Synthesis of C9,C10-Diheteroarylated Phenanthrenes via Palladium-Catalyzed C-H Bond Activation

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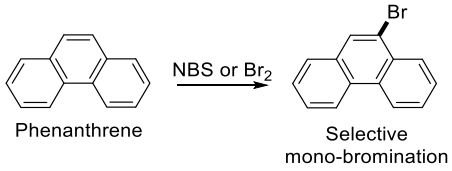
Synthesis of C9,C10-diheteroarylated phenanthrenes via palladium-catalyzed C-H bond activations

Bilel Bouzayani,[a,b] Ridha Ben Salem,*[b] Jean-François Soulé,*[a] and Henri Doucet*[a]

Abstract: The reactivity of positions C9 and C10 of 9- or 10-bromophenanthrenes in palladium-catalyzed direct heteroarylations was investigated. A wide variety of heteroarenes such as thiazoles, (benzo)thiophenes, (benzo)furans, pyrroles, selenophenes or imidazopyridazines was successfully introduced at phenanthrene C9-position *via* palladium-catalyzed direct arylations, using 0.5-0.1 mol% of phosphine-free $Pd(OAc)_2$ catalyst. Then, C10-bromination of the 9-heteroarylated phenanthrenes, followed by a second palladium-catalyzed direct heteroarylation gives access to symmetrical and non-symmetrical 9,10-di(heteroaryl)phenanthrenes.

Introduction

Phenanthrene is one of the most stable fused aromatics with a high resonance energy, employed as unit for the preparation of conjugated systems with a high energy gap [1]. Among phenanthrene derivatives, those bearing heteroarenes at positions C9 and/or C10 are of considerable interest for material chemistry as they are employed as building blocks for access to compounds with photochromic,[2a,2b] molecular rotor [2c] or fluorescence properties [2d]. It is well known that phenanthrene in the presence of *N*-bromosuccinimide or bromine affords selectively 9-bromophenanthrene in high yield, without significant formation of 9,10-dibromophenanthrene [3a,3b]; (Scheme 1). A similar reactivity was observed with other polyaromatic compounds such as a dibenzofluoranthene [3c]. Therefore, the development of simple and reliable routes, using readily accessible 9-bromophenanthrene derivatives as building block, for access to (poly)functionalized phenanthrenes is highly desirable.



Scheme 1. Synthesis of 9-bromophenanthrene

Currently, 9- and 10-heteroarylated phenanthrenes are generally prepared *via* Pd-catalyzed Suzuki or Negishi couplings [4]. However, these reactions require the preliminary preparation of an organometallic (or boron) derivative of an aryl derivative, and provide an organometallic salt (MX) as by-product. Since two decades, the Pd-catalyzed direct (poly)heteroarylation, *via* C–H bond activation of several polyaromatic compounds using aryl halides as aryl source has emerged as a powerful alternative method for the preparation of bi- and poly-(hetero)aryls [5,6]. Compared to the more classical Suzuki, Stille, or Negishi Pd-catalyzed reactions, [7] C–H bond functionalization reactions are often more attractive, as no prior preparation of an organometallic derivative is required, reducing the number of steps to prepare these compounds. However, so far only a few examples of Pd-catalyzed heteroarylations of 9-halophenanthrenes, *via* the C-H bond activation of heteroarenes, have been described [8]. Li et al. employed a mixture of 2 mol% of $Pd(OAc)_2$ associated to 4 mol% PPh_3 for the coupling of 9-bromoanthracene with imidazo[1,2-*a*]pyrimidine [8a]; whereas, Gryko et al. performed this reactions in the absence of phosphine ligand [8e]. Similarly, Fagnou et al. employed a mixture of 2 mol% of $Pd(OAc)_2$ and 4 mol% of PCy_3 to promote the coupling of 9-bromoanthracene with a thiazole derivative [8c]. In 2015, Langer et al. reported the coupling of 9-bromoanthracene with an imidazole derivative using 5 mol% of $PdCl_2(PPh_3)_2$ catalyst in the presence of 1.2 equiv. of CuI, and 0.3 equiv. of PivOH as additive and K_2CO_3 as base [8d]. A few examples of metal-catalyzed heteroarylations of phenanthrenes, proceeding *via* base deprotonation of (benzo)oxazoles or (benzo)thiazoles, have also been reported [9]. It should be mentioned that for all these procedures, the substrate scope was not studied in detail, as only one or two specific heteroarenes were employed. Moreover, to our knowledge, the Pd-catalyzed direct 9,10-diheteroarylation of phenanthrene has not been described yet.

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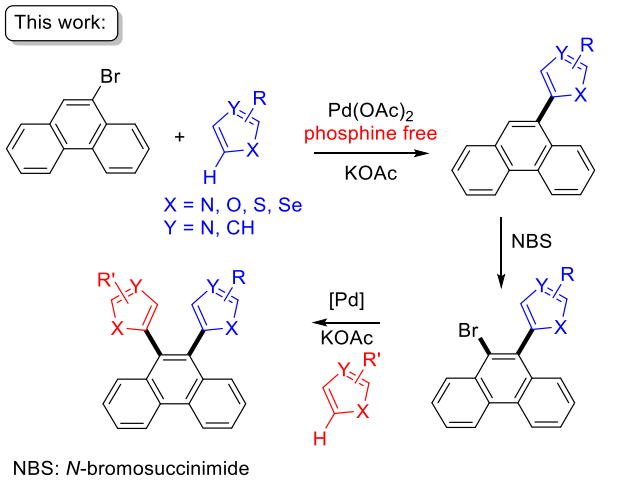
Here, we wish to report on the access i) to a wide variety of 9-heteroarylated phenanthrenes using Pd-catalyzed direct arylation reactions, and ii) to symmetrical and non-symmetrical 9,10-diheteroarylated phenanthrenes *via* successive Pd-catalyzed direct heteroarylations (Scheme 2).

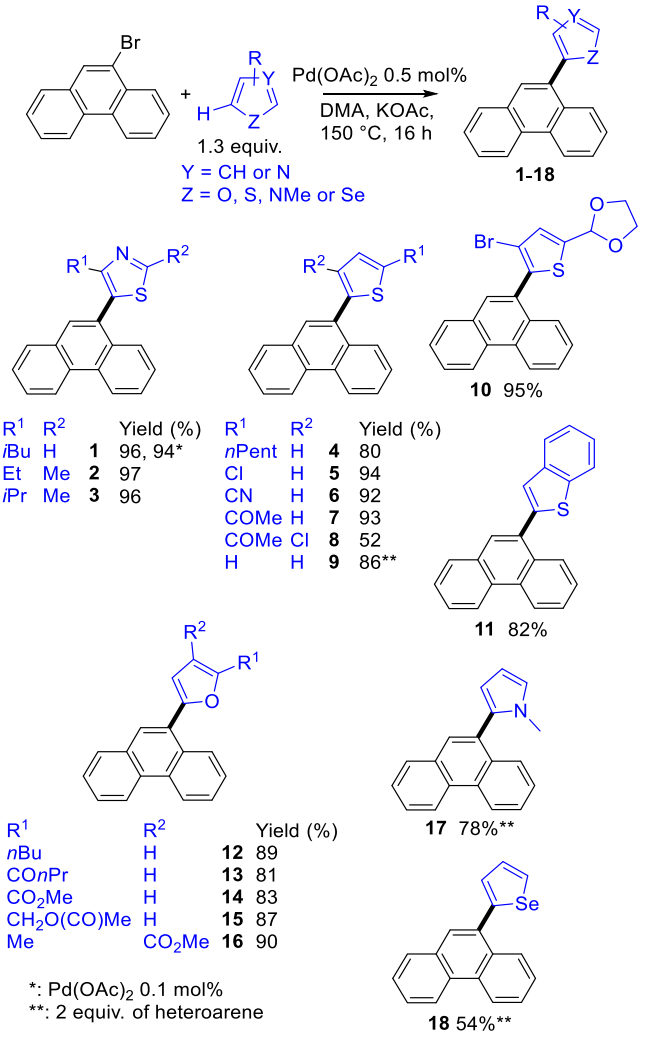


Scheme 2. Access to 9,10-diheteroarylated phenanthrenes *via* successive Pd-catalyzed direct heteroarylations

Results and Discussion

In 2003, de Vries et al. reported that, when $Pd(OAc)_2$ is employed as the catalyst precursor, at elevated temperature, soluble palladium(0) colloids or nanoparticles are formed, which are very efficient catalysts in the Suzuki or Heck reactions [10]. From 2008, we have reported that the coupling of aryl bromides with several heteroaromatics with a variety of aryl halides proceed nicely under the de Vries conditions [11], but we had not employed phenanthrene derivatives. First, we examined the reactivity of a set or heteroarenes for coupling with 9-bromophenanthrene using our previously reported phosphine-free Pd-catalyst conditions [11]. Starting from, a slight excess of 2-isobutylthiazole (1.3 equiv.) with respect to 9-bromophenanthrene, in the presence of 0.5 or 0.1 mol% $Pd(OAc)_2$ catalyst, KOAc as the base, and DMA as the solvent at 150°C, the desired product **1** was obtained in 96% and 94% yields, respectively (Scheme 3). No formation of side-products was detected in the course of this reaction.

Then, the reactivity of a set of heteroarenes for reaction with 9-bromophenanthrene, under the same conditions, was examined. The reaction of 4-methylthiazoles bearing ethyl or isopropyl substituents at C2-position with 9-bromophenanthrene in the presence of 0.5 mol% $Pd(OAc)_2$ catalyst gave **2** and **3** in 97% and 96% yields, respectively. In the presence of thiophene derivatives bearing pentyl, chloro, cyano or acetyl substituents at C2-position, the regioselective arylation at thienyl C5-position was observed affording **4**-**7** in 80-94% yields (Scheme 3). A C2-substituted thiophene derivative containing also a chloro-substituent at C4-position was tolerated affording **8**, without cleavage of the C-Cl bond. The mono-arylation of thiophene with 9-bromophenanthrene was also examined. The desired product **9** could be selectively obtained in 86% yield, using 2 equiv. of this heteroarene. A thiophene derivative bearing acetal- and bromo-substituents at C2- and C4-positions gave the corresponding coupling product **10** without deprotection of the acetal unit and without cleavage of the thienyl C-Br bond. From benzothiophene, the regioselective C2-arylation was observed affording **11** in 82% yield. Then, the reactivity of a set of furan derivatives was examined. From furan derivatives bearing methyl, *n*butyl, butyryl, ester or methyl acetate substituents at C2-position, the desired (phenanthren-9-yl)furan derivatives **12**-**16** were obtained in 81-90% yields. The reaction of 2 equiv. of 1-methylpyrrole or selenophene with 9-bromophenanthrene, under the same reaction conditions, was also successful to afford **17** and **18** in 78% and 54% yields, respectively.



R^1	R^2		Yield (%)
*i*Bu	H	**1**	96, 94*
Et	Me	**2**	97
*i*Pr	Me	**3**	96

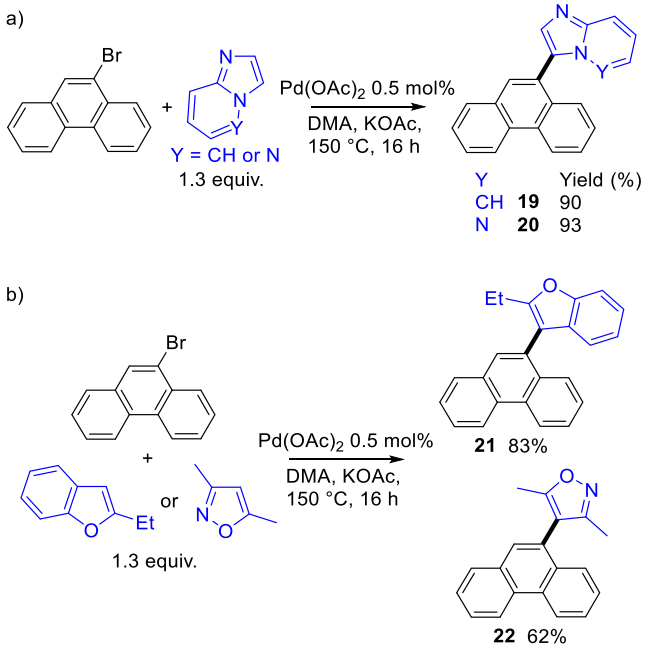
R^1	R^2		Yield (%)
*n*Pent	H	**4**	80
Cl	H	**5**	94
CN	H	**6**	92
COMe	H	**7**	93
COMe	Cl	**8**	52
H	H	**9**	86**

R^1	R^2		Yield (%)
*n*Bu	H	**12**	89
CO*n*Pr	H	**13**	81
CO_2Me	H	**14**	83
$CH_2O(CO)Me$	H	**15**	87
Me	CO_2Me	**16**	90

*: $Pd(OAc)_2$ 0.1 mol%
**: 2 equiv. of heteroarene

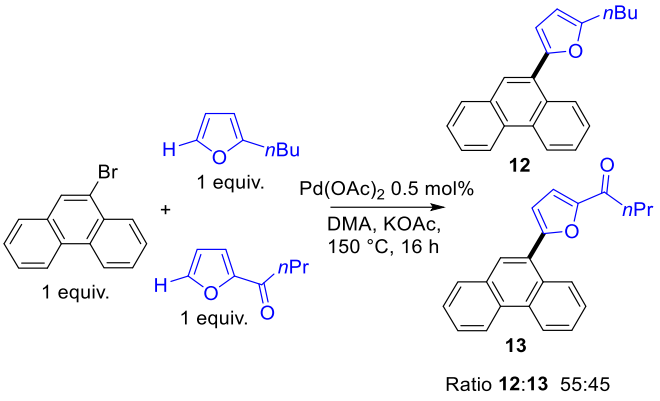
Scheme 3. Pd-catalyzed direct heteroarylations of 9-bromophenanthrenes with heteroarenes

The C3-arylation of both imidazo[1,2-*a*]pyridine and imidazo[1,2-*a*]pyrimidine with 9-bromophenanthrene, using again 0.5 mol% $Pd(OAc)_2$ catalyst, also proceeded with complete regioselectivity affording **19** and **20** in very high yields (Schema 4, a). The reaction is not limited to the arylation at α-position of an heteroelement of heterocycles. For example, the coupling of 9-bromophenanthrene with 2-ethylbenzofuran gave the *β*-arylated benzofuran derivative **21** in 83% yield; and from 3,5-dimethylisoxazole, the C4-arylated compound **22** was obtained in 62% yield (Schema 4, b).



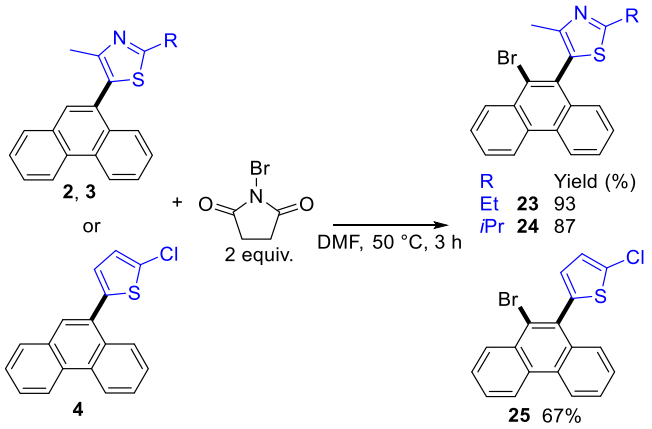
Scheme 4. Pd-catalyzed direct heteroarylations of 9-bromophenanthrenes with imidazopyridine, imidazopyrimidine, a benzofuran and an isoxazole

In order to determine the electronic influence of heteroarene substituents on the reaction rate, a competition experiment was performed (Scheme 5). Using an equimolar mixture of furan derivatives bearing *n*butyl and butyryl C2-substituents, the formation of products **12** and **13** in 55:45 ratio was observed, revealing that an electron-donating substituent on furan slightly favors the reactions.



Scheme 5. Competition reaction for Pd-catalyzed direct heteroarylation of 9-bromophenanthrene

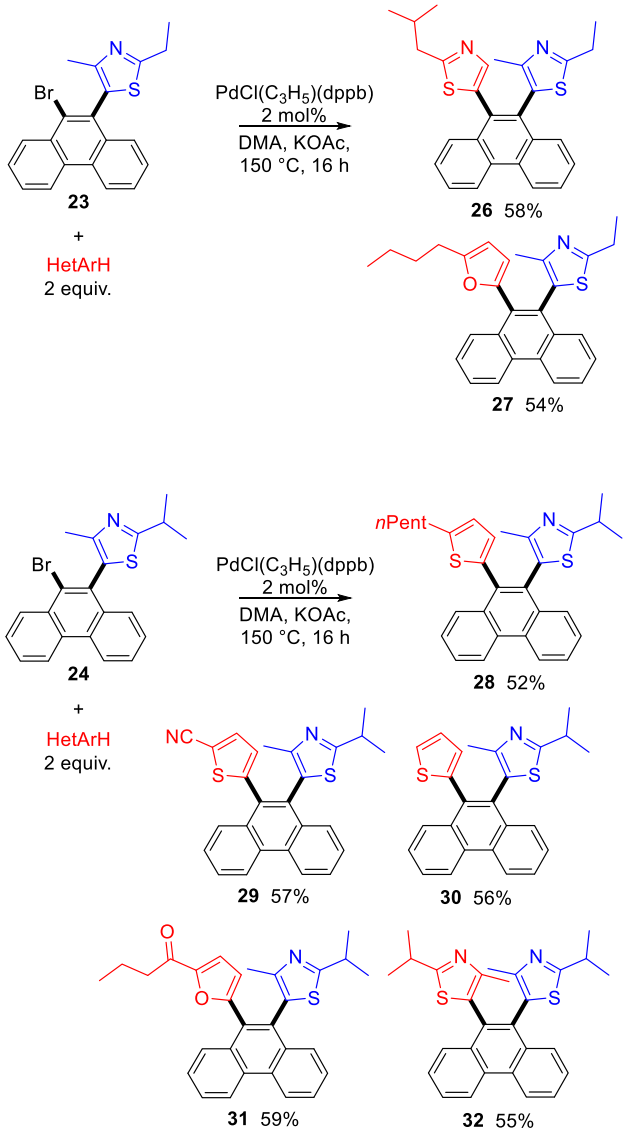
In order to prepare symmetrical and non-symmetrical C9,C10-diheteroarylated phenanthrenes, which might be useful for the preparation of photochromic compounds,[2a,2b] the reactivity of 2-ethyl-4-methyl-5-(phenanthren-9-yl)thiazole **2** with *N*-bromosuccinimide (NBS) was studied (Scheme 6). At room temperature, a poor conversion of **2** and a low yield in the desired 10-bromophenanthrene derivative **23** was observed; whereas, the reaction performed at 50°C during 3 h afforded **23** in a high 93% yield. A similar yield in **24** was obtained by reaction of **3** with NBS. From 2-chloro-5-(phenanthren-9-yl)thiophene **4**, under the same reaction conditions, the 10-bromo-substituted phenanthrene **25** was obtained in 67% yield.



Scheme 6. Reaction of **2** and **4** with *N*-bromosuccinimide

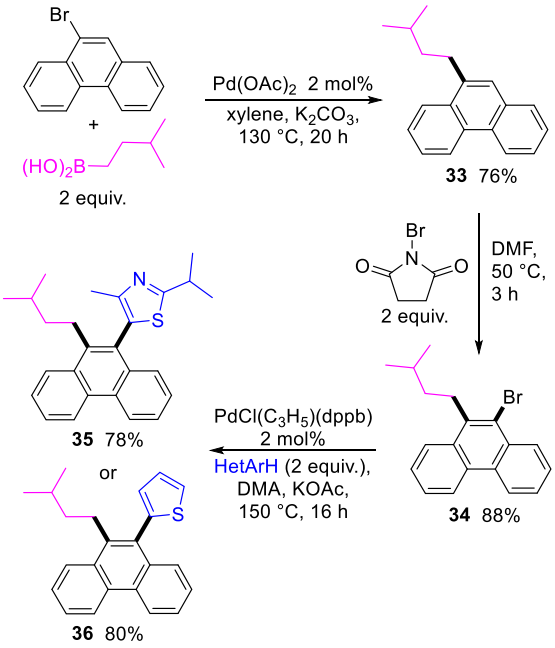
Then, the Pd-catalyzed direct heteroarylation of **23** at C10-position with 2-isobutylthiazole was investigated (Scheme 7). Our first attempt using 1 mol% $Pd(OAc)_2$ catalyst afforded the target product **26** in low yield due to a poor conversion of **23**. On the other hand, the use of 2 mol% of the thermally more stable catalyst $PdCl(C_3H_5)(dppb)$ [12] gave **26** in higher 58% yield with a good conversion of **23**. From **23** and 2-*n*butylfuran, the phenanthrene derivative **27** bearing furan and thiazole units

at C9 and C10 positions was obtained in 54% yield. The reaction of **24** with a set of thiophenes, and with a furan derivative also provided the desired 9,10-diheteroarylated phenanthrenes **28**-**31** in 52-59% yields. Finally, the reaction of **24** with 2-isopropyl-4-methylthiazole gave access to the symmetrical 9,10-bis(2-isopropyl-4-methylthiazol-5-yl)phenanthrene **32** in 55% yield.



Scheme 7. Palladium-catalyzed direct heteroarylations of 10-bromophenanthrene derivatives

Finally, the influence of an isopentyl substituent at C9-position of 10-bromophenanthrene on heteroarylation reaction was investigated (Scheme 8). 9-Bromo-10-isopentylphenanthrene **34** was prepared from 9-bromophenanthene *via* Suzuki coupling followed by bromination with NBS. The reaction of **34** with 2-isopropyl-4-methylylthiazole and thiophene afforded the desired C10-heteroarylated phenanthrenes bearing an isopentyl substituent at C9 position **35** and **36** in 78% and 80% yields, respectively.



Scheme 8. Palladium-catalyzed direct heteroarylations of a bromophenanthrene derivative

Conclusions

In summary, we have demonstrated that using as little as 0.5 mol% of $Pd(OAc)_2$ as the catalyst precursor, 9-bromophenanthrene can be heteroarylated at C9-position, *via* a C-H bond activation of heteroarenes. A wide variety of heteroarenes such as thiazoles, (benzo)thiophenes, selenophenes, (benzo)furans, pyrroles, imidazopyridazine or isoxazoles was successfully employed, and the reaction tolerated useful functional groups on the heteroarenes such as chloro, bromo, cyano, acetyl, butyryl, methyl acetate or ester substituents. This phosphine-free catalyst procedure is environmentally and economically attractive, as 1) there is no need to eliminate phosphine residues at the end of the reaction, 2) this C-H bond functionalization reaction does not no require the preparation of an organometallic derivative, reducing the number of synthetic steps and the mass of waste products, 3) the major waste of theses couplings is the relatively non-toxic AcOH/KBr instead of metallic salts with more classical metal-catalyzed coupling reactions. Moreover, the reaction of some of the 9-heteroarylated phenanthrenes with *N*-bromosuccinimide provided the 10-bromophenanthrene derivatives, which were successfully employed for access to symmetrical or non-symmetrical 9,10-di(heteroaryl)phenanthrenes. This methodology appears to be very promising for the sustainable synthesis of 9,10-diheteroarylated phenanthrenes, and could certainly be applied to the preparation of some heteroarylated benzoanthracenes, pyrenes, chrysenes,

phenanthrophenantrenes or even coronene derivatives which are important structures in material chemistry.

Experimental Section

General

All reactions were performed in Schlenk tubes under argon. Potassium acetate 99+ was used. 9-Bromophenanthrene (98%) was purchased from Alfa. DMA (99%) was purchased from Acros. $Pd(OAc)_2$, $[Pd(C_3H_5)Cl]_2$, 1.4-bis(diphenylphosphino)butane (98%) were purchased from Alfa Aesar. The heteroarenes and 9-bromophenanthrene were used without purification. NMR spectra were recorded on Bruker GPX (400 MHz) spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (^{1}H: 7.26 and ^{13}C: 77.0). Flash chromatography was performed on silica gel (230-400 mesh).

Preparation of the $PdCl(C_3H_5)$(dppb) catalyst [12]

An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ = 19.3 (s).

General procedure for the synthesis of compounds 1-22

In a typical experiment, 9-bromophenanthrene (0.257 g, 1 mmol), the heteroarene (1.3 or 2 mmol) (see schemes), KOAc (0.196 g, 2 mmol) and $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) were dissolved in DMA (4 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography.

2-Isobutyl-5-(phenanthren-9-yl)thiazole (1) [8c]

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-isobutylthiazole (0.183 g, 1.3 mmol), **1** was obtained in 96% (0.304 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.21 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.90-7.83 (m, 3H), 7.74-7.58 (m, 4H), 3.03 (d, *J* = 7.2 Hz, 2H), 2.28 (m, 1H), 1.15 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 141.4, 135.5, 131.1, 131.0, 130.7, 130.4, 129.7, 128.8, 127.6, 127.3, 127.1, 127.0, 126.9, 126.2, 123.0, 122.6, 42.6, 29.9, 22.5.

2-Ethyl-4-methyl-5-(phenanthren-9-yl)thiazole (2)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.166 g, 1.3 mmol), **2** was obtained in 97% (0.294 g) yield as a yellow solid: mp 137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.80 (s, 1H), 7.66 (t, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 2H), 3.15 (q, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 1.52 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 149.6, 131.4, 131.2, 130.6, 130.5, 130.4, 128.8, 128.1, 127.9, 127.3, 127.0, 126.9, 126.8, 126.6, 123.0, 122.6, 27.1, 15.9, 14.4. elemental analysis: calcd (%) for $C_{20}H_{17}NS$ (303.42): C 79.17, H 5.65; found: C 79.04, H 5.34.

2-Isopropyl-4-methyl-5-(phenanthren-9-yl)thiazole (3)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-isopropyl-4-methylthiazole (0.183 g, 1.3 mmol), **3** was obtained in 96% (0.304 g) yield as a yellow solid: mp 129-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.2 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.81 (s, 1H), 7.76-7.58 (m, 4H), 3.43 (sept., *J* = 7.5 Hz, 1H), 2.29 (s, 3H), 1.52 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 149.5, 131.5, 131.2, 130.6, 130.5, 130.4, 128.8, 128.2, 127.6, 127.3, 127.0, 126.9, 126.8, 126.7, 123.0, 122.6, 33.5, 23.4, 16.0. elemental analysis: calcd (%) for $C_{21}H_{19}NS$ (317.45): C 79.46, H 6.03; found: C 79.50, H 5.89.

2-Pentyl-5-(phenanthren-9-yl)thiophene (4)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-pentylthiophene (0.200 g, 1.3 mmol), **4** was obtained in 80% (0.264 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.80 (d, *J* = 8.2 Hz, 1H), 8.58 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.05-8.00 (m, 2H), 7.80-7.67 (m, 4H), 7.30 (d, *J* = 3.3 Hz, 1H), 7.04 (d, *J* = 3.3 Hz, 1H), 3.03 (t, *J* = 7.4 Hz, 2H), 1.92 (quint., *J* = 7.4 Hz, 2H), 1.60-1.48 (sext., 4H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 139.3, 131.7, 131.6, 131.4, 131.0, 130.3, 129.0, 128.9, 127.5, 127.1, 127.0, 126.9 (*2), 126.8, 124.5, 123.1, 122.7, 31.7 (*2), 30.4, 22.8, 14.4. elemental analysis: calcd (%) for $C_{23}H_{22}S$ (330.49): C 83.59, H 6.71; found: C 83.67, H 6.58.

2-Chloro-5-(phenanthren-9-yl)thiophene (5)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-chlorothiophene (0.154 g, 1.3 mmol), **5** was obtained in 94% (0.276 g) yield as a green solid: mp 116-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.31 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.85 (s, 1H), 7.78-7.62 (m, 4H), 7.10 (d, *J* = 3.7 Hz, 1H), 7.08 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 131.1, 130.8, 130.7, 130.4, 130.2, 129.8, 129.4, 128.9, 127.3, 127.1, 127.0, 126.9, 126.5, 126.4, 123.1, 122.6. elemental analysis: calcd (%) for $C_{18}H_{11}ClS$ (294.80): C 73.34, H 3.76; found: C 73.17, H 3.58.

5-(Phenanthren-9-yl)thiophene-2-carbonitrile (6)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-thiophenecarbonitrile (0.142 g, 1.3 mmol), **6** was obtained in 92% (0.262 g) yield as a white solid: mp 169-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.78-7.62 (m, 5H), 7.31 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 137.6, 130.8, 130.7, 130.2, 130.0, 129.0, 128.5, 128.0, 127.9, 127.3, 127.2, 125.9, 123.2, 122.7, 114.3, 109.4. elemental analysis: calcd (%) for $C_{19}H_{11}NS$ (285.36): C 79.97, H 3.89; found: C 80.12, H 3.68.

1-(5-(Phenanthren-9-yl)thiophen-2-yl)ethan-1-one (7)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-acetylthiophene (0.164 g, 1.3 mmol), **7** was obtained in 93% (0.281 g) yield as a yellow solid: mp 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.71 (d, *J* = 8.2 Hz, 1H), 8.23 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.88 (s, 1H), 7.80 (d, *J* = 3.7 Hz, 1H), 7.75-7.60 (m, 4H), 7.33 (d, *J* = 3.7 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 150.7, 144.1, 132.7, 130.9, 130.7, 130.5, 130.2, 130.0, 129.4, 129.0, 128.7, 127.6, 127.2, 127.1, 127.0, 126.2, 123.1, 122.6, 26.8. elemental analysis: calcd (%) for $C_{20}H_{14}OS$ (302.39): C 79.44, H 4.67; found: C 79.58, H 4.39.

1-(4-Chloro-5-(phenanthren-9-yl)thiophen-2-yl)ethan-1-one (8)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 1-(4-chlorothiophen-2-yl)ethan-1-one (0.209 g, 1.3 mmol), **8** was obtained in 52% (0.175 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.7, Hz, 1H), 7.86 (s, 1H), 7.82 (d, *J* = 8.0, Hz, 1H), 7.80-7.60 (m, 5H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 143.4, 142.4, 132.6, 130.9, 130.8, 130.7, 130.5, 130.0, 129.2, 127.9, 127.3, 127.2 (*2), 127.1, 126.5, 125.3, 123.4, 122.7, 26.5. elemental analysis: calcd (%) for $C_{20}H_{13}ClOS$ (336.83): C 71.32, H 3.89; found: C 71.50, H 3.99.

2-(Phenanthren-9-yl)thiophene (9) [13]

From 9-bromophenanthrene (0.257 g, 1 mmol) and thiophene (0.168 g, 2 mmol), **9** was obtained in 86% (0.224 g) yield as a green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 8.37 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.98-7.92 (m, 2H), 7.80-7.65 (m, 4H), 7.53 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.39 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.29 (dd, *J* = 5.2, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 131.3, 131.2, 131.1, 130.8, 130.3, 129.2, 128.9, 127.8, 127.4, 127.1, 127.0, 126.9, 126.8, 126.7, 125.7, 123.0, 122.9.

2-(4-Bromo-5-(phenanthren-9-yl)thiophen-2-yl)-1,3-dioxolane (10)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-(4-bromothiophen-2-yl)-1,3-dioxolane (0.305 g, 1.3 mmol), **10** was obtained in 95% (0.390 g) yield as a yellow solid: mp 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.97-7.89 (m, 3H), 7.79-7.70 (m, 2H), 7.70-7.62 (m, 2H), 7.48 (s, 1H), 6.16 (s, 1H), 4.30-4.05 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 143.7, 131.0, 130.6 (m), 130.1, 129.3, 128.1, 127.6, 127.4, 127.3, 127.2, 127.1, 126.0, 123.2, 122.7, 114.7, 110.2, 99.4, 65.6. elemental analysis: calcd (%) for $C_{21}H_{15}BrO_2S$ (411.31): C 61.32, H 3.68; found: C 61.18, H 3.87.

2-(Phenanthren-9-yl)benzo[*b*]thiophene (11) [14]

From 9-bromophenanthrene (0.257 g, 1 mmol) and benzothiophene (0.174 g, 1.3 mmol), **11** was obtained in 82% (0.254 g) yield as a yellow solid: mp 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 8.40 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.02-7.89 (m, 4H), 7.80-7.63 (m, 4H), 7.56 (s, 1H), 7.55-7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 140.3, 140.2, 131.2, 131.1, 130.9, 130.7, 130.4, 129.6, 129.0, 127.3, 127.1, 126.9, 126.8, 126.7, 124.6, 124.4, 124.3, 123.7, 123.0, 122.6, 122.2.

2-Butyl-5-(phenanthren-9-yl)furan (12)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-butylfuran (0.161 g, 1.3 mmol), **12** was obtained in 89% (0.267 g) yield as a white solid: mp 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 8.58 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.07 (s, 1H), 7.99 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.78-7.60 (m, 4H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.88 (quint., *J* = 7.4 Hz, 2H), 1.57 (sext., *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 151.5, 131.6, 130.9, 130.1, 129.7, 128.9, 127.8, 126.9 (m), 126.8, 126.7, 126.6, 126.5, 123.1, 122.6, 110.4, 106.7, 30.4, 28.1, 22.5, 14.0. elemental analysis: calcd (%) for $C_{22}H_{20}O$ (300.40): C 87.96, H 6.71; found: C 87.80, H 6.49.

1-(5-(Phenanthren-9-yl)furan-2-yl)butan-1-one (13)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 1-(furan-2-yl)butan-1-one (0.179 g, 1.3 mmol), **13** was obtained in 81% (0.254 g) yield as a yellow solid: mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.70 (d, *J* = 8.2 Hz, 1H), 8.42 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.11 (s, 1H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.77-7.62 (m, 4H), 7.40 (d, *J* = 3.5 Hz, 1H), 6.91 (d, *J* = 3.5 Hz, 1H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.88 (sext., *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 157.1, 152.4, 130.9, 130.8, 130.7, 129.2, 129.1, 128.8, 127.8, 127.2, 127.1, 127.0, 126.0, 125.8, 123.2, 122.6, 118.5, 111.9, 40.5, 18.1, 14.0. elemental analysis: calcd (%) for $C_{22}H_{18}O_2$ (314.38): C 84.05, H 5.77; found: C 84.02, H 5.80.

Methyl 5-(phenanthren-9-yl)furan-2-carboxylate (14)

From 9-bromophenanthrene (0.257 g, 1 mmol) and methyl furan-2-carboxylate (0.164 g, 1.3 mmol), **14** was obtained in 83% (0.251 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.71 (d, *J* = 8.2 Hz, 1H), 8.41 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.12 (s, 1H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.76-7.61 (m, 4H), 7.43 (d, *J* = 3.5 Hz, 1H), 6.89 (d, *J* = 3.5 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 157.1, 144.0, 130.9, 130.7, 130.6, 129.2, 129.1, 128.8, 127.7, 127.2, 127.1, 126.9, 126.0, 125.9, 123.1, 122.6, 119.6, 111.6, 52.0. elemental analysis: calcd (%) for $C_{20}H_{14}O_3$ (302.33): C 79.46, H 4.67; found: C 79.34, H 4.50.

Methyl 2-(5-(phenanthren-9-yl)furan-2-yl)acetate (15)

From 9-bromophenanthrene (0.257 g, 1 mmol) and furfuryl acetate (0.182 g, 1.3 mmol), **15** was obtained in 87% (0.275 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 8.3 Hz, 1H), 8.71 (d, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.05 (s, 1H), 7.95 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.78-7.60 (m, 4H), 6.78 (d, *J* = 3.2 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 5.27 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 154.0, 149.4, 131.3, 130.8, 130.3, 129.5, 129.0, 127.7, 127.2 (m), 127.0, 126.7, 126.2, 123.1, 122.6, 112.5, 110.6, 58.4, 21.0. elemental analysis: calcd (%) for $C_{21}H_{16}O_3$ (316.36): C 79.73, H 5.10; found: C 79.48, H 4.89.

Methyl 2-methyl-5-(phenanthren-9-yl)furan-3-carboxylate (16)

From 9-bromophenanthrene (0.257 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate (0.182 g, 1.3 mmol), **16** was obtained in 90% (0.284 g) yield as a white solid: mp 159-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.01 (s, 1H), 7.92 (d, *J* = 8.0, Hz, 1H), 7.78-7.60 (m, 4H), 7.06 (s, 1H), 3.94 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 159.2, 151.1, 131.2, 130.8, 130.3, 129.2, 129.0, 127.5, 127.3, 127.0, 126.9, 126.8, 126.3, 125.9, 123.1, 122.6, 115.0, 110.2, 51.5, 14.0. elemental analysis: calcd (%) for $C_{21}H_{16}O_3$ (316.36): C 79.73, H 5.10; found: C 79.80, H 4.97.

1-Methyl-2-(phenanthren-9-yl)-pyrrole (17)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 1-methylpyrrole (0.249 g, 2 mmol), **17** was obtained in 78% (0.200 g) yield as a yellow solid: mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.78 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.80 (s, 1H), 7.78-7.56 (m, 5H), 6.88 (dd, *J* = 2.6, 1.8 Hz, 1H), 6.39-6.32 (m, 2H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4, 132.2, 131.4, 130.4, 130.3, 129.9, 129.8, 128.8, 127.0, 126.9, 126.8 (2C), 126.6, 122.8, 122.5, 122.4, 110.0, 107.6, 34.5. elemental analysis: calcd (%) for $C_{19}H_{15}N$ (257.34): C 88.68, H 5.88; found: C 88.69, H 5.82.

2-(Phenanthren-9-yl)selenophene (18)

From 9-bromophenanthrene (0.257 g, 1 mmol) and selenophene (0.262 g, 2 mmol), **18** was obtained in 54% (0.166 g) yield as a green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.2 Hz, 1H), 8.75 (d, *J* = 8.2 Hz, 1H), 8.38 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.20 (dd, *J* = 3.8, 3.0 Hz, 1H), 7.98-7.92 (m, 2H), 7.79-7.63 (m, 4H), 7.54-7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 133.1, 131.5, 131.4, 131.1, 130.7, 130.2, 130.0, 129.8, 129.0, 128.9, 127.1 (*2), 126.9, 126.8, 126.7, 122.9, 122.7. elemental analysis: calcd (%) for $C_{18}H_{12}Se$ (307.25): C 70.36, H 3.94; found: C 70.24, H 4.14.

3-(Phenanthren-9-yl)imidazo[1,2-a]pyridine (19) [8e]

From 9-bromophenanthrene (0.257 g, 1 mmol) and imidazo[1,2-*a*]pyridine (0.153 g, 1.3 mmol), **19** was obtained in 90% (0.265 g) yield as a white solid: mp 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 7.96-7.88 (m, 3H), 7.81-7.63 (m, 5H), 7.58-7.50 (m, 2H), 7.25 (dd, *J* = 9.0, 6.6 Hz, 1H), 6.71 (t, *J* = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 134.0, 131.3, 130.8, 130.7 (*2), 130.6, 129.0, 127.7, 127.3, 127.2, 127.1, 126.0, 125.0, 124.3, 124.2, 123.7, 123.3, 122.7, 118.1, 112.3.

3-(Phenanthren-9-yl)imidazo[1,2-b]pyridazine (20)

From 9-bromophenanthrene (0.257 g, 1 mmol) and imidazo[1,2-*a*]pyrimidine (0.155 g, 1.3 mmol), **20** was obtained in 93% (0.274 g) yield as a white solid: mp 259-261 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 8.32 (d, *J* = 3.3 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.08 (s, 1H), 8.03 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.79-7.60 (m, 4H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 9.2, 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 139.6, 134.7, 131.2, 130.9, 130.8, 130.7, 130.5, 129.1, 127.8, 127.5, 127.0, 126.9, 126.8, 126.3, 126.0, 124.6, 123.2, 122.7, 116.7. elemental analysis: calcd (%) for $C_{20}H_{13}N_3$ (295.35): C 81.34, H 4.44; found: C 81.50, H 4.31.

2-Ethyl-3-(phenanthren-9-yl)benzofuran (21)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 2-ethylbenzofuran (0.190 g, 1.3 mmol), **21** was obtained in 83% (0.267 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.83 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.84 (s, 1H), 7.80-7.67 (m, 3H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 8.1 Hz, 1H), 7.29-7.19 (m, 2H), 2.85 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 154.2, 131.8, 131.7, 130.8, 130.5, 130.4, 129.2, 129.0, 128.7, 127.0, 126.9 (2C), 126.8, 126.7, 123.7, 123.1, 122.8, 122.7, 120.2, 114.8, 111.0, 20.6, 13.0. elemental analysis: calcd (%) for $C_{24}H_{18}O$ (322.41): C 89.41, H 5.63; found: C 89.60, H 5.47.

3,5-Dimethyl-4-(phenanthren-9-yl)isoxazole (22)

From 9-bromophenanthrene (0.257 g, 1 mmol) and 3,5-dimethylisoxazole (0.126 g, 1.3 mmol), **22** was obtained in 62% (0.169 g) yield as a white solid: mp 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.78-7.56 (m, 6H), 2.34 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 160.2, 131.3, 131.1, 130.7, 130.4, 129.5, 128.6, 127.2, 127.1, 127.0, 126.9, 126.3, 125.9, 123.2, 122.6, 115.0, 11.5, 10.6. elemental analysis: calcd (%) for $C_{19}H_{15}NO$ (273.34): C 83.49, H 5.53; found: C 83.67, H 5.47.

5-(10-Bromophenanthren-9-yl)-2-ethyl-4-methylthiazole (23)

2-Ethyl-4-methyl-5-(phenanthren-9-yl)thiazole **2** (0.303 g, 1 mmol) and *N*-bromosuccinimide (0.356 g, 2 mmol) were dissolved in DMF (5 mL) under an argon atmosphere. The reaction mixture was stirred at 50 °C for 3 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **23** was obtained in 93% (0.355 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78-8.71 (m, 2H), 8.55 (d, *J* = 8.2 Hz, 1H), 7.80-7.67 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.57 (t, *J* = 7.0 Hz, 1H), 3.16 (q, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.52 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 150.3, 132.5, 131.5, 130.4, 129.7, 129.6, 129.2, 128.2, 128.1, 127.9, 127.6, 127.5, 127.2, 127.1, 122.8, 122.7, 27.1, 15.5, 14.2. elemental analysis: calcd (%) for $C_{20}H_{16}BrNS$ (382.32): C 62.83, H 4.22; found: C 62.90, H 4.07.

5-(10-Bromophenanthren-9-yl)-2-isopropyl-4-methylthiazole (24)

2-Isopropyl-4-methyl-5-(phenanthren-9-yl)thiazole **3** (0.317 g, 1 mmol) and *N*-bromosuccinimide (0.356 g, 2 mmol) were dissolved in DMF (5 mL) under an argon atmosphere. The reaction mixture was stirred at 50 °C for 3 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **24** was obtained in 87% (0.344 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78-8.71 (m, 2H), 8.55 (d, *J* = 8.0 Hz, 1H), 7.84-7.51 (m, 5H), 3.44 (sext., *J* = 7.5 Hz, 1H), 2.19 (s, 3H), 1.54 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.5, 150.2, 132.5, 131.5, 130.4, 129.8, 129.7, 129.2, 128.1, 127.9 (*2), 127.6, 127.5, 127.3, 127.2, 122.8, 122.7, 33.5, 23.3, 15.5. elemental analysis: calcd (%) for $C_{21}H_{18}BrNS$ (396.35): C 63.64, H 4.58; found: C 63.51, H 4.30.

2-(10-Bromophenanthren-9-yl)-5-chlorothiophene (25)

2-Chloro-5-(phenanthren-9-yl)thiophene **4** (0.295 g, 1 mmol) and *N*-bromosuccinimide (0.356 g, 2 mmol) were dissolved in DMF (5 mL) under an argon atmosphere. The reaction mixture was stirred at 50 °C for 3 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **25** was obtained in 67% (0.250 g) yield as a white solid: mp 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75-8.69 (m, 2H), 8.54 (d, *J* = 8.2 Hz, 1H), 7.82-7.62 (m, 4H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 3.7 Hz, 1H), 6.89 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 132.9, 131.4, 130.7, 130.2, 129.5, 129.4, 128.2, 128.1, 127.9, 127.5 (*2), 127.2, 127.1, 126.1, 122.7, 122.6. elemental analysis: calcd (%) for $C_{18}H_{10}BrClS$ (373.69): C 57.85, H 2.70; found: C 57.79, H 2.78.

2-Ethyl-5-(10-(2-isobutylthiazol-5-yl)phenanthren-9-yl)-4-methylthiazole (26)

5-(10-Bromophenanthren-9-yl)-2-ethyl-4-methylthiazole **23** (0.191 g, 0.5 mmol), 2-isobutylthiazole (0.141 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **26** was obtained in 58% (0.128 g) yield as a white solid: mp 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.2 Hz, 2H), 7.86 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.79-7.72 (m, 2H), 7.68 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.64-7.58 (m, 2H), 7.53 (s, 1H), 2.99 (q, *J* = 7.5 Hz, 2H), 2.89 (d, *J* = 7.2 Hz, 2H), 2.11 (m, 1H), 2.10 (s, 3H), 1.38 (t, *J* = 7.5 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 171.3, 150.3, 142.4, 132.8, 131.7, 131.3, 130.6, 130.5, 130.0, 129.9, 127.6, 127.5, 127.4, 127.3, 127.2 (2C), 126.4, 122.8, 122.7, 42.2, 30.0, 26.9, 22.2, 22.1, 15.7, 14.1. elemental analysis: calcd (%) for $C_{27}H_{26}N_2S_2$ (442.64): C 73.26, H 5.92; found: C 73.38, H 6.04.

5-(10-(5-Butylfuran-2-yl)phenanthren-9-yl)-2-ethyl-4-methylthiazole (27)

5-(10-Bromophenanthren-9-yl)-2-ethyl-4-methylthiazole **23** (0.191 g, 0.5 mmol), 2-butylfuran (0.124 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **27** was obtained in 54% (0.115 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.2 Hz, 2H), 7.94 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.77-7.55 (m, 5H), 6.20 (d, *J* = 3.1 Hz, 1H), 6.04 (d, *J* = 3.1 Hz, 1H),), 3.02 (q, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.59 (quint., *J* = 7.4 Hz, 2H), 1.42 (t, *J* = 7.5 Hz, 3H), 1.39 (sext., *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 156.3, 150.1, 148.3, 131.5, 131.4, 130.9, 130.6, 130.5, 129.2, 127.5, 127.3 (m), 127.2, 127.0, 126.9, 122.7, 122.6, 111.8, 106.0, 30.3, 27.7, 26.9, 22.1, 15.5, 14.3, 13.8. elemental analysis: calcd (%) for $C_{28}H_{27}NOS$ (425.59): C 79.02, H 6.39; found: C 79.20, H 6.12.

2-Isopropyl-4-methyl-5-(10-(5-pentylthiophen-2-yl)phenanthren-9-yl)thiazole (28)

5-(10-Bromophenanthren-9-yl)-2-isopropyl-4-methylthiazole **24** (0.198 g, 0.5 mmol), 2-pentylthiophene (0.154 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **28** was obtained in 52% (0.122 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.80-7.64 (m, 3H), 7.60 (t, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 3.31 (sept., *J* = 7.5 Hz, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H), 1.69 (quint., *J* = 7.5 Hz, 2H), 1.50-1.30 (m, 10H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 149.9, 146.9, 136.5, 134.0, 132.3, 131.5, 130.5, 130.3, 129.1, 128.3, 127.9, 127.2 (m), 127.1, 126.9, 126.7, 123.4, 122.7, 122.5, 33.4, 31.5, 31.2, 30.0, 23.3, 23.2, 22.4, 15.9, 14.1. elemental analysis: calcd (%) for $C_{30}H_{31}NS_2$ (469.71): C 76.71, H 6.65; found: C 76.87, H 6.80.

5-(10-(2-Isopropyl-4-methylthiazol-5-yl)phenanthren-9-yl)thiophene-2-carbonitrile (29)

5-(10-Bromophenanthren-9-yl)-2-isopropyl-4-methylthiazole **24** (0.198 g, 0.5 mmol), 2-thiophenecarbonitrile (0.109 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **29** was obtained in 57% (0.121 g) yield as a white solid: mp 178-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.2 Hz, 2H), 7.85-7.55 (m, 7H), 7.01 (d, *J* = 3.7 Hz, 1H), 3.29 (sept., *J* = 7.5 Hz, 1H), 2.11 (s, 3H), 1.45-1.36 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 150.4, 147.1, 137.0, 131.2, 131.1, 130.7, 130.6, 130.5, 130.2, 129.0, 128.0, 127.8, 127.6, 127.4 (m), 126.9, 125.4, 122.8, 114.0, 110.5, 33.4, 23.2, 23.1, 15.8. elemental analysis: calcd (%) for $C_{26}H_{20}N_2S_2$ (424.58): C 73.55, H 4.75; found: C 73.60, H 4.67.

2-Isopropyl-4-methyl-5-(10-(thiophen-2-yl)phenanthren-9-yl)thiazole (30)

5-(10-Bromophenanthren-9-yl)-2-isopropyl-4-methylthiazole **24** (0.198 g, 0.5 mmol), thiophene (0.084 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **30** was obtained in 56% (0.112 g) yield as a white solid: mp 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.80-7.55 (m, 5H), 7.37 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.98 (dd, *J* = 3.5, 1.1 Hz, 1H), 3.27 (sept., *J* = 7.5 Hz, 1H), 2.12 (s, 3H), 1.45-1.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 149.9, 139.2, 133.5, 132.2, 131.5, 130.5, 130.4, 129.3, 128.6, 127.8, 127.3 (m), 127.2, 127.0, 126.4, 126.2, 122.7, 122.5, 33.3, 23.3, 23.2, 15.8. elemental analysis: calcd (%) for $C_{25}H_{21}NS_2$ (399.57): C 75.15, H 5.30; found: C 75.32, H 5.01.

1-(5-(10-(2-Isopropyl-4-methylthiazol-5-yl)phenanthren-9-yl)furan-2-yl)butan-1-one (31)

5-(10-Bromophenanthren-9-yl)-2-isopropyl-4-methylthiazole **24** (0.198 g, 0.5 mmol), 1-(furan-2-yl)butan-1-one (0.138 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **31** was obtained in 59% (0.133 g) yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.78-7.67 (m, 3H), 7.61 (t, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 3.5 Hz, 1H), 6.46 (d, *J* = 3.5 Hz, 1H), 3.30 (sept., *J* = 7.5 Hz, 1H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H), 1.76 (sext., *J* = 7.5 Hz, 2H), 1.45-1.35 (m, 6H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 177.4, 154.4, 152.8, 150.3, 131.1, 130.9, 130.6, 130.5, 130.4, 129.1, 128.0, 127.7, 127.5 (m), 127.4, 126.8, 125.6, 122.8, 117.2, 113.8, 40.4, 33.3, 23.2, 23.1, 17.7, 15.6, 13.9. elemental analysis: calcd (%) for $C_{29}H_{27}NO_2S$ (453.60): C 76.79, H 6.00; found: C 76.90, H 6.12.

9,10-bis(2-isopropyl-4-methylthiazol-5-yl)phenanthrene (32)

5-(10-Bromophenanthren-9-yl)-2-isopropyl-4-methylthiazole **24** (0.198 g, 0.5 mmol), 2-isopropyl-4-methylylthiazole (0.141 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **32** was obtained in 55% (0.125 g) yield as a green solid: mp 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, *J* = 8.2 Hz, 2H), 7.75 (t, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 8.0 Hz, 2H), 3.28 (sept., *J* = 7.5 Hz, 2H), 2.14 (s, 6H), 1.40-1.34 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.5, 149.9, 131.2, 130.6, 130.5, 127.5, 127.4, 127.1, 126.1, 122.8, 33.4, 23.4, 23.1, 16.0. elemental analysis: calcd (%) for $C_{28}H_{28}N_2S_2$ (456.67): C 73.64, H 6.18; found: C 73.45, H 6.01.

9-Isopentylphenanthrene (33) [15]

9-bromophenanthrene (0.514 g, 2 mmol), 3-methyl-1-butylboronic acid (0.464 g, 4 mmol), K_2CO_3 (0.552 g, 4 mmol) and $Pd(OAc)_2$ (8.8 mg, 0.04 mmol) were dissolved in xylene (5 mL) under an argon atmosphere. The reaction mixture was stirred at 130 °C for 20 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **33** was obtained in 76% (0.377 g) yield as a white solid: mp 89-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 6.3 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 6.4 Hz, 1H), 7.71-7.58 (m, 5H), 3.15 (t, *J* = 7.6 Hz, 2H), 1.86-1.70 (m, 3H), 1.08 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 132.0,

131.3, 130.7, 129.6, 128.0, 126.6, 126.5, 126.1, 125.8 (2C), 124.5, 123.2, 122.4, 39.6, 31.3, 28.4, 22.7.

9-Bromo-10-isopentylphenanthrene (34) [15]

9-Isopentylphenanthrene **33** (0.248 g, 1 mmol) and *N*-bromosuccinimide (0.356 g, 2 mmol) were dissolved in DMF (5 mL) under an argon atmosphere. The reaction mixture was stirred at 50 °C for 3 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **34** was obtained in 88% (0.288 g) yield as a white solid: mp 91-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 6.6 Hz, 1H), 8.54 (d, *J* = 6.6 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.76-7.58 (m, 4H), 3.44 (t, *J* = 7.6 Hz, 2H), 1.98-1.87 (m, 1H), 1.74-1.64 (m, 2H), 1.16 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 131.3, 130.9, 130.5, 130.0, 128.6, 127.5, 127.3, 126.7, 126.6, 125.1, 124.1, 123.3, 122.5, 38.2, 32.1, 28.9, 22.5.

5-(10-Isopentylphenanthren-9-yl)-2-isopropyl-4-methylthiazole (35)

9-Bromo-10-isopentylphenanthrene **34** (0.164 g, 0.5 mmol), 2-isopropyl-4-methylylthiazole (0.141 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **35** was obtained in 78% (0.151 g) yield as a white solid: mp 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 6.6 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.75-7.68 (m, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.58-7.50 (m, 2H), 3.50-3.38 (m, 1H), 3.11-2.90 (m, 2H), 2.16 (s, 3H), 1.64-1.54 (m, 3H), 1.53 (d, *J* = 7.6 Hz, 6H), 0.93 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 149.5, 139.3, 132.2, 131.0, 130.7, 129.5, 127.0, 126.9, 126.8, 126.7, 126.5, 126.1, 125.7, 125.4, 123.2, 122.5, 39.5, 33.6, 28.8, 23.5, 23.4, 22.3, 15.6. elemental analysis: calcd (%) for $C_{26}H_{29}NS$ (387.59): C 80.57, H 7.54; found: C 80.74, H 7.34.

2-(10-Isopentylphenanthren-9-yl)thiophene (36)

9-Bromo-10-isopentylphenanthrene **34** (0.164 g, 0.5 mmol), thiophene (0.084 g, 1 mmol), KOAc (0.098 g, 1 mmol) and $PdCl(C_3H_5)$(dppb) (6.1 mg, 0.01 mmol) were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography. Product **36** was obtained in 80% (0.132 g) yield as a white solid: mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 6.6 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.76-7.66 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.59-7.46 (m, 3H), 7.25 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 3.07-2.94 (m, 2H), 1.72-1.54 (m, 3H), 0.91 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 138.5, 133.1, 130.8, 130.6, 129.2, 128.7, 128.1, 127.2, 127.0, 126.8, 126.6, 126.5, 125.9, 125.8, 125.4, 123.1, 122.2, 40.4, 28.8, 22.4, 22.3. elemental analysis: calcd (%) for $C_{23}H_{22}S$ (330.49): C 83.59, H 6.71; found: C 83.60, H 6.49.

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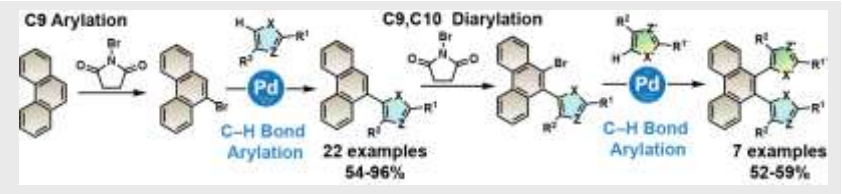

Successive palladium-catalyzed direct heteroarylations of 9- and 10-bromophenanthrenes provides a convenient route for access to symmetrical and non-symmetrical 9,10-di(heteroarylated) phenanthrenes. . A wide variety of heteroarenes such as thiazoles, (benzo)thiophenes, (benzo)furans, pyrroles, selenophenes or imidazopyridazines was successfully employed.

C-H bond functionalization

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Synthesis of C9,C10-diheteroarylated phenanthrenes via palladium-catalyzed C-H bond activations