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Synthesis of polybenzoquinazolines via an intramolecular dehydration of photocyclization

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ABSTRACT

Benzo[*h*]-naphth[1,2-*f*]quinazolines and benzo[*h*]-phenanthren[9,10-*f*]quinazoines were synthesized from intermediates 4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines and 4-(2-hydroxyphenyl)-5-(phenanthren-1-yl) pyrimidines by the intramolecular dehydration of photocyclization. The intermediates were obtained by the condensation of 3-arylchromone with formamidine, acetamidine or guanidine refluxing in ethanol, respectively. Irradiation of the corresponding intermediates by a high-pressure mercury lamp in 19:1 (v/v) EtOH–H_2O or 18:1:1 (v/v) EtOH–H_2O-Dioxane lead to target products. This photocyclization showed advantages including catalyst-free and mild reaction condition. Moreover, water was the only by-product of this reaction. The crystal structure of 2-amino-12-methoxy-benzo[*h*]-naphth[1,2-*f*]quinazoline was determined and the fluorescence properties of these polybenzoquinazolines were also investigated.

1. Introduction

The quinazoline skeleton is a key structural element due to its wide applications, for example, they have been reported to possess pharmaceutical activities[1] such as antidepressant, anti-cancer, enzymatic inhibitors, and antiviral. In addition, fused quinazolines belong to heterocyclic aromatic compounds (HACs),[2] which contain one or more nitrogen, sulfur, or oxygen atoms and are present along with polycyclic aromatic hydrocarbons (PAHs). As we known, PAHs can be used as functional organic materials such as electronic devices and optoelectronic devices,[3] because they are affinitive with their molecular, electronic and π-conjugated structures. Meanwhile, the scientific community is always interested in HACs mainly due to the unique properties and potential applications of some of them in the field of materials science.[4] HACs are also applied in the synthetic chemistry as a catalyst.[5] Specially, the aromatic ring framework of HACs are contributed by the lone pair of electrons of nitrogen atoms, which can lead to fabulous physical and chemical properties, for instance, fluorescence and higher carrier mobility.[6]

In recent years, the syntheses of dibenzo[*f*,*h*]quinazolines have been developed.[7] Dibenzo[*f*,*h*]quinazolines were achieved by the reaction of 4,5-*o*,*o*-dihaloarylpyrimidines with Me_6Sn_2 as the organometallic reagent and $Pd(PPh_3)_4$ as the catalyst in dioxane solution at 140 °C.[7a] In 1999, the same group synthesized dibenzo[*f*,*h*]quinazolines by the PIFA (phenyliodine(III) bis(trifluoroacetate)) mediated regioselective oxidative coupling of 4,5-diarylpyrimidines.[7b] Furthermore, dibenzo[*f*,*h*]quinazolines were also obtained from 4-(2-chlorophenyl)-2,6-dimethoxy-5-(2,5-dimethoxyphenyl)pyrimidine with tri(cyclohexyl)phosphine as ligand, in the presence of palladium(II) acetate as a transition-metal catalyst and cesium carbonate as a base.[7c] These methods required metal catalysts, or special oxidant. As for the polybenzoquinazolines, only dibenzo[*f*,*h*]quinazolines were reported, and three or more benzene rings fused quinazoline had not been disclosed to date. Herein, an efficient methodology for the synthesis of benzo[*h*]-naphth[1,2-*f*]quinazolines and benzo[*h*]-phenanthren[9,10-*f*]quinazoines **5** via the photocyclization of 4-(2-hydroxyph-enyl)-5-(naphthalen-1-yl) pyrimidines and 4-(2-hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidines **4** (Scheme 1) was reported.

Encouraged by our previous work, 2*H*-phenanthro[9,10-*c*]pyrazoles[8a] and dibenzo[*f*,*h*][1,2,4]triazolo[3,4-*b*]quinazolines[8b] were prepared by the dehydration of photocyclization of 3,4-diaryl-1*H*-pyrazoles and 6-phenyl-7-(2-hydroxyphenyl)- 1,2,4-triazolo[4,3-*a*] pyrimidines. In order to synthesize larger π-conjugated system of fused quinazolines and explore their distinctive properties, we hypothesized that benzo[*h*]-naphth[1,2-*f*]quinazolines and benzo[*h*]-phenanthren[9,10-*f*]quinazoines **5** would be given from 4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines and 4-(2-

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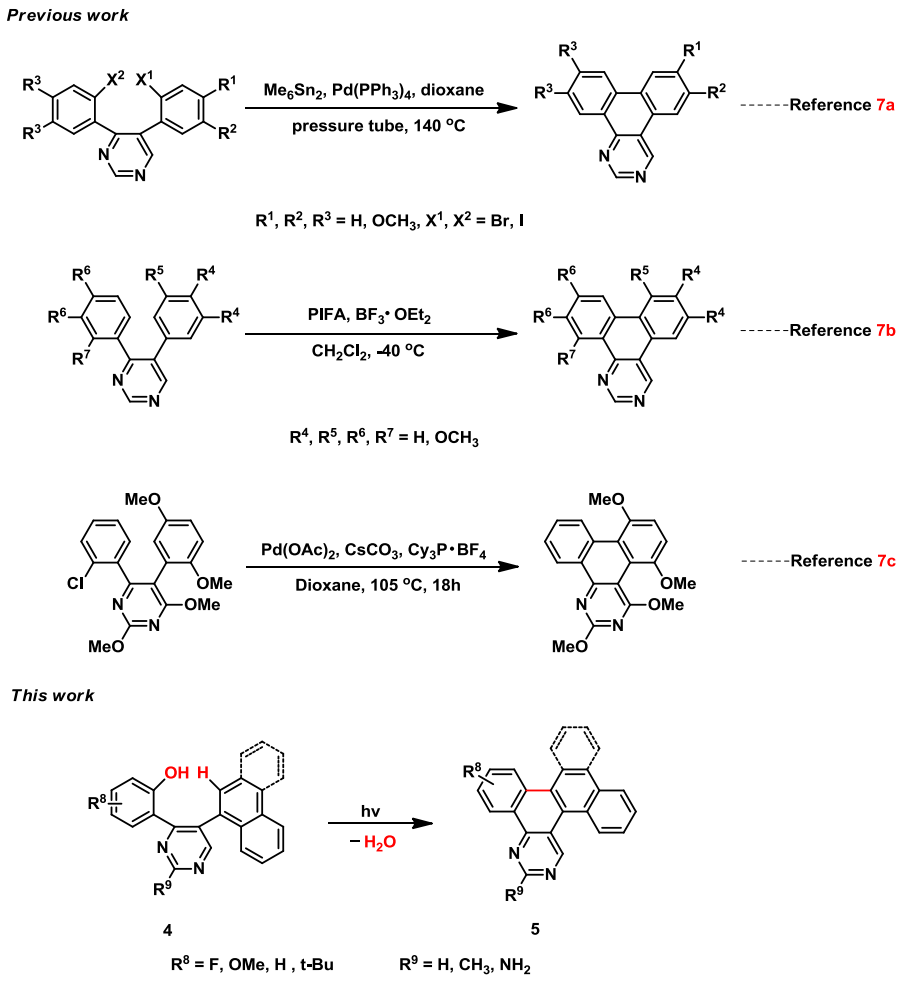


Scheme 1. Reported Approachs and Our Strategy.

hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidines **4** through the intramolecular dehydration of photocyclization.

2. Results and discussion

2.1. Synthesis of the intermediates (4)

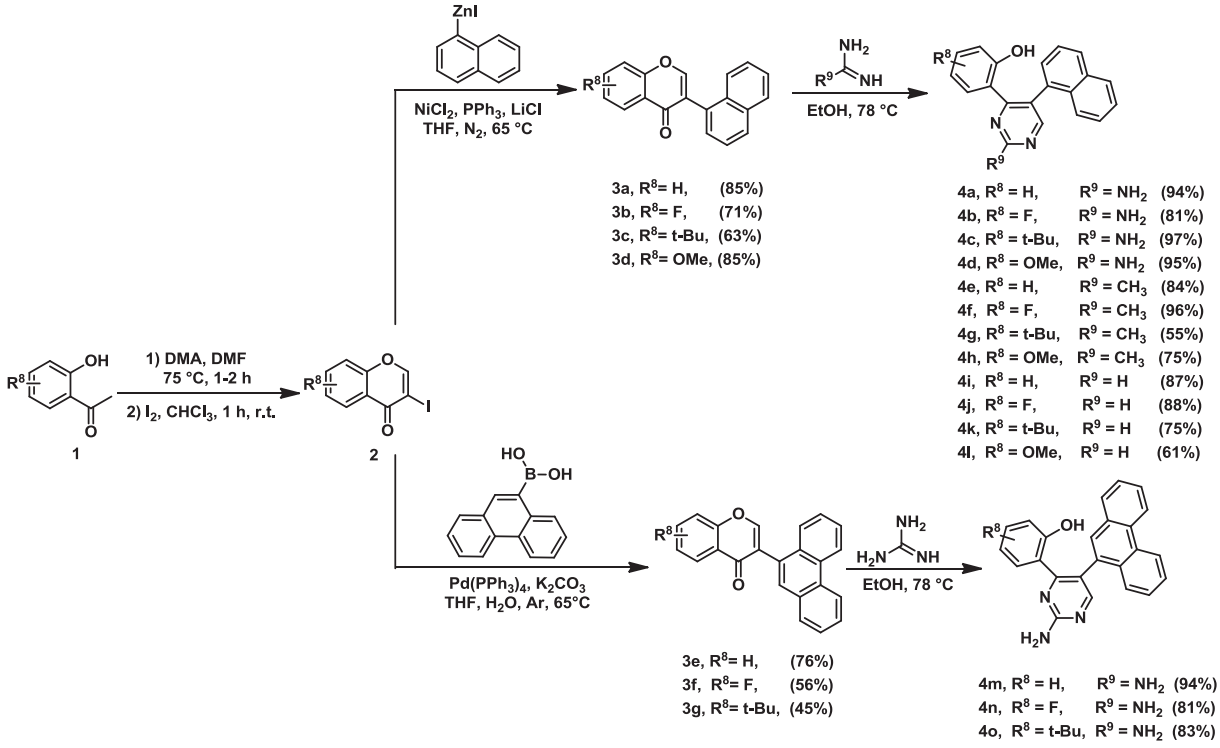
Following the literature procedure,[9,10] 3-iodochromones **2** were got via a two-step procedure: condensation reaction of *o*-hydroxyacetophenones **1** with DMF/DMA in DMF, subsequently cyclization reaction with I_2. Negishi cross-coupling reactions were used for synthesis 3-(1-naphthyl)chromones **3a**–**d** in 63–85% yields with Nickel(II) chloride and triphenylphosphine.[10] A methodology namely Suzuki coupling[11] was used to obtain 3-(9-phenanthrenyl) chromones **3e**–**g** in 45–76% yields. Based on our previous work of the condensation of isoflavones and guanidine,[12] the corresponding intermediates 4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines **4a**–**l** and 4-(2-hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidines **4m**–**o** were obtained in 55–97% yields by the condensation of **3** with formamidine acetate, acetamidine hydrochloride or guanidine hydrochloride in ethanol at 78 °C (Scheme 2).

2.2. Optimization of the solvents in photocyclization reaction

In our initial investigation, **5a** was obtained in 18% yield by the irradiation of **4a** (0.1 mmol) with a high-pressure mercury lamp (500 W) in ethanol (100 mL) under an argon atmosphere for 15 h (Table 1, entry 1). Then, the reaction conditions were optimized (Table 1). When *tert*-butanol or methanol was used as solvent, **5a** was afforded in lower yields (entries 2 and 3, 15% and 13%). Only a trace amount of **5a** was observed in acetonitrile (entry 4). Ethanol-water (19:1 v/v) was used as solvent resulted in 33% yield of **5a** (entry 5), the reason was that the addition of water was favorable to excited state intramolecular proton transfer (ESIPT).[13] While ethanol–water (2:1 v/v) was used as solvent, the yield of **5a** decreased to 25% (entry 6). Only a trace amount of **5a** was detected when a mixture of ethanol and 1% HCl (1:1 v/v) was used as solvent (entry 7). The irradiation time was increased to 25 and 35 h, the yield of **5a** separately increased to 47% and 68% (entries 8 and 9). Subsequently, continue to increase the irradiation time to 40 h, the yield decreased to 65% (entry 10). Due to poor solubility, the corresponding intermediates **4** (1 mmol) could not be dissolved in ethanol–water (100 mL, 19:1 v/v). We could not attempt higher concentration of **4** (10^{-2} M). In addition, the corresponding intermediates **4m**–**o** (0.1 mmol) were irradiated in ethanol-dioxane-water (100 mL, 18:1:1 v/v) because of the poor solubility in ethanol–water (100 mL, 19:1 v/v).

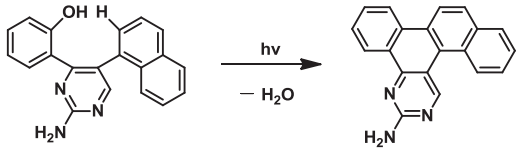
2.3. Scope of substrates

With the optimized reaction conditions in hand, we commenced to explore the substrate scope, and the results were depicted in Table 2. Generally, the corresponding intermediates 4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines and 4-(2-



Scheme 2. Preparation of Intermediates **4a**–**o**.

Table 1
Optimization of the photocyclization reaction of **4a**[a]



4a **5a**

Entry	Solvent	Time (h)	Yield[b]/%
1	EtOH	15	18
2	MeOH	15	15
3	*t*-BuOH	15	13
4	MeCN	15	Trace
5	EtOH–H_2O(19:1)	15	33
6	EtOH–H_2O(2:1)	15	25
7	EtOH–1% HCl (1:1)	15	Trace
8	EtOH–H_2O(19:1)	25	47
9	**EtOH–H_2O(19:1)**	**35**	**68**
10	EtOH–H_2O(19:1)	40	65

The optimization condition was in bold.
[a] Reaction conditions: The intermediate **4a** (0.1 mmol, 10^{-3} M) was dissolved in different solvents (100 mL) and irradiated with a high pressure mercury lamp (500 W) under an argon atmosphere in quartz tubes.
[b] Yield of isolated product after column chromatography based on **4a**.

hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidines **4** carrying electron-donating substituents gave the corresponding products in higher yields than those with electron-withdrawing groups.

For example, **5h** was obtained in 51% yield and it beared a methoxy group. Nevertheless, the fluoro containing product **5f** was obtained in only 30% yield (Table 2). As we know, the solubility of these compounds was poor in chloroform and dichloromethane, due to their larger π-conjugated system.[14] When *tert*-butyl group was introduced into the desired products, the solubility was notably improved. We provided an efficient method for the synthesis of benzo[*h*]-naphth[1,2-*f*] quinazolines **5a**–**l** and benzo[*h*]-phenanthren[9,10-*f*]quinazoines **5m**–**o**. Fortunately, **5d** was recrystallized from ethyl acetate and the structure was further confirmed by single-crystal X-ray diffraction.

Based on previous work of photocyclization reactions,[13] a reasonable mechanism for the preparation of polybenzoquinazolines **5** can be formulated. It is illustrated in Scheme 3. Firstly, under UV light, compound **4** undergoes excited state from the phenolic form to the keto form **6** by intramolecular proton transfer. Secondly, intermediate **7** is then formed under UV irradiation, the subsequent dehydration of which delivered **5** as the product.

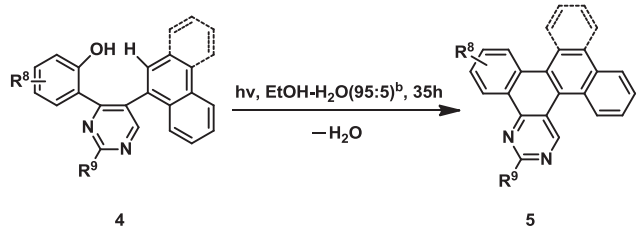
2.4. Fluorescence properties of products

The fluorescent properties of compounds **5** were subsequently investigated in ethanol and in the solid state. The emission spectra of **5** showed blue-purple fluorescence ($\lambda_{Em\ max}$=405–459 nm) in Table 3. The emissions maxima of **5a**, **5b**, **5c** and **5d**, bearing an amino-group in the 2-position of pyrimidine ring, were 431–438 nm. Compounds **5e**–**l**, carrying a methyl group or H atom in the 2-position of pyrimidine ring, had emission maxima at 405–423 nm. The bathochromic shift of emissions was in close contact with the substituents (H, Me, NH_2) on pyrimidine ring, whereas was unrelated to the substituents (H, F, OMe, *t*-Bu) on aromatic ring. For **5m**, **5n** and **5o**, the emission maxima had a bathochromic shift due to the expanded π conjugated.[15] In addition, these compounds also fluoresced in the solid state and showed in Table 3 (solid). The emission maxima of **5c** and **5o** were 593 and 597 nm. The majority of product **5** were at the range from 406 to 484 nm.

3. Conclusion

In summary, an efficient tactic for synthesis of benzo[*h*]-naphth[1,2-*f*] quinazolines and benzo[*h*]-phenanthren[9,10-*f*]quinazoines

Table 2
Synthesis of polybenzoquinazolines 5 via intramolecular dehydration of Photocyclization[a]



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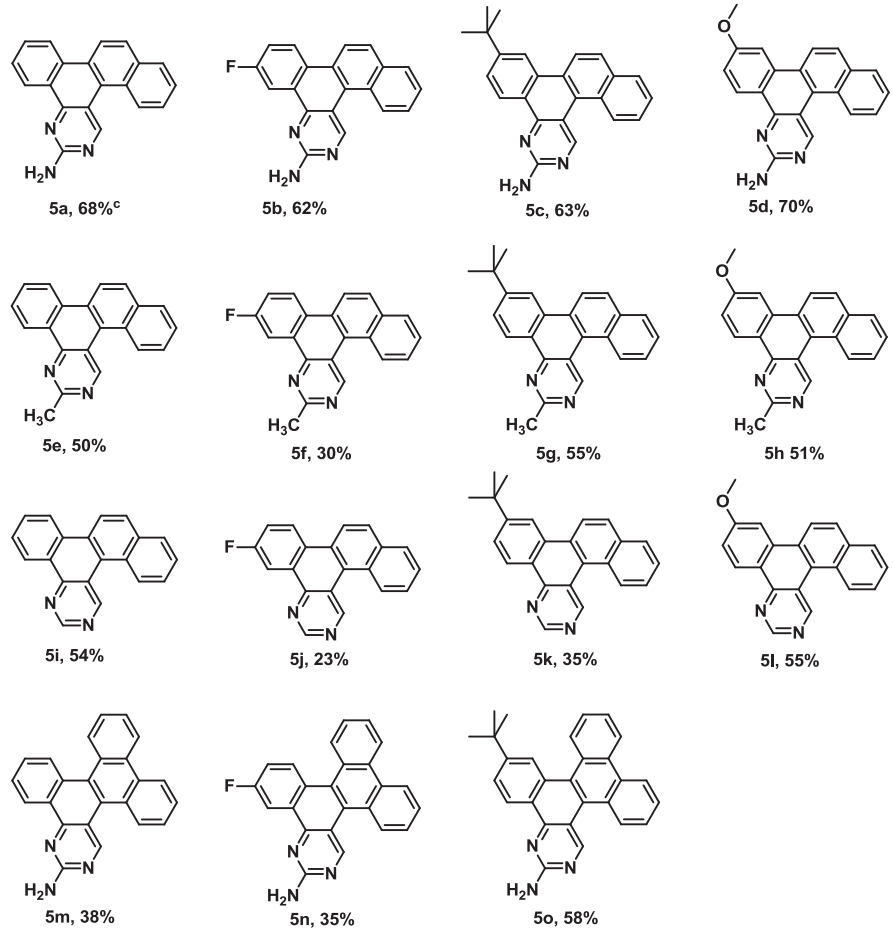
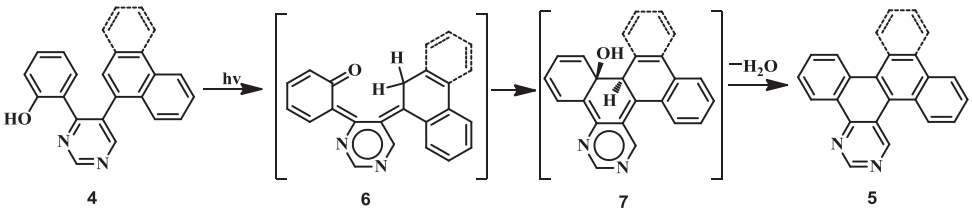


[a] Reaction condition: The intermediate **4** (0.1 mmol, 10^{-3} M) was dissolved in di erent solvents (100 mL) and irradiated with a high pressure mercury lamp (500 W) under an argon atmosphere in quartz tubes.
[b] Reaction solvent was 18:1:1 (v/v/v) EtOH-dioxane-H_2O for **5m**, **5n** and **5o**.
[c] Yield of isolated product after column chromatography based on **4**.

by intramolecular photocyclization of 4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines and 4-(2-hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidines was developed. Compared with the cyclizations of metal catalysts and oxidant reaction, the intramolecular dehydration of photocyclization was mild, catalyst-free and good yields. In addition, only water was formed and utilized the light as an ideal clean reagent.[16] The target products showed blue-purple fluorescence ($\lambda_{Em\ max}$=405–459 nm) in ethanol and possessed larger Stokes shift. In the solid state, the majority of products also had blue-purple fluorescence and the minority of



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Scheme 3. Plausible Mechanism for the Photocyclization Reaction.

Table 3
Spectroscopic properties of target products

Compd	λ_{ex} [nm]	(Solution) λ_{em} [nm]	Stokes shift [cm^{-1}]	λ_{ex} [nm]	(Solid) λ_{em} [nm]	Stokes shift [cm^{-1}]
5a	281	435	12,598	370	443	4454
5b	280	438	12,883	366	445	4850
5c	277	432	12,952	370	593	10,164
5d	279	431	12,640	369	570	9556
5e	261	413	14,101	370	423	3386
5f	260	420	14,652	368	440	4447
5g	267	410	13,062	382	406	1547
5h	271	406	12,270	366	438	4491
5i	259	415	14,514	368	441	4498
5j	258	423	15,119	367	448	4927
5k	267	414	13,299	367	404	2495
5l	272	405	12,073	366	439	4543
5m	292	457	12,364	367	484	5794
5n	294	459	12,227	378	468	5088
5o	294	452	11,890	372	597	10,131

products (**5c** and **5o**) possessed yellow-orange fluorescence. The molecular structure of target compounds was slightly tilted from planarity. This method as well provided facile construction of HACs that were applicable for screening of fundational organic materials.

4. Experimental section

4.1. General remarks

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Thin-layer chromatography was performed on precoated silica gel 60 GF254 plates. Silica gel (200–300 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on 300 MHz, 400 or 600 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (δ 2.50 ppm). Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were recorded on 75 MHz, 100 or 150 MHz spectrometer and the spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak) or DMSO-d_6 (δ 39.5 ppm, the middle peak). Coupling constants (J) are reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was recorded using the electron-spray ionization (ESI) technique. The absorbance and fluorescence spectra were measured in ethanol. Melting points were measured with a X-5 micro-melting point apparatus and were uncorrected. IR spectra were recorded with a Nicollet 170SX FTIR spectrophotometer with KBr pellets. The excitation wavelength and fluorescence spectra were measured in ethanol.

4.2. Preparation of 3-arylchromones 3a–d

Preparation of the 1-naphthylzinc Iodide: A dried 25 mL flask was charged with acetonitrile (5 mL), cobalt bromide (219 mg, 1 mmol), zinc dust (877.5 mg, 13.5 mmol), allylchloride (1.95 mmol, 0.15 mL)and 50 μL of trifluoroacetic acid, the mixture was stirred for 5 min at room temperature. Then 1-iodonaphthalene (5 mmol, 0.73 mL) was added and the reaction mixture was stirred for 1 h at room temperature.

Preparation of the 3-(1-naphthyl)chromones 3a–d: These reactions carried out as referred in the literature.[10] After tetrahydrofuran (THF) drying with Na/benzophenone, daretilled under N_2 atmosphere to use. A hot-oven dried Schlenk tube was charged with substituted 3-iodochromone **2** (0.5 mmol), $NiCl_2$ (1.9 mg, 0.015 mmol), PPh_3 (7.9 mg, 0.03 mmol), LiCl (31.5 mg, 0.75 mmol) followed by THF (3 mL) solvent under an argon atmosphere. The reaction mixture was stirred at 65 °C for 5 min, 1-naphthylzinc iodide (0.55 mmol) was added and stirred at 65 °C for 1 h. The reaction mixture was quenched with 10% HCl (2 mL), and extracted with CH_2Cl_2 (2×15 mL). The combined CH_2Cl_2 extract was washed with 10% HCl (5 mL), brine (5 mL), and dried over $MgSO_4$. The organic layer was concentrated under vacuo to give the crude product. The crude product was purified over silica gel using petroleum ether: ethyl acetate as eluent to give substituted 3-(1-naphthyl) chromones **3a–d**.

*4.2.1. 3-(Naphthalen-1-yl)chromone (**3a**).* Colorless powder. Yield 115.6 mg (85%). Mp 124–126 °C. IR (KBr) 3043, 1642, 1609, 1564, 1506, 1460, 1348, 1282, 1162, 1112, 776, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J=8.0 Hz, 1H), 7.98 (s, 1H), 7.87 (t, J=8.0 Hz, 2H), 7.73–7.66 (m, 2H), 7.51–7.39 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 156.5, 154.3, 133.8, 133.7, 132.5, 129.9, 129.3, 128.5, 128.3, 126.5, 126.4, 126.0, 125.7, 125.4, 125.4, 125.4, 124.5, 118.2. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{19}H_{12}O_2Na$ 295.0735, found 295.0741.

*4.2.2. 6-Fluoro-3-(naphthalen-1-yl)chromone (**3b**).* Colorless powder. Yield 102.9 mg (71%). Mp 176–178 °C. IR (KBr) 3051, 1651, 1613, 1564, 1477, 1315, 1269, 1244, 1108, 772, 727 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.98–7.89 (m, 3H), 7.73–7.70 (m, 1H), 7.57–7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 159.7(d, $^1J_{C-F}$=245.31 Hz), 154.4, 152.8, 133.7, 132.4, 129.4, 129.4, 128.5, 128.3, 126.4, 126.1, 125.6 (d, $^3J_{C-F}$=7.48 Hz), 125.5, 125.4, 124.8, 122.1 (d, $^2J_{C-F}$=25.48 Hz), 120.4 (d, $^3J_{C-F}$=7.98 Hz), 111.2 (d, $^2J_{C-F}$=23.41 Hz). HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{19}H_{11}FO_2Na$ 313.0641, found 313.0638.

*4.2.3. 7-tert-Butyl-3-(naphthalen-1-yl)chromone (**3c**).* Colorless powder. Yield 103.3 mg (63%). Mp 173–175 °C. IR (KBr) 3049, 2952, 2875, 1629, 1560, 1419, 1346, 1280, 1174, 1120, 900, 779, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J=8.6 Hz, 1H), 8.02 (s, 1H), 7.92 (t, J=8.0 Hz, 2H), 7.76 (d, J=8.2 Hz, 1H), 7.58–7.41 (m, 6H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 158.3, 156.6, 154.1, 133.6, 132.4, 130.0, 129.1, 128.3, 128.2, 126.0, 125.9, 125.7, 125.3, 123.3, 122.0, 114.4, 35.4, 31.0. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{23}H_{21}O_2$ 329.1542, found 329.1535.

*4.2.4. 7-Methoxy-3-(naphthalene-1-yl)chromone (**3d**).* Colorless powder. Yield 128.4 mg (85%). Mp 193–194.0 °C. IR (KBr) 3073, 2924, 2854, 1641, 1570, 1493, 1464, 1385, 1361, 1268, 1219, 1161, 1110, 1076, 991, 906, 852, 789, 759, 698 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.43 (s, 1H), 8.06–7.99 (m, 3H), 7.67–7.46 (m, 5H), 7.24 (s, 1H), 7.15–7.12 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.4, 164.4, 158.4, 155.3, 133.6, 132.9, 132.6, 130.8, 129.1, 128.8, 128.6, 127.4,

126.6, 126.4, 125.9, 124.7, 118.0, 115.4, 101.3, 56.7. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{20}H_{14}O_3Na$ 325.0841, found 325.0841.

4.3. Preparation of 3-arylchromones 3e–g[11]

A mixture of substrated 3-iodochromone (2 mmol), 9-phenanthracenylboronic acid (488.4 mg, 2.2 mmol) and K_2CO_3 (552 mg, 4 mmol) in THF (20 mL) and water (5 mL) was added with $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol) under an argon atmosphere. The reaction mixture was stirred at 60–65 °C and monitored by TLC. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (100 mL) and water (50 mL). The organic layer was washed with water (50 mL) and brine (50 mL) and then dried by $MgSO_4$. Upon removal of the solvent, the corresponding 3-(9-Phenanthryl)chromones **3e–g** was obtained after chromatography on silica gel (petrol ether–ethyl acetate).

*4.3.1. 3-(Phenanthren-9-yl)chromone (**3e**).* Brown powder. Yield 489.4 mg (76%). Mp 192–194 °C. IR (KBr) 3051, 1638, 1609, 1564, 1493, 1464, 1369, 1344, 1302, 1128, 851, 756, 718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, J=13.4, 8.3 Hz, 2H), 8.39 (dd, J=8.0, 1.3 Hz, 1H), 8.13 (s, 1H), 7.91 (d, J=7.8 Hz, 1H), 7.83–7.49 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 157.1, 156.6, 154.2, 133.9, 131.4, 131.3, 130.9, 130.6, 129.4, 129.0, 128.8, 127.2, 126.8, 126.6, 126.5, 126.3, 125.7, 125.4, 124.5, 123.0, 122.7, 118.2. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{23}H_{14}O_2Na$ 345.0891, found 345.0897.

*4.3.2. 6-Fluoro-3-(phenanthren-9-yl)chromone (**3f**).* Colorless powder. Yield 380.8 mg (56%). Mp 209–211 °C. IR (KBr) 3070, 1629, 1579, 1467, 1344, 1298, 1245, 1141, 939, 881, 823, 727 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, J=14.3, 8.3 Hz, 2H), 8.10 (s, 1H), 7.99 (dd, J=8.0, 2.8 Hz, 1H), 7.88 (d, J=7.7 Hz, 1H), 7.83–7.55 (m, 7H), 7.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 159.7 (d, $^1J_{C-F}$=245.6 Hz), 154.3, 152.7, 131.2, 131.0, 130.8, 130.5, 129.4, 128.7, 128.5, 127.2, 126.8, 126.4, 125.4 (d, $^3J_{C-F}$=7.1 Hz), 125.0, 123.0, 122.0, 122.1 (d, $^2J_{C-F}$=25.4 Hz), 120.3 (d, $^3J_{C-F}$=8.0 Hz), 111.2 (d, $^2J_{C-F}$=23.39 Hz). HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{23}H_{14}FO_2$ 341.0978, found 341.0965.

*4.3.3. 7-tert-Butyl-3-(phenanthren-9-yl)chromone (**3g**).* Colorless powder. Yield 340.2 mg (45%). Mp 221–223 °C. IR (KBr) 3059, 2954, 2871, 1633, 1558, 1423, 1357, 1296, 1201, 1136, 887, 842, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, J=13.1, 8.3 Hz, 2H), 8.30 (d, J=8.5 Hz, 1H), 8.08 (s, 1H), 7.89 (d, J=7.7 Hz, 1H), 7.80 (d, J=8.1 Hz, 1H), 7.74–7.53 (m, 7H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 158.3, 156.7, 154.0, 131.3, 131.2, 130.7, 130.3, 129.1, 129.0, 128.6, 127.0, 126.7, 126.6, 126.5, 126.0, 125.6, 123.3, 122.8, 122.5, 122.0, 114.4, 35.4, 31.0. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{27}H_{23}O_2$ 379.1698, found 379.1688.

4.4. Preparation for the synthesis of 4-(2-hydroxyphenyl)-5-(naphthalene-1-yl) pyrimidines 4a–l and 4-(2-hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidines 4m–o

Based on the literature procedure.[12] Formamidine acetate, acetamidine hydrochloride or guanidine hydrochloride (6 mmol) was added to an EtOH (150 mL) solution of the substrated 3-arylchromones **3** (2 mmol). The mixture was stirred at 78 °C and NaOH (1M, EtOH) was added dropwise to make the pH of the mixture between 8 and 9. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was concentrated by rotary evaporation to give crude compounds **4.** It was dissolved with CH_2Cl_2 (150 mL) and water (50 mL) and adjusted to neutral. The organic layer was separated and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography (ethyl acetate–petroleum ether) on silica gel (200–300 mesh) to afford the desired product.

*4.4.1. 2-Amino-4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidine (**4a**).* Yellow powder. Yield 588.4 mg (94%). Mp 241–243 °C. IR (KBr) 3383, 3329, 3155, 3055, 1659, 1575, 1527, 1448, 1386, 1340, 1215, 1165, 1109, 935, 840, 752 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 11.72 (s, 1H), 8.21 (s, 1H), 7.92 (d, J=8.1 Hz, 1H), 7.89 (d, J=8.2 Hz, 1H), 7.59 (d, J=8.4 Hz, 1H), 7.47 (dd, J=14.9, 7.1 Hz, 2H), 7.39 (t, J=7.3 Hz, 1H), 7.34 (d, J=6.6 Hz, 1H), 7.12 (s, 2H), 7.01–6.96 (m, 1H), 6.75 (dd, J=7.9, 1.3 Hz, 1H), 6.72 (d, J=8.0 Hz, 1H), 6.28 (t, J=7.3 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.0, 161.5, 161.3, 157.4, 135.2, 133.3, 131.6, 130.7, 129.6, 128.2, 127.9, 127.8, 126.3, 125.9, 125.6, 125.1, 121.4, 119.7, 117.7, 116.9. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{16}N_3O$ 314.1293, found 314.1286.

*4.4.2. 2-Amino-4-(2-hydroxy-5-fluorophenyl)-5-(naphthalen-1-yl) pyrimidine (**4b**).* Yellow powder. Yield 536.2 mg (81%). Mp 271–273 °C. IR (KBr) 3386, 3334, 3165, 2924, 2854, 1658, 1564, 1519, 1436, 1342, 1257, 1205, 1110, 931, 871, 813, 767, 657 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 11.31 (s, 1H), 8.26 (s, 1H), 7.94 (d, J=8.1 Hz, 1H), 7.91 (d, J=8.2 Hz, 1H), 7.61 (d, J=8.4 Hz, 1H), 7.49 (dd, J=14.8, 6.9 Hz, 2H), 7.42 (t, J=7.5 Hz, 1H), 7.38 (d, J=6.9 Hz, 1H), 7.15 (s, 2H), 6.86 (td, J=8.5, 3.2 Hz, 1H), 6.70 (dd, J=8.9, 4.9 Hz, 1H), 6.55 (dd, J=10.1, 3.1 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 162.0, 161.7, 161.1, 154.7, 153.9 (d, $^1J_{C-F}$=231.9 Hz), 134.7, 133.3, 131.5, 128.2, 127.9, 126.3, 126.0, 125.6, 125.1, 122.5 (d, $^3J_{C-F}$=7.5 Hz), 119.90, 117.68 (d, $^3J_{C-F}$=7.9 Hz), 117.2 (d, $^2J_{C-F}$=22.6 Hz), 115.3 (d, $^2J_{C-F}$=24.6 Hz). HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{15}FN_3O$ 332.1199, found 332.1190.

*4.4.3. 2-Amino-4-(2-hydroxy-4-tert-butylphenyl)-5-(naphthalen-1-yl)pyrimidine (**4c**).* Colorless powder. Yield 715.9 mg (97%). Mp 216–218 °C. IR (KBr) 3473, 3300, 3140, 2957, 2864, 1637, 1562, 1481, 1425, 1380, 1205, 1099, 1024, 952, 786, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 13.27 (s, 1H), 8.28 (s, 1H), 7.91 (d, J=8.2 Hz, 2H), 7.64 (d, J=8.4 Hz, 1H), 7.50 (m, 2H), 7.40 (t, J=7.6 Hz, 1H), 7.34 (d, J=6.9 Hz, 1H), 6.94 (s, 1H), 6.63 (d, J=8.5 Hz, 1H), 6.20 (d, J=9.0 Hz, 1H), 5.34 (s, 2H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.6, 159.8, 159.7, 156.1, 131.3, 133.8, 132.0, 130.1, 128.4, 128.0, 126.7, 126.2, 125.8, 125.3, 120.7, 115.7, 115.4, 115.0, 34.6, 30.7. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{24}H_{24}N_3O$ 370.1919, found 370.1916.

*4.4.4. 2-Amino-4-(2-hydroxy-4-methoxyphenyl)-5-(naphthalen-1-yl)pyrimidine (**4d**).* Colorless powder. Yield 651.7 mg (95%). Mp 215–217 °C. IR (KBr) 3417, 3304, 3142, 2926, 2839, 1625, 1552, 1487, 1437, 1375, 1285, 1207, 1151, 1031, 962, 842, 783, 729 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 13.43 (s, 1H), 8.15 (s, 1H), 7.96 (d, J=4.9 Hz, 1H), 7.95 (d, J=5.0 Hz, 1H), 7.56–7.52 (m, 2H), 7.49 (t, J=7.3 Hz, 1H), 7.41–7.38 (m, 2H), 7.22 (s, 2H), 6.57 (d, J=9.0 Hz, 1H), 6.32 (d, J=2.6 Hz, 1H), 5.76 (dd, J=9.0, 2.6 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 162.0, 161.8, 161.6, 161.2, 160.7, 135.7, 133.4, 131.5, 130.8, 128.4, 128.0, 127.8, 126.5, 126.1, 125.9, 125.0, 118.0, 112.1, 104.8, 101.8, 55.0. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{21}H_{18}N_3O_2$ 344.1399, found 344.1391.

*4.4.5. 2-Methyl-4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidine (**4e**).* Colorless powder. Yield 524.2 mg (84%). Mp 146–148 °C. IR (KBr) 3182, 3057, 2925, 2852, 1556, 1500, 1442, 1390, 1299, 1247, 1166, 1043, 962, 750 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.67 (s, 1H), 7.91 (t, J=8.6 Hz, 2H), 7.64 (d, J=8.2 Hz, 1H), 7.44 (m, 3H), 7.36 (d, J=6.9 Hz, 1H), 7.03 (t, J=8.1 Hz, 2H), 6.74 (d, J=8.0 Hz, 1H), 6.50 (t, J=7.4 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (150 MHz,

DMSO-d_6) δ 165.6, 163.3, 159.0, 155.9, 133.9, 133.1, 131.1, 130.5, 129.9, 129.3, 128.3, 128.2, 127.8, 126.3, 125.9, 125.3, 125.1, 123.5, 118.2, 116.2, 25.4. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{21}H_{16}N_2ONa$ 335.1160, found 335.1152.

*4.4.6. 2-Methyl-4-(2-hydroxy-5-fluorophenyl)-5-(naphthalen-1-yl) pyrimidine (**4f**).* Yellow powder. Yield 633.6 mg (96%). Mp 146–148 °C. IR (KBr) 3113, 3045, 2924, 2852, 1558, 1498, 1437, 1384, 1253, 1180, 1122, 1049, 952, 871, 771, 709, 655 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 13.34 (s, 1H), 8.68 (s, 1H), 7.98 (d, J=8.3 Hz, 1H), 7.93 (d, J=8.2 Hz, 1H), 7.57 (dd, J=8.1, 7.2 Hz, 1H), 7.50 (t, J=7.5 Hz, 1H), 7.44 (d, J=8.4 Hz, 1H), 7.41–7.36 (m, 2H), 6.71 (dd, J=9.0, 5.0 Hz, 1H), 6.82 (m, 1H), 6.40 (dd, J=10.7, 3.0 Hz, 1H), 2.90 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 165.0 (s, 2H), 161.5, 161.4(d, $^4J_{C-F}$=2.4 Hz), 156.3, 154.6 (d, $^1J_{C-F}$=234.8 Hz), 133.9, 133.8, 131.1, 129.5, 128.8, 127.9, 127.6, 127.2, 126.6, 125.8, 124.7, 119.7 (d, ^2J=23.3 Hz), 119.4 (d, $^3J_{C-F}$=7.7 Hz), 117.8 (d, $^3J_{C-F}$=7.7 Hz, 2H), 115.7 (d, $^2J_{C-F}$=25.4 Hz), 25.5. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{21}H_{16}FN_2O$ 331.1247, found 331.1239.

*4.4.7. 2-Methyl-4-(2-hydroxy-4-tert-butylphenyl)-5-(naphthalen-1-yl)pyrimidine (**4g**).* Yellow powder. Yield 404.8 mg (55%). Mp 130–132 °C. IR(KBr): 3209, 3055, 2963, 2877, 1616, 1554, 1433, 1367, 1309, 1215, 1105, 1047, 945, 864, 783, 684 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 13.86 (s, 1H), 8.58 (s, 1H), 7.95 (m, 2H), 7.53 (m, 3H), 7.39 (m, 2H), 6.98 (s, 1H), 6.66 (d, J=8.1 Hz, 1H), 6.23 (d, J=7.7 Hz, 1H), 2.89 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.4, 161.0, 160.4, 156.6, 134.7, 133.8, 131.4, 130.0, 128.9, 128.5, 127.5, 127.1, 126.9, 126.4, 125.7, 125.1, 115.7, 115.4, 114.9, 34.7, 30.7, 25.5. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{25}H_{25}N_2O$ 369.1967, found 369.1960.

*4.4.8. 2-Methyl-4-(2-hydroxy-4-methoxyphenyl)-5-(naphthalen-1-yl)pyrimidine (**4h**).* Yellow powder. Yield 489.1 mg (75%). Mp 147–149 °C. IR (KBr) 3182, 3051, 2927, 2841, 1581, 1527, 1440, 1382, 1276, 1157, 1029, 962, 839, 779, 713 cm^{-1}. ^1H NMR (600 MHz, CDCl) δ 14.36 (s, 1H), 8.54 (s, 1H), 7.94 (d, J=8.3 Hz, 1H), 7.92 (d, J=8.1 Hz, 1H), 7.54 (t, J=7.6 Hz, 1H), 7.49 (t, J=7.9 Hz, 2H), 7.38 (t, J=6.8 Hz, 2H), 6.65 (d, J=9.1 Hz, 1H), 6.45 (s, 1H), 5.75 (d, J=9.0 Hz, 1H), 3.67 (s, 3H), 2.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.3, 163.1, 163.0, 162.2, 160.7, 134.9, 133.8, 131.6, 131.2, 129.0, 128.5, 127.4, 126.9, 126.5, 126.4, 125.8, 125.1, 110.6, 106.1, 102.0, 55.09, 25.40. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{22}H_{19}N_2O_2$ 343.1447, found 343.1440.

*4.4.9. 4-(2-Hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidine (**4i**).* Yellow powder. Yield 518.5 mg (87%). Mp 120–122 °C. IR (KBr) 3205, 3053, 1608, 1560, 1500, 1448, 1386, 1249, 1161, 1035, 956, 854, 759 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 13.08 (s, 1H), 9.25 (s, 1H), 8.75 (s, 1H), 7.96 (d, J=8.3 Hz, 1H), 7.93 (d, J=8.2 Hz, 1H), 7.54 (t, J=7.6 Hz, 1H), 7.50 (dd, J=13.1, 7.8 Hz, 2H), 7.39 (t, J=7.2 Hz, 2H), 7.10 (t, J=7.7 Hz, 1H), 6.98 (d, J=8.2 Hz, 1H), 6.75 (d, J=8.2 Hz, 1H), 6.19 (t, J=7.7 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 162.7, 161.2, 160.0, 155.3, 134.3, 133.8, 132.7, 131.0, 130.9, 130.3, 129.3, 128.7, 127.6, 127.2, 126.6, 125.8, 124.9, 118.6, 118.4, 117.7. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{15}N_2O$ 299.1184, found 299.1183.

*4.4.10. 4-(2-Hydroxy-5-fluorophenyl)-5-(naphthalen-1-yl)pyrimidine (**4j**).* Yellow powder. Yield 556.1 mg (88%). Mp 123–125 °C. IR (KBr) 3107, 3053, 1624, 1550, 1446, 1371, 1256, 1191, 1109, 1047, 966, 873, 773, 653 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 12.87 (s, 1H), 9.27 (s, 1H), 8.79 (s, 1H), 8.00 (d, J=8.3 Hz, 1H), 7.94 (d, J=8.2 Hz, 1H), 7.60–7.55 (m, 1H), 7.51 (t, J=7.3 Hz, 1H), 7.45–7.35 (m, 3H), 6.92 (dd, J=9.0, 5.0 Hz, 1H), 6.82 (ddd, J=9.1, 7.6, 3.0 Hz, 1H), 6.41 (dd, J=10.6, 3.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.5, 161.2, 155.4, 155.3, 155.0 (d, $^1J_{C-F}$=233.9 Hz), 133.8, 133.5, 131.2, 130.8, 129.7, 128.8, 127.5, 127.3, 126.7, 125.7, 124.5, 119.9 (d, $^2J_{C-F}$=23.5 Hz), 119.5 (d, $^3J_{C-F}$=7.7 Hz), 117.7 (d, $^3J_{C-F}$=8.0 Hz), 115.6 (d, $^2J_{C-F}$=25.8 Hz). HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{14}FN_2O$ 317.1090, found 317.1079.

*4.4.11. 4-(2-Hydroxy-4-tert-butylphenyl)-5-(naphthalen-1-yl)pyrimidine (**4k**).* Colorless powder. Yield 531.1 mg (75%). Mp 175–177 °C. IR (KBr) 3193, 3039, 2958, 2869, 1622, 1562, 1510, 1438, 1384, 1284, 1222, 1022, 935, 869, 786 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 13.44 (s, 1H), 9.22 (s, 1H), 8.68 (s, 1H), 8.01–7.93 (m, 2H), 7.58–7.49 (m, 3H), 7.42 (d, J=7.2 Hz, 1H), 7.38 (d, J=6.9 Hz, 1H), 7.00 (s, 1H), 6.68 (d, J=8.5 Hz, 1H), 6.23 (d, J=8.6 Hz, 1H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.8, 160.4, 156.9, 155.0, 134.5, 133.8, 131.2, 130.5, 129.9, 129.2, 128.6, 127.5, 127.1, 126.5, 125.8, 125.0, 116.0, 115.5, 114.8, 34.7, 30.7. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{24}H_{23}N_2O$ 355.1810, found 355.1801.

*4.4.12. 4-(2-Hydroxy-4-methoxyphenyl)-5-(naphthalen-1-yl)pyrimidine (**4l**).* Colorless powder. Yield 400.2 mg (61%). Mp 122–124 °C. IR (KBr) 3188, 3062, 2932, 2844, 1606, 1558, 1434, 1382, 1259, 1201, 1159, 1037, 962, 783 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 13.89 (s, 1H), 9.17 (s, 1H), 8.64 (s, 1H), 7.97 (d, J=8.3 Hz, 1H), 7.93 (d, J=8.2 Hz, 1H), 7.58–7.54 (m, 1H), 7.53–7.47 (m, 2H), 7.42–7.38 (m, 2H), 6.65 (d, J=9.2 Hz, 1H), 6.46 (d, J=2.6 Hz, 1H), 5.77 (dd, J=9.2, 2.7 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.1, 162.9, 162.4, 160.6, 154.9, 134.7, 133.9, 131.6, 131.2, 129.9, 129.2, 128.6, 127.4, 127.1, 126.6, 125.8, 125.0, 110.6, 106.4, 102.1, 55.1. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{21}H_{17}N_2O_2$ 329.1290, found 329.1291.

*4.4.13. 2-Amino-4-(2-hydroxyphenyl)-5-(phenanthren-9-yl)pyrimidine (**4m**).* Yellow powder. Yield 682.4 mg (94%). Mp >300 °C. IR (KBr) 3402, 3323, 3161, 3066, 1651, 1571, 1494, 1446, 1383, 1207, 1039, 948, 821, 744 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ 11.92 (s, 1H), 8.83 (m, 2H), 8.29 (s, 1H), 7.92 (d, J=7.7 Hz, 1H), 7.75 (s, 1H), 7.69 (t, J=7.4 Hz, 1H), 7.64 (m, 3H), 7.50 (t, J=7.4 Hz, 1H), 7.17 (s, 2H), 6.96 (t, J=7.4 Hz, 1H), 6.92 (d, J=7.8 Hz, 1H), 6.71 (d, J=8.0 Hz, 1H), 6.23 (t, J=7.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.1, 161.6, 157.6, 134.0, 131.2, 131.0, 137.1, 130.1, 129.6, 129.5, 128.7, 128.4, 127.1, 127.1, 127.0, 126.9, 126.2, 123.3, 122.9, 121.4, 119.6, 117.8, 117.1. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{24}H_{17}N_3ONa$ 386.1269, found 386.1255.

*4.4.14. 2-Amino-4-(2-hydroxy-5-fluorophenyl)-5-(phenanthren-9-yl)pyrimidine (**4n**).* Yellow powder. Yield 617.2 mg (81%). Mp 294.5–296.5 °C. IR (KBr) 3410, 3336, 3178, 3068, 1656, 1566, 1504, 1442, 1359, 1253, 1205, 1112, 1033, 964, 885, 817, 767, 723 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 11.46 (s, 1H), 8.84 (t, J=8.3 Hz, 2H), 8.32 (d, J=2.8 Hz, 1H), 7.92 (d, J=7.4 Hz, 1H), 7.77 (s, 1H), 7.73–7.61 (m, 4H), 7.52 (t, J=7.5 Hz, 1H), 7.17 (s, 2H), 6.80 (t, J=8.5 Hz, 1H), 6.75–6.62 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 162.2, 161.8, 161.3, 154.6 (d, $^1J_{C-F}$=231.8 Hz), 153.5, 133.4, 133.1, 130.7, 130.0, 129.5, 128.6, 128.5, 127.1, 127.0, 126.9 (d, $^3J_{C-F}$=8.0 Hz), 126.1, 123.2, 122.8, 122.7, 122.7, 119.9, 117.7(d, $^3J_{C-F}$=7.9 Hz), 117.2(d, $^2J_{C-F}$=22.7 Hz), 115.3(d, $^2J_{C-F}$=24.4 Hz). HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{24}H_{17}FN_3O$ 382.1356, found 382.1338.

*4.4.15. 2-Amino-4-(2-hydroxy-4-tert-butylphenyl)-5-(phenanthren-9-yl)pyrimidine (**4o**).* Colorless powder. Yield 695.5 mg (83%). Mp 282.5–284.5 °C. IR (KBr) 3475, 3278, 3141, 3063, 2960, 2869, 1624, 1581, 1545, 1481, 1425, 1369, 1207, 1107, 1035, 947, 808, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 13.50 (s, 1H), 8.76 (t, J=8.3 Hz, 2H), 8.32 (s, 1H), 7.85 (d, J=7.9 Hz, 1H), 7.75–7.58 (m, 5H), 7.51–7.44 (m, 1H), 6.96 (d, J=2.0 Hz, 1H), 6.90 (d, J=8.6 Hz, 1H), 6.16 (dd, J=8.6, 2.1 Hz,

1H), 5.48 (s, 2H), 1.11 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 162.1, 160.9, 159.0, 154.6, 134.4, 131.3, 130.9, 130.1, 129.6, 129.2, 128.6, 128.2, 127.15, 127.14, 127.1, 127.0, 126.1, 123.4, 122.9, 118.4, 116.6, 115.0, 114.4, 34.2, 30.5. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{28}H_{26}N_3O$ 420.2076, found 420.2057.

4.5. General procedure for the synthesis of benzo[*h*]-naphth[1,2-*f*] quinazolines and benzo[*h*]-phenanthren[9,10-*f*]quinazoines 5

4-(2-hydroxyphenyl)-5-(naphthalen-1-yl)pyrimidines **4a**–**l** (0.1 mmol) was added to a EtOH-water (19:1) solution (100 mL), the solution was contained in 100 mL quartz tubes, deaerated by bubbling argon for 30 min and irradiated with a high pressure mercury lamp (500 W) for 35 h at 20 °C. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using petrol ether: ethyl acetate (or petrol ether: diethyl ether: dichloromethane) as eluent to give the corresponding products **5a**–**l**. Due to the poor solubility of **4m**–**o**, we used EtOH-dioxane-water (18:1:1) solution as solvent. The other procedure for the synthesis of **5m**–**o** was same with that of **5a**–**l** and **5a**–**5o** characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS.

*4.5.1. 2-Amino-benzo[h]-naphth[1,2-f]quinazoline (**5a**).* Yellow powder. Yield 120.4 mg (68%). Mp 230–232 °C. IR (KBr) 3452, 3298, 3190, 3053, 2924, 2858, 1730, 1624, 1560, 1460, 1390, 1232, 1126, 1045, 954, 808, 748 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6), δ 7.20 (s, 2H), 7.64 (t, J=7.3 Hz, 1H), 7.69 (t, J=7.3 Hz, 1H), 7.76 (t, J=7.4 Hz, 1H), 7.99 (d, J=8.8 Hz, 1H), 8.07 (d, J=7.8 Hz, 1H), 8.66 (dd, J=15.6, 8.7 Hz, 2H), 8.75 (d, J=8.3 Hz, 1H), 9.11 (d, J=7.9 Hz, 1H), 9.63 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6), δ 113.1, 121.0, 123.6, 124.7, 124.8, 125.1, 126.4, 126.6, 127.2, 127.6, 128.2, 128.3, 128.4, 130.6, 132.6, 133.2, 152.5, 159.4, 160.7; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{14}N_3$ 296.1188, found 296.1183.

*4.5.2. 2-Amino-13-fluoro-benzo[h]-naphth[1,2-f]quinazoline (**5b**).* Colorless powder. Yield 116.4 mg (62%). Mp 237–239 °C. IR (KBr) 3384, 3289, 3068, 2925, 2864, 1726, 1618, 1570, 1518, 1454, 1380, 1265, 1176, 1085, 1043, 952, 877, 786, 727, 671 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (s, 1H), 8.77 (dd, J=9.2, 5.3 Hz, 1H), 8.65 (dd, J=10.3, 2.9 Hz, 1H), 8.60 (t, J=7.9 Hz, 2H), 8.05 (d, J=7.3 Hz, 1H), 7.95 (d, J=8.9 Hz, 1H), 7.73–7.60 (m, 3H), 7.23 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.4 (d, $^1J_{C-F}$=243.9 Hz), 160.6, 159.9, 159.5, 151.4 (d, $^4J_{C-F}$=3.5 Hz), 133.0, 130.2 (d, $^3J_{C-F}$=8.2 Hz), 129.3, 128.3, 128.0, 127.5, 126.7 (d, $^3J_{C-F}$=6.5 Hz), 126.3, 124.4, 124.3, 120.9, 118.9(d, $^2J_{C-F}$=23.0 Hz), 113.4, 109.3, 109.1 (d, $^2J_{C-F}$=22.5 Hz). HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{13}FN_3$ 314.1094, found 314.1093.

*4.5.3. 2-Amino-12-tert-butyl-benzo[h]-naphth[1,2-f]quinazoline (**5c**).* Yellow powder. Yield 210.6 mg (63%). Mp 228–229 °C. IR (KBr) 3492, 3290, 3136, 2952, 2864, 1631, 1566, 1471, 1421, 1315, 1251, 933, 842, 792, 750, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 9.09 (d, J=8.5 Hz, 1H), 8.67 (d, J=8.2 Hz, 1H), 8.60 (d, J=8.6 Hz, 2H), 8.01 (d, J=7.7 Hz, 1H), 7.96 (d, J=8.8 Hz, 1H), 7.79 (d, J=8.5 Hz, 1H), 7.67–7.58 (m, 2H), 5.49 (s, 2H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.0, 159.7, 153.8, 153.4, 133.5, 133.0, 129.9, 128.4, 127.8, 126.9, 126.5, 126.4, 126.3, 126.1, 125.5, 125.3, 125.1, 120.7, 119.0, 114.7, 35.5, 31.4. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{24}H_{22}N_3$ 352.1814, found 352.1805.

*4.5.4. 2-Amino-12-methoxy-benzo[h]-naphth[1,2-f]quinazoline (**5d**).* Yellow powder. Yield 136.5 mg (71%). Mp 233–234.0 °C. IR (KBr) 3396, 3311, 3182, 2933, 2835, 1645, 1564, 1465, 1294, 1231, 1155, 1036, 939, 866, 796, 744, 669 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6), δ 4.02 (s, 3H), 7.10 (s, 2H), 7.36 (d, 1H, J=8.9 Hz), 7.64 (t, 1H, J=7.3 Hz), 7.68 (t, 1H, J=7.2 Hz), 7.99 (d, 1H, J=8.8 Hz), 8.07 (d, 1H, J=7.8 Hz), 8.13 (d, 1H, J=1.8 Hz), 8.64 (d, 1H, J=8.3 Hz) 8.70 (d, 1H, J=9.0 Hz), 9.00 (d, 1H, J=8.9 Hz), 9.57 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6), δ 161.4, 160.7, 159.2, 152.5, 134.6, 133.4, 128.3, 128.2, 127.8, 126.6, 126.4, 125.7, 124.5, 122.3, 121.4, 116.4, 112.2, 105.5, 55.6; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{21}H_{16}N_3O$ 326.1293, found 326.1290.

In order to further investigation of product structures, the crystal structure of **5d** was determined (Fig. 1). The average distance of atoms C2 to C21, N1 and N2 from the least square plane (C2–C21, N1, N2) was 0.2129 Å. The distances of atoms N2, C21 and C14 from the least square plane (C2–C21, N1, N2) were 0.4914 Å, 0.5488 and −0.5354 Å, respectively. The dihedral angle between ring E (C11–C16) and A (C18–C21, N1, N2) was 29.6° (Fig. 1). Owing the reason of the repulsion between contiguous H15 and H21 atoms in space (Fig. 1a), the molecular structure of polycyclic ring system of **5d** was slightly tilted from planarity (Fig. 1 b). It indicated that the atoms of polycyclic ring system for **5a**–**5o** were also slightly tilted from planarity. The crystallographic data and selected bond length, angles and torsion angles were summarized in Tables 3 and 4, respectively. Crystallographic data were deposited in CSD under CCDC-1449149 registration number and were available free of charge upon request to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: þ44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

*4.5.5. 2-Methyl-benzo[h]-naphth[1,2-f]quinazoline (**5e**).* Yellow powder. Yield 88.2 mg (50%). Mp 185–187 °C. IR (KBr) 3037, 2922, 2852, 1921, 1562, 1508, 1429, 1371, 1242, 1039, 956, 866, 806, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 9.32 (d, J=7.8 Hz, 1H), 8.69 (d, J=8.0 Hz, 1H), 8.58 (d, J=8.1 Hz, 1H), 8.52 (d, J=8.8 Hz, 1H), 8.00 (t, J=7.5 Hz, 2H), 7.84 (t, J=7.3 Hz, 1H), 7.75 (t, J=7.3 Hz, 1H), 7.70–7.54 (m, 2H), 3.01 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 157.5, 151.3, 133.5, 132.9, 130.7, 129.4, 129.1, 128.7, 128.6, 128.1, 127.6, 127.5, 127.1, 126.5, 125.5, 124.2, 123.1, 120.7, 118.6, 26.1.

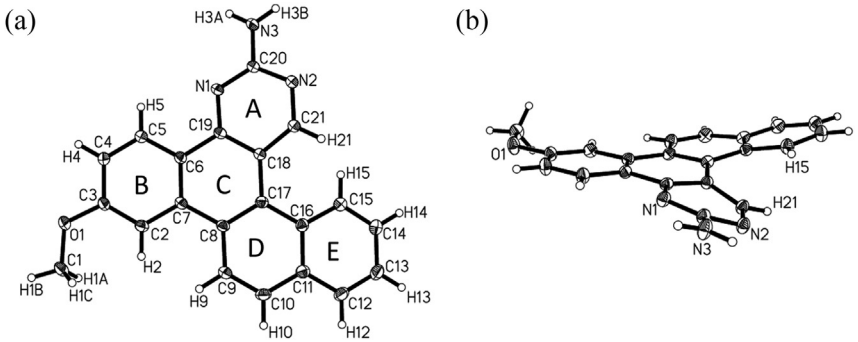

Fig. 1. Molecular structure of compound **5d** (recrystallized from ethyl acetate). (a) From vertical direction of the molecular plane; (b) From parallel direction of the molecular plane.

Table 4
Crystallographic data for compound **5d**

Empirical formula	$C_{21}H_{15}N_3O$
Formula weight	325.36
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a=18.237(10) Å b=13.871(8) Å c=14.473(9) Å alpha=90.00 deg. beta=121.706(9) deg. gamma=90.00 deg.
Volume (Å^3)	3115(3)
Z, Calculated density (g cm^{-3})	8, 1.388
Absorption coefficient (mm^{-1})	0.088
F(000)	1360
Crystal size, mm	0.36×0.31×0.22
Theta range for data collection	1.97–25.10 deg.
Limiting indices	$-21\leq h\leq 21$, $-14\leq k\leq 16$, $-17\leq l\leq 17$
Reflections collected/unique	7714/2771 [R(int)=0.0442]
Completeness to theta	99.8%
Max. and min. transmission	0.9808 and 0.9694
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2771/0/228
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	$R1$=0.0543, w$R2$=0.1542
R indices (all data)	$R1$=0.0843, w$R2$=0.1738
Largest diff. peak and hole	0.227 and −0.181 e. Å^{-3}

HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{21}H_{15}N_2$ 295.1235, found 295.1228.

*4.5.6. 2-Methyl-13-fluoro-benzo[h]-naphth[1,2-f]quinazoline (**5f**).* White powder. Yield 56.2 mg (30%). Mp 240–242 °C. IR (KBr) 3028, 2954, 1934, 1894, 1562, 1510, 1423, 1361, 1251, 1178, 1116, 1016, 939, 894, 852, 804, 744 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.99 (dd, J=9.8, 2.8 Hz, 1H), 8.74 (d, J=8.4 Hz, 1H), 8.62 (dd, J=9.0, 5.1 Hz, 1H), 8.53 (d, J=8.9 Hz, 1H), 8.06 (d, J=4.4 Hz, 1H), 8.05 (d, J=3.0 Hz, 1H), 7.74–7.69 (m, 1H), 7.66 (t, J=7.1 Hz, 1H), 7.59 (td, J=9.0, 2.8 Hz, 1H), 3.01 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.0, 162.7 (d, $^1J_{C-F}$=274.7 Hz), 157.8, 150.5 (d, $^4J_{C-F}$=4.0 Hz), 133.4, 131.3 (d, $^3J_{C-F}$=8.5 Hz), 129.5 (d, $^2J_{C-F}$=15.1 Hz), 129.0, 128.7, 127.8, 127.5, 127.3, 126.86, 125.7 (d, $^3J_{C-F}$=8.0 Hz), 123.7, 120.6, 119.4, 119.3, 119.1, 110.6(d, $^2J_{C-F}$=22.8 Hz), 26.1. HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{21}H_{14}FN_2$ 313.1141, found 313.1134.

*4.5.7. 2-Methyl-12-tert-butyl-benzo[h]-naphth[1,2-f]quinazoline (**5g**).* Yellow powder. Yield 115.5 mg (55%). Mp 196–198 °C. IR (KBr) 3063, 2958, 2866, 1566, 1497, 1433, 1367, 1269, 1230, 1035, 927, 840, 796, 758, 686 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 9.27 (d, J=8.7 Hz, 1H), 8.74 (d, J=8.2 Hz, 1H), 8.67–8.62 (m, 2H), 8.05 (d, J=4.5 Hz, 1H), 8.03 (s, 1H), 7.85 (d, J=8.5 Hz, 1H), 7.66 (dt, J=14.5, 7.0 Hz, 2H), 3.01 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 157.4, 154.0, 151.3, 133.4, 132.6, 129.4, 128.5, 128.4, 128.3, 127.6, 126.9, 126.8, 126.3, 125.7, 125.2, 124.3, 120.6, 119.0, 118.3, 35.5, 31.4, 26.1. HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{25}H_{23}N_2$ 351.1861, found 351.1852.

*4.5.8. 2-Methyl-12-methoxy-benzo[h]-naphth[1,2-f]quinazoline (**5h**).* Colorless powder. Yield 99.1 mg (62%). Mp 198–200 °C. IR (KBr) 3039, 2931, 2842, 1614, 1570, 1497, 1429, 1371, 1286, 1225, 1186, 1128, 1064, 1043, 960, 926, 781, 839, 688 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 9.22 (d, J=8.9 Hz, 1H), 8.71 (d, J=8.1 Hz, 1H), 8.43 (d, J=8.9 Hz, 1H), 8.00 (dd, J=13.2, 8.3 Hz, 2H), 7.91 (d, J=1.8 Hz, 1H), 7.73–7.57 (m, 2H), 7.33 (dd, J=8.9, 2.1 Hz, 1H), 4.04 (s, 3H), 2.97 (s, 3H)· ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 161.8, 157.3, 151.3, 134.7, 133.5, 129.4, 128.5, 128.4, 127.7, 127.6, 127.4, 127.0, 126.5, 124.8, 123.2, 120.7, 117.5, 116.4, 105.4, 55.5, 26.1; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{22}H_{17}N_2O$ 325.1341, found 325.1339.

*4.5.9. Benzo[h]-naphth[1,2-f]quinazoline (**5i**).* Colorless powder. Yield 90.7 mg (54%). Mp 179–181 °C. IR (KBr) 3045, 1944, 1739, 1606, 1566, 1512, 1456, 1413, 1336, 1230, 1161, 1103, 1039, 950, 873, 800, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 9.39 (s, 1H), 9.26 (d, J=7.9 Hz, 1H), 8.64 (d, J=8.0 Hz, 1H), 8.53 (d, J=8.1 Hz, 1H), 8.46 (d, J=8.7 Hz, 1H), 7.97 (t, J=7.5 Hz, 2H), 7.83 (t, J=7.4 Hz, 1H), 7.74 (t, J=7.5 Hz, 1H), 7.69–7.58 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 154.7, 151.1, 133.5, 132.9, 131.0, 129.4, 129.3, 129.1, 128.7, 128.6, 127.8, 127.5, 127.3, 126.7, 125.5, 123.8, 123.2, 121.1, 120.7, 58.4. HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{20}H_{13}N_2$ 281.1079, found 281.1077.

*4.5.10. 13-Fluoro-benzo[h]-naphth[1,2-f]quinazoline (**5j**).* Colorless powder. Yield 41.1 mg (23%). Mp 254–256 °C. IR (KBr) 3055, 1612, 1564, 1517, 1462, 1411, 1255, 1176, 1096, 1026, 800 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.19 (s, 1H), 9.45 (s, 1H), 8.99 (dd, J=9.7, 2.8 Hz, 1H), 8.77 (d, J=8.4 Hz, 1H), 8.67 (dd, J=9.0, 5.1 Hz, 1H), 8.57 (d, J=8.9 Hz, 1H), 8.11 (d, J=8.8 Hz, 1H), 8.07 (d, J=7.9 Hz, 1H), 7.75 (t, J=7.5 Hz, 1H), 7.69 (t, J=7.2 Hz, 1H), 7.63 (td, J=9.0, 2.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{C-F}$=247.5 Hz), 157.7, 154.7, 150.4(d, $^4J_{C-F}$=3.9 Hz), 133.4, 131.3(d, $^3J_{C-F}$=8.3 Hz), 129.6, 129.5, 129.4, 128.7, 128.3, 127.5, 127.4, 126.7, 125.7 (d, $^3J_{C-F}$=8.6 Hz), 123.3, 121.6, 120.6, 119.7 (d, $^2J_{C-F}$=23.3 Hz), 110.7 (d, $^2J_{C-F}$=22.6 Hz). HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{20}H_{12}FN_2$ 299.0985, found 299.0983.

*4.5.11. 12-tert-Butyl-benzo[h]-naphth[1,2-f]quinazoline (**5k**).* Yellow powder. Yield 70.6 mg (35%). Mp 166–168 °C. IR (KBr) 3049, 2958, 2924, 2862, 1612, 1560, 1504, 1458, 1415, 1369, 1259, 1107, 1026,920, 842, 798, 734 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.40 (s, 1H), 9.23 (d, J=8.6 Hz, 1H), 8.72 (d, J=8.3 Hz, 1H), 8.66–8.62 (m, 2H), 8.06–8.02 (m, 2H), 7.87 (d, J=8.3 Hz, 0H), 7.66 (m, 2H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 154.7, 154.3, 151.1, 133.4, 132.6, 129.5, 129.1, 128.9, 128.6, 127.5, 127.1, 126.8, 126.4, 126.0, 125.2, 123.9, 120.7, 120.6, 119.1, 35.6, 31.4. HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{24}H_{21}N_2$ 337.1705, found 337.1701.

*4.5.12. 12-Methoxy-benzo[h]-naphth[1,2-f]quinazoline (**5l**).* Colorless powder. Yield 102.3 mg (55%). Mp 227–228.5 °C. IR (KBr) 3047, 2983, 2916, 2844, 1614, 1570, 1513, 1419, 1342, 1285, 1227, 1170, 1053, 926, 844, 787, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 9.37 (s, 1H), 9.25 (d, J=8.9 Hz, 1H), 8.76 (d, J=8.2 Hz, 1H), 8.51 (d, J=8.9 Hz, 1H), 8.04 (d, J=8.5 Hz, 2H), 7.98 (s, 1H), 7.72–7.69 (m, 1H), 7.69–7.63 (m, 1H), 7.39 (d, J=8.8 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 157.3, 154.8, 151.2, 134.9, 133.6, 129.6, 129.1, 128.7, 128.3, 127.7, 127.5, 127.3, 126.8, 124.6, 123.2, 120.8, 120.1, 116.6, 105.7, 55.6. HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{21}H_{14}N_2O$ 311.1184, found 311.1181.

*4.5.13. 2-Amino-benzo[h]-phenanthren[9,10-f]quinazoline (**5m**).* Yellow powder. Yield 78.7 mg (38%). Mp 186–188 °C. IR (KBr) 3462, 3311, 3190, 2353, 1728, 1641, 1591, 1489, 1423, 1375, 1286, 1217, 1149, 1064, 738 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 9.09 (d, J=7.7 Hz, 1H), 8.81 (s, 2H), 8.59 (d, J=7.7 Hz, 2H), 8.40 (d, J=4.7 Hz, 1H), 7.81 (t, J=6.8Hz, 1H), 7.71 (m, 5H), 7.20 (s, 2H)· ^{13}C NMR (150 MHz, DMSO-d_6) δ 161.0, 159.8, 152.4, 131.5, 130.3, 129.8, 129.6, 128.9, 128.8, 128.4, 128.0, 127.7, 127.3, 127.2, 127.1, 127.0, 126.5, 126.4, 125.6, 124.9, 123.9, 123.0, 112.7. HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for $C_{24}H_{16}N_3$ 346.1344, found 346.1337.

*4.5.14. 2-Amino-5-fluoro-benzo[h]-phenanthren[9,10-f]quinazoline (**5n**).* Yellow powder. Yield 76.2 mg (35%). Mp 284–286 °C. IR (KBr) 3502, 3286, 3159, 1618, 1583, 1440, 1379, 1211, 1114, 1047, 974, 916, 819, 738 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.82 (t, J=7.0 Hz, 2H), 8.68 (dd, J=10.1, 2.9 Hz, 1H), 8.61 (dd, J=9.0, 5.4 Hz,

1H), 8.50 (d, J=8.0 Hz, 1H), 8.34 (d, J=7.9 Hz, 1H), 7.70 (m, 5H), 7.24 (s, 2H)·^{13}C NMR (150 MHz, DMSO-d_6) δ 161.0, 160.5(d, $^{1}J_{C-F}$=244.5 Hz), 160.0, 151.4(d, $^{4}J_{C-F}$=3.6 Hz),130.9, 130.9, 130.8, 130.2, 129.6, 128.8, 128.3, 128.1, 127.6, 127.3, 127.2, 127.1, 127.0, 126.5, 125.0, 123.8(d, $^{3}J_{C-F}$=10.9 Hz), 122.5, 118.0(d, $^{2}J_{C-F}$=23.1 Hz), 112.9, 109.3(d, $^{2}J_{C-F}$=22.5 Hz). HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{24}H_{15}FN_3$ 386.1069, found 346.1059.

*4.5.15. 2-Amino-12-tert-butyl-benzo[h]-phenanthren[9,10-f]quinazoline (**5o**).* Yellow powder. Yield 139.5 mg (58%). Mp 232–234 °C. IR (KBr) 3496, 3302, 3186, 2922, 2858, 1722, 1622, 1571, 1485, 1440, 1373, 1273, 1227, 1165, 1114, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 9.09 (d, J=8.6 Hz, 1H), 8.71 (m, 4H), 8.41 (d, J=7.5 Hz, 1H), 7.77 (d, J=8.5 Hz, 1H), 7.66 (m, 4H), 5.51 (s, 2H), 1.47 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 160.1, 153.2, 152.8, 132.4, 130.9, 130.5, 129.3, 128.9, 128.2, 128.0, 127.2, 127.0, 126.8, 126.6, 126.4, 125.7, 125.4, 125.1, 124.8, 124.6, 123.7, 123.7, 114.5, 35.4, 31.3. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{28}H_{24}N_3$ 402.1970, found 402.1948.

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Supplementary data

Supplementary data related to this article can be found, in the online version at http://dx.doi.org/10.1016/j.tet.2016.04.080.

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