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Synthesis of Phenacene–Helicene Hybrids by Directed Remote Metalation

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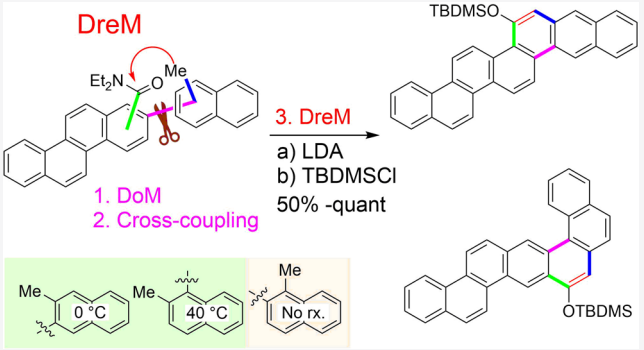
ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) with six and seven rings were synthesized *via* directed metalation and cross-coupling of chrysenyl *N*,*N*-diethyl carboxamides with *o*-tolyl and methylnaphthalenyl derivatives. In the presence of competing *ortho* sites, the site selectivity in iodination of chrysenyl amides by directed *ortho* metalation (DoM) was influenced by the lithium base. The catalyst ligand bite angle was presumably important in the cross-coupling of sterically hindered bulky PAHs. Subsequent directed remote metalation of biaryls under standard conditions and at elevated temperatures afforded various fused six- and seven-ring PAHs, all in good yields and with fluorescent properties.



1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) with extended π-conjugation find their applications in catalysis,[1,2] nonlinear optics,[3] circularly polarized luminescence,[4] organic electronic materials,[5] and optoelectronic devices.[6−9] PAHs are used as the synthetic building blocks for carbon-rich materials such as fullerenes, nanographenes, and nanotubes.[10,11] The intriguing photophysical properties of spiral PAHs have led to development of methods for the synthesis of novel, helically twisted PAHs[12] and C_3-symmetric spiro-annulated molecules.[13] The discovery of superconductivity in metal-doped PAHs[14] and an increasing variety of material properties in PAH adducts[15,16] has revived the purpose of preparing large or small PAHs which are/are not sterically congested. The material properties of PAHs are often controlled by frontier molecular orbitals that are influenced by the modes of ring fusion, geometry, dopant,[17] and functionalities in their periphery.[18−21] Synthesis of the aromatic core in nonlinear and nonplanar directions may lead to interesting new packing arrangements and different electronic properties.[22,23] Therefore, exploration of new approaches to synthesize these organic molecules in high purity and large scale is deemed important.

Apart from the general methods reported for the preparation of PAHs,[24,25] representative examples of the recent approaches include cross-couplings followed by metal-catalyzed intramolecular cyclizations,[26−29] C−H activation,[30,31] oxidative alkene arylation of *o*-aryl styrenes,[32,33] photochemical cyclizations,[34−37] directional synthesis using transient directing groups,[38] π-annulation reactions,[39] APEX (annulative π-extension) reactions,[40] from cycloaddition reactions of aryne precursors,[41−43] alkyne [2 + 2 + 2] cycloisomerizations,[44−46] and Diels−Alder reactions[47,48] among other protocols.[49−52]

The combinations of directed metalation and cross-couplings are well explored as a versatile and efficient route for the synthesis of phenanthrenes (Scheme 1).[53−55] Directed *ortho* metalation (DoM)[56] has proved to be an efficient method for the prefunctionalization of substrates required for cross-coupling, while the Suzuki−Miyaura cross-coupling has been the preferred reaction to make biaryls. The biaryls thus obtained can be cyclized by metalating the remote position through directed remote metalation (DreM) to form various aromatic structures, for example, the phenanthrene natural product gymnopusin.[57,58]

However, examples of DreM with moieties larger than phenyl in the biaryl substrates are scarce. One example of remote metalation of *N*,*N*-diethyl-2-(3-methylnaphthalen-2-yl)benzamide exists for the synthesis of tetraphene (benzo[*a*]-anthracene, Scheme 2a), while DreM on 2-methylnaphthalen-1-yl failed (Scheme 2b).[59] An attempt to make chrysene from 1-methylnaphthalen-2-yl benzamide gave a fluorenone instead (Scheme 2c).[60] Fluorenones are usually formed only in the absence of an *ortho* (peri)-methyl group in the biaryls.[58] These intriguing results in the presence of three regioisomers of the methylnaphthalenyl moiety inspired us to do a systematic exploration of the DreM reaction on methylnaphthalenyl-containing biaryl derivatives to make larger PAHs. Addition-

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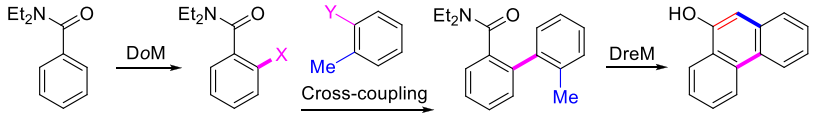
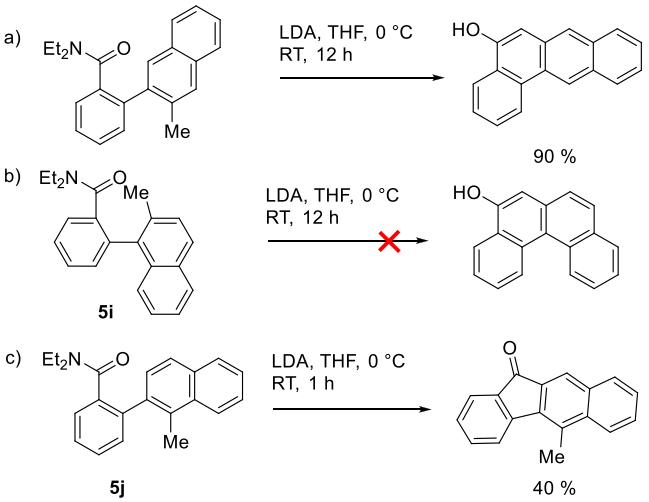
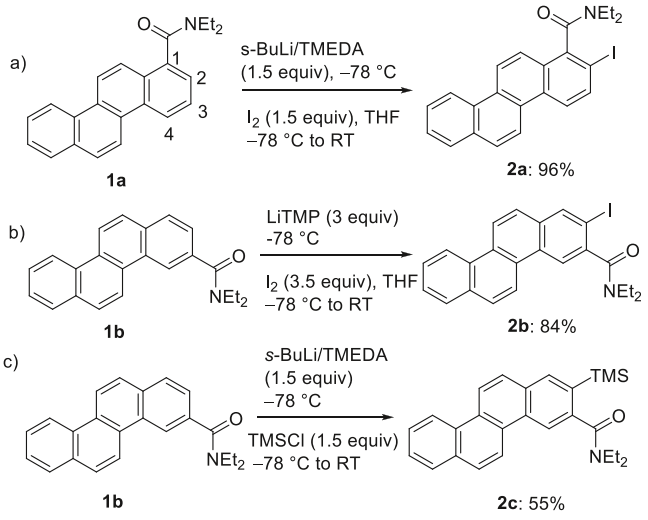
Scheme 1. Synthesis of Phenanthrenes by Directed Metalation and Cross-Coupling Strategies



Scheme 2. DreM Resulting in Different Products Depending on the Connecting Position of the Naphthyl Group. Examples (a,b) by Fu, *et al.*[59] and Example (c) by Lorentzen, *et al.*[63]



Scheme 3. Electrophilic Substitution of *N,N*-Diethylchrysenecarboxamides by DoM



ally, the detailed mechanism of DreM explaining the driving force behind the kinetic complex-induced proximity effect (CIPE) pathway and the thermodynamic pathway based on acid strength of protons is still unclear.[58,61]

Herein, we report the synthesis of six- and seven-ring PAHs using directed metalation (D*o*M and DreM) and Suzuki–Miyaura cross-coupling of chrysenyl carboxamides with *o*-tolyl and the three regioisomers of methylnapthalenes. The bulky and sterically hindered PAH substrates pose a challenge for the cross-coupling reaction; for instance, the catalysts reported for *ortho*-substituted anthracene derivatives are not commercially available,[62] and simple catalysts[59] give modest yields. Thus, new reaction conditions had to be found without compromising the yields.

2. RESULTS AND DISCUSSION

The required *N,N*-diethyl chrysenecarboxamides (**1a** and **1b**) were prepared from the corresponding chrysenecarboxylic acids.[64] To prefunctionalize the substrates for cross-coupling, *N,N*-diethylchrysene-1-carboxamide (**1a**) and *N,N*-diethylchrysene-3-carboxamide (**1b**) were subjected to *s*-BuLi/TMEDA-mediated D*o*M protocol. However, D*o*M and subsequent electrophilic quench with Br_2 and $B(OCH_3)_3$ in separate experiments were unsuccessful on both **1a** and **1b**. This was unanticipated as similar bromination on chrysenes with the *N,N*-diethylcarbamate directing group was reported in good yields.[60] Thereafter, I_2 was used as an electrophile; besides, iodo substrates are more reactive in the Suzuki–Miyaura cross-coupling. *N,N*-diethyl-2-iodochrysene-1-carboxamide (**2a**) was obtained from **1a** in excellent yield using *s*-BuLi/TMEDA and 1 M I_2 in THF (Scheme 3a). Under identical conditions, however, **1b** afforded *N,N*-diethyl-2-iodochrysene-3-carboxamide (**2b**) in poor yield (30%) because of the formation of a complex mixture of unexpected side products, including traces of C-4 iodination. An *in situ* quench (ISQ) reaction of **1b** with *s*-BuLi/TMEDA and TMSCl also resulted in poor yield of the silylated product **2c** and traces of the C-4 substituted product (Scheme 3c), indicating competitive side reactions in the metalation of **1b**. Thereupon, a weaker and sterically bulkier LiTMP base gave the desired iodo product **2b** regioselectively in good yield (Scheme 3b). It is worth mentioning, in this context, that our previous D*o*M study on chrysene-3-yl *N,N*-diethyl-*O*-carbamate with *s*-BuLi/TMEDA afforded only the C2-iodination product regioselectively in excellent yield.[60] In D*o*M reactions, *s*-BuLi (pK_a = 51) and LiTMP (pK_a = 37.3)[65] are the most commonly used bases.[66] In the present work, they were chosen over LDA (pK_a = 35.7)[67] based on their base strength, for the previous studies reported pK_a > 37.2 for *ortho* C–H bonds in monosubstituted benzenes with strong DMGs.[65]

With the iodo-coupling partners **2a** and **2b** in hand, focus was on the preparation of the three regioisomers of methylnaphthalenyl boronates. For the synthesis of boronate-coupling partners, 1-bromo-2-methylnaphthalene (**3a**), 2-bromo-1-methylnaphthalene (**3b**), and 3-methylnaphthalen-2-yl trifluoromethanesulfonate (**3c**) were prepared according to literature procedures (Supporting Information, Scheme S1).[27,68−70] Initially, the bromo-methylnaphthalenes were all converted to boronic acids (**S6**–**S8**) by lithium–halogen exchange reactions and used further without purification (Supporting Information, Scheme S2).[71] However, considering the ease of handling and purification of boronic esters, compounds **3a**–**3c** were subjected to Miyaura borylation using a reported procedure,[72] to synthesize the pinacol esters **4a**–**4c** in good yields, as shown in Scheme 4.

Initial cross-coupling experiments conducted on **2a**–**2b** with commercially available *o*-tolyl boronic acid, in the presence of $PdCl_2$(dppf) and Na_2CO_3 in DME and H_2O, afforded the

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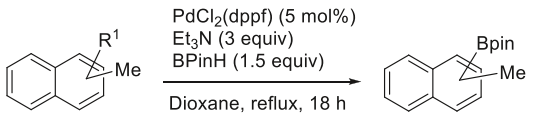
Scheme 4. Preparation of Methylnaphthalenyl Boron Pinacolate Cross-Coupling Partners



3a: 1-Br-2-CH_3
3b: 2-Br-1-CH_3
3c: 2-OTf-3-CH_3

4a: 1-BPin-2-CH_3, 68%
4b: 2-BPin-1-CH_3, 78%
4c: 2-BPin-3-CH_3, 74%

cross-coupled product in 90 and 77% yields, respectively (Table 1).[63] Unfortunately, these conditions failed for both methylnaphthalenyl boronic acid and the boron pinacolate (BPin) analogues **4b**–**4c** (Supporting Information, Table S1). In most of these experiments, the dehalogenated side product was observed, inferring a slower transmetalation step going from *o*-tolylboronates to methylnapthalenylboronates. Several cross-coupling conditions using available catalysts, bases, and solvents were attempted in search of suitable reaction conditions to cross-couple these *ortho*-substituted bulky substrates (Supporting Information, Tables S1 and S2).

Contemplating the observations from these unsuccessful experiments made us question the relative influence of electronic and steric factors. The ligand bite angle (β), described in Figure 1, has been considered important for Suzuki–Miyaura cross-coupling of sterically demanding substrates.[62,73] These substrates required a wide bite-angled *trans*-spanning ligand to allow trans conformation at the metal center. However, the Pd center must undergo a *trans* to *cis* isomerization before the reductive elimination. Excessively large bite angles can deform the catalyst.[74] On the other hand, extremely small bite angles, as in $PdCl_2$(dppm) (Figure 1), might be unsuitable for an efficient reductive elimination because of reduced electron density at the metal center.[75] Presuming that a ligand with a narrow bite angle could be effective, leading directly to a *cis* conformation at the metal center, we chose the $PdCl_2$(dppe) catalyst as a compromise for further experiments.

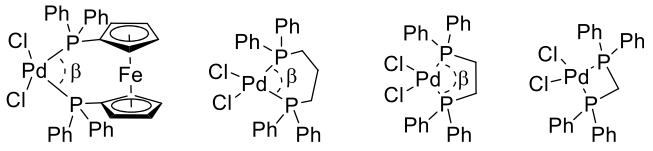
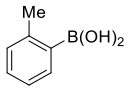
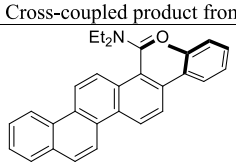
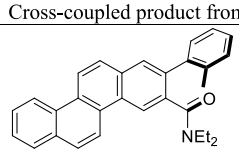
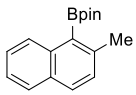
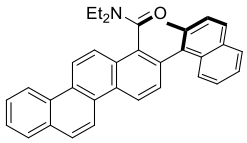
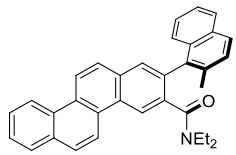
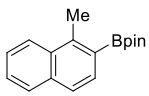
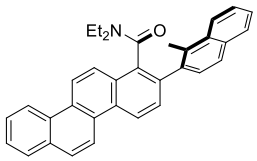
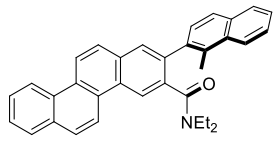
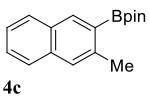
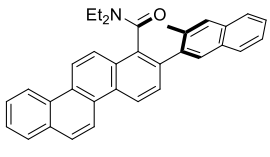
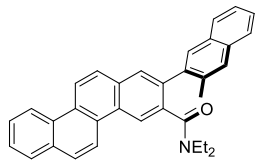


Figure 1. Ligand bite angle (β°) for selected catalysts: $PdCl_2$(dppf),[76] $PdCl_2$(dppp),[76,77] $PdCl_2$(dppe),[77,78] and $PdCl_2$(dppm)[78]

Fortunately, the chosen catalyst $PdCl_2$(dppe) was suitable for cross-coupling of all our bulky PAH substrates (Table 1). The use of BPins and anhydrous reaction conditions (dry solvent and molecular sieves) were helpful to avoid deboronation, which is usually observed in such cross-coupling reactions. Both Cs_2CO_3 (preferable) and KO^{t}Bu (in ^{t}BuOH as the solvent) can be used for the reaction. The experiments were initially conducted in toluene to avoid hydrodehalogenation usually observed in polar protic solvents. The yields

Table 1. Products from the Suzuki–Miyaura Cross-Coupling Reactions

Boronate	Cross-coupled product from **2a**	Cross-coupled product from **2b**
	 **5a**: 90%[a]	 **5e**: 77%[a]
 **4a**	 **5b**: 66%[b] 62%[c]	 **5f**: 46%[b] 10%[c]
 **4b**	 **5c**: quant.[b] 76%[c]	 **5g**: 93%[b] 78%[c]
 **4c**	 **5d**: 81%[b] 82%[c]	 **5h**: 81%[b] 71%[c]

[a]**2a**/**2b** (1 equiv), boronate (1.5 equiv), $PdCl_2$(dppf) (5 mol %), Na_2CO_3 (3 equiv). DME/H_2O, 90 °C. [b]**2a**/**2b** (1 equiv), boronate (1.5 equiv), $PdCl_2$(dppe) (5 mol %), Cs_2CO_3 (3 equiv). DMF, 4 Å MS, 120 °C. [c]Same conditions as *b*, but in toluene at 110 °C.

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obtained were acceptable with exception of **5f** (10%). The addition of the Ag_2O additive or changing the base to K_3PO_4 did not improve the yield of **5f**, but changing the solvent to DMF increased the yield significantly. The yields of remaining cross-coupling experiments were also improved; therefore, $PdCl_2$(dppe) with Cs_2CO_3 in DMF with 4 Å molecular sieves is the preferable condition to cross-couple the methylnaphthalenyl BPin derivatives with **2a-2b** in good to excellent yields (Table 1).

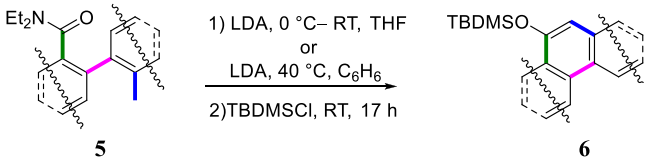
Thereon, DreM of biaryls **5a−5h** was studied to synthesize larger six- and seven-ring PAHs. Compounds **5a**, **5d**, **5e**, and **5h** were cyclized neatly using the regular DreM conditions of excess LDA in THF at 0 °C (Table 2). As phenols are sometimes prone to oxidation, forming quinones, the DreM reaction products were protected by one-pot addition of 1 M TBDMSCl to the reaction mixture at RT. The remaining biaryls failed to cyclize under regular DreM conditions. However, a slight increase in temperature to 40 °C after the addition of LDA afforded **6b** and **6f** in good to moderate yields. To avoid unwanted reactivity of the Li base with THF at elevated temperatures[79] and facilitate the addition of LDA at 40 °C, these experiments were conducted in benzene.[80] Direct addition of LDA at 40 °C afforded slightly higher yields (Table 2). Unfortunately, compounds **5c** and **5g** did not form products by increasing the temperature. Ultimately, biaryl **5g** was exposed to LDA in refluxing benzene that led to partial decomposition of the substrate, but no trace of the desired product.

In these DreM experiments, reactivity was determined by the regioisomeric methylnaphthalenyl groups. The 3-methylnaphthalen-2-yl group (**5d**, **5h** → **6d**, **6h**) reacted readily at 0 °C, while the 2-methylnaphthalen-1-yl group (**5b**, **5f** → **6b**, **6f**) reacted at 40 °C. The 1-methylnaphthalen-2-yl group (**5c** and **5g**) failed to cyclize at all. Besides, attached to a simple benzamide (**5j**), the 1-methylnaphthalen-2-yl group formed a fluorenone.[63] Although all of these biaryls display some atropisomerism, there is no indication that this variation in reactivity occurs from rotational barriers.[63]

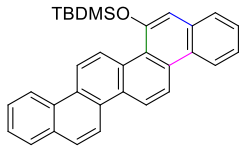
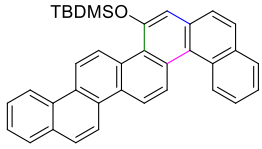
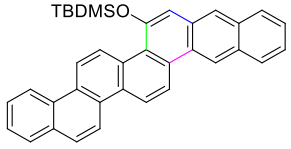
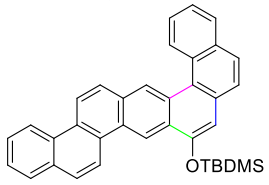
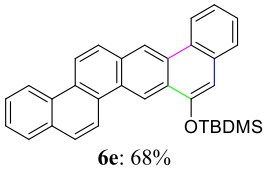
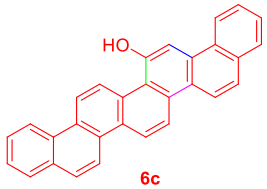
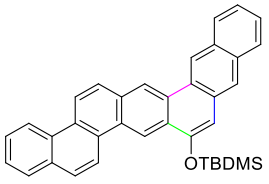
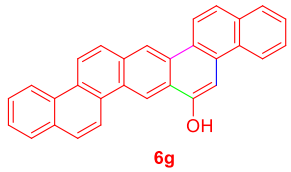
The mechanism of DreM on biarylic benzamides, as proposed by Snieckus and Mortier,[81] involves the first metalation at the *ortho* position of the benzamide (DoM-site) at low temperatures. At temperatures above −30 °C, *ortho* metalation is expected to rapidly equilibrate toward metalation of the DreM sites on the other aryl moiety (remote and lateral positions). This is then followed by a cyclization reaction with the amide group. A few quench experiments were performed to gain more insight into this reactivity. By this proposed mechanism, our ISQ experiments trap the metalation site after equilibration. Compound **5d** underwent ISQ with TMSCl at 0 °C, resulting in bis-silylation of the methyl group (**7**, Scheme 5). Deuterium quench experiments and ISQ experiments with TMSCl on compounds **5c** and **5g** were unsuccessful. A stronger base such as *n*-BuLi decomposed the starting material. Apparently, **5c** and **5g** lack a favorable deprotonation site, and stronger bases deprotonate indiscriminately, decomposing the starting material.

ISQ of **5j** (Scheme 5) gave a silylated product (**8**) and a second TLC spot with a complex NMR spectrum, explaining the moderate yield of product **8**. The exact position of the silyl group in ISQ product **8** could not be determined from its overlapping spectrum of atropdiastereomers, but an HMBC 2D-NMR experiment of the product displayed a correlation between the amide carbonyl and *ortho*-H on benzamide, excluding silylation *ortho* to the amide (DoM position). The integral of the methyl group (3H) and lack of an HMBC correlation between the methyl-C and TMS-H ruled out

Table 2. PAHs Synthesized from DreM on Cross-Coupled Products 6a−6i

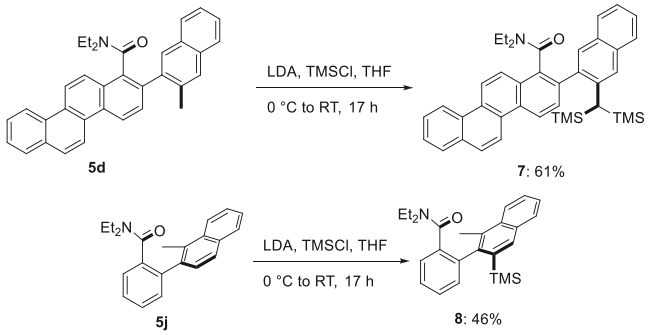


5 6

DreM at RT[a]	DreM at 40 °C[b]
 **6a**: 63%	 **6b**: 85% 62% (0 to 40 °C)[c]
 **6d**: quant	 **6f**: 50% 44% (0 to 40 °C)[c]
DreM of **5c** and **5g** failed to form:	
 **6e**: 68%	 **6c**
 **6h**: 54%	 **6g**

[a]LDA (3 equiv), THF, 0 °C, 30 min, then RT, 1 h, TBDMSCl (3.1 equiv), RT, 17 h. [b]LDA (3.5 equiv), 40 °C, benzene, 1 h, TBDMSCl (3.5 equiv), 40 °C, 14 h. [c]LDA (3.5 equiv), 0 °C, benzene, 40 °C, 1 h, TBDMSCl (3.5 equiv), RT, 17 h.

Scheme 5. ISQ Experiments on Selected Substrates



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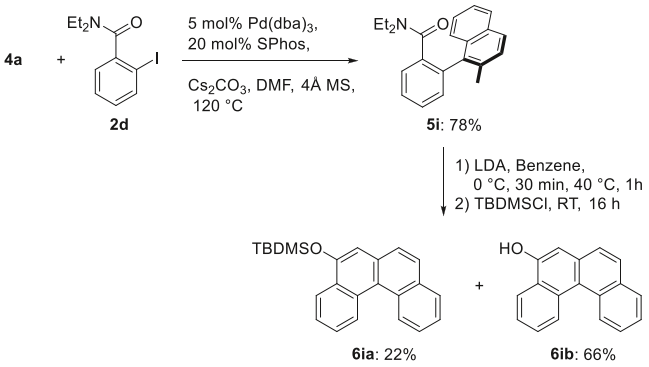
silylation on the methyl group. Increased rotational barriers, resulting in sharp signals of two atropisomers, make it reasonable to assume silylation in 3′ position, as drawn in product **8** (Scheme 5). Apparently, **5j** is deprotonated on the ring instead of on the methyl group during the DreM reaction, explaining the formation of fluorenone (Scheme 2c).[60]

The successful synthesis of **6b** and **6f** prompted us to reinvestigate the DreM of **5i** (Scheme 2b).[59] The yield of **5i** (Scheme 6) was improved from 25 to 78% by changing the

Scheme 6. Reinvestigated Synthesis of 6ib



cross-coupling reaction conditions of **4a** and **2d** (Supporting Information, Scheme S3). This catalyst also increased the yield of **5j** to quantitative. Following DreM reaction of biaryl **5i** did indeed give the cyclized product at 40 °C for a combined yield of 88%. However, direct derivatization of the free phenol with TBDMSCl was less efficient, giving unprotected **6ib** as the major product.

To further increase the scope of this methodology, we attempted to cross-couple two chrysenes toward the synthesis of a fused nine-ring PAH. Already, at the Miyaura borylation step on 2-bromo-3-methylchrysene, solubility became an issue, and poor yield (23%) of the BPin analogue was afforded with a solvent change. The cross-coupled product obtained in traces was practically insoluble, and further experiments were abandoned. Strategic substitutions to increase solubility will be necessary in order to make even larger PAH systems.

2.1. Fluorescence Measurements of Products 6. The final PAHs displayed a bluish fluorescence in UV light. Fluorescence spectra are dependent on the molecular shape, rigidness, and planarity;[82] although of similar size, the DreM products (Table 2) display a variety of geometrical arrangements of the benzene rings. Although most of the molecules should be planar, the carbo-[4]helicene end of **6b** and **6f** will be twisted out of plane. Torsion angles within [4]helicenes and carbo-[4]helicene substructures are reported from 23 to 33°, depending on substitution patterns.[29,83−86] Absorption, fluorescence, and excitation spectra were measured from 1×10^{-6} M sample solutions in $CHCl_3$. The normalized spectra are given in Figure 2, while λ_{max} and Stokes shifts are given in Table 3. $CHCl_3$ was chosen as the solvent because of solubility issues. Although $CHCl_3$ has significant absorption below 250 nm, it should not affect the fluorescence spectra. The lower part of the absorption spectra is affected, but the main absorption is clearly visible.

Although acenes have regular strong bathochromic shifts of about 100 nm per ring, the effect is much smaller for phenacenes.[82,87,88] We observed a small red shift in the absorption spectra for each benzene ring added and an

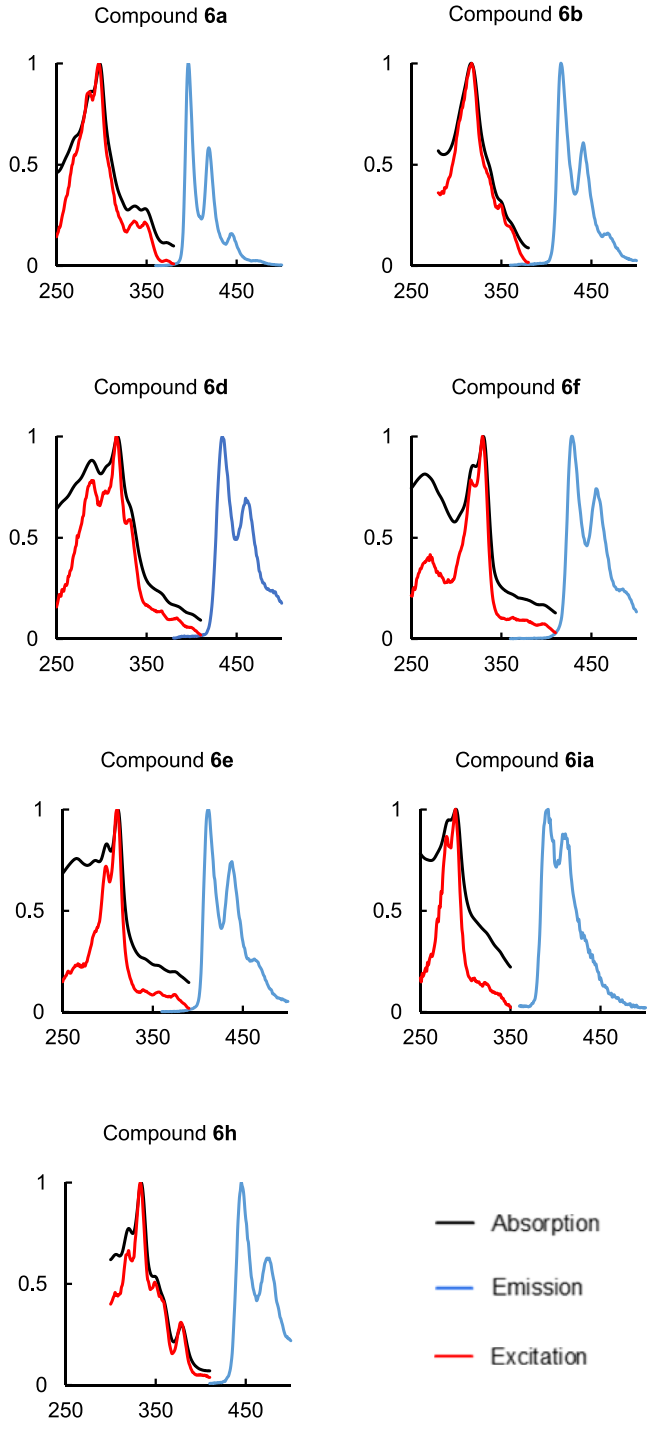


Figure 2. Plots showing UV−vis absorption and fluorescence spectra of PAHs dissolved in $CHCl_3$ with normalized intensity on the *y*-axis and wavelengths in nanometer on the *x*-axis.

additional 11−16 nm for a terminal anthracene moiety in the molecule. The emission spectra also showed similar perturbations between the molecules, but with a slightly stronger bathochromic shift when the anthracene moiety was present at the end of the molecule. [6]Phenacene derivative **6a** had a 98 nm Stokes shift. Chang *et al.* measured the Stokes shift of [6]phenacene to 90 nm, while some analogues with substituents on the terminal ring had 90−95 nm Stokes shift.[89] Despite the variety in shape, our compounds gave similar spectra with 98−102 nm Stokes shift. Only compounds **6d** and

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Table 3. Stokes Shift of the Synthesized PAHs

compound	λ_{abs} (nm)	λ_{exc} (nm)	λ_{emis} (nm)	Stokes shift (nm)	Stokes shift (cm^{-1})
6a	298	297	396	98	102,041
6b	317	317	416	99	101,010
6d	318	316	434	116	86,207
6e	311	311	412	101	99,010
6f	330	329	428	98	102,041
6h	334	333	445	111	90,090
6ia	290	289	392	102	98,039

6h, with a terminal anthracene moiety, deviate with 116 and 111 nm Stokes shift. The expected nonplanarity of **6b** and **6f** gave no visible impact on the spectra. It should be noted that a photophysical study of [6]phenacene by laser excitation in a glass matrix at 77 K found some weak absorption bands close to the fluorescence peak and calculated the Stokes shift to 4 nm.[90]

Benzo[*c*]phenanthrene (3,4-benzophenanthrene) is reported to have a quantum yield of 0.12 and a similar fluorescence spectrum to **6ia**.[87] In our experiments at 1×10^{-6} M solution, **6ib** had a fluorescence too weak to be measured, and **6ia** had much lower signal strength than the other compounds. Although quantum yields were not measured, **6a**–**6h** must have good quantum yields to give this difference in signal strength.

3. CONCLUSIONS

In this first study to expand directed metalation and cross-coupling strategies to the synthesis of medium-sized PAHs, we can observe several effects of the larger PAH systems. Although most of the extra bulk of the PAHs should point away from the catalyst in the cross-couplings, these molecules still have more steric hindrance than the well-explored biphenyls used in phenanthrene synthesis. Rather than a further increase in the catalyst's ligand bite angle, apparently a smaller bite angle was beneficial in these systems. Although DreM is usually performed at 0 °C (with a slow increase to room temperature during the experiment), we found that some configurations needed 40 °C to react. This demonstrated that the DreM reaction is not limited to flat PAHs but can also generate twisted out-of-plane PAHs. *In situ* quench experiments on selected biaryls reveal that the 1-methylnaphthalen-2-yl substituent fails to get deprotonated at the methyl group. Further studies will be needed to determine if this is due to an unfavorable conformation blocking the directing effect of the amide group or a pK_a effect of the naphthalenyl group.

4. EXPERIMENTAL INFORMATION

4.1. General Information. All the reactions were conducted under an inert N_2 atmosphere, in oven-dried glassware. The anhydrous solvents THF, DMF, toluene, and benzene were purchased commercially and used as supplied. All other solvents were dried over molecular sieves before use. BuLi (molar solution in cyclohexane) was titrated for accurate concentration. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) and di-isopropyl amine (DIIPA) were distilled before use and stored over KOH. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (pinBH) was purchased commercially and used as it is. Anhydrous TBDMSCl was purchased as 1 M solution in THF and used as it is. The synthesized compounds were purified using silica gel 40–63 μm. Routine TLC analysis was carried out on silica gel-coated aluminum sheets that were purchased from Merck KGaA. Plates were viewed with a 254 nm ultraviolet lamp. ^{1}H NMR spectra were obtained on a 400 MHz Bruker AVANCE III spectrometer. ^{13}C NMR spectra were obtained at 100 MHz. All NMR spectra were processed using Topspin NMR software. All chemical shift values are reported in parts per million (ppm) relative to the solvent signal and were determined in $CDCl_3$ + TMS ($CDCl_3$ at 7.26 ppm, ^{1}H NMR and 77.2 ppm, ^{13}C NMR) or $C_2D_2Cl_4$ (5.91 ppm, ^{1}H NMR and 73.78 ppm, ^{13}C NMR) or DMSO-d_6 (2.50 ppm, ^{1}H NMR and 39.52 ppm, ^{13}C NMR) with coupling constant (J) values reported in Hertz. The notation of signals is proton: δ chemical shift in ppm (multiplicity, J value(s), number of protons). Carbon: δ chemical shift in ppm (number of carbons). If assignment is ambiguous, for example, in the case of overlapping signals, a range of shifts is reported as the multiplet. Peaks due to solvent impurities in the region of 0–5 ppm (^{1}H NMR)/0–40 ppm (^{13}C NMR) are left unassigned. The ^{1}H NMR spectrum of EtOAc solvent impurities is also included. High-resolution mass spectra (HRMS) were obtained using either the positive and/or negative electrospray ionization (ESI) technique or time-of-flight (TOF) mass detection. IR spectra were recorded on an Agilent Carey 600 FTIR spectrometer using KBr pellets. Melting points of recrystallized samples were recorded on a Stuart Scientific melting point apparatus SMP3 and are uncorrected. UV–visible absorption spectra of recrystallized samples were measured on a VWR UV-1600PC spectrophotometer. Fluorescence emission and excitation spectra of recrystallized samples were measured on an F-7000 FL spectrophotometer.

4.2. General Procedures. The following general procedures A–D cover the important reactions applied and discussed in the main article. Any deviation from the general procedure, reference to applied procedures, and detailed amounts of reagents and yields are given for each compound together with the characterization of compounds.

4.2.1. General Procedure A for DoM. In an inert dry N_2 atmosphere, *s*-BuLi (1.5 equiv, 1.13 M in cyclohexane) was added to compound **1** (1 equiv) in anhydrous THF at −78 °C. The reaction mixture was stirred for 30 min before an electrophile (1.5 equiv) was added to it at −78 °C. The reaction mixture was allowed to reach RT in 15 h. After completion of the reaction, the mixture was quenched with satd. aq. NH_4Cl (50 mL). The crude product was extracted into EtOAc (3 × 50 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product **2** was purified using column chromatography (EtOAc in heptane).

4.2.2. General Procedure B for Borylation of Methylnapthalenes. An oven-dried round bottom flask was fitted with a condenser and purged with N_2 to maintain an inert atmosphere. Starting material **3** (1 equiv) and $PdCl_2$(dppf) (5 mol %) were fed into the reaction flask and stirred in anhydrous dioxane at RT for 10 min. After the addition of triethyl amine (3 equiv) and pinacol borane (1.5 equiv), the reaction mixture was refluxed using a heating mantle for 17 h. At the end, the reaction mixture was brought to RT and filtered through a pad of Celite. To the reaction mixture was added water (50 mL), and the crude product was extracted into EtOAc (3 × 50 mL). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was purified by flash chromatography to afford product **4** (initially eluted with pure heptane to remove the starting material, and then, silica was deactivated with 5% Et_3N in heptane to elute the product).

4.2.3. General Procedure C for Cross-Coupling. An oven-dried round bottom flask was fitted with a condenser and purged with N_2 to maintain an inert atmosphere. A mixture of *N*,*N*-diethyl-2-iodochrysene carboxamide **2a**/**2b** (1 equiv) and $PdCl_2$(dppe) (5 mol %) was stirred in anhydrous DMF at RT for 10 min. Methylnaphthalenyl BPin (**4a**–**4c**) was added followed by the addition of Cs_2CO_3 (3 equiv). The reaction mixture was refluxed at 120 °C using a heating mantle for 24 h. After completion of the reaction, it was cooled down to RT and filtered through a pad of Celite to remove Pd black. To the reaction mixture was added water (10 mL), and the crude product was extracted into EtOAc (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was purified using column chromatography (EtOAc in heptane).

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4.2.4. General Procedure D for DreM. An oven-dried round bottom flask was purged with N_2 before unsymmetrical biaryl **5** (1 equiv) was dissolved in anhydrous THF. The solution was brought to 0 °C, and a freshly prepared LDA (3.0 equiv of *n*-BuLi was added to 3.1 equiv of diisopropyl amine in anhydrous THF stirred at 0 °C for 15 min) was added dropwise to it. The reaction mixture was stirred at 0 °C for 30 min before allowing it to reach RT where again it was stirred for 1 h. At this point, 1 M TBDMSCl (3.1 equiv) was slowly added, and the mixture was stirred at RT for 17 h. After completion of the reaction, it was quenched with satd. aq NH_4Cl (10 mL). The product was extracted into EtOAc (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was purified using flash column chromatography (EtOAc or DCM in heptane).

4.2.5. General Procedure E for DreM at 40 °C. An oven-dried round bottom flask was purged with N_2 before unsymmetrical biaryl **5** (1 equiv) was dissolved in anhydrous benzene. The solution was brought to 40 °C using a heating mantle, and freshly prepared LDA (3.5 equiv of *n*-BuLi was added to 3.6 equiv of diisopropyl amine in anhydrous benzene stirred at 0 °C for 15 min) was added dropwise to it. The reaction mixture was stirred at 40 °C for 1 h. Then, 1 M TBDMSCl (3.5 equiv) was slowly added, and the mixture was stirred at 40 °C for 14 h. After completion of the reaction, the reaction mixture was brought to RT and quenched with satd. aq. NH_4Cl (10 mL). The product was extracted into EtOAc (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was purified using column chromatography (EtOAc in heptane).

4.2.6. General Procedure for UV−Visible and Fluorescence Spectroscopic Measurements. For end products **6a−6ia**, stock solutions of 10^{-3} M $CHCl_3$ were prepared, which were half-diluted in the same solvent to 10^{-6} M. These solutions were used to record the maximum absorption wavelength by scanning the sample from 200 to 900 nm.

Using the same 10^{-6} M solutions, the emission spectra of all the samples were recorded at maximum absorption wavelength. The excitation spectra were then measured using maximum emission wavelength. All the data from UV−visible absorption and fluorescence spectroscopy were plotted in normalized graphs to calculate the Stoke's shift.

4.3. Characterization of Compounds. *4.3.1. N,N-Diethylchrysene-1-carboxamide (**1a**).* Chrysene-1-carboxylic acid (0.732 g, 2.69 mmol), $SOCl_2$ (0.59 mL, 8.06 mmol), and a drop of DMF as the catalyst were heated to reflux in toluene (15 mL) for 16 h. After cooling down to RT, the solvent was evaporated *in vacuo* to yield crude chrysene-1-carbonyl chloride as a yellow solid that was subsequently used in the next step.

Diethyl amine (0.84 mL, 8.06 mmol) was added slowly to a solution of chrysene-1-carbonyl chloride (2.69 mmol) in THF (60 mL) at 0 °C. The reaction mixture was refluxed in an oil bath for 16 h. After cooling down to RT, the reaction mixture was quenched with 1 M HCl (60 mL) and extracted with Et_2O (3 × 60 mL). The combined organic layer was washed with satd aq $NaHCO_3$ (60 mL) and brine (60 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was purified using column chromatography (20% EtOAc in heptane) to obtain **1a** (0.84 g, 99%) as an off-white solid.

mp 156.5−158.3 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 8.8 Hz, 1H), 8.78 (d, J = 8.2 Hz, 1H), 8.77 (d, J = 9.2 Hz, 1H), 8.72 (d, J = 9.1 Hz, 1H), 8.04 (d, J = 9.1 Hz, 1H), 8.02−7.98 (m, 2H), 7.75−7.70 (m, 2H), 7.68−7.64 (m, 1H), 7.55 (dd, J = 1.0, 7.0 Hz, 1H), 3.96−3.88 (br m, 1H), 3.64−3.56 (br m, 1H), 3.19−3.11 (br m, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 135.9, 132.3, 130.9, 130.5, 128.7, 128.4 (2C), 128.3, 127.9, 127.0, 126.7, 126.2, 123.9, 123.8, 123.77, 123.3, 122.4, 121.2, 43.3, 39.2, 14.4, 13.2.

FTIR (KBr, cm^{-1}): 2965 (w), 1619 (vs), 1594 (s), 1465 (s), 1287 (s), 1101 (s), 774 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{23}H_{22}ON$, 328.1696 [M + H]$^+$; found, 328.1698.

*4.3.2. N,N-Diethylchrysene-3-carboxamide (**1b**).* Chrysene-3-carboxylic acid (1.68 g, 6.12 mmol), $SOCl_2$ (3.25 mL, 18.6 mmol), and a drop of DMF as the catalyst were heated to reflux in toluene (20 mL) for 16 h. After cooling down to RT, the solvent was evaporated *in vacuo* to yield crude chrysene-3-carbonyl chloride as a yellow solid that was subsequently used in the next step.

Diethyl amine (1.93 mL, 18.6 mmol) was added slowly to the solution of chrysene-3-carbonyl chloride (6.18 mmol) in THF (60 mL) at 0 °C. The reaction mixture was refluxed in an oil bath for 16 h. After cooling down to RT, the reaction mixture was quenched with 1 M HCl (100 mL) and extracted with Et_2O (3 × 100 mL). The combined organic layer was washed with satd aq $NaHCO_3$ (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was purified using column chromatography (20% EtOAc in heptane) to obtain **1b** (2.03 g, quant) as an off-white solid.

mp 156.5−157.7 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 8.71 (d, J = 9.0 Hz, 1H), 8.69 (d, J = 9.2 Hz, 1H), 8.67 (d, J = 8.9 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 6.9 Hz, 1H), 7.97 (s, 1H), 7.95 (d, J = 7.0 Hz, 1H), 7.70−7.60 (m, 2H), 7.63 (dd, J = 1.2, 8.1 Hz, 1H), 3.66 (br s, 2H), 3.33 (br s, 2H), 1.35 (br s, 3H), 1.16 (br s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 171.6, 135.3, 132.3, 132.2, 130.4, 130.2, 128.7, 128.6 (2C), 128.2, 127.7, 126.9, 126.8, 126.6, 124.2, 123.1, 122.2, 121.4, 121.0, 43.5, 39.5, 14.3, 13.1.

FTIR (KBr, cm^{-1}): 2975 (w), 1623 (vs), 1425 (s), 1283 (s), 1094 (s), 828 (s), 762 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{23}H_{22}ON$, 328.1696 [M + H]$^+$; found, 328.1702.

*4.3.3. N,N-Diethyl-2-iodochrysene-1-carboxamide (**2a**).* Following general procedure A, compound **1a** (873 mg, 2.67 mmol) in anhydrous THF (35 mL) was treated with *s*-BuLi (3.55 mL, 4.01 mmol, 1.13 M in cyclohexane) and TMEDA (0.60 mL, 4.01 mmol) for 30 min before adding I_2 (4 mL, 4.01 mmol, 1 M in anhydrous THF) at −78 °C and then warmed to RT over 8 h. Standard workup (eluent: 20% EtOAc in heptane) afforded product **2a** as an off-white solid (1.16 g, 96%).

mp 238.6−241.0 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, J = 8.2 Hz, 1H), 8.72 (d, J = 9.3 Hz, 1H), 8.61 (d, J = 9.1 Hz, 1H), 8.45 (d, J = 8.9 Hz, 1H), 8.03 (d, J = 8.9 Hz, 1H), 8.01 (d, J = 9.1 Hz, 1H), 7.99 (dd, J = 1.1, 9.1 Hz, 1H), 7.91 (d, J = 9.3 Hz, 1H), 7.74−7.69 (m, 1H), 7.67−7.63 (m, 1H), 4.03−3.95 (m, 1H), 3.66−3.95 (m, 1H), 3.19−3.14 (m, 2H) 1.46 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.7, 140.9, 136.2, 132.5, 130.4, 130.3, 129.9, 128.7, 128.4, 128.3, 128.1, 127.2, 127.0, 125.0, 124.1, 123.3, 123.25, 120.8, 91.8, 43.2, 39.2, 14.1, 12.7.

FTIR (KBr, cm^{-1}): 2963 (w), 1616 (vs), 1436 (m), 1274 (s), 1099 (m), 811 (s), 752 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{23}H_{21}ONI$, 454.0662 [M + H]$^+$; found, 454.0662.

*4.3.4. N,N-Diethyl-2-iodochrysene-3-carboxamide (**2b**).* Following general procedure A, compound **1b** (500 mg, 1.53 mmol) in anhydrous THF (15 mL) was treated with freshly prepared LiTMP (4.58 mmol in anhydrous THF) for 1.5 h before adding I_2 (5.35 mL, 5.35 mmol, 1 M in anhydrous THF) at −78 °C and then warmed to RT over 16 h. Standard workup (eluent: 20% EtOAc in heptane) afforded the product **2b** as an off-white solid (0.58 g, 84%).

mp 224.7−226.5 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71−8.67 (m, 2H), 8.58 (s, 1H), 8.56 (d, J = 9.2 Hz, 1H), 8.43 (s, 1H), 7.99−7.95 (m, 2H), 7.82 (d, J = 9.1 Hz, 1H), 7.71−7.67 (m, 1H), 7.66−7.62 (m, 1H), 4.00−3.97 (br m, 1H), 3.42−3.39 (br m, 1H), 3.25−3.17 (br m, 2H) 1.40 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.4, 140.2, 139.0, 133.3, 132.4, 130.4, 129.9, 128.8, 128.7, 128.2, 127.9, 127.1, 126.9, 125.6, 123.2, 123.0, 121.5, 120.6, 90.2, 43.1, 39.3, 14.1, 12.7.

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FTIR (KBr, cm^{-1}): 2965 (w), 1635 (vs), 1423 (s), 1279 (s), 1106 (m), 823 (s), 812 (s), 756 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{23}H_{21}ONI$, 454.0662 $[M + H]^+$; found, 454.0666.

*4.3.5. N,N-Diethyl-2-(trimethylsilyl)chrysene-3-carboxamide (**2c**).* Following general procedure A, compound **1a** (108 mg, 0.33 mmol) and TMSCl (0.06 mL, 0.50 mmol) in anhydrous THF (4 mL) were treated with *s*-BuLi (0.44 mL, 0.50 mmol, 1.13 M in cyclohexane) and TMEDA (0.07 mL, 0.50 mmol) for 30 min at −78 °C and then warmed to RT over 7 h. Standard workup with EtOAc (3 × 10 mL) and column chromatography (15−20% EtOAc in heptane) afforded the product **2c** (73 mg, 55%) as an off-white solid.

mp 166.9−169.0 °C (cyclohexane + DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 8.3 Hz, 1H), 8.75 (d, J = 9.1 Hz, 1H), 8.65 (d, J = 9.1 Hz, 1H), 8.58 (s, 1H), 8.23 (s, 1H), 8.02 (d, J = 8.9 Hz, 2H), 8.00 (dd, J = 1.0, 7.0 Hz, 1H), 7.74−7.70 (m, 1H), 7.67−7.63 (m, 1H), 3.70 (q, J = 7.0 Hz, 2H), 3.27 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H), 0.43 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 172.9, 140.4, 136.6, 135.8, 132.4, 131.4, 130.6, 130.1, 129.0, 128.7, 128.0, 127.8, 127.3, 127.0, 126.7, 123.3, 122.0, 121.0, 120.1, 43.8, 39.4, 14.2, 13.1, 0.1.

FTIR (KBr, cm^{-1}): 2966 (w), 1633 (vs), 1457 (m), 1283 (s), 1243 (m), 1112 (m), 861 (s), 839 (vs), 749 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{26}H_{30}ONSi$, 400.2091 $[M + H]^+$; found, 400.2093.

*4.3.6. N,N-Diethyl-2-iodobenzamide (**2d**).* Following general procedure A, benzamide (386 mg, 2.18 mmol) in anhydrous THF (3 mL) was added slowly to a solution of *s*-BuLi (2.90 mL, 3.27 mmol, 1.13 M in cyclohexane) and TMEDA (0.49 mL, 3.27 mmol) in anhydrous THF (2 mL) and stirred for 30 min before adding I_2 (3.27 mL, 1 M in anhydrous THF) at −78 °C. The reaction mixture was warmed to RT over 6 h. Standard workup with EtOAc (3 × 10 mL) and column chromatography (20% EtOAc in heptane) afforded the product **2d** (0.46 g, 68%) as a yellow oil.

Characterization data were in accordance with the literature.[91]

*4.3.7. 4,4,5,5-Tetramethyl-2-(2-methylnaphthalen-1-yl)-1,3,2-dioxaborolane (**4a**).* Following general procedure B, 1-bromo-2-methyl naphthalene[69] (**3a**, 2.08 g, 9.05 mmol) was stirred with $PdCl_2$(dppf) (0.37 g, 5 mol %) for 10 min in dioxane (36 mL), pinacol borane (1.97 mL, 13.6 mmol) and Et_3N (3.78 mL, 27.2 mmol) were added at RT, and heated to reflux. After completion of the reaction, workup afforded **4a** (1.67 g, 68%) as an off-white solid. A second experiment using 3.12 g of **3a** afforded **4a** in 65% yield.

mp 92.4−94.5 °C (cyclohexane + DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.5 Hz, 1H), 7.76 (dd, J = 1.3, 7.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.46−7.42 (m, 1H), 7.40−7.36 (m, 1H), 7.28 (d, J = 8.5 Hz, 1H), 2.62 (s, 3H), 1.49 (s, 12H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.5, 136.8, 131.5, 129.7, 128.6, 128.3 (2C), 127.6, 126.1, 124.7, 84.1 (2C), 25.2 (3C), 25.1, 22.8. The NMR data are in accordance with literature values.[92−94]

FTIR (KBr, cm^{-1}): 2975 (w), 1507 (m), 1467 (m), 1303 (m), 1258 (m), 1144 (m), 1132 (m), 857 (vs), 843 (vs), 816 (vs), 742 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{17}H_{22}O_2B$, 269.1713 $[M + H]^+$; found, 269.1707.

*4.3.8. 4,4,5,5-Tetramethyl-2-(1-methylnaphthalen-2-yl)-1,3,2-dioxaborolane (**4b**).* Following general procedure B, 2-bromo-1-methyl naphthalene[69] (**3b**, 2.97 g, 13.4 mmol) was stirred with $PdCl_2$(dppf) (0.49 g, 5 mol %) for 10 min in dioxane (40 mL), pinacol borane (2.93 mL, 20.2 mmol) and Et_3N (5.62 mL, 40.3 mmol) were added at RT, and heated to reflux. After completion of the reaction, workup afforded **4b** (2.82 g, 78%) as an off-white solid. A second experiment using 2 g of **3b** gave product **4b** in 77% yield.

mp 83.2−84.1 °C (cyclohexane + DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.83−8.80 (m, 1H), 8.04−8.01 (m, 1H), 8.00 (d, J = 7.0 Hz, 1H), 7.57−7.50 (m, 2H), 7.34 (dd, J = 0.8, 7.0 Hz, 1H), 2.72 (s, 3H), 1.43 (s, 12H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.3, 137.2, 135.8, 132.6, 129.2, 126.2 (3C), 125.5, 124.4, 83.8 (2C), 25.1 (4C), 20.1.

FTIR (KBr, cm^{-1}): 2979 (w), 1344 (w), 1291 (m), 1145 (m), 1114 (m), 858 (s), 849 (s), 760 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{17}H_{22}O_2B$, 269.1713 $[M + H]^+$; found, 269.1707.

4.3.9. 4,4,5,5-Tetramethyl-2-(3-methylnaphthalen-2-yl)-1,3,2-dioxaborolane (4c). Following general procedure B, 2-methylnaphthalen-3-yl trifluoromethanesulfonate[27] (**3c**, 1.00 g, 3.45 mmol) was stirred with $PdCl_2$(dppf) (141 mg, 5 mol %) for 10 min in dioxane (15 mL), pinacol borane (0.60 mL, 4.13 mmol) and Et_3N (1.5 mL, 10.4 mmol) were added at RT, and heated to reflux. After completion of the reaction, workup afforded **4c** (0.68 g, 74%) as an off-white solid. A second experiment using 2.02 g of **3c** afforded product **4c** in 66% yield.

mp 61.3−62.8 °C (cyclohexane + DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.60 (s, 1H), 7.50−7.45 (m, 1H), 7.42−7.38 (m, 1H), 2.70 (s, 3H), 1.41 (s, 12H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.5, 137.5 (2C), 135.1, 131.2, 128.4, 127.3, 127.1, 127.0, 125.0, 83.7 (2C), 25.1 (4C), 22.8. The NMR data are in accordance with literature values.[95]

FTIR (KBr, cm^{-1}): 2976 (w), 1350 (s), 1329 (s), 1147 (s), 1135 (s), 1031 (m), 960 (m), 856 (m), 754 (m), 750 (m).

HRMS (ESI/TOF) m/z: calcd for $C_{17}H_{22}O_2B$, 269.1713 $[M + H]^+$; found, 269.1706.

*4.3.10. N,N-Diethyl-2-(o-tolyl)chrysene-1-carboxamide (**5a**).* Compound **2a** (110 mg, 0.24 mmol), $PdCl_2$(dppf) (9 mg, 5 mol %), *o*-tolyl boronic acid (40 mg, 0.29 mmol), and Na_2CO_3 (77 mg, 0.73 mmol) were all added in sequence to DME (5 mL) and then H_2O (2 mL). The reaction mixture was stirred at 85 °C for 17 h. After completion of the reaction, workup following standard procedure B (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5a** (91 mg, 90%) as a brown solid (major/minor rotamers = 56:44).

mp 205.2−210.3 °C (cyclohexane + DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.85−8.73 (br m, 8H), 8.05−8.00 (br m, 6H), 7.75−7.71 (m, 2H), 7.68−7.56 (br m, 5H), 7.30−7.18 (br m, 7H), 3.93 (br, 2H), 3.25−2.78 (br, 6H), 2.31 (s, 3H), 2.26 (s, 3H, minor), 0.93−0.77 (12H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 169.2, 169.1, 139.9, 138.6, 138.1, 136.7, 135.4, 135.2, 134.9, 134.6, 132.3, 131.5, 130.5 (2C), 130.2, 129.9, 129.2, 129.1, 128.7 (2C), 128.3, 128.2, 128.0 (2C), 127.9, 127.0 (2C), 126.7 (2C), 125.8, 124.7, 123.5 (2C), 123.3, 122.8, 122.4 (2C), 121.2 (2C), 42.9, 42.4, 38.0, 37.8, 20.6, 20.5, 14.0 (2C), 12.1, 11.8.

FTIR (KBr, cm^{-1}): 2976 (w), 2929 (w), 1622 (s), 1438 (m), 1271 (s), 1220 (m), 1099 (m), 796 (s), 761 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{30}H_{28}ON$, 418.2165 $[M + H]^+$; found, 418.2167.

*4.3.11. N,N-Diethyl-2-(2-methylnaphthalen-1-yl)chrysene-1-carboxamide (**5b**).* According to general procedure C, **2a** (104 mg, 0.23 mmol), $PdCl_2$(dppe) (7 mg, 5 mol %), BPin **4a** (123 mg, 0.46 mmol), and Cs_2CO_3 (224 mg, 0.69 mmol) were all added in sequence to anhydrous DMF (3 mL) containing 4 Å molecular sieves. After completion of the reaction, standard workup (eluent: 15% EtOAc in heptane) afforded the cross-coupled product **5b** (71 mg, 66%) as a brown solid (major/minor rotamers = 83:17).

mp 91.3−94.8 °C (cyclohexane + DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.94 (d, J = 8.5 Hz, 1H), 8.81 (d, J = 9.0 Hz, 2H), 8.80 (d, J = 9.1 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 8.06 (d, J = 9.2 Hz, 1H), 8.04−8.02 (m, 1H), 7.89−7.87 (m, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.76−7.72 (m, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.69−7.68 (m, 1H), 7.66−7.63 (m, 1H, minor), 7.48 (d, J = 8.4 Hz, 1H), 7.42−7.39 (m, 2H), 7.31−7.27 (m, 1H), 3.79−3.74 (m, 1H), 3.21−3.16 (m, 1H), 2.84−2.79 (m, 2H), 2.43 (s, 3H), 2.34 (s, 3H, minor), 0.92 (app t, J = 7.0 Hz, 3H, minor), 0.71 (t, J = 7.1 Hz, 3H), 0.39 (t, J = 7.1 Hz, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, major isomer): δ = 168.7, 136.4, 135.9, 135.0, 134.7, 132.6, 132.4, 131.8, 130.5, 130.1, 129.3, 129.1, 128.7, 128.4, 128.3, 128.2, 127.9, 127.89, 127.8, 127.0, 126.7,

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126.0, 125.4, 124.6, 124.5, 123.4, 123.3, 122.4, 121.2, 42.9, 37.3, 21.5, 13.9, 11.4.

FTIR (KBr, cm^{-1}): 2925 (w), 1630 (s), 1439 (m), 1273 (m), 1097 (m), 812 (s), 752 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{34}H_{30}ON$, 468.2322 $[M + H]^+$; found, 468.2322.

*4.3.12. N,N-Diethyl-2-(1-methylnaphthalen-2-yl)chrysene-1-carboxamide (**5c**).* According to general procedure C, **2a** (94 mg, 0.21 mmol), $PdCl_2$(dppe) (6 mg, 5 mol %), BPin **4b** (111 mg, 0.42 mmol), and Cs_2CO_3 (205 mg, 0.63 mmol) were all added in sequence to anhydrous DMF (3 mL) containing 4 Å molecular sieves. After completion of the reaction, standard workup (eluent: 15% EtOAc in heptane) afforded the cross-coupled product **5c** (97 mg, quant) as a red solid (major/minor rotamers = 77:13).

mp 194.5−198.1 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (d, J = 7.9 Hz, 1H, minor), 8.86 (d, J = 8.6 Hz, 1H), 8.81 (app dd, J = 3.2, 9.6 Hz, 2H), 8.77 (d, J = 9.2 Hz, 1H), 8.13−8.10 (m, 2H), 8.05 (d, J = 9.1 Hz, 1H), 8.02 (br d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 7.00 Hz, 1H), 7.76−7.72 (m, 1H, major, 1H minor), 7.69 (d, J = 8.6 Hz, 1H, minor), 7.69−7.65 (m, 1H, major, 1H, minor), 7.58−7.52 (m, 1H, major, 1H, minor), 7.47−7.42 (m, 2H, major, 2H, minor), 7.36 (dd, J = 0.6, 7.2 Hz, 1H, minor), 7.29 (d, J = 7.1 Hz, 1H, minor), 3.81−3.74 (m, 1H, major, 1H, minor), 3.36−3.27 (m, 1H, minor), 3.13−3.00 (m, 2H), 2.96−2.88 (m, 2H, minor), 2.78 (s, 3H, major), 2.77 (s, 3H, minor), 2.50−2.41 (m, 1H), 0.93 (t, J = 7.1 Hz, 3H, minor), 0.71 (t, 3H, J = 7.1 Hz, 3H), 0.54 (t, J = 7.1 Hz, 3H), 0.52 (t, J = 7.1 Hz, 1H, minor).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.2 (major), 168.8 (minor), 136.6, 135.7, 135.6, 135.4, 134.8, 134.6, 134.5, 132.9, 132.6, 132.5, 132.4, 131.9, 130.5, 130.2, 130.1, 130.06, 129.6, 129.3, 128.7, 128.67 (2C), 128.5, 128.4, 128.3, 128.27, 127.9, 126.9 (2C), 126.7, 126.3, 126.2, 126.1, 125.7, 125.6, 125.5, 125.2, 124.8, 124.76, 124.7, 123.7, 123.4, 123.3, 122.7, 122.5, 121.2 (2C), 43.0 (minor), 42.7 (major), 38.0 (major), 37.7 (minor), 19.7 (2C), 14.1 (minor), 13.8 (major), 12.0 (major), 11.7 (minor).

FTIR (KBr, cm^{-1}): 2973 (w), 2930 (w), 1626 (s), 1481 (m), 1274 (s), 1097 (m), 806 (vs), 760 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{34}H_{30}ON$, 468.2322 $[M + H]^+$; found, 468.2324.

*4.3.13. N,N-Diethyl-2-(3-methylnaphthalen-2-yl)chrysene-1-carboxamide (**5d**).* According to general procedure C, **2a** (104 mg, 0.23 mmol), $PdCl_2$(dppe) (7 mg, 5 mol %), BPin **4c** (123 mg, 0.46 mmol), and Cs_2CO_3 (224 mg, 0.69 mmol) were all added in sequence to anhydrous DMF (3 mL) containing 4 Å molecular sieves. After completion of the reaction, standard workup (eluent: 15% EtOAc in heptane) afforded cross-coupled product **5d** (87 mg, 81%) as an off-white solid (major/minor rotamers = 51:49). A second experiment using 1.16 g of **2a** gave **5d** in 58% yield.

mp 208.7−212.4 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87−8.72 (m, 8H), 8.19 (s, 1H), 8.13−8.01 (m, 6H), 7.94−7.92 (br d, J = 7.5 Hz, 1H), 7.85−7.62 (m, 12H), 7.52−7.45 (m, 4H), 3.81 (br s, 2H), 3.42−3.33 (br m, 1H), 3.17−3.01 (br m, 4H), 2.79−2.72 (br m, 1H), 2.47 (s, 3H, major), 2.44 (s, 3H, minor), 0.98 (br m, 3H), 0.76 (br t, J = 6.6 Hz, 3H), 0.65−0.57 (br m, 6H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ = 169.1 (major), 169.0 (minor), 139.2, 136.9, 136.5, 135.0, 134.8, 133.5, 133.3, 133.1, 132.3 (2C), 131.8, 131.3, 130.6, 130.5, 130.0, 129.3, 129.0, 128.7 (2C), 128.5, 128.4, 128.2, 127.9, 127.85, 127.3, 127.0, 126.9, 126.7, 126.3, 126.0, 125.6, 125.4, 124.8, 124.5, 123.4, 123.3 (2C), 122.8, 122.5, 121.2, 42.9, 42.6, 38.2, 37.7, 21.1, 14.0 (2C), 11.9, 11.7.

FTIR (KBr, cm^{-1}): 2969 (w), 2927 (w), 1628 (vs), 1469 (m), 1422 (m), 1276 (s), 1097 (m), 798 (s), 744 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{34}H_{30}ON$, 468.2322 $[M + H]^+$; found, 468.2325.

*4.3.14. N,N-Diethyl-2-(o-tolyl)chrysene-3-carboxamide (**5e**).* Compound **2b** (65 mg, 0.14 mmol), $PdCl_2$(dppf) (6 mg, 5 mol %), *o*-tolyl boronic acid (24 mg, 0.17 mmol), and Na_2CO_3 (46 mg, 0.43 mmol) were all added in sequence to DME (2 mL) and then H_2O (1 mL). The reaction mixture was stirred at 85 °C for 17 h. After completion of the reaction, workup according to standard procedure B (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5e** (46 mg, 77%) as an off-white solid with a mixture of rotamers.

mp 195.4−199.0 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (s, 1H), 8.79 (d, J = 8.3 Hz, 1H), 8.78 (d, J = 9.1 Hz, 1H), 8.72 (d, J = 9.1 Hz, 1H), 8.04 (d, J = 9.1 Hz, 1H), 8.02 (app d, J = 1.3, 8.0 Hz, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.89 (s, 1H), 7.75−7.71 (m, 1H), 7.68−7.64 (m, 1H), 7.31−7.24 (br, 4H), 3.89 (br s, 1H), 3.19−2.90 (br, 3H), 2.33 (br s, 3H), 0.95 (br s, 3H), 0.77 (br s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.4, 132.4, 130.6, 130.3, 129.6, 128.8 (2C), 128.6, 128.2, 127.94, 127.9 (2C), 127.0 (2C), 126.9 (2C), 126.7, 123.3 (2C), 122.4, 121.2, 42.6 (2C), 38.2 (2C), 20.5, 13.9 (2C), 11.9 (2C).

FTIR (KBr, cm^{-1}): 2969 (w), 2930 (w), 1637 (vs), 1470 (s), 1433 (s), 1281 (s), 1096 (s), 1081 (m), 822 (m), 813 (s), 753 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{30}H_{28}ON$, 418.2165 $[M + H]^+$; found, 418.2167.

*4.3.15. N,N-Diethyl-2-(2-methylnaphthalen-1-yl)chrysene-3-carboxamide (**5f**).* According to general procedure C, **2b** (106 mg, 0.22 mmol), $PdCl_2$(dppe) (7 mg, 5 mol %), BPin **4a** (118 mg, 0.44 mmol), and Cs_2CO_3 (216 mg, 0.66 mmol) were all added in sequence to anhydrous DMF (3 mL) containing 4 Å molecular sieves. After completion of the reaction, standard workup (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5f** (48 mg, 46%) as a pale brown solid with a mixture of rotamers.

mp 237.4−240.8 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (s, 1H), 8.82 (d, J = 8.9 Hz, 2H), 8.75 (d, J = 9.1 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.99 (s, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.77−7.73 (m, 1H), 7.70−7.66 (m, 1H), 7.47 (br d, J = 8.4 Hz, 2H), 7.42−7.38 (m, 1H), 7.33−7.29 (br m, 1H), 3.65−2.49 (br m, 4H), 2.41 (s, 3H), 0.94 (s, 3H), 0.36 (br t, J = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.8, 137.0, 135.3, 135.0, 132.8, 132.4, 132.1, 131.9, 130.9, 130.6, 129.6, 128.8, 128.7, 128.2, 128.0, 127.8, 127.1, 127.0, 126.7, 125.5, 124.6, 123.3, 122.4, 121.1, 43.1, 37.9, 21.4, 14.0, 11.4.

FTIR (KBr, cm^{-1}): 2969 (w), 2929 (w), 1629 (vs), 1467 (m), 1425 (s), 1282 (s), 1067 (m), 818 (s), 749 (s).

HRMS (ESI/TOF) m/z: calcd for $C_{34}H_{30}ON$, 468.2322 $[M + H]^+$; found, 468.2322.

*4.3.16. N,N-Diethyl-2-(1-methylnaphthalen-2-yl)chrysene-3-carboxamide (**5g**).* According to general procedure C, **2b** (107 mg, 0.24 mmol), $PdCl_2$(dppe) (7 mg, 5 mol %), BPin **4b** (127 mg, 0.47 mmol), and Cs_2CO_3 (231 mg, 0.71 mmol) were all added in sequence to anhydrous DMF (3 mL) containing 4 Å molecular sieves. After completion of the reaction, standard workup (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5g** (103 mg, 93%) as a brown solid with a mixture of rotamers.

mp 228.0−230.0 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 8.77 (app dd, J = 2.6, 9.1 Hz, 3H), 8.16−7.82 (br m, 3H), 8.05 (br d, J = 9.1 Hz, 1H), 8.02 (br d, J = 7.9 Hz, 1H), 8.00 (br d, J = 9.1 Hz, 1H), 7.74−7.64 (br m, 3H), 7.59−7.55 (br m, 1H), 7.49−7.27 (br m, 3H), 3.76 (br s, 1H), 3.31−3.16 (br, 1H), 2.89−2.46 (br, 2H), 2.79 (s, 3H), 1.01−0.37 (br m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.3, 137.1, 136.3, 135.7, 134.9, 134.4, 132.9, 132.5, 132.4, 131.8, 131.5, 131.3, 130.5, 130.2, 129.6, 129.1, 128.7, 128.6, 128.1, 127.9, 127.0, 126.9, 126.6, 126.2, 126.0, 125.7, 125.5, 124.8, 124.2, 123.8, 123.2, 122.4, 121.9, 121.5, 121.2, 42.8, 38.1, 19.7, 13.6, 11.8.

FTIR (KBr, cm^{-1}): 2975 (w), 1618 (m), 1426 (m), 1275 (m), 767 (s), 748 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{34}H_{30}ON$, 468.2322 $[M + H]^+$; found, 468.2324.

*4.3.17. N,N-Diethyl-2-(3-methylnaphthalen-2-yl)chrysene-3-carboxamide (**5h**).* According to general procedure C, **2b** (83 mg, 0.18 mmol), $PdCl_2$(dppe) (5 mg, 5 mol %), BPin **4c** (98 mg, 0.37 mmol),

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and Cs_2CO_3 (179 mg, 0.55 mmol) were all added in sequence to anhydrous DMF (3 mL) containing 4 Å molecular sieves. After completion of the reaction, standard workup (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5h** (69 mg, 81%) as a pale brown solid with a mixture of rotamers.

mp 225.4−230.8 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 8.86 (br s, 1H), 8.78 (d, J = 8.3 Hz, 1H), 8.77 (d, J = 9.2 Hz, 1H), 8.75 (d, J = 9.1 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 8.03−7.99 (m, 2H), 7.97 (s, 1H), 7.83 (br d, J = 7.8 Hz, 2H), 7.79 (s, 1H), 7.75−7.71 (m, 1H), 7.68−7.65 (m, 1H), 7.52−7.44 (m, 2H), 3.77−2.92 (br m, 4H), 2.50 (s, 3H), 0.96 (br s, 3H), 0.57 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.3, 136.3, 133.3, 132.4, 131.8, 131.5, 130.5, 130.0, 129.6, 128.7 (2C), 128.6, 128.1, 127.9 (2C), 127.0 (2C), 126.9 (2C), 126.7, 126.2, 125.5, 123.2, 122.4, 121.1, 42.7, 38.2, 21.1, 13.9, 11.8.

FTIR (KBr, cm^{-1}): 2974 (w), 1634 (s), 1624 (s), 1424 (s), 1285 (m), 1094 (m), 1068 (m), 889 (s), 811 (s), 748 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{34}H_{30}ON$, 468.2322 [M + H]$^+$; found, 468.2324.

*4.3.18. N,N-Diethyl-2-(2-methylnaphthalen-1-yl)benzamide (**5i**).* According to general procedure C, **2d** (145 mg, 0.48 mmol), $Pd_2(dba)_3$ (22 mg, 5 mol %), SPhos (39 mg, 20 mol %), BPin **4a** (154 mg, 0.57 mmol), and Cs_2CO_3 (468 mg, 1.44 mmol) were all added in sequence to anhydrous DMF (4 mL) containing 4 Å molecular sieves. After completion of the reaction (17 h), standard workup (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5i** (118 mg, 78%) as a red solid of a mixture of rotamers. A second experiment using 1.32 g of **2d** gave **5i** in 60% yield.

Characterization data were in accordance with the literature.[23]

mp 137.8−138.8 °C (DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.54−7.43 (m, 3H), 7.39−7.28 (m, 5H), 3.47−2.60 (br, 4H), 2.31 (s, 3H), 0.86 (br s, 3H), 0.27 (t, J = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.6, 138.1, 137.1, 135.3, 132.6, 131.8, 131.3, 128.7 (2C), 127.9, 127.5 (2C), 126.4, 125.4, 124.6, 42.9, 37.7, 21.3, 13.9, 11.4.

FTIR (KBr, cm^{-1}): 2972 (m), 1627 (vs), 1459 (vs), 1432 (vs), 1290 (vs), 1081 (s), 826 (vs), 783 (vs), 767 (vs).

HRMS (ESI/TOF) m/z: calcd for $C_{22}H_{23}ONNa$, 340.1672 [M + Na]$^+$; found, 340.1675.

*4.3.19. N,N-Diethyl-2-(1-methylnaphthalen-2-yl)benzamide (**5j**).* According to general procedure C, **2d** (1.33 g, 4.39 mmol), $Pd_2(dba)_3$ (200 mg, 5 mol %), SPhos (360 mg, 20 mol %), BPin **4b** (1.42 g, 5.28 mmol), and Cs_2CO_3 (4.30 g, 13.2 mmol) were all added in sequence to anhydrous DMF (40 mL) containing 4 Å molecular sieves. After completion of the reaction (17 h), standard workup (eluent: 20% EtOAc in heptane) afforded the cross-coupled product **5j** (1.389 g, quant) as a pale red oil as a mixture of rotamers (solidified slowly to a red solid).

Characterization data were in accordance with the literature.[25]

mp 89.3−91.7 °C (DCM).

HRMS (ESI/TOF) m/z: calcd for $C_{22}H_{23}ONNa$, 340.1672 [M + H]$^+$; found, 340.1675.

*4.3.20. (Benzo[c]picen-7-yloxy)(tert-butyl)dimethylsilane (**6a**).* Compound **5a** (94 mg, 0.23 mmol) in anhydrous THF (3 mL) was added to freshly prepared LDA (0.56 mmol, 0.56 M in anhydrous THF) at 0 °C and stirred for 30 min. The reaction mixture was then stirred at RT for 1 h; TBDMSCl (0.56 mL, 0.56 mmol, 1 M in THF) was added and left to react at RT for 17 h and subsequently quenched with satd aq NH_4Cl solution (10 mL). The product had poor solubility and was hence extracted with toluene (3 × 10 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, and evaporated to dryness under reduced pressure. The crude product was washed with acetone to obtain the pure TBDMS-protected product **6a** (70 mg, 63%) as an off-white solid.

mp 261.0−263.0 °C (acetone).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 9.99 (d, J = 9.6 Hz. 1H), 8.97 (d, J = 9.4, 1H), 8.89 (d, J = 9.5 Hz, 1H), 8.84 (d, J = 8.3 Hz, 1H), 8.79 (d, J = 9.5 Hz, 1H), 8.77 (d, J = 10.0 Hz, 1H), 8.71−8.69 (m, 1H), 8.00−7.96 (m, 2H), 7.81−7.79 (m, 1H), 7.72−7.68 (m, 1H), 7.64−7.60 (m, 1H), 7.57−7.53 (m, 2H), 7.35 (s, 1H), 1.08 (s, 9H), 0.28 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $C_2D_2Cl_4$): δ = 152.1, 132.5, 131.8, 130.8, 130.0, 129.4, 129.1, 128.5, 127.9, 127.7, 127.65, 127.1, 126.9, 126.7, 126.67 (2C), 126.4, 124.7, 124.0, 123.3, 123.1, 122.6, 121.8, 121.7, 120.1, 114.7, 26.1 (3C), 18.6, −3.8 (2C).

FTIR (KBr, cm^{-1}): 2957 (w), 2927 (w), 1615 (w), 1441 (m), 1284 (m), 1252 (m), 1104 (s), 837 (vs), 762 (vs).

UV−vis ($CHCl_3$): λ_{max} = 298 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 297 nm; λ_{em} = 396 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{32}H_{30}OSi$, 458.2060 [M]$^+$; found, 458.2059.

*4.3.21. tert-Butyl(dibenzo[a,m]picen-17-yloxy)dimethylsilane (**6b**).* Following general procedure E, LDA (0.53 mmol, 0.53 M in anhydrous C_6H_6) was added to solution of **5b** (71 mg, 0.15 mmol) in anhydrous C_6H_6 (2 mL) at 40 °C. The reaction mixture was then stirred for 2 h before adding TBDMSCl (0.53 mL, 0.53 mmol, 1 M in THF) at 40 °C and left to react for 16 h at the same temperature. Standard workup (eluent: 5% EtOAc in heptane) afforded the TBDMS-protected product **6b** (66 mg, 85%) as a red solid.

mp 236.6−238.2 °C (DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (d, J = 9.5 Hz, 1H), 9.20 (d, J = 9.4 Hz, 1H), 9.03 (d, J = 8.4 Hz, 1H), 8.92 (d, J = 8.3 Hz, 1H), 8.88 (d, J = 9.5 Hz, 1H), 8.87 (d, J = 9.6 Hz, 1H), 8.83 (d, J = 9.2 Hz, 1H), 8.02 (app d, J = 9.0 Hz, 3H), 7.90 (app d, J = 8.6 Hz, 1H), 7.78−7.60 (m, 5H), 7.48 (s, 1H), 1.20 (s, 9H), 0.40 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.6, 132.9, 132.1, 131.6, 131.5, 130.5, 130.3, 129.1, 129.0, 128.7, 128.6, 128.4, 128.1, 128.1, 127.9, 127.8, 127.4, 127.2, 126.7, 126.6, 126.3, 125.8, 125.4, 124.9, 123.4, 123.0, 122.0, 121.3, 120.0, 115.4, 26.4 (3C), 18.9, −3.5 (2C).

FTIR (KBr, cm^{-1}): 2926 (w), 2856 (w), 1596 (s), 1532 (m), 1424 (s), 1361 (s), 1259 (vs), 1199 (s), 1105 (vs), 1061 (s), 838 (vs), 781 (vs).

UV−vis ($CHCl_3$): λ_{max} = 317 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 317 nm; λ_{em} = 416 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{36}H_{33}OSi$, 509.2295 [M + H]$^+$; found, 509.2281.

*4.3.22. tert-Butyl(dibenzo[b,m]picen-7-yloxy)dimethylsilane (**6d**).* Following general procedure D, LDA (0.46 mmol, 0.46 M in anhydrous THF) was added to solution of **5d** (71 mg, 0.15 mmol) in anhydrous THF (2 mL). After reaction with TBDMSCl (0.47 mL, 0.47 mmol, 1 M in THF), standard workup (eluent: 30% DCM in heptane) afforded the TBDMS-protected product **6d** (77 mg, quant) as a brown solid.

mp 310.4−312.7 °C (DCM).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 9.95 (d, J = 9.7 Hz, 1H), 9.21 (s, 1H), 9.08 (d, J = 9.5, 1H), 9.02 (d, J = 9.3 Hz, 1H), 8.84 (d, J = 8.4 Hz, 1H), 8.80 (d, J = 9.3 Hz, 1H), 8.76 (d, J = 9.8 Hz, 1H), 8.27 (s, 1H), 8.11 (d, J = 7.5 Hz, 1H), 8.01−7.97 (m, 3H), 7.72−7.68 (m, 1H), 7.64−7.61 (m, 1H), 7.52−7.45 (m, 2H), 7.40 (s, 1H), 1.08 (s, 9H), 0.31 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $C_2D_2Cl_4$): δ = 151.9, 132.1, 131.8, 131.0, 130.9, 130.6, 129.94, 129.9, 129.1, 128.6, 128.5, 127.9, 127.8, 127.7, 127.1, 127.08, 126.8, 126.7, 126.1, 124.9, 124.8, 123.8, 123.3, 122.9, 122.2, 122.0, 121.7, 120.2, 113.8, 99.4, 26.1 (3C), 18.6, −3.8 (2C).

FTIR (KBr, cm^{-1}): 2928 (w), 2857 (w), 1617 (s), 1440 (s), 1261 (vs), 1220 (vs), 1167 (s), 1107 (s), 878 (s), 849 (vs), 814 (s), 780 (s).

UV−vis ($CHCl_3$): λ_{max} = 318 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 316 nm; λ_{em} = 434 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{36}H_{33}OSi$, 509.2295 [M + H]$^+$; found, 509.2286.

*4.3.23. tert-Butyl(dibenzo[c,k]tetraphen-13-yloxy)dimethylsilane (**6e**).* According to general procedure D, **5e** (46 mg, 0.11 mmol) in anhydrous THF (2 mL) was added to LDA (0.28 mmol, 0.28 M in anhydrous THF) at 0 °C and stirred for 30 min. After reaction with TBDMSCl (0.28 mL, 0.28 mmol, 1 M in THF), standard workup

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(eluent: 10% EtOAc in heptane) afforded the protected product **6e** (34 mg, 68%) as a brown solid.

mp 227.4−229.1 °C (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (s, 1H), 9.19 (s, 1H), 8.89 (d, J = 9.0 Hz, 1H), 8.79 (d, J = 9.3 Hz, 1H), 8.78 (d, J = 8.12 Hz, 1H), 8.72 (d, J = 9.2 Hz, 1H), 8.20 (d, J = 9.2 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 8.03 (dd, J = 0.7, 8.0 Hz, 1H), 7.78−7.76 (m, 1H), 7.75−7.70 (m, 1H), 7.67−7.63 (m, 1H), 7.62−7.56 (m, 2H), 7.09 (s, 1H), 1.30 (s, 9H), 0.45 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.1, 133.2, 132.5, 131.0, 130.8, 130.4, 129.1, 128.7, 128.68, 128.2, 128.0, 127.9, 127.8, 127.4, 127.36, 127.2, 126.9, 126.5, 124.9, 123.3, 122.9, 122.3, 121.8, 121.4, 117.9, 110.8, 26.3 (3C), 18.8, −3.9 (2C).

FTIR (KBr, cm^{-1}): 2956 (w), 2926 (w), 1613 (s), 1553 (s), 1455 (vs), 1311 (vs), 1252 (s), 1190 (s), 1104 (vs), 890 (s), 835 (vs), 812 (vs), 780 (vs), 750 (vs).

UV−vis ($CHCl_3$): λ_{max} = 311 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 412 nm; λ_{em} = 311 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{32}H_{31}OSi$, 459.2139 [M + H]$^+$; found 459.2133.

*4.3.24. (Benzo[a]naphtho[2,1-k]tetraphen-15-yloxy)(tert-butyl)-dimethylsilane (**6f**).* According to general procedure E, **5f** (26 mg, 0.06 mmol) in anhydrous C_6H_6 (1 mL), LDA (0.2 mmol. 0.2 M in anhydrous C_6H_6), and TBDMSCl (0.2 mL, 0.2 mmol, 1 M in THF) gave, after completed reaction and standard workup (eluent: 5% EtOAc in heptane), the TBDMS-protected product **6f** (14 mg, 50%) as a red solid along with traces of the unprotected product.

mp 220.1−223.5 °C (cyclohexane + DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H), 9.71 (s, 1H), 9.28 (d, J = 8.5 Hz, 1H), 8.94 (d, J = 9.1 Hz, 1H), 8.82 (d, J = 8.3 Hz, 1H), 8.77 (d, J = 9.2 Hz, 1H), 8.26 (d, J = 9.2 Hz, 1H), 8.14 (d, J = 8.9 Hz, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.79−7.73 (m, 3H), 7.69−7.60 (m, 2H), 7.20 (s, 1H), 1.31 (s, 9H), 0.48 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.5, 132.8, 132.6, 132.0, 130.8, 130.78, 130.7, 130.3, 128.9, 128.8 (2C), 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.2, 126.9, 126.8, 126.5 (2C), 125.1, 123.4, 122.8, 121.8, 121.5, 117.6, 111.5, 26.3 (3C), 18.8, −3.9 (2C).

FTIR (KBr, cm^{-1}): 2953 (w), 2925 (w), 1596 (s), 1422 (m), 1257 (s), 1104 (s), 849 (vs), 750 (s).

UV−vis ($CHCl_3$): λ_{max} = 330 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 329 nm; λ_{em} = 428 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{36}H_{33}OSi$, 509.2295 [M + H]$^+$; found, 509.2289.

*4.3.25. tert-Butyldimethyl(naphtho[1,2-c]pentaphen-8-yloxy)-silane (**6h**).* Following general procedure D, LDA (0.51 mmol, 0.51 M in anhydrous THF), **5h** (80 mg, 0.17 mmol) in anhydrous THF (3 mL), and TBDMSCl (0.56 mL, 0.56 mmol, 1 M in THF) gave, after completed reaction and standard workup (eluent: 30% DCM in heptane), the protected product **6h** (48 mg, 54%) as a brown solid.

mp 246.3−248.1 °C (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63 (s, 1H), 9.27 (s, 1H), 9.20 (s, 1H), 8.85 (d, J = 9.0 Hz, 1H), 8.79 (d, J = 8.40 Hz, 1H), 8.76 (d, J = 9.2 Hz, 1H), 8.24 (d, J = 9.1 Hz, 1H), 8.14 (s, 1H), 8.14−8.12 (m, 1H), 8.08 (d, J = 9.0 Hz, 1H), 8.01 (dd, J = 0.9, 8.0 Hz, 1H), 7.99−7.97 (m, 1H), 7.75−7.70 (m, 1H), 7.67−7.63 (m, 1H), 7.57−7.50 (m, 2H), 7.09 (s, 1H), 1.30 (s, 9H), 0.47 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 149.9, 132.8, 132.5, 131.8, 131.2, 131.1, 130.8, 130.5, 129.4, 128.7, 128.63, 128.6, 128.5, 128.4, 127.8, 127.8, 127.3, 126.9, 126.7, 126.5, 126.1, 125.1, 124.7, 123.3, 122.6, 121.9, 121.89, 121.3, 117.9, 110.4, 26.3 (3C), 18.8, −3.9 (2C).

FTIR (KBr, cm^{-1}): 2955 (w), 2927 (w), 1620 (vs), 1447 (m), 1341 (m), 1252 (s), 1208 (s), 1098 (vs), 888 (vs), 744 (vs).

UV−vis ($CHCl_3$): λ_{max} = 334 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 333 nm; λ_{em} = 445 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{36}H_{33}OSi$, 509.2295 [M + H]$^+$; found, 509.2288.

*4.3.26. (Benzo[c]phenanthren-5-yloxy)(tert-butyl)dimethylsilane (**6ia**).* Freshly prepared LDA (0.72 mmol, 0.72 M in anhydrous C_6H_6) was added to solution of **5i** (65 mg, 0.21 mmol) in anhydrous C_6H_6 (2 mL) at 0 °C and stirred for 30 min. The reaction mixture was then stirred at 40 °C for 1 h before adding TBDMSCl (0.72 mL, 0.72 mmol, 1 M in THF) at RT and left to react for 17 h. Workup similar to standard procedure C (gradient elution 5%−15% EtOAc in heptane) afforded the TBDMS-protected product **6ia** (16 mg, 22%) as a red oil and unprotected product **6ib** (33 mg, 66%) as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$, **6ia**): δ = 9.12 (d, J = 8.4 Hz, 1H), 9.05 (d, J = 8.5 Hz, 1H), 8.45 (dd, J = 1.3, 8.0 Hz, 1H), 7.99 (dd, J = 1.3, 8.0 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.73−7.70 (m, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.69−7.63 (m, 3H), 7.59−7.55 (m, 1H), 7.18 (s, 1H), 1.16 (s, 9H), 0.38 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.3, 132.7, 131.9, 130.5, 129.3, 128.7, 128.0, 127.7, 127.5, 126.5, 126.47, 126.3, 125.6, 125.1, 123.1, 122.9, 111.7, 26.1, 18.7, −4.0.

FTIR (KBr, cm^{-1}): 2956 (w), 2928 (w), 1599 (m), 1254 (m), 1093 (m), 855 (m), 833 (m).

UV−vis ($CHCl_3$): λ_{max} = 290 nm.

Fluorescence ($CHCl_3$): λ_{ex} = 289 nm; λ_{em} = 392 nm.

HRMS (ESI/TOF) m/z: calcd for $C_{24}H_{27}OSi$, 359.1826 [M + H]$^+$; found, 359.1825.

*4.3.27. Benzo[c]phenanthren-5-ol (**6ib**).* Characterization data were in accordance with the literature.[96]

mp 100.6−103.5 °C (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.14 (d, J = 8.5 Hz, 1H), 9.05 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 7.8 Hz, 1H), 7.99 (dd, J = 1.2, 7.9 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.73−7.63 (m, 4H), 7.59−7.55 (m, 1H), 7.09 (br s, 1H), 5.71 (br s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 150.1, 132.6, 131.8, 130.5, 128.7, 128.0, 127.9, 127.4, 126.8, 126.4, 126.1, 126.0, 125.7, 125.0, 122.7, 122.3, 107.4.

FTIR (KBr, cm^{-1}): 3388 (w), 1697 (s), 1674 (s), 1586 (s), 1426 (m), 1276 (m), 1224 (m), 753 (s).

HRMS (ESI) m/z: calcd for $C_{18}H_{11}O_2$, 259.0765 [M − H + O]$^-$; found, 259.0764.

*4.3.28. 2-(3-(bis(Trimethylsilyl)methyl)naphthalen-2-yl)-N,N-diethylchrysene-1-carboxamide (**7**).* Similar to general procedure D, **5d** (96 mg, 0.21 mmol) and TMSCl (0.08 mL, 0.64 mmol) in anhydrous THF (5 mL) were treated with LDA (0.62 mmol, 0.62 M in anhydrous THF) for 1.5 h at 0 °C and warmed to RT over 17 h. Standard workup (gradient elution 5%−15% EtOAc in heptane) afforded the disilylated product 7 (77 mg, 61%) as an off-white solid.

mp 223.0−226.5 °C (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (d, J = 8.7 Hz, 1H), 8.81 (d, J = 6.7 Hz, 1H), 8.79 (d, J = 8.6 Hz, 2H), 8.08 (d, J = 9.1 Hz, 1H), 8.07 (d, J = 9.3 Hz, 1H), 8.03 (dd, J = 1.0, 7.9 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.77−7.66 (m, 4H), 7.64 (s, 1H), 7.55 (s, 1H), 7.50−7.45 (m, 1H), 7.41−7.37 (m, 1H), 3.78−3.69 (m, 1H), 3.47−3.38 (m, 1H), 3.31−3.14 (m, 2H), 2.11 (s, 1H), 1.00−0.94 (m, 6H), 0.13 (s, 9H), 0.10 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.6, 141.5, 138.9, 136.0, 135.4, 133.2, 132.4, 130.8, 130.5, 129.9, 129.7, 128.7, 128.65, 128.6, 128.4, 128.2, 127.9, 127.4, 127.1, 127.0, 126.98, 126.8, 126.0, 125.0, 124.6, 123.3, 122.3, 122.25, 121.3, 42.6, 37.1, 24.0, 13.8, 12.5, 1.4 (3C), 1.2 (3C).

FTIR (KBr, cm^{-1}): 2951 (w), 2896 (w), 1638 (vs), 1438 (s), 1247 (vs), 1095 (m), 839 (vs), 746 (vs).

HRMS (ESI) m/z: calcd for $C_{40}H_{46}ONSi_2$, 612.3112 [M + H]$^+$; found, 612.3119.

*4.3.29. N,N-Diethyl-2-(1-methyl-3-(trimethylsilyl)naphthalen-2-yl)benzamide (**8**).* Similar to the general procedure D, **5j** (123 mg, 0.39 mmol) and TMSCl (0.15 mL, 1.20 mmol) in anhydrous THF (3 mL) were treated with freshly prepared LDA (1.16 mmol, 1.16 M in anhydrous THF) at 0 °C for 1.5 h and then stirred at RT for 16 h. Standard workup (eluent: 30% EtOAc in heptane) afforded product **8** (70 mg, 46%) as a brown amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$, major rotamer): δ = 8.05 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.73−7.68 (m, 1H), 7.67−7.65 (m, 1H), 7.55−7.53 (m, 1H), 7.53−7.49 (m, 1H), 7.43−7.41 (m, 1H), 7.42 (s, 1H), 7.33−7.30 (m, 1H), 3.71−3.61 (m, 1H), 2.98−2.89 (m, 1H), 2.72 (s, 3H), 2.67−2.58 (m, 1H), 2.42−2.33 (m, 1H), 0.55 (t, J = 7.1 Hz, 3H), 0.36−0.32 (m, 3H), 0.33 (s, 9H).

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$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, major rotamer): δ = 170.6, 142.9, 138.8, 136.0, 135.2, 134.2, 134.1, 133.0, 132.5, 131.8, 128.6, 126.8, 126.3, 126.2, 125.7, 125.4, 124.8, 43.0, 37.9, 19.7, 12.9, 11.9, 0.3 (3C).

FTIR (KBr, cm^{-1}): 2957 (m), 2935 (m), 1633 (vs), 1479 (vs), 1460 (vs), 1440 (vs), 1288 (vs), 1243 (vs), 1138 (s), 1112 (s), 1094 (s), 990 (s), 854 (vs).

HRMS (ESI/TOF) *m/z*: calcd for $C_{25}H_{32}ONSi$, 390.2248 $[M + H]^+$; found, 390.2251.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01097.

Overview of applied literature procedures for starting materials, unsuccessful cross-coupling experiments, additional cross-coupling experiments to make **5i** and **5j**, and NMR spectra of the compounds (PDF)

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Notes

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