JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

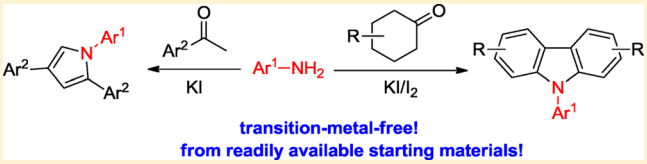
Carbazole and Triarylpyrrole Synthesis from Anilines and Cyclohexanones or Acetophenones under Transition-Metal-Free Condition

Jun Wu,[†,‡] Xiangui Chen,[†,‡] Yanjun Xie,[†] Yanjun Guo,[†] Qian Zhang,[†] and Guo-Jun Deng*[,†]

[†]Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, P.R. China

Supporting Information

ABSTRACT: An efficient strategy for carbazoles and 1,2,4-triarylpyrroles synthesis from anilines and cyclohexanones or acetophenones under transition-metal-free conditions is developed. A variety of disubstituted 9-arylcarbazoles were synthesized in moderate to good yields promoted by KI/I_2 using anilines as the nitrogen and aryl source. Meanwhile, a variety of 1,2,4-triarylpyrroles were also selectively synthesized from anilines and acetophenones in the presence of KI alone.



INTRODUCTION

Carbazoles are a class of important nitrogen-containing heterocyclic compounds, many of which widely exist in natural products and pharmaceutical drugs.[1] In addition, the carbazole moiety has found wide applications as a key building block in photophysical materials,[2] such as polymeric light-emitting diodes (PLEDs) and organic light-emitting devices (OLEDs).[3] Although there are a large number of classic methods for the synthesis of the carbazole scaffold, the development of efficient approaches for the preparation of structurally diverse carbazoles is a field of constant interest.[4]

Traditionally, the carbazole synthesis mainly relied on the Fischer–Borsche synthesis using arylhydrazines and cyclohexanones via a sequence of condensation, cyclization, and dehydrogenation under acidic and oxidative conditions.[5] The transition-metal-catalyzed intramolecular Cadogan cyclization of 2-nitrobiaryls at high temperatures using excess of either phosphines, phosphites, or carbon monooxide could provide an alternative approach to substituted carbazoles.[6] Recently, Kürti and co-workers realized a low-temperature and transition-metal-free intramolecular amination starting from readily available 2-nitrobiaryls using PhMgBr as the reducing reagent.[7] Alternatively, transition-metal-catalyzed intramolecular oxidative C–H bond amination of 2-aminobiaryls provided an efficient approach for construction-substituted carbazole derivatives.[8] Very recently, indole-to-carbazole transformations in the presence of transition metals have attracted much attention because indoles are readily available starting materials.[9] The Miura group developed a Pd-catalyzed [2 + 2 + 2] cycloaddition of indoles with diarylacetylenes to give tetraarylated carbazoles.[10] In addition, the Itami and Lei groups cooperatively found that a Pd–Cu–Ag trimetallic system could convert indoles to carbazoles using electron-deficient alkenes.[11] In the meantime, we developed an efficient indole-to-carbazole strategy from indoles, ketones, and nitroolefins under metal-free conditions.[12]

Anilines probably are the most readily available nitrogen-containing aromatic compounds and are widely used as synthons in organic synthesis. Therefore, carbazole synthesis based on simple and diverse anilines is a very attractive approach. The one-pot domino N–H/C–H bond activation using anilines and 1,2-dihaloarenes could be realized under Pd-catalyzed conditions (Figure 1a).[13] The Pd-catalyzed double amination of 2,2′-dihalo-1,1′-biaryls also could successfully convert anilines into substituted carbazoles (Figure 1b).[14] The copper-catalyzed amine insertion into cyclic diphenyleneiodoniums provided an alternative approach for substituted carbazoles (Figure 1c).[15] Recently, Yorimitsu and co-workers reported an efficient carbazole synthetic route via nucleophilic substitution of dibenzothiophene dioxides with anilines under transition-metal-free conditions (Figure 1d).[16] These reactions provide carbazole and functionalized carbazoles from readily available anilines in high yields and good selectivity. However, in most cases, highly functionalized arenes and/or expensive transition-metal catalyst are required, which severely limits the application of this strategy. Therefore, the development of carbazole synthesis based on simple anilines and other readily available starting materials under transition-metal-free conditions is still a challenging topic.

In recent years, we and others have successfully converted cyclohexanones to amines or anilines via a dehydrogenation strategy.[17] We also developed a novel method for carbazole synthesis from arylureas and cyclohexanones under transition-metal-free conditions.[18] In this kind of transformation, the whole carbazole moiety (except the nitrogen atom) comes from two equivalents of nonaromatic cyclohexanones via dehydro-

Received: March 8, 2017
Published: May 5, 2017

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743–5750

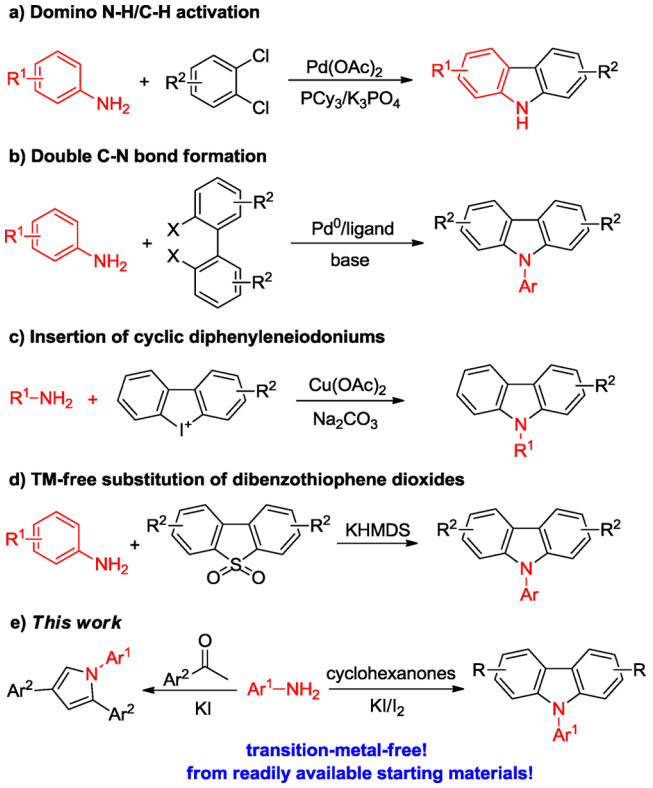


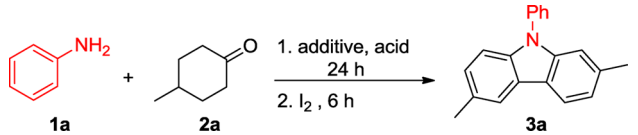
Figure 1. Carbazole synthesis based on anilines.

genation−tautomerization sequence. However, arylureas are much less available chemicals, and only a few of them are commercially available. Furthermore, only part of arylurea was introduced into the corresponding products, which lowered the reaction atom economy. To develop a more general approach for carbazole synthesis using readily available starting materials, herein we disclose a novel route for the synthesis of substituted carbazoles from cyclohexanones and anilines under transition-metal-free conditions. This strategy also could be used for 1,2,4-triarylpyrroles synthesis when acetophenones were employed (Figure 1e).

RESULTS AND DISCUSSION

Our study was initiated by using aniline (**1a**, 0.2 mmol) and 4-methylcyclohexanone (**2a**, 0.5 mmol, 1.5 equiv) as the starting materials to determine the optimal reaction conditions (Table 1). On the basis of our previous study, KI/I_2 was used as the promoter to initiate this kind of reaction. However, the desired product was obtained in moderate yield due to substituted pyrrole also being obtained (Table 1, entry 1). This means the dehydrogenation reaction is not completed under the reaction conditions using aniline as the nitrogen source. Because iodine could play an important role in the dehydrogenation step, we conducted this kind of reaction via a one-pot, two-step process. Iodine was added after the reaction was stirred for 24 h at the given temperature with the aid of various iodide-containing additives. Among the various iodide-containing additives investigated, KI showed the best efficiency to give the corresponding product **3a** in 76% isolated yield (entry 5). Acid plays an important role in this kind of transformation, and no desired product was obtained when methanesulfonic acid was replaced with acetic acid (entry 7). Several other organic acids were also investigated, and all of them are efficient to give

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3a**

entry	additive	acid	solvent	yYield[b] (%)
1	KI/I_2	CH_3SO_3H	toluene	50
2	NaI	CH_3SO_3H	toluene	64
3	NH_4I	CH_3SO_3H	toluene	52
4	I_2	CH_3SO_3H	toluene	56
5	KI	CH_3SO_3H	toluene	76
6	NIS	CH_3SO_3H	toluene	31
7	KI	CH_3COOH	toluene	NR
8	KI	p-TsOH	toluene	61
9	KI	CF_3COOH	toluene	72
10	KI	$ClSO_3H$	toluene	63
11	KI	CH_3SO_3H	*p*-xylene	44
12	KI	CH_3SO_3H	mesitylene	43
13	KI	CH_3SO_3H	chlorobenzene	63
14	KI	CH_3SO_3H	1,2-dichlorobenzene	33
15	KI	CH_3SO_3H	$Cl_2CHCHCl_2$	30
16	KI	CH_3SO_3H	DMF	trace
17	KI	CH_3SO_3H	NMP	trace
18[c]	KI	CH_3SO_3H	toluene	60

[a]Conditions: step 1, **1a** (0.2 mmol), **2a** (0.5 mmol), additive (0.1 mmol), acid (0.1 mmol), toluene (1 mL), 160 °C, 24 h, under oxygen; step 2, I_2 (25 mol %) was added and the mixture was further stirred under O_2 at 160 °C for 6 h. [b]Isolated yield based on **1a**. [c]At 150 °C. NR = no reaction.

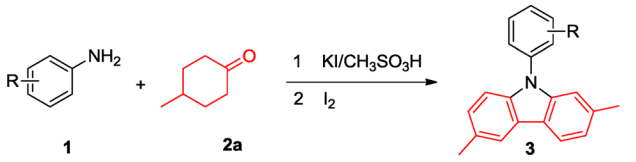
the product in good yield (entries 8−10). Solvent screening showed that lower yield was observed when the reaction was carried out in poor polar solvents such as *p*-xylene, mesitylene, and chlorobenzene (entries 11−13). No desired product was obtained when strongly polar solvents were used (entries 16 and 17). Decreasing the reaction temperature decreased the reaction yield to 60% (entry 18).

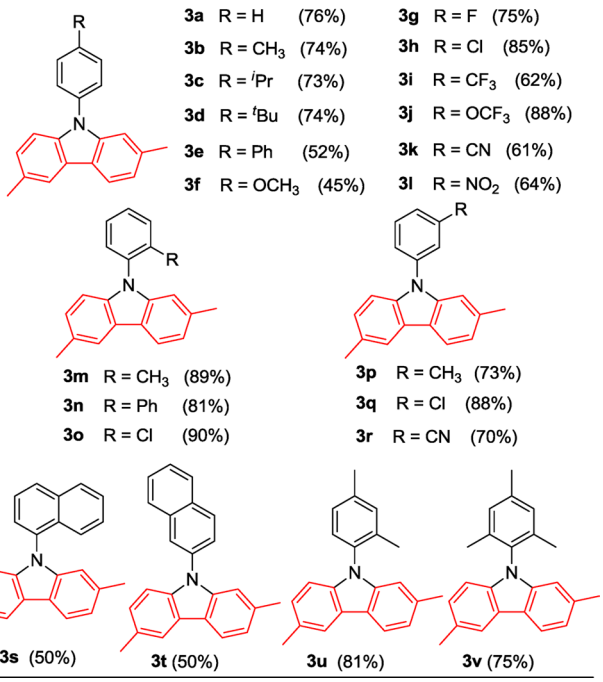
Under the optimized reaction conditions, various substituted anilines were employed (Table 2). A wide range of para-substituted anilines containing electron-withdrawing or electron-donating groups smoothly reacted with 4-methylcyclohexanone (**2a**) to give the corresponding carbazole derivatives in moderate to good yields (**3b**−**3l**). Functional groups such as trifluoromethyl, trifluoromethoxy, fluoro, and chloro were all well-tolerated. Meanwhile, strong electron-withdrawing cyano and nitro groups both were tolerated to give **3k** and **3l** in 61% and 64% yields, respectively. Interestingly, high yields were obtained when the substituents were located at the ortho position of the amino group (**3m**−**3o**). 1-Naphthylamine and 2-naphthylamine also could react smoothly with **2a** to give **3s** and **3t**, respectively, in moderate yields. To our delight, multisubstituted anilines such as 2,4-dimethylaniline and 2,4,6-trimethylaniline are also suitable substrates to afford the desired products **3u** and **3v** in 81% and 75% yields, respectively.

To further examine the scope and limitations of the reaction, several cyclohexanones were investigated under the optimized reaction conditions (Table 3). When simple cyclohexanone (**2b**) was reacted with **1a**, the product of 9-phenyl-9*H*-carbazole (**3w**) was obtained in only 41% yield. Moderate to good yields were obtained when alkyl substituents were employed at the para position. When 4-phenylcyclohexanone was used as the

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750

Table 2. Reaction of Substituted Anilines (1) with 2a[a]





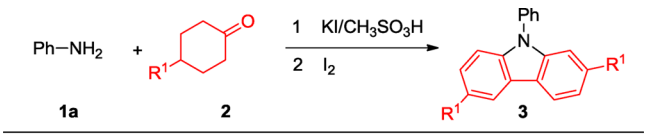
[a]Conditions: **1** (0.2 mmol), **2a** (0.5 mmol), KI (0.1 mmol), CH_3SO_3H (0.1 mmol), toluene (1 mL), 160 °C under O_2 for 24 h; after cooling to room temperature, I_2 (25 mol %) was added and the mixture was further stirred under O_2 at 160 °C for 6 h; isolated yield based on **1**.

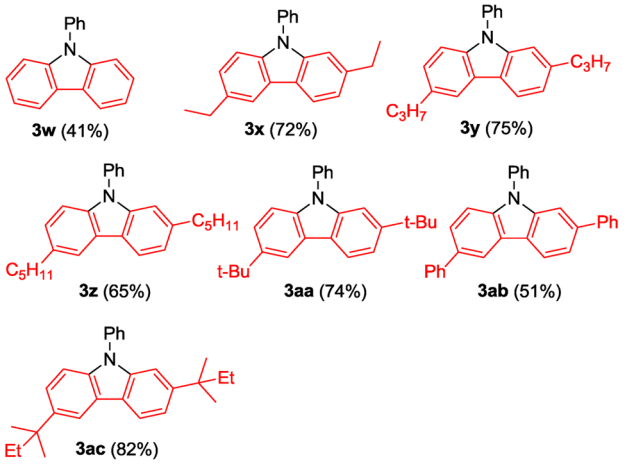
substrate, the corresponding product **3ab** was obtained in 51% yield.

In early years, some methods were reported to synthesize pyrroles from aromatic amines and ketones in the presence of transition metals.[19] However, a similar reaction under transition-metal-free conditions is rare. In addition, we found that aromatic ketones can also react with anilines to give 1,2,4-triaryl-substituted pyrrole compounds promoted by 50 mol % KI (Table 4).[20] When aniline (**1a**, 0.3 mmol, 1.5 equiv) reacted with acetophenone (**4a**, 0.4 mmol) under air at 160 °C using 1,1,2,2-tetrachloroethane as the solvent, the desired product 1,2,4-triphenyl-1*H*-pyrrole (**5a**) was observed in 85% yield. Good yields were obtained when electron-donating groups were present at the para position of anilines (**5b**−**5e**). Functional groups such as fluoro and chloro were compatiable to give the corresponding products **5g** and **5h** in 71% and 80% yields, respectively. The position of the methyl group significant affected the reaction yields, and much lower yield was obtained when the methyl group was located at the meta position (**5b**, **5i**, and **5j**). Moderate to good yields were obtained when substituted acetophenones were employed under the optimized reaction conditions.

A plausible reaction mechanism to rationalize this transformation is illustrated in Scheme 1. Condensation and dehydration reactions of two cyclohexanones under acidic conditions afford an unsaturated ketone intermediate **A**.[21] Subsequent condensation of **A** with **1a** provides an imine

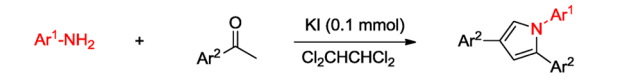
Table 3. Reaction of 1a with Substituted Cyclohexanones (2)[a]

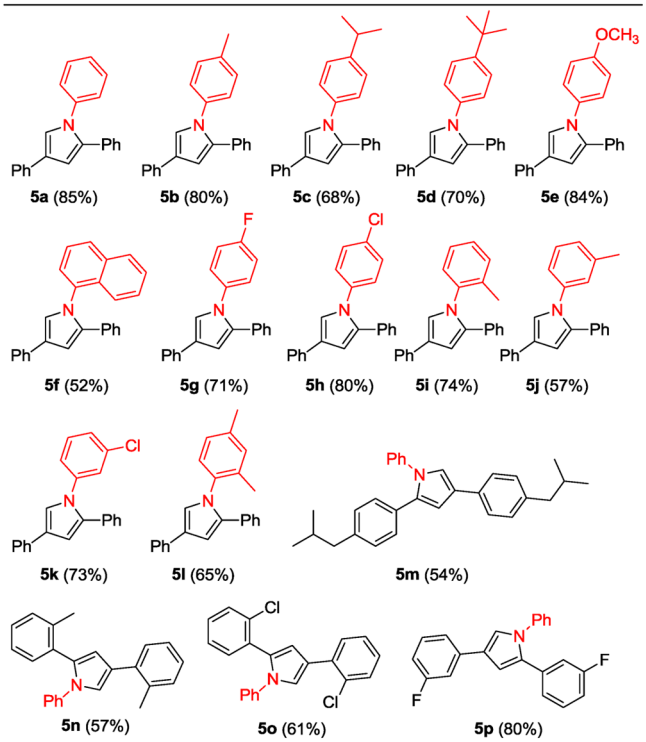




[a]Conditions: **1a** (0.2 mmol), **2** (0.5 mmol), KI (0.1 mmol), CH_3SO_3H (0.1 mmol), toluene (1 mL), 160 °C under O_2 for 24 h; after cooling to room temperature, I_2 (25 mol %) was added and the mixture was further stirred under O_2 at 160 °C for 6 h; isolated yield based on **1a**.

Table 4. Reaction of Substituted Anilines (1) with Acetophenone (4)[a]

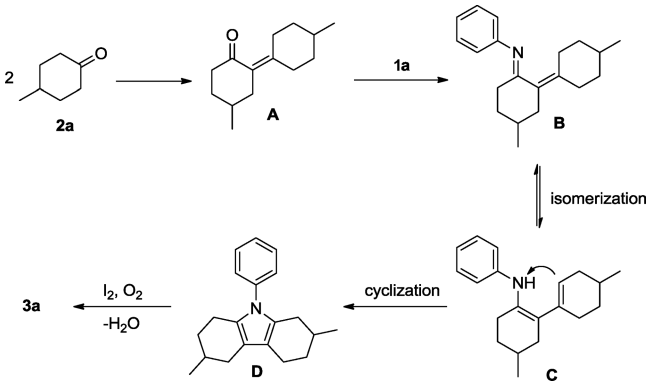




[a]Conditions: **1** (0.3 mmol), **4** (0.4 mmol), KI (0.1 mmol), 1,1,2,2-tetrachloroethane (0.5 mL), 160 °C under air for 30 h; isolated yield based on **4**.

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750

Scheme 1. Plausible Mechanism for the Reaction



intermediate **B**. Isomerization of **B** affords an enamine intermediate **C**, which can convert into a pyrrole intermediate **D** via cyclization procedure. A dehydrogenative tautomerization reaction under oxidative conditions provides the final product **3a**.[22] Intermediates **A**, **B**, **C**, and **D** could be detected by HRMS.

CONCLUSION

In summary, we have developed a novel approach for the synthesis of *N*-aryl-substituted carbazoles from anilines and cyclohexanones by a one-pot, two-step process. According to this strategy, a series of 2,6-disubstituted 9-arylcarbazoles were synthesized in moderate to good yields in the absence of transition-metal catalyst under oxygen atmosphere. Readily available anilines acted as the nitrogen and aryl source in this kind of transformation. Both of the aryl rings come from cyclohexanones. Meanwhile, 1,2,4-triaryl-substituted pyrroles were successfully prepared from anilines and acetophenones using KI as the promoter under air. This method affords a simple approach for unsymmetrical triaryl-substituted pyrroles from readily available starting materials. The mechanism and the further synthetic applications of this reaction are in progress in our laboratory.

EXPERIMENTAL SECTION

General Information. All experiments were carried out under an atmosphere of oxygen. Flash column chromatography was performed over silica gel 48−75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$, chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). HRMS analyses were performed on Thermo Scientific LTQ Orbitrap XL. The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, and HRMS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR, and MS data with those of literature. All reagents were used as received from commercial sources without further purification.

General Procedure for the Synthesis of Carbazoles. An oven-dried reaction tube was charged with aromatic amines (0.2 mmol), KI (16.7 mg, 0.1 mmol), methanesulfonic acid (CH_3SO_3H, 7 uL, 0.1 mmol), 4-substituted cyclohexanone (0.5 mmol), and toluene (1 mL). The resulting solution was sealed under oxygen and stirred at 160 °C for 24 h. After cooling to room temperature, I_2 (12.7 mg, 25 mol %) was added and the resulting solution was sealed under oxygen again and stirred at 160 °C for 6 h. The volatiles were removed under vacuum, and the residue was purified by column chromatography (petroleum ether) to give the pure product.

General Procedure for the Synthesis of Pyrroles. An oven-dried reaction tube was charged with aromatic amines (0.3 mmol), KI (16.7 mg, 0.1 mmol), acetophenone (0.4 mmol), and 1,1,2,2-tetrachloroethane (0.5 mL). The resulting solution was sealed under air and stirred at 160 °C for 30 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (petroleum ether) to give the pure product.

2,6-Dimethyl-9-phenyl-9H-carbazole (***3a***).[18] White solid (41.2 mg, yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.55−7.53 (m, 2H), 7.47−7.42 (m, 1H), 7.25 (d, J = 2.4 Hz, 1H), 7.20−7.15 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.5, 139.2, 138.0, 136.0, 129.8, 129.1, 127.1, 127.1, 126.6, 123.6, 121.2, 120.9, 119.9, 119.9, 109.8, 109.3, 22.1, 21.4; MS (EI) m/z (%): 271.1 (100), 254.1, 241.0, 127.2, 77.0.

2,6-Dimethyl-9-(p-tolyl)-9H-carbazole (***3b***).[18] Colorless liquid (42.2 mg, yield 74%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 7.6 Hz, 1H), 7.87 (s, 1H), 7.42−7.36 (m, 4H), 7.23 (d, J = 5.2 Hz, 1H), 7.18−7.14 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.47 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.7, 139.4, 137.0, 135.9, 135.3, 130.4, 128.9, 126.9, 126.6, 123.5, 121.0, 120.8, 119.9, 119.8, 109.8, 109.3, 22.0, 21.4, 21.2; MS (EI) m/z (%): 285 (100), 254, 192, 142, 77.

9-(4-Isopropylphenyl)-2,6-dimethyl-9H-carbazole (***3c***). Yellow solid (45.7 mg, yield 73%), mp 36−38 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.46−7.42 (m, 4H), 7.25 (d, J = 4.0 Hz, 1H), 7.18−7.16 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 3.07−3.00 (m, 1H), 2.53 (s, 3H), 2.47 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.8, 141.6, 139.4, 135.8, 135.5, 128.9, 127.7, 126.9, 126.5, 123.5, 121.0, 120.8, 119.9, 119.83, 109.8, 109.4, 33.9, 24.0, 22.1, 21.4; MS (EI) m/z (%): 313 (100), 298, 283, 194, 77; HRMS(ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{24}N$, 314.1903; found, 314.1902.

9-(4-(tert-Butyl)phenyl)-2,6-dimethyl-9H-carbazole (***3d***). White solid (48.4 mg, yield 74%), mp 159−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.61−7.57 (m, 2H), 7.47−7.44 (m, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.19−7.16 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.1, 141.6, 139.3, 135.8, 135.2, 128.9, 126.6, 126.5, 126.5, 123.5, 121.0, 120.8, 119.8, 119.8, 109.9, 109.5, 34.7, 31.4, 22.1, 21.4; MS (EI) m/z (%): 327 (100), 312, 297, 194, 142; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{26}N$, 328.2059; found, 328.2059.

9-([1,1′-Biphenyl]-4-yl)-2,6-dimethyl-9H-carbazole (***3e***). Yellow solid (36.1 mg, yield 52%), mp 168−170 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, J = 7.6 Hz, 1H), 7.90 (s, 1H), 7.82−7.80 (m, 2H), 7.71−7.69 (m, 2H), 7.63−7.61 (m, 2H), 7.53−7.49 (m, 2H), 7.42−7.39 (m, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 0.8 Hz, 1H), 7.22−7.19 (m, 1H), 7.10 (d, J = 8.0 Hz, 1H), 2.55 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.5, 140.4, 140.0, 139.2, 137.2, 136.1, 129.3, 128.9, 128.5, 127.6, 127.27, 127.2, 126.7, 123.7, 121.3, 121.1, 120.0, 119.95, 109.9, 109.5, 22.2, 21.4; MS (EI) m/z (%): 347 (100), 291, 254, 152, 77; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{22}N$, 348.1747; found, 348.1755.

9-(4-Methoxyphenyl)-2,6-dimethyl-9H-carbazole (***3f***).[18] Colorless liquid (27 mg, yield 45%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.44−7.41 (m, 2H), 7.20−7.17 (m, 2H), 7.12−7.08 (m, 3H), 7.06 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 2.53 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.7, 142.0, 139.7, 135.9, 130.6, 128.9, 128.5, 126.5, 123.3, 120.9, 120.7, 119.9, 119.8, 115.0, 109.7, 109.3, 55.5, 22.1, 21.4; MS (EI) m/z (%): 301 (100), 286, 242, 150, 120.

9-(4-Fluorophenyl)-2,6-dimethyl-9H-carbazole (***3g***). White solid (43.4 mg, yield 75%), mp 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.50−7.47 (m, 2H), 7.29−7.27 (m, 1H), 7.26−7.23 (m, 1H), 7.18 (d, J = 1.2 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 2.53 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.5 (d, J = 245.6 Hz),141.7, 139.4, 136.1, 133.9 (d, J = 3.1 Hz), 129.3, 128.95, 128.9, 126.7, 123.5, 121.3, 120.9, 120.0 (d, J = 3.3 Hz), 116.7 (d, J = 22.6 Hz), 109.5, 109.1, 22.1, 21.3; MS (EI) $m/$

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750

z (%): 289 (100), 272, 192, 143, 95; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{17}FN$, 290.1339; found, 290.1345.

9-(4-Chlorophenyl)-2,6-dimethyl-9H-carbazole (**3h**).[18] Colorless liquid (52.0 mg, yield 85%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.57−7.54 (m, 2H), 7.50−7.46 (m, 2H), 7.22 (d, J = 8.4 Hz, 1H), 7.19−7.17 (m, 1H), 7.14 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.3, 139.0, 136.6, 136.1, 132.6, 130.0, 129.5, 128.3, 126.8, 123.7, 121.5, 121.1, 120.0, 120.0, 109.6, 109.1, 22.1, 21.3; MS (EI) *m/z* (%): 305 (100), 290, 268, 192, 127.

2,6-Dimethyl-9-(4-(trifluoromethyl)phenyl)-9H-carbazole (**3i**).[18] White solid (42.0 mg, yield 62%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.97 (d, J = 7.6 Hz, 1H), 7.88 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 7.21−7.19 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 2.54 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.4, 140.9, 138.6, 136.3, 130.0, 128.8 (q, J = 32.7 Hz), 127.0 (q, J = 3.4 Hz), 126.9, 126.7 (q, J = 270.7 Hz), 124.0, 121.9, 121.4, 120.1, 120.1, 109.6, 109.2, 22.1, 21.3; MS (EI) *m/z* (%): 339 (100), 324, 268, 192, 127.

2,6-Dimethyl-9-(4-(trifluoromethoxy)phenyl)-9H-carbazole(**3j**).[18] Colorless liquid (62.5 mg, yield 88%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.58−7.55 (m, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 6.4 Hz, 1H), 7.20−7.17 (m, 1H), 7.15 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.7, 141.3, 139.0, 136.6, 136.2, 129.6, 128.3, 126.8, 123.7, 122.4, 121.6, 121.1, 120.6 (q, J = 257.0 Hz), 120.1, 120.0, 109.5, 109.1, 22.1, 21.3; MS (EI) *m/z* (%): 355 (100), 340, 242, 177, 127.

4-(2,6-Dimethyl-9H-carbazol-9-yl)benzonitrile (**3k**). White solid (36.1 mg, yield 61%), mp 190−192 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.90−7.87 (m, 3H), 7.73−7.69 (m, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 7.22−7.19 (m, 1H), 7.13 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.4, 140.5, 138.2, 136.6, 133.9, 130.5, 127.1, 126.9, 124.3, 122.4, 121.7, 120.3, 120.2, 118.5, 110.1, 109.7, 109.2, 22.2, 21.4; MS (EI) *m/z* (%): 296 (100), 297, 207, 192, 140; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{17}N_2$, 297.1386; found, 297.1385.

2,6-Dimethyl-9-(4-nitrophenyl)-9H-carbazole (**3l**).[18] Orange solid (40.5 mg, yield 64%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.50−8.48 (m, 1H), 8.47−8.46 (m, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.79−7.78 (m, 1H), 7.77−7.75 (m, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.28 (s, 1H), 7.23−7.21 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 2.54 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.5, 144.2, 140.4, 138.1, 136.6, 130.7, 127.1, 126.5, 125.5, 124.5, 122.5, 121.8, 120.3, 120.2, 109.7, 109.3, 22.2, 21.3; MS (EI) *m/z* (%): 316 (100), 286, 255, 192, 127.

2,6-Dimethyl-9-(o-tolyl)-9H-carbazole (**3m**). Colorless solid (50.7 mg, yield 89%), mp 37−39 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.47−7.36 (m, 3H), 7.33 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.80 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.8, 139.5, 137.4, 136.3, 135.9, 131.4, 129.3, 128.7, 128.5, 127.2, 126.6, 123.2, 120.8, 120.6, 120.0, 119.9, 109.8, 109.4, 22.1, 21.4, 17.6; MS (EI) *m/z* (%): 285 (100), 268, 254, 192, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{20}N$, 286.1590; found, 286.1590.

9-([1,1′-Biphenyl]-2-yl)-2,6-dimethyl-9H-carbazole (**3n**). White solid (56.2 mg, yield 81%), mp 139−142 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, J = 7.6 Hz, 1H), 7.77 (s, 1H), 7.67−7.65 (m, 1H), 7.60−7.51 (m, 2H), 7.47−7.45 (m, 1H), 7.06−7.02 (m, 3H), 7.01−6.96 (m, 4H), 6.91 (d, J = 8.0 Hz, 1H), 6.84 (s, 1H), 2.46 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.8, 141.0, 139.5, 138.74, 135.6, 135.1, 131.5, 129.8, 128.6, 128.6, 128.5, 128.0, 127.8, 127.2, 126.4, 123.3, 120.8, 120.7, 119.7, 119.6, 110.1, 109.5, 22.0, 21.4; MS (EI) *m/z* (%): 347 (100), 291, 254, 152, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{20}N$, 322.1590; found, 322.1588.

9-(2-Chlorophenyl)-2,6-dimethyl-9H-carbazole (**3o**).[18] Colorless liquid (55.0 mg, yield 90%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.97 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.67−7.65 (m, 1H), 7.47−7.44 (m, 3H), 7.17 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.95−6.92 (m, 1H), 6.84 (s, 1H), 2.53 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.5, 139.2, 136.0, 135.3, 133.7, 131.0, 130.9, 129.6, 129.2, 128.0, 126.6, 123.5, 121.3, 120.9, 120.0, 119.9, 110.0, 109.5, 22.1, 21.4; MS (EI) *m/z* (%): 305 (100), 290, 241, 192, 127.

2,6-Dimethyl-9-(m-tolyl)-9H-carbazole (**3p**).[18] Colorless liquid (41.6 mg, yield 73%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 7.6 Hz, 1H), 7.87 (s, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 6.8 Hz, 2H), 7.07 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.6, 139.8, 139.3, 137.89, 135.9, 129.5, 129.0, 128.0, 127.6, 126.6, 124.1, 123.5, 121.1, 120.9, 119.9, 119.9, 109.8, 109.4, 22.1, 21.4, 21.4; MS (EI) *m/z* (%): 285 (100), 268, 254, 192, 134.

9-(3-Chlorophenyl)-2,6-dimethyl-9H-carbazole (**3q**). Colorless solid (53.7 mg, yield 88%), mp 33−36 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 7.6 Hz, 1H), 7.87 (s, 1H), 7.57−7.56 (m, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.47−7.44 (m, 1H), 7.44−7.41 (m, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.21−7.18 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.2, 139.3, 138.8, 136.2, 135.3, 130.7, 129.6, 127.3, 127.1, 126.8, 125.1, 123.8, 121.6, 121.1, 120.0, 120.0, 109.6, 109.2, 22.1, 21.4; MS (EI) *m/z* (%): 305 (100), 290, 254, 192, 121; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{17}ClN$, 306.1044; found, 306.1047.

3-(2,6-Dimethyl-9H-carbazol-9-yl)benzonitrile (**3r**). Colorless liquid (41.5 mg, yield 70%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, J = 8.0 Hz, 1H), 7.88−7.85 (m, 2H), 7.83−7.79 (m, 1H), 7.73−7.68 (m, 2H), 7.23 (d, J = 6.8 Hz, 1H), 7.21−7.28 (m, 1H), 7.14 (s, 1H), 7.11 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.8, 139.2, 138.5, 136.4, 131.3, 130.8, 130.4, 130.1, 126.9, 124.0, 122.1, 121.3, 120.2, 120.1, 120.0, 114.1, 109.3, 108.8, 22.1, 21.3; MS (EI) *m/z* (%): 296 (100), 279, 192, 140, 102; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{17}N_2$, 297.1386; found, 297.1386.

2,6-Dimethyl-9-(naphthalen-1-yl)-9H-carbazole (**3s**). Colorless liquid (32.1 mg, yield 50%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (s, 1H), 8.01 (d, J = 10.8 Hz, 2H), 7.95 (s, 1H), 7.68−7.64 (m, 1H), 7.62−7.60 (m, 1H), 7.55−7.51 (m, 1H), 7.34−7.28 (m, 2H), 7.12−7.08 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.77 (s, 1H), 2.54 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.9, 140.6, 136.1, 134.9, 134.4, 131.1, 129.1, 128.9, 128.5, 127.0, 126.8, 126.7, 126.0, 123.7, 123.5, 121.2, 120.8, 120.0, 120.0, 110.2, 109.9, 22.1, 21.5; MS (EI) *m/z* (%): 321 (100), 305, 291, 145, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{20}N$, 322.1590; found, 322.1589.

2,6-Dimethyl-9-(naphthalen-2-yl)-9H-carbazole (**3t**). White solid (32.1 mg, yield 50%), mp 53−56 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, J = 8.4 Hz, 1H), 8.01−7.95 (m, 3H), 7.92−7.90 (m, 2H), 7.66−7.64 (m, 1H), 7.60−7.56 (m, 2H), 7.31 (d, J = 8.4 Hz, 1H), 7.23−7.18 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 2.55 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.7, 139.4, 136.0, 135.5, 134.0, 132.3, 129.7, 129.3, 127.9, 127.8, 126.7, 126.7, 126.3, 125.4, 125.2, 123.7, 121.3, 121.0, 120.0, 119.9, 109.8, 109.4, 22.1, 21.4; MS (EI) *m/z* (%): 321 (100), 291, 192, 152, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{20}N$, 322.1590; found, 322.1588.

9-(2,4-Dimethylphenyl)-2,6-dimethyl-9H-carbazole (**3u**). Colorless solid (48.5 mg, yield 81%), mp 43−46 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.26−7.15 (m, 4H), 7.05 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.80 (s, 1H), 2.53 (s, 3H), 2.45 (s, 6H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.9, 139.6, 138.4, 137.0, 135.9, 133.6, 132.1, 129.0, 128.6, 127.9, 126.5, 123.3, 120.7, 120.5, 119.9, 119.9, 109.8, 109.4, 22.0, 21.4, 21.2, 17.5; MS (EI) *m/z* (%): 299 (100), 282, 268, 133, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{22}N$, 300.1747; found, 300.1749.

9-Mesityl-2,6-dimethyl-9H-carbazole (**3v**). White solid (47.0 mg, yield 75%), mp 141−143 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.06−7.04 (m, 3H), 6.81 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 2.53 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H), 1.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.2, 138.9, 138.3, 137.9, 136.0, 132.2, 129.4, 128.6, 126.7, 123.2, 120.7, 120.5, 120.1, 120.0, 109.5, 109.1, 22.1, 21.5, 21.2, 17.5;

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750

MS (EI) m/z (%): 313 (100), 296, 192, 140, 77; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{24}N$, 314.1903; found, 314.1908.

*9-Phenyl-9H-carbazole (**3w**, CAS no. 1150-62-5).*[23] White solid (20.0 mg, yield 41%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.15 (d, J = 7.6 Hz, 2H), 7.62−7.55 (m, 4H), 7.48−7.44 (m, 1H), 7.41−7.38 (m, 4H), 7.30−7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.9, 137.7, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.9, 109.7; MS (EI) m/z (%): 243.1 (100), 166.0, 120.6, 108.5, 77.0.

*2,6-Diethyl-9-phenyl-9H-carbazole (**3x**).*[18] Colorless liquid (43.1 mg, yield 72%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, J = 8.0 Hz, 1H), 7.91 (s, 1H), 7.61−7.57 (m, 2H), 7.56−7.54 (m, 2H), 7.46−7.42 (m, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.24−7.21 (m, 1H), 7.20 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 2.83 (q, J = 7.6 Hz, 2H), 2.77 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H), 1.27 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.6, 141.5, 139.4, 138.1, 135.9, 129.8, 127.1, 127.1, 125.6, 123.6, 121.3, 120.1, 120.0, 118.7, 109.4, 108.6, 29.6, 28.9, 16.5, 16.2; MS (EI) m/z (%): 299, 284 (100), 269, 135, 77.

*9-Phenyl-2,6-dipropyl-9H-carbazole (**3y**).*[18] Colorless liquid (49.1 mg, yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00 (d, J = 7.6 Hz, 1H), 7.88 (s, 1H), 7.61−7.57 (m, 2H), 7.56−7.54 (m, 2H), 7.46−7.42 (m, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.19−7.17 (m, 2H), 7.09 (d, J = 8.0 Hz, 1H), 2.76 (t, J = 7.6 Hz, 2H), 2.70 t, J = 7.6 Hz, 2H), 1.77−1.71 (m, 2H), 1.71−1.65 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.4, 140.9, 139.5, 138.1, 134.2, 129.8, 127.1, 127.0, 126.1, 123.5, 121.3, 120.6, 119.8, 119.4, 109.3, 109.2, 38.8, 38.1, 25.4, 25.1, 13.89, 13.9; MS (EI) m/z (%): 327, 298 (100), 269, 254, 192.

*2,6-Dipentyl-9-phenyl-9H-carbazole (**3z**).*[18] Colorless liquid (49.8 mg, yield 65%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.62−7.58 (m, 2H), 7.57−7.54 (m, 2H), 7.47−7.43 (m, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.20−7.17 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 2.78 (t, J = 7.8 Hz, 2H), 2.71 (t, J = 7.8 Hz, 2H), 1.73−1.69 (m, 2H), 1.67−1.63 (m, 2H), 1.39−1.35 (m, 4H), 1.34−1.30 (m, 4H), 0.91 (t, J = 5.4 Hz, 3H), 0.87 (t, J = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.4, 141.2, 139.4, 138.1, 134.5, 129.8, 127.1, 127.0, 126.1, 123.5, 121.3, 120.6, 119.9, 119.3, 109.3, 109.1, 36.7, 36.0, 32.0, 31.8, 31.6, 31.6, 22.6, 22.6, 14.1, 14.0; MS (EI) m/z (%): 383, 326 (100), 269, 192, 77.

*2,6-Di-tert-butyl-9-phenyl-9H-carbazole (**3aa**).*[18] White solid (52.6 mg, yield 74%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (d, J = 1.6 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.62−7.58 (m, 2H), 7.57−7.55(m, 2H), 7.47−7.44 (m, 1H), 7.44−7.42 (m, 1H), 7.39 (d, J = 1.2 Hz, 1H), 7.35−7.30 (m, 2H), 1.45 (s, 9H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.4, 142.8, 141.3, 139.3, 138.1, 129.8, 127.0, 127.0, 123.2, 123.1, 121.2, 119.6, 117.8, 116.2, 109.1, 106.0, 35.2, 34.7, 32.0, 31.8; MS (EI) m/z (%): 355, 340 (100), 243, 127, 77.

*2,6,9-Triphenyl-9H-carbazole (**3ab**).*[18] White solid (48.5 mg, yield 51%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.36 (d, J = 1.2 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.75−7.72 (m, 2H), 7.69−7.61 (m, 7H), 7.60 (d, J = 1.2 Hz, 1H), 7.57−7.55 (m, 1H), 7.51−7.42 (m, 6H), 7.37−7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.0, 141.9, 141.9, 140.8, 139.7, 137.6, 133.7, 130.0, 128.8, 128.7, 127.6, 127.6, 127.3, 127.2, 127.1, 126.6, 125.5, 123.7, 122.7, 120.6, 119.8, 118.8, 110.0, 108.4.

*2,6-Di-tert-pentyl-9-phenyl-9H-carbazole (**3ac**).*[18] Colorless liquid (62.8 mg, yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm δ 8.04 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 1.2 Hz, 1H), 7.62−7.56 (m, 4H), 7.46−7.42 (m, 1H), 7.37−7.42 (m, 2H), 7.32 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 1.78−1.72 (q, J = 7.4 Hz, 2H), 1.68 (q, J = 7.4 Hz, 2H), 1.41 (s, 6H), 1.32 (s, 6H), 0.71 (t, J = 7.6 Hz, 3H), 0.67 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.8, 141.2, 141.0, 139.2, 138.2, 129.75, 126.9, 126.9, 123.7, 123.1, 121.2, 119.4, 118.3, 117.0, 109.0, 106.9, 38.4, 37.9, 37.4, 37.2, 29.1, 28.9, 9.3, 9.2; MS (EI) m/z (%): 383, 354 (100), 324, 243, 134.

*1,2,4-Triphenyl-1H-pyrrole (**5a**, CAS no. 15811-37-7).*[20] White solid (50.2 mg, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61−7.58 (m, 2H), 7.39−7.28 (m, 5H), 7.25−7.17 (m, 9H), 6.75 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm)δ 140.4, 135.2, 134.8, 132.7, 129.1, 128.7, 128.3, 128.1, 126.8, 126.5, 125.8, 125.7, 125.6, 125.1, 120.9, 108.8; MS (EI) m/z (%): 295 (100), 280, 191, 104, 77.

*2,4-Diphenyl-1-(p-tolyl)-1H-pyrrole (**5b**).*[20] White solid (49.5 mg, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59−7.57 (m, 2H), 7.37−7.33 (m, 2H), 7.22−7.17 (m, 7H), 7.13−7.07 (m, 4H), 6.73 (d, J = 2.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.8, 136.6, 135.2, 134.7, 132.8, 129.6, 128.7, 128.3, 128.1, 126.4, 125.7, 125.5, 125.3, 125.1, 120.9, 108.5, 21.0; MS (EI) m/z (%): 309 (100), 294, 232, 191, 77.

*1-(4-Isopropylphenyl)-2,4-diphenyl-1H-pyrrole (**5c**).* Yellow solid (45.8 mg, yield 68%), mp 97−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60−7.58 (m, 2H), 7.38−7.34 (m, 2H), 7.23−7.18 (m, 9H), 7.14−7.11 (m, 2H), 6.73 (d, J = 1.6 Hz, 1H), 2.96−2.89 (m, 1H), 1.26 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.6, 138.0, 135.3, 134.8, 132.8, 128.7, 128.3, 128.0, 127.0, 126.4, 125.7, 125.5, 125.3, 125.1, 121.0, 108.4, 33.6, 23.9; MS (EI) m/z (%): 337 (100), 322, 294, 191, 77; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{24}N$, 338.1903; found, 338.1906.

*1-(4-(tert-Butyl)phenyl)-2,4-diphenyl-1H-pyrrole (**5d**).* White solid (49.2 mg, yield 70%), mp 159−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60−7.57 (m, 2H), 7.38−7.32 (m, 4H), 7.23−7.17 (m, 7H), 7.15−7.11 (m, 2H), 6.73 (d, J = 1.6 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.9, 137.7, 135.3, 134.8, 132.8, 128.7, 128.3, 128.1, 126.4, 125.9, 125.7, 125.3, 125.1, 125.1, 121.0, 108.5, 34.6, 31.3; MS (EI) m/z (%): 351 (100), 336, 321, 191, 77; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{26}N$, 352.2060; found, 352.2059.

*1-(4-Methoxyphenyl)-2,4-diphenyl-1H-pyrrole (**5e**).*[20] White solid (54.6 mg, yield 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60−7.58 (m, 2H), 7.38−7.34 (m, 2H), 7.24−7.12 (m, 9H), 6.88−6.85 (m, 2H), 6.73 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.3, 135.3, 134.9, 133.5, 132.8, 128.7, 128.2, 128.1, 126.9, 126.4, 125.7, 125.2, 125.1, 121.1, 114.2, 108.1, 55.4; MS (EI) m/z (%): 325 (100), 310, 191, 102, 77.

*1-(Naphthalen-1-yl)-2,4-diphenyl-1H-pyrrole (**5f**).*[24] White solid (35.9 mg, yield 52%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91−7.85 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.52−7.36 (m, 6H), 7.26−7.19 (m, 2H), 7.10−7.04 (m, 5H), 6.89 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.1, 136.7, 135.2, 134.2, 132.6, 130.7, 128.7, 128.4, 128.1, 128.0, 127.4, 127.1, 126.6, 126.4, 125.8, 125.6, 125.2, 125.1, 123.4, 122.6, 107.3; MS (EI) m/z (%): 345 (100), 328, 241, 191, 77.

*1-(4-Fluorophenyl)-2,4-diphenyl-1H-pyrrole (**5g**).* White solid (44.4 mg, yield 71%), mp 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60−7.57 (m, 2H), 7.39−7.35 (m, 2H), 7.24−7.15 (m, 9H), 7.05−7.00 (m, 2H), 6.73 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 162.5, 160.0, 136.5 (d, J = 3.0 Hz), 135.0 (d, J = 7.3 Hz), 132.5, 128.7, 128.3, 128.2, 127.3 (d, J = 8.5 Hz), 126.7, 125.9, 125.6, 125.1, 120.9, 115.9 (d, J = 22.6 Hz), 108.7; MS (EI) m/z (%): 313 (100), 209, 191, 108, 75; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}FN$, 314.1340; found, 314.1339.

*1-(4-Chlorophenyl)-2,4-diphenyl-1H-pyrrole (**5h**).*[20] White solid (52.7 mg, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59−7.56 (m, 2H), 7.38−7.34 (m, 2H), 7.30−7.26 (m, 2H), 7.24−7.10 (m, 9H), 6.73 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.8, 134.9, 134.8, 132.4, 132.4, 129.2, 128.7, 128.3, 128.2, 126.8, 126.7, 126.0, 125.9, 125.1, 120.6, 109.1; MS (EI) m/z (%): 329 (100), 293, 191, 146, 102.

*2,4-Diphenyl-1-(o-tolyl)-1H-pyrrole (**5i**).*[25] White solid (45.8 mg, yield 74%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61−7.59 (m, 2H), 7.38−7.25 (m, 5H), 7.22−7.12 (m, 7H), 7.07 (d, J = 2.0 Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.8, 135.7, 135.2, 135.3, 132.9, 130.9, 128.7, 128.2, 128.1, 128.1, 127.2, 126.6, 126.3, 125.7, 125.1, 125.0, 121.0, 106.8, 17.6; MS (EI) m/z (%): 309 (100), 293, 281, 191, 91.

*2,4-Diphenyl-1-(m-tolyl)-1H-pyrrole (**5j**).*[20] White solid (35.2 mg, yield 57%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.60−705 (m, 2H), 7.38−7.34 (m, 2H), 7.23−7.16(m, 8H), 7.09 (d, J = 6.4 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.74 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.2, 139.1, 135.2, 134.7, 132.7, 128.7, 128.7, 128.2,

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750

128.1, 127.5, 126.5, 126.1, 125.8, 125.4, 125.1, 122.9, 120.9, 108.6, 21.3; MS (EI) *m/z* (%): 309 (100), 294, 191, 146, 102.

*1-(3-Chlorophenyl)-2,4-diphenyl-1H-pyrrole (**5k**).*[20] White solid (48.1 mg, yield 73%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59−7.57 (m, 2H), 7.38−7.35 (m, 2H), 7.29−7.25 (m, 2H), 7.24−7.16 (m, 8H), 7.02−6.99 (m, 1H), 6.73 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.4, 134.8, 134.8, 134.6, 132.3, 129.9, 128.8, 128.7, 128.3, 128.2, 126.9, 126.8, 126.0, 125.5, 125.1, 124.0, 120.6, 109.3; MS (EI) *m/z* (%): 329 (100), 293, 191, 146, 102.

*1-(2,4-Dimethylphenyl)-2,4-diphenyl-1H-pyrrole (**5l**).* White solid (42,0 mg, yield 65%), mp 109−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59−7.57 (m, 2H), 7.36−7.32 (m, 2H), 7.19−7.11 (m, 7H), 7.04−6.99 (m, 3H), 6.77 (s, 1H), 2.33 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.9, 137.2, 135.7, 135.4, 135.1, 133.0, 131.5, 128.7, 128.1, 127.8, 127.2, 127.2, 126.2, 125.6, 124.9, 121.2, 106.7, 21.1, 17.5; MS (EI) *m/z* (%): 323 (100), 308, 246, 191, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{22}N$, 324.1747; found, 324.1742.

*2,4-Bis(4-isobutylphenyl)-1-phenyl-1H-pyrrole (**5m**).* Colorless liquid (44.0 m, yield 54%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51−7.48 (m, 2H), 7.35−7.26 (m, 3H), 7.22−7.19 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.70 (s, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.91−1.80 (m, 2H), 0.92 (d, *J* = 6.4 Hz, 6H), 0.88 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.5, 140.0, 139.2, 134.8, 132.6, 130.2, 129.4, 128.9, 128.8, 128.0, 126.6, 125.6, 125.4, 124.8, 120.3, 108.3, 45.1, 45.1, 30.3, 30.1, 22.4, 22.3; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{34}N$, 408.2686; found, 408.2685.

*1-Phenyl-2,4-di-o-tolyl-1H-pyrrole (**5n**).* Colorless liquid (36.9 mg, yield 57%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50−7.48 (m, 1H), 7.25−7.09 (m, 13H), 6.48 (d, *J* = 2.0 Hz, 1H), 2.54 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.4, 137.5, 135.1, 133.0, 132.5, 131.3, 130.7, 130.1, 128.9, 128.8, 127.7, 126.0, 125.9, 125.4, 124.7, 124.4, 120.8, 112.4, 21.6, 20.3; MS (EI) *m/z* (%): 323 (100), 308, 206, 194, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{22}N$, 324.1747; found, 324.1747.

*2,4-Bis(2-chlorophenyl)-1-phenyl-1H-pyrrole (**5o**).* White solid (44.3 mg, yield 61%), mp 88−91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61−7.59 (m, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.46−7.43 (m, 1H), 7.35−7.33 (m, 1H), 7.29−7.25 (m, 3H), 7.23−7.12 (m, 7H), 6.80 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.1, 134.3, 133.8, 132.7, 132.0, 131.6, 130.5, 130.1, 129.9, 129.7, 128.9, 128.9, 126.8, 126.5, 126.3, 124.7, 122.8, 122.0, 113.0; MS (EI) *m/z* (%): 363 (100), 328, 291, 225, 145; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}Cl_2N$, 364.0654; found, 364.0656.

*2,4-Bis(3-fluorophenyl)-1-phenyl-1H-pyrrole (**5p**).* Colorless liquid (53.0 mg, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39−7.27 (m, 6H), 7.24−7.16 (m, 4H), 6.94−6.84 (m, 4H), 6.73 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.1 (d, *J* = 84.6 Hz), 161.7 (d, *J* = 85.7 Hz), 139.8, 137.3 (d, *J* = 8.2 Hz), 134.5 (d, *J* = 8.4 Hz), 133.7, 130.1 (d, *J* = 8.6 Hz), 129.6 (d, *J* = 8.6 Hz), 129.2, 127.3, 125.6, 124.6, 123.9, 121.8, 120.6, 114.9 (d, *J* = 22.4 Hz), 113.5 (d, *J* = 21.1 Hz), 112.6 (d, *J* = 21.2 Hz), 111.8 (d, *J* = 21.8 Hz), 109.1; MS (EI) *m/z* (%): 331 (100), 227, 209, 154, 77; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}F_2N$, 332.1245; found, 332.1242.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00556.

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gjdeng@xtu.edu.cn. Fax: (+86)-0731-5829-2251. Phone: (+86)-0731-5829-8280

ORCID

Guo-Jun Deng: 0000-0003-2759-0314

Author Contributions

‡J.W. and X.C. contributed equally to this work

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21372187, 21502160, and 21572194), the Program for Innovative Research Cultivation Team in University of Ministry of Education of China (1337304), the Hunan Provincial Innovative Foundation for Postgraduate (CX2015B202), and the Undergraduate-Investigated-Study and Innovated-Experiment Plan of Hunan Province.

■ REFERENCES

(1) (a) Schmidt, A. W.; Reddy, K. R.; Knolker, H.-J. *Chem. Rev.* **2012**, *112*, 3193. (b) Liu, K.; Zhang, S. *ACS Med. Chem. Lett.* **2015**, *6*, 894.

(2) (a) Blouin, N.; Leclerc, M. *Acc. Chem. Res.* **2008**, *41*, 1110. (b) Qian, X.; Zhu, Y. Z.; Chang, W. Y.; Song, J.; Pan, B.; Lu, L.; Gao, H. H.; Zheng, J. Y. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9015.

(3) (a) *Organic Light Emitting Devices: Synthesis, Properties, and Applications*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, Germany, 2006. (b) Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943. (c) Li, J.; Grimsdale, A. *Chem. Soc. Rev.* **2010**, *39*, 2399.

(4) For selected reviews, see: (a) Knolker, H. J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303. (b) Roy, J.; Jana, A. K.; Mal, D. *Tetrahedron* **2012**, *68*, 6099. (c) Bauer, I.; Knolker, H. J. *Top. Curr. Chem.* **2011**, *309*, 203.

(5) (a) Robinson, R. *Chem. Rev.* **1963**, *63*, 373. (b) Robinson, R. *Chem. Rev.* **1969**, *69*, 227 and references cited therein..

(6) (a) Cadogan, J.; Cameron-Wood, M.; Mackie, R.; Searle, R. *J. Chem. Soc.* **1965**, 4831. (b) Iddon, B.; Meth-Cohn, O.; Scriven, E.; Suschitzky, H.; Gallagher, P. *Angew. Chem.* **1979**, *91*, 965; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (c) Soderberg, B. C. G. *Curr. Org. Chem.* **2000**, *4*, 727. (d) Smitrovich, J. H.; Davies, I. W. *Org. Lett.* **2004**, *6*, 533. (e) Freeman, A.; Urvoy, M.; Criswell, M. *J. Org. Chem.* **2005**, *70*, 5014. (f) Sanz, R.; Escribano, J.; Pedrosa, M.; Aguado, R.; Arnáiz, F. *Adv. Synth. Catal.* **2007**, *349*, 713. (g) Majgier-Baranowska, H.; Williams, J. D.; Li, B.; Peet, N. P. *Tetrahedron Lett.* **2012**, *53*, 4785.

(7) Gao, H. Y.; Xu, Q. L.; Yousufuddin, M.; Ess, D. H.; Kürti, L. *Angew. Chem., Int. Ed.* **2014**, *53*, 2701.

(8) (a) Forke, R.; Jäger, A.; Knölker, H. J. *Org. Biomol. Chem.* **2008**, *6*, 2481. (b) Knölker, H. J. *Chem. Lett.* **2009**, *38*, 8. (c) Gensch, T.; Roennefahrt, M.; Czerwonka, R.; Jaeger, A.; Kataeva, O.; Bauer, I.; Knölker, H. J. *Chem. - Eur. J.* **2012**, *18*, 770. (d) Huet, L.; Forke, R.; Jäger, A.; Knölker, H. J. *Synlett* **2012**, *23*, 1230. (e) Hesse, R.; Gruner, K. K.; Kataeva, O.; Schmidt, A. W.; Knölker, H. J. *Chem. - Eur. J.* **2013**, *19*, 14098. (f) Kumar, V. P.; Gruner, K. K.; Kataeva, O.; Knölker, H. J. *Angew. Chem.* **2013**, *125*, 11279; *Angew. Chem., Int. Ed.* **2013**, *52*, 11073. (g) Hernandez-Perez, A. C.; Collins, S. K. *Angew. Chem.* **2013**, *125*, 12928; *Angew. Chem., Int. Ed.* **2013**, *52*, 12696.

(9) For selected examples on carbazole synthesis from indoles, see: (a) Shi, L.; Zhong, X.; She, H.; Lei, Z.; Li, F. *Chem. Commun.* **2015**, *51*, 7136. (b) Jia, J.; Shi, J.; Zhou, J.; Liu, X.; Song, Y.; Xu, H. E.; Yi, W. *Chem. Commun.* **2015**, *51*, 2925. (c) Kong, A.; Han, X.; Lu, X. *Org. Lett.* **2006**, *8*, 1339. (d) Markad, S. B.; Argade, N. P. *Org. Lett.* **2014**, *16*, 5470. (e) Zheng, X.; Lv, L.; Lu, S.; Wang, W.; Li, Z. *Org. Lett.* **2014**, *16*, 5156. (f) Saunthwal, R. K.; Patel, M.; Kumar, S.; Danodia, A. K.; Verma, A. K. *Chem. - Eur. J.* **2015**, *21*, 18601. (g) Naykode, M. S.; Humne, V. T.; Lokhande, P. D. *J. Org. Chem.* **2015**, *80*, 2392. (h) Yuan, Z. G.; Wang, Q.; Zheng, A.; Zhang, K.; Lu, L. Q.; Tang, Z. L.; Xiao, W. J. *Chem. Commun.* **2016**, *52*, 5128. (i) Samala, S.; Mandadapu, A. K.; Saifuddin, M.; Kundu, B. *J. Org. Chem.* **2013**, *78*, 6769.

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750

(10) Yamashita, M.; Horiguchi, H.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 7481.
(11) Ozaki, K.; Zhang, H.; Ito, H.; Lei, A. W.; Itami, K. *Chem. Sci.* **2013**, *4*, 3416.
(12) Chen, S. P.; Li, Y. X.; Ni, P. H.; Huang, H. W.; Deng, G. J. *Org. Lett.* **2016**, *18*, 5384.
(13) (a) Iwaki, T.; Yasuhara, A.; Sakamoto, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1505. (b) Bedford, R. B.; Betham, M. *J. Org. Chem.* **2006**, *71*, 9403. (c) Ackermann, L.; Althammer, A. *Angew. Chem.* **2007**, *119*, 1652; *Angew. Chem., Int. Ed.* **2007**, *46*, 1627.
(14) (a) Nozaki, K.; Takahashi, K.; Nakano, K.; Hiyama, T.; Tang, H. Z.; Fujiki, M.; Yamaguchi, S.; Tamao, K. *Angew. Chem.* **2003**, *115*, 2097; *Angew. Chem., Int. Ed.* **2003**, *42*, 2051. (b) Kitawaki, T.; Hayashi, Y.; Chida, N. *Heterocycles* **2005**, *65*, 1561. (c) Kuwahara, A.; Nakano, K.; Nozaki, K. *J. Org. Chem.* **2005**, *70*, 413. (d) Kitawaki, T.; Hayashi, Y.; Ueno, A.; Chida, N. *Tetrahedron* **2006**, *62*, 6792. (e) Ou, Y.; Jiao, N. *Chem. Commun.* **2013**, *49*, 3473.
(15) Zhu, D. Q.; Liu, Q.; Luo, B. L.; Chen, M. H.; Pi, R. B.; Huang, P.; Wen, S. J. *Adv. Synth. Catal.* **2013**, *355*, 2172.
(16) Bhanuchandra, M.; Murakami, K.; Vasu, D.; Yorimitsu, H.; Osuka, A. *Angew. Chem.* **2015**, *127*, 10372; *Angew. Chem., Int. Ed.* **2015**, *54*, 10234.
(17) For selected examples on transformation of cyclohexanones to anilines, see: (a) Barros, M. T.; Dey, S. S.; Maycock, C. D.; Rodrigues, P. *Chem. Commun.* **2012**, *48*, 10901. (b) Hong, W. P.; Iosub, A. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 13664. (c) Hajra, A.; Wei, Y.; Yoshikai, N. *Org. Lett.* **2012**, *14*, 5488. (d) Zhao, J. W.; Huang, H. W.; Wu, W. Q.; Chen, H. J.; Jiang, H. F. *Org. Lett.* **2013**, *15*, 2604. (e) Girard, S. A.; Hu, X.; Knauber, T.; Zhou, F.; Simon, M.-O.; Deng, G. J.; Li, C. J. *Org. Lett.* **2012**, *14*, 5606. (f) Xie, Y.; Liu, S.; Liu, Y.; Wen, Y.; Deng, G.-J. *Org. Lett.* **2012**, *14*, 1692.
(18) Wu, J.; Xie, Y. J.; Chen, X. G.; Deng, G. J. *Adv. Synth. Catal.* **2016**, *358*, 3206.
(19) (a) Cadierno, V.; Gimeno, J.; Nebra, N. *Chem. - Eur. J.* **2007**, *13*, 9973. (b) Zhao, M.; Wang, F.; Li, X. W. *Org. Lett.* **2012**, *14*, 1412. (c) Li, B.-L.; Hu, H.-C.; Mo, L.-P.; Zhang, Z.-H. *RSC Adv.* **2014**, *4*, 12929.
(20) 1,2,4-Triarylpyrroles could be synthesized from anilines and acetophenones promoted by a stoichiometric amount of I_2, see: Xu, H.; Wang, F. J.; Xin, M.; Zhang, Z. *Eur. J. Org. Chem.* **2016**, *2016*, 925.
(21) (a) Eshelby, J. J.; Parsons, P. J.; Crowley, P. J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 191. (b) Yatluk, Y. G.; Sosnovskikh, V. Y.; Suvorov, A. L. *Russ. J. Org. Chem.* **2004**, *40*, 763.
(22) (a) Cao, X. X.; Cheng, X. F.; Bai, Y.; Liu, S. W.; Deng, G. J. *Green Chem.* **2014**, *16*, 4644. (b) Xie, Y. J.; Wu, J.; Che, X. Z.; Chen, Y.; Huang, H. W.; Deng, G. J. *Green Chem.* **2016**, *18*, 667.
(23) Li, H.; Wang, Y.; Yuan, K.; Tao, Y.; Chen, R.; Zheng, C.; Zhou, X.; Li, J.; Huang, W. *Chem. Commun.* **2014**, *50*, 15760.
(24) Li, X.; Chen, M.; Xie, X.; Sun, N.; Li, S.; Liu, Y. *Org. Lett.* **2015**, *17*, 2984.
(25) Potikha, L. M.; Kovtunenko, V. A. *Chem. Heterocycl. Compd.* **2006**, *42*, 741.

DOI: 10.1021/acs.joc.7b00556
J. Org. Chem. 2017, 82, 5743−5750