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Exclusive 1,2-Aryl Shift in Platinum(II) Chloride-Catalyzed Cyclization of 1-(Indol-2-yl)-2,3-allenols

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Abstract: An efficient cyclization of 1-(indole-2-yl)-2,3-allenols in the presence of platinum(II) chloride leading to polysubstituted carbazoles *via* 1,2-methyl or an exclusive 1,2-aryl migration of the metal-carbene intermediate was observed. The reaction proceeds *via* the intermediacy of a metal carbene intermediate, which induces the carbon-carbon bond cleavage *via* 1,2-migration to afford the products.

Keywords: allenes; carbenes; cyclization; platinum

Introduction

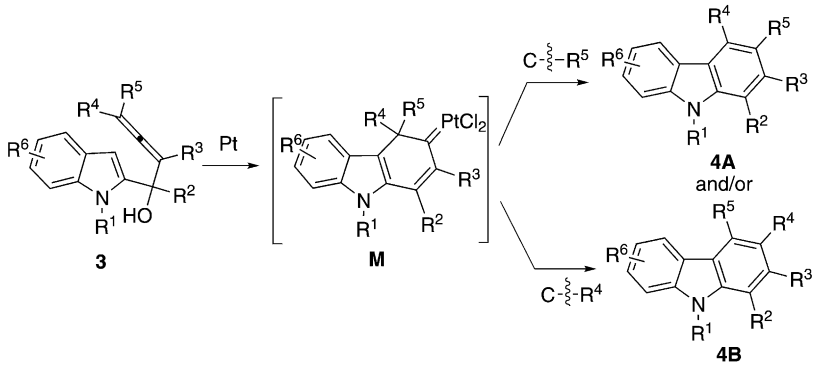
Selective C–C bond cleavage,[1] which is synthetically attractive, poses a great challenge due to the inherent strength of the C–C bond as well as the selectivity over the often accompanying C–H bond activation.[2] As we know, there are three major approaches for the cleavage of carbon-carbon bonds with transition metals: (i) direct oxidative addition of carbon-carbon bonds with low-valent transition metals or their complexes;[3] (ii) β-carbon elimination of carbon-metal species such as M–C–C–C or heteroatom-metal species such as M–O–C–C;[4] (iii) rearrangement *via* the intermediacy of such carbocations.[5] To the best our knowledge, examples of highly selective cleavage reactions of C–C bonds *via* the 1,2-carbon migration of metal-carbene intermediates are still quite limited.[6]

On the other hand, tricyclic carbazole derivatives are well-known alkaloids present in plants, and many of these compounds show biological activities, such as antioxidative, antitumor, antibacterial, antimicrobial, psychotropic, antihistaminic, antiinflammatory, and antibiotic activities.[7] In addition, carbazole derivatives are also widely used as organic materials with special thermal,[8] electrical,[9] optical,[9,10] electroluminescent,[11] hole-transporting, and light-emitting properties.[12] The important potentials of these carbazole derivatives have made them attractive targets for organic synthesis.[13]

Despite the fact that there are many useful synthetic procedures to prepare carbazoles, there remain some limitations:[14] (a) the yields usually are not very good, (b) harsh reaction conditions are usually needed and some processes cannot tolerate functional groups, (c) the starting materials are not readily available, (d) the atom economy is rather poor, and (e) it is non-regioselective in some of the well-recognized protocols. Thus, the development of mild, efficient and regiocontrolled diversified method for the preparation of carbazole alkaloids, which is suitable for introduction of specific substituent(s) to any position of the captioned skeleton is still of high current interest. Recently, we have described an approach to the carbazole skeleton through a Pt-catalyzed cyclization of 1-(indol-2-yl)-2,3-allenols.[15] According to our own observations and literature data, a possible mechanistic pathway involving a Pt-carbene intermediate **M**[6,16] has been proposed for this transformation (Scheme 1). We reasoned that 4,4-disubstitution of carbon groups may be implemented to check the intermediacy of the metal carbene **M** and the subsequent carbon-carbon single bond cleavage *via* 1,2-migration. If it is operative, this protocol may provide a method to introduce the substituent to any location of the carbazole skeleton providing that the selective carbon-carbon bond cleavage may be realized (Scheme 1).

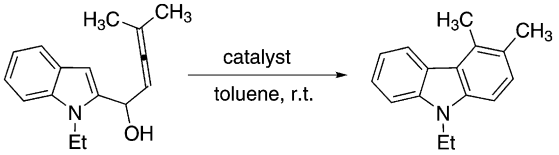
Results and Discussion

To this end, we have tested the cyclization of 4,4-dimethyl-substituted 2,3-allenol **5a** to avoid the issue of selectivity in the first place (Table 1). The reaction



Scheme 1.

Table 1. Optimization of the reaction conditions for the reaction of 4,4-dimethyl-substituted 2,3-allenol **5a**.

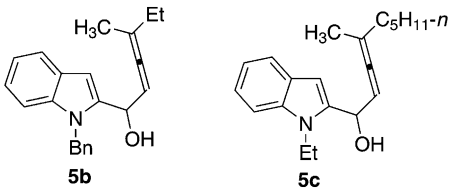


Entry	Catalyst	Solvent	NMR yield of **6a** [%][a]	Recovery of **5a** [%]
1	$AuCl_3$	toluene	20	–
2	$AuCl(PPh_3)$ (5 mol%)/AgOTf (5 mol%)	toluene	11	–
3	$PtCl_4$	toluene	43	–
4	$PtCl_2$	toluene	86	–
5	$PtCl_2$	xylenes	74	–
6	$PtCl_2$	DCE	22	44
7	$PtCl_2$	CH_2Cl_2	47	15
8	$PtCl_2$	THF	8	46
9	$PtCl_2$	dioxane	40	16
10	$PtCl_2$	acetonitrile	–	–
11[b]	$PtCl_2$	toluene	69	–
12[c]	$PtCl_2$	toluene	14	73
13[d]	$PtCl_2$	toluene	49	15

[a] 1H NMR yield of 6a and recovery of 5a obtained by using CH_2Br_2 as internal standard.
[b] The reaction temperature was 40 °C.
[c] The reaction temperature was 5 °C.
[d] $PtCl_2$ (3 mol%) was used.

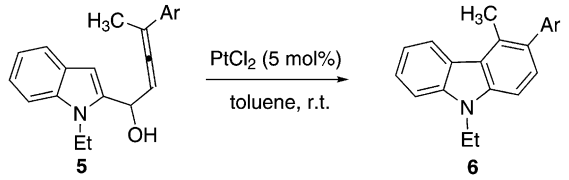
with $AuCl_3$ or $AuCl(PPh_3)$ (5 mol%)/$AgBF_4$ (5 mol%) afforded carbazole **6a** in a very low yield (entries 1 and 2, Table 1). Interestingly, $PtCl_4$ catalyzed this transformation affording **6a** in 43% yield (entry 3, Table 1). Then, it was observed that the reaction of **5a** with $PtCl_2$ (5 mol%) in toluene afforded carbazole **6a** in a surprising 86% NMR yield as the only product indicating the smooth 1,2-methyl migration (entry 4, Table 1), which is different from the previous report.[16f] Next, several solvents were tested for the $PtCl_2$-catalyzed reaction of **5a** at room temperature: xylenes was also effective affording **6a** in 74% NMR yield (entry 5, Table 1); other solvents failed to afford better yields (entries 6–10, Table 1). At a higher temperature (40 °C), the yield of **6a** was slightly lower and the reaction at 5 °C led to incomplete conversion (entries 11 and 12, Table 1). When 3 mol% $PtCl_2$ was used, the yield of **6a** was only 49% with **5a** being recovered in 15% (entry 13, Table 1).

However, the reaction of 4,4-dialkyl-substituted allenols **5b** and **5c** afforded a mixture of two regioisomers with very low yields (Scheme 2).



Scheme 2.

Table 2. $PtCl_2$-catalyzed cyclization reaction of 4-aryl-4-methyl-substituted 1-(indol-2-yl)-2,3-allenols *via* an aryl-carbon bond cleavage.[a]



Entry	Ar	Time [h]	Isolated yield of **6** [%]
1	Ph (**5d**)	24	67 (**6d**)
2	*p*-$MeOC_6H_4$ (**5e**)	6	87 (**6e**)
3	*m*-$MeOC_6H_4$ (**5f**)	12	75 (**6f**)
4	*p*-ClC_6H_4 (**5g**)	24	72 (**6g**)
5	*p*-FC_6H_4 (**5h**)	25	77 (**6h**)
6	2-furyl (**5i**)	4	61 (**6i**)
7	2-thienyl (**5j**)	13	83 (**6j**)

[a] *Reaction conditions:* mixture of 0.4 mmol of **5** and $PtCl_2$ (5 mol%) in 2 mL of toluene under N_2.

After some trials, we were able to establish the highly selective carbon-carbon single bond cleavage reaction of 4-aryl-4-alkyl-substitued allenols with the results shown in Table 2. Different carbazoles were afforded in moderate to good yields with the aromatic group serving as the 1,2-migration group exclusively, which was established by the X-ray diffraction study of **6m**[17] (Figure 1). Electronic effects of substituents on the phenyl ring showed no obvious impact on the yields (entries 2–5, Table 1): both *meta* and *para* substituted substrates such as **5e–h** afforded the corresponding products **6e–h** (entries 2–5, Table 2). It is worthy of note that the Ar group could also be a heterocyclic group such as 2-furyl or 2-thienyl (entries 6 and 7, Table 2). The thienyl-substituted carbazoles such as **6j** are particularly useful in the generation of short-wavelength absorption or emission for designing

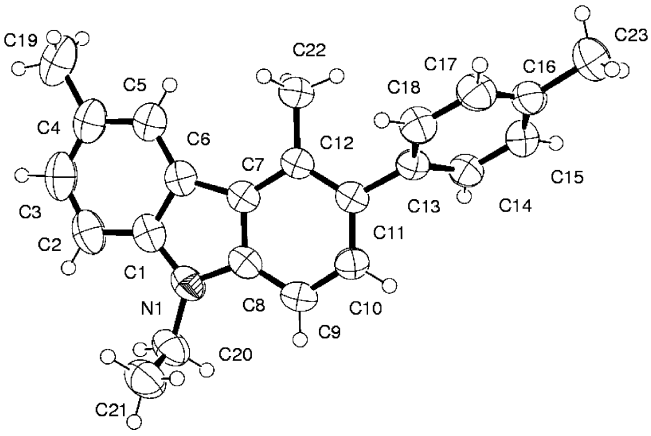
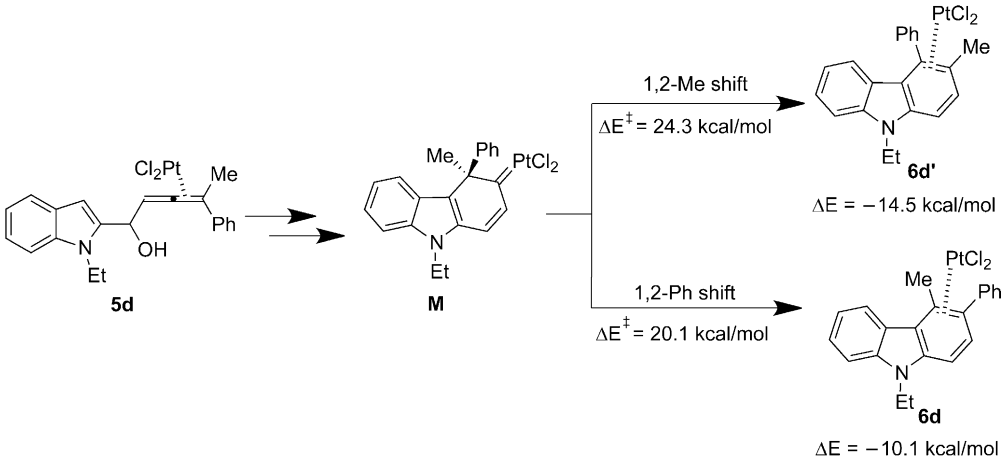


Figure 1. ORTEP representation of **6m**.

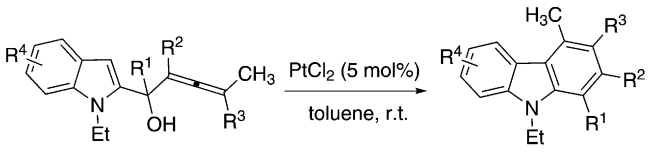
blue light-emitting materials.[18] In addition, it is capable of exhibiting the bifunctional properties of light emission and hole transport, which is potentially useful for highly efficient non-doped light-emitting diodes (OLEDs).[18c]

The migration for the aryl group and that for the methyl group from Pt-carbene intermediate **M** has been studied with DFT calculations. As a visual presentation of the data, the energy barrier of aryl migration is found to be lower than that of the competing methyl migration by 4.2 kcal mol^{-1}, thus, correctly accounting for the observed exclusive formation of **6d** as the final product in the experiment. Although the methyl migration product is computed to be thermodynamically more stable, its formation is kinetically less favorable.

Substituents may also be introduced to 1- or 2-position of the carbazole ring in **6k** and **6l** by installing R^1 and/or R^2 groups in the starting allenols. Moreover, different substituents may also be introduced to the original indole part by using 1-(poly-substituted indol-2-yl)-2,3-allenols. Thus, it was clearly demonstrated



Scheme 3. Methyl migration vs. phenyl migration: energies are relative to **M**.



5 6

R^1 = Me, R^2 = H, R^3 = Ph, R^4 = H (**5k**)	83% (**6k**)
R^1 = H, R^2 = Me, R^3 = Me, R^4 = H (**5l**)	55% (**6l**)
R^1 = H, R^2= H, R^3 = *p*-MeC_6H_4, R^4 = 5-Me (**5m**)	83% (**6m**)
R^1 = H, R^2 = H, R^3 = Me, R^4 = 5-OMe (**5n**)	70% (**6n**)
R^1 = H, R^2 = H, R^3 = Me, R^4 = 7-Me (**5o**)	72% (**6o**)

Scheme 4. Synthesis of differently poly-substituted carbazoles

that this method allows, in principle, the assembly of substituent(s) to any location of the carbazole (Scheme 4).

The reactions of **5p–5r** were tested. However, no reaction occurred (Scheme 5). Furthermore, the reaction of substrate **5s** afforded **6p** in a very low yield (3%). The major product is the cycloisomerization product **8** (55%). In order to prevent the cycloisomerization involving the hydroxy group, this functionality was protected with a methyl group. However, the yield of **6p** was still low (5%) with **9** being recovered in 63%.

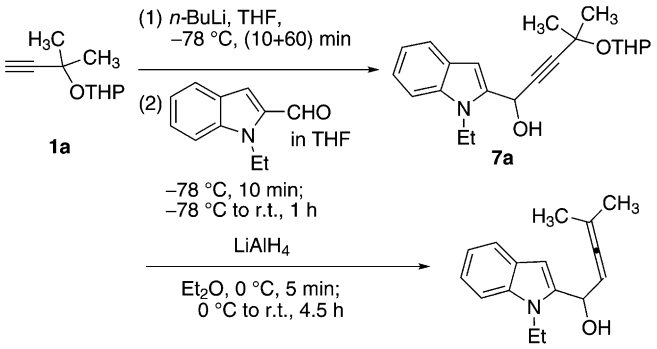
Conclusions

We have reported a new modular synthesis of carbazoles *via* the Pt-catalyzed cyclization of poly- substituted 1-(indol-2-yl)-2,3-allenols. Through these experiments, it is further confirmed that the reaction proceeds through a unique metal carbene intermediate. Selective C–C bond cleavage has been realized: compared with the methyl group, aryl groups migrate exclusively. The new methodology may find wide applications in organic synthesis, in projects oriented towards drug discovery and new organic materials based on carbazoles due to the mild reaction conditions, easy availability of the starting materials, and the potential of the products. Further studies on the scope, selectivity, and synthetic applications of this reaction are being carried out in our laboratory.

Experimental Section

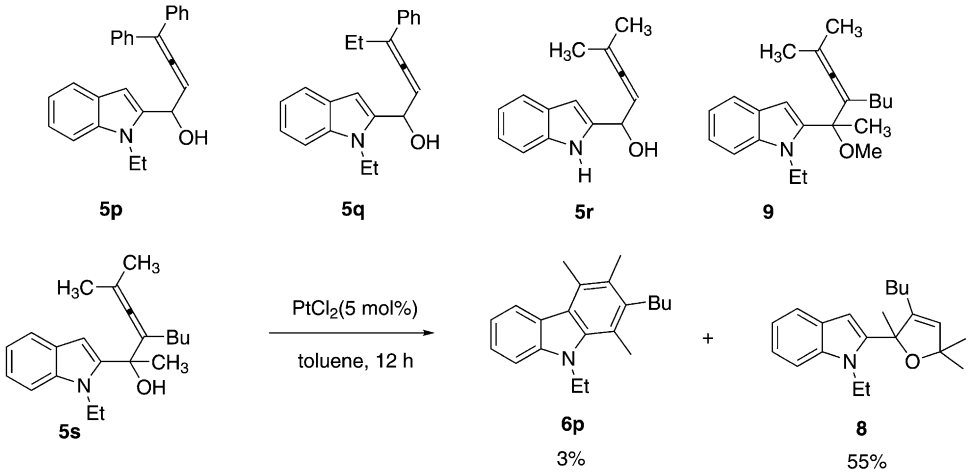
Toluene and THF were refluxed in the presence of sodium using diphenyl ketone as indicator and distilled right before use. $PtCl_2$ was purchased from Alfa. Compounds **5a–f**, **5h**, **5k**, **5m–5p**, and **5r** were prepared as described below.

1-(1-Ethyl-1*H*-indol-2-yl)-4-methylpenta-2,3-dien-1-ol (5a); Typical Procedure[15,19]



1a 7a **5a** (51%)

To a solution of **1a** (1.0901 g, 6.5 mmol) and THF (25 mL) was added dropwise *n*-BuLi (2.6 mL, 2.5 M in hexane, 6.5 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 (1.2101 g, 7.0 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 a sa-



5p **5q** **5r** **9** **5s** **6p** 3% **8** 55%

Scheme 5.

turated aqueous solution of NH_4Cl (20 mL), and extracted with diethyl ether (20 mL × 3). The ether layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The product **7a** was then used without further purification.

To an ice-cold suspension of $LiAlH_4$ (0.2501 g, 6.5 mmol) in dry Et_2O (15 mL) under N_2 was added dropwise a solution of **7a** prepared in the previous step in Et_2O (5 mL) within 5 min. Then the mixture was allowed to warm up to room temperature. After being stirred for 4.5 h, the resulting mixture was quenched with water. The aqueous layer was extracted with diethyl ether (15 mL × 3), washed with water (20 mL × 3) and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) gave **5a**; as a solid; yield: 0.7995 g (combined yield from **1a** to **5a** is 51%); mp 98–99 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (dt, J = 7.8 and 1.1 Hz, 1H, ArH), 7.34 (dd, J = 8.3 and 0.80 Hz, 1H, ArH), 7.25–7.17 (m, 1H, ArH), 7.13–7.05 (m, 1H, ArH), 6.50 (s, 1H, ArH), 5.55–5.44 (m, 1H, CH=), 5.38 (t, J = 5.9 Hz, 1H, CH), 4.42–4.18 (m, 2H, NCH_2), 2.07 (d, J = 6.0 Hz, 1H, OH), 1.81 [d, J = 3.0 Hz, 3H, one CH_3 from $(CH_3)_2C$=], 1.77 [d, J = 0.9 Hz, 3H, one CH_3 from $(CH_3)_2C$=], 1.42 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.9, 140.4, 137.0, 127.3, 121.7, 120.9, 119.4, 109.3, 100.8, 100.0, 92.3, 65.4, 38.4, 20.6, 20.5, 15.4; IR (KBr): ν = 3356, 3045, 2979, 2934, 2901, 1967, 1612, 1537, 1460, 1347, 1315, 1221, 1164, 1129, 1075 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 242 (M^+ + 1, 13.80), 241 (M^+, 77.84), 118 (100); anal. calcd. for $C_{16}H_{19}NO$: C 79.63, H 7.94, N 5.80, found: C 79.74, H 8.07, N 5.73.

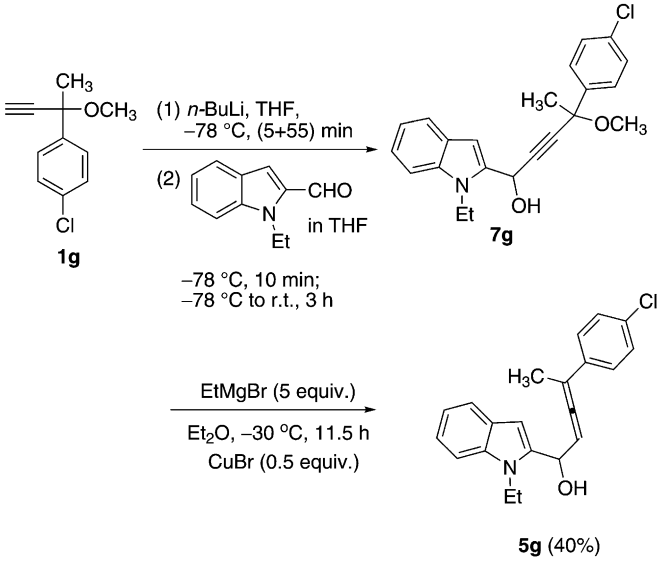
4-(4-Chlorophenyl)-1-(1-ethyl-1*H*-indol-2-yl)penta-2,3-dien-1-ol (5g); Typical Procedure

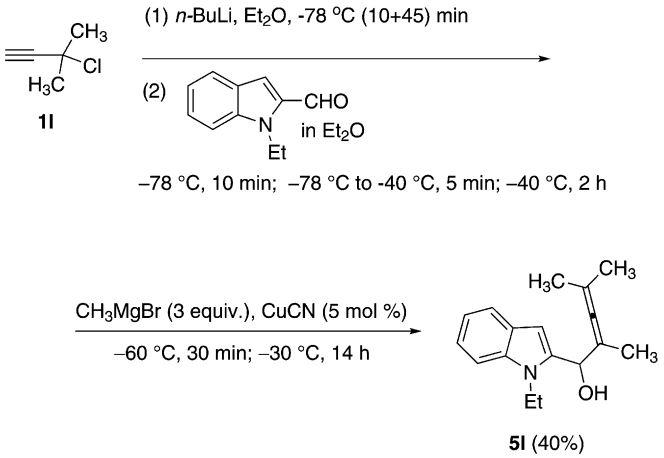
To a solution of **1g** (1.9419 g, 10 mmol) and THF (25 mL) was slowly added dropwise *n*-BuLi (4.0 mL, 2.5 M in hexane, 10 mmol) at −78 °C with stirring under a nitrogen atmosphere within 5 min. After being stirred for 55 min at −78 °C, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (1.7319 g, 10 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, filtered, concentrated under vacuum. Column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded **7g** that was used as such in the next step.

To a solution of CuBr (0.7524 g, 5 mmol) and **7g** prepared above in Et_2O (20 mL) was added dropwise a solution of EtMgBr (70 mL, 0.71 M in Et_2O, 50 mmol) at −30 °C with stirring under a nitrogen atmosphere within 25 min. After the addition, the reaction mixture was stirred for 11 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. Fifration, evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 ~ 10/1) afforded **5g** as a solid; yield: 1.3587 g (combined yield from **1g** to **5g** is 40%); mp 122–123 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 7.5 Hz, 1H, ArH), 7.52–7.26 (m, 6H, ArH), 7.25–7.13 (m, 1H, ArH), [(6.69, s), (6.62, s), 1H, ArH], 6.10–5.97 (m, 1H, CH=), 5.62–5.48 (m, 1H, CH), 4.48–4.13 (m, 2H, NCH_2), 2.52–2.30 (m, 1H, OH), [2.25 (d, J = 2.4 Hz), 2.20 (d, J = 2.4 Hz), 3H, CH_3], 1.45 (t, J = 7.1 Hz, 3H, CH_3); IR (neat): ν = 3531, 3410, 3055, 2981, 2933, 2899, 1951, 1657, 1611, 1592, 1537, 1489, 1460, 1409, 1347, 1315, 1267, 1221, 1165, 1128, 1094, 1062, 1012 cm^{-1}; MS (70 eV, EI): *m/z* (%) = 339 [M^+(^{37}Cl), 33.68], 337 [M^+(^{35}Cl), 100]; anal. calcd. for $C_{21}H_{20}NClO$: C 74.66, H 5.97, N 4.15; found: C 74.74, H 5.96, N 4.07.

1-(1-Ethyl-1*H*-indol-2-yl)-2,4-dimethylpenta-2,3-dien-1-ol (5l);[20] Typical Procedure

To a solution of **1l** (1.1210 g, 10 mmol) in Et_2O (50 mL) was added dropwise *n*-BuLi (4 mL, 2.5 M in hexane, 10 mmol) at −78 °C with stirring under a nitrogen atmosphere within 10 min. After being stirred for 45 min at −78 °C, a solution of 1-ethyl-1*H*-indole-2-carbaldehyde (1.7352 g, 10 mmol) in anhydrous Et_2O (10 mL) was added dropwise at this temperature within 5 min. Then the mixture was allowed to warm up to −40 °C within 2 h. CuCN (52.5 mg, 0.58 mmol) was then added at −60 °C, followed by the addition of a solution of CH_3MgBr (10 mL, 3 M in Et_2O, 30 mmol) dropwise at





−60 °C with stirring under a nitrogen atmosphere within 30 min. After the addition was over, the reaction mixture was stirred for 14 h at −30 °C as monitored by TLC, quenched with a 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 = 10/1) afforded **5l** as a liquid; yield: 1.0203 g (combined yield from **1l** to **5l** is 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (dt, J = 7.8 and 0.9 Hz, 1H, ArH), 7.32 (d, J = 8.3 and 0.8 Hz, 1H, ArH), 7.24–7.15 (m, 1H, ArH), 7.12–7.03 (m, 1H, ArH), 6.45 (s, 1H, ArH), 5.18 (s, 1H, CH), 4.38–4.20 (m, 2H, NCH_2), 2.27 (bs, 1H, OH), 1.80 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.38 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.5, 138.9, 137.0, 127.3, 121.5, 120.7, 119.2, 109.2, 101.0, 100.1, 68.3, 38.3, 20.84, 20.78, 16.3, 15.3; IR (neat): ν = 3405, 3050, 2980, 2930, 2898, 2870, 1974, 1654, 1611, 1541, 1461, 1413, 1363, 1346, 1316, 1221, 1164, 1125, 1077, 1038 cm^{-1}; MS (70 eV, EI): m/z (%) = 256 (M^+, 7.59), 255 (M^+, 36.58), 118 (100); HR-MS: m/z = 255.1618, calcd. for $C_{17}H_{21}NO$ (M^+): 255.1623.

Synthesis of Carbazoles;[15] Typical Procedure for 9-Ethyl-3,4-dimethyl-9*H*-carbazole (6a)

To a dry Schlenk tube were added $PtCl_2$ (5.2 mg, 0.02 mmol), **5a** (96.0 mg, 0.40 mmol), and toluene (2 mL) sequentially under N_2. After continuous stirring for 10 h at room temperature, the reaction was complete as monitored by TLC. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) afforded **6a** as a liquid; yield: 64.5 mg (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.1 Hz, 1H, ArH), 7.50–7.31 (m, 2H, ArH), 7.30–7.09 (m, 3H, ArH), 4.30 (q, J = 7.2 Hz, 2H, NCH_2), 2.80 (s, 3H, $ArCH_3$), 2.47 (s, 3H, $ArCH_3$), 1.37 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 138.6, 131.5, 127.7, 126.2, 124.7, 123.5, 122.9, 121.7, 118.3, 108.0, 105.4, 37.2, 19.5, 16.5, 13.6; IR (neat): ν = 3049, 2974, 2932, 2859, 1618, 1596, 1492, 1470, 1460, 1381, 1343, 1331, 1317, 1290, 1267, 1244, 1173, 1150, 1116, 1099, 1079, 1028 cm^{-1}; MS (70 eV, EI): m/z (%) = 224 (M^++1, 13.30), 223 (M^+, 70.45), 208 (100); HR-MS: m/z = 223.1365, calcd. for $C_{16}H_{17}N$ (M^+): 223.1361.

9-Ethyl-4-methyl-3-phenyl-9*H*-carbazole (6d): The reaction of $PtCl_2$ (4.0 mg, 0.015 mmol) and **5d** (91.0 mg, 0.30 mmol) in toluene (1.4 mL) at room temperature for 24 h afforded **6d** (silica gel, petroleum ether/ethyl acetate = 20/1) as a solid; yield: 57.6 mg (67%); mp 126–127 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.1 Hz, 1H, ArH), 7.55–7.20 (m, 10H, ArH), 4.40 (q, J = 7.2 Hz, 2H, NCH_2), 2.83 (s, 3H, $ArCH_3$), 1.46 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 140.2, 139.1, 133.1, 130.7, 130.3, 127.9, 127.8, 126.2, 125.0, 123.7, 123.0, 121.8, 118.7, 108.2, 105.7, 37.4, 18.2, 13.7; IR (KBr): ν = 3053, 2975, 2925, 1621, 1591, 1479, 1470, 1447, 1383, 1344, 1332, 1298, 1254, 1191, 1156, 1106, 1083, 1027, 1011 cm^{-1}; MS (70 eV, EI): m/z (%) = 286 (M^++1, 20.93), 285 (M^+, 91.60), 270 (100); anal. calcd. for $C_{21}H_{19}N$: C 88.38, H 6.71, N 4.91; found: C 88.45, H 6.80, N 5.02.

9-Ethyl-3-(4-methoxyphenyl)-4-methyl-9*H*-carbazole (6e): The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **5e** (98.1 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 6 h afforded **6e** (silica gel, petroleum ether/ethyl acetate = 40:1) as a solid; yield: 80.4 mg (87%); mp 136–138 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.1 Hz, 1H, ArH), 7.50–7.10 (m, 7H, ArH), 6.98–6.88 (m, 2H, ArH), 4.32 (q, J = 7.2 Hz, 2H, NCH_2), 3.80 (s, 3H, OCH_3), 2.75 (s, 3H, $ArCH_3$), 1.37 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 140.2, 139.0, 134.8, 132.8, 131.2, 130.9, 127.9, 125.0, 123.8, 123.0, 121.8, 118.7, 113.4, 108.2, 105.6, 55.3, 37.4, 18.2, 13.8; IR (KBr): ν = 3039, 2974, 2943, 1603, 1591, 1515, 1484, 1470, 1382, 1333, 1277, 1245, 1176, 1156, 1106, 1038 cm^{-1}; MS (70 eV, EI): m/z (%) = 316 (M^++1, 24.94), 315 (M^+, 100); anal. calcd. for $C_{22}H_{21}NO$: C 83.78, H 6.71, N 4.44; found: C 83.82, H 6.72, N 4.39.

9-Ethyl-4-methyl-3-(*m*-tolyl)-9*H*-carbazole (6f): The reaction of $PtCl_2$ (2.8 mg, 0.01 mmol) and **5f** (61.2 mg, 0.19 mmol) in toluene (1.0 mL) at room temperature for 12 h afforded **6f** (silioca gel, petroleum ether/ethyl acetate = 50/1) as a liquid; yield: 43.2 mg (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.1 Hz, 1H, ArH), 7.55–7.12 (m, 9H, ArH), 4.40 (q, J = 7.2 Hz, 2H, NCH_2), 2.82 (s, 3H, $ArCH_3$), 2.43 (s, 3H, $ArCH_3$), 1.45 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 140.2, 139.1, 137.5, 133.3, 131.0, 130.7, 127.8, 127.4, 127.0, 125.0, 123.8, 123.1, 121.8, 118.7, 108.2, 105.6, 37.4, 21.5, 18.2, 13.8; IR (neat): ν = 3047, 2971, 2917, 2866, 1692, 1622, 1594, 1480, 1467, 1449, 1382, 1344, 1333, 1257, 1154, 1100 cm^{-1}; MS (70 eV, EI): m/z (%) = 300 (M^++1, 24.39), 299 (M^+, 99.80), 284 (100); HR-MS: m/z = 299.1674, calcd. for $C_{22}H_{21}N$ (M^+): 299.1674.

3-(4-Chlorophenyl)-9-ethyl-4-methyl-9*H*-carbazole (6g): The reaction of $PtCl_2$ (4.0 mg, 0.015 mmol) and **5g** (98.5 mg, 0.29 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded **6g** (silica gel, petroleum ether/ethyl acetate = 40/1) as a solid; yield: 67.2 mg (72%); mp 175–176 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, J = 7.5 Hz, 1H, ArH), 7.55–7.20 (m, 9H, ArH), 4.40 (q, J = 7.2 Hz, 2H, NCH_2), 2.80 (s, 3H, $ArCH_3$), 1.45 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8, 140.2, 139.2, 132.2, 131.8, 131.5, 130.7, 128.1, 127.5, 125.1, 123.7, 123.0, 121.8, 118.8, 108.3, 105.8, 37.4, 18.1, 13.7; IR (KBr): ν = 3051, 2967, 1618, 1591, 1478, 1382, 1332, 1253, 1155, 1085 cm^{-1}; MS (70 eV, EI): m/z (%) = 321 [M^+(^{37}Cl), 29.74], 319 [M^+(^{35}Cl), 88.64], 306 [M^+−CH_3(^{37}Cl), 33.46], 304 [M^+−CH_3(^{35}Cl), 100]; anal. calcd. for $C_{21}H_{18}NCl$: C 78.86, H 5.67, N 4.38; found: C 78.71, H 5.45, N 4.38.

9-Ethyl-3-(4-fluorophenyl)-4-methyl-9*H*-carbazole (6h): The reaction of $PtCl_2$ (4.4 mg, 0.017 mmol) and **5h** (97.1 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 25 h afforded **6h** (silica gel, petroleum ether/ethyl acetate = 40/1) as a solid; yield: 70.2 mg (77%); mp 160–161 °C (ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, J = 7.8 Hz, 1H, ArH), 7.56–7.42 (m, 2H, ArH), 7.41–7.20 (m, 5H, ArH), 7.13 (t, J = 8.7 Hz, 2H, ArH), 4.40 (q, J = 7.3 Hz, 2H, NCH_2), 2.80 (s, 3H, $ArCH_3$), 1.45 (t, J = 7.2 Hz, 3H, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −117.0; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.7 (d, J = 243.3 Hz), 140.2, 139.2, 138.3 (d, J = 4.0 Hz), 132.0, 131.6 (d, J = 7.5 Hz), 130.8, 127.7, 125.1, 123.7, 123.0, 121.8, 118.8, 114.7 (d, J = 21.2 Hz), 108.3, 105.7, 37.4, 18.1, 13.7; IR (KBr): ν = 3051, 2967, 1591, 1478, 1462, 1382, 1332, 1323, 1290, 1253, 1185, 1155, 1085, 1014 cm^{-1}; MS (70 eV, EI): m/z (%) = 304 (M^++

1, 18.10), 303 (M^+, 81.52), 288 (100); anal. calcd. for $C_{21}H_{18}FN$: C 83.14, H 5.98, N 4.62; Found: C 83.34, H 5.88, N 4.49.

9-Ethyl-3-(2-furyl)-4-methyl-9*H*-carbazole (6i): The reaction of $PtCl_2$ (4.9 mg, 0.018 mmol) and **5i** (88.0 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 4 h afforded **6i** (silica gel, petroleum ether/ethyl acetate = 40/1) as a liquid; yield: 50.7 mg (61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (d, J = 7.8 Hz, 1H, ArH), 7.74 (d, J = 8.7 Hz, 1H, ArH), 7.61 (dd, J = 1.8 and 0.9 Hz, 1H, ArH), 7.58–7.45 (m, 2H, ArH), 7.38–7.28 (m, 2H, ArH), 6.59 (dd, J = 3.6 and 1.8 Hz, 1H, ArH), 6.52 (dd, J = 3.3 and 0.9 Hz, 1H, ArH), 4.39 (q, J = 7.1 Hz, 2H, NCH_2), 3.05 (s, 3H, $ArCH_3$), 1.46 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.7, 141.3, 140.2, 139.4, 131.6, 126.5, 125.1, 123.8, 123.1, 122.2, 122.0, 118.9, 111.0, 108.3, 107.8, 105.9, 37.4, 18.1, 13.7; IR (neat): ν = 3051, 2975, 2931, 1618, 1592, 1485, 1471, 1384, 1345, 1331, 1319, 1291, 1252, 1194, 1152, 1106, 1079, 1026, 1003 cm^{-1}; MS (70 eV, EI): m/z (%) = 276 (M^++1, 20.99), 275 (M^+, 100); HR-MS: m/z = 275.1311, calcd. for $C_{19}H_{17}NO$ (M^+): 275.1310.

9-Ethyl-4-methyl-3-(thiophen-2-yl)-9*H*-carbazole (6j): The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **5j** (91.2 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 13 h afforded **6j** (silica gel, petroleum ether/ethyl acetate = 100/1) as a liquid; yield: 71.3 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, J = 7.8 Hz, 1H, ArH), 7.65–7.46 (m, 3H, ArH), 7.45–7.39 (m, 1H, ArH), 7.38–7.29 (m, 2H, ArH), 7.25–7.15 (m, 1H, ArH), 7.14–7.10 (m, 1H, ArH), 4.42 (q, J = 7.2 Hz, 2H, NCH_2), 3.01 (s, 3H, $ArCH_3$), 1.49 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.0, 140.2, 139.4, 132.1, 128.6, 126.9, 126.8, 125.1, 125.0, 124.8, 123.7, 123.0, 121.9, 118.9, 108.3, 105.7, 37.4, 18.1, 13.7; IR (neat): ν = 3051, 2975, 2925, 1618, 1589, 1485, 1470, 1424, 1383, 1330, 1288, 1269, 1248, 1221, 1153, 1105, 1078, 1027 cm^{-1}; MS (70 eV, EI): m/z (%) = 292 (M^++1, 21.45), 291 (M^+, 100); HR-MS: m/z = 291.1083, calcd. for $C_{19}H_{17}NS$ (M^+): 291.1082.

9-Ethyl-1,4-dimethyl-3-phenyl-9*H*-carbazole (6k): The reaction of $PtCl_2$ (4.2 mg, 0.016 mmol) and **5k** (96.2 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 24 h afforded **6k** (silica gel/petroleum ether/ethyl acetate = 40/1) as a liquid; yield: 75.6 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (d, J = 7.8 Hz, 1H, ArH), 7.66–7.55 (m, 6H, ArH), 7.54–7.45 (m, 1H, ArH), 7.44–7.35 (m, 1H, ArH), 7.30 (s, 1H, ArH), 4.72 (q, J = 7.2 Hz, 2H, NCH_2), 2.95 (s, 6H, $ArCH_3$), 1.56 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3, 140.9, 137.8, 133.2, 131.1, 130.2, 128.3, 127.9, 126.2, 124.9, 124.1, 123.0, 122.6, 118.8, 116.8, 108.4, 39.2, 20.0, 18.1, 15.5; IR (neat): ν = 3052, 3018, 2972, 2926, 2870, 1601, 1575, 1484, 1463, 1396, 1377, 1340, 1308, 1244, 1155, 1105, 1074, 1028, 1005 cm^{-1}; MS (70 eV, EI): m/z (%) = 300 (M^++1, 22.16), 299 (M^+, 91.39), 284 (M^+-CH_3, 100); HR-MS: m/z = 299.1674, calcd. for $C_{22}H_{21}N$ (M^+): 299.1674.

9-Ethyl-2,3,4-trimethyl-9*H*-carbazole (6l): The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **5l** (78.5 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 12 h afforded **6l** (by double chromatography on silica gel: first round eluent petroleum ether/ethyl acetate = 10/1, second round eluent: petroleum ether/ethyl acetate = 200/1) as a liquid; yield: 40.3 mg (55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.4 Hz, 1H, ArH), 7.50–7.30 (m, 2H, ArH), 7.26–7.15 (m, 1H, ArH), 7.10 (s, 1H, ArH), 4.32 (q, J = 7.2 Hz, 2H, NCH_2), 2.85 (s, 3H, $ArCH_3$), 2.50 (s, 3H, $ArCH_3$), 2.37 (s, 3H, $ArCH_3$), 1.39 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9, 138.1, 134.7, 131.4, 125.4, 124.2, 123.7, 122.5, 119.9, 118.2, 107.9, 106.9, 37.1, 22.3, 17.0, 15.0, 13.7; IR (neat): ν = 3044, 3973, 2936, 2873, 1621, 1599, 1470, 1464, 1376, 1348, 1330, 1311, 1288, 1265, 1207, 1181, 1139, 1098, 1029 cm^{-1}; MS (70 eV, EI): m/z (%) = 238 (M^++1, 12.57), 237 (M^+, 66.11), 222 (100); HR-MS: m/z = 237.1519, calcd. for $C_{17}H_{19}N$ (M^+): 237.1517.

9-Ethyl-4,6-dimethyl-3-(*p*-tolyl)-9*H*-carbazole (6m): The reaction of $PtCl_2$ (3.9 mg, 0.015 mmol) and **5m** (99.4 mg, 0.30 mmol) in toluene (1.5 mL) at room temperature for 16 h afforded **6m** (silica gel, petroleum ether/ethyl acetate = 100/1) as a solid; yield: 77.8 mg (83%); mp 128–129 °C (CH_2Cl_2/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (s, 1H, ArH), 7.41–7.20 (m, 8H, ArH), 4.35 (q, J = 7.2 Hz, 2H, NCH_2), 2.81 (s, 3H, $ArCH_3$), 2.56 (s, 3H, $ArCH_3$), 2.43 (s, 3H, $ArCH_3$), 1.42 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 139.3, 138.5, 135.7, 132.8, 130.7, 130.2, 128.7, 127.8, 127.7, 126.2, 124.0, 123.1, 121.6, 107.9, 105.6, 37.4, 21.6, 21.2, 18.3, 13.7; IR (KBr): ν = 3020, 2974, 2919, 2865, 1624, 1595, 1573, 1489, 1474, 1449, 1382, 1345, 1308, 1257, 1226, 1154, 1112, 1010 cm^{-1}; MS (70 eV, EI): m/z (%) = 314 (M^++1, 25.61), 313 (M^+, 100); anal. calcd. for $C_{23}H_{23}N$: C 88.13, H 7.40, N 4.47; found: C 88.18, H 7.42, N 4.38.

9-Ethyl-6-methoxy-3,4-dimethyl-9*H*-carbazole (6n): The reaction of $PtCl_2$ (4.1 mg, 0.015 mmol) and **5n** (82.0 mg, 0.30 mmol) in toluene (2.0 mL) at room temperature for 12 h afforded **6n** (silica gel, petroleum ether/ethyl acetate = 40/1) as a liquid: yield: 53.6 mg (70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 2.1 H, 1H, ArH), 7.38–7.27 (m, 2H, ArH), 7.23–7.11 (m, 2H, ArH), 4.33 (q, J = 7.2 Hz, 2H, NCH_2), 3.99 (s, 3H, $ArOCH_3$), 2.86 (s, 3H, $ArCH_3$), 2.53 (s, 3H, $ArCH_3$), 1.41 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 139.3, 135.4, 131.4, 127.8, 125.7, 123.9, 121.6, 113.0, 108.3, 107.2, 105.5, 56.3, 37.3, 19.5, 16.4, 13.6; IR (neat): ν = 2973, 2933, 2829, 1625, 1602, 1575, 1494, 1476, 1379, 1321, 1306, 1269, 1225, 1209, 1164, 1149, 1040 cm^{-1}; MS (70 eV, EI): m/z (%) = 253 (M^+, 74.52), 238 (100); HR-MS: m/z = 253.1471, calcd. for $C_{17}H_{19}NO$ (M^+): 253.1467.

9-Ethyl-1,5,6-trimethyl-9*H*-carbazole (6o): The reaction of $PtCl_2$ (5.4 mg, 0.02 mmol) and **5o** (101.1 mg, 0.40 mmol) in toluene (2.0 mL) at room temperature for 16 h afforded **6o** (by double chromatography on silica gel: first round eluent petroleum ether/ethyl acetate = 50/1, second round eluent: petroleum ether/ethyl acetate = 100/1) as a liquid; yield: 68.1 mg (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, J = 7.8 H, 1H, ArH), 7.30 (d, J = 8.1 Hz, 1H, ArH), 7.19 (d, J = 8.1 Hz, 2H, ArH), 7.16–7.08 (m, 1H, ArH), 4.60 (q, J = 7.1 Hz, 2H, NCH_2), 2.85 (s, 3H, $ArCH_3$), 2.83 (s, 3H, $ArCH_3$), 2.50 (s, 3H, $ArCH_3$), 1.41 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 138.9, 131.2, 128.1, 127.7, 126.4, 124.5, 122.0, 120.9, 119.5, 118.5, 105.6, 39.3, 20.4, 19.6, 16.6, 15.5; IR (neat) ν = 2967, 2931, 2866, 1587, 1494, 1485, 1460, 1404, 1378, 1327, 1310, 1281, 1263, 1243, 1176, 1120, 1047 cm^{-1}; MS (70 eV, EI): m/z (%) = 238 (M^++1, 10.80), 237 (M^+, 57.23), 222 (M^+-CH_3, 100); HR-MS: m/z = 237.1519, calcd. for $C_{17}H_{19}N$ (M^+): 237.1517.

Supporting Information

The preparations of compounds **5d–5f**, **5h**, **5k**, **5m–5s**, **5i**, **5j**, **6p**, **8**, and **9** and ^{1}H and ^{13}C NMR spectra of all starting materials and products are given in the Supporting Information.

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