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A new procedure for the preparation of 2-vinylindoles and their [4+2] cycloaddition reaction

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ABSTRACT

A new approach for the synthesis of 2-vinylindole derivatives by 5-*exo* mode cyclization of 2-(3-silyloxymethylallenyl)anilines was developed. The starting allenylanilines were easily prepared by the Stille coupling of *o*-iodoaniline and allenylstannanes. The formed 2-vinylindole derivatives were transformed into several carbazole derivatives via the [4+2] cycloaddition reaction with suitable dienophiles.

1. Introduction

In our previous studies, we developed a new procedure for the generation of the reactive indole-2,3-quinodimethane intermediates **2** from the allenylanilines **1** via the S_N2'-type reaction in the 5-*endo*-type manner (Fig. 1).[1] This method was entirely different from the well-known ones[2] that took advantage of the 1,4-elimination-type or related reactions of the 2,3-disubstituted indole derivatives. The indole-2,3-quinodimethane intermediates **2** were successively captured by several dienophiles in the same reaction vessel to afford the tetrahydro- and dihydrocarbazole derivatives **3**.

We envisaged that the similar S_N2'-type reaction of allenylanilines **4** via the 5-*exo* mode ring-closing reaction would furnish the 2-vinylindole derivatives **5**,[3] which are known to be a useful component for the syntheses of some drugs[4] and natural products.[5] We now describe a new entry for the preparation of 2-vinylindole frameworks and their [4+2] cycloaddition leading to an alternative method for the construction of the carbazole derivatives **6**.

2. Results and discussion

At the beginning of this project, the Stille coupling reaction[6] of the *N*-(*tert*-butoxycarbonyl)-2-iodoaniline (**7**) and 3-(*tert*-butyldimethylsilyloxymethyl)-1-(tributylstannyl)allene derivatives **8** was conducted for the preparation of the *N*-(*tert*-butoxycarbonyl)-2-{3-(*tert*-butyldimethylsilyloxymethyl)allenyl} aniline derivatives **9**. According to a previous procedure,[1,7] **7** was treated with allenylstannane **8a**[8] in DMF in the presence of 3 mol % of $Pd_2(dba)_3$, tri-2-furylphosphine (TFP, 24 mol %), and CuI (10 mol %) at room temperature for 2 h to produce the allenylaniline derivative **9a** in 79% yield (Table 1, entry 1). Other allenylstannanes **8b**–**d** (R^1=Me, Et, CH_2OBn: R^2=H) gave the corresponding allenylanilines **9b**–**d** in good yields (entries 2–4). The tetrasubstituted derivatives **9e**,**f** (R^1=CH_2OBn: R^2=Bu, $(CH_2)_4OPMB$) were produced in moderate yields from **7** and the tetrasubstituted allenylstannanes **8e**,**f** (entries 5 and 6).

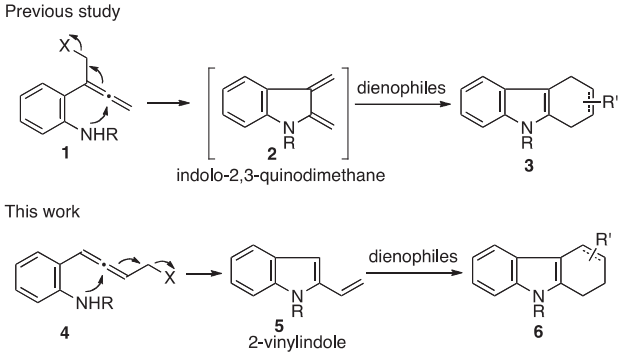

Fig. 1. Formation of carbazole derivatives based on S_N2' cyclization and Diels–Alder reaction.

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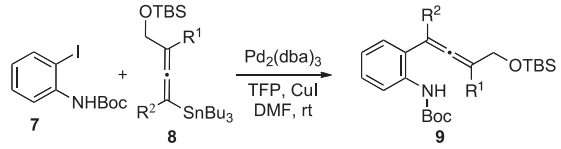
Table 1
Stille coupling of *o*-iodoaniline **7** and allenylstannanes **8**

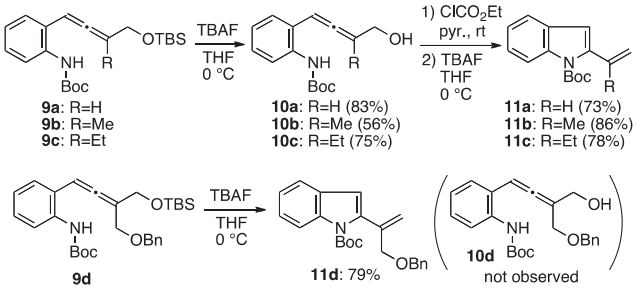


7 8 9

Entry	Allene	R^1	R^2	Time (h)	Product	Yield (%)
1	**8a**	H	H	2	**9a**	79
2	**8b**	Me	H	3	**9b**	90
3	**8c**	Et	H	5	**9c**	78
4	**8d**	CH_2OBn	H	4	**9d**	88
5	**8e**	CH_2OBn	Bu	12	**9e**	49
6[a]	**8f**	CH_2OBn	$(CH_2)_4OPMB$	6	**9f**	50

[a] The reaction was heated at 70 °C.

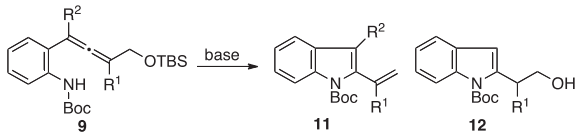
With the required allenylanilines **9** in hand, the ring-closing reaction for the construction of 2-vinylindole derivatives **11** was examined (Scheme 1). After removing the TBS group of the 1,3-disubstituted allene derivative **9a** with TBAF in THF at 0 °C, the resulting **10a** (83%) was successfully converted into *N*-(*tert*-butoxycarbonyl)-2-vinylindole (**11a**) in 73% yield by ethoxycarbonylation followed by TBAF treatment. The 1,1,3-trisubstituted allene derivatives **9b** and **9c** having a methyl or ethyl group on the vinyl position also provided the corresponding 2-vinylindole derivatives **11b** and **11c** in good yields. TBAF treatment of the 1,1,3-trisubstituted allene derivative **9d** directly and unexpectedly produced the 2-vinylindole derivative **11d** in 79% yield. This was in sharp contrast to the cases in which the desilylated products **10a**–**c** were obtained upon exposure of **9a**–**c** to TBAF.



Scheme 1. Formation of 2-vinylindoles **11**.

Based on the direct conversion of the allenylaniline **9d** to 2-vinylindole **11d**, we reinvestigated the one-step conversion of allenylanilines **9** into **11** (Table 2). Treatment of the allenylaniline **9a** with TBAF in THF at room temperature (not at 0 °C) afforded the desired 2-vinylindole derivative **11a** in 83% yield (entry 1).[9] At a higher temperature (45 °C), *N*-(*tert*-butoxycarbonyl)-2-(2-hydroxy-1-alkylethyl)indole derivatives **12b**,**c** were obtained instead of **11b**,**c** (entries 2 and 3). On the other hand, the tetrasubstituted allene derivatives **9e**,**f** were converted to the desired 2-vinyl-3-substituted indole derivatives **11e** (62%) and **11f** (73%) at 0 °C (entries 4 and 5). K_2CO_3 was used as a base for the formation of the indole derivatives from the allenylanilines in previous papers.[1,7] Thus, K_2CO_3 was again found to be a suitable base for the transformation of the allenylanilines **9b**,**c** to 2-vinylindoles **11b**,**c**. In fact, **11b**,**c** were obtained in satisfactory yields when **9b**,**c** were reacted with K_2CO_3 in DMF at rather higher reaction temperatures (85–110 °C)(entries 6–8).[10]

Table 2
S_N2' cyclization of 2-(4-silyloxybuta-1,2-dienyl)anilines **9**

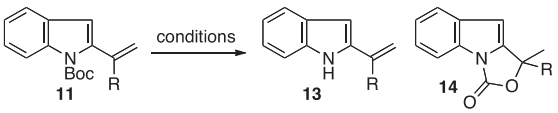


9 11 12

Entry	Substrate	R^1	R^2	Base	Solvent	Temp (°C)	Time (h)	Product (%)
1	**9a**	H	H	TBAF	THF	rt	0.2	**11a** (83)
2	**9b**	Me	H	TBAF	THF	45	5	**12b** (50)
3	**9c**	Et	H	TBAF	THF	45	5	**12c** (45)
4	**9e**	CH_2OBn	Bu	TBAF	THF	0	0.5	**11e** (62)
5	**9f**	CH_2OBn	$(CH)_2OPMB$	TBAF	THF	0	0.5	**11f** (73)
6	**9b**	Me	H	K_2CO_3	DMF	110	4	**11b** (66)
7	**9b**	Me	H	K_2CO_3/ Et_2CO_3	DMF	85	4	**11b** (80)
8	**9c**	Et	H	K_2CO_3/ Et_2CO_3	DMF	95	5	**11c** (85)

By taking the [4+2] cycloaddition reaction of the 2-vinylindoles, in particular the compounds having a substituent on the vinyl position (R≠H), into account, we tried to remove a Boc group on the nitrogen atom of the indole nucleus, which should be predicted to disturb the planarity due to the nonbonding interaction with an R group. Treatment of 2-vinylindole **11b** (R=Me) with TFA in CH_2Cl_2[11] at room temperature afforded 1,1-dimethyloxazolo[3,4-*a*]indol-3(1*H*)-one (**14b**) in 76% yield (Table 3, entry 1). Similar results were observed under other acidic conditions (HCl in AcOEt,[11,12] and TMSCl, NaI in CH_3CN,[13] entries 2 and 3). In contrast to these acidic conditions, exposure to KOH in MeOH at 70 °C gave the desired 2-vinylindole derivatives **13b**–**d** in moderate to high yields (entries 4–6).

Table 3
Deprotection of A/-Boc group of 2-vinylindoles **11**

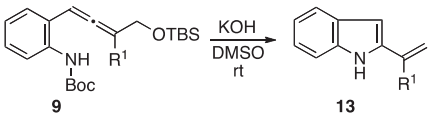


11 13 14

Entry	Substrate	R	Additive	Solv.	Temp	Time (h)	Product (%)
1	**11b**	Me	TFA	CH_2Cl_2	rt	1	**14b** (76)
2	**11b**	Me	HCl	AcOEt	rt	6	**14b** (45)
3	**11b**	Me	TMSCl, NaI	CH_3CN	rt	0.5	**14b** (85)
4	**11b**	Me	KOH	MeOH	70 °C	5	**13b** (92)
5	**11c**	Et	KOH	MeOH	70 °C	5	**13c** (56)
6	**11d**	CH_2OBn	KOH	MeOH	70 °C	5	**13d** (83)

The experimental results summarized in Tables 2 and 3 revealed that the one-step conversion of **9** into **11** required basic conditions, and a Boc group of **11** could also be removed by the base treatment. Thus, the direct one-step transformation of **9** into **13** would be attainable under proper basic conditions. After screening several basic conditions, we finally established the following conditions that treatment of **9a**–**d** with KOH in DMSO at room temperature producing the desired **13a**–**d** in satisfactory yields as expected (Table 4, entries 1–4).

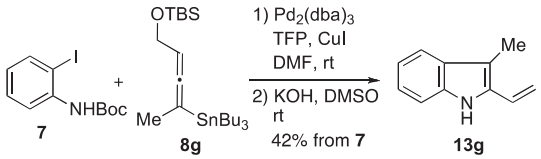
Table 4
Formation of 2-vinylindoles **13**



9 13

Entry	Substrate	R	Time (h)	Product (%)
1	**9a**	H	0.25	**13a** (76)
2	**9b**	Me	6	**13b** (73)
3	**9c**	Et	6	**13c** (75)
4	**9d**	CH_2OBn	10	**13d** (90)

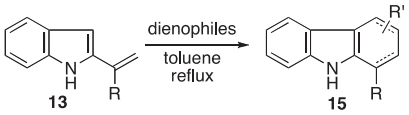
In addition, the successive Stille coupling reaction and KOH treatment offered a more efficient synthesis of 3-methyl-2-vinylindole (**13g**) (42%) as shown in Scheme 2.[14,15]

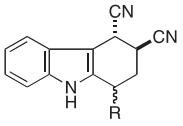
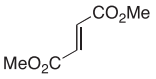
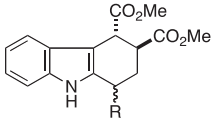
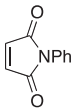
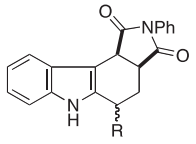
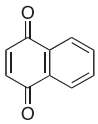
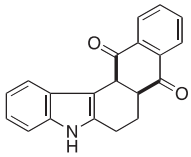
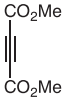
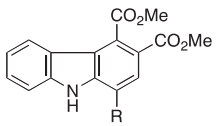


Scheme 2. Formation of 3-metyl-2-vinylindoles (**13g**).

Finally, the application of 2-vinylindoles **13** for the synthesis of the carbazole derivatives was invesitagted (Table 5).[3f,16] A suspension of 2-vinylindole (**13a**)[17] and fumaronitrile in toluene was heated under reflux to afford the desired tetrahydrocarbazole derivative **15a** (R=H) in 60% yield (entry 1). The methyl congener **15b** (R=Me) was also obtained from **13b**[17b,18] in 65% yield as a mixture of two isomers (1:2) (entry 2). Dimethyl fumarate, *N*-phenylmaleimide, and 1,4-naphthoquinone were found to be proper dienophiles for the formation of the corresponding tetrahydrocarbazole derivatives **15c–h** (entries 3–8). In the case of the dimethyl acetylenedicarboxylate, the initially formed dihydrocarbazoles were oxidized resulting in the production of **15i,j** in moderate yields (entries 9 and 10).

Table 5
Diels–Alder reaction of 2-vinylindole derivatives **13**



Entry	Dienophile	Product and yield
1		
2		**15a**: R=H (60%) **15b**: R=Me (65%, dr=2:1)[a]
3		
4		**15c**: R=Me (62%, dr=5:1)[a] **15d**: R=Et (49%, dr=2:1)[a]
5		
6		**15e**: R=H (49%)
7		**15f**: R=Me (95%, dr=3:2)[a] **15g**: R=Et (87%, dr=1:1)[a]
8		 **15h** (58%)
9		
10		**15i**: R=Me (48%) **15j**: R=Et (48%)

[a]Diastereomeric ratios were determined by isolated yields.

3. Conclusions

In summary, we have developed a novel and efficient procedure for the formation of the 2-vinylindole derivatives[19] from *N*-(*tert*-butoxycarbonyl)-2-{3-(*tert*-butyldimethylsilyloxymethyl)allenyl} aniline derivatives, which were easily prepared from the Stille coupling of the *N*-(*tert*-butoxycarbonyl)-*o*-iodoaniline and allenylstannanes, via a 5-*exo* mode cyclization under basic conditions. In addition, these 2-vinylindole derivatives could be applied to the syntheses of the carbazole derivatives.

4. Experimental

4.1. General

Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in $CDCl_3$ unless otherwise indicated. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal standard. All reactions were carried out under a nitrogen atmosphere. Silica gel (silica gel 60, 230–400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

4.2. Preparation of propargyl alcohol derivative

4.2.1. 1-Benzyloxy-2-(tert-butyldimethylsilyloxy)methyl-3-butyn-2-ol. To a solution of 1-benzyloxy-3-(*tert*-butyldimethylsilyloxy) propan-2-one[20] (60 mg, 0.20 mmol) in Et_2O (1 mL) was added ethynyl magnesium bromide (0.50 M in THF, 0.60 mL, 0.30 mmol) at 0 °C. After stirring for 1.5 h at the same temperature, the reaction mixture was quenched by saturated aqueous NH_4Cl, extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (9:1) to give 1-benzyloxy-2-(*tert*-butyldimethylsilyloxy)methyl-3-butyn-2-ol (49 mg, 76%) as a colorless oil. IR 3547, 3308 cm^{-1}; ^1H NMR δ 7.35–7.25 (m, 5H), 4.64 (s, 2H), 3.78, 3.71 (ABq, J_{AB}=9.7 Hz, 2H), 3.61, 3.57 (ABq, J_{AB}=9.6 Hz, 2H), 3.01 (s, 1H), 2.43 (s, 1H), 0.90 (s, 9H), 0.085 (s, 3H), 0.081 (s, 3H); ^{13}C NMR δ 137.8, 128.4, 127.70, 127.68, 83.8, 73.7, 72.8, 72.7, 70.4, 66.7, 25.8, 18.3, −5.40, −5.44; EIMS *m*/*z* 320 (M^+, 18); EI HRMS calcd for $C_{18}H_{28}O_3Si$ 320.1808, found 320.1799.

4.3. General procedure for the preparation of propargyl alcohols

^{n}BuLi (1.3 M in hexane, 0.25 mL, 0.34 mmol) was added to a solution of 1-hexyne derivative (0.41 mmol) in THF (0.7 mL) at −78 °C and the mixture was stirred for 1 h at −40 °C. 1-Benzyloxy-3-(*tert*-butyldimethylsilyloxy)propan-2-one (100 mg, 0.34 mmol) was added to the mixture and then the reaction mixture was warmed to room temperature. After stirring until the complete disappearance of the starting material (monitored by TLC), the mixture was quenched by water, extracted Et_2O. The extract was

washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (15:1) to give the corresponding propargyl alcohols.

4.3.1. 1-Benzyloxy-2-(tert-butyldimethylsilyloxy)methyl-3-octyn-2-ol. Colorless oil; IR 3545, 2245 cm^{-1}; ^1H NMR δ 7.36–7.27 (m, 5H), 4.65, 4.62 (ABq, J_{AB}=9.3 Hz, 2H), 3.75 (d, J=9.6 Hz, 1H), 3.66 (d, J=9.6 Hz, 1H), 3.56, 3.54 (ABq, J_{AB}=9.3 Hz, 2H), 2.91 (br s, 1H), 2.21 (t, J=6.9 Hz, 2H), 1.51–1.46 (m, 2H), 1.43–1.37 (m, 2H), 0.95–0.90 (m, 12H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR δ 138.1, 128.3, 127.61, 127.58, 85.7, 79.8, 73.5, 73.0, 70.5, 66.8, 30.6, 25.8, 21.9, 18.4, 18.3, 13.6, −5.41, −5.43; EIMS m/z 376 (M^+, 3.4); EI HRMS calcd for $C_{22}H_{36}O_3Si$ 376.2434, found 376.2428.

4.3.2. 1-Benzyloxy-2-(tert-butyldimethylsilyloxy)methyl-8-(p-methoxybenzyloxy)-3-octyne-2-ol. Colorless oil; IR 3545, 2243 cm^{-1}; ^1H NMR δ 7.34–7.24 (m, 7H), 6.87 (d, J=9.2 Hz, 2H), 4.63 (s, 2H), 4.41 (s, 2H), 3.80 (s, 3H), 3.74 (d, J=9.8 Hz, 1H), 3.66 (d, J=9.8 Hz, 1H), 3.56, 3.53 (ABq, J_{AB}=9.6 Hz, 2H), 3.44 (t, J=6.6 Hz, 2H), 2.23 (t, J=7.5 Hz, 2H), 1.71–1.66 (m, 2H), 1.63–1.57 (m, 2H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR δ 159.0, 138.1, 130.6, 129.2, 128.3, 127.59, 127.56, 113.7, 85.3, 80.1, 73.5, 73.0, 72.5, 70.4, 69.4, 66.8, 55.2, 28.8, 25.8, 25.2, 18.5, 18.3, −5.41, −5.44; DART MS m/z 513 (M^++1, 69); DART HRMS calcd for $C_{30}H_{45}O_5Si$ 513.3036, found 513.3041.

4.3.3. 1-(tert-Butyldimethylsilyloxy)-3-pentyn-2-ol. To a solution of 2-(*tert*-butyldimethylsilyloxy)acetaldehyde[21] (800 mg, 4.6 mmol) in Et_2O (9 mL) was added propynyl magnesium bromide (0.50 M in THF, 10 mL, 5.0 mmol) at 0 °C. After stirring for 2.5 h at the same temperature, the reaction mixture was quenched by saturated aqueous NH_4Cl, extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (9:1) to give 1-(*tert*-butyldimethylsilyloxy)-3-pentyn-2-ol (690 mg, 70%) as a colorless oil. IR 3545, 2359 cm^{-1}; ^1H NMR δ 4.35 (s, 1H), 3.71 (dd, J=10.0, 3.7 Hz, 1H), 3.57 (dd, J=10.0, 7.8 Hz, 1H), 2.61–2.60 (m, 1H), 1.83 (d, J=1.8 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR δ 81.8, 67.2, 63.2, 30.3, 25.8, 18.3, 3.5, −5.4; DART MS m/z 215 (M^++1, 39); DART HRMS calcd for $C_{11}H_{23}O_2Si$ 215.1467, found 215.1470.

4.4. General procedure for preparation of allenylstannanes

To a solution of propargyl alcohol derivative (1.0 mmol) in CH_2Cl_2 (10 mL) were added Et_3N (0.28 mL, 2.0 mmol) and MsCl (0.10 mL, 1.3 mmol) at 0 °C. The reaction mixture was stirred for 1 h, quenched by addition of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of $^iPr_2NH$ (0.24 mL, 1.6 mmol) in THF (10 mL) was added ^{n}BuLi (1.5 M hexane solution, 0.93 mL, 1.4 mmol) at −30 °C. After 30 min, Bu_3SnH (0.40 mL, 1.5 mmol) was added. The reaction mixture was stirred for 30 min at the same temperature and then cooled to −78 °C. $CuBr\cdot SMe_2$ (310 mg, 1.5 mmol) was then added to the reaction mixture and stirring for 30 min at −78 °C. The crude mesylate in THF (3.0 mL) was added to the reaction mixture and the mixture was stirred for 20 min at the same temperature. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane and then hexane/AcOEt (50:1) to give the corresponding allenylstannane **8**.

*4.4.1. 4-(tert-Butyldimethylsilyloxy)-1-(tributylstannyl)-1,2-butadiene (**8a**)*[8]. Colorless oil; IR 1929 cm^{-1}; ^1H NMR δ 5.12 (dt, J=6.4, 2.7 Hz, 1H), 4.78–4.73 (m, 1H), 4.22–4.12 (m, 2H), 1.62–1.26 (m, 12H), 1.00–0.85 (m, 24H), 0.08 (s, 6H).

*4.4.2. 4-(tert-Butyldimethylsilyloxy)-3-methyl-1-(tributylstannyl)-1,2-butadiene (**8b**).* Colorless oil; IR 1936 cm^{-1}; ^1H NMR δ 5.05–5.00 (m, 1H), 4.11–4.10 (m, 2H), 1.66 (td, J=10.7, 3.7 Hz, 3H), 1.57–0.88 (m, 36H), 0.07 (s, 6H); ^{13}C NMR δ 206.2, 88.4, 75.8, 66.2, 28.9, 27.2, 25.9, 18.4, 15.2, 13.7, 10.5, −5.3; EIMS m/z 488 (M^+, 8.2); EI HRMS calcd for $C_{23}H_{48}OSiSn$ 488.2496, found 488.2494.

*4.4.3. 4-(tert-Butyldimethylsilyloxy)-3-ethyl-1-(tributylstannyl)-1,2-butadiene (**8c**).* Colorless oil; IR 1933 cm^{-1}; ^1H NMR δ 5.11 (tt, J=4.1, 2.3 Hz, 1H), 4.15 (td, J=6.9, 2.3 Hz, 2H), 2.06–1.90 (m, 2H), 1.59–1.47 (m, 6H), 1.35–1.26 (m, 6H), 1.02 (t, J=7.3 Hz, 3H), 0.94–0.87 (m, 24H), 0.06 (s, 6H); ^{13}C NMR δ 205.6, 95.1, 76.7, 65.3, 29.0, 27.2, 26.0, 21.5, 18.4, 13.7, 12.4, 10.4, −5.2, −5.3; EIMS m/z 502 (M^+, 6.5); EI HRMS calcd for $C_{24}H_{50}OSiSn$ 502.2653, found 502.2648.

*4.4.4. 3-Benzyloxymethyl-4-(tert-butyldimethylsilyloxy)-1-(tributylstannyl)-1,2-butadiene (**8d**).* Colorless oil; IR 1934 cm^{-1}; ^1H NMR δ 7.25–7.17 (m, 5H), 5.10–5.09 (m, 1H), 4.42 (s, 2H), 4.15–4.14 (m, 2H), 4.05–4.02 (m, 2H), 1.45–1.39 (m, 6H), 1.26–1.17 (m, 6H), 0.97–0.78 (m, 24H), −0.02 (s, 6H); ^{13}C NMR δ 205.6, 138.7, 128.2, 127.7, 127.3, 90.3, 76.9, 71.4, 69.0, 62.3, 29.0, 27.2, 25.9, 18.4, 13.7, 10.5, −5.3; DART MS m/z 595 (M^++1, 34); DART HRMS calcd for $C_{30}H_{55}O_2SiSn$ 595.2993, found 595.2987.

*4.4.5. 1-Benzyloxy-2-(tert-butyldimethylsilyloxymethyl)-4-(tributylstannyl)-2,3-octadiene (**8e**).* Colorless oil; IR 1936 cm^{-1}; ^1H NMR δ 7.27–7.17 (m, 5H), 4.45 (d, J=11.6 Hz, 1H), 4.39 (d, J=11.6 Hz, 2H), 4.14–3.97 (m, 4H), 2.06–2.02 (m, 2H), 1.54–0.81 (m, 43H), −0.02 (s, 6H); ^{13}C NMR δ 199.7, 138.9, 128.2, 127.6, 127.2, 94.2, 92.1, 71.2, 69.8, 62.6, 32.6, 32.5, 29.0, 27.5, 27.3, 25.9, 22.3, 18.4, 13.7, 10.3, −5.3; EIMS m/z 650 (M^+, 1.4); EI HRMS calcd for $C_{34}H_{62}O_2SiSn$ 650.3541, found 650.3533.

*4.4.6. 1-Benzyloxy-2-(tert-butyldimethylsilyloxymethyl)-8-(p-methoxybenzyloxy)-4-(tributylstannyl)-2,3-octadiene (**8f**).* Colorless oil; IR 1936 cm^{-1}; ^1H NMR δ 7.28–7.16 (m, 7H), 6.78 (d, J=8.7 Hz, 2H), 4.45, 4.40 (ABq, J_{AB}=11.4 Hz, 2H), 4.34 (s, 2H), 4.16–3.97 (m, 4H), 3.71 (s, 3H), 3.36 (t, J=6.4 Hz, 2H), 2.11–2.01 (m, 2H), 1.61–1.55 (m, 2H), 1.49–0.80 (m, 38H), −0.01 (s, 6H); ^{13}C NMR δ 199.6, 159.0, 138.8, 130.7, 129.1, 128.2, 127.5, 127.2, 113.6, 94.0, 92.3, 72.4, 71.2, 69.9, 69.5, 62.5, 55.1, 32.6, 32.4, 29.0, 27.5, 27.0, 25.9, 18.3, 13.7, 10.3, −5.3; FABMS m/z 787 (M^++1, 0.1); FAB HRMS calcd for $C_{42}H_{71}O_4SiSn$ 787.4144, found 787.4148.

4.5. Palladium(0)-catalyzed coupling reaction of iodoaniline 7 with allenylstannane 8

To a solution of iodoaniline **7** (320 mg, 1.0 mmol) and allenylstannane **8** (1.1 mmol) in DMF (10 mL) were added TFP (56 mg, 0.24 mmol), CuI (19 mg, 0.10 mmol), and $Pd_2(dba)_3$ (27 mg, 0.030 mmol) at room temperature. After stirring until the complete disappearance of the starting material (monitored by TLC), the mixture was quenched by addition of 10% aqueous NH_3 solution, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane/Et_2O to give the corresponding 2-allenylaniline **9**. The chemical yields were summarized in Table 1.

*4.5.1. N-(tert-Butoxycarbonyl)-2-[4-(tert-butyldimethylsilyloxy)-1,2-butadienyl]aniline (**9a**).* Yellow oil; IR 3392, 1950, 1724 cm^{-1}; ^1H NMR δ 7.89 (d, J=7.8 Hz, 1H), 7.39 (br s, 1H), 7.23–7.19 (m, 1H), 7.18–7.16 (m, 1H), 7.03–6.99 (m, 1H), 6.36 (td, J=6.4, 3.2 Hz, 1H), 5.69–5.65 (m, 1H), 4.34–4.31 (m, 2H), 1.51 (s, 9H), 0.89 (s, 9H), 0.08

(s, 6H); ^{13}C NMR δ 204.5, 153.1, 136.1, 129.1, 127.9, 123.4, 122.5, 121.4, 95.5, 93.7, 80.1, 60.6, 28.3, 25.8, 18.3, −5.2, −5.3; DART MS *m*/*z* 376 (M^++1, 100); DART HRMS calcd for $C_{21}H_{34}NO_3Si$ 376.2308, found 376.2305.

*4.5.2. N-(tert-Butoxycarbonyl)-2-[4-(tert-butyldimethylsilyloxy)-3-methyl-1,2-butadienyl]aniline (**9b**).* Colorless oil; IR 3393, 1948, 1726 cm^{-1}; ^{1}H NMR δ 7.95 (d, *J*=8.2 Hz, 1H), 7.61 (br s, 1H), 7.22–7.17 (m, 1H), 7.12 (dd, *J*=7.8, 1.8 Hz, 1H), 7.01–6.97 (m, 1H), 6.28–6.26 (m, 1H), 4.22 (dd, *J*=12.4, 3.2 Hz, 1H), 4.18 (dd, *J*=12.4, 3.2 Hz, 1H), 1.83 (d, *J*=3.2 Hz, 3H), 1.51 (s, 9H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR δ 201.8, 153.0, 136.5, 129.4, 127.6, 122.9, 122.5, 120.6, 103.8, 93.4, 80.0, 64.3, 28.4, 25.8, 18.3, 15.5, −5.36, −5.38; EIMS *m*/*z* 389 (M^+, 4.7); EI HRMS calcd for $C_{22}H_{35}NO_3Si$ 389.2386, found 389.2384.

*4.5.3. N-(tert-Butoxycarbonyl)-2-[3-(tert-butyldimethylsilyloxymethyl)-1,2-pentadienyl]aniline (**9c**).* Yellow oil; IR 3396, 1960, 1728 cm^{-1}; ^{1}H NMR δ 7.97 (d, *J*=7.8 Hz, 1H), 7.66 (s, 1H), 7.21–7.17 (m, 1H), 7.13–7.11 (m, 1H), 7.00–6.97 (m, 1H), 6.38–6.37 (m, 1H), 4.25–4.24 (m, 2H), 2.17–2.11 (m, 2H), 1.51 (s, 9H), 1.11 (t, *J*=7.3 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR δ 201.1, 152.9, 136.6, 129.3, 127.6, 122.9, 122.3, 120.4, 110.6, 95.3, 80.0, 63.5, 28.3, 25.8, 22.4, 18.3, 12.0, −5.36, −5.40; FABMS *m*/*z* 404 (M^++1, 9.5); FAB HRMS calcd for $C_{23}H_{38}NO_3Si$ 404.2621, found 404.2625.

*4.5.4. N-(tert-Butoxycarbonyl)-2-[3-benzyloxymethyl-4-(tert-butyldimethylsilyloxy)-1,2-butadienyl]aniline (**9d**).* Colorless oil; IR 3398, 1952, 1724 cm^{-1}; ^{1}H NMR δ 7.88 (d, *J*=8.2 Hz, 1H), 7.42 (br s, 1H), 7.27–7.15 (m, 6H), 7.11 (dd, *J*=7.8, 1.4 Hz, 1H), 6.97 (td, *J*=7.8, 1.4 Hz, 1H), 6.36 (tt, *J*=3.2, 1.8 Hz, 1H), 4.51 (s, 2H), 4.30 (d, *J*=3.2 Hz, 2H), 4.13 (d, *J*=1.8 Hz, 2H), 1.43 (s, 9H), 0.82 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR δ 202.4, 153.1, 137.8, 136.4, 129.3, 128.3, 127.9, 127.7, 127.6, 123.2, 122.4, 121.3, 105.6, 94.5, 80.0, 72.1, 67.9, 61.3, 28.3, 25.8, 18.3, −5.37, −5.39; FABMS *m*/*z* 518 (M^++23, 2.4); FAB HRMS calcd for $C_{29}H_{41}NNaO_4Si$ 518.2703, found 518.2710.

*4.5.5. N-(tert-Butoxycarbonyl)-2-[1-benzyloxy-2-(tert-butyldimethylsilyloxymethyl)-2,3-octadien-4-yl]aniline (**9e**).* Colorless oil; IR 3421, 1960, 1718 cm^{-1}; ^{1}H NMR δ 7.92 (d, *J*=7.3 Hz, 1H), 7.63–7.62 (m, 1H), 7.27–7.14 (m, 7H), 7.00–6.98 (m, 1H), 4.57, 4.53 (ABq, J_{AB}=12.4, 2H), 4.20, 4.16 (ABq, J_{AB}=12.4 Hz, 2H), 4.08–4.04 (ABq, J_{AB}=11.9 Hz, 2H), 2.31 (t, *J*=7.8 Hz, 2H), 1.53–1.27 (m, 13H), 0.85 (t, *J*=7.3 Hz, 2H), 0.81 (s, 9H), −0.02 (s, 3H), −0.04 (s, 3H); ^{13}C NMR δ 198.7, 153.4, 138.1, 135.9, 128.3, 127.7, 127.64, 127.56, 127.5, 127.2, 122.8, 121.1, 104.8, 103.4, 80.0, 72.0, 67.7, 61.8, 33.8, 30.1, 28.4, 25.8, 22.4, 18.2, 14.0, −5.35, −5.42; FABMS *m*/*z* 552 (M^++1, 0.5); FAB HRMS calcd for $C_{33}H_{50}NO_4Si$ 552.3509, found 552.3507.

*4.5.6. N-(tert-Butoxycarbonyl)-2-[1-benzyloxy-2-(tert-butyldimethylsilyloxymethyl)-8-(p-methoxybenzyloxy)-2,3-octadien-4-yl]aniline (**9f**).* Colorless oil; IR 3420, 1954, 1718 cm^{-1}; ^{1}H NMR δ 7.97 (d, *J*=8.2 Hz, 1H), 7.67 (br s, 1H), 7.28–7.17 (m, 9H), 7.01 (t, *J*=7.8 Hz, 1H), 6.85 (d, *J*=8.7 Hz, 2H), 4.58 (s, 2H), 4.40 (s, 2H), 4.24, 4.19 (ABq, J_{AB}=12.4 Hz, 2H), 4.12, 4.07 (ABq, J_{AB}=12.4 Hz, 2H), 3.79 (s, 3H), 3.41 (t, *J*=6.4 Hz, 2H), 2.40–2.35 (m, 2H), 1.68–1.51 (m, 4H), 1.47 (s, 9H), 0.84 (s, 9H), 0.01 (s, 3H), −0.01 (s, 3H); ^{13}C NMR δ 198.6, 159.0, 153.4, 138.0, 135.9, 130.6, 129.2, 129.0, 128.4, 128.3, 127.7, 127.6, 126.9, 122.8, 121.1, 113.7, 104.6, 103.7, 80.1, 72.5, 72.0, 69.8, 67.6, 61.7, 55.2, 33.8, 29.4, 28.4, 25.8, 24.6, 18.2, −5.36, −5.42; FABMS *m*/*z* 710 (M^++23, 0.5); FAB HRMS calcd for $C_{41}H_{57}NNaO_6Si$ 710.3853, found 710.3845.

4.6. General procedure for the treatment of allenylanilines 9 with TBAF in THF

To a solution of allenylaniline **9** (0.10 mmol) in THF (1 mL) was added TBAF (0.50 M in THF, 1.0 mL, 0.50 mmol) at 0 °C. After stirring at 0–40 °C until the complete disappearance of the starting material (monitored by TLC), the mixture was quenched by saturated aqueous NH_4Cl, extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (9:1) to give indole products. The chemical yields were summarized in Scheme 1 and Table 2.

*4.6.1. N-(tert-Butoxycarbonyl)-2-(4-hydroxy-1,2-butadien-2-yl)aniline (**10a**).* Yellow oil; IR 3396, 1944, 1728 cm^{-1}; ^{1}H NMR δ 7.85 (br s, 1H), 7.32 (br s, 1H), 7.23 (t, *J*=7.2 Hz, 1H), 7.17 (d, *J*=7.2 Hz, 1H), 7.05 (t, *J*=7.2 Hz, 1H), 6.40 (br s, 1H), 5.78 (q, *J*=5.8 Hz, 1H), 4.30 (br s, 2H), 1.52 (s, 9H); ^{13}C NMR δ 204.7, 153.0, 136.2, 129.3, 128.1, 123.79, 123.77, 121.7, 95.3, 94.3, 81.1, 60.3, 28.4; DART MS *m*/*z* 262 (M^++1, 100); DART HRMS calcd for $C_{15}H_{20}NO_3$ 262.1443, found 262.1443.

*4.6.2. N-(tert-Butoxycarbonyl)-2-(4-hydroxy-3-methyl-1,2-butadienyl)aniline (**10b**).* Colorless oil; IR 3377, 1948, 1728 cm^{-1}; ^{1}H NMR δ 7.91 (br s, 1H), 7.59 (br s, 1H), 7.21 (t, *J*=7.6 Hz, 1H), 7.13 (d, *J*=7.6 Hz, 1H), 7.01 (t, *J*=7.6 Hz, 1H) 6.34 (br s, 1H), 4.19 (dd, *J*=13.4, 2.7 Hz, 1H), 4.14 (dd, *J*=13.4, 2.7 Hz, 1H), 1.86 (d, *J*=3.1 Hz, 3H), 1.52 (s, 9H); ^{13}C NMR δ 201.2, 153.0, 136.5, 129.4, 128.0, 123.3, 122.4, 120.8, 104.3, 94.3, 80.7, 63.9, 28.3, 15.8; EIMS *m*/*z* 275 (M^+, 4.0); EI HRMS calcd for $C_{16}H_{21}NO_3$ 275.1521, found 275.1516.

*4.6.3. N-(tert-Butoxycarbonyl)-2-(3-hydroxymethyl-1,2-pentadienyl) aniline (**10c**).* Yellow oil; IR 3373, 1944, 1728 cm^{-1}; ^{1}H NMR δ 7.94 (br s, 1H), 7.62 (br s, 1H), 7.23–7.20 (m, 1H), 7.14 (dd, *J*=7.6, 1.4 Hz, 1H), 7.01 (t, *J*=7.6 Hz, 1H), 6.45 (s, 1H), 4.23 (dd, *J*=13.4, 2.7 Hz, 1H), 4.20 (dd, *J*=13.4, 2.7 Hz, 1H), 2.22–2.10 (m, 2H), 1.52 (s, 9H), 1.12 (t, *J*=7.8 Hz, 3H); ^{13}C NMR δ 200.6, 152.8, 136.4, 129.4, 127.9, 123.2, 123.1, 120.6, 111.3, 96.1, 80.7, 62.9, 28.2, 22.8, 12.0; DART MS *m*/*z* 290 (M^++1, 30); DART HRMS calcd for $C_{17}H_{24}NO_3$ 290.1756, found 290.1737.

*4.6.4. 1-(tert-Butoxylcarbonyl)-2-vinyl-1H-indole (**11a**).* Colorless oil; IR 1724 cm^{-1}; ^{1}H NMR δ 8.07 (d, *J*=8.2 Hz, 1H), 7.50 (d, *J*=7.8 Hz, 1H), 7.28–7.21 (m, 3H), 6.72 (s, 1H), 5.69 (dd, *J*=17.4, 1.4 Hz, 1H), 5.28 (dd, *J*=11.0, 1.8 Hz, 1H), 1.69 (s, 9H); ^{13}C NMR δ 150.5, 139.8, 136.6, 129.4, 129.2, 124.1, 122.9, 120.4, 115.8, 115.6, 106.9, 84.2, 28.2; EIMS *m*/*z* 243 ($M^{+\cdot}$ 8.6); EI HRMS calcd for $C_{15}H_{17}NO_2$ 243.1259, found 243.1552.

*4.6.5. 2-(3-Benzyloxyprop-1-en-2-yl)-1-(tert-butoxylcarbonyl)-1H-indole (**11d**).* Colorless oil; IR 1728 cm^{-1}; ^{1}H NMR δ 8.08 (d, *J*=8.1 Hz, 1H), 7.50 (d, *J*=7.3 Hz, 1H), 7.31–7.18 (m, 7H), 6.54 (s, 1H), 5.48 (d, *J*=1.3 Hz, 1H), 5.40 (d, *J*=1.3 Hz, 1H), 4.53 (s, 2H), 4.29 (s, 2H), 1.58 (s, 9H); ^{13}C NMR δ 150.2, 140.4, 139.3, 138.2, 136.7, 129.2, 128.3, 127.7, 127.5, 124.2, 122.8, 120.4, 116.3, 115.4, 110.3, 84.0, 72.3, 72.1, 28.0; EIMS *m*/*z* 363 (M^+, 9.7); EI HRMS calcd for $C_{23}H_{25}NO_3$ 363.1834, found 363.1838.

*4.6.6. 2-(3-Benzyloxyprop-1-en-2-yl)-1-(tert-butoxylcarbonyl)-3-butyl-1H-indole (**11e**).* Colorless oil; IR 1724 cm^{-1}; ^{1}H NMR δ 8.02 (d, *J*=8.2 Hz, 1H), 7.45 (d, *J*=7.6 Hz, 1H), 7.21–7.16 (m, 7H), 5.60 (s, 1H), 5.19 (s, 1H), 4.49 (s, 2H), 4.11 (s, 2H), 2.60–2.58 (m, 2H), 1.52–1.48 (m, 11H), 1.34–1.28 (m, 2H), 0.86–0.81 (m, 3H); ^{13}C NMR δ 159.1, 139.1, 138.3, 135.9, 134.1, 130.0, 128.3, 127.6, 127.5, 124.2, 122.4, 121.9, 119.1, 116.5, 115.6, 83.7, 72.6, 72.4, 33.1, 28.1, 24.3, 23.1, 14.0; EIMS *m*/*z* 419 (M^+, 4.4); EI HRMS calcd for $C_{27}H_{33}NO_3$ 419.2460, found 419.2459.

*4.6.7. 1-(tert-Butoxylcarbonyl)-2-(3-benzyloxyprop-1-en-2-yl)-3-[4-(p-methoxybenzyloxy)methyl]-1H-indole (**11f**).* Colorless oil; IR 1722 cm^{-1}; ^{1}H NMR δ 8.09 (d, *J*=8.2 Hz, 1H), 7.51 (d, *J*=6.9 Hz, 1H), 7.31–7.19 (m, 9H), 6.87–6.85 (m, 2H), 5.664–5.660 (m, 1H), 5.261–5.257 (m, 1H), 4.54 (s, 2H), 4.41 (s, 2H), 4.18 (s, 2H), 3.79 (s, 3H),

3.45–3.41 (m, 2H), 2.69–2.66 (m, 2H), 1.70–1.67 (m, 4H), 1.58 (s, 9H); ^{13}C NMR δ 159.0, 150.1, 139.0, 138.2, 135.9, 134.2, 130.6, 129.9, 129.2, 128.3, 127.6, 127.5, 124.2, 122.4, 121.5, 119.1, 116.6, 115.5, 113.7, 83.7, 72.6, 72.5, 72.4, 69.8, 55.2, 29.9, 28.0, 27.4, 24.3; EIMS *m*/*z* 555 (M^+, 57); EI HRMS calcd for $C_{35}H_{41}NO_5$ 555.2985, found 555.2988.

*4.6.8. 1-(tert-Butoxycarbonyl)-2-(1-hydroxypropan-2-yl)-1H-indole (**12b**).* Colorless oil; IR 3468, 1740 cm^{-1}; ^{1}H NMR δ 8.26 (br s, 1H), 7.55 (d, *J*=7.8 Hz, 1H), 7.33 (d, *J*=8.2 Hz, 1H), 7.16–7.12 (m, 1H), 7.09–7.05 (m, 1H), 6.31 (s, 1H), 4.25 (dd, *J*=10.5, 6.9 Hz, 1H), 4.19 (dd, *J*=10.5, 6.9 Hz, 1H), 3.30 (sex, *J*=6.9 Hz, 1H), 1.48 (s, 9H), 1.42 (d, *J*=6.9 Hz, 3H); ^{13}C NMR δ 153.4, 140.7, 135.9, 128.2, 121.4, 120.1, 119.6, 110.6, 99.0, 82.5, 71.2, 32.8, 27.7, 16.4; EIMS *m*/*z* 275 (M^+, 93); EI HRMS calcd for $C_{16}H_{21}NO_3$ 275.1521, found 275.1525.

*4.6.9. 1-(tert-Butoxycarbonyl)-2-(1-hydroxybutan-2-yl)-1H-indole (**12c**).* Yellow oil; IR 3468, 1740 cm^{-1}; ^{1}H NMR δ 8.19 (br s, 1H), 7.55 (d, *J*=7.8 Hz, 1H), 7.34 (d, *J*=8.2 Hz, 1H), 7.16–7.12 (m, 1H), 7.09–7.06 (m, 1H), 6.31 (s, 1H), 4.31 (dd, *J*=10.5, 6.4 Hz, 1H), 4.24 (dd, *J*=10.5, 5.5 Hz, 1H), 3.07–3.01 (m, 1H), 1.86–1.72 (m, 2H), 1.46 (s, 9H), 0.95 (t, *J*=7.3 Hz, 3H); ^{13}C NMR δ 153.4, 139.3, 135.9, 128.3, 121.3, 120.0, 119.6, 110.6, 100.0, 82.4, 69.8, 40.3, 27.7, 24.4, 11.8; DART MS *m*/*z* 290 (M^++1, 99); DART HRMS calcd for $C_{17}H_{24}NO_3$ 290.1756, found 290.1760.

4.7. General procedure for the cyclization of allenylanilines 10

To a solution of alcohol **10** (0.10 mmol) in pyridine (0.3 mL), was added ethyl chloroformate (0.018 mL, 0.20 mmol) at 0 °C. The reaction mixture was stirred for 30 min at the same temperature and concentrated to dryness. The residue was a short pad of silica gel with hexane/AcOEt (15:1) to give the crude carbonate. To a solution of the crude carbonate in THF (1 mL) was added TBAF (0.10 mL, 0.30 mmol) at 0 °C. After stirring for 1 h, the mixture was quenched by saturated aqueous NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (20:1) to give 2-vinylindole **11**. The chemical yields were summarized in Scheme 1.

*4.7.1. 1-(tert-Butoxylcarbonyl)-2-(propen-2-yl)indole (**11b**).* Colorless oil; IR 1728 cm^{-1}; ^{1}H NMR δ 8.08 (d, *J*=7.9 Hz, 1H), 7.49 (d, *J*=7.6 Hz, 1H), 7.28–7.25 (m, 1H), 7.22–7.19 (m, 1H), 6.44 (s, 1H), 5.17 (br s, 2H), 2.09 (s, 3H), 1.65 (s, 9H); ^{13}C NMR δ 150.1, 142.9, 139.2, 136.8, 129.2, 124.0, 122.8, 120.4, 115.3, 115.1, 108.3, 83.9, 28.0, 23.2; EIMS *m*/*z* 257 (M^+, 74); EI HRMS calcd for $C_{16}H_{19}NO_2$ 257.1416, found 257.1414.

*4.7.2. 2-(1-Buten-2-yl)-1-(tert-butoxylcarbonyl)-1H-indole (**11c**).* Yellow oil; IR 1728 cm^{-1}; ^{1}H NMR δ 8.10 (d, *J*=8.2 Hz, 1H), 7.49 (d, *J*=7.8 Hz, 1H), 7.29–7.25 (m, 1H), 7.22–7.19 (m, 1H), 6.42 (s, 1H), 5.16–5.14 (m, 2H), 2.40 (q, *J*=7.3 Hz, 2H), 1.63 (s, 9H), 1.04 (t, *J*=7.3 Hz, 3H); ^{13}C NMR δ 150.1, 145.5, 141.8, 136.8, 129.2, 123.9, 122.7, 120.3, 115.3, 113.3, 109.1, 83.8, 29.6, 28.0, 12.9; EIMS *m*/*z* 271 (M^+, 10); EI HRMS calcd for $C_{17}H_{21}NO_2$ 271.1572, found 271.1570.

*4.7.3. Treatment of **9b** with K_2CO_3 in DMF.* To a solution of **9b** (46 mg, 0.12 mmol) in DMF (1 mL) was added K_2CO_3 (26 mg, 0.18 mmol) at room temperature. After stirring at 110 °C for 4 h, the mixture was quenched by water, extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (9:1) to afford **11b** (20 mg, 66%).

*4.7.4. Treatment of **9** with K_2CO_3 and Et_2CO_3 in DMF.* To a solution of allenylaniline **9** (0.12 mmol) in DMF (1 mL) were added K_2CO_3 (20 mg, 0.14 mmol) and Et_2CO_3 (0.14 mL, 1.2 mmol) at room temperature. After stirring at 85–95 °C until the complete disappearance of the starting material (monitored by TLC), the mixture was quenched by saturated aqueous NH_4Cl, extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (9:1) to afford vinylindole **11**. The chemical yields were summarized in Table 2.

*4.7.5. 3-Methyl-2-vinyl-1H-indole (**13g**).* To a solution of 1-(*tert*-butyldimethylsilyloxy)-3-pentyn-2-ol (64 mg, 0.30 mmol) in CH_2Cl_2 (3 mL) were added Et_3N (0.084 mL, 0.60 mmol) and MsCl (0.030 mL, 0.39 mmol) at 0 °C. The reaction mixture was stirred for 1 h, quenched by addition of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of ^{i}Pr$_2$NH (0.072 mL, 0.48 mmol) in THF (3 mL) was added ^{n}BuLi (1.5 M hexane solution, 0.28 mL, 0.42 mmol) at −30 °C. After 30 min, Bu_3SnH (0.12 mL, 0.45 mmol) was added. The reaction mixture was stirred for 30 min at the same temperature and then cooled to −78 °C. CuBr·SMe$_2$ (93 mg, 0.45 mmol) was then added to the reaction mixture and stirring for 30 min at −78 °C. The crude mesylate in THF (1.0 mL) was added to the reaction mixture and the mixture was stirred for 20 min at the same temperature. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was a short pad of silica gel with hexane/AcOEt (50:1) to give the crude 1-(*tert*-butyldimethylsilyloxy)-3-(tributylstannyl)-2,3-pentadiene. To a solution of iodoaniline **7** (25 mg, 0.078 mmol) and the crude 1-(*tert*-butyldimethylsilyloxy)-3-(tributylstannyl)-2,3-pentadiene in DMF (1 mL) were added TFP (4.3 mg, 0.018 mmol), CuI (1.5 mg, 7.8×10^{-3} mmol) and $Pd_2(dba)_3$ (2.2 mg, 2.3×10^{-3} mmol) at room temperature. After stirring for 12 h at the same temperature, the mixture was quenched by addition of 10% aqueous NH_3 solution, and extracted with Et_2O. The extract was washed with water, brine, dried, and concentrated to dryness. To a solution of the crude allenylanilines in DMSO (1 mL) was added KOH (22 mg, 0.39 mmol) at room temperature. After stirring for 20 min, the reaction mixture was quenched by water and extracted with Et_2O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (20:1) to afford **13g** (13 mg, 42% from **7**) as colorless needles. Mp 81.5–82 °C (hexane); IR 3474 cm^{-1}; ^{1}H NMR δ 7.96 (br s, 1H), 7.53 (d, *J*=8.2 Hz, 1H), 7.29 (d, *J*=8.2 Hz, 1H), 7.20–7.07 (m, 2H), 6.86 (dd, *J*=17.9, 11.0 Hz, 1H), 5.43 (d, *J*=17.9 Hz, 1H), 5.24 (d, *J*=11.0 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR δ 136.1, 132.1, 129.4, 129.0, 125.6, 123.0, 119.4, 119.0, 110.6, 110.4, 8.6; EIMS *m*/*z* 157 (M^+, 92); EI HRMS calcd for $C_{11}H_{11}N$ 157.0891, found 157.0893.

*4.7.6. 1,1-Dimethyloxazolo[3,4-a]indol-3(1H)-one (**14b**).* TMSCl (0.015 mL, 0.12 mmol) was added to a solution of NaI (18 mg, 0.12 mmol) in acetonitrile (0.2 mL). After stirring for 20 min, a solution of compound **11b** (10 mg, 0.039 mmol) in acetonitrile (0.2 mL) was added to the reaction mixture and further stirred for 30 min. The reaction mixture was quenched by addition of methanol and water, extracted with CH_2Cl_2. The extract was washed with water, brine, dried, and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (19:1) to afford compound **14b** (6.7 mg, 85%) as colorless crystals mp 64.5–65 °C (CH_2Cl_2); IR 1782 cm^{-1}; ^{1}H NMR δ 7.95 (d, *J*=8.1 Hz, 1H), 7.57 (d, *J*=8.1 Hz, 1H), 7.37–7.29 (m, 2H), 6.30 (s, 1H), 1.78 (s, 6H); ^{13}C NMR δ 149.3, 145.4, 134.5, 129.9, 124.0, 123.8, 121.4, 112.9, 96.2, 83.6, 27.6; EIMS *m*/*z* 201 (M^+, 90); EI HRMS calcd for $C_{12}H_{11}NO_2$ 201.0790, found 201.0793.

*4.7.7. Treatment of **11b** with TFA in CH_2Cl_2.* To a solution of **11b** (20 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was added TFA (0.6×10^{-2} mL, 0.11 mmol) at room temperature. After stirring for 1 h, the mixture was quenched by saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2. The extract was washed with water and brine, dried and

concentrated to dryness. The residue was chromatographed with hexane/AcOEt (19:1) to afford **14b** (15 mg, 76%).

*4.7.8. Treatment of **11b** with HCl in AcOEt.* To a solution of HCl (4 mmol) in AcOEt (1 mL) was added **11b** (20 mg, 0.10 mmol) at room temperature. After stirring for 6 h, the mixture was quenched by saturated aqueous $NaHCO_3$, extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (19:1) to afford **14b** (9.0 mg, 45%).

4.8. General procedure for the deprotection of Boc group of 2-vinylindole 11

KOH (22 mg, 0.40 mmol) was added to a solution of **11** (0.10 mmol) in methanol (1 mL). After stirring for5 h at 70 °C, the reaction mixture was cooled and concentrated. The residue was chromotographed with hexane/AcOEt (9:1) to afford compound **13**. The chemical yields were summarized in Table 3.

*4.8.1. 2-(Propen-2-yl)-1H-indole (**13b**)*[17b,18]. Colorless crystals; IR 3448 cm^{-1}; ^1H NMR δ 8.17 (s, 1H), 7.57 (d, J=7.8 Hz, 1H), 7.33 (t, J=8.1 Hz, 1H), 7.20–7.16 (m, 1H), 7.09–7.06 (m, 1H), 6.55 (d, J=1.2 Hz, 1H), 5.30 (br s, 1H), 5.08 (d, J=1.2 Hz, 1H), 2.19 (s, 3H).

*4.8.2. 2-(Buten-2-yl)-1H-indole (**13c**).* Colorless needles, mp 85.5–86 °C (hexane); IR 3475, 3427 cm^{-1}; ^1H NMR δ 8.14 (br s, 1H), 7.57 (d, J=7.8 Hz, 1H), 7.33 (d, J=8.2 Hz, 1H), 7.19–7.15 (m, 1H), 7.08 (t, J=8.2 Hz, 1H), 6.56 (s, 1H), 5.31 (s, 1H), 5.09 (s, 1H), 2.55 (q, J=7.3 Hz, 2H), 1.22 (t, J=7.3 Hz, 3H); ^{13}C NMR δ 141.5, 138.1, 136.3, 128.8, 122.5, 120.7, 119.9, 110.6, 108.0, 100.7, 27.0, 13.3; EIMS m/z 171 (M^+, 22); EI HRMS calcd for $C_{12}H_{13}N$ 171.1048, found 171.1046.

*4.8.3. 2-[3-(Benzyloxy)propen-2-yl]-1H-indole (**13d**).* Colorless crystals, mp 93–94 °C (CH_2Cl_2); IR 3475, 3427 cm^{-1}; ^1H NMR δ 8.69 (br s, 1H), 7.59–7.55 (m, 1H), 7.38–7.28 (m, 6H), 7.19–7.13 (m, 1H), 7.10–7.04 (m, 1H), 6.65 (dd, J=2.0, 0.8 Hz, 1H), 5.64 (s, 1H), 5.32–5.31 (m, 1H), 4.60 (br s, 2H), 4.43 (br s, 2H); ^{13}C NMR δ 137.7, 136.6, 136.2, 135.8, 128.5, 128.4, 128.0, 127.9, 122.4, 120.6, 120.0, 113.5, 110.8, 100.3, 72.2, 71.8; EIMS m/z 263 (M^+, 86); EI HRMS calcd for $C_{18}H_{17}NO$ 263.1310, found 263.1312.

*4.8.4. Treatment of **9** with KOH in DMSO.* KOH (22 mg, 0.40 mmol) was added to a solution of **9** (0.10 mmol) in DMSO (1 mL). After stirring for 0.25–10 h at room temperature, the reaction mixture was concentrated. The residue was chromotographed with hexane/AcOEt (9:1) to afford compound **13**. The chemical yields were summarized in Table 4.

*4.8.5. 2-Vinyl-1H-indole (**13a**)*[17b,c]. Colorless crystals; IR 3475 cm^{-1}; ^1H NMR δ 8.16 (br s, 1H), 7.56 (d, J=7.8 Hz, 1H), 7.33 (d, J=8.2 Hz, 1H), 7.20–7.16 (m, 1H), 7.10–7.06 (m, 1H), 6.74 (dd, J=17.9, 11.0 Hz, 1H), 6.50 (s, 1H), 5.53 (d, J=17.9 Hz, 1H), 5.26 (d, J=11.0 Hz, 1H).

4.9. General procedure for synthesis of carbazole derivatives

To a solution of 2-vinylindole **13** (0.058 mmol) in toluene (0.6 mL) was added dienophiles (0.29 mmol). After the reaction mixture was heated under reflux until the complete disappearance of the starting material (monitored by TLC), the mixture was cooled and concentrated. The residue was chromatographed with hexane/AcOEt to give the corresponding carbazole derivatives **15**. The chemical yields were summarized in Table 5.

4.9.1. (3R,4S*)-1,2,3,4-Tetrahydro-1H-carbazole-3,4-dicarbonitrile (**15a**).* Colorless needles; mp 168.5–169 °C (hexane/AcOEt); IR 3470 cm^{-1}; ^1H NMR δ 11.72 (br s, 1H), 7.51 (d, J=7.8 Hz, 1H), 7.35 (d, J=8.2 Hz, 1H), 7.13–7.08 (m, 1H), 7.07–7.03 (m, 1H), 4.83 (d, J=6.0 Hz, 1H), 3.87 (dt, J=6.0, 4.1 Hz, 1H), 2.94–2,81 (m, 2H), 2.25–2.22 (m, 2H); ^{13}C NMR δ 135.7, 134.5, 125.1, 121.5, 120.0, 119.23, 119.20, 117.2, 111.3, 99.6, 28.7, 27.2, 23.6, 20.0; DART MS m/z 222 (M^++1, 54); DART HRMS calcd for $C_{14}H_{12}N_3$ 222.1031, found 222.1028.

4.9.2. (1R,3R*,4S*)- and (1R*,3S*,4R*)-1,2,3,4-Tetrahydro-1-methyl-1H-carbazole-3,4-dicarbonitrile (**15b**).* Major diastereomer; Colorless needles; mp 204–205 °C (AcOEt); IR 3468, 2247 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.3 (br s, 1H), 7.53 (d, J=7.9 Hz, 1H), 7.36 (d, J=7.9 Hz, 1H), 7.13 (t, J=7.9 Hz, 1H), 7.06 (t, J=7.9 Hz, 1H), 4.82 (d, J=4.5 Hz, 1H), 3.98–3.96 (m, 1H), 3.15–3.11 (m, 1H), 2.37 (dt, J=13.7, 6.9 Hz, 1H), 1.88–1.83 (m, 1H), 1.37 (d, J=6.9 Hz, 3H); ^{13}C NMR δ 138.9, 135.9, 125.1, 121.6, 120.1, 119.3, 119.2, 117.4, 111.4, 99.4, 31.3, 27.7, 27.1, 25.8, 19.1; DART MS m/z 236 (M^++1, 20); DART HRMS calcd for $C_{15}H_{14}N_3$ 236.1188, found 236.1199.

Minor diastereomer; Colorless needles; mp 257.5–259 °C (AcOEt); IR 3470, 2361 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.2 (br s, 1H), 7.51 (d, J=7.3 Hz, 1H), 7.31 (d, J=7.3 Hz, 1H), 7.07 (t, J=7.3 Hz, 1H), 7.01 (t, J=7.3 Hz, 1H), 4.76 (dd, J=10.5, 2.3 Hz, 1H), 3.75–3.69 (m, 1H), 3.10–3.01 (m, 1H), 2.34 (ddd, J=13.2, 5.5, 2.7 Hz, 1H), 1.79–1.70 (m, 1H), 1.25 (d, J=6.9 Hz, 3H); ^{13}C NMR δ 138.6, 135.9, 124.8, 121.4, 120.5, 119.3, 119.2, 117.2, 111.4, 99.0, 33.4, 29.3, 28.4, 27.4, 18.7; DART MS m/z 236 (M^++1, 81); DART HRMS calcd for $C_{15}H_{14}N_3$ 236.1188, found 236.1200.

4.9.3. (1R,3R*,4S*)- and (1R*,3S*,4R*)-Dimethyl 1,2,3,4-tetrahydro-1-methyl-9H-carbazole-3,4-dicarboxylate (**15c**).* Major diastereomer; Colorless needles; mp 148–149 °C (AcOEt); IR 3472, 1728 cm^{-1}; ^1H NMR δ 7.86 (br s, 1H), 7.61 (d, J=7.8 Hz, 1H), 7.30–7.28 (m, 1H), 7.16–7.13 (m, 1H), 7.12–7.08 (m, 1H), 4.37 (d, J=4.2 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.46 (dt, J=6.8, 4.2 Hz, 1H), 3.10 (sex, J=6.8 Hz, 1H), 2,36 (dt, J=13.4, 6.8 Hz, 1H), 2.05 (ddd, J=13.4, 6.8, 4.2 Hz, 1H), 1.37 (d, J=6.8 Hz, 3H); ^{13}C NMR δ 174.1, 174.0, 138.7, 135.8, 126.9, 121.5, 119.6, 119.0, 110.6, 104.8, 52.10, 52.08, 40.8, 40.5, 31.2, 26.0, 20.0; DART MS m/z 302 (M^++1, 88); DART HRMS calcd for $C_{17}H_{20}NO_4$ 302.1392, found 302.1392.

Minor diastereomer; Colorless needles; mp 129.5–130 °C (AcOEt); IR 3472, 1734 cm^{-1}; ^1H NMR δ 7.92 (br s, 1H), 7.51 (d, J=7.8 Hz, 1H), 7.30 (d, J=7.8 Hz, 1H), 7.16–7.12 (m, 1H), 7.09–7.06 (m, 1H), 4.19 (dd, J=10.3, 2.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.32 (ddd, J=12.9, 10.3, 2.4 Hz, 1H), 3.20–3.14 (m, 1H), 2.44 (ddd, J=10.3, 5.1, 2.4 Hz, 1H), 1.76–1.60 (m, 1H), 1.35 (d, J=7.1 Hz, 3H); ^{13}C NMR δ 174.2, 174.1, 138.8, 135.9, 126.8, 121.5, 119.7, 118.9, 110.7, 104.6, 52.10, 52.06, 44.0, 40.5, 34.1, 26.0, 20.0; EIMS m/z 301 (M^+, 55); EI HRMS calcd for $C_{17}H_{19}NO_4$ 301.1314, found 301.1316.

4.9.4. (1R,3R*,4S*)- and (1R*,3S*,4R*)-Dimethyl 1,2,3,4-tetrahydro-1-ethyl-9H-carbazole-3,4-dicarboxylate (**15d**).* Major diastereomer; Yellow oil; IR 3472, 1728 cm^{-1}; ^1H NMR δ 7.87 (br s, 1H), 7.61 (d, J=7.8 Hz, 1H), 7.28 (d, J=7.8 Hz, 1H), 7.14 (t, J=7.8 Hz, 1H), 7.10 (t, J=7.8 Hz, 1H) 4.36 (d, J=5.0 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.48–3.44 (m, 1H), 2.96–2.89 (m, 1H), 2.29 (ddd, J=13.3, 7.8, 6.0 Hz, 1H), 2.14 (ddd, J=13.3, 5.3, 3.7 Hz, 1H), 1.92–1.83 (m, 1H), 1.71–1.62 (m, 1H), 1.06 (t, J=7.3 Hz, 3H); ^{13}C NMR δ 174.14, 174.12, 137.9, 135.8, 126.9, 121.6, 119.7, 119.0, 110.5, 105.5, 52.12, 52.10, 41.0, 40.5, 32.7, 27.9, 27.3, 11.5; EIMS m/z 315 (M^+, 44); EI HRMS calcd for $C_{18}H_{21}NO_4$ 315.1471, found 315.1465.

Minor diastereomer; Colorless needles; mp 131–132 °C (hexane/AcOEt); IR 3472, 1732 cm^{-1}; ^1H NMR δ 7.94 (br s, 1H), 7.49 (d, J=7.9 Hz, 1H), 7.30 (d, J=7.9 Hz, 1H), 7.14 (t, J=7.9 Hz, 1H), 7.08 (t, J=8.2 Hz, 1H), 4.17 (dd, J=10.7, 2.7 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.27 (ddd, J=12.9, 10.7, 2.7 Hz, 1H), 3.04–2.99 (m, 1H), 2.48 (ddd, J=10.7, 4.1, 2.7 Hz, 1H), 1.98–1.93 (m, 1H), 1.67–1.61 (m, 1H), 1.56–1.53 (m, 1H), 1.02 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 174.14, 174.12,

137.9, 135.8, 126.9, 121.6, 119.7, 119.0, 110.5, 105.5, 52.11, 52.10, 41.0, 40.5, 32.7, 27.9, 27.3, 11.5; DART MS *m/z* 316 (M^++1, 82); DART HRMS calcd for $C_{18}H_{22}NO_4$ 316.1549, found 316.1544.

4.9.5. (3aR,10cR*)-1,3,3a,4,5,10c-Hexahydro-1,3-dioxo-2-phenyl-6H-pyrrolo[3,4-c]carbazole (**15e**)*[16b]. Yellow crystals; IR 3470, 1715 cm^{-1}; ^1H NMR δ 7.99–7.97 (m, 1H), 7.95 (br s, 1H), 7.41–7.37 (m, 2H), 7.34–7.29 (m, 2H), 7.24–7.20 (m, 2H), 7.19–7.14 (m, 2H), 4.47 (d, *J*=7.8 Hz, 1H), 3.60–3.55 (m, 1H), 2.82–2.78 (m, 2H), 2.70–2.62 (m, 1H), 2.11–2.02 (m, 1H).

4.9.6. (3aR,10cR*)-1,3,3a,4,5,10c-Hexahydro-1,3-dioxo-5-methyl-2-phenyl-6H-pyrrolo[3,4-c]carbazole (**15f**)*[16f]. Major diastereomer; Yellow crystals; IR 3474, 1713 cm^{-1}; ^1H NMR δ 8.04 (br s, 1H), 8.01–7.98 (m, 1H), 7.39–7.16 (m, 8H), 4.48 (dd, *J*=8.1, 1.5 Hz, 1H), 3.64–3.57 (m, 1H), 3.07–2.96 (m, 1H), 2.76–2.68 (m, 1H), 1.77–1.66 (m, 1H), 1.41 (d, *J*=7.0 Hz, 3H).

Minor diastereomer; Yellow crystals; IR 3470, 1715 cm^{-1}; ^1H NMR δ 8.03–8.00 (m, 2H), 7.48–7.14 (m, 8H), 4.42 (dd, *J*=8.0, 1.0 Hz, 1H), 3.46 (td, *J*=8.0, 5.8 Hz, 1H), 3.16–3.09 (m, 1H), 2.44 (dt, *J*=12.1, 5.8 Hz, 1H), 2.12–2.01 (m, 1H), 1.37 (d, *J*=6.8 Hz, 3H).

4.9.7. (3aR,5R*,10cR*)- and (3aR*,5S*,10cR*)-1,3,3a,4,5,10c-Hexahydro-1,3-dioxo-5-ethyl-2-phenyl-6H-pyrrolo[3,4-c]carbazole (**15g**).* Major diastereomer; Colorless needles; mp 189–190 °C (AcOEt); IR 3474, 1713 cm^{-1}; ^1H NMR δ 8.05 (br s, 1H), 8.01–8.00 (m, 1H), 7.40–7.38 (m, 2H), 7.33–7.32 (m, 2H), 7.23–7.15 (m, 4H), 4.46 (dd, *J*=8.2, 1.7 Hz, 1H), 3.62 (dt, *J*=8.2, 4.8 Hz, 1H), 2.91–2.86 (m, 1H), 2.69 (dt, *J*=13.4, 4.8 Hz, 1H), 2.01–1.97 (m, 1H), 1.78 (ddd, *J*=13.4, 7.8, 4.8 Hz, 1H), 1.68–1.61 (m, 1H), 1.10 (d, *J*=7.8 Hz, 3H); ^{13}C NMR δ 178.1, 175.9, 137.9, 135.7, 131.9, 128.9, 128.3, 126.8, 126.3, 122.1, 120.3, 120.2, 110.6, 103.5, 40.0, 39.9, 31.6, 26.7, 25.6, 11.1; DART MS *m/z* 345 (M^++1, 64); DART HRMS calcd for $C_{22}H_{21}N_2O_2$ 345.1603, found 345.1586.

Minor diastereomer; Colorless needles; mp 183.5–185 °C (AcOEt); IR 3470, 1713 cm^{-1}; ^1H NMR δ 8.03–8.01 (m, 1H), 7.99 (br s, 1H), 7.45–7.42 (m, 2H), 7.39–7.26 (m, 4H), 7.23–7.15 (m, 2H), 4.45 (dd, *J*=8.7, 1.4 Hz, 1H), 3.46 (dt, *J*=8.7, 6.4 Hz, 1H), 2.93–2.87 (m, 1H), 2.35–2.32 (m, 2H), 1.82–1.74 (m, 1H), 1.61–1.53 (m, 1H), 1.09 (d, *J*=7.3 Hz, 3H); ^{13}C NMR δ 178.7, 175.9, 138.3, 135.8, 132.0, 129.1, 128.4, 127.0, 126.3, 122.2, 120.3, 120.29, 120.27, 110.6, 102.7, 39.55, 39.46, 34.4, 28.1, 27.8, 12.1; EIMS *m/z* 344 (M^+,100); EI HRMS calcd for $C_{22}H_{20}N_2O_2$ 344.1525, found 344.1533.

4.9.8. (7aR,13aR*)-6,7,7a,8,13,13a-Hexahydro-8,13-dioxo-5H-naphtho[2,3-c]carbazole (**15h**).* Red needles; mp 75–78 °C (CH_2Cl_2); IR 3468, 1688 cm^{-1}; ^1H NMR δ 8.08 (dd, *J*=7.2, 1.4 Hz, 1H), 8.02 (dd, *J*=7.2, 1.4 Hz, 1H), 7.88 (br s, 1H), 7.70–7.64 (m, 2H), 7.49 (d, *J*=7.6 Hz, 1H), 7.22 (d, *J*=7.9 Hz, 1H), 7.10–7.08 (m, 1H), 7.06–7.04 (m, 1H), 4.56–4.55 (m, 1H), 3.53–3.50 (m, 1H), 3.03–2.98 (m, 1H), 2.84–2.80 (m, 1H), 2.65–2.60 (m, 1H), 2.07–2.02 (m, 1H); ^{13}C NMR δ 197.7, 197.4, 135.8, 134.7, 134.5, 134.09, 134.06, 134.0, 127.1, 126.9, 126.6, 121.6, 120.0, 118.8, 110.5, 105.9, 48.3, 47.3, 23.9, 20.6; DART MS *m/z* 302 (M^++1, 33); DART HRMS calcd for $C_{20}H_{16}NO_2$ 302.1181, found 302.1183.

*4.9.9. Dimethyl 1-methyl-9H-carbazole-3,4-dicarboxylate (**15i**)*[22]. Yellow crystals; IR 3468, 1717 cm^{-1}; ^1H NMR δ 8.36 (br s, 1H), 7.90–7.86 (m, 2H), 7.45–7.43 (m, 2H), 7.27–7.21 (m, 1H), 4.14 (s, 3H), 3.93 (s, 3H), 2.56 (s, 3H).

*4.9.10. Dimethyl 1-ethyl-9H-carbazole-3,4-dicarboxylate (**15j**).* Yellow needles; mp 170–171 °C (hexane); IR 3460, 1734 cm^{-1}; ^1H NMR δ 8.41 (br s, 1H), 7.42–7.40 (m, 1H), 7.34–7.20 (m, 1H), 7.26 (s, 1H), 7.19–7.12 (m, 2H), 4.03 (s, 3H), 3.80 (s, 3H), 2.98–2.90 (m, 2H), 1.02 (t, *J*=7.2 Hz, 3H); ^{13}C NMR δ 170.2, 166.9, 140.82, 139.86, 127.9, 127.0, 126.5, 125.9, 121.9, 121.6, 120.8, 119.5, 118.5, 111.0, 52.9, 52.3, 24.0, 13.5; EIMS *m/z* 311 (M^+, 40); EI HRMS calcd for $C_{18}H_{17}NO_4$ 311.1158, found 311.1153.

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