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Synthesis of Phenanthrenes and Polycyclic Heteroarenes by Transition-Metal Catalyzed Cycloisomerization Reactions

Victor Mamane, Peter Hannen, and Alois Fürstner*[a]

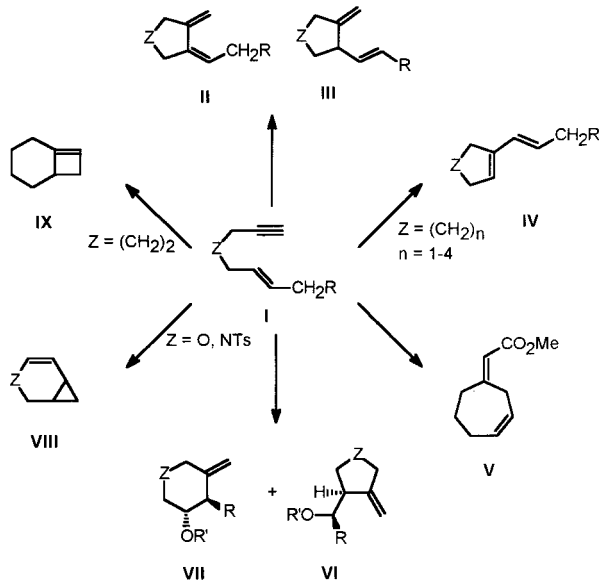
Abstract: Readily available biphenyl derivatives containing an alkyne unit at one of their *ortho*-positions are converted into substituted phenanthrenes on exposure to catalytic amounts of either $PtCl_2$, AuCl, $AuCl_3$, $GaCl_3$ or $InCl_3$ in toluene. This 6-*endo*-dig cyclization likely proceeds through initial π-complexation of the alkyne unit followed by interception of the resulting η^2-metal species by the adjacent arene ring. The reaction is inherently modular, allowing for substantial structural variations and for the incorporation of substituents at any site of the phenanthrene product. Moreover, it is readily extended to the heterocyclic series as exemplified by the preparation of benzoindoles, benzocarbazoles, naphthothiophenes, as well as bridgehead nitrogen heterocycles such as pyrrolo[1,2-*a*]quinolines. Depending on the chosen catalyst, biaryls bearing halo-alkyne units can either be converted into the corresponding 10-halo-phenanthrenes or into the isomeric 9-halo-phenanthrenes; in the latter case, the concomitant 1,2-halide shift is best explained by assuming a metal vinylidene species as the reactive intermediate. The scope of this novel method for the preparation of polycyclic arenes is illustrated by the total synthesis of a series of polyoxygenated phenanthrenes that are close relatives of the anticancer agent combretastatin A-4, as well as by the total synthesis of the aporphine alkaloid O-methyl-dehydroisopiline and its naturally occurring symmetrical dimer.

Keywords: arenes · homogeneous catalysis · natural products · phenanthrenes · platinum

Introduction

The potential of platinum chloride and related salts to induce highly selective skeletal rearrangements of polyunsaturated compounds was recognized only recently.[1,2] Though seemingly trivial, $PtCl_x$ ($x = 2, 4$) is able to catalyze an amazingly broad spectrum of C–C-bond formations that allow to convert enynes **I** and related substrates into a myriad of carbo- and heterocyclic products (e.g. **II**–**IX**). Prototype examples are depicted in Scheme 1.[1–13] All of these transformations are triggered by the high affinity of Pt^{II} for π-systems and benefit from the excellent compatibility of the late transition metal with many polar functional groups. Such $PtCl_2$-catalyzed processes are inherently atom economical, result in a significant increase in structural complexity, are operationally simple, safe, and convenient to perform even on a larger scale, and therefore meet many of the stringent criteria imposed upon contemporary organic synthesis.[14]

In pursuit of our previous investigations in this field,[4,15,16] we now report a flexible approach to phenanthrenes and various heteroarenes based on the metal-induced carbocyclization of alkynylated biaryl derivatives.[17–22] While $PtCl_2$ again turns out to be a privileged catalyst in this context,



Scheme 1. Prototype examples of cycloisomerization reactions of enynes catalyzed by $PtCl_2$.

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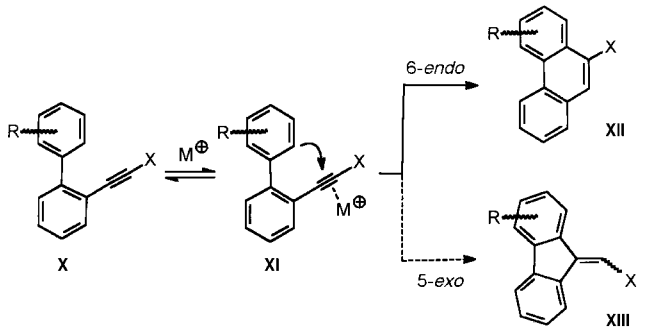
other metal salts such as $InCl_3$, $GaCl_3$, and $AuCl_x$ ($x = 1, 3$) also show appreciable activity in certain cases.[23–25] Applications to the total synthesis of aporphine alkaloids and polyoxygenated phenanthrenes related to the potent antitumor agent combretastatin A-4 illustrate the favorable application profile of this method.

Results and Discussion

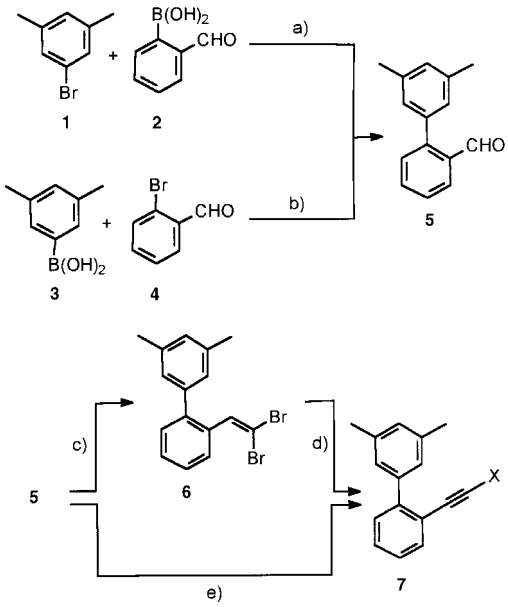
Conceptual background and catalyst screening: Addition of an electrophilic metal salt or metal complex to a biphenyl derivative bearing an alkyne unit at one of its *ortho*-positions should engender an equilibrium between the substrate **X** and the η^2-metal complex **XI** thereof;[26] if the latter is intercepted by the adjacent aromatic ring, a C–C-bond formation with concomitant release of the catalyst will ensue. Since the required substrates are readily accessible by established metal-catalyzed cross coupling reactions, a flexible entry into 9-alkylidene fluorene derivatives **XIII** or the corresponding phenanthrenes **XII** should result, depending on whether the reaction follows the 5-*exo*- or a 6-*endo* pathway (Scheme 2).



Scheme 2. Concept of the new phenanthrene synthesis by cycloisomerization of biaryls bearing an alkyne unit at one of their *ortho*-positions.

To probe the viability and outcome of the envisaged cycloisomerization process, suitable model compounds were prepared as depicted in Scheme 3. Specifically, 1-bromo-3,5-dimethylbenzene **1** was subjected to a Suzuki reaction[27] with 2-formyl-benzeneboronic acid **2** to give the biphenyl derivative **5** in good yield. The same product can be obtained by inverting the donor- and acceptor sites via the palladium catalyzed cross coupling of 3,5-dimethylbenzeneboronic acid **3** with 2-bromobenzaldehyde **4**. The formyl group in **5** served as a handle to install the required alkyne; this was achieved either in one step on treatment with lithiated trimethylsilyl diazomethane[28] or by following the Corey–Fuchs protocol.[29] While these methods provide similar yields of **7a** (X = H), the latter method can also be diverted to the synthesis of end-capped products (X ≠ H) by trapping of the lithiated intermediate derived from dibromide **6** with different electrophiles. Unless stated otherwise, all substrates used in this study have been prepared analogously.

Screening of a set of different metal species for their capacity to induce the desired cycloisomerization gave several



Scheme 3. Representative example for the preparation of the required substrates. a) $[Pd(PPh_3)_4]$ cat., Na_2CO_3, DME/EtOH/H_2O, reflux, 80%. b) $[Pd(PPh_3)_4]$ cat., CsF, DME, reflux, 76%. c) CBr_4, PPh_3, CH_2Cl_2, quant. d) *n*BuLi, THF, −78 °C, 81%. e) LDA, Me_3SiCHN_2, THF, −78 °C → RT, 70%.

hits (Table 1). In line with our expectations, $PtCl_2$ proved highly effective, furnishing the corresponding phenanthrenes **8** in good yields. Likewise, cationic platinum complexes formed in situ from $[PtCl_2(PhCN)_2]$ and suitable halide sequestering agents ($AgBF_4$, $AgSbF_6$, NH_4PF_6),[13,16,30] as well as $AuCl_3$,[25,31] $GaCl_3$,[23] and $InCl_3$[32] showed appreciable activity, whereas $RhCl_3$, $RuCl_3$, and various ruthenium complexes resulted in low conversions and/or poor selectivities. Although it is difficult to rationalize the subtle outcome of the individual entries in Table 1, all salts found to be catalytically competent exhibit a "soft" character and a high affinity for π-bonds. Moreover it is important to note that heating of alkyne **10** in toluene at 80 °C for 22 h in the absence of any catalyst does not result in ring closure (Table 1, entry 5). This control experiment makes clear that the observed reactions are not just thermal electrocyclization processes but definitely require assistance by a soft Lewis acid.[33]

The whole set of substrates investigated showed a pronounced preference for 6-*endo*-dig cyclization to give phenanthrenes over the conceivable 5-*exo* mode. The only exception was compound **7c** in which the strongly electron withdrawing ester group on the alkyne not only diminishes the reaction rate but also overturns this inherent bias and enforces a 1,4-addition which formally corresponds to the 5-*exo* pathway (**8c**/**9c** = 5:95). Likewise, the tolane derivative **7d** gave a mixture of both possible isomers, that is, the phenanthrene **8d** and the 9-alkylidene fluorene derivative **9d**, in a ≈3:2 ratio.

Preparative scope—Phenanthrenes, helicenes, heteroarenes: The examples compiled in Table 2 show the generality of this novel entry into phenanthrenes. In principle, the method allows the introduction of substituents at any posi-

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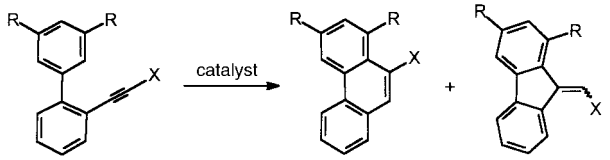
Table 1. Screening of the activity and selectivity of different catalysts in the cycloisomerization of the *ortho*-alkynylated biphenyl derivatives. All reactions were performed in toluene at 80 °C unless stated otherwise.



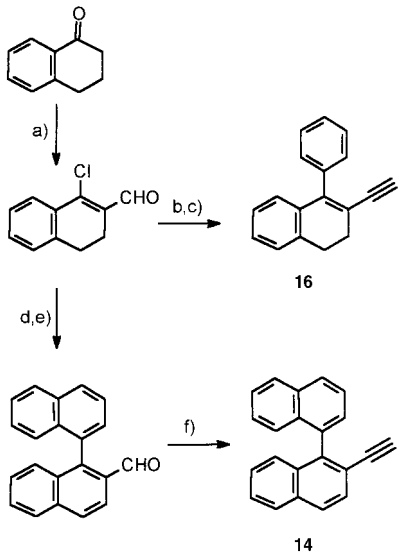
8 9

Entry	Substrate	R	X	Catalyst[a]	GC [%]	**8**:**9**	Yield[b] [%]
1	**7a**	Me	H	$PtCl_2$	100	97:3	64
2	**7b**	Me	Me	$PtCl_2$	100	100:0	89
3	**7c**	Me	COOMe	$PtCl_2$	73	5:95	
4	**7d**	Me	C_6H_4OMe	$PtCl_2$	100	60:40	87[c]
5	**10**	OMe	H	–	0		
6				$GaCl_3$	100	96:4	53
7				$InCl_3$	100	44:56	44
8				$AuCl_3$	100	97:3	95
9				$PtCl_2$	100	95:5	76
10				$PtCl_2(PhCN)_2$/ 2 $AgSbF_6$	100[d]	87:13	56
11				$PtCl_2(PhCN)_2$/ 2 $AgBF_4$	100[d]	92:8	82
12				$[PtCl_2(PhCN)_2]$/ 2 NH_4PF_6	62[e]	90:10	
13				$[RuCl_2(CO)_3]_2$	52	67:33	
14				$[(cymene)(PCy_3)RuCl_2]/2\,AgBF_4$	100	30:70	17
15				$[Cp^*Ru(MeCN)_3]PF_6$	0		
16				$RuCl_3$	0		
17				$RhCl_3$	0		

[a] Using 5 mol % of the monomeric complexes or 2.5 mol % of the dimeric complexes, respectively. [b] Refers to isolated yield of the major compound. [c] Inseparable mixture of **8d** and **9d**. [d] In CH_2Cl_2 at ambient temperature. [e] In CH_2Cl_2 at reflux.

tion except C-9 (a way to derivatize C-9 is outlined below). Entry 8 illustrates that partly saturated analogues are equally accessible. The required alkyne **16** was prepared in three simple steps starting from α-tetralone as shown in Scheme 4. This route also opens access to helicenes as illustrated by the synthesis of the parent pentahelicene **15** (entry 7). In view of the inherent flexibility of the approach, however, it can be expected that more elaborated and differently functionalized helical compounds are also within reach.[34]

Along similar lines, the individual phenyl rings in the starting material can be formally replaced by heteroarene units (entries 12–25). Although in the case of the N-unprotected pyrrole derivatives **26a**,**b** one might expect that the nitrogen atom acts as the nucleophile, exclusive carbocyclization with formation of 1*H*-benzo[*g*]indoles **27a**,**b** was observed. A simple change of the connectivity pattern in the substrate opens access to the isomeric pyrrolo[1,2-*a*]quinoline skeleton **31** bearing the heteroatom in the bridgehead position. In this series, however, $PtCl_2$ is not necessarily the best catalyst; only in the case of the terminal alkyne **30a** was it found to be effective (entry 18), whereas all substrates bearing an internal alkyne required the use of either $GaCl_3$ or $InCl_3$ for productive cyclization (entries 19–25).



Scheme 4. a) $POCl_3$, DMF, 58 %. b) $PhB(OH)_2$, $[Pd(OAc)_2]$ cat., K_2CO_3, Bu_4NBr, H_2O, 45 °C, 90 %. c) LDA, Me_3SiCHN_2, THF, −78 °C, 84 %. d) Naphthylboronic acid, $Pd(OAc)_2$ cat., K_2CO_3, Bu_4NBr, H_2O, 45 °C, 79 %. e) DDQ, benzene, reflux, 59 %. f) LDA, Me_3SiCHN_2, THF, −78 °C → RT, 90 %.

While benzo-annulated carbazole derivatives are only rarely found in nature, these heterocycles attracted considerable interest as antitumor agents in medicinal chemistry.[35] Specifically, compounds **29** and **38** are active against leukemia, renal tumor, colon cancer, and malignant melanoma cell lines.[36] Their synthesis was easy to accomplish by platinum-catalyzed cycloisomerizations (Scheme 5). Thus, a Fischer indole synthesis secured 2-(2-iodophenyl)indole **33**[74] in good yield which, after Sonogashira coupling[37] with propyne and subsequent N-methylation of **34** under standard conditions, furnished alkyne **28** and set the stage for the envisaged ring closure. This reaction proceeded exquisitely well, providing the targeted benzo[*a*]carbazole **29** in 93 % yield. Substrate **36** cyclized with similar ease, although small amounts of the isomeric product **39** formed upon attack of the unprotected indole N-atom onto the alkyne accompanied the major benzocarbazole **37** in this case. N-Sulfonylation of **37** gave the known antitumor agent **38** in excellent overall yield.

Mechanistic considerations: In a formal sense this new phenanthrene synthesis is reminiscent of the *endo*-selective cyclizations of dienylalkynes **XIV** and related substrates catalyzed either by $[(\eta^6\text{-cymene})(PPh_3)RuCl_2]$ or $[W(CO)_5]$·THF (Scheme 6).[38–40] These reactions likely involve vinylidene complexes **XV**[41] which undergo a 6π-elec-

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Table 2. Formation of phenanthrenes and heterocyclic congeners by cyclization of *ortho*-alkynylated biaryls. All reactions were carried out with 5 mol% of the catalyst in toluene at 80°C.

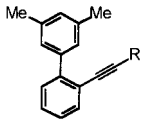
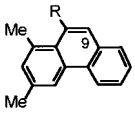
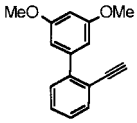
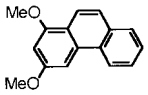
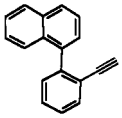
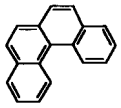
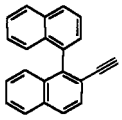
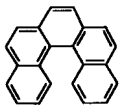
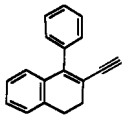
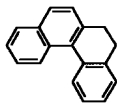
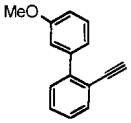
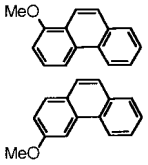
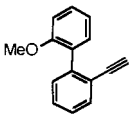
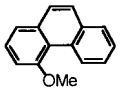
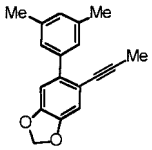
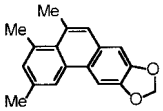
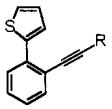
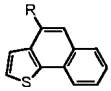
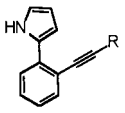
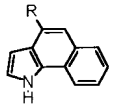
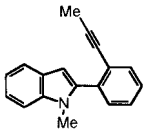
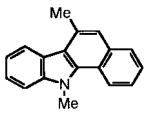
Entry	Substrate	Catalyst	Products	R	Yield [%]
1		$PtCl_2$		H (**8a**)	73
2	**7**	$PtCl_2$		Me (**8b**)	89
3		$PtCl_2$		Ph (**8e**)	82
4		$PtCl_2$		**11**	76
5	**10**	$AuCl_3$			95
6		$PtCl_2$		**13**	65
7		$PtCl_2$		**15**	56
8		$PtCl_2$		**17**	75
9		$PtCl_2$		**19a,b**	70 (1:4)
10		$PtCl_2$		**21**	55
11		$PtCl_2$		**23**	94
12		$PtCl_2$		H (**25a**)	54
13	**24**	$GaCl_3$		Ph (**25b**)	83
14		$InCl_3$		Ph (**25b**)	88
15		$PtCl_2$		H (**27a**)	63
16	**26**	$PtCl_2$		Me (**27b**)	76
17		$PtCl_2$		**29**	93

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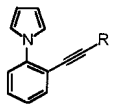
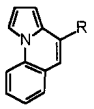
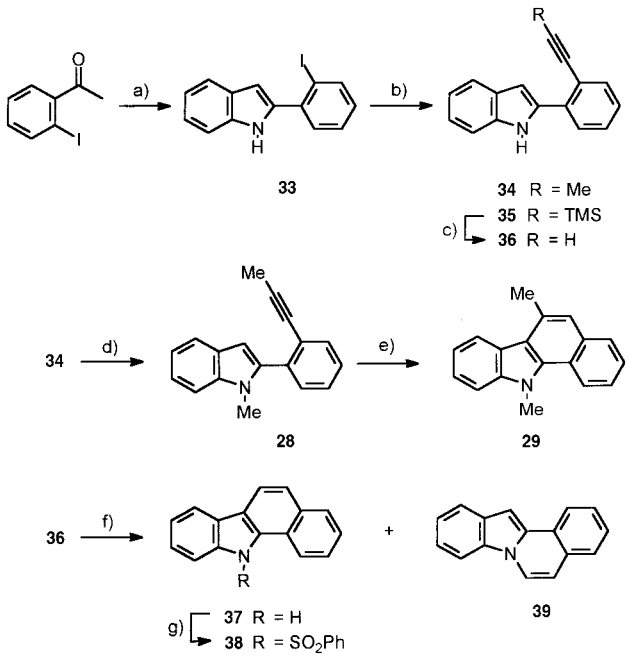
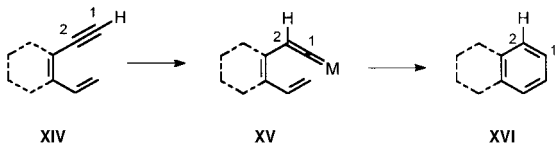
Table 2. (Continued)

Entry	Substrate	Catalyst	Products	R	Yield [%]
18		$PtCl_2$		H (**31a**)	56
19		$GaCl_3$		Me (**31b**)	74
20		$InCl_3$		Me (**31b**)	78
21		$GaCl_3$		Ph (**31c**)	94
22	**30**	$InCl_3$		Ph (**31c**)	90
23		$GaCl_3$		C_6H_{13} (**31d**)	80
24		$InCl_3$		C_6H_{13} (**31d**)	91
25		$InCl_3$		$SiMe_3$ (**31e**)	64



Scheme 5. a) i) $PhNHNH_2$, 150 °C; ii) $ZnCl_2$, 180 °C, 73 %, ref. [74]. b) i) Propyne, $[PdCl_2(PPh_3)_2]$ cat., CuI cat., Et_3N, 64 % (**34**); *or* ii) $Me_3SiC{\equiv}CH$, $[PdCl_2(PPh_3)_2]$ cat., CuI cat., Et_3N, 61 % (**35**). c) K_2CO_3, MeOH, quant. d) NaH, MeI, THF, 83 %. e) $PtCl_2$ cat., toluene, 80 °C, 93 %. f) $PtCl_2$ cat., toluene, 80 °C, 75 % (**37**) + 11 % (**39**). g) NaH, $PhSO_2Cl$, THF, 86 %.

trocyclization to form the new arene ring in product **XVI**. Since only terminal alkynes can afford such intermediates via metal complexation followed by a 1,2-hydride shift (cf. **XIV** → **XV**), however, the scope of this method is inherently limited.



Scheme 6. Electrocyclization reactions via metal vinylidene intermediates.

The platinum-catalyzed phenanthrene synthesis, in contrast, works equally well or even better with non-terminal alkynes as evident from the examples compiled in Table 2, suggesting that the activation of the π-system by coordination to Pt^{II} rather than the formation of metal vinylidenes triggers the observed ring closure. Whether the interaction of the triple bond with the metal template engenders a "Friedel–Crafts"-type alkylation manifold[16,42] or if platinum-carbenes[5] are involved as the actual reactive intermediates cannot yet be decided.

Natural product synthesis—Phenanthrenes related to combretastatin A-4: Tubulin as the major protein component of the microtubules constitutes a formidable target in search for anti-cancer chemotherapeutics. With the *Vinca* alkaloids, paclitaxel (Taxol) and docetaxel (Taxotère), drugs binding to tubulin have already entered clinical use.[43] Another very promising class of antineoplastic agents affecting this subcellular target are the so-called combretastatins, a family of natural products isolated from the South African willow tree *Combretum caffrum* and closely related species such as *C. apiculatum*, *C. molle*, and *C. psidioides*.[44] Most active among them is the stilbene derivative combretastatin A-4 (**40**) which is an exceptionally strong inhibitor of tubulin polymerization (IC_{50} ~2–3 μM) ligating the colchicine binding site of the protein.[45,46] Combretastatin A-4 and three derivatives thereof are presently in phase II or phase I clinical trials and several additional analogues undergo intense preclinical development.[47]

In view of the relevance of these compounds, we focused our attention on the polyoxygenated phenanthrene derivatives **41** and **42** (Scheme 7) which derive from the same *Combretum* species.[48,49] Notably, the oxygenation/methylation pattern of **41** is identical to that of combretastatin A-4, whereas **42** lacks only one MeO substituent in the A-ring. Moreover, many other closely related phenanthrenes have been isolated from various plant sources, many of which have not yet been assessed in detail for possible tubulin binding or cytotoxicity.[50] Pertinent examples are compound **44** derived from *Alnus maximowiezii*,[51] and phenanthrene **43** isolated from the orchid *Bulbophyllum vaginatum*[52] which have been included in the present study as simplified yet naturally occurring analogues of the lead compound **40**.

Our total synthesis of these products started from commercial 2,3,4-trimethoxybenzeneboronic acid (**46**) as a common building block which was cross coupled with either 5-benzyloxy-2-bromo-4-methoxy-benzaldehyde (**45a**), 2-bromo-5-methoxy-benzaldehyde (**45b**), or 2-bromobenzaldehyde (**45c**) to give the corresponding formylated biphenyl derivatives **47a–c** in high yields (Scheme 8, Table 3). These Suzuki reactions were best performed by following a procedure recently developed in this laboratory for the cross coupling of electron rich areneboronic acids which operates in

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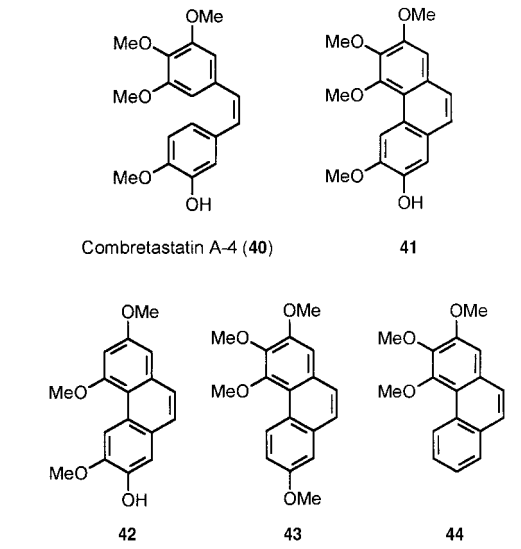
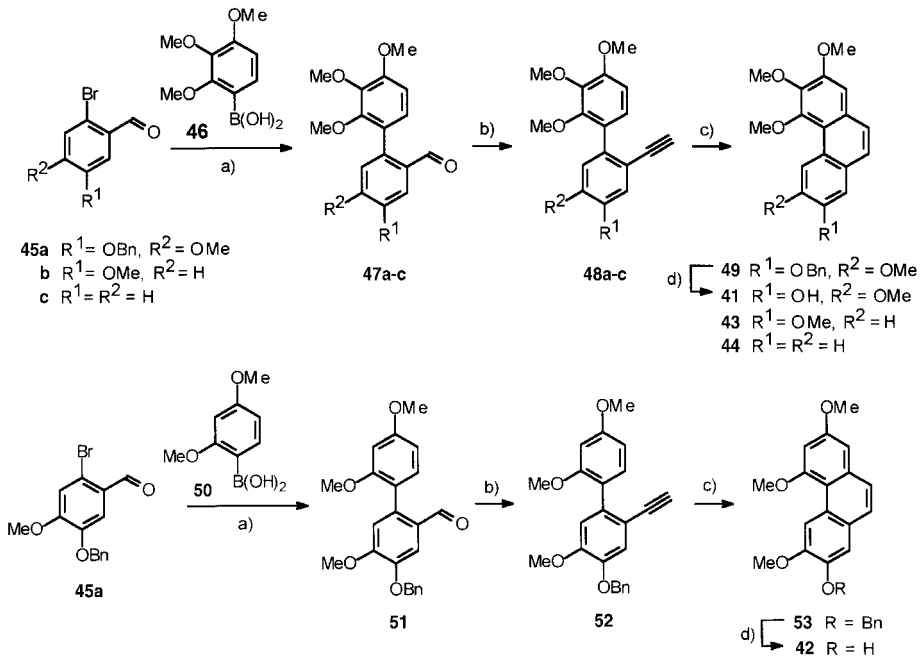


Scheme 7. Combretastatin A-4 and structurally related phenanthrenes.



Scheme 8. a) $[Pd(PPh_3)_4]$ cat., LiCl, Na_2CO_3, DME/H_2O, 80 °C, see Table 3. b) LDA, Me_3SiCHN_2, THF, −78 °C → RT, see Table 3. c) $PtCl_2$ cat., toluene, 80 °C, see Table 3. d) H_2 (1 atm), Pd/C, EtOAc, 96 % (**41**), 79 % (**42**).

Table 3. Preparation of phenanthrenes related to combretastatin A-4 according to Scheme 8.

Aldehydes	Alkynes	Catalyst	Phenanthrenes
47a (87 %)	**48a** (74 %)	$PtCl_2$	**49** (70 %)
47b (89 %)	**48b** (93 %)	$PtCl_2$	**43** (86 %)
47c (85 %)	**48c** (84 %)	$PtCl_2$	**44** (63 %)
		AuCl	**44** (73 %)
51 (88 %)	**52** (79 %)	$PtCl_2$	**53** (73 %)

aqueous DME as the medium in the presence of excess LiCl and Na_2CO_3.[53] The preparation of product **51** lacking one of the methoxy groups in the A-ring proceeded analogously using boronic acid **50** and bromide **45a** as the starting materials. The aldehyde groups were then reacted with lithiated trimethylsilyl diazomethane.[28] In line with our expectations, the resulting terminal alkynes **48a–c** and **52** cyclized to the desired substituted phenanthrene derivatives in good to excellent yields on treatment with catalytic amounts of $PtCl_2$ in toluene at 80 °C. In the case of substrate **48c**, the catalytic performance of AuCl was also investigated and found to rival that of $PtCl_2$ in terms of yield and reaction rate. Hydrogenolytic cleavage of the benzyl ether in **49** afforded phenanthrene **41** as the closest conceivable congener of combretastatin A-4. The structure of this natural product in the solid state is depicted in Figure 1.

Various intermediates of this synthesis route have been obtained in form of single crystals suitable for X-ray analysis. Representative structures are shown in Figures 2–4. Notable, though not surprising, is the twist of their biaryl axes as expressed in the torsional angles between the planes through the individual phenyl rings of 48.7° in aldehyde **47a**, 59.0° in aldehyde **47b**, and 72.8° in alkyne **48c**. Because the platinum-catalyzed cycloisomerization process forces the arene rings into coplanarity, it was of interest to estimate the rotational barrier of the central C–C-bond in alkyne **48c**. Ab initio calculations (B3LYP/6-31G*) suggest that the pertinent transition state is about 7.2 kcal mol^{-1} higher in energy than the minimum ground state conformation.

Cyclization of allenes: Due to the high reactivity of cumulated π-bonds in general it was envisaged that biphenyls bearing an allene rather than an alkyne unit at one of their *ortho*-positions might also qualify as substrates for metal-catalyzed cycloisomerization reactions.[54] Suitable compounds allowing to probe this aspect were prepared by a Sonogashira coupling of iodide **54** (see Scheme 9) with propargyl alcohol followed by standard elaboration of the resulting product **55a** according to literature procedures.[55,56]

In striking contrast to the alkyne series, allenes **56a**,**b** (Scheme 9) underwent even thermal electrocyclization with formation of the desired phenanthrenes **57a**,**b**; this fact is deemed to reflect the strain inherent to their 1,2-diene moieties (Table 4, entries 1 and 6). However, addition of $InCl_3$ or $GaCl_3$ (5 mol %) accelerated the reaction (entries 2, 3, 7) while $PtCl_2$ afforded product mixtures (entry 4). Interestingly, the major products were identified as the isomeric pyrrolo-azepines **58** and **59**. This rather unusual cyclization involving the terminal rather than the central C-atom of the allene moiety is favored by a cationic Pt^{II} species formed in

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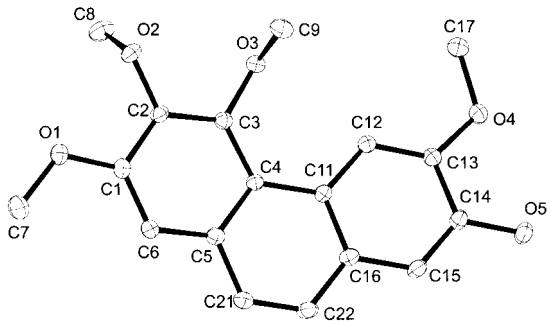


Figure 1. Molecular structure of compound **41**. Anisotropic displacement parameters are drawn at the 50% probability level. Selected bond length in Å. C(4)−C(11) 1.4616(19), C(5)−C(21) 1.431(2), C(21)−C(22) 1.352(2), C(16)−C(22) 1.434(2).

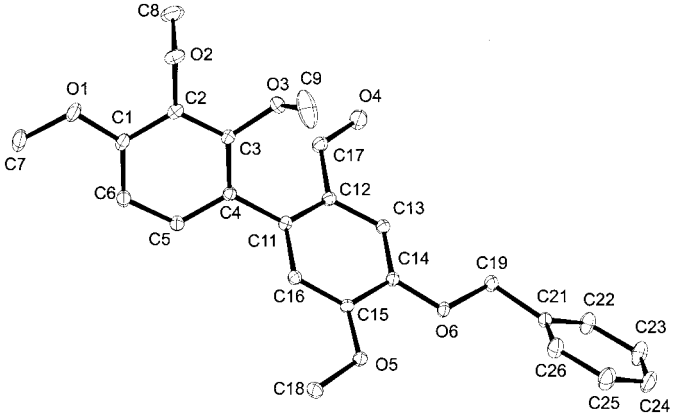


Figure 2. Molecular structure of compound **47a**. Anisotropic displacement parameters are drawn at the 50% probability level. Selected bond lengths in Å and bond angles in °. C(4)−C(11) 1.4839(13), C(12)−C(17) 1.4755(13), C(17)−O(4) 1.2161(12), C(3)-C(4)-C(11) 121.97(8), C(12)-C(11)-C(4) 123.67(8), C(11)-C(12)-C(17) 121.63(8), O(4)-C(17)-C(12) 123.38(9).

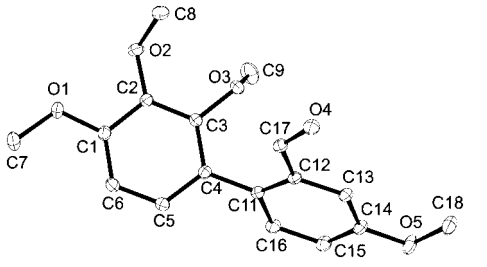


Figure 3. Molecular structure of compound **47b**. Anisotropic displacement parameters are drawn at the 50% probability level. Selected bond lengths in Å and bond angles in °. C(4)−C(11) 1.4888(12), C(11)−C(12) 1.4040(12), C(12)−C(17) 1.4816(12), C(17)−O(4) 1.2173(11), C(3)-C(4)-C(11) 120.35(8), C(12)-C(11)-C(4) 122.44(8), C(11)-C(12)-C(17) 120.72(8), O(4)-C(17)-C(12) 123.83(8).

situ from $[PtCl_2(PhCN)_2]$ (2.5 mol%) and $AgBF_4$ (5 mol%). The mechanistic background as well as the scope of this previously unknown skeletal reorganization remain to be explored.

Halophenanthrenes—Halide retention versus 1,2-halide migration regime: The scope of the present method could be considerably extended by using biaryls with a lateral haloalkyne unit as the substrates, since the resulting 10-halophenanthrenes are ideally suited for further elaboration. However, such compounds were found to react poorly on exposure to $PtCl_2$ under the standard conditions, affording rather complex product mixtures. In an attempt to improve on this result, a set of different metal species was screened for catalytic activity. While $RuCl_3$, $OsCl_3$, $CoCl_2$, $RhCl_3$, $IrCl_3$, $NiCl_2$, CuCl, and AgOTf resulted in marginal conversions and/or discouraging product distributions, $InCl_3$[32] was found to effect the desired transformation in good to excellent yields and high selectivity. Representative examples are compiled in Table 5.

Another hit in our screening was AuCl. Surprisingly, though, treatment of substrate **60** (X = Br, I) with this salt afforded the corresponding 9-halo-phenanthrenes **68** rather than the expected 10-halo-phenanthrenes **61**. This outcome is best explained by assuming the formation of a metal vinylidene as the reactive intermediate via a concomitant 1,2-halide shift (Scheme 10). Only recently were such species proposed in the literature to rationalize related halide walk phenomena.[57]

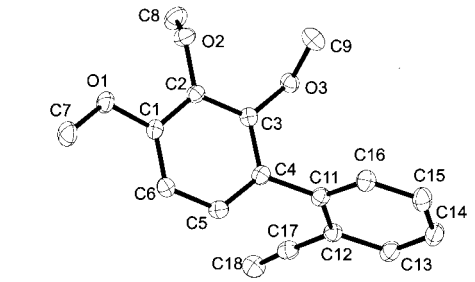
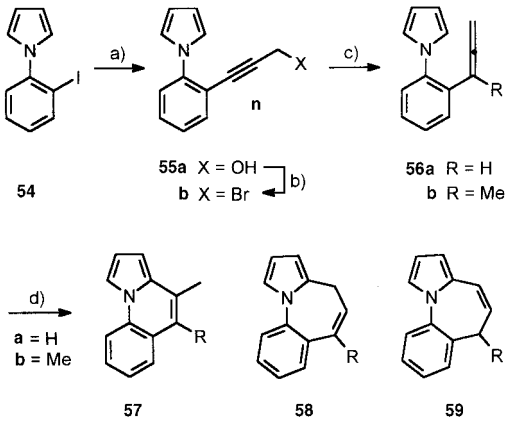


Figure 4. Molecular structure of compound **48c**. Anisotropic displacement parameters are drawn at the 50% probability level. Selected bond lengths in Å and bond angles in °. C(4)−C(11) 1.497(2), C(11)−C(12) 1.406(2), C(12)−C(17) 1.448(2), C(17)−C(18) 1.189(2), C(5)-C(4)-C(11) 122.41(14), C(12)-C(11)-C(4) 122.49(14), C(11)-C(12)-C(17) 121.26(14), C(18)-C(17)-C(12) 176.31(18).



Scheme 9. a) Propargyl alcohol, $[PdCl_2(PPh_3)_2]$ cat., CuI cat., Et_3N, 60 °C, 94%. b) CBr_4, PPh_3, CH_2Cl_2, 0 °C, 87%. c) i) PPh_3, diisopropyl azodicarboxylate (DIAD), *ortho*-nitrobenzenesulfonyl hydrazide, THF, −15 °C → RT, 65% (**55a**→**56a**) *or* ii) MeMgCl, CuCN, LiCl, THF, −78 °C, 71% (**55b**→**56b**). d) See Table 4.

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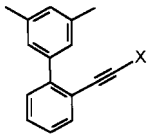
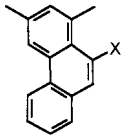
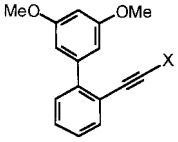
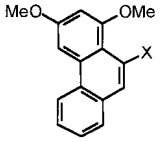
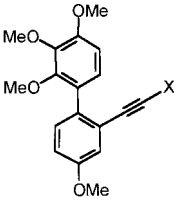
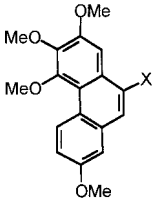
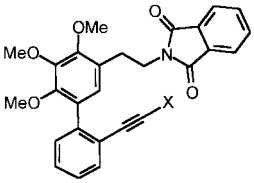
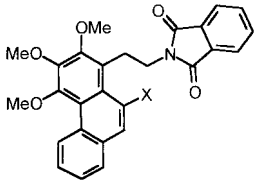
Table 4. Cycloisomerization reactions of allenes, see Scheme 9.

Entry	Substrate	Catalyst	Conditions	Product (Yield [%])
1	**56a**	–	$ClCH_2CH_2Cl$, 80 °C, 15 h	**57a** (43)
2	**56a**	$InCl_3$	$ClCH_2CH_2Cl$, 80 °C, 5 h	**57a** (84)
3	**56a**	$GaCl_3$	$ClCH_2CH_2Cl$, 80 °C, 15 h	**57a** (68)
4	**56a**	$PtCl_2$	$ClCH_2CH_2Cl$, 80 °C, 15 h	**58a** (52), **59a** (32)
5	**56a**	$[(PhCN)_2PtCl_2]/2\,AgBF_4$	CH_2Cl_2, 20 °C, 4 h	**58a** (70)
6	**56b**	–	$ClCH_2CH_2Cl$, 80 °C, 7 h	**57b** (77)
7	**56b**	$InCl_3$	$ClCH_2CH_2Cl$, 80 °C, 3 h	**57b** (83)
8	**56b**	$PtCl_2$	CH_2Cl_2, 20 °C, 30 h	**58b** (45), **59b** (12)
9	**56b**	$[PtCl_2(PhCN)_2]/2\,AgBF_4$	CH_2Cl_2, 20 °C, 7 h	**58b** (80)

Table 5. Formation of 10-halophenanthrenes. All reactions were carried out with 5 mol% of $InCl_3$ in toluene at 80 °C unless stated otherwise.

Entry	Substrate	Product	X	Yield [%]
1		**60** 	Cl (**61a**)	95
2			Br (**61b**)	7
3		**62** 	Cl (**63a**)	90
4			Br (**63b**)	59[a]
5			I (**63c**)	mixture
6		**64** 	Cl (**65**)	81
7		**66** 	Cl (**67a**)	78[b]
8			Br (**67b**)	87[b]

[a] GC yield. [b] Using 1 equiv $InCl_3$.

This unexpected result illustrates the subtle balance between different scenarios in metal catalyzed skeletal rearrangement reactions. As discussed above, the available mechanistic information makes vinylidene intermediates highly unlikely when biaryls bearing terminal, internal, or halogenated alkynes are exposed to either Pt^{II}, Au^{III}, Ga^{III} or In^{III} as the promoters. The AuCl-catalyzed 1,2-halide shift experiments, however, show that generalizations have to be met with caution as seemingly small changes (e.g. Au^{I} versus Au^{III}) can open additional reaction channels and thereby provide access to complementary substitution patterns in the products formed. From the preparative point of view, however, this unexpected way to functionalize C-9 is particularly gratifying because this position is the only one beyond reach of our novel phenanthrene synthesis otherwise.

Total synthesis of aporphine alkaloids: 10-Halophenanthrenes constitute versatile building blocks for the formation of various types of alkaloids such as aporphines or aristolactams. This notion is exemplified by the first total synthesis of O-methyl-dehydroisopiline **74** (see Scheme 11) isolated from the leaves of the annonaceous plant *Gutteria ouregon*,[58,59] and its symmetrical dimer **75**, a secondary metabolite of the tropical trees *Polyalthia bullata*[60] and *Phoenicanthus obliqua*.[61] These compounds are prototype members of the aporphine family, an important class of isoquinoline alkaloids endowed with an impressive number of biological activities.[18,62]

Selective iodination of commercial bromo-trimethoxybenzene **69** furnished compound **70**[87] which underwent a regioselective activation of its C–I bond in the presence of a catalyst formed in situ from $[Pd(OAc)_2]$ and tri-*ortho*-tolylphosphine (see Scheme 11). The resulting organopalladium species reacted with commercial N-vinyl-phthalimide in a standard Heck reaction[63,64] to afford the corresponding enamide which was chemoselectively hydrogenated in the presence of Crabtree's catalyst[65] without damaging the residual bromide function. The resulting compound **71** allowed for a subsequent Suzuki coupling with commercial 2-formyl-benzeneboronic acid to give the highly functionalised biphenyl derivative **72** in 94% yield.[27,66] Conversion of its aldehyde group into the desired bromoalkyne **66b** followed standard procedures and set the stage for the envisaged carbocyclization to form the phenanthrene core. As expected, this key transformation worked exquisitely well in the presence of $InCl_3$ in toluene at 80 °C. The phthalimide protecting group in product **67b** thus formed was cleaved off by hydrazinolysis to give compound **73** which is set up for a smooth intramolecular amination reaction[67] in the presence of CuI and CsOAc as the promoters forging the heterocyclic ring. This high yielding step completed the first total synthesis of O-methyl-dehydroisopiline

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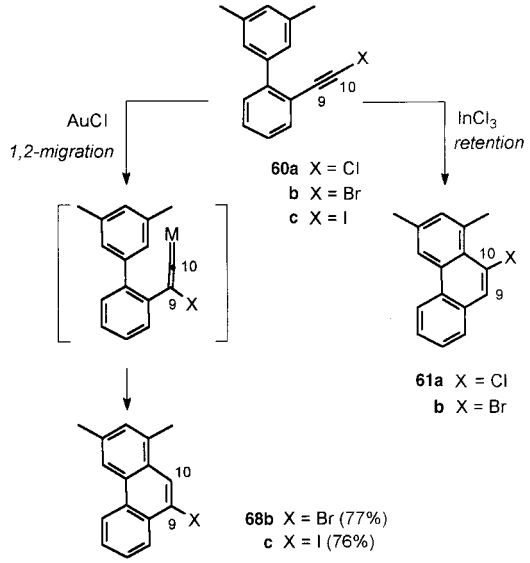
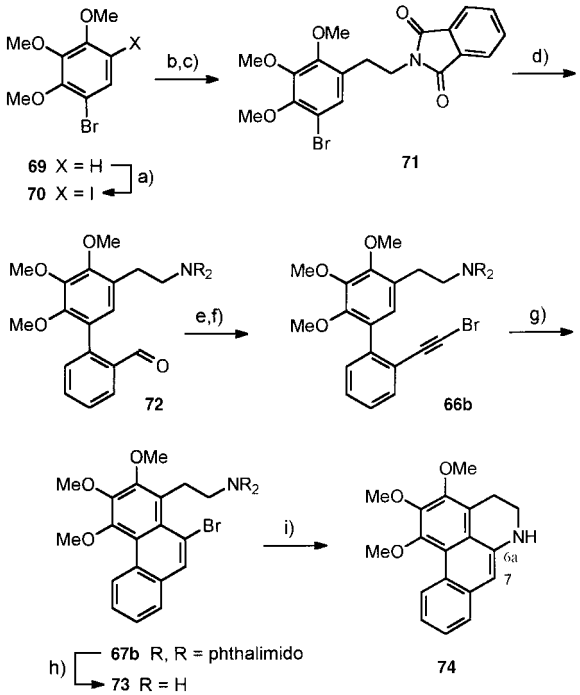


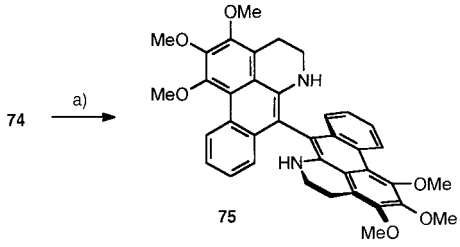
Scheme 10. Synthesis of 9-halo- or 10-halophenanthrenes by metal catalyzed cycloisomerizations.

74. The spectroscopic data of this prototype 6a,7-dihydroaporphine derivative are in excellent agreement with the proposed structure.[58,68] It is worth mentioning, however, that **74** is rather unstable when exposed to air, as can be judged from the rather rapid coloration of the sample.

Because of the enamine-like behavior of 6a,7-dehydroaporphines[69] it was anticipated that a selective activation of the 7-position in **74** might be possible, thus allowing to convert this compound directly to the corresponding symmetrical dimer **75** (Scheme 12). While the use of $PhI(OAc)_2$, $Hg(OAc)_2$, I_2, or air, which were previously recommended for such purposes,[70] was unsuccessful in our hands leading either to no conversion or to a rapid degradation of the starting material, we were pleased to find that a combination of $CuCl_2 \cdot 2H_2O$ and *tert*-$BuNH_2$ in MeOH effected the desired oxidative coupling in satisfactory yields.[71] The spectral data of the somewhat sensitive 7,7′-bisaporphine derivative **75** match those reported in the literature.[60]



Scheme 11. a) I_2, HgO, CH_2Cl_2, RT, 81%. b) $Pd(OAc)_2$ cat., P(*o*-tolyl)$_3$ cat., *N*-vinyl-phthalimide, $(iPr)_2NEt$, MeCN, 100°C, 51%. c) [Ir(cod)(pyridine)(PCy_3)]PF_6 cat., H_2 (1 atm), CH_2Cl_2, quant. d) 2-Formyl-benzeneboronic acid **2**, $[Pd(OAc)_2]$ cat., Cy_2P(*o*-biphenyl) cat., K_3PO_4, toluene, 100°C, 94%. e) CBr_4, PPh_3, CH_2Cl_2, 0°C, 88%. f) DBU, DMSO, 15°C, 79%. g) $InCl_3$ (1 equiv), toluene, 80°C, 87%. h) Hydrazine, MeOH, reflux, quant. i) CuI, CsOAc, DMSO, 71%.



Scheme 12. a) $CuCl_2 \cdot 2H_2O$, *t*$BuNH_2$, MeOH, 86%.

Experimental Section

General: All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF, DMA (Desmodur, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.24 ppm; CD_2Cl_2: δ_C = 53.8 ppm; residual CH_2Cl_2 in CD_2Cl_2: δ_H = 5.32 ppm). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Gallenkamp melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

Substrates

2′-(2,2-Dibromo-vinyl)-3,5-dimethyl-biphenyl (6): CBr_4 (3.30 g, 10 mmol) was added to a solution of PPh_3 (4.50 g, 20.0 mmol) in CH_2Cl_2 (60 mL) and the resulting yellow mixture was stirred for 10 min at 0°C. A solution of 2-(3,5-dimethylphenyl)benzaldehyde (**5**; 840 mg, 4.0 mmol)[17] in CH_2Cl_2 (40 mL) was slowly introduced and stirring was continued for 1 h at that temperature. The reaction was then quenched with brine, the aqueous layer was repeatedly extracted with CH_2Cl_2, the combined organic phases were dried (Na_2SO_4) and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc 95:5) to give dibromide **6** as a yellow syrup (1.40 g, quant.). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, J = 5.2, 2.1 Hz, 1H), 7.38 (m, 3H), 7.24 (s, 1H), 7.03 (s, 1H), 6.96 (s, 2H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 139.7, 137.4, 133.4, 129.4, 128.8, 128.7, 128.2, 127.0, 126.5, 90.0, 21.0; IR (KAP): $\tilde{\nu}$ = 3060, 3023, 2946, 2916, 2858, 1602, 1469, 1447, 851, 758 cm^{-1}; MS (EI): *m*/*z* (%): 366 (1) [M^+], 285 (10), 206 (100), 191 (20).

2-Ethynyl-3′,5′-dimethylbiphenyl (7a): *n*BuLi (1.6 M in THF, 2.35 mL, 3.75 mmol) was added to a solution of dibromide **6** (531 mg, 1.50 mmol) in THF (8 mL) at −78°C and stirring was continued at that temperature for 5 h. The cold mixture was quenched with water, the aqueous phase was repeatedly extracted with *tert*-butyl methyl ether, the combined or-

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ganic layers were dried over Na_2SO_4 and evaporated, and the crude product was purified by flash chromatography (hexanes/EtOAc 98:2) to give alkyne **7a** as a colorless syrup (250 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, 1H, J = 7.3 Hz), 7.38 (m, 2H), 7.29 (m, 1H), 7.22 (s, 2H), 7.03 (s, 1H), 3.05 (s, 1H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 139.8, 137.0, 133.4, 129.2, 128.8, 128.5, 126.7, 126.4, 120.0, 82.6, 79.6, 20.9; IR (KAP): $\tilde{\nu}$ = 3284, 3060, 3026, 2917, 2859, 2105, 1602, 1482, 1470, 1443, 1376, 851, 760, 649, 600 cm^{-1}; MS (EI): m/z (%): 206 (100) [M^+], 191 (95), 165 (14); elemental analysis calcd (%) for $C_{16}H_{14}$ (206.29): C 93.16, H 6.84; found: C 92.97, H 6.90.

All other substrates were prepared analogously. For details and for a compilation of the spectroscopic and analytical data of compounds **7b–d**, **10**, **12**, **16**, **18**, **20**, **22**, **24a**, **26a**, **26b**, **30a**, **30d**, **30e**, see Supporting Information in ref. [17]). The data of all other new compounds are compiled below.

[1,1′]Binaphthalenyl-2-carbaldehyde:[72] A suspension of 1-chloro-3,4-dihydro-naphthalene-2-carbaldehyde (1.925 g, 10 mmol),[73] 1-naphthyl boronic acid (1.9 g, 11 mmol), tetrabutylammonium bromide (3.22 g, 10 mmol), [$Pd(OAc)_2$] (45 mg, 0.2 mmol) and K_2CO_3 (2.45 g, 25 mmol) in degassed water (20 mL) was vigorously stirred for 2 h at 45 °C. After cooling, the mixture was diluted with water (60 mL), the aqueous phase was extracted with EtOAc, the combined organic layers were dried over Na_2SO_4 and evaporated, and the crude product was purified by flash chromatography (hexanes/EtOAc 9:1) to give 3,4-dihydro-[1,1′]binaphthalenyl-2-carbaldehyde as a yellow solid (2.25 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.42 (s, 1H), 7.96 (t, J = 8.7 Hz, 2H), 7.65–7.20 (m, 7H), 7.00 (dd, J = 7.4, 6.9 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 3.07 (m, 2H), 2.89 (m, 1H), 2.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0, 27.6, 125.0, 125.8, 126.2, 126.65, 126.7, 127.8, 128.0, 128.3, 128.35, 128.8, 130.1, 132.5, 132.8, 133.4, 134.9, 135.7, 138.0, 152.9, 193.0; IR (KBr): $\tilde{\nu}$ = 3061, 3016, 2954, 2937, 2852, 2828, 2740, 1660, 1605, 1564, 1504, 1453, 1429, 787 cm^{-1}; MS (EI): m/z (%): 284 (100) [M^+], 267 (46), 255 (60), 239 (33), 128 (22).

DDQ (1.0 g, 4.4 mmol) was added to a solution of the aldehyde described above (1.0 g, 3.5 mmol) in benzene (20 mL) and the mixture was heated at reflux for 5 h. After cooling to ambient temperature, the mixture was filtered, the filtrate was washed with NaOH (1 M, 3 × 30 mL) and the aqueous phase was extracted with toluene. The combined organic phases were dried over Na_2SO_4 and evaporated, and the crude product was purified by flash chromatography (hexanes/EtOAc 98:2) to give [1,1′]binaphthalenyl-2-carbaldehyde as a white solid (580 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.68 (s, 1H), 8.16 (d, J = 8.6 Hz, 1H), 8.03 (m, 2H), 7.96 (m, 2H), 7.62 (m, 2H), 7.52 (m, 2H), 7.36 (m, 3H), 7.22 (d, J = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.3, 144.7, 135.9, 133.3, 133.1, 132.8, 132.7, 131.9, 129.0, 128.7, 128.65, 128.5, 128.1, 128.0, 127.5, 126.8, 126.6, 126.1, 126.0, 124.8, 121.9; IR (KBr): $\tilde{\nu}$ = 3056, 2848, 2754, 1687, 1618, 1594, 1504, 1456, 1429, 783 cm^{-1}; MS (EI): m/z (%): 282 (100) [M^+], 265 (23), 252 (63), 126 (34).

2-Ethynyl-[1,1′]binaphthalenyl (14): nBuLi (1.6 M in hexane, 270 μL, 0.43 mmol) was added to a solution of diisopropylamine (65 μL, 0.46 mmol) in THF (2 mL) at 0 °C. After 10 min, the mixture was cooled to −78 °C before $TMSCHN_2$ (2 M in hexane, 215 μL, 0.43 mmol) was added dropwise and stirring was continued for 30 min. A solution of [1,1′]binaphthalenyl-2-carbaldehyde (101 mg, 0.36 mmol) in THF (1 mL) was then added dropwise and the mixture was allowed to reach ambient temperature overnight. The reaction was quenched with water, the aqueous layer was extracted with *tert*-butyl methyl ether and the combined organic phases were washed with water and brine, dried over Na_2SO_4 and evaporated. The crude product was purified by flash chromatography (hexanes/EtOAc 99:1) to give alkyne **14** (90 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (m, 4H), 7.63 (t, J = 8.6 Hz, 1H), 7.48 (m, 3H), 7.26 (m, 3H), 6.71 (d, J = 8.6 Hz, 1H), 2.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 136.9, 133.9, 133.5, 133.2, 132.9, 129.3, 128.6, 128.5, 128.45, 128.4, 128.3, 128.2, 127.4, 127.1, 127.0, 126.5, 126.45, 126.2, 125.8, 120.5, 83.5, 81.2; IR (KBr): $\tilde{\nu}$ = 3270, 3056, 2096, 1592, 1503, 781 cm^{-1}; MS (EI): m/z (%): 278 (100) [M^+], 138 (27); elemental analysis calcd (%) for $C_{22}H_{14}$ (278.36): C 94.93, H 5.07; found: C 94.86, H 5.02.

2-(2-Phenylethynyl-phenyl)-thiophene (24b): Colorless syrup; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (m, 3H), 7.52 (m, 2H), 7.39 (m, 5H), 7.34 (t, J = 8 Hz, 1H), 7.16 (t, J = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6, 136.4, 134.1, 131.8, 129.4, 128.8, 128.7, 127.6, 127.5, 127.2, 126.3, 123.8, 121.0, 94.1, 89.9; IR (KAP): $\tilde{\nu}$ = 3102, 3057, 3030, 2925, 2852, 2214, 1598, 1491, 1474, 1442, 1423, 853, 831, 753, 688 cm^{-1}; MS (EI): m/z (%): 260 (100) [M^+], 226 (10), 215 (32), 129 (13); elemental analysis calcd (%) for $C_{18}H_{12}S$ (260.35): C 83.04, H 4.65; found: C 83.11, H 4.61.

1-(2-Prop-1-ynyl-phenyl)-pyrrole (30b): Propyne was bubbled for 3 min into a mixture of 1-(2-iodophenyl)pyrrole (**54**; 10.0 g, 37.2 mmol, see below), piperidine (80 mL), [$PdCl_2(PPh_3)_2$] (1.30 g, 1.86 mmol), and CuI (355 mg, 1.86 mmol), leading to the discoloration of the solution and the formation of a white precipitate. Bubbling was discontinued at that stage and the resulting mixture was stirred under the remaining propyne atmosphere for 12 h at ambient temperature during which it turned black. For work-up, the flask was vented, the reaction mixture was filtered through a short pad of silica gel which was carefully rinsed with *tert*-butyl methyl ether (500 mL). The filtrate was successively washed with water (400 mL) and brine (200 mL) before it was dried over Na_2SO_4. Evaporation of the solvent gave a dark liquid which was filtered again through a pad of silica gel (ca. 100 g). The silica gel was carefully rinsed with hexane/EtOAc (99:1) and the filtrate was evaporated. The remaining orange liquid was purified by short-path distillation in vacuo to give product **30b** as a pale yellow liquid (6.20 g, 93%). B.p. 70–75 °C (3 × 10^{-2} Torr); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.7, 1.4 Hz, 1H), 7.35 (dt, J = 7.9, 1.3 Hz, 1H), 7.30 (dd, J = 7.9, 1.4 Hz, 1H), 7.24 (dt, J = 7.5, 1.5 Hz, 1H), 7.13 (t, J = 2.1 Hz, 2H), 6.34 (t, J = 2.1 Hz, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 133.6, 128.1, 125.7, 124.4, 121.2, 118.3, 108.7, 90.5, 4.2; IR (KAP): $\tilde{\nu}$ = 3134, 3102, 3067, 3033, 2954, 2914, 2247, 2225, 1849, 1599, 1568, 1501, 1477, 760, 725 cm^{-1}; MS (EI): m/z (%): 181 (100) [M^+], 154 (21), 77 (10); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.08, H 6.17, N 7.64.

1-(2-Phenylethynyl-phenyl)-1*H*-pyrrole (30c): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.70 (d, J = 7.6 Hz, 1H), 7.53–7.30 (m, 8H), 7.22 (t, J = 2.1 Hz, 2H), 6.39 (t, J = 2.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8, 134.3, 132.1, 130.2, 129.4, 129.2, 127.1, 125.7, 123.6, 122.4, 118.7, 110.0, 94.3, 87.2; IR (KAP): $\tilde{\nu}$ = 3136, 3102, 3062, 3034, 2926, 2852, 2219, 1596, 1570, 1502, 1489, 1447, 755, 724, 689 cm^{-1}; MS (EI): m/z (%): 243 (100) [M^+], 217 (5); elemental analysis calcd (%) for $C_{18}H_{13}N$ (243.31): C 88.86, H 5.39, N 5.76; found: C 88.74, H 5.31, N 5.67.

2-(2-Trimethylsilanylethynyl-phenyl)-1*H*-indole (35): A mixture of 2-(2-iodo-phenyl)-1*H*-indole (**33**; 542 mg, 1.7 mmol),[74] trimethylsilylacetylene (400 μL, 2.8 mmol), [$PdCl_2(PPh_3)_2$] (50 mg, 0.07 mmol), and CuI (13.3 mg, 0.07 mmol) in Et_3N (6 mL) was stirred at ambient temperature for 3 h. The mixture was diluted with *tert*-butyl methyl ether and washed with aq. sat. NH_4Cl and brine. After drying over Na_2SO_4 and evaporation of the solvent, the residue was purified by flash chromatography (hexanes/EtOAc 98:2) to give product **35** as a colorless solid (300 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (br s, 1H), 7.69 (dd, J = 8, 0.8 Hz, 1H), 7.52 (dd, J = 7.8, 0.6 Hz, 1H), 7.44 (dd, J = 7.7, 1.2 Hz, 1H), 7.10 (m, 2H), 7.01 (dt, J = 7.8, 0.8 Hz, 1H), 6.85 (d, J = 1.4 Hz, 1H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 136.2, 134.5, 133.4, 129.2, 128.2, 127.7, 126.9, 122.6, 120.7, 120.1, 117.9, 110.9, 105.7, 101.7, 99.2, −0.2; IR (KBr): $\tilde{\nu}$ = 3417, 3048, 2960, 2897, 2154, 1592, 1560, 1470, 1447, 1249, 864, 842, 762, 743 cm^{-1}; MS (EI): m/z (%): 289 (81) [M^+], 274 (100), 258 (44); elemental analysis calcd (%) for $C_{19}H_{19}NSi$ (289.45): C 78.84, H 6.62, N 4.84; found: C 78.76, H 6.54, N 4.91.

2-(2-Ethynyl-phenyl)-1*H*-indole (36): K_2CO_3 (690 mg, 5 mmol) was added to a solution of compound **35** (180 mg, 0.623 mmol) in MeOH (20 mL). After stirring at ambient temperature for 3 h, the mixture was filtered and the product was extracted with *tert*-butyl methyl ether, the combined organic layers were washed with water, dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc 9:1) to give **36** as a colorless syrup (130 mg, quant.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.51 (br s, 1H), 7.76 (dd, J = 8, 0.9 Hz, 1H), 7.62 (m, 2H), 7.43 (m, 2H), 7.28 (dt, J = 7.6, 1.2 Hz, 1H), 7.18 (dt, J = 7.1, 1.2 Hz, 1H), 7.10 (dt, J = 7, 1 Hz, 1H), 6.98 (dd, J = 2.2, 0.9 Hz, 1H), 3.51 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 136.6, 136.5, 135.1, 134.1, 129.7, 128.5, 128.1, 127.4, 122.8, 120.8, 120.2, 117.7, 111.2, 102.3, 83.8, 82.0; IR (KBr): $\tilde{\nu}$ = 3439, 3427, 3286, 3055, 2098, 1595, 1562, 1535, 1470, 1448, 1403, 750 cm^{-1}; MS (EI): m/z (%): 217 (100) [M^+], 189 (13); elemental analysis calcd (%) for $C_{16}H_{11}N$ (217.27): C 88.45, H 5.10, N 6.45; found: C 88.40, H 5.04, N 6.39.

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2-(2-Prop-1-ynyl-phenyl)-1*H*-indole (34): ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.60 (br s, 1H), 7.74 (dd, J = 8, 0.9 Hz, 1H), 7.61 (dd, J = 7.9, 0.9 Hz, 1H), 7.50 (dd, J = 8, 0.8 Hz, 1H), 7.41 (dt, J = 8.2, 0.8 Hz, 1H), 7.36 (dd, J = 8, 1.4 Hz, 1H), 7.24 (dt, J = 8, 1.3 Hz, 1H), 7.18 (dt, J = 8.1, 1.1 Hz, 1H), 7.08 (dt, J = 7.9, 0.9 Hz, 1H), 6.94 (dd, J = 2.2, 0.9 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 137.1, 136.4, 134.4, 133.1, 128.5, 128.4, 127.9, 127.3, 122.5, 120.6, 120.2, 111.1, 101.8, 91.0, 78.8, 4.5; IR (KBr): $\tilde{\nu}$ = 3407, 3054, 2910, 2845, 2227, 1616, 1595, 1532, 1471, 1446, 760 cm^{-1}; MS (EI): m/z (%): 231 (100) [M^+], 204 (12); elemental analysis calcd (%) for $C_{17}H_{13}N$ (231.29): C 88.28, H 5.67, N 6.06; found: C 88.20, H 5.75, N 6.12.

1-Methyl-2-(2-prop-1-ynyl-phenyl)-1*H*-indole (28): A solution of compound **34** (105 mg, 0.24 mmol) in THF (1 mL) was added to a suspension of NaH (13.1 mg, 0.546 mmol) in THF (1 mL) at ambient temperature and the resulting mixture was heated under reflux for 30 min. After cooling to ambient temperature, freshly distilled methyl iodide (34 μL, 0.546 mmol) was added and the resulting mixture was stirred overnight. A standard extractive work-up followed by flash chromatography (hexanes/EtOAc 9:1) gave product **28** as a colorless syrup (92 mg, 83%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.61 (dd, J = 7.8, 0.9 Hz, 1H), 7.55 (m, 1H), 7.38 (m, 3H), 7.23 (dt, J = 8.2, 1.2 Hz, 1H), 7.12 (dt, J = 7.9, 1 Hz, 1H), 6.53 (d, J = 0.7 Hz, 1H), 3.64 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 140.5, 138.0, 135.0, 132.9, 131.4, 128.3, 128.2, 128.1, 127.6, 124.9, 121.5, 120.5, 119.7, 109.7, 102.1, 89.4, 18.6, 31.0, 4.2; IR (KBr): $\tilde{\nu}$ = 3056, 3022, 2948, 2913, 2848, 2229, 1609, 1542, 1466, 1429, 739 cm^{-1}; MS (EI): m/z (%): 245 (100) [M^+], 230 (50), 202 (15); elemental analysis calcd (%) for $C_{18}H_{15}N$ (245.32): C 88.13, H 6.16, N 5.71; found: C 88.11, H 6.12, N 5.76.

Phenanthrenes and polycyclic heterocycles—Representative procedure for $PtCl_2$-catalyzed cycloisomerization reactions

1,3,10-Trimethyl-6,7-methylenedioxy-phenanthrene (23): A solution of alkyne **22** (528 mg, 2.0 mmol) and $PtCl_2$ (26.6 mg, 0.1 mmol) in toluene (10 mL) was stirred for 24 h at 80 °C under Ar until GC showed complete conversion of the substrate. For work up, the solvent was evaporated and the residue was purified by flash chromatography (hexanes) to give phenanthrene **23** as a colorless solid (495 mg, 94%). M.p. 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.87 (s, 1H), 7.24 (s, 1H), 7.09 (s, 1H), 6.98 (s, 1H), 5.98 (s, 2H), 2.83 (s, 3H), 2.82 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 147.0, 135.5, 134.4, 131.7, 131.6, 131.4, 129.0, 127.8, 125.4, 120.9, 104.0, 100.9, 100.7, 26.1, 25.7, 21.1; IR (KBr): $\tilde{\nu}$ = 2965, 2931, 2904, 1614, 1596, 1504, 1490, 1460, 1438, 1233, 1039, 942, 876 cm^{-1}; MS (EI): m/z (%): 264 (100) [M^+], 249 (18), 189 (11); elemental analysis calcd (%) for $C_{18}H_{16}O_2$ (264.33): C 81.79, H 6.10; found: C 81.75, H 6.13.

3,5-Dimethylphenanthrene (8a):[75] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 8.3 Hz), 8.45 (s, 1H), 7.96 (m, 2H), 7.78 (d, J = 9.1 Hz, 1H), 7.75–7.60 (m, 2H), 7.36 (s, 1H), 2.79 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4, 135.1, 134.3, 131.6, 130.1, 129.3, 128.5, 128.1, 126.0, 125.9, 125.4, 122.6, 122.4, 120.3, 21.7, 19.5; IR (KBr): $\tilde{\nu}$ = 3047, 3007, 2962, 2918, 2853, 1616, 1604, 1504, 1462, 1425, 1377, 858, 817, 754 cm^{-1}; MS (EI): m/z (%): 206 (100) [M^+], 223 (18), 191 (42).

1,3,10-Trimethylphenanthrene (8b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (dd, J = 7.8, 1.5 Hz), 8.45 (s, 1H), 7.76 (dd, J = 7.8, 1.5 Hz, 1H), 7.56 (m, 2H), 7.48 (s, 1H), 7.27 (s, 1H), 2.99 (s, 6H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4, 134.7, 133.3, 132.3, 131.4, 131.4, 129.5, 128.1, 126.9, 126.0, 125.2, 122.5, 121.2, 114.0, 26.3, 25.7, 21.1; IR (KBr): $\tilde{\nu}$ = 3042, 2970, 2911, 2855, 1613, 1600, 1571, 1494, 1462, 1450, 1439, 876, 751 cm^{-1}; MS (EI): m/z (%): 220 (100) [M^+], 205 (40), 189 (11); elemental analysis calcd (%) for $C_{17}H_{16}$ (220.32): C 92.68, H 7.32; found: C 92.47, H 7.28.

1,3-Dimethyl-10-phenyl-phenanthrene (8e): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (dd, J = 8.2, 1.3 Hz, 1H), 8.50 (d, J = 0.5 Hz, 1H), 7.81 (dd, J = 7.8, 1.7 Hz, 1H), 7.62 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.56 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.53 (s, 1H), 7.41 (m, 3H), 7.20 (d, J = 0.6 Hz, 1H), 2.58 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4, 138.7, 136.0, 135.6, 132.5, 132.0, 131.0, 130.2, 129.9, 129.3, 129.2, 128.3, 127.8, 126.7, 126.3, 122.9, 121.2, 25.2, 21.7.

1,3-Dimethoxy-phenanthrene (11):[76] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 9 Hz, 1H), 7.80 (dd, J = 9.2, 1.9 Hz, 1H), 7.60–7.45 (m, 4H), 6.60 (d, J = 2.1 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 157.5, 133.2, 132.6, 130.0, 129.0, 127.0, 126.3, 124.0, 123.5, 120.7, 118.9, 98.1, 95.7, 56.1, 55.9; IR (KBr): $\tilde{\nu}$ = 3050, 3000, 2958, 2936, 2834, 1619, 1601, 1579, 1521, 1505, 1466, 1454, 1424, 1403, 1269, 1153, 815, 750 cm^{-1}; MS (EI): m/z (%): 238 (100) [M^+], 223 (8), 195 (24), 180 (14), 163 (6), 152 (22).

Benzo[*c*]phenanthrene (13):[77] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04 (d, J = 8.4 Hz, 2H), 7.92 (dd, J = 7.9, 1.4 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.59 (dt, J = 6.9, 1.5 Hz, 2H), 7.52 (dt, J = 7, 1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.0, 132.4, 131.8, 128.2, 127.6, 127.1, 126.5, 125.8, 125.5; IR (KBr): $\tilde{\nu}$ = 3049, 3008, 1600, 1519, 1495, 833, 746 cm^{-1}; MS (EI): m/z (%): 228 (100) [M^+], 113 (25).

Dibenzo[*c*,*g*]phenanthrene (15): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 8.4 Hz, 2H), 7.95–7.75 (m, 8H), 7.51 (dt, J = 6.9, 1 Hz, 2H), 7.27 (m, 2H); ^{13}C (100 MHz, $CDCl_3$): δ = 132.6, 132.3, 130.8, 129.1, 127.8, 127.5, 127.3, 127.0, 126.4, 126.3, 124.4; IR (KBr): $\tilde{\nu}$ = 3044, 839, 746 cm^{-1}; MS (EI): m/z (%): 277 (100) [M^+–H], 138 (37).

5,6-Dihydro-benzo[*c*]phenanthrene (17):[78] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.37 (m, 2H), 7.25 (m, 2H), 7.19 (t, J = 7.3 Hz, 1H), 2.82 (m, 2H), 2.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.3, 136.8, 133.8, 133.5, 131.3, 129.7, 128.3, 128.25, 127.4, 127.2, 126.5, 126.1, 125.7, 125.6, 125.2, 124.5, 30.2, 29.1; IR (KAP): $\tilde{\nu}$ = 3050, 2937, 2892, 2834, 1619, 1594, 1510, 1485, 1448, 1428, 1381, 813, 791, 757, 737 cm^{-1}; MS (EI): m/z (%): 230 (100) [M^+], 215 (18), 202 (8).

1-Methoxyphenanthrene (19a):[80] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 8.2, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 7.82 (dd, J = 7.6, 1.4 Hz, 1H), 7.67 (d, J = 9.1 Hz, 1H), 7.60–7.45 (m, 3H), 6.94 (d, J = 7.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 132.6, 131.9, 130.4, 128.9, 127.0, 126.9, 126.7, 126.4, 123.6, 123.5, 120.7, 115.4, 106.2, 56.1; IR (KBr): $\tilde{\nu}$ = 3051, 3001, 2956, 2935, 2831, 1620, 1608, 1597, 1522, 1463, 1434, 1253, 803, 754 cm^{-1}; MS (EI): m/z (%): 208 (100) [M^+], 193 (39), 165 (64).

3-Methoxyphenanthrene (19b):[76,79,80] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, J = 7.6, 1H), 7.99 (d, J = 2.4 Hz, 1H), 7.80 (dd, J = 9.2, 7.7 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.60–7.45 (m, 3H), 7.18 (dd, J = 8.6, 2.1 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 133.2, 132.1, 131.3, 129.6, 128.2, 126.4, 126.25, 126.2, 125.7, 124.2, 122.3, 116.3, 103.7, 55.1; MS (EI): m/z (%): 208 (100) [M^+], 193 (24), 165 (60); IR (KBr): $\tilde{\nu}$ = 3070, 3008, 2964, 2929, 2831, 1619, 1602, 1507, 1455, 1438, 1425, 1224, 843, 745 cm^{-1}.

4-Methoxyphenanthrene (21):[81] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (dd, J = 8.6, 0.6 Hz), 7.80 (dd, J = 7.7, 1.6 Hz), 7.70–7.40 (m, 6H), 7.09 (d, J = 9.1, 1H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 134.3, 132.4, 130.0, 128.2, 127.9, 127.6, 126.7, 126.1, 126.0, 125.5, 121.2, 120.5, 108.0, 55.4; IR (KBr): $\tilde{\nu}$ = 3138, 3048, 2995, 2962, 2939, 2835, 1609, 1598, 1569, 1449, 1431, 1417, 1245, 823, 739, 713 cm^{-1}; MS (EI): m/z (%): 208 (100) [M^+], 193 (27), 165 (55).

Naphtho[1,2-*b*]thiophene (25a):[82] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, J = 8.1, 7.6 Hz, 1H), 7.92 (dd, J = 8.5, 1 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.55 (dd, J = 8, 1.2 Hz, 1H), 7.50 (dt, J = 4.1, 1.3 Hz, 2H), 7.45 (d, J = 5.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.42, 137.39, 130.8, 129.1, 128.8, 126.6, 125.6, 125.3, 125.1, 125.0, 123.6, 122.0.

4-Phenyl-naphtho[1,2-*b*]thiophene (25b): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.21 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 7.7 Hz, 1H), 7.77 (s, 1H), 7.70 (dd, J = 8.1, 1.6 Hz, 1H), 7.64–7.45 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 138.9, 137.2, 137.0, 131.8, 129.9, 129.6, 129.3, 129.0, 128.3, 127.4, 126.8, 125.9, 125.8, 125.4, 124.2; IR (KBr): $\tilde{\nu}$ = 3048, 1492, 1470, 1446, 1436, 882, 779, 733, 682 cm^{-1}; MS (EI): m/z (%): 260 (100) [M^+], 215 (20); elemental analysis calcd (%) for $C_{18}H_{12}S$ (260.35): C 83.04, H 4.65; found: C 83.12, H 4.52.

1*H*-Benzo[*g*]indole (27a):[83] ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.93 (br s, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.44 (m, 2H), 7.35 (dt, J = 7, 1.2 Hz, 1H), 7.22 (t, J = 2.8 Hz, 1H), 6.60 (dd, J = 3, 2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 131.2, 131.1, 129.5, 126.4, 126.2, 124.6, 123.1, 122.5, 121.5, 121.3, 120.1, 104.9; IR (KBr): $\tilde{\nu}$ = 3428, 3414, 3065, 3045, 2960, 2925, 2852, 1623, 1594, 1568, 1528, 1494, 1469, 1450, 811, 721, 688 cm^{-1}; MS (EI): m/z (%): 167 (100) [M^+], 139 (22).

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4-Methyl-1*H*-benzo[*g*]indole (27b): ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.95 (br s, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.39 (dt, J = 7, 1.3 Hz, 1H), 7.31 (dt, J = 6.9, 1.2 Hz, 1H), 7.23 (t, J = 2.8 Hz, 1H), 7.20 (s, 1H), 6.34 (dd, J = 3, 2.2 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 131.7, 131.0, 128.8, 125.5, 125.3, 124.6, 122.8, 121.4, 120.1, 120.0, 103.3, 19.7; IR (KBr): $\tilde{\nu}$ = 3418, 3048, 2982, 2935, 2912, 2850, 1570, 1531, 1497, 1433, 1382, 744, 729, 699 cm^{-1}; MS (EI): m/z (%): 181 (100) [M^+], 152 (15), 90 (10), 77 (10); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.07, H 6.11, N 7.63.

Pyrrolo[1,2-*a*]quinoline (31a):[84] ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.79 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 1.5 Hz, 1H), 7.54 (dd, J = 7.8, 1.3 Hz, 1H), 7.40 (dt, 8.5, 1.5 Hz, 1H), 7.22 (dt, J = 7.9, 1 Hz, 2H), 6.88 (d, J = 9.3 Hz, 1H), 6.67 (dd, J = 3.6, 3 Hz, 1H), 6.41 (dd, J = 3.7, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 134.2, 131.8, 129.3, 128.5, 124.6, 124.3, 119.6, 119.3, 114.9, 113.4, 112.7, 103.5; IR (KBr): $\tilde{\nu}$ = 3146, 3104, 3052, 2956, 2925, 2853, 1605, 1551, 1508, 1486, 1448, 1421, 801, 751, 702 cm^{-1}; MS (EI): m/z (%): 167 (100) [M^+], 139 (12).

4-Methyl-pyrrolo[1,2-*a*]quinoline (31b): ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.91 (m, 2H), 7.65 (dd, J = 7.8, 1.3 Hz, 1H), 7.50 (dt, J = 7.3, 1.4 Hz, 1H), 7.35 (dt, J = 7.9, 1 Hz, 1H), 6.87 (s, 1H), 6.82 (dd, J = 3.7, 3 Hz, 1H), 6.57 (dd, J = 3.8, 1.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.7, 128.5, 127.5, 125.1, 124.2, 118.0, 114.7, 113.1, 113.0, 101.9, 18.7; IR (KBr): $\tilde{\nu}$ = 3142, 3097, 3052, 2944, 2913, 2850, 1607, 1541, 1486, 1458, 1419, 866, 840, 773, 753, 739, 703 cm^{-1}; MS (EI): m/z (%): 181 (100) [M^+], 152 (10), 77 (7); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.10, H 6.21, N 7.67.

4-Phenyl-pyrrolo[1,2-*a*]quinoline (31c): ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.00 (m, 1H), 7.97 (s, 1H), 7.76 (m, 3H), 7.70–7.45 (m, 4H), 7.40 (dt, J = 7.9, 1 Hz, 1H), 7.06 (s, 1H), 6.84 (dd, J = 3.8, 3 Hz, 1H), 6.64 (dd, J = 3.9, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_2C_2): δ = 139.8, 133.4, 129.5, 129.3, 129.1, 128.8, 128.4, 125.0, 124.5, 118.7, 114.8, 113.5, 113.4, 104.0; IR (KBr): $\tilde{\nu}$ = 3142, 3102, 3058, 2924, 2853, 1602, 1537, 1489, 1453, 1418, 1336, 868, 839, 783, 750, 739, 700 cm^{-1}; MS (EI): m/z (%): 243 (100) [M^+]; elemental analysis calcd (%) for $C_{18}H_{13}N$ (243.31): C 88.86, H 5.39, N 5.76; found: C 88.80, H 5.47, N 5.72.

4-Hexyl-pyrrolo[1,2-*a*]quinoline (31d): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.3 Hz, 2H), 7.52 (dd, J = 7.8, 1.4 Hz), 7.36 (dt, J = 7.2, 1.4 Hz, 1H), 7.20 (dd, J = 7.9, 1 Hz, 1H), 6.74 (s, 1H), 6.71 (s, 1H), 6.48 (br s, 1H), 2.71 (t, J = 7.4 Hz, 2H), 1.70 (m, 2H), 1.39 (m, 2H), 1.28 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.1, 131.1, 127.6, 126.4, 124.0, 123.0, 116.0, 113.6, 111.9, 111.7, 100.6, 32.1, 31.4, 29.0, 28.4, 22.3, 13.7; IR (KAP): $\tilde{\nu}$ = 3142, 3101, 2955, 2923, 2852, 1540, 1487, 1455, 1422, 1385, 835, 753, 736, 700 cm^{-1}; MS (EI): m/z (%): 251 (65) [M^+], 208 (9), 194 (20), 181 (100); elemental analysis calcd (%) for $C_{18}H_{21}N$ (251.37) C 86.01, H 8.42, N 5.57; found: C 85.91, H 8.36, N 5.53.

4-Trimethylsilyl-pyrrolo[1,2-*a*]quinoline (31e): ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.92 (s, 1H), 7.88 (dd, J = 3.1, 1.6 Hz, 1H), 7.69 (dd, J = 7.8, 1.2 Hz, 1H), 7.54 (dt, J = 7.3, 1.5 Hz, 1H), 7.35 (dt, J = 7.5, 0.9 Hz, 1H), 7.19 (s, 1H), 7.01 (t, J = 3.1 Hz, 1H), 6.62 (dd, J = 3.8, 1.2 Hz, 1H), 0.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 133.9, 131.0, 129.3, 128.9, 124.2, 124.1, 114.7, 113.1, 112.1, 104.3, −0.8; elemental analysis calcd (%) for $C_{15}H_{17}NSi$ (239.40): C 75.26, H 7.16, N 5.85; found: C 75.20, H 7.10, N 5.93.

6,11-Dimethyl-11*H*-benzo[*a*]carbazole (29): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.69 (m, 1H), 8.29 (d, J = 8 Hz, 1H), 7.93 (m, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.52 (m, 3H), 7.41 (s, 1H), 7.30 (dt, J = 8.1, 0.9 Hz, 1H), 4.37 (s, 3H), 2.99 (d, J = 0.9 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 141.0, 135.7, 133.7, 132.2, 128.5, 124.9, 124.4, 124.3, 123.5, 122.3, 122.2, 121.4, 120.6, 119.6, 118.5, 109.1, 34.2, 21.5; IR (KBr): $\tilde{\nu}$ = 3072, 3056, 2985, 2921, 2852, 1558, 1524, 1469, 1428, 738 cm^{-1}; MS (EI): m/z (%): 245 (100) [M^+], 230 (30); elemental analysis calcd (%) for $C_{18}H_{15}N$ (245.32): C 88.13, H 6.16; found: C 88.08, H 6.10.

11*H*-Benzo[*a*]carbazole (37): ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.90 (br s, 1H), 8.15 (m, 3H), 8.02 (d, J = 8 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.61 (m, 2H), 7.55 (t, J = 8.2 Hz, 1H), 7.43 (dt, J = 7.6, 1 Hz, 1H), 7.30 (dt, J = 7.6, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 138.2, 135.1, 132.6, 129.1, 125.8, 125.4, 125.1, 124.2, 121.3, 120.7, 120.3, 120.1, 119.9, 119.4, 118.5, 111.3; IR (KBr): $\tilde{\nu}$ = 3437, 1627, 1561, 1529, 1460, 1442, 818, 739 cm^{-1}; MS (EI): m/z (%): 217 (100) [M^+], 189 (6); elemental analysis calcd (%) for $C_{16}H_{11}N$ (217.27): C 88.45, H 5.10; found: C 88.36, H 5.12.

Indolo[2,1-*a*]isoquinoline (39): Separated from isomer **37** by flash chromatography (hexanes/EtOAc 95:5). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.17 (dd, J = 8.6, 1.2 Hz, 1H), 8.12 (d, J = 7.4 Hz, 1H), 7.82 (m, 2H), 7.59 (dd, J = 7.5, 1.5 Hz, 1H), 7.49 (m, 2H), 7.32 (m, 2H), 7.29 (s, 1H), 6.74 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 133.3, 127.8, 127.4, 126.3, 126.0, 125.5, 124.6, 122.2, 121.0, 120.8, 119.3, 119.1, 108.3, 107.1, 91.4; IR (KBr): $\tilde{\nu}$ = 3055, 2962, 2924, 2853, 1540, 1487, 1477, 1460, 1452, 787, 739 cm^{-1}; MS (EI): m/z (%): 217 (100) [M^+], 189 (7); elemental analysis calcd (%) for $C_{16}H_{11}N$ (217.27): C 88.45, H 5.10; found: C 88.41, H 5.08.

11-Benzenesulfonyl-11*H*-benzo[*a*]carbazole (38): A solution of compound **37** (50 mg, 0.24 mmol) in THF (0.5 mL) was slowly added to a suspension of NaH (7.5 mg, 0.313 mmol) in THF (0.5 mL) at ambient temperature and the resulting mixture was heated under reflux for 30 min. After cooling to ambient temperature, freshly distilled benzenesulfonyl chloride (32 μL, 0.264 mmol) was introduced. After stirring overnight, the reaction mixture was hydrolyzed and extracted with *tert*-butyl methyl ether. After drying of the combined organic phases over Na_2SO_4 and evaporation of the solvent, the residue was purified by flash chromatography (hexanes/EtOAc 98:2) to give **38** as a colorless solid (72 mg, 86%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.96 (d, J = 8.7 Hz, 1H), 8.30 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.71 (dd, J = 7.6, 0.5 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (dt, J = 7.7, 1.1 Hz, 1H), 7.36 (dt, 7.5, 0.8 Hz, 1H), 7.25 (m, 1H), 6.94 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 141.8, 138.0, 134.5, 134.2, 133.5, 130.2, 128.5, 128.0, 127.9, 127. 0, 126.9, 126.4, 126.2, 126.0, 125.1, 119.8, 119.6, 117.6; IR (KBr): $\tilde{\nu}$ = 3059, 1460, 1446, 1366, 1179, 817, 751, 578 cm^{-1}; MS (EI): m/z (%): 357 (20) [M^+], 216 (100), 189 (6); elemental analysis calcd (%) for $C_{22}H_{15}NO_2S$ (357.43): C 73.93, H 4.23, N 3.92; found: C 73.89, H 4.28, N 3.84.

Phenanthrenes related to combretastatin A-4

2,3,4-Tetramethoxy-2′-carboxy-biphenyl (47c): A solution of Na_2CO_3 (9.16 g, 87 mmol) in degassed water (40 mL) was added to a solution of 2-bromo-benzaldehyde (**45c**; 4.0 g, 22 mmol), 2,3,4-trimethoxy-phenylboronic acid (**46**; 6.9 g, 32 mmol), [Pd(PPh$_3$)$_4$] (1.25 g, 1.1 mmol) and LiCl (2.75 g, 65 mmol) in DME (150 mL). The resulting suspension was stirred at 80 °C for 12 h before it was diluted with water. The aqueous phase was extracted with *tert*-butyl methyl ether, the combined organic layers were dried over Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc 9:1) to yield product **47c** as a white solid (4.98 g, 85%). M.p. 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.85 (d, J = 0.6 Hz, 1H), 8.00 (dd, J = 7.8, 1.5 Hz, 1H), 7.62 (dt, J = 7.5, 1.5 Hz, 1H), 7.47 (m, 1H), 7.37 (dd, J = 7.8, 1.5 Hz, 1H), 6.98 (d, J = 8.7 Hz, 1H), 6.78 (d, J = 8.7 Hz, 1H), 3.93 (s, 6H), 3.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.4, 154.1, 151.2, 142.1, 141.4, 133.9, 133.5, 131.3, 127.6, 126.9, 125.6, 124.6, 107.5, 61.1, 60.7, 56.1; IR (KAP): $\tilde{\nu}$ = 2996, 2936, 2839, 2750, 1696, 1597, 1466, 1411, 1283, 1096, 765 cm^{-1}; MS (EI): m/z (%): 272 (100) [M^+], 257 (12), 241 (60), 198 (13), 115 (21); elemental analysis calcd (%) for $C_{16}H_{16}O_4$ (272.3): C 70.58, H 5.92; found: C 70.63, H 6.04.

4-(Benzyloxy)-2′,3′,4′,5-tetramethoxy-2-carboxy-biphenyl (47a): Prepared analogously; colorless solid (110 mg, 87%); m.p. 143–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.69 (s, 1H), 7.59 (s, 1H), 7.45 (m, 5H), 6.95 (d, J = 8.4 Hz, 1H), 6.83 (s, 1H), 6.75 (d, J = 8.4 Hz, 1H), 5.23 (s, 2H), 3.95 (s, 3H), 3.92 (s, 6H), 3.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.2, 154.0, 153.9, 151.5, 147.8, 142.2, 137.0, 136.5, 128.6, 128.1, 127.63, 127.2, 125.9, 124.3, 113.6, 110.3, 107.3, 70.9, 61.1, 60.8, 56.2; IR (KAP): $\tilde{\nu}$ = 2931, 2856, 2836, 2776, 1680, 1594, 1491, 1454, 1254, 1015 cm^{-1}; MS (EI): m/z (%): 408 (61) [M^+], 377 (23), 317 (100), 91 (39); elemental analysis calcd (%) for $C_{24}H_{24}O_6$ (408.45): C 70.58, H 5.92; found: C 70.68, H 5.99.

2,3,4,4′-Tetramethoxy-2′-carboxy-biphenyl (47b): Prepared analogously; pale yellow solid (125 mg, 89%); m.p. 102–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 7.50 (d, J = 2.7 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 8.4, 3 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 3.92 (s, 6H), 3.90 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.3, 159.1, 153.9, 151.4, 142.1, 134.7, 134.3, 132.5, 125.7, 124.4, 121.2, 109.5, 107.5, 61.1, 60.6, 56.1, 55.6; IR (KAP): $\tilde{\nu}$ = 2974, 2940, 2844, 2752, 1682, 1597, 1484, 1459, 1436, 1420, 1405 cm^{-1}; MS (EI): m/z

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(%): 302 (100) [M^+], 287 (14), 271 (67), 228 (14); elemental analysis calcd (%) for $C_{17}H_{18}O_5$ (302.33): C 67.54, H 6.00; found: C 67.66, H 5.91.

4-(Benzyloxy)-2′,4′,5-trimethoxy-2-carboxy-biphenyl (51): Prepared analogously; colorless solid (1.04 g, 88%); m.p. 120–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.62 (s, 1H), 7.56 (s, 1H), 7.48 (d, J = 7.5 Hz, 2H), 7.35 (m, 3H), 7.17 (d, J = 8.1 Hz, 1H), 6.79 (s, 1H), 6.59 (dd, J = 8.4, 2.4 Hz, 1H), 6.54 (d, J = 2.1, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 161.2, 157.7, 154.0, 147.7, 137.2, 136.6, 132.1, 128.6, 128.1, 127.6, 127.3, 119.2, 113.7, 110.1, 104.7, 98.5, 70.8, 56.2, 55.2; IR (KAP): $\tilde{\nu}$ = 2933, 2865, 1669, 1594, 1497, 1455, 1436, 1455, 1436, 1393, 1380, 1347, 1306, 1287, 1274, 1254, 1208 cm^{-1}; MS (EI): m/z (%): 378 (50) [M^+], 287 (100), 91 (37); elemental analysis calcd (%) for $C_{23}H_{22}O_5$ (378.43): C 73, H 5.86; found: C 72.88, H 5.82.

2,3,4-Trimethoxy-2′-ethynyl-biphenyl (48c): nBuLi (1.6 M in hexanes, 4.13 mL, 6.61 mmol) was added to a solution of diisopropylamine (1 mL, 7.16 mmol) in THF (10 mL) at 0 °C. After stirring for 1 h, the mixture was cooled to −78 °C before TMS-diazomethane (2 M in hexanes, 3.3 mL, 6.61 mmol) was added dropwise. After stirring for 1 h, a solution of aldehyde **47c** (1.5 g, 5.5 mmol) in THF (20 mL) was introduced and the resulting mixture was stirred overnight while reaching ambient temperature. The reaction was quenched with water, the aqueous phase was extracted with EtOAc, the combined organic layers were washed with brine before being dried over Na_2SO_4, and the solvent was evaporated to give alkyne **48c** as a white solid (1.25 g, 84%). M.p. 89–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (m, 1H), 7.33 (m, 3H), 7.00 (d, J = 8.7 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 3.9 (s, 3H), 3.66 (s, 3H), 2.97 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 151.6, 142.1, 141.4, 133.0, 128.4, 127.4, 126.9, 125.4, 122.0, 106.7, 83.2, 79.7, 61.1, 61.0, 56.0; IR (KAP): $\tilde{\nu}$ = 3274, 3004, 2965, 2939, 2840, 1600, 1591, 1502, 1479, 1458, 1432, 1410, 1308, 1289, 1269, 1098 cm^{-1}; MS (EI): m/z (%): 268 (100) [M^+], 253 (15), 237 (15), 222 (31), 210 (17), 139 (33); elemental analysis calcd (%) for $C_{17}H_{16}O_3$ (268.32): C 76.10, H 6.01; found: C 75.88, H 6.04.

Analogously have been obtained:

4-(Benzyloxy)-2′,3′,4′,5-tetramethoxy-2-ethynyl-biphenyl (48a): Pale yellow solid (423 mg, 74%); m.p. 121–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (m, 2H), 7.35 (m, 3H), 7.13 (s, 1H), 7.04 (d, J = 8.7 Hz, 1H), 6.86 (s, 1H), 6.71 (d, J = 8.7 Hz, 1H), 5.16 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.68 (s, 3H), 2.83 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 152.0, 150.3, 147.3, 142.5, 137.2, 135.7, 129.0, 128.4, 127.8, 127.5, 126.0, 118.1, 114.2, 114.0, 107.0, 83.7, 78.6, 71.5, 61.5, 61.4, 56.4, 56.4; IR (KAP): $\tilde{\nu}$ = 3287, 3007, 2936, 2841, 2098, 1596, 1561, 1517, 1492, 1453, 1434, 1415, 1381, 1357, 1289, 1278, 1257, 1207, 1144, 1098, 1065, 1014 cm^{-1}; MS (EI): m/z (%): 404 (54) [M^+], 313 (100), 239 (11), 91 (18); elemental analysis calcd (%) for $C_{25}H_{24}O_5$ (404.47): C 74.24, H 5.98; found: C 74.12, H 5.94.

2,3,4,4′-Tetramethoxy-2′-ethynyl-biphenyl (48b): Pale yellow solid (278 mg, 93%); m.p. 103–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 4.2 Hz, 1H), 7.11 (d, J = 2.7 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 6.94 (dd, J = 8.4, 2.7 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H), 3.65 (s, 3H), 2.96 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 153.2, 151.7, 142.1, 133.9, 131.5, 127.1, 125.6, 122.7, 117.4, 115.2, 106.6, 83.2, 79.5, 76.6, 61.0, 56.0, 55.4; IR (KAP): $\tilde{\nu}$ = 3226, 3007, 2938, 2835, 2103, 1597, 1572, 1561, 1476, 1460, 1440, 1414, 1402, 1288, 1273, 1233, 1206, 1096, 1078, 1037, 1005 cm^{-1}; MS (EI): m/z (%): 298 (100) [M^+], 283 (18), 267 (17), 252 (30), 237 (23), 169 (18), 126 (19); elemental analysis calcd (%) for $C_{18}H_{18}O_4$ (298.34): C 72.47, H 6.08; found: C 72.36, H 6.15.

4-(Benzyloxy)-2′,4′,5-trimethoxy-2-ethynyl-biphenyl (52): Pale yellow solid (740 mg, 79%); m.p. 127–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (m, 2H), 7.36 (m, 3H), 7.22 (dd, J = 6, 3 Hz, 1H), 7.12 (s, 1H), 6.85 (s, 1H), 6.55 (m, 2H), 5.16 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.78 (s, 3H), 2.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 158.2, 150.3, 147.1, 137.3, 135.8, 132.2, 129.0, 128.3, 127.8, 122.6, 118.1, 114.4, 114.3, 104.5, 99.3, 83.8, 77.0, 71.5, 56.4, 56.0, 55.8; IR (KAP): $\tilde{\nu}$ = 3261, 3014, 2937, 2097, 1597, 1579, 1564, 1515, 1498, 1466, 1454, 1443, 1430, 1415, 1385, 1337, 1306, 1203 cm^{-1}; MS (EI): m/z (%): 374 (48) [M^+], 283 (100), 91 (20); elemental analysis calcd (%) for $C_{24}H_{22}O_4$ (374.44): C 76.99, H 5.92; found: C 76.87, H 5.98.

2,3,4-Trimethoxyphenanthrene (44): A suspension of $PtCl_2$ (3 mg, 0.011 mmol) and alkyne **48c** (60 mg, 0.22 mmol) in toluene (10 mL) was stirred at 80 °C for 12 h. Evaporation of the solvent followed by flash chromatography (hexanes/EtOAc 10:1) of the crude product gave product **44** as an off-white solid (38 mg, 63%). The use of AuCl (2.6 mg, 0.011 mmol) under otherwise identical conditions provided product **44** (44 mg, 73%). M.p. 86–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.50 (d, J = 9.5 Hz, 1H), 7.84 (dd, J = 7.8, 1.5 Hz, 1H), 7.59 (m, 4H), 7.10 (s, 1H), 4.04 (s, 3H), 4.03 (s, 3H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 152.5, 142.9, 131.8, 130.2, 129.9, 128.4, 127.2, 126.7, 126.5, 125.5, 119.0, 105.2, 61.3, 60.3, 55.9; IR (KAP): $\tilde{\nu}$ = 2928, 2839, 2619, 1597, 1564, 1515, 1496, 1467, 1442, 1417, 1388, 1345, 1307, 1266, 1245, 1222, 1125 cm^{-1}; MS (EI): m/z (%): 268 (100) [M^+], 253 (40), 225 (19), 210 (31), 139 (31); elemental analysis calcd (%) for $C_{17}H_{16}O_3$ (268.32): C 76.1, H 6.01; found: C 75.99, H 6.07.

7-Benzyloxy-2,3,4,6-tetramethoxy-phenanthrene (49): White solid (74 mg, 70%); m.p. 125–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.03 (s, 1H), 7.47–7.43 (m, 2H), 7.42 (s, 1H), 7.41 (s, 1H), 7.29 (m, 3H), 7.17 (s, 1H), 7.00 (s, 1H), 5.24 (s, 2H), 4.03 (s, 3H), 3.97 (s, 3H), 3.96 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.6, 151.6, 149.3, 147.3, 142.6, 137.0, 129.5, 128.6, 127.9, 127.4, 127.0, 126.2, 124.7, 118.6, 110.5, 108.0, 105.2, 70.7, 61.4, 60.5, 55.9, 55.8, 14.2; IR (KAP): $\tilde{\nu}$ = 2996, 2930, 2827, 1614, 1570, 1516, 1503, 1475, 1463, 1434, 1419, 1400, 1384, 1351, 1293, 1269, 1244, 1208, 1160, 1125 cm^{-1}; MS (EI): m/z (%): 404 (69) [M^+], 313 (100), 298 (16), 254 (12), 91 (18); elemental analysis calcd (%) for $C_{25}H_{24}O_5$ (404.47): C 74.24, H 5.98; found: C 74.15, H 6.91.

2,3,4,7-Tetramethoxyphenanthrene (43): Colorless solid (138 mg, 86%); m.p. 149–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.41 (d, J = 9.12 Hz, 1H), 7.58 (s, 2H), 7.25 (m, 2H), 7.07 (s, 1H), 4.03 (s, 3H), 4.01 (s, 3H), 4.00 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 151.8, 151.8, 142.9, 133.4, 129.1, 128.4, 127.1, 126.7, 124.2, 119.2, 116.8, 108.7, 105.2, 61.3, 60.2, 55.9, 55.3; IR (KAP): $\tilde{\nu}$ = 3005, 2929, 2837, 1611, 1566, 1520, 1497, 1473, 1454, 1431, 1420, 1399, 1383, 1346, 1303, 1273, 1223 cm^{-1}; MS (EI): m/z (%): 298 (100) [M^+], 283 (33), 255 (11), 240 (35), 197 (13), 169 (17), 148 (10); elemental analysis calcd (%) for $C_{18}H_{18}O_4$ (298.34): C 72.47, H 6.08; found: C 72.08, H 5.96.

7-Benzyloxy-2,4,6-trimethoxy-phenanthrene (53): Off-white solid (71 mg, 73%); m.p. 154–155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.12 (s, 1H), 7.53 (m, 4H), 7.35 (m, 3H), 7.24 (s, 1H), 6.86 (d, J = 2.7 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H), 5.30 (s, 2H), 4.10 (s, 3H), 4.08 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 157.6, 149.5, 147.2, 137.5, 135.2, 129.0, 128.2, 127.8, 127.7, 127.3, 125.8, 125.4, 115.8, 110.9, 109.8, 101.6, 99.6, 71.1, 56.3, 56.2, 55.8; IR (KAP): $\tilde{\nu}$ = 2999, 2963, 2936, 2837, 1618, 1578, 1521, 1503, 1481, 1468, 1457, 1407, 1382, 1370, 1295, 1271 cm^{-1}; MS (EI): m/z (%): 374 (55) [M^+], 283 (100), 255 (12), 240 (10), 91 (16); elemental analysis calcd (%) for $C_{24}H_{22}O_4$ (374.44): C 76.99, H 5.92; found: C 77.11, H 6.03.

7-Hydroxy-2,3,4,6-tetramethoxyphenanthrene (41): A suspension of compound **49** (100 mg, 0.25 mmol) and Pd/C (10 mg, 10% w/w) in EtOAc (16 mL) was stirred for 3 d under an atmosphere of H_2 (1 atm). The catalyst was filtered off, the filtrate was evaporated and the crude product was purified by flash chromatography (hexanes/EtOAc 9:1) to give product **41** as a pale yellow solid (74 mg, 96%). M.p. 168–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.00 (s, 1H), 7.52 (dd, J = 15.3, 9 Hz, 2H), 7.32 (s, 1H), 7.09 (s, 1H), 5.89 (s, 1H), 4.11 (s, 3H), 4.05 (s, 3H), 4.04 (s, 3H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.1, 151.9, 147.1, 145.0, 142.9, 129.7, 128.1, 126.6, 125.3, 124.4, 119.1, 111.6, 107.4, 105.7, 77.6, 61.7, 60.8, 56.2; IR (KBr): $\tilde{\nu}$ = 3435, 3005, 2935, 2836, 1633, 1605, 1572, 1523, 1504, 1479, 1463, 1435, 1421, 1408, 1388, 1353, 1276 cm^{-1}; MS (EI): m/z (%): 314 (100) [M^+], 299 (42), 271 (15), 256 (28); elemental analysis calcd (%) for $C_{18}H_{18}O_5$ (314.34): C 68.78, H 5.77; found: C 68.71, H 5.73.

7-Hydroxy-2,4,6-trimethoxy-phenanthrene (42): Prepared analogously; pale yellow solid (60 mg, 79%); m.p. 171–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.02 (s, 1H), 7.51 (dd, J = 23.4, 8.7 Hz, 2H), 7.27 (s, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 5.80 (s, 1H), 4.02 (s, 3H), 4.01 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 157.7, 146.8, 144.5, 135.0, 127.9, 127.9, 125.6, 125.1, 116.1, 111.4, 108.6, 101.7, 99.6, 56.2, 56.1, 55.8; IR (KBr): $\tilde{\nu}$ = 3434, 3158, 3010, 2962, 2934, 2840, 1612, 1581, 1529, 1503, 1486, 1464, 1451, 1443, 1417, 1394, 1374, 1361 cm^{-1}; MS (EI): m/z (%): 284 (100) [M^+], 269 (22), 241 (12), 237 (20), 142 (14); elemental analysis calcd (%) for $C_{17}H_{16}O_4$ (284.31): C 71.82, H 5.67; found: C 71.75, H 5.57.

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Preparation and cyclization of allenes

1-(2-Iodophenyl)pyrrole (54): 2,5-Dimethoxytetrahydrofuran (15.5 mL, 119.7 mmol) was added over a period of 10 min to a refluxing solution of 2-iodoaniline (25.0 g, 114.0 mmol) and glacial HOAc (25 mL). Once the addition was complete, reflux was continued for 5 min before the acetic acid was distilled off under reduced pressure and the remaining brown residue was purified by a short-path distillation in vacuo (3×10^{-2} Torr). The fraction distilling at 80–90 °C was collected to give product **54** as a pale yellow liquid (21.7 g, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.97 (dd, $J=8$, 1.4 Hz, 1H), 7.43 (dt, $J=7.7$, 1.4 Hz, 1H), 7.33 (dd, $J=7.8$, 1.6 Hz, 1H), 7.12 (dt, $J=7.5$, 1.7 Hz, 1H), 6.84 (t, $J=2.1$ Hz, 2H), 6.36 (t, $J=2.1$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=143.7$, 139.6, 128.9, 128.5, 127.7, 121.8, 108.8, 95.4; IR (KAP): $\tilde{\nu}=3127$, 3101, 3057, 1581, 1494, 1466, 1438, 760, 725 cm^{-1}; MS (EI): *m*/*z* (%): 269 (100) [M^+], 142 (23), 115 (46).

3-(2-Pyrrol-1-yl-phenyl)-prop-2-yn-1-ol (55a): A mixture of iodide **54** (2.7 g, 10 mmol), propargyl alcohol (0.88 mL, 15 mmol), [$PdCl_2(PPh_3)_2$] (175 mg, 0.25 mmol), Et_3N (30 mL) and CuI (95 mg, 0.5 mmol) was stirred at 60 °C for 3 h. The reaction was quenched at ambient temperature with water and the aqueous phase was extracted with EtOAc. After drying of the combined organic layers over Na_2SO_4 and evaporation of the solvent, the crude product was purified by flash chromatography (hexanes/EtOAc 3:1) to give compound **55a** as a colorless syrup (1.85 g, 94 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.59$ (dd, $J=7.6$, 1.5 Hz, 1H), 7.42 (dt, $J=7.3$, 1.6 Hz, 1H), 7.32 (m, 2H), 7.13 (t, $J=2.1$ Hz, 2H), 6.33 (t, $J=2.2$ Hz, 2H), 4.42 (d, $J=6.2$ Hz, 2H), 1.85 (t, $J=6.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=142.8$, 134.7, 130.3, 127.1, 125.7, 122.3, 118.0, 110.1, 92.9, 83.0, 52.1; IR (KAP): $\tilde{\nu}=3339$, 3127, 3103, 3062, 2911, 2861, 2230, 1599, 1569, 1501, 1477, 1447, 1332, 762, 728 cm^{-1}; MS (EI): *m*/*z* (%): 197 (50) [M^+], 196 (100), 178 (16), 167 (77); elemental analysis calcd (%) for $C_{13}H_{11}NO$ (197.24): C 79.17, H 5.62, N 7.10; found: C 79.16, H 5.66, N 6.97.

1-[2-(3-Bromo-prop-1-ynyl-phenyl)-1*H*-pyrrole (55b): CBr_4 (6.0 g, 18 mmol) was added to a solution of alcohol **55a** (2.96 g, 15 mmol) and PPh_3 (4.85 g, 18.45 mmol) in CH_2Cl_2 (75 mL) at 0 °C. After stirring for 45 min, the solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc 99:1) to give product **55b** as a pale yellow syrup (3.4 g, 87 %). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=7.60$ (dd, $J=$ 7.7, 1.5 Hz, 1H), 7.47 (dt, $J=7.5$, 1.6 Hz, 1H), 7.34 (m, 2H), 7.24 (t, $J=$ 2.2 Hz, 2H), 6.34 (t, $J=2.2$ Hz, 2H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=142.5$, 134.5, 130.3, 126.4, 125.0, 121.7, 116.7, 109.8, 88.9, 83.8, 15.5.

1-(2-Propa-1,2-dienyl-phenyl)-1*H*-pyrrole (56a): DIAD (220 μL, 1.518 mmol) was added to a solution of PPh_3 (400 mg, 1.518 mmol) in THF (5 mL) at −15 °C. The resulting mixture was stirred for 5 min before a solution of alcohol **55a** (230 mg, 1.168 mmol) in THF (3 mL) was introduced. After an additional 10 min, a solution of *ortho*-nitrobenzenesulfonylhydrazide (330 mg, 1.518 mmol)[85] in THF (5 mL) was added and the reaction was stirred at −15 °C for 1 h and at 23 °C overnight. The solvent was evaporated and the residue was purified by flash chromatography (hexanes) to give **56a** as a colorless syrup (137 mg, 65 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.59$ (d, $J=7.3$ Hz, 1H), 7.37 (m, 1H), 7.30 (m, 2H), 6.86 (t, $J=2.1$ Hz, 2H), 6.33 (t, $J=2.1$ Hz, 2H), 6.02 (t, $J=$ 6.8 Hz, 1H), 5.18 (d, $J=6.8$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=$ 211.1, 139.3, 130.7, 128.5, 128.4, 128.1, 127.6, 123.3, 109.8, 89.8, 79.3; IR (KAP): $\tilde{\nu}=3129$, 3102, 3066, 2923, 1940, 1600, 1578, 1478, 1327, 851, 761, 726 cm^{-1}; MS (EI): *m*/*z* (%): 181 (93) [M^+], 180 (100), 152 (18); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.08, H 6.17, N 7.68.

1-[2-(1-Methyl-propa-1,2-dienyl)-phenyl]-1*H*-pyrrole (56b): MeMgCl (2.7 M in THF, 6.4 mL, 17.3 mmol) was added to a suspension of CuCN (1.55 g, 17.3 mmol) and anhydrous LiCl (1.47 g, 34.6 mmol) in THF (30 mL) at 0 °C. After being stirred at that temperature for 30 min, the mixture was cooled to −78 °C and a solution of compound **55b** (1.5 g, 5.77 mmol) in THF (5 mL) was added. After 1 h at −78 °C, the reaction was quenched with aqueous saturated solution of NH_4Cl. A standard extractive work-up followed by flash chromatography (hexanes) afforded compound **56b** as a pale yellow syrup (800 mg, 71 %). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=7.40$–7.20 (m, 4H), 6.80 (t, $J=2.1$ Hz, 2H), 6.30 (t, $J=2.1$ Hz, 2H), 4.74 (q, $J=3.2$ Hz, 2H), 1.60 (t, $J=3.2$ Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=208.9$, 138.9, 134.6, 130.0, 128.0, 127.2, 126.5, 121.9, 109.7, 98.7, 73.9, 17.7; IR (KAP): $\tilde{\nu}=3132$, 3102, 3064, 2979, 2921, 2854, 1949, 1500, 1330, 1071, 850, 762, 725 cm^{-1}; MS (EI): *m*/*z* (%): 195 (47) [M^+], 180 (94), 167 (14), 152 (12); elemental analysis calcd (%) for $C_{14}H_{13}N$ (195.27): C 86.12, H 6.71, N 7.17; found: C 86.05, H 6.77, N 7.10.

4-Methyl-pyrrolo[1,2-*a*]quinoline (57a, R = H): ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=7.91$ (m, 2H), 7.65 (dd, $J=7.8$, 1.3 Hz, 1H), 7.50 (dt, $J=7.3$, 1.4 Hz, 1H), 7.35 (dt, $J=7.9$, 1 Hz, 1H), 6.87 (s, 1H), 6.82 (dd, $J=3.7$, 3 Hz, 1H), 6.57 (dd, $J=3.8$, 1.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=132.7$, 128.5, 127.5, 125.1, 124.2, 118.0, 114.7, 113.1, 113.0, 101.9, 18.7; IR (KBr): $\tilde{\nu}=3142$, 3097, 3052, 2944, 2913, 2850, 1607, 1541, 1486, 1458, 1419, 866, 840, 773, 753, 739, 703 cm^{-1}; MS (EI): *m*/*z* (%): 181 (100) [M^+], 152 (10), 77 (7); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.10, H 6.21, N 7.67.

4,5-Dimethyl-pyrrolo[1,2-*a*]quinoline (57b, R = Me): ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=7.92$ (dd, $J=8.3$, 1.1 Hz, 1H), 7.86 (m, 2H), 7.50 (dt, $J=8.2$, 1.4 Hz, 1H), 7.39 (dt, $J=8.2$, 1.2 Hz, 1H), 6.77 (dd, $J=3.7$, 3 Hz, 1H), 6.50 (dd, $J=3.8$, 1.4 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=132.7$, 132.4, 126.6, 125.0, 124.9, 124.2, 123.4, 120.8, 114.1, 112.3, 111.7, 100.7, 14.9, 13.6; IR (KBr): $\tilde{\nu}=3136$, 3101, 3071, 2999, 2920, 2859, 1599, 1537, 1487, 1461, 748, 696 cm^{-1}; MS (EI): *m*/*z* (%): 195 (100) [M^+], 180 (40); elemental analysis calcd (%) for $C_{14}H_{13}N$ (195.26): C 86.12, H 6.71, N 7.17; found: C 85.91, H 6.79, N 6.98.

6*H*-Benzo[*f*]pyrrolo[1,2-*a*]azepine (58a, R = H): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.50$ (dd, $J=8.1$, 1.1 Hz), 7.40–7.20 (m, 3H), 6.99 (dd, $J=2.9$, 1.8 Hz, 1H), 6.55 (d, $J=10.3$ Hz, 1H), 6.31 (t, $J=3.1$ Hz, 1H), 6.22 (td, $J=10.3$, 6.5 Hz, 1H), 5.92 (dd, $J=3.2$, 1.4 Hz, 1H), 3.25 (d, $J=6.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=140.1$, 135.6, 133.3, 129.3, 128.1, 127.2, 126.3, 124.8, 123.0, 122.8, 110.6, 110.4, 33.0; IR (KAP): $\tilde{\nu}=3062$, 3028, 2925, 2872, 2827, 1574, 1492, 1452, 774, 706 cm^{-1}; MS (EI): *m*/*z* (%): 180 (100) [M^+], 152 (11); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.26, H 6.18, N 7.85.

6-Methyl-4*H*-benzo[*f*]pyrrolo[1,2-*a*]azepine (58b, R = Me): ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=7.56$ (dd, $J=7.7$, 1.6 Hz, 1H), 7.45 (dd, $J=7.9$, 1.5 Hz, 1H), 7.38 (dt, $J=7.2$, 1.6 Hz, 1H), 7.33 (dt, $J=7.6$, 1.6 Hz, 1H), 6.97 (dd, $J=2.9$, 1.8 Hz, 1H), 6.25 (t, $J=3.2$ Hz, 1H), 6.10 (dt, $J=6.9$, 1.4 Hz, 1H), 5.88 (dd, $J=3.2$, 1.7 Hz, 1H), 3.07 (br s, 2H), 2.15 (d, $J=$ 0.5 Hz, 3H); ^{1}H NMR (400 MHz, C_6D_6): $\delta=7.56$ (dd, $J=7.7$, 1.6 Hz, 1H), 7.21 (m, 1H), 7.16 (m, 1H), 6.94 (m, 2H), 6.83 (dd, $J=2.9$, 1.8 Hz, 1H), 6.36 (t, $J=3.2$ Hz, 1H), 5.95 (dd, $J=3.3$, 1.7 Hz, 1H), 5.74 (dt, $J=$ 6.8, 1.4 Hz, 1H), 2.84 (d, $J=6.8$ Hz, 2H), 1.78 (t, $J=0.6$ Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta=137.8$, 137.5, 132.7, 132.6, 127.6, 127.3, 127.2, 124.4, 123.4, 119.5, 109.2, 102.9, 24.7, 22.2; IR (KAP): $\tilde{\nu}=3102$, 3062, 3030, 2962, 2920, 2878, 2855, 2829, 1645, 1601, 1574, 1492, 1450, 1419, 759, 713, 699 cm^{-1}; MS (EI): *m*/*z* (%): 194 (100) [M^+], 180 (31); elemental analysis calcd (%) for $C_{14}H_{13}N$ (195.27): C 86.12, H 6.71, N 7.17; found: C 85.97, H 6.78, N 7.05.

4*H*-Benzo[*f*]pyrrolo[1,2-*a*]azepine (59a, R = H): ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.30$ (m, 4H), 7.22 (dd, $J=2.9$, 1.8 Hz, 1H), 6.53 (d, $J=$ 10.2 Hz, 1H), 6.39 (t, $J=3$ Hz, 1H), 6.30 (dd, $J=3.5$, 1.7 Hz, 1H), 5.97 (td, $J=10.2$, 6.6 Hz, 1H), 3.28 (d, $J=6.6$ Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=140.1$, 135.6, 133.3, 129.3, 128.1, 127.2, 126.3, 124.8, 123.0, 122.8, 110.6, 110.4, 33.0; IR (KAP): $\tilde{\nu}=3102$, 3036, 2955, 2918, 1849, 1636, 1587, 1495, 1460, 1415, 757, 719 cm^{-1}; MS (EI): *m*/*z* (%): 180 (100) [M^+], 152 (20); elemental analysis calcd (%) for $C_{13}H_{11}N$ (181.24): C 86.15, H 6.12, N 7.73; found: C 86.22, H 6.15, N 7.65.

6-Methyl-6*H*-benzo[*f*]pyrrolo-[1,2-*a*]azepine (59b, R = Me): ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.25$–7.10 (m, 4H), 7.01 (dd, $J=2.9$, 1.7 Hz, 1H), 6.26 (dd, $J=10.2$, 1 Hz, 1H), 6.18 (t, $J=3.4$ Hz, 1H), 6.10 (dd, $J=4.8$, 1.6 Hz, 1H), 5.51 (dd, $J=10.2$, 6 Hz, 1H), 3.24 (q, $J=7.2$, 6 Hz, 1H), 1.25 (d, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=16.9$, 35.1, 109.1, 109.8, 120.2, 122.3, 124.7, 125.0, 126.6, 127.1, 132.6, 132.7, 138.9, 139.0.

Haloalkynes

2-Chloroethynyl-3′,5′-dimethyl-biphenyl (60a): A solution of LiHMDS (239 mg, 1.43 mmol) in THF (1 mL) was added dropwise to a solution of aldehyde **5** (100 mg, 0.48 mmol) and dichloromethyl diethylphosphonate (116 mg, 0.52 mmol)[86] in THF (4 mL) at −78 °C. After stirring for 1 h, the reaction was quenched with water, the aqueous phase was extracted

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with *tert*-butyl methyl ether, and the combined organic layers were washed with brine before being dried over Na_2SO_4. Evaporation of the solvents followed by flash chromatography (hexanes) of the crude material furnished product **60a** as a pale yellow oil (101 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.53$ (d, $J = 7.2$ Hz, 1H), 7.36 (d, $J = 4.8$, 2H), 7.25 (m, 1H), 7.19 (s, 2H), 7.01 (s, 1H), 2.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.7$, 140.2, 133.7, 129.7, 129.3, 128.9, 127.1, 127.0, 120.5, 69.3, 21.5; IR (KAP): $\tilde{\nu} = 3025$, 2917, 2216, 1603, 1468, 1443, 849, 755, 701, 670 cm^{-1}; MS (EI): *m/z* (%): 240 (18) [M^+], 225 (18), 205 (100), 198 (47); elemental analysis calcd (%) for $C_{16}H_{13}Cl$ (240.73): C 79.83, H 5.44; found: C 79.76, H 5.33.

2′-Chloro-ethynyl-3,5-dimethoxy-biphenyl (62a): Prepared analogously (246 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.57$ (dd, $J = 7.7$, 1.7 Hz, 1H), 7.39 (m, 2H), 7.30 (m, 1H), 6.74 (d, $J = 2.3$ Hz, 2H), 6.51 (t, $J = 2.3$ Hz, 1H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.5$, 144.3, 142.1, 133.7, 129.5, 128.8, 127.2, 120.4, 107.3, 100.3, 70.7, 69.1, 55.5, 49.5; IR (KBr): $\tilde{\nu} = 3064$, 3000, 2959, 2937, 2835, 2214, 1605, 1595, 1470, 1451, 1437, 1416, 833, 753, 690 cm^{-1}; MS (EI): *m/z* (%): 272 (0.4) [M^+], 237 (100), 209 (24), 165 (18); elemental analysis calcd (%) for $C_{16}H_{13}ClO_2$ (272.73): C 70.46, H 4.80; found: C 70.55, H 4.76.

2,3,4,4′-Tetramethoxy-2-chloroethynyl-biphenyl (64a): Prepared analogously; off-white solid (495 mg, 90%); m.p. 103–104°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (d, $J = 8.7$ Hz, 1H), 7.07 (d, $J = 2.7$ Hz 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 6.93 (dd, $J = 8.7$ Hz, 2.5 Hz, 1H), 6.71 (d, $J = 8.4$ Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.6$, 153.6, 152.1, 142.5, 134.3, 131.8, 127.3, 125.9, 123.1, 117.5, 115.4, 107.1, 77.0, 70.1, 69.5, 61.4, 56.4, 55.8; IR (KAP): $\tilde{\nu} = 3009$, 2955, 2936, 2853, 2214, 1597, 1562, 1479, 1463, 1289, 1279, 1079 cm^{-1}; MS (EI): *m/z* (%): 332 (100) [M^+], 317 (19), 301 (23), 286 (31), 271 (27); elemental analysis calcd (%) for $C_{18}H_{17}O_4Cl$ (332.78): C 64.97, H 5.15; found: C 65.08, H 5.21.

2-Bromoethynyl-3′,5′-dimethyl-biphenyl (60b): A solution of DBU (2.45 mL, 16.4 mmol) in DMSO (20 mL) was added to a cooled solution of compound **6** (2.0 g, 5.5 mmol) in DMSO (200 mL) at such a rate as to maintain the internal temperature below 15°C. The resulting mixture was stirred for 1 h before the reaction was quenched with aq. HCl (0.5 M) at 0°C. Extraction of the aqueous layer with CH_2Cl_2 was followed by successive washing of the combined organic phases with sat. aq. $NaHCO_3$, water and brine. After drying over Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc 4:1) to give product **60b** as a yellow oil (1.43 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60$ (dt, $J = 7.5$ Hz, 0.9 Hz, 1H), 7.44 (d, $J = 1.2$, 1H), 7.42 (m, 1H), 7.31 (m, 1H), 7.27 (s, 2H), 7.08 (d, $J = 1.2$ Hz, 1H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.8$, 140.1, 137.7, 133.8, 129.7, 129.4, 129.0, 127.2, 127.0, 121.1, 80.1, 52.6, 21.8; IR (KAP): $\tilde{\nu} = 3022$, 2915, 2858, 2194, 1602, 1443, 849, 755, 701, 686 cm^{-1}; MS (EI): *m/z* (%): 284 (9) [M^+], 205 (100), 189 (35), 178 (7), 165 (6); elemental analysis calcd (%) for $C_{16}H_{13}Br$ (285.18): C 67.39, H 4.59; found: C 67.30, H 4.65.

2′-Bromo-ethynyl-3,5-dimethoxy-biphenyl (62b): Prepared analogously (341 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (d, $J = 7.7$ Hz, 1H), 7.42 (m, 2H), 7.32 (m, 1H), 6.78 (d, $J = 2.3$ Hz, 2H), 6.53 (t, $J = 2.3$ Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.1$, 143.8, 141.6, 133.4, 129.0, 128.5, 126.8, 120.5, 106.8, 100.0, 79.3, 55.1, 52.1; IR (KBr): $\tilde{\nu} = 3056$, 3007, 2958, 2834, 2191, 1601, 1562, 1492, 1469, 1449, 1435, 1416, 1204, 1155, 834, 816, 751, 689 cm^{-1}; MS (EI): *m/z* (%): 318 (0.2) [$M(^{81}Br)^+$], 316 (0.17) [$M(^{79}Br)^+$], 237 (100), 209 (21), 194 (15), 178 (10), 165 (14), 151 (11); elemental analysis calcd (%) for $C_{16}H_{13}BrO_2$ (317.18): C 60.59, H 4.13; found: C 60.54, H 4.12.

2-Iodoethynyl-3′,5′-dimethyl-biphenyl (60c): $AgNO_3$ (12.4 mg, 0.073 mmol) was added to a solution of *N*-iodosuccinimide (196 mg, 0.87 mmol) and biphenyl **7a** (150 mg, 0.73 mmol) in THF (6 mL) and the resulting mixture was stirred in the dark for 1.5 h. Quenching with aq. sat. $Na_2S_2O_3$ was followed by extraction with CH_2Cl_2 and drying of the combined organic phases over Na_2SO_4. Evaporation of the solvent and subsequent flash chromatography of the residue (hexanes/EtOAc 9:1) yielded product **60c** as a pale yellow oil (242 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51$ (m, 1H), 7.34 (m, 2H), 7.23 (m, 3H), 7.00 (q, $J = 0.6$ Hz, 1H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.8$, 139.7, 137.5, 133.9, 129.3, 129.2, 128.9, 127.0, 126.7, 121.6, 93.9, 21.4, 8.8; IR (KAP): $\tilde{\nu} = 3025$, 2914, 2858, 2166, 1602, 1468, 1442, 849, 755, 700 cm^{-1}; MS (EI): *m/z* (%): 332 (13) [M^+], 206 (18), 205 (100), 202 (20), 189 (41), 178 (11), 101 (12); elemental analysis calcd (%) for $C_{16}H_{13}I$ (332.18): C 57.85, H 3.94; found: C 57.68, H 3.85.

10-Halophenanthrenes

10-Chloro-2,3,4,7-tetramethoxy-phenanthrene (65): A solution of chloroalkyne **64** (150 mg, 0.45 mmol) and $InCl_3$ (100 mg, 0.45 mmol) in toluene (2.5 mL) was stirred at 80°C for 16 h. The mixture was adsorbed on silica gel, put on top of a silica gel column, and the product was eluted (hexanes/EtOAc 19:1) to give phenanthrene **65** as a bright yellow solid (122 mg, 81%). M.p. 105–106°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.39$ (d, $J = 9.3$ Hz, 1H), 7.73 (s, 1H), 7.61 (s, 1H), 7.23 (dd, $J = 9.3$ Hz, 3 Hz, 1H), 7.11 (d, $J = 3$ Hz, 1H), 4.04 (s, 6H), 3.98 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.5$, 152.1, 151.8, 143.5, 133.0, 130.3, 128.4, 126.3, 126.1, 123.3, 120.5, 117.1, 107.9, 102.2, 61.3, 60.3, 55.9, 55.3; IR (KAP): $\tilde{\nu} = 3006$, 2964, 2937, 2840, 1620, 1559, 1492, 1453, 1419, 1397, 1367, 1298, 1278, 1252, 1228, 1088 cm^{-1}; MS (EI): *m/z* (%): 332 (100) [M^+], 317 (30), 274 (30), 231 (13), 203 (14); elemental analysis calcd (%) for $C_{18}H_{17}O_4Cl$ (332.78): C 64.97, H 5.15; found: C 64.88, H 5.06.

10-Chloro-1,3-dimethyl-phenanthrene (61a): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.62$ (dd, $J = 7.5$, 0.6 Hz, 1H), 8.43 (s, 1H), 7.80 (s, 1H), 7.75 (dd, $J = 7.5$, 1.4 Hz, 1H), 7.60 (m, 2H), 7.31 (s, 1H), 3.11 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.5$, 135.9, 133.6, 133.3, 131.6, 130.4, 129.6, 128.1, 127.2, 127.1, 126.6, 123.2, 121.5, 26.2, 21.6; IR (KBr): $\tilde{\nu} = 3051$, 2965, 2935, 2913, 2852, 1616, 1594, 1462, 1449, 1439, 1381, 873, 735 cm^{-1}; MS (EI): *m/z* (%): 240 (100) [M^+], 225 (25), 205 (31), 189 (30).

10-Bromo-1,3-dimethyl-phenanthrene (61b): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.56$ (dd, $J = 8.2$, 1.2 Hz, 1H), 8.39 (d, $J = 1.6$ Hz, 1H), 8.06 (s, 1H), 7.69 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.59 (dd, $J = 8.4$, 7.0 Hz, 1H), 7.53 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.28 (d, $J = 1.6$, 1H), 3.05 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.3$, 136.0, 133.6, 133.1, 132.7, 131.9, 129.8, 127.2, 127.0, 126.7, 123.2, 121.5, 118.5, 26.5, 21.5; IR (KBr): $\tilde{\nu} = 3056$, 3024, 2971, 2934, 2916, 2852, 1617, 1570, 1494, 1461, 1446, 1374, 877, 743 cm^{-1}; MS (EI): *m/z* (%): 286 (98) [$M(^{81}Br)^+$], 284 (100) [$M(^{79}Br)^+$], 271 (17), 269 (17), 205 (37), 189 (37), 101 (20); elemental analysis calcd (%) for $C_{16}H_{13}Br$ (285.19): C 67.39, H 4.59; found: C 67.46, H 4.47.

10-Chloro-1,3-dimethoxy-phenanthrene (63a): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.51$ (dd, $J = 6.9$, 2.6 Hz, 1H), 7.74 (m, 2H), 7.69 (s, 1H), 7.58 (m, 2H), 7.27 (s, 1H), 6.75 (d, $J = 2.3$ Hz, 1H), 4.03 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.1$, 158.4, 135.1, 132.1, 128.5, 127.9, 127.5, 127.4, 126.4, 126.3, 123.2, 100.1, 96.6, 56.1, 55.4; IR (KBr): $\tilde{\nu} = 3119$, 3062, 2998, 2958, 2939, 2826, 1615, 1593, 1578, 1454, 1414, 1269, 1214, 1168, 826, 775 cm^{-1}; MS (EI): *m/z* (%): 272 (100) [M^+], 229 (26), 186 (17); elemental analysis calcd (%) for $C_{16}H_{13}ClO_2$ (272.73): C 70.46, H 4.80; found: C 70.48, H 4.67.

1,2-Halide shift reactions

9-Bromo-1,3-dimethyl-phenanthrene (68b): A solution of AuCl (4.9 mg, 0.021 mmol) and bromoalkyne **60b** (30 mg, 0.105 mmol) in toluene (1 mL) was stirred at 80°C for 20 h. The mixture was then adsorbed on silica gel and added on top of a silica gel column. Flash chromatography (hexanes/EtOAc 7:3) afforded product **68b** as a pale yellow solid (30 mg, quant.). M.p. 98–99°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.66$ (m, 1H), 8.33 (m, 1H), 8.30 (m, 1H), 8.24 (d, $J < 1$ Hz, 1H), 7.65 (m, 2H), 7.27 (m, 1H), 2.67 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 136.4$, 134.0, 131.4, 130.21, 130.17, 130.0, 129.2, 128.0, 127.2, 127.1, 126.8, 123.1, 120.8, 120.6, 22.1, 19.6; IR (KAP): $\tilde{\nu} = 3069$, 3014, 2965, 2941, 2917, 2853, 1616, 1598, 1492, 1456, 1441, 867, 749 cm^{-1}; MS (EI): *m/z* (%): 284 (100) [M^+], 271 (13), 205 (43), 189 (43), 101 (18); elemental analysis calcd (%) for $C_{16}H_{13}Br$ (285.18): C 67.39, H 4.59; found: C 65.05, H 5.03.

9-Iodo-1,3-dimethyl-phenanthrene (68c): Prepared analogously; colorless solid (38 mg, 76%); m.p. 100–101°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.61$ (m, 1H), 8.56 (s, 1H), 8.30 (s, 1H), 8.18 (m, 1H), 7.64 (m, 1H), 7.62 (m, 1H), 7.26 (s, 1H), 2.67 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 136.7$, 134.9, 133.8, 133.1, 131.9, 130.8, 130.6, 130.1, 130.0, 127.5, 127.2, 123.1, 120.6, 97.7, 22.1, 19.6; IR (KAP): $\tilde{\nu} = 3062$, 3009, 2970, 2935, 2914, 2856, 1612, 1588, 1566, 1510, 1487, 1456, 1439, 1412 cm^{-1}; MS (EI): *m/z* (%): 332 (100) [M^+], 317 (4), 205 (25), 189 (19), 178 (5), 101

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(8); elemental analysis calcd (%) for $C_{16}H_{13}I$ (332.18): C 57.85, H 3.94; found: C 57.69, H 3.87.

Aporphine alkaloids

2-[2-(5-Bromo-2,3,4-trimethoxy-phenyl)-ethyl]-isoindole-1,3-dione (71): A mixture of iodide **70** (2.0 g, 5.39 mmol),[87] *N*-vinylphthalimide (1.12 g, 6.47 mmol), tri-*ortho*-tolylphosphine (50 mg, 0.16 mmol), $[Pd(OAc)_2]$ (30 mg, 0.135 mmol) and diisopropylethylamine (1.4 mL, 8.085 mmol) in MeCN (20 mL) was stirred at 100 °C for 20 h. A standard extractive work-up followed by flash chromatography of the residue (hexanes/EtOAc 6:1) gave 2-[2-(5-bromo-2,3,4-trimethoxy-phenyl)-vinyl]-isoindole-1,3-dione as a yellow solid (1.15 g, 51 %) which shows the following spectroscopic and analytical data: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (m, AA′XX′, 2H), 7.77 (m, AA′XX′, 2H), 7.73 (d, $J = 15.2$ Hz, 1H), 7.44 (s, 1H), 7.34 (d, $J = 15.2$ Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 164.7$, 134.6, 131.8, 123.9, 123.7, 118.8, 114.3, 112.1, 61.3; IR (KBr): $\tilde{\nu} = 3105$, 3047, 2998, 2942, 2866, 1778, 1717, 1648, 1459, 1379, 1221, 1006, 953, 882, 720, 529 cm^{-1}; MS (EI): *m*/*z* (%): 419 (100) [$M(^{81}Br)^+$], 417 (100) [$M(^{79}Br)^+$], 404 (24), 402 (23), 323 (27), 308 (24), 160 (37), 104 (27), 76 (22); elemental analysis calcd (%) for $C_{19}H_{16}BrNO_5$ (418.24): C 54.56, H 3.86, N 3.35; found: C 54.44, H 3.78, N 3.31.

A solution of $[Ir(cod)(pyridine)(PCy_3)]PF_6$ (80 mg, 0.1 mmol) in CH_2Cl_2 (4 mL) was added to a solution of the alkene described above (836 mg, 2 mmol) in CH_2Cl_2 (4 mL) and the resulting yellow mixture was degassed by two freeze/thaw cycles. After stirring overnight under an atmosphere of H_2, the color turned to orange indicating the completion of the reaction. The solvent was evaporated and the crude product was purified by flash chromatography (hexanes/EtOAc 4:1) to give product **71** as a colorless syrup (840 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.82$ (m, AA′XX′, 2H), 7.71 (m, AA′XX′, 2H), 7.08 (s, 1H), 3.90 (s, 3H), 3.88 (t, $J = 7.2$ Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 2.91 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.1$, 151.9, 150.2, 147.4, 133.8, 132.1, 128.5, 127.9, 123.1, 111.0, 61.0, 60.9, 60.8, 38.2, 28.7; IR (KBr): $\tilde{\nu} = 2991$, 2943, 2868, 2827, 1772, 1714, 1613, 1465, 1401, 1366, 1219, 1111, 1010, 871, 720, 531 cm^{-1}; MS (EI): *m*/*z* (%): 421 (92) [$M(^{81}Br)^+$], 419 (91) [$M(^{79}Br)^+$], 340 (18), 274 (98), 272 (100), 261 (62), 259 (81), 246 (44), 244 (45), 178 (25), 160 (36); elemental analysis calcd (%) for $C_{19}H_{18}BrNO_5$ (420.25): C 54.30, H 4.32, N 3.33; found: C 54.37, H 4.28, N 3.26.

5′-[2-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-ethyl]-2′,3′,4′-trimethoxy-biphenyl-2-carbaldehyde (72): A degassed solution of bromide **71** (420 mg, 1 mmol), 2-formylbenzeneboronic acid **2** (225 mg, 1.5 mmol), K_3PO_4 (424 mg, 2 mmol), $[Pd(OAc)_2]$ (2.3 mg, 0.01 mmol) and 2-(dicyclohexylphosphino)biphenyl (14 mg, 0.04 mmol) in toluene (4 mL) was stirred at 100 °C for 15 h. The mixture was cooled to ambient temperature and *tert*-butyl methyl ether was added. The mixture was washed with NaOH (1 M) and the aqueous layer were extracted with *tert*-butyl methyl ether. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography (hexanes/EtOAc 4:1) to give biphenyl **72** as a colorless syrup (420 mg, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$ (m, AA′XX′, 2H), 7.69 (m, AA′XX′, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.14 (dd, $J = 7.6$, 0.9 Hz, 1H), 6.76 (s, 1H), 3.99 (s, 3H), 3.94 (m, 2H), 3.84 (s, 3H), 3.48 (s, 3H), 3.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.2$, 168.1, 152.8, 150.4, 146.0, 141.2, 133.9, 133.4, 132.2, 130.9, 127.7, 127.3, 126.9, 126.8, 126.6, 123.1, 61.1, 60.8, 60.6, 38.4, 29.1; IR (KBr): $\tilde{\nu} =$ 2937, 2849, 2752, 1772, 1713, 1597, 1393, 1112, 1006, 719 cm^{-1}; MS (EI): *m*/*z* (%): 445 (100) [M^+], 414 (29), 298 (47), 285 (87), 267 (26), 160 (26); elemental analysis calcd (%) for $C_{26}H_{23}NO_6$ (445.46): C 70.10, H 5.20, N 3.14; found: C 70.03, H 5.28, N 3.06.

2-[2-(2′-Bromoethynyl-4,5,6-trimethoxy-biphenyl-3-yl)-ethyl]-isoindole-1,3-dione (66b): CBr_4 (485 mg, 1.46 mmol) was added to a solution of PPh_3 (765 mg, 2.92 mmol) in CH_2Cl_2 (4 mL) at 0 °C and the resulting orange mixture was stirred for 10 min. A solution of aldehyde **72** (260 mg, 0.584 mmol) in CH_2Cl_2 (6 mL) was then introduced and the mixture was stirred at 0 °C for 1 h before it was quenched with brine. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic phases were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc 9:1) to give 2-{2-[2′-(2,2-Dibromo-vinyl)-4,5,6-trimethoxy-biphenyl-3-yl]-ethyl}-isoindole-1,3-dione as a colorless syrup (310 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81$ (m, AA′XX′, 2H), 7.68 (m, AA′XX′, 2H), 7.63 (dd, $J =$ 7.4, 1.3 Hz, 1H), 7.31 (m, 2H), 7.16 (s, 1H), 7.06 (dd, $J = 7.2$, 1.3 Hz, 1H), 6.66 (s, 1H), 3.97 (s, 3H), 3.94 (t, $J = 7.3$ Hz, 2H), 3.83 (s, 3H), 3.56 (s, 3H), 2.97 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.1$, 152.2, 150.6, 145.9, 137.6, 132.2, 135.1, 133.8, 132.3, 130.1, 129.1, 128.4, 128.1, 127.0, 126.6, 126.5, 123.1, 90.3, 61.1, 61.0, 60.9, 38.6, 29.0.

A solution of DBU (390 μL, 1.548 mmol) in DMSO (1 mL) was slowly added to a solution of the dibromide prepared above (310 mg, 0.516 mmol) in DMSO (50 mL) at 15 °C. After stirring for 1 h at that temperature, the reaction was quenched at 0 °C with HCl (0.5 M, 5 mL) and extracted with CH_2Cl_2 (4 × 15 mL). The combined organic layers were successively washed with sat. aq. $NaHCO_3$, water and brine. After drying over Na_2SO_4 and evaporation of the solvent, the residue was purified by flash chromatography (hexanes/EtOAc 4:1) to give bromoalkyne **66b** as a colorless syrup (212 mg, 79 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.82 (m, AA′XX′, 2H), 7.69 (m, AA′XX′, 2H), 7.50 (dd, $J = 7.2$, 1.8 Hz, 1H), 7.27 (m, 2H), 7.12 (dd, $J = 7.2$, 1.8 Hz, 1H), 6.81 (s, 1H), 3.99 (s, 3H), 3.93 (t, $J = 7.7$ Hz, 2H), 3.89 (s, 3H), 3.63 (s, 3H), 2.97 (t, $J = 7.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.1$, 152.0, 150.6, 146.0, 141.2, 133.7, 132.6, 132.3, 130.0, 129.4, 128.3, 126.9, 126.5, 126.2, 123.1, 122.4, 79.6, 51.7, 38.6, 29.0; IR (KBr): $\tilde{\nu} = 3062$, 2938, 2869, 2194, 1769, 1714, 1397, 1109, 1004, 722 cm^{-1}; MS (EI): *m*/*z* (%): 521 (34) [$M(^{81}Br)^+$], 519 (33) [$M(^{79}Br)^+$], 361 (29), 359 (30), 293 (38), 280 (75), 262 (100); elemental analysis calcd (%) for $C_{27}H_{22}BrNO_5$ (520.37): C 62.32, H 4.26, N 2.69; found: C 62.19, H 4.30, N 2.55.

2-[2-(10-Bromo-2,3,4-trimethoxy-phenanthren-1-yl)-ethyl]-isoindole-1,3-dione (67b): A solution of bromoalkyne **66b** (200 mg, 0.384 mmol) and $InCl_3$ (85 mg, 0.384 mmol) in toluene (2 mL) was stirred at 80 °C for 16 h. After cooling, the solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc 4:1) to give bromophenanthrene **67b** as a pale yellow solid (173 mg, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.40$ (dd, $J = 8.6$, 0.7 Hz, 2H), 7.75 (m, AA′XX′, 2H), 7.65–7.45 (m, 5H), 4.18 (t, $J = 7.6$ Hz, 2H), 4.03 (s, 3H), 3.89 (s, 3H), 3.93 (s, 3H), 3.89 (s and t, $J = 7.9$ Hz, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 168.2, 153.1, 151.0, 146.2, 134.4, 133.6, 132.3, 131.5, 129.1, 127.6, 127.3, 127.1, 127.0, 126.6, 124.6, 122.8, 116.6, 61.0, 60.9, 60.8, 39.3, 27.1; IR (KBr): $\tilde{\nu} = 3059$, 2936, 2856, 1768, 1709, 1391, 1111, 997, 723 cm^{-1}; MS (EI): *m*/*z* (%): 521 (55) [$M(^{81}Br)^+$], 519 (54) [$M(^{79}Br)^+$], 361 (99), 359 (100); elemental analysis calcd (%) for $C_{27}H_{22}BrNO_5$ (520.37): C 62.32, H 4.26, N 2.69; found: C 62.27, H 4.28, N 2.58.

2-(10-Bromo-2,3,4-trimethoxy-phenanthren-1-yl)-ethylamine (73): A solution of hydrazine monohydrate (152 μL, 3.13 mmol) in MeOH (3 mL) was added to a solution of phthalimide **67b** (163 mg, 0.313 mmol) in MeOH (12 mL) and the resulting mixture was heated at reflux for 4 h. For work up, the solvent was evaporated and the residue was purified by filtration through Celite (methyl *tert*-butyl ether) to give amine **73** as a pale yellow oil (120 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.40$ (dd, $J = 8.3$, 0.6 Hz, 1H), 8.08 (s, 1H), 7.70 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.57 (m, 2H), 4.08 (s, 3H), 3.99 (s, 3H), 3.88 (s, 3H), 3.64 (t, $J = 7.5$ Hz, 2H), 3.11 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.8$, 149.9, 145.6, 131.7, 130.9, 128.6, 126.7, 126.5, 126.4, 126.1, 125.2, 124.1, 116.7, 60.6, 60.1, 43.2, 31.7; IR (KBr): $\tilde{\nu} = 3055$, 2933, 2854, 1630, 1572, 1451, 1392, 750 cm^{-1}; MS (EI): *m*/*z* (%): 361 (13), 309 (100), 294 (23); elemental analysis calcd (%) for $C_{19}H_{20}BrNO_3$ (390.27): C 58.47, H 5.17, N 3.59; found: C 58.38, H 5.22, 3.52.

1,2,3-Trimethoxy-5,6-dihydro-4*H*-dibenzo[*de*,*g*]quinoline, O-methyl dehydroisopiline (74): A solution of amine **73** (92 mg, 0.236 mmol) in DMSO (2 mL) was added to a suspension of CsOAc (227 mg, 1.18 mmol) and CuI (90 mg, 0.472 mmol) in benzene (100 μL) and the resulting mixture was stirred for 16 h. For work up, CH_2Cl_2 and aq. sat. NH_4OH were added and the organic layer was separated and washed with water and brine. After drying over Na_2SO_4 and evaporation of the solvents, the residue was purified by flash chromatography (CH_2Cl_2/EtOAc 99:1) to give product **74** as a pale yellow syrup (52 mg, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.40$ (d, $J = 8.6$ Hz, 1H), 7.58 (dd, $J = 8$, 1.5 Hz, 1H), 7.44 (dt, $J = 7.8$, 1.1 Hz, 1H), 7.35 (dt, $J = 8.5$, 1.6 Hz, 1H), 6.79 (s, 1H), 4.06 (s, 3H), 3.98 (s, 6H), 3.47 (t, $J = 6.0$ Hz, 2H), 3.24 (t, $J = 6.1$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.1$, 148.4, 146.4, 140.6, 133.6, 127.1, 126.3, 125.8, 125.1, 123.0, 121.2, 120.4, 105.1, 61.3, 60.9, 60.2, 40.7, 24.1; IR (KBr): $\tilde{\nu} = 3374$, 2933, 2832, 1623, 1391, 749 cm^{-1}; MS (EI): *m*/*z* (%): 309 (100) [M^+], 294 (26), 266 (11).

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7,7′-Bisdehydro-O-methylisopiline (75): A solution of *tert*-butylamine (14 μL, 0.128 mmol) in MeOH (0.5 mL) was added to a solution of $CuCl_2{\cdot}2H_2O$ (11.1 mg, 0.064 mmol) in degassed MeOH (0.5 mL). The resulting mixture was stirred for 10 min before a solution of compound **74** (10 mg, 0.032 mmol) in MeOH (1 mL) was introduced and stirring was continued for 14 h. For work up, the mixture was successively washed with conc. HCl (0.5 mL), sat. aq. NH_4OH (1 mL), and water (5 mL). The resulting suspension was extracted with CH_2Cl_2 (3×5 mL) and the combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (CH_2Cl_2/EtOAc 99:1) to give crude product **75** which was 92% pure (9.4 mg, 86%). An analytically pure sample was obtained by preparative HPLC (Nucleosil 5-120-C18/A, MeOH/water 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.57$ (dd, $J = 8.6$, 0.6 Hz, 2H), 7.35 (ddd, $J = 8.8$, 6.4, 1.6 Hz, 2H), 7.22 (ddd, $J = 8.4$, 6.4, 1.2 Hz, 2H), 7.15 (dd, $J = 8.2$, 1.3 Hz, 2H), 4.14 (s, 6H), 4.06 (s, 6H), 4.00 (s, 6H), 3.34–3.14 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 151.1$, 148.6, 146.7, 139.6, 132.7, 126.8, 125.5, 123.9, 123.1, 121.9, 120.2, 61.3, 60.9, 60.4, 40.6, 23.9; MS (EI): *m*/*z* (%): 616 (100) [M^+], 308 (12), 294 (12).

X-ray Crystal structure analyses

Phenanthrene 41: $C_{18}H_{18}O_5$, $M_r = 314.32$, colorless plate, crystal size 0.16×0.13×0.05 mm, orthorhombic, space group *Pbca*, $a = 18.9776(3)$, $b = 7.68670(10)$, c = 21.5379(4) Å, $V = 3141.84(9)$ Å^3, $T = 100$ K, $Z = 8$, $\rho_{calcd} = 1.329$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.097$ mm^{-1}, Nonius KappaCCD diffractometer, $3.43 < \theta < 33.15°$, absorption correction ($T_{min} = 1.00/T_{max} = 1.00$), 27423 measured reflections, 5977 independent reflections, 3883 reflections with $I > 2\sigma(I)$, structure solved by the direct method and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.0598$ [$I > 2\sigma(I)$], $wR_2 = 0.1508$, 280 parameters, H atoms riding, $S = 1.007$, residual electron density +0.407/−0.259 e Å^{-3}.

CCDC-229866 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Aldehyde 47a: $C_{24}H_{24}O_6$, $M_r = 408.43$, colorless plate, crystal size 0.32×0.20×0.20 mm, triclinic, space group $P\bar{1}$, $a = 10.072(2)$, $b = 10.160(2)$, $c = 10.887(2)$ Å, $\alpha = 100.51(3)$, $\beta = 108.78(3)$, $\gamma = 95.33(3)°$, $V = 1023.2(4)$ Å^3, $T = 100$ K, $Z = 2$, $\rho_{calcd} = 1.326$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.095$ mm^{-1}, Nonius KappaCCD diffractometer, $3.20 < \theta < 33.19°$, absorption correction ($T_{min} = 1.00/T_{max} = 1.00$), 20536 measured reflections, 7730 independent reflections, 6461 reflections with $I > 2\sigma(I)$, Structure solved by the direct method and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.0465$ [$I > 2\sigma(I)$], $wR_2 = 0.1356$, 275 parameters, H atoms riding, $S = 0.880$, residual electron density +0.625/−0.599 e Å^{-3}.

CCDC-229865 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Aldehyde 47b: $C_{17}H_{18}O_5$, $M_r = 302.31$, colorless plate, crystal size 0.21×0.18×0.11 mm, triclinic, space group $P\bar{1}$, $a = 8.44670(10)$, $b = 10.2568(2)$, $c = 10.6614(2)$ Å, $\alpha = 62.9260(10)$, $\beta = 84.0730(10)$, $\gamma = 66.9360(10)°$, $V = 753.53(2)$ Å^3, $T = 100$ K, $Z = 2$, $\rho_{calcd} = 1.332$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.098$ mm^{-1}, Nonius KappaCCD diffractometer, $2.96 < \theta < 33.13°$, absorption correction ($T_{min} = 1.00/T_{max} = 1.00$), 16534 measured reflections, 5696 independent reflections, 4548 reflections with $I > 2\sigma(I)$, Structure solved by the direct method and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.0432$ [$I > 2\sigma(I)$], $wR_2 = 0.1352$, 271 parameters, H atoms riding, $S = 1.035$, residual electron density +0.447/0.326 e Å^{-3}.

CCDC-229867 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Alkyne 48c: $C_{17}H_{16}O_3$, $M_r = 268.30$, white plate, crystal size 0.16×0.12×0.06 mm, monoclinic, space group $P2_1/n$, $a = 9.7595(2)$, $b = 7.9407(2)$, $c = 17.7294(4)$ Å, $\beta = 91.1470(10)°$, $V = 1373.70(5)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calcd} = 1.297$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.088$ mm^{-1}, Nonius KappaCCD diffractometer, $4.18 < \theta < 33.10°$, absorption correction ($T_{min} = 0.99/T_{max} = 1.00$), 18928 measured reflections, 5170 independent reflections, 3285 reflections with $I > 2\sigma(I)$, Structure solved by the direct method and refined by least-squares using Chebyshev weights on F_o^2 to $R_1 = 0.0661$ [$I > 2\sigma(I)$], $wR_2 = 0.1628$, 184 parameters, H atoms riding, $S = 1.004$, residual electron density +0.441/−0.274 e Å^{-3}.

CCDC-229864 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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