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Graphical Abstract

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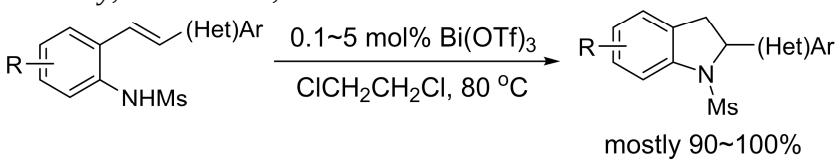

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ABSTRACT

An efficient $Bi(OTf)_3$-mediated intramolecular hydroamination of 2-aminostilbenes for the synthesis of various 2-arylindolines has been developed. Various advantages using $Bi(OTf)_3$ as a catalyst, such as the operationally easy, simple, and safe procedure, good to excellent chemical yields, and the use of relatively low catalyst loading are noteworthy.

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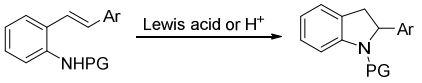
1. Introduction

Indolines are a ubiquitous structural motif of a wide range of naturally occurring and biologically active alkaloids.[1] Consequently, a number of methods have been reported for the construction of these privileged structures and new, more efficient synthetic methods still continue to be vigorously pursued. Intramolecular hydroamination[2] of aminoolefins is one of the efficient, straightforward, and atom economic methods for the synthesis of nitrogen-containing heterocycles through the addition of an N–H bond across a C=C bond.[3] In general, 2-allylanilines have been used as an unactivated alkenyl amine substrate for transition-metal-[4] or Brønsted acid-catalyzed[5] intramolecular hydroamination to afford 2-methylindoline derivatives. In contrast, 2-aminostilbenes have been scarcely used as a substrate for intramolecular hydroamination (Scheme 1). The Zhao group reported only a single example (Ar = Ph, PG = Ts) using a catalytic amount of TfOH, which is very corrosive, toxic, moisture sensitive, and difficult to handle.[5a] While Fe-catalyzed intramolecular hydroamination of aminoolefins for the synthesis of pyrrolidines was successfully developed,[6] cyclohydroamination of 2-aminostilbenes required the excess amount of $FeCl_3$, additives (e.g., benzophenone), and an electron-rich aryl group at the alkene moiety (Ar containing at least one MeO group) to afford indolines in low to moderate yields.[7] During the course of our recent studies on the indole synthesis under the $FeCl_3$/DDQ system, we also uncovered that the use of only $FeCl_3 \cdot 6H_2O$ in the absence of DDQ led to the corresponding indoline product in 40% yield.[8]

$Bi(OTf)_3$ has emerged as a versatile green Lewis acid for diverse organic reactions[9] due to its numerous advantages: commercial availability, low cost, low toxicity, air- and moisture-stability, and easy recovery/reuse.[10] Only a handful of $Bi(OTf)_3$-catalyzed hydroamination reactions have been reported in literature,[11] and, to the best of our knowledge, $Bi(OTf)_3$-catalyzed synthesis of indolines has not yet been exploited.



PG = Ts, Ar = Ph : 20 mol% TfOH, 75% yield (a single example, ref. 5a)
PG = Ac, Ar = 3,4-$(MeO)_2C_6H_3$: 1~3 equiv $FeCl_3$, 37~78% yields (ref. 7)
PG = Ts, Ar = Ph : 10 mol% $FeCl_3 \cdot H_2O$, 40% yield (our preliminary results, ref. 8)
PG = Ms, Ar = **(hetero)aryl : 0.1~5 mol% $Bi(OTf)_3$: mostly 90~100% yields** - ***This work***

Scheme 1. Hydroamination of 2-aminostilbenes for the synthesis of 2-arylindolines.

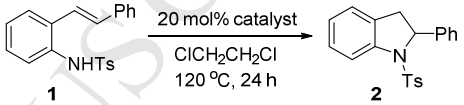
In parallel with our efforts to develop efficient synthetic methods for heterocyclic synthesis,[8, 12] we were interested in developing a new and mild protocol for the formation of indoline skeletons. Herein we report an efficient $Bi(OTf)_3$-mediated intramolecular hydroamination of 2-aminostilbenes for the synthesis of various 2-arylindolines. The operationally simple and straightforward procedure, the use of relatively low loading of $Bi(OTf)_3$, and good to excellent chemical yields are particularly noteworthy. Various advantages of main-group metal salt, $Bi(OTf)_3$ render this protocol an effective alternative or complementary to the known methods utilizing a transition-metal or Brønsted acid.

2. Results and discussion

We began our investigations on a variety of Lewis acids using **1** as the test substrate (Table 1, entries 1-18). Gratifyingly, it was found that $Cu(OTf)_2$, $In(OTf)_3$, $InCl_3$, and $Bi(OTf)_3$ showed comparably good reactivities to give the corresponding indoline **2** in 74-88% yields (entries 1, 3, 5, and 7). However, while reducing the amount of the catalysts (20 mol% → 5 mol%) generally decreased the yield of **2** (entries 2, 4, and 6), $Bi(OTf)_3$ proved to be superior to others to afford **2** in 86% yield (entry 8). Decreasing the reaction temperature significantly reduced the yield (entry 9). Other solvents were examined (entries 21-22): no reaction occurred in Lewis basic polar solvents and $ClCH_2CH_2Cl$ was identified as the most effective solvent.

For metal salts with weakly coordinating counterions, the generation of Brønsted acids through hydrolysis is well-documented,[13] and there are several examples of $Bi(OTf)_3$-catalyzed reactions wherein TfOH is the real catalyst.[14] Supporting this claim, TfOH indeed displayed a similar catalytic activity (entry 19), whereas this reaction failed with HCl (entry 20).

Table 1
Optimization studies



1 2

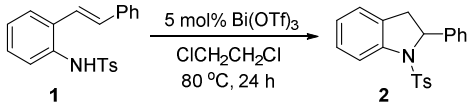
Entry	Catalyst	Yield (%)[a]	Entry	Catalyst	Yield (%)[a]
1	$Cu(OTf)_2$	74	12	$Fe(OTf)_2$	(0)
2[b]	$Cu(OTf)_2$	61	13	$Sc(OTf)_3$	(10)
3	$In(OTf)_3$	77	14	$Yb(OTf)_3$	(0)
4[b]	$In(OTf)_3$	43	15	AgOTf	64
5	$InCl_3$	88	16	$Sn(OTf)_2$	(6)
6[b]	$InCl_3$	75	17	$Zn(OTf)_2$	(0)
7	$Bi(OTf)_3$	77	18	$Mg(OTf)_2$	(0)
8[b]	**$Bi(OTf)_3$**	**86**	19[d]	TfOH	62
9[b-c]	$Bi(OTf)_3$	44	20[d]	HCl	(0)
10	$BiCl_3$	23	21[b, e]	$Bi(OTf)_3$	44
11	$FeCl_3 \cdot 6H_2O$	59	22[b, f]	$Bi(OTf)_3$	(0)

[a] Isolated yields. Values in parentheses indicate a ^1H NMR yield using trichloroethylene as an internal standard.
[b] Using 5 mol% catalyst.
[c] At 80 °C.
[d] Using 10 mol% catalyst at 80 °C.
[e] In toluene.
[f] In 1,4-dioxane, MeCN, EtOAc, acetone, or DMF.

To confirm that either adventitious water alone or Lewis acid-Lewis base (-NH- in substrate **1**) interaction contribute to the in situ generation of TfOH, several control experiments have been performed (Table 2). The addition of an equimolar amount of base to $Bi(OTf)_3$ resulted in only slightly lower yield of **2** (entry 1 vs entry 2). However, increasing the amount of base gave very low or no conversion (entries 3-4). In addition, the reaction was completely suppressed in the presence of dehydrating agents such as molecular sieves and anhydrous Na_2SO_4 (entries 5-6). On the contrary, the reaction of **1** took place smoothly in the presence of catalytic amounts of water (entries 7-9). These findings suggest that, most likely, $Bi(OTf)_3$ serves as a source of Brønsted acid, TfOH which could be the real catalytic species, through either hydrolysis or hydration of the triflate salt with residual moisture. Given that TfOH is very corrosive, toxic, moisture sensitive, and thus difficult to handle, the contrasting features of $Bi(OTf)_3$ provide an operationally simple, safe, and practical alternative.

Table 2

Additive effect



1 2

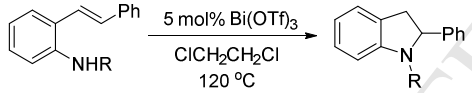
Entry	Additive	Yield (%)[a]
1	-	44
2	5 mol% 2,6-lutidine	36
3	10 mol% 2,6-lutidine	(20)
4	15 mol% 2,6-lutidine	(0)
5	MS 4Å (500 mg/mmol)	(0)
6	Na_2SO_4 (500 mg/mmol)	(0)
7	5 mol% H_2O	56
8	10 mol% H_2O	54
9	20 mol% H_2O	36

[a] Isolated yields. Values in parentheses indicate a ^{1}H NMR yield using trichloroethylene as an internal standard.

Next, we explored the effect of substituents on the nitrogen atom (Table 3). Basicity of nitrogen atom exerted a great influence on the reaction outcome, and the sulfonyl group was effective. Among sulfonyl groups, the Ms (methanesulfonyl) group was revealed as the substituent of choice for this reaction with regard to reaction time and product yield (entries 1-4). Lowering the reaction temperature to 80 °C still resulted in an excellent yield of **2a**, albeit requiring a longer reaction time (entry 6). Reducing a catalyst loading led to an incomplete conversion (entry 7). In the case of an *N*-Boc substrate, only Boc-deprotected starting material was obtained quantitatively, providing further evidence for the in situ generation and involvement of TfOH during the reaction (entry 12).

Table 3

Effect of substituents on the nitrogen atom

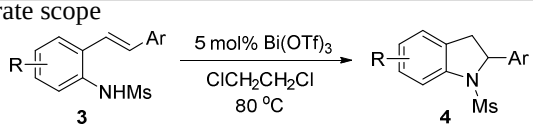


Entry	R	Time (h)	Yield (%)[a]	Entry	R	Time (h)	Yield (%)[a]
1	Ts (**1**)	24	86 (**2**)	8	Ac	24	(27)[e]
2	Bs	12	99	9	Bz	24	(13)[e]
3	Ns	24	99	10	CO_2Et	24	(60)[e]
4	Ms (**3a**)	6	98 (**4a**)	11	Cbz	24	(0)[f]
5[b]	Ms (**3a**)	8	96 (**4a**)	12	Boc	1	(0)[g]
6[c]	Ms (**3a**)	24	99 (**4a**)	13	H	24	(0)[f]
7[d]	Ms (**3a**)	24	62[e] (**4a**)				

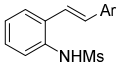
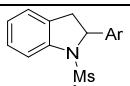
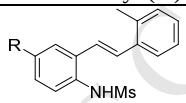
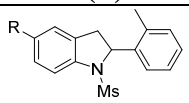
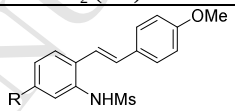
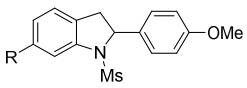
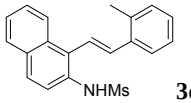
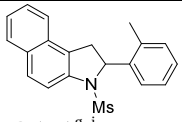
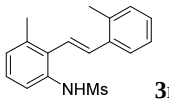
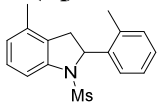
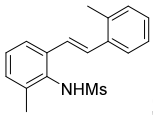
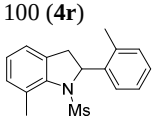
[a] Isolated yields. Values in parentheses indicate a ^{1}H NMR yield using trichloroethylene as an internal standard.
[b] Performed at 100 °C.
[c] Performed at 80 °C.
[d] Using 2 mol% catalyst.
[e] Unreacted starting material remained in 15-80%.
[f] No reaction occurred.
[g] *N*-Boc deprotected starting material was obtained quantitatively.

Table 4

Substrate scope



3 4

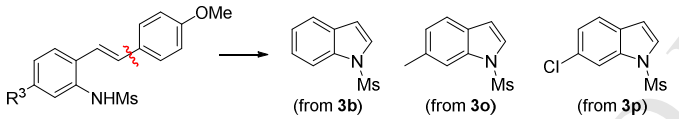
Entry	Ar, R	Time (h)	Yield (%)[a]
			
1	Ar = Ph (**3a**)	24/6[b]	99/98[b] (**4a**)
2	Ar = 4-$MeOC_6H_4$ (**3b**)	6[c]/24[d]	99[c]/86[d] (**4b**)
3	Ar = 4-MeC_6H_4 (**3c**)	4	99 (**4c**)
4	Ar = 3-MeC_6H_4 (**3d**)	4	97 (**4d**)
5	Ar = 2-MeC_6H_4 (**3e**)	4	100 (**4e**)
6[b]	Ar = 4-ClC_6H_4 (**3f**)	24	86 (**4f**)
7[e]	Ar = 4-$NO_2C_6H_4$ (**3g**)	24	-[f] (**4g**)
8	Ar = 1-naphthyl (**3h**)	24	92 (**4h**)
9	Ar = 3-thienyl (**3i**)	6	92 (**4i**)
			
10[b]	R = MeO (**3j**)	24	44 (**4j**)[g]
11	R = Me (**3k**)	6	93 (**4k**)
12	R = Cl (**3l**)	2	99 (**4l**)
13	R = NO_2 (**3m**)	24	97 (**4m**)
			
14	R = MeO (**3n**)	24	37 (**4n**)
15	R = Me (**3o**)	1[d]/6 d[g]	91[d]/90[h] (**4o**)
16	R = Cl (**3p**)	24	-[i]
	 **3q**		
17[b]		24	73 (**4q**)[g, j]
	 **3r**		
18		24	100 (**4r**)
	 **3s**		
19		24	78 (**4s**)[g]

[a] Isolated yields.
[b] Performed at 120 °C.
[c] Using 1 mol% $Bi(OTf)_3$.
[d] Using 0.5 mol% $Bi(OTf)_3$.
[e] Using 20 mol% $Bi(OTf)_3$ at 120 °C.
[f] No reaction occurred.
[g] Unreacted starting material **3** was recovered in 5-25% yields.
[h] Using 0.1 mol% $Bi(OTf)_3$.
[i] *N*-Ms-6-Chloroindole was obtained in 58% yield along with 38% of recovered **3p**.
[j] The corresponding indole, *N*-Ms-2-(*o*-tolyl)-3*H*-benzo[*e*]indole was obtained in 13% yield.

With the optimized conditions and substituent on the nitrogen atom in hand, we set out to explore the substituent effect (Ar) at the alkene moiety (Table 4, entries 1-9). A variety of *N*-Ms-2-aminostilbenes underwent intramolecular hydroamination smoothly to afford the corresponding indolines in good to

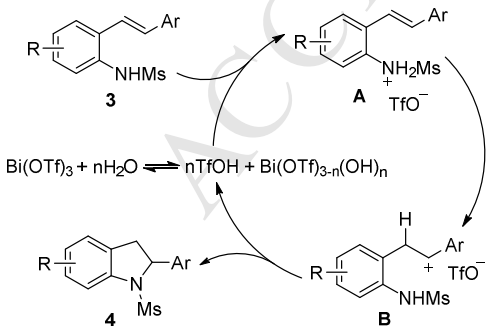
excellent yields. Electron-rich and -neutral, and moderately electron-deficient aryl groups irrespective of the position of their substituents were well tolerated, showing little steric dependence. In the case of a substrate with a strongly electron-donating substituent (e.g., MeO), catalyst loading could be successfully reduced to 0.5 mol% (entry 2). In contrast, strongly electron-withdrawing aryl substituents, such as NO_2, led to no reaction even under higher both catalyst loading and reaction temperature (entry 7), alluding to the involvement of a protonation of a tethered alkene.[15] Both naphthyl and heteroaryl moiety could also be incorporated as a substituent at the alkene terminus (entries 8-9).

Subsequently, we also investigated the effects of substituents (R) residing on the aniline aromatic moiety (entries 10−19). With little steric influence, both moderately electron-donating and electron-withdrawing substituents were well tolerated, whereas a strongly electron-donating substituent (e.g., OMe) gave an adverse effect, leading to low yields of the products along with some decomposition of the substrate (entries 10 and 14). In the case of substrate **3o**, catalyst loading could be significantly reduced to 0.1 mol% to afford **4o** in 90% yield, albeit requiring a long reaction time (entry 15). Very interestingly, when Ar = 4-$MeOC_6H_4$ (e.g., **3b**, **3o**, **3p**), increasing a catalyst loading led to the cleavage of C-C bond and oxidation to afford the corresponding 2-unsubstituted indoles, which cannot be fully elucidated at this stage (Scheme 2): from **3b**: 0% (0.5 and 1 mol% Bi), trace (5 mol% Bi), 63% (10 mol% Bi at 120 °C); from **3o**: 0% (0.1 and 0.5 mol% Bi), 5% (1 mol% Bi), 14% (5 mol% Bi); from **3p**: 58% (5 mol% Bi), 87% (10 mol% Bi at 120 °C).



Scheme 2.

Unfortunately, terminal and trisubstituted alkene derivatives were not suitable for this hydroamination to give the corresponding indolines in very low yields (<30%) or an unidentified dimerized product (when Ar = H). When an alkyl group is substituted at the alkene (e.g., Ar = *n*Hex), complex mixture was obtained along with 30% of recovered substrate.



Scheme 3. Proposed mechanism.

Based on the related mechanisms established for the $Bi(OTf)_3$-[11] and TfOH-catalyzed[5a, 15] hydroamination reactions, a plausible mechanistic proposal is outlined in Scheme 3. TfOH is generated through either hydrolysis or hydration of $Bi(OTf)_3$ with adventitious water. Intermediate **A** resulted from the protonation at the nitrogen atom of a mesylamide moiety of **3** undergoes an intramolecular proton transfer to afford a stable benzylic carbocation intermediate **B**. Subsequent intramolecular nucleophilic attack by the *o*-sulfonamide group toward a carbocation gives an indoline product **4** and regenerates the catalytically active TfOH.

3. Conclusion

In summary, we developed a simple and efficient $Bi(OTf)_3$-mediated intramolecular hydroamination of 2-aminostilbenes for the synthesis of various 2-arylindolines. The salient features of this protocol are the operationally easy, simple, and safe procedure, good to excellent chemical yields, and the use of relatively low loading of $Bi(OTf)_3$. This reaction represents a rare and attractive system for main-group metal-catalyzed intramolecular hydroamination with various advantages of $Bi(OTf)_3$, and thus an effective alternative or complementary to the known methods utilizing a transition-metal or Brønsted acid for related transformations.

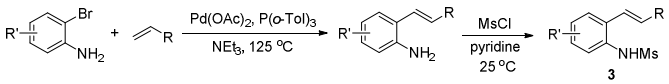
4. Experimental section

4.1. General information

Nuclear Magnetic Resonance spectra were recorded on 400 MHz instruments. Spectra were recorded in $CDCl_3$ solution referenced to TMS or solvent residual peak. High Resolution Mass Spectra were measured using EI at 70 eV. GC-MS spectra were recorded with EI ionization and an Elite-1 column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, the following method was used: The method starts with the injection temperature T_0 (50 °C), after holding this temperature for 5 min, the column is heated to the temperature T_1 (ramp, 300 °C, 10 °C/min) and hold for additional 10 min. Flash chromatography was performed on silica gel 230-400 mesh. All catalysts were purchased from Sigma-Aldrich or Strem and used as received. Unless otherwise noted, all commercially obtained reagents and solvents were used as received. Anhydrous DMF, toluene, $ClCH_2CH_2Cl$, and 1,4-dioxane were purchased from Sigma-Aldrich in a SureSeal™ bottle and used as received. Acetone, EtOAc, and MeCN were distilled from CaH_2 immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV.

Preparation and spectral data of substrates **1**, **3a**, and other *N*-substituted compounds in Table 3 are available in our previous report.[12r]

4.2. General procedure for the preparation of *N*-Ms-2-aminostilbenes 3



In step 1, the requisite 2-styrylanilines were prepared following the method reported in our previous papers.[8, 12r, 12u-v] In step 2, to a solution of 2-styrylaniline (1 equiv) in pyridine (0.2 M) was added methanesulfonyl chloride (1.1 equiv) at 0 °C. After being stirred at 25 °C for 2 hours, the reaction mixture was poured into water and then the product was extracted with CH_2Cl_2 (three times), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the corresponding product **3**.

*4.2.1. (E)-N-(2-Styrylphenyl)methanesulfonamide (**3a**)*[12r]

99% (step 1), 92% (step 2), a white solid (EtOAc : *n*-Hexane = 1:8 (step 1), 1:3 (step 2)), mp 109-110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (s, 3H), 6.77 (br s, 1H), 7.06 (d, J = 16.4 Hz, 1H), 7.29-7.34 (m, 4H), 7.38 (t, J = 7.4 Hz, 2H), 7.50 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.9, 122.6, 125.0, 126.8, 126.9, 127.0, 128.3, 128.7, 128.8, 132.3, 132.9, 133.3, 136.6; MS (EI) *m*/*z* 273 (M^+), 194, 165, 152, 139, 117, 97, 89, 82, 63, 51.

*4.2.2. (E)-N-(2-(4-Methoxystyryl)phenyl)methanesulfonamide (**3b**)*

77% (step 1), 87% (step 2), a white solid (EtOAc : *n*-Hexane = 1:4 (step 1), 1:2 (step 2)), mp 110-111 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.02 (s, 3H), 3.84 (s, 3H), 6.49 (br s, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 16.0 Hz, 1H), 7.15 (d, J = 16.0 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 6.8 Hz, 1H), 7.61 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.9, 55.3, 114.2, 120.2, 124.8, 126.8, 128.1, 128.3, 129.4, 132.5, 132.6, 133.1, 159.8 (1 carbon is missing due to overlapping); MS (EI) *m*/*z* 303 (M^+), 224, 209, 193, 180, 165, 152, 127, 117, 96, 89, 77, 63, 51.

*4.2.3. (E)-N-(2-(4-Methylstyryl)phenyl)methanesulfonamide (**3c**)*

73% (step 1), 78% (step 2), a white solid (EtOAc : *n*-Hexane = 1:7 (step 1), 1:3 (step 2)), mp 144-145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.01 (s, 3H), 6.62 (br s, 1H), 7.03 (d, J = 16.0 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 16.0 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 40.0, 121.4, 124.8, 126.7, 126.8, 127.0, 128.5, 129.5, 132.4, 133.1, 133.2, 133.8, 138.4; MS (EI) *m*/*z* 287 (M^+), 208, 193, 178, 165, 152, 128, 117, 103, 90, 77, 65, 51.

*4.2.4. (E)-N-(2-(3-Methylstyryl)phenyl)methanesulfonamide (**3d**)*

37% (step 1), 40% (step 2), a white solid (EtOAc : *n*-Hexane = 1:7 (step 1), CH_2Cl_2 : Et_2O : *n*-Hexane = 2:1:4 (step 2)), mp 86-87 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.40 (s, 3H), 3.02 (s, 3H), 6.65 (br s, 1H), 7.03 (d, J = 16.0 Hz, 1H), 7.13 (d, J = 6.8 Hz, 1H), 7.26-7.37 (m, 6H), 7.51 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 39.8, 122.3, 124.1, 125.1, 126.80, 126.83, 127.4, 128.5, 128.6, 129.1, 132.4, 132.9, 133.3, 136.6, 138.4; MS (EI) *m*/*z* 287 (M^+), 208, 193, 178, 165, 152, 128, 117, 103, 89, 77, 65, 51.

*4.2.5. (E)-N-(2-(2-Methylstyryl)phenyl)methanesulfonamide (**3e**)*

50% (step 1), 67% (step 2), a white solid (EtOAc : *n*-Hexane = 1:7 (step 1), 1:3 (step 2)), mp 120-121 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 3.02 (s, 3H), 6.55 (br s, 1H), 7.18 (d, J = 16.4 Hz, 1H), 7.21-7.35 (m, 6H), 7.51 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 40.0, 123.9, 124.5, 125.6, 126.4, 126.8, 127.3, 128.3, 128.8, 130.5, 131.0, 132.4, 133.4, 135.7, 136.0; MS (EI) *m*/*z* 287 (M^+), 208, 193, 178, 165, 152, 130, 115, 102, 91, 77, 65, 51.

*4.2.6. (E)-N-(2-(4-Chlorostyryl)phenyl)methanesulfonamide (**3f**)*

48% (step 1), 93% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:3 (step 2)), mp 121-122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.02 (s, 3H), 6.79 (br s, 1H), 7.00 (d, J = 16.0 Hz, 1H), 7.27-7.38 (m, 3H), 7.33 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.6 Hz, 3H), 7.65 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.9, 123.3, 125.1, 126.9, 127.0, 128.0, 128.90, 128.94, 131.3, 132.3, 133.3, 133.9, 135.2; MS (EI) *m*/*z* 307 (M^+), 228, 193, 165, 139, 125, 117, 96, 89, 82, 75, 63, 51.

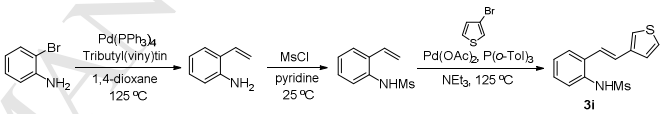
*4.2.7. (E)-N-(2-(4-Nitrostyryl)phenyl)methanesulfonamide (**3g**)*

49% (step 1), 81% (step 2), an orange solid (EtOAc : *n*-Hexane = 1:5 (step 1), 1:2 (step 2)), mp 211-212 °C; ^{1}H NMR (acetone-d_6, 400 MHz) δ 3.04 (s, 3H), 7.36 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 16.4 Hz, 1H), 7.42 (td, J = 2.0, 7.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 8.8 Hz, 3H), 7.98 (d, J = 16.4 Hz, 1H), 8.27 (d, J = 9.2 Hz, 2H), 8.47 (br s, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 40.0, 124.8, 127.3, 127.6, 127.7, 128.4, 129.1, 129.5, 130.2, 133.5, 136.3, 145.1, 147.8; MS (EI) *m*/*z* 318 (M^+), 239, 193, 165, 139, 127, 117, 90, 77, 63, 51.

*4.2.8. (E)-N-(2-(2-(Naphthalen-1-yl)vinyl)phenyl)methanesulfonamide (**3h**)*

61% (step 1), 90% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:3 (step 2)), mp 161-162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.03 (s, 3H), 6.52 (br s, 1H), 7.32-7.38 (m, 3H), 7.50-7.57 (m, 4H), 7.76-7.79 (m, 2H), 7.84-7.90 (m, 3H), 8.17 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.0, 123.4, 124.0, 125.0, 125.6, 125.7, 125.9, 126.3, 127.0, 127.2, 128.7, 128.9, 130.0, 131.2, 132.6, 133.4, 133.6, 134.2 (1 carbon is missing due to overlapping); MS (EI) *m*/*z* 323 (M^+), 244, 215, 202, 189, 166, 152, 139, 127, 121, 107, 89, 77, 63, 51.

*4.2.9. (E)-N-(2-(2-(Thiophen-3-yl)vinyl)phenyl)methanesulfonamide (**3i**)*



3i

Both step 1 and step 3 were performed following the method reported in our previous papers.[8, 12r, 12u-v] In step 2, *N*-mesylation of 2-styrylaniline was conducted in the same way as step 2 of General Procedure. 54% (step 1), 87% (step 2), 25% (step 3), a white solid (CH_2Cl_2: *n*-Hexane = 2:1 (step 1), EtOAc : *n*-Hexane = 1:2 (step 2 & step 3)), mp 103-104 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.02 (s, 3H), 6.59 (br s, 1H), 7.07 (d, J = 16.4 Hz, 1H), 7.16 (d, J = 16.4 Hz, 1H), 7.25-7.35 (m, 4H), 7.39 (d, J = 4.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.9, 122.4, 123.6, 124.9, 125.0, 126.5, 126.7, 126.9, 128.5, 132.3, 133.2, 139.6 (1 carbon is missing due to overlapping); MS (EI) *m*/*z* 279 (M^+), 200, 171, 167, 154, 129, 116, 100, 89, 77, 63, 51.

*4.2.10. (E)-N-(4-Methoxy-2-(2-methylstyryl)phenyl)methanesulfonamide (**3j**)*

In step 1, the requisite 2-vinylaniline was prepared from 2-iodo-4-methoxy-1-nitrobenzene following the method reported by Driver and co-workers.[16] In step 2: 90 %, (EtOAc : *n*-Hexane = 1:3), a white solid, mp 124-125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 2.94 (s, 3H), 3.85 (s, 3H), 6.58 (br s, 1H), 6.84 (dd, J = 2.8, 8.4 Hz, 1H), 7.18-7.28 (m, 6H), 7.36 (d, J = 8.8 Hz, 1H), 7.62-7.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 39.7, 55.5, 111.7, 113.8, 124.3, 125.6, 125.9, 126.4, 128.2, 129.1, 130.3, 130.5, 135.6, 135.8, 136.0, 158.9; MS (EI) *m*/*z* 317 (M^+), 238, 223, 207, 194, 180, 165, 152, 132, 115, 96, 91, 83, 65, 52.

*4.2.11. (E)-N-(4-Methyl-2-(2-methylstyryl)phenyl)methanesulfonamide (**3k**)*

35% (step 1, using 2-bromo-4-methylaniline), 74% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:3 (step 2)), mp 141-142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.40 (s, 3H), 2.44 (s, 3H), 3.00 (s, 3H), 6.34 (br s, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.19-7.26 (m, 4H), 7.28 (d, J = 16.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.59-7.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ

19.9, 21.1, 39.7, 124.2, 125.6, 126.0, 126.3, 127.3, 128.1, 129.4, 130.1, 130.4, 130.7, 133.1, 135.8, 135.9, 137.1; MS (EI) *m/z* 301 (M^+), 222, 207, 178, 165, 152, 130, 110, 103, 91, 83, 77, 65, 51.

*4.2.12. (E)-N-(4-Chloro-2-(2-methylstyryl)phenyl)methanesulfonamide (**3l**)*

64% (step 1, using 2-bromo-4-chloroaniline), 83% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:3 (step 2)), mp 157-158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 3.01 (s, 3H), 6.51 (br s, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.19-7.32 (m, 5H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.59-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 40.1, 122.6, 125.6, 126.36, 126.43, 126.9, 128.5, 128.6, 130.6, 131.8, 132.0, 132.6, 134.3, 135.2, 136.2; MS (EI) *m/z* 321 (M^+), 242, 207, 191, 178, 165, 151, 128, 115, 102, 89, 76, 65, 51.

*4.2.13. (E)-N-(2-(2-Methylstyryl)-4-nitrophenyl)methanesulfonamide (**3m**)*

30% (step 1, using 2-bromo-4-nitroaniline), 35% (step 2), a yellow solid (CH_2Cl_2 : Et_2O : *n*-Hexane = 3:1:5 (step 1), CH_2Cl_2 : *n*-Hexane = 2:1 (step 2)), mp 177-178 °C; ^{1}H NMR (acetone-d_6, 400 MHz) δ 2.47 (s, 3H), 3.21 (s, 3H), 7.24 (s, 3H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.74 (br s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.55 (s, 1H), 8.95 (br s, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 20.0, 41.0, 123.0, 123.5, 124.0, 126.8, 127.1, 129.3, 131.3, 132.6, 132.8, 136.6, 137.3, 141.9, 145.7 (1 carbon is missing due to overlapping); MS (EI) *m/z* 332 (M^+), 253, 236, 207, 178, 165, 152, 128, 115, 102, 91, 77, 63, 51.

*4.2.14. (E)-N-(5-Methoxy-2-(4-methoxystyryl)phenyl)methanesulfonamide (**3n**)*

In step 1, the requisite 2-vinylaniline was prepared from 2-bromo-5-methoxy-1-nitrobenzene following the method reported by Driver and co-workers.[16] In step 2: 56 %, (EtOAc : *n*-Hexane = 1:3), a white solid, mp 112-113 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.02 (s, 3H), 3.83 (s, 6H), 6.65 (br s, 1H), 6.81 (d, *J* = 6.8 Hz, 1H), 6.89 (d, *J* = 16.8 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 16.0 Hz, 1H), 7.08 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 39.8, 55.3, 55.5, 109.1, 112.8, 114.2, 119.7, 124.3, 127.79, 127.81, 129.6, 131.0, 134.2, 159.5, 159.6; MS (EI) *m/z* 333 (M^+), 254, 238, 223, 208, 196, 180, 167, 152, 139, 127, 120, 105, 91, 77, 63, 51.

*4.2.15. (E)-N-(2-(4-Methoxystyryl)-5-methylphenyl)methanesulfonamide (**3o**)*

60% (step 1, using 2-bromo-5-methylaniline), 69% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), 1:3 (step 2)), mp 149-150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.02 (s, 3H), 3.84 (s, 3H), 6.36 (br s, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 16.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 16.0 Hz, 1H), 7.31 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 39.9, 55.3, 114.2, 120.2, 125.3, 126.6, 127.8, 128.0, 129.6, 131.7, 132.9, 138.6, 159.7 (1 carbon is missing due to overlapping); MS (EI) *m/z* 317 (M^+), 238, 223, 208, 194, 180, 165, 152, 130, 112, 103, 84, 77, 63, 51.

*4.2.16. (E)-N-(5-Chloro-2-(4-methoxystyryl)phenyl)methanesulfonamide (**3p**)*

72% (step 1, using 2-iodo-5-chloroaniline), 73% (step 2), a white solid (EtOAc : *n*-Hexane = 1:6 (step 1), CH_2Cl_2 : *n*-Hexane = 2:1 (step 2)), mp 141-142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.06 (s, 3H), 3.85 (s, 3H), 6.54 (br s, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.53 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 40.1, 55.3, 114.2, 119.0, 123.9, 126.7, 127.8, 128.2, 129.1, 130.5, 133.1, 133.5, 134.1, 159.9; MS (EI) *m/z* 337 (M^+), 258, 223, 208, 180, 152, 128, 112, 96, 89, 76, 63, 51.

*4.2.17. (E)-N-(1-(2-Methylstyryl)naphthalen-2-yl)methanesulfonamide (**3q**)*

32% (step 1, using 2-amino-1-bromonaphthalene[17]), 86% (step 2), a white solid (CH_2Cl_2 : *n*-Hexane = 1:1 (step 1), Et_2O : *n*-Hexane = 1:1 (step 2)), mp 194-195 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 3.04 (s, 3H), 7.02 (br s, 1H), 7.15 (d, *J* = 16.8 Hz, 1H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.24-7.27 (m, 1H), 7.28-7.35 (m, 2H), 7.48-7.55 (m, 2H), 7.75-7.77 (m, 1H), 7.82-7.87 (m, 3H), 8.05 (dd, *J* = 1.4, 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 40.3, 119.6, 122.8, 125.1, 125.3, 125.50, 125.51, 126.5, 127.0, 128.3, 128.7, 129.1, 130.8, 131.1, 131.7, 132.5, 135.1, 136.1, 136.7; MS (EI) *m/z* 337 (M^+), 258, 243, 207, 191, 167, 139, 127, 115, 96, 73, 63, 51.

*4.2.18. (E)-N-(3-Methyl-2-(2-methylstyryl)phenyl)methanesulfonamide (**3r**)*

77% (step 1, using 2-bromo-3-methylaniline), 63% (step 2), a white solid (Et_2O : *n*-Hexane = 1:1 (step 1 & step 2)), mp 81-82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.40 (s, 3H), 3.02 (s, 3H), 6.85 (br s, 1H), 6.86 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.8 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.21-7.28 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.62-7.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9, 20.9, 39.8, 117.3, 124.1, 125.4, 126.4, 126.5, 128.1, 128.5, 128.9, 130.6, 134.4, 135.0, 135.2, 135.9, 137.9; MS (EI) *m/z* 301 (M^+), 222, 207, 191, 178, 165, 152, 144, 130, 115, 103, 91, 77, 65, 51.

*4.2.19. (E)-N-(2-Methyl-6-(2-methylstyryl)phenyl)methanesulfonamide (**3s**)*

59% (step 1, using 2-iodo-6-methylaniline[18]), 92% (step 2), a white solid (EtOAc : *n*-Hexane = 1:15 (step 1), EtOAc : *n*-Hexane = 1:3 (step 2)), mp 126-127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 2.47 (s, 3H), 3.03 (s, 3H), 6.32 (br s, 1H), 7.19-7.23 (m, 4H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 16.4 Hz, 1H), 7.43 (d, *J* = 16.4 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.63-7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 19.9, 41.7, 124.4, 125.3, 126.0, 126.4, 128.0, 128.4, 129.2, 130.5, 131.7, 135.88, 135.92, 137.2, 138.5 (1 carbon is missing due to overlapping); MS (EI) *m/z* 301 (M^+), 222, 207, 191, 178, 165, 152, 130, 115, 103, 91, 77, 65, 51.

4.3. General procedure for the $Bi(OTf)_3$-mediated intramolecular hydroamination of *N*-Ms-2-aminostilbenes 3 for the synthesis of 2-arylindolines 4

To a solution of **3** (0.03~0.8 mmol, 1 equiv) in $ClCH_2CH_2Cl$ (0.3~8 mL, 0.1 M) in pressure tube were added $Bi(OTf)_3$ (0.1~5 mol %). The resulting mixture was stirred at 80 or 120 °C for the reported time under Ar atmosphere. After the reaction was completed, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product **4**. All reactions were carried out 2-4 times repetitively and the average values of the yields are given.

*4.3.1. N-Ts-2-Phenylindoline (**2**)*[8]

86%, a white solid (EtOAc : *n*-Hexane = 1:5), mp 83-84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 2.81 (dd, *J* = 2.8, 16.0 Hz, 1H), 3.21 (dd, *J* = 10.2, 15.8 Hz, 1H), 5.26 (dd, *J* = 3.0, 9.8 Hz, 1H), 6.97-6.98 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.17-7.24 (m, 6H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 37.9, 64.7, 116.5, 124.5,

125.0, 126.0, 127.1, 127.6, 127.9, 128.6, 129.5, 131.1, 135.3, 141.8, 142.6, 143.8; MS (EI) *m/z* 349 (M^+), 194, 165, 152, 139, 116, 91, 77, 65, 51.

4.3.2. N-Bs-2-Phenylindoline

99%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 115-116 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.83 (dd, *J* = 2.8, 16.0 Hz, 1H), 3.22 (dd, *J* = 10.2, 16.2 Hz, 1H), 5.29 (dd, *J* = 2.6, 10.2 Hz, 1H), 6.99-7.00 (m, 2H), 7.17-7.24 (m, 6H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.8, 64.8, 116.4, 124.6, 125.1, 126.0, 127.0, 127.7, 127.9, 128.6, 128.9, 131.1, 132.9, 138.2, 141.7, 142.4; MS (EI) *m/z* 335 (M^+), 194, 165, 152, 141, 116, 91, 77, 65, 51.

4.3.3. N-Ns-2-Phenylindoline

99%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 193-194 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.92 (dd, *J* = 2.0, 16.4 Hz, 1H), 3.35 (dd, *J* = 10.2, 16.2 Hz, 1H), 5.35 (dd, *J* = 2.2, 9.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.14-7.26 (m, 6H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.8, 65.2, 115.5, 124.0, 125.0, 125.5, 126.1, 128.07, 128.09, 128.2, 128.7, 130.8, 140.9, 141.6, 144.1, 150.0; MS (EI) *m/z* 380 (M^+), 194, 165, 152, 139, 122, 116, 91, 76, 65, 51.

*4.3.4. N-Ms-2-Phenylindoline (**4a**)*

99% (80 °C for 24 h), 98% (120 °C for 6 h), a white solid (EtOAc : *n*-Hexane = 1:4), mp 187-188 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.67 (s, 3H), 3.12 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.79 (dd, *J* = 10.6, 16.2 Hz, 1H), 5.42 (dd, *J* = 3.2, 10.0 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.25- 7.33 (m, 6H), 7.43 (d, *J* = 8.0 Hz, 1H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.8, 38.0, 65.1, 114.0, 123.8, 125.4, 126.2, 128.12, 128.13, 128.8, 130.1, 141.7, 142.1; MS (EI) *m/z* 273 (M^+), 194, 165, 152, 139, 116, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{15}H_{15}NNaO_2S$ 296.0716, found 296.0714.

*4.3.5. N-Ms-2-(4-Methoxyphenyl)indoline (**4b**)*

99% (1 mol% $Bi(OTf)_3$ for 6 h), 86% (0.5 mol% $Bi(OTf)_3$ for 24 h), a white solid (EtOAc : *n*-Hexane = 1:2), mp 117-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (s, 3H), 3.10 (dd, *J* = 2.6, 16.2 Hz, 1H), 3.76 (dd, *J* = 10.4, 16.0 Hz, 1H), 3.78 (s, 3H), 5.39 (dd, *J* = 3.2, 10.0 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.22-7.26 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.88, 37.93, 55.2, 64.7, 113.8, 114.1, 123.6, 125.3, 127.6, 128.1, 130.2, 134.1, 141.6, 159.4; MS (EI) *m/z* 303 (M^+), 224, 209, 193, 180, 165, 152, 133, 116, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{16}H_{17}NNaO_3S$ 326.0821, found 326.0821.

*4.3.6. N-Ms-2-(p-Tolyl)indoline (**4c**)*

99%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 96-97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.65 (s, 3H), 3.10 (dd, *J* = 3.0, 16.2 Hz, 1H), 3.77 (dd, *J* = 10.0, 16.4 Hz, 1H), 5.39 (dd, *J* = 3.0, 10.2 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.20-7.24 (m, 4H), 7.41 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 37.8, 38.0, 64.9, 113.9, 123.7, 125.3, 126.2, 128.1, 129.4, 130.2, 137.9, 139.1, 141.7; MS (EI) *m/z* 287 (M^+), 208, 193, 178, 165, 152, 139, 128, 117, 103, 90, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{16}H_{17}NNaO_2S$ 310.0872, found 310.0874.

*4.3.7. N-Ms-2-(m-Tolyl)indoline (**4d**)*

97%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 121-122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 2.68 (s, 3H), 3.08 (dd, *J* = 3.2, 16.4 Hz, 1H), 3.76 (dd, *J* = 10.2, 16.2 Hz, 1H), 5.37 (dd, *J* = 3.4, 10.6 Hz, 1H), 7.04-7.12 (m, 4H), 7.17-7.24 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 37.7, 38.1, 65.1, 114.1, 123.0, 123.8, 125.3, 126.8, 128.1, 128.7, 128.8, 130.2, 138.5, 141.8, 142.2; MS (EI) *m/z* 287 (M^+), 208, 193, 178, 165, 152, 130, 116, 103, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{16}H_{17}NNaO_2S$ 310.0872, found 310.0870.

*4.3.8. N-Ms-2-(o-Tolyl)indoline (**4e**)*

100%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 171-172 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 2.77 (s, 3H), 2.88 (dd, *J* = 3.6, 16.0 Hz, 1H), 3.78 (dd, *J* = 10.4, 16.0 Hz, 1H), 5.60 (dd, *J* = 3.8, 10.2 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.06-7.14 (m, 4H), 7.21-7.26 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 37.7, 37.8, 61.8, 114.2, 124.0, 125.1, 125.6, 126.5, 127.6, 128.1, 129.9, 130.7, 133.9, 141.0, 142.0; MS (EI) *m/z* 287 (M^+), 208, 193, 178, 165, 152, 130, 116, 103, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{16}H_{17}NNaO_2S$ 310.0872, found 310.0871.

*4.3.9. N-Ms-2-(4-Chlorophenyl)indoline (**4f**)*

86%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 131-132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.74 (s, 3H), 3.05 (dd, *J* = 3.2, 16.4 Hz, 1H), 3.79 (dd, *J* = 10.4, 16.4 Hz, 1H), 5.38 (dd, *J* = 3.4, 10.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.24-7.30 (m, 5H), 7.44 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.5, 38.0, 64.4, 114.3, 124.2, 125.4, 127.5, 128.3, 129.0, 129.7, 133.8, 140.9, 141.5; MS (EI) *m/z* 307 (M^+), 228, 193, 165, 137, 117, 102, 96, 91, 82, 75, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{15}H_{14}ClNNaO_2S$ 330.0326, found 330.0328.

*4.3.10. N-Ms-2-(Naphthalen-1-yl)indoline (**4h**)*

92%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 145-146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.93 (s, 3H), 3.07 (dd, *J* = 3.4, 16.2 Hz, 1H), 4.01 (dd, *J* = 10.6, 16.2 Hz, 1H), 6.17 (dd, *J* = 3.6, 10.4 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.4, 38.4, 62.5, 115.2, 122.8, 123.1, 124.5, 125.5, 125.7, 126.3, 128.21, 128.24, 129.2, 129.5, 130.4, 134.1, 137.8, 141.8 (1 carbon is missing due to overlapping); MS (EI) *m/z* 323 (M^+), 244, 228, 215, 202, 189, 166, 153, 128, 121, 114, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{19}H_{17}NNaO_2S$ 346.0872, found 346.0869.

*4.3.11. N-Ms-2-(Thiophen-3-yl)indoline (**4i**)*

92%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 140-141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.54 (s, 3H), 3.10 (d, *J* = 16.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 16.0 Hz, 1H), 5.52 (d, *J* = 9.6 Hz, 1H), 6.91 (d, *J* = 5.2 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 7.19-7.26 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.9, 37.7, 61.0, 114.0, 122.9, 123.7, 125.4, 125.5, 126.8, 128.2, 130.2, 141.1, 142.0; MS (EI) *m/z* 279 (M^+), 200, 167, 154, 129, 116, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{13}H_{13}NNaO_2S_2$ 302.0280, found 302.0281

*4.3.12. N-Ms-5-Methoxy-2-(o-tolyl)indoline (**4j**)*

44%, a beige solid (EtOAc : *n*-Hexane = 1:4), mp 194-195 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 2.80 (s, 3H), 2.86 (dd, *J* = 3.6, 16.0 Hz, 1H), 3.78 (s, 3H), 3.79 (dd, *J* = 10.0, 16.0 Hz, 1H), 5.59 (dd, *J* = 3.4, 10.2 Hz, 1H), 6.73 (s, 1H), 6.80 (dd, *J* = 2.2, 9.0 Hz, 1H), 7.10-7.17 (m, 3H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 36.7, 38.0, 55.7, 62.2, 111.5, 113.0, 115.8, 125.1, 126.5, 127.5, 130.6, 131.8, 133.7, 135.4, 141.0, 157.1; MS (EI) *m/z* 317 (M^+),

238, 223, 207, 194, 180, 165, 152, 132, 118, 103, 96, 91, 77, 65, 52; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{17}H_{19}NNaO_3S$ 340.0978, found 340.0980.

*4.3.13. N-Ms-5-Methyl-2-(o-tolyl)indoline (**4k**)*

93%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 156-157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.42 (s, 3H), 2.80 (s, 3H), 2.87 (dd, *J* = 3.6, 16.0 Hz, 1H), 3.79 (dd, *J* = 10.4, 16.0 Hz, 1H), 5.60 (dd, *J* = 3.6, 10.4 Hz, 1H), 6.99 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.11-7.17 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 20.9, 37.1, 37.7, 62.0, 114.3, 125.1, 126.2, 126.4, 127.5, 128.6, 130.1, 130.6, 133.8, 133.9, 139.7, 141.1; MS (EI) *m/z* 301 (M^+), 222, 207, 178, 165, 152, 130, 115, 103, 91, 77, 65, 53; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{17}H_{19}NNaO_2S$ 324.1029, found 324.1027.

*4.3.14. N-Ms-5-Chloro-2-(o-tolyl)indoline (**4l**)*

99%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 177-178 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 2.79 (s, 3H), 2.91 (dd, *J* = 3.6, 16.4 Hz, 1H), 3.79 (dd, *J* = 10.6, 16.2 Hz, 1H), 5.65 (dd, *J* = 3.4, 10.6 Hz, 1H), 7.11-7.19 (m, 4H), 7.22-7.24 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 37.5, 37.9, 62.1, 115.1, 125.0, 125.7, 126.6, 127.8, 128.1, 129.2, 130.8, 131.9, 134.0, 140.4, 140.8; MS (EI) *m/z* 321 (M^+), 242, 207, 191, 178, 165, 151, 139, 125, 116, 102, 89, 77, 63, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{16}H_{16}ClNNaO_2S$ 344.0482, found 344.0482.

*4.3.15. N-Ms-5-Nitro-2-(o-tolyl)indoline (**4m**)*

97%, a light yellow solid (EtOAc : *n*-Hexane = 1:2), mp 169-170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 2.78 (s, 3H), 3.06 (dd, *J* = 3.2, 16.4 Hz, 1H), 3.87 (dd, *J* = 10.6, 16.6 Hz, 1H), 5.83 (dd, *J* = 3.8, 11.0 Hz, 1H), 7.15-7.21 (m, 4H), 7.51 (d, *J* = 9.2 Hz, 1H), 8.07 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 37.1, 39.9, 62.4, 112.5, 121.5, 124.9, 125.2, 126.8, 128.4, 131.0, 131.2, 134.5, 139.5, 143.8, 147.8; MS (EI) *m/z* 332 (M^+), 253, 207, 178, 165, 152, 139, 128, 115, 102, 89, 77, 63, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{16}H_{16}N_2NaO_4S$ 355.0723, found 355.0721.

*4.3.16. N-Ms-6-Methoxy-2-(4-methoxyphenyl)indoline (**4n**)*

37%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 87-88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (s, 3H), 3.02 (dd, *J* = 2.2, 15.8 Hz, 1H), 3.68 (dd, *J* = 10.0, 15.6 Hz, 1H), 3.78 (s, 3H), 3.82 (s, 3H), 5.38 (dd, *J* = 2.8, 9.6 Hz, 1H), 6.60 (dd, *J* = 1.8, 8.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.2, 37.9, 55.2, 55.6, 65.6, 100.6, 109.1, 114.0, 122.0, 125.5, 127.6, 134.1, 142.8, 159.3, 160.1; MS (EI) *m/z* 333 (M^+), 254, 239, 223, 208, 196, 180, 167, 152, 146, 139, 127, 121, 106, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{17}H_{19}NNaO_4S$ 356.0927, found 356.0926.

*4.3.17. N-Ms-2-(4-Methoxyphenyl)-6-methylindoline (**4o**)*

91% (0.5 mol% $Bi(OTf)_3$ for 1 h), 90% (0.1 mol% $Bi(OTf)_3$ for 6 days), a white solid (EtOAc : *n*-Hexane = 1:3), mp 164-165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.62 (s, 3H), 3.04 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.71 (dd, *J* = 10.4, 16.0 Hz, 1H), 3.78 (s, 3H), 5.38 (dd, *J* = 2.6, 10.2 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 37.6, 37.9, 55.2, 65.0, 114.0, 114.6, 124.4, 124.9, 127.3, 127.6, 134.2, 138.2, 141.7, 159.3; MS (EI) *m/z* 317 (M^+), 238, 223, 208, 194, 180, 165, 152, 146, 130, 119, 103, 97, 89, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{17}H_{19}NNaO_3S$ 340.0978, found 340.0979.

4.3.18. N-Ms-6-Chloroindole

58%, a colorless solid (EtOAc : *n*-Hexane = 1:3), mp 111-112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.13 (s, 3H), 6.69 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 3.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.0, 108.6, 113.2, 122.4, 124.2, 126.6, 129.1, 130.8, 135.1; MS (EI) *m/z* 229 (M^+), 150, 123, 114, 97, 88, 73, 63, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_9H_8ClNNaO_2S$ 251.9856, found 251.9854.

*4.3.19. N-Ms-2-(o-Tolyl)-2,3-dihydro-1H-benzo[e]indole (**4q**)*

73%, a white solid (EtOAc : *n*-Hexane = 1:4), mp 179-180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 3H), 2.85 (s, 3H), 3.22 (dd, *J* = 4.2, 16.2 Hz, 1H), 4.13 (dd, *J* = 10.6, 16.2 Hz, 1H), 5.79 (dd, *J* = 4.2, 10.6 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.17 (td, *J* = 1.2, 7.2 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.42 (td, *J* = 0.8, 7.4 Hz, 1H), 7.50 (td, *J* = 0.9, 7.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 2H), 7.88 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 36.7, 37.7, 62.5, 115.1, 123.1, 123.6, 124.8, 125.3, 126.6, 127.1, 127.6, 128.7, 129.3, 130.4, 130.7, 131.1, 133.8, 139.5, 141.2; MS (EI) *m/z* 337 (M^+), 258, 243, 228, 207, 191, 167, 141, 127, 115, 91, 73, 63, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{20}H_{19}NNaO_2S$ 360.1029, found 360.1027.

4.3.20. N-Ms-2-(o-Tolyl)-3H-benzo[e]indole

13%, a brown solid (EtOAc : *n*-Hexane = 1:4), mp 152-153 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 2.92 (s, 3H), 7.15 (s, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.40 (td, *J* = 1.2, 7.2 Hz, 1H), 7.54 (td, *J* = 1.2, 7.4 Hz, 1H), 7.62 (td, *J* = 1.0, 7.5 Hz, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5, 41.3, 110.2, 114.7, 123.2, 125.1, 125.3, 125.5, 125.7, 126.6, 127.0, 128.5, 129.3, 129.8, 130.3, 130.7, 132.2, 133.7, 139.2, 139.4; MS (EI) *m/z* 335 (M^+), 256, 207, 127, 113, 96, 89, 73, 63, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{20}H_{17}NNaO_2S$ 358.0872, found 358.0874.

*4.3.21. N-Ms-4-Methyl-2-(o-tolyl)indoline (**4r**)*

100%, a white solid (EtOAc : *n*-Hexane = 1:3), mp 127-128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.19 (s, 3H), 2.44 (s, 3H), 2.81 (s, 3H), 2.83 (dd, *J* = 4.0, 16.4 Hz, 1H), 3.71 (dd, *J* = 10.6, 16.2 Hz, 1H), 5.65 (dd, *J* = 3.8, 10.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 7.11-7.21 (m, 4H), 7.31 (dd, *J* = 1.2, 6.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.7, 19.4, 36.9, 37.5, 61.8, 111.7, 125.1, 125.2, 126.5, 127.5, 128.3, 128.5, 130.7, 133.8, 135.2, 141.4, 141.8; MS (EI) *m/z* 301 (M^+), 222, 207, 191, 178, 165, 152, 130, 110, 103, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{17}H_{19}NNaO_2S$ 324.1029, found 324.1027.

*4.3.22. N-Ms-7-Methyl-2-(o-tolyl)indoline (**4s**)*

78%, a white solid (CH_2Cl_2 : *n*-Hexane = 1:1), mp 140-141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 2.61 (s, 3H), 2.74 (d, *J* = 16.0 Hz, 1H), 2.94 (s, 3H), 3.91 (dd, *J* = 8.6, 15.8 Hz, 1H), 5.80 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 7.04-7.07 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.12-7.16 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 20.1, 38.2, 38.6, 63.5, 122.9, 124.4, 126.1, 126.7, 127.3, 130.6, 130.7, 131.0, 133.8, 134.2, 139.9, 141.1; MS (EI) *m/z* 301 (M^+), 222, 207, 178, 165, 152, 130, 110, 103, 91, 77, 65, 51; HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{17}H_{19}NNaO_2S$ 324.1029, found 324.1028.

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Supplementary Material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/

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