Total Syntheses of Carazostatin, Hyellazole, and Carbazoquinocins B−F

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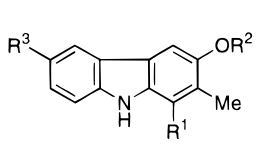
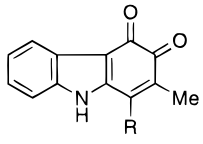
Total syntheses of carazostatin (**1**), hyellazole (**2a**), and carbazoquinocins B−F (**3b**−**f**) have been completed. The cross-coupling reaction between 3-iodoindole **8** and vinylstannane **11b** gave the 3-alkenylindole **7**. Treatment of **7** with ethynylmagnesium bromide, followed by etherification of the resulting alcohol **12** with MOMCl, yielded the 3-alkenyl-2-propargylindole **6**. The compound **6** was treated with *t*-BuOK in *t*-BuOH at 90 °C to obtain the desired carbazoles **4** together with the *N*-deprotected carbazole **13** through an allene-mediated electrocyclic reaction. The carbazole **13a**, derived from **4a** or **4c**, was converted into the triflate **24** in two steps. The triflate **24** was subjected to the Suzuki cross-coupling reaction with either 9-heptyl-9-BBN or phenylboronic acid in the presence of a palladium catalyst to produce the 1-heptylcarbazole **25a** and the 1-phenylcarbazole **25b**. Cleavage of the ether bond of **25a** yielded carazostatin (**1**). Cleavage of the ether bond of **25b** followed by *O*-methylation gave hyellazole (**2a**). Oxidation of carazostatin (**1**) with benzene seleninic anhydride afforded carbazoquinocin C (**3c**). In a similar way, carbazoquinocins B and D−F (**3b,d**−**f**) were synthesized, respectively.

Since 1979, new highly substituted carbazole alkaloids have been found by several groups in different terrestrial plants.[1] Hyellazoles (**2**) were isolated from blue-green algae *Hyella caespitosa* by Moore, representing the first carbazole alkaloids of marine origin.[2,3] Carazostatin (**1**), a free radical scavenger, was isolated from *Streptomyces chromofuscus* by Kato in 1989.[4,5] Carbazoquinocins A−F (**3**), found in *Streptomyces violaceus* 2448-SVT2 by Seto in 1995, have the *o*-quinone structure and possess antioxidation properties.[6,7] These novel alkaloids attracted considerable interest among synthetic organic chemists because of their potent biological activities.[8]



1: R^1=*n*-C_7H_{15}, R^2=R^3=H
2a: R^1=Ph, R^2=Me, R^3=H
2b: R^1=Ph, R^2=Me, R^3=Cl



3a: R=$(CH_2)_2CHMeCH_2Me$
3b: R=$(CH_2)_4CHMe_2$
3c: R=$(CH_2)_6Me$
3d: R=$(CH_2)_4CHMeCH_2Me$
3e: R=$(CH_2)_5CHMe_2$
3f: R=$(CH_2)_6CHMe_2$

We are currently interested in the synthesis of heteroaromatic compounds containing a nitrogen atom by thermal electrocyclic reactions[9] of either conjugated hexatriene or monoazahexatriene systems including one double bond of an aromatic or heteroaromatic portion.[8g,10]

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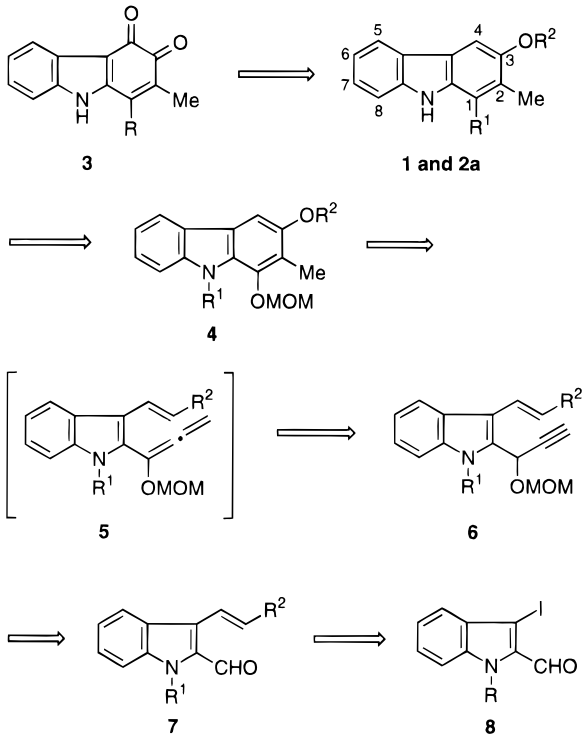
S0022-3263(96)02038-5 CCC: $14.00

Scheme 1



In the course of our study to develop a more efficient strategy for synthesizing these carbazole alkaloids than the previous synthesis of hyellazoles by the thermal electrocyclic reaction of the 2,3-bisalkenylindoles,[3a,b] we found that these 3-oxygenated carbazole alkaloids have a methyl group at the 2-position. On the basis of this finding, we envisaged that an electrocyclic reaction of an allene intermediate **5**, possessing an appropriate functional group in order to introduce an alkyl or aryl group to the 1-position of carbazole as depicted in retrosynthetic Scheme 1, might be more reactive without using an oxidative agent than the reaction of the 2,3-bisalkenylindole system for producing these alkaloids. The 3-alkenyl-2-propargylindole **6** was selected as a precursor of allene intermediate **5**. It would be derived from 3-iodoindole **8** in several steps, and then carbazoquinocines **3** would be obtained from carazostatin (**1**) and its related compounds. In this paper, we describe total synthesis of carazostatin (**1**), hyellazole (**2a**), and carbazoquinocins B−F (**3b**−**f**) together with details of the preliminary report.[11]

For the synthesis of the precursor 3-alkenyl-2-propargylindole **6**, 3-iodoindole-2-carboxaldehyde (**10**) (Scheme 2), prepared from 2-formylindole (**9**) according to the reported procedure[12] as the starting material, was converted into the *N*-(benzenesulfonyl)indole **8a** (83%). Cross-coupling reaction between **8a** and the alkenylstannane **11a** (or **11b**) in the presence of bis(triphenylphosphine)palladium(II) chloride [$Pd(PPh_3)_2Cl_2$] gave the 3-alkenylindoles **7a** (84%) and **7b** (67%), respectively. Treatment of **7a** (or **7b**) with ethynylmagnesium bromide followed by treatment of the resulting alcohol **12a** (or **12b**) with chloromethyl methyl ether (MOMCl) produced the 3-alkenyl-2-propargylindoles **6a** (80% from **7a**) and **6b** (97% from **7b**). On the other hand, 3-iodoindole **10** was converted into the *N*-MOM-indole **8b** in good yield (96%). Cross-coupling reaction between **8b** and the alkenylstannane **11a** (or **11b**) in a similar manner gave the 3-alkenylindoles **7c** (89%) and **7d** (94%). Treatment of **7c** (or **7d**) with ethynylmagnesium bromide followed by treatment of the resulting alcohol **12c** (or **12d**) with MOMCl produced the 3-alkenyl-2-propargylindoles **6c** (85% from **7c**) and **6d** (70% from **7d**).

We next attempted the construction of the trisubstituted carbazole nucleus by using two types of *N*-protecting groups of the indole nitrogen atom (Scheme 2). The 3-alkenyl-2-propargylindole **6a** was heated at 90 °C in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide according to the previous reported method[13] for allene generation to yield the expected carbazole **4a** (43%) together with the *N*-deprotected carbazole **13a** (41%). In a similar way, 2-propargylindole **6b** gave the carbazole **4b** (20%) and *N*-deprotected carbazole **13b** (57%), respectively. By contrast, heating of the 3-alkenyl-2-propargylindole **6c** in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide produced only the *N*-MOM-carbazole **4c** (92%). Also in the case of the 2-propargylindole **6d**, only the *N*-MOM-carbazole **4d** was obtained (96%). In the former case, it was considered that the *N*-benzenesulfonyl group was perhaps removed partly by potassium *tert*-butoxide[14] during this reaction, but both protecting groups seemed to be good groups for this reaction. Fortunately, this benzo annelation proceeded without elimination of the MOM oxy group.

Investigation of the proposed mechanism is shown in Scheme 3. 3-Iodoindole **8a** was treated with ethynylmagnesium bromide to obtain the propargyl alcohol **14** (99%), which was converted into the MOM ether **15** (89%). Treatment of **15** with potassium *tert*-butoxide in *tert*-butyl alcohol at 90 °C for 3 h produced the allenylindole **16** in good yield (79%) with retention of the MOM ether.[15] However, the cross-coupling reaction between **16** and the alkenylstannane **11a** (or **11b**) failed. Thus, although it is undeniable that this benzo annelation proceeds through an ionic process, at present it is considered to proceed by initial generation of an allene intermediate which undergoes electrocyclic reaction to give the trisubstituted carbazole.

Studies to introduce an alkyl group into the 1-position of carbazole were done with carbazoles **4b** and **13b** (Scheme 4). Cleavage of the MOM ether of **4b** and **13b** with trimethylsilyl chloride (TMSCl) and sodium iodide (NaI)[16] gave 1-hydroxycarbazoles **17** (94%) and **18** (85%), respectively. The phenols **17** and **18** were converted into the triflates **19** (96%) and **20** (98%), which were subjected to the Suzuki cross-coupling reaction.[17] The reaction between **20** and 9-heptyl-9-borabicyclo[3.3.1]nonane (**21**) [prepared from 9-borabicyclo[3.3.1]nonane (9-BBN) and 1-heptene] proceeded in the presence of a palladium catalyst to yield the 1-heptylcarbazole **22** (53%). A

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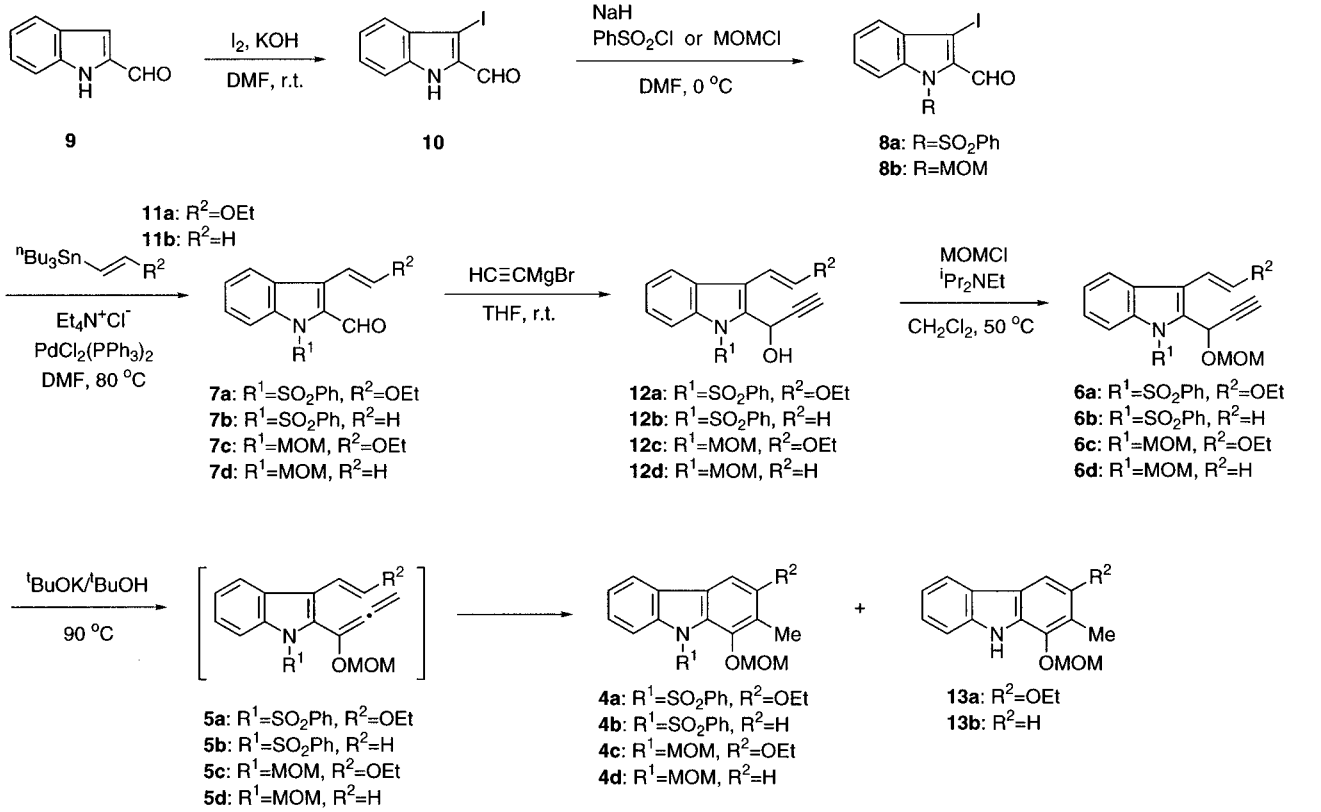
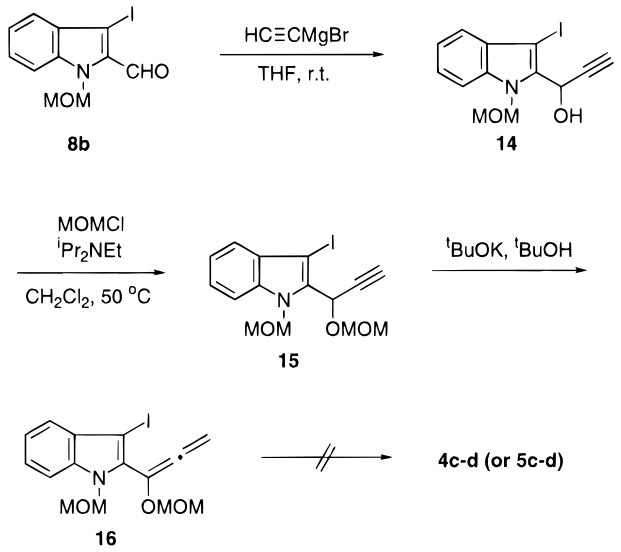
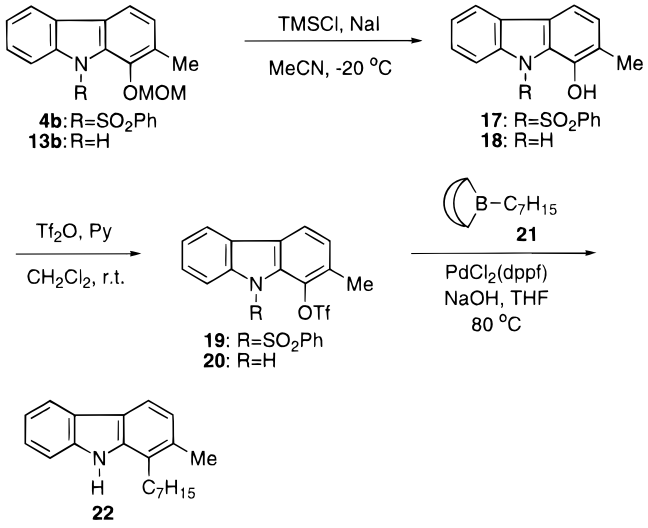
Scheme 2



Scheme 3



Scheme 4



similar reaction between **19** and **21** was unsuccessful because of steric hindrance.

On the basis of this model experiment, the *N*-protecting groups of carbazoles **4a,c** were removed to form the carbazole **13a** (98% from **4a** and 61% from **4c**) for the synthesis of natural products (Scheme 5). Treatment of **13a** with TMSCl and NaI followed by treatment of trifluoromethanesulfonyl anhydride (Tf_2O) and pyridine gave the triflate **24** (85% from **13a**). Subsequent cross-coupling reaction between **24** and **21** in the presence of a palladium catalyst gave the 1-heptylcarbazole **25a** (85%), which was treated with boron tribromide (BBr_3) to produce carazostatin (**1**) (90%). Furthermore, the cross-coupling reaction between **24** and phenylboronic acid in the presence of a palladium catalyst also gave the 1-phenylcarbazole **25b** (96%), which was treated with BBr_3 followed by *O*-methylation with methyl iodide[3i] to produce hyellazole (**2a**) (86% from **25b**). The spectroscopic data and physical data of carazostatin (**1**) and hyellazole (**2a**) were virtually identical with those reported for the natural[2,4] and synthetic[3,5] products. Carbazoquinocin C (**3c**) was readily obtained from carazostatin (**1**) by using benzeneseleninic anhydride [$(PhSeO)_2O$][18] as the oxidizing agent (95%). Thus, a synthetic route to

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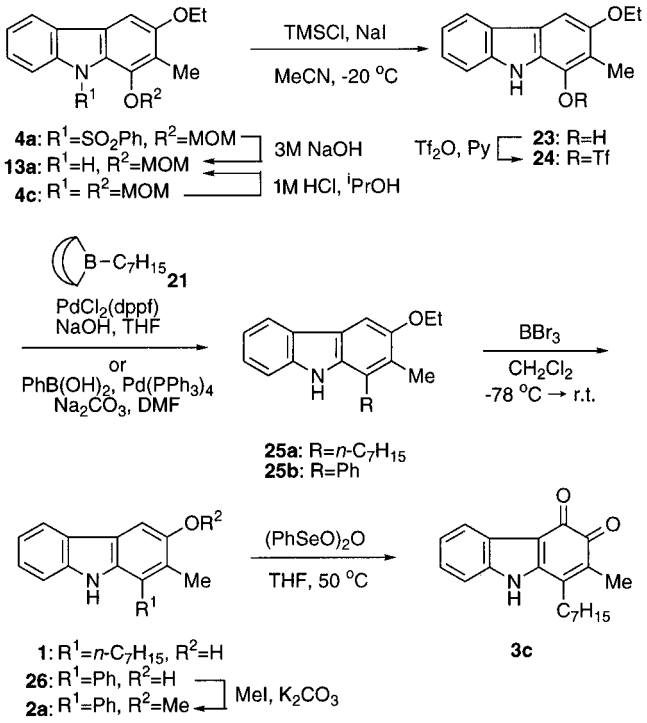
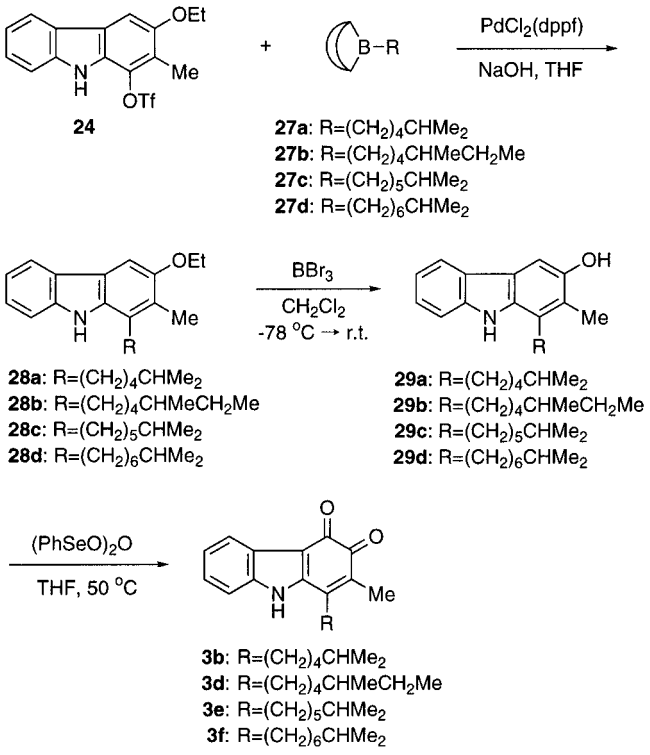
Scheme 5



Scheme 6



carbazoquinocins B (**3b**), D (**3d**), E (**3e**), and F (**3f**) is available.

Finally, the triflate **24** was subjected to the cross-coupling reaction with 9-alkyl-9-BBN **27a**−**d** in a similar manner to give the 1-alkylcarbazoles **28a**−**d** (56−78%). Subsequent treatment of **28a**−**d** with BBr_3 afforded 3-hydroxycarbazoles **29a**−**d** (64−97%), which were oxidized by $(PhSeO)_2O$ in the same way to yield carbazoquinocins B (**3b**, 90%), D (**3d**, 84%), E (**3e**, 70%), and F (**3f**, 92%), respectively (Scheme 6). The spectroscopic details of synthetic carbazoquinocins B−F (**3b**−**f**) were identical with those reported for natural products.[6] R_f values of synthetic carbazoquinocins B and D were consistent with those of authentic samples in various solvent systems. Although the melting points of all synthetic carbazoquinocins B−F (**3b**−**f**) were slightly higher than those of natural products, exact measurement of melting points is difficult because of dark-colored substances.

In conclusion, a new benzo annelation method based on the allene-mediated electrocyclic reaction of 2,3-functionalized indoles provides an effective route to the highly-functionalized carbazole ring, as shown for the total syntheses of carazostatin (**1**), hyellazole (**2a**), and carbazoquinocins B−F (**3b**−**f**). As regards hyellazole, this key reaction furnished more effective results than those of our previous synthesis.[3a,b] Moreover, the first total syntheses of carbazoquinocins B, C, E, and F (**3b,c,e,f**) were demonstrated.

Experimental Section

General. Most reactions were conducted in flame-dried glassware under argon atmosphere. All air-sensitive reactions were run under argon atmosphere. THF was freshly distilled from sodium benzophenone ketyl. DMF was freshly distilled under reduced pressure after drying over CaH_2. Silica gel (60−100 mesh, Merck Art 7734) was used for column chromatography. Melting points are uncorrected. ^1H NMR (60 MHz) and ^{13}C NMR were taken in $CDCl_3$ with Me_4Si as an internal standard unless otherwise stated. Low- and high-resolution mass spectra were measured at 70 eV (EI).

3-Iodoindole-2-carboxaldehyde (10). An ice-cooled solution of I_2 (1.67 g, 6.6 mmol) in DMF (30 mL) was added to a solution of 2-formylindole (**9**) (0.96 g, 6.6 mmol) and powdered KOH (1.3 g, 23.8 mmol). After stirring at rt for 4 h, the mixture was poured into a solution of 28% NH_4OH (100 mL) and $NaHSO_3$ (1 g, 9.6 mmol) in water (1.5 L). The precipitates were separated by filtration to give the 3-iodoindole **10** (1.45 g, 81%): mp 193−194 °C (from EtOH); IR (KBr) 3330, 1653 cm^{-1}; ^1H NMR δ 7.08−7.70 (m, 4 H), 9.77 (s, 1 H); MS *m*/*z* 271 (M^+). Anal. Calcd for C_9H_6NOI: C, 39.88; H, 2.23; N, 5.17. Found: C, 40.01; H, 2.33; N, 5.06.

***N*-(Benzenesulfonyl)-3-iodoindole-2-carboxaldehyde (8a).** An ice-cooled solution of 3-iodoindole **10** (500 mg, 1.84 mmol) in DMF (15 mL) was added to a suspension of 60% NaH (89 mg, 2.21 mmol) in DMF (5 mL). After stirring at the same temperature for 30 min, a solution of benzenesulfonyl chloride (0.28 mL, 2.21 mmol) was added to the above mixture. The reaction mixture was stirred at the same temperature for 2 h and then treated with water (30 mL). The mixture was extracted with EtOAc. The EtOAc layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography (silica gel, 30 g) using EtOAc−hexane (3:7, v/v) as an eluent to give the *N*-(benzenesulfonyl)indole **8a** (632 mg, 83%): mp 189.5−191 °C (from EtOAc); IR (KBr) 1688, 1368 cm^{-1}; ^1H NMR δ 7.15−8.31 (m, 9 H), 10.33 (s, 1 H); MS *m*/*z* 411 (M^+). Anal. Calcd for $C_{15}H_{10}NO_3IS$: C, 43.81; H, 2.45; N, 3.41. Found: C, 43.92; H, 2.55; N, 3.40.

3-Iodo-*N*-(methoxymethyl)indole-2-carboxaldehyde (8b). An ice-cooled solution of 3-iodoindole **10** (1.45 g, 5.3 mmol) in DMF (20 mL) was added to a suspension of 60% NaH (276 mg, 6.9 mmol) in DMF (10 mL). After stirring at rt for 30 min, a solution of MOMCl (1.6 mL, 21.4 mmol) was added to the above mixture. The reaction mixture was stirred at rt for 12 h and then poured into ice water. The mixture was extracted with EtOAc. The EtOAc layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography (silica gel, 50 g) using EtOAc−hexane (1:9, v/v) as an eluent to give the *N*-MOM-indole **8b** (1.58 g, 94%): mp 81−

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83.5 °C (from EtOAc); IR (KBr) 1611 cm^{-1}; ^1H NMR δ 3.26 (s, 3 H), 5.88 (s, 2 H), 7.02−7.58 (m, 4 H), 9.92 (s, 1 H); MS *m/z* 315 (M^+). Anal. Calcd for $C_{11}H_{10}NO_2I$: C, 41.93; H, 3.20; N, 4.45. Found: C, 42.05; H, 3.31; N, 4.40.

Palladium-Catalyzed Cross-Coupling Reaction between the 3-Iodoindole 8 and the Alkenyltri-*n*-butyltin 11. A typical example of **7a** is represented as follows, and other examples of **7b**−**d** show the compound name, yield, and physical data.

***N*-(Benzenesulfonyl)-3-(2-ethoxyethenyl)indole-2-carboxaldehyde (7a).** A solution of (2-ethoxyethenyl)tri-*n*-butyltin (**11a**) (818 mg, 2.27 mmol) was added to a suspension of 3-iodoindole **8a** (620 mg, 1.51 mmol), $Et_4N^+Cl^-$ (250 mg, 1.51 mmol), and $Pd(PPh_3)_2Cl_2$ (53 mg, 0.076 mmol) in DMF (5 mL). After stirring at 80 °C for 2 h, the reaction mixture was treated with 30% aqueous KF solution at rt. The mixture was stirred for 30 min and then filtered with Celite. The filtrate was extracted with EtOAc. The EtOAc layer was washed with water and brine and dried over Na_2SO_4. The organic layer was removed, and the residue was purified by column chromatography (silica gel, 30 g) using EtOAc−hexane (1:9, v/v) as an eluent to give the 3-(ethoxyethenyl)indole **7a** (448 mg, 84%): mp 122−124 °C (from EtOAc); IR (KBr) 1668, 1368 cm^{-1}; ^1H NMR δ 1.36 (t, 3 H, *J* = 7 Hz), 3.97 (q, 2 H, *J* = 7 Hz), 6.45 (d, 1 H, *J* = 14 Hz), 7.21−7.78 (m, 3 H), 7.53 (d, 1 H, *J* = 14 Hz), 8.07−8.32 (m, 6 H), 10.48 (s, 1 H); MS *m/z* 355 (M^+). Anal. Calcd for $C_{19}H_{17}NO_4S$: C, 64.21; H, 4.82; N, 3.94. Found: C, 64.23; H, 5.00; N, 3.89.

***N*-(Benzenesulfonyl)-3-ethenylindole-2-carboxaldehyde (7b).** A similar cross-coupling reaction between **8a** and **11b** was carried out as above to give the 3-ethenylindole **7b** (67%): mp 152.5−154 °C (from EtOAc); IR (KBr) 1676, 1367 cm^{-1}; ^1H NMR δ 5.71 (dd, 1 H, *J* = 2, 12 Hz), 5.93 (dd, 1 H, *J* = 2, 18 Hz), 7.25 (dd, 1 H, *J* = 12, 18 Hz), 7.28−8.31 (m, 9 H), 10.52 (s, 1 H); MS *m/z* 311 (M^+). Anal. Calcd for $C_{17}H_{13}NO_3S$: C, 65.58; H, 4.21; N, 4.50. Found: C, 65.63; H, 4.25; N, 4.61.

3-(2-Ethoxyethenyl)-*N*-(methoxymethyl)indole-2-carboxaldehyde (7c). A similar cross-coupling reaction between **8b** and **11a** was carried out as above to give the 3-(ethoxyethenyl)indole **7c** (89%): oil; IR (KBr) 1611 cm^{-1}; ^1H NMR δ 1.42 (t, 3 H, *J* = 7 Hz), 3.30 (s, 3 H), 4.02 (q, 2 H, *J* = 7 Hz), 5.91 (s, 2 H), 6.23 (d, 1 H, *J* = 12 Hz), 6.99 (d, 1 H, *J* = 12 Hz), 7.09−7.79 (m, 4 H), 10.02 (s, 1 H); MS *m/z* 259 (M^+). HRMS Calcd for $C_{15}H_{17}NO_3$: 259.1208. Found: 259.1191.

3-Ethenyl-*N*-(methoxymethyl)indole-2-carboxaldehyde (7d). A similar cross-coupling reaction between **8b** and **11b** was carried out as above to give the 3-(ethoxyethenyl)-indole **7d** (89%): oil; IR (KBr) 1611 cm^{-1}; ^1H NMR δ 3.27 (s, 3 H), 5.61 (d, 1 H, *J* = 10 Hz), 5.89 (d, 1 H, *J* = 10 Hz), 5.88 (s, 2 H), 6.94−7.91 (m, 5 H), 10.08 (s, 1 H); MS *m/z* 215 (M^+). HRMS Calcd for $C_{13}H_{13}NO_2$: 215.0946. Found: 215.0953.

Reaction of the 2-Formylindole 7 with Ethynylmagnesium Bromide. A typical example of **12a** is represented as follows, and other examples of **12b**−**d** show the compound name, yield, and physical data.

***N*-(Benzenesulfonyl)-3-(2-ethoxyethenyl)-2-(1-hydroxyprop-2-yn-1-yl)indole (12a).** An ice-cooled solution of ethynylmagnesium bromide (1.0 M in THF, 9.1 mL, 9.14 mmol) was added to a solution of (ethoxyethenyl)indole **7a** (500 mg, 1.41 mmol) in THF (15 mL). After stirring at rt for 2 h, the mixture was treated with aqueous NH_4OH solution (saturated) and extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 30 g) using EtOAc−hexane (3:17, v/v) as an eluent to give the propargyl alcohol **12a** (501 mg, 82%) as an oil: IR (neat) 3288, 2116, 1369, 1024 cm^{-1}; ^1H NMR δ 1.33 (t, 3 H, *J* = 7 Hz), 2.60 (d, 1 H, *J* = 3 Hz), 3.97 (q, 2 H, *J* = 7 Hz), 4.39 (br d, 1 H, *J* = 10 Hz, exchangeable with D_2O), 5.81 (d, 1 H, *J* = 8 Hz), 5.99 (br dd, 1 H, *J* = 3, 10 Hz), 6.90 (d, 1 H, *J* = 8 Hz), 7.01−8.03 (m, 9 H); MS *m/z* 381 (M^+). HRMS Calcd for $C_{21}H_{19}NO_4S$: 381.1034. Found: 381.1045.

***N*-(Benzenesulfonyl)-3-ethenyl-2-(1-hydroxyprop-2-yn-1-yl)indole (12b).** The same procedure as above was carried out by using **7b** (99%): oil, IR (neat) 3496, 3282, 2118, 1367 cm^{-1}; ^1H NMR δ 2.63 (d, 1 H, *J* = 2 Hz), 4.29 (d, 1 H, *J* = 10 Hz, exchangeable with D_2O), 5.60 (dd, 1 H, *J* = 2, 10 Hz), 5.73 (dd, 1 H, *J* = 2, 16 Hz), 6.17 (dd, 1 H, *J* = 2, 10 Hz), 6.94 (dd, 1 H, *J* = 10, 16 Hz), 7.02−8.18 (m, 9 H); MS *m/z* 337 (M^+). HRMS Calcd for $C_{21}H_{19}NO_4S$: 337.0772. Found: 337.0790.

3-(Ethoxyethenyl)-2-(1-hydroxyprop-2-yn-1-yl)-*N*-(methoxymethyl)indole (12c). The same procedure as above was carried out by using **7c** (89%): oil; IR (neat) 3432, 3282 cm^{-1}; ^1H NMR δ 1.31 (t, 3 H, *J* = 7 Hz), 2.56 (d, 1 H, *J* = 2 Hz), 3.19 (s, 3 H), 3.88 (q, 2 H, *J* = 7 Hz), 4.17 (d, 1 H, *J* = 2 Hz), 5.45 (d, 1 H, *J* = 10 Hz), 5.89 (d, 1 H, *J* = 12 Hz), 5.77−5.92 (m, 1 H), 6.06 (d, 1 H, *J* = 10 Hz), 6.79 (d, 1 H, *J* = 12 Hz), 7.07−7.71 (m, 4 H); MS *m/z* 285 (M^+). HRMS Calcd for $C_{17}H_{19}NO_3$: 285.1364. Found: 285.1345.

3-Ethenyl-2-(1-hydroxyprop-2-yn-1-yl)-*N*-(methoxymethyl)indole (12d). The same procedure as above was carried out by using **7d** (94%): oil; IR (neat) 3283, 2116 cm^{-1}; ^1H NMR δ 2.53 (d, 1 H, *J* = 2 Hz), 3.18 (s, 3 H), 4.16 (d, 1 H, *J* = 8 Hz), 5.29 (dd, 2 H, *J* = 2, 11 Hz), 5.42 (d, 1 H, *J* = 10 Hz), 5.61 (dd, 1 H, *J* = 2, 16 Hz), 5.76 (dd, 1 H, *J* = 2, 8 Hz), 6.01 (d, 1 H, *J* = 10 Hz), 6.82 (dd, 1 H, *J* = 11, 16 Hz), 6.99−7.89 (m, 4 H); MS *m/z* 241 (M^+). HRMS Calcd for $C_{15}H_{15}NO_2$: 241.1102. Found: 241.1099.

Preparation of the *O*-MOM Ether 6. A typical example of **6a** is represented as follows, and other examples of **6b**−**d** show the compound name, yield, and physical data.

***N*-(Benzenesulfonyl)-3-(2-ethoxyethenyl)-2-[1-[(methoxymethyl)oxy]prop-2-yn-1-yl]indole (6a).** A solution of MOMCl (0.36 mL, 4.72 mmol) was added to a solution of propargyl alcohol **12a** (360 mg, 0.94 mmol) and *i*-Pr_2NEt (0.98 mL, 5.64 mmol) in CH_2Cl_2 (15 mL). The solution was stirred at 50 °C for 12 h, cooled to rt, and treated with water. The mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (3:17, v/v) as an eluent to give the MOM ether **6a** (395 mg, 97%) as an oil: IR (neat) 3288, 2116, 1373 cm^{-1}; ^1H NMR δ 1.34 (t, 3 H, *J* = 7 Hz), 2.60 (d, 1 H, *J* = 3 Hz), 3.40 (s, 3 H), 3.92 (q, 2 H, *J* = 7 Hz), 4.63 (d, 1 H, *J* = 7 Hz), 4.95 (d, 1 H, *J* = 7 Hz), 6.17 (d, 1 H, *J* = 13 Hz), 6.55 (d, 1 H, *J* = 3 Hz), 7.07 (d, 1 H, *J* = 13 Hz), 7.09−8.28 (m, 9 H); MS *m/z* 425 (M^+). HRMS Calcd for $C_{23}H_{23}NO_5S$: 425.1296. Found: 425.1305.

***N*-(Benzenesulfonyl)-3-ethenyl-2-[1-[(methoxymethyl)-oxy]prop-2-yn-1-yl]indole (6b).** The same procedure as above was carried out by using **12b** to give the MOM ether **6b** (98%): oil; IR (neat) 3300, 2128, 1375 cm^{-1}; ^1H NMR δ 2.60 (d, 1 H, *J* = 2 Hz), 3.39 (s, 3 H), 4.62 (d, 1 H, *J* = 7 Hz), 4.94 (d, 1 H, *J* = 7 Hz), 5.45 (dd, 1 H, *J* = 2, 12 Hz), 5.75 (dd, 1 H, *J* = 2, 18 Hz), 6.60 (d, 1 H, *J* = 2 Hz), 7.25 (dd, 1 H, *J* = 12, 18 Hz), 7.18−8.27 (m, 9 H); MS *m/z* 381 (M^+). HRMS Calcd for $C_{21}H_{19}NO_4S$: 381.1034. Found: 381.1033.

3-(Ethoxyethenyl)-*N*-(methoxymethyl)-2-[1-[(methoxymethyl)oxy]prop-2-yn-1-yl]indole (6c). The same procedure as above was carried out by using **12c** to give the MOM ether **6c** (95%): oil; IR (neat) 3273, 2114 cm^{-1}; ^1H NMR δ 1.29 (t, 3 H, *J* = 7 Hz), 2.53 (d, 1 H, *J* = 2 Hz), 3.21 (s, 3 H), 3.29 (s, 3 H), 3.82 (q, 2 H, *J* = 7 Hz), 4.44 (d, 1 H, *J* = 6 Hz), 4.74 (d, 1 H, *J* = 6 Hz), 5.57 (s, 2 H), 5.79 (d, 1 H, *J* = 2 Hz), 5.88 (d, 1 H, *J* = 12 Hz), 6.71 (d, 1 H, *J* = 12 Hz), 6.83−7.51 (m, 4 H); MS *m/z* 329 (M^+). HRMS Calcd for $C_{19}H_{23}NO_4$: 329.1626. Found: 329.1641.

3-Ethenyl-*N*-(methoxymethyl)-2-[1-[(methoxymethyl)-oxy]prop-2-yn-1-yl]indole (6d). The same procedure as above was carried out by using **12d** to give the MOM ether **6d** (74%): oil; IR (neat) 3279, 2116 cm^{-1}; ^1H NMR δ 2.60 (d, 1 H, *J* = 2 Hz), 3.29 (s, 3 H), 3.36 (s, 3 H); 4.53 (d, 1 H, *J* = 7 Hz), 5.42 (dd, 1 H, *J* = 2, 11 Hz), 5.65 (s, 2 H), 5.65 (dd, 1 H, *J* = 2, 18 Hz), 5.92 (d, 1 H, *J* = 2 Hz), 6.91 (dd, 1 H, *J* = 11, 18 Hz), 7.05−7.83 (m, 4 H); MS *m/z* 285 (M^+). HRMS Calcd for $C_{17}H_{19}NO_3$: 285.1364. Found: 285.1372.

Preparation of the Carbazoles 4 and 13. A typical example of **4a** and **13a** is represented as follows, and other examples of **4b**−**d** show the compound name, yield, and physical data.

***N*-(Benzenesulfonyl)-3-ethoxy-1-[(methoxymethyl)oxy]-2-methylcarbazole (4a) and 3-Ethoxy-1-[(methoxymethyl)oxy]-2-methylcarbazole (13a).** A solution of the MOM ether **6a** (310 mg, 0.73 mmol) in THF (1 mL) was added to a solution of *t*-BuOK (245 mg, 2.2 mmol) in *t*-BuOH (4 mL). The stirred solution was heated at 90 °C for 3 h. After being cooled to rt, the solution was treated with aqueous NH_4Cl solution (saturated). The mixture was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (1:19, v/v) as an eluent to give the *N*-(benzenesulfonyl)carbazole **4a** (126 mg, 41%) and the carbazole **13a** (89 mg, 43%), respectively.

4a: mp 131.5−133 °C (from Et_2O−hexane); IR (KBr) 1363 cm^{-1}; ^1H NMR δ 1.40 (t, 3 H, $J = 7$ Hz), 2.30 (s, 3 H), 3.49 (s, 3 H), 3.97 (q, 2 H, $J = 7$ Hz), 5.38 (s, 2 H), 6.75 (s, 1 H), 6.83−7.59 (m, 8 H), 8.00−8.26 (m, 1 H); MS *m*/*z* 425 (M^+). Anal. Calcd for $C_{23}H_{23}NO_5S$: C, 64.92; H, 5.45; N, 3.29. Found: C, 65.04, H, 5.46; N, 3.15.

13a: IR (neat) 3331 cm^{-1}; ^1H NMR δ 1.49 (t, 3 H, $J = 7$ Hz), 2.34 (s, 3 H), 3.67 (s, 3 H), 4.10 (q, 2 H, $J = 7$ Hz), 5.13 (s, 2 H), 6.87−7.40 (m, 4 H), 7.78−7.99 (m, 1 H), 8.97 (br s, 1 H); MS *m*/*z* 285 (M^+). HRMS Calcd for $C_{17}H_{19}NO_3$: 285.1364. Found: 285.1378.

***N*-(Benzenesulfonyl)-1-[(methoxymethyl)oxy]-2-methylcarbazole (4b) and 1-[(methoxymethyl)oxy]-2-methylcarbazole (13b).** The same procedure as above was carried out by using **6b** to give the *N*-(benzenesulfonyl)carbazole **4b** (20%) and the carbazole **13b** (57%), respectively.

4b: mp 137−139.5 °C (from EtOAc−hexane); IR (KBr) 1373 cm^{-1}; ^1H NMR δ 2.44 (s, 3 H), 3.50 (s, 3 H), 5.36 (s, 2 H), 6.78−7.72 (m, 10 H), 8.05−8.28 (m, 1 H); MS *m*/*z* 381 (M^+). Anal. Calcd for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67. Found: C, 66.29; H, 4.98; N, 3.69.

13b: oil; ^1H NMR δ 2.40 (s, 3 H), 3.67 (s, 3 H), 5.15 (s, 2 H), 6.91 (d, 1 H, $J = 8$ Hz), 6.95−7.53 (m, 3 H), 7.62 (d, 1 H, $J = 8$ Hz), 7.84−8.07 (m, 1 H), 9.20 (br s, 1 H); MS *m*/*z* 241 (M^+). HRMS Calcd for $C_{15}H_{15}NO_2$: 241.1102. Found: 241.1099.

3-Ethoxy-*N*-(methoxymethyl)-1-[(methoxymethyl)oxy]-2-methylcarbazole (4c). The same procedure as above was carried out by using **6c** to give the *N*,*O*-bis(methoxymethyl)-carbazole **4c** (92%): oil; ^1H NMR δ 1.46 (t, 3 H, $J = 7$ Hz), 2.35 (s, 3 H), 3.24 (s, 3 H), 3.53 (s, 3 H), 4.08 (q, 2 H, $J = 7$ Hz), 5.08 (s, 2 H), 5.89 (s, 2 H), 6.99−7.94 (m, 5 H); MS *m*/*z* 329 (M^+). HRMS Calcd for $C_{19}H_{23}NO_4$: 329.1626. Found: 329.1638.

***N*-(Methoxymethyl)-1-[(methoxymethyl)oxy]-2-methylcarbazole (4d).** The same procedure as above was carried out by using **6d** to give the *N*,*O*-bis(methoxymethyl)carbazole **4d** (96%): oil; ^1H NMR δ 2.48 (s, 3 H), 3.32 (s, 3 H), 3.62 (s, 3 H), 5.15 (s, 2 H), 5.97 (m, 6 H); MS *m*/*z* 285 (M^+). HRMS Calcd for $C_{17}H_{19}NO_3$: 285.1364. Found: 285.1360.

2-(1-Hydroxyprop-2-yn-1-yl)-3-iodo-*N*-(methoxymethyl)indole (14). A solution of ethynylmagnesium bromide (0.5 M in THF, 7.0 mL, 3.5 mmol) was added to an ice-cooled solution of *N*-MOM-indole **8b** in THF (15 mL) under stirring. After stirring at 0 °C for 1 h, the solution was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 30 g) using EtOAc−hexane (3:7, v/v) as an eluent to give the propargyl alcohol **14** (1.07 g, 99%): mp 101−102 °C (from Et_2O−hexane); IR (KBr) 3291, 2110 cm^{-1}; ^1H NMR δ 2.63 (d, 1 H, $J = 2$ Hz), 3.28 (s, 3 H), 4.00 (br d, 1 H, $J = 8$ Hz, exchangeable with D_2O), 5.52 (d, 1 H, $J = 8$ Hz), 5.82 (dd, 1 H, $J = 2, 8$ Hz), 6.15 (d, 1 H, $J = 8$ Hz), 7.10−7.65 (m, 4 H); MS *m*/*z* 341 (M^+). Anal. Calcd for $C_{13}H_{12}NO_2I$: C, 45.77; H, 3.55, N, 4.11. Found: C, 45.78; H, 3.58; N, 4.08.

3-Iodo-*N*-(methoxymethyl)-2-[1-[(methoxymethyl)oxy]-prop-2-yn-1-yl]indole (15). A stirred solution of the propargyl alcohol **14** (1.2 g, 3.5 mmol), MOMCl (1.87 mL, 24.6 mmol), and *i*-Pr_2NEt (4.9 mL, 28.0 mmol) in CH_2Cl_2 (30 mL) was heated at 50 °C for 12 h. The solution was treated with water, and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (1:9, v/v) as an eluent to give the MOM ether **15** (1.2 g, 89%) as an oil: IR (neat) 3261, 2110 cm^{-1}; ^1H NMR δ 2.65 (d, 1 H, $J = 2$ Hz), 3.30 (s, 3 H), 3.41 (s, 3 H), 4.56 (d, 1 H, $J = 6$ Hz), 4.87 (d, 1 H, $J = 6$ Hz), 5.74 (s, 2 H), 5.95 (d, 1 H, $J = 2$ Hz), 7.02−7.63 (m, 4 H); MS *m*/*z* 385 (M^+). HRMS Calcd for $C_{15}H_{16}NO_3I$: 385.0174. Found: 385.0193.

3-Iodo-*N*-(methoxymethyl)-2-[1-[(methoxymethyl)oxy]-allen-1-yl]indole (16). A stirred solution of the MOM ether **15** (40 mg, 0.1 mmol) in THF (0.5 mL) was added to a solution of *t*-BuOK (35 mg, 0.31 mmol) in *t*-BuOH (3 mL). The solution was heated at 90 °C for 3 h. After being cooled to rt, the solution was treated with aqueous NH_4Cl solution (saturated). The mixture was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography using EtOAc−hexane (1:4, v/v) as an eluent to give the allenylindole **16** (33 mg, 83%) as an oil: IR (neat) 1961 cm^{-1}; ^1H NMR δ 3.25 (s, 3 H), 3.50 (s, 3 H), 4.99 (s, 2 H), 5.57 (s, 2 H), 5.62 (s, 2 H), 7.02−7.64 (m, 4 H); MS *m*/*z* 385 (M^+). HRMS Calcd for $C_{15}H_{16}NO_3I$: 385.0174. Found: 385.0168.

Preparation of the 1-Hydroxycarbazoles 17, 18, and 23 from the *O*-MOM Ethers 4b and 13a,b. A typical example of **23** is represented as follows, and other examples of **17** and **18** show the compound name, yield, and physical data.

3-Ethoxy-1-hydroxy-2-methylcarbazole (23). TMSCl (160 μL, 1.26 mmol) was added to a stirred suspension of the carbazole **13a** (239 mg, 0.84 mmol) and NaI (189 mg, 1.26 mmol) in MeCN (8 mL) at −20 °C. After the further addition of TMSCl (105 μL, 0.84 mmol) and NaI (124 mg, 0.84 mmol) at −20 °C, the mixture was stirred for 5 min and then the mixture was treated with MeOH. After removal of the solvent, water and EtOAc were added to the residue for extraction. The EtOAc layer was washed with 10% aqueous Na_2CO_3 solution and brine and then dried over Na_2SO_4. The organic layer was concentrated, and the residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (3:17, v/v) as an eluent to give the 1-hydroxycarbazole **23** (127 mg, 63%): mp 153−155 °C (from CH_2Cl_2−light petroleum); IR (KBr) 3154, 3346 cm^{-1}; ^1H NMR δ 1.44 (t, 3 H, $J = 7$ Hz), 2.25 (br s, 3 H), 4.08 (q, 2 H, $J = 7$ Hz), 4.88 (br s, 1 H, exchangeable with D_2O), 6.91−7.40 (m, 3 H), 7.25 (s, 1 H), 7.73−8.08 (m, 1 H); MS *m*/*z* 241 (M^+), 212 ($M^+ - 28$). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.60; H, 6.41; N, 6.00.

***N*-(Benzenesulfonyl)-1-hydroxy-2-methylcarbazole (17).** The same procedure as above was carried out by using **4b** to give the 1-hydroxycarbazole **17** (94%): mp 116−118 °C (from CH_2Cl_2−light petroleum); IR (KBr) 3155, 1370 cm^{-1}; ^1H NMR δ 2.43 (s, 3 H), 6.73−7.65 (m 10 H), 8.06−8.29 (m, 1 H), 9.20 (br s, 1 H, exchangeable with D_2O); MS *m*/*z* 337 (M^+). Anal. Calcd for $C_{19}H_{15}NO_3S$: C, 67.64; H, 4.48; N, 4.15. Found: C, 67.69; H, 4.35; N, 4.01.

1-Hydroxy-2-methylcarbazole (18). The same procedure as above was carried out by using **13b** to give the 1-hydroxycarbazole **18** (85%): mp 145−146.5 °C (from CH_2Cl_2−hexane); IR (KBr) 3158 cm^{-1}; ^1H NMR δ 2.34 (s, 3 H), 4.71 (br s, 1 H, exchangeable with D_2O), 6.80−7.68 (m, 5 H), 7.83−8.25 (m, 1 H); MS *m*/*z* 197 (M^+). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.24; H, 5.73; N, 6.99.

Preparation of the *O*-Triflates 19, 20, and 24. A typical example of **24** is represented as follows, and other examples of **19** and **20** show the compound name, yield, and physical data.

3-Ethoxy-2-methyl-1-[(trifluoromethanesulfonyl)oxy]-carbazole (24). Tf_2O (55 μL, 0.33 mmol) was added to a stirred solution of the 1-hydroxycarbazole **23** (66 mg, 0.27 mmol) and pyridine (66 μL, 0.81 mmol) in CH_2Cl_2 under cooling with ice. After stirring at rt for 2 h, the solution was treated with water. The mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with water and brine and then dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (1:19, v/v) as an eluent to give the triflate **24** (85%): mp 131−132 °C (from CH_2Cl_2−hexane); IR (KBr) 1400,

1073 cm^{-1}; ^1H NMR δ 1.44 (t, 3 H, J = 7 Hz), 2.34 (s, 3 H), 4.06 (q, 2 H, J = 7 Hz), 6.99−7.44 (m, 3 H), 7.23 (s, 1 H), 7.70−8.12 (m, 1 H); MS m/z 373 (M^+). Anal. Calcd for $C_{16}H_{14}NO_4F_3S$: C, 51.47; H, 3.78; N, 3.75. Found: C, 51.63; H, 3.59; N, 3.82.

***N*-(Benzenesulfonyl)-2-methyl-1-[(trifluoromethanesulfonyl)oxy]carbazole (19).** The same procedure as above was carried out by using **17** to give the triflate **19** (96%): mp 153−155 °C (from Et_2O); IR (KBr) 1419, 1080 cm^{-1}; ^1H NMR δ 2.26 (s, 3 H), 6.91−7.74 (m, 10 H), 7.99−8.25 (m, 1 H); MS m/z 469 (M^+). Anal. Calcd for $C_{20}H_{14}NO_5F_3S_2$: C, 51.17; H, 3.01; N, 2.98. Found: C, 51.06; H, 2.89; N, 3.11.

1-[(Trifluoromethanesulfonyl)oxy]-2-methylcarbazole (20). The same procedure as above was carried out by using **18** to give the triflate **20** (98%): mp 86−87 °C (from light petroleum ether); IR (KBr) 1406, 1070 cm^{-1}; ^1H NMR δ 2.49 (s, 3 H), 6.95 (d, 1 H, J = 8 Hz), 7.00−7.46 (m, 3 H), 7.78−8.02 (m, 1 H), 7.80 (d, 1 H, J = 8 Hz), 8.19 (br s, 1 H); MS m/z 329 (M^+). Anal. Calcd for $C_{14}H_{10}NO_3F_3S$: C, 51.06; H, 3.06; N, 4.25. Found: C, 51.15; H, 2.87; N, 4.26.

1-Heptyl-2-methylcarbazole (22). A solution of 9-heptyl-9-BBN (**21**) [prepared from 1-heptene (38 μL, 0.27 mmol) in THF (1 mL) with 9-BBN (0.5 M in THF, 0.54 mL, 0.27 mmol) at rt for 4 h] was added by cannula to a stirred suspension of the triflate **20** (60 mg, 0.18 mmol), 3 M NaOH (0.18 mL, 0.54 mmol), and $PdCl_2$(dppf) (9 mg, 0.014 mmol) in THF (1.5 mL). The mixture was heated at 80 °C for 3 h. After being cooled to rt, the mixture was treated with water and EtOAc. The EtOAc layer was separated, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 10 g) using EtOAc−hexane (2:98, v/v) as an eluent to give the 1-heptylcarbazole **22** (27 mg, 53%): mp 50−52 °C (from hexane); ^1H NMR (500 MHz) δ 0.90 (t, 3 H, J = 7.2 Hz), 1.15−1.70 (m, 10 H), 2.48 (s, 3 H), 2.88 (t, 2 H, J = 7.9 Hz), 7.04 (d, 1 H, J = 8 Hz), 7.20 (t, 1 H, J = 7.3 Hz), 7.38 (t, 1 H, J = 7.3 Hz), 7.44 (d, 1 H, J = 7.3 Hz), 7.79 (d, 1 H, J = 8 Hz), 8.00 (d, 1 H, J = 7.3 Hz); MS m/z 279 (M^+). Anal. Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01. Found: C, 86.03; H, 9.06; N, 4.87.

3-Ethoxy-1-[(methoxymethyl)oxy]-2-methylcarbazole (13a) from 4a. A mixture of the *N*-(benzenesulfonyl)-carbazole **4a** (833 mg, 1.96 mmol) and aqueous 3 M NaOH solution (30 mL, 90 mmol) in MeOH (50 mL) and THF (15 mL) was refluxed for 18 h. After being cooled to rt, the mixture was acidified with concd HCl. The mixture was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (5:95, v/v) as an eluent to give the carbazole **13a** (550 mg, 98%).

3-Ethoxy-1-[(methoxymethyl)oxy]-2-methylcarbazole (13a) from 4c. A solution of *N*-[(methoxymethyl)oxy]-carbazole **4c** (85 mg, 0.258 mmol) and 1 M HCl (1 mL) in *i*-PrOH (1 mL) and THF (2 mL) was refluxed for 15 h. After being cooled to rt, the solution was neutralized with aqueous Na_2CO_3 solution (saturated). The mixture was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 5 g) using EtOAc−hexane (1:19, v/v) as an eluent to give the carbazole **13a** (45 mg, 61%).

3-Ethoxy-1-heptyl-2-methylcarbazole (25a). A solution of 9-heptyl-9-BBN [prepared from 9-BBN (0.5 M in THF, 0.58 mL, 0.29 mmol) and 1-heptene (40 μL, 0.29 mmol) in THF (1 mL) at 0 °C for 4 h] was added to a mixture of the triflate **24** (71 mg, 0.19 mmol), 3 M NaOH (0.19 mL, 0.57 mmol), and $PdCl_2$(dppf) (6 mg, 0.01 mmol) in THF (1.5 mL) by cannula. The stirred mixture was heated at 80 °C for 1.5 h. After being cooled to rt, the mixture was treated with aqueous 30% H_2O_2 solution (3 mL) and aqueous 3 M AcONa solution (3 mL). The mixture was further stirred for 30 min and then extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 10 g) using EtOAc−hexane (1:19 v/v) as an eluent to give the 1-heptylcarbazole **25a** (52 mg, 85%): mp 80.5−82.5 °C (from pentane); ^1H NMR δ 0.87 (t, 3 H, J = 7.1 Hz), 1.24−1.39 (m, 7 H), 1.42−1.54 (m, 2 H), 1.49 (t, 3 H, J = 6.7 Hz), 2.36 (s, 3 H), 2.88 (t, 2 H, J = 7.9 Hz, 4.14 (q, 2 H, J = 6.7 Hz), 7.17 (t, 1 H, J = 7.6 Hz), 7.35 (t, 1 H, J = 7.6 Hz), 7.38 (s, 1 H), 7.42 (d, 1 H, J = 7.6 Hz), 7.76 (br s, 1 H) 7.97 (d, 1 H, J = 7.6 Hz); MS m/z 323 (M^+). Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.71; H, 8.94; N, 4.49.

3-Ethoxy-2-methyl-1-phenylcarbazole (25b). A stirred suspension of the triflate **24** (49 mg, 0.13 mmol), phenylboronic acid (19 mg, 0.16 mmol), 2 M Na_2CO_3 (0.13 mL, 0.26 mmol), and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) in DME (1 mL) was heated at 100 °C for 1 h. After being cooled to rt, the mixture was treated with water, and then the mixture was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 10 g) using EtOAc−hexane (1:9, v/v) as an eluent to give the 1-phenylcarbazole **25b** (38 mg, 96%) as an oil: ^1H NMR δ 1.49 (t, 3 H, J = 7 Hz), 2.23 (s, 3 H), 4.20 (q, 2 H, J = 7 Hz), 7.00−7.58 (m, 4 H), 7.43 (s, 5 H), 7.77−8.01 (m, 1 H); MS m/z 301 (M^+). HRMS Calcd for $C_{21}H_{19}NO$: 301.1466. Found: 301.1482.

1-Heptyl-3-hydroxy-2-methylcarbazole (Carazostatin, 1). A solution of BBr_3 (29 μL, 0.31 mmol) in CH_2Cl_2 (2 mL) was added at −78 °C to a stirred solution of 3-ethoxycarbazole **25a** (50 mg, 0.15 mmol) in CH_2Cl_2 (2 mL). After being warmed to rt gradually, the solution was stirred for 4 h and then treated with water. The mixture was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (1:9, v/v) as an eluent to give the carazostatin (**1**) (41 mg, 90%): mp 159−160 °C (from CH_2Cl_2−light petroleum) (lit.[4,5] mp 162−163 °C); IR (KBr) 3350 cm^{-1}; ^1H NMR (400 MHz) δ 0.90 (t, 3 H, J = 6.8 Hz), 1.20−1.50 (m, 8 H), 1.60−1.69 (m, 2 H), 2.38 (s, 3 H), 2.89 (t, 2 H, J = 7 Hz), 7.17 (t, 1 H, J = 7 Hz), 7.31 (s, 1 H), 7.33−7.46 (m, 2 H), 7.74 (br s, 1 H), 7.94 (d, 1 H, J = 7 Hz); MS m/z 295 (M^+). Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.33; H, 8.72; N, 4.81.

3-Hydroxy-2-methyl-1-phenylcarbazole (26).[3i] The same procedure as above was carried out by using **25b** to give the hydroxycarbazole **26** (90%). The solvent system for column chromatography used EtOAc−hexane (15:85, v/v): mp 171−173 °C (from $CHCl_3$−hexane); IR (KBr) 3310 cm^{-1}; ^1H NMR (400 MHz) δ 2.23 (s, 3 H), 7.16 (t, 1 H, J = 7 Hz), 7.26−7.57 (m, 7 H), 7.48 (s, 1 H), 7.58 (br s, 1 H), 7.97 (d, 1 H, J = 7.8 Hz); MS m/z 273 (M^+). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.52; H, 5.69; N, 4.98.

Hyellazole (2a). A stirred suspension of 3-hydroxycarbazole **26** (13 mg, 0.048 mmol), CH_3I(1.26 mL, 20.3 mmol), and K_2CO_3 (134 mg, 0.96 mmol) in Me_2CO (10 mL) was heated at 60 °C for 12 h. After being cooled to rt, the solvent was removed. The residue was extracted with EtOAc. The EtOAc layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 10 g) using EtOAc−hexane (1:19, v/v) as an eluent to give the hyellazole (**2a**) (13 mg, 95%): mp 129−130 °C (from hexane) (lit.[2,3] mp 133−134 °C); IR (KBr) 3310 cm^{-1}; ^1H NMR (400 MHz) δ 2.21 (s, 3 H), 4.00 (s, 3 H), 7.18 (t, 1 H, J = 6.9 Hz), 7.24−7.56 (m, 7 H), 7.51 (s, 1 H), 7.60 (br s, 1 H), 8.02 (d, 1 H, J = 7.8 Hz); MS m/z 287 (M^+). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.45; H, 6.01; N, 4.74.

Carbazoquinocin C (3c). A solution of carazostatin (**1**) (22 mg, 0.074 mmol) in THF (1 mL) was added to a stirred suspension of 70% $(PhSeO)_2O$ (38 mg, 0.074 mmol) in THF (3 mL). The mixture was stirred at 50 °C for 30 min. After being cooled to rt, the reaction mixture was diluted with MeOH−$CHCl_3$ (1:9) (50 mL). The mixture was washed with aqueous 10% Na_2CO_3 solution, water, and brine. The $CHCl_3$ layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, 10 g) using EtOAc as an eluent to give the carbazoquinocin C (**3c**) (22 mg, 95%): mp 227−229 °C (from EtOAc) (lit.[6] mp 210−212 °C); IR (KBr) 1649, 1632, 1474, 1256, 760 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 0.86 (t, 3 H, J = 7.1 Hz), 1.22−1.38 (m, 6 H), 1.42−1.49 (m, 2 H), 1.52−1.60 (m, 2 H), 1.91 (s, 3 H), 2.67 (t, 2 H, J = 7.5 Hz), 7.22−7.26 (m, 2 H), 7.50−7.53 (m, 1 H), 7.85−7.86 (m, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 183.5, 172.6, 145.8,

142.2, 137.2, 133.0, 125.7, 124.0, 123.8, 120.2, 113.4, 111.0, 31.2, 28.9, 28.5, 28.4, 28.0, 22.0, 13.8, 11.4; MS *m*/*z* 311 ($M^+ + 2$), 309 (M^+). Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.55; H, 7.60; N, 4.51.

Cross-Coupling Reaction between the Triflate 24 and 9-Alkyl-9-BBN 27. A typical example of **28a** is represented as follows, and other examples of **28b**−**d** show the compound name, yield, and physical data.

3-Ethoxy-2-methyl-1-(5-methylhexyl)carbazole (28a). A solution of 9-(5-methylhexyl)-9-BBN (**27a**) [prepared from 9-BBN (0.5 M n THF, 0.96 mL, 0.48 mmol) and 5-methyl-1-hexene (68 μL, 0.48 mmol) in THF (1 mL) at 0 °C for 4 h] was added to a mixture of the triflate **24** (91 mg, 0.24 mmol), 3 M NaOH (0.24 mL, 0.72 mmol), and $PdCl_2$(dppf) (8 mg, 0.012 mmol) in THF (1.5 mL) by cannula. The stirred mixture was heated at 80 °C for 1.5 h. After being cooled to rt, the mixture was treated with aqueous 30% H_2O_2 solution (3 mL) and aqueous 3 M AcONa solution (3 mL). The mixture was further stirred for 30 min and then extracted with EtOAc. The EtOAc was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc−hexane (1:19 v/v) as an eluent to give the 1-(5-methylhexyl)carbazole **28a** (60 mg, 76%): mp 79−81 °C (from pentane); ^{1}H NMR (500 MHz) δ 0.88 (d, 6 H, J = 6.7 Hz), 1.22−1.28 (m, 2 H), 1.43−1.51 (m, 2 H), 1.49 (t, 3 H, J = 7 Hz), 1.52−1.67 (m, 3 H), 2.41 (s, 3 H), 2.88 (t, 2 H, J = 7.9 Hz), 4.13 (q, 2 H, J = 7 Hz), 7.17 (t, 1 H, J = 7.9 Hz), 7.35 (t, 1 H, J = 7.9 Hz), 7.38 (s, 1 H), 7.42 (d, 1 H, J = 7.9 Hz), 7.76 (br s, 1 H), 7.97 (d, 1 H, J = 7.9 Hz); MS *m*/*z* 323 (M^+). Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.50; H, 9.11; N, 4.36.

3-Ethoxy-2-methyl-1-(5-methylheptyl)carbazole (28b). The same procedure as above was carried out by using 9-(5-methylheptyl)-9-BBN (**27b**) (prepared from 9-BBM and 5-methyl-1-heptane[20]) (78%): mp 72−74 °C (from pentane); ^{1}H NMR (500 MHz) δ 0.86 (d, 3 H, J = 6.4 Hz), 0.87 (t, 3 H, J = 8.5 Hz), 1.13−1.19 (m, 2 H), 1.31−1.54 (m, 5 H), 1.49 (t, 3 H, J = 7 Hz), 1.59−1.66 (m, 2 H), 2.36 (s, 3 H), 2.89 (t, 2 H, J = 8 Hz), 4.14 (q, 2 H, J = 7 Hz), 7.17 (t, 1 H, J = 7.5 Hz), 7.35 (t, 1 H, J = 7.5 Hz), 7.38 (s, 1 H), 7.42 (d, 1 H, J = 7.5 Hz), 7.76 (br s, 1 H), 7.87 (d, 1 H, J = 7.5 Hz); MS *m*/*z* 337 (M^+). Anal. Calcd for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 81.89; H, 9.35; N, 3.99.

3-Ethoxy-2-methyl-1-(6-methylheptyl)carbazole (28c). The same procedure as above was carried out by using 9-(6-methylheptyl)-9-BBN (**27c**) (prepared from 9-BBM and 6-methyl-1-heptene[21]) (72%): mp 90.5−92.5 °C (from pentane); ^{1}H NMR (500 MHz) δ 0.87 (d, 6 H, J = 6.4 Hz), 1.16−1.20 (m, 2 H), 1.32−1.38 (m, 2 H), 1.41−1.46 (m, 2 H), 1.49 (t, 3 H, J = 7 Hz), 1.63−1.69 (m, 2 H), 2.36 (s, 3 H), 2.89 (t, 2 H, J = 7.9 Hz), 4.14 (q, 2 H, J = 7 Hz), 7.17 (t, 1 H, J = 8.3 Hz), 7.35 (t, 1 H, J = 8.3 Hz), 7.38 (s, 1 H), 7.45 (d, 1 H, J = 8.3 Hz), 7.76 (br s, 1 H), 7.97 (d, 1 H, J = 8.3 Hz); MS *m*/*z* 337 (M^+). Anal. Calcd for $C_{23}H_{31}NO$: C, 81.85; H, 9.26; N, 4.15. Found: C, 82.01; H, 9.13; N, 4.18.

3-Ethoxy-2-methyl-1-(7-methyloctyl)carbazole (28d). The same procedure as above was carried out by using 9-(7-methyloctyl)-9-BBN (**27d**) (prepared from 9-BBM and 7-methyl-1-octene[22]) (56%): mp 70−72 °C (from pentane); ^{1}H NMR (500 MHz) δ 0.86 (d, 6 H, J = 7.3 Hz), 1.13−1.18 (m, 2 H), 1.25−1.37 (m, 4 H), 1.40−1.55 (m, 3 H), 1.48 (t, 3 H, J = 7 Hz), 1.60−1.67 (m, 2 H), 2.35 (s, 3 H), 2.86 (t, 2 H, J = 8 Hz), 4.12 (q, 2 H, J = 7 Hz), 7.17 (t, 1 H, J = 7.4 Hz), 7.34 (t, 1 H, J = 7.4 Hz), 7.37 (s, 1 H), 7.40 (d, 1 H, J = 7.4 Hz), 7.75 (br s, 1 H), 7.97 (d, 1 H, J = 7.4 Hz); MS *m*/*z* 351 (M^+). Anal. Calcd for $C_{24}H_{33}NO$: C, 82.00; H, 9.46; N, 3.98. Found: C, 81.96; H, 9.48; N, 4.00.

Cleavage of the Ethyl Ether 28 by BBr_3. A typical example of **29a** is represented as follows, and other examples of **29b**−**d** show the compound name, yield, and physical data.

3-Hydroxy-2-methyl-1-(5-methoxyhexyl)carbazole (29a). A solution of BBr_3 (27 μL, 0.29 mmol) in CH_2Cl_2 (12 mL) was added at −78 °C to a stirred solution of 3-ethoxycarbazole **28a** (47 mg, 0.15 mmol) in CH_2Cl (3 mL). After being warmed to rt gradually, the mixture was extracted with EtOAc. The EtOAc was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, 10 g) using EtOAc−hexane (3:17, v/v) as an eluent to give the 3-hydroxycarbazole **29a** (39 mg, 91%): mp 157−159 °C (from CH_2Cl_2−light petroleum); IR (KBr) 3473, 3379 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.89 (d, 6 H, J = 6.7 Hz), 1.23−1.28 (m, 2 H), 1.44−1.50 (m, 2 H), 1.52−1.67 (m, 3 H), 2.37 (s, 3 H), 2.88 (t, 2 H, J = 7.9 Hz), 7.16 (t, 1 H, J = 7 Hz), 7.33 (s, 1 H), 7.36 (t, 1 H, J = 7 Hz), 7.41 (d, 1 H, J = 7 Hz), 7.74 (br s, 1 H), 7.93 (d, 1 H, J = 7 Hz); MS *m*/*z* 295 (M^+). Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.25; H, 8.54; N, 4.60.

3-Hydroxy-2-methyl-1-(5-methylheptyl)carbazole (29b). The same procedure as above was carried out by using **28b** (97%): mp 162−164 °C (from CH_2Cl_2−light petroleum); IR (KBr) 3475, 3369 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.86 (d, 3 H, J = 6.4 Hz), 0.87 (t, 3 H, J = 7.3 Hz), 1.12−1.21 (m, 2 H), 1.28−1.54 (m, 5 H), 1.59−1.67 (m, 2 H), 2.37 (s, 3 H), 2.89 (t, 2 H, J = 7.9 Hz), 7.16 (t, 1 H, J = 7 Hz), 7.33 (s, 1 H), 7.35 (t, 1 H, J = 7 Hz), 7.41 (d, 1 H, J = 7 Hz), 7.74 (br s, 1 H), 7.93 (d, 1 H, J = 7 Hz); MS *m*/*z* 309 (M^+). Anal. Calcd for $C_{21}H_{27}NO$: C, 81.51; H, 8.79; N, 4.52. Found: C, 81.49; H, 8.79; N, 4.56.

3-Hydroxy-2-methyl-1-(6-methylheptyl)carbazole (29c). The same procedure as above was carried out by using **28c** (64%): mp 163−165 °C (from $CHCl_3$−hexane); IR (KBr) 3474, 3367 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.87 (d, 6 H, J = 6.4 Hz), 1.15−1.20 (m, 2 H), 1.35−1.37 (m, 2 H), 1.39−1.47 (m, 2 H), 1.51−1.57 (m, 1 H), 1.62−1.69 (m, 2 H), 2.37 (s, 3 H), 2.88 (t, 2 H, J = 8.1 Hz), 4.54 (br s, 1 H), 7.16 (t, 1 H, J = 8 Hz), 7.33 (s, 1 H), 7.35 (t, 1 H, J = 8 Hz), 7.41 (d, 1 H, J = 8 Hz), 7.74 (br s, 1 H), 7.93 (d, 1 H, J = 8 Hz); MS *m*/*z* 309 (M^+). Anal. Calcd for $C_{21}H_{27}NO$: C, 81.51; H, 8.79; N, 4.52. Found: C, 81.62; H, 8.60; N, 4.67.

3-Hydroxy-2-methyl-1-(7-methyloctyl)carbazole (29d). The same procedure as above was carried out by using **28d** (74%): mp 160−162 °C ($CHCl_3$−hexane); IR (KBr) 3477, 3366 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.86 (d, 6 H, J = 6.4 Hz), 1.15−1.18 (m, 2 H), 1.25−1.34 (m, 4 H), 1.43−1.53 (m, 3 H), 1.60−1.68 (m, 2 H), 2.37 (s, 3 H), 2.87 (t, 2 H, J = 8.1 Hz), 7.16 (t, 1 H, J = 8 Hz), 7.31 (s, 1 H), 7.36 (t, 1 H, J = 8 Hz), 7.40 (d, 1 H, J = 8 Hz), 7.78 (br s, 1 H), 7.91 (d, 1 H, J = 8 Hz); MS *m*/*z* 323 (M^+). Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.70; H, 8.95; N, 4.14.

Oxidation of the 3-Hydroxycarbazole 29 to Carbazoquinocins B and D−F (3b,d−f). A typical procedure of **3b** is represented as follows, and other examples of **3d**−**f** show the compound name, yield, and physical data.

Carbazoquinocin B (3b). A solution of 3-hydroxycarbazole **29a** (34 mg, 0.12 mmol) in THF (2 mL) was added to a stirred suspension of 70% $(PhSeO)_2O$ (59 mg, 0.12 mmol) in THF (4 mL). The mixture was stirred at 50 °C for 30 min. After being cooled to rt, the reaction mixture was diluted with MeOH−$CHCl_3$ (1:9) (50 mL). The mixture was washed with aqueous 10% Na_2CO_3 solution, water, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, 20 g) using EtOAc as an eluent to give the carbazoquinocin B (**3b**) (32 mg, 90%): mp 240−243 °C (from EtOAc) (lit.[6] mp 213−217 °C); IR (KBr) 1639, 1624, 1466, 1250, 754 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.87 (t, 6 H, J = 9.8 Hz), 1.16−1.24 (m, 2 H), 1.43−1.55 (m, 5 H), 1.91 (s, 3 H), 2.67 (t, 2 H, J = 8.2 Hz), 7.23−7.27 (m, 2 H), 7.51−7.54 (m, 1 H), 7.84−7.87 (m, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 183.5, 172.7, 145.5, 142.0, 137.0, 133.0, 125.6, 124.1, 123.9, 120.2, 113.3, 111.0, 38.2, 28.7, 28.0, 27.4, 26.8, 22.4 (2C), 11.4; MS *m*/*z* 311 ($M^+ + 2$), 309 (M^+). Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.77; H, 7.36; N, 4.73.

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Carbazoquinocin D (3d). The same procedure as above was carried out by using **29b** (84%): mp 231−233 °C (from EtOAc) (lit.[6] mp 208−210 °C); IR (KBr) 1639, 1625, 1465, 1249, 754 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 0.82 (t, 3 H, J = 7 Hz), 0.83 (d, 3 H, J = 6.4 Hz), 1.09−1.18 (m, 2 H), 1.25−1.35 (m, 4 H), 1.39−1.58 (m, 3 H), 1.91 (s, 3 H), 2.67 (t, 2 H, J = 7.5 Hz), 7.21−7.27 (m, 2 H), 7.51−7.53 (m, 1 H), 7.84−7.87 (m, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 183.5, 172.6, 145.7, 142.1, 137.1, 133.0, 125.6, 124.1, 123.8, 120.2, 113.3, 111.0, 35.8, 33.7, 28.8, 28.7, 28.0, 26.5, 19.0, 11.4, 11.1; MS m/z 325 ($M^+ + 2$), 323 (M^+). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33. Found: C, 77.98; H, 7.70; N, 4.15.

Carbazoquinocin E (3e). The same procedure as above was carried out by using **29c** (70%): mp 226−228 °C (from EtOAc) (lit.[6] mp 209−210 °C); IR (KBr) 1639, 1624, 1468, 1259, 754 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 0.85 (d, 6 H, J = 6.4 Hz), 1.14−1.19 (m, 2 H), 1.29−1.35 (m, 2 H), 1.40−1.61 (m, 5 H), 1.91 (s, 3 H), 2.67 (t, 2 H, J = 8 Hz), 7.21−7.25 (m, 2 H), 7.49−7.53 (m, 1 H), 7.83−7.86 (m, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 183.4, 172.6, 145.5, 142.1, 137.1, 133.0, 125.6, 124.1, 123.9, 120.2, 113.3, 111.0, 38.3, 29.2, 28.4, 28.0, 27.3, 26.7, 22.4 (2C), 11.4; MS m/z 325 ($M^+ + 2$), 323 (M^+). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33. Found: C, 78.03; H, 7.64; N, 4.41.

Carbazoquinocin F (3f). The same procedure as above was carried out by using **29d** (92%): mp 229−231 °C (from EtOAc) (lit.[6] mp 208−210 °C); IR (KBr) 1639, 1624, 1464, 1250, 752 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 0.83 (d, 6 H, J = 6.7 Hz), 1.10−1.17 (m, 2 H), 1.21−1.35 (m, 4 H), 1.42−1.61 (m, 5 H), 1.91 (s, 3 H), 2.67 (t, 2 H, J = 8 Hz), 7.21−7.27 (m, 2 H), 7.49−7.54 (m, 1 H), 7.83−7.89 (m, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 183.4, 172.7, 145.5, 142.0, 136.0, 133.0, 125.6, 124.1, 123.9, 120.2, 113.3, 111.0, 38.3, 29.1, 28.9, 28.4, 28.0, 27.2, 26.6, 22.4 (2C), 11.4; MS m/z 339 ($M^+ + 2$), 337 (M^+). Anal. Calcd for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15. Found: C, 78.15; H, 8.08; N, 4.20.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of **3b**−**f** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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