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Catalytic C-2 Allylation of Indoles by Electronic Modulation of the Indole Ring and its Application to the Synthesis of Functionalized Carbazoles

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Abstract: We report a palladium-catalyzed C-2 allylation of indoles and subsequent cyclization of the allylated indoles. The electronic effects of chloro and ester groups that can be readily installed at the C-3 position of indoles facilitated a highly efficient C–H allylation at the C-2 position. The resulting 2-allyl-3-chloroindoles were found to be suitable substrates for benzannulation reactions with alkynes and norbornadiene as an acetylene synthon. This approach, utilizing readily available indoles, allyl acetates, and norbornadiene, allows a rapid access to complex carbazoles.

Keywords: allylation; annulation; carbazoles; indoles; palladium

Introduction

Indole is an important heterocyclic core, frequently found in natural products and pharmaceuticals.[1] In the past decade, much progress has been made towards the functionalization of indoles by directly installing the desired functional group in the heterocyclic ring.[2–5] Particularly, direct C–H allylation reactions facilitate the synthesis of allylated indoles, a key structural motif in many natural products.[6] Furthermore, owing to the facile transformation of the allyl group into various functional groups, the catalytic allylation strategy is useful for the synthesis of complex indole compounds and annulated heterocycles.[7]

Consistent with the general reactivity of indoles, allylation preferentially occurs at the C-3 position, which is more nucleophilic than the C-2 position.[8–10] To enable the C-2 selective allylation of indoles, a directing group strategy has been developed previously (Figure 1 A).[4g,h,11] Although the desired C-2-regioselectivity was achieved, only two types of directing groups, the 2-pyrimidyl and *N*,*N*-dialkylcarbamoyl groups, have proven effective. Moreover, the substituents at the C-3 position significantly hindered the directing group-assisted allylation.[12]

We postulated that modification of the electronic nature of the electron-rich indole ring with electron-withdrawing groups (EWGs) could promote the C-2 allylation of indoles.[13] Based on our recent results in the C–H alkylation of pyrazoles, we surmised that the

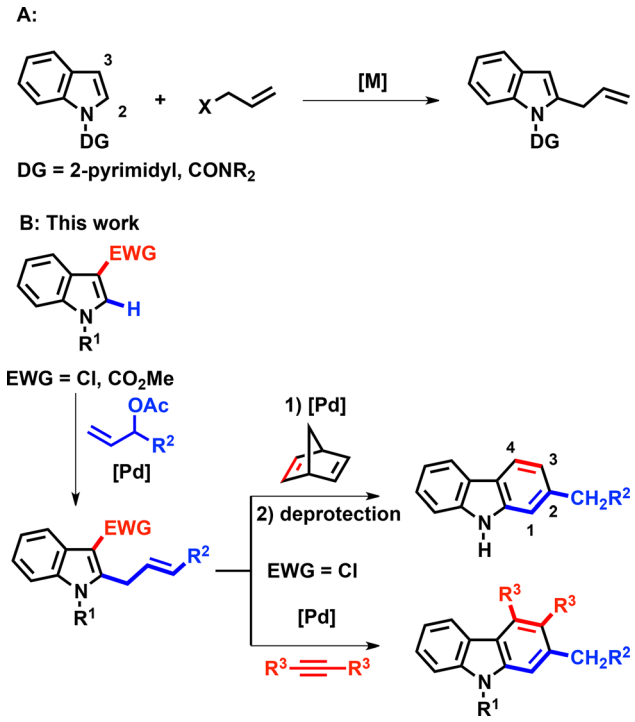


Figure 1. A: Directing group-assisted C-2-allylation of indoles. **B:** C-2 allylation enabled by the effect of electron-withdrawing groups and subsequent cyclization to give carbazoles.

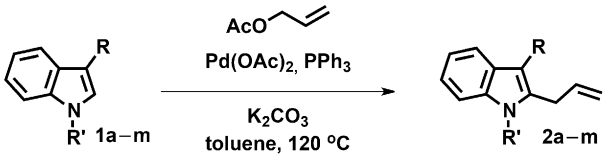
electronic effect of appropriately positioned electron-withdrawing groups should facilitate C–H allylation at the indole C-2 position.[14] For example, a chloro group installed at the indole C-3 position should enable the formation of synthetically useful 2-allyl-3-chloroindoles *via* C–H allylation (Figure 1 B). While 2-allyl-3-haloindoles have proven useful in the annulation of indoles, their preparation relies on the cyclization reactions of iodoanilines, rather than taking advantage of readily available indoles.[15] In addition, only the annulation reactions of iodoindoles with alkynes have been examined until now, leaving open the possibility that carbazoles with a variety of substitution patterns could be synthesized from haloindoles and unsaturated hydrocarbons.[16]

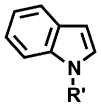
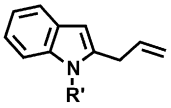
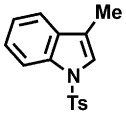
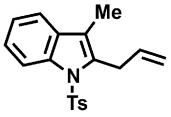
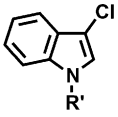
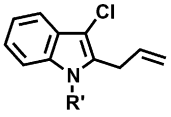
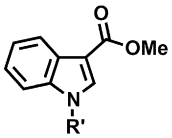
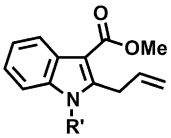
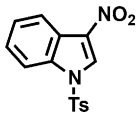
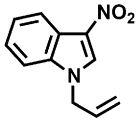
Herein, we report the catalytic C–H allylation of indoles at the C-2 position in high yields. The chloro and ester groups were utilized as electron-withdrawing substituents. C–H allylation was carried out using readily available functionalized allyl acetates.[17] In the case of chloro substrates, the resulting 2-allyl-3-chloroindoles were converted to carbazoles by sequential cyclization and isomerization reactions. In addition to internal alkynes, norbornadiene can be employed as an acetylene synthon in the retro-Diels–Alder reaction.[18–20] This represents a new approach to the synthesis of 2-alkylcarbazoles, where an allyl group and norbornadiene merge to form a benzene ring in the carbazole heterocycle.[21,22]

Results and Discussion

First, the electronic effects of electron-withdrawing groups on C-2 allylation reactions of indoles were evaluated using a catalytic system derived from $Pd(OAc)_2$ and PPh_3 (Table 1).[23] We propose that the C-2 allylation of indoles occurs *via* π-allyl palladium complexes, similar to the C–H allylation of electron-deficient arenes (see the Supporting Information for the proposed mechanism).[24] *N*-Methylindole **1a** did not produce appreciable amounts of either the C-2 allylation product **2a** or the corresponding C-3 allylation product (entry 1). An electron-withdrawing group attached to the nitrogen atom had a positive impact on the allylation; the reactions of *N*-tosylindole **1b** and carbamoylindole **1c** produced the corresponding C-2 allylation products **2b** and **2c** in 11% and 18% yields, respectively (entries 2 and 3). The formation of the corresponding C-3 allylation products was not observed in these cases. The low yield of **2c** suggests that the *N*,*N*-dimethylcarbamoyl group is not an efficient directing group in the Pd-catalyzed reaction, in contrast to its strong effect in the Rh-catalyzed reactions.[11c] In addition, the low yield of the 3-methyl variant **1d** indicates that simply blocking the C-3 position does not considerably increase the yield

Table 1. C-2 allylation of indoles by electronic modulation of the indole ring.[a]



Entry	Reactant	Product (Yield)
		
1	R' = Me (1a)	2a (0%)
2	Ts (1b)	2b (11%)
3	$CONMe_2$ (1c)	2c (18%)
4	 1d	 2d (34%)
		
5	R' = Ts (1e)	2e (>99%)
6	SO_2Ph (1f)	2f (97%)
7	SO_2NMe_2 (1g)	2g (>99%)[b]
		
8	R' = Me (1h)	2h (71%)[c]
9	Ts (1i)	2i (74%)
10	SO_2Ph (1j)	2j (76%)
11	SO_2NMe_2 (1k)	2k (66%)[c]
12	Ns (1l)	2l (63%)
13	$CONMe_2$ (1m)	2m (61%)
14	 1n	 3 (52%)

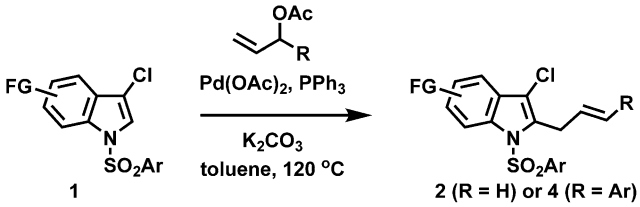
[a] *Reaction conditions:* indole (0.40 mmol), allyl acetate (0.60 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), K_2CO_3 (1.0 mmol), toluene (0.40 M), 120 °C, 14 h.
[b] The reaction was carried out for 36 h to ensure complete consumption of the starting material.
[c] The reaction was carried out at 130 °C.

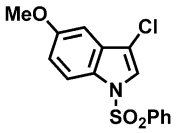
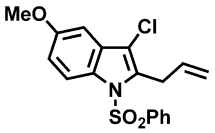
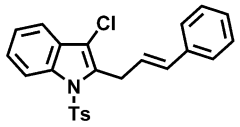
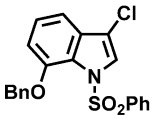
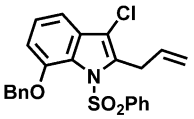
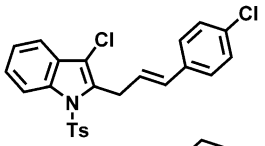
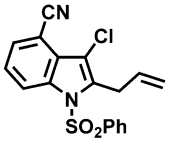
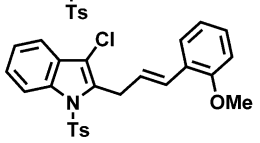
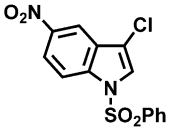
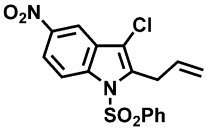
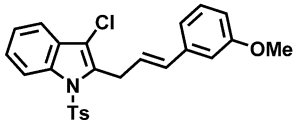
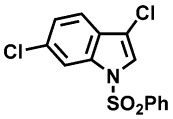
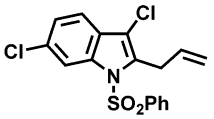
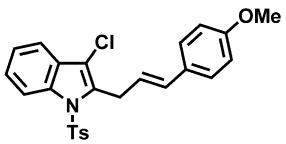
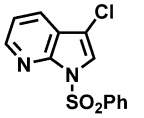
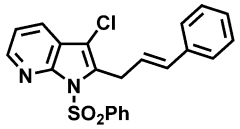
of C-2 allylation (entry 4). Crucially, when a chloro substituent was attached to the indole C-3 position, the allylation product **2e** was obtained in almost quantitative yield (entry 5). Common indole protecting groups, namely benzenesulfonyl and *N*,*N*-dimethylaminosulfamoyl, were tolerated in the reac-

tion (entries 6 and 7). Furthermore, a series of experiments using 3-carboxylate counterparts **1h–1m** revealed that the ester group too promoted the C–H allylation of indoles, but to a lesser extent than the chloro group (entries 8–13). These results show that in the allylation reactions of indole-3-carboxylates, the electronic effect of protecting groups at N-1 is not as significant as the effect exerted by the ester group at C-3. The reactions of indoles possessing other carbonyl groups, such as formyl and acetyl groups, were not efficient because of an olefin isomerization reaction of the allylation products (Table S2 in the Supporting Information). However, functional groups that are either less electron-withdrawing (Br, I) or more electron-withdrawing (CN, NO_2) than the chloro and ester groups gave low yields of allylation products, showing the importance of the fine balance of the electronic effects in Pd-catalyzed C–H functionalization reactions.[25] When *N*-tosylated 3-nitroindole **1n** was subjected to the reaction conditions, it underwent deprotection followed by *N*-allylation, furnishing **3** as the major product (entry 14).

The C-2 selective allylation worked well for indoles bearing electron-donating and electron-withdrawing substituents on the benzene ring (Table 2). Alkoxy, cyano, nitro and chloro groups were compatible with the allylation conditions (entries 1–5). Notably, an azaindole derivative **1t** was allylated to generate the corresponding product **2t** in 89% yield (entry 6). Both cinnamyl acetate and its regioisomeric secondary ace-

Table 2. Scope of the C–H allylation of 3-chloroindoles.[a]



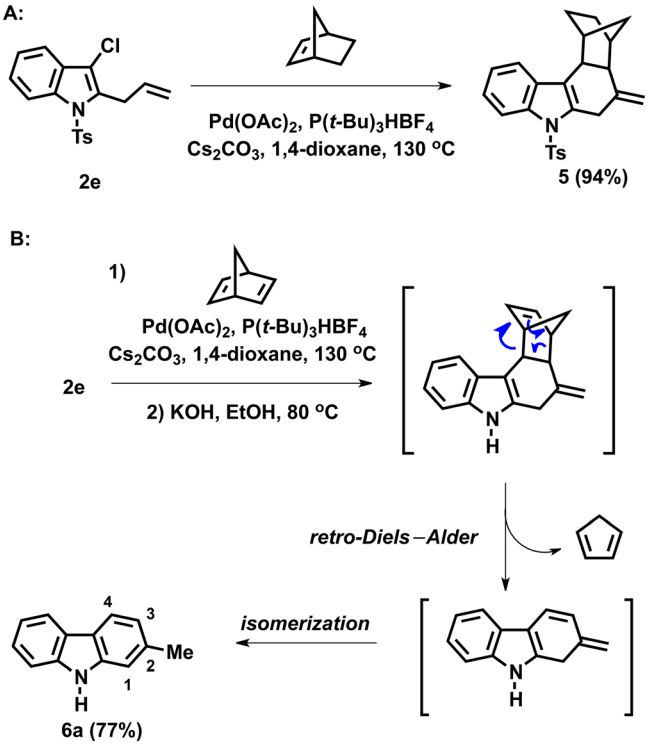
Entry	Reactant	Product	Yield	Entry	Reactant	Product	Yield
1	 1o		2o (86%)	7[b]	1e		4a (75%, 95%[c])
2	 1p		2p (80%)	8	1e		4b (65%)
3	 1q		2q (89%)	9	1e		4c (92%)
4	 1r		2r (77%)	10	1e		4d (69%)
5	 1s		2s (89%)	11	1e		4e (70%)
6	 1t		2t (89%)	12	1t		4f (83%)[c]

[a] *Reaction conditions:* indole (0.40 mmol), allyl acetate (0.60 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), K_2CO_3 (1.0 mmol), toluene (0.40 M), 120 °C, 14 h.
[b] The reaction was carried out for 42 h to ensure complete consumption of the starting material.
[c] The reaction was carried out with cinnamyl acetate.

tate gave the linear isomer **4a**, consistent with the results obtained in the allylation of pyrazoles (entry 7).[14a] Therefore, depending on the preparation method preferred for allyl acetates, either primary or secondary acetates could be used for the C-2 allylation of indoles. Several allyl aryl acetates were competent allyl group donors and afforded **4b**–**4e** in good to high yields (entries 8–11). Also, the reaction of azaindole **1t** and cinnamyl acetate resulted in the synthesis of **4f** in 83% yield.

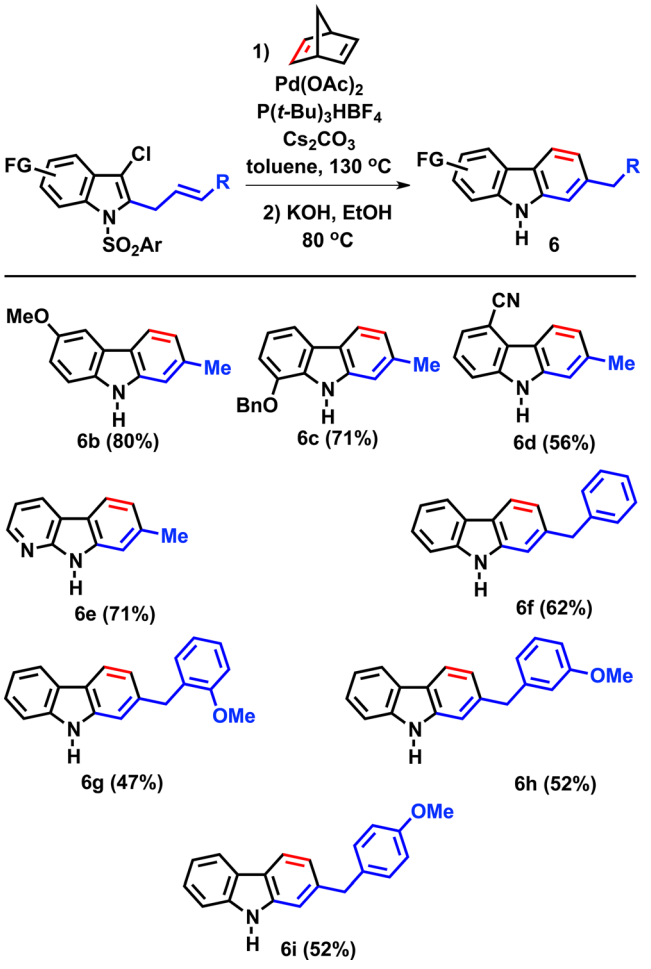
After establishing a general method to afford 2-allyl-3-chloroindoles, we examined their amenability to annulation reactions. Due to the lack of general approaches to prepare 2-allyl-3-chloroindoles, reactions of these functionalized indoles were not investigated earlier. In order to identify new two-carbon units that could undergo annulation reactions with 2-allyl-3-chloroindoles, we first carried out a cyclization reaction with norbornene (Scheme 1A). The formation of cyclized product **5** illustrated that strained alkenes could be viable partners for the annulation of 2-allyl-3-chloroindoles. The diene counterpart, norbornadiene has been used as an acetylene synthon, instead of gaseous polymerizable acetylene, in Pd-catalyzed annulation reactions.[19] We envisioned that the annulation of 2-allyl-3-chloroindoles with norbornadiene, followed by retro-Diels–Alder and isomerization reactions, should afford aromatized carbazole structures (Scheme 1B). Gratifyingly, it was feasible to perform a tandem sequence of these reactions to eventually form the carbazole **6a**. The annulation with norbornadiene was efficient in both 1,4-dioxane and toluene (77% and 72% yields, respectively). In agreement with previous studies using norbornadiene, the following characteristics were observed: (i) an excess of norbornadiene was essential for high efficiency; presumably it increases complexation with the Pd complexes and prevents additional reactions with the remaining strained olefinic portion of the cyclized product (see the Supporting Information for details); and (ii) the retro-Diels–Alder reaction was better facilitated when the indole protecting group was removed.[19c]

Using the two-step sequence, we synthesized a variety of carbazoles from 2-allyl-3-chloroindoles (Table 3). It is noteworthy that the newly formed carbazole benzene rings possess a methyl or benzyl sub-



Scheme 1. Annulation of chloroindole **2e** with norbornene and norbornadiene.

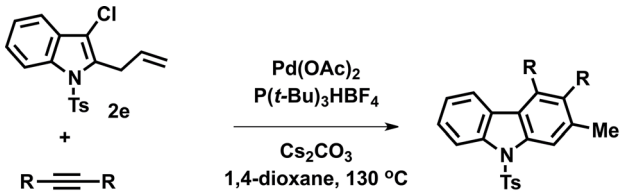
Table 3. Synthesis of carbazoles by annulation with norbornadiene as an acetylene synthon.[a]



[a] *Reaction conditions:* 1) indole (0.20 mmol), norbornadiene (1.2 mmol), $Pd(OAc)_2$ (10 mol%), $P(t\text{-}Bu)_3HBF_4$ (22 mol%), Cs_2CO_3 (0.40 mmol), toluene (0.20 M), 130 °C, 14 h; 2) KOH (0.60 mmol), EtOH (0.20 M), 80 °C, 14 h.

stituent at the C-2 position, which is difficult to introduce using a convergent approach.[26] Alkoxy and cyano groups were tolerated in the cyclization process (**6b–6d**). Azaindole **2t** was successfully transformed to pyridoindole **6e**. In addition to allyl-substituted indoles, cinnamyl-substituted indoles could also be used for cyclization, ultimately furnishing 2-benzyl-substituted carbazoles (**6f–6i**).

Encouraged by these results, we further explored the utility of 2-allyl-3-chloroindoles for the synthesis of highly substituted carbazoles. In light of the results obtained by the Larock group, where a 2-allyl-3-iodoindole reacted with internal alkynes to give carbazoles in moderate yields, we attempted the cyclization of the chloro-substituted variant **2e** (Scheme 2).[15a] In the presence of $Pd(OAc)_2$ and $P(t\text{-}Bu)_3HBF_4$, both diaryl- and dialkylacetylenes led to the formation of their corresponding carbazoles, **7a** and **7b**, in good yields. This result suggests that 2-allyl-3-chloroindoles can be alternatively employed in cyclization reactions in place of their iodide counterparts.



Scheme 2. Synthesis of carbazoles by annulation with internal alkynes.

Conclusions

In conclusion, we have developed a catalytic C-2 allylation reaction of indoles by taking advantage of electron-withdrawing groups at the C-3 position. The chloro and ester groups that can be easily installed by the electrophilic substitution of indoles, enabled allylation at the C-2 position in a highly efficient manner, providing an alternative to the directing group-assisted C–H allylation reactions. This general approach for the preparation of 2-allyl-3-chloroindoles facilitated the development of new annulation reactions of indoles. 2-Allyl-3-chloroindoles were smoothly converted to the corresponding carbazoles by a Pd-catalyzed cyclization with norbornadiene and alkynes. In the reaction with norbornadiene, retro-Diels–Alder and isomerization reactions took place to furnish 2-methyl- and 2-benzyl-substituted carbazoles. This result represents the first catalytic reaction between 2-allyl-3-chloroindoles and a strained alkene to give carbazoles. This strategy based on C–H allylation complements the annulation methods for the synthesis of carbazoles from indoles, and allows the systematic preparation of new, fused indole-containing compounds.

Experimental Section

General Procedure A for the *N*-Protection of Indoles

To a stirred solution of the indole (1.0 equiv.) in THF (and/or DMF) at 0 °C under a nitrogen atmosphere was added 60% sodium hydride in oil. After stirring for 20 min at 0 °C, a protecting reagent was added dropwise, and the resulting mixture was stirred for 16 h at 25 °C. The reaction mixture was treated with water (15 mL) and EtOAc (20 mL) and transferred to a 125-mL separatory funnel. The organic layer was collected, and the aqueous layer was extracted with EtOAc (25 mL × 2). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired indole.

General Procedure B for the C–H Allylation of Indoles

To an 8-mL glass vial equipped with a magnetic stir bar were sequentially added K_2CO_3 (138 mg, 1.0 mmol), the indole substrate (0.40 mmol), allyl acetate (0.60 mmol), toluene (1.00 mL, 0.40 M), $Pd(OAc)_2$ (4.50 mg, 0.020 mmol) and PPh_3 (21.0 mg, 0.080 mmol). The reaction mixture was purged with nitrogen through a Teflon-lined cap. Then, the cap was replaced with a new Teflon-lined solid cap. The reaction vial was moved to a preheated reaction block (120 or 130 °C). After stirring for 14 h, the reaction mixture was cooled to 25 °C and concentrated. The residue was purified by flash column chromatography to provide the desired product.

General Procedure C for the Synthesis of Carbazoles from 2-Allyl-3-chloroindoles

To an 8-mL glass vial equipped with a magnetic stir bar were sequentially added Cs_2CO_3 (130 mg, 0.40 mmol), the 2-allyl-3-chloroindole substrate (0.20 mmol), norbornadiene (122 μL, 1.2 mmol), toluene or 1,4-dioxane (1.00 mL, 0.20 M), $Pd(OAc)_2$ (4.50 mg, 0.020 mmol) and $P(t\text{-}Bu)_3HBF_4$ (12.8 mg, 0.044 mmol). The reaction mixture was purged with nitrogen through a Teflon-lined cap. Then, the cap was replaced with a new Teflon-lined solid cap. The reaction vial was moved to a preheated reaction block (130 °C). After stirring for 14 h, the reaction mixture was cooled to 25 °C and filtered through a short pad of silica gel. The solvent was evaporated, and the crude material was transferred to an 8-mL glass vial. Then, EtOH (1.00 mL, 0.20 M) and KOH (33.7 mg, 0.60 mmol) were added. The reaction vial was moved to a preheated reaction block (80 °C). After stirring for 14 h, the reaction mixture was cooled to 25 °C. The reaction mixture was treated with water (15 mL) and EtOAc (20 mL) and transferred to a 125-mL separatory funnel. The organic layer was collected and the aqueous layer was extracted with EtOAc (25 mL × 2). The combined organic layers were washed with brine (20 mL), dried over sodium

sulfate, and filtered. The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired carbazole.

1-Tosyl-1*H*-indole (1b):[27] Following the general procedure A, 1*H*-indole (1.00 g, 8.54 mmol), THF (10.0 mL), DMF (10.0 mL), 60% sodium hydride in oil (376 mg, 9.39 mmol), and 4-methylbenzene-1-sulfonyl chloride (1.79 g, 9.39 mmol) were used. Flash column chromatography (hexanes/EtOAc = 9:1) provided indole **1b** as a yellow solid; yield: 937 mg (40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (dd, J = 8.2, 0.7 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.62–7.45 (m, 2H), 7.36–7.28 (m, 1H), 7.25–7.14 (m, 3H), 6.65 (d, J = 3.6 Hz, 1H), 2.33 (s, 3H).

***N*,*N*-Dimethyl-1*H*-indole-1-carboxamide (1c):**[28] Following the general procedure A, 1*H*-indole (1.00 g, 8.54 mmol), THF (10.0 mL), 60% sodium hydride in oil (376 mg, 9.39 mmol), and dimethylcarbamic chloride (0.865 mL, 9.39 mmol) were used. Flash column chromatography (hexanes/EtOAc = 3:1) provided indole **1c** as a pink solid; yield: 1.31 g (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 3.4 Hz, 1H), 7.31–7.26 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 3.5 Hz, 1H), 3.10 (s, 6H).

3-Methyl-1-tosyl-1*H*-indole (1d):[29] Following the general procedure A, 3-methyl-1*H*-indole (1.00 g, 7.62 mmol), DMF (10.0 mL), 60% sodium hydride in oil (335 mg, 8.38 mmol), and 4-methylbenzene-1-sulfonyl chloride (1.60 g, 8.38 mmol) were used. Flash column chromatography (hexanes/EtOAc = 18:1) provided indole **1d** as a yellow solid; yield: 776 mg (36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 7.4 Hz, 1H), 7.38–7.28 (m, 2H), 7.25–7.12 (m, 3H), 2.33 (s, 3H), 2.24 (s, 3H).

3-Chloro-1-tosyl-1*H*-indole (1e):[30] Following the general procedure A, 3-chloro-1*H*-indole (615 mg, 4.06 mmol), DMF (6.00 mL), 60% sodium hydride in oil (179 mg, 4.47 mmol), and 4-methylbenzene-1-sulfonyl chloride (852 mg, 4.47 mmol) were used. Flash column chromatography (hexanes/EtOAc = 19:1) provided indole **1e** as a white solid; yield: 994 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.61–7.46 (m, 2H), 7.42–7.28 (m, 2H), 7.25–7.18 (m, 2H), 2.35 (s, 3H).

3-Chloro-1-(phenylsulfonyl)-1*H*-indole (1f):[31] Following the general procedure A, 3-chloro-1*H*-indole (1.89 g, 12.5 mmol), THF (10.0 mL), 60% sodium hydride in oil (548 mg, 13.7 mmol), and benzenesulfonyl chloride (1.95 mL, 13.7 mmol) were used. Flash column chromatography (hexanes/EtOAc = 19:1) provided indole **1f** as a white solid; yield: 2.19 g (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.2 Hz, 2H), 7.66–7.27 (m, 7H).

3-Chloro-*N*,*N*-dimethyl-1*H*-indole-1-sulfonamide (1g): Following the general procedure A, 3-chloro-1*H*-indole (1.00 g, 6.60 mmol), THF (10.0 mL), DMF (2.50 mL), 60% sodium hydride in oil (343 mg, 8.58 mmol), and dimethylsulfamoyl chloride (0.85 mL, 7.92 mmol) were used. Flash column chromatography (hexanes/EtOAc = 11:1) provided indole **1g** as a brown solid; yield: 0.76 g (45%); mp 105–108 °C. IR (film): ν = 3136, 1469, 1445, 1414, 1389, 1274, 1203 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 6.9 Hz, 1H), 7.45 (s, 1H), 7.42–7.32 (m, 2H), 2.85 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.6, 127.6, 125.5, 123.4, 123.3, 119.0, 114.0, 111.5, 38.6; HR-MS (ESI): m/z = 259.0305, calcd. for $C_{10}H_{12}ClN_2O_2S$ $[M+H]^+$: 259.0303.

Methyl 1-methyl-1*H*-indole-3-carboxylate (1h):[32] Following the general procedure A, methyl 1*H*-indole-3-carboxylate (3.00 g, 17.1 mmol), THF (25.0 mL), 60% sodium hydride in oil (451 mg, 11.3 mmol), and iodomethane (1.17 mL, 18.8 mmol) were used. Flash column chromatography (hexanes/EtOAc = 5:1) provided indole **1h** as a white solid; yield: 1.58 g (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21–8.13 (m, 1H), 7.79 (s, 1H), 7.38–7.27 (m, 3H), 3.91 (s, 3H), 3.84 (s, 3H).

Methyl 1-tosyl-1*H*-indole-3-carboxylate (1i):[33] To a stirred solution of methyl 1*H*-indole-3-carboxylate (1.00 g, 5.71 mmol), triethylamine (1.04 mL, 7.42 mmol) and DMAP (27.9 mg, 0.228 mmol) in CH_2Cl_2 (20.0 mL) under a nitrogen atmosphere was added 4-methylbenzene-1-sulfonyl chloride (1.09 g, 5.71 mmol). The mixture was stirred for 14 h at 25 °C. The reaction mixture was treated with a saturated aqueous solution of $NaHCO_3$ (15 mL) and CH_2Cl_2 (20 mL) and transferred to a 125-mL separatory funnel. The organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2 (25 mL × 2). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated, and the residue was purified by flash column chromatography (hexanes/EtOAc = 6:1) to provide indole **1i** as a white solid; yield: 890 mg (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 8.16–8.10 (m, 1H), 7.99–7.93 (m, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.41–7.27 (m, 4H), 3.93 (s, 3H), 2.36 (s, 3H).

Methyl 1-(phenylsulfonyl)-1*H*-indole-3-carboxylate (1j):[34] Following the general procedure A, methyl 1*H*-indole-3-carboxylate (1.00 g, 5.71 mmol), THF (5.00 mL), DMF (5.00 mL), sodium hydride 60% in oil (274 mg, 6.85 mmol), and benzenesulfonyl chloride (0.729 mL, 5.71 mmol) were used. Flash column chromatography (hexanes/EtOAc = 6:1) provided indole **1j** as a white solid; yield: 1.15 g (64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 8.17–8.10 (m, 1H), 8.00–7.92 (m, 3H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.41–7.31 (m, 2H), 3.93 (s, 3H).

Methyl 1-(*N*,*N*-dimethylsulfamoyl)-1*H*-indole-3-carboxylate (1k): Following the general procedure A, methyl 1*H*-indole-3-carboxylate (5.00 g, 28.5 mmol), THF (10.0 mL), DMF (10.0 mL), 60% sodium hydride in oil (1.37 g, 34.2 mmol), and dimethylsulfamoyl chloride (3.06 mL, 28.5 mmol) were used. Flash column chromatography (hexanes/EtOAc = 6:1) provided indole **1k** as a white solid; yield: 7.20 g (89%); mp 96–98 °C. IR (film): ν = 3140, 2953, 1714, 1392, 1204, 1172 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (dd, J = 5.9, 3.2 Hz, 1H), 8.15 (s, 1H), 7.94 (dd, J = 6.2, 3.0 Hz, 1H), 7.42–7.33 (m, 2H), 3.94 (s, 3H), 2.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.4, 135.6, 133.0, 127.2, 125.1, 124.1, 122.0, 113.7, 111.5, 51.7, 38.6; HR-MS (ESI): m/z = 283.0750, calcd. for $C_{12}H_{15}N_2O_4S$ $[M+H]^+$: 283.0747.

Methyl 1-[(4-nitrophenyl)sulfonyl]-1*H*-indole-3-carboxylate (1l): Following the general procedure A, methyl 1*H*-indole-3-carboxylate (1.00 g, 5.71 mmol), THF (10.0 mL), 60% sodium hydride in oil (320 mg, 7.99 mmol), and 4-nitrobenzene-1-sulfonyl chloride (1.90 g, 8.57 mmol) were used. Crystallization (hexanes/EtOAc) provided indole **1l** as a yellow solid; yield: 1.44 g (70%); mp 211–213 °C. IR

(film): ν = 3105, 1717, 1534, 1404, 1387, 1349, 1201 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.9 Hz, 2H), 8.24 (s, 1H), 8.19–8.09 (m, 3H), 7.96 (d, J = 7.6 Hz, 1H), 7.47–7.34 (m, 2H), 3.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.8, 151.0, 142.9, 134.8, 131.6, 128.5, 128.0, 126.2, 125.2, 124.9, 122.7, 115.2, 113.2, 52.0; HR-MS (ESI): m/z = 361.0485, calcd. for $C_{16}H_{13}N_2O_6S$ $[M+H]^+$: 361.0489.

Methyl 1-(dimethylcarbamoyl)-1*H*-indole-3-carboxylate (1m): Following the general procedure A, methyl 1*H*-indole-3-carboxylate (1.00 g, 5.71 mmol), THF (10.0 mL), 60% sodium hydride in oil (251 mg, 6.28 mmol), and dimethylcarbamic chloride (0.578 mL, 6.28 mmol) were used. Flash column chromatography (hexanes/EtOAc = 2:1) provided indole **1m** as a white solid; yield: 1.23 g (87%); mp 115–117 °C. IR (film): ν = 3138, 3072, 3025, 2956, 2851, 1682, 1209 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23–8.14 (m, 1H), 8.01 (s, 1H), 7.67–7.58 (m, 1H), 7.40–7.29 (m, 2H), 3.93 (s, 3H), 3.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 153.6, 135.8, 132.2, 126.6, 124.5, 123.3, 121.8, 113.4, 110.8, 51.4, 38.4; HR-MS (ESI): m/z = 247.1079, calcd. for $C_{13}H_{15}N_2O_3$ $[M+H]^+$: 247.1077.

3-Nitro-1-tosyl-1*H*-indole (1n): Following the general procedure A, 3-nitro-1*H*-indole (300 mg, 1.85 mmol), DMF (5.00 mL), 60% sodium hydride in oil (88.8 mg, 22.2 mmol), and 4-methylbenzene-1-sulfonyl chloride (423 mg, 2.22 mmol) were used. Flash column chromatography (hexanes/EtOAc = 10:1) provided **1n** as a yellow solid; yield: 444 mg (76%); mp 175–177 °C. IR (film): ν = 3142, 2925, 2855, 1491, 1477, 1383, 1359, 1296 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.28–8.21 (m, 1H), 8.04–7.97 (m, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.52–7.41 (m, 2H), 7.33 (d, J = 8.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.9, 133.8, 133.6, 133.2, 130.6, 128.0, 127.6, 126.9, 126.0, 121.8, 121.3, 113.7, 21.8; HR-MS (ESI): m/z = 317.0590, calcd. for $C_{15}H_{13}N_2O_4S$ $[M+H]^+$: 317.0591.

3-Chloro-5-methoxy-1-(phenylsulfonyl)-1*H*-indole (1o): Following the general procedure A, 3-chloro-5-methoxy-1*H*-indole (970 mg, 5.34 mmol), THF (5.00 mL), DMF (5.00 mL), 60% sodium hydride in oil (256 mg, 6.41 mmol), and benzenesulfonyl chloride (0.68 mL, 5.34 mmol) were used. Flash column chromatography (hexanes/EtOAc = 9:1) provided indole **1o** as a white solid; yield: 1.15 g (67%); mp 142–144 °C. IR (film): ν = 3131, 1479, 1446, 1372, 1216, 1169 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 7.5 Hz, 2H), 7.59–7.49 (m, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.04–6.89 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 137.7, 134.2, 129.5, 129.5, 128.7, 126.9, 123.0, 115.6, 115.0, 114.1, 100.8, 55.8; HR-MS (ESI): m/z = 322.0302, calcd. for $C_{15}H_{13}ClNO_3S$ $[M+H]^+$: 322.0299.

7-(Benzyloxy)-3-chloro-1-(phenylsulfonyl)-1*H*-indole (1p): Following the general procedure A, 7-(benzyloxy)-3-chloro-1*H*-indole (1.15 g, 4.45 mmol), THF (5.00 mL), DMF (5.00 mL), 60% sodium hydride in oil (214 mg, 5.34 mmol), and benzenesulfonyl chloride (0.57 mL, 4.45 mmol) were used. Flash column chromatography (hexanes/EtOAc = 17:1) provided indole **1p** as a light yellow solid; yield: 1.35 g (76%); mp 134–136 °C. IR (film): ν = 3151, 3062, 2937, 2877, 1368, 1341, 1228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.58 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.40–7.35 (m, 3H), 7.33–7.27 (m, 4H), 7.21–7.12 (m, 2H), 6.74 (d, J = 7.4 Hz, 1H), 5.01 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 139.6, 136.1, 133.3, 131.4, 128.9, 128.6, 128.3, 128.0, 127.3, 124.9, 124.7, 123.8, 111.7, 111.6, 108.9, 70.8; HR-MS (ESI): m/z = 398.0612, calcd. for $C_{21}H_{17}ClNO_3S$ $[M+H]^+$: 398.0612.

3-Chloro-1-(phenylsulfonyl)-1*H*-indole-4-carbonitrile (1q): Following the general procedure A, 3-chloro-1*H*-indole-4-carbonitrile (1.01 g, 5.70 mmol), THF (5.00 mL), DMF (5.00 mL), 60% sodium hydride in oil (228 mg, 5.70 mmol), and benzenesulfonyl chloride (0.73 mL, 5.70 mmol) were used. Crystallization (hexanes/EtOAc) provided indole **1q** as a white solid; yield: 1.28 g (71%); mp 119–120 °C. IR (film): ν = 3145, 3125, 2231, 1417, 1379, 732 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.72 (s, 1H), 7.62 (t, J = 8.4 Hz, 2H), 7.57–7.39 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 134.9, 134.3, 130.3, 129.8, 127.5, 127.0, 125.7, 125.4, 118.3, 116.3, 112.6, 103.6; HR-MS (ESI): m/z = 338.9967, calcd. for $C_{15}H_9ClN_2NaO_2S$ $[M+Na]^+$: 338.9965.

3-Chloro-5-nitro-1-(phenylsulfonyl)-1*H*-indole (1r): Following the general procedure A, 3-chloro-5-nitro-1*H*-indole (725 mg, 3.69 mmol), THF (5.00 mL), DMF (5.00 mL), 60% sodium hydride in oil (177 mg, 4.43 mmol), and benzenesulfonyl chloride (0.5 mL, 3.69 mmol) were used. Crystallization (hexanes/EtOAc) provided indole **1r** as a beige solid; yield: 471 mg (38%); mp 199–201 °C. IR (film): ν = 3106, 1525, 1448, 1382, 1346, 1293 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, J = 1.9 Hz, 1H), 8.28 (dd, J = 9.1, 2.1 Hz, 1H), 8.13 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 7.8 Hz, 2H), 7.73 (s, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7, 137.3, 136.8, 135.0, 129.9, 128.6, 127.1, 125.3, 121.1, 116.0, 114.5, 114.3; HR-MS (EI): m/z = 335.9969, calcd. for $C_{14}H_9ClN_2O_4S$ $[M]^+$: 335.9966.

3,6-Dichloro-1-(phenylsulfonyl)-1*H*-indole (1s): Following the general procedure A, 3,6-dichloro-1*H*-indole (1.00 g, 5.38 mmol), THF (10.0 mL), 60% sodium hydride in oil (194 mg, 4.85 mmol), and benzenesulfonyl chloride (0.83 mL, 6.46 mmol) were used. Flash column chromatography (hexanes/EtOAc = 18:1) provided indole **1s** as a white solid; yield: 0.64 g (36%); mp 160–163 °C. IR (film): ν = 3142, 1605, 1581, 1448, 1420, 1372, 1306, 1269 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 1.1 Hz, 1H), 7.92–7.86 (m, 2H), 7.63–7.53 (m, 2H), 7.52–7.43 (m, 3H), 7.31–7.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6, 134.6, 134.4, 132.2, 129.7, 127.1, 127.0, 124.8, 122.9, 120.1, 114.0, 113.9; HR-MS (EI): m/z = 324.9732, calcd. for $C_{14}H_9Cl_2NO_2S$ $[M]^+$: 324.9726.

3-Chloro-1-(phenylsulfonyl)-1*H*-pyrrolo[2,3-*b*]pyridine (1t): Following the general procedure A, 3-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (1.00 g, 6.55 mmol), THF (10 mL), 60% sodium hydride in oil (393 mg, 9.83 mmol), and benzenesulfonyl chloride (1.00 mL, 7.86 mmol) were used. Flash column chromatography (hexanes/EtOAc = 8:1) provided indole **1t** as a white solid; yield: 1.76 g (92%); mp 146–148 °C. IR (film): ν = 3148, 3060, 2360, 2341, 1395, 1381, 1284, 1200 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (dd, J = 4.7, 1.3 Hz, 1H), 8.23–8.16 (m, 2H), 7.88 (dd, J = 7.9, 1.5, 1H), 7.73 (s, 1H), 7.63–7.56 (m, 1H), 7.54–7.47 (m, 2H), 7.30–7.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.2, 145.8, 138.0, 134.4, 129.2, 128.1, 127.8, 122.6, 121.1, 119.5, 110.3; HR-MS (ESI): m/z = 293.0147, calcd. for $C_{13}H_{10}ClN_2O_2S$ $[M+H]^+$: 293.0146.

2-Allyl-1-tosyl-1*H*-indole (2b):[7b] Purification by flash column chromatography (hexanes/EtOAc = 10:1) provided allylated indole **2b** as a yellow oil; yield: 14 mg (11%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 6.9 Hz, 1H), 7.24–7.16 (m, 4H), 6.39 (s, 1H), 6.12–5.97 (m, 1H), 5.25–5.15 (m, 2H), 3.77 (d, J = 6.6 Hz, 2H), 2.34 (s, 3H).

2-Allyl-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide (2c):[33b] Purification by flash column chromatography (hexanes/EtOAc = 6:1) provided allylated indole **2c** as a yellow oil; yield: 16 mg (18%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.5 Hz, 1H), 7.25–7.00 (m, 3H), 6.38 (s, 1H), 6.08–5.80 (m, 1H), 5.26–4.99 (m, 2H), 3.63 (d, J = 6.3 Hz, 2H), 3.01 (br s, 6H).

2-Allyl-3-methyl-1-tosyl-1*H*-indole (2d):[35] Purification by flash column chromatography (hexanes/EtOAc = 19:1) provided allylated indole **2d** as a yellow solid; yield: 44 mg (34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27–8.06 (m, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.43–7.36 (m, 1H), 7.33–7.27 (m, 1H), 7.25–7.19 (m, 1H), 7.15 (d, J = 8.1 Hz, 2H), 5.98 (ddt, J = 17.0, 10.2, 5.8 Hz, 1H), 5.08–4.94 (m, 2H), 3.79 (d, J = 5.8 Hz, 2H), 2.32 (s, 3H), 2.14 (s, 3H).

2-Allyl-3-chloro-1-tosyl-1*H*-indole (2e): Purification by flash column chromatography (hexanes/EtOAc = 18:1) provided allylated indole **2e** as a white solid; yield: 140 mg (quantitative); mp 76–78 °C. IR (film): ν = 3078, 2923, 2854, 1597, 1449, 1372, 1258, 1218 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.39–7.28 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.08–5.92 (m, 1H), 5.17–5.03 (m, 2H), 3.88 (d, J = 5.8 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 135.5, 135.4, 134.2, 133.7, 129.9, 127.8, 126.6, 125.5, 124.2, 118.3, 117.0, 115.1, 114.4, 30.1, 21.6; HR-MS (ESI): m/z = 346.0676, calcd. for $C_{18}H_{17}ClNO_2S$ $[M+H]^+$: 346.0663.

2-Allyl-3-chloro-1-(phenylsulfonyl)-1*H*-indole (2f): Purification by flash column chromatography (hexanes/EtOAc = 15:1) provided allylated indole **2f** as a yellow oil; yield: 129 mg (97%). IR (film): ν = 3069, 1449, 1429, 1375, 1310, 1295, 1258, 1221 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 7.3 Hz, 2H), 7.57–7.46 (m, 2H), 7.44–7.28 (m, 4H), 6.11–5.90 (m, 1H), 5.20–5.02 (m, 2H), 3.90 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 135.4, 134.2, 134.1, 133.6, 129.3, 127.8, 126.5, 125.6, 124.3, 118.4, 117.1, 115.1, 114.6, 30.1; HR-MS (EI): m/z = 331.0434, calcd. for $C_{17}H_{14}ClNO_2S$ $[M]^+$: 331.0428.

2-Allyl-3-chloro-*N*,*N*-dimethyl-1*H*-indole-1-sulfonamide (2g): Purification by flash column chromatography (hexanes/EtOAc = 18:1) provided allylated indole **2g** as a yellow oil; yield: 126 mg (quantitative). IR (film): ν = 3079, 2924, 2854, 1449, 1414, 1372, 1261, 1223 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.00 (m, 1H), 7.62–7.53 (m, 1H), 7.39–7.28 (m, 2H), 6.07–5.91 (m, 1H), 5.17–5.06 (m, 2H), 3.87 (d, J = 5.8 Hz, 2H), 2.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.7, 134.4, 133.7, 127.0, 125.0, 123.6, 118.2, 116.7, 115.0, 112.6, 38.4, 30.0; HR-MS (EI): m/z = 298.0542, calcd. for $C_{13}H_{15}ClN_2O_2S$ $[M]^+$: 298.0537.

Methyl 2-allyl-1-methyl-1*H*-indole-3-carboxylate (2h): Purification by flash column chromatography (hexanes/EtOAc = 8:1) provided allylated indole **2h** as a yellow solid; yield: 65 mg (71%); mp 81–82 °C. IR (film): ν = 3075, 2996, 2947, 2841, 1694, 1533, 1213 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19–8.10 (m, 1H), 7.37–7.27 (m, 2H), 7.25–7.20 (m, 1H), 6.06–5.89 (m, 1H), 5.11 (dd, J = 10.2, 1.4 Hz, 1H), 4.98 (dd, J = 17.2, 1.4 Hz, 1H), 4.07 (d, J = 5.7 Hz, 2H), 3.93 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 146.0, 136.8, 133.9, 126.5, 122.4, 121.9, 121.8, 116.6, 109.4, 104.1, 50.9, 29.9, 29.8; HR-MS (ESI): m/z = 230.1179, calcd. for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1176.

Methyl 2-allyl-1-tosyl-1*H*-indole-3-carboxylate (2i): Purification by flash column chromatography (hexanes/EtOAc = 8:1) provided allylated indole **2i** as a yellow solid; yield: 109 mg (74%); mp 79–81 °C. IR (film): ν = 2951, 1712, 1451, 1382, 1233, 1175, 1090 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28–8.13 (m, 1H), 8.13–8.00 (m, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.38–7.28 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.03 (ddt, J = 17.2, 10.1, 6.0 Hz, 1H), 5.19–5.03 (m, 2H), 4.33 (d, J = 6.0 Hz, 2H), 3.93 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.0, 146.7, 145.5, 135.9, 135.8, 134.7, 130.0, 127.3, 126.7, 125.0, 124.4, 121.9, 116.9, 114.6, 112.0, 51.5, 30.6, 21.6; HR-MS (ESI): m/z = 370.1102, calcd. for $C_{20}H_{20}NO_4S$ $[M+H]^+$: 370.1108.

Methyl 2-allyl-1-(phenylsulfonyl)-1*H*-indole-3-carboxylate (2j): Purification by flash column chromatography (hexanes/EtOAc = 8:1) provided allylated indole **2j** as a yellow solid; yield: 108 mg (76%); mp 92–94 °C. IR (film): ν = 3081, 3007, 2951, 1713, 1449, 1383, 1233 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27–8.17 (m, 1H), 8.14–8.04 (m, 1H), 7.82 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.38–7.28 (m, 2H), 6.02 (ddt, J = 17.2, 10.1, 6.0 Hz, 1H), 5.21–5.00 (m, 2H), 4.33 (d, J = 6.0 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.9, 146.6, 138.7, 135.9, 134.5, 134.3, 129.4, 127.2, 126.6, 125.1, 124.5, 122.0, 116.9, 114.6, 112.2, 51.6, 30.6; HR-MS (ESI): m/z = 356.0946, calcd. for $C_{19}H_{18}NO_4S$ $[M+H]^+$: 356.0951.

Methyl 2-allyl-1-(*N*,*N*-dimethylsulfamoyl)-1*H*-indole-3-carboxylate (2k): Purification by flash column chromatography (hexanes/EtOAc = 7:1) provided allylated indole **2k** as a yellow solid; yield: 85 mg (66%); mp 62–65 °C. IR (film): ν = 3082, 3055, 2951, 2852, 1699, 1556, 1451 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22–8.09 (m, 1H), 8.09–8.00 (m, 1H), 7.41–7.28 (m, 2H), 6.11–5.90 (m, 1H), 5.18–4.99 (m, 2H), 4.30 (d, J = 5.8 Hz, 2H), 3.97 (s, 3H), 2.84 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 147.0, 136.3, 134.7, 126.7, 124.7, 124.1, 121.8, 116.4, 114.6, 110.7, 51.5, 38.3, 30.6; HR-MS (ESI): m/z = 323.1062, calcd. for $C_{15}H_{19}N_2O_4S$ $[M+H]^+$: 323.1060.

Methyl 2-allyl-1-[(4-nitrophenyl)sulfonyl]-1*H*-indole-3-carboxylate (2l): Purification by flash column chromatography (hexanes/EtOAc = 7:1) provided allylated indole **2l** as a yellow solid; yield: 101 mg (63%); mp 131–134 °C. IR (film): ν = 3106, 2952, 2924, 2853, 1713, 1534, 1387 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 9.0 Hz, 2H), 8.20–8.12 (m, 1H), 8.12–8.05 (m, 1H), 7.98 (d, J = 9.0 Hz, 2H), 7.42–7.30 (m, 2H), 6.01 (ddt, J = 17.1, 10.2, 6.0 Hz, 1H), 5.12 (dd, J = 17.1, 1.5 Hz, 1H), 5.08 (dd, J = 10.1, 1.43 Hz, 1H), 4.33 (d, J = 6.0 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 150.7, 146.3, 143.8, 135.7, 134.3, 128.1, 127.4, 125.7, 125.2, 124.7, 122.4, 117.4, 114.4, 113.4, 51.8, 30.5; HR-MS (ESI): m/z = 399.0668, calcd. for $C_{19}H_{15}N_2O_6S$ $[M-H]^-$: 399.0656.

Methyl 2-allyl-1-(dimethylcarbamoyl)-1*H*-indole-3-carboxylate (2m): Purification by flash column chromatography (hexanes/EtOAc = 6:1) provided allylated indole **2m** as a yellow solid; yield: 70 mg (61%); mp 84–85 °C. IR (film):

ν = 3079, 2949, 2854, 1697, 1456, 1386, 1271 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.23–8.05 (m, 1H), 7.37–7.13 (m, 3H), 6.04–5.78 (m, 1H), 5.21–5.02 (m, 2H), 4.33 (d, J = 12.9 Hz, 1H), 3.95 (s, 3H), 3.93–3.83 (m, 1H), 3.21 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 152.6, 145.0, 134.4, 133.9, 126.2, 123.7, 122.7, 122.1, 116.9, 110.4, 106.7, 51.1, 38.4, 36.8, 30.1; HR-MS (ESI): m/z = 287.1391, calcd. for $C_{16}H_{19}N_2O_3$ $[M+H]^+$: 287.1390.

2-Allyl-3-chloro-5-methoxy-1-(phenylsulfonyl)-1*H*-indole (2o): Purification by flash column chromatography (hexanes/EtOAc = 16:1) provided allylated indole **2o** as a yellow oil; yield: 124 mg (86%); IR (film): ν = 3080, 3005, 2937, 2835, 1615, 1479, 1448, 1372 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.0 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.00–6.87 (m, 2H), 6.09–5.87 (m, 1H), 5.17–5.04 (m, 2H), 3.90–3.81 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 138.4, 134.8, 134.0, 133.6, 129.9, 129.3, 128.9, 126.5, 117.1, 116.3, 114.7, 114.6, 100.4, 55.8, 30.2; HR-MS (EI): m/z = 361.0536, calcd. for $C_{18}H_{16}ClNO_3S$ $[M]^+$: 361.0534.

2-Allyl-7-(benzyloxy)-3-chloro-1-(phenylsulfonyl)-1*H*-indole (2p): Purification by flash column chromatography (hexanes/EtOAc = 18:1) provided allylated indole **2p** as a yellow solid; yield: 141 mg (80%); mp 98–99 °C. IR (film): ν = 3085, 3068, 3035, 2940, 1494, 1352, 1271 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.4 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.38–7.27 (m, 5H), 7.25–7.18 (m, 2H), 7.18–7.11 (m, 2H), 6.76–6.65 (m, 1H), 6.16–5.94 (m, 1H), 5.25–5.10 (m, 2H), 4.92 (s, 2H), 4.02 (d, J = 6.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7, 141.2, 137.3, 136.3, 134.3, 132.7, 130.5, 128.6, 128.5, 127.9, 127.5, 126.2, 125.5, 125.1, 117.2, 114.2, 111.1, 109.8, 70.7, 31.0; HR-MS (ESI): m/z = 438.0927, calcd. for $C_{24}H_{21}ClNO_3S$ $[M+H]^+$: 438.0925.

2-Allyl-3-chloro-1-(phenylsulfonyl)-1*H*-indole-4-carbonitrile (2q): Purification by flash column chromatography (hexanes/EtOAc = 9:1) provided allylated indole **2q** as a yellow oil; yield: 127 mg (89%); IR (film): ν = 3082, 2227, 1448, 1423, 1380, 1359, 1262, 1240 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.66–7.55 (m, 2H), 7.50–7.37 (m, 3H), 6.04–5.84 (m, 1H), 5.18–5.05 (m, 2H), 3.92 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0, 137.8, 135.6, 134.7, 132.6, 130.5, 129.7, 127.2, 126.6, 125.1, 119.4, 117.8, 116.7, 112.8, 102.6, 30.0; HR-MS (EI): m/z = 356.0388, calcd. for $C_{18}H_{13}ClN_2O_2S$ $[M]^+$: 356.0381.

2-Allyl-3-chloro-5-nitro-1-(phenylsulfonyl)-1*H*-indole (2r): Purification by flash column chromatography (hexanes/EtOAc = 10:1) provided allylated indole **2r** as a yellow solid; yield: 116 mg (77%); mp 121–124 °C. IR (film): ν = 3087, 1524, 1447, 1382, 1345, 1268 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.43 (d, J = 2.2 Hz, 1H), 8.33 (d, J = 9.2 Hz, 1H), 8.24 (dd, J = 9.3, 2.2 Hz, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 6.03–5.87 (m, 1H), 5.15–5.01 (m, 2H), 3.90 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7, 138.1, 138.0, 137.6, 134.8, 132.6, 129.8, 127.9, 126.7, 120.5, 117.8, 115.4, 114.8, 114.4, 30.1; HR-MS (ESI): m/z = 394.0638, calcd. for $C_{17}H_{17}ClN_3O_4S$ $[M+NH_4]^+$: 394.0623.

2-Allyl-3,6-dichloro-1-(phenylsulfonyl)-1*H*-indole (2s): Purification by flash column chromatography (hexanes/EtOAc = 19:1) provided allylated indole **2s** as a white solid; yield: 130 mg (89%); mp 98–101 °C. IR (film): ν = 3078, 2925, 2853, 1448, 1420, 1378, 1291, 1277 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, J = 1.0 Hz, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.49–7.39 (m, 3H), 7.33–7.26 (m, 1H), 6.05–5.85 (m, 1H), 5.13–5.04 (m, 2H), 3.84 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 135.6, 134.7, 134.3, 133.1, 131.5, 129.5, 126.5, 126.2, 124.9, 119.1, 117.2, 115.2, 114.0, 30.0; HR-MS (EI): m/z = 365.0045, calcd. for $C_{17}H_{13}Cl_2NO_2S$ $[M]^+$: 365.0039.

2-Allyl-3-chloro-1-(phenylsulfonyl)-1*H*-pyrrolo[2,3-*b*]pyridine (2t): Purification by flash column chromatography (hexanes/EtOAc = 9:1) provided allylated indole **2t** as a yellow solid; yield: 119 mg (89%); mp 93–95 °C. IR (film): ν = 3070, 2924, 1582, 1449, 1398, 1380, 1331, 1276 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.43 (dd, J = 4.8, 3.2 Hz, 1H), 8.22–8.13 (m, 2H), 7.78 (dd, J = 7.8, 1.6 Hz, 1H), 7.59–7.51 (m, 1H), 7.49–7.41 (m, 2H), 7.25–7.18 (m, 1H), 6.17–6.02 (m, 1H), 5.20–5.09 (m, 2H), 4.05–3.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.9, 145.2, 138.7, 135.3, 134.2, 133.7, 128.9, 128.2, 126.6, 120.0, 119.5, 117.3, 110.5, 29.8; HR-MS (ESI): m/z = 333.0460, calcd. for $C_{16}H_{14}ClN_2O_2S$ $[M+H]^+$: 333.0459.

1-Allyl-3-nitro-1*H*-indole (3): Purification by flash column chromatography (hexanes/EtOAc = 7:1) provided *N*-allylated indole **3** as a yellow solid; yield: 53 mg (52%); mp 82–85 °C. IR (film): ν = 3132, 1484, 1458, 1445, 1371, 1351, 1307, 1210 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.33–8.25 (m, 1H), 8.11 (s, 1H), 7.44–7.33 (m, 3H), 6.09–5.94 (m, 1H), 5.37 (d, J = 10.2 Hz, 1H), 5.24 (d, J = 17.1 Hz, 1H), 4.79 (d, J = 5.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.3, 131.1, 130.5, 124.7, 124.4, 121.1, 121.0, 120.0, 110.9, 110.1, 49.9; HR-MS (ESI): m/z = 203.0815, calcd. for $C_{11}H_{11}N_2O_2$ $[M+H]^+$: 203.0815.

3-Chloro-2-cinnamyl-1-tosyl-1*H*-indole (4a): Purification by flash column chromatography (hexanes/EtOAc = 12:1) provided allylated indole **4a** as a yellow solid; yield: 160 mg (95%); mp 104–107 °C. IR (film): ν = 3056, 3028, 2924, 1449, 1372, 1178, 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.55–7.47 (m, 1H), 7.46–7.27 (m, 5H), 7.24–7.15 (m, 2H), 7.09 (d, J = 8.3 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 6.28 (dt, J = 15.9, 6.1 Hz, 1H), 4.04 (d, J = 6.0 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 137.1, 135.6, 135.5, 134.3, 132.1, 129.9, 128.5, 127.7, 127.3, 126.6, 126.3, 125.6, 125.3, 124.2, 118.4, 115.1, 114.3, 29.2, 21.6; HR-MS (ESI): m/z = 439.1246, calcd. for $C_{24}H_{24}ClN_2O_2S$ $[M+NH_4]^+$: 439.1242.

3-Chloro-2-[3-(4-chlorophenyl)allyl]-1-tosyl-1*H*-indole (4b): Purification by flash column chromatography (hexanes/EtOAc = 18:1) provided allylated indole **4b** as a yellow solid; yield: 119 mg (65%); mp 98–101 °C. IR (film): ν = 3053, 2980, 2924, 1491, 1449, 1371, 1249 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.55–7.47 (m, 1H), 7.40–7.29 (m, 2H), 7.25–7.17 (m, 4H), 7.10 (d, J = 8.0 Hz, 2H), 6.37 (d, J = 16.1 Hz, 1H), 6.27 (dt, J = 15.9, 5.5 Hz, 1H), 4.02 (d, J = 5.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 135.62, 135.59, 135.5, 134.0, 132.9, 130.9, 129.9, 128.6, 127.7, 127.5, 126.6, 126.1, 125.7, 124.2, 118.4, 115.1, 114.4, 29.2, 21.6; HR-MS (ESI): m/z = 473.0856, calcd. for $C_{24}H_{23}Cl_2N2O_2S$ $[M+NH_4]^+$: 473.0852.

3-Chloro-2-[3-(2-methoxyphenyl)allyl]-1-tosyl-1*H*-indole (4c): Purification by flash column chromatography (hexanes/EtOAc = 8:1) provided allylated indole **4c** as a yellow solid;

yield: 167 mg (92%); mp 74–76 °C. IR (film): ν = 3051, 2936, 2836, 1597, 1488, 1454, 1373 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.29–8.14 (m, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.55–7.47 (m, 1H), 7.40–7.28 (m, 3H), 7.22–7.08 (m, 3H), 6.92–6.79 (m, 3H), 6.29 (dt, J = 16.0, 6.6 Hz, 1H), 4.06 (d, J = 6.6 Hz, 2H), 3.82 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 145.1, 135.6, 135.4, 134.6, 129.8, 128.4, 127.8, 127.1, 126.8, 126.6, 126.1, 125.9, 125.4, 124.1, 120.6, 118.3, 115.1, 114.1, 110.8, 55.5, 29.8, 21.5; HR-MS (ESI): m/z = 469.1367, calcd. for $C_{25}H_{26}ClN_2O_3S$ $[M+NH_4]^+$: 469.1347.

3-Chloro-2-[3-(3-methoxyphenyl)allyl]-1-tosyl-1*H*-indole (4d): Purification by flash column chromatography (hexanes/EtOAc = 8:1) provided allylated indole **4d** as a yellow solid; yield: 125 mg (69%); mp 127–129 °C. IR (film): ν = 3031, 2933, 2834, 2359, 1372, 1308 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 7.3 Hz, 1H), 7.40–7.29 (m, 2H), 7.18 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 7.2 Hz, 1H), 6.81–6.71 (m, 2H), 6.39 (d, J = 16.1 Hz, 1H), 6.33–6.21 (m, 1H), 4.03 (d, J = 5.8 Hz, 2H), 3.79 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 145.2, 138.6, 135.6, 135.5, 134.2, 132.1, 130.0, 129.5, 127.8, 126.7, 125.64, 125.59, 124.2, 119.0, 118.4, 115.2, 114.4, 113.2, 111.4, 55.3, 29.2, 21.6; HR-MS (ESI): m/z = 452.1086, calcd. for $C_{25}H_{23}ClNO_3S$ $[M+H]^+$: 452.1082.

3-Chloro-2-[3-(4-methoxyphenyl)allyl]-1-tosyl-1*H*-indole (4e): Purification by flash column chromatography (hexanes/EtOAc = 17:1) provided allylated indole **4e** as a yellow oil; yield: 126 mg (70%). IR (film): ν = 3033, 3003, 2956, 2933, 2836, 1373 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 7.1 Hz, 1H), 7.39–7.29 (m, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.38 (d, J = 15.9 Hz, 1H), 6.23–6.09 (m, 1H), 4.02 (d, J = 6.1 Hz, 2H), 3.80 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 145.1, 135.6, 135.4, 134.6, 131.5, 129.93, 129.89, 127.8, 127.4, 126.6, 125.5, 124.2, 123.1, 118.3, 115.1, 114.1, 113.9, 55.3, 29.2, 21.6; HR-MS (ESI): m/z = 452.1100, calcd. for $C_{25}H_{23}ClNO_3S$ $[M+H]^+$: 452.1082.

3-Chloro-2-cinnamyl-1-(phenylsulfonyl)-1*H*-pyrrolo[2,3-*b*]pyridine (4f): Purification by flash column chromatography (hexanes/EtOAc = 6:1) provided allylated indole **4f** as a yellow solid; yield: 136 mg (83%); mp 118–120 °C. IR (film): ν = 3059, 2360, 2341, 1398, 1380 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.8 Hz, 1H), 8.18 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.37–7.28 (m, 6H), 7.25–7.19 (m, 2H), 6.52–6.37 (m, 2H), 4.18 (d, J = 4.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 145.3, 138.8, 137.0, 135.6, 134.1, 132.5, 128.9, 128.6, 128.4, 127.6, 126.7, 126.4, 125.5, 120.1, 119.6, 110.5, 29.0; HR-MS (ESI): m/z = 409.0788, calcd. for $C_{22}H_{18}ClN_2O_2S$ $[M+H]^+$: 409.0772.

5-Methylene-7-tosyl-2,3,4,4a,5,6,7,11c-octahydro-1*H*-1,4-methanobenzo[*c*]carbazole (5): Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided carbazole **5** as a yellow oil; yield: 76 mg (94%). IR (film): ν = 3068, 2953, 2871, 1452, 1369, 1217 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, J = 6.8 Hz, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.40 (d, J = 6.9 Hz, 1H), 7.25–7.14 (m, 4H), 5.01–4.84 (m, 2H), 3.91 (d, J = 18.6 Hz, 1H), 3.56 (d, J = 18.4 Hz, 1H), 2.97 (d, J = 7.8 Hz, 1H), 2.56 (d, J = 8.2 Hz, 1H), 2.37–2.26 (m, 5H), 2.14–2.07 (m, 1H), 1.68–1.61 (m, 1H), 1.49–1.41 (m, 2H), 1.10 (d, J = 10.3 Hz, 1H), 0.92 (d, J = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 144.7, 136.9, 135.9, 134.7, 129.9, 129.8, 126.4, 124.1, 123.5, 121.8, 118.6, 114.9, 111.6, 49.4, 44.3, 43.7, 42.2, 35.0, 31.9, 31.5, 28.2, 21.7; HR-MS (ESI): m/z = 404.1689, calcd. for $C_{25}H_{26}NO_2S$ $[M+H]^+$: 404.1679.

2-Methyl-9*H*-carbazole (6a):[36] The reaction was carried out with 2-allyl-3-chloroindole **2e**. Purification by flash column chromatography (hexanes/EtOAc = 19:1) provided carbazole **6a** as a yellow solid; yield: 28 mg (77%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.4 Hz, 1H), 7.99–7.86 (m, 2H), 7.45–7.32 (m, 2H), 7.24–7.17 (m, 2H), 7.06 (d, J = 7.6 Hz, 1H), 2.53 (s, 3H).

6-Methoxy-2-methyl-9*H*-carbazole (6b):[37] The reaction was carried out with 2-allyl-3-chloroindole **2o**. Purification by flash column chromatography (hexanes/EtOAc = 12:1) provided carbazole **6b** as a yellow solid; yield: 34 mg (80%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.0 Hz, 1H), 7.77 (br s, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 8.7 Hz, 1H), 7.14 (s, 1H), 7.09–6.99 (m, 2H), 3.94 (s, 3H), 2.52 (s, 3H).

1-(Benzyloxy)-7-methyl-9*H*-carbazole (6c): The reaction was carried out with 2-allyl-3-chloroindole **2p**. Purification by flash column chromatography (hexanes/EtOAc = 18:1) provided carbazole **6c** as a yellow solid; yield: 41 mg (71%); mp 114–115 °C. IR (film): ν = 3416, 3034, 2915, 2868, 1578, 1452, 1261, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (br s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.58–7.49 (m, 2H), 7.48–7.36 (m, 3H), 7.22 (s, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 5.26 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9, 139.7, 137.1, 136.0, 129.9, 128.8, 128.3, 128.1, 124.7, 121.4, 121.1, 120.3, 119.7, 113.0, 111.1, 106.9, 70.5, 22.2; HR-MS (ESI): m/z = 288.1388, calcd. for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1383.

7-Methyl-9*H*-carbazole-4-carbonitrile (6d): The reaction was carried out with 2-allyl-3-chloroindole **2q**. Purification by flash column chromatography (hexanes/EtOAc = 6:1) provided carbazole **6d** as a yellow solid; yield: 23 mg (56%); mp 134–136 °C. IR (film): ν = 3332, 2921, 2854, 2219, 1438, 1325 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.43 (d, J = 8.1 Hz, 1H), 8.25 (br s, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.31–7.26 (m, 1H), 7.15 (d, J = 8.1 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.6, 139.3, 138.4, 124.9, 124.5, 123.9, 122.2, 121.5, 119.1, 118.9, 115.2, 111.1, 103.4, 22.3; HR-MS (EI) : m/z = 206.0845, calcd. for $C_{14}H_{10}N_2$ $[M]^+$: 206.0844.

7-Methyl-9*H*-pyrido[2,3-*b*]indole (6e):[38] The reaction was carried out with 2-allyl-3-chloroindole **2t**. Purification by flash column chromatography (hexanes/EtOAc = 1:1) provided carbazole **6e** as a yellow solid; yield: 26 mg (71%). ^1H NMR (300 MHz, DMSO-d_6): δ = 11.68 (s, 1H), 8.51–8.30 (m, 2H), 8.01 (d, J = 6.4 Hz, 1H), 7.30 (s, 1H), 7.22–7.11 (m, 1H), 7.04 (d, J = 6.9 Hz, 1H), 2.47 (s, 3H).

2-Benzyl-9*H*-carbazole (6f): The reaction was carried out with 2-allyl-3-chloroindole **4a**. Purification by flash column chromatography (hexanes/EtOAc = 18:1) provided carbazole **6f** as a yellow solid; yield: 32 mg (62%); mp 189–190 °C. IR (film): ν = 3398, 3022, 2921, 1462, 1443, 1343 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 7.7 Hz, 1H), 8.01–7.85 (m, 2H), 7.42–7.36 (m, 2H), 7.34–

7.28 (m, 2H), 7.26–7.16 (m, 5H), 7.11 (d, J=7.9 Hz, 1H), 4.16 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ=141.9, 140.2, 139.9, 139.1, 128.9, 128.5, 126.0, 125.3, 122.5, 120.7, 120.2, 120.0, 119.9, 118.6, 111.0, 110.9, 41.8; HR-MS (ESI): m/z=258.1283, calcd. for $C_{19}H_{16}N$ $[M+H]^+$: 258.1277.

2-(2-Methoxybenzyl)-9*H*-carbazole (6g): The reaction was carried out with 2-allyl-3-chloroindole **4c**. Purification by flash column chromatography (hexanes/EtOAc=10:1) provided carbazole **6g** as a yellow solid; yield: 27 mg (47%); mp 148–149 °C. IR (film): ν=3410, 2360, 1491, 1460, 1440, 1242 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.04 (d, J=7.7 Hz, 1H), 7.98 (d, J=7.9 Hz, 1H), 7.85 (br s, 1H), 7.43–7.33 (m, 2H), 7.26–7.18 (m, 3H), 7.17–7.10 (m, 2H), 6.96–6.88 (m, 2H), 4.16 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.4, 140.0, 139.6, 139.3, 130.5, 130.1, 127.5, 125.4, 123.4, 121.5, 121.0, 120.6, 120.2, 120.1, 119.4, 110.9, 110.6, 110.5, 55.5, 36.3; HR-MS (ESI): m/z=288.1378, calcd. for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1383.

2-(3-Methoxybenzyl)-9*H*-carbazole (6h): The reaction was carried out with 2-allyl-3-chloroindole **4d**. Purification by flash column chromatography (hexanes/EtOAc=16:1) provided carbazole **6h** as a yellow solid; yield: 30 mg (52%); mp 172–174 °C. IR (film): ν=3405, 2936, 2360, 1595, 1461, 1441 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.05 (d, J=7.7 Hz, 1H), 7.99 (d, J=7.9 Hz, 1H), 7.86 (br s, 1H), 7.44–7.34 (m, 2H), 7.29–7.21 (m, 2H), 7.17 (s, 1H), 7.12 (d, J=8.0 Hz, 1H), 6.91–6.75 (m, 3H), 4.13 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=159.8, 143.2, 140.0, 139.7, 139.2, 129.6, 125.6, 123.4, 121.7, 121.6, 121.0, 120.3, 120.2, 119.5, 114.9, 111.4, 110.9, 110.6, 55.3, 42.5; HR-MS (ESI): m/z=288.1386, calcd. for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1383.

2-(4-Methoxybenzyl)-9*H*-carbazole (6i): The reaction was carried out with 2-allyl-3-chloroindole **4e**. Purification by flash column chromatography (hexanes/EtOAc=7:1) provided carbazole **6i** as a yellow solid; yield: 30 mg (52%); mp 199–200 °C. IR (film): ν=3397, 2360, 1609, 1511, 1461, 1444 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.03 (d, J=7.8 Hz, 1H), 8.00–7.91 (m, 2H), 7.42–7.36 (m, 2H), 7.23–7.17 (m, 3H), 7.15 (s, 1H), 7.09 (d, J=8.0 Hz, 1H), 6.84 (d, J=8.6 Hz, 2H), 4.10 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ=157.5, 140.1, 139.8, 139.5, 133.7, 129.8, 125.1, 122.4, 120.5, 120.0, 119.9, 119.7, 118.5, 113.8, 110.9, 110.7, 55.0, 40.8; HR-MS (ESI): m/z=288.1390, calcd. for $C_{20}H_{18}NO$ $[M+H]^+$: 288.1383.

3,4-Diethyl-2-methyl-9-tosyl-9*H*-carbazole (7a): To an 8-mL glass vial equipped with a magnetic stir bar were sequentially added Cs_2CO_3 (130 mg, 0.40 mmol), **2e** (69.2 mg, 0.20 mmol), hex-3-yne (182 µL, 1.6 mmol), 1,4-dioxane (1.00 mL, 0.20 M), $Pd(OAc)_2$ (4.50 mg, 0.020 mmol) and P(t-Bu)$_3$HBF$_4$ (12.8 mg, 0.044 mmol). The reaction mixture was purged with nitrogen through a Teflon-lined cap. Then, the cap was replaced with a new Teflon-lined solid cap. The reaction vial was moved to a preheated reaction block (130 °C). After stirring for 20 h, the reaction mixture was cooled to 25 °C and concentrated. The residue was purified by flash column chromatography (hexanes/EtOAc=19:1) to provide carbazole **7a** as a white solid; yield: 69 mg (88%); mp 179–182 °C. IR (film): ν=2968, 2931, 2872, 1442, 1368, 1174 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.36 (d, J=8.2 Hz, 1H), 8.06 (s, 1H), 7.98 (d, J=7.7 Hz, 1H), 7.71 (d, J=8.2 Hz, 2H), 7.43 (t, J=7.8 Hz, 1H), 7.34 (t, J=7.2 Hz, 1H), 7.11 (d, J=8.1 Hz, 2H), 3.15 (q, J=7.5 Hz, 2H), 2.78 (q, J=7.5 Hz, 2H), 2.53 (s, 3H), 2.27 (s, 3H), 1.31 (t, J=7.5 Hz, 3H), 1.19 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=144.7, 138.5, 137.13, 137.07, 136.3, 136.2, 135.3, 129.7, 126.8, 126.6, 126.1, 123.8, 122.4, 122.3, 114.9, 114.2, 22.8, 21.8, 21.6, 21.4, 15.0, 14.3; HR-MS (ESI): m/z=392.1688, calcd. for $C_{24}H_{26}NO_2S$ $[M+H]^+$: 392.1679.

2-Methyl-3,4-diphenyl-9-tosyl-9*H*-carbazole (7b): Following the procedure to prepare **7a**, Cs_2CO_3 (130 mg, 0.40 mmol), **2e** (69.2 mg, 0.20 mmol), 1,2-diphenylethyne (285 mg, 1.6 mmol), 1,4-dioxane (1.00 mL, 0.20 M), $Pd(OAc)_2$ (4.50 mg, 0.020 mmol) and P(t-Bu)$_3$HBF$_4$ (12.8 mg, 0.044 mmol) were used. Purification by flash column chromatography (hexanes/EtOAc=19:1) provided carbazole **7b** as a white solid; yield: 64 mg (66%); mp 254–256 °C. IR (film): ν=3055, 1592, 1443, 1371, 1230, 1175 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.35–8.25 (m, 2H), 7.82 (d, J=8.3 Hz, 2H), 7.33 (t, J=7.8 Hz, 1H), 7.23–7.05 (m, 10H), 7.01 (d, J=6.5 Hz, 2H), 6.95 (t, J=7.6 Hz, 1H), 6.45 (d, J=7.9 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=145.0, 139.7, 139.1, 138.6, 137.8, 137.6, 136.14, 136.12, 135.4, 130.4, 129.9, 128.2, 127.7, 127.1, 126.8, 126.60, 126.56, 126.3, 123.4, 122.4, 122.0, 114.8, 114.6, 22.5, 21.7; HR-MS (ESI): m/z=488.1671, calcd. for $C_{32}H_{26}NO_2S$ $[M+H]^+$: 488.1679.

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