Supplementary Information

Iron mediated divergent reductive coupling reactions of heteroarenes

with alkenes

Cong Zhang,^a Yuhang He,^a Guanghui An^{a*}

^a School of Chemistry and Materials Science, Heilongjiang University,

Harbin 150080, China.

Email: chemagh@163.com; gmli 2000@163.com

Table of Contents

1.	General Information	S2
2.	Substrate Structures	S2
3.	Preparation of Fe(dibm) ₃	S3
4.	Optimization of C2 Alkylation	S4
5.	Optimization of Reductive Alkylation	S7
6.	General Procedures for Synthesis of Compounds	
7.	Cyclohexyl Radical Capture Experiment	S10
8.	Prove the Formation of Ph(<i>i</i> -PrO)SiH ₂	S10
9.	Unsuccessful Substrates	S11
10.	Characterization Data of the Compounds	S12
11.	Reference	S26
12.	Copies of ¹ H and ¹³ C NMR Spectra	S27

General Information 1.

Unless otherwise noted, all reagents were obtained from commercial suppliers (Adamas-beta) and used without further purification. The reaction product was isolated by column chromatography on a silica gel (236-400 mesh) column using petroleum ether (PE) with a boiling range from 60 to 90 °C and EtOAc. ¹H, ¹³C NMR and ¹⁹F NMR spectra were recorded on 400, 101, 376 MHz NMR spectrometers using CDCl3 and DMSO-d6 as solvent. In addition, 1H, and 13C NMR spectra used tetramethylsilane as the internal standard and the ¹⁹F NMR spectra used trifluoroacetic acid as the internal standard. HRMS were made by means of ESI. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were performed in air.

2. **Substrate Structures**



S2

Scheme S1. Substrate Structures

3. Preparation of Fe(dibm)₃



Iron(III) diisobutyrylmethane. To a biphasic mixture of 2,6-dimethylheptane-3,5-dione (2.60 g, 16.6 mmol, 3.0 equiv) and NaOAc (1.36 g, 16.6 mmol, 3.0 equiv) in an aqueous solution of EtOH (1:1 EtOH:H₂O, 42 mL) was added ground FeCl₃•6H₂O (1.50 g, 5.55 mmol, 1.0 equiv). A red slurry formed and the reaction mixture was heated at 60 °C with stirring for 1 h. The slurry was cooled at room temperature over 10 min, cooled at 0 °C for 15 min, and then filtered to give an orange powder. The orange powder was rinsed with H₂O, collected, placed in an Erlenmeyer flask, and heated with an aqueous solution of EtOH (9:1 EtOH:H₂O, 30 mL) using a heat gun until fully dissolved to give a red, homogenous solution. The solution was cooled to room temperature and then to 0 °C to give red crystals, which were filtered and rinsed with a -78 °C aqueous solution of EtOH (9:1 EtOH:H₂O, 10 mL) to furnish Fe(dibm)₃ as a red crystalline solid (1.20 g, 2.31 mmol, 14%).¹

4. Optimization of C2 Alkylation

Table S1. Screening of Catalyst^a

		catalyst (30 mol%) CF ₃ SO ₃ H (50 mol%) PhSiH ₃ (3 equiv)	
N +		THF/MeOH (1 mL) rt, 24 h	
1a	2a		3a
Entry		Catalyst	Yield(%) ^b
1		Fe(acac) ₃	29
2		Fe(dibm) ₃	45
3		Fe(dpm) ₃	31
4		Mn(dpm) ₃	20
5		$Co(acac)_2(II)$	N.R
6		$Co(acac)_2(III)$	N.R
7		$Ni(acac)_2$	N.R
8		Salen-Co	N.R
9		Co 1	N.R
10		Co 2	13
11		Co 3	N.R
12		Co 4	N.R
13		Co 5	N.R
14		Co 6	N.R
15		Co 7	N.R

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), catalyst (30 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under air for 24 h. ^{*b*}Isolated products. N.R.=No reaction.



Scheme S2. Catalysts

Table S2. Screening of Acid Additives^a

+	Fe(dibm) ₃ (30 mol%) acid (50 mol%) PhSiH ₃ (3 equiv)		
N		THF/MeOH (1 mL) rt, 24 h	N
1a	2a		3a
Entry	Acid		Yield(%) ^b
1	CF ₃ SO ₃ H		45
2	CF ₃ COOH		12
3	ClCH ₂ COOH		<5
4	CH ₃ COOH		<5
5	C ₆ H ₅ COOH		37
6	TsOH•H ₂ O		37
7		HFIP	<5

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (30 mol%), acid (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under air 24 h. ^{*b*}Isolated products. N.R.=No reaction.

 Table S3. The Amount of Acid^a

+		Fe(dibm) ₃ (30 mol%) CF ₃ SO ₃ H (X equiv) PhSiH ₃ (3 equiv) THF/MeOH (1 mL) rt, 24 h		
1a	2a		3a 🎽	
Entry	CF ₃ SO ₃ H (equiv)		Yield(%) ^b	
1		0.8	24	
2		0	6	
3		0.5	45	

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (30 mol%), CF₃SO₃H (X equiv) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under air 24 h. ^{*b*}Isolated products. N.R.=No reaction.

Table S4. Screening of Solvent^a

	+ Fe(dibm) ₃ (30 mol%) CF ₃ SO ₃ H (50 mol%) PhSiH ₃ (3 equiv) solvent (1 mL) rt, 24 h	
1a	2a	3a
Entry	Solvent	Yield(%) ^b
1	THF/EtOH (4:1)	49
2	EtOH	37
3	HFIP	15
4	THF/HFIP (4:1)	14
5	THF/MeOH (4:1)	45
6	THF/TBA (4:1)	25
7	TBA	14
8	THF	13
9	<i>i</i> -PrOH	43
10	THF/ <i>i</i> -PrOH (4:1)	63
11	THF/ <i>i</i> -PrOH (8:1)	67
12	THF/ <i>i</i> -PrOH (6:1)	69
13	THF/i-PrOH (2:1)	62
14	THF/ <i>i</i> -PrOH (1:1)	69

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (30 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of solvent under air 24 h. ^{*b*}Isolated products. N.R.=No reaction. TBA= tert-butanol. HFIP= 1,1,1,3,3,3-hexafluoro-2-propanol. THF= tetrahydrofuran.

Table S5. Screening of Temperature and Gas Environment^a

	+	Fe(dibm) ₃ (30 mol%) CF ₃ SO ₃ H (50 mol%) PhSiH ₃ (3 equiv) ➤	
N		THF/ <i>i</i> -PrOH (1 mL) gas , temp , 24 h	N
1a	2a		3a
Entry	Temp(°C)	Gas	Yield(%) ^b
1	20	Ar	47
2	20	Air	69
3	40	Air	64
4	60	Air	53

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (30 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/*i*-PrOH (6:1) under gas environment 24 h. ^{*b*}Isolated products. N.R.=No reaction.

5. Optimization of Reductive Alkylation

Table S6. Screening of Catalyst^a

F N F	-	catalyst (50 mol%) CF ₃ SO ₃ H (50 mol%) PhSiH ₃ (3 equiv) THF/MeOH (1 mL) Ar, rt, 24 h	F NH
1i	2a		5j
Entry	Catalyst		Yield(%) ^b
1	Fe(acac) ₃		72
2	Fe(e	dibm) ₃	77
3	Fe(dpm) ₃	37
4	Mn	(dpm) ₃	33
5	$Co(acac)_2(II)$		N.R
6	Co(acac) ₂ (III)		N.R
7	$Ni(acac)_2$		N.R
8	Sal	en-Co	N.R
9	C	Co 2	N.R
10	C	Co 5	N.R

^{*a*}Reaction conditions: **1i** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), catalyst (50 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under Ar reaction for 24 h. ^{*b*}Isolated products. N.R.=No reaction.

Table S7. Screening of Acid Additives^a

F	F	e(dibm) ₃ (50 mol%) acid (50 mol%) PhSiH ₃ (3 equiv) THF/MeOH (1 mL) Ar, rt, 24 h F	
1	i 2a	5j	
Entry	Acid	Yield(%) ^b	
1	CF ₃ SO ₃ H	77	
2	CF ₃ COOH	I N.R	
3	ClCH ₂ COO	N.R	
4	CH ₃ COOH	I N.R	
5	C ₆ H ₅ COOI	H N.R	
6	TsOH•H ₂ O	29	

^{*a*}Reaction conditions: **1i** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (50 mol%), acid (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under Ar reaction for 24 h. ^{*b*}Isolated products. N.R.=No reaction.

Table S8. Screening of Solvent^a



^{*a*}Reaction conditions: **1i** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (50 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of solvent under Ar reaction for 24 h. ^{*b*}Isolated products. N.R.=No reaction.

THF= tetrahydrofuran. TFE= trifluoroethanol.

Table S9. Screening of Gas Environment^a

F +	-	Fe(dibm) ₃ (50 mol%) CF ₃ SO ₃ H (50 mol%) PhSiH ₃ (3 equiv) THF/MeOH (1 mL) gas, rt, 24 h F	
1 i	2a	5j	
Entry	Gas	Yield(%) ^b	
1	O ₂	N.R	
2	Ar	77	
3	Air	30	

^aReaction conditions: **1i** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (50 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under Ar reaction for 24 h. ^bIsolated products. N.R.=No reaction.

6. General Procedures for Synthesis of Compounds

6.1 Procedures for Synthesis of Compounds (3a-3u)

A Schlenk flask was charged with heterocycle **1** (0.2 mmol, 1.0 equiv), $Fe(dibm)_3$ (30 mol%), and olefin **2** (3 equiv), THF/*i*-PrOH (6:1, 1 mL), CF₃SO₃H (neat, 50 mol%) and PhSiH₃ (3 equiv) was added sequentially, and the mixture was stirred vigorously at rt in air for 24 h. The reaction mixture was then cooled to rt and quenched with saturated aqueous solution of NaHCO₃. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel to give the pure product.

6.2 Procedures for Synthesis of Compounds (4a-4b and 5a-5m)

A Schlenk flask was charged with heterocycle 1 (0.2 mmol, 1.0 equiv), $Fe(dibm)_3$ (50 mol%), and olefin 2 (3 equiv). The flask was evacuated and backfilled with argon for 3 times. THF/MeOH (4:1, 1 mL), CF_3SO_3H (neat, 50 mol%) and PhSiH₃ (3 equiv) was added sequentially, and the mixture was stirred vigorously at rt for 24 h. The reaction mixture was then cooled to rt and quenched with saturated aqueous solution of NaHCO₃. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel to give the pure product.

7. Cyclohexyl Radical Capture Experiment

7.1 TEMPO Inhibition Experiment



A Schlenk flask was charged with heterocycle **1a** (0.2 mmol, 1.0 equiv), Fe(dibm)₃ (30 mol%), TEMPO (1.6 mmol, 8.0 equiv) and olefin **2** (3 equiv), THF/*i*-PrOH (6:1, 1 mL), CF₃SO₃H (neat, 50 mol%) and PhSiH₃ (3 equiv) was added sequentially, and the mixture was stirred vigorously at rt in air for 24 h. The target product yield is inhibited.

7.2 1,1-Diphenylethylene Inhibition Experiment



A Schlenk flask was charged with heterocycle **1a** (0.2 mmol, 1.0 equiv), $Fe(dibm)_3$ (30 mol%), 1,1diphenylethylene (0.2 mmol, 1.0 equiv) and olefin **2** (3 equiv), THF/i-PrOH (6:1, 1 mL), CF_3SO_3H (neat, 50 mol%) and PhSiH₃ (3 equiv) was added sequentially, and the mixture was stirred vigorously at rt in air for 24 h. Product **6** was obtained with a yield of 16%. The structure of **6** is confirmed by ¹H NMR analysis as follows.

8. Prove the Formation of Ph(*i*-PrO)SiH₂



Figure S1. Prove the Formation of Ph(*i*-PrO)SiH₂

9. Unsuccessful Substrates

Table S10. Unsuccessful Substrates of C2-Alkylation^{a,b}



^{*a*}Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (30 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/*i*-PrOH (6:1) under air 24 h. ^{*b*}Isolated products. N.R.=No reaction.

Table S11. Unsuccessful C4 Reductive Alkylation^{a,b}



^aReaction conditions: **1** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), Fe(dibm)₃ (50 mol%), CF₃SO₃H (50 mol%) and PhSiH₃ (3 equiv) was added in 1 mL of THF/MeOH (4:1) under Ar reaction for 24 h. ^bIsolated products. N.R.=No reaction.

10. Characterization Data of the Compounds



4-methyl-2-(1-methylcyclohexyl)quinoline (3a): Eluent: 100% petroleum ether (PE); Yellow Oil, 69% yield, 32.9 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.32 (s, 1H), 2.69 (s, 3H), 2.35 (dd, J = 13.1, 7.9 Hz, 2H), 1.66 – 1.54 (m, 4H), 1.46 (s, 4H), 1.29 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 168.2, 147.6, 143.5, 130.0, 128.5, 126.5, 125.3, 123.4, 119.3, 77.3, 77.0, 76.7, 41.3, 37.2, 26.4, 22.9, 19.4, 19.0. HRMS (ESI) m/z calcd for C₁₇H₂₂N⁺ [M+H]⁺: 240.1747; found: 240.1745.



2-cyclohexyl-4-methylquinoline (3b): Eluent: PE/EtOAc (50:1); Colorless oil, 43% yield, 19.5 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H),

7.50 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 2.94 – 2.84 (m, 1H), 2.70 (s, 3H), 2.03 (d, J = 12.0 Hz, 2H), 1.91 (d, J = 12.8 Hz, 2H), 1.81 (d, J = 12.7 Hz, 1H), 1.70 – 1.57 (m, 2H), 1.55 – 1.30 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5, 147.6, 144.3, 129.5, 129.0, 127.1, 125.4, 123.6, 120.3, 77.4, 77.1, 76.7, 47.6, 32.9, 26.6, 26.2, 18.9. HRMS (ESI) m/z calcd for C₁₆H₂₀N⁺ [M+H]⁺: 226.1590; found: 226.1587.



2-(bicyclo[2.2.1]hept-5-en-2-yl)-4-methylquinoline (3c): Eluent: PE/EtOAc (100:1); Colorless oil, 82% yield, 38.6 mg; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.35 (s, 1H), 6.29 (dd, *J* = 5.8, 3.0 Hz, 1H), 6.23 (dd, *J* = 5.7, 2.8 Hz, 1H), 2.98 (s, 2H), 2.88 (dd, *J* = 8.5, 4.3 Hz, 1H), 2.64 (s, 3H), 2.34 (dt, *J* = 11.4, 3.9 Hz, 1H), 1.76 (d, *J* = 8.0 Hz, 1H), 1.45 (ddd, *J* = 11.2, 8.8, 2.2 Hz, 1H), 1.24 (d, *J* = 7.9 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.6, 147.4, 144.2, 138.4, 137.3, 129.7, 129.5, 126.9, 126.0, 124.4, 123.1, 48.9, 46.5, 45.5, 42.1, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 31.3, 18.6. HRMS (ESI) m/z calcd for C₁₇H₁₈N⁺ [M+H]⁺: 236.1434; found: 236.1433.



4-methyl-2-(octan-2-yl)quinoline (3d): Eluent: PE/EtOAc (100:1); Yellow oil, 59% yield, 29.9 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 3.05 (q, *J* = 7.1 Hz, 1H), 2.70 (s, 3H), 1.83 (tdd, *J* = 13.4, 9.0, 5.9 Hz, 1H), 1.67 (dq, *J* = 19.1, 6.1 Hz, 1H), 1.37 (d, *J* = 6.9 Hz, 3H), 1.33 – 1.15 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 147.6, 144.2, 129.6, 128.9, 127.0, 125.4, 123.6, 120.2, 77.4, 77.1, 76.7, 43.0, 37.1, 31.8, 29.5, 27.7, 22.6, 20.8, 18.9, 14.1. HRMS (ESI) m/z calcd for C₁₈H₂₆N⁺ [M+H]⁺: 256.2060; found: 256.2056.



2-(dodecan-2-yl)-4-methylquinoline (3e): Eluent: PE/EtOAc (50:1); Colorless oil, 49% yield, 30.5 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 3.05 (q, *J* = 7.1 Hz, 1H), 2.70 (s, 3H), 1.82 (qd, *J* = 10.1, 9.1, 6.3 Hz, 1H), 1.67 (tt, *J* = 13.3, 6.0 Hz, 1H), 1.39 – 1.19 (m, 19H), 0.88 (t, *J* = 6.8 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 167.0, 147.7, 144.1, 129.6, 128.9, 127.0, 125.3, 123.6, 120.2, 77.3, 77.0, 76.7, 43.0, 37.1, 31.9, 29.8, 29.6, 29.6, 29.6, 29.3, 27.7, 22.7, 20.8, 18.8, 14.1. HRMS (ESI) m/z calcd for C₂₂H₃₄N⁺ [M+H]⁺:312.2686; found: 312.2683.



4-methyl-2-(4-phenylbutan-2-yl)quinoline (3f): Eluent: PE/EtOAc (20:1); Colorless oil, 45% yield, 24.9 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 8.04 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.32 (s, 1H), 7.25 (t, J = 7.5 Hz, 2H), 7.16 (t, J = 7.4 Hz, 3H), 3.01 (q, J = 7.0 Hz, 1H), 2.67 (s, 3H), 2.57 (ddd, J = 14.0, 10.0, 6.2 Hz, 1H), 2.45 (dq, J = 10.2, 5.7, 4.9 Hz, 1H), 2.12 (dddd, J = 13.6, 9.8, 6.0, 4.1 Hz, 1H), 1.91 (ddt, J = 12.9, 9.9, 6.3 Hz, 1H), 1.32 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 166.2, 147.6, 144.8, 142.6, 129.6, 129.5, 128.7, 127.1, 126.1, 126.0, 124.5, 121.2, 41.8, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 38.5, 33.7, 21.1, 18.7. HRMS (ESI) m/z calcd for C₂₀H₂₂N⁺ [M+H]⁺: 276.1747; found: 276.1745.



2-methyl-2-(4-methylquinolin-2-yl)propan-1-ol (3g): Eluent: PE/EtOAc (9:1); Colorless oil, 57% yield, 24.5 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 8.01 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.48 (s, 1H), 4.73 (t, J = 5.6 Hz, 1H), 3.65 (d, J = 5.6 Hz, 2H), 2.65 (s, 3H), 1.33 (s, 6H). ¹³C NMR (101 MHz, DMSO- d_6) δ 167.3, 147.0, 144.1, 129.7, 129.4, 126.7, 126.1, 124.3, 120.3, 70.8, 43.3, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 25.2, 18.9. HRMS (ESI) m/z calcd for C₁₄H₁₈NO⁺ [M+H]⁺: 216.1383; found: 216.1382.



4-methyl-2-(tetrahydro-2H-pyran-2-yl)quinoline (3h): Eluent: PE/EtOAc (9:1); Colorless oil, 61% yield, 27.6 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 8.04 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (s, 1H), 4.48 (dd, J = 11.0, 2.4 Hz, 1H), 4.06 (d, J = 11.1 Hz, 1H), 3.64 – 3.52 (m, 1H), 2.67 (s, 3H), 2.03 – 1.93 (m, 1H), 1.92 – 1.83 (m, 1H), 1.75 – 1.44 (m, 4H). ¹³C NMR (101 MHz, DMSO- d_6) δ 162.3, 147.1, 145.1, 129.7, 129.6, 127.5, 126.5, 124.6, 119.2, 80.9, 68.3, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 32.5, 26.0, 23.6, 18.8. HRMS (ESI) m/z calcd for C₁₅H₁₈NO⁺ [M+H]⁺: 228.1383; found: 228.1380.



tert-butyl 4-methyl-4-(4-methylquinolin-2-yl)piperidine-1-carboxylate (3i): Eluent: PE/EtOAc (9:1); Colorless oil, 63% yield, 42.8 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 7.87 (m, 2H), 7.77 – 7.62 (m, 1H), 7.61 – 7.46 (m, 1H), 7.40 – 7.22 (m, 1H), 3.73 (s, 2H), 3.25 (s, 2H), 2.73 (d, *J* = 13.3 Hz, 3H), 2.49 (s, 2H), 1.74 (s, 2H), 1.48 (d, *J* = 12.9 Hz, 9H), 1.37 (d, *J* = 13.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.0, 155.1, 147.4, 144.2, 130.0, 128.9, 126.6, 125.7, 123.5, 119.2, 79.2, 41.4, 39.8, 36.2, 29.1, 28.5, 19.1. HRMS (ESI) m/z calcd for C₂₁H₂₉N₂O₂+ [M+H]+: 341.2224; found: 341.2220.



(2*R*,5*S*)-2-methyl-5-(2-(4-methylquinolin-2-yl)propan-2-yl)cyclohexan-1-one (3j): Eluent: PE/EtOAc (20:1); Colorless oil, 33% yield, 19.2 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.49 (s, 1H), 2.68 (s, 3H), 2.36 (dt, *J* = 12.7, 6.3 Hz, 1H), 2.29 – 2.15 (m, 2H), 1.98 (ddd, *J* = 12.5, 5.8, 3.0 Hz, 1H), 1.89 (d, *J* = 11.5 Hz, 1H), 1.63 – 1.46 (m, 2H), 1.37 (d, *J* = 12.7 Hz, 6H), 1.22 – 1.11 (m, 1H), 0.84 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 212.6, 167.5, 146.9, 144.4, 129.9, 129.5, 126.6, 126.2, 124.3, 119.9, 49.2, 44.2, 43.8, 43.7, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 34.7, 26.7, 24.8, 24.0, 18.9, 14.8. HRMS (ESI) m/z calcd for C₂₀H₂₆NO⁺ [M+H]⁺: 296.2009; found: 296.2007.



2-(4-methyl-4-(4-methylquinolin-2-yl)cyclohexyl)propan-2-ol (3k): Eluent: PE/EtOAc (9:1); Yellow oil, 46% yield, 27.3 mg; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.51 (d, *J* = 6.4 Hz, 1H), 4.07 (s, 1H), 2.66 (s, 3H), 1.94 (d, *J* = 12.6 Hz, 2H), 1.77 (t, *J* = 11.7 Hz, 4H), 1.33 (d, *J* = 9.8 Hz, 5H), 1.22 (dd, *J* = 13.2, 9.5 Hz, 1H), 1.09 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.9, 147.0, 144.3, 129.8, 129.3, 126.7, 126.0, 124.3, 119.4, 71.1, 48.9, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 36.9, 27.6, 23.1, 23.0, 18.9. HRMS (ESI) m/z calcd for C₂₀H₂₈NO⁺ [M+H]⁺: 298.2165; found: 298.2162.



3,7-dimethyl-7-(4-methylquinolin-2-yl)octan-1-ol (3l): Eluent: PE/EtOAc (9:1); Colorless oil, 65% yield, 38.7 mg; ¹**H NMR** (400 MHz, CDCl₃) δ 8.07 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.29 (s, 1H), 3.60 (qd, J = 10.4, 9.9, 3.6 Hz, 2H), 2.68 (s, 3H), 1.80 – 1.73 (m, 2H), 1.54 – 1.40 (m, 8H), 1.33 – 1.03 (m, 6H), 0.79 (d, J = 6.4 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.2, 147.3, 143.6, 129.9, 128.7, 126.5, 125.4, 123.4, 119.3, 77.4, 77.1, 76.8, 61.1, 43.5, 41.0, 39.8, 37.8, 29.2, 27.9, 22.1, 19.6, 19.1. **HRMS (ESI)** m/z calcd for C₂₀H₃₀NO⁺ [M+H]⁺: 300.2322; found: 300.2321.



8-methyl-2-(1-methylcyclohexyl)quinoline (3m): Eluent: PE/EtOAc (100:1); Colorless oil, 50% yield, 23.8 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.50 (dd, *J* = 16.5, 7.8 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 2.81 (s, 3H), 2.49 – 2.37 (m, 2H), 1.66 – 1.54 (m, 4H), 1.53 – 1.41 (m, 4H), 1.29 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 146.4, 137.5, 136.0, 128.9, 126.1, 125.3, 125.1, 118.4, 77.4, 77.0, 76.7, 41.8, 37.4, 30.0, 26.5, 23.0, 17.8. HRMS (ESI) m/z calcd for C₁₇H₂₂N⁺ [M+H]⁺: 240.1747; found: 240.1745.



6-methyl-2-(1-methylcyclohexyl)quinoline (3n): Eluent: PE/EtOAc (50:1);Yellow oil, 66% yield, 31.6 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 11.2, 8.9 Hz, 2H), 7.58 – 7.41 (m, 3H), 2.54 (s, 3H), 2.37 (dd, *J* = 11.9, 6.4 Hz, 2H), 1.73 – 1.58 (m, 4H), 1.48 (s, 4H), 1.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.6, 146.3, 135.3, 135.2, 131.1, 129.1, 126.3, 126.1, 118.7, 77.4, 77.1, 76.7, 41.4, 37.3, 29.2, 26.4, 22.9, 21.5. HRMS (ESI) m/z calcd for C₁₇H₂₂N⁺ [M+H]⁺: 240.1747; found: 240.1743.



5-bromo-2-(1-methylcyclohexyl)quinoline (30): Eluent: PE/EtOAc (50:1); Colorless oil, 43% yield, 26.0 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 2.36 (dd, *J* = 12.2, 6.9 Hz, 2H), 1.63 (d, *J* = 12.6 Hz, 4H), 1.45 (s, 4H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.4, 148.5, 135.3, 129.4, 129.3, 129.1, 125.8, 121.6, 120.0, 77.4, 77.0, 76.7, 41.5, 37.1, 29.3, 26.3, 22.9. HRMS (ESI) m/z calcd for C₁₆H₁₉BrN⁺ [M+H]⁺: 304.0695; found: 304.0693.



4-chloro-2-(1-methylcyclohexyl)quinoline (3p): Eluent: PE/EtOAc (100:1); Colorless oil, 53% yield, 27.3 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 4.4 Hz, 2H), 2.35 (dd, *J* = 12.3, 6.3 Hz, 3H), 1.70 – 1.58 (m, 8H), 1.48 (s, 4H), 1.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 148.6, 142.4, 129.8, 129.8, 126.6, 124.6, 123.7, 119.0, 77.3, 77.0, 76.7, 41.7, 37.1, 29.2, 26.2, 22.9. HRMS (ESI) m/z calcd for C₁₆H₁₉ClN⁺ [M+H]⁺: 260.1201; found: 260.1200.



2-(1-methylcyclohexyl)quinolin-6-amine (3q): Eluent: PE/EtOAc (4:1); Brown oil, 43% yield, 20.8 mg; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.84 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 11.1 Hz, 1H), 6.74 (s, 1H), 5.43 (s, 2H), 2.24 (d, *J* = 8.6 Hz, 2H), 1.58 – 1.40 (m,

4H), 1.41 – 1.29 (m, 4H), 1.17 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.6, 146.9, 141.5, 133.9, 129.9, 128.2, 121.6, 118.9, 105.3, 41.0, 40.6, 40.4, 40.2, 40.0, 39.7, 39.6, 39.3, 37.2, 29.9, 26.3, 23.0. HRMS (ESI) m/z calcd for C₁₆H₂₁N₂⁺ [M+H]⁺: 241.1699; found: 241.1697.



(2-(1-methylcyclohexyl)quinolin-8-yl)boronic acid (3r): Eluent: PE/EtOAc (4:1); Yellow oil, 44% yield, 23.5 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.91 (s, 2H), 8.39 (d, *J* = 6.9 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 8.7 Hz, 2H), 2.29 (dd, *J* = 11.3, 6.8 Hz, 2H), 1.82 – 1.65 (m, 4H), 1.52 (d, *J* = 7.9 Hz, 4H), 1.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.4, 167.9, 151.2, 137.9, 137.8, 130.4, 126.1, 125.9, 118.7, 77.4, 77.0, 76.7, 41.7, 37.3, 29.2, 26.2, 22.8. HRMS (ESI) m/z calcd for C₁₆H₂₁BNO₂⁺ [M+H]⁺: 270.1660; found: 270.1656.



2-(1-methylcyclohexyl)benzo[d]thiazole (3s): Eluent: PE/EtOAc (100:1); Colorless oil, 43% yield, 19.8 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 2.31 – 2.14 (m, 2H), 1.74 – 1.47 (m, 8H), 1.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.7, 153.3, 134.9, 125.6, 124.5, 122.7, 121.5, 77.4, 77.0, 76.7, 42.1, 38.5, 29.8, 25.8, 22.7. HRMS (ESI) m/z calcd for C₁₄H₁₈NS⁺ [M+H]⁺: 232.1154; found: 232.1151.



2-(1-methylcyclohexyl)benzo[h]quinoline (3t): Eluent: 100% petroleum ether (PE); Colorless oil, 58% yield, 31.8 mg; ¹H NMR (400 MHz, CDCl₃) δ 9.42 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.81 – 7.66 (m, 4H), 7.62 (d, *J* = 8.4 Hz, 1H), 2.54 (dd, *J* = 10.9, 6.3 Hz, 2H), 1.79 – 1.64 (m, 4H), 1.61 – 1.47 (m, 4H), 1.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 145.3, 135.8, 133.7, 132.0, 127.7, 127.6, 126.7, 126.6, 125.1, 124.7, 123.9, 119.0, 77.4, 77.1, 76.7, 41.8, 37.5, 30.1, 26.5, 23.0. HRMS (ESI) m/z calcd for C₂₀H₂₂N⁺ [M+H]⁺: 276.1747; found: 276.1743.



heptan-2-yl 2-((5-chloro-2-(1-methylcyclohexyl)quinolin-8-yl)oxy)acetate (3u): Eluent: PE/EtOAc (50:1); Colorless oil, 63% yield, 54.1 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 8.40 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 5.15 – 4.99 (m, 2H), 4.86 (q, J = 6.2 Hz, 1H), 2.28 (s, 2H), 1.60 – 1.48 (m, 4H), 1.44 – 1.29 (m, 6H), 1.23 – 1.07 (m, 12H), 0.76 (t, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 168.8, 168.1, 153.1, 140.0, 133.2, 126.1, 125.0, 122.4, 120.9, 112.6, 71.9, 67.0, 41.9, 40.6, 40.4, 40.2, 39.9, 39.7, 39.5, 39.3, 37.0, 35.6, 31.5, 29.5, 26.2, 24.7, 22.8, 22.4, 20.2, 14.3. HRMS (ESI) m/z calcd for C₂₅H₃₅CINO₃⁺ [M+H]⁺: 432.2300; found: 432.2298.



2-(1-methylcyclohexyl)quinoline (4a): Eluent: PE/EtOAc (100:1); Yellow oil, 39% yield, 17.4 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.01 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.55 – 7.42 (m, 2H), 2.37 (dd, *J* = 12.0, 6.5 Hz, 2H), 1.69 – 1.57 (m, 4H), 1.46 (s, 4H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.6, 147.7, 135.8, 129.4, 128.9, 127.2, 126.3, 125.6, 118.7, 77.4, 77.0, 76.7, 41.6, 37.2, 29.2, 26.4, 22.9. HRMS (ESI) m/z calcd for C₁₆H₂₀N⁺ [M+H]⁺: 226.1590; found: 226.1589.



4-(1-methylcyclohexyl)-1,2,3,4-tetrahydroquinoline (4b): Eluent: PE/EtOAc (100:1); Yellow oil, 30% yield, 13.6 mg; ¹**H NMR** (400 MHz, DMSO-*d*₆) δ 6.83 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 6.33 (t, *J* = 7.2 Hz, 1H), 5.60 (d, *J* = 3.5 Hz, 1H), 3.21 (ddt, *J* = 16.5, 12.2, 4.9 Hz, 2H), 2.50 (d, *J* = 11.0 Hz, 2H), 2.08 (d, *J* = 13.7 Hz, 1H), 1.57 – 1.24 (m, 10H), 0.69 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 146.0, 130.9, 127.1, 120.8, 113.8, 113.2, 40.6, 40.3, 40.1, 39.9, 39.7, 39.5, 39.3, 38.9, 37.4, 37.0, 35.8, 26.4, 22.6, 22.2, 21.8. **HRMS (ESI)** m/z calcd for C₁₆H₂₄N⁺ [M+H]⁺: 230.1903; found: 230.1900.



2-cyclohexylquinoline (5a-C2): Eluent: PE/EtOAc (100:1); Yellow oil, 46% yield, 19.3 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (t, J = 8.4 Hz, 2H), 7.76 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 2.92 (tt, J = 12.0, 3.3 Hz, 1H), 2.02 (d, J = 11.9 Hz, 2H), 1.89 (d, J = 12.8 Hz, 2H), 1.79 (d, J = 12.5 Hz, 1H), 1.63 (qd, J = 12.4, 2.6 Hz, 2H), 1.47 (qd, J = 12.7, 2.9 Hz, 2H), 1.33 (qt, J = 12.8, 3.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 147.8, 136.3, 129.3, 129.0, 127.5, 127.0, 125.6, 119.6, 77.4, 77.1, 76.8, 47.7, 32.9, 26.6, 26.1. HRMS (ESI) m/z calcd for C₁₅H₁₈N⁺ [M+H]⁺: 212.1434; found: 212.1430.



4-cyclohexyl-1,2,3,4-tetrahydroquinoline (5a): Eluent: PE/EtOAc (100:1); Yellow oil, 29% yield, 12.5 mg; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.85 – 6.70 (m, 2H), 6.48 – 6.24 (m, 2H), 5.59 (s, 1H), 3.18 – 3.06 (m, 2H), 2.37 (dt, *J* = 8.3, 4.6 Hz, 1H), 1.93 – 1.79 (m, 1H), 1.76 – 1.47 (m, 6H), 1.47 – 1.33 (m, 1H), 1.21 – 0.73 (m, 5H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 145.3, 129.7, 126.9, 122.6, 114.5, 113.7, 41.5, 40.6, 40.4, 40.2, 40.0, 39.8, 39.5, 39.3, 38.1, 31.8, 29.3, 26.7, 26.7, 26.6, 23.0. HRMS (ESI) m/z calcd for C₁₅H₂₂N⁺ [M+H]⁺: 216.1747; found: 216.1745.



2-(dodecan-2-yl)quinoline (5b-C2): Eluent: PE/EtOAc (50:1); Yellow oil, 33% yield, 19.9 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.02 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 3.08 (h, *J* = 7.0 Hz, 1H), 1.88 – 1.73 (m, 1H), 1.72 – 1.60 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 4H), 1.24 (d, *J* = 16.7 Hz, 15H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 147.8, 136.3, 129.2, 129.0, 127.5, 127.0, 125.6, 119.6, 77.4, 77.1, 76.7, 43.1, 37.2,

31.9, 29.8, 29.6, 29.6, 29.6, 29.4, 27.7, 22.7, 20.9, 14.2. **HRMS (ESI)** m/z calcd for C₂₁H₃₂N⁺ [M+H]⁺: 298.2529; found: 298.2528.



4-(dodecan-2-yl)-1,2,3,4-tetrahydroquinoline (5b): Eluent: PE/EtOAc (50:1); Yellow oil, 34% yield, 20.3 mg; ¹**H NMR** (400 MHz, DMSO- d_{δ}) δ 6.83 (dd, J = 27.3, 7.5 Hz, 2H), 6.39 (t, J = 7.1 Hz, 2H), 5.54 (s, 1H), 3.12 (d, J = 6.9 Hz, 2H), 2.58 (d, J = 6.2 Hz, 1H), 1.84 (s, 1H), 1.65 (dq, J = 17.3, 6.0, 5.2 Hz, 2H), 1.34 (s, 1H), 1.22 (s, 17H), 0.83 (t, J = 6.7 Hz, 3H), 0.70 (d, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, DMSO- d_{δ}) δ 146.2, 128.4, 126.6, 123.3, 115.2, 114.0, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.3, 35.1, 34.8, 31.8, 29.8, 29.5, 29.5, 29.2, 27.4, 22.6, 22.5, 15.7, 14.4. HRMS (ESI) m/z calcd for C₂₁H₃₆N⁺ [M+H]⁺: 302.2842; found: 302.2840.



2-(4-phenylbutan-2-yl)quinoline (5c-C2): Eluent: PE/EtOAc (9:1); Colorless oil, 49% yield, 25.6 mg; ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.07 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 6.1 Hz, 3H), 3.17 (h, *J* = 6.9 Hz, 1H), 2.66 (m, *J* = 13.7, 10.4, 6.1 Hz, 1H), 2.54 (m, *J* = 10.5, 5.4 Hz, 1H), 2.21 (m, *J* = 10.4, 8.2, 5.5 Hz, 1H), 2.02 (m, *J* = 13.2, 10.5, 6.3 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 147.9, 142.5, 136.5, 129.3, 129.1, 128.4, 128.3, 127.5, 127.0, 125.8, 125.7, 119.7, 77.4, 77.1, 76.8, 42.6, 38.8, 34.0, 21.0. HRMS (ESI) m/z calcd for C₁₉H₂₀N⁺ [M+H]⁺: 262.1590; found: 262.1587.



4-(4-phenylbutan-2-yl)-1,2,3,4-tetrahydroquinoline (5c): Eluent: PE/EtOAc (9:1); Colorless oil, 25% yield, 13.3 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 7.30 – 7.20 (m, 2H), 7.15 (d, J = 6.4 Hz, 3H), 6.86 – 6.75 (m, 2H), 6.39 (dd, J = 11.6, 7.7 Hz, 2H), 5.55 (s, 1H), 3.19 – 3.06 (m, 2H), 2.65 (dq, J = 12.3, 6.1, 5.7 Hz, 2H), 2.52 (d, J = 6.7 Hz, 1H), 1.91 (dt, J = 12.2, 6.7 Hz, 1H), 1.68 (ddq, J = 17.3, 11.3, 6.7, 6.2 Hz, 3H), 1.57 – 1.41 (m, 1H), 0.78 (d, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.2, 142.8, 128.4, 128.3, 128.3, 126.6, 125.7, 124.5, 117.1 114.4, 77.3, 77.0, 76.7, 40.6 39.6, 36.9, 35.1, 34.1 22.6 15.1. HRMS (ESI) m/z calcd for C₁₉H₂₄N⁺ [M+H]⁺: 266.1903; found: 266.1902.



tert-butyl 4-methyl-4-(1,2,3,4-tetrahydroquinolin-4-yl)piperidine-1-carboxylate (5d): Eluent: PE/EtOAc (9:1); Yellow solid, 73% yield, 48.0 mg, m.p. 115.1-116.6 °C; ¹H NMR (400 MHz, DMSO d_6) δ 6.89 – 6.81 (m, 1H), 6.76 (d, J = 7.4 Hz, 1H), 6.42 (d, J = 7.6 Hz, 1H), 6.33 (t, J = 7.4 Hz, 1H), 5.63 (d, J = 4.4 Hz, 1H), 3.63 (d, J = 13.3 Hz, 2H), 3.20 (ddt, J = 25.1, 12.3, 5.6 Hz, 2H), 2.93 (s, 1H), 2.45 (d, J = 6.9 Hz, 1H), 2.08 (d, J = 13.8 Hz, 1H), 1.56 – 1.10 (m, 15H), 0.78 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 154.4, 146.1, 131.1, 127.4, 120.1, 113.9, 113.3, 78.8, 60.2, 45.0, 40.6, 40.4, 40.1, 39.9, 39.7, 39.5, 39.3, 38.8, 35.9, 28.6, 22.5, 20.2, 14.6. HRMS (ESI) m/z calcd for C₂₀H₃₁N₂O₂⁺ [M+H]⁺: 331.2380; found: 331.2378.



2-(4-methyl-4-(1,2,3,4-tetrahydroquinolin-4-yl)cyclohexyl)propan-2-ol (5e): Eluent: PE/EtOAc (9:1); Yellow solid, 38% yield, 21.7 mg, m.p. 103.9-104.6 °C; ¹H NMR (400 MHz, DMSO- d_6) δ 6.83 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 7.3 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 6.32 (t, J = 7.2 Hz, 1H), 5.67 – 5.52 (m, 1H), 3.94 (s, 1H), 3.26 – 3.17 (m, 2H), 2.33 – 2.26 (m, 1H), 2.13 (d, J = 13.7 Hz, 1H), 1.51 (dq, J = 30.9, 10.2, 5.8 Hz, 5H), 1.34 – 1.02 (m, 5H), 0.97 (s, 6H), 0.73 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6)

δ 146.0, 131.2, 127.2, 120.8, 113.8, 113.3, 71.0, 49.1, 47.7, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 37.3, 37.0, 36.2, 27.6, 23.3, 22.7, 20.0. **HRMS (ESI)** m/z calcd for C₁₉H₃₀NO⁺ [M+H]⁺: 288.2322; found: 288.2320.



2-methyl-4-(1-methylcyclohexyl)-1,2,3,4-tetrahydroquinoline (5f): Eluent: PE/EtOAc (100:1); Yellow solid, 45% yield, 21.7 mg, m.p. 49.4-51.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 3.05 – 2.85 (m, 2H), 2.01 (ddd, *J* = 13.1, 10.0, 3.0 Hz, 1H), 1.64 (dq, *J* = 12.6, 7.9 Hz, 2H), 1.40 (ddd, *J* = 41.0, 20.5, 9.0 Hz, 10H), 1.21 (d, *J* = 6.1 Hz, 3H), 0.68 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 131.2, 126.3, 126.0, 117.7, 115.4, 77.4, 77.0, 76.7, 49.9, 38.5, 37.0, 36.3, 35.7, 26.4, 22.4, 22.2, 19.6. HRMS (ESI) m/z calcd for C₁₇H₂₆N⁺ [M+H]⁺: 244.2060; found: 244.2057.



6-methoxy-2-methyl-4-(1-methylcyclohexyl)-1,2,3,4-tetrahydroquinoline (5g): Eluent: PE/EtOAc (4:1); Yellow oil, 47% yield, 25.5 mg; ¹H NMR (400 MHz, DMSO- d_6) δ 7.09 (d, J = 8.5 Hz, 1H), 6.77 (dd, J = 8.5, 2.8 Hz, 1H), 6.64 (d, J = 2.9 Hz, 1H), 5.23 (d, J = 4.8 Hz, 1H), 3.98 (d, J = 4.9 Hz, 1H), 3.72 (s, 3H), 2.54 (s, 1H), 2.49 (s, 1H), 2.14 (s, 3H), 1.53 – 0.91 (m, 11H), 0.59 (s, 3H). ¹³C NMR (101 MHz, DMSO- d_6) δ 167.4, 157.0, 138.4, 127.7, 126.9, 118.1, 111.9, 63.4, 55.6, 40.6, 40.4, 40.1, 39.9, 39.7, 39.5, 39.3, 36.1, 36.0, 35.3, 26.2, 25.4, 21.9, 21.8. HRMS (ESI) m/z calcd for C₁₈H₂₈NO⁺ [M+H]⁺: 274.2165; found: 274.2161.



4-(1-methylcyclohexyl)-1,2,3,4-tetrahydroquinoline-2-carbaldehyde (5h): Eluent: PE/EtOAc (100:1); Yellow solid, 47% yield, 24.3 mg, m.p. 141.2-142.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.33 (s, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.40 (s, 1H), 5.83 – 5.63 (m, 1H), 3.55 (d, *J* = 6.2 Hz, 1H), 1.68 – 1.49 (m, 4H), 1.42 (dq, *J* = 25.2, 15.9, 13.0 Hz, 6H), 1.30 – 1.08 (m, 2H), 0.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 186.3, 140.3, 130.7, 127.2, 121.1, 119.4, 114.6, 77.4, 77.0, 76.7, 48.7, 42.2, 34.9, 34.4, 26.4, 22.0, 21.9, 19.7. HRMS (ESI) m/z calcd for C₁₇H₂₄NO⁺ [M+H]⁺: 258.1852; found: 258.1850.



6-chloro-8-(1-methylcyclohexyl)-5,6,7,8-tetrahydroimidazo[1,2-b]pyridazine (5i): Eluent: PE/EtOAc (9:1); Colorless oil, 56% yield, 28.3 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, J = 1.5 Hz, 1H), 6.98 (d, J = 1.5 Hz, 1H), 3.11 – 3.04 (m, 1H), 3.02 – 2.97 (m, 2H), 1.64 – 1.38 (m, 10H), 1.25 (s, 1H), 0.85 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.5, 136.4, 126.3, 117.6, 77.3, 77.0, 76.7, 37.9, 35.4, 35.1, 32.2, 25.9, 21.8, 21.6. HRMS (ESI) m/z calcd for C₁₃H₂₁ClN₃⁺ [M+H]⁺: 254.1419; found: 254.1416.



8-fluoro-4-(1-methylcyclohexyl)-1,2,3,4-tetrahydroquinoline (5j): Eluent: PE/EtOAc (100:1); Colorless oil, 77% yield, 38.1 mg; ¹H NMR (400 MHz, CDCl₃) δ 6.86 (dd, J = 10.9, 8.5 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.47 (q, J = 7.7 Hz, 1H), 4.04 (s, 1H), 3.45 (dd, J = 11.5, 3.7 Hz, 2H), 2.70 (s, 1H), 2.31 – 2.18 (m, 1H), 1.77 – 1.48 (m, 7H), 1.45 – 1.22 (m, 4H), 0.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.6 (d, J = 236.2 Hz), 133.4 (d, J = 11.3 Hz), 126.2 (d, J = 2.8 Hz), 124.4 (d, J = 3.4 Hz), 113.4 (d, J = 7.4 Hz), 112.2 (d, J = 18.1 Hz), 77.4, 77.0, 76.7, 39.0, 37.5, 37.2, 36.0, 26.3, 22.3, 22.3, 21.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -64.12. HRMS (ESI) m/z calcd for C₁₆H₂₃FN⁺ [M+H]⁺: 248.1809; found: 248.1808.



7-(8-fluoro-1,2,3,4-tetrahydroquinolin-4-yl)-3,7-dimethyloctan-1-ol (5k): Eluent: PE/EtOAc (9:1); Colorless oil, 36% yield, 22.2 mg; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.81 (dd, J = 11.3, 8.2 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.33 (q, J = 7.7 Hz, 1H), 5.54 (s, 1H), 4.31 (t, J = 5.0 Hz, 1H), 3.41 (m, 2H), 3.32 – 3.17 (m, 2H), 2.58 (s, 1H), 2.05 (d, J = 13.5 Hz, 1H), 1.48 (m, 3H), 1.35 – 1.12 (m, 6H), 1.06 (d, J = 8.7 Hz, 1H), 0.83 (d, J = 7.9 Hz, 6H), 0.76 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.4 (d, J =235.0 Hz), 134.0 (d, J = 11.5 Hz), 126.5 (d, J = 2.0 Hz), 123.9 (d, J = 3.6 Hz), 112.7 (d, J = 7.3 Hz), 112.5, 59.3, 42.5, 41.2, 40.6, 40.4, 40.4, 40.1, 39.9, 39.7, 39.5, 39.3, 38.3, 38.2, 37.4, 29.5, 27.7, 27.7, 26.1, 22.9, 21.3, 20.1. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -62.16. HRMS (ESI) m/z calcd for C₁₉H₃₁FNO⁺ [M+H]⁺: 308.2384; found: 308.2380.



8-fluoro-2-(octan-2-yl)quinoline (5l): Eluent: PE/EtOAc (100:1); Colorless oil, 40% yield, 21.0 mg; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.33 (d, *J* = 9.9 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.57 – 7.45 (m, 3H), 3.04 (q, *J* = 6.9 Hz, 1H), 1.75 (dq, *J* = 13.5, 9.2, 6.8 Hz, 1H), 1.59 (dq, *J* = 13.5, 7.7, 7.0 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.23 – 1.09 (m, 8H), 0.78 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.5, 157.5 (d, *J* = 254.2 Hz), 137.5 (d, *J* = 11.5 Hz), 136.8, 128.9 (d, *J* = 2.7 Hz), 126.1 (d, *J* = 7.5 Hz), 124.2, 121.8, 114.1 (d, *J* = 18.0 Hz), 113.9, 42.5, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.3, 36.8, 31.6, 29.2, 27.5, 22.5, 21.0, 14.3. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -50.13. HRMS (ESI) m/z calcd for C₁₇H₂₃FN⁺ [M+H]⁺: 260.1809; found: 260.1807.



heptan-2-yl 2-((5-chloro-4-(1-methylcyclohexyl)-1,2,3,4-tetrahydroquinolin-8-yl)oxy)acetate (5m): PE/EtOAc (50:1); Yellow oil, 10% yield, 8.7 mg; ¹H NMR (400 MHz, CDCl₃) δ 6.53 (d, J = 8.5 Hz, 1H), 6.45 (d, J = 8.4 Hz, 1H), 5.03 (h, J = 6.5 Hz, 1H), 4.68 (s, 1H), 4.57 – 4.54 (m, 2H), 3.03 – 2.93 (m, 2H), 2.60 (ddd, J = 17.4, 12.6, 5.8 Hz, 1H), 2.07 – 1.99 (m, 1H), 1.64 – 1.19 (m, 22H), 0.95 (s, 3H), 0.87 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.6, 143.1, 137.5, 127.4, 119.4, 114.8, 110.3, 77.4, 77.4, 77.0, 76.7, 72.5, 66.6, 59.7, 35.8, 34.8, 34.6, 31.6, 26.4, 25.4, 25.0, 22.5, 21.7, 21.5, 20.0, 18.3, 14.0. HRMS (ESI) m/z calcd for C₂₅H₃₉ClNO₃⁺ [M+H]⁺: 436.2613; found: 436.2611.



(2-cyclohexylethene-1,1-diyl)dibenzene (6): Eluent: PE; Colorless oil, 16% yield, 8.2 mg; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (dt, J = 16.7, 7.1 Hz, 3H), 7.27 – 7.14 (m, 7H), 5.92 (d, J = 10.0 Hz, 1H), 2.18 – 2.11 (m, 1H), 1.69 (d, J = 5.2 Hz, 5H), 1.28 – 1.13 (m, 5H). HRMS (ESI) m/z calcd for C₂₀H₂₃⁺ [M+H]⁺: 263.1794; found: 263.1791.

11. Reference

 J. C. Lo, J. Gui, Y. Yabe, C. M. Pan and P. S. Baran, Functionalized olefin cross-coupling to construct carbon-carbon bonds, *Nature*, 2014, 516, 343-348.

12. Copies of ¹H and ¹³C NMR Spectra

¹H NMR spectrum (400 MHz, CDCl₃) of **3a**



¹H NMR spectrum (400 MHz, CDCl₃) of **3b**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3b**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3c**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3c**



¹H NMR spectrum (400 MHz, CDCl₃) of **3d**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3d**



¹H NMR spectrum (400 MHz, CDCl₃) of **3e**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3e**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3f**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3f**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3g**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3g**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3h**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3h**



¹H NMR spectrum (400 MHz, CDCl₃) of **3i**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3i**



¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **3**j



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3j**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3**k



¹³C NMR spectrum (101 MHz, DMSO-*d*₆) of **3**k



¹H NMR spectrum (400 MHz, CDCl₃) of 3l



¹³C NMR spectrum (101 MHz, CDCl₃) of **3**l



¹H NMR spectrum (400 MHz, CDCl₃) of 3m



¹³C NMR spectrum (101 MHz, CDCl₃) of **3m**



¹H NMR spectrum (400 MHz, CDCl₃) of **3n**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3n**



¹H NMR spectrum (400 MHz, CDCl₃) of 30



¹³C NMR spectrum (101 MHz, CDCl₃) of **30**



¹H NMR spectrum (400 MHz, CDCl₃) of **3p**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3p**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3**q



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3q**



¹H NMR spectrum (400 MHz, CDCl₃) of 3r





¹H NMR spectrum (400 MHz, CDCl₃) of **3s**



¹³C NMR spectrum (101 MHz, CDCl₃) of **3s**



¹H NMR spectrum (400 MHz, CDCl₃) of 3t



¹³C NMR spectrum (101 MHz, CDCl₃) of **3t**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **3u**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **3u**



¹H NMR spectrum (400 MHz, CDCl₃) of 4a



¹³C NMR spectrum (101 MHz, CDCl₃) of 4a



¹H NMR spectrum (400 MHz, DMSO- d_6) of **4b**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **4b**



¹H NMR spectrum (400 MHz, CDCl₃) of (**5a-C2**)



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

¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **5a**



¹³C NMR spectrum (101 MHz, DMSO-*d*₆) of **5a**







¹³C NMR spectrum (101 MHz, CDCl₃) of (**5b-C2**)



¹H NMR spectrum (400 MHz, DMSO- d_6) of **5b**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **5b**



¹H NMR spectrum (400 MHz, CDCl₃) of (5c-C2)





¹³C NMR spectrum (101 MHz, CDCl₃) of (5c-C2)



¹H NMR spectrum (400 MHz, DMSO- d_6) of **5**c



¹³C NMR spectrum (101 MHz, CDCl₃) of **5c**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **5d**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **5d**



¹H NMR spectrum (400 MHz, DMSO- d_6) of **5**e



¹³C NMR spectrum (101 MHz, DMSO-*d*₆) of **5**e



1 H NMR spectrum (400 MHz, CDCl₃) of **5**f



¹H NMR spectrum (400 MHz, DMSO- d_6) of **5g**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **5g**



¹H NMR spectrum (400 MHz, CDCl₃) of **5h**





^{13}C NMR spectrum (101 MHz, CDCl_3) of 5h



1 H NMR spectrum (400 MHz, CDCl₃) of **5**i



¹³C NMR spectrum (101 MHz, CDCl₃) of **5**i



¹H NMR spectrum (400 MHz, CDCl₃) of **5**j





¹⁹F NMR spectrum (376 MHz, CDCl₃) of **5j**



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **5**k



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 fl (ppm)

¹⁹F NMR spectrum (376 MHz, DMSO- d_6) of **5**k



¹H NMR spectrum (400 MHz, DMSO- d_6) of **5**I



¹³C NMR spectrum (101 MHz, DMSO- d_6) of **5**I







-50.13

¹H NMR spectrum (400 MHz, CDCl₃) of **5m**



^{13}C NMR spectrum (101 MHz, CDCl₃) of **5m**

