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# Efficient synthesis of carbazoles *via* PtCl<sub>2</sub>-catalyzed RT cyclization of 1-(indol-2-yl)-2,3-allenols: scope and mechanism<sup>†</sup>

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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, antimicrobial, psychotropic, anti-histaminic, anti-inflammatory, and antibiotic.<sup>1</sup> In addition, carbazole derivatives are also widely used as organic materials with special thermal,<sup>2</sup> electrical,<sup>3</sup> optical,<sup>3,4</sup> electroluminescent,<sup>5</sup> hole-transporting, and light-emitting properties.<sup>6</sup> The important potential applications of these carbazole derivatives have made them attractive targets for organic synthesis.<sup>7</sup> 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;<sup>8</sup> (b) reductive cyclization of o-nitrobiphenyl derivatives9 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,<sup>7a,7f,7g</sup> 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<sub>2</sub> make this type of reaction much less attractive; (d) Pd-catalyzed pyrrole formation via N,N-diarylamines (d1),<sup>10</sup> 2-aminobiphenyl (d2),<sup>11</sup> 1,1'-biphenyl-2,2'-diyl ditriflate or 2,2'-dihalobiphenyl (with primary amines) (d3),<sup>12</sup> have also been reported for the





Scheme 1 Main strategies for the synthesis of carbazoles.

construction of carbazoles; however, the starting materials such as *o*-haloanilines, arynes<sup>10a,10b</sup> and boronic acids<sup>11,12</sup> with preexisting 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,<sup>13</sup> nevertheless, require not-readily-available starting materials such as diynamides and the regioselectivity is rather poor (1 : 1 to 6 : 1).

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

Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027 Zhejiang, People's Republic of China. E-mail: masm@sioc.ac.cn; Fax: (+86) 21-62609305 †Electronic supplementary information (ESI) available: The spectroscopic data (<sup>1</sup>H and <sup>13</sup>C) for all the new compounds. See DOI: 10.1039/ c1ob06474f

 
 Table 1
 PtCl2-catalyzed cyclization reaction of 4-non-substituted 1-(indol-2-yl)-2,3-allenols

$R^{3}$ $N$ $R^{1}$ $R^{2}$ $\frac{PtCl_{2} (5 \text{ mol}\%)}{toluene}$ $1$				$ \begin{array}{c} R^{3} \swarrow \\ & \\ & \\ & \\ & \\ & \\ R^{1} \\ 2 \\ \end{array} $	
	1			Time	Vield of <b>?</b>
Entry	$\mathbb{R}^1$	R <sup>2</sup>	R <sup>3</sup>	(h)	$(\%)^a$
1	Et	Н	H (1a)	4	70 ( <b>2a</b> )
2	Et	$n-C_4H_9$	H (1b)	3	74 ( <b>2b</b> )
3	Et	allyl	H (1c)	3	74 ( <b>2</b> c)
4	Et	Ph	H (1d)	4	70 ( <b>2d</b> )
5	Et	p-MeC <sub>6</sub> H <sub>4</sub>	H (1e)	16	69 ( <b>2e</b> )
6	Et	p-MeOC <sub>6</sub> H <sub>4</sub>	H (1f)	15	76 ( <b>2f</b> )
7	Et	COOMe	H (1g)	36	67 ( <b>2g</b> )
8	Et	CONMe <sub>2</sub>	H (1h)	24	83 ( <b>2h</b> )
9	Et	CH <sub>2</sub> OH	H (1i)	23	64 ( <b>2i</b> )
10	Et	CH <sub>2</sub> OEt	H (1j)	12	84 ( <b>2j</b> )
11	Et	CH <sub>2</sub> OAc	H (1k)	24	81 (2k)
12	Et	CH <sub>2</sub> OCOOMe	H (11)	13	77 ( <b>2I</b> )
13	Et	$n-C_4H_9$	4-Me	18	77 ( <b>2m</b> )
			(1m)		
14	Et	Ph	5-Me (1n)	17	70 ( <b>2n</b> )
15	Et	CH <sub>2</sub> OH	4-Me (10)	20	81 ( <b>20</b> )
16	Et	CH <sub>2</sub> OH	7-Me (1p)	21	68 ( <b>2p</b> )
17	Et	OBn	H (1q)	11	60 ( <b>2q</b> )
18	Me	$n-C_4H_9$	H (1r)	4	81 ( <b>2r</b> )
19	Me	Ph	H (1s)	4	71 ( <b>2s</b> )
20	Ph	Ph	H (1t)	19	78 ( <b>2t</b> )
21	PMP	Ph	H (1u)	16	72 ( <b>2u</b> )
<sup>a</sup> Isolated yield.					

skeleton, is still of high current interest. On the other hand, Ptcatalyzed reactions have recently been demonstrated to be powerful tools in synthetic organic chemistry<sup>14</sup> owing to their extraordinary potential for functional group tolerance.<sup>15</sup> 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.<sup>16</sup> Due to the ready availability of the starting allenols with their strong substituentloading 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)-2,3allenols

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);<sup>17</sup> in addition, this reaction tolerates many functional groups, such as COOMe, CONMe<sub>2</sub> and CH<sub>2</sub>OH (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<sup>2</sup> is CH<sub>2</sub>OEt, CH<sub>2</sub>OAc or CH<sub>2</sub>OCOOMe. Moreover, as expected, different substituents may be loaded onto the indole ring to give the corresponding carbazole derivatives smoothly (entries 13–16).

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

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  $\mathbb{R}^3$  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 preintroduced 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  $\alpha$ -allenol 1-(1-ethyl-5-methyl-1*H*-indol-2-yl)deca-4deutero-2,3-dien-1-ol **3f-D** (98% D): firstly, oxidation of non-1yn-3-ol afforded the corresponding alkynone,<sup>18</sup> which was subsequently reduced with LiAlD<sub>4</sub>.<sup>19</sup> The tetrahydropyranyloxy-



Scheme 2 Preparation of 3f-D.

The reaction of **3f-D** in toluene under the catalysis of PtCl<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub>O 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.<sup>21</sup>



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)-2,3allenols 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**

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectra were recorded with an instrument operated at 300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR. CDCl<sub>3</sub> was used as solvent in all NMR experiments. Chemical shifts ( $\delta$ ) 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 precoated 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<sub>2</sub> 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<sup>23</sup>

To a 10 mL dried three-necked flask were added Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (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<sub>2</sub>SO<sub>4</sub>, 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%).<sup>18</sup> liquid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  187.6, 81.4, 78.3, 45.4, 31.4, 28.5, 23.7, 22.4, 14.0.

To a suspension of LiAlD<sub>4</sub> (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<sub>2</sub> 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<sub>4</sub>, filtered, evaporated, and purified by chromatography on silica gel to afford 3-deutero-1-nonyn-3-ol (2.997 g, 84%): liquid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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);<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>16</sup>

1-(1-Ethyl-1*H*-indol-2-yl)-2-(*p*-tolyl)buta-2,3-dien-1-ol
 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<sub>4</sub>Cl (20 mL) and THF (4 mL) was added 1-bromo-3-(4-methylphenyl)prop-2-vne (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<sub>2</sub>O, extracted with diethyl ether (20 mL $\times$ 3), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. 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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>=), 4.62-4.27 (m, 2H, NCH<sub>2</sub>), 3.11 (d, *J* = 7.8 Hz, 1H, OH), 2.53 (s, 3H, ArCH<sub>3</sub>), 1.62 (t, J = 7.1 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ 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) v (cm<sup>-1</sup>) 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<sup>+</sup>+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-1H-indol-2-yl)-2-(4-methoxyphenyl)-buta-2,3dien-1-ol (1f). The reaction of 1-ethyl-1H-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<sub>4</sub>Cl solution (20 mL) at 0 °C for 11 h afforded 1f (1.1015 g, 69%) (petroleum ether/ethyl acetate =  $10/1 \sim 5/1$ ): oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>=), 4.48-4.21 (m, 2H, NCH<sub>2</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 2.35 (bs, 1H, OH), 1.44 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 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<sub>21</sub>H<sub>21</sub>NO<sub>2</sub> (M<sup>+</sup>): 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<sub>4</sub>Cl solution (20 mL) at 0 °C for 17 h afforded **1j** (1.1099 g, 81%) (petroleum ether/ethyl acetate =  $10/1 \sim 5/1$ ): oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 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<sub>2</sub>=), 4.20 (dq, J = 7.2 and 1.5 Hz, 2H, NCH<sub>2</sub>), 4.08 (dt, J = 11.2 and 1.8 Hz, 1H, one proton from CH<sub>2</sub>OC), 3.97 (dt, J = 11.1 and 2.0 Hz, 1H, one proton from CH<sub>2</sub>OC), 3.57–3.39 (m, 2H, OCH<sub>2</sub>), 3.29–3.19 (m, 1H, OH), 1.34 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>), 1.19 (t, J = 6.9 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 14.64), 271 (M<sup>+</sup>, 75.93), 182 (100); HRMS Calcd for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub> (M<sup>+</sup>): 271.1572, Found: 271.1571.

(4) 2-((1-Ethyl-1H-indol-2-yl)(hydroxy)methyl)buta-2,3-dienyl acetate (1k). The reaction of 1-ethyl-1H-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<sub>4</sub>Cl solution (20 mL) at 0 °C for 20 h afforded 1k (0.6988 g, 61%) (petroleum ether/ethyl acetate = 10/ $1 \sim 5/1$ ): oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>=), 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<sub>2</sub>OAc), 4.22 (q, J = 7.2 Hz, 2H, NCH<sub>2</sub>), 3.01-2.68 (m, 1H, OH), 1.92 (s, 3H, COCH<sub>3</sub>), 1.36 (t, J = 7.2Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 3425, 3039, 2980, 2925, 1960, 1739, 1606, 1543, 1461, 1378, 1347, 1316, 1233, 1165, 1027; MS (70 ev, EI) m/z (%) 286 (M<sup>+</sup>+1, 19.08), 285 (M<sup>+</sup>, 93.58), 182 (100); HRMS Calcd for C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub> (M<sup>+</sup>): 285.1365, Found: 285.1366.

(5) 2-((1-Ethyl-1*H*-indol-2-yl)(hydroxy)methyl)buta-2,3-dienyl methyl carbonate (11). The reaction of 1-ethyl-1H-indole-2carbaldehyde (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<sub>4</sub>Cl solution (20 mL) at 0 °C for 11 h afforded 11 (0.7103 g, 61%) (petroleum ether/ethyl acetate =  $10/1 \sim 5/1$ ): oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>=), 4.78 (dt, J = 12.0 and 1.8 Hz, 1H, one proton from CH<sub>2</sub>OCOO), 4.59 (dt, J = 12.3 and 2.3 Hz, 1H, one proton from CH2OCOO), 4.35-4.18 (m, 2H, NCH2), 3.69 (s, 3H, COOCH<sub>3</sub>), 2.53 (d, *J* = 6.3 Hz, 1H, OH), 1.37 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>);  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 8.92), 301 (M<sup>+</sup>, 46.48), 182 (100); HRMS Calcd for C<sub>17</sub>H<sub>19</sub>NO<sub>4</sub> (M<sup>+</sup>): 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<sub>4</sub>Cl solution (20 mL) at 0 °C for 12 h afforded **1m** (1.1462 g, 81%) (petroleum ether/ethyl acetate = 20/1): oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>—), 4.23 (d, *J* = 7.2 Hz, 2H, NCH<sub>2</sub>), 2.53 (s, 3H, ArCH<sub>3</sub>), 2.29 (d, *J* = 5.7 Hz, 1H, OH), 2.07–1.79 (m, 2H, CH<sub>2</sub>), 1.51–1.21 (m, 7H, 2×CH<sub>2</sub>+CH<sub>3</sub>), 0.86 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>, 38.24), 266 (100); HRMS Calcd for C<sub>19</sub>H<sub>25</sub>NO (M<sup>+</sup>): 283.1936, Found: 283.1935.

(7) 1-(1-(4-Methoxybenzyl)-1*H*-indol-2-yl)-2-phenyl-buta-2,3dien-1-ol (1u). The reaction of 1-(4-methoxybenzyl)-1H-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<sub>4</sub>Cl solution (20 mL) at 0 °C for 10 h afforded 1u (1.3000 g, 91%) (petroleum ether/ ethyl acetate =  $5/1 \sim 3/1$ ): oil;<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 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<sub>2</sub>), 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 = 8.4Hz, 1H, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 3422, 3055, 2937, 2841, 1941, 1612, 1582, 1512, 1495, 1461, 1420, 1348, 1315, 1246, 1176, 1034; MS (70 ev, EI) m/z (%) 382 (M<sup>+</sup>+1, 8.05), 381 (M<sup>+</sup>, 25.66), 121 (100); HRMS Calcd for  $C_{26}H_{23}NO_2$  (M<sup>+</sup>): 381.1729, Found: 381.1731.

#### 3. Synthesis of 1-(1-ethyl-1*H*-indol-2-yl)-2-(benzyloxy)buta-2,3dien-1-ol (1q)<sup>22</sup>

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-1H-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<sub>4</sub>Cl (20 mL), and extracted with diethyl ether (25 mL×3). The combined organic layer was washed with water and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. After filtration and evaporation, the residue was purified by column chromatography on alkali-Al<sub>2</sub>O<sub>3</sub> (petroleum ether/ethyl acetate =  $5/1 \sim 3/1$ ) to give 1q (1.8125 g, 57%): oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>=), 5.48 (d, J = 7.2Hz, 1H, CH), 4.76 (d, J = 12.0 Hz, 1H, one proton from OCH<sub>2</sub>), 4.71 (d, J = 12.0 Hz, 1H, one proton from OCH<sub>2</sub>), 4.36–4.14 (m, 2H, NCH<sub>2</sub>), 2.46 (d, J = 7.5 Hz, 1H, OH), 1.36 (t, J = 7.2

Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 3416, 3033, 2979, 2929, 2865, 1959, 1612, 1537, 1459, 1380, 1347, 1316, 1218, 1164, 1014; MS (70 ev, EI) *m/z* (%) 320 (M<sup>+</sup>+1, 3.24), 319 (M<sup>+</sup>, 14.10), 172 (100); HRMS Calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub> (M<sup>+</sup>): 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<sub>4</sub>Cl (20 mL), and extracted with diethyl ether (25 mL×3). The ether layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated *in vacuo*. The product 9c was then used without further purification.



To an ice-cold suspension of LiAlH<sub>4</sub> (0.2357 g, 6 mmol) in dry Et<sub>2</sub>O (25 mL) under N<sub>2</sub> was added dropwise a solution of 9c prepared in the previous step in Et<sub>2</sub>O (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  $\times$  3) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. 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); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 2.50–2.30 (m, 1H, CH(Me)<sub>2</sub>), [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<sub>2</sub>), [1.09 (d, J = 6.6 Hz), 1.04 (d, J = 6.6 Hz), 6H, 2×CH<sub>3</sub>]; IR (KBr) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 4.37), 255 (M<sup>+</sup>, 22.59), 237 (M<sup>+</sup>-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,<sup>23</sup> prepared from 3-deutero-1nonyn-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<sub>4</sub> (0.1247 g, 3.3 mmol) in Et<sub>2</sub>O (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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 2.43 (s, 3H, ArCH<sub>3</sub>), 2.15–1.98 (m, 3H, CH<sub>2</sub>+OH), 1.50–1.20 (m, 11H, 4×CH<sub>2</sub>+CH<sub>3</sub>), 0.95–0.80 (m, 3H, CH<sub>3</sub>); IR (neat) v (cm<sup>-1</sup>); 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<sup>+</sup>+1, 19.69), 312 (M<sup>+</sup>, 96.31), 212 (M<sup>+</sup>-C<sub>7</sub>H<sub>14</sub>D, 100); Elemental analysis calcd for C<sub>21</sub>H<sub>28</sub>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<sub>4</sub> (0.2001 g, 5 mmol) in Et<sub>2</sub>O (30 mL) afforded **3h** (0.4047 g, combined yield from **8a** to **3h** is 34%) (petroleum ether/ethyl acetate =  $10/1 \sim 5/1$ ): solid; m.p. 125–126 °C (ethyl acetate/n-hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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 $\geq$ 5.57 (m, 1H, CH), 5.56–5.34 (m, 2H, CH=), 4.43–4.19 (m, 2H, NCH<sub>2</sub>), 2.54 (s, 3H, ArCH<sub>3</sub>), 2.12–2.02 (m, 1H, OH), 1.84–1.68 (m, 3H, CH<sub>3</sub>C=), 1.41 (t, J = 7.4 Hz, 3H, CH<sub>3</sub>); IR (KBr) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 17.43), 241 (M<sup>+</sup>, 100); Elemental analysis calcd for C<sub>16</sub>H<sub>19</sub>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<sub>4</sub> (0.1565 g, 4 mmol) in Et<sub>2</sub>O (30 mL) afforded 3i (0.3860 g, combined yield from 8f to 3i is 31%) (petroleum ether/ethyl acetate = 10/1): solid; 65.3–66.9 °C (ethyl acetate/n-hexane); <sup>1</sup>H NMR m.p. (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.24–7.04 (m, 2H, ArH), 6.91 (d, J = 6.6Hz, 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<sub>2</sub>), 2.55 (s, 3H, ArCH<sub>3</sub>), 2.20–2.01 (m, 3H, NCH<sub>2</sub>+OH), 1.55–1.20 (m, 11H, 4×CH<sub>2</sub>+CH<sub>3</sub>), 0.97–0.84 (m, 3H, CH<sub>3</sub>); IR (KBr) v (cm<sup>-1</sup>) 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<sub>2</sub>O, 100); Elemental analysis calcd for C<sub>21</sub>H<sub>29</sub>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<sub>4</sub> (0.0891 g, 2 mmol) in Et<sub>2</sub>O (20 mL) afforded **3j** (0.2297 g, combined yield from **8f** to **3j** is 31%) (petroleum ether/ethyl acetate = 10/1-5/1): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 2.37 (bs, 1H, OH), 2.19–2.00 (m, 2H, CH<sub>2</sub>), 1.55–1.19 (m, 11H, 4×CH<sub>2</sub>+CH<sub>3</sub>), 1.00–0.83 (m, 3H, CH<sub>3</sub>); IR

(neat) v (cm<sup>-1</sup>) 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<sup>+</sup>(<sup>81</sup>Br), 37.58), 375 (M<sup>+</sup>(<sup>79</sup>Br), 38.74), 145 (100); Elemental analysis calcd for C<sub>20</sub>H<sub>26</sub>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-2,3dien-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<sub>4</sub>Cl (20 mL), and extracted with diethyl ether (25 mL×3). The ether layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>O (50 mL) was added dropwise a solution of EtMgBr in Et<sub>2</sub>O (50 mL, 1 M in Et<sub>2</sub>O, 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, guenched with saturated ammonium chloride solution (30 mL), extracted with ether (3  $\times$  30 mL), washed with water, and dried over anhydrous Na2SO4. 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); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 2.14 (d, J = 6.6 Hz, 1H, OH), 1.41 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); IR (KBr) v (cm<sup>-1</sup>) 3321, 3045, 2985, 1953, 1489, 1460, 1347, 1314, 1221, 1161, 1101, 1026; MS (70 ev, EI) m/z (%) 290 (M<sup>+</sup>+1, 8.67), 289 (M<sup>+</sup>, 40.09), 198 (100); Elemental analysis calcd for C<sub>20</sub>H<sub>19</sub>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-2,3dien-1-ol (31)<sup>24</sup>

To a solution of 3-chloronon-1-vne (1.1902 g, 7.5 mmol) in Et<sub>2</sub>O (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-1H-indole-2-carbaldehyde (1.2995 g, 7.5 mmol) in anhydrous Et<sub>2</sub>O (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<sub>3</sub>MgBr in Et<sub>2</sub>O (7.5 mL, 3 M in Et<sub>2</sub>O, 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 ( $3 \times 30$  mL), washed with water, and dried over anhydrous Na2SO4. Filtration, evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded **31** (0.4652 g, 20%): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 2.24 (d, J = 5.7Hz, 1H, OH), 2.06 (q, J = 6.9 Hz, 2H, CH<sub>2</sub>), 1.68 (d, J = 2.7Hz, 3H, CH<sub>3</sub>C =), 1.46–1.20 (m, 11H, 4×CH<sub>2</sub>+CH<sub>3</sub>), 0.91–0.82 (m, 3H,  $CH_3$ ); IR (neat) v (cm<sup>-1</sup>) 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<sup>+</sup>, 9.76), 293 (M<sup>+</sup>-H<sub>2</sub>O, 69.25), 208 (100); Elemental analysis calcd for C<sub>21</sub>H<sub>29</sub>NO: C, 80.98; H, 9.38; N, 4.50; Found: C, 80.74, H, 9.49; N, 4.38.

#### 7. Synthesis of carbazoles<sup>16</sup>

(1) 9-Ethyl-2-p-tolyl-9H-carbazole (2e). Typical procedure: to a dry Schlenk tube were added sequentially PtCl<sub>2</sub> (4.1 mg, 0.015 mmol), 1e (92.5 mg, 0.31 mmol), and toluene (1.5 mL) under N2. 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/l) afforded 2e (60.2 mg, 69%): solid; m.p. 146-147 °C (ethyl acetate/n-hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 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<sub>2</sub>), 2.40 (s, 3H, ArCH<sub>3</sub>), 1.41 (t, J = 7.4 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 19.16), 285 (M<sup>+</sup>, 83.40), 270 (100); Elemental analysis calcd for C<sub>21</sub>H<sub>19</sub>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)-9H-carbazole (2f). The reaction of PtCl<sub>2</sub> (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/l), solid; m.p. 132–133 °C (ethyl acetate/n-hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) & 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<sub>2</sub>), 3.85 (s, 3H, ArOCH<sub>3</sub>), 1.43 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-</sup> 3051, 2974, 2943, 2835, 1618, 1601, 1558, 1519, 1491, 1458, 1328, 1247, 1180; MS (70 ev, EI) m/z (%) 302 (M<sup>+</sup>+1, 22.89), 301 (M<sup>+</sup>, 100), 286 (M<sup>+</sup>-CH<sub>3</sub>, 81.17); Elemental analysis calcd for C<sub>21</sub>H<sub>19</sub>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<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>OEt), 4.31 (q, *J* = 7.3 Hz, 2H, NCH<sub>2</sub>), 3.59 (q, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>), 1.38 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.28 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 15.28), 253 (M<sup>+</sup>, 77.23), 208 (100); HRMS Calcd for C<sub>17</sub>H<sub>19</sub>NO (M<sup>+</sup>): 253.1467, Found: 253.1467.

(4) 2-Acetoxymethyl-9-ethyl-9*H*-carbazole (2k). The reaction of PtCl<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>OAc), 4.38 (q, J = 7.3 Hz, 2H, NCH<sub>2</sub>), 2.20 (s, 3H, COCH<sub>3</sub>), 1.47 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 19.59), 267 (M<sup>+</sup>, 100); HRMS Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub> (M<sup>+</sup>): 267.1259, Found: 267.1262.

(5) 2-(Methoxycarbonyloxy)methyl-9-ethyl-9*H*-carba-zole (21). The reaction of PtCl<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>OCOOMe), 4.29 (q, *J* = 7.2 Hz, 2H, NCH<sub>2</sub>), 3.78 (s, 3H, COOCH<sub>3</sub>), 1.37 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 19.16), 283 (M<sup>+</sup>, 100); HRMS Calcd for  $C_{17}H_{17}NO_3$  (M<sup>+</sup>): 283.1208, Found: 283.1209.

(6) 9-Ethyl-2-butyl-5-methyl-9H-carbazole (2m). The reaction of PtCl<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 2.99 (s, 3H, ArCH<sub>3</sub>), 2.96 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>), 1.95–1.75 (m, 2H, CH<sub>2</sub>), 1.65–1.45 (m, 5H,  $CH_2+CH_3$ ), 1.10 (t, J = 7.2 Hz, 3H,  $CH_3$ ); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) & 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) v (cm<sup>-1</sup>) 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<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>Ar), 4.25 (q, J = 7.2 Hz, 2H, NCH<sub>2</sub>), 1.36 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 2979, 2937, 2871, 1636, 1601, 1579, 1501, 1460, 1371, 1327, 1189, 1118, 1029; MS (70 ev, EI) m/z (%) 302 (M<sup>+</sup>+1, 12.17), 301 (M<sup>+</sup>, 53.18), 210 (100); HRMS Calcd for C<sub>21</sub>H<sub>19</sub>NO (M<sup>+</sup>): 301.1467, Found: 301.1472.

(8) 9-(4-Methoxybenzyl)-2-phenyl-9*H*-carbazole (2u). The reaction of PtCl<sub>2</sub> (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); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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 = 9.0Hz, 2H, ArH), 5.48 (s, 2H, NCH<sub>2</sub>), 3.72 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v  $(cm^{-1})$  1609, 1599, 1561, 1511, 1487, 1458, 1435, 1326, 1247, 1175; MS (70 ev, EI) m/z (%) 364 (M<sup>+</sup>+1, 10.47), 363 (M<sup>+</sup>, 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/l): liquid; <sup>1</sup>H NMR (300 MHz,

CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 3.97 (heptet, J = 0.9 Hz, 1H, CH(Me)<sub>2</sub>), 1.49 (d, J = 6.9 Hz, 6H, CH<sub>3</sub>), 1.42 (t, J = 7.3 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 3063, 2964, 2877, 1615, 1594, 1576, 1498, 1471, 1460, 1433, 1381, 1329, 1250, 1154, 1088; MS (70 ev, EI) *m/z* (%) 238 (M<sup>+</sup>+1, 13.09), 237 (M<sup>+</sup>, 67.34), 222 (100); HRMS Calcd for C<sub>17</sub>H<sub>19</sub>N (M<sup>+</sup>): 237.1517, Found: 237.1517.

(10) 9-Ethyl-4-phenyl-9*H*-carbazole (4e). The reaction of PtCl<sub>2</sub> (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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 1.51 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 15.90), 271 (M<sup>+</sup>, 69.49), 256 (100); HRMS Calcd for C<sub>20</sub>H<sub>17</sub>N (M<sup>+</sup>): 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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (s, 1H, ArH), 7.42–7.19 (m, 4H, ArH), 6.99 (d, J = 6.9 Hz, 0.06H, ArH), 4.35  $(q, J = 7.1 \text{ Hz}, 2H, \text{ NCH}_2), 3.21 (t, J = 8.0 \text{ Hz}, 2H, \text{ ArCH}_2),$ 2.56 (s, 3H, ArCH<sub>3</sub>), 1.93-1.76 (m, 2H, CH<sub>2</sub>), 1.62-1.47 (m, 2H, CH<sub>2</sub>), 1.46–1.28 (m, 7H, 2×CH<sub>2</sub>+CH<sub>3</sub>), 0.91 (t, J = 6.9 Hz, 3H, CH<sub>3</sub>);  $^{13}\mathrm{C}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  140.4, 138.4, 138.1, 127.8, 126.1, 125.1, 123.0, 122.8, 120.5, 118.9 (t,  $J_{D-C} = 23.0$ 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) v (cm<sup>-1</sup>) 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<sup>+</sup>+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<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 3.13 (s, 6H, ArCH<sub>3</sub>), 1.47 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  140.4, 132.3, 125.2, 122.4, 122.3, 106.2, 37.2, 26.2, 13.3; IR (neat) v (cm<sup>-1</sup>) 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<sup>+</sup>+1, 10.84), 223 (M<sup>+</sup>, 60.31), 208 (M<sup>+</sup>-CH<sub>3</sub>, 100); HRMS Calcd for C<sub>16</sub>H<sub>17</sub>N (M<sup>+</sup>): 223.1361, Found: 223.1363.

(13) 9-Ethyl-4-hexyl-5-methyl-9*H*-carbazole (4i). The reaction of PtCl<sub>2</sub> (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/l): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 3.37 (t, *J* = 8.0 Hz, 2H, ArCH<sub>2</sub>), 3.00 (s, 3H, ArCH<sub>3</sub>), 1.83–1.68 (m, 2H, CH<sub>2</sub>), 1.51–1.38 (m, 5H, CH<sub>2</sub>+CH<sub>3</sub>), 1.37–1.25 (m, 4H, 2×CH<sub>2</sub>), 0.90 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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) v (cm<sup>-1</sup>) 2961, 2926, 2856, 1593, 1569, 1496, 1474, 1449, 1389, 1317, 1152; MS (70 ev, EI) *m/z* (%) 294 (M<sup>+</sup>+1, 23.25), 293 (M<sup>+</sup>, 100); HRMS Calcd for C<sub>21</sub>H<sub>27</sub>N (M<sup>+</sup>): 293.2144, Found: 293.2143.

(14) 3-Bromo-9-ethyl-5-hexyl-9H-carbazole (4j). The reaction of PtCl<sub>2</sub> (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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>), 3.15 (t, J = 7.8 Hz, 2H, ArCH<sub>2</sub>), 1.90-1.72 (m, 2H, CH<sub>2</sub>), 1.60-1.25 (m, 9H,  $3 \times CH_2 + CH_3$ ), 0.91 (t, J = 6.8 Hz, 3H,  $CH_3$ ); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 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<sup>+</sup>(<sup>81</sup>Br), 100), 357 ( $M^+$ (<sup>79</sup>Br), 94.91); HRMS Calcd for  $C_{20}H_{24}N^{79}Br$ (M<sup>+</sup>): 357.1092, Found: 357.1091.

(15) 9-Ethyl-4-hexyl-2-methyl-9H-carbazole (41). The reaction of PtCl<sub>2</sub> (3.1 mg, 0.012 mmol) and 31 (61.0 mg, 0.20 mmol) in toluene (1.0 mL) at rt for 21 h afforded 41 (44.7 mg, 78%) (petroleum ether/ethyl acetate = 80/1): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, J = 8.1 Hz, 1H, ArH), 7.47-7.36 (m, 2H, ArH), 7.25-7.18 (m, 1H, ArH), 7.07 (s, 1H, ArH), 6.85 (s, 1H, ArH), 4.33 (q, J = 7.2 Hz, 2H, NCH<sub>2</sub>), 3.16  $(t, J = 7.8 \text{ Hz}, 2\text{H}, \text{ArCH}_2), 2.54 (s, 3\text{H}, \text{ArCH}_3), 1.89-1.76 (m, 300)$ 2H, CH<sub>2</sub>), 1.58–1.30 (m, 9H, 3×CH<sub>2</sub>+CH<sub>3</sub>), 0.90 (t, J = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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) v (cm<sup>-1</sup>) 2961, 2927, 2853, 1618, 1600, 1573, 1471, 1460, 1374, 1347, 1328, 1251, 1191, 1158, 1113, 1026; MS (70 ev, EI) m/z (%) 294 (M<sup>+</sup>+1, 22.55), 223 (M<sup>+</sup>, 94.79), 223 (100); HRMS Calcd for C<sub>21</sub>H<sub>27</sub>N (M<sup>+</sup>): 293.2144, Found: 293.2150.

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