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Vicinally Diiodinated PAHs

Selective Vicinal Diiodination of Polycyclic Aromatic Hydrocarbons

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Abstract: Vicinally diiodinated polycyclic aromatic hydrocarbons (I_2-PAHs) are accessible from the corresponding diborylated B_2-PAHs through boron/iodine exchange. The B_2-PAHs have been prepared via twofold electrophilic borylation reactions templated by a vicinally disilylated benzene. Our protocol is applicable to fluorenes, acenes, annulated acenes, oligoaryls, and even [5]helicene. Using B_2-naphthalene as the example, we have shown that the reaction scope can, in principle, be expanded to include the synthesis of vicinally dibrominated and dihydroxylated PAHs. The usefulness of the building blocks provided by our method in the field of optoelectronic materials was demonstrated by the successful conversion of I_2-fluoranthene to the analogous doubly alkynylated fluoranthene emitter.

The importance of aryl halides as building blocks in organic synthesis can hardly be overestimated. Particularly valuable are vicinally dihalogenated derivatives, which offer the possibility of annulating an additional ring onto the pre-existing arene scaffold. While simple *ortho*-dihalogenated benzenes are in large supply, already the next higher 2,3-dihalonaphthalenes require tedious syntheses. As an example, three different access routes to 2,3-dibromonaphthalene (**1^{Br}**) have been elaborated and optimized, but each of them still has its shortcomings in terms of atom economy, reaction times and temperatures, or yields (Scheme 1, top):[1] (1) Naphthalene is protected on one of its rings through Diels-Alder reactions with 2 equiv. of hexachlorocyclopentadiene (HCCPD). Subsequent bromination occurs selectively in the β positions of the diadduct **A**, and a thermally induced retro-cycloaddition reaction finally liberates the target compound together with the environmentally malignant HCCPD (overall yield of **1^{Br}**: 20 %).[2–4] (2) *ortho*-Phthalaldehyde is converted to 2,3-dibromonaphthalene through the assembly of a second benzene ring by following a sequence of Corey–Fuchs, HBr elimination (cf. **B**), and Bergman cyclization reactions (overall yield: 30 %).[5] (3) Monolithiation of 1,2,4,5-tetrabromobenzene in the presence of excess furan gives the corresponding dibromoepoxynaphthalene **C** via a benzyne intermediate. Reduction of **C** using Zn/$TiCl_4$ furnishes the desired **1^{Br}** (overall yield: 62 %[6]).[6–10] In our hands, the benzyne route (3) turned out to be the most efficient one, if 2,3-dibromonaphthalene is to be synthesized from scratch. With environmental concerns set aside, the main bottleneck of route (1) is the synthesis of the protected naphthalene **A**, because it forms only at high temperatures and in equilibrium with its constituents.[2,3] **A** has meanwhile been commercialized so that this problem is remedied, which underscores the considerable demand for **1^{Br}** in the chemical community.[11]

This demand results from the numerous applications of 2,3-dibromonaphthalene as a synthetic building block across fields as varied as pharmaceuticals[12] and organic optoelectronic materials: (1) *Introduction of new (cooperating) substituents* in the naphthalene scaffold, such as Lewis basic –OR/SR groups or electropositive $-SiMe_3$/$SnMe_3$ moieties.[6,13,14] (2) *Consecutive C–C- or C–N-coupling reactions* to immediately generate oligonaphthylenes or π-expanded (hetero)arenes.[9,10,13,15–17] (3) *Mono- or dialkynylations* with subsequent cyclization reactions to furnish naphthopentalenes as well as naphthannulated (hetero)aromatics.[8,18,19] (4) *Br_2 elimination to liberate 2,3-naphthalyne*,[11,13,20] followed by [4+2]-cycloadditions to prepare polycyclic aromatic hydrocarbons (PAHs) and triptycenes.[7,11,21–24] It is to be emphasized at this point that 2,3-dibromonaphthalene not only provides rare access to 2,3-naphthalyne (via Br_2 elimination), but also to 3-bromo-1,2-naphthalyne (via HBr elimination). The respective trapping products still contain one Br atom at the naphthalene fragment, which can be employed for further transformations or renders the product itself a potential aryne precursor.[21,22]

Given the remarkably diverse uses even of the moderately large naphthalene system **1^{Br}**, it is desirable to be able to employ also larger vicinally dibrominated PAHs. In 2019, two optimized protocols for the synthesis of 2,3-dibromoanthracene (**2^{Br}**; Scheme 1, middle) have been disclosed: Bettinger's five-

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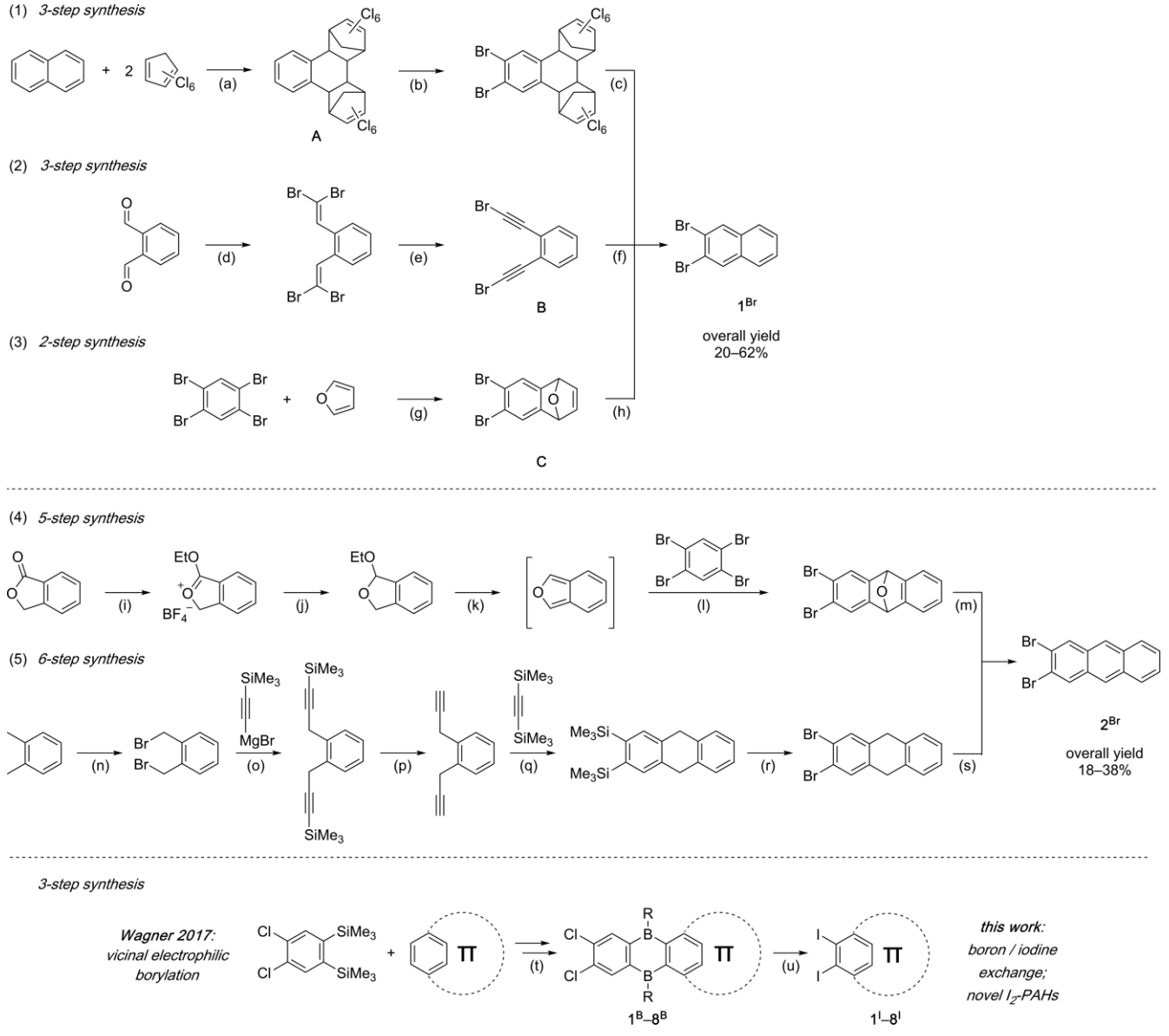

Scheme 1. Syntheses of 2,3-dibromonaphthalene **1^{Br}**, 2,3-dibromoanthracene **2^{Br}**, and the diiodinated PAHs presented herein. Reagents and conditions for **1^{Br}** and **2^{Br}**. (a) 160 °C, 120 h. (b) Br_2, Fe, tetrachloroethane, reflux, 3 h. (c) Continuous high-vacuum distillation, 220 °C. (d) CBr_4, PPh_3, CH_2Cl_2, 0 °C, 2 h. (e) KO*t*Bu, H_2O, THF, –78 °C, 5 min. (f) γ-Terpinene, *o*-dichlorobenzene, 180 °C, 2 h. (g) *n*BuLi, toluene, –25 °C, 3 h to r.t., 12 h. [h] Zn/$TiCl_4$, THF, reflux, 18 h. (i) $[Et_3O]BF_4$, 1,2-dichloroethane, r.t., 72 h. (j) $LiAlH_4$, EtOH, THF, r.t., 2 h. (k) MeLi, cat. *i*Pr_2NH, Et_2O, r.t., 3 h. (l) MeLi, Et_2O, reflux, 17 h. (m) Zn/$TiCl_4$, THF, 0 °C to reflux, 17 h. (n) NBS, CH_3CN, irradiation by a spotlight (500 W), 2 h. (o) CuI, THF, reflux, 14 h. (p) $AgNO_3$, NaCN, H_2O, EtOH, r.t., 30 min. (q) $[CoCp(CO)_2]$, irradiation by a spotlight (500 W), 5 h. (r) NBS, CH_3CN, r.t., 16 h. (s) DDQ, toluene, reflux, 4 h. Reagents and conditions for **1^{B}**–**8^{B}** (R = Br, OH, or Mes) and **1^{I}**–**8^{I}**. (t) 1) BBr_3, *n*-hexane, sealed ampoule, 120 °C, 2.5 d (R = Br). For R = Mes: 2) MesMgBr in THF, toluene, 0 °C to r.t., 17 h. For R = OH: 2) H_2O, toluene, 0 °C to r.t., 17 h. (u) I_2, K_2CO_3, CH_3CN, 80 °C, 17 h. Best results were achieved with R = Mes; the by-products 2-iodomesitylene and 1,2-dichloro-4,5-diiodobenzene can be recycled.

step approach starts from readily available phthalide to generate an isobenzofuran intermediate and is therefore reminiscent of the benzyne route (3) to **1^{Br}** (overall yield of **2^{Br}**: 18 %).[25] The synthesis put forward by Bunz and co-workers involves a Vollhardt cyclization of bis(propargyl)benzene with bis(trimethylsilyl)acetylene, followed by bromodesilylation and oxidation (yield over 6 steps from 1,2-dimethylbenzene: 38 %).[26] The general application fields of **2^{Br}** are very similar to those outlined above for its naphthalene congener **1^{Br}**.[15,16,18,23,27]

Our group now reports the first versatile strategy that is general enough to prepare a large variety of vicinally dihalogenated PAHs by applying always the same reaction sequence (Scheme 1, bottom). We are exploiting our previous observation that a broad palette of PAHs undergoes vicinal electrophilic diborylation upon treatment with 4,5-dichloro-1,2-bis(trimethylsilyl)benzene and BBr_3 (Scheme 1, bottom).[28] The resulting B_2-PAHs **1^{B}**–**8^{B}** can afterwards be converted into the aimed-for I_2-PAH products **1^{I}**–**8^{I}** via straightforward boron/iodine exchange ("H.C. Brown chemistry"; Figure 1).[29]

The regioselectivity of the dihalogenation process is governed by three factors: (1) The vicinally disilylated benzene precursor leads to a corresponding vicinally diborylated intermedi-

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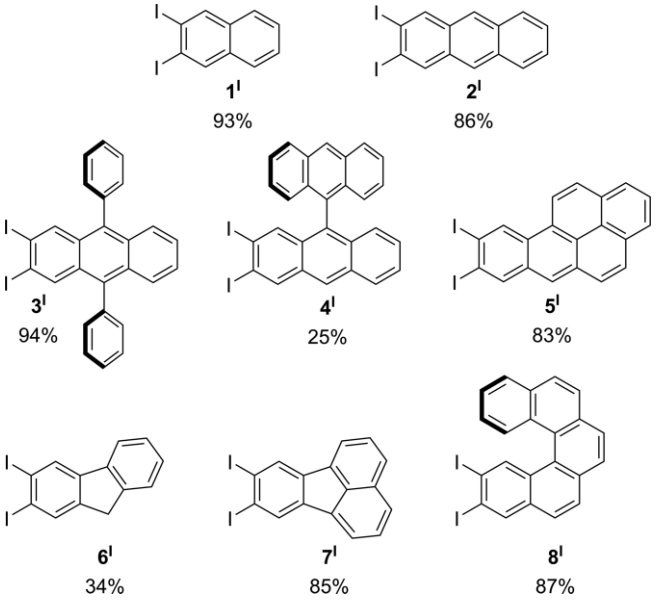


Figure 1. Diiodinated PAHs **1^{I}**–**8^{I}** obtained via the synthesis protocol shown in Scheme 1 (bottom). Yields are given relative to the respective B_2-PAH precursor.

ate, which imprints its substitution pattern onto the PAH in the process of assembling a strain-free, six-membered B_2C_4 ring. (2) For steric reasons, the preferred sites of attack on each PAH have H atoms in neighboring positions. (3) No substituent scrambling occurs during boron/halogen exchange. These factors, together with the nodal structure of the PAH's HOMO,[28] provide a set of reliable selection rules to predict which types of vicinally dihalogenated PAHs are accessible by our method. As a proof-of-principle, the precursor borane **1^{BOH}** (R = OH) has been transformed both to 2,3-dibromo- and 2,3-diiodonaphthalene (see below and the Supporting Information). In all other cases, only the vicinally diiodinated PAHs have been prepared, because C–I bonds tend to be more reactive than C–Br bonds in subsequent halogen/metal exchanges,[30] Pd-catalyzed cross-couplings,[31] and radical reactions.[32] As an additional advantage, the higher molecular mass of the aryl iodides reduces weighing errors when working with small quantities. Compared to electrophilic aromatic chlorination or bromination, iodination reactions are less efficiently catalyzed by conventional Lewis acids (an exception being $CuCl_2$)[33] and therefore often require the addition of strong oxidants,[34] which limits the functional group tolerance. Given that the boron/halogen exchange is equally facile for X = Cl, Br, and I, the detour via our double electrophilic borylation reaction appears particularly justified for synthesizing the otherwise harder-to-get iodo derivatives.[35]

The transformations of the B_2-PAHs **1^{BMes}**–**8^{BMes}** (R = Mes) to the I_2-PAHs **1^{I}**–**8^{I}** were achieved by heating a mixture of the respective aryl borane, excess I_2, and K_2CO_3 in CH_3CN to 80 °C for 17 h.[36] The corresponding aryl iodides were isolated in yields of 25–94 % after (flash) column chromatography. The following points are noteworthy: (1) In most cases, a much shorter reaction time should be sufficient. We opted for "17 h" with the sole reason to guarantee full conversion especially in those cases were more valuable PAHs are to be diiodinated.[37] The current protocol can conveniently be carried out overnight and by working in simple septum-capped microwave vials. (2) Due to the weak electrophilicity of I_2, overiodination as a possible consequence of longer reaction times was never an issue. In contrast, the corresponding boron/bromine exchange on **1^{BOH}** (R = OH) tends to furnish the desired 2,3-dibromonaphthalene contaminated with triply brominated side products (see the Supporting Information for more details). (3) We initially assumed that it would be most practical to quench the primary bromoborane products **1^{BBr}**–**8^{BBr}** (R = Br) with H_2O and perform the boron/halogen exchange on the borinic acids **1^{BOH}**–**8^{BOH}**. However, already the borinic acid **2^{BOH}** was so poorly soluble that the crude lump always enclosed some unreacted anthracene, which was impossible to separate from the 2,3-diiodoanthracene target product by chromatographic workup. The problem was solved through the introduction of solubilizing mesityl substituents to generate **1^{BMes}**–**8^{BMes}**. The steric demand of the Mes groups had no negative impact on the subsequent iodination step and a stock solution of the Grignard reagent required for their introduction is stable enough to be stored for months under an inert atmosphere. (4) In addition to the aimed-for I_2-PAHs, chromatographic workup also furnishes 1,2-dichloro-4,5-diiodobenzene and 2-iodomesitylene in yields of > 90 % and sufficient purity to be recycled for the synthesis of 4,5-dichloro-1,2-bis(trimethylsilyl)benzene and MesMgI. Our diiodination protocol is thus considerably more atom economic than it seems at first glance.

The ^{1}H NMR spectra of **1^{I}**–**8^{I}** show one (or two, depending on the symmetry) characteristic singlets assignable to the protons occupying the positions adjacent to the iodination sites. Cross peaks with one (or two) ^{13}C resonances in the typical shift range of iodinated aryl-C atoms (102.6–105.9 ppm) have been detected in all cases in the HMBC experiments. The remaining ^{1}H/^{13}C signal patterns of **1^{I}**–**8^{I}** are similar to those of the respective pristine PAHs.

X-ray crystal structure determinations were carried out for all products except the known compounds **1^{I}** and **2^{I}** (see Figure 2 and the Supporting Information).[26,38,39] Key structural features will exemplarily be discussed for the diiodo[5]helicene **8^{I}** and compared to those of its diborylated precursor **8^{BMes}**. Compound **8^{I}** crystallizes with four crystallographically independent molecules in the asymmetric unit (**8$^{I}_{A}$**–**8$^{I}_{D}$**). The individual I–C bond lengths of **8$^{I}_{A}$**–**8$^{I}_{D}$** are the same within the experimental error margins (av. 2.10 Å). The intramolecular I···I distances vary only slightly between 3.674(4) and 3.692(4) Å and are thus 0.6 Å smaller than the double van der Waals radius of iodine (4.30 Å[40,41]). A somewhat crowded situation within the I–C–C–I fragment is also indicated by the associated torsion angles of –7(4)° to 13(5)° and the moderately expanded internal I–C–C bond angle of av. 123.1°. We take the shortest distance between the best plane through the heteroatom-substituted benzene ring and the centroid of the C–C bond at the opposite end of the respective [5]helicene as the helix pitch. For **8$^{I}_{A}$**–**8$^{I}_{D}$**, values of 2.86, 3.06, 3.15, and 3.15 Å have been determined, which attest to a certain sensitivity of this parameter to even subtle packing effects. The average value of 3.06 Å, however, is almost identical to that of the pristine [5]helicene (2.90 Å) and

also the B_2-substituted $\mathbf{8}^{\mathbf{BMes}}$ (2.96 Å; own structure determinations, see the Supporting Information). We therefore conclude that possible steric interactions with the neighboring bulky mesityl substituent do not increase the helix pitch.

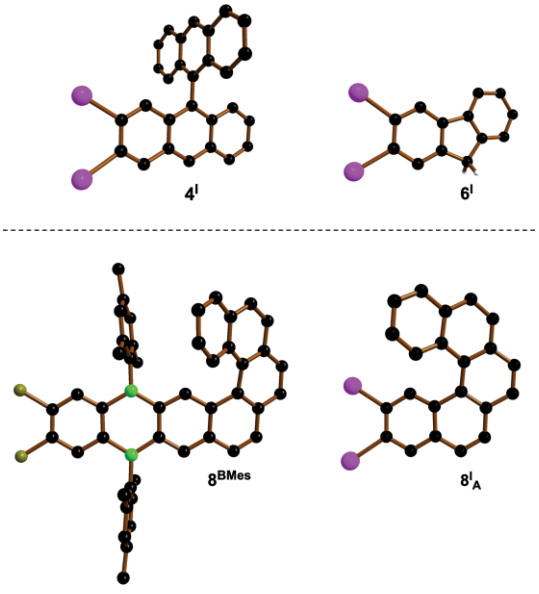
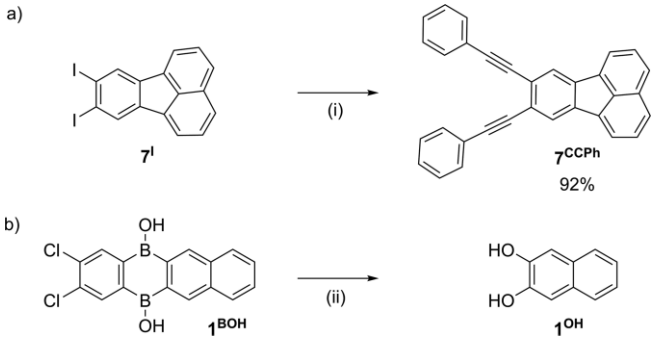


Figure 2. Molecular structures of $\mathbf{4}^{\mathbf{I}}$, $\mathbf{6}^{\mathbf{I}}$, $\mathbf{8}^{\mathbf{BMes}}$, and $\mathbf{8}^{\mathbf{I}}_{\mathbf{A}}$ in the solid state (B: bright green, Cl: olive-green, I: magenta).[42] H atoms, except those of the CH_2 group of $\mathbf{6}^{\mathbf{I}}$, are omitted for clarity. Selected averaged I–C bond lengths [Å]: $\mathbf{4}^{\mathbf{I}}$: 2.104, $\mathbf{6}^{\mathbf{I}}$: 2.093, $\mathbf{8}^{\mathbf{I}}_{\mathbf{A}}$: 2.09.

As a representative follow-up reaction, we conducted the double Sonogashira alkynylation of $\mathbf{7}^{\mathbf{I}}$, which proceeded with yields of 92 % to afford $\mathbf{7}^{\mathbf{CCPh}}$ (Scheme 2a), a versatile precursor for further annulations (see the related examples mentioned above).



Scheme 2. Syntheses of $\mathbf{7}^{\mathbf{CCPh}}$ and $\mathbf{1}^{\mathbf{OH}}$. Reagents and conditions. (i) 3.5 equiv. phenylacetylene, 16 mol-% CuI, 6 mol-% $Pd(PPh_3)_2Cl_2$, THF/iPr_2NH (4:1), 90 °C, 5 h. (ii) 4 equiv. *m*-CPBA, H_2O/EtOH (1:2), 0 °C to r.t., 6 h, quantitative conversion.

We finally demonstrated that the scope of our B_2-PAHs goes beyond the synthesis of aryl halides and reaches out to vicinally dihydroxylated PAHs: upon treatment with *m*-chloroperbenzoic acid (*m*-CPBA), $\mathbf{1}^{\mathbf{BOH}}$ is readily transformed to 2,3-dihydroxynaphthalene $\mathbf{1}^{\mathbf{OH}}$ (Scheme 2b).[43] Compounds of this kind have been used by Bunz and co-workers for the preparation of N-heteroacenes.[15]

Based on a boron/iodine exchange protocol, we devise a universal method for the vicinal diiodination of PAHs. A set of selection rules to predict the specific iodination sites is provided. Remarkably, these sites differ from the positions that are commonly attacked by halogens, i.e., the 1-positions of naphthalenes, the 9,10-positions of anthracenes, the localized double bonds of phenanthrene substructures, and the benzylic hydrogen atoms of fluorenes.[44] Except I_2-naphthalene ($\mathbf{1}^{\mathbf{I}}$) and I_2-anthracene ($\mathbf{2}^{\mathbf{I}}$), none of the I_2-PAHs presented herein have so far been accessible. Owing to this lack of alternatives, the moderate yields obtained in the borylation steps seem an affordable price to pay for obtaining synthetic building blocks as useful as $\mathbf{1}^{\mathbf{I}}$–$\mathbf{8}^{\mathbf{I}}$.

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Keywords: Halogenation · Iodine · Polycyclic aromatic hydrocarbons · Synthetic methods

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