SUPPORTING INFORMATION

For

Pd/Cu-Catalyzed Cascade C(sp³)-H Arylation and Intramolecular C-N Coupling: A One-Pot Synthesis of 3,4-2H-quinolinone Skeletons

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Supporting Information Placeholder

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I General Consideration

General Experimental Section

$^1$H NMR and $^{13}$C NMR data were obtained on Bruker 600 M nuclear resonance spectrometers unless otherwise specified, respectively. CDCl$_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H NMR spectrum as 0.00 ppm. The data of $^1$H NMR was reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiple and $br$ = broad), coupling constant ($J$ values) in Hz and integration. Chemical shifts for $^{13}$C NMR spectra were recorded in ppm from TMS using the central peak of CDCl$_3$ (77.2 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gels with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS (ESI) analysis was performed by Analytical Instrumentation Center, Peking University. The analytical data for the known compounds were found to match with the literature data.

General Preparation for Chemicals

The ortho halogen substituted phenyl iodides were all purchased from Ark. The metal catalyst Pd(OAc)$_2$, Cul, and Ni(OAc)$_2$ were purchased from Energy. $K_3$PO$_4$ was purchased from Sinopharm Chemical Reagent Co. Ltd. 1,2-dichloro Benzene(o-DCB) was purchased from Tianjin Guangfu Chemical Reagent Co. Ltd. and used directly without further purification. t-AmylOH was purchased from Alfa and used directly without further purification.

II General Procedure for Synthesis of Amides

Scheme a General Procedure for Synthesis of Amides

The starting materials were prepared according to literature methods$^1$. To a solution of Acid in CHCl$_3$ (30 mL) was added oxalyl chloride (0.35 mL, 4 mmol) slowly at room temperature and 3 drops of DMF was added to the mixture. The resulting mixture was refluxed for 3 h. After cooled to room temperature, the mixture was evaporated in vacuo carefully to give the crude acid chloride, which was used directly for the next step without further purification.

The acid chloride was added dropwise to a solution of aromatic methyl amine (2 mmol) and Et$_3$N (0.2 mL, 3 mmol) in CH$_2$Cl$_2$ (20 mL). The mixture was stirred overnight at room temperature. Then the mixture was diluted with CH$_2$Cl$_2$ (10 mL), washed successively with water, saturated aqueous NaHCO$_3$, and brine. The organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/Petro ether (60-90 °C) (1:2, v/v), to afford corresponding starting materials.
III Initial Study on Amides with Different Protecting Group

Scheme S1 Initial Study on Amides with Different Protecting Group

\[
\begin{array}{c}
\text{R}1 \quad \text{O} \quad \text{N} \\
\text{H} \quad \text{H} \\
\text{1} \quad \text{2a} \quad \text{3} \\
\end{array}
\]

\[\begin{align*}
1 & : 10 \text{ mmol}, \\
2a & : 1.5 \text{ equiv}, \\
Pd(OAc)_2 & : 10 \text{ mol %}, \\
K_2CO_3 & : 0.2 \text{ equiv}, \\
DCE & : 1.0 \text{ mL}, \\
100^\circ C. & \\
\end{align*}\]

IV Standard Procedure for Cascade C-H Arylation and C-N Coupling Reaction

To an oven-dried Schlenk tube equipped with magnetic stir bar was added by amides (0.1 mmol), Pd(OAc)$_2$ (2.23 mg, 0.01 mmol), CuI (1.0 mg, 0.005 mmol) and K$_3$PO$_4$ (42.4 mg, 0.2 mmol). Then 0.9 mL of o-DCB and 0.1 mL of t-AmylOH were added sequentially and 2-halogen phenyl iodide (0.15 mmol) was injected into the resulted mixture with a micro injector. The resulting mixture was stirred at 140 °C in oil bath for 24 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as the eluent.

V Procedure for Deprotection.

This procedure was prepared according to literature methods$^1$.

To a solution of 3a (0.2 mmol) in THF (3 mL), cooled to -78 °C, LDA (0.4 mmol) was added dropwise upon stirring. After 25 min stirring at -78 °C, a stream of dry oxygen gas was bubbled into the solution for 20 min. After 50 mg of NH$_4$Cl and H$_2$O were added, the cooling bath was removed and the mixture was allowed to warm to room temperature. After filtering, the mixture was evaporated in vacuo. The residue was subjected to flash column chromatography on silica-gel (eluent; Hexane/EtOAc = 3/1) to give 5 as a white solid.

VI Preliminary Mechanistic Study

1, General Procedure for Eqs 3-5

To an oven-dried Schlenk tube equipped with magnetic stir bar was added by amides 1o (0.1 mmol), Pd(OAc)$_2$ (2.23 mg, 0.01 mmol), CuI (1.0 mg, 0.005 mmol) (for eq 3) or CuI (1.0 mg, 0.005 mmol) (for eq 4) or Pd(OAc)$_2$ (2.23 mg, 0.01 mmol) (for eq 5), and K$_3$PO$_4$ (42.4 mg, 0.2 mmol). Then 0.9 mL of o-DCB and 0.1 mL of t-AmylOH were added sequentially. The resulting mixture was stirred at 140 °C in oil bath for 24 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as the eluent.

2, General Procedure for Eqs 6-8

To an oven-dried Schlenk tube equipped with magnetic stir bar was added by amides 1p (0.1 mmol),
Pd(OAc)$_2$ (2.23 mg, 0.01 mmol), CuI (1.0 mg, 0.005 mmol) (for eq 6) or CuI (1.0 mg, 0.005 mmol) (for eq 7) or Pd(OAc)$_2$ (2.23 mg, 0.01 mmol) (for eq 8), and K$_3$PO$_4$ (42.4 mg, 0.2 mmol). Then 0.9 mL of o-DCB and 0.1 mL of t-AmylOH were added sequentially. The resulting mixture was stirred at 140 °C in oil bath for 24 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as the eluent.

3, General Procedure for Eq 9
To an oven-dried Schlenk tube equipped with magnetic stir bar was added by amides 1o (0.1 mmol), Pd(OAc)$_2$ (2.23 mg, 0.01 mmol), CuI (1.0 mg, 0.005 mmol), K$_3$PO$_4$ (42.4 mg, 0.2 mmol). Then 0.9 mL of o-DCB and 0.1 mL of t-AmylOH were added sequentially and 1,2-dibromo benzene (0.15 mmol) was injected into the resulted mixture with a micro injector. The resulting mixture was stirred at 140 °C in oil bath for 24 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as the eluent.

4, General Procedure for Eqs 10-11
To an oven-dried Schlenk tube equipped with magnetic stir bar was added by 1a (0.1 mmol), Pd(OAc)$_2$ (2.23 mg, 0.01 mmol), CuI (1.0 mg, 0.005 mmol), K$_3$PO$_4$ (42.4 mg, 0.2 mmol) and TEMPO (0.1 equivalent (eq 10) or 1.0 equivalent (eq 11)). Then 0.9 mL of o-DCB and 0.1 mL of t-AmylOH were added sequentially and 2-bromo iodobenzene (0.15 mmol) was injected into the resulted mixture with a micro injector. The resulting mixture was stirred at 140 °C in oil bath for 24 h. After the reaction was finished, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The resulting mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as the eluent.

Reference
VII Characterization Data for Substrates and Products

![Chemical structural formula](attachment:image)

N-(pyridin-2-ylmethyl)pivalamide (1a), 307.2 mg, 80%, colorless oil, \( R_f = 0.21 \) (PE/EtOAc = 1/1).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.54 (d, \( J = 4.6 \) Hz, 1H), 7.67 (t, \( J = 7.6 \) Hz, 1H), 7.26 (d, \( J = 7.8 \) Hz, 1H), 7.22 - 7.18 (m, 1H), 7.05 (s, 1H), 4.54 (d, \( J = 4.7 \) Hz, 2H), 1.26 (s, 9H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 178.7, 156.7, 149.1, 136.8, 122.4, 122.2, 44.5, 38.9, 27.7.


N-(quinolin-8-yl)pivalamide (1a-1), 387.6 mg, 85%, colorless oil, \( R_f = 0.45 \) (PE/EtOAc = 5/1).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 10.28 (s, 1H), 8.81 (dd, \( J = 9.4, 5.9 \) Hz, 2H), 8.16 (d, \( J = 8.2 \) Hz, 1H), 7.56 - 7.47 (m, 2H), 7.45 (dd, \( J = 8.2, 4.2 \) Hz, 1H), 1.43 (s, 9H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 177.4, 148.4, 139.0, 136.5, 134.9, 128.1, 127.6, 121.7, 121.4, 116.3, 40.5, 27.89.


N-(2-(4,5-dihydrooxazol-2-yl)phenyl)pivalamide (1a-2), 369.1 mg, 75%, white solid, \( R_f = 0.42 \) (PE/EtOAc = 3/1).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 12.23 (s, 1H), 8.81 (d, \( J = 8.5 \) Hz, 1H), 7.85 (d, \( J = 7.9 \) Hz, 1H), 7.45 (d, \( J = 8.2 \) Hz, 1H), 7.06 (t, \( J = 7.6 \) Hz, 1H), 4.39 (t, \( J = 9.4 \) Hz, 2H), 4.16 (t, \( J = 9.5 \) Hz, 2H), 1.34 (s, 9H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 178.5, 164.8, 140.5 132.6, 129.3, 122.1, 119.9, 113.4, 66.3, 54.8, 40.7, 27.9.


N-(2-(pyridin-2-yl)propan-2-yl)pivalamide (1a-3), 308.2 mg, 70%, colorless oil, \( R_f = 0.34 \) (PE/EtOAc = 1/1).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.52 (d, \( J = 4.5 \) Hz, 1H), 8.18 (s, 1H), 7.72 (t, \( J
= 7.7 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.22 – 7.15 (m, 1H), 1.75 (s, 6H), 1.26 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 177.9, 165.2, 147.7, 137.2, 121.9, 119.7, 56.1, 39.6, 27.9, 27.5.

HRMS (ESI): found: 221.1657 ([M+H]$^+$), calcd. Chemical Formula: C$_{13}$H$_{21}$N$_2$O, Exact Mass: 221.1654.

![N-pivaloylpycolinamide](attachment:1a-4.png)

N-pivaloylpycolinamide (1a-4), 321.4 mg, 78%, white solid, $R_f$ = 0.18 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 11.11 (s, 1H), 8.62 (d, J = 4.4 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.93 (t, J = 7.7 Hz, 1H), 7.60 – 7.46 (m, 1H), 1.36 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 176.3, 161.9, 148.9, 148.4, 138.1, 127.6, 123.3, 41.0, 27.2.

HRMS (ESI): found: 207.1137 ([M+H]$^+$), calcd. Chemical Formula: C$_{11}$H$_{15}$N$_2$O$_2$, Exact Mass: 207.1134.

![2,2-dimethyl-N-(pyridin-2-ylmethyl)butanamide](attachment:1b.png)

2,2-dimethyl-N-(pyridin-2-ylmethyl)butanamide (1b), 346.1 mg, 84%, colorless oil, $R_f$ = 0.25 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 11.11 (s, 1H), 8.62 (d, J = 4.4 Hz, 1H), 7.4 (s, 1H), 7.23 – 7.16 (m, 1H), 7.01 (s, 1H), 4.55 (d, J = 4.7 Hz, 2H), 1.60 (d, J = 7.5 Hz, 2H), 1.22 (s, 6H), 0.84 (t, J = 7.5 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 178.0, 156.8, 149.1, 136.9, 122.4, 122.3, 44.6, 42.6, 34.0, 25.1, 9.3.

HRMS (ESI): found: 207.1494 ([M+H]$^+$), calcd. Chemical Formula: C$_{12}$H$_{19}$N$_2$O$_2$, Exact Mass: 207.1497.

![2,2-dimethyl-N-(pyridin-2-ylmethyl)pentanamide](attachment:1c.png)

2,2-dimethyl-N-(pyridin-2-ylmethyl)pentanamide (1c), 387.2 mg, 88%, colorless oil, $R_f$ = 0.27 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.54 (d, J = 4.1 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.01 (s, 1H), 4.54 (d, J = 4.5 Hz, 2H), 1.56 – 1.50 (m, 2H), 1.30 – 1.23 (m, 2H), 1.22 (s, 6H), 0.88 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 178.1, 156.8, 149.1, 136.8, 122.4, 122.2, 44.5, 43.8, 42.3, 25.6, 18.2, 14.7.

HRMS (ESI): found: 221.1659 ([M+H]$^+$), calcd. Chemical Formula: C$_{13}$H$_{21}$N$_2$O, Exact Mass: 221.1654.
1-methyl-N-(pyridin-2-ylmethyl)cyclopropanecarboxamide (1d), 247.1 mg, 65%, colorless oil, 
$R_f = 0.20$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J = 4.3$ Hz, 1H), 7.67 (dd, $J = 10.8, 4.5$ Hz, 1H), 7.26 (s, 1H), 7.19 (s, 1H), 7.11 (s, 1H), 4.57 (d, $J = 4.7$ Hz, 2H), 1.41 (s, 3H), 1.23 (q, $J = 3.5$ Hz, 2H), 0.60 (q, $J = 3.7$ Hz, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.2, 156.8, 149.2, 136.9, 122.4, 122.3, 44.9, 19.8, 19.3, 16.2.


2,2-dimethyl-3-phenyl-N-(pyridin-2-ylmethyl)propanamide (1e), 444.9 mg, 83%, colorless oil, 
$R_f = 0.28$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 4.6$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.17 (dd, $J = 14.2, 8.9$ Hz, 5H), 7.11 (d, $J = 7.1$ Hz, 2H), 6.80 (s, 1H), 4.50 (d, $J = 4.8$ Hz, 2H), 2.88 (s, 2H), 1.24 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 177.2, 156.6, 149.0, 138.2, 136.3, 130.3, 127.9, 126.3, 122.3, 122.2, 46.8, 44.5 43.5, 25.2.

HRMS (ESI): found: 269.1657 ([M+H]$^+$), calcd. Chemical Formula: C$_{17}$H$_{21}$N$_2$O, Exact Mass: 269.1654.

2,2-dimethyl-N-(pyridin-2-ylmethyl)-3-(3,4,5-trifluorophenyl)propanamide (1f), 495.9 mg, 
77%, white solid, $R_f = 0.28$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J = 4.7$ Hz, 1H), 7.65 (td, $J = 7.7, 1.4$ Hz, 1H), 7.19 (dd, $J = 11.1, 7.5$ Hz, 2H), 6.93 (s, 1H), 6.77 – 6.65 (m, 2H), 4.48 (d, $J = 4.7$ Hz, 2H), 2.79 (s, 2H), 1.24 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 176.3, 156.1, 151.5 (dd, $J = 9.7, 4.1$ Hz), 149.8 (dd, $J = 9.8, 4.0$ Hz), 149.08 (s), 139.4 (t, $J = 15.3$ Hz), 137.7 (t, $J = 15.2$ Hz), 136.87 (s), 134.6 (td, $J = 7.3, 4.9$ Hz), 122.52, 122.20, 114.0 (dd, $J = 16.3, 4.1$ Hz), 46.1, 44.4, 43.7, 25.3.

HRMS (ESI): found: 323.1376 ([M+H]$^+$), calcd. Chemical Formula: C$_{17}$H$_{18}$F$_3$N$_2$O, Exact Mass: 323.1371.
2,2-dimethyl-3-(naphthalen-2-yl)-N-(pyridin-2-ylmethyl)propanamide (1g), 921.6 mg, 72%, white solid, $R_f = 0.29$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.58 (s, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.44 – 7.36 (m, 2H), 7.25 (d, $J = 7.1$ Hz, 1H), 7.08 (dd, $J = 14.2$, 6.9 Hz, 2H), 6.78 (s, 1H), 4.50 (d, $J = 4.8$ Hz, 2H), 3.05 (s, 2H), 1.29 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 177.2, 156.6, 149.0, 136.7, 136.0, 133.4, 128.9, 128.8, 127.6, 127.4, 125.9, 125.4, 122.3, 122.0, 47.0, 44.6, 43.9, 25.4.


2-ethyl-N-(pyridin-2-ylmethyl)-2-(4-(trifluoromethyl)benzyl)butanamide (1h), 574.1 mg, 82%, white solid, $R_f = 0.31$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J = 4.7$ Hz, 1H), 7.64 (td, $J = 7.7$, 1.5 Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.18 (dd, $J = 13.4$, 6.9 Hz, 4H), 6.80 (s, 1H), 4.49 (ddd, $J = 37.2$, 16.1, 4.9 Hz, 2H), 3.19 (d, $J = 13.1$ Hz, 1H), 2.63 (d, $J = 13.1$ Hz, 1H), 1.93 (dq, $J = 14.8$, 7.4 Hz, 1H), 1.45 (dq, $J = 14.8$, 7.4 Hz, 1H), 1.14 (s, 3H), 0.90 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.8, 156.4, 149.1, 142.4, 136.7, 136.0, 128.6 (q, $J = 32.0$ Hz), 127.1 (s), 125.3, 124.8 (q, $J = 3.6$ Hz), 123.5, 122.4, 122.3, 47.7, 45.8, 44.5, 33.0, 19.7, 9.1.


2-(4-bromobenzyl)-2-methyl-N-(pyridin-2-ylmethyl)butanamide (1i), 504.2 mg, 70%, white solid, $R_f = 0.30$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 3.9$ Hz, 1H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.30 – 7.23 (m, 3H), 7.18 (t, $J = 7.2$ Hz, 2H), 6.96 (d, $J = 7.9$ Hz, 2H), 6.77 (s, 1H), 4.57 – 4.37 (m, 2H), 3.07 (d, $J = 13.2$ Hz, 1H), 2.54 (d, $J = 13.2$ Hz, 1H), 1.94 – 1.73 (m, 2H), 1.42 (dd, $J = 13.7$, 7.2 Hz, 1H), 1.12 (s, 3H), 0.88 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 176.0, 156.5, 149.1, 137.2, 136.8, 132.0, 131.0, 122.4, 122.3, 120.3, 47.6, 45.4, 44.5, 32.9, 19.7, 9.2.

2-ethyl-2-methyl-4-phenyl-N-(pyridin-2-ylmethyl)butanamide (1j), 449.9 mg, 76%, white solid, \( R_f = 0.35 \) (PE/EtOAc = 1/1). \( ^1H \) NMR (600 MHz, CDCl₃) \( \delta \) 8.55 (d, \( J = 4.7 \) Hz, 1H), 7.67 (t, \( J = 7.7 \) Hz, 1H), 7.29 (d, \( J = 7.8 \) Hz, 1H), 7.24 (d, \( J = 7.3 \) Hz, 2H), 7.22 – 7.18 (m, 1H), 7.16 (t, \( J = 6.5 \) Hz, 3H), 7.07 (s, 1H), 4.66 – 4.50 (m, 2H), 2.58 (td, \( J = 13.0, 4.9 \) Hz, 1H), 2.48 (td, \( J = 12.9, 4.4 \) Hz, 1H), 1.97 (td, \( J = 13.1, 4.5 \) Hz, 1H), 1.83 – 1.65 (m, 3H), 1.59 – 1.48 (m, 1H), 1.28 (s, 3H), 0.87 (t, \( J = 7.4 \) Hz, 3H).

\( ^{13}C \) NMR (151 MHz, CDCl₃) \( \delta \) 176.9, 156.8, 149.1, 142.7, 136.9, 128.5, 128.5, 125.9, 122.5, 122.4, 46.3, 44.5, 42.2, 32.8, 31.3, 20.7, 9.0.


N-(pyridin-2-ylmethyl)isobutyramide (1k), 284.8 mg, 80%, colorless oil, \( R_f = 0.18 \) (PE/EtOAc = 1/1). \( ^1H \) NMR (600 MHz, CDCl₃) \( \delta \) 8.54 (d, \( J = 4.1 \) Hz, 1H), 7.67 (t, \( J = 7.6 \) Hz, 1H), 7.26 (s, 1H), 7.23 – 7.18 (m, 1H), 6.84 (s, 1H), 4.56 (d, \( J = 4.6 \) Hz, 2H), 2.55 – 2.40 (m, 1H), 1.21 (d, \( J = 6.9 \) Hz, 6H).

\( ^{13}C \) NMR (151 MHz, CDCl₃) \( \delta \) 177.2, 156.8, 149.1, 142.7, 136.9, 128.5, 128.5, 125.9, 122.5, 46.3, 44.4, 35.7, 19.8.


2-methyl-N-(pyridin-2-ylmethyl)butanamide (1l), 284.2 mg, 74%, colorless oil, \( R_f = 0.19 \) (PE/EtOAc = 1/1). \( ^1H \) NMR (600 MHz, CDCl₃) \( \delta \) 8.54 (d, \( J = 4.4 \) Hz, 1H), 7.67 (t, \( J = 7.6 \) Hz, 1H), 7.27 (t, \( J = 3.6 \) Hz, 1H), 7.22 – 7.15 (m, 1H), 6.78 (s, 1H), 4.57 (d, \( J = 4.8 \) Hz, 2H), 2.33 – 2.12 (m, 1H), 1.71 (td, \( J = 14.6, 7.4 \) Hz, 1H), 1.54 – 1.41 (m, 1H), 1.18 (d, \( J = 6.9 \) Hz, 3H), 0.91 (t, \( J = 7.4 \) Hz, 3H).

\( ^{13}C \) NMR (151 MHz, CDCl₃) \( \delta \) 176.7, 156.7, 149.1, 136.9, 122.5, 122.3, 44.4, 43.3, 27.5, 17.6, 12.1.

N-(2-(pyridin-2-yl)propan-2-yl)propionamide (1m), 291.8 mg, 76%, white solid, $R_f = 0.15$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.51 (d, $J = 4.2$ Hz, 1H), 7.72 (dd, $J = 10.7, 4.4$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 1H), 7.22 – 7.13 (m, 1H), 2.30 (q, $J = 7.6$ Hz, 2H), 1.76 (s, 6H), 1.18 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 173.1, 164.8, 147.7, 137.2, 121.9, 119.6, 56.4, 30.9, 27.7, 10.0.


N-((1-(pyridin-2-yl)ethyl)pivalamide (1n), 329.6 mg, 80%, white solid, $R_f = 0.25$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.54 (d, $J = 4.2$ Hz, 1H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.21 – 7.16 (m, 2H), 5.18 – 5.03 (m, 1H), 1.45 (d, $J = 6.7$ Hz, 3H), 1.23 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 177.9, 161.4, 149.1, 136.9, 122.4, 121.7, 49.7, 38.8, 27.7, 22.9.

HRMS (ESI): found: 207.1499 ([M+H]$^+$), calcd. Chemical Formula: C$_{12}$H$_{19}$N$_2$O, Exact Mass: 207.1494.

N-(pyrimidin-2-ylmethyl)pivalamide (1o), 320.4 mg, 84%, colorless oil, $R_f = 0.20$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.6$ Hz, 2H), 7.22 (t, $J = 4.7$ Hz, 1H), 7.09 (s, 1H), 4.69 (d, $J = 4.0$ Hz, 2H), 1.29 (d, $J = 0.9$ Hz, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 178.7, 166.3, 157.3, 119.6, 45.5, 38.9, 27.7.


3-(2-bromophenyl)-2,2-dimethyl-N-(pyridin-2-ylmethyl)propanamide (1p), 442.9 mg, 64%, colorless oil, $R_f = 0.25$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 4.6$ Hz, 1H), 7.66 (t, $J = 7.7$ Hz, 1H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.18 (dd, $J = 16.7, 6.8$ Hz, 2H), 7.05 (t, $J = 7.4$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.92 (s, 1H), 4.54 (d, $J = 4.8$ Hz, 2H), 3.15 (s, 2H), 1.30 (s, 6H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 177.3, 156.5, 149.1, 138.2, 136.9, 133.0, 131.9, 128.0, 127.1, 126.2, 122.4, 122.3, 44.7, 44.6, 44.4, 25.2.

HRMS (ESI): found: 347.0762 ([M+H$^+$]), calcd. Chemical Formula: C$_{17}$H$_{20}$BrN$_2$O, Exact Mass: 347.0757.

N-(2-bromophenyl)-N-(pyridin-2-ylmethyl)pivalamide (1q), 387.5mg, 56%, colorless oil, $R_f$ = 0.52 (PE/EtOAc = 3/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (d, $J = 4.2$ Hz, 1H), 7.71 (t, $J = 7.7$ Hz, 1H), 7.49 – 7.42 (m, 2H), 7.23 – 7.18 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.79 (t, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 7.9$ Hz, 1H), 5.27 (s, 2H), 1.19 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.2, 157.7, 149.3, 146.9, 136.6, 132.6, 127.5, 122.9, 122.4, 121.6, 121.3, 114.7, 69.0, 40.4, 28.8.

HRMS (ESI): found: 347.0761 ([M+H$^+$]), calcd. Chemical Formula: C$_{17}$H$_{20}$BrN$_2$O, Exact Mass: 347.0757.

3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3a), 21.8 mg, 82%, colorless oil, $R_f$ = 0.65 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (d, $J = 4.8$ Hz, 1H), 7.57 (td, $J = 7.7$, 1.7 Hz, 1H), 7.16 – 7.13 (m, 2H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.05 (d, $J = 7.9$ Hz, 1H), 6.96 (d, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 1H), 5.26 (s, 2H), 2.85 (s, 2H), 1.26 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.6, 157.6, 149.5, 139.5, 137.0, 128.5, 127.5, 125.0, 123.0, 122.2, 120.7 115.2, 48.9, 40.3, 37.5, 24.7.

HRMS (ESI): found: 267.1499 ([M+H$^+$]), calcd. Chemical Formula: C$_{17}$H$_{19}$N$_2$O, Exact Mass: 267.1495.

3-ethyl-3-methyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3b), 21.8 mg, 78%, colorless oil, $R_f$ = 0.67 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (d, $J = 4.0$ Hz, 1H), 7.58 (dd, $J = 10.8$, 4.5 Hz, 1H), 7.12 (ddd, $J = 21.4$, 14.5, 8.0 Hz, 4H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.91
(d, J = 8.1 Hz, 1H), 5.38 (d, J = 16.5 Hz, 1H), 5.15 (d, J = 16.4 Hz, 1H), 2.86 (q, J = 15.7 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.25 (s, 3H), 0.92 (t, J = 7.5 Hz, 3H).

$^1^C$ NMR (151 MHz, CDCl$_3$) δ 175.2, 157.7, 149.5, 139.6, 137.0, 128.5, 127.5, 125.0, 123.1, 122.2, 120.8, 115.2, 48.9, 40.9, 37.5, 29.2, 22.0, 8.4.


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3-methyl-3-propyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3c), 21.8 mg, 74%, Colorless oil, $R_f = 0.68$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (d, J = 4.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.14 (dt, J = 15.9, 6.7 Hz, 3H), 7.07 (d, J = 7.9 Hz, 1H), 6.98 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 5.37 (d, J = 16.5 Hz, 1H), 5.15 (d, J = 16.4 Hz, 1H), 2.87 (q, J = 15.6 Hz, 2H), 1.51 (ddd, J = 18.0, 12.8, 4.7 Hz, 2H), 1.37 (ddt, J = 25.9, 13.2, 6.1 Hz, 2H), 1.26 (s, 3H), 0.88 (t, J = 7.3 Hz, 3H).

$^1^C$ NMR (151 MHz, CDCl$_3$) δ 175.2, 157.7, 149.5, 139.5, 137.0, 128.5, 127.5, 125.0, 123.0, 122.3, 120.8, 115.1, 48.9, 40.8, 38.9, 38.1, 22.6, 17.4, 14.7.


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1’-(pyridin-2-ylmethyl)-1’H-spirocyclopropane-1,3’-quinolin-2’(4’H)-one (3d), (conformation isomer), 17.2 mg, 65%, Colorless oil, $R_f = 0.57$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (dd, J = 10.3, 4.3 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.11 – 7.03 (m, 2H), 6.98 (dt, J = 14.9, 7.4 Hz, 1H), 6.91 (dd, J = 18.1, 8.2 Hz, 1H), 5.36 – 5.23 (m, 2H), 2.91 (s, 1H), 2.43 (dd, J = 8.3, 5.1 Hz, 1H), 1.45 (dt, J = 20.6, 10.3 Hz, 1H), 1.39 (s, 1H), 0.87 (s, 1H), 0.80 (s, 1H).

$^1^C$ NMR (151 MHz, CDCl$_3$) δ 172.9, 171.7, 157.5, 149.5, 149.5, 139.7, 137.0, 136.6, 127.8, 127.6, 126.9, 125.0, 124.9, 122.6, 122.3, 121.3, 121.0, 115.6, 115.5, 49.13, 48.3, 34.8, 28.1, 24.5, 20.7, 20.6, 19.7, 14.7.

HRMS (ESI): found: 265.1345 ([M+H]$^+$), calcd. Chemical Formula: C$_{17}$H$_{17}$N$_2$O, Exact Mass: 265.1343.

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3-benzyl-3-methyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3e), 25.6 mg, 75%, colorless oil, Rf = 0.71 (PE/EtOAc = 1/1). \( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.59 (d, \( J = 4.5 \) Hz, 1H), 7.59 (t, \( J = 7.7 \) Hz, 1H), 7.28 (t, \( J = 7.2 \) Hz, 2H), 7.26 – 7.22 (m, 1H), 7.19 – 7.09 (m, 6H), 7.03 – 6.95 (m, 2H), 5.30 (dd, \( J = 70.0, 16.4 \) Hz, 2H), 3.00 (d, \( J = 13.3 \) Hz, 1H), 2.87 – 2.75 (m, 2H), 2.69 (d, \( J = 15.8 \) Hz, 1H), 1.22 (s, 3H).

\( ^{13} \)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 175.0, 157.5, 149.5, 139.5, 136.9, 130.9, 128.8, 128.1, 127.6, 126.7, 124.7, 123.3, 122.3, 121.0, 115.4, 49.07, 41.8, 41.7, 36.6, 22.5.


3-methyl-1-(pyridin-2-ylmethyl)-3-(3,4,5-trifluorobenzyl)-3,4-dihydroquinolin-2(1H)-one (3f), 29.3 mg, 74%, colorless oil, Rf = 0.72 (PE/EtOAc = 1/1). \( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.58 (d, \( J = 4.4 \) Hz, 1H), 7.61 (t, \( J = 7.6 \) Hz, 1H), 7.20 – 7.12 (m, 4H), 7.03 (d, \( J = 6.1 \) Hz, 2H), 6.80 (t, \( J = 7.2 \) Hz, 2H), 5.26 (dd, \( J = 40.4, 16.2 \) Hz, 2H), 3.00 (d, \( J = 13.6 \) Hz, 1H), 2.80 (d, \( J = 15.6 \) Hz, 1H), 2.75 – 2.69 (m, 2H), 1.22 (s, 3H).

\( ^{13} \)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 173.9, 157.1, 151.6 (dd, \( J = 9.7, 4.0 \) Hz), 149.9 (dd, \( J = 9.7, 4.0 \) Hz), 149.6, 139.6 (t, \( J = 15.2 \) Hz), 139.3, 138.0 (t, \( J = 15.2 \) Hz), 137.0 (d, \( J = 8.0 \) Hz), 133.5 (td, \( J = 7.5, 4.9 \) Hz), 128.6 (s), 127.9, 124.2, 123.5 (d, \( J = 4.8 \) Hz), 122.5 (d, \( J = 5.5 \) Hz), 121.2, 115.6, 114.7 (dd, \( J = 16.4, 4.1 \) Hz), 49.2, 41.9, 41.7, 37.0, 22.8.


3-methyl-3-(naphthalen-1-ylmethyl)-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3g), 25.7 mg, 68%, colorless oil, Rf = 0.75 (PE/EtOAc = 1/1). \( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.59 (d, \( J = 4.0 \) Hz, 1H), 7.82 (d, \( J = 7.6 \) Hz, 1H), 7.77 (dd, \( J = 14.0, 8.1 \) Hz, 2H), 7.61 – 7.54 (m, 2H),
7.50 – 7.42 (m, 2H), 7.29 (d, J = 8.3 Hz, 1H), 7.19 – 7.10 (m, 4H), 7.05 – 6.96 (m, 2H), 5.32 (dd, J = 77.7, 16.3 Hz, 2H), 3.19 (d, J = 13.3 Hz, 1H), 2.99 (d, J = 13.3 Hz, 1H), 2.86 (d, J = 15.8 Hz, 1H), 2.72 (d, J = 15.8 Hz, 1H), 1.28 (s, 3H).

$^1$H NMR (151 MHz, CDCl$_3$) δ 175.0, 157.5, 149.6, 139.5, 137.1, 134.6, 133.4, 132.4, 129.5, 129.3, 128.8, 127.8, 127.7, 127.6, 126.1, 125.7, 124.8, 123.3, 122.3, 121.0, 115.4, 49.1, 42.1, 42.0, 36.7, 22.6.


3-ethyl-1-(pyridin-2-ylmethyl)-3-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinolin-2(1H)-one (3h), 20.4 mg, 48%, Colorless oil, $R_f$ = 0.75 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (d, J = 4.1 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.12 (q, J = 7.7 Hz, 3H), 6.98 (dd, J = 7.4, 3.3 Hz, 2H), 5.37 (d, J = 16.3 Hz, 1H), 5.15 (d, J = 16.7 Hz, 1H), 5.29 (d, J = 13.4 Hz, 1H), 2.83 (d, J = 13.4 Hz, 1H), 2.76 (s, 2H), 1.66 (dt, J = 14.8, 7.4 Hz, 1H), 1.57 (dd, J = 14.4, 7.1 Hz, 1H), 0.98 (t, J = 7.4 Hz, 3H).

$^1$C NMR (151 MHz, CDCl$_3$) δ 173.1, 157.34, 149.5, 141.8, 139.1, 137.0, 131.1, 129.0 (dd, J = 6.0, 3.0 Hz), 128.8, 127.6, 125.4, 125.0 (dd, J = 7.3, 3.6 Hz), 124.4, 123.5, 123.3, 122.4, 121.7, 121.1, 115.3, 49.0, 45.6, 40.0, 34.2, 27.7, 8.7.


3-(4-bromobenzyl)-3-ethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3i), 17.4 mg, 40%, colorless oil, $R_f$ = 0.75 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.57 (d, J = 4.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.10 (dt, J = 18.0, 8.3 Hz, 5H), 6.97 (dd, J = 11.4, 7.8 Hz, 2H), 5.36 (d, J = 16.2 Hz, 1H), 5.16 (d, J = 16.2 Hz, 1H), 3.17 (d, J = 13.5 Hz, 1H), 2.74 (d, J = 14.3 Hz, 3H), 1.65 (dt, J = 14.7, 7.3 Hz, 1H), 1.55 (dd, J = 14.3, 7.2 Hz, 1H), 0.96 (t, J = 7.4 Hz, 3H).

$^1$C NMR (151 MHz, CDCl$_3$) δ 173.3, 157.5, 149.5, 139.1, 137.0, 136.6, 132.6, 131.2, 128.7, 127.5, 124.6, 123.3, 122.3, 121.0, 115.3, 49.0, 45.5, 39.7, 34.2, 27.6, 8.7.

3-ethyl-3-phenethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3j), 19.2 mg, 52%, colorless oil, Rf = 0.75 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.57 (d, J = 4.2 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.27-7.24 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 6.3 Hz, 5H), 7.12 (t, J = 8.7 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 5.28 (q, J = 16.4 Hz, 2H), 2.96 (q, J = 15.6 Hz, 2H), 2.71 (td, J = 12.9, 4.7 Hz, 1H), 2.61 (td, J = 12.9, 4.8 Hz, 1H), 1.93 (dd, J = 12.7, 4.7 Hz, 1H), 1.87 (dd, J = 13.0, 4.6 Hz, 1H), 1.81 – 1.70 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 173.9, 157.6, 149.6, 142.6, 139.3, 137.0, 128.6, 128.5, 127.5, 126.0, 124.7, 123.1, 122.3, 120.9, 115.1, 49.0, 44.1, 36.3, 35.3, 30.6, 27.3, 8.4. HRMS (ESI): found: 371.2127 ([M+H]+), calcd. Chemical Formula: C25H27N2O, Exact Mass: 371.2120.

3-methyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3k), 8.8 mg, 35%, colorless oil, Rf = 0.62 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.58 (d, J = 4.2 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.15 (dd, J = 24.9, 7.2 Hz, 4H), 7.00 – 6.93 (m, 2H), 5.41 (d, J = 16.5 Hz, 1H), 5.15 (d, J = 16.5 Hz, 1H), 3.02 (q, J = 10.9 Hz, 1H), 2.81 (dd, J = 12.4, 8.5 Hz, 2H), 1.34 (d, J = 5.4 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 175.2, 157.4, 149.6, 142.6, 139.3, 137.0, 128.6, 128.5, 128.4, 127.5, 126.0, 124.7, 123.1, 122.4, 120.9, 115.1, 49.2, 40.2, 37.4, 24.7. HRMS (ESI): found: 253.1348 ([M+H]+), calcd. Chemical Formula: C16H17N2O, Exact Mass: 253.1342.

3-ethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3l), 10.6 mg, 40%, colorless oil, Rf = 0.63 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.57 (d, J = 4.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.16 (t, J = 8.9 Hz, 2H), 7.11 (d, J = 7.5 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.27 (s, 2H), 3.09 (dd, J = 15.5, 5.4 Hz, 1H), 2.80 (dd, J = 15.5, 8.8 Hz, 1H), 2.66 – 2.56 (m, 1H), 1.97 – 1.90 (m, 1H), 1.57 – 1.50 (m, 1H), 1.05 (t, J = 7.5 Hz, 3H).
\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3 \] \( \delta \) 173.0, 157.5, 149.3 (s), 139.7, 137.0, 128.3, 127.6, 125.5, 123.1, 122.3, 121.0, 115.5, 48.8, 42.4, 30.4, 22.9, 11.7.


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\text{1-(2-(pyridin-2-yl)propan-2-yl)-3,4-dihydroquinolin-2(1H)-one (3m), 15.2 mg, 57%, colorless oil, } R_f = 0.57 \text{ (PE/EtOAc = 1/1).} \] 
\[ ^{1}H \text{ NMR (600 MHz, CDCl}_3 \] \( \delta \) 8.52 (d, \( J = 4.5 \text{ Hz}, 1\text{H}), 7.54 (t, \( J = 7.6 \text{ Hz}, 1\text{H}), 7.28 (s, 1\text{H}), 7.10 – 7.05 (m, 2\text{H}), 6.76 – 6.70 (m, 2\text{H}), 6.50 (d, \( J = 8.8 \text{ Hz}, 1\text{H}), 3.75 (s, 3\text{H}), 2.82 (t, \( J = 6.4 \text{ Hz}, 2\text{H}), 2.51 (t, \( J = 6.4 \text{ Hz}, 2\text{H}), 1.94 (s, 6\text{H}).

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3 \] \( \delta \) 174.0, 166.5, 148.5, 140.6, 136.3, 131.9, 127.1, 125.8, 123.3, 121.2, 120.3, 65.0, 36.3, 28.9, 26.1.


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\text{6-methoxy-1-(2-(pyridin-2-yl)propan-2-yl)-3,4-dihydroquinolin-2(1H)-one (3m-OMe), 15.7 mg, 53%, colorless oil, } R_f = 0.63 \text{ (PE/EtOAc = 1/1).} \] 
\[ ^{1}H \text{ NMR (600 MHz, CDCl}_3 \] \( \delta \) 8.61 (d, \( J = 4.2 \text{ Hz}, 1\text{H}), 7.57 (t, \( J = 7.7 \text{ Hz}, 1\text{H}), 7.20 – 7.10 (m, 4\text{H}), 7.00 (t, \( J = 7.8 \text{ Hz}, 1\text{H}), 6.93 (t, \( J = 7.3 \text{ Hz}, 1\text{H}), 6.70 (d, \( J = 8.1 \text{ Hz}, 1\text{H}), 6.38 (q, \( J = 7.0 \text{ Hz}, 1\text{H}), 2.90 (d, \( J = 15.3 \text{ Hz}, 1\text{H}), 2.70 (d, \( J = 15.3 \text{ Hz}, 1\text{H}), 1.84 (d, \( J = 7.1 \text{ Hz}, 3\text{H}), 1.27 (s, 3\text{H}), 1.16 (s, 3\text{H}).

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3 \] \( \delta \) 174.2, 166.4, 148.5, 140.6, 136.3, 131.9, 127.1, 125.8, 123.3, 121.2, 120.3, 65.0, 36.3, 28.9, 26.5.


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\text{3,3-dimethyl-1-(1-(pyridin-2-yl)ethyl)-3,4-dihydroquinolin-2(1H)-one (3n), 17.4 mg, 62%, colorless oil, } R_f = 0.68 \text{ (PE/EtOAc = 1/1).} \] 
\[ ^{1}H \text{ NMR (600 MHz, CDCl}_3 \] \( \delta \) 8.57 (d, \( J = 4.2 \text{ Hz}, 1\text{H}), 7.57 (t, \( J = 7.7 \text{ Hz}, 1\text{H}), 7.20 – 7.10 (m, 4\text{H}), 7.00 (t, \( J = 7.8 \text{ Hz}, 1\text{H}), 6.93 (t, \( J = 7.3 \text{ Hz}, 1\text{H}), 6.70 (d, \( J = 8.1 \text{ Hz}, 1\text{H}), 6.38 (q, \( J = 7.0 \text{ Hz}, 1\text{H}), 2.90 (d, \( J = 15.3 \text{ Hz}, 1\text{H}), 2.70 (d, \( J = 15.3 \text{ Hz}, 1\text{H}), 1.84 (d, \( J = 7.1 \text{ Hz}, 3\text{H}), 1.27 (s, 3\text{H}), 1.16 (s, 3\text{H}).

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$^{13}$C NMR (151 MHz, CDCl$_3$) δ 176.1, 160.7, 149.1, 137.9, 136.6, 128.6, 126.8, 126.6, 122.9, 121.9, 121.4, 117.0, 52.9, 40.3, 37.9, 25.0, 24.0, 15.5.


![Chemical Structure]

3,3-dimethyl-1-(pyrimidin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (3o), 19.5 mg, 73%, colorless oil, $R_f$ = 0.56 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.65 (d, $J$ = 4.8 Hz, 2H), 7.15 (dd, $J$ = 11.7, 6.5 Hz, 2H), 7.10 (s, 1H), 6.98 (d, $J$ = 7.3 Hz, 1H), 6.72 (d, $J$ = 8.1 Hz, 1H), 5.36 (s, 2H), 2.87 (s, 2H), 1.26 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.9, 157.6, 139.8, 129.5, 128.5, 127.3, 125.3, 123.7, 119.4, 114.5, 48.6, 40.4, 37.4, 24.7.


methyl 3,3-dimethyl-2-oxo-1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinoline-7-carboxylate (4a), 25.3 mg, 78%, colorless oil, $R_f$ = 0.45 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.59 (d, $J$ = 4.3 Hz, 1H), 7.68 (d, $J$ = 7.6 Hz, 1H), 7.62 (s, 1H), 7.59 (s, 1H), 7.23 (d, $J$ = 7.7 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.08 (d, $J$ = 7.9 Hz, 1H), 5.30 (s, 2H), 3.84 (s, 3H), 2.91 (s, 2H), 1.26 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.4, 166.7, 157.0, 149.7, 139.8, 137.0, 130.4, 129.7, 128.6, 124.4, 122.4, 120.7, 116.0, 52.3, 48.8, 40.39 (s), 37.4 24.7.

HRMS (ESI): found: 325.1557 ([M+H]$^+$), calcd. Chemical Formula: C$_{19}$H$_{21}$N$_2$O$_3$, Exact Mass: 325.1553.
3,3-dimethyl-7-nitro-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4b), 22.4 mg, 72%, colorless oil, $R_f = 0.58$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 4.6$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.63 (t, $J = 7.7$ Hz, 1H), 7.31 (d, $J = 8.2$ Hz, 1H), 7.19 (dd, $J = 12.8$, 7.0 Hz, 2H), 5.30 (s, 2H), 2.95 (s, 2H), 1.27 (s, 7H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.1, 156.2, 149.9, 147.8, 140.8, 137.1, 132.3, 129.0, 122.7, 121.3, 118.0, 110.4, 48.9, 40.3, 37.3, 24.7.

HRMS (ESI): found: 312.1349 ([M+H]$^+$), calcd. Chemical Formula: C$_{17}$H$_{18}$N$_3$O$_3$, Exact Mass: 312.1343.

3,3-dimethyl-2-oxo-1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinoline-7-carbonitrile (4c), 20.4 mg, 70%, colorless oil, $R_f = 0.57$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 4.4$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.31 – 7.22 (m, 3H), 7.23 – 7.17 (m, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 5.23 (s, 2H), 2.91 (s, 2H), 1.26 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.1, 156.3, 149.8, 140.6, 137.2, 130.5, 129.2, 126.9, 122.7, 121.1, 118.8, 118.3, 111.5, 48.9, 40.4, 37.3, 24.6.


3,3-dimethyl-1-(pyridin-2-ylmethyl)-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1H)-one (4d), 25.4 mg, 76%, colorless oil, $R_f = 0.64$ (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J = 3.9$ Hz, 1H), 7.60 (td, $J = 7.7$, 1.4 Hz, 1H), 7.39 (d, $J = 11.2$ Hz, 2H), 7.20 – 7.13 (m, 1H), 7.07 (dd, $J = 24.1$, 8.1 Hz, 2H), 5.27 (s, 2H), 2.90 (s, 2H), 1.27 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.6, 156.9, 149.7, 142.4, 131.1, 129.0, 125.4, 125.4 (d, $J = 4.0$ Hz), 125.1 (d, $J = 5.8$ Hz), 124.9 (q, $J = 3.9$ Hz), 123.3, 122.6, 121.0, 48.9, 40.0, 37.4, 24.7.

HRMS (ESI): found: 335.1377 ([M+H]$^+$), calcd. Chemical Formula: C$_{18}$H$_{18}$F$_{3}$N$_3$O, Exact Mass: 335.1374.
3,3-dimethyl-1-(pyridin-2-ylmethyl)-7-((trifluoromethoxy)-3,4-dihydroquinolin-2(1H)-one (4e), 23.8 mg, 68%, colorless oil, Rf = 0.63 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.57 (d, J = 4.0 Hz, 1H), 7.60 (t, J = 7.1 Hz, 1H), 7.20 – 7.06 (m, 3H), 6.83 (d, J = 8.0 Hz, 1H), 5.23 (s, 2H), 2.84 (s, 2H), 1.26 (s, 6H).

13C NMR (151 MHz, CDCl3) δ 175.4, 156.9, 149.6, 148.6, 140.9, 137.1, 129.2, 123.5, 122.5, 121.19, 114.9, 108.9, 48.9, 39.8, 37.5, 24.7.


7-fluoro-3,3,7-trimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4f), 21.3 mg, 75%, colorless oil, Rf = 0.65 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.57 (d, J = 4.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.23 – 7.11 (m, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.88 (t, J = 6.9 Hz, 2H), 6.80 (d, J = 8.6 Hz, 1H), 5.24 (s, 2H), 2.83 (s, 2H), 1.26 (s, 6H).

13C NMR (151 MHz, CDCl3) δ 175.5, 157.7, 149.5, 139.4, 137.3, 133.1, 129.4, 123.5, 122.9, 122.5, 120.8, 115.6, 115.9, 48.9, 39.8, 37.5, 24.7.


3,3,7-trimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4g), 21.0 mg, 75%, colorless oil, Rf = 0.66 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) 1H NMR (600 MHz, CDCl3) δ 8.59 (d, J = 4.5 Hz, 1H), 7.59 (td, J = 7.7, 1.5 Hz, 1H), 7.22 – 7.08 (m, 1H), 7.04 (t, J = 7.1 Hz, 2H), 6.80 (d, J = 7.5 Hz, 1H), 6.70 (s, 1H), 5.25 (s, 2H), 2.81 (s, 2H), 2.22 (s, 3H), 1.26 (s, 6H).

13C NMR (151 MHz, CDCl3) δ 175.8, 157.7, 149.5, 139.5, 137.3, 137.1, 128.4, 123.7, 122.2, 122.0, 120.6, 115.9, 48.9, 39.9, 37.6, 24.7, 21.6.

tert-butyl (3,3-dimethyl-2-oxo-1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinolin-6-yl)carbamate (4h), 25.2 mg, 66%, colorless oil, RF = 0.55 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.56 (d, J = 4.3 Hz, 1H), 7.57 (t, J = 7.7 Hz, 1H), 7.35 (s, 1H), 7.20 – 7.11 (m, 1H), 7.04 (d, J = 7.9 Hz, 1H), 6.93 (dd, J = 8.7, 2.1 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 6.39 (s, 1H), 5.24 (s, 2H), 2.82 (s, 2H), 1.50 (s, 9H), 1.25 (s, 6H).

13C NMR (151 MHz, CDCl3) δ 175.4, 157.7, 153.0, 149.5, 137.1, 135.1, 133.7, 126.0, 122.3, 120.9, 119.2, 117.6, 115.7, 80.7, 48.9, 40.56, 37.6, 28.5, 24.8.


6-methoxy-3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4i), 23.4 mg, 79%, colorless oil, RF = 0.65 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) 1H NMR (600 MHz, CDCl3) δ 8.58 (d, J = 4.7 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.06 (d, J = 7.9 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 6.64 (dd, J = 8.8, 2.6 Hz, 1H), 5.24 (s, 2H), 3.75 (s, 3H), 2.82 (s, 2H), 1.26 (s, 6H).

13C NMR (151 MHz, CDCl3) δ 175.2, 157.7, 155.5, 149.5, 137.1, 133.1, 126.6, 122.3, 120.8, 116.2, 114.7, 111.7, 55.6, 49.0, 40.5, 37.5, 24.7.


6-chloro-3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4j), 21.0 mg, 70%, colorless oil, RF = 0.62 (PE/EtOAc = 1/1). 1H NMR (600 MHz, CDCl3) δ 8.59 (d, J = 3.7 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.07 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 7.6 Hz, 2H), 5.21 (s, 2H), 2.82 (s, 2H), 1.25 (s, 6H).

13C NMR (151 MHz, CDCl3) δ 175.5, 156.9, 149.7, 140.8, 137.1, 133.1, 129.4, 123.5, 122.9, 122.5, 120.8, 115.6, 48.9, 39.8, 37.5, 24.7.
HRMS (ESI): found: 301.1109 ([M+H]^+), calcd. Chemical Formula: C$_{17}$H$_{18}$ClN$_2$O, Exact Mass: 301.1112.

6-bromo-3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroquinolin-2(1H)-one (4k), 25.2 mg, 73%, colorless oil, $R_f$ = 0.65 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.56 (d, $J = 4.0$ Hz, 1H), 7.59 (s, 1H), 7.07 (d, $J = 7.9$ Hz, 1H), 6.82 (d, $J = 8.7$ Hz, 1H), 5.23 (s, 2H), 2.82 (s, 2H), 1.25 (s, 6H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.3, 157.2, 149.6, 138.7, 137.1, 131.3, 130.4, 127.2, 122.5, 121.0, 117.0, 115.7, 48.9, 40.0, 37.5, 24.7.  
HRMS (ESI): found: 345.0601 ([M+H]^+), calcd. Chemical Formula: C$_{17}$H$_{18}$BrN$_2$O, Exact Mass: 345.0607.

3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydro-1,8-naphthyridin-2(1H)-one (4l), 15.0 mg, 56%, colorless oil, $R_f$ = 0.53 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.52 (s, 1H), 8.18 (s, 1H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.10 (d, $J = 5.5$ Hz, 1H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.92 (t, $J = 5.3$ Hz, 1H), 5.49 (s, 2H), 2.83 (s, 2H), 1.26 (s, 6H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.9, 158.2, 149.4, 146.4, 136.5, 136.4, 121.7, 120.4, 119.8, 118.5, 46.4, 38.8, 37.7, 24.9.  

3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydrothieno[3,4-b]pyridin-2(1H)-one (4m), 19.0 mg, 70%, colorless oil, $R_f$ = 0.68 (PE/EtOAc = 1/1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.55 (d, $J = 4.0$ Hz, 1H), 7.60 (t, $J = 7.1$ Hz, 1H), 7.19 – 7.07 (m, 2H), 6.91 (d, $J = 2.0$ Hz, 1H), 6.47 (d, $J = 2.9$ Hz, 1H), 5.16 (s, 2H), 2.79 (s, 2H), 1.26 (s, 6H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 174.7, 157.4, 149.40, 139.30, 137.0, 127.9, 122.5, 121.3, 119.9, 104.0, 49.9, 38.6, 36.7, 25.5.
HRMS (ESI): found: 273.1068 ([M+H]^+), calcd. Chemical Formula: C_{15}H_{17}N_{2}OS, Exact Mass: 273.1061.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 3,3-dimethyl-2-oxo-1-(pyridin-2-ylmethyl)-1,2,3,4-tetrahydroquinoxaline-7-carboxylate (4n), 39.3 mg, 70%, colorless oil, R_f = 0.58 (PE/EtOAc = 1/1).

{^1}H NMR (600 MHz, CDCl_3) \( \delta \) 8.54 (s, 1H), 7.82 (d, \( J = 7.5 \) Hz, 1H), 7.79 (s, 1H), 7.59 (t, \( J = 7.5 \) Hz, 1H), 7.30 (t, \( J = 9.7 \) Hz, 2H), 7.26 (s, 1H), 7.17 – 7.10 (m, 2H), 6.91 (d, \( J = 8.2 \) Hz, 1H), 6.88 (s, 1H), 5.32 (s, 2H), 2.95 (s, 2H), 2.92 (s, 2H), 2.51 (dd, \( J = 19.0, 8.4 \) Hz, 1H), 2.42 (d, \( J = 11.6 \) Hz, 1H), 2.31 (s, 1H), 2.19 – 2.11 (m, 1H), 2.07 (s, 1H), 2.02 (d, \( J = 11.9 \) Hz, 1H), 1.97 (d, \( J = 11.9 \) Hz, 1H), 1.65 (s, 4H), 1.51 – 1.42 (m, 2H), 1.28 (s, 6H), 0.92 (s, 3H).

{^{13}}C NMR (151 MHz, CDCl_3) \( \delta \) 220.8, 175.4, 165.1, 157.0, 149.70, 149.0, 140.1, 138.2, 137.6, 137.0, 131.1, 129.3, 128.7, 126.5, 124.9, 122.4, 121.7, 121.0, 118.9, 116.6, 50.7, 48.9, 48.1, 44.4, 40.5, 38.2, 37.4, 36.0, 31.8, 29.6, 26.5, 26.0, 24.7, 21.8, 14.0.

HRMS (ESI): found: 563.2919 ([M+H]^+), calcd. Chemical Formula: C_{36}H_{39}N_{2}O_{4}, Exact Mass: 563.2911.

3,3-dimethyl-3,4-dihydroquinoxaline-2(1H)-one (5), 11.3 mg, 65%, white solid, R_f = 0.54 (PE/EtOAc = 3/1). {^1}H NMR (600 MHz, CDCl_3) \( \delta \) 7.88 (s, 1H), 7.20 – 7.11 (m, 2H), 6.98 (t, \( J = 7.4 \) Hz, 1H), 6.74 (d, \( J = 7.8 \) Hz, 1H), 2.80 (s, 2H), 1.21 (s, 6H).

{^{13}}C NMR (151 MHz, CDCl_3) \( \delta \) 176.6, 137.0, 128.6, 127.5, 123.5, 123.1, 114.7, 40.4, 37.5, 24.5.

VIII NMR Spectra

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