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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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 crystal structure analysis. 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, 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 the cobalt-promoted insertion of carbon monoxide into an ortho-C(sp²)–H bond of aldimine and azobenzene substrates. Subsequently, various stoichiometric metal-promoted C–H bond activation reactions involving cyclometallated species were published. In 1970, the palladium-catalyzed chlorination of an ortho-C(sp²)–H bond of azobenzene reported by Fahey is another important discovery. Subsequently, Jordan (1989), Moore (1992) and Murai (1993) reported breakthroughs in catalytic C–H activationfunctionalization methods involving Zr- and Ru-based catalysts. During the last 20 years, research on transition-metal-catalyzed C–H bond activation reactions has advanced at a rapid rate.

Pertinently, the transition-metal-catalyzed sp²/sp³ C–H activationfunctionalization is considered to be a remarkable synthetic strategy to functionalize small organic molecules. The catalytic C–H functionalization of sp²/sp³ C–H bonds of small organic molecules has been accomplished with or without the help of a directing group. In particular, directing-group-aided sp² and sp³ C–H activationfunctionalization 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 sp² and sp³ C–H activationfunctionalization of carboxamides are considered benchmark strategies. 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). 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.

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

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$_{Ar}$) reactions. 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. The 2- and 7-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. Impressed by the chemical transformations carried out on the pyrene core and driven by the importance of the pyrene derivatives in chemical sciences, 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). 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 and Assembly of the C1,C2-Disubstituted Pyrene Motif 4a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Yield of 4a (%)</th>
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<tr>
<td>1</td>
<td>Pd(OAc)$_2$</td>
<td>Ag$_2$CO$_3$</td>
<td>o-xylene 135</td>
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<tr>
<td>2</td>
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<td>40</td>
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<tr>
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<td>K$_2$CO$_3$</td>
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<tr>
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<td>o-xylene 135</td>
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<td>1,2-DCE 130</td>
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<tr>
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<td>o-xylene 130</td>
<td>22</td>
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<td>o-xylene 130</td>
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<td>AgOAc</td>
<td>o-xylene 130</td>
<td>60</td>
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<tr>
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<td>AgOAc</td>
<td>o-xylene 130</td>
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<td>Ni(OAc)$_2$</td>
<td>NaHCO$_3$</td>
<td>toluene 160</td>
<td>15</td>
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</tr>
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* 0.2 mmol of 3a.

h 0.4 mmol of 3a.

i 0.6 mmol of 3a.
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-amino-pyrene 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(sp2)–H functionalization of 2a (C2-position, Table 1). We performed optimization reactions by employing the standard Pd(II)-catalyzed sp2-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 Ag2CO3 or K2CO3, 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 Ag2CO3 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 Cs2CO3 as an additive instead of Ag2CO3 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 K2CO3 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-
ent palladium catalysts such as Pd(TFA)₂ and Pd(MeCN)₂Cl₂ 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, NO₂, 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
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(sp²)–H functionalization of 2b at the C10-position. We then performed the 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 Ph and various aryl iodides containing different electron-donating and electron withdrawing substituents (e.g., OMe, Me, OEt, Ac, COOEt, 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-ido-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 (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. 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-
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/H₂O 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

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-

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**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

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

A dry round-bottomed flask containing amine (9 mmol, 0.9 equiv) and Et$_3$N (11 mmol, 1.1 equiv) was stirred for 5–10 min under a nitrogen atmosphere. The reaction flask 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).

Synthesis of Carboxamide 2b

An appropriate amount of picolinic acid (10 mmol), N-[3-dimethylamino propyl]-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-amino pyrene (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 Amination of the Carboxamide 2b and Preparation of Compounds 5

A mixture of carboxamide 2b (0.2 mmol, 1 equiv), an appropriate vinyl 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 aminated 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 allyl iodide (0.56 mmol, 4 equiv), anhydrous K$_2$CO$_3$ (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 allyl 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).
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 mixture was heated at reflux 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.¹³κ

Directing Group Removal/Amide Hydrolysis and Preparation of Compound 13

A solution of NaOH (60 mg of NaOH) in EtOH/H₂O (10:1 v/v, 3.3 mL) 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 C–H arylated 1-aminopyrene derivative 13 (d, J = 8.55–8.54 (m, 1 H), 8.49 (d, J = 9.0 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), 7.40 (s, 3 H)).

IR (DCM): 3348, 2940, 1725, 1675, 1528 cm⁻¹.

¹³C NMR (~101 MHz, CDCl₃): 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, 124.9, 124.6, 123.5, 123.1, 121.1, 120.5, 115.7, 25.6.


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%).

IR (DCM): 3275, 2924, 1670, 1595, 1519, 1346 cm⁻¹.

¹³C NMR (~101 MHz, CDCl₃): 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, 2 H), 8.27 (d, J = 8.6 Hz, 2 H), 8.17 (t, J = 7.6 Hz, 1 H), 8.05 (d, J = 8.3 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 1 H), 7.66 (t, J = 7.8 Hz, 1 H), 7.56 (dd, J = 8.3 Hz, J' = 4.2 Hz, 1 H).


2-(4-Chlorophenyl)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%).

IR (DCM): 3348, 2936, 1663, 1528, 1490 cm⁻¹.

¹³C NMR (~101 MHz, CDCl₃): 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, 127.4, 127.0, 126.8, 126.3, 126.1, 125.7, 124.5, 124.3, 123.1, 123.0, 122.4, 121.7, 116.8.

HRMS (ESI): m/z [M + H⁺]⁺ calcd for C₁₃H₁₇ClNO₂S: 345.0961; found: 345.0962.

Methyl 4-((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%).

IR (DCM): 3348, 3296, 1725, 1675, 1528 cm⁻¹.

¹³C NMR (~101 MHz, CDCl₃): 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, 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.


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 (68 mg, 70%).

IR (DCM): 3348, 3296, 1725, 1675, 1528 cm⁻¹.

¹³C NMR (~101 MHz, CDCl₃): 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, J = 8.1 Hz, J' = 4.1 Hz, 1 H), 3.86 (s, 3 H).


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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 (67 mg, 71%).

IR (DCM): 3338, 1665, 1515, 1482, 1324 cm⁻¹.


13C NMR (~126 MHz, CDCl3): δ = 168.3, 167.4, 160.0, 148.0, 148.9, 138.9, 138.7, 132.5, 130.6, 130.3, 129.8, 129.0, 128.5, 128.1, 127.9, 127.6, 127.4, 126.8, 124.7, 123.9, 115.7, 115.6, 115.2, 114.9, 114.6, 114.4, 114.3, 113.1, 112.8, 112.6, 112.5, 112.3, 112.1, 111.8, 111.5, 111.6.


2-(3-(Dihydrobenzo[b][1,4]dioxin-6-yl)-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%).

IR (DCM): 3338, 2924, 1667, 1516, 1481 cm⁻¹.


13C NMR (~101 MHz, CDCl3): δ = 168.3, 168.2, 160.1, 148.0, 148.9, 138.9, 138.7, 132.5, 130.6, 130.3, 129.8, 129.0, 128.5, 128.1, 127.9, 127.6, 127.4, 126.8, 124.7, 123.9, 115.7, 115.6, 115.2, 114.9, 114.6, 114.3, 113.1, 112.8, 112.6, 112.5, 112.3, 112.1, 111.8, 111.5, 111.6, 64.3, 64.2.

2-Phenyl-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 (40 mg, 55%).

IR (DCM): 3344, 1667, 1519, 1483 cm⁻¹.


1C NMR (~101 MHz, CDCl3): δ = 168.3, 168.2, 160.1, 148.0, 148.9, 138.9, 138.7, 132.5, 130.6, 130.3, 129.8, 129.0, 128.5, 128.1, 127.9, 127.6, 127.4, 126.8, 124.7, 123.9, 115.7, 115.6, 115.2, 114.9, 114.6, 114.3, 113.1, 112.8, 112.6, 112.5, 112.3, 112.1, 111.8, 111.5, 111.6.


2-(4-Isopropylphenyl)-N-(quinolin-8-yl)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 (38 mg, 55%).

IR (DCM): 3357, 2959, 1662, 1519, 1481 cm⁻¹.


N-(Quinolin-8-yl)-2-(p-toly)pyrene-1-carboxamide (4j)

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

IR (DCM): 3355, 3052, 1690, 1536, 1321 cm⁻¹.

2-(3-Chlorophenyl)-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%).

\[
\begin{align*}
\text{IR (DCM): } & 3333, 1667, 1519, 1483, 1325 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{N}_2\text{O}_2: 479.1760; \text{ found: 479.1775}. \\
\end{align*}
\]

2-(3-Methoxyphenyl)-N-(quinolin-8-yl)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).

\[
\begin{align*}
\text{IR (DCM): } & 3316, 1667, 1519, 1483, 1325 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{N}_2\text{O}_2: 479.1760; \text{ found: 479.1780}. \\
\end{align*}
\]

N-(quinolin-8-yl)-2-(m-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 (61 mg, 66%).

\[
\begin{align*}
\text{IR (DCM): } & 3337, 1665, 1516, 1482, 1324 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{N}_2\text{O}_2: 493.1624; \text{ found: 493.1627}. \\
\end{align*}
\]

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%).

\[
\begin{align*}
\text{IR (DCM): } & 3337, 2923, 1668, 1518, 1483 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{N}_2\text{O}_2: 493.1624; \text{ found: 493.1627}. \\
\end{align*}
\]

2-(3-Chlorophenyl)-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%).

\[
\begin{align*}
\text{IR (DCM): } & 3337, 1665, 1519, 1483, 1324 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{N}_2\text{O}_2: 493.1624; \text{ found: 493.1627}. \\
\end{align*}
\]

2-(3-Fluorophenyl)-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%).

\[
\begin{align*}
\text{IR (DCM): } & 3337, 2924, 1667, 1519, 1483 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{N}_2\text{O}_2: 493.1624; \text{ found: 493.1627}. \\
\end{align*}
\]

2-(3-Bromopyridin-2-yl)-(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).

\[
\begin{align*}
\text{IR (DCM): } & 3334, 2917, 1682, 1536, 1332 \text{ cm}^{-1}. \\
\text{HRMS (ESI): } & m/z [M + H]^+ \text{ calcd for C}_{33}\text{H}_{25}\text{BrN}_2: 528.0711; \text{ found: 528.0685}. \\
\end{align*}
\]
1H NMR (400 MHz, CDCl 3): δ = 7.15–7.11 (m, 3 H), 6.55–6.54 (m, 1 H), 3.74 (s, 3 H).

IR (DCM): 3475, 3352, 1667, 1602, 1517 cm–1.

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

IR (DMC): 3475, 3352, 1667, 1602, 1517 cm–1.

1H 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 (s, 3 H).

1C NMR (101 MHz, DMSO-d 6): δ = 162.2, 159.6, 149.8, 147.4, 144.3, 137.1, 136.5, 131.3, 131.3, 130.4, 129.4, 129.0, 127.7, 126.6, 126.4, 126.2, 126.1, 125.4, 124.8, 124.3, 124.0, 121.8, 121.8, 121.4, 113.7, 113.2, 55.1.

HRMS (ESI): m/z [M + H]+ calcd for C 29H 21N 2O 2: 413.1603; 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%).

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

IR (DMC): 3325, 3040, 1690, 1517, 1478 cm–1.

1H 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, J = 7.7 Hz, J' = 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).

1C 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, 126.2, 126.1, 125.0, 125.3, 124.7, 124.3, 124.0, 122.1, 121.9, 21.3.

HRMS (ESI): m/z [M + H]+ calcd for C 29H 34F 3N 2O 2: 471.1709; found: 471.1716.

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

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

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

IR (DMC): 3328, 2921, 1671, 1521, 1486 cm–1.

1H 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, J' = 7.7 Hz, J = 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).

1C NMR (101 MHz, DMSO-d 6): δ = 166.5, 161.8, 149.5, 147.4, 144.2, 137.1, 135.6, 133.6, 131.9, 131.3, 131.0, 130.2, 129.5, 129.5, 129.2, 128.1, 127.7, 126.7, 126.4, 126.3, 126.2, 125.4, 124.8, 124.3, 124.0, 121.8, 121.8, 121.4, 113.7, 113.2, 55.1.

**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%).

$R_f = 0.4\ (\text{EtOAc/hexane = 20:80}); \text{mp} 171–173^\circ\text{C}.$

IR (DCM): 3296, 2926, 1674, 1511 cm$^{-1}$.  
$\delta = 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, $J = 7.6\ Hz, J = 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).

HRMS (ESI): $[M + H]^+\text{calcd for C}_{29}H_{21}N_2O: 413.1654; \text{found: 413.1669.}$

**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%).

$R_f = 0.5\ (\text{EtOAc/hexane = 20:80}); \text{mp} 158–160^\circ\text{C}.$

IR (DCM): 3452, 3344, 1682, 1605, 1517 cm$^{-1}$.  
$\delta = 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), 3.6 (s, 3\ H).

HRMS (ESI): $[M + H]^+\text{calcd for C}_{30}H_{21}N_2O_2: 441.1603; \text{found: 441.1624.}$

**N-(10-(4-Acetylphenyl)pyren-1-yl)picolinamide (5i)**
By following the general procedure, compound 5i was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 25:75) as a brown solid (54 mg, 61%).

$R_f = 0.3\ (\text{EtOAc/hexane = 20:80}); \text{mp} 158–160^\circ\text{C}.$

IR (DCM): 3396, 3296, 2951, 1780, 1716, 1678, 1512 cm$^{-1}$.  
$\delta = 8.4\ Hz, 1\ 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).

HRMS (ESI): $[M + H]^+\text{calcd for C}_{28}H_{19}N_2O: 399.1497; \text{found: 399.1511.}$

**Methyl 4-(((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%).

$R_f = 0.3\ (\text{EtOAc/hexane = 20:80}); \text{mp} 125–127^\circ\text{C}.$

IR (DCM): 3500, 1716, 1678, 1512, 1434 cm$^{-1}$.  
$\delta = 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), 7.93\ (s, 1\ H), 7.84–7.80\ (m, 1\ H), 7.47 (d, J = 8.6\ Hz, 2\ H), 7.38–7.35\ (m, 1\ H), 6.77 (d, J = 7.6\ Hz, 2\ H), 3.78 (q, J = 7.0\ Hz, 2\ H), 1.35 (t, J = 7.3\ Hz, 3\ H).

HRMS (ESI): $[M + H]^+\text{calcd for C}_{30}H_{21}N_2O_2: 457.1552; \text{found: 457.1535.}$

**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 = 25:75) as a brown solid (58 mg, 64%).

$R_f = 0.3\ (\text{EtOAc/hexane = 20:80}); \text{mp} 125–127^\circ\text{C}.$

IR (DCM): 3500, 1716, 1678, 1512, 1434 cm$^{-1}$.  
$\delta = 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), 7.93\ (s, 1\ H), 7.84–7.80\ (m, 1\ H), 7.47 (d, J = 8.6\ Hz, 2\ H), 7.38–7.35\ (m, 1\ H), 6.77 (d, J = 7.6\ Hz, 2\ H), 3.78 (q, J = 7.0\ Hz, 2\ H), 1.35 (t, J = 7.3\ Hz, 3\ H).

HRMS (ESI): $[M + H]^+\text{calcd for C}_{30}H_{21}N_2O_2: 457.1552; \text{found: 457.1535.}$
By following the general procedure, compound 5m was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (55 mg, 65%).

HRMS (ESI): m/z [M + H]+ calcd for C_{30}H_{23}BrN_{2}O: 433.1100; found: 433.1108.

IR (DCM): 1686, 1590, 1517, 1486 cm\(^{-1}\).

\(^{13}\)C NMR (~101 MHz, CDCl\(_3\)): \[\delta = 161.9, 149.3, 148.0, 147.5, 137.6, 134.8, 131.9, 131.8, 131.2, 130.6, 129.9, 129.8, 129.6, 127.8, 126.9, 126.8, 126.5, 126.4, 126.2, 125.3, 124.8, 124.5, 122.0, 118.6, 110.3.\]

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

By following the general procedure, compound 5m was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a brown solid (36 mg, 42%).

IR (DCM): 3483, 2925, 1686, 1517, 1252 cm\(^{-1}\).

\(^{1}H\) NMR (400 MHz, DMSO-d\(_6\)): \[\delta = 9.98 (s, 1 H), 8.44–8.38 (m, 2 H), 8.33–8.18 (m, 5 H), 8.08 (t, \(J = 7.6 \text{ Hz}, 1 \text{ H})\), 7.98–7.95 (m, 3 H), 7.59–7.55 (m, 1 H), 7.19 (s, 1 H), 7.06–7.12 (m, 1 H), 6.92 (d, \(J = 7.6 \text{ Hz}, 1 \text{ H})\), 2.04 (s, 3 H), 1.90 (s, 3 H).\]

HRMS (ESI): m/z [M + H]+ calcd for C_{20}H_{15}N_{2}O_{4}: 424.1470; found: 424.1467.

N-(10-(4-Chlorophenyl)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 (38 mg, 53%).

IR (DCM): 3483, 2925, 1678, 1517, 1486 cm\(^{-1}\).

\(^{1}H\) NMR (400 MHz, DMSO-d\(_6\)): \[\delta = 10.20 (s, 1 H), 8.79 (d, \(J = 8.3 \text{ Hz}, 1 \text{ H})\), 8.43–8.42 (m, 2 H), 8.30–8.23 (m, 2 H), 7.68–7.69 (m, 2 H), 7.59–7.56 (m, 1 H), 7.38 (d, \(J = 4.2 \text{ Hz}, 2 \text{ H})\), 7.35 (d, \(J = 4.2 \text{ Hz}, 2 \text{ H})\).\]

HRMS (ESI): m/z [M + H]+ calcd for C_{30}H_{23}BrN_{2}O: 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%).

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

\(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \[\delta = 9.75 (s, 1 H), 8.65 (d, \(J = 8.4 \text{ Hz}, 1 \text{ H})\), 8.31–8.26 (m, 2 H), 8.19 (d, \(J = 7.4 \text{ Hz}, 2 \text{ H})\), 8.13–8.06 (m, 3 H), 8.01 (t, \(J = 7.6 \text{ Hz}, 1 \text{ H})\), 7.93 (s, 1 H), 7.83 (td, \(J = 7.7 \text{ Hz}, 1 \text{ H}\), \(J = 1.6 \text{ Hz}\)), 7.41–7.38 (m, 1 H), 7.16 (s, 2 H), 6.59 (s, 2 H), 2.20 (s, 6 H).\]

HRMS (ESI): m/z [M + H]+ calcd for C_{27}H_{23}ClN_{2}O_{2}: 415.1777; found: 415.1774.

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**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%).

\[ R_f = 0.5 \text{ (EtOAc/hexane = 20:80); mp 156–160°C.} \]

**HRMS (ESI):** m/z [M + H]^+ calcd for C_{29}H_{38}NO: 378.2134; found: 378.2136.

2-Butyl-N-(quinolinin-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%).

\[ R_f = 0.5 \text{ (EtOAc/hexane = 20:80); mp 167–169°C.} \]

**HRMS (ESI):** m/z [M + H]^+ calcd for C_{36}H_{36}NO: 543.2708; found: 543.2711.
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).


N-(10-Butylpyryl-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%).


N-(10-Pentylypyren-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%).


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).


N-(10-Pentylypyren-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%).


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).

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, 70%, 0.15 mmol scale).

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

\(^{1}C\) NMR (~101 MHz, CDCl\(_3\)): \(\delta = 123.2, 122.8, 115.9, 114.3, 21.4\).

1H NMR (400 MHz, CDCl\(_3\)):
\(\delta = 8.07–8.02 (m, 2 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 \(\text{NH}_2\) signal could not be clearly located in the proton NMR spectrum.

\(^{1}C\) NMR (~101 MHz, CDCl\(_3\)): \(\delta = 123.7, 123.2, 122.8, 115.8, 114.3, 35.5, 33.7, 22.5, 14.1\).

HRMS (ESI): \(m/z [M + H]^+\) calcd for C\(_{20}\)H\(_{14}\)NO: 324.1388; found: 324.1373.

Conflict of Interest
The authors declare no conflict of interest.

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Supporting Information
Supporting information for this article is available online at https://doi.org/10.1055/a-1472-0881.

References

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).

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

1H NMR (400 MHz, CDCl\(_3\)): \(\delta = 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), 1.74–1.70 (m, 2 H), 1.50–1.44 (m, 2 H), 1.02 (t, \(J = 7.4\) Hz, 3 H).

\(^{1}C\) NMR (~101 MHz, CDCl\(_3\)): \(\delta = 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\(_{30}\)H\(_{24}\)N\(_{2}\): 350.1909; found: 350.1897.


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.