Supporting Information

Visible-Light-Induced Radical Cascade Cyclization of

2-Isocyanobiaryls via 1,5-hydrogen atom transfer (1,5-HAT)

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1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All of the reactions were carried out in pressure tubes. Except for the specially mentioned dry solvent, all the solvents were treated according to general methods. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. Product purification was done using silica gel column chromatography. Thin-layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2 mm), while column chromatography characterization was performed with silica gel (100-200 mesh). ¹H NMR and ¹³C NMR spectra were recorded with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. ¹H NMR spectra were recorded at 400 or 600 MHz (Varian) and ¹³C NMR spectra were recorded at 100 or 150 MHz (Varian). ¹⁹F NMR spectra were recorded at 376 MHz. Shifts are reported in ppm downfield from CDCl₃ (δ =7.26 ppm) for ¹H NMR and chemical shifts for ¹³C NMR spectra are reported in ppm relative to the central CDCl₃ (δ = 77.0 ppm). Coupling constants were given in Hz. The following notations were used: br-broad, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, dd-doublet of doublet, dt-doublet of triplet, td-triplet of doublet. HRMS spectra were recorded a MicrOTOF-QIII (Bruker.Daltonics). Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China). 2-Isocyanobiaryls and hydroxamic acid derivatives were synthesized according to the literature.

2. Condition optimization

Table 1. Optimization of reaction conditions for 3aa.^a



Entry	Photocatalyst	Light source	Solvent	Base	Yield(%) ^b
1	<i>fac</i> -Ir(ppy) ₃	450-455 nm	DMSO	DABCO	79
2	<i>fac</i> -Ir(ppy) ₃	450-455 nm	DMSO	NaHCO ₃	trace
3	<i>fac</i> -Ir(ppy) ₃	450-455 nm	DMSO	K ₂ CO ₃	trace
4	<i>fac</i> -Ir(ppy) ₃	450-455 nm	DMSO	DIPEA	73
5	<i>fac</i> -Ir(ppy) ₃	450-455 nm	DMSO	-	81
6	Ph-PTZ	450-455 nm	DMSO	-	93
7	Ru(bpy) ₃ PF ₆	450-455 nm	DMSO	-	70

8	Ru(bpy) ₃ Cl ₂	450-455 nm	DMSO	-	N.R.
9	EosinY	450-455 nm	DMSO	-	trace
10	4CzIPN	450-455 nm	DMSO	-	trace
11	4CzTPN	450-455 nm	DMSO	-	trace
12	Ir(ppy) ₂ (dtbbpy)PF ₆	450-455 nm	DMSO	-	61
13	[Ir{dFCF3ppy}2(bpy)]PF6	450-455 nm	DMSO	-	67
14	Ph-PTZ	450-455 nm	DMF	-	51
15	Ph-PTZ	450-455 nm	DMA	-	43
16	Ph-PTZ	450-455 nm	THF	-	trace
17	Ph-PTZ	450-455 nm	MeCN	-	50
18	Ph-PTZ	450-455 nm	DCM	-	trace
19	Ph-PTZ	450-455 nm	Dioxane	-	77
20	Ph-PTZ	450-455 nm	Acetone	-	41
21	Ph-PTZ	390-395 nm	DMSO	-	79
22	Ph-PTZ	420-425 nm	DMSO	-	88
23	Ph-PTZ	520-525 nm	DMSO	-	73
24 ^c	Ph-PTZ	450-455 nm	DMSO	-	78
25 ^d	Ph-PTZ	450-455 nm	DMSO	-	92
26 ^e	Ph-PTZ	450-455 nm	DMSO	-	69
$27^{\rm f}$	Ph-PTZ	450-455 nm	DMSO	-	93
28	-	450-455 nm	DMSO	-	trace
29	Ph-PTZ	Dark conditions	DMSO	-	N.R.
30 ^g	Ph-PTZ	450-455 nm	DMSO	-	N.R.

^aReaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), Solvent (1.0 mL), Photocatalyst (5 mol%), Base (2.0 equiv.), 12 W LEDs, at rt for 24 h under Ar. ^b Isolated yield. ^cPC (2 mol%). ^dPC (10 mol%). ^c12 h. ^f36 h. ^gOpen to air. N.R. = no reaction.

3. Experimental information

3.1 Synthesis of 2-isocyanobiaryls



Following a literature procedures ¹:

Step 1: Biaryl-2-amines (**S3**): 2-bromoaniline (**S1**, 10 mmol), aryl boronic acid (**S2**, 15 mmol), $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 0.02 equiv.) and K_2CO_3 (40 mmol) were placed in a dry three necked flask under Ar. Then, EtOH (12 mL) and H₂O (12 mL) were added and the mixture was stirred at 80 °C for 4 h. The mixture was then cooled to room temperature and diluted with EtOAc. The organic layer was washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

Step 2: Formamides (S4): S3 (3 mmol) and THF (6 mL) were added into a flask and cooled S3 to 0 °C. Acetic formic anhydride (2.5 mL), which was prepared from the reaction of acetic anhydride with formic acid (1.1 equiv.) at 55 °C for 2 h, was added dropwise into the solution of S3 at 0 °C. After the addition was completed, the mixture was warmed to room temperature and stirred for 1 h. Then, the mixture was treated with saturated solution of NaHCO₃ and extracted with EtOAc three times. The extract was dried and concentrated under vacuum to give formamide S4. These materials were used for the subsequent dehydration without further purification.

Step 3: 2-Isocyanobiaryl (**S5**): THF (6 mL), NEt₃ (2 mL), **S4** (2.8 mmol) were added to an oven-dried two-neck flask under N₂ atmosphere. After cooling the reaction mixture to 0 °C by using ice bath, POCl₃ (0.8 mL) was added via syring pump for a period of 2 h. After the addition was complete, the resulted mixture was stirred at 0 °C for an additional 1 h. Then, the mixture was quenched with saturated solution of NaHCO₃ and extracted with EtOAc (25 mL \times 3). The combined organic layer was dried (MgSO₄), filtered and evaporated followed by a silica gel column chromatography.

3.2 Preparation of hydroxamic acid derivatives



Following a literature procedures ²:

Step 1: To a solution of carboxylic acid (1.0 equiv.) and 3-5 drops of anhydrous DMF in anhydrous CH_2Cl_2 (0.5 M) at 0 °C, oxalyl chloride (1.5 equiv.) was added dropwise over 10 minutes. The reaction was vigorously stirred at room temperature for 3 h. The solvent was removed in vacuum. Anhydrous CH_2Cl_2 was added to remove the residual of oxalyl chloride in vacuum. Then the resulting acyl chloride was redissolved in anhydrous acetonitrile and used directly for the next step without further purification.

Step 2: A solution of the N-(tert-butyl)hydroxylamine hydrochloride in anhydrous THF (0.4 M) was cooled to 0 °C, treated with DIPEA (2.0 equiv.) and stirred for 15 minutes. The acyl

chloride (1.0 equiv.) in anhydrous acetonitrile was added dropwise over 15 minutes and the mixture was allowed to warm to room temperature overnight. The mixture was diluted with saturated NaHCO₃ and EtOAc and the layers were separated. The aqueous layer was extracted twice with EtOAc and the combined organic layers were washed with 1 M HCl, saturated NaHCO₃ and brine, successively, and then evaporated. Purification by column chromatography on silica gel eluting with petroleum ether and EtOAc gave the hydroxylamine.

Step 3: To a solution of hydroxylamine (1.1 equiv.) in anhydrous CH_2Cl_2 (0.35 M) at 0 °C, Et₃N (1.5 equiv.) was added dropwise. 4-trifluoromethyl-benzoyl chloride (1.0 equiv.) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 2 h. The mixture was diluted with saturated NaHCO₃ and CH_2Cl_2 and the layers were separated. The aqueous layer was extracted twice with CH_2Cl_2 and the combined organic layers were washed with 1 M HCl, saturated NaHCO₃ and brine, successively, and then evaporated. Purification by column chromatography on silica gel eluting with petroleum ether and EtOAc gave the hydroxamide compounds 2.

3.3 General procedure for the synthesis of desired products 3 and 4 (3aa as an example)



To an oven-dried 10 mL glass tube equipped with a stir bar, was added **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.) and photocatalyst Ph-PTZ (5 mol%). The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs (450 nm) for 24 h. After completion of the reaction, 5.0 mL water was added and extracted by ethyl acetate (3×5.0 mL). The combined organic layer was washed with brine (5.0 mL) and then dried over anhydrous Na₂SO₄ and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel eluting with hexane/ethyl acetate or hexane/dichloromethane.

4. Scale-Up synthesis of 3aa



To an oven-dried 50 mL schlenk tube equipped with a stir bar, was added **1a** (6 mmol, 1.0 equiv.), **2a** (9 mmol, 1.5 equiv.) and photocatalyst Ph-PTZ (5 mol%). The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (20 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs (450 nm) for 24 h. After completion of the reaction, 50 mL water was added and extracted by ethyl acetate (3×10 mL). The combined organic layer was

washed with brine (10 mL) and then dried over anhydrous Na₂SO₄ and evaporated in vacuum. The residue was directly purified by a silica gel column chromatography using ethyl acetate/petroleum as the eluent to afford product **3aa** (1.86 g, 89%).

5. Diversity of the products 5.1 C–H alkylation



The product **3aa** (20.0 mg, 1.0 equiv.), 1-AdCOOH (20.7 mg, 2.0 equiv.), AgOAc (2.8 mg, 0.3 equiv.) and $K_2S_2O_8$ (46.0 mg, 3.0 equiv.) were weighed into a Schlenk tube, then a mixture of acetone/water (1.0 mL, 0.5:0.5) was added through the side-arm by syringe. The mixture was stirred at 50 °C for 3 h. After reaction, the mixture was cooled to room temperature. Then saturated NaHCO₃ solution (10 mL) was added, and it was extracted with CH₂Cl₂ (10 mL × 3), washed with saturated brine (20 mL), and dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography affording the desired product **5**.

5.2 Alcoholysis



The product **3aa** (15.0 mg, 1.0 equiv.) were added into a Schlenk tube, then H_2SO_4 (con. 0.13 mL, 55.0 equiv.), and MeOH (0.72 mL) was added through the side-arm by syringe. The mixture was stirred at 90 °C for 3 h. After reaction, the mixture was cooled to room temperature. It was neutralized with saturated NaHCO₃ solution, extracted with CH₂Cl₂ (15 mL × 3), and washed with saturated brine (10 mL), then dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography affording the desired product **6**.

5.3 Hydrolysis



The product **3aa** (15.0 mg, 0.03 mmol) were added to an aqueous solution of HCl (4 N, 3 mL). The mixture was flushed at 100 $^{\circ}$ C in oil bath for 3 h. After reaction, the mixture was cooled

to room temperature. It was adjusted pH with saturated NaHCO₃ solution, extracted with ethyl acetate (15 mL \times 3), and washed with saturated brine (10 mL), then dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography affording the desired product 7.

6. Control experiments



To an oven-dried 10 mL glass tube equipped with a stir bar, was added **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), photocatalyst Ph-PTZ (5 mol%) and TEMPO (0.30 mmol, 3.0 equiv.) were added. The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs (450 nm) for 24 h using electronic fan to cool the tube. When 3.0 equiv. of TEMPO was subjected into the reaction of **1a** with **2a** under the standard conditions, no corresponding product **3aa** was formed by TLC analysis. And the radical adduct with TEMPO was detected by HRMS (ESI-TOF).



To an oven-dried 10 mL glass tube equipped with a stir bar, was added 1a (0.10 mmol, 1.0 equiv.), 2a (0.15 mmol, 1.5 equiv.), photocatalyst Ph-PTZ (5 mol%). The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, 1,1-diphenylethylene (0.30 mmol, 3.0 equiv.) and anhydrous DMSO (1.0 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs (450 nm) for 24 h using electronic fan to cool the tube. When 3.0 equiv. of 1,1-diphenylethylene was subjected into the reaction of 1a with 2a under the standard conditions, a trace amount of product 3aa was formed by TLC analysis. And the radical adduct with 1,1-diphenylethylene was detected by HRMS (ESI-TOF).



Figure S2. HRMS spectra of the radical adduct with 1,1-diphenylethylene

7. Light on/off experiments

In a reaction vial equipped with a PTFE-coated magnetic stir bar, 2-isocyanobiaryls **1a** (0.1 mmol, 1.0 equiv.), hydroxamic acid derivatives **2a** (0.15 mmol, 1.5 equiv.) and Ph-PTZ (5 mol%) were dissolved in anhydrous DMSO (1.0 mL). The reaction vial was placed in 12 W Blue LEDs (450-455 nm) and irradiated with visible light for 3 h and without light for 3 h at room temperature under Ar. The product yield for the reaction was determined each time by ¹H NMR experiment using 1,3,5-trimethoxy benzene as internal standard.



Figure S3. Light on/off experiments

8. Stern-Volmer fluorescence quenching experiments

DMSO was degassed with a stream of argon for 30 min. Ph-PTZ (4.0 μ mol) was dissolved in 1.0 mL DMSO to prepare a 4×10⁻³ M solution. 100 μ L of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the solution of quencher **1a** or **2a** in DMSO (1.5 mL, 10 mM) was added in increasing amounts (0, 100 μ L, 200 μ L, 300 μ L, 400 μ L, 500 μ L) to the volumetric flasks and the volume of volumetric flasks were adjusted to 10 mL by adding DMSO. All solutions were excited at 318 nm and the emission intensity at 445 nm was observed. All fluorescence measurements were recorded by a F-98 FL Spectrophotometer.



Figure S4. The emission quenching spectrum of Ph-PTZ by various concentrations of quencher 1a.



Figure S5. The emission quenching spectrum of Ph-PTZ by various concentrations of quencher 2a.



Figure S6. Stern-Volmer plot for the emission quenching of Ph-PTZ by various concentrations of quencher 1a or 2a.

9. Cyclic voltammetry experiments

Cyclic voltammetry experiments were performed using a CHI660E Electrochemical workstation with a glassy carbon working electrode (3 mm in diameter), a saturated calomel reference electrode, and a platinum electrode as the counter electrode in a 50 mL glass vial fitted. Solutions of **1a** and **2a** in DMSO (0.01 M) were tested with tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) as electrolyte.



Figure S7. Cyclic voltammogram of 1a in DMSO



Figure S8. Cyclic voltammogram of 2a in DMSO

10. References

[1] B. Zhang, C. Mück-Lichtenfeld, C. G. Daniliuc and A. Studer, 6-Trifluoromethyl-Phenanthridines through Radical Trifluoromethylation of Isonitriles, *Angew. Chem.*, 2013, **125**, 10992 - 10995.

[2] H. Chen, L. Guo and S. Yu, Primary, Secondary, and Tertiary γ -C(sp³)-H Vinylation of Amides via Organic Photoredox-Catalyzed Hydrogen Atom Transfer, *Org. Lett.*, 2018, **20**, 6255-6259.

11. Characterization of the products *N*-(*tert*-butyl)-4-methyl-4-(phenanthridin-6-yl)pentanamide (3aa)



White solid, mp: 160-162 °C; 32.4 mg, 93% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.70 – 8.64 (m, 2H), 8.53 (dd, J = 8.2, 1.4 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.72 – 7.61 (m, 3H), 5.08 (s, 1H), 2.53 – 2.48 (m, 2H), 1.95 (dd, J = 10.2,

6.2 Hz, 2H), 1.71 (s, 6H), 1.23 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.6, 163.9, 141.7, 132.8, 129.2, 128.5, 127.4, 126.6, 125.6, 125.5, 123.6, 122.4, 121.9, 120.7, 49.9, 42.2, 37.6, 32.6, 28.5, 27.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₉N₂O 349.2274; Found 349.2271.

N-(tert-butyl)-4-methyl-4-(8-methylphenanthridin-6-yl)pentanamide (3ba)



White solid, mp: 154-156 °C; 31.2 mg, 86% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, J = 8.4 Hz, 1H), 8.49 (dd, J = 8.1, 1.4 Hz, 1H), 8.41 (s, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.69 – 7.58 (m, 3H), 5.08 (s, 1H), 2.61 (s, 3H), 2.53 – 2.47 (m, 2H), 1.97 – 1.92 (m, 2H),

1.71 (s, 6H), 1.24 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.8, 163.6, 141.4, 135.1, 130.6, 130.2, 129.1, 126.9, 126.2, 125.5, 123.8, 122.4, 121.8, 120.5, 49.8, 42.2, 37.6, 32.6, 28.5, 27.7, 21.2. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2433.

*N-(tert-*butyl)-4-(8-butylphenanthridin-6-yl)-4-methylpentanamide (3ca)



Yellow solid, mp: 158-160 °C; 34.3 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, J = 8.5 Hz, 1H), 8.49 (dd, J = 8.2, 1.5 Hz, 1H), 8.42 (d, J = 1.7 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.69 – 7.58 (m, 3H), 5.08 (s, 1H), 2.87 (t, J = 7.7 Hz, 2H), 2.54 – 2.48 (m, 2H), 1.99 – 1.92 (m, 2H), 1.78 – 1.73 (m, 2H), 1.72 (s, 6H), 1.43 (q, J

= 7.5 Hz, 2H), 1.24 (s, 9H), 0.98 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.8, 164.7, 142.5, 141.1, 131.9, 130.6, 130.1, 128.0, 126.7, 126.6, 124.8, 123.5, 122.9, 121.5, 50.9, 43.3, 38.8, 36.1, 33.6, 29.5, 28.78, 22.3, 14.0. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₃₇N₂O 405.2900; Found 405.2903.

*N-(tert-*butyl)-4-(8-(*tert-*butyl)phenanthridin-6-yl)-4-methylpentanamide (3da)



White solid, mp: 157-159 °C; 36.4 mg, 90% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.64 – 8.59 (m, 2H), 8.50 (dd, J = 8.1, 1.5 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.87 (dd, J = 8.7, 2.0 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.63 – 7.57 (m, 1H), 5.08 (s, 1H), 2.56 – 2.50 (m, 2H), 1.97 (dd, J = 9.8, 6.6 Hz, 2H), 1.73 (s, 6H), 1.48 (s, 9H),

1.23 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.7, 164.0, 148.2, 141.6, 130.5, 129.0, 126.9, 126.7, 125.5, 123.5, 122.4, 122.3, 121.6, 120.5, 49.8, 42.1, 38.1, 34.2, 32.7, 30.4, 28.5, 27.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₃₇N₂O 405.2900; Found 405.2904.

N-(tert-butyl)-4-(8-methoxyphenanthridin-6-yl)-4-methylpentanamide (3ea)



Yellow solid, mp: 166-168 °C; 33.7 mg, 89% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, J = 9.1 Hz, 1H), 8.46 – 8.41 (m, 1H), 8.07 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 2.6 Hz, 1H), 7.61 (m, 2H), 7.43 (dd, J = 9.1, 2.5 Hz, 1H), 5.10 (s, 1H), 4.00 (s, 3H), 2.53 – 2.47 (m,

2H), 1.98 – 1.91 (m, 2H), 1.72 (s, 6H), 1.23 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.6, 164.0, 157.7, 142.0, 130.2, 128.0, 127.4, 126.7, 125.8, 124.5, 123.5, 121.2, 119.7, 108.8, 55.6, 50.9, 43.2, 38.4, 33.6, 29.4, 28.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O₂ 379.2380; Found 379.2382.

N-(tert-butyl)-4-methyl-4-(8-phenoxyphenanthridin-6-yl)pentanamide (3fa)



Yellow oil; 35.2 mg, 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 9.0 Hz, 1H), 8.46 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.09 (d, *J* = 2.6 Hz, 2H), 7.64 (m, 2H), 7.53 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.20 (m, 1H), 7.17 – 7.08 (m, 2H), 5.10 (s, 1H), 2.37 – 2.29 (m, 2H), 1.97 – 1.89 (m, 2H), 1.59 (s, 6H), 1.25 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.6, 163.2, 155.4, 154.6, 129.2, 129.1, 128.5, 126.9, 125.9, 124.6, 123.8, 123.1, 122.2, 120.8, 120.4, 118.4,

114.0, 49.8, 42.0, 37.6, 32.6, 28.2, 27.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{33}N_2O_2$ 441.2531; Found 441.2532.

N-(tert-butyl)-4-methyl-4-(8-phenylphenanthridin-6-yl)pentanamide (3ga)



Colorless oil; 31.8 mg, 75% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.85 (d, J = 1.9 Hz, 1H), 8.74 (d, J = 8.6 Hz, 1H), 8.55 (dd, J = 8.1, 1.4 Hz, 1H), 8.12 (d, J = 7.9 Hz, 1H), 8.05 (dd, J = 8.5, 1.8 Hz, 1H), 7.76 (dd, J = 7.3, 1.7 Hz, 2H), 7.72 (t, J = 8.0 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 5.08 (s, 1H), 2.59 – 2.53 (m, 2H), 2.00 (t, J = 8.4 Hz, 2H), 1.77 (s,

6H), 1.22 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.6, 164.1, 139.6, 138.2, 131.8, 129.1, 128.2, 127.8, 127.4, 126.8, 126.4, 125.8, 124.9, 124.0, 122.5, 122.2, 120.7, 49.9, 42.3, 37.9, 32.6, 28.7, 27.7, 22.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₉H₃₃N₂O 425.2587; Found 425.2583.

*N-(tert-*butyl)-4-(8-fluorophenanthridin-6-yl)-4-methylpentanamide (3ha)



White solid, mp: 132-134 °C; 32.3 mg, 88% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.67 (dd, J = 9.2, 5.7 Hz, 1H), 8.46 (dd, J = 8.2, 1.5 Hz, 1H), 8.26 (dd, J = 11.3, 2.6 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.69 (m, 1H), 7.62 (m, 1H), 7.55 (m,1H), 5.13 (s, 1H), 2.49 – 2.44 (m, 2H), 1.98 – 1.93 (m, 2H), 1.69 (s, 6H), 1.24 (s, 9H). ¹⁹F

NMR (376 MHz, Chloroform-*d*) δ -111.69. ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.5, 164.2 (d, J = 4.0 Hz), 160.4 (d, J = 247.0 Hz), 130.5 (d, J = 1.8 Hz), 130.3, 128.3, 127.1, 125.7 (d, J = 7.6 Hz), 125.3 (d, J = 8.6 Hz), 123.0, 121.5, 118.8 (d, J = 23.6 Hz), 112.6 (d, J = 22.4 Hz), 51.0, 43.2, 38.4, 33.5, 29.3, 28.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₈FN₂O 367.2180; Found 367.2182.

*N-(tert-*butyl)-4-(8-chlorophenanthridin-6-yl)-4-methylpentanamide (3ia)



White solid, mp: 137-139 °C; 35.6 mg, 93% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.58 (m, 2H), 8.46 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.62 (m, 1H), 5.12 (s, 1H), 2.50 – 2.44 (m, 2H), 1.98 – 1.93 (m, 2H), 1.70 (s, 6H), 1.25 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.5, 163.9,

142.7, 132.33, 132.29, 130.3, 130.1, 128.8, 127.1, 127.0, 125.4, 124.7, 122.8, 121.6, 51.0, 43.2, 38.6, 33.6, 29.4, 28.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}CIN_2O$ 383.1885; Found 383.1883.

N-(tert-butyl)-4-(8-cyanophenanthridin-6-yl)-4-methylpentanamide (3ja)



White solid, mp: 201-203 °C; 32.1 mg, 86% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.96 (d, J = 1.6 Hz, 1H), 8.73 (d, J = 8.6 Hz, 1H), 8.49 (dd, J = 8.3, 1.4 Hz, 1H), 8.12 (dd, J = 8.2, 1.4 Hz, 1H), 7.94 (dd, J = 8.6, 1.6 Hz, 1H), 7.78 (m, 1H), 7.67 (m, 1H), 5.18 (s, 1H), 2.50 – 2.42 (m, 2H), 2.01 – 1.95 (m, 2H), 1.69 (s, 6H), 1.24 (s,

9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.2, 164.4, 143.6, 136.7, 132.8, 130.9, 130.5, 130.2, 127.5, 124.4, 123.9, 122.2, 122.1, 118.9, 109.9, 51.0, 43.3, 38.6, 33.5, 29.5, 28.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₂₈N₃O 374.2227; Found 374.2225.

N-(tert-butyl)-4-methyl-4-(10-methylphenanthridin-6-yl)pentanamide (3ka)

		O ∐	
N [×]	X >	́_Ń	

White solid, mp: 141-143 °C; 33.7 mg, 93% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.74 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.1 Hz, 1H), 7.71 – 7.55 (m, 4H), 5.05 (s, 1H), 3.12 (s, 3H), 2.54 – 2.46 (m, 2H), 1.94 (dd, J = 10.0, 6.3 Hz, 2H), 1.71 (s,

6H), 1.22 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.7, 164.2, 142.9, 134.8, 132.8, 132.4, 129.4, 126.6, 125.4, 125.1, 124.8, 124.7, 124.6, 123.6, 49.8, 42.3, 37.9, 32.6, 28.9, 27.7, 26.2. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2435.

*N-(tert-*butyl)-4-methyl-4-(1-methylphenanthridin-6-yl)pentanamide (3la)



Yellow solid, mp: 180-182 °C; 30.1 mg, 83% yield. ¹H NMR (400 MHz, Chloroform-*d*) & 8.89 (d, *J* = 8.5 Hz, 1H), 8.71 – 8.66 (m, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.77 (m, 1H), 7.67 (m, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 5.07 (s, 1H), 3.09 (s, 3H), 2.54 –

2.47 (m, 2H), 1.99 – 1.91 (m, 2H), 1.71 (s, 6H), 1.23 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.7, 164.3, 144.2, 135.1, 134.4, 130.9, 128.9, 128.6, 127.5, 127.31, 127.26, 125.7, 125.6, 123.2, 50.9, 43.0, 38.8, 33.7, 29.6, 28.7, 26.6. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2433.

*N-(tert-*butyl)-4-methyl-4-(2-methylphenanthridin-6-yl)pentanamide (3ma)



White solid, mp: 176-178 °C; 30.8 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.64 (m, 2H), 8.31 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.77 (m, 1H), 7.64 (m, 1H), 7.52 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.10 (s, 1H), 2.61 (s, 3H), 2.52 – 2.46 (m, 2H), 1.97 – 1.91 (m, 2H),

1.70 (s, 6H), 1.23 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.8, 163.9, 141.1, 136.5, 133.6, 130.1, 129.9, 129.4, 127.6, 126.3, 124.7, 123.2, 122.9, 121.3, 50.9, 43.1, 38.7, 33.6, 29.5, 28.7, 22.0. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2430.

*N-(tert-*butyl)-4-methyl-4-(3-methylphenanthridin-6-yl)pentanamide (3na)



White solid, mp: 183-185 °C; 29.7 mg, 82% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 – 8.60 (m, 2H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.62 (m, 1H), 7.49 – 7.41 (m, 1H), 5.12 (s, 1H), 2.58 (s, 3H), 2.53 – 2.46 (m, 2H), 1.94

(dd, J = 10.0, 6.2 Hz, 2H), 1.70 (s, 6H), 1.24 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.8, 165.0, 142.9, 138.6, 133.9, 129.7, 129.5, 128.4, 127.6, 126.0, 124.3, 122.8, 121.5, 121.1, 50.9, 43.2, 38.7, 33.6, 29.5, 28.8, 21.4. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2430.

N-(tert-butyl)-4-methyl-4-(4-methylphenanthridin-6-yl)pentanamide (30a)



White solid, mp: 181-183 °C; 27.9 mg, 77% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.66 (dd, J = 17.3, 8.4 Hz, 2H), 8.39 (d, J = 8.1 Hz, 1H), 7.77 (m, 1H), 7.65 (m, 1H), 7.57 (d, J = 7.1 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 5.02 (s, 1H), 2.86 (s, 3H), 2.55 – 2.48 (m, 2H),

 $1.97 - 1.92 \text{ (m, 2H)}, 1.72 \text{ (s, 6H)}, 1.22 \text{ (s, 9H)}. {}^{13}\text{C NMR} \text{ (100 MHz, Chloroform-}d\text{) } \delta \text{ 172.7, 163.3, 141.2, 138.2, 134.2, 129.4, 129.1, 127.5, 126.29, 126.27, 124.3, 123.3, 123.1, 119.5, 50.9, 43.9, 38.4, 33.5, 29.5, 28.7, 18.3. HRMS (ESI) m/z: [M+H]^+ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2431.$

*N-(tert-*butyl)-4-(2-methoxyphenanthridin-6-yl)-4-methylpentanamide (3pa)



White solid, mp: 171-173 °C; 29.5 mg, 78% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 – 8.58 (m, 2H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 2.7 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 8.9, 2.7 Hz, 1H), 5.08 (s,

1H), 4.01 (s, 3H), 2.52 – 2.45 (m, 2H), 1.93 (t, J = 8.3 Hz, 2H), 1.69 (s, 6H), 1.22 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.7, 162.3, 158.3, 138.1, 133.4, 131.6, 129.2, 127.6, 126.6, 124.8, 124.4, 123.0, 118.3, 102.6, 55.7, 50.9, 43.0, 38.6, 33.6, 29.6, 28.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O₂ 379.2380; Found 379.2383.

N-(tert-butyl)-4-(3-methoxyphenanthridin-6-yl)-4-methylpentanamide (3qa)

Yellow solid, mp: 172-174 °C; 30.3 mg, 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dd, J = 19.1, 8.4 Hz, 2H), 8.40 (d, J = 9.0 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.49 (d, J = 2.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 5.04 (s,

1H), 3.99 (s, 3H), 2.54 – 2.46 (m, 2H), 1.95 – 1.89 (m, 2H), 1.71 (s, 6H), 1.22 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.5, 164.5, 158.9, 143.3, 133.0, 128.6, 126.6, 124.4, 122.6, 121.9, 121.5, 116.6, 116.4, 109.0, 54.5, 49.8, 42.2, 37.5, 32.5, 28.6, 27.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O₂ 379.2380; Found 379.2383.

*N-(tert-*butyl)-4-(3-(*tert-*butyl)phenanthridin-6-yl)-4-methylpentanamide (3ra)



White solid, mp: 186-188 °C; 35.6 mg, 88% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.64 (t, *J* = 8.6 Hz, 2H), 8.46 (d, *J* = 8.7 Hz, 1H), 8.07 (s, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.70 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 5.02 (s, 1H), 2.54 –

2.48 (m, 2H), 1.93 (t, J = 8.1 Hz, 2H), 1.72 (s, 6H), 1.47 (s, 9H), 1.21 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.7, 164.9, 151.8, 142.8, 133.8, 129.5, 127.6, 126.1, 126.0, 125.0, 124.4, 122.9, 121.4, 121.0, 50.9, 43.3, 38.5, 34.9, 33.6, 31.4, 29.6, 28.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₃₇N₂O 405.2900; Found 405.2904.

*N-(tert-*butyl)-4-(2-cyanophenanthridin-6-yl)-4-methylpentanamide (3sa)



White solid, mp: 204-206 °C; 31.7 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.85 (d, *J* = 1.8 Hz, 1H), 8.71 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.62 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.76 (m, 1H), 5.10 (s, 1H), 2.54 –

2.47 (m, 2H), 1.97 – 1.92 (m, 2H), 1.70 (s, 6H), 1.22 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.2, 168.9, 144.3, 132.7, 131.3, 130.7, 130.0, 128.0, 127.9, 127.6, 125.0, 123.7, 122.9, 119.3, 110.0, 51.0, 43.8, 38.4, 33.4, 29.5, 28.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₂₈N₃O 374.2227; Found 374.2229.

N-(tert-butyl)-4-(7,9-dimethoxyphenanthridin-6-yl)-4-methylpentanamide (3ta)



Yellow solid, mp: 187-189 °C; 34.3 mg, 84% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 5.13 (s, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 2.48 – 2.35 (m, 2H), 1.99 – 1.90 (m, 2H), 1.54 (s, 6H), 1.23 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.7, 164.6,

161.1, 158.5, 142.7, 137.9, 129.7, 128.7, 126.0, 122.6, 122.2, 113.0, 99.2, 95.7, 55.6, 54.9, 50.8, 44.9, 38.5, 34.8, 29.0, 28.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}N_2O_3$ 409.2486; Found 409.2488.

N-(tert-butyl)-4-methyl-4-(7,8,9-trimethoxyphenanthridin-6-yl)pentanamide (3ua)



White solid, mp: 203-205 °C; 34.2 mg, 78% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.74 (s, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 5.20 (s, 1H), 4.10 (s, 3H), 4.01 (s, 3H), 3.93 (s, 3H), 2.43 (t, 2H), 1.95 (t, J = 8.4 Hz, 2H), 1.55 (s, 6H), 1.25 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.6, 164.2, 155.3, 151.4, 142.5,

142.2, 131.7, 129.7, 128.2, 126.2, 122.2, 121.7, 115.8, 98.5, 61.2, 56.1, 50.9, 44.9, 38.4, 34.7, 28.9, 28.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₃₄N₂O₄ 439.2591; Found 439.2587.

N-isopropyl-4-methyl-4-(phenanthridin-6-yl)pentanamide (4aa)



White solid, mp: 155-157 °C; 30.1 mg, 90% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.66 (dd, J = 15.2, 8.4 Hz, 2H), 8.53 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.65 (m, 3H), 5.17 (s, 1H), 3.96 (h, J = 6.7 Hz, 1H), 2.55 – 2.49 (m, 2H),

2.01 (dd, J = 10.2, 6.2 Hz, 2H), 1.72 (s, 6H), 1.04 (s, 3H), 1.02 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 172.5, 164.9, 142.7, 133.8, 130.1, 129.6, 128.4, 127.6, 126.7, 126.5, 124.6, 123.4, 123.0, 121.7, 43.3, 41.1, 38.7, 32.9, 29.4, 22.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₂H₂₇N₂O

335.2118; Found 335.2115.

N-cyclohexyl-4-methyl-4-(phenanthridin-6-yl)pentanamide (4ba)



White solid, mp: 180-182 °C; 34.1 mg, 91% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.69 – 8.62 (m, 2H), 8.52 (dd, J = 8.2, 1.4 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.79 (m, 1H), 7.72 – 7.60 (m, 3H), 5.21 (s, 1H), 3.65 (m, 1H), 2.55 – 2.48 (m, 2H), 2.04 – 1.98

(m, 2H), 1.80 (dd, J = 12.8, 3.7 Hz, 2H), 1.71 (s, 6H), 1.65 – 1.53 (m, 3H), 1.29 (m, 2H), 1.10 (m, 1H), 1.02 – 0.93 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.3, 163.9, 141.7, 132.8, 129.1, 128.5, 127.4, 126.6, 125.6, 125.4, 123.5, 122.4, 122.0, 120.7, 46.9, 42.2, 37.7, 32.1, 31.9, 28.4, 24.5, 23.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₅H₃₁N₂O 375.2431; Found 375.2433.

N-benzyl-4-methyl-4-(phenanthridin-6-yl)pentanamide (4ca)



White solid, mp: 140-142 °C; 33.6 mg, 88% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (dd, J = 15.0, 8.4 Hz, 2H), 8.51 (d, J = 7.4 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.63 (m, 3H), 7.31 – 7.24 (m, 3H), 7.22 – 7.16 (m, 2H), 5.81 (s, 1H), 4.32 (d, J = 5.6 Hz, 2H), 2.59 – 2.53 (m, 2H), 2.12

(dd, J = 10.0, 6.2 Hz, 2H), 1.72 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.3, 163.8, 137.3, 132.9, 129.0, 128.6, 127.6, 127.4, 126.8, 126.6, 126.4, 125.7, 125.4, 123.5, 122.4, 122.0, 120.7, 52.4, 42.5, 42.2, 37.9, 31.8, 28.3. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₂₇N₂O 383.2118; Found 383.2116.

N-isopropyl-3-(1-(phenanthridin-6-yl)cyclohexyl)propenamide (4da)



White solid, mp: 124-126 °C; 34.1 mg, 91% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.70 (m, 2H), 8.54 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.63 (t, *J* = 7.3 Hz, 2H), 4.89 (s, 1H), 3.87 (h, *J* = 6.8 Hz, 1H), 2.73 (t, *J* = 10.4 Hz, 2H), 2.55 (t, *J* = 8.3 Hz, 2H), 1.84 (q, *J* = 8.7 Hz, 4H),

1.62 (t, J = 6.8 Hz, 2H), 1.55 – 1.44 (m, 4H), 0.95 (s, 3H), 0.93 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.3, 163.5, 142.8, 133.8, 130.2, 129.5, 128.4, 127.2, 126.7, 126.4, 124.9, 123.2, 123.0, 121.7, 47.3, 41.1, 37.4, 35.8, 31.9, 26.6, 22.9, 22.6. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₅H₃₁N₂O 375.2431; Found 375.2435.

N-(tert-butyl)-3-(1-(phenanthridin-6-yl)cyclohexyl)propenamide (4ea)



White solid, mp: 130-132 °C; 34.6 mg, 89% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.70 (t, *J* = 8.0 Hz, 2H), 8.54 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.63 (m, 2H), 4.87 (s, 1H), 2.77 – 2.68 (m, 2H), 2.57 – 2.50 (m, 2H), 1.82 (m, 4H), 1.62 (m, 2H), 1.55 – 1.43 (m, 4H), 1.14 (s, 9H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 172.5, 163.6, 142.8, 133.8, 130.2, 129.5, 128.4, 127.2, 126.7, 126.4, 125.0, 123.2, 123.0, 121.7, 50.8, 47.2, 37.5, 35.7, 32.5, 28.6, 26.6, 22.9. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₆H₃₃N₂O 389.2587; Found 389.2585.

*N-(tert-*butyl)-4-ethyl-4-(phenanthridin-6-yl)octanamide (4fa)



Yellow oil; 36.4 mg, 90% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.69 (m, 2H), 8.54 (dd, J = 8.2, 1.5 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.72 – 7.61 (m, 3H), 5.15 (s, 1H), 2.50 (m, 2H), 2.28 – 2.12 (m, 4H), 1.98 (m, 2H), 1.27 (s, 9H), 1.26 – 1.20 (m, 2H), 1.14 – 1.06 (m, 2H), 0.80 (t, J = 7.3 Hz, 6H). ¹³C NMR (100

MHz, Chloroform-*d*) δ 173.1, 163.8, 142.7, 133.6, 130.3, 129.5, 128.3, 126.9, 126.6, 126.5, 125.4, 123.2, 123.0, 121.7, 50.9, 49.6, 37.2, 33.4, 33.3, 30.0, 28.8, 26.6, 23.5, 14.0, 9.0. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₃₇N₂O 405.2900; Found 405.2904.

*N-(tert-*butyl)-4-(phenanthridin-6-yl)pentanamide (4ga)



Colorless oil; 28.4 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, J = 8.2 Hz, 1H), 8.55 (dd, J = 8.3, 1.4 Hz, 1H), 8.34 (d, J = 8.1 Hz, 1H), 8.14 (dd, J = 8.2, 1.4 Hz, 1H), 7.83 (m, 1H), 7.70 (m, 2H), 7.62 (m, 1H), 5.18 (s, 1H), 3.99 – 3.89 (m, 1H),

2.56 – 2.47 (m, 1H), 2.20 – 2.12 (m, 2H), 2.09 – 2.03 (m, 1H), 1.48 (d, J = 6.9 Hz, 3H), 1.27 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.6, 164.5, 143.6, 133.1, 130.3, 129.8, 128.5, 127.4, 126.4, 125.8, 125.2, 123.4, 122.6, 121.9, 51.0, 35.8, 35.6, 31.6, 28.8, 20.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₂H₂₇N₂O 335.2118; Found 335.2116.

*N-(tert-*butyl)-4-(phenanthridin-6-yl)hexanamide (4ha)



Colorless oil; 30.0 mg, 86% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, J = 8.3 Hz, 1H), 8.57 (dd, J = 8.2, 1.4 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.71 (m, 2H), 7.63 (m, 1H), 5.10 (s, 1H), 3.82 – 3.72 (m, 1H), 2.45 (m, 1H), 2.27 – 2.20 (m, 1H), 2.10 – 2.03 (m, 2H), 1.98 – 1.91

(m, 1H), 1.85 (m, 1H), 1.25 (s, 9H), 0.89 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.5, 164.0, 132.9, 130.3, 129.8, 128.5, 127.4, 126.4, 126.1, 125.9, 123.3, 122.6, 121.9, 51.0, 35.5, 29.9, 28.7, 28.5, 12.3. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₉N₂O 349.2214; Found 349.2219.

*N-(tert-*butyl)-4-(phenanthridin-6-yl)heptanamide (4ia)



Colorless oil; 31.9 mg, 88% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, J = 8.3 Hz, 1H), 8.56 (dd, J = 8.2, 1.4 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.83 (m, 1H), 7.71 (m, 2H), 7.62 (m, 1H), 5.12 (s, 1H), 3.85 (m, 1H), 2.45 (m, 1H), 2.26 - 2.19 (m, 1H), 2.09 - 2.00 (m, 2H), 1.97 - 1.89 (m, 1H), 1.78 (m, 1H), 1.43 - 1.29 (m, 2H), 1.25 (s, 9H), 0.86 (t, J = 7.3 Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 172.5, 164.2, 143.7, 132.9, 130.3, 129.8, 128.5, 127.4, 126.4, 126.0, 125.8, 123.3, 122.6, 121.9, 50.9, 37.9, 35.5, 30.2, 28.8, 20.9, 14.3. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₁N₂O 363.2431; Found 363.2433.

*N-(tert-*butyl)-4-(phenanthridin-6-yl)-5-phenylpentanamide (4ja)



Yellow oil; 32.8 mg, 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, J = 8.3 Hz, 1H), 8.55 (d, J = 8.2 Hz, 1H), 8.22 (dd, J = 13.9, 8.2 Hz, 2H), 7.81 – 7.72 (m, 2H), 7.67 – 7.60 (m, 2H), 7.18 – 7.12 (m, 4H), 7.10 – 7.05 (m, 1H), 5.06 (s, 1H), 4.15 (m, 1H), 3.43 (dd, J = 13.5, 7.2 Hz, 1H), 3.09 (dd, J = 13.5, 7.0 Hz, 1H), 2.50 (m, 1H), 2.27 – 2.19 (m, 1H), 2.09 – 2.03 (m, 1H), 1.96 – 1.89 (m, 1H), 1.23 (s, 9H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 172.2, 163.2, 140.7, 132.9, 130.2, 129.9, 129.2, 128.5, 128.2, 127.3, 126.5, 125.9, 125.8, 125.6, 123.4, 122.5, 122.0, 50.9, 41.5, 35.3, 30.1, 28.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₈H₃₁N₂O 411.2431; Found 411.2430.

*N-(tert-*butyl)-2-(1-(phenanthridin-6-yl)ethoxy)acetamide (4ka)



Colorless oil; 26.9 mg, 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, J = 8.3 Hz, 1H), 8.58 (dd, J = 8.1, 1.5 Hz, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.87 (m, 1H), 7.78 – 7.73 (m, 1H), 7.70 (m, 2H), 6.66 (s, 1H), 5.42 (q, J =

6.7 Hz, 1H), 3.96 (d, J = 4.1 Hz, 2H), 1.83 (d, J = 6.7 Hz, 3H), 1.32 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.8, 159.5, 133.6, 130.8, 130.1, 128.9, 127.4, 125.7, 124.0, 123.9, 122.9, 122.0, 79.5, 69.3, 50.9, 28.8, 20.9. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₅N₂O₂ 337.1911; Found 337.1914.

*N-(tert-*butyl)-2-(phenanthridin-6-yl(phenyl)methoxy)acetamide (4la)



Colorless oil; 29.9 mg, 75% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, J = 8.3, 1.2 Hz, 1H), 8.27 (s, 1H), 7.49 – 7.43 (m, 3H), 7.37 – 7.33 (m, 4H), 7.31 – 7.27 (m, 3H), 7.19 (m, 1H), 6.11 (s, 1H), 4.74 (s, 1H), 3.80 (d, J = 1.4 Hz, 2H), 1.24 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.4, 137.8, 136.0, 133.9, 132.5, 130.1, 129.2, 129.13, 129.06, 128.6, 128.2, 126.9,

124.8, 120.9, 84.0, 70.2, 51.1, 28.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}N_2O_2$ 399.2067; Found 399.2065.

N-(tert-butyl)-3,3-dimethyl-4-(phenanthridin-6-yl)butanamide (4ma)

White solid, mp: 203-204 °C; 31.0 mg, 89% yield. ¹H NMR (600 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 8.68 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.60 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.37 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.87 (m, 1H), 7.74 (m, 2H), 7.68 (m, 1H), 3.42

(s, 2H), 2.22 (s, 2H), 1.53 (s, 9H), 1.08 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.5, 160.6, 133.0, 130.8, 128.9, 128.5, 127.5, 127.2, 126.9, 126.7, 123.6, 122.5, 122.2, 51.0, 47.3, 41.4, 36.4, 29.8, 29.2. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₉N₂O 349.2274; Found 349.2278.

4-(9-((3r,5r,7r)-adamantan-1-yl)phenanthridin-6-yl)-N-(tert-butyl)-4-methylpentanamide (5)



Colorless oil; 20.9 mg, 76% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.69 – 8.51 (m, 3H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.53 (m, 3H), 5.08 (s, 1H), 2.49 (t, *J* = 8.3 Hz, 2H), 2.19 (s, 3H), 2.09 (d, *J* = 2.9 Hz, 6H), 1.94 (d, *J* = 7.9 Hz, 2H), 1.89 – 1.81 (m, 6H), 1.70 (s, 6H), 1.22 (s, 9H). ¹³C NMR (100 MHz,

Chloroform-d) & 172.9, 164.9, 152.7, 143.1, 133.9, 130.3, 128.2, 127.5, 126.5, 124.4, 124.0, 122.9, 121.8, 118.5, 51.0, 43.3, 43.2, 38.8, 37.0, 36.9, 33.8, 29.8, 29.61, 29.59, 29.0, 28.8. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₃H₄₂N₂O 483.3370; Found 483.3374.

methyl 4-methyl-4-(phenanthridin-6-yl)pentanoate (6)



White solid, mp: 140-142 °C; 11.2 mg, 85% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.69 (d, J = 7.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.75 – 7.59 (m, 3H), 3.57 (s, 3H), 2.57 – 2.48 (m, 2H), 2.28 – 2.20 (m, 2H), 1.74 (s, 6H). ¹³C NMR (150 MHz,

Chloroform-*d*) δ 174.7, 164.7, 134.2, 130.2, 129.9, 128.7, 127.7, 127.0, 126.6, 124.5, 123.5, 123.2, 121.8, 51.6, 43.3, 38.0, 30.3, 29.5. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₁NO₂ 308.1645; Found 308.1643.

4-methyl-4-(phenanthridin-6-yl)pentanoic acid (7)



White solid, mp: 135-136 °C; 11.4 mg, 90% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, J = 7.1 Hz, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.56 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.79 – 7.62 (m, 3H), 2.58 – 2.47 (m, 2H), 2.44 – 2.35 (m,

2H), 1.77 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 177.7, 165.4, 134.5, 130.6, 129.2, 129.1, 128.1, 127.4, 126.8, 124.5, 123.8, 123.3, 121.9, 43.5, 38.5, 30.9, 29.4. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₉NO₂ 294.1489; Found 294.1486.



Figure S10. ¹³C NMR spectra (100 MHz, CDCl₃) of compound 3aa



Figure S12. ¹³C NMR spectra (100 MHz, CDCl₃) of compound 3ba



Figure S14. ¹³C NMR spectra (100 MHz, CDCl₃) of compound 3ca



Figure S16. ¹³C NMR spectra (100 MHz, CDCl₃) of compound 3da







Figure S19. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3fa





Figure S22. ¹³C NMR spectra (100 MHz, CDCl₃) of compound 3ga





¹⁰ ⁰ ⁻¹⁰ ⁻²⁰ ⁻³⁰ ⁻⁴⁰ ⁻⁵⁰ ⁻⁶⁰ ⁻⁷⁰ ⁻⁸⁰ ⁻⁹⁰ ⁻¹⁰⁰ ⁻¹¹⁰ ⁻¹²⁰ ⁻¹³⁰ ⁻¹⁴⁰ ⁻¹⁵⁰ ⁻¹⁶⁰ ⁻¹⁷⁰ ⁻¹⁸⁰ ⁻¹⁹⁰ ⁻²⁰⁰ ⁻²¹⁰ **Figure S24.** ¹⁹F NMR spectra (376 MHz, CDCl₃) of compound **3ha**



Figure S26. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ia



Figure S28. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ja



Figure S30. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ka



Figure S32. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3la



Figure S34. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ma



Figure S36. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3na



Figure S38. ¹H NMR spectra (400 MHz, CDCl₃) of compound 30a



Figure S40. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3pa



Figure S42. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3qa



Figure S44. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ra



Figure S46. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3sa



Figure S48. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ta



Figure S50. ¹H NMR spectra (400 MHz, CDCl₃) of compound 3ua



Figure S52. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4aa



Figure S54. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ba



Figure S56. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ca



Figure S58. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4da



Figure S60. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ea



Figure S62. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4fa



Figure S64. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ga



Figure S66. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ha



Figure S68. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ia



Figure S70. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ja



Figure S72. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4ka



Figure S74. ¹H NMR spectra (400 MHz, CDCl₃) of compound 4la



Figure S76. ¹H NMR spectra (600 MHz, CDCl₃) of compound 4ma



Figure S78. ¹H NMR spectra (400 MHz, CDCl₃) of compound 5



Figure S80. ¹H NMR spectra (400 MHz, CDCl₃) of compound 6



Figure S82. ¹H NMR spectra (400 MHz, CDCl₃) of compound 7

