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Article

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Directed Metalation – Suzuki-Miyaura Cross-coupling Strategies. Regioselective Synthesis of Hydroxylated 1-Methyl-phenanthrenes

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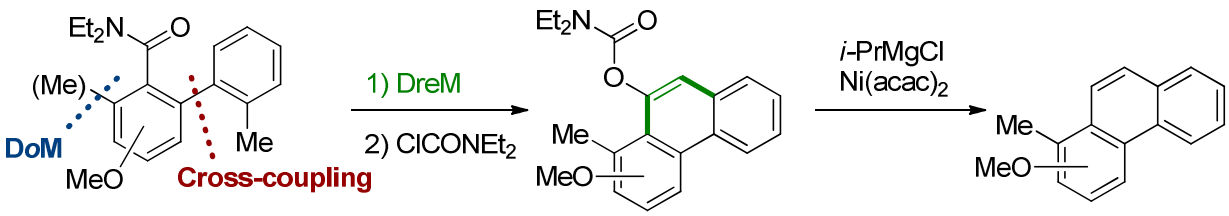
Graphics:



Abstract

A general, efficient, and regioselective synthesis of a series of hydroxylated 1-methylphenanthrenes **9** by a combined directed *ortho* metalation (DoM) – Suzuki-Miyaura cross-coupling – directed remote metalation (DreM) sequence is reported. Diversity to this methodology was achieved by a regioselective DoM rather than DreM reaction, affording more highly substituted phenanthrols (Table 2). Application of the turbo-Grignard reagent

(iPrMgCl•LiCl) in the Ni-catalyzed Corriu-Kumada reaction gave efficient decarbamoylation (Tables 3 and 4). Additional features are the TMS protecting group and halo-induced ipso-desilylation tactics applied to the regioselective synthesis of phenanthrenes (Scheme 2).

Introduction

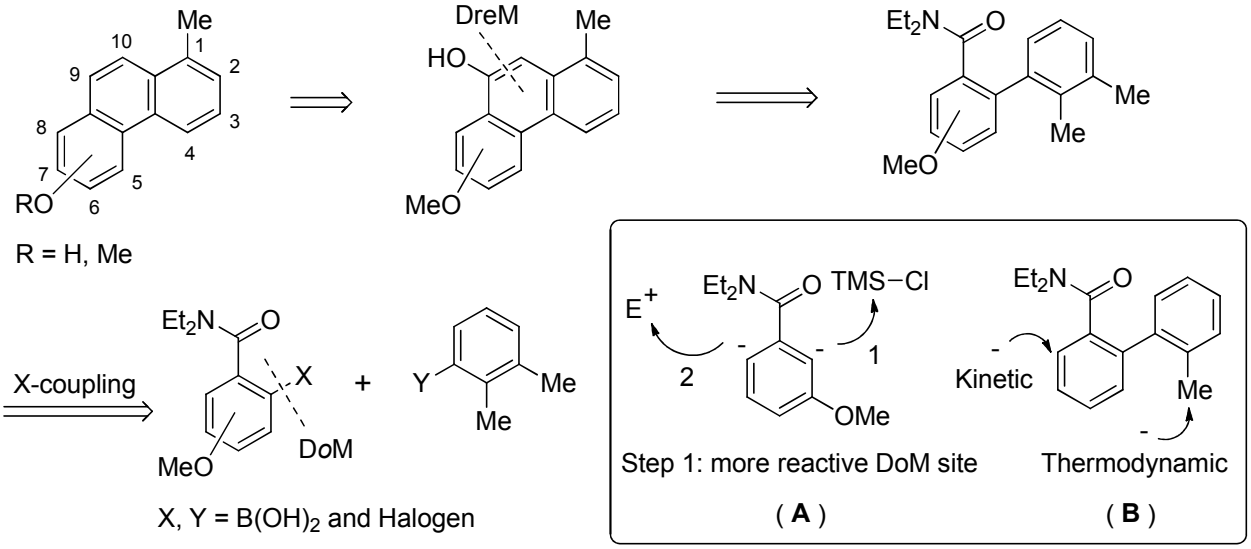
The phenanthrene nucleus represents one of the myriad of ring systems of polycyclic aromatic hydrocarbons (PAHs),[1] and is present in large classes of natural products,[2] including a large group of alkaloids.[3] Substituted phenanthrenes have been exploited as anti-viral[4] and anti-cancer agents,[5,6] fluorescent probes for DNA[7] as antioxidant resveratrol analogues,[8] and in material science areas.[9] Unfortunately phenanthrenes, as most classes of PAHs, are also persistent pollutants in the environment,[10,11] e.g., annelids on tidal flats concentrate phenanthrene in their excrements,[12] phenanthrene-based synthetic musk fragrances have been found in shrimps,[13] and metabolites of phenanthrenes have been detected in goat's milk.[14] Among the many fractions of PAHs in oil sources currently under study,[11,15] alkylated PAHs have been established to cause general detrimental environmental effects[10,16] and in particular are toxic to marine life.[17,18]

In the substantial body of literature on the construction of phenanthrenes,[19] the dominant classical Pschorr[20] and the more recent Mallory photo-[21] and oxidative cyclizations[22] have been augmented by an evolving number of transition metal catalyzed methods,[6,16,23] including the popular Suzuki-Miyaura cross-coupling reaction.[24] Furthermore, phenanthrenes have been prepared from functionalized biphenyls by [4+2] benzannulation reactions[25] and by McMurry-like reactions.[26]

As part of our efforts to advance directed *ortho* metalation (DoM) reactions in aromatic and

heteroaromatic synthesis,[27,28] we have devised combined metalation-cross-coupling strategies,[29] which have had particular relevance to the construction of phenanthrene derivatives.[30,31,32] In continuation of these efforts, we report herein a general route for the regioselective construction of 1-methyl-phenanthrenes bearing various positional hydroxy-substitutents by taking advantage of sequential DoM – Suzuki-Miyaura cross-coupling – directed remote metalation (DreM) reactions. Its retrosynthetic analysis is depicted in Scheme 1. In the penultimate step, the selective removal of the incipient 9-OH of the phenanthrol is carried out by transfer hydrogenation of the corresponding triflate or β-hydride induced excision of the corresponding *O*-carbamate under Ni-catalyzed conditions, a procedure of considerable as yet unfulfilled promise.[33,34] In this work, we also advantageously adapted the silicon protection tactic for most reactive DoM sites[35,36] (**A**, Scheme 1) and the regioselective *ipso*-halodesilylation. Finally, we report on an apparent kinetic - thermodynamic *ortho* - remote metalation selectivity (**B**) which allows the additional regioselective electrophile introduction into biaryl systems and thence leads to more highly substituted phenanthrenes.

Scheme 1: The regioselective synthesis of substituted phenanthrenes by the DoM – cross-coupling – DreM strategy: Retrosynthetic analysis



Results and discussion

The results of Suzuki-Miyaura cross-coupling reactions of benzamides **1** with tolyl and xylyl derivatives **2** to give substituted biaryls **3** are summarized in Table 1. In many cases, both the cross-coupling of benzamide-derived boronic acid with halotoluene and the inverted reaction of halo benzamide with toluene-derived boronic acid were carried out to compare efficiency of the respective routes. In addition, three different conditions were applied to establish generality. The boronic acid benzamides **1,** X = $B(OH)_2$ and bromobenzamides **1,** X = Br were prepared by DoM reactions using standard procedures while the boronic acids **2,** Y = $B(OH)_2$ were obtained by metal-halogen exchange from the corresponding commercially available bromotoluenes followed by quench with a boron electrophile. Boronic acids **1a, c, g** were prepared by using tri-isopropyl boronate, [B(*i*-OPr)$_3$] as the electrophile which has the advantage of being more bench-stable than $B(OMe)_3$. However, the sterically hindered **1d** gave poor yields of product with B(*i*-OPr)$_3$

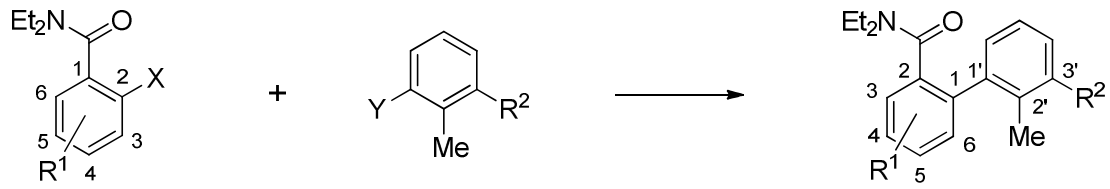
and therefore required the use of $B(OMe)_3$. This reaction was difficult to reproduce, requiring a careful quench at –40 °C to avoid decomposition of the product during workup.

The commercial bromotoluenes **2a** and **2b** conveniently served a double purpose since they were also used as cross-coupling partners. Two cases of iodotoluene coupling reaction were tested (entries 7, 9). To comment briefly, cross-coupling of unsubstituted boronic acid benzamides with bromoarenes (entries 1, 2) or vice versa (entries 3, 4) under two different sets of conditions proceeded in high yields to give both mono methyl and dimethyl biaryls. A slightly buttressing influence of the 6-OMe group may be responsible for the lower yield (74%) of the biaryl product (entry 5). Interestingly, in moving from the 2,2′-substituted biaryl **3a-c** to the considerably more hindered 2,2′,6-substituted series **3d**, **3e**, the yields of products remained very good in both coupling partner combinations (entries 6-10).[37] The ^{1}H NMR-spectra of all biphenyls indicated the presence of rotamers, more pronounced in the more crowded biphenyls.[38]

The cross-coupling reactions of the 4-OMe boronic acid benzamide and bromobenzamides series proved to be unexceptional providing modest to good yields of biaryl products **3f** and **3g** (entries 11-16). While the 3-OMe benzamide 2-boronic acid **1d** was prepared by DoM chemistry using the less hindered $B(OMe)_3$ reagent, the corresponding halogenated products **1e**, **1f** and **1h** were obtained via metalation and quench with Br_2 or I_2. Interestingly, using Br_2 as the electrophile seemed to consistently lead to poor yields in this approach (see also Scheme 2). Therefore, an alternative tactic was adopted and both **1e** and **1f** were conveniently synthesized by the selective *ipso*-bromo and -iodo desilylation method[39] of the corresponding silylated derivative **1k** (Scheme 2) which was readily available on multigram scale. The requisite boronic acid and bromo derivatives **1i** and **1j** were obtained by DoM chemistry using the silicon-protection of most reactive metalation site method[35, 36] followed by a second metalation and boronation or

bromination. Cross-coupled products **3h** and **3i** were subsequently desilylated with TBAF into **3k** (Table 3**)** and **3l** (Table 2) in high yields for further use. The Suzuki-Miyaura coupling reaction of **1d** with iodo toluene **2e** proceeded in modest yields with $Pd(PPh_3)_4$ both under aqueous conditions,[31] and even less efficiently under anhydrous conditions (K_3PO_4/DMF) previously developed in our laboratories,[40] but was considerably improved even in reactions with the bromotoluene **2b** using the Buchwald reaction under anhydrous conditions (entries 7 and 6).[37] Finally (entry 21), the fluorinated compound **2f** was coupled with **1f** to obtain biphenyl **3j** in good yields in order to extend the range of substituents.

Table 1. The Suzuki-Miyaura cross-coupling route to biaryl amides **3a-i**

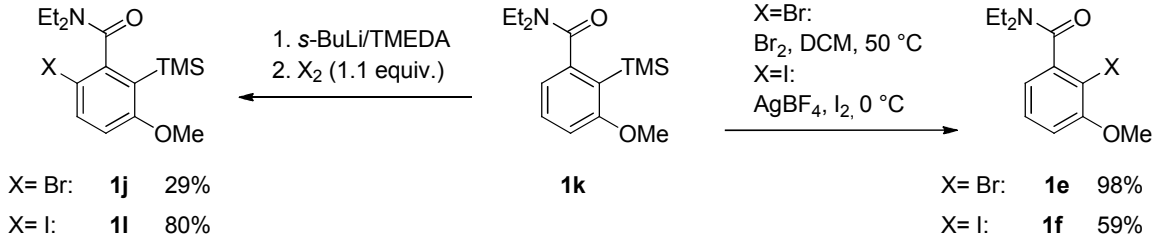


Entry	Compd.	X	R^1	Compd.	Y	R^2	Compd.	R^1	R^2	Cond.[a]	Yield[b] (%)
1	**1a**	$B(OH)_2$	H	**2a**	Br	H	**3a**	H	H	A	89
2	**1a**	$B(OH)_2$	H	**2b**	Br	Me	**3b**	H	Me	A	95
3	**1b**	Br	H	**2c**	$B(OH)_2$	H	**3a**	H	H	C	70-86
4	**1b**	Br	H	**2d**	$B(OH)_2$	Me	**3b**	H	Me	C	quant.
5	**1c**	$B(OH)_2$	6-OMe	**2b**	Br	Me	**3c**	3-OMe	Me	A	74
6	**1d**	$B(OH)_2$	3-OMe	**2b**	Br	Me	**3d**	6-OMe	Me	B	71
7	**1d**	$B(OH)_2$	3-OMe	**2e**	I	Me	**3d**	6-OMe	Me	A	47
8	**1e**	Br	3-OMe	**2c**	$B(OH)_2$	H	**3e**	6-OMe	H	B	73

9	**1f**	I	3-OMe	**2c**	$B(OH)_2$	H	**3e**	6-OMe	H	B	82-97
10	**1e**	Br	3-OMe	**2d**	$B(OH)_2$	Me	**3d**	6-OMe	Me	B	61-73
11	**1g**	$B(OH)_2$	4-OMe	**2a**	Br	H	**3f**	5-OMe	H	A	40
12	**1g**	$B(OH)_2$	4-OMe	**2b**	Br	Me	**3g**	5-OMe	Me	A	46
13	**1h**	Br	4-OMe	**2c**	$B(OH)_2$	H	**3f**	5-OMe	H	B	44
14	**1h**	Br	4-OMe	**2c**	$B(OH)_2$	H	**3f**	5-OMe	H	C	76-89
15	**1h**	Br	4-OMe	**2d**	$B(OH)_2$	Me	**3g**	5-OMe	Me	B	67
16	**1h**	Br	4-OMe	**2d**	$B(OH)_2$	Me	**3g**	5-OMe	Me	C	71
17	**1i**	$B(OH)_2$	5-OMe, 6-TMS	**2b**	Br	Me	**3h**	3-TMS, 4-OMe	Me	A	83
18	**1j**	Br	5-OMe, 6-TMS	**2c**	$B(OH)_2$	H	**3i**	3-TMS, 4-OMe	H	B	64
19	**1j**	Br	5-OMe, 6-TMS	**2c**	$B(OH)_2$	H	**3i**	3-TMS, 4-OMe	H	C	81
20	**1l**	I	5-OMe, 6-TMS	**2c**	$B(OH)_2$	H	**3i**	3-TMS, 4-OMe	H	C	95
30	**1f**	I	3-OMe	**2f**	$B(OH)_2$	H, 5-F	**3j**	6-OMe	H, 5´-F	B	75

[a]Conditions: **A**: 3 mol% $Pd(PPh_3)_4$, DME/2 M Na_2CO_3, 100 °C, 18-20h. **B**: 5 mol% Pd_2dba_3, S-Phos, PhMe/K_3PO_4, 100 °C, 20-28 h. **C**: 4 mol% $Pd(dppf)Cl_2$*DCM, dioxane/2M K_2CO_3 (3/1), 90-100 °C, 16 h. [b]Yields of isolated products.

Scheme 2. Si-protection and *ipso*-desilylation routes to benzamides **1e, 1f, 1j** and **1l**



X= Br: **1j** 29%
X= I: **1l** 80%

1k

X= Br: **1e** 98%
X= I: **1f** 59%

In the course of the studies involving the conversion of the biaryl amides **3** into the corresponding phenanthrenes (Table 3), we observed the formation of products **4e** and **4g** under *s*-BuLi/TMEDA metalation and MeI quench conditions (Scheme 3). Formation of compound **4e** is expected by the kinetic C-3 deprotonation under the standard and widely used DoM *s*-BuLi/TMEDA conditions for tertiary amides[28] while the formation of C-3 ethyl derivative **4g** is likely the result of an intermolecular C-3 anion (**3f**) - C-3 methyl (**4e**) proton exchange followed by methylation of the resulting tolyl anion.[41] The formation of **4g** is a function of the rate of addition of the MeI reagent as expected since the incipient C-3 methyl anion is formed competitively with the original C-3 methylation.

Scheme 3. DoM reaction of **3f** and slow stepwise quench with MeI

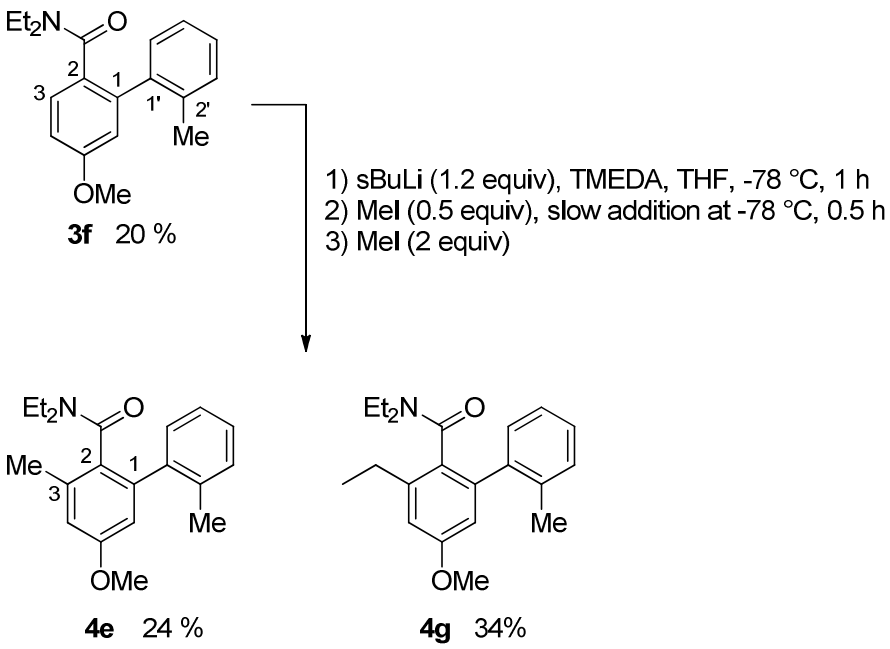
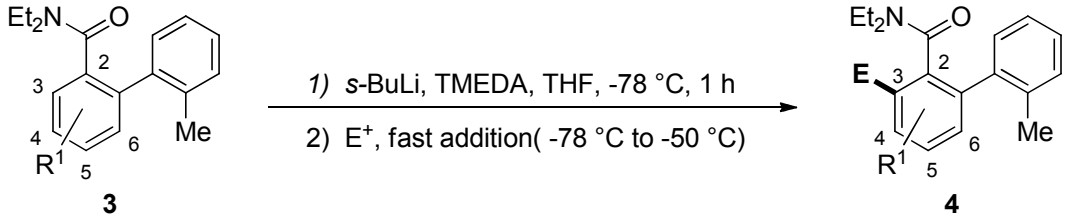


Table 2. DoM reactions on biaryl amides **3**. Synthesis of compounds **4a-f**



Entry	Compound	R^1	E^+	Product	E	Yield[a] (%)
1	**3a**	H	MeI	**4a**	Me	85-95
2	**3a**	H	C_2Cl_6	**4b**	Cl	70
3	**3a**	H	TMSCl	**4c**	TMS	92
4	**3e**	6-OMe	MeI	**4d**	Me	78-82
5	**3f**	5-OMe	MeI	**4e**	Me	77-94
6	**3l**[b]	4-OMe	MeI	**4f**	Me	72-89

[a]Yields of isolated products. [b]Desilylation of **3i** (Table 1) with TBAF gave **3l** in 83% yield.

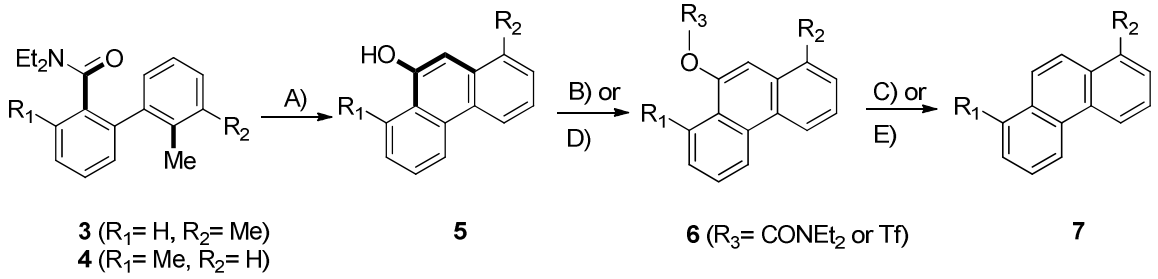
The C-3 anion of **3f** was efficiently trapped to give **4e** in high yield by a procedure involving fast quench with neat MeI. In consideration of the potential value of this result for general substituted phenanthrene synthesis, it was generalized using two other electrophiles and for four biaryl substrates (Table 2) which does not require further comment.

With a series of biaryl amides in hand, the transformation to phenanthrols and eventually to the oxygenated 1-methyl phenanthrenes was undertaken and the results are summarized in Table 3. Application of the standard LDA conditions of the DreM procedure[30,31] to the 2′,3′-dimethyl biaryl amide **3b** afforded the 1-methylphenanthren-9-ol **5a** in 68% yield of recrystallized material. The isomeric 3,2′-dimethyl biaryl amide **4a**, by treatment under the same LDA conditions, furnished the 8-methylphenanthren-9-ol **5b** in 89% yield of crude material. However **5b** was significantly less stable than **5a** and partly decomposed during flash chromatography, and even Kugelrohr distillation, giving rapidly decreased yields upon purification. Therefore, rapid carbamoylation of the crude phenanthrols from the methoxy dimethyl biaryl benzamides **4e**, **4d** and **3d,g,k,c** was undertaken and directly furnished the corresponding phenanthrol O-carbamates **6c-e, g-i** respectively, without isolation of the respective phenanthrols, in modest to good yields. In two cases, the corresponding triflates (**6b** and **6f**) were also prepared. A study of the rotational barriers[38] of the starting biaryls may shed light upon the observed variations in yields. In this context, it is noted that the *o*-silylated amide **3h** required desilylation to **3k** before corresponding DreM reaction to **5i** could be achieved. The silylated derivative **3h** is expected to give desilylated phenanthrylamine product.[42] Furthermore, in some cases 2 equivalents of LDA were required to

effect the DreM transformation (e.g. **4d**, **4e** and **4f**) as expected from the acidic C-H sites present in these molecules.

Finally, one unexpected DreM transformation not related to the major aim of this work, **3j → 8** (entry 12), was observed. Although biphenyl 2-amides lacking a 2′-Me group are known to form fluorenones,[43] this represents, to our knowledge, the first example of a 2-amido-2′-Me biphenyl forming a fluorenone derivative under DreM conditions and suggests higher equilibrating acidity of C-6′ H over C-2′ methyl hydrogens under the LDA conditions. This result suggests an overriding DMG = F effect as already established for DMG = OMe.[44]

Table 3. Transformation of biaryls **3-4** to phenanthrenes **7**

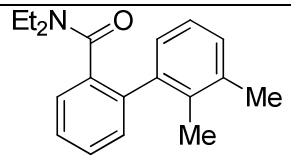
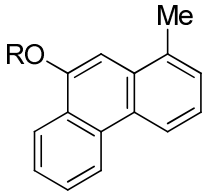
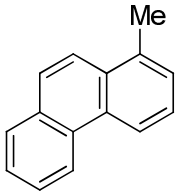


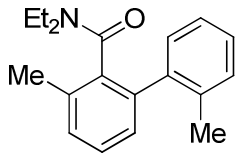
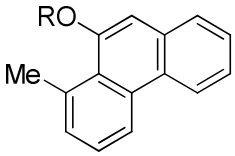
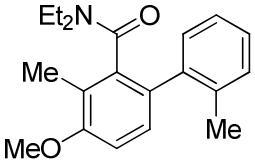
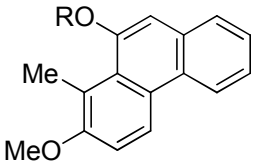
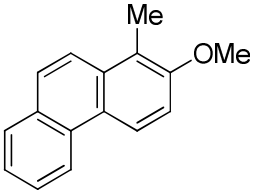
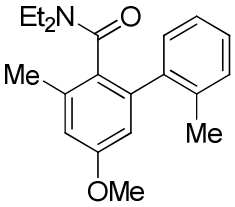
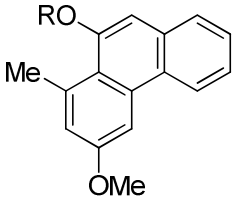
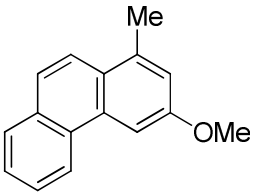
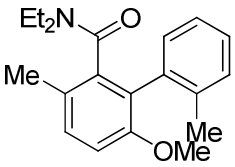
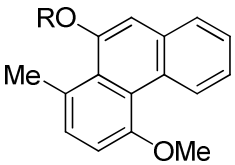
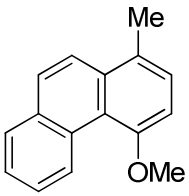
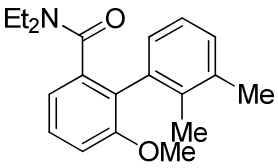
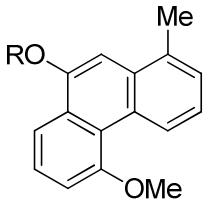
3 (R_1= H, R_2= Me)
4 (R_1= Me, R_2= H)

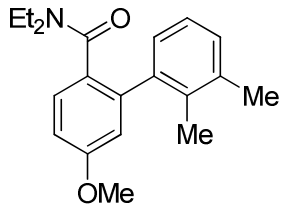
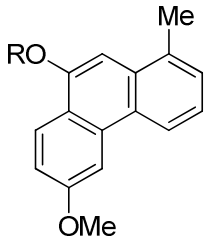
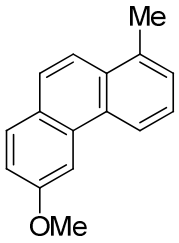
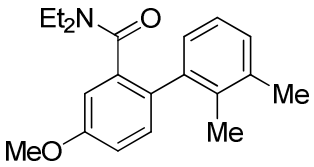
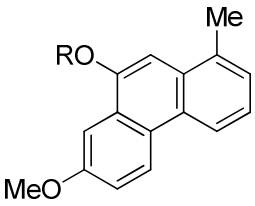
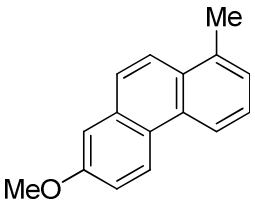
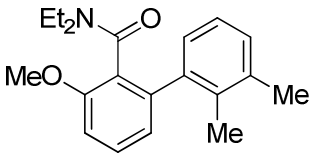
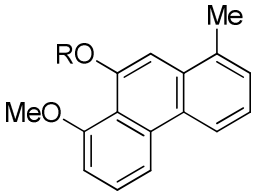
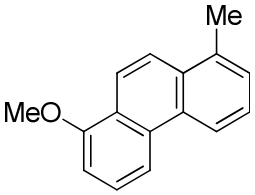
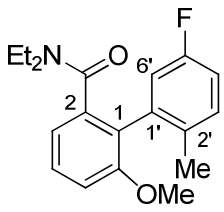
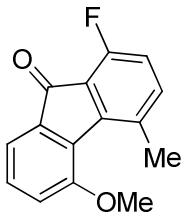
5

6 (R_3= $CONEt_2$ or Tf)

7

Entry	Biaryl	Cond.[a]	Phenanthrene	Yield (%)	Cond.[a]	Phenanthrene	Yield (%)[b]
							
1	**3b**	A	**5a** R = H	68			
2		A, B	**6a** R = $CONEt_2$	82	C	**7a**	97

3	 **4a**	A	 **5b**	R = H	89[c]				
4	 **4f**	A,D	 **6b**	R = Tf	55	E	 **7b**	73	
5	 **4e**	A,B	 **6c**	R = $CONEt_2$	40-44	C	 **7c**	75[e]	
6	 **4d**	A,B	 **6d**	R = $CONEt_2$	40-52	C	 **7d**	88[e]	
7	 **3d**	A,B	 **6e**	R = $CONEt_2$	77				
8		A,D	**6f**	R = Tf	92	E	**7e**	75	

9		**3g**	A,B		**6g**	R = $CONEt_2$	74-77	C		**7f**	83[e]
10		**3k**[d]	A,B		**6h**	R = $CONEt_2$	92	C		**7g**	79
11		**3c**	A,B		**6i**	R = $CONEt_2$	81	C		**7h**	67
12		**3j**	A		**8**		79-97				65

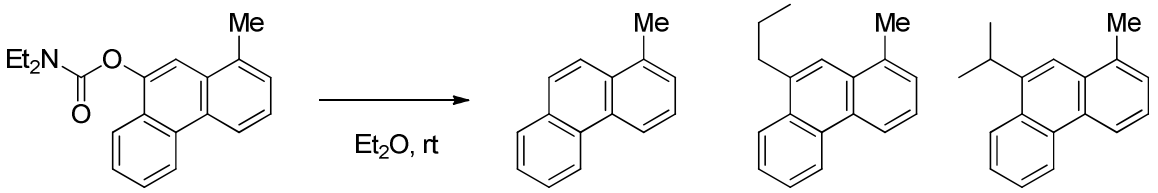
[a]**A:** 2.5 equiv LDA, THF, 0 °C- r.t.; **B:** 1) NaH, THF, 0 °C-r.t. 2) $Et_2NC(O)Cl$; **C:** 10% $Ni(acac)_2$, Et_2O, 2 equiv *i*PrMgCl•LiCl in THF, r.t.; **D:** CH_2Cl_2, pyridine (1.2 equiv), Tf_2O (1.2 equiv), r.t., 8-12 h.; **E:** $Pd(OAc)_2$ (2 mol%), PPh_3 (4 mol%), Et_3N (3 equiv), DMF (10 mL/mmol), HCO_2H (2 equiv), 80 °C, 1 h. [b]Yields after flash chromatography. [c]Yield of crude product after extraction. The compound underwent rapid decomposition upon attempted purification by flash

chromatography. [d]Desilylation of **3h** with TBAF gave **3k** in 94% yield (see Experimental Section). [e]The compound is contaminated with cross-coupled propyl and isopropyl group products. See Experimental section for details.

For the generalizion of the final reductive scission of the O-aryl carbamates **6** to the oxygenated 1-methylphenanthrenes **7**, an optimization study was carried out (Table 4). In the original work on the development of the Ni-catalyzed Kumada-Corriu cross-coupling reaction, Kumada had observed that Grignard reagents bearing β-hydrogens effect β-hydride transfer reactions and thereby reductive cleavage of aryl halides.[45,46] In our laboratories, we discovered this reaction for the *O*-carbamates.[33] In spite of the knowledge that the *O*-carbamate is the most powerful DMG and its promise in indole and scale-up chemistry,[33,47] this reaction remains broadly unexploited.[48] Initial optimization studies on model compound **6a** (Table 4) using commercially available *i*PrMgCl or *i*PrMgCl•LiCl (turbo-Grignard)[49,50] failed in THF solution at 10 mol % $Ni(acac)_2$ loading (entry 1). However, in spite of using both reagents as THF solutions, reductive cleavage was observed in Et_2O as reaction solvent at room temperature. While *i*PrMgCl produced mixtures of the desired decarbamoylated **7a**, together with the normal (**7i**) and isomeric (**7j**) Kumada-Corriu cross-coupled products[46] in varying amounts (entries 2 and 3), rapid injection of *i*PrMgCl•LiCl afforded high ratios of **7a** to the two coupled products (entries 4 and 5). The *i*PrMgCl•LiCl complex is considered to be more nucleophilic compared to *i*PrMgCl,[50] and its use in a Grignard reaction has shown increased amounts of reduction products[51] but to our knowledge, this result constitutes the first intentional use of the turbo-Gringard reagent as a hydride source. For small-scale experiments, the higher 10 mol% catalyst loading is recommended to achieve fast completion of the reaction although, as gleaned from the

experiments, large scale reactions should be feasible with low catalyst loading and thereby avoidance of environmental problems with excessive Ni residues. Although the cross-coupled products (**7i**, **7j**) were not isolated, they were readily identified on GC-MS by their main fragment from EI ionization arose from alkyl chain cleavages.

Table 4. Optimization of the reductive O-decarbamoylation of compound **6a** to **7a**



6a **7a** **7i** **7j**

Entry	Ni(acac)$_2$ (mol%)	Grignard[a]	equiv	time	Product ratios (%)[b]		
					7a	**7i**	**7j**
1	10	*i*PrMgCl•LiCl[c]	2	1.5 h	No reaction		
2	3	*i*PrMgCl[d]	2	1 h	48	33	18
3	2	*i*PrMgCl	4	4 h	77	14	8
4	10	*i*PrMgCl•LiCl	2	15 min	98	2	0
5	1	*i*PrMgCl•LiCl	2	22 h	97	2	1

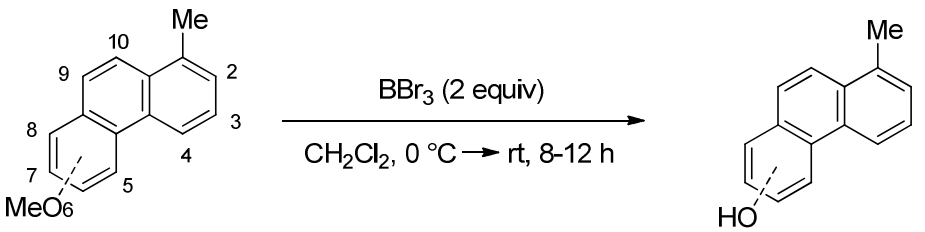
[a]All Grignard reagents were commercial solutions in THF: *i*PrMgCl (1 M) and *i*PrMgCl•LiCl (14 w%). [b]Ratios of products by GC/MS analysis. [c]Reaction were carried out in THF. [d]Grignard reagent was added slowly (see Experimental Section).

The optimized conditions were then applied to the phenanthrene *O*-carbamates **6a, c-e, g-i** (Table 3, conditions C) to give good to quantitative yields of 1-methylphenanthrenes **7a, c, g-h**.

Unfortunately, the reaction revealed its sensitivity as compounds **7c-d** and **7f** contained significant amounts of cross-coupled products. Presumably, due to steric hindrance by a peri-type effect, **7h** was obtained in lower yield. In the case of triflates **6b** and **6f**, reductive cleavage by hydride transfer from formic acid (condition E)[30] gave products **7b** and **7e** respectively. Although proceeding in very good yield, this method is less desirable due to its greater expense in the synthesis of the triflate **6f** compared to the *O*-carbamate derivative **6e**. In contrast, the byproducts formed in the reductive decarbamoylation route (cases **7i** and **7j**) were very difficult to separate from the desired phenanthrenes, and therefore the triflate procedure has merit when absolute purity is more important than cost.

To summarize, the reductive decarbamoylation completed the efficient regioselective synthesis of the series of ring A 2-, 3-, and 4-OMe 1-methylphenanthrenes as single isomers **7b-d**. Furthermore, the synthetic "walking tour" of OMe groups provided the isomeric C-ring OMe substituted 1-methylphenanthrenes **7e-h** by the regioselective DoM – cross-coupling – DreM strategy. It is of interest to note that, although the further transformation of **5b** into the corresponding phenanthrene **7a** was not pursued, reductive excision of the $OCONEt_2$ group from the isomeric derivatives of **5a** (**6a**) and **5b** gives the same molecule. This observation is perhaps a conceptual element of broader utility in PAH synthesis and certainly of step economy value since **3b** is simpler to prepare than the isomeric **4a**.

Scheme 4. Demethylation of 1-methylphenanthrenes **7** to phenanthrols **9**



7h	(8-OMe)	8-Methylphenanthren-1-ol	**9a**	57%
7g	(7-OMe)	8-Methylphenanthren-2-ol	**9b**	94%
7f	(6-OMe)	8-Methylphenanthren-3-ol	**9c**	87%

As previously noted, phenanthrols are unstable to aerial oxidation to varying degrees. To conclude our study, reliable[52] BBr_3 deprotection[53] on three methoxy derivatives **7f, 7g,** and **7h** was carried out to afford the corresponding phenols **9c, 9b** and **9a** respectively (Scheme 4) in order to demonstrate the relative higher stability of non 9-hydroxy phenanthrenes and the ability to make such products available as standards for PAH environmental and metabolism studies.[17] In summary, we have provided a systematic study of a general, efficient, and regioselective synthesis of phenanthrenes which allows the preparation of this class of PAHs with minimal handling of potentially carcinogenic materials, and without using Lewis-acid and other powerful reagents and harsh conditions. The route involves application of the combined DoM – Suzuki-Miyaura cross-coupling – DreM strategy to give a significant number of phenanthrenes (Tables 1 and 3) via the intermediate phenanthrols which are subjected to conversion to the corresponding triflates and O-carbamates followed by Ni-catalyzed scission. In addition, previously developed silicon protecting group and ipso-desilylation reactions have been applied (Scheme 2) and a new DoM over DreM reaction of 2-amido-2'-methyl biphenyls has been uncoverd (Table 2) which invite further application in aromatic synthesis.

Experimental Section

General

Melting points were measured in capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on 400 or 500 MHz spectrometers. The chemical shifts of ^{1}H and ^{13}C NMR signals are quoted relative to internal C*H*Cl_3 (δ = 7.26) and *C*DCl_3 (δ =77.0), DMSO-d_6 (δ = 2.50 and 45.0), acetone-d_6 (δ = 2.05 and 29.8 / 206.3) or tetramethylsilane (δ = 0.0). ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, etc.), coupling constant (Hz) and relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). The GC-MS analyses were performed under EI conditions. High resolution mass spectra were obtained on a EI or ESI Time of Flight Mass Spectrometer. All reactions involving alkyllithiums were carried out under argon in flame-dried glassware, using syringe-septum cap techniques. Anhydrous THF and Et_2O were obtained by treatment using solvent purification system with final drying through molecular sieves under argon. All purchased chemicals were used without further purification. Alkyllithiums were titrated before use.[54] Flash column chromatography was carried out using silica gel (particle size: 40-60 μm, 60A).

General Synthetic Procedures

The starting benzamides (*N,N*-diethyl-2-methoxybenzamide, *N,N*-diethyl-3-methoxybenzamide, *N,N*-diethyl-4-methoxybenzamide and **1b**) were synthesized from the corresponding benzoic acids using $SOCl_2$ and $HNEt_2$[55] and the spectral and analytical data of the products matched those that have been reported.[56]

The benzamide boronic acids **1a, 1c, 1d, 1g** and **1i** were synthesized according to general procedure **A** and were used directly without further purification. The synthesis and subsequent

cross-coupling of compound **1d** was difficult to reproduce, despite the care taken to avoid decomposition.

Ortho-tolyl (**2c**) and –xylyl (**2d**) boronic acids as well as 5-fluoro-2-methylbenzene boronic acid (**2f**) were purchased from Sigma Aldrich, as were the corresponding bromides and iodides (**2a**, **2b, 2e**).

Compounds **3a, 3f, 3e** were synthesized as reported,[30] as were compounds **3b, 5a** and **7a.**[31]

The more highly substituted biaryls exhibited rotamers, resulting in not well defined ^{1}H NMR spectra. For some biaryls VT NMR studies in DMSO solution indicated coalescence of certain peaks and for some biaryls not all of the carbon peaks were observed in the ^{13}C NMR.

For the synthesis of some final phenanthrenes, the Ni-catalyzed decarbamoylation reaction leads to linear and rearranged i-PrMgCl coupling rather than decarbamoylation. In some cases, it was not possible to fully eradicate this impurity from the desired product and these are indicated where relevant.

General Procedure – Directed *ortho* Metalation (A): To a solution of TMEDA (1.0-2.2 equiv) in THF (5-10 mL / mmol) cooled to 0 ^{o}C was added a solution of *s*-BuLi (1.0-2.2 equiv) and the mixture was cooled to -78 °C. The starting material (1.0 equiv) in THF (5-10 mL / mmol) was added dropwise while keeping the internal temperature below -70 °C. The reaction mixture was stirred for 1 hour, or the time indicated in the specific procedure, and then the electrophile was added, either neat or as a solution in THF. The cooling bath was removed and the reaction mixture was warmed to room temperature. Saturated solution of NH_4Cl was added (10 mL / mmol) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined, dried ($MgSO_4$) and evaporated to dryness. The residue was purified via column chromatography.

General Procedure – Directed remote Metalation (B): Under argon LDA in THF (1.1-2.5 equiv) was either prepared at 0 °C using *n*-BuLi (1.1-2.5 equiv) and diisopropylamine [DIPA] (1.1-2.5 equiv) in THF (10-30 mL / mmol) or commercial LDA solution (2.0 M in ethylbenzene/THF/heptane, 1.1-2.5 equiv) was utilized. The starting material (1.0 equiv) was dissolved in dry THF (5-10 mL / mmol) and added to the LDA solution dropwise at -20-0 °C. The solution was stirred for 4-24 h and quenched with saturated NH_4Cl solution (20 mL / mmol). The mixture was extracted with CH_2Cl_2 (3 x 20 mL), dried ($MgSO_4$) and evaporated to dryness in vacuo. The residue was purified via column chromatography or taken directly onto the next step.

General Procedure – Cross-coupling I (C): The starting halide (1.0 equiv) and the boronic acid (1.2-2.0 equiv) were dissolved in degassed dioxane / 2M aqueous K_2CO_3 mixture (10 mL dioxane / mmol substrate; 4-6 equiv K_2CO_3). To this solution was added $Pd(dppf)Cl_2*CH_2Cl_2$ complex (4-5 mol%) and the mixture was immersed into a preheated oil bath at 90-100 °C and maintained at this temperature for 16 h. Water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were dried ($MgSO_4$) and evaporated to dryness. The residue was purified by column chromatography.

General Procedure – Cross-coupling II (D): The starting halide (1.0 equiv) and boronic acid (1.1-1.5 equiv) were dissolved in toluene (7-10 mL / mmol) and degassed for 5-10 mins by bubbling argon through the solution. K_3PO_4 (4.0-5.0 equiv) was added, followed by Pd_2dba_3 (2-3 mol%) and SPhos (5-10 mol%). The reaction mixture was immersed in a preheated oilbath at 110 °C and the temperature maintained overnight. The reaction mixture was filtered, washed with EtOAc and after evaporation the residue was purified via column chromatography.

General Procedure – Cross-coupling III (E): The starting halide (1.0 equiv) and the boronic acid (1.2-2.5 equiv) were dissolved in degassed dimethoxyethane and 2M aqueous Na_2CO_3 mixture (7-10 mL dimethoxyethane /mmol substrate; 4-6 equiv Na_2CO_3). To this solution was added $Pd(PPh_3)_4$ (3-5 mol%) and the solution was maintained at reflux temperature overnight (16 h). The mixture was extracted with diethylether (3 x 10 mL/mmol substrate). Organic layers were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography.

General Procedure – Desilylation (F): The starting biaryl (1.0 equiv) was dissolved in dry THF (5-10 mL / mmol) and TBAF was added (1 M in THF, 2-3 equiv). After the reaction was complete according to TLC (2-16 h) the solvent was evaporated. The residue was purified via column chromatography.

General Procedure – Detriflation (G): The starting triflate (1.0 equiv) is dissolved in DMF (10 mL / mmol) and the mixture is degassed by bubbling argon through with a needle for 5-10 mins. Then were added Et_3N (3.0 equiv), HCO_2H (2.0 equiv), $PdOAc_2$ (2 mol%) and PPh_3 (4 mol%). The mixture was placed in a preheated oilbath at 80 ^oC for 1 h. The mixture was cooled to r.t. and H_2O (15 mL / mmol) was added and the mixture was extracted with CH_2Cl_2 (2 x 20 mL). After evaporating to dryness, the residue was purified via column chromatography.

General Procedure – Decarbamoylation (H): The starting material (1 equiv) was dissolved in dry Et_2O (20 mL/mmol) and $Ni(acac)_2$ (10 mol%) was added. The suspension was cooled to 0 ^oC and *i*-PrMgCl*LiCl (2.5 equiv, solution in THF) was added. The mixture was allowed to warm to room temperature overnight. Then, H_2O (20 mL / mmol) was added, the layers separated and the

aqueous layer extracted with CH_2Cl_2 (2 x 20 mL). The combined organics were dried ($MgSO_4$) and evaporated. The residue was purified via column chromatography.

General Procedure – BBr_3 Demethylation (I): The phenanthrene was dissolved in dry CH_2Cl_2 (50 mL / mmol). The solution was cooled to 0 °C, and BBr_3 (2.0 equiv) was added dropwise. The icebath was removed and the mixture stirred at room temperature overnight. Water (20 mL) was added and the organic layer separated. The aqueous layer was additionally extracted with CH_2Cl_2 (2 x 20 mL). The organic layers were combined, dried ($MgSO_4$) and after evaporation the residue was purified via column chromatography.

***N,N*-Diethyl-2-bromo-3-methoxy-benzamide (1e):**

The title compound was synthesized by dissolving **1k** (2.50 g, 8.95 mmol, 1.0 equiv) in CCl_4 (50 mL). At 0 ^oC Br_2 (483 µL, 9.39 mmol, 1.05 equiv) was added and the mixture was warmed to 50 ^oC for 2 h. After cooling to room temperature the solution was evaporated and the residue subjected to column chromatography using pentane / Et_2O (1:1 to 0:1 gradient). The title compound was isolated as a colorless oil (2.5 g, 98%). Physical and spectral data are in agreement with those reported.[57]

***N,N*-Diethyl-2-iodo-3-methoxy-benzamide (1f):**

The title compound was synthesized by dissolving **1k** (280 mg, 1.0 mmol, 1.0 equiv) in MeOH (10 mL) and adding $AgBF_4$ (202 mg, 1.1 mmol, 1.1 equiv). At 0 ^oC I_2 (305 mg, 1.2 mmol, 1.2 equiv) was added and the mixture was warmed to room temperature and stirred at this temperature overnight. The next day, EtOAc was added (20 mL) and the suspension was filtered and evaporated to dryness. EtOAc (50 mL) was added and washed with 2M HCl (10 mL) and

H_2O (20 mL). The organic layer was dried ($MgSO_4$), evaporated and the residue subjected to column chromatography using hexanes / EtOAc (2:1 to 1:1 gradient). The title compound was isolated as a colorless oil (197 mg, 59%). ^{1}H NMR data are similar to those reported but obtained in C_6D_6.[58] ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.31 (t, *J* = 7.9 Hz, 1H), 6.80 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.77 (dd, *J* = 1.0, 8.2 Hz, 1H), 3.88 (s, 3H), 3.80-3.90 (m, 1H), 3.22-3.34 (m, 1H), 3.02-3.19 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 12.4, 13.8, 38.8, 42.6, 56.5, 85.1, 110.3, 119.1, 129.8, 144.7, 158.2, 169.9; MS (EI, DIP) *m/z* 333 (M^+, 61), 332 (56), 261 (100), 218 (15), 206 (34), 195 (30), 165 (19), 135 (19); FTIR (neat, cm^{-1}) 2972, 2934, 1628, 1562, 1424, 1296, 1262, 1053, 786; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{12}H_{16}INO_2$ calcd 333.0226, found 333.0215.

***N,N*-Diethyl-2-bromo-4-methoxy-benzamide (1h):**

The title compound was synthesized according to general procedure **A** using TMEDA (1.52 mL, 10.13 mmol, 1.05 equiv), *s*-BuLi (1.33M in cyclohexane, 7.62 mL, 10.13 mmol, 1.05 equiv) in THF (25 mL), *N,N*-diethyl-4-methoxybenzamide (2.00 g, 9.65 mmol, 1.0 equiv) in THF (5 mL), and Br_2 (522 μL, 10.13 mmol, 1.05 equiv). After standard workup, with an additional wash with sodium thiosulfate (sat., 20 mL), the residue was purified via column chromatography using CH_2Cl_2/Et_2O (10/0 to 10/1 gradient). The title compound was isolated as a colorless oil (1.19 g, 43%): ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.15 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 2.4, 8.5 Hz, 1H), 3.79 (s, 4H [-OC*H*$_3$ + -NC*H*]), 3.32 (br s, 1H), 3.14 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 12.5, 13.9, 39.0, 42.7, 55.5, 113.6, 117.9, 119.8, 128.2, 131.1, 160.0, 168.5; MS (EI, DIP) *m/z* 286/284 (M^+, 20), 215/213 (100), 172/170 (15), 135 (26); FTIR (KBr, cm^{-1}) 2973, 2935, 1633, 1601, 1564, 1469,

1427, 1288, 1195, 1032, 884; HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{12}H_{17}BrNO_2$ calcd 286.0443, found 286.0442.

***N,N*-Diethyl-6-bromo-3-methoxy-2-trimethylsilyl-benzamide (1j):**

The title compound was synthesized according to general procedure **A** using TMEDA (650 µL, 4.31 mmol, 1.2 equiv), *s*-BuLi (1.35M in cyclohexane, 3.18 mL, 4.31 mmol, 1.2 equiv) in THF (20 mL), **1k** (1.0 g, 3.58 mmol, 1.0 equiv) in THF (5 mL), and Br_2 (202 µL, 3.93 mmol, 1.1 equiv) in THF (5 mL). After standard workup, with an additional wash with sodium thiosulfate (sat., 20 mL), the residue was purified via column chromatography using pentane/Et_2O (5/1 to 3/1 gradient). The title compound was isolated as a colorless oil that solidifies on standing (375 mg, 29%): Mp 99-100 °C (hexanes / Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.46 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 3.91 (sex, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 3.01-3.27 (m, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 0.3, 12.0, 13.1, 38.7, 42.8, 55.3, 111.3, 111.4, 127.3, 134.5, 143.7, 163.9, 168.5; MS (EI, DIP) *m/z* 359/357 (M^+, 7), 344/342 (100), 287/285 (9), 219 (29); FTIR (KBr, cm^{-1}) 2975, 1639, 1461, 1413, 1380, 1286, 1244, 1057, 846; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{15}H_{24}BrNO_2Si$ calcd 357.0760, found 357.0759.

***N,N*-Diethyl-3-methoxy-2-trimethylsilylbenzamide (1k):**

The title compound was synthesized according to general procedure **A** using TMEDA (1.65 mL, 11.0 mmol, 1.1 equiv), *s*-BuLi (1.4M in cyclohexane, 7.5 mL, 10.5 mmol, 1.05 equiv) in THF (25 mL), *N*,*N*-diethyl-3-methoxybenzamide (2.07 g, 10.0 mmol, 1.0 equiv) in THF (10 mL), and TMSCl (4.0 mL, 31.5 mmol, 3.15 equiv). After standard workup, the residue was purified via column chromatography using pentane/Et_2O (5/1 to 3/1 to 1/1 gradient). The title compound was

isolated as a pale yellow solid (2.12 g, 76%). Mp 51-52 °C (hexanes, lit. 54-55 °C [hexanes]);[36] ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.30 (t, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 3.61 (br s, 1H), 3.40 (br s, 1H), 3.21 (br s, 1H), 3.13 (br s, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 0.4, 12.7, 13.6, 38.9, 43.3, 55.1, 109.7, 118.8, 124.3, 130.4, 144.5, 164.8, 171.7.

***N,N*-Diethyl-6-iodo-3-methoxy-2-trimethylsilyl-benzamide (1l):**

The title compound was synthesized according to general procedure **A** using TMEDA (335 µL, 2.23 mmol, 1.3 equiv), *s*-BuLi (1.4M in cyclohexane, 1.5 mL, 2.1 mmol, 1.2 equiv) in THF (10 mL), **1k** (480 mg, 1.72 mmol, 1.0 equiv) in THF (10 mL), and I_2 (570 mg, 2.25 mmol, 1.3 equiv) in THF (2 mL). After standard workup, with an additional wash with sodium thiosulfate (sat., 20 mL), the residue was purified via column chromatography using pentane/Et_2O (5/1 to 3/1 gradient). The title compound was isolated as a colorless solid (556 mg, 80%): Mp 108-109 °C (Et_2O, lit. 100-101 °C [hexanes]);[36] ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.73 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 8.7 Hz, 1H), 3.93 (sex, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 3.01-3.27 (m, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 0.4, 12.0, 13.1, 38.9, 43.0, 55.3, 84.3, 111.8, 127.5, 141.2, 147.5, 164.8, 170.1.

***N,N*-Diethyl-2'-methylbiphenyl-2-carboxamide (3a):**

The title compound was synthesized according to general procedure **E** using **1a** (2.42 g, 10.9 mmol, 1.4 equiv), **2a** (1.21 g, 7.1 mmol, 1.0 equiv), 2M aqueous K_2CO_3 (20 mL, 40.00 mmol, 5.6 equiv), $Pd(PPh_3)_4$ (246 mg, 0.213 mmol, 3.0 mol%) in 35 mL of dimethoxyethane and 5 ml ethanol. After standard workup, the residue was purified via column chromatography using heptane/Ethyl acetate (2/1) to afford the title product as a colorless oil that solidifies (1.74 g, 89%

yield): Mp 65-66.5 °C (cyclohexane, lit. 67-68 °C [hexanes][30]); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) □ 7.36-7.48 (m, 2H), 7.28-7.35 (m, 1H), 7.18-7.28 (m, 3H), 7.05-7.17 (m, 2H), 3.18 (br s, 2H), 2.93 (br s, 2H), 2.13 (s, 3H), 0.88 (br s, 3H), 0.67 (br s, 3 H); ^{13}C-NMR (100 MHz, DMSO-d_6) □ 12.2, 14.0, 20.4, 37.9, 42.5, 125.4, 126.6, 127.7, 128.0, 128.6, 129.9, 130.3, 130.5, 136.2, 137.8, 138.3, 139.7, 169.4; MS (EI, DIP) *m/z* 267 (M^+, 22), 266 (22), 195 (M^+, 100), 167 (40), 165 (69), 152 (45); FTIR (KBr, cm^{-1}) 2965, 1631, 1428, 755; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{18}H_{21}NO$ calcd 267.1623, found 267.1635.

***N,N*-Diethyl-3-methoxy-2',3'-dimethylbiphenyl-2-carboxamide (3c):**

Compound **1c** was synthesized according to general procedure **A** using TMEDA (2.7 mL, 18.0 mmol, 1.20 equiv), *s*-BuLi (1.23 M in cyclohexane, 14.6 mL, 18.0 mmol, 1.20 equiv) in THF (30 mL), *N,N*-diethyl-2-methoxybenzamide (3.1 g, 15.0 mmol, 1.0 equiv) in THF (30 mL), and tri*iso*propylborate (8.3 mL, 36 mmol, 2.4 equiv). After standard workup (quench with sat. aq. NH_4Cl and ether extraction) the crude **1c** (3.94 g, 104%) was isolated and used in the next step without further purification.

The title compound **3c** was synthesized according to general procedure **E** using **1c** (3.94 g, 15 mmol, 1.5 equiv), **2b** (1.83 g, 9.89 mmol, 1.00 equiv), 2M aqueous Na_2CO_3 (40 mL), $Pd(PPh_3)_4$ (347 mg, 0.3 mmol, 3.0 mol%) in 40 mL of dimethoxyethane. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (2/1) to afford the title product as a colorless oil that solidifies (2.28 g, 74% yield): Mp 123-124 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers major (A) and minor **(**B**))** □ 7.26-7.38 (A + B, m, 3H), 7.03-7.14 (A + B, m, 3H), 7.00 (B, t, *J* = 7.5 Hz, 1H), 6.88-6.94 (A + B, m, 2H), 6.85 (A, d, *J* = 4.2 Hz, 1H), 6.84 (B, d, *J* = 4.4 Hz, 1H), 6.79 (B, d, *J* = 7.6 Hz, 1H), 3.86 (B, s, 3H), 3.85 (A, s, 3H), 3.78 (A + B, sex, *J* = 6.8 Hz, 2H), 3.26 (A, sex, *J* = 7.1 Hz, 1H), 3.10 (B, sex, *J* =

7.0 Hz, 1H), 2.65-2.97 (A + B, m, 4H), 2.28 (B, s, 3H), 2.27 (A, s, 3H), 2.08 (B, s, 3H), 2.06 (A, s, 3H), 1.03 (A, t, *J* = 7.1 Hz, 3H), 0.88 (B, t, *J* = 7.1 Hz, 3H), 0.52-0.67 (A + B, m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 11.5, 11.6, 13.5, 13.5, 17.0, 17.3, 20.4, 20.5, 37.3, 37.5, 42.1, 42.4, 55.3, 55.6, 109.2, 109.3, 122.0, 123.2, 124.0, 124.9, 125.8, 126.0, 126.4, 128.3, 128.8, 128.9, 128.9, 129.0, 133.2, 136.0, 136.4, 136.8, 138.3, 139.4, 139.7, 141.1, 155.2, 155.9, 167.2, 167.4; MS (EI, DIP) *m/z* 311 (M^+, 2), 280 (2), 239 (100), 224 (7), 196 (10), 181 (7), 165 (12), 152 (8); FTIR (KBr, cm-1) 2980, 2930, 1627, 1461, 1285, 1256, 1067; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{20}H_{25}NO_2$ calcd 311.1885, found 311.1879.

***N,N*-Diethyl-6-methoxy-2',3'-dimethylbiphenyl-2-carboxamide (3d):**

The title compound was synthesized according to general procedure **D** using **1e** (400 mg, 1.40 mmol, 1.0 equiv), **2d** (300 mg, 2.00 mmol, 1.4 equiv), K_3PO_4 (1.40 g, 6.60 mmol, 4.7 equiv), Pd_2dba_3 (32 mg, 0.035 mmol, 2.5 mol%) and SPhos (32 mg, 0.080 mmol, 5.7 mol%) in 10 mL toluene. After standard workup, the residue was purified via column chromatography using hexanes /EtOAc (3/1 to 1/1 gradient) to afford the title product as a colorless oil (310 mg, 71% yield): ^{1}H NMR (400 MHz, 70 °C, d_6-DMSO) □ 7.40 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 2H), 3.70 (s, 3H), 2.75-3.30 (m, 4H), 2.25 (s, 3H), 1.93 (s, 3H), 0.91 (br s, 3H), 0.61 (br s, 3H); ^{13}C NMR (100 MHz, 70 °C, d_6-DMSO) □ 11.0, 13.0, 15.8, 19.4, 36.6, 41.4, 55.1, 110.7, 117.3, 123.7, 126.8, 128.1 (2C), 134.9, 138.4, 156.1, 167.9; MS (EI, DIP) *m/z* 311 (M^+, 29), 239 (83), 238 (100), 224 (24), 209 (6), 195 (11), 181 (13), 165 (16), 152 (13); FTIR (KBr, cm^{-1}) 2970, 2931, 1634, 1457, 1427, 1314, 1296, 1059; HRMS (EI-TOF) m/z: $[M-H]^+$ for $C_{20}H_{24}NO_2$ calcd 310.1807, found 310.1795.

***N,N*-Diethyl-6-methoxy-2'-methylbiphenyl-2-carboxamide (3e):**

The title compound was synthesized according to general procedure **D** using **1f** (1.44 g, 4.08 mmol, 1.0 equiv), **2c** (832 mg, 6.11 mmol, 1.5 equiv), K_3PO_4 (3.46 g, 16.30 mmol, 4.0 equiv), Pd_2dba_3 (85 mg, 0.093 mmol, 2.3 mol%) and SPhos (135 mg, 0.33 mmol, 8.0 mol%) in 35 mL of toluene. After standard workup, the residue was purified via column chromatography using pentane /Et_2O (1/1) to afford the title product as a colorless oil that solidifies (1.01 g, 82% yield). Physical and spectral data are in agreement with those reported:[30] Mp 110.5-112.5 °C (hexanes / Et_2O, lit. 105-107 °C [hexane][30]); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) □ 7.41 (t, *J* = 8.0 Hz, 1H), 7.15-7.22 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.98-7.06 (m, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 2.70-3.35 (m, 4H), 2.04 (s, 3H), 0.93 (br s, 3H), 0.61 (t, *J* = 6.0 Hz, 3 H); ^{13}C-NMR (100 MHz, DMSO-d_6, 70 °C) □ 12.1, 14.0, 20.0, 37.6, 42.4, 56.2, 111.8, 118.3, 125.2, 127.7, 129.3, 129.6, 135.9, 137.6, 139.4, 157.1, 168.9; FTIR (KBr, cm^{-1}) 2971, 2932, 1632, 1460, 1427, 1296, 1256, 1059; MS (EI, DIP) *m/z* 297 (M^+, 48), 225 (100), 224 (90), 210 (45), 181 (27), 166 (42), 152 (29), 84 (55); HRMS (EI-TOF) m/z: $[M]^+$ for $C_{19}H_{23}NO_2$ calcd 297.1729, found 297.1718.

***N,N*-Diethyl-5-methoxy-2',3'-dimethylbiphenyl-2-carboxamide (3g):**

The title compound was synthesized according to general procedure **C** using **1h** (143 mg, 0.50 mmol, 1.0 equiv), **2d** (225 mg, 1.50 mmol, 3.0 equiv), 2M aqueous K_2CO_3 (1.5 mL, 3.00 mmol, 6.0 equiv), Pd(dppf)Cl_2*CH_2Cl_2 (20 mg, 0.024 mmol, 4.9 mol%) in 5 mL of dioxane. After standard workup, the residue was purified via column chromatography using hexanes/EtOAc (9/1 to 5/1 gradient) to afford the title product as a colorless oil (110 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$, one aromatic proton exhibits a very broad peak and is only visible when the spectrum intensity is increased**)** □ 7.29 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.04 (t, *J* =

7.5 Hz, 1H), 6.92 (dd, *J* = 2.5, 8.4 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 2.40-3.75 (m, 4H), 2.29 (s, 3H), 2.11 (s, 3H), 0.89 (br s, 3H), 0.67 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 11.7, 13.7, 17.1, 20.5, 37.9, 42.5, 55.3, 112.7, 115.5, 124.6, 127.5, 129.1, 129.7, 136.9, 159.1, 170.2 MS (EI, DIP) *m/z* 311 (M^+, 11), 240 (100), 211 (24), 196 (42), 165 (24), 153 (25); FTIR (KBr, cm^{-1}) 2934, 1633, 1455, 1379, 1288, 1223, 1109, 1035; HRMS (EI-TOF) m/z: $[M-H]^+$ for $C_{20}H_{24}NO_2$ calcd 310.1807, found 310.1792.

***N,N*-Diethyl-4-methoxy-3-trimethylsilyl-2',3'-dimethylbiphenyl-2-carboxamide (3h):**

Compound **1i** was synthesized according to general procedure **A** using TMEDA (3.1 mL, 20.7 mmol, 1.30 equiv), *s*-BuLi (1.23 M in cyclohexane, 16.8 mL, 20.7 mmol, 1.30 equiv) in THF (40 mL), **1k** (4.45 g, 15.9 mmol, 1.0 equiv) in THF (30 mL), and tri*iso*propylborate (11.0 mL, 47.8 mmol, 3.0 equiv). After standard workup (quench with sat. aq. NH_4Cl and ether extraction) the crude **1i** (5.32 g, 103%) was isolated and used in the next step without further purification.

The title compound **3h** was synthesized according to general procedure **E** using **1i** (5.32 g, 15.9 mmol, 1.4 equiv), **2b** (2.09 g, 11.3 mmol, 1.00 equiv), 2M aqueous Na_2CO_3 (40 mL), $Pd(PPh_3)_4$ (394 mg, 0.34 mmol, 3.0 mol%) in 80 mL of dimethoxyethane. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (6/1) to afford the title product as a colorless oil that solidifies (3.59 g, 83% yield); Mp 95-96 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers major (A) and minor **(B))** □ 7.08-7.15 (B, m, 1H), 7.03 (A, d, *J* = 8.5 Hz, 1H), 6.98 (B, d, *J* = 8.3 Hz, 1H), 6.93 (A + B, d, *J* = 7.2 Hz, 2H), 6.89 (B, d, *J* = 7.5 Hz, 1H), 6.84 (A, t, *J* = 7.8 Hz, 1H), 6.75 (A, d, *J* = 7.5 Hz, 1H), 6.72 (A, d, *J* = 4.2 Hz, 1H), 6.70 (B, d, *J* = 4.3 Hz, 1H), 3.71 (A, s, 3H), 3.70 (B, s, 3H), 3.50-3.65 (A + B, m, 2H), 3.02 (B, sex, *J* = 7.0 Hz, 1H), 2.91 (A, sex, *J* = 7.0 Hz, 1H), 2.65 (B, sex, *J* = 7.1 Hz, 1H), 2.54 (A, sex, *J* = 7.0 Hz, 1H), 2.46 (A, sex, *J* = 6.5 Hz, 1H), 2.35 (B, sex, *J* = 6.5 Hz, 1H), 2.15

(A, s, 3H), 2.11 (B, s, 3H), 1.96 (A, s, 3H), 1.86 (B, s, 3H), 0.83 (B, t, J = 7.2 Hz, 3H), 0.68 (A, t, J = 7.2 Hz, 3H), 0.40 (A, t, J = 7.1 Hz, 3H), 0.22 (B, t, J = 7.1 Hz, 3H), 0.14 (B, s, 9H), 0.13 (A, s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 0.6, 0.7, 10.7, 11.4, 12.8, 12.9, 17.1, 17.7, 20.4, 20.7, 37.0, 37.6, 42.4, 42.5, 55.1, 55.2, 109.0, 109.2, 123.8, 123.9, 124.8, 124.8, 127.1, 128.6, 128.7, 129.5, 130.2, 131.7, 132.0, 133.3, 133.6, 136.5, 136.7, 137.2, 138.8, 140.0, 142.8, 143.3, 163.8, 163.9, 169.2, 169.5; MS (EI, DIP) *m/z* 383 (M^+, 6), 368 (100), 311 (9), 295 (7); FTIR (KBr, cm^{-1}) 2980, 2933, 1633, 1429, 1282, 1239, 1061; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{23}H_{33}NO_2Si$ calcd 383.2281, found 383.2293.

***N,N*-Diethyl-4-methoxy-3-trimethylsilyl-2'-methylbiphenyl-2-carboxamide (3i):**

The title compound was synthesized according to general procedure **C** using **1l** (550 mg, 1.36 mmol, 1.0 equiv), **2c** (370 mg, 2.72 mmol, 2.0 equiv), 2M aqueous K_2CO_3 (4 mL, 8.00 mmol, 5.9 equiv), Pd(dppf)Cl_2*CH_2Cl_2 (54 mg, 0.066 mmol, 4.9 mol%) in 14 mL of dioxane. After standard workup, the residue was purified via column chromatography using hexanes/EtOAc (9/1 to 5/1 gradient) to afford the title product as a colorless oil that solidifies (475 mg, 95% yield): Mp 74-77 °C (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers major (A) and minor **(B))** □ 7.41 (A, d, J = 7.4 Hz, 1H), 7.00-7.28 (A + B, m, 9H), 6.86 (A, d, J = 4.7 Hz, 1H), 6.84 (B, d, J = 5.2 Hz, 1H), 3.84 (B, s, 3H), 3.84 (A, s, 3H), 3.66-3.80 (A + B, m, 2H), 3.20 (B, sex, J = 7.0 Hz, 1H), 3.06 (A, sex, J = 7.0 Hz, 1H), 2.85 (B, sex, J = 7.0 Hz, 1H), 2.71 (A, sex, J = 7.0 Hz, 1H), 2.60 (A, sex, J = 6.7 Hz, 1H), 2.51 (B, sex, J = 6.7 Hz, 1H), 2.22 (A, s, 3H), 2.15 (B, s, 3H), 0.99 (B, t, J = 7.1 Hz, 3H), 0.84 (A, t, J = 7.1 Hz, 3H), 0.55 (A, t, J = 7.1 Hz, 3H), 0.39 (B, t, J = 7.0 Hz, 3H), 0.29 (A, s, 9H), 0.28 (B, s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 0.6, 0.6, 10.8, 11.4, 12.8, 20.3, 20.4, 36.9, 37.4, 42.2, 42.3, 55.0, 55.1, 108.9, 109.1, 123.9, 124.1, 124.7, 125.2, 127.0, 127.3, 129.0, 129.5, 129.5, 129.8, 131.3, 131.5, 131.6, 132.9, 135.0, 138.6,

138.7, 140.0, 142.8, 143.3, 163.8, 169.1, 169.3; MS (EI, DIP) *m/z* 369 (M^+, 17), 354 (92), 297 (15), 264 (27), 219 (100), 131 (33), 108 (32); FTIR (KBr, cm^{-1}) 2975, 1633, 1452, 1425, 1284, 1242, 1059; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{22}H_{31}NO_2Si$ calcd 369.2124, found 369.2125.

***N,N*-Diethyl-6-methoxy-2'-methyl-5´-fluorobiphenyl-2-carboxamide (3j):**

The title compound was synthesized according to general procedure **D** using **1f** (166 mg, 0.5 mmol, 1.0 equiv), **2f** (115 mg, 0.75 mmol, 1.5 equiv), K_3PO_4 (530 mg, 2.5 mmol, 5.0 equiv), Pd_2dba_3 (10 mg, 0.011 mmol, 2.2 mol%) and SPhos (16 mg, 0.039 mmol, 7.8 mol%) in 4 mL of toluene. After standard workup, the residue was purified via column chromatography using pentane /Et_2O (2/1 to 1/1 gradient) to afford the title product as a pale yellow solid (119 mg, 75% yield): Mp 113-114 °C (cyclohexane); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) □ 7.42 (t, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 6.2, 8.3 Hz, 1H), 7.13 (dd, *J* = 0.6, 8.3 Hz, 1H), 6.99 (dt, *J* = 2.8, 8.6 Hz, 1H), 6.89 (dd, *J* = 0.9, 7.6 Hz, 1H), 6.82 (dd, *J* = 2.4, 9.8 Hz, 1H), 3.73 (s, 3H), 2.80-3.40 (br m, 4H), 2.00 (s, 3H), 0.94 (br s, 3H), 0.65 (t, *J* = 6.8 Hz, 3H); *Despite measurement of dilute and concentrated samples, and varying the number of scans, NMR solvents as well as the temperature, a ^{13}C-NMR showing adequate signal intensities could not be obtained;* MS (EI, DIP) *m/z* 315 (M^+, 87), 242 (100), 183 (9), 74 (29); FTIR (KBr, cm^{-1}) 2973, 2934, 1632, 1574, 1462, 1427, 1297, 1256, 1059, 891, 801; HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{19}H_{23}FNO_2$ calcd 316.1713, found 316.1712.

***N,N*-Diethyl-4-methoxy-2',3'-dimethylbiphenyl-2-carboxamide (3k):**

The title compound was synthesized according to general procedure **F** with **3h** (3.37 g, 8.79 mmol, 1.0 equiv) and TBAF (1M in THF, 21.6 mL, 2.46 equiv) in THF (18 mL). After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (1/1) to

afford the title compound as a colorless solid (2.56 g, 94%): Mp 102-103 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) □ 6.85-7.24 (m, 6H), 3.85 (s, 3H), 3.72 (br s, 1H), 2.50-3.20 (m, 3H), 2.28 (s, 3H), 2.08 (br s, 3H), 0.50-1.05 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 11.7, 13.7, 17.1, 20.6, 37.9, 42.4, 55.4, 114.2, 128.9, 136.8, 158.6, 169.9; MS (EI, DIP) *m/z* 311 (M^+, 5), 282 (1), 239 (55), 238 (100), 224 (10), 211 (13), 196 (14), 181 (11), 165 (11), 152 (13); FTIR (KBr, cm^{-1}): 3059, 2971, 2929, 1627, 1479, 1461, 1292, 1230, 1077, 1042; HRMS (EI-TOF) m/z: $[M-H]^+$ for $C_{20}H_{24}NO_2$ calcd 310.1807, found 310.1800.

_N,N_-Diethyl-4-methoxy-2'-methylbiphenyl-2-carboxamide (3l):

The title compound was synthesized according to general procedure **F** with **3i** (1.19 g, 3.21 mmol, 1.0 equiv) and TBAF (1M in THF, 3.5 mL, 1.1 equiv) in THF (30 mL). After standard workup, the residue was purified via column chromatography using hex/EtOAc (7/1 to 1/1 gradient) to afford the title compound as a colorless oil (796 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) □ 7.07-7.24 (m, 5H), 6.94 (dd, J = 2.6, 8.4 Hz, 1H), 6.90 (s, 1H), 3.85 (s, 3H), 3.73 (br s, 1H), 2.50-3.35 (m, 3H), 2.21 (s, 3H), 0.89 (br s, 3H), 0.68 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 11.7, 13.7, 20.2, 37.8, 42.2, 55.4, 111.3, 114.2, 125.2, 127.0, 130.0, 131.4, 138.1, 158.7, 169.8; MS (EI, DIP) *m/z* 297 (M^+, 4), 224 (100), 197 (44), 182 (38), 165 (29), 153 (33); FTIR (KBr, cm^{-1}) 3058, 2971, 2933, 2836, 1635, 1566, 1456, 1379, 1289, 1229, 1082, 1002, 831; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{19}H_{23}NO_2$ calcd 297.1729, found 297.1720.

_N,N_-Diethyl-3-methyl-2'-methylbiphenyl-2-carboxamide (4a):

The title compound was synthesized according to general procedure **A** by dissolving **3a** (1.73 g, 6.47 mmol, 1.0 equiv) in THF (60 mL) and adding TMEDA (1.16 mL, 7.76 mmol, 1.2 equiv) and *s*-BuLi (1.16 M in cyclohexane, 6.69 mL, 7.76 mmol, 1.2 equiv) at -78 °C. After 1 hr MeI (2.00

mL, 35.3 mmol, 5.0 equiv) in THF (5 mL) was precooled to -78 °C and added all at once. After standard workup, the residue was purified via column chromatography using heptane:ethyl acetate (2/1). The title compound was isolated as a colorless oil (1.73 g, 95%): ^{1}H NMR (400 MHz, $CDCl_3$, two rotamers, ~1/1 ratio) □ 7.35-7.50 (m, 2H), 6.94-7.34 (m, 12H), 3.56-3.76 (m, 2H), 3.13-3.30 (m, 1H), 2.78-3.11 (m, 4H), 2.60-2.77 (m, 1H), 2.35 (s, 6H), 2.23 (s, 3H), 2.16 (s, 3H), 1.00 (br s, 3H), 0.82 (br s, 3H), 0.70 (br s, 3H), 0.60 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) □ 11.4, 11.7, 13.5, 13.6, 19.4, 19.5, 20.2, 37.1, 37.5, 41.8, 42.2, 124.3, 125.4, 126.9, 127.3, 127.5, 128.0, 128.4, 129.1, 129.8, 130.0, 131.1, 133.8, 134.8, 136.4, 136.6, 137.2, 137.8, 138.7, 138.8, 140.1, 169.3, 169.4; MS (EI, DIP) *m/z* 281 (M^+, 14), 266 (34), 209 (100), 165 (66); FTIR (KBr, cm^{-1}) 2972, 2931, 1630, 1492, 1283; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{19}H_{23}NO$ calcd 281.1780, found 281.1772.

***N,N*-Diethyl-3-chloro-2'-methylbiphenyl-2-carboxamide (4b):**

The title compound was synthesized according to general procedure **A** using TMEDA (120 μL, 0.80 mmol, 2.1 equiv), *s*-BuLi (1.1 M in cyclohexane, 730 μL, 0.80 mmol, 2.1 equiv) in THF (1.0 mL), **3a** (100 mg, 0.37 mmol, 1.0 equiv) in THF (1.0 mL), and C_2Cl_6 (266 mg, 1.12 mmol, 3.0 equiv), in THF (0.5 mL). After standard workup, the residue was purified via column chromatography using CH_2Cl_2/Et_2O (10/0 to 10/1 gradient). The title compound was isolated as a colorless solid (79 mg, 70%): Mp 87 °C (cyclohexane); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) □ 7.39-7.55 (m, 2H), 7.08-7.32 (m, 5H), 3.44 (sext, *J* = 6.6 Hz, 1H), 2.75-3.33 (m, 3H), 2.12 (s, 3H), 0.96 (br s, 3H), 0.64 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6, 70 °C) □ 11.9, 13.8, 20.3, 37.6, 42.4, 125.4, 128.4, 128.7, 129.4, 129.8, 130.3, 136.5, 165.7; MS (EI, DIP) *m/z* 301 (M^+, 3), 264 (41), 229 (32), 219 (100), 165 (48), 131 (79), 114 (14), 100 (25), 69 (99); FTIR

(KBr, cm^{-1}) 2977, 2929, 2870, 1634, 1464, 1283; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{18}H_{20}ClNO$ calcd 301.1233, found 301.1253.

***N,N*-Diethyl-3-trimethylsilyl-2'-methylbiphenyl-2-carboxamide (4c):**

The title compound was synthesized according to general procedure **A** using TMEDA (120 µL, 0.80 mmol, 2.1 equiv), *s*-BuLi (1.1 M in cyclohexane, 730 µL, 0.80 mmol, 2.1 equiv) in THF (1.0 mL), **3a** (100 mg, 0.37 mmol, 1.0 equiv) in THF (1.0 mL), and TMSCl (140 µL, 1.12 mmol, 3.0 equiv). After standard workup, the residue was purified via column chromatography using CH_2Cl_2/Et_2O (100/0 to 95/5 gradient). The title compound was isolated as a colorless oil (116 mg, 92%): ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) □ 7.60 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.08-7.36 (m, 4H), 3.56 (sex, *J* = 6.6 Hz, 1H), 2.96 (br s, 1H), 2.71 (br s, 2H), 2.18 (br s, 3H), 0.76 (br s, 3H), 0.57 (br s, 3H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, 2 rotamers) □ -0.1, 0.0, 10.9, 11.5, 12.6, 12.6, 19.8, 20.0, 36.2, 37.0, 41.9 (2 x C), 124.5, 125.0, 126.6, 126.7, 127.3 (2 x C), 127.5, 127.5, 128.9, 129.1, 129.8, 129.8, 130.2, 130.3, 130.9, 133.5, 133.7, 134.7, 135.9, 137.,4 138.3, 138.3, 141.7 (2 x C), 169.2 (2 x C); MS (EI, DIP) *m/z* 339 (M^+, 26), 324 (100), 267 (70), 264 (29), 251 (48), 235 (14), 219 (74), 195 (17), 178 (19), 165 (33), 131 (52), 73 (34), 69 (72); FTIR (neat, cm^{-1}) 2962, 1626, 1439, 1281, 1246; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{29}NOSi$ calcd 339.2018, found 339.2027.

***N,N*-Diethyl-6-methoxy-3-methyl-2'-methylbiphenyl-2-carboxamide (4d):**

According to general procedure **A**, TMEDA (2.2 equiv, 3.33 mmol, 500 µL), *s*-BuLi (2.2 equiv, 3.33 mmol, 3.1 mL, 1.05 M in cyclohexane) in 5 mL of THF, **3e** (1.0 equiv, 1.51 mmol, 450 mg) in THF (3 mL) were used. After a deprotonation time of 1 h, MeI (3.0 equiv, 4.50 mmol, 282 µL) was added all at once. Subsequent standard workup and flash column chromatography

(CH_2Cl_2:Et_2O, 12:1) gave 366 mg (78%) of **4d** as a pale yellow oil that solidifies over time. It is possible to separate the rotamers via column chromatography, but the purified material converts back to a mixture over time: ^{1}H NMR (400 MHz, $CDCl_3$, rotamer A) □ 7.06-7.25 (m, 4H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H), 3.58-3.72 (m, 1H), 3.30 (sex, *J* = 7.0 Hz, 1H), 2.97 (sex, *J* = 7.0 Hz, 1H), 2.85 (sex, *J* = 6.7 Hz, 1H), 2.27 (s, 3H), 2.13 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.60 (t, *J* = 7.1 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$, rotamer B) □ 7.30-7.40 (m, 1H), 7.12-7.24 (m, 4H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 3.62 (sex, *J* = 6.6 Hz, 1H), 3.06 (sex, *J* = 7.0 Hz, 1H), 2.86 (sex, *J* = 6.6 Hz, 1H), 2.67 (sex, *J* = 7.0 Hz, 1H), 2.27 (s, 3H), 2.12 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.61 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rotamer A) □ 11.4, 13.6, 18.5, 20.1, 36.9, 42.2, 55.7, 110.6, 124.3, 125.4, 127.1, 127.5, 128.6, 129.7, 130.1, 135.8, 137.9, 138.3, 154.8, 168.7; ^{13}C NMR (100 MHz, $CDCl_3$, rotamer B) □ 11.5, 13.5, 18.6, 19.4, 37.0, 41.6, 55.5, 110.3, 125.3, 126.0, 126.2, 127.3, 128.9, 130.2, 131.3, 134.8, 136.6, 138.3, 154.7, 168.8; MS (ESI) *m/z* 312 (M^+ + H, 100); FTIR (KBr, cm^{-1}) 2967, 2935, 1620, 1473, 1460, 1291, 1251, 1060, 759; HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{20}H_{26}NO_2$ calcd 312.1958, found 312.1956.

***N,N*-Diethyl-5-methoxy-3-methyl-2'-methylbiphenyl-2-carboxamide (4e):**

According to general procedure **A**, TMEDA (2.2 equiv, 3.33 mmol, 500 µL), *s*-BuLi (2.2 equiv, 3.33 mmol, 3.4 mL, 0.97 M in cyclohexane) in 8 mL of THF, **3f** (1.0 equiv, 1.51 mmol, 450 mg) in THF (3 mL) were used. After a deprotonation time of 1 h, MeI (3.0 equiv, 4.50 mmol, 282 µL) was added all at once. Subsequent standard workup and flash column chromatography (hexanes:EtOAc, 2:1) gave the title compound as a colorless oil (360 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers ~ 1:1) δ 7.34-7.45 (m, 1H), 7.00-7.25 (m, 7H), 6.75 (d, *J* = 2.1 Hz, 2H), 6.64 (s, 1H), 6.55 (s, 1H), 3.80 (s, 6H), 3.63 (br s, 2H), 3.21 (br s, 1H), 3.05 (br s,

1H), 2.92 (br s, 1H), 2.84 (br s, 2H), 2.69 (br s, 1H), 2.32 (s, 6H), 2.26 (s, 3H), 2.18 (s, 3H), 0.98 (br s, 3H), 0.81 (br s, 3H), 0.68 (br s, 3H), 0.58 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 11.7, 13.6, 13.7, 19.7, 19.7, 20.3 (2C), 37.2, 37.4, 41.9, 42.3, 55.2 (2C), 112.2, 113.2, 114.6, 114.7, 124.3, 125.4, 127.5 (2C), 128.2, 129.8, 130.0, 131.0, 134.6, 134.6, 135.6, 135.6, 136.5, 137.7, 137.7, 138.7, 158.2, 158.3, 158.8, 158.9, 169.4 (2C); MS (EI, DIP) *m/z* 311 (M^+, 4), 296 (12), 239 (100), 196 (16), 165 (17); FTIR (KBr, cm^{-1}) 2971, 2837, 1632, 1462, 1380, 1327, 1284, 1206, 1164, 1050, 857 HRMS (EI-TOF) m/z: $[M]^+$ for $C_{20}H_{25}NO_2$ calcd 311.1885, found 311.1881.

***N,N*-Diethyl-4-methoxy-3-methyl-2'-methylbiphenyl-2-carboxamide (4f):**

According to general procedure **A**, TMEDA (2.2 equiv, 2.40 mmol, 360 µL), *s*-BuLi (2.2 equiv, 2.40 mmol, 2.0 mL, 1.20 M in cyclohexane) in 10 mL of THF, **3l** (1.0 equiv, 1.09 mmol, 325 mg) in THF (10 mL) were used. After a deprotonation time of 1 h, MeI (3.0 equiv, 3.28 mmol, 205 µL) was added all at once. Subsequent standard workup and flash column chromatography (CH_2Cl_2:Et_2O, 12:1) gave **4f** as a pale yellow oil that solidifies (303 mg, 89%): Mp 114-115 °C (*c*yclohexane); ^{1}H NMR (400 MHz, DMSO-d_6, 70 ^{o}C) δ 7.06-7.23 (m, 4H), 6.95-7.05 (m, 2H), 3.86 (s, 3H), 3.45 (sex, *J* = 6.6 Hz, 1H), 3.05 (sex, *J* = 6.5 Hz, 1H), 2.91 (sex, *J* = 6.6 Hz, 1H), 2.77 (sex, *J* = 6.5 Hz, 1H), 2.12 (br s, 3H), 2.09 (s, 3H), 0.85 (br s, 3H), 0.62 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 70 ^{o}C) δ 12.1, 13.3, 13.8, 20.5, 37.4, 42.2, 56.2, 110.5, 122.4, 125.2, 127.6, 128.8, 130.1, 130.4, 136.7, 138.5, 139.8, 157.1, 168.5; MS (EI, DIP) *m/z* 311 (M^+, 20), 297 (24), 263 (19), 239 (48), 219 (100, 131 (29); FTIR (KBr, cm^{-1}) 2973, 2836, 1631, 1468, 1379, 1286, 1222, 1139, 1087; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{20}H_{25}NO_2$ calcd 311.1885, found 311.1884.

***N,N*,3-Triethyl-5-methoxy-2'-methylbiphenyl-2-carboxamide (4g):**

According to general procedure **A**, a solution of **3f** (1.0 equiv, 4.02 mmol, 1.19 g) in THF (10 mL) was slowly added to a mixture of TMEDA (1.2 equiv, 4.82 mmol, 0.72 mL) and s-BuLi (1.2 equiv, 4.82 mmol, 3.92 mL) in THF (10 mL) while the temperature was kept below -74 °C. After 1 h deprotonation time MeI (4.8 equiv, 19.3 mmol, 1.20 mL) was slowly added. After approx. 0.4 mL of MeI was added, due to a fire alarm the reaction mixture was left at -78 °C for 30 min. before addition of MeI to the now blood red mixture was continued. After standard workup the product was fractionated by flash chromatography (heptane:EtOAc, 2:1) into **4g** (254 mg, colorless oil), a mixture of **4g** and **4e** (377 mg) and a mixture of **4e** and **3f** (346 mg). From integrations of the relative ^{1}H-NMR spectra this corresponded to 34% **4g**, 24% **4e** and 20% starting material (**3f**): ^{1}H-NMR (400 MHz, $CDCl_3$, mixture of two rotamers, ~1:1 ratio**)** δ 7.41 (d, *J* = 6.9 Hz, 1H), 7.02-7.24 (m, 7H), 6.76-6.86 (m, 2H), 6.64 (s, 1H), 6.54 (s, 1H), 3.79 (s, 6H), 3.52-3.72 (m, 1H), 3.12-3.26 (m, 1H), 2.98-3.12 (m, 1H), 2.86-2.98 (m, 1H), 2.76-2.86 (m, 2H), 2.50-2.76 (m, 5H), 2.26 (s, 3H), 2.17 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 6H), 0.94 (t, *J* = 6.4 Hz, 3H). 0.78 (t, *J* = 6.6 Hz, 3H), 0.66 (t, *J* = 6.7 Hz, 3H), 0.53 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2, 11.5, 13.4, 13.6, 14.8, 14.9, 20.2 (2C), 26.0, 26.3, 37.0, 37.3, 41.9, 42.2, 55.1 (2C), 111.8, 112.6, 113.0 (2C), 124.2, 125.3, 127.4 (2C), 128.2, 128.7, 129.1, 129.7, 130.0, 130.9, 134.6, 137.6, 138.4, 138.7, 140.0, 141.7, 142.7, 158.4, 159.0, 169.1, 169.3; MS (EI, DIP) *m/z* 325 (M^+, 6), 296 (16), 253 (100); FTIR (KBr, cm^{-1}) 2968, 2934, 1627, 1597, 1456, 1423, 1285, 1205, 1163, 1035; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{27}NO_2$ calcd 325.2042, found 325.2031.

8-Methylphenanthren-9-ol (5b):

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 2.37 mL, 16.9 mmol, 2.75 equiv; *n*-BuLi, 2.04 M, 7.52 mL, 15.3 mmol, 2.5 equiv) in THF (50 mL) and **4a** (1.73g, 6.14 mmol, 1.0 equiv) in THF (15 mL). The reaction was stirred at 0 ^{o}C for 1.5 h and after a standard workup, the residual solids was purified by flash chromatography using heptane/ethyl acetate (4/1 to 3/1 gradient) to give 5b as a tan solid (1.1343 g, 89%) that darkened rapidly when wet. *Due to rapid decomposition, no clean ^{1}H NMR nor a melting point could be obtained. Additionally, the Ms indicated the oxidized 9,10-phenanthraquinone as the major component as described below*: ^{1}H-NMR (400 MHz, acetone-d_6) δ 9.11 (br s, 1H), 8.69 (d, J = 6.4 Hz, 1H), 8.67 (d, J = 6.4 Hz, 1H), 7.69 (dd, J = 1.4, 7.9 Hz, 1H), 7.41-7.59 (m, 4H), 7.15 (s, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 24.7, 106.4, 121.0, 123.0, 123.5, 125.9, 126.6, 126.8, 129.9, 133.1, 136.0, 153.8; MS (EI, DIP) oxidized diquinone *m/z* 245 ($[M + Na]^+$, 100), 223 (8); FTIR (KBr, cm^{-1}) 3412, 1671, 1591, 1454, 1224, 760; HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{15}H_{13}O$ calcd 209.0961, found 209.0958.

***N*,*N*-Diethyl-1-methylphenanthren-9-yl diethylcarbamate (6a):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 2.08 mL, 14.8 mmol, 2.75 equiv; *n*-BuLi, 2.04 M, 6.62 mL, 13.5 mmol, 2.5 equiv) in THF (45 mL) and **3b** (1.52 g, 5.40 mmol, 1.0 equiv) in THF (15 mL). The reaction was stirred at 0 ^{o}C for 1 h, followed by a standard workup to yield 1.17 g of residue. The residue (1.15 g) was subjected directly to a carbamoylation reaction, by dissolving the residue in THF (25 mL) and after cooling to 0 ^{o}C, NaH (60%, 0.331g, 8.28 mmol, 1.5 equiv) was added. After stirring for 15 mins, diethylcarbamoyl chloride (1.40 mL, 11.0 mmol, 2.0 equiv) was added in one portion and the

reaction mixture stirred overnight at room temperature. After quenching with sat. aq. NH_4Cl (30 mL) and diethylether extraction (3 x 30 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography using heptane/ethyl acetate (4/1 to 2.5/1, gradient) as eluent. The title compound was obtained as a colorless solid (1.36 g, 82%): Mp 99-100 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* =8.1 Hz, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.76 (s, 1H), 7.59-7.61 (m, 2H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 3.68 (q, *J* = 7.0 Hz, 2H), 3.50 (q, *J* = 7.0 Hz, 2H), 2.74 (s, 3H), 1.44 (t, *J* = 6.9 Hz, 3H), 1.29 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.5, 20.0, 42.0, 42.3, 114.1, 120.7, 121.9, 123.2, 125.7, 126.6, 126.9, 127.0, 128.0, 128.8, 130.8, 131.9, 134.6, 145.6, 154.3; MS (EI, DIP) *m/z* 307 (M^+, 59), 189 (8), 179 (51), 178 (58), 100 (100); FTIR (KBr, cm^{-1}) 1717; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{20}H_{21}NO_2$ calcd 307.1572, found 307.1562.

7-Methoxy-8-methylphenanthren-9-yl trifluoromethanesulfonate (6b):

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 694 µL, 4.95 mmol, 2.75 equiv; *n*-BuLi, 1.1 M, 4.09 mL, 4.5 mmol, 2.5 equiv) in THF (20 mL) and **4f** (560 mg, 1.80 mmol, 1.0 equiv) in THF (7 mL). The reaction was stirred at -20 ^{o}C for 15 min and then room temperature for another hour. After a standard workup, the residual colorless solid was directly used for next step without further purification. The residue was dissolved in CH_2Cl_2 (30 mL) and cooled to 0 ^{o}C. The solution is treated with pyridine (218 µL, 2.70 mmol, 1.50 equiv) and triflic anhydride (454 µL, 2.70 mmol, 1.50 equiv). The solution was warmed to room temperature overnight, added water (40 mL) and extracted with CH_2Cl_2 (2 x 25 mL). The organic phases was combined, dried ($MgSO_4$) and evaporated to dryness. The residue was purified via column chromatography using heptane/ethyl acetate (5/1) eluent to afford the desired

product as an amorphous brown solid (363 mg, 55%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.57 (t, *J* = 9.6 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.72 (s, 1H), 7.60-7.70 (m, 1H), 7.50-7.60 (m, 1H), 7.39 (d, *J* = 9.2 Hz, 1H), 3.99 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 56.3, 113.0, 116.5, 120.0, 120.7, 122.1, 122.4, 126.0, 126.6, 127.1, 127.9, 128.5, 129.0, 130.3, 144.6, 157.1; MS (EI, DIP) *m/z* 370 (M^+, 10), 237 (100); FTIR (KBr, cm^{-1}) 2955, 2845, 1595, 1421, 1279, 1213, 1164, 1026, 818; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{17}H_{13}F_3O_4S_1$ calcd 370.0486, found 370.0465.

***N*,*N*-Diethyl-6-methoxy-8-methylphenanthren-9-yl diethylcarbamate (6c):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 240 µL, 1.72 mmol, 2.2 equiv; *n*-BuLi, 2.15 M, 800 µL, 1.72 mmol, 2.2 equiv) in THF (22 mL) and **4e** (243 mg, 0.78 mmol, 1.0 equiv) in THF (5 mL). The reaction was stirred at 0 ^{o}C for 1 h and after a standard workup, the residue is subjected directly to a carbamoylation reaction, by dissolving the residue in THF (10 mL) and after cooling to 0 ^{o}C, NaH (60%, 47 mg, 1.17 mmol, 1.5 equiv) was added. After stirring for 30 mins, diethylcarbamoyl chloride (150 µL, 1.17 mmol, 1.5 equiv) was added in one portion and the reaction mixture stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (2 x 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2) .The title compound was obtained as a brown solid (115 mg, 44%): Mp 112-114 °C (*c*yclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52-8.59 (m, 1H), 7.99 (d, *J* = 2.3 Hz, 1H), 7.75-7.81 (m, 1H), 7.51-7.60 (m, 2H), 7.26 (s, 1H), 7.05 (d, *J* = 1.7 Hz, 1H), 4.00 (s, 3H), 3.60 (q, *J* = 7.1 Hz, 2H), 3.47 (q, *J* = 7.1 Hz, 2H), 2.81 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.3, 23.7, 41.7, 42.0, 55.2, 102.5, 116.9, 120.4, 121.6, 123.0, 125.6, 126.8,

127.8, 128.8, 132.0, 134.6, 135.7, 147.2, 154.8, 157.8; MS (EI, DIP) *m/z* 337 (M^+, 71), 284 (10), 219 (35), 165 (12), 100 (100), 72 (22); FTIR (KBr, cm^{-1}) 2972, 2935, 1716, 1609, 1465, 1419, 1377, 1262, 1219, 1155, 1051; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{23}NO_3$ calcd 337.1678, found 337.1677.

***N*,*N*-Diethyl-5-methoxy-8-methylphenanthren-9-yl diethylcarbamate (6d):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 353 µL, 2.51 mmol, 2.2 equiv; *n*-BuLi, 2.27 M, 1.10 mL, 2.51 mmol, 2.2 equiv) in THF (30 mL) and **4d** (355 mg, 1.14 mmol, 1.0 equiv) in THF (7 mL). The reaction was stirred at 0 ^oC for 1 h and after a standard workup, the residue is subjected directly to a carbamoylation reaction, by dissolving the residue in THF (15 mL) and after cooling to 0 ^oC, NaH (60%, 55 mg, 1.37 mmol, 1.2 equiv) was added. After stirring for 15 mins, diethylcarbamoyl chloride (174 µL, 1.37 mmol, 1.2 equiv) was added in one portion and the reaction mixture stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (3 x 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2+5% Et_2O gradient) .The title compound was obtained as a brown oil (200 mg, 52%): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 1.8, 7.1 Hz, 1H), 7.50-7.64 (m, 2H), 7.42 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 4.07 (s, 3H), 3.60 (q, *J* = 7.1 Hz, 2H), 3.48 (q, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.3, 23.6, 41.6, 42.0, 55.8, 108.8, 120.5, 123.5, 125.4, 125.7, 126.0, 127.3, 128.7, 128.8, 129.1, 130.4, 131.8, 146.7, 154.7, 157.3; MS (EI, DIP) *m/z* 337 (M^+, 19), 264 (29), 219 (100), 166 (5), 131 (36), 100 (33); FTIR (KBr, cm^{-1}) 2971, 2873, 1713,

1632, 1453, 1384, 1267, 1157, 1072, 1049, 959; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{23}NO_3$ calcd 337.1678, found 337.1670.

***N*,*N*-Diethyl-5-methoxy-1-methylphenanthren-9-yl diethylcarbamate (6e):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 900 µL, 6.40 mmol, 2.5 equiv; *n*-BuLi, 1.92 M, 3.32 mL, 6.40 mmol, 2.5 equiv) in THF (8 mL) and **3d** (800 mg, 2.57 mmol, 1.0 equiv) in THF (8 mL). The reaction was stirred at 0 ^oC for 1 h and after a standard workup, the residue is subjected directly to a carbamoylation reaction, by dissolving the residue in THF (4 mL) and after cooling to 0 ^oC, NaH (60%, 120 mg, 2.99 mmol, 1.2 equiv) was added. After stirring for 15 mins, diethylcarbamoyl chloride (360 µL, 2.83 mmol, 1.1 equiv) was added in one portion and the reaction mixture stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (3 x 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2+5% Et_2O gradient) .The title compound was obtained as a colorless solid (1.08 g, 77%): Mp 129-130 °C (*c*yclohexane); ^1H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 8.6 Hz, 1H), 7.80 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.51 (dd, J = 7.1, 8.6 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 4.12 (s, 3H), 3.67 (q, J = 7.0 Hz, 2H), 3.49 (q, J = 7.0 Hz, 2H), 2.75 (s, 3H), 1.43 (t, J = 6.9 Hz, 3H), 1.29 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.5, 20.5, 42.0, 42.3, 55.8, 109.0, 114.3, 115.0, 122.5, 125.4, 126.6, 126.7, 127.4, 128.9, 129.5, 130.9, 133.7, 145.2, 154.4, 158.9; MS (EI, DIP) *m/z* 337 (M^+, 48), 285 (13), 264 (20), 219 (100), 131 (26), 100 (62); FTIR (KBr, cm^{-1}) 2972, 2935, 1716, 1575, 1455, 1291, 1267, 1151, 1049, 1025, 746; HRMS (EI-TOF) m/z: $[M]^+$for $C_{21}H_{23}NO_3$ calcd 337.1678, found 337.1686.

5-Methoxy-1-methylphenanthren-9-yl trifluoromethanesulfonate (6f):

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 316 µL, 2.4 mmol, 2.4 equiv; *n*-BuLi, 2.17 M, 1.03 mL, 2.2 mmol, 2.2 equiv) in THF (30 mL) and **3d** (311 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL). The reaction was stirred at 0 ^{o}C overnight and after a standard workup, the residual colorless solid is directly used for next step without further purification. The residue is dissolved in CH_2Cl_2 (10 mL) and cooled to 0 ^{o}C. The solution is treated with pyridine (100 µL, 1.24 mmol, 1.24 equiv) and triflic anhydride (200 µL, 1.19 mmol, 1.19 equiv). The solution was warmed to room temperature overnight, and evaporated to dryness. The residue was purified via column chromatography using pentane/DCM (7/1) eluent to afford the desired product as a colorless solid (340 mg, 92%). The compound was converted without further purification to **7e**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.55 (d, J = 8.7 Hz, 1H), 8.07 (s, 1H), 7.83 (t, J = 8.1 Hz, 1H), 7.63-7.72 (m, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 4.15 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.6, 57.2, 111.9, 113.7, 116.3, 122.5, 127.3, 127.4, 128.7, 129.3, 129.7, 130.2, 135.8, 144.4, 159.4.

***N*,*N*-Diethyl-6-methoxy-1-methylphenanthren-9-yl diethylcarbamate (6g):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 350 µL, 2.0 mmol, 2.5 equiv; *n*-BuLi, 1.92 M, 1.30 mL, 2.50 mmol, 2.5 equiv) in THF (4 mL) and **3d** (312 mg, 1.00 mmol, 1.0 equiv) in THF (4 mL). The reaction was stirred at 0 ^{o}C for 1 h and after a standard workup, the residue is subjected directly to a carbamoylation reaction, by dissolving the residue in THF (6 mL) and after cooling to 0 ^{o}C, NaH (60%, 60 mg, 1.5 mmol, 1.5 equiv) was added. After stirring for 15 mins, diethylcarbamoyl chloride (190 µL, 1.5 mmol, 1.5 equiv) was added in one portion and the reaction mixture stirred overnight at room temperature.

After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (3 x 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2+5% Et_2O gradient) .The title compound was obtained as a colorless solid (252 mg, 77%): Mp 130-131.5 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 2.2 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.27 (dd, *J* = 2.3, 9.0 Hz, 1H), 4.02 (s, 3H), 3.66 (q, *J* = 6.8 Hz, 2H), 3.49 (q, *J* = 6.9 Hz, 2H), 2.72 (s, 3H), 1.42 (t, *J* = 6.7 Hz, 3H), 1.29 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.5, 20.0, 42.0, 42.3, 55.4, 104.5, 111.7, 116.9, 120.7, 121.7, 123.5, 125.2, 128.0, 128.2, 131.4, 133.5, 134.7, 145.7, 154.3, 158.7; MS (EI, DIP) *m/z* 337 (M^+, 33), 209 (41), 166 (42), 100 (100), 72 (42); FTIR (KBr, cm^{-1}) 2976, 1713, 1617, 1459, 1381, 1265, 1235, 1157; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{23}NO_3$ calcd 337.1678, found: 337.1678.

***N*,*N*-Diethyl-7-methoxy-1-methylphenanthren-9-yl diethylcarbamate (6h):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 3.00 mL, 21.5 mmol, 2.75 equiv; *n*-BuLi, 2.04 M, 9.57 mL, 19.5 mmol, 2.5 equiv) in THF (60 mL) and **3k** (2.43 g, 7.81 mmol, 1.0 equiv) in THF (15 mL). The reaction was stirred at -20 ^{o}C for 15 min and then room temperature for another hour. After a standard workup, the colorless residue was subjected directly to a carbamoylation reaction, by dissolving the residue in THF (40 mL) and after cooling to 0 ^{o}C, NaH (60%, 468 mg, 11.7 mmol, 1.5 equiv) was added. After stirring for 15 mins, diethylcarbamoyl chloride (2.00 mL, 15.7 mmol, 2.0 equiv) was added in one portion and the reaction mixture stirred overnight at room temperature. After quenching with sat. aq. NH_4Cl (50 mL) and diethylether extraction (3 x 50 mL), then dried ($MgSO_4$) and evaporated, residue was subjected to column chromatography using heptane/ethyl acetate (3/1) as

eluent. The title compound was obtained as a colorless solid (2.42 g, 92%): Mp 112.5-113.5 °C (hexanes / DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 9.1 Hz, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 7.78 (s, 1H), 7.49 (t, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.31 (dd, *J* = 9.1, 2.7 Hz, 1H), 3.95 (s, 3H), 3.67 (br s, 2H), 3.51 (br s, 2H), 2.73 (s, 3H), 1.44 (br s, 3H), 1.31 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.5, 19.9, 42.0, 42.3, 55.2, 102.3, 114.6, 117.2, 120.2, 125.0, 125.7, 126.3, 127.0, 128.3, 128.8, 129.6, 134.6, 145.0, 154.2, 158.3; MS (EI, DIP) *m/z* 337 (M^+, 58), 237 (8), 209 (29), 166 (42), 100 (100), 72 (36); FTIR (KBr, cm^{-1}) 2986, 1703, 1275, 1155, 865, 793; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{23}NO_3$ calcd 337.1678, found 337.1664.

***N*,*N*-Diethyl-8-methoxy-1-methylphenanthren-9-yl diethylcarbamate (6i):**

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 2.54 mL, 18.1 mmol, 2.75 equiv; *s*-BuLi, 1.16 M, 14.2 mL, 16.5 mmol, 2.5 equiv) in THF (55 mL) and **3c** (2.05 g, 6.58 mmol, 1.0 equiv) in THF (20 mL). The reaction was stirred at -20 °C for 15 min and then room temperature for another hour. Standard workup yielded 1.60 g of residue. A part of the residue (0.98 g, 4.11 mmol, 1.0 equiv) was subjected directly to a carbamoylation reaction, by dissolving the residue in THF (50 mL) and after cooling to 0 °C, NaH (60%, 0.23g, 5.76 mmol, 1.4 equiv) was added. After stirring for 15 mins, diethylcarbamoyl chloride (0.83 mL, 6.55 mmol, 1.6 equiv) was added in one portion and the reaction mixture stirred overnight at room temperature. After quenching with sat. aq. NH_4Cl (50 mL) and diethyleter extraction (3 x 50 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography using heptane/ethyl acetate (3/1 to 2/1, gradient) as eluent. The title compound was obtained as a colorless solid (1.13 g, 81%): Mp 166-167 °C (hexanes / DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.51 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.57 (s, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.02 (d, *J* = 7.0 Hz, 1H), 3.93 (s, 3H), 3.61 (br s, 2H), 3.48 (br s, 2H), 2.72 (s, 3H), 1.39 (br s, 3H), 1.28 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.1, 19.7, 41.7, 41.9, 55.7, 107.4, 115.5, 115.9, 118.2, 121.4, 125.6, 127.0, 128.0, 128.7, 131.0, 134.1, 134.3, 145.4, 155.2, 156.2; MS (EI, DIP) *m/z* 337 (M^+, 85), 179 (27), 178 (31), 165 (23), 100 (100); FTIR (KBr, cm^{-1}) 1713; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{21}H_{23}NO_3$ calcd 337.1678, found 337.1686.

2-Methoxy-1-methylphenanthrene (7b):

The title compound was synthesized according to general procedure **G** using **6b** (358 mg, 0.967 mmol, 1.00 equiv), Et_3N (410 µL, 2.90 mmol, 3.0 equiv), HCO_2H (80 µL, 2.1 mmol, 2.2 equiv), $PdOAc_2$ (11.2 mg, 0.050 mmol, 5 mol%) and PPh_3 (26.3 mg, 0.100 mmol, 10 mol%) in DMF (15 mL). After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (10/1 to 5/1 gradient) to afford the title compound as a colorless solid (157 mg, 73%). Further recrystallization from heptane afforded colorless crystals (103 mg, 48%): Mp 161.5-162.2 °C (heptane, lit. 160.5-161 °C [ethanol][59]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.57 (d, *J* = 9.1 Hz, 1H), 7.95 (d, *J* = 9.2 Hz, 1H), 7.87 (dd, *J* = 1.3, 7.8 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.60-7.70 (m, 1H), 7.50-7.60 (m, 1H), 7.34 (d, *J* = 9.1 Hz, 1H), 3.99 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 56.3, 111.8, 120.8, 121.5, 122.3, 122.7, 124.6, 125.6, 126.6, 127.2, 128.4, 130.6, 130.8, 132.0, 155.5; MS (EI, DIP) *m/z* 245 ($[M+Na]^+$, 15), 217 (8), 157 (8), 125 (10); FTIR (KBr, cm^{-1}) 2941, 1607, 1467, 1271, 1208, 1097, 809, 743; HRMS (ESI-TOF) m/z: $[M+Na]^+$ for $C_{16}H_{14}ONa$ calcd 245.0942, found 245.0941.

3-Methoxy-1-methylphenanthrene (7c):

The title compound was synthesized according to general procedure **H** using **6c** (120 mg, 0.36 mmol, 1.0 equiv), $Ni(acac)_2$ (10 mg, 0.04 mmol, 10 mol%), *i*-PrMgCl*LiCl (1.0 M in THF, 1.6 mL, 1.60 mmol, 4.5 equiv) in Et_2O (7 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (8/1) to afford the title compound as a colorless solid (59 mg, 75%). The product is contaminated with approximately 20% of impurities that could not be removed neither via column chromatography nor via recrystallization: Mp 70-71 °C (DCM / hexanes, lit. 90 °C [alcohol][60]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 2.1 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.58-7.73 (m, 3H), 7.13 (br s, 1H), 4.02 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.3, 101.8, 118.0, 122.6, 122.9, 124.2, 126.0, 126.4, 128.5, 130.1, 131.8, 132.1, 136.7, 157.8; MS (EI, DIP) *m/z* 222 (M^+, 83), 219 (100), 207 (10), 179 (29), 131 (20); FTIR (KBr, cm^{-1}) 2957, 1611, 1463, 1263, 1209, 1054, 862, 811; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{16}H_{14}O$ calcd 222.1045, found 222.1047.

4-Methoxy-1-methylphenanthrene (7d):

The title compound was synthesized according to general procedure **H** using **6d** (190 mg, 0.56 mmol, 1.0 equiv), $Ni(acac)_2$ (15 mg, 0.058 mmol, 10 mol%), *i*-PrMgCl*LiCl (0.6 M in THF, 2.35 mL, 1.41 mmol, 2.5 equiv) in Et_2O (12 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (10/1) to afford the title compound as a colorless solid (110 mg, 88%). The product is contaminated with approximately 24% of impurities that could not be removed via column chromatography:^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 8.6 Hz, 1H), 7.92-7.98 (m, 2H), 7.84 (d, J = 9.1 Hz, 1H), 7.61-7.73 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 4.13 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9,

55.7, 107.9, 123.0, 125.3, 125.8, 126.3, 126.7, 127.6, 127.8, 128.1, 128.8, 130.6, 132.4, 132.8, 157.4; MS (EI, DIP) *m/z* 222 (M^+, 99), 207 (55), 179 (43), 100 (23), 86 (68), 84 (100); FTIR (KBr, cm^{-1}) 2932, 1573, 1449, 1244, 1204, 1100, 821; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{16}H_{14}O$ calcd 222.1045, found 222.1051.

5-Methoxy-1-methylphenanthrene (7e):

The title compound was synthesized according to general procedure **G** using **6f** (290 mg, 0.78 mmol, 1.0 equiv), Et_3N (330 µL, 2.35 mmol, 3.0 equiv), HCO_2H (60 µL, 1.59 mmol, 2.0 equiv), $PdOAc_2$ (3.5 mg, 0.016 mmol, 2 mol%) and PPh_3 (8.2 mg, 0.031 mmol, 4 mol%) in DMF (8 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (1/0 to 20/1 gradient) to afford the title compound as a colorless solid (130 mg, 75%): Mp 72-74 °C (Et_2O, lit. 76-77 °C [alcohol][61]); ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 9.1 Hz, 1H), 7.79 (d, J = 9.1 Hz, 1H), 7.53-7.63 (m, 3H), 7.50 (d, J = 7.1 Hz, 1H), 7.18 (dd, J = 2.7, 6.3 Hz, 1H), 4.15 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 55.7, 108.4, 121.2, 121.5, 123.5, 125.8, 126.4, 126.8, 126.9, 127.3, 130.4, 131.3, 133.9, 134.3, 158.8; MS (EI, DIP) *m/z* 222 (M^+, 81), 219 (100), 207 (28), 131 (25), 88 (37), 70 (43); FTIR (KBr, cm^{-1}) 3053, 2927, 1574, 1453, 1265, 1105, 1053, 824; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{16}H_{14}O$ calcd 222.1045, found 222.1041.

6-Methoxy-1-methylphenanthrene (7f):

The title compound was synthesized according to general procedure **H** using **6g** (160 mg, 0.47 mmol, 1.0 equiv), $Ni(acac)_2$ (14 mg, 0.054 mmol, 11 mol%), *i*-PrMgCl*LiCl (1.0 M in THF, 1.2 mL, 1.18 mmol, 2.5 equiv) in Et_2O (12 mL). After standard workup, the residue was purified via

column chromatography using pentane/CH_2Cl_2 (6/1) to afford the title compound as a colorless solid (88 mg, 83%). The product is contaminated with approximately 16% of impurities that could not be removed neither via column chromatography nor via recrystallization: Mp 77-80 °C (*c*yclohexane, lit. 84-85 °C [methanol][62]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 2.3 Hz, 1H), 7.68 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 3.3 Hz, 1H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.35-7.41 (m, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.10 (dd, *J* = 2.5, 8.7 Hz, 1H), 3.87 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 55.4, 104.1, 116.7, 120.4, 120.8, 125.6, 126.3, 126.4, 127.7, 129.7, 129.9, 131.1, 131.9, 134.8, 158.4; MS (EI, DIP) *m/z* 222 (M^+, 100), 219 (15), 207 (30), 179 (35), 88 (37); FTIR (KBr, cm^{-1}) 2956, 1616, 1601, 1462, 1231, 1170, 1035, 831; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{16}H_{14}O$ calcd 222.1045, found 222.1036.

7-Methoxy-1-methylphenanthrene (7g):

The title compound was synthesized according to general procedure **H** using **6h** (2.20 g, 6.52 mmol, 1.0 equiv), $Ni(acac)_2$ (168 mg, 0.654 mmol, 10 mol%), *i*-PrMgCl*LiCl (0.97 M in THF, 16.8 mL, 16.3 mmol, 2.5 equiv) in Et_2O (90 mL). After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (9/1) to afford the title compound as a colorless solid (1.14 g, 79%). Further recrystallization from cyclohexane afforded colorless crystals (845 mg, 58%): Mp 136 °C (cyclohexane, lit. 134-135 °C[methanol][63]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.9 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.24-7.33 (m, 2H), 3.98 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.4, 108.3, 117.2, 120.4, 123.4, 124.6, 125.0, 126.2, 126.2, 126.8, 129.8, 130.5, 133.0, 134.8, 158.1; MS (EI, DIP) *m/z* 222 (M^+, 100),

207 (11), 179 (53), 178 (26), 152 (7); FTIR (KBr, cm^{-1}) 2949, 1599, 1270, 1174, 1031, 854, 795; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{16}H_{14}O$ calcd 222.1045, found 222.1035.

1-Methoxy-8-methylphenanthrene (7h):

The title compound was synthesized according to general procedure **H** using **6i** (1.28 g, 3.79 mmol, 1.0 equiv), $Ni(acac)_2$ (97.5 mg, 0.38 mmol, 10 mol%), *i*-PrMgCl*LiCl (0.97 M in THF, 8.5 mL, 8.2 mmol, 2.2 equiv) in Et_2O (70 mL). The reaction is left stirring overnight. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (9/1) to afford the title compound as a colorless solid (563 mg, 67%). Further recrystallization from cyclohexane afforded colorless crystals (385 mg, 46%): Mp 123-124 °C (cyclohexane, lit. 119.8-121 °C [water/methanol][64]); ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.3 Hz, 1H), 8.29 (t, J = 7.9 Hz, 2H), 7.96 (d, J = 9.5 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 8.3 Hz, 1H), 7.45 (d, J = 7.0 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 4.05 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.7, 105.5, 115.3, 120.1, 121.4, 122.0, 122.9, 126.0, 126.6, 127.7, 130.0, 131.0, 131.8, 134.8, 155.9; MS (EI, DIP) *m/z* 222 (M^+, 100), 207 (43), 179 (60), 152 (13); FTIR (KBr, cm^{-1}) 2964, 1599, 1263, 1248, 765; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{16}H_{14}O$ Calcd 222.1045, found 222.1051.

1-Fluoro-4-methyl-5-methoxyfluorenone (8):

The title compound was synthesized according general procedure **B** from prepared LDA (DIPA, 185 µL, 1.30 mmol, 1.2 equiv; *n*-BuLi, 2.33 M, 555 µL, 1.30 mmol, 1.2 equiv) in THF (2.5 mL) and **3j** (340 mg, 1.08 mmol, 1.0 equiv) in THF (2.5 mL). The reaction was stirred at 0 °C for 1 h and after a standard workup, the residue was subjected to column chromatography

(pentane:CH_2Cl_2, 1:1) .The title compound was obtained as a bright yellow solid (207 mg, 97%): Mp 164-167 °C (Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 1.0, 7.1 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.16-7.24 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 55.3, 116.5 (d, J_F = 20.4 Hz), 116.8, 118.7, 130.6, 131.0, 136.4, 140.8, 140.9, 143.8, 154.2, 156.9, 159.5, 190.7; MS (EI, DIP) *m/z* 242 (M^+, 100), 227 (38), 170 (16); FTIR (KBr, cm^{-1}) 2935, 1712, 1616, 1591, 1441, 1273, 1187, 1063; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{15}H_{11}FO_2$ calcd 242.0743, found 242.0746.

8-Methylphenanthren-1-ol (9a):

The title compound was synthesized according to general procedure **I** with **7h** (222 mg, 1.0 mmol, 1.0 equiv) and BBr_3 (1M in CH_2Cl_2, 2.0 mL, 2.0 mmol, 2.0 equiv) in CH_2Cl_2 (70 mL). After standard workup, the residue was purified via column chromatography using CH_2Cl_2 to afford the title compound as a colorless solid (118 mg, 57%): Mp >165 °C, dec. (DCM, lit. 171-172 °C [?][65]); ^{1}H NMR (400 MHz, d_6-acetone) δ 9.08 (s, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.29 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 9.4 Hz, 1H), 7.43-7.57. (m, 3H), 7.10 (d, *J* = 7.6 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, d_6-acetone) δ 20.9, 111.9, 116.1, 122.3, 123.1, 123.2, 123.8, 127.9, 128.9, 129.5, 132.1, 132.8, 134.0, 136.5, 155.6; MS (EI, DIP) *m/z* 208 (M^+, 100), 179 (25), 165 (52), 152 (13); FTIR (KBr, cm^{-1}) 3260, 2360, 1600, 1453, 1293, 1246, 767; HRMS (EI-TOF) m/z: $[M]^+$ for $C_{15}H_{12}O$ calcd 208.0888, found 208.0879.

8-Methylphenanthren-2-ol (9b):

The title compound was synthesized according to general procedure **I** with **7g** (100 mg, 0.45 mmol, 1.0 equiv) and BBr_3 (1M in CH_2Cl_2, 0.92 mL, 0.92 mmol, 2.05 equiv) in CH_2Cl_2 (35 mL).

After standard workup, the residue was purified via trituration with hexanes to afford the title compound as a colorless solid (96 mg, 94%): Mp 187-189 °C, melt/dec. (hexanes, lit. 187-188 °C [petroleum][66]); ^{1}H NMR (400 MHz, d_6-acetone) δ 8.75 (s, 1H), 8.65 (d, *J* = 8.9 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.28 (dd, *J* = 2.6, 8.9 Hz, 1H), 2.70 (s, 3H) ^{13}C-NMR (100 MHz, d_6-acetone) δ 20.9, 113.0, 119.2, 122.1, 125.0, 126.1, 126.6, 127.8, 128.1, 128.4, 131.4, 132.6, 135.3, 136.5, 158.0; MS (EI, DIP) *m/z* 208 (M^+, 100), 178 (12), 152 (9); FTIR (KBr, cm^{-1}) 3369, 1617, 1468, 1259, 955, 865 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ for $C_{15}H_{12}O$ calcd 208.0888, found 208.0876.

8-Methylphenanthren-3-ol (9c):

The title compound was synthesized according to general procedure **I** with **7f** (70 mg, 0.31 mmol, 1.0 equiv) and BBr_3 (1M in CH_2Cl_2, 0.66 mL, 0.92 mmol, 2.1 equiv) in CH_2Cl_2 (10 mL). After standard workup, the residue was purified via column chromatography using CH_2Cl_2 to afford the title compound as a colorless solid (57 mg, 87%). The product is contaminated with approx. 15% cross-coupled compound carried over from **7f** that could not be removed via column chromatography: ^{1}H-NMR (400 MHz, d_6-acetone) δ 9.77 (d, *J* = 8.5 Hz, 1H), 8.82 (s, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.19 (d, *J* = 2.2 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.77-7.85 (m, 2H), 7.46-7.58 (m, 2H), 7.28 (dd, *J* = 2.3, 8.6 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, d_6-acetone)**:** δ = 21.0, 108.5, 119.0, 121.5, 122.8, 127.5, 127.6, 128.4, 129.6, 131.5, 131.9, 133.0, 134.2, 136.4, 158.4; MS (EI, DIP) *m/z* 208 (M^+, 100), 178 (11), 152 (8); HRMS (EI-TOF) m/z: $[M]^+$ for $C_{15}H_{12}O$ calcd 208.0888, found 208.0887.

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Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds are provided in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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