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Pd(II)-Catalyzed Directing-Group-Aided C–H Arylation and Alkylation of Pyrene Core: Synthesis of C1,C2- and C1,C10-Disubstituted Pyrene Motifs

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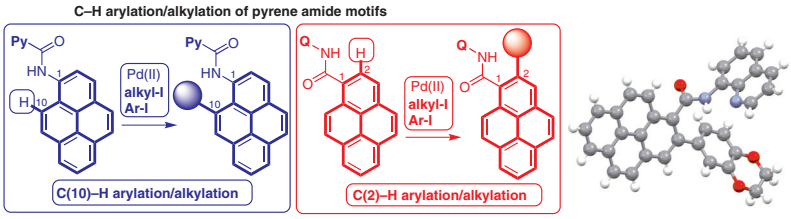

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Abstract We report the application of the Pd(II)-catalyzed, directing-group-aided C–H arylation/alkylation tactics to functionalize the pyrene core, especially, the relatively inaccessible C2 and K-region C10 positions of the pyrene core and augmentation of the library of pyrene derivatives with C1,C2- and C1,C10-disubstituted pyrene motifs. The Pd(II)-catalyzed β-C–H arylation/alkylation of the C2-position of pyrene-1-carboxamide possessing an 8-aminoquinoline directing group yielded various C1,C2-disubstituted pyrenes. Similarly, the Pd(II)-catalyzed selective γ-C–H arylation/alkylation of the C10-position of *N*-(pyren-1-yl)picolinamide, possessing a picolinamide directing group, yielded various C1,C10-disubstituted pyrenes. Examples of C(9)–H arylation of pyrene-1-carboxamide and the removal of the directing group after the C–H arylation/alkylation reactions were also shown. The structures of representative pyrene derivatives were confirmed by the X-ray structure analysis. Given the importance of the pyrene derivatives in various fields of chemical sciences, this report is a contribution towards augmentation of the library of pyrene derivatives with C1,C2- and C1,C10-disubstituted pyrene amide motifs.

Key words C–H activation, C–H arylation/alkylation, C–H functionalization, bidentate directing group, carboxamides, palladium, pyrene

During an era when cross-coupling reactions were ubiquitous in organic synthesis,[1,2] there were some pioneering efforts at direct functionalization of C–H bonds in small organic molecules to achieve C–C bond construction. In 1955 and 1956 Murahashi reported[3] the cobalt-promoted insertion of carbon monoxide into an *ortho*-C(sp^2)–H bond of aldimine and azobenzene substrates. Subsequently, various stoichiometric metal-promoted C–H bond activation reactions involving cyclometallated species were published.[4] In 1970, the palladium-catalyzed chlorination of an *ortho*-C(sp^2)–H bond of azobenzene reported by Fahey is another important discovery.[5] Subsequently, Jordan (1989), Moore (1992) and Murai (1993) reported breakthroughs in catalytic C–H activation/functionalization methods involving Zr- and Ru-based catalysts.[6–8] During the last 20 years, research on transition-metal-catalyzed C–H bond activation reactions has advanced at a rapid rate.[9–11]

Pertinently, the transition-metal-catalyzed sp^2/sp^3 C–H activation/functionalization is considered to be a remarkable synthetic strategy to functionalize small organic molecules. The catalytic C–H functionalization of sp^2/sp^3 C–H bonds of small organic molecules has been accomplished with or without the help of a directing group.[9–15] In particular, directing-group-aided sp^2 and sp^3 C–H activation/functionalization strategies have received significant attention in organic synthesis because the strategy makes it feasible to functionalize the required substrates with site-selectivity or regioselectivity as well as stereoselectivity. Along this line, the Pd(II)-catalyzed bidentate directing group (BDG)-aided site-selective sp^2 and sp^3 C–H activation/functionalization of carboxamides are considered benchmark strategies.[11–15] The site-selective C–H functionalization of carboxamides derived from carboxylic acid substrates were achieved with the help of 8-aminoquinoline type BDGs (introduced by Daugulis).[11–15] On the other hand, the site-selective C–H functionalization of carboxamides derived from amine substrates were achieved with the help of picolinamide type BDGs.[11–15]

Due to the superior fluorescence properties, efficient excimer emission, and high charge-carrier mobility, pyrene and its derivatives have received much attention in various fields of chemical sciences including organic-, supramolecular and materials chemistry.[16–19] Markedly, pyrenes are important building blocks to assemble materials such as organic light-emitting diodes (OLEDs), organic semiconducting materials for OFETs, supramolecular sensors, and solar cells. Almost all types of photoelectric devices have been investigated using various pyrene-based organic materials.[16b–d,18] It is documented that the optoelectronic and pho-

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tophysical properties of pyrenes are strongly dependent on the respective substituents and their positions.[16,17,19] Consequently, several methodologies have been developed to functionalize the multiple reactive positions of pyrene core.[16,17]

The 1-, 3-, 6- and 8-positions of pyrene are known as 'active/common sites' and these sites have electron-rich density and readily undergo electrophilic aromatic substitution (S_EAr) reactions.[16b] Generally, pyrene derivatives have been synthesized by introducing substitutions at these active/common sites. The 2- and 7-positions of pyrene are known as 'nodal plane positions and uncommon or inaccessible sites' and these are relatively difficult to functionalize (Figure 1).[16b] It may be noted that the Friedel–Crafts *tert*-butylation and Ir-catalyzed direct borylation reactions have been carried out at these positions. The 4-, 5-, 9- and 10-positions of pyrene are known as 'the K-region sites' and it may be noted that oxidation and Pd-catalyzed oxidative direct arylation reactions have been carried out at these positions and these results have been summarized by Feng and Yamato.[16b]

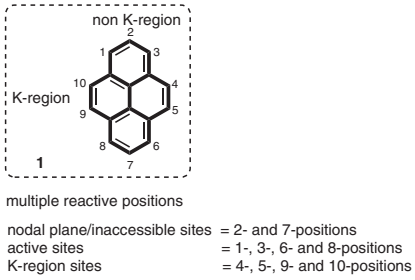
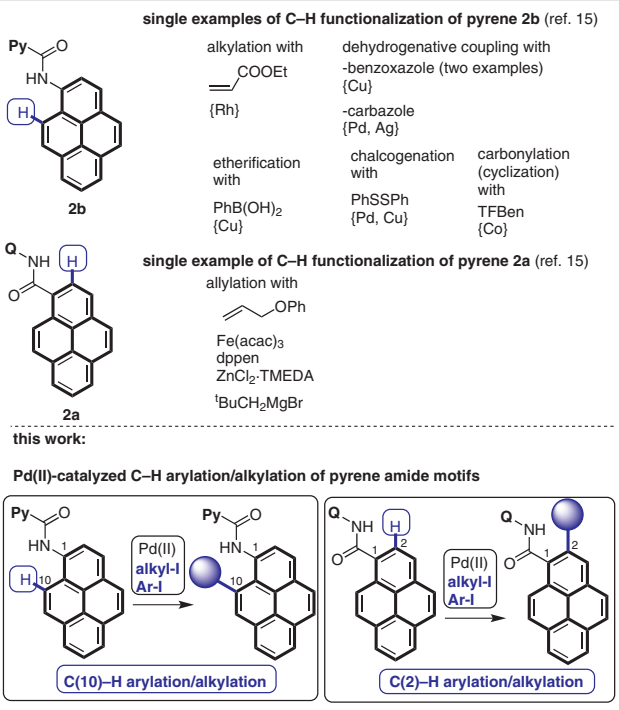


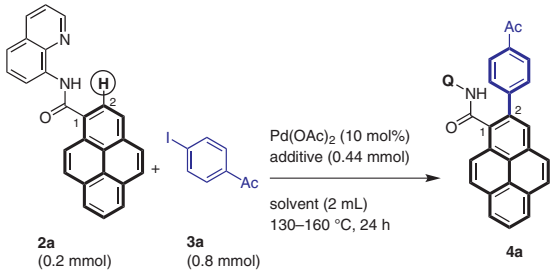
Figure 1 K-Region and non-K-region of the pyrene motif



Scheme 1 Theme of this work: C–H arylation/alkylation of pyrene amide motifs

Impressed by the chemical transformations carried out on the pyrene core and driven by the importance of the pyrene derivatives in chemical sciences,[15–19] we intended to take forward the functionalization of the pyrene core through the directing-group-aided C–H functionalization route to assemble new pyrene amide motifs. A few instances of functionalization of the pyrene core through the directing-group-aided C–H functionalization have been reported. Nevertheless, the available reports provided only single examples of functionalization of the pyrene core (Scheme 1).[15] We wanted to contribute to the development of this field by performing the bidentate directing-group-aided site-selective C–H arylation and alkylation of the relatively inaccessible C2 position and K-region C10 position of pyrene amides **2a** and **2b**, respectively. To our knowledge, the bidentate directing-group-aided site-selective C–H arylation and alkylation C2 position and C10 position of pyrene amides have not yet been explored. In a continuation of our interest in C–H activation reactions, herein we report the

Table 1 Optimization of the C–H Arylation of Pyrene Carboxamide **2a** and Assembly of the C1,C2-Disubstituted Pyrene Motif **4a**



Entry	Catalyst	Additive	Solvent	*T* (°C)	Yield of **4a** (%)
1	$Pd(OAc)_2$	Ag_2CO_3	*o*-xylene	135	38
2	$Pd(OAc)_2$	Cs_2CO_3	*o*-xylene	135	40
3	$Pd(OAc)_2$	K_2CO_3	*o*-xylene	135	51
4	$Pd(OAc)_2$	AgOAc	*o*-xylene	135	70
5	$Pd(OAc)_2$	AgOAc	1,2-DCE	130	65
6[a]	$Pd(OAc)_2$	AgOAc	*o*-xylene	130	22
7[b]	$Pd(OAc)_2$	AgOAc	*o*-xylene	130	35
8[c]	$Pd(OAc)_2$	AgOAc	*o*-xylene	130	47
9	$Pd(TFA)_2$	AgOAc	*o*-xylene	130	60
10	$Pd(MeCN)_2Cl_2$	AgOAc	*o*-xylene	130	53
11	$Ni(OTf)_2$	$NaHCO_3$	toluene	160	15

[a] 0.2 mmol of **3a**.
[b] 0.4 mmol of **3a**.
[c] 0.6 mmol of **3a**.

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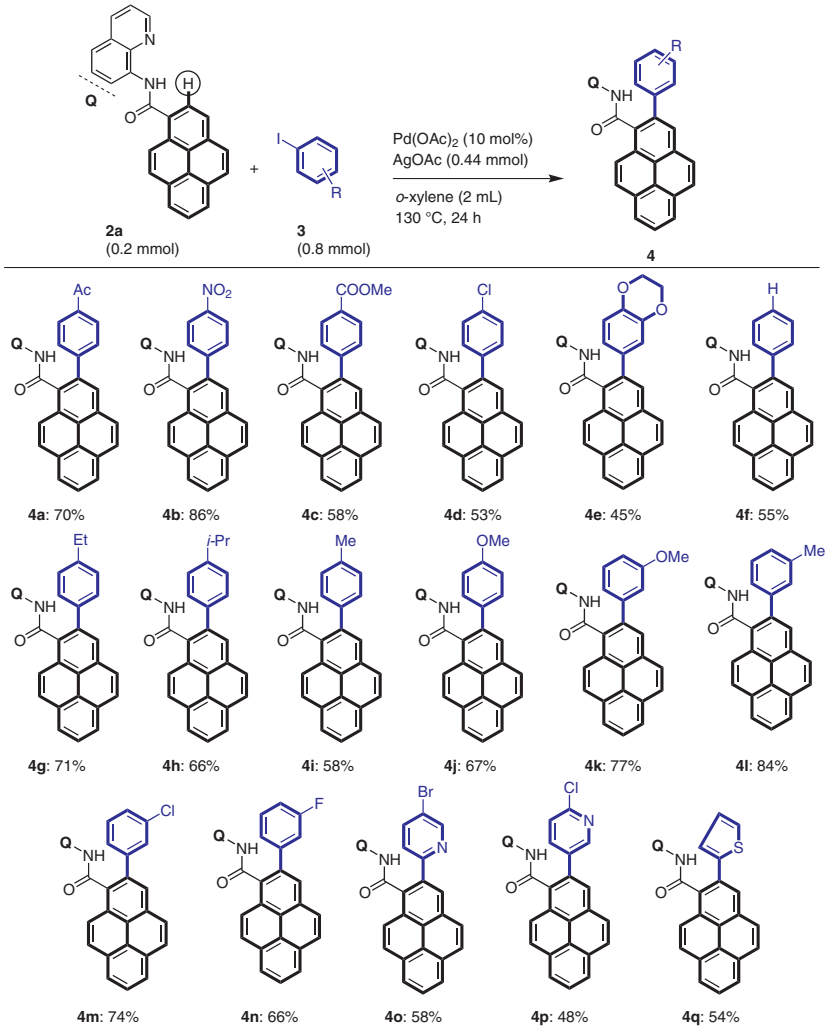
Pd(II)-catalyzed, directing-group-aided arylation/alkylation of C(2)–H bond of pyrene-1-carboxamide motif **2a** linked with 8-aminoquinoline DG, and C(10)–H bond of 1-aminopyrene motif **2b** linked with a picolinamide DG, and the assembly of various C1,C2- and C1,C10-disubstituted pyrene amide motifs.

Starting with the assembly of C1,C2- and C1,C10-disubstituted pyrene motifs via the Pd(II)-catalyzed, directing-group-aided C–H arylation/alkylation reaction, initially we prepared the pyrene-1-carboxamide **2a** possessing 8-aminoquinoline directing group, which enabled the selective β-C(sp^2)–H functionalization of **2a** (C2-position, Table 1). We performed optimization reactions by employing the standard Pd(II)-catalyzed sp^2 β-C–H arylation conditions.[11–13] Typically, the directing group 8-aminoquinoline-aided C–H functionalization of carboxamides have been carried out by using a Pd(II) catalyst and an additive such as AgOAc or Ag_2CO_3 or K_2CO_3, which function as a halide ion scavenger.[11–13]

First, a mixture of pyrene-1-carboxamide **2a**, ArI (**3a**) and $Pd(OAc)_2$ catalyst (10 mol%) in the presence of Ag_2CO_3 as an additive in *o*-xylene was heated at 135 °C for 24 h, which yielded the C(2)–H arylated pyrene-1-carboxamide **4a** in satisfactory yield (38%, Table 1, entry 1). Next, the same reaction was carried out in the presence of Cs_2CO_3 as an additive instead of Ag_2CO_3 and this reaction also yielded the C(2)–H arylated pyrene-1-carboxamide **4a** in satisfactory yield (40%, entry 2).

The Pd(II)-catalyzed arylation of pyrene-1-carboxamide **2a** by using K_2CO_3 as an additive yielded the C(2)–H arylated pyrene-1-carboxamide **4a** in an improved yield (51%, Table 1, entry 3). The Pd(II)-catalyzed arylation of **2a** in the presence of AgOAc as an additive in *o*-xylene or 1,2-DCE at 130–135 °C yielded **4a** in 65–70% yields (entries 4 and 5). The Pd(II)-catalyzed arylation of **2a** by using different amounts of **3a** (1–3 equiv) yielded the product **4a** in 22–47% yields (entries 6–8). The arylation of **2a** by using differ-



Scheme 2 Assembly of C1,C2-disubstituted pyrene carboxamide motifs **4a–q** via the Pd(II)-catalyzed, 8-aminoquinoline-directed C–H arylation of **2a**

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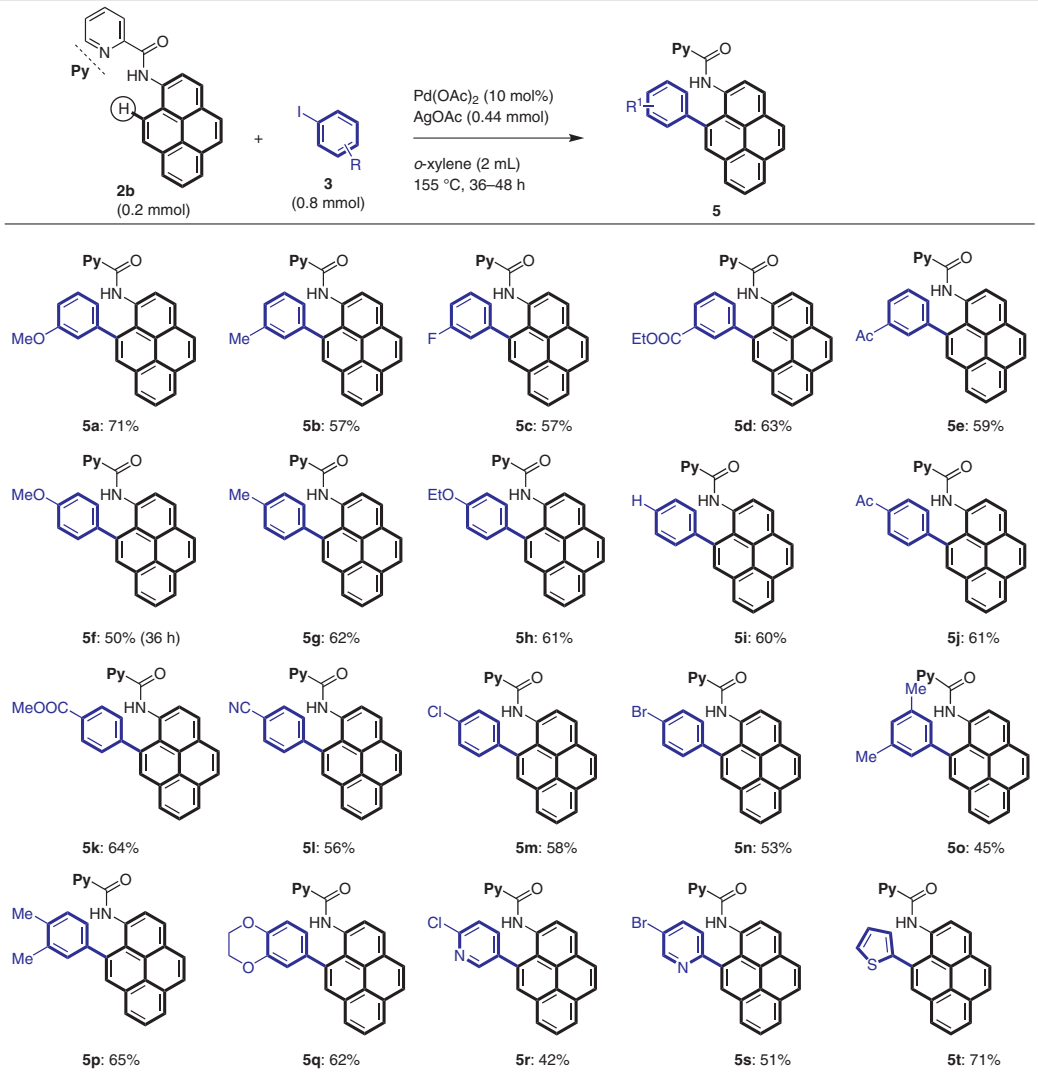
ent palladium catalysts such as $Pd(TFA)_2$ and $Pd(MeCN)_2Cl_2$ yielded the product **4a** in 53–60% yields (entries 9 and 10). The C–H arylation of **2a** under the $Ni(OTf)_2$-catalyzed reaction conditions yielded **4a** in only 15% yield (entry 11).

Having the optimized reaction conditions in hand for the Pd(II)-catalyzed C(2)–H arylation of **2a**, we wanted to enrich the library of pyrene-1-carboxamide via the Pd(II)-catalyzed C(2)–H arylation reaction. Towards this, we carried out the Pd(II)-catalyzed C(2)–H arylation of **2a** using a variety of aryl iodides (Scheme 2). Arylation of **2a** with aryl iodides containing different electron-withdrawing substituents (e.g., Ac, NO_2, COOMe and Cl) at the *para*-position yielded the corresponding C(2)–H arylated pyrene-1-carboxamides **4a–d** in moderate to good yields (53–86%, Scheme 2). Next, the Pd(II)-catalyzed C(2)–H arylation of pyrene-1-carboxamide **2a** with 6-iodo-2,3-dihydrobenzo[*b*][1,4]dioxine, PhI and aryl iodides containing different electron-donating substituents (e.g., Et, *i*-Pr, Me and OMe) at the *para*-position yielded the corresponding C(2)–H arylated pyrene-1-carboxamides **4e–j** in moderate to good yields (45–71%, Scheme 2).

We then performed the Pd(II)-catalyzed C(2)–H arylation of pyrene-1-carboxamide **2a** with aryl iodides containing different electron-donating or electron-withdrawing substituents (e.g., OMe, Me, Cl and F) at the *meta*-position, which yielded the corresponding C(2)–H arylated pyrene-1-carboxamides **4k–n** in 66–84% yields (Scheme 2). Furthermore, the Pd(II)-catalyzed C(2)–H arylation of pyrene-1-carboxamide **2a** with different heteroaryl iodides also yielded the corresponding C(2)–H arylated pyrene-1-carboxamides **4o–q** in satisfactory to moderate yields (48–58%, Scheme 2). The structures of representative pyrene derivatives **4a** and **4e** were confirmed by the X-ray structure analysis (Figure 2).



Scheme 3 Assembly of C1,C10-disubstituted pyrene carboxamide motifs **5a–t** via the Pd(II)-catalyzed, picolinamide-directed C–H arylation of **2b**

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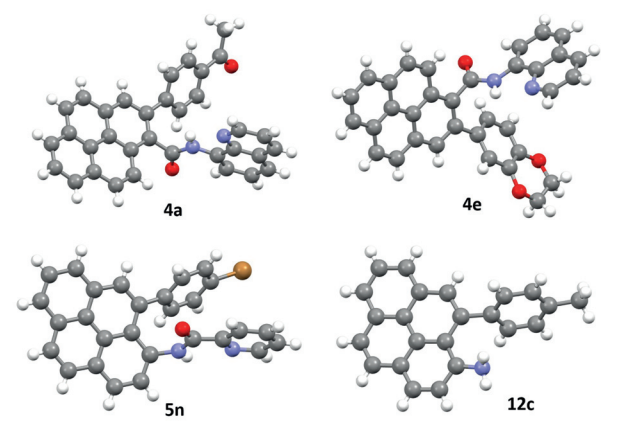
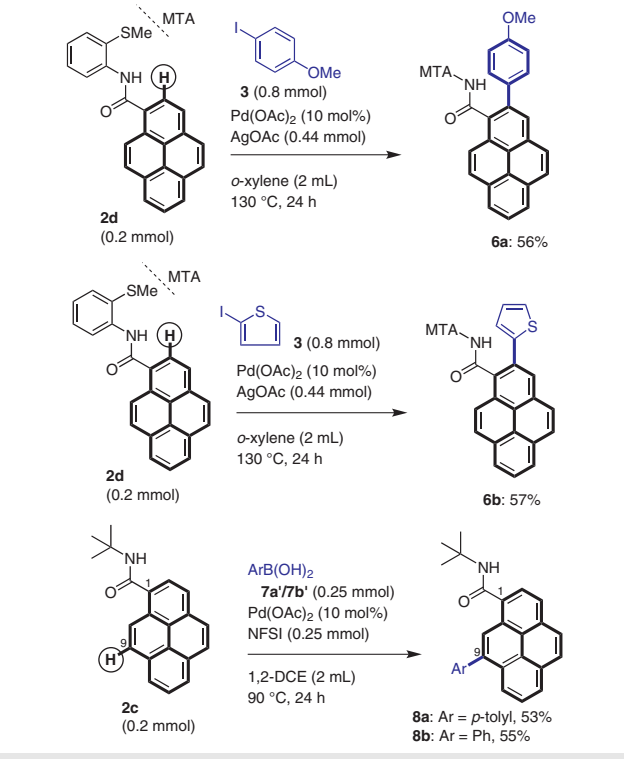


Figure 2 X-ray (ball and stick model) crystal structures of compounds **4a**, **4e**, **5n** and **12c**

After assembling various C(2)–H arylated pyrene-1-carboxamides **4a–q**, we then planned to expand the scope of this work and enrich the library of 1-aminopyrene core by assembling various C(10)–H arylated 1-aminopyrene-based motifs (Scheme 3). Towards this end, we prepared *N*-(pyren-1-yl)picolinamide (**2b**), possessing a picolinamide directing group, which will enable the γ-C(sp^2)–H functionalization of **2b** at the C10-position. We then performed the



Scheme 4 Assembly of pyrene carboxamide motifs **6a**,**b** and **8a**,**b** via the Pd(II)-catalyzed C–H arylation of **2c**,**d**

Pd(II)-catalyzed C(10)–H arylation of **2b** by using a variety of aryl iodides (Scheme 3). The Pd(II)-catalyzed C(10)–H arylation of **2b** with aryl iodides containing different electron-donating or electron-withdrawing substituents (e.g., OMe, Me, F, COOEt and Ac) at the *meta*-position yielded the corresponding C(10)–H arylated *N*-(pyren-1-yl)picolinamides **5a–e** in moderate to good yields (57–71%, Scheme 3).

The Pd(II)-catalyzed C(10)–H arylation of **2b** with PhI and various aryl iodides containing different electron-donating and electron withdrawing substituents (e.g., OMe, Me, OEt, Ac, COOMe, CN, Cl and Br) at the *para*-position yielded the corresponding C(10)–H arylated *N*-(pyren-1-yl)picolinamides **5f–n** in moderate to good yields (50–64%, Scheme 3). The Pd(II)-catalyzed C(10)–H arylation of **2b** with disubstituted aryl iodides and 6-iodo-2,3-dihydrobenzo[*b*][1,4]dioxine yielded the corresponding C(10)–H arylated *N*-(pyren-1-yl)picolinamides **5o–q** in satisfactory to good yields (45–65%, Scheme 3). Furthermore, the C(10)–H arylation of **2b** with different heteroaryl iodides also yielded the corresponding C(10)–H arylated *N*-(pyren-1-yl)picolinamides **5r–t** in satisfactory to good yields (42–71%, Scheme 3). The structure of representative pyrene carboxamide **5n** was confirmed by X-ray crystal structure analysis (Figure 2).

We then explored the possibility of using other directing groups similar to 8-aminoquinoline. Accordingly, we prepared the pyrene-1-carboxamide **2d**, possessing 2-(methylthio)aniline as the directing group[11] (Scheme 4). We then performed the Pd(II)-catalyzed C(10)–H arylation of **2d** with different aryl iodides (Scheme 4), which also afforded the corresponding products **6a**,**b** in 56–57% yields. Furthermore, we also attempted the functionalization at the C9-position of the pyrene core by using the procedure reported by Yang and You for the 1-naphthylamine system.[10l] In this regard, we treated pyrene-1-carboxamide **2c** with *p*-tolylboronic acid in the presence of the Pd(OAc)$_2$ catalyst and NFSI as an additive in 1,2-DCE at 90 °C for 24 h, which afforded the corresponding C(9)–H arylated pyrene-1-carboxamide **8a** in 53% yield (Scheme 4). Similarly, the reaction of pyrene-1-carboxamide **2c** with phenylboronic acid in the presence of the Pd(OAc)$_2$ catalyst and NFSI as an additive in 1,2-DCE at 90 °C for 24 h afforded the C(9)–H arylated pyrene-1-carboxamides **8b** in 55% yield (Scheme 4).

To further extend the substrate scope and enrich the library of pyrene-1-carboxamide and 1-aminopyrene core, we attempted the Pd(II)-catalyzed alkylation of C(2)–H and C(10)–H bonds of pyrene amides **2a** and **2b**, respectively. Towards this, we carried out the Pd(II)-catalyzed C(2)–H alkylation of pyrene-1-carboxamide **2a** with different alkyl iodides, which successfully yielded the corresponding C(2)–H alkylated pyrene-1-carboxamides **10a–d** in good yields (70–74%, Scheme 5). Similarly, the Pd(II)-catalyzed C(10)–H alkylation of *N*-(pyren-1-yl)picolinamide (**2b**) with differ-

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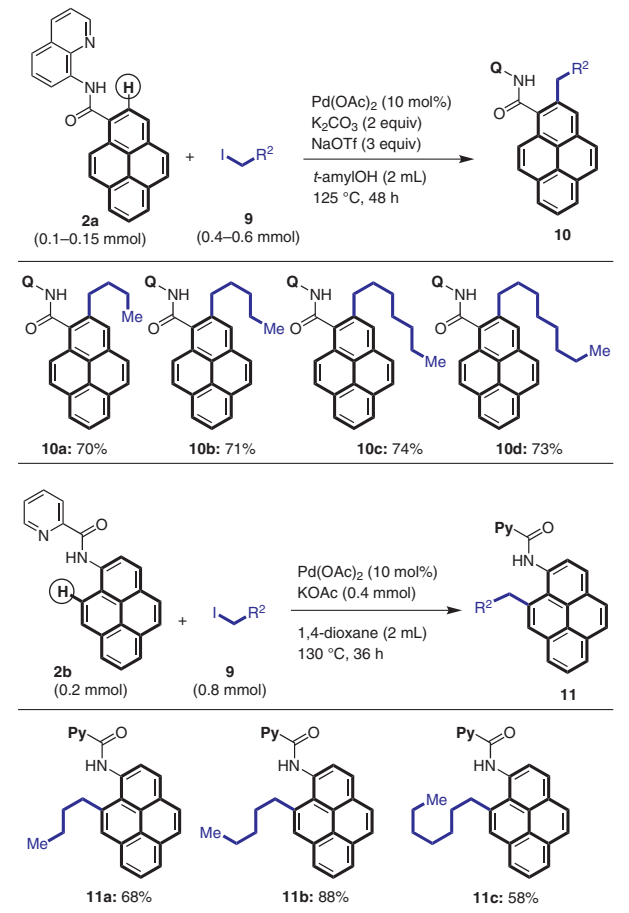
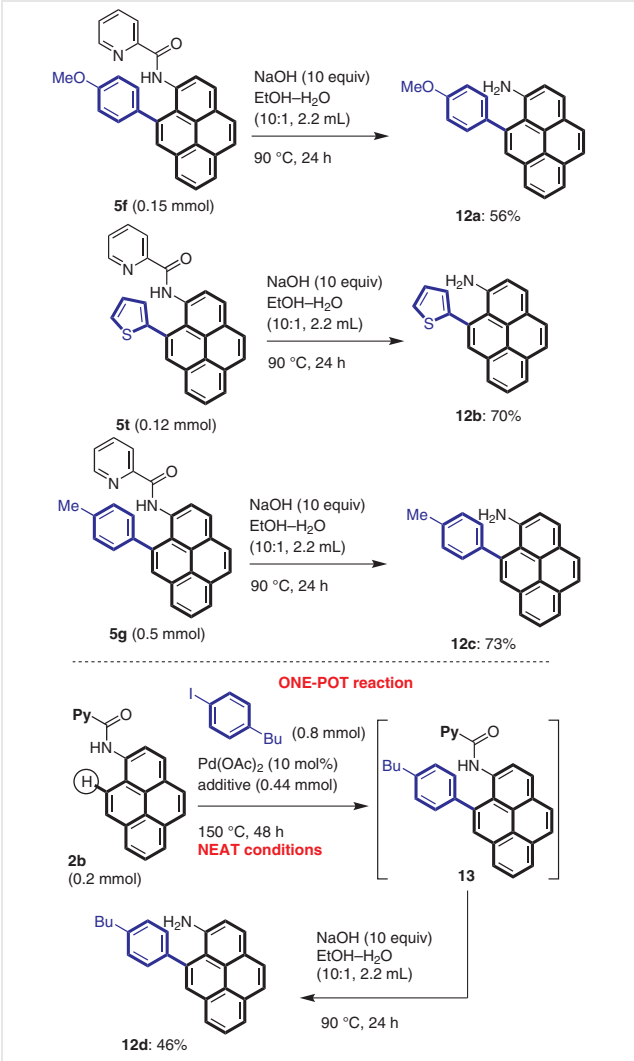
ent alkyl iodides yielded the corresponding C(10)–H alkylated *N*-(pyren-1-yl)picolinamide **11a–c** in good yields (58–88%, Scheme 5).

We also attempted the removal of the directing group after the C–H arylation of the pyrene amides. In this regard, the C(10)–H arylated *N*-(pyren-1-yl)picolinamide **5f** was subjected to different amide hydrolysis conditions. Of the limited number of attempts that were carried out, we found that heating a mixture of *N*-(pyren-1-yl)picolinamide **5f** and NaOH in EtOH/H_2O at 90 °C for 24 h yielded the C(10)–H arylated 1-aminopyrene derivative **12a** in 56% yield (Scheme 6). Similarly, the NaOH-mediated hydrolysis of the C–H arylated *N*-(pyren-1-yl)picolinamides **5g**,**t** yielded the corresponding C(10)–H arylated 1-aminopyrene derivatives **12b**,**c** in 70–73% yields (Scheme 6). Finally, compound **12d** was obtained via one-pot sequential C–H arylation of **2b** under standard reaction conditions and neat conditions followed by NaOH-mediated hydrolysis (Scheme 6). The structures of representative pyrene derivative **12c** was unequivocally established by X-ray crystal structure analysis (Figure 2).[20]



Scheme 5 Assembly of C1,C2- and C1,C10-disubstituted pyrene carboxamide motifs **10a–d** and **11a–c** via C–H alkylation of the pyrene core

In summary, we have shown the application of the Pd(II)-catalyzed, directing-group-aided C–H arylation/alkylation tactics to functionalize the relatively inaccessible C2 and K-region C10 positions of the pyrene core. The Pd(II)-catalyzed β-C–H arylation/alkylation of the C2-position of pyrene-1-carboxamide, possessing an 8-aminoquinoline directing group, afforded various C1,C2-disubstituted pyrene motifs. Similarly, the Pd(II)-catalyzed selective γ-C–H arylation/alkylation of the C10-position of *N*-(pyren-1-yl)picolinamide possessing a picolinamide directing group afforded various C1,C10-disubstituted pyrene motifs. Examples of C(9)–H arylation of pyrene-1-carboxamide and the removal of the directing group after the C–H arylation reactions were also shown. The structures of representative pyrene derivatives were confirmed by X-ray crystal structure analysis. Given the importance of the pyrene deriva-



Scheme 6 Trials on the removal of the directing group and one-pot sequential C–H arylation of pyrene carboxamide **2b** followed by directing group removal

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tives in various fields of chemical sciences, this report is a contribution towards augmentation of the library of pyrene derivatives with C1,C2- and C1,C10-disubstituted pyrene amide motifs. While we have obtained a library of new C1,C2- and C1,C10-disubstituted pyrene amide motifs, currently, we are studying their structure and photophysical properties and exploring their application, the results of which will be reported in due course.

^{1}H and ^{13}C{^{1}H} NMR spectra of compounds were recorded (using TMS as an internal standard) with 400 or 500 and ca. 101 or ca. 126 MHz spectrometers, respectively. The HRMS analysis data of samples were obtained with a QTOF mass analyzer by using electrospray ionization (ESI) method. IR spectra of samples were recorded as neat or thin films. Column chromatography purification was carried out on silica gel (100–200 mesh). Reactions were conducted in anhydrous solvents under a nitrogen atmosphere when required. Organic layers obtained after workup were dried by using anhydrous Na_2SO_4. Thin-layer chromatography (TLC) analyses were performed on silica gel (silica gel 60 F_{254} plates) or alumina plates and components were visualized by observation under irradiation with a UV lamp or iodine vapor. Isolated yields of all the products are reported. Yields of isolated compounds were not optimized. In all of the cases, after the Pd(II)-catalyzed reactions, the respective crude reaction mixtures were subjected to the column chromatographic purification to afford the pure samples. Some pyrene amide products contain some inseparable adventitious grease and hexane residuals or adventitious moisture peaks in the ^{1}H/^{13}C NMR spectra. Adventitious grease and hexane residuals seem to get trapped with the pyrene amide compounds during handling/sample purification. While we have tried to purify all the samples to get pure compounds, the C–H functionalized pyrene compounds and the starting material pyrene compounds have similar R_f values and thus, their separation in column chromatography was found to be a difficult task. Accordingly, we have repeated column chromatography purification for most of the cases to obtain samples with the highest possible purity.

Synthesis of Carboxamides 2a, 2c, 2d; General Procedure

A dry round-bottomed flask containing amine (9 mmol, 0.9 equiv) and Et_3N (11 mmol, 1.1 equiv) was stirred for 5–10 min under a nitrogen atmosphere. To the reaction flask was then added anhydrous DCM (20 mL) followed by dropwise addition of the corresponding acid chloride, which was prepared from pyrene-1-carboxylic acid (10 mmol) and $SOCl_2$ (9 equiv) after refluxing for 12 h. The reaction mixture was then stirred overnight and, after this period, the reaction mixture was diluted with DCM (10–15 mL) and washed with water (10–15 mL) and twice with saturated aqueous $NaHCO_3$ solution (10–15 mL). The combined organic layers were washed with 1 N HCl (2 × 20 mL) to remove excess amine, then dried over anhydrous Na_2SO_4, and concentrated under vacuum to afford the corresponding carboxamides.

Synthesis of Carboxamide 2b

An appropriate amount of picolinic acid (10 mmol), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (1.1 equiv), 1-hydroxybenzotriazole hydrate (1.1 equiv) in DCM (20 mL) was stirred for 1 h at 0 °C under a nitrogen atmosphere. Then, an appropriate amount of 1-aminopyrene (1 equiv) was added to the above mixture and stirred for 16–24 h at room temperature. The resulting solution was then subjected to aqueous workup and washed with aqueous $NaHCO_3$ solution (two times). The resulting solution mixture was concentrated and purified on silica gel column chromatography (EtOAc/hexane) to give the corresponding carboxamide.

Pd(II)-Catalyzed Arylation of Carboxamides 2a/2d and Preparation of Compounds 4/6

A mixture of an appropriate carboxamide (0.2 mmol, 1 equiv), an appropriate aryl iodide (0.8 mmol, 4 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol%) and AgOAc (0.44 mmol, 2.0–2.2 equiv) in *o*-xylene (2 mL) was heated at 130 °C for 24 h in a 10 mL capacity sealed (pressure) tube (the pressure tube was flushed with nitrogen atmosphere for 2 min and it was sealed with a PTFE-lined cap, and then the tube was heated). After the reaction period, the reaction mixture was concentrated under vacuum and purification of the resulting reaction mixture by column chromatography on neutral alumina or silica gel (EtOAc/hexane) furnished the corresponding arylated carboxamide (see the corresponding Tables/Schemes for specific examples).

Pd(II)-Catalyzed Arylation of the Carboxamide 2b and Preparation of Compounds 5

A mixture of carboxamide **2b** (0.2 mmol, 1 equiv), an appropriate aryl iodide (0.8–1.0 mmol, 4–5 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol%) and AgOAc (0.44 mmol, 2.2 equiv) in *o*-xylene (2 mL) was heated at 150 °C for 36–48 h in a 10 mL capacity sealed (pressure) tube (the pressure tube was flushed with nitrogen atmosphere for 2 min and it was sealed with a PTFE-lined cap, and then the tube was heated). After the reaction period, the reaction mixture was concentrated under vacuum and purification of the resulting reaction mixture by column chromatography on silica gel (EtOAc/hexane) furnished the corresponding arylated carboxamide (see the corresponding Tables/Schemes for specific examples).

Pd(II)-Catalyzed Alkylation of Carboxamide 2a and Preparation of Compounds 10

A mixture of carboxamide **2a** (0.14 mmol, 1 equiv), an appropriate alkyl iodide (0.56 mmol, 4 equiv), anhydrous K_2CO_3 (0.28 mmol, 2 equiv), NaOTf (0.42 mmol, 3 equiv), $Pd(OAc)_2$ (10 mol%, 3.4 mg), and *t*-AmylOH (2.0 mL) was added in a 10 mL capacity sealed (pressure) tube. The pressure tube was flushed with nitrogen atmosphere for 2 min, sealed with a PTFE-lined cap, and then the tube was heated at 125 °C for 48 h. After the reaction period, the reaction mixture was concentrated under vacuum and purification of the resulting reaction mixture by column chromatography on silica gel (EtOAc/hexane) furnished the corresponding alkylated carboxamide **10** (see the corresponding Tables/Schemes for specific examples).

Pd(II)-Catalyzed Alkylation of Carboxamide 2b and Preparation of Compounds 11

A mixture of **2b** carboxamide (0.2 mmol, 1 equiv), an appropriate alkyl iodide (0.8 mmol, 4.0 equiv), anhydrous KOAc (0.4 mmol, 2 equiv), $Pd(OAc)_2$ (10 mol%, 4.5 mg), and 1,4-dioxane (2.0 mL) was added in a 10 mL capacity sealed (pressure) tube. The pressure tube was flushed with nitrogen atmosphere for 2 min, sealed with a PTFE-lined cap, and then heated at 130 °C for 36 h. After the reaction period, the reaction mixture was concentrated under vacuum and purification of the resulting reaction mixture by column chromatography on neutral alumina or silica gel (EtOAc/hexane) furnished the corresponding alkylated carboxamide **11** (see the corresponding Tables/Schemes for specific examples).

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Pd(II)-Catalyzed Arylation of Carboxamides 2c and Preparation of Compounds 8a,b

A mixture of carboxamide **2c** (0.2 mmol, 1 equiv), an appropriate boronic acid (0.25 mmol, 1.25 equiv), NFSI (0.25 mmol, 1.25 equiv), and $Pd(OAc)_2$ (10 mol%, 4.5 mg) was suspended in 1,2-DCE (2.0 mL) in a 10 mL capacity sealed (pressure) tube. The pressure tube was flushed with N_2 for 2 min and sealed with a PTFE-lined cap, and then the tube was heated at 90 °C for 24 h. After the reaction period, the mixture was filtered through a Celite® pad and washed with DCM (10–15 mL). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to afford the corresponding arylated carboxamide **8** (see the corresponding Tables/Schemes for specific examples). The structures of compounds **8a**,**b** were assigned based on reports of a similar compound prepared under Cu-catalyzed reaction involving aryliodonium salts as arylating reagent.[15k]

Directing Group Removal/Amide Hydrolysis and Preparation of Compound 13

A solution of NaOH (60 mg of NaOH) in EtOH/H_2O (10:1 v/v, 3.3 mL) containing an appropriate arylated carboxamide **5** (0.15 mmol) was heated at reflux for 24 h. The reaction mixture was then cooled to r.t. and the mixture was subjected to evaporation (to evaporate EtOH), then the solution was diluted with water (5 mL) and the product was extracted with EtOAc (3 × 5 mL). The organic layers were combined, dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane) to afford the corresponding C–H arylated 1-aminopyrene derivative **13** (see the corresponding Tables/Schemes for specific examples).

***N*-(2-(Methylthio)phenyl)pyrene-1-carboxamide (2d)**

By following the general procedure, compound **2d** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (521 mg, 71%, 2 mmol scale).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 149–151 °C.

IR (DCM): 3275, 2925, 1682, 1513, 1436 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (s, 1 H), 8.79–8.72 (m, 2 H), 8.31 (d, *J* = 7.9 Hz, 1 H), 8.26–8.19 (m, 4 H), 8.15 (d, *J* = 8.9 Hz, 1 H), 8.09–8.05 (m, 2 H), 7.58 (d, *J* = 7.7 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 7.22–7.18 (m, 1 H), 2.40 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.0, 138.7, 133.0, 133.0, 131.2, 130.7, 130.7, 129.1, 129.0, 129.0, 127.1, 126.5, 126.1, 126.0, 125.9, 124.9, 124.9, 124.7, 124.6, 124.4, 120.9, 19.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{17}NNaOS$: 390.0929; found: 390.0922.

2-(4-Acetylphenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4a)

By following the general procedure, compound **4a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (68 mg, 70%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 249–251 °C.

IR (DCM): 3338, 1679, 1519, 1483, 1264 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1 H), 8.99 (d, *J* = 7.5 Hz, 1 H), 8.55–8.54 (m, 1 H), 8.49 (d, *J* = 9.2 Hz, 1 H), 8.27–8.25 (m, 3 H), 8.19 (d, *J* = 9.0 Hz, 2 H), 8.14–8.06 (m, 3 H), 7.95 (d, *J* = 8.2 Hz, 2 H), 7.90 (d, *J* = 8.3 Hz, 2 H), 7.62 (t, *J* = 8.1 Hz, 1 H), 7.55 (d, *J* = 8.2 Hz, 1 H), 7.36 (dd, ^{1}*J* = 8.2 Hz, ^{2}*J* = 4.2 Hz, 1 H), 2.52 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 196.8, 166.8, 147.1, 144.7, 137.4, 135.2, 135.0, 134.8, 133.3, 130.9, 130.3, 130.1, 129.7, 128.6, 128.3, 128.1, 127.8, 127.4, 126.8, 126.3, 126.0, 125.5, 125.0, 124.9, 124.9, 123.5, 123.1, 123.0, 121.1, 120.5, 115.7, 25.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{23}N_2O_2$: 491.1760; found: 491.1779.

2-(4-Nitrophenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4b)

By following the general procedure, compound **4b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a pale-yellow solid (84 mg, 86%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 237–239 °C.

IR (DCM): 2924, 1670, 1595, 1519, 1341 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.61 (s, 1 H), 8.73 (d, *J* = 4.0 Hz, 1 H), 8.61 (d, *J* = 7.5 Hz, 1 H), 8.47 (s, 1 H), 8.43–8.32 (m, 7 H), 8.27 (d, *J* = 8.6 Hz, 2 H), 8.17 (t, *J* = 7.6 Hz, 1 H), 8.05 (d, *J* = 8.6 Hz, 2 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.66 (t, *J* = 7.8 Hz, 1 H), 7.56 (dd, ^{1}*J* = 8.3 Hz, ^{2}*J* = 4.2 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 167.5, 148.2, 147.6, 147.2, 138.3, 136.3, 134.8, 134.2, 132.0, 131.2, 130.8, 130.3, 129.6, 129.4, 128.9, 127.9, 127.3, 127.0, 126.8, 126.3, 126.1, 125.7, 124.5, 124.3, 124.1, 123.6, 123.6, 122.4, 121.7, 116.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{20}N_3O_3$: 494.1505; found: 494.1520.

Methyl 4-(1-(Quinolin-8-ylcarbamoyl)pyren-2-yl)benzoate (4c)

By following the general procedure, compound **4c** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (58 mg, 58%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 160–162 °C.

IR (DCM): 3348, 2940, 1725, 1675, 1528 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1 H), 8.99 (d, *J* = 7.5 Hz, 1 H), 8.54 (d, *J* = 3.1 Hz, 1 H), 8.48 (d, *J* = 9.2 Hz, 1 H), 8.26–8.23 (m, 3 H), 8.17 (d, *J* = 9.0 Hz, 1 H), 8.12–8.03 (m, 5 H), 7.89 (d, *J* = 7.8 Hz, 1 H), 7.63–7.59 (m, 1 H), 7.53 (d, *J* = 8.2 Hz, 1 H), 7.34 (dd, ^{1}*J* = 8.1 Hz, ^{2}*J* = 4.1 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 167.9, 166.9, 148.1, 145.6, 138.4, 136.2, 136.0, 134.4, 131.9, 131.3, 131.1, 130.7, 129.7, 129.5, 129.3, 129.1, 129.1, 128.8, 127.8, 127.3, 127.0, 126.5, 126.0, 125.9, 124.5, 124.2, 124.0, 122.2, 121.6, 116.9, 52.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{23}N_2O_3$: 507.1709; found: 507.1695.

2-(4-Chlorophenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4d)

By following the general procedure, compound **4d** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (51 mg, 53%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 237–239 °C.

IR (DCM): 3348, 2936, 1663, 1528, 1490 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1 H), 9.01–9.00 (m, 1 H), 8.56 (dd, ^{1}*J* = 4.1 Hz, ^{2}*J* = 1.4 Hz, 1 H), 8.47 (d, *J* = 9.2 Hz, 1 H), 8.27–8.24 (m, 3 H), 8.19–8.05 (m, 5 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.64 (t, *J* = 7.8 Hz, 1 H), 7.58–7.56 (m, 1 H), 7.38 (dd, ^{1}*J* = 8.3 Hz, ^{2}*J* = 4.2 Hz, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H).

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^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.0, 148.1, 139.3, 138.4, 136.2, 135.9, 134.4, 133.7, 132.0, 131.4, 131.1, 130.7, 129.2, 129.0, 128.8, 128.6, 127.9, 127.3, 127.1, 126.5, 126.1, 126.0, 125.9, 124.6, 124.2, 123.9, 122.2, 121.6, 116.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{20}ClN_2O$: 483.1264; found: 483.1252.

2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4e)

By following the general procedure, compound **4e** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (45 mg, 45%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 248–250 °C.

IR (DCM): 3338, 2924, 1667, 1516, 1323 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1 H), 9.04 (d, *J* = 7.6 Hz, 1 H), 8.59 (d, *J* = 4.0 Hz, 1 H), 8.48 (d, *J* = 9.2 Hz, 1 H), 8.26–8.23 (m, 3 H), 8.19–8.11 (m, 4 H), 8.05 (t, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.9 Hz, 1 H), 7.55 (d, *J* = 8.2 Hz, 1 H), 7.39–7.34 (m, 2 H), 7.29–7.26 (m, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 4.17–4.16 (m, 4 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.3, 148.0, 143.4, 143.2, 138.5, 136.7, 136.1, 134.7, 134.2, 131.9, 131.4, 131.1, 130.7, 129.0, 128.8, 128.8, 127.8, 127.4, 127.2, 126.3, 125.8, 125.7, 124.7, 124.3, 123.6, 122.6, 121.8, 121.5, 118.5, 117.2, 116.7, 64.3, 64.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{23}N_2O_3$: 507.1709; found: 507.1724.

2-Phenyl-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4f)

By following the general procedure, compound **4f** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (49 mg, 55%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 218–220 °C.

IR (DCM): 3342, 1667, 1519, 1483, 1325 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 8.97 (dd, ^1J = 7.6 Hz, ^2J = 1.0 Hz, 1 H), 8.52 (dd, ^1J = 4.1 Hz, ^2J = 1.4 Hz, 1 H), 8.47 (d, *J* = 9.3 Hz, 1 H), 8.27 (s, 1 H), 8.23 (t, *J* = 7.9 Hz, 2 H), 8.17–8.03 (m, 5 H), 7.83–7.77 (m, 2 H), 7.60–7.56 (m, 1 H), 7.50 (d, *J* = 8.3 Hz, 1 H), 7.34–7.31 (m, 3 H), 7.18 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (~126 MHz, $CDCl_3$): δ = 168.2, 148.0, 140.8, 138.4, 137.3, 136.1, 134.6, 131.9, 131.6, 131.2, 130.8, 129.4, 129.0, 128.9, 128.8, 128.4, 127.8, 127.5, 127.3, 127.2, 126.4, 126.3, 125.9, 125.8, 124.7, 124.4, 123.8, 121.8, 121.5, 116.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{21}N_2O$: 449.1654; found: 449.1649.

2-(4-Ethylphenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4g)

By following the general procedure, compound **4g** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (67 mg, 71%).

R_f = 0.6 (EtOAc/hexane = 20:80); mp 205–207 °C.

IR (DCM): 3338, 1665, 1515, 1482, 1324 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1 H), 9.02 (d, *J* = 7.6 Hz, 1 H), 8.55–8.49 (m, 2 H), 8.30 (s, 1 H), 8.26–8.23 (m, 2 H), 8.19–8.05 (m, 5 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.33 (dd, ^1J = 8.4 Hz, ^2J = 4.0 Hz, 1 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 2.53 (q, *J* = 7.6 Hz, 2 H), 1.05 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.4, 147.9, 143.5, 138.4, 138.1, 137.3, 135.9, 134.7, 131.9, 131.5, 131.1, 130.7, 129.4, 129.0, 128.8, 128.8, 128.0, 127.8, 127.3, 127.1, 126.4, 126.2, 125.8, 125.7, 124.7, 124.3, 123.6, 121.8, 121.4, 116.6, 28.5, 15.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{25}N_2O$: 477.1967; found: 477.1982.

2-(4-Isopropylphenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4h)

By following the general procedure, compound **4h** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (65 mg, 66%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 160–162 °C.

IR (DCM): 3337, 2959, 1662, 1519, 1481 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1 H), 9.03 (dd, ^1J = 7.6 Hz, ^2J = 0.9 Hz, 1 H), 8.55–8.51 (m, 2 H), 8.28 (s, 1 H), 8.24–8.22 (m, 2 H), 8.18–8.03 (m, 5 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 7.49 (dd, ^1J = 8.3 Hz, ^2J = 0.9 Hz, 1 H), 7.32–7.28 (m, 1 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 2.80–2.72 (m, 1 H), 1.05 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.3, 148.0, 147.8, 138.3, 138.2, 137.3, 135.8, 134.7, 131.9, 131.4, 131.0, 130.6, 129.4, 128.9, 128.8, 128.7, 127.6, 127.2, 127.1, 126.4, 126.3, 126.2, 125.7, 125.6, 124.7, 124.3, 123.6, 121.7, 121.3, 116.4, 33.6, 23.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{27}N_2O$: 491.2123; found: 491.2142.

***N*-(Quinolin-8-yl)-2-(*p*-tolyl)pyrene-1-carboxamide (4i)**

By following the general procedure, compound **4i** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (54 mg, 58%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 195–197 °C.

IR (DCM): 3355, 3052, 1690, 1536, 1321 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1 H), 9.04 (d, *J* = 7.5 Hz, 1 H), 8.54 (dd, ^1J = 4.0 Hz, ^2J = 1.4 Hz, 1 H), 8.48 (d, *J* = 9.2 Hz, 1 H), 8.27–8.21 (m, 3 H), 8.16–8.03 (m, 5 H), 7.72 (d, *J* = 7.9 Hz, 2 H), 7.62 (t, *J* = 8.1 Hz, 1 H), 7.51 (d, *J* = 8.2 Hz, 1 H), 7.32 (dd, ^1J = 8.2 Hz, ^2J = 4.2 Hz, 1 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 2.26 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.4, 148.0, 138.4, 137.9, 137.2, 136.0, 134.7, 131.9, 131.5, 131.1, 130.7, 129.3, 129.2, 128.0, 128.8, 128.7, 127.8, 127.3, 127.2, 126.4, 126.3, 125.8, 125.7, 124.7, 124.3, 123.6, 121.9, 121.5, 116.7, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{23}N_2O$: 463.1810; found: 463.1791.

2-(4-Methoxyphenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4j)

By following the general procedure, compound **4j** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a pale-yellow solid (64 mg, 67%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 178–180 °C.

IR (DCM): 3336, 2932, 1682, 1521, 1321 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1 H), 9.05 (d, *J* = 7.5 Hz, 1 H), 8.55–8.54 (m, 1 H), 8.48 (d, *J* = 9.2 Hz, 1 H), 8.26–8.22 (m, 3 H), 8.16 (d, *J* = 9.1 Hz, 2 H), 8.12–8.03 (m, 3 H), 7.75 (d, *J* = 7.7 Hz, 2 H), 7.62 (t, *J* = 7.9 Hz, 1 H), 7.53 (d, *J* = 8.2 Hz, 1 H), 7.33 (dd, ^1J = 7.8 Hz, ^2J = 4.0 Hz, 1 H), 6.91 (d, *J* = 7.8 Hz, 2 H), 3.71 (s, 3 H).

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^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.5, 159.1, 148.0, 138.4, 136.9, 136.1, 134.7, 133.2, 131.9, 131.5, 131.1, 130.7, 130.6, 129.0, 128.8, 128.8, 127.8, 127.3, 127.2, 126.4, 126.3, 125.8, 125.7, 124.7, 124.3, 123.5, 121.9, 121.5, 116.6, 113.9, 55.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{23}N_2O_2$: 479.1760; found: 479.1775.

2-(3-Methoxyphenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4k)

By following the general procedure, compound **4k** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (73 mg, 77%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 201–203 °C.

IR (CH_2Cl_2): 3337, 1665, 1516, 1482, 1324 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1 H), 9.03 (d, *J* = 7.6 Hz, 1 H), 8.55 (d, *J* = 3.9 Hz, 1 H), 8.50 (d, *J* = 9.2 Hz, 1 H), 8.29 (s, 1 H), 8.23 (d, *J* = 7.6 Hz, 2 H), 8.18–8.14 (m, 2 H), 8.11–8.03 (m, 3 H), 7.61 (t, *J* = 7.9 Hz, 1 H), 7.52 (d, *J* = 8.3 Hz, 1 H), 7.41–7.39 (m, 2 H), 7.33 (dd, ^1J = 8.0 Hz, ^2J = 4.0 Hz, 1 H), 7.26–7.24 (m, 1 H), 6.77 (d, *J* = 7.9 Hz, 1 H), 3.75 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.3, 159.5, 148.0, 142.2, 138.4, 137.1, 136.1, 134.7, 131.9, 131.5, 131.1, 130.7, 129.4, 129.1, 128.9, 128.8, 127.8, 127.3, 127.1, 126.3, 126.2, 125.9, 125.8, 124.7, 124.3, 123.8, 122.0, 121.9, 121.5, 116.7, 114.5, 113.9, 55.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{23}N_2O_2$: 479.1760; found: 479.1780.

***N*-(Quinolin-8-yl)-2-(*m*-tolyl)pyrene-1-carboxamide (4l)**

By following the general procedure, compound **4l** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (57 mg, 84%, 0.15 mmol scale).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 186–188 °C.

IR (DCM): 3333, 1667, 1519, 1483, 1325 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 1 H), 9.01 (d, *J* = 7.6 Hz, 1 H), 8.56 (d, *J* = 4.0 Hz, 1 H), 8.51 (d, *J* = 9.2 Hz, 1 H), 8.28 (s, 1 H), 8.26–8.23 (m, 2 H), 8.17 (d, *J* = 9.2 Hz, 2 H), 8.13–8.04 (m, 3 H), 7.63–7.59 (m, 3 H), 7.52 (d, *J* = 8.2 Hz, 1 H), 7.34 (dd, ^1J = 8.2 Hz, ^2J = 4.2 Hz, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.01 (d, *J* = 7.6 Hz, 1 H), 2.30 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.3, 148.0, 140.7, 138.4, 137.9, 137.5, 136.1, 134.7, 131.9, 131.6, 131.1, 130.7, 130.2, 129.0, 128.8, 128.7, 128.2, 128.2, 127.8, 127.3, 127.2, 126.5, 126.3, 125.8, 125.7, 124.7, 124.4, 123.7, 121.8, 121.5, 116.6, 21.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{23}N_2O$: 463.1810; found: 463.1827.

2-(3-Chlorophenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4m)

By following the general procedure, compound **4m** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (71 mg, 74%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 218–220 °C.

IR (DCM): 3334, 2923, 1668, 1519, 1483 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.96 (s, 1 H), 8.95 (dd, ^1J = 7.6 Hz, ^2J = 1.0 Hz, 1 H), 8.57 (dd, ^1J = 4.1 Hz, ^2J = 1.6 Hz, 1 H), 8.48 (d, *J* = 9.2 Hz, 1 H), 8.26–8.23 (m, 3 H), 8.19–8.16 (m, 2 H), 8.12–8.04 (m, 3 H), 7.80 (t, *J* = 1.8 Hz, 1 H), 7.63–7.58 (m, 2 H), 7.52 (dd, ^1J = 8.4 Hz, ^2J = 1.1 Hz, 1 H), 7.35 (dd, ^1J = 8.3 Hz, ^2J = 4.2 Hz, 1 H), 7.18 (t, *J* = 7.7 Hz, 1 H), 7.14–7.12 (m, 1 H).

^{13}C NMR (~126 MHz, $CDCl_3$): δ = 167.8, 148.2, 142.6, 138.4, 136.1, 135.8, 134.5, 134.3, 132.0, 131.4, 131.2, 130.8, 129.6, 129.5, 129.3, 129.1, 128.9, 127.8, 127.6, 127.5, 127.3, 127.1, 126.5, 126.0, 126.0, 125.9, 124.7, 124.3, 124.0, 122.0, 121.6, 116.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{20}ClN_2O$: 483.1264; found: 483.1261.

2-(3-Fluorophenyl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4n)

By following the general procedure, compound **4n** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (61 mg, 66%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 217–219 °C.

IR (DCM): 3342, 1667, 1519, 1483, 1423 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1 H), 9.00 (d, *J* = 7.6 Hz, 1 H), 8.54 (d, *J* = 3.9 Hz, 1 H), 8.47 (d, *J* = 9.2 Hz, 1 H), 8.21–8.10 (m, 5 H), 8.06–8.01 (m, 3 H), 7.62–7.54 (m, 3 H), 7.50 (d, *J* = 8.3 Hz, 1 H), 7.33–7.25 (m, 2 H), 6.91 (t, *J* = 8.1 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 167.9, 162.7 (d, $J_{C–F}$ = 245 Hz), 148.1, 143.0 (d, $J_{C–F}$ = 5.3 Hz), 138.3, 136.1, 135.8 (d, $J_{C–F}$ = 1.5 Hz), 134.5, 131.9, 131.3, 131.1, 130.7, 129.9 (d, $J_{C–F}$ = 8.4 Hz), 129.2, 129.0, 128.8, 127.8, 127.3, 127.0, 126.5, 126.0, 125.8, 125.3 (d, $J_{C–F}$ = 2.5 Hz), 124.6, 124.1, 123.9, 122.1, 121.6, 116.7, 116.5 (d, $J_{C–F}$ = 22.0 Hz), 114.4 (d, $J_{C–F}$ = 21.0 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{20}FN_2O$: 467.1560; found: 467.1574.

2-(5-Bromopyridin-2-yl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4o)

By following the general procedure, compound **4o** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (61 mg, 58%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 115–117 °C.

IR (DCM): 3338, 2924, 1667, 1519, 1483 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 1 H), 9.05 (d, *J* = 7.3 Hz, 1 H), 8.70 (d, *J* = 1.8 Hz, 1 H), 8.57–8.51 (m, 3 H), 8.27–8.06 (m, 7 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.77 (dd, ^1J = 8.4 Hz, ^2J = 2.2 Hz, 1 H), 7.67 (t, *J* = 8.0 Hz, 1 H), 7.59 (d, *J* = 7.7 Hz, 1 H), 7.38 (dd, ^1J = 8.3 Hz, ^2J = 4.2 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.3, 156.6, 150.6, 148.2, 139.0, 138.5, 136.1, 134.7, 134.4, 132.0, 131.3, 131.1, 130.8, 129.2, 129.0, 127.9, 127.3, 127.3, 126.7, 126.0, 125.9, 125.7, 125.2, 124.6, 124.6, 124.1, 122.1, 121.6, 119.8, 116.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{19}BrN_3O$: 528.0711; found: 528.0685.

2-(6-Chloropyridin-3-yl)-*N*-(quinolin-8-yl)pyrene-1-carboxamide (4p)

By following the general procedure, compound **4p** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (23 mg, 48%, 0.1 mmol scale).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 135–137 °C.

IR (DCM): 3344, 2917, 1682, 1536, 1332 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.64 (s, 1 H), 8.78 (d, *J* = 2.3 Hz, 1 H), 8.74 (dd, ^1J = 4.2 Hz, ^2J = 1.5 Hz, 1 H), 8.62–8.60 (m, 1 H), 8.47 (s, 1 H), 8.43–8.30 (m, 7 H), 8.23 (dd, ^1J = 8.2 Hz, ^2J = 2.5 Hz, 1 H), 8.16 (t, *J* = 7.6 Hz, 1 H), 7.79–7.77 (m, 1 H), 7.69–7.65 (m, 1 H), 7.60–7.57 (m, 2 H).

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^{13}C NMR (~101 MHz, $CDCl_3$): δ = 167.4, 150.7, 149.7, 148.3, 139.5, 138.3, 136.3, 135.5, 134.1, 132.1, 132.0, 131.4, 131.2, 130.7, 129.6, 129.4, 129.0, 127.9, 127.3, 126.9, 126.8, 126.3, 126.1, 125.8, 124.4, 124.2, 124.1, 123.8, 122.5, 121.7, 117.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{19}ClN_3O$: 484.1217; found: 484.1205.

N-(Quinolin-8-yl)-2-(thiophen-2-yl)pyrene-1-carboxamide (4q)

By following the general procedure, compound **4q** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (48 mg, 54%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 221–223 °C.

IR (DCM): 3332, 2921, 1667, 1525, 1467 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.54 (s, 1 H), 8.83 (d, *J* = 7.4 Hz, 1 H), 8.72 (d, *J* = 4.0 Hz, 1 H), 8.56 (s, 1 H), 8.43–8.25 (m, 7 H), 8.16–8.15 (m, 1 H), 7.79 (d, *J* = 8.2 Hz, 1 H), 7.74–7.72 (m, 1 H), 7.63–7.56 (m, 3 H), 7.12–7.10 (m, 1 H).

^{13}C NMR (~101 MHz, DMSO-d_6): δ = 167.8, 149.6, 141.8, 138.8, 137.1, 134.7, 131.8, 131.4, 131.2, 130.6, 129.8, 129.5, 129.3, 128.5, 128.4, 128.4, 128.2, 127.8, 127.6, 127.5, 127.4, 126.8, 126.5, 126.3, 124.6, 123.8, 1235, 123.2, 122.7, 118.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{19}N_2OS$: 455.1218; found: 455.1199.

N-(10-(3-Methoxyphenyl)pyren-1-yl)picolinamide (5a)

By following the general procedure, compound **5a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a brown solid (61 mg, 71%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 167–169 °C.

IR (DCM): 3475, 3352, 1667, 1602, 1517 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 8.69 (d, *J* = 8.3 Hz, 1 H), 8.32–8.28 (m, 2 H), 8.18 (d, *J* = 7.6 Hz, 2 H), 8.12–8.06 (m, 3 H), 8.04–7.98 (m, 1 H), 7.94 (s, 1 H), 7.82 (t, *J* = 7.6 Hz, 1 H), 7.40–7.37 (m, 1 H), 7.15–7.11 (m, 3 H), 6.55–6.54 (m, 1 H), 3.74 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.2, 159.6, 149.8, 147.4, 144.3, 137.1, 136.5, 131.3, 131.3, 130.3, 129.4, 129.4, 127.7, 126.6, 126.4, 126.3, 126.1, 126.0, 125.4, 124.8, 124.3, 124.0, 122.0, 121.8, 121.4, 113.7, 113.2, 55.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{21}N_2O_2$: 429.1603; found: 429.1593.

N-(10-(*m*-Tolyl)pyren-1-yl)picolinamide (5b)

By following the general procedure, compound **5b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (46 mg, 57%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 167–169 °C.

IR (DCM): 3325, 3040, 1690, 1517, 1478 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1 H), 8.71 (d, *J* = 8.4 Hz, 1 H), 8.31–8.26 (m, 2 H), 8.20–8.18 (m, 2 H), 8.12–8.05 (m, 3 H), 8.01 (t, *J* = 7.6 Hz, 1 H), 7.93 (s, 1 H), 7.81 (td, ^1J = 7.7 Hz, ^2J = 1.1 Hz, 1 H), 7.39–7.36 (m, 3 H), 7.14 (t, *J* = 7.6 Hz, 1 H), 6.81 (d, *J* = 7.6 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.1, 149.8, 147.3, 142.9, 137.9, 137.0, 136.8, 131.4, 131.3, 130.4, 129.7, 129.4, 128.3, 127.8, 127.6, 126.6, 126.5, 126.3, 126.1, 126.0, 125.9, 125.3, 124.7, 124.3, 124.0, 122.1, 121.9, 21.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{21}N_2O$: 413.1654; found: 413.1639.

N-(10-(3-Fluorophenyl)pyren-1-yl)picolinamide (5c)

By following the general procedure, compound **5b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (47 mg, 57%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 195–197 °C.

IR (DCM): 3328, 2921, 1671, 1521, 1486 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1 H), 8.70 (d, *J* = 8.4 Hz, 1 H), 8.35–8.34 (m, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.22–8.18 (m, 2 H), 8.13–8.00 (m, 4 H), 7.92 (s, 1 H), 7.84 (td, ^1J = 7.7 Hz, ^2J = 1.7 Hz, 1 H), 7.43–7.36 (m, 2 H), 7.25–7.23 (m, 1 H), 7.16–7.10 (m, 1 H), 6.73–6.68 (m, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.9 (d, J_{C-F} = 245.2 Hz), 162.0, 149.6, 147.4, 145.2 (d, J_{C-F} = 7.8 Hz), 137.2, 135.2 (d, J_{C-F} = 1.7 Hz), 131.6, 131.3, 131.2, 130.1, 129.7 (d, J_{C-F} = 8.5 Hz), 129.4, 127.8, 126.6, 126.4, 126.3, 126.2, 125.7, 125.1, 125.0 (d, J_{C-F} = 2.8 Hz), 124.9, 124.4, 123.9, 122.0, 121.8, 115.9 (d, J_{C-F} = 21.8 Hz), 113.5 (J_{C-F} = 20.8 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{18}FN_2O$: 417.1403; found: 417.1393.

Ethyl 3-(3-(Picolinamido)pyren-4-yl)benzoate (5d)

By following the general procedure, compound **5d** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (59 mg, 63%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 157–159 °C.

IR (DCM): 3328, 2921, 1671, 1521, 1486 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1 H), 8.68 (d, *J* = 8.4 Hz, 1 H), 8.36–8.31 (m, 2 H), 8.23 (d, *J* = 7.3 Hz, 1 H), 8.18–8.09 (m, 5 H), 8.04 (t, *J* = 7.6 Hz, 1 H), 7.96 (s, 1 H), 7.81 (td, ^1J = 7.7 Hz, ^2J = 1.6 Hz, 1 H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.66–7.64 (m, 1 H), 7.39–7.36 (m, 1 H), 7.24 (t, *J* = 7.7 Hz, 1 H), 4.45–4.39 (m, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 166.5, 161.8, 149.5, 147.4, 143.2, 137.1, 135.6, 133.6, 131.9, 131.3, 131.0, 130.7, 130.2, 129.5, 129.5, 128.1, 128.1, 127.7, 126.7, 126.4, 126.3, 126.2, 125.7, 124.9, 124.4, 124.1, 121.9, 121.9, 61.01, 14.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{23}N_2O_3$: 471.1709; found: 471.1716.

N-(10-(3-Acetylphenyl)pyren-1-yl)picolinamide (5e)

By following the general procedure, compound **5e** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (52 mg, 59%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 168–170 °C.

IR (DCM): 3440, 1686, 1602, 1513, 1248 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.03 (s, 1 H), 8.42 (d, *J* = 8.3 Hz, 1 H), 8.36–8.21 (m, 6 H), 8.11 (t, *J* = 7.6 Hz, 1 H), 8.01 (s, 1 H), 7.99 (s, 1 H), 7.93–7.86 (m, 2 H), 7.67 (d, *J* = 7.5 Hz, 1 H), 7.56–7.53 (m, 1 H), 7.41 (d, *J* = 7.9 Hz, 1 H), 7.28 (t, *J* = 7.7 Hz, 1 H), 2.46 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 197.9, 161.8, 149.3, 147.4, 143.4, 137.3, 136.9, 135.5, 133.4, 131.9, 131.2, 130.8, 130.1, 129.6, 129.0, 128.5, 127.7, 126.8, 126.5, 126.4, 126.3, 126.3, 126.2, 125.7, 125.0, 124.6, 124.3, 122.2, 121.8, 26.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{21}N_2O_2$: 441.1603; found: 441.1589.

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N-(10-(4-Methoxyphenyl)pyren-1-yl)picolinamide (5f)

By following the general procedure, compound **5f** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (42 mg, 50%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 171–173 °C.

IR (CH_2Cl_2): 3396, 2951, 1678, 1556, 1514 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.98 (s, 1 H), 8.80 (d, *J* = 8.4 Hz, 1 H), 8.32–8.29 (m, 2 H), 8.22–8.19 (m, 2 H), 8.15–8.01 (m, 4 H), 7.95 (s, 1 H), 7.87–7.83 (m, 1 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 7.41–7.38 (m, 1 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 3.63 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.0, 159.0, 150.0, 147.5, 137.0, 136.2, 135.2, 131.6, 131.5, 131.3, 130.4, 130.1, 129.2, 127.7, 126.5, 126.5, 126.3, 126.1, 125.8, 125.2, 124.6, 124.3, 123.4, 121.9, 121.7, 113.8, 55.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{21}N_2O_2$: 429.1603; found: 429.1588.

N-(10-(*p*-Tolyl)pyren-1-yl)picolinamide (5g)

By following the general procedure, compound **5g** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (51 mg, 62%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 158–160 °C.

IR (DCM): 3348, 3048, 1682, 1521, 1325 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1 H), 8.75 (d, *J* = 8.4 Hz, 1 H), 8.31–8.26 (m, 2 H), 8.19 (d, *J* = 7.7 Hz, 2 H), 8.13–8.05 (m, 3 H), 8.01 (t, *J* = 7.6 Hz, 1 H), 7.93 (s, 1 H), 7.8 (td, ^1J = 7.7 Hz, ^2J = 1.6 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.38–7.35 (m, 1 H), 7.06 (d, *J* = 7.8 Hz, 2 H), 2.13 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.0, 150.0, 147.4, 140.0, 137.0, 136.7, 136.6, 131.5, 131.3, 130.4, 129.3, 129.0, 128.9, 127.8, 126.5, 126.3, 126.1, 125.8, 125.3, 124.7, 124.3, 123.6, 121.9, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{21}N_2O$: 413.1654; found: 413.1669.

N-(10-(4-Ethoxyphenyl)pyren-1-yl)picolinamide (5h)

By following the general procedure, compound **5h** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (53 mg, 61%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 148–150 °C.

IR (DCM): 3296, 2926, 1674, 1511, 1495 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1 H), 8.79 (d, *J* = 8.4 Hz, 1 H), 8.30–8.29 (m, 2 H), 8.19–8.17 (m, 2 H), 8.12–7.99 (m, 4 H), 7.93 (s, 1 H), 7.84– 8.0 (m, 1 H), 7.47 (d, *J* = 8.6 Hz, 2 H), 7.38–7.35 (m, 1 H), 6.77 (d, *J* = 8.6 Hz, 2 H), 3.78 (q, *J* = 7.0 Hz, 2 H), 1.35 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.0, 158.4, 150.0, 147.5, 137.0, 136.3, 135.0, 131.6, 131.5, 131.3, 130.4, 130.1, 129.2, 127.8, 126.5, 126.5, 126.3, 126.1, 125.7, 125.2, 124.6, 124.3, 123.3, 121.9, 121.7, 114.2, 63.1, 14.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{23}N_2O_2$: 443.1760; found: 443.1775.

N-(10-Phenylpyren-1-yl)picolinamide (5i)

By following the general procedure, compound **5i** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (48 mg, 60%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 167–169 °C.

IR (DCM): 3347, 2923, 1678, 1511, 839 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1 H), 8.75 (d, *J* = 8.4 Hz, 1 H), 8.31 (d, *J* = 8.4 Hz, 1 H), 8.25 (d, *J* = 4.6 Hz, 1 H), 8.22–8.00 (m, 6 H), 7.94 (s, 1 H), 7.81 (td, ^1J = 7.6 Hz, ^2J = 1.4 Hz, 1 H), 7.57 (d, *J* = 7.3 Hz, 2 H), 7.38 –7.35 (m, 1 H), 7.28–7.24 (m, 2 H), 7.04 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.0, 149.8, 147.5, 142.9, 137.0, 136.6, 131.7, 131.5, 131.3, 130.3, 129.3, 129.0, 128.3, 127.7, 126.9, 126.5, 126.5, 126.3, 126.1, 125.9, 125.4, 124.8, 124.3, 123.6, 121.9, 121.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{19}N_2O$: 399.1497; found: 399.1511.

N-(10-(4-Acetylphenyl)pyren-1-yl)picolinamide (5j)

By following the general procedure, **5j** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a brown solid (54 mg, 61%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 158–160 °C.

IR (DCM): 3452, 3344, 1682, 1605, 1517 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (s, 1 H), 8.56 (d, *J* = 8.3 Hz, 1 H), 8.25 (d, *J* = 8.3 Hz, 1 H), 8.18–8.13 (m, 3 H), 8.09–8.04 (m, 3 H), 8.00–7.98 (m, 1 H), 7.87 (s, 1 H), 7.79–7.76 (m, 3 H), 7.57 (d, *J* = 7.8 Hz, 2 H), 7.30–7.28 (m, 1 H), 2.36 (s, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 197.3, 161.9, 149.5, 148.0, 147.4, 137.1, 135.5, 135.3, 131.5, 131.2, 130.8, 130.0, 129.6, 129.1, 128.3, 127.7, 126.7, 126.5, 126.3, 126.3, 126.1, 125.8, 125.1, 124.5, 124.3, 122.0, 121.9, 26.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{21}N_2O_2$: 441.1603; found: 441.1624.

Methyl 4-(3-(Picolinamido)pyren-4-yl)benzoate (5k)

By following the general procedure, compound **5k** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25: 75) as a brown solid (58 mg, 64%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 125–127 °C.

IR (DCM): 3500, 1716, 1678, 1512, 1434 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 8.61 (d, *J* = 8.3 Hz, 1 H), 8.29 (d, *J* = 8.4 Hz, 1 H), 8.22–8.20 (m, 2 H), 8.15–8.05 (m, 4 H), 8.02 (t, *J* = 7.6 Hz, 1 H), 7.92 (s, 1 H), 7.88 (d, *J* = 8.3 Hz, 2 H), 7.79 (td, ^1J = 7.6 Hz, ^2J = 1.6 Hz, 1 H), 7.60 (d, *J* = 8.2 Hz, 2 H), 7.32–7.28 (m, 1 H), 3.87 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 166.6, 162.0, 149.5, 147.8, 147.5, 137.1, 135.7, 131.5, 131.3, 131.0, 130.1, 129.6, 129.5, 128.9, 128.5, 127.7, 126.7, 126.4, 126.4, 126.3, 125.9, 125.8, 125.1, 124.4, 124.4, 122.0, 121.9, 51.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{21}N_2O_3$: 457.1552; found: 457.1535.

N-(10-(4-Cyanophenyl)pyren-1-yl)picolinamide (5l)

By following the general procedure, compound **5l** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (47 mg, 56%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 213–215 °C.

IR (DCM): 3322, 2924, 2226, 1679, 1513 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (s, 1 H), 8.56 (d, *J* = 8.3 Hz, 1 H), 8.35–8.32 (m, 2 H), 8.26 (d, *J* = 7.5 Hz, 1 H), 8.19–8.10 (m, 4 H), 8.06 (t, *J* = 7.6 Hz, 1 H), 7.93–7.89 (m, 2 H), 7.65 (d, *J* = 8.3 Hz, 2 H), 7.53–7.48 (m, 3 H).

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^{13}C NMR (~101 MHz, $CDCl_3$): δ = 161.9, 149.3, 148.0, 147.5, 137.6, 134.8, 131.9, 131.8, 131.2, 130.6, 129.9, 129.8, 129.6, 127.8, 126.9, 126.8, 126.6, 126.5, 126.4, 126.2, 125.3, 124.8, 124.5, 122.0, 118.6, 110.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{29}H_{18}N_3O$: 424.1450; found: 424.1467.

N-(10-(4-Chlorophenyl)pyren-1-yl)picolinamide (5m)

By following the general procedure, **5m** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (37 mg, 58%, 0.15 mmol scale).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 200–202 °C.

IR (DCM): 3440, 3332, 1678, 1517, 1486 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.04 (s, 1 H), 8.44–8.40 (m, 3 H), 8.33 (d, *J* = 7.5 Hz, 1 H), 8.28 (d, *J* = 7.5 Hz, 1 H), 8.25–8.19 (m, 2 H), 8.09 (t, *J* = 7.6 Hz, 1 H), 7.99–7.97 (m, 3 H), 7.62–7.58 (m, 1 H), 7.44 (d, *J* = 8.2 Hz, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.0, 149.5, 147.7, 141.5, 137.2, 135.4, 133.2, 131.7, 131.3, 131.2, 130.3, 130.2, 129.4, 128.5, 127.8, 126.6, 126.4, 126.4, 126.3, 126.3, 125.6, 124.9, 124.4, 123.9, 121.9, 121.7.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{28}H_{18}ClN_2O$: 433.1108; found: 433.1100.

N-(10-(4-Bromophenyl)pyren-1-yl)picolinamide (5n)

By following the general procedure, compound **5n** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (50 mg, 53%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 165–167 °C.

IR (DCM): 3325, 2959, 1678, 1521, 1467 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.08 (s, 1 H), 8.46–8.29 (m, 6 H), 8.26–8.21 (m, 2 H), 8.11 (t, *J* = 7.6 Hz, 1 H), 8.00–7.96 (m, 3 H), 7.63–7.60 (m, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (~126 MHz, $CDCl_3$): δ = 161.0, 148.4, 146.8, 140.9, 136.2, 134.3, 130.6, 130.4, 130.3, 130.1, 129.6, 129.1, 128.4, 126.7, 125.6, 125.4, 125.3, 124.6, 123.9, 123.4, 123.0, 120.9, 120.7, 120.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{28}H_{18}BrN_2O$: 477.0603; found: 477.0607.

N-(10-(3,5-Dimethylphenyl)pyren-1-yl)picolinamide (5o)

By following the general procedure, compound **5o** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (38 mg, 45%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 165–167 °C.

IR (DCM): 3313, 1678, 1511, 1434, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1 H), 8.65 (d, *J* = 8.4 Hz, 1 H), 8.31–8.28 (m, 2 H), 8.19 (d, *J* = 7.4 Hz, 2 H), 8.13–8.06 (m, 3 H), 8.01 (t, *J* = 7.6 Hz, 1 H), 7.93 (s, 1 H), 7.83 (td, ^1J = 7.7 Hz, 1 H, ^2J = 1.6 Hz), 7.41–7.38 (m, 1 H), 7.16 (s, 2 H), 6.59 (s, 1 H), 2.20 (s, 6 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.1, 149.8, 147.2, 142.9, 137.8, 136.9, 131.4, 131.3, 131.1, 130.4, 129.5, 128.4, 127.8, 126.8, 126.6, 126.5, 126.3, 126.0, 125.9, 125.3, 124.7, 124.3, 122.4, 121.8, 21.2.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{30}H_{23}N_2O$: 427.1810; found: 427.1826.

N-(10-(3,4-Dimethylphenyl)pyren-1-yl)picolinamide (5p)

By following the general procedure, compound **5p** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (55 mg, 65%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 148–150 °C.

IR (DCM): 3428, 1686, 1590, 1517, 1128 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.88 (s, 1 H), 8.44–8.38 (m, 2 H), 8.33–8.18 (m, 5 H), 8.08 (t, *J* = 7.6 Hz, 1 H), 7.98–7.95 (m, 3 H), 7.59–7.55 (m, 1 H), 7.19 (s, 1 H), 7.15–7.12 (m, 1 H), 6.92 (d, *J* = 7.6 Hz, 1 H), 2.04 (s, 3 H), 1.90 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.0, 150.0, 147.3, 140.5, 136.9, 136.8, 136.4, 135.3, 131.4, 131.3, 130.5, 130.3, 129.7, 129.4, 127.8, 126.6, 126.5, 126.3, 126.3, 126.3, 126.0, 125.8, 125.2, 124.7, 124.3, 124.1, 122.2, 121.8, 19.5, 19.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{30}H_{23}N_2O$: 427.1810; found: 427.1801.

N-(10-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)pyren-1-yl)picolinamide (5q)

By following the general procedure, compound **5q** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (56 mg, 62%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 192–194 °C.

IR (DCM): 3448, 2925, 1686, 1517, 1252 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.06 (s, 1 H), 8.79 (d, *J* = 8.3 Hz, 1 H), 8.43–8.42 (m, 1 H), 8.30–8.23 (m, 2 H), 8.18 (d, *J* = 7.1 Hz, 1 H), 8.11–7.98 (m, 4 H), 7.92 (s, 1 H), 7.86 (t, ^1J = 7.7 Hz, 1 H, ^2J = 1.6 Hz), 7.44–7.41 (m, 1 H), 7.10–7.06 (m, 2 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 4.20–4.13 (m, 2 H), 3.98–3.91 (m, 2 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 161.9, 150.1, 147.5, 143.4, 143.0, 137.2, 136.2, 136.0, 131.5, 131.5, 131.3, 130.4, 129.2, 127.7, 126.5, 126.3, 126.1, 125.9, 125.3, 124.7, 124.3, 123.4, 122.3, 122.1, 121.7, 118.0, 117.3, 64.3, 64.2.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{30}H_{21}N_2O_3$: 457.1552; found: 457.1541.

N-(10-(6-Chloropyridin-3-yl)pyren-1-yl)picolinamide (5r)

By following the general procedure, compound **5r** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a brown solid (36 mg, 42%).

R_f = 0.3 (EtOAc/hexane = 20:80); mp 194–196 °C.

IR (DCM): 3323, 1678, 1513, 1274, 842 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1 H), 8.72 (s, 1 H), 8.65 (d, *J* = 8.3 Hz, 1 H), 8.43 (d, *J* = 4.4 Hz, 1 H), 8.23–8.17 (m, 3 H), 8.09–7.97 (m, 4 H), 7.88 (t, *J* = 7.6 Hz, 1 H), 7.81 (s, 1 H), 7.56 (d, *J* = 8.1 Hz, 1 H), 7.47 (t, *J* = 6.2 Hz, 1 H), 6.99 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 161.6, 150.1, 149.1, 148.4, 148.0, 139.4, 137.6, 137.5, 132.3, 131.3, 131.2, 130.7, 129.8, 129.4, 127.7, 126.7, 126.6, 126.5, 126.3, 126.1, 125.2, 124.4, 123.7, 123.4, 122.0, 121.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{27}H_{17}ClN_3O$: 434.1060; found: 434.1045.

N-(10-(5-Bromopyridin-2-yl)pyren-1-yl)picolinamide (5s)

By following the general procedure, compound **5s** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a brown solid (48 mg, 51%).

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R_f = 0.3 (EtOAc/hexane = 20:80); mp 175–177 °C.

IR (DCM): 3344, 2936, 1682, 1521, 1236 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1 H), 8.80–8.79 (m, 1 H), 8.50–8.47 (m, 2 H), 8.33 (d, *J* = 8.3 Hz, 1 H), 8.26 (d, *J* = 7.6 Hz, 1 H), 8.19–8.12 (m, 4 H), 8.10–8.03 (m, 2 H), 7.87 (td, ^1J = 7.7 Hz, ^2J = 1.6 Hz, 1 H), 7.60 (dd, ^1J = 8.4 Hz, ^2J = 2.4 Hz, 1 H), 7.49–7.45 (m, 1 H), 7.42 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.5, 160.2, 150.6, 149.3, 147.9, 138.7, 137.4, 134.7, 132.4, 131.2, 130.6, 130.0, 129.9, 127.8, 126.9, 126.5, 126.4, 126.4, 126.2, 125.6, 125.5, 125.4, 124.7, 122.8, 122.1, 118.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{17}BrN_3O$: 478.0555; found: 478.0538.

N-(10-(Thiophen-2-yl)pyren-1-yl)picolinamide (5t)

By following the general procedure, compound **5t** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (57 mg, 71%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 148–150 °C.

IR (DCM): 3428, 2932, 1675, 1513, 1321 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.31 (s, 1 H), 8.84 (d, *J* = 8.4 Hz, 1 H), 8.41 (d, *J* = 4.3 Hz, 1 H), 8.32 (d, *J* = 8.4 Hz, 1 H), 8.23 (d, *J* = 7.6 Hz, 2 H), 8.15–8.01 (m, 5 H), 7.88–7.84 (m, 1 H), 7.44–7.41 (m, 1 H), 7.25 (dd, ^1J = 7.6 Hz, ^2J = 0.9 Hz, 1 H), 7.17 (dd, ^1J = 5.2 Hz, ^2J = 0.9 Hz, 1 H), 6.91 (dd, ^1J = 5.2 Hz, ^2J = 3.6 Hz, 1 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.2, 150.0, 147.6, 143.8, 137.1, 133.5, 131.7, 131.3, 129.9, 129.1, 128.6, 127.8, 127.6, 127.2, 126.4, 126.3, 126.3, 126.0, 125.8, 125.7, 124.9, 124.6, 123.4, 122.0, 121.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{17}N_2OS$: 405.1062; found: 405.1073.

2-(4-Methoxyphenyl)-*N*-(2-(methylthio)phenyl)pyrene-1-carboxamide (6a)

By following the general procedure, compound **6a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (53 mg, 56%).

R_f = 0.4 (EtOAc/hexane = 20:80); mp 151–153 °C.

IR (DCM): 3348, 2925, 1667, 1582, 1509 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 8.1 Hz, 1 H), 8.49 (s, 1 H), 8.44 (d, *J* = 9.2 Hz, 1 H), 8.25–8.04 (m, 7 H), 7.76 (d, *J* = 8.6 Hz, 2 H), 7.46–7.38 (m, 2 H), 7.14–7.10 (m, 1 H), 7.02 (d, *J* = 8.6 Hz, 2 H), 3.83 (s, 3 H), 2.05 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.5, 159.4, 138.4, 136.3, 133.1, 133.0, 132.0, 131.1, 130.6, 129.1, 128.9, 128.7, 127.1, 126.3, 126.3, 126.1, 125.9, 125.8, 124.8, 124.5, 124.3, 123.5, 120.8, 114.3, 55.4, 18.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{24}NO_2S$: 474.1528; found: 474.1538.

N-(2-(Methylthio)phenyl)-2-(thiophen-2-yl)pyrene-1-carboxamide (6b)

By following the general procedure, compound **6b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (51 mg, 57%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 167–169 °C.

IR (DCM): 3336, 2921, 1678, 1509, 1428 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69–8.64 (m, 2 H), 8.39–8.36 (m, 2 H), 8.28–8.25 (m, 2 H), 8.21–8.19 (m, 2 H), 8.14–8.06 (m, 2 H), 7.55 (d, *J* = 3.1 Hz, 1 H), 7.50–7.41 (m, 3 H), 7.17–7.12 (m, 2 H), 2.08 (s, 3 H).

^{13}C NMR (~101 MHz, DMSO-d_6): δ = 168.2, 141.9, 135.6, 135.1, 132.3, 131.4, 131.2, 130.7, 129.7, 129.2, 129.1, 128.4, 128.0, 128.0, 127.6, 127.6, 127.3, 127.0, 127.0, 126.5, 126.3, 126.3, 125.6, 125.3, 123.9, 123.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{20}NOS_2$: 450.0986; found: 450.0999.

N-(*tert*-Butyl)-9-(*p*-tolyl)pyrene-1-carboxamide (8a)

By following the general procedure, compound **8a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (41 mg, 53%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 161–163 °C.

IR (DCM): 3259, 2959, 1675, 1632, 1540 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 8.30 (d, *J* = 7.9 Hz, 1 H), 8.25 (d, *J* = 7.6 Hz, 1 H), 8.16–8.13 (m, 2 H), 8.10–8.06 (m, 2 H), 7.99 (t, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 7.9 Hz, 2 H), 7.40 (d, *J* = 7.8 Hz, 2 H), 6.00–5.99 (m, 1 H), 2.54 (s, 3 H), 1.59 (s, 9 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 169.6, 140.6, 137.9, 137.3, 132.6, 132.1, 131.4, 130.2, 130.1, 129.2, 128.6, 128.1, 127.0, 126.1, 125.9, 124.9, 124.7, 124.7, 124.6, 124.3, 124.1, 52.3, 29.1, 21.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{26}NO$: 392.2014; found: 392.1998.

N-(*tert*-Butyl)-9-phenylpyrene-1-carboxamide (8b)

By following the general procedure, compound **8b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (41 mg, 55%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 158–160 °C.

IR (DCM): 3340, 2925, 1707, 1673, 1518 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1 H), 8.27–8.22 (m, 2 H), 8.14–7.97 (m, 5 H), 7.69 (d, *J* = 7.1 Hz, 2 H), 7.60 (t, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 6.08 (s, 1 H), 1.59 (s, 9 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 169.5, 140.8, 140.6, 132.6, 132.1, 131.4, 130.2, 130.0, 128.6, 128.5, 128.0, 127.6, 127.0, 126.1, 125.9, 124.9, 124.8, 124.6, 124.6, 124.2, 124.1, 52.3, 29.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{24}NO$: 378.1858; found: 378.1845.

2-Butyl-*N*-(quinolin-8-yl)pyrene-1-carboxamide (10a)

By following the general procedure, compound **10a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (41 mg, 70%, 0.14 mmol scale).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 167–169 °C.

IR (DCM): 3342, 2954, 1667, 1515, 1479 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.29 (s, 1 H), 9.23 (dd, ^1J = 7.6 Hz, ^2J = 1.2 Hz, 1 H), 8.64 (dd, ^1J = 4.2 Hz, ^2J = 1.6 Hz, 1 H), 8.27 (d, *J* = 9.2 Hz, 1 H), 8.24–8.19 (m, 3 H), 8.15–8.07 (m, 4 H), 8.02 (t, *J* = 7.6 Hz, 1 H), 7.73 (t, *J* = 8.1 Hz, 1 H), 7.65 (dd, ^1J = 8.3 Hz, ^2J = 1.2 Hz, 1 H), 7.43 (dd, ^1J = 8.3 Hz, ^2J = 4.2 Hz, 1 H), 3.21 (t, *J* = 8.0 Hz, 2 H), 1.98–1.90 (m, 2 H), 1.48–1.41 (m, 2 H), 0.9 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (~126 MHz, $CDCl_3$): δ = 168.8, 148.3, 138.5, 137.3, 136.3, 134.6, 132.4, 131.8, 130.9, 130.5, 128.6, 128.3, 128.1, 128.0, 127.5, 127.0, 125.9, 125.7, 125.6, 125.4, 124.4, 124.3, 123.0, 122.1, 121.7, 34.3, 33.9, 22.8, 14.0.

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HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{25}N_2O$: 429.1967; found: 429.1948.

2-Pentyl-*N*-(quinolin-8-yl)pyrene-1-carboxamide (10b)

By following the general procedure, compound **10b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid (31 mg, 71%, 0.1 mmol scale).

R_f = 0.6 (EtOAc/hexane = 20:80); mp 148–150 °C.

IR (DCM): 3343, 2926, 1669, 1515, 1480 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.28 (s, 1 H), 9.23 (dd, ^1J = 7.6 Hz, ^2J = 1.1 Hz, 1 H), 8.64 (dd, ^1J = 4.2 Hz, ^2J = 1.6 Hz, 1 H), 8.28–8.19 (m, 4 H), 8.15–8.01 (m, 4 H), 8.03 (t, *J* = 7.6 Hz, 1 H), 7.73 (t, *J* = 7.8 Hz, 1 H), 7.64 (dd, ^1J = 8.3 Hz, ^2J = 1.1 Hz, 1 H), 7.2 (dd, ^1J = 8.3 Hz, ^2J = 4.2 Hz, 1 H), 3.20 (t, *J* = 7.8 Hz, 2 H), 1.97–1.92 (m, 2 H), 1.42–1.28 (m, 4 H), 0.82 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (~126 MHz, $CDCl_3$): δ = 167.7, 147.3, 137.5, 136.3, 135.3, 133.6, 131.4, 130.8, 129.9, 129.5, 127.5, 127.3, 127.0, 127.0, 126.5, 126.0, 124.9, 124.7, 124.5, 124.4, 123.4, 123.3, 122.0, 121.1, 120.7, 115.8, 33.1, 30.8, 28.7, 21.5, 12.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{27}N_2O$: 443.2123; found: 443.2107.

2-Heptyl-*N*-(quinolin-8-yl)pyrene-1-carboxamide (10c)

By following the general procedure, compound **10c** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 10:80) as a pale-yellow solid (52 mg, 74%, 0.15 mmol scale).

R_f = 0.7 (EtOAc/hexane = 20:80); mp 108–110 °C.

IR (DCM): 3346, 2925, 1707, 1673, 1518 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1 H), 9.26 (dd, ^1J = 7.6 Hz, ^2J = 1.2 Hz, 1 H), 8.63 (dd, ^1J = 4.2 Hz, ^2J = 1.6 Hz, 1 H), 8.29 (d, *J* = 9.2 Hz, 1 H), 8.22–8.16 (m, 3 H), 8.14–8.00 (m, 5 H), 7.73 (t, *J* = 8.1 Hz, 1 H), 7.63 (dd, ^1J = 8.3 Hz, ^2J = 1.2 Hz, 1 H), 7.40 (dd, ^1J = 8.3 Hz, ^2J = 4.2 Hz, 1 H), 3.22 (t, *J* = 8.0 Hz, 2 H), 1.98–1.92 (m, 2 H), 1.46–1.38 (m, 2 H), 1.32–1.25 (m, 2 H), 1.22–1.16 (m, 4 H), 0.8 (t, 3 H, *J* = 6.8 Hz).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.8, 148.3, 138.5, 137.4, 136.3, 134.6, 132.5, 131.8, 131.0, 130.5, 128.6, 128.3, 128.1, 127.5, 127.0, 125.9, 125.8, 125.6, 125.5, 124.5, 124.3, 123.0, 122.2, 121.7, 116.9, 34.2, 32.2, 31.7, 29.7, 29.2, 22.6, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{31}N_2O$: 471.2436; found: 471.2423.

2-Octyl-*N*-(quinolin-8-yl)pyrene-1-carboxamide (10d)

By following the general procedure, compound **10d** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 10:90) as a pale-yellow solid (35 mg, 73%, 0.1 mmol scale).

R_f = 0.7 (EtOAc/hexane = 20:80); mp 152–154 °C.

IR (DCM): 3359, 2932, 1655, 1528, 1475 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.44 (s, 1 H), 8.92 (dd, ^1J = 7.5 Hz, ^2J = 1.1 Hz, 1 H), 8.76 (dd, ^1J = 4.2 Hz, ^2J = 1.6 Hz, 1 H), 8.48 (dd, ^1J = 8.3 Hz, ^2J = 1.5 Hz, 1 H), 8.37–8.31 (m, 3 H), 8.28–8.16 (m, 4 H), 8.11 (t, *J* = 7.6 Hz, 1 H), 7.84 (dd, ^1J = 8.3 Hz, ^2J = 1.1 Hz, 1 H), 7.79–7.75 (m, 1 H), 7.62 (dd, ^1J = 8.2 Hz, ^2J = 4.2 Hz, 1 H), 3.12–3.08 (m, 2 H), 1.86–1.82 (m, 2 H), 1.34–0.97 (m, 10 H), 0.71 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 168.8, 148.3, 138.5, 137.4, 136.3, 134.6, 132.5, 131.8, 131.0, 130.5, 128.6, 128.3, 128.1, 127.5, 127.0, 125.9, 125.8, 125.6, 125.5, 124.5, 124.3, 123.0, 122.1, 121.7, 116.9, 34.2, 32.2, 31.8, 29.7, 29.4, 29.2, 22.6, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{33}N_2O$: 485.2593; found: 485.2571.

***N*-(10-Butylpyren-1-yl)picolinamide (11a)**

By following the general procedure, compound **11a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 15:85) as a brown solid (51 mg, 68%).

R_f = 0.6 (EtOAc/hexane = 20:80); mp 144–146 °C.

IR (DCM): 3396, 2951, 1678, 1556, 1514 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.8 (s, 1 H), 8.72 (d, *J* = 4.3 Hz, 1 H), 8.53 (d, *J* = 8.3 Hz, 1 H), 8.45 (d, *J* = 7.8 Hz, 1 H), 8.23 (d, *J* = 8.3 Hz, 1 H), 8.16–8.13 (m, 1 H), 8.08–8.03 (m, 3 H), 8.01–7.96 (m, 2 H), 7.91 (s, 1 H), 7.56–7.53 (m, 1 H), 3.48 (t, *J* = 7.9 Hz, 2 H), 1.78–1.72 (m, 2 H), 1.32–1.26 (m, 2 H), 0.84 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.5, 150.2, 148.1, 137.7, 136.5, 131.2, 130.9, 130.8, 130.2, 129.8, 127.7, 127.0, 126.8, 126.6, 126.1, 125.7, 125.3, 124.8, 124.7, 124.1, 124.1, 122.7, 38.0, 33.9, 22.7, 13.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{23}N_2O$: 379.1810; found: 379.1794.

***N*-(10-Pentylpyren-1-yl)picolinamide (11b)**

By following the general procedure, compound **11b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (69 mg, 88%).

R_f = 0.5 (EtOAc/hexane = 20:80); mp 128–130 °C.

IR (DCM): 3352, 2936, 1686, 1513, 1325 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.79 (s, 1 H), 8.74–8.73 (m, 1 H), 8.53 (d, *J* = 8.3 Hz, 1 H), 8.46 (d, *J* = 7.8 Hz, 1 H), 8.25 (d, *J* = 8.3 Hz, 1 H), 8.17–8.15 (m, 1 H), 8.11–8.05 (m, 3 H), 8.02–7.97 (m, 2 H), 7.94 (s, 1 H), 7.59–7.56 (m, 1 H), 3.50 (t, *J* = 8.0 Hz, 2 H), 1.80–1.76 (m, 2 H), 1.28–1.22 (m, 4 H), 0.78 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.5, 150.2, 148.1, 137.8, 136.6, 131.2, 130.9, 130.8, 130.2, 129.9, 127.8, 127.0, 126.8, 126.6, 126.1, 125.7, 125.4, 124.9, 124.8, 124.2, 124.1, 122.8, 38.4, 31.8, 31.6, 22.6, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{25}N_2O$: 393.1967; found: 393.1957.

***N*-(10-Heptylpyren-1-yl)picolinamide (11c)**

By following the general procedure, compound **11c** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (48 mg, 58%).

R_f = 0.6 (EtOAc/hexane = 20:80); mp 132–134 °C.

IR (DCM): 3375, 2928, 1690, 1517, 1321 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.77 (s, 1 H), 8.73 (d, *J* = 4.6 Hz, 1 H), 8.52 (d, *J* = 8.2 Hz, 1 H), 8.46 (d, *J* = 7.8 Hz, 1 H), 8.24 (d, *J* = 8.2 Hz, 1 H), 8.15 (d, *J* = 7.5 Hz, 1 H), 8.09–8.06 (m, 3 H), 8.01–7.97 (m, 2 H), 7.92 (s, 1 H), 7.58–7.55 (m, 1 H), 3.48 (t, *J* = 7.8 Hz, 2 H), 1.78–1.74 (m, 2 H), 1.22–1.13 (m, 8 H), 0.84 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 162.5, 150.2, 148.1, 137.8, 136.6, 131.2, 130.9, 130.8, 130.2, 129.9, 127.8, 127.0, 126.8, 126.6, 126.1, 125.7, 125.4, 124.8, 124.8, 124.1, 124.1, 122.8, 38.4, 31.9, 31.9, 29.7, 29.2, 22.6, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{29}N_2O$: 421.2280; found: 421.2265.

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10-(4-Methoxyphenyl)pyren-1-amine (12a)

By following the general procedure, compound **12a** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 5:95) as a brown solid (27 mg, 56%, 0.15 mmol scale).

R_f = 0.8 (EtOAc/hexane = 20:80); mp 134–136 °C.

IR (DCM): 3484, 3386, 1601, 1510, 1450 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–7.91 (m, 5 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 7.72 (s, 1 H), 7.54 (d, *J* = 7.9 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 1 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 3.94 (s, 3 H). The NH_2 signal could not be clearly located in the proton NMR spectrum.

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 159.2, 142.8, 137.1, 135.6, 132.4, 131.2, 130.3, 129.1, 128.0, 127.4, 127.1, 126.2, 125.2, 124.2, 123.8, 123.3, 122.8, 115.9, 114.5, 113.9, 55.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{18}NO$: 324.1388; found: 324.1373.

10-(Thiophen-2-yl)pyren-1-amine (12b)

By following the general procedure, compound **12b** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 5:95) as a brown solid (25 mg, 70%, 0.12 mmol scale).

R_f = 0.8 (EtOAc/hexane = 20:80); mp 169–171 °C.

IR (DCM): 3471, 3398, 2928, 1617, 1452 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.3 Hz, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 7.97–7.91 (m, 4 H), 7.83 (d, *J* = 8.8 Hz, 1 H), 7.52 (d, *J* = 5.2 Hz, 1 H), 7.28–7.26 (m, 2 H), 7.22–7.20 (m, 1 H), 4.25 (br s, 2 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 144.3, 143.0, 132.4, 131.2, 130.7, 129.1, 128.0, 127.6, 127.3, 127.1, 126.3, 126.2, 125.6, 124.4, 124.0, 123.2, 123.0, 116.2, 114.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{14}NS$: 300.0847; found: 300.0844.

10-(*p*-Tolyl)pyren-1-amine (12c)

By following the general procedure, compound **12c** was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 5:95) as a red solid (112 mg, 73%, 0.5 mmol).

R_f = 0.9 (EtOAc/hexane = 20:80); mp 150–152 °C.

IR (DCM): 3494, 3398, 1617, 1513, 1452 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–7.93 (m, 5 H), 7.87–7.84 (m, 1 H), 7.73–7.72 (m, 1 H), 7.53–7.51 (m, 2 H), 7.37–7.35 (m, 2 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 4.13 (br s, 2 H), 2.53 (s, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 143.0, 140.5, 137.5, 132.4, 131.3, 129.2, 129.1, 128.9, 128.0, 127.4, 127.1, 126.2, 125.3, 124.1, 123.8, 123.2, 122.8, 115.9, 114.3, 21.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{18}N$: 308.1439; found: 308.1428.

10-(4-Butylphenyl)pyren-1-amine (12d)

Compound **12d** was obtained via a one-pot sequential C–H arylation of **2b** under standard reaction conditions and neat conditions, followed by NaOH-mediated hydrolysis procedure. After the standard work-up procedure and purification by column chromatography on silica gel (EtOAc/hexane = 5:95) as a red solid (32 mg, 46%, 0.2 mmol scale from **2b**).

R_f = 0.9 (EtOAc/hexane = 20:80); mp 142–144 °C.

IR (DCM): 3490, 3394, 1613, 1513, 1421 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06–8.01 (m, 2 H), 8.00–7.90 (m, 3 H), 7.83 (d, *J* = 8.8 Hz, 1 H), 7.72 (s, 1 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 1 H), 4.13 (s, 2 H), 2.77 (t, *J* = 7.8 Hz, 2 H), 1.77–1.70 (m, 2 H), 1.50–1.44 (m, 2 H), 1.02 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (~101 MHz, $CDCl_3$): δ = 143.0, 142.5, 140.7, 137.5, 132.4, 131.2, 129.0, 128.9, 128.5, 128.0, 127.4, 127.1, 126.2, 125.3, 124.1, 123.7, 123.2, 122.8, 115.8, 114.3, 35.5, 33.7, 22.5, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{24}N$: 350.1909; found: 350.1897.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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(20) CCDC 2068244 (**4a**), 2068245 (**4e**), 2068246 (**5n**), and 2068247 (**12c**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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