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PAPER

Efficient synthesis of carbazoles *via* $PtCl_2$-catalyzed RT cyclization of 1-(indol-2-yl)-2,3-allenols: scope and mechanism†

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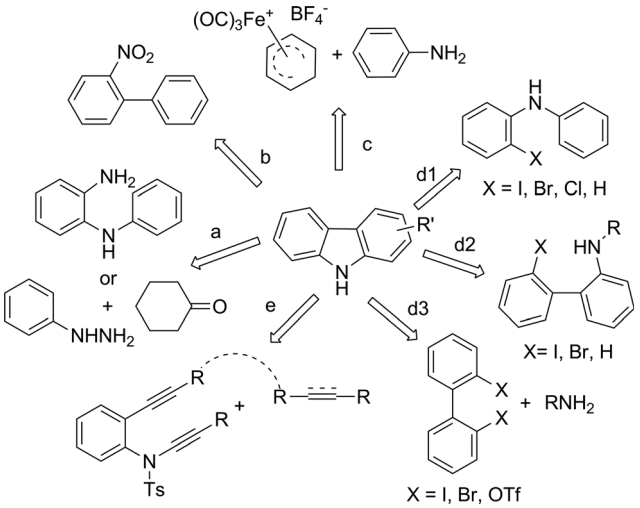
A detailed study on the scope of the efficient $PtCl_2$-catalyzed synthesis of carbazoles from 1-(indol-2-yl)-2,3-allenols is described. Through isotopic labeling experiments, it is confirmed that the reaction proceeds through a unique metal carbene intermediate, which undergoes subsequent highly selective 1,2-hydrogen migration to afford carbazoles. The reaction shows wide scope and allows the introduction of a variety of different substituents at different positions on the carbazole due to the substituent-loading capability of both indole and the allene moiety.

Introduction

Tricyclic carbazole derivatives are well-known alkaloids present in plants, and many of these compounds show biological activities such as anti-oxidative, anti-tumor, anti-bacterial, anti-microbial, psychotropic, anti-histaminic, anti-inflammatory, and antibiotic.[1] In addition, carbazole derivatives are also widely used as organic materials with special thermal,[2] electrical,[3] optical,[3,4] electroluminescent,[5] hole-transporting, and light-emitting properties.[6] The important potential applications of these carbazole derivatives have made them attractive targets for organic synthesis.[7] Scheme 1 schematically presents some of the well-established protocols: (a) classical methods are the Fischer–Borsche synthesis from phenylhydrazone and the Graebe–Ullmann synthesis involving 2-(*N*-phenylamino)anilines; however, the yields and regioselectivity are low;[8] (b) reductive cyclization of *o*-nitrobiphenyl derivatives[9] requires high temperature (>140 °C) and it is almost non-regioselective; (c) the tricarbonyliron cyclohexadienylium salts may react with the arylamines *via* electrophilic aromatic substitution followed by oxidative cyclization to afford carbazoles,[7a,7f,7g] which has already been applied in the total synthesis of various naturally occurring carbazole alkaloids. However, utilization of stoichiometric amounts of tricarbonyliron and oxidant such as MnO_2 make this type of reaction much less attractive; (d) Pd-catalyzed pyrrole formation *via* *N*,*N*-diarylamines (d1),[10] 2-aminobiphenyl (d2),[11] 1,1′-biphenyl-2,2′-diyl ditriflate or 2,2′-dihalobiphenyl (with primary amines) (d3),[12] have also been reported for the construction of carbazoles; however, the starting materials such as *o*-haloanilines, arynes[10a,10b] and boronic acids[11,12] with pre-existing and extensive substitution are difficult to prepare, thus, these methods lacks atom economy/efficiency as well as regioselectivity in some cases; (e) inter- or intramolecular alkyne cyclotrimerizations,[13] nevertheless, require not-readily-available starting materials such as diynamides and the regioselectivity is rather poor (1 : 1 to 6 : 1).



Scheme 1 Main strategies for the synthesis of carbazoles.

For biological screening, the diversity in carbazole synthesis, especially the regioselectivity of the installation of substituents onto each of the nine positions of the carbazole skeleton, is very challenging and important. Thus, the development of a mild, efficient and regio-controlled diversified method for the preparation of carbazole alkaloids, which is suitable for the introduction of specific substituent(s) to any position of the carbazole

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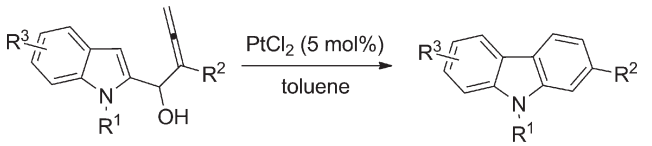
Table 1 $PtCl_2$-catalyzed cyclization reaction of 4-non-substituted 1-(indol-2-yl)-2,3-allenols



1 2

	1				
Entry	R^1	R^2	R^3	Time (h)	Yield of **2** (%)[a]
1	Et	H	H (**1a**)	4	70 (**2a**)
2	Et	*n*-C_4H_9	H (**1b**)	3	74 (**2b**)
3	Et	allyl	H (**1c**)	3	74 (**2c**)
4	Et	Ph	H (**1d**)	4	70 (**2d**)
5	Et	*p*-MeC_6H_4	H (**1e**)	16	69 (**2e**)
6	Et	*p*-$MeOC_6H_4$	H (**1f**)	15	76 (**2f**)
7	Et	COOMe	H (**1g**)	36	67 (**2g**)
8	Et	$CONMe_2$	H (**1h**)	24	83 (**2h**)
9	Et	CH_2OH	H (**1i**)	23	64 (**2i**)
10	Et	CH_2OEt	H (**1j**)	12	84 (**2j**)
11	Et	CH_2OAc	H (**1k**)	24	81 (**2k**)
12	Et	$CH_2OCOOMe$	H (**1l**)	13	77 (**2l**)
13	Et	*n*-C_4H_9	4-Me (**1m**)	18	77 (**2m**)
14	Et	Ph	5-Me (**1n**)	17	70 (**2n**)
15	Et	CH_2OH	4-Me (**1o**)	20	81 (**2o**)
16	Et	CH_2OH	7-Me (**1p**)	21	68 (**2p**)
17	Et	OBn	H (**1q**)	11	60 (**2q**)
18	Me	*n*-C_4H_9	H (**1r**)	4	81 (**2r**)
19	Me	Ph	H (**1s**)	4	71 (**2s**)
20	Ph	Ph	H (**1t**)	19	78 (**2t**)
21	PMP	Ph	H (**1u**)	16	72 (**2u**)

[a] Isolated yield.

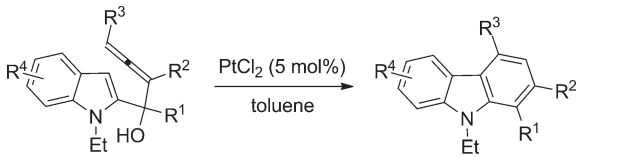
skeleton, is still of high current interest. On the other hand, Pt-catalyzed reactions have recently been demonstrated to be powerful tools in synthetic organic chemistry[14] owing to their extraordinary potential for functional group tolerance.[15] Moreover, these processes are conveniently performed under mild reaction conditions and no significant redox chemistry is involved. Recently, in a communication, we have described a novel approach to the carbazole skeleton through a Pt-catalyzed cyclization of 1-(indol-2-yl)-2,3-allenols.[16] Due to the ready availability of the starting allenols with their strong substituent-loading capability, this method meets the requirement of diversity, selectivity, and is atom economical by just releasing one molecule of water. In this paper, we wish to disclose our recent comprehensive studies on the scope and mechanism.

Results and discussion

Cyclization reaction of 4-non-substituted 1-(indol-2-yl)-2,3-allenols

In the preliminary study, we investigated the generality of the cyclization of various 4-non-substituted 1-(indol-2-yl)-2,3-allenols. Some of the typical results are listed in Table 1: the protecting groups of nitrogen on the indole moiety may be an alkyl (entries 1–19) or an aryl group (entries 20 and 21); R^2 may be H (entry 1), an alkyl (entries 2, 13, and 18), an aryl (entries 4–6, 14, and 19–21), or a benzyloxyl group (entry 17); the reaction of **1c** is especially noteworthy since this reaction shows an interesting exclusive cyclization of the allene instead of the alkene functionality (entry 3);[17] in addition, this reaction tolerates many functional groups, such as COOMe, $CONMe_2$ and CH_2OH (entries 7–9, 15 and 16); in entries 10–12, it should also be noted that the secondary hydroxyl group was exclusively eliminated to form the carbazole ring even when R^2 is CH_2OEt, CH_2OAc or $CH_2OCOOMe$. Moreover, as expected, different substituents may be loaded onto the indole ring to give the corresponding carbazole derivatives smoothly (entries 13–16).

Table 2 $PtCl_2$-catalyzed cyclization reaction of 4-mono-substituted 1-(indol-2-yl)-2,3-allenols



3 4

	3					
Entry	R^1	R^2	R^3	R^4	Time (h)	Yield of **4** (%)[a]
1	H	H	*n*-C_5H_{11}	H (**3a**)	2	83 (**4a**)
2	H	H	Me	H (**3b**)	2	86 (**4b**)
3	H	H	*i*-C_3H_7	H (**3c**)	20	38 (**4c**)
4	H	H	Bn	H (**3d**)	5	50 (**4d**)
5	H	H	Ph	H (**3e**)	14	92 (**4e**)
6	H	H	*n*-C_6H_{13}	5-Me (**3f**)	2	75 (**4f**)
7	H	H	*n*-C_6H_{13}	5-OMe (**3g**)	3	75 (**4g**)
8	H	H	Me	4-Me (**3h**)	20	85 (**4h**)
9	H	H	*n*-C_6H_{13}	4-Me (**3i**)	12	81 (**4i**)
10	H	H	*n*-C_6H_{13}	5-Br (**3j**)	16	75 (**4j**)
11	Me	H	*n*-C_6H_{13}	H (**3k**)	2	81 (**4k**)
12	H	Me	*n*-C_6H_{13}	H (**3l**)	21	78 (**4l**)

[a] Isolated yield.

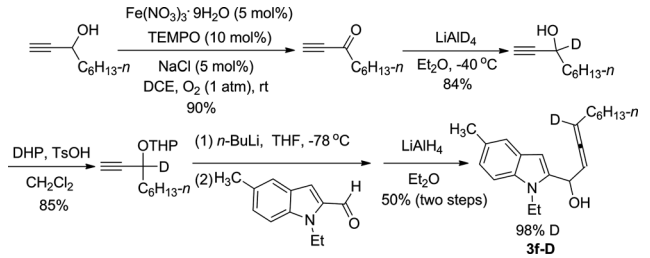
Cyclization reaction of 4-mono-substituted 1-(indol-2-yl)-2,3-allenols

The scope of the reaction with regard to the 4-mono-substituted 1-(indol-2-yl)-2,3-allenols was also examined. The yields are better when R^3 is a normal alkyl group (entries 1, 2 and 6–12, Table 2) or an aryl group (entry 5, Table 2) than those with an isopropyl (entry 3, Table 2) or benzyl group, probably due to the steric effect (entry 4, Table 2). Different substituents may be pre-introduced to the indole ring (entries 6–10, Table 2). The tertiary alcohol **3k** can also smoothly afford the corresponding carbazole **4k** in 81% yield (entry 11, Table 2). Meanwhile, the substitutions can also be introduced to the 2-position of 2,3-allenols (entry 12, Table 2).

Mechanistic study

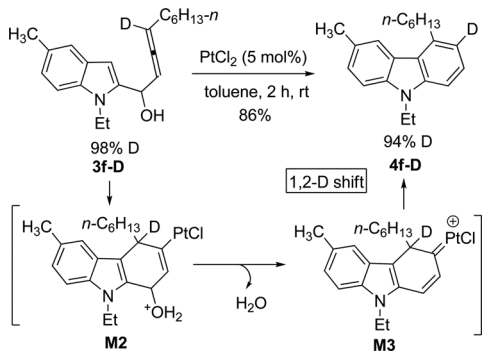
In order to unveil the mechanism, we then prepared the deuterium-labeled *α*-allenol 1-(1-ethyl-5-methyl-1*H*-indol-2-yl)deca-4-deutero-2,3-dien-1-ol **3f-D** (98% D): firstly, oxidation of non-1-yn-3-ol afforded the corresponding alkynone,[18] which was subsequently reduced with $LiAlD_4$.[19] The tetrahydropyranyloxy-

protected propargylic alcohol reacted with n-BuLi to generate the corresponding 1-alkynyl lithium, which was treated with the carbonyl group of indole-2-carbaldehyde, followed by reduction with $LiAlH_4$ to afford **3f-D** (Scheme 2).[20]



Scheme 2 Preparation of **3f-D**.

The reaction of **3f-D** in toluene under the catalysis of $PtCl_2$ (5 mol%) at rt proceeded smoothly affording **4f-D** in 86% yield with 94% D-incorporation at the 3-position of the newly formed phenyl ring. This result led us to propose the mechanism shown in Scheme 3: the reaction of $PtCl_2$ with **3f-D** would form intermediate **M2** *via* the coordination of the allene moiety with the platinum atom followed by nucleophilic attack of indolyl C3 to the metal-activated electrophilic C=C double bond. Subsequent protonation of the hydroxyl group followed by elimination of H_2O affords cyclic vinylic platinum carbene intermediate **M3**. Subsequent 1,2-D shift of carbene intermediate **M3** would afford the final product **4f-D**. The mechanism must be different from that which we previously observed in the Au-catalyzed reaction of 1-arylalka-2,3-dienyl acetates.[21]



Scheme 3 Isotopic distribution experiment and mechanism.

Conclusion

In conclusion, we have reported a new modular synthesis of carbazoles *via* the Pt-catalyzed cyclization of 1-(indol-2-yl)-2,3-allenols that involves 1,2-H migration of a metal carbene intermediate, and demonstrated that this methodology allows for the synthesis of carbazoles with a variety of substituents at almost any position on the rings. Through this study, we have demonstrated that this new methodology for the synthesis of the potentially useful carbazole substructure may find wide applications in organic synthesis and in particular in projects oriented towards drug discovery and new organic materials based on carbazoles. Further studies on the synthetic applications of this reaction are being carried out in our laboratory and will be reported in due course.

Experimental section

General information

^1H and ^{13}C nuclear magnetic resonance spectra were recorded with an instrument operated at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR. $CDCl_3$ was used as solvent in all NMR experiments. Chemical shifts (δ) are given in parts per million (ppm). Infrared spectra were recorded on a FT-IR spectrometer. Mass spectra were obtained in EI mode. HRMS was carried out in EI mode. Thin layer chromatography was performed on pre-coated glass-back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. Toluene and THF were refluxed in the presence of sodium using diphenyl ketone as indicator and distilled right before use. $PtCl_2$ was purchased from Alfa.

For the analytical data of **1a–1d**, **1g–1i**, **1n–1p**, **1r–1t**, **3a–3b**, **3d**, **3f–3g**, **3k**, **2a–2d**, **2g–2i**, **2n–2p**, **2r–2t**, **4a–4b**, **4d**, **4f–4g**, and **4k**, see the supporting information of ref. 16.

1. Synthesis of 3-deutero-1-nonyn-3-ol[23]

To a 10 mL dried three-necked flask were added $Fe(NO_3)_3{\cdot}9H_2O$ (202.5 mg, 0.5 mmol), TEMPO (156.1 mg, 1.0 mmol), NaCl (19.2 mg, 0.5 mmol), non-1-yn-3-ol (1.4002 g, 10 mmol) and DCE (10 mL) under an atmosphere of oxygen. The resulting mixture was stirred at room temperature with oxygen from a balloon until the reaction was complete as monitored by TLC (petroleum ether/ethyl acetate = 10/1). The resulting mixture was diluted with diethyl ether (30 mL), dried over anhydrous Na_2SO_4, and filtered through a short column of silica gel to remove the inorganic salts. After evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 40/1) to afford 1-nonyn-3-one (1.2420 g, 90%).[18] liquid, ^1H NMR (300 MHz, $CDCl_3$) δ 3.21 (s, 1H), 2.57 (t, J = 7.8 Hz, 2H), 1.70–1.58 (m, 2H), 1.40–1.19 (m, 6H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.6, 81.4, 78.3, 45.4, 31.4, 28.5, 23.7, 22.4, 14.0.

To a suspension of $LiAlD_4$ (0.941 g, 23 mmol) in 40 mL of ether was added dropwise a solution of 1-nonyn-3-one (3.501 g, 25 mmol) in 20 mL of ether under N_2 at −78 °C over 30 min. The resulting mixture was stirred at −78 °C for another 1 h and quenched with water. The resulting mixture was extracted with ether. The combined extracts were dried over $MgSO_4$, filtered, evaporated, and purified by chromatography on silica gel to afford 3-deutero-1-nonyn-3-ol (2.997 g, 84%): liquid, ^1H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 1H), 1.92 (s, 1H), 1.80–1.60 (m, 2H), 1.48–1.38 (m, 2H), 1.39–1.20 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 85.0, 72.8, 37.5, 31.7, 28.9, 24.9, 22.5, 14.0.

2. Synthesis of 4-non-substituted 1-(indol-2-yl)-2,3-allenols 1e–1f, 1j–1m and 1u[16]

(1) 1-(1-Ethyl-1*H*-indol-2-yl)-2-(*p*-tolyl)buta-2,3-dien-1-ol (1e). Typical procedure: to a mixture of 1-ethyl-1*H*-indole-2-

carbaldehyde (0.8712 g, 5 mmol) and indium powder (1.1421 g, 10 mmol) in a saturated aqueous solution of NH_4Cl (20 mL) and THF (4 mL) was added 1-bromo-3-(4-methylphenyl)prop-2-yne (1.5812 g, 7.5 mmol) with vigorously stirring at 0 °C. After 10 h, the reaction was complete as monitored by TLC, the mixture was quenched with 20 mL of H_2O, extracted with diethyl ether (20 mL×3), and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **1e** (1.3094 g, 86%): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 1H, ArH), 7.60–7.53 (m, 1H, ArH), 7.52–7.42 (m, 3H, ArH), 7.41–7.27 (m, 3H, ArH), 6.70 (s, 1H, ArH), 6.04–5.90 (m, 1H, CH), 5.58 (dd, J = 12.2 and 2.6 Hz, 1H, one proton from CH_2═), 5.50 (dd, J = 12.0 and 2.4 Hz, 1H, one proton from CH_2═), 4.62–4.27 (m, 2H, NCH_2), 3.11 (d, J = 7.8 Hz, 1H, OH), 2.53 (s, 3H, $ArCH_3$), 1.62 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.0, 139.3, 137.0, 136.9, 129.2, 127.2, 126.3, 121.8, 121.0, 119.3, 109.3, 109.0, 101.6, 82.6, 65.1, 38.3, 21.0, 15.4; IR (neat) ν (cm^{-1}) 3405, 3050, 2976, 2921, 2859, 1941, 1611, 1540, 1511, 1460, 1380, 1347, 1316, 1263, 1221, 1188, 1164, 1139, 1125, 1079, 1042; MS (70 ev, EI) *m/z* (%) 304 (M^++1, 22.67), 303 (M^+, 100); HRMS Calcd for $C_{21}H_{21}NO$ (M^+): 303.1623, Found: 303.1624.

The following compounds **1f**, **1j–1m** and **1u** were prepared according to this procedure.

(2) 1-(1-Ethyl-1*H*-indol-2-yl)-2-(4-methoxyphenyl)-buta-2,3-dien-1-ol (1f). The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (0.8701 g, 5 mmol), indium powder (1.1412 g, 10 mmol), and 3-bromo-1-(4-methoxylphenyl)propyne (1.6910 g, 7.5 mmol) in THF (4 mL) and saturated aqueous NH_4Cl solution (20 mL) at 0 °C for 11 h afforded **1f** (1.1015 g, 69%) (petroleum ether/ethyl acetate = 10/1 ~ 5/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dt, J = 7.9 and 0.9 Hz, 1H, ArH), 7.37–7.31 (m, 1H, ArH), 7.28–7.16 (m, 3H, ArH), 7.09–7.03 (m, 1H, ArH), 6.83–6.75 (m, 2H, ArH), 6.43 (s, 1H, ArH), 5.76 (s, 1H, CH), 5.42 (dd, J = 11.9 and 2.9 Hz, 1H, one proton from CH_2═), 5.34 (dd, J = 12.0 and 2.7 Hz, 1H, one proton from CH_2═), 4.48–4.21 (m, 2H, NCH_2), 3.74 (s, 3H, OCH_3), 2.35 (bs, 1H, OH), 1.44 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 158.7, 139.3, 137.0, 127.7, 127.2, 126.1, 121.8, 121.0, 119.4, 114.0, 109.3, 108.7, 101.7, 82.7, 65.3, 55.2, 38.4, 15.4; IR (neat) ν (cm^{-1}) 3424, 3057, 2973, 2943, 2841, 1941, 1607, 1573, 1510, 1460, 1414, 1347, 1315, 1249, 1180, 1035; MS (70 ev, EI) *m/z* (%) 320 (M^++1, 22.32), 319 (M^+, 100); HRMS Calcd for $C_{21}H_{21}NO_2$ (M^+): 319.1572, Found: 319.1570.

(3) 2-(Ethoxymethyl)-1-(1-ethyl-1*H*-indol-2-yl)buta-2,3-dien-1-ol (1j). The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (0.8701 g, 5 mmol), indium powder (1.2104 g, 10 mmol), and 1-bromo-4-ethoxybut-2-yne (1.3402 g, 7.5 mmol) in THF (4 mL) and saturated aqueous NH_4Cl solution (20 mL) at 0 °C for 17 h afforded **1j** (1.1099 g, 81%) (petroleum ether/ethyl acetate = 10/1~5/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.54 (m, 1H, ArH), 7.30 (dd, J = 8.4 and 0.6 Hz, 1H, ArH), 7.24–7.14 (m, 1H, ArH), 7.13–7.05 (m, 1H, ArH), 6.47 (s, 1H, ArH), 5.57–5.48 (m, 1H, CH), 4.99 (q, J = 2.1 Hz, 2H, CH_2═), 4.20 (dq, J = 7.2 and 1.5 Hz, 2H, NCH_2), 4.08 (dt, J = 11.2 and 1.8 Hz, 1H, one proton from CH_2OC), 3.97 (dt, J = 11.1 and 2.0 Hz, 1H, one proton from CH_2OC), 3.57–3.39 (m, 2H, OCH_2), 3.29–3.19 (m, 1H, OH), 1.34 (t, J = 7.2 Hz, 3H, CH_3), 1.19 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 139.0, 136.9, 127.4, 121.4, 120.7, 119.3, 109.2, 102.7, 100.5, 78.5, 69.5, 66.9, 65.9, 38.3, 15.03, 15.00; IR (neat) ν (cm^{-1}) 3416, 3055, 2975, 2931, 2871, 1958, 1610, 1540, 1480, 1460, 1412, 1373, 1347, 1316, 1271, 1222, 1164, 1138, 1124, 1092, 1036, 1014; MS (70 ev, EI) *m/z* (%) 272 (M^++1, 14.64), 271 (M^+, 75.93), 182 (100); HRMS Calcd for $C_{17}H_{21}NO_2$ (M^+): 271.1572, Found: 271.1571.

(4) 2-((1-Ethyl-1*H*-indol-2-yl)(hydroxy)methyl)buta-2,3-dienyl acetate (1k). The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (0.6954 g, 4 mmol), indium powder (1.1412 g, 10 mmol), and 4-bromobut-2-ynyl acetate (1.5612 g, 7.5 mmol) in THF (4 mL) and saturated aqueous NH_4Cl solution (20 mL) at 0 °C for 20 h afforded **1k** (0.6988 g, 61%) (petroleum ether/ethyl acetate = 10/1~5/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.51 (m, 1H, ArH), 7.31 (d, J = 8.1 Hz, 1H, ArH), 7.26–7.14 (m, 1H, ArH), 7.13–7.02 (m, 1H, ArH), 6.25 (d, J = 1.2 Hz, 1H, ArH), 5.50–5.41 (m, 1H, CH), 5.15–5.01 (m, 2H, CH_2═), 4.68 (d, J = 12.0 Hz, 1H, one proton from CH_2OAc), 4.54 (d, J = 12.0 Hz, 1H, one proton from CH_2OAc), 4.22 (q, J = 7.2 Hz, 2H, NCH_2), 3.01–2.68 (m, 1H, OH), 1.92 (s, 3H, $COCH_3$), 1.36 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.2, 170.8, 138.2, 137.1, 127.2, 121.8, 120.9, 119.5, 109.3, 102.5, 100.9, 80.4, 66.0, 62.2, 38.5, 20.8, 15.1; IR (neat) ν (cm^{-1}) 3425, 3039, 2980, 2925, 1960, 1739, 1606, 1543, 1461, 1378, 1347, 1316, 1233, 1165, 1027; MS (70 ev, EI) *m/z* (%) 286 (M^++1, 19.08), 285 (M^+, 93.58), 182 (100); HRMS Calcd for $C_{17}H_{19}NO_3$ (M^+): 285.1365, Found: 285.1366.

(5) 2-((1-Ethyl-1*H*-indol-2-yl)(hydroxy)methyl)buta-2,3-dienyl methyl carbonate (1l). The reaction of 1-ethyl-1*H*-indole-2-carbaldehyde (0.6752 g, 4 mmol), indium powder (1.2105 g, 10 mmol), and 4-bromobut-2-ynyl methyl carbonate (1.2452 g, 6.0 mmol) in THF (4 mL) and saturated aqueous NH_4Cl solution (20 mL) at 0 °C for 11 h afforded **1l** (0.7103 g, 61%) (petroleum ether/ethyl acetate = 10/1~5/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dt, J = 7.6 and 1.0 Hz, 1H, ArH), 7.32 (dd, J = 8.1 and 0.9 Hz, 1H, ArH), 7.25–7.16 (m, 1H, ArH), 7.13–7.04 (m, 1H, ArH), 6.47 (s, 1H, ArH), 5.56–5.45 (m, 1H, CH), 5.19–5.04 (m, 2H, CH_2═), 4.78 (dt, J = 12.0 and 1.8 Hz, 1H, one proton from CH_2OCOO), 4.59 (dt, J = 12.3 and 2.3 Hz, 1H, one proton from CH_2OCOO), 4.35–4.18 (m, 2H, NCH_2), 3.69 (s, 3H, $COOCH_3$), 2.53 (d, J = 6.3 Hz, 1H, OH), 1.37 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 155.5, 138.1, 137.1, 127.2, 121.9, 120.9, 119.5, 109.4, 102.2, 100.9, 80.5, 65.7, 65.6, 54.9, 38.4, 15.1; IR (neat) ν (cm^{-1}) 3487, 3056, 2957, 2883, 1960, 1748, 1611, 1540, 1461, 1375, 1347, 1264, 1165, 1139, 1126, 1106, 1080, 1037, 1014; MS (70 ev, EI) *m/z* (%) 302 (M^++1, 8.92), 301 (M^+, 46.48), 182 (100); HRMS Calcd for $C_{17}H_{19}NO_4$ (M^+): 301.1314, Found: 301.1312.

(6) 1-(1-Ethyl-4-methyl-1*H*-indol-2-yl)-2-butylbuta-2,3-dien-1-ol (1m). The reaction of 1-ethyl-4-methyl-1*H*-indole-2-carbaldehyde (0.9359 g, 5 mmol), indium powder (1.1512 g, 10 mmol), and 1-bromohept-2-yne (1.3219 g, 7.5 mmol) in THF (4 mL) and saturated aqueous NH_4Cl solution (20 mL) at 0 °C for

12 h afforded **1m** (1.1462 g, 81%) (petroleum ether/ethyl acetate = 20/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.05 (m, 2H, ArH), 6.88 (d, J = 6.6 Hz, 1H, ArH), 6.44 (s, 1H, ArH), 5.26 (t, J = 2.4 Hz, 1H, CH), 5.10–4.91 (m, 2H, CH_2═), 4.23 (d, J = 7.2 Hz, 2H, NCH_2), 2.53 (s, 3H, $ArCH_3$), 2.29 (d, J = 5.7 Hz, 1H, OH), 2.07–1.79 (m, 2H, CH_2), 1.51–1.21 (m, 7H, 2×CH_2+CH_3), 0.86 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.1, 138.2, 136.8, 130.3, 127.1, 121.9, 119.6, 107.0, 99.5, 80.4, 67.6, 38.5, 29.7, 28.3, 22.3, 18.6, 15.1, 13.9; IR (neat) ν (cm^{-1}) 3416, 3050, 2957, 2930, 2871, 1956, 1606, 1587, 1541, 1495, 1456, 1429, 1378, 1350, 1296, 1235, 1159, 1128, 1080, 1031; MS (70 ev, EI) m/z (%) 283 (M^+, 38.24), 266 (100); HRMS Calcd for $C_{19}H_{25}NO$ (M^+): 283.1936, Found: 283.1935.

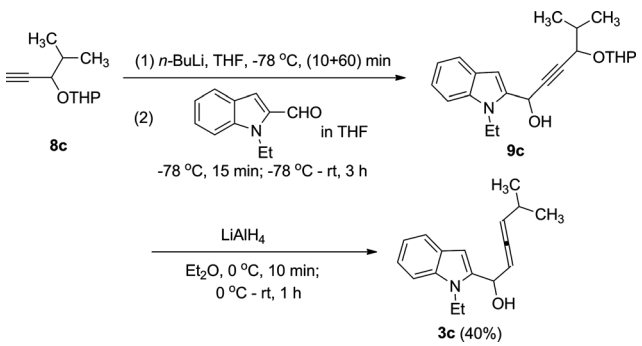
(7) 1-(1-(4-Methoxybenzyl)-1*H*-indol-2-yl)-2-phenyl-buta-2,3-dien-1-ol (1u). The reaction of 1-(4-methoxybenzyl)-1*H*-indole-2-carbaldehyde (0.9912 g, 4 mmol), indium powder (1.0125 g, 8 mmol), and 3-bromo-1-phenylpropyne (1.1925 g, 6 mmol) in THF (4 mL) and saturated aqueous NH_4Cl solution (20 mL) at 0 °C for 10 h afforded **1u** (1.3000 g, 91%) (petroleum ether/ethyl acetate = 5/1∼3/1): oil;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.50 (m, 1H, ArH), 7.33–7.24 (m, 1H, ArH), 7.21–7.02 (m, 7H, ArH), 7.01–6.91 (m, 2H, ArH), 6.83–6.74 (m, 2H, ArH), 6.50 (s, 1H, ArH), 5.69 (dt, J = 8.3 and 2.6 Hz, 1H, CH), 5.49 (d, J = 2.4 Hz, 2H, NCH_2), 5.40 (dd, J = 12.2 and 2.9 Hz, 1H, one proton from CH_2═), 5.32 (dd, J = 12.0 and 2.7 Hz, 1H, one proton from CH_2═), 3.75 (s, 3H, OCH_3), 2.29 (d, J = 8.4 Hz, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 158.9, 139.9, 138.2, 133.7, 130.0, 128.3, 127.5, 127.1, 127.0, 126.4, 122.3, 121.0, 119.7, 114.1, 109.6, 109.1, 102.4, 82.8, 64.8, 55.3, 46.4; IR (neat) ν (cm^{-1}) 3422, 3055, 2937, 2841, 1941, 1612, 1582, 1512, 1495, 1461, 1420, 1348, 1315, 1246, 1176, 1034; MS (70 ev, EI) m/z (%) 382 (M^++1, 8.05), 381 (M^+, 25.66), 121 (100); HRMS Calcd for $C_{26}H_{23}NO_2$ (M^+): 381.1729, Found: 381.1731.

3. Synthesis of 1-(1-ethyl-1*H*-indol-2-yl)-2-(benzyloxy)buta-2,3-dien-1-ol (1q)[22]

Typical procedure: to a solution of benzyloxylpropa-1,2-diene (1.6012 g, 11 mmol) in THF (30 mL) was added dropwise n-BuLi (4 mL, 2.5 M in hexane, 10 mmol) at −40 °C with stirring under a nitrogen atmosphere within 10 min. After being stirred for 50 min at −40 °C, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (1.7412 g, 10 mmol) in THF (10 mL) was added dropwise at this temperature within 20 min. Then the mixture was allowed to warm up to room temperature, quenched with a saturated aqueous solution of NH_4Cl (20 mL), and extracted with diethyl ether (25 mL×3). The combined organic layer was washed with water and dried over anhydrous K_2CO_3. After filtration and evaporation, the residue was purified by column chromatography on alkali-Al_2O_3 (petroleum ether/ethyl acetate = 5/l∼3/1) to give **1q** (1.8125 g, 57%): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 1H, ArH), 7.38–7.26 (m, 6H, ArH), 7.24–7.16 (m, 1H, ArH), 7.13–7.04 (m, 1H, ArH), 6.52 (s, 1H, ArH), 5.61 (d, J = 2.4 Hz, 2H, CH_2═), 5.48 (d, J = 7.2 Hz, 1H, CH), 4.76 (d, J = 12.0 Hz, 1H, one proton from OCH_2), 4.71 (d, J = 12.0 Hz, 1H, one proton from OCH_2), 4.36–4.14 (m, 2H, NCH_2), 2.46 (d, J = 7.5 Hz, 1H, OH), 1.36 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 138.2, 136.92, 136.90, 133.2, 128.4, 127.9, 127.8, 127.4, 121.7, 121.0, 119.3, 109.3, 101.0, 93.6, 71.0, 67.0, 38.5, 15.2; IR (neat) ν (cm^{-1}) 3416, 3033, 2979, 2929, 2865, 1959, 1612, 1537, 1459, 1380, 1347, 1316, 1218, 1164, 1014; MS (70 ev, EI) m/z (%) 320 (M^++1, 3.24), 319 (M^+, 14.10), 172 (100); HRMS Calcd for $C_{21}H_{21}NO_2$ (M^+): 319.1572, Found: 319.1574.

4. Synthesis of 4-mono-substituted 1-(indol-2-yl)-2,3-allenols 3c, 3f-D, and 3h–3j

(1) 1-(1-Ethyl-1*H*-indol-2-yl)-5-methylhexa-2,3-dien-1-ol (3c). Typical procedure: to a solution of **8c** (1.1012 g, 6 mmol) and THF (25 mL) was added dropwise n-BuLi (2.5 mL, 2.5 M in hexane, 6 mmol) at −78 °C with stirring under a nitrogen atmosphere within 10 min. After being stirred for 1 h at −78 °C, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (1.0354 g, 6 mmol) in anhydrous THF (5 mL) was added dropwise at this temperature within 15 min. Then the mixture was allowed to warm up to room temperature, quenched with a saturated aqueous solution of NH_4Cl (20 mL), and extracted with diethyl ether (25 mL×3). The ether layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated *in vacuo*. The product **9c** was then used without further purification.

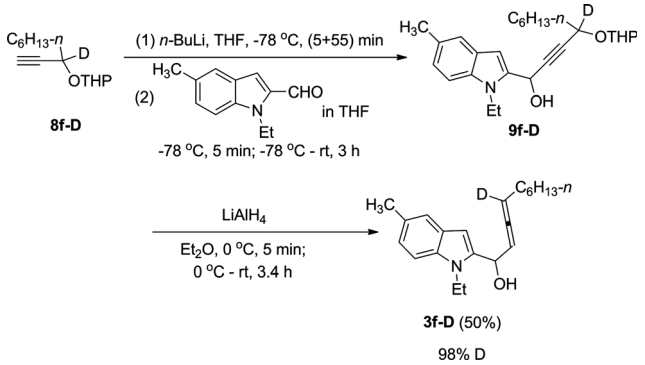


To an ice-cold suspension of $LiAlH_4$ (0.2357 g, 6 mmol) in dry Et_2O (25 mL) under N_2 was added dropwise a solution of **9c** prepared in the previous step in Et_2O (5 mL) within 10 min. Then the mixture was allowed to warm up to room temperature. After being stirred for 1 h, the resulting mixture was quenched with water. The aqueous layer was extracted with diethyl ether (15 mL × 3) and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) gave **3c** (0.6167 g, combined yield from **8c** to **3c** is 40%): solid; m.p. 71.2–72.5 °C (ethyl acetate/n-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.0 and 0.8 Hz, 1H, ArH), 7.35 (dd, J = 8.3 and 0.8 Hz, 1H, ArH), 7.28–7.18 (m, 1H, ArH), 7.15–7.05 (m, 1H, ArH), [(6.51, s), (6.50, s), 1H, ArH], 5.78–5.66 (m, 1H, CH), 5.58–5.48 (m, 1H, CH═), 5.47–5.37 (m, 1H, CH═), 4.47–4.20 (m, 2H, NCH_2), 2.50–2.30 (m, 1H, $CH(Me)_2$), [2.09 (d, J = 6.6 Hz), 2.06 (d, J = 6.6 Hz), 1H, OH], 1.43 (t, J = 7.2 Hz, 3H, CH_2), [1.09 (d, J = 6.6 Hz), 1.04 (d, J = 6.6 Hz), 6H, 2×CH_3]; IR (KBr) ν (cm^{-1}) 3374, 3047, 2961, 2930, 2866, 1962, 1610, 1540, 1460, 1420, 1379, 1347, 1315, 1220, 1165, 1127, 1078, 1041; MS (70 ev, EI) m/z (%) 256 (M^++1, 4.37), 255 (M^+, 22.59), 237 (M^+-OH, 76.37), 222 (100); Elemental analysis calcd (%) for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49; Found: C, 80.11, H, 8.17; N, 5.27.

Compounds **3f-D** and **3h–3j** were prepared according to this procedure.

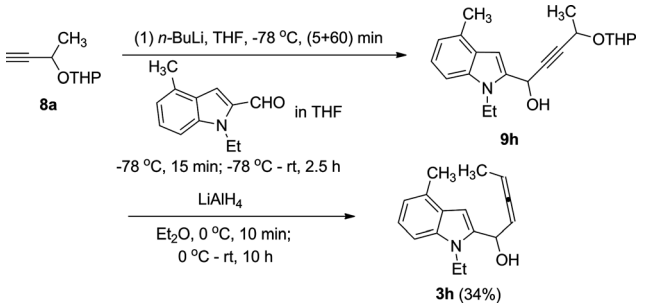
(2) 1-(1-Ethyl-5-methyl-1*H*-indol-2-yl)-4-deuterodeca-2,3-dien-1-ol (3f-D). The reaction of **8f-D**,[23] prepared from 3-deutero-1-nonyn-3-ol described in the Experimental Part 1 of this manuscript (0.7225 g, 3.2 mmol)/THF (15 mL), n-BuLi (1.3 mL, 2.5 M in hexane, 3.3 mmol), and 1-ethyl-5-methyl-1*H*-indole-2-carbaldehyde (0.5910 g, 3.2 mmol)/THF (5 mL) afforded **9f-D**. The product **9f-D** was then used without further purification.

The reaction of **9f-D** and $LiAlH_4$ (0.1247 g, 3.3 mmol) in Et_2O (25 mL) afforded **3f-D** (0.4881 g, combined yield from **8f-D** to **3f-D** is 50%, 98% D) (petroleum ether/ethyl acetate = 10/1): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.34 (m, 1H, ArH), 7.22 (d, J = 8.4 Hz, 1H, ArH), 7.03 (dd, J = 8.4 Hz and 1.5 Hz, 1H, ArH), [(6.40, s)(6.39, s), 1H, ArH], 5.65–5.55 (m, 1H, CH), 5.45–5.35 (m, 1H, CH═), 4.40–4.15 (m, 2H, NCH_2), 2.43 (s, 3H, $ArCH_3$), 2.15–1.98 (m, 3H, CH_2+OH), 1.50–1.20 (m, 11H, 4×CH_2+CH_3), 0.95–0.80 (m, 3H, CH_3); IR (neat) ν (cm^{-1}); 3385, 2955, 2927, 2856, 1955, 1573, 1542, 1483, 1456, 1415, 1378, 1347, 1299, 1270, 1224, 1181, 1159, 1126, 1113, 1079; MS (70 ev, EI) *m/z* (%) 313 (M^++1, 19.69), 312 (M^+, 96.31), 212 (M^+-$C_7H_{14}D$, 100); Elemental analysis calcd for $C_{21}H_{28}NOD$: C, 80.72; H, 9.68; N, 4.48; Found: C, 80.59, H, 9.60; N, 4.36.



(3) 1-(1-Ethyl-4-methyl-1*H*-indol-2-yl)penta-2,3-dien-1-ol (3h). The reaction of **8a** (0.8315 g, 5 mmol)/THF (35 mL), n-BuLi (2 mL, 2.5 M in hexane, 5 mmol) and 1-ethyl-4-methyl-1*H*-indole-2-carbaldehyde (0.9412 g, 5 mmol)/THF (5 mL) afforded **9h**. The product **9h** was then used without further purification.

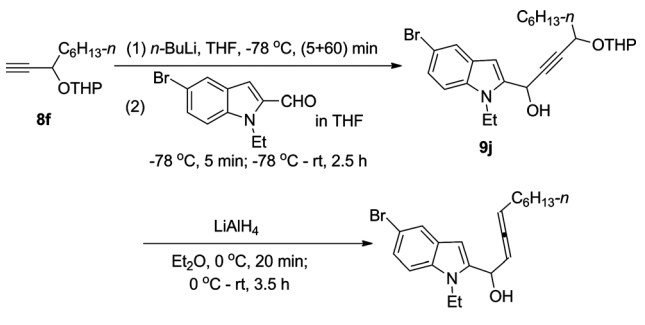
The reaction of **9h** and $LiAlH_4$ (0.2001 g, 5 mmol) in Et_2O (30 mL) afforded **3h** (0.4047 g, combined yield from **8a** to **3h** is 34%) (petroleum ether/ethyl acetate = 10/1∼5/1): solid; m.p. 125–126 °C (ethyl acetate/n-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.23–7.07 (m, 2H, ArH), 6.89 (d, J = 7.2 Hz, 1H, ArH), [(6.52, s), (6.48, s), 1H, ArH], 5.70≥5.57 (m, 1H, CH), 5.56–5.34 (m, 2H, CH═), 4.43–4.19 (m, 2H, NCH_2), 2.54 (s, 3H, $ArCH_3$), 2.12–2.02 (m, 1H, OH), 1.84–1.68 (m, 3H, CH_3C═), 1.41 (t, J = 7.4 Hz, 3H, CH_3); IR (KBr) ν (cm^{-1}) 3312, 2979, 2936, 2898, 1967, 1604, 1584, 1537, 1495, 1467, 1448, 1430, 1368, 1349, 1277, 1238, 1159, 1150, 1081; MS (70 ev, EI) *m/z* (%) 242 (M^++1, 17.43), 241 (M^+, 100); Elemental analysis calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80; Found: C, 79.62, H, 7.98; N, 5.64.



(4) 1-(1-Ethyl-4-methyl-1*H*-indol-2-yl)deca-2,3-dien-1-ol (3i). The reaction of **8f** (0.9124 g, 4 mmol)/THF (25 mL), n-BuLi (1.7 mL, 2.5 M in hexane, 4 mmol), and 1-ethyl-4-methyl-1*H*-indole-2-carbaldehyde (0.7412 g, 4 mmol)/THF (5 mL) afforded **9i**. The product **9i** was then used without further purification.

The reaction of **9i** and $LiAlH_4$ (0.1565 g, 4 mmol) in Et_2O (30 mL) afforded **3i** (0.3860 g, combined yield from **8f** to **3i** is 31%) (petroleum ether/ethyl acetate = 10/1): solid; m.p. 65.3–66.9 °C (ethyl acetate/n-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.04 (m, 2H, ArH), 6.91 (d, J = 6.6 Hz, 1H, ArH), [(6.524, s)(6.515, s), 1H, ArH], 5.71–5.59 (m, 1H, CH), 5.54–5.37 (m, 2H, CH═), 4.43–4.19 (m, 2H, NCH_2), 2.55 (s, 3H, $ArCH_3$), 2.20–2.01 (m, 3H, NCH_2+OH), 1.55–1.20 (m, 11H, 4×CH_2+CH_3), 0.97–0.84 (m, 3H, CH_3); IR (KBr) ν (cm^{-1}) 3312, 2954, 2926, 2854, 1964, 1588, 1534, 1495, 1455, 1432, 1368, 1350, 1287, 1233, 1158, 1147; MS (70 ev, EI) *m/z* (%) 311 (M^+, 4.60), 293 (M^+-H_2O, 100); Elemental analysis calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.38; N, 4.50; Found: C, 80.98, H, 9.50; N, 4.47.

(5) 1-(5-Bromo-1-ethyl-1*H*-indol-2-yl)deca-2,3-dien-1-ol (3j). The reaction of **8f** (0.4601 g, 2 mmol)/THF (10 mL), n-BuLi (0.8 mL, 2.5 M in hexane, 2 mmol) and 1-ethyl-5-bromo-1*H*-indole-2-carbaldehyde (0.5035 g, 2 mmol)/THF (5 mL) afforded **9j**. The product **9j** was then used without further purification.



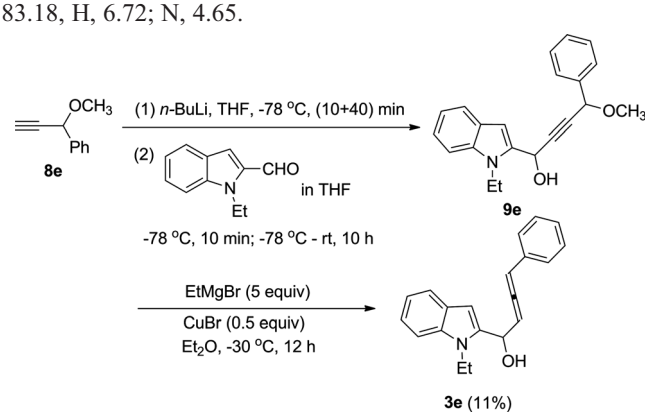
The reaction of **9j** and $LiAlH_4$ (0.0891 g, 2 mmol) in Et_2O (20 mL) afforded **3j** (0.2297 g, combined yield from **8f** to **3j** is 31%) (petroleum ether/ethyl acetate = 10/1–5/1): liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (t, J = 1.5 Hz, 1H, ArH), 7.29 (dd, J = 8.7 and 1.8 Hz, 1H, ArH), 7.18 (d, J = 9.0 Hz, 1H, ArH), [(6.42, s)(6.41, s), 1H, ArH], 5.65–5.53 (m, 1H, CH), 5.52–5.42 (m, 1H, CH═), 5.41–5.31 (m, 1H, CH═), 4.38–4.08 (m, 2H, NCH_2), 2.37 (bs, 1H, OH), 2.19–2.00 (m, 2H, CH_2), 1.55–1.19 (m, 11H, 4×CH_2+CH_3), 1.00–0.83 (m, 3H, CH_3); IR

(neat) ν (cm^{-1}) 3355, 2955, 2927, 2855, 1964, 1609, 1567, 1540, 1462, 1447, 1410, 1379, 1349, 1326, 1265, 1216, 1160, 1146, 1128, 1113, 1079; MS (70 ev, EI) *m/z* (%) 377 (M^+(^{81}Br), 37.58), 375 (M^+(^{79}Br), 38.74), 145 (100); Elemental analysis calcd for $C_{20}H_{26}NBrO$: C, 65.13; H, 7.16; N, 3.62; C, 65.33; H, 7.46; N, 3.30.

5. Synthesis of 1-(1-ethyl-1*H*-indol-2-yl)-4-phenylbuta-2,3-dien-1-ol (3e)

To a solution of **8e** (1.4657 g, 10 mmol) and THF (25 mL) was slowly added dropwise n-butyl lithium (4.0 mL, 2.5 M in hexane, 10 mmol) at −78 °C with stirring under a nitrogen atmosphere within 10 min. After being stirred for 40 min at −78 °C, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (1.7314 g, 10 mmol) in anhydrous THF (5 mL) was added dropwise at this temperature within 10 min. Then the mixture was allowed to warm up to room temperature, quenched with the addition a saturated aqueous solution of NH_4Cl (20 mL), and extracted with diethyl ether (25 mL×3). The ether layer was dried over anhydrous Na_2SO_4, filtrated, concentrated *in vacuo*, and column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) afforded **9e**, which was then used in the next step.

To a solution of CuBr (0.7251 g, 5 mmol) and **9e** in Et_2O (50 mL) was added dropwise a solution of EtMgBr in Et_2O (50 mL, 1 M in Et_2O, 50 mmol) at −30 °C with stirring under a nitrogen atmosphere within 40 min. After the addition, the reaction mixture was stirred for 12 h as monitored by TLC at this temperature, quenched with saturated ammonium chloride solution (30 mL), extracted with ether (3 × 30 mL), washed with water, and dried over anhydrous Na_2SO_4. Filtration, evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1–10/1) afforded **3e** (0.3225 g, 11%): solid; m.p. 122–123 °C (ethyl acetate/n-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H, ArH), 7.43–7.18 (m, 7H, ArH), 7.11 (t, J = 7.4 Hz, 1H, ArH), 6.58 (s, 1H, ArH), 6.48 (dd, J = 6.5 and 2.3 Hz, 1H, CH═), 6.12 (t, J = 6.2 Hz, 1H, CH═), 5.63–5.50 (m, 1H, CH), 4.48–4.18 (m, 2H, NCH_2), 2.14 (d, J = 6.6 Hz, 1H, OH), 1.41 (t, J = 7.2 Hz, 3H, CH_3); IR (KBr) ν (cm^{-1}) 3321, 3045, 2985, 1953, 1489, 1460, 1347, 1314, 1221, 1161, 1101, 1026; MS (70 ev, EI) *m/z* (%) 290 (M^++1, 8.67), 289 (M^+, 40.09), 198 (100); Elemental analysis calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84; Found: C, 83.18, H, 6.72; N, 4.65.



6. Synthesis of 1-(1-ethyl-1*H*-indol-2-yl)-2-methyldeca-2,3-dien-1-ol (3l)[24]

To a solution of 3-chlorononon-1-yne (1.1902 g, 7.5 mmol) in Et_2O (25 mL) was added dropwise n-BuLi (3 mL, 2.5 M in hexane, 7.5 mmol) at −78 °C with stirring under a nitrogen atmosphere within 10 min. After being stirred for 40 min at −78 °C, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (1.2995 g, 7.5 mmol) in anhydrous Et_2O (5 mL) was added dropwise at this temperature within 5 min. Then the mixture was allowed to warm up to −40 °C within 1.2 h. CuCN (34.0 mg, 0.38 mmol) was then added at −60 °C, followed by the addition of a solution of CH_3MgBr in Et_2O (7.5 mL, 3 M in Et_2O, 22.5 mmol) dropwise at −60 °C with stirring under a nitrogen atmosphere within 15 min. After the addition was over, the reaction mixture was stirred for 21 h at −30 °C as monitored by TLC, quenched with saturated ammonium chloride solution (30 mL), extracted with ether (3 × 30 mL), washed with water, and dried over anhydrous Na_2SO_4. Filtration, evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded **3l** (0.4652 g, 20%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H, ArH), 7.31 (d, J = 8.1 Hz, 1H, ArH), 7.25–7.14 (m, 1H, ArH), 7.13–7.01 (m, 1H, ArH), 6.44 (s, 1H, ArH), 5.46–5.37 (m, 1H, CH═), 5.26–5.18 (m, 1H, CH), 4.26 (q, J = 7.2 Hz, 2H, NCH_2), 2.24 (d, J = 5.7 Hz, 1H, OH), 2.06 (q, J = 6.9 Hz, 2H, CH_2), 1.68 (d, J = 2.7 Hz, 3H, CH_3C =), 1.46–1.20 (m, 11H, 4×CH_2+CH_3), 0.91–0.82 (m, 3H, CH_3); IR (neat) ν (cm^{-1}) 3401, 2959, 2926, 2855, 1971, 1656, 1614, 1563, 1537, 1459, 1372, 1346, 1315, 1227, 1168, 1123, 10100; MS (70 ev, EI) *m/z* (%) 311 (M^+, 9.76), 293 (M^+-H_2O, 69.25), 208 (100); Elemental analysis calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.38; N, 4.50; Found: C, 80.74, H, 9.49; N, 4.38.

7. Synthesis of carbazoles[16]

(1) 9-Ethyl-2-*p*-tolyl-9*H*-carbazole (2e). Typical procedure: to a dry Schlenk tube were added sequentially $PtCl_2$ (4.1 mg, 0.015 mmol), **1e** (92.5 mg, 0.31 mmol), and toluene (1.5 mL) under N_2. After continuous stirring for 16 h at rt, the reaction was complete as monitored by TLC. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) afforded **2e** (60.2 mg, 69%): solid; m.p. 146–147 °C (ethyl acetate/n-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15–8.04 (m, 2H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.49–7.40 (m, 2H, ArH), 7.37 (d, J = 7.8 Hz, 1H, ArH), 7.33–7.14 (m, 3H, ArH), 4.35 (q, J = 7.2 Hz, 2H, NCH_2), 2.40 (s, 3H, $ArCH_3$), 1.41 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.45, 140.38, 139.4, 139.1, 136.8, 129.5, 127.4, 125.5, 122.8, 122.0, 120.6, 120.4, 118.9, 118.4, 108.4, 106.7, 37.5, 21.1, 13.8; IR (KBr) ν (cm^{-1}) 3057, 3023, 2975, 2919, 1627, 1600, 1564, 1519, 1491, 1470, 1457, 1442, 1383, 1348, 1327, 1251, 1231, 1124, 1086, 1053; MS (70 ev, EI) *m/z* (%) 286 (M^++1, 19.16), 285 (M^+, 83.40), 270 (100); Elemental analysis calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91; Found: C, 88.06, H, 6.57; N, 5.14.

The following compounds were prepared according to this procedure.

(2) 9-Ethyl-2-(4-methoxyphenyl)-9*H*-carbazole (2f). The reaction of $PtCl_2$ (14.0 mg, 0.05 mmol) and **1f** (320.0 mg, 1.0 mmol) in toluene (5.0 mL) at rt for 15 h afforded **2f** (230.1 mg, 76%) (petroleum ether/ethyl acetate = 40/1), solid; m.p. 132–133 °C (ethyl acetate/n-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15–8.04 (m, 2H, ArH), 7.70–7.60 (m, 2H, ArH), 7.52 (d, J = 0.9 Hz, 1H, ArH), 7.50–7.35 (m, 3H, ArH), 7.27–7.18 (m, 1H, ArH), 7.06–6.96 (m, 2H, ArH), 4.37 (q, J = 7.2 Hz, 2H, NCH_2), 3.85 (s, 3H, $ArOCH_3$), 1.43 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 140.5, 140.3, 138.8, 134.8, 128.5, 125.4, 122.8, 121.7, 120.6, 120.3, 118.8, 118.2, 114.2, 108.4, 106.5, 55.3, 37.4, 13.8; IR (KBr) ν (cm^{-1}) 3051, 2974, 2943, 2835, 1618, 1601, 1558, 1519, 1491, 1458, 1328, 1247, 1180; MS (70 ev, EI) m/z (%) 302 (M^++1, 22.89), 301 (M^+, 100), 286 (M^+-CH_3, 81.17); Elemental analysis calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65; Found: C, 83.82, H, 6.56; N, 4.54.

(3) 2-(Ethoxymethyl)-9-ethyl-9*H*-carbazole (2j). The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **1j** (82.0 mg, 0.3 mmol) in toluene (1.5 mL) at rt for 12 h afforded **2j** (64.5 mg, 84%) (petroleum ether/ethyl acetate = 20/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12–7.98 (m, 2H, ArH), 7.48–7.31 (m, 3H, ArH), 7.25–7.14 (m, 2H, ArH), 4.69 (s, 2H, CH_2OEt), 4.31 (q, J = 7.3 Hz, 2H, NCH_2), 3.59 (q, J = 7.0 Hz, 2H, OCH_2), 1.38 (t, J = 7.2 Hz, 3H, CH_3), 1.28 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.12, 140.08, 136.3, 125.4, 122.7, 122.3, 120.3, 120.2, 118.7, 108.4, 107.5, 73.4, 65.6, 37.4, 15.3, 13.7; IR (neat) ν (cm^{-1}) 3054, 3022, 2974, 2931, 2867, 1630, 1602, 1573, 1497, 1480, 1443, 1379, 1327, 1302, 1235, 1178, 1157, 1102, 1020, 1001; MS (70 ev, EI) m/z (%) 254 (M^++1, 15.28), 253 (M^+, 77.23), 208 (100); HRMS Calcd for $C_{17}H_{19}NO$ (M^+): 253.1467, Found: 253.1467.

(4) 2-Acetoxymethyl-9-ethyl-9*H*-carbazole (2k). The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **1k** (85.1 mg, 0.3 mmol) in toluene (1.5 mL) at rt for 24 h afforded **2k** (64.7 mg, 81%) (petroleum ether/ethyl acetate = 10/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (t, J = 5.1 Hz, 2H, ArH), 7.60–7.40 (m, 3H, ArH), 7.36–7.24 (m, 2H, ArH), 5.37 (s, 2H, CH_2OAc), 4.38 (q, J = 7.3 Hz, 2H, NCH_2), 2.20 (s, 3H, $COCH_3$), 1.47 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 140.2, 139.8, 133.2, 125.7, 122.8, 122.5, 120.4, 119.3, 118.8, 108.5, 108.4, 67.1, 37.4, 21.0, 13.7; IR (neat) ν (cm^{-1}) 3053, 2976, 2883, 1738, 1631, 1602, 1574, 1499, 1445, 1379, 1327, 1235, 1157, 1133, 1122, 1087, 1024; MS (70 ev, EI) m/z (%) 268 (M^++1, 19.59), 267 (M^+, 100); HRMS Calcd for $C_{17}H_{17}NO_2$ (M^+): 267.1259, Found: 267.1262.

(5) 2-(Methoxycarbonyloxy)methyl-9-ethyl-9*H*-carba-zole (2l). The reaction of $PtCl_2$ (6.1 mg, 0.023 mmol) and **1k** (151.1 mg, 0.5 mmol) in toluene (2.5 mL) at rt for 13 h afforded **2k** (109.0 mg, 77%) (petroleum ether/ethyl acetate = 20/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10–8.00 (m, 2H, ArH), 7.50–7.32 (m, 3H, ArH), 7.26–7.15 (m, 2H, ArH), 5.34 (s, 2H, $CH_2OCOOMe$), 4.29 (q, J = 7.2 Hz, 2H, NCH_2), 3.78 (s, 3H, $COOCH_3$), 1.37 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 140.3, 139.8, 132.5, 125.8, 123.0, 122.5, 120.45, 120.40, 119.2, 118.8, 108.5, 108.4, 70.5, 54.7, 37.4, 13.7; IR (neat) ν (cm^{-1}) 2975, 2949, 2895, 1747, 1631, 1603, 1574, 1481, 1443, 1379, 1327, 1266, 1188, 1157, 1134, 1087, 1001; MS (70 ev, EI) m/z (%) 284 (M^++1, 19.16), 283 (M^+, 100); HRMS Calcd for $C_{17}H_{17}NO_3$ (M^+): 283.1208, Found: 283.1209.

(6) 9-Ethyl-2-butyl-5-methyl-9*H*-carbazole (2m). The reaction of $PtCl_2$ (8.0 mg, 0.03 mmol) and **1m** (172.5 mg, 0.6 mmol) in toluene (3 mL) at rt for 18 h afforded **2m** (124.9 mg, 77%) (petroleum ether/ethyl acetate = 80/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 1H, ArH), 7.51–7.40 (m, 1H, ArH), 7.39–7.30 (m, 2H, ArH), 7.21 (d, J = 7.8 Hz, 1H, ArH), 7.11 (d, J = 6.9 Hz, 1H, ArH), 4.43 (q, J = 7.2 Hz, 2H, NCH_2), 2.99 (s, 3H, $ArCH_3$), 2.96 (t, J = 7.8 Hz, 2H, $ArCH_2$), 1.95–1.75 (m, 2H, CH_2), 1.65–1.45 (m, 5H, CH_2+CH_3), 1.10 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 140.2, 140.0, 133.0, 124.8, 122.3, 121.5, 120.2, 119.6, 107.7, 105.8, 37.3, 36.4, 34.3, 22.5, 20.8, 14.0, 13.7; IR (neat) ν (cm^{-1}) 3048, 2955, 2929, 2856, 1623, 1597, 1585, 1500, 1488, 1447, 1378, 1322, 1273, 1252, 1221, 1188, 1165, 1152, 1138, 1106, 1080, 1013; MS (70 ev, EI) m/z (%) 266 (M^++1, 21.33), 265 (M^+, 100); HRMS Calcd for $C_{19}H_{23}N$ (M^+): 265.1830, Found: 265.1830.

(7) 2-(Benzyloxy)-9-ethyl-9*H*-carbazole (2q). The reaction of $PtCl_2$ (3.0 mg, 0.01 mmol) and **1q** (64.5 mg, 0.2 mmol) in toluene (1 mL) at rt for 11 h afforded **2q** (36.5 mg, 60%) (petroleum ether/ethyl acetate = 20/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03–7.91 (m, 2H, ArH), 7.49 (d, J = 7.2 Hz, 2H, ArH), 7.44–7.25 (m, 5H, ArH), 7.23–7.14 (m, 1H, ArH), 6.97–6.88 (m, 2H, ArH), 5.16 (s, 2H, OCH_2Ar), 4.25 (q, J = 7.2 Hz, 2H, NCH_2), 1.36 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 141.1, 140.0, 137.1, 128.5, 127.9, 127.6, 124.3, 123.0, 121.1, 119.5, 118.8, 117.0, 108.1, 107.6, 94.2, 70.5, 37.4, 13.6; IR (neat) ν (cm^{-1}) 2979, 2937, 2871, 1636, 1601, 1579, 1501, 1460, 1371, 1327, 1189, 1118, 1029; MS (70 ev, EI) m/z (%) 302 (M^++1, 12.17), 301 (M^+, 53.18), 210 (100); HRMS Calcd for $C_{21}H_{19}NO$ (M^+): 301.1467, Found: 301.1472.

(8) 9-(4-Methoxybenzyl)-2-phenyl-9*H*-carbazole (2u). The reaction of $PtCl_2$ (40.1 mg, 0.15 mmol) and **1u** (912.4 mg, 2.39 mmol) in toluene (8 mL) at rt for 16 h afforded **2u** (623.3 mg, 72%) (petroleum ether/ethyl acetate = 40/1): solid; m.p. 123–124 °C (ethyl acetate/n-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (t, J = 8.9 Hz, 2H, ArH), 7.66 (d, J = 7.2 Hz, 2H, ArH), 7.56 (s, 1H, ArH), 7.53–7.29 (m, 6H, ArH), 7.28–7.18 (m, 1H, ArH), 7.10 (d, J = 8.7 Hz, 2H, ArH), 6.78 (d, J = 9.0 Hz, 2H, ArH), 5.48 (s, 2H, NCH_2), 3.72 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 142.1, 141.2, 141.1, 139.3, 129.1, 128.7, 127.6, 127.5, 127.0, 125.8, 122.8, 122.2, 120.6, 120.4, 119.3, 118.9, 114.1, 109.0, 107.4, 55.2, 46.0; IR (KBr) ν (cm^{-1}) 1609, 1599, 1561, 1511, 1487, 1458, 1435, 1326, 1247, 1175; MS (70 ev, EI) m/z (%) 364 (M^++1, 10.47), 363 (M^+, 37.22), 121 (100); Elemental analysis calcd for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.85; Found: C, 86.16, H, 5.91; N, 3.78.

(9) 9-Ethyl-4-isopropyl-9*H*-carbazole (4c). The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **3c** (78.0 mg, 0.31 mmol) in toluene (1.5 mL) at rt for 20 h afforded **4c** (27.2 mg, 38%) (petroleum ether/ethyl acetate = 100/1): liquid; ^{1}H NMR (300 MHz,

$CDCl_3$) δ 8.22 (d, J = 7.8 Hz, 1H, ArH), 7.51–7.38 (m, 3H, ArH), 7.33–7.25 (m, 1H, ArH), 7.24–7.20 (m, 1H, ArH), 7.16 (d, J = 7.5 Hz, 1H, ArH), 4.37 (q, J = 7.1 Hz, 1H, NCH_2), 3.97 (heptet, J = 0.9 Hz, 1H, $CH(Me)_2$), 1.49 (d, J = 6.9 Hz, 6H, CH_3), 1.42 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 140.1, 139.9, 125.7, 124.8, 123.1, 122.6, 120.2, 118.7, 114.7, 108.2, 106.0, 37.4, 30.3, 22.6, 13.7; IR (neat) ν (cm^{-1}) 3063, 2964, 2877, 1615, 1594, 1576, 1498, 1471, 1460, 1433, 1381, 1329, 1250, 1154, 1088; MS (70 ev, EI) *m/z* (%) 238 (M^++1, 13.09), 237 (M^+, 67.34), 222 (100); HRMS Calcd for $C_{17}H_{19}N$ (M^+): 237.1517, Found: 237.1517.

(10) 9-Ethyl-4-phenyl-9*H*-carbazole (4e). The reaction of $PtCl_2$ (4.2 mg, 0.015 mmol) and **3e** (84.1 mg, 0.29 mmol) in toluene (1.5 mL) at rt for 14 h afforded **4e** (72.2 mg, 92%) (petroleum ether/ethyl acetate = 20/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.67 (m, 2H, ArH), 7.65–7.52 (m, 5H, ArH), 7.51–7.43 (m, 3H, ArH), 7.17 (dd, J = 7.2 and 1.2 Hz, 1H, ArH), 7.10–6.98 (m, 1H, ArH), 4.45 (q, J = 7.3 Hz, 2H, NCH_2), 1.51 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 140.2, 140.0, 137.8, 129.2, 128.3, 127.4, 125.4, 125.3, 122.5, 120.5, 120.3, 118.4, 108.2, 107.3, 37.5, 13.7; IR (neat) ν (cm^{-1}) 3052, 3028, 2975, 2932, 2896, 1618, 1591, 1572, 1504, 1469, 1458, 1449, 1383, 1324, 1293, 1262, 1223, 1180, 1152, 1117, 1083, 1027; MS (70 ev, EI) *m/z* (%) 272 (M^++1, 15.90), 271 (M^+, 69.49), 256 (100); HRMS Calcd for $C_{20}H_{17}N$ (M^+): 271.1361, Found: 271.1361.

(11) 3-Deutero-9-ethyl-4-hexyl-6-methyl-9*H*-carbazole (4f-D). The reaction of $PtCl_2$ (4.2 mg, 0.015 mmol) and **3f-D** (93.2 mg, 0.3 mmol) in toluene (2 mL) at rt for 2 h afforded **4f-D** (75.2 mg, 86%, 94% D) (petroleum ether/ethyl acetate = 100/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (s, 1H, ArH), 7.42–7.19 (m, 4H, ArH), 6.99 (d, J = 6.9 Hz, 0.06H, ArH), 4.35 (q, J = 7.1 Hz, 2H, NCH_2), 3.21 (t, J = 8.0 Hz, 2H, $ArCH_2$), 2.56 (s, 3H, $ArCH_3$), 1.93–1.76 (m, 2H, CH_2), 1.62–1.47 (m, 2H, CH_2), 1.46–1.28 (m, 7H, 2×CH_2+CH_3), 0.91 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 138.4, 138.1, 127.8, 126.1, 125.1, 123.0, 122.8, 120.5, 118.9 (t, $J_{D\text{-}C}$ = 23.0 Hz), 107.8, 105.9, 37.3, 34.4, 31.8, 29.63, 29.55, 22.7, 21.6, 14.2, 13.7; IR (neat) ν (cm^{-1}) 2955, 2928, 2858, 1594, 1576, 1489, 1467, 1379, 1348, 1326, 1306, 1266, 1229, 1151, 1131, 1114, 1080; MS (70 ev, EI) *m/z* (%) 295 (M^++1, 22.85), 294 (M^+, 100); HRMS Calcd for $C_{21}H_{26}DN$ (M^+): 294.2206, Found: 294.2201.

(12) 9-Ethyl-4,5-dimethyl-9*H*-carbazole (4h). The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **3h** (73.0 mg, 0.30 mmol) in toluene (1.5 mL) at rt for 20 h afforded **4h** (57.7 mg, 85%) (petroleum ether/ethyl acetate = 80/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.39 (m, 2H, ArH), 7.35 (d, J = 7.5 H, 2H, ArH), 7.10 (dd, J = 7.2 Hz and 0.3 Hz, 2H, ArH), 4.41 (q, J = 7.2 Hz, 2H, NCH_2), 3.13 (s, 6H, $ArCH_3$), 1.47 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 132.3, 125.2, 122.4, 122.3, 106.2, 37.2, 26.2, 13.3; IR (neat) ν (cm^{-1}) 3063, 3041, 2965, 2930, 1616, 1592, 1574, 1498, 1484, 1450, 1442, 1388, 1371, 1345, 1318, 1252, 1213, 1152, 1074, 1049, 1036; MS (70 ev, EI) *m/z* (%) 224 (M^++1, 10.84), 223 (M^+, 60.31), 208 (M^+-CH_3, 100); HRMS Calcd for $C_{16}H_{17}N$ (M^+): 223.1361, Found: 223.1363.

(13) 9-Ethyl-4-hexyl-5-methyl-9*H*-carbazole (4i). The reaction of $PtCl_2$ (2.8 mg, 0.01 mmol) and **3i** (62.1 mg, 0.20 mmol) in toluene (1.0 mL) at rt for 12 h afforded **4i** (47.5 mg, 81%) (petroleum ether/ethyl acetate = 80/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.34 (m, 2H, ArH), 7.33–7.26 (m, 2H, ArH), 7.11–7.02 (m, 2H, ArH), 4.38 (q, J = 7.1 Hz, 2H, NCH_2), 3.37 (t, J = 8.0 Hz, 2H, $ArCH_2$), 3.00 (s, 3H, $ArCH_3$), 1.83–1.68 (m, 2H, CH_2), 1.51–1.38 (m, 5H, CH_2+CH_3), 1.37–1.25 (m, 4H, 2×CH_2), 0.90 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 140.6, 138.1, 132.6, 125.2, 125.1, 122.4, 121.2, 106.1, 106.0, 37.3, 37.2, 32.5, 31.8, 29.1, 25.4, 22.6, 14.1, 13.3; IR (neat) ν (cm^{-1}) 2961, 2926, 2856, 1593, 1569, 1496, 1474, 1449, 1389, 1317, 1152; MS (70 ev, EI) *m/z* (%) 294 (M^++1, 23.25), 293 (M^+, 100); HRMS Calcd for $C_{21}H_{27}N$ (M^+): 293.2144, Found: 293.2143.

(14) 3-Bromo-9-ethyl-5-hexyl-9*H*-carbazole (4j). The reaction of $PtCl_2$ (2.9 mg, 0.011 mmol) and **3j** (75.0 mg, 0.20 mmol) in toluene (1.0 mL) at rt for 16 h afforded **4j** (53.6 mg, 75%) (petroleum ether/ethyl acetate = 40/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 1.2 Hz, 1H, ArH), 7.51 (dd, J = 8.6 and 2.0 Hz, 1H, ArH), 7.39 (t, J = 7.8 Hz, 1H, ArH), 7.29–7.20 (m, 2H, ArH), 7.02 (d, J = 7.2 Hz, 1H, ArH), 4.28 (q, J = 7.2 Hz, 2H, NCH_2), 3.15 (t, J = 7.8 Hz, 2H, $ArCH_2$), 1.90–1.72 (m, 2H, CH_2), 1.60–1.25 (m, 9H, 3×CH_2+CH_3), 0.91 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 138.9, 138.5, 127.6, 126.2, 125.3, 124.6, 119.9, 111.5, 109.6, 106.3, 37.6, 34.3, 31.8, 29.5, 22.7, 14.2, 13.7; IR (neat) ν (cm^{-1}) 2961, 2929, 2856, 1615, 1592, 1573, 1499, 1470, 1455, 1417, 1380, 1330, 1304, 1270, 1247, 1150, 1115, 1066, 1008; MS (70 ev, EI) *m/z* (%) 359 (M^+(^{81}Br), 100), 357 (M^+(^{79}Br), 94.91); HRMS Calcd for $C_{20}H_{24}N^{79}Br$ (M^+): 357.1092, Found: 357.1091.

(15) 9-Ethyl-4-hexyl-2-methyl-9*H*-carbazole (4l). The reaction of $PtCl_2$ (3.1 mg, 0.012 mmol) and **3l** (61.0 mg, 0.20 mmol) in toluene (1.0 mL) at rt for 21 h afforded **4l** (44.7 mg, 78%) (petroleum ether/ethyl acetate = 80/1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H, ArH), 7.47–7.36 (m, 2H, ArH), 7.25–7.18 (m, 1H, Ar*H*), 7.07 (s, 1H, ArH), 6.85 (s, 1H, ArH), 4.33 (q, J = 7.2 Hz, 2H, NCH_2), 3.16 (t, J = 7.8 Hz, 2H, $ArCH_2$), 2.54 (s, 3H, $ArCH_3$), 1.89–1.76 (m, 2H, CH_2), 1.58–1.30 (m, 9H, 3×CH_2+CH_3), 0.90 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 139.9, 138.2, 135.5, 124.3, 122.9, 122.2, 121.1, 118.6, 118.4, 108.1, 106.3, 37.3, 34.5, 31.8, 29.8, 29.6, 22.7, 22.1, 14.1, 13.7; IR (neat) ν (cm^{-1}) 2961, 2927, 2853, 1618, 1600, 1573, 1471, 1460, 1374, 1347, 1328, 1251, 1191, 1158, 1113, 1026; MS (70 ev, EI) *m/z* (%) 294 (M^++1, 22.55), 223 (M^+, 94.79), 223 (100); HRMS Calcd for $C_{21}H_{27}N$ (M^+): 293.2144, Found: 293.2150.

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