Supporting Information

One-pot approach to pyrido-4-phenanthridinones via Pd-catalyzed annulation of 4-quinolones with 2-bromobenzyl bromides

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**Experimental**

**Materials and methods**

All the chemicals used for synthesis were commercially purchased and used without further purification. The $^1$H and $^{13}$C NMR spectra were recorded in DMSO on a 400 MHz, 100 MHz Bruker spectrometers respectively. Chemical shifts are given in parts per million ($\delta$-scale) and coupling constants are given in Hertz (Hz). The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). IR spectra was recorded on an FT-IR (Bruker). Melting points were recorded on METTLER FP 51 apparatus in open capillary tubes and these are uncorrected. Elemental analyses were conducted on a Perkin Elmer 2400 series II Elemental CHNS analyser. LC-MS analyses were performed on waters Q-TOF micro mass spectrometer. The reaction courses were monitored by TLC on silica gel precoated F254 Merck plates. Developed plates were examined with UV lamps (254 nm).

**General procedure for the synthesis of phenanthridinone derivatives**

To a mixture of 4-quinolones 1 (1 mmol), 2-bromobenzyl bromides 5/8 (1.5 mmol) and $K_2$CO$_3$ (2 mmol) in dry DMF (3 ml) was stirred for 2 h at 80 °C. After the solution was cooled to room temperature, TBAB (1.5 equiv), $K_2$CO$_3$ (1.5 equiv), and Pd(OAc)$_2$ (10 mol %) were added to the reaction vessel under argon, and the mixture was heated at 80 °C for 3 h. After completion of the reaction, the mixture was cooled and diluted with water. This was extracted with EtOAc. The combined organic extracts were washed with water and the brine solution, dried with anhydrous Na$_2$SO$_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel with chloroform/methanol (9:1 v/v) as eluent to give the desired products.
X-ray crystal structure of compound 11b (CCDC 1848481)

X-ray crystal structure of compound 11d (CCDC 1848482)
4-Oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7a)

White solid, 0.126 g (90%), mp 222-224 °C; IR (KBr) νmax 3433, 2922, 1673, 1619 cm⁻¹;
¹H NMR (400 MHz, DMSO-d₆): δ 8.66 (s, 1H, ArH), 8.39 (dd, 1H, J = 1.6, 7.6 Hz, ArH), 8.15
(dd, 1H, J = 1.2, 8.4 Hz, ArH), 8.08 (d, 1H, J = 8.0 Hz, ArH), 7.51 (t, 1H, J = 7.6 Hz, ArH), 7.48-7.41
(m, 2H, ArH), 7.35 (d, 1H, J = 7.6 Hz, ArH), 5.53 (s, 2H, N-CH₂), 4.26 (q, 2H, J = 7.6 Hz,
CH₂), 1.30 (t, 3H, J = 6.8 Hz, CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 173.1, 164.8, 148.8, 136.2,
129.9, 129.5, 129.0, 128.7, 128.3, 126.76, 126.70, 126.4, 125.7, 125.0, 123.7, 111.6, 60.4, 53.2,
15.1; Mass (ESI) m/z; 305.1 [M]+; Anal. Calcd for C₁₉H₁₅NO₃: C, 74.74; H, 4.95; N, 4.59 %;
Found. C, 74.70; H, 4.92; N, 4.64 %.

2-Fluoro-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7b)

Light yellow solid, 0.117 g (85%), mp 230-232 °C; IR (KBr) νmax 3423, 2924, 1721, 1603
cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.67 (s, 1H, ArH), 8.34 (dd, 1H, J = 3.2, 6.4 Hz, ArH),
8.15-8.13 (m, 1H, ArH), 7.78 (dd, 1H, J = 3.2, 5.6 Hz, ArH), 7.49-7.46 (m, 2H, ArH), 7.36 (t, 1H,
J = 4.8 Hz, ArH), 5.56 (s, 2H, N-CH₂), 4.26 (q, 2H, J = 6.8 Hz, CH₂), 1.30 (t, 3H, J = 6.4 Hz,
CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 172.8, 165.2, 161.1, 158.7, 150.9, 136.3, 134.8, 133.6,
130.5, 130.3, 128.8, 128.2, 122.1, 121.7, 121.4, 120.9, 120.8, 111.6, 111.4, 110.4, 60.2, 56.8, 14.7;
HRMS (TOF-ES+) m/z [M+H]+ calcd for C₁₀H₁₄FNO₃ 323.0958, found 324.0253.

2-Chloro-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7c)

White solid, 0.116 g (86%), mp 226-228 °C; IR (KBr) νmax 3458, 2929, 1680, 1630 cm⁻¹;
¹H NMR (400 MHz, DMSO-d₆): δ 8.67 (s, 1H, ArH), 8.44 (d, 1H, J = 2.4 Hz, ArH), 8.16 (t, 1H,
J = 5.6 Hz, ArH), 8.02 (d, 1H, J = 2.8 Hz, ArH), 7.47 (t, 2H, J = 4.4 Hz, ArH), 7.35 (t, 1H, J = 4.4
Hz, ArH), 5.55 (s, 2H, N-CH₂), 4.26 (q, 2H, J = 6.8 Hz, CH₂), 1.30 (t, 3H, J = 7.2 Hz, CH₃); ¹³C
APT (100 MHz, DMSO-d₆): δ 172.2, 164.8, 149.4, 135.3, 131.0, 130.2, 129.9, 129.1, 127.7, 127.1,
126.8, 126.4, 124.9, 124.3, 111.4, 60.5, 53.1, 14.7; Anal. Calcd for C₁₀H₁₄ClNO₃: C, 67.16; H,
4.15; N, 4.12 %; Found. C, 67.13; H, 4.14; N, 4.17 %.

2-Ethoxy-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7d)

Yellow solid, 0.104 g (78%), mp 243-245 °C; IR (KBr) νmax 3421, 2930, 1720, 1609 cm⁻¹;
¹H NMR (400 MHz, DMSO-d₆): δ 8.58 (s, 1H, ArH), 8.12-8.09 (m, 1H, ArH), 7.93 (d, 1H, J = 2.8
Hz, ArH), 7.53 (d, 1H, J = 2.8 Hz, ArH), 7.44-7.42 (m, 2H, ArH), 7.32 (t, 1H, J = 4.4 Hz, ArH),
5.52 (s 2H, N-CH₂), 4.28-4.16 (m, 4H, CH₂), 1.41 (t, 3H, J = 6.4 Hz, CH₃), 1.30 (t, 3H, J = 6.8
Hz, CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 172.9, 156.7, 149.2, 135.1, 133.7, 133.5, 131.5, 130.3,
Anal. Calcd for C$_{21}$H$_{19}$NO$_4$: C, 72.19; H, 5.48; N, 4.01 %; Found. C, 72.16; H, 5.46; N, 4.05 %.

2-Methoxy-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthidine-5-carboxylic acid ethyl ester (7e)

Light brown solid, 0.108 g (80%), mp 220-222 °C; IR (KBr) $\nu_{\text{max}}$ 3410, 2920, 1675, 1615 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 8.61 (s, 1H, ArH), 8.14-8.12 (m, 1H, ArH), 7.99 (d, 1H, $J = 2.8$ Hz, ArH), 7.58 (d, 1H, $J = 3.6$ Hz, ArH), 7.46-7.44 (m, 2H, ArH), 7.35-7.33 (m, 1H, ArH), 5.54 (s, 2H, N-CH$_2$), 4.25 (q, 2H, $J = 7.2$ Hz, CH$_2$), 3.92 (s, 3H, OCH$_3$), 1.30 (t, 3H, $J = 7.2$ Hz, CH$_3$); $^{13}$C APT (100 MHz, DMSO-$_d_6$): $\delta$ 172.8, 164.9, 157.6, 147.6, 130.8, 130.3, 129.7, 129.0, 127.9, 126.9, 126.7, 124.2, 115.8, 110.2, 106.8, 70.45, 56.17, 53.17, 15.0; Anal. Calcd for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18 %; Found. C, 71.58; H, 5.09; N, 4.23 %.

4-Oxo-2-trifluoromethyl-4H,8H-pyrido[3,2,1-de]phenanthidine-5-carboxylic acid ethyl ester (7f)

White solid, 0.098 g (75%), mp 233-235 °C; IR (KBr) $\nu_{\text{max}}$ 3455, 2928, 1678, 1626 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 8.74 (s, 1H, ArH), 8.64 (d, 1H, $J = 2.0$ Hz, ArH), 8.35 (d, 1H, $J = 1.2$ Hz, ArH), 8.28 (t, 1H, $J = 4.4$ Hz, ArH), 7.50-7.48 (m, 2H, ArH), 7.38-7.35 (m, 1H, ArH), 5.60 (s, 2H, N-CH$_2$), 4.27 (q, 2H, $J = 7.6$ Hz, CH$_2$), 1.31 (t, 3H, $J = 7.2$ Hz, CH$_3$); $^{13}$C APT (100 MHz, DMSO-$_d_6$): $\delta$ 172.4, 161.5, 149.9, 130.4, 130.2, 129.2, 126.8, 124.6, 112.5, 109.1, 70.26, 60.68, 52.98, 14.84; Anal. Calcd for C$_{20}$H$_{14}$F$_3$NO$_3$: C, 64.34; H, 3.78; N, 3.75 %; Found. C, 64.30; H, 3.75; N, 3.80 %.

4-Oxo-2-trifluoromethoxy-4H,8H-pyrido[3,2,1-de]phenanthidine-5-carboxylic acid ethyl ester (7g)

White solid, 0.090 g (70%), mp 219-221 °C; IR (KBr) $\nu_{\text{max}}$ 3428, 2923, 1718, 1607 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 8.71 (s, 1H, ArH), 8.41 (d, 1H, $J = 2.4$ Hz, ArH), 8.18 (t, 1H, $J = 4.8$ Hz, ArH), 7.95 (d, 1H, $J = 1.6$ Hz, ArH), 7.49 (t, 2H, $J = 7.2$ Hz, ArH), 7.37 (t, 1H, $J = 4.4$ Hz, ArH), 5.58 (s, 2H, N-CH$_2$), 4.26 (q, 2H, $J = 7.2$ Hz, CH$_2$), 1.30 (t, 3H, $J = 7.2$ Hz, CH$_3$); $^{13}$C APT (100 MHz, DMSO-$_d_6$): $\delta$ 172.3, 164.6, 149.5, 146.2, 135.0, 130.5, 130.3, 129.8, 129.2, 128.3, 127.0, 126.8, 124.5, 121.9, 120.1, 116.6, 111.4, 70.1, 60.5, 53.0, 14.6; Anal. Calcd for C$_{20}$H$_{14}$F$_3$NO$_4$: C, 61.70; H, 3.62; N, 3.60 %; Found. C, 61.67; H, 3.59; N, 3.64 %.

1,2-Difluoro-4-Oxo-4H,8H-pyrido[3,2,1-de]phenanthidine-5-carboxylic acid ethyl ester (7h)

White solid, 0.097 g (65%), mp 228-230 °C; IR (KBr) $\nu_{\text{max}}$ 3435, 2923, 1678, 1621 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 8.72 (s, 1H, ArH), 8.14 (t, 1H, $J = 4.4$ Hz, ArH), 8.00 (t, 1H, $J$
= 8.8 Hz, ArH), 7.54-7.52 (m, 2H, ArH), 7.45-7.42 (m, 1H, ArH), 5.49 (s, 2H, N-CH₂), 4.26 (q, 2H, J = 7.2 Hz, CH₂), 1.30 (s, 3H, J = 7.6 Hz, CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 164.4, 162.0, 156.2, 149.4, 142.0, 133.8, 133.6, 131.0, 130.5, 129.4, 127.2, 127.0, 112.6, 112.4, 111.3, 60.57, 53.41, 15.0; Anal. Calcd for C₁₉H₁₃F₂NO₃: C, 66.86; H, 3.84; N, 4.10 %; Found. C, 66.81; H, 3.80; N, 4.15 %.

1,2-Dichloro-4-Oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7i)

White solid, 0.081 g (62%), mp 245-247 °C; IR (KBr) v max 3435, 2929, 1671, 1622 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.76 (s, 1H, ArH), 8.48-8.46 (m, 1H, ArH), 8.23 (s, 1H, ArH), 7.55-7.52 (m, 2H, ArH), 7.49-7.47 (m, 1H, ArH), 5.33 (s, 2H, N-CH₂), 4.25 (q, 2H, J = 7.6 Hz, CH₂), 1.29 (t, 3H, J = 6.8 Hz, CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 164.5, 150.7, 134.5, 133.6, 133.2, 130.4, 128.9, 128.4, 122.6, 114.6, 114.5, 111.0, 107.5, 107.2, 97.8, 60.6, 56.6, 14.7; Anal. Calcd for C₁₉H₁₃Cl₂NO₃: C, 60.98; H, 3.50; N, 3.74 %; Found. C, 60.95; H, 3.47; N, 3.80 %.

1,2-Dimethoxy-4-Oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7j)

White solid, 0.079 g (60%), mp 234-236 °C; IR (KBr) v max 3460, 2926, 1686, 1631 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.45 (s, 1H, ArH), 8.28 (d, 1H, J = 8.0 Hz, ArH), 7.38-7.34 (m, 1H, ArH), 7.31-7.29 (m, 2H, ArH), 6.77 (s, 1H, ArH), 5.14 (s, 2H, N-CH₂), 4.19 (q, 2H, J = 8.4 Hz, CH₂), 4.09 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 1.27 (t, 3H, J = 8.0 Hz, CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 165.1, 147.6, 141.0, 129.6, 128.9, 128.3, 127.2, 126.4, 126.0, 113.2, 70.27, 60.67, 60.09, 56.75, 56.57, 54.18, 14.84; Anal. Calcd for C₂₁H₁₉NO₃: C, 69.03; H, 5.24; N, 3.83 %; Found. C, 69.01; H, 5.20; N, 3.87 %.

10-Fluoro-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7k)

White solid, 0.104 g (70%), mp 242-244 °C; IR (KBr) v max 3420, 2930, 1715, 1607 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.80 (s, 1H, ArH), 8.14 (t, 1H, J = 9.2 Hz, ArH), 7.77 (d, 1H, J = 6.0 Hz, ArH), 7.71 (dd, 1H, J = 4.8, 6.0 Hz, ArH), 7.33-7.31 (m, 2H, ArH), 6.86 (d, 1H, J = 7.2 Hz, ArH), 5.64 (s, 2H, N-CH₂), 4.22 (q, 2H, J = 7.2 Hz, CH₂), 1.26 (t, 3H, J = 8.0 Hz, CH₃); ¹³C APT (100 MHz, DMSO-d₆): δ 164.7, 161.5, 159.2, 148.8, 130.3, 129.1, 127.4, 126.7, 124.4, 115.2, 114.9, 110.7, 110.6, 110.4, 60.5, 53.1, 14.7; Anal. Calcd for C₁₉H₁₄FNO₃: C, 70.58; H, 4.36; N, 4.33 %; Found. C, 70.53; H, 4.34; N, 4.38 %.

10-Chloro-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7l)

White solid, 0.102 g (65%), mp 247-249 °C; IR (KBr) v max 3418, 2925, 1720, 1604 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 8.53 (s, 1H, ArH), 8.45 (d, 1H, J = 2.5 Hz, ArH), 7.52-7.49 (m, 2H,
ArH), 7.18 (dd, 1H, J = 1.5, 6.5 Hz, ArH), 7.11 (d, 1H, J = 9.0 Hz, ArH), 6.72 (d, 1H, J = 8.5 Hz, ArH), 5.42 (s, 2H, N-CH₂), 4.38 (q, 2H, J = 7.2 Hz, CH₂), 1.40 (t, 3H, J = 7.0 Hz, CH₃); ¹³C NMR (125.7 MHz, CDCl₃): δ 173.0, 165.0, 149.5, 137.2, 135.4, 133.1, 133.0, 131.8, 130.1, 130.0, 128.1, 128.0, 127.4, 117.8, 111.9, 61.1, 54.4, 14.3; Anal. Calcd for C₁₉H₁₄ClNO₃: C, 67.16; H, 4.15; N, 4.12 %; Found. C, 67.13; H, 4.10; N, 4.15 %.

10-Methoxy-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7m)

White solid, 0.120 g (78%), mp 242-244 ºC; IR (KBr) νmax 3458, 2926, 1709, 1624 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.80 (s, 1H, ArH), 7.93 (dd, 1H, J = 2.8, 6.0 Hz, ArH), 7.66-7.61 (m, 2H, ArH), 7.53 (dd, 1H, J = 4.4, 5.2 Hz, ArH), 6.92 (dd, 1H, J = 2.8, 6.0 Hz, ArH), 6.35 (d, 1H, J = 3.2 Hz, ArH), 5.62 (s, 2H, N-CH₂), 4.23 (q, 2H, J = 6.8 Hz, CH₂), 3.62 (s, 3H, OCH₃), 1.27 (t, 3H, J = 7.2 Hz, CH₃); ¹³C NMR (100 MHz, DMSO-d₆): δ 172.1, 159.0, 149.8, 135.7, 135.1, 134.0, 129.9, 121.2, 121.0, 120.3, 120.2, 114.7, 114.6, 111.9, 111.1, 110.9, 109.8, 59.9, 56.0, 55.3, 14.1; Anal. Calcd for C₂₀H₁₇NO₄: C, 71.63; H, 5.11; N, 4.18 %; Found. C, 71.59; H, 5.10; N, 4.22 %.

10-Methoxy-4-oxo-2-trifluoromethyl-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7n)

White solid, 0.104 g (74%), mp 224-226 ºC; IR (KBr) νmax 3451, 2923, 1702, 1602 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.67 (s, 1H, ArH), 8.43 (s, 1H, ArH), 8.23 (s, 1H, ArH), 8.14 (d, 1H, J = 8.8 Hz, ArH), 7.02 (dd, 1H, J = 2.0, 6.8 Hz, ArH), 6.89 (s, 1H, ArH), 5.51 (s, 2H, N-CH₂), 4.27 (q, 2H, J = 7.2 Hz, CH₂), 3.84 (s, 3H, OCH₃), 1.31 (t, 3H, J = 7.2 Hz, CH₃); ¹³C NMR (100 MHz, DMSO-d₆): δ 171.9, 164.5, 160.4, 149.3, 149.1, 137.2, 131.3, 127.8, 126.5, 125.7, 125.4, 122.5, 121.2, 120.7, 119.0, 114.7, 111.9, 111.5, 110.9, 60.0, 55.4, 52.6, 14.2; HRMS (TOF-ES+) m/z [M+H]+ calcd for C₂₁H₁₆F₃NO₄ 403.1031, found 404.0100.

2-Ethoxy-10-Methoxy-4-oxo-4H,8H-pyrido[3,2,1-de]phenanthridine-5-carboxylic acid ethyl ester (7o)

Yellow solid, 0.079 g (55%), mp 227-229 ºC; IR (KBr) νmax 3433, 2924, 1690, 1606 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 8.55 (s, 1H, ArH), 8.01 (d, 1H, J = 6.8 Hz, ArH), 7.77 (s, 1H, ArH), 7.44 (s, 1H, ArH), 6.99 (d, 1H, J = 8.0 Hz, ArH), 6.87 (s, 1H, ArH), 5.45 (s, 2H, N-CH₂), 4.23 (m, 4H, CH₂), 3.77 (s, 3H, OCH₃), 1.34 (m, 6H, CH₃); Anal. Calcd for C₂₂H₂₁NO₄: C, 69.64; H, 5.58; N, 3.69 %; Found. C, 69.60; H, 5.53; N, 3.75 %.
4-Oxo-4H,7H-9,11-dioxo-6a-aza-benzo[fg]cyclopenta[b]anthracene-5-carboxylic acid ethyl ester (9a)

White solid, 0.096 g (60%), mp 235-237 °C; IR (KBr) $\tilde{\nu}_{\text{max}}$ 3422, 2927, 1715, 1618 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.74 (s, 1H, ArH), 8.28 (dd, 1H, $J = 1.6, 6.4$ Hz, ArH), 7.74-7.70 (m, 1H, ArH), 7.45-7.43 (m, 1H, ArH), 7.35 (s, 1H, ArH), 6.51 (s, 1H, ArH), 6.04 (s, 2H, CH$_2$), 5.52 (s, 2H, N-CH$_2$), 4.23 (q, 2H, $J = 7.2$ Hz, CH$_2$), 1.27 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 172.9, 164.4, 149.6, 148.1, 147.7, 139.0, 132.8, 128.2, 127.1, 126.5, 125.0, 117.0, 112.6, 110.3, 107.9, 102.3, 59.7, 55.8, 14.2; Anal. Calcd for C$_{20}$H$_{15}$NO$_5$: C, 68.76; H, 4.33; N, 4.01 %; Found. C, 68.72; H, 4.29; N, 4.07 %.

2-Fluoro-4-oxo-4H,7H-9,11-dioxo-6a-aza-benzo[fg]cyclopenta[b]anthracene-5-carboxylic acid ethyl ester (9b)

White solid, 0.093 g, (60%), mp 238-240 °C; IR (KBr) $\tilde{\nu}_{\text{max}}$ 3424, 2928, 1689, 1605 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.74 (s, 1H, ArH), 8.28 (dd, 1H, $J = 1.6, 6.4$ Hz, ArH), 7.74-7.70 (m, 1H, ArH), 7.45-7.43 (m, 1H, ArH), 7.35 (s, 1H, ArH), 6.51 (s, 1H, ArH), 6.04 (s, 2H, CH$_2$), 5.52 (s, 2H, N-CH$_2$), 4.23 (q, 2H, $J = 7.2$ Hz, CH$_2$), 1.27 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 172.9, 164.4, 149.6, 148.1, 147.7, 139.0, 132.8, 128.2, 127.1, 126.5, 125.0, 117.0, 112.6, 110.3, 107.9, 102.3, 59.7, 55.8, 14.2; Anal. Calcd for C$_{20}$H$_{14}$FNO$_5$: C, 65.40; H, 3.84; N, 3.81 %; Found. C, 65.35; H, 3.83; N, 3.85 %.

1-(1-Bromo-naphthalen-2-ylmethyl)-4-oxo-1,4-dihydro-quinoline-3-carboxylic acid ethyl ester (11a)

White solid, 0.148 g (74%), mp 277-279 °C; IR (KBr) $\tilde{\nu}_{\text{max}}$ 3425, 2923, 1679, 1604 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.93 (s, 1H, ArH), 8.32-8.28 (m, 2H, ArH), 7.97 (d, 1H, $J = 3.2$ Hz, ArH), 7.54 (d, 1H, $J = 4.4$ Hz, ArH), 7.36 (s, 1H, ArH), 6.55 (s, 1H, ArH), 6.04 (s, 2H, CH$_2$), 5.54 (s, 2H, N-CH$_2$), 4.23 (q, 2H, $J = 7.2$ Hz, CH$_2$), 1.27 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 178.5, 164.5, 157.5, 150.2, 139.3, 132.9, 131.6, 128.9, 128.4, 127.2, 126.7, 126.3, 59.9, 57.2, 14.2; Anal. Calcd for C$_{23}$H$_{18}$BrNO$_3$: C, 65.40; H, 3.84; N, 3.81 %; Found. C, 65.35; H, 3.83; N, 3.85 %.

1-(1-Bromo-naphthalen-2-ylmethyl)-6-methyl-4-oxo-1,4-dihydro-quinoline-3-carboxylic acid ethyl ester (11b)

Brown solid, 0.138 g (71%), mp 288-290 °C; IR (KBr) $\tilde{\nu}_{\text{max}}$ 3450, 2828, 1690, 1638 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.90 (s, 1H, ArH), 8.31 (d, 1H, $J = 8.4$ Hz, ArH), 8.08 (s, 1H,
ArH), 7.96 (d, 1H, $J = 8.0$ Hz, ArH), 7.89 (d, 1H, $J = 8.4$ Hz, ArH), 7.75 (t, 1H, $J = 7.2$ Hz, ArH), 7.63 (t, 1H, $J = 7.6$ Hz, ArH), 7.47 (dd, 1H, $J = 1.6, 7.2$ Hz, ArH), 7.28 (d, 1H, $J = 8.4$ Hz, ArH), 6.88 (d, 1H, $J = 8.4$ Hz, ArH), 5.88 (s, 2H, N-CH$_2$), 4.24 (q, 2H, $J = 7.2$ Hz, CH$_2$), 2.38 (s, 3H, CH$_3$), 1.29 (t, 3H, $J = 7.2$ Hz, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 172.9, 164.5, 149.6, 137.1, 134.7, 134.0, 133.5, 133.0, 131.5, 128.6, 128.5, 128.4, 128.1, 127.2, 126.2, 125.9, 124.0, 121.5, 117.1, 110.3, 59.7, 56.9, 20.4, 14.2; Anal. Calcd for C$_{24}$H$_{20}$BrNO$_3$: C, 64.01; H, 4.48; N, 3.11 %; Found. C, 64.00; H, 4.45; N, 3.16 %.

1-(1-Bromo-naphthalen-2-ylmethyl)-6-ethoxy-4-oxo-1,4-dihydro-quinoline-3-carboxylic acid ethyl ester (11c)

Yellow solid, 0.128 g (70%), mp 278-280 °C; IR (KBr) $\nu_{\text{max}}$ 3455, 2926, 1726, 1627 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 8.88 (s, 1H, ArH), 8.31 (d, 1H, $J = 8.0$ Hz, ArH), 7.97 (d, 1H, $J = 7.6$ Hz, ArH), 7.90 (d, 1H, $J = 8.4$ Hz, ArH), 7.77-7.73 (m, 1H, ArH), 7.69 (d, 1H, $J = 2.8$ Hz, ArH), 7.64 (t, 1H, $J = 7.2$ Hz, ArH), 7.33 (d, 1H, $J = 9.2$ Hz, ArH), 7.26 (dd, 1H, $J = 3.2, 6.0$ Hz, ArH), 6.87 (d, 1H, $J = 8.8$ Hz, ArH), 5.90 (s, 2H, N-CH$_2$), 4.24 (q, 2H, $J = 7.2$ Hz, CH$_2$), 4.11 (q, 2H, $J = 6.8$ Hz, CH$_2$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 172.5, 164.6, 155.9, 148.9, 136.9, 133.5, 133.4, 133.2, 133.0, 131.5, 129.6, 128.7, 128.5, 128.4, 128.3, 127.7, 127.2, 126.3, 126.2, 125.8, 123.9, 122.2, 121.4, 119.0, 109.4, 107.5, 63.5, 59.7, 57.0, 28.3, 14.4, 14.2; Anal. Calcd for C$_{25}$H$_{22}$BrNO$_4$: C, 64.01; H, 4.48; N, 3.11 %; Found. C, 64.00; H, 4.45; N, 3.16 %.

1-(1-Bromo-naphthalen-2-ylmethyl)-6-fluoro-4-oxo-1,4-dihydro-quinoline-3-carboxylic acid ethyl ester (11d)

Light brown solid, 0.150 g (78%), mp 280-282 °C; IR (KBr) $\nu_{\text{max}}$ 3457, 2930, 1677, 1622 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 8.95 (s, 1H, ArH), 8.31 (d, 1H, $J = 8.8$ Hz, ArH), 7.97-7.92 (m, 2H, ArH), 7.90 (d, 1H, $J = 8.8$ Hz, ArH), 7.77-7.73 (m, 1H, ArH), 7.66-7.62 (m, 1H, ArH), 7.59-7.54 (m, 1H, ArH), 7.47 (dd, 1H, $J = 4.0, 5.2$ Hz, ArH), 6.93 (d, 1H, $J = 8.8$ Hz, ArH), 5.92 (s, 2H, N-CH$_2$), 4.24 (q, 2H, $J = 7.2$ Hz, CH$_2$), 1.27 (t, 3H, $J = 6.8$ Hz, CH$_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 172.2, 164.3, 160.4, 158.0, 150.1, 135.8, 133.5, 132.6, 131.5, 130.0, 128.7, 128.5, 128.4, 127.2, 126.2, 124.0, 121.6, 121.2, 121.0, 120.3, 120.2, 111.2, 110.9, 109.9, 59.9, 57.2, 14.2; Anal. Calcd for C$_{23}$H$_{17}$BrFNO$_3$: C, 60.81; H, 3.77; N, 3.08 %; Found. C, 60.77; H, 3.79; N, 3.10 %.
$^1$H NMR Spectrum of 6a

$^1$H NMR expand Spectrum of 6a
$^{13}$C NMR Spectrum of $6a$

IR Spectrum of $7a$
$^1\text{H NMR}$ Spectrum of 7a

$^1\text{H NMR}$ expand Spectrum of 7a
$\text{C NMR Spectrum of 7a}$

$\text{H-H COSY spectrum of compound 7a}$
HSQC spectrum of compound 7a

HMBC spectrum of compound 7a
Mass Spectrum of 7a

\(^1\)H NMR Spectrum of 7b
$^{1}$H NMR expand Spectrum of $7b$

$^{13}$C NMR Spectrum of $7b$
Mass Spectrum of 7b

$^1$H NMR Spectrum of 7c
$^{13}$C NMR Spectrum of 7c

$^1$H NMR Spectrum of 7d
$^{13}$C NMR Spectrum of $7d$

$^1$H NMR Spectrum of $7e$
$^{13}$C NMR Spectrum of 7f

$^1$H NMR Spectrum of 7g
$^1$H NMR Spectrum of 7h

$^{13}$C NMR Spectrum of 7g
\(^1^H\) NMR expand Spectrum of \(7k\)

\(^{13}C\) NMR Spectrum of \(7k\)
$^1$H NMR Spectrum of 71

$^1$H NMR expand Spectrum of 71
$^{13}$C NMR Spectrum of 7l

$^1$H NMR Spectrum of 7m
$^{13}$C NMR Spectrum of 7m

$^1$H NMR Spectrum of 7n
$^{13}$C NMR Spectrum of 7n

Mass Spectrum of 7n
Mass Spectrum of 9b
\(^{13}\)C NMR Spectrum of 9b

\(^{1}\)H NMR Spectrum of 11a
$^{13}$C NMR Spectrum of 11b

$^1$H NMR Spectrum of 11c
$^{13}$C NMR Spectrum of 11c

$^1$H NMR Spectrum of 11d
$^{13}$C NMR Spectrum of 11d