Synthetic, physical and computational chemistry of propeller-shaped polycyclic aromatic hydrocarbons

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Chapter 2

Synthesis of a Pyrene-based π-extended Triple Helicene

Abstract

The synthesis of large polycyclic aromatic hydrocarbons is a challenging endeavour. On the one hand, it can be difficult to install functional groups on the required positions, and on the other hand, the poor solubility of compounds presents an important bottleneck. This Chapter shows the synthesis of the large, pyrene-based propellerene tripyrenylene, using chemical conversions that circumvent these issues. The synthesis starts with pyrene, which is converted to 4-hydroxypyrene using a ring-contraction/ring-expansion sequence, using optimized purification procedures, which allows access to this material on a gram scale. Then, after conversion to an *ortho*-TMS triflate, using a palladium catalysed aryne trimerization, the desired propellerene is made by stitching three pyrene molecules together in one step. The methodology outlined in this Chapter allows future access to other, large PAHs with trifold symmetry.

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van der Ham A., Brouwer A. M., Filippov D. V., Overkleeft H. S., Schneider G. F. Positional effect of π-Extension in Triple Helicenes. **Manuscript in preparation.**

Helicenes, by virtue of their non-planar structure, show interesting physicochemical properties, which has prompted their application in, *e.g.*, chirality sensing,[1-3] asymmetric catalysts,[4-6] and chiro-optical materials. Their implementation is, however, hampered due to their poor photo-stability and low racemization barriers.[7,8] Recent years have therefore seen a shift towards the synthesis of molecules that incorporate helicene motifs, but do not suffer from these shortcomings, primarily by making the molecules more rigid. Approaches to this end include the introduction of heteroatomic functionalities, as well as the fusion of additional benzene rings into so-called π-extended helicenes,[9-13] and the merger of multiple helicene motifs into a single molecule, yielding double,[14-21] triple,[22,23] and even quadruple helicenes (Fig. 2.1).[24] Of these, the triple helicenes, for which the term propellerenes was coined in the previous Chapter, are of particular interest, with hexabenzotriphenylene (HBT; Fig. 2.1), *i.e.*, showing the highest dichroism dissymmetry factor of all known helicenes and helicinoids.[25]

Evidently, the photo-optical properties of aromatic molecules are driven by the size of the conjugated system, and the relationship between these two provides an important guiding principle for the rational design of photo-optical materials.[26-28] The relationship between the size of conjugated systems and photo-optical properties were already investigated by Woodward and Fieser halfway through the last century,[29,30] and have more recently been documented for monohelicenes[31,32] and multiple helicenes.[33] Nonetheless, a systematic study on the effect of π-extension on the properties of helicenes *vis-à-vis* propellerenes appears absent in the literature. Intrigued by the work of Hosokawa *et al.* who synthesized a π-extended hexapole [5]helicene (Fig. 2.1), tripyrenylene **1** was chosen as target molecule, not only to study the effect of π-extension on the properties of propellerenes, but also to investigate whether or not the position of the π-extension is of importance on the photo-optical properties.
This Chapter describes all the work that went into the synthesis of tripyrenylene **1**, the conformational and spectroscopic properties of which will be studied in the following Chapter.

Synthesis outline. Tripyrenylene **1**, is a triphenylene-class propellerene. By far the most popular approach nowadays to synthesize molecules of this class is the palladium(0) catalyzed trimerization of arynes (Scheme 2.1A).[34,35] Given the reactive nature of arynes they have to be generated *in situ*, which can be achieved in an elegant way by treating *ortho*-TMS triflates with a fluoride source, typically CsF or TBAF. The driving forces of this reaction are the formation of a strong Si–F bond, and the cleavage of a triflate group. Although synthesis of the required precursors can be lengthy, this is more than offset by mild reaction conditions, large functional group tolerance, and generally high yields obtainable, all explaining the popularity of this reaction. Indeed, this strategy allows access to structures not attainable *via* any other route. Scheme 2.1B gives a retro-synthetic analysis for the synthesis of tripyrenylene **1**. In short, synthesis of **1** requires *ortho*-TMS triflate precursor **9**, which in turn was to be obtained from 4-hydroxypyrene **4**.

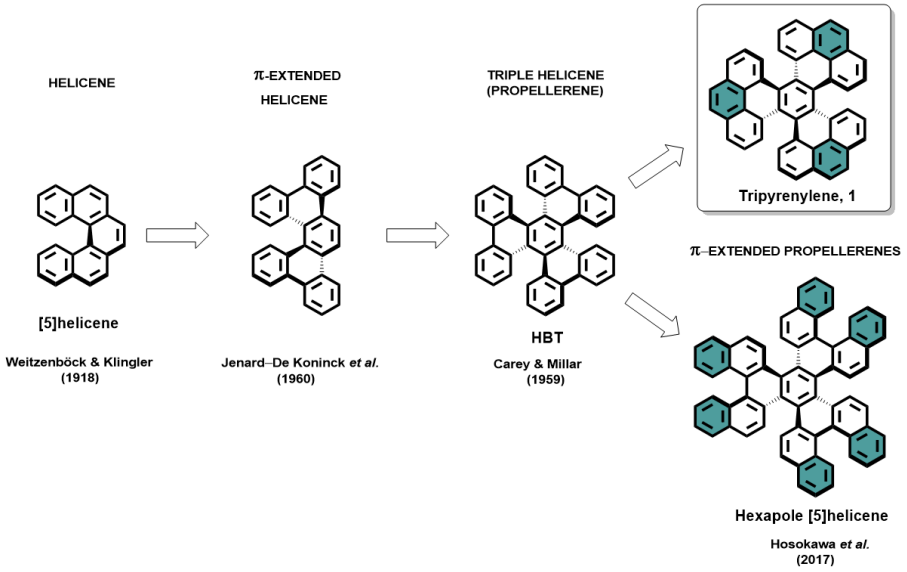
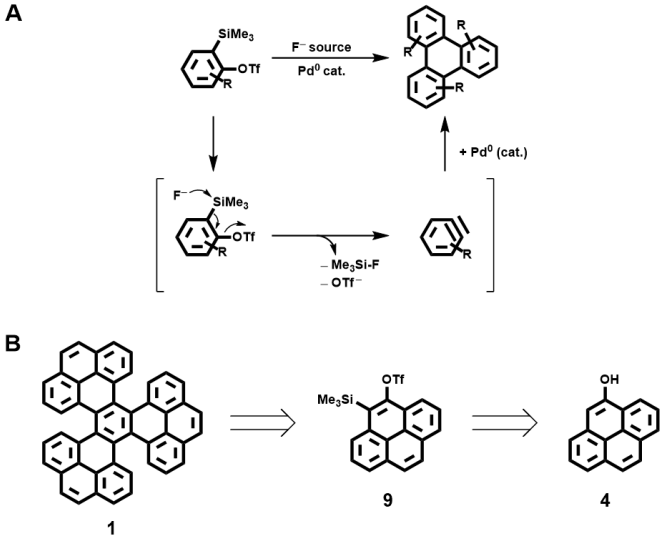
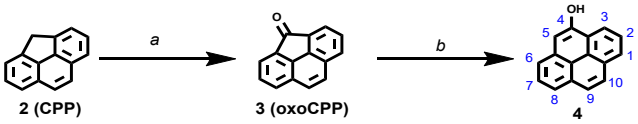


Figure 2.1 Schematic representation of the π-extension of a helicene structure. Names and dates given are related to the first identification of the compound.



Scheme 2.1 (A) General scheme for the palladium(0) catalyzed trimerization of arynes to yield PAHs with a trifold symmetry. A more detailed description is given in Chapter 3. (B) Retro-synthetic analysis for the synthesis of tripyrenylene **1**.

*Synthesis of 4-hydroxypyrene **4***. Synthesis of the required 4-hydroxypyrene **4** was found to be more challenging than expected. Selective derivatization of pyrene on the C-4 position poses a serious synthetic challenge, due to the nature of the molecule, which precludes direct oxidation protocols (For numbering see Scheme 2.2). Electrophilic and radical substitution on pyrene occurs almost exclusively at C-1, after which further derivatization takes place on C-6 or C-8. Exceptions to this rule are the Friedel-Crafts alkylation with tert-butyl chloride, which gives substitution at C-2 followed by C-7 due to steric factors.[36] The only transformations known to date to achieve direct C-4 functionalization are methylation using methyllithium under UV irradiation,[37] and the palladium catalyzed arylation using arylboroxines.[38] Interestingly, a picolinamide directing strategy showed the possibility for selective formation of a C–C bound on the C-4 position of pyrene.[39] Unfortunately, none of these routes are amendable for the introduction of an hydroxyl group at C-4. The most common way of introducing substituents on C-4 is by first reducing pyrene to 1,2,3,6,7,8-hexahydropyrene with sodium metal in refluxing amyl alcohol, followed by substitution and back oxidation with DDQ; an approach developed by Vollmann in the 1930's.[40] A multistep approach to get **4** *via* this route was recently reported and involves the initial introduction of bromine on the desired position, followed by substitution with methoxide and demethylation.[41] Although this, and other procedures,[42-46] yield 4-hydroxypyrene, they all suffer from a large number of steps and unsatisfactory overall yields, making them unattractive for the envisioned large scale synthesis of propellerene **1**. Fortuitously, it was found possible to obtain 4-hydroxypyrene **4** in 50% yield from 4*H*-4-oxocyclopenta[*d,e,f*]phenanthrene (oxoCPP, **3**) by treating it with TMS-azidomethane to affect a Tiffeneau-Demjanov-like rearrangement.[47] The required oxoCPP **3** could be synthesized in 70% yield from CPP **2** by careful oxidation with *t*BuOOH in the presence of a catalytic amount of CrO_3 (Scheme 2.2).[48]

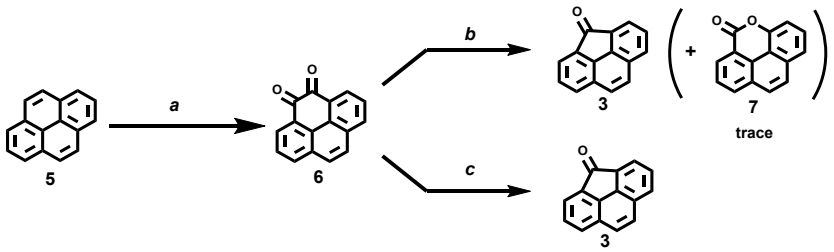


2 (CPP) 3 (oxoCPP) 4

Scheme 2.2 Synthesis of 4-hydroxypyrene **4** from CPP **2**. *Reagents and conditions*: a) *t*BuOOH, CrO_3 (cat.), DCM:H_2O, 70%; b) $TMSCHN_2$, $BF_3{\cdot}Et_2O$, DCM, -78°C → rt, 50%.

Despite the successfulness of this sequence, commercial samples of CPP **2** are relatively expensive, currently on the order of €400 / gram, precluding large-scale synthesis *via* this route. A search through literature shows that, ever since the first extraction of **2** by Kruber from anthracene oil in 1934,[49] much effort has been put into its synthesis, all starting from different parent PAH structures (SI Scheme S2.1).[40,50-57] Unfortunately, all of these are either lengthy, poor yielding, or require the use of hazardous chemicals, making them unamendable for large-scale synthesis.[50-52] A more efficient synthesis route was therefore desired to obtain oxoCPP **3**. This was found possible using a two-step procedure starting from pyrene **5** yielding the desired **4** in 15% overall yield (Scheme 2.3).

*Synthesis of oxoCPP **3***. The first step in the synthesis of oxoCPP **3** was the oxidation of pyrene **5** to the 4,5-dione **6** using a $NaIO_4/RuCl_3$ system. The oxidation of pyrene using this system has been reported several times, including a detailed description of the procedure on a 15 gram scale by Walsh *et al.*[58] One of the drawbacks associated with this reaction is the formation of an intractable residue which is difficult to filter off, seriously hampering the work-up. It was found, however, that by careful addition of the $NaIO_4$ oxidant as an aqueous solution, rather than as a solid, to a solution of **5** and $RuCl_3$ in DCM:THF, and stopping the addition when heating up of the reaction becomes noticeable by touch, a much finer residue is obtained. This residue can then be filtered off using a standard glass fritted filter, significantly expediting the work-up procedure, without negatively affecting the yield (~50%). The product can be purified by column chromatography over silica gel using neat DCM as eluent, which can be recovered and reused to reduce the total amount of solvent needed (Scheme 2.4 and Fig. 2.3A). The next crucial step in the synthesis is then the direct conversion of **6** to mono-ketone **3**.



Scheme 2.3 Synthesis of oxoCPP. *Reagents and conditions*: a) $NaIO_4$, $RuCl_3$, DCM:MeCN:H_2O, rt, 3 hrs (50%); b) PbO, 245 - 260°C, vac., 3 hrs., 4 - 8%; c) 1M NaOH, reflux, 3 d., 30%.

This conversion was initially tried by pyrolysis of **6** at 245 – 260 °C in an evacuated tube in the presence of lead(II) oxide (Scheme 2.3), a procedure described in 1949 by James W. Cook.[59] This resulted in the fractional sublimation of starting material and the desired product as a yellow crystalline sublimate (Fig. 2.2). The latter could, however, only be obtained in poor yields (2 – 8%). When performed on a larger scale, trace amounts of phenanthrene-4,5-lactone **7** were also obtained, whose identity was confirmed by comparison with an authentic sample, prepared by a classic Baeyer–Villiger oxidation of oxoCPP (See Experimental). It was attempted to extant the lead(II) oxide pyrolysis to other substrates, but this ultimately proved unsuccessful (Scheme S2.3). As a final attempt, the benzilic acid rearrangement of **6** was tried, as originally described by the aforementioned Anschütz and Japp in 1878 (Scheme 2.3).[60] Boiling of a suspension of **6** in an aqueous 1M NaOH solution for three days yielded the desired compound **4** in 30% yield as a bright yellow sublimate on the walls of the reaction flask, as well as in the air-cooled condenser fitted to it (Fig. 2.3B and 2.3C). Boiling for a longer period of time did not produce any more material, nor did use of a more concentrated (10M) NaOH solution (10% yield).

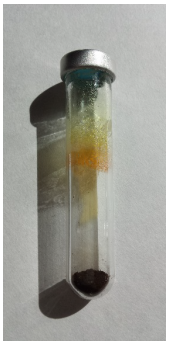


Figure 2.2 Vacuum tube showing fractional sublimation of **3** (yellow) and **6** (orange).

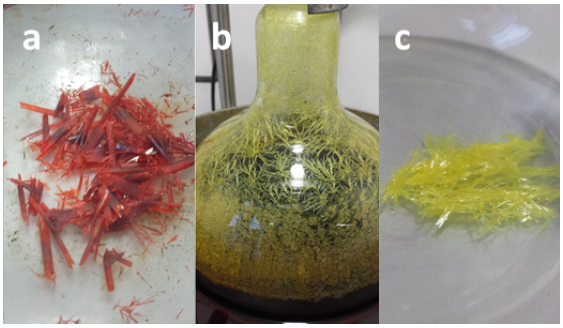
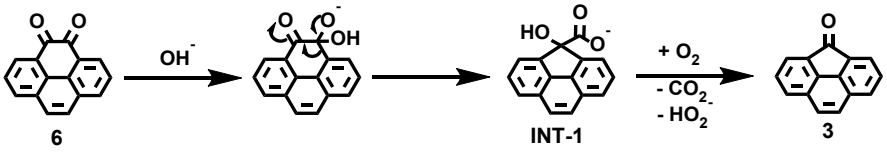


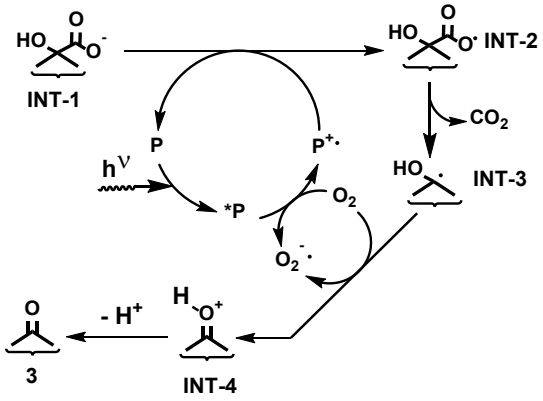
Figure 2.3 Images of the different compounds. a) Crystals of pyrene-4,5-dione **6**; b) deposition of oxoCPP **3** on the wall of a flask; c) recovered, sublimated product **3**.

*Mechanism for the **6** → **3** conversion.* The reaction scheme and proposed mechanism for the conversion of **6** to **3** are given in Scheme 2.4. The reaction starts with the formation of a hydrate, which undergoes a benzilic acid rearrangement to yield an α-hydroxycarboxylic acid intermediate (**INT-1**). This intermediate then undergoes oxidative decarboxylation by oxygen from the air to form **3**. The requirement of oxygen for this conversion was supported by the fact that no product formation was observed when the reaction was performed under an inert atmosphere. In addition, when the reaction was performed in the dark, no product could be isolated. As no dedicated light source was used, it was suspected that the known photo-sensitizability of phenanthrene played a role in this reaction.[61,62] Indeed, examples of self-sensitization of phenanthrene derivatives are known in literature.[63] Based on literary precedent regarding the oxidative decarboxylation of α-hydroxycarboxylates,[64-71] the reaction is presumed to proceed as shown in Scheme 2.4. In short, the reaction is initiated by excitation of molecules containing a phenanthrene moiety **P** (*i.e.* **6** or **3**). The excited species ***P** then undergoes a single electron transfer (SET) to aerial oxygen to produce a superoxide radical and a radical cationic phenanthrene species $\mathbf{P}^{+\cdot}$. The cationic species reacts with carboxylate (**INT-1**) to yield a carboxyl anion radical intermediate (**INT-2**), which is accompanied by re-formation of the ground state phenanthrene species **P**. The radical intermediate (**INT-2**) decomposes with hemolytic C–C bond cleavage, resulting in the formation of CO_2 and a secondary alcohol radical (**INT-3**). Another SET with aerial oxygen generates protonated carbonyl (**INT-4**) and another radical proton. Finally, proton abstraction from **INT-4** gives the ketone product **3**. The superoxide radicals are expected to be quenched in the form of hydrogen peroxide anion. As substituted glycolic acids, like the one supposed to be formed here, are known to be attacked by hydrogen peroxide only slowly, its role is suspected by be insignificant under the present reaction conditions.[72] Moreover, despite exhaustive testing, direct treatment of **6** with different peroxides and superoxides, in different solvents and under various reaction conditions, did not provide any identifiable products. Lastly, addition of $KMnO_4$ as oxidizing agent also did not increase the yield of **3**.

Reaction scheme



Proposed mechanism



Scheme 2.4 Reaction scheme and proposed mechanism for the *in situ* formation and oxidative decarboxylation of benzylic acids.

Custom reaction vessel. To facilitate the easy recovery of the sublimated oxoCPP product, a custom reaction vessel was designed (Fig. 2.4). The vessel consists of a 1 L Duran glass beaker with a flat flange (DN120) fitted with an O-ring, and a raised, flat flange lid with a single ground joint neck, which are affixed using a stainless-steel quick release clamp. The neck is fitted with a glass tube (l = 15 cm) which serves as both a condensing and sublimation tube. After the reaction, the lid is removed and the product washed out with DCM. Simple drying and evaporation of the solvent then provides the pure product, eliminating the need for further purification.

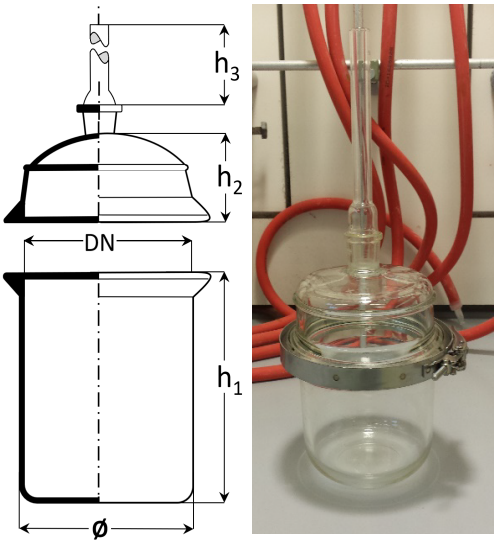
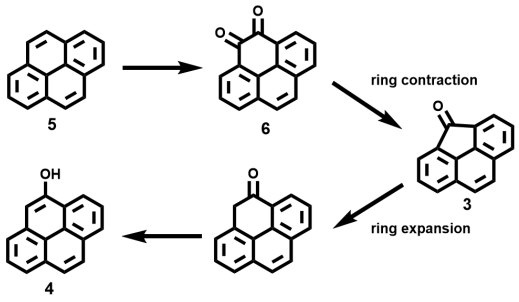


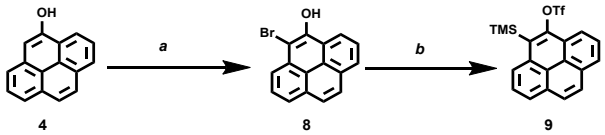
Figure 2.4 Custom reaction vessel for the facile recovery of sublimated material. DN 120, ø = 13 cm, h_1 = 12½ cm, h_2 = 7½ cm, h_3 = 15 cm.

It is interesting to note here that by performing a consecutive ring contraction and ring expansion reaction, a formal reduction of only one of the ketones in pyrene-4,5-dione **6** is achieved, as well as the formal installation of a hydroxide on the C-4 position of pyrene **5** (Scheme 2.5). In addition, with an efficient and economical route to **3** in hand, direct reduction also provided an expedient route to CPP **2** (Scheme S2.2), a valuable precursor in itself.



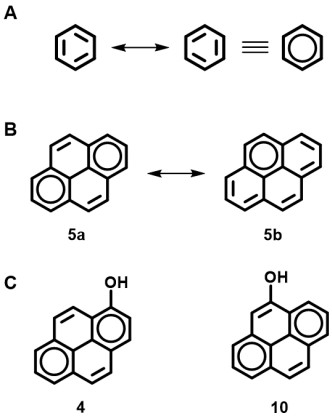
Scheme 2.5 Schematic representation of the conversion of pyrene to 4-hydroxypyrene, illustrating how consecutive ring contraction and ring expansion result in the selective reduction of a single ketone.

Precursor synthesis. With 4-hydroxypyrene **4** in hand, the next step was to selectively *ortho*-brominate it (Scheme 2.6). Bromination, however, proved cumbersome, with overbromination taking place when using most common bromination reagents. This observation was attributed to the enolic character of the hydroxyl group on the C-4 position (See Scheme 2.2 for numbering), which is related to the Clar sextet rule.



Scheme 2.6 Synthesis of propellerene **1** from 4-hydroxypyrene 4. *Reagents and conditions*: a) Br_2, CS_2, -10˚C, 94%; b) i) HMDS, PhMe, reflux, 3 hrs; ii) *n*-BuLi, THF, -78˚C; iii) Tf_2O, -78˚C, 47% over three steps.

Like explained in the introduction, the π electrons in an aromatic system are delocalized, *i.e*. an aromatic ring is said to have more than one resonance structure (Scheme 2.7A). With polycyclic aromatic system, several resonance structures can be drawn in which different rings have localized and delocalized electrons, illustrated for pyrene **5** in Scheme 2.7B. The Clar sextet rule states that: the resonance structure of a polycyclic aromatic system that possesses the greatest number of isolated 6-π electron systems contributes most to the observed chemistry of the overall system.[73] Thus, when both 4-hydroxypyrene **4** and 1-hydroxypyrene **10** are drawn with their Clar sextets it is apparent that in the case of 1-hydroxypyrene **10** the hydroxyl group is attached to a ring which bears a Clar sextet, whereas in the case of 4-hydroxypyrene it is not (Scheme 2.7C). The importance of this seemingly minor difference can be illustrated experimentally using NMR spectroscopy. Thus, when both 1-hydroxy and 4-hydroxypyrene are dissolved in acetone-d_6 in the presence of a small amount of acid, the ^{1}H signal corresponding to the C-5 proton in 4-hydroxypyrene 4 is observed to disappear rapidly ($t_{½}$ ≈ 1 min.). The corresponding C-2 proton in 1-hydroxypyrene **10**, however, showed no exchange even after standing at room temperature for 48 hours (Fig. 2.5A).



Scheme 2.7 Explanation of the Clar sextet rule. (A) The two resonance structures of benzene, with the π-electrons at different locations. The equivalent structure is drawn with a Clar sextet notation. (B) The two resonance structures of pyrene **5**, drawn with Clar sextets. The Clar sextet rule predicts structure **5a**, having two isolated π-sextets, to dominate the observed chemistry of **5**. (C) The structures of 4-hydroxypyrene 5 and 1-hydroxypyrene 12 drawn in their most favorable Clar structure. It is apparent that in **4** the hydroxyl functionality is on a localized π-bond, whereas in **10** it is on an Clar sextet, explaining the lesser reactivity of the latter.

Nonetheless, both compounds show phenolic character, demonstrated by a negative linear relationship between the resonance frequency of the hydroxyl proton and temperature (Fig. 2.5B). Temperature coefficients of -0.04 and -0.01 ppm K^{-1} for 4-hydroxypyrene **4** and 1-hydroxypyrene **10** respectively are typical values for phenols in polar solvents.

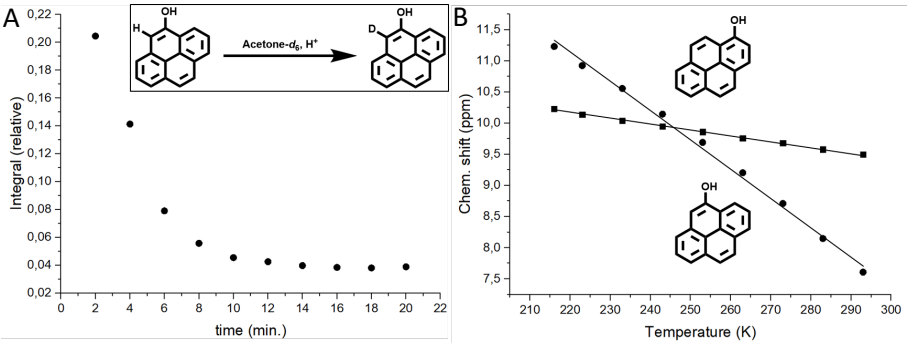
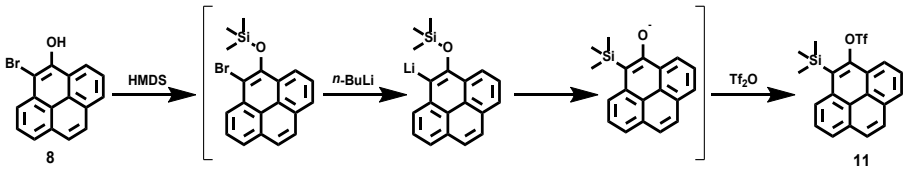


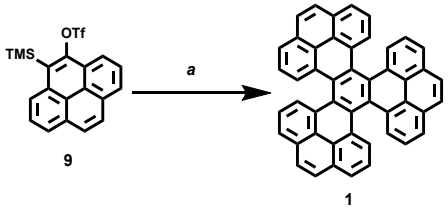
Figure 2.5 (A) Deuteration of 4-hydroxypyrene **4** over time as represented by a decrease of the relative intensity of the ^{1}H resonance corresponding to the C-5 proton (0.55 M in Ace-d_6, approx. 3 eq. of HCl added as a 4.0 M solution in dry dioxane). (B) ^{1}H chemical shift of the hetero-proton on 1-hydroxypyrene **10** (■) and 4-hydroxypyrene **4** (●) at different temperatures (0.55 M in $CDCl_3$). All spectra recorded at a frequency of 500 MHz.

Bromination of **4** was ultimately found possible using elemental bromine in CS_2 at –10°C, given the *ortho*-brominated product **8** in 94% yield. A three-step-one-pot procedure involving *ortho*-lithiation, retro-Brook rearrangement and quenching of the resultant phenolate with triflic anhydride then afford *ortho*-TMS triflate **9** in an overall yield of 47% (Scheme 2.8).



Scheme 2.8 Three-step-one-pot reaction for the conversion of *ortho*-bromophenol **7** to *ortho*-TMS triflate **8.**

Treatment of **9** with CsF in the presence of a palladium(0) catalyst affords tripyrenylene **1**, as a bright yellow solid in 47% yield (Scheme 2.9).



Scheme 2.9 Synthesis of tripyrenylene **1.** *Reagents and conditions*: a) CsF, $Pd_2(dba)_3$, MeCN:Et_2O, rt, o/n, 47%.

To conclude, this Chapter described the optimized synthesis of tripyrenylene from pyrene in six steps with an overall yield of 1.6%. The Chapter started by describing the economical, gram scale synthesis of oxoCPP in two steps from pyrene. By using a single solvent in the chromatography step, the total amount of solvent required was reduced. In addition, by designing a custom reaction vessel, analytically pure product could be obtained, circumventing the need for additional purification. A mechanism was proposed to explain the direct conversion of pyrene-4,5-dione to oxoCPP. The oxoCPP was converted to 4-hydroxypyrene in a ring-expansion reaction, allowing installation of an hydroxyl functionality on an otherwise difficult to access position. From the 4-hydroxypyrene, tripyrenylene could be successfully synthesized, by the merger of three pyrene moieties into a single molecule in one step. The aforementioned oxoCPP was also used to make CPP on a gram-scale in a single reduction step, constituting an improvement over known procedures.

The methodology outlined here, being: i) a consecutive ring-contraction/ring-opening of a vicinal dione, ii) conversion of the resultant phenol to an *ortho*-TMS triflate, and iii) a palladium catalyzed trimerization therewith, constitutes a generally applicable sequence to obtain large PAHs with trifold symmetry on a useful scale. The conformational behavior, physicochemical and spectroscopic properties of tripyrenylene **1** will now be studied in depth in the following Chapter.

References

(1) Hasan, M.; Borovkov, V. Helicene-based chiral auxiliaries and chirogenesis. *Symmetry* **2018,** *10* (1), 10.

(2) Hembury, G. A.; Borovkov, V. V.; Inoue, Y. Chirality-sensing supramolecular systems. *Chem. Rev.* **2008,** *108* (1), 1.

(3) Yang, Y.; Da Costa, R. C.; Fuchter, M. J.; Campbell, A. J. Circularly polarized light detection by a chiral organic semiconductor transistor. *Nat. Photonics* **2013,** *7* (8), 634.

(4) Yamamoto, K.; Shimizu, T.; Igawa, K.; Tomooka, K.; Hirai, G.; Suemune, H.; Usui, K. Rational design and synthesis of [5]helicene-derived phosphine ligands and their application in Pd-catalyzed asymmetric reactions. *Sci. Rep.* **2016,** *6* (1), 1.

(5) Aillard, P.; Voituriez, A.; Marinetti, A. Helicene-like chiral auxiliaries in asymmetric catalysis. *Dalton T.* **2014,** *43* (41), 15263.

(6) Stetsovych, O.; Švec, M.; Vacek, J.; Chocholoušová, J. V.; Jančařík, A.; Rybáček, J.; Kosmider, K.; Stará, I. G.; Jelínek, P.; Starý, I. From helical to planar chirality by on-surface chemistry. *Nat. Chem.* **2017,** *9* (3), 213.

(7) Isla, H.; Crassous, J. Helicene-based chiroptical switches. *Compt. Rend. Chim.* **2016,** *19* (1-2), 39.

(8) Bosson, J.; Gouin, J.; Lacour, J. Cationic triangulenes and helicenes: synthesis, chemical stability, optical properties and extended applications of these unusual dyes. *Chem. Soc. Rev.* **2014,** *43* (8), 2824.

(9) Buchta, M.; Rybáček, J.; Jančařík, A.; Kudale, A. A.; Buděšínský, M.; Chocholoušová, J. V.; Vacek, J.; Bednárová, L.; Císařová, I.; Bodwell, G. J. Chimerical pyrene-based [7]helicenes as twisted polycondensed aromatics. *Chem. Eur. J.* **2015,** *21* (24), 8910.

(10) Nakakuki, Y.; Hirose, T.; Sotome, H.; Miyasaka, H.; Matsuda, K. Hexa-peri-hexabenzo [7]helicene: Homogeneously π-extended helicene as a primary substructure of helically twisted chiral graphenes. *J. Am. Chem. Soc.* **2018,** *140* (12), 4317.

(11) Evans, P. J.; Ouyang, J.; Favereau, L.; Crassous, J.; Fernández, I.; Perles, J.; Martín, N. Synthesis of a helical bilayer nanographene. *Angew. Chem. Int. Ed.* **2018,** *57* (23), 6774.

(12) Cruz, C. M.; Castro-Fernández, S.; Maçôas, E.; Cuerva, J. M.; Campaña, A. G. Undecabenzo [7]superhelicene: a helical nanographene ribbon as a circularly polarized luminescence emitter. *Angew. Chem. Int. Ed.* **2018,** *57* (45), 14782.

(13) Hu, Y.; Paternò, G. M.; Wang, X.-Y.; Wang, X.-C.; Guizzardi, M.; Chen, Q.; Schollmeyer, D.; Cao, X.-Y.; Cerullo, G.; Scotognella, F. π-Extended pyrene-fused double [7]carbohelicene as a chiral polycyclic aromatic hydrocarbon. *J. Am. Chem. Soc.* **2019,** *141* (32), 12797.

(14) Chen, F.; Tanaka, T.; Hong, Y. S.; Mori, T.; Kim, D.; Osuka, A. Closed pentaaza [9]helicene and hexathia [9]/[5]helicene: Oxidative fusion reactions of ortho-phenylene-bridged cyclic hexapyrroles and hexathiophenes. *Angew. Chem.* **2017,** *129* (46), 14880.

(15) Hashimoto, S.; Nakatsuka, S.; Nakamura, M.; Hatakeyama, T. Construction of a highly distorted benzene ring in a double helicene. *Angew. Chem. Int. Ed.* **2014,** *53* (51), 14074.

(16) Sakamaki, D.; Kumano, D.; Yashima, E.; Seki, S. A facile and versatile approach to double N-heterohelicenes: Tandem oxidative C-N couplings of N-heteroacenes via cruciform dimers. *Angew. Chem.* **2015,** *127* (18), 5494.

(17) Ferreira, M.; Naulet, G.; Gallardo, H.; Dechambenoit, P.; Bock, H.; Durola, F. A naphtho-fused double [7]helicene from a maleate-bridged chrysene trimer. *Angew. Chem. Int. Ed.* **2017,** *56* (12), 3379.

(18) Tanaka, H.; Ikenosako, M.; Kato, Y.; Fujiki, M.; Inoue, Y.; Mori, T. Symmetry-based rational design for boosting chiroptical responses. *Commun. Chem.* **2018,** *1* (1), 1.

(19) Liu, X.; Yu, P.; Xu, L.; Yang, J.; Shi, J.; Wang, Z.; Cheng, Y.; Wang, H. Synthesis for the mesomer and racemate of thiophene-based double helicene under irradiation. *J. Org. Chem.* **2013,** *78* (12), 6316.

(20) Wang, X.-Y.; Wang, X.-C.; Narita, A.; Wagner, M.; Cao, X.-Y.; Feng, X.; Müllen, K. Synthesis, structure, and chiroptical properties of a double [7]heterohelicene. *J. Am. Chem. Soc.* **2016,** *138* (39), 12783.
(21) Katayama, T.; Nakatsuka, S.; Hirai, H.; Yasuda, N.; Kumar, J.; Kawai, T.; Hatakeyama, T. Two-step synthesis of boron-fused double helicenes. *J. Am. Chem. Soc.* **2016,** *138* (16), 5210.
(22) Hosokawa, T.; Takahashi, Y.; Matsushima, T.; Watanabe, S.; Kikkawa, S.; Azumaya, I.; Tsurusaki, A.; Kamikawa, K. Synthesis, structures, and properties of hexapole helicenes: assembling six [5]helicene substructures into highly twisted aromatic systems. *J. Am. Chem. Soc.* **2017,** *139* (51), 18512.
(23) Berezhnaia, V.; Roy, M.; Vanthuyne, N.; Villa, M.; Naubron, J.-V. r.; Rodriguez, J.; Coquerel, Y.; Gingras, M. Chiral nanographene propeller embedding six enantiomerically stable [5]helicene units. *J. Am. Chem. Soc.* **2017,** *139* (51), 18508.
(24) Fujikawa, T.; Segawa, Y.; Itami, K. Synthesis and structural features of quadruple helicenes: highly distorted π systems enabled by accumulation of helical repulsions. *J. Am. Chem. Soc.* **2016,** *138* (10), 3587.
(25) Tanaka, H.; Kato, Y.; Fujiki, M.; Inoue, Y.; Mori, T. Combined experimental and theoretical study on circular dichroism and circularly polarized luminescence of configurationally robust D_3-symmetric triple pentahelicene. *J. Phys. Chem. A* **2018,** *122* (37), 7378.
(26) Griffiths, J. *Colour and constitution of organic molecules*; Academic press, **1976**.
(27) Fabian, J.; Hartmann, H. *Light absorption of organic colorants: theoretical treatment and empirical rules*; Springer Science & Business Media, **2013**.
(28) Nishimoto, K. A MO theoretical study of organic dyes I. Effect of chemical softness on the electronic spectra. *Bull. Chem. Soc. Jap.* **1993,** *66* (7), 1876.
(29) Woodward, R. B. Structure and the absorption spectra of α,ß-unsaturated ketones. *J. Am. Chem. Soc.* **1941,** *63* (4), 1123.
(30) Fieser, L. F.; Fieser, M.; Rajagopalan, S. Absorption spectroscopy and the structures of the diosterols. *J. Org. Chem.* **1948,** *13* (6), 800.
(31) Rulíšek, L.; Exner, O.; Cwiklik, L.; Jungwirth, P.; Starý, I.; Pospíšil, L.; Havlas, Z. On the convergence of the physicochemical properties of [n]helicenes. *J. Phys. Chem. C* **2007,** *111* (41), 14948.
(32) Nakai, Y.; Mori, T.; Inoue, Y. Theoretical and experimental studies on circular dichroism of carbo [n] helicenes. *J. Phys. Chem. A* **2012,** *116* (27), 7372.
(33) Mori, T. Chiroptical properties of symmetric double, triple, and multiple helicenes. *Chem. Rev.* **2021,** *121* (4), 2373.
(34) Pozo, I.; Guitián, E.; Pérez, D.; Peña, D. Synthesis of nanographenes, starphenes, and sterically congested polyarenes by aryne cyclotrimerization. *Acc. Chem. Res.* **2019**.
(35) Guitián, E.; Pérez, D.; Peña, D. In *Palladium in Organic Synthesis*; Springer, 2005.
(36) Rodenburg, L.; Brandsma, R.; Tintel, C.; Van Thuijl, J.; Lugtenburg, J.; Cornelisse, J. Synthesis and properties of nitro derivatives of 2-tert-butyl-and 2,7-di-tert-butylpyrene. *Recl. Trav. Chim. Pays-Bas* **1986,** *105* (5), 156.
(37) Peake, D. A.; Oyler, A. R.; Heikkila, K. E.; Liukkonen, R. J.; Engroff, E. C.; Carlson, R. M. Alkyl aromatic synthesis: Nucleophilic alkyl lithium addition. *Synth. Comm.* **1983,** *13* (1), 21.
(38) Mochida, K.; Kawasumi, K.; Segawa, Y.; Itami, K. Direct arylation of polycyclic aromatic hydrocarbons through palladium catalysis. *J. Am. Chem. Soc.* **2011,** *133* (28), 10716.
(39) Odani, R.; Hirano, K.; Satoh, T.; Miura, M. Copper-mediated dehydrogenative biaryl coupling of naphthylamines and 1, 3-azoles. *J. Org. Chem.* **2013,** *78* (21), 11045.
(40) Vollmann, H.; Becker, H.; Corell, M.; Streeck, H. Beiträge zur Kenntnis des Pyrens und seiner Derivate. *Liebigs Ann. Chem.* **1937,** *531* (1), 1.
(41) Sun, W.; Tang, X.; Li, J.; He, M.; Zhang, R.; Han, X. e.; Zhao, Y.; Ni, Z. A novel 4-hydroxypyrene-based "off–on" fluorescent probe with large Stokes shift for detecting cysteine and its application in living cells. *Tet. Lett.* **2020,** *61* (6), 151467.
(42) Newman, M. S. Syntheses in the pyrene field. *J. Org. Chem.* **1951,** *16* (6), 860.

(43) Okamoto, T.; Shudo, K.; Miyata, N.; Kitahara, Y.; Nagata, S. Reactions of K-region oxides of carcinogenic and non-carcinogenic aromatic hydrocarbonds - Comparative studies on reactions with nucleophiles and acid-catalyzed reactions. *Chem. Pharm. Bull.* **1978,** *26* (7), 2014.
(44) Nashed, N. T.; Bax, A.; Loncharich, R. J.; Sayer, J. M.; Jerina, D. M. Methanolysis of K-region arene oxides - Comparison between acid-catalyzed and methodide ion addition-reactions. *J. Am. Chem. Soc.* **1993,** *115* (5), 1711.
(45) Vanduuren, B. L.; Witz, G.; Agarwal, S. C. Synthesis and photorearrangement of 4,5-epoxy-4,5-dihydropyrene. *J. Org. Chem.* **1974,** *39* (8), 1032.
(46) Barton, D. H. R.; Sammes, P. G.; Weingarten, G. G.. Photochemical transformations .29. Steric compression effects in synthesis and reaction of 4-amino-5-methylphenanthrene. *J. Chem. Soc. C* **1971**, (4), 729.
(47) Aoyama, T.; Shioiri, T. New Methods and Reagents in Organic Synthesis. 17. Trimethylsilydiazomethane (TMSCHN2) as a Stable and Safe Substitute for Hazardous Diazomethane. Its Application to the Arndt-Eistert Synthesis. *Chem. Pharm. Bull.* **1981,** *29* (11), 3249.
(48) Harvey, R. G.; Abu-Shqara, E.; Yang, C. X. Synthesis of ketone and alcohol derivatives of methylene-bridged polyarenes, potentially new classes of active metabolites of carcinogenic hydrocarbons. *J. Org. Chem.* **1992,** *57* (23), 6313.
(49) Kruber, O. Über neue Kohlenwasserstoffe aus dem Anthracenöl des Steinkohlenteers. *Chem. Ber.* **1934,** *67* (6), 1000.
(50) Yang, C. X.; Harvey, R. G. Synthesis of 4 H-Cyclopenta[def]phenanthrene. *Polycycl. Arom. Comp.* **1992,** *2* (4), 229.
(51) Minabe, M.; Yoshida, M.; Takayanagi, T. A facile synthesis of 4*H*-cyclopenta[def]phenanthrene. *Bull. Chem. Soc. Jap.* **1988,** *61* (3), 995.
(52) Minaba, M.; Suzuki, K. 4*H*-Cyclopenta[def]phenanthrene. *J. Synth. Org. Chem. Jap.* **1986,** *44* (5), 421.
(53) Kazuo, S. *Technol. Repts. Tohoku Univ.* **1954,** *19*, 63.
(54) Suzuki, K.; Kajigaeshi, S.; Kato, S. Studies on fluorene derivatives .X. Studies on 4, 4', 4"-tribromotribiphenylenepropane and 4'-bromotribiphenylenepropane. *J. Synth. Org. Chem. Jap.* **1958,** *16* (6), 304.
(55) Graebe, C.; Aubin, C. Ueber Diphensäureanhydrid und über o-Diphenylenketoncarbonsäure. *Liebigs Ann. Chem.* **1888,** *247* (3), 257.
(56) Kim, J.; Jin, Y.; Song, S.; Kim, I.; Suh, H. Synthesis of 4H-Cyclopenta[def]phenanthrene from 1-naphthylacetic Acid. *Chem. Lett.* **2009,** *38* (10), 1008.
(57) Medenwald, H. Synthese des 1-Aza-pyrens und des Phenanthrylen-(4.5)-methans. *Chem. Ber.* **1953,** *86* (2), 287.
(58) Walsh, J. C.; Williams, K. L. M.; Lungerich, D.; Bodwell, G. J. Synthesis of Pyrene-4, 5-dione on a 15 g Scale. *Eur. J. Org. Chem.* **2016,** *2016* (36), 5933.
(59) Cook, J. W.; Stephenson, E. F. M. 181. Polycyclic aromatic hydrocarbons. Part XXXIII. Synthesis of naphtho(1′: 2′-1: 2)fluorene and naphtho(2′:1′-2:3)fluorene. *J. Chem. Soc. (Resumed)* **1949**, 842.
(60) Anschütz, R.; Japp, F. R. Ueber die Oxydation des Phenanthrenchinons mittelst Kaliumpermanganat. *Ber. Dtsch. Chem. Ges.* **1878,** *11* (1), 211.
(61) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. Oxygen quenching of aromatic triplet states in solution. Part 1. *J. Chem. Soc. Faraday Trans.* **1973,** *69*, 708.
(62) Horspool, W. M.; Lenci, F. *CRC Handbook of Organic Photochemistry and Photobiology, Volumes 1 & 2*; CRC press, 2003.
(63) Montanaro, S.; Lhiaubet-Vallet, V.; Iesce, M.; Previtera, L.; Miranda, M. A. A mechanistic study on the phototoxicity of atorvastatin: singlet oxygen generation by a phenanthrene-like photoproduct. *Chem. Res. Tox.* **2009,** *22* (1), 173.
(64) Pink, J. M. O., University of British Columbia, **1969**.
(65) He, S.; Chen, X.; Zeng, F.; Lu, P.; Peng, Y.; Qu, L.; Yu, B. Visible-light-promoted oxidative decarboxylation of arylacetic acids in air: Metal-free synthesis of aldehydes and ketones at room temperature. *Chin. Chem. Lett.* **2020,** *31* (7), 1863.

(66) Nakayama, H.; Itoh, A. Aerobic photo-decarboxylation of α-hydroxy carboxylic acid derivatives under visible light irradiation in the presence of catalytic iodine. *Tet. Lett.* **2008,** *49* (17), 2792.
(67) Lemmetyinen, H.; Koskikallio, J.; Lindblad, M.; Kuzmin, M. G. A mechanism involving two photoinduced transients for the photocyanation of phenanthrene in the presence of oxygen and potassium cyanide-18-crown—6 ether in anhydrous acetonitrile. *Acta Chem. Scand. A* **1982,** *36* (5).
(68) Lemmetyinen, H. J. Kinetic analysis of aromatic photocyanation: naphthalene, biphenyl, and phenanthrene. *J. Chem. Soc. Perkin T. 2* **1983,** (8), 1269.
(69) Bhattacherjee, A.; Sneha, M.; Lewis-Borrell, L.; Tau, O.; Clark, I. P.; Orr-Ewing, A. J. Picosecond to millisecond tracking of a photocatalytic decarboxylation reaction provides direct mechanistic insights. *Nat. Comm.* **2019,** *10* (1), 1.
(70) Joshi, P. C.; Pathak, M. A. The role of active oxygen ($^1O_2$ and $O^{\cdot 2-}$) induced by crude coal tar and its ingredients used in photochemotheraphy of skin diseases. *J. Invest. Dermat.* **1984,** *82* (1).
(71) Rahman, M.; Mukherjee, A.; Kovalev, I. S.; Kopchuk, D. S.; Zyryanov, G. V.; Tsurkan, M. V.; Majee, A.; Ranu, B. C.; Charushin, V. N.; Chupakhin, O. N. Recent advances on diverse decarboxylative reactions of amino acids. *Adv. Synth. Cat.* **2019,** *361* (10), 2161.
(72) Witzemann, E. J. The oxidation of alpha-and beta-hydroxybutyric acids with hydrogen peroxide. *J. Am. Chem. Soc.* **1926,** *48* (1), 211.
(73) Clar, E. Aromatic sextet. **1972**.
(74) Kim, J.; Park, S. H.; Cho, S.; Jin, Y.; Kim, J.; Kim, I.; Lee, J. S.; Kim, J. H.; Woo, H. Y.; Lee, K. Low-bandgap poly (4H-cyclopenta[def]phenanthrene) derivatives with 4, 7-dithienyl-2, 1, 3-benzothiadiazole unit for photovoltaic cells. *Polymer* **2010,** *51* (2), 390.
(75) Jin, Y.; Kim, Y.; Kim, S. H.; Song, S.; Woo, H. Y.; Lee, K.; Suh, H. Novel green-light-emitting polymers based on cyclopenta[def]phenanthrene. *Macromol.* **2008,** *41* (15), 5548.
(76) Song, S.; Jin, Y.; Kim, S. H.; Kim, J. H.; Lee, K.; Suh, H. Synthesis and characterization of novel conjugated polymer with 4H-cyclopenta[def]phenanthrene and the sulfanyl group. *Polym. J.* **2009,** *41* (2), 138.
(77) Kim, J.; Park, S. H.; Kim, J.; Cho, S.; Kim, I.; Lee, K.; Suh, H. Syntheses and characterization of new low-band gap polymers containing 4H-cyclopenta[def]phenanthrene unit and 4,7-di(thien-2-yl)-2*H*-benzimidazole-2-spirocyclohexane for photovoltaic device. *Synth. Met.* **2011,** *161* (13-14), 1336.
(78) Shin, Y. R.; Lee, W. H.; Park, J. B.; Kim, J. H.; Lee, S. K.; Shin, W. S.; Hwang, D. H.; Kang, I. N. Synthesis and characterization of new low band-gap polymers containing electron-accepting acenaphtho [1,2-c]thiophene-S,S-dioxide groups. *J. Polym. Sci. Pol. Chem.* **2016,** *54* (4), 498.
(79) Liu, T.; Zhang, H.-X.; Xia, B.-H. Theoretical studies of the electronic structures and optical properties of stable blue-emitting polymer based on 4H-cyclopenta-[def]-phenanthrene. *Polymer* **2008,** *49* (8), 2077.
(80) Shinohara, A.; Pan, C.; Guo, Z.; Zhou, L.; Liu, Z.; Du, L.; Yan, Z.; Stadler, F.; Wang, L.; Nakanishi, T. Viscoelastic Conjugated Polymer Fluids. *Angew. Chem.* **2019**.
(81) Song, S.; Kim, C.; Park, S. H.; Kim, I.; Lee, K.; Jin, Y.; Suh, H. Synthesis and characterization of polycyclopentaphenanthrene with carbazole or oxidiazole pendant units. *Polym. J.* **2012,** *44* (4), 347.
(82) Song, S.; Jin, Y.; Kim, J.; Park, S. H.; Kim, S. H.; Lee, K.; Suh, H. A novel conjugated polymer based on cyclopenta[def]phenanthrene backbone with spiro group. *Polymer* **2008,** *49* (26), 5643.
(83) Song, S.; Jin, Y.; Kim, K.; Kim, S. H.; Shim, Y. B.; Lee, K.; Suh, H. Novel cyclopenta [def] phenanthrene based blue emitting oligomers for OLEDs. *Tet. Lett.* **2008,** *49* (22), 3582.
(84) Suh, H.; Jin, Y.; Park, S. H.; Kim, D.; Kim, J.; Kim, C.; Kim, J. Y.; Lee, K. Stabilized Blue Emission from Organic Light-Emitting Diodes Using Poly (2, 6-(4, 4-bis (2-ethylhexyl)-4*H*-cyclopenta[def]phenanthrene)). *Macromol.* **2005,** *38* (15), 6285.

(85) Kim, J.; Kim, S. H.; Kim, J.; Kim, I.; Jin, Y.; Kim, J. H.; Woo, H. Y.; Lee, K.; Suh, H. Di-aryl substituted poly (cyclopenta[def]phenanthrene) derivatives containing carbazole and triphenylamine units in the main chain for organic light-emitting diodes. *Macromol. Res.* **2011,** *19* (6), 589.

(86) Jin, Y.; Yoo, C.; Kim, K.; Song, S.; Kim, J.; Kim, J.; Suh, H. Novel efficient blue materials with 4*H*-cyclopenta[def]phenanthrene for OLEDs. *Synth. Met.* **2008,** *158* (10), 417.

(87) Jang, S. H.; Tai, T. B.; Park, J. H.; Jeong, H. J.; Chun, E. J.; Kim, Y.-H.; Lee, S.-G.; Singh, O. M.; Yoon, Y. J.; Kwon, S. K. Synthesis and characterization of highly conjugated cyclopenta [def] phenanthrene-based polymers. *Macromol. Res.* **2010,** *18* (2), 185.

(88) Ono, A.; Suzuki, N.; Kamimura, J. Hydrogenolysis of diaryl and aryl alkyl ketones and carbinols by sodium borohydride and anhydrous aluminum (III) chloride. *Synth.* **1987,** *1987* (8), 736.

(89) Gálová M. and Lux L., Aluminum halides in nonaqueous solvents. I. Basic polarographic characteristics. *Chem. Zvesti* **1975**, *29 (3)*, 279.

(90) Hu, J.; Zhang, D.; Harris, F. W. Ruthenium (III) chloride catalyzed oxidation of pyrene and 2, 7-disubstitued pyrenes: An efficient, one-step synthesis of pyrene-4,5-diones and pyrene-4, 5, 9, 10-tetraones. *J. Org. Chem.* **2005,** *70* (2), 707.

(91) Kestens, V.; Auclair, G.; Drozdzewska, K.; Held, A.; Roebben, G.; Linsinger, T. Thermodynamic property values of selected polycyclic aromatic hydrocarbons measured by differential scanning calorimetry. *J. Therm. Anal. Calorim.* **2010,** *99* (1), 245.

(92) Kimura, T.; Minabe, M.; Suzuki, K. Rearrangements and ring expansions of 4*H*-cyclopenta[def]phenanthrene derivatives. *J. Org. Chem.* **1978,** *43* (6), 1247.

(93) Baeyer, A. Mittheilungen aus dem chemischen Laboratorium der Akademie der Wissenschaften in München. *Ber. Dtsch. Chem. Ges.* **1877,** *10* (1), 123.

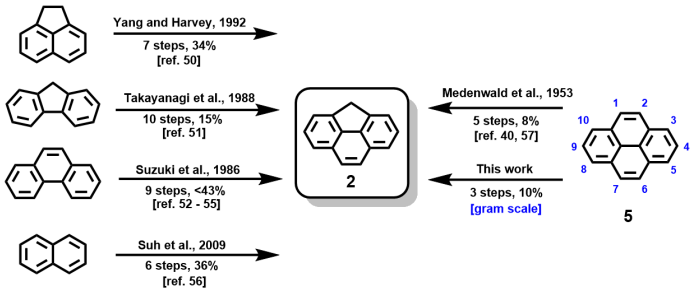
(94) Sieglitz, A.; Schidlo, W. Über Abkömmlinge des 4.5-Methylen-phenanthrens. *Chem. Ber.* **1963,** *96* (4), 1098.

(95) van den Braken—van Leersum, A. M.; Tintel, C.; Van't Zelfde, M.; Cornelisse, J.; Lugtenburg, J. Spectroscopic and photochemical properties of mononitropyrenes. *Recl. Trav. Chim. Pays-Bas* **1987,** *106* (4), 120.

(96) Ott, R.; Zinke, A. Zur Kenntnis des Coronens. *Monatsh. Chem. Verw. Tl.* **1953,** *84* (6), 1132.

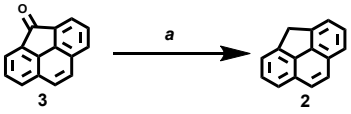
Supplementary results

Reduction of oxoCPP ***3***. The 4*H*-cyclopenta[*def*]phenanthrene (CPP) **2** motive holds interesting properties for the synthesis of photovoltaic[74] and electroluminescent polymers,[75-81] as well as for the production of organic light emitting diodes (OLEDs).[82-87] Interest in this motive stems from the low HOMO-LUMO gap of CPP **2**,[79] allowing its use in high frequency applications. Synthesis of these polymers usually starts from the parent CPP molecule **2**. As such many have attempted to synthesize it, with varying success (Scheme S2.1).[40,50-57] With a successful synthetic route in hand to access large amounts of oxoCPP, it became interesting to see whether it could be directly reduced to CPP **2**.



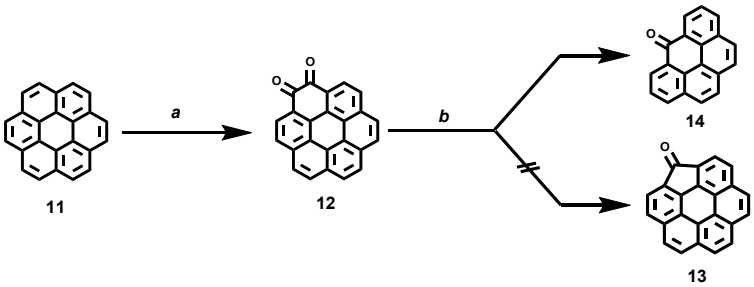
Scheme S2.1 Summary of the literature procedures for the synthesis of CPP and the procedure described in this Chapter for the synthesis of oxoCPP.

A procedure for the direct reduction of **3** to **2** *via* a Wolff-Kishner reaction could be found in literature, with a reported yield of 60%.[57] Given the hazardous nature of hydrazine, conversion was tried using $Al(BH_4)_3$ instead, generated *in situ* by adding a solution of $AlCl_3$ in anhydrous THF to a mixture of $NaBH_4$ and **3** (Scheme 2.8).[88] Gratifyingly, the reduced product could thus be obtained on a one gram scale, with a slightly increased yield of 65% (Scheme S2.2). After work-up, the product could be purified by a standard silica gel column using neat pentane as eluent. As with the purification of **6**, solvent used for the chromatography could be retrieved and reused, reducing the total amount of solvent needed. The yield of the product was found to be highly influenced by the purity of the solution of $AlCl_3$ in THF. When insufficiently dry reagents were used, brown colored solutions were obtained, which resulted in significantly lower yields of the desired product (10 – 30%).[89]



Scheme S2.2 The direct reduction of oxoCPP to CPP. *Reagents and conditions*: a) $NaBH_4$, $AlCl_3$, THF, -78°C → reflux, 3 d., 65%.

Lead(II) oxide mediated pyrolysis. In an attempt to expand the scope of the PbO mediated pyrolysis of germinal diones, coronen-1,2-dione **12** was subjected to the same conditions. Unexpectedly, instead of ring contracted product **13**, decomposed compound **14** was the only identifiable product obtained in low yield (1.9%; Scheme S2.3).

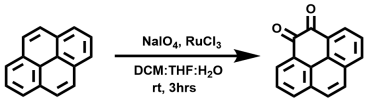


Scheme S2.3 PbO mediated pyrolysis of coronen-1,2-dione. *Reagents and conditions*: a) $Na_2Cr_2O_7$, $PhNO_2$:HOAc, 120°C, 1 hr, 76%; b) PbO, 265°C, vac., 3 hrs, 1.9%.

Experimental

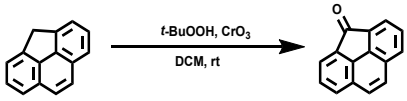
General. All reagents were obtained from commercial sources and were used as received. Solvents used were stored over 4 Å molecular sieves. Reactions were monitored by TLC analysis using Merck 25 DC plastikfolien 60 F254 with detection by using an aqueous solution of $KMnO_4$ (7%) and K_2CO_3 (2%) followed by charring at ~150 °C. Column chromatography was performed on Fluka silica gel (0.04–0.063 mm). High-resolution mass spectra were recorded by direct injection (2 µL of a 2 µM solution in water/acetonitrile; 50:50; v/v and 0.1% formic acid) on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 250 °C). The high-resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan). Melting points were recorded on a Stuart scientific SMP3 melting point apparatus and are uncorrected. All NMR experiments were performed on a Bruker AV500 NMR instrument equipped with a BBFO probe head for 5 mm outer diameter tubes. Spectra were recorded at 500 MHz for ^1H, 125 MHz for ^{13}C and 470 MHz for ^{19}F. All deuterated solvents were obtained from a commercial source (Eurisotope) and were used as received. Chemical shifts are given in ppm (δ) relative to TMS (0 ppm), and coupling constants (*J*) are given in Hertz (Hz).

Pyrene-4,5-dione (6)



A solution of $NaIO_4$ (28 g, 130 mmol) in H_2O (500 mL) was added dropwise to a vigorously stirred solution of pyrene (6 g, 30 mmol) and $RuCl_3 \cdot xH_2O$ (600 mg, 3.0 mmol) in DCM (250 mL) and THF (250mL). The addition took approximately 1 hr and was stopped whenever heating of the solution became noticeable by touch. The resultant dark brown suspension was stirred at room temperature for 3 hours and then poured into water (1 L) and the layers separated. The aqueous layer extracted twice with DCM (300 mL) and the organic layer washed twice with water (300 mL). The organic layer was dilute with DCM (400 mL) and filtered through a glass fritted funnel. The residue was rinsed twice with DCM (200 mL) and the combined organic layers were washed with brine (500 mL) and evaporated under reduced pressure to afford a brown-orange residue. The residue was eluted over a silica gel column using neat DCM (R_f = 0.5) as eluent to provide the dione as bright orange crystals. Yield: 3.5 g, 15 mmol, 50%. ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 (dd, J = 7.4, 1.2 Hz, 1H), 8.17 (dd, J = 8.0, 1.2 Hz, 1H), 7.84 (s, 1H), 7.75 (t, J = 7.7 Hz, 1H). HRMS (ESI-TOF) m/z: calc'd for $C_{16}H_9O_2$ [M+H]+: 233.06025 found 233.05950. m.p. 300 °C (dec.), lit. 299 – 302 °C.[90]

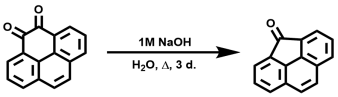
4*H*-cyclopenta[*def*]phenanthren-4-one (4)



4*H*-Cyclopenta[*def*]phenanthrene (500 mg, 2.63 mmol, 1.0 eq) was added to a solution of CrO_3 (13 mg, 0.13 mmol, 0.05 eq.) and aqueous tBuOOH (2.4 mL, 70%, 18.3 mmol, 6.9 eq) in DCM (30 mL). The reaction mixture stirred at room temperature for 3 hrs. The solution was then cooled to 0ºC and added dropwise to a vigorously stirred solution 10% aqueous $Na_2S_2O_5$ solution and stirred for 1 hour. The layers were then separated and the organic layer washed with brine, dried over Na_2SO_4 and evaporated on celite. The product was purified over a silica column using DCM:Pentane (1:3; R_f = 0.3) to provide the product as bright yellow needlesStarting material was also eluted in the first couple of fractions, which was recovered and used for another run of the reaction. Over a total of four cycles, a cumulative yield of 383 mg (1.86 mmol, 71%) of oxoCPP was obtained. ^1H NMR (500MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.0 Hz,

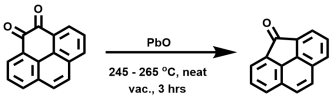
2H), 7.64 (s, 2H), 7.49 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (125MHz, $CDCl_3$) 193.62, 158.69, 138.95, 132.92, 130.68, 129.08, 127.21, 125.29, 122.35. HRMS (ESI-TOF) m/z: calc'd for $C_{15}H_9O$ [M+H]+: 205.06534 found 205.06473. m.p. 170 – 171 °C, lit. 170 °C.[91]

Benzilic Acid Rearrangement of Pyrene-4,5-dione



In a 2 L round bottom flask, fitted with a ground glass joint tube (l = 15 cm), a suspension of pyrene-4,5-dione (5 g, 21.5 mmol) in aqueous NaOH (1.0 M, 1 L) was refluxed for 3 days with vigorous stirring in contact with air. The flask was allowed to cool to room temperature and the product, which had sublimated as a yellow crystalline solid in the reflux condenser was washed out with DCM to provide an initial yield of 1 g (4.9 mmol, 23%). Material which had collected on the walls of the flask was washed down with DCM, separated from the aqueous reaction mixture, dried over $MgSO_4$, filtered and purified by elution over a silica gel column with 1:10 DCM:Pentane (R_f = 0.3) provided additional product (310 mg, 1.5 mmol, 7%).

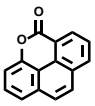
4*H*-cyclopenta[*def*]phenanthren-4-one via Pyrolysis of Pyrene-4,5-dione with PbO



A flame-dried vial charged with an intimate mixture of pyrene-4,5-dione (100 mg, 0.43 mmol) and yellow lead(II) oxide (1 g, 4.5 mmol, 10 eq.) in one portion. The vial was sealed with a shrink cap and evacuated. The vial was then heated on a metal block at 265 °C for 3 hours at which point all starting material had been consumed (as per TLC). After cooling to room temperature the vial was purged with N_2. The bright yellow crystalline sublimate was scraped off, and the residue washed with DCM (3x 10 mL) and filtered. Elution over a silica gel column with EtOAc:pentane (1:30; R_f = 0.5) gave the title compound as the only product. Yield: 7 mg, 0.17 mmol, 8.0%.

Leaving the reaction overnight did not increase the yield. When the reaction was performed on a larger scale (1 g, 4.3 mmol), trace amount of a slightly more polar compound was also obtained, which was putatively assigned as phenanthrene-1,10-lactone (5*H*-naphtho[8,1,2-*cde*]chromen-5-one) based on its ^1H and ^{13}C NMR spectra (Fig. S2.1). The identity was confirmed by comparison of the spectra with those obtained for an authentic sample which was made as follows: oxoCPP (132 mg, 0.65 mmol) was suspended in glacial acetic acid (6 mL) and concentrated sulfuric acid (1.5 mL) slowly added to it. Stirring was continued until all material had dissolved. Then, aqueous hydrogen peroxide (30%, 0.5mL) was added which caused the solution to take on a dark red color. The solution was stirred in contact with air for 10 min. at which point the dark red color had faded and stirring of the pale yellow solution continued for another 3 hours. The resultant suspension was filtered, and the residue taken up in chloroform (~10 mL) which was found to consist of a mixture of starting material and product (TLC, eluent 1:1 DCM:Pentane, R_f = 0.73). The filtrate was poured on ice (~100 mL) and extracted with chloroform (2x 50 mL). The combined organic layers were washed with sat. $NaHCO_3$ (50 mL), dried over Na_2SO_4 and evaporated to dryness. The residue thus obtained was nearly pure lactone. The combined residues were then purified by column chromatography over silica gel using DCM:Pentane (1:3 → 1:1) as eluent to provide the product as a white solid (66 mg, 0.30 mmol, 46%) together with recovery of starting material (19 mg, 0.09 mmol, 14%).

5*H*-naphtho[8,1,2-*cde*]chromen-5-one (7)



^{1}H NMR (300 MHz, Ace-d_6) δ 8.60 (dd, *J* = 7.8, 1.2Hz, 1H), 8.52 (dd, *J* = 7.8, 1.2Hz, 1H), 8.110 (s, 1H), 8.107 (s, 1H), 8.06 (t, *J* = 7.8Hz, 1H), 7.98 (dd, *J* = 7.8, 1.2Hz, 1H), 7.91 (t, *J* = 7.8Hz, 1H), 7.63 (dd, *J* = 7.8, 1.2Hz, 1H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 7.8, 1.2Hz, 1H), 8.21 (dd, *J* = 7.8, 1.2Hz, 1H), 7.85 (t, *J* = 7.8Hz, 1H), 7.82 (dd, *J* = 11.4, 4.7Hz, 2H), 7.75 (s, 1H), 7.74 (dd, *J* = 7.8, 1.2Hz, 1H), 7.52-7.49 (m, *J* = 7.8Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.42, 150.42, 132.80, 131.26, 129.72, 128.71, 128.53, 127.63, 127.56, 127.10, 126.40, 122.63, 119.79, 113.98, 113.04. HRMS (ESI-TOF) m/z: calc'd for $C_{16}H_8O_2$ [M+H]+: 221.05971 found 221.05952. m.p. 194 – 195 °C, lit. 200.5 – 201.5 °C.[92]

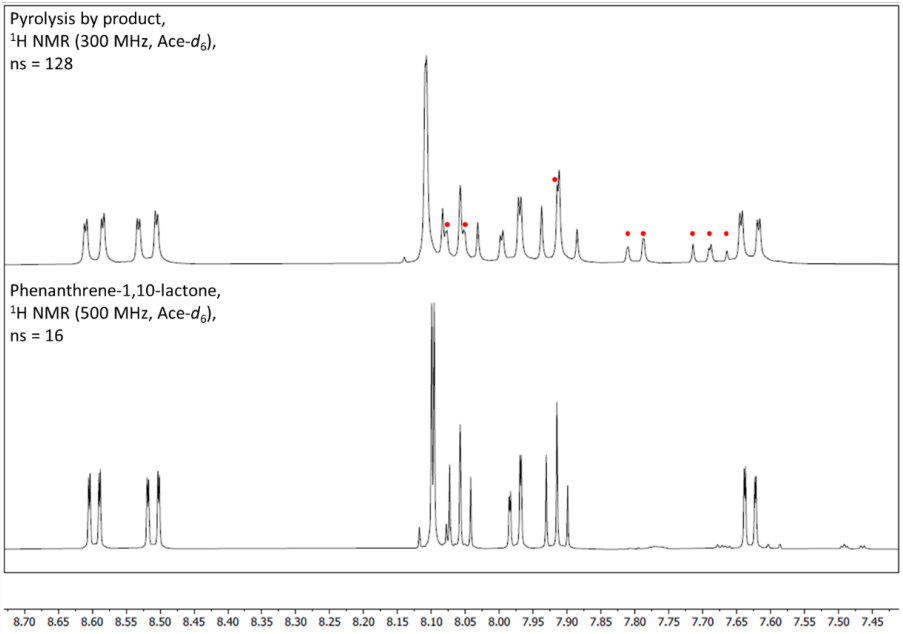
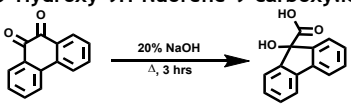


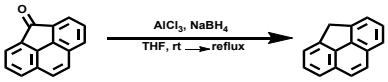
Figure S2.1 ^{1}H spectra of the product isolated in trace amount from the PbO pyrolysis of pyrene-4,5-dione (above) and that obtained for pure phenanthrene-1,10-lactone (below). Signals indicated with red dots in the upper spectrum correspond to residual pyrene-4,5-dione starting material.

9-Hydroxy-9H-fluorene-9-carboxylic acid (15)[93]



A suspension of phenanthrene-9,10-dione (0.96 g, 4.61 mmol) in aqueous NaOH (20% (2 g in 8 ml water), 48 mmol, 10 eq) was heated at 100°C for 3 hrs with vigorous stirring in contact with air. The dark suspension was diluted with an equal portion of water (10 ml), yielding a brown-green suspension. Careful neutralization with concentrated H_2SO_4 caused almost complete dissolution of the precipitate, at which point it was filtered while still warm. Further addition of H_2SO_4 yielded the glycolic acid as a pale yellow precipitate, which was filtered and dried in contact with air. Yield: 0.81 g, 3.60 mmol, 78.0%. ^{1}H NMR (500MHz, 1N NaOD in D_2O) δ 7.55 (dt, J = 7.50, 1.0Hz, 1H), 7.29 (dt, J = 7.50, 1.0Hz, 1H), 7.24 (td, J = 7.50, 1.0Hz, 1H), 7.15 (td, J = 7.50, 1.0Hz, 1H). ^{13}C NMR (125MHz, 1N NaOD in D_2O) δ 179.30, 147.72, 140.45, 129.13, 128.22, 123.20, 120.27, 84.26.

4*H*-Cyclopenta[*def*]phenanthrene (2)

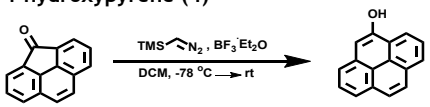


A 250 ml round bottom flask was flame dried under high vacuum, back-purged with argon and allowed to cool to room temperature. The flask was then charged with commercial, sublimated, anhydrous $AlCl_3$ (5g, mmol), cooled on an acetone/liquid nitrogen bath to -80 °C under dry nitrogen provided by a Schlenk line, and anhydrous THF* (75ml) added slowly. Minor gas formation was observed upon addition, which quickly cleared up. The flask was allowed to attain room temperature and the contents dissolved by manually swirling the flask. This yielded a near colorless 0.5 M solution of $AlCl_3$ in THF, which was used immediately in the reaction.*
A flame dried two-necked flask, fitted with a reflux condenser and closed off with rubber septa was purged with argon, cooled on an ice bath and charged with oxoCPP (1.6 g, 8.09 mmol) and granulated $NaBH_4$ (1.43 g, 38 mmol, 4.8eq).* To this was added the solution as prepared above (43.3 ml, 21.3 mmol, 2.6 eq), which was accompanied by minor evanescence. The flask was then put under a positive pressure of N_2 provided by a Schlenk line and the contents stirred. After approximately 10 minutes the yellow color had faded and the solution attained a grey color. The ice bath was thereupon replaced with an oil bath and heated to reflux (70 °C) for 3 days. The solution was then poured unto ice (~100 ml), extracted with DCM, the organic fractions washed with $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and eluted over a silica gel column using neat pentane to provide CPP as a colorless, crystalline plates (1.0 g, 5.26 mmol, 65%). ^{1}H NMR (400MHz, Ace-d_6) δ 7.89 (s, 2H), 7.86 (d, *J* = 8.00 Hz, 2H), 7.74 (d, *J* = 8.00 Hz, 2H), 7.66 (t, *J* = 8.00 Hz, 2H), 4.37 (s, 2H). HRMS (ESI-TOF) m/z: calc'd for C16H10 [M+H]+: 191.08608 found 191.08549. m.p. 113 – 114 °C, lit. 113.5 – 114.5 °C.[94]

* Anhydrous, ≥99.9%, inhibitor-free THF was obtained from Sigma Aldrich with a reported water content < 0.005%.

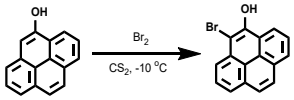
* Use of granulated $NaBH_4$ is preferred as much heavier evanescence is observed when using powdered $NaBH_4$. A slightly lower yield (60%) was observed when reducing 9-fluorenone with powered $NaBH_4$.

4-hydroxypyrene (4)



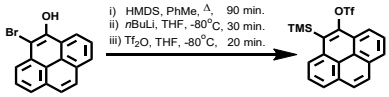
To a stirred mixture of 4*H*-cyclopenta[*d,e,f*]phenanthren-4-one (162 mg, 0.78 mmol) and $BF_3{\cdot}Et_2O$ (150 ul, 1.2 mmol, 1.5 eq) in DCM (10ml) was added trimethylsilyldiazomethane (2M in hexanes, 600 uL, 1.2 mmol, 1.5 eq) in DCM (15 mL) at -78°C over 20 minutes. The mixture was allowed to slowly attain room temperature overnight and then, poured into ice cold water (30 mL). The organic layer was separated and the aqueous layer extracted with chloroform (1x 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and charged on celite. The compound was eluted over a silica gel column using 1:50 EtOAC:pentane as eluent, to yield the title compound as a pale yellow solid which turns brown upon standing in contact with air. An analytical sample was obtained by recrystallization of the product from pentane:Et_2O. Yield: 86 mg, 0.39 mmol, 50.5%. m.p. 203-206 °C (dec.) ^{1}H NMR (500MHz, Acetone-d_6) δ 9.46 (brs, 1H), 8.64 (dd, J = 8.0, 1.0Hz, 1H), 8.29 (dd, J = 7.5, 1.0Hz, 1H), 8.11 (ABq, 2H, $\Delta\delta_{AB}$ = 0.025, J_{AB} = 9.0Hz), 8.09—8.04 (m, 2H), 7.94 (t, J = 7.5Hz, 1H), 7.51 (s, 1H). ^{13}C NMR (125MHz, Acetone-d_6) δ 152.94, 133.44, 132.02, 131.02, 131.90, 128.31, 127.89, 127.14, 126.56, 126.35, 126.31, 126.30, 123.90, 123.10, 121.50, 120.63. HRMS (ESI-TOF) m/z: calc'd for $C_{16}H_{11}O$ $[M+H]^+$: 219.08044, found 219.08025. m.p. 181 °C (dec.).

4-bromo-5-hydroxypyrene (8)



To a solution of 4-hydroxypyrene (360 mg, 1.7 mmol) in CS_2 (35 ml) at -10 °C was added dropwise a solution of Br_2 in CS_2 (0.3M, 5.5 ml, 1.7 mmol, 1 eq) and the solution stirred under an argon atmosphere for 6 hours. The solution was then quenched by the dropwise addition of sat. $Na_2S_2O_4$ (10 ml) at -10 °C. The organic phase was then separated, washed with brine and charged on celite. The compound was eluted over a silica gel column using EtOAc:Pentane (1:20) as eluent, to provide the title compound in the form of fine, pale yellow needles. Yield: 464 mg, 1.56 mmol, 94%. ^{1}H NMR (500 MHz, Ace-d_6) δ 8.79 (s, 1H), 8.63 (dd, J = 1.0, 8.0Hz, 1H), 8.33 (dd, J = 1.0, 7.5 Hz, 1H), 8.24 (dd, J = 1.0, 7.5 Hz, 1H), 8.07 (dd, J = 1.0, 7.5 Hz, 1H), 8.041 (s, 1H), 8.039 (s, 1H), 8.037 (t, J = 8.0Hz, 1H), 7.999 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, Ace-d_6) δ 150.09, 132.35, 132.28, 131.42, 128.67, 128.43, 128.11, 127.69, 127.34, 126.31, 125.13, 125.12, 124.38, 122.42, 121.62, 104.73. The compound was found to be unstable upon standing in contact with air and was used without further characterization.

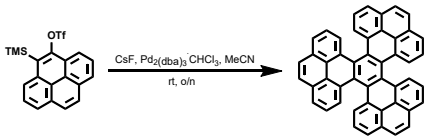
5-(trimethylsilyl)pyren-4-yl trifluoromethanesulfonate (9)



A solution of 4-bromo-5-hydroxypyrene (0.220 g, 0.74 mmol) and HMDS (0.17 mL, 0.43 mmol) in THF (5 mL) was refluxed for 90 minutes. The solvent and excess reagent were then removed under reduced pressure to yield a colorless oil. [^{1}H NMR (300MHz, $CDCl_3$) δ 8.62 (dd, J = 1.2, 7.8Hz, 1H), 8.48 (dd, J = 1.8, 7.8Hz, 1H), 8.22 (dd, J = 0.9, 7.5Hz, 1H), 8.13 (dd, J = 1.2, 7.5Hz, 1H), 8.09-8.01 (m, 4H), 0.54 (s, 9H)]. The residue was dissolved in THF (5 mL) and the solution cooled to -80 °C using an Ace:liquid N_2 bath. Then, *n*-BuLi in hexanes (0.77 mL, 2.46 M, 1.90 mmol, 2.6 eq.) added in one portion, stirring continued for 30 minutes and Tf_2O (0.16 mL, 0.93 mmol) then added. Stirring was continued for another 20 min. and the reaction then quenched by the addition of cold sat. $NaHCO_3$ (~5 mL). The layers were separated, the aqueous layer

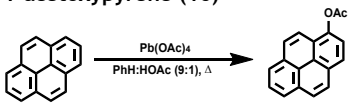
extracted with Et_2O (2x 10 mL), and the combined organic layers dried over Na_2SO_4, filtered and concentrated under reduced pressure. Column chromatography over silica gel (Et_2O:hexane, 1:500) afforded the product as a white solid. Yield: 143 mg, 0.35 mmol, 47%. ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 7.95, 0.90 Hz, 1H), 8.42 (d, *J* = 7.90 Hz, 1H), 8.26 (dd, *J* = 7.65, 0.85 Hz, 1H), 8.09 (t, *J* = 7.85 Hz, 1H), 8.06 (s, 1H), 8.05 (s, 1H), 8.03 (t, *J* = 7.65 Hz, 1H), 0.73 (s, 9H). ^{13}C NMR (125 MHz, $CHCl_3$) δ 148.76, 133.91, 131.63, 131.54, 131.07, 128.11, 127.66, 127.13, 126.94, 126.52, 126.33, 126.22, 125.86, 125.15, 124.02, 119.67, 119.00 (q, $^1J_{CF}$ = 320.68 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ 72.52. HRMS (ESI-TOF) m/z: calc'd for $C_{20}H_{18}F_3O_3SSi$ $[M+H]^+$: 423.06925, found 423.06906.

Tripyrenylene (1)-*C*$_2$



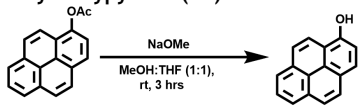
The compound obtained above (143 mg, 0.35 mmol) was dissolved in a mixture of dry MeCN (7 mL) and dry Et_2O (2 mL) together with $Pd_2(dba)_3{\cdot}CHCl_3$ (20 mg, 0.018 mmol). Then, finely powdered anhydrous CsF (170 mg, 1.1 mmol) was added in one portion and the mixture stirred at room temperature overnight under a N_2 atmosphere. The resulting suspension was allowed to settle, the supernatant withdrawn and the residue successively washed with MeCN (2x 5 mL) and Et_2O (1x 10 mL). The residue was then taken up in DCM (~10 mL), evaporated onto celite using a rotary evaporator at room temperature, and eluted over a short silica gel column using DCM:Pentane (1:10 → 1:3). Fractions containing the product (TLC, DCM:Pentane (1:10), R_f = 0.3) were evaporated at room temperature using a rotary evaporator to provide the title compound as a dark orange solid. Yield: 33 mg, 54.9 μmol, 47.1%. ^1H NMR (500 MHz, Tol-d_8) δ 8.43 (d, *J* = 8.0 Hz, 1H), 7.87 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.85 (s, 1H), 7.40 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, DCM-d_2) δ 131.83, 130.33, 128.78, 128.36, 127.35, 126.17, 125.35, 124.61. HRMS (ESI-TOF) m/z: calc'd for $C_{48}H_{25}$ $[M+H]^+$: 601.19563, found 601.19508.

1-acetoxypyrene (16)[95]



A solution of pyrene (3.0 g, 14.8 mmol) and $Pb(OAc)_4$ (7.3 g, 16.5 mmol) in glacial AcOH (12 mL) and anhydrous benzene (100 mL) was stirred under reflux for 3 h. The mixture was cooled, diluted with toluene (250 mL) and washed with H_2O (3 × 250 mL). The organic layer was charged on celite and eluted over a silica gel column using neat toluene as eluent to afford the 1-acetoxypyrene as a white solid (1.62g, 6.22mmol, 37.7%).^1H NMR (300MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 3H), 7.93 (ABq , ΔδAB = 0.03, J_{AB} = 9.0Hz, 2H), 7.83 – 7.90 (m, 3H), 7.68 (d, *J* = 13.5, 1H), 2.42 (s, 3H). ^{13}C NMR (126MHz, $CDCl_3$) δ 169.84, 144.25, 131.03, 130.86, 129.26, 128.09, 127.01, 126.96, 126.20, 125.50, 125.14, 124.96, 124.43, 123.03, 120.13, 119.68, 77.41, 77.16, 76.90, 21.06.

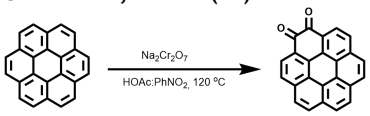
1-hydroxypyrene (10)



To a solution of 1-acetoxypyrene (646 mg, 2.48 mmol) in MeOH:THF (5:5) was added NaOMe (135 mg, 2.5 mmol) and the resultant bright yellow suspension stirred for 3 hrs. The reaction was quenched by the addition of 1M HCl (10 ml) and extracted with EtOAc. The organic phase

was dried over MgSO4, filtered, evaporated to driedness to provide 1-hydroxypyrene in quantitative yield. ^{1}H NMR (300MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.53 (d, *J* = 9.3Hz, 1H), 8.09-8.03 (m, 4H), 7.91 (ABq , ΔδAB = 0.108, J_{AB} = 9.0Hz, 2H), 7.91 (t, *J* = 7.8Hz, 1H) 7.67 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$) δ 152.76, 132.74, 132.72, 128.20, 126.95, 126.88, 126.74, 126.59, 125.92, 125.53, 125.02, 124.83, 124.59, 122.27, 119.60, 113.90.

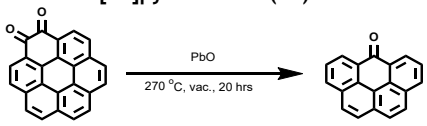
Coronene-1,2-dione (12)[96]

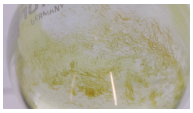


Over the course of 1 h a solution of $Na_2Cr_2O_7$ (4 g, 13.4 mmol) in glacial acetic acid (30 mL) was added dropwise to a boiling solution (~120 °C) of coronene (1 g, 3.3 mmol) in nitrobenzene (30 mL) and glacial acetic acid (5 ml). Another 30ml of glacial acetic acid were added and the solution allowed to cool to room temperature, and then further cooled on ice. The precipitate was collected by vacuum filtration and the residue washed with acetic acid, dilute H_2SO_4 and cold water. Yield of fine, dark-purple crystals 834 mg, 2.52 mmol, 76.5%. Of all solvents tried, only DMSO provided enough dissolution to allow for NMR measurements (Fig. S2.2 – S2.6).* ^{1}H NMR (850 MHz, DMSO-d6) 8.50 (s, 2H), 8.40 (d, *J* = 0.85, 8.0Hz, 2H), 8.33 (d, *J* = 8.5Hz, 2H), 8.28 (d, *J* = 8.0Hz, 2H), 8.15 (d, *J* = 8.5Hz, 2H). ^{13}C NMR (213MHz, DMSO-d_6) 178.86, 130.98, 129.91, 129.89, 128.18, 127.91, 127.76, 127.21, 126.08, 123.97, 122.64. Residual coronene signals were also observed: ^{1}H NMR (850 MHz, DMSO-d_6) 9.06 (s, 2H). ^{13}C NMR (213MHz, DMSO-d_6) 128.33, 126.38, 121.57. MALDI-TOF calc'd 330.068, found 329.760.

* The compound also dissolves in acetic acid with a brown color, in trifluoroacetic acid with a purple color and sulfuric acid with a dark-green color.

6*H*-Benzo[*cd*]pyren-6-one (14)





An intimate mixture of coronene-1,2-dione (700 mg, 2.12 mmol) and lead(II) oxide (7.7 g, 34.5 mmol, 16.3 eq.) was divided over four vials which had previously been flame dried under vacuum. The vials were shrink capped and evacuated to high vacuum prior to being heated on an aluminum heating block at 270 °C for 20 hours. Fine yellow crystals sublimated on the walls of the tubes above the metal block. The vials were allowed to attain room temperature, purged with argon and the contents extracted with chloroform. The extracts were evaporated on celite on a rotary evaporator and flushed over a silica gel column using neat DCM as eluent. The product eluting at R_f = 0.5 was isolated in the form of fine, yellow needles and identified as 6*H*-benzo[*cd*]pyren-6-one by 1D and 2D NMR (Fig. S2.7 and S2.8). Yield: 12.1 mg, 0.04 mmol, 1.9%. ^{1}H NMR (850 MHz, DMSO-d_6) 8.76 (d, *J* = 8.5Hz, 2H), 8.59 (d, *J* = 8.5Hz, 2H), 8.36 (d, *J* = 8.5Hz, 2H), 8.24 (d, *J* = 8.5Hz, 2H), 8.03 (t, *J* = 8.5Hz, 2H). ^{13}C NMR (HSQC, HMBC, 213MHz, DMSO-d_6) 182.93, 134.76, 131.83, 130.77, 128.40, 128.84, 128.71, 127.02, 126.97, 126.93, 119.86.

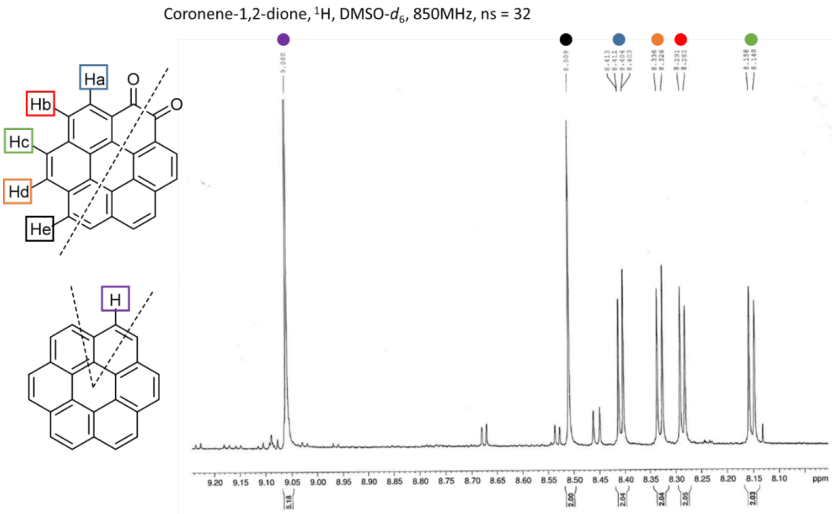


Figure S2.2 ^{1}H spectrum of coronene-1,2-dione **12** with protons indicated. Also observed is the signal of residual coronene starting material.

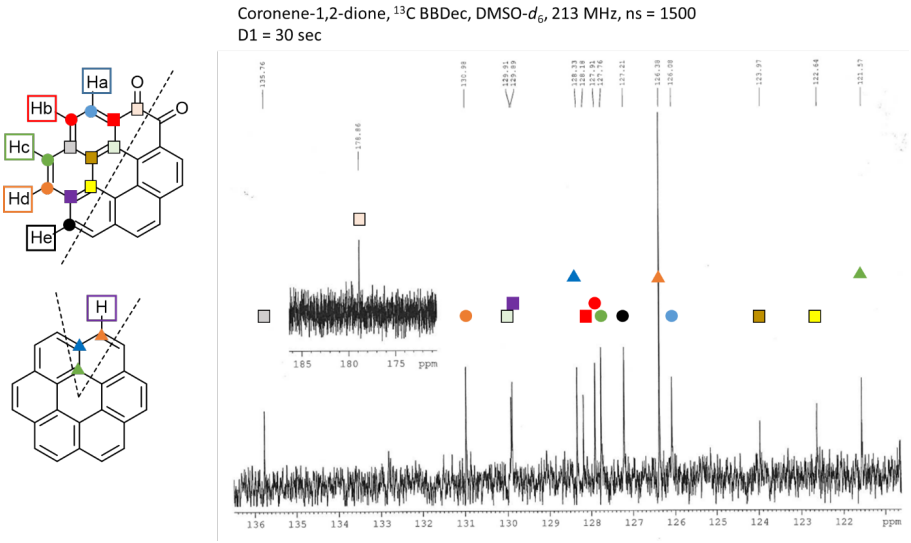


Figure S2.3 ^{13}C{^{1}H} spectrum of coronene-1,2-dione **12** with individual carbon signals labelled. Also observed are signals of residual coronene starting material.

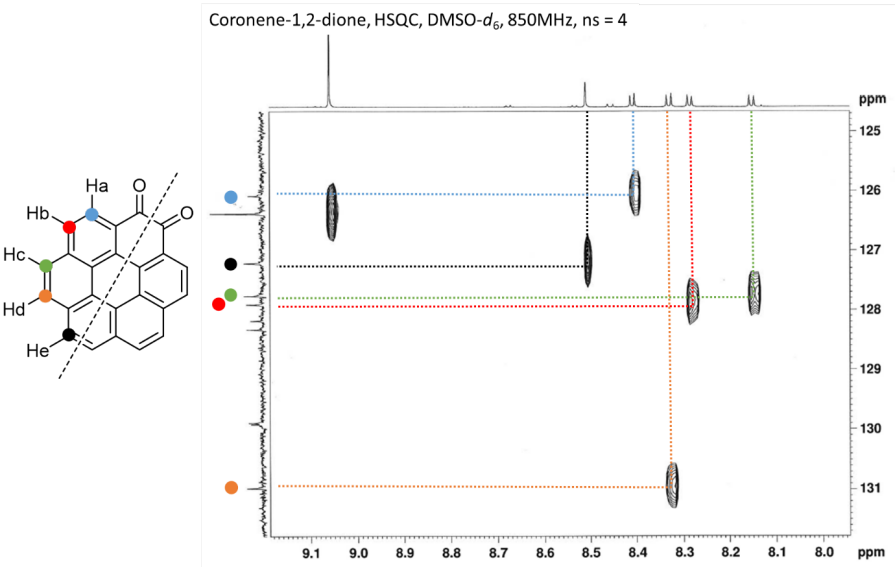


Figure S2.4 Part of the HSQC spectrum of coronene-1,2-dione **12** showing $^{1}J_{CH}$ couplings.

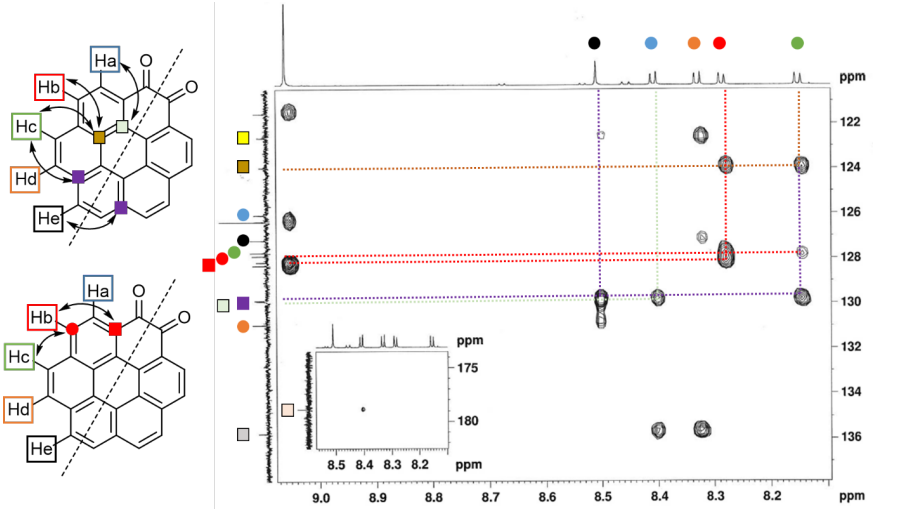


Figure S2.5 Part of the HMBC spectrum of coronene-1,2-dione **12** showing selected $^{3}J_{CH}$ couplings.

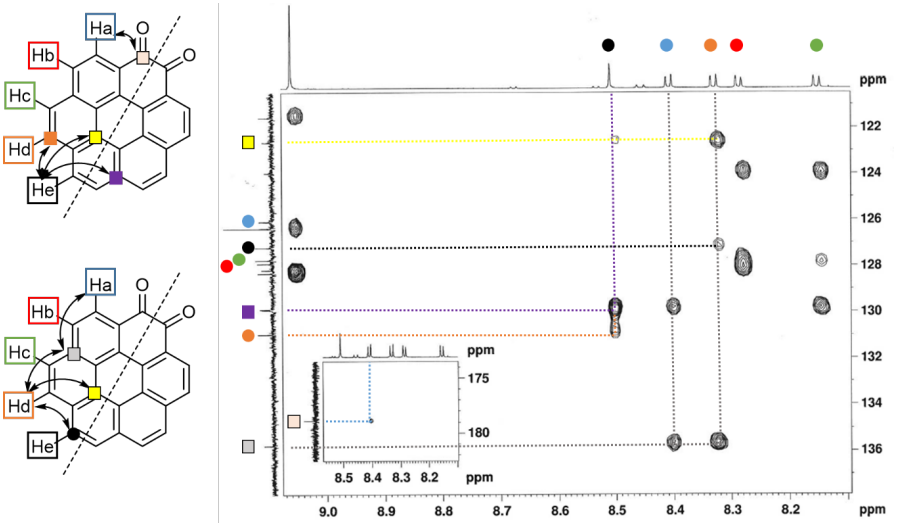


Figure S2.6 Part of the HMBC spectrum of coronene-1,2-dione **12** showing selected $^{3}J_{CH}$ couplings.

Figure S2.7 ^{1}H spectrum of 6*H*-benzo[cd]pyrenone **14**. Also observed are signals of unidentified side-product.

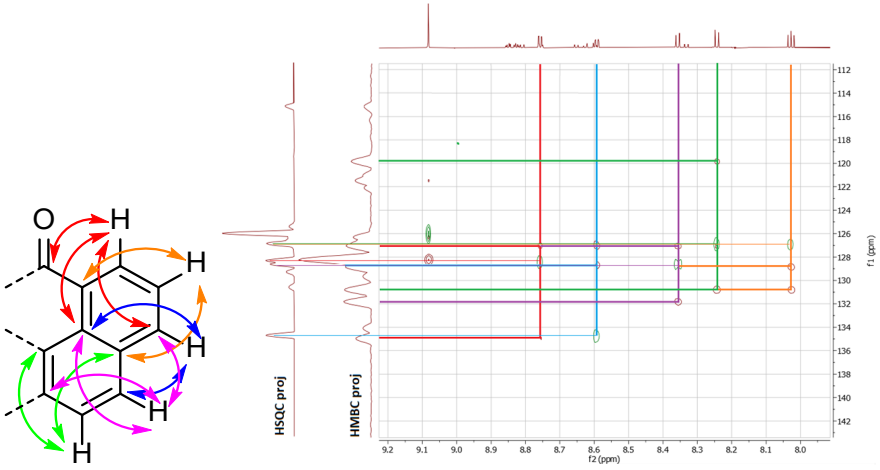


Figure S2.8 Overlay of the HSQC and HMBC spectra of 6*H*-benz[*cd*]pyrenone **14** showing $^{1}J_{CH}$ and $^{3}J_{CH}$ correlations as red and green cross peaks respectively. Note that there is cross peak overlap for the proton resonance at 8.24 ppm, due to $^{3}J_{CH}$ correlation across the symmetry plane (green lines).