Preparation of Vinylogous 2-Sulfonylindolines by the Palladium-Catalyzed Heteroannulation of *o*-Iodoanilines with Dienyl Sulfones and Their Further Transformation to Indoles and Carbazoles

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The palladium-catalyzed heteroannulation of *o*-iodoanilines with dienyl sulfones provides a convenient route to vinylogous 2-sulfonylindolines **3**. The reaction proceeds in DMF/water in the presence of potassium carbonate and catalytic palladium(II) acetate and is compatible with both electron-donating and -withdrawing substituents in the *para* position of the aniline, and with an alkyl substituent at C-2 of the dienyl sulfone. The indolines underwent oxidation with DDQ to afford the corresponding indoles **4**. The latter were then employed as dienes in Diels−Alder reactions with dimethyl acetylenedicarboxylate (DMAD), methyl propiolate, or methyl acrylate. In the case of the latter two dienophiles, the cycloadditions were highly regioselective, affording the corresponding 1,3-products (with respect to the relative positions of the sulfone and ester groups), exclusively. The cycloadducts from acetylenic dienophiles were converted to the corresponding carbazoles by elimination of the sulfone moiety with DBU, and that from methyl acrylate was subjected to reductive desulfonylation and oxidation to the corresponding carbazole with DDQ. The method thus provides access to carbazoles with various substituents at the 3-, 4-, and 6-positions.

The Heck reaction[1] provides a versatile method for the coupling of vinyl or aryl halides with alkenes to afford conjugated products in the presence of catalytic amounts of palladium(0) species.[2] When dienes are employed in place of alkenes, a π-allylpalladium intermediate is formed that can undergo either elimination of the metal or substitution by an appropriate nucleophile such as a secondary amine (Scheme 1).[1a,b] Furthermore, in cases where the amine (or other nucleophile) is tethered to the aryl halide precursor, the possibility arises for heteroannulations with acetylenes,[3] dienes,[4] allenes,[5] and vinylcyclopropanes and cyclobutanes[6] to afford the corresponding nitrogen heterocycles. Many types of unsaturated substrates have been investigated in Heck reactions and related palladium-catalyzed coupling reactions. However, there are relatively few examples where unsaturated sulfones[7,8] have been employed in this context. In particular, it appears that the use of dienyl sulfones in palladium-catalyzed heteroannulation reactions has not yet been reported. Since the sulfone group is a useful functionality that can be either exploited in further transformations of the products[7a] or removed at the end of a synthetic sequence by appropriate desulfonylation methods,[9] such processes are of potential value in the synthesis of various types of heterocycles.

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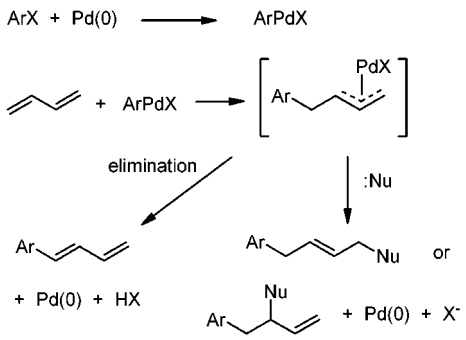
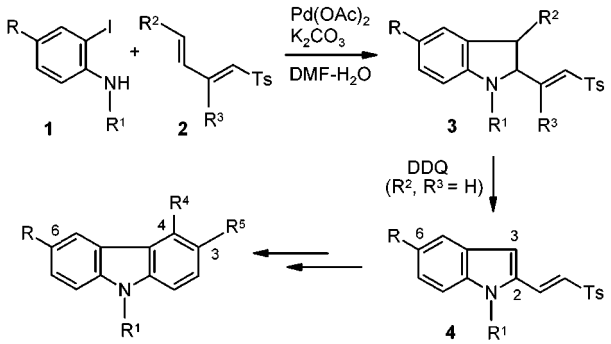
Scheme 1



Scheme 2

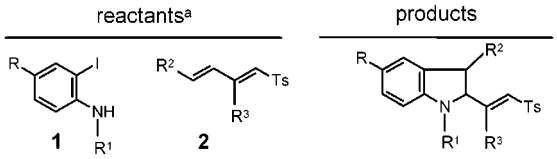


We now report that the palladium-catalyzed reactions of variously *p*-substituted *o*-iodoanilines **1** with dienyl sulfones **2** afford vinylogous 2-sulfonylindolines **3**.[10] We also report that the products **3** undergo facile oxidation with DDQ to the corresponding indoles **4**, which in turn can be employed as dienes in highly regioselective Diels−Alder cycloaddditions that lead, after desulfonylation, to carbazoles containing substituents at the 3-, 4-, and/or 6-positions (Scheme 2). Indole and carbazole ring systems comprise the core structures of numerous naturally occurring alkaloids[11] and synthetic analogues of medicinal importance. Thus, the development of new methods for their synthesis is of current interest.

Results and Discussion

The results of the heteroannulation of *o*-iodoanilines **1** with dienyl sulfones **2** to afford vinylogous sulfonylindolines **3** is summarized in Table 1. In general, the reactions were performed in aqueous DMF solution containing potassium carbonate and 5−10 mol % of palladium diacetate. The addition of triphenylphosphine to the reaction mixture to reduce the palladium diacetate to Pd(0) did not improve the yields of the corresponding indolines **3**. Presumably, oxidation of a small amount of the dienyl sulfone (or other component of the reaction mixture) with Pd(II) in situ generates the required Pd(0) catalyst. Since some polymerization of the dienyl sulfone **2** accompanied the cyclization, slightly better yields were obtained when an excess of **2** was employed. The reactions were conducted at room temperature because heating resulted in more complex product mixtures and lower yields of **3**.

Table 1. Heteroannulation of *o*-Iodoanilines 1 with Dienyl Sulfones 2



entry	R	R^1	R^2	R^3	no.	reaction time (days)	isolated yield (%)[a,b]
1	H	H	H	H	**3a**	5	31[c]
2	H	Cbz	H	H	**3b**	5	83
3	H	Ts	H	H	**3c**	5	66
4	H	*t*-Boc	H	H	**3d**	5	41
5	H	Cbz	H	Me	**3e**	6	66
6	H	Cbz	Me	H	**3f**	16	
7	Me	Cbz	H	H	**3g**	8	81
8	Me	Cbz	H	Me	**3h**	12	53
9	Me	Cbz	Me	H	**3i**	19	
10	OMe	Cbz	H	H	**3j**	12	78
11	OMe	Cbz	H	Me	**3k**	11	25
12	CO_2Me	Cbz	H	H	**3l**	0.5	73

[a] An excess of **2** was generally employed to compensate for its competing partial polymerization. [b] The yield is based on **1**. [c] Product **3a** underwent rapid oxidation to **4a** upon exposure to air.

When *o*-iodoaniline, a primary amine, was used in the heteroannulation, a relatively poor yield of the indoline **3a** was obtained (Table 1, entry 1). Moreover, the product was readily oxidized to the corresponding indole **4a** upon exposure to air (Scheme 3). Several *N*-protected *o*-iodoanilines were then investigated, and the use of the *N*-carbobenzyloxy (*N*-Cbz) derivative (entry 2) proved more efficacious than the corresponding *N*-*p*-toluenesulfonyl (*N*-Ts) or *N*-*tert*-butoxycarbonyl (*N*-*t*-Boc) analogues (entries 3 and 4, respectively). Thus, all further experiments were conducted with *N*-Cbz-anilines. The N-protected indolines **3b**−**d** were stable toward aerial oxidation.

In general, an additional methyl substituent in the 2-position of the dienyl sulfone **2** (R^3 = Me) resulted in

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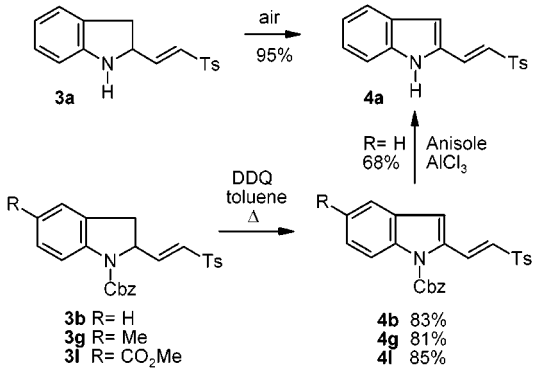
Scheme 3



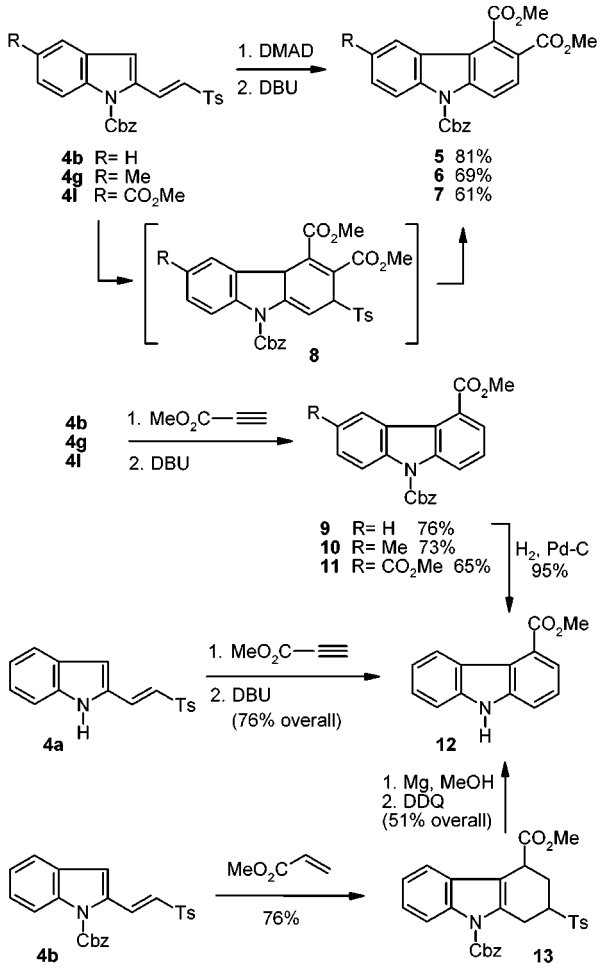
lower yields of **3** compared to the corresponding unsubstituted dienyl sulfone (compare entries 2 vs 5, and 7 vs 8 and 10 vs 11). The presence of a 4-methyl substituent (R^2 = Me) suppressed the reaction completely, and no indoline product was obtained even after prolonged reaction times (entries 6 and 9). When the unsubstituted dienyl sulfone (**2**, R^2, R^3 = H) was employed, the vinyl sulfone moieties in the indoline products **3** were formed as the *trans*-isomers, as evidenced by relatively large coupling constants J_{trans} of ca. 15 Hz. The absence of an NOE between the vinyl methyl group and the olefinic hydrogen atom in each of **3e**, **3h**, and **3k** suggests the *E*-configuration, where these two substituents are *trans*.

The heteroannulation reaction proved compatible with both electron-donating and -withdrawing substituents in the *para* position of the *o*-iodoaniline **1**. Thus, comparable yields of **3** were produced when the unsubstituted dienyl sulfone was allowed to react with *o*-iodoanilines containing a methyl (entry 7), methoxy (entry 10), ester (entry 12), or no *p*-substituent (entry 2). However, we noted that the electron-withdrawing ester group (entry 12) resulted in the fastest reaction time.

The oxidation of indolines **3b**, **3g**, and **3l** to indoles **4b**, **4g**, and **4l**, respectively, was smoothly achieved with DDQ[12] in refluxing toluene (Scheme 3), regardless of the nature of the substituent at the 6-position. Furthermore, deprotection of **4b** with anisole in the presence of a Lewis acid[13] provided a more efficient preparation of the free indole **4a** (Scheme 3) than the cyclization of unprotected *o*-iodoaniline in entry 1 of Table 1, followed by aerial oxidation of **3a**. Attempted deprotection of **4b** via hydrogenolysis resulted in simultaneous hydrogenation of the vinyl sulfone moiety.

We then investigated the Diels−Alder cycloadditions of the variously substituted indole derivatives with representative dienophiles (Scheme 4). The symmetrical dienophile dimethyl acetylenedicarboxylate (DMAD) reacted readily with **4b**, **4g**, and **4l** in refluxing toluene. The inclusion of a small amount of the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) improved the yields of the cycloaddition products, presumably by suppressing competing polymer formation. The initial cycloadducts **8** could not be isolated in a pure state because of partial double bond isomerization. However, when the crude product mixtures were treated with DBU in dichloromethane, elimination of

Scheme 4



p-toluenesulfinic acid occurred, resulting in aromatization to afford carbazoles **5**, **6**, and **7**, respectively, in good to excellent yield.

The similar cycloaddition of indoles **4b**, **4g**, and **4l** with the unsymmetrical dienophile methyl propiolate, followed by elimination with DBU, produced carbazoles **9**, **10**, and **11**, respectively, as single regioisomers (Scheme 4). Carbazole **9** was unequivocally identified as the indicated regioisomer by hydrogenolysis of the Cbz protecting group to afford **12**. Since both **12**, where the ester moiety occupies the 4-position, and the corresponding 3-isomer **14** are known compounds,[14] the structural assignment of **12** and therefore also that of **9** were easily confirmed. The structure of the 6-methyl derivative **10** could not be obtained unequivocally by NMR spectroscopy because of overlapping signals. However, an X-ray crystallographic structure of **10** clearly indicated the same regiochemistry as was observed in **9**. Carbazole **11** was easily distinguished from its regioisomer **15** by NMR spectroscopy, since the symmetrical structure of the latter would be expected to produce ^{1}H and ^{13}C NMR spectra considerably simpler than those of the actual product **11**. The cycloaddition of the unprotected indole **4a** with methyl propiolate, followed by treatment with DBU, provided carbazole **12**, which was identical to the sample obtained previously from the hydrogenolysis of **9**, in 76% yield.

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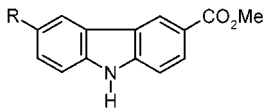


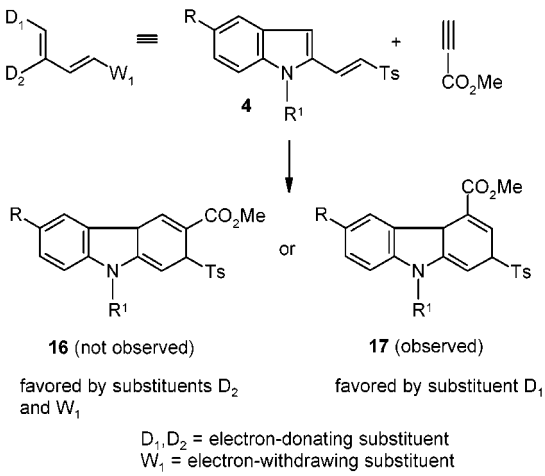
14 R= H
15 R= CO_2Me

We also investigated the Diels−Alder reaction of the N-Cbz-protected indole **4b** with methyl acrylate (Scheme 4). The cycloadduct **13** was obtained with high regioselectivity but with undetermined stereochemistry. Attempts to eliminate *p*-toluenesulfinic acid cleanly from **13** with DBU and other bases failed. The mixture was therefore subjected to reductive desulfonylation and removal of the Cbz protecting group with magnesium in refluxing methanol,[15] followed by oxidation with DDQ, to afford carbazole **12**, again identical to the products derived from **9** and **4a**.

The regiochemistry of the above Diels−Alder reactions deserves further comment. Frontier MO analyses have been reported of interactions between variously substituted dienes and dienophiles containing an electron-withdrawing group.[16a] In general, an electron-donating group in the 1-position of the diene produces chiefly the 1,2-disubstituted cycloadduct (with respect to the diene and dienophile substituents), whereas a similar substituent in the 2-position favors the 1,4-regioisomer. An electron-withdrawing group at the 1- or 4-position of the diene affords mainly the 1,2-isomer. In the present case, the diene unit of the sulfonylindoles **4** can be considered to possess donating groups at both the 1- and 2-positions (D_1 = *o*-nitrogen-substituted aryl group; D_2 = nitrogen substituent, respectively) and a withdrawing group at the 4-position (W_1 = sulfone moiety) (Scheme 5). Thus, the nitrogen atom and sulfone group of **4** are expected to direct the cycloaddition with an unsymmetrical dienophile such as methyl propiolate to produce **16** preferentially, whereas the aryl substituent, as well as any steric interactions between the sulfone group and the dienophile ester moiety, are expected to favor the formation of **17** (Scheme 5). The exclusive formation of products derived from **17** suggests that the latter effects are dominant.[16b]

Other cycloaddition mechanisms were also considered. A stepwise process involving diradical intermediates was ruled out on the basis of the salutary effects of BHT, a radical inhibitor, upon the yields of the cycloadducts. Although a stepwise dipolar mechanism cannot be completely ruled out, the lack of observable effects upon the reaction rate or regiochemistry of the cycloaddition caused by the presence of electron-donating, -withdrawing, or no substituents at C-6 of the indole moiety (i.e., compare **4b**, **4g**, and **4l** in Scheme 4) suggests that charged intermediates are not produced in the reaction. It has also been established that dienyl sulfones are capable of both normal and inverse electron demand in Diels−Alder cycloadditions.[7d,17] Although the reactions of dienes **4** with electron-deficient dienophiles such as methyl propiolate or methyl acrylate are expected to proceed with normal electron demand, we nevertheless

Scheme 5



tested the possibility of inverse demand by attempting the reaction of **4b** with an electron-rich dienophile. Thus, when **4b** was refluxed in neat *n*-butyl vinyl ether[18] for extended periods, no cycloadduct was obtained. The preference of **4b** for reactions with electron-deficient dienophiles therefore indicates that **4b** undergoes cycloadditions via normal electron demand.

In conclusion, the palladium-catalyzed heteroannulation of *o*-iodoanilines with dienyl sulfones provides a convenient route to vinylogous 2-sulfonylindolines. The method is compatible with both electron-donating and -withdrawing substituents in the *para* position of the aniline and with an alkyl substituent at C-2 of the dienyl sulfone. The indolines are readily oxidized to indoles with DDQ, which can then be employed in highly regioselective Diels−Alder reactions. The resulting cycloadducts afford the corresponding carbazoles after elimination of the sulfone moiety. Other synthetically useful transformations of sulfonylindoles **4** are under continued investigation.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in deuteriochloroform and are reported relative to residual chloroform or TMS as the internal standard, unless otherwise indicated. Mass spectra were obtained by EI at 70 eV. Chromatography refers to flash chromatography on silica gel (230−400 mesh), unless otherwise noted. The following materials were prepared by literature procedures: (*E*)-1-(*p*-toluenesulfonyl)-1,3-butadiene,[19] 2-methyl-1-(*p*-toluenesulfonyl)-1,3-butadiene,[19] 1-(*p*-toluenesulfonyl)-1,3-pentadiene,[19] *N*-(*p*-toluenesulfonyl)-2-iodoaniline,[20] *N*-*t*-Boc-2-iodoaniline,[21] 2-iodo-4-toluidine,[22] 4-amino-3-iodophenol,[23] and methyl 4-amino-3-iodobenzoate.[24]

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(16) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1976; Chapter 4. (b) Semiempirical MO calculations (AM1) indicated that the diene HOMO of **4** (R = H, R^1 = Ac) has a larger coefficient at C-3 of the indole moiety than at the α-position of the sulfone group. This leads to the expectation that **16** would be the dominant regioisomer, in contrast to experimental results.

(17) The dual electron demand nature of 2-(phenylsulfonyl)-1,3-dienes in Diels−Alder reactions has been studied extensively: (a) Bäckvall, J.-E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396. 1-(Arylsulfonyl)-1,3-dienes have also been reported to undergo cycloadditions with both electron-deficient and electron-rich dienophiles. (b) For cycloaddition with methyl acrylate, see: Cuvigny, T.; Hervé du Penhoat, C.; Julia, M. *Tetrahedron* **1986**, *42*, 5321. (c) For cycloaddition with *N*-(1-cyclohexenyl)piperidine, see: Flitsch, W.; Lubisch, W.; Rosche, J. *Liebigs. Ann. Chem.* **1987**, 655.

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N-Carbobenzyloxy-2-iodoaniline. 2-Iodoaniline was treated with benzyl chloroformate under standard conditions[25] to afford the corresponding Cbz derivative in 80% yield: mp 60.5−62 °C; IR (film) 1740, 1206 cm^{-1}; ^1H NMR (200 MHz) δ 8.07 (d, J = 8.2 Hz, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.42−7.25 (m, 6 H), 7.04 (broad s, 1 H), 6.80 (t, J = 7.4 Hz, 1 H), 5.22 (s, 2 H); MS m/z (%) 353 (M^+, 16), 245 (94), 91 (88), 90 (100). Anal. Calcd for $C_{14}H_{12}INO_2$: C, 47.61; H, 3.43; N, 3.97. Found: C, 47.73; H, 3.32; N, 3.95.

***N*-Carbobenzyloxy-2-iodo-4-toluidine.** 2-Iodo-4-toluidine was treated with benzyl chloroformate under standard conditions[25] to afford the corresponding Cbz derivative in 96% yield: mp 65.5−66 °C; IR (film) 1736, 1690, 1217, 1200 cm^{-1}; ^1H NMR (200 MHz) δ 7.89 (d, J = 8.2 Hz, 1 H), 7.60 (d, J = 1.9 Hz, 1 H), 7.44−7.33 (m, 5 H), 7.13 (d, J = 8.5 Hz, 1 H), 6.93 (broad s, 1 H), 5.23 (s, 2 H), 2.26 (s, 3 H); MS m/z (%) 367 (M^+, 25), 259 (87), 91 (91), 77 (100). Anal. Calcd for $C_{15}H_{14}INO_2$: C, 49.07; H, 3.84; N, 3.82. Found: C, 48.73; H, 3.48; N, 3.73.

***N*-Carbobenzyloxy-4-methoxy-2-iodoaniline.** 4-Amino-3-iodophenol was treated with benzyl chloroformate under standard conditions[25] to afford the corresponding Cbz derivative in 93% yield: mp 143−144 °C; IR (film) 3350, 1698, 1233, 1207 cm^{-1}; ^1H NMR (DMSO-d_6, 200 MHz) δ 9.76 (s, 1 H), 8.86 (broad s, 1 H), 7.38−7.30 (m, 5 H), 7.24 (d, J = 2.6 Hz, 1 H), 7.1 (d, J = 8.8 Hz, 1 H), 6.77 (dd, J = 8.5, 2.7 Hz, 1 H), 5.01 (s, 2 H); MS m/z (%) 369 (M^+, 5), 260 (44), 91 (100). Anal. Calcd for $C_{14}H_{12}INO_3$: C, 45.55; H, 3.28; N, 3.80. Found: C, 45.51; H, 3.05; N, 3.69.

The above product (1.5 g, 4.0 mmol) and KOH (283 mg, 5.05 mmol) were dissolved in anhydrous DMSO (50 mL). Dimethyl sulfate (0.42 mL 4.0 mmol) was added, and the solution was stirred for 24 h. Ether (100 mL) was then added, followed by a small amount of chloroform to form a homogeneous mixture. The mixture was washed with saturated NaCl solution, dried ($MgSO_4$), and evaporated. Chromatography of the crude product (hexanes−ethyl acetate, 2:1) afforded *N*-Cbz-4-methoxy-2-iodoaniline (675 mg, 43%): mp 95−98 °C; IR (film) 1706, 1694, 1283, 1257, 1237, 1220 cm^{-1}; ^1H NMR (200 MHz) δ 7.82 (d, J = 10.1 Hz, 1 H), 7.43−7.29 (m, 6 H), 6.90 (dd, J = 9.1, 2.7 Hz, 1 H), 6.74 (broad s, 1 H), 5.21 (s, 2 H), 3.77 (s, 3 H); MS m/z (%) 383 (M^+, 71), 275 (100), 260 (86). Anal. Calcd for $C_{15}H_{14}INO_3$: C, 47.02; H, 3.68; N, 3.66. Found: C, 46.60; H, 3.22; N, 3.63.

Methyl *N*-Carbobenzyloxy-4-amino-3-iodobenzoate. Methyl 4-amino-3-iodobenzoate was treated with benzyl chloroformate under standard conditions[25] to afford the corresponding Cbz derivative in 70% yield: mp 99−102 °C; IR (film) 1742, 1720, 1203 cm^{-1}; ^1H NMR (200 MHz) δ 8.43 (dd, J = 2.0, 0.4 Hz, 1 H), 8.23 (d, J = 8.6 Hz, 1 H), 8.00 (dd, J = 8.8, 2.0 Hz, 1 H), 7.42−7.38 (m, 5 H), 7.26 (s, 1 H), 5.24 (s, 2 H), 3.90 (s, 3 H); MS m/z (%) 411 (M^+, 15), 303 (100), 272 (99), 91 (89). Anal. Calcd for $C_{16}H_{14}INO_4$: C, 46.74; H, 3.43; N, 3.41. Found: C, 46.62; H, 3.38; N, 3.33.

2-[(*E*)-2-(*p*-Toluenesulfonyl)ethenyl]indoline (3a) (Table 1, entry 1) and 2-[(*E*)-2-(*p*-Toluenesulfonyl)ethenyl]indole (4a). *o*-Iodoaniline (250 mg, 1.14 mmol), (*E*)-1-(*p*-toluenesulfonyl)-1,3-butadiene (237 mg, 1.14 mmol), K_2CO_3 (157 mg, 1.14 mmol), and 10 mol % of $Pd(OAc)_2$ were dissolved in DMF−H_2O (5 mL, 10:1). The reaction mixture was stirred at room temperature under argon for 5 days. Chloroform (5 mL) was added, the mixture was filtered through Celite, the filtrate was concentrated in vacuo, and the residue was purified by chromatography (elution with ethyl acetate−hexanes, 2:1) to afford indoline **3a** (105 mg, 31%) as a dark oil. Indoline **3a** was readily oxidized upon exposure to air while stirring for 1 h in chloroform to give indole **4a** (100 mg, 95%) as a dark solid: IR (film) 3351, 1606, 1301, 1137 cm^{-1}; ^1H NMR (200 MHz) δ 8.5 (s, 1 H), 7.83 (d, J = 8.4 Hz, 2 H), 7.69 (d, J = 15.4 Hz, 1 H), 7.62 (m, 1 H), 7.36−7.30 (m, 3 H), 7.23−7.08 (m, 1 H), 6.87 (s, 1 H), 6.70 (d, J = 15.4 Hz, 1 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz) δ 144.4, 138.1, 137.9, 132.1, 131.1, 130.1, 128.2, 127.6, 125.3, 124.4, 121.8, 120.9, 111.4, 110.6, 21.6; MS m/z (%) 297 (M^+, 1), 232 (100), 218 (65), 140 (89); HRMS calcd for $C_{17}H_{15}NO_2S$ 297.0824, found 297.0849.

***N*-Carbobenzyloxy-2-[(*E*)-2-(*p*-toluenesulfonyl)ethenyl]-indoline (3b). Typical Procedure (Table 1, entry 2).** *N*-Cbz-2-iodoaniline (182 mg, 0.516 mmol), (*E*)-1-(*p*-toluenesulfonyl)-1,3-butadiene (214 mg, 1.03 mmol), K_2CO_3 (71 mg, 0.51 mmol), and 10 mol % of $Pd(OAc)_2$ were added to DMF−H_2O (6 mL, 10:1). The reaction mixture was stirred at room temperature under argon for 5 days. Chloroform (10 mL) was added, and the reaction mixture was filtered and concentrated in vacuo. The crude material was purified by chromatography (hexanes−ethyl acetate, 2:1), to afford **3b** (183 mg, 83%, based on *N*-Cbz-2-iodoaniline) as a white crystalline solid: mp 145.5−146.5 °C (from dichloromethane−hexanes); IR (film) 1711, 1317, 1145 cm^{-1}; ^1H NMR (200 MHz) δ 7.69 (d, J = 8.4 Hz, superimposed on m, 3 H), 7.32−7.16 (m, 9 H), 7.12−6.85 (m, 2 H), 6.37 (d, J = 15.2 Hz, 1 H), 5.23−4.90 (m, 3 H), 3.50 (dd, J = 16.1, 10.5 Hz, 1 H), 2,88 (dd, J = 16.4, 2.9 Hz, 1 H), 2.42 (s, 3 H); MS m/z (%) 433 (M^+, 11), 389 (16), 208 (33), 91 (100). Anal. Calcd for $C_{25}H_{23}NO_4S$: C, 69.26; H, 5.30; N, 3.20. Found: C, 68.81; H, 4.93; N, 3.24.

The other products in Table 1 were prepared similarly. The properties of the products **3c**−**l** are given below.

***N*-(*p*-Toluenesulfonyl)-2-[(*E*)-(2-*p*-toluenesulfonyl)ethenyl]indoline (3c) (Table 1, entry 3).** Mp 158−159 °C (from dichloromethane-hexanes); IR (film) 1596, 1349, 1314, 1163, 1136 cm^{-1}; ^1H NMR (200 MHz) δ 7.76 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 1 H), 7.50 (d, J = 8.4 Hz, 2 H), 7.37−7.15 (m, 6 H), 7.05 (m, 1 H), 6.95 (dd, J = 14.8, 5.1 Hz, 1 H), 6.68 (dd, J = 14.9, 1.3, 1 H), 4.93−4.87 (m, 1 H), 3.00 (dd, J = 15.7, 10.1 Hz, 1 H), 2.70 (dd, J = 16.5, 3.0 Hz, 1 H), 2.45 (s, 3 H), 2.36 (s, 3 H); MS m/z (%) 453 (M^+, 70), 299 (87), 154 (99), 76.4 (100). Anal. Calcd for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.09. Found: C, 63.55; H, 5.11; N, 3.05.

***N*-(*tert*-Butyloxycarbonyl)-2-[(*E*)-(2-*p*-toluenesulfonyl)-ethenyl]indoline (3d) (Table 1, entry 4).** White solid foam; IR (film) 1702, 1601, 1384, 1316, 1141 cm^{-1}; ^1H NMR (200 MHz) δ 7.74 (d, J = 8.4 Hz, superimposed on m,3 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 7.4 Hz, 1 H), 7.12 (d, J = 8.4 Hz, 1 H), 7.00−6.82 (m, 2 H), 6.37 (d, J = 14.9 Hz, 1 H), 5.1−4.9 (m, 1 H), 3.47 (dd, J = 16.2, 10.6 Hz, 1 H), 2.86 (dd, J = 16.4, 3.1 Hz, 1 H), 2.42 (s, 3 H), 1.35 (s, 9 H); ^{13}C NMR (100 MHz) δ 151.7, 144.5, 143.7, 137.3, 131.0, 130.0, 129.9, 127.9, 127.8, 124.9, 123.0, 115.1, 58.7, 33.8, 29.7, 28.0, 21.6; MS m/z (%) 399 (M^+, 2), 343 (22), 142 (100); HRMS calcd for $C_{22}H_{25}NO_4S$ 399.1504, found 399.1515.

***N*-Carbobenzyloxy-2-[(*E*)-1-methyl-2-(*p*-toluenesulfonyl)ethenyl]indoline (3e) (Table 1, entry 5).** Mp 126−127 °C; IR (film): 1711, 1316, 1147; ^1H NMR (200 MHz) δ 7.69 (d, J = 8.4 Hz, superimposed on m, 3 H), 7.36−6.94 (m, 10 H), 6.26 (s, 1 H), 5.20 (d, J = 11.8 Hz, 1 H), 5.17−4.87 (m, 1 H), 4.84 (dd, J = 10.3, 3.9 Hz,1 H), 3.51 (dd, J = 16.5, 10.9 Hz, 1 H), 2.84 (dd, J = 16.6, 4.0 Hz, 1 H), 2.41 (s, 3 H), 2.07 (d, J = 1.2 Hz, 3 H); MS m/z (%) 447 (M^+, 21), 403 (29), 208 (71), 91 (100). Anal. Calcd for $C_{26}H_{25}NO_4S$: C, 69.78; H, 5.63; N, 3.13. Found: C, 69.72; H, 5.77; N, 3.17.

***N*-Carbobenzyloxy-6-methyl-2-[(*E*)-(2-*p*-toluenesulfonyl)ethenyl]indoline (3g) (Table 1, entry 7).** Mp 139.5−140.5 °C (from dichloromethane−hexanes); IR (film) 1710, 1318, 1146 cm^{-1}; ^1H NMR (200 MHz) δ 7.69 (d, J = 8.2 Hz, superimposed on m, 3 H), 7.36−7.25 (m, 7 H), 7.05−6.85 (m, 3 H), 6.35 (d, J = 15.6 Hz, 1 H) 5.25−4.9 (m, 3 H), 3.45 (dd, J = 16.7, 10.4 Hz, 1 H), 2.83 (dd, J = 16.4, 3.1 Hz, 1 H), 2.42 (s, 3 H), 2.29 (s, 3 H);^{13}C NMR (50 MHz) δ 152.3, 144.4, 143.4, 138.7, 137.0, 135.6, 133.1, 131.0, 129.8, 128.5, 128.4. 128.2, 128.0, 127.6, 127.3, 125.6, 115.0, 67.5, 58.7, 34.0, 21.6, 20.8; MS m/z (%) 447 (M^+, 23), 403 (61), 91 (100); HRMS calcd for $C_{26}H_{25}NO_4S$ 447.1504, found 447.1489.

***N*-Carbobenzyloxy-6-methyl-2-[(*E*)-1-methyl-2-(*p*-toluenesulfonyl)ethenyl]indoline (3h) (Table 1, entry 8).** Oil; IR (film) 1710, 1635, 1313, 1302, 1147 cm^{-1}; ^1H NMR (200 MHz) δ 7.81 (d, J = 8.4 Hz, superimposed on m, 3 H),

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7.42−7.13 (m, 7 H), 6.97 (d, J = 9.1 Hz, 1 H), 6.92 (s, 1 H), 6.25 (s, 1 H), 5.21−5.13 (m, 1 H), 5.05−4.86 (m, 1 H), 4.81 (dd, J = 10.8, 3.6 Hz, 1 H), 3.47 (dd, J = 16.6, 11.1 Hz, 1 H), 2.80 (dd, J = 16.6, 3.8 Hz, 1 H), 2.40 (s, 3 H), 2.28 (s, 3 H), 2.05 (d, J = 1.2 Hz, 3 H); ^{13}C (100 MHz) δ 154.8, 144.0, 139.1, 135.7, 133.1, 130.4, 129.8, 129.7, 128.6, 128.5, 128.2, 127.8, 127.2, 127.0, 125.7, 125.4, 114.7, 67.4, 64.6, 34.2, 21.5, 20.8, 13.7; MS *m*/*z* (%) 461 (M^+, 45), 434 (59), 418 (79), 91 (100); HRMS calcd for $C_{27}H_{27}NO_4S$ 461.1661, found 461.1671

***N*-Carbobenzyloxy-6-methoxy-2-[(*E*)-(2-*p*-toluenesulfonyl)ethenyl]indoline (3j) (Table 1, entry 10).** Mp 141−142.5 °C; IR (film) 1706, 1320, 1145 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.69 (d, J = 8.0 Hz, superimposed on m, 3 H), 7.31−7.17 (m, 7 H), 6.90 (dd, J = 14.9, 6.5 Hz, 1 H), 6.71 (s, superimposed on m, 2 H), 6.35 (d, J = 15.4 Hz, 1 H), 5.19−4.92 (m, 3 H), 3.77 (s, 3 H), 3.48 (dd, J = 16.2, 10.3 Hz, 1 H), 2.84 (dd, J = 16.5, 2.7 Hz, 1 H), 2.42 (s, H); ^{13}C NMR (50 MHz) δ 156.3, 152.4, 144.4, 143.3, 137.0, 135.7, 131.1, 129.9, 128.8, 128.5, 128.3, 128.2, 127.9, 127.7, 115.9, 112.8, 111.2, 67.5, 58.9, 55.7, 34.2, 21.6; MS *m*/*z* (%) 463 (M^+, 5), 419 (6), 328 (8), 91 (100); HRMS calcd for $C_{26}H_{25}NO_5S$ 463.1453, found 463.1489.

***N*-Carbobenzyloxy-6-methoxy-2-[(*E*)-(1-methyl-2-*p*-toluenesulfonyl)ethenyl]indoline (3k) (Table 1, entry 11).** Oil; IR (film) 1708, 1315, 1146 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.70 (d, J = 8.4 Hz, superimposed on m, 3 H), 7.36−7.20 (m, 7 H), 6.68 (s superimposed on m, 2 H), 6.27 (s, 1 H), 5.24−4.79 (m, 3 H), 3.77 (s, 3 H), 3.49 (dd, J = 16.8, 10.9 Hz, 1 H), 2.81 (dd, J = 16.8, 3.8 Hz, 1 H), 2.42 (s, 3 H), 2.07 (d, J = 1.2 Hz, 3 H); ^{13}C NMR (50 MHz) δ 156.2, 154.6, 144.0, 139.0, 135.7, 129.7, 129.6, 128.6, 128.4, 128.3, 128.2, 127.8, 127.0, 125.8, 115.6, 112.7, 111.1, 67.3, 64.7, 55.7, 34.2, 21.6, 13.7; MS *m*/*z* (%) 477 (M^+, 39), 433 (22), 342 (63), 91 (100); HRMS calcd for $C_{27}H_{27}NO_5S$ 477.1610, found 477.1594.

Methyl *N*-Carbobenzyloxy-2-[(*E*)-(2-*p*-toluenesulfonyl)-ethenyl]indoline-6-carboxylate (3l) (Table 1, entry 12). Mp 189−190 °C (from dichloromethane−hexanes); IR (film) 1711, 1609, 1323, 1145 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.92 (d, J = 9.1 Hz, 1 H), 7.82 (s, 1 H), 7.68 (d, J = 8.2 Hz, 2 H), 7.36−7.24 (m, 8 H), 6.90 (dd, J = 14.9, 6.6 Hz, 1 H), 6.36 (d, J = 14.9 Hz, 1 H), 5.25−5.01 (m, 3 H), 3.89 (s, 3 H), 3.51 (dd, J = 16.2, 10.8 Hz, 1 H), 2.92 (dd, J = 16.7, 3.0 Hz, 1 H), 2.43 (s, 3 H); MS *m*/*z* (%) 491 (M^+, 2), 447 (19), 91 (100). Anal. Calcd for $C_{27}H_{25}NO_6S$: C, 65.97; H, 5.13; N, 2.85. Found: C, 66.15; H, 5.14; N, 2.86.

***N*-Carbobenzyloxy-2-[(*E*)-(2-*p*-toluenesulfonyl)ethenyl]-indole (4b).** Indoline **3b** (590 mg, 1.36 mmol) and DDQ (618 mg, 2.72 mmol) were refluxed 18 h in toluene (25 mL) under an argon atmosphere. The reaction mixture was concentrated in vacuo, and the residue was separated by chromatography (elution with hexanes−ethyl acetate−chloroform, 4:2:1) to yield indole **4b (**486 mg, 83%) as a white crystalline solid: mp 186−187 °C (from dichloromethane−hexanes); IR (film) 1726, 1314, 1141 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.31 (d, J = 15.9 Hz, 1 H), 8.12 (d, J = 8.4 Hz, 1 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.59−7.20 (m, 10 H), 6.95 (s, 1 H), 6.79 (d, J = 15.4 Hz, 1 H), 5.51 (s, 2 H), 2.42 (s, 3 H); MS *m*/*z* (%) 431 (M^+, 7), 387 (16), 232 (76), 141 (86), 91 (100). Anal. Calcd for $C_{25}H_{21}NO_4S$: C, 69.59; H, 4.91; N, 3.25. Found: C, 69.67; H, 5.22; N, 3.35.

***N*-Carbobenzyloxy-6-methyl-2-[(*E*)-(2-*p*-toluenesulfonyl)ethenyl]indole (4g).** Indoline **3g** (110 mg, 0.246 mmol) was treated with DDQ (111 mg, 0.489 mmol) as in the preparation of **4b** to afford indole **4g** (88 mg, 81%) as a white crystalline solid: mp 163−164.5 °C (from dichloromethane−hexanes); IR (film) 1726, 1602, 1314, 1135 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.32 (d, J = 15.2 Hz, 1 H), 7.99 (d, J = 8.5 Hz, 1 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.54−7.43 (m, 5 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.30 (s, 1 H), 7.15 (d, J = 8.9 Hz, 1 H), 6.87 (s, 1 H), 6.77 (d, J = 15.2 Hz, 1 H), 5.50 (s, 2 H), 2.44 (s, 3 H), 2.40 (s, 3 H); MS *m*/*z* (%) 445 (M^+,1), 290 (69), 246 (68), 154 (100), 91 (89). Anal. Calcd for $C_{26}H_{23}NO_4S$: C, 70.09; H, 5.20; N, 3.14. Found: C, 69.97; H, 5.13; N, 3.20.

Methyl *N*-Carbobenzyloxy-2-[(*E*)-(2-*p*-toluenesulfonyl)-ethenyl]indole-6-carboxylate (4l). Indoline **3l** (120 mg, 0.244 mmol) was treated with DDQ (110 mg, 0.485 mmol) as in the preparation of **4b** to afford indole **4l** (101 mg, 85%) as a white crystalline solid: mp 180−182 °C (from dichloromethane-hexanes); IR (film) 1705, 1609, 1314, 1287, 1149 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.34−8.14 (m, 3 H), 8.01 (dd, J = 9.0, 1.6 Hz, 1 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.55−7.42 (m, 5 H), 7.32 (d, J = 8.5 Hz, 2 H), 6.97 (s, 1 H), 6.82 (d, J = 15.2 Hz, 1 H), 5.53 (s, 2 H), 3.93 (s, 3 H), 2.44 (s, 3 H); MS *m*/*z* (%) 489 (M^+, 1), 445 (6), 199 (61), 91 (100). Anal. Calcd for $C_{27}H_{23}NO_6S$: C, 66.24; H, 4.74; N, 2.86. Found: C, 66.23; H, 4.39; N, 2.93.

Alternative Preparation of 4a. Indole **4b** (45 mg, 0.10 mmol) was dissolved in dichloromethane (5 mL) and cooled to 0 °C. $AlCl_3$ (41 mg, 0.31 mmol) and anisole (0.07 mL, 0.6 mmol) were added. The reaction mixture was stirred for 2 h and was then washed with aqueous NH_4OH, dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by chromatography (hexanes−ethyl acetate, 10:1) to afford a dark solid (21 mg, 68%) with a ^{1}H NMR spectrum and TLC that were identical to those of **4a** obtained by the oxidation of indoline **3a** (vide supra).

Dimethyl *N*-Carbobenzyloxy-carbazole-3,4-dicarboxylate (5). Indole **4b** (125 mg, 0.290 mmol), DMAD (0.36 mL, 2.9 mmol), and BHT (10 mg) were refluxed in toluene (5 mL) under an argon atmosphere for 18 h. The reaction mixture was concentrated in vacuo, and the residue was dissolved in 5 mL of dichloromethane. DBU (0.04 mL, 0.3 mmol) was added to the reaction mixture dropwise over 5 min. The reaction mixture was stirred for 2 h, concentrated in vacuo, and separated by chromatography (elution with hexanes−ethyl acetate, 5:1) to afford carbazole **5** (97 mg, 81%, based on **4b**) as a white crystalline solid: mp 215−216 °C (from dichloromethane−hexanes); IR (film) 1733, 1266, 1150 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.46 (d, J = 8.9 Hz, 1 H), 8.33 (d, J = 8.0 Hz, 1 H), 8.15 (d, J = 8.9 Hz, 1 H), 7.83 (d, J = 8.7 Hz, 1 H), 7.56−7.38 (m, 7 H), 5.60 (s, 2 H), 4.15 (s, 3 H), 3.96 (s, 3 H); MS *m*/*z* (%) 417 (M^+, 1), 373 (60), 164 (43), 91 (100). Anal. Calcd for $C_{24}H_{19}NO_6$: C, 69.06; H, 4.59; N, 3.36. Found: C, 68.81; H, 4.53; N, 3.39.

Dimethyl *N*-Carbobenzyloxy-6-methylcarbazole-3,4-dicarboxylate (6). Indole **4g** (137 mg, 0.308 mmol), DMAD (0.38 mL, 3.1 mmol), and BHT (7 mg) were refluxed in toluene (5 mL) under an argon atmosphere for 18 h. The product was treated with DBU and worked up as in the preparation of **5** to afford carbazole **6** (92 mg, 69%, based on **4g**) as a white crystalline solid: mp 112−112.5 °C (from dichloromethane−hexanes); IR (film) 1732, 1712 1306, 1248, 1151 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.43 (d, J = 8.9 Hz 1 H), 8.18 (d, J = 8.7 Hz, 1 H), 8.13 (d, J = 8.9 Hz, 1 H), 7.65−7.28 (m, 7 H), 5.58 (s, 2 H), 4.15 (s, 3 H), 3.96 (s, 3 H), 2.49 (s, 3 H); MS *m*/*z* (%) 431 (M^+, 1), 387 (64), 178 (74), 91 (100). Anal. Calcd for $C_{25}H_{21}NO_6$: C, 69.60; H, 4.91; N, 3.25. Found: C, 69.34; H, 5.04; N, 3.21.

Trimethyl *N*-Carbobenzyloxy-carbazole-3,4,6-tricarboxylate (7). Indole **4l** (114 mg, 0.233 mmol), DMAD (0.29 mL, 2.3 mmol), and BHT (5 mg) were refluxed in toluene (5 mL) under an argon atmosphere for 18 h. The product was treated with DBU and worked up as in the preparation of **5** to afford carbazole **7** (67 mg, 61%, based on **4l**) as a white crystalline solid: mp 165−167 °C (from dichloromethane−hexanes); IR (film) 2946, 1717, 1263, 1147 cm^{-1}; ^{1}H NMR (400 MHz) 8.51 (d, J = 1.3 Hz, 1 H), 8.44 (d, J = 8.9 Hz, 1 H), 8.36 (d, J = 8.9 Hz, 1 H), 8.20 (dd, J = 8.9, 1.7 Hz, 1 H), 8.17 (d, J = 8.9 Hz, 1 H), 7.55 (dd, 8.0, 1.8 Hz, 1 H), 7.50−7.41 (m, 4 H), 5.61 (s, 2 H), 4.20 (s, 3 H), 3.97 (s, 3 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.9, 166.6, 165.8, 151.6, 141.7, 141.6, 134.3, 129.7, 129.6, 129.4, 129.2, 129.0, 128.9, 126.0, 123.5, 123.1, 122.6, 122.2, 116.9, 116.1, 69.8, 53.1, 52.6, 52.3; MS *m*/*z* (%) 475 (M^+, <1), (431 (28), 310 (33), 91 (100); HRMS calcd for $C_{26}H_{21}NO_8$ 475.1267, found 475.1245.

Methyl *N*-Carbobenzyloxy-carbazole-4-carboxylate (9). Indole **4b** (90 mg, 0.21 mmol), methyl propiolate (0.19 mL, 2.1 mmol), and BHT (5 mg) were refluxed in toluene (5 mL) under an argon atmosphere for 18 h. The reaction mixture was concentrated in vacuo, and the residue was dissolved in 5 mL of dichloromethane. DBU (0.04 mL, 0.29 mmol) was added to the reaction mixture dropwise over 5 min. The reaction mixture was stirred for 2 h, concentrated in vacuo, and

separated by chromatography (elution with hexanes−ethyl acetate, 5:1) to afford carbazole **9** (57 mg, 76%, based on **4b**) as a white crystalline solid: mp 123.5−125 °C (from dichloromethane−hexanes); IR (film) 1717, 1321, 1142 cm^{-1}; ^1H NMR (400 MHz) δ 8.68 (d, J = 8.9 Hz, 1 H), 8.63 (d, J = 8.4 Hz, 1 H), 8.35 (d, J = 8.4 Hz, 1 H), 7.88 (d, J = 7.7 Hz, 1 H), 7.55−7.33 (m, 8 H), 5.60 (s, 2 H), 4.06 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.1, 152.1, 139.2, 138.9, 135.0, 128.9, 128.7, 128.6, 128.1, 126.2, 125.9, 125.5, 124.8, 124.7, 124.4, 123.4, 120.1, 115.9, 69.0, 52.0; MS *m*/*z* (%) 359 (M^+, 0.2), 315 (29), 164 (63), 91 (100); HRMS calcd for $C_{22}H_{17}NO_4$ 359.1158, found 359.1122.

When a 5-fold excess of DBU was employed, simultaneous deprotection of the Cbz group occurred to afford **12** (vide infra) in 65% yield.

Methyl *N*-Carbobenzyloxy-6-methylcarbazole-4-carboxylate (10). Indole **4g** (105 mg, 0.236 mmol), methyl propiolate (0.21 mL, 2.4 mmol), and BHT (5 mg) were refluxed in toluene (5 mL) under an argon atmosphere for 18 h. The product was treated with DBU and worked up as in the preparation of **9** to afford carbazole **10** (63 mg, 73%, based on **4g**) as a white crystalline solid: mp 99−100 °C (from dichloromethane−hexanes); IR (film) 1727, 1301, 1146 cm^{-1}; ^1H NMR (200 MHz) δ 8.62 (d, J = 8.6 Hz 1 H), 8.46 (s, 1 H), 8.22 (d, J = 8.7 Hz, 1 H), 7.86 (d, J = 8.7 Hz, 1 H), 7.60−7.28 (m, 7 H), 5.58 (s, 2 H), 4.07 (s, 3 H), 2.52 (s, 3 H); MS *m*/*z* (%) 373 (M^+, 4), 329 (65), 178 (85), 91 (100). Anal. Calcd for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.13; N, 3.75. Found: C, 73.84; H, 4.94; N, 3.80. See Supporting Information for X-ray crystallographic data for **10**.

Dimethyl *N*-Carbobenzyloxy-carbazole-4,6-dicarboxylate (11). Indole **4l** (79 mg, 0.16 mmol), methyl propiolate (0.14 mL, 1.6 mmol), and BHT (4 mg) were refluxed in toluene (4 mL) under an argon atmosphere for 18 h. The product was treated with DBU and worked up as in the preparation of **9** to afford carbazole **11** (44 mg, 65%, based on **4l**) as a white crystalline solid: mp 246−250 °C; IR (film) 1717, 1311, 1238 cm^{-1}; ^1H NMR (200 MHz) δ 9.41 (s, 1 H), 8.63 (d, J = 8.4 Hz, 1 H), 8.41 (d, J = 8.9 Hz, 1 H), 8.20 (d, J = 8.9 Hz, 1 H), 7.95 (d, J = 7.7 Hz, 1 H) 7.62−7.31 (m, 6 H), 5.61 (s, 2 H), 4.11 (s, 3 H), 3.99 (s, 3 H); ^{13}C NMR (100 MHz) δ 167.8, 167.2, 151.8, 141.7, 139.7, 134.6, 129.3, 129.0, 128.9, 128.7, 128.2, 128.0, 126.9, 126.4, 125.8, 125.3, 124.3, 120.1, 115.6, 69.4, 52.5, 52.2; MS *m*/*z* (%) 417 (M^+, 1), 373 (88), 164 (50), 91 (100); HRMS calcd for $C_{24}H_{19}NO_6$ 417.1212, found 417.1232.

Methyl Carbazole-4-carboxylate (12). Carbazole **9** (35 mg, 0.097 mmol) was dissolved in methanol (5 mL), 5% Pd−C (10 mg) was added, and the reaction mixture was stirred for 16 h under 1 atm of hydrogen, maintained with a balloon. The reaction mixture was filtered through Celite, concentrated in vacuo, and purified by chromatography (hexanes−ethyl acetate, 2:1) to afford carbazole **12** (21 mg, 95%): mp 94−96 °C (lit.[14a] 96−97 °C); IR (film) 3386, 1717, 1258 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 10.7 (s, 1 H), 8.86 (d, J = 7.7 Hz, 1 H), 7.84−7.76 (m, 2 H), 7.57−7.40 (m, 3 H), 7.19 (m, 1 H), 4.02 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.4, 140.2, 130.0, 129.4, 126.8, 125.7, 125.3, 124.8, 122.7, 121.9, 119.8, 114.9, 110.3, 52.1; MS *m*/*z* (%) 225 (M^+, 10), 194 (91), 166 (82), 89 (100); HRMS calcd for $C_{14}H_{11}NO_2$ 225.0790, found 225.0790.

Alternatively, indole **4a** (90 mg, 0.30 mmol), methyl propiolate (0.27 mL, 3.0 mmol), and BHT (4 mg) were refluxed in toluene (5 mL) under an argon atmosphere for 18 h. The reaction mixture was concentrated in vacuo, and the residue was dissolved in 5 mL of dichloromethane. DBU (0.04 mL, 0.30 mmol) was added to the reaction mixture dropwise over 5 min. The reaction mixture was stirred for 2 h, concentrated in vacuo, and separated by chromatography (elution with hexanes−ethyl acetate, 5:1) to afford carbazole **12** (51 mg, 76%), identical (^1H NMR, TLC) to the sample prepared above.

Methyl *N*-Carbobenzyloxy-2-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydrocarbazole-4-carboxylate (13). Indole **4b** (212 mg, 0.492 mmol), methyl acrylate (0.48 mL, 5.3 mmol), and BHT (11 mg) were refluxed in toluene (10 mL) under an argon atmosphere for 18 h. The reaction mixture was concentrated in vacuo and separated by chromatography (elution with hexanes−ethyl acetate, 5:1) to afford **13** (192 mg, 76%, based on **4b**) as a white crystalline solid: mp 216−216.5 °C (from dichloromethane−hexanes); IR (film) 1726, 1712, 1307, 1136 cm^{-1}; ^1H NMR (400 MHz) 8.12 (d, J = 8.5 Hz, 1 H), 7.70 (d, J = 8.2 Hz, 2 H), 7.51−7.32 (m, 5 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.28−7.20 (m, 3 H), 5.44 (s, 2 H), 3.80−3.90 (m, 1 H), 3.76 (s, 3 H), 3.51 (dd, J = 17.2, 4.6 Hz, 1 H), 3.30−3.40 (m, 1 H), 3.15 (m, 1 H), 2.77 (dd, J = 12.4, 5.7 Hz, 1 H), 2.47 (s, 3 H), 2.03 (q, J = 12.3 Hz, 1 H); MS *m*/*z* (%) 517 (M^+, 1), 488 (1), 168 (28), 91 (100). Anal. Calcd for $C_{29}H_{27}NO_6S$ C, 67.30; H, 5.26; N, 2.71. Found C, 66.90; H, 5.04; N, 2.71.

Conversion of Tetrahydrocarbazole 13 to Carbazole 12. Magnesium powder (36 mg, 1.5 mg atom) was added to refluxing methanol (4 mL), followed by tetrahydrocarbazole **13** (80 mg, 0.15 mmol). The mixture was refluxed for an additional 20 h and was then filtered through Celite and concentrated in vacuo. Toluene (5 mL) was added to the residue along with DDQ (34 mg, 0.15 mmol), and the mixture was refluxed for 16 h. It was then concentrated in vacuo and separated by chromatography (hexanes−ethyl acetate, 5:1) to afford carbazole **12** (17 mg, 51%). The ^1H NMR spectrum and TLC of the product were identical to those of **12** obtained from the deprotection of **9** (vide supra).

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of new compounds without satisfactory elemental analyses and X-ray crystallographic data for **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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