JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

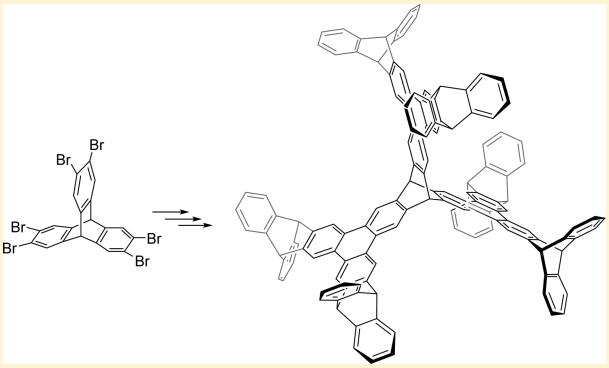
Synthesis of Triphenylene-Based Triptycenes via Suzuki–Miyaura Cross-Coupling and Subsequent Scholl Reaction

Dennis Reinhard, Frank Rominger, and Michael Mastalerz*

Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 273, 69120 Heidelberg, Germany

Supporting Information

ABSTRACT: A two-step method (Suzuki–Miyaura cross-coupling, followed by Scholl oxidation) to triphenylene-based triptycenes is described, rendering a variety of π-extended triptycenes accessible in high yields and without the necessity of column chromatography purification. The versatility of this reaction has been demonstrated in the synthesis of a super-triptycene in only four steps and high yields.



Triptycenes with extended conjugated π-planes have gained interest due to their high intramolecular free volume (IMFV)[1] as precursors for 1D and 2D porous polymers,[2,3] supramolecular porous materials[4] such as organic molecules with intrinsic microporosities (OMIMs), fluorescent markers for in vivo studies,[5] and for organic electronics.[6] The most frequently used reactions to construct such π-extended triptycenes are condensation reactions, e.g., of diketones with diamine moieties.[7] Examples of π-extended triptycenes with exclusively aromatic hydrocarbon scaffolds are much rarer.[1,8] In 2009, King and co-workers have reported for the first time triphenylene-based triptycenes (TBTs), which have been synthesized by the reaction of hexabromotriptycene **1** with biphenylene zirconium reagents to give the corresponding TBTs in 9% yield.[9] Later, the yield could be improved to 28% by using bis(*tert*-butyl)-biphenylene stannane instead of the corresponding zirconium reagent in a palladium-catalyzed reaction.[10] However, the scope of these reactions is limited to three compounds and the yields are not satisfying. Furthermore, one has to take into account that the required organometallic species first have to be synthesized in a multiple-step sequence and that the zirconium reagents are chemically labile.[11]

It is well-known that substituted triphenylenes can be synthesized from the corresponding *o*-terphenyls either by photoirradiation in the presence of an oxidant such as I_2[12] or by using organic or metal-based oxidative reagents, such as DDQ or $FeCl_3$,[13,14] often referred to as the Scholl oxidation.[15] In general, triphenylenes can be synthesized in high yields by the Scholl oxidation, if some guidelines concerning substitution effects are taken into account.[16]

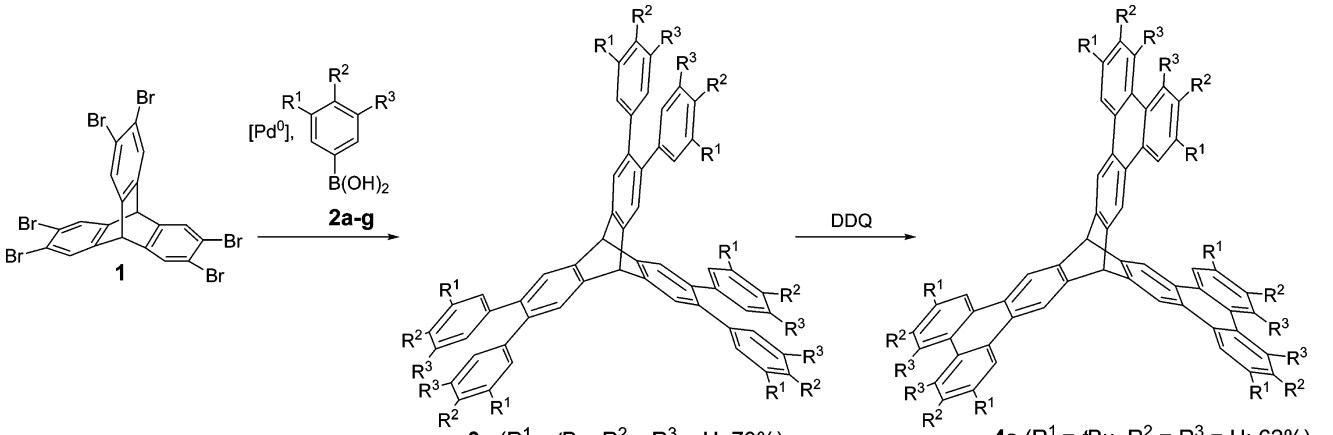
Since *o*-terphenyls are easily accessible by 2-fold Suzuki–Miyaura cross-coupling of 1,2-dibromoarenes with arylboronic esters or acids,[17] we developed a two-step method from hexabromotriptycene **1** to synthesize TBTs, generally in higher yields than by previously described methods. In addition, in most cases, no column chromatographic workup procedures were necessary.

The first step of the reaction sequence was the 6-fold palladium-catalyzed transformation of hexabromotriptycene **1**[3] to the corresponding tris(terphenyls) **3a–3g** (Scheme 1). All compounds could be isolated in yields of 61–95%. With the exception for dodecamethoxyterphenyl **3f**, no column chromatographic purification was necessary: after dispersing the crude products in methanol and sonicating the suspension, the white solids were collected by filtration, washed with methanol and *n*-pentane, and precipitated from $CHCl_3$ and MeOH to give compounds **3a–3g** in pure form. This was proved by NMR spectroscopy and elemental analyses (see the Experimental Section and Supporting Information). Compounds **3a** and **3b** have been additionally characterized by single-crystal X-ray analysis (see the Supporting Information). To directly compare this method with the methods by King and co-workers,[9,10] we first investigated compound **4a** in the Scholl reaction. The oxidation reaction was performed in an analogous manner to a protocol of Rathore et al.,[13] where methanesulfonic acid was added dropwise to a cooled solution (0 °C) of **3a** in dry DCM, followed by the addition of 4.5–5 equiv of DDQ in one portion. After 10–15 min, the reaction was quenched and the crude product washed with methanol, *n*-hexane, and *n*-pentane to give, after drying, 62% of **3a** as an off-white solid. The combined yield of 43% is significantly higher

Received: July 3, 2015
Published: August 20, 2015

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342–9348

Scheme 1. Two-Step Synthesis of Triphenylene Triptycenes[b]



[a]**4g** was the observed main product but could not be isolated by common methods. [b]For detailed reaction conditions, see the Experimental Section.

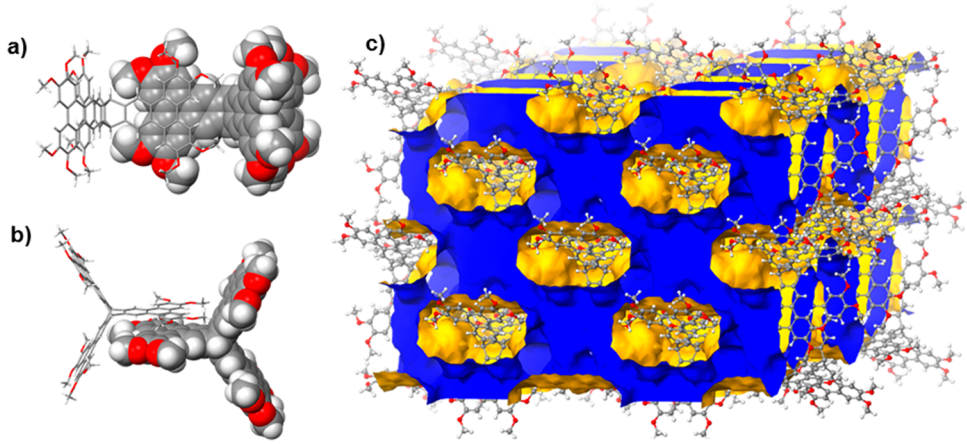


Figure 1. X-ray structure analysis of triphenylene triptycene **4e**. (a, b) Packing of two adjacent molecules by $\pi-\pi$ stacking. (c) Voids (blue) of the crystal for a 3 × 3 × 3 unit cell described by the Connolly surface area for a probe with radius 1.2 Å. Enclathrated chloroform molecules have been omitted for clarity.

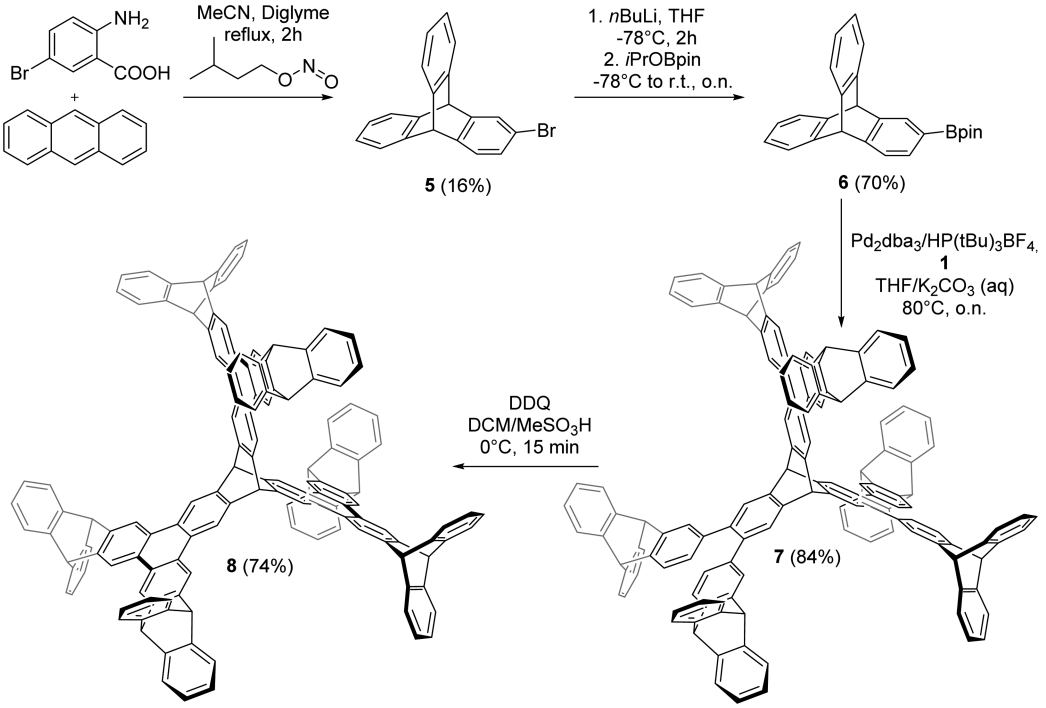
than by the "zirconium or stannylene routes" published before.[9,10]

It has previously been shown that the position of the *tert*-butyl group has only a minor effect on the performance of the Scholl reaction and also inhibits vicinal reactions and polymerization processes.[16] Therefore, we tested **3b** under the same cyclization conditions as **3a** and obtained the corresponding triphenylene compound **4b** in an even higher yield of 71%. Substrates bearing methoxy groups in *para*- or *ortho*-positions to the formed C−C bonds can usually be converted in very high, sometimes quantitative, yields in the oxidative C−C coupling.[13] Indeed, the hexamethoxy compound **3c** and the veratrole derivative **3e** were converted to the corresponding triphenylenes **4c** and **4e** in 51% and 48% yield, respectively. For **4e**, single crystals of sufficient quality for analysis by X-ray diffraction have been grown from chloroform (see Figure 1; for crystallographic data, see the Supporting Information). Through $\pi-\pi$-stacking (the closest distance of two atoms of adjacent π-planes is d = 3.55 Å), **4e** is packed in a manner that large three-dimensional voids (blue surface in Figure 1) are formed, making the compound interesting as a precursor for porous supramolecular solids, which will be studied and reported in due course.

Rathore et al. have also reported that terphenyls with methoxy groups *meta* to the formed C−C bond can be converted under typical Scholl conditions in 60% yield.[13] However, when we tried to apply these conditions for **3d**, the starting material was fully consumed, but no 3-fold oxidized product **4d** was detected at all. Neither changing the acid from $MeSO_3H$ to $BF_3{\cdot}Et_2O$ in the DDQ oxidation reaction nor using anhydrous $FeCl_3$ in nitromethane as oxidative reagent led to isolable amounts of **4d**. These observations are in accordance to the guidelines provided before for Scholl oxidation.[16] A similar result has been found when applying the DDQ methods for

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342−9348

Scheme 2. Synthesis of Supertriptycene 8



compound **3f**, where each cross-coupled aromatic ring bears methoxy groups in the 3- and 5-positions. In this case no formation of **4f** was detected: With $MeSO_3H$ the reaction gave an unidentifiable product mixture, while with $BF_3{\cdot}Et_2O$ only starting material could be recovered. The conversion of nonsubstituted terphenyl **3g** to **4g** is hampered, probably because of a low solubility of intermediates and the product. Although, by ^1H NMR spectroscopy of the crude product, the formation of **4g** as the main product has been observed (Supporting Information), the compound could not be purified by common methods. This once more confirms the results for unsubstituted terphenyls in Scholl oxidation reactions made before by King et al. It should also be mentioned that, for **4g**, the zirconium method of King et al. is the method of choice because no intermolecular oxidative coupling can occur.[9]

To demonstrate the applicability of the new route, we envisioned to use it for the synthesis of supertriptycene congener **8** in only four steps (Scheme 2).[8] Triptycenyl pinacolboronate **6** was accessible in 70% yield from 2-bromotriptycene **5**, which was synthesized according to an early described procedure of Friedman and Logullo, in 16% yield by a Diels–Alder reaction of anthracene and 5-bromo anthranilic acid.[18] Suzuki–Miyaura cross-coupling of **6** with hexabromide **1** gave hexatriptycenyl triptycene **7** in 84% yield. The subsequent oxidative cyclodehydrogenation of **7** gave **8** in 74% yield. As described above, no column chromatography was necessary for the purification of both compounds. It is worth mentioning that no formation of other regioisomers of **8** has been observed, which most probably can be explained by the fused-*ortho* effect,[19] which suppresses the oxidative bond formation *ortho* to the bridgeheads.

To conclude, we have presented a two-step method, which allows access to triphenylene triptycenes in high yields. In almost all cases, the products were isolated in pure form, even without applying column chromatographic purifications. In accordance to observations made before for the Scholl reaction, only terphenyls with a certain substitution pattern of electron-donating groups allow a good conversion to the final products. Larger structures, such as supertriptycene **8**, can be synthesized by this method in high yields.

EXPERIMENTAL SECTION

General Remarks. All reagents including the arylboronic acids **2a–g** and solvents were commercially available and used without further purification. Hexabromotriptycene **1** was synthesized analogous to the literature known procedure from King et al.[3] For thin-layer chromatography, silica gel 60 F_{254} plates were used and examined under UV-light irradiation (254 and 365 nm). Flash column chromatography was performed on flash silica gel (particle size: 0.04–0.063 mm) using light petroleum ether, toluene, ethyl acetate, and DCM. Melting points are not corrected. NMR spectra were recorded on 600 MHz (^1H NMR: 600 MHz; ^{13}C NMR: 151 MHz), 500 MHz (^1H NMR: 500 MHz; ^{13}C NMR: 126 MHz), 400 MHz (^1H NMR: 400 MHz; ^{13}C NMR: 101 MHz), and 300 MHz spectrometers (^1H NMR: 300 MHz, ^{13}C NMR: 75 MHz) at 298 K, unless otherwise mentioned. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm) or $C_2H_2Cl_4$ (δ_H = 5.963 ppm, δ_C = 73.78 ppm) in the corresponding deuterated solvent. IR spectra were recorded on a Fourier transform spectrophotometer equipped with a Ge ATR crystal. UV–vis spectra were recorded on double-beam UV–vis spectrophotometers utilizing either double or single monochromators and photomultiplier tube detectors. MS and HRMS (MALDI and DART) experiments were carried out in positive mode on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer equipped with a 9.4 T superconducting magnet and interfaced to a dual ESI/MALDI source. Crystal structure analysis was accomplished on a diffractometer with a molybdenum source (λ(Mo$K\alpha$) = 0.71073 Å). Data processing and absorption correction (SADABS)[20] were accomplished by standard methods. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXL software.[21] All non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms were treated using appropriate riding models. All crystallographic information files (CCDC 1409998 (**3a**), CCDC 1409999 (**3b**), and CCDC 1410000 (**4e**)) have been deposited in the

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342–9348

Cambridge Crystallographic Data Centre and can be downloaded free of charge via www.ccdc.camac.uk/data_request/cif.

2-Bromotriptycene 5.[18] To a refluxing solution of anthracene (4.13 g, 23.1 mmol, 1.00 equiv) in MeCN (90 mL) were added solutions of isoamylnitrite (3.43 mL, 25.5 mmol, 1.10 equiv) in MeCN (1.5 mL) and 5-bromoanthranilic acid (5.50 g, 25.5 mmol, 1.10 equiv) in 120 mL of 5:1 (v/v) MeCN/diglyme concurrently over a period of 2 h. The mixture was then refluxed another 2 h until MeCN was distilled off. After cooling to r.t., 50 mL of 4:1 (v/v) MeOH/H_2O was added. Crystallized anthracene was then removed by filtration. The mother liquor was left overnight, and the precipitate was filtered off. The off-white crude product was further purified by column chromatography (SiO_2; light petroleum ether/DCM 20:1) to give **5** as a colorless solid (1.22 g, 3.65 mmol, 16%): mp 159−160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 1.8, 1H), 7.38 (dd, J = 5.3, 3.2, 4H), 7.24 (d, J = 7.9, 1H), 7.11 (dd, J = 7.8, 1.9, 1H), 7.01 (dd, J = 5.3, 3.2, 4H), 5.39 (s, 1H), 5.37 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 144.9, 144.7, 144.6, 128.1, 127.0, 125.6, 125.5, 125.2, 123.9, 123.8, 118.7, 53.9, 53.7 ppm; HRMS (DART) m/z: $[M]^+$ Calcd for $C_{20}H_{13}Br$ 332.01951; Found 332.01915. The analytical data are in accordance to those published before.[18,22]

2-Triptycenylboronic Acid Pinacol Ester 6. In an oven-dried and argon-purged Schlenk flask, 2-bromotriptycene **5** (1.00 g, 3.00 mmol, 1.00 equiv) was dissolved in dry THF (10 mL), and *n*-BuLi (1.6 M in hexanes, 2.06 mL, 1.10 equiv) was added dropwise at −78 °C. After stirring for 2 h at the same temperature, isopropoxyboronic acid pinacol ester (0.80 mL, 3.90 mmol, 1.3 equiv) was added, and the mixture was warmed to r.t. overnight. The reaction was quenched by addition of sat. aq. NH_4Cl solution (15 mL). After phase separation and extraction with DCM (3 × 15 mL), the organic layer was washed twice with H_2O and brine, dried over $MgSO_4$, and solvent was removed in vacuum to give the crude product as a colorless residue. Purification via flash column chromatography on silica gel (light petroleum ether/ethyl acetate 40:1) yielded **6** as a colorless solid (799 mg, 2.10 mmol, 70%): mp 266−268 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H, *H*-1), 7.48 (dd, J = 7.3, 1.0, 1H, *H*-3), 7.40 (d, J = 7.3, 1H, *H*-4), 7.38−7.32 (m, 4H, *H*-5,8,11,14), 6.97 (m, 4H, *H*-6,7,12,13), 5.43 (s, 1H, *H*-10), 5.42 (s, 1H, *H*-9) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7 (*C*-4a), 145.3 (*C*-8a,10a,10b,14a), 145.0, 144.8 (*C*-9a), 132.5 (*C*-3), 129.6 (*C*-1), 125.4 (*C*-6,7,12,13), 125.3 (*C*-6,7,12,13), 123.8 (*C*-5,8,11,14), 123.8 (*C*-5,8,11,14), 123.3 (*C*-4), 83.8 ($OC(CH_3)_2$), 54.5 (*C*-10), 54.2 (*C*-10), 25.0 ($-CH_3$) ppm; FT IR (ATR): $\bar{\nu}$ 3073 (w), 2991 (w), 2981 (w), 2953 (w), 1615 (w), 1603 (w), 1572 (w), 1493 (w), 1458 (m), 1417 (m), 1385 (m), 1372 (m), 1352 (s), 1327 (m), 1311 (m), 1291 (m), 1270 (m), 1215 (w), 1195 (w), 1166 (m), 1146 (s), 1121 (m), 1109 (w), 1097 (w), 1070 (m), 1022 (w), 1005 (w), 983 (w), 962 (w), 944 (w), 926 (w), 913 (w), 889 (w), 877 (w), 858 (m), 830 (w), 797 (w), 771(w), 750 (s), 738 (s), 701 (w), 683 (m), 650 (m), 634 (m), 624 (m), 612 (w) cm^{-1}; HRMS (DART) m/z: $[M+NH_4]^+$ Calcd for $C_{26}H_{29}BNO_2$ 398.22904; Found 398.22794. Anal. Calcd for $C_{26}H_{25}BO_2 \cdot H_2O$: C, 78.40, H, 6.83. Found: C, 78.76, H, 6.57.

General Procedure for Suzuki−Miyaura Cross-Coupling Reactions (GP1). In a screw capped vessel, hexabromotriptycene **1** (250 mg, 344 μmol, 1.00 equiv) and arylboronic acid **2a−g** (6.60−9.00 equiv) were dissolved to 10 mL of a degassed 1:1-mixture (v/v) of THF and 1 M aq. K_2CO_3 solution. After addition of Pd_2dba_3 (37.8 mg, 41 μmol, 12 mol %) and $HP(tBu)_3BF_4$ (29.9 mg, 103 μmol, 30 mol %), the vessel was purged with argon, and the mixture was stirred for 16 h at 80 °C. After cooling to r.t., EtOAc (10 mL) was added and the phases were separated. The organic layer was washed with saturated aqueous NH_4Cl solution, H_2O, and brine and dried over $MgSO_4$, and solvents were evaporated in vacuum to give the crude product as a yellow residue. After dispersing in methanol, sonication and filtration, the product was washed with MeOH (3 × 10 mL) and *n*-pentane (3 × 20 mL) to give **3a−g** as a white powder.

2,3,6,7,12,13-Hexa-((3′-*tert*-butyl)phenyl)triptycene 3a. According to **GP1**, hexabromotriptycene **1** and 3-(*tert*-butyl)-phenylboronic acid **2a** (500 mg, 2.84 mmol, 7.8 equiv) gave, after workup, **3a** as a colorless solid (266 mg, 0.25 mmol, 70%): mp 351 °C (under dec.); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (s, 6H, tript-*H*), 7.19−7.14 (m, 12H, Ar-*H*-4′,5′), 7.04 (m, 6H, Ar-*H*-6′), 6.95 (m, 6H, Ar-*H*-2′), 5.69 (s, 2H, bridgehead-*H*), 1.06 (s, 54H, $-C(CH_3)_3$) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.4 (ArC-C(CH_3)), 144.3 (triptC), 141.3 (triptC-Ar), 138.6 (ArC-1′), 128.3 (ArC-2′), 127.8 (ArC-5′), 126.7 (ArC-6′), 125.9 (triptC-H), 123.1 (ArC-4′), 53.4 (bridgehead-C), 34.5 (Ar-$C(CH_3)_3$), 31.3 (Ar-$C(CH_3)_3$) ppm; FT IR (ATR): $\bar{\nu}$ 2961 (m), 2904 (w), 2867 (w), 1737 (w), 1603 (w), 1580 (w), 1460 (m), 1415 (w), 1362 (m), 1268 (w), 1217 (w), 1203 (w), 1093 (w), 893 (w), 865 (w), 795 (s), 708 (s) cm^{-1}; UV−vis λ_{max}/nm (log) 251 (5.18) sh 292 (4.59); HRMS (MALDI) m/z: $[M]^+$ Calcd for $C_{80}H_{86}$ 1046.67240; Found 1046.67117. Anal. Calcd for $C_{80}H_{86} \cdot 1/3H_2O$: C, 91.21, H, 8.29. Found: C, 91.22, H, 8.14.

2,3,6,7,12,13-Hexa-((4′-*tert*-butyl)phenyl)triptycene 3b. According to **GP1**, hexabromotriptycene **1** and 4-(*tert*-butyl)-phenylboronic acid **2b** (544 mg, 2.84 mmol, 9.0 equiv) gave, after workup, **3b** as a colorless solid (302 mg, 0.29 mmol, 84%): mp 297 °C (under dec.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 6H, tript-*H*), 7.17 (d, J = 8.4 Hz, 12H, Ar-*H*-3′), 7.00 (d, J = 8.4 Hz, 12H, Ar-*H*-2′), 5.57 (s, 2H, bridgehead-*H*), 1.27 (s, 54H, $-C(CH_3)_3$) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.1 (ArC-C(CH_3)), 144.1 (triptC), 138.7 (ArC-1′), 137.7 (triptC-Ar), 129.7 (ArC-2′), 126.1 (triptC-H), 124.7 (ArC-3′), 53.4 (bridgehead-C), 34.5 (Ar-$C(CH_3)_3$), 31.5 ppm (Ar-$C(CH_3)_3$); FT IR (ATR) $\bar{\nu}$ 3028 (w), 2961 (m), 2904 (w), 2867 (w), 1515 (w), 1462 (s), 1417 (w), 1393 (w), 1362 (m), 1268 (m), 1201 (w), 1113 (m), 1013 (w), 944 (w), 901 (w), 854 (w), 834 (s), 826 (s), 801 (w), 759 (w), 750 (w), 712 (w), 667 (w) cm^{-1}; UV−vis λ_{max}/nm (log) 254 (5.15) sh 292 (4.47); HRMS (MALDI) m/z: $[M]^+$ Calcd for $C_{80}H_{86}$ 1046.67240; Found 1046.67203. Anal. Calcd for $C_{80}H_{86} \cdot 1/3H_2O$: C, 91.21, H, 8.29. Found: C, 91.27, H, 8.28.

2,3,6,7,12,13-Hexa-(3′-methoxyphenyl)triptycene 3c. According to **GP1**, hexabromotriptycene **1** and 3-methoxyphenylboronic acid **2c** (340 mg, 2.27 mmol, 6.6 equiv) gave, after workup, **3c** as an off-white solid (193 mg, 0.22 mmol, 63%): mp 248 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (s, 6H, tript-*H*), 7.11 (t, J = 7.9 Hz, 6H, Ar-*H*-5′), 6.72 (m, 12H, Ar-*H*-4′,6′), 6.62 (m, 6H, Ar-*H*-2′) 5.65 (s, 2H, bridgehead-*H*), 3.59 (s, 18H, OCH_3) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.2 (ArC-OMe), 144.3 (tript-C), 142.9 (Ar-C-1′), 137.8 (triptC-Ar), 129.0 (ArC-5), 125.1 (triptC-H), 122.5 (ArC-4′/6′), 115.1 (ArC-2′), 112.9 (ArC-4′/6′), 55.2 (OCH_3), 53.3 (bridgehead-C) ppm; FT IR (ATR): $\bar{\nu}$ 2955 (w), 2936 (w), 2832 (w), 1601 (s), 1578 (s), 1488 (w), 1466 (s), 1429 (m), 1389 (w), 1319 (w), 1287 (s), 1262 (m), 1242 (m), 1209 (s), 1177 (m), 1034 (s), 995 (w), 860 (m), 785 (s), 703 (s), 634 (w) cm^{-1}; UV−vis λ_{max}/nm (log) 248 (5.04), 283 (4.55); HRMS (MALDI) m/z: $[M]^+$ Calcd for $C_{62}H_{50}O_6$ 890.36019; Found 890.35953. Anal. Calcd for $C_{62}H_{50}O_6$: C, 83.57, H, 5.66. Found: C, 83.34, H, 5.65.

2,3,6,7,12,13-Hexa-(4′-methoxyphenyl)triptycene 3d. According to **GP1**, hexabromotriptycene **1** and 4-methoxyphenylboronic acid **2d** (361 mg, 2.40 mmol, 7.0 equiv) gave, after workup and precipitation from $CHCl_3$ with MeOH, **3d** as an off-white solid (270 mg, 0.30 mmol, 88%): mp 241 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (s, 6H, tript-*H*), 7.01 (d, J = 8.7 Hz, 12H, Ar-*H*-3′), 6.74 (d, J = 8.8 Hz, 12H, Ar-*H*-2′), 5.59 (s, 2H, bridgehead-*H*), 3.77 (s, 18H, OCH_3) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.3 ppm (ArC-OMe), 144.1 (tript-C), 137.3 (triptC-Ar), 134.3 (ArC-1′), 131.1 (ArC-3′), 126.1 (triptC-H), 113.5 (ArC-2′), 55.3 (O-CH_3), 53.3 (bridgehead-C) ppm; FT IR (ATR): $\bar{\nu}$ 3012 (w), 2952 (w), 2932 (w), 2832 (w), 1607 (m), 1576 (w), 1513 (s), 1462 (s), 1440 (m), 1421 (w), 1391 (w), 1289 (m), 1244 (s), 1176 (s), 1107 (w), 1044 (m), 1026 (m), 905 (w), 850 (w), 828 (s), 812 (m), 789 (m), 779 (m), 763 (w), 734 (w), 685 (w) cm^{-1}; UV−vis λ_{max}/nm (log) 260 (5.04) sh 290 (4.57); HRMS (MALDI) m/z: $[M]^+$ Calcd for $C_{62}H_{50}O_6$ 890.36019; Found 890.35946. Anal. Calcd for $C_{62}H_{50}O_6 \cdot H_2O$: C, 81.92, H, 5.77. Found: C, 81.54, H, 5.72.

2,3,6,7,12,13-Hexakis-((3′,4′-dimethoxyphenyl)triptycene 3e. According to **GP1**, hexabromotriptycene **1** and (3,4-dimethoxyphenyl)boronic acid **2e** (433 mg, 2.40 mmol, 7.0 equiv) gave, after workup procedure, **3e** as a colorless solid (309 mg, 0.29 mmol, 84%): mp 197 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 6H, tript-*H*),

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342−9348

6.74 (d, J = 8.3 Hz, 6H, Ar-*H*-5′), 6.71 (dd, J = 8.3, 1.6 Hz, 6H, Ar-*H*-6′), 6.56 (d, J = 1.6 Hz, 6H, Ar-*H*-2′), 5.65 (s, 2H, bridgehead-*H*), 3.84 (s, 18H, Ar-OCH_3-4′), 3.57 (s, 18H, Ar-OCH_3-3′) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.3 (Ar*C*-OMe), 147.8 (Ar*C*-OMe), 144.1 (triptC), 137.5 (triptC-Ar), 134.4 (Ar*C*-1′), 125.9 (triptC-H), 122.0 (Ar*C*-6′), 113.6 (Ar*C*-2′), 110.9 (Ar*C*-5′), 56.0 (OCH_3), 55.8 (OCH_3), 53.3 (bridgehead-*C*) ppm; FT IR (ATR): $\tilde{\nu}$ 2991 (w), 2934 (w), 2832 (w), 1605 (w), 1578 (w), 1558 (w), 1541 (w), 1513 (s), 1464 (s), 1407 (m), 1329 (w), 1242 (s), 1170 (s), 1138 (s), 1058 (w), 1026 (s), 975 (w), 883 (m), 856 (m), 809 (m), 791 (w), 765 (m), 734 (w), 665 (w), 610 (w) cm^{-1}; UV−vis λ_{max}/nm (log) 265 (4.89) sh 286 (4.78); HRMS (MALDI) m/z: [M]$^+$ Calcd for $C_{68}H_{62}O_{12}$ 1070.42358; Found 1070.42624. Anal. Calcd for $C_{68}H_{62}O_{12}$: C, 76.24, H, 5.83. Found: C, 75.94, H, 5.65.

2,3,6,7,12,13-Hexakis-((3′,5′-dimethoxyphenyl)triptycene 3f. According to **GP1**, hexabromotriptycene **1** and (3,5-dimethoxyphenyl)boronic acid **2f** (556 mg, 3.09 mmol, 9.0 equiv) gave, after workup, column chromatography on silica gel (PE/EA 2:1), and precipitation from $CHCl_3$ with MeOH, **3f** as a colorless solid (327 mg, 0.31 mmol, 89%): mp 345 °C (under dec.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 6H, triptC-*H*), 6.30 (s, 18H, Ar-*H*-2′,4′), 5.63 (s, 2H, bridgehead-*H*), 3.60 (s, 36H, Ar-OCH_3-3′,5′) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 (Ar*C*-OMe), 144.3 (Ar*C*-1′), 143.5 (tript-*C*), 137.8 (triptC-Ar), 125.8 (triptC-H), 108.0 (Ar*C*-2′), 99.4 (Ar*C*-4′), 55.4 (OCH_3), 53.3 (bridgehead-*C*) ppm; FT IR (ATR): $\tilde{\nu}$ 2997 (w), 2936 (w), 2834 (w), 1588 (s), 1454 (m), 1423 (m), 1391 (m), 1350 (w), 1319 (w), 1287 (w), 1250 (w), 1203 (s), 1150 (s), 1085 (w), 1060 (s), 1038 (m), 991 (w), 930 (w), 907 (w), 891 (w), 869 (w), 834 (m), 695 (m) cm^{-1}; UV−vis λ_{max}/nm (log) 240 (5.06) sh 292 (4.43); HRMS (MALDI) m/z: [M]$^+$ Calcd for $C_{68}H_{62}O_{12}$ 1070.42358; Found 1070.42113. Anal. Calcd for $C_{68}H_{62}O_{12}$: C, 76.24, H, 5.83. Found: C, 76.32, H, 5.98.

2,3,6,7,12,13-Hexaphenyltriptycene 3g. According to **GP1**, hexabromotriptycene **1** and phenylboronic acid **2g** (371 mg, 3.09 mmol, 9.0 equiv) gave, after workup, **3g** as a colorless solid (227 mg, 0.32 mmol, 93%): mp > 400 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (s, 6H, tript-*H*), 7.18−7.16 (m, 18H, 3′,4′,5′-*H*), 7.10−7.09 (m, 12H, 2′,6′-*H*), 5.65 (s, 2H, bridgehead-*H*) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.3 (tript-*C*), 141.6 (Ar*C*-1′), 137.9 (triptC-Ar), 130.1 (Ar*C*-2′), 128.0 (Ar*C*-3′), 126.5 (tript-*C*H), 126.2 (Ar*C*-4′), 53.3 (bridgehead-*C*) ppm; FT IR (ATR): $\tilde{\nu}$ 3081 (w), 3059 (w), 3024 (w), 2946 (w), 1601 (w), 1495 (w), 1466 (m), 1444 (w), 1395 (w), 1262 (w), 1195 (w), 1075 (w), 1020 (w), 903 (w), 805 (w), 761 (m), 695 (s), 634 (w) cm^{-1}; UV−vis λ_{max}/nm (log) 250 (4.99) sh 289 (4.35); HRMS (MALDI) m/z: [M]$^+$ Calcd for $C_{56}H_{38}$ 710.29680; Found 710.29800. Anal. Calcd for $C_{56}H_{38}\cdot 1/2H_2O$: C, 93.43, H, 5.46. Found: C, 93.50, H, 5.52.

2,3,6,7,12,13-Hexakis-(triptycen-2′-yl)triptycene 7. According to **GP1**, hexabromotriptycene **1** (110 mg, 0.15 mmol, 1.00 equiv) and 2-triptycenylboronic acid pinacol ester **6** (379 mg, 1.00 mmol, 6.60 equiv) were mixed in 5 mL of 1:1 (v/v) THF/K_2CO_3 (1M, aq.). Pd_2dba_3 (21 mg, 0.02 mmol, 0.15 equiv) and HP(tBu)$_3BF_4$ (16 mg, 0.05 mmol, 0.36 equiv) were added and heated for the given time. After standard workup, followed by precipitation from hot $CHCl_3$ with MeOH, **7** was obtained as a colorless solid (224 mg, 0.13 mmol, 84%): mp > 400 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (m, 12H, *H*-5′,11′), 7.32 (s, 6H, tript-*H*), 7.17 (m, 12H, *H*-8′,14′), 7.01 (m, 30H, *H*-1′, *H*-6′,7′,12′,13′), 6.92 (d, 6H, *H*-4′), 6.44 (d, 6H, *H*-3′), 5.40 (s, 2H, bridgehead-*H*-9,10), 5.29 (s, 6H, bridgehead-*H*-9′), 5.03 (s, 6H, bridgehead-*H*-10′) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.5 (*C*-8′a,10′a,10′b,14′a), 145.4 (*C*-8′a,10′a,10′b,14′a), 144.9 (*C*-9′a), 144.0 (triptC-4a,8a,9a,10a,10b,14a), 143.4 (*C*-4′a), 138.3 (*C*-2′), 137.6 (triptC-tript′), 126.9 (*C*-3′), 125.9 (triptC-H), 125.3 (*C*-1′), 125.1 (*C*-6′,7′,12′,13′), 123.7 (*C*-8′,14′), 123.5 (*C*-5′,11′), 123.0 (*C*-4′), 54.1 (bridgehead-*C*-10′), 53.8 (bridgehead-*C*-9′), 53.2 (bridgehead-*C*-9,10) ppm; FT IR (ATR): $\tilde{\nu}$ 3065 (w), 3038 (w), 3018 (w), 2955 (w), 1711 (w), 1456 (s), 1417 (w), 1387 (w), 1360 (w), 1313 (w), 1295 (w), 1283 (w), 1217 (w), 1187 (w), 1158 (w), 1119 (w), 1087 (w), 1022 (w), 934 (w), 922 (w), 901 (w), 881 (w), 860 (w), 828 (w), 795 (w), 783 (w), 738 (s), 708 (w), 669 (w), 661 (w), 630 (s), 624 (s) cm^{-1}; UV−vis λ_{max}/nm (log) 267 (5.28) sh 292 (4.50); MS (MALDI) m/z 1767.69 [M + H]$^+$; Anal. Calcd for $C_{140}H_{86}\cdot H_2O$: C, 94.14, H, 4.97. Found: C, 93.77, H, 5.10.

General Procedure for Scholl Oxidative Cyclodehydration Reactions (GP2). In a oven-dried and argon-purged Schlenk flask, 1 mL of $MeSO_3H$ was added dropwise to a solution of **3a−c** in 9 mL of dry DCM, and DDQ (3.3−5.0 equiv) was added in one portion under ice-bath cooling. After stirring for 5−20 min at 0 °C or r.t., the reaction was stopped by pouring the dark green to blue mixture into 25−50 mL of a saturated $NaHCO_3$ solution, which was stirred vigorously for another 20 min. The organic layer was separated, and the aqueous phase was extracted with DCM (2 × 15 mL). The combined organic extract was washed twice with water (20 mL) and brine (20 mL) and dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to give the crude product **4a−f** as an off-white to brownish residue.

10,21-((6′,11′-Di-*tert*-butyl)triphenylen-2′,3′-yl)-10,21-dihydro-(2,7,13,18-tetra-*tert*-butyl)tetrabenzo[*a*,*c*,*l*,*n*]pentacene 4a. According to **GP2**, DDQ (26.2 mg, 115 μmol, 3.5 equiv) was added to a solution of **3a** (35 mg, 33 μmol, 1.0 equiv) in DCM/$MeSO_3H$, and the mixture was stirred for 10 min at 0 °C. After workup, the crude product was washed with n-hexane and n-pentane, to obtain **4a** as a colorless solid (21.5 mg, 21 μmol, 62%); mp > 400 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.93 (s, 6H, *H*-1′,4′,9,11,20,22), 8.70 (d, J = 1.5 Hz, 6H, *H*-5′,12′,1, 8,12,19), 8.50 (d, J = 8.7 Hz, 6H, *H*-8′,9′,4,5,15,16), 7.66 (dd, J = 8.6, 1.5 Hz, 6H, *H*-7′,10′,3,6,14,17), 6.55 (s, 2H, bridgehead-*H*), 1.54 (s, 54H, −C(CH_3)$_3$) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.3 (*C*-6′,10′,2,7,13,18), 143.1 (*C*-2′,3′,9a,10a,20a,21a), 129.2 (*C*-4′b,12′a,8a,11b,19a,22b), 128.4 (*C*-4′a,12′b,8b,11a,19b,22a), 127.6 (*C*-8′a,8′b,4a,4b,15a,15b), 124.9 (*C*-7′,10′,3,6,14,17), 123.0 (*C*-8′,9′,4,5,15,16), 119.3 (*C*-5′,12′,1,8,12,19), 118.5 (*C*-1′,4′,9,11,20,22), 54.3 (bridgehead-*C*), 35.2 (*C*(CH$_3$)$_3$), 31.7 (C(CH_3)$_3$) ppm; FT IR (ATR): $\tilde{\nu}$ 2953 (s), 2902 (m), 2867 (w), 1615 (w), 1493 (m), 1484 (m), 1460 (m), 1405 (m), 1362 (m), 1262 (s), 1203 (w), 1128 (w), 969 (w), 879 (m), 814 (s), 779 (w), 728 (m), 665 (w), 646 (w), 632 (m) cm^{-1}; UV−vis λ_{max}/nm (log) 266 (5.31), 277 (5.22), 318 (4.65) ; MS (MALDI) m/z 1041.63 [M + H]$^+$; Anal. Calcd for $C_{80}H_{80}\cdot H_2O$: C, 90.69, H, 7.80. Found: C, 90.55, H, 7.79.

10,21-((7′,10′-Di-*tert*-butyl)triphenylen-2′,3′-yl)-10,21-dihydro-(3,6,14,17-tetra-*tert*-butyl)tetrabenzo[*a*,*c*,*l*,*n*]pentacene 4b. According to **GP2**, DDQ (26.2 mg, 115 μmol, 3.5 equiv) was added to a solution of **3b** (35 mg, 33 μmol, 1.0 equiv) in DCM/$MeSO_3H$, and the mixture was stirred for 12 min at 0 °C. After workup, the crude product was washed with n-hexane and n-pentane, giving a colorless solid. After precipitation from hot $CHCl_3$/MeOH, **4b** was obtained as a colorless solid (23 mg, 21 μmol, 67%); mp > 400 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 6H, *H*-1′,4′,9,11,20,22), 8.62 (d, J = 8.8 Hz, 6H, *H*-5′,12′,1,8,12,19), 8.60 (s, 6H, *H*-8′,9′,4,5,15,16), 7.70 (dd, J = 8.7, 2.0 Hz, 6H, *H*-6′,10′,2,7,13,18), 6.15 (s, 2H, bridgehead-*H*), 1.49 (s, 54H, −C(CH_3)$_3$) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4 (*C*-7′,10′,3,6,14,17), 143.0 (*C*-2′,3′,9a,10a,20a,21a), 129.6 (*C*-8′a,8′b,4a,4b,15a,15b), 127.8 (*C*-4′b,12′a,8a,11b,19a,22b/4′a,12′b,8b,11a,19b,22a), 127.7 (*C*-4′b,12′a,8a,11b, 19a,22b/4′a,12′b,8b,11a,19b,22a), 125.0 (*C*-6′,10′,2,7,13,18), 123.2 (*C*-5′,12′,1,8,12,19), 119.0 (*C*-8′,9′,4,5,15,16), 118.4 (*C*-1′,4′,9,11,20,22), 54.5 (bridgehead-*C*), 35.1 (*C*(CH$_3$)$_3$), 31.6 (C(CH_3)$_3$) ppm; FT IR (ATR): $\tilde{\nu}$ 2961 (s), 2904 (w), 2867 (w), 1741 (w), 1717 (w), 1615 (w), 1582 (w), 1542 (w), 1513 (w), 1470 (s), 1417 (m), 1401 (m), 1362 (m), 1305 (w), 1264 (s), 1217 (w), 1203 (w), 1174 (w), 1144 (w), 1111 (w), 1042 (w), 1022 (w), 946 (w), 934 (w), 922 (w), 909 (w), 879 (s), 852 (w), 840 (w), 812 (s), 787 (w), 742 (w), 720 (w), 699 (w), 683 (w), 669 (w), 646 (w), 634 (w), 606 (s) cm^{-1}; UV−vis λ_{max}/nm (log) 268 (5.25), 279 (5.25), 339 (4.03), 355 (3.96); MS (MALDI) m/z 1041.64 [M + H]$^+$; Anal. Calcd for $C_{80}H_{80}\cdot 1/3\ H_2O$: C, 91.78, H, 7.76. Found: C, 91.64, H, 7.58.

10,21-(6′,11′-Dimethoxytriphenylen-2′,3′-yl)-10,21-dihydro-(2,7,13,18-tetramethoxy)tetrabenzo[*a*,*c*,*l*,*n*]pentacene 4c. To a solution of **3c** (29 mg, 33 μmol, 1.0 equiv) in dry DCM (9 mL) and methanesulfonic acid (1 mL) was added DDQ (37 mg, 165 μmol, 5.0

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342−9348

equiv), and the mixture was stirred for 10 min at 0 °C. After quenching and standard workup, the crude product was washed with *n*-hexane and *n*-pentane. Purification via column chromatography on silica gel (toluene/ethyl acetate) gave **4c** as an off-white solid (15 mg, 17 μmol, 51%); mp > 400 °C; ^{1}H NMR (600 MHz, $C_2D_2Cl_4$): δ 8.71 (s, 6H, *H*-1′,4′,9,11,20,22), 8.38 (d, *J* = 8.8 Hz, 6H, *H*-8′,9′,4,5,15,16), 8.02 (d, *J* = 2.4 Hz, 6H, *H*-5′,12′,1,8,12,19), 7.19 (dd, *J* = 8.8, 2.5 Hz, 6H, *H*-7′,10′,3,6,14,17), 6.18 (s, 2H, bridgehead-*H*), 4.02 (s, 18H, OCH_3) ppm; ^{13}C NMR (151 MHz, $C_2D_2Cl_4$): δ 158.2 (*C*-6′,10′,2,7,13,18), 143.2 (*C*-2′,3′,9a,10a,20a,21a), 130.0 (*C*-4′b,12′a,8a,11b,19a,22b), 128.0 (*C*-4′a,12′b,8b,11a,19b,22a), 124.6 (*C*-8′,9′,4,5,15,16), 124.0 (*C*-8′a,8′b,4a,4b,15a,15b), 118.7 (*C*-1′,4′,9,11,20,22), 115.8 (*C*-7′,10′,3,6,14,17), 106.0 (*C*-5′,12′,1,8,12,19), 55.8 (OCH_3), 54.1 (bridgehead-*C*) ppm; FT IR (ATR): $\bar{\nu}$ 2959 (w), 2930 (w), 2832 (w), 1711 (w), 1613 (s), 1582 (w), 1495 (s), 1462 (m), 1452 (m), 1429 (m), 1413 (s), 1299 (w), 1270 (m), 1234 (s), 1205 (m), 1174 (m), 1148 (w), 1111 (m), 1101 (m), 1046 (s), 999 (w), 973 (w), 881 (m), 850 (m), 836 (m), 801 (s), 781 (m), 716 (w), 683 (w), 622 (w) cm^{-1}; UV−vis λ_{max}/nm (log) 272 (4.63), 321 (4.04), 348 (3.37), 367 (3.34); HRMS (MALDI) *m*/*z*: $[M]^+$ Calcd for $C_{62}H_{44}O_6$ 884.31379; Found 884.31526. Anal. Calcd for $C_{62}H_{44}O_6 \cdot 2.5\ H_2O$: C, 80.07, H, 5.31. Found: C, 79.80, H, 5.18.

10,21-(6′,7′,10′,11′-Tetramethoxytriphenylen-2′,3′-yl)-10,21-dihydro-(2,3,6,7,13,14,17,18-octamethoxy)tetrabenzo-[*a*,*c*,*l*,*n*]pentacene 4e. To a solution of **3e** (106 mg, 99 μmol, 1.0 equiv) in dry DCM (30 mL) and methanesulfonic acid (3 mL) was added DDQ (74 mg, 327 μmol, 3.3 equiv), and the mixture was stirred for 10 min at 0 °C. After quenching and standard workup, the crude product was washed with MeOH and *n*-pentane. The crude product was further purified by recrystallization from hot $CHCl_3$, and **4c** was obtained as colorless crystalline solid (51 mg, 48 μmol, 48%); mp > 400 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 373 K): δ 8.66 (s, 6H, *H*-1′,4′,9,11,20,22), 8.09 (s, 6H, *H*-8′,9′,4,5,15,16), 7.82 (s, 6H, *H*-5′,12′,1,8,12,19), 6.17 (s, 2H, bridgehead-*H*), 4.17 (s, 18H, OCH_3-7′,10′,3,6,14,17), 4.08 (s, 18H, OCH_3-6′,11′,2,7,13,18) ppm; ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 373 K): δ 150.0 (*C*-7′,10′,3,6,14,17), 149.6 (*C*-6′,11′,2,7,13,18), 142.4 (*C*-2′,3′,9a,10a,20a,21a), 126.9 (*C*-4′a,12′b,8b,11a,19b,22a), 124.4 (*C*-8′a,8′b,4a,4b,15a,15b), 123.9 (*C*-4′b,12′a,8a,11b,19a,22b), 117.7 (*C*-1′,4′,9,11,20,22), 106.7 (*C*-8′,9′,4,5,15,16), 106.1 (*C*-5′,12′,1,8,12,19), 56.7 (OCH_3), 56.5 (OCH_3), 54.3 (bridgehead-*C*) ppm; FT IR (ATR): $\bar{\nu}$ 2993 (w), 2932 (w), 2826 (w), 1739 (w), 1713 (w), 1617 (m), 1509 (s), 1493 (m), 1462 (m), 1448 (m), 1415 (s), 1382 (w), 1333 (w), 1258 (s), 1211 (s), 1197 (s), 1170 (m), 1148 (s), 1036 (s), 975 (w), 956 (w), 899 (w), 875 (w), 838 (s), 816 (m), 789 (w), 765 (m), 722 (w), 683 (w), 618 (s) cm^{-1}; UV−vis λ_{max}/nm (log) 283 (5.30), 314 (4.95), 327 (4.94) sh 347 (4.22); HRMS (MALDI) *m*/*z*: $[M]^+$ Calcd for $C_{68}H_{56}O_{12}$ 1064.37663; Found 1064.37334. Anal. Calcd for $C_{68}H_{56}O_{12} \cdot 1.5\ H_2O$: C, 74.78, H, 5.45. Found: C, 74.85, H, 5.51.

10,21-[6′,7′,10′,11′-Di(9″,10″-dihydroanthracen-9″,10″-yl)-triphenylen-2′,3′-yl]-10,21-dihydro-(2,3,6,7,13,14,17,18-tetra-(9″,10″-dihydroanthracen-9″,10″-yl)tetrabenzo[*a*,*c*,*l*,*n*]-pentacene 8. To a solution of **7** (30 mg, 17 μmol, 1.0 equiv) in dry DCM (9 mL) and methanesulfonic acid (1 mL) was added DDQ (13.5 mg, 59 μmol, 3.5 equiv), and the mixture was stirred for 15 min at 0 °C. After quenching and standard workup, the crude product was washed with *n*-hexane and *n*-pentane, giving a colorless solid (22 mg, 13 μmol, 74%); mp > 400 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 6H, *H*-1′,4′,9,11,20,22), 8.58 (s, 6H, *H*-5′,12′,1,8,12,19), 8.50 (s, 6H, *H*-8′,9′,4,5,15,16), 7.47−7.42 (m, 24H, *H*-1″,4″,5″,8″), 7.03−6.98 (m, 24H, *H*-2″,3″,6″,7″*H*), 6.04 (s, 2H, core bridgehead-*H*-10,21), 5.62 (s, 6H, bridgehead-*H*-9″), 5.59 (s, 6H, bridgehead-*H*-10″) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1 (*C*-4″a,8″a,9″a,10″a), 143.2 (*C*-6′,11′,2,7,13,18/7′,10′,3,6,14,17), 143.2 (*C*-6′,11′,2,7,13,18/7′,10′,3,6,14,17), 142.6 (*C*-2′,3′,9a,10a,20a,21a), 127.8 (*C*-4′a,12′b,8b,11a,19b,22a), 127.5 (*C*-4′b,12′a,8a,11b,19a,22b/8′a,8′b,4a,4b,15a,15b), 127.4 (*C*-4′b,12′a,8a,11b,19a,22b/8′a,8′b,4a,4b,15a,15b), 125.5 (*C*-2″,3″,6″,7″), 123.9 (*C*-1″,4″,5″,8″), 118.2 (*C*-1′,4′,9,11,20,22), 118.0 (*C*-5′,12′,1,8,12,19), 118.0 (*C*-8′,9′,4,5,15,16), 54.4 (core bridgehead *C*-10,21), 54.4 (bridgehead *C*-9″), 54.3 (bridgehead *C*-10″) ppm; FT IR (ATR): $\bar{\nu}$ 3067 (w), 3040 (w), 3020 (w), 2953 (w), 2924 (w), 1737 (w), 1711 (w), 1680 (w), 1588 (w), 1472 (w), 1458 (m), 1423 (m), 1376 (w), 1338 (w), 1295 (w), 1260 (w), 1203 (w), 1189 (w), 1164 (w), 1156 (w), 1093 (w), 1024 (w), 1001 (w), 973 (w), 934 (w), 920 (w), 881 (m), 797 (w), 740 (s), 689 (w), 669 (w), 634 (m), 626 (s) cm^{-1}; UV−vis λ_{max}/nm (log) 282 (5.29), 312 (4.99), 323 (4.96) sh 345 (4.40); MS (MALDI) *m*/*z* 1761.64 $[M + H]^+$; Anal. Calcd for $C_{140}H_{80} \cdot 2H_2O$: C, 93.51, H, 4.71. Found: C, 93.48, H, 4.70.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01520.

^{1}H, ^{13}C, and 2D NMR spectra of all new compounds (**3a**−**3g**, **4a**−**4c**, **4e**, **5**−**8**) and single-crystal X-ray diffraction data of **3a**, **3b**, and **4e** (PDF)

Crystallographic data for **3a**, **3b**, and **4e** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.mastalerz@oci.uni-heidelberg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank "Deutsche Forschungsgemeinschaft" and "Fonds der Chemischen Industrie" for financial support. We would like to thank Michael Ganschow for preliminary experiments.

■ REFERENCES

(1) (a) Long, T. M.; Swager, T. M. *Adv. Mater.* **2001**, *13*, 601−604. (b) Tsui, N. T.; Paraskos, A. J.; Torun, L.; Swager, T. M.; Thomas, E. L. *Macromolecules* **2006**, *39*, 3350−3358.

(2) (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321−5322. (b) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864−11873. (c) Nesterov, E. E.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 10083−10088. (d) Swager, T. M. *Acc. Chem. Res.* **2008**, *41*, 1181−1189. (e) McKeown, N. B.; Budd, P. M. *Macromolecules* **2010**, *43*, 5163−5176. (f) Ghanem, B. S.; Hashem, M.; Harris, K. D. M.; Msayib, K. J.; Xu, M.; Budd, P. M.; Chaukura, N.; Book, D.; Tedds, S.; Walton, A.; McKeown, N. B. *Macromolecules* **2010**, *43*, 5287−5294. (g) Ghanem, B. S.; Msayib, K. J.; McKeown, N. B.; Harris, K. D. M.; Pan, Z.; Budd, P. M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. *Chem. Commun.* **2007**, 67−69.

(3) (a) Kissel, P.; Murray, D. J.; Wulftange, W. J.; Catalano, V. J.; King, B. T. *Nat. Chem.* **2014**, *6*, 774−778. (b) Bhola, R.; Payamyar, P.; Murray, D. J.; Kumar, B.; Teator, A. J.; Schmidt, M. U.; Hammer, S. M.; Saha, A.; Sakamoto, J.; Schlüter, a. D.; King, B. T. *J. Am. Chem. Soc.* **2013**, *135*, 14134−14141.

(4) (a) Kohl, B.; Rominger, F.; Mastalerz, M. *Org. Lett.* **2014**, *16*, 704−707. (b) Taylor, R. G. D.; Carta, M.; Bezzu, C. G.; Walker, J.; Msayib, K. J.; Kariuki, B. M.; McKeown, N. B. *Org. Lett.* **2014**, *16*, 1848−1851. (c) Abbott, L. J.; McDermott, A. G.; Del Regno, A.; Taylor, R. G. D.; Bezzu, C. G.; Msayib, K. J.; McKeown, N. B.; Siperstein, F. R.; Runt, J.; Colina, C. M. *J. Phys. Chem. B* **2013**, *117*, 355−364. (d) Del Regno, A.; Siperstein, F. R. *Microporous Mesoporous Mater.* **2013**, *176*, 55−63. (e) Abbott, L. J.; McKeown, N. B.; Colina, C. M. *J. Mater. Chem. A* **2013**, *1*, 11950.

(5) Zhang, C.; Liu, Y.; Xiong, X.-Q.; Peng, L.-H.; Gan, L.; Chen, C.-F.; Xu, H.-B. *Org. Lett.* **2012**, *14*, 5912−5915.

(6) Biegger, P.; Stolz, S.; Intorp, S. N.; Zhang, Y.; Engelhart, J. U.; Rominger, F.; Hardcastle, K. I.; Lemmer, U.; Qian, X.; Hamburger, M.; Bunz, U. H. F. *J. Org. Chem.* **2015**, *80*, 582−589.

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342−9348

(7) (a) Chong, J. H.; MacLachlan, M. J. *J. Org. Chem.* **2007**, *72*, 8683−8690. (b) Cao, J.; Zhu, X.-Z.; Chen, C.-F. *J. Org. Chem.* **2010**, *75*, 7420−7423. (c) Jiang, Y.; Chen, C.-F. *Synlett* **2010**, *2010*, 1679−1681. (d) Roy, X.; Chong, J. H.; Patrick, B. O.; MacLachlan, M. J. *Cryst. Growth Des.* **2011**, *11*, 4551−4558. (e) Mastalerz, M.; Sieste, S.; Cenić, M.; Oppel, I. M. *J. Org. Chem.* **2011**, *76*, 6389−6393. (f) Jiang, Y.; Chen, C.-F. *Eur. J. Org. Chem.* **2011**, *2011*, 6377−6403. (g) Meng, Z.; Han, Y.; Wang, L.-N.; Xiang, J.-F.; He, S.-G.; Chen, C.-F. *J. Am. Chem. Soc.* **2015**, *137*, 9739−9745. (h) Kohl, B.; Over, L. C.; Lohr, T.; Vasylyeva, M.; Rominger, F.; Mastalerz, M. *Org. Lett.* **2014**, *16*, 5596−5599. (i) White, N. G.; MacLachlan, M. J. *J. Org. Chem.* **2015**, *80*, 8390−8397.

(8) (a) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641−1654. (b) Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675−6679. (c) Shahlai, K.; Hart, H. *J. Org. Chem.* **1991**, *56*, 6905−6912. (d) Patney, H. K. *Synthesis* **1991**, *1991*, 694−696. (e) Zhu, X.-Z.; Chen, C.-F. *J. Org. Chem.* **2005**, *70*, 917−924. (f) Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301−3315. (g) Zhu, P.-C.; Liu, Y.; Peng, L.-H.; Zhang, C. *Tetrahedron Lett.* **2014**, *55*, 521−524.

(9) Hilton, C. L.; Jamison, C. R.; Zane, H. K.; King, B. T. *J. Org. Chem.* **2009**, *74*, 405−407.

(10) Kumar, B.; Strasser, C. E.; King, B. T. *J. Org. Chem.* **2012**, *77*, 311−316.

(11) Hilton, C. L.; King, B. T. *Organometallics* **2006**, *25*, 4058−4061.

(12) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1−456.

(13) Zhai, L.; Shukla, R.; Wadumethrige, S. H.; Rathore, R. *J. Org. Chem.* **2010**, *75*, 4748−4760.

(14) (a) Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, a. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851−858. (b) Naarmann, H.; Hanack, M.; Mattmer, R. *Synthesis* **1994**, *1994*, 477−478. (c) Mahoney, S. J.; Ahmida, M. M.; Kayal, H.; Fox, N.; Shimizu, Y.; Eichhorn, S. H. *J. Mater. Chem.* **2009**, *19*, 9221. (d) Bai, W.; Lin, J. *Synth. Commun.* **2011**, *41*, 903−906.

(15) (a) Scholl, R.; Mansfeld, J. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734−1746. (b) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357−379. (c) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem., Int. Ed.* **2013**, *52*, 9900−9930.

(16) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279−2288.

(17) (a) Suzuki, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6722−6737. (b) Von der Saal, W.; Engh, R. a.; Eichinger, A.; Gabriel, B.; Kucznierz, R.; Sauer, J. *Arch. Pharm.* **1996**, *329*, 73−82. (c) Dong, C. G.; Hu, Q. S. *J. Am. Chem. Soc.* **2005**, *127*, 10006−10007.

(18) Friedman, L.; Logullo, F. M. *J. Org. Chem.* **1969**, *34*, 3089−3092.

(19) Tanida, H.; Muneyuki, R. *Tetrahedron Lett.* **1964**, *5*, 2787−2790.

(20) Sheldrick, G. M. *SADABS 2012/1: Program for Absorption Correction*; Bruker Analytical X-ray Division: Madison, WI, 2012.

(21) (SHELXL-2014/7 (Sheldrick, 2014) Program for Structure Refinement): Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

(22) Chen, Z.; Swager, T. M. *Macromolecules* **2008**, *41*, 6880−6885.

DOI: 10.1021/acs.joc.5b01520
J. Org. Chem. 2015, 80, 9342−9348