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Synthesis of Substituted Phenanthrene by Iron(III)-Catalyzed Intramolecular Alkyne−Carbonyl Metathesis

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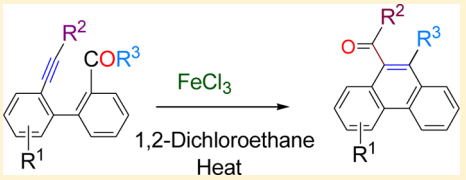
Supporting Information

ABSTRACT: An efficient synthesis of functionalized phenanthrenes has been developed for the first time involving an iron(III)-catalyzed intramolecular coupling of 2′-alkynyl-biphenyl-2-carbaldehydes. A broad range of functionalized phenanthrene derivatives could be obtained in the present method in moderate to good yields with high chemo- and regioselectivity. This transformation can also be applied to the synthesis of an angularly fused tetracyclic compound. This method offers several advantages such as high selectivity, mild reaction conditions, and easy availability of starting materials.

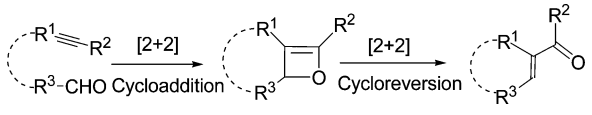


The construction of phenanthrene skeleton has attracted considerable attention due to their occurrence in numerous natural products.[1] Compounds having this structural motif also exhibit interesting biological roles such as antimalarial,[2] anticancer,[3] and emetic activity.[4] Moreover, they are also very useful in material science because of their photoconductivity, photochemical and electroluminescent properties.[5] In addition, synthesis of phenanthrene motif is the key step in the preparation of several phenanthrene based alkaloids such as phenanthroindolizidine, phenanthroquinolizidine, etc.[6] Therefore, numerous synthetic methods have been developed from time to time in order to improve the efficiency of synthesis of phenanthrene skeleton. Among them, the preparations of stilbene followed by aryl−aryl coupling reactions are the most extensively studied approaches to afford the phenanthrene skeleton. The aryl−aryl bonds are generally formed using Pschorr reaction, photocyclization, radical and other oxidative coupling reactions.[7]

A second, frequently utilized strategy involves aryl−aryl coupling followed by various intramolecular cyclization via aldol condensation, McMurry coupling, ring closing alkene metathesis and DDQ oxidation reactions to afford phenanthrene molecules.[8] Other strategies for the phenanthrene synthesis are based on metal induced carbocylization of alkynylated biaryl derivatives,[9] and metal-catalyzed intramolecular [4 + 2] cycloaddition of biaryl compounds with alkynes.[10] Very recently, the coupling of terminal alkynes with *N*-tosylhydrazones[11] in the presence of $CuBr_2$ (10 mol %), TBAB (20 mol %) and LiO^tBu (4 equiv), and a three-component carbocyclization of biphenyl-2-carbaldehydes/alkynes/piperidine in the presence of Zn/CuI/TFA have also been reported to achieve phenanthrene derivatives.[12] Despite these advances, some of the above said methods suffer from one or more limitations such as low yields, poor regioselecivity, drastic reaction conditions, use of expensive and large excess of toxic reagents in most cases. Therefore, the development of new, mild and environmentally friendly approaches for the regioselective synthesis of functionalized phenanthrene still remains as a highly desirable goal in organic synthesis.

The Wittig reaction and its variants are among the most powerful strategies for the construction of carbon−carbon double bonds in organic synthesis.[13] With regard to this aspect, very recently, alkyne−carbonyl metathesis, i.e., the addition of C−O double bond to C−C triple bonds for the construction of α,β-unsaturated carbonyl compounds, has been recognized as an atom economical alternative to the Wittig reaction.[14] Although this reaction seems to be very useful, but has been less exploited and only introduced very recently in organic synthesis. This alkyne−carbonyl metathesis is considered to be proceeding via a [2 + 2] cycloaddition and cycloreversion process in the presence of Lewis or strong Brønsted acids (Scheme 1).

Scheme 1. Intramolecular Alkyne−Carbonyl Metathesis



A delicate design of intramolecular version of this reaction would allow the constructing of complex carbo- and heterocyclic compounds from easily available starting materials. Despite the potential of this reaction, only a few examples of the intramolecular version of this reaction have been reported.[15] During our recent study in this area,[15a] we envisaged that the phenanthrene skeleton could be synthesized via intramolecular alkyne−carbonyl metathesis from a substituted 2′-alkynyl-biphenyl-2-carbaldehyde (Scheme 2). Herein, we report an efficient synthetic route to 9-acyl phenanthrenes under mild conditions through the intra-

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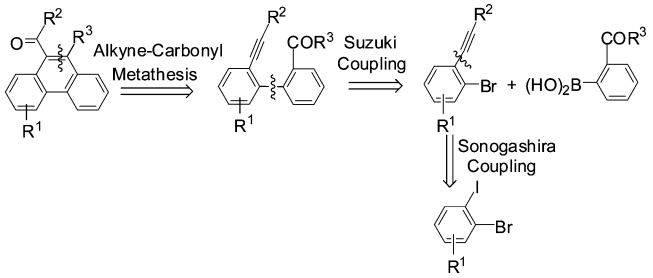
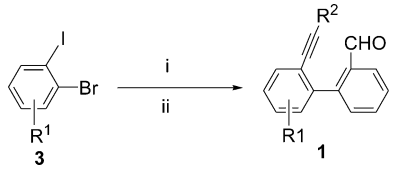
Scheme 2. Design of Phenanthrene Synthesis by Alkyne–Carbonyl Metathesis



molecular alkyne–carbonyl metathesis of 2′-alkynyl-biphenyl-2-carbaldehyde in presence of catalytic amount of $FeCl_3$.

The required substrate, 2′-alkynyl-biphenyl-2-carbaldehyde **1**, has been prepared by a two-step transformation in high yield starting from 1-bromo-2-iodobenzene **3** derivatives, as outlined in Scheme 3. The Sonogashira coupling of 1-bromo-2-iodobenzene with terminal alkynes followed by Suzuki–Miyaura coupling with 2-formyl phenylboronic acid afforded the desired starting materials in very high yield.

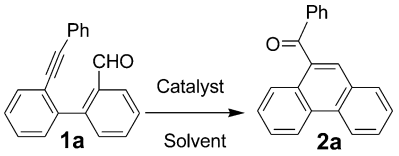
Scheme 3. Preparation of 2′-Alkynyl-biphenyl-2-carbaldehydes[a]



[a]Reaction conditions: (i) Aryl/alkyl acetylene, $BuNH_2$, $Pd(PPh_3)_4$, CuI, THF. (ii) 2-Formyl phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, EtOH, toluene.

To explore the possibility of the alkyne–carbonyl metathesis in biaryl system, we began our investigations using 2′-alkynyl-biphenyl-2-carbaldehyde **1a** to optimize the suitable conditions with various catalysts. The results are summarized in Table 1. In view of the high catalytic activity of $FeCl_3$ for the alkyne–carbonyl metathesis in our previous work and related work reported by others,[14g,15a,b] we first examined the intramolecular alkyne–aldeyhde coupling of **1a** in the presence of anhydrous $FeCl_3$. The reaction did not procced with 5 mol % $FeCl_3$ in 1,2-dichloroethane at room temperature; however, heating to 60 °C for 12 h resulted in the formation of the desired phenanthrene **2b** in 40% yield (Table 1, entry 2). We were delighted to find that the reaction temperature played a crucial role for the efficiency of this reaction, and yield was dramatically improved to 86% when the reaction mixture was heated to reflux for 3 h in the presence of 5 mol % of anhydrous $FeCl_3$ (Table 1, entry 3). Further, increasing the temperature and amount of catalyst loading from 5 to 10 mol % did not have a beneficial effect. Other iron catalysts such as $FeCl_3{\cdot}6H_2O$, $FeBr_3$ and $Fe(OTf)_3$ were also investigated, and they gave a lower yield of the desired product (Table 1, entries 5–7). $Fe(acac)_3$ did not show any catalytic activity toward this coupling reaction (Table 1, entry 8). We also screened other solvents such as $MeNO_2$, CH_3CN, THF and toluene, but only inferior results were obtained. In addition, other commonly used Lewis acids such as $InCl_3$, AgOTf and $AuCl_3$ also produced the desired product but failed to improve the yield

Table 1. Optimization of Reaction Conditions[a]



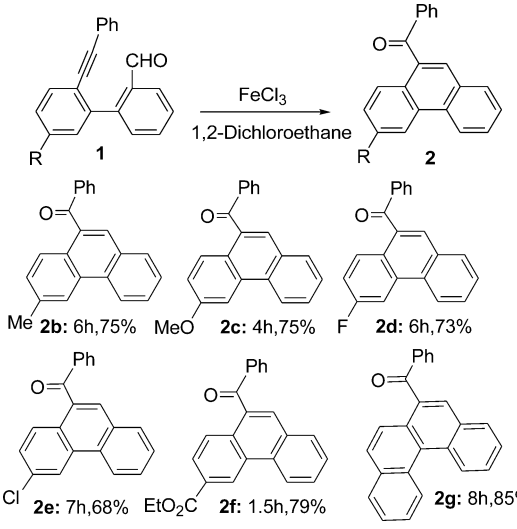
entry	catalyst (mol %)	time (h)	temperature	yield (%)
1	$FeCl_3$ (5)	12	rt	nr
2	$FeCl_3$ (5)	12	**60 °C**	40
3	**$FeCl_3$ (5)**	**3**	**reflux**	**86**
4	$FeCl_3$(10)	3	reflux	86
5	$FeCl_3{\cdot}6H2O$ (5)	5	reflux	83
6	$FeBr_3$ (5)	6	reflux	44
7	$Fe(OTf)_3$ (5)	7	reflux	45
8	$Fe(acac)_3$ (5)	8	reflux	nr
9	$lnCl_3$ (5)	4	reflux	85
10	AgOTf(5)	6	reflux	82
11	$AuCl_3$ (5)	6	reflux	74
12	TfOH (5)	4	reflux	86

[a]Conditions: Substrate **1a** (0.5 mmol), catalyst (0.025 mmol) and 1,2-dichloroethane (3 mL).

(Table 1, entries 9–11). These results demonstrated that anhydrous $FeCl_3$ exhibited higher catalytic activity for this particular transformation, with only 5 mol % required for achieving high yield. Strong Brønsted acid such as TfOH provided similar results (Table 1, entry 12); however, because of the ease of operation and economical, sustainable, and environmentally friendly nature of iron,[16] we employed iron as the catalyst for this transformation.

With these encouraging results in hand, this intramolecular coupling strategy has been investigated using various substituted 2′-alkynyl-biphenyl-2-carbaldehydes to synthesize a diverse range of functionalized phenanthrenes under the optimized reaction conditions. In terms of structural features, first we explored the substituent effects on the biphenyl ring attached to the alkyne motif of the starting material (Table 2).

Table 2. Intramolecular Alkyne–Carbonyl Metathesis of a Variety of Substituted Biphenyls[a]



[a]Conditions: Substrate (0.5 mmol), $FeCl_3$ (0.025 mmol) and 1,2-dichloroethane (3 mL).

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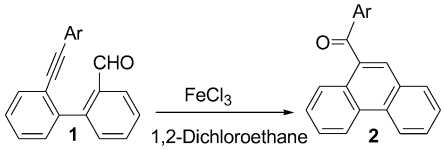
To our delight, biaryls possessing electron-donating groups such as −Me and −OMe or electron-withdrawing groups such as −F, −Cl and $-CO_2Et$ were smoothly reacted under this reaction conditions and gave the desired products **2b**−**2f** in good yields (68−79%).

Along these lines, it is notable that halide substituted phenanthrene derivatives would be very useful substrates for further synthetic transformations by transition metal catalyzed cross-coupling reactions. Moreover, a benzene fused biaryl was also efficiently converted to the desired angularly fused tetracyclic compound **2g** in high yield, 85% (Table 2). These results further demonstrated the potential of the reaction for the synthesis of a higher polycyclic aromatic hydrocarbon (PAH).

We also investigated a variety of substituents in the aryl alkyne moiety of 2′-alkynyl-biphenyl-2-carbaldehyde (Table 3).

Table 3. Iron-Catalyzed Synthesis of Substituted Phenanthrene[a]



entry	Ar	time (h)	yield of **2** (%)
1	*p*-Me-C_6H_4 **1h**	6	**2h** (57)
2	*p*-Cl-C_6H_4 **1i**	6	**2i** (83)
3	*m*-NO_2-C_6H_4 **2j**	1.5	**2j** (77)[b]
4	6-MeO-2-Naphthyl **2k**	8	**2k** (56)

[a]Conditions: Substrate 1 (0.5 mmol), $FeCl_3$ (0.025 mmol) and 1,2-dichloroethane (3 mL), [b]Carried out at 60 °C.

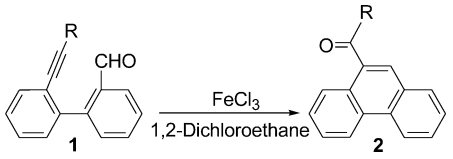
Alkynes bearing an electron-donating group such as *p*-Me (Table 3, entry 1) and electron-withdrawing groups such as *p*-Cl and *m*-NO_2 groups (Table 3, entries 2 and 3) were easily converted to the desired phenanthrenes in good to high yields (57−77%). Notably, 2-naphthyl bearing alkyne motif was also applicable to this cyclization reaction to give the product **2k** in 56% yield (Table 3, entry 4).

Next, we studied a few substrates possessing an alkyl group at one of the terminus of biaryl alkynes to show the versatility of this reaction (Table 4). Interestingly, this strategy was also equally applicable to the internal alkynes bearing an alkyl group such as **1l**, **1m** and **1n** bearing an alkyl group affording the desired phenanthrenes **2l**, **2m** and **2n** in moderate yields as 64, 60, and 45%, respectively.

Finally, the intramolecular coupling of biphenyl possessing an alkyne and a ketone group instead of an aldehyde has also been explored to show the generality of this reaction for the direct synthesis of 9,10-substituted phenanthrene. We were delighted to find that the optimized reaction conditions were so robust and versatile that the ketone could also be used as a substrate to synthesize 9,10-substituted phenanthrene **2o** in high yield, 85% (Scheme 4) in 15 h. However, because of the lesser reactivity of ketone, the reaction was sluggish compared to aldehyde.

In general, this method is quite simple and high yielding, and only a catalytic amount of $FeCl_3$ (5 mol %) is required for this process. This reaction worked smoothly and efficiently with a wide range of functional groups containing substrates. These results indicated that there is no significant electronic effect of substituents. Moreover, the products obtained in this method

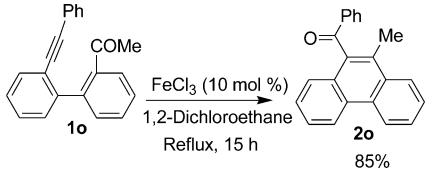
Table 4. Intramolecular Coupling of Carbonyl with Aliphatic Alkynes[a]



Entry	R	Time (h)	Yield of **2**(%)
1	C_6H_{13} **1l**	6	**2l** (64%)
2	CH_2CH_2OMe **1m**	4	**2m** (60%)
3	**1n**	7	**2n** (45%)[b,c]

[a]Conditions: substrates (0.5 mmol),1,2-dichloroethane and $FeCl_3$ (0.025 mmol). [b]Reaction was performed at 60 °C. [c]Performed in $MeNO_2$ solvents.

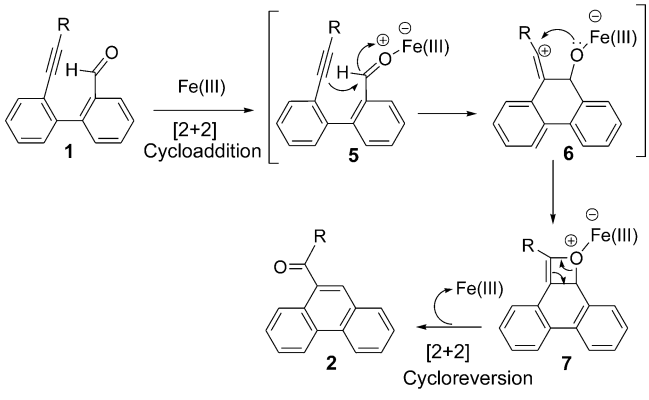
Scheme 4. Phenanthrene Synthesis with Coupling of Alkyne and Ketone



are 9-acyl phenanthrene derivatives, which are generally made by Friedel−Crafts acylation of phenanthrenes. So, employing this approach, the Friedel−Crafts acylation reaction could be avoided to synthesize 9-acyl phenanthrene. Unfortunately, terminal alkyne did not undergo this reaction. All of the products were characterized by spectroscopic methods, and product **2b** (CCDC no. 881041) was further confirmed by X-ray crystallography (see the Supporting Information).

On the basis of the above experimental results, a plausible catalytic cycle is proposed to illustrate the formation of product (Scheme 5). Presumably, the reaction may proceed through formation of an oxetene intermediate **7** via an intramolecular [2 + 2] cycloaddition, and a subsequent cycloreversion of oxetene intermediate producing the product. The definite role of the iron catalyst is not known; however, we believed that the catalytic cycle begins with the coordination of $FeCl_3$ to the

Scheme 5. Plausible Mechanism for the Formation of Phenanthrene



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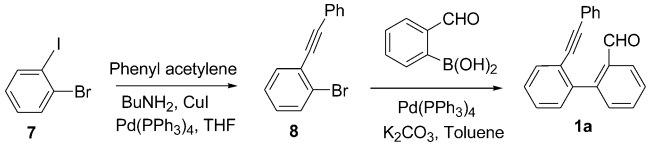
carbonyl group of **1**, which enhances the electrophilicity of carbonyl carbon. Then subsequent intramolecular nucleophilic attack by the alkyne moiety onto the polarized carbonyl carbon generating a vinylic carbocation intermediate **6**, which immediately cyclized by nucleophilic attack of the carbonyl oxygen center forming an oxetene intermediate **7**. Then a subsequent [2 + 2] cycloreversion of oxetene intermediate leading to the substituted phenanthrene and regenerating the iron salts for the next catalytic cycle. It is interesting to note that while the internal alkyne undergoes smooth coupling with carbonyl group in the presence of iron, no such coupling takes place with terminal alkyne. These results can be explained considering the greater stability of secondary vinylic carbocation generating from internal alkyne. However, because of the instability of generating primary vinylic carbocation, terminal alkyne does not participate in this reaction. Moreover, aryl substituted internal alkynes in general produced higher yield compared to the alkyl substituted terminal alkyne. This result further supported the formation of vinylic intermediate **6**.

In summary, we have developed an efficient iron-catalyzed intramolecular alkyne−carbonyl metathesis reaction for the regioselective synthesis of multisubstituted phenanthrene skeletons. The advantages of this new method are the ease of the substrate preparation, operational simplicity, high atom economy, and use of inexpensive and environmentally friendly $FeCl_3$ (5 mol %) as catalyst. This coupling reaction is compatible with a wide range of functional groups such as methyl, methoxy, fluoride, chloride and ester groups. Moreover, variation of functional groups was proven possible in all the rings of phenanthrene motif. In addition, this method also works for the synthesis of a tetracyclic compound. Considering these, the present synthetic strategy of phenanthrene may find application toward the synthesis of many biologically active molecules and new polycyclic aromatic compounds.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were recorded with 300 and 500 MHz spectrometer in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include the following: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets and brs = broad singlet. ^{13}C NMR spectra were recorded with spectrometer in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. High-resolution mass spectra (HRMS) were obtained using a TOF spectrometer using simultaneous electrospray (ESI) method. The molecular fragments are quoted as the relation between mass and charge (m/z). IR (infrared spectroscopy) was recorded with an FT-IR spectrometer. The routine monitoring of reactions was performed with silica gel coated glass slides and precoated Al plate, which were analyzed with iodine and UV light, respectively. All reactions involving moisture-sensitive reactants were executed with oven-dried glassware. Anhydrous $FeCl_3$ was purchased from Alfa aesar, Germany (98%) and SRL, India (98%).

Representative Experimental Procedure for the Preparation of 2′-Alkynyl-biphenyl-2-carbaldehydes (1a).



Step 1. Preparation of 1-Bromo-2-(phenylethynyl)benzene (7). To a solution of compound **7** (1 g, 3.53 mmol) in THF, $Pd(PPh_3)_4$ (0.05 equiv), CuI (0.1 equiv), $BuNH_2$ (1.4 equiv) and phenyl acetylene (1.2 equiv) were added successively under argon atmosphere. The mixture was stirred at 70 °C for 11 h. After completion of reaction (monitored by TLC), the mixture was cooled and solvent was evaporated under reduced pressure. To this mixture, water was added (20 mL) and then extracted with dichloromethane and dried over anhydrous Na_2SO_4. The crude compound was purified using silica gel (60−120 mesh) column chromatography (petroleum ether/EtOAc) to afford compound **8** (760 mg, 84%) as colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, J = 7.0 Hz, 1H), 7.11−7.31 (m, 4H), 7.46−7.54 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 88.2, 94.1, 122.0, 127.2, 128.5, 128.6, 128.8, 129.4, 129.5, 131.9, 132.6, 132.7, 133.4 ppm.

Step 2. Preparation of 2′-(Phenylethynyl)biphenyl-2-carbaldehyde (1a). The compound **8** (1 g, 3.9 mmol), 2-formyl phenylboronic acid (770 mg, 4.3 mmol) and $Pd(PPh_3)_4$ (0.02 equiv, 90 mg) were suspended in toluene (5 mL). Then ethanol (5 mL) and K_2CO_3 (2.5 M) were added to it. The mixture was stirred thoroughly under argon atmosphere and heated to 90 °C for 18 h. After completion of reaction, toluene was evaporated under reduced pressure and crude product was extracted with ethyl acetate. The crude mixture was partitioned between ethyl acetate (25 mL) and brine (25 mL), and the aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over Na_2SO_4, and solvent was removed under reduced pressure to yield the crude product **1a** as dark red liquid (770 mg, 70%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15−7.18 (m, 2H), 7.22−7.25 (m, 2H), 7.40−7.46 (m, 4H), 7.55 (t, J = 7.5 Hz, 2H), 7.62−7.70 (m, 2H), 8.09 (d, J = 7.7 Hz, 2H), 9.93 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 88.4, 93.1, 123.8, 127.0, 128.4, 128.6, 130.4, 131.4, 132.1, 133.6, 140.4, 144.5, 192.0 ppm; HRMS calcd. for $C_{21}H_{14}NaO$ [M + Na] 305.0942, found 305.0940.

The compounds **1b−1o** were synthesized by similar procedure. Spectral data of compounds **1b−1o** are given below:

5′-Methyl-2′-(phenylethynyl)biphenyl-2-carbaldehyde (1b). Yield 70%, orange-red liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.18−7.21 (m, 2H), 7.23−7.26 (m,5H), 7.46 (d, J = 7.6 Hz, 1H), 7.54−7.58 (m, 2H), 7.64−7.69 (m, 1H), 8.13 (d, J = 7.7 Hz, 1H), 9.99 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 88.4, 93.1, 120.8, 122.9, 126.8, 128.2, 128.3, 129.1, 131.1, 131.2, 131.3, 131.9, 133.5, 134.3, 138.7, 140.2, 144.5, 191.9 ppm; HRMS calcd. for $C_{22}H_{16}NaO$ [M + Na] 319.1099, found 319.1105.

5′-Methoxy-2′-(phenylethynyl)biphenyl-2-carbaldehyde (1c). Yield 75%, orange-red liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.95−6.99 (m, 2H), 7.15−7.17 (m, 2H), 7.22−7.26 (m. 3H), 7.45 (d, J = 7.5 Hz, 1H), 7.52−7.59 (m, 2H), 7.64−7.69 (m, 1H), 8.11 (d, J = 7.7 Hz, 1H), 9.97 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 88.2, 92.3, 114.0, 115.9, 116.1, 123.1, 126.8, 128.1, 128.2, 128.3, 131.1, 133.4, 133.5, 134.2, 141.9, 144.2, 159.6, 191.8 ppm; HRMS calcd. for $C_{22}H_{16}NaO_2$ [M + Na] 335.1048, found 335.1053.

5′-Fluoro-2′-(phenylethynyl)biphenyl-2-carbaldehyde (1d). Yield 70%, brown solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14−7.16 (m, 4H), 7.22−7.25 (m, 3H), 7.42 (d, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.61−7.64 (m, 1H), 7.67−7.70 (m, 1H), 8.09 (d, J = 7.5 Hz, 1H), 9.94 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.1, 93.3, 115.4, 115.6, 117.2, 117.5, 119.9, 120.0, 122.4, 127.1, 128.1, 128.2, 128.4, 128.6, 130.0, 130.9, 131.2, 133.6, 133.7, 133.8, 134.1, 142.6, 142.9, 149.7, 160.4, 163.8, 191.2 ppm; HRMS calcd. for $C_{21}H_{14}FO$ [M + H] 301.1029, found 301.1025.

5′-Chloro-2′-(phenylethynyl)biphenyl-2-carbaldehyde (1e). Yield 80%, yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12−7.17 (m, 2H), 7.22−7.79 (m, 3H), 7.40 (s, 1H), 7.43 (s, 2H), 7.55−7.60 (m, 2H), 7.69 (t, J = 6.9 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 9.94 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.1, 94.6, 122.3, 127.1, 128.2, 128.4, 128.6, 128.7, 130.1, 131.0, 131.2, 132.9, 133.6, 134.1, 134.3, 141.9, 142.7, 191.2 ppm; HRMS calcd. for $C_{21}H_{14}ClO$ [M + H] 317.0733, found 317.0738.

Ethyl 2′-formyl-6-(phenylethynyl)biphenyl-3-carboxylate (1f). Yield 50%, faint yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41

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(t, J = 7.1 Hz, 3H), 4.41 (q, J = 7.1 Hz, 2H), 7.15−7.18 (m, 2H), 7.22− 7.31 (m, 3H), 7.45 (d J = 7.6 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.67−7.72 (m, 2H), 8.11 (d, J = 6.9 Hz, 3H), 9.92 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 61.4, 87.7, 96.7, 122.1, 127.2, 128.1, 128.3, 128.6, 128.9, 129.1, 130.1, 131.0, 131.3, 131.4, 131.9, 133.7, 134.2, 140.5, 143.3, 165.7, 191.3 ppm; HRMS calcd. for $C_{24}H_{18}NaO_3$ [M + H] 377.1154, found 377.1159.

*2-[2-(Phenylethynyl)naphthalen-1-yl]benzaldehyde (**1g**).* Yield 65%, faint yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.0 Hz, 2H), 7.21−7.26 (m, 3H), 7.43 (s, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.50−7.53 (m, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.91 (d, J = 8.5 Hz, 2H), 8.19 (d, J = 7.5 Hz, 1H), 9.66 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 89.0, 94.9, 121.7, 122.8, 126.3, 126.8, 127.1, 127.3, 128.0, 128.3, 128.4, 128.5, 128.5, 131.4, 132.1, 132.8, 132.9, 133.7, 135.2, 138.4, 142.9, 191.8 ppm; HRMS calcd. for $C_{25}H_{16}NaO$ [M + Na] 355.1099, found 355.1094.

*2′-(p-Tolylethynyl)biphenyl-2-carbaldehyde (**1h**).* Yield 80%, orange oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.04−7.08 (m, 4H), 7.39−7.45 (m, 4H), 7.54 (t, J = 7.5 Hz, 1H), 7.63−7.68 (m, 2H), 8.09 (d, J = 7.5 Hz, 1H), 9.94 ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 87.7, 94.2, 119.8, 124.1, 127.0, 128.3, 129.2, 130.3, 131.3, 131.4, 132.0, 133.5, 134.4, 138.7, 140.3,144.5, 191.9 ppm; HRMS calcd. for $C_{22}H_{16}NaO$ [M + Na] 319.1099, found 319.1106.

*2′-[(4-Chlorophenyl)ethynyl]biphenyl-2-carbaldehyde (**1i**).* Yield 50%, yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, J = 10.7 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.34 (s, 1H), 7.42−7.45 (m, 2H), 7.52−7.57 (m, 2H), 7.62−7.70 (m, 2H), 8.08 (d, J = 7.7 Hz, 1H), 9.91 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 89.1, 92.6, 121.1, 122.9, 123.4, 126.8, 127.3, 128.2, 128.4, 128.6, 129.5, 130.2, 131.0, 131.2, 131.9, 132.4, 132.6, 133.4, 134.5, 140.4, 144.1, 191.7 ppm; HRMS calcd. for $C_{21}H_{13}ClNaO$ [M + Na] 339.0553, found 335.0559.

*2′-[(3-nitrophenyl)ethynyl]biphenyl-2-carbaldehyde (**1j**).* Yield 70%, yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.52 (m, 6H), 7.60 (t, J = 7.5 Hz, 1H), 7.66−7.74 (m, 2H), 8.0 (s, 1H), 8.11 (d, J = 7.2 Hz, 2H), 9.92 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 90.7, 91.2, 122.7, 123.0, 124.5, 126.1, 127.0, 128.4, 128.5, 129.3, 129.3, 130.3, 131.3, 132.1, 133.6, 134.3, 136.8, 140.8, 143.9, 148.1, 191.7 ppm; HRMS calcd. for $C_{21}H_{13}NNaO_3$ [M + Na] 350.0793, found 350.0794.

*2′-[(6-Methoxynaphthalen-2-yl)ethynyl]biphenyl-2-carbaldehyde (**1k**).* Yield 70%, yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.06 (s, 1H), 7.10−7.17 (m, 2H), 7.39−7.47 (m, 3H), 7.49 (s, 1H), 7.57 (s, 1H), 7.61 (d, J = 5.9 Hz, 2H), 7.65−7.72 (m, 3H), 8.12 (d, J = 7.7 Hz, 1H), 9.97 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 87.9, 94.5, 105.8, 119.3, 123.9, 126.7, 126.9, 128.2, 128.3, 128.3, 128.5, 129.4, 130.3, 131.1, 131.3, 131.9, 133.5, 134.2, 134.3, 140.2, 144.4, 158.4, 191.9 ppm; HRMS calcd. for $C_{26}H_{18}NaO_2$ [M + Na] 385.1204, found 385.1209.

*2′-(1-Octynyl)biphenyl-2-carbaldehyde (**1l**).* Yield 75%, yellowish-red oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83−0.88 (m, 2H), 1.08−1.15 (m, 4H), 1.21−1.35 (m, 4H), 2.15 (t, J = 6.9 Hz, 2H), 7.30−7.40 (m, 4H), 7.47−7.52 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 8.03 (d, J = 7.7 Hz, 1H), 9.85 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 19.4, 22.6, 28.2, 28.4, 31.6, 79.5, 95.6, 124.6, 126.8, 127.8, 128.1, 128.2, 130.2, 131.2, 132.1, 133.5, 134.3, 140.3, 144.8, 192.0 ppm; HRMS calcd. for $C_{21}H_{22}NaO$ [M + Na] 313.1568, found 313.1574.

*2′-(4-Methoxybut-1-ynyl)biphenyl-2-carbaldehyde (**1m**).* Yield 60%, yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (t, J = 6.5 Hz, 2H), 3.14−3.19 (m, 5H), 7.21−7.29 (m, 4H), 7.38−7.42 (m, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 9.75 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 58.5, 70.2, 80.3, 91.8, 124.0, 126.6, 126.9, 128.0, 128.0, 128.8, 130.1, 131.1, 131.7,132.1, 133.4, 134.1, 140.2, 144.4, 191.8 ppm; HRMS calcd. for $C_{18}H_{16}NaO_2$ [M + Na] 287.1048, found 287.1048.

*2′-(cyclohexylethynyl)biphenyl-2-carbaldehyde (**1n**).* Yield 60%, brown-yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15−1.24 (m, 5H), 1.36−1.54 (m, 5H), 2.32−2.34 (m, 1H), 7.26−7.33 (m, 4H), 7.42−7.47 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 8.02 (d, J = 7.7 Hz, 1H), 9.84 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 25.8, 29.4, 31.9, 79.5, 99.2, 124.5, 126.6, 127.6, 127.9, 128.0, 129.0, 129.7, 129.9, 131.1, 131.9, 133.4, 134.1, 134.4, 140.2, 144.7, 191.8 ppm; HRMS calcd. for $C_{21}H_{20}NaO$ [M + Na] 311.1412, found 311.1417.

*1-[2′-(Phenylethynyl)biphenyl-2-yl] ethanone (**1o**).* Yield 73%, yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.17 (s, 3H), 7.22−7.28 (m, 5H), 7.32−7.44 (m, 4H), 7.48 (t, J = 7.5 Hz, 1H), 7.55 (q, J = 7.5 Hz, 1H), 7.62−7.66 (m, 1H), 7.76 (d, J = 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.4, 88.6, 93.2, 122.4, 123.1, 127.5, 127.7, 128.1, 128.3, 128.5, 129.2, 129.5, 130.9, 131.0, 131.1, 131.4, 132.2, 132.8, 139.9, 140.3, 143.9, 202.1 ppm; HRMS calcd. for $C_{22}H_{16}NaO$ [M + H] 319.1099, found 319.1105.

General Experimental Procedure for the Synthesis of Phenanthrene. *Representative Experimental Procedure for the synthesis of Phenanthrene-9-yl (phenyl)methanone (**2a**).* Compound **1a** (140 mg, 0.5 mmol) was taken in a 10 mL round-bottom flask containing 3 mL of dry 1,2-dichloroethane. Anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) was added to it, and the reaction mixture was heated to reflux for 4 h under an Ar atmosphere. After completion of the reaction (TLC), dichloroethane was distilled out under reduced pressure and the residue was purified by silica gel (mesh 60−120) column chromatography (petroleum ether/EtOAc) to afford **2a** (121 mg, 0.43 mmol, 86%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (t, J = 7.5 Hz, 2H), 7.59−7.65 (m, 3H), 7.70−7.78 (m, 2H), 7.88 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.0 Hz, 2H), 8.15 (d, J = 8.0 Hz, 1H), 8.77 (dd, J = 18.0 Hz, 8.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.9, 123.1, 126.8, 127.3, 127.3, 128.4, 128.7, 129.3, 129.5, 129.6, 130.2, 130.6, 130.8, 131.5, 133.5, 135.5, 138.4, 198.0; HRMS calcd. for $C_{21}H_{15}O$ [M + H] 283.1123, found 283.1128.

*1-(6-Methylphenanthrene-9-yl)ethanone (**2b**).* Compound **1b** (155 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 6 h to afford **2b** (113 mg, 0.38 mmol, 75%) as a yellow solid: mp 130 °C; IR (KBr) 3063, 2360, 1665, 1252, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (s, 3H), 7.42 (d, J = 8.5 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.73 (t, J = 7.0 Hz, 1H), 7.79 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 1H), 8.56 (s, 1H), 8.73 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 122.8, 126.6, 127.1, 127.4, 128.2, 128.4, 128.6, 129.1, 129.6, 130.4, 130.6, 130.9, 131.2, 133.4, 135.4, 137.2, 138.4, 198.2 ppm; HRMS calcd. for $C_{22}H_{17}O$ [M + H] 297.1279, found 297.1281.

*(6-Methoxyphenanthrene-9-yl)(phenyl)methanone (**2c**).* Compound **1c** (156 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 6 h to afford **2c** (119 mg, 0.38 mmol, 75%) as a yellow liquid: IR (KBr) 2924, 2322, 1655, 1617, 1229, 1062, 724 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (s, 3H), 7.23 (dd, J = 9.1 Hz, 2.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H), 7.69−7.75 (m, 2H), 7.86 (d, J = 7.3 Hz, 1H), 7.96 (d, J = 7.1 Hz, 2H), 8.09 (d, J = 9.1 Hz, 1H), 8.12 (s, 1H), 8.65 (d, J = 8.3 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4, 104.5, 117.0, 122.7, 123.9, 127.1, 127.2, 127.9, 128.1, 128.5, 129.5, 130.4, 130.5, 130.7, 132.3, 133.3, 135.1, 138.3, 158.7, 198.0 ppm; HRMS calcd. for $C_{22}H_{17}O_2$ [M + H] 313.1229, found 313.1233.

*(6-Fluorophenanthrene-9-yl)(phenyl)methanone (**2d**).* Compound **1d** (150 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 6 h to afford **2d** (111 mg, 0.37 mmol, 73%) as a yellow solid: mp 98 °C; IR (KBr) 1651, 1594, 1250, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.35 (m, 1H), 7.46−7.52 (m, 3H), 7.65 (q, J = 7.2 Hz, 2H), 7.72−7.78 (m, 1H), 7.82 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H), 8.18 (dd, J = 9.1 Hz, 5.9 Hz, 1H), 8.35 (dd, J = 10.9 Hz, 2.5 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 107.9, 108.2, 116.0, 116.3, 122.9, 16.0, 127.7, 128.4, 128.6, 128.8, 128.9, 129.0, 129.6, 130.3, 130.4, 130.6,132.5, 132.6, 133.4, 134.7, 138.1, 160.1, 163.4, 197.5; HRMS calcd. for $C_{21}H_{13}FNaO$ [M + Na] 323.0848, found 323.0853.

*(6-Chlorophenanthrene-9-yl)(phenyl)methanone (**2e**).* Compound **1e** (158 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the

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synthesis of **2a** for 6 h to afford **2e** (108 mg, 0.34 mmol, 68%) as a yellow solid: mp 120 °C; IR (KBr) 1651, 1594, 1254, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, J = 7.6 Hz, 2H), 7.55 (s, 1H), 7.61−7.68 (m, 2H), 7.75 (t, J = 7.2 Hz, 1H), 7.86 (s, 1H), 7.89 (s, 1H), 7.94 (d, J = 7.2 Hz, 2H), 8.11 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 8.71 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.6, 122.7, 127.7, 127.8, 128.1, 128.6, 128.7, 129.6, 129.7, 130.3, 130.3, 130.4, 131.9, 133.4, 133.5, 134.6, 138.0, 197.4 ppm; HRMS calcd. for $C_{21}H_{14}ClO$ [M + H] 317.0733, found 317.0736.

*Ethyl-10-Acetylphenanthrene-3-carboxylate (**2f**).* Compound **1f** (185 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 1.5 h to afford **2f** (144 mg, 0.39 mmol, 79%) as a yellowish white solid: mp 110 °C; IR (KBr) 3064, 2983, 2252, 1710, 1660, 1255, 910, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.48 (t, J = 7.1 Hz, 3H), 4.49 (q, J = 7.1 Hz, 2H), 7.45−7.50 (m, 2H), 7.60−7.68 (m, 2H), 7.79 (t, J = 7.1 Hz, 1H), 7.88−7.95 (m, 4H), 8.18 (s, 1H), 8.83 (d, J = 8.3 Hz, 1H), 9.49 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 61.3, 123.0, 125.3, 126.7, 127.0, 127.7, 128.6, 128.7, 129.0, 129.7, 130.2, 130.4, 131.5, 132.1, 133.6, 134.8, 138.0, 166.6, 197.4 ppm; HRMS calcd. for $C_{24}H_{19}O_3$ [M + H] 355.1334, found 355.1328.

*Benzo[c]phenanthrene-6-yl (phenyl)methanone (**2g**).* Compound **1g** (166 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 8 h to afford **2g** (143 mg, 0.43 mmol, 85%) as a yellow oil: IR (KBr) 2919, 1655, 1594, 1265, 748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, J = 7.5 Hz, 2H), 7.60−7.69 (m, 3H), 7.72−7.79 (m, 2H), 7.88 (d, J = 8.9 Hz, 1H), 7.98−8.04 (m, 5H), 8.07 (s, 1H), 9.14 (d, J = Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.7, 126.3, 126.5, 126.5, 127.6, 127.9, 128.2, 128.3, 128.4, 128.6, 128.8, 129.2, 130.5, 131.1, 131.5, 133.3, 133.5, 138.2, 198.1 ppm; HRMS calcd. for $C_{25}H_{16}NaO$ [M + Na] 355.1099, found 355.1104.

*Phenanthrene-9-yl (p-tolyl)methanone (**2h**).* Compound **1h** (148 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 5 h to afford **2h** (86 mg, 0.29 mmol, 57%) as a yellow oil: IR (KBr) 3063, 2924, 2251, 1651, 1604, 908, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.28 (d, J = 8.0 Hz, 2H), 7.56−7.77 (m, 4H), 7.85−7.90 (m, 4H), 8.11 (d, J = 8.2 Hz, 1H), 8.75 (t, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 122.7, 122.9, 126.6, 127.1, 127.1, 128.1, 128.7, 129.2, 129.4, 129.4, 130.1, 130.6, 131.2, 135.6, 135.7, 144.4, 197.6 ppm; HRMS calcd. for $C_{22}H_{17}O$ [M + H] 297.1279, found 297.1282.

*(4-Chlorophenyl)(phenanthrene-9-yl)methanone (**2i**).* Compound **1i** (158 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 6 h to afford **2i** (133 mg, 0.42 mmol, 83%) as a yellow oil: IR (KBr) 3059, 2922, 1651, 1585, 1084, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 8.6 Hz, 2H), 7.55−7.76 (m, 5H), 7.84 (s, 1H), 7.89 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 8.2 Hz, 1H), 8.75 (t, J = 9.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.7, 123.0, 126.5, 127.2, 127.3, 128.5, 128.9, 129.1, 129.3, 129.6, 130.0, 130.6, 131.3, 131.8, 134.9, 136.5, 139.9, 196.6 ppm; HRMS calcd. for $C_{21}H_{14}ClO$ [M + H] 317.0733, found 317.0733.

*(3-Nitrophenyl)(phenanthrene-9-yl)methanone (**2j**).* Compound **1j** (164 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in 1,2-dichloroethane as described for the synthesis of **2a** for 1.5 h to afford **2j** (128 mg, 0.39 mmol, 77%) as a faint yellow solid: mp 122 °C; IR (KBr) 3076, 2361, 1655, 1537, 1348, 1254, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (t, J = 7.8 Hz, 3H), 7.70−7.80 (m, 2H), 7.85−7.90 (m, 2H), 8.18 (dd, J = 16.7 Hz, 8.2 Hz, 2H), 8.44 (d, J = 6.2 Hz, 1H), 8.71−8.78 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.8, 123.2, 124.9, 126.3, 127.4, 127.4, 127.5, 127.6, 128.9, 129.0, 129.7, 129.8, 130.4, 130.8, 131.7, 133.7, 135.8, 139.8, 148.4, 195.3 ppm; HRMS calcd. for $C_{21}H_{14}NO_3$ [M + H] 328.0974, found 328.0970.

*(6-Methoxynaphthalene-2-yl)(phenanthren-9-yl)methanone (**2k**).* Compound **1k** (181 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 8 h to afford **2k** (101 mg, 0.28 mmol, 56%) as a yellow oil: IR (KBr) 2924, 2322, 1655, 1617, 1300, 1062, 748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.14−7.18 (m, 2H), 7.51−7.62 (m, 2H), 7.65−7.70 (m,3H), 7.75 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.92 (s, 1H), 8.15 (d, J = 8.6 Hz, 2H), 8.30 (s, 1H), 8.77 (t, J = 9.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4, 105.6, 1058, 119.7, 122.7, 123.0, 126.1, 126.7, 127.1, 127.2, 127.7, 128.2, 128.6, 129.5, 130.2, 130.6, 131.2, 131.3, 132.9, 133.5,135.9, 137.6, 158.0, 160.0, 197.8 ppm; HRMS calcd. for $C_{26}H_{19}O_2$ [M + H] 363.1385, found 363.1379.

*1-(Phenanthrene-9-yl)heptan-1-one (**2l**).* Compound **1l** (145 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane as described for the synthesis of **2a** for 6 h to afford **2l** (93 mg, 0.32 mmol, 64%) as a faint yellow oil: IR (KBr) 3063, 2929, 2252, 1693, 908, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89−0.93 (m, 3H), 1.31−1.45 (m, 6H), 1.81−1.86 (m, 2H), 3.13 (t, J = 7.5 Hz, 2H), 7.64−7.74 (m, 4H), 7.95 (d, J = 6.93 Hz, 1H), 8.08 (s, 1H), 8.50−8.53(m, 1H), 8.66−8.74 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0, 22.5, 24.7, 29.0, 31.2, 42.4, 122.6, 122.8, 126.5, 127.0, 127.4, 128.4, 128.6, 128.7, 129.6, 129.8, 130.8, 131.6, 132.7, 135.7, 205.2 ppm; HRMS calcd. for $C_{21}H_{22}NaO$ [M + Na] 313.1568, found 313.1572.

*3-Methoxy-1-(phenanthrene-9-yl)propan-1-one (**2m**).* Compound **1m** (132 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry 1,2-dichloroethane solvent at 60 °C following the procedure as described for the synthesis of **2a** for 4 h to afford **2m** (79 mg, 0.30 mmol, 60%) as a faint yellow solid: mp 70 °C; IR (KBr) 2886, 2360, 1664, 1114, 747, 723 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.38 (t, J = 6.3 Hz, 2H), 3.41 (s, 3H), 3.91 (t, J = 6.2 Hz, 2H), 7.59−7.75 (m, 4H), 7.92 (d, J = 7.9 Hz, 1H), 8.13 (s, 1H), 8.58−8.71 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.2, 58.9, 68.2, 122.6, 122.7, 126.6, 127.0, 127.4, 128.2, 128.7, 129.5, 129.7, 129.9, 130.7, 131.7, 135.1, 202.6 ppm; HRMS calcd. for $C_{18}H_{16}NaO_2$ [M + Na] 287.1048, found 287.1051.

*Cyclohexyl (phenanthrene-9-yl)methanone (**2n**).* Compound **1n** (144 mg, 0.5 mmol) and anhydrous $FeCl_3$ (4.0 mg, 0.025 mmol) were treated in dry nitromethane at 60 °C following the procedure as described for the synthesis of **2a** for 7 h to afford **2n** (66 mg, 0.23 mmol, 45%) as a yellow oil: IR (KBr) 3072, 2921, 2850, 1681, 1444, 728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26−1.45 (m, 4H), 1.52−1.75 (m, 2H), 1.83−1.88 (m, 2H), 1.98−2.03 (m, 2H), 3.24−3.33 (m, 1H), 7.60−7.76 (m, 4H), 7.93−7.96 (m, 2H), 8.22 (dd, J = 8.0 Hz, 1.42 Hz, 1H), 8.71 (t, J = 9.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8, 26.0, 28.9, 50.0, 122.7, 122.9, 126.4, 126.9, 127.1, 127.3, 128.3, 128.8, 129.5, 130.2, 130.7, 131.4, 136.6, 208.7 ppm; HRMS calcd. for $C_{21}H_{21}O$ [M + H] 289.1592, found 289.1596.

*(10-Methylphenanthren-9-yl)(phenyl)methanone (**2o**).* Compound **1o** (156 mg, 0.5 mmol) and anhydrous $FeCl_3$ (8.0 mg, 0.05 mmol) were treated in dry 1,2-dichloroethane solvent as described for the synthesis of **2a** for 15 h to afford **2o** (133 mg, 0.43 mmol, 85%) as a yellow solid: mp 164 °C; IR (KBr) 3047, 2918, 2845, 2358, 1664, 1574, 1591, 1239, 1163, 883 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.57 (s, 3H), 7.42−7.49 (m, 3H), 7.55−7.63 (m, 3H), 7.69−7.76 (m, 2H), 7.93 (d, J = 7.5 Hz, 2H), 8.15 (d, J = 8.0 Hz, 1H), 8.77 (dd, J = 22.7 Hz, 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.1, 122.9, 123.2, 125.0, 126.1, 126.5, 127.2, 127.3, 129.0, 129.1, 129.4 ppm; HRMS calcd. for $C_{22}H_{16}NaO$ [M + Na] 319.1099, found 319.1103.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of **2b** (CIF) and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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