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Article

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One-Pot Cascade Synthesis of Substituted Carbazoles from Indoles, Ketones and Alkenes Using Oxygen as the Oxidant

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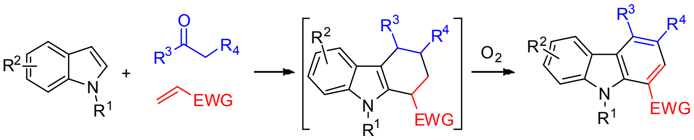


cascade synthesis
atom-economy
green oxidant

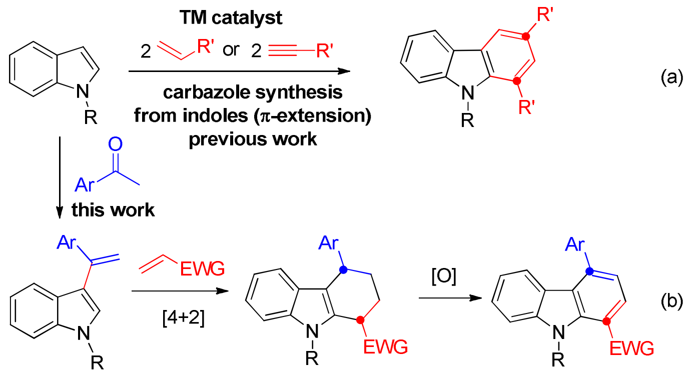
ABSTRACT: An efficient one-pot two-step indole-to-carbazole strategy has been developed. This transition metal-free methodology uses oxygen as the sole oxidant and starts from cheap and readily available indoles, ketones and alkenes. The present protocol efficiently enables the assembly of a diverse array of substituted carbazole products with good regioselectivity and broad tolerance of functional groups.

INTRODUCTION

The construction of complex molecules starting from easily available chemicals is of great significance in the context of ongoing green chemistry. Cascade synthesis has thereby attracted much attentions in the past few decades, which provides versatile capabilities to form a plurality of C-C and C-Het bonds in a one-pot manner.[1] Due to the high importance of carbazoles in medicinal chemistry[2] and material science,[3] one-pot cascade synthesis of substituted carbazoles has been widely developed. While at the early stage, the carbazole synthesis mainly relies on the Fischer-Borsche synthesis via a multi-step procedure,[4] in recent years, intramolecular cross coupling by transition-metal (TM) catalysis for carbazole synthesis has gained great interest. Aryl halides and 2-haloanilines or 1,2-dihaloarenes could be directly used as the coupling partners for carbazole synthesis via *in situ* formation of diarylamines in the presence of palladium catalyst.[5] The Cadogan cyclization of 2-nitrobiaryls at high temperatures using either excess of phosphines, phosphites or carbon monooxide could provide an alternative approach to substituted carbazoles.[6] A recent research showed that this kind of reaction could be realized from 2-nitrobiaryls and PhMgBr under mild and TM-free reaction conditions.[7]

Indole-to-carbazole strategy via, for example, Diels-Alder reaction by multi-step synthesis[8] represents one of concise cascade methods, which also formed three C-C bonds in one-pot through transition-metal-catalyzed π-extension of indoles with alkenes or alkynes[9] (Scheme 1a). In view of our previous indole-template synthesis,[10] we speculate a cascade access to carbazoles through three-component assembly of readily available indoles, ketones and alkenes: the established 3-vinylindole, in situ generated through dehydrative condensation of ketone and indole, [10a-b] undergoes formal [4+2] cycloaddition with alkenes to form tetrahydrocarbazole intermediate, followed by dehydrogenative aromatization to give the target carbazoles (Scheme 1b).

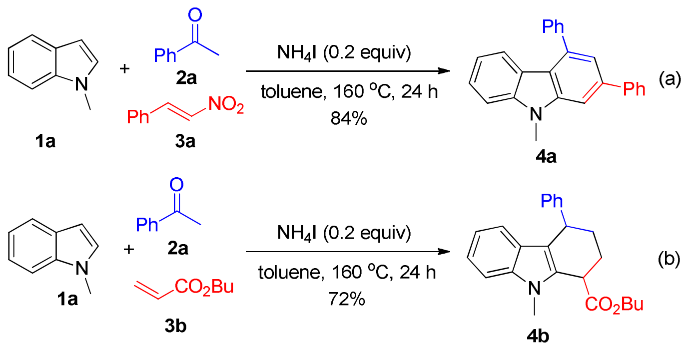
Scheme 1. Carbazole Formation from Indoles.



RESULTS AND DISSCUSSION

Recently, we developed the indole-based three-component reaction for the carbazole assembly using nitrostyrene with a NH_4I-based catalytic system.[11] While nitrostyrene **3a** exclusively afforded the carbazole **4a** with the nitro removed in excellent yield (Scheme 2a), the initial experiment of butyl acrylate (**3b**) indicated that it gave tetrahydrocarbazole **4b** as the main product although the reaction was performed under an oxygen atmosphere for prolonged reaction time (Scheme 2b). We reason that the dehydrogenative aromatization could be achieved under an oxygen-based system in a one-pot manner.[12]

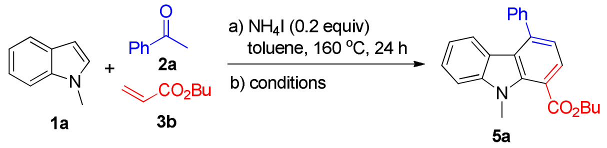
Scheme 2. Initial Attempts on Carbazole Formation from Indoles.



We thus screened a series of conditions to promote the dehydrogenation process using oxygen as the sole oxidant (Table 1). The yield of carbazole **5a** was enhanced to

24% by simply prolonging the reaction time under oxygen (entry 1), which indicates the dehydrogenation could be achieved by oxygen. A series of iodine reagents such as elemental iodine, KI, NaI, and NIS (*N*-Iodosuccinimide) were screened (entries 2-5),[13,14] which showed that elemental iodine (entry 2) and KI (entry 3) enhanced the yield of **5a**. Then, we speculated that Brφnsted acid as an additive could promote the desired reaction.[15] Among those acids tested (entries 6-10), TsOH gave the best result (entry 7). Increasing the amounts of KI and TsOH further enhanced the yield of **5a** to 89% (entry 11). The reaction performed under air atmosphere afforded very low yield of the products (entry 12). As a contrast, excessive NH_4I used in the first step instead of the combination of NH_4I and KI showed lower efficiency for the cascade carbazole formation. Finally, we detected certain amount of tetrahydrocarbazole **4b** when the reaction was conducted at lowered temperature (entries 13,14). Thus 160 °C is indeed required for the dehydrogenative step.

Table 1. Optimization for the One-Pot Synthesis of Carbazole.[a]



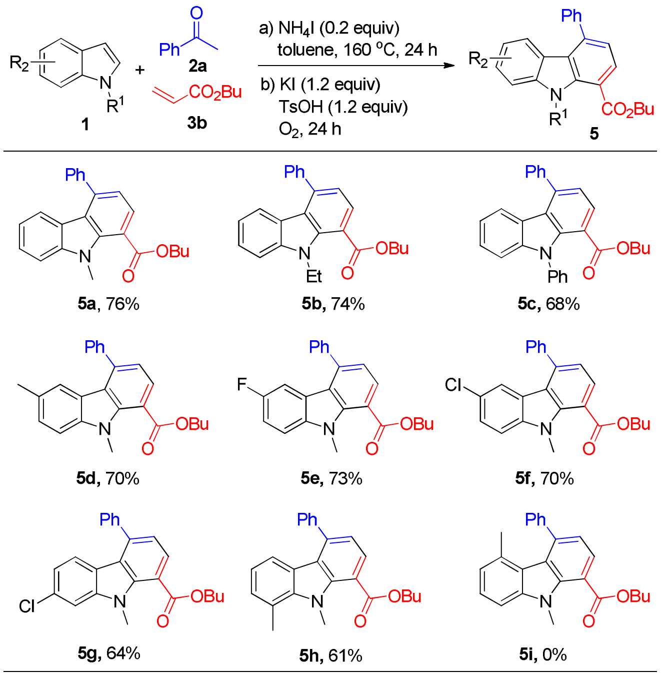
entry	[I]	additive	atmosphere	yield (%)[b]
1	-	-	O_2	24
2	I_2	-	O_2	34
3	KI	-	O_2	41
4	NaI	-	O_2	37
5	NIS	-	O_2	38

6	KI	AcOH	O_2	45
7	KI	TsOH	O_2	62
8	KI	TFA	O_2	48
9	KI	CH_3SO_3H	O_2	17
10	KI	TfOH	O_2	trace
11[c]	KI	TsOH	O_2	89 (trace)
12	KI	TsOH	air	32
13[d]	-	TsOH	O_2	69
14[c,e]	KI	TsOH	O_2	71 (16)
15[c,f]	KI	TsOH	O_2	56 (20)

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3b** (0.4 mmol, 2.0 equiv), NH_4I (0.04 mmol, 20 mol %), toluene (0.5 mL, sealed tube), 160 °C, 24 h. Then [I] (0.04 mmol, 20 mol %), additive (1.0 equiv) added, under O_2, 160 °C, 24 h, [b] GC yield based on **1a** was given and GC yield of **4b** in the parentheses. [c] KI (0.24 mmol, 1.2 equiv), TsOH (0.24 mmol, 1.2 equiv) . [d] NH_4I (1.5 equiv) was used in the first step and TsOH (0.24 mmol, 1.2 equiv) was used in the second step. [e] The reaction was performed at 150 °C. [f] The reaction was performed at 140 °C.

With the optimized reaction conditions in hand, subsequently, a series of substituted indoles were tested for the annulation/aromatization sequence (Table 2). Generally, both *N*-alkylindoles and *N*-arylindoles can smoothly proceed to give the corresponding products in good yields (**5a**-**5c**). The carbazole products **5d**-**5h** were afforded in moderate yield when *N*-methylindoles bearing different substituent such as alkyl and halogen at C5, C6, or C7 were employed. Unfortunately, no desired product can be obtained when a methyl group was located at C4 position (**5i**).

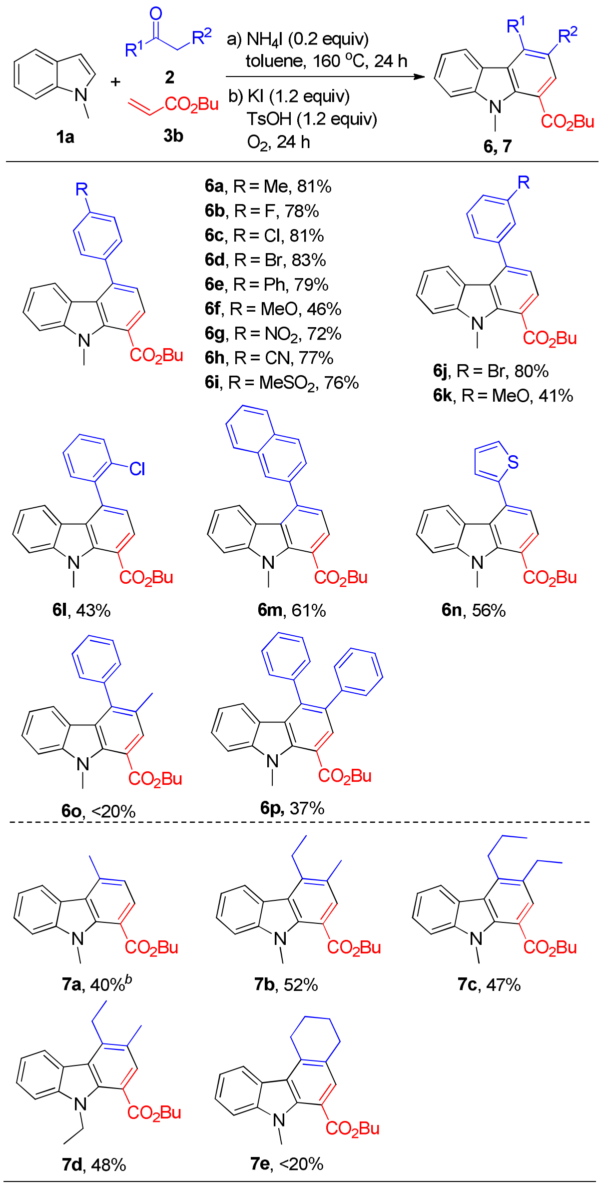
Table 2. The Scope of Indoles.[a]



[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3b** (0.4 mmol, 2.0 equiv), catalyst (0.04 mmol, 20 mol %), toluene (0.5 mL, sealed tube), 160 °C, 24 h. Then KI (0.24 mmol, 1.2 equiv), TsOH (0.24 mmol, 1.2 equiv) added, under O_2, 160 °C, 24 h.

To further examine the scope and limitations of the reaction, we tested various ketones for this kind of reaction (Table 3). Moderate to good yields of carbazoles were obtained with wide tolerance of ketones bearing halogen (F, Cl, and Br), nitro, nitrile, sulfone, et al. (**6a-6k**). Steric effect of the ketones was clearified by chloro-substituted phenylethanone. While 1-(2-chlorophenyl)ethanone gave relatively low yield (**6l**), para-occupied substrate afforded the corresponding carbazole **6c** with excellent yield. To our delight, 1-(Naphthalen-2-yl)ethanone and 1-(thiophen-2-yl)ethanone also reacted, delivering the corresponding carbazoles **6m** and **6n** in 61% and 56% yield, respectively. Other aromatic ketones featured low reactivity. For example propiophenone gave less than 20% GC yield and 1,2-diphenylethanone afforded the corresponding product **6p** in 37% yield. After screening various aromatic ketones, a series of aliphatic ketones were also investigated. In general, lower yields were obtained when aliphatic ketones were used (**7a-7d**). When cyclohexanone was employed, the corresponding product **7e** was obtained in less than 20% yield, while competitive amounts of tetrahydrocarbazole were observed.

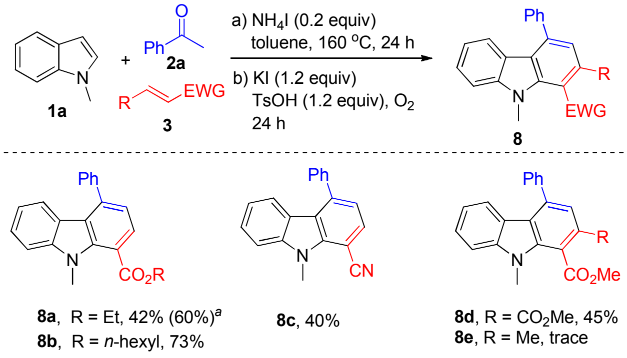
Table 3. The Scope of Ketones.[a]



[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv), **3b** (0.4 mmol, 2.0 equiv), catalyst (0.04 mmol, 20 mol %), toluene (0.5 mL, sealed tube), 160 °C, 24 h. Then KI (0.24 mmol, 1.2 equiv), TsOH (0.24 mmol, 1.2 equiv) added, under O_2, 160 °C, 24 h. [b] 5 equiv of acetone were used.

Then we subjected a range of electron-withdrawing alkenes to the two-step sequence to test the one-pot carbazole synthesis (Scheme 3). When ethyl acrylate was used, we found the yield increased with the amount of ethyl acrylate increased. For example, 42% yield was given under the standard reaction conditions (2 equiv of ethyl acrylate) while 4.0 equiv of ethyl acrylate afford 60% yield of the corresponding carbazole **8a**. These observations may be attributed to the low boiling point of this substrate (99.8 ^{o}C) while the reaction temperature is much higher (160 ^{o}C). We also found *n*-hexyl acrylate gave 73% yield (similar with *n*-Bu-acrylate 76%). Acrylonitrile reacted smoothly to give **8c**, albeit in moderate yields. Dimethyl fumarate also worked in this reaction system, giving carbazole **8d** in 45% yield. Unfortunately, no carbazoles could be obtained when using (*E*)-methyl but-2-enoate and methyl cinnamate.

Scheme 3. Carbazole Synthesis from Electron-Withdrawing Alkenes.

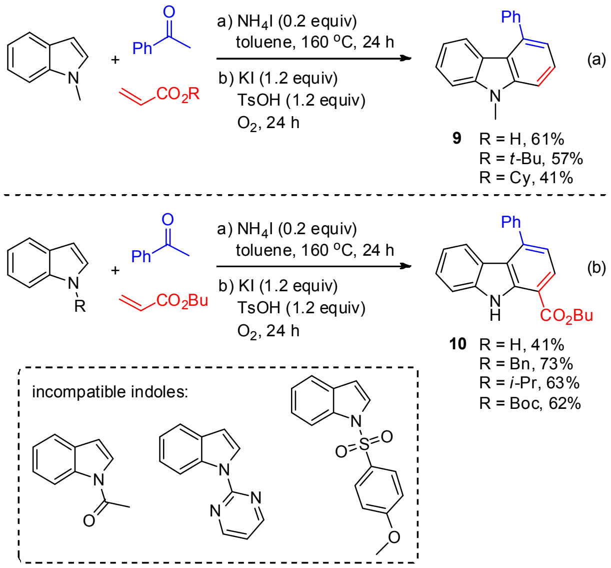


^{a} 4.0 equiv of ethyl acrylate were used.

Unexpectedly, when acrylic acid, *tert*-butyl acrylate, and cyclohexyl acrylate were used, decarbonylation readily occurred and thereby the same carbazole product **9** was obtained (Scheme 4a). While *N*-methyl indoles reacted well, *N*-benzylindole, *N*-isopropylindole, and *N*-Boc indole exclusively afforded *N*-H carbazole **10** with the benzyl group, isopropyl group, and Boc group removed under the present system, the yields of which were even much higher than that from *N*-H indole (Scheme 4b).

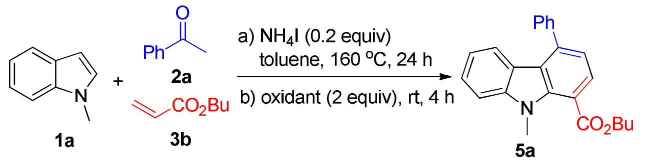
Unfortunately, in the present system electron-deficient indoles bearing *N*-protecting group such as acyl, pyrimidin-2-yl, and sulfonyl afforded neither *N*-protected carbazole nor *N*-H carbazole product (Scheme 4b).

Scheme 4. Unexpected Results of the Three-Component Reaction.



This carbazole synthesis was realized using sealed tube with oxygen as the sole oxidant at a very high temperature, which makes it lack of practicality especially for scale-up synthesis. To solve this problem, the dehydrogenative step of the reaction was performed at room temperature by using an oxidant other than oxygen (Scheme 5). Remarkably, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) smoothly afforded the carbazole **5a** in 58% yield, and the 5 mmol scale reaction also gave moderate yield by DDQ. When using other oxidants, while Dess-Martin reagent afforded 36% yield, 1,4-benzoquinone (BQ) or potassium persulfate ($K_2S_2O_8$) did not promote the dehydrogenative step at all.

Scheme 5. Oxidant Screening for the Dehydrogenative Step

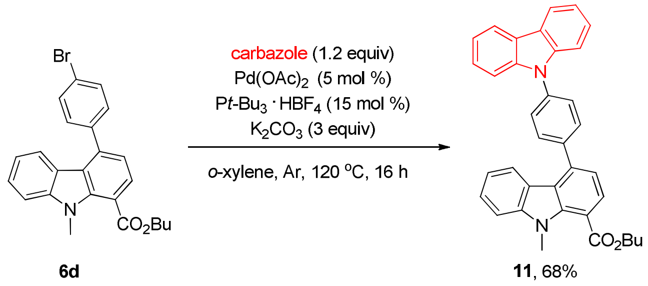


oxidant	yield
DDQ	58% (54%, 965 mg)[a]
Dess-Martin reagent	36%
BQ or $K_2S_2O_8$	0

[a] 5 mmol scale reaction

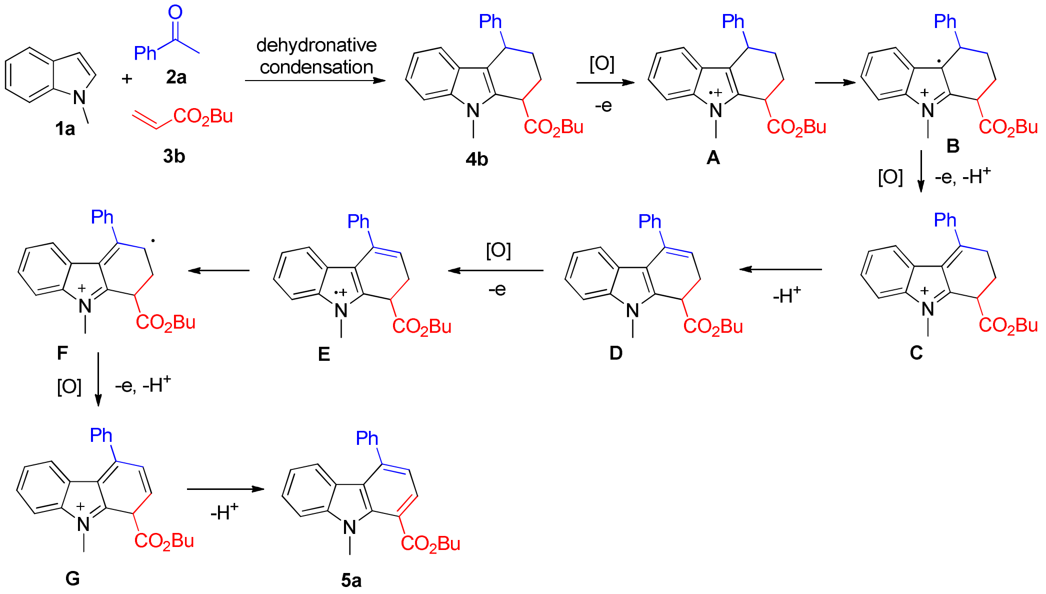
To further illuminate the synthetic utility of this protocol, further transformation of **6d** was investigated (Scheme 6). Cross-coupling of **6d** with cabarzole under palladium-catalysis conditions afforded the adduct **11** bearing two carbazole functionalities in moderate yield, which indicates the present work would be applied to the synthesis of certain optoelectronic materials.[16]

Scheme 6. Coupling of Two Carbazoles.



Regarding the reaction mechanism, dehydronative condensation would be the first step, affording the tetrahydrocarbazole intermediate product **4b**. In an iodine reagent-involved dehydrogenative process, a single-electron oxidative pathway would be plausible.[13] As shown in Scheme 7, nitrogen-centered radical **A**, formed through single-electron oxidation form tetrahydrocarbazole, undergoes single-electron shift to give intermediate **B**. Further single-electron oxidation and deprotonation of **B** forms intermediate **C**, which further proceeds through deprotonation and tautomerization to generate dihydrocarbazole **D**. The second single-electron oxidative dehydrogenation of **D** occurs through the intermediate **E**, **F**, and **G** to give the final product **5a**.

Scheme 7. Possible Reaction Pathway.



CONCLUSION

In summary, we have developed efficient three-component assembly of substituted carbazoles through one-pot twe-step sequence. This indole-to-carbazole protocol involves a cascade of condensation, [4+2] annulation, and dehydrogenative aromatization. It features advantages including easily available starting materials, metal-free conditions, high regioselectivity, and wide functional group tolerance. Moreover, molecular oxygen was used as the sole oxidant in the dehydrogenative procedure.

EXPERIMENTAL SECTION

General information. All reactions were carried out under the standard conditions unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer, and the chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Generally, chloroform was used as the solvent with TMS as the internal standard. GC−MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). The structure of known compounds was further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those in literature. Melting points were measured with a melting point instrument and were uncorrected. All reagents were obtained from commercial suppliers and used without further purification.

General procedure for carbazole synthesis. Ammonium iodide (5.8 mg, 0.04 mmol) was added to a 20 mL oven-dried reaction vessel. The reaction vessel was added 1-methyl-1*H*-indole (25.0 μL, 0.2 mmol), acetophenone (70.4 μL, 0.6 mmol), butyl acrylate (57.4 μL, 0.4 mmol), and toluene (0.5 mL) by syringe. The reaction vessel was stirred at 160 ^{o}C for 24 h. After cooling to room temperature, KI (39.8 mg, 0.24 mmol) and *p*-toluenesulfonic acid (45.7 mg, 0.24 mmol) were added to the reaction vessel. The reaction vessel was purged with oxygen gas for three times and was stirred at 160 ^{o}C for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 10:1) to yield the desired product **5a** as colorless liquid (54.3 mg, 76% yield). $R_f = 0.31$ (10:1 petroleum ether/dichloromethane).

General procedure for carbazole synthesis in 5 mmol scale using DDQ as the oxidant. To a 25 mL pressure tube with Teflon cover was added ammonium iodide (145 mg, 1.0 mmol), 1-methyl-1*H*-indole (656 mg, 5 mmol), acetophenone (1.80 g, 15 mmol), butyl acrylate (1.28 g, 10 mmol), and toluene (4 mL). The reaction mixture was stirred at 160 °C for 24 h. After cooling to room temperature, the mixture was moved into a 50 mL flask and toluene (5 mL) and DDQ (2.27 g, 10 mmol) were added. The reaction was stirred at room temperature for 4 h. After completion, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 10:1) to yield the desired product **5a** as colorless liquid (965 mg, 54% yield). $R_f = 0.31$ (10:1 petroleum ether/dichloromethane).

9-Methyl-2,4-diphenyl-9*H*-carbazole (**4a**, CAS: 1256609-04-7)[17]. White solid (56.0 mg, 84% yield), mp 129-131 °C. $R_f = 0.48$ (200:1 petroleum ether/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76-7.74 (m, 2H), 7.69-7.66 (m, 2H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.55-7.44 (m, 6H), 7.41-7.33 (m, 4H), 7.00-6.96 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.8, 141.7, 141.6, 141.2, 138.7, 137.8, 129.2, 128.7, 128.4, 127.5, 127.5, 127.1, 125.5, 122.2, 122.1, 120.2, 119.4, 118.6, 108.2, 105.8, 28.9; IR spectrum (ν_{max}, cm^{-1}) 3044, 2932, 1588, 1468, 1421, 1323, 1077, 697; HRMS calcd. for $C_{25}H_{19}N$ $[M+H]^+$ 334.1590, found 334.1592.

Butyl-9-methyl-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazole-1-carboxylate [**4b** (dr = 4:5)]. Pale yellow liquid (56.3 mg, 78% yield). R_f = 0.32 (200:1 petroleum ether/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30-7.20 (m, 5H), 7.17-7.09 (m, 2H), 6.92-6.78 (m, 2H), 4.22-4.11 (m, 3H), 3.94-3.91 (m, 1H), 3.67 (s, 3H), 2.42-2.35 (m, 1H), 2.22-2.08 (m, 2H), 1.97-1.88 (m, 1H), 1.65-1.58 (m, 2H), 1.40-1.26 (m, 2H), 0.94-0.88(m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.2, 146.0, 145.5, 137.5, 137.4, 133.2, 133.1, 128.2, 128.2, 128.1, 128.1, 126.4, 126.2, 126.1, 125.9, 121.4, 121.3, 119.8, 119.5, 118.8, 118.7, 113.2, 112.5, 108.7, 108.7, 65.1, 40.6, 39.2, 39.1, 37.9, 31.9, 30.7, 30.6, 30.3, 29.7, 29.6, 26.7, 23.7, 19.1, 13.6, 13.6; IR spectrum (ν_{max}, cm^{-1}) 2932, 1725, 1469, 1244, 1166, 740, 700; HRMS calcd. for $C_{24}H_{27}NO_2$ $[M+H]^+$ 362.2115, found 362.2112.

Butyl-9-methyl-4-phenyl-9*H*-carbazole-1-carboxylate (5a). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.89 (d, J = 7.6 Hz, 1H), 7.58-7.49 (m, 5H), 7.44-7.42 (m, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.00-6.96 (m, 1H), 4.45 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 1.87-1.80 (m, 2H), 1.58-1.49 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 142.7, 141.3, 140.6, 139.5, 128.9, 128.5, 127.9, 127.8, 126.2, 122.6, 122.2, 122.1, 120.1, 119.3, 114.5, 109.1, 65.1, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1707, 1467, 1243, 1068, 748, 700; HRMS calcd. for $C_{24}H_{23}NO_2$ $[M+H]^+$ 358.1802, found 358.1798.

Butyl-9-ethyl-4-phenyl-9*H*-carbazole-1-carboxylate (5b). Colorless liquid (54.9 mg, 74% yield). R_f = 0.31 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (d, J = 7.6 Hz, 1H), 7.57-7.40 (m, 7H), 7.29 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6. 99-6.94 (m, 1H), 4.56 (q, J = 7.1 Hz, 2H), 4.45 (t, J = 6.8 Hz, 2H), 1.87-1.80 (m, 2H), 1.59-1.49 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.3, 141.6, 141.3, 140.7, 137.6, 128.9, 128.5, 127.9, 127.6, 126.1, 122.9, 122.4, 122.3, 119.9, 119.3, 115.0, 109.2, 65.3, 40.0, 30.8, 19.3, 13.8, 13.7; IR spectrum (ν_{max}, cm^{-1}) 2958, 1709, 1457, 1241, 1068, 750, 700; HRMS calcd. for. $C_{25}H_{25}NO_2$ [M+H]$^+$ 372.1958, found 372.1956.

Butyl-4,9-diphenyl-9*H*-carbazole-1-carboxylate (5c). Colorless liquid (57.0 mg, 68% yield). R_f = 0.32 (petroleum ether/dichloromethane = 6:1).^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 (d, J = 7.6 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.56-7.53 (m, 5H), 7.46-7.43 (m, 3H), 7.38 (d, J = 8.0 Hz, 1H), 7.32-7.30 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.03-6.99 (m, 1H), 3.61 (t, J = 6.8 Hz, 2H), 1.47-1.40 (m, 2H), 1.32-1.23 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 142.7, 140.9, 140.5, 139.8, 138.4, 129.7, 129.0, 128.6, 128.0, 127.5, 127.2, 126.8, 126.3, 123.0, 122.6, 122.2, 121.2, 120.2, 116.0, 110.1, 64.8, 30.5, 19.1, 13.7; IR spectrum (ν_{max}, cm^{-1}) 2958, 1718, 1455, 1255, 1135, 756, 702; HRMS calcd. for. $C_{29}H_{25}NO_2$ [M+H]$^+$ 420.1958, found 420.1954.

Butyl -6,9-dimethyl-4-phenyl-9*H*-carbazole-1-carboxylate (5d). Colorless liquid (51.9 mg, 70% yield). R_f = 0.31 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, J = 7.6 Hz, 1H), 7.58-7.50 (m, 5H), 7.32 (d, J = 8.4 Hz, 1H), 7.26-7.23 (m, 1H), 7.09-7.06 (m, 2H), 4.44 (t, J = 6.8 Hz, 2H), 3.88 (s, 3H), 2.28 (s, 3H), 1.87-1.79 (m, 2H), 1.57-1.50 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 141.3, 141.1, 140.7, 139.7, 129.0, 128.6, 128.4, 127.9, 127.7, 127.5, 122.5, 122.2, 122.2, 119.8, 114.4, 108.8, 65.1, 33.6, 30.9, 21.4, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1708, 1473, 1247, 1069, 756, 701; HRMS calcd. for. $C_{25}H_{25}NO_2$ $[M+H]^+$ 372.1958, found 372.1958.

Butyl-6-fluoro-9-methyl-4-phenyl-9*H*-carbazole-1-carboxylate (5e). Colorless liquid (54.8 mg, 73% yield). R_f = 0.32 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.57-7.51 (m, 5H), 7.37-7.33 (m, 1H), 7.19-7.14 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.98-6.95 (m, 1H), 4.45 (t, *J* = 6.6 Hz, 2H), 3.90 (s, 3H), 1.87-1.80 (m, 2H), 1.55-1.49 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 157.0 (d, *J* =233.7 Hz), 141.6, 140.2, 140.0, 139.1, 128.8, 128.7, 128.4, 128.2, 122.5 (d, *J* =10 Hz), 122.2 (d, *J* =4 Hz), 120.0, 114.8, 113.9 (d, *J* =25.5 Hz), 109.7 (d, *J* =9.1 Hz), 107.9 (d, *J* =25.0 Hz), 65.2, 33.7, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2957, 1699, 1474, 1249, 1134, 753, 700; HRMS calcd. for. $C_{24}H_{22}FNO_2$ $[M+H]^+$ 376.1707, found 376.1707.

Butyl-6-chloro-9-methyl-4-phenyl-9*H*-carbazole-1-carboxylate (5f). Light yellow solid (54.7 mg, 70% yield), mp 85-87 ^{o}C. R_f = 0.30 (petroleum ether/dichloromethane = 8:1).^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.57-7.52 (m, 5H), 7.39-7.33 (m, 2H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.44 (t, *J* = 6.6 Hz, 2H), 3.89 (s, 3H), 1.87-1.80 (m, 2H), 1.60-1.49 (m, 2H), 1.02 (t, *J* =7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 141.6, 141.1, 140.0, 139.9, 128.8, 128.7, 128.5, 128.3, 126.2, 124.8, 123.2, 121.8, 121.8, 120.4, 114.8, 110.1, 65.3, 33.7, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2928, 1697, 1466, 1243, 1066, 757, 704; HRMS calcd. for. $C_{24}H_{22}ClNO_2$ $[M+H]^+$ 392.1412, found 392.1412.

Butyl-7-chloro-9-methyl-4-phenyl-9*H*-carbazole-1-carboxylate (5g). Colorless liquid (52.4 mg, 67% yield). R_f = 0.32 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.53-7.49 (m, 5H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.95-6.92 (m, 1H), 4.44 (t, *J* = 6.8 Hz, 2H), 3.88 (s, 3H), 1.87-1.80 (m, 2H), 1.58-1.49 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 143.3, 141.2, 140.2, 139.7, 138.2, 132.1, 128.8, 128.6, 128.1, 123.0, 122.2, 120.7, 120.6, 119.9, 114.9, 109.3, 65.3, 33.7, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2955, 1701, 1384, 1241, 1068, 755, 702; HRMS calcd. for $C_{24}H_{22}ClNO_2$ $[M+H]^+$ 392.1412, found 392.1402.

Butyl-8,9-dimethyl-4-phenyl-9*H*-carbazole-1-carboxylate (5h). Light yellow solid (45.3 mg, 61% yield), mp 94-96 ^{o}C. R_f = 0.34 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.52-7.50 (m, 5H), 7.16-7.07 (m, 3H), 6.86 (t, *J* = 7.6 Hz, 1H), 4.45 (t, *J* = 6.6 Hz, 2H), 3.96 (s, 3H), 2.82 (s, 3H), 1.87-1.80 (m, 2H), 1.58-1.50 (m, 2H), 10.2 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 143.4, 142.5, 141.4, 140.7, 129.4, 128.9, 128.5, 128.0, 127.9, 123.7, 123.3, 121.3, 120.8, 120.2, 120.0, 114.6, 65.0, 38.2, 30.9, 20.4, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2955, 1706, 1453, 1235, 1063, 751, 701; HRMS calcd. for $C_{25}H_{25}NO_2$ $[M+H]^+$ 372.1958, found 372.1956.

Butyl-9-methyl-4-(p-tolyl)-9*H*-carbazole-1-carboxylate (6a). Colorless liquid (60.1 mg, 81% yield). R_f = 0.32 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.47-7.39 (m, 5H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.02-6.98 (m, 1H), 4.44 (t, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 2.49 (s, 3H), 1.87-1.79 (m, 2H), 1.59-1.49 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 142.7, 141.5, 139.5, 137.7, 137.6, 129.2, 128.8, 127.8, 126.1, 122.7, 122.3, 122.2, 120.2, 119.3, 114.4, 109.1, 65.1, 33.6, 30.9, 21.4, 19.3, 3.8; IR spectrum (ν_{max}, cm^{-1}) 2955, 1706, 1466, 1138, 1067, 793, 730; HRMS calcd. for. $C_{25}H_{25}NO_2$ [M+H]$^+$ 372.1958, found 372.1955.

Butyl-4-(4-fluorophenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6b) . Pale yellow liquid (58.5 mg, 78% yield). R_f = 0.34 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 2H), 7.44 (d, *J* =4.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 2H), 7.05 (d, *J* =8.0 Hz, 1H), 7.03-6.99 (m, 1H), 4.45 (t, *J* =6.6 Hz, 2H), 3.91 (s, 3H), 1.87-1.80 (m, 2H), 1.60-1.49 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 162.7 (d, *J* =245.3 Hz), 142.7, 140.2, 139.4, 136.6 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 8.0 Hz), 127.8, 126.3, 122.7, 122.0, 122.0, 120.1, 119.4, 115.5(d, *J* = 21.3 Hz), 114.8, 109.2, 65.2, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2957, 1708, 1466, 1244, 1068, 748, 732; HRMS calcd. for. $C_{24}H_{22}FNO_2$ [M+H]$^+$ 376.1707, found 376.1704.

Butyl-4-(4-chlorophenyl)-9-methyl-9*H*-carbazole-1carboxylate (6c). Pale yellow liquid (63.3 mg, 81% yield). R_f = 0.35 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.51-7.50 (m, 4H), 7.45 (d, *J* = 4.4 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.06-7.00 (m, 2H), 4.45 (t, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 1.87-1.80 (m, 2H), 1.59-1.50 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.7, 139.8, 139.4, 139.1, 134.0, 130.4, 128.8, 127.8, 126.4, 122.5, 122.0, 121.9, 120.0, 119.5, 114.9, 109.2, 65.2, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2957, 1707, 1466, 1243, 1068, 821, 732; HRMS calcd. for. $C_{24}H_{22}ClNO_2$ [M+H]$^+$ 392.1412, found 392.1400.

Butyl-4-(4-bromophenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6d). Colorless liquid (72.4 mg, 83% yield). R_f = 0.34 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.45-7.43 (m, 4H), 7.35 (d, J = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 4.44 (t, J = 6.8 Hz, 2H), 3.90 (s, 3H), 1.87-1.79 (m, 2H), 1.58-1.50 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.7, 139.8, 139.5, 139.4, 131.7, 130.7, 127.8, 126.4, 122.4, 122.1, 122.0, 121.8, 120.0, 119.5, 114.9, 109.2, 65.2, 33.5, 30.8, 19.3, 3.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1705, 1465, 1244, 1068, 792, 731; HRMS calcd. for. $C_{24}H_{22}BrNO_2$ [M+H]$^+$ 436.0907, found 436.0902.

Butyl-4-([1,1'-biphenyl]-4-yl)-9-methyl-9*H*-carbazole-1-carboxylate (6e). CCDC number: 1500913. White solid (68.4 mg, 79% yield), mp 126-128 ^{o}C. R_f = 0.31 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.90 (d, J = 8.0 Hz, 1H), 7.78-7.72 (m, 4H), 7.64 (d, J = 8.4 Hz, 2H), 7.51-7.40 (m, 5H), 7.38 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.02-6.98 (m, 1H), 4.45 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 1.87-1.80 (m, 2H), 1.58-1.51 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 142.8, 140.9, 140.7, 140.7, 139.6, 139.5, 129.4, 128.9, 127.9, 127.5, 127.2, 127.1, 126.2, 122.6, 122.3, 122.1, 120.1, 119.4, 114.6, 109.1, 65.2, 33.6, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1706, 1463, 1247, 1067, 819, 730; HRMS calcd. for. $C_{30}H_{27}NO_2$ [M+H]$^+$ 434.2115, found 434.2112.

Butyl-4-(4-methoxyphenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6f). Colorless liquid (35.6 mg, 46% yield). R_f = 0.30 (petroleum ether/dichloromethane = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H), 7.43-7.42 (m, 3H), 7.08-7.05 (m, 3H), 7.02-6.98 (m, 1H), 4.44 (t, J = 6.6 Hz, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 1.86-1.80 (m, 2H), 1.58-1.48 (m, 2H), 1.01 (t, J = 7.4Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 159.5, 142.7, 141.2, 139.5, 133.0, 130.1, 127.9, 126.1, 122.8, 122.3, 122.2, 120.2, 119.3, 114.2, 113.9, 109.1, 65.1, 55.3, 33.6, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2958, 1700, 1463, 1243, 1069, 832, 753; HRMS calcd. for $C_{25}H_{25}NO_3$ $[M+H]^+$ 388.1907, found 388.1889.

Butyl-9-methyl-4-(4-nitrophenyl)-9*H*-carbazole-1-carboxylate (6g). Yellow liquid (57.9 mg, 72% yield). R_f = 0.34 (petroleum ether/dichloromethane = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.40 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 3.6 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.04-7.00 (m, 1H), 4.47 (t, J = 6.8 Hz, 2H), 3.93 (s, 3H), 1.88-1.81 (m, 2H), 1.60-1.51 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 147.6, 147.4, 142.7, 139.3, 138.3, 130.0, 127.7, 126.7, 123.8, 122.1, 121.7, 121.4, 119.7, 119.7, 115.8, 109.5, 65.4, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2957, 1706, 1515, 1342, 1066, 851, 730; HRMS calcd. for $C_{24}H_{22}N_2O_4$ $[M+H]^+$ 403.1652, found 403.1656.

Butyl-4-(4-cyanophenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6h). White solid (58.8 mg, 77% yield), mp 104-106 ^{o}C. R_f = 0.36 (petroleum ether/dichloromethane =2:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.89 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4

Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 3.6 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.06-7.01 (m, 2H), 4.46 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 1.88-1.81 (m, 2H), 1.57-1.49 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.7, 145.5, 142.8, 139.4, 138.8, 132.4, 129.9, 127.8, 126.6, 122.2, 121.7, 121.5, 119.7, 119.7, 118.8, 115.6, 111.9, 109.4, 65.4, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2928, 2224, 1714, 1466, 1245, 1067, 751, ; HRMS calcd. for $C_{25}H_{22}N_2O_2$ $[M+H]^+$ 383.1754, found 383.1754.

Butyl-9-methyl-4-(4-(methylsulfonyl)phenyl)-9*H*-carbazole-1-carboxylate (6i). Pale yellow liquid (66.1 mg, 76% yield). R_f = 0.34 (petroleum ether/dichloromethane =1:3). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 4.0 Hz, 2H), 7.28-7.25 (m, 1H), 7.06-7.00 (m, 2H), 4.46 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 3.19(s, 3H), 1.88-1.80 (m, 2H), 1.58-1.51 (m, 2H), 1,02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 146.4, 142.7, 140.0, 139.3, 138.6, 130.0, 127.7, 127.6, 126.6, 122.1, 121.7, 121.4, 119.8, 119.7, 115.6, 109.4, 65.3, 44.5, 33.5, 30.8, 19.2, 13.7; IR spectrum (ν_{max}, cm^{-1}) 2925, 1705, 1466, 1246, 1146, 1067, 748; HRMS calcd. for $C_{25}H_{25}NO_4S$ $[M+H]^+$ 436.1577, found 436.1576.

Butyl-4-(3-bromophenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6j). Colorless liquid (69.8 mg, 80% yield). R_f = 0.31 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 1.8 Hz, 1H), 7.65-7.62 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.07-7.01 (m, 2H), 4.45 (t, *J* = 6.6 Hz, 2H), 3.91 (s, 3H), 1.87-1.80 (m, 2H), 1.58-1.51 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.7, 142.7, 139.4, 131.9, 131.0, 130.0, 127.8, 127.7, 126.4, 122.5, 122.5, 122.0, 121.8, 119.9, 119.7 115.1, 109.2, 65.2, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1707, 1464, 1241, 1138, 1066, 731; HRMS calcd. for $C_{24}H_{22}BrNO_2$ $[M+H]^+$ 436.0907, found 436.0904.

Butyl-4-(3-methoxyphenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6k). White solid (31.7 mg, 41% yield), mp 90-92 ^{o}C. R_f = 0.30 (petroleum ether/dichloromethane =6:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.46-7.38 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.11-7.09 (m, 2H), 7.06-6.98 (m, 2H), 4.45 (t, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 3.84 (s, 3H), 1.87-1.80 (m, 2H), 1.59-1.49 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 159.7, 142.7, 142.0, 141.1, 139.5, 129.6, 127.8, 126.2, 122.6, 122.4, 122.1, 121.4, 119.9, 119.4, 114.6, 114.2, 113.8, 109.1, 65.2, 55.3, 33.6, 30.9, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2957, 1715, 1468, 1222, 1032, 794, 706; HRMS calcd. for $C_{25}H_{25}NO_3$ $[M+H]^+$ 388.1907, found 388.1907.

Butyl-4-(2-chlorophenyl)-9-methyl-9*H*-carbazole-1-carboxylate (6l). Colorless liquid (33.6 mg, 43% yield). R_f = 0.28 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.47-7.41 (m, 5H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.01-6.97 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 4.45 (t, *J* = 6.6 Hz, 2H), 3.93 (s, 3H), 1.88-1.80 (m, 2H), 1.57-1.50 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.6, 139.2, 139.2, 137.8, 133.4, 131.0, 129.8, 129.4, 127.7, 127.0, 126.3, 123.2, 122.0, 121.6, 119.8, 119.7, 115.1, 109.1, 65.2, 33.5, 30.9, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1709, 1469, 1240, 1137, 1077, 748; HRMS calcd. for. $C_{24}H_{22}ClNO_2$ $[M+H]^+$ 392.1412, found 392.1422.

Butyl-9-methyl-4-(naphthalen-2-yl)-9*H*-carbazole-1-carboxylate (6m). Colorless liquid (49.7 mg, 61% yield). R_f = 0.30 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04-7.89 (m, 5H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.59-7.54 (m, 2H), 7.46-7.40 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 4.46 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 1.88-1.81 (m, 2H), 1.59-1.50 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 142.8, 141.2, 139.6, 138.1, 133.5, 132.9, 128.2, 128.0, 127.9, 127.8, 127.6, 127.4, 126.4, 126.2, 126.2, 122.7, 122.3, 122.1, 120.4, 119.4, 114.6, 109.1, 65.2, 33.6, 30.9, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1705, 1463, 1247, 1067, 819, 730; HRMS calcd. for. $C_{28}H_{25}NO_2$ $[M+H]^+$ 408.1958, found 408.1956.

Butyl-9-methyl-4-(thiophen-2-yl)-9*H*-carbazole-1-carboxylate (6n). Yellow solid (40.7 mg, 56% yield), mp 85-87 °C. R_f = 0.27 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.50-7.49 (m, 1H), 7.47-7.45 (m, 2H), 7.32-7.30 (m, 1H), 7.23-7.20 (m, 2H), 7.08-7.04 (m, 1H), 4.44 (t, *J* = 6.8 Hz, 2H), 3.90 (s, 3H), 1.86-1.79 (m, 2H), 1.57-1.50 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.7, 141.3, 139.4, 133.4, 127.5, 127.3, 127.0, 126.5, 126.1, 123.6, 122.2, 122.0, 121.4, 119.6, 115.3, 109.2, 65.2, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2956, 1698, 1469, 1243, 1066, 728, 700; HRMS calcd. for. $C_{22}H_{21}NO_2S$ $[M+H]^+$ 364.1366, found 364.1363.

Butyl-9-methyl-3,4-diphenyl-9H-carbazole-1-carboxylate (6p). Pale yellow liquid (32.0 mg, 37% yield). R_f = 0.43 (petroleum ether/dichloromethane =7:1). 1H NMR (400 MHz, CDCl3, ppm) δ 7.93 (s, 1H), 7.46-7.41 (m, 2H), 7.38-7.36 (m, 3H), 7.28-7.25 (m, 2H), 7.20-7.15 (m, 5H), 6.94-6.90 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.45 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 1.86-1.79 (m, 2H), 1.57-1.46 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 143.0, 140.8, 139.1, 139.0, 138.4, 131.9, 130.3, 130.0, 129.9, 128.3, 127.5, 127.4, 126.1, 126.0, 123.8, 122.6, 122.4, 119.4, 114.6, 109.0, 65.3, 33.5, 30.8, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2930, 1713, 1467, 1392, 1247, 1070, 758; HRMS calcd. for. $C_{30}H_{27}NO_2$ $[M+H]^+$ 434.2115, found 434.2108.

Butyl-4,9-dimethyl-9*H*-carbazole-1-carboxylate (7a). Colorless liquid (23.6 mg, 40% yield). R_f = 0.33 (petroleum ether/dichloromethane =8:1). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.18 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.53-7.46 (m, 2H), 7.30-7.27 (m, 1H), 7.01 (d, J = 8.0 Hz, 1H), 4.40 (t, J = 6.8 Hz, 2H), 3.88 (s, 3H), 2.90 (s, 3H), 1.84-1.77 (m, 2H), 1.58-1.46 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 142.5, 139.3, 137.7, 128.1, 125.7, 123.4, 123.0, 122.5, 120.2, 119.7, 113.4, 109.1, 65.0, 33.6, 30.8, 21.3, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2958, 1712, 1469, 1213, 1068, 747, 728; HRMS calcd. for. $C_{19}H_{21}NO_2$ $[M+H]^+$ 296.1645, found 296.1641.

Butyl-4-ethyl-3,9-dimethyl-9*H*-carbazole-1-carboxylate (7b). Colorless liquid (33.6 mg, 52% yield). R_f = 0.34 (petroleum ether/dichloromethane =7:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.52-7.49 (m, 2H), 7.30-7.27 (m, 1H), 4.40 (t, J = 6.8 Hz, 2H), 3.85 (s, 3H), 3.30 (q, J = 7.5 Hz, 2H), 2.50 (s, 3H), 1.85-1.78 (m, 2H), 1.54-1.47 (m, 2H), 1.37 (t, J = 7.6 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.0, 142.9, 142.2, 138.5, 130.3, 125.6, 125.5, 123.2, 122.5, 122.2, 119.6, 112.9, 109.2, 650, 33.5, 30.9, 23.4, 19.3, 18.5, 13.8, 12.8; IR spectrum (ν_{max}, cm^{-1}) 2960, 1705, 1571, 1466, 1227, 1060, 739; HRMS calcd. for. $C_{21}H_{25}NO_2$ $[M+H]^+$ 324.1958, found 324.1958.

Butyl-3-ethyl-9-methyl-4-propyl-9*H*-carbazole-1-carboxylate (7c). Colorless liquid (33.0 mg, 47% yield). R_f = 0.35 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.51-7.44 (m, 2H), 7.29-7.25 (m, 1H), 4.41 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.26-3.21 (m, 2H), 2.89-2.82 (m, 2H), 1.85-1.74 (m, 4H), 1.56-1.47 (m, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 1.18 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.1, 142.9, 140.3, 138.3, 132.2, 129.0, 125.5, 123.4, 122.4, 122.4， 119.6, 113.2, 109.2, 65.0, 33.5, 31.8, 30.8, 25.3, 22.8, 19.3, 16.4, 14.6, 13.8; IR spectrum (ν_{max}, cm^{-1}) 2959, 1714, 1574, 1466, 1404, 1228, 1064; HRMS calcd. for. $C_{23}H_{29}NO_2$ $[M+H]^+$ 352.2271, found 352.2268.

Butyl-4,9-diethyl-3-methyl-9*H*-carbazole-1-carboxylate (7d). Colorless liquid (32.5 mg, 47% yield). R_f = 0.33 (petroleum ether/dichloromethane =8:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.49 (d, J = 4.0 Hz, 2H), 7.29-7.27 (m, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.41 (t, J = 6.6 Hz, 2H), 3.30 (q, J = 7.6 Hz, 2H), 2.49 (s, 3H), 1.85-1.78 (m, 2H), 1.54-1.49 (m, 2H), 1.39-1.31 (m, 6H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ 168.5, 142.0, 141.7, 136.5, 130.0, 125.4, 125.4, 123.4, 122.6, 122.5, 119.5, 113.4, 109.3, 65.1, 39.8, 30.8, 23.4, 19.3, 18.5, 13.8, 13.6, 12.8; IR spectrum (ν_{max}, cm^{-1}) 2963, 1713, 1458, 1208, 1109, 1062, 734; HRMS calcd. for. $C_{22}H_{27}NO_2$ [M+H]$^+$ 338.2115, found 338.2111.

Ethyl-9-methyl-4-phenyl-9*H*-carbazole-1-carboxylate (8a). Pale yellow liquid (27.6 mg, 42% yield). R$_f$ = 0.32 (petroleum ether/dichloromethane = 8:1). ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.57-7.49 (m, 5H), 7.45-7.43 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.00-6.96 (m, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ 167.9, 142.7, 141.4, 140.6, 139.5, 129.0, 128.5, 127.9, 127.9, 126.2, 122.6, 122.2, 122.2, 120.1, 119.4, 114.5, 109.1, 61.3, 33.6, 14.4; IR spectrum (ν_{max}, cm^{-1}) 2956, 1707, 1390, 1242, 1068, 749, 701; HRMS calcd. for. $C_{22}H_{19}NO_2$ [M+H]$^+$ 330.1489, found 330.1486.

Hexyl-9-methyl-4-phenyl-9H-carbazole-1-carboxylate (8b). Colorless liquid (56.2 mg, 73% yield). R$_f$ = 0.40 (petroleum ether/dichloromethane =10:1). ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 7.89(d, *J* = 7.6 Hz, 1H), 7.58-7.51(m, 5H), 7.45-7.44(m, 2H), 7.33(d, *J* = 8.0 Hz, 1H), 7.10(d, *J* = 7.6 Hz, 1H), 7.01-6.96(m, 1H), 4.44 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 1.88-1.81(m, 2H), 1.53-1.46(m, 2H), 1.39-1.31(m, 4H), 0.94-0.89(m, 3H); ^{13}C NMR (100 MHz, CDCl3, ppm) δ 167.9, 142.7, 141.3, 140.6, 139.4, 128.9, 128.5, 127.9, 127.8, 126.2, 122.6, 122.2, 122.1, 120.1, 119.3, 114.5, 109.1, 65.5, 33.6, 31.5, 28.8, 25.7, 22.6, 14.0; IR spectrum (ν_{max}, cm^{-1}) 2957, 1709, 1459, 1218, 1069, 733, 700; HRMS calcd. for. $C_{26}H_{27}NO_2$ $[M+H]^+$ 386.2115, found 386.2109.

9-Methyl-4-phenyl-9*H*-carbazole-1-carbonitrile (8c). White solid (22.6 mg, 40% yield), mp 127-129 °C. R_f = 0.42 (petroleum ether/dichloromethane =10:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76 (d, J = 8.0 Hz, 1H), 7.56-7.56 (m, 5H), 7.50-7.44 (m, 2H), 7.36(d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.05-7.01 (m, 1H), 4.27 (s ,3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.7, 141.8, 140.3, 139.8, 131.3, 128.7, 128.7, 128.4, 126.9, 122.5, 122.2, 121.5, 120.7, 120.0, 119.1, 108.8, 91.6, 30.7; IR spectrum (ν_{max}, cm^{-1}) 3049, 2216, 1467, 1305, 1023, 747, 698; HRMS calcd. for. $C_{20}H_{14}N_2$ $[M+H]^+$ 283.1230, found 283.1229.

Dimethyl-9-methyl-4-phenyl-9*H*-carbazole-1,2-dicarboxylate (8d). Yellow solid (33.6 mg, 45% yield), mp 185-187 °C. Rf = 0.34 (petroleum ether/dichloromethane =6:1). 1H NMR (400 MHz, CDCl3, ppm) δ 7.77 (s, 1H), 7.58-7.45 (m, 6H), 7.42-7.36 (m, 2H), 6.99 (t, J = 7.6 Hz, 1H), 4.11 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H); 13C NMR (100 MHz, CDCl3, ppm) δ 169.8, 166.9, 143.0, 140.0, 138.1, 136.7, 129.0, 128.6, 128.1, 127.4, 125.4, 124.2, 123.0, 122.0, 121.1, 119.5, 117.5, 108.8, 52.9, 52.5, 30.4; IR spectrum (ν_{max}, cm^{-1}) 2952, 1731, 1712, 1387, 1233,1082, 744; HRMS calcd. for. $C_{23}H_{19}NO_4$ $[M+Na]^+$ 396.1206, found 396.1207.

9-Methyl-4-phenyl-9*H*-carbazole (**9**, CAS: 1314146-23-0)[18]. Colorless liquid (21.1 mg, 41% yield). R_f = 0.51 (petroleum ether/EtOAc =100:1). ^{1}H NMR (400 MHz,

$CDCl_3$, ppm) δ 7.63 (d, J = 7.6 Hz, 2H), 7.54-7.47 (m, 5H), 7.43-7.37 (m, 3H), 7.11 (d, J = 7.2 Hz, 1H), 6.99-6.95 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.4, 141.3, 141.2, 137.7, 129.2, 128.4, 127.4, 125.5, 125.4, 122.4, 122.3, 120.6, 120.2, 118.5, 108.2, 107.3, 29.1; IR spectrum (ν_{max}, cm^{-1}) 3051, 2925, 1467, 1320, 1151, 755,700; HRMS calcd. for $C_{19}H_{15}N$ [M+H]$^+$ 258.1277, found 258.1276.

Butyl-4-phenyl-9*H*-carbazole-1-carboxylate (10). White solid (43.2 mg, 63% yield), mp 116-118 °C. R_f = 0.49 (petroleum ether/dichloromethane =5:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.19 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.63-7.62 (m, 2H), 7.57-7.47 (m, 5H), 7.39 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 4.46 (t, J = 6.6 Hz, 2H), 1.88-1.81 (m, 2H), 1.60-1.51 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 142.8, 140.6, 140.5, 139.9, 128.9, 128.5, 128.1, 127.1, 126.3, 122.3, 122.1, 121.9, 120.3, 119.5, 110.9, 110.6, 64.7, 30.9, 19.3, 13.8; IR spectrum (ν_{max}, cm^{-1}) 3401, 2917, 1670, 1455, 1253, 1145, 730; HRMS calcd. for $C_{23}H_{21}NO_2$ [M+H]$^+$ 344.1645, found 344.1646.

Butyl-4-(4-(9H-carbazol-9-yl)phenyl)-9-methyl-9*H*-carbazole-1-carboxylate (11). Colorless liquid (71.0 mg, 68% yield). R_f = 0.33 (50:1 petroleum ether/ EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, J = 7.6 Hz, 2H), 7.94 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.53-7.46 (m, 5H), 7.33 (t, J = 7.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.11-7.07 (m, 1H), 4.47 (t, J = 6.6 Hz, 2H), 3.94 (s, 3H), 1.89-1.82 (m, 2H), 1.60-1.51 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 142.8, 140.8, 140.3, 139.7, 139.5, 137.4, 130.5, 127.9, 127.0, 126.4, 126.0, 123.5, 122.6, 122.0, 122.0, 120.4, 120.1, 119.6, 114.9, 109.8, 109.3, 65.3, 33.6, 30.9, 19.3, 13.8; IR spectrum (v_{max}, cm^{-1}) 2956, 1709, 1521, 1451, 1247, 1069, 749; HRMS calcd. for. $C_{36}H_{30}N_2O_2$ $[M+H]^+$ 523.2380, found 523.2372.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc

^{1}H NMR and ^{13}C NMR spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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