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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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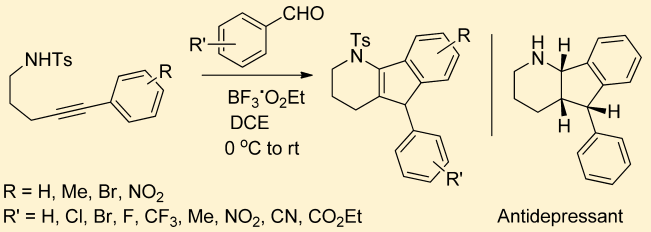
Supporting Information

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 the antidepressant agent (±)-5-phenyl-2,3,4,4a,5,9b-hexahydro-1*H*-indeno[1,2-*b*]pyridine.



INTRODUCTION

The tetrahydro-1*H*-indeno[1,2-*b*]pyridines are a class of nitrogen heterocycles containing a piperidine ring fused to 2,3-dihydro-1*H*-indene. Many of these molecules possess biological activity, like other nitrogen-containing alkaloids. For example, hexahydroindenopyridine (**1**; HHIP) is part of new class of compounds known for their antidepressant action[1] and inhibition of 11β-hydroxysteroid dehydrogenase enzyme 1 (11β-HSD1).[2] On the other hand, the 2,4a,9,9a-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

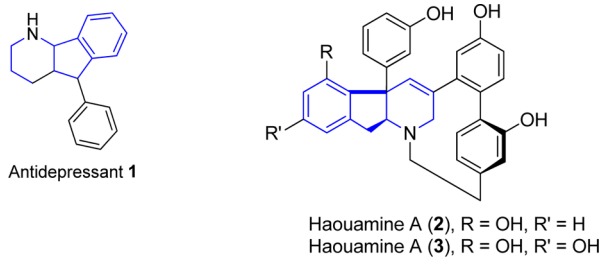
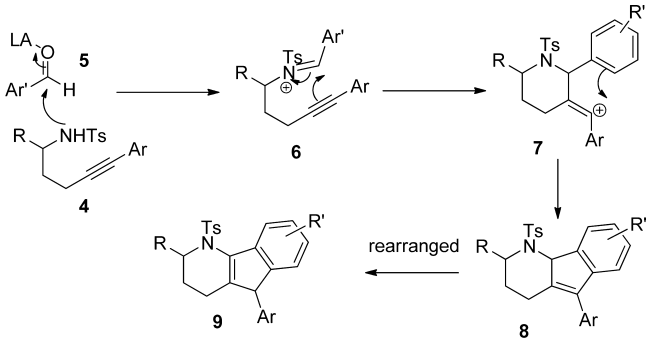


Figure 1. Biologically important indeno[1,2-*b*]pyridine.

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 is still in demand.

Cascade reactions are gaining importance in organic synthesis due to their ability to form complex molecular frameworks.[5] Similarly, the Friedel–Crafts reaction is one of the most important reactions 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 efficient methodologies for the synthesis of variously substituted heterocyclic compounds. Jin and co-workers have reported the triflic acid catalyzed cascade cyclization of arenyl enynes via acetylene cation cyclization and Friedel–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). A tandem aza-Prins cyclization and Friedel–Crafts type reaction may provide product **8**. The product **8** may rearrange to give the more stable enamide **9**.

Scheme 1. Possible Reaction Pathways



RESULTS AND DISCUSSION

In a 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 the 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 *p*-chlorobenzalde-

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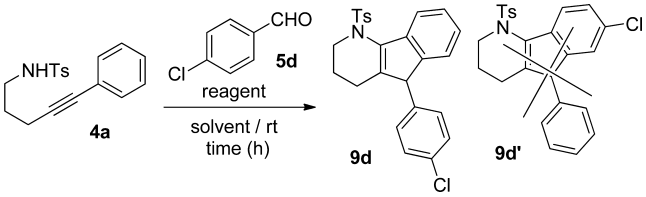
hyde in dichloromethane with 2 equiv of boron trifluoride etherate and 5-(4-chlorophenyl)-1-tosyl-2,3,4,5-tetrahydro-1*H*-indeno[1,2-*b*]pyridine (**9d**) was obtained in 45% yield in 12 h, instead of the proposed product 7-chloro-5-phenyl-1-tosyl-2,3,4,5-tetrahydro-1*H*-indeno[1,2-*b*]pyridine (**9d′**). The structure of compound **9d** was determined from NMR and X-ray crystallographic analysis (see the Supporting Information).[11] To optimize the reaction conditions, different reagents and solvents were screened and the results are summarized in Table 1. The reaction with 1 equiv of $BF_3{\cdot}OEt_2$ gave a 38%

Table 1. Optimization of the Reaction Conditions



entry	reagent (amt (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 yields. Compounds were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectrometry. [b]No reaction; starting material was recovered.

yield. The same reaction with 2 equiv of $BF_3{\cdot}OEt_2$ in 1,2-dichloroethane (DCE) gave a 70% yield, but in toluene it produced only a 30% yield. The reaction was also performed under 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, the starting material was recovered in 98% yield. Similarly, the metal salts $InCl_3$ and $FeCl_3$ gave 18 and 20% yields, respectively. Brønsted acids such as camphorsulfonic acid (CSA) failed to give the desired product, but starting material was recovered in 96% yield. On the other hand, triflic acid (TfOH) gave a 20% yield.

With these optimized conditions in hand, we further examined the scope of the reaction with a variety of substrates (Table 2). It was observed from 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, an aldehyde having a 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, a mixture of unidentified byproducts were observed. In contrast, a substrate (entry 15) having an electron-withdrawing nitro group on the aromatic ring failed to give the product. This is due to the destabilization of carbocation **10** formed during the reaction (Scheme 2). The structures of the products was determined by ^{1}H and ^{13}C NMR and X-ray crystallographic analysis of **9d,e**, **k,n** (see the Supporting Information).[11] The sharp downfield shift of the C-5H proton of compounds **9b,e** (δ 5.04 ppm) is due to the electron-withdrawing effect of ortho-substituted chloride and bromide groups on the aromatic ring. An ethyl-substituted alkyne (entry 16) gave trans product **9p** with respect to ethyl and phenyl at the 2- and 5-positions, the stereochemistry of which was determined by X-ray crystallographic analysis (see the Supporting Information).[11] The structures of the products in Table 2 are in contrast to the proposed structure in which the aromatic ring of the aldehyde is taking part in the Friedel−Crafts reaction (Scheme 1). However, in reality the aromatic ring of the alkyne side chain is taking part in the 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 nucleophilic attack by an alkyne group, which is subsequently attacked by a tosylamide group to form intermediate **11**, which after decomposition generates carbocation **12**. The carbocation **12** is attacked by an aryl group to give the Friedel−Crafts products **9a−r**.

There is an unexpected result in the reaction of alkyne **4a** with phenylacetaldehyde (**5o**) and 2-phenylpropanal (**5p**) (Table 3, entries 19 and 20), where sulfonamide-substituted aromatized products **9s,t** were obtained in 71 and 74% yields, respectively. The structures of compounds **9s,t** were determined from ^{1}H and ^{13}C NMR, COSEY, and HMQC analysis of compound **9s** (see the Supporting Information). Compound **9s** shows a broad singlet at δ 4.44 ppm in ^{1}H NMR and 18 signals in the aromatic region of ^{13}C NMR. Moreover, the proton at δ 4.44 ppm does not correlate with carbon in an HMQC analysis (see the Supporting Information). This indicates that this peak belongs to the −NH− proton of the −NHTs group. It was observed from 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,t** is shown in Scheme 3. In this case, aldehyde **5** enolized under Lewis acidic conditions, which subsequently reacted with alkyne **4** to form the Diels−Alder adduct **13**, which after aromatization gave naphthalene derivatives **9s,t**.[12]

The former strategy has been successfully applied to the synthesis of (±)-5-phenyl-2,3,4,4a,5,9b-hexahydro-1*H*-indeno-[1,2-*b*]pyridine (**1**). The compound **1** is considered as an antidepressant agent.[1a] The synthesis started with the reduction of (±)-**9a** with sodium cyanoborohydride and trifluoroacetic acid in dichloromethane to give diastereomeric mixtures of *cis*-(±)-**14a** and *trans*-(±)-**14b**, in 60 and 10% yields, respectively (Scheme 4). Compound (±)-**14a** after deprotection of the tosyl group with sodium naphthalenide gave the 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

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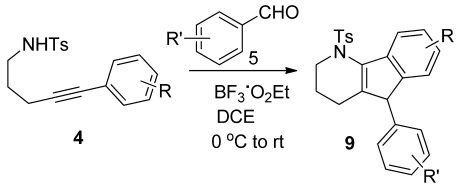
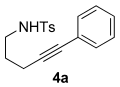
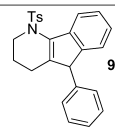
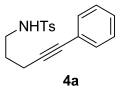
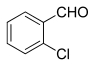
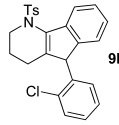
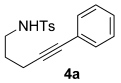
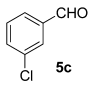
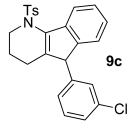
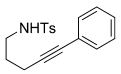
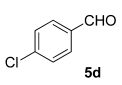
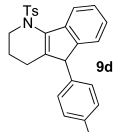
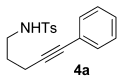
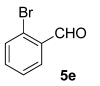
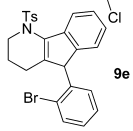
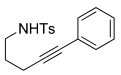
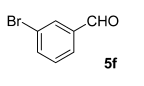
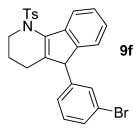
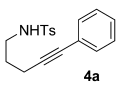
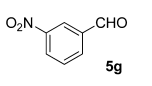
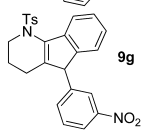
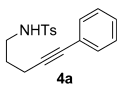
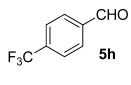
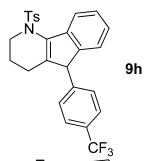
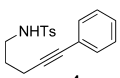
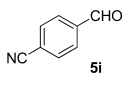
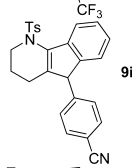
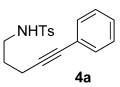
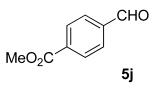
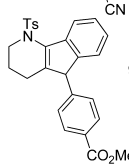
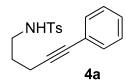
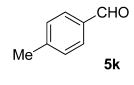
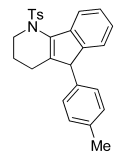
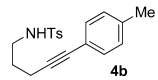
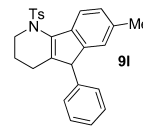
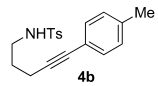
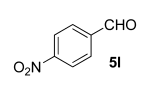
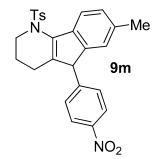
Table 2. Synthesis of Tetrahydro-1*H*-indeno[1,2-*b*]pyridine



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
8	 **4a**	 **5h**	 **9h**	61
9	 **4a**	 **5i**	 **9i**	78
10	 **4a**	 **5j**	 **9j**	75

Sl.No.	amide **4**	aldehyde **5**	product **9**	yield (%)[a]
11	 **4a**	 **5k**	 **9k**	87
12	 **4b**	 **5a**	 **9l**	57
13	 **4b**	 **5l**	 **9m**	56
14	**4c**	**5a**	**9n**	52
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 yields. Compounds were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectrometry.

indicates that in both compounds the configuration of the ring junction is same. As seen from the mechanism of formation of (±)-**14a** and (±)-**14b** from (±)-**9a** after protonation and subsequent addition of hydride, the stereochemistry of the ring junction should be cis (Scheme 5). Out of the two possible transition states **15a**,**b**, in their chair conformation, transition state **15a** is more favored 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.

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J. Org. Chem. 2016, 81, 8736−8743

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

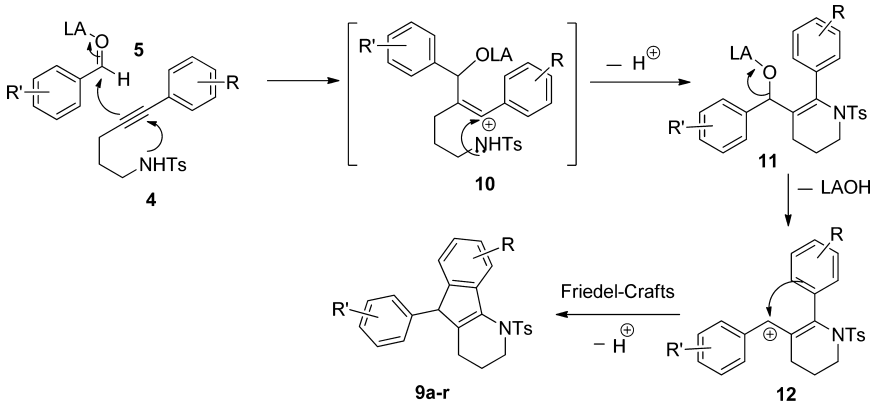
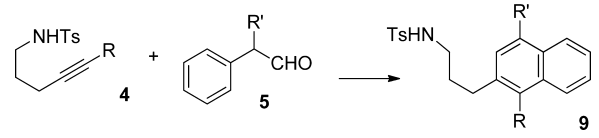
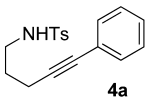
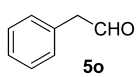
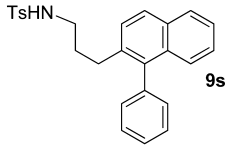
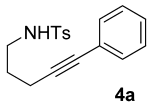
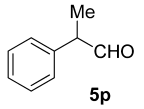
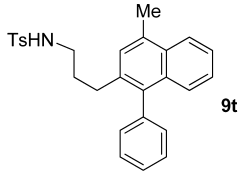
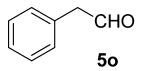
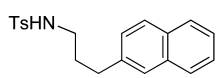


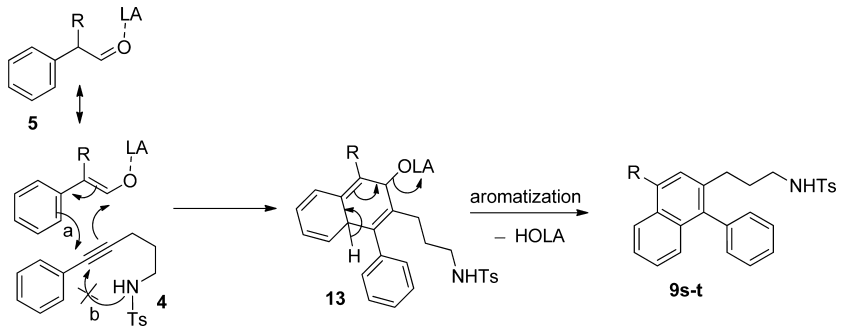
Table 3. Formation of Naphthalene Derivatives



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 yields. Compounds were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectrometry.

Scheme 3. Mechanism for the Formation of Naphthalene Derivatives



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). However, there was no such NOE correlation between the hydrogens C-9bH and C-5H in compound (±)-**14b**. Therefore, the configuration of the C-9bH and C-5H protons of compound (±)-**14b** is trans.

CONCLUSIONS

In conclusion, we have developed a mild and efficient method for the synthesis of tetrahydro-1*H*-indeno[1,2-*b*]-pyridine via a 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

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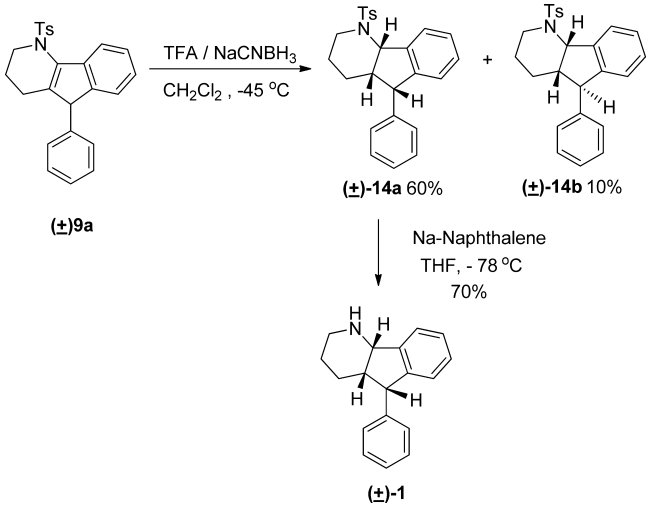
Scheme 4. Total Synthesis of (±)-5-Phenyl-2,3,4,4*a*,5,9*b*-hexahydro-1*H*-indeno[1,2-*b*]pyridine



synthesis of the biologically active molecule (±)-5-phenyl-2,3,4,4a,5,9b-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 infrared (FT-IR) spectra were recorded as neat liquids 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 a Q-TOF mass spectrometer.

Synthesis of Sulfonamide. The starting materials, 4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamide (**4a**−**f**) derivatives, were prepared by the literature procedure.[13] Compounds **4a**,**f** 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 alkynamine (100 mg, 0.3 mmol) in dry 1,2-dichloroethane (2 mL) was added benzaldehyde (35 mg, 0.33 mmol) at 0 °C, followed by $BF_3{\cdot}OEt_2$ (84 mg, 0.6 mmol). The reaction mixture was warmed to room temperature and kept for 12 h. After completion of the reaction, as determined by TLC,

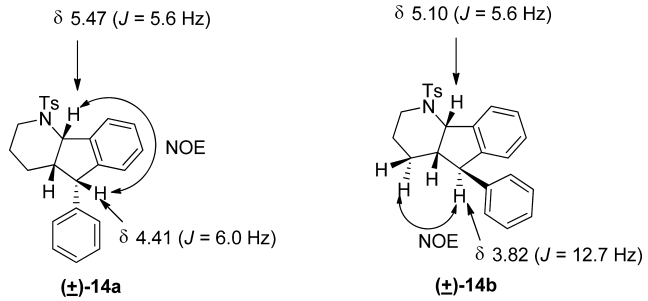


Figure 2. Coupling constants and NOE of compounds (±)-**14a** and (±)-**14b**.

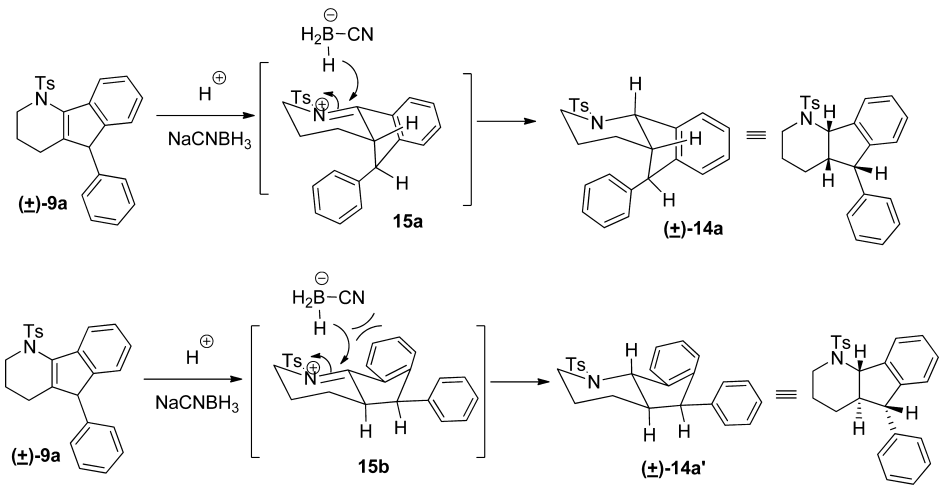
dichloroethane was added to the reaction mixture, which was then washed with saturated sodium bicarbonate and brine solutions and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by column chromatography using ethyl acetate and hexane as eluents.

*4-Methyl-N-(5-(p-tolyl)pent-4-yn-1-yl)benzenesulfonamide (**4b**):* colorless solid; mp 99−101 °C; 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 °C; R_f (hexane/EtOAc 4/2) 0.6; yield 262 mg, 67%; ^1H 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%; ^1H 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

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



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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%; ^1H 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%; ^1H 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%; ^1H 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%; ^1H NMR (600 MHz, $CDCl_3$) 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%; ^1H 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%; ^1H 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%; ^1H 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%; ^1H 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 °C; R_f (hexane/EtOAc 9/1) 0.45; yield 91 mg, 61%; ^1H 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.

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J. Org. Chem. 2016, 81, 8736−8743

*4-(1-Tosyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridin-5-yl)-benzonitrile (**9i**):* colorless solid; mp 154−156 °C; 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%; ^{1}H 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 114 mg, 87%; ^{1}H 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 °C; 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 130−132 °C; 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 °C; 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**):* colorless 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 101 mg, 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,

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J. Org. Chem. 2016, 81, 8736−8743

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 °C; R_f (hexane/EtOAc 9/1) 0.5; yield 60 mg, 60%; ^1H 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 °C; R_f (hexane/EtOAc 9/1) 0.21; yield 10 mg, 10%; ^1H 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 °C; R_f (DCM/MeOH 9/1) 0.33; yield 43 mg, 70%; ^1H 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00988.

Crystallographic data (CIF)
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Crystallographic data (CIF)
Crystallographic data (CIF)
^1H and ^{13}C NMR spectra of all new compounds and X-ray crystallographic data of compounds **9d,e,k,n,p** (PDF)
HRMS spectra of all new compounds (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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