Supporting Information

Metal- and Photosensitizer-free Cross-Dehydrogenative Coupling through Photoinduced Energy Transfer

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1. General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. The light source (Kessil PR160L-390 nm; Kessil PR160L-427 nm; A160WE TUNA BLUE) were purchased from Kessil. Thin layer chromatography (TLC) with Merck TLC silica gel 60 F254 plate was used to check reaction progress. ¹H and ¹³C NMR spectra were recorded on a Bruker UltraShield Plus 600 MHz (151 MHz) instrument, which uses the deuterium lock signal to reference the spectra. ¹⁹F NMR spectra were recorded on a Bruker 700 MHz spectrometer. The solvent residual peaks, e.g., of chloroform (CDCl₃: δ 7.26 ppm and δ 77.23 ppm), were used as references. Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doubletof doublet, etc), coupling constant (J/Hz) and integration. HRMS (ESI) spectra were obtained using a Waters Q-Tof premier[™] mass spectrometer. Ultraviolet-visible (UVvis) spectrometry was performed by Agilent Cary 5000 series UV-vis-NIR spectrometer. Fluorescence quenching was performed on VARIAN CARY Eclipse fluorescence spectrophotometer.

2. Table of Reaction Optimization

Table S1. Screening of oxidant ^a	
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		+	Oxidant (2.0 equiv) <u>TFA (1.0 equiv)</u> DCE/H ₂ O N ₂ , blue LEDs, 6h		
	1a	2a		3a	
entry ^a			Oxidant		yield (%) ^b
1	DTBP				56
2	DCP				88
3	H_2O_2				23
4	TBPB				95
5	BPO				90
6	TBHP				15
7	Air				70
8 ^c	DTBP				73
9 ^c			H_2O_2		71

^a Reaction conditions: 1a (0.2 mmol), 2a (0.2 mL), oxidant (2.0 equiv.), TFA (0.2 mmol), H₂O (200

 μL), and DCE (2.0 mL) under N_2 at room temperature (25 °C), blue LEDs for 6 h. $^{\it b}$ Determined by

¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ^c Reaction time: 18

h.

Table S2. Screening of acid^a

		+	TBPB (2.0 equiv) Acid (1.0 equiv) DCE/H ₂ O N ₂ , blue LEDs, 6h		
	1a	2a		3a	
entry ^a			Acid		yield $(\%)^b$
1	H ₃ PO ₄				68
2	TFA				95
3	TfOH				90
4	HCl				37
5	CH ₃ COOH				65
6	TsOH				88

^a Reaction conditions: 1a (0.2 mmol), 2a (0.2 mL), TBPB (2.0 equiv.), Acid (0.2 mmol), H₂O (200

µL), and DCE (2.0 mL) under N₂ at room temperature (25 °C), blue LEDs for 6 h. ^b Determined by

¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Screening of solvent^a

	1a	+ 🔶 2a	TBPB (2.0 equiv) <u>TFA (1.0 equiv)</u> Solvent N ₂ , blue LEDs, 6h	3a	
entry ^a			solvent		yield $(\%)^b$
1^c	DCE				56
2	Toluene				49
3	DMSO				25
4	MeCN				75
5	Acetone				83
6	EA				70
7	DCE/H ₂ O (10:1)				95
8	$DCE/H_2O(5:1)$				92
9		DCI	$E/H_2O(1:1)$		67

^{*a*} Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mL), TBPB (2.0 equiv.), TFA (0.2 mmol), solvent (2.0 mL), H₂O (200 μL) under N₂ at room temperature (25 °C), blue LEDs for 6 h. ^{*b*} Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*} Without water.

3. General procedure

To a 10 mL vial equipped with a Teflon septum and a magnetic stir bar was added heteroarene (1) (0.20 mmol, 1.0 equiv.), alkane (2) (0.2 mL), *tert*-Butyl peroxybenzoate (TBPB) (76 μ L, 0.40 mmol, 2.0 equiv.), TFA (15 μ L, 0.20 mmol, 1.0 equiv.), H₂O (200 μ L) and 2.0 mL of dichloroethane (DCE). The above mixture was vigorously stirred under the irradiation of 40 W blue LEDs in N₂ atmosphere for 6 hours. After completion, the reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The collected organic layer was washed with brine, dried with sodium sulfate. After the solvent was removed under reduced pressure, the crude product was purified by preparative thin layer chromatography or flash column chromatography.

4. Characterization data of products



2-cyclohexyl-4-methylquinoline (3a)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a colorless oil (42.75 mg, 95%).

¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 2.88 (t, J = 12.1 Hz, 1H), 2.67 (s, 3H), 2.06 - 1.97 (m, 2H), 1.89 (d, J = 13.1 Hz, 2H), 1.79 (d, J = 12.9 Hz, 1H), 1.68 - 1.58 (m, 2H), 1.47 (q, J = 12.9 Hz, 2H), 1.37 - 1.30 (m, 1H).
¹³C NMR (151 MHz, CDCl₃) δ 166.59, 147.72, 144.34, 129.59, 129.03, 127.14, 125.46,

123.65, 120.35, 47.70, 32.95, 26.69, 26.25, 18.94.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}N^+$ 226.1596; Found 226.1597.

2-cyclohexyl-6-fluoro-4-methylquinoline (3b)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow solid (34.02 mg, 70%).

¹**H** NMR (600 MHz, CDCl₃) δ 8.03 (dd, J = 8.8, 5.7 Hz, 1H), 7.51 (d, J = 9.8 Hz, 1H),

7.41 (t, J = 8.6 Hz, 1H), 7.17 (s, 1H), 2.85 (t, J = 12.0 Hz, 1H), 2.61 (s, 3H), 1.99 (d, J

= 12.8 Hz, 2H), 1.88 (d, J = 12.9 Hz, 2H), 1.78 (d, J = 12.9 Hz, 1H), 1.61 (q, J = 12.6 Hz, 2H), 1.45 (q, J = 12.9 Hz, 2H), 1.32 (d, J = 12.8 Hz, 1H).
¹³C NMR (151 MHz, CDCl₃) δ 165.91 (d, J = 3.0 Hz), 160.07 (d, J = 246.1 Hz), 144.79, 143.80 (d, J = 4.5 Hz), 131.91 (d, J = 9.1 Hz), 127.78 (d, J = 9.1 Hz), 121.00, 118.91 (d, J = 25.7 Hz), 107.26 (d, J = 21.1 Hz), 47.52, 32.92, 26.66, 26.22, 18.97.
¹⁹F NMR (659 MHz, CDCl₃) δ -114.57.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₆H₁₈FN⁺ 244.1457; Found 244.1451.



4-chloro-2-cyclohexylquinoline (3c)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a colorless oil (38.22 mg, 78%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.42 (s, 1H), 2.91 (d, *J* = 11.9 Hz, 1H), 2.02 (d, *J* = 12.4 Hz, 2H), 1.90 (d, *J* = 13.1 Hz, 2H), 1.79 (d, *J* = 12.9 Hz, 1H), 1.61 (q, *J* = 13.8, 12.7 Hz, 2H), 1.46 (q, *J* = 12.9 Hz, 2H), 1.34 (t, *J* = 14.5 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 166.94, 148.74, 142.82, 130.33, 129.40, 126.75, 125.27, 124.04, 119.93, 47.51, 32.83, 26.57, 26.14.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₆ClN⁺ 246.1044; Found 246.1047.



4-bromo-2-cyclohexylquinoline (3d)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a colorless oil (41.62 mg, 72%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.13 (d, *J* = 8.3 Hz, 1H), 8.05 (s, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.63 (s, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 2.90 (s, 1H), 2.03 (d, *J* = 12.5 Hz, 2H), 1.90 (d, *J* = 12.8 Hz, 2H), 1.79 (d, *J* = 12.8 Hz, 1H), 1.61 (q, *J* = 12.6 Hz, 2H), 1.46 (q, *J* = 12.8 Hz, 2H), 1.34 (t, *J* = 12.9 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 166.86, 148.53, 134.40, 130.39, 129.44, 127.06, 126.70, 126.64, 123.84, 47.33, 32.84, 26.56, 26.13.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₆BrN⁺ 290.0539; Found 290.0536.



4,7-dichloro-2-cyclohexylquinoline (3e)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (45.20 mg, 81%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.21 – 7.99 (m, 2H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.40 (s, 1H), 2.86 (t, *J* = 11.9 Hz, 1H), 2.01 (d, *J* = 12.8 Hz, 2H), 1.90 (d, *J* = 13.1 Hz, 2H), 1.79 (d, *J* = 13.0 Hz, 1H), 1.61 (t, *J* = 12.4 Hz, 2H), 1.45 (q, *J* = 12.9 Hz, 2H), 1.33 (t, *J* = 12.8 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 168.27, 149.20, 142.68, 136.35, 128.47, 127.69, 125.45,

123.77, 120.28, 47.44, 32.71, 26.52, 26.10.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₅Cl₂N⁺ 280.0654; Found 280.0658.



2-bromo-4-cyclohexylquinoline (3f)

Obtained as a yellow oil (39.30 mg, 68%).

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

¹**H NMR** (600 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57

(t, J = 7.4 Hz, 1H), 7.38 (s, 1H), 3.28 (t, J = 9.2 Hz, 1H), 1.97 (dd, J = 38.7, 8.8 Hz,

4H), 1.85 (d, *J* = 13.2 Hz, 1H), 1.53 (q, *J* = 10.6, 10.0 Hz, 4H), 1.34 (d, *J* = 12.1 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 156.53, 148.99, 142.71, 130.04, 129.74, 126.76, 125.94, 123.42, 122.33, 39.19, 33.55, 26.93, 26.28.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₆BrN⁺ 290.0539; Found 290.0542.



1-cyclohexylisoquinoline (3g)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow oil (33.34 mg, 79%).

¹H NMR (600 MHz, CDCl₃) δ 8.48 (d, J = 5.5 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.83
- 7.78 (m, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 5.4 Hz, 1H), 3.56 (t, J = 10.7 Hz, 1H), 1.96 (dd, J = 29.6, 12.9 Hz, 4H), 1.87 - 1.80 (m, 3H), 1.57 - 1.50 (m, 2H), 1.44 - 1.36 (m, 1H).
¹³C NMR (151 MHz, CDCl₃) δ 165.83, 142.01, 136.52, 129.68, 127.68, 126.94, 126.41,

124.87, 119.02, 41.67, 32.72, 27.02, 26.38.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₇N⁺ 212.1434; Found 212.1439.



6-chloro-1-cyclohexylisoquinoline (3h)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow oil (43.12 mg, 88%).

¹H NMR (600 MHz, CDCl₃) δ 8.53 – 8.42 (m, 1H), 8.19 – 8.09 (m, 1H), 7.76 (s, 1H),
7.49 (d, J = 9.0 Hz, 1H), 7.37 (d, J = 5.6 Hz, 1H), 3.48 (t, J = 11.6 Hz, 1H), 1.93 (t, J = 11.3 Hz, 4H), 1.81 (d, J = 11.9 Hz, 3H), 1.51 (q, J = 13.0 Hz, 2H), 1.41 – 1.34 (m, 1H).
¹³C NMR (151 MHz, CDCl₃) δ 165.93, 143.13, 137.35, 135.82, 127.84, 126.70, 126.35, 124.57, 118.08, 41.78, 32.67, 26.91, 26.28.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₆ClN⁺ 246.1044; Found 246.1047.



4-chloro-1-cyclohexylisoquinoline (3i)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow solid (44.10 mg, 90%).

¹**H** NMR (600 MHz, CDCl₃) δ 8.52 (s, 1H), 8.23 (t, *J* = 7.4 Hz, 2H), 7.77 (t, *J* = 8.0

Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 3.62 – 3.44 (m, 1H), 1.97 – 1.92 (m, 4H), 1.81 (t, J =

12.0 Hz, 3H), 1.52 (q, *J* = 13.1 Hz, 2H), 1.39 (t, *J* = 12.9 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 164.82, 140.79, 133.90, 130.66, 127.74, 127.26, 126.32,

125.17, 124.30, 41.62, 32.70, 26.93, 26.30.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₆ClN⁺ 246.1044; Found 246.1045



methyl 1-cyclohexylisoquinoline-3-carboxylate (3j)

Prepared according to general procedure. Eluent: PE/(EA) (6:1).

Obtained as a white solid (46.81 mg, 87%).

¹H NMR (600 MHz, CDCl₃) δ 8.39 (s, 1H), 8.29 – 8.25 (m, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.73 – 7.68 (m, 2H), 4.02 (s, 3H), 3.60 – 3.53 (m, 1H), 1.95 (p, J = 14.2, 12.4 Hz, 6H), 1.81 (d, J = 12.5 Hz, 1H), 1.57 – 1.50 (m, 2H), 1.43 (t, J = 12.8 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 166.99, 166.22, 140.78, 136.12, 130.20, 129.13, 127.86, 125.06, 122.52, 52.78, 42.17, 32.35, 26.90, 26.18.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₇H₁₉NO₂⁺ 270.1489; Found 270.1490.



5-bromo-1-cyclohexylisoquinoline (3k)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (46.82 mg, 81%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.58 (d, *J* = 5.9 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 5.9 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 3.58 – 3.51 (m, 1H), 1.94 (d, *J* = 16.1 Hz, 5H), 1.81 (t, *J* = 11.1 Hz, 4H), 1.53 – 1.48 (m, 2H), 1.38 (d, *J* = 12.9 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 166.19, 143.40, 135.60, 133.48, 127.54, 127.16, 124.59, 122.72, 117.81, 41.88, 32.82, 26.96, 26.31.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₆BrN⁺ 290.0539; Found 290.0533.



4-chloro-2-cyclohexylquinazoline (3l)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (22.14 mg, 45%).

¹**H NMR** (600 MHz, CDCl₃) δ 10.72 (s, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 7.76 (q, *J* = 17.1, 12.4 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 2.71 (s, 1H), 2.06 (d, *J* = 12.3 Hz, 2H), 1.93 (d, *J* = 13.0 Hz, 2H), 1.81 (d, *J* = 12.4 Hz, 1H), 1.71 (q, *J* = 11.7 Hz, 2H), 1.45 (q, *J* = 12.7 Hz, 2H), 1.40 – 1.33 (m, 1H).

¹³**C NMR** (151 MHz, CDCl₃) δ 163.63, 159.97, 149.47, 134.91, 127.44, 126.57, 126.41, 120.94, 44.89, 30.73, 26.09, 25.83.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₄H₁₅ClN₂⁺ 246.7393; Found 246.7390.



1,4-dicyclohexylphthalazine (3m)

Prepared according to general procedure. Eluent: PE/ (EA) (6:1).

Obtained as a white solid (47.04 mg, 80%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.22 – 8.09 (m, 1H), 7.89 – 7.77 (m, 1H), 3.50 – 3.39 (m, 1H), 2.07 – 1.92 (m, 6H), 1.81 (d, *J* = 12.7 Hz, 1H), 1.51 (q, *J* = 12.5, 11.5 Hz, 2H), 1.38 (q, *J* = 12.6 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 161.94, 131.26, 125.08, 124.34, 40.58, 32.46, 27.03, 26.38.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₆N₂⁺ 295.2169; Found 295.2166.



2-cyclohexylbenzo[d]thiazole (3n)

Prepared according to general procedure. Eluent: PE/(EA) (10:1).

Obtained as a colorless oil (30.38 mg, 70%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.11 (t, *J* = 11.7 Hz, 1H), 2.21 (d, *J* = 12.1 Hz, 2H), 1.89 (d, *J* = 13.3 Hz, 2H), 1.77 (d, *J* = 13.0 Hz, 1H), 1.64 (q, *J* = 12.6 Hz, 2H), 1.45 (q, *J* = 12.8 Hz, 2H), 1.33 (t, *J* = 12.7 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 177.73, 153.24, 134.67, 125.91, 124.62, 122.68, 121.68, 43.59, 33.57, 26.21, 25.93.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}NS^+$ 218.0998; Found 218.0995.



5,5'-di-tert-butyl-6,6'-dicyclohexyl-3,3'-bipyridine (30)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (63.95 mg, 74%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.21 (s, 2H), 7.12 (s, 2H), 2.77 (t, *J* = 11.2 Hz, 2H), 2.03

(d, J = 12.5 Hz, 4H), 1.88 (d, J = 12.9 Hz, 5H), 1.78 (d, J = 12.6 Hz, 2H), 1.62 (q, J =

12.3 Hz, 5H), 1.52 – 1.43 (m, 5H), 1.38 (s, 19H).

¹³C NMR (151 MHz, CDCl₃) δ 165.67, 160.70, 156.45, 117.61, 115.99, 46.80, 35.05, 33.26, 30.89, 26.84, 26.41.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₀H₄₄N₂⁺ 433.3538; Found 433.3540.



4-cyclohexyl-2-phenylquinoline (3p)

Prepared according to general procedure. Eluent: PE/ (DCM) (2:1).

Obtained as a colorless solid (30.42 mg, 53%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.22 (d, *J* = 7.5 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.54 (q, *J* = 7.1 Hz, 3H), 7.46 (t, *J* = 7.3 Hz, 1H), 3.39 (t, *J* = 11.2 Hz, 1H), 2.09 (d, *J* = 11.9 Hz, 2H), 1.97 (d, *J* = 12.6 Hz, 2H), 1.88 (d, *J* = 13.4 Hz, 1H), 1.60 (dq, *J* = 25.5, 12.9 Hz, 4H), 1.42 – 1.34 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.32, 154.16, 148.44, 140.14, 130.60, 129.20, 129.11, 128.81, 127.68, 125.96, 125.90, 122.88, 115.57, 39.18, 33.70, 27.00, 26.36.
HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₁N⁺ 288.1752; Found 288.1758.



6-cyclohexylphenanthridine (3q)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (40.19 mg, 77%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.65 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.36 - 8.29 (m, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.70 (dt, *J* = 14.5, 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 3.63 (t, *J* = 11.3 Hz, 1H), 2.10 (d, *J* = 12.0 Hz, 2H), 1.98 (t, *J* = 12.6 Hz, 4H), 1.86 (d, *J* = 12.8 Hz, 1H), 1.59 (q, *J* = 12.8 Hz, 2H), 1.46 (d, *J* = 12.9 Hz, 1H).

¹³**C NMR** (151 MHz, CDCl₃) δ 165.39, 143.99, 133.12, 130.03, 128.49, 127.17, 126.24, 125.73, 124.83, 123.45, 122.68, 121.92, 42.11, 32.42, 27.01, 26.45.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₁₉N⁺ 262.1596; Found 262.1600.



ethyl 2,6-dicyclohexylisonicotinate (3r)

Prepared according to general procedure. Eluent: PE/(EA) (6:1).

Obtained as a white solid (54.18 mg, 86%).

¹**H** NMR (600 MHz, CDCl₃) δ 7.50 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 11.5

Hz, 2H), 1.95 (d, *J* = 12.3 Hz, 4H), 1.84 (d, *J* = 12.9 Hz, 4H), 1.74 (d, *J* = 12.8 Hz, 2H),

1.51 (q, *J* = 12.6, 11.3 Hz, 4H), 1.45 – 1.38 (m, 7H), 1.31 – 1.24 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 166.88, 166.22, 138.37, 117.25, 61.57, 46.70, 33.08,

26.64, 26.21, 14.41.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₉NO₂⁺ 316.2271; Found 316.2270.



2,6-dicyclohexyl-4-phenylpyridine (3s)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (52.95 mg, 83%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.18 (s, 2H), 2.77 (t, *J* = 11.3 Hz, 2H), 2.06 – 1.96 (m, 4H), 1.87 (d, *J* = 12.8 Hz, 4H), 1.77 (d, *J* = 12.8 Hz, 2H), 1.56 (q, *J* = 12.6 Hz, 4H), 1.46 (q, *J* = 12.7 Hz, 4H), 1.31 (q, *J* = 12.8 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 166.35, 149.12, 139.73, 128.99, 128.59, 127.25, 116.11, 46.88, 33.33, 26.77, 26.33.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₉N⁺ 320.2373; Found 320.2367.



2-cyclohexyl-4,6-dimethylpyrimidine (3t)

Prepared according to general procedure. Eluent: PE/(EA) (3:1).

Obtained as a colorless oil (36.85 mg, 91%).

¹**H NMR** (600 MHz, CDCl₃) δ 6.81 (s, 1H), 2.78 (t, *J* = 11.9 Hz, 1H), 2.43 (s, 7H), 1.97 - 1.90 (m, 2H), 1.82 (d, *J* = 13.0 Hz, 2H), 1.67 (dd, *J* = 48.8, 13.7 Hz, 3H), 1.39 (q, *J* = 12.8 Hz, 2H), 1.30 (d, *J* = 12.7 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 174.04, 166.43, 117.46, 47.76, 32.06, 26.43, 26.06, 24.18.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₂H₁₈N₂⁺ 191.1504; Found 191.1508.



5,7-dichloro-8-cyclohexyl-4-(4-fluorophenoxy)quinoline (3u)

Prepared according to general procedure. Eluent: PE/(EA) (6:1).

Obtained as a yellow solid (63.02 mg, 81%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.96 (s, 1H), 7.50 (s, 1H), 7.16 (t, *J* = 7.7 Hz, 2H), 7.12 - 7.08 (m, 2H), 6.52 (d, *J* = 2.3 Hz, 1H), 2.69 (t, *J* = 10.8 Hz, 1H), 1.88 (d, *J* = 12.4 Hz, 2H), 1.82 (d, *J* = 12.1 Hz, 2H), 1.72 (d, *J* = 12.8 Hz, 1H), 1.49 – 1.32 (m, 5H), 1.25 (t, *J* = 12.5 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 169.68, 162.49, 159.98 (d, J = 244.6 Hz), 151.49, 150.43 (d, J = 3.0 Hz), 134.91, 130.03, 128.76, 127.61, 122.07 (d, J = 9.1 Hz), 117.15 (d, J = 24.2 Hz), 117.13, 105.83, 47.35, 32.48, 26.42, 25.98.

¹⁹**F NMR** (659 MHz, CDCl₃) δ -117.36.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₁₈Cl₂FNO⁺ 390.0822; Found 390.0818.

2,6-dichloro-8-cyclohexyl-9-methyl-9H-purine (3v)

Prepared according to general procedure. Eluent: PE/(EA) (3:1).

Obtained as a white solid (43.74 mg, 77%).

¹**H NMR** (600 MHz, CDCl₃) δ 3.84 (s, 3H), 2.91 (t, *J* = 11.6 Hz, 1H), 1.99 (dd, *J* =

29.4, 12.6 Hz, 4H), 1.85 (q, *J* = 12.5 Hz, 3H), 1.43 (dq, *J* = 25.6, 12.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 163.23, 154.82, 151.80, 149.67, 130.32, 37.04, 30.90,

29.37, 26.08, 25.61.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₂H₁₄Cl₂N₄⁺ 285.0668; Found 285.0668.



2-cyclopentyl-4-methylquinoline (4a)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (38.82 mg, 92%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.17 (s, 1H), 3.38 – 3.28 (m, 1H), 2.67 (s, 3H), 2.20 – 2.12 (m, 2H), 1.88 (s, 4H), 1.75 (s, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 166.00, 147.61, 144.20, 129.58, 129.01, 127.06, 125.45, 123.63, 120.75, 48.91, 33.68, 26.16, 18.92.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₇N⁺ 212.1440; Found 212.1443.



2-cycloheptyl-4-methylquinoline (4b)

Prepared according to general procedure. Eluent: PE/(EA) (10:1).

Obtained as a colorless oil (45.41 mg, 95%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 3.04 (t, *J* = 9.8 Hz, 1H), 2.67 (s, 3H), 2.04 (dd, *J* = 10.3, 6.0 Hz, 2H), 1.88 – 1.78 (m, 4H), 1.77 – 1.71 (m, 2H), 1.64 (t, *J* = 8.4 Hz, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 168.21, 147.45, 144.54, 129.53, 129.09, 127.07, 125.48, 123.66, 120.42, 49.68, 35.21, 28.12, 27.61, 18.98.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}N^+$ 240.1747; Found 240.1744.



2-cyclooctyl-4-methylquinoline (4c)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow oil (45.66 mg, 92%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 3.11 (t, *J* = 9.7 Hz, 1H), 2.67 (s, 3H), 1.98 (dd, *J* = 13.9, 8.3 Hz, 2H), 1.87 (dd, *J* = 22.8, 13.8 Hz, 4H), 1.75 – 1.61 (m, 8H).

¹³C NMR (151 MHz, CDCl₃) δ 168.93, 147.45, 144.46, 129.56, 129.06, 127.02, 125.46, 123.65, 120.79, 47.66, 33.66, 26.56, 26.29, 18.99.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₂₃N⁺ 254.1903; Found 254.1903.



2-cyclododecyl-4-methylquinoline (4d)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a white solid (55.62 mg, 90%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.00 – 7.86 (m, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.41 (m, 1H), 7.13 (s, 1H), 3.19 – 3.01 (m, 1H), 2.68 (s, 3H), 1.91 (dq, *J* = 12.8, 6.6 Hz, 2H), 1.74 (dd, *J* = 13.1, 5.8 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.52 – 1.43 (m, 7H), 1.40 – 1.31 (m, 10H). ¹³**C NMR** (151 MHz, CDCl₃) δ 166.81, 147.79, 143.89, 129.74, 128.88, 127.08, 125.38, 123.63, 121.53, 43.23, 30.28, 24.08, 24.02, 23.85, 23.52, 23.05, 18.93.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for C₂₂H₃₁N⁺ 310.2527; Found 310.2527.

2-((3r,5r,7r)-adamantan-1-yl)-4-methylquinoline (4e)

Prepared according to *general procedure* with 2 equiv of adamantane. Eluent: PE/ (EA)

(10:1).

Obtained as a white solid (47.09 mg, 85%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.33 (s, 1H), 2.69 (s, 3H), 2.13 (d, *J* = 22.4 Hz, 9H), 1.83 (s, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 168.83, 147.66, 143.68, 130.09, 128.75, 126.84, 125.45, 123.56, 118.66, 41.94, 39.69, 37.05, 28.99, 19.13.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N^+$ 278.1903; Found 278.1900.



4-methyl-2-(1-methylcyclopentyl)quinoline (4f)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a colorless oil (29.70 mg, 66%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.23 – 8.01 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J*

= 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.30 (s, 1H), 2.69 (s, 3H), 2.38 – 2.24 (m, 2H),

1.78 (d, *J* = 46.5 Hz, 6H), 1.42 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.11, 147.22, 143.75, 129.97, 128.86, 126.73, 125.50, 123.52, 120.22, 50.18, 39.25, 28.53, 24.72, 19.08.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₆H₁₉N⁺ 226.1596; Found 226.1594.

2-(hexan-2-yl)-4-methylquinoline (4g)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as yellow oil (37.11 mg, 76%).

(C₂:C₃ = 2:1) C₂ and C₃ products were obtained as an inseparable mixture. Ratio of C₂: C₃ was determined by the integration of methyl group peaks at **3.06-3.01 ppm** (m, 1H) for C₂ product and **2.86-2.81 ppm** (m, 1H) for C₃ product.

Data for C₂ product: ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.3 Hz, 1H), 7.95 (d, J

= 8.2 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H),

7.12 (s, 1H), 3.03 (h, J = 6.8 Hz, 1H), 2.69 (s, 3H), 1.86 – 1.58 (m, 3H), 1.37 – 1.25 (m,

2H), 1.34(d, *J* = 6.8 Hz, 3H), 1.23 – 1.12 (m, 1H), 0.85 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.06, 147.68, 144.38, 129.63, 129.03, 125.50, 125.34, 123.69, 120.28, 43.05, 36.94, 30.10, 22.97, 20.94, 19.00, 14.17.

Data for C₃ product: ¹**H NMR** (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.12 (s, 1H), 2.84 (p, *J* = 7.0 Hz, 1H), 2.69 (s, 3H), 1.86 – 1.58 (m, 2H), 1.37 – 1.25 (m, 3H), 1.23 – 1.12 (m, 1H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.94, 147.72, 144.10, 129.68, 128.96, 127.16, 125.46, 123.69, 120.84, 50.43, 37.82, 28.68, 20.99, 19.00, 14.40, 12.38.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₆H₂₁N⁺ 228.1747; Found 228.1747.

4-methyl-2-(pentan-2-yl)quinoline (4h)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow oil (29.82 mg, 70%).

 $(C_2:C_3 = 3:1)$ C₂ and C₃ products were obtained as an inseparable mixture. Ratio of C₂:

C₃ was determined by the integration of methyl group peaks at **3.11 – 3.02 ppm** (m, 1H)

for C_2 product and 2.77 – 2.71 ppm (m, 1H) for C_3 product.

Data for C₂ product: ¹**H NMR** (40 0 MHz, CDCl₃) δ 8.07 (t, J = 7.9 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.12 (s, 1H), 3.06 (h, J = 7.1 Hz, 1H), 2.68 (s, 1H), 1.84 – 1.74 (m, 1H), 1.69 – 1.61 (m, 1H), 1.43 – 1.32 (m, 1H), 1.35 (d, J = 7.0 Hz, 3H), 1.28 – 1.18 (m, 1H), 0.90 (t, J = 7.3 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 167.02, 147.66, 144.39, 129.61, 129.04, 127.15, 125.51,
123.68, 120.28, 42.57, 39.44, 21.02, 20.87, 19.00, 14.34.

Data for C₃ product: ¹**H NMR** (400 MHz, CDCl₃) δ 8.09 (t, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 2.74 (p, *J* = 7.4 Hz, 1H), 2.68 (s, 1H), 1.84 – 1.74 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H) ¹³**C NMR** (101 MHz, CDCl₃) δ 165.74, 147.73, 144.12, 129.68, 128.97, 127.18, 125.48,

123.70, 120.86, 52.31, 28.37, 19.00, 12.38.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₉N⁺ 214.1590; Found 214.1588.

4-methyl-2-(2-methylhexan-2-yl)quinoline (4i)

Prepared according to general procedure. Eluent: PE/(EA) (10:1).

Obtained as a yellow oil (30.85 mg, 64%).

¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.1 Hz, 1H), 7.49 (t, J = 7.1 Hz, 1H), 2.69 (s, 3H), 1.81 – 1.75 (m, 2H), 1.43 (s, 6H), 1.26 – 1.22 (m, 2H), 1.11 – 1.05 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H).
¹³C NMR (151 MHz, CDCl₃) δ 168.41, 147.49, 143.44, 130.15, 128.71, 126.62, 125.45, 123.53, 119.47, 43.42, 41.09, 27.96, 27.20, 23.57, 19.15, 14.20.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}N^+$ 242.1830; Found 242.1835.



4-methyl-2-(tert-pentyl)quinoline (4j)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow oil (32.81 mg, 77%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.07 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.31 (s, 1H), 2.69 (s, 3H), 1.85 (q, J = 7.3

Hz, 2H), 1.44 (s, 6H), 0.77 - 0.70 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 168.16, 147.50, 143.45, 130.13, 128.72, 126.60, 125.46, 123.51, 119.51, 41.33, 35.97, 27.48, 19.11, 9.39.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for C₁₅H₁₉N⁺ 214.1590; Found 214.1592.

2-(2,3-dimethylbutan-2-yl)-4-methylquinoline (4k)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow oil (31.33 mg, 69%).

¹H NMR (600 MHz, CDCl₃) δ 8.06 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.65 (s, 1H), 7.49 (s, 1H), 7.30 (s, 1H), 2.69 (s, 3H), 2.29 (s, 1H), 1.38 (s, 6H), 0.81 (d, *J* = 6.6 Hz, 6H).
¹³C NMR (151 MHz, CDCl₃) δ 169.00, 147.39, 143.23, 130.16, 128.70, 126.62, 125.44, 123.52, 119.75, 43.98, 37.23, 23.82, 19.17, 18.09.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}N^+$ 228.3510; Found 228.3519.



4-methyl-2-(tetrahydrofuran-2-yl)quinoline (4l)

Prepared according to general procedure. Eluent: PE/ (EA) (3:1).

Obtained as a yellow solid (25.57 mg, 60%).

¹**H** NMR (600 MHz, CDCl₃) δ 8.22 – 8.04 (m, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (s, 1H), 5.16 (d, *J* = 6.7 Hz, 1H), 4.18 (q, *J* = 6.9 Hz, 1H), 4.04 (q, *J* = 7.0 Hz, 1H), 2.72 (s, 3H), 2.58 – 2.44 (m, 1H), 2.06 (dd, *J* = 18.8, 6.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 163.20, 147.35, 145.21, 129.62, 129.32, 127.60, 126.00, 123.83, 118.73, 82.17, 69.42, 33.48, 26.13, 19.07.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₄H₁₅NO⁺ 214.1226; Found 214.1223.



2-(1,4-dioxan-2-yl)-4-methylquinoline (4m)

Prepared according to general procedure. Eluent: PE/(EA) (3:1).

Obtained as a yellow solid (36.64 mg, 80%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (s, 1H), 4.97 – 4.83 (m, 1H), 4.23 (d, *J* = 11.6 Hz, 1H), 4.00 (q, *J* = 12.1, 11.7 Hz, 2H), 3.89 – 3.76 (m, 2H), 3.70 – 3.60 (m, 1H), 2.72 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 157.92, 147.38, 145.35, 129.91, 129.43, 127.75, 126.36, 123.82, 119.23, 78.90, 71.23, 67.21, 66.56, 19.00.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₄H₁₅NO₂⁺ 230.1175; Found 230.1172.



4-methyl-2-(tetrahydro-2H-pyran-2-yl)quinoline (4n)

Prepared according to general procedure. Eluent: PE/ (EA) (10:1).

Obtained as a yellow solid (35.41 mg, 78%).

¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.46 (s, 1H), 4.61 (d, J = 11.2 Hz, 1H), 4.21 (d, J = 11.2 Hz, 1H), 3.75 - 3.64 (m, 1H), 2.71 (s, 3H), 2.10 (d, J = 13.1 Hz, 1H), 1.98 (s, 1H), 1.76 (t, J = 9.1 Hz, 2H), 1.67 - 1.58 (m, 2H).
¹³C NMR (151 MHz, CDCl₃) δ 162.27, 147.28, 145.16, 129.76, 129.21, 127.67, 125.98,

123.79, 118.94, 81.78, 69.06, 32.94, 26.02, 23.88, 18.99.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₇NO⁺ 228.1383; Found 228.1383.

2-(tert-butoxymethyl)-4-methylquinoline (40)

Prepared according to general procedure. Eluent: PE/(EA) (6:1).

Obtained as a yellow oil (32.98 mg, 72%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.68

(t, *J* = 7.6 Hz, 1H), 7.54 – 7.50 (m, 2H), 4.73 (s, 2H), 2.72 (s, 3H), 1.34 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 160.43, 147.23, 145.02, 129.41, 127.61, 125.93, 123.85,

120.21, 74.16, 66.14, 27.85, 19.02.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₅H₁₉NO⁺ 230.1539; Found 230.1538.



2-(1-(tert-butoxy)ethyl)-4-methylquinoline (4p)

Prepared according to general procedure. Eluent: PE/(EA) (6:1).

Obtained as a yellow solid (37.42 mg, 77%).

¹**H** NMR (600 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.68 (t, J

= 7.5 Hz, 1H), 7.56 (s, 1H), 7.52 (t, J = 7.3 Hz, 1H), 4.92 (q, J = 5.9 Hz, 1H), 2.72 (s,

3H), 1.46 (d, *J* = 6.6 Hz, 3H), 1.19 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 166.80, 147.05, 144.89, 129.44, 129.19, 127.51, 125.83,

123.85, 119.09, 74.80, 72.28, 28.63, 25.11, 19.11.

2-((2-methoxyethoxy)methyl)-4-methylquinoline (4q)

Prepared according to general procedure. Eluent: PE/(EA) (6:1).

Obtained as a yellow oil (32.34 mg, 66%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.69

(t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.50 (s, 1H), 4.84 (s, 2H), 3.81 – 3.71 (m,

2H), 3.67 – 3.56 (m, 2H), 3.42 (s, 3H), 2.72 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.77, 147.31, 145.37, 129.54, 127.72, 126.24, 123.88, 120.27, 74.82, 72.01, 70.26, 59.23, 19.01.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₄H₁₇NO₂⁺ 232.1332; Found 232.1330.



N-methyl-N-((4-methylquinolin-2-yl)methyl)formamide (4r)

Prepared according to general procedure. Eluent: PE/(EA) (1:1).

Obtained as a colourless oil (32.10 mg, 75%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 3.17 (d, *J* = 18.6 Hz, 6H), 2.73 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.40, 154.07, 146.53, 145.83, 130.31, 129.79, 128.18, 127.34, 123.84, 121.23, 39.18, 35.86, 18.94.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₃H₁₄N₂ONa⁺ 237.0998; Found 237.0996.



N-methyl-N-((4-methylquinolin-2-yl)methyl)acetamide (4s)

Prepared according to general procedure. Eluent: PE/(EA) (1:1).

Obtained as a colourless oil (32.83 mg, 72%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.04 (dd, *J* = 14.7, 8.5 Hz, 1H), 7.98 (dd, *J* = 14.2, 8.4 Hz, 1H), 7.71 (dt, *J* = 14.7, 7.6 Hz, 1H), 7.55 (dt, *J* = 14.9, 7.6 Hz, 1H), 7.24 (s, 1H), 7.11 (s, 0H), 4.85 (s, 1H), 4.75 (s, 1H), 3.05 (s, 3H), 2.72 – 2.65 (m, 3H), 2.20 (d, *J* = 9.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 171.61, 171.11, 157.69, 156.86, 147.83, 147.29, 146.11,
145.66, 129.84, 129.64, 129.51, 129.48, 127.60, 127.49, 126.51, 126.31, 123.91,
123.83, 120.86, 118.75, 56.97, 53.28, 36.30, 34.54, 21.94, 21.83, 19.07, 18.92.
HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₄H₁₆N₂O⁺ 229.1335; Found 229.1331.

2-benzyl-4-methylquinoline (4t)

Prepared according to general procedure. Eluent: PE/(EA) (10:1).

Obtained as a yellow solid (24.70 mg, 53%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.31 (q, *J* = 7.3 Hz, 4H), 7.23 (t, *J* = 6.7 Hz, 1H), 7.07 (s, 1H), 4.32 (s, 2H), 2.62 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 160.88, 147.39, 145.20, 139.33, 129.50, 129.37, 128.77, 127.03, 126.64, 126.03, 123.79, 122.34, 45.41, 18.91.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N^+$ 234.1204; Found 234.2255.

2-(4-chlorobenzyl)-4-methylquinoline (4u)

Prepared according to general procedure. Eluent: PE/(EA) (10:1).

Obtained as a colorless oil (23.50 mg, 44%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 4H), 7.04 (s, 1H), 4.26 (s, 2H), 2.63 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 160.30, 147.58, 145.24, 137.87, 132.49, 130.65, 129.56, 129.50, 128.87, 127.04, 126.12, 123.82, 122.19, 44.75, 18.90.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₇H₁₄ClN⁺ 268.0893; Found 268.0892.

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2-(3-(5-bromo-2-methoxyphenyl)adamantan-1-yl)-4-methylquinoline (4v)

Prepared according to *general procedure* with 2 equiv of 1-(5-Bromo-2-methoxyphenyl)adamantane (differin precursor). Eluent: PE/ (EA) (3:1).

Obtained as a white solid (76.53 mg, 83%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.40 (s, 1H), 7.36 (s, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 3.81 (s, 3H), 2.70 (s, 3H), 2.39 (s, 2H), 2.35 (s, 2H), 2.20 (d, *J* = 12.3 Hz, 4H), 2.14 (d, *J* = 11.9 Hz, 4H), 1.85 (s, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 168.32, 158.01, 147.62, 143.76, 140.26, 130.09, 129.91,
129.60, 128.78, 126.86, 125.51, 123.54, 118.67, 113.45, 113.38, 55.36, 44.52, 41.16,
40.66, 39.76, 38.27, 36.30, 29.62, 19.13.

HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₇H₂₈BrNO⁺ 462.4310; Found 462.4313.

5. Mechanistic studies

5.1 Free radical-trapping experiment



A 10 mL oven-dried quartz tube equipped with a magnetic stirrer was charged with lepidine (**1a**, 26.4 μ L, 0.20 mmol, 1.0 equiv.), cyclohexane (**2a**, 0.10 mL), *tert*-Butyl peroxybenzoate (TBPB) (76 μ L, 1.0 mmol, 2.0 equiv.), TFA (15 μ L, 0.20 mmol, 1.0 equiv.), TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, 0.60 mmol, 3.0 equiv.), H₂O (200 μ L), and 1,2-dichloroethane (DCE, 2.0 mL). The reaction vessel was exposed to 40 W blue LEDs irradiation at room temperature under N₂ atmosphere with stirring for 6 h. After the reaction was stopped, no desired product **3a** was detected in the mixture, while an adduct (**5**) of TEMPO with a cyclohexyl radical was formed, which was detected by HRMS. The model reaction was completely inhibited, indicating that a radical pathway was involved in the reaction.



Figure S1. HRMS analysis of 5

5.2 Light on/off experiment

The reaction between **1a** and **2a** was conducted under the standard conditions on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (40 W, blue LEDs) followed by stirring in the absence of light. At the end of each period, a small portion (100 to 150 μ L) of the reacting solution was taken by a syringe, basified with sat NaHCO₃ (aq), extracted with EtOAc, and the volatiles were removed under reduced pressure to obtain the crude sample, which was taken for ¹H NMR analysis.





Figure S2. Time frame for the yield of 1a to 3a

From the light on/off experiments, we found that the reaction needed continual irradiation of light, and thus it is not a photo-initiated reaction. Finding suggest that a radical chain pathway is unlikely.

5.3 UV-Vis spectroscopic investigation

Preparation. Two formulated solutions were prepared with degassed DCE in 10 mL volumetric flasks. For flask A, lepidine (**1a**, 4MeQL, 1.0 mmol, 132 μ L), was added; for flask B, lepidine (**1a**, 4MeQL, 1.0 mmol, 132 μ L) and TFA (76 μ L, 1.0 mmol) were added. All these flasks were diluted to 10 mL to set the concentration to be 0.10 M.

UV-Vis spectrometric experiments. A quartz cuvette $(1 \text{ cm} \times 1 \text{ cm} \times 3.5 \text{ cm})$ was filled with 2 mL of the abovementioned 0.10 M solutions from flasks A and B to perform the UV-vis experiment (500 nm to 200 nm). The resulting spectra are shown in Figure S3.



Figure S3. UV-Vis spectra of lepidine with and without acid.

5.4 Stern-Volmer plot

5.4.1: Fluorescent change with the addition of TBPB without and with acid (*all the fluorescence spectra were obtained at 320 nm exciting wavelength*) and the concentration of the lepidine is 0.1μ M.


Figure S4. fluorescence quenching of TBPB without acid.



Figure S5. fluorescence quenching of TBPB with acid.

5.4.2 Stern-Volmer plot without and with acid



Figure S6. Stern-Volmer analysis of TBPB and lepidine with acid.



Figure S7. Stern-Volmer analysis of TBPB and lepidine without acid.

5.5 NMR analysis in CDCl₃



Figure S8. Complete conversion of TBPB to *t*-BuOH and acetone under blue LEDs irradiation in 8 h in CDCl₃.

6. NMR Spectra





¹⁹F NMR of **3b** (376 MHz, CDCl₃)









¹H NMR of **3d** (600MHz, CDCl₃)









¹³C NMR of **3d** (151MHz, CDCl₃)



¹H NMR of **3e** (600MHz, CDCl₃)





2. 88 2. 286 2. 286 2. 02 2. 02 2. 02 2. 02 2. 02 1. 99 1. 99 1. 78 1. 59 1. 78 1. 59 1. 78 1. 7

¹³C NMR of **3e** (151MHz, CDCl₃)



¹H NMR of **3f** (600MHz, CDCl₃)





4 3.29 3.28 3.26 3.26

¹ H NMR of $3g$	(600MHz,	CDCl ₃)
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¹H NMR of **3h** (600MHz, CDCl₃)



23.50 3.45 3.46 3.46 3.46 3.46 3.46 1.95 1.195 1.128 1.











 $\begin{array}{c} -4.02\\ 3.55\\ 3.55\\ 3.55\\ 3.57\\ 3.57\\ 1.97\\ 1.97\\ 1.97\\ 1.19\\ 1.97\\ 1.58\\ 1.57\\ 1.58\\ 1.57\\ 1.58$



¹³C NMR of **3j** (151MHz, CDCl₃)





3.56 3.54 3.52 3.52 3.52 3.52 1.95 1.95 1.92 1.79 1.79 1.779 1.53 1.179 1.133 1.133





¹³C NMR of **3k** (151MHz, CDCl₃)







¹H NMR of **3n** (600MHz, CDCl₃)









¹H NMR of **30** (600MHz, CDCl₃)



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¹H NMR of **3p** (600MHz, CDCl₃)



3. 340 3. 375 3. 379 3. 377 3. 377 3. 379 5.





¹³C NMR of **3p** (151MHz, CDCl₃)



${}^{1}\text{H NMR of 3q (600MHz, CDCl_{3})} \\ {}^{5}\text{H NMR of 3q (}{}^{600MHz, CDCl_{3})} \\ {}^{5}\text{H NMR of 3q (}{}^{600MZ, CDCl_{3})} \\ {}^{5}\text{H NMR of 3q (}{}^{60MZ, CDCl_{3})} \\ {}^{5}\text{H NMR of 3q (}{}^{6}\text{H NMR of 3q (}{}^{6}\text{H NMR of 3q (}{}^{6}\text{H NMR of 3q (}{$







¹³C NMR of **3q** (151MHz, CDCl₃)







-7.50











¹H NMR of **3s** (600MHz, CDCl₃)







 $\begin{array}{c} 2, 79\\ 2, 27\\ 2, 27\\ 2, 204\\ 2,$



¹H NMR of **3u** (600MHz, CDCl₃)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

III

¹⁹F NMR of **3u** (376 MHz, CDCl₃)



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)





¹ H NMR of 4a (600MHz, CDCl ₃)	3. 35 3. 34 3. 33		2. 19 2. 18 2. 17 2. 17 1. 75	
	à			
		1		.
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 f1 (ppm)	3.5 3	3.0 2	.5 2.0 1.5	1.0 0.5 0.0 -0.5
¹³ C NMR of 4a (151MHz, CDCl ₃)			18. 91	33. 68 26. 16 18. 92

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)





S67





¹H NMR of **4f** (600MHz, CDCl₃)







 $\begin{array}{c} -2.\ 69\\ 2.\ 35\\ 2.\ 33\\ 2.\ 33\\ 2.\ 33\\ -1.\ 74\\ -1.\ 42\\ \end{array}$










S75











S80



S81

¹H NMR of 4r (600MHz, CDCl₃)





 $\times \frac{3, 18}{3, 15}$ -2.73

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)











__2.63

¹H NMR of **4v** (600MHz, CDCl₃)

