Tandem reaction to 3-(2-quinolyl) chromones from ynones and quinoline N-oxides under transition metal- and additive-free conditions

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1. General Information

All the solvents were used without further purification. The other commercial chemicals were used without further purification. All reactions were performed under an inert atmosphere of nitrogen in flame-dried glassware, unless otherwise stated. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel’s permanganate. Preparative TLC was performed on 1.0 mm silica gel. $^1$H NMR spectra were recorded on Bruker DRX-500 instrument (500 MHz). $^{13}$C NMR spectra were recorded on Bruker DRX-500 instrument (126 MHz) were fully decoupled by broad band proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 Mass spectrometer using using EI or ESI-TOF (electrospray ionization-time of flight). NMR spectra were recorded in CDCl$_3$. $^1$H NMR spectra were referenced to residual CHCl$_3$ at 7.26 ppm, and $^{13}$C NMR spectra were referenced to the central peak of CDCl$_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.
2. Experimental Section

2.1 Procedure for the Preparation of 1

To a solution of the acyl chloride (1.0 mmol) and terminal alkyne (1.1 mmol) in an anhydrous THF (5 mL) under N₂ protection, was added PdCl₂(PPh₃)₂ (14 mg, 2 mol %) and CuI (7.6 mg, 4 mol %). After stirring for 1 min, Et₃N (1.5 mmol) was added and the mixture was stirred for 15 h at r.t. When the reaction was complete (Monitored by TLC), distilled H₂O was added. The mixture was extracted with CH₂Cl₂. The organic phase was collected, dried (Na₂SO₄), and concentrated. The residue was purified by column chromatography [silica gel, PE/EtOAc (50:1)].

1-(2-fluorophenyl)-4,4-dimethylpent-2-yn-1-one (1k). (15.6 mg, 75%). Yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 8.02 – 7.94 (m, 1H), 7.57 – 7.46 (m, 1H), 7.25 – 7.17 (m, 1H), 7.15 – 7.05 (m, 1H), 1.34 – 1.31 (m, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 174.6, 161.9 (d, J = 261.8 Hz), 135.2 (d, J = 9.3 Hz), 131.8, 125.7 (d, J = 8.1 Hz), 124.0 (d, J = 4.0 Hz), 116.9 (d, J = 21.9 Hz), 103.8 (d, J = 2.8 Hz), 79.7, 29.9, 27.9; ¹³C NMR (126 MHz, CDCl₃) δ 174.6, 161.9 (d, J = 261.8 Hz), 135.2 (d, J = 9.3 Hz), 131.8, 125.7 (d, J = 8.1 Hz), 124.0 (d, J = 4.0 Hz), 116.9 (d, J = 21.9 Hz), 103.8 (d, J = 2.8 Hz), 79.7, 29.9, 27.9. HRMS (ESI-TOF) m/z: calcd for C₁₃H₁₃FNaO⁺ (M+Na)⁺: calculated 227.0843, found 227.0839.
1-(2-fluoro-4-(trifluoromethyl)phenyl)-3-phenylprop-2-yn-1-one (1m). (25.6 mg, 86%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.20 (t, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 7.3$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.47 – 7.38 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.7, 161.5 (d, $J = 263.4$ Hz), 136.6 (qd, $J = 33.8$, 8.5 Hz), 133.3, 132.4, 131.3, 128.7, 122.5 (qd, $J = 273.7$, 2.3 Hz), 121.5 (d, $J = 2.3$ Hz), 121.0 (p, $J = 3.8$ Hz), 119.6, 114.7 (dq, $J = 25.4$, 3.8 Hz), 94.4 (d, $J = 3.2$ Hz), 88.2. HRMS (ESI-TOF) m/z: calcld for C$_{16}$H$_8$F$_4$NaO$^+$ (M+Na)$^+$: calculated 315.0403, found 315.0404.

1-(2-fluoro-4-methoxyphenyl)-3-phenylprop-2-yn-1-one (1n). (20.1 mg, 79%)$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.08 (t, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 7.1$ Hz, 2H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 6.81 – 6.72 (m, 1H), 6.69 – 6.61 (m, 1H), 3.87 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.9, 165.5 (d, $J = 11.8$ Hz), 163.8 (d, $J = 262.3$ Hz), 133.4 (d, $J = 2.3$ Hz), 133.0, 130.6, 128.5, 120.2, 118.8 (d, $J = 8.0$ Hz), 110.4 (d, $J = 2.8$ Hz), 102.2 (d, $J = 25.4$ Hz), 92.0 (d, $J = 3.2$ Hz), 88.3, 55.9. HRMS (ESI-TOF) m/z: calcld for C$_{16}$H$_{11}$FNaO$^+$ (M+Na)$^+$: calculated 277.0635, found 277.0631.
2.2 Optimization of the Reaction Conditions

2.2.1 Table S1 Screening of the reaction conditions (Condition A)\textsuperscript{a}

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp °C</th>
<th>Yield (%)\textsuperscript{b}</th>
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<td>DMF</td>
<td>120</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>CH\textsubscript{3}CN</td>
<td>120</td>
<td>82</td>
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<tr>
<td>3</td>
<td>tert-butanol</td>
<td>120</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>MTBE</td>
<td>120</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>120</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>1,4-dioxane</td>
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<tr>
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<tr>
<td>12\textsuperscript{e}</td>
<td>toluene</td>
<td>120</td>
<td>90</td>
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</table>

\textsuperscript{a} Reaction condition: 1a (0.1 mmol), 2a (0.15 mmol), solvent (0.5 mL) at a corresponding temperature under an air atmosphere.

\textsuperscript{b} Isolated yield based on 1a.

\textsuperscript{c} 2a (0.2 mmol) was used.

\textsuperscript{d} 2a (0.1 mmol) was used.

\textsuperscript{e} Under nitrogen atmosphere. DMF = N,N-Dimethyl formamide. MTBE = Methyl tertiary butyl ether. DCE = 1,2-Dichloroethane.
2.2.2 Table S2 Screening of the reaction conditions (Condition B)\textsuperscript{a}

\begin{align*}
\text{Entry} & \quad \text{Solvent} & \quad \text{Base} & \quad \text{Yield (\%)\textsuperscript{b}} \\
1 & \text{DMF} & \text{Li}_2\text{CO}_3 & 50 \\
2 & \text{DMF} & \text{Na}_2\text{CO}_3 & 30 \\
3 & \text{DMF} & \text{K}_2\text{CO}_3 & 44 \\
4 & \text{DMF} & \text{Cs}_2\text{CO}_3 & 43 \\
5 & \text{DMF} & \text{NaHCO}_3 & 25 \\
6 & \text{DMF} & \text{KHCO}_3 & 30 \\
7 & \text{DMF} & \text{Na}_3\text{PO}_4 & 75 \\
8 & \text{DMF} & \text{K}_3\text{PO}_4 & 64 \\
9 & \text{DMF} & \text{KOA}c & 0 \\
10 & \text{DMF} & \text{LiOH} & 65 \\
11 & \text{DMF} & \text{KO'Bu} & 5 \\
12 & \text{DMF} & \text{Et}_3\text{N} & 10 \\
13 & \text{DMF} & \text{DBU} & \text{trace} \\
14 & \text{DMF} & \text{-} & \text{trace} \\
15 & \text{DMSO} & \text{Na}_3\text{PO}_4 & 39 \\
16 & \text{DMA} & \text{Na}_3\text{PO}_4 & 50 \\
17 & \text{NMP} & \text{Na}_3\text{PO}_4 & 55 \\
18 & \text{THF} & \text{Na}_3\text{PO}_4 & 20 \\
19 & \text{CH}_3\text{CN} & \text{Na}_3\text{PO}_4 & 30 \\
20 & \text{tert-butanol} & \text{Na}_3\text{PO}_4 & 35 \\
21 & \text{MTBE} & \text{Na}_3\text{PO}_4 & 25 \\
22 & \text{toluene} & \text{Na}_3\text{PO}_4 & 15 \\
23 & \text{DMPU} & \text{Na}_3\text{PO}_4 & 70 \\
24 & \text{DMF} & \text{Na}_3\text{PO}_4 & 74 \\
\end{align*}

\textsuperscript{a} \text{1o} (0.1 mmol), \text{2a} (0.15 mmol), solvent (0.5 mL), base (2 equiv), under air atmosphere for 12 h. \textsuperscript{b} Isolated yield. \textsuperscript{c} at 120 °C.
2.3 Procedure for the Synthesis of 3a

2.3.1 Condition A

A dried 10 mL Schlenk tube was charged with 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-one 1a (22.4 mg, 0.1 mmol, 1 equiv), quinoline N-oxide 2a (21.8 mg, 0.15 mmol, 1.5 equiv), and toluene (0.5 mL). The reaction mixture was heated to 120 °C for 12 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature. The solvent was concentrated under vacuum, and the resulting residue was purified by preparative thin layer chromatography (PTLC) with acetate : hexane = 1 : 4 to give the corresponding products 2-phenyl-3-(quinolin-2-yl)-4H-chromen-4-one (3a) (32.1 mg, 92%) as a white solid. 

1H NMR (500 MHz, CDCl₃) δ 8.34 – 8.28 (m, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.29 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.7 Hz, 2H); 

13C NMR (126 MHz, CDCl₃) δ 177.32 , 163.26 , 156.09 , 153.63 , 148.07 , 136.13 , 133.89 , 132.78 , 130.28 , 129.43 , 129.33 , 129.27 , 128.10 , 127.48 , 127.11 , 126.69 , 126.21 , 125.27 , 124.15 , 123.75 , 123.07 , 117.97; HRMS (EI) for C₂₄H₁₆NO₂⁺ (M+H)⁺: calculated 350.1176, found 350.1176.

2.3.2 Condition B

A dried 10 mL Schlenk tube was charged with 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-one 1o (24.1 mg, 0.1 mmol, 1 equiv), quinoline N-oxide 2a (21.8 mg, 0.15 mmol, 1.5 equiv), Na₃PO₄ (32.6 mg, 0.2 mmol, 2 equiv), and DMF (0.5 mL). The reaction mixture was heated to 100 °C for 12 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was concentrated under vacuum, and the resulting residue was purified by preparative thin layer chromatography (PTLC) with acetate : hexane = 1 :
4 to give the corresponding product **2-phenyl-3-(quinolin-2-yl)-4H-chromen-4-one (3a)** (26.2 mg, 75%) as a white solid.

![Structure 3b](image)

**2-(4-fluorophenyl)-3-(quinolin-2-yl)-4H-chromen-4-one (3b).** (31.6 mg, 86%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.34 – 8.31 (m, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.71 – 7.66 (m, 1H), 7.60 – 7.55 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.46 – 7.41 (m, 2H), 6.91 (t, J = 8.6 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.2, 163.5 (d, J = 252.3 Hz), 162.2, 156.0, 153.4, 148.1, 136.3, 134.0, 131.5 (d, J = 8.7 Hz), 129.5, 129.4, 128.9 (d, J = 3.4 Hz), 127.5, 127.1, 126.8, 126.2, 125.4, 124.1, 123.7, 123.0, 117.9, 115.3 (d, J = 21.9 Hz); HRMS (EI) for C$_{24}$H$_{15}$NO$_2$ (M+H)$^+$: calculated 368.1081, found 368.1081. (Condition A).

![Structure 3c](image)

**2-(4-chlorophenyl)-3-(quinolin-2-yl)-4H-chromen-4-one (3c).** (30.0 mg, 78%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.32 – 8.28 (m, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.85 – 7.80 (m, 1H), 7.76 – 7.71 (m, 1H), 7.70 – 7.65 (m, 1H), 7.58 – 7.53 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.37 – 7.33 (m, 2H), 7.19 – 7.15 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.2, 162.0, 156.0, 153.3, 148.1, 136.5, 136.3, 134.0, 131.3, 130.6, 129.5, 129.4, 128.5, 127.5, 127.2, 126.9, 126.2, 125.4, 124.0, 123.7, 123.2, 117.9; HRMS (EI) for C$_{24}$H$_{15}$ClNO$_2$ (M+H)$^+$: calculated 384.0786, found 384.0785. (Condition A).

![Structure 3d](image)
3-(quinolin-2-yl)-2-(p-tolyl)-4H-chromen-4-one (3d). (29.8 mg, 82%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.32 – 8.28 (m, 1H), 8.15 (d, $J$ = 8.4 Hz, 1H), 8.00 (d, $J$ = 8.4 Hz, 1H), 7.82 (d, $J$ = 8.1 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.69 – 7.64 (m, 1H), 7.58 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.31 (d, $J$ = 8.3 Hz, 2H), 7.00 (d, $J$ = 8.1 Hz, 2H), 2.26 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.3, 163.3, 156.1, 153.9, 148.1, 140.7, 136.2, 133.8, 129.9, 129.5, 129.3, 129.2, 128.8, 127.5, 127.1, 126.6, 126.2, 125.2, 124.2, 123.7, 122.7, 117.9, 21.3; HRMS (EI) for C$_{25}$H$_{18}$NO$_2$+ (M+H)$^+$: calculated 364.1332, found 364.1329. (Condition A).

![Image of 3e](image)

2-(4-propylphenyl)-3-(quinolin-2-yl)-4H-chromen-4-one (3e). (31.3 mg, 80%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 – 8.20 (m, 1H), 8.06 (d, $J$ = 8.4 Hz, 1H), 7.90 (d, $J$ = 8.5 Hz, 1H), 7.74 (d, $J$ = 8.2 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.60 – 7.55 (m, 1H), 7.48 (d, $J$ = 8.5 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.39 (d, $J$ = 8.4 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.24 (d, $J$ = 8.1 Hz, 2H), 6.92 (d, $J$ = 8.0 Hz, 2H), 2.44 – 2.37 (m, 2H), 1.46 (h, $J$ = 7.3 Hz, 2H), 0.77 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.34, 163.34, 156.07, 153.90, 148.11, 145.42, 136.11, 133.76, 130.07, 129.47, 129.24, 129.20, 128.22, 127.46, 127.12, 126.62, 126.18, 125.14, 124.21, 123.75, 122.70, 117.92, 37.68, 23.98, 13.60; HRMS (EI) for C$_{27}$H$_{22}$NO$_2$+ (M+H)$^+$: calculated 392.1645, found 392.1643. (Condition A).

![Image of 3f](image)

2-(4-methoxyphenyl)-3-(quinolin-2-yl)-4H-chromen-4-one (3f). (31.9 mg, 84%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.23 – 8.19 (m, 1H), 8.08 (d, $J$ = 8.4 Hz, 1H), 7.94 (d, $J$ = 8.6 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.65 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.38 (d, $J$ = 8.4 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.27 (d, $J$ = 8.9 Hz, 2H), 6.61 (d, $J$ = 8.9 Hz, 2H), 3.63 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.3, 162.9, 161.1, 156.0, 154.1, 148.1, 136.2, 133.7, 131.3, 131.0, 129.5, 129.3, 127.5, 127.1, 126.7, 126.1, 125.1, 124.9, 124.2, 123.7, 117.8, 113.6, 55.2; HRMS (EI) for C$_{25}$H$_{18}$NO$_3$+ (M+H)$^+$: calculated 380.1281, found 380.1282. (Condition A).
2-(3-fluorophenyl)-3-(quinolin-2-yl)-4H-chromen-4-one (3g). (30.1 mg, 82%). White solid. Ethyl acetate : hexane = 1 : 4. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.33 – 8.28 (m, 1H), 8.19 (d, \(J = 8.4\) Hz, 1H), 7.95 (d, \(J = 8.4\) Hz, 1H), 7.86 – 7.80 (m, 1H), 7.78 – 7.71 (m, 1H), 7.70 – 7.64 (m, 1H), 7.60 – 7.51 (m, 3H), 7.49 – 7.45 (m, 1H), 7.26 – 7.22 (m, 1H), 7.16 – 7.07 (m, 2H), 7.02 – 6.97 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.2, 162.2 (d, \(J = 247.0\) Hz), 161.7, 156.0, 153.1, 136.3, 134.9 (d, \(J = 8.1\) Hz), 134.1, 129.7 (d, \(J = 8.1\) Hz), 129.5, 129.4, 127.6, 127.2, 126.9, 126.3, 125.5, 125.2 (d, \(J = 3.1\) Hz), 124.0, 123.7, 118.0, 117.3 (d, \(J = 21.2\) Hz), 116.3 (d, \(J = 23.8\) Hz), 100.0; HRMS (EI) for C\(_{24}\)H\(_{15}\)FNO\(_2\) (M+H): calculated 368.1081, found 368.1081. (Condition A).

3-(quinolin-2-yl)-2-(thiophen-3-yl)-4H-chromen-4-one (3h). (34.8 mg, 98%). White solid. Ethyl acetate : hexane = 1 : 4; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.30 – 8.23 (m, 2H), 8.07 (d, \(J = 8.4\) Hz, 1H), 7.91 – 7.86 (m, 1H), 7.75 – 7.69 (m, 2H), 7.61 – 7.55 (m, 2H), 7.52 (d, \(J = 8.4\) Hz, 1H), 7.48 – 7.46 (m, 1H), 7.45 – 7.40 (m, 1H), 7.12 – 7.07 (m, 1H), 6.80 – 6.76 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.53, 157.85, 155.83, 153.80, 148.26, 136.71, 133.87, 133.68, 129.64, 129.57, 127.61, 127.41, 127.31, 126.95, 126.07, 125.55, 125.16, 123.95, 123.64, 121.84, 117.82; HRMS (EI) for C\(_{22}\)H\(_{14}\)NO\(_2\)S (M+H): calculated 356.0740, found 356.0740. (Condition A).

2-butyl-3-(quinolin-2-yl)-4H-chromen-4-one (3i). (18.4 mg, 56%). White solid. Ethyl acetate : hexane = 1 : 4. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.29 – 8.25 (m, 1H), 8.23 (d, \(J = 8.4\) Hz, 1H), 8.11 (d, \(J = 8.4\) Hz, 1H), 7.87 (d, \(J = 8.0\) Hz, 1H), 7.75 – 7.70 (m, 1H), 7.70 – 7.66 (m, 1H), 7.61 (d, \(J = 8.4\) Hz, 1H), 7.60 –
7.54 (m, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.43 – 7.37 (m, 1H), 2.78 – 2.71 (m, 2H), 1.79 – 1.70 (m, 2H), 1.34 – 1.24 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 176.8, 169.3, 156.0, 153.7, 148.1, 135.7, 133.5, 129.4, 129.3, 127.6, 127.3, 126.6, 126.1, 125.0, 124.2, 123.8, 123.1, 117.7, 32.3, 29.5, 22.3, 13.6; HRMS (EI) for C$_{22}$H$_{20}$NO$_2$ $^+$(M+H)$^+$: calculated 330.1489, found 330.1491. (Condition A).

![3j](image)

**2-cyclopropyl-3-(quinolin-2-yl)-4H-chromen-4-one (3j).** (27.3 mg, 87%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.21 – 8.16 (m, 2H), 8.08 (d, J = 8.3 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.68 – 7.64 (m, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.54 – 7.48 (m, 1H), 7.35 – 7.29 (m, 2H), 2.17 – 2.09 (m, 1H), 1.34 – 1.28 (m, 2H), 0.98 – 0.91 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 176.0, 168.7, 155.4, 153.8, 136.0, 133.4, 129.4, 129.3, 127.6, 127.3, 126.7, 126.2, 125.0, 124.6, 123.8, 122.8, 117.3, 12.9, 9.5; HRMS (EI) for C$_{24}$H$_{16}$NO$_2$ $^+$(M+H)$^+$: calculated 314.1176, found 314.1177. (Condition A).

![3k](image)

**2-(tert-butyl)-3-(quinolin-2-yl)-4H-chromen-4-one (3k).** (9.9 mg, 30%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 – 8.09 (m, 2H), 8.03 (d, J = 8.6 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.67 – 7.63 (m, 1H), 7.63 – 7.59 (m, 1H), 7.53 – 7.48 (m, 1H), 7.46 – 7.40 (m, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.34 – 7.29 (m, 1H), 1.14 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.6, 172.2, 155.9, 155.1, 147.7, 135.6, 133.6, 129.6, 129.4, 127.6, 127.3, 126.7, 125.9, 124.9, 124.8, 123.1, 123.0, 117.6, 39.2, 29.5; HRMS (EI) for C$_{22}$H$_{20}$NO$_2$ $^+$(M+H)$^+$: calculated 330.1489, found 330.1490. (Condition A).
**5-fluoro-2-phenyl-3-(quinolin-2-yl)-4H-chromen-4-one (3l).** (28.0 mg, 76%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 8.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.67 – 7.60 (m, 2H), 7.55 – 7.48 (m, 2H), 7.41 – 7.35 (m, 3H), 7.31 – 7.26 (m, 1H), 7.22 – 7.16 (m, 2H), 7.11 – 7.03 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 175.6 (d, $J$ = 1.8 Hz), 162.4, 160.9 (d, $J$ = 265.9 Hz), 157.1 (d, $J$ = 3.5 Hz), 153.1, 148.0, 136.1, 133.9 (d, $J$ = 10.7 Hz), 132.2, 130.4, 129.4, 129.2, 128.1, 127.5, 127.2, 126.8, 124.2, 123.8, 114.2 (d, $J$ = 10.1 Hz), 113.9 (d, $J$ = 4.5 Hz), 112.1 (d, $J$ = 20.6 Hz); HRMS (EI) for C$_{24}$H$_{15}$FNO$_2^+$ (M+H)$^+$ : calculated 368.1081, found 368.1081. (Condition A).

**2-phenyl-3-(quinolin-2-yl)-7-(trifluoromethyl)-4H-chromen-4-one. (3m).** (30 mg, 72%). Yellow solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$ = 8.2 Hz, 1H), 8.17 (d, $J$ = 8.4 Hz, 1H), 7.99 (d, $J$ = 8.4 Hz, 1H), 7.91 (s, 1H), 7.83 (d, $J$ = 8.1 Hz, 1H), 7.68 (t, $J$ = 8.4 Hz, 2H), 7.55 (t, $J$ = 7.5 Hz, 1H), 7.48 (d, $J$ = 8.4 Hz, 1H), 7.43 (d, $J$ = 7.7 Hz, 2H), 7.31 (t, $J$ = 7.4 Hz, 1H), 7.21 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 176.3, 163.9, 155.4, 152.9, 148.1, 136.3, 135.3 (q, $J$ = 33.3 Hz), 132.1, 130.6, 129.4, 129.2, 128.1, 127.5, 127.2, 126.8, 125.9, 123.8, 123.6, 123.0 (q, $J$ = 273.0 Hz), 121.5 (q, $J$ = 3.3 Hz), 115.9 (q, $J$ = 4.1 Hz). HRMS (EI) for C$_{25}$H$_{15}$F$_3$NO$_2^+$ (M+H)$^+$ : calculated 418.1049, found 418.1049.

**8-chloro-2-phenyl-3-(quinolin-2-yl)-4H-chromen-4-one (3o).** (33.9 mg, 89%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.14 – 8.11 (m, 1H), 8.10 (d, $J$ = 8.4 Hz, 1H), 7.91
(d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.62 – 7.57 (m, 1H), 7.49 – 7.45 (m, 1H), 7.42 – 7.37 (m, 3H), 7.30 (t, J = 7.9 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.13 (t, J = 7.7 Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) 3176.9, 163.0, 153.2, 151.8, 148.1, 136.4, 134.0, 132.2, 130.7, 129.8, 129.5, 128.7, 128.2, 127.5, 127.2, 126.9, 125.3, 125.1, 124.8, 124.0, 123.1, 122.9; HRMS (EI) for C\(_{24}\)H\(_{15}\)ClINO\(_2^+\) (M+H)\(^+\): calculated 384.0786, found 384.0787. (Condition B).

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\begin{array}{c}
\text{3p} \\
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{N} \\
\text{3p}
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\]

7-chloro-2-phenyl-3-(quinolin-2-yl)-4\(H\)-chromen-4-one (3p). (30.3 mg, 79%). White solid. ethyl acetate : hexane = 1 : 4. \(^1\)H NMR (500 MHz, CDCl\(_3\)) 98.24 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.61 (d, J = 1.9 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 1H), 7.22 – 7.17 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) 3176.5, 163.4, 156.2, 153.2, 148.1, 139.9, 136.3, 132.4, 130.5, 129.5, 129.4, 129.3, 128.2, 127.7, 127.5, 127.2, 126.8, 126.2, 124.0, 123.3, 122.3, 118.1; HRMS (EI) for C\(_{24}\)H\(_{15}\)ClINO\(_2^+\) (M+H)\(^+\): calculated 384.0786, found 384.0785. (Condition B).

\[
\begin{array}{c}
\text{4a} \\
\begin{array}{c}
\text{Br} \\
\text{O} \\
\text{N}
\end{array}
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\]

3-(3-bromoquinolin-2-yl)-2-phenyl-4\(H\)-chromen-4-one (4a). (26.6 mg, 62%). White solid. ethyl acetate : hexane = 1 : 4. \(^1\)H NMR (500 MHz, CDCl\(_3\)) 98.40 (s, 1H), 8.33 – 8.28 (m, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.71 – 7.66 (m, 1H), 7.61 – 7.53 (m, 2H), 7.52 – 7.48 (m, 2H), 7.48 – 7.42 (m, 1H), 7.33 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) 3176.7, 162.7, 156.2, 153.5, 146.6, 139.1, 134.0, 132.6, 130.5, 129.8, 129.5, 128.7, 128.5, 128.2, 127.7, 126.6, 126.2, 125.3, 123.5, 122.9, 119.8, 118.0; HRMS (EI) for C\(_{24}\)H\(_{14}\)BrKNO\(_2^+\) (M+K)\(^+\): calculated 465.9839, found 465.9834. (Condition A).
3-(3-methylquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4b). (21.8 mg, 60%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.31 – 8.27 (m, 1H), 8.01 (d, $J$ = 8.4 Hz, 1H), 7.97 (s, 1H), 7.79 – 7.71 (m, 2H), 7.65 – 7.57 (m, 2H), 7.54 – 7.48 (m, 1H), 7.48 – 7.39 (m, 3H), 7.31 – 7.24 (m, 1H), 7.19 (t, $J$ = 7.7 Hz, 2H), 2.31 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.2, 162.1, 156.2, 154.7, 146.7, 136.3, 133.9, 132.6, 131.3, 130.4, 129.2, 128.7, 128.5, 128.2, 128.0, 126.8, 126.7, 126.2, 125.2, 123.6, 122.6, 118.0, 19.0; HRMS (EI) for C$_{25}$H$_{18}$NO$_2$+ (M+H)$^+$ : calculated 364.1332, found 364.1334. (Condition A).

3-(4-chloroquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4c). (29.0 mg, 76%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.25 – 8.19 (m, 1H), 8.17 – 8.11 (m, 1H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.65 – 7.57 (m, 1H), 7.57 (s, 1H), 7.58 – 7.50 (m, 1H), 7.49 (d, $J$ = 8.0 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.27 – 7.19 (m, 1H), 7.15 (t, $J$ = 7.6 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.06, 163.75, 156.07, 153.49, 148.74, 142.41, 143.04, 132.60, 130.48, 130.21, 129.74, 129.23, 128.22, 127.68, 126.19, 125.43, 125.41, 124.21, 123.91, 123.64, 122.23, 118.01; HRMS (EI) for C$_{24}$H$_{15}$ClNO$_2$+ (M+H)$^+$ : calculated 384.0786, found 384.0786. (Condition A).

3-(4-methylquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4d). (34.2 mg, 94%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 – 8.20 (m, 1H), 7.93 – 7.87 (m, 1H), 7.85 (d,
\[ J = 8.3 \text{ Hz, 1H}, 7.66 - 7.60 \text{ (m, 1H)}, 7.57 - 7.52 \text{ (m, 1H)}, 7.51 - 7.43 \text{ (m, 2H)}, 7.38 - 7.34 \text{ (m, 3H)}, 7.29 \text{ (s, 1H)}, 7.22 - 7.18 \text{ (m, 1H)}, 7.11 \text{ (t, } J = 7.6 \text{ Hz, 2H)}, 2.61 \text{ (d, } J = 1.0 \text{ Hz, 3H)}; ^{13}\text{C NMR (126 MHz, CDCl}_3) \delta 177.5, 163.1, 156.1, 153.3, 147.8, 144.3, 133.8, 132.9, 130.2, 130.0, 129.2, 129.0, 128.1, 127.3, 126.4, 126.2, 125.2, 124.7, 123.7, 123.6, 123.1, 117.9, 18.8; \text{ HRMS (EI) for } C_{25}H_{18}NO_2^+ (M+H)^+ : \text{ calculated } 364.1332, \text{ found } 364.1334. (\text{Condition A}).

\begin{center}
4e
\end{center}

3-(6-bromoquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4e). (37.7 mg, 88%). White solid. ethyl acetate : hexane = 1 : 4. \(^1\text{H NMR (500 MHz, CDCl}_3) \delta 8.25 - 8.20 \text{ (m, 1H)}, 7.98 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.89 \text{ (d, } J = 2.1 \text{ Hz, 1H)}, 7.72 \text{ (d, } J = 9.0 \text{ Hz, 1H)}, 7.68 - 7.60 \text{ (m, 2H)}, 7.50 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.44 \text{ (d, } J = 8.5 \text{ Hz, 1H)}, 7.40 - 7.35 \text{ (m, 1H)}, 7.32 - 7.28 \text{ (m, 2H)}, 7.26 - 7.20 \text{ (m, 1H)}, 7.15 - 7.10 \text{ (m, 2H)}; ^{13}\text{C NMR (126 MHz, CDCl}_3) \delta 177.15, 163.55, 156.09, 154.15, 146.59, 135.04, 134.00, 132.84, 132.70, 131.10, 130.40, 129.52, 129.24, 128.19, 128.16, 126.21, 125.38, 125.10, 123.69, 122.72, 120.64, 118.01; \text{ HRMS (EI) for } C_{24}H_{25}BrNO_2^+ (M+H)^+ : \text{ calculated } 428.0281, \text{ found } 428.0281. (\text{Condition A}).

\begin{center}
4f
\end{center}

3-(6-methylquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4f). (31.3, 86%). White solid. ethyl acetate : hexane = 1 : 4. \(^1\text{H NMR (500 MHz, CDCl}_3) \delta 8.24 - 8.21 \text{ (m, 1H)}, 7.97 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.76 \text{ (d, } J = 8.6 \text{ Hz, 1H)}, 7.66 - 7.60 \text{ (m, 1H)}, 7.50 - 7.46 \text{ (m, 2H)}, 7.41 - 7.38 \text{ (m, 1H)}, 7.36 \text{ (d, } J = 8.3 \text{ Hz, 2H)}, 7.36 - 7.30 \text{ (m, 2H)}, 7.22 - 7.17 \text{ (m, 1H)}, 7.13 - 7.07 \text{ (m, 2H)}, 2.44 \text{ (s, 3H)}; ^{13}\text{C NMR (126 MHz, CDCl}_3) \delta 177.3, 163.2, 156.1, 152.6, 146.7, 136.6, 135.4, 133.8, 132.9, 131.6, 130.2, 129.2, 129.1, 128.0, 127.1, 126.3, 126.2, 125.2, 124.1, 123.8, 123.1, 117.9, 21.6; \text{ HRMS (EI) for } C_{25}H_{18}NO_2^+ (M+H)^+ : \text{ calculated } 364.1332, \text{ found } 364.1331. (\text{Condition A}).
3-(6-methoxyquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4g). (32.6 mg, 86%). White solid. ethyl acetate : hexane = 1 : 4. H NMR (500 MHz, CDCl₃) δ 8.24 – 8.21 (m, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.24 – 7.17 (m, 2H), 7.11 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 2.7 Hz, 1H), 3.83 (s, 3H); C NMR (126 MHz, CDCl₃) δ 177.4, 163.2, 157.9, 156.1, 150.9, 144.2, 134.9, 133.8, 132.9, 130.8, 130.2, 129.6, 129.3, 128.2, 128.0, 126.2, 125.2, 124.4, 123.8, 122.1, 117.9, 105.0, 55.5; HRMS (EI) for C₂₅H₁₈NO₃⁺ (M+H)⁺ : calculated 380.1281, found 380.1283. (Condition A).

3-(6-nitroquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4h). (30.0 mg, 76%). White solid. ethyl acetate : hexane = 1 : 4. H NMR (500 MHz, CDCl₃) δ 8.72 (d, J = 2.5 Hz, 1H), 8.35 – 8.32 (m, 1H), 8.28 – 8.23 (m, 2H), 7.97 (d, J = 9.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.34 – 7.29 (m, 2H), 7.29 – 7.23 (m, 1H), 7.16 (t, J = 7.7 Hz, 2H); C NMR (126 MHz, CDCl₃) δ 177.0, 164.2, 157.7, 156.1, 149.9, 145.6, 137.7, 134.3, 132.5, 131.1, 130.7, 129.3, 128.3, 126.2, 125.8, 125.6, 124.3, 123.6, 122.9, 122.3, 118.1; HRMS (EI) for C₂₄H₁₅N₂O₄⁺ (M+H)⁺ : calculated 395.1026, found 395.1025. (Condition A).

3-(8-methylquinolin-2-yl)-2-phenyl-4H-chromen-4-one (4i). (31.3 mg, 86%). White solid. ethyl acetate : hexane = 1 : 4. H NMR (500 MHz, CDCl₃) δ 8.26 – 8.23 (m, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.34 (d, J = 6.7 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.22 – 7.17 (m, 1H), 7.10 (t, J = 7.7 Hz, 2H), 2.29
(s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.3, 164.4, 156.1, 151.9, 146.9, 137.4, 135.8, 133.8, 133.7, 129.9, 129.3, 129.1, 127.9, 127.1, 126.3, 126.2, 125.4, 125.2, 124.0, 123.9, 123.2, 118.0, 17.6; HRMS (EI) for $C_{25}H_{18}NO_2^+$ (M+H)$^+$. calculated 364.1332, found 364.1331. (Condition A).

![4j](image)

3-(8-(benzyloxy)quinolin-2-yl)-2-phenyl-4H-chromen-4-one (4j). (40.1 mg, 88%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, $J$ = 7.9 Hz, 1H), 8.06 (d, $J$ = 8.4 Hz, 1H), 7.61 (t, $J$ = 8.6 Hz, 2H), 7.46 (d, $J$ = 8.4 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.27 (d, $J$ = 8.0 Hz, 1H), 7.23 – 7.17 (m, 4H), 7.16 (d, $J$ = 5.8 Hz, 1H), 7.12 (d, $J$ = 7.6 Hz, 4H), 6.82 (d, $J$ = 7.6 Hz, 1H), 5.09 (s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.4, 163.8, 156.0, 154.1, 152.2, 140.5, 137.2, 135.7, 133.8, 133.3, 129.9, 129.5, 128.5, 128.3, 127.9, 127.4, 126.8, 126.6, 125.2, 124.8, 123.8, 123.3, 119.9, 117.9, 111.3, 70.7; HRMS (EI) for $C_{31}H_{22}NO_3^+$ (M+H)$^+$. calculated 456.1594, found 456.1590. (Condition A).

![4k](image)

3-(isoquinolin-1-yl)-2-phenyl-4H-chromen-4-one (4k). (17.5mg, 50%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.52 (d, $J$ = 5.7 Hz, 1H), 8.33 – 8.27 (m, 1H), 7.88 (d, $J$ = 8.4 Hz, 1H), 7.84 (d, $J$ = 8.3 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.68 – 7.60 (m, 3H), 7.53 – 7.44 (m, 2H), 7.36 – 7.30 (m, 2H), 7.25 (t, $J$ = 7.4 Hz, 1H), 7.14 (t, $J$ = 7.8 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.3, 163.2, 156.3, 154.6, 142.5, 136.2, 134.0, 132.7, 130.4, 130.2, 128.7, 128.6, 128.1, 127.6, 127.1, 126.5, 126.3, 125.4, 123.5, 121.6, 120.8, 118.0; HRMS (EI) for $C_{24}H_{16}NO_2^+$ (M+H)$^+$. calculated 350.1176, found 350.1177. (Condition B).
3-(4-bromoisoquinolin-1-yl)-2-phenyl-4H-chromen-4-one (4l). (32.9 mg, 75%). White solid. ethyl acetate : hexane = 1 : 4. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.63 (s, 1H), 8.23 – 8.19 (m, 1H), 8.11 (d, \(J = 8.5\) Hz, 1H), 7.80 (d, \(J = 8.4\) Hz, 1H), 7.71 – 7.65 (m, 2H), 7.54 (d, \(J = 8.1\) Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.10 (t, \(J = 7.7\) Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.1, 163.4, 156.3, 154.2, 144.2, 135.0, 134.1, 132.5, 131.5, 130.6, 129.8, 128.6, 128.3, 127.0, 126.4, 126.3, 125.5, 123.4, 121.0, 119.8, 118.1; HRMS (EI) for C\(_{24}\)H\(_{25}\)BrNNaO\(_2\)(M+Na): calculated 450.0100, found 450.0095. (Condition B).

3-(5-bromoisoquinolin-1-yl)-2-phenyl-4H-chromen-4-one (4m). (18.1 mg, 43%). White solid. ethyl acetate : hexane = 1 : 4. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.54 (d, \(J = 5.9\) Hz, 1H), 8.24 – 8.18 (m, 1H), 7.93 (d, \(J = 5.9\) Hz, 1H), 7.86 (d, \(J = 7.4\) Hz, 1H), 7.80 (d, \(J = 8.3\) Hz, 1H), 7.72 – 7.66 (m, 1H), 7.55 (d, \(J = 8.4\) Hz, 1H), 7.40 (t, \(J = 7.5\) Hz, 1H), 7.29 – 7.22 (m, 3H), 7.19 (d, \(J = 6.4\) Hz, 1H), 7.09 (t, \(J = 7.7\) Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.2, 163.5, 156.3, 155.2, 143.8, 135.4, 134.1, 134.0, 132.5, 130.6, 129.8, 128.6, 128.3, 128.0, 126.4, 126.3, 125.5, 123.4, 122.0, 121.3, 119.8, 118.1; HRMS (EI) for C\(_{24}\)H\(_{25}\)BrNO\(_2\)(M+H): calculated 428.0281, found 428.0281. (Condition B).
3-(5-methylpyridin-2-yl)-2-phenyl-4H-chromen-4-one (4n). (10.7 mg, 34%). White solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 4.7$ Hz, 1H), 8.31 – 8.27 (m, 1H), 7.75 – 7.71 (m, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.53 – 7.50 (m, 1H), 7.48 – 7.42 (m, 1H), 7.41 – 7.33 (m, 3H), 7.27 (t, $J = 7.6$ Hz, 2H), 7.20 – 7.16 (m, 1H), 2.12 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 176.96 , 162.19 , 156.20 , 152.67 , 147.24 , 137.92 , 133.84 , 133.80 , 132.82 , 130.41 , 128.69 , 128.17 , 126.24 , 125.19 , 123.55 , 123.01 , 122.38 , 117.98 , 18.68; HRMS (EI) for C$_{21}$H$_{16}$NO$_2$+ (M+H)$^+$ : calculated 314.1176, found 314.1177. (Condition B).

2.4 Procedure for the Gram-Scale Preparation of 3a

A dried 100 mL Schlenk tube was charged with 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-one 1a (1.12 g, 5 mmol, 1 equiv), quinoline N-oxide 2a (1.09 g, 7.5 mmol, 1.5 equiv), and toluene (25 mL). The reaction mixture was heated to 120 °C for 12 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature. The solvent was concentrated under vacuum, and the resulting residue was purified by flash chromatograpy with acetate : hexane = 1 : 4 to give the corresponding products 2-phenyl-3-(quinolin-2-yl)-4H-chromen-4-one (3a) (1.59 g, 91%) as a white solid.

2.5 Procedure for the Preparation of 5

A dried 10 mL Schlenk tube was charged with 1,3-diphenylprop-2-yn-1-one 1r (20.7 mg, 0.1 mmol, 1 equiv), quinoline N-oxide 2a (21.8 mg, 0.15 mmol, 1.5 equiv), and toluene (0.5 mL). The reaction mixture was heated to 120 °C for 12 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature. The solvent was concentrated under vacuum, and the resulting residue was purified by preparative thin layer chromatograpy (PTLC) with acetate : hexane = 1 : 4 to give the corresponding products 1,3-diphenyl-2-(quinolin-2(1H)-ylidene)propane-1,3-dione (5a) (31.6 mg, 90%) as a yellow solid.
1,3-diphenyl-2-(quinolin-2(1H)-ylidene)propane-1,3-dione (5a). (31.6 mg, 90%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 1.7$ Hz, 2H), 7.72 – 7.65 (m, 3H), 7.61 (d, $J = 7.3$ Hz, 2H), 7.45 – 7.37 (m, 3H), 7.21 (d, $J = 7.0$ Hz, 1H), 7.12 (q, $J = 7.2$ Hz, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.65 , 192.79 , 154.43 , 142.56 , 142.15 , 138.33 , 136.41 , 131.65 , 131.42 , 129.77 , 129.29 , 128.14 , 127.74 , 127.71 , 125.07 , 123.69 , 119.79 , 118.62 , 106.10; HRMS (EI) for C$_{24}$H$_{17}$NO$_2$+ (M+H)$^+$ : calculated 352.1332, found 352.1333.

1,3-bis(4-fluorophenyl)-2-(quinolin-2(1H)-ylidene)propane-1,3-dione (5b). (32.9 mg, 85%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.9 (q, $J = 9.5$ Hz, 2H), 7.7 – 7.6 (m, 5H), 7.5 – 7.4 (m, 3H), 6.8 (t, $J = 7.9$ Hz, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 195.8 , 191.1 , 164.5 (d, $J = 254.5$ Hz), , 163.4 (d, $J = 257.0$ Hz), 154.3 , 138.7, 138.5, 138.3, 136.2 , 131.7, 131.6, 130.2, 127.7 , 125.2 , 123.7 , 119.5 , 118.5, 114.8 (d, $J = 21.7$ Hz). HRMS (EI) for C$_{24}$H$_{16}$F$_2$NO$_2$+ (M+H)$^+$ : calculated 388.1144, found 388.1145.

2-(quinolin-2(1H)-ylidene)-1,3-di-p-tolylpropane-1,3-dione (5c). (18.1 mg, 48%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 9.5$ Hz, 1H), 7.74 (d, $J = 9.5$ Hz, 1H), 7.64 (d, $J = 6.9$ Hz, 3H), 7.58 (d, $J = 7.7$ Hz, 2H), 7.41 – 7.35 (m, 1H), 7.34 (d, $J = 7.6$ Hz, 2H), 6.99 –
6.88 (m, 4H), 2.22 (d, J = 21.2 Hz, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.3, 191.8, 154.2, 142.2, 139.9, 139.6, 139.1, 137.8, 136.6, 131.5, 129.5, 129.1, 128.5, 128.1, 127.6, 124.8, 123.5, 119.8, 118.5, 106.1, 21.4, 21.3. HRMS (EI) for C$_{26}$H$_{22}$NO$_2$$^+$ (M+H)$^+$ : calculated 380.1645, found 380.1644.

![5d](image)

2-(4-chloroquinolin-2(1H)-ylidene)-1,3-diphenylpropane-1,3-dione (5d). (17.2 mg, 45%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.13 (s, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.4 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 6.8 Hz, 2H), 7.21 (t, J = 7.0 Hz, 1H). 7.16 – 7.01 (m, 5H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.1, 189.8, 154.7, 142.2, 140.9, 138.6, 136.1, 131.7, 131.3, 129.7, 129.3, 128.5, 127.7 (d, J = 2.1 Hz), 125.9, 125.4, 123.8, 120.0, 118.8, 107.6. HRMS (EI) for C$_{24}$H$_{17}$ClNO$_2$$^+$ (M+H)$^+$ : calculated 386.0942, found 386.0943.

![5e](image)

2-(4-methylquinolin-2(1H)-ylidene)-1,3-diphenylpropane-1,3-dione (5e). (20.1 mg, 55%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.83 (d, J = 9.3 Hz, 2H), 7.67 (d, J = 5.9 Hz, 2H), 7.60 (s, 2H), 7.47 – 7.42 (m, 1H), 7.39 (s, 2H), 7.20 (s, 1H), 7.10 (s, 5H), 2.62 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.9, 192.9, 153.9, 147.5, 142.8, 142.4, 136.1, 131.3, 129.6, 129.3, 128.1, 127.7, 124.9, 124.2, 124.0, 119.1, 119.0, 105.5, 19.6. HRMS (EI) for C$_{25}$H$_{20}$NO$_2$$^+$ (M+H)$^+$ : calculated 366.1489, found 366.1487.
2-(8-methylquinolin-2(1H)-ylidene)-1,3-diphenylpropane-1,3-dione (5f). (22.3 mg, 60%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (s, 2H), 7.62 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 2H), 7.44 – 7.38 (m, 2H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.11 (m, $J = 6.8$, 5.8 Hz, 5H), 2.79 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.7, 192.7, 154.1, 142.7, 142.2, 138.8, 135.6, 132.2, 131.3, 129.6, 129.3, 128.2, 127.7, 127.7, 126.8, 125.5, 124.8, 123.7, 119.3, 106.3, 17.2. HRMS (EI) for C$_{25}$H$_{20}$NO$_2$+(M+H)$^+$: calculated 366.1489, found 366.1488.

(E)-1-(2-chlorophenyl)-3-phenyl-2-(quinolin-2(1H)-ylidene)propane-1,3-dione (5g). (26.6 mg, 69%). Yellow solid. ethyl acetate : hexane = 1 : 4. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.4$ Hz, 1H), 7.82 (s, 1H), 7.70 (t, $J = 5.6$ Hz, 3H), 7.59 (s, 2H), 7.48 – 7.41 (m, 1H), 7.30 – 7.10 (m, 4H), 7.05 – 6.92 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 197.1, 189.8, 154.7, 142.2, 140.9, 138.6, 136.1, 131.7, 131.3, 131.1, 129.7, 129.3, 128.5, 127.7, 125.9, 125.4, 123.8, 120.0, 118.8, 107.6. HRMS (EI) for C$_{24}$H$_{17}$ClNO$_2$+(M+H)$^+$: calculated 386.0942, found 386.0944.

2.6 Procedure for the Preparation of 6

A dried 50 mL Schlenk tube was charged with 20 mL of H$_2$O were added sequentially the ynone 1a (224.3 mg, 1 mmol, 1 equiv), quinoline N-oxide 2a (218 mg, 1.5 mmol, 1.5 equiv). The resulting mixture was stirred at 100 ºC, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was extracted by ethyl acetate and dried by Na$_2$SO$_4$ and then concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product 1-(2-fluorophenyl)-3-phenyl-2-(quinolin-2-yl)propane-1,3-dione (6) (296 mg) in 80% yield as a yellow solid.
(E)-1-(2-fluorophenyl)-3-phenyl-2-(quinolin-2(1H)-ylidene)propane-1,3-dione (6). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.41 (s, 1H), 7.97 (d, $J$ = 8.0 Hz, 1H), 7.88 (s, 1H), 7.77 – 7.55 (m, 5H), 7.48 – 7.39 (m, 1H), 7.24 (s, 2H), 7.16 (d, $J$ = 6.7 Hz, 2H), 7.06 (q, $J$ = 6.7, 6.1 Hz, 1H), 6.88 (t, $J$ = 7.2 Hz, 1H), 6.69 (t, $J$ = 9.2 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 196.88, 188.10, 158.46 (d, $J$ = 248.9 Hz), 154.47, 142.04, 138.61, 136.07, 131.71, 131.40, 130.91, 129.39, 128.77, 127.71, 127.67, 125.32, 123.81, 123.34 (d, $J$ = 2.5 Hz), 119.83, 118.68, 115.43 (d, $J$ = 22.7 Hz), 107.50; HRMS (EI) for C$_{24}$H$_{17}$FNO$_2$$^+$ (M+H)$^+$: calculated 370.1238, found 370.1237.
2.7 Crystal Data and structure Refinement for 4a

Crystal structure and data of 4a (CCDC 1940117, Displacement ellipsoids are drawn at the 50% probability level.)

Table S3 Crystal data and structure refinement for exp_7038.

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Reference:

3. \(^1\)H and \(^{13}\)C NMR Spectra

1k