Visible-Light-Mediated Photoredox Minisci C-H Alkylation with

Alkyl Boronic Acids Using Molecular Oxygen as an Oxidant

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1. General Information

Reagents were purchased from commercial sources and were used as received. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (36 W, $\lambda_{max} = 470$ nm) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.



Figure S1 Photograph of the Photocatalytic reactor used for reactions conducted under blue LED irradiation.

2. Preparation of Photocatalyst

The photocatalyst was synthesized according to literature report.¹ The spectral data of the photocatalyst is consistent with the literature data. The other photocatalysts (Eosin Y, Fluorescein, 4CzIPN, $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, $Ru(bpy)_3(PF_6)_2$, $Ir(ppy)_3$ and Mes-Acr) are commercially available.



Ru(bpy)32+



fac-lr(ppy)₃



 $R_1 = H, R_2 = H, R_3 = t$ -Bu lr(ppy)₂(dtbbpy)⁺ $R_1 = F, R_2 = CF_3, R_3 = t$ -Bu lr[dF(CF₃)ppy]₂(dtbbpy)⁺



Fluorescein

.CN

NC

C

4CzIPN





Figure 2 The structures of photocatalysts.

Cz =

3. Investigation of the Key Reaction Parameters

Table S1: Screening of photocatalysts^a

	+ B(OH) ₂	1 mol % photocatalyst 2.0 equiv TFA	
		36 W blue LED, rt, 24 h	
 entrv	2, 3.0 equiv	photocatalyst	vield (%) ^b
1	[Ir(d	[Ir(dtbbpy)(ppv)2][PF4]	
2	L	$fac-Ir(ppy)_3$	NR
3	$[Ru(bnv)_2](PF_4)_2$		21
4	[]	$Ru(bpy)_{2} = 6H_{2}O$	10
5°	4CzIPN		NR
6°		Fosin-V	42
			74

7°	Mes-Acr	45
8°	Fluorescein	NR
9	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	94

^aGeneral conditions: **1** (0.3 mmol), **2** (0.9 mmol), photocatalyst (0.003 mmol), TFA (0.6 mmol), DCE (3.0 mL), rt, O₂ atmosphere, 24 h. ^bYields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard. ^cPhotocatalyst (0.015 mmol). NR = no reaction.

Table S2: Screening of different solvents^a

1, 1.0 equiv 2, 3.0 e	(OH) ₂ 1 mol % Ir[dF(CF ₃)ppy] ₂ (dtbbp 2.0 equiv TFA solvent (0.1 M), O ₂ 36 W blue LED, rt, 24 h	$y)PF_6$
entry	solvent	yield (%) ^b
1	CH ₃ CN	90
2	DMSO	88
3	acetone	77
4	DCE	94

^aGeneral conditions: **1** (0.3 mmol), **2** (0.9 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), TFA (0.6 mmol), solvent (3.0 mL), rt, O₂ atmosphere, 24 h. ^bYields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard.

	+ B(OH) ₂	1 mol % Ir[dF(CF ₃ 2.0 equ DCE (0. 36 W blue I	3)ppy]₂(dtbbpy)PF ₆ uiv TFA 1 M), O₂ FD, rt, 24 b	
1 , 1.0 equiv	2 , x equiv		, , , , , , , , , , , , , , , , , ,	3
entry		x eq. 2	yiel	d (%) ^b
1		1.0		48
2		1.5		69
3		2.0		83
4		3.0		94
5		5.0		94

Table S3: Screening of the amount of cyclohexylboronic acid (2)^a

^aGeneral conditions: **1** (0.3 mmol), **2** (0.3x mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), TFA (0.6 mmol), DCE (3.0 mL), rt, O₂ atmosphere, 24 h. ^bYields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard.

Table S4: Screening of the amount of TFA^a

1 , 1.0 equiv	+ 2, 3.0 equiv	1 mol % lr[dF(CF ₃)ppy] ₂ (dtbbpy x equiv TFA DCE (0.1 M), O ₂ 36 W blue LED, rt, 24 h		\supset
entry		x eq. TFA	yield (%) ^b	
1		0.5	34	
2		1.0	56	
3		1.5	79	
4		2.0	94	
5		3.0	94	

^aGeneral conditions: **1** (0.3 mmol), **2** (0.9 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.003 mmol), TFA (0.3x mmol), DCE (3.0 mL), rt, O₂ atmosphere, 24 h. ^bYields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard.

4. Investigation of the Mechamism

4.1 Control experiments

Table S5

1, 1.0 equiv	+ B(OH) ₂ 1 mol % Ir[dF(CF) 2, 3.0 equiv 1 mol % Ir[dF(CF) 2 .0 eq DCE (0) 36 W blue	F_3)ppy] ₂ (dtbbpy)PF ₆ <u>quiv TFA</u> 0.1 M), O ₂ LED, rt, 24 h 3
entry	control conditions	yield (%)
1	w/o photocatalyst	NR
2	w/o light	NR
3	w/o TFA	NR
4	air	35
4	Ar	<5
5	standard conditions, w/all	94

Yields were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard.

4.2 TEMPO, BHT and 1,1-diphenylethylene were used as radical scavengers



Scheme S1

To a 10 mL glass vial was added Ir[dF(CF₃)ppy)]₂(dtbbpy)PF₆ (3.36mg, 0.003 mmol, 1 mol %), **1** (0.3 mmol, 1.0 equiv), **2** (0.9 mmol, 3.0 equiv), TEMPO (117 mg, 0.75 mmol, 2.5 equiv), BHT (165mg, 0.75 mmol, 2.5 equiv), or 1,1-diphenylethylene (135 mg, 0.75 mmol, 2.5 equiv), TFA (45 μ L, 0.6 mmol, 2.0 equiv) and 3.0 mL of DCE. The reaction mixture was degassed by bubbling with O₂ for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The yields of corresponding alkylated product **3** were determined by ¹H NMR spectroscopy with dibromomethane as an internal standard. The corresponding product of radical trapping, 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (**46**) and 3,5-di-tert-butyl-1-methyl-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (**47**), were detected by HR-MS (positive mode ESI).



Figure S3. HR-ESI mass spectra of 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (46).



Figure S4. HR-ESI mass spectra of 2,6-di-tert-butyl-4-(cyclohexylmethyl)phenol (47).

4.3 Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a CARY VARIAN luminescence spectrophotometer. All $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ solutions were excited at 350 nm and the emission intensity was collected at 475 nm. In a typical experiment, to a 3 × 10⁻⁶ M solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in acetone was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



Figure S5. (a). UV-vis absorption spectra. (b). $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching with **1** and **2**. (c). $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching with O₂.

4.4 Light/dark experiment

Eight standard reaction mixtures in 10 mL glass vials were charged with Ir[dF(CF₃)ppy)]₂(dtbbpy)PF₆ (3.36mg, 0.003 mmol, 1 mol %), 1 (0.3 mmol, 1.0 equiv), 2 (0.9mmol, 3.0 equiv), TFA (45 µL, 0.6 mmol, 2.0 equiv) and 3.0 mL of DCE. The reaction mixtures were degassed by bubbling with O_2 for 15 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an

additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h, then, a vial was removed for analysis and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yield was determined by ¹H NMR spectroscopy using dibromomethane as the internal standard.



Figure S6. Light/dark experiment.





Scheme S2. Proposed mechanism for direct C-H alkylation of heteroarenes.

5. Experimental Procedures and Product Characterization

5.1 General Procedure for the alkylation of N-heteroarenes.

To a 10 mL glass vial was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.36mg, 0.003 mmol, 1 mol %), *N*-heteroarene (0.3 mmol, 1.0 equiv), alkyl boronic acids (0.9 mmol, 3.0 equiv), TFA (45 µL, 0.6 mmol, 1.5 equiv) and 3.0 mL of DCE. The reaction mixture was degassed by bubbling with O₂ for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was diluted with 10 mL of aqueous 1 M NaHCO₃ solution, and extracted with DCM (3×20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

5.2. Product Characterization

2-cyclohexyl-4-methylquinoline (3).

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (58.7 mg, 87%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.15 (s, 1H), 2.87 (t, J = 12.0 Hz, 1H), 2.65 (s, 3H), 2.01 (d, J = 12.4 Hz, 2H), 1.88 (d, J = 12.4 Hz, 2H), 1.78 (d, J = 12.4 Hz, 1H), 1.62 (dd, J = 25.2, 12.4 Hz, 2H), 1.46 (dd, J = 25.2, 12.8 Hz, 2H), 1.39 – 1.29 (m, 1H). ¹³C **NMR** (100 MHz, CDCl₃) δ 166.6, 147.8, 144.2, 129.6, 128.9, 127.1, 125.4, 123.6, 120.3, 47.7, 32.9, 26.7, 26.2, 18.9. **HRMS** (ESI) calcd for C₁₆H₂₀N [M + H]⁺ 226.1590, found 226.1595.

2-cyclohexylquinoline (4a) and 2,4-dicyclohexylquinoline (4b).



1:0.64

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (31.4 mg, 43%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 40/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.10 – 7.99 (m, 3.27H), 7.76 (dd, J = 8.0, 1.2 Hz, 1H), 7.70 – 7.60 (m, 1.68H), 7.50 – 7.43 (m, 1.65H), 7.32 (d, J = 8.4 Hz, 1H), 7.20 (s, 0.64H), 3.31 – 3.26 (m, 0.66H), 2.99 – 2.81 (m, 1.68H), 2.02 (dd, J = 6.4, 5.2 Hz, 5.11H), 1.96 – 1.85 (m, 5.34H), 1.82 – 1.75 (m, 2.15H), 1.66 – 1.59 (m, 3.18H), 1.58 – 1.50 (m, 3.21H), 1.45 (ddd, J = 12.8, 9.2, 2.8 Hz, 3.29H), 1.38 – 1.31 (m, 2.07H). ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 166.7, 153.5, 148.1, 147.9, 136.4, 129.9, 129.3, 129.0, 128.7, 127.5, 127.1, 125.8, 125.7, 125.3, 122.9, 119.7, 115.9, 47.9, 47.8, 39.1, 33.7, 33.0, 32.9, 27.1, 26.7, 26.6, 26.4, 26.3, 26.2.

HRMS (ESI) calcd for $C_{15}H_{18}N [M + H]^+$ 212.1434, found 212.1433 and $C_{21}H_{28}N [M + H]^+$ 294.2216, found 294.2216.

4-chloro-2-cyclohexylquinoline (5).



According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (52.9 mg, 72%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.16 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.41 (s, 1H), 2.88 (tt, J = 12.0, 3.2 Hz, 1H), 2.02 (d, J = 11.6 Hz, 2H), 1.89 (d, J = 12.8 Hz, 2H), 1.78 (d, J = 12.4 Hz, 1H), 1.60 (ddd, J = 24.8, 12.4, 2.8 Hz, 2H), 1.52 - 1.39 (m, 2H), 1.38 - 1.29 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.9, 148.8, 142.7, 130.2, 129.4, 126.7, 125.2, 123.9, 119.9, 47.5, 32.8, 26.5, 26.1.

HRMS (ESI) calcd for $C_{15}H_{17}ClN [M + H]^+ 246.1044$, found 246.1046.

4-bromo-2-cyclohexylquinoline (6).



According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (59.8 mg, 69%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.14 – 8.09 (m, 1H), 8.06 – 8.00 (m, 1H), 7.74 – 7.68 (m, 1H), 7.62 (s, 1H), 7.59 – 7.53 (m, 1H), 2.88 (tt, J = 12.0, 3.2 Hz, 1H), 2.02 (dd, J = 13.2, 1.6 Hz, 2H), 1.94 – 1.85 (m, 2H), 1.83 – 1.75 (m, 1H), 1.61 (qd, J = 12.4, 2.8 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.38 – 1.28 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.9, 148.6, 134.3, 130.3, 129.5, 126.9, 126.6, 126.5, 123.8, 47.4, 32.8, 26.5, 26.1.

HRMS (ESI) calcd for $C_{15}H_{17}BrN [M + H]^+ 290.0539$, found 290.0540.

7-chloro-4-cyclohexyl-2-methylquinoline (7).



According to the *general procedure*.

Yellow oil (45.1 mg, 58%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.00 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.39 (dd, J = 9.2, 2.1 Hz, 1H), 7.14 (s, 1H), 3.20 (t, J = 9.6 Hz, 1H), 2.69 (s, 3H), 1.99 – 1.88 (m, 4H), 1.84 (d, J = 14.0 Hz, 1H), 1.49 (d, J = 11.2 Hz, 4H), 1.32 (ddd, J = 12.6, 8.0, 3.6 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 160.1, 153.4, 148.8, 134.6, 128.5, 126.1, 124.3, 123.6, 118.6, 38.9, 33.6, 26.9, 26.3, 25.6.

HRMS (ESI) calcd for $C_{16}H_{19}ClN [M + H]^+ 260.1201$, found 260.1200.

1-cyclohexylisoquinoline (8).



According to the *general procedure*. The spectral Data is consistent with the literature data.³ Yellow oil (26.6 mg, 42%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 7/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.48 (d, J = 5.6 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.48 (d, J = 5.6 Hz, 1H), 3.56 (t, J = 11.2 Hz, 1H), 1.96 (t, J = 15.6 Hz, 4H), 1.89 – 1.75 (m, 3H), 1.54 (dd, J = 24.0, 11.6 Hz, 2H), 1.41 (dd, J = 17.6, 7.6 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 165.9, 142.1, 136.5, 129.7, 127.7, 126.9, 126.4, 124.9, 119.0, 41.7, 32.7, 27.0, 26.4.

HRMS (ESI) calcd for $C_{15}H_{18}N [M + H]^+ 212.1434$, found 212.1434.

4-bromo-1-cyclohexylisoquinoline (9).



According to the *general procedure*. The spectral Data is consistent with the literature data.³ Yellow oil (35.5 mg, 41%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 60/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 8.21 (dd, J = 11.6, 8.8 Hz, 2H), 7.77 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 3.52 (t, J = 11.6 Hz, 1H), 1.95 (t, J = 12.0 Hz, 4H), 1.81 (t, J = 11.2 Hz, 3H), 1.53 (dd, J = 25.6, 12.8 Hz, 2H), 1.44 – 1.35 (m, 1H). ¹³**C** NMR (100 MHz, CDCl₃) δ 165.5, 143.8, 135.0, 130.9, 127.9, 127.8, 127.0, 125.2, 117.7, 41.6, 32.7, 26.9, 26.3. HRMS (ESI) calcd for C₁₅H₁₇BrN [M + H]⁺ 290.0539, found 290.0538.

6-cyclohexylphenanthridine (10).



According to the *general procedure*. The spectral data is consistent with the literature data.³ Colorless oil (72.8 mg, 93%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 8.0 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.64 (dt, J = 19.6, 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 3.57 (tt, J = 11.2, 3.0 Hz, 1H), 2.06 (d, J = 11.2 Hz, 2H), 2.01 – 1.88 (m, 4H), 1.82 (d, J = 12.4 Hz, 1H), 1.54 (qd, J = 13.2, 6.8 Hz, 2H), 1.43 (ddd, J = 12.8, 5.6, 2.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 143.9, 133.0, 130.0, 129.9, 128.4, 127.1, 126.2, 125.6, 128.4 124.8, 123.4, 122.6, 121.9, 42.0, 32.4, 26.9, 26.4. **HRMS** (ESI) calcd for $C_{19}H_{20}N [M + H]^+$ 262.1590, found 262.1592.

4-cyclohexylquinazoline (11).



According to the *general procedure*. The spectral data is consistent with the literature data.³ Yellow oil (42.6 mg, 67%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 2/1).

¹**H NMR** (400 MHz, CDCl₃) δ 9.26 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 3.57 (t, J = 11.6 Hz, 1H), 1.96 (s, 4H), 1.87 – 1.75 (m, 3H), 1.56 – 1.46 (m, 2H), 1.45 – 1.36 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 175.2, 154.9, 150.2, 133.4, 129.5, 127.5, 124.3, 123.4, 41.4, 32.2, 26.7, 26.1. **HRMS** (ESI) calcd for C₁₄H₁₇N₂ [M + H]⁺ 213.1386, found 213.1384.

1-cyclohexylphthalazine (12).



According to the *general procedure*. The spectral data is consistent with the literature data.² Yellow oil (32.4 mg, 51%).

*R*_f 0.30 (CH₂Cl₂/MeOH, 2/1).

¹**H NMR** (400 MHz, CDCl₃) δ 9.39 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.04 – 7.81 (m, 3H), 3.51 (t, J = 11.2 Hz, 1H), 2.01 (dd, J = 33.6, 11.6 Hz, 6H), 1.83 (d, J = 11.6 Hz, 1H), 1.54 (dd, J = 25.2, 12.8 Hz, 2H), 1.46 – 1.36 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 163.6, 150.2, 132.3, 131.7, 127.2, 126.7, 125.1, 123.6, 40.8, 32.4, 26.9, 26.2.

HRMS (ESI) calcd for $C_{14}H_{17}N_2$ [M + H]⁺ 213.1386, found 213.1386.

2-cyclohexyl-4-phenylpyridine (13).



According to the *general procedure*. Yellow oil (39.1 mg, 55%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.57 (d, J = 5.2 Hz, 1H), 7.62 (dd, J = 8.0, 1.2 Hz, 2H), 7.52 – 7.38 (m, 3H), 7.36 (d, J = 0.8 Hz, 1H), 7.30 (dd, J = 5.2, 1.6 Hz, 1H), 2.77 (tt, J = 11.6, 3.2 Hz, 1H), 2.07 – 1.94 (m, 2H), 1.88 (dd, J = 9.6, 3.2 Hz, 2H), 1.81 – 1.71 (m, 1H), 1.59 (ddd, J = 24.8, 12.4, 2.8 Hz, 2H), 1.50 – 1.38 (m, 2H), 1.36 – 1.26 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 167.1, 149.6, 148.9, 138.9, 129.1, 128.9, 127.1, 119.3, 119.2, 46.8, 33.1, 26.7, 26.2.

HRMS (ESI) calcd for $C_{17}H_{20}N [M + H]^+ 238.1590$, found 238.1590.

4-(tert-butyl)-2-cyclohexylpyridine (14).



According to the *general procedure*. The spectral data is consistent with the literature data.³ Yellow oil (41.0 mg, 63%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 10/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.43 (d, J = 5.2 Hz, 1H), 7.12 (s, 1H), 7.09 (d, J = 5.2 Hz, 1H), 2.68 (tt, J = 11.6, 3.2 Hz, 1H), 1.94 (d, J = 11.6 Hz, 2H), 1.86 (d, J = 12.8 Hz, 2H), 1.75 (d, J = 12.4 Hz, 1H), 1.55 (ddd, J = 24.4, 12.4, 2.4 Hz, 2H), 1.48 – 1.34 (m, 3H), 1.30 (s, 9H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.4, 160.4, 148.9, 118.3, 118.1, 46.9, 34.8, 33.2, 30.7, 26.8, 26.2. HRMS (ESI) calcd for C₁₅H₂₄N [M + H]⁺ 218.1903, found 218.1902.

2-cyclohexyl-6-phenylpyridine and 2,4-dicyclohexyl-6-phenylpyridine (15).



According to the *general procedure*. The spectral data is consistent with the literature data.⁴ Clear oil (38.5 mg, 48%).

 $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.01 (t, J = 8.0 Hz, 3.2H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1.2H), 7.48 – 7.41 (m, 3.2H), 7.40 – 7.32 (m, 2H), 7.07 (d, J = 7.6 Hz, 1H), 6.93 (s, 0.6H), 2.87 – 2.69 (m, 1.6H), 2.60 – 2.44 (m, 0.6H), 2.02 (d, J = 12.4 Hz, 3.4H), 1.87 (d, J = 13.2 Hz, 5.2H), 1.76 (d, J = 12.8 Hz, 2.2H), 1.59 (ddd, J = 24.8, 12.4, 2.8 Hz, 3.6H), 1.49 – 1.38 (m, 5.2H), 1.36 – 1.27 (m, 2.2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.5, 157.5, 156.6, 156.5, 140.5, 140.1, 136.9, 128.7, 128.7, 128.6, 128.5, 127.2, 127.1, 119.3, 118.1, 117.8, 116.8, 46.8, 46.7, 44.4, 33.84, 33.2, 33.1, 26.8, 26.7, 26.4, 26.3, 26.1.

HRMS (ESI) calcd for $C_{17}H_{20}N [M + H]^+$ 238.1590, found 238.1587 and $C_{23}H_{30}N [M + H]^+$ 320.2373, found 320.2369.

diethyl 4-cyclohexylpyridine-2,6-dicarboxylate (16).



According to the *general procedure*. Yellow solid (69.5 mg, 76%). M.p. = 72 - 73 °C. $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 4/1). ¹**H** NMR (400 MHz, CDCl₃) δ 8.13 (s, 2H), 4.49 (q, J = 7.2 Hz, 4H), 2.68 (t, J = 11.6 Hz, 1H), 1.92 (t, J = 13.6 Hz, 4H), 1.79 (d, J = 12.8 Hz, 1H), 1.51 – 1.40 (m, 10H), 1.29 (d, J = 12.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 159.6, 148.7, 126.6, 62.3, 43.9, 33.4, 26.4, 25.8, 14.3. HRMS (ESI) calcd for C₁₇H₂₄NO₄ [M + H]⁺ 306.1700, found 306.1702.

2-cyclohexylbenzo[d]thiazole (17).

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (35.2 mg, 54%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.97 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 3.10 (tt, J = 11.6, 3.6 Hz, 1H), 2.20 (dd, J = 13.6, 2.0 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.76 (ddd, J = 12.8, 4.8, 2.4 Hz, 1H), 1.64 (ddd, J = 24.8, 12.4, 3.2 Hz, 2H), 1.44 (ddt, J = 25.2, 12.4, 3.2 Hz, 2H), 1.37 – 1.27 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 177.7, 153.2, 134.7, 125.9, 124.6, 122.7, 121.6, 43.6, 33.5, 26.2, 25.9.

HRMS (ESI) calcd for $C_{13}H_{16}NS [M + H]^+ 218.0998$, found 218.0999.

2-cyclohexyl-5-methoxybenzo[d]thiazole (18).



According to the general procedure.

Yellow oil (35.6 mg, 48%).

 $R_{\rm f}$ 0.45 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 7.04 (dd, J = 8.8, 2.4 Hz, 1H), 3.86 (s, 3H), 3.05 (tt, J = 11.6, 3.6 Hz, 1H), 2.18 (dd, J = 13.6, 2.0 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.76 (ddd, J = 12.4, 4.8, 2.4 Hz, 1H), 1.62 (ddd, J = 24.4, 12.4, 3.2 Hz, 2H), 1.49 – 1.37 (m, 2H), 1.36 – 1.28 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 175.2, 157.3, 147.7, 135.9, 123.1, 115.0, 104.4, 55.9, 43.4, 33.5, 26.2, 25.9.

HRMS (ESI) calcd for C₁₄H₁₈NOS [M + H]⁺ 248.1104, found 248.1104.

6-chloro-7-cyclohexylimidazo[1,2-b]pyridazine (19).

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (52.2 mg, 74%).

 $R_{\rm f}$ 0.35 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.72 (s, 1H), 6.86 (s, 1H), 3.36 (t, *J* = 9.6 Hz, 1H), 2.09 (d, *J* = 8.4 Hz, 2H), 1.90 (d, *J* = 6.4 Hz, 2H), 1.82 (d, *J* = 13.2 Hz, 1H), 1.51 (d, *J* = 11.2 Hz, 4H), 1.36 – 1.27 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 148.2, 147.5, 138.1, 133.3, 117.3, 114.7, 38.9, 32.2, 26.4, 26.1.

HRMS (ESI) calcd for $C_{12}H_{15}CIN_3 [M + H]^+ 236.0949$, found 236.0948.

3-bromo-6-chloro-7-cyclohexylimidazo[1,2-b]pyridazine (20).

According to the *general procedure*. Yellow oil (62.0 mg, 66%). $R_f 0.50$ (Petroleum ether/EtOAc, 20/1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.72 (s, 1H), 6.92 (s, 1H), 3.35 (s, 1H), 2.06 (d, J = 7.2 Hz, 2H), 1.89 (s, 2H), 1.82 (d, J = 12.8 Hz, 1H), 1.52 (p, J = 12.0 Hz, 4H), 1.38 – 1.28 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 148.6, 148.5, 138.7, 133.6, 115.1, 101.3, 38.5, 32.2, 26.3, 26.0. **HRMS** (ESI) calcd for C₁₂H₁₄BrClN₃ [M + H]⁺ 314.0054, found 314.0056.

4-cyclohexyl-2,6-dimethylpyridine (21).



According to the general procedure.

Colorless oil (34.2 mg, 60%).

 $R_{\rm f}$ 0.30 (Petroleum ether/EtOAc, 7/1).

¹**H NMR** (400 MHz, CDCl₃) δ 6.83 (d, J = 5.2 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.45 (d, J = 5.6 Hz, 6H), 1.95 (d, J = 12.0 Hz, 2H), 1.84 (d, J = 8.8 Hz, 2H), 1.69 (dd, J = 29.2, 12.4 Hz, 3H), 1.44 – 1.31 (m, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 174.0, 166.4, 117.4, 47.7, 32.0, 26.4, 26.0, 24.1. **HRMS** (ESI) calcd for C₁₂H₁₉N₂ [M + H]⁺ 191.1543, found 191.1543.

5-bromo-4,6-dicyclohexylpyrimidine (22).



According to the *general procedure*. White solid (58.9 mg, 61%). M.p. = 108 – 109 °C.

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.91 (s, 1H), 3.21 (t, J = 11.6 Hz, 2H), 1.86 (t, J = 11.2 Hz, 8H), 1.76 (d, J = 12.0 Hz, 2H), 1.59 (d, J = 8.8 Hz, 4H), 1.48 – 1.38 (m, 4H), 1.36 – 1.31 (m, 2H). ¹³**C** NMR (100 MHz, CDCl₃) δ 172.0, 156.3, 121.4, 44.6, 31.1, 26.4, 26.0. HRMS (FSI) calcd for C₁ H₂BrN₂ [M + H]⁺ 323 1117 found 323 1120

HRMS (ESI) calcd for $C_{16}H_{24}BrN_2 [M + H]^+$ 323.1117, found 323.1120.

2-cyclohexylquinazolin-4(3H)-one (23).



According to the *general procedure C*. The spectral Data is consistent with the literature data.⁴ White solid (56.1 mg, 82%). M.p. = 189 - 190 °C.

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 2/1).

¹**H NMR** (400 MHz, CDCl₃) δ 12.04 (s, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.81 – 7.68 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 2.75 (ddd, J = 12.0, 7.6, 3.2 Hz, 1H), 2.06 (d, J = 12.0 Hz, 2H), 1.93 (d, J = 11.6 Hz, 2H), 1.86 – 1.75 (m, 3H), 1.53 – 1.38 (m, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 164.5, 160.5, 149.7, 134.8, 127.5, 126.4, 126.3, 120.9, 45.0, 30.6, 26.2, 25.8. **HRMS** (ESI) calcd for C₁₄H₁₇N₂O [M + H]⁺ 229.1335, found 229.1335.

2-ethyl-4-methylquinoline (24).



According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.⁵

Yellow oil (27.7 mg, 54%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.56 – 7.45 (m, 1H), 7.15 (s, 1H), 2.95 (q, J = 7.6 Hz, 2H), 2.67 (s, 3H), 1.38 (t, J = 7.6 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 163.7, 147.7, 144.3, 129.3, 129.0, 126.8, 125.4, 123.6, 121.6, 32.2, 18.7, 14.1.

HRMS (ESI) calcd for $C_{12}H_{14}N [M + H]^+ 172.1121$, found 172.1122.

4-methyl-2-propylquinoline (25).

According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.²

Yellow oil (33.9 mg, 61%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.54 – 7.44 (m, 1H), 7.13 (s, 1H), 2.96 – 2.85 (m, 2H), 2.66 (s, 3H), 1.92 – 1.75 (m, 2H), 1.02 (t, J = 7.6 Hz, 3H). ¹³**C** NMR (100 MHz, CDCl₃) δ 162.7, 147.8, 144.2, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 41.3, 23.4, 18.8, 14.2.

HRMS (ESI) calcd for $C_{13}H_{16}N [M + H]^+$ 186.1277, found 186.1279.

2-butyl-4-methylquinoline (26).



According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.²

Yellow oil (37.6 mg, 63%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.70 – 7.61 (m, 1H), 7.53 – 7.45 (m, 1H), 7.14 (s, 1H), 2.98 – 2.87 (m, 2H), 2.67 (s, 3H), 1.78 (tt, J = 7.6, 6.8 Hz, 2H), 1.51 – 1.37 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 162.9, 147.9, 144.2, 129.5, 129.1, 126.9, 125.5, 123.7, 122.2, 39.1, 32.3, 22.9, 18.8, 14.1. **HRMS** (ESI) calcd for C₁₄H₁₈N [M + H]⁺ 200.1434, found 200.1435.

4-methyl-2-pentylquinoline (27).

According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.⁵

Yellow oil (44.7 mg, 70%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.04 (dd, J = 8.4, 0.8 Hz, 1H), 7.93 (dd, J = 8.4, 0.8 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.48 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.13 (s, 1H), 3.21 – 2.84 (m, 2H), 2.66 (s, 3H), 1.91 – 1.70 (m, 2H), 1.47 – 1.26 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 147.8, 144.2, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.4, 31.9, 29.9, 22.7, 18.8, 14.1.

HRMS (ESI) calcd for $C_{15}H_{20}N [M + H]^+ 214.1590$, found 214.1589.

2-hexyl-4-methylquinoline (28).

According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.²

Yellow oil (46.3 mg, 68%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.14 (s, 1H), 3.00 – 2.85 (m, 2H), 2.67 (s, 3H), 1.79 (dt, J = 15.6, 7.6 Hz, 2H), 1.43 (d, J = 6.8 Hz, 2H), 1.35 – 1.27 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 162.9, 147.9, 144.2, 129.5, 129.1, 126.9, 125.5, 123.7, 122.2, 39.5, 31.9, 30.2, 29.4, 22.7, 18.8, 14.2.

HRMS (ESI) calcd for $C_{16}H_{22}N [M + H]^+ 228.1747$, found 228.1747.

4-methyl-2-octylquinoline (29).



According to the general procedure. 3 mL DMSO was used as the solvent.

Yellow oil (55.8 mg, 73%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.96 (d, J = 8.4 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.58 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 7.46 – 7.36 (m, 1H), 7.05 (s, 1H), 2.90 – 2.75 (m, 2H), 2.58 (s, 3H), 1.71 (dt, J = 15.6, 7.6 Hz, 2H), 1.37 – 1.17 (m, 10H), 0.79 (t, J = 6.8 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 162.9, 147.8, 144.2, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.4, 31.9, 30.2, 29.7, 29.6, 29.3, 22.8, 18.8, 14.2.

HRMS (ESI) calcd for $C_{18}H_{26}N [M + H]^+ 256.2060$, found 256.2060.

4-methyl-2-phenethylquinoline (30).



According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.²

Yellow oil (55.6 mg, 75%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.07 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.20 (t, J = 6.4 Hz, 1H), 7.09 (s, 1H), 3.29 – 3.19 (m, 2H), 3.17 – 3.09 (m, 2H), 2.65 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 161.6, 147.9, 144.4, 141.8, 129.5, 129.2, 128.6, 128.5, 127.0, 126.1, 125.7, 123.7, 122.4, 41.1, 36.1, 18.8. **HRMS** (ESI) calcd for C₁₈H₁₈N [M + H]⁺ 248.1434, found 248.1434.

2-isopentyl-4-methylquinoline (31).

According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.³

Yellow oil (25.6 mg, 40%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.15 (s, 1H), 2.98 – 2.86 (m, 2H), 2.67 (s, 3H), 1.77 – 1.60 (m,

3H), 0.98 (d, J = 5.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.3, 37.4, 28.4, 22.7, 18.8. HRMS (ESI) calcd for C₁₅H₂₀N [M + H]⁺ 214.1590, found 214.1593.

2-cyclopropyl-4-methylquinoline (32).



According to the *general procedure*. 3 mL DMSO was used as the solvent. The spectral Data is consistent with the literature data.²

Yellow oil (26.4 mg, 48%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 8.4, 1.2 Hz, 1H), 7.63 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.45 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 6.99 (s, 1H), 2.65 (s, 3H), 2.20 (ddd, J = 9.6, 8.4, 5.2 Hz, 1H), 1.16 – 1.10 (m, 2H), 1.10 – 1.03 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 147.9, 143.9, 129.3, 129.1, 126.9, 125.1, 123.7, 119.9, 18.8, 18.1, 10.1. HRMS (ESI) calcd for C₁₃H₁₄N [M + H]⁺ 184.1121, found 184.1122.

2-cyclobutyl-4-methylquinoline (33).

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (31.9 mg, 54%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.17 (s, 1H), 3.82 (p, J = 8.8 Hz, 1H), 2.65 (s, 3H), 2.50 – 2.36 (m, 4H), 2.11 (tt, J = 18.0, 9.2 Hz, 1H), 2.00 – 1.87 (m, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 164.7, 147.7, 144.2, 129.6, 129.0, 126.9, 125.5, 123.6, 120.3, 42.7, 28.3, 18.8, 18.4. **HRMS** (ESI) calcd for C₁₄H₁₆N [M + H]⁺ 198.1277, found 198.1279.

2-cyclopentyl-4-methylquinoline (34).

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (53.2 mg, 84%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.96 – 7.86 (m, 1H), 7.70 – 7.60 (m, 1H), 7.53 – 7.42 (m, 1H), 7.16 (s, 1H), 3.41 – 3.22 (m, 1H), 2.65 (s, 3H), 2.16 (ddd, J = 16.0, 9.6, 2.4

Hz, 2H), 1.93 - 1.81 (m, 4H), 1.80 - 1.70 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 147.6, 144.2, 129.5, 128.9, 127.0, 125.4, 123.6, 120.7, 48.9, 33.7, 26.1, 18.9. HRMS (ESI) calcd for C₁₅H₁₈N [M + H]⁺ 212.1434, found 212.1435.

2-isopropyl-4-methylquinoline (35).

According to the *general procedure*. The spectral data is consistent with the literature data.² Yellow oil (50.0 mg, 90%).

 $R_{\rm f}$ 0.70 (Petroleum ether/EtOAc, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.16 (s, 1H), 3.29 – 3.13 (m, 1H), 2.67 (s, 3H), 1.38 (d, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 147.6, 144.4, 129.6, 129.0, 127.1, 125.5, 123.6, 119.8, 37.3, 22.6, 18.9.

HRMS (ESI) calcd for $C_{13}H_{16}N [M + H]^+$ 186.1277, found 186.1279.

(S)-2-(sec-butyl)-4-methylquinoline (36).

According to the *general procedure*. The spectral Data is consistent with the literature data.² Yellow oil (49.0 mg, 82%).

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 20/1).

¹**H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 0.8 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.49 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.13 (s, 1H), 3.03 – 2.88 (m, 1H), 2.67 (s, 3H), 1.91 – 1.76 (m, 1H), 1.76 – 1.61 (m, 1H), 1.35 (d, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.8, 147.7, 144.3, 129.6, 129.0, 127.1, 125.5, 123.7, 120.3, 44.7, 30.0, 20.5, 18.9, 12.4.

HRMS (ESI) calcd for $C_{14}H_{18}N [M + H]^+ 200.1434$, found 200.1435.

5,7-dichloro-2-cyclohexyl-4-(4-fluorophenoxy)quinolone (39).



According to the *general procedure*. The spectral Data is consistent with the literature data.² White solid (49.0 mg, 42%). M.p. = 92 - 93 °C. $R_{\rm f}$ 0.60 (Petroleum ether/EtOAc, 40/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.95 (t, J = 1.6 Hz, 1H), 7.49 (t, J = 1.6 Hz, 1H), 7.22 – 7.06 (m, 4H), 6.52 (s, 1H), 2.69 (t, J = 11.2 Hz, 1H), 1.85 (dd, J = 23.6, 11.6 Hz, 4H), 1.72 (d, J = 12.4 Hz, 1H), 1.50 – 1.32 (m, 4H), 1.26 (t, J = 12.0 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 169.7, 162.4, 159.9 (d, J = 244 Hz), 151.5, 150.4, 134.8, 129.9, 128.7, 127.6, 122.1, 122.0, 117.1 (d, J = 24 Hz), 105.8, 47.4, 32.5, 26.4, 25.9.

HRMS (ESI) calcd for $C_{21}H_{19}Cl_2FNO [M + H]^+$ 390.0822, found 390.0821

(S)-11-cyclohexyl-4-ethyl-4-hydroxy-1,12-dihydro-14*H*-pyrano[3',4':6,7]indolizino[1,2b]quinoline-3,14(4*H*)-dione (40).



According to the *general procedure*. The spectral Data is consistent with the literature data.⁶ Yellow solid (52.9 mg, 41%).

 $R_{\rm f}$ 0.60 (DCM/MeOH, 20/1). M.p. = 221–223 °C.

¹**H NMR** (400 MHz, CDCl₃) δ 8.32 – 8.16 (m, 2H), 7.79 (t, J = 7.6 Hz, 1H), 7.72 – 7.61 (m, 2H), 5.76 (d, J = 16.4 Hz, 1H), 5.42 (s, 2H), 5.31 (d, J = 16.4 Hz, 1H), 3.83 (s, 1H), 3.66 (s, 1H), 2.00 (s, 4H), 1.95 – 1.84 (m, 4H), 1.58 (dd, J = 25.2, 12.4 Hz, 3H), 1.51 – 1.42 (m, 1H), 1.04 (t, J = 7.6 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 174.1, 157.7, 153.6, 152.5, 150.4, 148.7, 146.7, 130.9, 130.0, 127.8, 127.1, 123.8, 118.4, 97.8, 72.9, 66.5, 50.8, 31.9, 31.7, 29.8, 27.1, 26.1, 7.9. **HRMS** (ESI) calcd for C₂₆H₂₇N₂O₄ [M + H]⁺ 431.1965, found 431.1969.

5-((1,4-diazepan-1-yl)sulfonyl)-1-cyclohexylisoquinoline (41).



According to the *general procedure*. The spectral Data is consistent with the literature data.⁴ Brown solid (52.6 mg, 47%). M.p. = 110– 111 °C. $R_f 0.30$ (DCM/MeOH, 20/1). ¹**H NMR** (400 MHz, CDCl₃) δ 8.62 (d, J = 6.0 Hz, 1H), 8.48 (d, J = 8.8 Hz, 1H), 8.28 (dd, J = 14.4, 6.8 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 3.58 (dd, J = 11.6, 2.8 Hz, 1H), 3.54 – 3.44 (m, 4H), 3.31 (s, 1H), 3.12 – 2.92 (m, 4H), 2.00 – 1.77 (m, 9H), 1.62 – 1.46 (m, 2H), 1.46 – 1.34 (m, 1H). 47.4, 47.3, 42.1, 32.8, 30.6, 26.8, 26.2. **HRMS** (ESI) calcd for $C_{20}H_{28}N_3O_2S$ [M + H]⁺ 374.1897, found 374.1899.

2-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)ethyl 2-cyclohexylnicotinate (42).



According to the *general procedure*. Yellow oil (86.8 mg, 65%).

 $R_{\rm f}$ 0.40 (Petroleum ether/EtOAc, 4/1).

¹**H** NMR (400 MHz, CDCl₃) δ 9.05 (d, J = 1.6 Hz, 1H), 8.03 (dd, J = 8.4, 2.4 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.81 – 6.73 (m, 2H), 4.60 – 4.46 (m, 4H), 2.78 (tt, J = 11.6, 3.2 Hz, 1H), 2.01 – 1.93 (m, 2H), 1.88 (dd, J = 9.2, 3.2 Hz, 2H), 1.79 – 1.73 (m, 1H), 1.59 (d, J = 3.2 Hz, 6H), 1.57 – 1.49 (m, 2H), 1.46 – 1.37 (m, 2H), 1.35 – 1.27 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 171.5, 165.2, 154.0, 150.5, 137.5, 129.2, 127.3, 123.0, 120.8, 120.3, 79.4, 63.2, 62.6, 46.9, 32.7, 26.5, 26.0, 25.4.

HRMS (ESI) calcd for $C_{24}H_{29}CINO_5 [M + H]^+ 446.1729$, found 446.1732.

ethyl 4-(8-chloro-2-cyclohexyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11ylidene)piperidine-1-carboxylate (43).



According to the *general procedure*. The spectral Data is consistent with the literature data.² White solid (72.4 mg, 52%). M.p. = 105 - 106 °C.

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 4/1).

¹**H NMR** (400 MHz, CDCl₃) δ 7.34 (d, J = 8.0 Hz, 1H), 7.14 (dt, J = 9.2, 5.0 Hz, 3H), 6.96 (d, J = 8.0 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.84 (s, 2H), 3.32 (dddd, J = 16.8, 13.1, 9.6, 5.6 Hz, 2H), 3.10 (ddd, J = 13.2, 9.6, 3.2 Hz, 2H), 2.86 – 2.73 (m, 2H), 2.68 (dd, J = 15.6, 7.2 Hz, 1H), 2.49 (s, 1H), 2.41 – 2.28 (m, 3H), 1.96 – 1.88 (m, 2H), 1.82 (d, J = 12.4 Hz, 2H), 1.73 (d, J = 12.4 Hz, 1H), 1.48 – 1.34 (m, 4H), 1.26 (t, J = 7.2 Hz, 4H). ¹³**C NMR** (100 MHz, CDCl₃) δ 163.7, 155.8, 155.6, 140.0, 138.2, 138.1, 137.4, 134.6, 132.8, 130.6, 130.3, 128.9, 126.1, 118.9, 61.4, 46.1, 45.0, 34.0, 32.4, 31.9, 31.5, 30.7, 26.7, 26.5, 26.2, 14.8.

HRMS (ESI) calcd for $C_{28}H_{34}ClN_2O_2$ [M + H]⁺ 465.2303, found 465.2308.

8-cyclohexyl-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (44).



According to the *general procedure*. The spectral Data is consistent with the literature data.⁷ White solid (33.8 mg, 43%). M.p. =299 - 300 °C.

*R*_f 0.30 (DCM/MeOH, 20/1).

¹**H** NMR (400 MHz, CDCl₃) δ 3.64 (s, 3H), 3.48 (s, 3H), 2.90 (tt, J = 12.0, 3.6 Hz, 1H), 2.13 – 2.04 (m, 2H), 1.92 – 1.85 (m, 2H), 1.78 – 1.70 (m, 2H), 1.68 (d, J = 3.2 Hz, 1H), 1.48 – 1.37 (m, 2H), 1.34 – 1.29 (m, 1H). ¹³**C** NMR (100 MHz, CDCl₃) δ 160.0, 155.8, 151.8, 149.3, 106.7, 39.0, 31.5, 30.3, 28.4, 26.1, 25.8.

HRMS (ESI) calcd for $C_{13}H_{19}N_4O_2$ [M + H]⁺ 263.1503, found 263.1502.

2-cyclohexyl-3-hydroxynaphthalene-1,4-dione (45)



According to the *general procedure*. The spectral data is consistent with the literature data.⁴ Yellow solid (55.3 mg, 72%). M.p. =128 - 129 °C.

 $R_{\rm f}$ 0.50 (Petroleum ether/EtOAc, 10/1).

¹**H** NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.50 (s, 1H), 3.08 (tt, J = 12.4, 3.2 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.81 (d, J = 12.4 Hz, 2H), 1.73 (d, J = 9.2 Hz, 1H), 1.61 (d, J = 12.4 Hz, 2H), 1.44 – 1.28 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 184.7, 182.1, 153.0, 135.0, 133.3, 132.8, 129.3, 128.0, 127.0, 126.0, 35.2, 29.3, 26.8, 26.1.

HRMS (ESI) calcd for $C_{16}H_{17}O_3 [M + H]^+ 257.1172$, found 257.1171.

6. Gram-scale Reaction



Scheme S3

To an oven dried Schlenk tube was added $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (90 mg, 0.08 mmol, 1 mol %), **1** (1.17 g, 8.0 mmol, 1.0 equiv), 2 (3.54 g, 12 mmol, 1.5 equiv), TFA (0.9 mL, 12 mmol, 1.5 equiv) and 80 mL of DMSO. The tube was evacuated and backfilled with O₂ (this process was repeated three times). The mixture was then stirred rapidly and irradiated with two 36 W Blue LEDs (approximately 2 cm away from the light source) at room temperature for 48 h. The reaction mixture was diluted with 60 mL of aqueous 1 M NaHCO₃ solution, and extracted with DCM (3 ×

100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na_2SO_4 , and concentrated in vacuo. After purification by flash column chromatography on silica gel, the product was obtained in 81% yield.

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NMR Spectra





















70

60 50 40

80

30 20

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10

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210 200 190 180 170 160 150 140 130 120 110 100 f1 (ppm)









































































