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# Gold-Catalyzed Sequential Alkyne Activation: One-Pot Synthesis of NH-Carbazoles via Cascade Hydroarylation of Alkyne/6-Endo-Dig Carbocyclization Reactions

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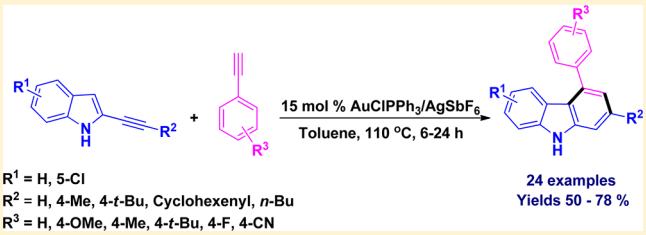
Supporting Information

**ABSTRACT:** A simple and efficient one-pot protocol for the synthesis of NH-carbazoles has been described. The strategy comprises a one-pot reaction involving the treatment of 2-alkynyl indoles with arylacetylenes in the presence of an Au–Ag combination catalyst. The salient feature of the strategy involves sequential activation of terminal and internal alkynes leading to the cascade hydroarylation of terminal alkynes and 6-endo-dig carbocyclization reactions. The generality of the method has been demonstrated by using a series of 2-alkynyl indoles and arylacetylenes.




In recent years, the gold-catalyzed reactions[1] involving the addition of a wide variety of nucleophiles (C/N/O) to a terminal or internal alkyne in an intramolecular or intermolecular format has offered opportunities for the development of new methodologies for the synthesis of N-heterocycles in a one-pot procedure. Nitrogen heterocycles are structural constituents of many natural products, medicinally important compounds,[2] and organic materials.[3] Among them, carbazoles are an important class of heteroaromatic compounds present in many bioactive natural products (carbazomycins/mahanimbine[4]), pharmaceuticals,[5] and materials,[6] and they possess a broad spectrum of biological activities.[7] Therefore, synthesis of carbazoles has remained a subject of intense investigation in recent years.[8] However, despite being an attractive synthetic target, a one-pot synthesis of NH-carbazoles from readily available materials is scarcely available.[9] Strategies for the multistep synthesis reported in the literature suffer from drawbacks such as low yields and poor generality.[10]

In a continuation of our efforts on the one-pot synthesis of diverse heterocycles from 2-alkynyl indoles,[11] which acts as a combined source for both a nucleophile (indole) and an electrophile (an internal alkyne), we embarked on yet another application involving the construction of 2,4 -substituted NH-carbazoles by treating the 2-alkynyl indole with a terminal aryl alkyne. We envisioned that initially the terminal alkyne may undergo hydroarylation[12] with 2-alkynyl indole via metal-catalyzed activation to form an enyne intermediate, which may then undergo intramolecular carbocyclization to afford NH-carbazoles. For the metal catalyzed activation of the terminal alkyne, we proposed the use of Au(I) salts, as they have been widely used to promote cyclization,[13] cycloaddition,[14] cycloisomerization,[15] and rearrangements.[16]

In our initial experiments, treatment of 2-alkynyl indole **1a** with a terminal alkyne **2a** in the presence of 5 mol % of either $AuClPPh_3$ or $AuCl_3$ as a catalyst was unsuccessful (entries 1 and 2). This prompted us to carry out the desired cyclization by employing a catalytic combination of Au(I) and Ag(I) salts. In recent years, gold-catalyzed reactions in the presence of Ag(I) salts have been demonstrated to promote intramolecular cyclization involving an alkyne and a nucleophile via an efficient cationic gold species.[1] Accordingly, the 2-alkynyl indole **1a** was treated with the terminal alkyne **2a** in DCE at 90 °C in the presence of 5 mol % $AuClPPh_3/AgSbF_6$. After overnight stirring, a new product was isolated in 45% yield with a molecular weight of 319.1 Da (entry 3, Table 1). The structure of the product was elucidated by NMR studies that led to its identification as 2,4-diphenyl-9*H*-carbazole **3aa**.

Once the structure was determined, we then proceeded to optimize the reaction conditions with a view to enhance the yield of **3aa**, and the results have been summarized in Table 1. Switching to other solvents such as toluene and acetonitrile (ACN) in the presence of 5 mol % catalyst loading afforded **3aa** in 55% and 42% isolated yield, respectively (entries 4 and 5). However, increasing the catalyst loading to 15 mol % in toluene afforded **3aa** in an improved yield of 71% (entry 6). Replacing Au(I) with Au(III) catalyst furnished **3aa** in reduced yields (entries 7 and 8), thereby suggesting that in comparison to Au(III), the Au(I) catalyst produced better results. These

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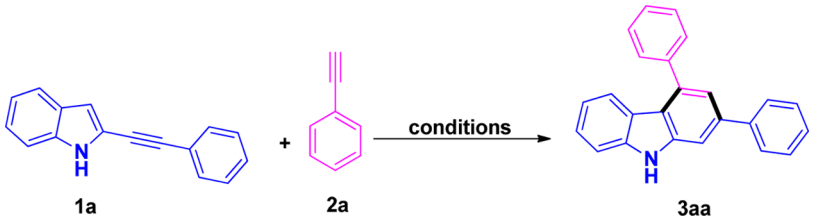
**Table 1. Optimization of the Reaction Condition for the Synthesis of 3aa**




| entry | catalyst/solvent | temp (°C) | time (h) | yield[a] (%) |
|---|---|---|---|---|
| 1 | 5 mol % $AuClPPh_3$, DCE | 90 | 10 | NR[b] |
| 2 | 5 mol % $AuCl_3$, DCE | 90 | 10 | NR[b] |
| 3 | 5 mol % $AuClPPh_3/AgSbF_6$, DCE | 90 | 10 | 45 |
| 4 | 5 mol % $AuClPPh_3/AgSbF_6$, toluene | 110 | 10 | 55 |
| 5 | 5 mol % $AuClPPh_3/AgSbF_6$, ACN | 85 | 10 | 42 |
| **6** | **15 mol % $AuClPPh_3/AgSbF_6$, toluene** | **110** | **10** | **71** |
| 7 | 5 mol % $AuCl_3$/AgOTf, DCE | 90 | 12 | 35 |
| 8 | 5 mol % $AuCl_3$/AgOTf, toluene | 110 | 10 | 41 |
| 9 | 5 mol % $AuCl_3/AgSbF_6$, toluene | 110 | 24 | NR[b] |
| 10 | 5 mol % $AuClPPh_3$/AgOTf, toluene | 110 | 16 | 45 |
| 11 | 15 mol % $AuClPPh_3$/AgOTf, toluene | 110 | 16 | 52 |
| 12 | 5 mol % $AuClPPh_3/AgNO_3$, toluene | 110 | 24 | NR[b] |
| 13 | 10 mol % $InCl_3$, DCE | 90 | 9.5 | 41 |
| 14 | 15 mol % $InCl_3$, toluene | 90 | 9 | 47 |
| 15 | 5 mol % $PdCl_2(PPh_3)_2$, $PPh_3$, toluene | 110 | 24 | NR[b] |
| 16 | 5 mol % $Pd_2(dba)_3$, toluene | 110 | 24 | NR[b] |
| 17 | 5 mol % $AgSbF_6$, toluene | 110 | 24 | NR[b] |

[a]Isolated yield. [b]NR = no reaction.

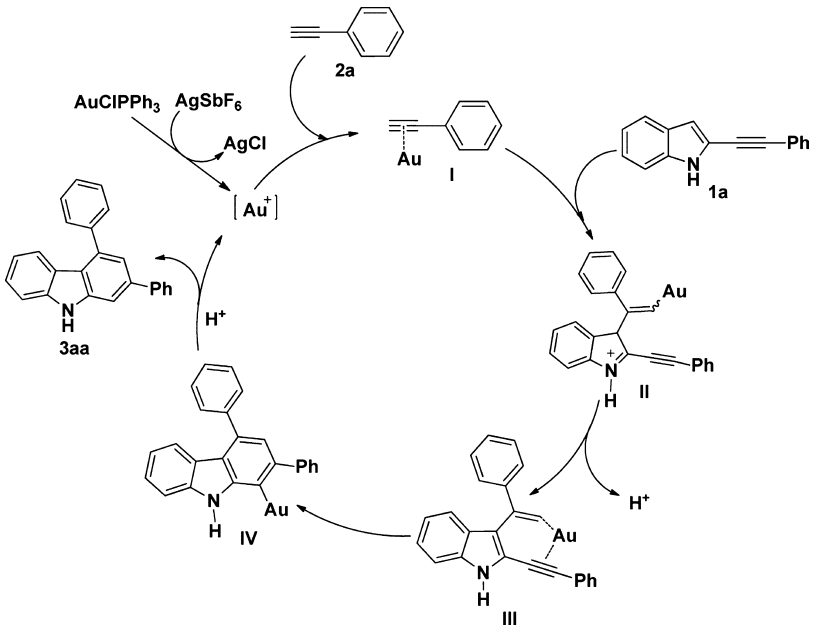



**Figure 1.** Plausible mechanism for the synthesis of **3aa**.

findings are in accordance with the observation reported earlier by Toste et al.[17] Further, replacing $AuClPPh_3$ with 5 mol % of the combination of $AuCl_3/AgSbF_6$ failed to afford the desired product (entry 9, Table 1). We next examined the reaction conditions by replacing $AgSbF_6$ with other Ag salts. Employing 5 and 15 mol % AgOTf furnished **3aa** in 45% and 52% isolated yields (entries 10 and 11), whereas $AgNO_3$ failed to afford **3aa** (entry 12). Replacing Au(I) catalyst with $InCl_3$ furnished **3aa** in moderate yields (entries 13 and 14), whereas employing Pd catalysts failed to even promote the formation of **3aa** (entries 15 and 16). Controlled experiments without the addition of Au catalysts failed to furnish **3aa** (entry 17). Thus, among the many reaction conditions screened, 15 mol % $AuClPPh_3/AgSbF_6$ in toluene was found to be the optimal conditions for the synthesis of NH-carbazoles in one-pot (entry 6, in bold).

A plausible mechanism for the formation of **3aa** via the $AuClPPh_3/AgSbF_6$ catalyzed reaction is depicted in Figure 1. Initially, a cationic Au complex obtained[18] from mixing


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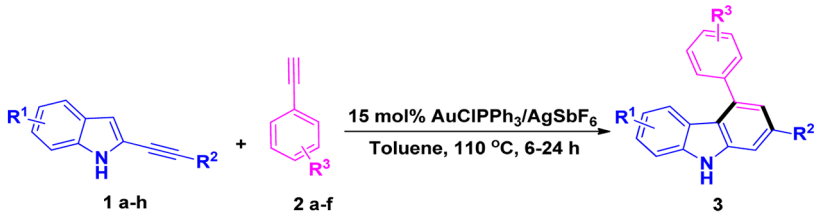
**Table 2. Substrate Scope for the Gold Catalyzed One-Pot Synthesis of Carbazoles 3[a]**




1a = $R^1$ = H, $R^2$ = Ph
1b = $R^1$ = H, $R^2$ = 4-Me-Ph
1c = $R^1$ = H, $R^2$ = 4-*t*-Bu-Ph
1d = $R^1$ = H, $R^2$ = *n*-Bu
1e = $R^1$ = H, $R^2$ = Cyclohexenyl
1f = $R^1$ = 5-Cl, $R^2$ = Ph
1g = $R^1$ = 5-Cl, $R^2$ = 4-*t*-Bu-Ph
1h = $R^1$ = 5-Cl, $R^2$ = 4-Me-Ph

2a = $R^3$ = H
2b = $R^3$ = 4-*t*-Bu
2c = $R^3$ = 4-Me
2d = $R^3$ = 4-OMe
2e = $R^3$ = 4-F
2f = $R^3$ = 4-CN

| entry | 1 | 2 | time (h) | 3 | yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** | **2a** | 8 | **3aa** | 71 |
| 2 | **1a** | **2b** | 7.5 | **3ab** | 70 |
| 3 | **1a** | **2c** | 8 | **3ac** | 66 |
| 4 | **1a** | **2d** | 7 | **3ad** | 72 |
| 5 | **1b** | **2a** | 8 | **3ba** | 70 |
| 6 | **1b** | **2b** | 6.5 | **3bb** | 76 |
| 7 | **1b** | **2c** | 7 | **3bc** | 71 |
| 8 | **1c** | **2a** | 8.5 | **3ca** | 78 |
| 9 | **1c** | **2b** | 7.5 | **3cb** | 69 |
| 10 | **1c** | **2c** | 8 | **3cc** | 74 |
| 11 | **1c** | **2d** | 7 | **3cd** | 70 |
| 12 | **1c** | **2e** | 15 | **3ce** | 58 |
| 13 | **1c** | **2f** | 24 | **3cf** | 52 |
| 14 | **1d** | **2a** | 9.5 | **3da** | 60 |
| 15 | **1d** | **2b** | 8.5 | **3db** | 53 |
| 16 | **1d** | **2c** | 9 | **3dc** | 50 |
| 17 | **1e** | **2a** | 8.5 | **3ea** | 67 |
| 18 | **1e** | **2b** | 8 | **3eb** | 65 |
| 19 | **1e** | **2d** | 8 | **3ed** | 68 |
| 20 | **1f** | **2a** | 6.5 | **3fa** | 75 |
| 21 | **1f** | **2c** | 6 | **3fc** | 70 |
| 22 | **1g** | **2a** | 6.5 | **3ga** | 68 |
| 23 | **1h** | **2a** | 7 | **3ha** | 72 |
| 24 | **1h** | **2e** | 16 | **3he** | 56 |

[a]Reaction conditions: 1 equiv of **1**, 1.2 equiv of **2**, 5 mL of toluene, and 15 mol % of $AuClPPh_3/AgSbF_6$

$AuClPPh_3$ and $AgSbF_6$ in a 1:1 ratio activates the terminal alkyne **2a**, which is then followed by its hydroarylation with **1a** to afford a C-3 alkenylated indole intermediate **II**. The metal present in **II** subsequently coordinates with the internal alkyne present at the C-2 position of the indole to afford intermediate **III**. This in turn activates the alkyne toward intramolecular nucleophilic attack by the alkenyl carbon (at the C-3 position of the indole) via 6-endo-dig carbocyclization mode to furnish intermediate **IV**. Later on, further protodemetalation affords **3aa** with the regeneration of catalyst. Having established the optimized conditions for the synthesis of NH-carbazoles, we next explored the reaction of a variety of substituted 2-alkynyl indoles **1a**–**h** and phenylacetylenes **2a**–**f** to examine the scope and limitations of the cascade hydroarylation–6-endo-dig carbocyclization reactions. The $R^3$ in **2** (Table 2) represents substitution on the terminal aryl alkyne comprising electron-donating and -withdrawing substituents, whereas the $R^2$ in **1** represents substitution on internal alkynes linked to the C-2 of the indole and comprises both aliphatic and aromatic moieties. The $R^1$ in **1** represents substitution on the aromatic ring and comprises either a 5-Cl group or H.

The results demonstrated that a wide range of terminal alkynes bearing both electron-withdrawing and electron-donating groups ($R^3$) were found to be suitable substrates for the cyclization and gave the corresponding products in moderate to excellent yields. For example, terminal alkynes bearing *t*-butyl, methyl, or methoxyl substituents provided the desired products in good yields (**3ab**, **3ac**, **3ad**, and **3cc**). Terminal alkynes containing a halogen atom (F) or electron-withdrawing substituents (CN) as $R^3$ also underwent the cyclization smoothly to afford the corresponding product in moderate yields (**3he**, **3ce**, and **3cf**). The moderate yield may be attributed to the poor $\pi$-coordination between the gold catalyst and alkynes bearing either halogen or electron-withdrawing groups, thereby leading to the weak activation of alkynes toward nucleophilic attack. Similarly, in the internal alkynes **2**, the presence of an aromatic ring as $R^2$ furnished products in good yields, whereas the presence of aliphatic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substitutents (*n*-butyl and cyclohexenyl) gave corresponding products in moderate yields. Introduction of the 5-Cl group, instead of the 5-H group, in the aromatic ring of the indole had no effect on the yield of the corresponding **3**. Replacing phenylacetylenes **2** with aliphatic terminal alkynes failed to give desired products. All 24 NH-carbazoles with diverse substitutions ($R^1$, $R^2$, and $R^3$) were synthesized in isolated yields ranging from 50 to 78% (Table 2).

In conclusion, we have developed an efficient gold catalyzed annulation reaction that allows the assembly of NH-carbazoles from two readily accessible building blocks, 2-alkynyl indoles and terminal alkynes, in moderate to good yields. The strategy involves tandem gold-catalyzed reactions leading to two C−C bonds forming via sequential hydroarylaion of the alkyne and 6-endo-dig carbocyclization. The methodology allows direct synthesis of NH-carbazoles with three-point diversity.

## EXPERIMENTAL SECTION

**I. General Information and Methods.** All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with 300 and 400 MHz spectrometers for $^1$H NMR and 75 and 100 MHz for $^{13}$C NMR. Chemical shifts ($\delta$) are given in parts per million relative to the residual signals of tetramethylsilane in $CDCl_3$ or deuterated solvent $CDCl_3$ for $^1$H and $^{13}$C NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). High resolution mass spectra were taken with a 3000 mass spectrometer and MALDI-TOF/TOF Analyzer. Column chromatography was performed using silica gel (100−200 mesh) as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). The purity and characterization of these compounds were further established using HR/EI mass spectroscopy. Melting points were measured on a capillary melting point apparatus and are uncorrected.

**II. Synthesis of 2-Ethynyl-1*H*-indoles 1a−h.** Starting materials **1a−h** were prepared according to the literature procedure.[19] The characterization data of compounds **1a−f** and **1h** were reported previously by us.[11]

*2-((4-(tert-Butyl)phenyl)ethynyl)-5-chloro-1H-indole (**1g**).* Yellow solid. $R_f$ = 0.58 (10:90 ethyl acetate/hexane). Yield: 67% (0.661 g). Mp: 158−160 °C. FT-IR (KBr): 3028, 2964, 1648, 1534, 1458 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.10 (s, 1H), 7.46−7.35 (m, 5H), 6.94 (s, 1H), 6.77 (s, 1H), 6.68 (d, $J$ = 0.9 Hz, 1H), 1.32 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 151.8, 146.4, 143.8, 131.4, 131.2, 125.6, 121.9, 119.9, 117.7, 108.9, 100.9, 92.5, 81.4, 34.9, 31.3. HRMS (ESI): calcd for $C_{20}H_{19}ClN$ [M + H], 308.1206; found, 308.1214.

**III. Typical Procedure for the Synthesis of NH-Carbazoles.** A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with the 2-alkynyl indole **1a−h** (1.0 equiv), phenylacetylenes **2a−f** (1.2 equiv), and 10 mL of freshly dried toluene. The resulting solution was purged with $N_2$ for 10 min followed by the addition of $Au(PPh_3)Cl$ (0.15 mmol) and $AgSbF_6$ (0.15 mmol) under the $N_2$ atmosphere. The reaction mixture was transferred to an oil bath and continued to stir at 110 °C. After being allowed to stir vigorously for the appropriate time, the reaction mixture was removed from the oil bath and cooled to room temperature and filtered through a bed of Celite-R, diluted with water (50 mL), and extracted with ethyl acetate (3 × 30 mL). The resulting organic solution was washed with brine (25 mL), dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel flash column chromatography using EtOAc/hexane as the eluent to afford **3**.

*Characterization Data of All Final Compounds (**3aa−3he**). 2,4-Diphenyl-9H-carbazole (**3aa**).* Gray solid. $R_f$ = 0.48 (10:90 ethyl acetate/hexane). Yield: 71% (0.208 g). Mp: 170−172 °C. FT-IR (KBr): 3399, 2927, 1613, 1324, 755 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.20 (s, 1H), 7.74−7.68 (m, 4H), 7.63 (s, 1H), 7.55−7.44 (m, 6H), 7.41−7.36 (m, 4H), 7.00 (t, $J$ = 7.8 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 141.7, 141.3, 140.7, 140.3, 139.2, 138.1, 129.4, 129.0, 128.6, 127.8, 127.7, 127.4, 125.9, 122.9, 122.6, 121.0, 120.3, 119.4, 110.6, 108.1. HRMS (MALDI-TOF/TOF): calcd for $C_{24}H_{17}N$ [M$^{+\bullet}$], 319.1355; found, 319.1352.

*4-(4-(tert-Butyl)phenyl)-2-phenyl-9H-carbazole (**3ab**).* Pale yellow solid. $R_f$ = 0.42 (10:90 ethyl acetate/hexane). Yield: 70% (0.242 g). Mp: 203−205 °C. FT-IR (KBr): 3397, 2932, 1600, 1403, 1321, 832 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.16 (s, 1H), 7.72 (d, $J$ = 7.6 Hz, 2H), 7.65−7.55 (m, 6H), 7.49−7.33 (m, 6H), 7.02 (t, $J$ = 6.8 Hz, 1H), 1.46 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.8, 141.8, 140.7, 140.3, 139.1, 138.3, 138.1, 129.1, 129.0, 127.7, 127.3, 125.9, 125.5, 123.0, 122.7, 121.2, 120.3, 119.3, 110.6, 107.9, 34.9, 31.7. HRMS (ESI): calcd for $C_{28}H_{26}N$ [M + H], 376.2065; found, 376.2055.

*2-Phenyl-4-(p-tolyl)-9H-carbazole (**3ac**).* White solid. $R_f$ = 0.44 (10:90 ethyl acetate/hexane). Yield: 66% (0.202 g). Mp: 133−135 °C. FT-IR (KBr): 3417, 2922, 1601, 1453, 1411, 1322 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.19 (s, 1H), 7.71 (d, $J$ = 7.1 Hz, 2H), 7.60−7.55 (m, 4H), 7.48−7.36 (m, 8H), 7.00 (t, $J$ = 6.9 Hz, 1H), 2.49 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 141.8, 140.7, 140.4, 139.2, 138.4, 138.1, 137.5, 129.4, 129.3, 129.0, 127.7, 127.3, 125.8, 123.1, 122.7, 121.1, 120.3, 119.4, 110.6, 107.9, 21.5. HRMS (ESI): calcd for $C_{25}H_{20}N$ [M + H], 334.1596; found, 334.1593.

*4-(4-Methoxyphenyl)-2-phenyl-9H-carbazole (**3ad**).* White solid. $R_f$ = 0.48 (10:90 ethyl acetate/hexane). Yield: 72% (0.231 g). Mp: 121−123 °C. FT-IR (KBr): 3397, 2923, 1606, 1451, 1320, 748 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.17 (s, 1H), 7.69 (d, $J$ = 7.6 Hz, 2H), 7.61−7.55 (m, 4H), 7.44 (t, $J$ = 7.3 Hz, 2H), 7.35 (d, $J$ = 4.6 Hz, 4H), 7.07 (d, $J$ = 8.2 Hz, 2H), 7.00 (t, $J$ = 7.5 Hz, 1H), 3.91 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 159.4, 141.8, 140.7, 140.4, 139.2, 137.8, 133.8, 130.8, 130.5, 129.0, 127.7, 127.3, 125.8, 123.1, 122.6, 121.1, 120.4, 119.4, 114.1, 113.9, 110.6, 107.9, 55.6. HRMS (MALDI-TOF/TOF): calcd for $C_{25}H_{19}NO$ [M$^{+\bullet}$], 349.1461; found, 349.1474.

*4-Phenyl-2-(p-tolyl)-9H-carbazole (**3ba**).* White solid. $R_f$ = 0.46 (10:90 ethyl acetate/hexane). Yield: 70% (0.214 g). Mp: 131−133 °C. FT-IR (KBr): 3434, 2923, 1606, 1454, 1320 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.21 (s, 1H), 7.71 (d, $J$ = 6.6 Hz, 2H), 7.65 (d, $J$ = 8.5 Hz, 3H), 7.59−7.51, (m, 5H), 7.44−7.34 (m, 3H), 7.29 (d, $J$ = 9.7 Hz, 1H), 7.02 (t, $J$ = 7.0 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 141.5, 140.7, 140.4, 139.2, 138.8, 138.1, 137.2, 129.7, 129.4, 128.6, 127.8, 127.5, 125.8, 123.0, 122.5, 120.9, 120.1, 119.4, 114.3, 110.6, 107.9, 21.3. HRMS (ESI): calcd for $C_{25}H_{20}N$ [M + H], 334.1596; found, 334.1591.

*4-(4-(tert-Butyl)phenyl)-2-(p-tolyl)-9H-carbazole (**3bb**).* White solid. $R_f$ = 0.46 (10:90 ethyl acetate/hexane). Yield: 76% (0.272 g). Mp: 198−200 °C. FT-IR (KBr): 3400, 2955, 1606, 1457, 1325, 1115 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.17 (s, 1H), 7.63−7.53 (m, 8H), 7.42−7.31 (m, 3H), 7.27−7.25 (m, 2H), 7.00 (t, $J$ = 7.1 Hz, 1H), 2.40 (s, 3H), 1.44 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 150.8, 140.8, 140.4, 139.2, 138.9, 138.4, 138.1, 137.1, 129.7, 129.1, 127.5, 125.8, 125.5, 123.2, 122.7, 121.1, 120.2, 119.3, 110.5, 107.7, 34.9, 31.7, 21.3. HRMS (ESI): calcd for $C_{29}H_{28}N$ [M + H], 390.2222; found, 390.2220.

*2,4-di-p-Tolyl-9H-carbazole (**3bc**).* White solid. $R_f$ = 0.42 (10:90 ethyl acetate/hexane). Yield: 71% (0.227 g). Mp: 140−142 °C. FT-IR (KBr): 3392, 2942, 1604, 1455, 1273 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.11 (s, 1H), 7.61−7.53 (m, 6H), 7.35−7.32 (m, 5H), 7.25 (d, $J$ = 8.9 Hz, 2H), 7.01−6.96 (m, 1H), 2.48 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 140.7, 140.3, 139.1, 138.9, 138.4, 137.4, 137.1, 129.7, 129.4, 129.3, 127.5, 125.7, 123.1, 122.6, 120.9, 120.1, 119.3, 110.6, 107.7, 21.6, 21.3. HRMS (ESI): calcd for $C_{26}H_{22}N$ [M + H], 348.1752; found, 348.1741.

*2-(4-(tert-Butyl)phenyl)-4-phenyl-9H-carbazole (**3ca**).* White solid. $R_f$ = 0.51 (10:90 ethyl acetate/hexane). Yield: 78% (0.269 g). Mp: 178−180 °C. FT-IR (KBr): 3404, 2928, 1606, 1456, 1396, 1322 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.18 (s, 1H), 7.69−7.64 (m, 4H), 7.61 (d, $J$ = 1.3 Hz, 1H), 7.56−7.47 (m, 6H), 7.42−7.33 (m, 3H), 6.98 (t, $J$ = 6.9 Hz, 1H), 1.37 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 150.4, 141.5, 140.7, 140.3, 139.1, 138.8, 138.0, 129.4, 128.6, 127.8, 127.3, 126.0, 125.8, 123.0, 122.5, 121.0, 120.1, 119.3, 110.6, 107.9, 34.7, 31.6. HRMS (MALDI-TOF/TOF): calcd for $C_{28}H_{25}N$ [M$^{+\bullet}$], 375.1981; found, 375.1987.


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*2,4-bis(4-(tert-Butyl)phenyl)-9H-carbazole (**3cb**).* White solid. $R_f$ = 0.50 (10:90 ethyl acetate/hexane). Yield: 69% (0.274 g). Mp: 198−200 °C. FT-IR (KBr): 3393, 2942, 1606, 1458, 1382, 1270 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.66 (s, 1H), 7.64 (s, 2H), 7.60 (d, *J* = 4.7 Hz, 2H), 7.56 (s, 2H), 7.53 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.41−7.36 (m, 3H), 7.00 (t, *J* = 6.9 Hz, 1H), 1.44 (s, 9H), 1.37 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 150.7, 150.5, 140.8, 140.3, 139.0, 138.9, 138.4, 138.0, 129.0, 127.3, 125.9, 125.7, 125.5, 123.1, 122.6, 121.1, 120.1, 119.3, 110.5, 107.7, 34.9, 34.7, 31.7, 31.6. HRMS (MALDI-TOF/TOF): calcd for $C_{32}H_{33}N$ [$M^{+\bullet}$], 431.2613; found, 431.2603.

*2-(4-(tert-Butyl)phenyl)-4-(p-tolyl)-9H-carbazole (**3cc**).* Pale yellow solid. $R_f$ = 0.46 (10:90 ethyl acetate/hexane). Yield: 74% (0.265 g). Mp: 174−176 °C. FT-IR (KBr): 3391, 2920, 1606, 1450, 1278, 1140 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.59−7.54 (m, 4H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.39−7.33 (m, 5H), 6.99 (t, *J* = 7.1 Hz, 1H), 2.49 (s, 3H), 1.37 (s, 9H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 150.3, 140.6, 140.2, 139.0, 138.8, 138.4, 137.9, 137.3, 129.3, 129.2, 127.2, 125.8, 125.6, 123.0, 122.5, 120.9, 120.0, 119.2, 110.5, 107.7, 34.7, 31.5, 21.5. HRMS (ESI): calcd for $C_{29}H_{28}N$ [M + H], 390.2222; found, 390.2223.

*2-(4-(tert-Butyl)phenyl)-4-(4-methoxyphenyl)-9H-carbazole (**3cd**).* Pale yellow solid. $R_f$ = 0.52 (10:90 ethyl acetate/hexane). Yield: 70% (0.261 g). Mp: 182−184 °C. FT-IR (KBr): 3394, 2923, 1602, 1455, 1320. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.66 (s, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.58 (d, *J* = 3.3 Hz, 2H), 7.54 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.41−7.34 (m, 3H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 6.9 Hz, 1H), 3.92 (s, 3H), 1.37 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 159.4, 150.4, 140.8, 140.4, 139.1, 138.9, 137.7, 133.9, 130.5, 127.3, 125.9, 125.7, 123.2, 122.5, 121.0, 120.3, 119.3, 114.1, 110.6, 107.7, 55.6, 34.7, 31.6. HRMS (ESI): calcd for $C_{29}H_{28}NO$ [M + H], 406.2171; found, 406.2146.

*2-(4-(tert-Butyl)phenyl)-4-(4-fluorophenyl)-9H-carbazole (**3ce**).* Gray solid. $R_f$ = 0.54 (10:90 ethyl acetate/hexane). Yield: 58% (0.210 g). Mp: 176−178 °C. FT-IR (KBr): 3345, 2920, 1608, 1450, 1278 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.58−7.53 (m, 5H), 7.42−7.37 (m, 3H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.29−7.25 (m, 1H), 7.17−7.13 (m, 3H), 6.93 (t, *J* = 7.2 Hz, 1H), 1.30 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 150.5, 140.7, 140.4, 139.2, 138.7, 137.4, 136.9, 131.1, 131.0, 127.3, 126.0, 125.9, 122.9, 122.3, 121.0, 120.1, 119.5, 115.7, 115.4, 110.7, 108.1, 34.8, 31.6. HRMS (MALDI-TOF/TOF): calcd for $C_{28}H_{24}FN$ [$M^{+\bullet}$], 393.1887; found, 393.1868.

*4-(2-(4-(tert-Butyl)phenyl)-9H-carbazol-4-yl)benzonitrile (**3cf**).* Gray solid. $R_f$ = 0.58 (10:90 ethyl acetate/hexane). Yield: 52% (0.191 g). Mp: 172−174 °C. FT-IR (KBr): 3391, 2920, 2240, 1600, 1450, 1290 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.85−7.79 (m, 3H), 7.67−7.63 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45−7.38 (m, 4H), 7.31 (s, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 1.38 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 150.7, 146.4, 140.8, 140.4, 139.2, 138.4, 135.7, 132.7, 132.5, 130.3, 128.9, 127.3, 126.2, 126.0, 122.3, 122.0, 120.7, 119.6, 119.5, 119.2, 111.5, 111.0, 109.0, 34.8, 31.6. HRMS (MALDI-TOF/TOF): calcd for $C_{29}H_{24}N_2$ [$M^{+\bullet}$], 400.1934; found, 400.1927.

*2-Butyl-4-phenyl-9H-carbazole (**3da**).* Black liquid. $R_f$ = 0.42 (10:90 ethyl acetate/hexane). Yield: 60% (0.165 g). FT-IR (neat): 3385, 2927, 1600, 1461, 1251, 1172 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.53−7.44 (m, 4H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.32−7.27 (m, 1H), 7.20 (s, 1H), 6.94 (t, *J* = 6.8 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 1.75−1.65 (m, 2H), 1.27 (d, *J* = 10.3 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 141.7, 141.3, 140.6, 140.1, 137.6, 129.5, 128.6, 127.7, 125.4, 124.3, 123.8, 123.3, 122.4, 122.3, 119.2, 119.0, 110.6, 109.4, 36.4, 34.3, 22.8, 14.3. HRMS (MALDI-TOF/TOF): calcd for $C_{22}H_{21}N$ [$M^{+\bullet}$], 299.1668; found, 299.1666.

*2-Butyl-4-(4-(tert-butyl)phenyl)-9H-carbazole (**3db**).* Black liquid. $R_f$ = 0.46 (10:90 ethyl acetate/hexane). Yield: 53% (0.173 g). FT-IR (neat): 3382, 2925, 1606, 1456, 1212, 841 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.59−7.50 (m, 5H), 7.37−7.27 (m, 2H), 7.18 (s, 1H), 6.99−6.95 (m, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.75−1.65 (m, 2H), 1.43 (s, 9H), 1.41−1.37 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 150.4, 141.1, 140.5, 139.9, 138.5, 137.5, 128.9, 125.3, 125.2, 123.3, 122.5, 122.3, 119.0, 118.9, 110.3, 109.0, 36.2, 34.8, 34.1, 31.6, 22.6, 14.1. HRMS (ESI): calcd for $C_{26}H_{30}N$ [M + H], 356.2378; found, 356.2348.

*2-Butyl-4-(p-tolyl)-9H-carbazole (**3dc**).* Black liquid. $R_f$ = 0.54 (10:90 ethyl acetate/hexane). Yield: 50% (0.144 g). FT-IR (neat): 3394, 2923, 1602, 1466, 1246, 1175 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.53−7.50 (m, 3H), 7.30−7.19 (m, 4H), 7.05 (s, 1H), 6.96−6.92 (m, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.72−1.64 (m, 2H), 1.42−1.35 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 141.2, 140.5, 140.0, 138.7, 137.5, 137.2, 129.4, 129.2, 128.6, 125.2, 123.3, 122.3, 119.0, 118.9, 110.5, 109.1, 36.2, 34.2, 22.7, 21.5, 14.2. HRMS (ESI): calcd for $C_{23}H_{24}N$ [M + H], 314.1909; found, 314.1896.

*2-(Cyclohex-1-en-1-yl)-4-phenyl-9H-carbazole (**3ea**).* Pale yellow solid. $R_f$ = 0.5 (10:90 ethyl acetate/hexane). Yield: 67% (0.199 g). Mp: 134−136 °C. FT-IR (KBr): 3398, 2925, 1602, 1461, 1246, 1172 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.53−7.44 (m, 4H), 7.40 (s, 1H), 7.36 (s, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.18 (s, 1H), 6.95 (t, *J* = 7.1 Hz, 1H), 6.26 (s, 1H), 2.53 (s, 2H), 2.24 (d, *J* = 3.0 Hz, 2H), 1.84−1.80 (m, 2H), 1.69 (d, *J* = 5.1 Hz, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 141.7, 140.9, 140.5, 140.3, 137.4, 137.0, 129.4, 128.6, 127.6, 125.5, 125.4, 123.2, 122.3, 119.2, 119.1, 110.5, 106.0, 34.0, 32.1, 22.5, 14.3. HRMS (MALDI-TOF/TOF): calcd for $C_{24}H_{21}N$ [$M^{+\bullet}$], 323.1668; found, 323.1666.

*4-(4-(tert-Butyl)phenyl)-2-(cyclohex-1-en-1-yl)-9H-carbazole (**3eb**).* Pale yellow solid. $R_f$ = 0.44 (10:90 ethyl acetate/hexane). Yield: 65% (0.227 g). Mp: 161−163 °C. FT-IR (KBr): 3395, 2928, 1602, 1466, 1246, 1155 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.59−7.51 (m, 5H), 7.37−7.30 (m, 3H), 7.19 (s, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H), 2.52 (s, 2H), 2.24 (s, 2H), 1.80 (d, *J* = 5.1 Hz, 2H), 1.69 (d, *J* = 5.4 Hz, 2H), 1.43 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 150.6, 140.9, 140.5, 140.3, 138.7, 137.4, 137.1, 129.0, 128.5, 125.7, 125.4, 125.3, 123.3, 122.5, 119.8, 119.2, 119.1, 114.3, 110.5, 105.8, 34.9. 31.7, 28.0, 26.2, 23.4, 22.5. HRMS (MALDI-TOF/TOF): calcd for $C_{28}H_{29}N$ [$M^{+\bullet}$], 379.2294; found, 379.2292.

*2-(Cyclohex-1-en-1-yl)-4-(4-methoxyphenyl)-9H-carbazole (**3ed**).* Pale yellow solid. $R_f$ = 0.52 (10:90 ethyl acetate/hexane). Yield: 68% (0.221 g). Mp: 143−145 °C. FT-IR (KBr): 3391, 2925, 1603, 1461, 1245, 1172 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 4.9 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.16 (s, 1H), 7.05 (t, *J* = 7.9 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.26 (s, 1H), 3.92 (s, 3H), 2.53 (s, 2H), 2.24 (s, 2H), 1.82 (d, *J* = 4.9 Hz, 2H), 1.70 (d, *J* = 5.2 Hz, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 159.3, 140.9, 140.5, 140.3, 137.1, 137.0, 134.1, 130.5, 125.4, 125.3, 123.3, 122.3, 119.9, 119.2, 119.1, 114.0, 110.5, 105.7, 55.6, 28.0, 26.2, 23.4, 22.5. HRMS (ESI): calcd for $C_{25}H_{24}NO$ [M + H], 354.1858; found, 354.1832.

*6-Chloro-2,4-diphenyl-9H-carbazole (**3fa**).* Pale yellow solid. $R_f$ = 0.5 (10:90 ethyl acetate/hexane). Yield: 75% (0.210 g). Mp: 181−183 °C. FT-IR (KBr): 3381, 2935, 1605, 1390, 1278, 1150 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.61 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 3H), 7.49−7.45 (m, 3H), 7.38 (s, 2H), 7.32 (d, *J* = 2.8 Hz, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 141.5, 141.2, 140.7, 139.9, 138.6, 138.3, 129.2, 129.0, 128.8, 128.2, 127.7, 127.6, 126.0, 124.7, 124.1, 122.1, 121.4, 119.5, 111.5, 108.3. HRMS (ESI): calcd for $C_{24}H_{17}ClN$ [M + H], 354.1050; found, 354.1041.

*6-Chloro-2-phenyl-4-(p-tolyl)-9H-carbazole (**3fc**).* Pale brown solid. $R_f$ = 0.56 (10:90 ethyl acetate/hexane). Yield: 70% (0.204 g). Mp: 178−180 °C. FT-IR (KBr): 3395, 2920, 1607, 1400, 1251, 1145 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.57−7.53 (m, 4H), 7.45 (t, *J* = 7.1 Hz, 2H), 7.37−7.34 (m, 4H), 7.30 (s, 2H), 2.50 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 141.6, 141.3, 139.9, 138.6, 138.4, 137.9, 137.8, 129.5, 129.1, 129.0, 127.7, 127.5, 125.9, 124.7, 124.3, 122.2, 121.5, 119.5, 111.5, 108.1, 21.6. HRMS (MALDI-TOF/TOF): calcd for $C_{25}H_{18}ClN$ [$M^{+\bullet}$], 367.1122; found, 367.1125.

*2-(4-(tert-Butyl)phenyl)-6-chloro-4-phenyl-9H-carbazole (**3ga**).* Gray solid. $R_f$ = 0.52 (10:90 ethyl acetate/hexane). Yield: 68% (0.221 g). Mp: 152−154 °C. FT-IR (KBr): 3386, 2925, 1607, 1461,


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1252, 1165 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.18 (s, 1H), 7.62−7.54 (m, 5H), 7.42−7.28 (m, 5H), 7.07 (d, $J$ = 7.9 Hz, 2H), 7.02−6.91 (m, 2H), 1.26 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 150.4, 141.0, 140.6, 139.6, 138.4, 138.0, 130.3, 129.5, 129.0, 128.6, 127.9, 127.3, 127.1, 125.8, 125.7, 124.5, 124.0, 121.9, 121.1, 119.1, 113.8, 111.3, 107.8, 34.6, 31.3. HRMS (MALDI-TOF/TOF): calcd for $C_{28}H_{24}ClN$ [$M^{+\bullet}$], 409.1591; found, 409.1606.

*6-Chloro-4-phenyl-2-(p-tolyl)-9H-carbazole (**3ha**)*. Gray solid. $R_f$ = 0.48 (10:90 ethyl acetate/hexane). Yield: 72% (0.210 g). Mp: 182−184 °C. FT-IR (KBr): 3395, 2925, 1600, 1464, 1246, 1172 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.16 (s, 1H), 7.64−7.52 (m, 10H), 7.43 (s, 1H), 7.35 (s, 1H), 7.25 (d, $J$ = 7.7 Hz, 2H), 2.40 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 141.3, 140.8, 139.9, 138.7, 138.6, 138.3, 137.4, 129.8, 129.2, 128.8, 128.1, 127.5, 125.9, 124.7, 124.2, 122.1, 121.2, 119.3, 111.5, 108.0, 21.3. HRMS (MALDI-TOF/TOF): calcd for $C_{25}H_{18}ClN$ [$M^{+\bullet}$], 367.1122; found, 367.1123.

*6-Chloro-4-(4-fluorophenyl)-2-(p-tolyl)-9H-carbazole (**3he**)*. Gray solid. $R_f$ = 0.54 (10:90 ethyl acetate/hexane). Yield: 56% (0.171 g). Mp: 178−180 °C. FT-IR (KBr): 3392, 2920, 1607, 1455, 1195 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (s, 1H), 7.59 (d, $J$ = 8.3 Hz, 5H), 7.41 (s, 1H), 7.31 (s, 3H), 7.28−7.24 (m, 4H), 2.41 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 141.3, 139.9, 138.6, 138.5, 137.5, 137.1, 136.8, 130.9, 130.8, 129.8, 127.5, 126.0, 124.8, 124.0, 121.8, 121.3, 119.2, 115.9, 115.6, 111.6, 108.2, 21.3. HRMS (MALDI-TOF/TOF): calcd for $C_{25}H_{17}ClFN$ [$M^{+\bullet}$], 385.1028; found, 385.1043.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Copies of $^1H$ and $^{13}C$ NMR spectra of all final 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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