The [4+2] Annulation of *o*-Acylamino-aryl MBH Carbonates with Coumarins: Facile Access to Tetrahydrochromeno[4,3-b]quinolin-6-ones

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Supporting Information

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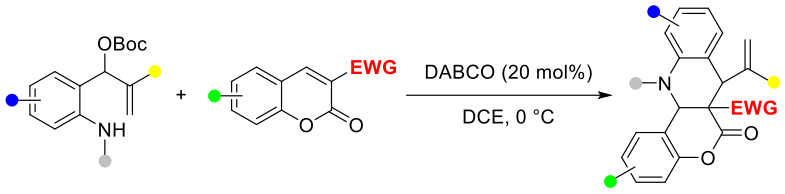
1. General experimental information

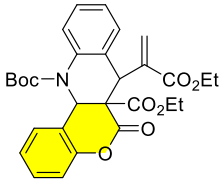
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). Melting points products were recorded on a Büchi Melting Point B-545. The HRMS were recorded by Thermo Scientific LTQ Orbitrap XL.

2. General experimental procedures for synthesis of compounds 3.



In an ordinary vial charged with a magnetic stirring bar, *o*-acylamino-aryl MBH carbonates **1** (0.1 mmol, 1.0 equiv), coumarins **2** (0.12 mmol, 1.2 equiv), DABCO (0.02 mmol, 0.2 equiv) and DCE (1 mL) was added, and then the mixture was stirred at 0 °C for 2 h. the products **3** were isolated by flash chromatography on silica gel.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3a)



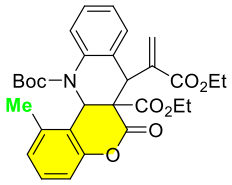
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (47.1 mg, 90% yield); m.p. 143.5-146.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.17 (m, 2H), 7.17 – 7.08 (m, 2H), 6.97 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.48 (s, 1H), 5.86 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.15 (s, 1H), 4.31 – 4.14 (m, 2H), 4.09 – 3.95 (m, 2H), 1.48 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.2, 164.1, 153.8, 150.3, 136.8, 136.4, 131.9, 131.8, 130.3, 129.4, 127.5, 127.4, 125.6, 124.8, 121.0, 116.8, 82.3, 63.1, 61.4, 59.9, 54.5, 44.3, 28.4, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{29}H_{31}NO_8Na^+$ $[M+Na]^+$: 544.19419; found: 544.19440.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-1-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3b)



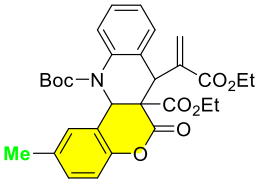
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (48.0 mg, 90% yield); m.p. 145.5-148.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.13 – 7.06 (m, 1H), 6.98 – 6.93 (m, 1H), 6.79 – 6.75 (m, 1H), 6.47 (s, 1H), 5.83 (s, 1H), 5.37 (d, *J* = 1.1 Hz, 1H), 5.14 (s, 1H), 4.31 – 4.13 (m, 2H), 4.11 – 3.93 (m, 2H), 2.31 (s, 3H), 1.48 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.3, 164.3, 153.9, 150.2, 140.8, 136.9, 136.5, 132.0, 131.5, 129.5, 129.4, 127.5, 127.4, 125.7, 125.5, 118.0, 117.1, 82.3, 63.1, 61.4, 60.0, 54.3, 44.3, 28.4, 21.3, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{30}H_{33}NO_8Na^+$ $[M+Na]^+$: 558.20984; found: 565.09491, 558.20990.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3c)



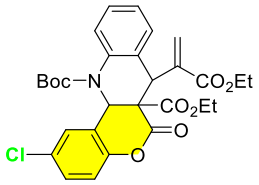
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (47.1 mg, 88% yield); m.p. 134.5-137.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.1 Hz, 1H), 7.28 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.13 – 7.05 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.46 (s, 1H), 5.82 (s, 1H), 5.37 (s, 1H), 5.14 (s, 1H), 4.26 – 4.14 (m, 2H), 4.09 – 3.97 (m, 2H), 2.32 (s, 3H), 1.49 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.3, 164.3, 153.9, 148.2, 136.9, 136.5, 134.5, 132.1, 131.9, 130.8, 129.5, 129.4, 127.5, 127.4, 125.6, 120.6, 116.5, 82.3, 63.1, 61.4, 60.0, 54.5, 44.4, 28.5, 28.4, 21.0, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{30}H_{33}NO_8Na^+$ $[M+Na]^+$: 558.20984; found: 558.21014.

12-(tert-butyl) 6a-ethyl 2-chloro-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3d)



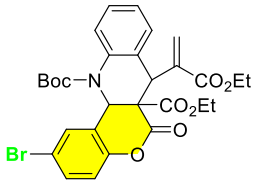
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (52.5 mg, 95% yield); m.p. 150.9-154.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.6 Hz, 1H), 7.30 – 7.18 (m, 4H), 7.15 – 7.08 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.46 (s, 1H), 5.80 (s, 1H), 5.35 (t, *J* = 1.1 Hz, 1H), 5.14 (s, 1H), 4.29 – 4.13 (m, 2H), 4.12 – 4.00 (m, 2H), 1.50 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 165.9, 153.8, 148.8, 136.6, 136.2, 131.9, 131.6, 130.4, 130.0, 129.5, 129.5, 127.7, 127.4, 125.8, 122.6, 118.2, 82.8, 77.5, 77.2, 76.8, 63.4, 61.5, 59.7, 54.2, 44.4, 28.4, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{29}H_{30}ClNO_8Na^+$ $[M+Na]^+$: 578.15522, 580.15226; found: 578.15558, 580.15350.

12-(tert-butyl) 6a-ethyl 2-bromo-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3e)



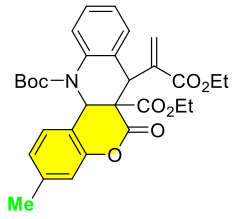
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (52.4 mg, 87% yield); m.p. 155.0-158.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.08 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.46 (d, *J* = 0.8 Hz, 1H), 5.79 (s, 1H), 5.35 (t, *J* = 1.1 Hz, 1H), 5.14 (d, *J* = 1.1 Hz, 1H), 4.32 – 4.14 (m, 2H), 4.13 – 3.96 (m, 2H), 1.51 (s, 9H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 165.9, 163.5, 153.8, 149.3, 136.6, 136.2, 134.5, 133.3, 131.9, 129.5, 129.4, 127.7, 127.4, 125.8, 123.0, 118.6, 117.4, 82.9, 77.5, 77.2, 76.8, 63.4, 61.5, 59.8, 54.1, 44.4, 28.4, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{29}H_{30}BrNO_8Na^+$ $[M+Na]^+$: 622.10470, 624.10265; found: 622.10516, 624.10321.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3f)



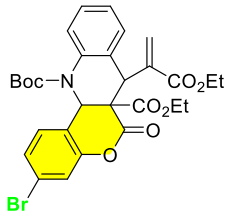
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (45.5 mg, 85% yield); m.p. 147.0-151.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.13 – 7.07 (m, 1H), 6.95 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.47 (s, 1H), 5.83 (s, 1H), 5.37 (d, *J* = 1.0 Hz, 1H), 5.14 (s, 1H), 4.29 – 4.14 (m, 2H), 4.13 – 3.91 (m, 2H), 2.31 (s, 3H), 1.48 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.3, 164.3, 153.8, 150.2, 140.8, 136.8, 136.5, 132.0, 131.5, 129.4, 129.4, 127.5, 127.4, 125.7, 125.5, 118.0, 117.1, 82.2, 63.1, 61.4, 60.0, 54.3, 44.3, 28.4, 21.3, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{30}H_{33}NO_8Na^+$ $[M+Na]^+$: 558.20984; found: 558.21033.

12-(tert-butyl) 6a-ethyl 3-bromo-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3g)



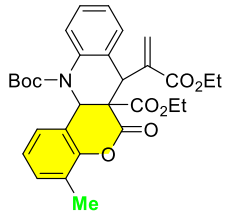
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (47.9 mg, 80% yield); m.p. 181.6-182.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.26 – 7.16 (m, 3H), 7.12 (dd, *J* = 6.6, 1.6 Hz, 2H), 6.46 (s, 1H), 5.81 (s, 1H), 5.34 (s, 1H), 5.14 (s, 1H), 4.31 – 4.14 (m, 2H), 4.12 – 3.93 (m, 2H), 1.47 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 165.9, 163.4, 153.8, 150.7, 136.6, 136.2, 133.3, 131.8, 129.5, 129.4, 128.0, 127.6, 127.3, 125.7, 123.3, 120.1, 120.0, 82.5, 63.4, 61.5, 59.8, 54.1, 44.4, 28.3, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{29}H_{30}BrNO_8Na^+$ $[M+Na]^+$: 622.10470, 624.10265; found: 622.10504, 624.10315.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-4-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3h)



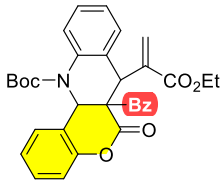
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (43.9 mg, 82% yield); m.p. 181.2-183.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.30 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.16 – 7.07 (m, 2H), 7.06 – 6.99 (m, 1H), 6.48 (s, 1H), 5.85 (s, 1H), 5.39 (s, 1H), 5.14 (s, 1H), 4.30 – 4.13 (m, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.48 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.3, 164.2, 153.8, 148.6, 136.9, 136.5, 131.9, 131.7, 129.4, 129.2, 127.4, 127.3, 126.1, 125.5, 124.3, 120.8, 82.3, 62.9, 61.4, 59.7, 54.7, 44.1, 28.4, 15.7, 14.2, 13.7.

HRMS (ESI) Calcd. for $C_{30}H_{33}NO_8Na^+$ $[M+Na]^+$: 558.20984; found: 558.21033.

tert-butyl 6a-benzoyl-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6a,12a-dihydro-6H-chromeno[4,3-b]quinoline-12(7H)-carboxylate (3i)



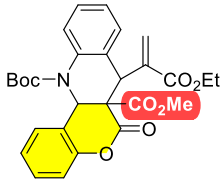
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (52.0 mg, 94% yield); m.p. 127.9-130.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.51 – 7.44 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 7.12 – 7.06 (m, 1H), 6.94 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.64 (d, *J* = 1.0 Hz, 1H), 6.37 (s, 1H), 5.75 (d, *J* = 1.2 Hz, 1H), 5.15 (s, 1H), 4.21 – 3.94 (m, 2H), 1.36 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 166.9, 166.7, 153.7, 150.0, 136.7, 136.1, 132.7, 132.1, 130.9, 130.3, 130.0, 128.9, 128.5, 128.2, 127.1, 126.8, 125.1, 125.1, 121.7, 116.7, 82.5, 62.9, 61.5, 54.8, 43.5, 28.1, 14.1.

HRMS (ESI) Calcd. for $C_{33}H_{31}NO_7Na^+$ $[M+Na]^+$: 576.19927; found: 576.19934.

12-(tert-butyl) 6a-methyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3j)



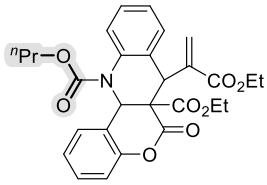
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (47.0 mg, 93% yield); m.p. 178.5-180.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.09 (m, 2H), 6.96 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.48 (s, 1H), 5.93 (s, 1H), 5.40 (t, *J* = 1.0 Hz, 1H), 5.13 (s, 1H), 4.31 – 4.15 (m, 2H), 3.62 (s, 3H), 1.48 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.7, 164.0, 153.8, 150.1, 136.6, 136.5, 131.8, 131.7, 130.3, 129.8, 129.5, 127.6, 127.4, 125.7, 125.0, 121.0, 116.9, 82.4, 61.5, 59.8, 54.3, 53.8, 44.6, 28.4, 14.3.

HRMS (ESI) Calcd. for $C_{28}H_{29}NO_8Na^+$ $[M+Na]^+$: 530.17854; found: 530.17859.

6a-ethyl 12-propyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3k)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (47.5 mg, 95% yield); m.p. 170.7-172.0 °C.

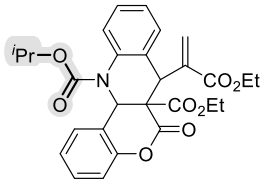
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.26 – 7.19 (m, 2H), 7.18 – 7.11 (m, 2H), 6.97 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.47 (s, 1H), 5.87 (s, 1H), 5.33 (t, *J* = 1.0 Hz, 1H),

5.17 (s, 1H), 4.29 – 4.11 (m, 4H), 4.08 – 3.99 (m, 2H), 1.72 – 1.62 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.1, 164.0, 155.1, 150.3, 136.8, 135.9, 131.9, 131.9, 130.4, 129.6, 129.4, 127.8, 126.9, 125.9, 124.9, 120.7, 116.9, 68.4, 63.2, 61.4, 59.7, 54.9, 44.4, 22.3, 14.3, 13.7, 10.5.

HRMS (ESI) Calcd. for $C_{28}H_{29}NO_8Na^+$ $[M+Na]^+$: 530.17854; found: 530.17877.

6a-ethyl 12-isopropyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3l)



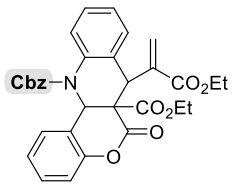
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford yellow solid (48.2 mg, 94% yield); m.p. 143.0-145.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.38 – 7.25 (m, 7H), 7.25 – 7.18 (m, 2H), 7.16 – 7.05 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.28 (s, 1H), 5.87 (s, 1H), 5.28 – 5.13 (m, 4H), 4.30 – 4.09 (m, 2H), 4.09 – 3.94 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.0, 163.9, 154.9, 150.3, 136.5, 135.8, 135.7, 132.0, 131.9, 130.5, 129.6, 129.6, 128.7, 128.5, 128.4, 127.9, 126.9, 126.0, 124.9, 120.5, 116.9, 68.4, 63.2, 61.4, 59.7, 55.0, 44.3, 14.3, 14.2, 13.6.

HRMS (ESI) Calcd. for $C_{28}H_{29}NO_8Na^+$ $[M+Na]^+$: 530.17854; found: 530.17865.

12-benzyl 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3m)



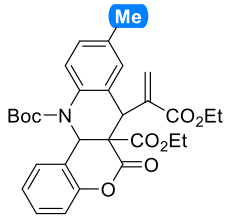
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford yellow solid (50.1 mg, 90% yield); m.p. 150.8-152.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.34 (s, 2H), 7.14 – 7.08 (m, 1H), 7.06 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.93 – 6.87 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.63 – 6.51 (m, 2H), 5.91 (t, *J* = 1.3 Hz, 1H), 5.01 – 4.83 (m, 1H), 4.39 – 4.14 (m, 2H), 3.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.98 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 165.6, 151.9, 144.3, 137.9, 135.1, 134.4, 130.6, 129.3, 128.1, 124.0, 123.9, 123.4, 123.2, 122.9, 108.3, 85.9, 70.6, 68.8, 61.3, 26.3, 21.8, 14.3.

HRMS (ESI) Calcd. for $C_{32}H_{29}NO_8Na^+$ $[M+Na]^+$: 578.17854; found: 578.17865.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-9-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3n)



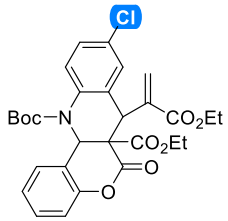
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (47.0 mg, 88% yield); m.p. 133.6-138.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.18 – 7.10 (m, 2H), 7.03 (d, *J* = 2.0 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.54 – 6.38 (m, 1H), 5.85 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.10 (s, 1H), 4.28 – 4.13 (m, 2H), 4.08 – 3.96 (m, 2H), 2.29 (s, 3H), 1.47 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.2, 164.2, 153.9, 150.3, 136.9, 135.2, 133.9, 131.8, 131.7, 130.2, 129.7, 129.4, 128.4, 127.0, 124.8, 121.1, 116.7, 82.1, 63.0, 61.3, 59.9, 54.5, 44.3, 28.4, 20.9, 14.2, 13.6.

HRMS (ESI) Calcd. for $C_{30}H_{33}NO_8Na^+$ $[M+Na]^+$: 558.20984; found: 558.21045.

12-(tert-butyl) 6a-ethyl 9-chloro-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3o)



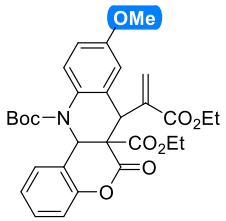
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (49.0 mg, 88% yield); m.p. 135.7-138.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 7.18 – 7.11 (m, 2H), 6.99 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.50 (s, 1H), 5.87 (s, 1H), 5.38 (t, *J* = 1.0 Hz, 1H), 5.08 (s, 1H), 4.30 – 4.14 (m, 2H), 4.10 – 3.95 (m, 2H), 1.48 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 166.0, 164.0, 153.6, 150.2, 136.4, 135.0, 133.4, 131.6, 130.8, 130.4, 129.6, 129.1, 128.5, 127.7, 125.0, 120.7, 116.9, 82.8, 63.2, 61.5, 59.5, 54.5, 43.8, 28.3, 14.3, 13.7.

HRMS (ESI) Calcd. for $C_{29}H_{30}ClNO_8Na^+$ $[M+Na]^+$: 578.15522, 580.15226; found: 578.15558, 580.15356.

12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-9-methoxy-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3p)



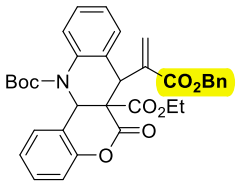
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (51.2 mg, 93% yield); m.p. 160.2-163.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.19 – 7.15 (m, 1H), 7.15 – 7.11 (m, 1H), 6.95 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.77 – 6.69 (m, 2H), 6.47 (d, *J* = 0.9 Hz, 1H), 5.84 (s, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 5.10 (d, *J* = 1.1 Hz, 1H), 4.27 – 4.15 (m, 2H), 4.09 – 3.97 (m, 2H), 3.76 (s, 3H), 1.46 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 166.2, 164.0, 157.1, 154.0, 150.2, 136.6, 133.2, 131.7, 130.2, 129.6, 129.3, 128.4, 124.8, 121.1, 116.7, 114.2, 113.2, 82.0, 77.4, 77.2, 76.9, 63.0, 61.4, 60.0, 55.5, 54.5, 44.6, 28.3, 14.2, 13.6.

HRMS (ESI) Calcd. for $C_{30}H_{34}NO_9^+$ $[M+H]^+$: 552.22280; found: 552.22229.

12-(tert-butyl) 6a-ethyl 7-(3-(benzyloxy)-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3q)



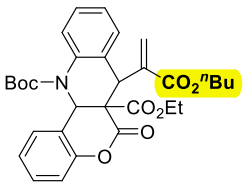
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (49.6 mg, 85% yield); m.p. 160.0-162.5 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.36 – 7.32 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.14 (m, 1H), 7.14 – 7.09 (m, 1H), 6.96 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.54 (s, 1H), 5.89 (s, 1H), 5.43 (d, *J* = 1.0 Hz, 1H), 5.21 (d, *J* = 1.4 Hz, 2H), 5.19 (s, 1H), 4.01 – 3.85 (m, 2H), 1.48 (s, 9H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 166.2, 164.1, 153.8, 150.3, 136.6, 136.5, 135.8, 131.8, 131.8, 130.2, 129.9, 129.5, 128.7, 128.4, 128.3, 127.5, 127.4, 125.6, 124.8, 121.0, 116.8, 82.4, 67.1, 63.1, 59.9, 54.5, 44.3, 28.4, 13.6.

HRMS (ESI) Calcd. for $C_{34}H_{33}NO_8^+$ $[M+H]^+$: 584.2278934, found 584.22797.

12-(tert-butyl) 6a-ethyl 7-(3-butoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3r)



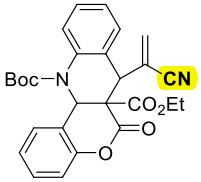
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (43.9 mg, 80% yield); m.p. 144.3-146.7 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.17 – 7.13 (m, 1H), 7.13 – 7.09 (m, 1H), 6.96 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.46 (d, *J* = 0.9 Hz, 1H), 5.87 (s, 1H), 5.37 (d, *J* = 1.1 Hz, 1H), 5.15 (d, *J* = 1.1 Hz, 1H), 4.21 – 4.10 (m, 2H), 4.08 – 3.98 (m, 2H), 1.72 – 1.65 (m, 2H), 1.48 (s, 9H), 1.45 – 1.40 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 166.2, 164.1, 153.9, 150.3, 136.9, 136.5, 131.9, 131.8, 130.2, 129.5, 129.3, 127.5, 127.4, 125.6, 124.8, 121.0, 116.8, 82.3, 65.3, 63.1, 59.9, 54.5, 44.3, 30.7, 28.4, 19.3, 13.9, 13.7.

HRMS (ESI) Calcd. for $C_{31}H_{36}NO_8^+$ $[M+H]^+$: 550.24354, found 550.24384.

12-(tert-butyl) 6a-ethyl 7-(1-cyanovinyl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3s)



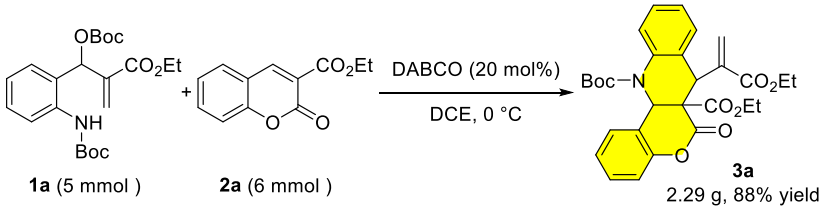
It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (28.5 mg, 60% yield); m.p. 184.3-186.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.28 – 7.23 (m, 3H), 7.22 – 7.13 (m, 2H), 6.95 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.19 (s, 1H), 6.15 (d, *J* = 1.0 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.65 (s, 1H), 4.35 – 4.13 (m, 2H), 1.48 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.0, 153.4, 149.5, 136.2, 130.9, 130.3, 129.4, 128.6, 128.1, 127.4, 125.9, 125.5, 121.2, 121.2, 119.6, 117.6, 116.8, 82.8, 63.7, 60.1, 53.4, 47.7, 28.4, 13.8.

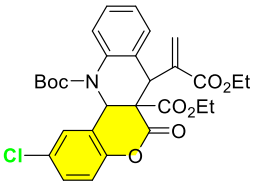
HRMS (ESI) Calcd. for $C_{27}H_{26}N_2O_6Na^+$ $[M+Na]^+$: 497.16831; found: 497.16797.

3. Scale-up experiment

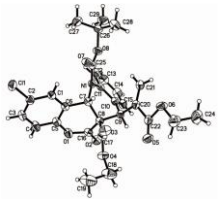


In an ordinary vial charged with a magnetic stirring bar, **1a** (6.0 mmol, 1.2 equiv), **2a** (5.0 mmol, 1.0 equiv), DABCO (1.0 mmol, 0.2 equiv) and DCE (50 mL) was added, and then the mixture was stirred at 0 °C for 2 h. the products **3a** were isolated by flash chromatography on silica gel with yields of 88%.

4. X-ray crystal data for compound 3a



3d

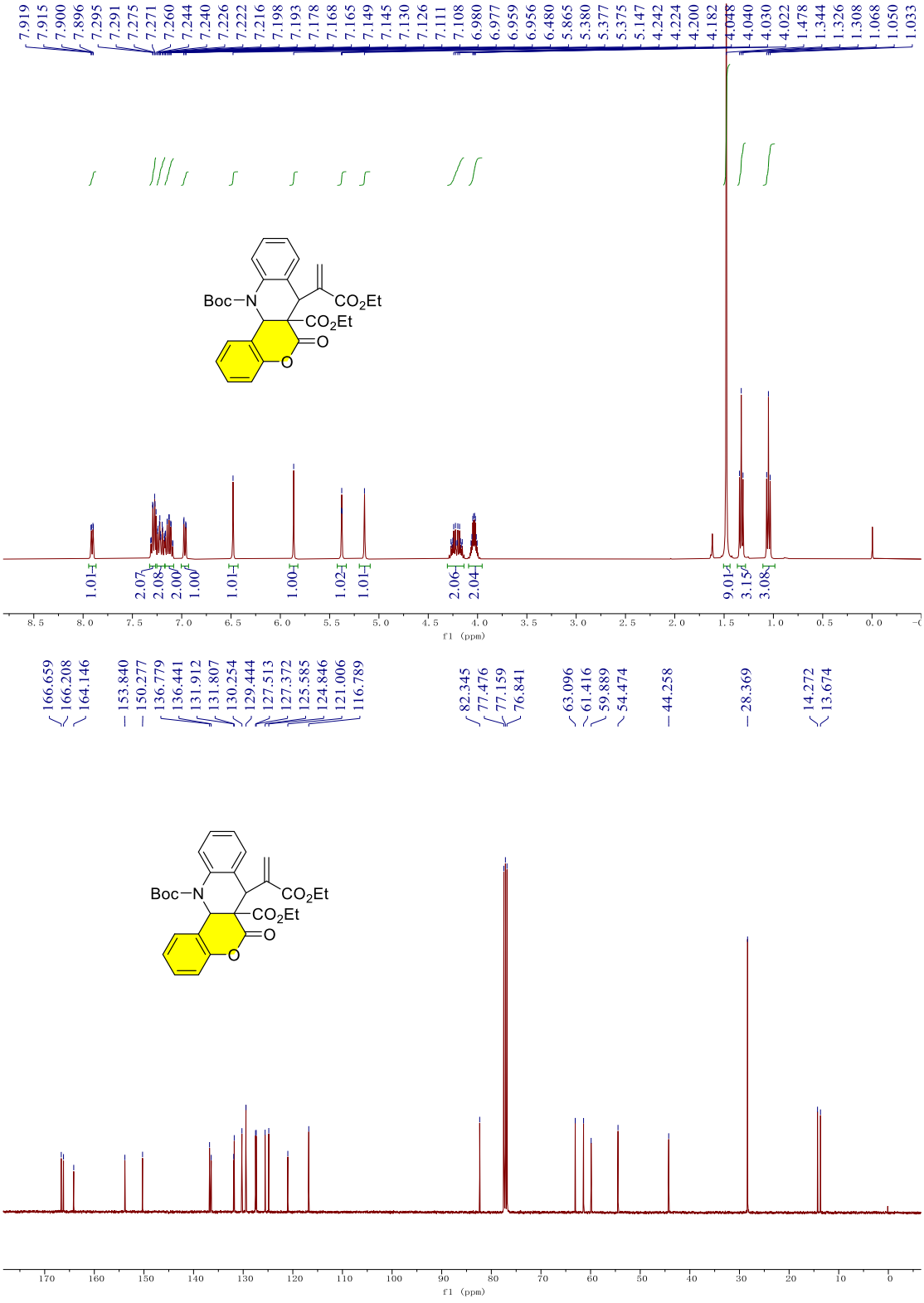


3d, CCDC(2360827)

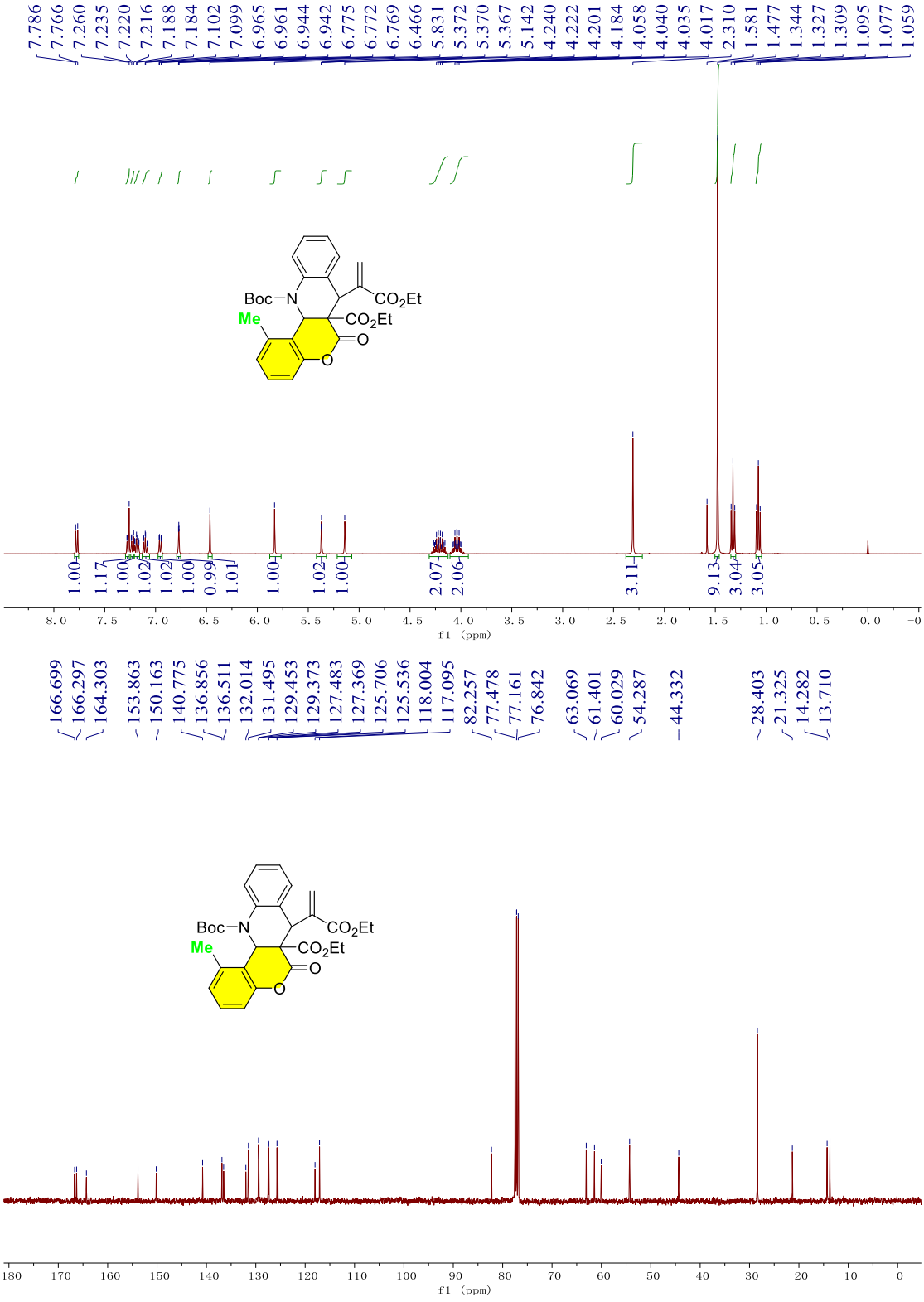
Identification code	**3d**
Empirical formula	**$C_{29}H_{30}ClNO_8$**
Formula weight	**555.99**
Temperature/K	**293(2)**
Crystal system	**triclinic**
Space group	**P-1**
a/Å	**11.3573(5)**
b/Å	**15.0998(6)**
c/Å	**17.5183(8)**
α /°	**99.383(4)**
β /°	**106.340(4)**
γ /°	**94.093(4)**
Volume/Å3	**2822.5(2)**
Z	**4**
ρ calcg/cm3	**1.308**
μ /mm-1	**1.626**
F(000)	**1168.0**
Crystal size/mm3	**0.14 × 0.12 × 0.1**
Radiation	**CuKα (λ = 1.54184)**
2Θ range for data collection/°	**7.226 to 134.116**
Index ranges	**-12≤h≤13, -18≤k≤18, -19≤l≤20**
Reflections collected	**21101**
Independent reflections	**10075 [Rint = 0.0338, Rsigma = 0.0448]**
Data/restraints/parameters	**10075/35/753**
Goodness-of-fit on F2	**1.025**
Final R indexes [I>=2σ (I)]	**R1 = 0.0568, wR2 = 0.1550**
Final R indexes [all data]	**R1 = 0.0753, wR2 = 0.1751**
Largest diff. peak/hole / e Å-3	**0.58/-0.31**

5. The copies of ^{1}H NMR and ^{13}C NMR for compounds 3a-3s

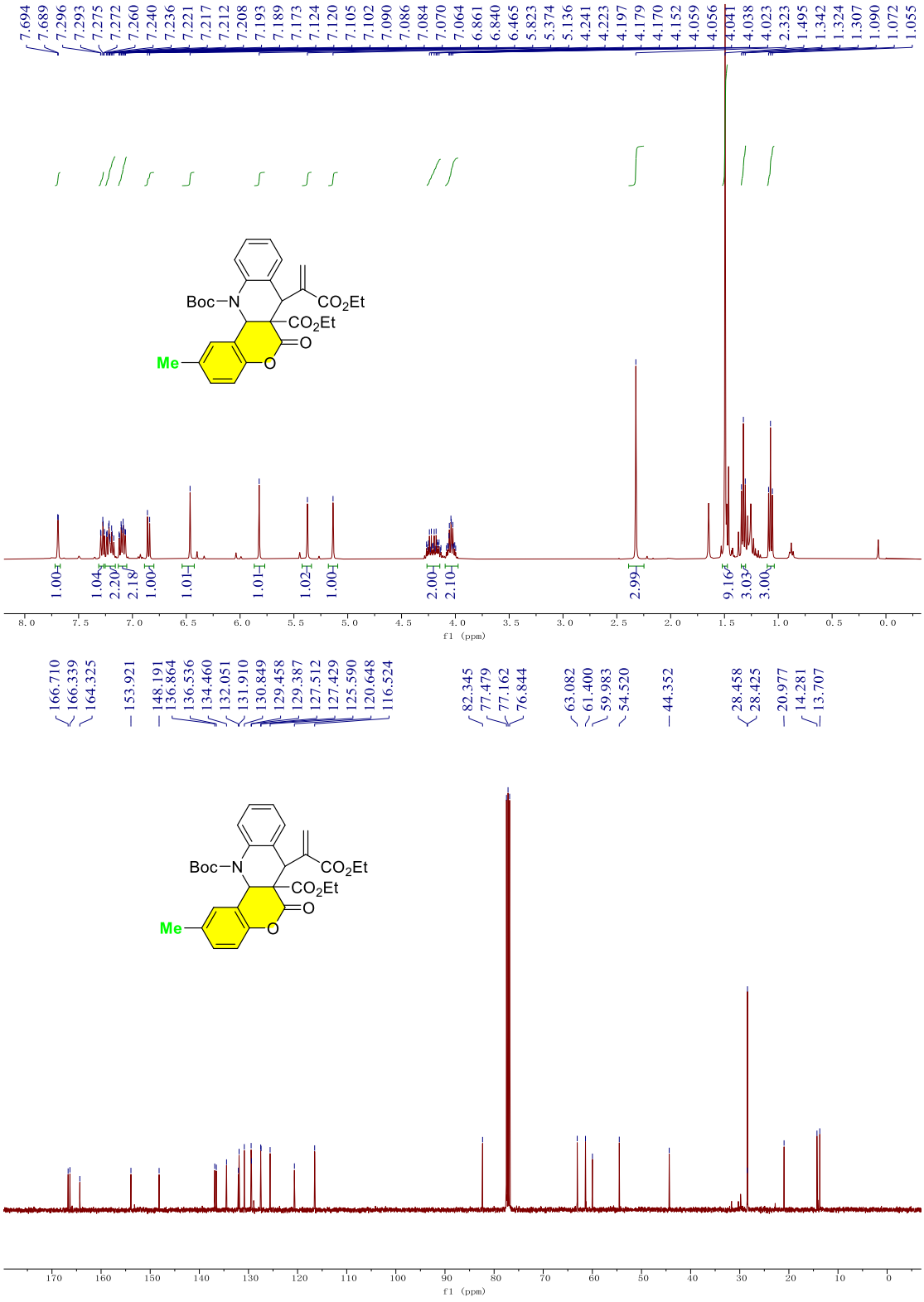
12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3a)



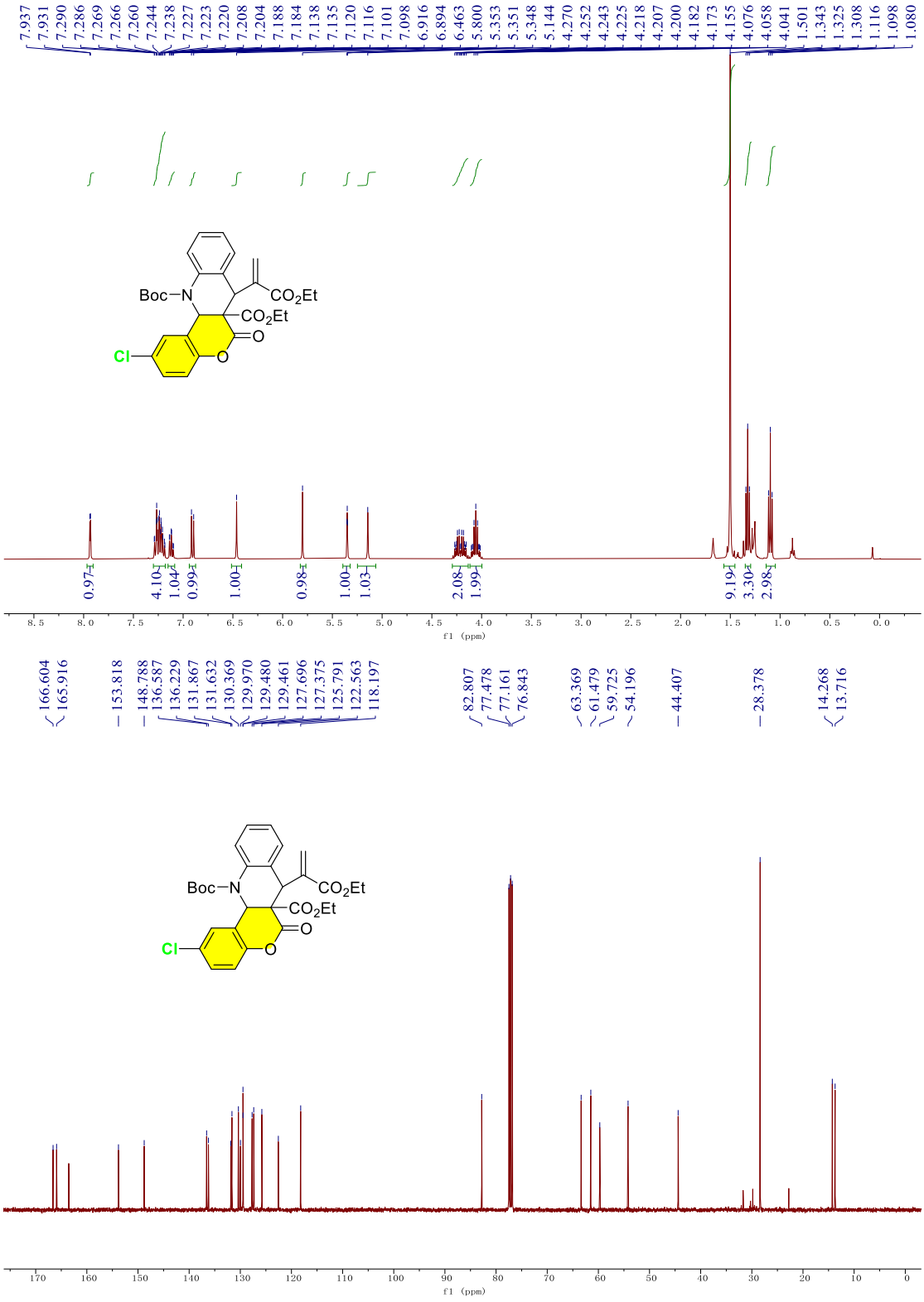
12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-1-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3b)



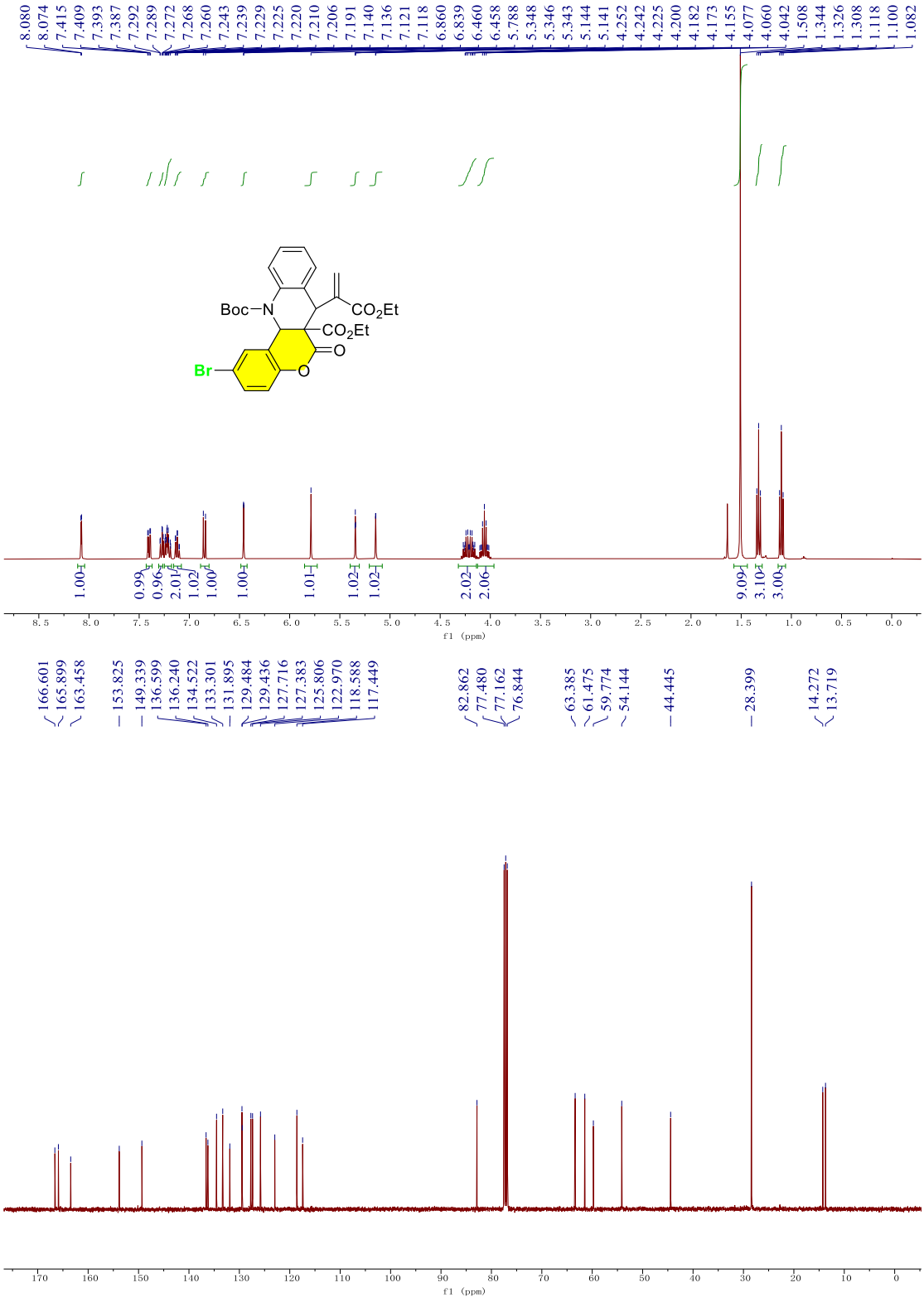
12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-2-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3c)



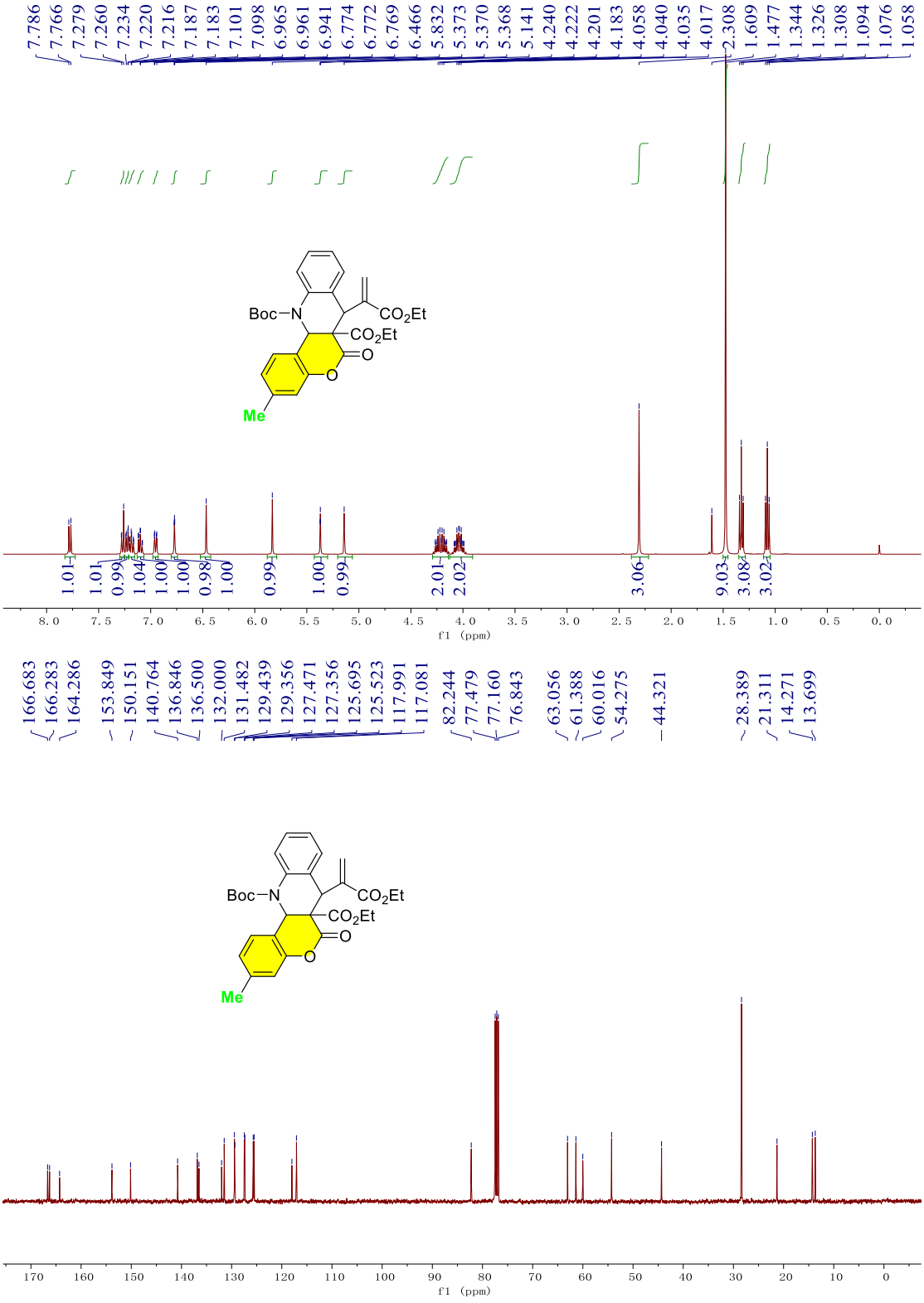
12-(tert-butyl) 6a-ethyl 2-chloro-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3d)



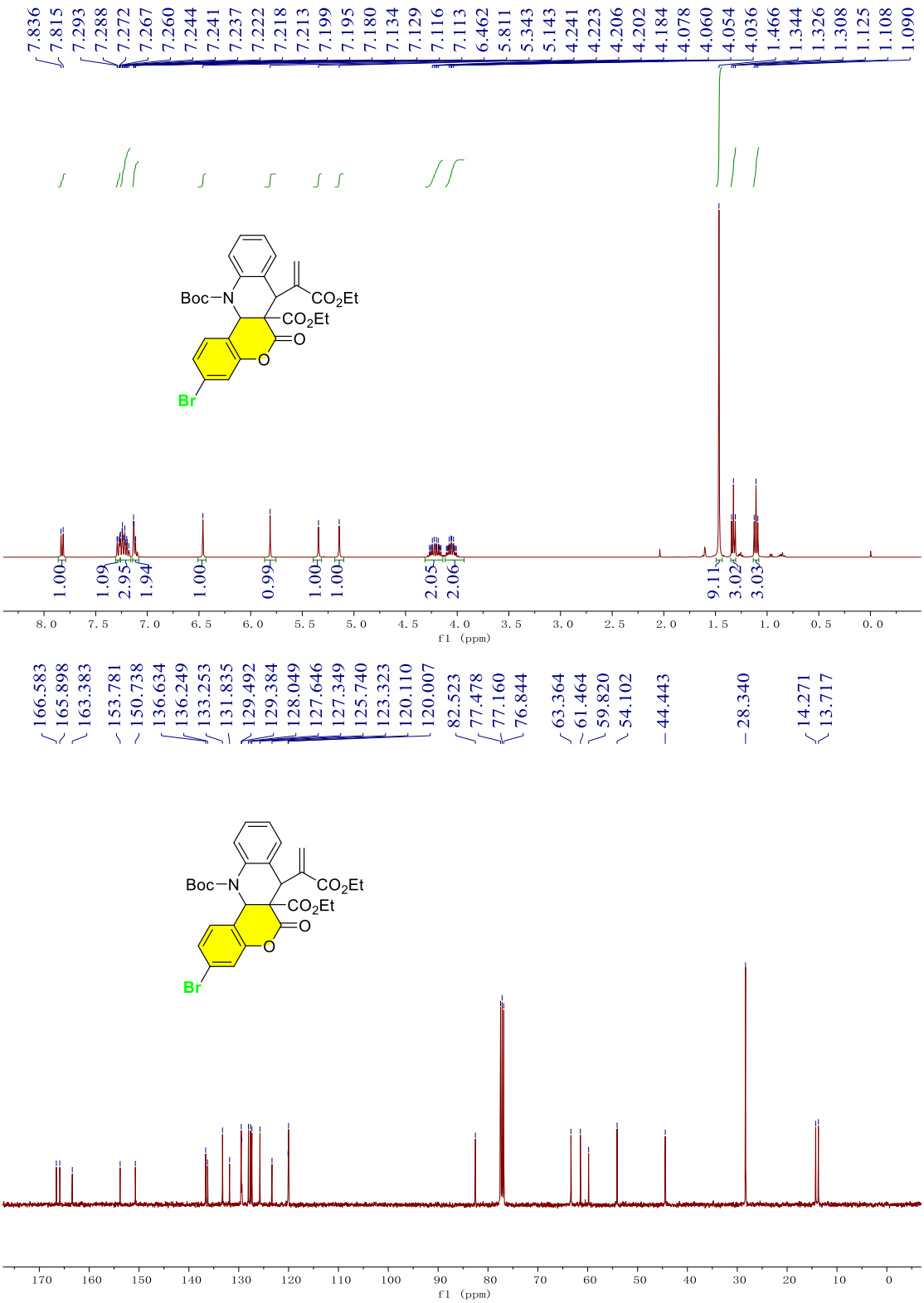
12-(tert-butyl) 6a-ethyl 2-bromo-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3e)



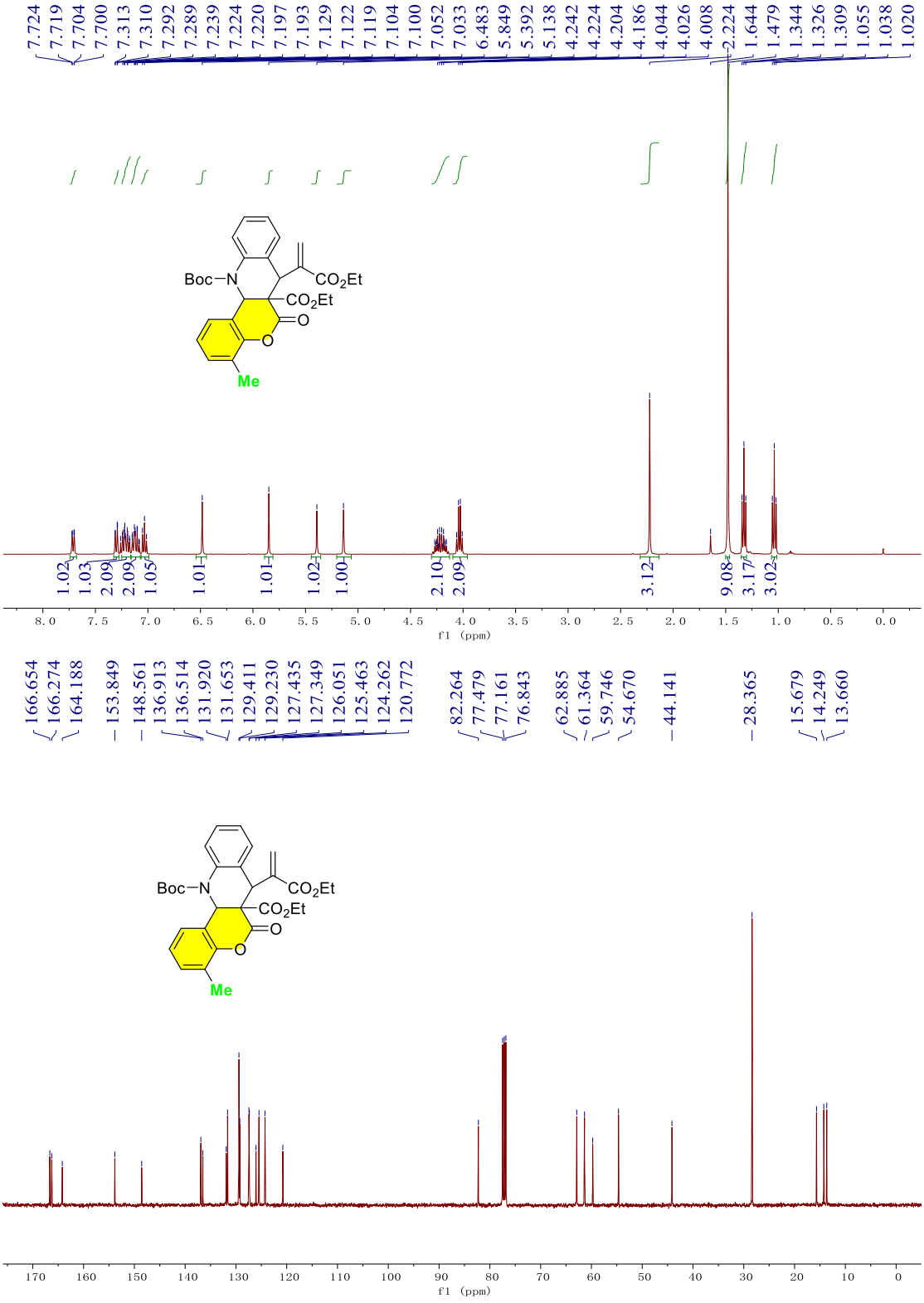
12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3f)



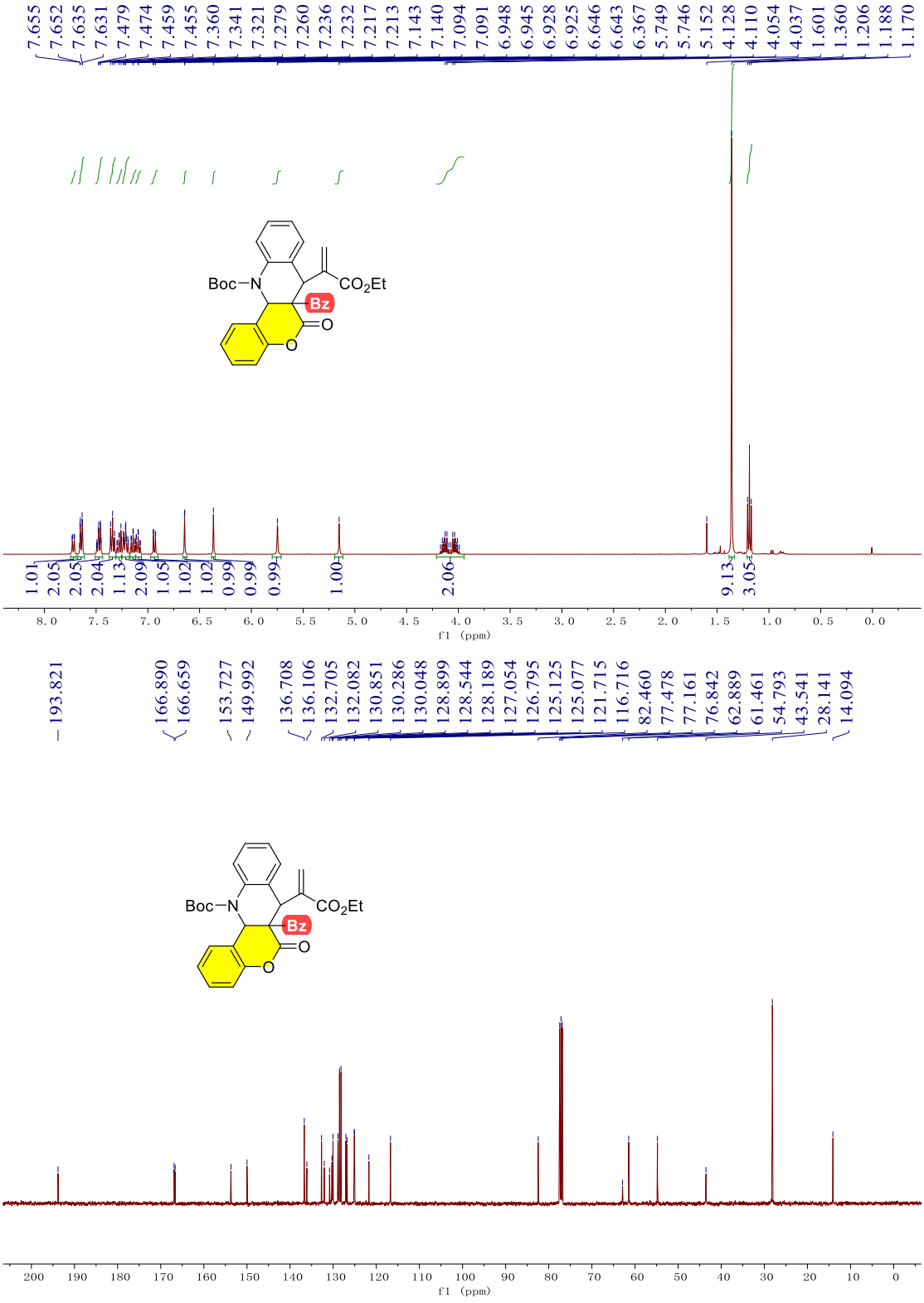
12-(tert-butyl) 6a-ethyl 3-bromo-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3g)



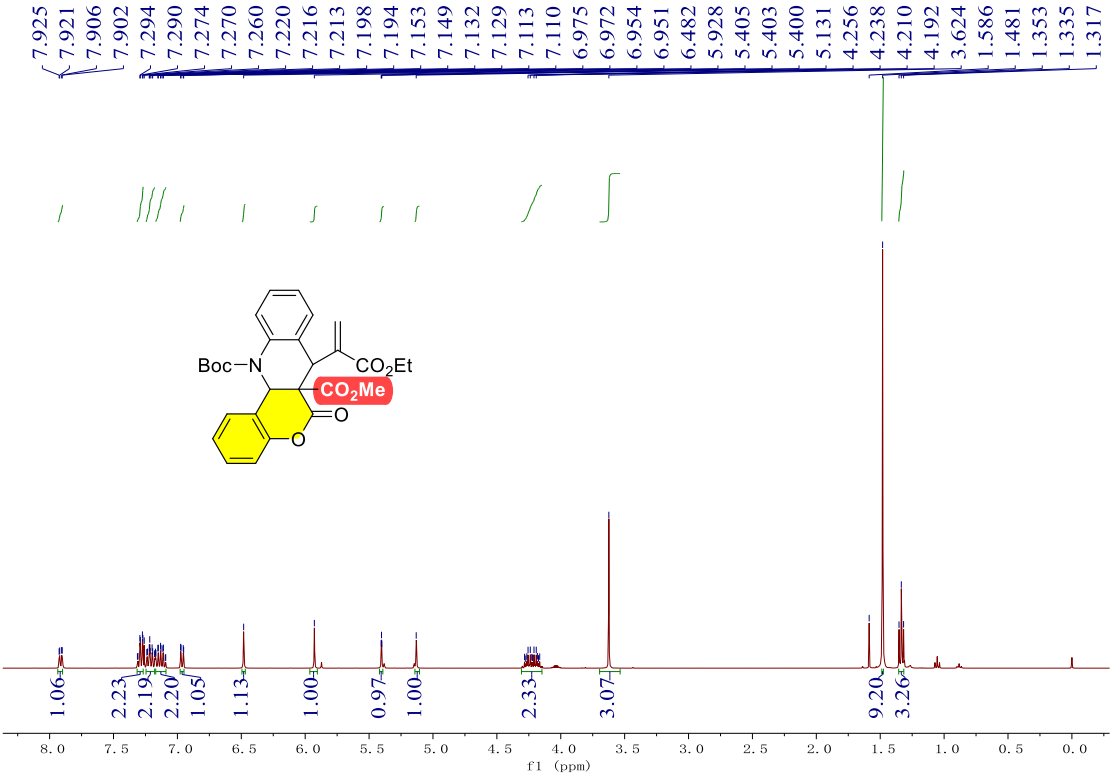
12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-4-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3h)

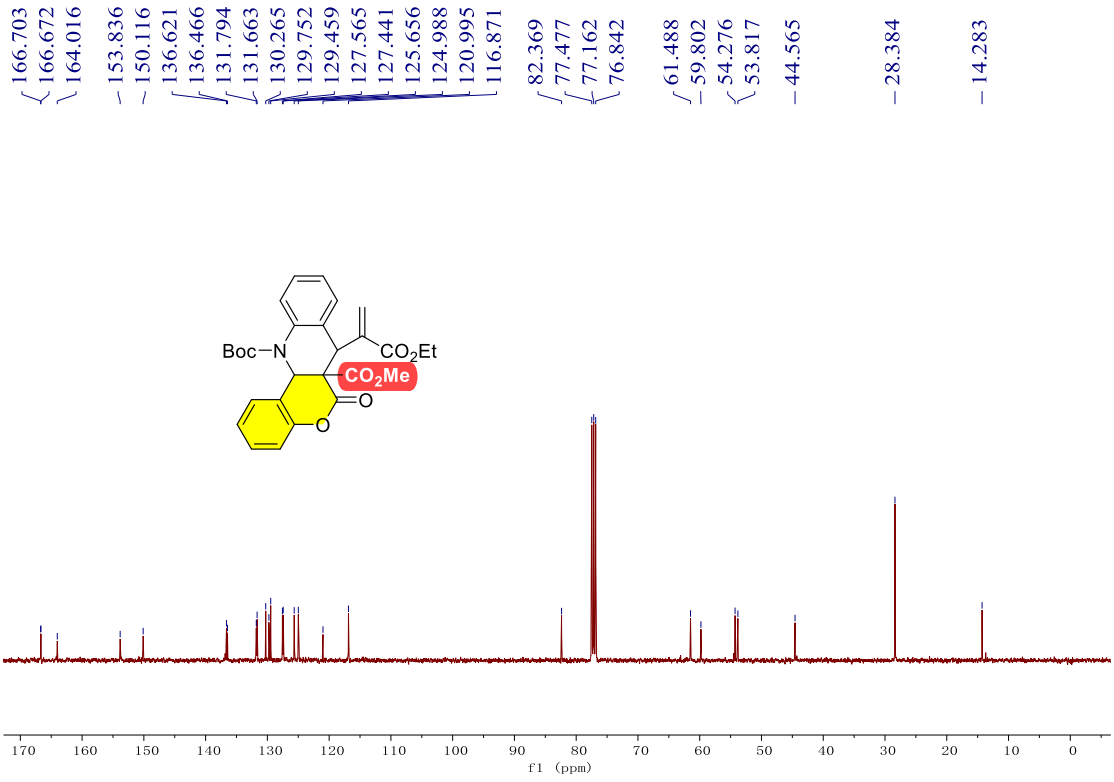


tert-butyl 6a-benzoyl-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6a,12a-dihydro-6H-chromeno[4,3-b]quinoline-12(7H)-carboxylate (3i)

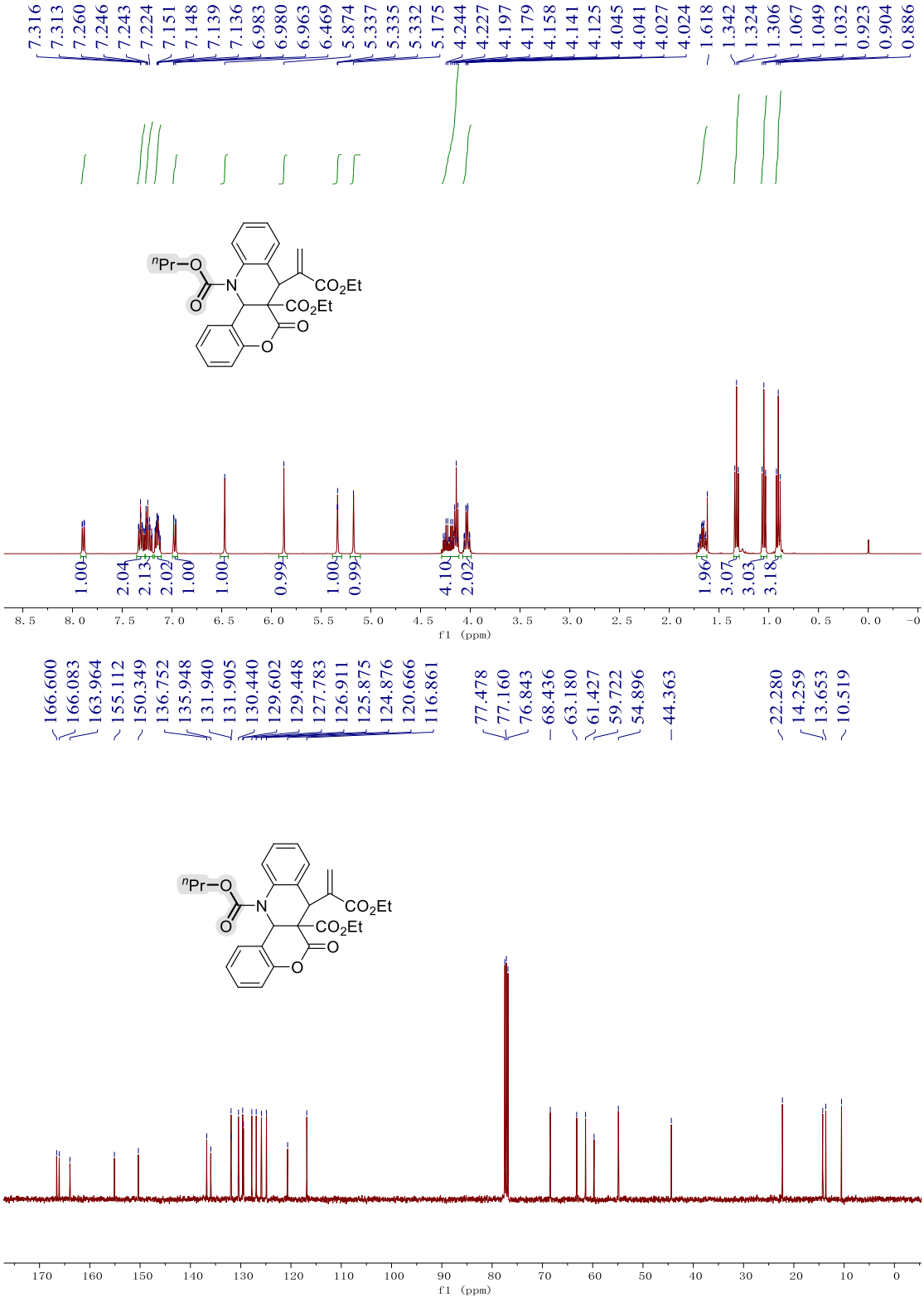


12-(tert-butyl) 6a-methyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3j)

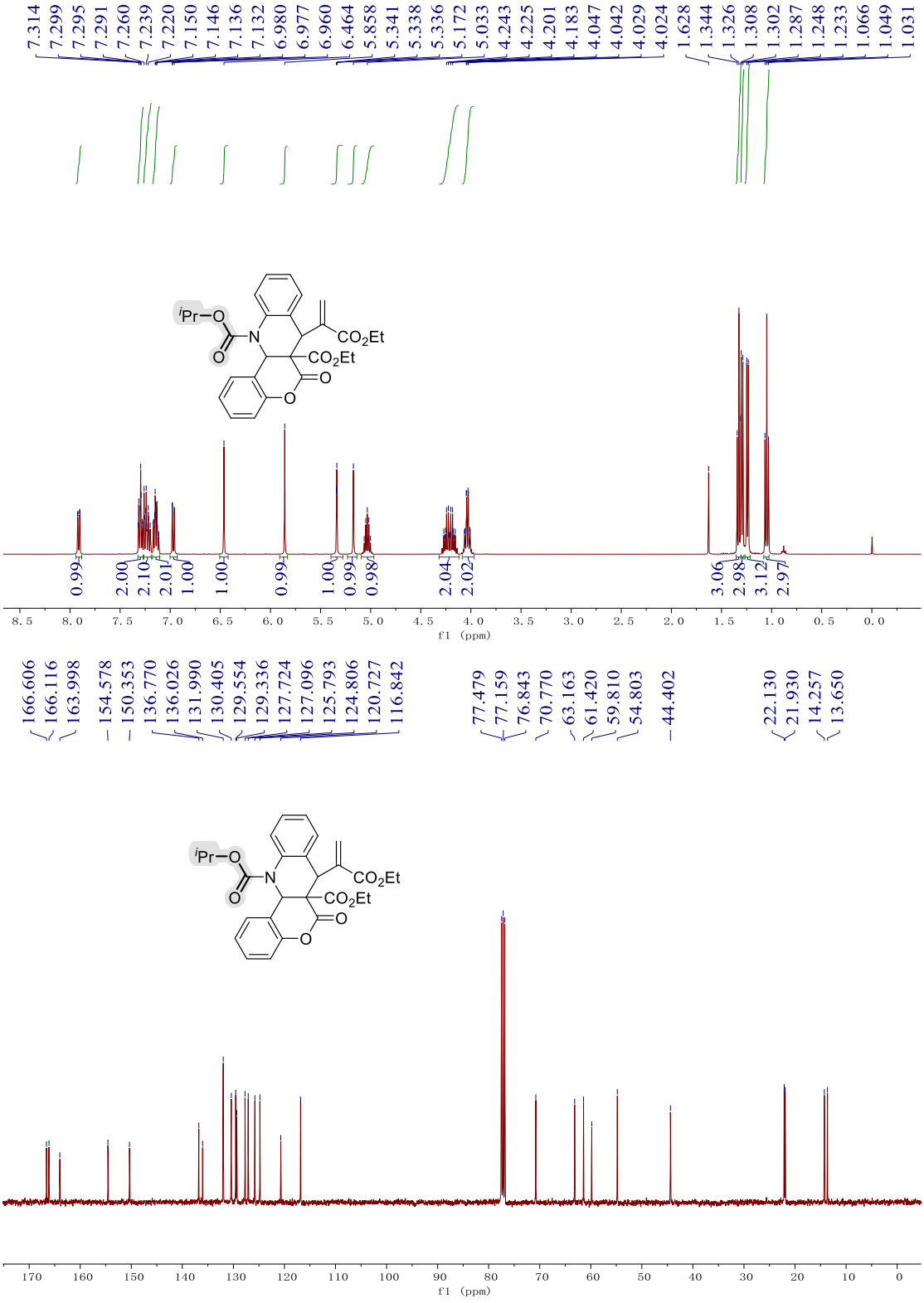




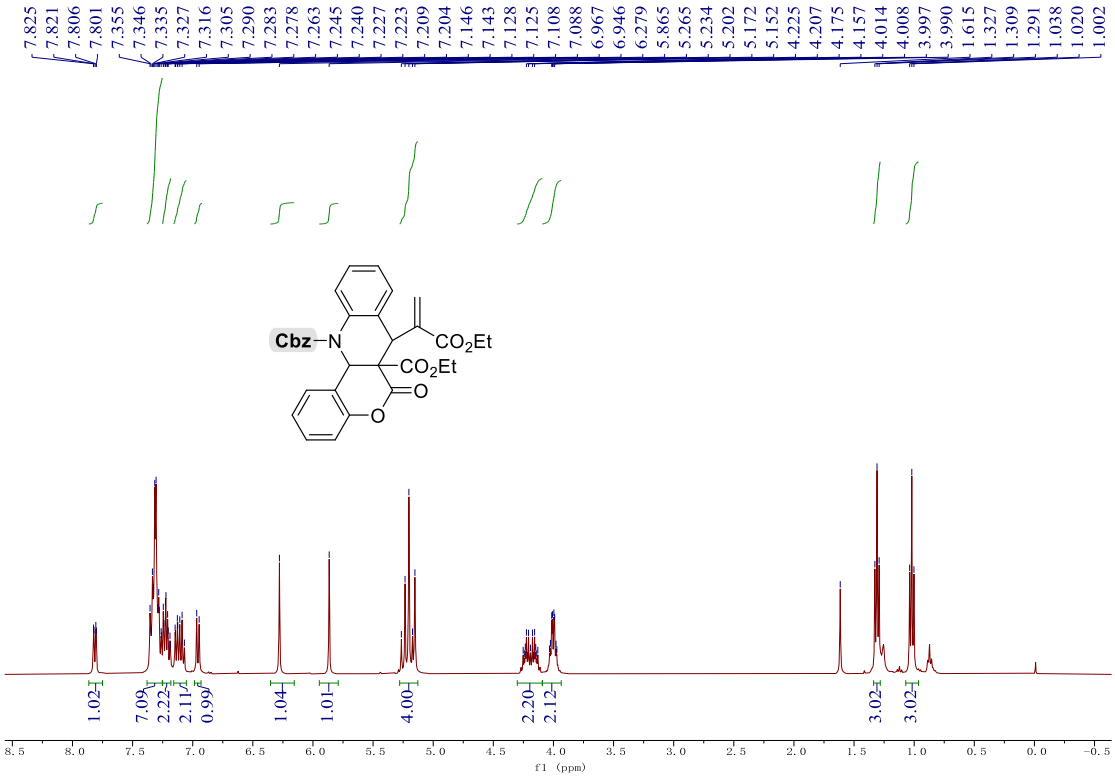
6a-ethyl 12-propyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3k)

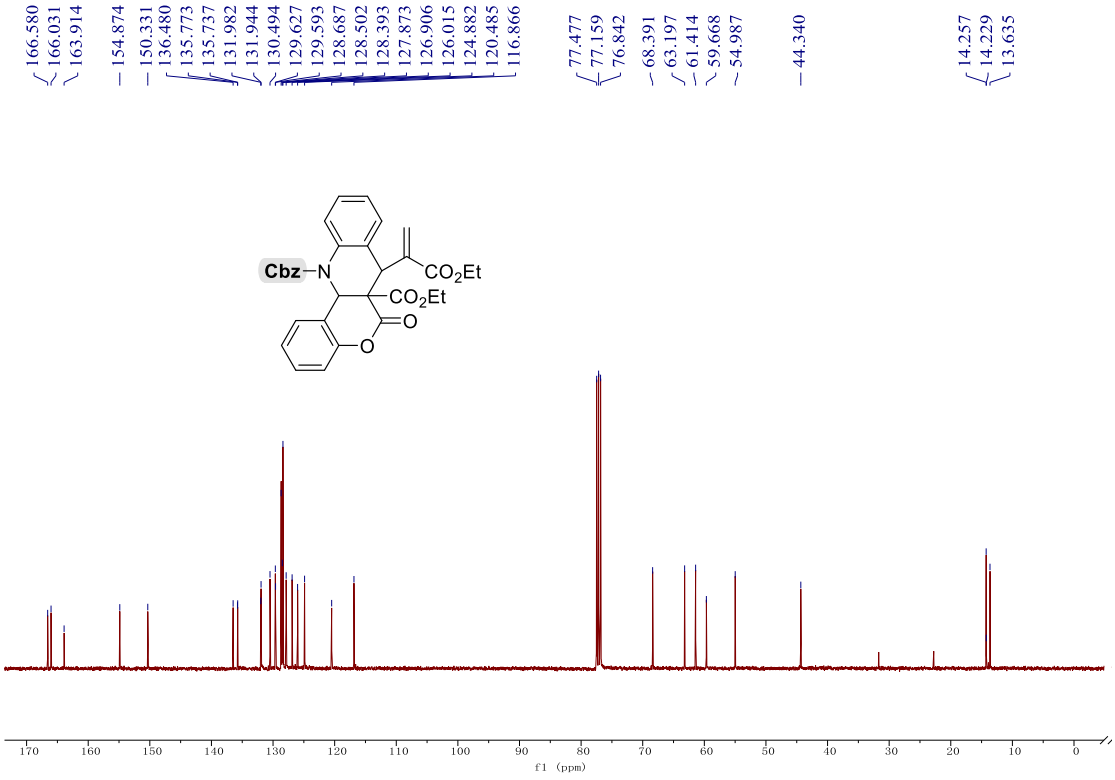


6a-ethyl 12-isopropyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3l)

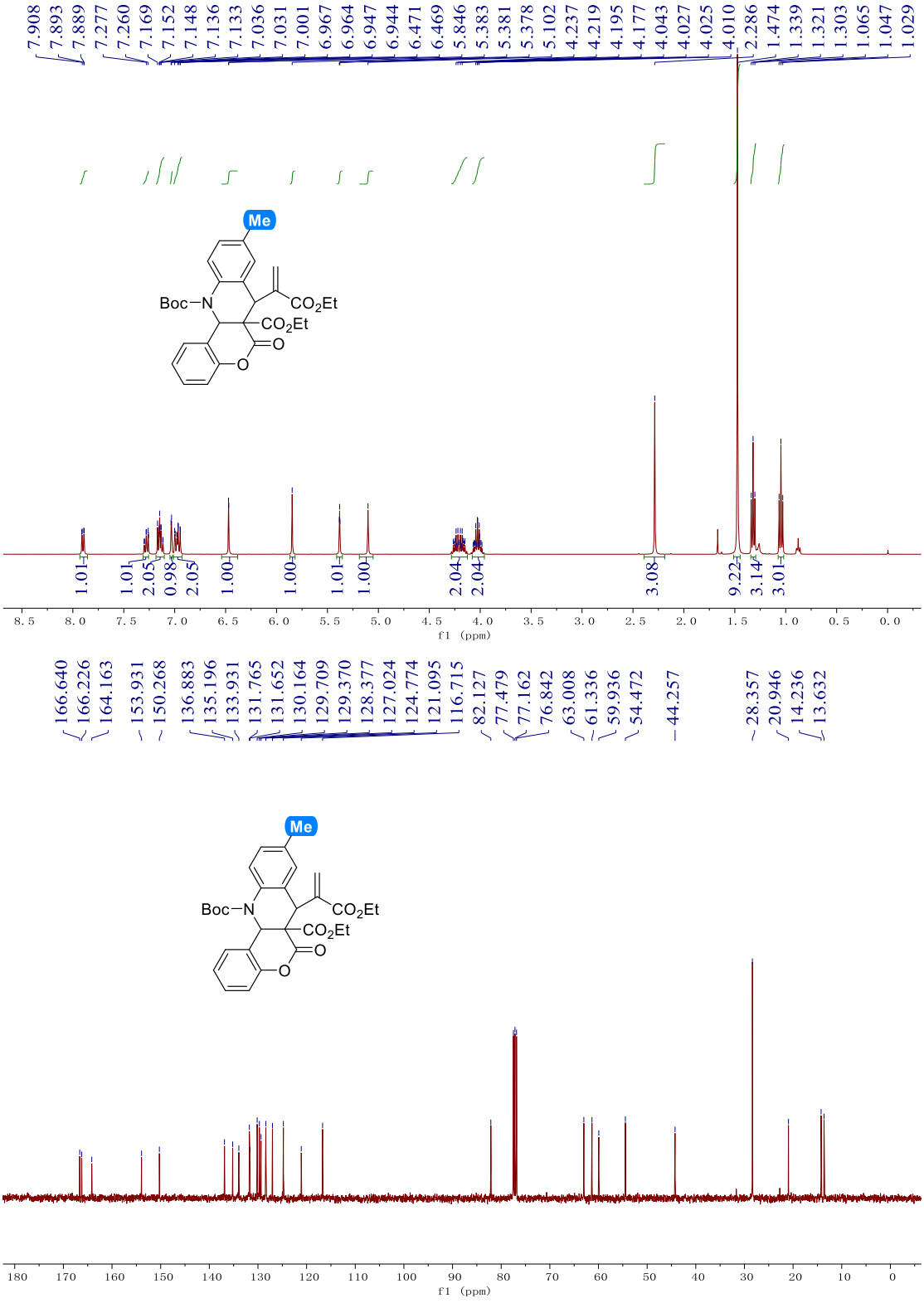


12-benzyl 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3m)

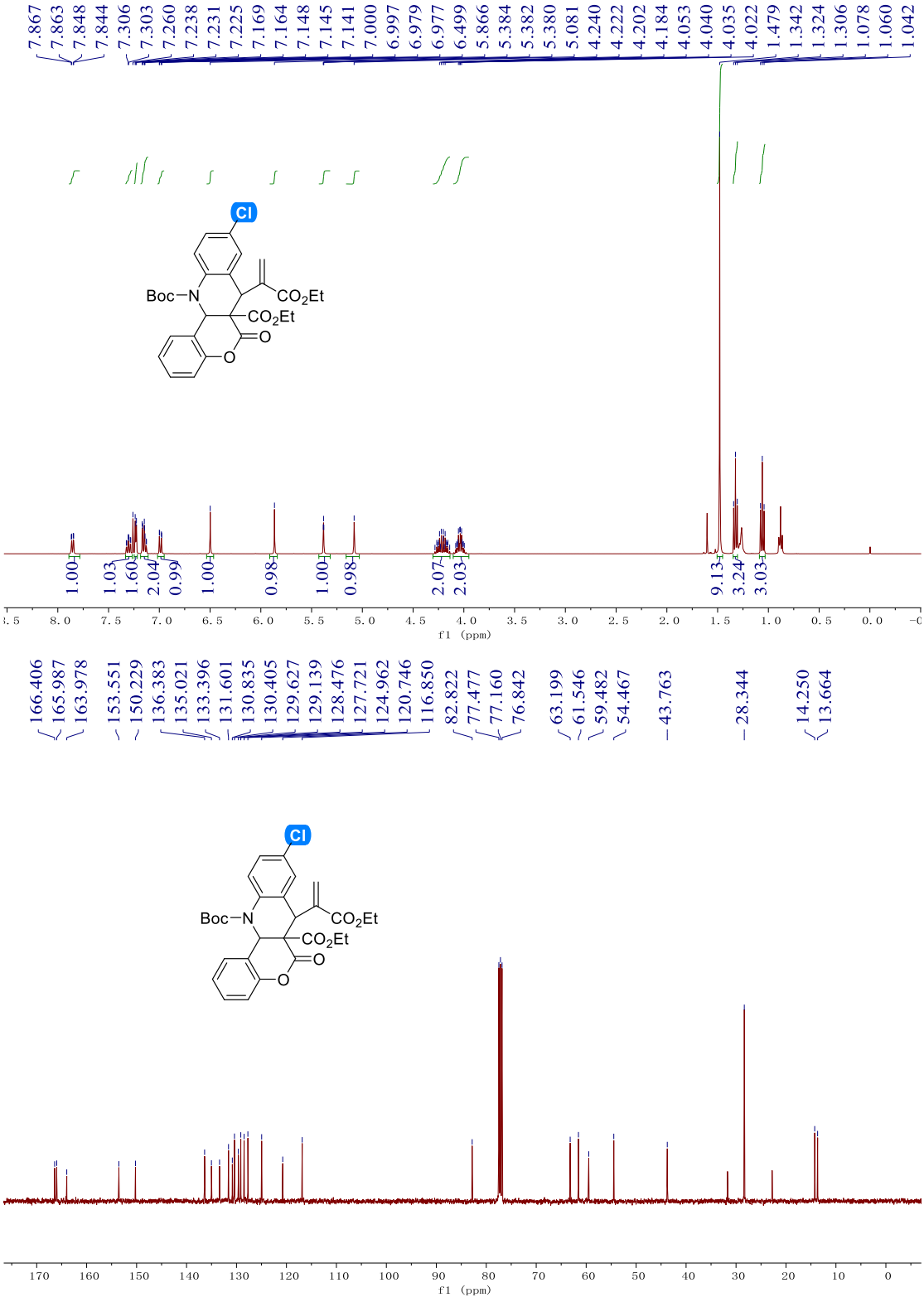




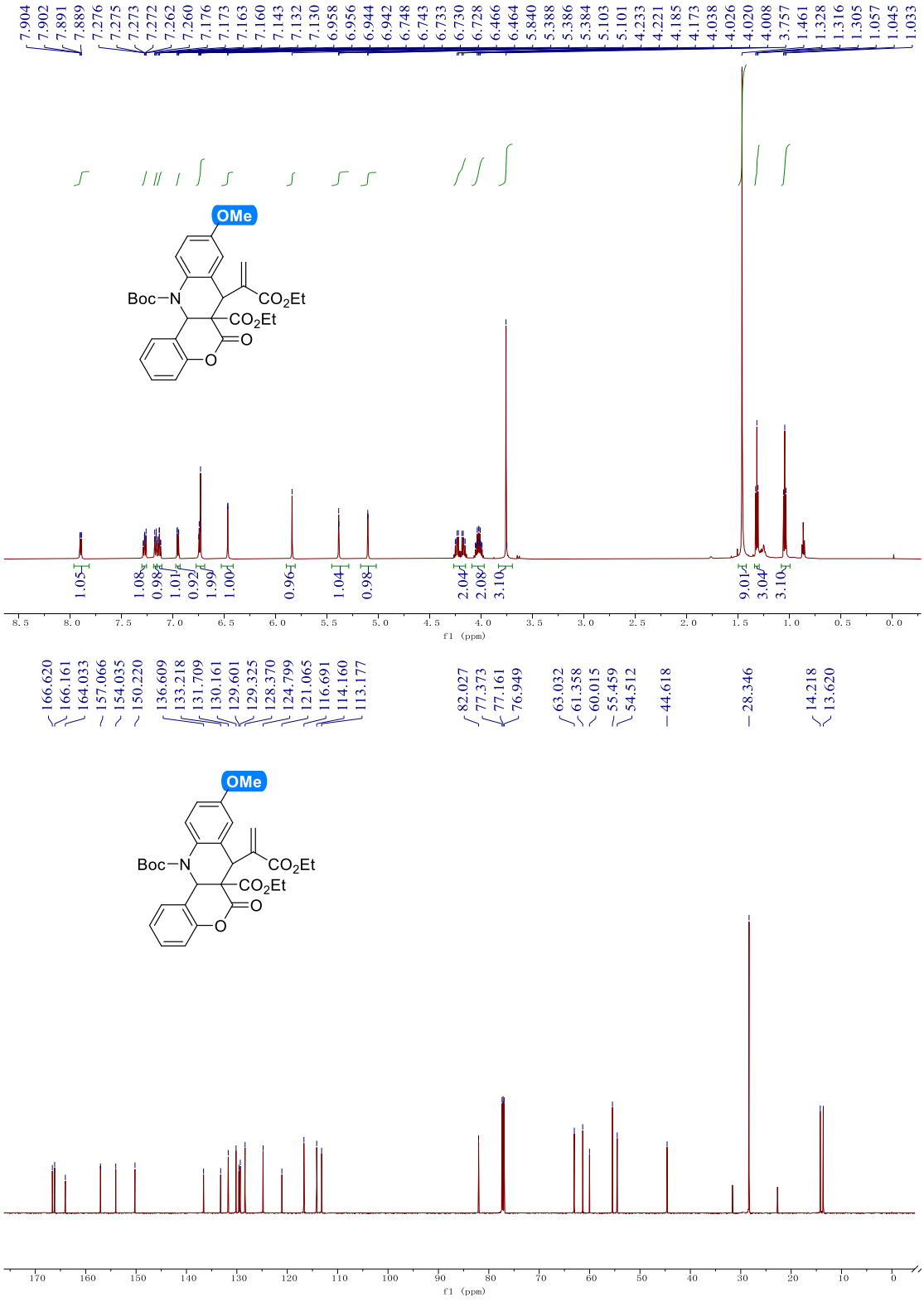
12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-9-methyl-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3n)



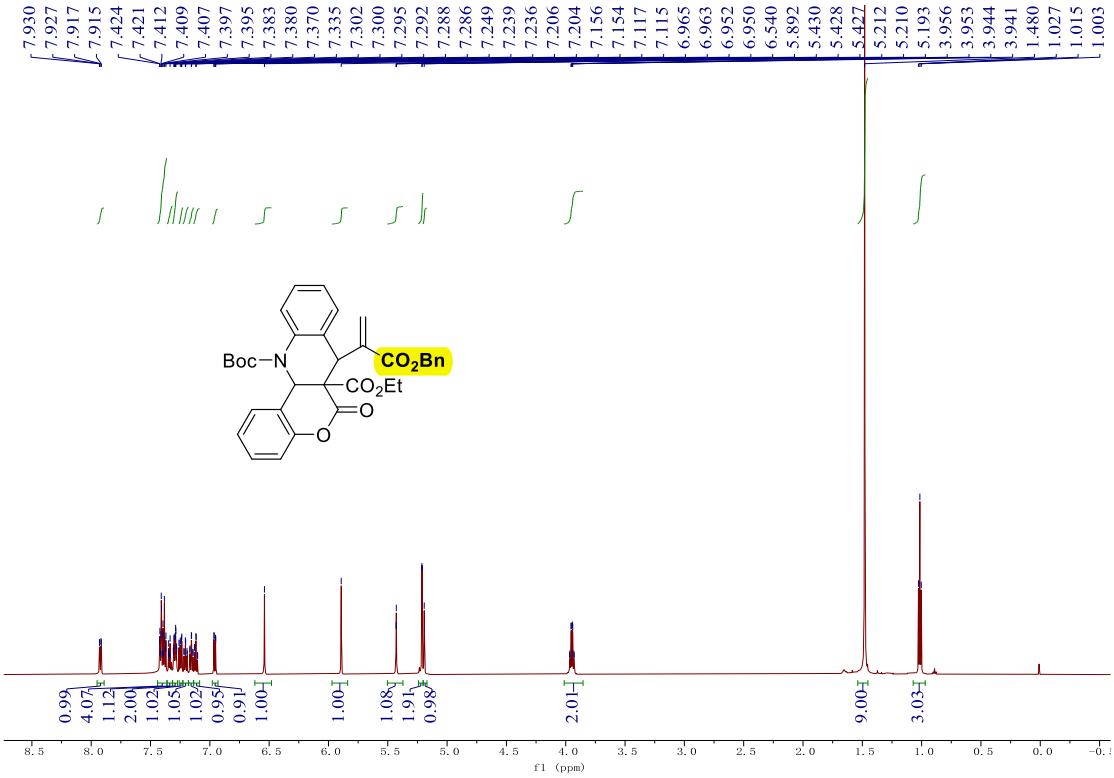
12-(tert-butyl) 6a-ethyl 9-chloro-7-(3-ethoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3o)

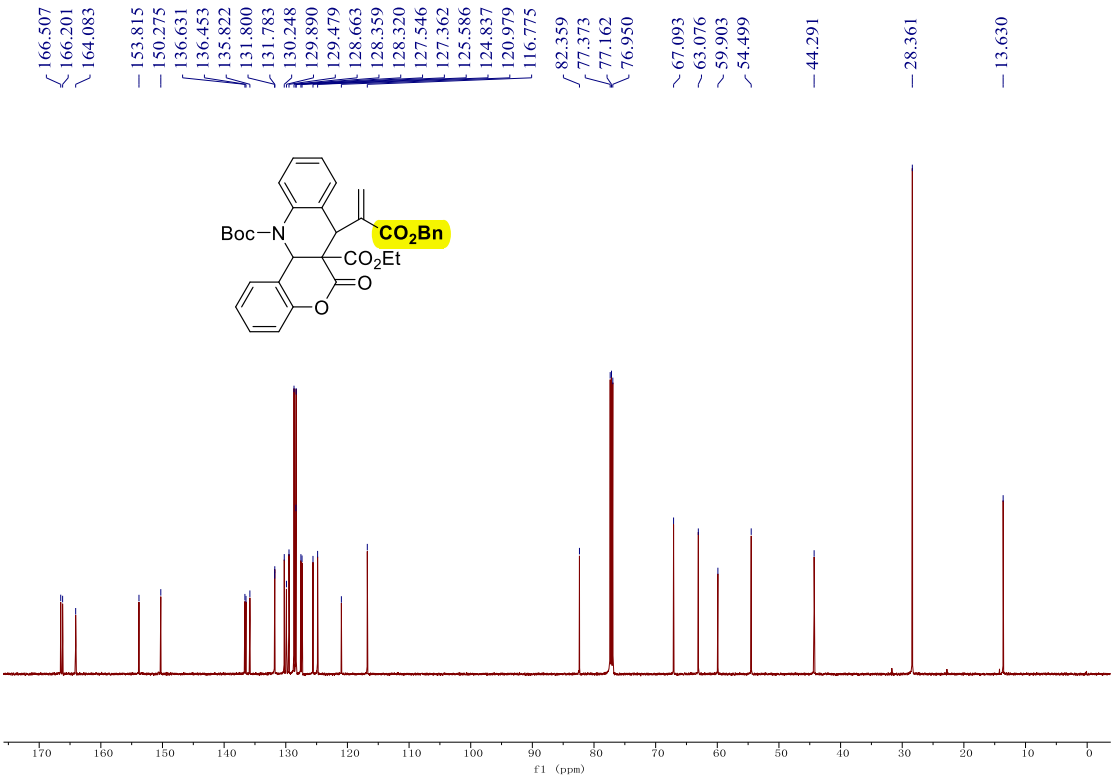


12-(tert-butyl) 6a-ethyl 7-(3-ethoxy-3-oxoprop-1-en-2-yl)-9-methoxy-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3p)

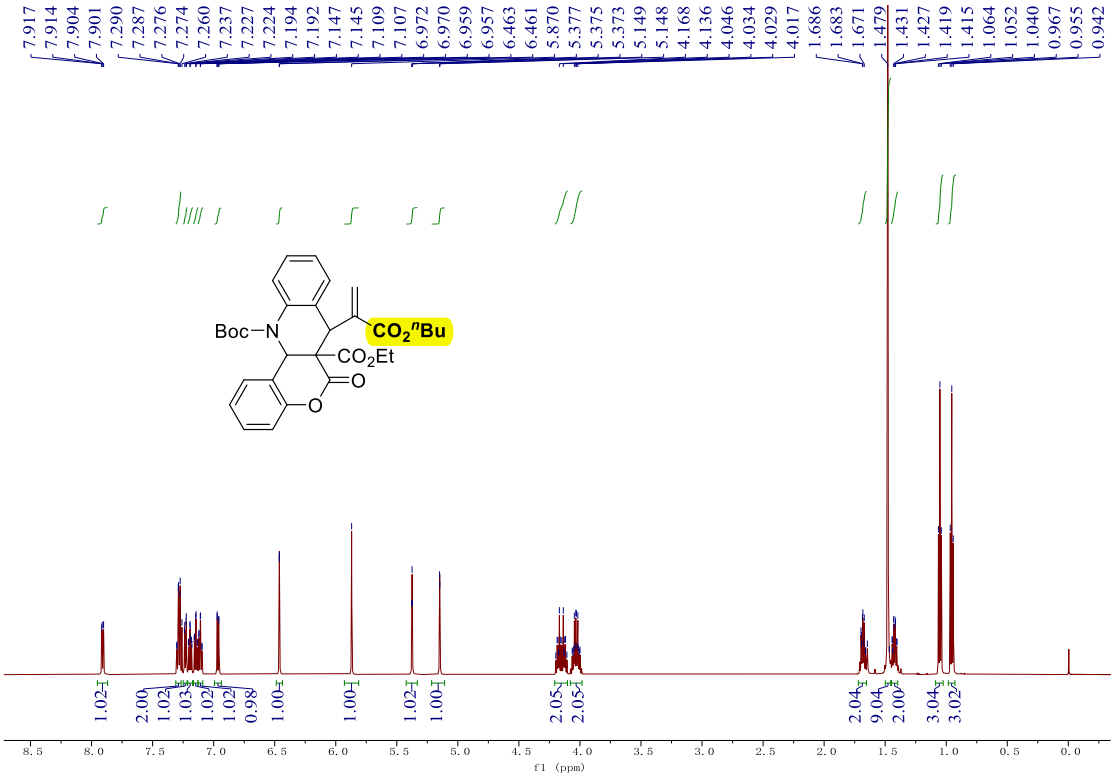


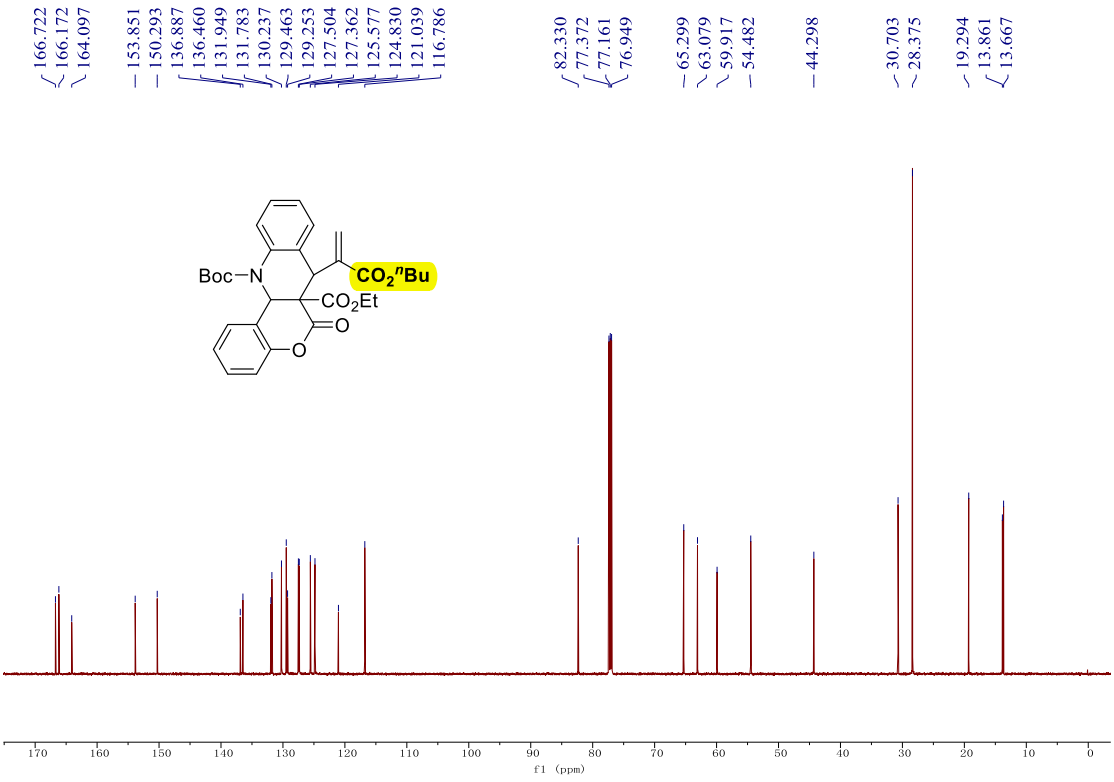
12-(tert-butyl) 6a-ethyl 7-(3-(benzyloxy)-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3q)





12-(tert-butyl) 6a-ethyl 7-(3-butoxy-3-oxoprop-1-en-2-yl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3r)





12-(tert-butyl) 6a-ethyl 7-(1-cyanovinyl)-6-oxo-6H-chromeno[4,3-b]quinoline-6a,12(7H,12aH)-dicarboxylate (3s)