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Assessing Carbazole Derivatives as Single-Electron Photoreductants

Tyler D. Weinhold, Natalie A. Reece,‡ Kevin Ribeiro,‡ Maredh Lopez Ocasio, Noelle Watson, Kenneth Hanson, and Ashley R. Longstreet*

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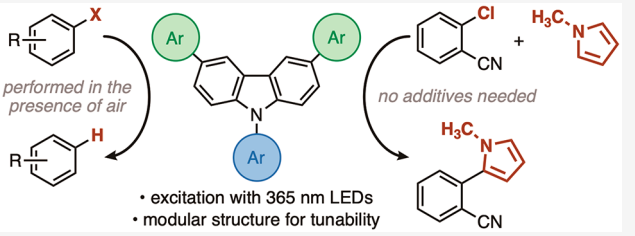
ABSTRACT: The electron-donating capabilities of carbazoles have stimulated interest in their use as photoinduced single-electron reductants. Due to the modularity of the carbazole, a further broadening and understanding of their reactivity could be achieved by manipulating the structure. Herein, eight carbazole derivatives were synthesized, characterized, and assessed as single-electron photoreductants in the hydrodehalogenation of aryl halides and the arylation of *N*-methylpyrrole.



Since their discovery in 1872,[1] carbazoles have been utilized across multiple disciplines for potential medicinal[2] and opto/electronic applications[3] due in part to their modular structure and unique physical properties. The strong excited state reducing capabilities of carbazole derivatives have also facilitated their involvement in photochemical reactions.[4−14] Simple carbazoles such as carbazoles **1a−c** and **2a** (Figure 1)

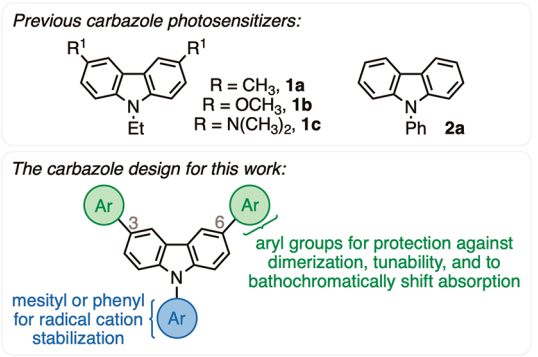


Figure 1. Examples of carbazole derivatives used as single-electron photoreductants.

make excellent single-electron reductants due to their excited state reduction potentials ranging from as low as −2.75 (**1c**)[8] to −1.91 V (**2a**)[15] vs SCE, enabling their ability to participate as photosensitizers in the reduction of secondary benzoates and *m*-(trifluoromethyl)benzoates[10−13,16] and aryl chlorides.[8]

While previously reported carbazoles **1a−c** and **2a** (Figure 1) have promising characteristics,[8,11−13] there are some limitations. For example, excitation of carbazoles **1a** and **1b** requires high energy, ultraviolet light, and specialized glassware.[11−13] Such light sources are typically expensive, and the high-energy, short wavelengths of light can cause undesirable side reactions to occur. Carbazoles that lack substitution in the 3 and 6 positions, such as carbazole **2a** (Figure 1), are also known to dimerize or undergo other side reactions upon oxidization.[15,17−19] This leads to short radical cation lifetimes and limits the electrochemical reversibility necessary for photocatalysts. Carbazole **1c** is a powerful photoreductant, but the same amine groups that give the carbazole its reducing power also cause the oxidation potential of the radical cation to be low (+0.27 V vs SCE)[8] in comparison to other carbazoles (+0.84 and +1.423 V vs SCE for **1b** and **2a**, respectively),[8,15] which can limit its reversibility.

Due to their demonstrated potential to facilitate photoinduced single-electron reductions, our group focused on developing a library of carbazole derivatives with a modular structure and favorable photophysical and electrochemical properties to study how different functionalities affect their reactivity and to broaden their application as photosensitizers. Herein, we report the synthesis and photophysical characterization of eight carbazole derivatives. The derivatives were then evaluated as photocatalysts in the hydrodehalogenation of aryl halides and the arylation of *N*-methylpyrrole.

The carbazole design included the addition of aryl groups at positions 3 and 6 to protect against irreversible dimerization and to bathochromically shift absorption (Figure 1). The installation of electron-rich or -poor aryl groups also enables tuning of the redox properties of the carbazole. In addition, the design incorporated a phenyl or mesityl group on the carbazole nitrogen (Figure 1) to stabilize the radical cation[18] and sterically protect the radical intermediate from dimerization and other side reactions.

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Scheme 1. Synthesis of Carbazole Derivatives 3a−h

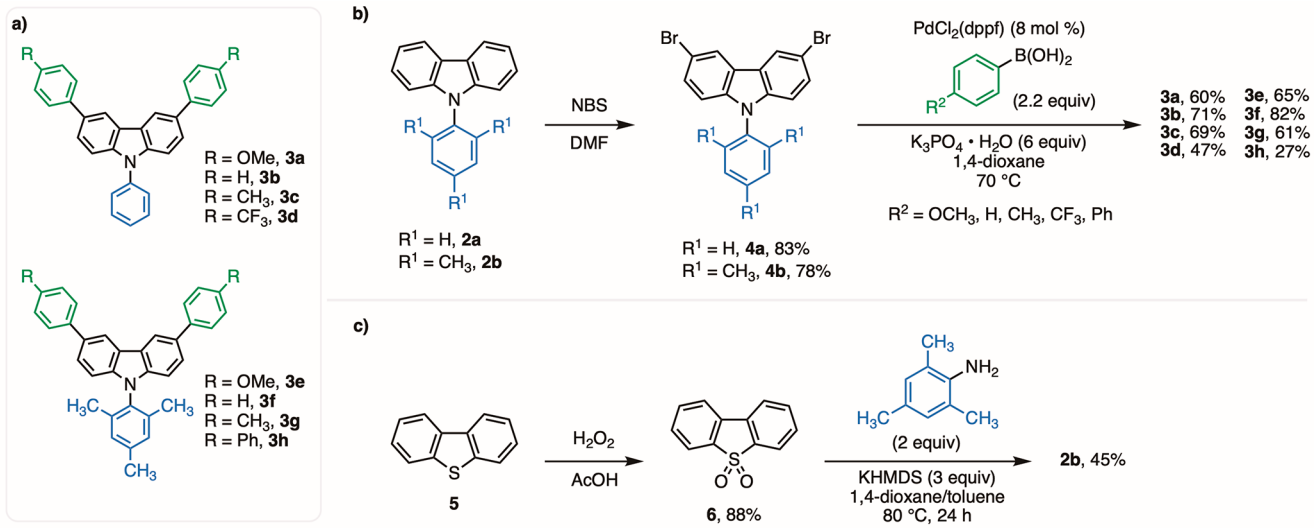

Table 1. Photophysical Data for Carbazoles 3a−h in MeCN

carbazole	λ_{abs} (nm)	λ_{em} (nm)	τ (ns)[a]	Φ_F	k_r ($\times 10^7$ s^{-1})[b]	k_{nr} ($\times 10^8$ s^{-1})[c]	$E_{1/2}$ ($PC^{+\bullet}/PC$) (V vs SCE)	$E_{1/2}$ ($PC^{+\bullet}/PC^*$) (V vs SCE)[d]
3a	262	398	6.8	0.15	2.1	1.3	1.00	−2.12
3b	258	388	6.9	0.16	2.3	1.2	1.13	−2.07
3c	260	392	6.8	0.15	2.3	1.2	1.09	−2.07
3d	298	386	6.0	0.21	3.4	1.3	1.27	−1.95
3e	262	398	7.0	0.09	1.2	1.3	1.00	−2.11
3f	258	387	7.1	0.10	1.4	1.3	1.15	−2.05
3g	259	390	7.3	0.18	2.5	1.1	1.10	−2.08
3h	298	393	6.1	0.28	4.5	1.2	1.16	−2.00

[a]Lifetime of excited states determined from single-exponential fits. [b]Radiative decay (k_r) calculated using $k_r = \Phi_F/\tau$. [c]Nonradiative decay (k_{nr}) calculated using $k_{nr} = (1 - \Phi_F)/\tau$. [d]Calculated using eq 1 in the Supporting Information.

The eight carbazole derivatives (**3a−h**, Scheme 1a) were synthesized from the parent carbazole (**2a** and **2b**) in two steps starting with the bromination of the 3 and 6 positions with *N*-bromosuccinimide (NBS) to generate carbazole **4a** and **4b** in 83% and 78% yields, respectively (Scheme 1b). Once brominated, carbazoles **4a** and **4b** were derivatized further by installing aryl groups in the 3 and 6 positions through a Suzuki coupling of commercially available boronic acids to produce carbazoles **3a−h** in 27−82% yield. The low yield observed for **3h** was likely due to the loss of the product after multiple purification attempts by both column chromatography and recrystallization.

While the parent carbazole bearing the *N*-phenyl group (**2a**) was commercially available, the other parent containing the *N*-mesityl group (**2b**) was synthesized in two steps from dibenzothiophene (**5**, Scheme 1c). Dibenzothiophene (**5**) was first oxidized to sulfone **6** in 88% yield using hydrogen peroxide. The *N*-mesityl group could then be installed to sulfone **6** using an adapted procedure reported by Bhanuchandra et al. to produce the desired carbazole **2b** in 45% yield.[20]

Next, we turned our attention toward the photophysical properties of carbazoles **3a−h**. The absorbance maxima (λ_{abs}) for carbazoles **3a−h** are in the 250−300 nm range (Table 1) with an additional lower energy absorbance observed between 360 and 370 nm (Figures S3−S10), enabling excitation with 365 nm light-emitting diodes (LEDs). All compounds emit at ∼390 nm with lifetimes (τ) of 6−7 ns. The small Stokes shift, nanosecond lifetime, and lack of excited state quenching by oxygen (vida infra) are consistent with fluorescence from the singlet excited state of the molecules. The >1 ns lifetime is advantageous for bimolecular photoinduced electron transfer (PET) events.[21] In fact, Stern−Volmer analysis indicated that the excited state of carbazole **3a** is readily quenched by 4-bromobenzonitrile (**7a**), presumably via a PET mechanism (Figure S2). The excited state reduction potentials ranged from −1.95 to −2.12 V vs SCE (Table 1) with the most positive and negative being with the electron-withdrawing CF_3 and electron-donating OCH_3 substituents, respectively.

The quantum yield of florescence (Φ_F) values varied from 0.09 to 0.28 for carbazoles **3a−h** (Table 1). When comparing *N*-phenyl carbazoles **3a** and **3b** to their *N*-mesityl counterparts (**3e** and **3f**), a decrease in Φ_F was observed from 0.15 and 0.16 to 0.09 and 0.10, respectively. This decrease in value was not observed when comparing carbazole **3c** to **3g**. The increased conjugation in carbazole **3h** led to a higher Φ_F value of 0.28, which can be attributed to an increase in the radiative rate constant (k_r).

To demonstrate their photocatalytic capabilities, the carbazole derivatives were applied toward the hydrodehalogenation of aryl bromides and chlorides. The proposed mechanism would involve the reduction of the aryl halides to their corresponding aryl radicals via an oxidative quenching of the carbazole excited state (Scheme S1). Hydrogen-atom transfer (HAT) would then occur between the generated aryl radical and a hydrogen donor to produce the final product.[22]

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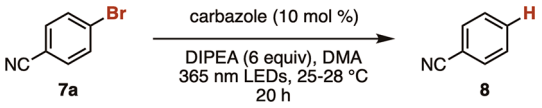
Under 365 nm irradiation and in the presence of *N*,*N*-diisopropylethylamine (DIPEA) as a hydrogen-atom donor, carbazoles **3a**–**d** reduced 4-bromobenzonitrile (**7a**) to benzonitrile (**8**) in 83–87% yield in 20 h (Table 2, entries 1–4). From the ^{1}H NMR spectrum, acetaldehyde was observed as a byproduct, which suggests DIPEA was acting as a hydrogen-atom donor. There was also no significant change in the yield between carbazole **3a** with the *N*-phenyl (85%, entry 1) versus carbazole **3e** with the *N*-mesityl (82%, entry 5). When commercially available carbazole **2a** was employed, benzonitrile (**8**) was only produced in 55% yield (entry 6) owing to the importance of the added aryl groups in the 3 and 6 positions. Both the carbazole and light were essential for the success of the reaction because their absence resulted in 7% yield (entry 7) and no reaction (entry 8), respectively. There was no significant difference in the yield when the reaction with carbazole **3a** was performed in the presence of air or sparged with Ar (entry 9), further supporting that the singlet excited state is responsible for the photoreactivity. When the loading of carbazole **3a** is reduced by one-half, the efficiency of hydrodehalogenation is maintained (entry 10).

Table 2. Screening Carbazoles 3a–e for Activity in the Hydrodehalogenation of 4-Bromobenzonitrile[a]

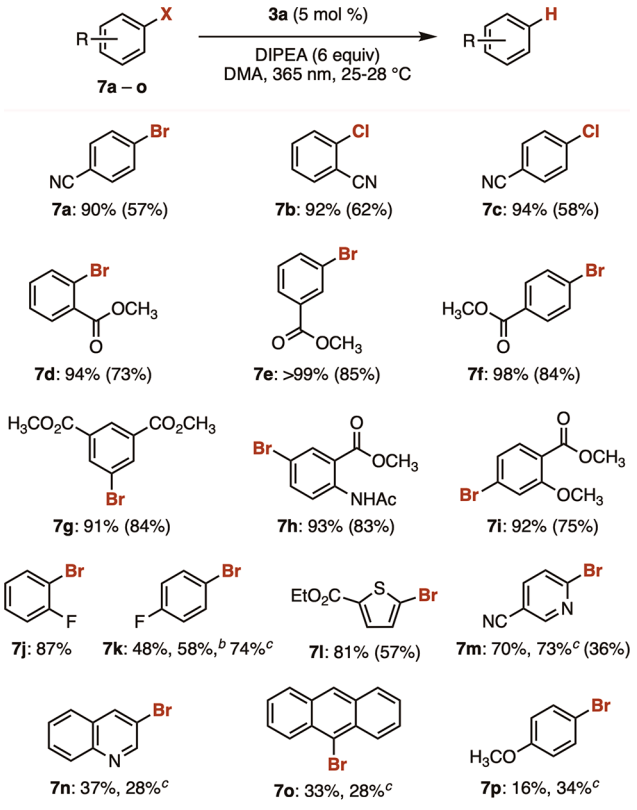


entry	carbazole	deviation from standard conditions	yield (%)[b]
1	**3a**		85 (87[c])
2	**3b**		85
3	**3c**		83
4	**3d**		87
5	**3e**		82
6	**2a**		55
7		no carbazole added	7
8	**3a**	no light or ambient light	NR
9	**3a**	sparged with Ar	84
10	**3a**	5 mol % (0.02 mmol) of **3a** was used	90[c]

[a]Reaction conditions: **7a** (0.4 mmol), carbazole (0.04 mmol), DIPEA (2.4 mmol), *N*,*N*-dimethylacetamide (DMA, 4 mL). Reactions were irradiated with 365 nm LEDs for 20 h. [b]Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]Yields determined by GC using dodecane as an internal standard. Internal standards were added after the reactions were removed from the 365 nm light source. NR = no reaction.

The hydrodehalogenation conditions with carbazole **3a** were then applied toward other aryl bromides and chlorides (Table 3). In addition to 4-bromobenzonitrile (**7a**), 2-chlorobenzonitrile (**7b**) and 4-chlorobenzonitrile (**7c**) were both readily reduced to benzonitrile (**8**) in 94% and 92% yields, respectively. Due to the volatility of **8**, isolated yields for substrates **7a**–**c** were >30% lower than the calibrated GC yields. Methyl benzoate substrates **7d**–**f** also reduced to methyl benzoate in 94–99% yield regardless of the position of the bromine substituent. Other benzoate derivatives including dimethyl 5-bromoisophthalate (**7g**) and methyl benzoates with the inclusion of moderate electron-donating groups (**7h** and **7i**) were also reduced in 91%, 93%, and 92% yields, respectively.

Table 3. Substrate Scope for the Hydrodehalogenation of Aryl Bromides and Chlorides[a]



[a]Reaction conditions: Substrates **7a**–**p** (0.4 mmol), **3a** (0.02 mmol), DIPEA (2.4 mmol), DMA (4 mL). Reactions were irradiated with 365 nm LEDs for 20 h. Yields determined by GC using dodecane as an internal standard. The internal standard was added after the reactions were removed from the 365 nm light source. Isolated yields were performed at a 1.0 mmol scale and are reported in parentheses. [b]Carbazole **3e** (0.02 mmol, 5 mol %) was used in lieu of **3a**. [c]Carbazole **3h** (0.02 mmol, 5 mol %) was used in lieu of **3a**.

When assessing *ortho*- and *para*-fluorobenzene derivatives **7j** and **7k**, carbazole **3a** was shown to generate the corresponding products in 87% and 48% yields, respectively. The electron-deficient thiophene (**7l**) and pyridine (**7m**) substrates were reduced to the corresponding products in 81% and 70% yields, respectively. However, the product from substrate **7m** could only be isolated in 36% yield due to a difficult separation between the product and the byproducts that formed due to the degradation of carbazole **3a**. The products of substrates **7n** and **7o** were observed to decompose in the presence of 365 nm light, which was attributed to their low yields. Lastly, carbazole **3a** could not readily reduce the electron-rich 4-bromoanisole (**7p**), producing the product in only 16% yield.

After identifying the more challenging substrates, we performed additional screenings to determine how well other carbazole derivatives reduced 1-bromo-4-fluorobenzene (**7k**, Table 3 and Table S1). When carbazole **3h** was employed as the photocatalyst, a significant improvement in yield was observed (74%) relative to that for **3a** (48%). When **3h** was applied toward other low-yielding substrates, the yield for substrate **7p** improved more than 2-fold from 16% to 34% (Table 3) while other substrates (**7m**–**o**) showed no significant improvements.

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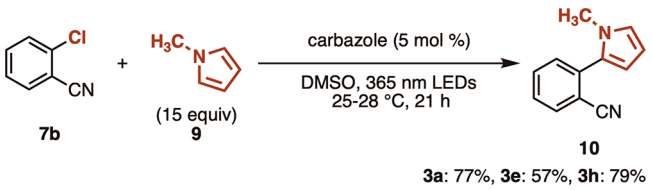
In the arylation of 5-membered heterocycles, highly reducing photocatalysts, such as carbazole **1c**, typically require the addition of a base or a sacrificial electron donor with a low oxidation potential to facilitate the reduction of the oxidized photocatalyst.[8,22−24] To assess the reversibility and whether the oxidation potentials of the radical cations for carbazoles **3a**, **3e**, and **3h** were sufficient to forego the need for such additives, we applied the carbazoles as photocatalysts in the arylation of *N*-methylpyrrole (**9**) with 2-chlorobenzonitrile (**7b**) (Scheme 2). After being irradiated for 21 h with 365 nm light, product **10** was produced in 77%, 57%, and 79% yield with carbazoles **3a**, **3e**, and **3h**, respectively.

Scheme 2. Arylation of *N*-Methylpyrrole (9) with 2-Chlorobenzonitrile (7b).[a]



[a]Reaction conditions: Substrate **7b** (0.5 mmol), carbazole (0.025 mmol), *N*-methylpyrrole (7.5 mmol), DMSO (5 mL). Reactions were sparged with Ar for 10 min before being irradiated with 365 nm light for 21 h. Isolated yields are shown.

In conclusion, we synthesized eight carbazole derivatives with varying photocatalytic capabilities. Their design allowed the carbazoles to successfully reduce electron-deficient aryl bromides and chlorides with a 365 nm light source and in the presence of air. In addition, the carbazoles could participate in the arylation of *N*-methylpyrrole without additional additives presumably due to the carbazoles exhibiting favorable oxidation potentials. The modularity of the carbazole will provide the opportunity for further improvements to the carbazole structure, and further experiments to understand the mechanism of the reaction process will allow us to explore and develop new, valuable chemical transformations.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from Sigma-Aldrich, Oakwood Chemicals, or Fisher Scientific and used as received without further purification unless otherwise noted. All reactions were performed with magnetic stirring and a preheated oil bath if heating was necessary. LED strip lights were purchased from Waveform Lighting (product number 7021.65). High-resolution mass spectra (HRMS) for substrates **3a−c** and **3e−g** were obtained through the Chemical Purification Analysis and Screening Core Facility (CPAS) at the University of South Florida (USF) on a QTOF mass spectrometer with direct infusion. HRMS for substrates **3d** and **3h** were obtained on an Orbitrap mass spectrometer with direct infusion. Elemental analysis was performed by Atlantic Microlabs. Melting points were measured using a DigiMelt MPA160 apparatus. Gas chromatography (GC) analysis was performed with a Thermo Fisher gas chromatograph equipped with a flame ionization detector (FID) and a 100% dimethyl polysiloxane column (0.25 mm diameter and 0.25 μm film thickness). ^{1}H, ^{13}C, and ^{18}F NMR spectra were obtained on a JEOL 400 MHz spectrometer. NMR chemical shifts are reported as δ values in ppm relative to TMS in $CDCl_3$ for all ^{1}H spectra, relative to $CDCl_3$ for all ^{13}C spectra, and relative to fluorobenzene (−112.96 ppm)[25] for all ^{18}F spectra. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, m = multiplet), coupling constants in Hertz (Hz), integration.

General Information for Photophysical Characterization. Absorption spectra were recorded on an Agilent 8453 UV−vis photodiode array spectrometer in a 1 × 1 cm quartz cuvette. An Edinburgh FLS980 fluorescence spectrometer was used to record steady-state emission data. Solutions of each sample were prepared using acetonitrile and measured in a 1 × 1 cm quartz cuvette at room temperature. Samples were excited using 295 nm light from a housed 450 W Xe lamp/single grating 1800 λ mm^{-1}, 250 nm blaze Czerny−Turner monochromator; the resulting sample emission was detected by a Peltier-cooled Hamamatsu R928 photomultiplier tube. Time-resolved emission data were collected using the same spectrometer employed for steady-state emission measurements. Time-correlated single-photon counting (TCSPC; 1024 channels) was used to acquire the emission decay traces with 10 000 counts collected for each lifetime measurement. An Edinburgh EPL-360 ps pulsed light-emitting diode (360 ± 10 nm, pulse width 892 ps) operated at 10 MHz was used to excite the samples. The Edinburgh software package was used to fit the emission decay data for each sample with a single-exponential function, $y = A_1 e^{-kx} + y_0$. A Hamamatsu Quantaurus-QY Spectrometer was used to measure the quantum yield of each sample at room temperature. Solutions of the samples were prepared using acetonitrile and measured in quartz tubes (12.5 cm long with a diameter of 0.8 cm). Samples were excited using 295 nm light from a 150 W xenon arc lamp. A back-illuminated cooled 1024 channel CCD detector was used to record the resulting sample emission.

Carbazole Synthesis. *Dibenzothiophene 5,5-Dioxide (**6**).* **6** was prepared according to a previously reported procedure with some modifications.[26] Dibenzothiophene (**5**, 9.21 g, 50 mmol), a solution of 30% hydrogen peroxide (26 mL), and acetic acid (8.6 mL, 150 mmol) were added a round-bottom flask with a stir bar. The round-bottom flask was equipped with a Vigreux column and heated to reflux. After 4 h, the reaction was cooled to room temperature. Once cooled, a white crystalline solid had formed and was collected by vacuum filtration. The solid was dried under high vacuum at 50 °C for 24 h to yield dibenzothiophene 5,5-dioxide (9.53 g, 88%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 7.7 Hz, 2H), 7.61 (td, J = 7.6, 1.2 Hz, 2H), 7.50 (td, J = 7.6, 1.1 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 137.6, 134.0, 131.6, 130.4, 122.2, 121.7. Spectra were in accordance with those described in the literature.[26]

*9-Mesityl-9H-carbazole (**2b**).* **2** was prepared according to a previously reported procedure with some modifications.[20] A round-bottom flask containing dibenzothiophene 5,5-dioxide (**6**, 5.41 g, 25.0 mmol) and a stir bar was dried under vacuum at 50 °C for 1 h. The flask was then placed under an Ar atmosphere by evacuating and filling the flask with Ar three times. To the flask was then added 1,4-dioxane (75 mL), 2,4,6-trimethylaniline (7.0 mL, 50 mmol), and then a 0.7 M KHMDS solution in toluene (110 mL, 77 mmol) at room temperature. The reaction was heated to 80 °C. After 18 h, the reaction was quenched with saturated NH_4Cl (20 mL). The reaction mixture was then passed through Celite (ca. 120 g) using Et_2O to rinse. The filtrate was concentrated under vacuum, and the resulting solid was recrystallized from Et_2O/MeOH to yield **2b** (3.20 g, 45%) as a tan crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H), 1.81 (s, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 140.6, 138.6, 137.9, 131.9, 129.5, 126.0, 123.0, 120.5, 119.4, 109.6, 21.3, 17.7. Spectra were in accordance with those described in the literature.[27]

*3,6-Dibromo-9-phenyl-9H-carbazole (**4a**).* NBS (13.1 g, 73.5 mmol) was slowly added to a solution of 9-phenyl-9*H*-carbazole (**2a**, 8.72 g, 35.9 mmol) in DMF (150 mL). After stirring overnight at room temperature, water (150 mL) was added to the mixture to precipitate the product. The product was collected by vacuum filtration and recrystallized from THF/MeOH to yield **4a** (11.9 g, 83%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 1.9 Hz, 2H), 7.58 (t, J = 7.6 Hz, 2H), 7.49−7.41 (m, 5H), 7.21 (d, J = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.9, 136.8, 130.2, 129.5, 128.2, 127.0, 124.0, 123.3, 113.1, 111.6. Spectra were in accordance with those described in the literature.[28]

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*3,6-Dibromo-9-mesityl-9H-carbazole (**4b**).* A solution of 9-mesityl-9*H*-carbazole (**2b**, 2.28 g, 8.00 mmol) in DMF (16 mL) was cooled in an ice bath before adding NBS (2.91 g, 16.4 mmol). After stirring overnight at room temperature, water (150 mL) was added to the mixture to precipitate the product. The product was collected by vacuum filtration and recrystallized from THF/MeOH to yield **4b** (2.76 g, 78%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.07 (s, 2H), 6.83 (d, J = 8.6 Hz, 2H), 2.41 (s, 3H), 1.78 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 139.5, 139.2, 137.5, 131.0, 129.7, 129.6, 123.6, 123.5, 112.7, 111.3, 21.3, 17.4. Anal. Calcd for $C_{21}H_{17}Br_2N$: C, 56.91; H, 3.87; N, 3.16. Found: C, 56.97; H, 3.90; N, 3.20. Mp 240−245 °C.

*3,6-Bis(4-methoxyphenyl)-9-phenyl-9H-carbazole (**3a**).* A Schlenk flask containing **4a** (6.02 g, 15.0 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.980 g, 1.20 mmol), K_3PO_4·H_2O (20.7 g, 90.0 mmol), 4-methoxyphenylboronic acid (5.01 g, 33.0 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with argon three times. To the flask was added anhydrous 1,4-dioxane (60 mL). The reaction was heated to 70 °C. After stirring overnight, the reaction mixture was passed through Celite using hexanes to rinse. The filtrate was concentrated under vacuum, and the product was purified by recrystallization (Et_2O/MeOH) to afford **3a** (4.12 g, 60%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 1.8 Hz, 2H), 7.69−7.55 (m, 10H), 7.50−7.41 (m, 3H), 7.04−6.99 (m, 4H), 3.86 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.8, 140.5, 137.8, 134.7, 133.3, 130.1, 128.4, 127.6, 127.0, 125.5, 124.1, 118.5, 114.4, 110.2, 55.5. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{26}NO_2$ 456.1958. Found: 456.1958. Mp 168−170 °C.

*3,6,9-Triphenyl-9H-carbazole (**3b**).* A Schlenk flask containing **4a** (1.00 g, 2.5 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.163 g, 0.200 mmol), K_3PO_4·H_2O (3.45 g, 15.00 mmol), phenylboronic acid (0.671 g, 5.50 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with argon three times. To the flask was added anhydrous 1,4-dioxane (10 mL). The reaction was heated to 70 °C. After stirring overnight, the reaction mixture was passed through Celite using hexanes to rinse. The filtrate was concentrated under vacuum, and the product was purified by recrystallization in CH_2Cl_2/MeOH to afford **3b** (0.703 g, 71%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, J = 1.8 Hz, 2H), 7.76−7.57 (m, 10H), 7.54−7.44 (m, 7H), 7.35 (t, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 142.0, 140.9, 137.7, 133.7, 130.1, 128.9, 127.7, 127.5, 127.1, 126.8, 125.8, 124.1, 119.0, 110.3. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{22}N$ 396.1747. Found: 396.1733. Mp 144−146 °C.

*9-Phenyl-3,6-di-p-tolyl-9H-carbazole (**3c**).* A Schlenk flask containing **4a** (1.00 g, 2.5 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.163 g, 0.200 mmol), K_3PO_4·H_2O (3.45 g, 15.00 mmol), *p*-tolylboronic acid (0.748 g, 5.50 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with argon three times. To the flask was added anhydrous 1,4-dioxane (10 mL). The reaction was heated to 70 °C. After stirring overnight, the reaction mixture was passed through Celite using hexanes to rinse. The filtrate was concentrated under vacuum, and the product was purified by recrystallization in CH_2Cl_2/MeOH to afford **3c** (0.728 g, 69%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 1.4 Hz, 2H), 7.68−7.56 (m, 10H), 7.50−7.43 (m, 3H), 7.32−7.25 (m, 4H), 2.41 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 140.7, 139.2, 137.8, 136.4, 133.6, 130.1, 129.7, 127.6, 127.3, 127.1, 125.6, 124.1, 118.7, 110.2, 21.2. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{26}N$ 424.2060. Found: 424.2060. Mp 165−168 °C.

*9-Phenyl-3,6-bis(4-(trifluoromethyl)phenyl)-9H-carbazole (**3d**).* A Schlenk flask containing **4a** (1.20 g, 3.0 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.196 g, 0.24 mmol), K_3PO_4·H_2O (4.15 g, 18.0 mmol), 4-(trifluoromethyl)phenylboronic acid (1.25 g, 6.60 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with argon three times. To the flask was added anhydrous 1,4-dioxane (8 mL). The reaction was heated to 70 °C. After stirring overnight, the reaction mixture was passed through Celite using hexanes to rinse. The filtrate was concentrated under vacuum, and the product was purified by recrystallization in Et_2O/MeOH to afford **3d** (0.744 g, 47%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 1.8 Hz, 2H), 7.83 (d, J = 8.3 Hz, 4H), 7.78−7.57 (m, 10H), 7.57−7.45 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.4, 141.5, 137.4, 132.4, 129.0, 128.7, 128.1, 127.6, 127.2, 125.9 (m), 124.1, 123.2, 119.3, 110.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.1 (s). HRMS (ESI/Orbitrap) m/z: $[M]^+$ calcd for $C_{32}H_{19}F_6N$ 531.1422. Found: 531.1414. Anal. Calcd for $C_{32}H_{19}F_6N$: C, 72.31; H, 3.60; N, 2.64. Found: C, 72.20; H, 3.70; N, 2.71. Mp 205−208 °C.

*9-Mesityl-3,6-bis(4-methoxyphenyl)-9H-carbazole (**3e**).* A Schlenk flask containing **4b** (1.33 g, 3.0 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.196 g, 0.24 mmol), K_3PO_4·H_2O (4.15 g, 18.0 mmol), 4-methoxyphenylboronic acid (1.00 g, 6.60 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with argon three times. To the flask was added anhydrous 1,4-dioxane (24 mL). The reaction was heated to 70 °C. After stirring overnight, the reaction mixture was passed through Celite using hexanes to rinse. The filtrate was concentrated under vacuum, and the product was purified by recrystallization in Et_2O/MeOH to afford **3e** (0.977 g, 65%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 1.8 Hz, 2H), 7.71−7.63 (m, 4H), 7.60 (dd, J = 8.4, 1.8 Hz, 2H), 7.11 (s, 2H), 7.07−6.97 (m, 6H), 3.88 (s, 6H), 2.44 (s, 3H), 1.89 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.7, 140.2, 138.7, 137.8, 134.9, 132.8, 131.9, 129.5, 128.4, 125.5, 123.6, 118.6, 114.3, 109.9, 55.5, 21.3, 17.6. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{35}H_{32}NO_2$ 498.2428. Found: 498.2434. Mp 211−213 °C.

*9-Mesityl-3,6-diphenyl-9H-carbazole (**3f**).* A Schlenk flask containing K_3PO_4·H_2O (1.38 g, 6.00 mmol) and a stir bar was flame dried under vacuum. Once cool, **4b** (0.443 g, 1.0 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.065 g, 0.080 mmol), K_3PO_4·H_2O (1.38 g, 6.00 mmol), and phenylboronic acid (0.33 g, 2.2 mmol) were added under a positive stream of Ar. The flask was evacuated and refilled with Ar three times before adding anhydrous 1,4-dioxane (8 mL) followed by H_2O (0.18 mL, 5 equiv) that had been sparged with Ar. The reaction was heated to 70 °C. After stirring for 3 h, water was added and the reaction mixture was extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under vacuum. The product was purified by column chromatography (0−2.5% EtOAc/hexanes) to afford **3f** (0.36 g, 82%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 1.1 Hz, 2H), 7.78−7.70 (m, 4H), 7.64 (dd, J = 8.5, 1.8 Hz, 2H), 7.52−7.43 (m, 4H), 7.37−7.30 (m, 2H), 7.11 (s, 2H), 7.03 (dd, J = 8.4, 0.7 Hz, 2H), 2.44 (s, 3H), 1.89 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 142.2, 140.6, 138.8, 137.8, 133.2, 131.8, 129.6, 128.9, 127.5, 126.6, 125.8, 123.7, 119.2, 110.0, 21.4, 17.7. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{28}N$ 438.2216. Found: 438.2215. Melting point was difficult to determine due to what appeared to be sublimation of the solid at temperatures > 105 °C.

*9-Mesityl-3,6-di-p-tolyl-9H-carbazole (**3g**).* A Schlenk flask containing **4b** (1.11 g, 2.5 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.163 g, 0.200 mmol), K_3PO_4·H_2O (3.45 g, 15.00 mmol), *p*-tolylboronic acid (0.748 g, 5.50 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with argon three times. To the flask was added anhydrous 1,4-dioxane (10 mL). The reaction was heated to 70 °C. After stirring overnight, the reaction mixture was passed through Celite using hexanes to rinse. The filtrate was concentrated under vacuum, and the product was purified by recrystallization in CH_2Cl_2/MeOH to afford **3g** (0.713 g, 61%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 2H), 7.71−7.60 (m, 6H), 7.31 (d, J = 7.9 Hz, 4H), 7.13 (s, 2H), 7.03 (d, J = 8.4 Hz, 2H), 2.46 (s, 3H), 2.45 (s, 6H), 1.91 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 140.4, 139.4, 138.7, 137.9, 136.2, 133.1, 131.9, 129.6, 129.6, 127.3, 125.7, 123.7, 118.9, 109.9, 21.4, 21.2, 17.7. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{35}H_{32}N$ 466.2529. Found: 466.2513. Mp 225−228 °C.

*3,6-Di([1,1′-biphenyl]-4-yl)-9-mesityl-9H-carbazole (**3h**).* A Schlenk flask containing **4b** (0.443 g, 1.0 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.065 g, 0.080 mmol), K_3PO_4·H_2O (1.38 g, 6.00 mmol), 4-biphenylboronic acid (0.436 g, 2.2 mmol), and a stir bar was placed under an argon atmosphere by evacuating and filling the flask with

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argon three times. To the flask was added anhydrous 1,4-dioxane (8 mL). The reaction was heated to 70 °C. After stirring overnight, water was added and the reaction mixture was extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under vacuum. The product was purified by column chromatography (0−10% EtOAc/hexanes) and then further by recrystallization (Et_2O/MeOH) to afford **3h** (0.157 g, 27%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 1.7 Hz, 2H), 7.82 (d, J = 8.3 Hz, 4H), 7.76−7.65 (m, 10H), 7.47 (t, J = 7.6 Hz, 4H), 7.36 (t, J = 7.4 Hz, 2H), 7.12 (s, 2H), 7.05 (d, J = 8.4 Hz, 2H), 2.45 (s, 3H), 1.91 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 141.2, 141.0, 140.7, 139.4, 138.8, 137.8, 132.7, 131.8, 129.6, 129.0, 127.8, 127.6, 127.3, 127.2, 125.8, 123.7, 119.1, 110.1, 21.4, 17.7. HRMS (ESI/Orbitrap) m/z: $[M]^+$ calcd for $C_{45}H_{35}N$ 589.2770. Found: 589.2753. Anal. Calcd for $C_{45}H_{35}N$: C, 91.64; H, 5.98; N, 2.37. Found: C, 91.83; H, 5.86; N, 2.51. Mp 200−202 °C.

Procedures for the Hydrodehalogenation of Aryl Bromides and Chlorides. *Method A.* To a flask containing the substrate (1.0 mmol) and DIPEA (1.0 mL, 6.0 mmol) was added a solution of carbazole **3a** in DMA (5.0 mM, 10 mL, 0.050 mmol). The reaction mixture was split between two 7 mL vials and irradiated with 365 nm LED lights for 20 h. The reaction mixture was then added to a separatory funnel with H_2O (20 mL) and aq HCl (1 M, 5 mL). The mixture was extracted with Et_2O (3 × 10 mL), and the organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum. The product was purified by column chromatography (5−10% EtOAc/hexanes).

Method B. To a 7 mL vial containing the substrate (0.40 mmol) and DIPEA (0.42 mL, 2.4 mmol) was added a solution of carbazole **3a** or **3h** in DMA (5.0 mM, 4.0 mL, 0.020 mmol). After irradiating the reaction mixture for 20 h with 365 nm LED lights, dodecane was added (0.40 mmol, 0.091 mL). Approximately 20 μL of the crude mixture was dissolved in EtOAc (1 mL) and analyzed by GC-FID.

*Benzonitrile from **7a**.* Method A was used with 4-bromobenzonitrile (**7a**, 0.182 g, 1.00 mmol) to yield benzonitrile (**8**) as an oil (0.059 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.57 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 132.8, 132.2, 129.2, 118.9, 112.4. Spectra were in accordance with those described in the literature.[29] Method B was also used with 4-bromobenzonitrile (**7a**, 0.073 g, 0.40 mmol). The yield was determined by the ratio of product to dodecane to be 90%.

*Benzonitrile from **7b**.* Method A was used with 2-chlorobenzonitrile (**7b**, 0.138 g, 1.00 mmol) to yield benzonitrile (**8**) as an oil (0.064 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.57 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 132.8, 132.2, 129.2, 118.9, 112.4. Spectra were in accordance with those described in the literature.[29] Method B was also used with 2-chlorobenzonitrile (**7b**, 0.055 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 92%.

*Benzonitrile from **7c**.* Method A was used with 4-chlorobenzonitrile (**7c**, 0.138 g, 1.00 mmol) to yield benzonitrile (**8**) as an oil (0.060 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.57 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 132.8, 132.2, 129.2, 118.9, 112.4. Spectra were in accordance with those described in the literature.[29] Method B was also used with 4-chlorobenzonitrile (**7c**, 0.055 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 94%.

*Methyl Benzoate from **7d**.* Method A was used with methyl 2-bromobenzoate (**7d**, 0.215 g, 1.00 mmol) to yield methyl benzoate as an oil (0.099 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.2, 133.0, 130.2, 129.6, 128.4, 52.2. Spectra were in accordance with those described in the literature.[30] Method B was also used with methyl 2-bromobenzoate (**7d**, 0.086 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 94%.

*Methyl Benzoate from **7e**.* Method A was used with methyl 3-bromobenzoate (**7e**, 0.215 g, 1.00 mmol) to yield methyl benzoate as an oil (0.115 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.2, 133.0, 130.2, 129.6, 128.4, 52.2. Spectra were in accordance with those described in the literature.[30] Method B was also used with methyl 3-bromobenzoate (**7e**, 0.086 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be >99%.

*Methyl Benzoate from **7f**.* Method A was used with methyl 4-bromobenzoate (**7f**, 0.215 g, 1.00 mmol) to yield methyl benzoate as an oil (0.114 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 167.2, 133.0, 130.2, 129.6, 128.4, 52.2. Spectra were in accordance with those described in the literature.[30] Method B was also used with methyl 4-bromobenzoate (**7f**, 0.086 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 98%.

*Dimethyl Isophthalate from **7g**.* Method A was used with dimethyl 5-bromoisophthalate (**7g**, 0.273 g, 1.00 mmol) to yield dimethyl isophalate as a solid (0.163 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (t, J = 1.8 Hz, 1H), 8.22 (d, J = 8.0, 1.7 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 3.95 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.3, 133.8, 130.8, 130.6, 128.7, 52.4. Spectra were in accordance with those described in the literature.[22] Method B was also used with dimethyl 5-bromoisophthalate (**7g**, 0.109 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 91%.

*Methyl 2-Acetamidobenzoate from **7h**.* Method A was used with methyl 2-acetamido-5-bromobenzoate (**7h**, 0.272 g, 1.00 mmol) to yield methyl 2-acetamidobenzoate as a solid (0.161 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.06 (br s, 1H), 8.70 (dd, J = 8.6, 1.1 Hz, 1H), 8.01 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.06 (t, J = 7.7 Hz, 1H), 3.91 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 169.1, 168.8, 141.6, 134.7, 130.8, 122.4, 120.3, 114.7, 52.4, 25.5. Spectra were in accordance with those described in the literature.[31] Method B was also used with methyl 2-acetamido-5-bromobenzoate (**7h**, 0.109 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 93%.

*Methyl 2-Methoxybenzoate from **7i**.* Method A was used with methyl 4-bromo-2-methoxybenzoate (**7i**, 0.245 g, 1.00 mmol) to yield methyl 2-methoxybenzoate as an oil (0.124 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, J = 7.9 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.01−6.92 (m, 2H), 3.89 (s, 3H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.7, 159.1, 133.5, 131.6, 120.1, 119.9, 111.9, 55.9, 52.0. Spectra were in accordance with those described in the literature.[32] Method B was also used with methyl 4-bromo-2-methoxybenzoate (**7i**, 0.098 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 92%.

*Fluorobenzene from **7j**.* Method B was used only due to the volatility of the product with 1-bromo-2-fluorobenzene (**7j**, 0.044 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 87%.

*Fluorobenzene from **7k**.* Method B was used only due to the volatility of the product with 1-bromo-4-fluorobenzene (**7k**, 0.044 g, 0.40 mmol) and carbazole **3h**. The calibrated yield was determined by the ratio of product to dodecane to be 74%.

*Ethyl 2-Thiophenecarboxylate from **7l**.* Method A was used with ethyl 5-bromo-2-thiophenecarboxylate (**7l**, 0.235 g, 1.00 mmol) to yield ethyl 2-thiophenecarboxylate as an oil (0.089 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.54 (dd, J = 4.0, 0.9 Hz, 1H), 7.10 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.4, 134.2, 133.4, 132.3, 127.8, 61.3, 14.5. Spectra were in accordance with those described in the literature.[33] Method B was also used with ethyl 5-bromo-2-thiophenecarboxylate (**7l**, 0.062 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 81%.

*3-Cyanopyridine from **7m**.* Method A was used with 2-bromo-5-cyanopyridine (**7m**, 0.183 g, 1.00 mmol) to yield 3-cyanopyridine as a solid (0.037 g, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (dd, J =

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2.2, 0.9 Hz, 1H), 8.84 (dd, J = 5.0, 1.7 Hz, 1H), 8.03−7.95 (m, 1H), 7.53−7.41 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 153.1, 152.6, 139.4, 123.8, 116.6, 110.3. Spectra were in accordance with those described in the literature.[34] Method B was also used with 2-bromo-5-cyanopyridine (**7m**, 0.073 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 70%.

*Quinoline from **7n**.* Method B was used due to the product being difficult to isolate with 3-bromoquinoline (**7n**, 0.083 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 37%.

*Anthracene from **7o**.* Method B was used only due to the product being difficult to isolate with 9-bromoanthracene (**7o**, 0.103 g, 0.40 mmol) and carbazole **3a**. The calibrated yield was determined by the ratio of product to dodecane to be 33%.

*Anisole from **7p**.* Method B was used only due to the volatility of the product with 4-bromoanisole (**7p**, 0.050 mL, 0.40 mmol) and carbazole **3h**. The calibrated yield was determined by the ratio of product to dodecane to be 34%.

Arylation of *N*-Methylpyrrole. *2-(1-Methyl-1H-pyrrol-2-yl)-benzonitrilepyrrole (**10**) from **3a**.* *N*-Methylpyrrole (**9**) was distilled before use. To a 7 mL vial containing **3a** (0.011 g, 0.025 mmol) was added a solution of 2-chlorobenzonitrile (**7b**) in DMSO (0.1 M, 5 mL, 0.5 mmol) and *N*-methylpyrrole (**9**, 0.67 mL, 7.5 mmol). The reaction mixture was sparged with Ar for 10 min and then irradiated at 365 nm for 21 h. Once finished, the reaction mixture was added to a separatory funnel with H_2O (40 mL) and brine (10 mL) and extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum. The product was purified by column chromatography to yield **10** (0.070 g, 77%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.45−7.36 (m, 2H), 6.79 (dd, J = 2.7, 1.8 Hz, 1H), 6.41 (dd, J = 3.7, 1.7 Hz, 1H), 6.24 (dd, J = 3.7, 2.7 Hz, 1H), 3.61 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 136.9, 133.6, 132.5, 130.9, 130.0, 127.5, 124.9, 118.7, 112.8, 111.5, 108.4, 34.9. Spectra were in accordance with those described in the literature.[35]

*2-(1-Methyl-1H-pyrrol-2-yl)benzonitrilepyrrole (**10**) from **3e**.* *N*-Methylpyrrole (**9**) was distilled before use. To a 7 mL vial containing **3e** (0.012 g, 0.025 mmol) was added a solution of 2-chlorobenzonitrile (**7b**) in DMSO (0.1 M, 5 mL, 0.5 mmol) and *N*-methylpyrrole (**9**, 0.67 mL, 7.5 mmol). The reaction mixture was sparged with Ar for 10 min and then irradiated at 365 nm for 21 h. Once finished, the reaction mixture was added to a separatory funnel with H_2O (40 mL) and brine (10 mL) and extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum. The product was purified by column chromatography to yield **10** (0.052 g, 57%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.45−7.36 (m, 2H), 6.79 (dd, J = 2.7, 1.8 Hz, 1H), 6.41 (dd, J = 3.7, 1.7 Hz, 1H), 6.24 (dd, J = 3.7, 2.7 Hz, 1H), 3.61 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 136.9, 133.6, 132.5, 130.9, 130.0, 127.5, 124.9, 118.7, 112.8, 111.5, 108.4, 34.9. Spectra were in accordance with those described in the literature.[35]

*2-(1-Methyl-1H-pyrrol-2-yl)benzonitrilepyrrole (**10**) from **3h**.* *N*-Methylpyrrole (**9**) was distilled before use. To a 7 mL vial containing **3h** (0.015 g, 0.025 mmol) was added a solution of 2-chlorobenzonitrile (**7b**) in DMSO (0.1 M, 5 mL, 0.5 mmol) and *N*-methylpyrrole (**9**, 0.67 mL, 7.5 mmol). The reaction mixture was sparged with Ar for 10 min and then irradiated at 365 nm for 21 h. Once finished, the reaction mixture was added to a separatory funnel with H_2O (40 mL) and brine (10 mL) and extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated under vacuum. The product was purified by column chromatography to yield **10** (0.072 g, 79%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.45−7.36 (m, 2H), 6.79 (dd, J = 2.7, 1.8 Hz, 1H), 6.41 (dd, J = 3.7, 1.7 Hz, 1H), 6.24 (dd, J = 3.7, 2.7 Hz, 1H), 3.61 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 136.9, 133.6, 132.5, 130.9, 130.0, 127.5, 124.9, 118.7, 112.8, 111.5, 108.4, 34.9. Spectra were in accordance with those described in the literature.[35]

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c02312.

Additional reaction setup details, proposed mechanism for the hydrodehalogenation reaction, Stern−Volmer quenching study, addition optimization data, carbazole absorbance and emission spectra, cyclic voltammograms, GC-FID traces, and ^1H and ^{13}C NMR spectra of all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Ashley R. Longstreet − *Department of Chemistry, Biochemistry, and Physics, The University of Tampa, Tampa, Florida 33606, United States;* orcid.org/0000-0001-7487-5385; Email: alongstreet@ut.edu

Authors

Tyler D. Weinhold − *Department of Chemistry, Biochemistry, and Physics, The University of Tampa, Tampa, Florida 33606, United States*

Natalie A. Reece − *Department of Chemistry, Biochemistry, and Physics, The University of Tampa, Tampa, Florida 33606, United States*

Kevin Ribeiro − *Department of Chemistry, Biochemistry, and Physics, The University of Tampa, Tampa, Florida 33606, United States*

Maredh Lopez Ocasio − *Department of Chemistry, Biochemistry, and Physics, The University of Tampa, Tampa, Florida 33606, United States*

Noelle Watson − *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States*

Kenneth Hanson − *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States;* orcid.org/0000-0001-7219-7808

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.2c02312

Author Contributions

‡N.A.R. and K.R.: These authors contributed equally to this article.

Notes

The authors declare no competing financial interest.

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