Supporting Information

Photosensitizer-Free, Harnessing Sunlight for Highly Efficient Consecutive [3+2]/[4+2] Annulation to Fused Benzobicyclic Skeletons

Nengneng Zhou, a Yixiang Cheng, a Jin Xie*,a and Chengjian Zhu*,a,b

(a State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Material, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China; E-mail: xie@nju.edu.cn or cjzhu@nju.edu.cn
b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai, 200032, P. R. China)

Table of Contents

General information ..................................................................................................................................................2
General procedure for sunlight-promoted cascade annulation of unsaturated α-bromocarbonyls with o-alkynylanilines ..................................................................................................................2
Trapping experiment with TEMPO ......................................................................................................................2
The light on/off experiments ...............................................................................................................................3
UV/Vis measurement ............................................................................................................................................3
The crystallographic data ....................................................................................................................................4
Characterization of products ..............................................................................................................................4
Copies of $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR spectra ..........................................................................................12
**General Information:** All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. $^1$H NMR, $^{13}$C NMR spectra and $^{19}$F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts ($\delta$) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high-resolution mass spectrometer in the ESI mode.

**General procedure for sunlight-promoted cascade annulation of unsaturated $\alpha$-bromocarbonyls with o-alkynylanilines**

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1 (0.1 mmol), 2 (2 equiv, 0.2 mmol), K$_2$CO$_3$ (2 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH$_3$CN was added with syringe under Ar. The tube was placed exposed to sunlight at room temperature for 2-3 h. After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products 3.

**Trapping experiment with TEMPO**

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1 (0.1 mmol), 2 (2 equiv, 0.2 mmol), K$_2$CO$_3$ (2 equiv, 0.2 mmol), TEMPO (2 equiv). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH$_3$CN was added with syringe under Ar. The tube was placed exposed to sunlight at room temperature. However, products 3a could not be detected, the corresponding alkylfragment of the halides were formed. Which suggests that the initiation of this radical chain is best achieved via photoinduction.

**The HRMS (ESI) for the important intermediate 10**

![Image of the intermediate 10]

HRMS [5 + H]$^+$: Caled: 356.2431; Found: 356.2429.
The light on/off experiments
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1 (0.1 mmol), 2 (2 equiv, 0.2 mmol), K$_2$CO$_3$ (2 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH$_3$CN was added with syringe under Ar. The tube was placed at a distance (app. 5 cm) from 33 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the indicated reaction time, 50 μL of the reaction mixture aliquot was collected at different points. The $^1$H NMR analysis was calculated using 4,4'-dimethylbenzophenone as the internal standard.

UV/Vis measurement
The corresponding NK salts generated in situ from 1a and KH occurred bathochromic shift from the UV-vis absorption, which showed much stronger absorption range from 325-375 nm than any of 1a, 2a and product 3aa.
Figure 1: Absorption spectra of the reagents of the model reaction (c = 10^{-4} \text{ mol/L}, recorded in MeCN in 1 mm path length quartz cuvettes using a Shimadzu UV-3600 UV-visible spectrophotometer).

The crystallographic data

![Crystal Structure Image]

<table>
<thead>
<tr>
<th>Identification code</th>
<th>3ac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C26 H29 N O6 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>483.56</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>triclinic, P-1</td>
</tr>
</tbody>
</table>
| Unit cell dimensions | a = 9.8833(13) Å \( \alpha = 61.578(2) \)  
                        | b = 12.3066(16) Å \( \beta = 71.152(2) \)  
                        | c = 12.4078(15) Å \( \gamma = 72.508(2) \) |
| Volume              | 1236.4(3) Å³ |
| Z, Calculated density | 2, 1.299 g/cm³ |
| Absorption coefficient | 0.172 mm⁻¹ |
| F(000)              | 512 |
| Limiting indices    | -11<=h<=11, -14<=k<=14, -13<=l<=14 |
| Data / parameters   | 4328 /311 |
| Goodness-of-fit on F² | 0.982 |
| Final R indices [I>2sigma(I)] | R1 = 0.058, wR2 = 0.198 |

Characterization of products

**diethyl 5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(3aa)**. Yellow solid; (41.7 mg, 89%); mp: 145-146 °C; \( R_f = 0.32 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.81 \) (dd, \( J = 8.4 \) Hz, \( J = 1.2 \) Hz, 1H), 7.59-7.55 (m, 3H), 7.28-7.21 (m, 3H), 7.14-7.10 (m, 1H), 6.15 (d, \( J = 2.4 \) Hz, 1H), 4.61 (dd, \( J = 13.2 \) Hz, \( J = 4.8 \) Hz, 1H), 4.24-4.08 (m, 4H), 3.04 (m, 1H), 2.82-2.78 (m, 2H), 2.37 (s, 3H), 1.82-1.76 (m, 1H), 1.28-1.19 (m, 6H) ppm; \(^{13}\)C NMR (100.6 MHz, CDCl₃): \( \delta = 170.8, 169.8, 143.9, 142.2, 137.0, 135.9, 129.8, 129.2, 127.0, 125.7, 125.0, 124.4, 123.4, 121.1, 65.3, 61.7, 61.6, 51.4, 39.6, 37.2, 21.5, 14.1, 14.0 \) ppm. HRMS
(ESI): m/z Calcd for C_{25}H_{28}NO_{6}S [M+H^+] :470.1632, found 470.1635.

**diethyl 5-((4-bromophenyl)sulfonyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ba).** Yellow solid; (43.2 mg, 81%); mp: 123-125 °C; R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.79 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.61-7.50 (m, 5H), 7.17-7.13 (m, 1H), 6.18 (d, J = 1.6 Hz, 1H), 4.60 (dd, J = 13.2 Hz, J = 4.4 Hz, 1H), 4.23-4.08 (m, 4H), 3.07 (t, J = 13.2 Hz, 1H), 2.83-2.78 (m, 2H), 1.83-1.76 (m, 1H), 1.28-1.20 (m, 6H) ppm; ^13C NMR (100.6 MHz, CDCl_3): δ 170.7, 169.7, 141.8, 138.9, 135.4, 132.4, 129.3, 128.5, 128.1, 125.9, 125.4, 124.4, 123.7, 121.7, 65.3, 61.80, 61.77, 51.5, 39.7, 37.2, 14.06 ppm. HRMS (ESI): m/z Calcd for C_{24}H_{24}BrNO_{6}S [M+H^+] : 534.0580, found 534.0582.

**diethyl 5-(methylsulfonyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ca).** Yellow solid; (30.7 mg, 78%); mp: 146-148 °C; R_f = 0.38 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.75 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.69 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.30 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H), 7.18-7.14 (m, 1H), 6.30 (d, J = 2.4 Hz, 1H), 4.60 (dd, J = 13.2 Hz, J = 4.8 Hz, 1H), 4.28-4.13 (m, 4H), 3.32-3.23 (m, 1H), 3.06-2.96 (m, 2H), 2.94 (s, 3H), 1.90 (dd, J = 13.2 Hz, J = 8.8 Hz, 1H), 1.31-1.26 (m, 6H) ppm; ^13C NMR (100.6 MHz, CDCl_3): δ 170.7, 170.0, 142.1, 135.8, 129.6, 126.2, 125.0, 123.1, 121.7, 65.4, 61.9, 61.8, 51.1, 40.8, 39.9, 37.2, 14.1 ppm. HRMS (ESI): m/z Calcd for C_{19}H_{23}NO_{6}S [M+H^+] : 394.1319, found 394.1317.

**diethyl 5-(phenylsulfonyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3da).** Yellow oil; (38.7 mg, 85%); R_f = 0.35 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.81 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.69-7.67 (m, 2H), 7.59-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.29-7.25 (m, 1H), 7.15-7.11 (m, 1H), 6.15 (d, J = 1.6 Hz, 1H), 4.61 (dd, J = 13.2 Hz, J = 4.0 Hz, 1H), 4.23-4.05 (m, 4H), 3.06 (m, 1H), 2.82-2.74 (m, 2H), 1.82-1.76 (m, 1H), 1.27-1.19 (m, 6H) ppm; ^13C NMR (100.6 MHz, CDCl_3): δ 170.8, 169.8, 142.1, 140.0, 135.7, 133.0, 129.2, 126.9, 125.8, 125.1, 124.4, 123.5, 121.3, 65.3, 61.7, 51.4, 39.6, 37.2, 14.04 ppm. HRMS (ESI): m/z Calcd for C_{24}H_{25}NO_{6}S [M+H^+] : 456.1475, found 456.1476.
diethyl 8-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(3ea).

Yellow solid; (42.1 mg, 87%); mp: 133-135 °C; Rf = 0.33 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.70 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 1.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.08 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 6.12 (d, J = 1.6 Hz, 1H), 4.57 (dd, J = 13.2 Hz, J = 4.4 Hz, 1H), 4.22-4.05 (m, 4H), 3.02 (t, J = 13.2 Hz, 1H), 2.79-2.68 (m, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.80-1.73 (m, 1H), 1.27-1.19 (m, 6H) ppm; 13C NMR (100.6 MHz, CDCl3): δ 170.8, 169.9, 143.8, 142.4, 137.0, 134.7, 133.5, 130.1, 129.7, 127.0, 125.9, 124.4, 123.2, 120.9, 65.3, 61.7, 61.6, 51.5, 39.5, 37.2, 21.5, 20.8, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for C26H29NO6S [M+H]+:484.1788, found 484.1790.

diethyl 8-fluoro-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(3fa).

Yellow solid; (39.0 mg, 80%); mp: 113-115 °C; Rf = 0.33 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.81 (dd, J = 9.2 Hz, J = 5.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.25-7.22 (m, 3H), 7.04-6.96 (m, 1H), 6.14 (d, J = 2.4 Hz, 1H), 4.53 (dd, J = 13.2 Hz, J = 4.8 Hz, 1H), 4.26-4.05 (m, 4H), 3.01 (t, J = 13.2 Hz, 1H), 2.77 (dd, J = 12.8 Hz, J = 6.8 Hz, 1H), 2.73-2.64 (m, 1H), 2.38 (s, 3H), 1.77 (dd, J = 12.8 Hz, J = 9.2 Hz, 1H), 1.27-1.19 (m, 6H) ppm; 13C NMR (100.6 MHz, CDCl3): δ 170.5, 169.5, 159.9 (d, J = 243.6 Hz), 144.1, 141.6 (d, J = 2.3 Hz), 136.7,131.9 (d, J = 2.7 Hz), 129.8, 127.0, 126.8 (d, J = 8.2 Hz), 125.4 (d, J = 8.2 Hz), 122.8, 116.4, 116.2, 111.7, 111.4, 65.3, 61.8, 61.7, 52.3, 39.0, 37.2, 21.5, 14.04, 13.98 ppm; 19F NMR (376 MHz, CDCl3): -116.86 ppm. HRMS (ESI): m/z Calcd for C25H26FNO6S [M+H]+:488.1538, found 488.1536.

diethyl 8-chloro-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(3ga).

Yellow solid; (41.7 mg, 83%); mp: 133-135 °C; Rf = 0.33 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.78 (d, J = 9.2 Hz, 1H), 7.56-7.53 (m, 3H), 7.25-7.22 (m, 3H), 7.04-6.96 (m, 1H), 6.17 (d, J = 2.4 Hz, 1H), 4.58 (dd, J = 13.6 Hz, J = 4.8 Hz, 1H), 4.24-4.06 (t, J = 13.6 Hz, 4H), 3.00 (m, 1H), 2.79 (dd, J = 12.8 Hz, J = 7.6 Hz, 1H), 2.74-2.65 (m, 1H), 2.38 (s, 3H), 1.80-1.73 (m, 1H), 1.79 (dd, J = 12.8 Hz, J = 8.8 Hz, 1H), 1.28-1.19 (m, 6H) ppm; 13C NMR (100.6 MHz, CDCl3): δ 170.5, 169.6, 144.2, 141.2, 136.6, 134.4, 130.6, 129.9, 129.0, 127.0, 125.8, 125.4, 124.9, 122.6,
65.3, 61.83, 61.76, 51.2, 39.2, 37.1, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for C\textsubscript{25}H\textsubscript{26}ClNO\textsubscript{6} [M+H\textsuperscript{+}]: 504.1242, found 504.1244.

\[
\begin{array}{c}
\text{Ts} \quad \text{Br} \\
\text{EtCO2} \\
\text{EtCO2}
\end{array}
\]

diethyl 8-bromo-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ha). Yellow solid; (42.7 mg, 78%); mp: 123-124 °C; R\textsubscript{f} = 0.31 (petroleum ether/ethyl acetate 10:1); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.73-7.69 (m, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.36 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 7.24 (dd, J = 8.0 Hz, 2H), 6.16 (d, J = 2.4 Hz, 1H), 4.58 (dd, J = 13.6 Hz, J = 4.8 Hz, 1H), 4.23-4.06 (m, 4H), 3.00 (t, J = 12.8 Hz, 1H), 2.79 (dd, J = 12.8 Hz, J = 7.6 Hz, 1H), 2.73-2.65 (m, 1H), 2.39 (s, 3H), 1.80-1.73 (m, 1H), 1.79 (dd, J = 12.8 Hz, J = 9.2 Hz, 1H), 1.28-1.19 (m, 6H) ppm; \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}): δ 170.5, 169.6, 144.2, 141.1, 136.6, 134.9, 131.9, 129.9, 128.4, 127.0, 126.0, 125.2, 122.6, 118.3, 65.3, 61.83, 61.77, 51.2, 39.2, 37.1, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for C\textsubscript{25}H\textsubscript{26}BrNO\textsubscript{6} [M+H\textsuperscript{+}]: 548.0737, found 548.0709.

\[
\begin{array}{c}
\text{Ts} \quad \text{CF}_3 \\
\text{CO2} \\
\text{EtCO2}
\end{array}
\]

diethyl 5-tosyl-8-(trifluoromethyl)-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ia). Yellow solid; (39.2 mg, 73%); mp: 178-181 °C; R\textsubscript{f} = 0.31 (petroleum ether/ethyl acetate 10:1); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.93 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.47 (dd, J = 8.8 Hz, J = 8.8 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 6.26 (d, J = 2.4 Hz, 1H), 4.65 (dd, J = 13.2 Hz, J = 4.8 Hz, 1H), 4.24-4.08 (m, 4H), 3.03 (t, J = 18.8 Hz, 1H), 2.89-2.77 (m, 2H), 2.40 (s, 3H), 1.87-1.81 (m, 1H), 1.79-1.73 (m, 1H), 1.29-1.21 (m, 6H) ppm; \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}): δ 170.5, 169.6, 144.4, 141.1, 136.8, 136.5, 130.0, 127.0, 126.6 (q, J = 33 Hz), 125.6 (q, J = 3.6 Hz), 123.9, 123.8 (q, J = 270.1 Hz), 123.2, 123.0 (q, J = 3.7 Hz), 122.8, 65.4, 61.9, 51.2, 39.6, 37.0, 21.6, 14.06, 14.00 ppm; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): --62.55 ppm. HRMS (ESI): m/z Calcd for C\textsubscript{26}H\textsubscript{26}F\textsubscript{3}NO\textsubscript{6} [M+H\textsuperscript{+}]: 538.1506, found 538.1508.

\[
\begin{array}{c}
\text{Ts} \quad \text{H} \\
\text{CO2} \\
\text{EtCO2}
\end{array}
\]

diethyl 7-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ja). Yellow solid; (42.0 mg, 87%); mp: 167-169 °C; R\textsubscript{f} = 0.38 (petroleum ether/ethyl acetate 10:1); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.63 (s, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.22
(dd, J = 8.4 Hz, J = 0.8 Hz, 2H), 6.94 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 6.07 (d, J = 2.4 Hz, 1H), 4.57 (dd, J = 13.2 Hz, J = 4.0 Hz, 1H), 4.22-4.07 (m, 4H), 3.04-2.98 (m, 1H), 2.79-2.74 (m, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 1.79-1.73 (m, 1H), 1.27-1.18 (m, 6H) ppm; 13C NMR (100.6 MHz, CDCl₃): δ 170.9, 170.0, 143.8, 142.3, 139.4, 137.1, 135.8, 129.7, 127.0, 126.1, 125.5, 124.8, 120.8, 120.0, 65.3, 61.7, 61.6, 51.5, 39.6, 37.2, 21.7, 21.5, 14.1, 14.0 ppm. HRMS (ESI): m/z Calcd for C₂₆H₂₉NO₆S [M+H⁺]:484.1788, found 484.1786.

**diethyl 7-chloro-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ka).**

Yellow solid; (44.8 mg, 89%); mp: 142-144 °C; R_f = 0.39 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl₃): δ = 7.86 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 9.6 Hz, 2H), 7.09 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 6.13 (d, J = 2.4 Hz, 1H), 4.59 (dd, J = 13.2 Hz, J = 4.8 Hz, 1H), 4.23-4.06 (m, 4H), 3.03-2.96 (m, 1H), 2.83-2.71 (m, 2H), 2.39 (s, 3H), 1.82-1.79 (m, 1H), 1.77-1.73 (m, 1H), 1.28-1.19 (m, 6H) ppm; 13C NMR (100.6 MHz, CDCl₃): δ 170.6, 169.7, 144.3, 141.3, 136.7, 136.5, 134.7, 129.9, 127.0, 126.7, 125.2, 124.0, 121.7, 121.6, 65.3, 61.8, 61.7, 51.2, 39.5, 37.0, 21.6, 14.05, 14.00 ppm. HRMS (ESI): m/z Calcd for C₂₅H₂₇ClNO₆S [M+H⁺]:504.1242, found 504.1243.

**diethyl 3a-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ab).**

Yellow solid; (43.0 mg, 89%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl₃): δ = 7.76 (d, J = 7.6 Hz, 2H), 7.59-7.52 (m, 2H), 7.31-7.29 (m, 2H), 7.17-7.12 (m, 2H), 7.01-6.91 (m, 1H), 6.00 (s, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.32-4.18 (m, 4H), 3.21 (d, J = 8.0 Hz, 1H), 2.74 (d, J = 5.6 Hz, 1H), 2.41 (s, 3H), 2.46 (d, J = 13.6 Hz, 1H), 2.26 (d, J = 13.6 Hz, 1H), 1.31-1.25 (m, 6H), 1.23 (s, 3H) ppm; 13C NMR (100.6 MHz, CDCl₃): δ 171.1, 170.8, 146.8, 143.9, 137.9, 135.6, 129.9, 129.1, 126.9, 126.7, 123.1, 120.6, 119.2, 118.9, 65.0, 61.88, 61.85, 57.5, 43.6, 43.4, 22.6, 21.5, 14.1 ppm. HRMS (ESI): m/z Calcd for C₂₆H₂₇ClNO₆S [M+H⁺]:504.1242, found 504.1243.

**diethyl 4-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ac).**

Yellow solid; (10 mg, 21%); mp: 145-146 °C; R_f = 0.33 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl₃): δ = 7.70 (d, J = 7.6 Hz, 1H), 7.38-7.33 (m, 1H), 7.26-7.18 (m, 4H), 7.04 (d, J = 8.0 Hz, 1H), 5.57 (d, J = 2.8 Hz, 1H), 4.24 (dd, J = 7.2 Hz, J = 3.6 Hz, 1H), 4.22-4.08 (m,
diethyl 4-methyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ac').

Yellow solid; (30 mg, 62%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.81 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.60-7.54 (m, 3H), 7.30-7.26 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.15-7.11 (m, 1H), 6.20 (d, J = 2.4 Hz, 1H), 4.73-4.67 (m, 1H), 4.24-4.05 (m, 4H), 2.94-2.88 (m, 1H), 2.64 (dd, J = 13.2 Hz, J = 7.6 Hz, 1H), 2.37 (s, 3H), 1.94 (dd, J = 13.2 Hz, J = 8.4 Hz, 1H), 1.27-1.19 (m, 6H), 0.98 (d, J = 6.8 Hz, 3H) ppm; ^13C NMR (100.6 MHz, CDCl_3): δ 170.9, 170.0, 143.7, 139.7, 137.2, 133.5, 129.7, 129.3, 127.0, 125.9, 125.3, 124.9, 123.5, 122.3, 65.5, 61.7, 61.6, 53.1, 43.7, 35.3, 21.5, 14.05, 14.00, 13.4 ppm. HRMS (ESI): m/z Calcd for C_{26}H_{29}NO_6S [M+H]^+:484.1788, found 484.1790.

diethyl 4,4-dimethyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3ae').

Yellow solid; (43.3 mg, 87%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.79 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.58-7.55 (m, 3H), 7.30-7.26 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 4.0 Hz, 1H), 5.62 (s, 1H), 4.43-4.38 (m, 1H), 4.37-4.15 (m, 4H), 3.38 (d, J = 16.4 Hz, 1H), 3.02 (d, J = 16.4 Hz, 1H), 2.36 (s, 3H), 1.36 (t, J = 6.8 Hz, 3H), 1.28 (t, J = 6.8 Hz, 3H), 0.89 (s, 3H) ppm; ^13C NMR (100.6 MHz, CDCl_3): δ 171.4, 169.9, 144.4, 143.6, 136.5, 134.5, 133.8, 133.2, 129.4, 129.3, 127.4, 123.8, 119.3, 63.2, 62.4, 61.9, 38.3, 23.7, 21.5, 19.6, 14.2, 14.1 ppm. HRMS (ESI): m/z Calcd for C_{27}H_{31}NO_6S [M+H]^+:498.1945, found 498.1947.

dimethyl 5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate (3af). Yellow solid; (37.0 mg, 84%); mp: 145-146 °C; R_f = 0.32 (petroleum ether/ethyl acetate 3:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.79 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.58-7.55 (m, 3H), 7.28-7.21 (m, 3H), 7.14-7.10 (m, 1H), 6.14 (d, J = 2.0 Hz, 1H), 4.60 (dd, J = 13.2 Hz, J = 4.0 Hz, 1H), 3.75 (s,
ethyl 2-acetyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (3ag). Yellow solid; (10 mg, 22%); mp: 145-146 °C; Rf = 0.35 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.81 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.60-7.55 (m, 3H), 7.28-7.21 (m, 3H), 7.15-7.11 (m, 1H), 6.17 (d, J = 2.0 Hz, 1H), 4.60 (dd, J = 13.2 Hz, J = 4.0 Hz, 1H), 4.20-4.07 (m, 2H), 3.05-2.99 (m, 1H), 2.85-2.77 (m, 2H), 2.38 (s, 3H), 2.20 (s, 3H), 1.68-1.61 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H) ppm; 13C NMR (100.6 MHz, CDCl3): δ 201.3, 171.2, 144.0, 143.0, 136.9, 136.0, 129.8, 129.3, 127.0, 125.6, 125.0, 124.6, 123.3, 120.8, 72.2, 61.8, 51.4, 39.4, 35.8, 26.6, 21.5, 14.1 ppm. HRMS (ESI): m/z Calcd for C24H25NO5S [M+H]+: 440.1526, found 440.1528.

ethyl 2-acetyl-5-tosyl-3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2-carboxylate (3ag'). Yellow solid; (30 mg, 67%); mp: 145-146 °C; Rf = 0.32 (petroleum ether/ethyl acetate 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.79 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.31-7.26 (m, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.07-6.99 (m, 2H), 5.92 (s, 1H), 4.45-4.17 (m, 4H), 3.54-3.49 (m, 1H), 3.15-3.11 (m, 1H), 2.38 (s, 3H), 1.37 (t, J = 3.2 Hz, 3H), 1.32 (s, 3H), 1.29 (t, J = 3.2 Hz, 3H) ppm; 13C NMR (100.6 MHz, CDCl3): δ 170.9, 168.9, 143.9, 141.8, 139.3, 137.9, 136.5, 134.7, 129.6, 129.5, 129.4, 127.3, 126.3, 124.1, 120.2, 119.9, 62.9, 62.1, 43.1, 24.7, 21.6, 14.2, 13.9 ppm. HRMS (ESI): m/z Calcd for C24H25NO5S [M+H]+: 440.1526, found 440.1528.
14.1 ppm. HRMS (ESI): m/z Calcd for C_{26}H_{27}NO_{6}S [M+H^+]:482.1632, found 482.1635.

\[
\text{diethyl 4-butyl-5-tosyl-2H-cyclopenta[c]quinoline-2,2(3H,5H)-dicarboxylate.}
\]
Yellow solid (3ai); (40.8 mg, 78%); mp: 145-146 °C; \( R_f = 0.32 \) (petroleum ether/ethyl acetate 10:1); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.78 \) (d, \( J = 8.0 \) Hz, 1H), 7.67 (d, \( J = 8.4 \) Hz, 2H), 7.31-7.26 (m, 2H), 7.20 (d, \( J = 8.0 \) Hz, 2H), 7.03-7.00 (m, 2H), 5.82 (s, 1H), 4.45-4.17 (m, 4H), 3.50 (d, \( J = 17.6 \) Hz, 1H), 3.14 (d, \( J = 17.6 \) Hz, 1H), 2.37 (s, 3H), 1.56-1.48 (m, 1H), 1.38-1.27 (m, 6H), 0.96-0.98 (m, 1H), 0.90-0.70 (m, 4H), 0.57 (t, \( J = 7.2 \) Hz, 3H) ppm; \(^{13}\text{C} \) NMR (100.6 MHz, CDCl\(_3\)): \( \delta = 170.9, 169.0, 143.9, 141.8, 139.0, 138.0, 136.5, 134.8, 129.6, 129.5, 128.9, 127.4, 127.1, 126.2, 123.8, 119.5, 62.8, 62.7, 62.1, 43.2, 36.4, 31.0, 21.9, 21.5, 14.2, 14.1, 13.4 \) ppm. HRMS (ESI): m/z Calcd for C_{29}H_{33}NO_{6}S [M+H^+]:524.2101, found 524.2103.

\[
\text{diethyl 3,3a,4,5-tetrahydro-2H-cyclopenta[c]quinoline-2,2-dicarboxylate(4).}
\]
Yellow solid; (26.8 mg, 85%); mp: 166-168 °C; \( R_f = 0.38 \) (petroleum ether/ethyl acetate 10:1); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.45 \) (dd, \( J = 7.6 \) Hz, \( J = 1.6 \) Hz, 1H), 7.07-7.03 (m, 1H), 6.69-6.65 (m, 1H), 6.56 (dd, \( J = 8.0 \) Hz, \( J = 1.2 \) Hz, 1H), 6.02 (d, \( J = 2.8 \) Hz, 1H), 4.25-4.14 (m, 4H), 4.10 (s, 1H), 3.53 (dd, \( J = 10.4 \) Hz, \( J = 2.8 \) Hz, 1H), 3.25-3.16 (m, 1H), 2.97-2.91 (m, 2H), 1.89 (dd, \( J = 13.2 \) Hz, \( J = 9.2 \) Hz, 1H), 1.30-1.24 (m, 6H) ppm; \(^{13}\text{C} \) NMR (100.6 MHz, CDCl\(_3\)): \( \delta = 171.6, 170.8, 144.7, 143.7, 129.6, 126.1, 117.6, 116.4, 114.9, 65.8, 61.6, 61.5, 48.0, 41.4, 37.2, 14.13, 14.10 \) ppm. HRMS (ESI): m/z Calcd for C_{18}H_{21}NO_{4} [M+H^+]:316.1543, found 316.1545.
Copies of $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR
Ms-N\(\text{CO}_2\text{Et}\)\(\text{CO}_2\text{Et}\) 3ca

Ms-N\(\text{CO}_2\text{Et}\)\(\text{CO}_2\text{Et}\) 3ca
Ts-N

CO₂Et

CO₂Et

H₃C

3ja

Ts-N

CO₂Et

CO₂Et

H₃C

3ja

N
C
O₂
Et

N
C
O₂
Et

Tₘ

C₃
Ja

Tₘ

C₃
Ja
Ts-\text{N-}CO_2\text{Et}CO_2\text{Et}

3ac'

Ts-\text{N-}CO_2\text{Et}CO_2\text{Et}

3ac'
Ts-N

Ac

CO₂Et

3ag