Aerobic, metal-free synthesis of 6H-chromeno[4,3-b]quinolin-6-ones

Nhan N. H. Ton, Ha V. Dang, Nam T. S. Phan and Tung T. Nguyen*

Faculty of Chemical Engineering, HCMC University of Technology, VNU-HCM

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

Email: tungtn@hcmut.edu.vn

1. General procedure

Products are synthesized following the typical procedure unless notice: a 2-amino carbonyl compound (0.2 mmol) and a 4-hydroxycoumarin derivative or a cyclic 1,3-diketone (0.8 mmol) were added to a pressurized vial equipped with a magnetic stir bar. Subsequently, the mixture was charged with acetic acid (2 mL). The vial was purged with O₂ for 5 min. The reaction mixture was placed into a pre-heated bath (120 °C) and stirred for a given period. The value of temperature shown is of the heating bath. Upon completion, the reaction mixture was cooled to room temperature and added diphenyl ether (34 mg, 0.2 mmol) internal standard. The crude mixture was diluted with ethyl acetate (30 mL). The organic phase was washed with brine (4 x 10 mL). The organic layer was subsequently dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography.
2. Studies of reaction conditions

![Chemical structure](image)

| Entry | Solvent       | Oxidant | Temp. (°C) | Molar ratio | Yield of 1, % |
|-------|---------------|---------|------------|-------------|---------------|
| 1     | TFA           | O₂      | 120        | 2:1         | 78            |
| 2     | AcOH          | O₂      | 120        | 2:1         | 86            |
| 3     | PivOH         | O₂      | 120        | 2:1         | 54            |
| 4     | CH₃CH₂COOH    | O₂      | 120        | 2:1         | 69            |
| 5     | H₂O           | O₂      | 120        | 2:1         | 23            |
| 6d    | AcOH/glycerol | O₂      | 120        | 2:1         | 31            |
| 7     | AcOH          | DTBP    | 120        | 2:1         | 76            |
| 8     | AcOH          | H₂O₂    | 120        | 2:1         | 47            |
| 9     | AcOH          | TBHP    | 120        | 2:1         | 37            |
|       |               |         |            |             |               |
|       |               |         |            |              |               |
| 10    | AcOH          | TBHP in H₂O | 120   | 2:1     | 31            |
| 11    | AcOH          | cumyl   | 120        | 2:1         | 28            |
|       |               |         |            |              |               |
| 12    | AcOH          | tert-butyl | 120 | 2:1    | 18            |
| Entry | Reagents                  | Conditions | Molar Ratio | Yield |
|-------|---------------------------|------------|-------------|-------|
| 13    | AcOH, TEMPO               | 120°C, 2:1 | 18          |
| 14    | AcOH, K$_2$S$_2$O$_8$     | 120°C, 2:1 | 63          |
| 15    | AcOH, O$_2$               | 100°C, 2:1 | 69          |
| 16    | AcOH, O$_2$               | 80°C, 2:1  | 39          |
| 17    | AcOH, O$_2$               | 120°C, 1:1 | 47          |
| 18    | AcOH, O$_2$               | 120°C, 1:2 | 57          |
| 19    | AcOH, O$_2$               | 120°C, 1:3 | 77          |
| 20    | AcOH, O$_2$               | 120°C, 1:4 | 88          |
| 21    | AcOH, O$_2$               | 120°C, 1:4 | 95          |
| 22    | AcOH, O$_2$               | 120°C, 1:4 | 96          |

**Table Notes:**

- Entry [a]: 2-Aminobenzyl alcohol (0.2 mmol), solvent (1 mL), 16 h.
- Molar ratio is of 2-aminobenzyl alcohol:4-hydroxycoumarin.
- Yields are GC yields using diphenyl ether internal standard.
- Acetic acid (0.2 mmol) in glycerol.
- 2 mL solvent.
- 3 mL solvent.
- TFA = trifluoroacetic acid; AcOH = acetic acid; PivOH = pivalic acid; DTBP = di-tert-butylperoxide; TBHP = tert-butylhydrogen peroxide; TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

**3. Details in synthesis of 6H-Chromeno[4,3-\(b\)]quinolin-6-one and copies of NMRs**

**6H-Chromeno[4,3-\(b\)]quinolin-6-one (1, entry 1, Table 2)**
2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 4-hydroxycoumarin (0.8 mmol, 130 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 10:1), 45 mg (92%) of a yellow solid was obtained. This compound is known.\textsuperscript{1}

\[ R_f = 0.4 \text{ (hexanes/EtOAc 10:1)}. \]

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, ppm) \( \delta 9.22 \) (s, 1H), \( 8.79 \) (d, \( J = 7.5 \) Hz, 1H), \( 8.24 \) (d, \( J = 8.4 \) Hz, 1H), \( 8.02 \) (d, \( J = 7.9 \) Hz, 1H), \( 7.92 \) (t, \( J = 7.4 \) Hz, 1H), \( 7.62 \) (dt, \( J = 24.9, 7.6 \) Hz, 2H), \( 7.52 - 7.34 \) (m, 2H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}, ppm) \( \delta 161.4, 152.7, 151.1, 149.7, 141.1, 133.4, 132.4, 129.6, 129.4, 127.4, 127.3, 125.3, 125.0, 119.7, 117.4, 115.8. \)

\textsuperscript{1}Y. Weng, H. Zhou, C. Sun, Y. Xie, W. Su, \textit{J. Org. Chem.} 2017, 82, 9047–9053.
Fig. S1 $^1$H spectrum of 6H-chromeno[4,3-b]quinolin-6-one.
Fig. S2 $^{13}$C spectrum of $6H$-chromeno[4,3-$b$]quinolin-6-one.

If 2-aminobenzyl amine (0.2 mmol, 24 mg) was used, 42 mg (85%) of a yellow solid was also obtained. Characterization of the compound proved that the reaction gave the same product compared to that of 2-aminobenzyl alcohol.

*Scale up for 2 mmol:* To a 100 mL round bottom flask charged with a magnetic stir bar was added 2-aminobenzyl alcohol (2 mmol, 246 mg), 4-hydroxycoumarin (8 mmol, 1.3 g), and acetic acid (10 mL). After purging O$_2$, the flask was capped, placed into a preheated oil bath (120 °C), and vigorously stirred. The reaction was stopped after every
one hour to check the reaction progress and charged O$_2$. After 5 hours, the reaction was cooled to room temperature and diluted with ethyl acetate (50 mL). The organic phase was washed multiple times with brine (4 x 30 mL). The organic layer was subsequently dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography (eluent hexanes/ethyl acetate 10:1) to afford 445 mg (90%) of the pure product.

*Scale up for 50 mmol:* To a 1 L two-necked, round bottom flask equipped with a magnetic stir bar and a reflux condenser was added 2-aminobenzyl alcohol (50 mmol, 6.16 g), 4-hydroxycoumarin (100 mmol, 1.62 g), and acetic acid (250 mL). The flask was capped, connected to an oxygen ballon, placed into a preheated oil bath (120 °C), and vigorously stirred. The reaction was stopped after every two hours to check the reaction progress and charged O$_2$. After 12 hours, the reaction was cooled to room temperature and diluted with ethyl acetate (500 mL). The organic phase was washed multiple times with brine (4 x 100 mL). The organic layer was subsequently dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude solid was recrystallized using a mixture of hexanes/ethyl acetate solvents, affording 11 g (88%) of the yellow crystals.

2-Chloro-6$H$-chromeno[4,3-$b$]quinolin-6-one (2, entry 2, Table 2)
2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 6-chloro-4-hydroxycoumarin (0.8 mmol, 157 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 20:1), 42 mg (76 %) of a yellow solid was obtained. This compound is known.\(^1\) \(R_f = 0.3\) (hexanes/EtOAc 20:1).

\(^1\)H NMR (500 MHz, CDCl\(_3\), ppm) \(\delta\) 9.24 (s, 1H), 8.77 (d, \(J = 2.5\) Hz, 1H), 8.26 (d, \(J = 8.6\) Hz, 1H), 8.05 (d, \(J = 8.2\) Hz, 1H), 7.98 – 7.93 (m, 1H), 7.68 (t, \(J = 7.2\) Hz, 1H), 7.54 (dd, \(J = 8.7, 2.6\) Hz, 1H), 7.35 (d, \(J = 8.7\) Hz, 1H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), ppm) \(\delta\) 160.9, 151.1, 148.5, 141.3, 133.7, 132.3, 130.7, 129.7, 129.5, 127.9, 127.6, 124.9, 121.0, 118.9, 115.6. One carbon signal could not be located.

**Fig. S3** \(^1\)H spectrum of 2-chloro-6\(H\)-chromeno[4,3-\(b\)]quinolin-6-one.
**Fig. S4** $^{13}$C spectrum of 2-chloro-6$H$-chromeno[4,3-$b$]quinolin-6-one.

**2-Bromo-6$H$-chromeno[4,3-$b$]quinolin-6-one (3, entry 3, Table 2)**

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 6-bromo-4-hydroxycoumarin (0.8 mmol, 193 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 20:1), 51 mg (78 %) of a yellow solid was obtained. Due to poor solubility, the compound was characterized in a mixture of CDCl$_3$ dropped small amount of acetone.
$R_f = 0.3$ (hexanes/EtOAc 20:1).

$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 9.25 (s, 1H), 8.94 (d, $J = 2.4$ Hz, 1H), 8.27 (d, $J = 8.7$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.97 (s, 1H), 7.73 – 7.66 (m, 2H), 7.30 (d, $J = 8.7$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 160.8, 151.6, 151.1, 141.3, 135.1, 133.7, 129.7, 129.5, 128.0, 127.9, 127.6, 121.4, 119.2, 118.1, 115.6. One carbon signal could not be located.

HRMS cacld. for $C_{16}H_8BrNaO_2$ [M + Na]$^+$: 347.9631; found: 347.9628.

**Fig. S5** $^1$H spectrum of 2-bromo-6$H$-chromeno[4,3-$b$]quinolin-6-one.
2-Methyl-6H-chromeno[4,3-b]quinolin-6-one (4, entry 4, Table 2)

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 6-methyl-4-hydroxycoumarin (0.8 mmol, 141 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 15:1), 44 mg (85%) of a yellow solid was obtained. This compound is known. A small amount (~7%) of an unidentified impurity raised from 2-aminobenzyl alcohol could not be completely removed.

Fig. S6 $^{13}$C spectrum of 2-bromo-6H-chromeno[4,3-b]quinolin-6-one.
$R_f = 0.4$ (hexanes/EtOAc 15:1).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.22 (s, 1H), 8.58 (s, 1H), 8.25 (d, $J = 8.6$ Hz, 1H), 8.02 (d, $J = 8.2$ Hz, 1H), 7.92 (t, $J = 7.7$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.29 (d, $J = 8.3$ Hz, 1H), 2.52 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 161.6, 151.1, 150.9, 149.8, 141.2, 134.8, 133.37, 133.36, 129.51, 129.47, 127.36, 127.32, 125.0, 119.2, 117.2, 115.9, 21.0.

**Fig. S7** $^1$H spectrum of 2-methyl-$6H$-chromeno[4,3-$b$]quinolin-6-one.
Fig. S8 $^{13}$C spectrum of 2-methyl-6H-chromeno[4,3-b]quinolin-6-one.

2-ethyl-6H-chromeno[4,3-b]quinolin-6-one (5, entry 5, Table 2)

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 6-ethyl-4-hydroxycoumarin (0.8 mmol, 152 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 20:1), 46 mg (84%) of a light yellow solid was obtained.

$R_f = 0.3$ (hexanes/EtOAc 20:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 9.24 (s, 1H), 8.61 (d, $J = 2.0$ Hz, 1H), 8.26 (d, $J = 8.6$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.93 (ddd, $J = 8.4, 6.9, 1.3$ Hz, 1H), 7.68 – 7.62 (m, 1H), 7.44 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 2.83 (q, $J = 7.6$ Hz, 2H), 1.36 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 161.6, 151.1, 151.0, 149.9, 141.2, 133.3, 132.3, 129.52, 129.46, 127.34, 127.28, 123.9, 119.3, 117.3, 115.9, 28.5, 15.8. One carbon signal could not be located.

HRMS cacld. for C$_{18}$H$_{14}$NO$_2$ [M + H]$^+$: 276.1019; found: 276.1025.

Fig. S9 $^1$H spectrum of 2-ethyl-6$H$-chromeno[4,3-b]quinolin-6-one.
Fig. S10 $^{13}$C spectrum of 2-ethyl-6H-chromeno[4,3-b]quinolin-6-one.

3-Methyl-6H-chromeno[4,3-b]quinolin-6-one (6, entry 6, Table 2)

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 7-methyl-4-hydroxycoumarin (0.8 mmol, 141 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 15:1), 45 mg (86%) of a yellow solid was obtained.

$R_f = 0.4$ (hexanes/EtOAc 15:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 9.21 (s, 1H), 8.65 (d, $J$ = 8.0 Hz, 1H), 8.22 (d, $J$ = 8.6 Hz, 1H), 8.01 (d, $J$ = 8.1 Hz, 1H), 7.91 (ddd, $J$ = 8.4, 6.9, 1.3 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.26 (d, overlapping with CHCl$_3$ signal, 1H), 7.20 (s, 1H), 2.50 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 161.7, 152.7, 151.2, 149.9, 143.6, 141.1, 133.3, 129.48, 129.46, 127.2, 126.2, 125.0, 117.6, 117.1, 115.6, 21.8. One carbon signal could not be located.

HRMS cacl. for $C_{17}H_{12}NO_2$ [M + H]$^+$: 262.0863; found: 262.0858.

Fig. S11 $^1$H spectrum of 3-methyl-6$H$-chromeno[4,3-$b$]quinolin-6-one.
3-Methoxy-6H-chromeno[4,3-b]quinolin-6-one (7, entry 7, Table 2)

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 7-methoxy-4-hydroxycoumarin (0.8 mmol, 154 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 20:1), 41 mg (75%) of a yellow solid was obtained.

R<sub>f</sub> = 0.4 (hexanes/EtOAc 20:1).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.18 (s, 1H), 8.68 (d, $J = 8.8$ Hz, 1H), 8.20 (d, $J = 8.6$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.90 (dd, $J = 11.3$, 4.2 Hz, 1H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.00 (dd, $J = 8.8$, 2.4 Hz, 1H), 6.88 (d, $J = 2.4$ Hz, 1H), 3.93 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 163.2, 161.7, 154.1, 151.3, 149.9, 141.2, 133.3, 129.5, 129.3, 126.91, 126.89, 126.5, 115.0, 112.77, 112.75, 101.4, 55.8.

HRMS cacld. for C$_{17}$H$_{12}$NO$_3$ [M + H]$^+$: 278.0812; found: 278.0808.

**Fig. S13** $^1$H spectrum of 3-methoxy-6$H$-chromeno[4,3-b]quinolin-6-one.
Fig. S14 $^{13}$C spectrum of 3-methoxy-6H-chromeno[4,3-b]quinolin-6-one.

5-Methyl dibenzo[b,h][1,6]naphthyridin-6(5H)-one (8, entry 8, Table 2)

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 4-hydroxy-1-methylquinolin-2(1H)-one (0.8 mmol, 140 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 5:1), 46 mg (89%) of a yellow solid was obtained. $R_f = 0.4$ (hexanes/EtOAc 5:1). This compound is known.$^2$
$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 9.32 (s, 1H), 9.09 (dd, $J = 8.1$, 1.6 Hz, 1H), 8.25 (d, $J = 8.6$ Hz, 1H), 8.05 (d, $J = 8.1$ Hz, 1H), 7.87 (dd, $J = 8.4$, 6.8, 1.3 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.41 (dd, $J = 7.8$, 5.6 Hz, 2H), 3.82 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 161.9, 150.3, 149.2, 139.7, 138.8, 132.1, 131.6, 129.4, 129.2, 127.3, 126.7, 125.9, 123.0, 121.1, 119.5, 114.7, 29.9.

Fig. S15 $^1$H spectrum of 5-methyldibenzo[$b,h$][1,6]naphthyridin-6(5$H$)-one.

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2 R. R. Rajawinslin, S. D. Gawande, V. Kavala, Y.-H. Huang, C.-W. Kuo, T.-S. Kuo, M.-L. Chen, C.-H. He, C.-F. Yao, *RSC Adv.* 2014, 4, 37806–37811.
**Fig. S16** $^{13}$C spectrum of 5-methyldibenzo[$b,h$][1,6]naphthyridin-6($5H$)-one.

**9-Chloro-$6H$-chromeno[4,3-$b$]quinolin-6-one (9, entry 9, Table 2)**

2-Amino-4-chlorobenzyl alcohol (0.2 mmol, 32 mg), 4-hydroxycoumarin (0.8 mmol, 130 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 10:1), 46 mg (81%) of a yellow solid was obtained. This compound is known.$^1$

$R_f = 0.4$ (hexanes/EtOAc 10:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 9.18 (s, 1H), 8.73 (d, $J = 7.7$ Hz, 1H), 8.22 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 161.0, 152.8, 151.3, 150.6, 140.9, 139.8, 132.8, 130.5, 128.7, 128.6, 125.6, 125.4, 125.1, 119.3, 117.5, 115.9.

**Fig. S17** $^1$H spectrum of 9-chloro-6$H$-chromeno[4,3-$b$]quinolin-6-one.
**Fig. S18** $^{13}$C spectrum of 9-chloro-6$H$-chromeno[4,3-\textit{b}]quinolin-6-one.

11-Methyl-6$H$-chromeno[4,3-\textit{b}]quinolin-6-one (10, entry 10, Table 2)

2-Amino-3-methylbenzyl alcohol (0.2 mmol, 27 mg), 4-hydroxycoumarin (0.8 mmol, 130 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 20:1), 46 mg (90%) of a yellow solid was obtained. This compound is known.$^{1}$

$R_f = 0.4$ (hexanes/EtOAc 20:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 9.04 (s, 1H), 8.70 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.75 (d, $J$ = 8.2 Hz, 1H), 7.67 (d, $J$ = 6.9 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.49 – 7.42 (m, 1H), 7.38 (t, $J$ = 7.4 Hz, 1H), 7.32 (d, $J$ = 8.2 Hz, 1H), 2.85 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) δ 161.6, 152.7, 150.1, 148.4, 141.1, 137.8, 133.2, 132.1, 127.34, 127.31, 127.2, 125.2, 124.9, 120.1, 117.4, 115.4, 17.9.

Fig. S19 $^1$H spectrum of 11-methyl-6$H$-chromeno[4,3-]$b$quinolin-6-one.
Fig. S20 $^{13}$C spectrum of 11-methyl-6H-chromeno[4,3-b]quinolin-6-one.

7-Phenyl-6H-chromeno[4,3-b]quinolin-6-one (11, entry 11, Table 2)

2-Aminobenzhydrol (0.2 mmol, 40 mg), 4-hydroxycoumarin (0.8 mmol, 130 mg), AcOH (2.0 mL), 120 °C, 3 h. After column chromatography (hexanes/ethyl acetate 10:1), 56 mg (86 %) of a yellow solid was obtained. This compound is known.$^3$

$R_f = 0.4$ (hexanes/EtOAc 10:1).

$^3$ D. Garella, A. Barge, D. Upadhyaya, Z. Rodríguez, G. Palmisano, G. Cravotto, *Synth. Commun.* **2010**, *40*, 120–128.
$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 8.87 (dd, $J$ = 7.9, 1.5 Hz, 1H), 8.26 (d, $J$ = 8.5 Hz, 1H), 7.88 (ddd, $J$ = 8.2, 6.7, 1.3 Hz, 1H), 7.60 – 7.51 (m, 5H), 7.51 – 7.46 (m, 1H), 7.45 – 7.40 (m, 1H), 7.33 (d, $J$ = 8.2 Hz, 1H), 7.31 – 7.28 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 159.4, 155.6, 152.7, 150.4, 150.1, 137.0, 132.8, 132.3, 129.5, 128.28, 128.25, 128.1, 128.03, 127.94, 127.1, 125.7, 124.6, 119.86, 117.0, 113.2.

Fig. S21 $^1$H spectrum of 7-phenyl-6$H$-chromeno[4,3-\textit{b}]quinolin-6-one.
Fig. S22 $^{13}$C spectrum of 7-phenyl-6$H$-chromeno[4,3-$b$]quinolin-6-one.

7-Methyl-6$H$-chromeno[4,3-$b$]quinolin-6-one (12, Scheme 3)

2’-Aminoacetophenone (2.0 mmol, 270 mg), 4-hydroxycoumarin (0.5 mmol, 81 mg), AcOH (5 mL), 120 °C, 24 h. After column chromatography (hexanes/ethyl acetate 25:1), 48 mg (37 %) of a yellow solid was obtained.

$R_f = 0.4$ (hexane/EtOAc 25:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 8.79 (dd, $J = 7.9$, 1.2 Hz, 1H), 8.30 (d, $J = 8.6$ Hz, 1H), 8.18 (d, $J = 8.4$ Hz, 1H), 7.87 (t, $J = 7.6$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.56 (td, $J = 7.5$, 1.5 Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.2$ Hz, 1H), 3.32 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 161.0, 154.6, 152.4, 150.0, 149.7, 132.6, 132.1, 130.3, 127.9, 127.0, 125.7, 125.4, 124.6, 119.9, 116.7, 114.1, 16.9.

Fig. S23 $^1$H spectrum of 7-methyl-$6H$-chromeno[4,3-$b$]quinolin-6-one.
Fig. S24 $^{13}$C spectrum of 7-methyl-6$H$-chromeno[4,3-$b$]quinolin-6-one.

11$H$-Indeno[1,2-$b$]quinolin-11-one (13, Scheme 3)

2-Aminobenzyl alcohol (0.2 mmol, 25 mg), 1,3-indanedione (0.4 mmol, 58.5 mg), AcOH (2.0 mL), 120 °C, 24 h. After column chromatography (hexanes/ethyl acetate 30:1), 32 mg (70 %) of an orange solid was obtained. This compound is known.$^2$
$R_f = 0.4$ (hexane/EtOAc 30:1).

$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 8.35 (s, 1H), 8.09 (dd, $J = 11.5$, 8.0 Hz, 2H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 7.4$ Hz, 1H), 7.76 (td, $J = 7.8$, 1.5 Hz, 1H), 7.68 (td, $J = 7.5$, 0.8 Hz, 1H), 7.52 (dt, $J = 13.2$, 4.1 Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 190.9, 162.1, 150.7, 143.9, 137.5, 135.6, 132.5, 132.1, 131.6, 130.5, 129.9, 127.7, 127.3, 127.1, 124.2, 121.9.

Fig. S25 $^1$H spectrum of 11$H$-indenoo[1,2-$b$]quinolin-11-one.
Fig. S26 $^{13}$C spectrum of 11H-indeno[1,2-b]quinolin-11-one.

3,4-Dihydroacridin-1(2H)-one (14, Scheme 3)

$\text{R}_f = 0.4$ (hexane/EtOAc 25:1).
$^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 8.86 (s, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.94 (d, $J = 8.1$ Hz, 1H), 7.85 – 7.78 (t, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 3.36 – 3.30 (m, 2H), 2.84 – 2.78 (m, 2H), 2.32 – 2.24 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 197.9, 162.0, 149.7, 137.1, 132.3, 129.7, 128.6, 126.8, 126.7, 126.3, 39.1, 33.5, 21.8.

Fig. S27 $^1$H spectrum of 3,4-dihydroacridin-1(2H)-one.
Fig. S28 $^{13}$C spectrum of 3,4-dihydroacridin-1(2H)-one.

5-Methyl-3,4-dihydroacridin-1(2H)-one (15, Scheme 3)

2-Amino-3-methylbenzyl alcohol (0.2 mmol, 27 mg), cyclohexane-1,3-dione (0.4 mmol, 45 mg), AcOH (2.0 mL), 30 °C, 24 h. After column chromatography (hexanes/ethyl acetate 20:1), 23 mg (55 %) of a light yellow solid was obtained. $R_f = 0.7$ (hexanes/EtOAc 10:1).
^1H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 8.79 (s, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.63 (d, $J = 7.0$ Hz, 1H), 7.42 (dd, $J = 8.0$, 7.0 Hz, 1H), 3.35 – 3.29 (m, 2H), 2.83 – 2.75 (m, 2H), 2.80 (s, 3H), 2.29 – 2.22 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm) $\delta$ 198.3, 160.9, 148.8, 137.1, 136.7, 132.3, 127.7, 126.8, 126.3, 126.0, 39.2, 33.7, 21.9, 17.9.

![Fig. S29 $^1$H spectrum of 5-methyl-3,4-dihydroacridin-1(2H)-one.](image-url)
Fig. S30 $^{13}$C spectrum of 5-methyl-3,4-dihydroacridin-1(2H)-one.

4. List of substrates which gave unacceptable yields or no products.

Fig. S31 Unreacting substrates.