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SYNTHESIS OF INDOLINES AND QUINOLINE *VIA* CYCLIZATION OF *N*-ARYLSULFONYL-2-ALLYLANILINES CATALYZED BY BRØNSTED ACID

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Abstract - *N*-Arylsulfonyl-2-allylanilines underwent the intramolecular hydroamination to produce indolines or quinoline in the presence of catalytic amount of triflic acid with good yield. The scope of the reaction was extended to other *N*-protected aminoalkenes.

INTRODUCTION

Hydroamination of alkenes and alkynes,[1] the addition of an N-H bond across a carbon-carbon multiple bond, offers an efficient, atom-economical route to nitrogen-containing molecules. Various approaches using the catalysts of alkali metals,[2] Brønsted acid,[3] early transition metals (group IV),[4] late transition metals,[5] and organo-f-element metal complexes (lanthanide complexes),[6] have been extensively studied to develop efficient and selective catalysts for this simple but challenging transformation. These reactions are particularly interesting from the standpoint of green chemistry because hydroamination displays perfect atom economy. On the other hand, both of indolines and quinolines are a class of substances with an importance as lead structure for psychodysleptics, strong analgesics, analeptics, antihistaminics, and anorectics.[2d, 7] In recent years, The various methods for synthesizing indolines and indoline scaffolds have been reported.[5a, 8] Herein, we would like to report a strategy for the efficient synthesis of indolines or quinoline catalyzed by Brønsted acid.

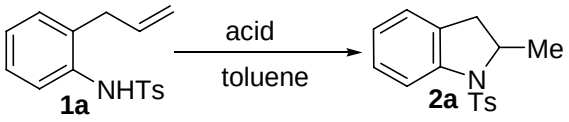
RESULTS AND DISCUSSION

Initially the formation of indolines was investigated using **1a** as a test substrate for screening a series of protic Brønsted acids and solvents, as shown in Table 1. We carried out the experiment in the absence of TfOH in toluene; **1a** was not consumed at all (Table 1, Entry 1). When acetic acid (Table 1, Entry 2) or trifluroacetic acid (Table 1, Entry 4) was employed, no reaction occurred in toluene at 80°C after 3 h. Treatment of **1a** with TsOH or H_3PO_4 under the same conditions gave **2a** in rather low yield of 19% and

30%, respectively (Table 1, Entries 3 and 5), and recovered the unreacted starting material. However, in the presence of a catalytic amount of H_2SO_4 or TfOH, we observed the cyclization with good yield in benzene, toluene or xylene (Table 1, Entries 6, 7, 10 and 11). In contrast, no product of **2a** in H_2O or DMF was obtained (Table 1, Entries 16 and 18). And also the cyclization of **1a** occurred only slightly in THF, CH_3CN or DME (Table 1, Entries 14, 15 and 17). It seems that the lowering acidity of TfOH in those Lewis-basic solvents prevents the protonation of the nitrogen.

Screening of several solvents revealed that toluene was one of the best solvents for this direct intramolecular cyclization. To gain insight on the effect of the electron density of the aromatic ring, a series of the 2-allyl- *N*-tosylanilines bearing different substitutents at a *para* position on the phenyl ring were prepared from the tosylation of the corresponding *N*-allylic amines by a Claisen rearrangement.[9] Under optimized reaction conditions, reaction of the *para* substituted 2-allyl-*N*-tosylanilines in the presence of triflic acid(20 mol%) as a catalyst furnished the substituted indoline derivatives in good yields through 5-*exo*-trig cyclization route[10] (Table 2). These results also showed that these substrates with withdrawing groups on the phenyl ring took longer reaction time. The reason should be that the electron-withdrawing group decreases the electron density of the phenyl ring to deactivate effect of the protonation of nitrogen atom. Using the **1h** synthesized according to the literature[11] as a substrate resulted in formation of the product of 2-phenyl-*N*-tosylindoline (**2h**) *via* a 5-*endo*-trig cyclization in 75% yield (Table 2, Entry 8).

Table 1. Screening the reaction conditions for acid-catalyzed cyclization of **1a**[a]



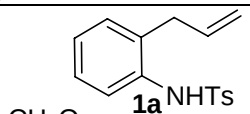
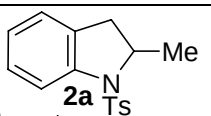
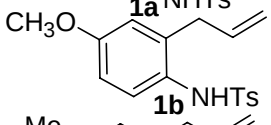
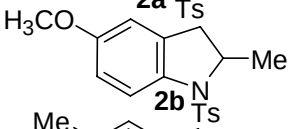
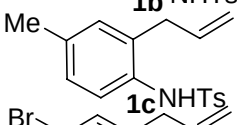
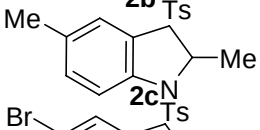
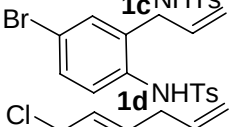
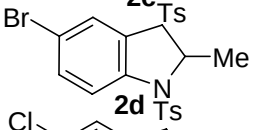
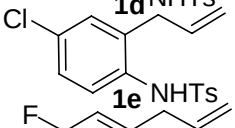
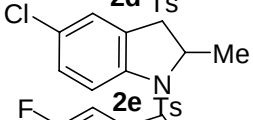
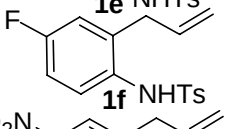
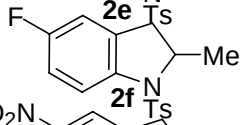
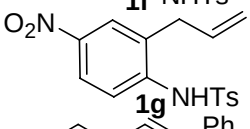
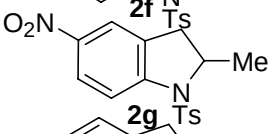
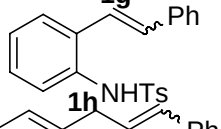
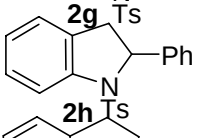
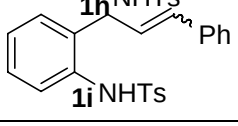
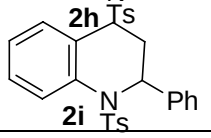
1a **2a**

Entry	Acid	Solvent	Time (h)	Temp. (°C)	Yield (%)
1	none	toluene	3	80	0 [b]
2	HOAc	toluene	3	80	0 [b]
3	*p*-TsOH·H_2O	toluene	3	80	19
4	TFA	toluene	3	80	0 [b]
5	H_3PO_4	toluene	3	80	30
6	H_2SO_4	toluene	3	80	87
7	TfOH	toluene	3	80	98
8	TfOH	toluene	24	rt	38
9	TfOH	toluene	3	110	92
10	TfOH	benzene	3	80	96

11	TfOH	xylene	3	145	69
12	TfOH	CH_2Cl_2	3	40	81
13	TfOH	$CHCl_3$	3	62	60
14	TfOH	THF	3	67	5
15	TfOH	DME	3	86	3
16	TfOH	H_2O	3	100	0[b]
17	TfOH	CH_3CN	3	83	7
18	TfOH	DMF	3	153	0[b]

[a] All reactions were run in the presence of 20 mol% acid. [b] Starting material was not consumed.

Table 2. TfOH catalyzed cyclization of **1** in toluene [a]

Entry	Tosylamide	Product	Time (h)	Yield (%)
1	 **1a**	 **2a**	3	98
2	 **1b**	 **2b**	0.5	88
3	 **1c**	 **2c**	1	92
4	 **1d**	 **2d**	3.5	94
5	 **1e**	 **2e**	3.5	81
6	 **1f**	 **2f**	5	90
7	 **1g**	 **2g**	8	89
8	 **1h**	 **2h**	1	75
9	 **1i**	 **2i**	1	86

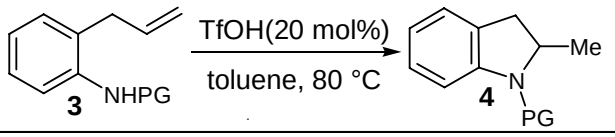
[a] Conditions: TfOH (20 mol %), 80°C, toluene.

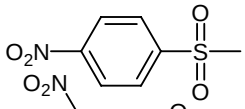
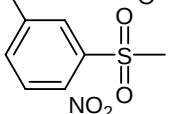
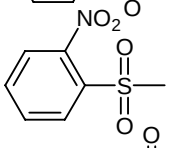
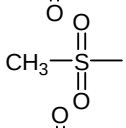
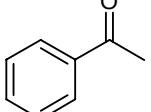
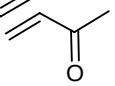
The reason is that the stable benzylic cation intermediate was formed through protonation of **1h**. Compound (**1i**) prepared by a Wittig olefination,[12] (Table 2, Entry 9) which could form a six-member ring through an intermediate of benzylic stabilized cation, underwent the Markovnikov cyclization to yield 2-phenyl-*N*-tosyl-1,2,3,4-tetrahydroquinoline (**2i**) *via* a 6-*endo*-trig cyclization in 86% yield within one

hour, and deprotecting cyclization product also obtained in 12% yield, but no 5-*exo*-trig cyclization product was detected.

To evaluate the scope of the acid-catalyzed cyclization, several *N*-protected-2-allylanilines were prepared to examine the effects of protecting groups on the nitrogen atom of the substrates. After screening the substrates of **3a-d**, we found that the different position of nitro group on phenyl ring of the sulfonamides has little effect on the yields of the corresponding products (Table 3). To evaluate further the influence of the electronic properties of the nitrogen and activating group on this reaction, the substrates containing more labile activating groups were examined. *N*-benzoyl-2-allylaniline (**3e)** was prepared.[13] In refluxing toluene，**3e** was transformed to *N*-benzoyl-2-methylindoline in good yield, with stoichiometric amount of triflic acid in 3 days. Treatment of *N*-acryloyl-2-allylaniline (**3f**) with 1 equiv. of TfOH gave only trace cyclization product in refluxing toluene in 24 h, because **3f** was easy to polymerize. Carbamate (**3g**) also was tested, no cyclization product was obtained. The substrate (**3g**) was easy to be deprotected in this strongly acidic condition. When the transformation of substrate (**3h**) was carried out with 0.2 equiv. of TfOH, no cyclization occurred. Protonation of free amine (**3h**) led to lose the reactivity.

Table 3. Variation of protecting groups



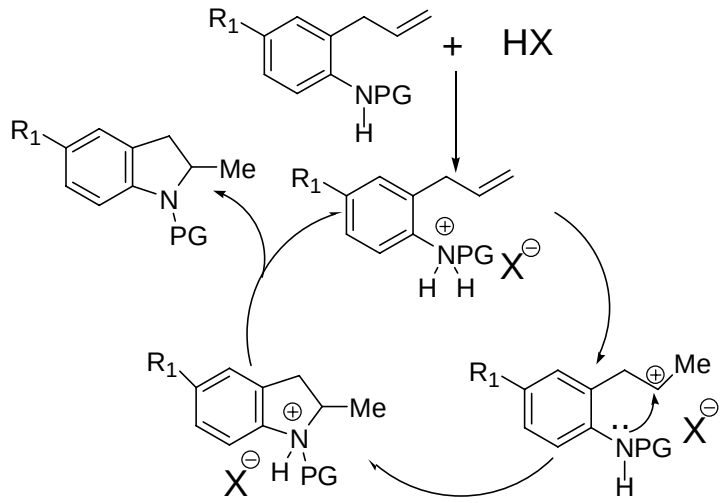
Substrate	PG	Time (h)	Yield (%)
3a		3	85
3b		3	92
3c		3	88
3d		3	84
3e		72	68[a]
3f		24	trace[a]
3g	Cbz	24	0[b]
3h	H	3	0[c]

[a] Reaction temperature was 110°C with 1 equiv. of TfOH.

[b] Starting material was consumed. [c] Starting material was not consumed.

Although the reaction mechanism is not exactly clear up to now. A possible mechanism of the cyclization comprise the following steps according to literature (Scheme 1):[14] (1) a proton adds to the nitrogen atom of the protected amino group, (2) intramolecular proton transfers from the nitrogen to the carbon of the double bond to form a stable carbon cation intermediate, (3) nucleophilic attack of the nitrogen to the positively charged carbon gives a cyclic amine and regenerates the acid catalyst.

Scheme 1. Proposed reaction mechanism



CONCLUSION

We have established that acid-catalyzed cyclization of *N*-protected-2-allylanilines is a highly atom economical route for the rapid and efficient assembly of 2-substituted indolines or tetrahydroquinoline.

EXPERIMENTAL

General procedure for the trifilic acid-catalyzed hydroamination of *N*-protected 2-allylanilines.

Acid (0.2 mmol, 0.2 equiv.) was added to a solution of substrate (1.0 mmol, 1 equiv.) in dry toluene (1.00 mL) by syringe and the vial was placed in an oil bath that was preheated to 80°C. At the end of the reaction, the mixture was allowed to cool to rt. Triethylamine (3 mmol) was added, after the usual work-up, and the product was isolated by flash chromatography (silica gel, AcOH/n-hexane=1/12).

2-Methyl-*N*-tosylindoline (2a): 98% yield, identical in mp, IR and ^{1}H NMR spectra with those of a sample prepared according to the literature.[15]

5-Methoxy-2-methyl-*N*-tosylindoline (2b): a white solid, 88% yield, mp 46-47°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.48 (m, 3H), 7.16-7.14 (m, 2H), 6.77-6.74 (m, 1H), 6.60 (m, 1H), 4.31 (m, 1H), 3.76 (s, 3H), 2.74 (dd, *J*=6.0, 17.4 Hz, 1H), 2.41 (m, 4H), 1.38 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 143.6, 135.0, 134.4, 133.7, 129.5, 127.0, 118.5, 112.8, 111.0, 58.7, 55.6, 36.3, 23.2, 21.5; IR(KBr, cm^{-1}) 3030, 2926, 2836, 1736, 1597, 1489, 1351, 1164, 1090, 1033, 813, 750, 669;

MS (EI) (*m/z*) 317, 162, 147, 132, 118, 104, 91, 77, 65, 51, 39; HMRS Calcd for $C_{17}H_{19}NO_3S$: 340.0986 [M^++Na]. Found: 340.0978; *Anal*. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.06; H, 5.95; N, 4.67.

2, 5-Dimethyl-*N*-tosylindoline (2c): a colorless oil, 92% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (m, 3H), 7.15 (m, 2H), 7.01 (m, 1H), 6.85 (m, 1H), 4.31 (ddq, *J*=2.7, 6.6, 9.6 Hz, 1H), 2.81 (dd, *J*=9.6, 15.9 Hz, 1H), 2.39 (dd, *J*=2.7, 15.9 Hz, 1H), 2.34 (m, 3H), 2.27 (m, 3H), 1.40 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ143.6, 138.7,135.3, 134.2, 131.9, 129.5, 128.3, 127.0, 125.9, 117.0, 58.6, 36.2, 23.3, 21.5, 21.0; IR (KBr, cm^{-1}) 2957, 2924, 2853, 1597, 1486, 1349, 1164, 1090, 983, 813, 666, 614, 584, 542; MS (EI) (*m/z*) 301, 286, 239, 210, 195, 155, 146, 131, 105, 91, 77, 65, 51, 43; HMRS Calcd for $C_{17}H_{19}NO_2S$: 387.9973 [M^++Na]. Found: 387.9973; *Anal*. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.92; H, 6.40; N, 4.37.

5-Bromo-2-methyl-*N*-tosylindoline (2d): a white solid, 94% yield, mp 84-85°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (m, 3H), 7.32 (m, 1H), 7.18 (m, 3H), 4.33 (ddq, *J*=2.4, 6.3, 9.3 Hz, 1H), 2.52 (dd, *J*=9.3, 15.9 Hz, 1H), 2.42 (dd, *J*=2.4, 15.9 Hz, 1H), 2.36 (s, 3H), 1.42 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 140.4, 135.1, 133.9, 130.7, 129.7, 128.4, 126.9, 118.3, 117.2, 58.8, 36.0, 23.4, 21.5; IR (KBr, cm^{-1}) 2957, 2924, 2853, 1736, 1597, 1470, 1353, 1168, 1097, 814, 725, 666, 581, 540; MS (EI) (*m/z*) 367, 365, 352, 350, 211, 210, 169, 155, 132, 131, 117, 91, 77, 65, 57, 43; HMRS Calcd for $C_{16}H_{16}NO_2BrS$: 324.1039 [M^++Na]. Found: 324.1029; *Anal*. Calcd for $C_{16}H_{16}NO_2BrS$: C, 52.47; H, 4.40; N, 3.82. Found: C, 52.55; H, 4.47; N, 3.57.

5-Chloro-2-methyl-*N*-tosylindoline (2e): a white solid, 81% yield, mp 81-82°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 3H), 7.19-7.01 (m, 4H), 4.34 (m, 1H), 2.85 (dd, *J*=9.6,16.5 Hz, 1H), 2.43-2.35 (m, 4H), 1.41 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 140.0, 135.1, 133.6, 129.7, 129.6, 127.8, 127.0, 125.4, 118.0, 58.8, 36.1, 23.3, 21.5; IR(KBr, cm^{-1}) 2963, 2927, 2852, 1598, 1472, 1353, 1165, 1090, 814, 666, 582; MS (EI) (*m/z*) 321, 166, 151, 131, 91, 89, 77, 65, 51, 39; HMRS Calcd for $C_{16}H_{16}NO_2ClS$: 344.0498 [M^++Na]. Found: 344.0482; *Anal*. Calcd for $C_{16}H_{16}NO_2ClS$: C, 59.71; H, 5.01; N, 4.35. Found: C, 59.92; H, 5.23; N, 4.16.

5-Fluoro-2-methyl-*N*-tosylindoline (2f): a white solid, 90% yield, mp 116-117°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.50 (m, 3H), 7.19-7.16 (m, 2H), 6.93-6.74 (m, 2H), 4.36 (m, 1H), 2.80 (dd, *J*=9.3, 16.2 Hz, 1H), 2.41-2.34 (m, 4H), 1.40 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 144.1, 137.3, 134.9, 134.0, 129.6, 127.0, 118.5, 114.4, 112.4, 112.4, 36.2, 23.2, 21.5; IR(KBr, cm^{-1}) 2970, 2926, 2859, 1594, 1481, 1348, 1164, 1084, 668, 589; MS (EI) (*m/z*) 305, 290, 226, 150, 135, 109, 91, 65, 51, 39; HMRS Calcd for $C_{16}H_{16}NO_2FS$: 328.0789 [M^++Na]. Found: 328.0778; *Anal*. Calcd for $C_{16}H_{16}NO_2FS$: C, 62.93; H, 5.28; N, 4.59. Found: C, 63.03; H, 5.27; N, 4.34.

5-Nitro-2-methyl-*N*-tosylindoline (2g): a white solid, 89% yield, mp 122-123°C (from hexane); ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.14-8.11 (m, 1H), 7.94-7.93(m, 1H), 7.72-7.63 (m, 3H), 7.26-7.23 (m, 2H), 4.49 (ddt, *J*=3.3, 6.6, 9.6 Hz, 1H), 3.12 (dd, *J*=9.6, 16.2 Hz, 1H), 2.63 (dd, *J*=3.3, 16.2 Hz, 1H), 2.38 (s, 3H), 1.50 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 144.7, 144.3, 135.2, 132.2, 130.0, 126.9, 124.6, 121.2, 115.2, 59.7, 35.8, 23.4, 21.5; IR(KBr, cm^{-1}) 3089, 2970, 2927, 2852, 1712, 1598, 1518, 1338, 1166, 1074, 749, 666; MS (EI) (*m/z*) 332, 317, 177, 155, 131, 91, 89, 77, 65, 51, 43. HMRS Calcd for $C_{16}H_{16}N_2O_4S$: $[M^+$+H]:333.0920 Found: 333.0904; *Anal*. Calcd for $C_{16}H_{16}N_2O_4S$: C, 57.82; H, 4.85; N, 8.43. Found: C, 68.08; H, 5.01; N, 8.40.

2-Phenyl-*N*-tosylindoline (2h): a white solid, 75% yield, mp 101-102°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (m, 1H), 7.52 (m, 2H), 7.29-7.03 (m, 10H), 5.42 (dd, *J*=2.7, 10.2 Hz, 1H), 3.26 (dd, *J*=10.2, 16.2 Hz, 1H), 2.86 (dd, *J*=2.7, 16.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 142.8, 142.0, 135.5, 131.2, 129.6, 128.6, 127.9, 127.6, 127.1, 126.0, 125.1, 124.6, 116.5, 64.9, 38.0, 21.5; IR (KBr, cm^{-1}) 3064, 3031, 2920, 2852, 1598, 1494, 1478, 1460, 1355, 1168, 1091, 1028, 814, 756, 576; MS (EI) (*m/z*) 349, 272, 194, 180, 165, 91, 89, 65, 51, 39; HMRS Calcd for $C_{21}H_{19}NO_2S$: 350.1209 $[M^+$+H]. Found: 350.1209; *Anal*. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.19; H, 5.65; N, 3.93.

2-Phenyl-*N*-tosyl-1,2,3,4-tetrahydroquinoline (2i): a white solid, 86% yield, mp 109-110°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.42 (m, 2H), 7.33-7.08 (m, 9H), 6.96 (m, 1H), 5.35 (t, *J*=7.2 Hz, 1H), 2.38 (s, 3H), 2.35-2.29 (m, 1H), 2.23-2.12 (m, 1H), 1.89-1.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 142.5, 136.3, 136.2, 134.0, 129.5, 128.5, 128.0, 127.2, 127.0, 126.9, 126.7, 126.1, 125.6, 59.7, 31.9, 25.4, 21.6; IR (KBr, cm^{-1}) 3062, 3029, 2948, 2844, 1599, 1486, 1454, 1347, 1164, 1090, 972, 813, 759, 660, 584, 570, 549; MS (EI) (*m/z*) 363, 341, 299, 284, 208, 193, 155, 130, 91, 77, 71, 65, 51, 39; HMRS Calcd for $C_{22}H_{21}NO_2S$: 386.1183 $[M^+$+Na]. Found: 386.1185; *Anal*. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found: C, 72.66; H, 5.85; N, 3.89.

2-Methyl-*N*-(4-nitrobenzenesulfonyl)indoline (4a): a white solid, 85% yield, mp 137-138°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J*=8.7 Hz, 2H), 7.87 (d, *J*=8.7 Hz, 2H), 7.69-7.66 (m, 1H), 7.27-7.07 (3H, m), 4.37 (ddq, *J*=2.4, 6, 9.3 Hz, 1H), 2.91 (dd, *J*=9.3, 16.2 Hz, 1H), 2.50 (dd, *J*=2.4, 16.2 Hz, 1H), 1.46 (d, J=6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 144.0, 140.1, 131.4, 128.1, 125.6, 125.3, 124.1, 123.7, 116.9, 59.0, 36.1, 23.4; IR(KBr, cm^{-1}) 3104, 2958, 2924, 2853, 1604, 1531, 1349, 1309, 1171, 1087, 740; MS (EI) (*m/z*) 318, 303, 186, 132, 117, 91, 76, 65; HMRS Calcd for $C_{15}H_{14}N_2O_4S$: 319.0742$[M^+$+H]. Found: 319.0747; *Anal*. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.88; H, 4.57; N, 8.64.

2-Methyl-*N*-(3-nitrobenzenesulfonyl)indoline (4b): a white solid, 92% yield, mp 104-105°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56-7.06 (m, 8H), 4.42 (ddq, *J*=2.7, 6.3, 9.3 Hz, 1H), 2.94 (dd, *J*=9.3, 16.2 Hz, 1H), 2.52 (dd, *J*=2.7, 16.2 Hz, 1H), 1.47 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 148.2, 140.4, 140.1, 132.3, 130.3, 129.2, 128.1, 127.3, 125.6, 125.2, 122.2, 116.8, 50.1, 36.2, 23.4; IR(KBr, cm^{-1}) 3082, 2926, 1605, 1533, 1479, 1352, 1176, 1127, 762; MS (EI) (*m/z*) 318, 303, 299, 269, 216, 132, 91, 89, 77, 39; HMRS Calcd for $C_{15}H_{14}N_2O_4S$: 319.0742 [M^++H]. Found: 319.0747; *Anal*. Calcd for $C_{15}H_{14}N2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.88; H, 4.65; N, 8.75.

2-Methyl-*N*-(2-nitrobenzenesulfonyl)indoline (4c): a white solid, 88% yield, mp 107-108°C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.03 (m, 8H), 4.71 (ddq, *J*=1.2, 6.3, 9 Hz, 1H), 3.29 (dd, *J*=9, 15.9 Hz, 1H), 2.58 (dd, *J*=1.2, 15.9 Hz, 1H), 1.40 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 139.7, 133.8, 132.0, 131.3, 130.5, 128.6, 127.8, 125.7, 124.7, 124.0, 115.8, 59.4, 36.2, 23.1; IR(KBr, cm^{-1}) 3096, 2922, 2851, 1592, 1545, 1478, 1371, 1172, 1126, 756, 597; MS (EI) (*m/z*) 318, 186, 165, 132, 117, 91, 65, 39; HMRS Calcd for $C_{15}H_{14}N_2O_4S$: 319.0742 [M^++H]. Found: 319.0747; *Anal*. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.88; H, 4.61; N, 8.70.

2-Methyl-*N*-mesylindoline (4d): 84% yield, identical in IR and ^{1}H NMR spectra with those of a sample prepared according to the literature.[16]

2-Methyl-*N*-benzoylindoline (4e): 88% yield, identical in mp, IR and ^{1}H NMR spectra with those of a sample prepared according to the literature.[17]

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