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Oxidative synthesis of *ortho*-quinones from hydroxy-PAHs by stabilized formulation of 2-iodoxybenzoic acid (SIBX)

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ABSTRACT

Polycyclic aromatic phenols (PAPs or hydroxy-PAHs) are conveniently converted into their corresponding *ortho*-quinones using commercially available stabilized iodoxybenzoic acid (SIBX). SIBX provides a safer and commercially available alternative to IBX and displays the same selectivity with comparable or better yields in the oxidative dearomatization of phenols to *ortho*-quinone, including examples where formation of *para*-quinones is feasible. This *ortho*-selectivity from all positions of a hydroxy-group allowed for simple synthesis of the prerequisite hydroxy-PAHs by either photochemical cyclization of stilbenes or Pt-catalyzed cycloisomerization. The later synthesis involved a four-step sequence where suitably substituted biphenyls were prepared by Suzuki-Miyaura cross-coupling, followed by the Corey–Fuchs protocol and cycloisomerization by a catalytic amount of $PtCl_2$. 2- and 4-methylphenanthene were also prepared for the first time using this method.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) become environmental pollutants when introduced into the aquatic environment through accidental oil spills or discharge of produced water from the offshore oil wells [1]. Small PAHs (2–5 rings) are partly soluble in water and are increasingly released to the ocean towards the tail production from offshore oil wells [2]. Petrogenic sources such as crude oil and coal contain substantial amounts of low molecular weight PAHs and their alkylated homologs predominate over the unsubstituted parent PAHs [3]. Moreover, alkylated phenanthrenes are known to be more toxic than phenanthrene [4] and the position of the alkyl groups on PAHs affects the toxicity of fish embryos [4,5].

The major metabolic pathways of polycyclic aromatic hydrocarbons (PAHs) by cytochrome P450 (CYP) and other metabolic enzymes involve radical cations, diol-epoxides, and *ortho*-quinones [6,7]. The metabolic processes from the medium-sized benzo [*a*] pyrene [7] to the smaller naphthalene [8] and even benzene [9] involve these three main intermediate-type species to form quinone isomers. *Ortho*-quinones are highly reactive and may form conjugates or covalent adducts with DNA [10]. Some studies also show that the point of oxidation varies from species to species for the same PAH due to the presence of various cytochrome isoforms [11]. Thus different regio-specificities were found from the various CYPs, influencing the toxicity of the mother PAHs.

These kinds of environmental and metabolic studies depend on organic synthesis to provide chemicals for exposure studies and/or reference compounds to help analyze the fate of the mother PAHs in organisms. Pure compounds are also needed as standards to identify the same compounds in a more complex matrix in exposure studies. The need for *ortho*-quinones motivated this study on the transformation of readily available small (2–4 rings) hydroxy-PAHs to *ortho*-quinone metabolites which are used to study their effect on fish embryos [12].

Quinones may be synthesized by different oxidizing agents from phenols. For instance, oxidation of phenols by Fremy's radical (potassium nitrosodisulfonate) [13] or methyltrioxorhenium (VII), $MeReO_3$-catalyzed oxidation [14], leads to the formation of either *para*-quinones, or *ortho*-quinones if the position *para* to hydroxy is blocked. Oxidation of phenols to polycyclic aromatic quinones with powdered Oxone® in the presence of catalytic amounts of 2-iodobenzenesulfonic acid (pre-IBS) give high yields and good *ortho*-selectivity, but with some formation of *para*-quinones when feasible (See Fig. 2) [15].

Pettus and colleagues [16] reported regioselective oxidation of phenols with stoichiometric amounts of iodoxybenzoic acid (IBX)

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to *ortho*-quinones. IBX has also been used for the synthesis of bioactive compounds such as flavonoid derivatives in high yield [17]. Harvey and colleagues [18] found that oxidation of polycyclic aromatic phenols by stoichiometric amounts of IBX in non-aqueous DMF afforded *ortho*-quinones in moderate yields, while oxidation with [bis(trifluoro-acetoxy)iodo]benzene (BTI) in aqueous DMF gave *para*-quinones. Herein we report the use of commercially available stabilized IBX (SIBX) as a non-explosive version of IBX [19,20], to synthesize *ortho*-quinones from a wide selection of 2–4 -ring hydroxy-PAHs by a modified procedure at room temperature avoiding DMF.

2. Result and discussion

Chrysenols are readily available through oxidative photochemical cyclization of stilbenoids. 1-, 2-, and 3-chrysenol (**5a-c**) were prepared as previously described [21], as well as 3-phenanthrenol (**6c**) [22]. 6-Chrysenol (**5d**) was prepared by a reaction between iodonaphthalene and 2-chloro-acetophenone [23].

A serious drawback of photochemical cyclization of stilbenes is the lack of selectivity between the 2- and 4-positions (Fig. 1) unless blocking-groups or eliminative protocols are used [24]. To avoid a very difficult separation of isomers, we decided to make 2- and 4-hydroxyphenanthrene **(6b,a)** by Pt-catalyzed cycloisomerization of biaryls with an *ortho*-alkyne unit [25], as described below. This method depends on regioselectivity between the 1- and 3-position of the product but are regiospecific for the 2- and 4-position and is thus a complementary method to photocyclization (Fig. 1).

The synthesis of **6a,b** along with the corresponding methylphenanthrenes (**4c,d**) are described in Scheme 1. Initially, 2-bromobenzaldehyde was subjected to a Suzuki-Miyaura cross-coupling reaction [26] with commercially available phenylboronic acids to give the biphenyl derivatives **1a-d.** Conversion of the aldehydes to alkynes **3** was achieved by following the Corey–Fuchs protocol [27]. In general, good to excellent yields were obtained over the two steps of alkynylation to give products **3a-d**. Cycloisomerization [25,28] of **3a-d** with 5 mol% of $PtCl_2$ at 80 °C in toluene for 12 h resulted in formation of the desired carbon-carbon bond. This cyclization proceeded well, providing the targeted 4- and 2-methoxyphenanthrene (**4a,b** respectively). Similarly, 4- and 2-methylphenanthrene (**4c,d**) were prepared by the same method. It should be noted that the analogous cyclization of 1-ethynyl-2-phenylnaphthalenes to chrysenes was previously reported to give higher yields under microwave heating to 150 °C in a sealed tube than ordinary reflux conditions, which leads to incomplete

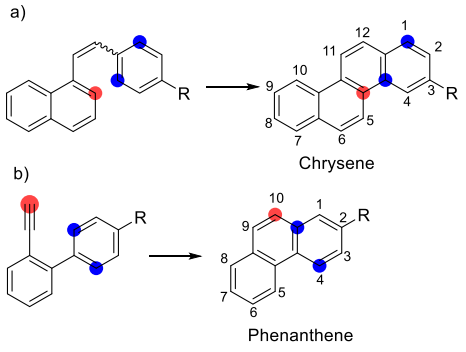


Fig. 1. Substituted PAHs are usually prepared either by a) photochemical 6π-electrocyclization or b) transition metal-catalyzed cyclization of alkyne. Both methods have two possible reaction sites (blue dots). A single product is obtained when one site is blocked by the substituent, or both sites are identical by symmetry. Different scaffolds make this happen in a) the 1- and 3-positions or b) the 2- and 4-positions.

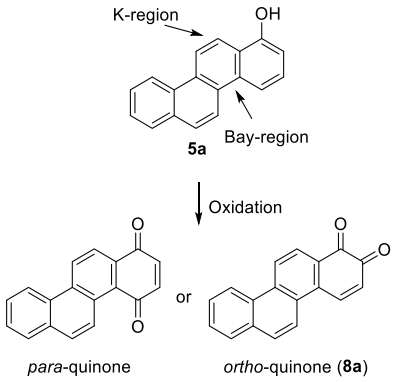


Fig. 2. Structural regions of chrysene, and possible oxidations of 1-chrysenol (**5a**).

conversion [29]. Finally, **4a,b** were readily demethylated using BBr_3 to 4- and 2-phenanthrenol **(6a,b)**.

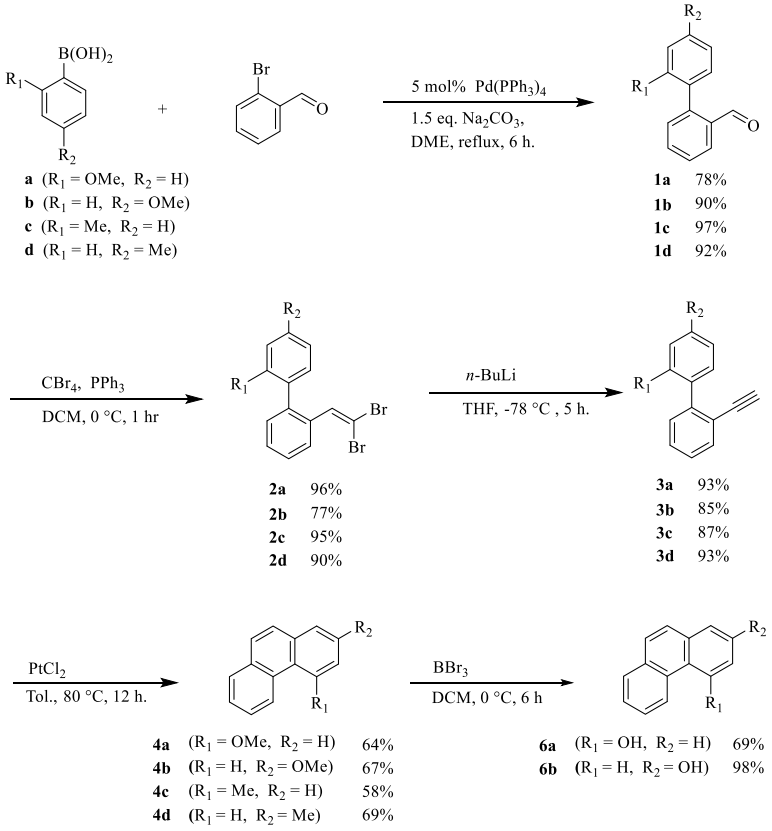
The synthesized chrysenols (**5a-d**), phenanthrols (**6a-c**) and commercially available 2-and 1-naphthol (**7a,b**) were used as starting materials to study the selectivity of SIBX and provide the desired *ortho*-quinones.

From previous studies of IBX oxidation [18,30] phenols have been shown to react with IBX to produce intermediates, which transfer oxygen to the *ortho*-site via rearrangement, eventually forming *ortho*-quinones. Other oxidants will usually form *para*-quinones or a mixture of the two isomers (Fig. 2) from phenols at the 1- or 4-positions [15,18,31]. However, the use of IBX rises safety concerns related to its preparation and violent decomposition under impact or heating [32]. Mixing IBX with benzoic acid and isophthalic acid creates a stabilized formulation (SIBX) that is now commercially available. Quideau and co-workers [19] used SIBX to safely oxidize alcohols into aldehydes and ketones with yields comparable to those obtained with IBX, and SIBX were as effective and selective as IBX in various solvents in different transformations [33].

We dissolved the hydroxy-PAHs in anhydrous THF, added 1 equivalent of SIBX and stirred the suspension at room temperature in darkness to provide *ortho*-quinones (Table 1). Chrysenols reacted slowly and needed 48 h, while the more reactive phenanthrols and naphthols had completed the reaction overnight.

Chrysen-1-ol **5a** (entry 1) was oxidized to **8a** without traces of *para*-quinone. The same *ortho*-selectivity was observed for phenanthrene (entry 5) and naphthalene (entry 9). Oxidation of hydroxy-groups in 2- and 3-position cannot form *para*-quinones. This oxidation to *ortho*-quinones is still often referred to as regioselective [15,18]. This refers to the lack of over-oxidation that break the quinone-ring and digest parts of the molecule. SIBX provided efficient conversion of the hydroxy-group in 2-position (entry 2, 6, 8) to ortho-quinones. The similar conversion of **6b**–**9b** was achieved in even higher yields with oxone®/pre-IBS [15].

PAHs have common structural regions that behave similarly in metabolism and have similar reactivity (Fig. 2). The bay-region are important for carcinogenicity, while the K-region is typically the most chemically reactive place for oxidations [11]. In our examples, the bay-region can be accessed from a hydroxy-group in both 3-position and 4-position (entry 3, 5, 7). The K-region, which usually are more chemically reactive due to less aromatic stabilization of the double bond, were accessed in entry 4 where **5d** was converted to **8c** in 94%. The K-region of phenanthrene is highly reactive. Phenanthrene-9,10-dione is not included in this study, as it can be accessed directly from phenanthene [34].



Scheme 1. Preparation of methyl- and hydroxy-phenanthrenes.

The *ortho*-selectivity of SIBX allows for a simplified synthesis of starting materials from either photochemical cyclization of stilbenes (1- and 3-position) or Pt-catalyzed cycloisomerization of *o*-ethynebiphenyls (2- and 4-position) (Fig. 1).

Phenanthrenes **6a,b,c** have previously been oxidized by IBX in DMF to the corresponding ortho-quinones (51–62%) [18]. Our higher yields (entry 5, 6, 7) suggest that SIBX in THF is preferable not only for safety and convenience, but also to give better conversion.

Naphthalene-1,2-quinone (**10**) is reported to co-elute with 2-iodobenzoic acid formed in the IBX reaction, making purification difficult [16]. We observed the same problem, together with some decomposition of **10** on the column. However, after extraction, the crude product could be recrystallized from EtOAc, providing orthoquinone **10** in excellent yield from both 2-position (entry 8, 85%) and 1-position (entry 9, 93%).

3. Conclusion

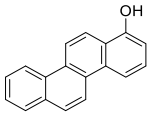
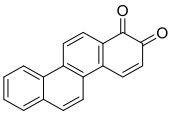
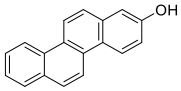
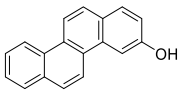
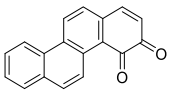
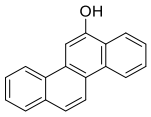
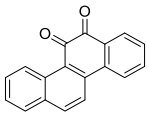
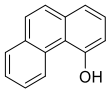
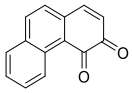
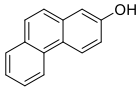
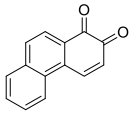
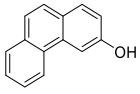
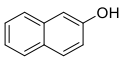
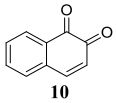
Ortho-quinones are common metabolites of PAHs. Stabilized IBX (SIBX) oxidizes hydroxy-PAHs to the corresponding *ortho*-quinones in yields equal to or better than IBX. This provides safe reaction conditions and easy workup with good to excellent yields. The strong regioselectivity of SIBX in this oxidation reaction allows for a choice in starting materials that are readily available from either photochemical oxidation of stilbenes, or Pt-catalyzed cycloisomerization of *o*-ethynebiphenyls.

4. Experimental section

4.1. General

All reactions were carried out under N_2 and in oven-dried glassware. The anhydrous solvents were purchased commercially (THF, Et_2O, CH_2Cl_2, MeCN, DMF, Toluene). SIBX is "Stabilized IBX", a non-explosive white powder composed of benzoic acid (22%), isophthalic acid (29%), and *o*-iodoxybenzoic acid itself (49%) [19], was purchased from Sigma-Aldrich as containing 45 wt% IBX. The photochemical reactions were performed in a 400 W medium pressure mercury-lamp supplied by Photochemical reactor Ltd. The synthesized compounds were purified by flash chromatography using silica gel 40–63 μm. Solvent volumes in the general procedures were scaled in accordance with the amount of starting material. NMR spectra were recorded on a 400 MHz Bruker AVANCE III spectrometer. Chemical shifts (δ) are given in ppm relative to the TMS signal (0.00 ppm) for ^{1}H NMR and the solvent signal for ^{13}C NMR ($CDCl_3$ at 77.0 ppm and DMSO-d_6 at 39.52 ppm) with coupling constants (J) in Hz. Compounds **1a**, **1b, 6a, 6c, 9a** and **10** have chemical shift in ppm related to the solvent peak (7.26 ppm) in $CDCl_3$. All NMR spectra were processed using Topspin NMR software. Melting points were measured on Büchi MP-3 melting point apparatus (uncorrected). IR spectra were measured as neat compound on an Agilent Carey 630 FTIR with an ATR sampling module. Absorption strength was designated as vs (very strong), s (strong), m (medium) or w (weak). HRMS analysis were performed on an Orbitrap Exploris 120 with a APCI probe by

Table 1
Oxidation of hydroxy-PAHs by SIBX to *ortho*-quinones.

Entry	Hydroxy-PAH	*Ortho*-quinone	Yield (%)
1	 **5a**	 **8a**	58
2	 **5b**	**8a**	42
3	 **5c**	 **8b**	60
4	 **5d**	 **8c**	94
5	 **6a**	 **9a**	59
6	 **6b**	 **9b**	84
7	 **6c**	**9a**	77
8	 **7a**	 **10**	85
9	 **7b**	**10**	93

Thermo Fischer Scientific; or an JMS T100 GC-AccuTOF™ EI-TOF from JEOL.

4.2. General procedure A for Suzuki-Miyaura cross-coupling to biphenyls **1** [26]

To a solution of 2-bromobenzaldehyde (1.00 g, 5.40 mmol) in DMF (40 mL) was added substituted phenylboronic acid (1.2 equiv), tetrakis-(triphenylphosphine)-palladium (5 mol%) and Na_2CO_3 (1.5 equiv.). The solution was stirred and refluxed at 153 °C in an oil bath for 6 h. After completed reaction, the solution was cooled to room temperature, then partitioned between satd. $NaHCO_3$ (14 mL) and EtOAc (14 mL), and the mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (heptane/diethyl ether = 95:5) to afford the products (**1a-d).**

4.2.1. 2-(2-Methoxyphenyl)benzaldehyde ***(1a)***

Following general procedure A, (2-methoxyphenyl) boronic acid (1.97 g, 13.0 mmol) and 2-bromobenzaldehyde (2.00 g, 10.8 mmol) afforded the cross-coupled product 1a (1.81 g, 78%) as yellow oil. NMR data were in agreement with previously reported data [25].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3H), 6.98 (d, J = 8.2 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.30 (dd, J = 7.3, 1.7 Hz, 1H), 7.37 (dd, J = 6.5, 1.2 Hz, 1H), 7.43 (td, J = 7.8 Hz, 1.8 Hz, 1H), 7.48 (td, J = 7.6 Hz, 1.1 Hz, 1H), 7.64 (td, J = 7.6 Hz, 1.5 Hz, 1H), 8.02 (dd, J = 7.8, 1.1 Hz, 1H), 9.82 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 110.5, 120.9, 126.5, 126.7, 127.6, 129.8, 131.1, 131.3, 133.6, 133.9, 141.7, 156.4, 192.5 ppm; IR (ATR): 3061 (w), 3003 (w), 2937 (w), 2837 (w), 2750 (w), 1692 (vs), 1594 (m), 1496 (m), 1477 (m), 1433 (m), 1393 (w), 1251 (s), 1233 (s), 1195 (m), 1024 (m), 1002 (w), 828 (m), 750 (vs), 729 (m) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0910; found 213.0910.

4.2.2. 2-(4-Methoxyphenyl)benzaldehyde (**1b**)

Following general procedure A, (4-methoxyphenyl) boronic acid (2.95 g, 19.5 mmol) and 2-bromobenzaldehyde (3.00 g, 16.2 mmol) afforded **1b** (3.10 g, 90%) as yellow liquid. NMR spectral data were in agreement with those previously reported [35].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 7.00 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.43 (m, 2H), 7.60 (t, J = 7.7 Hz, 1H), 8.00 (d, J = 7.8, 1H), 9.99 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 113.8127.2, 127.5, 129.9, 130.7, 131.2, 133.4, 133.6, 145.5, 159.6, 192.4 ppm; IR (ATR): 3063 (w), 3028 (w), 2954 (w), 2923 (w), 2837 (w), 1688 (s), 1609 (m), 1596 (m), 1514 (m), 1474 (m), 1391 (w), 1244 (s), 1177 (m), 1032 (m), 999 (w), 834 (m), 764 (m), 713 (w) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0910; found 213.0910.

4.2.3. 2-(2-Methylphenyl)benzaldehyde (**1c**)

Following general procedure A, (2-methylphenyl) boronic acid (2.20 g, 16.2 mmol) and 2-bromobenzaldehyde (2.50 g, 13.5 mmol) afforded the cross-coupled product **1c** (2.53 g, 97%) as yellow liquid. ^{1}H NMR data were in agreement with those previously reported [36].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 7.11 (dd, J = 7.5 Hz, 1.2 Hz, 1H), 7.17–7.28 (m, 4H), 7.42 (t, J = 7.6 Hz, 1H), 7.56 (td, J = 7.6 Hz, 1.5 Hz, 1H), 7.95 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 9.67 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8, 127.1, 127.2, 128.8, 129.7, 130.4, 133.2, 133.3, 134.4, 137.6, 145.6192.0 ppm; IR (ATR): 3061 (w), 2927 (w), 2857 (w), 1691 (vs), 1594 (m), 1571 (m), 1450 (m), 1394 (m), 1247 (s), 1195 (m), 1078 (w), 1004 (w), 822 (m), 754 (s), 702 (w) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_{13}O$ $[M+H]$+197.0961; found 197.0961.

4.2.4. 2-(4-Methylphenyl)benzaldehyde (**1d**)

Following general procedure A, (4-methylphenyl) boronic acid (2.20 g, 16.2 mmol) and 2-bromobenzaldehyde (3.07 g, 16.6 mmol) afforded **1d** (3.02 g, 92%) as yellow liquid. NMR data were in agreement with those previously reported [37].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.26 (s, 4H), 7.41–7.47 (m, 2H), 7.60 (td, J = 7.5 Hz, 1.5 Hz, 1H), 8.00 (dd, J = 7.8 Hz, 1.1 Hz, 1H), 9.99 (s, 1H) ppm: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 127.39, 127.4, 129.0, 130.6, 133.4, 133.6, 134.7, 137.91, 145.8, 192.4 ppm; IR (ATR): 3025 (w), 2920 (w), 2847 (w), 2750 (w), 1689 (vs), 1596 (m), 1515 (m), 1475 (m), 1448 (m), 1252 (m), 1193 (m), 1160 (w), 1043 (w), 1005 (m), 821 (s), 761 (s), 714 (w) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_{13}O$ $[M+H]^+$ 197.0961; found 197.0961.

4.3. General procedure B for synthesis of 2-(2,2-dibromovinyl)-1, 1′-biphenyl derivatives **2** [25]

CBr_4 (2.5 equiv.) was added to a solution of PPh_3 (5 equiv.) in CH_2Cl_2 (150 mL) and the resulting yellow mixture was stirred for 10 min at 0 °C. A solution of phenyl benzaldehyde **1** (1.00 g, 5.09 mmol) in CH_2Cl_2 (50 mL) was slowly added and stirring was continued for 1 h. The reaction was then quenched with brine. The aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL), the combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) to obtain dibromide derivatives **2a-d**.

4.3.1. 2-(2,2-Dibromovinyl)-2′-methoxy-1,1′-biphenyl (**2a**)

Following general procedure B, a solution of **1a** (1.81 g, 8.53 mmol) in CH_2Cl_2 was slowly added to a mixture of CBr_4 (7.07 g, 21.3 mmol) and PPh_3 (11.2 g, 42.7 mmol) in CH_2Cl_2. After completion of the reaction, workup afforded **2a** (2.90 g, 96%) as a yellow viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 6.96 (dd, J = 8.2, 0.8 Hz, 1H), 7.02 (td, J = 7.5, 1.0 Hz, 1H), 7.13 (s, 1H), 7.13 (dd, J = 7.6, 1.7 Hz, 1H), 7.29–7.31 (m, 1H), 7.34–7.40 (m, 3H), 7.64–7.67 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 89.9, 83.1, 110.9, 120.6, 127.1, 128.35, 128.4, 129.1, 129.4, 130.5, 131.3, 135.2, 137.4, 138.1, 156.6 ppm; IR (ATR): 3058 (w), 3019 (w), 2932 (w), 2833 (w), 1601 (m), 1460 (m), 1432 (m), 1236 (s), 1177 (m), 1123 (w), 1027 (m), 887 (m), 834(m), 807 (m), 782 (m), 744 (vs) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{15}H_{13}Br_2O$ $[M+H]^+$ 366.9328; found 366.9329.

4.3.2. 2-(2,2-Dibromovinyl)-4′-methoxy-1,1′-biphenyl (**2b**)

Following general procedure B, a solution of **1b** (3.10 g, 14.6 mmol) in CH_2Cl_2 was slowly added to a mixture of CBr_4 (12.1 g, 36.5 mmol) and PPh_3 (19.1 g, 42.7 mmol) in CH_2Cl_2. After completion of the reaction, workup afforded **2b** (4.01 g, 77%) as a colorless viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 6.96–6.98 (m, 2H), 7.21 (s, 1H), 7.25–7.28 (m, 2H), 7.33–7.39 (m, 3H), 7.65–7.67 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 90.5, 113.7, 126.7, 128.6, 129.2129.8, 130.7,12.5, 133.8, 137.7, 140.8, 159.2 ppm; IR (ATR): 3059 (w), 3021 (w), 3000 (w), 2931 (w), 2835 (w), 1604 (m), 1511 (m), 1456 (m), 1439 (m), 1240 (s), 1176 (m), 1105 (m), 1030 (m), 835 (s), 808 (m), 763 (s), 746 (m), 687 (m) cm^{-1}; HRMS (APCI) *m/z*: Calcd for $C_{15}H_{13}Br_2O$ $[M+H]^+$ 366.9328; found 366.9329.

4.3.3. 2-(2,2-Dibromovinyl)-2′-methyl-1,1′-biphenyl (**2c**)

Following general procedure B, a solution of **1c** (2.00 g, 10.2 mmol) in CH_2Cl_2 was slowly introduced to a mixture of CBr_4 (8.5 g, 25.5 mmol) and PPh_3 (13.4 g, 51.0 mmol) in CH_2Cl_2. After completion of the reaction, workup afforded **2c** (3.42 g, 95%) as a yellow viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 7.01 (s, 1H), 7.07 (d, J = 7.4 Hz, 1H), 7.19–7.29 (m, 4H), 7.37–7.39 (m, 2H), 7.74–7.76 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 90.4, 125.6, 127.1, 128.4, 128.6129.6, 129.9, 130.1, 134.5, 136.3, 136.6, 139.8, 141.3 ppm; IR (ATR): 3055 (w), 3022 (w), 2919 (w), 2863 (w), 1596 (w), 1514 (w), 1472 (m), 1444 (m), 1251 (w), 1184 (w), 1006 (m), 887 (m), 858 (m), 820 (s), 783 (m), 755 (s) 698 (w) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{15}H_{13}Br_2$ $[M+H]^+$ 350.9379; found 350.9379.

4.3.4. 2-(2,2-Dibromovinyl)-4′-methyl-1,1′-biphenyl (**2d**)

Following general procedure B, a solution of **1d** (3.00 g, 15.3 mmol) in CH_2Cl_2 was slowly introduced to a mixture of CBr_4 (12.7 g, 38.2 mmol) and PPh_3 (20.1 g, 76.5 mmol) in CH_2Cl_2. After completion of the reaction, workup afforded **2d** (4.92 g, 90%) as a colorless viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 7.19 (s, 1H), 7.20 (s, 4H), 7.30–7.35 (m, 3H), 7.63–7.56 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 90.5, 126.8, 128.6, 129.2, 129.4, 129.7, 129.8, 133.1, 137.2, 137.6, 141.0 ppm; IR (ATR): 3051 (w), 3018 (w), 1590 (w), 1483 (w), 1437 (m), 1311 (w), 1278 (w), 1188 (m), 1114 (s), 1026 (w), 996 (m), 859 (w), 753 (m), 718 (s), 693 (vs) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{15}H_{13}Br_2$ $[M+H]^+$ 350.9379; found 350.9379.

4.4. General procedure C for the synthesis of alkynes **3** [25]

A 2.5 M *n*-BuLi solution of in hexane (2.5 equiv.) was added to a solution of 2'-(2,2-Dibromo-vinyl)-biphenyl derivative, **2a-d** (1.0 g, 1 equiv.) in THF (15 mL) at −78 °C. Stirring was continued at that temperature for 5 h under N_2 atmosphere. The cold mixture was quenched with water and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* before the crude product was purified by flash chromatography (heptane/ethyl acetate 98:2) to give the alkyne **3a-d**.

*4.4.1. 2-Ethynyl-2′-methoxy-1,1′-biphenyl **(3a)***

Compound **2a** (2.90 g, 8.19 mmol) in THF (45 mL) was treated with *n*-BuLi (8.19 mL, 20.5 mmol, 2.5 M in hexane) according to the general procedure C to obtain **3a** (1.50 g, 93%) as colorless viscous oil. NMR date were in agreement with those previously reported [25].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92 (s, 1H), 3.78 (s, 3H), 6.99 (dd, J = 8.3 Hz, 0.8 Hz, 1H),7.03 (t, J = 7.5 Hz, 1.0 Hz, 1H), 7.27–7.42 (m, 5H), 7.60 (dd, J = 7.7 Hz, 0.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 79.1, 83.1, 111.0, 120.2, 122.0, 126.9, 128.4, 129.1, 129.5, 130.3, 131.2, 132.9, 141.6, 156.7 ppm; IR (KBr): 3282 (s), 3062 (w), 2956 (m), 2934 (m), 2934 (m), 2835 (m), 2106 (w), 2054 (w), 1696 (w), 1602 (m), 1499 (m), 1474 (m), 1431 (m), 1252 (s), 1234 (s), 1180 (m), 1028 (m), 753 (vs) cm^{-1}; HRMS(EI,TOF) *m/z*: Calcd for $C_{15}H_{12}O$ $[M]^+$ 208.0883; found 208.0892.

*4.4.2. 2-Ethynyl-4′-methoxy-1,1′-biphenyl **(3b)***

Compound **2b** (4.00 g, 11.4 mmol) in THF (63 mL) was treated with *n*-BuLi (11.4 mL, 28.6 mmol, 2.5 M in hexane) according to the general procedure C to obtain **3b** (1.87 g, 85%) as liquid. NMR data were in agreement with those previously reported [38].

^{1}H NMR (400 MHz, *CDCl$_3$*): δ = 3.03 (s, 1H), 3.80 (s, 3H), 6.94 (dt, J = 8.8 Hz, 2.1 Hz, 2H), 7.21–7.25 (m, 1H), 7.31–7.35 (m, 2H), 7.51 (dt, J = 8.8 Hz, 2.1 Hz, 2H), 7.58 (d, J = 7.4 Hz, 1H) ppm; ^{13}C NMR (*CDCl$_3$*): δ = 55.1, 80.0, 80.3, 113.4, 120.2, 126.5, 128.9, 129.4, 130.3132.6, 133.8, 143.9, 159.1 ppm; IR (KBr): 3283 (s), 3059 (m), 2956 (m), 2933 (m), 2835 (m), 2103 (w), 2053 (w), 1610 (m), 1516 (m), 1476 (m), 1440 (m), 1293 (m), 1245 (s), 1178 (m), 1133 (w), 1035 (m), 833 (m), 760 (s) cm^{-1}; HRMS(EI_TOF) *m/z*: Calcd for $C_{15}H_{12}O$ $[M]^+$ 208.0883; found 208.0894.

*4.4.3. 2-Ethynyl-2′-methyl-1,1′-biphenyl **(3c)***

Compound **2c** (2.12 g, 6.00 mmol) in THF (32 mL) was treated with *n*-BuLi (6.00 mL, 15.0 mmol, 2.5 M in hexane) according to the general procedure C to obtain **3c** (1.02 g, 87%) as a liquid.

^{1}H NMR (400 MHz, *CDCl$_3$*): δ = 2.17 (s, 3H), 2.87 (s, 1H), 7.17–7.27 (m, 5H), 7.28 (td, J = 7.6 Hz, 1.5 Hz, 1H), 7.36 (td, J = 7.5 Hz, 1.5 Hz, 1H), 7.58 (dd, J = 7.6 Hz, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 79.9, 82.6, 121.7, 125.3, 126.9, 127.6, 128.5, 129.5, 129.7, 132.8, 136.0, 140.4, 144.9 ppm; IR (KBr): 3286 (s), 3060 (m), 2957 (m), 2927 (m), 2871 (m), 2230 (w), 2108 (w), 1922 (w), 1595 (w), 1474 (m), 1439 (m), 1265 (w), 1123 (m), 1006 (m), 864 (w), 757 (s), 726 (m) cm^{-1}; HRMS(EI-TOF) *m/z*: Calcd for $C_{15}H_{11}$ $[M - H]^+$ 191.0866; found 191.0878.

*4.4.4. 2-Ethynyl-4′-methyl-1,1′-biphenyl **(3d)***

Compound **2d** (4.92 g, 13.8 mmol) in THF (75 mL) was treated with *n*-BuLi (13.8 mL, 34.5 mmol, 2.5 M in hexane) according to the general procedure C to obtain **3d** (2.48 g, 93%) as a liquid.

^{1}H NMR (400 MHz, *CDCl$_3$*): δ = 2.27 (s, 3H), 2.90 (s, 1H), 7.09–7.15 (m, 3H), 7.22–7.24 (m, 2H), 7.37 (dt, J = 8.1 Hz, 1.8 Hz, 2H), 7.48 (dt, J = 7.7 Hz, 0.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 80.1, 83.2, 120.3, 126.7, 128.7, 128.9, 129.0, 129.5, 133.8, 137.2, 137.3, 144.3 ppm; IR (KBr): 3283 (s), 3057 (m), 3023 (m), 2956 (m), 2923 (m), 2863 (m), 2105 (w), 1904 (w), 1614 (w), 1516 (m), 1476 (m), 1440 (m), 1185 (m), 1104 (m), 1005 (m), 821 (s), 761 (vs), 681 (m) cm^{-1}; HRMS(EI-TOF) *m/z*: Calcd for $C_{15}H_{11}$ $[M - H]^+$ 191.0866; found 191.0897.

*4.5. General procedure D for $PtCl_2$-catalyzed cycloisomerization into phenanthrenes **4***

A solution of alkyne **3** (1 g, 1 equiv.) and 5 mol% $PtCl_2$ in toluene (45 mL) was heated at 80 °C for 12 h under N_2 until TLC showed complete conversion of the substrate. After cooling to room temperature, the solvent was removed *in vacuo*, and the residue was purified by flash column chromatography on silica gel eluting with heptane: ethyl acetate (95:5) to afford phenanthrene **4**.

*4.5.1. 4-Methoxylphenanthrene **(4a)***

Compound **3a** (1.51 g, 7.73 mmol) and 5 mol% $PtCl_2$ (102 mg) were stirred in refluxing toluene (65 mL) according to the general procedure D to obtain **4a** (1.02 g, 64%) as white crystals. Mp. 91–92 °C (Heptane). NMR data were in agreement with those previously reported [18,25,39].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.14 (s, 3H), 7.15–7.17 (m, 1H), 7.52–7.55 (m, 2H), 7.56–7.64 (m, 2H), 7.72 (q, J = 8.8 Hz, 2H), 7.89 (dd, J = 7.89, 1.6 Hz, 1H), 9.66 (dt, J = 8.6, 0.6 Hz 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 108.3, 120.8, 121.6, 125.9, 126.4, 126.5, 127.1, 128.0, 128.3, 128.6, 130.4, 132.7, 134.6, 158.9 ppm; IR (ATR): 3048 (w), 2920 (w), 2937 (w), 2836 (w), 1598 (w), 1568 (m), 1524 (m), 1448 (m), 1429 (m), 1299 (m), 1241 (m), 1202 (w), 1071 (s), 954 (m), 821 (s), 737 (s), 711 (m), cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0961; found 209.0959.

*4.5.2. 2-Methoxyphenenthrene **(4b)***

Compound **3b** (2.00 g, 10.3 mmol) and 5 mol% $PtCl_2$ (0.14 g) were stirred in refluxing toluene (85 mL) according to the general procedure D to obtain **4b** (1.43 g, 67%) as white crystals. Mp. 93–94 °C (Heptane). NMR data were in agreement with those previously reported [25,39,40].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3H), 7.24–7.30 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.61 (td, J = 7.7 Hz, 1.4 Hz, 1H), 7.69 (q, J = 14.9 Hz, 8.8 Hz, 2H), 7.85 (dd, J = 8.0, 0.9 Hz, 1H), 8.58 (d, J = 8.7, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 108.6, 117.1, 122.2, 124.3, 124.7, 125.6, 126.5, 126.7, 127.6, 128.6, 130.5, 131.0, 133.5, 158.3 ppm; IR (ATR): 3054 (w), 3001 (w), 2956 (w), 2937 (w), 2839 (w), 1613 (m), 1467 (m), 1438 (m), 1358 (m), 1259 (m), 1173 (m), 1033 (s), 855 (s), 810 (m), 748 (s), 709 (m), cm^{-1}; HRMS(EI) *m/z*: Calcd for $C_{15}H_{12}O$ [M]+ 208.0883; found 208.0891.

*4.5.3. 4-Methylphenanthrene **(4c)***

Compound **3c** (2.08 g, 10.8 mmol) and 5 mol% $PtCl_2$ (0.14 g) were stirred in refluxing toluene (90 mL) according to the general procedure D to obtain **4c** (1.21 g, 58%) as white crystals. Mp. 50.2–51.8 °C (Methanol + Acetone, v/v, 2:1) (Lit [39]. 52.0–52.3 °C). ^{1}H NMR data were in agreement with those previously reported [39].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.16 (s, 3H), 7.47–7.51 (m, 2H), 7.57–7.65 (m, 2H), 7.72 (s, 2H), 7.76–7.79 (m, 1H), 7.92 (dd, J = 7.3 Hz, 2.1 Hz, 1H), 8.92 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.5, 125.6, 125.8, 125.9, 127.1, 127.5, 127.6, 128.1, 128.8, 130.2, 131.3, 131.7, 133.6, 133.8, 135.6 ppm; IR (ATR): 3047 (w), 2960 (w), 2875 (w), 1663 (w), 1597 (w), 1438 (m), 1375 (m), 1294 (w), 1214 (w), 1165 (m), 862 (m), 820 (s), 793 (m), 734 (vs), 708 (s), 666 (w) cm^{-1}; HRMS(EI-TOF) *m/z*: Calcd for $C_{15}H_{12}$ $[M]^+$ 192.0934; found 192.0949.

*4.5.4. 2-Methylphenanthrene **(4d)***

Compound **3d** (2.47 g, 12.9 mmol) and 5 mol% $PtCl_2$ (0.17 g) were stirred in refluxing toluene (110 mL) according to the general procedure D to obtain **4d** (1.71 g, 69%) as yellow crystals. Mp 52–53 °C (Methanol) (Lit [39]. 56.7–57.2 °C). ^{1}H NMR data were in agreement with those previously reported [39].

^{1}H NMR (400 MHz, $CDCl_3$), δ = 2.56 (s, 3H), 7.48 (dd, J = 8.5 Hz, 1.7 Hz, 1H), 7.56 (td, 7.4 Hz, 1,3 Hz, 1H), 7.63 (td, J = 7.7 Hz, 1.5 Hz, 1H), 7.65–7.72 (m, 3H), 7.86 (dd, J = 7.7 Hz, 1.2 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.64 (d, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 122.4, 122.5, 126.1, 126.4, 126.6, 127.9, 128.16, 128.19, 128.3, 128.5, 130.3, 131.7, 132.2, 136.3 ppm; IR (ATR): 3016

(w), 2911 (w), 2857 (w), 1617 (w), 1460 (w), 1304 (w), 1247 (m), 1141 (w), 889 (m), 811 (s), 776 (m), 742 (vs), 710 (s), 674 (m) cm^{-1}; HRMS(EI-TOF) *m/z*: Calcd for $C_{15}H_{12}$ $[M]^+$ 192.0934; found 192.0945.

4.5.5. 3-Methoxyphenanthrene ***(4e)*** *[22]*

A solution of 4-methoxystilbene (0.5 g, 2.38 mmol), iodine (0.66 g, 2.62 mmol), and potassium carbonate (3.29 g, 23.8 mmol) in cyclohexane (1.2 L) was irradiated by 400 W medium pressure mercury lamp until the starting material was completely consumed (14 h). The solvent was removed *in vacuo* and the residue was dissolved in dichloromethane (100 mL). The solution was washed with 10% $Na_2S_2O_3$ (120 mL), dried over Na_2SO_4, and the solvent was removed *in vacuo*. The residue was separated by column chromatography (heptane: ethyl acetate, 80:20) to give **4e** (186 mg, 75%) as a yellow solid. Mp. 93–94 °C (Heptane) (Lit [41]. 95 °C). NMR data were in agreement with those previously reported [22,40].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3H); 7.15–7.18 (m, 1H); 7.48–7.61 (m, 4H); 7.72 (d, J = 8.7 Hz, 1H); 7.79 (dd, J = 6.6 Hz, 2.6 Hz, 1H); 7.97 (d, J = 2.4 Hz, 1H); 8.52 (dd, J = 8.0 Hz, 0.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 104.0, 116.7, 122.7, 124.6, 126.1, 126.6, 126.7, 128.6, 129.8, 130.0, 131.6, 132.4, 158.5 ppm; IR (ATR): 3069 (w), 3008 (w), 2964 (w), 2929 (w), 2830 (w), 1616 (m), 1506 (m), 1453 (m), 1362 (m), 1220 (s), 1177 (m), 1094 (w), 1027 (s), 839 (s), 799 (m), 742 (s) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{15}H_{13}O$ $[M+H]^+$ 209.0961; found 209.0960.

4.6. General procedure E for deprotection of methoxy to phenanthrenols ***6***

To a solution of methoxyphenenthrene **(4)** (1.00 g, 4.81 mmol) in CH_2Cl_2 (30 mL) at 0 °C under nitrogen atmosphere was added BBr_3 (1.5 equiv., 7.21 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The reaction was quenched with water (80 mL) at 0 °C and diluted with DCM (40 mL) and 1 M NaOH (15 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 70 mL). The organic layers were combined, washed with water (100 mL) and brine (100 mL), dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with heptane–EtOAc (9:1) to afford **6.**

4.6.1. Phenanthren-4-ol ***(6a)***

Following general procedure E, BBr_3 (1.5 equiv., 7.21 mmol) was added dropwise to a solution of compound **4a** (1.00 g, 4.81 mmol) in dry DCM (30 mL) to afford **6a** (535 mg, 69%) as white crystals. Mp. 113–114 °C (Heptane). NMR data were in agreement with those previously reported [42].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 1H), 6.99 (dd, J = 7.6, 1.2 Hz, 1H),7.43 (t, J = 7.8 Hz, 1H), 7.50 (dd, J = 7.8, 1.2 Hz, 1H), 7.59 (td, J = 7.4, 1.2 Hz, 1H), 7.65 (td, J = 7.8 Hz, 1H), 7.72 (q, J = 15.7, 8.8 Hz, 2H), 7.89 (dd, J = 7.8, 1.6 Hz, 1H), 9.64 (dd, J = 8.5, 0.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.2, 119.4, 121.8, 126.0, 126.3, 126.5, 127.0, 128.0, 128.2, 128.5, 130.3, 132.6, 135.0, 154.3 ppm; IR (ATR): 3507 (s), 3137 (w), 3049 (w), 3016 (w), 2924 (w), 1597 (w), 1568 (m), 1440 (m), 1413 (m), 1339 (m), 1309 (m), 1285 (m), 1222 (m), 1162 (w), 1092 (m), 1002 (m), 824 (s), 738 (s), 711 (s), cm^{-1} HRMS(APCI) *m/z*: Calcd for $C_{14}H_{11}O$ $[M+H]^+$ 195.0804; found 195.0804.

4.6.2. Phenanthren-2-ol ***(6b)***

Following general procedure E, BBr_3 (1.5 equiv., 7.21 mmol) was added dropwise to a solution of compound **4b** (1.00 g, 4.81 mmol) in dry DCM (30 mL) to afford **6b** (0.925 g, 98%) as white crystals. Mp. 162.4–163.8 °C. (Heptane). NMR data were in agreement with those previously reported [18].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.06 (s, 1H), 7.19–7.23 (m, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.58–7.64 (m, 2H), 7.70 (d, J = 8.8 Hz, 1H), 7.84 (dd, J = 7.9, 0.8 Hz, 1H), 8.56 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.8, 116.6, 122.21 124.6, 124.8, 125.7, 126.0, 126.7, 128.6, 130.4, 131.0, 133.6, 154.1 ppm; IR (ATR): 3242 (m), 3048 (w), 1615 (m), 1570 (m), 1526 (m), 1498 (m), 1461 (m), 1442 (m), 1369 (m), 1302 (m), 1243 (m), 1227 (m), 1166 (m), 1094 (w), 1034 (w), 948 (m), 871 (m), 809 (s), 746 (s), 708 (m) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_{11}O$ $[M+H]^+$ 195.0804; found 195.0804.

4.6.3. Phenanthren-3-ol ***(6c)***

Following general procedure E, BBr_3 (1.5 equiv., 0.72 mmol) was added dropwise to a solution of compound **4e** (100 mg, 0.48 mmol) in dry DCM (3 mL) to afford **6c** (63 mg, 68%) as white crystals. Mp. 112 °C (Heptane). NMR data were in agreement with those previously reported [43].

^{1}H NMR ($CDCl_3$), δ = 5.08 (s, 1H), 7.17 (dd, J = 8.6 Hz, 2.5 Hz, 1H), 7.57–7.64 (m, 3H), 7.68 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.86 (dd, 7.0 Hz, 1.9 Hz, 1H), 8.04 (d, 2.4 Hz, 1H), 8.54 (d, J = 8.0, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 106.4, 116.7, 122.7, 124.6, 126.2, 126.6, 126.8, 128.6, 129.5, 130.3, 131.9, 132.4, 154.3 ppm; IR (ATR): 3482 (m), 3412 (w), 3047 (w), 3020 (w), 2926 (w), 1618 (m), 1507 (m), 1436 (m), 1341 (w), 1280 (w), 1216 (m), 1196 (m), 1178 (s), 1139 (m), 833 (s), 741 (s), 708 (w), 694 (m) cm^{-1}; HRMS(APCI-Neg) *m/z*: Calcd for $C_{14}H_9O$ $[M-H]^-$ 193.0659; found 193.0658.

4.7. General procedure F for oxidation to ortho-quinones with SIBX

To a stirred solution of phenol (1 equiv. 200 mg, 0.82 mmol) in dry THF (*ca.* 0.05 M) was added 45 wt% SIBX (1 equiv., 0.82 mmol) and the resulting white suspension was stirred under nitrogen in the dark at room temperature. A color change was generally observed within 30 min. Stirring was continued until TLC showed starting material was completely disappeared, usually evidenced by a clear red solution. After stirring in the dark at room temperature for 48 h, the white suspension was filtered off and washed with CH_2Cl_2 (2 × 30 mL). The resulting red solution was poured into water (40 mL). After separation, the aqueous layer was further extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (4 × 30 mL). The resulting solution was washed with water (40 mL), brine (30 mL), dried over Na_2SO_4, filtered, and evaporated to dryness giving a residue that was purified by flash column chromatography (EtOAc: Heptane; 1:2 for chrysene quinones, 1:3 for phenanthrene quinones) to afford the *ortho*-quinones.

4.7.1. Chrysene-1,2-dione ***(8a)***

Following general procedure F, SIBX (688 mg, 1.23 mmol) was added to a solution of compound **5a** (300 mg, 1.23 mmol) in dry THF (25 mL) to afford **8a** (148 mg, 58%) as a brown solid. Mp. 237–239 °C (dec.) (Lit [44]. 250–251 °C (dec.)). ^{1}H NMR data were in agreement with reported values [44].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.56 (d, J = 10.6 Hz, 1H), 7.72–7.77 (m, 2H), 7.92–7.96 (m, 2H), 8.14 (d, J = 9.2 Hz, 1H), 8.34 (d, J = 8.7 Hz, 1H), 8.39 (d, J = 10.6 Hz, 1H), 8.69–8.73 (m, 1H), 8.82 (d, J = 8.6, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 121.3, 124.0, 125.1, 125.4, 127.9, 128.0, 128.6, 128.7, 128.8, 129.2, 129.4, 130.3, 131.5, 132.2, 134.5, 139.5, 178.6, 180.1 ppm; IR (ATR): 3060 (w), 2923 (w), 1663 (s), 1646 (s), 1575 (m), 1524 (m), 1409 (m), 1349 (m), 1303 (m), 1287 (s), 1257 (m), 1010 (s), 850 (m), 794 (s), 760 (s), 751(s) 663 (w)cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{18}H_{11}O_2$ $[M+H]^+$ 259.0754; found 259.0753.

*4.7.2. Chrysene-1,2-dione **(8a)***

Following general procedure F, SIBX (459 mg, 0.82 mmol) was added to a solution of compound **5b** (200 mg, 0.82 mmol) in dry THF (16 mL) to afford **8a** (90.0 mg, 42%) as brown solid. Spectral data were identical to those in chapter 4.7.1.

*4.7.3. Chrysene-3,4-dione **(8b)***

Following general procedure F, SIBX (1.84 g, 3.27 mmol) was added to a solution of compound **5c** (800 mg, 3.27 mmol) in dry THF (65 mL) to afford **8b** (506 mg, 60%) as a red solid. Mp. 199–202 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (d, J = 9.9 Hz, 1H), 7.57 (dd, J = 9.6, 2.4, 2H), 7.66–7.74 (m, 2H), 7.92 (dd, J = 7.2, 2.6 Hz, 1H), 7.98 (d, J = 9.5, 1H), 8.64 (dd, J = 8.1, 1.5 Hz, 1H), 8.98 (d, J = 8.4 Hz, 1H), 9.34 (d, J = 9.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 123.3, 123.6, 126.6, 127.85, 127.89, 128.1, 128.43, 128.44, 129.3, 130.8, 132.2, 131.6, 131.7, 136.0, 146.1, 180.6, 181.4 ppm; IR (ATR): 3057 (w), 2925 (w), 1655 (s), 1619 (w), 1577 (m), 1488 (m), 1412 (m), 1339 (m), 1222 (m), 835 (m), 824 (s), 739 (s), 700 (m) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{18}H_{11}O_2$ $[M+H]^+$ 259.0754; found 259.0755.

*4.7.4. Chrysene-5,6-dione **(8c)***

Following general procedure F, SIBX (184 mg, 0.33 mmol) was added to a solution of compound **5d** (80.0 mg, 0.33 mmol) in dry THF (7 mL) to afford **8c** (79.0 mg, 94%) as orange crystals. Mp. 190–192 °C (Lit [45]. 189–191 °C). ^{1}H NMR data were in agreement with those previously reported [45].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (td, J = 7.5 Hz, 0.8 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 8.7 Hz, 2H), 8.15 (dd, J = 5.9, 1.3 Hz, 1H), 8.17 (d, J = 5.8 Hz, 1H), 9.40 (dd, J = 8.8, 0.7, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.1.125.2, 125.9, 127.2, 127.6,128.7, 129.9, 130.0, 130.7, 130.8, 132.2, 133.8, 136.0, 136.6, 137.3, 137.8, 182.0, 184.2 ppm; IR (ATR): 3054 (w), 2931 (w), 1656 (s), 1614 (w), 1592 (s), 1485 (m), 1445 (m), 1363 (m), 1297 (m), 1281 (m), 1204 (s), 919 (m), 836 (m), 816 (m), 750 (s), 713 (m) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{18}H_{11}O_2$ $[M+H]^+$ 259.0754; found 259.0754.

*4.7.5. Phenanthrene-3,4-dione **(9a)***

Following general procedure F, SIBX (90 mg, 0.16 mmol) was added to a solution of compound **6a** (30.0 mg, 0.16 mmol) in dry THF (3 mL) for 14 h to afford **9a** (18.9 mg, 59%) as a brown solid. Mp 132–133 °C (Lit [18]. 131–132 °C) ^{1}H NMR data are in agreement with those previously reported [18,46].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.49 (d, 1H, J = 10.0 Hz), 7.41 (d, J = 8.3 Hz, 1H), 7.51 (d, J = 10.0 Hz, 1H), 7.58 (td, J = 7.6 Hz, 1.10 Hz, 1H), 7.73 (td, J = 8.0 Hz, 1.4 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H); 9.44 (dd, J = 8.8H, 0.68 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.3, 126.8, 127.0, 127.91, 127.94, 128.9, 131.3, 132.5, 134.7, 136.4, 137.4, 146.7, 181.2, 181.3 ppm; IR (ATR): 2841 (m), 2677 (m), 2562 (m), 1687 (s), 1647 (m), 1584 (m), 1425 (s), 1327 (s), 1293 (s), 1187 (m), 935 (s), 708 (s), 684 (m) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_9O_2$ $[M+H]^+$ 209.0597; found 209.0595.

*4.7.6. Phenanthrene-3,4-dione **(9a)***

Following general procedure F, SIBX (90 mg, 0.16 mmol) was added to a solution of compound **6c** (30 mg, 0.16 mmol) in dry THF (3 mL) for 14 h to afford **9a** (25.0 mg, 77% yield) as brown solid. Spectral data were identical to those in chapter 4.7.5.

*4.7.7. Phenanthrene-1,2-dione **(9b)***

Following general procedure F, SIBX (90 mg, 0.16 mmol) was added to a solution compound **6b** (30.0 mg, 0.16 mmol) in dry THF 3 mL) for 14 h to obtain **9b** (27.0 mg, 84%) as a red solid. Mp. 196–199 °C (Lit [18,46]. 201–203 °C). ^{1}H NMR data were in agreement with those previously reported [18,46].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.58 (d, J = 10.5 Hz, 1H), 7.67–7.72 (m, 2H), 7.89–7.93 (m, 1H), 7.97 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.27–8.30 (m, 1H), 8.34 (d, J = 10.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.5, 124.3, 127.6, 128.5, 129.3, 129.5, 129.7, 131.3, 131.8, 137.2, 139.4, 179.4, 180.7 ppm; IR (ATR): 2923 (s), 2852 (m), 1655 (s), 1647(s), 1577 (m), 1331 (m), 1284 (m), 978 (m), 850 (m), 750 (s), 736 (m) cm^{-1}; HRMS(APCI) *m/z*: Calcd for $C_{14}H_9O_2$ $[M+H]^+$ 209.0597; found 209.0596.

*4.7.8. Naphtalene-1,2-dione **(10)***

Following general procedure F, SIBX (466 mg, 0.83 mmol) was added to a stirred solution of compound **7a** (120 mg, 0.83 mmol) in THF (16 mL) for 14 h. Avoiding flash chromatography, the crude solid after extraction was recrystallized from EtOAc to obtain **10** (113 mg, 85%) as red solid. Mp.121–124 °C (EtOAc) (Lit [19]. 126–129 °C, lit [47]. 144–146 °C). NMR data were in agreement with those previously reported [47].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.44 (d, J = 10.1 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 10.1 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.5, 1.1 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.0, 129.8, 130.3, 130.9, 131.7, 134.8, 135.8, 145.4, 178.9, 180.9 ppm; IR (ATR): 3369 (m), 3053 (w), 3016 (w), 2972 (m), 2881 (w), 1695 (m), 1652 (s), 1586 (w), 1459 (m), 1399 (m), 1286 (m), 1246 (m), 1087 (m), 1045 (vs), 879 (m), 848 (m), 795 (m), 762 (m), 681(m) cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{10}H_7O_2$, 159.0441 $[M + H]^+$; found, 159.0441.

*4.7.9. Naphtalene-1,2-dione **(10)***

Following general procedure F, SIBX (466 mg, 0.83 mmol) was added to a stirred solution of compound **7b** (120 mg, 0.83 mmol) in THF (16 mL) for 14 h. Avoiding flash chromatography, the crude solid after extraction was recrystallized from EtOAc to obtain **10** (123 mg, 93%) as a red solid. Spectral data were identical to those in chapter 4.7.8.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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