Synthesis X. Zhao et al. Special Topic

Photoinduced Cross-Coupling of Amines with 1,2-Diiodobenzene and Its Application in the Synthesis of Carbazoles

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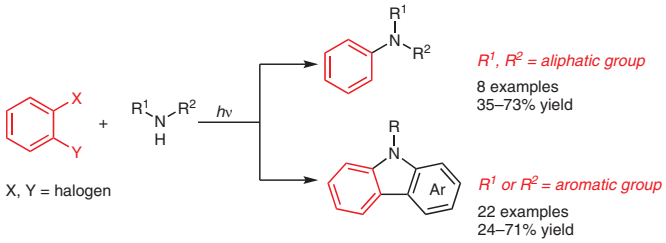

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Abstract A facile and efficient process for the preparation of various tertiary aminobenzenes and carbazole derivatives via photoinduced cross-coupling of amines with 1,2-diiodobenzene is reported. Mechanistic investigations indicate that the transformation proceeds via nucleophilic addition of an amine to the benzyne intermediate accompanied with a proton transfer process, followed by an oxidative cyclization of the generated diphenylamine to furnish the corresponding carbazole products.

Key words aminobenzenes, cross-coupling, carbazoles, oxidative cyclization

Aminobenzenes represent one of the most common subunits present in various organic compounds across pharmaceutical and materials sciences;[1] numerous methodologies have therefore been developed for their preparation. Among all the synthetic protocols, amination of benzene halides provides the most attractive method to generate C(sp^2)–N bonds. For example, the transition-metal-catalyzed (usually a Pd-based catalyst) C(sp^2)–N cross-coupling reactions,[2] e.g., the Buchwald–Hartwig and Ullmann–Goldberg reactions,[3] have been extensively studied over the past decades. Furthermore, Fu and co-workers have dedicated many years to the study of different types of copper-catalyzed photoinduced C–N coupling reactions.[4] In 2016, Johannes developed a visible-light catalytic cross-coupling of primary aryl amines with aryl halides.[5] However, techniques that do not employ metal catalysts to directly achieve the arylation of amines under mild conditions are still rare and attractive.

Carbazoles, as one of the particularly important classes of nitrogen-containing functional compounds, are a significant area of research due to their presence in the frameworks of a wide spectrum of natural products and biologically active molecules (Figure 1).[6] Moreover, many carbazoles have been proven to be key motifs in the synthesis of electrical and thermal materials.[7] Consequently, tremendous efforts have been devoted toward the development of strategies for the construction of carbazole frameworks. All these tactics can generally be classified into two categories: (i) construction of the central pyrrolyl ring via intramolecular C–C or C–N coupling,[8] and (ii) installation of a new aromatic ring onto an indole derivative via inter- or intramolecular benzannulation.[9] However, most of these procedures require complex and expensive metal catalysts (such as Pd and Ru), harsh reaction conditions, or complicated steps. Therefore, developing an inexpensive and practical method to access carbazoles is still in high demand.

Over the past decades, direct addition of amines to the triple bond of a benzyne intermediate has been extensively studied to access various nitrogen-containing products (Scheme 1);[8a,10,11] however, formation of the benzyne intermediate often requires a strong base (e.g., organolithium reagents), thereby limiting wider application of the process. Based on previous literature,[12] the benzyne intermediate could be easily obtained from a dihalobenzene precursor under photoirradiation. Hence, we envisioned that an intermolecular cross-coupling might take place via a nucleophilic addition process between aminobenzenes and halobenzenes to furnish nitrogen-containing compounds under the irradiation of ultraviolet light. In this report, we

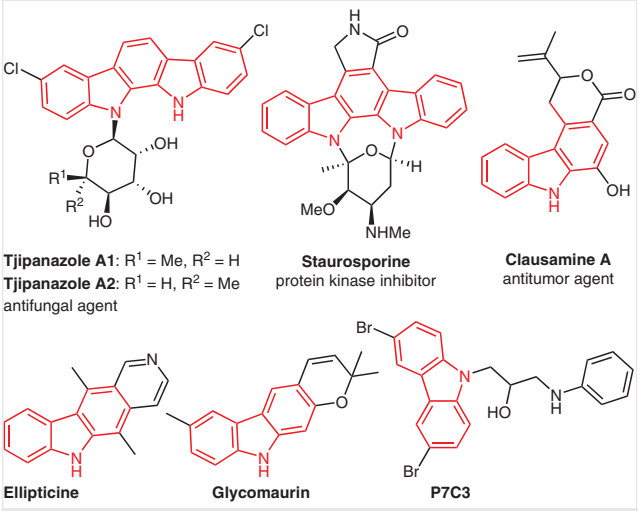
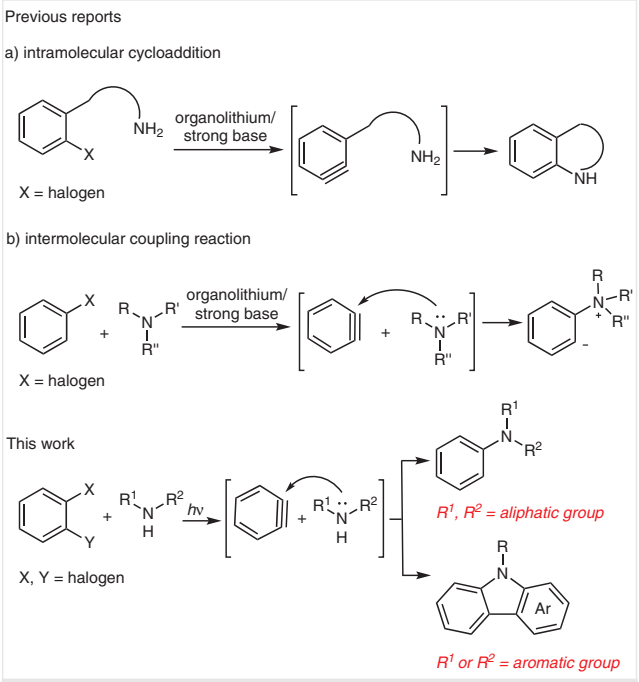


Figure 1 Representative carbazole-based natural products and bioactive carbazole derivatives

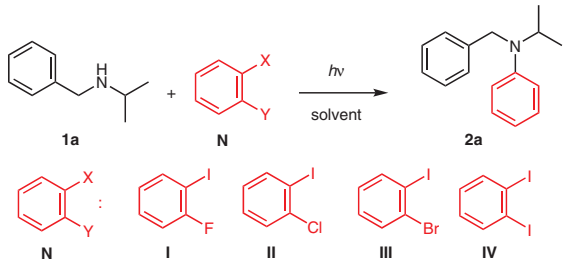


Scheme 1 Previous reports and the design of this cross-coupling reaction

describe our findings on this facile photochemical method to access diverse tertiary aminobenzenes and carbazoles from simple starting materials.

The proposed cross-coupling was initially explored by using *N*-benzylpropan-2-amine (**1a**) as a nucleophile and 1-fluoro-2-iodobenzene (**I**) as the benzyne precursor (Table 1). Exposure of a degassed heptane solution of both **1a** and **I** in a glass container to irradiation using a low-pressure mercury lamp (λ = 300 nm) led to the desired cross-coupling product **2a** being isolated in 27% yield (entry 1). In order to gauge the reactivity of **1a**, other dihalobenzenes such as **II** and **III** were employed, with the desired product **2a** being obtained (entries 2 and 3). The reaction with 1,2-diiodobenzene (**IV**) showed a much better result than with the other dihalobenzenes (entry 4). When the reaction was carried out without protection of the nitrogen, a dramatic decrease in the yield was observed, probably due to the strong radical-scavenging activity of air (entry 5). Subsequent solvent screening revealed that the reaction conducted in heptane afforded **2a** in a higher yield than in other media (entries 6–14). Notably, polar solvents such as methanol and acetonitrile showed a negative effect on the photoreaction. Moreover, changing the glass vessel to a quartz tube led to an appreciable decrease in the yield, which indicated that

Table 1 Optimization of the Reaction Conditions[a]

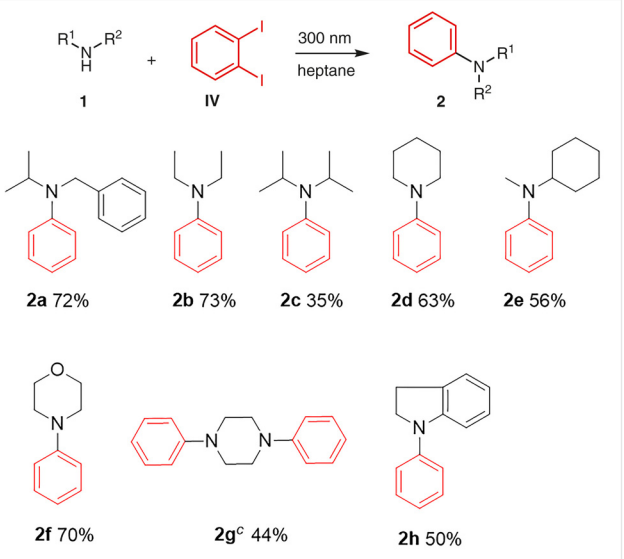


Entry	N	hν	Solvent	Yield (%)[b]
1	**I**	300 nm	heptane	27
2	**II**	300 nm	heptane	35
3	**III**	300 nm	heptane	42
4	**IV**	**300 nm**	**heptane**	**72**
5[c]	**IV**	300 nm	heptane	18
6	**IV**	300 nm	1,2-DCE	45
7	**IV**	300 nm	hexane	67
8	**IV**	300 nm	THF	40
9	**IV**	300 nm	1,4-dioxane	42
10	**IV**	300 nm	toluene	39
11	**IV**	300 nm	MeCN	22
12	**IV**	300 nm	MeOH	25
13[c]	**IV**	300 nm	DMSO	28
14	**IV**	300 nm	DMF	34
15[d]	**IV**	300 nm	heptane	48
16[e]	**IV**	350 nm	heptane	40
17	**IV**	HPML	heptane	46
18	**IV**	MPML	heptane	42

[a] Reaction conditions: **1a** (0.2 mmol), **N** (0.1 mmol), solvent (10 mL), glass tube, N_2 atmosphere (unless otherwise noted), 6–8 h.
[b] Yield of isolated product.
[c] Reaction conducted under an air atmosphere.
[d] Reaction conducted in a quartz tube.
[e] Reaction time: 24 h.

the favorable wavelength for reaction was no less than 300 nm (entry 15). However, a longer reaction time was required to completely consume **1a** when the light-emitting spectrum was chosen at 350 nm (entry 16). Other light sources, for example, a high-pressure mercury lamp (HPML) and a medium-pressure mercury lamp (MPML), did not improve the yield of **2a** (entries 17 and 18).

With optimized conditions in hand, the substrate scope with respect to the amine partner was screened. As revealed in Scheme 2, diverse types of tertiary aminobenzenes were readily prepared in moderate to high yields by employing aliphatic amines with 1,2-diiodobenzene (**IV**). In addition to **2a**, N-phenylated products **2b** and **2c** could be successfully prepared from their corresponding secondary amines in 73% and 35% yields, respectively. Cyclic amines also readily tolerated the reaction conditions and provided the corresponding aminobenzenes **2d–f** in good yields. It is noteworthy that aliphatic amine **1g**, containing two nitrogen atoms, underwent the cross-coupling reaction with **IV** on both nitrogen atoms to afford product **2g** in moderate yield, even when the loading of **1g** was reduced to 1 equivalent. Next, the reaction between benzocyclic amine **1h** and **IV** was tested, and delightfully, the reaction proceeded successfully under the optimized conditions to deliver **2h** in 50% yield.



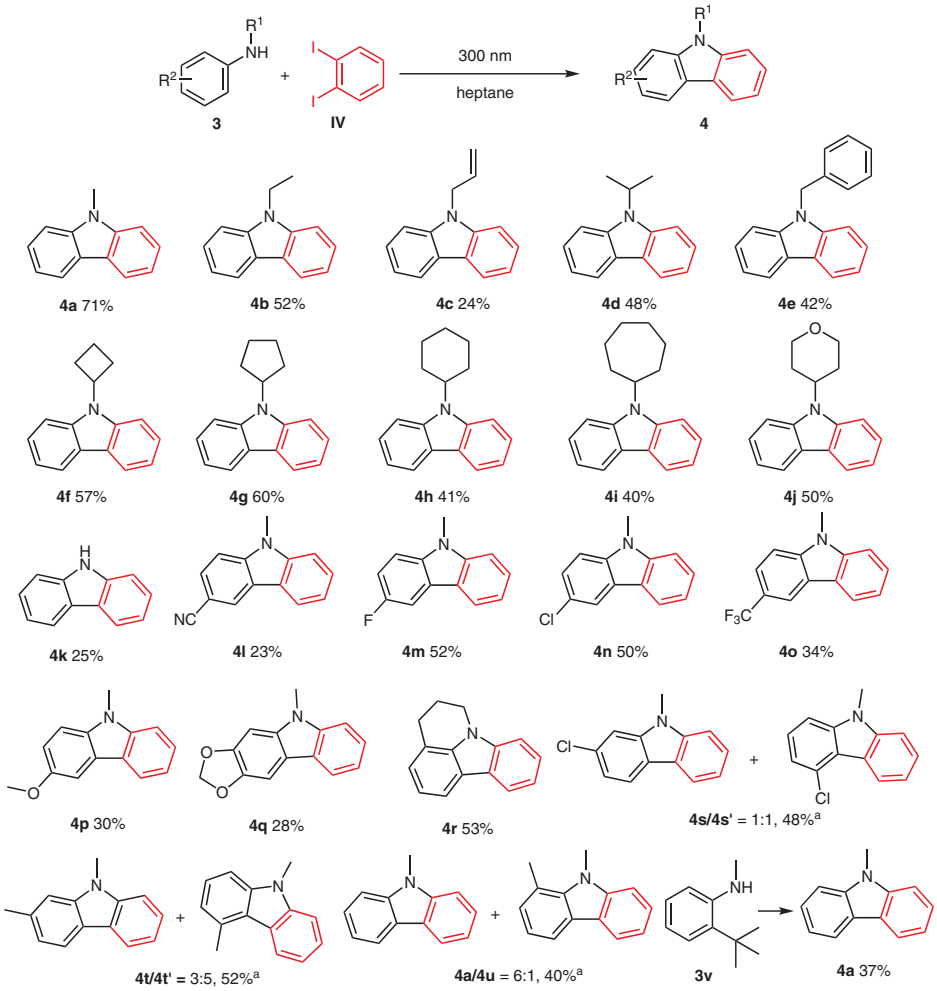
Scheme 2 Photoinduced cross-coupling between 1,2-diiodobenzene and different aliphatic amines. Unless otherwise noted, all reactions were conducted under the optimized conditions: **1** (0.2 mmol), **IV** (0.1 mmol), heptane (10 mL), glass tube, N_2 atmosphere, λ = 300 nm, 6–10 h; reactions were monitored by TLC. Yields are those of isolated products. [a] The amount of **1g** was decreased to 1.0 equivalent.

Subsequently, we turned our attention to the photochemical behavior of N-substituted secondary phenylamines. In general, such a photoreaction protocol led to the formation of carbazole derivatives, which may stem from the oxidative cyclization of the in situ formed diphenylamine intermediates.[13] With this assumption in mind, a series of carbazoles was synthesized to demonstrate the application of this reaction model. As shown in Scheme 3, it was notable that the desired *N*-methylcarbazole (**4a**) could be readily prepared from substrate **3a** in a yield of up to 71%. Replacing the methyl group with other substituents, such as ethyl, allyl, 2-propyl and benzyl, delivered the corresponding products **4b–e** smoothly in yields of 24–52%. Furthermore, we were satisfied to find that four- to seven-membered aliphatic rings, as well as a six-membered oxo-heterocyclic ring were tolerated in this transformation, giving the corresponding carbazole derivatives **4f–j** in moderate yields. As for the photoreaction of non-substituted phenylamine (**3k**), the carbazole product **4k** was isolated in 25% yield, indicating that this photoreaction was applicable to primary phenylamines, albeit in a weak manner.

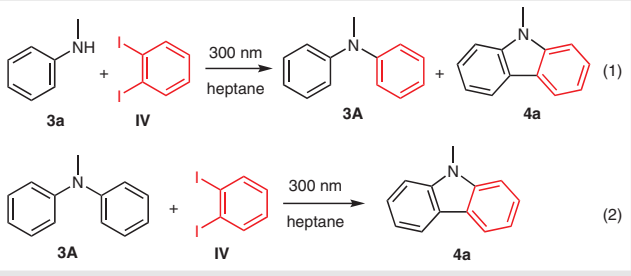
Next, diverse structural variations of R^1 and R^2 were evaluated. For example, compound **3l** bearing a strong electron-withdrawing cyano group at the *para* position afforded the desired product **4l** in a low yield of 23%. Similarly, *p*-halo- and *p*-trifluoromethyl-substituted substrates were also tolerated under the photoreaction conditions, providing the corresponding products **4m**, **4n** and **4o** in 52%, 50% and 34% yields, respectively. In addition, substrates **3p** and **3q** furnished products **4p** and **4q** in yields of 30% and 28%, respectively. Remarkably, the substrate scope could be extended to tetrahydroquinoline (**3r**), which was successfully transformed into product **4r** in a moderate 53% yield. Furthermore, substrate **3s** bearing a *meta*-chlorine atom gave a mixture of two regioisomers **4s** and **4s′** in a ratio of 1:1, while the *meta*-methyl-substituted reactant **3t** provided **4t** and **4t′** in a ratio of 3:5 and an overall yield of 52%.[13d,e,14] According to the literature,[13d,e] *o*- substituted compounds could also afford two products. As expected, the *o*-methyl-substituted substrate **3u** delivered two carbazole derivatives: 1,9-dimethyl-9*H*-carbazole (**4u**) and product **4a**, which may be generated via elimination of the methyl group. As for substrate **3v** with a bulkier *o*-*tert*-butyl group, **4a** was obtained as the exclusive product, probably due to the strong steric effect.

In order to gain more insight into this photochemical reaction, control experiments were carried out by using **3a** as a model substrate with 1,2-diiodobenzene (**IV**). To our delight, after a reduced irradiation time of 2 hours, a small amount of *N*-methyl-*N*-phenylaminobenzene (**3A**) was isolated (Scheme 4, eq 1). A deeper investigation identified **3A** as an important intermediate which could be finally converted into the carbazole **4a** when exposed to the standard reaction conditions (Scheme 2, eq 2).

Based on the control experiments and the relevant literature,[8a,10,11] a tentative reaction mechanism is proposed in Scheme 5. Upon absorbing the energy of UV light, 1,2-diiodobenzene (**IV**) is excited to form the benzyne interme-



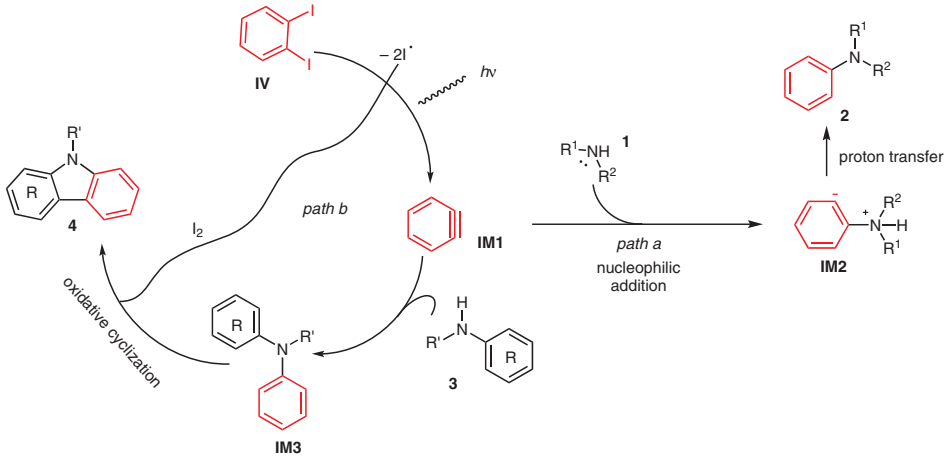
Scheme 3 Photoinduced preparation of carbazole derivatives. Unless otherwise noted, all reactions were conducted under the optimized conditions: **3** (0.2 mmol), **IV** (0.1 mmol) in heptane (10 mL), glass tube, N_2 atmosphere, λ = 300 nm, 8–12 h; reactions were monitored by TLC. Yields are those of isolated products. [a] The ratio of the generated mixture was determined by NMR spectroscopy.



Scheme 4 Control experiments

diate **IM1** by eliminating two iodine radicals, which probably couple with each other to afford an iodine molecule. On the other hand, as a good nucleophile, the nitrogen lone pair electrons of amine **1** interact with the triple bond of **IM1** to deliver **IM2**. An intramolecular proton transfer in **IM2** then takes place to give tertiary aminobenzene product **2** (Scheme 5, path a). As for aminobenzene **3**, formation of the tertiary aminobenzene **IM3** is followed by an oxidative cyclization process, with the generated iodine as an oxidant, to give the final carbazole derivative **4** (Scheme 5, path b).

In summary, we have developed a novel cross-coupling reaction to achieve the arylation of secondary aliphatic amines as well as secondary aminobenzenes. This synthetic protocol provides an efficient method to access tertiary aminobenzenes and carbazoles. Moreover, the reaction is triggered by UV light and the developed conditions are mild and tolerate readily accessible starting materials. Mechanistic investigations disclosed that the generated benzyne intermediate was trapped by the secondary amine nucleophiles to give the tertiary adducts, while the final carbazole products were produced by oxidative cyclization of diphenylamines, which were generated from the secondary aminobenzenes in a one-pot reaction.



Scheme 5 Proposed mechanism

All solvents were purified according to the reported procedures.[15] Thin-layer chromatography (TLC) was performed with Merck GF254 silica gel precoated TLC plates. Flash column chromatography was performed using Merck silica gel (200–300 mesh), eluting with petroleum ether/EtOAc. Melting points were determined using a Mettler–Toledo capillary melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on a Bruker AV-400 instrument, with $CDCl_3$ as the solvent and TMS as the internal standard. ^{1}H NMR chemical shifts are reported in parts per million relative to the chemical shift of $CDCl_3$ at 7.26 ppm, followed by multiplicity (standard abbreviations) and integration. ^{13}C NMR spectra are reported relative to the central signal of the $CDCl_3$ triplet at 77.16 ppm. HRMS (ESI) spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

Cross-Coupling Products 2; General Procedure

Under an N_2 atmosphere, substrate **1** (0.2 mmol) and 1,2-diiodobenzene (**IV**) (0.1 mmol) were placed in a dry glass tube. Heptane (10 mL) was added and the well-stirred mixture was irradiated under UV light (300 nm) until the reaction was complete (TLC monitoring). The solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford the coupling product **2**.

N-Benzyl-*N*-isopropylaniline (2a)

Yield: 16.2 mg (72%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 4 H), 7.28–7.18 (m, 3 H), 6.79–6.68 (m, 3 H), 4.45 (s, 2 H), 4.30 (dq, *J* = 13.2, 6.6 Hz, 1 H), 1.25 (d, *J* = 6.6 Hz, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.41, 140.90, 129.23, 128.53, 126.52, 126.36, 116.51, 113.31, 48.52, 48.30, 20.00.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}NNa$: 248.1410; found: 248.1415.

N,*N*-Diethylaniline (2b)

Yield: 10.9 mg (73%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.22 (m, 2 H), 6.73 (d, *J* = 8.1 Hz, 2 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 3.39 (q, *J* = 7.1 Hz, 4 H), 1.26–1.16 (m, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.92, 129.37, 115.50, 112.01, 44.44, 12.68.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{16}N$: 150.1277; found: 150.1272.

N,*N*-Diisopropylaniline (2c)

Yield: 6.2 mg (35%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 8.4, 7.4 Hz, 2 H), 6.93 (d, *J* = 8.1 Hz, 2 H), 6.81 (t, *J* = 7.2 Hz, 1 H), 3.80 (sept, *J* = 6.7 Hz, 2 H), 1.24 (d, *J* = 6.7 Hz, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.11, 128.53, 119.66, 118.48, 47.73, 21.46.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{20}N$: 178.1590; found: 178.1592.

1-Phenylpiperidine (2d)

Yield: 10.1 mg (63%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.23 (m, 2 H), 6.96 (d, *J* = 7.9 Hz, 2 H), 6.83 (t, *J* = 7.3 Hz, 1 H), 3.20–3.13 (m, 4 H), 1.72 (dt, *J* = 11.3, 5.7 Hz, 4 H), 1.58 (qd, *J* = 6.3, 2.2 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.39, 129.13, 119.33, 116.68, 50.83, 26.00, 24.46.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{16}N$: 162.1277; found:162.1275.

N-Cyclohexyl-*N*-methylaniline (2e)

Yield: 10.6 mg (56%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.21 (m, 2 H), 6.81 (d, *J* = 8.3 Hz, 2 H), 6.71 (t, *J* = 7.2 Hz, 1 H), 3.59 (tt, *J* = 11.3, 3.4 Hz, 1 H), 2.80 (s, 3 H), 1.90–1.78 (m, 4 H), 1.71 (d, *J* = 13.0 Hz, 1 H), 1.43 (qdd, *J* = 12.7, 10.7, 2.6 Hz, 4 H), 1.22–1.10 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.31, 129.21, 116.37, 113.31, 58.28, 31.29, 30.18, 26.35, 26.09.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{20}N$: 190.1590; found: 190.1585.

4-Phenylmorpholine (2f)

Yield: 11.4 mg (70%); white solid; mp 49.0–49.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (dt, *J* = 9.8, 4.9 Hz, 2 H), 6.91 (dd, *J* = 17.8, 7.7 Hz, 3 H), 3.88 (dd, *J* = 10.7, 5.9 Hz, 4 H), 3.22–3.11 (m, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.42, 129.32, 120.18, 115.85, 67.08, 49.50.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{14}NO$: 164.1070; found: 164.1065.

1,4-Diphenylpiperazine (2g)

Yield: 10.5 mg (44%); white solid; mp 153.5–154.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 8.6, 7.4 Hz, 4 H), 6.99 (d, *J* = 7.9 Hz, 4 H), 6.90 (t, *J* = 7.3 Hz, 2 H), 3.35 (s, 8 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.41, 129.34, 120.21, 116.49, 49.58.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}N_2$: 239.1543; found: 239.1545.

1-Phenylindoline (2h)

Yield: 9.8 mg (50%); pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.33 (m, 2 H), 7.24 (dd, *J* = 7.3, 6.4 Hz, 2 H), 7.18 (dd, *J* = 15.5, 6.0 Hz, 2 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 7.01–6.95 (m, 1 H), 6.76 (td, *J* = 7.3, 0.9 Hz, 1 H), 3.97 (t, *J* = 8.5 Hz, 2 H), 3.14 (t, *J* = 8.4 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.14, 144.23, 131.38, 129.27, 127.18, 125.15, 121.00, 118.93, 117.73, 108.21, 52.18, 28.28.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}N$: 196.1121; found: 196.1119.

Carbazoles 4; General Procedure

Under an N_2 atmosphere, substrate **3** (0.2 mmol) and 1,2-diiodobenzene (**IV**) (0.1 mmol) were placed in a dry glass tube. Heptane (10 mL) was added and the well-stirred mixture was irradiated under UV light (300 nm) until the reaction was complete (TLC monitoring). The solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford the corresponding carbazole **4**.

9-Methyl-9*H*-carbazole (4a)

Yield: 12.9 mg (71%); white solid; mp 91.5–92.5 °C. The yield of **4a** starting from **3v** was 6.7 mg (37%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.8 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 8.1 Hz, 2 H), 7.30–7.20 (m, 2 H), 3.87 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.11, 125.80, 122.89, 120.44, 118.95, 108.55, 29.22.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{12}N$: 182.0964; found: 182.0964.

9-Ethyl-9*H*-carbazole (4b)

Yield: 10.2 mg (52%); white solid; mp 69–70 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.8 Hz, 2 H), 7.64–7.39 (m, 4 H), 7.28 (t, *J* = 7.4 Hz, 2 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 1.47 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.03, 125.72, 123.03, 120.54, 118.85, 108.54, 77.37, 76.95, 37.62, 13.93.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}N$: 196.1121; found: 196.1120.

9-Allyl-9*H*-carbazole (4c)

Yield: 5.0 mg (24%); white solid; mp 52–53 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.8 Hz, 2 H), 7.46 (t, *J* = 7.3 Hz, 2 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.24 (d, *J* = 7.1 Hz, 2 H), 6.01 (ddd, *J* = 21.9, 10.1, 4.9 Hz, 1 H), 5.17 (d, *J* = 9.3 Hz, 1 H), 5.05 (d, *J* = 18.1 Hz, 1 H), 4.97–4.89 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.52, 132.45, 125.83, 123.07, 120.49, 119.16, 116.93, 108.91, 45.41.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}N$: 208.1121; found: 208.1115.

9-Isopropyl-9*H*-carbazole (4d)

Yield: 10.0 mg (48%); white solid; mp 120.5–121.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.8 Hz, 2 H), 7.53 (t, *J* = 9.0 Hz, 2 H), 7.49–7.42 (m, 2 H), 7.23 (t, *J* = 7.4 Hz, 2 H), 5.08–4.94 (m, 1 H), 1.73 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.54, 125.45, 123.40, 120.45, 118.63, 110.10, 46.78, 20.95.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}N$: 210.1277; found: 210.1277.

9-Benzyl-9*H*-carbazole (4e)

Yield: 10.8 mg (42%); white solid; mp 121.5–122.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.8 Hz, 2 H), 7.47–7.42 (m, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.30–7.22 (m, 5 H), 7.19–7.14 (m, 2 H), 5.53 (s, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.78, 137.30, 128.90, 127.57, 126.53, 125.98, 123.14, 120.52, 119.33, 109.02, 46.67.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}N$: 258.1277; found: 258.1271.

9-Cyclobutyl-9*H*-carbazole (4f)

Yield: 12.6 mg (57%); white solid; mp 100.5–101.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.8 Hz, 2 H), 7.60 (d, *J* = 8.3 Hz, 2 H), 7.49–7.41 (m, 2 H), 7.23 (dd, *J* = 11.0, 3.9 Hz, 2 H), 5.20 (quin, *J* = 8.8 Hz, 1 H), 3.18–2.96 (m, 2 H), 2.73–2.58 (m, 2 H), 2.16–1.93 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.23, 125.49, 123.40, 120.41, 118.88, 110.32, 50.13, 29.40, 15.37.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}N$: 222.1277; found: 222.1275.

9-Cyclopentyl-9*H*-carbazole (4g)

Yield: 14.1 mg (60%); white solid; mp 76.5–77.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.7 Hz, 2 H), 7.45 (ddd, *J* = 12.3, 9.5, 4.7 Hz, 4 H), 7.25–7.19 (m, 2 H), 5.16 (quin, *J* = 8.9 Hz, 1 H), 2.49–2.31 (m, 2 H), 2.23–2.01 (m, 4 H), 1.96–1.78 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.73, 125.42, 123.38, 120.49, 118.68, 109.94, 55.81, 29.15, 25.49.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{17}NNa$: 258.1253; found: 258.1252.

9-Cyclohexyl-9*H*-carbazole (4h)

Yield: 10.2 mg (41%); white solid; mp 142–143 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.7 Hz, 2 H), 7.61 (d, *J* = 8.2 Hz, 2 H), 7.48 (t, *J* = 7.7 Hz, 2 H), 7.26 (dd, *J* = 9.8, 5.1 Hz, 2 H), 4.54 (tt, *J* = 12.1, 3.6 Hz, 1 H), 2.52–2.38 (m, 2 H), 2.04 (t, *J* = 13.2 Hz, 4 H), 1.90 (d, *J* = 12.8 Hz, 1 H), 1.65–1.53 (m, 2 H), 1.50–1.40 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.81, 125.37, 123.38, 120.39, 118.60, 110.34, 55.51, 30.86, 26.66, 25.82.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{20}N$: 250.1590; found: 250.1589.

9-Cycloheptyl-9*H*-carbazole (4i)

Yield: 10.5 mg (40%); white solid; mp 145–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.7 Hz, 2 H), 7.58 (d, *J* = 8.2 Hz, 2 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 7.28 (t, *J* = 7.4 Hz, 2 H), 4.75 (tt, *J* = 11.0, 4.0 Hz, 1 H), 2.65–2.44 (m, 2 H), 2.13 (ddd, *J* = 13.5, 7.2, 3.3 Hz, 2 H), 1.98 (dt, *J* = 9.6, 6.3 Hz, 2 H), 1.92–1.68 (m, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.53, 125.38, 123.29, 120.42, 118.57, 100.06, 57.48, 33.20, 27.89, 26.58.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{22}N$: 264.1747; found: 264.1749.

9-(Tetrahydro-2*H*-pyran-4-yl)-9*H*-carbazole (4j)

Yield: 12.6 mg (50%); white solid; mp 217.5–218.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 7.7 Hz, 2 H), 7.61 (d, *J* = 8.3 Hz, 2 H), 7.52–7.44 (m, 2 H), 7.26 (t, *J* = 7.4 Hz, 2 H), 4.75 (tt, *J* = 12.4, 4.3 Hz, 1 H), 4.25 (dd, *J* = 11.6, 4.7 Hz, 2 H), 3.67 (td, *J* = 12.1, 1.8 Hz, 2 H), 2.82 (qd, *J* = 12.6, 4.7 Hz, 2 H), 1.88 (dd, *J* = 12.9, 2.5 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.54, 125.60, 123.48, 120.53, 118.99, 110.07, 68.17, 52.36, 30.62.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{18}NO$: 252.1383; found: 252.1385.

9*H*-Carbazole (4k)

Yield: 4.2 mg (25 %); white solid; mp 243–244 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (t, *J* = 9.3 Hz, 3 H), 7.48–7.41 (m, 4 H), 7.30–7.22 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.59, 125.97, 123.47, 120.47, 119.58, 110.71.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{10}N$: 168.0808; found: 168.0805.

9-Methyl-9*H*-carbazole-3-carbonitrile (4l)

Yield: 4.7 mg (23%); white solid; mp 92–93 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 1.0 Hz, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 7.71 (dd, *J* = 8.5, 1.5 Hz, 1 H), 7.60–7.54 (m, 1 H), 7.45 (t, *J* = 8.8 Hz, 2 H), 7.36–7.30 (m, 1 H), 3.89 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 142.70, 141.65, 129.12, 127.33, 125.34, 123.07, 121.96, 120.83, 120.78, 120.57, 109.27, 109.24, 101.68, 29.49.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}N_2$: 207.0917; found: 207.0915.

1-Fluoro-9-methyl-9*H*-carbazole (4m)

Yield: 10.3 mg (52%); white solid; mp 150–151 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.8 Hz, 1 H), 7.75 (dd, *J* = 8.9, 2.5 Hz, 1 H), 7.50 (t, *J* = 7.7 Hz, 1 H), 7.40 (d, *J* = 8.2 Hz, 1 H), 7.31 (dd, *J* = 8.8, 4.2 Hz, 1 H), 7.22 (ddd, *J* = 11.4, 7.2, 2.7 Hz, 2 H), 3.85 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.39 (d, *J* = 234.9 Hz), 141.91, 137.50, 126.39, 123.22 (d, *J* = 9.6 Hz), 122.44 (d, *J* = 4.1 Hz), 120.68, 118.92, 113.49 (d, *J* = 25.5 Hz), 109.02 (d, *J* = 9.1 Hz), 108.85, 106.14 (d, *J* = 23.7 Hz), 29.39.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}FN$: 200.0870; found: 200.0872.

3-Chloro-9-methyl-9*H*-carbazole (4n)

Yield: 10.8 mg (50%); white solid; mp 40–41 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 4.7, 2.8 Hz, 2 H), 7.57–7.50 (m, 1 H), 7.47–7.40 (m, 2 H), 7.34–7.27 (m, 2 H), 3.84 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.51, 139.38, 126.49, 125.78, 124.43, 123.93, 121.95, 120.60, 120.11, 119.32, 109.50, 108.81, 29.29.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}ClN$: 216.0575; found: 216.0580.

9-Methyl-3-(trifluoromethyl)-9*H*-carbazole (4o)

Yield: 8.5 mg (34%); white solid; mp 55.5–56.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (s, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 7.71 (dd, *J* = 8.6, 1.1 Hz, 1 H), 7.58–7.51 (m, 1 H), 7.45 (d, *J* = 8.3 Hz, 2 H), 7.34–7.28 (m, 1 H), 3.88 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 142.46, 141.70, 126.79, 125.48 (q, *J* = 271.2 Hz), 121.18 (q, *J* = 32.2 Hz), 122.51, 122.49, 122.65 (q, *J* = 3.6 Hz), 120.69, 119.93, 117.98 (q, *J* = 4.1 Hz), 109.03, 108.61, 29.41.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}F_3N$: 250.0838; found: 250.0836.

3-Methoxy-9-methyl-9*H*-carbazole (4p)

Yield: 6.3 mg (30%); white solid; mp 97.5–98.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.8 Hz, 1 H), 7.60 (d, *J* = 2.4 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.37 (d, *J* = 8.2 Hz, 1 H), 7.31 (d, *J* = 8.8 Hz, 1 H), 7.20 (t, *J* = 7.4 Hz, 1 H), 7.13 (dd, *J* = 8.8, 2.5 Hz, 1 H), 3.94 (s, 3 H), 3.84 (d, *J* = 6.0 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.69, 141.62, 136.23, 125.77, 123.14, 122.68, 120.38, 118.46, 114.93, 109.24, 108.66, 103.46, 56.29, 29.32.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}NO$: 212.1070; found: 212.1069.

5-Methyl-5*H*-[1,3]dioxolo[4,5-*b*]carbazole (4q)

Yield: 6.3 mg (28%); white solid; mp 127–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.8 Hz, 1 H), 7.47 (s, 1 H), 7.37 (q, *J* = 7.3 Hz, 2 H), 7.21–7.14 (m, 1 H), 6.89 (s, 1 H), 6.02 (s, 2 H), 3.79 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.48, 142.14, 140.85, 136.91, 124.17, 123.07, 119.40, 118.77, 115.86, 108.54, 101.16, 99.71, 90.27, 29.47.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{12}NO_2$: 226.0863; found: 226.0865.

5,6-Dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole (4r)

Yield: 11.0 mg (53%); white solid; mp 86–87 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.8 Hz, 1 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.52–7.42 (m, 1 H), 7.36 (d, *J* = 8.1 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 7.3 Hz, 1 H), 4.27–4.12 (m, 2 H), 3.06 (t, *J* = 6.1 Hz, 2 H), 2.29 (dt, *J* = 12.0, 6.0 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.95, 137.89, 125.35, 123.08, 122.92, 120.97, 120.95, 120.63, 118.84, 118.60, 118.06, 108.30, 41.04, 25.04, 22.51.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}NNa$: 230.0940; found: 230.0933.

2-Chloro-9-methyl-9*H*-carbazole (4s) and 4-Chloro-9-methyl-9*H*-carbazole (4s')

Combined yield (1:1 mixture of regioisomers): 10.3 mg (48%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 7.9 Hz, 0.47 H), 8.04 (d, *J* = 7.8 Hz, 0.47 H), 7.96 (d, *J* = 8.3 Hz, 0.45 H), 7.56–7.45 (m, 1 H), 7.38 (dd, *J* = 17.0, 9.1 Hz, 2 H), 7.32–7.23 (m, 1.69 H), 7.20 (ddd, *J* = 9.9, 6.3, 1.3 Hz, 1 H), 3.82 (dd, *J* = 13.7, 5.4 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 142.17, 141.65, 141.38, 141.10, 131.57, 128.90, 126.35, 126.10, 125.99, 123.19, 122.37, 121.91, 121.47, 121.21, 120.38, 120.10, 119.80, 119.51, 119.47, 119.44, 108.78, 108.76, 108.39, 106.92, 29.40, 29.29.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{11}ClN$: 216.0575; found: 216.0585.

2,9-Dimethyl-9*H*-carbazole (4t) and 4,9-Dimethyl-9*H*-carbazole (4t')

Combined yield (3:5 mixture of regioisomers): 10.1 mg (52%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 7.9 Hz, 0.64 H), 8.20–8.02 (m, 0.78 H), 7.67–7.28 (m, 4.77 H), 7.21–7.06 (m, 1 H), 3.85 (d, *J* = 11.9 Hz, 3 H), 3.06–2.95 (m, 1.91 H), 2.67 (s, 1.15 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.52, 141.12, 141.09, 140.99, 135.90, 133.47, 125.54, 125.19, 125.11, 123.49, 122.95, 122.65, 121.35, 120.56, 120.44, 120.06, 120.05, 118.88, 118.81, 108.75, 108.40, 108.26, 106.10, 29.09, 28.99, 22.39, 20.94.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}N$: 196.1121; found: 196.1126.

9-Methyl-9*H*-carbazole (4a) and 1,9-Dimethyl-9*H*-carbazole (4u)

Combined yield (6:1 mixture of regioisomers): 7.3 mg (40%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.8 Hz, 2 H), 8.09 (d, *J* = 7.8 Hz, 0.18 H), 7.97 (d, *J* = 7.6 Hz, 0.18 H), 7.55–7.49 (m, 2 H), 7.48–7.46 (m, 0.18 H), 7.42 (d, *J* = 8.2 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 0.19 H), 7.32–7.25 (m, 2 H), 7.24–7.21 (m, 0.17 H), 7.20 (d, *J* = 7.0 Hz, 0.17 H), 7.13 (t, *J* = 7.4 Hz, 0.18 H), 4.13 (s, 0.5 H), 3.87 (s, 3 H), 2.88 (s, 0.5 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.75, 141.10, 139.81, 128.92, 125.79, 125.68, 123.63, 123.03, 122.87, 120.50, 120.43, 120.11, 119.17, 118.97, 118.94, 118.34, 108.65, 108.54, 32.42, 29.19, 20.52.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}N$: 196.1121; found: 196.1124.

***N*-Methyl-*N*-phenylaniline (3A)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.35 (m, 4 H), 7.16 (dd, *J* = 8.6, 0.9 Hz, 4 H), 7.08 (t, *J* = 7.3 Hz, 2 H), 3.43 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.12, 129.27, 121.35, 120.53, 40.30.

The analytical data match those reported in the literature.[2c]

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609444.

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