JOC The Journal of Organic Chemistry

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General Method for the Synthesis of Functionalized Tetrabenzo[8]circulenes

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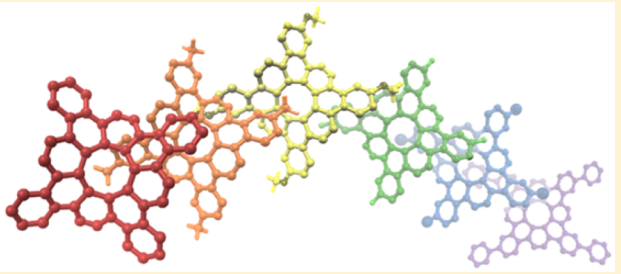
Supporting Information

ABSTRACT: Functionalized derivatives of the saddle-shaped molecule tetrabenzo[8]circulene were successfully synthesized through a Diels–Alder/oxidative cyclodehydrogenation approach. This methodology improves on our previously reported synthesis, affording products containing both electron-rich and electron-poor functional groups from readily available starting materials in a more efficient manner. The optoelectronic effects that result from the introduction of this functionality are presented and briefly discussed.



Nonplanar polycyclic aromatic hydrocarbons (PAHs) have received considerable attention over the last several decades due to the unique supramolecular and electronic properties that result from their contorted structures.[1] This nonplarity typically results from the installation of non-hexagonal rings into an otherwise hexagonal framework. The concept is best illustrated by the [*n*]circulene family of molecules in which a central *n*-membered ring is surrounded by *n* fused benzenoid rings.[2−5] Notably, these molecules are planar when the central ring is six-membered[3] but distort into bowl-shaped[4] and saddle-shaped[5] structures if this ring is smaller or larger, respectively. The largest known member of this family, [8]circulene,[5b,c] and its stable analogue, tetrabenzo[8]circulene,[5d−f] have been known for several years. However, despite their unique structures, [8]circulenes have yet to receive significant attention, likely due to the lack of methodology to generate functionalized derivatives. This is particularly relevant considering the extensive literature detailing the synthesis and electronic properties of the analogous hetero[8]circulenes[6] and the vast theoretical investigations of such structures.[7] To address this limitation, we describe a general method for the synthesis of a number of functionalized tetrabenzo[8]circulene derivatives (**1a**–**f**) and detail the optoelectronic properties that result from the varied functionalization.

In our initial synthesis of the parent structure (**1a**), we chose to utilize a palladium-catalyzed arylation reaction for the final step of our synthetic procedure (Figure 1).[8] The reaction methodology was expected to provide high functional group tolerance; however, the substrate scope was limited with decomposition observed for a range of substrates. Furthermore, overly complex synthetic precursors were required to install the appropriately placed chlorine atoms required for the final bond closure, limiting the quantity of material that could be produced. Oxidative cyclodehydrogenation reactions (which would circumvent the need for chlorine atoms) were originally avoided due to a similar substrate producing rearrangement products rather than the desired bond closures.[9] Nevertheless,

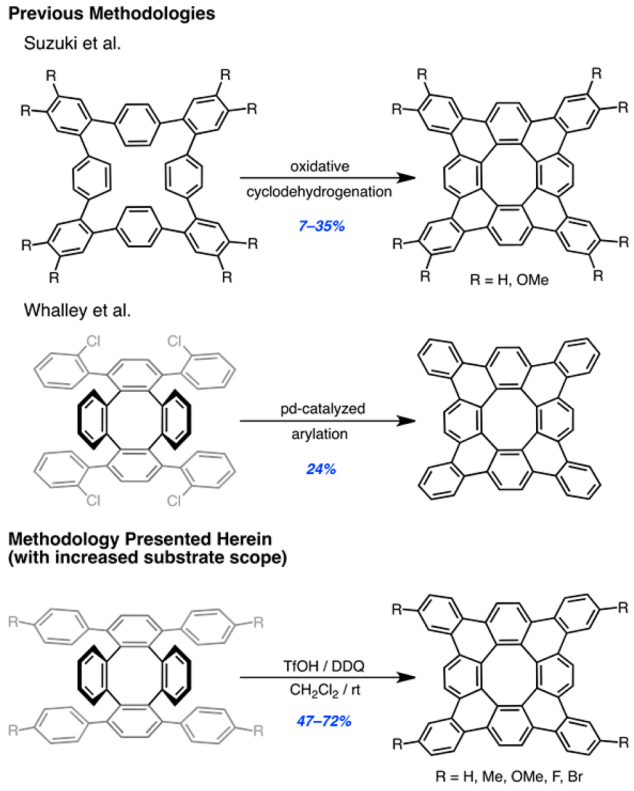


Figure 1. A comparison of the more efficient methodology described in this paper to both our previously reported synthesis and that of Suzuki.

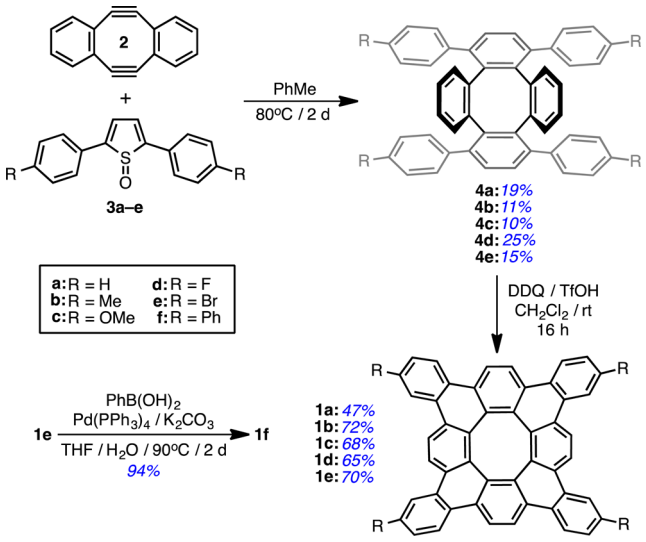
Received: September 12, 2016
Published: November 4, 2016

DOI: 10.1021/acs.joc.6b02244
J. Org. Chem. 2016, 81, 12001−12005

the development of new oxidative cyclodehydrogenation conditions,[10] an increase in the number of nonplanar aromatics generated through such methods,[11] and the synthesis of tetrabenzo[8]circulene and the higher-yielding octamethyltetrabenzo[8]circulene by Suzuki (Figure 1)[5d] compelled us to evaluate the potential of these reactions. While common methods employing $FeCl_3$ in CH_2Cl_2, $CuCl_2$, and $AlCl_3$ in CS_2 or $Cu(OTF)_2$ and $AlCl_3$ in CS_2 displayed some promise, these conditions ultimately proved insufficient as partially closed products dominated crude reaction mixtures, and the desired product was isolated in low yields. To our surprise, however, the use of TfOH and DDQ in CH_2Cl_2 for the conversion of **4a** into **1a** (Scheme 1) produced the desired product in a much higher yield and in a more energy-efficient manner than in our previously reported method. It is important to note that while completion of the reaction was observed by TLC in as little as 15 min, our best yields were obtained by allowing reactions to continue for 16 h. With the oxidative coupling reaction proving successful for the synthesis of the parent compound, we then directed our attention to determining the substrate scope of this methodology.

As illustrated in Scheme 1, functional groups are most easily introduced through the use of substituted 2,5-diarylthiophene-

Scheme 1. Synthesis of Functionalized Tetrabenzo[8]circulenes



1-oxides (**3a–e**), which we were able to synthesize through a zirconium-mediated cyclization reaction recently developed in our lab.[12] These thiophene oxides were reacted via a Diels–Alder reaction with the Sondheimer–Wong diyne (**2**)[13] in toluene at 80 °C to produce a range of substituted tetraphenylene derivatives (**4a–e**). While we expected the removal of the chlorine atoms from the dienophile to positively impact the yield of the Diels–Alder reaction due to decreased steric effects and planarization of the substrate, this was not the case. However, we do observe a correlation between reaction yield and the electronic nature of the diene, consistent with an inverse demand Diels–Alder reaction; yields of the electron-rich tetramethoxylated species (**4c**) and electron-poor tetrafluorinated species (**4d**) are 10 and 25%, respectively.

Subsequent oxidative cyclodehydrogenation reactions of **4a–e** were successfully accomplished using TfOH and DDQ in CH_2Cl_2 at room temperature with isolated yields ranging from 47 to 72%. Although electron-donating groups typically facilitate these reactions,[14] no significant correlation was observed between the electronic nature of the functional group and the reaction yield. We initially rationalized this to be a result of the positioning of the functional groups *meta* to the site of bond closure rather than *para*, which was done to guarantee the formation of only a single regioisomer from the oxidative cyclodehydrogenation reaction. When the methoxy group was moved to the position *para* to the site of bond formation (**4c′**), we observed no change in reaction yield. Interestingly, however, we only observe the single desired regioisomer, indicating that the functional groups retain their directing effects. While the absence of a correlation between the electronic nature of a substituent is surprising, it also facilitates an increase in the functional group tolerance of the reaction. For example, compounds outfitted with electron-withdrawing fluorine (**4d**) and bromine (**4e**) atoms were successfully converted to the corresponding tetrabenzo[8]circulene derivatives **1d** and **1e**, respectively, in yields comparable to those achieved with electron-donating substituents. The main factor in this reaction appears to be the presence of a functional group (no matter its electronic nature) as we only observe a significant decrease in yield for the formation of the parent compound, **1a**. While this is likely a result of the functional groups sterically inhibiting intermolecular bond formation during the coupling reaction, we were unable to confirm the presence of any dimers/oligomers in the mass spectral analysis of the crude reaction mixture that produced **1a**. It is important to note that attempts to furnish the desired **4d** via the earlier reported oxidative cyclodehydrogenation conditions afforded only unreacted starting material.

The synthesis of the tetrabrominated compound, **1e**, is particularly relevant as it provides a means for late-stage diversification through metal-catalyzed cross-coupling reactions. The effectiveness of these potential modifications is illustrated by the conversion of **1e** to **1f** through the use of standard, unoptimized Suzuki–Miyaura cross-coupling conditions, which provided the tetraphenylated derivative in near quantitative yield.

The effect of functionalization on the optoelectronic properties of the substrate has been investigated through UV–vis and cyclic voltammetry (CV). In the UV–vis spectra of **1a–1f** (Figure 2), we see little change in the molar absorptivity

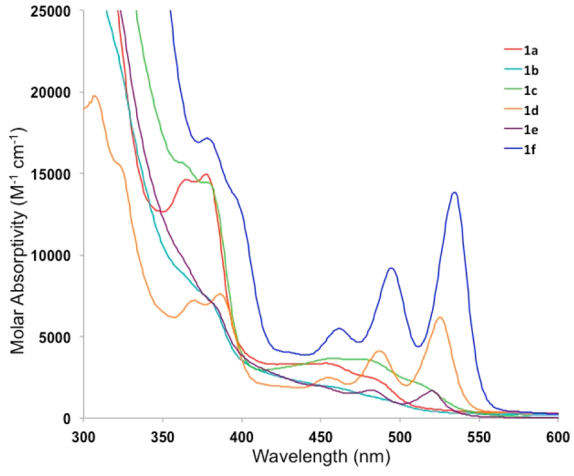


Figure 2. UV–vis absorption spectra of tetrabenzo[8]circulenes **1a–1f** in CH_2Cl_2 (~50 μM).

DOI: 10.1021/acs.joc.6b02244
J. Org. Chem. 2016, 81, 12001–12005

as functionalization is introduced (with the exception of **1f**, which is the only species where the π-system has been extended). However, an increase in the fine structure for the halogenated and phenylated substrates is observed. This observation is likely an electronic effect resulting in the clearly visible vibronic progression in the UV−vis spectrum. Such observations have been made both computationally[15] and experimentally[16] in regards to similar contorted aromatic ring systems. Interestingly, the band edge of the low-energy transitions for each of the substrates consistently appears at ca. 550 nm. These optical gaps are in agreement with the electrochemical data obtained from CV (Table 1), which consistently provide HOMO−LUMO gaps of 2.22 ± 0.01 eV (with the exception of the fluorinated derivative, **1d**, which has a gap of 2.29 eV). The energy levels of these orbitals also appear to change very little (ca. 0.06 eV), again with the exception of fluorinated derivative **1d**.

Table 1. Electrochemical Data of 1a−f[a]

	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)
1a	0.44	−1.79	−5.24	−3.01	2.23
1b	0.39	−1.83	−5.19	−2.97	2.22
1c	0.38	−1.83	−5.18	−2.97	2.21
1d	0.54	−1.75	−5.34	−3.05	2.29
1e	0.39	−1.83	−5.19	−2.97	2.22
1f	0.45	−1.77	−5.25	−3.03	2.22

[a]All potentials were measured in CH_2Cl_2 containing 0.05 M tetrabutylammonium tetrakis(pentafluorophenyl)borate as the supporting electrolyte, and values are referenced versus a ferrocene/ferrocenium redox couple. E_{ox} and E_{red} are the average of the anionic and cationic current peak maxima for the reversible first oxidation and reduction couple, respectively. HOMO and LUMO values were calculated on the basis of the oxidation of a ferrocene reference in vacuum (4.8 V). Additional oxidation and reduction potentials are provided in the Supporting Information.

In conclusion, we have demonstrated a route to functionalized tetrabenzo[8]circulene derivatives, which provides access to substrates containing both electron-rich and electron-poor functional groups. While these functional groups have little effect on the energetics of the frontier molecular orbitals, we envision that the methodology demonstrated herein will provide a foundation for further investigation of the electronic and supramolecular properties inherent to these topologically unique structures.

EXPERIMENTAL SECTION

General Methods. Anhydrous and anaerobic solvents were obtained from alumina-based purification columns. Dibenzocyclooctadiyne (**2**)[13] and 2,5-diarylthiophene-1-oxides (**3a−e**)[12] were synthesized according to literature procedures. All other reagents were obtained from commercial sources and were used as received. All reactions were run under a nitrogen atmosphere and monitored by TLC by using silica gel 60 F_{254} precoated plates. Column chromatography was performed on an automated system using normal phase silica columns. ^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were recorded on a 500 MHz spectrometer at room temperature, and peaks were calibrated against an internal TMS standard unless otherwise noted. High-resolution mass spectra were recorded on a Q-TOF mass spectrometer. Low-resolution mass spectra were recorded on a MALDI-TOF-MS or a 70-VSE EI/CI/FD/FI mass spectrometer. Electrochemical potentials were obtained on a potentiostat interfaced to a computer using in-house software. UV−vis spectra were obtained on a single monochromator instrument.

General Procedure for the Diels−Alder Reaction. A flame-dried 25 mL round-bottom flask equipped with a reflux condenser and a stir bar was charged with 2,5-diarylthiophene-1-oxide (2.1 equiv) and dibenzocyclooctadiyne (1 equiv) in anhydrous toluene. The reaction mixture was heated at 80 °C for 48 h. The crude reaction mixture was cooled to rt, and the solvent was removed under reduced pressure. Column chromatography afforded pure product as a red-yellow solid.

*1,4,9,12-Tetraphenyltetraphenylene (**4a**).* Following the general Diels−Alder procedure, **2** (472 mg, 2.36 mmol) and **3a** (1.22 g, 4.83 mmol) in toluene (20 mL) afforded a yellow solid (271 mg, 19%): mp 310−316 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.20; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (s, 4H), 7.15 (t, J = 7 Hz, 4H), 7.06−7.01 (m, 16H), 6.76 ppm (s, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 141.0, 140.5, 140.1, 139.1, 130.9, 130.8, 129.7, 127.5, 126.4, 125.4 ppm; HRMS ESI [M + 1] calcd for $C_{48}H_{33}$ 609.2582; found 609.2588.

*1,4,9,12-Tetra-p-tolyltetraphenylene (**4b**).* Following the general Diels−Alder procedure, **2** (52.7 mg, 0.263 mmol) and **3b** (155 mg, 0.553 mmol) in toluene (5 mL) afforded a yellow solid (19.2 mg, 11%): mp 370−377 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 3:7 v/v) R_f = 0.49; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 (s, 4H), 6.85 (m, 16H), 6.77 (m, 8H), 2.30 ppm (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 140.4, 140.3, 138.7, 138.1, 135.7, 130.8, 130.6, 129.6, 128.2, 125.3, 21.1 ppm; HRMS ESI [M + 1] calcd for $C_{52}H_{41}$ 665.3208; found 665.3227.

*1,4,9,12-Tetrakis(4-methoxyphenyl)tetraphenylene (**4c**).* Following the general Diels−Alder procedure, **2** (88.2 mg, 0.441 mmol) and **3c** (289 mg, 0.925 mmol) in toluene (7 mL) afforded an orange solid (31.0 mg, 10%): mp 380−385 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 3:2 v/v) R_f = 0.23; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 (s, 4H), 6.90 (d, J = 8.5 Hz, 8H), 6.77 (m, 8H), 6.58 (d, J = 8.5 Hz 8H), 3.75 ppm (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.3, 140.7, 140.6, 138.4, 133.7, 132.0, 131.1, 129.8, 125.6, 113.1, 55.2 ppm; HRMS ESI [M + 1] calcd for $C_{52}H_{41}O_4$ 729.3005; found 729.3004.

*1,4,9,12-Tetrakis(3-methoxyphenyl)tetraphenylene (**4c′**).* Following the general Diels−Alder procedure, **2** (122 mg, 0.611 mmol) and **3c′** (400 mg, 1.28 mmol) in toluene (10 mL) afforded a yellow solid (40.0 mg, 10%): mp 380−385 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 3:2 v/v) R_f = 0.24; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (s, 4H), 6.82 (m, 8H), 6.79 (s, 8H), 6.97 (dd, J = 8.5, 3 Hz, 4H), 6.35 (d, J = 8.5 Hz, 4H), 3.64 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.8, 142.2, 140.4, 140.2, 138.9, 130.8, 129.5, 128.4, 125.5, 123.7, 115.9, 112.5, 55.2 ppm; HRMS ESI [M + 1] calcd for $C_{52}H_{41}O_4$ 729.3005; found 729.3010.

*1,4,9,12-Tetrakis(4-fluorophenyl)tetraphenylene (**4d**).* Following the general Diels−Alder procedure, **2** (30.0 mg, 0.148 mmol) and **3d** (90.1 mg, 0.312 mmol) in toluene (5 mL) afforded a bright yellow solid (25.5 mg, 25%): mp 380−385 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.25; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (s, 4H), 6.91 (m, 8H), 6.81 (m, 4H), 6.77−6.72 ppm (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 161.9 (d, J = 245.0 Hz), 140.7, 140.1, 138.2, 136.9 (d, J = 3.8 Hz) 132.4 (d, J = 7.5 hz), 131.0, 129.9, 126.0, 114.6 ppm (d, J = 20 Hz); LRMS [M] calcd for $C_{48}H_{28}F_4$ 680.2; found 680.2. HRMS and accurate CHN analysis were attempted; however, the molecular ion was not observed, and accurate CHN was unable to be obtained.

*1,4,9,12-Tetrakis(4-bromophenyl)tetraphenylene (**4e**).* Following the general Diels−Alder procedure, **2** (23.1 mg, 0.115 mmol) and **3e** (100 mg, 0.242 mmol) in toluene (8 mL) afforded a bright red solid (15.4 mg, 15%): mp 380−385 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 (s, 4H), 7.20 (d, J = 8.5 Hz, 8H), 6.83 (m, 4H), 6.76 (d, J = 8.5 Hz, 8H) 6.73 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 140.4, 139.6, 139.5, 138.0, 132.2, 130.80, 130.76, 129.6, 126.0, 121.1 ppm. HRMS and accurate CHN analysis were attempted; however, the molecular ion was not observed, and accurate CHN was unable to be obtained.

General Procedure for the Oxidative Cyclodehydrogenation. A flame-dried 10 mL round-bottom flask equipped with a stir bar

DOI: 10.1021/acs.joc.6b02244
J. Org. Chem. 2016, 81, 12001−12005

was charged with tetraphenylene (1 equiv) and DDQ (5 equiv) in anhydrous CH_2Cl_2. Under vigorous stirring, triflic acid (20 equiv) was added dropwise to the reaction mixture. After being stirred at rt for 16 h, the reaction mixture was quenched with a solution of saturated $NaHCO_3$(aq). The organic layer was separated and extracted with CH_2Cl_2. The combined extract was dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography afforded pure product as a red-yellow solid.

*Tetrabenzo[8]circulene (**1a**).* Following the general oxidative cyclodehydrogenation procedure, **4a** (30.0 mg, 0.049 mmol), DDQ (55.9 mg, 0.246 mmol), and triflic acid (148 mg, 0.087 mL, 0.985 mmol) in CH_2Cl_2 (10 mL) afforded a yellow solid (14 mg, 47%): mp >420 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.20. To indicate purity, a ^{1}H NMR has been provided for reference (500 MHz, THF-d_8) δ = 8.16 (dd, J = 6.0, 3.0 Hz, 8H), 7.76 (s, 8H), 7.55 (dd, J = 6.0, 3.0 Hz, 8H). Spectral characterization was in agreement with our previously reported results.[5e]

*Tetramethyltetrabenzo[8]circulene (**1b**).* Following the general oxidative cyclodehydrogenation procedure, **4b** (8.0 mg, 0.01 mmol), DDQ (466 mg, 2.05 mmol), and triflic acid (36.1 mg, 21.3 μL, 0.241 mmol) in CH_2Cl_2 (2 mL) afforded an orange solid (5.6 mg, 72%): mp >420 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 3:7 v/v) R_f = 0.51; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.0 Hz, 4H), 7.87 (s, 4H), 7.64 (s, 4H), 7.62 (s, 4H), 7.37 (d, J = 8.0 Hz, 4H), 2.53 ppm (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 136.9, 134.1, 133.7, 129.5, 129.43, 129.41, 128.7, 127.2, 123.3, 123.2, 122.80, 122.78 ppm; HRMS ESI [M + 1] calcd for $C_{52}H_{33}$ 657.2582; found 657.2575.

*Tetramethoxytetrabenzo[8]circulene (**1c**).* From **4c**, following the general oxidative cyclodehydrogenation procedure, **4c** (24.0 mg, 0.033 mmol), DDQ (37.4 mg, 0.164 mmol), and triflic acid (98.8 mg, 58.3 μL, 0.658 mmol) in CH_2Cl_2 (6 mL) afforded a dark red solid (15.9 mg, 67%): mp >420 °C. From **4c′**, following the general oxidative cyclodehydrogenation procedure, **4c′** (33.9 mg, 0.047 mmol), DDQ (58 mg, 0.26 mmol), and triflic acid (153 mg, 90.2 μL, 1.02 mmol) in CH_2Cl_2 (6 mL) afforded a dark red solid (22.8 mg, 68%): mp >420 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 3:2 v/v) R_f = 0.25; ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.04 (d, J = 8.5 Hz, 4H), 7.66 (s, 4H), 7.62 (s, 4H), 7.53 (d, J = 2 Hz, 4H) 7.21 (dd, J = 8.5, 2 Hz, 4H) 3.93 ppm (s, 12H); this product proved to be too insoluble for ^{13}C NMR characterization; HRMS ESI [M + 1] calcd for $C_{52}H_{33}O_4$ 721.2379; found 721.2386.

*Tetrafluorotetrabenzo[8]circulene (**1d**).* Following the general oxidative cyclodehydrogenation procedure, **4d** (22.0 mg, 0.032 mmol), DDQ (36.7 mg, 0.162 mmol), and triflic acid (97.0 mg, 57.2 μL, 0.646 mmol) in CH_2Cl_2 (6 mL) afforded a fluorescent orange solid (14.0 mg, 65%): mp >420 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.19; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 (m, 4H), 7.77 (dd, J = 10.0, 2.5 Hz, 4H), 7.65 (s, 4H), 7.63 (s, 4H), 7.33 ppm (td, J = 9.0, 2.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 162.3 (d, J = 245.0), 134.5, 133.6, 130.6, 129.5, 129.4, 125.9, 125.3 (d, J = 7.5 Hz), 123.7, 123.6, 116.0 (d, J = 22.5 Hz), 108.5 ppm (d, J = 22.5 Hz). HRMS and accurate CHN analysis were attempted; however, the molecular ion was not observed, and accurate CHN was unable to be obtained. The spectroscopic data match that of material produced through our original palladium-catalyzed arylation methodology.

*Tetrabromotetrabenzo[8]circulene (**1e**).* Following the general oxidative cyclodehydrogenation procedure, **4e** (13.0 mg, 0.014 mmol), DDQ (16.0 mg, 0.070 mmol), and triflic acid (42.6 mg, 25.1 μL, 0.284 mmol) in CH_2Cl_2 (5 mL) afforded a bright orange solid (9.0 mg, 70%): mp >420 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.27; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.22 (d, J = 2.0 Hz, 4H), 7.95 (d, J = 8.5 Hz, 4H), 7.67 (dd, J = 8.5, 2 Hz, 4H), 7.62 (s, 4H), 7.61 ppm (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 134.2, 133.9, 130.9, 130.6, 129.4, 129.0, 128.1, 125.7, 124.8, 123.7, 123.6, 121.6 ppm. HRMS and accurate CHN analysis were attempted; however, the molecular ion was not observed, and accurate CHN was unable to be obtained.

*Procedure for the Preparation of Tetraphenyltetrabenzo[8]-circulene (**1f**).* In a two-neck round-bottom flask equipped with a stir bar and reflux condenser, 6 mL of THF and 3 mL of water were degassed by bubbling with nitrogen for 15 min. **1e** (5.0 mg, 5.5 μmol, 1 equiv), phenylboronic acid (3.0 mg, 24.6 μmol, 4.5 equiv), $Pd(PPh_3)_4$ (1.1 mg, 1.1 μmol, 20 mol %), and K_2CO_3 (9.0 mg, 65.5 μmol, 12 equiv) were added, and the reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was cooled to rt, and a solution of saturated NH_4Cl(aq) (5 mL) was added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The organic fractions were combined and dried over $MgSO_4$, and solvent was removed under reduced pressure to afford pure product as a bright fluorescent orange solid (4.6 mg, 94%): mp >420 °C; purified by column chromatography (SiO_2, CH_2Cl_2/hexanes, 1:4 v/v) R_f = 0.24; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.31 (d, J = 0.5 Hz, 4H), 8.20 (d, J = 8.5 Hz, 4H), 7.82 (dd, J = 8.5, 0.5 Hz, 4H), 7.78 (s, 4H), 7.76 (s, 4H), 7.71 (d, J = 8 Hz, 8H), 7.48 (t, J = 7.5 Hz, 8H), 7.38 ppm (t, 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 141.1, 140.3, 134.3, 134.2, 130.1, 129.8, 129.6, 128.9, 128.6, 127.7, 127.5, 127.4, 126.7, 123.6, 123.5, 121.4 ppm; MALDI-MS [M] calcd for $C_{72}H_{40}$ 904.31; found 904.23. HRMS and accurate CHN analysis were attempted; however, the molecular ion was not observed, and accurate CHN was unable to be obtained.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02244.

Copies of ^{1}H and ^{13}C NMR spectra for all compounds prepared by the present method and a full list of oxidation and reduction potentials obtained from CV (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to thank Bruce O'Rourke for assistance with HRMS data, and William Geiger for assistance with cyclic voltammetry. Support for the HRMS instrumentation was provided in part by the NIH, Grant No. S10-OD018126. S.E.A. thanks the UVM Women in Science Fellowship, and S.J.V.W. thanks the Paul Krapcho Award for summer research funding. A.C.W. thanks the University of Vermont for generous startup funding.

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DOI: 10.1021/acs.joc.6b02244
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