DOI: 10.1002/adsc.201500449

Indium(III)-Catalyzed Cyclization of Aromatic 5-Enynamides: Facile Synthesis of 2-Aminonaphthalenes, 2-Amino-1*H*-indenes, and 2,3-Dihydro-1*H*-indeno[2,1-*b*]pyridines

Ming-Chang P. Yeh,[a,*] Chia-Jung Liang,[a] Hsiao-Feng Chen,[a] and Yu-Ting Weng[a]

[a] Department of Chemistry, National Taiwan Normal University, 88 Ding-Jou Road, Section 4, Taipei 11677, Taiwan, Republic of China
Fax: (+886)-2-2932-4249; e-mail: cheyeh@ntnu.edu.tw

Received: May 6, 2015; Revised: July 30, 2015; Published online: October 14, 2015

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500449.

Abstract: Indium(III)-catalyzed cyclization reactions of aromatic 5-enynamides were studied. Indium triflate enabled the efficient synthesis of 2-aminonaphthalenes and 2-amino-1*H*-indenes from aromatic *N*-methyl-*N*-tosyl-ynamides bearing an *ortho*-vinyl and -isobutenyl group, respectively. The aromatic *N*-3-arylpropargylynamides bearing an *ortho-gem*-dihalovinyl subunit underwent a tandem cyclization/carbobromination reaction in the presence of indium tribromide to provide the dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine derivatives in good yields.

Keywords: amides; bromine; cyclization; indium

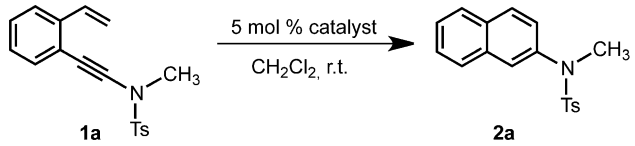
Introduction

In recent years, ynamides have emerged as versatile building blocks in organic synthesis.[1] Reactive keteniminium ions, generated *in situ* from the reaction of ynamides with a metal catalyst or an acid, are strong electrophilic anchors for cyclization with π-nucleophiles, providing an easy access to a variety of useful nitrogen-containing heterocycles.[2] Many transition metal catalysts, including Rh,[3] Pd,[4] Pt,[5] Cu,[6] Ag,[7] Co,[8] and gold,[9] have been employed for intramolecular cyclization of ynamides with an alkene or alkyne. In contrast to various transition metal-catalyzed cyclization reactions, acid-promoted intramolecular cyclizations of ynamides with tethered unsaturated C–C bonds were limited to the $HNTf_2$-catalyzed cyclization of aromatic ynamides,[10a] the TsOH-catalyzed cyclization of ynamides with an alkyne,[10b] the AgOTf-catalyzed cycloisomerization reactions of heteroaromatic ynamides[11a] and epoxy ynamides,[11b] and the $BF_3{\cdot}OEt_2$-promoted intramolecular ring-closing metathesis of ynamides bearing an aldehyde.[12] In this report, we describe our results on a simple catalytic process that transforms aromatic 5-enynamides, in the presence of a catalytic amount of InX_3 (X = OTf or Br), into nitrogen-containing bi- and tricycles. Under mild reaction conditions, aromatic ynamides bearing a vinyl group at the *ortho* position of the phenyl ring afforded 2-aminonaphthalenes, whereas 2-amino-1*H*-indenes were available in excellent yields from the cyclization of aromatic ynamides with an *ortho*-isobutenyl group. Moreover, the reaction of aromatic *N*-3-arylpropargyl-*ortho-gem*-dibromovinyl-ynamides with $InBr_3$ proceeded *via* a tandem enynamide cyclization/carbobromination to furnish the dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine derivatives.

Results and Discussion

Various synthetic methods for the synthesis of ynamides have been documented.[13] The aromatic 5-enynamide **1a**, as the cyclization precursor, was prepared starting from 2-bromobenzaldehyde (see the Supporting Information for details)[14] and was treated with a range of Brønsted and Lewis acids (Table 1). Our first optimization study consisted of subjecting 5 mol% of $HNTf_2$ to a solution of the 5-enynamide **1a** in CH_2Cl_2 (DCM) at 30 °C. After 2 min, **1a** led to the 2-aminonaphthalene derivative **2a** in 69% yield (Table 1, entry 1). On the other hand, reaction of **1a** with TfOH (5 mol%) in DCM at room temperature for 3 d produced **2a** in only 32% yield (Table 1, entry 2). Next, the use of 5 mol% of the Au(I) cation, formed *in situ* from $AuCl(PPh_3)$ and AgOTf, in DCM at room temperature for 5 d led to a 49% yield of **2a** (Table 1, entry 3). It has been known that AgOTf is capable of catalyzing intramolecular hydroarylation

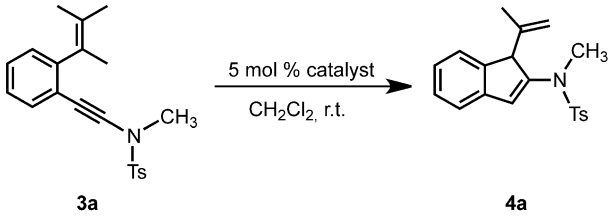
Table 1. Screen of catalysts for the formation of 2-aminonaphthalene **2a**.[a]



Entry	Catalyst	Time	Yield [%][b]
1	$NHTf_2$	2 min	69
2	TfOH	3 d	32
3	$Ph_3PAuCl/AgOTf$	5 d	49
4	AgOTf	2 d	47
5	$Fe(OTf)_3$	3 h	74
6	$Sc(OTf)_3$	18 h	71
7	$Sn(OTf)_2$	30 min	76
8	$In(OTf)_3$	8 h	94
9	$In(OTf)_3$[c]	13 h	75
10	$InCl_3$	1 d	N.R.

[a] *Reaction conditions:* **1a** (0.25 mmol), catalyst (1.25×10^{-2} mmol), DCM (2.5 mL).
[b] Yields obtained from column chromatography over silica gel.
[c] $In(OTf)_3$ (3 mol%) was used.

Table 2. Screen of catalysts for the formation of 2-amino-1*H*-indene **4a**.[a]



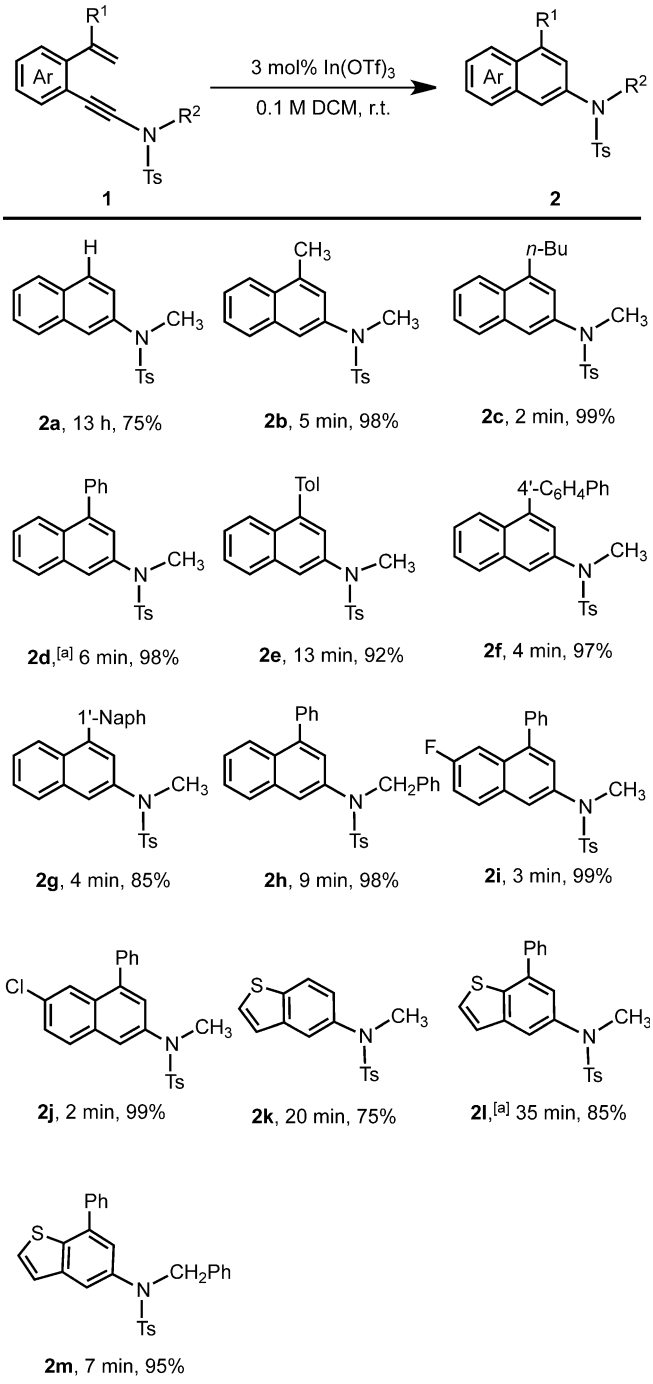
Entry	Catalyst	Time	Yield [%][b]
1	$In(OTf)_3$	10 min	98
2	$FeCl_3$	10 min	74
3	$Yb(OTf)_3$	10 d	84
4	$Sn(OTf)_2$	10 min	74
5	$NHTf_2$	45 min	55
6	$In(NTf_2)_3$	10 min	67
7	$SnCl_4$	10 min	51
8	BF_3•OEt	10 min	44
9	$InBr_3$	10 min	60

[a] *Reaction conditions:* **3a** (0.25 mmol), catalyst (1.25×10^{-2} mmol), DCM (2.5 mL).
[b] Yields obtained from column chromatography over silica gel.

of aromatic ynamide-tethered pyrroles to afford pyrrolo[1,2-*a*]quinolines in good yields.[11a] However, when subjected to 5 mol% of AgOTf in DCM for 2 d, **1a** delivered **2a** in only 47% yield (Table 1, entry 4). Other Lewis acids (5 mol%), including $Fe(OTf)_3$, $Sc(OTf)_3$, and $Sn(OTf)_2$, were capable of promoting the cycloisomerization reaction to produce **2a** in 71–76% yields (Table 1, entries 5–7). To our delight, when **1a** was treated with 5 mol% of $In(OTf)_3$ in DCM at room temperature for 8 h, **2a** was isolated in 94% yield (Table 1, entry 8). With a lower loading of $In(OTf)_3$ (3 mol%) in DCM, the reaction required a prolonged reaction time (13 h) but still provided **2a** in 75% yield (Table 1, entry 9). Unfortunately, the cycloisomerization reaction failed in the presence of $InCl_3$ and the reactant **1a** was recovered quantitatively. (Table 1, entry 10).

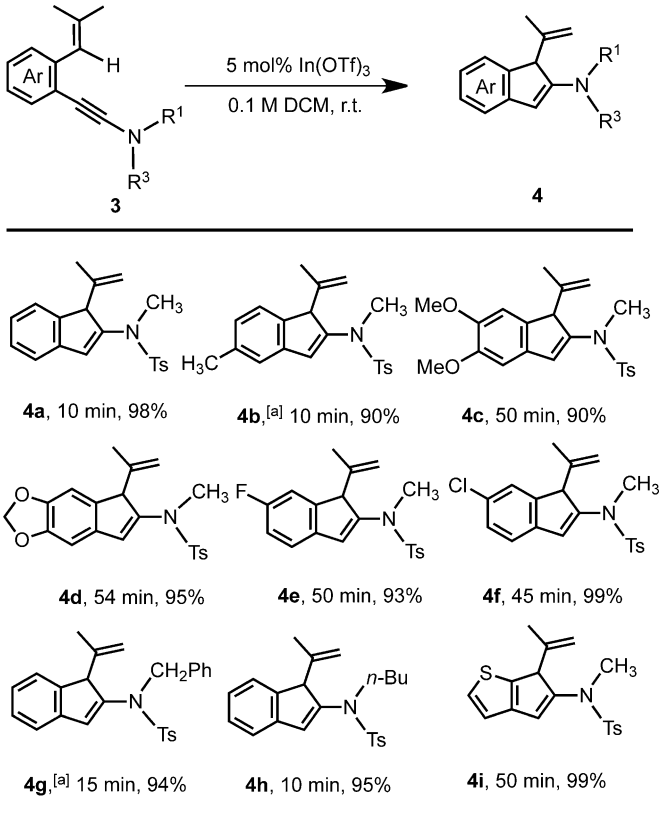
Next, the aromatic *ortho*-isobutenyl-substituted enynamide **3a** was investigated. Interestingly, treatment of **3a** with a catalytic amount of $In(OTf)_3$ (5 mol%) in DCM at room temperature under nitrogen for 10 min afforded a compound identified as the 2-amino-1*H*-indene derivative **4a** in 98% isolated yield after column chromatography over silica gel (Table 2, entry 1). Although various acids, including $FeCl_3$ (10 min, 74%), $Yb(OTf)_3$ (10 d, 84%), $Sn(OTf)_2$ (10 min, 74%), $NHTf_2$ (45 min, 55%), $In(NTf_2)_3$ (10 min, 67%), $SnCl_4$ (10 min, 51%), BF_3·OEt_2 (10 min, 44%), and $InBr_3$ (10 min, 60%), were capable of transforming **3a** into **4a** (Table 2 entries 2–9), 0.05 molar equiv. of $In(OTf)_3$ in DCM at room temperature for 10 min were the optimal reaction conditions, which delivered **4a** in 98% isolated yield. Therefore, $In(OTf)_3$ was chosen as the catalyst of performing the cycloisomerization reactions for both starting substrates **1** and **3**.

Having identified the optimal reaction conditions for the synthesis of 2-aminonaphthalene derivative **2a** and 2-amino-1*H*-indene derivative **4a**, a survey of various substrates was conducted to evaluate the scope and limitation of the cycloisomerization reactions. Results are summarized in Scheme 1 and Scheme 2, respectively. Unlike the parent substrate **1a** requiring a lengthy reaction time, aromatic 5-enynamides **1b–g**, having an alkyl or aryl group substituent at the internal olefin carbon, were more reactive and afforded the corresponding 2-aminonaphthalene derivatives **2b–g**[15] in minutes (2–13 min) and in excellent yields (85–99%). Compound **1h** bearing a benzyl protecting group on the nitrogen atom also cyclized efficiently to generate the desired product **2h** in 9 min and in 98% yield. The halogenated aromatic 5-enynamides, **1i** and **1j**, were also reactive and afforded quantitatively the desired cyclization products **2i** and **2j**, respectively. The *ortho*-vinyl-tethered thiophenylynamides **1k–m** were also tolerated and cycloisomerized to the corre-



[a] The structure is confirmed by X-ray diffraction analysis.

Scheme 1. Substrate scope of the $In(OTf)_3$-catalyzed cycloisomerization of **1**. *Reaction conditions*: **1a** (0.25 mmol), $In(OTf)_3$ (7.5×10^{-3} mmol), DCM (2.5 mL); isolated yields.



[a] The structure is confirmed by X-ray diffraction analysis.

Scheme 2. Substrate scope of the $In(OTf)_3$-catalyzed cycloisomerization of **3**. *Reaction conditions*: **3** (0.25 mmol), $In(OTf)_3$ (1.25×10^{-2} mmol), DCM (2.5 mL); isolated yields.

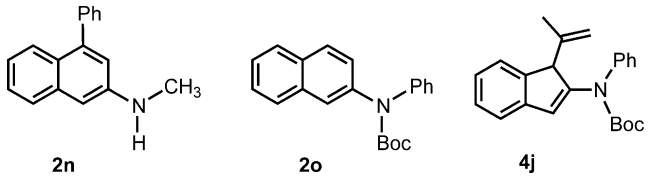
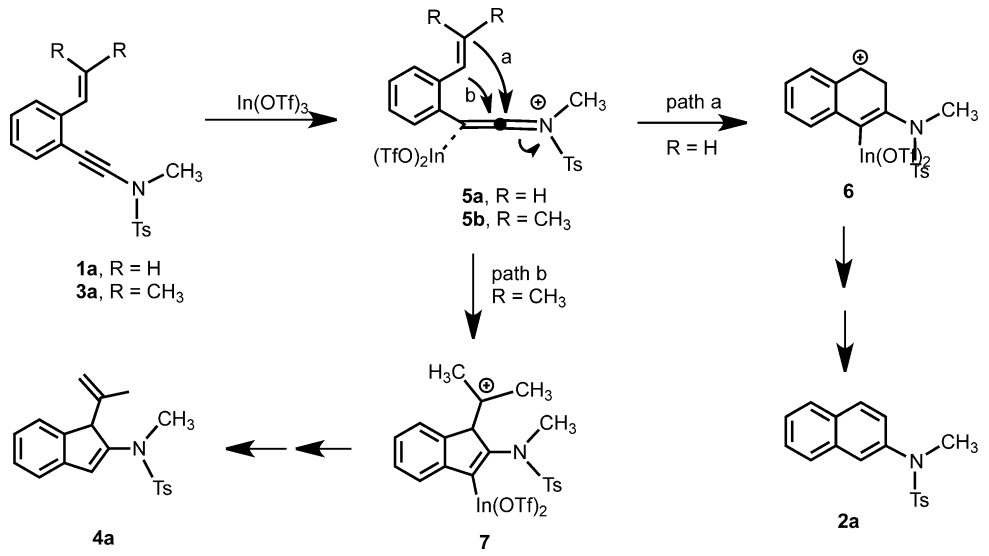


Figure 1. Structures of **2n**, **2o**, and **4j**.

sponding 5-aminobenzo[*b*]thiophenes **2k**–**m**[15] in 75–95% yields. To explore the possibility of deprotecting the *N*-tosyl group, compound **2d** was treated with sodium/naphthalene in THF at −78 °C.[16] The reaction was stirred for 30 min and delivered 4-phenyl-2-aminonaphthalene (**2n**) (Figure 1) in 54% yield after an aqueous work-up and column chromatography over silica gel. Moreover, substrate **1o**, bearing an *N*-Boc(Ph) group, was subjected to 3 mol% $In(OTf)_3$ in DCM. The cycloisomerization reaction required 70 min and afforded 2-aminonaphthalene derivative **2o** (Figure 1) in 64% isolated yield. Furthermore, it should be noted that an important gold(I)-catalyzed cyclization of aromatic ynamides with ethoxyethene was also known to afford 2-aminonaphthalenes in good yields.[17]

As revealed in Scheme 2, aromatic *ortho*-isobutenyl-substituted enynamides **3a**–**d** bearing an electron-neutral or electron-rich substituent on the phenyl ring were equally reactive and produced the desired 2-amino-1*H*-indenes **4a**–**d**[15] in excellent yields (90–98%). It is noteworthy that a fluorine or chlorine



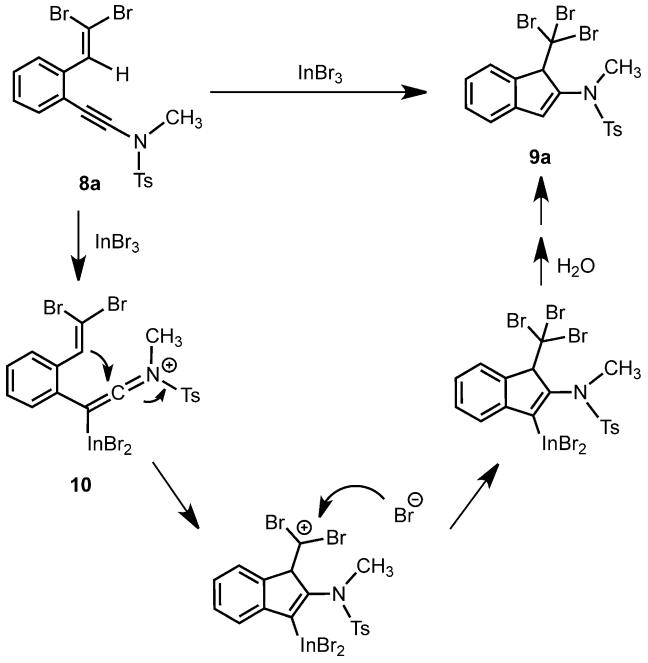
Scheme 3. Postulated reaction paths for the formation of **2** and **4**.

atom on the phenyl ring did not interfere with the reactivity of the catalyst and **3e** and **3f** delivered **4e** and **4f** in 93 and 99% yield, respectively. Switching the methyl protecting group to a benzyl (**3g**) or *n*-butyl group (**3h**) on the nitrogen atom did not show any influence on the cyclization. The corresponding 2-amino-1*H*- indene derivatives **4g**[15] and **4h** were isolated in respectively 94 and 95% yield. The 5-aminocyclopenta[*b*]thiophene derivative **4i** was also available in quantitative yield from the *ortho*-isobutenyl-substituted thiophenylynamide **3i**. When treated with 0.05 equiv. of $In(OTf)_3$ in DCM, substrate **3j**, bearing an *N*-Boc(Ph) tether, also gave the corresponding 2-amino-1*H*-indene derivatives **4j** (Figure 1) in 2 min and in 51% isolated yield. The current synthetic method employing a catalytic amount of $In(OTf)_3$ with the *ortho*-isobutenyl-tethered ynamides provides a good alternative to 3-alkenyl-substituted 2-aminoindenes, which may be applied to the synthesis of bioactive molecules.[18]

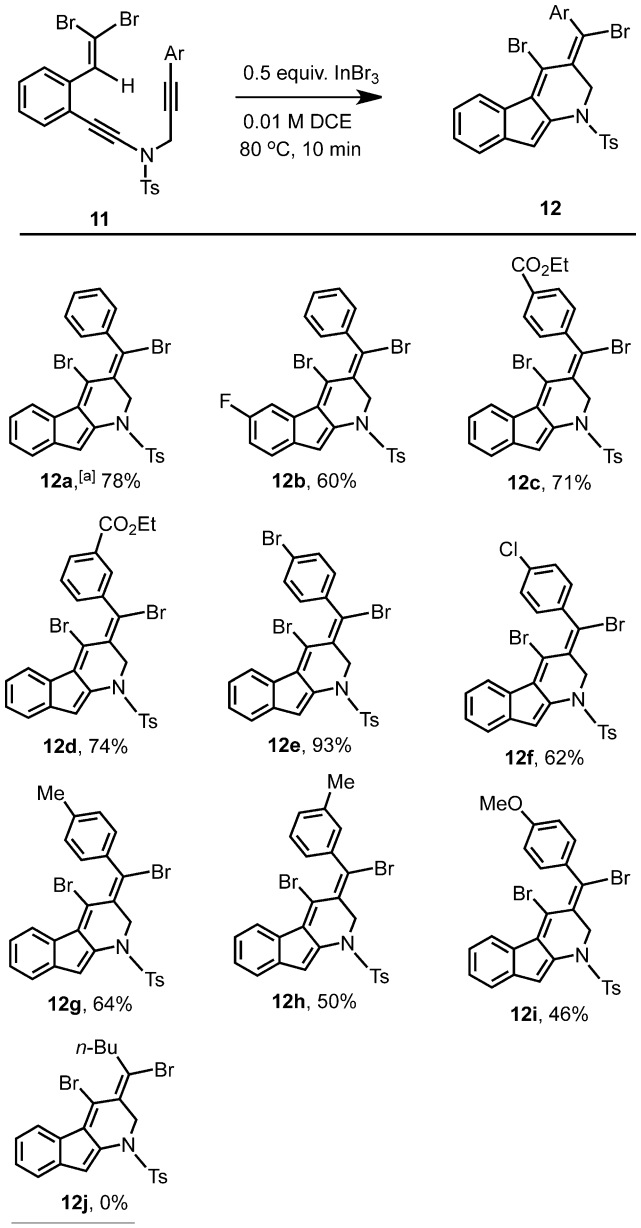
Formation of 2-aminonaphthalene **2a** and 2-amino-1*H*-indene **4a** can be explained by reaction paths depicted in Scheme 3. First, metalation of the electron-rich alkyne of the enynamide **1a** with $In(OTf)_3$ would form a reactive keteniminium ion **5**. Attack of the vinyl group at the α-position of **5a** (R = H) *via* a *6-exo-dig* fashion gives the benzylic cation **6**, which undergoes deprotonation followed by protodemetalation to produce **2a**, whereas a *5-exo-dig* cyclization of **5b** ($R = CH_3$) occurred, leading to the tertiary cationic intermediate **7**, which produces **4a** after deprotonation followed by protodemetalation. In both cases, the weakly nucleophilic anion (TfO^-, the conjugated base) does not add to the keteniminium ion **5** or at carbocation centers of **6** and **7**. It is worth mentioning that In(III)-promoted cyclization reactions of π-nucleophiles with alkynes for the construction of various carbocycles and heterocycles have also been studied.[19]

Next, substrate **8** possessing an *ortho-gem*-dibromovinyl subunit was investigated for the intramolecular cyclization reaction. Among the Lewis acids [$In(OTf)_3$, $FeCl_3$, $InBr_3$, and $AuCl(PPh_3)/AgOTf$] screened, $InBr_3$ was found to have a promising tendency to yield 1-tribromomethyl-2-amino-1*H*- indene derivative **9**. Thus, treatment of **8a** with 1.2 molar equiv. of $InBr_3$ at room temperature under nitrogen for 10 min produced the carbobromination product **9a**[15] in 60% yield (Scheme 4). Substrate **8b** bearing a fluorine at C-5 of the phenyl ring also gave the corresponding 1-tribromomethyl-2-amino-1*H*- indene **9b** in 55% yield. In this transformation, the activation of **8a** with $InBr_3$ would form the reactive keteniminium intermediate **10** (Scheme 5). Attack of the *gem*-dibromovinyl group at the α-carbon of the keteniminium ion **10** generated the transient carbonium ion. Addition of a bromide to the cation center followed by

Scheme 4. Synthesis of 1-tribromomethyl-2-amino- 1*H*-indenes **9a** and **9b**. *Reaction conditions*: **8** (0.20 mmol), $InBr_3$ (0.24 mmol), DCM (2.0 mL); isolated yields.



Scheme 5. Suggested mechanism for the formation of **9a**.

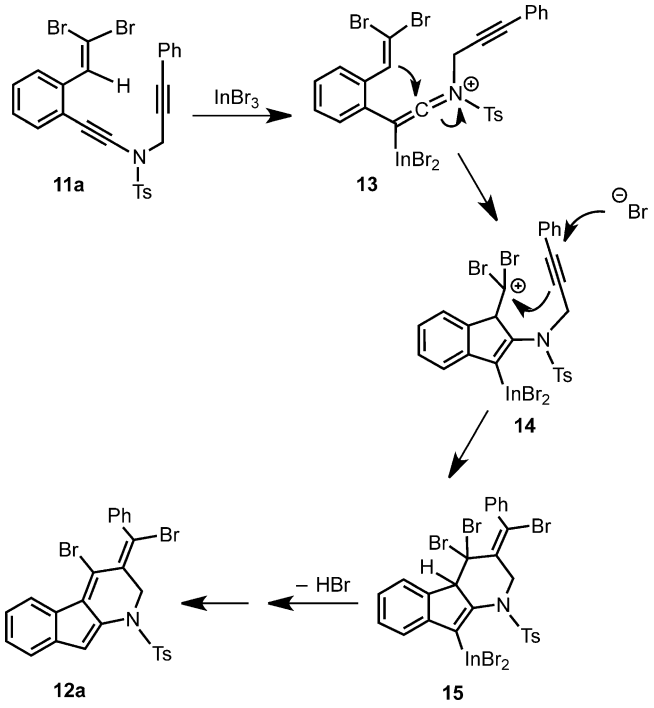


[a] The structure is confirmed by X-ray diffraction analysis.

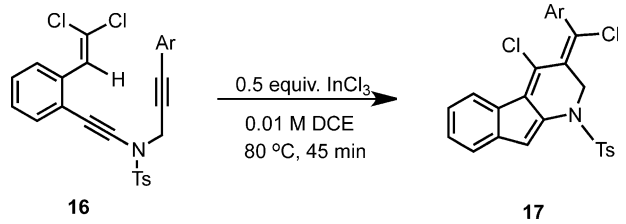
Scheme 6. Synthesis of the dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine derivatives **12**. *Reaction conditions:* **11** (0.2 mmol), $InBr_3$ (0.1 mmol), DCE (20 mL), 80 °C; isolated yields.

protodemetalation during an aqueous process furnished 1-tribromomethyl-2-amino-1*H*-indene derivative **9a**. Unfortunately, substrate **8c**, bearing an *N*-Boc(Ph) group, decomposed upon treatment with $InBr_3$ under the same reaction conditions. Interestingly, when switching the alkyl protecting group to a 3-phenylpropargyl moiety on the nitrogen atom, for example **11a**, a consecutive cyclization occurred to furnish the dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine derivative **12a** (Scheme 6). Thus, treatment of **11a** with 1.2 equiv. of $InBr_3$ in DCM at 30 °C for 10 min gave a 42% isolated yield of **12a**.[15] Compound **12** may have potential applications in medicinal chemistry since several indeno[2,1-*b*]pyridine-based compounds have been reported to possess pharmacological activities.[20] Further optimization studies had shown that the yield of **12a** increased to 78% when **11a** was treated with 0.5 molar equiv. of $InBr_3$ in dichloroethane (DCE) at a higher temperature (80 °C). Next, a series of aromatic *N*-3-arylpropargyl-*ortho-gem*-dibromovinyl-ynamides, **11b–i**, were submitted to the tandem cyclization conditions employing 0.5 molar equiv. of $InBr_3$ at 80 °C in DCE and the results are shown in Scheme 6. The cyclization proceeded smoothly with electron-neutral and electron-deficient 3-arylpropargyl groups to give the desired cyclization products in yields ranging from 60–78% (**12a–d**). Substrates with a halogen atom at the phenyl group, **11e** and **11f**, were also operative and delivered **12e** and **12f** in 93 and 62% yield, respectively. Substrates **11g–i**, containing electron-donating methyl and methoxy substituents on the phenyl ring, afforded the desired products in low yields (46–64%). Unfortunately, substrate **11j**, with an *n*-butyl substituent at the terminus of the alkyne, gave an unidentified mixture of compounds.

A suggested reaction path for the formation of the representative dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine **12a** from **11a** is shown in Scheme 7. The reactive keteniminium cation **13**, generated from metalation of the ynamide, was attacked by the pendant dibromoalkene by a *5-exo-dig* cycliza-



Scheme 7. Mechanism for the formation of the dibrominated 1*H*-indeno[2,1-*b*]pyridine derivative **12a**.



a : Ar = phenyl, 63%
b : Ar = 4-methylphenyl, 51%
c : Ar = 3-methylphenyl, 52%
d : Ar = 4-methoxyphenyl, 50%
e : Ar = 4-bromophenyl, 72%
f : Ar = 4-carbethoxyphenyl, 53%

Scheme 8. Synthesis of the dichlorinated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine derivatives **17**.

tion to afford the cation **14**. Then, an anti-addition of a bromide and the carbonium ion across the alkyne occurred, giving the tribrominated compound **15**, which underwent dehydrobromination followed by protodemetalation to furnish the dibrominated 2,3-dihydro-1*H*- indeno[2,1-*b*]pyridine derivative **12a**.

The cyclization reactions were also effective with aromatic *N*-3-arylpropargyl-*ortho-gem*-dichlorovinylynamides **16a–f**, albeit in slightly lower yields. Thus, treatment of ynamides **16a–f** with 0.5 molar equiv. of $InCl_3$ in DCE (0.01 M) at 80 °C for 45 min generated the desired products **17a–f**[15] in 50–72% yields (Scheme 8).

Conclusions

In conclusion, this report demonstrates a convenient method for the synthesis of 2-aminonaphthalenes and 2-amino-1*H*-indenes from aromatic *ortho*-alkenyl-ynamides employing indium triflate as the catalyst. The dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]- pyridines are available from indium tribromide-promoted ynamide cyclization/carbobromination of aromatic *N*-3-arylpropargyl-*ortho-gem*-dihalo-vinylynamides. These reactions have advantages as they involve milder reaction conditions, short reaction times, and good to excellent yields. Especially, the facile approach to the dibrominated 2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine derivatives from easily available starting substrates may have further applications.

Experimental Section

Typical Procedure for the Preparation of *N*,4-Dimethyl-*N*-(naphthalen-2-yl)benzenesulfonamide (2a) in Dichloromethane

To a solution of *N*,4-dimethyl-*N*-[(2-vinylphenyl)ethynyl]-benzenesulfonamide (**1a**) (78 mg, 0.25 mmol) in dichloromethane (2.5 mL) was added $In(OTf)_3$ (4.0 mg, 0.0075 mmol) at room temperature under nitrogen. The reaction mixture was stirred until no trace of **1a** was detected on TLC, and concentrated under reduced pressure to give a crude oil. The resulting crude mixture was purified by flash column chromatography [silica gel, 5% EtOAc in hexanes] to afford product **2a** as a pale yellow oil; yield: 58 mg (0.19 mmol, 75%).

The products **2b–m** were prepared in a similar manner.

***N*,4-Dimethyl-*N*-(naphthalen-2-yl)benzenesulfonamide (2a):** yield: 58 mg (0.19 mmol, 75%); yellow oil; IR (CH_2Cl_2): ν = 3055, 2925, 1598, 1466, 1356, 1162, 819, 752, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.72 (m, 1H), 7.51–7.46 (m,3H), 7.43 (d, J = 8.3 Hz, 2H), 7.30 (dd, J = 8.8, 2.2 Hz, 1H) 7.21 (d, J = 8.2 Hz, 2H), 3.26 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 139.2, 133.5, 133.2, 132.1, 129.3 (2C), 128.6, 127.9 (2C), 127.9, 127.6, 126.4, 126.3, 125.1, 124.6, 38.2, 21.5; MS (APCI): *m/e* (%) = 312.1 ($[M+H]^+$, 100), 249.2 (1), 198.1 (2), 157.1 (4); HR-MS (APCI): *m/e* = 312.1055, calcd. for $C_{18}H_{18}NO_2S$ $[M+H]^+$: 312.1058.

***N*,4-Dimethyl-*N*-(4-methylnaphthalen-2-yl)benzenesulfonamide (2b):** yield: 80 mg (0.25 mmol, 98%) white solid; mp 88–89 °C; IR (CH_2Cl_2): ν = 3064, 2924, 1600, 1466, 1350, 1170, 876, 806, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.54–7.46 (m, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.28 (s, 1H), 7.24–7.18 (m, 3H), 3.23 (s, 3H), 2.64 (s, 3H), 2.41(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 138.8, 135.4, 133.6, 133.4, 131.4, 129.3 (2C), 128.5, 127.9 (2C), 126.1, 126.1,126.0, 123.9, 122.6, 38.3, 21.5, 19.3; MS (ESI): *m/e* (%) = 326.05 ($[M+H]^+$, 100), 321.17 (9), 171.21 (32), 154.16 (2); HR-MS (ESI): *m/e* = 326.1220, calcd. for $C_{19}H_{20}NO_2S$ $[M+H]^+$: 326.1215.

***N*-(4-Butylnaphthalen-2-yl)-*N*,4-dimethylbenzenesulfonamide (2c):** yield: 91 mg (0.25 mmol, 99%); pale yellow solid; mp 76–77 °C; IR (CH_2Cl_2): ν = 3063, 2929, 2872, 1599, 1459, 1349, 1171, 808, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.3 Hz,1 H), 7.73 (d, J = 8.5 Hz, 1 H), 7.53–7.45 (m, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.35 (d, J = 2.1 Hz, 1 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 2.1 Hz, 1 H), 3.25 (s, 3 H), 3.00 (t, J = 7.8 Hz, 2 H), 2.40 (s, 3 H), 1.72–1.58 (m, 2 H), 1.40 (sextet, J = 7.44 Hz, 2 H), 0.95 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 140.1, 138.7, 133.8, 133.7, 130.8, 129.3 (2 C), 128.8, 127.9 (2 C), 126.1, 126.0, 124.9, 123.7, 123.0, 38.2, 32.7, 32.5, 22.7, 21.5, 14.0; MS (FAB): *m/e* (%) = 368.1 ($[M+H]^+$, 100), 367.1 (84), 303.2 (41), 228.2 (6), 212.2 (81), 129.1 (8); HR-MS (FAB): *m/e* = 368.1689, calcd. for $C_{22}H_{26}NO_2S$ $[M+H]^+$: 368.1684.

***N*,4-Dimethyl-*N*-(4-phenylnaphthalen-2-yl)benzenesulfonamide (2d):** yield: 95 mg (0.25 mmol, 98%); yellow solid; mp 153–155 °C; IR (CH_2Cl_2): ν = 3061, 2922, 1596, 1448, 1352, 1169, 920, 786, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.3 Hz, 1 H), 7.81 (d, J = 7.9 Hz, 1 H), 7.58 (d, J = 2.0 Hz, 1 H), 7.52–7.36 (m, 9 H), 7.23 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 2.1 Hz, 1 H), 3.27 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 141.2, 139.8, 138.5, 133.8, 133.7, 130.5, 129.9 (2 C), 129.4 (2 C), 128.4, 128.3 (2 C), 128.0 (2 C), 127.5, 126.5, 126.4, 125.9, 125.7, 124.6, 38.3, 21.5; MS (APCI): *m/e* (%) = 388.1 ($[M+H]^+$, 100), 343.1 (10), 311.1 (42), 223.1 (21), 186.1 (9), 122.0 (6); HR-MS (APCI): *m/e* = 388.1380, calcd. for $C_{24}H_{22}NO_2S$ $[M+H]^+$: 388.1371.

***N*,4-Dimethyl-*N*-(4-(*p*-tolyl)naphthalen-2-yl)benzenesulfonamide (2e):** yield: 78 mg (0.23 mmol, 92%); pale yellow solid; mp 129–130 °C; IR (CH_2Cl_2): ν = 3050, 2923, 1597, 1351, 1168, 922, 823, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.4 Hz, 1 H), 7.80 (d, J = 7.8 Hz, 1 H), 7.58 (d, J = 2.1 Hz, 1 H), 7.53–7.45 (m, 3 H), 7.42 (ddd, J = 8.3, 6.8, 1.3 Hz, 1 H), 7.28 (s, 4 H), 7.23 (d, J = 8.1 Hz, 2 H), 7.11 (d, J = 2.2 Hz, 1 H), 3.26 (s, 3 H), 2.44 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 141.2, 138.5, 137.3, 136.8, 133.8, 133.7, 130.6, 129.8 (2 C), 129.4 (2 C), 129.0 (2 C), 128.4, 128.0 (2 C), 126.4, 126.3, 125.9, 125.6, 124.5, 38.3, 21.5, 21.2; MS (FAB): *m/e* (%) = 402.1 ($[M+H]^+$, 100), 377.2 (40), 296.2 (10), 247.2 (96), 246.2 (87), 205.1 (28); HR-MS (FAB): *m/e* = 402.1518, calcd. for $C_{25}H_{24}NO_2S$ $[M+H]^+$: 402.1528.

***N*-{4-([1,1′-Biphenyl]-4-yl)naphthalen-2-yl}-*N*,4-dimethylbenzenesulfonamide (2f):** yield: 97 mg (0.24 mmol, 97%); yellow solid; mp 89–91 °C; IR (CH_2Cl_2): ν = 3060, 2925, 1598, 1488, 1349, 1168, 922, 845, 711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.2 Hz, 1 H), 7.83 (d, J = 7.9 Hz, 1 H), 7.73–6.65 (m, 4 H), 7.60 (d, J = 2.1 Hz, 1 H), 7.53–7.44 (m, 8 H), 7.42– 7.36 (m, 1 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 2.2 Hz, 1 H), 3.29 (s, 3 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 140.8, 140.7, 140.5, 138.8, 138.6, 133.9, 133.8, 130.5, 130.4 (2 C), 129.4 (2 C), 128.9 (2 C), 128.5, 128.0 (2 C), 127.5, 127.1 (2 C), 127.0 (2 C), 126.6, 126.5, 125.9, 125.8, 124.7, 38.3, 21.6; MS (FAB): *m/e* (%) = 464.1 ($[M+H]^+$, 100), 463.1 (78), 399.2 (31), 309.2 (76), 308.2 (71), 267.1 (31), 235.2 (13); HR-MS (FAB): *m/e* = 464.1687, calcd. for $C_{30}H_{26}NO_2S$ $[M+H]^+$: 464.1684.

***N*-([1,1′-Binaphthalen]-3-yl)-*N*,4-dimethylbenzenesulfonamide (2g):** yield: 93 mg (0.21 mmol, 85%); white solid; mp 170–171 °C; IR (CH_2Cl_2): ν = 3061, 2926, 1598, 1351, 1166, 917, 791, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 3.2 Hz, 1 H), 7.92 (d, J = 3.2 Hz, 1 H), 7.88 (d, J = 8.3 Hz, 1 H), 7.80 (d, J = 2.1 Hz, 1 H), 7.56 (dd, J = 8.2, 7.1 Hz, 1 H), 7.52–7.45 (m, 4 H), 7.38 (dd, J = 7.0, 1.1 Hz, 1 H), 7.36–7.26 (m, 4 H), 7.19 (d, J = 8.2 Hz. 2 H), 7.12 (d, J = 2.2 Hz, 1 H), 3.29 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 139.4, 138.3, 137.4, 133.7, 133.5 (2 C), 132.5, 131.7, 129.4 (2 C), 128.4, 128.2, 128.2, 127.9 (2 C), 127.7, 126.5, 126.5, 126.4, 126.3, 126.1, 125.9, 125.8, 125.5, 125.2, 38.2, 21.5; MS (ESI): *m/e* (%) = 438.06 ($[M+H]^+$, 100), 284.33 (16), 283.29 (65), 282.28 (15), 267.49 (4); HR-MS (ESI): *m/e* = 438.1528, calcd. for $C_{28}H_{24}NO_2S$ $[M+H]^+$: 438.1528.

***N*-Benzyl-4-methyl-*N*-(4-phenylnaphthalen-2-yl)benzenesulfonamide (2h):** yield: 114 mg (0.25 mmol, 98%); yellow solid; mp 56–58 °C; IR (CH_2Cl_2): ν = 3062, 3032, 2924, 1597, 1455, 1348, 1160, 919, 750, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.2 Hz, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.58 (d, J = 8.1 Hz, 2 H), 7.55 (s, 1 H), 7.47–7.36 (m, 5 H), 7.27 (d, J = 6.1 Hz, 6 H), 7.23–7.13 (m, 3 H), 6.95 (d, J = 1.9 Hz, 1 H), 4.83 (s 2 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 141.0, 139.7, 136.0, 135.8, 135.7, 133.7, 130.7, 129.9 (2 C), 129.5 (2 C), 128.5, 128.5 (2 C), 128.4 (2 C), 128.2 (2 C), 127.8 (3 C), 127.6, 127.5, 127.0, 126.6, 126.2, 125.7, 54.7, 21.5; MS (FAB): *m/e* (%) = 464.1 ($[M+H]^+$, 100), 463.1 (72), 399.2 (25), 308.2 (87), 231.1 (10), 202.1 (15); HR-MS (FAB): *m/e* = 464.1677, calcd. for $C_{30}H_{26}NO_2S$ $[M+H]^+$: 464.1684.

***N*-(6-Fluoro-4-phenylnaphthalen-2-yl)-*N*,4-dimethylbenzenesulfonamide (2i):** yield: 100 mg (0.25 mmol, 99%); white solid; mp 172–173 °C; IR (CH_2Cl_2): ν = 3060, 2926, 1600, 1350, 1169, 948, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 9.0, 5.8 Hz, 1 H), 7.60 (d, J = 2.0 Hz, 1 H), 7.52–7.40 (m, 6 H), 7.39–7.32 (m, 2 H), 7.30–7.22 (m, 3 H), 7.15 (d, J = 2.0 Hz, 1 H), 3.26 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (d, J = 246 Hz), 143.7, 140.6 (d, J = 6 Hz), 139.3, 137.9 (d, J = 3 Hz), 133.6, 131.5 (d, J = 9 Hz), 130.8 (d, J = 9 Hz), 130.7, 129.7 (2 C), 129.4 (2 C), 128.5 (2 C), 128.0 (2 C), 127.8, 126.5, 124.7, 116.8 (d, J = 26 Hz), 119.4 (d, J = 22 Hz), 38.2, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −113.7; MS (ESI): *m/e* (%) = 406.0 ($[M+H]^+$, 100), 374.6 (4), 251.3 (64), 230.90 (3); HR-MS (ESI): *m/e* = 406.1277, calcd. for $C_{24}H_{21}NO_2FS$ $[M+H]^+$: 406.1277.

***N*-[6-Chloro-4-phenylnaphthalen-2-yl]-*N*,4-dimethylbenzenesulfonamide (2j):** yield: 104 mg (0.25 mmol, 99%); white oil; IR (CH_2Cl_2): ν = 3058, 2926, 1736, 1593, 1351, 1170, 1089, 928 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 1.9 Hz, 1 H), 7.75 (d, J = 8.8 Hz, 1 H), 7.57 (d, J = 2.1 Hz, 1 H), 7.51–7.42 (m, 6 H), 7.38–7.34 (m, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 2.2 Hz, 1 H), 3.26 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 140.5, 139.1, 138.8, 133.6, 132.6, 132.0, 131.1, 129.9, 129.8 (2 C), 129.4 (2 C), 128.5 (2 C), 127.9 (2 C), 127.9, 127.4, 126.6, 124.8, 124.4, 38.1, 21.5; MS (ESI): *m/e* (%) = 423.9 ($[M+H+2]^+$, 37), 421.9 ($[M+H]^+$, 100), 414.6 (10), 356.8 (7), 267.3 (82), 229.2 (5); HR-MS (ESI): *m/e* = 422.0980, calcd. for $C_{24}H_{21}NO_2SCl$ $[M+H]^+$: 422.0982.

***N*-(Benzo[*b*]thiophen-5-yl)-*N*,4-dimethylbenzenesulfonamide (2k):** yield: 60 mg (0.19 mmol, 75%); brown solid; mp 101–102 °C; IR (CH_2Cl_2): ν = 3502, 2926, 2856, 1736, 1597, 1438, 1348, 1165, 938, 846, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.6 Hz, 1 H), 7.57 (d, J = 2.0 Hz, 1 H), 7.48 (d, J = 5.4 Hz, 1 H), 7.45 (d, J = 8.2 Hz, 2 H), 7.27 (d, J =

5.3 Hz, 1H), 7.24 (d, J=8.1 Hz, 2H), 7.05 (dd, J=8.6, 2.0 Hz, 1H), 3.23 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.5, 139.9, 138.6, 138.3, 133.5, 129.3 (2C), 128.0 (2C), 127.8, 123.9, 123.0, 122.6, 122.0, 38.6, 21.5; MS (ESI): *m/e* (%)=318.0 ([M+H]$^+$, 100), 279.1 (6), 248.6 (4), 163.2 (18); HR-MS (ESI): *m/e*=318.0623, calcd. for $C_{16}H_{16}NO_2S_2$ [M+H]$^+$: 318.0622.

***N*,4-Dimethyl-*N*-(7-phenylbenzo[*b*]thiophen-5-yl)benzenesulfonamide (2l):** yield: 84 mg (0.21 mmol, 85%); white solid;, mp 167–168 °C; IR (CH_2Cl_2): ν=3513, 3061, 2933, 1597, 1346, 1169, 895, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.56 (m, 3H), 7.52–7.44 (m, 5H), 7.44–7.38 (m, 1H), 7.34 (d, J=5.4 Hz, 1H), 7.26 (d, J=7.6 Hz, 2H), 7.03 (d, J=2.0 Hz, 1H), 3.26 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.6, 140.5, 139.8, 139.0, 137.8, 136.9, 133.7, 129.4 (2C), 128.8 (2C), 128.2, 128.1 (2C), 128.0 (2C), 127.9, 124.4, 122.9, 121.0, 38.7, 21.5; MS (FAB): *m/e* (%)=393.0 ([M]$^+$, 47), 329.1 (15), 238.1 (100), 210.1 (13), 197.1 (10), 165.1 (7); HR-MS (FAB): *m/e*=393.0857, calcd. for $C_{22}H_{19}NO_2S_2$ [M]$^+$: 393.0857.

***N*-Benzyl-4-methyl-*N*-(7-phenylbenzo[*b*]thiophen-5-yl)-benzenesulfonamide (2m):** yield: 112 mg (0.24 mmol, 95%); white oil; IR (CH_2Cl_2): ν=3032, 2926, 1697, 1351, 1164, 1093, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61 (d, J=8.2 Hz, 2H), 7.50–7.42 (m, 6H), 7.42–7.37 (m, 1H), 7.32–7.16 (m, 8H), 6.87 (d, J=1.8 Hz, 1H), 4.81 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.5, 140.5, 139.7, 138.2, 136.8, 136.2, 136.0, 135.8, 129.5 (2C), 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.2, 128.0 (2C), 127.9 (2C), 127.7, 127.6, 124.5, 124.4, 123.6, 55.2, 21.5; MS (ESI): *m/e* (%)=470.0 ([M+H]$^+$, 100), 447.2 (2), 315.2 (38), 286.2 (3); HR-MS (ESI): *m/e*=470.1248, calcd. for $C_{28}H_{24}NO_2S_2$ [M+H]$^+$: 470.1248.

Procedure for Deprotection of the *N*-Tosyl Group of 2d; Synthesis of *N*-Methyl-4-phenylnaphthalen-2-amine (2n)

To a flame-dried 25-mL round-bottom flask were added 8 equiv. of sodium (28 mg, 1.2 mmol) and naphthalene (154 mg, 1.2 mmol) in tetrahydrofuran (0.4 mL) at room temperature under nitrogen. After 15 min, the solution turned to a dark-green color. To this solution of sodium naphthalenide at –78 °C was added dropwise a solution of *N*,4-dimethyl-*N*-(4-phenylnaphthalen-2-yl)benzenesulfonamide (**2d**, 58 mg, 0.15 mmol) in tetrahydrofuran (0.4 mL). The reaction mixture was stirred until no trace of **2d** was detected on TLC (*ca.* 30 min). The reaction mixture was then quenched with 5 drops of saturated aqueous NH_4Cl solution at 0 °C and concentrated under reduced pressure to give a crude oil. The resulting crude mixture was purified by flash column chromatography [silica gel, 5% EtOAc in hexanes] to afford product **2n** as a yellow oil; yield: 19 mg (0.08 mmol, 54%).

***N*-Methyl-4-phenylnaphthalen-2-amine (2n):** yield: 19 mg (0.08 mmol, 54%); yellow oil; IR (CH_2Cl_2): ν=3418, 3056, 2897, 1714, 1621, 1500, 1409, 1233, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (t, J=7.9 Hz, 2H), 7.50–7.45 (m, 4H), 7.45–7.39 (m, 1H), 7.39–7.34 (m, 1H), 7.17–7.10 (m, 1H), 6.83 (s, 2H), 3.90 (s, 1H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.3, 141.2, 140.7, 135.8, 129.9 (2C), 128.1 (2C), 127.2, 126.3, 126.2, 125.9, 125.9, 122.0, 118.8, 103.7, 30.8; MS (ESI): *m/e* (%)=234.2 ([M+H]$^+$, 100), 219.3 (5); HR-MS (ESI): *m/e*=234.1282, calcd. for $C_{17}H_{16}N$ [M+H]$^+$: 234.1283.

***tert*-Butyl naphthalen-2-yl(phenyl)carbamate (2o):** yield: 51 mg (0.16 mmol, 64%); white solid; mp 114–116 °C; IR (CH_2Cl_2): ν=2978, 1712, 1596, 1495, 1317, 1163, 748, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84–7.76 (m, 2H), 7.76–7.69 (m, 1H), 7.62 (d, J=2.0 Hz, 1H), 7.48–7.41 (m, 2H), 7.39 (dd, J=8.8, 2.1 Hz, 1H), 7.36–7.29 (m, 2H), 7.29–7.22 (m, 2H), 7.22–7.14 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.9, 143.1, 140.6, 133.5, 131.3, 128.7 (2C), 128.3, 127.7, 127.5, 127.0 (2C), 126.2, 125.9, 125.7, 125.6, 124.8, 81.3, 28.3; MS (ESI): *m/e* (%)=342.1 ([M+Na]$^+$, 100), 286.1 (26), 264.2 (22), 218.3 (15); HR-MS (ESI): *m/e*=342.1470, calcd. for $C_{21}H_{21}NO_2Na$ [M+Na]$^+$: 342.1470.

Typical Procedure for the Preparation of *N*,4-Dimethyl-*N*-[1-(prop-1-en-2-yl)-1*H*-inden-2-yl]benzenesulfonamide (4a) in Dichloromethane

To a solution of *N*,4-dimethyl-*N*-{[2-(2-methylprop- 1-en-1-yl)phenyl]ethynyl}benzenesulfonamide (**3a**, 85 mg, 0.25 mmol) in dichloromethane (2.5 mL) was added $In(OTf)_3$ (7 mg, 0.012 mmol) at room temperature under nitrogen. The reaction mixture was stirred until no trace of **3a** was detected on TLC, then concentrated under reduced pressure to give a crude liquid. The resulting crude mixture was purified by flash column chromatography [silica gel, 20% EtOAc in hexanes] to afford product **4a** as a yellow oil; yield: 83 mg (0.25 mmol, 98%).

The products **4b–i** were prepared by the similar manner.

***N*,4-Dimethyl-*N*-[1-(prop-1-en-2-yl)-1*H*-inden-2-yl]benzenesulfonamide (4a):** yield: 83 mg (0.25 mmol, 98%); yellow oil; IR (CH_2Cl_2): ν=3069, 2971, 2356, 1918, 1644, 1597, 1463, 1358, 1169, 1089, 919, 889, 755, 670, 567 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61 (d, J=8.2 Hz, 2H), 7.26 (d, J=8.0 Hz, 2H), 7.24–7.19 (m, 2H), 7.18–7.11 (m, 2H), 6.23 (s, 1H), 5.24 (s, 1H), 5.09 (s, 1H), 4.74 (s, 1H), 3.11 (s, 3H), 2.41 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.7, 143.8, 143.3, 142.6, 142.2, 133,3, 129.5 (2C), 127.7 (2C), 126.9, 124.9, 122.9, 120.3, 119.8, 116.1, 59.7, 37.9, 21.5, 17.2; MS (ESI): *m/e* (%)=340.1 ([M+H]$^+$, 20), 279.3 (5), 102.1 (5); HR-MS (ESI): *m/e*=340.1364, calcd. for $C_{20}H_{22}NO_2S$ [M+H]$^+$: 340.1371.

***N*,4-Dimethyl-*N*-[5-methyl-1-(prop-1-en-2-yl)-1*H*-inden-2-yl]benzenesulfonamide (4b):** yield: 80 mg (0.23 mmol, 90%); white solid; mp 120–121 °C; IR (CH_2Cl_2): ν=3443, 3115, 2920, 2358, 1909, 1597, 1474, 1357, 1170, 803, 670, 571 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.60 (d, J=8.3 Hz, 2H), 7.26 (d, J=8.2 Hz, 2H), 7.16 (d, J=7.7 Hz, 1H), 7.01 (s, 1H), 6.97 (d, J=7.7 Hz, 1H), 6.18 (s, 1H), 5.22 (s, 1H), 5.07 (t, J=1.4 Hz, 1H), 4.70 (s, 1H), 3.10 (s, 3H), 2.41 (s, 3H), 2.35 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.8, 143.8, 142.9, 142.4, 140.5, 136.7, 133.5, 129.5 (2C), 127.8 (2C), 125.7, 122.7, 121.1, 119.9, 115.8, 59.5, 37.9, 21.5 (2C), 17.3; MS (EI, 70 eV): *m/e* (%)=353.1 ([M]$^+$, 100), 198.1 (40), 157.1 (100), 142.1 (35); HR-MS (EI, 70 eV): *m/e*=353.1444, calcd. for $C_{21}H_{23}NO_2S$ [M]$^+$: 353.1450.

***N*-[5,6-Dimethoxy-1-(prop-1-en-2-yl)-1*H*-inden-2-yl]-*N*,4-dimethylbenzenesulfonamide (4c):** yield: 90 mg (0.23 mmol, 90%); white solid; mp 132–133 °C; IR (CH_2Cl_2): ν=3344,

3079, 2938, 2254, 1921, 1644, 1597, 1491, 1354, 1299, 1167, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.60$ (d, $J =$ 8.2 Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.86 (s, 1H), 6.78 (s, 1H), 6.14 (s, 1H), 5.25 (s, 1H), 5.09 (s, 1H), 4.68 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.07 (s, 3H), 2.41 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.5$, 148.3, 147.5, 143.7, 142.9, 135.8 134.5, 133.2, 129.4 (2C), 127.7 (2C), 120.4, 116.1, 107.2, 104.2, 59.9, 56.2, 56.0, 38.0, 21.5, 17.0; MS (EI, 70 eV): *m/e* (%) = 399.2 ($[M]^+$, 40), 325.2 (20), 244.2 (100), 203.1 (100), 188.1 (15); HR-MS (EI, 70 eV): *m/e* = 399.1506, calcd. for $C_{22}H_{25}NO_4S$ $[M]^+$: 399.1504.

***N*,4-Dimethyl-*N*-(5-(prop-1-en-2-yl)-5-indeno[5,6-*d*][1,3]-dioxol-6-yl)benzenesulfonamide (4d):** yield: 91 mg (0.24 mmol, 95%); yellow oil; IR (CH_2Cl_2): $\nu = 3556$, 3370, 2974, 2917, 2204, 1500, 1470, 1355, 1165, 1039, 812 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 6.7$ Hz, 2H), 6.80 (s, 1H), 6.69 (s, 1H), 6.10 (s, 1H), 5.25 (s, 1H), 5.92 (d, $J = 1.5$ Hz, 1H), 5.22 (s, 1H), 5.07 (s, 1H), 4.64 (s, 1H), 3.06 (s, 3H), 2.41 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.4$, 146.8, 145.8, 143,7, 142.6, 137.2, 135.6, 133.2, 129.4 (2C), 127.7 (2C), 120.3, 116.2, 104.8, 101.6, 100.8, 59.7, 38.0, 21.5, 16.9; MS (EI, 70 eV): *m/e* (%) = 383.1 ($[M]^+$, 57), 228.1 (98), 187.1 (100), 157.1 (40), 129.1(80), 128.1 (65); HR-MS (EI, 70 eV): *m/e* = 383.1188, calcd. for $C_{21}H_{21}NO_4S$ $[M]^+$: 383.1191.

***N*-[6-Fluoro-1-(prop-1-en-2-yl)-1*H*-inden-2-yl]-*N*,4-dimethylbenzenesulfonamide (4e):** yield: 83 mg (0.23 mmol, 93%); yellow oil; IR (CH_2Cl_2): $\nu = 3456$, 3080, 2973, 2944, 2360, 1919, 1724, 1598, 1475, 1354, 1189, 1034, 864 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.63$ (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.13 (dd, $J = 8.2$, 5.0 Hz, 1H), 7.03 (dd, $J = 8.6$, 2.3 Hz, 1H), 6.94 (td, $J = 9.6$, 2.5 Hz, 1H), 6.20 (s, 1H), 5.27 (s, 1H), 5.13 (t, $J = 1.4$ Hz, 1H), 4.76 (s, 1H), 3.11 (s, 3H), 2.44 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.5$ (d, $J = 240$ Hz), 149.3 (d, $J = 4$ Hz), 145.4 (d, $J = 8$ Hz), 143.9, 142.1, 137.9, 133.3, 129.5 (2C), 127.7 (2C), 121,0 (d, $J = 8$ Hz),119.3, 116.6, 113.8 (d, $J = 23$ Hz), 110.9 (d, $J = 24$ Hz), 59.9 (d, $J = 2$ Hz), 37.9, 21.5, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -118.4$; MS (APCI): *m/e* (%) = 358.1 ($[M+H]^+$, 100), 319.2 (10), 279.2 (10), 229.1 (5), 203.1 (5); HR-MS (APCI): *m/e* = 358.1272, calcd. for $C_{20}H_{21}FNO_2S$ $[M+H]^+$: 358.1277.

***N*-[6-Chloro-1-(prop-1-en-2-yl)-1*H*-inden-2-yl]-*N*,4-dimethylbenzenesulfonamide (4f):** yield: 93 mg (0.25 mmol, 99%); yellow oil; IR (CH_2Cl_2): $\nu = 2973$, 2942, 2362, 1597, 1587, 1358, 1169, 866, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.60$ (d, $J = 8.2$ Hz, 2H), 7.28 (s, 1H), 7.26– 7.25 (m, 2H), 7.19 (dd, $J = 8.0$, 1.9 Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.19 (s, 1H), 5.24 (s, 1H), 5.10 (s, 1H), 4.73 (s, 1H), 3.10 (s, 3H), 2.41 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.0$, 144.9, 144.0, 141.9, 140.7, 130.8, 129.5 (2C), 127.7 (2C), 127.2. 123.5, 121.1, 120.5, 118.8, 116.7, 59.8, 37.8, 21.5, 17.2; MS (ESI): *m/e* (%) = 376.0 ($[M+2+H]^+$, 374.0 ($[M+H]^+$, 100), 219.1 (30); HR-MS (ESI): *m/e* = 374.0980, calcd. for $C_{20}H_{21}NO_2SCl$ $[M+H]^+$: 374.0982.

***N*-Benzyl-4-methyl-*N*-[1-(prop-1-en-2-yl)-1*H*-inden-2-yl]-benzenesulfonamide (4g):** yield: 98 mg (0.24 mmol, 94%); white solid; mp 128–129 °C; IR (CH_2Cl_2): $\nu = 3429$, 3066, 2971, 2340, 1643, 1596, 1566, 1456, 1352, 1164, 1090, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J =$ 8.2 Hz, 2H), 7.33 (d, $J = 7.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 2H), 7.19–7.10 (m, 4H), 7.07–7.03 (m, 1H), 6.55 (s, 1H), 5.16–5.12 (m, 2H), 4.98 (s, 1H), 4.48–4.44 (m, 2H), 2.37 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 146.3$, 143.8, 142.8, 142.5, 142.3, 136.3, 135.4, 129.4 (2C), 128.3 (2C), 128.0 (2C), 127.7 (2C), 127.5, 126.8, 124.8, 122.8, 122.0, 120.4, 116.4, 292, 52.8, 21.4, 16.6; MS (APCI): *m/e* (%) = 416.2 ($[M+H]^+$, 100); HR-MS (APCI): *m/e* = 416.1679, calcd. for $C_{26}H_{26}NO_2S$ $[M+H]^+$: 416.1684.

***N*-Butyl-4-methyl-*N*-[1-(prop-1-en-2-yl)-1*H*-inden-2-yl]-benzenesulfonamide (4h):** yield: 91 mg (0.24 mmol, 95%); yellow oil; IR (CH_2Cl_2): $\nu = 3459$, 3069, 2959, 2932, 2340, 1918, 1722, 1642, 1597, 1463, 1353, 1166, 1018, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.64$ (d, $J = 8.3$ Hz, 2H), 7.24–7.20 (m, 6H), 7.17–7.11 (m, 1H), 6.42 (s, 1H), 5.18 (s, 1H), 5.04 (s, 1H), 4.63 (s, 1H), 3.81–3.74 (m, 1H), 3.32–3.25 (m, 1H), 2.38 (s, 3H), 1.63–1.53 (m, 2H), 1.41–1.26 (m, 2H), 1.10 (s, 2H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 146.9$, 143.5, 143.1, 142.4, 135.4, 129.3 (2C), 127.7 (2C), 127.0, 124.9, 123.0, 121.8, 120.4, 116.4, 77.2, 59.3, 49.5, 30.5, 21.5, 19.9, 17.3, 13.6; MS (APCI): *m/e* (%) = 382.2 ($[M+H]^+$, 100); HR-MS (APCI): *m/e* = 382.1838, calcd. for $C_{23}H_{28}NO_2S$ $[M+H]^+$: 382.1841.

***N*,4-Dimethyl-*N*-(6-(prop-1-en-2-yl)-6*H*-cyclopenta[*b*]-thiophen-5-yl)benzenesulfonamide (4i):** yield: 86 mg (0.25 mmol, 99%); white solid; mp 89–90 °C; IR (CH_2Cl_2): $\nu = 3907$, 3427, 2926, 2357, 2012, 1698, 1453, 1346, 1164, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.60$ (d, $J =$ 8.3 Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.26 (s, 1H), 6.89 (d, $J = 4.8$ Hz, 1H), 6.14 (d, $J = 1.2$ Hz, 1H), 5.19 (s, 1H), 5.06 (t, $J = 1.5$ Hz, 1H), 4.78 (s, 1H), 3.04 (s, 3H), 2.42 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.4$, 145.3, 143.7, 142.6, 142.2, 133.0, 129.4 (2C), 127.9 (2C), 127.3, 119.4, 118.5, 115.9, 57.9, 38.5, 21.5, 17.6; MS (EI, 70 eV)**:** *m/e* (%) = 345.1 ($[M]^+$, 30), 325.2 (50), 279.2 (20), 239.2 (24), 190.1 (100), 149.1 (42), 134.1 (20); HR-MS (EI, 70 eV): *m/e* = 345.0851, calcd. for $C_{18}H_{19}NO_2S_2$ $[M]^+$: 345.0857.

***tert*-Butyl phenyl[1-(prop-1-en-2-yl)-1*H*-inden-2-yl]carbamate (4j)**: yield: 44 mg (0.13 mmol, 51%); brown oil; IR (CH_2Cl_2): $\nu = 2977$, 1718, 1594, 1459, 1317, 1157, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40$–7.31 (m, 2H), 7.31–7.24 (m, 1H), 7.24–7.20 (m, 2H), 7.20–7.13 (m, 3H), 7.07 (td, $J = 7.2$, 1.6 Hz, 1H), 6.28 (s, 1H), 5.00–4.95 (m, 1H), 4.89 (s, 1H), 4.56 (s, 1H), 1.44 (s, 9H), 1.37 (s, 3H); ^{13}C NMR (100 MHz,$CDCl_3$): $\delta = 153.2$, 149.8, 143.2, 142.6, 142.5, 142.1, 128.7 (2C), 128.1 (2C), 126.9 (2C), 124.2, 122.8, 120.2, 120.0, 115.6, 81.4, 57.9, 28.1, 17.7; MS (ESI)**:** *m/e* (%) = 370.0 ($[M+Na]^+$, 100), 347.8 (10), 292.1 (43), 180.7 (7); HR-MS (ESI): *m/e* = 370.1783, calcd. for $C_{23}H_{25}NO_2Na$ $[M+Na]^+$: 370.1783.

Typical Procedure for the Preparation of *N*,4-Dimethyl-*N*-[1-(tribromomethyl)-1*H*-inden-2-yl]benzenesulfonamide (9a) in Dichloromethane

To a solution of *N*-{[2-(2,2-dibromovinyl)phenyl]ethynyl}-*N*,4-dimethylbenzenesulfonamide (**8a**, 94 mg, 0.2 mmol) in dichloromethane (2.0 mL) was added $InBr_3$ (85 mg, 0.24 mmol) at room temperature under an atmosphere of nitrogen. The reaction mixture was stirred until no trace of **8a** was detected on TLC (*ca.* 10 min), and then concentrated under reduced pressure to give a crude liquid. The resulting crude mixture was purified by flash column chromatography

[silica gel, 20% EtOAc in hexanes] to afford product **9a** as a green solid; yield: 66 mg (0.12 mmol, 60%).

The product **9b** was prepared by a similar method.

***N*,4-Dimethyl-*N*-[1-(tribromomethyl)-1*H*-inden-2-yl]benzenesulfonamide (9a): yield:** 66 mg 0.12 mmol, 60%); green solid; mp 181–182 °C; IR (CH_2Cl_2): ν = 3067, 2914, 2361, 1920, 1701, 1598, 1464, 1352, 1168, 1088, 1031, 906 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.38 (td, J = 7.3, 0.7 Hz, 1H), 7.32–7.34 (m, 3H), 7.24 (d, J = 7.4 Hz, 1H), 6.29 (s, 1H),5.30 (m, 1H), 3.11 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 147.9, 141.6, 140.7, 132.1, 129.4 (2C), 129.3, 128.9, 128.1 (2C), 126.9, 125.8, 121.4, 69.2, 39.6, 28.8, 21.5; MS (APCI): *m/e* (%) = 553.8 ([M + 6 + H]$^+$, 10), 551.8 ([M + 4 + H]$^+$, 30), 549.9 ([M + 2 + H]$^+$, 30), 547.9 ([M + H]$^+$, 10), 265.1 (15), 233.1 (100), 216.1 (20); HR-MS (APCI): *m/e* = 547.8538, calcd. for $C_{18}H_{17}NO_2SBr_3$ [M + H]$^+$: 547.8530.

***N*-[6-Fluoro-1-(tribromomethyl)-1*H*-inden-2-yl]-*N*,4-dimethylbenzenesulfonamide (9b):** yield: 63 mg (0.11 mmol, 55%); green solid; mp 243–244 °C; IR (CH_2Cl_2): ν = 3072, 2940, 2358, 1598, 1473, 1460, 1351, 1163, 1087, 1026, 906 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, J = 9.6, 2.2 Hz, 1H), 7.56 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.17 (dd, J = 8.2, 5.2 Hz, 1H), 7.08 (td, J = 8.7, 2.4 Hz, 1H), 6.25 (s, 1H), 5.28 (s, 1H), 3.09 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (d, J = 245 Hz), 147.1, 144.0, 142.7 (d, J = 9 Hz),137.4, 132.2, 129.4 (2C), 128.5, 128.1 (2C), 122.0 (d, J = 8 Hz), 115.7 (d, J = 23 Hz), 115.4 (d, J = 26 Hz), 69.2, 38.8, 38.3, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −114.8; MS (FAB): *m/e* (%) = 570.8 ([M + 6]$^+$, 10), 568.8 ([M + 4]$^+$, 30), 566.8 ([M + 2]$^+$, 30), 564.8 ([M]$^+$, 10), 487.9 (25), 460.1 (5), 391.3 (5), 307.1 (35), 289.1 (20), 235.2 (10), 219.2 (5); HR-MS (FAB): *m/e* = 564.8353, calcd. for $C_{18}H_{15}NO_2SBr_3F$ [M]$^+$: 564.8358.

Typical Procedure for the Preparation of (*E*)-4-Bromo-3-[bromo(phenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12a) in 1,2-Dichloroethane

To a solution of *N*-{[2-(2,2-dibromovinyl)phenyl]ethynyl}-*N*-(3-phenylprop-2-yn-1-yl)tolylsulfonamide (**11a**, 0.11 mg, 0.20 mmol) in 1,2-dichloroethane (20 mL) was added $InBr_3$ (35 mg, 0.10 mmol) at 80 °C under an atmosphere of nitrogen. The reaction mixture was stirred until no trace of **11a** was detected on TLC in 10 min. The mixture was filtered through a bed of Celite® and concentrated to give a crude solid. The resulting crude mixture was purified by flash column chromatography [silica gel, 5% EtOAc in hexanes] to afford product **12a** as a red solid; yield: 88 mg (0.16 mmol, 78%).

The products **12b–i** (from 0.20 mmol of **11b–i** and 0.10 mml of $InBr_3$) and **17a–f** (from 0.15 mmol of **16a–f** and 0.075 mmol of $InCl_3$) were prepared by a similar method.

(*E*)-4-Bromo-3-[bromo(phenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12a): yield: 88 mg (0.16 mmol, 78%); red solid; mp 173–174 °C; IR (CH_2Cl_2): ν = 3059, 2914, 2355, 1601, 1447, 1352, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 7.4 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.31 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.24–7.16 (m, 6H), 7.03 (td, J = 7.6, 1.4 Hz, 1H), 6.85 (s, 1H), 6.72–6.65 (m, 2H), 5.04 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 143.0, 139.5, 137.3, 136.7, 135.9, 132.0, 131.7, 130.5 (2C), 129.9 (3C), 129.7, 128.8, 127.8 (2C), 127.2 (2C), 125.0, 124.6, 121.7, 119.3, 118.7, 55.5, 21.5; MS (EI, 70 eV): *m/e* (%) = 570.9 ([M + 4]$^+$, 27), 569.0 ([M + 2]$^+$, 59), 567.0 ([M]$^+$, 24), 412.0 (58), 334.1 (34), 254.2 (93); HR-MS (ESI): *m/e* = 566.9509, calcd. for $C_{26}H_{19}Br_2NO_2S$ [M]$^+$: 566.9503.

(*E*)-4-Bromo-3-[bromo(phenyl)methylene]-6-fluoro-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12b): Yield: 65 mg (0.12 mmol, 60%); red solid; mp 156–157 °C; IR (CH_2Cl_2): ν = 2918, 2848, 1581, 1463, 1362, 1274, 1167, 1088, 954 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.76 (dd, J = 9.9, 2.4 Hz, 1H), 7.32 (td, J = 6.8, 1.2 Hz, 1H), 7.21 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.09 (dd, J = 8.2, 5.2 Hz, 1H), 6.92 (ddd, J = 8.9, 8.2, 2.4 Hz, 1H), 6.81 (s, 1H), 6.67 (d, J = 7.1 Hz, 2H), 5.03 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0 (d, J = 243 Hz),144.2, 139.4, 138.6, 135.7, 133.6 (d, J = 9 Hz),132.6, 130.4 (2C), 130.0, 129.9 (2C), 128.5, 127.8 (2C), 127.1 (2C), 122.0 (d, J = 8 Hz), 119.9, 118.8, 115.5 (d, J = 22 Hz),112.9 (d, J = 26 Hz), 55.4, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −117.0; MS (EI, 70 eV): *m/e* (%) = 589.0 ([M + 4]$^+$, 22), 587.0 ([M + 2]$^+$, 44), 585.0 ([M]$^+$, 22), 458.0 (10), 431.9 (100), 352 (30), 351 (30), 272.1 (60), 271.1 (40), 244.1 (25); HR-MS (EI, 70 eV): *m/e* = 584.9407, calcd. for $C_{26}H_{18}FNO_2SBr_2$ [M]$^+$: 584.9407.

(*E*)-Ethyl 4-{bromo(4-bromo-1-tosyl-1*H*-indeno[2,1-*b*]pyridin-3(2*H*)-ylidene)methyl}benzoate (12c): yield: 90 mg (0.14 mmol, 71%); red solid; mp 163–165 °C; IR (CH_2Cl_2): ν = 3055, 2985, 1717, 1601, 1352, 1274, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.25–7.15 (m, 4H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.85 (s, 1H), 6.76 (d, J = 8.2 Hz, 2H), 5.03 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 144.3, 143.7, 142.9, 137.9, 136.6, 135.8, 131.9, 131.5, 130.3 (2C), 130.1, 129.9 (3C), 129.7, 128.9 (2C), 127.2 (2C), 125.2, 124.7, 121.8, 119.8, 117.7, 61.3, 55.3, 21.5, 14.2; MS (FAB): *m/e* (%) = 643.0 ([M + 4]$^+$, 67), 640.9 ([M + 2]$^+$, 100), 638.9 ([M$^+$], 45), 485.9 (44), 406.0 (9); HR-MS (FAB): *m/e* = 638.9702, calcd. for $C_{29}H_{23}Br_2NO_4S$ [M]$^+$: 638.9715.

(*E*)-Ethyl 3-{bromo(4-bromo-1-tosyl-1*H*-indeno[2,1-*b*]pyridin-3(2*H*)-ylidene)methyl}benzoate (12d): yield: 90 mg (0.15 mmol, 74%); red solid; mp 148–150 °C; IR (CH_2Cl_2): ν = 3066, 2979, 1717, 1601, 1447, 1351, 1240, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.61 (s, 1H), 7.25–7.15 (m, 5H), 7.03 (td, J = 7.6, 1.2 Hz, 1H), 6.84 (s, 1H), 6.70 (d, J = 7.8 Hz, 1H), 5.11 (br s, 1H), 4.95 (br s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.31 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 144.4, 143.0, 139.8, 137.8, 136.5, 135.9, 134.4, 132.0, 131.3, 130.7, 130.5, 129.9 (3C), 129.8, 129.7, 127.7, 127.2 (2C), 125.1, 124.7, 121.7, 119.6, 117.8, 61.3, 55.4, 21.4, 14.3; MS (ESI): *m/e* (%) = 666.0 ([M + 4 + Na]$^+$, 35), 664.0 ([M + 2 + Na]$^+$, 100), 662.0 ([M + Na]$^+$, 33), 397.4 (8), 274.3 (32), 264.1 (7); HR-MS (ESI): *m/e* = 661.9617, calcd. for $C_{29}H_{23}Br_2NO_4S$ [M + Na]$^+$: 661.9612.

(*E*)-4-Bromo-3-[bromo(4-bromophenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12e): yield: 121 mg (0.19 mmol, 93%); red solid; mp 162–163 °C; IR

(CH_2Cl_2): ν = 3063, 2920, 1913, 1600, 1447, 1352, 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.25–7.13 (m, 4H), 7.05 (td, J = 7.6, 1.3 Hz, 1H), 6.85 (s, 1H), 6.55 (d, J = 8.5 Hz, 2H), 5.01 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 143.0, 138.4, 137.7, 136.7, 135.8, 131.9, 131.9 (2C), 131.0 (2C), 129.9 (3C), 129.9, 129.5, 127.2 (2C), 125.2, 124.6, 124.4, 121.8, 119.7, 118.0, 55.4, 21.5; MS (FAB): *m/e* (%) = 648.8 ($[M+4]^+$, 100), 646.9 ($[M+2]^+$, 89), 644.8 ($[M]^+$, 31), 493.8 (53), 413.9 (19), 334.0 (18); HR-MS (FAB): *m/e* = 644.8622, calcd. for $C_{26}H_{18}Br_3NO_2S$ $[M]^+$: 644.8608.

(*E*)-4-Bromo-3-[bromo(4-chlorophenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12f): yield: 75 mg (0.13 mmol, 62%); red solid; mp 166–167 °C; IR (CH_2Cl_2): ν = 3053, 2919, 1600, 1449, 1352, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.27–7.14 (m, 6H), 7.04 (td, J = 7.6, 1.2 Hz, 1H), 6.85 (s, 1H), 6.61 (d, J = 8.5 Hz, 2H), 5.01 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 142.9, 138.0, 137.7, 136.6, 136.1, 135.8, 131.9, 131.7 (2C), 129.9 (2C), 129.9 (2C), 129.5, 128.1 (2C), 127.2 (2C), 125.2, 124.6, 121.8, 119.7, 118.0, 55.4, 21.5; MS (ESI): *m/e* (%) = 604.9 ($[M+4]^+$, 40), 602.8 ($[M+2]^+$, 50), 600.8 ($[M]^+$, 21), 447.9 (23), 368.0 (8); HR-MS (ESI): *m/e* = 600.9119, calcd. for $C_{26}H_{18}Br_2ClNO_2S$ $[M]^+$: 600.9114.

(*E*)-4-Bromo-3-[bromo(*p*-tolyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12g): yield: 74 mg (0.13 mmol, 64%); red solid; mp 188–189 °C; IR (CH_2Cl_2): ν = 3034, 2922, 1909, 1600, 1572, 1447, 1352, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.25–7.16 (m, 4H), 7.03 (td, J = 7.5, 1.4 Hz, 1H), 6.84 (s, 1H), 6.58 (d, J = 8.1 Hz, 2H), 5.02 (s, 2H), 2.34 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 143.0, 140.4, 137.1, 136.7, 136.7, 136.0, 132.2, 132.1, 130.5 (2C), 129.9 (2C), 129.6, 128.5 (2C), 128.2, 127.2 (2C), 125.0, 124.5, 121.6, 119.1, 119.1, 55.6, 21.4; MS (ESI): *m/e* (%) = 586.0 ($[M+4+H]^+$, 30), 584.0 ($[M+2+H]^+$, 73), 582.0 ($[M+H]^+$, 27), 504.0 (7), 419.3 (3), 348.0 (7), 311.1 (21); HR-MS (ESI): *m/e* = 581.9739, calcd. for $C_{27}H_{22}Br_2NO_2S$ $[M+H]^+$: 581.9738.

(*E*)-4-Bromo-3-[bromo(*m*-tolyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12h): 58 mg (0.10 mmol, 50%); red solid; mp 188–189 °C; IR (CH_2Cl_2): ν = 3055, 2919, 1600, 1574, 1449, 1352, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.25–7.16 (m, 4H), 7.12 (d, J = 7.6 Hz, 1H), 7.09–7.00 (m, 2H), 6.84 (s, 1H), 6.57 (s, 1/H), 6.45 (d, J = 7.5 Hz, 1H), 5.03 (s, 2H), 2.34 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 143.0, 139.5, 137.5, 137.2, 136.7, 136.0, 132.1, 132.1, 130.9, 130.7, 129.9 (2C), 129.6, 128.6, 127.7, 127.6, 127.3 (2C), 125.0, 124.6, 121.6, 119.1, 119.0, 55.5, 21.5, 21.2; MS (ESI): *m/e* (%) = 608.0 ($[M+4+Na]^+$, 45), 606.0 ($[M+2+Na]^+$, 100), 604.0 ($[M+Na]^+$, 40), 507.0 (12), 471.4 (18), 409.0 (26), 317.0 (30); HR-MS (ESI): *m/e* = 603.9563, calcd. for $C_{27}H_{21}Br_2NO_2NaS$ $[M+Na]^+$: 603.9557.

(*E*)-4-Bromo-3-[bromo(4-methoxyphenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (12i): yield: 55 mg (0.09 mmol, 46%); red solid; mp 175–176 °C; IR (CH_2Cl_2): ν = 3047, 2941, 2356, 1601, 157/4, 1448, 1351, 1252, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.25–7.15 (m, 4H), 7.03 (td, J = 7.5, 1.4 Hz, 1H), 6.83 (s, 1H), 6.69 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 5.01 (s, 2H), 3.80 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 144.1, 143.0, 136.9, 136.7, 136.0, 132.3 (2C), 132.1, 131.7, 129.9 (3C), 129.6, 127.6, 127.2 (2C), 125.0, 124.5, 121.6, 119.3, 119.1, 113.1 (2C), 55.7, 55.4, 21.5; MS (FAB): *m/e* (%) = 601.0 ($[M+4]^+$, 63), 598.9 ($[M+2]^+$, 100), 596.9 ($[M]^+$, 46), 443.9 (52), 364.0 (30); HR-MS (FAB): *m/e* = 596.9611, calcd. for $C_{27}H_{21}Br_2NO_3S$ $[M]^+$: 596.9609.

(*E*)-4-Chloro-3-[chloro(phenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (17a): yield: 45 mg (0.10 mmol, 63%); red solid; mp 145–146 °C; IR (CH_2Cl_2): ν = 3062, 2926, 2359, 1598, 1491, 1355, 1167 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.38–7.30 (m, 1H), 7.24–7.16 (m, 6H), 7.09–6.99 (m, 1H), 6.84 (s, 1H), 6.74 (d, J = 7.5 Hz, 2H), 4.99 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 142.7, 138.0, 137.8, 136.6, 135.4, 134.4, 131.2, 130.0 (3C), 129.8 (2C), 129.5, 128.9, 127.8 (2C), 127.1 (2C), 125.3, 125.1, 124.9, 121.6, 119.5, 52.0, 21.5; MS (ESI): *m/e* (%) = 504.0 ($[M+2+Na]^+$, 38), 502.0 ($[M+Na]^+$, 52), 439.5 (8), 397.4 (7), 337.1 (9), 321.0 (11); HR-MS (ESI): *m/e* = 502.0421, calcd. for $C_{26}H_{19}Cl_2NO_2NaS$ $[M+Na]^+$: 502.0411.

(*E*)-4-Chloro-3-[chloro(*p*-tolyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (17b): yield: 38 mg (0.08 mmol, 51%); red solid; mp 175–177 °C; IR (CH_2Cl_2): ν = 3059, 2927, 1597, 1447, 1353, 1169 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.23–7.15 (m, 4H), 7.05–6.98 (m, 3H), 6.83 (s, 1H), 6.64 (d, J = 8.1 Hz, 2H), 4.98 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 142.7, 140.4, 138.4, 136.6, 135.4, 135.0, 134.2, 131.2, 129.9 (2C), 129.8 (2C), 129.4, 129.2, 128.5 (2C), 127.1 (2C), 125.2, 124.8, 124.5, 121.6, 119.3, 52.0, 21.5, 21.4; MS (ESI): *m/e* (%) = 518.1 ($[M+2+Na]^+$, 12), 516.1 ($[M+Na]^+$, 17), 437.4 (5), 381.4 (3), 360.3 (11), 304.3 (12); HR-MS (ESI): *m/e* = 516.0555, calcd. for $C_{27}H_{21}Cl_2NO_2NaS$ $[M+Na]^+$: 516.0568.

(*E*)-4-Chloro-3-[chloro(*m*-tolyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (17c): yield: 39 mg (0.08 mmol, 52%); red solid; mp 119–120 °C; IR (CH_2Cl_2): ν = 3059, 2920, 1598, 1447, 1354, 1166 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.22–7.17 (m, 4H), 7.15 (d, J = 7.7 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.06–7.00 (m, 1H), 6.83 (s, 1H), 6.62 (s, 1H) 6.51 (d, J = 7.6 Hz, 1H), 4.98 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 142.7, 138.3, 137.8, 137.5, 136.6, 135.4, 134.3, 131.2, 130.7, 130.1, 129.9 (2C), 129.4, 129.1, 127.6, 127.1 (2C), 127.0, 125.2, 124.9, 124.8, 121.6, 119.3, 51.9, 21.5, 21.2; MS (EI, 70 eV): *m/e* (%) = 495.2 ($[M+2]^+$, 7), 493.2 ($[M^+]$, 4), 394.2 (18), 358.2 (3), 303.1 (6), 267.2 (19); HR-MS (EI, 70 eV): *m/e* = 493.0676, calcd. for $C_{27}H_{21}Cl_2NO_2S$ $[M]^+$: 493.0670.

(*E*)-4-Chloro-3-[chloro(*p*-tolyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (17d): yield: 39 mg 0.08 mmol, 50%); red solid; mp 166–167 °C; IR (CH_2Cl_2): ν = 3061, 2931, 1600, 1450, 1354, 1255, 1168 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.23–7.12 (m, 4H), 7.07–7.00 (m, 1H), 6.82 (s, 1H), 6.77–6.64 (m, 4H), 4.97 (s, 2H), 3.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 144.1, 142.7, 138.2, 136.6, 135.4, 134.0, 131.6 (2C), 131.2, 130.0, 129.9 (2C), 129.3 (2C), 127.1 (2C), 125.2, 124.8, 123.8, 121.6,

119.2, 113.1 (2C), 55.3, 52.2, 21.5; MS (EI, 70 eV): *m/e* (%) = 511.1 ([M+2]$^+$, 30), 509.2 ([M]$^+$, 35), 464.2 (4), 354.1 (100), 319.1 (25), 308.1 (23), 240.1 (13); HR-MS (EI, 70 eV): *m/e* = 509.0625, calcd. for $C_{27}H_{21}Cl_2NO_3S$ [M]$^+$: 509.0619.

(*E*)-4-Chloro-3-[chloro(4-bromophenyl)methylene]-1-tosyl-2,3-dihydro-1*H*-indeno[2,1-*b*]pyridine (17e): yield: 60 mg (0.11 mmol, 72%); red solid; mp 128–129 °C; IR (CH_2Cl_2): ν = 3072, 2921, 1600, 1449, 1353, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.24–7.16 (m, 4H), 7.04 (ddd, *J* = 7.6, 7.0, 1.9 Hz, 1H), 6.84 (s, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.96 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 142.7, 136.8, 136.6, 136.4, 135.3, 134.8, 131.3 (2C), 131.1 (3C), 129.9 (2C), 129.7, 128.1, 127.2 (2C), 125.8, 125.4, 125.0, 124.5, 121.7, 119.9, 51.9, 21.5; MS (EI, 70 eV): *m/e* (%) = 559.1 ([M+2]$^+$, 33), 557.1 ([M]$^+$, 18), 404.0 (100), 368.1 (14), 323.1 (22), 288.1 (21), 246.1 (28); HR-MS (EI, 70 eV): *m/e* = 556.9616, calcd. for $C_{26}H_{18}BrCl_2NO_2S$ [M]$^+$: 556.9619.

(*E*)-Ethyl 4-{chloro(4-chloro-1-tosyl-1*H*-indeno[2,1-*b*]pyridin-3(2*H*)-ylidene)methyl}benzoate (17f): yield: 44 mg (0.08 mmol, 53%); red solid; mp 156–157 °C; IR (CH_2Cl_2): ν = 3055, 2919, 2232, 1719, 1596, 1370, 1169 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.6 Hz, 2H), 7.78–7.72 (m, 3H), 7.23–7.18 (m, 4H), 7.03 (ddd, *J* = 7.6, 6.9, 1.9 Hz, 1H), 6.84 (s, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.98 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 144.4, 142.7, 142.1, 136.5, 136.3, 135.2, 134.9, 131.6, 131.0, 130.0 (2C), 129.7, 129.7 (2C), 128.9 (2C), 127.9, 127.1 (2C), 126.3, 125.4, 125.0, 121.7, 120.0, 61.3, 51.8, 21.5, 14.3; MS (EI, 70 eV): *m/e* (%) = 553.1 ([M+2]$^+$, 13), 551.2 ([M]$^+$, 17), 452.2 (5), 396.1 (100), 368.1 (26), 332.1 (19), 288.1 (47); HR-MS (EI, 70 eV): *m/e* = 551.0723, calcd. for $C_{29}H_{23}Cl_2NO_4S$ [M]$^+$: 551.0725.

Supporting Information

Spectroscopic characterization and copies of ^{1}H/^{13}C NMR spectra of compounds **1a–m**, **2a–m**, **3a–i**, **4a–i**, **8a**, **b**, **9a**, **b**, **11a–i**, **12a–i**, **16a–f**, and **17a–f** and X-ray crystallographic information files for compounds **2d**, **2l**, **4b**, **4g**, **9a**, **12a**, **17a**, and **17b** are available in the Supporting Information.

Acknowledgements

This work is supported by the Ministry of Science and Technology (NSC 101-2113M-003-002-MY3) and National Taiwan Normal University.

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