

Synthesis and Study of a Novel Family of Conjugated Carbazole-Centered Compounds with Potential Applications in Organic Light-Emitting Diodes (OLEDs)

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Abstract

Organic Light-Emitting Diodes (OLEDs) have been of great interest in various technological applications. Currently, there have been many successful syntheses of stable organic compounds capable of emitting red and green light. However, synthesis of stable blue light-emitting compounds has proven to be challenging and a complete color spectrum requires red, green, and blue light emitters. The present work focused on the synthesis of a novel family of carbazole-centered molecules with hopes of creating a stable blue light emitter. The parent compound is comprised of three subunit molecules, which have to be prepared individually. The subunit 4-bromodiphenylacetylene was prepared by a former research student while the subunits 2,7-dibromocarbazole (14 % yield) and 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene (dendron) (34 % yield) were synthesized in the lab. With the three subunits, an aryl boronate ester synthesis was performed to yield 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) diphenylacetylene (73 % yield), which will undergo a Suzuki coupling reaction to couple the subunits together and form the parent compound.

1. Introduction

Synthesis of organic molecules for use in organic light-emitting-diodes (OLEDs) has been an active area of study since researchers discovered their uses as alternatives to liquid crystal-based displays (LCD).^[1] Current conventional lighting sources have been both energy and economically inefficient.^[2] Using OLEDs as a replacement would reduce global electricity use by 50% and power consumption in the United States by 760 GW in 20 years.^[2]

The inspiration for the synthesis of organic compounds for use in OLEDs was derived from researchers Tang and Vanslyke who first constructed electroluminescent (EL) devices.^[10] Compared to liquid-crystal displays, the organic molecules in OLEDs are easier to synthesize and display fewer technological challenges for OLED manufacturers.^[2] Furthermore, manufacturing OLEDs over liquid-crystal displays is more cost effective and energy efficient than current light sources.^[3] To produce a full spectrum of colors, OLEDs need red, blue, and green light emitters. Red and green light emitters have been made commercially and tested to exhibit great stability.^[1] Blue light emitters, however, have concerned researchers because current blue light-emitting compounds have relatively short longevity and are limited in versatility.^[1] Synthesizing a novel compound with blue-light emitting properties will provide a new molecule for OLEDs that may help transition the move from LCD to OLED. This work is directed towards the synthesis of the

parent compound shown in **Figure 1**, which contains three subunits: the diphenylacetylene, the carbazole, and the dendron (blue, red, and green, respectively in **Figure 1**).

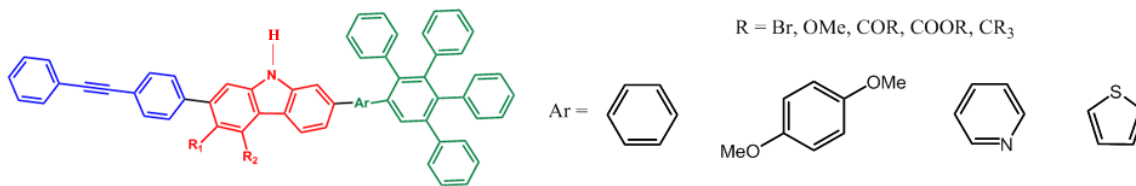


Figure 1. Parent Compound and Possible Different Functional Groups

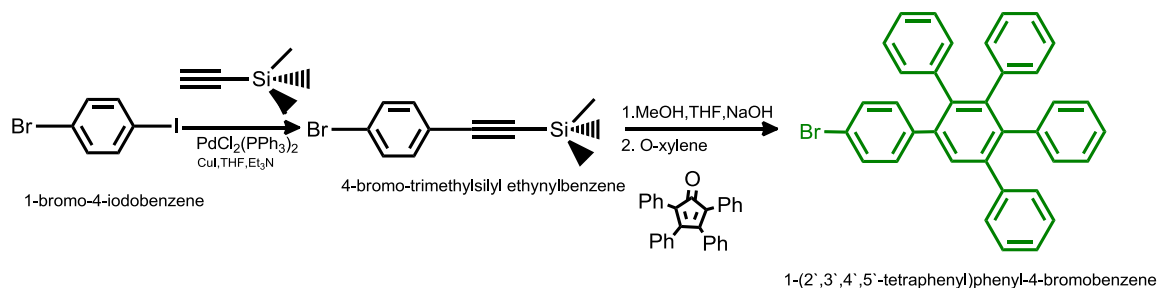
Carbazole-based derivatives have been excellent candidates for OLEDs because they are electron-rich and are among the best photoconductive polymeric materials.^[1] However, the carbazole by itself displays high instability and requires other functional groups such as the diphenylacetylene or the dendron to minimize decomposition.^[9] Diphenylacetylene is used to extend the conjugation of molecules to improve stability whereas the dendron is used to prevent a phenomenon called “pi-pi stacking”.^[9] This event occurs when pi electrons of aromatics interact with pi electrons from other aromatic molecules, which results in noncovalent attractions. Unlike many smaller aromatics, the dendron moiety is very bulky, which prevents it from being planar. Its size forces the outer rings of the dendron to rotate at an angle, which prevents pi electrons from interacting with other aromatic compounds. Once the parent molecule is synthesized, its properties can be studied via UV-vis, fluorescence spectroscopy and cyclic voltammetry. Light emission can be studied and tested in solution and in thin film form, as well as before and after exposure to air and heat. With these three subunits, the hypothesis was that the synthesized compound would have a longer longevity and stronger light-emitting properties than current blue light-emitting compounds.

To synthesize the parent compound, the three subunits needed to be prepared separately. The blue subunit precursor, 4-bromodiphenylacetylene (diphenylacetylene), was synthesized by a former research member using a modified procedure.^[5] The green precursor, 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene (dendron), was synthesized through a Sonogashira Coupling reaction and a Diels-Alder reaction.^[7] The red precursor, 2,7-dibromocarbazole (carbazole), was synthesized through a nitration reaction^[6] and a Cadogan Reductive Ring Closure.^[6] The subunits were borylated through an aryl boronate ester synthesis,^[4] and then they will be coupled to the carbazole through a Suzuki-Miyaura cross-coupling reaction.^[3] Herein describes our synthetic efforts towards the parent compound.

2. Results and Discussions

I. Synthesis of 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene

Synthesis of the dendron was achieved through a two-step process (**Scheme 1**). The first step was to synthesize 4-bromo-TMS ethynylbenzene from 1-bromo-4-iodobenzene through a Sonogashira coupling reaction.^[7] GC-MS analysis (**Figure 2**) displayed a peak at 5.747 min with m/z ratios of 254/256, which is indicative of 4-bromo-TMS ethynylbenzene. Two peaks are present in 1:1 ratio because of the two bromine isotopes (Br-79 and Br-81). The peaks at approximately 4.17 min and 5.08 min corresponded to the self-coupling of TMS-acetylene and 1-bromo-4-iodobenzene, respectively. The large peak at 5.08 min indicated that the reaction did not reach completion and needed more time. TLC was performed to determine the progress and estimated completion time of the reaction. Another GC-MS analysis was not needed because chromatography would separate out the product from the crude mixture. After isolating the product via column chromatography, the reaction produced a 92 % yield of 4-bromo-TMS ethynylbenzene. This yield was higher than the product yield of 65 % found by Huang *et al.*^[7]



Scheme 1. Synthesis of 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene (dendron)

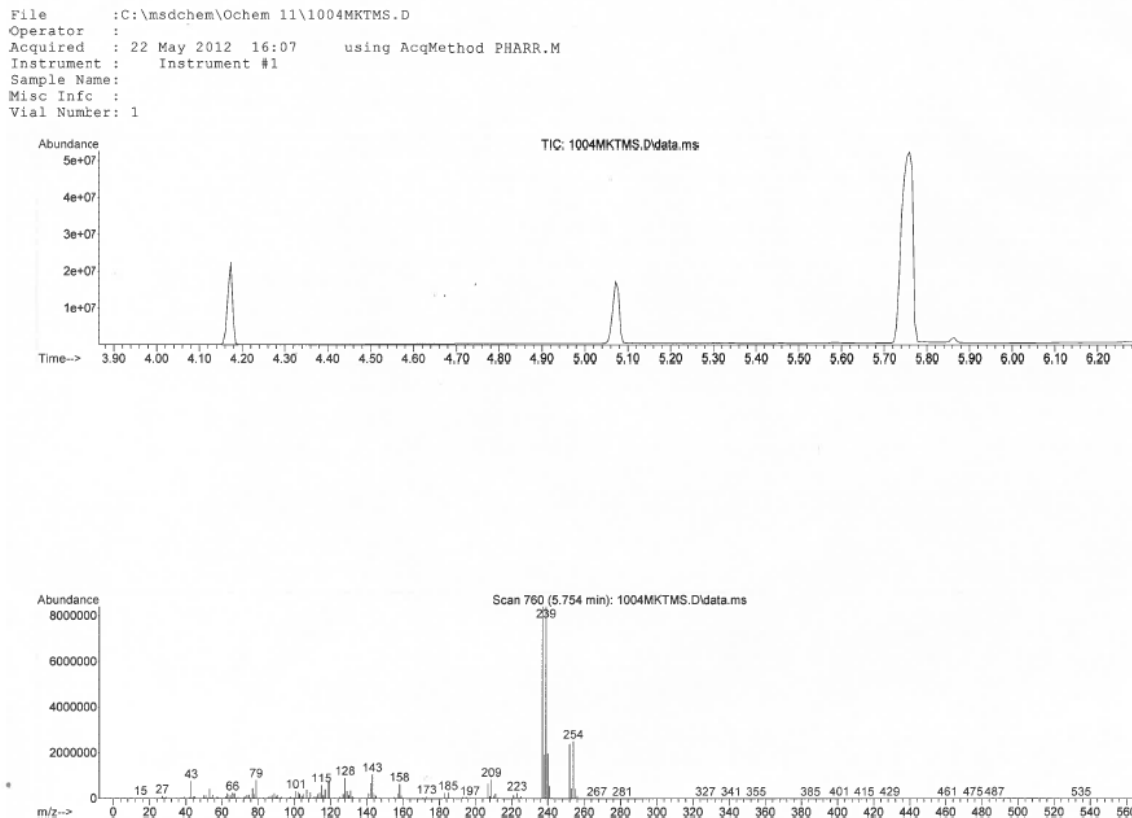
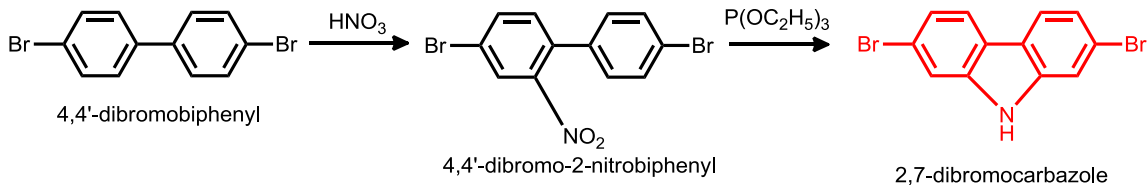


Figure 2. GC-MS Chromatogram (top panel) and Mass Spectrum (bottom panel) of the Crude Reaction Mixture from the Sonogashira Coupling Reaction

The second step was to synthesize the dendron from 4-bromo-TMS ethynylbenzene through a Diels-Alder reaction.^[7] GC-MS was not performed due to the large mass of the dendron subunit. Alternatively, melting point analysis was performed to determine the purity and identity of the product. The melting point of the analyte was 225-228°C, which fell within the range of the expected melting point for the dendron (223-226°C). This scheme produced a 34 % yield of the dendron, which was lower than the 47 % product yield found by Huang *et al.*^[7] Running multiple column chromatography systems to purify the product could account for the smaller yield.

II. Synthesis of 2,7-dibromocarbazole

Synthesis of the carbazole was achieved through a two-step process (**Scheme 2**).



Scheme 2. Synthesis of 2,7-dibromocarbazole.

The first step was to synthesize 4,4'-dibromo-2-nitrobiphenyl from 4,4'-dibromobiphenyl through a nitration reaction.^[6] GC-MS analysis (**Figure 3**) displayed a peak at 9.351 min with m/z ratios of 355/357/359, which is indicative of 4,4'-dibromo-2-nitrobiphenyl. These three peaks are present with a ratio of 1:2:1 because of the two bromine isotopes that can occupy both ends of the intermediate. The peak at 7.84 min corresponds to 4,4'-dibromobiphenyl, indicating that the reaction did not reach completion. The reaction continued until both the TLC and MS spectrum indicated that the reaction reached completion. The peak at 6.35 min corresponds to a compound that did not leave the column from a previous run. This reaction produced an 80. % yield of 4,4'-dibromo-2-nitrobiphenyl while the literature yield was 91 %.^[6]

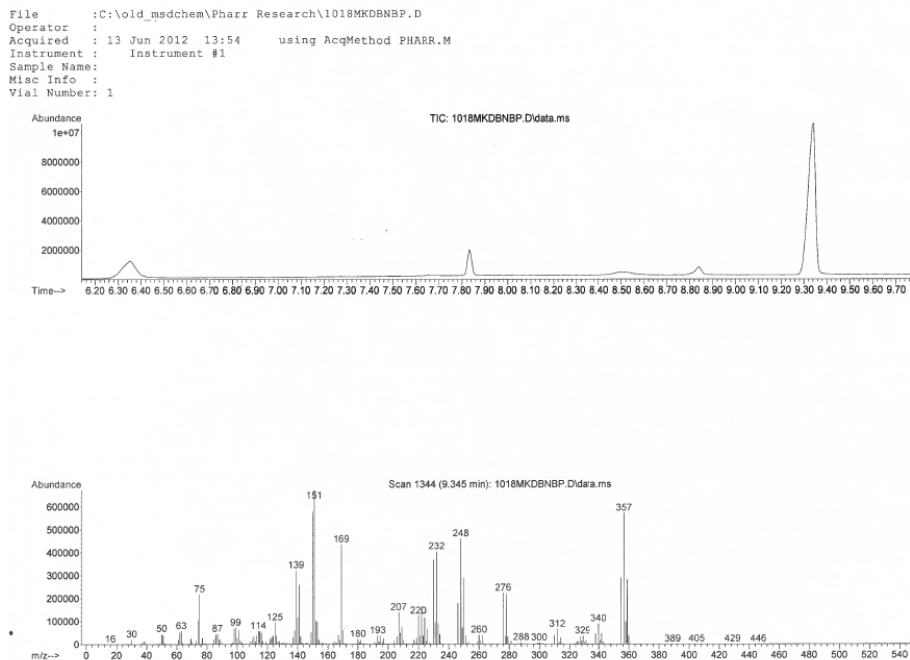


Figure 3. GC-MS Chromatogram (top panel) and Mass Spectrum (bottom panel) of the Crude Reaction Mixture from the Nitration Reaction

The second step was to synthesize the carbazole from 4,4'-dibromo-2-nitrobiphenyl via a Cadogan Reductive Ring Closure.^[6] After several purifications, GC-MS analysis (**Figure 4**) displayed a peak at approximately 6.670 min with m/z ratios of 325/327/329, which is indicative of 2,7-dibromocarbazole. These three peaks have a ratio of 1:2:1 for the same reasons as the first step of the carbazole synthesis. The product yield of this reaction was 14 % while the literature yield was 56 %.^[6] After letting the reaction proceed for the allotted time in the procedure, some of the starting reagent was present, which had to be separated out from the final product, which would decrease the product yield.

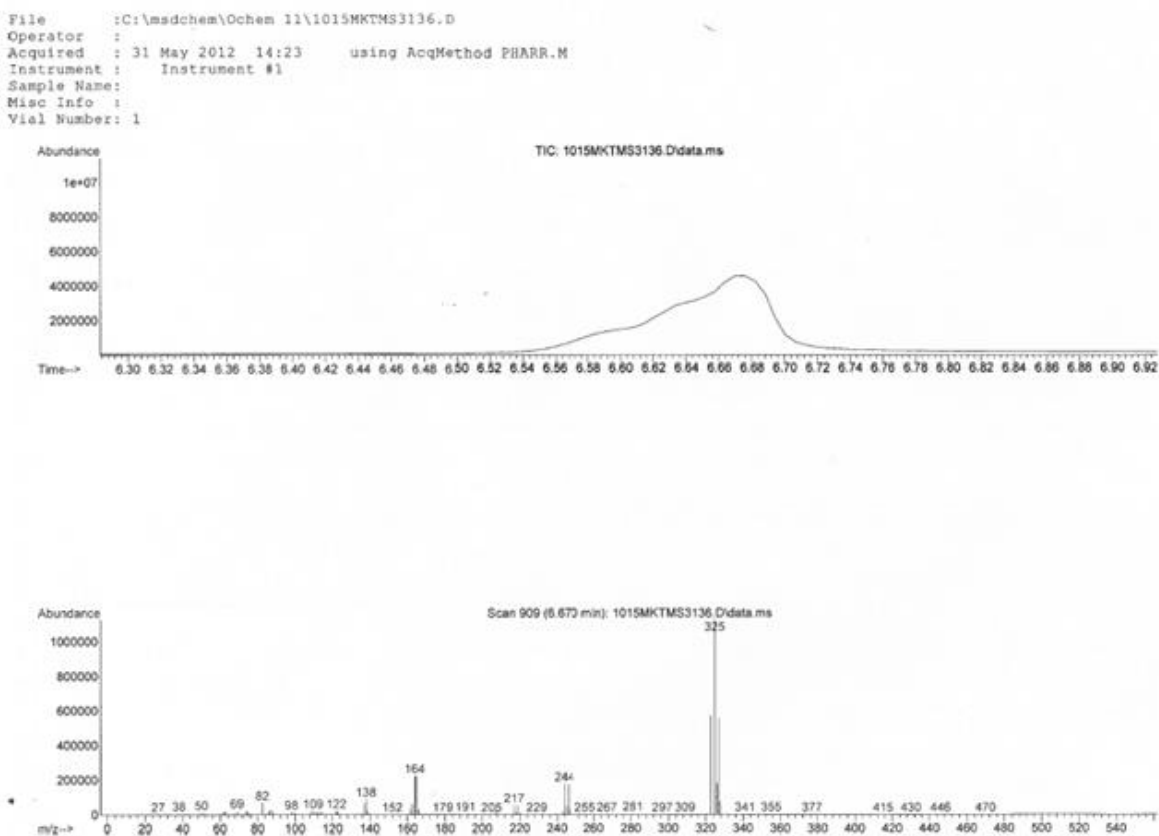
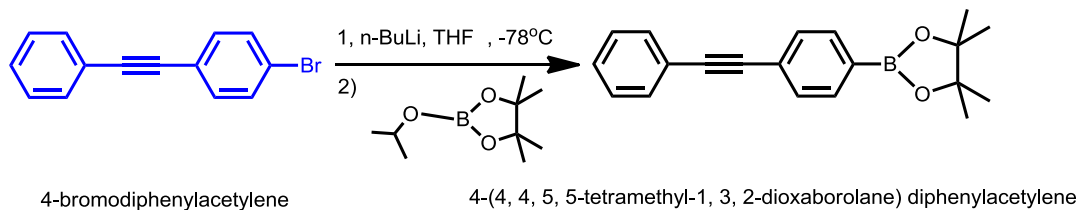


Figure 4. GC-MS Chromatogram (top panel) and Mass Spectrum (bottom panel) of the Reaction Mixture from the Cadogan Reductive Ring Closure Reaction

III. Synthesis of the borylated diphenylacetylene

To synthesize the proposed compound, the subunits needed to be borylated. Synthesis of 4-(4, 4, 5, 5-tetramethyl-1, 3, 2,-dioxaborolane) diphenylacetylene was achieved through an aryl boronate ester reaction (**Scheme 3**) using diphenylacetylene.^[8]



Scheme 3. Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) diphenylacetylene

GC-MS spectrum (**Figure 5**) displayed a lone peak at 19.488 min with a m/z ratio of 304, which is indicative of the 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) diphenylacetylene. ^1H NMR analysis was performed to further characterize the reaction product, which produced the spectrum in **Figure 6**. The signal at 1.377 ppm corresponds to the hydrogens in the four methyl groups (Ha) from the dioxaborolane.

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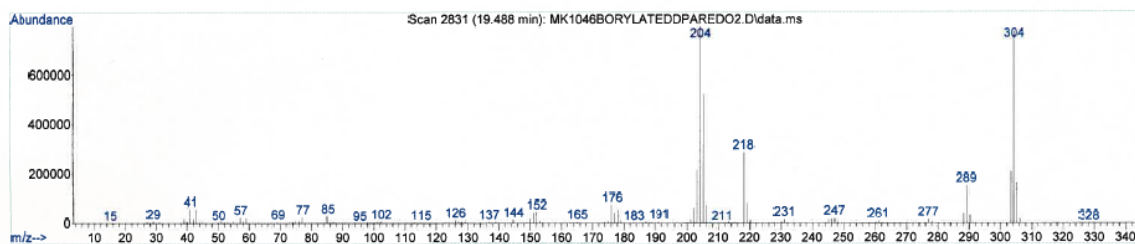
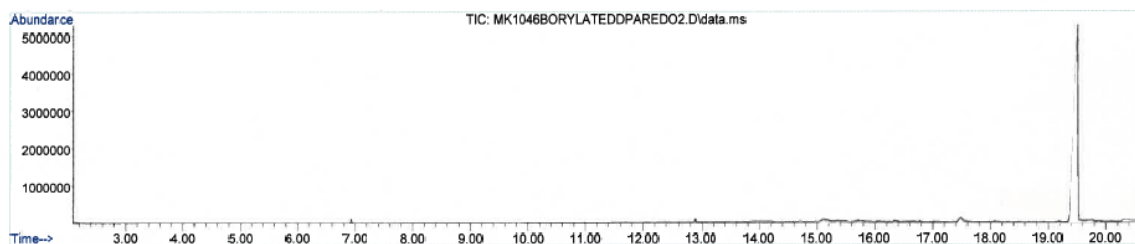


Figure 5. GC-MS Chromatogram (top panel) and Mass Spectrum (bottom panel) of the Reaction Mixture from the Aryl Boronate Ester Synthesis

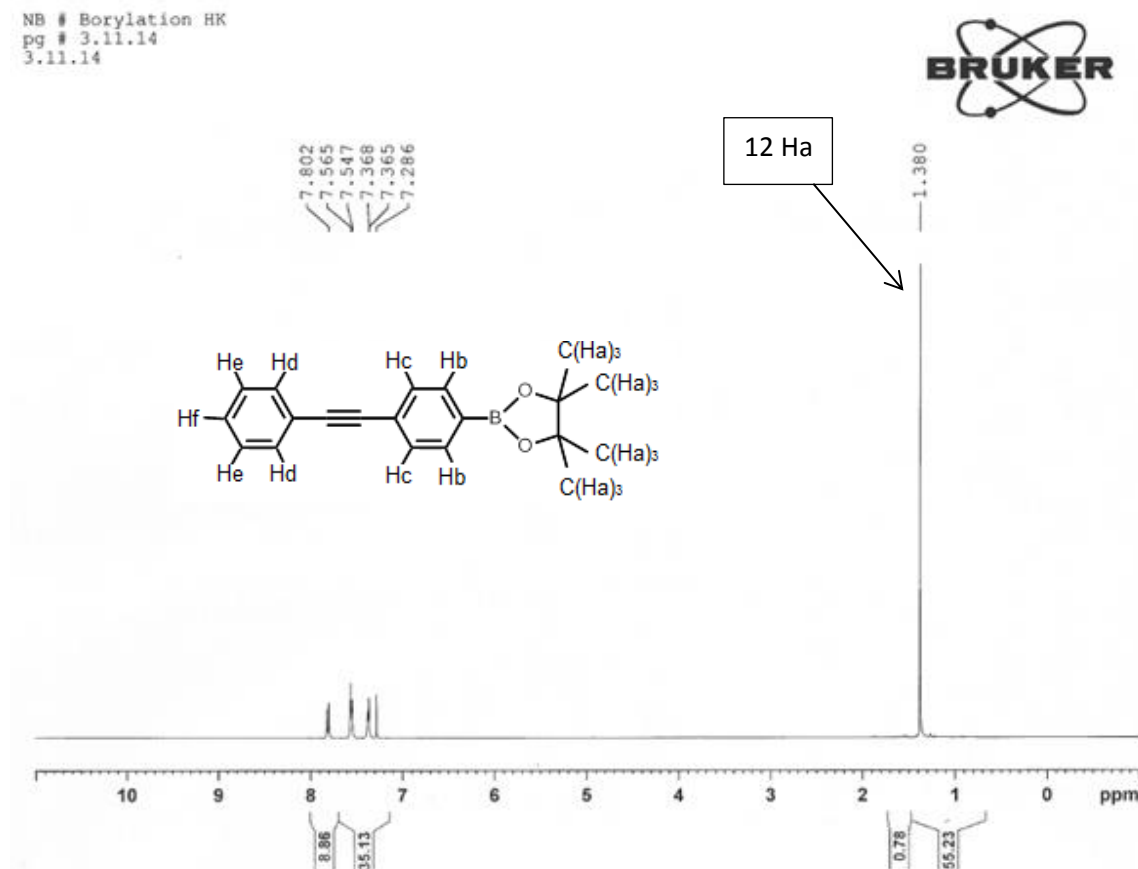


Figure 6. ^1H NMR Spectrum of the borylated diphenylacetylene with the Molecular Structure

Figure 7 shows a closer look at the ^1H NMR from 7.285 to 7.819 ppm, which correspond to the aromatic regions in the diphenylacetylene. In the aromatic region from right to left, a singlet is shown, which corresponds to the CHCl_3 or solvent peak, and an overlap of several peaks around 7.366 ppm is shown, which correspond to He and Hf because these hydrogens are shielded more than Hb, Hc, and Hd based on their positions on the molecule. The peaks from 7.547-7.565 ppm correspond to Hc and Hd while the doublet at around 7.802 ppm corresponds to Hb due to their positions on the molecule. With the results from the GC-MS and ^1H NMR, it was determined that the borylated diphenylacetylene was synthesized successfully and with high purity.

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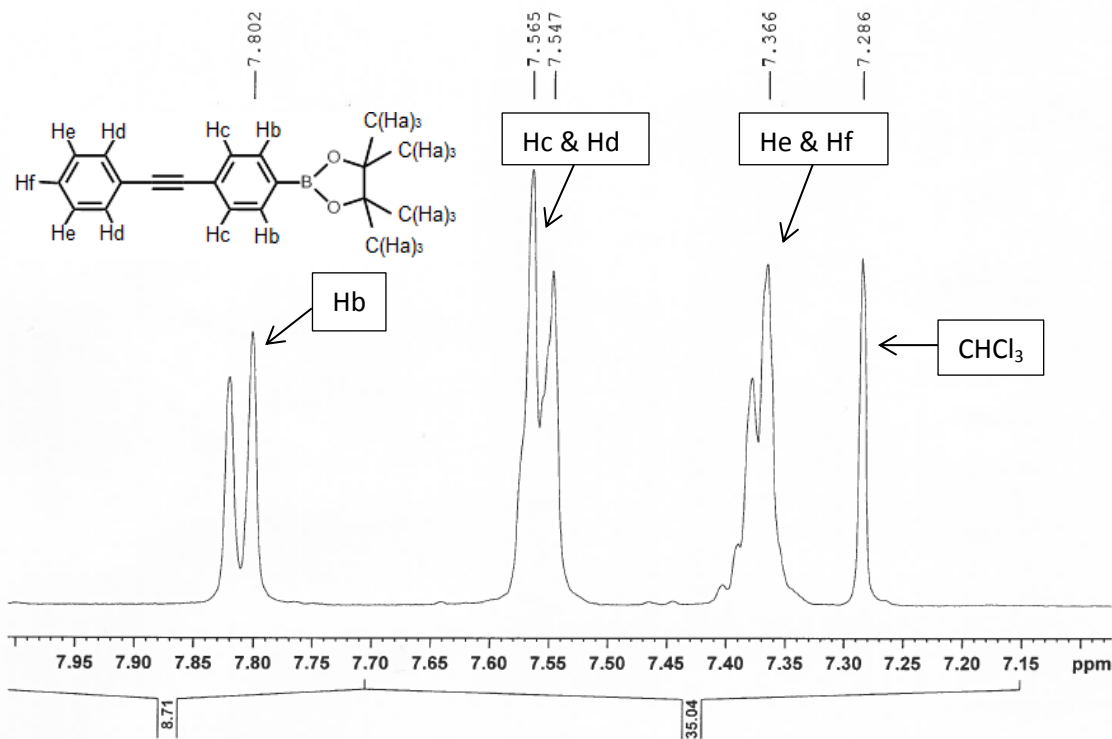


Figure 7. ^1H NMR Spectrum of the borylated diphenylacetylene (from 7.286 to 7.819 ppm) with the Molecular Structure

In conclusion, all three subunits were synthesized and characterized. Attempts at producing the borylated diphenylacetylene were successful and characterized via GC-MS and ^1H NMR. As of spring of 2014, attempts at producing the proposed compound were performed via a Suzuki-Miyaura coupling reaction.^[3]

3. Experimental:

Most solvents and reagents were purchased from Sigma Aldrich and did not require further preparation prior to use except for one exception. Tetrahydrofuran was dried over 4 Å molecular sieves that had been oven dried for a minimum of 24 hours and left to sit for 48 hours before use. An R-210 Rotary Evaporator was used to expedite the removal of solvents from the products. A Mel-Temp melting point apparatus was used to determine melting points. An HP 6890 Series GC System with an HP 5973 Mass Selective Detector was used to perform mass spectrometry. Chemstation Data Analysis program provided analysis of the MS chromatogram

and mass spectrum to determine the m/z ratios. A 400 MHz Avance III HD Nanobay Bruker NMR was used to perform ^1H NMR analysis.

I. Synthesis of 4-bromo-TMS ethynylbenzene^[7]

A solution of 1-bromo-4-iodobenzene (4.905 g, 17.34 mmol), copper(I) iodide (0.043 g, 0.0232 mmol), bis[triphenylphosphinepalladium(II)] chloride (0.024 g, 0.033 mmol), triethylamine (15 mL, 107.6 mmol), and dry tetrahydrofuran (50 mL) were added to a three neck flask and the mixture was degassed by bubbling nitrogen gas through the mixture for fifteen minutes. To the solution, trimethylsilyl(TMS)acetylene (2.5 mL, 0.0177 mmol) was added drop wise and the mixture was stirred for 20 hours, which resulted in a color change from clear yellow to opaque yellow. Afterwards, the solution was washed successively with 2 M hydrochloric acid (2X, 20 mL)/ distilled water (3X, 20 mL), dried with magnesium sulfate, and concentrated to afford a white solid (4.789 g, 18.8 mmol, 92 % yield) the next day. GC-MS: m/z 254/256 (1:1).

II. Synthesis of 1-(2',3',4',5'-tetraphenyl)phenyl-4-bromobenzene^[7]

A mixture of 4-bromo-TMS ethynylbenzene (4.789 g, 18.85 mmol), tetrahydrofuran (106.18 mL, 1.062 mol), and methanol (26.55 mL, 0.655 mol) were added to a round bottom flask. Sodium hydroxide (5 M, 8.85 mL) was added slowly to the mixture. The reaction was stirred for 1 hour at room temperature to form a clear yellow solution. Tetrahydrofuran was added. The mixture was washed successively with distilled water (3X, 10 mL)/ brine (3X, 5 mL), dried with magnesium sulfate, and concentrated. The remaining white precipitate was added to a stirring solution of tetraphenylcyclopentadienone (7.217 g, 19.97 mmol) and *o*-xylene (20 mL), then heated at 144°C for 70 hours. The resulting mixture was then loaded on a silica chromatography column and eluted with 3:1 hexane : dichloromethane, affording a white solid (3.448 g, 6.60 mmol, 47% yield) after concentration. Melting point: 225-228°C.

III. Synthesis of 4,4'-dibromo-2-nitrobiphenyl^[6]

A solution of 4,4'-dibromobiphenyl (10.024 g, 0.032 mol) and glacial acetic acid (150 mL) at 100°C was prepared in a round bottom flask. Fuming nitric acid (84 % nitric acid, 46 mL) and distilled water (3.75 mL) was added to the solution and the reaction mixture was stirred for 30 minutes. Afterwards, the solution was transferred to a beaker, which precipitated out a yellow product as it cooled. The precipitate was concentrated to afford a yellow solid (8.015 g, 0.024 mol, 80%). GC-MS: m/z 355/357/359 (1:2:1).

IV. Synthesis of 2,7-dibromocarbazole^[6]

A mixture of 4,4'-dibromo-2-nitrobiphenyl (8.015 g, 22.46 mmol) and triethyl phosphite (30 mL) was heated under reflux for 18 hours. The color of the solution changed from yellow to red. Excess triethyl phosphite was distilled off and the product was purified via column chromatography using 10:1 hexane : ethyl acetate as the solvent system. The isolated product was then left to evaporate, yielding a light peach-colored product (1.022 g, 3.14 mmol, 14 %). GC-MS: m/z 325/327/329 (1:2:1).

V. Synthesis of 4-(4, 4, 5, 5-tetramethyl-1, 3, 2,-dioxaborolane) diphenylacetylene^[8]

In a three neck flask degassed with nitrogen gas, 4-bromodiphenylacetylene (1.015 g, 3.93 mmol), 4, 4, 5, 5-tetramethyl-1, 3, 2,-dioxaborolane (1.2 mL, 8.27 mmol), and dry tetrahydrofuran (20 mL) were added together and stirred at -78°C for 15 minutes. Next, *n*-butyllithium (2.5 M in hexane, 3.2 mL) was added drop wise in the mixture for 30 minutes under the same temperature conditions, which resulted in a color change from orange to red. After 1-2 hours, the mixture was stirred at room temperature for 18 hours. The mixture was combined with 25 mL of distilled water and then successively washed with dichloromethane (3X, 20 mL)/ brine (3X, 20 mL). If two layers did not appear after a few minutes between washes, brine was added (~3 mL) to expedite the process. A foamy layer appeared in between the organic layer and aqueous layer, which was not extracted with the organic layers. The final combined organic layers were dried with magnesium sulfate and concentrated to afford a clear yellow solid (0.891 g, 2.9 mmol, 73 %). ¹H NMR (CDCl₃, 400MHz): δ 1.380 (singlet, 12 H) , 7.366 (triplet, 1 H), 7.368 (triplet, 2 H), 7.547 (doublet, 2 H), 7.565 (doublet, 2 H), 7.802 (doublet, 2 H). GC-MS: m/z 304.

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5. References:

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