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Palladium(II)-Catalyzed Tandem Cyclization/C−H Functionalization of Alkynes for the Synthesis of Functionalized Indoles

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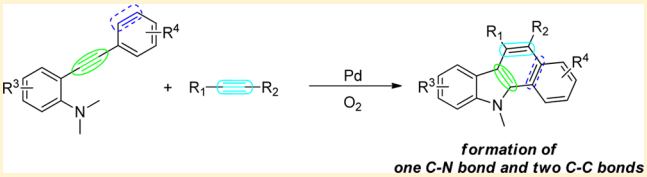
Supporting Information

ABSTRACT: A palladium-catalyzed tandem cyclization/C−H functionalization of two alkynes was accomplished to construct a series of polycyclic functionalized indoles. A range of internal alkynes bearing synthetically useful functional groups were tolerated. A good regioselectivity was observed when alkyl-substituted alkynes were introduced into the reaction system, and a single product was obtained. Molecular oxygen was used as the terminal oxidant in the approach, rendering the reaction more sustainable.

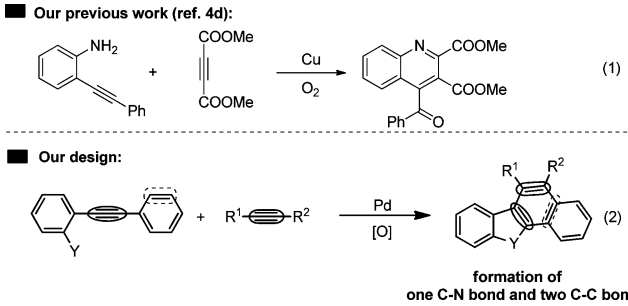


INTRODUCTION

Highly efficient construction of polysubstituted heterocyclic aromatic ring systems is an important research area in organic synthesis. A series of highly fused aromatic compounds with interesting biological and pharmacological activities have been reported to date.[1] Among these, polycyclic functionalized indoles have attracted great attention not only because of their remarkable biological activity but also because of their electrochemical and photochemical properties.[1a−d] In recent years, methodologies for the synthesis of indoles based on Pd-catalyzed cascade processes have gained great attention.[2] Nevertheless, despite the great interest of these transformations in synthesis, the development of alternative and facile approaches that may allow for the straightforward preparation of structurally diverse indoles from easily available starting materials needs to be pursued. In particular, to the best of our knowledge, the synthesis of polycyclic functionalized indoles by a palladium-catalyzed tandem cyclization/C−H functionalization of two different alkynes under oxidative conditions, a transformation in which one C−N bond as well as two C−C bonds form simultaneously, has not yet been reported (Scheme 1-2).

Palladium(II)-catalyzed functionalization of alkynes has emerged as an attractive strategy for the rapid generation of complex molecules due to its ability to form multiple carbon−carbon/carbon−heteroatom bonds in one step.[3] This versatility, combined with the broad functional-group compatibility and air- and moisture-tolerance, renders the Pd^{II}-catalyzed difunctionalization of alkynes a powerful tool in synthetic chemistry. Our group is persistently interested in metal-catalyzed functionalization of alkynes to prepare various functionalized heterocyclic compounds.[4] In our previous work, 4-carbonyl-quinolines were synthesized using amino-alkynes and but-2-ynedioate as substrates under copper-catalyzed oxidative conditions (Scheme 1-1). When tolane was introduced into our previous reaction, no product was detected. Then we envisioned that the reaction may occur if palladium catalysts were used. To our delight, we got a tetracyclic indole compound under the Pd-catalyzed conditions. Herein, we report an efficient preparation of polycyclic functionalized indoles using two different alkynes in one pot under Pd-catalyzed oxidative conditions (Scheme 1-2).

Scheme 1. Our Designed Route to Polycyclic Aromatic Hydrocarbons



RESULTS AND DISCUSSION

At the outset of our studies, we explored the effect of different reaction parameters on the tandem cyclization/C−H functionalization of alkynes **1a** and **2a**, which included palladium catalysts, oxidants, additives, and solvents (Table 1). Pd-catalyzed Cacchi cyclization of *o*-(1-alkynyl)anilines is a well-known process. The reaction has generally been performed under basic and nonoxidative conditions.[2b] However, Pd^0 is expected to be regenerated in the reductive elimination step; therefore, a suitable external oxidant is required to complete the

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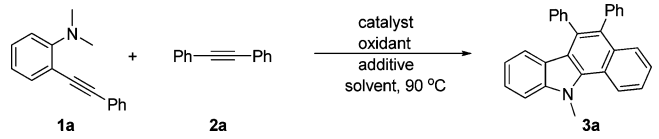
Table 1. Screening Optimal Conditions[a]



1a 2a 3a

entry	catalyst (mol %)	oxidant (2.0 equiv)	additive (equiv)	solvent	T (h)	yield (%)[b]
1	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$	NaOAc (2.0)	CH_3CN	12	n.r.[c]
2	$Pd(OAc)_2$ (10)	$PhI(OAc)_2$	NaOAc (2.0)	CH_3CN	12	15
3	$Pd(OAc)_2$ (10)	BQ	NaOAc (2.0)	CH_3CN	12	n.r.
4	$Pd(OAc)_2$ (10)	Ag_2CO_3	NaOAc (2.0)	CH_3CN	12	10
5	$Pd(OAc)_2$ (10)	$CuCl_2$	NaOAc (2.0)	CH_3CN	12	n.r.
6	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$	NaOAc (2.0)	DMF	12	20
7	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	NaOAc (2.0)	DMF	12	30
8	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	K_3PO_4 (2.0)	DMF	12	25
9	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	K_2CO_3 (2.0)	DMF	12	15
10	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	PivOH (2.0)	DMF	12	35
11	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	TBAB(1.0) + NaOAc (2.0)	DMF	12	40
12	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	TBAB(1.0) + PivOH (2.0)	DMF	12	45
13	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$	TBAB(1.0) + NaOAc (2.0) + PivOH (1.0)	DMF	12	50
14	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$ (20%) + O_2 (1 atm)	TBAB(1.0) + NaOAc (2.0) + PivOH (1.0)	DMF	12	55
15	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$ (20%) + O_2 (1 atm)	TBAB(1.0) + NaOAc (3.0) + PivOH (2.0)	DMF	12	60
16	$Pd(OAc)_2$ (10)	$Cu(OAc)_2{\cdot}CuCl_2$ (20%) + O_2 (1 atm)	TBAB(1.0) + NaOAc (3.0) + PivOH (2.0)	DMAc	12	68
17	$Pd(OAc)_2$ (10)	O_2 (1 atm)	TBAB(1.0) + NaOAc (3.0) + PivOH (2.0)	DMAc	12	56
18	$Pd(CF_3COO)_2$	$Cu(OAc)_2{\cdot}CuCl_2$ (20%) + O_2 (1 atm)	TBAB(1.0) + NaOAc (3.0) + PivOH (2.0)	DMAc	12	48
19	$PdCl_2$	$Cu(OAc)_2{\cdot}CuCl_2$ (20%) + O_2 (1 atm)	TBAB(1.0) + NaOAc (3.0) + PivOH (2.0)	DMAc	12	36

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), oxidant, additive, and solvent (2 mL) for 12 h. [b]Yield of isolated product. [c]n.r. = no reaction.

catalytic cycle in our designed route. Thus, we first paid more attention to the oxidants. Among the commonly used oxidants such as $Cu(OAc)_2$, $PhI(OAc)_2$, BQ, Ag_2CO_3, $CuCl_2$, and $Cu(OAc)_2{\cdot}CuCl_2$, $Cu(OAc)_2{\cdot}CuCl_2$ gave a better result. Then some additives were selected, and we found that pivalic acid (PivOH) and tetrabutylammonium bromide (TBAB) used as additives drastically imporved the yield of the product (entry 12). To our delight, a buffer system gave a better result, and a 50% yield was obtained (entry 13). When $Cu(OAc)_2{\cdot}CuCl_2$ was used as a cocatalyst and oxygen was used as the terminal oxidant, a similar result was observed (entry 14). After extensive screening of different parameters (see Table 1), the optimum reaction conditions were determined: $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2.CuCl_2$ (20 mol %), TBAB (1.0 equiv), PivOH (2.0 equiv), NaOAc (3.0 equiv), DMAc, O_2 (1 atm), 90 °C, 12 h, under which the highest yield (68%) was achieved (Table 1, entry 16).

With the optimized catalytic system in hand, we explored its scope in the tandem cyclization/C−H functionalization by employing differently substituted aminoalkynes **1** (Scheme 2). Several useful functional groups were tolerated, including chloro, bromo, fluoro, nitro, ether, and alkyl substituents. An electron-withdrawing substituent favored product formation, whereas an electron-donating group slightly hindered the reaction. When a naphthyl was embedded in the aminoalkyne, an 82% yield was obtained. When *N*-ethyl-*N*-methyl-2-(phenylethynyl)aniline was subjected to the reaction, a mixture of products (5:2) was observed with *N*-ethylindole as the major product, which meant the small group in aminoalkynes was easier to lose in the first cyclization step (see the mechanism). To our disappointment, when a substrate with an ortho-substituted group (R^2 = Cl) was used in the reaction, no product was observed because of the steric effect. When cyclohexenyl-substituted aminoalkyne **1n** was introduced into the reaction system, no reaction occurred.

The catalytic system was not restricted to the use of tolane **2a** but also allowed for efficient annulation of aryl-, alkyl-, or hydroxyl-substituted alkynes **2** (Scheme 3). Importantly, the annulation process occurred with high regioselectivity when using unsymmetrically alkyl or hydroxyl-substituted alkynes **2**. For instance, prop-1-ynylbenzene was reactive when subjected to the standard reaction conditions, and the structure of **3o** was determined by X-ray crystallographic analysis (see the Supporting Information). Importantly, unprotected propargyl alcohols were also tolerated, and a synthetically useful yield was obtained. However, a moderate regioselectivity was observed when two electronically distinct aryl groups were introduced into the alkynes **2** with low ratios of inseparable regioisomers.[5]

Given the good activity of the tandem cyclization/C−H functionalization, we became interested in understanding its mode of reaction. Thus, intramolecular competition experiments with meta-substituted substrates were conducted, but a poor regioselectivity was observed (Scheme 4). This means the steric effect is not obvious in the C−H functionalization step. Then, intermolecular competition experiments revealed the electron-deficient arylalkyne to be annulated preferentially as well as the electron-deficient aminoalkyne. These observations indicated that electron-deficient alkynes preferred to go through the tandem cyclization/C−H functionalization sequence in our reaction system (Scheme 5).

To gain additional insight into the mechanism, we synthesized the substrate **1q**. When **1q** was subjected to the reaction system, we found that the pyrrolidine ring of **1q** was opened and a pivalate ester was obtained (Scheme 6). According to the above observations, a plausible mechanism for the reaction of **1** with alkyne **2** is illustrated in Scheme 7. A sequence of events first involves the coordination of alkyne to

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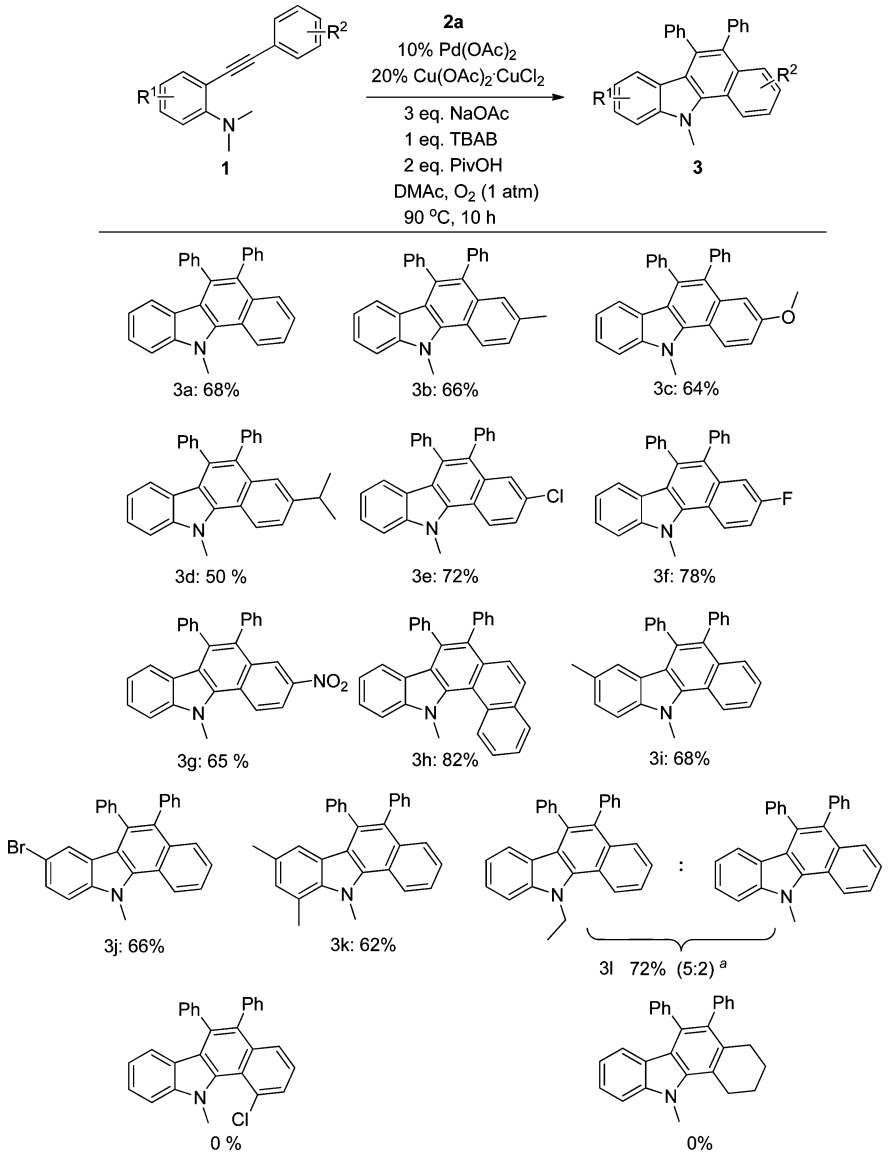
Scheme 2. Yields for the Isolated Products



[a]The ratio of the regioisomers was determined by ^{1}H NMR spectroscopy.

the Pd^{II} species. An anti addition of the tethered *N*,*N*-dimethylaniline to the triple bond through a formal 5-endodig mode affords intermediate **A**. Then the anion PivO attacks intermediate **A** to yield Pd^{II} intermediate **B**, which appears to be the key process for the cycloaromatization, and releases the compound PivOMe. The resulting intermediate **B** subsequently inserts into the less hindered alkyne C_{sp} center of alkyne **2** to produce vinylic palladium(II) intermediate **C**, which may illustrate the observed regioselectivity of the reaction.[3b,g] The formed vinylic palladium(II) intermediate **C** is suitable for base-promoted aromatic palladation[6] and subsequent proton abstraction to afford the seven-membered palladacycle **D**. Subsequent reductive elimination generates the cyclic product as well as a Pd^0 complex that can be reoxidized to the Pd^{II} species by copper salt and O_2 for the next catalytic cycle.

In summary, we have developed a palladium-catalyzed tandem cyclization/C−H functionalization of two different alkynes to synthesize polycyclic functionalized indoles. Molecular oxygen was used as the terminal oxidant in this process, rendering the reaction more sustainable. A range of internal alkynes bearing synthetically useful functional groups were tolerated. The highly selective conversion of alkyl-substituted alkynes is a strong testament to the beneficial features of this transformation. To the best of our knowledge, this study presents the first example in which the C−H functionalization and the Cacchi indole synthesis were combined and realized under oxidative conditions. Further applications of palladium-catalyzed oxidative C−H bond functionalization are ongoing in our laboratory.

■ EXPERIMENTAL SECTION

Column chromatography was carried out on silica gel. Unless noted, ^{1}H NMR spectra were recorded at 400 or 300 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded at 100 or 75 MHz in $CDCl_3$. IR spectra were recorded on an FT-IR spectrometer, and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high resolution mass spectra); high resolution mass spectrometry (HRMS) spectra was obtained on a

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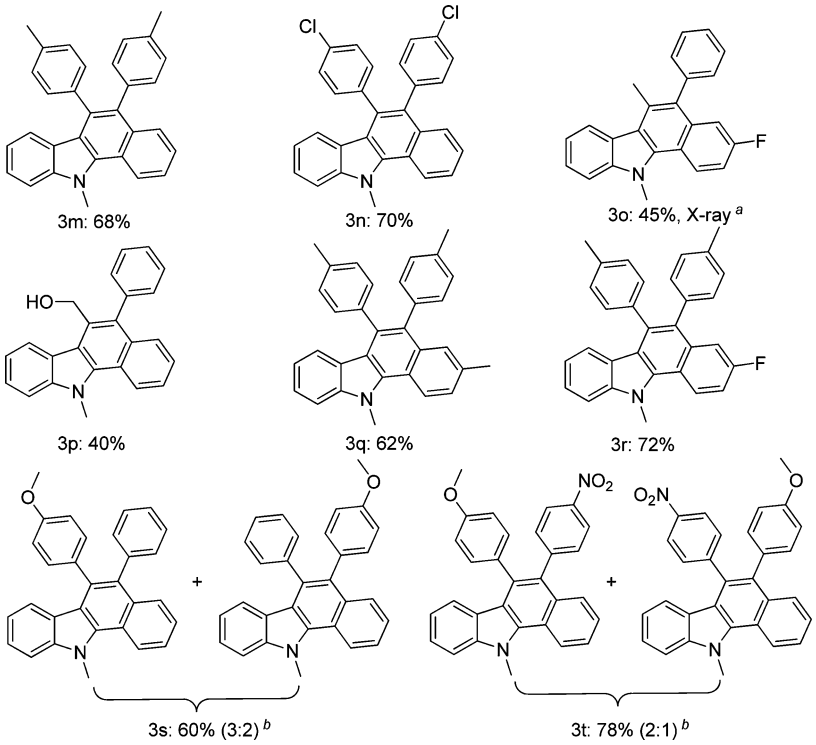
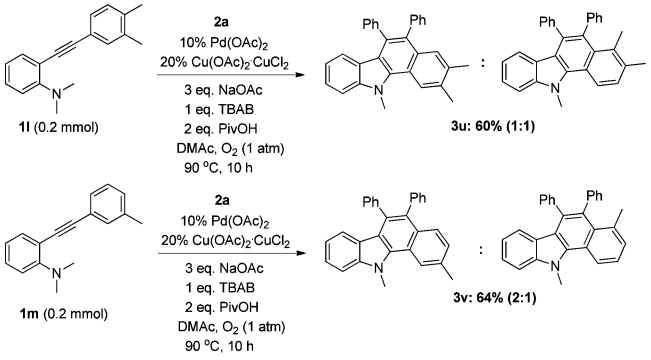
Scheme 3. Scope of Palladium-Catalyzed Cycloaromatization

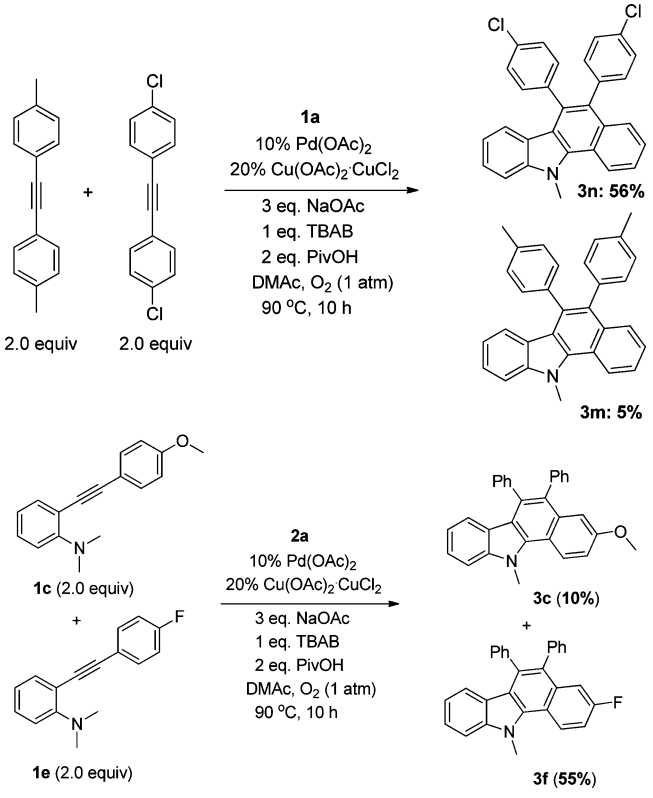


[a]The structure was determined by X-ray crystallographic analysis. [b]The ratio of the regioisomers was determined by ^{1}H NMR spectroscopy.[5].

Scheme 4. Intramolecular Competition Experiments with Meta-Substituted Aminoalkynes

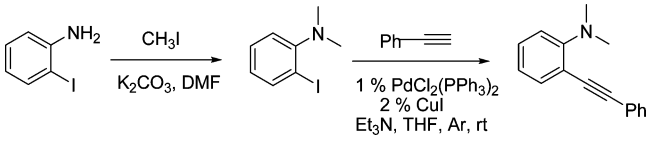


Scheme 5. Intermolecular Competition Experiments



Q-TOF instrument equipped with an ESI/APCI source; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

General Procedure for the Synthesis of Aminoalkynes 1. To a mixture of 2-iodoaniline (2.19 g, 10 mmol) and K_2CO_3 (2.0 equiv



2.76 g) in DMF was added CH_3I (3.0 equiv 4.26 g) dropwise. The reaction was stirred at room temperature overnight. Water was added to the mixture and extracted with ethyl acetate twice. The combined organic phase was washed with brine and dried over Na_2SO_4. The concentrated residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent (100:1) to get the product (2.22 g, 90%).

To a mixture of 2-iodo-*N*,*N*-dimethylaniline (2.22 g, 9.0 mmol), $PdCl_2(PPh_3)_2$ (63 mg, 1 mol %), and CuI (34 mg, 2 mol %) in THF (20 mL) were added ethynylbenzene (1.2 equiv, 1.1 g) and triethylamine (8.0 equiv, 0.73 g) under nitrogen atmosphere. The

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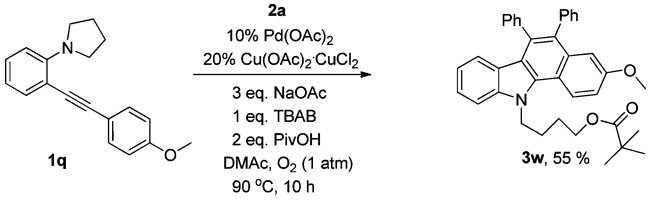
Scheme 6. Ring-Opening Reaction



reaction was performed at room temperature for 4−16 h and monitored by TLC analysis until the starting material was consumed. Saturated NH_4Cl solution was added to the mixture and extracted with ethyl acetate twice. The combined organic phase was washed with brine and dried over Na_2SO_4. The concentrated residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate as eluent (50:1) to get the product (1.89 g, 95%).

Characterization Data of Compound 1. *N,N-Dimethyl-2-(phenylethynyl)aniline* ***1a.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.54 (m, 3 H), 7.29−7.35 (m, 3 H), 7.22−7.26 (m, 1 H), 6.86−6.92 (m, 2 H), 2.99 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.7, 134.3, 131.2, 129.2, 128.2, 127.9, 123.8, 120.4, 116.9, 115.0, 94.7, 88.9, 43.4.

N,N-Dimethyl-2-(p-tolylethynyl)aniline ***1b.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.49 (m, 1 H), 7.42−7.44 (m, 2 H), 7.21−7.25 (m, 1 H), 7.13−7.15 (m, 2 H), 6.86−6.92 (m, 2 H), 2.99 (s, 6 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.6, 138.0, 134.2, 131.1, 129.0, 120.8, 120.4, 116.9, 115.3, 94.9, 88.1, 43.4, 21.5.

2-((4-Methoxyphenyl)ethynyl)-N,N-dimethylaniline ***1c.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.48 (m, 3 H), 7.20−7.25 (m, 1 H), 6.86−6.93 (m, 4 H), 3.81 (s, 3 H), 2.99 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.4, 154.5, 134.1, 132.7, 128.9, 120.5, 116.9, 116.0, 115.5, 113.9, 94.7, 87.4, 55.2, 43.5.

2-((4-Chlorophenyl)ethynyl)-N,N-dimethylaniline ***1d.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.48 (m, 3 H), 7.29−7.32 (m, 2 H), 7.23−7.26 (m, 1 H), 6.87−6.93 (m, 2 H), 2.99 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.8, 134.3, 133.9, 132.4, 129.5, 128.6, 122.4, 120.5, 116.9, 114.7, 93.5, 89.9, 43.5.

2-((4-Fluorophenyl)ethynyl)-N,N-dimethylaniline ***1e.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.52 (m, 3 H), 7.22−7.26 (m, 1 H), 7.01−7.05 (m, 2 H), 6.87−6.93 (m, 2 H), 2.99 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 161.1, 154.7, 134.2, 133.1, 133.0, 129.3, 120.5, 119.9, 116.9, 115.6, 115.4, 114.9, 93.5, 88.5, 43.5. HRMS (ESI) m/z: calcd for $C_{16}H_{14}NF$: M + H = 240.1183; found: 240.1179.

N,N-Dimethyl-2-((4-nitrophenyl)ethynyl)aniline ***1f.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19−8.22 (m, 2 H), 7.63−7.66 (m, 2 H), 7.48−7.51 (m, 1 H), 7.26−7.32 (m, 1 H), 6.89−6.95 (m, 2 H), 3.01 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.2, 146.7, 134.6, 131.7, 130.9, 130.3, 123.6, 120.4, 117.0, 113.5, 94.7, 92.8, 43.5.

N,N-Dimethyl-2-(naphthalen-1-ylethynyl)aniline ***1g.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, J = 7.6 Hz, 1 H), 7.81−7.87 (m, 2 H), 7.76−7.78 (m, 1 H), 7.57−7.63 (m, 2 H), 7.51−7.55 (m, 1 H), 7.44−7.48 (m, 1 H), 7.27−7.31 (m, 1 H), 6.93−6.99 (m, 2 H), 3.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.9, 134.4, 133.3, 130.0, 129.4, 128.5, 128.3, 126.7, 126.5, 126.4, 125.4, 121.7, 120.7, 117.2, 115.6, 93.9, 92.9, 43.8. HRMS (ESI) m/z: calcd for $C_{20}H_{17}N$: M + H = 272.1434; found: 272.1430.

N,N,4-Trimethyl-2-(phenylethynyl)aniline ***1h.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.54 (m, 2 H), 7.31−7.35 (m, 4 H), 7.04−7.06 (m, 1 H), 6.81−6.84 (m, 1 H), 2.95 (s, 3 H), 2.94 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.5, 134.5, 131.2, 129.9, 128.2, 127.9, 123.9, 116.9, 115.2, 94.4, 88.9, 43.7, 20.2.

4-Bromo-N,N-dimethyl-2-(phenylethynyl)aniline ***1i.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.53 (m, 2 H), 7.45 (s, 1 H), 7.32−7.37 (m, 3 H), 7.16−7.19 (m, 1 H), 6.81−6.83 (m, 1 H), 2.97 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 153.3, 133.5, 131.3, 129.0, 128.3, 125.0, 123.3, 118.1, 116.4, 95.6, 87.6, 43.4.

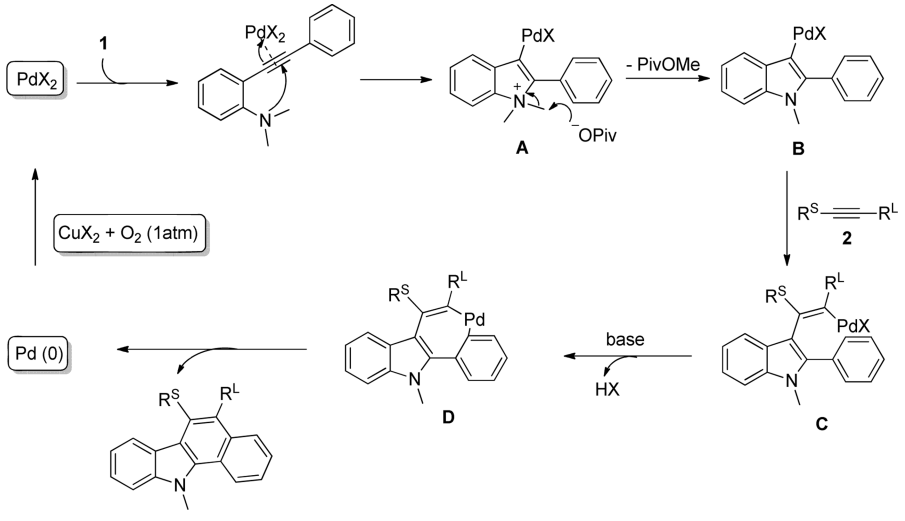
N,N,2,4-Tetramethyl-6-(phenylethynyl)aniline ***1j.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.53 (m, 2 H), 7.29−7.35 (m, 3 H), 7.13 (s, 1 H), 6.96 (s, 1 H), 2.94 (s, 6 H), 2.27 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 150.6, 136.8, 133.8, 132.3, 132.0, 131.0, 128.3, 127.9, 123.9, 120.5, 93.3, 88.9, 43.1, 20.5, 18.4; HRMS (ESI) m/z: calcd for $C_{18}H_{19}N$: M + H = 250.1590; found: 250.1593.

N-Ethyl-N-methyl-2-(phenylethynyl)aniline ***1k.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.54 (m, 3 H), 7.29−7.36 (m, 3 H), 7.21−7.25 (m, 1 H), 6.85−6.93 (m, 2 H), 3.42 (dd, J = 14.0, 7.2 Hz, 2 H), 2.87 (s, 3 H), 1.23 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 134.4, 131.3, 129.1, 128.3, 127.9, 123.9, 120.2, 117.6, 115.2, 94.2, 88.9, 50.4, 38.7, 12.9.

2-((3,4-Dimethylphenyl)ethynyl)-N,N-dimethylaniline ***1l.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.47 (m, 1 H), 7.31 (s, 1 H), 7.26−7.28 (m, 1 H), 7.19−7.23 (m, 1 H), 7.07−7.09 (m, 1 H), 6.85−6.90 (m, 2 H), 2.98 (s, 6 H), 2.24 (s, 3 H), 2.23 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.5, 136.8, 136.5, 134.1, 132.2, 129.5, 128.9, 128.7, 121.1, 120.4, 116.8, 115.3, 95.0, 87.9, 43.4, 19.7, 19.5; HRMS (ESI) m/z: calcd for $C_{18}H_{19}N$: M + H = 250.1590; found: 250.1586.

N,N-Dimethyl-2-(m-tolylethynyl)aniline ***1m.*** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.49 (m, 1 H), 7.33−7.35 (m, 2 H), 7.19−7.25 (m, 2 H), 7.10−7.12 (m, 1 H), 6.86−6.92 (m, 2 H), 2.99 (s, 6 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.7, 137.9, 134.2, 131.8, 129.1, 128.8, 128.3, 128.1, 123.6, 120.4, 116.8, 115.1, 94.8, 88.5, 43.4, 21.2; HRMS (ESI) m/z: calcd for $C_{17}H_{17}N$: M + H = 236.1434; found: 236.1436.

Scheme 7. Proposed Mechanism



2-(Cyclohex-1-en-1-ylethynyl)-N,N-dimethylaniline ***1n***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.38 (m, 1 H), 7.16−7.24 (m, 1 H), 6.82−6.88 (m, 2 H), 6.18−6.19 (m, 1 H), 2.93 (s, 6 H), 2.23−2.25 (m, 2 H), 2.12−2.16 (m, 2 H), 1.58−1.70 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.4, 134.2, 134.0, 128.6, 121.1, 120.4, 116.8, 115.7, 96.6, 86.0, 43.4, 29.1, 25.7, 22.3, 21.5.

2-((2-Chlorophenyl)ethynyl)-N,N-dimethylaniline ***1o***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.57 (m, 2 H), 7.39−7.42 (m, 1 H), 7.21−7.28 (m, 3 H), 6.87−6.93 (m, 2 H), 3.01 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.7, 135.5, 134.7, 133.1, 129.6, 129.2, 128.9, 126.3, 120.3, 116.9, 114.5, 94.0, 91.4, 43.6. HRMS (ESI) *m/z*: calcd for $C_{16}H_{14}NCl$: M + H = 256.0888; found: 256.0886.

2-((4-Isopropylphenyl)ethynyl)-N,N-dimethylaniline ***1p***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.48 (m, 3 H), 7.18−7.24 (m, 3 H), 6.85−6.91 (m, 2 H), 2.98 (s, 6 H), 2.86−2.93 (m, 1 H), 1.23−1.25 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.6, 148.9, 134.2, 131.2, 129.0, 126.4, 121.2, 120.4, 116.8, 115.3, 94.9, 88.1, 43.4, 34.0, 23.8; IR(neat, cm^{-1}): 2959, 2868, 2785, 1591, 1491, 1453, 1429, 1330, 1051, 948, 833, 752; HRMS (APCI) *m/z*: calcd for $C_{19}H_{22}N$: M + H = 264.1747; found: 264.1748.

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)pyrrolidine ***1q***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.42 (m, 3 H), 7.13−7.17 (m, 1 H), 6.84−6.87 (m, 2 H), 6.66−6.69 (m, 2 H), 3.80 (s, 3 H), 3.59−3.62 (m, 4 H), 1.93−1.96 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 150.2, 135.0, 132.2, 128.9, 116.9, 116.5, 113.9, 109.2, 92.2, 89.5, 55.3, 55.2, 50.4, 25.7; IR (neat, cm^{-1}): 2919, 2849, 1598, 1443, 1382, 1247, 1029, 831, 748; HRMS (APCI) *m/z*: calcd for $C_{19}H_{20}NO$: M + H = 278.1539; found: 278.1550.

Typical Procedure for the Synthesis of Product 3. To a solution of *N,N*-dimethyl-2-(phenylethynyl)aniline (44.2 mg, 0.200 mmol) and diphenylethyne (53.4 mg, 0.300 mmol) in DMAc (2 mL) were added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}CuCl_2$ (12.7 mg, 0.04 mmol), NaOAc (49.2 mg, 0.60 mmol), TBAB (64.4 mg, 0.20 mmol), and PivOH (44.8 mg, 0.40 mmol). The reaction mixture was then stirred for 12 h at 90 °C under O_2 atmosphere. The resulting mixture was quenched with water and extracted twice with EtOAc. The combined organic extracts were washed with water and brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by flash column chromatography using petroleum ether/ethyl acetate as eluent (30:1) afforded **3a** in 68% yield (52 mg) as a yellow solid.

Characterization Data of Compound 3. 11-Methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3a** (68%, 52 mg), mp = 222−224 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.4 Hz, 1 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 7.48−7.52 (m, 1 H), 7.43−7.45 (m, 1 H), 7.28−7.36 (m, 2 H), 7.10−7.21 (m, 10 H), 6.83−6.94 (m, 1 H), 6.56−6.58 (m, 1 H), 4.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 140.2, 139.6, 135.1, 134.9, 132.7, 131.8, 131.0, 130.2, 128.3, 127.9, 127.7, 127.5, 126.7, 126.2, 124.8, 124.7, 124.4, 123.1, 122.1, 121.9, 119.2, 117.7, 108.7, 34.4; IR (neat, cm^{-1}): 2920, 1597, 1430, 1383, 1069, 1025, 771; HRMS (APCI) *m/z*: calcd for $C_{29}H_{21}N$: M + H = 384.1747; found: 384.1762.

3,11-Dimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3b** (66%, 53 mg), mp > 200 °C, decomp; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.4 Hz, 1 H), 7.47−7.50 (m, 2 H), 7.34−7.42 (m, 2 H), 7.18−7.28 (m, 10 H), 6.89−6.93 (m, 1 H), 6.62−6.64 (m, 1 H), 4.41 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.1, 140.4, 139.7, 135.2, 134.9, 134.5, 132.9, 131.9, 130.5, 130.2, 127.9, 127.5, 126.7, 126.6, 126.1, 124.1, 123.2, 122.0, 121.8, 119.9, 119.2, 117.1, 108.6, 34.3, 21.8; IR (neat, cm^{-1}): 2919, 1589, 1430, 1384, 1068, 1021, 771; HRMS (APCI) *m/z*: calcd for $C_{30}H_{23}N$: M + H = 398.1903; found: 398.1909.

3-Methoxy-11-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3c** (64%, 53 mg), mp = 232−234 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69−8.72 (m, 1 H), 7.47−7.49 (m, 1 H), 7.33−7.37 (m, 1 H), 7.17−7.28 (m, 11 H), 7.05 (s, 1 H), 6.89−6.93 (m, 1 H), 6.61−6.63 (m, 1 H), 4.39 (s, 3 H), 3.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.7, 140.9, 140.4, 139.7, 135.5, 135.4, 134.4, 131.7, 130.2, 130.1, 127.9, 127.6, 126.7, 126.2, 123.9, 123.7, 123.3, 121.6, 119.2, 116.9, 116.3, 115.9, 108.6, 108.1, 55.0, 34.2; IR (neat, cm^{-1}): 2920, 1605, 1457, 1383, 1026, 755, 700; HRMS (APCI) *m/z*: calcd for $C_{30}H_{23}NO$: M + H = 414.1852; found: 414.1863.

3-Isopropyl-11-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3d** (50%, 42 mg), mp = 202−204 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75−8.77 (m, 1 H), 7.49−7.52 (m, 3 H), 7.34−7.38 (m, 1 H), 7.16−7.28 (m, 10 H), 6.89−6.93 (m, 1 H), 6.63−6.65 (m, 1 H), 4.43 (s, 3 H), 2.92−2.99 (m, 1 H), 1.23−1.25 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.3, 141.1, 140.4, 139.7, 135.3, 134.9, 133.0, 131.9, 130.9, 130.8, 130.2, 128.8, 127.9, 127.4, 126.6, 126.1, 125.2, 124.1, 123.9, 123.3, 122.2, 121.9, 120.4, 119.1, 117.2, 108.6, 34.3, 23.9; IR (neat, cm^{-1}): 2966, 2923, 1618, 1465, 1381, 1068, 1026, 741, 705; HRMS (APCI) *m/z*: calcd for $C_{32}H_{28}N$: M + H = 426.2216; found: 426.2223.

3-Chloro-11-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3e** (72%, 60 mg), mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66−8.68 (m, 1 H), 7.66 (s, 1 H), 7.48−7.51 (m, 2 H), 7.36−7.40 (m, 1 H), 7.13−7.29 (m, 10 H), 6.91−6.95 (m, 1 H), 6.62−6.64 (m, 1 H), 4.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 139.9, 138.8, 136.1, 134.8, 133.7, 131.7, 130.7, 130.3, 130.0, 127.9, 127.7, 127.1, 126.9, 126.5, 125.2, 124.7, 123.6, 122.9, 122.0, 119.5, 117.9, 108.8, 34.3; IR (neat, cm^{-1}): 2921, 1600, 1384, 1068, 1026, 745, 704; HRMS (APCI) *m/z*: calcd for $C_{29}H_{20}NCl$: M + H = 418.1357; found: 418.1375.

3-Fluoro-11-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3f** (78%, 63 mg), mp = 228−230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69−8.73 (m, 1 H), 7.46−7.48 (m, 1 H), 7.14−7.38 (m, 13 H), 6.91−6.94 (m, 1 H), 6.63−6.65 (m, 1 H), 4.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.1, 158.7, 141.0, 139.9, 139.0, 136.0, 135.1, 134.4, 134.3, 131.6, 130.5, 130.4, 130.0, 127.9, 127.7, 126.9, 126.5, 124.4, 124.3, 124.2, 123.0, 121.9, 119.4, 118.8, 117.2, 114.3, 114.1, 112.2, 112.0, 108.7, 34.2; IR (neat, cm^{-1}): 3056, 1623, 1446, 755, 721, 700; HRMS (APCI) *m/z*: calcd for $C_{29}H_{20}NF$: M + H = 402.1653; found: 402.1659.

11-Methyl-3-nitro-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3g** (65%, 56 mg), mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92−8.94 (m, 1 H), 8.67 (s, 1 H), 8.35−8.38 (m, 1 H), 7.50−7.60 (m, 1 H), 7.46−7.48 (m, 1 H), 7.18−7.33 (m, 10 H), 6.97−7.01 (m, 1 H), 6.68−6.69 (m, 1 H), 4.51 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.1, 141.9, 139.2, 137.8, 137.0, 134.3, 132.7, 131.6, 129.8, 128.1, 127.8, 127.2, 127.0, 125.9, 124.8, 124.2, 123.2, 122.6, 120.9, 119.9, 118.1, 109.1, 34.4; IR (neat, cm^{-1}): 2921, 1600, 1383, 1337, 1068, 1025, 770; HRMS (APCI) *m/z*: calcd for $C_{29}H_{20}N_2O_2$: M + H = 429.1598; found: 429.1614.

13-Methyl-7,8-diphenyl-13*H*-naphtho[1,2-a]carbazole **3h** (82%, 71 mg), mp = 214−216 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75−8.77 (m, 1 H), 7.93−7.95 (m, 1 H), 7.68−7.70 (m, 2 H), 7.58−7.63 (m, 3 H), 7.42−7.46 (m, 1 H), 7.22−7.29 (m, 10 H), 6.98−6.99 (m, 1 H), 6.74−6.76 (m, 1 H), 3.86 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.0, 139.9, 139.4, 139.2, 135.2, 132.2, 131.8, 130.8, 130.2, 128.4, 128.1, 127.9, 127.5, 126.8, 126.3, 126.1, 125.9, 125.8, 125.4, 125.3, 124.8, 122.2, 122.1, 120.2, 117.2, 110.8, 37.9; IR (neat, cm^{-1}): 2922, 1597, 1463, 1382, 1069, 1023, 754; HRMS (APCI) *m/z*: calcd for $C_{33}H_{23}N$: M + H = 434.1903; found: 434.1911.

8,11-Dimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3i** (68%, 54 mg), mp = 186−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.53−7.57 (m, 1 H), 7.36−7.41 (m, 2 H), 7.16−7.28 (m, 11 H), 6.38 (s, 1 H), 4.37 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.3, 139.6, 135.2, 134.9, 132.6, 131.8, 130.6, 130.2, 128.3, 127.8, 127.5, 126.6, 126.2, 125.8, 124.7, 124.6, 123.2, 122.0, 121.9, 117.5, 108.4, 34.4, 21.5; IR (neat, cm^{-1}): 2920, 1599, 1447, 1068, 1025, 796, 756, 698; HRMS (APCI) *m/z*: calcd for $C_{30}H_{23}N$: M + H = 398.1903; found: 398.1919.

8-Bromo-11-methyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3j** (66%, 60 mg), mp = 184−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.54−7.58 (m, 1 H), 7.39−7.44 (m, 1 H), 7.32−7.34 (m, 1 H), 7.15−7.28 (m, 11 H), 6.50 (s, 1 H), 4.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.6, 139.4, 139.3, 135.6, 134.6, 132.9, 131.7, 131.3, 129.9, 128.4, 128.1, 127.5, 127.0, 126.3, 125.2, 124.9, 124.6, 124.4, 124.0, 122.0, 121.8, 121.5, 116.9, 109.7, 34.4; IR (neat, cm^{-1}): 2920, 1427, 1382, 1067, 1025, 759, 701; HRMS (APCI) *m/z*: calcd for $C_{29}H_{20}NBr$: M + H = 462.0852; found: 462.0860.

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8,10,11-Trimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole **3k** (62%, 51 mg), mp = 239−240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, J = 8.4 Hz, 1 H), 7.68 (d, J = 8.4 Hz, 1 H), 7.55−7.59 (m, 1 H), 7.39−7.43 (m, 1 H), 7.18−7.28 (m, 11 H), 6.94 (s, 1 H), 6.21 (s, 1 H), 4.45 (s, 3 H), 2.84 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.4, 140.3, 139.6, 138.4, 134.7, 132.7, 131.8, 131.4, 130.2, 129.2128.9, 128.3, 127.8, 127.4, 126.6, 126.2, 125.1, 124.7, 124.4, 122.8, 121.6, 120.7, 119.8, 118.6, 38.6, 21.2, 20.5; IR (neat, cm^{-1}): 2921, 1598, 1448, 1383, 1102, 1070, 1025, 759, 700; HRMS (APCI) m/z: calcd for $C_{31}H_{25}N$: M + H = 412.2060; found: 412.2072.

3l (mixture, total yield: 72%, 56 mg) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (d, J = 9.0 Hz, 0.4 H), 8.64 (d, J = 9.0 Hz, 1 H), 7.64−7.73 (m, 1.4 H), 7.45−7.62 (m, 3.6 H), 7.42−7.43 (m, 3.7 H), 7.09−7.40 (m, 16.6 H), 6.90−6.95 (m, 2 H), 6.63−6.67 (m, 2 H), 4.88−4.95 (m, 2 H), 4.45 (s, 1.3 H), 1.75 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.4, 140.3, 139.6, 134.9, 133.9, 132.7, 131.8, 130.9, 130.2, 128.5, 128.3, 127.9, 127.4, 126.7, 126.2, 125.0, 124.8, 124.7, 124.4, 123.2, 122.0, 121.9, 121.8, 121.4, 119.3, 117.9, 108.7, 108.5, 40.8, 34.4, 15.1; IR (neat, cm^{-1}): 2921, 1600, 1441, 1382, 1069, 1026, 768, 700; HRMS (APCI) m/z: calcd for $C_{30}H_{23}N$: M + H = 398.1903; found: 398.1908; calcd for $C_{29}H_{21}N$: M + H = 384.1747; found: 384.1752.

11-Methyl-5,6-di-*p*-tolyl-11*H*-benzo[*a*]carbazole **3m** (68%, 56 mg), mp = 182−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 8.4 Hz, 1 H), 7.69 (d, J = 8.4 Hz, 1 H), 7.49−7.58 (m, 2 H), 7.35−7.42 (m, 2 H), 7.04−7.14 (m, 8 H), 6.91−6.95 (m, 1 H), 6.67−6.69 (m, 1 H), 4.42 (s, 3 H), 2.36 (s, 3 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 137.3, 136.6, 136.0, 135.5, 135.0, 134.9, 133.0, 131.6, 131.1, 129.9, 128.7, 128.4, 128.2, 124.7, 124.6, 124.3, 123.2, 122.1, 122.0, 121.9, 119.1, 118.0, 108.7, 34.4, 21.4, 21.2; IR (neat, cm^{-1}): 2919, 1599, 1460, 1429, 1383, 1068, 1025, 757; HRMS (APCI) m/z: calcd for $C_{31}H_{25}N$: M + H = 412.2060; found: 412.2075.

5,6-Bis(4-chlorophenyl)-11-methyl-11*H*-benzo[*a*]carbazole **3n** (70%, 63 mg), mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J = 8.4 Hz, 1 H), 7.56−7.62 (m, 2 H), 7.49−7.51 (m, 1 H), 7.37−7.44 (m, 2 H), 7.24−7.26 (m, 2 H), 7.19−7.22 (m, 2 H), 7.08−7.10 (m, 2 H), 7.03−7.05 (m, 2 H), 6.95−6.99 (m, 1 H), 6.68−6.70 (m, 1 H), 4.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.1, 138.4, 137.8, 135.2, 133.6, 132.9, 132.4, 131.5, 129.7, 128.4, 127.9, 125.1, 125.0, 124.6, 122.8, 122.2, 121.9, 121.7, 119.5, 117.3, 108.9, 34.3; IR (neat, cm^{-1}): 2923, 1489, 1090, 1017, 760; HRMS (APCI) m/z: calcd for $C_{29}H_{19}NCl_2$: M + H = 452.0967; found: 452.0986.

3-Fluoro-6,11-dimethyl-5-phenyl-11*H*-benzo[*a*]carbazole **3o** (45%, 30 mg), mp = 174−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70−8.74 (m, 1 H), 8.33 (d, J = 8.0 Hz, 1 H), 7.59−7.61 (m, 1 H), 7.50−7.55 (m, 3 H), 7.45−7.49 (m, 1 H), 7.25−7.34 (m, 4 H), 7.15−7.19 (m, 1 H), 4.41 (s, 3 H), 2.74 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.0, 140.1, 135.2, 131.2, 128.5, 127.1, 124.2, 124.1, 123.7, 122.4, 119.7, 117.9, 113.5, 113.3, 111.9, 111.6, 108.9, 34.4, 19.2; IR (neat, cm^{-1}): 2921, 1598, 1467, 1450, 1102, 1068, 1029, 769; HRMS (APCI) m/z: calcd for $C_{24}H_{18}NF$: M + H = 340.1496; found: 340.1498.

(11-Methyl-5-phenyl-11*H*-benzo[*a*]carbazole-6-yl)methanol **3p** (40%, 27 mg), mp = 170−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 8.4 Hz, 1 H), 8.43−8.75 (m, 1 H), 7.48−7.62 (m, 7 H), 7.34−7.43 (m, 4 H), 5.05−5.06 (m, 2 H), 4.43 (s, 3 H), 1.69 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 139.3, 135.9, 132.7, 132.2, 131.1, 130.7, 128.7, 128.3, 127.3, 125.1, 124.8, 124.7, 122.5, 122.3, 122.2, 122.0, 120.1, 117.2, 109.1, 61.2, 34.4; IR (neat, cm^{-1}): 3394, 2922, 1599, 1466, 1382, 1025, 755, 700; HRMS (APCI) m/z: calcd for $C_{24}H_{19}NO$: M + H = 338.1539; found: 338.1548.

3,11-Dimethyl-5,6-di-*p*-tolyl-11*H*-benzo[*a*]carbazole **3q** (62%, 52 mg), mp = 218−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 8.8 Hz, 1 H), 7.47−7.49 (m, 2 H), 7.33−7.40 (m, 2 H), 7.04−7.13 (m, 8 H), 6.89−6.94 (m, 1 H), 6.64−6.66 (m, 1 H), 4.39 (s, 3 H), 2.41 (s, 3 H), 2.36 (s, 3 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.0, 137.5, 136.7, 135.9, 135.4, 135.2, 135.0, 134.3, 133.3, 131.6, 130.6, 129.9, 128.6, 128.2, 127.5, 126.5, 124.0, 123.4, 121.9, 119.9, 119.1, 117.4, 108.6, 34.3, 21.8, 21.4, 21.3; IR (neat, cm^{-1}): 2920, 1469, 1381, 1330, 1113, 1024, 814, 753; HRMS (APCI) m/z: calcd for $C_{32}H_{27}N$: M + H = 426.2216; found: 426.2223.

3-Fluoro-11-methyl-5,6-di-*p*-tolyl-11*H*-benzo[*a*]carbazole **3r** (72%, 61 mg), mp = 217−218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69−8.74 (m, 1 H), 7.47 (d, J = 8.0 Hz, 1 H), 7.27−7.38 (m, 3 H), 7.03−7.12 (m, 8 H), 6.92−6.95 (m, 1 H), 6.66 (d, J = 8.0 Hz, 1 H), 4.35 (s, 3 H), 2.36 (s, 3 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.1, 158.7, 141.0, 137.0, 136.2, 136.1, 135.8, 135.0, 134.7, 134.6, 131.4, 130.6, 130.5, 129.8, 128.7, 128.4, 124.3, 124.2, 123.2, 122.0, 119.4, 118.8, 117.5, 114.2, 113.9, 112.3, 112.1, 108.7, 34.3, 21.4, 21.2; IR (neat, cm^{-1}): 2920, 1619, 1448, 1384, 1067, 1017, 755; HRMS (APCI) m/z: calcd for $C_{31}H_{24}NF$: M + H = 430.1966; found: 430.1973.

5-(4-Methoxyphenyl)-11-methyl-6-phenyl-11*H*-benzo[*a*]carbazole with 6-(4-methoxyphenyl)-11-methyl-5-phenyl-11*H*-benzo[*a*]-carbazole (3:2) **3s** (total yield: 60%, 49 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 8.0 Hz, 1 H), 7.68−7.74 (m, 1 H), 7.55−7.59 (m, 1 H), 7.50−7.57 (m, 1 H), 7.40−7.44 (m, 2 H), 7.09−7.43 (m, 8 H), 6.92−6.97 (m, 1 H), 6.79−6.83 (m, 1 H), 6.75−6.77 (m, 1 H), 4.43 (s, 3 H), 3.79 (s, 1.8 H), 3.76 (m, 1.2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.2, 157.9, 141.2, 140.4, 139.8, 135.1, 134.5, 133.1, 132.8, 132.7, 132.6, 131.8, 131.4, 131.2, 130.6, 130.2, 128.3, 127.9, 127.5, 126.7, 126.1, 124.8, 124.7, 124.6, 124.4, 123.2, 123.1, 122.1, 121.9, 121.8, 119.2, 118.1, 113.3, 112.9, 108.7, 55.1, 34.4; IR (neat, cm^{-1}): 2919, 1604, 1509, 1243, 1028, 745, 701; HRMS (APCI) m/z: calcd for $C_{30}H_{23}NO$: M + H = 414.1852; found: 414.1856.

5-(4-Methoxyphenyl)-11-methyl-6-(4-nitrophenyl)-11*H*-benzo[*a*]-carbazole with 6-(4-methoxyphenyl)-11-methyl-5-(4-nitrophenyl)-11*H*-benzo[*a*]carbazole (2:1) **3t** (total yield: 78%, 71 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80−8.84 (m, 1 H), 8.06−8.13 (m, 2 H), 7.72−7.74 (m, 0.4 H), 7.59−7.65 (m, 1 H), 7.53−7.56 (m, 1.8 H), 7.43−7.48 (m, 2.2 H), 7.39−7.41 (m, 0.7 H), 7.28−7.36 (m, 1.5 H), 7.01−7.06 (m, 1.5 H), 6.93−6.99 (m, 1.9 H), 6.74−6.79 (m, 2.9 H), 6.59−6.61 (m, 0.4 H), 4.44 (s, 3 H), 3.80 (s, 2 H), 3.77 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.6, 158.2, 147.9, 147.6, 146.7, 146.3, 141.2, 141.1, 135.5, 134.7, 132.8, 132.7, 132.5, 131.7, 131.5, 131.3, 131.0, 130.7, 130.6, 128.9, 128.4, 127.4, 125.3, 125.2, 125.0, 124.7, 123.2, 123.0, 122.8, 122.4, 122.2, 121.9, 121.8, 121.3, 119.6, 119.5, 117.9, 113.6, 113.2, 109.1, 108.9, 55.1, 34.4; IR (neat, cm^{-1}): 2920, 1596, 1512, 1344, 1244, 1028, 744; HRMS (APCI) m/z: calcd for $C_{30}H_{22}N_2O_3$: M + H = 459.1703; found: 459.1720.

2,3,11-Trimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole with 3,4,11-trimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole (1:1) **3u** (total yield: 60%, 49 mg), mp = 216−218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54−8.57 (m, 1 H), 7.40−7.50 (m, 3 H), 7.06−7.37 (m, 10 H), 6.87−6.92 (m, 1 H), 6.63 (d, J = 8.0 Hz, 0.5 H), 6.46 (d, J = 8.0 Hz, 0.5 H), 4.42 (s, 1.5 H), 4.37 (s, 1.5 H), 2.52 (s, 1.5 H), 2.40 (s, 1.5 H), 2.32 (s, 1.5 H), 1.88 (s, 1.5 H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.4, 141.7, 141.1, 140.9, 140.5, 139.8, 136.5, 135.9, 135.0, 134.8, 134.6, 134.4, 134.1, 134.0, 132.5, 131.9, 131.8, 131.6, 130.4, 130.3, 130.2, 127.9, 127.8, 127.7, 127.5, 127.4, 126.8, 126.6, 126.4, 126.1, 125.4, 124.2, 124.0, 123.3, 123.2, 122.0, 121.9, 121.8, 121.7, 120.6, 120.0, 119.3, 119.0, 117.2, 116.9, 108.8, 108.6, 34.8, 34.3, 21.6, 20.7, 20.3; IR (neat, cm^{-1}): 2919, 2858, 1600, 1446, 1383, 1069, 1025, 753, 701; HRMS (APCI) m/z: calcd for $C_{31}H_{25}N$: M + H = 412.2060; found: 412.2066.

2,11-Dimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole with 4,11-dimethyl-5,6-diphenyl-11*H*-benzo[*a*]carbazole (2:1) **3v** (total yield: 64%, 50 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72−8.74 (m, 0.5 H), 8.58 (s, 1 H), 7.36−7.61 (m, 5 H), 7.09−7.31 (17.5 H), 6.88−6.94 (m, 1.7 H), 6.65 (d, J = 8.0 Hz, 1 H), 6.44 (d, J = 8.0 Hz, 0.5 H), 4.47 (s, 3 H), 4.43 (s, 1.5 H), 2.63 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 140.3, 139.7, 137.1, 134.8, 134.3, 133.9, 132.1, 131.8, 131.2, 130.9, 130.3, 128.2, 127.9, 127.7, 127.4, 126.8, 126.7, 126.4, 126.2, 125.9, 124.5, 124.3, 123.2, 123.1, 122.1, 121.9, 121.4, 121.1, 119.3, 119.1, 117.8, 108.9, 108.7, 34.5, 22.2; IR (neat, cm^{-1}): 2919, 1598, 1437, 1384, 1068, 1025, 758, 700; HRMS (APCI) m/z: calcd for $C_{30}H_{23}N$: M + H = 398.1903; found: 398.1908.

4-(3-Methoxy-5,6-diphenyl-11*H*-benzo[*a*]carbazol-11-yl)butyl pivalate **3w** (55%, 61 mg), mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47−8.49 (m, 1 H), 7.48−7.51 (m, 1 H), 7.33−7.36 (m, 1 H), 7.18−7.29 (m, 11 H), 7.06 (s, 1 H), 6.89−6.93 (m, 1 H), 6.58−6.60 (m, 1 H), 4.83−4.87 (m, 2 H), 4.18−4.21 (m, 2 H), 3.70 (s, 3 H), 2.19−2.27

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(m, 2 H), 1.87−1.94 (m, 2 H), 1.18 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.6, 140.6, 140.4, 139.7, 135.6, 134.5, 134.4, 131.7, 130.6, 130.4, 130.1, 127.9, 127.6, 126.7, 126.3, 124.1, 123.4, 123.1, 121.8, 119.3, 116.7, 116.4, 116.2, 114.0, 108.6, 63.7, 55.1, 45.6, 38.7, 27.2, 26.6, 26.3; IR(neat, cm^{-1}): 2962, 2932, 1727, 1617, 1461, 1377, 1283, 1221, 1155, 1031, 743, 716; HRMS (APCI) *m*/*z*: calcd for $C_{38}H_{37}NO_3$: M + H = 556.2852; found: 556.2859.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Representative experimental procedures, X-ray crystallographic data of **3a** and **3o**, and ^{1}H NMR and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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