Aryne-based synthesis of cyclobutadiene-containing oligoacenes and related extended biphenylene derivatives

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Abstract. A novel aryne derived from a π-extended biphenylene, 2,3-didehydrobenzo[*b*]biphenylene, has been developed. The participation of this new aryne building block in [4+2] and palladium-catalyzed [2+2+2] cycloaddition reactions has been effectively applied to the synthesis of a variety of polycyclic conjugated hydrocarbons (PCHs) with appealing structures which combine (aromatic) benzene and (antiaromatic) cyclobutadiene (CBD) rings. Among them, a family of unsubstituted (or barely substituted) CBD-oligoacenes has been accessed by iterative Diels-Alder reactions of the new aryne with furans and/or isobenzofurans, followed by deoxygenative aromatization of the resulting epoxy-derivatives. The experimental and computational studies of the newly synthesized PCHs suggest an important degree of electron delocalization along the polycyclic skeleton, more pronounced in the linearly fused derivatives. Interestingly, the computed ACID plots reveal clockwise current density vectors at the peripheral bonds, originating from the σ contributions of the antiaromatic cyclobutadiene rings.

Keywords: Polycyclic conjugated hydrocarbons; Arynes; Cycloaddition reactions; Biphenylene; Cyclobutadiene-containing oligoacenes

Introduction

Polycyclic π-conjugated hydrocarbons (PCHs) have attracted wide attention from the scientific community due to their prominent role as organic semiconductors and electroactive materials for the development of organic electronics.[1] Linearly fused rigid systems, such as acenes, are considered paradigmatic organic semiconductors,[2] but their general use is hampered by the decreased chemical stability associated to the extension of the length of the acene, a feature that can be qualitatively explained on the basis of Clar's π-sextet rule.[3] Angularly fused phenes, starphenes[4] and other bent-shaped oligoacene derivatives[5] are also promising optoelectronic materials. Among the diverse families of PCHs, those containing fused four-membered cyclobutadienoid rings are particularly interesting due to the properties associated with the alternation of aromatic and antiaromatic ring currents in their structures. In this context, in addition to the fascinating linear, angular and helical [*N*]phenylenes,[6] profusely studied by Vollhardt and co-workers[7] among others, recent interest has aroused on the study of other polycyclic systems, including linear phenylene-containing oligoacenes[8,9] and heteroacenes,[10] derivatives with non-linear polycyclic aromatic moieties[11] or isomeric graphene nanostructures formed by fused biphenylene units.[12] Biphenylene-containing PCHs have been recently explored for single-molecule junctions,[13] or as potential singlet fission chromophores,[14] while the effect of the cyclobutadiene rings on Baird aromaticity and its influence in the triplet state energies of the resulting π-extended derivatives[15] have also been studied. Conversion of PCHs containing cyclobutadiene (CBD) rings into contorted benzenoid conjugated hydrocarbons, through metal-catalyzed C–C bond activation, has also been recently described.[16]

Some years ago, we applied our shortly before discovered palladium-catalyzed [2+2+2] cycloaddition of arynes[17] to the synthesis of tris(benzocyclobutadiene)triphenylene.[18] More recently, we used this biphenylene trimer as a probe for the site-selective covalent functionalization of a semiconductor surface.[19] Our renewed interest in PCHs containing four-membered rings, led us to plan the synthesis of π-extended derivatives, including CBD-containing oligoacenes, by means of cycloaddition reactions of a benzobiphenylene-based aryne building block, 2,3-didehydrobenzo[*b*]biphenylene (**1**), accessed from its Kobayashi-type aryne precursor[20] **2** (Scheme 1). Here we report the results of our synthetic study, and the preliminary evaluation of the electronic properties and aromatic character of the newly synthesized CBD-containing PCHs.

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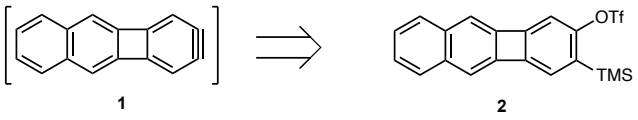
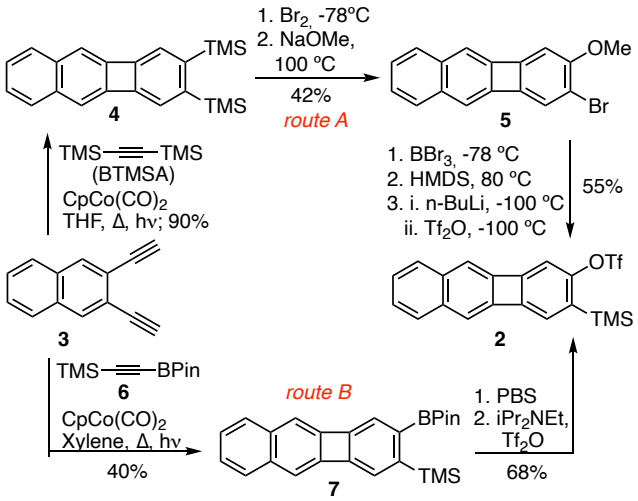


Scheme 1. 2,3-Didehydrobenzo[*b*]biphenylene (**1**) and its Kobayashi-type aryne precursor, **2**..

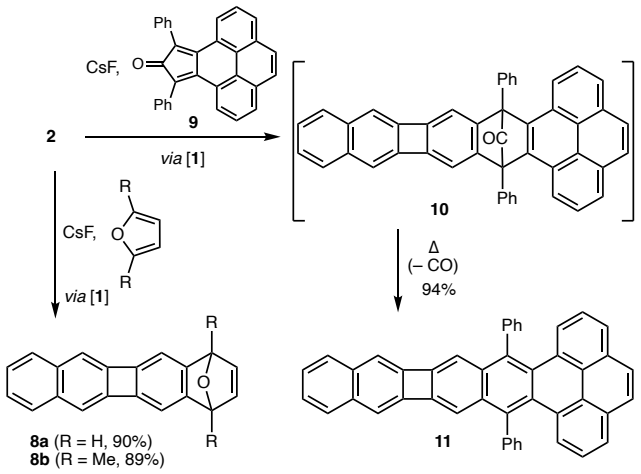
Results and Discussion

The synthesis of 3-(trimethylsilyl)benzo[*b*]-biphenylene-2-yl triflate (**2**) was achieved through the two alternative routes depicted in Scheme 2, both based in the construction of the 2,3-disubstituted benzo[*b*]biphenylene core by means of a cobalt(I)-catalyzed [2+2+2] cycloaddition of 2,3-diethynyl-naphthalene (**3**) with an appropriate alkyne. Thus, reaction of **3** with bis(trimethylsilyl)acetylene (BTMSA, used as co-solvent) in the presence of $CpCo(CO)_2$, under heating and irradiation, provided 2,3-bis(trimethylsilyl)benzo[*b*]biphenylene (**4**)[21] in a satisfactory 90% yield. For the transformation of **4** into triflate **2**, first we attempted the protocol previously developed for the synthesis of an analogous biphenylyne precursor,[18] which allowed the isolation of **2** in low yields and with scarce reproducibility. Better results were obtained when **4** was subjected to a double bromodesilylation followed by nucleophilic substitution of one of the bromine atoms by methoxide to yield **5**. Subsequent treatment with BBr_3 afforded an unstable *o*-bromophenol, which was directly subjected to the protocol developed in our group for the synthesis of *o*-(trimethylsilyl)aryl triflates[22] to give **2** (route A in Scheme 2; six steps and 20.7% yield from **3**). Alternatively, the Co(I)-catalyzed [2+2+2] cyclo-addition of **3** with the trimethylsilyl alkynylboronate **6**[23] afforded **7** in 40% yield. The *ipso*-hydroxylation of the arylboronic ester with sodium perborate, followed by triflation of the resulting phenol, allowed the straightforward synthesis of **2** in 68% yield (route B in Scheme 2; three steps and 27.2% overall yield from **3**).



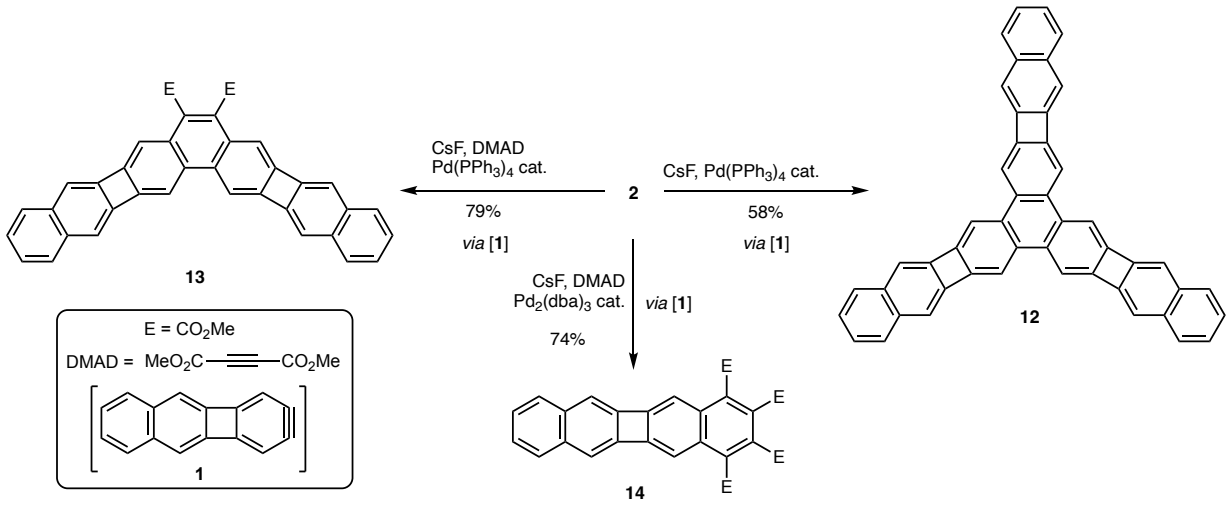
Scheme 2. Syntheses of 3-(trimethylsilyl)-benzo[*b*]biphenylene-2-yl triflate (**2**).

The efficiency of **2** as precursor of benzo[*b*]biphenylyne **1** was evaluated by means of trapping experiments with typical dienes, such as furans and cyclopentadienones (Scheme 3). In particular, treatment of **2** with CsF in the presence of excess furan (or 2,5-dimethylfuran) successfully afforded the corresponding [4+2] adducts **8a**[24] and **8b** in 90% and 89% isolated yields, respectively. On the other hand, the reaction of **2** with the polycyclic cyclopentadienone **9**[25] under aryne-forming conditions followed by heating of the resulting adduct **10** in refluxing 1,1,2,2-tetrachloroethane allowed the isolation of **11** in an excellent 94% yield, as the result of a Diels-Alder reaction between aryne **1** and diene **9**, and subsequent cheletropic extrusion of CO.



Scheme 3. Trapping of 2,3-didehydrobenzo[*b*]biphenylene (**1**) generated from *o*-silylaryl triflate **2**.

Next, we tested the performance of **1** under the conditions developed by our group for palladium-catalyzed [2+2+2] cycloaddition reactions of arynes.[4b,17] Thus, treatment of **2** with CsF in the presence of catalytic amounts of $Pd(PPh_3)_4$ resulted in the formation of a yellow solid, scarcely soluble in common organic solvents, which was identified as the cyclobutadiene-containing starphene **12** on the basis of its high resolution mass spectrum (Scheme 4). When the reaction was performed in the presence of dimethyl acetylene dicarboxylate (DMAD), compound **13** was isolated in a 79% yield, as the result of a [2+2+2] cycloaddition between two molecules of aryne **1** and one of the electron-deficient alkyne. In accordance to previous results with other arynes,[17b,26] the use of $Pd_2(dba)_3$ as the catalyst resulted in the selective formation of dibenzobiphenylene **14** by means of the reaction of one molecule of the aryne and two of the alkyne (Scheme 4).



Scheme 4. Palladium(0)-catalyzed [2+2+2] cycloaddition reactions of 2,3-didehydrobenzo[*b*]biphenylene (**1**).

Once proved the efficiency of triflate **2** as precursor of 2,3-didehydrobenzo[*b*]biphenylene (**1**), and the utility of this novel aryne for the easy access to π-extended cyclobutadiene-containing polycyclic conjugated systems, we decided to explore the use of this building block for the synthesis of oligoacene derivatives incorporating cyclobutadiene rings (CBD-oligoacenes). Elegant synthetic strategies recently developed by Swager,[8a,b] Xia,[8c,d,e] Miao[8f] or Gribble[24] have allowed the access to CBD-oligoacenes functionalized with large phenyl, alkyl and/or (trialkylsilyl)ethynyl substituents, as analogues of acenes in which the presence of four-membered rings into the linear π-backbone increases the number of Clar sextets, resulting in higher stability. The influence of the substituents in the molecular packing and electronic properties has been illustrated by some high-mobility derivatives,[8d,e] while the effect of the extension and (anti)aromaticity of the polycyclic conjugated core in charge transport has also been theoretically studied.[27] With those precedents in mind, and on the basis of our own work in the synthesis of long acenes,[28] we decided to approach the construction of unsubstituted (or barely substituted) CBD-oligoacenes from adequate endoxide-precursors, which would be accessed by iterative Diels-Alder reactions between biphenylene-based arynes and furans (or isobenzofurans).

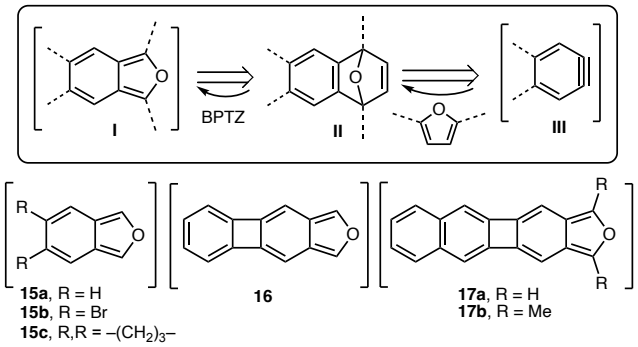
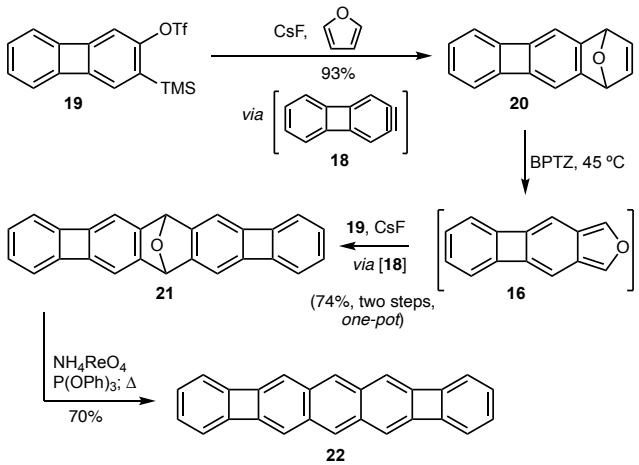


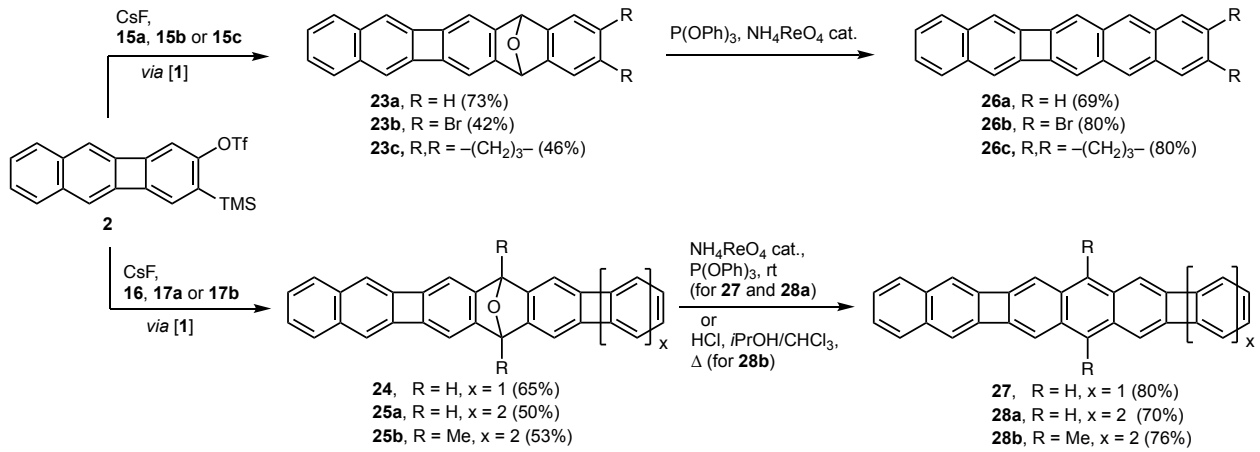
Figure 1. Isobenzofuran building blocks used in this work.

The highly reactive isobenzofurans **I** could be easily generated by gentle warming of epoxyacenes **II**, obtained by reaction of arynes **III** with furans, in the presence of 3,6-bis(pyridyl)-1,2,4,5-tetrazine (BPTZ)[29] (Figure 1). This approach was used in this work for accessing isobenzofuran (**15a**) and derivatives **15b**, **15c**, **16**, **17a** and **17b**.

As a proof of concept of our approach we first studied the reaction of biphenylyne **18**, whose generation from triflate **19** had been previously reported by our group,[18] with isobenzofuran **16** obtained from endoxyde **20**. The reaction afforded the epoxy-derivative **21** in a satisfactory 74% yield. Deoxygenative aromatization of **21** was successfully achieved by treatment with catalytic amounts of ammonium perrhenate in the presence of triphenylphosphite as oxygen scavenger,[30] affording **22** as a white, highly insoluble solid in 70% yield (Scheme 5). The identity of **22** was deduced on the basis of its HRMS and UV-vis spectra (see SI), being diagnostic the red shift of the lowest energy absorption band of **22** (λ_{max} = 451 nm) with respect to that of **21** (λ_{max} = 388 nm). The low solubility of **22** precluded the analysis by ^{1}H NMR.



Scheme 5. Synthesis of bis(benzocyclobuta)anthracene **22** by iterative Diels-Alder reactions of biphenylyne (**18**).



Scheme 6. Synthesis of cyclobutadiene-containing oligoacenes **26-28** by cycloaddition reactions of 2,3-didehydrobenzo[*b*]biphenylene (**1**).

Next, we studied the cycloaddition of benzo[*b*]biphenylyne (**1**) generated by fluoride-induced decomposition of triflate **2**, with *in situ* generated isobenzofurans **15**, **16** and **17**, obtaining the expected cycloadducts **23-25** in satisfactory yields, ranging from 42% for **23b** to 73% for **23a** (Scheme 6), as perfectly stable and soluble products which could be fully characterized. The deoxygenative aromatization of **23-25** was successfully performed by rhenium-catalyzed procedure mentioned above or by treatment with HCl and *i*PrOH (effective for the dimethyl-substituted **25b**), to afford the expected CBD-oligoacenes **26-28** in good yields (Scheme 6). Remarkably, the cyclopentene-fused derivative **26c** resulted soluble enough to successfully obtain its ^{1}H NMR spectrum in 1,1,2,2-tetrachloroethane-d_2. With regard to the other newly synthesized CBD-oligoacenes, although the lack of solubility precluded their characterization by NMR, their identity was confirmed by high resolution mass spectrometry and analysis of their UV-vis spectra. In particular, compounds such as **26a-c** or **28a-b** displayed similar spectra that those reported for previously described alkynyl or aryl-substituted analogues.[8]

Selected experimental data provided by the UV-vis and fluorescence spectra of the newly synthesized cyclobutadiene-containing PCHs are summarized in Table 1, together with the results of the computational estimation of the energy gaps (see SI for full details). The spectra of the [2+2+2] cycloadducts **12-14** show lowest energy absorptions in the range of 421 (for **14**) to 448 (for **13**) nm. With regard to the linearly fused derivatives, it is worth to note that while all the epoxy-oligoacenes **23-25** exhibit almost identical lowest energy absorptions around 405-410 nm, associated to the benzo[*b*]biphenylene chromophore, the corresponding deoxygenated CBD-oligoacenes show larger λ_{max} values (see Figure 2a, for **25b**/**28b**). The wavelength of these lowest absorptions increases with the size of the linear polycyclic system, from $\lambda_{max} \approx$ 440 nm for **26**, to 479 nm for **28b**. In all cases, the absorption is also significantly red-shifted with respect to that of anthracene (λ_{max} = 373 nm), the largest polycyclic benzenoid chromophore contained in each of the structures, demonstrating an important degree of electron delocalization along the polycyclic skeleton despite the presence of the antiaromatic cyclobutadiene moieties. Comparison of the spectra of the angularly shaped **13** with the linear analogue of similar size, **28**, suggests that the electron delocalization is more significant in the latter.

Table 1. Spectroscopic properties[a] and E_{gap} estimation of the new CBD-containing PCHs.

Comp.	λ_{max} (nm)	λ_{onset} (nm)	λ_{em} (nm)	$E_{gap(opt)}$[c] (eV)	$E_{gap(calc)}$[d] (eV)
11	459	465	464 (505)[b]	2.67	2.67
12	437	455	468	2.73	2.67
13	448	455	455	2.73	2.75
14	421	427	428	2.90	3.09
22	451	460	451	2.70	2.82
26a	433	441	468	2.80	2.79
26b	440	445	441	2.79	2.77
26c	436	440	441	2.81	2.75
27	458	473	459	2.62	2.73
28a	470	475	470 (599)[b]	2.60	2.67
28b	479	490	480 (616)[b]	2.53	2.54

[a] Measured in 1,2,4-trichlorobenzene, except the spectra of **11**, **13**, **14** and **26a**, measured in $CHCl_3$. [b] Measured in the solid state by means of an integrating sphere. [c] $E_{gap(opt)} = 1241/\lambda_{onset}$. [d] Calculated at the TDDFT/O3LYP/6-311+G(d,p) level.

With regard to the fluorescence, it is remarkable the very small Stokes shifts observed in the linear CBD-oligoacenes, ranging from 0 to 2 nm, which is indicative of the rigid structure of these compounds. As another interesting feature, the fluorescence spectra of solid **28a** and **28b** exhibit large bathochromic shifts with respect to measurements in solution (146 and 119 nm, respectively; see Figure 2b for **28b**), that are significantly larger than those observed for the same polycyclic systems provided with pendant phenyl and TIPS-ethynyl groups[8a] and may constitute a

preliminary evidence of effective electronic coupling between neighbouring molecules in the solid state.[31]

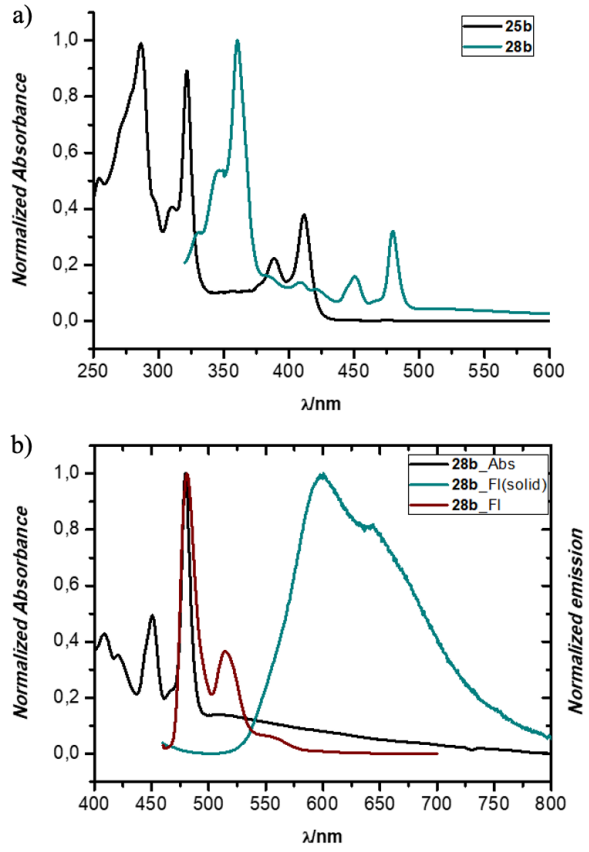


Figure 2. a) Overlay of the absorbance spectra of precursor **25b** (in $CHCl_3$) and CBD-oligoacene **28b** (in 1,2,4-trichlorobenzene). b) Absorbance and fluorescence spectra of **28b** in solution, and fluorescence in the solid state.

The structures and properties of the newly synthesized compounds were also computational studied. Optical gaps were calculated by TDDFT using the B3LYP and O3LYP functionals with the 6-311++G(d,p) basis set (see Table S1). While the B3LYP calculated gaps resulted, as expected, slightly overestimated, the use of the O3LYP functional, which is similar to the B3LYP but with a smaller percentage of exact HF, predicts smaller energy gaps that are in excellent agreement with the experimental values (within 0.2 eV for all compounds analyzed, see Tables 1 and S1).

Next, we studied the local and global aromaticity/antiaromaticity for the newly synthesized CBD-PCHs by NICS-*XY* scan calculations,[32] using the σ-only method[33] at the GIAO-B3LYP/6-311+G* level of theory (see SI for details). In all compounds, positive NICS values were observed for the four-membered rings, indicating their antiaromatic character. The paratropicity of the cyclobutadiene rings is more pronounced for compound **22** (NICS = 6 ppm), with single benzene rings fused to the CBD at the PCH termini, and for the angularly-fused systems **12** and **13** (NICS ≈ 5.5 ppm), while the bis(naphthocyclobuta)anthracene ring system **28**, previously studied by Xia and coworkers,[8c] presents peak NICS values of 3.9 ppm (for **28a**). On the other hand, the aromatic character of the different benzenoid rings in each PCH structure is affected by the presence of the antiaromatic cyclobutadienoids and the associated bond localization. To illustrate this feature, Figure 3 shows the NICS-*XY* scans of the 9-ring polycyclic systems of **12**, **13** and **28**, showing the terminal benzenoid rings as the less affected (more aromatic character), the rings directly attached to the CBDs as the less aromatic, and a significant difference in the aromatic character of the central ring of the polycyclic systems, being that of the linearly-fused CBD-oligoacene **28** the most aromatic.

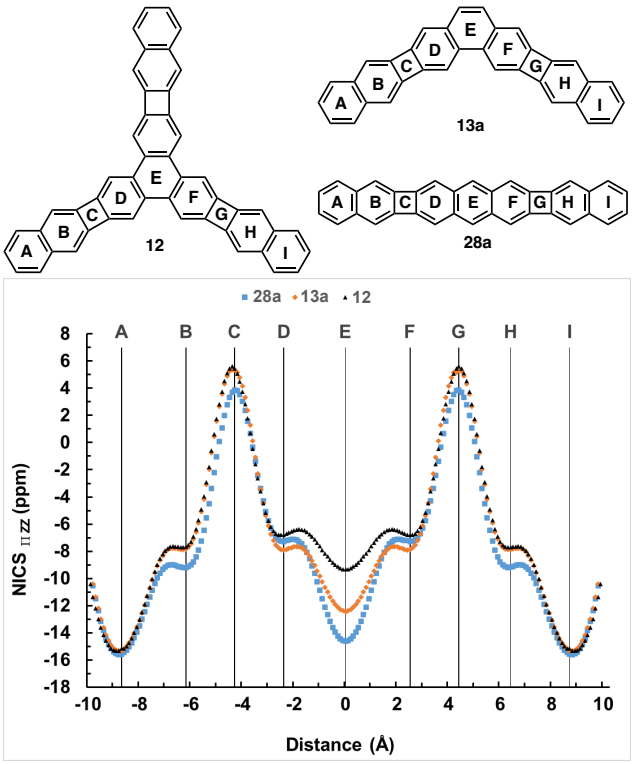


Figure 3. NICS-XY scans at the B3LYP/6-311+G(d,p) level, for **12**, **13** and **28** ring systems.

Finally, to visualize the local diatropic and paratropic ring currents induced by local aromaticity and antiaromaticity, we computed the anisotropy of the induced current density (ACID).[34] As a representative example, Figure 4a shows the ACID plot of **28a**; where clockwise current density vectors indicate aromaticity (black arrows) and anti-clockwise ones describe anti-aromaticity (red arrows). As expected, benzene units show clockwise ring currents, while anti-clockwise ring currents are observed in the cyclobutadiene rings. However, taking a closer look at the latter in Figure 4b, one can see the presence of clockwise current density vectors on the peripheral bonds of the four-membered rings, suggesting a global diatropic current loop that rounds the whole system. Figure 4c shows that these clockwise vectors come from the contributions of the σ system. The other studied compounds present similar features, and their ACID plots can be consulted in Figure S3 (SI).

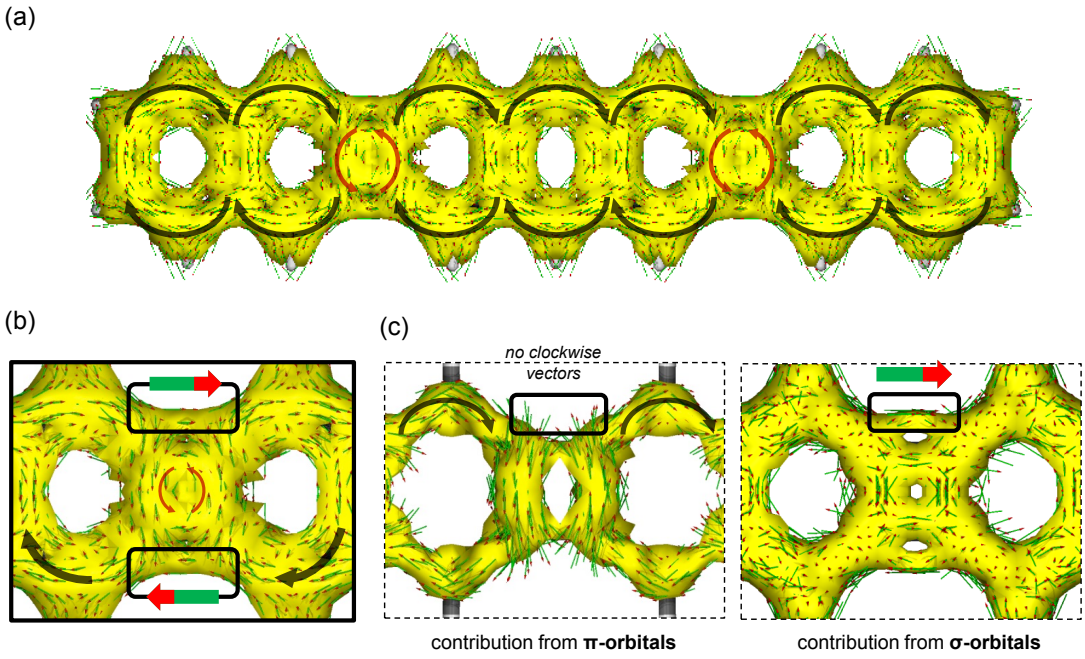


Figure 4. (a) ACID plot of 28a at isosurface value of 0.04. (b) Zoom in on the cyclobutadiene unit. (c) Contributions from π- and σ-type orbitals.

Conclusion

In conclusion, we have synthesized a family of extended cyclobutadiene-containing PCHs with diverse structures, by means of efficient [4+2] or palladium-catalyzed [2+2+2] cycloaddition reactions of a novel aryne building block derived from benzo[*b*]biphenylene. The set of extended phenylenes synthesized include CBD-oligoacenes (with up to nine linearly-fused rings), angularly-fused analogues and a star-shaped benzobiphenylene trimer. Importantly, our approach allowed the synthesis of stable, unsubstituted (or barely substituted) CBD-oligoacenes, which according to preliminary examination of their emission spectra might display effective electronic coupling in the solid state, as unsubstituted acenes do. Experimental and computational studies on the whole series of newly synthesized systems reveal an important degree of electron delocalization along the polycyclic skeletons despite the presence of the antiaromatic cyclobutadiene rings, with more pronounced delocalization observed in the linearly fused CBD-oligoacenes. The current density plotted onto the ACID isosurface indicates a complex pattern of currents that unveils the presence of clockwise peripherical current originating from the σ contributions of the four-membered rings, thus providing new insights into the aromatic and antiaromatic interactions within these intriguing molecular architectures.

Experimental Section

General methods

All reactions were carried out under argon using oven-dried glassware. Anhydrous THF, CH_2Cl_2 and ACN were taken from a MBraun SPS-800 Solvent Purification System. Xylene, *i*-Pr_2NEt and Tf_2O was dried by distillation over CaH_2. Furan was purchased from Sigma-Aldrich and filtered through neutral aluminium oxide (Brockmann I) and stored with molecular sieves (3 Å) under argon atmosphere. Finely powdered CsF was dried under vacuum at 100 °C, cooled under argon and stored in a glove-box. *n*-BuLi was titrated by using diphenyl acetic acid and 1,3-diphenylpropanylidene tosylhydrazine methods. $Pd(PPh_3)_4$ was prepared from $PdCl_2$ following a published procedure.[35] 2,3-Diethynylnaphthalene,[36] 9,11-diphenyl-10*H*-cyclopenta[*e*]pyren-10-one,[25] 3-(trimethylsilyl)biphenylen-2-yl triflate,[18] 1,4-dihydro-1,4-epoxy-naphthalene,[37] 1,4-dihydro-6,7-dibromo-1,4-epoxynaphthalene[38] and 2,3,5,8-tetrahydro-1*H*-5,8-epoxycyclopenta[*b*]naphthalene[39] were prepared following published procedures. Other commercial reagents were purchased from ABCR GmbH, Sigma-Aldrich or Fluorochem, and were used without further purification. TLC was performed on Merck silica gel 60 F_{254} and chromatograms were visualized with UV light (254 and 360 nm). Column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). Centrifugation was performed in a Hettich EBA21 centrifuge. ^1H, ^{19}F and ^{13}C NMR spectra were recorded at 300, 282 and 75 MHz (Varian Mercury-300 instrument), 400 and 101 MHz (Varian Inova 400) or 500 and 125 MHz (Varian Inova 500) respectively. Because of quadrupolar

relaxation, the carbon directly attached to the boron atom was not detected by ^{13}C NMR in compound **7**. Every experiment was performed at 298 K unless otherwise indicated. Low resolution mass spectra (EI) were obtained at 70 eV on a HP-5988A instrument, while high-resolution mass spectra (HR-MS) were obtained on a Micromass Autospec spectrometer. Atmospheric pressure chemical ionisation (APCI) HRMS were obtained on a Bruker Microtof, using either Direct Inlet Probe (DIP) or Flow Injection Analysis (FIA) for sample introduction. UV-Vis and fluorescence spectra were obtained on a Jasco V-630 and on a Fluoromax-2 spectrophotometers, respectively.

Experimental procedures and characterization data

2,3-Bis(trimethylsilyl)benzo[*b*]biphenylene (4): A solution of 2,3-diethynylnaphthalene (320 mg, 1.8 mmol) and $CpCo(CO)_2$ (50 mL, 0.36 mmol) in bis(trimethylsilyl)acetylene (BTMSA, 4 mL) and THF (16 mL) was slowly added (3 h, syringe pump) to a boiling solution of BTMSA (20 mL). Light from a projector lamp (300 W, 50% of its power) was directed at the reaction mixture during the addition. After refluxing and irradiation of the mixture for one additional hour, the solvents were removed under vacuum. The crude residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 9:1) to yield **4** as yellow solid (572 mg, 90 %). Spectroscopic data were identical to those reported in the literature for this compound.[36] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.26 (m, 4H), 6.98 (s, 2H), 0.38 (s, 18H) ppm.

2-Bromo-3-methoxybenzo[*b*]biphenylene (5): To a solution of 2,3-bis(trimethylsilyl)-benzo[*b*]biphenylene (**4**, 450 mg, 1.30 mmol) in dry CH_2Cl_2 (40 mL) cooled down to -78 °C, a solution of Br_2 (200 mL, 3.90 mmol) in CH_2Cl_2 (78 mL) was added dropwise (3 hours, addition funnel with pressure equalizing arm). After being stirred at -78 °C for 20 min, the reaction mixture was quenched with aq. $Na_2S_2O_5$ saturated solution (30 mL) and warmed up to room temperature. The organic layer was separated and concentrated in vacuo. The crude residue was subjected to sonication-assisted washing with hexane (2 x 5 mL) and CH_2Cl_2 (2 x 5 mL) to furnish 2,3-dibromobenzo[*b*]biphenylene (299 mg, 64%) as a white solid. ^1H NMR (353K, 300 MHz, $C_2D_2Cl_4$): δ = 7.51 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.31 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.19 (s, 2H), 7.03 (s, 2H). ^{13}C NMR-DEPT (353K, 75 MHz, $C_2D_2Cl_4$): δ = 150.5 (C), 145.2 (C), 135.6 (C), 129.4 (CH), 127.4 (CH), 125.2 (C), 124.8 (CH), 117.2 (CH). EM (EI^+), m/z (%): 359 ($[M]^+$,100), 280 ($[M]^+$- Br, 3), 274 ($[M]^+$- 2Br, 74). HR-MS (IEA) for $C_{16}H_8Br_2$ ($[M]^+$) Calcd.: 357.8993; Found: 357.9002.

To a solution of dibromobenzo[*b*]biphenylene (100 mg, 0.27 mmol) in DMSO (4 mL) and CH_3OH (300 mL), a solution of $NaOCH_3$ (600 mL, 0.5M in MeOH, 0.30 mmol) was added dropwise. Then the solution was heated at 100 °C for 16 h. After being cooled at room temperature, H_2O (30 mL) was added and the mixture was extracted with CH_2Cl_2 (2 x 20 mL), the organic layer dried with Na_2SO_4, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 9:1 to 8:2), yielding compound **5** as pale yellow solid (58 mg, 65 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49 - 7.41 (m, 2H), 7.28 - 7.21 (m, 2H), 7.11 (s, 1H), 6.91 (s, 1H), 6.81 (s, 1H), 6.68 (s, 1H), 3.90 (s, 3H). ^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 157.2 (C), 151.0 (C), 146.0 (C), 145.4 (C), 143.2 (C), 135.4 (C), 135.0 (C), 128.8 (CH), 128.6 (CH), 126.7 (CH), 126.3 (CH), 124.9 (CH), 115.5 (CH), 114.3 (CH), 111.4 (C), 106.0 (CH), 56.8 (CH_3). HR-MS (APCI-FIA-TOF) for $C_{17}H_{12}BrO$ ($[M+H]^+$) Calcd.: 311.0066; Found: 311.0064.

Trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]biphenylen-2-yl]silane (7): A solution of 2,3-diethynylnaphthalene (160 mg, 0.91 mmol), $CpCo(CO)_2$ (35 mL, 0.23 mmol) and trimethyl[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl]silane (**6**, 200 mg, 0.91 mmol), in a mixture of xylene (8 mL) and THF (3.5 mL), was slowly added (3 h, syringe pump) to a boiling solution of **6** (720 mg, 3,21 mmol) in xylene (12 mL). Light from a projector lamp (300 W, 50% of its power) was directed at the reaction mixture during the addition. After refluxing and irradiation of the mixture for one additional hour, the solvents were removed under vacuum. The crude residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 4:2) to yield trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]biphenylen-2-yl]silane **7** as orange solid (130 mg, 35 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.41 (m, 3H), 7.28 – 7.19 (m, 3H), 6.98 (s, 1H), 6.92 (s, 1H), 1.35 (s, 12H), 0.34 (s, 9H).^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 151.6 (C), 150.8 (C), 149.8 (C), 148.2 (C), 135.3 (C), 135.2 (C), 128.8 (CH), 128.7 (CH), 126.4 (CH), 126.3 (CH), 125.8 (CH), 124.4 (CH), 115.8 (CH), 115.5 (CH), 84.0 (C), 25.1 (CH_3), 1.00 (CH_3). HR-MS (APCI-DIP-TOF) for $C_{25}H_{29}BO_2Si$ ($[M]^+$) Calcd.: 400.2029; Found: 400.2031.

3-(Trimethylsilyl)benzo[*b*]biphenylene-2-yl trifluoromethanesulfonate (2). *Route A:* To a solution of 2-bromo-3-methoxybenzo[*b*]biphenylene (**5**, 230 mg, 0.76 mmol) in dry CH_2Cl_2 (27 mL) cooled to -78 °C, BBr_3 (1.30 mL, 1M in CH_2Cl_2, 1.30 mmol) was added. After 1 h, the reaction mixture was warmed up to room temperature and stirring was kept for 14 h. The reaction mixture was quenched with H_2O/ice and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried with Na_2SO_4, filtered and evaporated under reduced pressure. After observed the quantitative formation of phenol by TLC the crude was used in the next step without any further purification. The crude phenol, previously isolated, was dissolved in THF (5 mL), HMDS (175 mL, 0.83 mmol) was added and the reaction mixture was refluxed for 1.5 h. The solvent and excess HMDS were removed under reduced pressure. The crude residue was dissolved in dry THF (3 mL), the solution was cooled down to -100 °C and, then, *n*-BuLi (365 mL, 2.3 M, 0.84 mmol) was added dropwise. After warming up the reaction mixture to -80°C, it was cooled again to -100°C and Tf_2O (155 mL, 0.91 mmol) was added. The reaction mixture was allowed to reach -80 °C and then quenched with $NaHCO_3$ (aqueous saturated solution, 5 mL). After being warmed to room temperature, the phases were separated, the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic layers dried with Na_2SO_4, filtered and evaporated under reduced pressure. The crude residue was purified by column

chromatography on silica gel (hexane/CH_2Cl_2, 9:1) yielding triflate **2** as a pale yellow solid (177 mg, 55 %).

Route B: A solution of trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]biphenylen-2-yl]silane (**7**, 20 mg, 0.05 mmol) in THF (2 mL) was added to a solution of sodium perborate (PBS, 38 mg, 0.25 mmol) in H_2O (2 mL). After stirring at room temperature for 1 h, the reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL), the combined organic layers dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was used in the next step without any further purification.The residue was dissolved in dry CH_2Cl_2 (2.3 mL) and to the resulting solution, kept at -78 °C, freshly destilled *i*-Pr_2NEt (14 mL, 0.08 mmol) and Tf_2O (17 mL, 0.10 mmol) were successively added. After stirring for 1 h at -78 °C, the reaction mixture was allowed to reach room temperature and stirred for 2 h. The reaction mixture was quenched with aqueous $NaHCO_3$ (saturated solution, 2 mL), the phases were separated and the organic layer was extracted with CH_2Cl_2 (2 x 10 mL), the combined organic layers were dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 4:2) yielding triflate **2** as a pale yellow solid (0.015 g, 68 %).

2: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 2H), 7.32 – 7.28 (m, 2H), 7.05 (s, 1H), 7.02 (s, 1H), 7.00 (s, 1H), 6.92 (s, 1H), 0.36 (s, 9H). ^{19}F-NMR (282 MHz, $CDCl_3$) δ: -73.63. ^{13}C RMN-DEPT (101 MHz, $CDCl_3$): δ = 155.6 (C), 153.4 (C), 148.81 (C), 145.7 (C), 144.5 (C), 135.3 (C), 135.2 (C), 133.5 (C), 129.2 (CH), 129.0 (CH), 127.0 (CH), 126.8 (CH), 125.5 (CH), 117.2 (CH), 116.1 (CH), 111.9 (CH), -0.6 (CH_3). EM (EI^+), m/z (%): 422 ($[M]^+$, 50), 407 ($[M]^+$-CH_3, 1), 274 ($[M]^+$-SO_2CF_3, 33). HR-MS (IEA**)** for $C_{20}H_{17}O_3F_3SSi$($[M]^+$) Calcd.: 422.0620; Found: 422.0618.

1,4-Dihydro-1,4-epoxydibenzo[*b,h*]biphenylene (8a): To a solution of **2** (70 mg, 0.16 mmol) in dry CH_3CN (3.2 mL) placed in a Schlenk flask under argon, furan (230 mL, 3.17 mmol) and CsF (218 mg, 1.40 mmol) were successively added. The reaction mixture was stirred at room temperature for 14 hours. The solvent was evaporated and the residue was suspended in CH_2Cl_2 and passed through a SiO_2 plug to isolate **8a** as pale yellow solid (41 mg, 93%). The spectroscopic data were consistent with those from the literature.[24] ^{1}H NMR (300 MHz, CDCl3): δ = 7.39 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.20 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.02 (t, *J* = 1.0 Hz, 2H), 6.91 (s, 2H), 6.75 (s, 2H), 5.63 (s, 2H). EM (EI^+), m/z (%): 268 ($[M]^+$, 17), 242 ($[M]^+$-C_2H_2, 16), 83 (100). HR-MS (IEA) for $C_{20}H_{12}O$ ($[M]^+$) Calcd.: 268.0888; Found: 268.0898.

1,4-Dimethyl-1,4-dihydro-1,4-epoxydibenzo[*b,h*]biphenylene (8b): To a solution of **2** (67 mg, 0.16 mmol) in dry CH_3CN (3.2 mL) placed in a Schlenk flask under argon, 1,5-dimethylfuran (230 mL, 3.17 mmol) and anhydrous CsF (218 mg, 1.40 mmol) were successively added. The reaction mixture was stirred at room temperature for 14 hours. The solvent was evaporated and the residue was suspended in CH_2Cl_2 and passed through a SiO_2 plug to isolate **8b** as pale yellow solid (42 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (dt, *J* = 7.1, 3.5 Hz, 2H), 7.22 (dt, *J* = 5.9, 3.5 Hz, 2H), 6.82(s, 2H), 6.77 (s, 2H), 6.74 (s, 2H), 1.88 (s, 6H). ^{13}C NMR-DEPT (75 MHz, $CDCl_3$): δ: 155.1 (C), 148.1 (C), 146.5 (CH), 146.3 (C), 135.2 (C), 128.5 (CH), 126.1 (CH), 113.7 (CH), 111.8 (CH), 88.8 (C), 15.4 (CH_3). HR-MS (APCI-FIA-TOF) for $C_{22}H_{17}O$ ($[M+H]^+$) Calcd.: 297.1274; Found: 297.1271.

Dibenzo[*hi,mn*]naphthocyclobuta[1,2-*b*]tetracene (11). To a solution of **2** (30 mg, 0.07 mmol) and 9,11-diphenyl-10H-cyclopenta[*e*]pyren-10-one (**10**, 38 mg, 0.09 mmol) in a 2:1 mixture of CH_3CN and CH_2Cl_2 (3 mL), placed in a Schlenk flask under argon, anhydrous CsF (32 mg, 0.21 mmol) was added. The reaction mixture was stirred at room temperature for 14 hours. The solvent was evaporated and the crude product was suspended in CH_2Cl_2/Et_2O (3:1) and passed through a SiO_2. The resulting material was redisolved in $C_2H_2Cl_4$ and refluxed overnigth. The solvent was removed under reduced pressure and the resulting product was dried under vacuum to yield **11** as a bright yellow solid (38 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (s, 2H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.82 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.60 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.55 (s, 10H), 7.39 (s, 2H), 7.35 (d, *J* = 3.8 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.26 (s, 2H). ^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 146.7 (C), 145.9 (C), 142.5 (C), 137.5 (C), 135.5 (C), 133.8 (C), 132.6 (CH), 130.8 (C), 130.3 (C), 130.2 (C), 129.3 (CH), 129.1 (CH), 128.5 (CH), 127.7 (CH), 127.0 (CH), 126.5 (CH), 125.9 (C), 125.8 (CH), 124.8 (CH), 117.6 (CH), 115.8 (CH). EM (APCI), m/z (%): 579 ($[M]^+$, 100), 551 (23), 411(14). HR-MS (APCI-FIA-TOF) for $C_{46}H_{27}$ ($[M+H]^+$) Calcd.: 579.2107; Found: 579.2106. UV-Vis ($CHCl_3$): λ_{max} = 271, 304, 356, 384, 432, 459 nm.

Tris(naphthocyclobutadieno)triphenylene (12): To a solution of **2** (50 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in dry CH_3CN (3.5 mL), placed in a Schlenk flask under argon, anhydrous CsF (60 mg, 0.4 mmol) was added. The reaction mixture was stirred at room temperature for over 14 hours. The resulting suspension was concentrated under reduced pressure, the solid was collected by centrifugation subjected to sonication-assisted washing with portions of CH_3CN (2 x 2 mL), H_2O (2 mL), CH_3OH (2 x 2 mL), Et_2O (2 x 2 mL) and CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **12** as a yellow powder (14 mg, 58%). HR-MS (APCI-DIP-TOF) for $C_{48}H_{25}$ ($[M+H]^+$), Calcd.: 601.1951; Found: 601.1945.

Dimethyl naphtho[2',3':3,4]cyclobuta[1,2-*b*]naphtho[2'3':3,4]cyclobuta[1,2-*h*]phenanthrene-7-8-dicarboxylate (13): To a solution of **2** (30 mg, 0.07 mmol) and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) in dry CH_3CN (1 mL), placed in a Schlenk flask under argon, dimethyl acetylenedicarboxilate (DMAD, 12 mL, 0.10 mmol), and anhydrous CsF (32 mg, 0.21 mmol) were successively added. The reaction mixture was stirred at room temperature for over 14 hours. The resulting suspension was concentrated under reduced pressure, the solid was collected by centrifugation, subjected to sonication-assisted washing with portions of CH_3CN (2 x 2 mL), H_2O (2 mL), CH_3OH (2 x 2 mL), Et_2O (2 x 2 mL) and dried under vacuum to afford **13** as a yellow solid (15 mg, 79%). ^{1}H NMR (353K, 300 MHz, $C_2D_2Cl_4$): δ = 7.98 (s, 2H), 7.60 – 7.51 (m, 4H), 7.44 (s, 2H), 7.29 (dd, *J* = 6.1, 3.2 Hz, 4H), 7.26 (s, 2H), 7.22 (s, 2H), 3.94 (s, 6H). ^{13}C NMR-DEPT (353K, 75 MHz, $C_2D_2Cl_4$): δ = 168.9 (C), 149.9 (C), 148.9 (C), 146.6 (C), 146.5 (C), 136.2 (C), 136.1 (C), 134.5 (C), 130.7 (C), 130.2 (C), 129.6 (CH), 127.4 (CH),118.3 (CH), 116.1 (CH), 112.9 (CH), 53.1 (CH_3). EM (APCI), m/z (%): 542 ($[M]^+$, 100),

407 ([M]$^+$- 2CH_3, 10). HR-MS (APCI-DIP-TOF) for $C_{38}H_{22}O_4$ ([M]$^+$) Calcd.: 542.1513; Found: 542.1510. UV-Vis ($CHCl_3$): λ_{max} = 285, 339, 370, 394, 421, 448 nm.

Tetramethyl dibenzo[*b,h*]biphenylene-1,2,3,4-tetracarboxylate (14): To a solution of **2** (50 mg, 0.12 mmol) and $Pd_2(dba)_3$ (12 mg, 0.01 mmol) in dry CH_3CN (3.5 mL), placed in a Schlenk flask under argon, dimethyl acetylenedicarboxilate (DMAD, 73 mL, 0.6 mmol), and anhydrous CsF (55 mg, 0.36 mmol) were added. The reaction mixture was stirred at room temperature for over 14 hours. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (SiO_2; CH_2Cl_2) to isolate cycloadduct **14** as a yellow solid (43 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.37 (s, 3H), 7.33 (dd, *J* = 6.1, 3.3 Hz, 3H), 7.29 (s, 2H), 4.00 (s, 6H), 3.88 (s, 6H). ^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 167.5 (C), 166.7 (C), 150.4 (C), 145.0 (C), 135.7(C), 134.0 (C), 133.1 (C), 129.4 (CH), 127.9 (C), 127.2 (CH), 119.1 (CH), 114.2 (CH), 53.23 (CH_3), 53.18 (CH_3). EM, m/z (%): 484 ([M]$^+$, 100), 453 ([M]$^+$, -OCH_3, 40). HR-MS (APCI-DIP-TOF) for $C_{28}H_{20}O_8$ ([M]$^+$) Calcd.: 484.1153; Found: 484.1153. UV-Vis ($CHCl_3$): λ_{max} = 306, 395, 421 nm.

6,9-Dihydro-6,9-epoxybenzo[*b*]biphenylene (20): To a solution of **19**[4] (73 mg, 0.19 mmol) in dry CH_3CN (2 mL), placed in a Schlenk under argon, was added furan (428 mL, 5.88 mmol) and anhydrous CsF (120 mg, 0.78 mmol). The reaction mixture was stirred at room temperature for 14 hours. The solvent was evaporated and the residue was suspended in CH_2Cl_2 and passed through a SiO_2 plug to isolate **20** as a pale yellow solid (40 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00 (t, J = 1.1 Hz, 2H), 6.67 (s, 2H), 6.64 (dd, J = 4.8, 2.8 Hz, 2H), 6.46 (dd, J = 4.8, 2.9 Hz, 2H), 5.56 (d, J = 1.3 Hz, 2H). ^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 150.6(C), 150.2(C), 149.5(C), 142.9(CH), 128.0(CH), 116.2(CH), 112.5(CH), 82.6(CH). HR-MS (APCI-FIA-TOF) for $C_{16}H_{11}O$ ([M+H]$^+$) Calcd.: 219.0804; Found: 219.0806.

General procedure for the synthesis of oligoacene endoxides 21, 23-25

A solution of the corresponding epoxyacene and 3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine (BPTZ) in CH_2Cl_2, is stirred at 45 ºC until complete consumption of the starting epoxiacene (TLC monitoring), generating *in situ* the corresponding isobenzofuran (**15-17**). To this solution, kept at room temperature in a Schlenk flask, a solution of the aryne precursor (**2** or **19**, 1 equiv) in CH_3CN was added, followed by finely powdered, anhydrous CsF (5-10 equiv; addition of the solid under a positive flow of argon). The mixture is stirred at room temperature for 14 h, then the solvent is evaporated under reduced pressure and the desired endoxide is isolated either by quick chromatography in silica gel (for **21**, **23a**, **23b** and **23c**) or by centrifugation and repeated washing with different solvents (for **24**, **25a** and **25b**).

6,13-Dihydro-6,13-epoxybenzo[3,4]cyclobuta[1,2-*b*]benzo[3,4]cyclobuta[1,2-*i*]anthracene (21): Following the general procedure described above, compound **20** (40 mg, 0.18 mmol) and BPTZ (43 mg, 0.18 mmol) were reacted in CH_2Cl_2 (4.4 mL), and the resulting mixture was treated with triflate **19** (35 mg, 0.09 mmol) in CH_3CN (4.5 mL) and CsF (66 mg, 0.43 mmol). Filtration through a SiO_2 plug (CH_2Cl_2) afforded **21** as a pale yellow solid (23 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.67 (s, 4H), 6.66 – 6.62 (m, 4H), 6.49 – 6.45 (m, 4H), 5.70 (s, 2H). ^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 150.5 (C), 150.1 (C), 149.3 (C), 128.3 (CH), 116.5 (CH), 112.0 (CH), 83.0 (CH). HRMS (APCI-FIA-TOF) for $C_{26}H_{15}O$ ([M+H]$^+$) Calcd.: 343.1117; Found: 343.115. UV-Vis. (1,2,4-trichlorobenzene): λ_{max} = 355, 368, 388 nm.

7,12-Dihydro-7,12-epoxynaphtho[2',3':3,4]cyclobuta[1,2-*b*]anthracene (23a): Following the general procedure described above, 1,4-dihydro-1,4-epoxynaphthalene[37] (43 mg, 0.30 mmol) and BPTZ (71 mg, 0.30 mmol) were reacted in CH_2Cl_2 (2 mL), and the resulting mixture was treated with triflate **2** (50 mg, 0.12 mmol) in CH_3CN (2 mL) and CsF (182 mg, 1.2 mmol). Filtration through a SiO_2 plug (CH_2Cl_2) afforded **23a** as a white solid (28 mg, 73%). ^{1}H NMR (323K, 300 MHz, $CDCl_3$): δ = 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.23 – 7.17 (m, 2H), 7.07 – 7.01 (m, 2H), 6.95 (s, 2H), 6.76 (s, 2H), 5.93 (s, 2H). ^{13}C NMR-DEPT (323K, 75 MHz, $CDCl_3$): δ = 150.4(C), 149.3(C), 147.8(C), 146.1(C), 135.4(C), 128.7(CH), 126.3(CH), 120.4(CH), 114.3(CH), 113.3(CH), 82.9(CH). EM (EI$^+$), m/z (%): 318 ([M]$^+$, 100), 289 (92), 144 (48). HR-MS (IEA) for $C_{24}H_{14}O$ ([M]$^+$) Calcd.: 318.1045; Found: 318.1054.

9,10-Dibromo-7,12-dihydro-7,12-epoxynaphtho[2',3':3,4]cyclobuta[1,2-*b*]anthracene (23b): Following the general procedure described above, 6,7-dibromo-1,4-dihydro-1,4-epoxynaphthalene[38] (100 mg, 0.33 mmol) and BPTZ (79 mg, 0.33 mmol) were reacted in CH_2Cl_2 (8 mL), and the resulting mixture was treated with triflate **2** (75 mg, 0.18 mmol) in CH_3CN (8 mL) and CsF (81 mg, 0.53 mmol). Filtration through a SiO_2 plug (CH_2Cl_2) afforded **23b** as a green solid (36 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (s, 2H), 7.41 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.22 (dd, *J* = 5.9, 3.4 Hz, 2H), 6.95 (s, 2H), 6.81 (s, 2H), 5.90 (s, 2H). ^{13}C RMN-DEPT (75 MHz, $CDCl_3$): δ = 149.8 (C), 149.0(C), 148.9(C), 145.7(C), 135.3(C), 128.7(CH), 126.5(CH), 125.7(CH), 122.0(C), 114.8(CH), 113.4(CH), 82.3(CH). HR-MS (APCI-FIA-TOF) for $C_{24}H_{13}Br_2O$ ([M+H]$^+$) Calcd.: 474.9328; Found: 474.9325. UV-Vis (1,2,4-trichlorobenzene): λ_{max}, 363, 382, 404 nm.

2,3,4a,5,14,14a-Hexahydro-1H-5,14-epoxycyclopenta[*b*]naphtho[2',3':3,4]cyclobuta[1,2-*i*]anthracene (23c): Following the general procedure described above, 2,3,5,8-tetrahydro-1H-5,8-epoxycyclopenta[*b*]naphthalene,[39] (61 mg, 0.33 mmol) and BPTZ (79 mg, 0.33 mmol) were reacted in CH_2Cl_2 (8 mL), and the resulting mixture was treated with triflate **2** (75 mg, 0.18 mmol) in CH_3CN (8 mL) and CsF (81 mg, 0.53 mmol). Filtration through a SiO_2 plug (CH_2Cl_2) afforded **23c** as a yellow solid (30 mg, 46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.20 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.16 (s, 2H), 6.93 (s, 2H), 6.75 (s, 2H), 5.88 (s, 2H), 2.84 – 2.77 (m, 4H), 2.11 – 1.93 (m, 2H). ^{13}C NMR-DEPT (126 MHz, $CDCl_3$): δ = 151.16 2x(C), 150.98 2x(C), 149.32 2x(C), 146.43 2x(C), 142.43 2x(C), 135.58 2x(C), 128.85 2x(CH), 126.50 2x(CH), 117.28 2x(CH), 114.41 2x(CH), 113.41 2x(CH), 83.06 2x(CH), 32.98 2x(CH_2), 25.94(CH_2). HR-MS (APCI-FIA-TOF) for $C_{30}H_{16}O$ ([M]$^+$) Calcd.: 358.1352, Found: 358.1343.

6,15-Dihydro-6,15-epoxybenzo[3,4]cyclobuta[1,2-*b*]naphtho[2',3':3,4]-cyclobuta[1,2-*i*]anthracene (24): Following the general procedure described above, compound **20** (75 mg, 0.344 mmol) and BPTZ (80 mg, 0.344 mmol) were reacted in CH_2Cl_2 (8.5 mL), and the resulting mixture was treated with triflate **2** (50 mg, 0.12 mmol) in CH_3CN (8.5 mL) and CsF (90 mg, 0.59 mmol). The solid was collected by centrifugation, subjected to sonication-assisted washing with portions of CH_3CN (2x 2mL), H_2O (2 mL), CH_3OH (2 mL) and Et_2O (3 x 2 mL), and dried under vacuum to afford **24** as a pale yellow solid (30 mg, 65%). ^1H NMR (363K, 500 MHz, $C_2D_2Cl_4$): δ = 7.42 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.24 (dd, *J* = 6.0, 3.3 Hz, 2H), 6.96 (s, 2H), 6.81 (s, 2H), 6.74 (s, 2H), 6.69 (dd, *J* = 4.9, 2.8 Hz, 2H), 6.53 (dd, *J* = 4.8, 2.8 Hz, 2H), 5.76 (s, 2H). ^{13}C NMR-DEPT (363K, 126 MHz, $C_2D_2Cl_4$): δ = 151.0(C), 150.5(C), 150.3(C), 149.6(C), 149.3(C), 146.4(C), 135.7(C), 128.9(CH), 128.8(CH), 126.7(CH), 117.0(CH), 114.6(CH), 113.3(CH), 112.2(CH), 83.3(CH). HR-MS (APCI-FIA-TOF) for $C_{30}H_{16}O$ ($[M]^+$) Calcd.: 392.1196; Found: 392.1197. UV-Vis (1,2,4-trichlorobenzene): λ_{max} = 342, 364, 388, 409 nm.

7,16-Dihydro-7,16-epoxynaphtho[2',3':3,4]-cyclobuta[1,2-*b*]naphtho[2',3':3,4]cyclobuta[1,2-*i*]anthracene (25a): Following the general procedure described above, compound **8a** (32 mg, 0.12 mmol) and BPTZ (28 mg, 0.12 mmol) were reacted in CH_2Cl_2 (11 mL), and the resulting mixture was treated with triflate **2** (45 mg, 0.11 mmol) in CH_3CN (7 mL) and CsF (198 mg, 1.3 mmol). The solid was collected by centrifugation, subjected to sonication-assisted washing with portions of CH_3CN (2x 2mL), H_2O (2 mL), CH_3OH (2 mL) and Et_2O (3 x 2 mL), and dried under vacuum to afford **25a** as a pale yellow solid (25 mg, 50%).^1H NMR (363K, 500 MHz, $C_2D_2Cl_4$): δ = 7.35 (dd, J = 5.9, 3.3 Hz, 4H), 7.16 (dd, J = 6.0, 3.3 Hz, 4H), 6.91 (s, 4H), 6.74 (s, 4H), 5.76 (s, 2H). ^{13}C NMR-DEPT (363K, 126 MHz, $C_2D_2Cl_4$): δ = 150.2(C), 149.8(C), 146.3(C), 135.7(C), 128.9(CH), 126.7(CH), 114.7(CH), 113.4(CH), 83.3(CH). HR-MS (APCI-DIP-TOF) for $C_{34}H_{19}O$ ($[M+H]^+$) Calcd.: 443.1430; Found: 443.1427. UV-Vis ($CHCl_3$). λ_{max}: 286, 321, 388, 411 nm.

7,16-Dimethyl-7,16-dihydro-7,16-epoxynaphtho[2',3':3,4]cyclobuta[1,2-*b*]naphtho[2',3':3,4]cyclobuta[1,2-i]anthracene (25b): Following the general procedure described above, compound **8b** (25 mg, 0.08 mmol) and BPTZ (19 mg, 0.08 mmol) were reacted in CH_2Cl_2 (2.8 mL), and the resulting mixture was treated with triflate **2** (32 mg, 0.08 mmol) in CH_3CN (5 mL) and CsF (139 mg, 0.91 mmol). Flash chromatography (SiO_2, 1:3 hexane/CH_2Cl_2) afforded **25b** as a yellow solid (22 mg, 61%).^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 – 7.34 (m, 4H), 7.24 – 7.17 (m, 4H), 6.83 (s, 4H), 6.76 (s, 4H), 2.01 (s, 6H). δ = 153.1(C), 149.1(C), 146.1(C), 135.3 (C), 128.6(CH), 126.3(CH), 114.2(CH), 111.6(CH), 87.1(C), 14.0(CH_3). HR-MS (APCI-DIP-TOF) for $C_{36}H_{23}O$ ($[M+H]^+$) Calcd.: 471.1743; Found: 471.1741. UV-Vis ($CHCl_3$): λ_{max}, 285, 321, 387, 410 nm.

General procedure for the deoxygenative aromatization of endoxides 21, 23-25

Method A:[40] A solution of the oligoacene endoxide in a ^{i}PrOH/$CHCl_3$/HCl (37%) mixture is heated at 80 °C for 24 hours. Then, the reaction mixture is cooled to room temperature, washed with $NaHCO_3$ saturated solution, and extracted with $CHCl_3$. The combined organic layers are concentrated under reduced pressure, the solid is collected by centrifugation, subjected to sonication-assisted washing with CH_2Cl_2, CH_3OH and Et_2O, and dried under vacuum to afford the aromatized product.

Method B: A flame-dried flask is charged with NH_4ReO_4, $P(OPh)_3$ and dry toluene. After stirring for 20 min, the corresponding endoxide is added and the resulting mixture is stirred for 14 h. Then, the solvent is concentrated under reduced pressure, the solid is collected by centrifugation and subjected to sonication-assisted washing with portions of CH_2Cl_2, H_2O, CH_3OH, CH_2Cl_2, and dried under vacuum to afford the corresponding aromatic product.

Benzo[3,4]cyclobuta[1,2-*b*]benzo[3,4]cyclobuta[1,2-*i*]anthracene (22): Following method B described above, NH_4ReO_4 (2 mg, 0.007 mmol), $P(OPh)_3$ (28 mL, 0.1 mmol) and dry toluene (1 mL) were reacted with compound **21** (30 mg, 0.09 mmol) at 80 °C for 14 h. The isolated solid was washed with CH_2Cl_2 (1 x 2 mL), H_2O (2 mL) CH_3OH (2 mL) CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **22** as a yellow solid (20 mg, 70 %). HR-MS (APCI-FIA-TOF) for $C_{26}H_{15}$ ($[M+H]^+$) Calcd.: 327.1168; Found: 327.1170. UV-Vis (1,2,4-trichlorobenzene): l_{max} = 332, 342, 424, 451 nm.

Naphtho[2',3':3,4]cyclobuta[1,2-*b*]anthracene (26a): Following method B described above, NH_4ReO_4 (2.7 mg, 0.012 mmol), $P(OPh)_3$ (30 mL, 0.1 mmol) and dry toluene (4.7 mL) were reacted with compound **23a** (27 mg, 0.08 mmol) at reflux for 14 h. The isolated solid was washed with CH_2Cl_2 (1 x 2 mL), H_2O (2 mL) CH_3OH (2 mL) CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **26a** as a yellow solid (17.6 mg, 69 %). HR-MS (APCI-FIA-TOF) for $C_{24}H_{14}$ ($[M^+]$) Calcd.: 302.1090; Found: 302.1085. UV-Vis (1,2,4-trichlorobenzene): λ_{max}: 312, 327, 407, 433 nm.

9,10-Dibromonaphtho[2',3':3,4]cyclobuta[1,2-*b*]anthracene (26b): Following method B described above, NH_4ReO_4 (2 mg, 0.007 mmol), $P(OPh)_3$ (20 mL, 0.08 mmol) and dry toluene (3 mL) were reacted with compound **23b** (30 mg, 0.06 mmol) at 80 °C for 14 h. The isolated solid was washed with CH_2Cl_2 (1 x 2 mL), H_2O (2 mL) CH_3OH (2 mL) CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **26b** as a greenish yellow solid (24 mg, 80 %). HR-MS (APCI-DIP-TOF) for $C_{24}H_{12}Br_2$ ($[M+H]^+$) Calcd.: 457.9300; Found: 457.9298. UV-Vis (1,2,4-trichlorobenzene): λ_{max} = 322, 334, 345, 387, 414, 440 nm.

2,3-Dihydro-1H-cyclopenta[b]naphtho[2',3':3,4]cyclobuta[1,2-i]anthracene (26c): Following method B described above, NH_4ReO_4 (4.5 mg, 0.017 mmol), $P(OPh)_3$ (30 mL, 0.109 mmol) and dry toluene (4.2 mL) were reacted with compound **23c** (30 mg, 0.084 mmol) at reflux for 14 h. The isolated solid was washed with CH_2Cl_2 (1 x 2 mL), H_2O (2 mL) CH_3OH (2 mL) CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **26c** as a greenish solid (23 mg, 80 %). ^1H NMR (750 MHz, $C_2D_2Cl_4$): δ = 8.00 (s, 2H), 7.68 (s, 2H), 7.66 – 7.65 (dd, J = 6.0, 3.2 Hz, 2H), 7.39 (s, 2H), 7.38 (s, 2H), 7.35 (dd, *J* = 6.0, 3.2 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 4H), 2.17 (q, *J* = 7.3 Hz, 2H). HR-MS (APCI-DIP-TOF) for $C_{27}H_{18}$ ($[M]^+$) Calcd.: 342.1345; Found: 342.1403. UV-Vis ($CHCl_3$): λ_{max} = 371, 385, 411, 436 nm.

Benzo[3,4]cyclobuta[1,2-*b*]naphtho[2',3':3,4]cyclobuta[1,2-*i*]anthracene (27): Following method B described above (see section 1.2.13), NH_4ReO_4 (3 mg, 0.01 mmol), $P(OPh)_3$ (22 mL, 0.08 mmol) and dry toluene (3.4 mL) were reacted with compound **24** (27 mg, 0.07 mmol) at reflux for 14 h. The isolated solid was washed with CH_2Cl_2 (1 x 2 mL), H_2O (2 mL), CH_3OH (2 mL), CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **27** as a pale green solid (21 mg, 80%). HR-MS (APCI-DIP-TOF) for $C_{30}H_{16}$ ($[M]^+$) Calcd.: 376.1247; Found: 376.1251. UV-Vis (CH_2Cl_2): λ_{max} = 337, 348, 432, 458 nm.

Naphtho[2',3':3,4]cyclobuta[1,2-*b*]naphtho[2',3':3,4]cyclobuta[1,2-*i*]anthracene (28a): Following method B described above, NH_4ReO_4 (3 mg, 0.01 mmol), $P(OPh)_3$ (21 mL, 0.08 mmol) and dry toluene (4 mL) were reacted with compound **25a** (30 mg, 0.07 mmol) at reflux for 14 h. The isolated solid was washed with CH_2Cl_2 (1 x 2 mL), H_2O (2 mL), CH_3OH (2 mL), CH_2Cl_2 (2 x 2 mL), and dried under vacuum to afford **28a** as a yellow solid (21 mg, 70%). HR-MS (APCI-DIP-TOF) for $C_{34}H_{18}$ ($[M]^+$) Calcd.: 426.1403; Found: 426.1400.

7,16-Dimethylnaphtho[2',3':3,4]cyclobuta[1,2-*b*]naphtho[2',3':3,4]cyclobuta-[1,2-*i*]anthracene (28b): Following method A described above, a solution of compound **25b** (11 mg, 0.023 mmol) in ^{i}PrOH (0.7 mL), $CHCl_3$ (0.25 mL) and 37% aq. HCl (0.05 mL) was stirred at 80 °C for 12 h, then treated with satd. aq. $NaHCO_3$ (2 mL), and extracted with $CHCl_3$ (3 x 5 mL). The isolated solid, collected after concentration under reduced pressure and centrifugation, was washed with CH_2Cl_2 (1 x 2 mL), CH_3OH (2 mL), Et_2O (2 mL), and dried under vacuum to afford **28b** as an orange solid (8 mg, 76%). HR-MS (APCI-DIP-TOF) for $C_{33}H_{22}$ ($[M]^+$) Calcd.: 454.1716; Found: 454.1709. UV-Vis (1,2,4-trichlorobenzene): λ_{max} = 360, 459, 479 nm. Attempts to record a ^{1}H-NMR spectrum at 100 ^{0}C, led to decomposition.

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[40] Method A was attempted for the aromatization of **23-25**, but only worked satisfactorily for the dimethylated compound **25b**