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Extended Study of Visible Light-Induced Photocatalytic [4 + 2] Benzannulation: Synthesis of Polycyclic (Hetero)Aromatics

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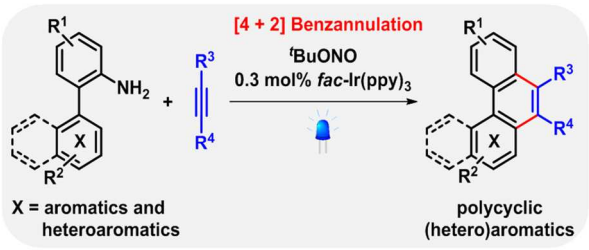
Abstract: Herein we report an extended study of [4 + 2] benzannulation reactions of 2-(hetero)aryl-substituted anilines with alkynes by visible light photocatalysis. The method requires the use of ^{t}BuONO as a diazotizing agent and 0.3 mol% of *fac*-Ir(ppy)$_3$ as a photocatalyst at room temperature. The reaction proceeded in a chemo- and regioselective manner with high functional group tolerance under mild conditions allowing the preparation of a wide variety of polycyclic (hetero)aromatic compounds, including phenanthrenes, in moderate to high yields. This procedure is amenable to gram-scale synthesis of 9-phenylphenanthrene.



- synthesis of library of polycyclic (hetero)aromatics
- chemo- and regioselective synthesis
- broad substrate scope with high functional group tolerance
- gram-scale synthesis

INTRODUCTION

Polycyclic aromatic and heteroaromatic compounds have received considerable attention because of their various biological and electronic properties and have been used as important structural motifs in many applications.[1] In particular, they have been applied to various electronic devices such as organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs).[2] In addition, polycyclic (hetero)aromatic systems constitute the core structures of many biologically active natural products, pharmaceuticals, and agrochemicals (Figure 1).[1a,3]

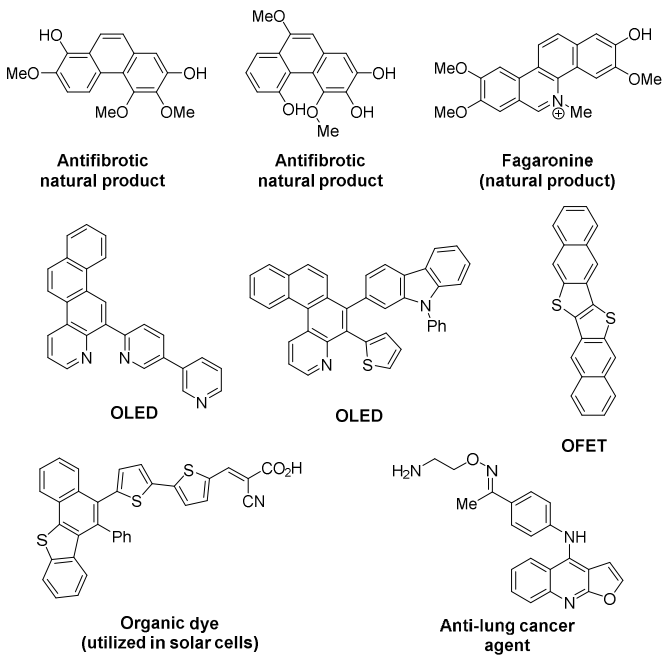


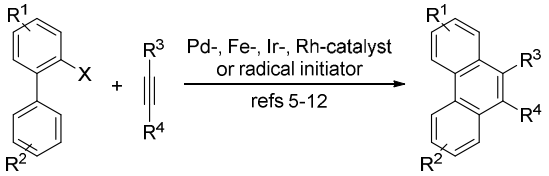
Figure 1. Examples of polycyclic (hetero)aromatic compounds and their applications.

Owing to their significant importance, numerous synthetic approaches to polycyclic (hetero)aromatics were reported so far.[4] Among them, the intermolecular [4 + 2] benzannulation

between a functionalized biaryl derivative and an alkyne has received much attention as a simple and straightforward method for the construction of polycyclic aromatic units such as phenanthrene units. In particular, the [4 + 2] benzannulation reaction of 2-functionalized 1,1′-biaryls with alkynes through the activation of the $C_{2'}$-H bond is perhaps one of the most atom-economical routes to phenanthrene derivatives requiring only one pre-functionalization of substrates (Scheme 1). In 1987, the Heck group first disclosed the Pd-catalyzed [4 + 2] benzannulation reaction of 2-iodobiphenyl with diphenylacetylene for the synthesis of 9,10-diphenylphenanthrene by using $Pd(OAc)_2$, PPh_3, and Et_3N at 100 °C.[5] In 1997, Larock et al. showed that the reaction could be further improved in terms of both yield and substrate scope by using NaOAc as base.[6] In 2010, the Glorius group developed a Pd-catalyzed decarboxylative reaction between 2-arylbenzoic acids and alkynes to afford phenanthrenes in the presence of a base and Ag_2CO_3 as an oxidant at 140 °C.[7] An iron-catalyzed reaction between 2-biaryl magnesium bromides and alkynes in the presence of 4,4′-di-*tert*-butyl-2,2′-bipyridyl as a ligand and 1,2-dichloroisobutane as an oxidant at room temperature was reported by Nakamura et al.[8] The Miura group developed an iridium-catalyzed coupling of 2-arylbenzoyl chlorides with alkynes in the presence of P(*t*-Bu)$_3$ as a ligand at 160 °C to afford phenanthrenes.[9] Recently, the same group reported rhodium-catalyzed oxidative benzannulation of (2-arylphenyl)boronic acids with alkynes for the synthesis of phenanthrenes by using $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$ at 100 ^oC under aerobic atmosphere.[10] In addition, Studer et al. reported the construction of the phenanthrene ring via base-promoted homolytic aromatic substitution of 2-aminobiaryls with alkynes in the presence of isoamyl nitrite as a diazotizing agent and substoichiometric amounts of tetrabutylammonium iodide (Bu_4NI) as a radical initiator at 70 °C.[11] Recently, the Cai group developed a similar method using ^{t}BuONO as a nitrite source and substoichiometric amounts of

ascorbic acid as the radical initiator at room temperature.[12] Despite these significant advances, these methods often suffer from harsh reaction conditions such as the use of strong bases, substoichiometric amounts of reagents, and high temperatures.

Scheme 1. Previous Work on Phenanthrene Synthesis by [4 + 2] Benzannulation of 2-Functionalized 1,1′-Biaryls with Alkynes

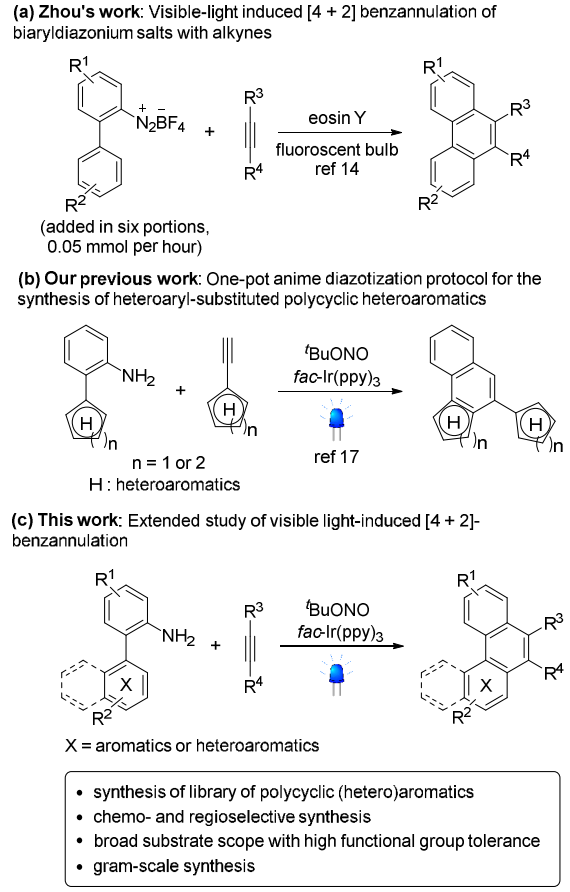


X = I (Heck and Larock et al.)[5,6]
= CO_2H (Glorious et al.)[7]
= MgBr (Nakamura et al.)[8]
= COCl (Miura et al.)[9]
= $B(OH)_2$ (Miura et al.)[10]
= NH_2 (Studer and Cai et al.)[11,12]

In another arena, visible light photocatalysis has recently attracted the renewed interest of synthetic chemists, owing to its environmental benignity and mechanistic versatility in a large number of synthetically important reactions.[13] In 2012, the Zhou group nicely developed a visible light-induced reaction of biaryldiazonium salts with alkynes using eosin Y as a photosensitizer [Scheme 2(a)].[14] However, the reaction suffered from a limited substrate scope due to the difficulties in preparing the starting biaryldiazonium tetrafluoroborate salts containing functional groups such as *N*-heterocycles.[15] Moreover, the process involved the portion wise addition of the diazonium salt (in six batches; 0.05 mmol per hour). Recently, we have overcome the limitation by utilizing one-pot amine diazotization protocol[16] and reported a visible light-induced [4 + 2] benzannulation between 2-heteroaryl-substituted anilines and heteroarylalkynes in the presence of ^{t}BuONO as diazotizing agent and a cyclometalated Ir(III) complex, *fac*-$Ir(ppy)_3$ as the photocatalyst to synthesize a new class of heteroaryl-substituted tricyclic heteroaromatic compounds, which are potential materials for many applications [Scheme 2(b)].[17]

Notably, the in situ generation of diazonium salt intermediates[16] from easily available amino substrates followed by radical cycloaddition with alkynes could be considered as an efficient and practical strategy for the synthesis of polycyclic heteroaromatic compounds. Herein, we present a detailed and extended study of the chemo- and regioselective [4 + 2] benzannulation reaction of 2-(hetero)aryl-substituted anilines with alkynes by visible light photocatalysis for the preparation of a variety of substituted tri- and tetracyclic (hetero)aromatic compounds [Scheme 2(c)].

Scheme 2. Visible Light-induced [4 + 2] Benzannulation for the Synthesis of Polycyclic (Hetero)Aromatics Including Phenanthrenes



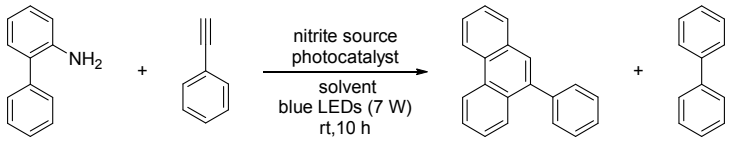
In particular, we focused our attention on the synthesis of phenanthrene derivatives because, although their synthetic methods have been widely investigated, more efficient and

practical alternatives are highly desirable. On the other hand, our strategy using in situ generated diazonium intermediates in the presence of the cyclometalated Ir(III) complex *fac*-Ir(ppy)$_3$ as the photocatalyst has a wide substrate scope with a simple and practical protocol.

RESULTS AND DISCUSSIONS

In order to optimize the reaction conditions, we started our investigation using 2-aminobiphenyl (**1a**) and phenylacetylene (**2a**) as model substrates for the synthesis of representative 9-phenyl phenanthrene (**3aa**) (Table 1). The reaction in the presence of 2.0 equiv of ^{t}BuONO and 1 mol% of *fac*-Ir(ppy)$_3$ in MeCN (1.0 M) under blue LEDs (7 W) at room temperature produced the desired phenanthrene **3aa** in 78% yield along with deaminated compound **4a** as a side product (Table 1, entry 1). Control experiments confirmed that the reaction requires visible light irradiation, a photocatalyst, and ^{t}BuONO (Table 1, entries 2-4). Next, several Ru- and Ir-based complexes were screened as photocatalysts, but no improvement was observed (entries 5-8). Eosin Y, used in the work by Zhou,[14] was also found to be less efficient than *fac*-Ir(ppy)$_3$ in this transformation (entry 9). Studies of the reagent stoichiometry revealed that the amount of ^{t}BuONO and the catalyst loading could be decreased to 1.5 equiv (entries 1, 10, and 11) and 0.3 mol% (entries 1, 12, and 13), respectively, without any loss in yield. Changing the nitrite source to isoamyl nitrite did not improve the yield of the reaction (entry 14). Notably, the choice of solvent was critical for success: among the examined solvents, including DCM, THF, DMF, and DMSO, only MeCN gave good results (entries 12 and 15-18). Moreover, base additives had a negative effect on the reaction; in particular, tertiary amine DBU completely inhibited the reaction probably by quenching of ^{t}BuONO (entries 19-21). Finally, the use of 1.5 equiv of alkyne at 1.0 M reaction concentration was found to be optimal (entries 12 and 22-26).

Table 1. Optimization of Reaction Conditions for Phenanthrene Synthesis[a]



1a **2a** **3aa** **4a**

entry	photocatalyst (mol%)	nitrite source (equiv)	solvent (concentration)	variations	Yield (%)[b]	
					3aa	**4a**
1	*fac*-Ir(ppy)$_3$ (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	–	78	10
2	*fac*-Ir(ppy)$_3$ (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	no light	20	6
3	--	^{t}BuONO (2)	MeCN (1.0 M)	–	17	5
4	*fac*-Ir(ppy)$_3$ (1.0)	–	MeCN (1.0 M)	–	--	--
5	Ru(bpy)$_3$Cl$_2$ (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	–	51	16
6	Ru(phen)$_3$Cl$_2$ (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	–	53	17
7	[Ir(dtb-bpy)(ppy)$_2$]PF$_6$ (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	–	65	14
8	*fac*-Ir(dFppy)$_3$ (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	–	71	15
9	eosin Y (1.0)	^{t}BuONO (2)	MeCN (1.0 M)	–	59	14
10	*fac*-Ir(ppy)$_3$ (1.0)	^{t}BuONO (3.0)	MeCN (1.0 M)	–	77	11
11	*fac*-Ir(ppy)$_3$ (1.0)	^{t}BuONO (1.5)	MeCN (1.0 M)	–	78	10
12	***fac*-Ir(ppy)$_3$ (0.3)**	**^{t}BuONO (1.5)**	**MeCN (1.0 M)**	–	**78**	**10**
13	*fac*-Ir(ppy)$_3$ (0.1)	^{t}BuONO (1.5)	MeCN (1.0 M)	–	68	14
14	*fac*-Ir(ppy)$_3$ (0.3)	isoamyl nitrite (1.5)	MeCN (1.0 M)	–	65	15
15	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	DCM (1.0 M)	–	26	61
16	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	THF (1.0 M)	–	16	74
17	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	DMF (1.0 M)	–	trace	53
18	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	DMSO (1.0 M)	–	trace	--
19	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (1.0 M)	K_2CO_3 (2 equiv)	48	15
20	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (1.0 M)	K_3PO_4 (2 equiv)	20	7
21	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (1.0 M)	DBU (2 equiv)	trace	8
22	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (0.5 M)	–	66	20
23	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (0.25 M)	–	57	28
24	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (2.0 M)	–	72	11
25	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (1.0 M)	1.2 equiv **2a**	60	20
26	*fac*-Ir(ppy)$_3$ (0.3)	^{t}BuONO (1.5)	MeCN (1.0 M)	3.0 equiv **2a**	78	10

[a]Reaction conditions: **1a** (0.1 mmol) and **2a** (0.15 mmol) were used unless otherwise stated;

[b]Yields were determined by gas chromatography using dodecane as an internal standard.

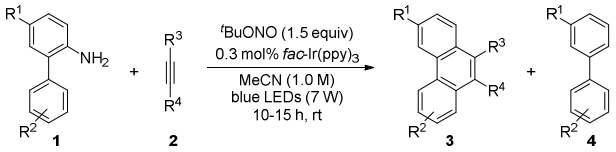
With the optimized conditions in hand, the substrate scope of the [4 + 2] benzannulation reaction for the synthesis of phenanthrene derivatives was examined (Table 2). First, the reaction of **1a** with various terminal and internal alkynes was investigated (entries 1-10). Phenylacetylenes substituted with electron-donating (Me and OMe) or -withdrawing (F and CF_3) groups reacted smoothly to afford the corresponding 9-aryl phenanthrene derivatives (**3ab**-**3ae**)

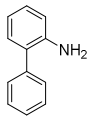
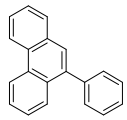
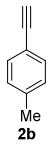
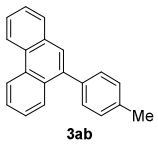
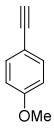
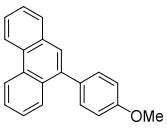
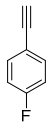
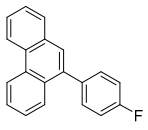
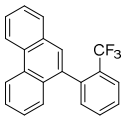
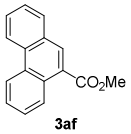
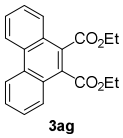
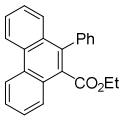
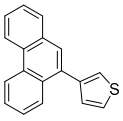
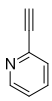
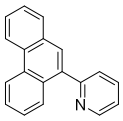
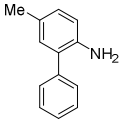
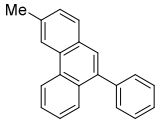
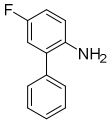
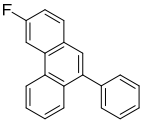
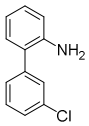
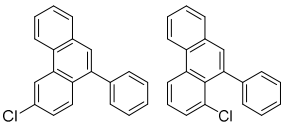
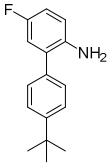
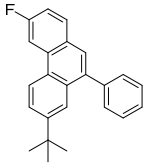
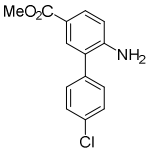
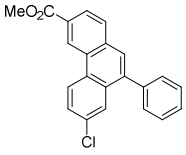
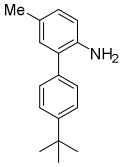
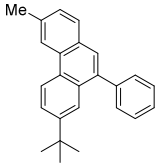
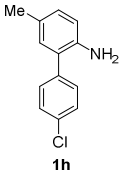
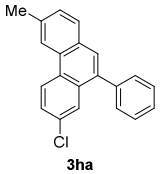
in moderate to high yields (entries 2-5). Notably, the reactivity of unsubstituted and electron-rich phenylacetylenes (**2a**-**2c**) was higher in this system than in the system using eosin Y as the photocatalyst reported by Zhou et al.[14] The reactions with ester-substituted alkynes, namely methyl propiolate (**2f**) and diethyl but-2-ynedioate (**2g**), also proceeded to give methyl phenanthrene-9-carboxylate (**3af**) and diethyl phenanthrene-9,10-dicarboxylate (**3ag**), respectively (entries 6 and 7). Another internal alkyne, namely ethyl 3-phenylpropiolate (**2h**), was also applicable to this reaction to generate the desired 9,10-disubstituted phenantherene **3ah**, albeit in relatively low yield (entry 8). Heteroaryl alkynes 3-ethynylthiophene (**2i**) and 2-ethynylpyridine (**2j**) reacted smoothly with **1a** to form the corresponding 9-heteroaryl-substituted phenantherenes (**3ai** and **3aj**) in moderate yields (entries 9 and 10). Unfortunately, diphenylacetylene and aliphatic alkyne 1-hexyne did not successfully undergo the [4 + 2] benzannulation with **1a** under the optimized conditions, probably because of the relative instability of the corresponding vinyl radical formed after the addition of 2-biphenyl radical to the corresponding alkyne.

Next, the scope of the reaction with respect to the 2-aminobiaryl substrates was examined using phenylacetylene (**2a**) as a coupling partner (Table 2, entries 11-17). The electronic nature and position of substituents did not significantly affect the efficiency of the transformation, and 2-aminobiaryls bearing electron-donating or -withdrawing substituents smoothly underwent benzannulation (entries 11 and 12). Moreover, the reaction of 3'-chloro-[1,1'-biphenyl]-2-amine (**1d**) produced a mixture of regioisomers **3da** and **3da′** in 55% overall yield, with **3da** as the major isomer (**3da**:**3da′** = 61:39) (entry 13). Diversely substituted biarylamines were also subjected to the reaction with **2a** under the optimized conditions, providing the corresponding phenanthrene derivatives (**3ea-3ha**) in 51-70% yield (entries 14-17). In general, the

corresponding deaminated products **4** were also obtained as the side products, and the numbers in parentheses indicate the yield of **4** in Table 2.

Table 2. Substrate Scope of 2-Biarylamines and Alkynes[a]

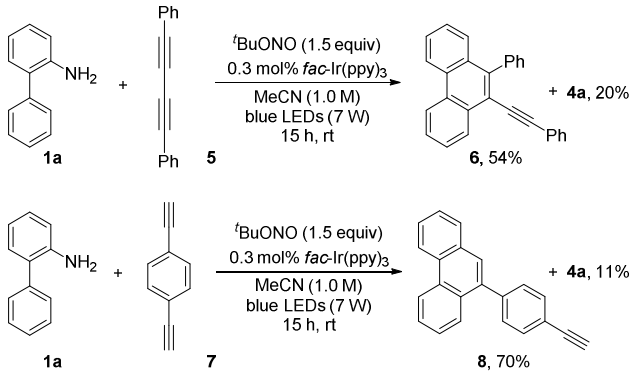


entry	amine (**1**)	alkyne (**2**)	product (**3**)	yield (%)[b]
1	 **1a**	 **2a**	 **3aa**	78 (10)
2	**1a**	 **2b**	 **3ab**	72 (11)
3	**1a**	 **2c**	 **3ac**	65 (13)
4	**1a**	 **2d**	 **3ad**	85 (5)
5	**1a**	 **2e**	 **3ae**	81 (6)
6	**1a**	 **2f**	 **3af**	64 (13)
7	**1a**	 **2g**	 **3ag**	48 (22)
8	**1a**	 **2h**	 **3ah**	31 (26)
9	**1a**	 **2i**	 **3ai**	70 (4)
10	**1a**	 **2j**	 **3aj**	62 (12)
11	 **1b**	**2a**	 **3ba**	71 (4)
12	 **1c**	**2a**	 **3ca**	56 (5)
13	 **1d**	**2a**	 **3da** **3da'**	55[c] (7)
14	 **1e**	**2a**	 **3ea**	70 (13)
15	 **1f**	**2a**	 **3fa**	51 (12)
16	 **1g**	**2a**	 **3ga**	60 (16)
17	 **1h**	**2a**	 **3ha**	57 (14)

[a]Reaction conditions: amine **1** (0.5 mmol), alkyne **2** (0.75 mmol), [t]BuONO (0.75 mmol), *fac*-Ir(ppy)$_3$ (0.015 mmol) and MeCN (0.5 mL); [b]yield of isolated phenanthrenes **3** is shown with the yield of corresponding deaminated side products **4** in parenthesis; [c]ratio of regioisomers (**3da**:**3da′** = **61**:**39**) was determined by ^{1}H NMR analysis of the crude reaction mixture.

Interestingly, the reactions using diynes as alkyne coupling partners proceeded with high chemoselectivity under the optimized conditions (Scheme 3). The reaction of **1a** with 1,4-diphenylbuta-1,3-diyne (**5**) provided the monobenzannulated product, 9-phenyl-10-(phenylethynyl)phenanthrene (**6**). In the reaction of **1a** with 1,4-diethynylbenzene (**7**), only one alkyne moiety participated in the reaction to give selectively **8** in 70% yield along with biphenyl **4a** as the side product. Notably, only monoannulated products **6** and **8** were obtained even when excess amount of **1a** (1.5 equiv) was used.

Scheme 3. Chemoselective [4 + 2] Benzannulation with Diynes[a,b]

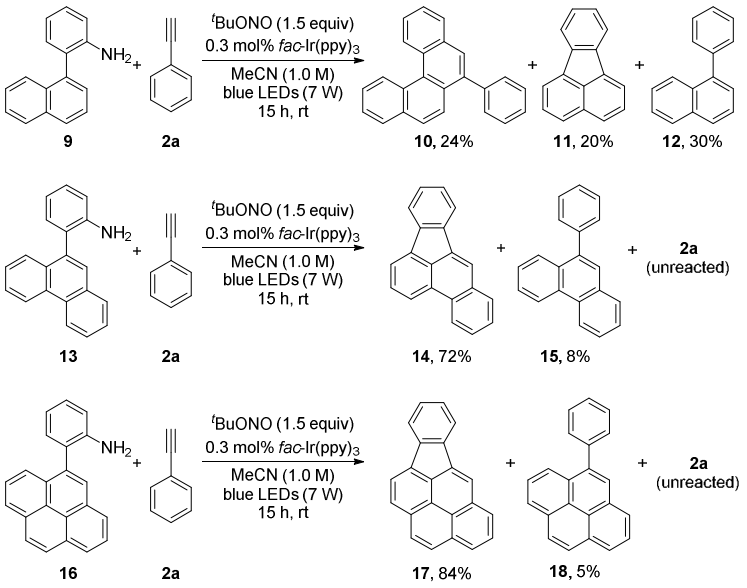


[a]Reaction conditions: **1a** (0.5 mmol), diyne (0.75 mmol), [t]BuONO (0.75 mmol), *fac*-Ir(ppy)$_3$ (0.015 mmol) and MeCN (0.5 mL); [b]yield of isolated products are shown.

Under the standard conditions, 2-polyaryl-substituted anilines showed different reactivities with **2a** depending on the electron density of the polyaromatic moiety. Whereas 2-

naphthyl-substituted aniline **9** produced [4 + 2] benzannulated product **10**, albeit in low yield, phenanthrene- and pyrene-substituted anilines (**13** and **16**) produced only cyclopenta-fused polycyclic aromatic hydrocarbons (**14** and **17**) by intramolecular aromatic substitution along with the formation of small amount of corresponding deaminated side products (Scheme 4).[18]

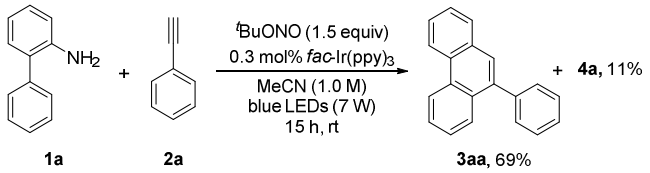
Scheme 4. Different Reactivity of 2-Polyaryl-substituted Anilines[a,b]



[a]Reaction conditions: 2-biarylamine (0.1 mmol), **2a** (0.15 mmol), ^{t}BuONO (0.15 mmol), *fac*-Ir(ppy)$_3$ (0.003 mmol) and MeCN (0.1 mL); [b]yields were determined by gas chromatography using dodecane as an internal standard.

To test the practicality of the method, we performed a gram-scale (10 mmol scale) reaction between **1a** and **2a** under the standard conditions (Scheme 5). In the event, **3aa** was produced in a yield similar to that reported for the 0.5 mmol scale reaction (Table 2, entry 1), demonstrating the feasibility of scaling up the process.

Scheme 5. Scale-up Experiment[a,b]

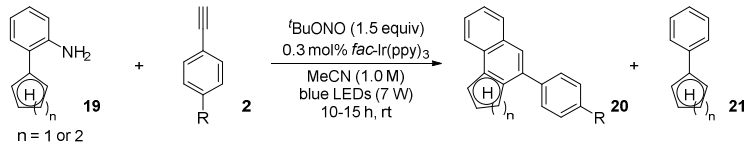


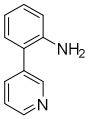
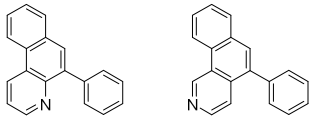
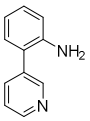
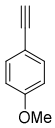
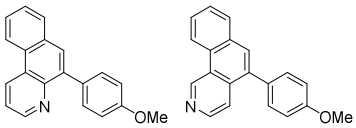
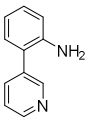
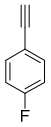
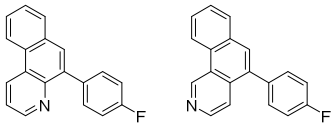
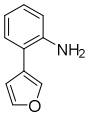
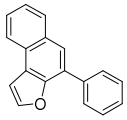
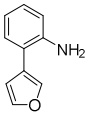
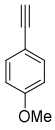
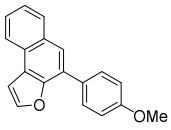
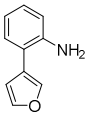
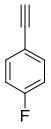
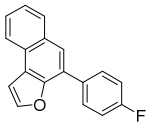
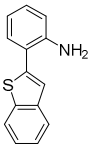
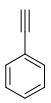
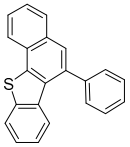
[a]Reaction conditions: **1a** (10 mmol), **2a** (15 mmol), ^{t}BuONO (15 mmol), *fac*-Ir(ppy) (0.3 mmol) and MeCN (10 mL); [b]isolated yield of **3aa** is shown.

As discussed in the introduction, this one-pot protocol based on the in situ generation of diazonium salts would allow for an expanded substrate scope. Generally, the isolation of diazonium salts from amines containing *N*-heterocycles under aqueous acidic conditions is a challenging task because of the formation of *N*-hydrochloride salts.[15] By this one-pot diazotization-[4 + 2] benzannulation protocol using ^{t}BuONO, 2-heteroaryl-substituted anilines **19** were successfully reacted with aryl-substituted alkynes **2** (Table 3). In these reactions, 2-30% of corresponding deaminated products **21** were obtained as the side products. 2-(Pyridin-3-yl)aniline (**19a**) reacted smoothly with phenylacetylene **2a** affording a mixture of two regioisomers (**20aa**:**20aa′** = 72:28) in 77% overall yield (Table 3, entry 1). Phenylacetylenes bearing electron-donating or -withdrawing groups (**2c** and **2d**) also participated in the [4 + 2] benzannulation reaction with **19a** to give the corresponding products in high yields (Table 3, entries 2 and 3). In all cases, the regioisomers could be easily separated by silica gel column chromatography. Notably, the reactions of 2-(furan-3-yl)aniline (**19b**) with phenylacetylenes **2a**, **2c**, and **2d** were highly regioselective producing only **20ba**, **20bc**, and **20bd**, respectively, in 54-71% yield (Table 3, entries 4-6). This high regioselectivity could be explained by the higher stability of the heterocyclic radical (**S4**) formed upon radical cyclization at the 2-position of the furan moiety as compared to that of the species (**S5**) arising from the radical cyclization at the 4-

position (see Scheme S1 in the SI). 2-(Benzo[*b*]thiophen-2-yl)aniline (**19c**) also participated in the [4 + 2] benzannulation reaction with **2a** producing the tetracyclic heteroaromatic compound **20ca** (Table 3, entry 7), which is the core structure of an organic dye for solar cells (Figure 1).[2a]

Table 3. Substrate Scope of 2-Heteroaryl-substituted Anilines and Alkynes[a]

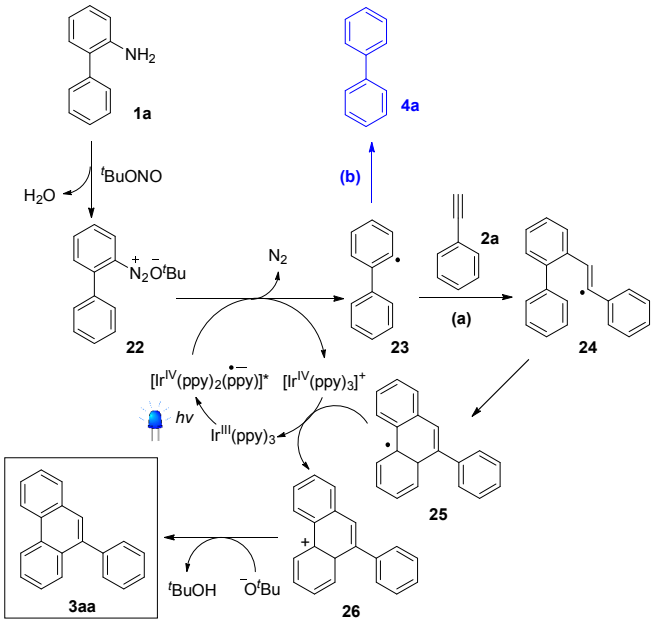


entry	amine (**15**)	alkyne (**2**)	product (**16**)	yield (%)[b]
1	 **19a**	 **2a**	 **20aa** **20aa'**	77 (4) (**20aa**:**20aa'** = 72:28)[c]
2	 **19a**	 **2c**	 **20ac** **20ac'**	70 (5) (**20ac**:**20ac'** = 66:34)[c]
3	 **19a**	 **2d**	 **20ad** **20ad'**	82 (6) (**20ad**:**20ad'** = 78:22)[c]
4	 **19b**	 **2a**	 **20ba**	60 (3)
5	 **19b**	 **2c**	 **20bc**	54 (7)
6	 **19b**	 **2d**	 **20bd**	71 (2)
7	 **19c**	 **2a**	 **20ca**	42 (30)

[a]Reaction scale: amine **19** (0.5 mmol), alkyne **2** (0.75 mmol), ^{t}BuONO (0.75 mmol), *fac*-Ir(ppy)$_3$ (0.015 mmol) and MeCN (0.5 mL); [b]yield of isolated polycyclic heteroaromatics **20** is shown with the yield of corresponding deaminated side products **21** in parenthesis; [c]ratio of regioisomers was determined by ^{1}H NMR analysis of the crude mixture.

A plausible reaction mechanism for the [4 + 2] benzannulation is shown in Scheme 6 with **1a** and **2a** as the model substrates. In situ diazotization of **1a** by ^{t}BuONO produces the corresponding diazonium salt **22**, which is reduced to biphenyl radical **23** by single-electron transfer from the excited species, [Ir^{IV}(ppy)$_2$(ppy)$^{\bullet-}$]*, formed from *fac*-Ir(ppy)$_3$ under visible light irradiation, with subsequent release of [Ir^{IV}(ppy)$_3$]$^+$. Addition of **23** to **2a** generates the corresponding vinyl radical **24**, which undergoes intramolecular cyclization to form **25**. Photocatalytic oxidation of **25** by [Ir^{IV}(ppy)$_3$]$^+$ followed by deprotonation gives the final product **3aa** along with the regeneration of the photocatalyst. The biphenyl side product probably results from H-atom abstraction by **23** from one of the many hydrogen donors present in the medium.

Scheme 6. Proposed Reaction Mechanism



In conclusion, we have expanded the scope of the [4 + 2] benzannulation of biarylamines with alkynes under mild visible light photocatalytic conditions. The process requires only ^{t}BuONO as the diazotization reagent and 0.3 mol% of *fac*-Ir(ppy)$_3$ as the photocatalyst. This one-pot diazotization protocol overcomes the problems of synthesizing N-containing polycyclic heteroaromatic compounds. The reaction was found to be highly chemo- and regioselective, and could be applied to the synthesis of a variety of polycyclic (hetero)aromatic compounds, obtained in moderate to high yields. Moreover, the reaction is amenable to gram-scale operations.

EXPERIMENTAL SECTION

General information. Acetonitrile was purchased from Sigma-Aldrich chemical company in Sure-Seal bottles and degassed by repeated sonication under light vacuum and replenishing the atmosphere with argon. *fac*-Ir(ppy)$_3$ was purchased from Sigma-Aldrich company. All other reagents required for the synthesis of the amino starting substrates and polycyclic (hetero)aromatic compounds were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, or Combi-Blocks companies. Flash column chromatography was performed using Merck silica gel 60 (70-230 mesh).

General analytical information. The synthesized amino substrates and polycyclic (hetero)aromatic compounds were characterized by ^{1}H, ^{13}C NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Bruker 600 MHz instrument (600 MHz for ^{1}H NMR and 151 MHz for ^{13}C NMR). Copies of ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and

were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet iS 10 ThermoFisher FT-IR spectrometer. Reactions were monitored by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector. Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. The mass analyzer type used for HRMS measurements is quadrupole.

General Experimental Procedure for the Synthesis of 2-Aminobiaryls (1b-1h). A Representative Experimental Procedure for the Synthesis of 5-methyl-[1,1'-biphenyl]-2-amine (1b).

An oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (116 mg, 2 mol%) in toluene:ethanol:H_2O (5:2:1; 58 mL in total). The 2-bromo-4-methylaniline (0.6 mL, 5 mmol, 1 equiv), K_2CO_3 (2.76 g, 4 equiv), and phenylboronic acid (915 mg, 1.5 equiv) were added to it. The round bottom flask connected with a reflux condenser was placed in the oil bath which was preheated at 100 °C and stirred for 16 h. The progress of the reaction was monitored by TLC and gas chromatography. After completion, the reaction mixture was diluted with dichloromethane (50 mL) and washed with brine (3 x 20 mL). Then, the organic layers were combined, dried over anhydrous $MgSO_4$, and concentrated in rotary evaporator. The desired product **1b** (817 mg, 89%) was purified by silica gel flash column chromatography using hexane/EtOAc as the eluent.

5-Methyl-[1,1'-biphenyl]-2-amine (1b):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.51 – 7.45 (m, 4H), 7.37 (tt, *J* = 6.9, 1.7 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.99 (s, 1H) 6.72 (d, *J* = 7.9 Hz, 1H), 3.66

(bs, 2H), 2.32 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.0, 139.7, 131.0, 129.1, 129.0, 128.8, 127.8, 127.7, 127.1, 115.8, 20.5; **IR (neat)**: ν_{max} = 3447, 3364, 3019, 2919, 1619, 1505, 1295, 814, 702 cm^{-1}; R_f 0.51 (hex/EtOAc, 4/1).

5-Fluoro-[1,1'-biphenyl]-2-amine (1c):[19] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.49 – 7.43 (m, 4H), 7.38 (tt, *J* = 6.7, 6.5 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.70 (dd, *J* = 9.5, 4.8 Hz, 1H), 3.64 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.3 (d, *J* = 236.4 Hz), 139.6, 138.6, 128.9, 128.9, 128.7 (d, *J* = 7.1 Hz), 127.6, 116.6 (d, *J* = 22.4 Hz), 116.4 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 22.2 Hz); **IR (neat)**: ν_{max} = 3454, 3369, 3057, 1600, 1504, 1270, 1178, 702 cm^{-1}; R_f 0.41 (hex/EtOAc, 4/1).

3'-Chloro-[1,1'-biphenyl]-2-amine (1d):[20] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.50 (s, 1H), 7.39 – 7.35 (m, 2H), 7.30 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.18 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 7.8, 7.4 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 3.74 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.4, 141.4, 134.7, 130.4, 130.1, 129.2, 129.0, 127.3, 127.3, 126.2, 118.8, 115.8; **IR (neat)**: ν_{max} = 3461, 3374, 3060, 1614, 1468, 1294, 745 cm^{-1}; R_f 0.51 (hex/EtOAc, 4/1).

4'-(*tert*-Butyl)-5-fluoro-[1,1'-biphenyl]-2-amine (1e):[21] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.69 (dd, *J* = 8.6, 4.9 Hz, 1H), 3.63 (bs, 2H), 1.36 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.3 (d, *J* = 236.4 Hz), 150.5, 139.7, 135.5, 128.7 (d, *J* = 7.1 Hz), 128.5, 125.8, 116.6 (d, *J* = 22.3 Hz), 116.3 (d, *J* = 7.7 Hz), 114.6 (d, *J* = 22.2 Hz), 34.6, 31.3; **IR (neat)**: ν_{max} = 3369, 2962, 1611, 1494, 1268, 1177, 840 cm^{-1}; R_f 0.49 (hex/EtOAc, 4/1).

Methyl 6-amino-4'-chloro-[1,1'-biphenyl]-3-carboxylate (1f):[22] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.19 (bs, 2H), 3.85 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)**

δ 167.1, 148.0, 136.8, 133.6, 132.3, 130.8, 130.4, 129.2, 125.1, 119.8, 114.6, 51.7; **IR (neat)**: ν_{max} = 3480, 3365, 3220, 2949, 1694, 1615, 1293, 1235, 835, 770, 739 cm^{-1}; $\boldsymbol{R_f}$ 0.27 (hex/EtOAc, 4/1).

4'-(*tert*-Butyl)-5-methyl-[1,1'-biphenyl]-2-amine (1g):[11] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.04 (s, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 3.69 (bs, 2H), 2.35 (s, 3H), 1.44 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.9, 141.2, 136.7, 131.1, 128.8, 128.8, 127.8, 127.7, 125.7, 115.8, 34.6, 31.5, 20.5; **IR (neat)**: ν_{max} = 3445, 3362, 2960, 1617, 1498, 1268, 811, 729 cm^{-1}; $\boldsymbol{R_f}$ 0.57 (hex/EtOAc, 4/1).

4'-Chloro-5-methyl-[1,1'-biphenyl]-2-amine (1h):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26 (s, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 3.90 (bs, 2H), 2.63 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.1, 138.2, 133.0, 130.9, 130.6, 129.5, 129.0, 128.0, 126.4, 116.1, 20.5; **IR (neat)**: ν_{max} = 3445, 3363, 3014, 2918, 1618, 1482, 1089, 812 cm^{-1}; $\boldsymbol{R_f}$ 0.51 (hex/EtOAc, 4/1).

General Experimental Procedure for the Synthesis of Polycyclic (Hetero)Aromatics (3, 6, 8 and 20). A Representative Experimental Procedure for the Synthesis of 9-phenylphenanthrene (3aa).

An oven-dried tube equipped with a magnetic stir bar was charged with **1a** (85 mg, 0.5 mmol, 1.0 equiv), **2a** (77 mg, 0.75 mmol, 1.5 equiv), *fac*-$Ir(ppy)_3$ (1 mg, 0.3 mol%), and MeCN (1.0 M, 0.5 mL). Next, ^{t}BuONO (77 mg, 0.75 mmol, 1.5 equiv) was added, and the tube was sealed with a silicone septum screw cap and irradiated by blue LEDs (7 W) at room temperature. The reaction progress was monitored by TLC and gas chromatography. After completion of the reaction, the mixture was diluted with DCM and filtered. The filtrate was concentrated by rotary

evaporator to give a residue that was subjected to flash column chromatography (SiO_2, hexane/ethyl acetate) to afford pure 9-phenylphenanthrene **3aa** (99 mg, 78%).

9-Phenylphenanthrene (3aa):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.69 (dd, *J* = 6.9, 6.9 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H) 7.64 (dd, *J* = 7.9, 6.9 Hz, 1H), 7.59 – 7.52 (m, 5H), 7.48 (tt, *J* = 7.3, 7.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.0, 139.0, 131.8, 131.4, 130.8, 130.3, 130.2, 128.9, 128.5, 127.7, 127.6, 127.1, 127.1, 126.8, 126.71, 126.65, 123.1, 122.7; **IR (neat)**: ν_{max} = 3057, 3021, 1594, 1491, 1451, 725, 701 cm^{-1}; R_f 0.59 (hex/EtOAc, 8/1).

9-(*p*-Tolyl)phenanthrene (3ab):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.85 (dd, *J* = 8.3 Hz, 1H), 8.79 (dd, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 1H), 7.78 (s, 1H), 7.76 – 7.71 (m, 2H), 7.69 (dd, *J* = 7.4, 6.8 Hz, 1H), 7.62 (dd, *J* = 8.1, 6.8 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 2.56 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.9, 138.0, 137.2, 131.8, 131.5, 130.8, 130.13, 130.09, 129.2, 128.8, 127.6, 127.2, 127.0, 126.7, 126.63, 126.58, 123.1, 122.7, 21.5; **IR (neat)**: ν_{max} = 3020, 2918, 1509, 1492, 906, 819, 723 cm^{-1}; R_f 0.49 (hex/EtOAc, 8/1).

9-(4-Methoxyphenyl)phenanthrene (3ac):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.79 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.62 (dd, *J* = 8.0, 7.7 Hz, 1H), 7.56 (dd, *J* = 8.2, 8.0 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.3, 138.6, 133.4, 131.9, 131.6, 131.3, 130.9, 130.1, 128.8, 127.66, 127.65, 127.2, 127.0, 126.7, 126.6, 123.1, 122.7, 114.0, 55.6; **IR (neat)**: ν_{max} = 3060, 2954, 2834, 1608, 1507, 1240, 1176, 1032, 725 cm^{-1}; R_f 0.46 (hex/EtOAc, 8/1).

9-(4-Fluorophenyl)phenanthrene (3ad):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.74 (d, *J* = 8.3 Hz, 1H), 7.90 (dd, *J* = 8.3, 7.9 Hz, 2H), 7.71 – 7.68 (m, 2H), 7.68 (s, 1H), 7.64 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.57 (dd, *J* = 7.1, 6.9 Hz, 1H), 7.52 (dd, *J* = 8.5, 8.1 Hz, 2H), 7.23 (dd, *J* = 8.7, 8.1 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.5 (d, *J* = 246.5 Hz), 137.9, 136.9 (d, *J* = 3.4 Hz), 131.8 (d, *J* = 7.9 Hz), 131.7, 131.3, 130.8, 130.2, 128.8, 127.9, 127.1, 126.91, 126.88, 126.8, 126.7, 123.2, 122.8, 115.4 (d, *J* = 21.3 Hz); **IR (neat)**: ν_{max} = 3062, 2926, 1605, 1505, 1219, 834, 726 cm^{-1}; R_f 0.49 (hex/EtOAc, 8/1).

9-(2-(Trifluoromethyl)phenyl)phenanthrene (3ae):[23] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.78 (d, *J* = 8.3 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 8.6, 8.3 Hz, 2H), 7.71 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.68 – 7.62 (m, 4H), 7.59 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.50 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.5, 135.6, 133.0, 132.0, 131.4, 131.2, 130.43, 130.40, 130.2 (q, *J* = 30.2 Hz, 1H), 129.0, 128.07, 128.05, 128.0, 127.3, 127.1, 126.70, 126.65, 126.4 (q, *J* = 5.2 Hz, 1H), 124.3 (q, *J* = 274.5 Hz, 1H), 122.9, 122.8; **IR (neat)**: ν_{max} = 3063, 1599, 1314, 1174, 1126, 767, 747 cm^{-1}; R_f 0.51 (hex/EtOAc, 8/1)

Methyl phenanthrene-9-carboxylate (3af):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.96 (d, *J* = 9.7 Hz, 1H), 8.72 (d, *J* = 9.1 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.48 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.74 (dd, *J* = 8.3, 8.0 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.63 (dd, *J* = 8.0, 7.9 Hz, 1H), 4.06 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.2, 132.6, 132.3, 130.8, 130.2, 130.1, 129.2, 129.1, 127.6, 127.2, 127.1, 126.8, 126.3, 123.0, 122.8, 52.4; **IR (neat)**: ν_{max} = 3060, 2948, 1712, 1528, 1445, 1252, 1210, 1026, 742 cm^{-1}; R_f 0.36 (hex/EtOAc, 8/1).

Diethyl phenanthrene-9,10-dicarboxylate (3ag):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 8.3 Hz, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 7.75 (dd, *J* = 8.3, 8.1 Hz, 2H), 7.7 (dd, *J* = 8.2, 8.1 Hz, 2H), 4.52 (q, *J* = 7.2 Hz, 4H), 1.46 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 168.1,

131.2, 130.1, 128.5, 127.8, 127.4, 127.0, 123.1, 62.2, 14.4; **IR (neat)**: ν_{max} = 2983, 1728, 1448, 1251, 1195, 1024, 761, 727 cm^{-1}; R_f 0.41 (hex/EtOAc, 4/1).

Ethyl 10-phenylphenanthrene-9-carboxylate (3ah):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.77 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 2H), 7.67-7.62 (m, 2H), 7.54 – 7.43 (m, 6H), 4.11 (q, *J* = 7.1 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.2, 138.1, 136.4, 130.8, 130.64, 130.60, 130.3, 129.9, 128.0, 127.9, 127.78, 127.76, 127.41, 127.39, 127.0, 126.8, 125.9, 122.8, 122.6, 61.1, 13.7; **IR (neat)**: ν_{max} = 2924, 1724, 1379, 1223, 1033, 760 cm^{-1}; R_f 0.38 (hex/EtOAc, 8/1).

9-Thienylphenanthrene (3ai): yellow solid; m. p. 57-58 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.78 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.71 – 7.66 (m, 2H), 7.62 (dd, *J* = 7.8, 7.7 Hz, 1H), 7.58 (dd, *J* =8.1, 7.9 Hz, 1H), 7.50 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.47 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.36 (dd, *J* = 4.8, 1.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.4, 133.8, 131.8, 131.4, 130.8, 130.2, 129.9, 128.8, 127.8, 127.1, 126.89, 126.85, 126.8, 126.7, 125.6, 123.9, 123.1, 122.8; **IR (neat)**: ν_{max} = 3075, 2925, 1598, 1492, 1449, 723, 661 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{12}S$ [M+] 260.0660, found 260.0657; R_f 0.49 (hex/EtOAc, 8/1).

2-(Phenanthren-9-yl)pyridine (3aj):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.83 (d, *J* = 4.9 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.72 – 7.60 (m, 4H), 7.58 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.37 (dd, *J* = 7.1, 4.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.6, 149.8, 137.4, 136.7, 131.6, 131.0, 130.7, 130.5, 129.2, 128.7, 127.3, 127.0, 126.9, 126.8, 126.7, 125.3, 123.2, 122.8, 122.4; **IR (neat)**: ν_{max} = 3057, 2925, 1585, 1470, 1429, 745, 725 cm^{-1}; R_f 0.31 (hex/EtOAc, 4/1).

3-Methyl-9-phenylphenanthrene (3ba):[11] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.55 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.49 (dd, *J* = 8.8, 7.9 Hz, 2H), 2.68 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.0, 137.8, 136.3, 131.3, 130.4, 130.1, 130.0, 129.5, 128.6, 128.5, 128.3, 127.4, 127.3, 126.9, 126.4, 126.2, 122.9, 122.3, 22.2; **IR (neat)**: ν_{max} = 3054, 3021, 2920, 1735, 1598, 1448, 893, 748, 709 cm^{-1}; R_f 0.51 (hex/EtOAc, 4/1).

3-Fluoro-9-phenylphenanthrene (3ca):[12] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.33 (dd, *J* = 11.0, 2.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 8.8, 8.6 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.47 (t, *J* = 6.7 Hz, 1H), 7.38 (ddd, *J* = 11.0, 8.6, 2.4 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.6 (d, *J* = 245.6 Hz), 140.6, 138.1, 131.43 (d, *J* = 8.4 Hz), 131.35, 130.7 (d, *J* = 8.9 Hz), 130.04, 130.01, 128.4, 128.3, 127.4, 127.1, 127.0, 126.8, 126.5, 123.1, 115.9 (d, *J* = 24.0 Hz), 107.7 (d, *J* = 22.3 Hz); **IR (neat)**: ν_{max} = 3056, 2927, 1738, 1597, 1500, 771, 710 cm^{-1}; R_f 0.62 (hex/EtOAc, 8/1).

2-(*tert*-Butyl)-6-fluoro-10-phenylphenanthrene (3ea): off-white solid; m. p. 120-121 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.57 (d, *J* = 8.7 Hz, 1H), 8.30 (d, *J* = 11.0 Hz, 1H), 7.96 (s, 1H), 7.86 (dd, *J* = 8.6, 8.4 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.65 (s, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.54 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 8.6, 8.4 Hz, 1H), 1.36 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.6 (d, *J* = 245.3 Hz), 150.0, 140.7, 138.2, 131.3 (d, *J* = 8.4 Hz), 131.1, 130.6 (d, *J* = 8.9 Hz), 130.0, 128.3, 128.0, 127.9, 127.4, 126.8, 124.7, 122.9, 122.7, 115.5 (d, *J* = 23.9 Hz), 107.4 (d, *J* = 22.3 Hz), 35.0, 31.3; **IR (neat)**: ν_{max} = 3057, 2962, 1595, 1492, 1181, 701 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{21}F$ [M+] 328.1627, found 328.1628; R_f 0.68 (hex/EtOAc, 8/1).

Methyl 7-chloro-9-phenylphenanthrene-3-carboxylate (3fa): pale green solid; m. p. 171-172 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.39 (s, 1H), 8.79 (d, *J* = 8.9 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.73 (s, 1H), 7.67 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.58 – 7.47 (m, 5H), 4.04 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.2, 140.4, 139.6, 134.2, 133.2, 132.4, 129.8, 129.3, 128.94, 128.86, 128.6, 128.2, 128.1, 128.0, 127.6, 127.0, 126.2, 125.0, 124.8, 52.4; **IR (neat)**: ν_{max} = 3025, 2950, 1715, 1436, 1271, 906, 699 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{15}ClO_2$ [M+] 346.0761, found 346.0758; $\boldsymbol{R_f}$ 0.35 (hex/EtOAc, 8/1).

2-(*tert*-Butyl)-6-methyl-10-phenylphenanthrene (3ga):[11] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.69 (d, *J* = 8.7 Hz, 1H), 8.48 (s, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (dd, *J* = 8.0, 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 2.65 (s, 3H), 1.35 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.1, 141.1, 137.9, 136.1, 130.9, 130.0, 129.9, 129.3, 128.4, 128.20, 128.16, 128.15, 127.4, 127.2, 124.4, 122.61, 122.59, 122.1, 34.9, 31.3, 22.2; **IR (neat)**: ν_{max} = 3053, 2961, 1739, 1617, 1597, 1371, 897, 701 cm^{-1}; $\boldsymbol{R_f}$ 0.68 (hex/EtOAc, 8/1).

2-Chloro-6-methyl-10-phenylphenanthrene (3ha):[11] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.68 (d, *J* = 8.9 Hz, 1H), 8.44 (s, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68 (s, 1H), 7.59 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.53 (m, 4H), 7.48 (dd, *J* = 5.76, 2.0 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H) 2.65 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.2, 136.9, 136.8, 132.5, 132.4, 130.0, 129.6, 129.4, 128.9, 128.7, 128.6, 128.53, 128.48, 127.5, 126.7, 125.9, 124.5, 122.2, 22.2; **IR (neat)**: ν_{max} = 3055, 2920, 1734, 1597, 1492, 895, 820, 701 cm^{-1}; $\boldsymbol{R_f}$ 0.62 (hex/EtOAc, 8/1).

9-Phenyl-10-(phenylethynyl)phenanthrene (6):[14] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.78 – 8.73 (m, 2H), 8.65 (d, *J* = 9.4 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.67 (m, 2H), 7.59 – 7.55 (m, 2H), 7.55 – 7.49 (m, 4H), 7.30 – 7.27 (m, 3H), 7.27 – 7.23 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.2, 140.0, 131.63, 131.59, 130.94, 130.89, 130.4, 129.9, 128.5, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 127.0, 123.7, 122.9, 122.8, 119.3, 98.4, 88.0; **IR (neat)**: ν_{max} = 3061, 1597, 1490, 1449, 754, 724, 690 cm^{-1}; R_f 0.51 (hex/EtOAc, 8/1).

9-(4-Ethynylphenyl)phenanthrene (8): pale-green oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.79 (d, *J* = 8.1 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.68 (m, 3H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.64 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.56 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 3.18 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.6, 138.1, 132.3, 131.6, 130.94, 130.85, 130.3, 128.9, 127.78, 127.77, 127.1, 127.0, 126.9, 126.83, 126.80, 123.2, 122.8, 121.4, 83.8, 77.9; **HRMS** m/z (EI) calc. for $C_{22}H_{14}$ [M+] 278.1096, found 278.1095; **IR (neat)**: ν_{max} = 3288, 3061, 2924, 2106, 1504, 838, 749, 733 cm^{-1}; R_f 0.54 (hex/EtOAc, 8/1).

5-Phenylbenzo[*f*]quinoline (20aa):[24] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.04 – 8.99 (m, 2H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.71 (dd, *J* = 7.5, 6.8 Hz, 1H), 7.68 (dd, *J* = 7.1, 6.8 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.48 (dd, *J* = 7.4, 7.4 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.6, 146.9, 139.9, 139.5, 131.6, 131.3, 130.9, 130.8, 129.7, 129.0, 128.2, 127.7, 127.6, 127.1, 126.0, 122.6, 121.3; **IR (neat)**: ν_{max} = 3056, 1740, 1599, 1442, 1239, 750, 702 cm^{-1}; R_f 0.68 (hex/EtOAc, 2/1).

5-Phenylbenzo[*h*]isoquinoline (20aa′): brown oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.13 (s, 1H), 8.84 (d, *J* = 8.1 Hz, 1H), 8.66 (d, *J* = 5.7 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.90 (s, 1H), 7.78 – 7.74 (m, 2H), 7.69 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.54 (m, 4H), 7.49 (dd, *J* = 6.0, 2.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 147.3, 145.5, 139.3, 137.3, 135.3, 131.93, 131.86, 130.1,

129.23, 129.16, 128.8, 128.1, 128.0, 127.9, 125.5, 122.0, 119.6; **IR (neat)**: ν_{max} = 3057, 2925, 1717, 1600, 1443, 1238, 750, 702 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{19}H_{13}N$ [M+] 255.1048, found 255.1047; $\boldsymbol{R_f}$ 0.38 (hex/EtOAc, 1/1).

5-(4-Methoxyphenyl)benzo[*f*]quinoline (20ac): brown solid; m. p. 140-141 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.03 (d, *J* = 8.3 Hz, 1H), 9.00 (d, *J* = 4.3 Hz, 1H), 8.65 (d, *J* = 7.9 Hz, 1H), 7.99 (s, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.58 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.3, 149.6, 147.1, 139.1, 132.3, 131.9, 131.8, 131.0, 130.9, 129.6, 128.9, 127.7, 127.0, 126.1, 122.6, 121.3, 113.8, 55.6; **IR (neat)**: ν_{max} = 2925, 1508, 1245, 1034, 831, 751 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{15}NO$ [M+] 285.1154, found 285.1152; $\boldsymbol{R_f}$ 0.68 (hex/EtOAc, 2/1).

5-(4-Methoxyphenyl)benzo[*h*]isoquinoline (20ac′): orange solid; m. p. 128-129 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.11 (s, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 8.66 (d, *J* = 5.6 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.86 (s, 1H), 7.77 (d, *J* = 5.6 Hz, 1H), 7.73 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.67 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.6, 147.2, 145.3, 136.9, 135.6, 132.0, 131.71, 131.70, 131.5, 131.2, 129.1, 129.0, 127.9, 125.5, 122.0, 119.6, 114.2, 55.6; **IR (neat)**: ν_{max} = 3037, 2925, 1609, 1512, 1246, 1032, 834, 751 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{15}NO$ [M+] 285.1154, found 285.1152; $\boldsymbol{R_f}$ 0.32 (hex/EtOAc, 1/1).

5-(4-Fluorophenyl)benzo[*f*]quinoline (20ad): yellow solid; m. p. 162-163 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.03 (d, *J* = 8.4 Hz, 1H), 8.99 (d, *J* = 4.3 Hz, 1H), 8.66 (d, *J* = 8.1 Hz, 1H), 7.98 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.70 (m, 3H), 7.69 (dd, *J* = 7.9, 7.7 Hz, 1H), 7.59 (dd, *J*

= 8.4, 4.3 Hz, 1H), 7.21 (dd, *J* = 8.8, 8.5 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.7 (d, *J* = 246.5 Hz), 149.6, 146.8, 138.4, 135.8 (d, *J* = 3.3 Hz), 132.4 (d, *J* = 7.9 Hz), 131.6, 131.3, 131.1, 129.7, 129.0, 127.8, 127.3, 126.1, 122.7, 121.4, 115.1 (d, *J* = 21.4 Hz); **IR (neat)**: ν_{max} = 3062, 2925, 1590, 1508, 1222, 834, 749 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{19}H_{12}FN$ [M+] 273.0954, found 273.0950; $\boldsymbol{R_f}$ 0.58 (hex/EtOAc, 2/1).

5-(4-Fluorophenyl)benzo[*h*]isoquinoline (20ad′): yellow sticky solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 10.11 (s, 1H), 8.82 (d, *J* = 8.3 Hz, 1H), 8.67 (d, *J* = 5.6 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 1H), 7.75 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.49 (dd, *J* = 8.8, 8.7 Hz, 2H), 7.23 (dd, *J* = 8.7, 8.2 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.8 (d, *J* = 247.6 Hz), 147.3, 145.5, 136.2, 135.3, 135.2 (d, *J* = 3.4 Hz), 132.0, 131.8, 131.7 (d, *J* = 8.0 Hz), 129.2, 129.16, 128.17, 128.0, 125.4, 122.0, 119.4, 115.8 (d, *J* = 21.5 Hz); **HRMS** m/z (EI) calc. for $C_{19}H_{12}FN$ [M+] 273.0954, found 273.0950; $\boldsymbol{R_f}$ 0.28 (hex/EtOAc, 1/1).

4-Phenylnaphtho[2,1-*b*]furan (20ba): yellow sticky solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.87 (s, 1H), 7.84 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 8.2, 8.0 Hz, 1H), 7.55 (dd, *J* = 7.8, 7.5 Hz, 2H), 7.52 (dd, *J* = 8.2, 8.0 Hz, 1H), 7.45 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 150.7, 144.5, 136.7, 131.1, 129.04, 129.02, 128.9, 128.2, 127.5, 126.9, 126.4, 125.1, 124.3, 123.7, 123.5, 106.0; **IR (neat)**: ν_{max} = 3062, 2925, 1590, 1508, 1222, 834, 749 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{12}O$ [M+] 244.0888, found 244.0891; $\boldsymbol{R_f}$ 0.51 (hex/EtOAc, 4/1).

4-(4-Methoxyphenyl)naphtho[2,1-*b*]furan (20bc): brown sticky solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.16 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.84 – 7.83 (m, 2H), 7.59 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.52 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 159.7, 150.7, 144.4,

131.1, 130.1, 129.1, 128.9, 127.2, 126.5, 126.1, 125.0, 123.6, 123.5, 123.4, 114.3, 106.0, 55.6; **IR (neat)**: ν_{max} = 2925, 2851, 1609, 1510, 1250, 1033, 831, 751 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{19}H_{14}O_2$ [M+] 274.0994, found 274.0991; $\boldsymbol{R_f}$ 0.69 (hex/EtOAc, 4/1).

4-(4-Fluorophenyl)naphtho[2,1-*b*]furan (20bd): white sticky solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.93 (dd, *J* = 8.6, 8.5 Hz, 2H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.81 (s, 1H), 7.60 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.23 (dd, *J* = 8.6, 8.5 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.9 (d, *J* = 247.7 Hz), 150.5, 144.6, 132.7 (d, *J* = 3.3 Hz), 131.0, 130.6 (d, *J* = 8.0 Hz), 129.0, 127.4, 126.5, 125.8, 125.2, 124.1, 123.7, 123.5, 115.8 (d, *J* = 21.4 Hz), 106.1; **IR (neat)**: ν_{max} = 3056, 2924, 2850, 1508, 1233, 833, 749 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{11}FO$ [M+] 262.0794, found 262.0796; $\boldsymbol{R_f}$ 0.66 (hex/EtOAc, 4/1).

6-Phenylbenzo[*b*]naphtho[2,1-*d*]thiophene (20ca):[2a] **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 9.4, 8.2 Hz, 2H), 7.67 (s, 1H), 7.63 (dd, *J* = 7.7, 7.3 Hz, 1H), 7.59 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.56 – 7.51 (m, 5H), 7.36 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.15 – 7.09 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.5, 139.4, 138.4, 137.6, 136.9, 132.7, 131.6, 130.9, 129.6, 128.8, 128.4, 128.0, 127.04, 126.95, 126.8, 125.8, 125.0, 124.5, 124.1, 122.9; **IR (neat)**: ν_{max} = 3055, 2921, 2849, 1492, 1431, 1248, 1029, 755 cm^{-1}; $\boldsymbol{R_f}$ 0.69 (hex/EtOAc, 4/1).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ^{1}H and ^{13}C NMR spectra for all 2-aminobiaryls (**1b**-**1h**), phenanthrene derivatives (**3**, **6** and **8**) and polycyclic heteroaromatic compounds (**20**).

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Notes

The authors declare no competing financial interest.

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