The development of corannulene-based blue emitters†

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Novel blue emitters were synthesized based on the fullerene fragment corannulene. 1,2-bis(corannulenylethynyl)benzene and 1,4-bis(corannulenylethynyl)benzene were designed, synthesized, and shown to exhibit significant red shifts in their absorption spectra as compared to that of the parent corannulene. Photoluminescence studies show both 1,2- bis(corannulenylethynyl)benzene and 1,4-bis(corannulenylethynyl)benzene gives enhanced blue luminescence compared to the parent corannulene structure. 1,4-bis(corannulenylethynyl)benzene was observed to give intense blue luminescence when excited at 400 nm. DFT and TD-DFT calculations were performed and shown to be consistent with the observed experimental results.

Introduction

The advancement of technology in various fields is reliant upon the discovery of new and promising materials. Organic molecules are desirable since they are light and flexible. Two classes of molecules that have spearheaded the area of organic materials are fullerenes and nanotubes. These molecules have shown promise in medicine, photovoltaics, optical limiters, organic light-emitting diodes, and many other emerging fields.[1] Due to the difficulty to selectively modify fullerenes and the complexity in the processing of nanotubes, neither has made it very far in commercial production.

A vast amount of research has focused on the development of fullerene and nanotube-based materials, conversely, the area of fullerene fragments has virtually been ignored in this endeavour. Corannulene (**1**)[2] (Fig. 1), which represents 1/3 of fullerene[60], is a molecule that has been known for almost forty years, but due to its lengthy original synthesis only microscopic quantities were available for analysis.[3] The pioneering work of Scott *et al.*,[4] Siegel *et al.*,[5] and others[6] has made it possible to obtain macroscopic quantities of corannulene and other fullerene fragments. Given the greater availability of these novel molecules many of the properties of corannulene have been uncovered.

Corannulene has been shown to have a significant dipole moment[7] and to form complexes with fullerenes,[8] various metals[9] and even molecular hydrogen.[10] Corannulene can accept up to four electrons, and it has been shown that each reduction causes significant changes in its absorption spectrum.[11] Several publications have reported on the fluorescence and phosphorescence properties of this unique molecule.[12] Corannulene's electrochromic and fluorescent properties suggest organic materials based on its molecular framework could show promise in the display industry.

To further advance organic light-emitting diode (OLED) technology there is a continual need to seek molecules that embody the necessary properties. Robust materials that emit blue light are in constant demand for various display applications.[13] Previous reports show extending the conjugation of corannulene causes a red shift in the absorption spectrum along with increased fluorescence.[5b] Bicorannulenylacetylene was synthesized and shown to give a strong blue fluorescence with a quantum yield of 0.57; more than eight times that of the parent corannulene (*ca.* $\Phi = 0.07$).[5b] Unfortunately, bicorannulenylacetylene rapidly decomposes, even at temperatures as low as −16 °C. Our research group looks to develop and further understand the potential of fullerene fragments as prominent organic-based materials. We designed two molecules, 1,2-bis(corannulenylethynyl)benzene (**5**) and 1,4-bis(corannulenylethynyl)benzene (**6**) for use as organic blue emitters. These molecules were designed to extend the conjugation between corannulene moieties, which is expected to cause a significant red shift in the absorption spectrum, further we expect these molecules will give enhanced luminescent properties.

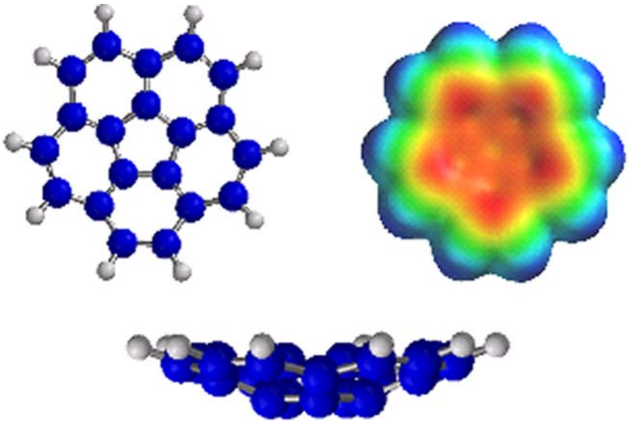

Fig. 1 Top view of corannulene (**1**) (top left). Side view of corannulene (bottom). Electron-density map of corannulene (top right, red indicates high electron density while blue represents low electron density.

Results and discussion

Corannulene (**1**) was prepared according to the published method.[5,6] **5** and **6** were synthesized according to Scheme 1. Bromocorannulene (**2**) was prepared from corannulene using

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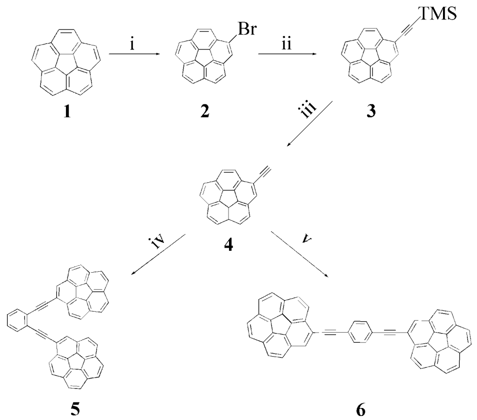
† Electronic supplementary information (ESI) available: ^{1}H NMR, ^{13}C NMR, MALDI-TOF and TGA/DSC data for compounds **5** and **6**. See DOI: 10.1039/b705621d



Scheme 1 *i*) IBr, DCE 90%, *ii*) TMS-acetylene, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3–THF, 12 h, 97%, *iii*) K_2CO_3, MeOH–CH_2Cl_2, 94%, *iv*) 1,2-$C_6H_4Br_2$, CuI, $Pd(PPh_3)_2Cl_2$, diisopropylamine–THF, 12 h, 15%, *v*) 1,4-$C_6H_4Br_2$, CuI, $Pd(PPh_3)_2Cl_2$, diisopropylamine–THF, 12 h, 12%.

iodobromide in anhydrous 1,2-dichloroethane in 90% yield. Sonogashira coupling of **2** with trimethylsilylacetylene was achieved in the presence of copper iodide, diisopropylamine, anhydrous THF and catalytic *trans*-dichlorobis(triphenylphosphine)palladium(II) in 97%. Deprotection of (trimethylsilylethynyl)corannulene (**3**) in methanol–THF and potassium carbonate provided ethynylcorannulene (**4**) in 94% yield. Pure **4** was immediately coupled with 1,2-dibromobenzene and 1,4-dibromobenzene due to the rapid decay of **4** in light and an open atmosphere. Sonogashira coupling of **4** with 1,2-dibromobenzene and 1,4-dibromobenzene gave 1,2-bis(corannulenylethynyl)benzene (**5**) and 1,4-bis(corannulenylethynyl)benzene (**6**) in 15% and 12% yield, respectively (Scheme 1). Upon purification, 3.9 μM CH_2Cl_2 solutions of **1**, **5**, and **6** were made and their absorption (Fig. 2) and emission spectra (Fig. 4 and Fig. 5) were recorded.[14]

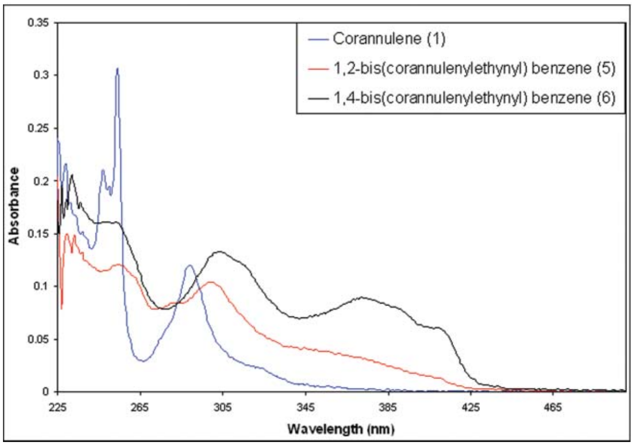


Fig. 2 Absorption spectra for corannulene (**1**), 1,2-bis(corannulenylethynyl)benzene (**5**) and 1,4-bis(corannulenylethynyl)benzene (**6**).

Compound **1** gives two prominent absorption bands centered at 254 nm (ε = 79 900), and 289 nm (ε = 30 900). Two prominent absorption bands were observed for **5** centered at 254 nm (ε = 31 300) and 299 nm (ε = 26 900) with a long tail that trails into the visible region of the spectrum. Compound **6** gives three prominent absorptions centered at 250 nm (ε = 41 700), 302 nm (ε = 34400), and 371 nm (ε = 23 300) with a broad shoulder trailing into the visible region of the spectrum.

Table 1 Calculated TD-DFT wavelength (nm) and oscillator strength, *f*, for most relevant transitions. Experimental values are added for comparison

Molecule	Experimental wavelength/nm	Calculated wavelength/nm	*f*
1	254	254	0.1907
1	289	283	0.2496
5	299	293	0.2819
6	250	244	0.1352
6	302	303	0.3153
6	371	401	1.7661

To gain insight into the absorption spectra we performed density functional theory (DFT) and time-dependent-density functional theory (TD-DFT) calculations on the geometry and absorption spectra for **1**, **5**, and **6**. We employed the B3LYP exchange–correlation functional with a 6–31G* basis set, as implemented in the Gaussian 03 suite of programs.[15] It has been shown that B3LYP theory with a 6–31G* basis set accurately reproduces bond lengths, bond angles and dihedral angles for corannulene, therefore we feel confident in the geometrical output.[16] TD-DFT calculations were also obtained at the B3LYP level of theory with a 6–31G* basis set. Calculated wavelengths and oscillator frequencies (*f*) are listed in Table 1.

The B3LYP/6–31G* geometry optimized structure for **5** places the outer rim of each corannulene moiety directly over the interior of the other corannulene (Fig. 3). This is similar to the X-ray crystallographic data of corannulene that places two corannulene units in a similar arrangement.[17] Each bowl is twisted (with a twist angle of *ca.* 7°)[18] with respect to the benzene ring. Compound **6** is calculated to be a planar structure with both corannulene moieties twisted less than 1° with respect to the benzene ring.

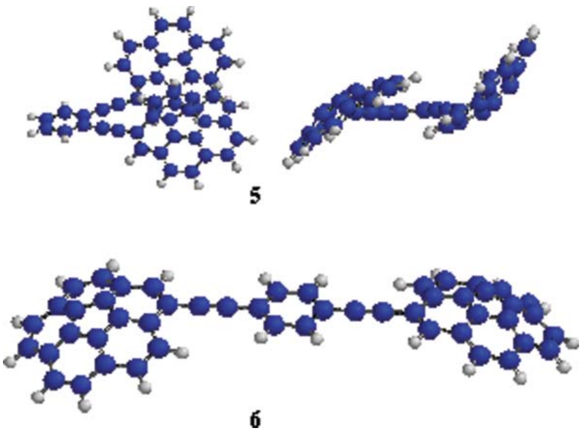


Fig. 3 B3LYP/6–31G* calculated geometries for **5** (top left and top right) and **6** (bottom).

According to TD-DFT calculations for **1**, significant transitions are predicted to be observed at 220 nm (*f* = 0.1335), 254 nm (*f* = 0.1907), and 283 nm (*f* = 0.2496). These calculated transitions correlate very well with the observed bands at 220 nm, 254 nm, and 286 nm.

TD-DFT calculations for **5** predict a transition at 293 nm ($f = 0.2819$), which is observed at 299 nm.[19] The HOMO-to-LUMO transition is predicted at 425 nm ($f = 0.225$) but this band is observed at 360 nm. We believe there are intramolecular bowl-to-bowl interactions which are not accounted for by the TD-DFT B3LYP level of theory, this leads to the inaccuracy of the HOMO-to-LUMO transition in structure **5**.

TD-DFT calculations of **6** predicts significant absorption bands centered at 244 nm ($f = 0.1352$), 303 nm ($f = 0.3153$) and 401 nm ($f = 1.7601$). These transitions correlate well with the observed absorption at 250, 302 and 371 nm. Comparing TD-DFT calculations with the observed absorption spectra we see that TD-DFT at the B3LYP level of theory does a relatively good job of predicting the effect of extended conjugation on corannulene-based structures.

As we expected, extending the conjugation of corannulene led to a significant red shift of the absorption spectrum. We further expected the fluorescence spectra for both **5** and **6** to emit at longer wavelength than the parent corannulene and give increased fluorescence. Compounds **1**, **5** and **6** were excited at 300 nm (Fig. 4) and 400 nm (Fig. 5). Exciting **1** at 300 nm gives low intensity blue fluorescence with two emission bands, one centered at 420 nm and the other centered at 440 nm, which is consistent with previous reports.[12]

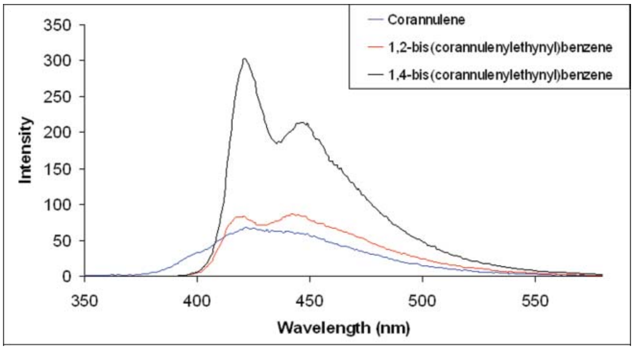


Fig. 4 Fluorescence spectra of corannulene (**1**), 1,2-bis(corannulenylethynyl)benzene (**5**) and 1,4-bis(corannulenylethynyl)benzene (**6**) excited at 300 nm.

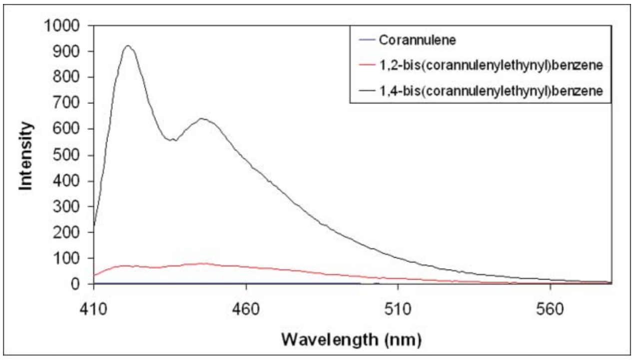
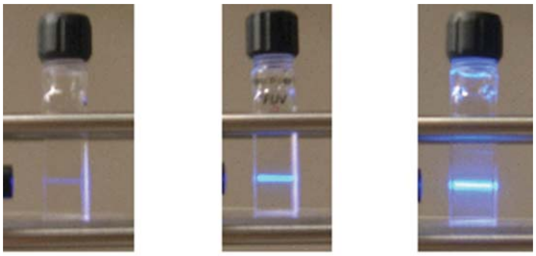


Fig. 5 Fluorescence spectra of corannulene (**1**), 1,2-bis(corannulenylethynyl)benzene (**5**) and 1,4-bis(corannulenylethynyl)benzene (**6**) excited at 400 nm.

Somewhat to our surprise **5** and **6** give similar emission spectra to the parent corannulene. Compounds **5** and **6** give two strong emissions at 420 nm and 440 nm, which is what was observed for corannulene. Although **5** and **6** do not give longer wavelength emissions, they do give higher fluorescence intensity. Excitation of **5** at 300 nm provides slightly higher fluorescence intensity (*ca.* $\Phi = 0.08$) to that of the parent corannulene, while **6** gives greatly increased fluorescence intensity (*ca.* $\Phi = 0.60$).[20] Excitation of corannulene at 400 nm gives no significant fluorescence. Excitation of **5** gives a slightly increased fluorescence compared to corannulene, while **6** gives a significantly stronger fluorescence intensity.

Compound **5**, which has each corannulene unit out of plane with respect to the benzene ring, has lower absorbance in the visible region of the absorption spectrum thus lower subsequent emission when excited at 400 nm. Compound **6**, on the other hand, has both corannulene units planar to the benzene ring providing stronger absorbance in the visible region of the absorption spectrum and a much higher emission when excited at 400 nm.

To determine the viability of these molecules as blue emitters we irradiated a sample vial of each with a 405 nm laser beam (Fig. 6). Irradiation of the corannulene solution gave light scattering without any significant observed fluorescence. Irradiation of **5** shows a soft light blue fluorescence, while irradiation of **6** shows a bright blue fluorescence.



1 **5** **6**

Fig. 6 Solution of corannulene (**1**) excited with 405 nm laser. 1,2-Bis-(corannulenylethynyl)benzene (**5**) excited with 405 nm laser. 1,4-Bis(corannulenylethynyl)benzene (**6**) excited with 405 nm laser.

Compounds **1**, **5**, and **6** are all stable to an open atmosphere and have shown no signs of degradation since they were originally synthesized (*ca.* 6 months). TGA/DSC analysis of **1** gives a sublimation trace between 200–300 °C. Both **5** and **6** show no significant changes up to 200 °C with only 30% loss of material after ramping to 600 °C.

Conclusions

We have studied the optical properties of corannulene (**1**), 1,2-bis(corannulenylethynyl)benzene (**5**) and 1,4-bis(corannulenylethnyl)benzene (**6**) to determine the effect of extended conjugation on the absorption and emission spectra of corannulene-based molecules. We have shown that by extending the conjugation of corannulene, we can increase the wavelength of absorption and greatly enhance its luminescence properties, thus making corannulene-based molecules a viable material for blue emission. Further, we determined these molecules are stable and have potential in OLED technology. We are in the process of designing and synthesizing other corannulene-based molecules for many other technological advances. We expect the further engineering of corannulene-based molecules that absorb further into the visible region will allow us to make corannulene-based materials that can be tuned throughout the full range of the absorption and emission spectrum.

Experimental

General experimental information

Column chromatography was carried out using an Isco Combiflash Companion column system with silica gel columns purchased from Silicycle Inc. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover MA, and used without further purification. Molecular masses were determined by a Bruker Biflex III matrix-assisted laser desorption–ionization time of flight mass spectrometer (MALDI-TOF-MASS) with a tetracyanonapthaquinone matrix. Absorption and emission spectra were measured in CH_2Cl_2 in a 1 cm path quartz cell using a Cary 50 UV-Vis spectrophotometer and a Cary Eclipse fluorescence spectrophotometer, respectively. Thermal gravametric analysis (TGA) and differential scanning calorimetry (DSC) was conducted using a Netzsch STA 409 PC/PG. A Power Technologies 405 nm, 2mW laser was used for luminescence studies.

Materials and synthesis

All chemicals were purchased from Acros Organics, and used without further purification unless otherwise noted. *trans*-Dichlorobis(triphenylphosphine)palladium(II) was purchased from Strem chemicals. Anhydrous solvents were obtained *via* an MBraun solvent-purification system.

Bromocorannulene (2)

To a solution of corannulene (1.0 g, 4 mmol) in anhydrous 1,2-dichloroethane (20 mL) under a blanket of nitrogen was added iodobromide (2.53 g, 12.2 mmol). The mixture was stirred at room temperature for a period of 12 h. The crude mixture was evaporated under reduced pressure and purified by column chromatography using a gradient cyclohexane–CH_2Cl_2 eluent to provide a yellowish solid (1.2 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.03$ (s, 1H), 7.93 (d, 1H, $J = 8.6$ Hz), 7.87–7.78 (m, 6H), 7.71 (d, $J = 8.6$ Hz, 1H) ^{13}C NMR ($CDCl_3$) $\delta = 122.1$, 126.7, 127.2, 127.7, 127.9, 128.0, 128.4 (2C), 128.8, 130.1, 130.9, 131.5, 131.8 (2C), 132.7, 135.5, 135.8, 136.4, 136.6. All spectroscopic data are consistent with published results.[5a]

(Trimethlysilylethynyl)corannulene (3)

In a dry box with an argon atmosphere, to a pressure vessel was added bromocorannulene (0.495 g, 1.5 mmol), copper iodide (0.032 g, 0.16 mmol), trimethylsilylacetylene (0.516 g, 5.27 mmol) *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.085 g, 1.2 mmol), triethylamine (30 mL) and anhydrous THF (30 mL). The pressure vessel was sealed and the reaction stirred for 12 h at 75 °C. The crude mixture was washed with 10% HCl (3 × 10 mL), and extracted with CH_2Cl_2 (25 mL). The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The crude mixture was purified by column chromatography using a gradient cyclohexane–CH_2Cl_2 eluent, which gave the title compound (0.524 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.16$ (s, 9H), 7.40–7.58 (m, 6H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.77 (s, 1H), 7.78 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$) $\delta = 0.3$, 98.4, 103.1, 121.2, 126.0, 126.5, 126.9, 127.0, 127.2, 127.3, 127.5, 130.0, 130.7, 130.9, 131.0, 131.6, 134.9, 135.2, 135.4, 135.5, 135.9. All spectroscopic data are consistent with published results.[5b]

Ethynylcorannulene(4)

To a stirred solution of potassium carbonate (0.627 g, 4.54 mmol) in methanol (15 mL) was added (trimethylsilylacetylene)corannulene (0.524 g, 1.5 mmol) dissolved in CH_2Cl_2 (10 mL). The reaction was stirred for 0.5 h at room temperature. The crude reaction was treated with water (50 mL), and extracted with CH_2CL_2 (3 × 15 mL). The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The crude mixture was purified by column chromatography using a cyclohexane eluent, which gave the title compound (0.386 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 3.38$ (s, 1H), 7.71–7.77 (m, 6H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.97–8.00 (m, 2H). ^{13}C NMR ($CDCl_3$) $\delta =$ 80.6, 81.8, 120.3, 126.0, 126.7, 127.3, 127.6, 127.7, 127.8, 130.2, 131.1, 131.2, 131.3, 131.4, 135.2, 135.6, 135.7. All spectroscopic data are consistent with published results.[5b]

1,2-Bis(corannulenylethynyl)benzene (5)

In a dry box with an argon atmosphere, to a pressure vessel was added ethynylcorannulene (0.389 g, 1.2 mmol), 1,2-dibromobenzene (0.141 g, 0.6 mmol), copper iodide (0.032 g, 0.16 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.085 g, 0.12 mmol) diisopropylamine (15 mL) and anhydrous THF (15 mL). The pressure vessel was sealed, and the reaction stirred for 12 h at 75° C. The crude mixture was washed with 10% HCl (3 × 10 mL), and extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The crude mixture was purified by column chromatography using a gradient cyclohexane–CH_2Cl_2 eluent, which gave the title compound (0.055 g, 15%). HRMS: calcd for $C_{50}H_{22}$, 622.1722 found [M+] 622.1778. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.10$ (d, $J = 8.8$ Hz, 1H), 7.46 (d, $J = 8.8$ Hz, 1H), 7.49 (d, $J = 8.8$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.72–7.81 (m, 5H), 8.08 (d, $J = 8.8$ Hz, 1H), 8.11 (s, 1H). ^{13}C NMR ($CDCl_3$) $\delta = 92.2$, 92.3, 121.4, 126.0, 126.3, 126.6, 127.1 (2C), 127.2, 127.4 (2C), 127.5, 128.3, 130.3, 130.8, 131.0, 131.1, 131.5 (2C), 132.2, 135.1, 135.4, 135.5, 135.7, 136.0.

1,4-Bis(corannulenylethynyl)benzene (6)

In a dry box with an argon atmosphere, to a pressure vessel was added ethynylcorannulene (0.389 g, 1.41 mmol), 1,4-dibromobenzene (0.145 g, 0.615 mmol), copper iodide (0.032 g, 1.2 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.085 g, 1.2 mmol), diisopropylamine (15 mL) and anhydrous THF (15 mL). The pressure vessel was sealed, and the reaction stirred for 12 h at 75 °C. The crude mixture was washed with 10% HCl (3 × 10 mL), extracted with CH_2Cl_2 (3 × 15 mL), and evaporated under reduced pressure. The crude mixture was purified by column chromatography using a gradient cyclohexane–CH_2Cl_2 eluent, which gave the title compound (0.043 g, 12%). HRMS: calcd for $C_{50}H_{22}$, 622.1722 found [M+] 622.1669. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.69$ (s, 2H), 7.74–7.88 (m, 7H), 8.05 (s, 1H), 8.11 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$) $\delta = 90.7$, 93.6, 121.3, 123.5, 126.0, 126.1, 126.8, 127.1, 127.3, 127.5, 127.6, 127.7, 130.3, 130.9, 131.0, 131.2, 131.3, 131.5, 131.9, 133.2, 135.4, 135.6, 135.9, 136.4.

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