Visible light-induced one-pot synthesis of trifluoromethyl/gem-difluoromethylene substituted cyclobutene derivatives

Xiao Hu,a Aishun Ding,a Dawen Xu,a,b,* Hao Guoa,*

a Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, PR China, E-mail: Hao_Guo@fudan.edu.cn

b Zhuhai Fudan Innovation Institute, Hengqin New Area, Zhuhai, Guangdong 519000, PR China, E-mail: 13210220024@fudan.edu.cn

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Figure S1. Spectral distribution of irradiance density for the purple LED strip
X-ray Crystallographic Details

The crystal samples were prepared by dissolving the respective compounds in ethyl acetate/petroleum ether solvent system. The solution was placed in the refrigerator, the crystals were grown by slow cooling. Data were collected on a single crystal X-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), an IMS microsource with MoKα radiation ($\lambda = 0.71073$ Å) and a Helios optic using the APEX3 software package. Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT. Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS. Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structures were solved using SHELXS or SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL in conjunction with SHELXLE. Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, and other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(Fo^2 - Fc^2)^2$ with the SHELXL weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. A split layer refinement was used for disordered groups and additional SIMU, DELU, RIGU, ISOR and SAME restraints were used, if necessary. Images of the crystal structures were generated with PLATON. Crystallographic data are provided free of charge by The Cambridge Crystallographic Data Centre.
Experimental Section

General information

All the photo reactions were carried out using purple LED strip (height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm at rt unless stated otherwise. $^1$H (400 MHz), $^{13}$C (101 MHz), and $^{19}$F (376 MHz) NMR spectra of samples in CDCl$_3$ were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics APEXIII ESI-FTICRMS spectrometer. Melting points were determined on a WRS-2 apparatus. Anhydrous DMF is commercially available from Energy®. Anhydrous DCM was distilled with CaH$_2$. Anhydrous THF was distilled with Na using benzophenone as monitor. 1m$^9$, 1o$^{10}$ and 1p$^{11}$ were synthesized according to literature procedures.

Typical Procedure I for the synthesis of substrates

Synthesis of 1-benzylquinolin-2(1H)-one (1a)

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\text{Quinolin-2(1H)-one (4.356 g, 30.0 mmol), 1-(bromomethyl)benzene (4.3 mL, 36.0 mmol), K}_2\text{CO}_3 (12.440 g, 90.0 mmol) and anhydrous DMF (30 mL) were added subsequently into a 120 mL of sealed tube. The mixture was stirred at 70 °C with an oil bath for 18 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3:1). After completion of the reaction, the mixture was cooled, diluted with ethyl acetate. The mixture was washed with H}_2\text{O (90 mL) and saturated aqueous NH}_4\text{Cl (30 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine, dried over MgSO}_4 and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1→3:1) afforded 1a}^{12}\text{ as a white solid (5.068 g, 72%). $^1$H NMR (400 MHz, CDCl}_3) \delta 7.74 (d, $J = 9.6$ Hz, 1 H), 7.56 (dd, $J = 7.8$, 1.0 Hz, 1 H), 7.46-7.37 (m, 1 H), 7.33-7.14 (m, 7 H),
\]
6.80 (d, J = 9.6 Hz, 1 H), 5.56 (s, 2 H).

The following compounds were synthesized according to Typical Procedure I.

1) 1-(4-Methoxybenzyl)quinolin-2(1H)-one (1b)

The reaction of quinolin-2(1H)-one (2.903 g, 20.0 mmol), 1-(bromomethyl)-4-methoxybenzene (3.7 mL, 25.4 mmol), K₂CO₃ (8.293 g, 60.0 mmol), and anhydrous DMF (20 mL) afforded 1b as a white solid (2.157 g, 41%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 9.2 Hz, 1 H), 7.53 (d, J = 7.6 Hz, 1 H), 7.46-7.38 (m, 1 H), 7.30 (d, J = 8.8 Hz, 1 H), 7.20-7.12 (m, 3 H), 6.85-6.80 (m, 2 H), 6.78 (d, J = 9.6 Hz, 1 H), 5.48 (s, 2 H), 3.73 (s, 3 H).

2) 1-(4-(Tert-butyl)benzyl)quinolin-2(1H)-one (1c)

The reaction of quinolin-2(1H)-one (2.904 g, 20.0 mmol), 1-(bromomethyl)-4-(tert-butyl)benzene (4.4 mL, 24.0 mmol), K₂CO₃ (8.293 g, 60.0 mmol), and anhydrous DMF (20 mL) afforded 1c as a white solid (3.177 g, 55%). Mp: 159.4-159.9 ºC (petroleum ether/ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 9.6 Hz, 1 H), 7.53 (dd, J = 8.0, 1.2 Hz, 1 H), 7.45-7.37 (m, 1 H), 7.33-7.27 (m, 3 H), 7.20-7.13 (m, 3 H), 6.79 (d, J = 9.2 Hz, 1 H), 5.51 (s, 2 H), 1.26 (s, 9 H); ¹³C NMR (101 MHz, CDCl₃) δ 162.4, 150.0, 139.5, 139.4, 133.1, 130.5, 128.7, 126.3, 125.6, 122.0, 121.6, 120.8, 115.0, 45.5, 34.3, 31.2; IR (neat) 1664, 1590, 1564, 1519, 1496, 1450, 1405 cm⁻¹; HRMS (ESI): calcd for C₂₀H₂₁NNaO⁺ [M+Na]⁺: 314.1515, found: 314.1507.

3) 1-(4-Methylbenzyl)quinolin-2(1H)-one (1d)
The reaction of quinolin-2(1H)-one (2.904 g, 20.0 mmol), 1-(bromomethyl)-4-methylbenzene (4.443 g, 24.0 mmol), K₂CO₃ (8.295 g, 60.0 mmol), and anhydrous DMF (20 mL) afforded 1d as a white solid (3.540 g, 71%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 9.6 Hz, 1 H), 7.53 (d, J = 7.6 Hz, 1 H), 7.45-7.36 (m, 1 H), 7.27 (d, J = 8.4 Hz, 1 H), 7.16 (t, J = 7.4 Hz, 1 H), 7.13-7.05 (m, 4 H), 6.79 (d, J = 10.0 Hz, 1 H), 5.51 (s, 2 H), 2.28 (s, 3 H).

4) 1-(4-Bromobenzyl)quinolin-2(1H)-one (1e)

The reaction of quinolin-2(1H)-one (1.452 g, 10.0 mmol), 1-(bromomethyl)-4-bromobenzene (3.000 g, 12.0 mmol), K₂CO₃ (4.147 g, 30.0 mmol), and anhydrous DMF (10 mL) afforded 1e as a white solid (2.129 g, 68%). Mp: 154.3-154.4 °C (petroleum ether/ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 9.2 Hz, 1 H), 7.57 (dd, J = 7.8, 1.4 Hz, 1 H), 7.47-7.38 (m, 3 H), 7.23-7.16 (m, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 6.79 (d, J = 9.6 Hz, 1 H), 5.50 (s, 2 H); ¹³C NMR (101 MHz, CDCl₃) δ 162.3, 139.7, 139.2, 135.4, 131.9, 130.7, 128.9, 128.4, 122.3, 121.6, 121.1, 120.9, 114.7, 45.3; IR (neat) 1651, 1589, 1564, 1489, 1451, 1401 cm⁻¹; HRMS (ESI): calcd for C₁₆H₁₂BrNNaO⁺ [M+Na⁺]: 335.9994, found: 335.9995.

5) 1-(4-Chlorobenzyl)quinolin-2(1H)-one (1f)

The reaction of quinolin-2(1H)-one (1.453 g, 10.0 mmol), 1-(bromomethyl)-4-chlorobenzene (3.330 g, 20.0 mmol), K₂CO₃ (4.472 g, 32.0 mmol), and anhydrous DMF (20 mL) afforded 1f as a white solid (2.540 g, 89%).
chlorobenzene (2.467 g, 12.0 mmol), K$_2$CO$_3$ (4.146 g, 30.0 mmol), and anhydrous DMF (10 mL) afforded 1f as a white solid (2.393 g, 89%). Mp: 148.8-149.1 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 9.6$ Hz, 1 H), 7.57 (dd, $J = 8.2$, 1.4 Hz, 1 H), 7.47-7.39 (m, 1 H), 7.29-7.23 (m, 2 H), 7.21 (d, $J = 7.2$ Hz, 2 H), 7.16 (d, $J = 8.8$ Hz, 2 H), 6.79 (d, $J = 9.6$ Hz, 1 H), 5.52 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.4, 139.7, 139.2, 134.9, 133.1, 130.7, 128.9, 128.0, 122.3, 121.6, 120.9, 114.7, 45.3; IR (neat) 1652, 1590, 1565, 1492, 1452, 1402 cm$^{-1}$; HRMS (ESI): calcd for C$_{16}$H$_{12}$ClNNaO$^+$ [M+Na]$^+$: 292.0500, found: 292.0505.

6) 1-(4-Fluorobenzyl)quinolin-2(1H)-one (1g)

The reaction of quinolin-2(1H)-one (2.903 g, 20.0 mmol), 1-(bromomethyl)-4-fluorobenzene (3.0 mL, 24.1 mmol), K$_2$CO$_3$ (8.295 g, 60.0 mmol), and anhydrous DMF (20 mL) afforded 1g as a white solid (3.081 g, 61%). Mp: 183.1-183.3 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 9.6$ Hz, 1 H), 7.57 (dd, $J = 7.6$, 1.2 Hz, 1 H), 7.44 (ddd, $J = 8.6$, 7.4, 1.4 Hz, 1 H), 7.24 (d, $J = 8.4$ Hz, 1 H), 7.23-7.16 (m, 3 H), 7.03-6.93 (m, 2 H), 6.80 (d, $J = 9.2$ Hz, 1 H), 5.52 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.4, 162.0 (C-F, $^1$J$_{C-F}$ = 246.3 Hz), 139.6, 139.3, 132.0 (C-F, $^4$J$_{C-F}$ = 3.5 Hz), 130.6, 128.9, 128.3 (C-F, $^3$J$_{C-F}$ = 8.2 Hz), 122.3, 121.6, 120.9, 115.7 (C-F, $^2$J$_{C-F}$ = 21.6 Hz), 114.8, 45.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -115.2 (ddd, $J = 13.5$, 8.5, 5.1 Hz); IR (neat) 1651, 1591, 1565, 1510, 1454, 1403 cm$^{-1}$; HRMS (ESI): calcd for C$_{16}$H$_{12}$FNNaO$^+$ [M+Na]$^+$: 276.0795, found: 276.0800.

7) 1-(4-Methoxycarbonylbenzyl)quinolin-2(1H)-one (1h)

The reaction of quinolin-2(1H)-one (4.355 g, 30.0 mmol), 1-(bromomethyl)-4-
methoxycarbonylbenzene (8.246 g, 36.0 mmol), K$_2$CO$_3$ (12.435 g, 90.0 mmol), and anhydrous DMF (30 mL) afforded 1h as a solid (6.072 g, 69%). Mp: 134.7-134.8 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.0$ Hz, 2 H), 7.76 (d, $J = 9.6$ Hz, 1 H), 7.58 (dd, $J = 7.8$, 1.0 Hz, 1 H), 7.45-7.37 (m, 1 H), 7.28 (d, $J = 7.6$ Hz, 2 H), 7.23-7.13 (m, 2 H), 6.81 (d, $J = 9.2$ Hz, 1 H), 5.61 (s, 2 H), 3.88 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.6, 162.3, 141.6, 139.7, 139.2, 130.7, 130.1, 129.2, 128.9, 126.5, 122.3, 121.5, 120.9, 114.7, 52.0, 45.7; IR (neat) 1720, 1653, 1613, 1590, 1565, 1452, 1435, 1403 cm$^{-1}$; HRMS (ESI): calcd for C$_{18}$H$_{16}$NO$_3$ $^+$ [M+H]$^+$: 294.1125, found: 294.1130.

8) 1-(4-Acetylbenzyl)quinolin-2(1H)-one (1i)

\[
\begin{array}{ccc}
\text{N} & \text{O} \\
\text{HO} & \text{Me} \\
\text{O} & \text{Me} \\
\end{array}
\xrightarrow{K_2CO_3 \text{ (3 equiv.)}}
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \text{Me} \\
\end{array}
\]

The reaction of quinolin-2(1H)-one (1.455 g, 10.0 mmol), 1-(bromomethyl)-4-acetylbenzene (2.560 g, 12.0 mmol), K$_2$CO$_3$ (4.146 g, 30.0 mmol), and anhydrous DMF (10 mL) afforded 1i as a solid (2.109 g, 76%). Mp: 157.1-157.3 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (d, $J = 8.4$ Hz, 2 H), 7.76 (d, $J = 9.6$ Hz, 1 H), 7.58 (dd, $J = 8.0$, 1.2 Hz, 1 H), 7.46-7.37 (m, 1 H), 7.30 (d, $J = 8.8$ Hz, 2 H), 7.23-7.14 (m, 2 H), 6.80 (d, $J = 9.2$ Hz, 1 H), 5.60 (s, 2 H), 2.54 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.4, 162.2, 141.7, 139.7, 139.1, 136.1, 130.6, 128.9, 128.7, 126.6, 122.3, 121.4, 120.8, 114.6, 45.6, 26.4; IR (neat) 1684, 1658, 1615, 1590, 1499, 1453, 1408 cm$^{-1}$; HRMS (ESI): calcd for C$_{18}$H$_{16}$NO$_2$ $^+$ [M+H]$^+$: 278.1176, found: 278.1177.

9) 1-(4-Formylbenzyl)quinolin-2(1H)-one (1j)

\[
\begin{array}{ccc}
\text{N} & \text{O} \\
\text{HO} & \text{CHO} \\
\end{array}
\xrightarrow{K_2CO_3 \text{ (3 equiv.)}}
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{CHC} \\
\end{array}
\]
The reaction of quinolin-2(1H)-one (725 mg, 5.0 mmol), 1-(bromomethyl)-4-formylbenzene (1.195 g, 6.0 mmol), K$_2$CO$_3$ (2.072 g, 15.0 mmol), and anhydrous DMF (5 mL) afforded 1j as a white solid (789 mg, 60%). Mp: 96.7-97.3 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.96 (s, 1 H), 7.82 (d, $J$ = 8.0 Hz, 2 H), 7.78 (d, $J$ = 9.6 Hz, 1 H), 7.60 (d, $J$ = 7.2 Hz, 1 H), 7.48-7.40 (m, 1 H), 7.37 (d, $J$ = 8.0 Hz, 2 H), 7.22 (t, $J$ = 7.4 Hz, 1 H), 7.16 (d, $J$ = 8.4 Hz, 1 H), 6.82 (d, $J$ = 9.6 Hz, 1 H), 5.64 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.6, 162.4, 143.4, 139.9, 139.2, 135.6, 130.8, 130.3, 129.1, 127.1, 122.5, 121.5, 121.0, 114.6, 45.8; IR (neat) 1697, 1651, 1608, 1590, 1496, 1452, 1403 cm$^{-1}$; HRMS (ESI): calcd for C$_{17}$H$_{13}$NNaO$_2$ $^+[M+Na]^+$: 286.0838, found: 286.0836.

10) 1-(4-Trifluoromethylbenzyl)quinolin-2(1H)-one (1k)

![Chemical Structure](attachment:image.png)

The reaction of quinolin-2(1H)-one (1.451 g, 10.0 mmol), 1-(bromomethyl)-4-trifluoromethylbenzene (2.870 g, 12.0 mmol), K$_2$CO$_3$ (4.246 g, 30.7 mmol), and anhydrous DMF (10 mL) afforded 1k as a white solid (2.074 g, 68%). Mp: 119.8-120.4 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J$ = 9.6 Hz, 1 H), 7.57 (dd, $J$ = 8.0, 1.2 Hz, 1 H), 7.54 (d, $J$ = 8.0 Hz, 2 H), 7.46-7.38 (m, 1 H), 7.33 (d, $J$ = 8.0 Hz, 2 H), 7.23-7.14 (m, 2 H), 6.80 (d, $J$ = 9.6 Hz, 1 H), 5.60 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.2, 140.4, 139.7, 139.1, 130.7, 129.5 (q, $J$ = 32.5 Hz), 128.9, 126.8, 125.6 (q, $J$ = 3.7 Hz), 123.9 (q, $J$ = 273.3 Hz), 122.3, 121.4, 120.8, 114.5, 45.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.5; IR (neat) 1652, 1590, 1564, 1496, 1459, 1419, 1402 cm$^{-1}$; HRMS (ESI): calcd for C$_{17}$H$_{13}$F$_3$NO$^+$ [M+H]$^+$: 304.0944, found: 304.0937.

11) 1-(4-Cyanobenzyl)quinolin-2(1H)-one (1l)
The reaction of quinolin-2(1H)-one (2.903 g, 20.0 mmol), 1-(bromomethyl)-4-cyanobenzene (4.705 g, 24.0 mmol), K$_2$CO$_3$ (8.294 g, 60.0 mmol), and anhydrous DMF (20 mL) afforded 11$^{13}$ as a solid (1.146 g, 22%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J$ = 9.6 Hz, 1 H), 7.63-7.56 (m, 3 H), 7.49-7.41 (m, 1 H), 7.32 (d, $J$ = 8.4 Hz, 2 H), 7.23 (t, $J$ = 7.4 Hz, 1 H), 7.12 (d, $J$ = 8.8 Hz, 1 H), 6.80 (d, $J$ = 9.2 Hz, 1 H), 5.60 (s, 2 H).

12) 1-Allylquinolin-2(1H)-one (1n)

The reaction of quinolin-2(1H)-one (1.453 g, 10.0 mmol), 2-bromo-1-propene (2.6 mL, 30.0 mmol), K$_2$CO$_3$ (4.143 g, 30.0 mmol), and anhydrous DMF (10 mL) afforded 1n$^{14}$ as an oil (1.204 g, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J$ = 9.6 Hz, 1 H), 7.59-7.48 (m, 2 H), 7.32 (d, $J$ = 8.4 Hz, 1 H), 7.25-7.17 (m, 1 H), 6.73 (d, $J$ = 9.2 Hz, 1 H), 6.02-5.89 (m, 1 H), 5.21 (dm, $J$ = 11.2 Hz, 1 H), 5.09 (dm, $J$ = 18.4 Hz, 1 H), 4.95 (dt, $J$ = 4.7, 1.7 Hz, 2 H).

13) 1-Benzyl-6-bromoquinolin-2(1H)-one (1s)

The reaction of 6-bromoquinolin-2(1H)-one (4.490 g, 20.0 mmol), 1-(bromomethyl) benzene (2.9 mL, 24.4 mmol), K$_2$CO$_3$ (8.293 g, 60.0 mmol), and anhydrous DMF (20 mL) afforded 1s$^{12}$ as a solid (3.737 g, 59%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J$ = 2.4 Hz, 1 H), 7.61 (d, $J$ = 9.6 Hz, 1 H), 7.44 (dd, $J$ = 9.0, 2.2 Hz, 1 H), 7.32-7.26 (m, 2 H), 7.25-7.15 (m, 3 H), 7.10 (d, $J$ = 9.2 Hz, 1 H), 6.80 (d, $J$ = 9.6 Hz, 1 H), 5.51 (s, 2
14) 1-Benzyl-6-chloroquinolin-2(1H)-one (1t)

The reaction of 6-chloroquinolin-2(1H)-one (899 mg, 5.0 mmol), 1-(bromomethyl)
benzene (0.7 mL, 5.9 mmol), K$_2$CO$_3$ (2.074 g, 15.0 mmol), and anhydrous DMF (5 mL)
afforded 1t as a white solid (1.025 g, 76%). Mp: 123.4-123.7 °C (petroleum ether/ethyl
acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 9.6$ Hz, 1 H), 7.51 (d, $J = 2.4$ Hz, 1
H), 7.33 (dd, $J = 8.8, 2.4$ Hz, 1 H), 7.31-7.14 (m, 6 H), 6.82 (d, $J = 9.2$ Hz, 1 H), 5.52
(s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.0, 138.3, 137.9, 135.8, 130.5, 128.8, 127.8,
127.6, 127.4, 126.4, 122.9, 121.9, 116.4, 46.0; IR (neat) 1659, 1587, 1558, 1488, 1454,
1428 cm$^{-1}$; HRMS (ESI): calcd for C$_{16}$H$_{12}$ClNNaO$^+$ [M+Na]$^+$: 292.0500, found:
292.0496.

**Synthesis of 1-benzyl-6-methylquinolin-2(1H)-one (1q)**

6-Methyl-2-chloroquinoline (1.780 g, 10.0 mmol) was refluxed in aq. HCl (6.0 M, 35
mL) for 24 h. The reaction mixture was cooled to room temperature, and it was
extracted with ethyl acetate and dried with MgSO$_4$. After concentration under reduced
pressure, the crude residue S1$^{15}$ was directly subjected to subsequent transformation
without further purification. The following step was synthesized according to **Typical
Procedure I**. The reaction of crude S1, 1-bromomethylbenzene (1.4 mL, 11.8 mmol),
K$_2$CO$_3$ (4.150 g, 30.0 mmol), and anhydrous DMF (10 mL) afforded 1q$^{12}$ as a white
solid (946 mg, 38%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 9.6$ Hz, 1 H), 7.34 (s,
1 H), 7.32-7.26 (m, 2 H), 7.21 (t, $J = 7.0$ Hz, 4 H), 7.14 (d, $J = 8.4$ Hz, 1 H), 6.78 (d, $J$
= 9.2 Hz, 1 H), 5.54 (s, 2 H), 2.36 (s, 3 H).

**Synthesis of 1-benzyl-6-phenylquinolin-2(1H)-one (1r)**
1s (1.565 g, 5.0 mmol), phenylboronic acid (1.123 g, 10.0 mmol), Pd(PPh₃)₄ (286 mg, 0.25 mmol), aq. Na₂CO₃ (2.0 M, 13 mL, 26 mmol), and THF (20 mL) were added subsequently into a 100 mL of sealed tube. The mixture was stirred at 100 °C with an oil bath for 24 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 4:1). After completion of the reaction, the mixture was cooled, diluted with ethyl acetate. The mixture was washed with H₂O (30 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over MgSO₄ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) afforded 1r as a white solid (1.403 g, 90%). Mp: 158.0-158.3 °C (petroleum ether/ethyl acetate). \(^\text{1}H\) NMR (400 MHz, CDCl₃) \(\delta\) 7.79 (d, \(J = 9.2\) Hz, 1 H), 7.75 (d, \(J = 2.0\) Hz, 1 H), 7.65 (dd, \(J = 8.8, 2.0\) Hz, 1 H), 7.60-7.53 (m, 2 H), 7.48-7.40 (m, 2 H), 7.39-7.27 (m, 4 H), 7.26-7.20 (m, 3 H), 6.84 (d, \(J = 9.6\) Hz, 1 H), 5.59 (s, 2 H); \(^{13}C\) NMR (101 MHz, CDCl₃) \(\delta\) 162.4, 139.6, 138.7, 136.3, 135.3, 129.5, 128.9, 128.8, 127.4, 127.3, 126.8, 126.6, 122.1, 121.2, 115.5, 46.0; IR (neat) 1656, 1589, 1566, 1486, 1453, 1426 cm\(^{-1}\); HRMS (ESI): calcd for C₂₂H₁₈NO\(^+\) [M+H]\(^+\): 312.1383, found: 312.1381.

Synthesis of 1-methyl-5-methoxycarbonylquinolin-2(1H)-one (1u)\(^{11,15}\)

5-Carboxyl-2-chloroquinoline (2.075 g, 10.0 mmol) was refluxed in aq. HCl (6.0 M, 35 mL) for 36 h. The reaction mixture was cooled to room temperature while forming a colorless solid which was filtered, washed with cool water and dried in vacuum to give crude S2\(^{16}\) as a white solid (1.823 g, 96%). S2 was used in the following step without further purification. To a solution of S2 (1.823 g, 9.64 mmol) in anhydrous DMF (10
mL) was slowly added NaH (60% wt. in mineral oil, 880 mg, 22.0 mmol) at 0 °C, the reaction was warmed to room temperature and stirred for 1 h. Then the suspension was cooled to 0 °C, followed by dropwise addition of MeI (1.4 mL, 22.5 mmol). The reaction was warmed to room temperature gradually and stirred for 12 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 1:1). After completion of the reaction, the mixture was washed with H2O (30 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with brine, dried over MgSO4 and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:1) afforded 1u as a white solid (1.793 g, 86%). Mp: 121.5-121.9 °C (petroleum ether/ethyl acetate). 1H NMR (400 MHz, CDCl3) δ 8.76 (d, J = 10.4 Hz, 1 H), 7.83 (dd, J = 7.2, 1.6 Hz, 1 H), 7.64-7.53 (m, 2 H), 6.80 (d, J = 10.0 Hz, 1 H), 3.98 (s, 3 H), 3.76 (s, 3 H); 13C NMR (101 MHz, CDCl3) δ 167.0, 161.5, 140.8, 136.0, 129.5, 128.6, 124.8, 123.2, 119.7, 118.2, 52.5, 29.8; IR (neat) 1716, 1648, 1608, 1583, 1482, 1456, 1428, 1418 cm⁻¹; HRMS (ESI): calcd for C12H12NO3⁺ [M+H]⁺: 218.0812, found: 218.0806.

Typical Procedure II for Condition A

Synthesis of 4-benzyl-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4a)

To an oven-dried 10 mL of sealed tube were added 1a (47 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), and anhydrous DCM (2 mL). The reaction was irradiated by purple LED (λ = 400-410 nm) under an argon atmosphere at room temperature. The reaction was completed after 24 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). TBAF (1.0 M in THF, 1 mL, 1.0 mmol) was added to the solution subsequently. The reaction mixture was stirred at 60 °C for 12 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). After completion of the
reaction, the mixture was washed with H₂O (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded 4a as a white solid (63 mg, 95%). Mp: 175.3-175.6 °C (petroleum ether/ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 7.6 Hz, 1 H), 7.47-7.38 (m, 1 H), 7.37-7.26 (m, 3 H), 7.25-7.17 (m, 4 H), 5.57 (AB, J_{AB} = 15.6 Hz, J_{BA} = 36.8 Hz, 2 H), 4.27-4.15 (m, 1 H), 3.47 (dd, J = 14.2, 4.6 Hz, 1 H), 3.35 (dd, J = 14.0, 1.6 Hz, 1 H); ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 148.4 (q, J = 3.3 Hz), 141.6, 136.3, 133.7, 130.6, 128.8, 127.3, 126.4, 125.5 (q, J = 278.0 Hz), 123.7 (d, J = 1.5 Hz), 122.6, 117.9, 116.5, 46.1, 43.7 (q, J = 32.9 Hz), 29.8 (q, J = 3.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -70.0 (d, J = 9.0 Hz); IR (neat) 1677, 1640, 1597, 1561, 1497, 1452 cm⁻¹; HRMS (ESI): calcd for C₁₉H₁₅F₃NO⁺ [M+H]⁺: 330.1100, found: 330.1093. Supplementary crystallographic data for 4a have been deposited at the Cambridge Crystallographic Data Center. CCDC: 2076890.

Ortep drawing with 50% ellipsoids for 4a
**Crystal data**: C_{19}H_{14}F_{3}NO, M = 329.31, T = 173(2) K, Space group: P2\(_1\)/c, a = 9.0542(7) Å, b = 10.0870(8) Å, c = 16.9352(14) Å, \(\alpha = 90^\circ\), \(\beta = 93.412(3)^\circ\), \(\gamma = 90^\circ\), V = 1543.9(2) Å\(^3\), Z = 4, R indices: R1 = 0.0511, wR2 = 0.1276.

The following compounds were synthesized according to Typical Procedure II.

1) **4-(4-Methoxybenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4b)**

![Chemical structure of 4b]

The reaction of 1b (53 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4b as a solid (61 mg, 85%). Mp: 157.4-157.8 °C (petroleum ether/ethyl acetate).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 7.6\) Hz, 1 H), 7.45 (t, \(J = 7.8\) Hz, 1 H), 7.38 (d, \(J = 8.4\) Hz, 1 H), 7.22 (t, \(J = 7.4\) Hz, 1 H), 7.16 (d, \(J = 8.4\) Hz, 2 H), 6.83 (d, \(J = 8.4\) Hz, 2 H), 5.51 (AB, \(J_{AB} = 15.0\) Hz, \(J_{AB} = 35.8\) Hz, 2 H), 4.27-4.15 (m, 1 H), 3.76 (s, 3 H), 3.47 (dd, \(J = 14.2, 4.6\) Hz, 1 H), 3.35 (d, \(J = 14.0\) Hz, 1 H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.8, 157.8, 148.3 (q, \(J = 2.7\) Hz), 141.7, 133.8, 130.6, 128.4, 127.9, 125.6 (q, \(J = 278.3\) Hz), 123.7, 122.6, 118.0, 116.5, 114.2, 55.3, 45.6, 43.7 (q, \(J = 32.9\) Hz), 29.8 (q, \(J = 2.3\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -70.0 (d, \(J = 8.6\) Hz); IR (neat) 1676, 1640, 1613, 1597, 1561, 1513, 1452 cm\(^{-1}\); HRMS (ESI): calcd for C\(_{20}\)H\(_{16}\)F\(_3\)NNaO\(_2\)\([M+Na]^+\): 382.1025, found: 382.1021.

2) **4-(4-(Tert-butyl)benzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4c)**

![Chemical structure of 4c]
The reaction of 1c (58 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4c as a white solid (66 mg, 86%). Mp: 182.5-182.7 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J$ = 7.6 Hz, 1 H), 7.45 (t, $J$ = 7.8 Hz, 1 H), 7.38 (d, $J$ = 8.8 Hz, 1 H), 7.31 (d, $J$ = 8.0 Hz, 2 H), 7.22 (t, $J$ = 7.4 Hz, 1 H), 7.14 (d, $J$ = 8.0 Hz, 2 H), 5.55 (brs, 2 H), 4.27-4.16 (m, 1 H), 3.47 (dd, $J$ = 14.2, 4.6 Hz, 1 H), 3.35 (d, $J$ = 14.0 Hz, 1 H), 1.27 (s, 9 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.7, 150.2, 148.3 (q, $J$ = 2.7 Hz), 141.7, 133.8, 133.2, 130.6, 126.2, 125.7, 125.5 (q, $J$ = 278.0 Hz), 123.6, 122.5, 117.9, 116.6, 145.8, 43.7 (q, $J$ = 32.8 Hz), 34.4, 31.3, 29.8 (q, $J$ = 3.2 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.0 (d, $J$ = 9.0 Hz); IR (neat) 1676, 1641, 1597, 1561, 1453 cm$^{-1}$; HRMS (ESI): calcd for C$_{23}$H$_{22}$F$_3$NNaO$^+$ [M+Na]$^+$: 408.1546, found: 408.1552.

3) 4-(4-Methylbenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4d)

The reaction of 1d (50 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4d as a white solid (61 mg, 88%). Mp: 149.2-149.5 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 7.6 Hz, 1 H), 7.47-7.39 (m, 1 H), 7.35 (d, $J$ = 8.4 Hz, 1 H), 7.21 (t, $J$ = 7.4 Hz, 1 H), 7.14 -7.06 (m, 4 H), 5.53 (AB, $J_{AB}$
= 15.0 Hz, $J_{BA} = 39.4$ Hz, 2 H), 4.27-4.15 (m, 1 H), 3.47 (dd, $J = 14.2, 4.6$ Hz, 1 H), 3.35 (dd, $J = 14.2, 1.8$ Hz, 1 H), 2.29 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.7, 148.3 (q, $J = 3.0$ Hz), 141.7, 136.9, 133.8, 133.3, 130.6, 129.5, 126.5, 125.5 (q, $J = 278.1$ Hz), 123.6, 122.5, 117.9, 116.5, 45.9, 43.7 (q, $J = 32.8$ Hz), 29.8 (q, $J = 2.6$ Hz), 21.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.0 (d, $J = 8.6$ Hz); IR (neat) 1675, 1641, 1597, 1561, 1515, 1500, 1452 cm$^{-1}$; HRMS (ESI): calcd for C$_{20}$H$_{16}$F$_{3}$NNaO$^+$ [M +Na]$^+$: 366.1076, found: 366.1073.

4) 4-(4-Bromobenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4e)

![Reaction scheme for 4e](image)

The reaction of 1e (63 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4e as a white solid (71 mg, 87%). Mp: 161.0-161.3 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 8.0$ Hz, 1 H), 7.49-7.39 (m, 3 H), 7.30-7.20 (m, 2 H), 7.08 (d, $J = 8.4$ Hz, 2 H), 5.51 (AB, $J_{AB} = 15.2$ Hz, $J_{BA} = 41.2$ Hz, 2 H), 4.28-4.16 (m, 1 H), 3.48 (dd, $J = 14.2, 4.6$ Hz, 1 H), 3.35 (dd, $J = 14.0, 1.6$ Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.6, 148.6 (q, $J = 2.9$ Hz), 141.5, 135.4, 133.7, 131.9, 130.7, 128.3, 125.5 (q, $J = 278.3$ Hz), 123.9, 122.8, 121.2, 118.0, 116.2, 45.6, 43.8 (q, $J = 32.9$ Hz), 29.8 (q, $J = 2.6$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.0 (d, $J = 8.6$ Hz); IR (neat) 1677, 1640, 1597, 1561, 1515, 1489, 1453 cm$^{-1}$; HRMS (ESI): calcd for C$_{19}$H$_{14}$BrF$_3$NO$^+$ [M+H]$^+$: 408.0205, found: 408.0210.

5) 4-(4-Chlorobenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4f)
The reaction of 1f (54 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4f as a white solid (69 mg, 95%). Mp: 186.1-186.2 °C (petroleum ether/ethyl acetate). 1H NMR (400 MHz, CDCl3) δ 7.61 (d, J = 7.6 Hz, 1 H), 7.49-7.41 (m, 1 H), 7.30-7.20 (m, 4 H), 7.14 (d, J = 8.4 Hz, 2 H), 5.53 (AB, JAB = 15.4 Hz, JBA = 40.6 Hz, 2 H), 4.28-4.16 (m, 1 H), 3.48 (dd, J = 14.0, 4.8 Hz, 1 H), 3.35 (dd, J = 14.0, 1.6 Hz, 1 H); 13C NMR (101 MHz, CDCl3) δ 157.7, 148.6 (q, J = 2.9 Hz), 141.5, 134.9, 133.7, 133.2, 130.7, 129.0, 127.9, 125.5 (q, J = 278.2 Hz), 123.9, 122.8, 118.0, 116.2, 45.5, 43.8 (q, J = 32.9 Hz), 29.8 (q, J = 2.8 Hz); 19F NMR (376 MHz, CDCl3) δ -70.0 (d, J = 8.6 Hz); IR (neat) 1675, 1640, 1597, 1561, 1492, 1452 cm⁻¹; HRMS (ESI): calcd for C19H14ClF3NO+ [M+H]+: 364.0711, found: 364.0710.

6) 4-(4-Fluorobenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4g)

The reaction of 1g (51 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4g as a white solid (66 mg, 96%). Mp: 181.0-181.2 °C (petroleum ether/ethyl acetate). 1H NMR (400 MHz, CDCl3) δ 7.61 (d, J = 7.6 Hz, 1 H), 7.45 (t, J = 7.4 Hz, 1 H), 7.31 (d, J = 8.8 Hz, 1 H), 7.25-7.15 (m, 3 H), 7.02-6.94 (m, 2 H), 5.53 (AB, JAB = 15.8 Hz, JBA = 34.2 Hz, 2 H), 4.27-4.16 (m, 1 H), 3.47 (dd, J = 14.0, 4.8 Hz, 1 H), 3.35
(dd, J = 14.0, 1.6 Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl₃) δ 162.0 (C-F, $^1J_{C-F} = 246.8$ Hz), 157.7, 148.5 (q, J = 2.8 Hz), 141.5, 133.7, 132.0 (C-F, $^4J_{C-F} = 2.7$ Hz), 130.6, 128.2 (C-F, $^3J_{C-F} = 8.1$ Hz), 125.5 (q, J = 278.2 Hz), 123.8, 122.7, 117.9, 116.2, 115.7 (C-F, $^2J_{C-F} = 21.7$ Hz), 45.4, 43.7 (q, J = 32.9 Hz), 29.8 (q, J = 2.9 Hz); $^{19}$F NMR (376 MHz, CDCl₃) δ -70.0 (d, J = 7.9 Hz), -115.1 (ddd, J = 13.3, 8.6, 5.2 Hz); IR (neat) 1674, 1641, 1597, 1562, 1510, 1452 cm⁻¹; HRMS (ESI): calcd for C₁₉H₁₃F₄NNaO⁺ [M+Na]⁺: 370.0825, found: 370.0823.

7) 4-(4-Methoxycarbonylbenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4h)

The reaction of 1h (59 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4h as a white solid (68 mg, 88%). Mp: 171.3-171.5 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.0 Hz, 2 H), 7.61 (d, J = 7.6 Hz, 1 H), 7.47-7.38 (m, 1 H), 7.29-7.20 (m, 4 H), 5.62 (AB, $J_{AB} = 13.2$ Hz, $J_{BA} = 48.4$ Hz, 2 H), 4.30-4.18 (m, 1 H), 3.88 (s, 3 H), 3.49 (dd, J = 14.2, 4.6 Hz, 1 H), 3.36 (dd, J = 14.2, 1.4 Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl₃) δ 166.6, 157.6, 148.7 (q, J = 2.6 Hz), 141.6, 141.4, 133.7, 130.7, 130.1, 129.3, 126.4, 125.5 (q, J = 278.4 Hz), 123.8, 122.8, 117.9, 116.2, 52.0, 46.0, 43.7 (q, J = 32.9 Hz), 29.8 (q, J = 2.9 Hz); $^{19}$F NMR (376 MHz, CDCl₃) δ -70.0 (d, J = 8.6 Hz); IR (neat) 1722, 1679, 1641, 1613, 1597, 1562, 1500, 1453, 1437, 1416 cm⁻¹; HRMS (ESI): calcd for C₂₁H₁₇F₃NO₃⁺ [M+H]⁺: 388.1155, found: 388.1148.

8) 4-(4-Acetylbenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4i)
The reaction of 1i (55 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4i as a white solid (67 mg, 91%). Mp: 136.6-136.7 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, $J = 8.4$ Hz, 2 H), 7.62 (d, $J = 7.6$ Hz, 1 H), 7.48-7.39 (m, 1 H), 7.29 (d, $J = 8.0$ Hz, 2 H), 7.26-7.20 (m, 2 H), 5.63 (AB, $J_{AB} = 15.4$ Hz, $J_{BA} = 38.2$ Hz, 2 H), 4.30-4.18 (m, 1 H), 3.49 (dd, $J = 14.0$, 4.8 Hz, 1 H), 3.36 (dd, $J = 14.0$, 1.6 Hz, 1 H), 2.56 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.4, 157.6, 148.7 (q, $J = 2.7$ Hz), 141.8, 141.5, 136.3, 133.7, 130.8, 128.9, 126.6, 125.5 (q, $J = 278.2$ Hz), 123.9, 122.8, 118.0, 116.2, 45.9, 43.8 (q, $J = 32.9$ Hz), 29.8 (q, $J = 2.5$ Hz), 26.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.0 (d, $J = 8.6$ Hz); IR (neat) 1678, 1640, 1609, 1597, 1561, 1453 cm$^{-1}$; HRMS (ESI): calcd for C$_{21}$H$_{17}$F$_3$NO$_2$ $^{+}$ [M+H]$^+$: 372.1206, found: 372.1207.

9) 4-(4-Formylbenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4j)

The reaction of 1j (53 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4j as a solid (52 mg, 73%). Mp: 168.1-168.6 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.96 (s, 1 H), 7.83 (d, $J = 8.4$ Hz, 2 H), 7.63 (d, $J = 7.6$ Hz, 1 H), 7.49-7.40 (m, 1 H), 7.36 (d, $J = 8.0$ Hz, 2 H), 7.24 (d, $J = 4.0$ Hz, 1 H), 7.22
(d, J = 5.6 Hz, 1 H), 5.65 (AB, \( J_{AB} = 16.0 \) Hz, \( J_{BA} = 39.6 \) Hz, 2 H), 4.31-4.19 (m, 1 H), 3.50 (dd, \( J = 14.0, 4.8 \) Hz, 1 H), 3.36 (dd, \( J = 14.2, 1.4 \) Hz, 1 H); \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 191.5, 157.6, 148.8 (q, \( J = 3.0 \) Hz), 143.4, 141.4, 135.6, 133.7, 130.8, 130.3, 127.0, 125.5 (q, \( J = 278.3 \) Hz), 123.9, 122.9, 117.9, 116.1, 46.0, 43.8 (q, \( J = 32.9 \) Hz), 29.8 (q, \( J = 2.8 \) Hz); \( ^{19} \)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -69.9 (d, \( J = 8.6 \) Hz); IR (neat) 1704, 1674, 1641, 1608, 1597, 1562, 1501, 1453 cm\(^{-1}\); HRMS (ESI): calcd for C\(_{20}\)H\(_{15}\)F\(_3\)NO\(_2\)\([M+H]^+\): 358.1049, found: 358.1044.

10) 4-(4-Trifluoromethylbenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4k)

The reaction of 1k (61 mg, 0.2 mmol), 2a (42 \( \mu \)L, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4k as a white solid (66 mg, 84%). Mp: 188.2-188.4 \( ^\circ \)C (petroleum ether/ethyl acetate). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.63 (d, \( J = 7.6 \) Hz, 1 H), 7.57 (d, \( J = 8.4 \) Hz, 2 H), 7.50-7.42 (m, 1 H), 7.31 (d, \( J = 8.0 \) Hz, 2 H), 7.29-7.21 (m, 2 H), 5.63 (AB, \( J_{AB} = 15.2 \) Hz, \( J_{BA} = 37.6 \) Hz, 2 H), 4.30-4.18 (m, 1 H), 3.49 (dd, \( J = 14.0, 4.8 \) Hz, 1 H), 3.36 (dd, \( J = 14.2, 1.4 \) Hz, 1 H); \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.6, 148.8 (q, \( J = 2.9 \) Hz), 141.4, 140.5, 133.7, 130.8, 129.7 (q, \( J = 32.3 \) Hz), 126.8, 125.8 (q, \( J = 3.2 \) Hz), 125.5 (q, \( J = 278.2 \) Hz) 123.97 (q, \( J = 273.1 \) Hz), 123.96, 122.9, 118.0, 116.1, 45.8, 43.8 (q, \( J = 32.9 \) Hz), 29.8 (q, \( J = 2.8 \) Hz); \( ^{19} \)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -62.6, -70.0 (d, \( J = 8.6 \) Hz); IR (neat) 1673, 1639, 1620, 1596, 1561, 1452, 1430 cm\(^{-1}\); HRMS (ESI): calcd for C\(_{20}\)H\(_{14}\)F\(_6\)NO\(_2\)\([M+H]^+\): 398.0974, found: 398.0985.

11) 4-(4-Cyanobenzyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4l)
The reaction of \(1\) (52 mg, 0.2 mmol), \(2\) (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded \(4\) as a white solid (64 mg, 90%). Mp: 229.3-229.6 °C (petroleum ether/ethyl acetate). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.64 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 7.60 (d, J = 8.0 \text{ Hz}, 2 \text{ H}), 7.50-7.42 (m, 1 \text{ H}), 7.31 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.18 (d, J = 8.4 \text{ Hz}, 1 \text{ H}), 5.62 (AB, \(J_{AB} = 16.6 \text{ Hz}, J_{BA} = 33.8 \text{ Hz}, 2 \text{ H}), 4.31-4.18 (m, 1 \text{ H}), 3.49 (dd, J = 14.0, 4.8 \text{ Hz}, 1 \text{ H}), 3.36 (dd, J = 14.2, 1.4 \text{ Hz}, 1 \text{ H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 157.5, 148.9 (q, J = 2.7 \text{ Hz}), 141.9, 141.3, 133.7, 132.7, 130.9, 127.2, 125.4 (q, J = 278.2 \text{ Hz}), 124.1, 123.0, 118.5, 118.0, 115.9, 111.4, 45.8, 43.8 (q, J = 32.9 \text{ Hz}), 29.8 (q, J = 2.6 \text{ Hz}); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -69.9 (d, J = 8.6 \text{ Hz}); IR (neat) 2229, 1672, 1639, 1595, 1557, 1509, 1451, 1435, 1415 \text{ cm}^{-1}; \) HRMS (ESI): calcd for C\(_{20}\)H\(_{14}\)F\(_3\)N\(_2\)O\(_3\)\([\text{M+H}]^+\): 355.1053, found: 355.1048.

12) 4-Methyl-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(IH)-one (4m)

The reaction of \(1\) (32 mg, 0.2 mmol), \(2\) (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded \(4\) as a white solid (39 mg, 76%). Mp: 111.2-111.8 °C (petroleum ether/ethyl acetate). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.63-7.56 (m, 2 \text{ H}), 7.45 (d, J = 9.2 \text{ Hz}, 1 \text{ H}), 7.29 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 4.24-4.12 (m, 1 \text{ H}), 3.75 (s, 3 \text{ H}), 3.42 (dd, J = 14.0, 4.8 \text{ Hz}, 1 \text{ H}), 3.29 (d, J = 14.0 \text{ Hz}, 1 \text{ H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 157.6, 147.7 (q, J = 3.7 \text{ Hz}), 142.1, 133.9, 130.6, 125.5 (q, J = 278.0 \text{ Hz}), 123.6 (q, J = 1.5 \text{ Hz}), 122.5, 117.7,
115.6, 43.6 (q, J = 33.0 Hz), 29.70 (q, J = 3.3 Hz), 29.68; 19F NMR (376 MHz, CDCl3) δ -70.1 (d, J = 7.9 Hz); IR (neat) 1674, 1639, 1596, 1562, 1453 cm⁻¹; HRMS (ESI): calcd for C13H11F3NO⁺ [M+H]⁺: 254.0787, found: 254.0786.

13) 4-Allyl-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4n)

The reaction of 1n (37 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4n as a solid (31 mg, 55%). Mp: 111.1-111.4 °C (petroleum ether/ethyl acetate). 

1H NMR (400 MHz, CDCl3) δ 7.60 (d, J = 7.6 Hz, 1 H), 7.58-7.51 (m, 1 H), 7.40 (d, J = 8.8 Hz, 1 H), 7.30-7.22 (m, 1 H), 6.03-5.89 (m, 1 H), 5.23 (dm, J = 11.2 Hz, 1 H), 5.10 (dm, J = 18.0 Hz, 1 H), 5.05-4.90 (m, 2 H), 4.25-4.13 (m, 1 H), 3.43 (dd, J = 14.4, 4.8 Hz, 1 H), 3.31 (dd, J = 14.0, 2.0 Hz, 1 H); 13C NMR (101 MHz, CDCl3) δ 157.2, 148.1 (q, J = 2.9 Hz), 141.5, 133.8, 131.9, 130.5, 125.5 (q, J = 278.2 Hz), 123.7, 122.5, 117.8, 117.1, 116.3, 44.7, 43.6 (q, J = 32.8 Hz), 29.7 (q, J = 2.8 Hz); 19F NMR (376 MHz, CDCl3) δ -70.1 (d, J = 8.6 Hz); IR (neat) 1676, 1639, 1597, 1561, 1452 cm⁻¹; HRMS (ESI): calcd for C15H13F3NO⁺ [M+H]⁺: 280.0944, found: 280.0950.

14) 4-Phenyl-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4o)

The reaction of 1o (44 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4o as a white solid (54 mg, 86%). Mp: 199.8-200.2 °C (petroleum ether/ethyl
acetate). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65-7.57 (m, 3 H), 7.56-7.49 (m, 1 H), 7.37-7.27 (m, 2 H), 7.26-7.19 (m, 2 H), 6.68 (d, $J = 8.8$ Hz, 1 H), 4.30-4.18 (m, 1 H), 3.47 (dd, $J = 14.0$, 4.8 Hz, 1 H), 3.34 (dd, $J = 14.2$, 1.4 Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.5, 148.8 (q, $J = 3.3$ Hz), 143.5, 137.7, 134.3, 130.2, 130.1 (d, $J = 5.6$ Hz), 129.0, 128.9 (d, $J = 1.6$ Hz), 125.6 (q, $J = 278.0$ Hz), 123.2, 122.7, 117.4, 117.3, 43.6 (q, $J = 33.0$ Hz), 29.8 (q, $J = 3.1$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -69.9 (d, $J = 8.6$ Hz); IR (neat) 1671, 1592, 1558, 1488, 1448 cm$^{-1}$; HRMS (ESI): calcd for C$_{18}$H$_{13}$F$_3$NO$^+$ [M+H]$^+$: 316.0944, found: 316.0940.

15) 4-Methyl-6-methoxy-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4p)

The reaction of 1p (38 mg, 0.2 mmol), 2a (104 μL, 1.0 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4p as a white solid (38 mg, 67%). Mp: 151.8-152.2 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, $J = 8.4$ Hz, 1 H), 6.90-6.83 (m, 2 H), 4.19-4.07 (m, 1 H), 3.92 (s, 3 H), 3.69 (s, 3 H), 3.38 (dd, $J = 13.6$, 4.8 Hz, 1 H), 3.25 (dd, $J = 13.6$, 1.6 Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.7, 157.9, 147.5 (q, $J = 3.1$ Hz), 143.9, 130.1, 125.6 (q, $J = 278.2$ Hz), 124.9, 111.8, 110.0, 100.1, 55.6, 43.5 (q, $J = 32.7$ Hz), 29.7, 29.5 (d, $J = 2.8$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -70.2 (d, $J = 9.8$ Hz); IR (neat) 1672, 1605, 1553, 1464, 1420 cm$^{-1}$; HRMS (ESI): calcd for C$_{14}$H$_{13}$F$_3$NO$^+$ [M+H]$^+$: 284.0893, found: 284.0889.

16) 4-Benzyl-7-methly-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4q)
The reaction of 1q (50 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4q as a white solid (32 mg, 46%). Mp: 149.1-149.6 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (s, 1 H), 7.33-7.27 (m, 2 H), 7.25-7.15 (m, 5 H), 5.56 (AB, $J_{AB} = 15.8$ Hz, $J_{BA} = 38.2$ Hz, 2 H), 4.25-4.13 (m, 1 H), 3.46 (dd, $J = 14.0$, 4.8 Hz, 1 H), 3.34 (dd, $J = 14.4$, 1.6 Hz, 1 H), 2.37 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.7, 148.1 (q, $J = 2.6$ Hz), 139.7, 136.5, 133.7, 132.4, 131.9, 128.8, 127.2, 126.4, 125.6 (q, $J = 278.1$ Hz), 123.4, 117.9, 116.4, 46.1, 43.6 (q, $J = 32.9$ Hz), 29.8 (q, $J = 2.6$ Hz), 20.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -69.9 (d, $J = 8.6$ Hz); IR (neat) 1674, 1641, 1607, 1558, 1497, 1454 cm$^{-1}$; HRMS (ESI): calcd for C$_{20}$H$_{16}$F$_3$NNaO$^+$ [M+Na]$^+$: 366.1076, found: 366.1069.

17) 4-Benzyl-7-phenyl-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4r)

The reaction of 1r (62 mg, 0.2 mmol), 2a (104 μL, 1.0 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4r as a solid (66 mg, 81%). Mp: 155.6-155.9 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 (s, 1 H), 7.66 (dd, $J = 9.0$, 2.2 Hz, 1 H), 7.55 (d, $J = 7.6$ Hz, 2 H), 7.44 (t, $J = 7.4$ Hz, 2 H), 7.39 (d, $J = 8.8$ Hz, 1 H), 7.37-7.27 (m, 3 H), 7.26-7.20 (m, 3 H), 5.59 (AB, $J_{AB} = 15.4$ Hz, $J_{BA} = 35.0$ Hz, 2 H), 4.31-4.19 (m, 1 H), 3.49 (dd, $J = 14.0$, 4.8 Hz, 1 H), 3.37 (d, $J = 14.4$ Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$)
δ 157.6, 148.4 (q, J = 3.0 Hz), 140.9, 139.3, 136.3, 135.6, 134.2, 129.6, 129.0, 128.8, 127.6, 127.3, 126.9, 126.5, 125.6 (q, J = 278.2 Hz), 121.5, 118.2, 116.9, 46.2, 43.7 (q, J = 32.8 Hz), 29.9 (q, J = 2.6 Hz); 19F NMR (376 MHz, CDCl3) δ -69.8 (dd, J = 8.3, 3.0 Hz); IR (neat) 1675, 1641, 1604, 1555, 1496, 1454, 1427 cm⁻¹; HRMS (ESI): calcd for C25H19F3NO⁺ [M+H⁺]: 406.1413, found: 406.1412.

18) 4-Benzyl-7-bromo-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(IH)-one (4s)

The reaction of 1s (63 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4s as a white solid (73 mg, 89%). Mp: 154.8-155.0 °C (petroleum ether/ethyl acetate). 1H NMR (400 MHz, CDCl3) δ 7.69 (s, 1 H), 7.49 (dd, J = 9.0, 1.4 Hz, 1 H), 7.34-7.27 (m, 2 H), 7.26-7.14 (m, 4 H), 5.54 (AB, JAB = 14.4 Hz, JBA = 38.8 Hz, 2 H), 4.27-4.13 (m, 1 H), 3.48 (dd, J = 14.2, 4.6 Hz, 1 H), 3.36 (d, J = 14.0 Hz, 1 H); 13C NMR (101 MHz, CDCl3) δ 157.3, 147.2 (q, J = 2.6 Hz), 140.5, 135.9, 135.2, 133.4, 128.9, 127.5, 126.4, 126.1, 125.3 (q, J = 278.4 Hz), 119.2, 118.2, 115.8, 46.2, 43.8 (q, J = 33.0 Hz), 30.0 (q, J = 2.6 Hz); 19F NMR (376 MHz, CDCl3) δ -69.9 (d, J = 8.6 Hz); IR (neat) 1679, 1640, 1590, 1549, 1496, 1454, 1423 cm⁻¹; HRMS (ESI): calcd for C19H13BrF3NNaO⁺ [M+Na⁺]: 430.0025, found: 430.0031.

19) 4-Benzyl-7-chloro-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(IH)-one (4t)
The reaction of 1t (54 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4t as a white solid (67 mg, 92%). Mp: 151.8-152.3 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 2.4$ Hz, 1 H), 7.36 (dd, $J = 9.2$, 2.4 Hz, 1 H), 7.34-7.20 (m, 4 H), 7.17 (d, $J = 7.2$ Hz, 2 H), 5.55 (AB, $J_{AB} = 15.6$ Hz, $J_{BA} = 39.6$ Hz, 2 H), 4.26-4.14 (m, 1 H), 3.48 (dd, $J = 14.2$, 4.6 Hz, 1 H), 3.35 (dd, $J = 14.4$, 1.6 Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.3, 147.3 (q, $J = 3.2$ Hz), 140.1, 135.9, 135.3, 130.7, 128.9, 128.4, 127.5, 126.4, 125.3 (q, $J = 3.2$ Hz), 123.0, 118.8, 117.9, 46.3, 43.8 (q, $J = 3.2$ Hz), 30.0 (q, $J = 3.2$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -69.9 (d, $J = 8.6$ Hz); IR (neat) 1677, 1595, 1552, 1496, 1455, 1426 cm$^{-1}$; HRMS (ESI): calcd for C$_{19}$H$_{13}$ClF$_3$NNaO$^+ [M+Na]^+$: 386.0530, found: 386.0532.

20) 4-Methyl-8-methoxycarbonyl-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (4u)

The reaction of 1u (43 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and TBAF (1.0 M in THF, 1 mL, 1.0 mmol) afforded 4u as a white solid (50 mg, 81%). Mp: 160.4-160.6 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (dd, $J = 6.4$, 1.6 Hz, 1 H), 7.65-7.54 (m, 2 H), 4.58-4.46 (m, 1 H), 3.96 (s, 3 H), 3.78 (s, 3 H), 3.43 (dd, $J = 14.4$, 4.8 Hz, 1 H), 3.15 (dd, $J = 14.4$, 1.2 Hz, 1 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.0, 157.0, 146.3 (q, $J = 3.3$ Hz), 142.7, 137.5, 129.4, 128.1, 125.7 (q, $J = 278.7$ Hz), 124.0, 119.1, 116.2, 52.6, 46.0 (q, $J = 31.6$ Hz), 30.1, 29.5 (q, $J = 3.0$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -70.4 (d, $J = 7.9$ Hz); IR (neat) 1720, 1672, 1628, 1586, 1561, 1460, 1438 cm$^{-1}$; HRMS (ESI): calcd for C$_{15}$H$_{13}$F$_3$NO$_3^+$ [M+H]$^+$: 312.0842, found: 312.0839.

Gram-scale reaction of 1a under Condition A
To an oven-dried 100 mL of sealed tube were added 1a (1.176 g, 5.0 mmol), 2 (1.0 mL, 9.6 mmol), thioxanthone (11 mg, 0.05 mmol), and anhydrous DCM (50 mL). The reaction was irradiated by purple LED (λ = 400-410 nm) under an argon atmosphere at room temperature. The reaction was completed after 24 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). TBAF (1.0 M in THF, 25 mL, 25 mmol) was added to the solution subsequently. The reaction mixture was stirred at 60 °C for 12 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). After completion of the reaction, the mixture was washed with H2O (50 mL) and saturated aqueous NH4Cl (20 mL) and extracted with ethyl acetate (50 mL x 3). The combined organic layer was washed with brine, dried over MgSO4 and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1→5:1) afforded 4a as a white solid (1.570 g, 95%).

Typical Procedure III for Condition B

Synthesis of 4-benzyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(IH)-one (5a)

To an oven-dried 10 mL of sealed tube were added 1a (47 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), and anhydrous DCM (2 mL). The reaction was irradiated by purple LED (λ = 400-410 nm) under an argon atmosphere at room temperature. The reaction was completed after 24 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). DCM was removed in vacuo, anhydrous THF (1
mL) and DBU (45 μL, 0.3 mmol) were added to the residue subsequently. The reaction mixture was stirred at 100 °C. The reaction was completed after 12 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). The mixture was cannulated under argon atmosphere to a 250 mL of Schlenk flask containing anhydrous THF (100 mL). LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol) was added to the solution at -78 °C. The reaction was stirred at this temperature for 30 min. The cooling bath was then removed and the reaction was quenched with H₂O (10 mL). The mixture was stirred for another 30 min until the reaction mixture reached room temperature. Then THF was removed by rotary evaporator, the residue was washed with saturated aqueous NH₄Cl (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded 5a as a white solid (51 mg, 82%). Mp: 112.2-112.4 °C (petroleum ether/ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.0 Hz, 1 H), 7.46-7.38 (m, 1 H), 7.35-7.26 (m, 3 H), 7.25-7.16 (m, 4 H), 5.57 (s, 2 H), 3.76 (s, 2 H); ¹³C NMR (101 MHz, CDCl₃) δ 157.9, 150.1 (dd, J = 294.3, 292.0 Hz), 147.8 (dd, J = 8.7, 3.6 Hz), 141.9, 136.5, 130.7, 129.1 (dd, J = 6.5, 5.1 Hz), 128.8, 127.2, 126.4, 124.5 (d, J = 5.6 Hz), 122.4, 116.5, 116.1, 90.1 (dd, J = 34.3, 23.1 Hz), 46.0, 32.2 (d, J = 5.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -83.9 (d, J = 44.4 Hz), -93.4 (d, J = 44.4 Hz); IR (neat) 1776, 1660, 1584, 1557, 1497, 1449, 1406 cm⁻¹; HRMS (ESI): calcd for C₁₉H₁₃F₂NNaO⁺ [M+Na]⁺: 332.0857, found: 332.0855. Supplementary crystallographic data for 5a have been deposited at the Cambridge Crystallographic Data Center. CCDC: 2076180.
Ortep drawing with 50% ellipsoids for 5a

**Crystal data:** C\textsubscript{19}H\textsubscript{13}F\textsubscript{2}NO, M = 309.30, T = 173(2) K, Space group: P-1, a = 8.982(5) Å, b = 13.786(5) Å, c = 13.975(3) Å, α = 112.81(3)°, β = 107.33(3)°, γ = 96.28(3)°, V = 1472.2(11) Å\textsuperscript{3}, Z = 4, R indices: R1 = 0.0541, wR2 = 0.1250.

The following compounds were synthesized according to Typical Procedure III.

1) 4-(4-Methoxybenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5b)

\[ \text{1b} + \text{2a} + \text{F}_3\text{C}-\text{Br} \xrightarrow{1} \text{thioxanthone} \text{DCM, 400-410 nm, rt, 24 h} \xrightarrow{2} \text{DBU (1.5 equiv.)} \text{THF, 100 °C, 12 h} \xrightarrow{3} \text{LiHMDS (25 equiv.) THF, -78 °C, 30 min} \]

The reaction of 1b (53 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (
mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5b as a white solid (47 mg, 69%). Mp: 169.0-169.5 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 7.6$ Hz, 1 H), 7.49-7.40 (m, 1 H), 7.15 (d, $J = 8.8$ Hz, 2 H), 6.82 (d, $J = 8.4$ Hz, 2 H), 5.51 (s, 2 H), 3.76 (s, 2 H), 3.75 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.8, 157.9, 150.1 (t, $J = 293.3$ Hz), 147.7 (dd, $J = 8.4$, 3.2 Hz), 141.9, 130.6, 129.2 (t, $J = 5.5$ Hz), 128.6, 127.8, 124.5 (d, $J = 5.6$ Hz), 122.4, 116.5, 116.1, 114.2, 90.1 (dd, $J = 34.3$, 23.3 Hz), 55.2, 45.5, 32.2 (d, $J = 5.9$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -84.0 (d, $J = 45.1$ Hz), -93.5 (d, $J = 45.1$ Hz); IR (neat) 1776, 1660, 1585, 1556, 1513, 1445 cm$^{-1}$; HRMS (ESI): calcd for C$_{20}$H$_{15}$F$_2$NNaO$_2^+$ [M+Na]$^+$: 362.0963, found: 362.0959.

2) 4-(4-(Tert-butyl)benzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(IH)-one (5c)

The reaction of 1c (58 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5c as a white solid (51 mg, 70%). Mp: 169.6-170.4 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 7.6$ Hz, 1 H), 7.45 (t, $J = 8.0$ Hz, 1 H), 7.37 (d, $J = 8.8$ Hz, 1 H), 7.31 (d, $J = 8.4$ Hz, 2 H), 7.22 (t, $J = 7.6$ Hz, 1 H), 7.13 (d, $J = 8.4$ Hz, 2 H), 5.55 (brs, 2 H), 3.77 (s, 2 H), 1.27 (s, 9 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.9, 150.12, 150.11 (t, $J = 293.2$ Hz), 147.7 (dd, $J = 8.9$, 3.4 Hz), 142.0, 133.4, 130.7, 129.2 (dd, $J = 6.4$, 5.1 Hz), 126.2, 125.7, 124.5 (d, $J = 5.5$ Hz), 122.4, 116.6, 116.1, 90.1 (dd, $J = 34.3$, 23.4 Hz), 45.8, 34.4, 32.3 (d, $J = 5.9$ Hz), 31.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -84.0 (d, $J = 45.1$ Hz), -93.5 (d, $J = 45.1$ Hz); IR (neat) 1776, 1660, 1585, 1556, 1513, 1445 cm$^{-1}$; HRMS (ESI): calcd for C$_{23}$H$_{21}$F$_2$NNaO$_2^+$ [M+Na]$^+$: 388.1483, found:
388.1478.

3) 4-(4-Methylbenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5d)

The reaction of 1d (50 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5d as a white solid (42 mg, 65%). Mp: 163.5-163.7 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.0$ Hz, 1 H), 7.47-7.39 (m, 1 H), 7.34 (d, $J = 8.4$ Hz, 1 H), 7.21 (t, $J = 7.4$ Hz, 1 H), 7.13-7.05 (m, 4 H), 5.54 (brs, 2 H), 3.76 (s, 2 H), 2.29 (s, 3 H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.9, 150.1 (t, $J = 293.5$ Hz), 147.7 (dd, $J = 8.5$, 2.6 Hz), 141.9, 136.9, 133.5, 130.6, 129.4, 129.2 (t, $J = 5.5$ Hz), 126.4, 124.5 (d, $J = 5.6$ Hz), 122.4, 116.5, 116.1, 90.1 (dd, $J = 34.2$, 23.2 Hz), 45.8, 32.2 (d, $J = 6.0$ Hz), 21.0;

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -84.0 (d, $J = 44.7$ Hz), -93.5 (d, $J = 44.4$ Hz);

IR (neat) 1776, 1660, 1586, 1557, 1515, 1502, 1449, 1407 cm$^{-1}$;


4) 4-(4-Bromobenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5e)

The reaction of 1e (63 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5e as a white solid (42 mg, 65%). Mp: 163.5-163.7 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 8.0$ Hz, 1 H), 7.47-7.39 (m, 1 H), 7.34 (d, $J = 8.4$ Hz, 1 H), 7.21 (t, $J = 7.4$ Hz, 1 H), 7.13-7.05 (m, 4 H), 5.54 (brs, 2 H), 3.76 (s, 2 H), 2.29 (s, 3 H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.9, 150.1 (t, $J = 293.5$ Hz), 147.7 (dd, $J = 8.5$, 2.6 Hz), 141.9, 136.9, 133.5, 130.6, 129.4, 129.2 (t, $J = 5.5$ Hz), 126.4, 124.5 (d, $J = 5.6$ Hz), 122.4, 116.5, 116.1, 90.1 (dd, $J = 34.2$, 23.2 Hz), 45.8, 32.2 (d, $J = 6.0$ Hz), 21.0;

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -84.0 (d, $J = 44.7$ Hz), -93.5 (d, $J = 44.4$ Hz);

IR (neat) 1776, 1660, 1586, 1557, 1515, 1502, 1449, 1407 cm$^{-1}$;

0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5e as a white solid (35 mg, 45%). Mp: 162.7-163.3 °C (petroleum ether/ethyl acetate).

1H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.6 Hz, 1 H), 7.49-7.38 (m, 3 H), 7.26-7.20 (m, 2 H), 7.08 (d, J = 8.4 Hz, 2 H), 5.52 (brs, 2 H), 3.77 (s, 2 H); 13C NMR (101 MHz, CDCl₃) δ 157.8, 150.2 (t, J = 294.3 Hz), 148.0 (dd, J = 8.5, 2.8 Hz), 141.7, 135.6, 131.9, 130.8, 129.1 (t, J = 5.7 Hz), 128.3, 124.7 (d, J = 5.6 Hz), 122.6, 121.1, 116.24, 116.16, 90.1 (dd, J = 34.4, 23.4 Hz), 45.5, 32.3 (d, J = 5.5 Hz); 19F NMR (376 MHz, CDCl₃) δ -83.7 (d, J = 44.0 Hz), -93.1 (d, J = 43.2 Hz); IR (neat) 1776, 1660, 1586, 1559, 1501, 1488, 1449, 1404 cm⁻¹; HRMS (ESI): calcd for C₁₉H₁₃BrF₂NO⁺ [M+H]⁺: 388.0143, found: 388.0146.

5) 4-(4-Chlorobenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5f)

The reaction of 1f (54 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5f as a solid (35 mg, 51%). Mp: 149.2-149.8 °C (petroleum ether/ethyl acetate).

1H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.6 Hz, 1 H), 7.45 (t, J = 7.4 Hz, 1 H), 7.30-7.20 (m, 4 H), 7.14 (d, J = 8.0 Hz, 2 H), 5.54 (brs, 2 H), 3.77 (s, 2 H); 13C NMR (101 MHz, CDCl₃) δ 157.8, 150.2 (dd, J = 294.3, 292.4 Hz), 148.0 (dd, J = 8.7, 3.2 Hz), 141.7, 135.0, 133.1, 130.8, 129.1 (dd, J = 6.7, 4.9 Hz), 129.0, 127.9, 124.7 (d, J = 5.6 Hz), 122.6, 116.3, 116.2, 90.1 (dd, J = 34.4, 23.3 Hz), 45.5, 32.3 (d, J = 5.7 Hz); 19F NMR (376 MHz, CDCl₃) δ -83.7 (d, J = 44.4 Hz), -93.2 (d, J = 43.2 Hz); IR (neat) 1775, 1660, 1586, 1557, 1492, 1449, 1406 cm⁻¹; HRMS (ESI): calcd for
C_{19}H_{13}ClF_2NO^+ [M+H]^+: 344.0648, found: 344.0639.

6) 4-(4-Fluorobenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5g)

![Chemical structure of 5g]

The reaction of 1g (51 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5g as a white solid (51 mg, 78%). Mp: 185.6-185.7 °C (petroleum ether/ethyl acetate).

H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 1 H), 7.49-7.41 (m, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.23 (t, J = 7.4 Hz, 1 H), 7.18 (dd, J = 8.4, 5.6 Hz, 2 H), 7.02-6.94 (m, 2 H), 5.53 (brs, 2 H), 3.76 (s, 2 H); C NMR (101 MHz, CDCl₃) δ 162.0 (C-F, J_C-F = 246.9 Hz), 157.8, 150.1 (t, J = 293.5 Hz), 147.9 (dd, J = 8.7, 3.2 Hz), 141.7, 132.2 (C-F, J_C-F = 2.8 Hz), 130.7, 129.1 (t, J = 5.6 Hz), 128.2 (C-F, J_C-F = 8.1 Hz), 124.6 (d, J = 5.6 Hz), 122.5, 116.3, 116.1, 115.7 (C-F, J_C-F = 21.7 Hz), 90.1 (dd, J = 34.4, 23.3 Hz), 45.4, 32.2 (d, J = 5.5 Hz); F NMR (376 MHz, CDCl₃) δ -83.8 (d, J = 44.4 Hz), -93.2 (d, J = 44.4 Hz), -115.2 (ddd, J = 13.2, 8.5, 4.9 Hz); IR (neat) 1777, 1658, 1607, 1584, 1556, 1510, 1450, 1407 cm⁻¹; HRMS (ESI): calcd for C_{19}H_{12}F_3NNaO^+ [M+Na]^+: 350.0763, found: 350.0761.

7) 4-(4-Acetylbenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5i)
The reaction of 1i (55 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5i as a white solid (43 mg, 61%). Mp: 165.8-166.2 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, $J = 8.4$ Hz, 2 H), 7.76 (d, $J = 7.6$ Hz, 1 H), 7.43 (t, $J = 7.4$ Hz, 1 H), 7.28 (d, $J = 8.8$ Hz, 2 H), 7.24 (d, $J = 3.6$ Hz, 1 H), 7.22 (d, $J = 4.8$ Hz, 1 H), 5.63 (brs, 2 H), 3.78 (s, 2 H), 2.56 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.4, 157.7, 150.2 (t, $J = 293.7$ Hz), 148.1 (dd, $J = 8.8$, 2.9 Hz), 142.0, 141.7, 136.3, 130.8, 129.0 (t, $J = 5.8$ Hz), 128.9, 126.6, 124.7 (d, $J = 5.2$ Hz), 122.6, 116.2, 90.1 (dd, $J = 34.5$, 23.6 Hz), 45.9, 32.3 (d, $J = 5.6$ Hz), 26.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -83.6 (d, $J = 42.5$ Hz), -93.0 (d, $J = 43.6$ Hz); IR (neat) 1776, 1659, 1609, 1586, 1559, 1450, 1409 cm$^{-1}$; HRMS (ESI): calcd for C$_{21}$H$_{16}$F$_2$NO$_2$ [M+H]$^+$: 352.1144, found: 352.1143.

8) 4-(4-Formylbenzyl)-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5j)

The reaction of 1j (53 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded
5j as a white solid (19 mg, 28%). Mp: 169.9-170.4 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.96 (s, 1 H), 7.82 (d, $J$ = 8.4 Hz, 2 H), 7.77 (d, $J$ = 8.0 Hz, 1 H), 7.44 (t, $J$ = 8.0 Hz, 1 H), 7.35 (d, $J$ = 8.0 Hz, 2 H), 7.26 (d, $J$ = 8.0 Hz, 1 H), 7.21 (d, $J$ = 8.8 Hz, 1 H), 5.65 (brs, 2 H), 3.78 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.6, 157.7, 150.2 (dd, $J$ = 294.6, 292.5 Hz), 148.2 (dd, $J$ = 8.9, 3.4 Hz), 143.6, 141.6, 135.6, 130.8, 130.2, 129.0 (dd, $J$ = 6.5, 5.1 Hz), 127.0, 124.7 (d, $J$ = 5.9 Hz), 122.7, 116.12, 116.09, 90.1 (dd, $J$ = 34.4, 23.1 Hz), 45.9, 32.3 (d, $J$ = 5.5 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -83.5 (d, $J$ = 43.2 Hz), -92.9 (d, $J$ = 43.6 Hz); IR (neat) 1776, 1703, 1660, 1609, 1586, 1560, 1450, 1407 cm$^{-1}$; HRMS (ESI): calcd for C$_{20}$H$_{14}$F$_2$NO$_2$ $^{[M+H]^+}$: 338.0987, found: 338.0991.

9) 4-Methyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5m)

The reaction of 1m (32 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5m as a white solid (27 mg, 57%). Mp: 107.1-107.6 °C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J$ = 8.0 Hz, 1 H), 7.59 (t, $J$ = 8.0 Hz, 1 H), 7.43 (d, $J$ = 8.8 Hz, 1 H), 7.32-7.24 (m, 1 H), 3.74 (s, 3 H), 3.70 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.7, 150.1 (dd, $J$ = 294.0, 292.0 Hz), 147.1 (dd, $J$ = 8.2, 3.8 Hz), 142.4, 130.7, 129.3 (dd, $J$ = 6.3, 5.1 Hz), 124.5 (d, $J$ = 5.5 Hz), 122.3, 115.8, 115.6, 115.6, 115.6, 90.1 (dd, $J$ = 34.3, 23.3 Hz), 32.1 (d, $J$ = 5.8 Hz), 32.1 (d, $J$ = 5.8 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -84.3 (d, $J$ = 45.1 Hz), -93.8 (d, $J$ = 45.9 Hz); IR (neat) 1776, 1655, 1586, 1557, 1452, 1415 cm$^{-1}$; HRMS (ESI): calcd for C$_{13}$H$_{10}$F$_2$NO$_2$ $^{[M+H]^+}$: 234.0725, found: 234.0724.

10) 4-Allyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5n)
The reaction of 1n (37 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5n as a white solid (19 mg, 37%). Mp: 106.5-106.7 °C (petroleum ether/ethyl acetate).

1H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 1 H), 7.59-7.51 (m, 1 H), 7.39 (d, J = 8.4 Hz, 1 H), 7.30-7.22 (m, 1 H), 6.03-5.89 (m, 1 H), 5.22 (dm, J = 11.6 Hz, 1 H), 5.08 (dm, J = 18.4 Hz, 1 H), 5.01-4.96 (m, 2 H), 3.72 (s, 2 H); 13C NMR (101 MHz, CDCl₃) δ 157.4, 150.1 (dd, J = 294.0, 292.0 Hz), 147.6 (dd, J = 8.8, 3.3 Hz), 141.8, 132.0, 130.6, 129.2 (dd, J = 6.4, 5.1 Hz), 124.5 (d, J = 5.5 Hz), 122.4, 117.0, 116.3, 116.0, 90.1 (dd, J = 34.5, 23.1 Hz), 44.7, 32.1 (d, J = 5.9 Hz); 19F NMR (376 MHz, CDCl₃) δ -84.2 (d, J = 45.1 Hz), -93.6 (d, J = 45.1 Hz); IR (neat) 1771, 1655, 1584, 1555, 1407 cm⁻¹; HRMS (ESI): calcd for C₁₅H₁₂F₂NO⁺ [M+H]⁺: 260.0881, found: 260.0877.

11) 4-Phenyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5o)

The reaction of 1o (44 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), and LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), anhydrous THF (100 mL) afforded
**5o** as a solid (41 mg, 69%). Mp: 216.1-216.9 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 8.0 Hz, 1 H), 7.64-7.56 (m, 2 H), 7.55-7.49 (m, 1 H), 7.37-7.29 (m, 1 H), 7.28 -7.19 (m, 3 H), 6.67 (d, $J$ = 8.8 Hz, 1 H), 3.75 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.6, 150.1 (t, $J$ = 293.7 Hz), 148.2 (dd, $J$ = 8.5, 2.8 Hz), 143.8, 137.9, 130.2, 129.7 (t, $J$ = 5.5 Hz), 129.0, 128.9, 124.0 (d, $J$ = 5.5 Hz), 122.5, 117.4, 115.5, 90.1 (dd, $J$ = 34.3, 23.2 Hz), 32.3 (d, $J$ = 5.5 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -83.9 (d, $J$ = 44.0 Hz), -93.4 (d, $J$ = 44.0 Hz); IR (neat) 1776, 1655, 1582, 1551, 1492, 1444, 1422 cm$^{-1}$; HRMS (ESI): calcd for C$_{18}$H$_{12}$F$_2$NO$^+$ [M+H$^+$]: 296.0881, found: 296.0878.

12) 4-Methyl-6-methoxy-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5p)

The reaction of **1p** (38 mg, 0.2 mmol), **2a** (104 μL, 1.0 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded **5p** as a solid (25 mg, 47%). Mp: 187.5-188.0 °C (petroleum ether/ethyl acetate). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 8.0 Hz, 1 H), 6.84 (dd, $J$ = 8.6, 2.2 Hz, 1 H), 6.81 (d, $J$ = 1.6 Hz, 1 H), 3.92 (s, 3 H), 3.67 (s, 3 H), 3.64 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.6, 157.9, 150.0 (t, $J$ = 293.1 Hz), 146.9 (dd, $J$ = 8.5, 2.7 Hz), 144.1, 125.8 (t, $J$ = 5.8 Hz), 125.7 (d, $J$ = 5.2 Hz), 109.9, 109.8, 100.0, 90.0 (dd, $J$ = 34.1, 23.1 Hz), 55.5, 31.9 (d, $J$ = 5.6 Hz), 29.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -84.8 (d, $J$ = 47.0 Hz), -94.2 (d, $J$ = 46.2 Hz); IR (neat) 1777, 1668, 1629, 1588, 1551, 1516, 1464, 1422 cm$^{-1}$; HRMS (ESI): calcd for C$_{14}$H$_{12}$F$_2$NO$_2$$^+$ [M+H$^+$]: 264.0831, found: 264.0829.

13) 4-Benzyl-7-methyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5q)
The reaction of 1\textsubscript{q} (50 mg, 0.2 mmol), 2\textsubscript{a} (42 \(\mu\)L, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 \(\mu\)L, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5\textsubscript{q} as a white solid (23 mg, 35%). Mp: 157.1-157.3 °C (petroleum ether/ethyl acetate).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.51 (s, 1 H), 7.33-7.27 (m, 2 H), 7.26-7.15 (m, 5 H), 5.57 (brs, 2 H), 3.76 (s, 2 H), 2.38 (s, 3 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 157.8, 150.1 (t, \(J = 293.2 \) Hz), 147.5 (dd, \(J = 8.6, 3.3 \) Hz), 139.9, 136.6, 132.1, 132.0, 129.1 (t, \(J = 5.7 \) Hz), 128.7, 127.2, 126.4, 124.2 (d, \(J = 5.2 \) Hz), 116.4, 116.1, 90.1 (dd, \(J = 34.3, 23.3 \) Hz), 46.0, 32.2 (d, \(J = 5.5 \) Hz), 20.6; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta\) -84.1 (d, \(J = 45.9 \) Hz), -93.7 (d, \(J = 44.7 \) Hz); IR (neat) 1775, 1660, 1585, 1560, 1454, 1435 cm\textsuperscript{-1}; HRMS (ESI): calcd for C\textsubscript{20}H\textsubscript{16}F\textsubscript{2}NO\textsuperscript{+} [M+H]\textsuperscript{+}: 324.1194, found: 324.1197.

14) 4-Benzyl-7-phenyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1\textsubscript{H})-one (5\textsubscript{r})

The reaction of 1\textsubscript{r} (62 mg, 0.2 mmol), 2\textsubscript{a} (104 \(\mu\)L, 1.0 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 \(\mu\)L, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5\textsubscript{r} as a solid (46 mg, 60%). Mp: 155.4-155.8 °C (petroleum ether/ethyl acetate). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.93 (s, 1 H), 7.66 (dd, \(J = 8.8, 2.0 \) Hz, 1 H), 7.57 (d, \(J = 7.2 \) Hz, 2 H), 7.44 (t, \(J = 7.6 \) Hz, 2 H), 7.41-7.30 (m, 3 H), 7.29-7.19 (m, 4 H), 5.60 (s,
2 H), 3.79 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.7, 150.2 (t, $J = 293.5$ Hz), 147.9 (dd, $J = 8.5, 3.1$ Hz), 141.1, 139.4, 136.5, 135.4, 129.6, 129.5, 129.0, 128.8, 127.6, 127.3, 126.8, 126.5, 122.3 (d, $J = 5.6$ Hz), 116.9, 116.4, 90.2 (dd, $J = 34.3, 23.2$ Hz), 46.1, 32.3 (d, $J = 5.9$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -83.7 (d, $J = 45.1$ Hz), -93.3 (d, $J = 45.1$ Hz); IR (neat) 1775, 1661, 1556, 1495, 1453, 1424 cm$^{-1}$; HRMS (ESI): calcd for C$_{25}$H$_{18}$F$_2$NO$^+$ [M+H$^+$]: 386.1351, found: 386.1355.

15) 4-Benzyl-7-bromo-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5s)

The reaction of 1s (63 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), and DBU (45 μL, 1.0 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded 5s as a solid (36 mg, 46%). Mp: 163.3-163.5 $^\circ$C (petroleum ether/ethyl acetate).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (s, 1 H), 7.49 (dd, $J = 9.0, 2.2$ Hz, 1 H), 7.33-7.13 (m, 6 H), 5.54 (s, 2 H), 3.77 (s, 2 H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.5, 150.2 (t, $J = 294.3$ Hz), 146.7 (dd, $J = 8.7, 3.0$ Hz), 140.8, 136.1, 133.5, 130.4 (t, $J = 5.6$ Hz), 128.9, 127.4, 126.9 (d, $J = 5.9$ Hz), 126.4, 118.2, 117.4, 115.6, 89.9 (dd, $J = 34.5, 23.6$ Hz), 46.1, 32.4 (d, $J = 5.6$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -83.2 (d, $J = 43.2$ Hz), -92.6 (d, $J = 43.6$ Hz); IR (neat) 1774, 1661, 1578, 1548, 1496, 1456, 1445, 1417 cm$^{-1}$; HRMS (ESI): calcd for C$_{19}$H$_{13}$BrF$_2$NO$^+$ [M+H$^+$]: 388.0143, found: 388.0160.

16) 4-Benzyl-7-chloro-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5t)
The reaction of \(1t\) (54 mg, 0.2 mmol), \(2a\) (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded \(5t\) as a solid (22 mg, 32%). Mp: 163.4-163.6 °C (petroleum ether/ethyl acetate). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.66 (s, 1 H), 7.36 (dd, \(J = 9.2, 2.4\) Hz, 1 H), 7.33-7.27 (m, 2 H), 7.26-7.20 (m, 2 H), 7.16 (d, \(J = 6.8\) Hz, 2 H), 5.55 (s, 2 H), 3.77 (s, 2 H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.5, 150.2 (t, \(J = 294.1\) Hz), 146.8 (dd, \(J = 8.7, 2.7\) Hz), 140.4, 136.1, 130.7, 130.4 (t, \(J = 5.8\) Hz), 128.9, 128.1, 127.4, 126.4, 123.8 (d, \(J = 6.0\) Hz), 117.9, 117.0, 89.9 (dd, \(J = 34.8, 23.4\) Hz), 46.2, 32.4 (d, \(J = 5.6\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -83.3 (d, \(J = 43.2\) Hz), -92.7 (d, \(J = 43.2\) Hz); IR (neat) 1777, 1661, 1550, 1496, 1454, 1422 cm\(^{-1}\); HRMS (ESI): calcd for C\(_{19}\)H\(_{13}\)ClF\(_2\)NO\(^+\) [M+H\(^+\)]\(^+\): 344.0648, found: 344.0649.

17) 4-Methyl-8-methoxycarbonyl-1-(difluoromethylene)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (5u)

The reaction of \(1u\) (43 mg, 0.2 mmol), \(2a\) (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), anhydrous DCM (2 mL), DBU (45 μL, 0.3 mmol), anhydrous THF (1 mL), LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol), and anhydrous THF (100 mL) afforded \(5u\) as a solid (38 mg, 66%). Mp: 161.3-161.5 °C (petroleum ether/ethyl acetate). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.66-7.56 (m, 3 H), 3.95 (s, 3 H), 3.76 (s, 3 H), 3.67 (s, 2 H).
H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.1, 157.1, 150.0 ($dd, J = 297.0, 288.5$ Hz), 145.6 ($dd, J = 8.5, 2.2$ Hz), 142.9, 132.2 (t, $J = 4.9$ Hz), 129.5, 129.1, 123.7, 118.8, 114.3, 91.1 ($dd, J = 38.9, 18.6$ Hz), 52.5 (d, $J = 3.3$ Hz), 32.4 (d, $J = 4.8$ Hz), 30.0; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -83.6 ($dd, J = 41.7$ Hz), -93.1 (d, $J = 41.4$ Hz); IR (neat) 1772, 1728, 1660, 1580, 1556, 1434 cm$^{-1}$; HRMS (ESI): calcd for C$_{15}$H$_{12}$F$_2$NO$_3$ $^{+}$ [M+H]$^+$: 292.0780, found: 292.0776.

**Mmol-scale reaction of 1a under Condition B**

To an oven-dried 50 mL of sealed tube were added 1a (471 mg, 2.0 mmol), 2a (415 μL, 4.0 mmol), thioxanthone (4.0 mg, 0.02 mmol), and anhydrous DCM (20 mL). The reaction was irradiated by purple LED ($\lambda = 400-410$ nm) under an argon atmosphere at room temperature. The reaction was completed after 24 h as monitored by TLC (petroleum ether/ethyl acetate/dichloromethane = 5:1:1). DCM was removed in vacuo, anhydrous THF (10 mL) and DBU (448 μL, 3.0 mmol) were added to the residue subsequently. The reaction mixture was stirred at 100 °C. The reaction was completed after 12 h as monitored by TLC (petroleum ether/ethyl acetate/dichloromethane = 5:1:1). The mixture was cannulated under argon atmosphere to a 2000 mL of Schlenk flask containing anhydrous THF (1000 mL). LiHMDS (1.0 M in THF, 50 mL, 50.0 mmol) was added to the solution at -78 °C. The reaction was stirred at this temperature for 30 min. The cooling bath was then removed and the reaction was quenched with H$_2$O (20 mL). The mixture was stirred for another 30 min until the reaction mixture reached room temperature. Then THF was removed by rotary evaporator, the residue was washed with saturated aqueous NH$_4$Cl (50 mL) and extracted with ethyl acetate (50 mL x 3). The combined organic layer was dried over MgSO$_4$ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (petroleum
ether/ethyl acetate/dichloromethane = 5:1:1) afforded 5a as a white solid (398 mg, 64%).

**Synthesis of (Z)-4-benzyl-1-((4-benzyl-3-oxo-3,4-dihydrocyclobuta[c]quinolin-1(2H)-ylidene)fluoromethyl)-1-(trifluoromethyl)-2,4-dihydrocyclobuta[c]quinolin-3(1H)-one (6a)**

![Chemical structure](image)

To an oven-dried 10 mL of sealed tube were added 1a (47 mg, 0.2 mmol), 2a (42 μL, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), and anhydrous DCM (2 mL). The reaction was irradiated by purple LED (λ = 400-410 nm) under an argon atmosphere at room temperature. The reaction was completed after 24 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). DCM was removed in vacuo, anhydrous THF (1 mL) and DBU (60 μL, 0.4 mmol) were added to the residue subsequently. The reaction mixture was stirred at 100 °C. The reaction was completed after 12 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). The mixture was cannulated under argon atmosphere to a 25 mL of Schlenk tube containing anhydrous THF (10 mL). LiHMDS (1.0 M in THF, 0.4 mL, 0.4 mmol) was added to the solution at -78 °C. The reaction was stirred at this temperature for 30 min. The cooling bath was then removed and the mixture was stirred for another 30 min until the reaction mixture reached room temperature. Then the reaction mixture was washed with H₂O (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2:1) afforded 6a as a white solid (27 mg, 22%). Mp: 193.9-194.2 °C (petroleum ether/ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.6 Hz, 1 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.54-7.46 (m, 1 H), 7.45-7.37 (m, 2 H), 7.36-7.15 (m, 13 H), 5.75-5.47 (m, 4 H), 3.85-3.62 (m, 4 H), ¹³C NMR (101 MHz, CDCl₃) δ 158.0, 157.6, 149.4, 148.1, 147.5, 144.9, 141.9
(d, \( J = 4.4 \) Hz), 136.4, 136.0, 133.6, 131.8, 131.1, 130.7, 128.9, 128.8, 127.4, 127.3, 126.4, 125.8, 125.7, 124.7 (d, \( J = 279.8 \) Hz), 124.6, 123.0, 122.5, 119.2 (d, \( J = 21.0 \) Hz), 117.4, 116.7, 116.5, 116.1, 55.0 (dd, \( J = 31.2, 28.1 \) Hz), 46.4, 46.2, 36.8, 34.8 (d, \( J = 9.6 \) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -70.8 (d, \( J = 6.0 \) Hz), -101.6; IR (neat) 1678, 1658, 1598, 1586, 1559, 1497, 1451, 1399 cm\(^{-1}\); HRMS (ESI): calcd for C\(_{38}\)H\(_{26}\)F\(_4\)N\(_2\)NaO\(_2\)\(^+\)[M+Na\(^+\)]: 641.1823, found: 641.1825.

Mechanistic verification experiments

Mechanistic verification experiments were conducted as depicted above. Subjecting 1a and 2a to standard photoreaction condition yielded 3a in an isolated yield of 96%. Treating 3a under standard elimination Condition A2 afforded 4a almost quantitatively (99% isolated yield). Meanwhile, treating 3a under standard elimination Conditions B2 and B3 also afforded 5a in an isolated yield of 82%. These results indicated that 3a was the common intermediate of Conditions A and B. Consequently, 4a was tested under standard elimination Condition B3. 5a was furnished in an isolated yield of 92%, demonstrating that 4a was another intermediate of Condition B. The above results are consistent with the initially proposed mechanism.

Procedure for the transformation of 1a into 3a

To an oven-dried 10 mL of sealed tube were added 1a (47 mg, 0.2 mmol), 2a (42 \( \mu \)L, 0.4 mmol), thioxanthone (0.4 mg, 0.002 mmol), and anhydrous DCM (2 mL). The reaction was irradiated by purple LED (\( \lambda = 400-410 \) nm) under an argon atmosphere at
room temperature. The reaction was completed after 24 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford 3a as a white solid (79 mg, 96%). Mp: 103.6-103.9 °C (petroleum ether/ethyl acetate).\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.15 (m, 6 H), 7.06-6.95 (m, 2 H), 6.92 (d, \(J = 8.4\) Hz, 1 H), 5.25 (AB, \(J_{AB} = 16.4\) Hz, \(J_{BA} = 67.6\) Hz, 2 H), 4.36-4.30 (m, 1 H), 3.62-3.48 (m, 2 H), 3.05-2.93 (m, 1 H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.3, 140.3, 136.3, 129.5, 129.4, 128.7, 127.2, 126.4, 124.0 (q, \(J = 279.1\) Hz), 123.2, 120.0, 115.9, 61.5 (q, \(J = 32.3\) Hz), 46.1, 42.3 (q, \(J = 1.9\) Hz), 38.4 (q, \(J = 1.9\) Hz), 32.5; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -76.8; IR (neat) 1667, 1602, 1499, 1462 cm\(^{-1}\); HRMS (ESI): calcd for C\(_{19}\)H\(_{15}\)BrF\(_3\)NO\(^+\) [M+H]\(^+\): 410.0362, found: 410.0378. Supplementary crystallographic data for 3a have been deposited at the Cambridge Crystallographic Data Center. CCDC: 2076891.

**Crystal data**: C\(_{19}\)H\(_{15}\)BrF\(_3\)NO, M = 410.23, T = 150(2) K, Crystal system: Monoclinic,
Space group: C2/c, \( a = 25.323(2) \, \text{Å}, b = 5.9171(4) \, \text{Å}, c = 25.206(2) \, \text{Å}, \alpha = 90^\circ, \beta = 114.569(2)^\circ, \gamma = 90^\circ, V = 3434.9(5) \, \text{Å}^3, Z = 8 \), R indices: \( R_1 = 0.0950, wR_2 = 0.1251 \).

Procedure for the transformation of 3a into 4a

To an oven-dried 10 mL of sealed tube were added 3a (82 mg, 0.2 mmol), TBAF (1.0 M in THF, 1 mL, 1.0 mmol), and anhydrous DCM (2 mL). The reaction mixture was stirred at 60 °C for 12 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). After completion of the reaction, the mixture was washed with H\(_2\)O (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over MgSO\(_4\) and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded 4a as a white solid (65 mg, 99%).

Procedure for the transformation of 3a into 5a

To an oven-dried 10 mL of sealed tube were added 3a (82 mg, 0.2 mmol), DBU (45 μL, 0.3 mmol), and anhydrous THF (1 mL). The reaction mixture was stirred at 100 °C for 12 h as monitored by TLC (petroleum ether/ethyl acetate = 5:1). The mixture was cannulated under argon atmosphere to a 250 mL of Schlenk flask containing anhydrous THF (100 mL). LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol) was added to the solution at -78 °C. The reaction was stirred at this temperature for 30 min. The cooling bath was then removed and the reaction was quenched with H\(_2\)O (10 mL). The mixture was stirred for another 30 min until the reaction mixture reached room temperature. Then
THF was removed by rotary evaporator, the residue was washed with saturated aqueous NH$_4$Cl (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over MgSO$_4$ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded 5a as a white solid (51 mg, 82%).

**Procedure for the transformation of 4a into 5a**

To an oven-dried 250 mL of Schlenk flask were added 4a (66 mg, 0.2 mmol) and anhydrous THF (100 mL) under argon atmosphere. LiHMDS (1.0 M in THF, 5 mL, 5.0 mmol) was added to the solution at -78 °C. The reaction was stirred at this temperature for 30 min. The cooling bath was then removed and the reaction was quenched with H$_2$O (10 mL). The mixture was stirred for another 30 min until the reaction mixture reached room temperature. Then THF was removed by rotary evaporator, the residue was washed with saturated aqueous NH$_4$Cl (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with brine, dried over MgSO$_4$ and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded 5a as a white solid (57 mg, 92%).
NMR Spectra

1a

NMR Spectra

1b

NMR Spectra
References


