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Iodine(III) Reagent-Mediated Intramolecular Amination of 2-Alkenylanilines to Prepare Indoles

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Abstract. A variety of 3-substituted and 2,3-disubstituted indoles were synthesized efficiently in good yields through the intramolecular amination of 2-alkenylanilines promoted by readily available iodine(III) reagents in a short reaction time. Mechanistic studies showed that the reaction pathway went through a nitrenium ion and that 3-acetoxy indoline was the key intermediate in the indole formation. The indole product was easily prepared on a gram scale and amination also proceeded smoothly using catalytic 3,5-dimethylphenyl iodine in the presence of *m*CPBA. Furthermore, the indolo[3,2-a]carbazole scaffold was prepared in good yield in six steps from commercial *ortho*-iodoaniline.

Keywords: amination; 2-alkenylaniline; hypervalent iodine compound; indole; C−N bond formation

Indole scaffolds are common in numerous biologically active natural products and synthetic compounds, including alkaloids, peptides and materials in sciences.[1] Therefore, the development of new methods to access privileged indole scaffolds has received much attention in synthetic chemistry.[2] Transition-metal catalysis has been applied in various elegant syntheses of indoles, using palladium,[3] rhodium,[4] and other catalysts[5]. Although the transition-metal-catalyzed strategies have shown high efficiency, metal-free strategies for indole preparation are also desirable due to their advantages with regard to purity requirements in biological and medicinal research.[6] Many metal-free indole synthesis methods have been developed,[7] but the most promising is the intramolecular amination of 2-alkenylanilines owing to the availablility of the starting materials, including C(sp^2)-H bond amination by sulfenium ions,[8] DDQ-mediated amination,[9] selenium-catalzyed oxidative amination using N-fluorobenzensulfonimide as oxidant,[10] and NIS-mediated intramolecular amination.[11] Hypervalent iodine(III) reagents are versatile tools for the construction of carbon-heteroatom bonds in modern organic oxidation chemistry and have recently received much attention in indole synthesis as alternatives to traditional transition-metal-based procedures.[12,13] Muñiz and coworkers reported a rapid and productive indole preparation *via* the intramolecular amination of 2-vinylanilines using a modified iodine(III) reagent under mild conditions (Scheme 1-A).[14] This successful process was based on a sterically congested hypervalent iodine compound from the family of Koser reagents, comprising iodosobenzene combined with 2,4,5-trisisopropylbenzene sulfonic acid. Modification of the Koser reagent anion to improve the reactivity of the iodine(III) reagent was key in this method. The modified Koser reagent anion is not readily commercially but could be prepared in one step from commercial materials[15]. However, 2-vinylaniline substrates were limited to monosubstituted terminal alkenes which were unable to afford 2- or 3-substitued and 2,3-disubstituted indoles. To prepare 2,3-disubstituted indoles, Muñiz *et al.* continued to develop an iodine(III) reagent-mediated intramolecular sequential electrophilic N−H and C−H bonds functionalization between the aniline and acetylene (Scheme 1-B).[16] The free 2,3-disubstituted indoles can be obtained in good yileds by the tracelesss tether removal under Ti(O^iPr)$_4$ combined with Mg and TMSCl. Although this methodoly resolved the preparation of 2,3-disubstituted indoles, it still suffered from multistep preparation of starting matials and deprotecting procedures. Based on the studies of electronic effects on iodine(III) compounds by Muñiz's group[17] and our research into hypervalent iodine compounds[18], we became interested in accessing such substituted indoles by using readily available iodine(III) reagents and simple operations. We surmised that the electronic and steric effects of iodobenzene in the iodine(III) reagents would directly affect their reactivity and the efficiency of amination of 2-vinylaniline, particularly, for polysubstitituted

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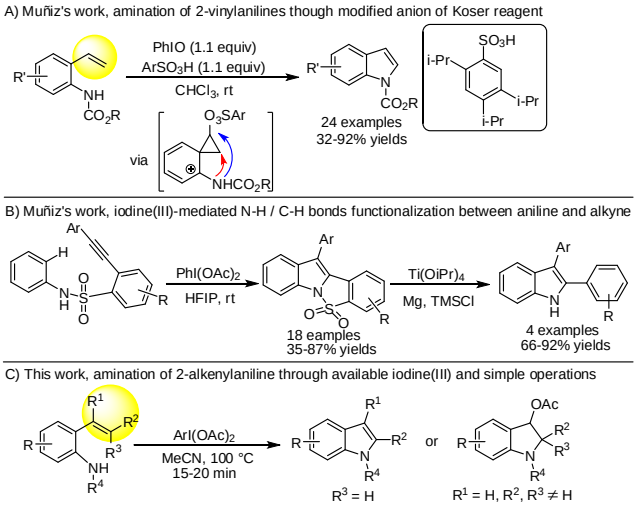
alkenes (Scheme 1-C). Herein, we report the synthesis of 2,3-disubstituted indoles *via* the 3,5-dimethyliodobenzene acetate-promoted intramolecuar amination of 2-alkenylanilines.



Scheme 1. Amination of 2-alkenylanilines to access indoles using iodine(III) reagents.

Initially, Koser reagent PhI(OH)OTs (**2a)** was used to investigate the intramolecular amination of **1a** to synthesize 3-methyl indole. However, this reaction resulted in a complex mixture with only 9% and 12% yields of **3a** obtained in DCM at rt and 80 °C, respectively (Table 1, entries 1 and 2). Pleasingly, product **3a** was afforded in 28% and 40% yields using $PhI(OOCF_3)_2$ (**2b)** and $PhI(OAc)_2$ (**2c)**, respectively, at 80 °C for 15 min (Table 1, entries 3 and 4). Solvent screening showed that MeCN gave the best result, with a 67% yield (Table 1, entries 5−9). Decreasing the amount of $PhI(OAc)_2$ to 2.0 equiv. afforded **3a** in 68% yield, which decreased to to 60% when using only 1.0 equiv. of $PhI(OAC)_2$ (Table 1, entries 10 and 11). The effect of temperature was also investigated (Table 1, entries 12−15). Product **3a** was obtained in 73% yield from the reaction at 100 °C. Finally, the substituent effect of the aryl group in iodine(III) reagent **2** (Figure 1) on the yield of **3a** was examined. Electron-donating or electron-withdrawing *para*-substituents had litte effect on the yield (Table 1, entries 16 and 17). Iodine(III) reagent **2f**, containing an electron-donating group at the aryl *meta*-position, resulted in a higher yield than iodine(III) reagent **2g**, with an electron-withdrawing group at the same position (Table 1, entries 18 and 19). Lower yields of **3a** were afforded when using iodine(III) reagents **2h** and **2i**, containing methoxy and trifluoromethyl groups, respectively (Table 1, entries 20 and 21). Interestingly, 3,5-dimethoxy-substituted iodine(III) reagent **2j** delivered product **3a** in 79% yield, while **2k**, containing trifluoromethyl groups, afforded **3a** in only 17% yield with recovery of substrate **1a** (Table 1, entries 22 and 23). Compared with reagents **2d-2k**, these results showed that iodine(III) reagents containing electron-danating group at *para*-, *meta*-, or *ortho*-positions gave better yields than their elecron-withdrawing groups counterparts, which were consistent with Muñiz's recent studies.[17] Pleasingly, **2l** and **2m** gave desired product **3a** in 85% and 84% yields, respectively (Table 1, entries 24 and 25). Notably, the reaction time of this transformation was less than 20 min. Therefore, optimal conditions for the preparation of indole **3a** were 2.0 equiv. of **2l** in MeCN at 100 °C for 15 min.

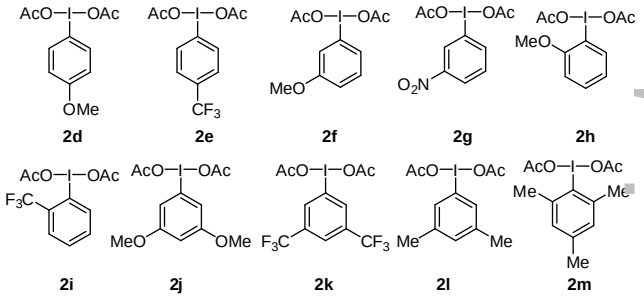
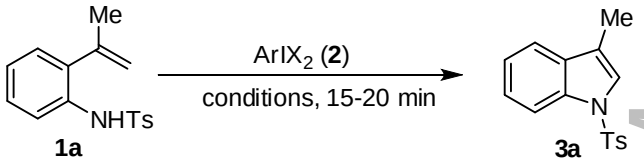


Figure 1. Iodine(III) reagents tested.

Table 1. Optimization of the reaction conditions.[a]



entry	2	solvent	T (°C)	**3a**, yield (%)[b]
1	**2a**	DCM	rt	9
2	**2a**	DCM	80	12
3	**2b**	DCM	80	28
4	**2c**	DCM	80	40
5	**2c**	toluene	80	32
6	**2c**	THF	80	49
7	**2c**	DMSO	80	56
8	**2c**	EtOAc	80	36
9	**2c**	MeCN	80	67
10	**2c**	MeCN	80	68[c]
11	**2c**	MeCN	80	60[d]
12	**2c**	MeCN	60	68
13	**2c**	MeCN	rt	59
14	**2c**	MeCN	100	73
15	**2c**	MeCN	120	69
16	**2d**	MeCN	100	62
17	**2e**	MeCN	100	59
18	**2f**	MeCN	100	68
19	**2g**	MeCN	100	27
20	**2h**	MeCN	100	51
21	**2i**	MeCN	100	29
22	**2j**	MeCN	100	79
23	**2k**	MeCN	100	17
24	**2l**	MeCN	100	87
25	**2m**	MeCN	100	84

[a] Reaction conditions: **1a** (0.2 mmol), **2** (entries 1−9, 3.0 equiv.; entries 12−25, 2.0 equiv.), solvent (2.5 mL), 15−20 min; [b] isolated yield; [c] **2c** (2.0 equiv.); [d] **2c** (1.0 equiv.).

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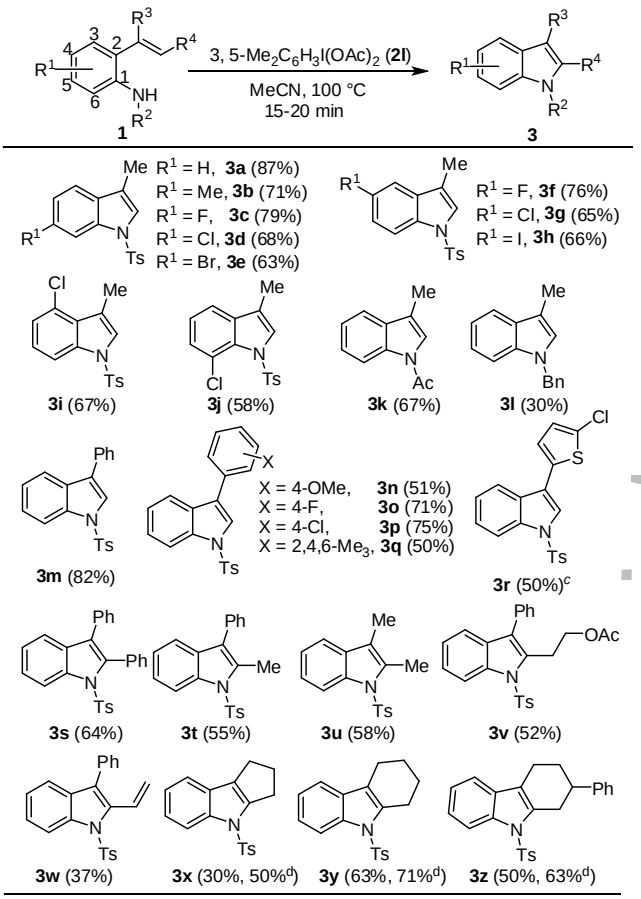
With optimized conditions in hand, we set out to explore the generality of this amination method for indole formation. The scope of aryl substituents on various 2-alkenylaniline substrates was examined (Table 2). A variety of 2-alkenylanilines bearing substituents at 3, 4, 5 or 6-positions on the aryl ring were well tolerated affording 3-methyl substituted indoles in good to high yields (**3a-j**). When the *N*-protecting group was replaced with an acetyl group, desired product **3k** was afforded in 67% yield. However, using benzyl protecting group afforded indole **3l** in only 30% yield. This result suggested that the *N*-protecting groups greatly influenced indole formation. Next, different alkenyl moieties in alkenylaniline **1** were also evaluated for the synthesis of diversely substituted indoles. Various 3-aryl substituted indoles were afforded in moderate to good yields (**3n-r**). The methoxy substituent resulted in a lower yield than fluoro and chloro substituents (**3n-p**). Furthermore, when a 2,4,6-trimethyl group was present on the aryl ring, desired product **3q** was obtained in 50% yield. Pleasingly, a thienyl subsituent afforded **3r** in 50% yield with the reaction necessarily ran at room temperature. Diverse 2,3-disubstituted indoles bearing aryl or alkyl with linear or cyclic groups were afforded in good yields (**3s-z**). For indole products **3x-z**, using the classic Fisher indole synthesis method gave higher yields. However, classic Fisher indole synthesis procedures were not compatible with ketones containing sensitive functional groups owing to their reactions with phenyl hydrazine. Compared to our method, the sensitive functional groups such as ester, and vinyl groups were compatible, affording the desired products in moderate yields (**3v-w**). These compounds could be applied in further useful transformations in organic synthesis.

Table 2. Scope of 2-alkenylanilines **1**.[a,b]



[a)] Reaction conditions: **1** (0.2 mmol), **2l** (2.0 equiv), MeCN (2.0 mL), 15−20 min; [b)] isolated yields; [c)] run at room temperature; [d)] isolated yields by Fisher indole synthesis from ketones and phenyl hydrazine in HOAc at 120 °C.

To probe the reaction mechanism, controlled experiments were performed. The addition of TEMPO (2.0 equiv.) under optimal conditions still afforded desired product **3a** in 91% yield (Scheme 2-1), indicating that the reaction did not involve a radical process. When substrate **1x** was reacted with iodine reagent **2l** at 100 °C for 15 min, products **3x** and **4x** were afforded in 30% and 26% yields, respectively (Scheme 2-2). The structure of **4x** was determined from 2D NMR spectra. Further experiments showed that compound **4x** was converted to compound **3x** in 40% yield under the optimal conditions while compound **3x** cannot convert to compound **4x** (Scheme 2-3). These results suggested that compound **4x** was a key intermediate in the formation of indole **3x**. Elimination of *cis* OAc and proton group revealed that the formation of indoles at last step was E1 elimination. When compound **5**, the precursor to **1a,** was treated under the optimal conditions, compound **6** and $TsNH_2$ were obtained in 52% and 55% yields, respectively (Scheme 2-4). Treatment of compound **5** with iodine(III) reagent **2l** in MeOH at 0 °C for 5 min gave compound **7** in 79% yield (Scheme 2-5). When aniline **8** containing an additional methyl protecting group was subjected to the optimal conditions even for 24 h, the reaction did not occur and aniline **8** was

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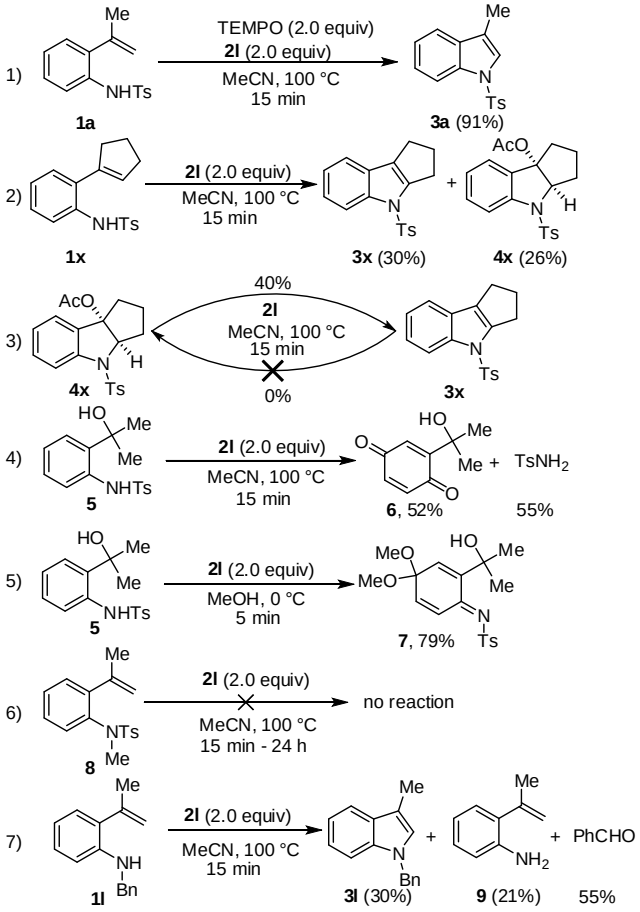
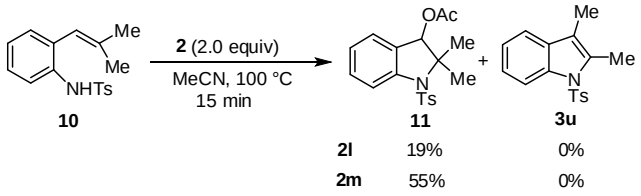
recovered in 90% yield (Scheme 2-6). Interestingly, aniline **1l** in Table 2 not only gave indole **3l** in 28% yield under the optimal conditions but also afforded aniline **9** and benzaldehyde in 21% and 55% yields, respectively (Scheme 2-7). Compound **9** and benzaldehyde might be generated from the oxidation of N-atom to imine group by iodine(III) reagent **2l** and a sequence of hydrolysis. These results suggested that the iodine(III) reagent initially oxidized the N-atom rather than the alkene during the indole formation.



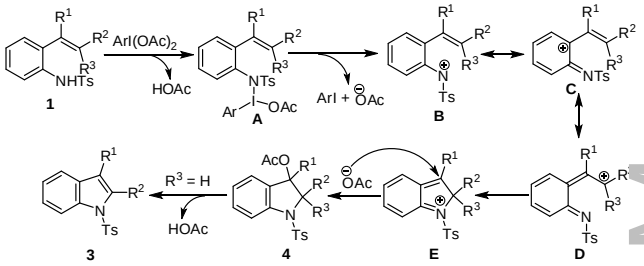
Scheme 2. Mechanistic studies.

According to the results shown in Scheme 2-2, a trisubstituted alkene might inhibit acetoxy elimination to afford a 3-oxygenated indoline or rearrangement product. As shown in Scheme 3, when aniline **10** was subjected to the optimal conditions, desired product **11** was obtained in 19% yield along with strarting material recovery, but rearrangement product **3u** was not observed. These results indicated that no carbocation should form at the 3-position of the indoline intermediate. To our delight, a 55% yield of product **11** was afforded when 2,4,6-trimethyl substituted iodine(III) reagent **2m** with was used.



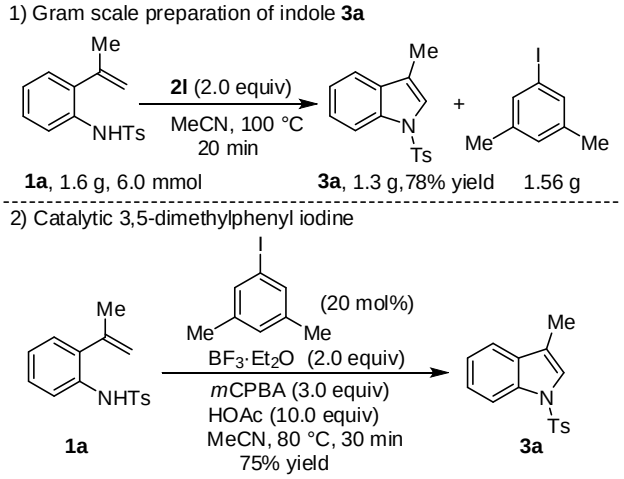
Scheme 3. Testing the trisubstituted alkene **10**.

Based on the experimental results, a plausible mechanism for the formation of indole **3** was proposed (Scheme 4). Iodine(III) reagent **2** combines with alkenylaniline **1** to form intermediate **A** eliminating acetic acid. Intermediate **A** then undergoes reductive elimination to generate nitrenium ion **B**,[16,19] as supported by the results in Schemes 2-4 and 2-5. Isomerization of **B** forms intermediate **C** and **D**. Intermediate **D** then undergoes intramolecular nucleophilic attack by the N-atom to give intermediate **E**. Trapping of intermediate **E** by an OAc anion results in 3-oxygenated indolines **4** or **9**. When R^2 or R^3 are protons, compound **4** undegoes E1 elimination to give indole product **3**.



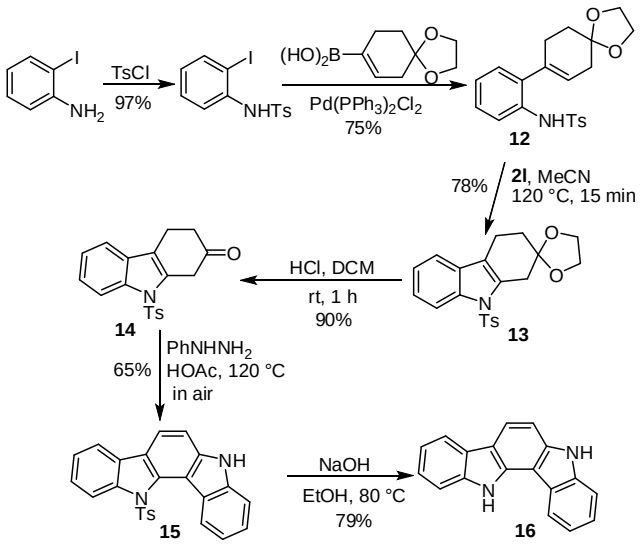
Scheme 4. Proposed mechanism.

These useful indole scaffolds encouraged us to perfom this method on a gram scale. When akene **1a** (1.6 g) was reacted with **2l**, indole **3a** (1.3 g) was obtained in 78% yield accompanied by 3,5-dimethylphenyl iodine (1.56 g) (Scheme 5-1). To avoid the large amount of aryliodine produced in this reaction, we attempted using a catalytic amount of aryliodine in the presence of *meta*-chloroperoxybenzoic acid (*m*CPBA) as terminal oxidant (Scheme 5-2). When 0.2 equiv. of 3,5-dimethylphenyl iodine was combined with $BF_3 \cdot Et_2O$ (2.0 equiv.) in the presence of 3.0 equiv. of *m*CPBA and HOAc in MeCN at 80 °C for 30 min, product **3a** was isolated in 75% yield.



Scheme 5. Gram scale preparation and use of catalytic 3,5-dimethylphenyl iodine.

As this method proved to be efficient for various substrates, we envisioned its application to the synthesis of indolocarbazole alkaloids. This family of compounds are found in many natural products, pharmaceuticals, photorefractive materials, and organic dyes, and have attracted much attention in synthetic and biological fields.[20] We postulated that indolo[3,2-a]carbazole[21] could be accessed from simple commercial *ortho*-iodoaniline. As shown in Scheme 6, 2-alkenylaniline **12** was prepared in 75% yield through the palladium-catalyzed cross-coupling of *N*-Ts-*o*-iodoaniline with alkenylboronic acid. When alkenylaniline **12** was subjected to the optimal conditions, desired indole **13** was afforded in 78% yield in 15 min. Compound **14** was obtained in 90% yield by the subsequent hydrolysis using concentrated HCl solution, and then underwent Fisher-indole synthesis by reacting with $PhNHNH_2$ in HOAc to give compound **15** in 65% yield. Removal of the Ts group with NaOH afforded indolo[3,2-a]carbazole **16** in 79% yield. This approach provides an alternative method to accessing indolocarbazole scaffolds.



Scheme 6. Synthesis of indolo[3,2-a]carbazole alkaloid.

In summary, we have developed a facile method for the synthesis of 3-substituted and 2,3-disubstituted indoles *via* the intramolecular amination of 2-alkenylanilines with readily available hypervalent iodine reagents. These reaction requires a short reaction time to provide a wide range of indoles in good yields. Mechanistic studies suggested that acetoxy-substituted indoline was the key intermediate in indole formation. Furthermore, the indole were easily prepared at the gram-scale and by catalysis with 3,5-dimethylphenyl iodine in the presence of *m*CPBA. Finally, indolo[3,2-a]carbazole was synthesized in good yield in six steps from commercial *ortho*-iodoaniline.

Experimental Section

General procedure for the synthesis of indole 3a: In a Teflon-sealed reaction flask was charged with 2-alkenylaniline **1a** (0.2 mmol) and 3,5-$Me_2C_6H_3I(OAc)_2$ **2l** (0.4 mmol, 2.0 equiv.) under air. MeCN (2.5 mL) was added. And then, the reaction vessel was sealed with a Teflon cap. The reaction mixture was stirred vigorously at 100 °C for 15−20 min until the substrate **1a** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (dry loading with SiO_2) using eluents (1:30 ethyl acetate:petroleum ether to 1:10) to provide product **3a** as a white solid (0.049 g, 87%). mp: 95−96 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.32−7.29 (m, 2H), 7.24−7.21 (m, 1H), 7.19 (d, J = 7.5 Hz, 2H), 2.32 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz $CDCl_3$): δ 144.6, 135.4, 135.2, 131.7, 129.7, 126.7, 124.5, 123.0, 122.9, 119.3, 118.5, 113.6, 21.4, 9.6; IR (thin film) 3456, 3014, 2954, 1612, 1458, 1210, 1009, 733 cm^{-1}; HRMS (ESI) *m/z* $C_{16}H_{16}NO_2S$ $(M+H)^+$ 286.0896, found 286.0899.

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Iodine(III) Reagent-Mediated Intramolecular Amination of 2-Alkenylanilines to Prepare Indoles

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