Intramolecular Oxidative Diaryl Coupling of Tetrasubstituted Diphenylamines for the Preparation of Bis(trifluoromethyl) Dimethyl Carbazoles

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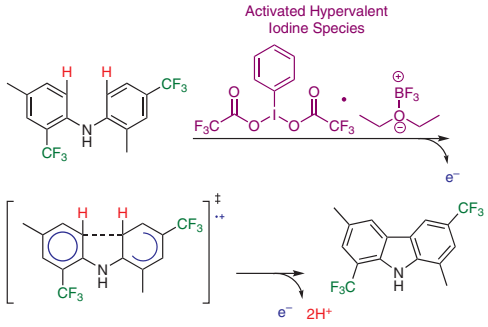

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Abstract Synthetic preparation of carbazoles can be challenging, requiring ring-building strategies and/or precious metal catalysts. Presented herein is a method for the preparation of carbazoles with the use of inexpensive and reliable hypervalent iodine chemistry. An oxidative single-electron-transfer (SET) event initiates cyclization for the preparation of our trifluoromethyl carbazoles. This method has been shown to be useful for a variety of bis(trifluoromethyl)carbazole isomers that are of primary interest for use as battery materials.

Key words intramolecular coupling, metal-free, electron-deficient carbazoles, hypervalent iodine

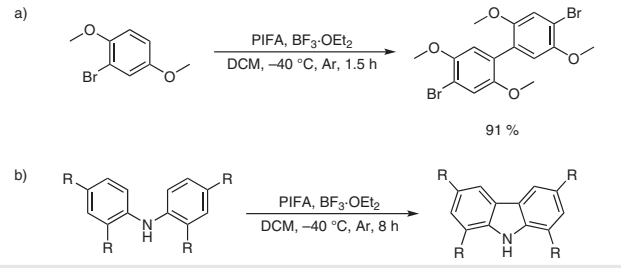
Carbazoles and their derivatives have a wide range of photochemical and electrochemical applications, including use as fluorescent probes or dyes for *in vitro* analyses,[1,2] organic light-emitting diodes (OLEDs) in solar cells and televisions,[3–8] and battery materials.[9,10] Additionally, recent scientific interest in carbazoles with biomedical applications has increased, with over 3,500 publications in the last five years.[11] This is due in part to their potential uses as therapies for neurodegeneration,[12,13] cancer,[14,15] pathogens,[16–18] inflammation,[19,20] and chronic health conditions.[21]

Our particular interest in carbazoles lies in their ability to undergo reversible electrochemical oxidation at high potentials.[22] Polymerization of the carbazole cation radical has been well documented,[23] but can be suppressed by blocking areas of high electron-spin density (i.e., at the 3- and 6-positions, and preferably at the 1- and 8-positions as well).[23] Functionalization also allows for modulation of oxidation potentials. In general, electron-withdrawing substituents have been shown to cause an increase in oxidation potential with the opposite being true for electron-donating substituents, although steric factors can also play a role.[22] Carbazoles containing two trifluoromethyl groups are of particular interest due to their oxidation potentials being well matched to the requirements for battery materials. Specifically, these high oxidation potentials would increase the energy density of redox-flow batteries and are near the optimal potential (4.3 V vs Li/Li^+) needed to function as redox shuttles in some lithium-ion batteries.[24] The desirability of this functionality prompted our investigation of different approaches for the synthesis of trifluoromethyl-containing carbazoles.

Derivatives of carbazoles have traditionally been prepared through ring-building strategies.[25] Alternatively, to substitute at particular ring positions, halogenation is first required. These methods require the use of precious metal catalysts,[26–28] increasing synthetic steps and involving purification undesirable for commercial applications. Synthetic routes involving radical chemistry have been documented; however, these methods have limitations. The Graebe–Ullmann synthesis[29] requires an *ortho*-amine for diazotization and subsequent cyclization of the diphenylamine to occur. Thermal decomposition releases nitrogen gas and forms a radical. Finally, radical rearrangement allows for formation of a new carbon–carbon bond to produce a carbazole. Hypervalent iodine chemistry has been utilized previously to form a carbon–nitrogen bond to intramolecularly cyclize biphenyls. Joining of the arenes requires N-substitution and the use of precious metal catalyst with Suzuki coupling.[30] These methods limit the variety of carbazoles that can

be synthesized because of their functional group sensitivity and involvement of harsh conditions. For these reasons, alternative methods to carbazole preparation are needed.

This method attempts to overcome these limitations with utilization of hypervalent iodine chemistry to prepare carbazoles by intramolecular cyclization of diphenylamines. This is done with the formation of a new carbon–carbon bond between the two aryl rings. The activated hypervalent iodine species, specifically [bis(trifluoroacetoxy)iodo]benzene boron trifluoride diethyl etherate (PIFA-BF_3·OEt_2), is capable of oxidizing electron-rich arenes and producing a cation radical to couple aromatic rings.[31] As shown in Scheme 1, oxidative diaryl coupling has provided swift, high-yielding reactions in low-temperature environments for a variety of aryl substrates.[31,32] The method presented herein utilizes similar conditions for carbazole formation. With the use of the activated hypervalent iodine species, oxidative diaryl coupling selectively forms an intramolecular bond, transforming bis(trifluoromethyl) diphenylamines into bis(trifluoromethyl) carbazoles.



Scheme 1 a) Example of high-yielding oxidative diaryl coupling; b) oxidative diaryl coupling for the preparation of trifluoromethyl carbazoles

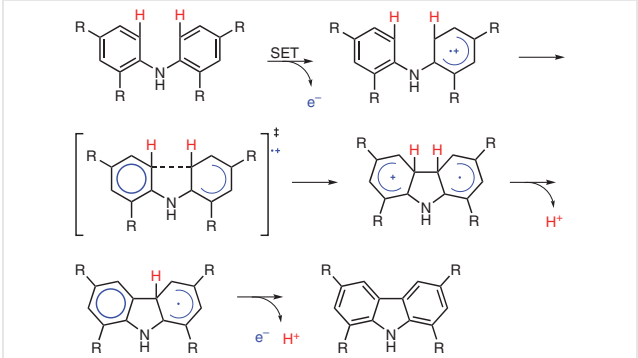
This synthetic route is advantageous for several reasons. It eliminates the need for a metal catalyst and reduces cost significantly. PIFA and BF_3·OEt_2, for instance, are considerably cheaper than palladium and allow for simpler purification. Having the synthetic methodology pass through commercially available aromatic starting materials also makes development of carbazoles more economically viable.

The diphenylamines were synthesized using Buchwald–Hartwig amination following a literature precedent.[33] Although method development for amination was beyond the scope of this work, it may be possible for this starting-material preparation to be modified to successfully prepare diphenylamines, as well as the subsequent carbazoles, without any use of a precious metal catalysis in the synthetic pathway. Nevertheless, bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] has been shown to be extremely robust in its formation of various amines and was utilized for its versatility in assembling a range of diphenylamines on a laboratory scale.[33,34]

The oxidative diaryl coupling was performed following a literature precedent,[31] as shown in Scheme 1. While oxidative diaryl coupling reactions have been well documented,[35] none have yet been applied to the preparation of carbazoles by isolated carbon–carbon bond formation without the use of precious metals. The reaction was performed under argon at –40 °C. PIFA and BF_3·OEt_2 were dissolved in methylene chloride and added dropwise to the cooled diphenylamine solution, also dissolved in methylene chloride. As the PIFA-BF_3·OEt_2 was added, a dramatic color change from yellow to deep blue-green was observed. This is indicative of formation of the cation radical.[36] After 8 hours, the mixture was quenched with saturated aqueous $NaHCO_3$, changing the color of the organic layer from a deep blue-green to a clear red-orange and was accompanied by mild gas evolution.

Reactions were allowed to run for 8 hours instead of the 1.5 hours shown in Scheme 1a. Additional pot time was required as the diphenylamines were not completely consumed even after 4 hours. Diphenylamine consumption was monitored by TLC. After 8 hours, complete consumption of diphenylamine for each isomer was confirmed. Additional reaction details for the Buchwald–Hartwig aminations and the oxidative diaryl couplings are provided below.

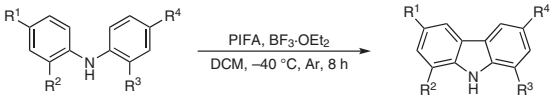
The expected reaction mechanism is shown in Scheme 2. This proposed mechanism is based on the cation radical Scholl reaction mechanism utilizing activated hypervalent iodine chemistry.[37,38] A cation radical is formed when a single-electron-transfer (SET) event occurs from the electron-rich diphenylamine to the electron-poor PIFA-BF_3·OEt_2. The cation radical is greatly stabilized by resonance. Only the most interesting of the resonance structures is shown at the top right of Scheme 2 for simplicity. This greater spin-density delocalization may be responsible for the increased reaction times observed when compared to the dimethoxybenzene analogues shown in Scheme 1a. The C–N–C bond angle distorts in the transition state as the neighboring nucleophilic arene reacts to form a new carbon–carbon bond, cyclizing the diphenylamine. Upon workup with $NaHCO_3$, deprotonation and quenching of the radical occurs to provide the desired carbazole.



Scheme 2 Proposed reaction mechanism. SET event to form resonance-stabilized diphenylamine cation radical. The neighboring nucleophilic arene reacts to form an intramolecular carbon–carbon bond, cyclizing the diphenylamine. Aqueous basic workup deprotonates and quenches cation radical, providing the desired carbazole.

Carbazole synthesis via oxidative diaryl coupling was attempted with all 2,2′,4,4′-isomers of bis(trifluoromethyl)dimethyldiphenylamine to yield the corresponding 1,3,6,8-substituted carbazoles, as shown in Table 1. The intent was to prepare tetrasubstituted carbazoles with two trifluoromethyl substituents.

Table 1 Isolated Yields for Prepared Carbazoles via Intramolecular Oxidative Diaryl Coupling



Reactant	Product	R^1	R^2	R^3	R^4	Yield (%)
1	**5**	Me	CF_3	CF_3	Me	60
2	**6**	Me	Me	CF_3	CF_3	–
3	**7**	CF_3	Me	Me	CF_3	60
4	**8**	Me	CF_3	Me	CF_3	49

This method provides appreciable yields for three of the four isomers. For *N*-[2,4-bis(trifluoromethyl)phenyl]-2,4-dimethylaninline (**2**), where both trifluoromethyl groups are on one phenyl ring, consumption was observed by TLC. However, formation of the desired 1,3-dimethyl-6,8-bis(trifluoromethyl)-9*H*-carbazole (**6**) was not observed. Instead, an abundance of byproducts was observed by HPLC and ^{1}H NMR spectroscopy. This byproduct formation may be due to localization of the cation radical to one of the aryl rings. This localization can be seen in the spin-density maps of the diphenylamine starting materials (Figure 1a) and resulting carbazoles (Figure 1b) prepared in Spartan '18.[39–41]

This method may be applicable to other diphenylamines with a lesser or greater degree of substitution for the preparation of carbazoles. Investigation into substituent type and quantity is needed to determine the universality of this method. Additionally, other SET initiators (whether hypervalent iodine species or otherwise) have not been attempted and further optimization of the reaction or workup may be possible to provide for simpler purification – aqueous washes and removal of iodobenzene *in vacuo*. Nevertheless, it is clear this method is extremely powerful for the synthesis of carbazoles by decreasing overall reaction costs and allowing for more commercially available materials to be utilized. This method of carbazole preparation will assist the fields of photochemistry, electrochemistry, and could provide pathways to materials in other fields such as medicinal and bioorganic chemistry.

Solvents listed as being dry and degassed were obtained from a solvent purification system equipped with drying (3 Å molecular sieve) and deoxygenating (Research Catalyst, Inc. GetterMax) columns. All other reagents and solvents were purchased from commercial sources (Millipore Sigma, Oakwood Chemical, Fischer Scientific, and AA Blocks) and used without further purification.

Silica gel (230–400 mesh) was used as a stationary phase for column chromatography. Commercial solvents were used as eluents. Eluent details are listed with the associated compound. TLC was performed on silica gel 60 F_{254}.

Characterization Methods

^{1}H, ^{13}C{^{1}H}, ^{19}F, and DEPT-90 NMR data were acquired on a Bruker Ascend 500 MHz instrument at ambient temperature. Chemical shift values are reported in ppm and coupling constants are reported in Hz. Abbreviations for multiplicity are: s = singlet, d = doublet, q = quartet, dd = doublet of doublets, dq = doublet of quartets, m = multiplet. All spectra were recorded in $CDCl_3$, referencing the residual solvent signal of 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C{^{1}H}. For ^{19}F spectra, 2 µL of hexafluorobenzene was added to the prepared samples in $CDCl_3$.

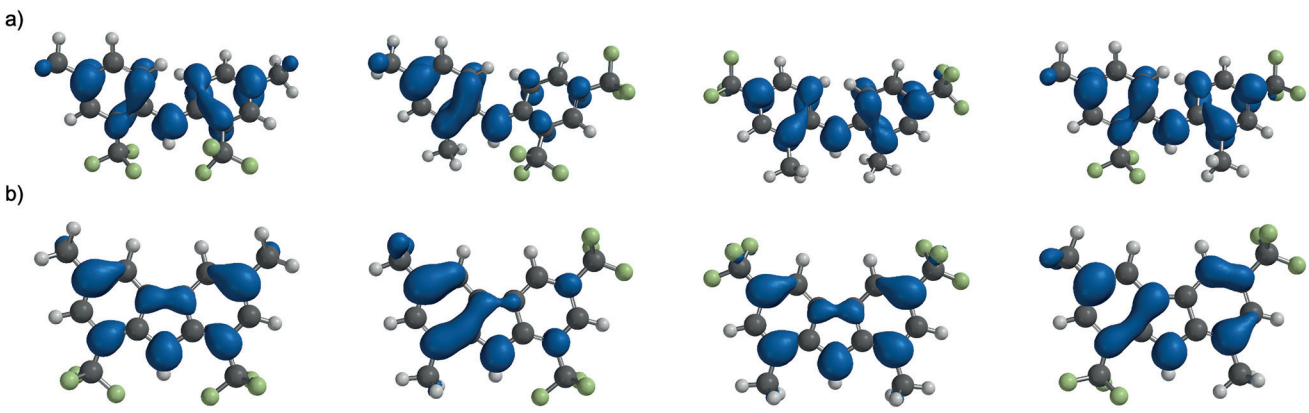


Figure 1 Electron spin density surfaces (blue) prepared in Spartan '18 following tandem Equilibrium Geometry and Energy calculations. Ball and stick representations – carbon (grey), hydrogen (white), fluorine (green) nitrogen (purple; hidden by surfaces). a) Diphenylamines left to right – compounds **1**, **2**, **3**, and **4**. Compound **2** has increased spin-density localization in favor of the ring with the methyl substituents. b) Carbazoles left to right – compounds **5**, **6**, **7**, and **8**. As with compound **2**, **6** has increased spin-density localization, favoring the ring with methyls.

Chemical shift values for ^{19}F spectra were then referenced to hexafluorobenzene's chemical shift in $CDCl_3$, –163.0 ppm, determined from a reported external standard.[42] NMR data were processed using a Bruker TopSpin academic license.

LC/MS analysis was performed on a 6224 TOF LC/MS system (Agilent Technologies), consisting of a 1200 HPLC (degasser, binary pump, thermostated column compartment, diode array detector (DAD) coupled to a 6224 accurate-mass time-of-flight mass spectrometer. The mass spectrometer was equipped with a Dual ESI source, and accurate mass data were obtained by internal calibration (reference ions 121.050873 and 922.009798 *m/z*) using a secondary nebulizer to continuously deliver the reference solution. Positive-ion mass spectral data were acquired in full-scan mode over the range of 100–3200 *m/z* using the following source parameters: gas temperature 325 °C, gas flow 11 L/min, nebulizer pressure 33 psig, VCap 3500 V, and fragmentor voltage 120 V. HPLC separations were achieved on a Phenomenex Kinetix EVO C18 column (3 × 100 mm, 2.6 µ) using a linear gradient of mobile phase B in A, a flow rate of 0.5 mL/min, and a column temperature of 40 °C. Mobile phase A was prepared by combining 400 mL ultrapure water with 12 mL methanol and 1.2 mL formic acid. Mobile phase B was prepared by combining 400 mL acetonitrile with 12 mL ultrapure water and 1.2 mL formic acid. The gradient program included an initial hold at 0% solvent B for 2 min, followed by a linear increase to 100% solvent B from 2–8 min, a hold at 100% solvent B from 8–9 min, and re-equilibration back to 0% B for a total run time of 15 min. In addition to MS detection, the DAD was used to acquire a UV chromatogram at 254 nm. Samples were analyzed using a 1–5 µL injection volume. Raw data were exported from Agilent MassHunter and processed in Microsoft Excel.

TGA data were acquired on a TA Instruments TGA 550 instrument. Method: isotherm at 20 °C for 3 min; +20 °C/min to 800 °C; isotherm at 800 °C for 3 min. Samples were loaded onto clean, tared platinum pans. Sample mass on platinum pan was measured prior to analysis. Between 2 mg and 10 mg of material was loaded for each run. Mass percent difference was measured across entire method. Data were processed using TA Instruments TRIOS software.

DSC data were acquired on a TA Instruments DSC 2500 instrument. Method: isotherm at 20 °C for 3 min; +10 °C/min to decomposition onset; isotherm at decomposition onset for 3 min. Samples were contained in hermetically sealed Tzero aluminum pans. Pans were pressed appropriately. Between 2 mg and 10 mg of material was loaded for each run. An empty hermetically sealed Tzero aluminum pan was used as temperature correction for all runs. Data were processed using TA Instruments TRIOS software. Endothermic processes are displayed down. Melting point was taken to be the range from onset to peak temperatures.

GC/MS data were acquired on an Agilent 7890A/5975C instrument. Method: split/splitless injector (ran at 50:1 split) at 250 °C; column flow rate 1.1 mL/min; ultra-high purity 5.0 helium; oven initial temp at 50 °C, initial time 5 min, first ramp at +10 °C/min to 200 °C, no hold, second ramp at +20 °C/min to final temp 320 °C, final temp time 15 min; MSD transfer line at 280 °C; electron impact ionization (69.9 eV) source at 230 °C, quadrupole at 150 °C, pressure < 6×10^{-6} torr. GC/MS data were processed using Agilent ChemStation MSD Data Analysis software.

Synthetic Procedures and Characterization Details

General Procedure for the Preparation of Tetrasubstituted Diphenylamines by Buchwald–Hartwig Amination[33]

$Pd(dba)_2$ (0.30 mmol), tri(*tert*-butyl)phosphonium tetrafluoroborate (0.30 mmol), and sodium *tert*-butoxide (4.50 mmol) were added to a dry, argon purged 100 mL round-bottom flask. The flask was sealed and continuously purged with argon while aryl bromide (3.00 mmol) and 50 mL of dry, degassed toluene were injected in the flask. After stirring for 15 min, the aniline (3.00 mmol) was injected to the flask. Purging was stopped, and the reaction mixture was stirred at room temperature overnight in the septum-sealed flask. Reaction completion was determined by TLC and GC/MS. Upon completion the reaction mixture was poured into a separatory funnel containing 75 mL of deionized water and 75 mL of ethyl acetate. The organic layer was separated, and the aqueous layer was extracted twice more with 50 mL of ethyl acetate. The three organic layers were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvents were removed by rotary evaporation. Purification was performed by column chromatography. Purified product was dried in a vacuum oven overnight at 40 °C and 75 torr.

Bis[4-methyl-2-(trifluoromethyl)phenyl]amine (1)

0.7714 g; 78%; 9:1 hexanes–ethyl acetate chromatography eluent; yellow solid.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 0.5 Hz, 2 H), 7.20 (dd, *J* = 0.6, 8.4 Hz, 2 H), 7.12 (d, *J* = 8.3 Hz, 2 H), 6.22 (s, 1 H), 2.34 (s, 6 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 138.84, 133.44, 131.22, 127.35 (q, J_{CF} = 5.2 Hz), 124.60 (q, J_{CF} = 272.6 Hz), 120.57, 119.87 (q, J_{CF} = 29.0 Hz), 20.71.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.09 (s, 6 F).

HPLC/HRMS (ESI): t_R = 6.76 min; *m/z* $[M + H]^+$ calcd for $[C_{16}H_{13}F_6N + H]^+$: 334.1025; found: 334.1034.

TGA/DSC: mp 54–58 °C.

N-[2,4-Bis(trifluoromethyl)phenyl]-2,4-dimethylaniline (2)

0.8138 g; 81%; 9:1 hexanes–ethyl acetate chromatography eluent; clear, red-orange oil.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.45 (dd, *J* = 1.5, 8.8 Hz, 1 H), 7.14–7.08 (m, 2 H), 7.06 (dd, *J* = 1.2, 8.0 Hz, 1 H), 6.67 (d, *J* = 8.8 Hz, 1 H), 6.10 (s, 1 H), 2.36 (s, 3 H), 2.17 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 147.18, 136.78, 134.74, 134.54, 132.30, 129.98 (q, J_{CF} = 3.7 Hz), 128.04, 126.60, 124.68 (q, J_{CF} = 285.9 Hz), 124.59 (dq, J_{CF} = 1.8, 6.4 Hz), 124.44 (q, J_{CF} = 285.0 Hz), 119.26 (q, J_{CF} = 33.7 Hz), 114.19, 113.62 (q, J_{CF} = 30.7 Hz), 21.11, 17.71.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.87 (s, 3 F), –64.07 (s, 3 F).

HPLC/HRMS (ESI): t_R = 7.49 min; *m/z* $[M + H]^+$ calcd for $[C_{16}H_{13}F_6N + H]^+$: 334.1025; found: 334.1021.

Bis[2-methyl-4-(trifluoromethyl)phenyl]amine (3)

0.7254 g; 73%; 3:1 hexanes–ethyl acetate chromatography eluent; orange-yellow solid.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (s, 2 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 5.47 (s, 1 H), 2.33 (s, 6 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 143.95, 128.15 (q, J_{CF} = 3.6 Hz), 127.78, 124.58 (q, J_{CF} = 271.1 Hz), 124.32 (q, J_{CF} = 3.7 Hz), 123.94 (q, J_{CF} = 32.7 Hz), 117.79, 17.89.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.95 (s, 6 F).

HPLC/HRMS (ESI): t_R = 7.15 min; *m/z* [M + H]$^+$ calcd for [$C_{16}H_{13}F_6N$ + H]$^+$: 334.1025; found: 334.1030.

TGA/DSC: mp 55–58 °C.

2-Methyl-*N*-[4-methyl-2-(trifluoromethyl)phenyl]-4-(trifluoromethyl)aniline (4)

0.8190 g; 82%; 9:1 hexanes–ethyl acetate chromatography eluent; clear, golden yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 1.4, 8.4 Hz, 2 H), 7.34 (dd, *J* = 1.4, 8.5 Hz, 1 H), 7.27 (dd, *J* = 1.3, 8.0 Hz, 1 H), 7.20 (d, *J* = 8.3 Hz, 1 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 5.83 (s, 1 H), 2.37 (s, 3 H), 2.29 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.74, 137.87, 133.53, 132.28, 128.01 (q, J_{CF} = 3.6 Hz), 127.48 (q, J_{CF} = 5.2 Hz), 126.47, 124.75 (q, J_{CF} = 265.2 Hz), 124.64 (q, J_{CF} = 268.2 Hz), 124.25 (q, J_{CF} = 3.7 Hz), 122.92 (q, J_{CF} = 32.5 Hz), 122.05, 120.75 (q, J_{CF} = 29.1 Hz), 115.76, 20.80, 17.67.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.60 (s, 3 F), –62.84 (s, 3 F).

HPLC/HRMS (ESI): t_R = 7.25 min; *m/z* [M + H]$^+$ calcd for [$C_{16}H_{13}F_6N$ + H]$^+$: 334.1025; found: 334.1033.

General Procedure for the Oxidative Diaryl Coupling of Trifluoromethyl-Containing Tetrasubstituted Carbazoles[31]

Diphenylamine (1.00 mmol) and 25 mL of dry, degassed methylene chloride were added to an oven-dried 250 mL round-bottom flask. The flask was sealed, purged with argon, and placed in an acetonitrile-dry ice bath to cool to –40 °C. PIFA (1.33 mmol) was dissolved in 50 mL of dry, degassed methylene chloride and charged into an additional funnel. The addition funnel was sealed and quickly fitted to the round-bottom flask. The apparatus was purged with argon for 15 min. $BF_3{\cdot}OEt_2$ (2.66 mmol) was injected to the addition funnel, and the apparatus was swirled for proper mixing. The PIFA-$BF_3{\cdot}OEt_2$ was added dropwise to the flask over 5 min. The mixture was left to stir for 8 h in the cold bath (maintained with additional dry ice as needed) under continuous argon purge. The mixture was poured into a separatory funnel with 150 mL of saturated sodium bicarbonate. The crude product was extracted from the mixture with three 50 mL portions of methylene chloride. Extracts were combined, washed with 100 mL of brine, and dried over anhydrous $MgSO_4$. Solvents were removed by rotary evaporation. Purification was performed by column chromatography. Purified product was dried in a vacuum oven overnight at 40 °C and 75 torr.

3,6-Dimethyl-1,8-bis(trifluoromethyl)-9*H*-carbazole (5)

0.2003 g; 60%; 19:1 hexanes–ethyl acetate chromatography eluent; white powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1 H), 7.98 (s, 2 H), 7.50 (s, 2 H), 2.56 (s, 6 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 134.11 (q, J_{CF} = 1.8 Hz), 129.42, 124.99 (q, J_{CF} = 4.3 Hz), 124.94 (q, J_{CF} = 272.6 Hz), 124.33, 124.18, 112.94 (q, J_{CF} = 29.2 Hz), 21.29.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –61.41 (s, 6 F).

HPLC/HRMS (ESI): t_R = 7.39 min; *m/z* [M + H]$^+$ calcd for [$C_{16}H_{13}F_6N$ + H]$^+$: 332.0869; found: 332.0871.

TGA/DSC: no melting point, compound decomposes at 98 °C.

1,8-Dimethyl-3,6-bis(trifluoromethyl)-9*H*-carbazole (7)

0.1997 g; 60%; 4:1 hexanes–ethyl acetate chromatography eluent; light yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (s, 2 H), 8.13 (s, 1 H), 7.52 (s, 2 H), 2.65 (s, 6 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.85 125.16 (q, J_{CF} = 271.5 Hz), 123.96 (q, J_{CF} = 3.4 Hz), 123.00 (q, J_{CF} = 32.1 Hz), 122.73, 120.95, 116.14 (q, J_{CF} = 4.0 Hz), 17.05.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –61.66 (s, 6 F).

HPLC/HRMS (ESI): t_R = 6.59 min; *m/z* [M + H]$^+$ calcd for [$C_{16}H_{13}F_6N$ + H]$^+$: 332.0869; found: 332.0878.

TGA/DSC: no melting point, compound decomposes at 149 °C.

1,6-Dimethyl-3,8-bis(trifluoromethyl)-9*H*-carbazole (8)

0.1607 g; 49%; 49:1 hexanes–ethyl acetate chromatography eluent; light yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.28 (s, 1 H), 8.15 (s, 1 H), 8.01 (s, 1 H), 7.52 (s, 1 H), 7.50 (s, 1 H), 3.04 (s, 3 H), 2.50 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.82, 134.02, 129.69, 125.45, 125.20 (q, J_{CF} = 271.4 Hz), 125.02 (q, J_{CF} = 271.5 Hz), 124.86 (q, J_{CF} = 4.3 Hz), 124.12, 124.01 (q, J_{CF} = 3.4 Hz), 122.73 (q, J_{CF} = 32.1 Hz), 121.50, 120.85, 115.77 (q, J_{CF} = 3.9 Hz), 112.97 (q, J_{CF} = 32.7 Hz), 21.30, 16.87.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –61.39 (s, 3 F), –61.64 (s, 3 F).

HPLC/HRMS (ESI): t_R = 6.85 min; *m/z* [M + H]$^+$ calcd for [$C_{16}H_{13}F_6N$ + H]$^+$: 332.0869; found: 332.0875.

TGA/DSC: no melting point, compound decomposes at 122 °C.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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References and Notes

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