2

Hz, 1 H), 2.01 (ddd, *J* = 18.6, 9.6 and 7.8 Hz, 1 H), 2.41 (s, 3 H), 3.49 (ddd, *J* = 13.2, 10.2 and 3.0 Hz, 1 H), 3.90 (ddd, *J* = 14.4, 5.4 and 3.0 Hz, 1 H), 4.24 (s, 1 H), 6.88 (s, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 7.12 (d, *J* = 7.2 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 7.20-7.22 (m, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 2 H), 8.03 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.0, 21.9, 22.1, 48.0, 55.4, 122.8, 123.7, 125.8, 126.9, 127.3, 127.5, 127.9, 128.1, 130.0, 130.2, 134.7, 137.3, 141.0, 142.0, 144.2, 145.9; IR (KBr, neat) 3059, 2926, 2856, 1596, 1457, 1352, 1164, 1093, 987, 811, 688 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}ClNO_2S$ $(M + H)^+$ 436.1133, found 436.1135.

*5-(4-Chlorophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9d**):*

Colorless solid; mp 159-161 °C; R_f (hexane/ EtOAc 9:1) 0.58; yield 97 mg, 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.23-1.29 (m, 1 H), 1.39-1.42 (m, 1 H), 1.84 (ddd, *J* = 18.6, 7.2 and 5.4 Hz, 1 H), 2.08 (ddd, *J* = 15.0, 7.8 and 4.2 Hz, 1 H), 2.42 (s, 3 H), 3.54 (ddd, *J* = 16.8, 9.6 and 3.0 Hz, 1 H), 3.79 (ddd, *J* = 14.4, 6.6 and 3.6 Hz, 1 H), 4.26 (s, 1 H), 6.88 (d, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 7.2 Hz, 1 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 7.21-7.26 (m, 4 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 7.8 Hz, 2 H), 8.00 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.8, 22.0, 47.8, 55.1, 122.6, 123.6, 125.7, 127.2, 128.0, 129.1, 129.6, 129.8, 132.9, 136.0, 136.9, 138.2, 138.3, 141.0, 144.1, 146.1; IR (KBr, neat) 3063, 2927, 2856, 1618, 1597, 1490, 1354, 1164, 1091, 1017, 986, 813, 766 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}ClNO_2S$ $(M + H)^+$ 436.1133, found 436.1135.

*5-(2-Bromophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9e**):*

Colorless solid; mp 182-184 °C; R_f (hexane/ EtOAc 9:1) 0.53; yield 81 mg, 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.30 (m, 1 H), 1.36-1.42 (m, 1 H), 1.86 (ddd, *J* = 19.2, 7.2 and 4.8 Hz, 1 H), 2.20 (ddd, *J* = 19.2, 7.6 and 4.0 Hz, 1 H), 2.42 (s, 3 H), 3.55 (ddd, *J* = 14.4, 6.4 and 3.2 Hz, 1 H), 3.80 (ddd, *J* = 14.0, 6.4 and 3.2 Hz, 1 H), 5.04 (s, 1 H), 6.43-6.46 (m, 1 H),

7.06-7.10 (m, 2 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.21-7.25 (m, 3 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.61-7.63 (m, 1 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 8.01 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.8, 22.0, 47.9, 54.2, 122.7, 123.6, 125.7, 127.2, 128.0, 128.1, 128.6, 128.7, 129.9, 133.1, 137.1, 138.5, 139.6, 141.1, 144.1, 146.2; IR (KBr, neat) 2959, 2927, 2854, 1594, 1466, 1353, 1164, 1093, 1026, 987, 811, 765 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}BrNO_2S$ $(M + H)^+$ 480.0627, found 480.0608.

*5-(3-Bromophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9f**):*

Colorless solid; mp 178-180 °C; R_f (hexane/ EtOAc 9:1) 0.54; yield 90 mg, 59%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10-1.21 (m, 1 H), 1.37-1.44 (m, 1 H), 1.84 (ddd, *J* = 18.8, 6.8 and 3.6 Hz, 1 H), 2.09 (ddd, *J* = 19.2, 8.0 and 4.0 Hz, 1 H), 2.41 (s, 3 H), 3.46 (ddd, *J* = 17.2, 7.2 and 3.2 Hz, 1 H), 3.89 (ddd, *J* = 14.4, 5.6 and 3.6 Hz, 1 H), 4.23 (s, 1 H), 6.98 (d, *J* = 7.6 Hz, 1 H), 7.06 (s, 1 H), 7.13 (d, *J* = 7.8 Hz, 1 H), 7.15-7.18 (m, 2 H), 7.29 (d, *J* = 7.8 Hz, 2 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.66 (d, *J* = 7.8 Hz, 2 H), 8.03 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.0, 21.9, 22.0, 47.9, 55.3, 122.7, 123.6, 125.7, 127.2, 127.3, 128.0, 129.9, 130.4, 130.5, 130.7, 137.1, 137.9, 140.9, 142.1, 144.2, 145.8; IR (KBr, neat) 2925, 2854, 1594, 1467, 1352, 1297, 1164, 1093, 1025, 988, 812, 765 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}BrNO_2S$ $(M + H)^+$ 480.0627, found 480.0625.

*5-(3-Nitrophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9g**):*

Colorless solid; mp 115-117 °C; R_f (hexane/ EtOAc 9:1) 0.28; yield 77 mg, 54%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18-1.22 (m, 1 H), 1.41-1.45 (m, 1 H), 1.83 (dt, *J* = 18.6 and 4.8 Hz, 1 H), 2.14(dt, *J* = 18.6 and 7.8 Hz, 1 H), 2.42 (s, 3 H), 3.49-3.54 (m, 1 H), 3.86 (dt, *J* = 14.4 and 4.8 Hz, 1 H), 4.39 (s, 1 H), 7.10 (d, *J* = 7.2 Hz, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 7.29 (d, *J* = 7.8 Hz, 2 H), 7.33 (d, *J* = 7.8 Hz, 1 H), 7.37 (t, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 2 H), 7.85 (s, 1 H), 8.04 (d, *J* = 7.8 Hz, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.8, 22.1, 47.8, 55.2, 122.5, 123.1, 123.6, 126.0, 127.6, 128.0, 130.0, 134.6, 135.8, 136.9, 137.9, 141.0, 142.2, 144.4, 145.4, 148.9; IR (KBr, neat) 3065, 2926, 2854, 1620, 1599, 1500, 1455, 1352, 1163, 1092, 987, 810, 740 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}N_2O_4S$ $(M + H)^+$ 447.1373, found 447.1370.

*1-Tosyl-5-(4-(trifluoromethyl)phenyl)-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9h**):*

Colorless solid; mp 166-168 ºC; R_f (hexane/ EtOAc 9:1) 0.45; yield 91 mg, 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25-1.33 (m, 1 H), 1.39-1.43 (m, 1 H), 1.83 (dt, *J* = 18.0 and 6.4 Hz, 1 H), 2.10 (dt, *J* = 19.2 and 7.2 Hz, 1 H), 2.42 (s, 3 H), 3.55 (ddd, *J* = 14.0, 6.8 and 3.2 Hz, 1 H), 3.80 (ddd, *J* = 14.0, 6.0 and 2.8 Hz, 1 H), 4.35 (s, 1 H), 7.06-7.11 (m, 3 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 8.01(d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.8, 22.0, 47.8, 55.4, 122.8, 123.7, 124.3 (q, *J* = 270.5 Hz), 125.8, 125.9 (q, *J* = 3.6 Hz), 125.9, 127.4, 128.1, 128.7, 129.5 (q, *J* = 32.3 Hz), 130.0, 136.0, 137.3, 137.8, 141.1, 144.3, 145.8; ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 99.27; IR (KBr, neat) 3065, 2926, 2853, 1617, 1459, 1326, 1164, 1123, 1066, 1018, 817, 733 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{23}F_3NO_2S$ $(M + H)^+$ 470.1396, found 470.1392.

*4-(1-Tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridin-5-yl)benzonitrile (**9i**):*

Colorless solid; mp 154-156 ºC; R_f (hexane/ EtOAc 4:1) 0.4; yield 106 mg, 78%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25-1.31 (m, 1 H), 1.40-1.44 (m, 1 H), 1.81 (dt, *J* = 15.0 and 6.6 Hz, 1 H), 2.11 (dt, *J* = 18.6 and 7.2 Hz, 1 H), 2.43 (s, 3 H), 3.55 (ddd, *J* = 14.4, 9.6 and 3.6 Hz, 1 H), 3.78 (ddd, *J* = 14.4, 7.2 and 3.0 Hz, 1 H), 4.34 (s, 1 H), 7.06-7.09 (m, 3 H), 7.17 (t, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.36 (t, *J* = 7.8 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 8.01 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.2, 21.9, 22.0, 47.8, 55.6, 111.2, 118.9, 122.9, 123.6, 125.9, 127.6, 128.1, 129.1, 129.9, 132.8,

136.0, 137.2, 137.7, 141.0, 144.3, 145.4, 145.9; IR (KBr, neat) 3064, 2925, 2855, 2228, 1604, 1499, 1458, 1352, 1298, 1164, 1092, 1022, 987, 816, 737 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{23}N_2O_2S$ $(M + H)^+$ 427.1475, found 427.1474.

*Methyl 4-(1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridin-5-yl)benzoate (**9j**):*

Colorless solid; mp 120-122 °C; R_f (hexane/ EtOAc 9:1) 0.37; yield 110 mg, 75%; ^1H NMR (600 MHz, $CDCl_3$) δ 1.20-1.30 (m, 1 H), 1.35-1.45 (m, 1 H), 1.81 (dt, *J* = 18.6 and 5.4 Hz, 1 H), 2.10 (dt, *J* = 18.6 and 7.8 Hz, 1 H), 2.42 (s, 3 H), 3.52-3.57 (m, 1 H), 3.78-3.84 (m, 1 H), 3.91 (s, 3 H), 4.34 (s, 1 H), 7.03 (d, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 7.2 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 2 H), 7.93 (d, *J* = 7.8 Hz, 2 H), 8.02 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 21.8, 22.0, 47.8, 52.3, 55.6, 122.7, 123.6, 125.7, 127.3, 128.0, 128.3, 129.2, 129.9, 130.3, 135.9, 137.2, 137.9, 141.0, 144.2, 145.4, 145.9, 167.0; IR (KBr, neat) 3063, 2956, 2852, 1925, 1729, 1606, 1494, 1459, 1352, 1275, 1159, 1106, 1020, 987, 814, 765 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{26}NO_4S$ $(M + H)^+$ 460.1577, found 460.1580.

*5-(p-Tolyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9k**):*

Colorless solid; mp 125-127 °C; R_f (hexane/ EtOAc 9:1) 0.50; yield 114mg, 87%; ^1H NMR (600 MHz, $CDCl_3$) δ 1.20-1.30 (m, 1 H), 1.32-1.45 (m, 1 H), 1.87 (dt, *J* = 19.2 and 5.4 Hz, 1 H), 2.07 (dt, *J* = 19.2 and 7.2 Hz, 1 H), 2.32 (s, 3 H), 2.41 (s, 3 H), 3.52-3.57 (m, 1 H), 3.78-3.82 (m, 1 H), 4.25 (s, 1 H), 6.85 (d, *J* = 7.2 Hz, 2 H), 7.06 (d, *J* = 7.2 Hz, 2 H), 7.11-7.15 (m, 2 H), 7.23 (d, *J* = 7.2 Hz, 2 H), 7.30-7.34 (m, 1 H), 7.66 (d, *J* = 7.2 Hz, 2 H), 8.00 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 21.3, 21.8, 22.1, 47.9, 55.5, 122.4, 123.6, 125.5, 126.9, 128.1, 128.2, 129.6, 129.8, 136.1, 136.5, 136.6, 136.7, 138.8, 141.0, 144.0, 146.8; IR (KBr, neat) 3061, 2927, 2853, 1606, 1458, 1352, 1298, 1165, 1092, 1022, 986, 765 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{26}NO_2S$ $(M + H)^+$ 416.1679, found 416.1678.

*7-Methyl-5-phenyl-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9l**):*

Colorless solid; mp 127-129 ºC; R_f (hexane/ EtOAc 9:1) 0.45; yield 72 mg, 57%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20-1.28 (m, 1 H), 1.34-1.40 (m, 1 H), 1.84 (dt, *J* = 19.2 and 6.0 Hz, 1 H), 2.06 (dt, *J* = 19.2 and 7.2 Hz, 1 H), 2.31 (s, 3 H), 2.41 (s, 3 H), 3.51-3.56 (m, 1 H), 3.80-3.84 (m, 1 H), 4.24 (s, 1 H), 6.95-6.96 (m, 3 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 7.19-7.38 (m, 5 H), 7.66 (t, *J* = 7.8 Hz, 2 H), 7.89 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 21.5, 21.8, 22.0, 47.9, 55.7, 122.2, 124.5, 127.1, 127.7, 128.1, 128.3, 128.9, 129.8, 135.3, 136.1, 136.6, 137.6, 138.3, 140.0, 144.0, 146.9; IR (KBr, neat) 2924, 2855, 1603, 1493, 1451, 1347, 1164, 1091, 985, 817, 737 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{26}NO_2S$ $(M + H)^+$ 416.1679, found 416.1683.

*7-Methyl-5-(4-nitrophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9m**):*

Colorless solid; mp 130-132ºC; R_f (hexane/ EtOAc 9:1) 0.35; yield 79 mg, 56%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25-1.30 (m, 1 H), 1.40-1.45 (m, 1 H), 1.80 (dt, *J* = 18.6 and 6.0 Hz, 1 H), 2.11 (dt, *J* = 18.6 and 7.2 Hz, 1 H), 2.31 (s, 3 H), 2.43 (s, 3 H), 3.53-3.57 (m, 1 H), 3.80 (dt, *J* = 11.4 and 3.0 Hz, 1 H), 4.36 (s, 1 H), 6.90 (s, 1 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.90 (d, *J* = 7.8 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 21.5, 21.8, 22.0, 47.8, 55.1, 122.6, 124.2, 124.5, 128.0, 128.3, 129.1, 129.9, 130.7, 135.8, 136.0, 137.6, 138.2, 144.3, 145.6, 147.2, 148.3; IR (KBr, neat) 2925, 2855, 1600, 1523, 1347, 1164, 1091, 814, 777 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{25}N_2O_4S$ $(M + H)^+$ 461.1530, found 461.1529.

*7-Bromo-5-phenyl-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9n**):*

Colorless solid; mp 180-182 ºC; R_f (hexane/ EtOAc 9:1) 0.42; yield 64 mg, 52%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18-1.27 (m, 1 H), 1.35-1.39 (m, 1 H), 1.84 (dt, *J* = 19.2 and 6.0 Hz, 1 H), 2.06 (dt, *J* = 19.2 and 7.2 Hz, 1 H), 2.42 (s, 3 H), 3.51-3.56 (m, 1 H), 3.81 (ddd, *J* = 14.4,

6.0 and 3.0 Hz, 1 H), 4.26 (s, 1 H), 6.93 (d, *J* = 7.2 Hz, 2 H), 7.24-7.30 (m, 6 H), 7.45 (d, *J* = 8.4 Hz, 1 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.0, 21.8, 22.0, 47.9, 55.8, 119.7, 124.0, 126.9, 127.5, 128.1, 128.2, 129.1, 129.9, 130.1, 135.9, 136.3, 138.8, 139.0, 140.0, 144.2, 148.6; IR (KBr, neat) 2924, 2855, 1603, 1451, 1347, 1164, 1091, 985, 816, 737 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}BrNO_2S$ $(M + H)^+$ 480.0627, found 480.0626.

*2-Ethyl-5-phenyl-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9p**):*

Crystalline solid; mp 169-171 °C; R_f (hexane/ EtOAc 9:1) 0.60; yield 102 mg, 81%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.2 Hz, 3 H), 1.03-1.07 (m, 1 H), 1.24-1.29 (m, 1 H), 1.34 (dd, *J* = 13.8 and 7.2 Hz, 1 H), 1.49-1.55 (m, 1 H), 1.78 (dd, *J* = 19.2 and 6.6 Hz, 1 H), 2.12 (dt, *J* = 19.2 and 8.4 Hz, 1 H), 2.38 (s, 3 H), 4.06-4.09 (m, 1 H), 4.20 (s, 1 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 7.15 (s, 2 H), 7.19 (d, *J* = 7.2 Hz, 2 H), 7.23-7.29 (m, 3 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.64 (d, *J* = 7.8 Hz, 2 H), 8.04 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.2, 19.1, 21.8, 22.2, 24.4, 55.8, 57.8, 122.6, 123.5, 125.4, 127.0, 127.1, 128.1, 128.2, 128.8, 129.7, 134.2, 135.6, 137.7, 139.7, 141.8, 143.9, 146.5; IR (KBr, neat) 3062, 2966, 2870, 1674, 1598, 1493, 1457, 1347, 1169, 1092, 1024, 949, 763 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{28}NO_2S$ $(M + H)^+$ 430.1835, found 430.1833.

*5-(4-Fluorophenyl)-1-tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine (**9r**):*

Colorless gum; R_f (hexane/ EtOAc 9:13) 0.58; yield 70 mg, 52%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.24-1.30 (m, 1 H), 1.38-1.42 (m, 1 H), 1.85 (dt, *J* = 18.6 and 6.6 Hz, 1 H), 2.08 (dt, *J* = 18.6 and 7.2 Hz, 1 H), 2.42 (s, 3 H), 3.55 (ddd, *J* = 12.0, 9.0 and 2.4 Hz, 1 H), 3.79 (ddd, *J* = 14.4, 6.6 and 3.6 Hz, 1 H), 4.27 (s, 1 H), 6.90-6.96 (m, 4 H), 7.11 (d, *J* = 7.2 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 7.20-7.25 (m, 2 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 8.00 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.2, 21.8, 22.0, 47.9,

55.1, 115.7 (d, *J* = 21.0 Hz), 122.6, 123.6, 125.7, 127.2, 128.1, 129.7 (d, *J* = 7.5 Hz), 129.8, 135.5, 136.1, 136.8, 138.4, 140.9, 144.1, 146.4, 162.1 (d, *J* = 244.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 39.16; IR (KBr, neat) 2924, 2854, 1601, 1507, 1459, 1352, 1161, 1093, 815, 735 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{23}FNO_2S$ $(M + H)^+$ 420.1428, found 420.1430.

*4-Methyl-N-(3-(1-phenylnaphthalen-2-yl)propyl)benzenesulfonamide (**9s**):*

Colurless solid; mp 183-185 °C; R_f (hexane/ EtOAc 4:1) 0.43; yield 94 mg, 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.57-1.60 (m, 2 H), 2.33 (s, 3 H), 2.44 (t, *J* = 7.2 Hz, 2 H), 2.72-2.76 (m, 2 H), 4.44 (brs, 1 H), 7.12 (d, *J* = 7.2 Hz, 2 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 7.24-7.27 (m, 3 H), 7.33-7.36 (m, 1 H), 7.38-7.42 (m, 3 H), 7.60 (d, *J* = 7.8 Hz, 2 H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 30.7, 31.3, 42.8, 125.3, 126.1, 126.6, 127.2, 127.5, 127.9, 128.5, 128.6, 129.8, 130.4, 130.5, 132.2, 133.1, 136.2, 137.9, 138.2, 139.2, 143.4; IR (KBr, neat) 3060, 2960, 2855, 1597, 1490, 1454, 1328, 1160, 1094, 1023, 817, 750 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{26}NO_2S$ $(M + H)^+$ 416.1679, found 416.1675.

*4-Methyl-N-(3-(4-methyl-1-phenylnaphthalen-2-yl)propyl)benzenesulfonamide (**9t**):*

Colorless solid; mp 108-110 °C; R_f (hexane/ EtOAc 4:1) 0.41; yield 101mg, 74%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.60-1.66 (m, 2 H), 2.41 (s, 3 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 2.70 (s, 3 H), 2.77-2.81 (m, 2 H), 4.37 (brs, 1 H), 7.17-7.19 (m, 3 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.33-7.35 (m, 2 H), 7.41-7.47 (m, 4 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.98 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.6, 21.7, 30.7, 31.3, 42.9, 124.0, 125.1, 125.8, 127.2, 127.3, 128.2, 128.5, 129.8, 130.6, 130.7, 131.3, 133.2, 134.0, 135.8, 136.6, 137.1, 139.5, 143.4; IR (KBr, neat) 3063, 2925, 2854, 1598, 1494, 1442, 1326, 1160, 1095, 1032, 760 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{28}NO_2S$ $(M + H)^+$ 430.1835, found 430.1834.

*5-Phenyl-1-tosyl-2,3,4,4a,5,9b-hexahydro-1H-indeno[1,2-b]pyridine (**14a**):*

Colorless solid; mp 74-76 ^{o}C; R_f (hexane/ EtOAc 9:1) 0.5; yield 60 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91-1.00 (m, 2 H), 125-1.28 (m, 2 H), 2.44 (s, 3 H), 2.46-2.50 (m, 1 H), 2.86 (t, *J* = 12.8 Hz, 1 H), 3.86 (d, *J* = 14.0 Hz, 1 H), 4.41 (d, *J* = 6.0 Hz, 1 H), 5.47 (d, *J* = 5.6 Hz, 1 H), 7.19-7.25 (m, 6 H), 7.27-7.34 (m, 5 H), 7.84 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.8, 22.4, 23.2, 42.0, 44.9, 52.7, 60.5, 124.1, 125.8, 127.1, 127.2, 127.4, 127.7, 128.4, 129.6, 130.0, 138.1, 138.7, 141.1, 142.2, 143.4; IR (KBr, neat) 3028, 2926, 2856, 1598, 1495, 1452, 1332, 1162, 1022, 719 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{26}NO_2S$ $(M + H)^+$ 404.1679, found 404.1678.

*5-Phenyl-1-tosyl-2,3,4,4a,5,9b-hexahydro-1H-indeno[1,2-b]pyridine (**14b**):*

Colorless solid; mp 69-71 ^{o}C; R_f (hexane/ EtOAc 9:1) 0.21; yield 10 mg, 10%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.57-1.61 (m, 2 H), 182-1.85 (m, 1 H), 1.97 (dd, *J* = 13.2 and 9.2 Hz, 1 H), 2.21-2.28 (m, 1 H), 2.31 (s, 3 H), 2.42-2.47 (m, 1 H), 3.12 (dt, *J* = 12.8 and 3.6 Hz, 1 H), 3.82 (d, *J* = 12.7 Hz, 1 H), 5.10 (d, *J* = 5.6 Hz, 1 H), 6.98 (d, *J* = 7.2 Hz, 3 H), 7.16-7.26 (m, 10 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 24.0, 25.3, 40.1, 41.8, 42.0, 60.6, 126.3, 127.2, 127.7, 128.3, 128.4, 128.5, 129.2, 129.3, 129.6, 130.1, 136.9, 138.1, 139.7, 142.5; IR (KBr, neat) 3027, 2924, 1600, 1492, 1449, 1336, 1159, 1099, 701 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{26}NO_2S$ $(M + H)^+$ 404.1679, found 404.1681.

*5-Phenyl-2,3,4,4a,5,9b-hexahydro-1H-indeno[1,2-b]pyridine (**1**):*

Colorless solid; mp 85-87^{o}C; R_f (DCM/ MeOH 9:1) 0.33; yield 43mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98-1.12 (m, 2 H), 122-1.43 (m, 2 H), 2.57-2.66 (m, 2 H), 2.87 (d, *J* = 12.4 Hz, 1 H), 4.39 (d, *J* = 6.0 Hz, 1 H), 4.55 (d, *J* = 5. Hz, 1 H), 7.22-7.28 (m, 5 H), 7.29-7.36 (m, 3 H), 7.49 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.9, 25.2, 41.5, 46.0, 53.2, 61.0, 123.7, 126.1, 126.8, 127.1, 127.3, 128.4, 129.7, 139.2, 143.5, 143.9; IR (KBr, neat)

3440, 2926, 2853, 1641, 1453, 1154, 1076, 1031, 775, 703 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{20}N$ $(M + H)^+$ 250.1590, found 250.1589.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of all new compounds and X-ray crystallographic data of compounds **9d**, **9e**, **9k**, **9n** and **9p** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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