# 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

Received: 09.03.2021 Accepted after revision: 31.03.2021 Published online: 31.03.2021 DOI: 10.1055/a-1472-0881; Art ID: ss-2021-f0113-st 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 $\mathrm{Pd}(\mathrm{II})$-catalyzed $\beta-\mathrm{C}-\mathrm{H}$ 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 $\gamma-\mathrm{C}-\mathrm{H}$ 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 $\mathrm{C}-\mathrm{H}$ 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 $\mathrm{C}-\mathrm{H}$ 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- $\mathrm{C}\left(\mathrm{sp}^{2}\right)-\mathrm{H}$ bond of aldimine and azobenzene substrates. Subsequently, various stoichiometric metal-promoted $\mathrm{C}-\mathrm{H}$ bond activation reactions involving cyclometallated species were published. ${ }^{4}$ In 1970, the palladium-catalyzed chlorination of an ortho-$\mathrm{C}\left(\mathrm{sp}^{2}\right)-\mathrm{H}$ bond of azobenzene reported by Fahey is another important discovery. ${ }^{5}$ Subsequently, Jordan (1989), Moore (1992) and Murai (1993) reported breakthroughs in cata-
lytic C-H activation/functionalization methods involving Zr - and Ru-based catalysts. ${ }^{6-8}$ During the last 20 years, research on transition-metal-catalyzed $\mathrm{C}-\mathrm{H}$ bond activation reactions has advanced at a rapid rate. ${ }^{9-11}$

Pertinently, the transition-metal-catalyzed $\mathrm{sp}^{2} / \mathrm{sp}^{3} \mathrm{C}-\mathrm{H}$ activation/functionalization is considered to be a remarkable synthetic strategy to functionalize small organic molecules. The catalytic C-H functionalization of $\mathrm{sp}^{2} / \mathrm{sp}^{3} \mathrm{C}-\mathrm{H}$ bonds of small organic molecules has been accomplished with or without the help of a directing group. ${ }^{9-15}$ In particular, directing-group-aided $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3} \mathrm{C}-\mathrm{H}$ 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 $\mathrm{Pd}(\mathrm{II})$-catalyzed bidentate directing group (BDG)aided site-selective $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3} \mathrm{C}-\mathrm{H}$ 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). ${ }^{1-15}$ 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. ${ }^{16 b-d, 18}$ It is documented that the optoelectronic and pho-
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 ( $\mathrm{S}_{\mathrm{E}} \mathrm{Ar}$ ) reactions. ${ }^{16 \mathrm{~b}}$ 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). ${ }^{16 \mathrm{~b}}$ It may be noted that the Friedel-Crafts tertbutylation and Ir-catalyzed direct borylation reactions have been carried out at these positions. The 4-, 5-, 9- and 10-

multiple reactive positions
nodal plane/inaccessible sites $=2$ - and 7 -positions active sites
$=1-, 3-$, $6-$ and 8 -positions
$=4-, 5-, 9-$ and 10 -positions
Figure 1 K-Region and non-K-region of the pyrene motif
single examples of C-H functionalization of pyrene $\mathbf{2 b}$ (ref. 15)

alkylation with
$\underset{\{R h\}}{\text { COOEt }}$
etherification
with $\mathrm{PhB}(\mathrm{OH})_{2}$ \{Cu\}

single example of C-H functionalization of pyrene $\mathbf{2 a}$ (ref. 15) allylation with
~OPh
Fe(acac)
$\mathrm{ZnCl}_{2} \cdot$ TMEDA
${ }^{\text {t }} \mathrm{BuCH}_{2} \mathrm{MgBr}$
this work:
Pd(II)-catalyzed C-H arylation/alkylation of pyrene amide motifs


Scheme 1 Theme of this work: C-H arylation/alkylation of pyrene amide motifs
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. ${ }^{16 \mathrm{~b}}$

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 $\mathrm{C}-\mathrm{H}$ functionalization route to assemble new pyrene amide motifs. A few instances of functionalization of the pyrene core through the di-recting-group-aided $\mathrm{C}-\mathrm{H}$ 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-groupaided site-selective $\mathrm{C}-\mathrm{H}$ arylation and alkylation of the relatively inaccessible C2 position and K-region C10 position of pyrene amides $\mathbf{2 a}$ and $\mathbf{2 b}$, 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 | $T\left({ }^{\circ} \mathrm{C}\right)$ | Yield of 4a (\%) |
| :---: | :--- | :--- | :--- | :---: | :--- |
| 1 | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ | o-xylene | 135 | 38 |
| 2 | $\mathrm{Pd}(\mathrm{OAC})_{2}$ | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ | o-xylene | 135 | 40 |
| 3 | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | $\mathrm{~K}_{2} \mathrm{CO}_{3}$ | o-xylene | 135 | 51 |
| 4 | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | AgOAc | o-xylene | 135 | 70 |
| 5 | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | AgOAc | 1,2-DCE | 130 | 65 |
| $6^{\text {a }}$ | $\mathrm{Pd}(\mathrm{OAC})_{2}$ | AgOAc | o-xylene | 130 | 22 |
| $7^{\text {b }}$ | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | AgOAc | o-xylene | 130 | 35 |
| $8^{\text {c }}$ | $\mathrm{Pd}(\mathrm{OAc})_{2}$ | AgOAc | o-xylene | 130 | 47 |
| 9 | $\mathrm{Pd}(\mathrm{TFA})_{2}$ | AgOAc | o-xylene | 130 | 60 |
| 10 | $\mathrm{Pd}(\mathrm{MeCN})_{2} \mathrm{Cl}_{2}$ | AgOAc | o-xylene | 130 | 53 |
| 11 | $\mathrm{Ni}(\mathrm{OTf})_{2}$ | NaHCO | toluene | 160 | 15 |

[^0]$\mathrm{Pd}(\mathrm{II})$-catalyzed, directing-group-aided arylation/alkylation of $\mathrm{C}(2)-\mathrm{H}$ bond of pyrene-1-carboxamide motif 2a linked with 8 -aminoquinoline DG , and $\mathrm{C}(10)-\mathrm{H}$ bond of 1 -aminopyrene motif $\mathbf{2 b}$ 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 $\operatorname{Pd}(\mathrm{II})$-catalyzed, directing-group-aided C-H arylation/alkylation reaction, initially we prepared the pyrene-1-carboxamide $\mathbf{2 a}$ possessing 8 -aminoquinoline directing group, which enabled the selective $\beta$ -$\mathrm{C}\left(\mathrm{sp}^{2}\right)-\mathrm{H}$ functionalization of $\mathbf{2 a}$ (C2-position, Table 1). We performed optimization reactions by employing the standard $\mathrm{Pd}(\mathrm{II})$-catalyzed $\mathrm{sp}^{2} \beta-\mathrm{C}-\mathrm{H}$ arylation conditions. ${ }^{11-13}$ Typically, the directing group 8-aminoquinoline-aided $\mathrm{C}-\mathrm{H}$ functionalization of carboxamides have been carried out by using a $\mathrm{Pd}(\mathrm{II})$ catalyst and an additive such as AgOAc or $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ or $\mathrm{K}_{2} \mathrm{CO}_{3}$, which function as a halide ion scavenger. ${ }^{11-13}$

First, a mixture of pyrene-1-carboxamide 2a, $\operatorname{ArI}$ ( $\mathbf{3 a}$ ) and $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst ( $10 \mathrm{~mol} \%$ ) in the presence of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ as an additive in 0 -xylene was heated at $135{ }^{\circ} \mathrm{C}$ for 24 h , which yielded the $\mathrm{C}(2)-\mathrm{H}$ arylated pyrene-1-carboxamide 4a in satisfactory yield ( $38 \%$, Table 1 , entry 1 ). Next, the same reaction was carried out in the presence of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ as an additive instead of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ and this reaction also yielded the $\mathrm{C}(2)$ - H arylated pyrene-1-carboxamide $\mathbf{4 a}$ in satisfactory yield ( $40 \%$, entry 2 ).

The $\mathrm{Pd}(\mathrm{II})$-catalyzed arylation of pyrene-1-carboxamide 2a by using $\mathrm{K}_{2} \mathrm{CO}_{3}$ as an additive yielded the $\mathrm{C}(2)$ - H arylated pyrene-1-carboxamide 4 a in an improved yield ( $51 \%$, Table 1, entry 3). The $\operatorname{Pd}(I I)$-catalyzed arylation of $\mathbf{2 a}$ in the presence of AgOAc as an additive in 0 -xylene or $1,2-\mathrm{DCE}$ at $130-135{ }^{\circ} \mathrm{C}$ yielded $4 \mathbf{a}$ in $65-70 \%$ yields (entries 4 and 5 ). The $\mathrm{Pd}(\mathrm{II})$-catalyzed arylation of $\mathbf{2 a}$ by using different amounts of $\mathbf{3 a}$ (1-3 equiv) yielded the product $\mathbf{4 a}$ in $22-$ $47 \%$ yields (entries 6-8). The arylation of 2a by using differ-


2a
( 0.2 mmol )


3
$\mathrm{Pd}(\mathrm{OAc})_{2}(10 \mathrm{~mol} \%)$ AgOAc ( 0.44 mmol )
$o$-xylene ( 2 mL )
$130^{\circ} \mathrm{C}, 24 \mathrm{~h}$


4a: $70 \%$

4b: $86 \%$

4g: 71\%


4c: $58 \%$


4i: $58 \%$


4d: 53\%


4j: 67\%


4e: $45 \%$


4k: 77\%


4f: 55\%


4I: $84 \%$


4m: 74\%


4n: 66\%


4o: 58\%


4p: 48\%


4q: $54 \%$

Scheme 2 Assembly of C1,C2-disubstituted pyrene carboxamide motifs 4a-q via the $\operatorname{Pd}$ (II)-catalyzed, 8-aminoquinoline-directed C-H arylation of $\mathbf{2 a}$
ent palladium catalysts such as $\mathrm{Pd}(\mathrm{TFA})_{2}$ and $\mathrm{Pd}(\mathrm{MeCN})_{2} \mathrm{Cl}_{2}$ yielded the product 4a in 53-60\% yields (entries 9 and 10). The $\mathrm{C}-\mathrm{H}$ arylation of $\mathbf{2 a}$ under the $\mathrm{Ni}(\mathrm{OTf})_{2}$-catalyzed reaction conditions yielded 4a in only $15 \%$ yield (entry 11 ).

Having the optimized reaction conditions in hand for the $\operatorname{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(2)-\mathrm{H}$ arylation of $\mathbf{2 a}$, we wanted to enrich the library of pyrene-1-carboxamide via the $\mathrm{Pd}(\mathrm{II})-$ catalyzed $\mathrm{C}(2)-\mathrm{H}$ arylation reaction. Towards this, we carried out the $\mathrm{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(2)-\mathrm{H}$ arylation of $\mathbf{2 a}$ using a variety of aryl iodides (Scheme 2). Arylation of 2a with aryl iodides containing different electron-withdrawing substituents (e.g., Ac, $\mathrm{NO}_{2}$, COOMe and Cl ) at the para-position yielded the corresponding $\mathrm{C}(2)-\mathrm{H}$ arylated pyrene-1-carboxamides 4a-d in moderate to good yields (53-86\%, Scheme 2). Next, the $\operatorname{Pd}(\mathrm{II})$-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, $i-\mathrm{Pr}, \mathrm{Me}$ and OMe ) at the para-position yielded the corresponding $\mathrm{C}(2)$-H arylated pyrene-1-carboxamides $\mathbf{4 e} \mathbf{e} \mathbf{j}$ in moderate to good yields ( $45-71 \%$, Scheme 2 ).

We then performed the $\mathrm{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(2)-\mathrm{H}$ arylation of pyrene-1-carboxamide 2a with aryl iodides containing different electron-donating or electron-withdrawing substituents (e.g., $\mathrm{OMe}, \mathrm{Me}, \mathrm{Cl}$ and F ) at the meta-position, which yielded the corresponding $\mathrm{C}(2)$-H arylated pyrene-1carboxamides $\mathbf{4 k} \mathbf{k} \mathbf{n}$ in 66-84\% yields (Scheme 2). Furthermore, the $\mathrm{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(2)-\mathrm{H}$ arylation of pyrene-1carboxamide 2a with different heteroaryl iodides also yielded the corresponding $\mathrm{C}(2)-\mathrm{H}$ arylated pyrene-1-carboxamides $\mathbf{4 0 - q}$ in satisfactory to moderate yields (48-58\%, Scheme 2). The structures of representative pyrene derivatives $\mathbf{4 a}$ and $\mathbf{4 e}$ were confirmed by the X-ray structure analysis (Figure 2).





MeOOC


5k: 64\%


5p: 65\%


5b: 57\%


5g: 62\%


5I: 56\%


5q: 62\%


5c: 57\%


5h: 61\%


5m: 58\%


5r: 42\%


5d: 63\%


5i: 60\%


5n: 53\%


5s: $51 \%$


5e: 59\%


5j: 61\%


50: $45 \%$


5t: 71\%

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


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

After assembling various $\mathrm{C}(2)-\mathrm{H}$ arylated pyrene-1-carboxamides $4 \mathbf{a}-\mathbf{q}$, we then planned to expand the scope of this work and enrich the library of 1-aminopyrene core by assembling various $\mathrm{C}(10)-\mathrm{H}$ 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 $\gamma-\mathrm{C}\left(\mathrm{sp}^{2}\right)-\mathrm{H}$ functionalization of $\mathbf{2 b}$ at the $\mathbf{C 1 0}$-position. We then performed the


2d
( 0.2 mmol )

$2 d$
( 0.2 mmol )


2c
2c
( 0.2 mmol )



$\mathrm{Pd}(\mathrm{OAc})_{2}(10 \mathrm{~mol} \%)$ $\mathrm{AgOAc}(0.44 \mathrm{mmol})$
o-xylene ( 2 mL )
$130^{\circ} \mathrm{C}, 24 \mathrm{~h}$


8b: $\mathrm{Ar}=\mathrm{Ph}, 55 \%$

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

The $\operatorname{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(10)-\mathrm{H}$ arylation of $\mathbf{2 b}$ with PhI and various aryl iodides containing different electron-donating and electron withdrawing substituents (e.g., OMe, $\mathrm{Me}, \mathrm{OEt}, \mathrm{Ac}, \mathrm{COOMe}, \mathrm{CN}, \mathrm{Cl}$ and Br ) at the para-position yielded the corresponding $\mathrm{C}(10)-\mathrm{H}$ arylated N -(pyren-1yl)picolinamides $\mathbf{5 f}-\mathbf{n}$ in moderate to good yields (50-64\%, Scheme 3). The $\operatorname{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(10)-\mathrm{H}$ arylation of $\mathbf{2 b}$ with disubstituted aryl iodides and 6-iodo-2,3-dihydrobenzo[b][1,4]dioxine yielded the corresponding $C(10)-\mathrm{H}$ arylated N -(pyren-1-yl)picolinamides $\mathbf{5 0}-\mathbf{q}$ in satisfactory to good yields (45-65\%, Scheme 3). Furthermore, the C(10)-H arylation of $\mathbf{2 b}$ with different heteroaryl iodides also yielded the corresponding $\mathrm{C}(10)-\mathrm{H}$ arylated N -(pyren-1-yl) picolinamides $5 \mathbf{r}-\mathbf{t}$ in satisfactory to good yields (42-71\%, Scheme 3). The structure of representative pyrene carboxamide $\mathbf{5 n}$ 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 $\mathrm{Pd}(\mathrm{II})$-catalyzed $\mathrm{C}(10)-\mathrm{H}$ arylation of $\mathbf{2 d}$ 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. ${ }^{101}$ In this regard, we treated pyrene-1-carboxamide 2c with $p$-tolylboronic acid in the presence of the $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst and NFSI as an additive in 1,2-DCE at $90^{\circ} \mathrm{C}$ for 24 h , which afforded the corresponding $\mathrm{C}(9)-\mathrm{H}$ 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 $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst and NFSI as an additive in 1,2 -DCE at $90{ }^{\circ} \mathrm{C}$ for 24 h afforded the $\mathrm{C}(9)-\mathrm{H}$ arylated pyrene-1-carboxamides $\mathbf{8 b}$ 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 $\mathrm{Pd}(\mathrm{II})$-catalyzed alkylation of $\mathrm{C}(2)-\mathrm{H}$ and $\mathrm{C}(10)-\mathrm{H}$ bonds of pyrene amides $\mathbf{2 a}$ and $\mathbf{2 b}$, 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 $\mathrm{C}(10)-\mathrm{H}$ 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 $\mathrm{C}-\mathrm{H}$ arylation of the pyrene amides. In this regard, the $\mathrm{C}(10)-\mathrm{H}$ arylated N -(pyren-1-yl)picolinamide $\mathbf{5 f}$ 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 $\mathbf{5 f}$ and NaOH in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ at $90^{\circ} \mathrm{C}$ for 24 h yielded the $\mathrm{C}(10)-$ 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 $\mathbf{5 g}$,t yielded the corresponding $\mathrm{C}(10)-\mathrm{H}$ 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 $\mathbf{2 b}$ 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). ${ }^{20}$



[^2]In summary, we have shown the application of the $\mathrm{Pd}(\mathrm{II})$-catalyzed, directing-group-aided $\mathrm{C}-\mathrm{H}$ arylation/alkylation tactics to functionalize the relatively inaccessible C2 and K-region C10 positions of the pyrene core. The $\mathrm{Pd}(\mathrm{II})$-catalyzed $\beta-\mathrm{C}-\mathrm{H}$ 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 $\gamma-\mathrm{C}-$ H arylation/alkylation of the C10-position of N -(pyren-1yl)picolinamide possessing a picolinamide directing group afforded various C1,C10-disubstituted pyrene motifs. Examples of $\mathrm{C}(9)-\mathrm{H}$ 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-

$5 f(0.15 \mathrm{mmol})$



$5 \mathrm{~g}(0.5 \mathrm{mmol})$

12b: $70 \%$

12c: $73 \%$


ONE-POT reaction
( 0.2 mmol )
NEAT condition
NEAT conditions

12d: 46\%

Scheme 6 Trials on the removal of the directing group and one-pot sequential C-H arylation of pyrene carboxamide $\mathbf{2 b}$ followed by directing group removal
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.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ 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 $\mathrm{Na}_{2} \mathrm{SO}_{4}$. Thin-layer chromatography (TLC) analyses were performed on silica gel (silica gel 60 $\mathrm{F}_{254}$ 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 $\operatorname{Pd}(\mathrm{II})$-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 ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ 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 ( $9 \mathrm{mmol}, 0.9$ equiv) and $\mathrm{Et}_{3} \mathrm{~N}$ ( $11 \mathrm{mmol}, 1.1$ 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 $\mathrm{SOCl}_{2}$ ( 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 $(10-15 \mathrm{~mL})$ and washed with water $(10-15 \mathrm{~mL})$ and twice with saturated aqueous $\mathrm{NaHCO}_{3}$ solution ( $10-$ $15 \mathrm{~mL})$. The combined organic layers were washed with $1 \mathrm{~N} \mathrm{HCl}(2 \times$ 20 mL ) to remove excess amine, then dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concentrated under vacuum to afford the corresponding carboxamides.

## Synthesis of Carboxamide 2b

An appropriate amount of picolinic acid ( 10 mmol ), N -(3-dimethyl-aminopropyl)- $N^{\prime}$-ethylcarbodiimide hydrochloride (1.1 equiv), 1-hydroxybenzotriazole hydrate ( 1.1 equiv) in DCM ( 20 mL ) was stirred for 1 h at $0{ }^{\circ} \mathrm{C}$ under a nitrogen atmosphere. Then, an appropriate amount of 1 -aminopyrene ( 1 equiv) was added to the above mixture and stirred for $16-24 \mathrm{~h}$ at room temperature. The resulting solution
was then subjected to aqueous workup and washed with aqueous $\mathrm{NaHCO}_{3}$ 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 ( $0.2 \mathrm{mmol}, 1$ equiv), an appropriate aryl iodide ( $0.8 \mathrm{mmol}, 4$ equiv), $\mathrm{Pd}(\mathrm{OAc})_{2}(4.5 \mathrm{mg}, 10 \mathrm{~mol} \%$ ) and $\operatorname{AgOAc}(0.44 \mathrm{mmol}, 2.0-2.2$ equiv) in $o$-xylene ( 2 mL ) was heated at $130^{\circ} \mathrm{C}$ 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 $\mathbf{2 b}$ ( $0.2 \mathrm{mmol}, 1$ equiv), an appropriate aryl iodide ( $0.8-1.0 \mathrm{mmol}, 4-5$ equiv), $\mathrm{Pd}(\mathrm{OAc})_{2}(4.5 \mathrm{mg}, 10 \mathrm{~mol} \%$ ) and $\mathrm{AgOAc}\left(0.44 \mathrm{mmol}, 2.2\right.$ equiv) in 0 -xylene ( 2 mL ) was heated at $150^{\circ} \mathrm{C}$ for $36-48 \mathrm{~h}$ 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 $\mathbf{2 a}$ ( $0.14 \mathrm{mmol}, 1$ equiv), an appropriate alkyl iodide ( $0.56 \mathrm{mmol}, 4$ equiv), anhydrous $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( $0.28 \mathrm{mmol}, 2$ equiv), $\mathrm{NaOTf}\left(0.42 \mathrm{mmol}, 3\right.$ equiv), $\operatorname{Pd}(\mathrm{OAc})_{2}(10 \mathrm{~mol} \%, 3.4 \mathrm{mg})$, 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 $125^{\circ} \mathrm{C}$ 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 $\mathbf{1 0}$ (see the corresponding Tables/Schemes for specific examples).

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

A mixture of $\mathbf{2 b}$ carboxamide ( $0.2 \mathrm{mmol}, 1$ equiv), an appropriate alkyl iodide ( $0.8 \mathrm{mmol}, 4.0$ equiv), anhydrous KOAc ( $0.4 \mathrm{mmol}, 2$ equiv), $\mathrm{Pd}(\mathrm{OAc})_{2}(10 \mathrm{~mol} \%, 4.5 \mathrm{mg})$, 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 $130^{\circ} \mathrm{C}$ 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 $\mathbf{1 1}$ (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 $\mathbf{2 c}$ ( $0.2 \mathrm{mmol}, 1$ equiv), an appropriate boronic acid ( $0.25 \mathrm{mmol}, 1.25$ equiv), NFSI ( $0.25 \mathrm{mmol}, 1.25$ equiv), and $\mathrm{Pd}(\mathrm{OAc})_{2}(10 \mathrm{~mol} \%, 4.5 \mathrm{mg})$ was suspended in 1,2-DCE ( 2.0 mL ) in a 10 mL capacity sealed (pressure) tube. The pressure tube was flushed with $\mathrm{N}_{2}$ for 2 min and sealed with a PTFE-lined cap, and then the tube was heated at $90{ }^{\circ} \mathrm{C}$ for 24 h . After the reaction period, the mixture was filtered through a Celite® pad and washed with DCM ( $10-15 \mathrm{~mL}$ ). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to afford the corresponding arylated carboxamide $\mathbf{8}$ (see the corresponding Tables/Schemes for specific examples). The structures of compounds $\mathbf{8 a}, \mathbf{b}$ were assigned based on reports of a similar compound prepared under Cu-catalyzed reaction involving aryliodonium salts as arylating reagent. ${ }^{15 k}$

## Directing Group Removal/Amide Hydrolysis and Preparation of Compound 13

A solution of $\mathrm{NaOH}(60 \mathrm{mg}$ of NaOH$)$ in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}(10: 1 \mathrm{v} / \mathrm{v}, 3.3 \mathrm{~mL})$ containing an appropriate arylated carboxamide $\mathbf{5}(0.15 \mathrm{mmol})$ 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 ( $3 \times 5 \mathrm{~mL}$ ). The organic layers were combined, dried with anhydrous $\mathrm{MgSO}_{4}$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane) to afford the corresponding C-H arylated 1 -aminopyrene derivative $\mathbf{1 3}$ (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 ( $521 \mathrm{mg}, 71 \%, 2 \mathrm{mmol}$ scale).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 149- $151^{\circ} \mathrm{C}$.
IR (DCM): 3275, 2925, 1682, 1513, $1436 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.08(\mathrm{~s}, 1 \mathrm{H}), 8.79-8.72(\mathrm{~m}, 2 \mathrm{H}), 8.31$ (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.26-8.19(\mathrm{~m}, 4 \mathrm{H}), 8.15(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.09-$ 8.05 (m, 2 H ), 7.58 (d, $J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.47(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.22-$ 7.18 (m, 1 H), 2.40 (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.0,138.7,133.0,133.0,131.2$, 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): $m / z[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{17} \mathrm{NNaOS}$ : 390.0929; found: 390.0922.

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

By following the general procedure, compound $\mathbf{4 a}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ 20:80) as a pale-yellow solid ( $68 \mathrm{mg}, 70 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 249- $251^{\circ} \mathrm{C}$.
IR (DCM): 3338, 1679, 1519, 1483, $1264 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=10.04(\mathrm{~s}, 1 \mathrm{H}), 8.99(\mathrm{~d}, \mathrm{~J}=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, $8.55-8.54(\mathrm{~m}, 1 \mathrm{H}), 8.49(\mathrm{~d}, \mathrm{~J}=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.27-8.25(\mathrm{~m}, 3 \mathrm{H}), 8.19$ $(\mathrm{d}, J=9.0 \mathrm{~Hz}, 2 \mathrm{H}), 8.14-8.06(\mathrm{~m}, 3 \mathrm{H}), 7.95(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.90(\mathrm{~d}$, $J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.62(\mathrm{t}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.55(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.36$ (dd, ${ }^{1}=8.2 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.52 (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=196.8,166.8,147.1,144.7,137.4$, 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 $\mathrm{C}_{34} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 491.1760; found: 491.1779.

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

By following the general procedure, compound $\mathbf{4 b}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $25: 75$ ) as a pale-yellow solid ( $84 \mathrm{mg}, 86 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); mp 237-239 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 2924, 1670, 1595, 1519, $1341 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz , DMSO- $d_{6}$ ): $\delta=10.61$ ( $\mathrm{s}, 1 \mathrm{H}$ ), 8.73 ( $\mathrm{d}, \mathrm{J}=4.0 \mathrm{~Hz}, 1$ H), 8.61 ( $\mathrm{d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.47 ( $\mathrm{s}, 1 \mathrm{H}$ ), $8.43-8.32(\mathrm{~m}, 7 \mathrm{H}), 8.27(\mathrm{~d}, J=$ $8.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.17(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.76(\mathrm{~d}, J=$ $8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.66(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.56\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}=4.2 \mathrm{~Hz}, 1\right.$ H).
${ }^{13} \mathrm{C}$ NMR ( $\left.\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=167.5,148.2,147.6,147.2,138.3$, 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 $\mathrm{C}_{32} \mathrm{H}_{20} \mathrm{~N}_{3} \mathrm{O}_{3}$ : 494.1505; found: 494.1520.

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

By following the general procedure, compound $\mathbf{4 c}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $58 \mathrm{mg}, 58 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 160-162 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3348, 2940, 1725, 1675, $1528 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.03(\mathrm{~s}, 1 \mathrm{H}), 8.99(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, $8.54(\mathrm{~d}, J=3.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.48(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.26-8.23(\mathrm{~m}, 3 \mathrm{H})$, 8.17 (d, $J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.12-8.03(\mathrm{~m}, 5 \mathrm{H}), 7.89(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H})$, $7.63-7.59(\mathrm{~m}, 1 \mathrm{H}), 7.53(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.34\left(\mathrm{dd},{ }^{1} J=8.1 \mathrm{~Hz},{ }^{2} \mathrm{~J}=\right.$ $4.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.9,166.9,148.1,145.6,138.4$, 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 $\mathrm{C}_{34} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 507.1709; found: 507.1695.

2-(4-Chlorophenyl)-N-(quinolin-8-yl)pyrene-1-carboxamide (4d) By following the general procedure, compound $\mathbf{4 d}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ 20:80) as a pale-yellow solid ( $51 \mathrm{mg}, 53 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 237-239 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3348, 2936, 1663, 1528, $1490 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=10.02$ (s, 1 H ), $9.01-9.00$ ( $\mathrm{m}, 1 \mathrm{H}$ ), 8.56 (dd, ${ }^{1} J=4.1 \mathrm{~Hz},{ }^{2} J=1.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.47 (d, $J=9.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $8.27-8.24$ (m, $3 \mathrm{H}), 8.19-8.05(\mathrm{~m}, 5 \mathrm{H}), 7.74(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.64(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1$ H), $7.58-7.56(\mathrm{~m}, 1 \mathrm{H}), 7.38\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.34(\mathrm{~d}$, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.0,148.1,139.3,138.4,136.2$, 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 $\mathrm{C}_{32} \mathrm{H}_{20} \mathrm{ClN}_{2} \mathrm{O}$ : 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 $\mathbf{4 e}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $45 \mathrm{mg}, 45 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 248-250^{\circ} \mathrm{C}$.
IR (DCM): 3338, 2924, 1667, 1516, $1323 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.02(\mathrm{~s}, 1 \mathrm{H}), 9.04(\mathrm{~d}, \mathrm{~J}=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, $8.59(\mathrm{~d}, J=4.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.48(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.26-8.23(\mathrm{~m}, 3 \mathrm{H})$, 8.19-8.11 (m, 4 H$), 8.05(\mathrm{t}, \mathrm{J}=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{t}, \mathrm{J}=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.55$ (d, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.39-7.34(\mathrm{~m}, 2 \mathrm{H}), 7.29-7.26(\mathrm{~m}, 1 \mathrm{H}), 6.81(\mathrm{~d}, J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.17-4.16(\mathrm{~m}, 4 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.3,148.0,143.4,143.2,138.5$, 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 $\mathrm{C}_{34} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 507.1709; found: 507.1724.

## 2-Phenyl- $\boldsymbol{N}$-(quinolin-8-yl)pyrene-1-carboxamide (4f)

By following the general procedure, compound $\mathbf{4 f}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $49 \mathrm{mg}, 55 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 218-220 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3342, 1667, 1519, 1483, $1325 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.96(\mathrm{~s}, 1 \mathrm{H}), 8.97\left(\mathrm{dd},{ }^{1} \mathrm{~J}=7.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}=\right.$ $1.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.52\left(\mathrm{dd},{ }^{1} J=4.1 \mathrm{~Hz},{ }^{2} J=1.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.47(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1$ H), $8.27(\mathrm{~s}, 1 \mathrm{H}), 8.23(\mathrm{t}, \mathrm{J}=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 8.17-8.03(\mathrm{~m}, 5 \mathrm{H}), 7.83-7.77$ (m, 2 H$), 7.60-7.56(\mathrm{~m}, 1 \mathrm{H}), 7.50(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.34-7.31(\mathrm{~m}, 3$ $\mathrm{H}), 7.18(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.2,148.0,140.8,138.4,137.3$, 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 $\mathrm{C}_{32} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}: 449.1654$; found: 449. 1649.

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

By following the general procedure, compound $\mathbf{4 g}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $67 \mathrm{mg}, 71 \%$ ).
$R_{f}=0.6$ (EtOAc/hexane $=20: 80$ ); mp 205-207 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3338, 1665, 1515, 1482, $1324 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.99(\mathrm{~s}, 1 \mathrm{H}), 9.02(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, 8.55-8.49 (m, 2 H ), $8.30(\mathrm{~s}, 1 \mathrm{H}), 8.26-8.23(\mathrm{~m}, 2 \mathrm{H}), 8.19-8.05(\mathrm{~m}, 5$ H), 7.71 ( $\mathrm{d}, \mathrm{J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.62(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1$ H), 7.33 (dd, $\left.{ }^{1} J=8.4 \mathrm{~Hz},{ }^{2} J=4.0 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.17(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 2.53$ $(\mathrm{q}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.05(\mathrm{t}, J=7.6 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.4,147.9,143.5,138.4,138.1$, 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 $\mathrm{C}_{34} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{O}$ : 477.1967; found: 477.1982.

## 2-(4-Isopropylphenyl)- $N$-(quinolin-8-yl)pyrene-1-carboxamide

 (4h)By following the general procedure, compound $\mathbf{4 h}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $65 \mathrm{mg}, 66 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 160-162 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3337, 2959, 1662, 1519, $1481 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.99(\mathrm{~s}, 1 \mathrm{H}), 9.03\left(\mathrm{dd},{ }^{1} J=7.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}=\right.$ $0.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.55-8.51(\mathrm{~m}, 2 \mathrm{H}), 8.28(\mathrm{~s}, 1 \mathrm{H}), 8.24-8.22(\mathrm{~m}, 2 \mathrm{H})$, $8.18-8.03(\mathrm{~m}, 5 \mathrm{H}), 7.74(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.49\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=0.9 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.32-7.28(\mathrm{~m}, 1 \mathrm{H}), 7.19(\mathrm{~d}, J=$ $8.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.80-2.72(\mathrm{~m}, 1 \mathrm{H}), 1.05(\mathrm{~d}, \mathrm{~J}=6.9 \mathrm{~Hz}, 6 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.3,148.0,147.8,138.3,138.2$, 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 $\mathrm{C}_{35} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}$ : 491.2123; found: 491.2142.

## $\mathbf{N}$-(Quinolin-8-yl)-2-(p-tolyl)pyrene-1-carboxamide (4i)

By following the general procedure, compound $\mathbf{4 i}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $54 \mathrm{mg}, 58 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $\left.=20: 80\right) ; \mathrm{mp} 195-197^{\circ} \mathrm{C}$.
IR (DCM): 3355, 3052, 1690, 1536, $1321 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.04(\mathrm{~s}, 1 \mathrm{H}), 9.04(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, $8.54\left(\mathrm{dd},{ }^{1} J=4.0 \mathrm{~Hz},{ }^{2} J=1.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.48(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.27-8.21$ (m, 3 H ), 8.16-8.03 (m, 5 H ), 7.72 (d, $J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.62(\mathrm{t}, J=8.1 \mathrm{~Hz}$, $1 \mathrm{H}), 7.51(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.32\left(\mathrm{dd},{ }^{1} \mathrm{~J}=8.2 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.18$ (d, J = 7.8 Hz, 2 H ), 2.26 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.4,148.0,138.4,137.9,137.2$, 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 $\mathrm{C}_{33} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}$ : 463.1810; found: 463.1791.

2-(4-Methoxyphenyl)- $N$-(quinolin-8-yl)pyrene-1-carboxamide (4j) By following the general procedure, compound $\mathbf{4} \mathbf{j}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = $25: 75$ ) as a pale-yellow solid ( $64 \mathrm{mg}, 67 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp $178-180^{\circ} \mathrm{C}$.
IR (DCM): 3336, 2932, 1682, 1521, $1321 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.02(\mathrm{~s}, 1 \mathrm{H}), 9.05(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, 8.55-8.54 (m, 1 H ), $8.48(\mathrm{~d}, \mathrm{~J}=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.26-8.22(\mathrm{~m}, 3 \mathrm{H}), 8.16$ (d, $J=9.1 \mathrm{~Hz}, 2 \mathrm{H}), 8.12-8.03(\mathrm{~m}, 3 \mathrm{H}), 7.75(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.62(\mathrm{t}$, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.33\left(\mathrm{dd},{ }^{1} J=7.8 \mathrm{~Hz},{ }^{2} J=4.0 \mathrm{~Hz}\right.$, $1 \mathrm{H}), 6.91(\mathrm{~d}, \mathrm{~J}=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.71(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.5,159.1,148.0,138.4,136.9$, 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 $\mathrm{C}_{33} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 479.1760; found: 479.1775.

## 2-(3-Methoxyphenyl)-N-(quinolin-8-yl)pyrene-1-carboxamide

 (4k)By following the general procedure, compound $\mathbf{4 k}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $73 \mathrm{mg}, 77 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 201-203 ${ }^{\circ} \mathrm{C}$.
IR $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 3337,1665,1516,1482,1324 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.04(\mathrm{~s}, 1 \mathrm{H}), 9.03(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, 8.55 (d, $J=3.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.50(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.29(\mathrm{~s}, 1 \mathrm{H}), 8.23$ (d, $J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.18-8.14(\mathrm{~m}, 2 \mathrm{H}), 8.11-8.03(\mathrm{~m}, 3 \mathrm{H}), 7.61(\mathrm{t}, J=7.9$ $\mathrm{Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.41-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.33\left(\mathrm{dd},{ }^{1} \mathrm{~J}=8.0\right.$ $\left.\mathrm{Hz},{ }^{2} J=4.0 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.26-7.24(\mathrm{~m}, 1 \mathrm{H}), 6.77(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.75$ (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.3,159.5,148.0,142.2,138.4$, 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 $\mathrm{C}_{33} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 479.1760; found: 479.1780.

## $\boldsymbol{N}$-(Quinolin-8-yl)-2-(m-tolyl)pyrene-1-carboxamide (41)

By following the general procedure, compound 41 was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $57 \mathrm{mg}, 84 \%, 0.15 \mathrm{mmol}$ scale).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp $186-188^{\circ} \mathrm{C}$.
IR (DCM): 3333, 1667, 1519, 1483, $1325 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.01(\mathrm{~s}, 1 \mathrm{H}), 9.01(\mathrm{~d}, \mathrm{~J}=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, 8.56 (d, $J=4.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.51 (d, $J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.28$ ( $\mathrm{s}, 1 \mathrm{H}$ ), $8.26-8.23$ (m, 2 H ), $8.17(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 2 \mathrm{H}), 8.13-8.04(\mathrm{~m}, 3 \mathrm{H}), 7.63-7.59(\mathrm{~m}, 3$ H), 7.52 (d, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.34\left(\mathrm{dd},{ }^{1} J=8.2 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.22$ ( $\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.01(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=168.3,148.0,140.7,138.4,137.9$, $137.5,136.1,134.7,131.9,131.6,131.1,130.7,130.2,129.0,128.8$, 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 $\mathrm{C}_{33} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}: 463.1810$; found: 463.1827.

## 2-(3-Chlorophenyl)- $\boldsymbol{N}$-(quinolin-8-yl)pyrene-1-carboxamide (4m)

By following the general procedure, compound $\mathbf{4 m}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = $20: 80$ ) as a pale-yellow solid ( $71 \mathrm{mg}, 74 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 218-220 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3334, 2923, 1668, 1519, $1483 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.96(\mathrm{~s}, 1 \mathrm{H}), 8.95\left(\mathrm{dd},{ }^{1} \mathrm{~J}=7.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}=\right.$ $1.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.57\left(\mathrm{dd},{ }^{1} J=4.1 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.48(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1$ H), 8.26-8.23 (m, 3 H$), 8.19-8.16(\mathrm{~m}, 2 \mathrm{H}), 8.12-8.04(\mathrm{~m}, 3 \mathrm{H}), 7.80(\mathrm{t}$, $J=1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.63-7.58(\mathrm{~m}, 2 \mathrm{H}), 7.52\left(\mathrm{dd},{ }^{1} J=8.4 \mathrm{~Hz},{ }^{2} J=1.1 \mathrm{~Hz}, 1\right.$ H), $7.35\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.18(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.14-$ 7.12 ( $\mathrm{m}, 1 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=167.8,148.2,142.6,138.4,136.1$, 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 $\mathrm{C}_{32} \mathrm{H}_{20} \mathrm{ClN}_{2} \mathrm{O}$ : 483.1264; found: 483.1261.

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

By following the general procedure, compound $\mathbf{4 n}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $61 \mathrm{mg}, 66 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 217-219^{\circ} \mathrm{C}$.
IR (DCM): 3342, 1667, 1519, 1483, $1423 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.03(\mathrm{~s}, 1 \mathrm{H}), 9.00(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, $8.54(\mathrm{~d}, J=3.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.47(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.21-8.10(\mathrm{~m}, 5 \mathrm{H})$, 8.06-8.01 (m, 3 H), 7.62-7.54 (m, 3 H$), 7.50(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.33-$ $7.25(\mathrm{~m}, 2 \mathrm{H}), 6.91(\mathrm{t}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.9,162.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=245 \mathrm{~Hz}\right), 148.1$, $143.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=5.3 \mathrm{~Hz}\right), 138.3,136.1,135.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.5 \mathrm{~Hz}\right), 134.5$, $131.9,131.3,131.1,130.7,129.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.4 \mathrm{~Hz}\right), 129.2,129.0,128.8$, $127.8,127.3,127.0,126.5,126.0,125.8,125.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.5 \mathrm{~Hz}\right), 124.6$, $124.1,123.9,122.1,121.6,116.7,116.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22.0 \mathrm{~Hz}\right), 114.4(\mathrm{~d}$, $\left.J_{\mathrm{C}-\mathrm{F}}=21.0 \mathrm{~Hz}\right)$.
HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{32} \mathrm{H}_{20} \mathrm{FN}_{2} \mathrm{O}: 467.1560$; found: 467.1574.

## 2-(5-Bromopyridin-2-yl)-N-(quinolin-8-yl)pyrene-1-carboxamide

 (40)By following the general procedure, compound $\mathbf{4 0}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = $20: 80$ ) as a pale-yellow solid ( $61 \mathrm{mg}, 58 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 115-117^{\circ} \mathrm{C}$.
IR (DCM): 3338, 2924, 1667, 1519, $1483 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=10.13(\mathrm{~s}, 1 \mathrm{H}), 9.05(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H})$, 8.70 (d, J = $1.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.57-8.51(\mathrm{~m}, 3 \mathrm{H}), 8.27-8.06(\mathrm{~m}, 7 \mathrm{H}), 7.84$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.77\left(\mathrm{dd},{ }^{1} J=8.4 \mathrm{~Hz},{ }^{2} J=2.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.67(\mathrm{t}, J=8.0$ $\mathrm{Hz}, 1 \mathrm{H}), 7.59(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.38\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right)$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.3,156.6,150.6,148.2,139.0$, 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 $\mathrm{C}_{31} \mathrm{H}_{19} \mathrm{BrN}_{3} \mathrm{O}$ : 528.0711; found: 528.0685.

## 2-(6-Chloropyridin-3-yl)- N -(quinolin-8-yl)pyrene-1-carboxamide

 (4p)By following the general procedure, compound $\mathbf{4 p}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = 20:80) as a pale-yellow solid ( $23 \mathrm{mg}, 48 \%, 0.1 \mathrm{mmol}$ scale).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp $135-137^{\circ} \mathrm{C}$.
IR (DCM): 3344, 2917, 1682, 1536, $1332 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=10.64(\mathrm{~s}, 1 \mathrm{H}), 8.78(\mathrm{~d}, \mathrm{~J}=2.3 \mathrm{~Hz}, 1$ H), $8.74\left(\mathrm{dd},{ }^{1} J=4.2 \mathrm{~Hz},{ }^{2} J=1.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.62-8.60(\mathrm{~m}, 1 \mathrm{H}), 8.47(\mathrm{~s}, 1$ H), $8.43-8.30(\mathrm{~m}, 7 \mathrm{H}), 8.23\left(\mathrm{dd},{ }^{1} J=8.2 \mathrm{~Hz},^{2} J=2.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.16(\mathrm{t}, J=$ $7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.79-7.77(\mathrm{~m}, 1 \mathrm{H}), 7.69-7.65(\mathrm{~m}, 1 \mathrm{H}), 7.60-7.57(\mathrm{~m}, 2$ H).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=167.4,150.7,149.7,148.3,139.5$, 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 $\mathrm{C}_{31} \mathrm{H}_{19} \mathrm{ClN}_{3} \mathrm{O}$ : 484.1217; found: 484.1205.

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

By following the general procedure, compound $\mathbf{4 q}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $48 \mathrm{mg}, 54 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 221-223 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3332, 2921, 1667, 1525, $1467 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=10.54$ ( $\mathrm{s}, 1 \mathrm{H}$ ), 8.83 (d, $J=7.4 \mathrm{~Hz}, 1$ H), 8.72 ( $\mathrm{d}, \mathrm{J}=4.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), $8.56(\mathrm{~s}, 1 \mathrm{H}), 8.43-8.25(\mathrm{~m}, 7 \mathrm{H}), 8.16-8.15$ (m, 1 H ), $7.79(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.74-7.72(\mathrm{~m}, 1 \mathrm{H}), 7.63-7.56(\mathrm{~m}, 3$ H), 7.12-7.10 (m, 1 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}$, DMSO- $d_{6}$ ): $\delta=167.8,149.6,141.8,138.8,137.1$, 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 $\mathrm{C}_{30} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{OS}$ : 455.1218; found: 455.1199.

## $\mathbf{N}$-(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 ( $61 \mathrm{mg}, 71 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); mp 167-169 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3475, 3352, 1667, 1602, $1517 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.86(\mathrm{~s}, 1 \mathrm{H}), 8.69(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, $8.32-8.28(\mathrm{~m}, 2 \mathrm{H}), 8.18$ (d, $J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.12-8.06(\mathrm{~m}, 3 \mathrm{H}), 8.04-$ $7.98(\mathrm{~m}, 1 \mathrm{H}), 7.94(\mathrm{~s}, 1 \mathrm{H}), 7.82(\mathrm{t}, \mathrm{J}=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.40-7.37(\mathrm{~m}, 1 \mathrm{H})$, 7.15-7.11 (m, 3 H ), 6.55-6.54 (m, 1 H ), 3.74 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.2,159.6,149.8,147.4,144.3$, $137.1,136.5,131.3,131.3,130.3,129.4,129.4,127.7,126.6,126.4$, $126.3,126.1,126.0,125.4,124.8,124.3,124.0,122.0,121.8,121.4$, 113.7, 113.2, 55.1.

HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{29} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{2}: 429.1603$; 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 ( $46 \mathrm{mg}, 57 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp $167-169{ }^{\circ} \mathrm{C}$.
IR (DCM): 3325, 3040, 1690, 1517, $1478 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.80(\mathrm{~s}, 1 \mathrm{H}), 8.71(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, 8.31-8.26 (m, 2 H), 8.20-8.18 (m, 2 H$), 8.12-8.05(\mathrm{~m}, 3 \mathrm{H}), 8.01(\mathrm{t}, \mathrm{J}=$ $7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.93(\mathrm{~s}, 1 \mathrm{H}), 7.81\left(\mathrm{td},{ }^{1} \mathrm{~J}=7.7 \mathrm{~Hz},{ }^{2} \mathrm{~J}=1.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.39-$ $7.36(\mathrm{~m}, 3 \mathrm{H}), 7.14(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.81(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.24(\mathrm{~s}, 3$ H).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.1,149.8,147.3,142.9,137.9$, 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 $\mathrm{C}_{29} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}: 413.1654$; found: 413.1639.

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

By following the general procedure, compound $\mathbf{5 b}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $47 \mathrm{mg}, 57 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 195-197^{\circ} \mathrm{C}$.
IR (DCM): 3328, 2921, 1671, 1521, $1486 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.80(\mathrm{~s}, 1 \mathrm{H}), 8.70(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.35-8.34(\mathrm{~m}, 1 \mathrm{H}), 8.30(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.22-8.18(\mathrm{~m}, 2 \mathrm{H}), 8.13-$ $8.00(\mathrm{~m}, 4 \mathrm{H}), 7.92(\mathrm{~s}, 1 \mathrm{H}), 7.84\left(\mathrm{td},{ }^{1} J=7.7 \mathrm{~Hz},{ }^{2} J=1.7 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.43-$ 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).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=162.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=245.2 \mathrm{~Hz}\right), 162.0$, $149.6,147.4,145.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=7.8 \mathrm{~Hz}\right), 137.2,135.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.7 \mathrm{~Hz}\right)$, $131.6,131.3,131.2,130.1,129.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.5 \mathrm{~Hz}\right), 129.4,127.8,126.6$, $126.4,126.3,126.2,125.7,125.1,125.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 124.9,124.4$, $123.9,122.0,121.8,115.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=21.8 \mathrm{~Hz}\right), 113.5\left(J_{\mathrm{C}-\mathrm{F}}=20.8 \mathrm{~Hz}\right)$.
HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{28} \mathrm{H}_{18} \mathrm{FN}_{2} \mathrm{O}: 417.1403$; 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 ( $59 \mathrm{mg}, 63 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp $157-159^{\circ} \mathrm{C}$.
IR (DCM): 3328, 2921, 1671, 1521, $1486 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.72(\mathrm{~s}, 1 \mathrm{H}), 8.68(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.36-8.31(\mathrm{~m}, 2 \mathrm{H}), 8.23(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.18-8.09(\mathrm{~m}, 5 \mathrm{H}), 8.04(\mathrm{t}$, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.96(\mathrm{~s}, 1 \mathrm{H}), 7.81\left(\mathrm{td},{ }^{1} J=7.7 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.71$ $(\mathrm{d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.66-7.64(\mathrm{~m}, 1 \mathrm{H}), 7.39-7.36(\mathrm{~m}, 1 \mathrm{H}), 7.24(\mathrm{t}, J=$ $7.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.45-4.39(\mathrm{~m}, 2 \mathrm{H}), 1.43(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.5,161.8,149.5,147.4,143.2$, $137.1,135.6,133.6,131.9,131.3,131.0,130.7,130.2,129.5,129.5$, 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 $\mathrm{C}_{31} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 471.1709; found: 471.1716.

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

By following the general procedure, compound $\mathbf{5 e}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = $20: 80$ ) as a brown solid ( $52 \mathrm{mg}, 59 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); mp $168-170^{\circ} \mathrm{C}$.
IR (DCM): 3440, 1686, 1602, 1513, $1248 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=10.03(\mathrm{~s}, 1 \mathrm{H}), 8.42(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1$ H), 8.36-8.21 (m, 6 H$), 8.11(\mathrm{t}, \mathrm{J}=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.01(\mathrm{~s}, 1 \mathrm{H}), 7.99(\mathrm{~s}, 1$ H), $7.93-7.86(\mathrm{~m}, 2 \mathrm{H}), 7.67(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.56-7.53(\mathrm{~m}, 1 \mathrm{H})$, $7.41(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.46$ (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=197.9,161.8,149.3,147.4,143.4$, 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 $\mathrm{C}_{30} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 441.1603; found: 441.1589.

## $\mathbf{N}$-(10-(4-Methoxyphenyl)pyren-1-yl)picolinamide (5f)

By following the general procedure, compound $\mathbf{5 f}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $42 \mathrm{mg}, 50 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 171-173 ${ }^{\circ} \mathrm{C}$.
IR ( $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ): 3396, 2951, 1678, 1556, $1514 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.98(\mathrm{~s}, 1 \mathrm{H}), 8.80(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.32-8.29$ (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, $J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.41-7.38(\mathrm{~m}, 1 \mathrm{H})$, 6.81 ( $\mathrm{d}, \mathrm{J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.63 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.0,159.0,150.0,147.5,137.0$, 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 $\mathrm{C}_{29} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 429.1603; found: 429.1588 .

## $\boldsymbol{N}$-(10-(p-Tolyl)pyren-1-yl)picolinamide (5g)

By following the general procedure, compound $\mathbf{5 g}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $51 \mathrm{mg}, 62 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 158- $160^{\circ} \mathrm{C}$.
IR (DCM): 3348, 3048, 1682, 1521, $1325 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.88(\mathrm{~s}, 1 \mathrm{H}), 8.75(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.31-8.26(\mathrm{~m}, 2 \mathrm{H}), 8.19(\mathrm{~d}, \mathrm{~J}=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.13-8.05(\mathrm{~m}, 3 \mathrm{H}), 8.01(\mathrm{t}$, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.93(\mathrm{~s}, 1 \mathrm{H}), 7.8\left(\mathrm{td},{ }^{1} J=7.7 \mathrm{~Hz},{ }^{2} \mathrm{~J}=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.46$ $(\mathrm{d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.38-7.35(\mathrm{~m}, 1 \mathrm{H}), 7.06$ (d, $J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 2.13$ (s, 3 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.0,150.0,147.4,140.0,137.0$, 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 $\mathrm{C}_{29} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}$ : 413.1654; found: 413.1669.

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

By following the general procedure, compound $\mathbf{5 h}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ 20:80) as a brown solid ( $53 \mathrm{mg}, 61 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 148- $150^{\circ} \mathrm{C}$.
IR (DCM): 3296, 2926, 1674, 1511, $1495 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.97$ (s, 1 H ), 8.79 (d, J = $8.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.30-8.29 (m, 2 H), 8.19-8.17 (m, 2 H ), 8.12-7.99 (m, 4 H ), 7.93 ( $\mathrm{s}, 1$ H), $7.84-8.0$ (m, 1 H), 7.47 (d, $J=8.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.38-7.35$ (m, 1 H ), 6.77 ( $\mathrm{d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), $3.78(\mathrm{q}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.35(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.0,158.4,150.0,147.5,137.0$, 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 $\mathrm{C}_{30} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 443.1760; found: 443.1775.

## $\mathbf{N}$-(10-Phenylpyren-1-yl)picolinamide (5i)

By following the general procedure, compound $\mathbf{5 i}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $48 \mathrm{mg}, 60 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 167-169 ${ }^{\circ} \mathrm{C}$.

IR (DCM): 3347, 2923, 1678, 1511, $839 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.85(\mathrm{~s}, 1 \mathrm{H}), 8.75(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.31(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.25(\mathrm{~d}, J=4.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.22-8.00(\mathrm{~m}, 6 \mathrm{H})$, $7.94(\mathrm{~s}, 1 \mathrm{H}), 7.81\left(\mathrm{td},{ }^{1} J=7.6 \mathrm{~Hz},{ }^{2} J=1.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.57(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2$ H), $7.38-7.35$ (m, 1 H ), $7.28-7.24(\mathrm{~m}, 2 \mathrm{H}), 7.04(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\left.\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=162.0,149.8,147.5,142.9,137.0$, 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 $\mathrm{C}_{28} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}$ : 399.1497; found: 399.1511.

## $\mathbf{N}$-(10-(4-Acetylphenyl)pyren-1-yl)picolinamide (5j)

By following the general procedure, $\mathbf{5 j}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=25: 75$ ) as a brown solid ( $54 \mathrm{mg}, 61 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); mp 158- $160^{\circ} \mathrm{C}$.
IR (DCM): 3452, 3344, 1682, 1605, $1517 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.54(\mathrm{~s}, 1 \mathrm{H}), 8.56(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, $8.25(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.18-8.13(\mathrm{~m}, 3 \mathrm{H}), 8.09-8.04(\mathrm{~m}, 3 \mathrm{H}), 8.00-$ 7.98 (m, 1 H$), 7.87$ (s, 1 H$), 7.79-7.76(\mathrm{~m}, 3 \mathrm{H}), 7.57(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H})$, 7.30-7.28 (m, 1 H), 2.36 ( $\mathrm{s}, 1 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=197.3,161.9,149.5,148.0,147.4$, 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 $\mathrm{C}_{30} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{2}$ : 441.1603; found: 441.1624.

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

By following the general procedure, compound $\mathbf{5 k}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ 25: 75) as a brown solid ( $58 \mathrm{mg}, 64 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); mp $125-127^{\circ} \mathrm{C}$.
IR (DCM): 3500, 1716, 1678, 1512, $1434 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.59(\mathrm{~s}, 1 \mathrm{H}), 8.61(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, $8.29(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.22-8.20(\mathrm{~m}, 2 \mathrm{H}), 8.15-8.05(\mathrm{~m}, 4 \mathrm{H}), 8.02(\mathrm{t}$, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.92(\mathrm{~s}, 1 \mathrm{H}), 7.88(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.79\left(\mathrm{td},{ }^{1} J=7.6\right.$ $\left.\mathrm{Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.60(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.32-7.28(\mathrm{~m}, 1 \mathrm{H}), 3.87$ ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=166.6,162.0,149.5,147.8,147.5$, 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 $\mathrm{C}_{30} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 457.1552; found: 457.1535.

## N -(10-(4-Cyanophenyl)pyren-1-yl)picolinamide (51)

By following the general procedure, compound $\mathbf{5 1}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $47 \mathrm{mg}, 56 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); mp 213-215 ${ }^{\circ} \mathrm{C}$.
IR (DCM): 3322, 2924, 2226, 1679, $1513 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.54(\mathrm{~s}, 1 \mathrm{H}), 8.56(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, $8.35-8.32(\mathrm{~m}, 2 \mathrm{H}), 8.26$ (d, $J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.19-8.10(\mathrm{~m}, 4 \mathrm{H}), 8.06(\mathrm{t}$, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.93-7.89(\mathrm{~m}, 2 \mathrm{H}), 7.65(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.53-7.48$ (m, 3 H ).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=161.9,149.3,148.0,147.5,137.6$, 134.8, 131.9, 131.8, 131.2, 130.6, 129.9, 129.8, 129.6, 127.8, 126.9, $126.8,126.6,126.5,126.4,126.2,125.3,124.8,124.5,122.0,118.6$, 110.3.

HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{29} \mathrm{H}_{18} \mathrm{~N}_{3} \mathrm{O}$ : 424.1450; found: 424.1467.

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

By following the general procedure, 5 m was obtained after purification by column chromatography on silica gel $($ EtOAc/hexane $=20: 80)$ as a brown solid ( $37 \mathrm{mg}, 58 \%, 0.15 \mathrm{mmol}$ scale).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 200-202{ }^{\circ} \mathrm{C}$.
IR (DCM): 3440, 3332, 1678, 1517, $1486 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=10.04$ (s, 1 H ), 8.44-8.40 (m, 3 H ), $8.33(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.28(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.25-8.19(\mathrm{~m}, 2 \mathrm{H})$, 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, $J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.21(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.0,149.5,147.7,141.5,137.2$, $135.4,133.2,131.7,131.3,131.2,130.3,130.2,129.4,128.5,127.8$, 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 $\mathrm{C}_{28} \mathrm{H}_{18} \mathrm{ClN}_{2} \mathrm{O}$ : 433.1108; found: 433.1100.

## $\boldsymbol{N}$-(10-(4-Bromophenyl)pyren-1-yl)picolinamide (5n)

By following the general procedure, compound $5 n$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = $20: 80$ ) as a brown solid ( $50 \mathrm{mg}, 53 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 165-167^{\circ} \mathrm{C}$.
IR (DCM): 3325, 2959, 1678, 1521, $1467 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=10.08$ (s, 1 H ), 8.46-8.29 (m, 6 H ), $8.26-8.21(\mathrm{~m}, 2 \mathrm{H}), 8.11(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.00-7.96(\mathrm{~m}, 3 \mathrm{H}), 7.63-$ $7.60(\mathrm{~m}, 1 \mathrm{H}), 7.39(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=161.0,148.4,146.8,140.9,136.2$, 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 $\mathrm{C}_{28} \mathrm{H}_{18} \mathrm{BrN}_{2} \mathrm{O}$ : 477.0603; found: 477.0607.

## $\mathbf{N}$-(10-(3,5-Dimethylphenyl)pyren-1-yl)picolinamide (50)

By following the general procedure, compound $\mathbf{5 0}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane = $20: 80$ ) as a brown solid ( $38 \mathrm{mg}, 45 \%$ ).
$R_{f}=0.5(\mathrm{EtOAc} /$ hexane $=20: 80) ; \mathrm{mp} 165-167^{\circ} \mathrm{C}$.
IR (DCM): 3313, 1678, 1511, 1434, $840 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.75(\mathrm{~s}, 1 \mathrm{H}), 8.65(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.31-8.28(\mathrm{~m}, 2 \mathrm{H}), 8.19(\mathrm{~d}, \mathrm{~J}=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 8.13-8.06(\mathrm{~m}, 3 \mathrm{H}), 8.01(\mathrm{t}$, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.93(\mathrm{~s}, 1 \mathrm{H}), 7.83\left(\mathrm{td},{ }^{1} J=7.7 \mathrm{~Hz}, 1 \mathrm{H},{ }^{2} \mathrm{~J}=1.6 \mathrm{~Hz}\right)$, $7.41-7.38$ (m, 1 H), 7.16 ( $\mathrm{s}, 2 \mathrm{H}), 6.59(\mathrm{~s}, 1 \mathrm{H}), 2.20(\mathrm{~s}, 6 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.1,149.8,147.2,142.9,137.8$, 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 $\mathrm{C}_{30} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}$ : 427.1810; found: 427.1826.

## $\boldsymbol{N}$-(10-(3,4-Dimethylphenyl)pyren-1-yl)picolinamide (5p)

By following the general procedure, compound $\mathbf{5 p}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $55 \mathrm{mg}, 65 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $\left.=20: 80\right) ; \mathrm{mp} 148-150^{\circ} \mathrm{C}$.
IR (DCM): 3428, 1686, 1590, 1517, $1128 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=9.88(\mathrm{~s}, 1 \mathrm{H}), 8.44-8.38(\mathrm{~m}, 2 \mathrm{H})$, 8.33-8.18 (m, 5 H), $8.08(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.98-7.95(\mathrm{~m}, 3 \mathrm{H}), 7.59-$ $7.55(\mathrm{~m}, 1 \mathrm{H}), 7.19(\mathrm{~s}, 1 \mathrm{H}), 7.15-7.12(\mathrm{~m}, 1 \mathrm{H}), 6.92(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H})$, 2.04 (s, 3 H ), 1.90 ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.0,150.0,147.3,140.5,136.9$, 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 $\mathrm{C}_{30} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}: 427.1810$; 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 $\mathbf{5 q}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $56 \mathrm{mg}, 62 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 192-194{ }^{\circ} \mathrm{C}$.
IR (DCM): 3448, 2925, 1686, 1517, $1252 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.06(\mathrm{~s}, 1 \mathrm{H}), 8.79(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, 8.43-8.42 (m, 1 H), 8.30-8.23 (m, 2 H$), 8.18(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.11-$ $7.98(\mathrm{~m}, 4 \mathrm{H}), 7.92(\mathrm{~s}, 1 \mathrm{H}), 7.86\left(\mathrm{t},{ }^{1} \mathrm{~J}=7.7 \mathrm{~Hz}, 1 \mathrm{H},{ }^{2} \mathrm{~J}=1.6 \mathrm{~Hz}\right), 7.44-$ $7.41(\mathrm{~m}, 1 \mathrm{H}), 7.10-7.06(\mathrm{~m}, 2 \mathrm{H}), 6.84(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.20-4.13$ (m, 2 H ), 3.98-3.91 (m, 2 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=161.9,150.1,147.5,143.4,143.0$, 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 $\mathrm{C}_{30} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}_{3}$ : 457.1552; found: 457.1541.

## $\mathbf{N}$-(10-(6-Chloropyridin-3-yl)pyren-1-yl)picolinamide (5r)

By following the general procedure, compound $\mathbf{5 r}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $25: 75$ ) as a brown solid ( $36 \mathrm{mg}, 42 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 194-196^{\circ} \mathrm{C}$.
IR (DCM): 3323, 1678, 1513, 1274, $842 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=9.72(\mathrm{~s}, 1 \mathrm{H}), 8.72(\mathrm{~s}, 1 \mathrm{H}), 8.65(\mathrm{~d}, \mathrm{~J}=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.43(\mathrm{~d}, \mathrm{~J}=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.23-8.17(\mathrm{~m}, 3 \mathrm{H}), 8.09-7.97(\mathrm{~m}$, $4 \mathrm{H}), 7.88(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.81(\mathrm{~s}, 1 \mathrm{H}), 7.56(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.47$ ( $\mathrm{t}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $6.99(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=161.6,150.1,149.1,148.4,148.0$, $139.4,137.6,137.5,132.3,131.3,131.2,130.7,129.8,129.4,127.7$, 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 $\mathrm{C}_{27} \mathrm{H}_{17} \mathrm{ClN}_{3} \mathrm{O}$ : 434.1060; found: 434.1045.

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

By following the general procedure, compound $\mathbf{5 s}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $25: 75$ ) as a brown solid ( $48 \mathrm{mg}, 51 \%$ ).
$R_{f}=0.3$ (EtOAc/hexane $\left.=20: 80\right) ; \mathrm{mp} 175-177^{\circ} \mathrm{C}$.
IR (DCM): 3344, 2936, 1682, 1521, $1236 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=9.80(\mathrm{~s}, 1 \mathrm{H}), 8.80-8.79(\mathrm{~m}, 1 \mathrm{H}), 8.50-$ 8.47 (m, 2 H ), 8.33 (d, $J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.26(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.19-$ 8.12 (m, 4 H), 8.10-8.03 (m, 2 H), 7.87 (td, $\left.{ }^{1} J=7.7 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right)$, $7.60\left(\mathrm{dd},{ }^{1} \mathrm{~J}=8.4 \mathrm{~Hz},{ }^{2} \mathrm{~J}=2.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.49-7.45(\mathrm{~m}, 1 \mathrm{H}), 7.42(\mathrm{~d}, J=$ 8.3 Hz, 1 H ).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=162.5,160.2,150.6,149.3,147.9$, $138.7,137.4,134.7,132.4,131.2,130.6,130.0,129.9,127.8,126.9$, $126.5,126.4,126.4,126.2,125.6,125.5,125.4,124.7,122.8,122.1$, 118.9.

HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{27} \mathrm{H}_{17} \mathrm{BrN}_{3} \mathrm{O}$ : 478.0555; found: 478.0538.

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

By following the general procedure, compound $\mathbf{5 t}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $57 \mathrm{mg}, 71 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp $148-150^{\circ} \mathrm{C}$.
IR (DCM): 3428, 2932, 1675, 1513, $1321 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=10.31(\mathrm{~s}, 1 \mathrm{H}), 8.84(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $8.41(\mathrm{~d}, J=4.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.32(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.23(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H})$, 8.15-8.01 (m, 5 H), 7.88-7.84 (m, 1 H), 7.44-7.41 (m, 1 H ), 7.25 (dd, $\left.{ }^{1} J=7.6 \mathrm{~Hz},{ }^{2} J=0.9 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.17\left(\mathrm{dd},{ }^{1} J=5.2 \mathrm{~Hz},{ }^{2} J=0.9 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.91$ (dd, ${ }^{1} J=5.2 \mathrm{~Hz},{ }^{2} J=3.6 \mathrm{~Hz}, 1 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.2,150.0,147.6,143.8,137.1$, 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 $\mathrm{C}_{26} \mathrm{H}_{17} \mathrm{~N}_{2} \mathrm{OS}$ : 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 ( $53 \mathrm{mg}, 56 \%$ ).
$R_{f}=0.4$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 151-153^{\circ} \mathrm{C}$.
IR (DCM): 3348, 2925, 1667, 1582, $1509 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.58(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.49(\mathrm{~s}, 1 \mathrm{H})$, $8.44(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.25-8.04(\mathrm{~m}, 7 \mathrm{H}), 7.76(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H})$, $7.46-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.14-7.10(\mathrm{~m}, 1 \mathrm{H}), 7.02(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.83(\mathrm{~s}$, $3 \mathrm{H}), 2.05$ ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.5,159.4,138.4,136.3,133.1$, 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 $\mathrm{C}_{31} \mathrm{H}_{24} \mathrm{NO}_{2} \mathrm{~S}: 474.1528$; found: 474.1538.

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

By following the general procedure, compound $\mathbf{6 b}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a brown solid ( $51 \mathrm{mg}, 57 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 167-169{ }^{\circ} \mathrm{C}$.
IR (DCM): 3336, 2921, 1678, 1509, $1428 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.69-8.64(\mathrm{~m}, 2 \mathrm{H}), 8.39-8.36(\mathrm{~m}, 2 \mathrm{H})$, 8.28-8.25 (m, 2 H), 8.21-8.19 (m, 2 H), 8.14-8.06 (m, 2 H ), 7.55 (d, $J=$ $3.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.50-7.41$ (m, 3 H ), 7.17-7.12 (m, 2 H ), 2.08 ( $\mathrm{s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}$, DMSO- $d_{6}$ ): $\delta=168.2,141.9,135.6,135.1,132.3$, 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 $\mathrm{C}_{28} \mathrm{H}_{20} \mathrm{NOS}_{2}$ : 450.0986; found: 450.0999.

## $\boldsymbol{N}$-(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 ( $41 \mathrm{mg}, 53 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 161-163^{\circ} \mathrm{C}$.
IR (DCM): 3259, 2959, 1675, 1632, $1540 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=8.50(\mathrm{~s}, 1 \mathrm{H}), 8.30(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, 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, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.40(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.00-$ 5.99 (m, 1 H), 2.54 (s, 3 H$), 1.59$ (s, 9 H ).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=169.6,140.6,137.9,137.3,132.6$, 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 $\mathrm{C}_{28} \mathrm{H}_{26} \mathrm{NO}$ : 392.2014; found: 392.1998.

## $\mathbf{N}$-(tert-Butyl)-9-phenylpyrene-1-carboxamide (8b)

By following the general procedure, compound $\mathbf{8 b}$ was obtained after purification by column chromatography on silica gel (EtOAc/hexane $=$ $20: 80$ ) as a pale-yellow solid ( $41 \mathrm{mg}, 55 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $=20: 80$ ); mp 158- $160^{\circ} \mathrm{C}$.
IR (DCM): 3340, 2925, 1707, 1673, $1518 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.51(\mathrm{~s}, 1 \mathrm{H}), 8.27-8.22(\mathrm{~m}, 2 \mathrm{H}), 8.14-$ 7.97 (m, 5 H), $7.69(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.60(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.54(\mathrm{~d}$, $J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.08(\mathrm{~s}, 1 \mathrm{H}), 1.59(\mathrm{~s}, 9 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=169.5,140.8,140.6,132.6,132.1$, 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 $\mathrm{C}_{27} \mathrm{H}_{24} \mathrm{NO}$ : 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 ( $41 \mathrm{mg}, 70 \%, 0.14 \mathrm{mmol}$ scale).
$R_{f}=0.5$ (EtOAc/hexane $\left.=20: 80\right)$; mp $167-169{ }^{\circ} \mathrm{C}$.
IR (DCM): 3342, 2954, 1667, 1515, $1479 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.29(\mathrm{~s}, 1 \mathrm{H}), 9.23\left(\mathrm{dd},{ }^{1} \mathrm{~J}=7.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}=\right.$ $1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.64\left(\mathrm{dd},{ }^{1} J=4.2 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.27(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1$ 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, $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.65\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=1.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.43\left(\mathrm{dd},{ }^{1} J=\right.$ $\left.8.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.21(\mathrm{t}, \mathrm{J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.98-1.90(\mathrm{~m}, 2 \mathrm{H})$, $1.48-1.41(\mathrm{~m}, 2 \mathrm{H}), 0.9(\mathrm{t}, \mathrm{J}=7.3 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.8,148.3,138.5,137.3,136.3$, 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.

HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{30} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{O}$ : 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 ( $31 \mathrm{mg}, 71 \%, 0.1 \mathrm{mmol}$ scale) .
$R_{f}=0.6$ (EtOAc/hexane $\left.=20: 80\right) ; \mathrm{mp} 148-150^{\circ} \mathrm{C}$.
IR (DCM): 3343, 2926, 1669, 1515, $1480 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.28(\mathrm{~s}, 1 \mathrm{H}), 9.23\left(\mathrm{dd},{ }^{1} J=7.6 \mathrm{~Hz},{ }^{2} J=\right.$ $1.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.64\left(\mathrm{dd},{ }^{1} J=4.2 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.28-8.19(\mathrm{~m}, 4 \mathrm{H})$, $8.15-8.01(\mathrm{~m}, 4 \mathrm{H}), 8.03(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.73(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.64$ (dd, ${ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=1.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.2\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right.$ ), $3.20(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.97-1.92(\mathrm{~m}, 2 \mathrm{H}), 1.42-1.28(\mathrm{~m}, 4 \mathrm{H}), 0.82(\mathrm{t}$, $J=7.2 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=167.7,147.3,137.5,136.3,135.3$, 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 $\mathrm{C}_{31} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}$ : 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 ( $52 \mathrm{mg}, 74 \%, 0.15 \mathrm{mmol}$ scale) .
$R_{f}=0.7$ (EtOAc/hexane $=20: 80$ ); mp $108-110^{\circ} \mathrm{C}$.
IR (DCM): 3346, 2925, 1707, 1673, $1518 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=10.32(\mathrm{~s}, 1 \mathrm{H}), 9.26\left(\mathrm{dd},{ }^{1} \mathrm{~J}=7.6 \mathrm{~Hz},{ }^{2} \mathrm{~J}=\right.$ $1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.63\left(\mathrm{dd},{ }^{1} J=4.2 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.29(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1$ H), 8.22-8.16 (m, 3 H), 8.14-8.00 (m, 5 H), $7.73(\mathrm{t}, \mathrm{J}=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.63$ (dd, $\left.{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=1.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.40\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} J=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right)$, $3.22(\mathrm{t}, \mathrm{J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.98-1.92(\mathrm{~m}, 2 \mathrm{H}), 1.46-1.38(\mathrm{~m}, 2 \mathrm{H}), 1.32-$ $1.25(\mathrm{~m}, 2 \mathrm{H}), 1.22-1.16(\mathrm{~m}, 4 \mathrm{H}), 0.8(\mathrm{t}, 3 \mathrm{H}, J=6.8 \mathrm{~Hz})$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.8,148.3,138.5,137.4,136.3$, $134.6,132.5,131.8,131.0,130.5,128.6,128.3,128.1,127.5,127.0$, $125.9,125.8,125.6,125.5,124.5,124.3,123.0,122.2,121.7,116.9$, 34.2, 32.2, 31.7, 29.7, 29.2, 22.6, 14.1.

HRMS (ESI): $m / z[M+H]^{+}$calcd for $\mathrm{C}_{33} \mathrm{H}_{31} \mathrm{~N}_{2} \mathrm{O}$ : 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 ( $35 \mathrm{mg}, 73 \%, 0.1 \mathrm{mmol}$ scale).
$R_{f}=0.7$ (EtOAc/hexane $=20: 80$ ); mp $152-154{ }^{\circ} \mathrm{C}$.
IR (DCM): 3359, 2932, 1655, 1528, $1475 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ): $\delta=10.44(\mathrm{~s}, 1 \mathrm{H}), 8.92\left(\mathrm{dd},{ }^{1} \mathrm{~J}=7.5 \mathrm{~Hz}\right.$, $\left.{ }^{2} J=1.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.76\left(\mathrm{dd},{ }^{1} J=4.2 \mathrm{~Hz},{ }^{2} J=1.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.48\left(\mathrm{dd},{ }^{1} J=8.3\right.$ $\left.\mathrm{Hz},{ }^{2} J=1.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.37-8.31(\mathrm{~m}, 3 \mathrm{H}), 8.28-8.16(\mathrm{~m}, 4 \mathrm{H}), 8.11(\mathrm{t}, \mathrm{J}=$ $7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.84\left(\mathrm{dd},{ }^{1} J=8.3 \mathrm{~Hz},{ }^{2} \mathrm{~J}=1.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.79-7.75(\mathrm{~m}, 1 \mathrm{H})$, 7.62 (dd, $\left.{ }^{1} \mathrm{~J}=8.2 \mathrm{~Hz},{ }^{2} \mathrm{~J}=4.2 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.12-3.08(\mathrm{~m}, 2 \mathrm{H}), 1.86-1.82(\mathrm{~m}$, $2 \mathrm{H}), 1.34-0.97(\mathrm{~m}, 10 \mathrm{H}), 0.71(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=168.8,148.3,138.5,137.4,136.3$, $134.6,132.5,131.8,131.0,130.5,128.6,128.3,128.1,127.5,127.0$, 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 $\mathrm{C}_{34} \mathrm{H}_{33} \mathrm{~N}_{2} \mathrm{O}: 485.2593$; 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 ( $51 \mathrm{mg}, 68 \%$ ).
$R_{f}=0.6$ (EtOAc/hexane $=20: 80$ ); mp $144-146^{\circ} \mathrm{C}$.
IR (DCM): 3396, 2951, 1678, 1556, $1514 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.8(\mathrm{~s}, 1 \mathrm{H}), 8.72(\mathrm{~d}, J=4.3 \mathrm{~Hz}, 1 \mathrm{H})$, $8.53(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.45(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.23(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, 8.16-8.13 (m, 1 H$), 8.08-8.03(\mathrm{~m}, 3 \mathrm{H}), 8.01-7.96(\mathrm{~m}, 2 \mathrm{H}), 7.91(\mathrm{~s}, 1$ H), 7.56-7.53 (m, 1 H$), 3.48(\mathrm{t}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 1.78-1.72(\mathrm{~m}, 2 \mathrm{H})$, $1.32-1.26(\mathrm{~m}, 2 \mathrm{H}), 0.84(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.5,150.2,148.1,137.7,136.5$, 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 $\mathrm{C}_{26} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}$ : 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 ( $69 \mathrm{mg}, 88 \%$ ).
$R_{f}=0.5$ (EtOAc/hexane $\left.=20: 80\right) ; \mathrm{mp} 128-130^{\circ} \mathrm{C}$.
IR (DCM): 3352, 2936, 1686, 1513, $1325 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=10.79(\mathrm{~s}, 1 \mathrm{H}), 8.74-8.73(\mathrm{~m}, 1 \mathrm{H}), 8.53$ $(\mathrm{d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.46(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.25(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H})$, 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$), 3.50(\mathrm{t}, \mathrm{J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.80-1.76(\mathrm{~m}, 2 \mathrm{H})$, $1.28-1.22(\mathrm{~m}, 4 \mathrm{H}), 0.78(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.5,150.2,148.1,137.8,136.6$, 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 $\mathrm{C}_{27} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{O}$ : 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 ( $48 \mathrm{mg}, 58 \%$ ).
$R_{f}=0.6($ EtOAc $/$ hexane $=20: 80) ; \mathrm{mp} 132-134{ }^{\circ} \mathrm{C}$.
IR (DCM): 3375, 2928, 1690, 1517, $1321 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=10.77(\mathrm{~s}, 1 \mathrm{H}), 8.73(\mathrm{~d}, \mathrm{~J}=4.6 \mathrm{~Hz}, 1 \mathrm{H})$, $8.52(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.46(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.24(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H})$, 8.15 (d, J = 7.5 Hz, 1 H ), 8.09-8.06 (m, 3 H), 8.01-7.97 (m, 2 H$), 7.92(\mathrm{~s}$, $1 \mathrm{H}), 7.58-7.55(\mathrm{~m}, 1 \mathrm{H}), 3.48(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.78-1.74(\mathrm{~m}, 2 \mathrm{H})$, $1.22-1.13(\mathrm{~m}, 8 \mathrm{H}), 0.84(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=162.5,150.2,148.1,137.8,136.6$, 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 $\mathrm{C}_{29} \mathrm{H}_{29} \mathrm{~N}_{2} \mathrm{O}$ : 421.2280; found: 421.2265.

## 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 ( $27 \mathrm{mg}, 56 \%, 0.15 \mathrm{mmol}$ scale) .
$R_{f}=0.8$ (EtOAc/hexane $\left.=20: 80\right) ; \mathrm{mp} 134-136^{\circ} \mathrm{C}$.
IR (DCM): 3484, 3386, 1601, 1510, $1450 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.07-7.91(\mathrm{~m}, 5 \mathrm{H}), 7.84(\mathrm{~d}, \mathrm{~J}=8.7 \mathrm{~Hz}, 1$ H), $7.72(\mathrm{~s}, 1 \mathrm{H}), 7.54(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.23(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.07$ (d, $J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.94(\mathrm{~s}, 3 \mathrm{H})$. The $\mathrm{NH}_{2}$ signal could not be clearly located in the proton NMR spectrum.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=159.2,142.8,137.1,135.6,132.4$, 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 $\mathrm{C}_{23} \mathrm{H}_{18} \mathrm{NO}: 324.1388$; 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 ( $25 \mathrm{mg}, 70 \%, 0.12 \mathrm{mmol}$ scale $)$.
$R_{f}=0.8$ (EtOAc/hexane $=20: 80$ ); mp 169-171 ${ }^{\circ} \mathrm{C}$. IR (DCM): 3471, 3398, 2928, 1617, $1452 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.07(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.02(\mathrm{~d}, J=8.2$ $\mathrm{Hz}, 1 \mathrm{H}), 7.97-7.91(\mathrm{~m}, 4 \mathrm{H}), 7.83(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, J=5.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.28-7.26(\mathrm{~m}, 2 \mathrm{H}), 7.22-7.20(\mathrm{~m}, 1 \mathrm{H}), 4.25$ (br s, 2 H ).
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=144.3,143.0,132.4,131.2,130.7$, 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 $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{NS}$ : 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 ( $112 \mathrm{mg}, 73 \%, 0.5 \mathrm{mmol}$ ).
$R_{f}=0.9$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 150-152^{\circ} \mathrm{C}$.
IR (DCM): 3494, 3398, 1617, 1513, $1452 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.07-7.93(\mathrm{~m}, 5 \mathrm{H}), 7.87-7.84(\mathrm{~m}, 1 \mathrm{H})$, $7.73-7.72(\mathrm{~m}, 1 \mathrm{H}), 7.53-7.51(\mathrm{~m}, 2 \mathrm{H}), 7.37-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.23(\mathrm{~d}, \mathrm{~J}=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.13$ (br s, 2 H$), 2.53$ ( $\mathrm{s}, 3 \mathrm{H}$ ).
${ }^{13} \mathrm{C}$ NMR $\left(\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=143.0,140.5,137.5,132.4,131.3$, 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 $\mathrm{C}_{23} \mathrm{H}_{18} \mathrm{~N}$ : 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 $\mathbf{2 b}$ 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 $(32 \mathrm{mg}, 46 \%, 0.2 \mathrm{mmol}$ scale from 2b).
$R_{f}=0.9$ (EtOAc/hexane $=20: 80$ ); $\mathrm{mp} 142-144{ }^{\circ} \mathrm{C}$.
IR (DCM): 3490, 3394, 1613, 1513, $1421 \mathrm{~cm}^{-1}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.06-8.01(\mathrm{~m}, 2 \mathrm{H}), 8.00-7.90(\mathrm{~m}, 3 \mathrm{H})$, $7.83(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.72(\mathrm{~s}, 1 \mathrm{H}), 7.53(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.36$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.23(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.13(\mathrm{~s}, 2 \mathrm{H}), 2.77(\mathrm{t}, J=7.8 \mathrm{~Hz}$, $2 \mathrm{H}), 1.77-1.70(\mathrm{~m}, 2 \mathrm{H}), 1.50-1.44(\mathrm{~m}, 2 \mathrm{H}), 1.02(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $\sim 101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=143.0,142.5,140.7,137.5,132.4$, $131.2,129.0,128.9,128.5,128.0,127.4,127.1,126.2,125.3,124.1$, 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 $\mathrm{C}_{26} \mathrm{H}_{24} \mathrm{~N}$ : 350.1909; found: 350.1897.

## Conflict of Interest

The authors declare no conflict of interest.

## Funding Information

S.A.B. thanks the Science and Engineering Research Board (SERB), the Department of Science and Technology (DST), New Delhi, India, for funding (Grant No. EMR/2017/002515). S.A.B. thanks IISER Mohali for funding initial part of this research. A.D. thanks IISER Mohali for providing a PhD fellowship.

## Acknowledgment

We thank IISER Mohali for use of the analytical (NMR, HRMS and Xray) facilities.

## Supporting Information

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

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[^0]:    ${ }^{\mathrm{a}} 0.2 \mathrm{mmol}$ of 3 a .
    ${ }^{\mathrm{b}} 0.4 \mathrm{mmol}$ of 3 a .
    ${ }^{c} 0.6 \mathrm{mmol}$ of 3 a .

[^1]:    Scheme 4 Assembly of pyrene carboxamide motifs $\mathbf{6 a , b}$ and $\mathbf{8 a}, \mathbf{b}$ via

[^2]:    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

