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Pd Catalyzed Insertion of Alkynes into Cyclic Diaryliodoniums: A Direct Access to Multi-substituted Phenanthrenes

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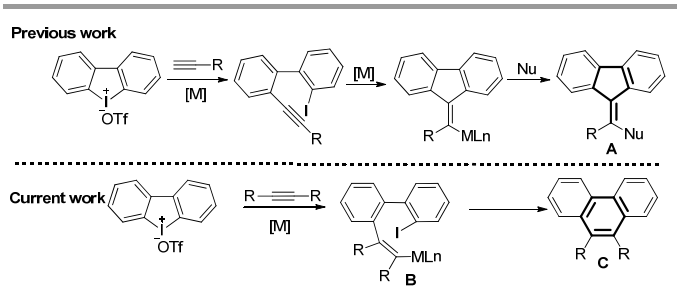
Cyclic diaryliodoniums remain unexplored compared to linear iodoniums. In our current work, internal alkynes were for the first time applied to react with cyclic iodoniums, catalyzed by Pd, resulting in a [4+2] benzannulation. Our work offers a new strategy to synthesize multi-substituted phenanthrene derivatives which are not easily accessed by conventional methods.

Introduction

Phenanthrenes have attracted considerable attention due to their vital molecular structure features in materials and important pharmacological activity.[1] A number of studies have suggested that these compounds may be potential anti-inflammatory,[2] anti-tumour,[3] and anti-tubercular agents.[4] Thus, the synthesis of phenanthrenes are of highly importance, and several synthetic strategies have been reported, including benzyne-alkyne-benzyne insertion,[5] intramolecular cyclizations,[6] and [4+2] benzannulation reaction.[7-9] These reported methods have some limitations, for example, either harsh or sensitive reaction conditions, narrow substitutents in the substrates, and toxicity of reagents. The [4+2] cycloaddition is the most straightforward method for the formation of phenanthrenes. Takahashi and co-workers demonstrated that aromatic phenanatrhenes were afforded by using chromium reagents and butyllithium.[7c] Recently, Nakamura reported that iron catalyzed [4+2] benzannulation between alkyne and 2-alkenylphenyl Grignard reagent.[8] Both of these two methods employed highly moisture sensitive organometallic reagents, increasing the difficulty to operate the reactions.

Compared to linear diaryliodoniums that are widely reported as arylating reagents,[10] cyclic diaryliodoniums have advantages because their arylated products themselves incorporate the iodoarenes which are inevitably produced and often discarded in the arylation with linear diaryiodoniums.[11] In addition, the incorporated iodoarene could be employed for further transformations to set up a cascade reaction. The synthesis of aromatic rings still remains a challenge while the reported methods have limitations including harsh conditions, multi-steps reactions, and low yields.[12-16] We are interested in the development of synthetic methods to build aromatic rings in one pot with cyclic diaryliodoniums.[17] Recently, we demonstrated that terminal alkynes were easily arylated by cyclic iodoniums, and then underwent further subsequent transformation to exclusively form a five member ring, generating fluorenes **A** (Scheme 1).[18] In this case, six membered ring formation was not observed although the intramolecular cyclization could make it happen. It is a question raised thereof how to realize a six membered ring formation with triple bonds. Heterocyclic ring formation with internal alkynes mediated by transition metals has been reported.[19] We hypothesized that a six membered benzene ring in phenanthrenes **C** might be accessed while internal alkynes were employed to replace terminal alkynes. In principle, the insertion of internal alkynes into cyclic iodoniums could generate intermediate species **B**, and a potential subsequent intramolecular coupling would form a middle six membered ring. Herein, we report Pd catalyzed insertion of internal alkynes into cyclic diphenyliodoniums featuring [4+2] benzannulation to afford multi-substituted phenanthrenes.



Scheme 1. The strategies to employ alkenes/alkynes to react with cyclic iodoniums.

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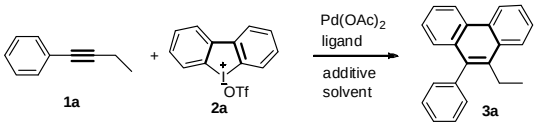
Electronic Supplementary Information (ESI) available: The details of experiments, characterisation of synthetic compounds, and copies of NMR spectra are available. See DOI: 10.1039/x0xx00000x

Results and discussion

To validate our hypothesis, alkyne **1a** and cyclic iodonium **2a** were employed at the outset of our study to investigate whether their reaction could generate a known compound, 9-ethyl-10-phenylphenantrhene **3a**.[7c] We were delighted to find that **3a** was obtained albeit at a low yield while using $Pd(OAc)_2$ as a catalyst in 1,2-dichloroethane (entry 1, table 1). Then, a series of polar and non-polar solvents were screened, with 1, 2-dichloroethane still remaining the best (entry 1-6). Further study indicated that the addition of bases was not necessary (entry 7). Moreover, additional zinc powder increased the yield of products obviously, implying that a reducing agent can accelerate the regeneration of palladium zero species (entry 8). A number of phosphine ligands were then screened, and tricyclohexylphosphine was found to significantly enhance the yield (entry 13). Not surprisingly, the yield decreased when Zn was withdrawn, confirming that Zn played a crucial role in the reactions (entry 14). In addition, Cu, another reductive metal also improved the yield, albeit not as much as zinc. The yield slightly decreased when temperature was decreased to 80 ℃ (entry 16).

Table 1. Optimization of the reaction conditions [a]



Entry	Ligand	Solvent	Additive	Yield (%)[b]
1	PPh_3	DCE	Na_2CO_3	32
2	PPh_3	*i*-PrOH	Na_2CO_3	trace
3	PPh_3	DMF	Na_2CO_3	20
4	PPh_3	DMSO	Na_2CO_3	21
5	PPh_3	NMP	Na_2CO_3	27
6	PPh_3	toluene	Na_2CO_3	ND
7	PPh_3	DCE	-	37
8	PPh_3	DCE	Zn	47
9	dppe	DCE	Zn	30
10	dppf	DCE	Zn	51
11	Bu_3P	DCE	Zn	48
12	$P(NMe_2)_3$	DCE	Zn	53
13	PCy_3	DCE	Zn	82
14	PCy_3	DCE	-	50
15	PCy_3	DCE	Cu	63
16[c]	PCy_3	DCE	Zn	62

[a] 1a (1.0 equiv), 2a (1.2 equiv), Pd(OAc)2 (10 mol %), ligand (0.3 equiv), with or without additive (1.0 equiv) , Ar, 100 °C, 15 h. [b] Isolated yield. [c] 80 °C. Notes: DCE, 1, 2-dichloroethane; NMP, N-methyl-2-pyrrolidone; dppe, 1,2-Bis-(diphenylphosphino)-ethane; dppf, 1,1'-Ferrocenebis-diphenylphosphine; ND, not detected.

With the optimal reaction conditions obtained, a variety of internal alkynes were investigated to react with the iodonium **2a** (Figure 1). The desired phenanthrenes were successfully obtained at modest to good yields while aryl alkyl alkynes were employed (**3a**-**3e**). A number of functional groups were compatible, including ester, amides and TMS (**3b-3e**) to be subject to the reaction conditions, providing opportunities for further functionalization of these phenanthrenes. Diaryl alkynes also underwent well [4+2] benzannulation reactions to generate the expected phenanthrenes (**3f-3k**). To our more delight, aliphatic alkynes were also successfully transformed to the expected products smoothly (**3l-3n**).

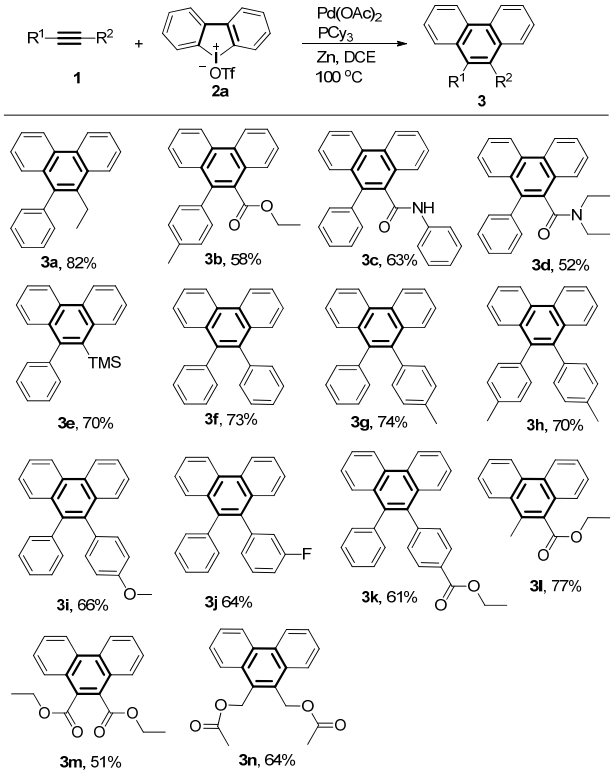


Figure 1. The scope of alkynes. Reaction condition: **1** (1.0 equiv), **2a** (1.2 equiv), and $Pd(OAc)_2$ (10 mol %), PCy_3 (0.3 equiv), Zn (1 equiv), Ar, DCE, 100℃, 15 h.

Next, a range of cyclic diaryliodoniums with different substituents were investigated to react with alkyne **1h** (Figure 2). Under the standard reaction conditions, the iodoniums with either electron donating or electron drawing groups attached were all transformed to the desired phenanthrenes at modest or good yields.

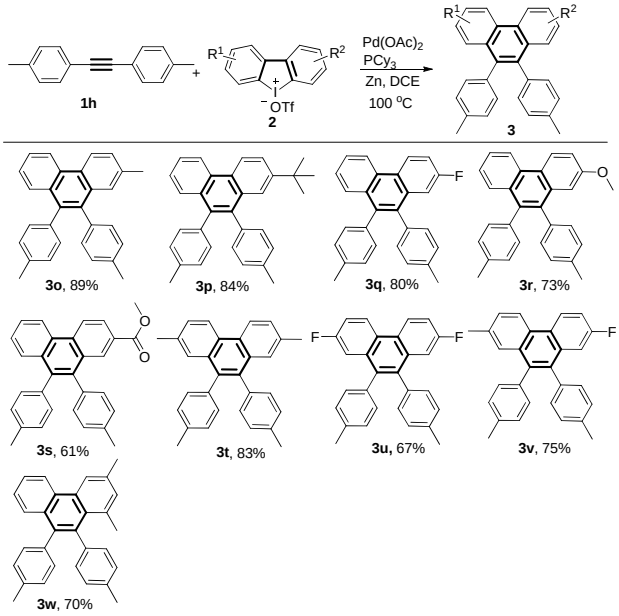
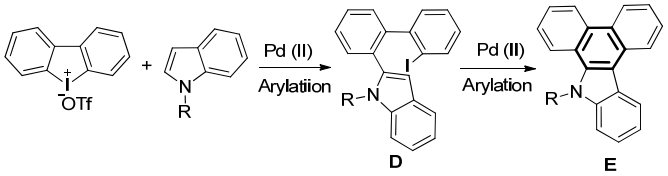


Figure 2. The scope of diaryliodoniums. Reaction conditions: **1a** (1.0 equiv), **2a** (1.2 equiv), and $Pd(OAc)_2$ (10 mol %), PCy_3 (0.3 equiv), Zn (1 equiv), Ar, DCE, 100℃, 15 h.

In our previous report, the reaction of cyclic diaryliodoniums with indoles was able to generate dibenzocarbazoles (Scheme 2).[17a] The 2,3-double bond of indoles acted as nucleophiles to proceed dual arylations. The final result of the reaction was the formation of a six membered benzene ring in a [4+2] pathway. A palladium species cycle with Pd(II/IV) was proposed therein for the transformation. However, the potential mechanism of our current reactions between the iodoniums and internal alkynes are believed to be different although resulting in the same six membered ring formation.



Scheme 2. Our previous work on the reaction of iodoniums and indoles.

To explore the mechanism of the reactions, two experiments were designed (Figure 3). Firstly, 4-methoxyphenylboronic acid was added additionally under the standard conditions to study whether the intermediate **B** in scheme 1 could be intercepted by the boronic acid to access **5**. However, only **3a** and boronic acid self coupled product **4** were observed, demonstrating that intramolecular cyclization was faster than an intermolecular coupling reaction with incoming boronic acid after in situ generation of a potential palladiums species. Secondly, it was also of our interest whether an intermediate **7** was able to generate while the reaction was performed at lower temperature to prevent the subsequent cyclization. However, only 2-iodobiphenyl **6** was obtained while the mixture of **1a** and **2a** were subjected to 60 °C, implying that the generation of **B** required high energy.

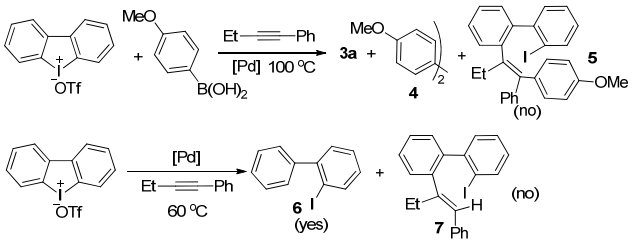
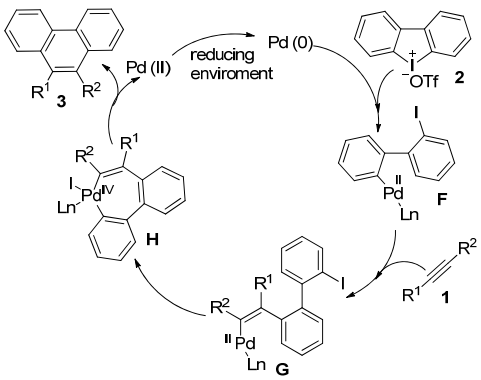


Figure 3. The experiments to investigate the reaction mechanism

Based on our above observation and previous work,[17a] a probable pathway involving a Pd (0/II/IV) catalytic cycle is proposed although the exact mechanism still needs to be further investigated (Scheme 3). First, the palladium reactive species **F** was formed via oxidative addition of cyclic liodoniums **2** with Pd (0) in situ reduced from Pd (II). Then, the insertion of **F** to the internal alkynes **1** afforded intermediate **G** that underwent a subsequent intermolecular oxidative addition to form Pd (IV) species **H**. It is worth-mentioning that palladium species **F** was easily produced even at low temperature. However, on one hand, the failure to obtain intermediate **7** in the above experiments implied that the formation of palladium species **G** from **F** required a high energy and had to be realized at high temperature. This might explain why only **6** was obtained from palladium species **F** at 60 °C (Figure 3). On the other hand, the formation of 5 was not observed in our above experiments. The result demonstrated that the formation of **H** from **G** was rapid once species **G** was generated at higher temperature. A final reductive elimination of **H** resulted in phenanthrene **3**. The generated palladium species after one reaction cycle is two valent, and it has to be reduced by reducing environments to regenerate Pd (0) for next reaction cycle. This was validated by the fact that additional metal zinc favoured the reactions.



Scheme 3. Proposed mechanism of the reaction.

Experimental

General information for the experiments: All reaction under standard conditions were carried out under argon atmosphere and monitored by thin layer chromatography. All the commercial available reagents, catalysts, and solvents and were without further purification unless stated otherwise. All

cyclic diaryliodoniums were prepared according to our previous work[18]. All products were purified by silica gel (200-300 mesh) column chromatography with petroleum ether (60-90℃) and dichloromethane as eluents. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ or DMSO-d_6 on Bruker Avance 400 spectrometer. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 77.16 for ^{13}C, and to DMSO-d_6 with 2.50 for ^{1}H and 39.5 for ^{13}C. Signals are abbreviated as follows: s, singlet; dd, doublet of doublets; d, doublet; t, triplet; q, quartet; m, multiplet.

9-Ethyl-10-phenylphenanthrene (3a)[7c]: To a sealed tube with an magnetic stirrer bar, was added **1a** (60 mg, 460 μmol), **2a** (237 mg, 553 μmol), $Pd(OAc)_2$ (10 mg, 10 % mol), PCy_3 (39 mg, 128 μmol), Zn (30 mg, 460 μmol) and 1,2-dichloroethane (3 mL). The reaction proceeded at 100℃ for 15 h under Ar before the mixture was diluted with CH_2Cl_2 and filtered via celite. The filtrate was concentrated in vacuo and the crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 20/1) to give **3a** (109 mg, 82% yield) as a white solid. 1H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.79 (m, 1H), 8.75 (d, J = 8.3 Hz, 2H), 8.25 – 8.16 (m, 1H), 7.74 – 7.66 (m, 2H), 7.54 (m, 4H), 7.43 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 8.5 Hz, 3H), 2.93 (q, J = 7.5 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H).13C NMR (101 MHz, $CDCl_3$) δ 140.6, 136.7, 136.1, 132.5, 130.7, 130.6, 130.2, 129.4, 128.5, 127.7, 127.2, 126.9, 126.4, 126.2, 125.8, 125.3, 123.2, 122.4, 23.6, 15.4.

Ethyl-10-(*p*-tolyl)-phenanthrene-9-carboxylate (3b)[12]: Obtained from **1b** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.79 – 7.57 (m, 4H), 7.51-7.49 (m, 1H), 7.32-7.25 (m, 4H), 4.15 (q, J = 7.2 Hz, 2H), 2.46 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 137.6, 136.6, 135.1, 131.1, 130.8, 130.7, 130.3, 129.9, 128.9, 128.1, 127.9, 127.5, 127.1, 126.9, 125.9, 122.9, 122.7, 61.3, 21.5, 13.9.

***N*-phenyl-10-(*p*-tolyl)-phenanthrene-9-carboxamide (3c)**: Obtained from **1c** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 8.4 Hz, 2H), 8.17 (d, J = 8.0 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.57 – 7.45 (m, 7H), 7.22 (t, J = 6.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 137.9, 137.3, 135.7, 133.4, 130.9, 130.8, 130.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.4, 128.2, 127.7, 127.4, 127.1, 126.5, 125.0, 122.9, 122.8, 120.7, 119.9. HRMS (ESI, *m/z*) calcd for $C_{27}H_{20}NO$ ($M + H^+$), 374.1545; found, 374.1555. MP: 109.1-110.8℃. IR (KBr) υ: 3056, 2826, 1693, 1682, 1256.

***N*,*N*-diethyl-10-(*p*-tolyl)-phenanthrene-9-carboxamide (3d)**: Obtained from **1d** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.74 – 7.58 (m, 5H), 7.53 – 7.46 (m, 2H), 7.43 (m, 2H), 7.35 (m , 1H), 3.91 (m, 1H), 3.26 – 3.13 (m, 1H), 2.93 (m, 1H), 2.78 (m, 1H), 0.82-0.79 (m, 3H), 0.69-0.67 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 131.5, 129.8, 128.9, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.5, 122.9, 122.7, 42.6, 37.6, 29.8, 13.9, 11.8. HRMS (ESI, *m/z*) calcd for $C_{25}H_{24}NO$ ($M + H^+$), 354.1858; found, 354.1866. MP: 100.8-101.7℃. IR (KBr) υ: 3056, 2823, 1671, 1256.

Trimethyl-(10-phenylphenanthren-9-yl)-silane (3e)[7c]: Obtained from **1e** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 – 8.69 (m, 3H), 8.32 (d, J = 8.0 Hz, 1H), 7.92 (t, J = 8.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.50 – 7.44 (m, 3H), 7.42 (d, J = 3.6 Hz, 2H), 7.38-7.35 (m, 2H), 0.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 131.5, 130.2, 129.7, 128.8, 128.4, 128.0, 127.9, 127.6, 127.5, 126.9, 126.4, 125.8, 125.7, 123.2, 122.6, 122.3, 2.8.

9, 10-Diphenylphenanthrene (3f)[14]: Obtained from **1f** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.4 Hz, 2H), 7.67 (m, 2H), 7.56 (m, 2H), 7.49 (m, 2H), 7.25 – 7.22 (m, 4H), 7.22 – 7.19 (m, 2H), 7.17 (d, J = 1.6 Hz, 2H), 7.15 (t, J = 1.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 137.3, 132.0, 131.2, 130.1, 128.0, 127.7, 126.7, 126.6, 126.5, 122.6.

9-Phenyl-10-(*p*-tolyl)phenanthrene (3g)[13]: Obtained from **1g** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 7.6 Hz, 2H), 7.61 – 7.43 (m, 4H), 7.23 (m, 3H), 7.19-7.13 (m, 2H), 7.04 (s, 4H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.4, 137.3, 136.6, 136.0, 132.2, 132.1, 131.2, 131.0, 130.2, 130.1, 128.5, 128.0, 127.9, 127.7, 126.7, 126.6, 126.5, 126.4, 122.6, 100.1, 21.3.

9, 10-Di-*p*-tolylphenanthrene (3h)[13]: Obtained from **1h** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.4 Hz, 2H), 7.67 (t, J = 7.6 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.08 (s, 8H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 136.7, 135.9, 132.3, 131.0, 130.0, 128.5, 128.0, 126.6, 126.3, 122.6, 77.5, 21.3.

9-(4-Methoxyphenyl)-10-phenylphenanthrene (3i)[7c]: Obtained from **1i** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.3 Hz, 2H), 7.66 (t, J = 7.5 Hz, 2H), 7.60 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.24 (m, 3H), 7.16 (d, J = 6.8 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 139.9, 137.6, 136.9, 132.3, 132.2, 132.0, 131.9, 131.1, 130.1, 130.0, 128.0, 127.9, 127.7, 126.7, 126.5, 126.4, 122.6, 113.1, 55.2.

9-(3-Fluorophenyl)-10-phenylphenanthrene (3j): Obtained from **1j** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.50 – 7.37 (m, 4H), 7.17 (m, 3H), 7.07 (m, 3H), 6.86 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 9.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 137.5, 136.0, 131.8, 131.5, 131.0 (d, J = 6.0 Hz), 130.2 (d, J = 9.2 Hz), 129.2 (d, J = 8.4 Hz), 128.0, 127.9, 127.8, 127.7, 127.1 (d, J = 2.8 Hz), 127.0, 126.9, 126.8, 126.7, 122.7 (d, J = 7.6 Hz), 118.2 (d, J = 21.2 Hz), 113.6 (d, J = 20.8 Hz). HRMS (ESI, *m/z*) calcd for $C_{26}H_{17}F$ (M^+), 348.1314; found, 348.1326. MP: 116.2-117.3℃. IR (KBr) υ: 3055, 2826, 1505, 1216.

Ethyl-4-(10-phenylphenanthren-9-yl)-benzoate (3k): Obtained from **1k** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 7.74 (m, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.55 (m, 3H), 7.34 – 7.26 (m, 5H), 7.20 (d, J = 6.8 Hz, 2H), 4.42 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 144.8, 139.2, 137.3, 136.3, 131.8, 131.4, 131.2, 131.0, 130.2,

130.1, 129.0, 128.7, 128.0, 127.9, 127.6, 126.9, 126.8, 126.7, 122.7, 122.6, 61.1, 14.5. HRMS (ESI, *m/z*) calcd for $C_{29}H_{23}O_2$ ($M + H^+$), 403.1698; found, 403.1681. MP: 107-108.4℃. IR (KBr) υ: 3056, 2980, 2823, 1715, 1378, 1256.

Ethyl-10-methylphenanthrene-9-carboxylate (3l)[14]: Obtained from **1l** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 11.7, 8.4 Hz, 2H), 8.13 (d, J = 7.6 Hz, 1H), 7.67 (m, 5H), 4.59 (q, J = 7.2 Hz, 2H), 2.71 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.4, 127.3, 127.2, 126.6, 125.3, 125.2, 123.1, 122.8, 61.6, 17.2, 14.5.

Diethyl-phenanthrene-9, 10-dicarboxylate (3m)[13]: Obtained from **1m** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (d, J = 7.6 Hz, 1H), 8.14 – 8.02 (m, 2H), 7.83 (d, J = 7.6 Hz, 1H), 7.71 (m, 3H), 7.59 – 7.49 (m, 1H), 4.89 – 4.11 (m, 4H), 1.45 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.4, 127.7, 126.8, 122.9, 62.0, 14.3.

Phenanthrene-9, 10-diylbis(methylene)-diacetate (3n)[20]**:** Obtained from **1n** and **2a** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.0 Hz, 2H), 8.19 (d, J = 8.0 Hz, 2H), 7.70 (t, J = 8.0 Hz, 4H), 5.83 (s, 4H), 2.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 131.1, 130.7, 130.5, 127.5, 127.4, 125.4, 123.1, 60.1, 21.1.

2-methyl-9, 10-di-*p*-tolylphenanthrene (3o)[15]: Obtained from **1h** and **2b** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 8.4 Hz, 1H), 7.65 (m, 1H), 7.58 (m, 1H), 7.53 – 7.43 (m, 2H), 7.38 (s, 1H), 7.08 (s, 8H), 2.45 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 137.1, 136.9, 136.8, 136.3, 135.7, 132.3, 131.9, 131.0, 130.1, 128.5, 128.4, 128.1, 127.9, 127.4, 126.2, 126.1, 122.5, 122.3, 21.8, 21.4, 21.3.

2-(*Tert*-butyl)-9, 10-di-*p*-tolylphenanthrene (3p): Obtained from **1h** and **2c** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 13.6, 8.4 Hz, 2H), 7.76 (M, 1H), 7.70 – 7.55 (m, 3H), 7.47 (M, 1H), 7.09 (d, J = 2.8 Hz, 8H), 2.36 (d, J = 1.6 Hz, 6H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 137.5, 137.2, 136.9, 136.7, 135.8, 135.7, 132.0, 131.0, 130.9, 129.9, 128.4, 128.3, 127.9, 126.3, 126.2, 124.5, 123.8, 122.4, 122.3, 34.9, 31.4, 21.5, 21.4. HRMS (ESI, *m/z*) calcd for $C_{32}H_{30}$ (M^+), 414.2348; found, 414.2359. MP:130.1-131.7℃. IR (KBr) υ: 3056, 2828, 1691, 1373, 1256.

2-Fluoro-9, 10-di-*p*-tolylphenanthrene (3q): Obtained from **1h** and **2d** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.65 (m, 2H), 7.71 – 7.61 (m, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.39 (m, 1H), 7.22 (m, 1H), 7.13 – 6.97 (m, 8H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, J = 245.1 Hz), 138.5, 136.7 (d, J = 4.0 Hz), 136.4, 136.2 (d, J = 3.3 Hz), 136.1, 134.0 (d, J = 8.5 Hz), 131.8, 131.0, 130.8, 129.8, 128.6, 128.4, 128.2, 126.6, 125.3, 124.9 (d, J = 8.7 Hz), 122.4, 115.2 (d, J = 23.9 Hz), 112.4 (d, J = 22.2 Hz), 21.4. HRMS (ESI, *m/z*) calcd for $C_{28}H_{21}F$ (M^+), 376.1627; found, 376.1637. MP: 110.2-111.5℃. IR (KBr) υ: 3056, 2824 1505, 1375, 1256, 1206.

2-Methoxy-9, 10-di-*p*-tolylphenanthrene (3r): Obtained from **1h** and **2e** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.66 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.30 (dd, J = 9.2, 2.4 Hz, 1H), 7.06 (s, 9H), 6.97 (d, J = 2.4 Hz, 1H), 3.74 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.24, 137.89, 136.88, 136.83, 136.70, 135.8, 133.8, 131.3, 130.9, 130.8, 130.1, 129.1, 128.8, 128.5, 128.4, 128.0, 126.4, 125.6, 124.4, 124.2, 122.0, 116.1, 109.1, 55.3, 21.4. HRMS (ESI, *m/z*) calcd for $C_{29}H_{24}O$ (M^+), 388.1827; found, 388.1829. MP: 126.4-127.9℃. IR (KBr) υ: 3056, 2956, 1255.

Methyl-9, 10-di-*p*-tolylphenanthrene-2-carboxylate (3s): Obtained from **1h** and **2f** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (m, 2H), 8.32 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.06 (m, 8H), 4.36 (q, J = 7.2 Hz, 2H), 2.33 (s, 6H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 138.1, 137.8, 136.4, 136.2, 136.1, 135.9, 133.2, 133.0, 131.9, 131.0, 130.9, 130.3, 129.5, 128.6, 128.5, 128.3, 128.1, 127.7, 126.7, 126.1, 123.2, 122.3, 61.1, 21.4, 14.4. HRMS (ESI, *m/z*) calcd for $C_{30}H_{24}O_2$ (M^+), 416.1776; found,416.1766. MP: 110.3-112.2℃. IR (KBr) υ: 3055, 2980, 2824, 1715, 1385, 1256.

2, 7-Dimethyl-9, 10-di-*p*-tolylphenanthrene (3t): Obtained from **1h** and **2g** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.33 (s, 2H), 7.05 (q, J = 8.0 Hz, 8H), 2.43 (s, 6H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 136.9, 135.8, 135.7, 132.0, 131.0, 128.3, 128.0, 127.9, 127.4, 122.3, 21.8, 21.4. HRMS (ESI, *m/z*) calcd for $C_{32}H_{30}$ (M^+), 386.2035; found, 386.2044. MP: 129.8-130.4℃. IR (KBr) υ: 3054, 2823, 1694, 1373, 1255.

2, 7-Difluoro-9, 10-di-*p*-tolylphenanthrene (3u): Obtained from **1h** and **2h** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 9.2, 5.6 Hz, 2H), 7.39 (m, 2H), 7.18 (dd, J = 11.2, 2.8 Hz, 1H), 7.07 (d, J = 8.0 Hz, 4H), 7.00 (d, J = 8.0 Hz, 4H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J = 245.1 Hz), 136.4, 135. 9, 130.6, 128.7, 126.4, 124.6 (d, J = 9.3 Hz), 115.6 (d, J = 24.2 Hz), 112.6 (d, J = 22.1 Hz), 21.4. HRMS (ESI, *m/z*) calcd for $C_{28}H_{20}F_2$ (M^+), 394.1533; found, 394.1529. MP: 127.2-128.9℃. IR (KBr) υ: 3054, 2825 1505, 1382, 1256, 1206.

2-Fluoro-7-methyl-9, 10-di-*p*-tolylphenanthrene (3v): Obtained from **1h** and **2i** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, J = 9.2, 5.6 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.21 – 7.14 (m, 1H), 7.08-7.00 (m, 8H), 2.42 (s, 3H), 2.34 (d, J = 4.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, J = 244.6 Hz), 138.3, 136.8 (d, J = 3.6 Hz), 136.5, 136.3, 136.2, 136.1, 135.9, 133.5 (d, J = 8.3 Hz), 131. 9, 130.8, 128.6, 128.4, 127.7, 127.6, 126.7, 124.6 (d, J = 8.6 Hz), 122.3, 115.1 (d, J = 23.9 Hz), 112.3 (d, J = 22.0 Hz), 21.8, 21.4, 21.3. HRMS (ESI, *m/z*) calcd for $C_{29}H_{23}F$ (M^+), 399.1784; found, 390.1777. MP: 113.6-114.8℃. IR (KBr) υ: 3056, 2825 1515, 1382, 1256.

1, 3-Dimethyl-9, 10-di-p-tolylphenanthrene (3w): Obtained from **1h** and **2j** following the procedure for the synthesis of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, J = 9.2, 5.6 Hz, 1H), 8.44 (s, 1H), 7.35 – 7.28 (m, 1H), 7.17 (s, 1H), 7.02-6.99 (m, 4H), 6.97 – 6.81 (m, 6H), 2.57 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.2, 137.0, 136.6, 135.9, 135.8, 135.7, 133.0, 131.3, 131.0, 130.9, 128.4, 127.8, 125.4, 125.3, 120.9, 115.1, 114.8, 112.1, 111.9, 25.2, 21.7, 21.3.

HRMS (ESI, *m/z*) calcd for $C_{32}H_{30}$ (M^+), 386.2035; found, 386.2043. MP: 132.4-133.6℃. IR (KBr) υ: 3055, 2830, 1695, 1374, 1256.

Conclusions

In summary, we have developed a new synthetic strategy to prepare a variety of multi-substituted phenanthrenes employing cyclic diaryliodoniums and internal alkynes at modest to good yields. A broad range of internal alkynes including aryl alkyl, diaryl, and dialkyl alkynes were viable for the reactions. A number of functional groups including fluoro, ether, ester and trimethylsilyl were well tolerated under the reaction conditions. Further investigation of the exact mechanism and the application of our new synthetic method is in progress.

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