Phosphine-Mediated [2+1] Cyclization of Coumarins for the Efficient Construction of cyclopropa[*c*]coumarin Scaffolds

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Supporting Information

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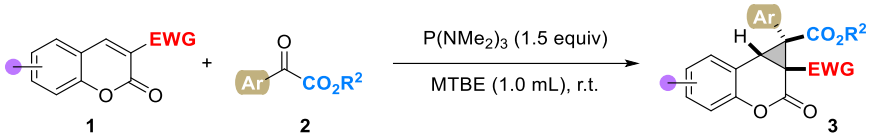
1. General experimental information

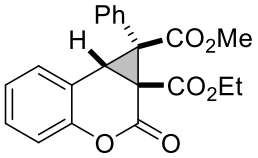
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent 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, coumarins **1** (0.1 mmol, 1.0 equiv), benzoylformates **2** (0.15 mmol, 1.5 equiv), $P(NMe_2)_3$ (0.15 mmol, 1.5 equiv) and MTBE (1.0 mL) was added. The reaction was performed without the requirement of anhydrous or inert atmosphere conditions, and then the mixture was stirred at r.t. for 10 h. the products **3** were isolated by flash chromatography on silica gel.

1a-ethyl 1-methyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3a)



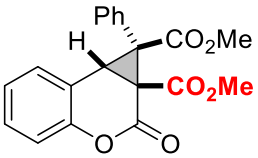
It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford white solid (31.8 mg, 87% yield); m.p. 164.4-166.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.22 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 7.04 – 6.91 (m, 2H), 6.65 – 6.59 (m, 1H), 4.33 (qd, *J* = 7.2, 2.5 Hz, 2H), 4.05 (s, 1H), 3.70 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 164.9, 160.4, 149.9, 130.6, 129.9, 129.4, 128.8, 128.7, 128.5, 125.1, 116.7, 116.6, 62.9, 53.8, 43.8, 42.5, 35.3, 14.1.

HRMS (ESI) Calcd. for $C_{21}H_{18}O_6Na^+$ $(M+Na)^+$ 389.0996, found 389.0992.

dimethyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3b)



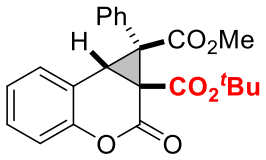
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (28.5 mg, 81% yield); m.p. 153.7-155.6 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H), 7.23 – 7.15 (m, 3H), 7.15 – 7.10 (m, 2H), 6.99 (s, 2H), 6.65 – 6.60 (m, 1H), 4.04 (s, 1H), 3.88 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 165.5, 160.3, 149.8, 130.6, 129.7, 129.5, 128.8, 128.8, 128.5, 125.1, 116.7, 116.5, 53.9, 53.7, 43.6, 42.6, 35.4.

HRMS (ESI) Calcd. for $C_{20}H_{16}O_6Na^+$ $(M+Na)^+$ 375.0839, found 375.0837.

1a-(tert-butyl) 1-methyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3c)



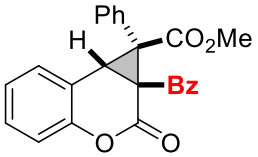
It was purified by flash chromatography (petroleum ether /EtOAc, 15:1) to afford white solid (32.8 mg, 83% yield); m.p. 176.2-178.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.19 – 7.15 (m, 3H), 7.13 – 7.08 (m, 2H), 7.02 – 6.89 (m, 2H), 6.64 – 6.57 (m, 1H), 4.04 (s, 1H), 3.71 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 163.7, 160.8, 149.9, 130.6, 130.2, 129.2, 128.8, 128.6, 128.4, 124.9, 116.9, 116.6, 83.6, 53.7, 45.0, 42.4, 35.1, 27.9.

HRMS (ESI) Calcd. for $C_{23}H_{22}O_6Na^+$ $(M+Na)^+$ 417.1309, found 417.1306.

methyl 1a-benzoyl-2-oxo-1-phenyl-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate (3d)



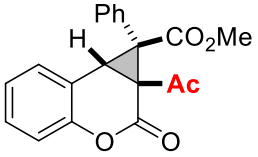
It was purified by flash chromatography (petroleum ether /EtOAc, 13:1) to afford white solid (39.5 mg, 99% yield, 20:1 d.r.); m.p. 173.8-176.6 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.63 – 7.54 (m, 2H), 7.48 – 7.42 (m, 2H), 7.27 – 7.21 (m, 3H), 7.21 – 7.19 (m, 1H), 7.19 – 7.06 (m, 3H), 6.74 – 6.68 (m, 1H), 4.19 (s, 1H), 3.61 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 189.3, 170.0, 161.5, 150.0, 135.0, 134.1, 130.8, 130.3, 129.6, 129.2, 129.1, 128.6, 128.6, 128.5, 125.3, 116.9, 116.4, 53.8, 47.0, 42.2, 36.0.

HRMS (ESI) Calcd. for $C_{25}H_{18}O_5Na^+$ $(M+Na)^+$ 421.1046, found 421.1043.

methyl 1a-acetyl-2-oxo-1-phenyl-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate (3e)



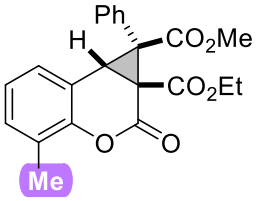
It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford white solid (31.6 mg, 94% yield, 8:1 d.r.); m.p. 162.2-163.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 1H), 7.22 – 7.17 (m, 3H), 7.15 – 7.11 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.67 – 6.61 (m, 1H), 3.99 (s, 1H), 3.69 (s, 3H), 2.67 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 169.1, 161.7, 149.7, 130.4, 130.0, 129.4, 129.0, 128.8, 128.6, 125.1, 116.9, 116.6, 53.7, 47.4, 45.8, 35.4, 30.5.

HRMS (ESI) Calcd. for $C_{20}H_{16}O_5Na^+$ $(M+Na)^+$ 359.0890, found 359.0890.

1a-ethyl 1-methyl 4-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3f)



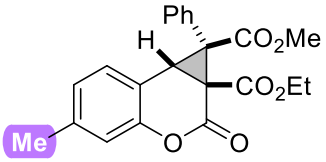
It was purified by flash chromatography (petroleum ether /EtOAc, 12:1) to afford white solid (29.6 mg, 78% yield); m.p. 152.1-154.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.12 – 7.08 (m, 2H), 7.08 – 7.05 (m, 1H), 7.03 – 7.00 (m, 1H), 7.00 – 6.93 (m, 2H), 4.33 (tq, *J* = 7.2, 3.5 Hz, 2H), 4.03 (s, 1H), 3.70 (s, 3H), 1.90 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 165.0, 160.6, 148.2, 130.8, 130.6, 130.0, 128.6, 128.3, 126.3, 126.1, 124.4, 116.2, 62.8, 53.8, 44.1, 42.3, 35.6, 15.4, 14.1.

HRMS (ESI) Calcd. for $C_{22}H_{20}O_6Na^+$ $(M+Na)^+$ 403.1152, found 403.1153.

1a-ethyl 1-methyl 5-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3g)



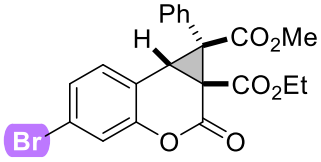
It was purified by flash chromatography (petroleum ether /EtOAc, 12:1) to afford white solid (29.5 mg, 78% yield); m.p. 143.2-144.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.15 – 7.10 (m, 2H), 7.05 – 6.96 (m, 3H), 6.46 – 6.41 (m, 1H), 4.32 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.00 (s, 1H), 3.69 (s, 3H), 2.25 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 165.0, 160.7, 149.7, 139.9, 130.7, 130.0, 128.6, 128.4, 125.9, 117.0, 113.4, 62.8, 53.7, 43.7, 42.5, 35.2, 21.3, 14.1.

HRMS (ESI) Calcd. for $C_{22}H_{20}O_6Na^+$ $(M+Na)^+$ 403.1152, found 403.1150.

1a-ethyl 1-methyl 5-bromo-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3h)



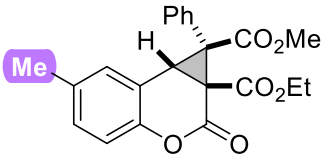
It was purified by flash chromatography (petroleum ether /EtOAc, 12:1) to afford white solid (32.3 mg, 73% yield); m.p. 173.7-175.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.18 – 7.14 (m, 2H), 7.03 – 6.95 (m, 2H), 6.80 (d, *J* = 1.9 Hz, 1H), 4.33 (qd, *J* = 7.1, 2.0 Hz, 2H), 4.00 (s, 1H), 3.70 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 164.6, 159.8, 150.2, 130.5, 129.9, 129.6, 129.0, 128.7, 128.2, 122.3, 119.9, 115.8, 63.0, 53.9, 43.4, 42.6, 34.9, 14.1.

HRMS (ESI) Calcd. for $C_{21}H_{17}BrO_6Na^+$ $(M+Na)^+$ 467.0101, 469.0080, found 467.0101, 469.0081.

1a-ethyl 1-methyl 6-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3i)



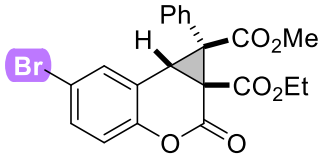
It was purified by flash chromatography (petroleum ether /EtOAc, 12:1) to afford White solid (28.2 mg, 74% yield); m.p. 152.4-154.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 1H), 7.23 – 7.17 (m, 1H), 7.16 – 7.10 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.98 – 6.94 (m, 1H), 6.51 (d, *J* = 8.3 Hz, 1H), 4.32 (qd, *J* = 7.2, 2.3 Hz, 2H), 3.99 (s, 1H), 3.70 (s, 3H), 2.37 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 165.0, 160.6, 147.9, 134.8, 130.6, 130.0, 129.0, 128.7, 128.5, 116.4, 116.2, 62.8, 53.8, 43.8, 42.5, 35.4, 20.9, 14.1.

HRMS (ESI) Calcd. for $C_{22}H_{20}O_6Na^+$ $(M+Na)^+$ 403.1152, found 403.1152.

1a-ethyl 1-methyl 6-bromo-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3j)



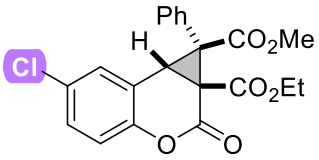
It was purified by flash chromatography (petroleum ether /EtOAc, 15:1) to afford White solid (36.7 mg, 83% yield); m.p. 162.7-165.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.4 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 7.08 – 6.94 (m, 2H), 6.51 (d, *J* = 8.7 Hz, 1H), 4.33 (qd, *J* = 7.1, 1.4 Hz, 2H), 4.00 (s, 1H), 3.70 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 164.6, 159.9, 148.9, 132.4, 131.4, 130.5, 129.5, 129.0, 128.7, 118.8, 118.4, 117.5, 63.0, 53.9, 43.4, 42.7, 34.8, 14.1.

HRMS (ESI) Calcd. for $C_{21}H_{17}BrO_6Na^+$ $(M+Na)^+$ 467.0101, 469.0080, found 467.0104, 469.0083.

1a-ethyl 1-methyl 6-chloro-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3k)



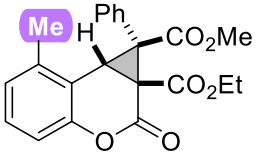
It was purified by flash chromatography (petroleum ether /EtOAc, 15:1) to afford White solid (33.7 mg, 74% yield); m.p. 160.5-162.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.5 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.12 (m, 3H), 7.05 – 6.96 (m, 2H), 6.57 (d, *J* = 8.7 Hz, 1H), 4.33 (qd, *J* = 7.2, 1.5 Hz, 2H), 4.00 (s, 1H), 3.70 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 164.6, 159.9, 148.4, 130.5, 130.2, 129.6, 129.5, 128.9, 128.7, 128.5, 118.3, 118.1, 63.0, 53.9, 43.4, 42.7, 34.8, 14.1.

HRMS (ESI) Calcd. for $C_{21}H_{17}ClO_6Na^+$ $(M+Na)^+$ 423.0606, 425.0576, found 423.0607, 425.0573.

1a-ethyl 1-methyl 7-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3l)



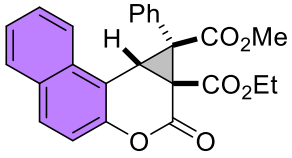
It was purified by flash chromatography (petroleum ether /EtOAc, 12:1) to afford White solid (29.4 mg, 77% yield); m.p. 162.1-164.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.15 – 7.09 (m, 2H), 7.04 – 6.94 (m, 3H), 6.48 – 6.40 (m, 1H), 4.32 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.00 (s, 1H), 3.69 (s, 3H), 2.25 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 165.1, 160.7, 149.8, 139.9, 130.7, 130.0, 128.7, 128.5, 125.9, 117.0, 113.5, 62.8, 53.8, 43.7, 42.5, 35.2, 21.3, 14.1.

HRMS (ESI) Calcd. for $C_{22}H_{20}O_6Na^+$ $(M+Na)^+$ 403.1152, found 403.1152.

1a-ethyl 1-methyl 2-oxo-1-phenyl-1,9c-dihydrobenzo[*f*]cyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3m)



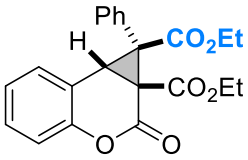
It was purified by flash chromatography (petroleum ether /EtOAc, 20:1) to afford White solid (32.5 mg, 78% yield); m.p. 167.3-169.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 – 8.24 (m, 1H), 7.89 – 7.82 (m, 1H), 7.78 – 7.71 (m, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.16 – 7.10 (m, 1H), 7.05 – 6.97 (m, 2H), 6.93 – 6.83 (m, 2H), 6.81 (d, *J* = 8.9 Hz, 1H), 4.52 (s, 1H), 4.36 (qd, *J* = 7.1, 5.3 Hz, 2H), 3.76 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 165.2, 160.4, 147.8, 131.5, 130.8, 130.4, 130.1, 129.9, 129.0, 128.8, 128.5, 128.3, 125.9, 122.9, 116.7, 110.0, 63.0, 53.9, 43.0, 42.7, 32.2, 14.2.

HRMS (ESI) Calcd. for $C_{25}H_{20}O_6Na^+$ $(M+Na)^+$ 439.1152, found 439.1151.

diethyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3n)



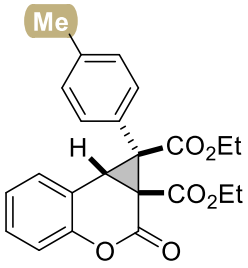
It was purified by flash chromatography (petroleum ether /EtOAc, 8:1) to afford White solid (29.9 mg, 79% yield); m.p. 158.7-160.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.14 – 7.06 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.66 – 6.58 (m, 1H), 4.37 – 4.28 (m, 2H), 4.25 – 4.17 (m, 1H), 4.13 – 4.06 (m, 1H), 4.04 (s, 1H), 1.36 (td, *J* = 7.1, 1.2 Hz, 3H), 1.17 (td, *J* = 7.1, 1.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.2, 164.9, 160.5, 149.9, 130.6, 130.0, 129.3, 128.8, 128.6, 128.4, 125.0, 116.8, 116.7, 62.9, 62.8, 43.7, 42.7, 35.1, 14.1, 14.0.

HRMS (ESI) Calcd. for $C_{22}H_{20}O_6Na^+$ $(M+Na)^+$ 403.1152, found 403.1151.

diethyl 2-oxo-1-(p-tolyl)-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3o)



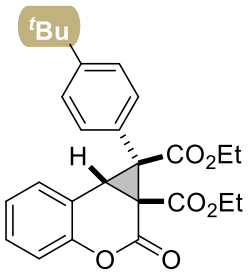
It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford White solid (34.1 mg, 87% yield); m.p. 155.2-158.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.18 (dd, *J* = 5.9, 3.4 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.65 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.32 (qd, *J* = 7.2, 1.7 Hz, 2H), 4.21 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.09 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.01 (s, 1H), 2.22 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 165.1, 160.5, 149.9, 138.5, 130.4, 129.3, 129.1, 128.8, 126.9, 124.9, 116.9, 116.7, 62.8, 62.7, 43.5, 42.5, 35.1, 21.3, 14.1, 14.0.

HRMS (ESI) Calcd. for $C_{23}H_{22}O_6Na^+$ $(M+Na)^+$ 417.1309, found 417.1303.

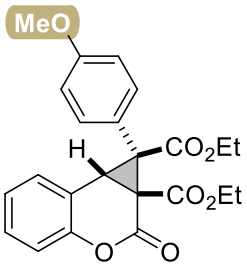
diethyl 1-(4-(tert-butyl)phenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3p)



It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford White solid (36.0 mg, 83% yield); m.p. 146.7-148.1 °C.

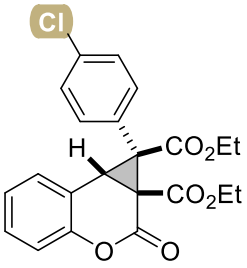
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.22 – 7.15 (m, 1H), 7.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.80 (dq, *J* = 10.7, 7.1 Hz, 1H), 1.30 (s, 9H), 0.83 (dt, *J* = 14.5, 7.1 Hz, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 163.8, 159.8, 152.3, 150.4, 129.4, 129.3, 129.2, 125.7, 124.8, 116.9, 115.9, 62.6, 62.5, 47.5, 39.9, 34.8, 32.0, 31.3, 13.6, 13.5.
HRMS (ESI) Calcd. for $C_{26}H_{28}O_6Na^+$ $(M+Na)^+$ 459.1778, found 459.1776.

diethyl 1-(4-methoxyphenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3q)



It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (33.6 mg, 82% yield); m.p. 166.7-168.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 5.7, 3.5 Hz, 1H), 7.18 (dd, *J* = 5.9, 3.4 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.69 – 6.58 (m, 3H), 4.32 (qd, *J* = 7.1, 0.9 Hz, 2H), 4.21 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.09 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.01 (s, 1H), 3.70 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 165.0, 160.5, 159.6, 149.9, 131.8, 129.3, 128.7, 125.0, 121.8, 116.8, 116.7, 113.8, 62.8, 62.7, 55.2, 43.6, 42.2, 35.1, 14.1, 14.0.
HRMS (ESI) Calcd. for $C_{23}H_{22}O_7Na^+$ $(M+Na)^+$ 433.12577, found 433.12549.

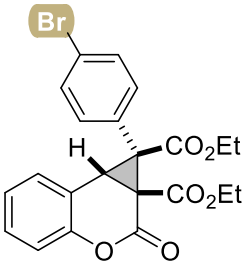
diethyl 1-(4-chlorophenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3r)



It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford White solid (37.3 mg, 90% yield); m.p. 158.7-161.2 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 1H), 7.25 – 7.17 (m, 2H), 7.12 – 7.05 (m, 2H), 6.97 – 6.83 (m, 2H), 6.71 – 6.63 (m, 1H), 4.32 (qd, *J* = 7.2, 1.0 Hz, 2H), 4.21 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.10 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.04 (s, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 164.6, 160.2, 149.8, 134.8, 131.9, 129.6, 128.8, 128.7, 128.6, 125.2, 116.9, 116.4, 63.1, 62.9, 43.8, 41.9, 35.1, 14.1, 14.0.
HRMS (ESI) Calcd. for $C_{22}H_{19}ClO_6Na^+$ $(M+Na)^+$ 437.0762, 439.0733, found 437.0761, 439.0726.

diethyl 1-(4-bromophenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-

dicarboxylate (3s)



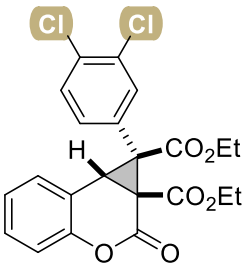
It was purified by flash chromatography (petroleum ether /EtOAc, 8:1) to afford White solid (36.9 mg, 81% yield); m.p. 180.2-182.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.26 – 7.23 (m, 2H), 7.23 – 7.17 (m, 2H), 6.85 (s, 2H), 6.72 – 6.65 (m, 1H), 4.32 (qd, *J* = 7.2, 1.9 Hz, 2H), 4.21 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.10 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.03 (s, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 164.6, 160.2, 149.8, 132.2, 131.7, 129.6, 129.2, 128.8, 125.2, 123.2, 116.9, 116.4, 63.1, 62.9, 43.7, 41.9, 35.1, 14.1, 14.0.

HRMS (ESI) Calcd. for $C_{22}H_{19}BrO_6Na^+$ $(M+Na)^+$ 481.0257, 483.0237, found 481.0258, 483.0237.

diethyl 1-(3,4-dichlorophenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3t)



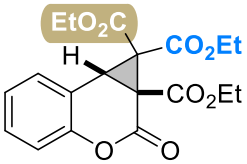
It was purified by flash chromatography (petroleum ether /EtOAc, 20:1) to afford white solid (39.5 mg, 88% yield); m.p. 175.2-177.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.93 (d, *J* = 59.6 Hz, 2H), 6.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.33 (qd, *J* = 7.1, 1.4 Hz, 2H), 4.26 – 4.20 (m, 1H), 4.15 – 4.07 (m, 1H), 4.04 (s, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 164.4, 159.9, 149.7, 133.3, 132.5, 132.4, 130.6, 130.3, 130.1, 129.9, 128.8, 125.4, 117.0, 116.0, 63.3, 63.0, 43.9, 41.2, 35.1, 14.1, 14.0.

HRMS (ESI) Calcd. for $C_{22}H_{18}Cl_2O_6Na^+$ $(M+Na)^+$ 471.0373, 473.0343, 475.0314, found 471.0377, 473.0346, 475.0304.

triethyl 2-oxocyclopropa[*c*]chromene-1,1,1a(2*H*,7b*H*)-tricarboxylate (3u)



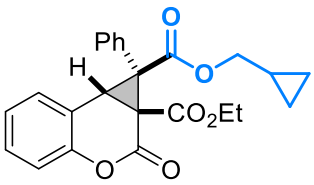
It was purified by flash chromatography (petroleum ether /EtOAc, 8:1) to afford white solid (28.7 mg, 76% yield); m.p. 147.4-149.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.20 – 7.15 (m, 1H), 7.03 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.34 – 4.24 (m, 4H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 1H), 1.31 (dt, *J* = 13.2, 7.1 Hz, 6H), 0.93 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 163.8, 163.1, 159.3, 150.2, 130.0, 129.5, 125.1, 117.1, 114.1, 63.4, 63.1, 62.8, 43.9, 40.8, 33.6, 14.1, 14.0, 13.5.

HRMS (ESI) Calcd. for $C_{19}H_{20}O_8Na^+$ $(M+Na)^+$ 399.1050, found 399.1050.

1-(cyclopropylmethyl) 1a-ethyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3v)



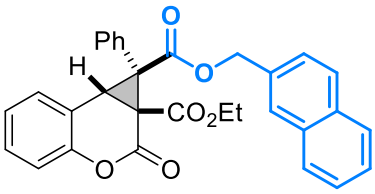
It was purified by flash chromatography (petroleum ether /EtOAc, 15:1) to afford white solid (32.7 mg, 81% yield); m.p. 143.5-147.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 1H), 7.22 – 7.15 (m, 3H), 7.15 – 7.07 (m, 2H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.67 – 6.58 (m, 1H), 4.38 – 4.28 (m, 2H), 4.04 (s, 1H), 3.99 (ddd, *J* = 11.3, 6.9, 1.2 Hz, 1H), 3.90 (ddd, *J* = 11.3, 7.0, 1.3 Hz, 1H), 1.35 (td, *J* = 7.1, 1.6 Hz, 3H), 1.06 – 0.97 (m, 1H), 0.51 – 0.42 (m, 2H), 0.20 – 0.11 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 164.9, 160.5, 149.9, 130.6, 130.1, 129.3, 128.8, 128.6, 128.4, 125.0, 116.8, 116.7, 71.1, 62.8, 43.6, 42.8, 35.2, 14.1, 9.5, 3.2, 3.1.

HRMS (ESI) Calcd. for $C_{24}H_{22}O_6Na^+$ $(M+Na)^+$ 429.1309, found 429.1309.

1a-ethyl 1-(naphthalen-2-ylmethyl) 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3w)



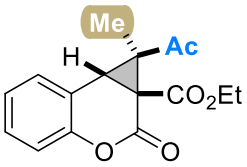
It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford white solid (38.4 mg, 87% yield); m.p. 160.2-161.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.72 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.52 (s, 1H), 7.49 – 7.44 (m, 2H), 7.25 – 7.20 (m, 2H), 7.20 – 7.17 (m, 2H), 7.17 – 7.13 (m, 2H), 7.04 (s, 2H), 6.67 – 6.61 (m, 1H), 5.35 – 5.24 (m, 2H), 4.30 – 4.14 (m, 2H), 4.09 – 4.04 (m, 1H), 1.23 (td, *J* = 7.1, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 164.9, 160.4, 149.9, 133.2, 133.1, 132.7, 130.7, 130.0, 129.4, 128.8, 128.7, 128.5, 128.4, 128.1, 127.8, 126.5, 126.4, 126.3, 125.1, 116.7, 116.6, 68.2, 62.9, 43.9, 42.7, 35.3, 14.0.

HRMS (ESI) Calcd. for $C_{31}H_{24}O_6Na^+$ $(M+Na)^+$ 515.1465, found 515.1468.

ethyl 1-acetyl-1-methyl-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1a(2*H*)-carboxylate (3x)



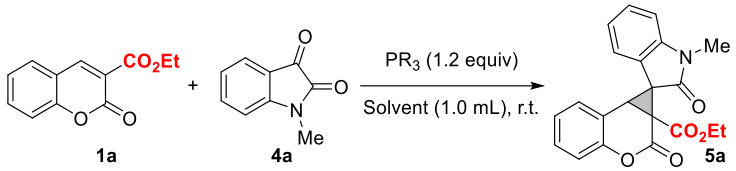
It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford white solid (24.0 mg, 83% yield); m.p. 162.8-164.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.23 – 7.17 (m, 1H), 7.08 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.25 – 4.16 (m, 2H), 3.74 (s, 1H), 2.45 (s, 3H), 1.30 – 1.26 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 203.6, 165.0, 160.6, 150.4, 129.4, 129.4, 125.4, 117.0, 116.4, 62.7, 42.9, 38.4, 33.7, 29.0, 13.9, 11.5.

HRMS (ESI) Calcd. for $C_{16}H_{16}O_5Na^+$ $(M+Na)^+$ 311.0890, found 311.0890.

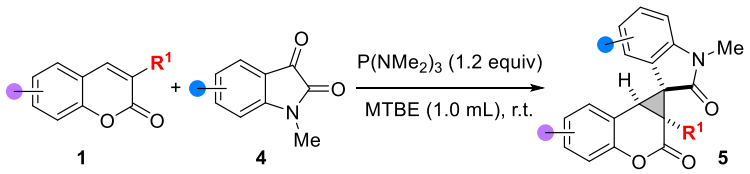
3. Table S1. Optimization of Reaction Condition for 1a and 4a[a].



Entry	PR_3	Solvent	Yield[b] (%)
1	$P(NMe_2)_3$	DCM	74
2	$P(NMe_2)_3$	MeCN	64
3	$P(NMe_2)_3$	THF	50
4	$P(NMe_2)_3$	Toluene	N.R.
5	$P(NMe_2)_3$	Et_2O	28
6	$P(NMe_2)_3$	Acetone	66
7	$P(NMe_2)_3$	MTBE	95
8	$P(NMe_2)_3$	EA	61
9	$P(OMe)_3$	MTBE	N.R.
10	PPh_3	MTBE	N.R.
11[c]	$P(NMe_2)_3$	MTBE	80
12[d]	$P(NMe_2)_3$	MTBE	59
13[e]	$P(NMe_2)_3$	MTBE	Messy

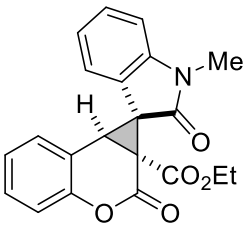
[a]Unless specified, the reactions were carried out with **1a** (0.1 mmol), **4a** (0.12 mmol) and PR_3 (0.12 mmol, 1.2 equiv) in 1.0 mL of solvent at r.t. for 18 h. [b]isolated yield. [c]**4a** (1.5 equiv) and $P(NMe_2)_3$ (1.5 equiv) were used. [d] 0 °C. [e]50 °C.

4. General experimental procedures for synthesis of compounds 5.



In an ordinary vial charged with a magnetic stirring bar, coumarins **1** (0.1 mmol, 1.0 equiv), isatins **4** (0.12 mmol, 1.2 equiv), $P(NMe_2)_3$ (0.12 mmol, 1.2 equiv) and MTBE (1.0 mL) was added. The reaction was performed without the requirement of anhydrous or inert atmosphere conditions, and then the mixture was stirred at r.t. for 18 h. the products **5** were isolated by flash chromatography on silica gel.

ethyl 1'-methyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5a)



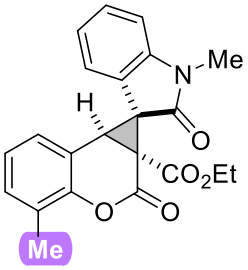
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (34.6 mg, 95% yield); m.p. 185.7-188.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.30 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.11 – 7.06 (m, 1H), 7.03 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.27 (qd, *J* = 7.1, 1.9 Hz, 2H), 3.87 (s, 1H), 3.16 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 163.8, 159.0, 152.0, 144.1, 130.0, 129.1, 124.7, 124.0, 122.6, 120.9, 116.5, 112.8, 108.9, 63.4, 43.0, 38.2, 36.3, 26.8, 14.2.

HRMS (ESI) Calcd. for $C_{21}H_{17}NO_5Na^+$ $(M+Na)^+$ 386.0999, found 386.0994.

ethyl 1',4-dimethyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5b)



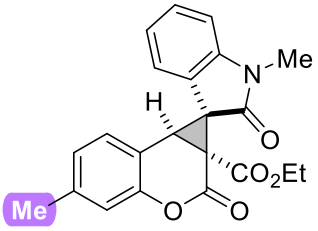
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (33.3 mg, 88% yield); m.p. 178.4-179.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 1H), 7.21 – 7.16 (m, 1H), 7.12 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.05 – 7.03 (m, 1H), 7.03 – 6.99 (m, 1H), 6.90 (dd, *J* = 7.9, 0.8 Hz, 1H), 4.27 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.86 (s, 1H), 3.15 (s, 3H), 2.41 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 163.9, 159.1, 150.3, 144.1, 131.4, 129.0, 126.6, 125.8, 124.1, 124.1, 122.5, 120.9, 112.4, 108.8, 63.3, 43.0, 38.1, 36.7, 26.8, 16.0, 14.2.

HRMS (ESI) Calcd. for $C_{22}H_{19}NO_5Na^+$ $(M+Na)^+$ 400.1155, found 400.1156.

ethyl 1',5-dimethyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5c)



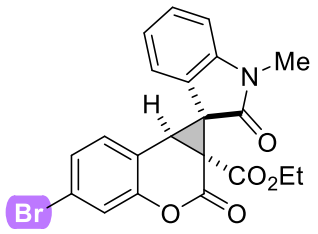
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (36.1 mg, 96% yield); m.p. 186.3-188.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.05 (m, 1H), 7.04 – 7.00 (m, 1H), 6.97 (d, *J* = 1.7 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.92 – 6.87 (m, 1H), 4.27 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.84 (s, 1H), 3.15 (s, 3H), 2.35 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 163.9, 159.3, 151.9, 144.0, 140.4, 129.0, 128.8, 125.6, 124.1, 122.5, 120.9, 116.8, 109.7, 108.8, 63.3, 43.0, 38.2, 36.3, 26.8, 21.5, 14.1.

HRMS (ESI) Calcd. for $C_{22}H_{19}NO_5Na^+$ $(M+Na)^+$ 400.1155, found 400.1158.

ethyl 5-bromo-1'-methyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5d)



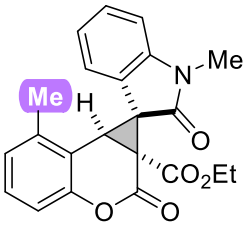
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (33.9 mg, 77% yield); m.p. 189.2-190.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 1H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.12 – 7.06 (m, 1H), 7.05 – 7.01 (m, 1H), 6.94 – 6.88 (m, 1H), 4.27 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.83 (s, 1H), 3.16 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 163.5, 158.4, 152.4, 144.1, 130.3, 129.3, 127.9, 123.6, 123.0, 122.7, 121.0, 119.8, 112.0, 109.0, 63.5, 42.6, 38.3, 35.7, 26.8, 14.1.

HRMS (ESI) Calcd. for $C_{21}H_{16}BrNO_5Na^+$ $(M+Na)^+$ 464.0104, 466.0084, found 464.0106, 466.0085.

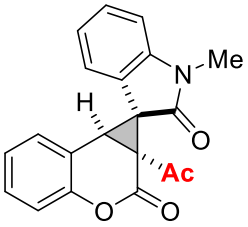
ethyl 1',7-dimethyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5e)



It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (35.2 mg, 93% yield); m.p. 178.5-179.7 °C.

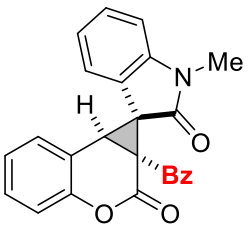
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.04 – 7.00 (m, 1H), 6.97 (d, *J* = 1.7 Hz, 1H), 6.95 – 6.92 (m, 1H), 6.92 – 6.88 (m, 1H), 4.27 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.84 (s, 1H), 3.16 (s, 3H), 2.35 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 163.9, 159.3, 151.9, 144.1, 140.5, 129.0, 128.8, 125.7, 124.1, 122.5, 120.9, 116.9, 109.7, 108.8, 63.3, 43.0, 38.2, 36.3, 26.8, 21.5, 14.2.
HRMS (ESI) Calcd. for $C_{22}H_{19}NO_5Na^+$ $(M+Na)^+$ 400.1155, found 400.1152.

1a-acetyl-1'-methyl-1a,7b-dihydro-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-2,2'-dione (5f)



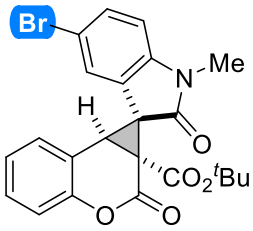
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (28.7 mg, 86% yield); m.p. 168.4-169.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 1H), 7.35 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H), 7.18 – 7.10 (m, 2H), 7.10 – 7.05 (m, 1H), 6.95 – 6.91 (m, 1H), 6.89 – 6.84 (m, 1H), 4.00 (s, 1H), 3.18 (s, 3H), 2.44 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 168.4, 160.9, 151.9, 144.1, 129.8, 129.3, 129.2, 124.8, 123.0, 122.8, 121.0, 116.3, 113.3, 109.0, 49.4, 38.4, 34.6, 31.0, 26.8.
HRMS (ESI) Calcd. for $C_{20}H_{15}NO_4Na^+$ $(M+Na)^+$ 356.0893, found 356.0892.

1a-benzoyl-1'-methyl-1a,7b-dihydro-2H-spiro[cyclopropa[c]chromene-1,3'-indoline]-2,2'-dione (5g)



It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (32.5 mg, 82% yield); m.p. 172.3-175.1 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.49 – 7.44 (m, 1H), 7.42 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 7.19 – 7.14 (m, 1H), 6.91 – 6.82 (m, 2H), 6.58 (d, *J* = 7.6 Hz, 1H), 3.90 (s, 1H), 3.24 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 189.2, 168.7, 160.1, 151.9, 143.5, 135.4, 134.2, 130.2, 130.0, 129.3, 128.8, 128.5, 124.9, 124.1, 122.6, 121.0, 116.6, 113.0, 108.9, 46.6, 38.3, 36.3, 27.0.
HRMS (ESI) Calcd. for $C_{25}H_{17}NO_4Na^+$ $(M+Na)^+$ 418.1050, found 418.1050.

tert-butyl 5'-bromo-1'-methyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5h)



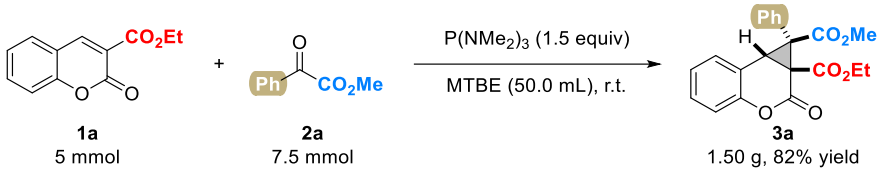
It was purified by flash chromatography (petroleum ether /EtOAc, 5:1) to afford white solid (32.7 mg, 74% yield); m.p. 175.9-178.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (d, *J* = 1.9 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 1H), 3.13 (s, 3H), 1.47 (s, 9H).

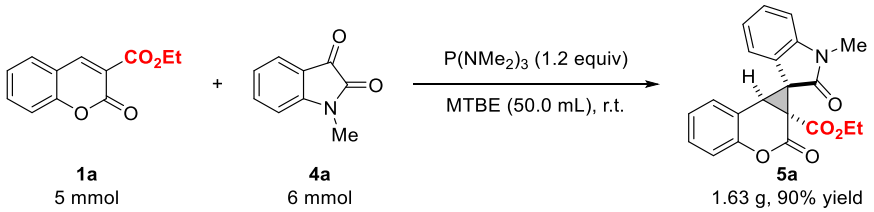
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 162.3, 158.8, 152.1, 143.0, 131.6, 130.0, 129.2, 126.2, 124.7, 124.6, 116.5, 115.0, 112.6, 110.1, 85.2, 44.0, 37.7, 36.6, 28.0, 26.9.

HRMS (ESI) Calcd. for $C_{21}H_{16}BrNO_5Na^+$ $(M+Na)^+$ 464.0104, 466.0084, found 464.0105, 466.0087.

5. Scale-up experiment

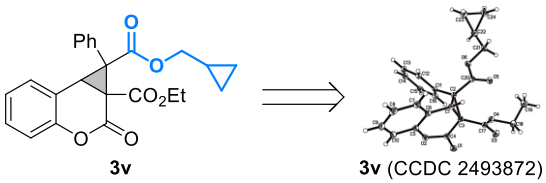


In an ordinary vial charged with a magnetic stirring bar, coumarins **1a** (5 mmol, 1.0 equiv), benzoylformates **2a** (7.5 mmol, 1.5 equiv), $P(NMe_2)_3$ (7.5 mmol, 1.5 equiv) and MTBE (50 mL) was added. The reaction was performed without the requirement of anhydrous or inert atmosphere conditions, and then the mixture was stirred at r.t. for 10 h. the products **3a** were isolated by flash chromatography on silica gel.



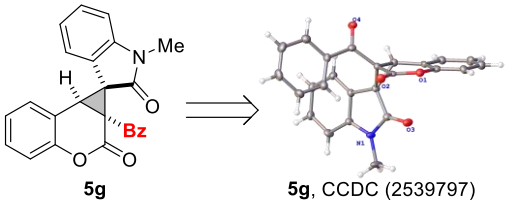
In an ordinary vial charged with a magnetic stirring bar, coumarins **1a** (5 mmol, 1.0 equiv), isatins **4a** (6 mmol, 1.2 equiv), $P(NMe_2)_3$ (6 mmol, 1.2 equiv) and MTBE (50 mL) was added. The reaction was performed without the requirement of anhydrous or inert atmosphere conditions, and then the mixture was stirred at r.t. for 18 h. the products **5a** were isolated by flash chromatography on silica gel.

6. X-ray crystal data for compound 3v



Identific code	**3v**
Empirical formula	$C_{24}H_{22}O_6$
Formula weight	406.41
Temperature/K	276.36(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.6132(3)
b/Å	9.9563(3)
c/Å	11.4160(3)
α/°	78.958(2)
β/°	70.028(3)
γ/°	86.994(3)
Volume/Å^3	1007.82(5)
Z	2
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	0.096
F(000)	428.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.508 to 52.742
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	19923
Independent reflections	4113 [R_{int} = 0.0297, R_{sigma} = 0.0216]
Data/restraints/parameters	4113/0/272
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0851
Final R indexes [all data]	R_1 = 0.0395, wR_2 = 0.0889
Largest diff. peak/hole / e Å^{-3}	0.24/-0.20

7. X-ray crystal data for compound 5g

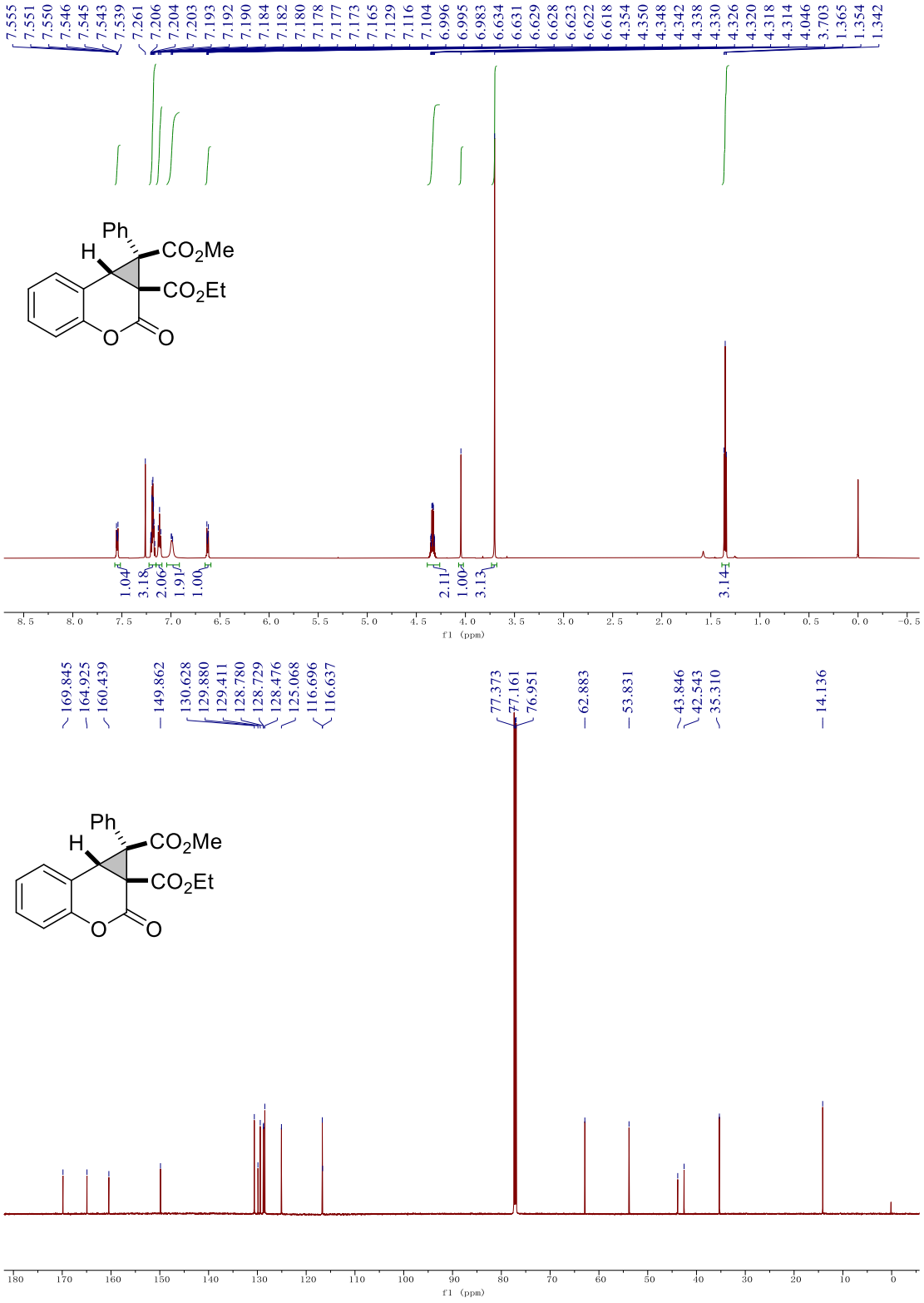


5g **5g**, CCDC (2539797)

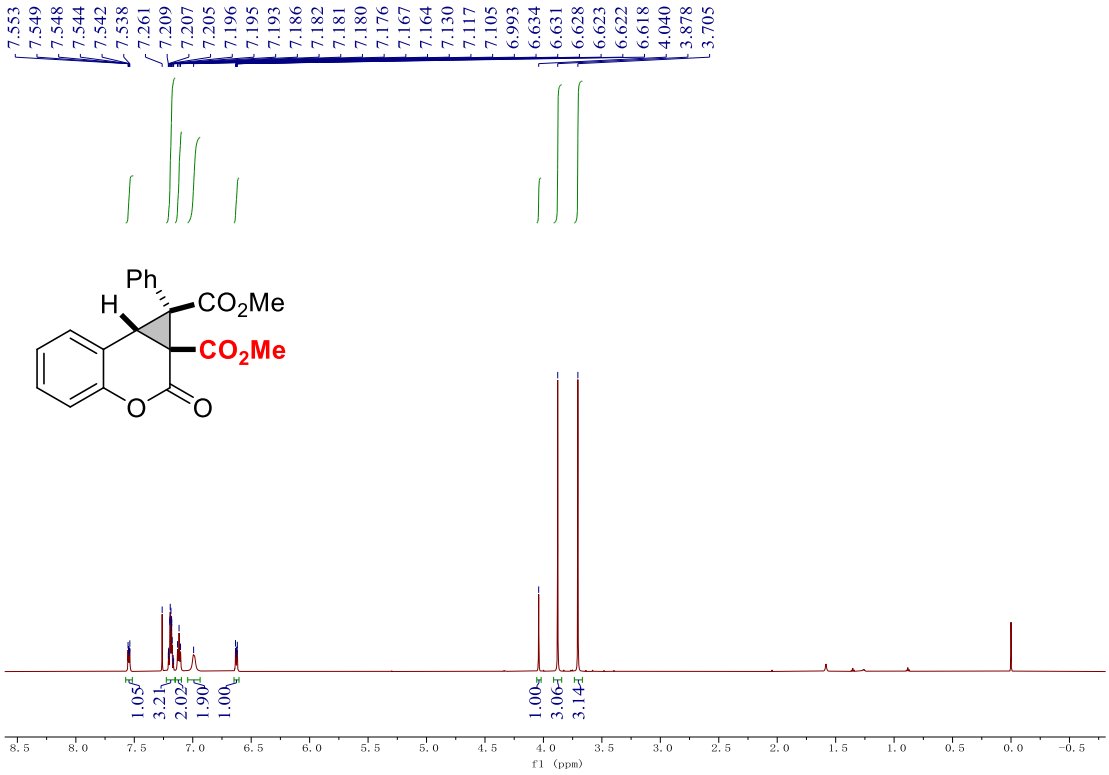
Identific code	**5g**
Empirical formula	$C_{26}H_{19}Cl_2NO_4$
Formula weight	480.32
Temperature/K	120.02(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.86524(12)
b/Å	25.0306(3)
c/Å	10.59161(15)
α/°	90
β/°	108.1518(15)
γ/°	90
Volume/Å^3	2233.34(6)
Z	4
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	2.905
F(000)	992.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.064 to 149.272
Index ranges	$-9 \le h \le 10$, $-31 \le k \le 30$, $-13 \le l \le 13$
Reflections collected	23985
Independent reflections	8200 [R_{int} = 0.0356, R_{sigma} = 0.0225]
Data/restraints/parameters	8200/15/625
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0728, wR_2 = 0.1980
Final R indexes [all data]	R_1 = 0.0733, wR_2 = 0.1986
Largest diff. peak/hole / e Å^{-3}	1.05/-0.46

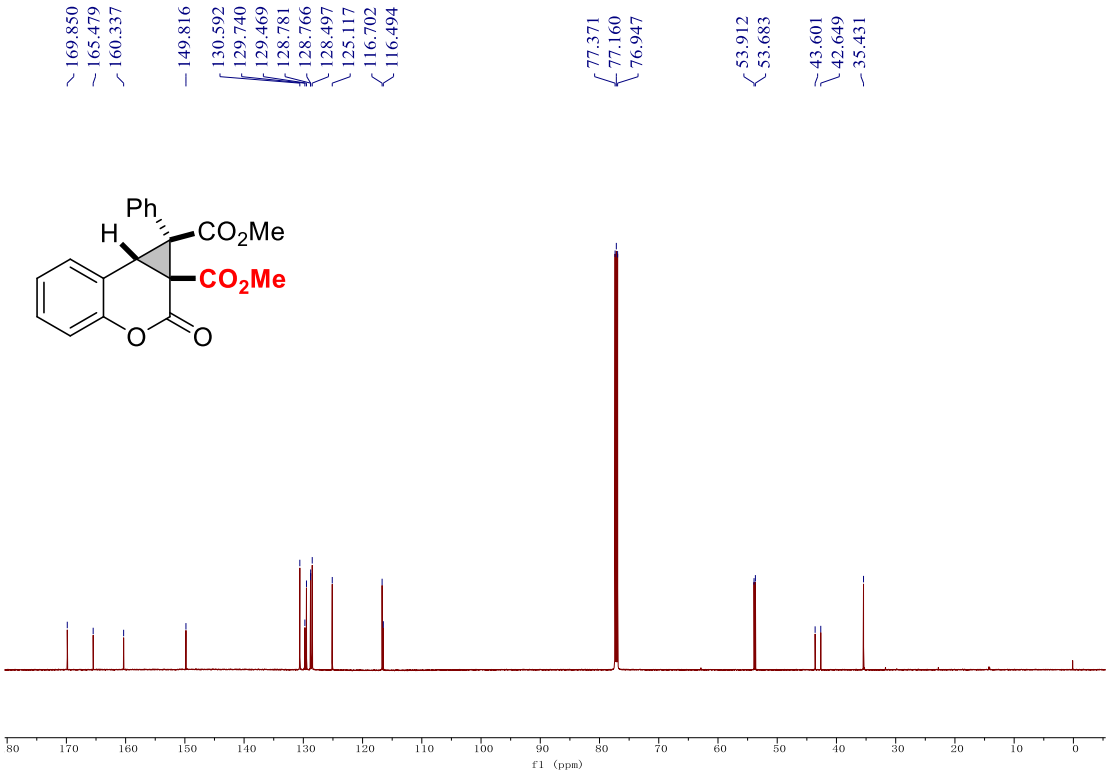
8. The copies of ^{1}H NMR and ^{13}C NMR for compounds 3a-3x, 5a-5h.

1a-ethyl 1-methyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3a)

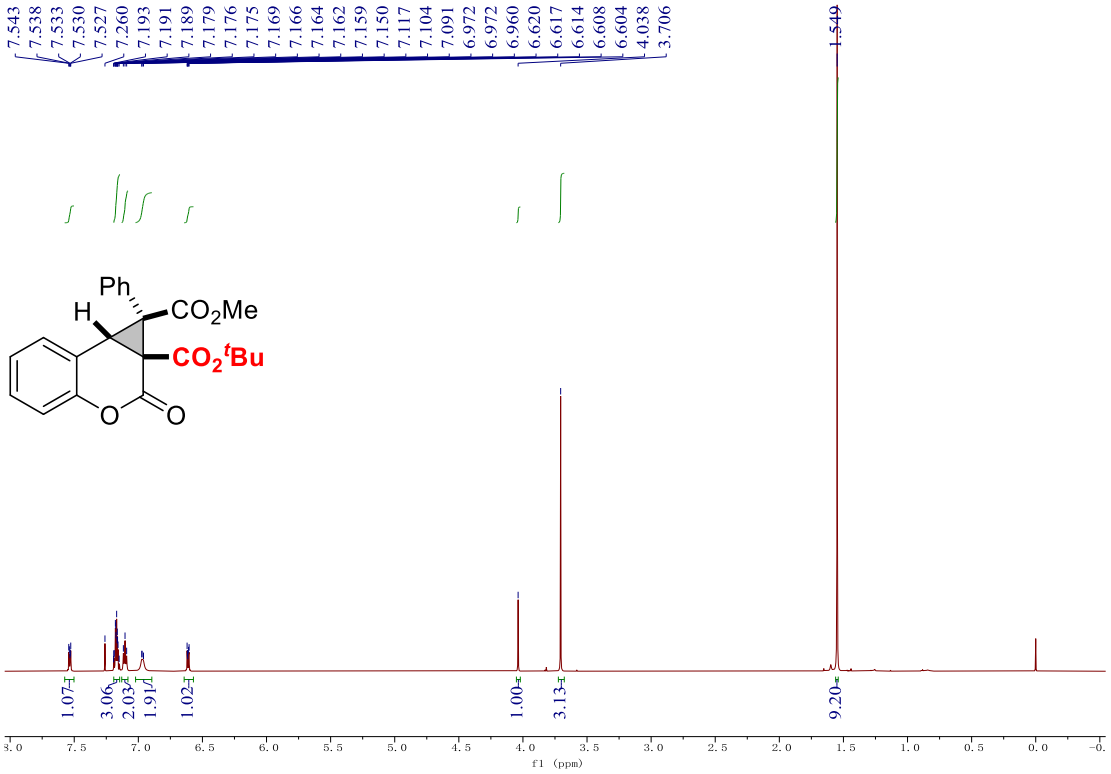


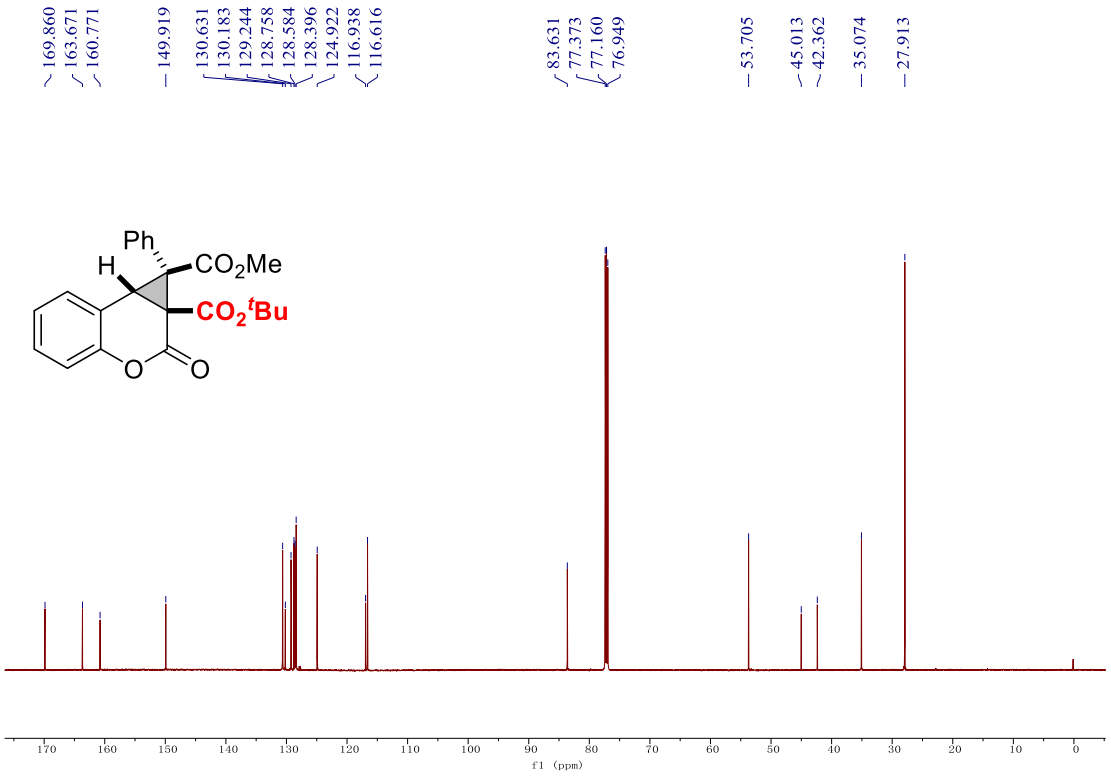
dimethyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3b)



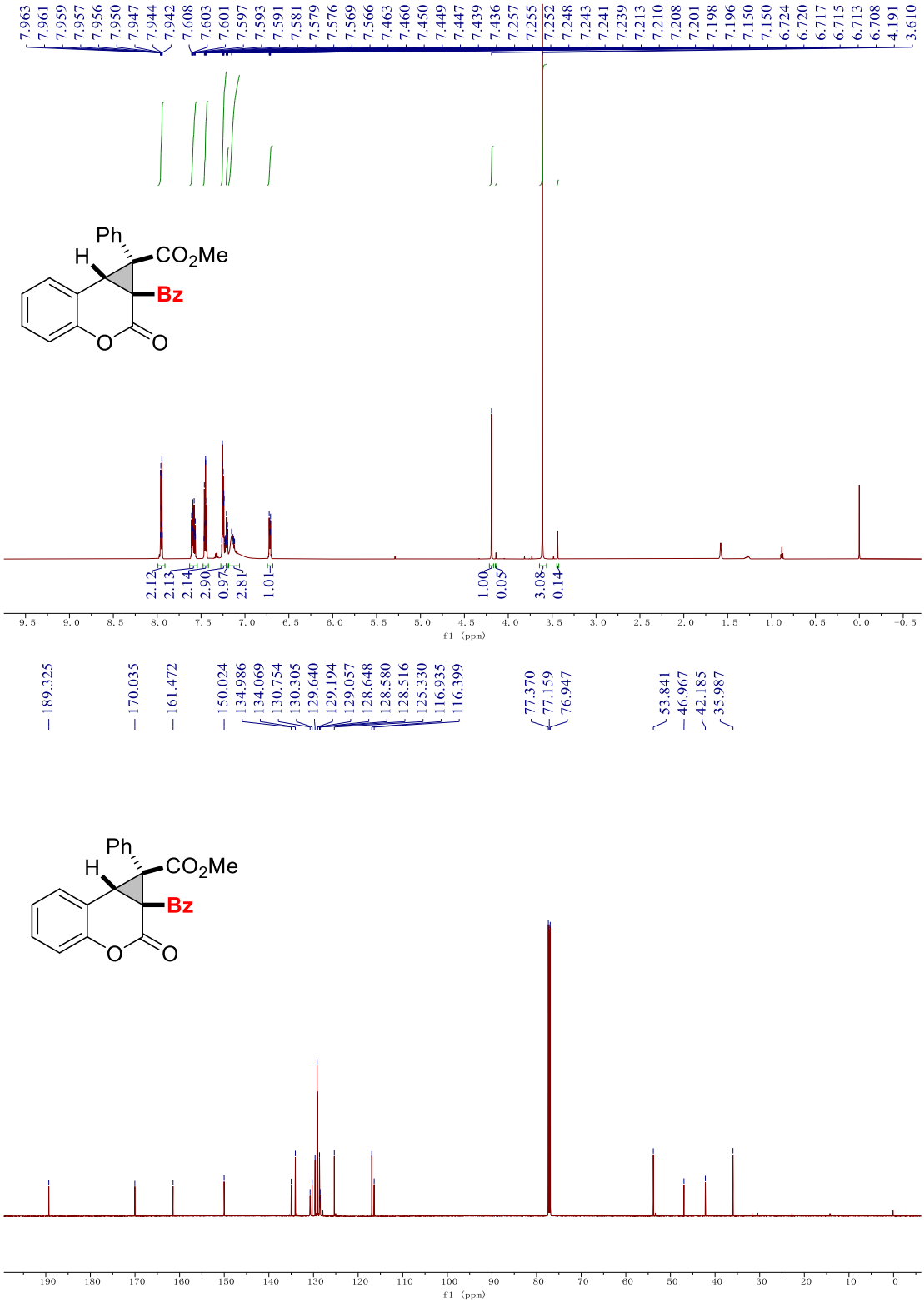


1a-(tert-butyl) 1-methyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3c)

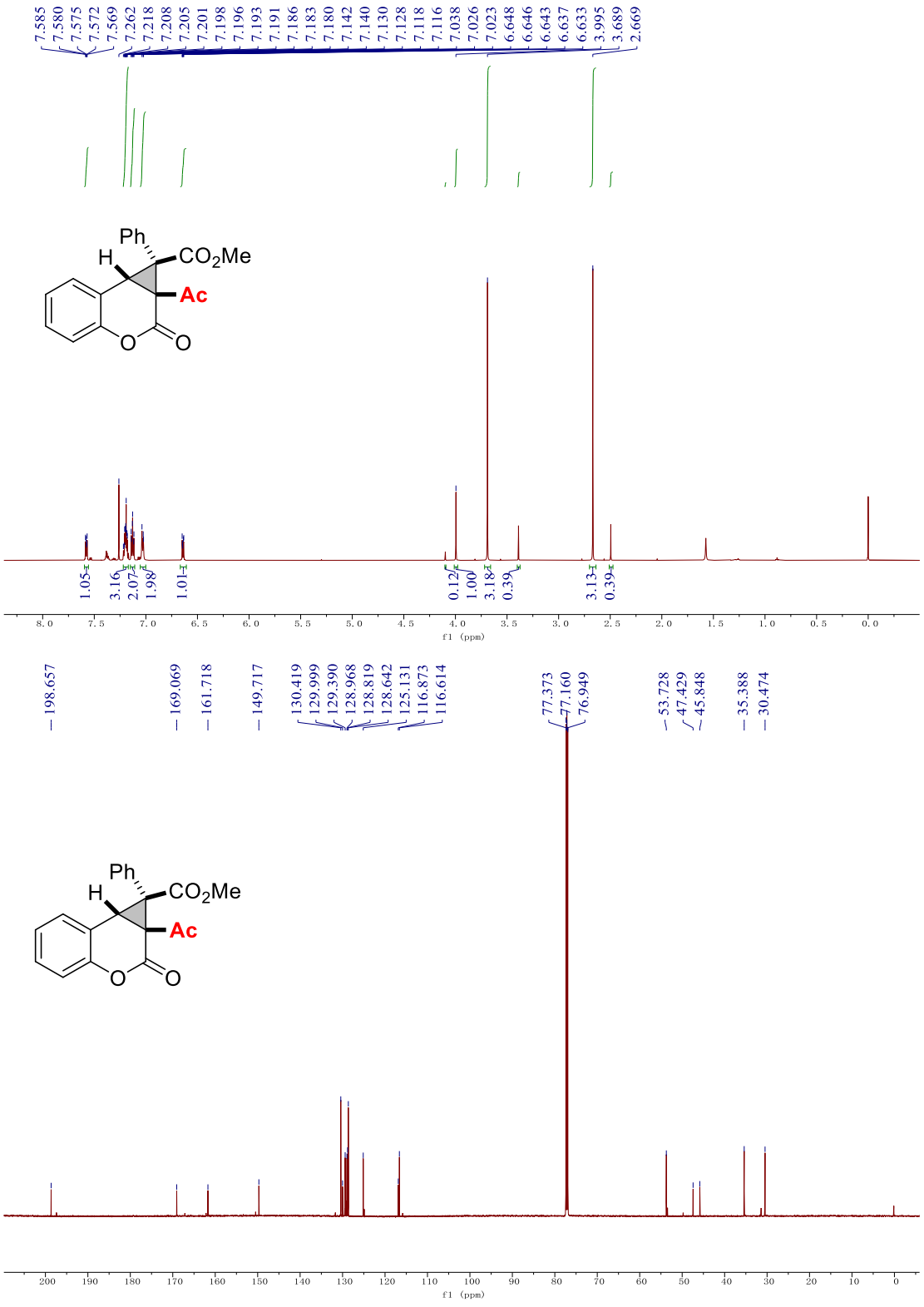




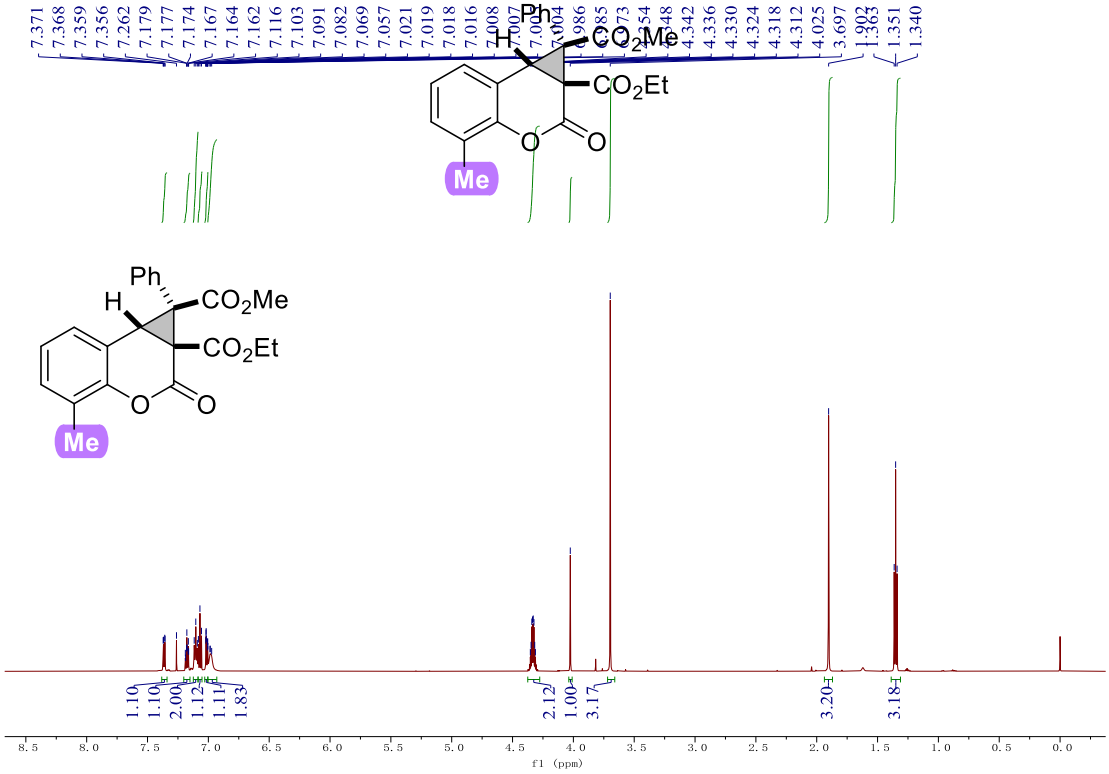
methyl 1a-benzoyl-2-oxo-1-phenyl-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate (3d)

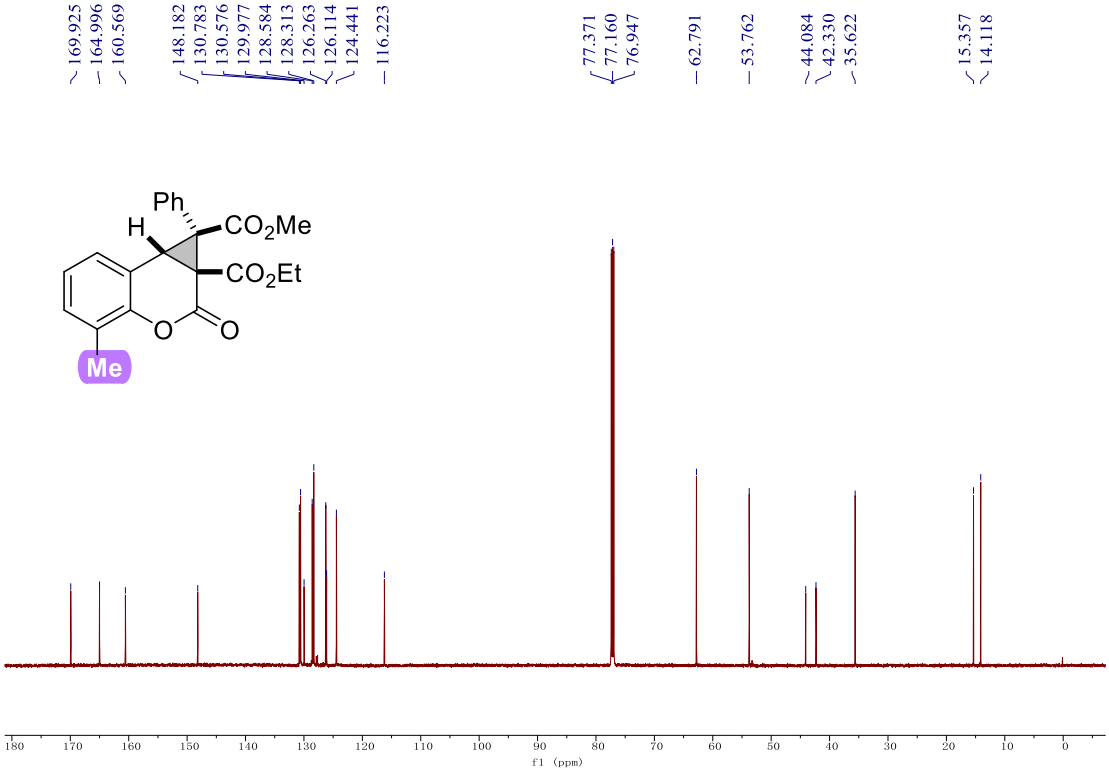


methyl 1a-acetyl-2-oxo-1-phenyl-1,1a,2,7b-tetrahydrocyclopropa[*c*]chromene-1-carboxylate (3e)

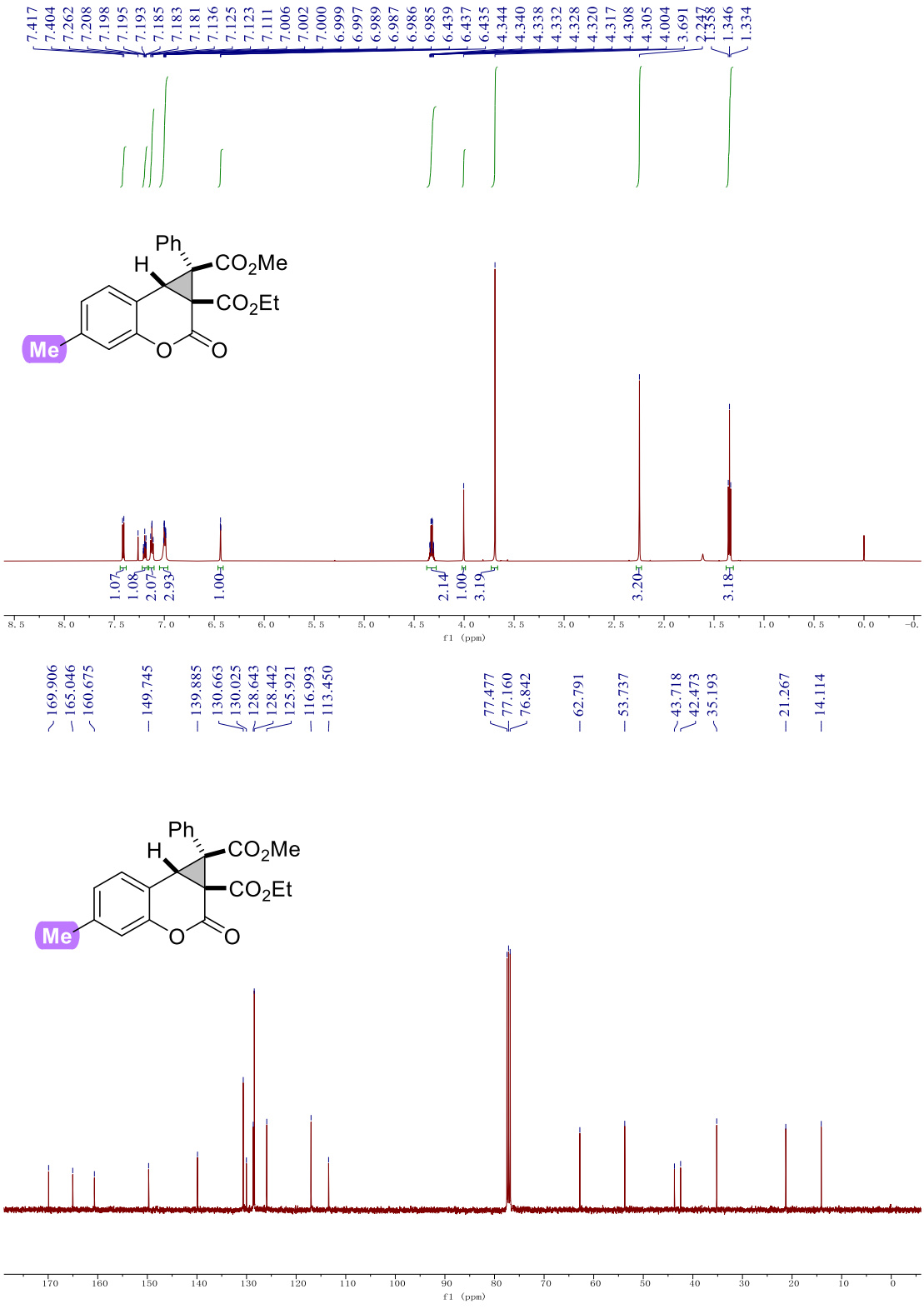


1a-ethyl 1-methyl 4-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3f)

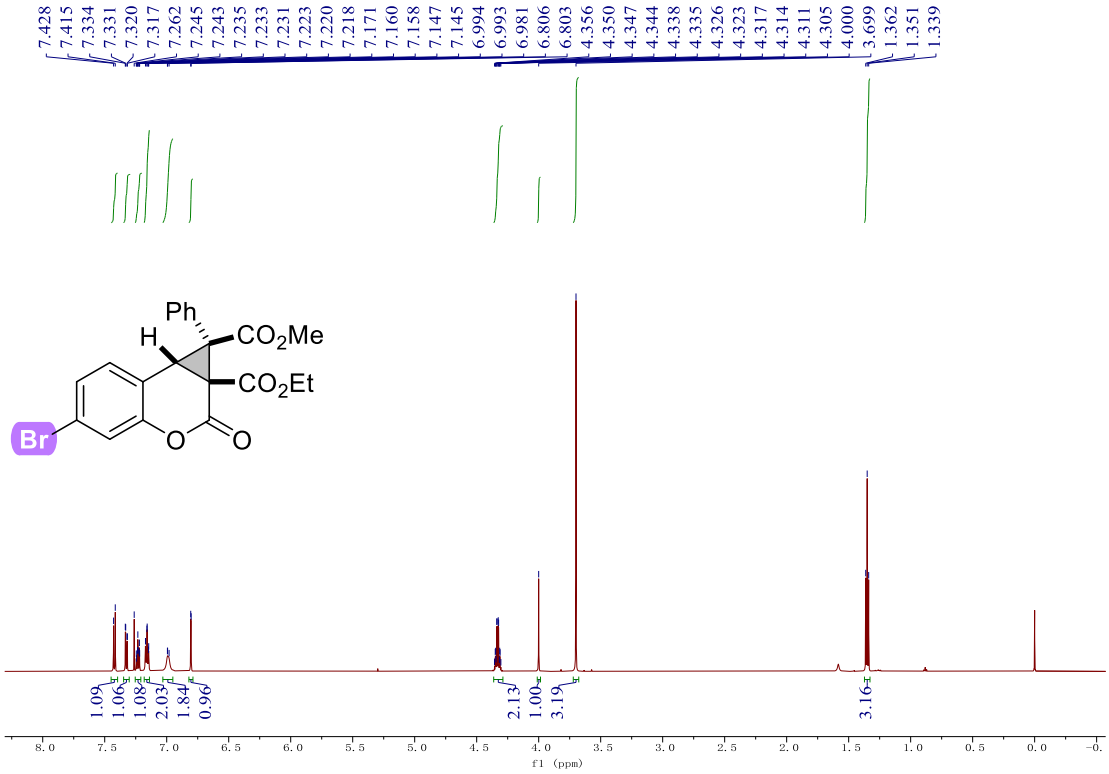


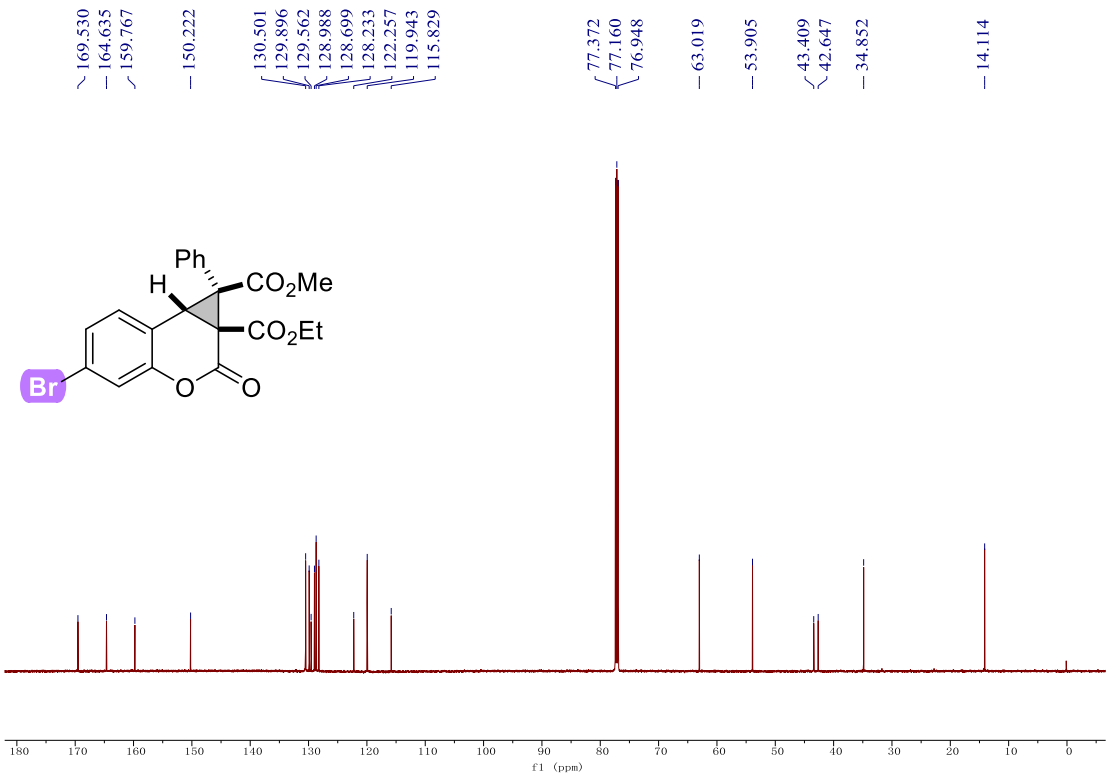


1a-ethyl 1-methyl 5-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3g)

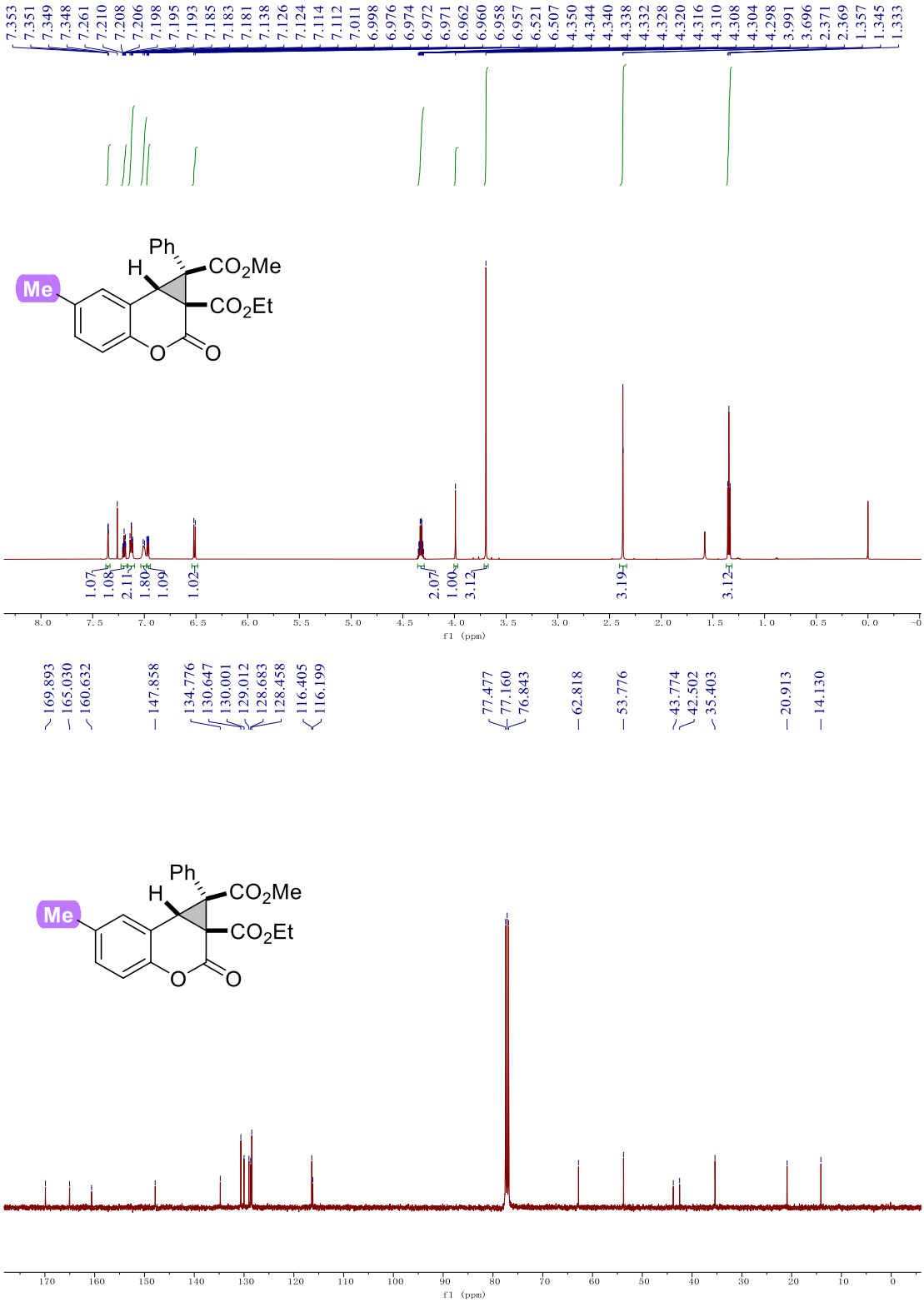


1a-ethyl 1-methyl 5-bromo-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3h)

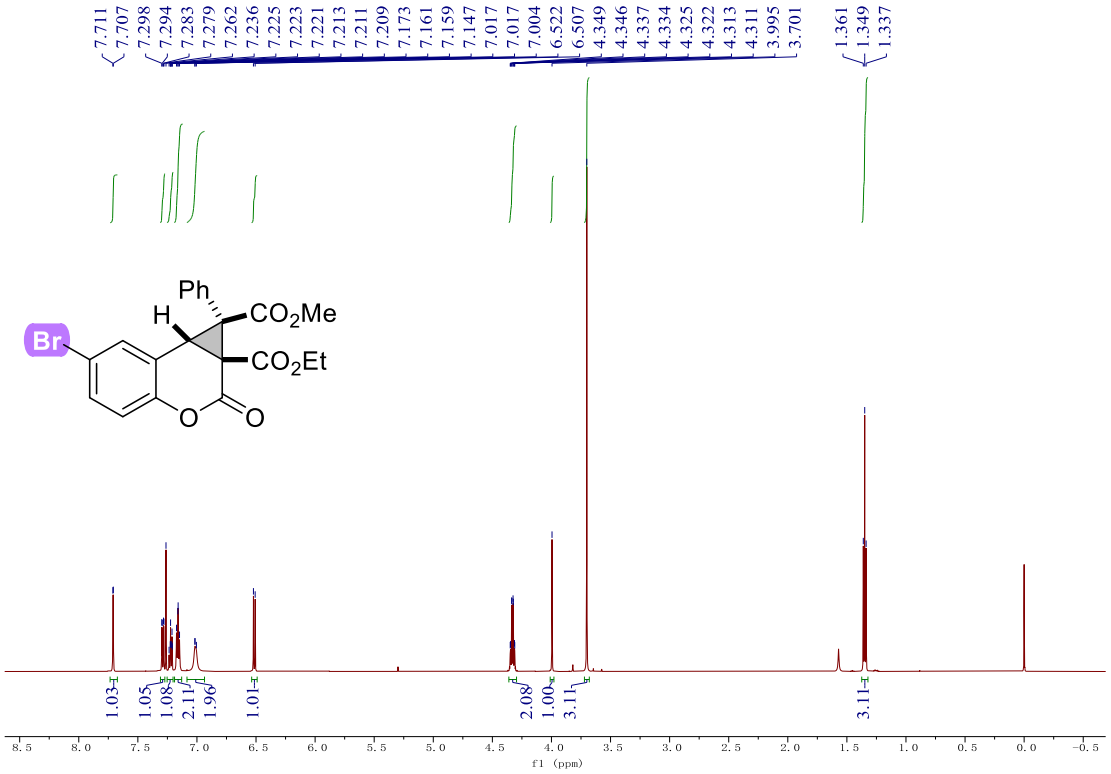


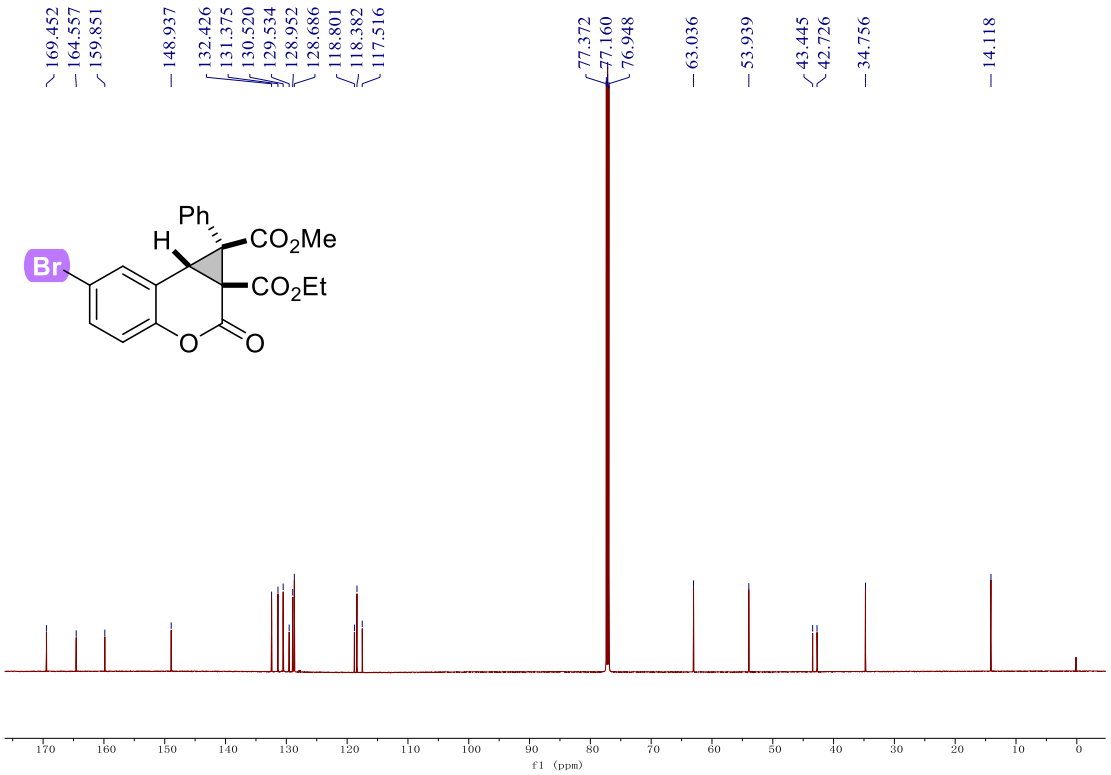


1a-ethyl 1-methyl 6-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3i)

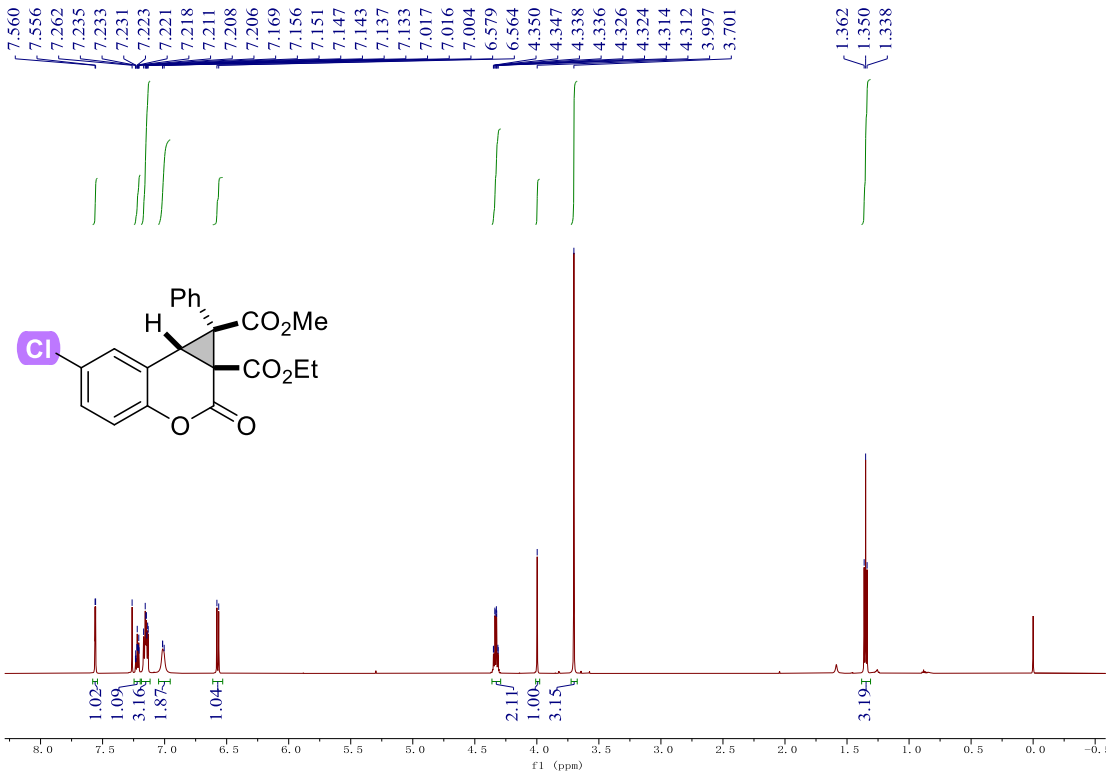


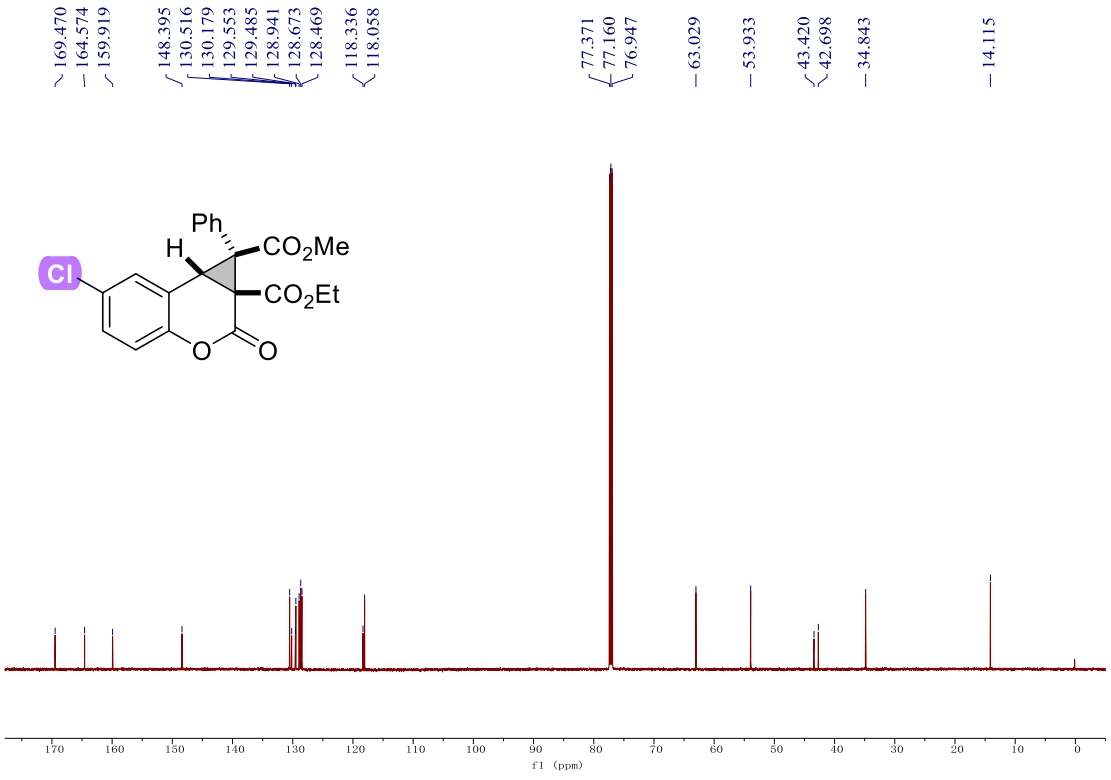
1a-ethyl 1-methyl 6-bromo-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3j)



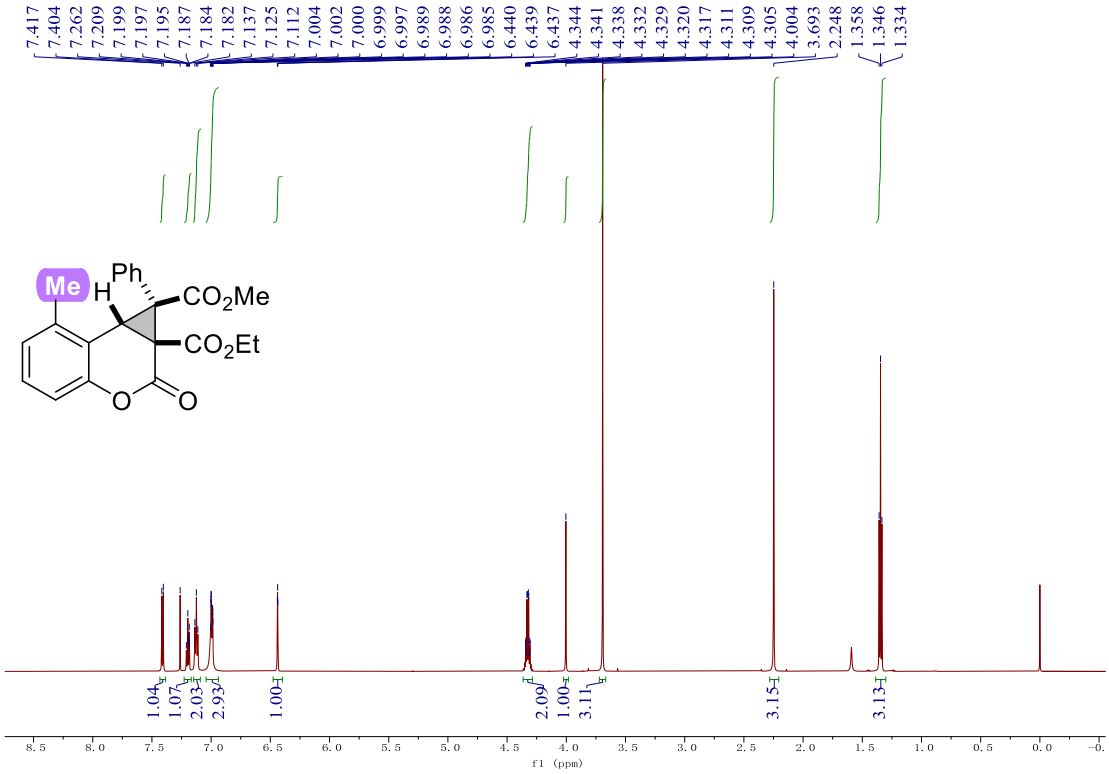


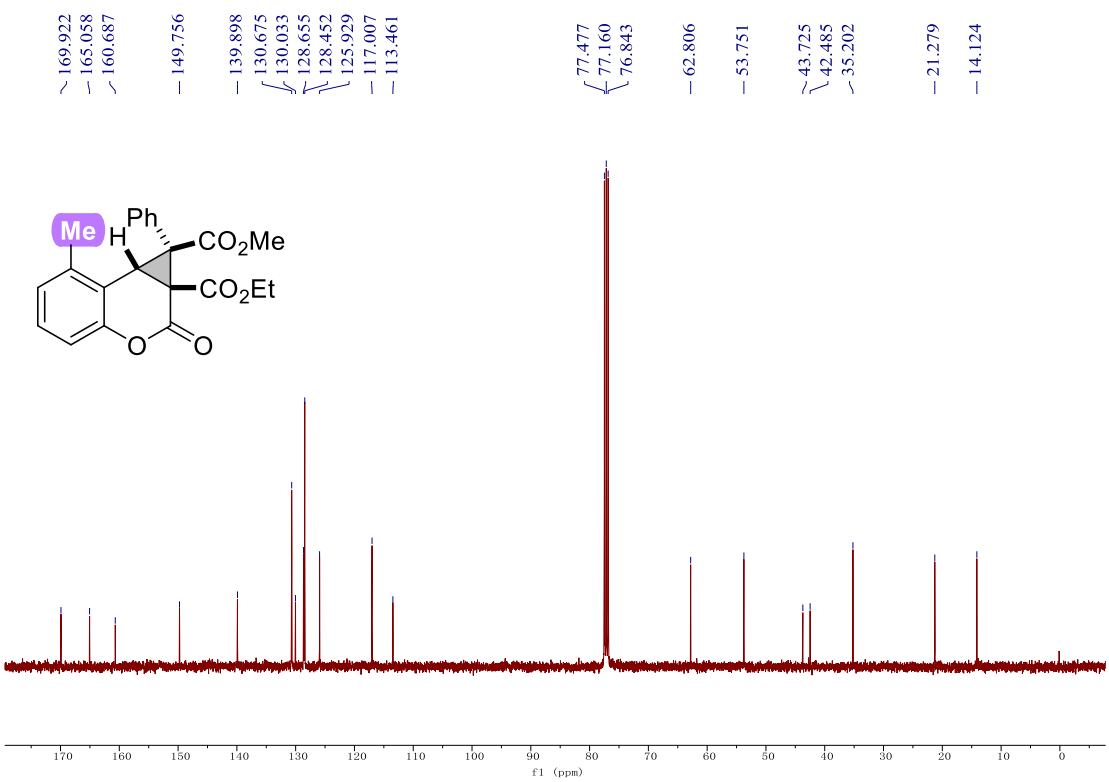
1a-ethyl 1-methyl 6-chloro-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3k)



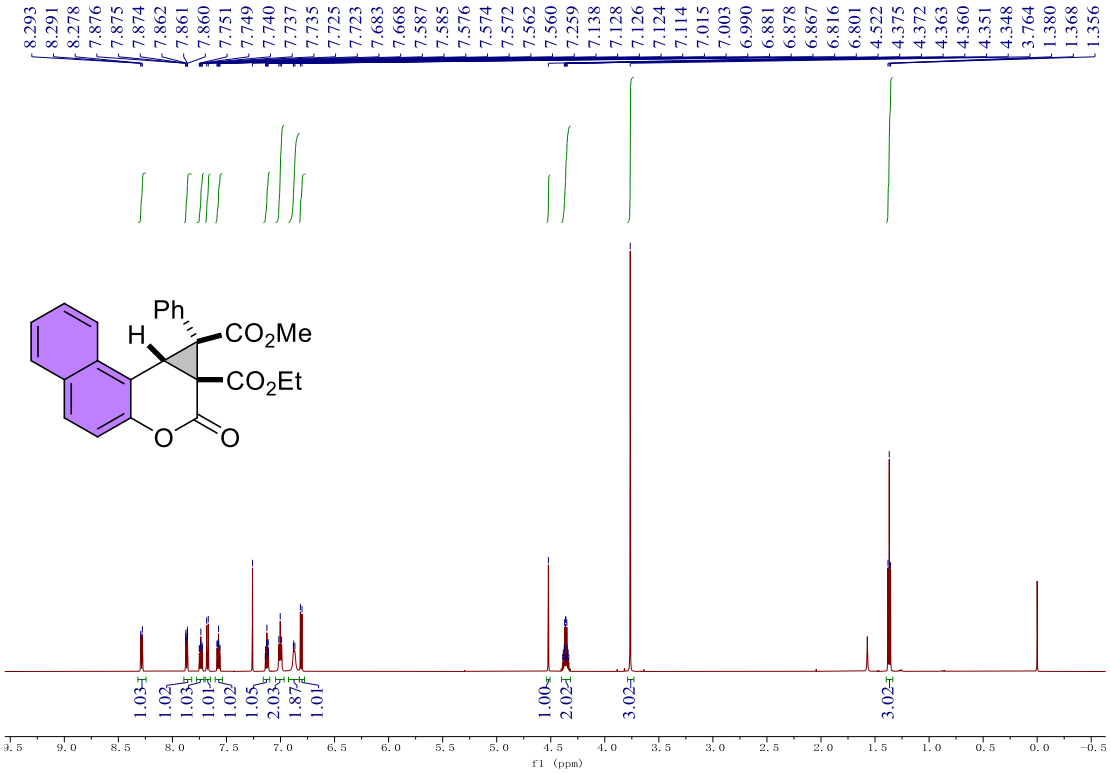


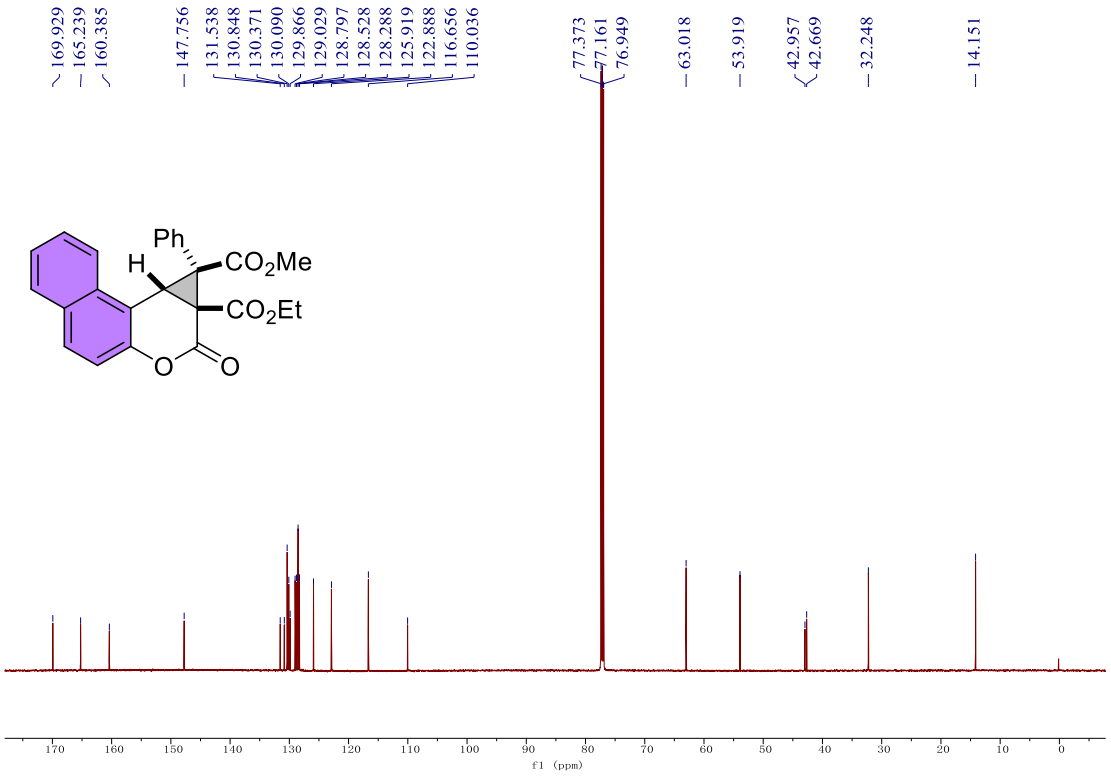
1a-ethyl 1-methyl 7-methyl-2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3l)



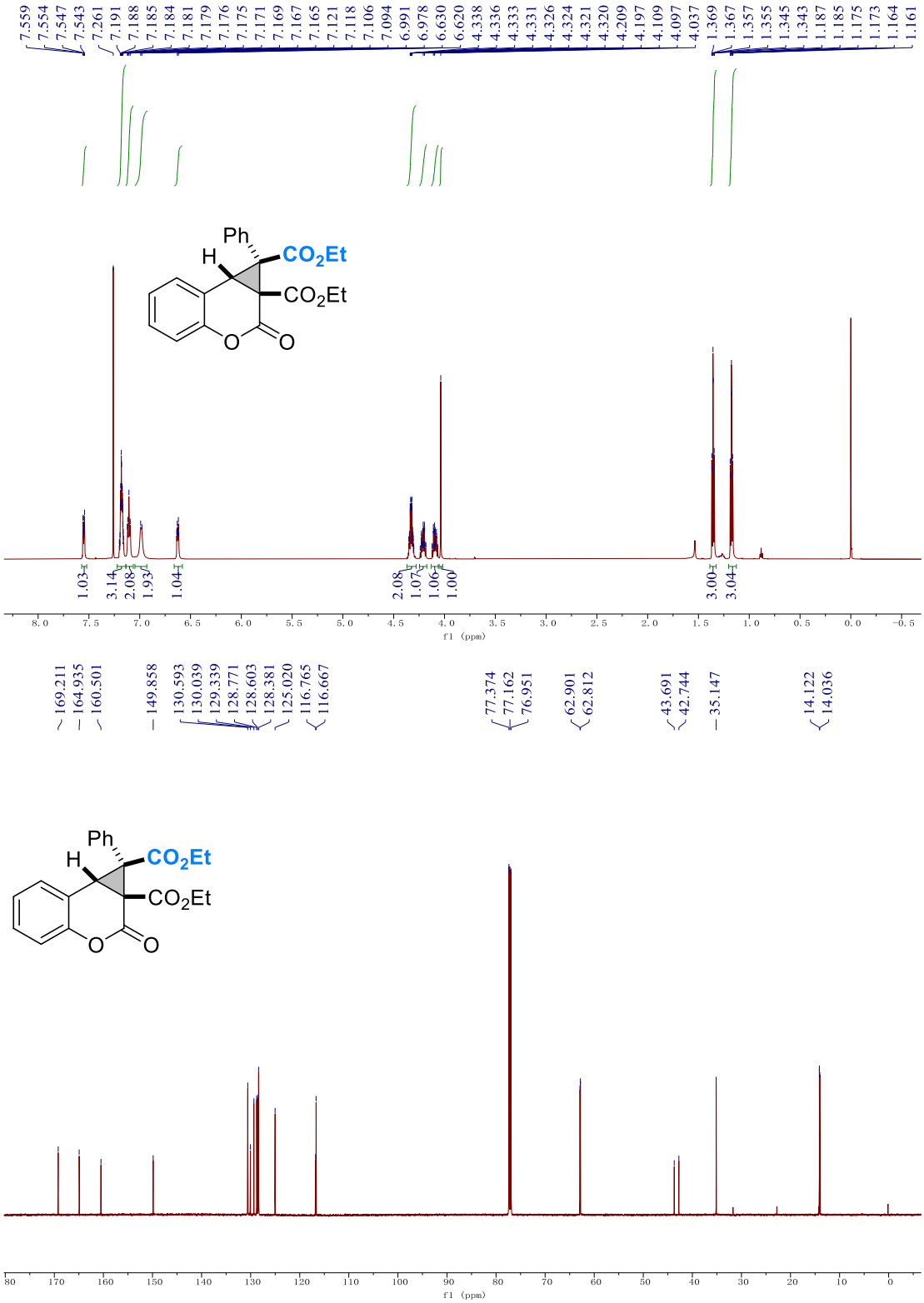


1a-ethyl 1-methyl 2-oxo-1-phenyl-1,9c-dihydrobenzo[*f*]cyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3m)

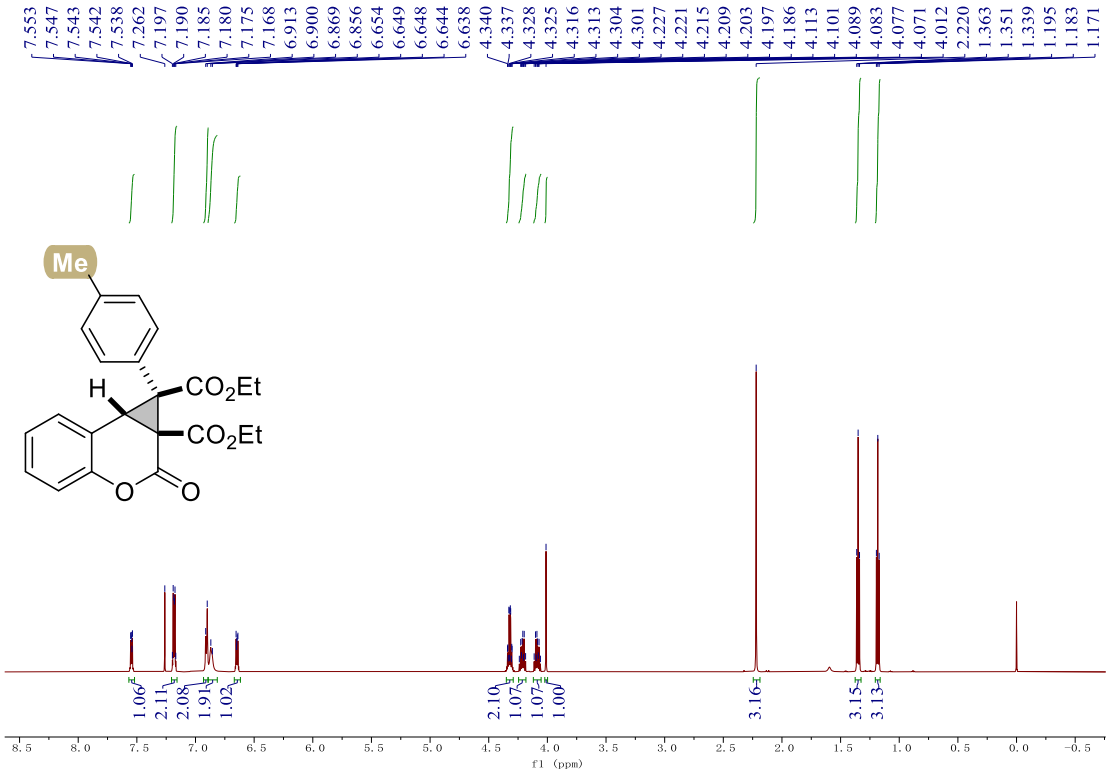


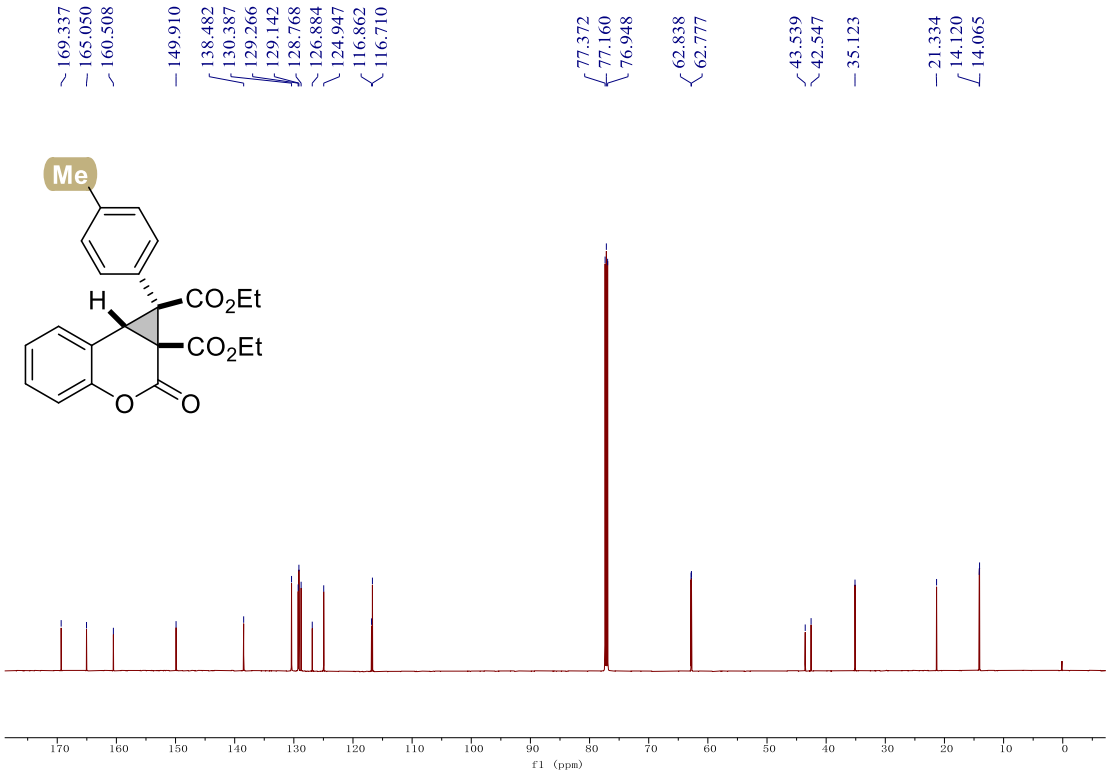


diethyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3n)

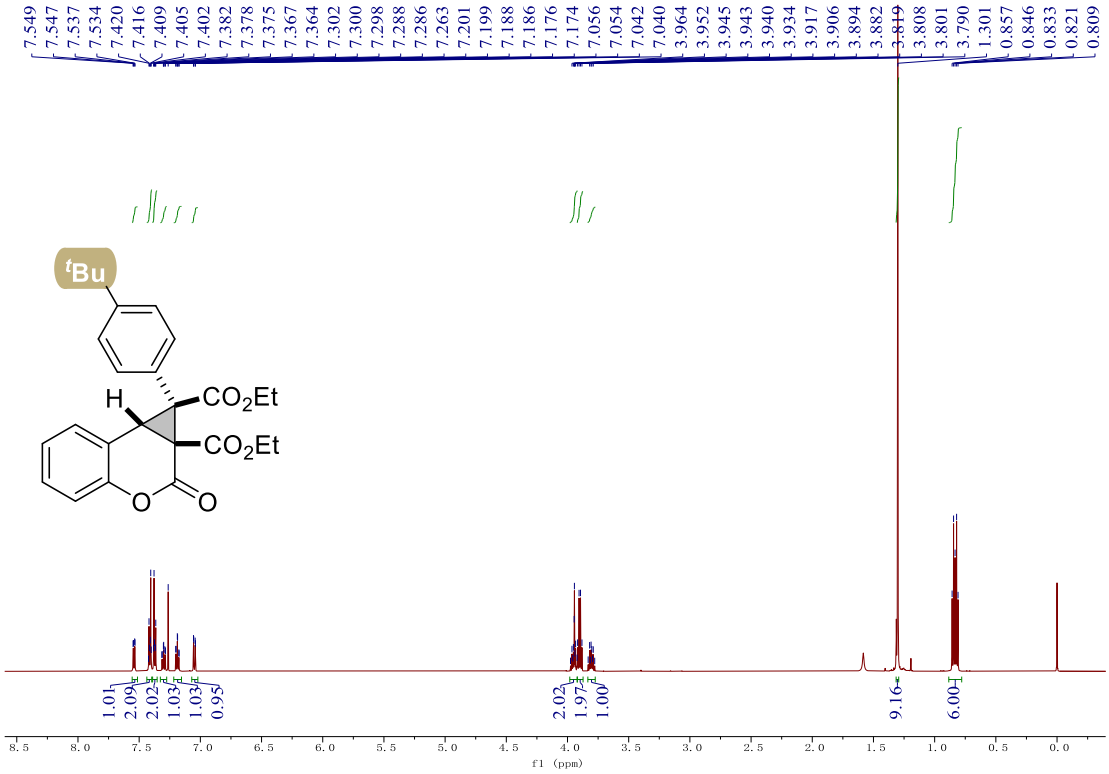


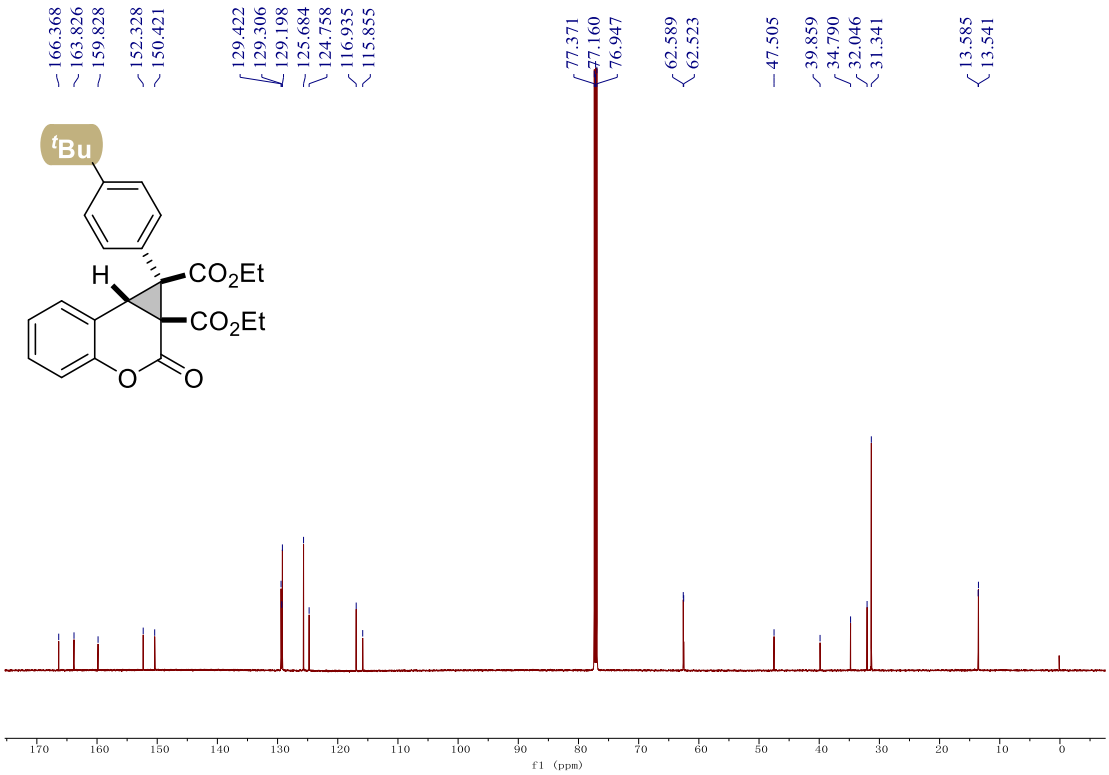
diethyl 2-oxo-1-(p-tolyl)-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3o)



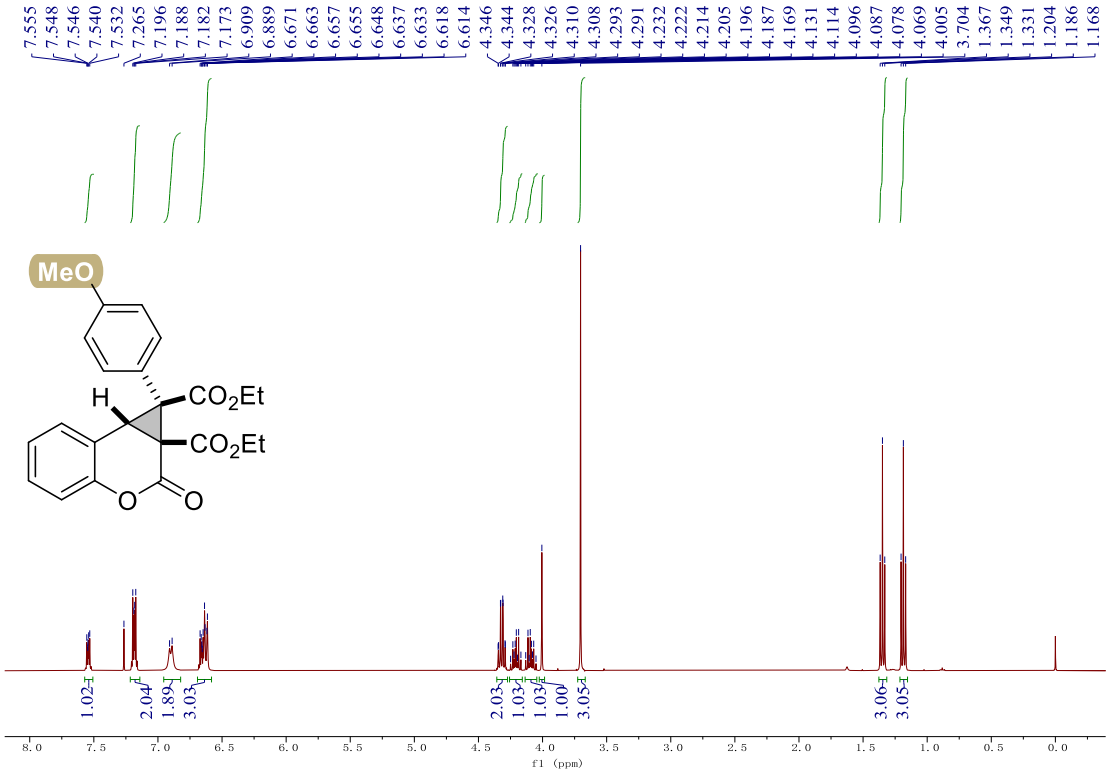


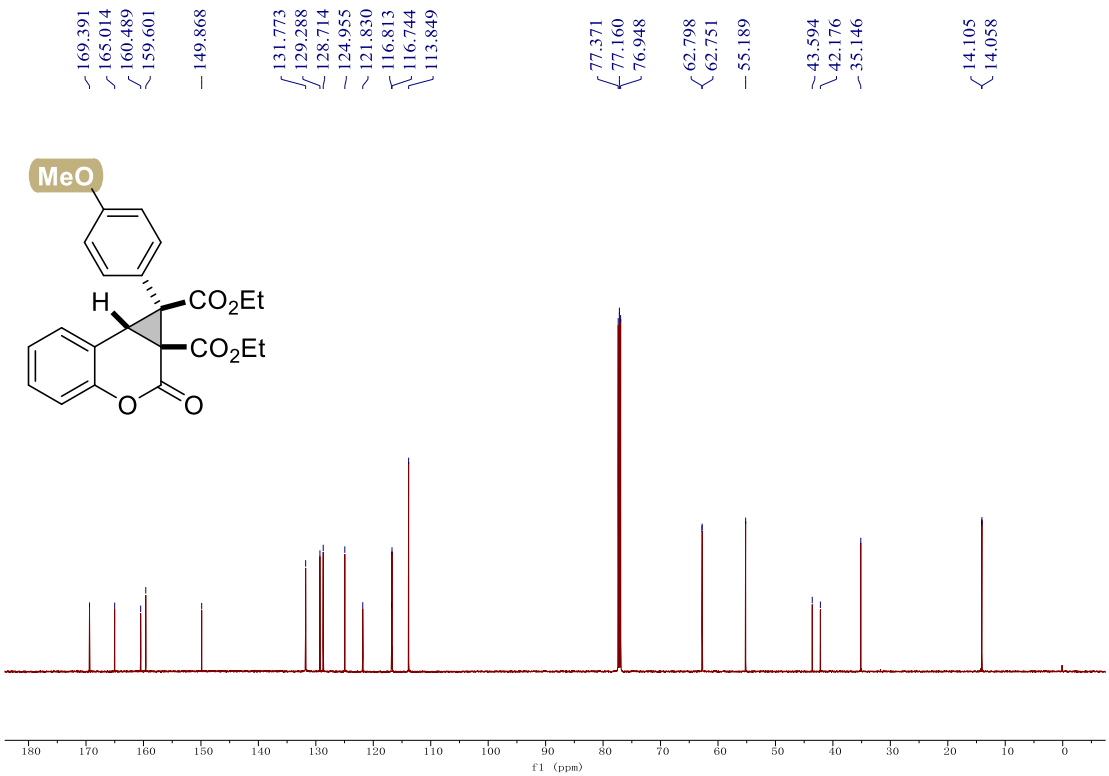
diethyl 1-(4-(tert-butyl)phenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3p)



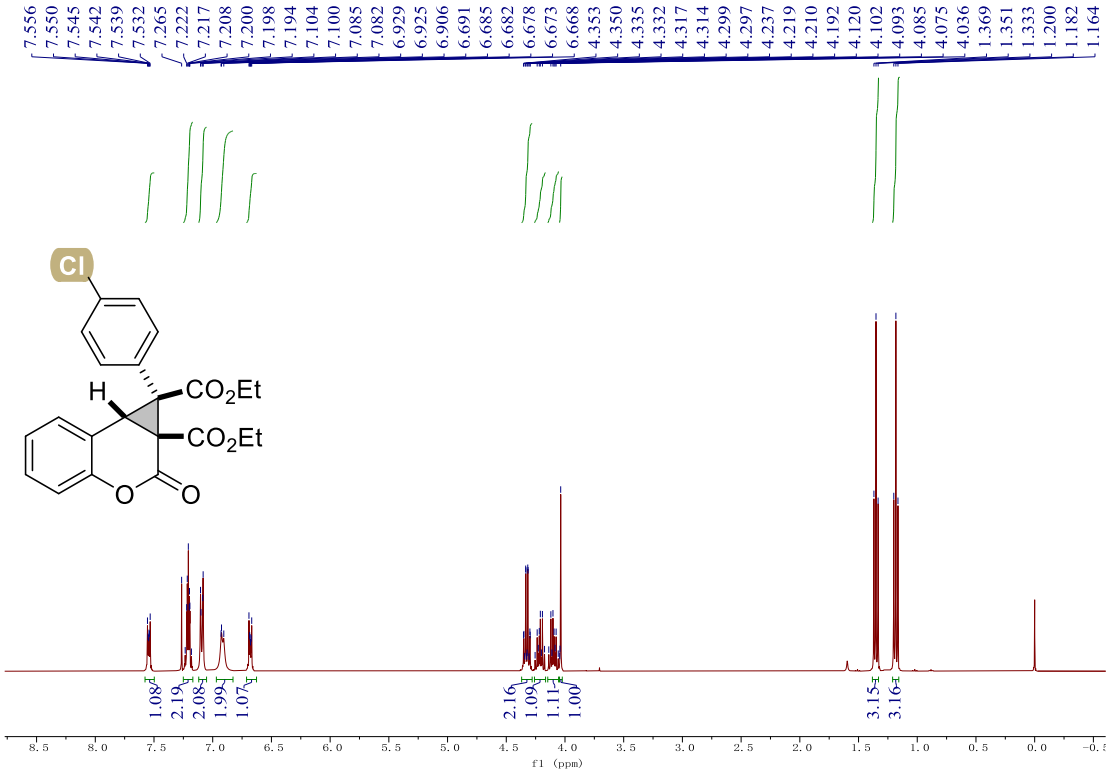


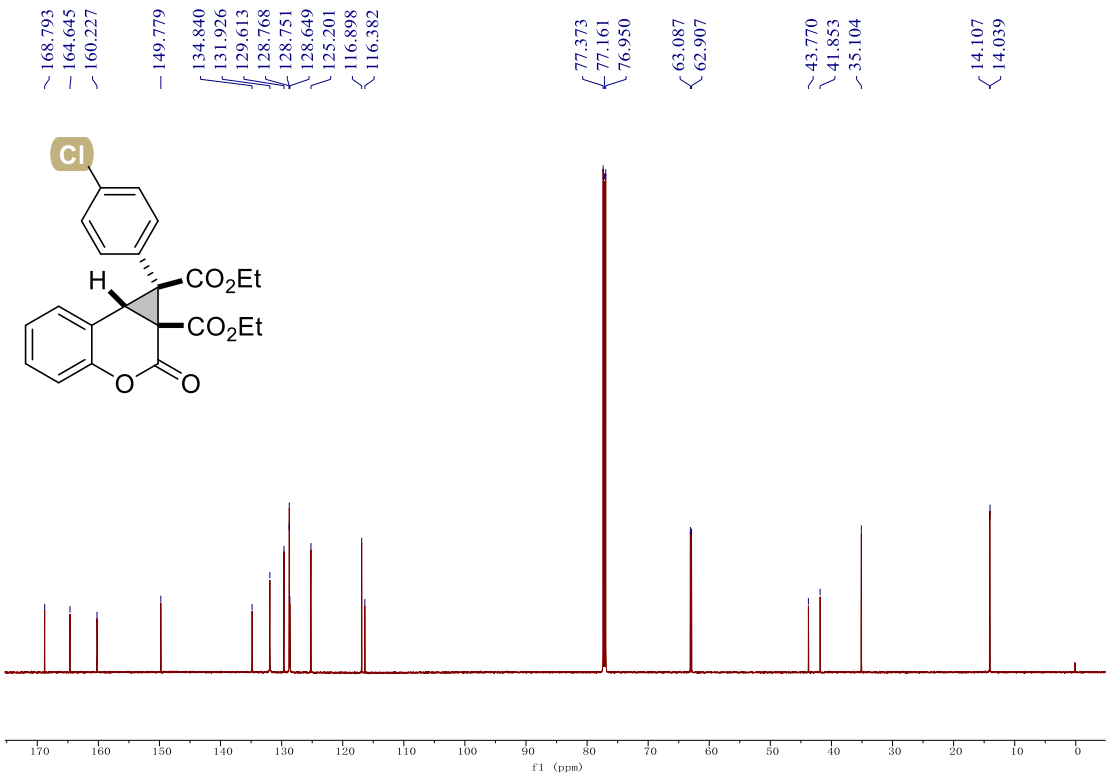
diethyl 1-(4-methoxyphenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3q)



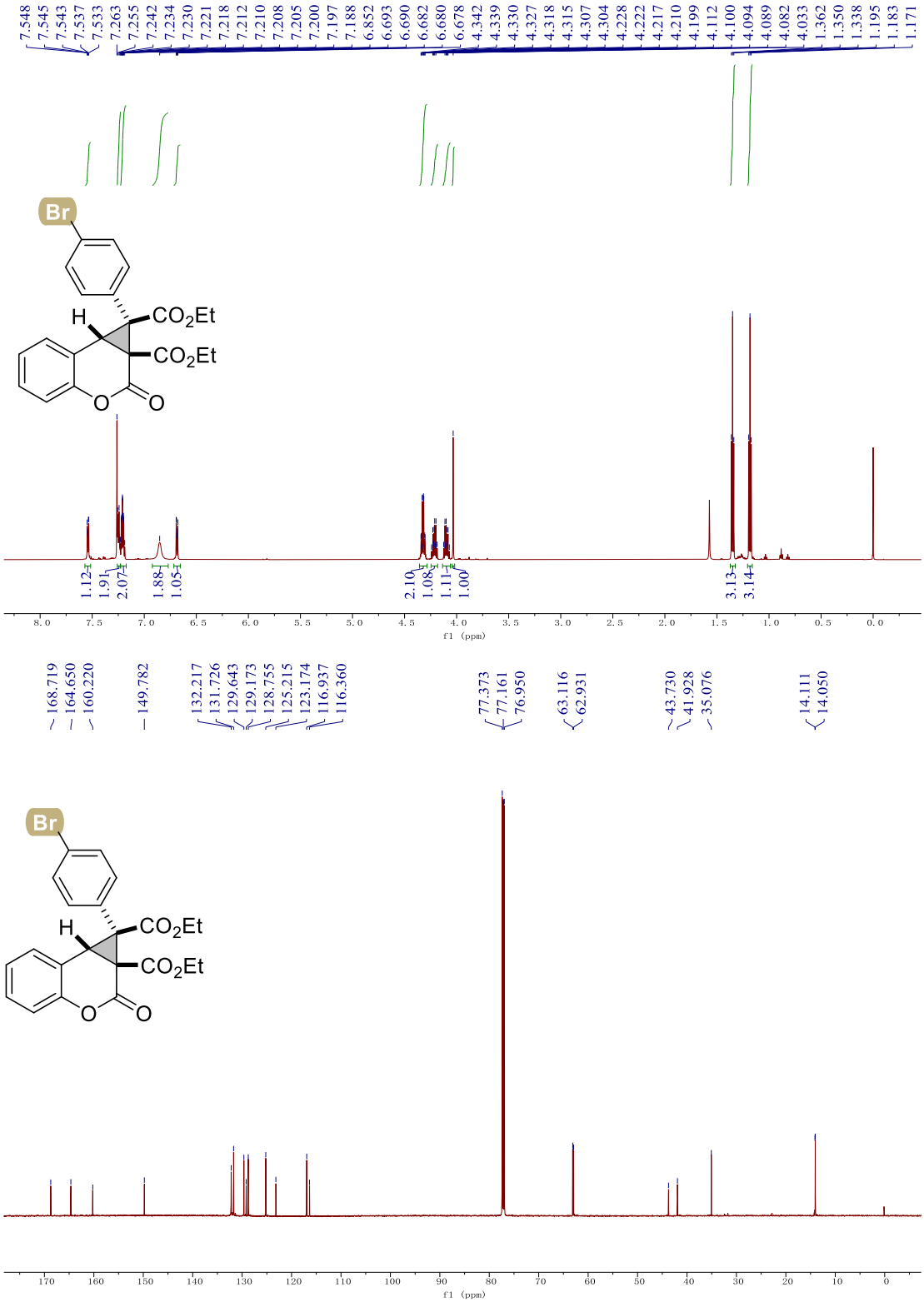


diethyl 1-(4-chlorophenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3r)

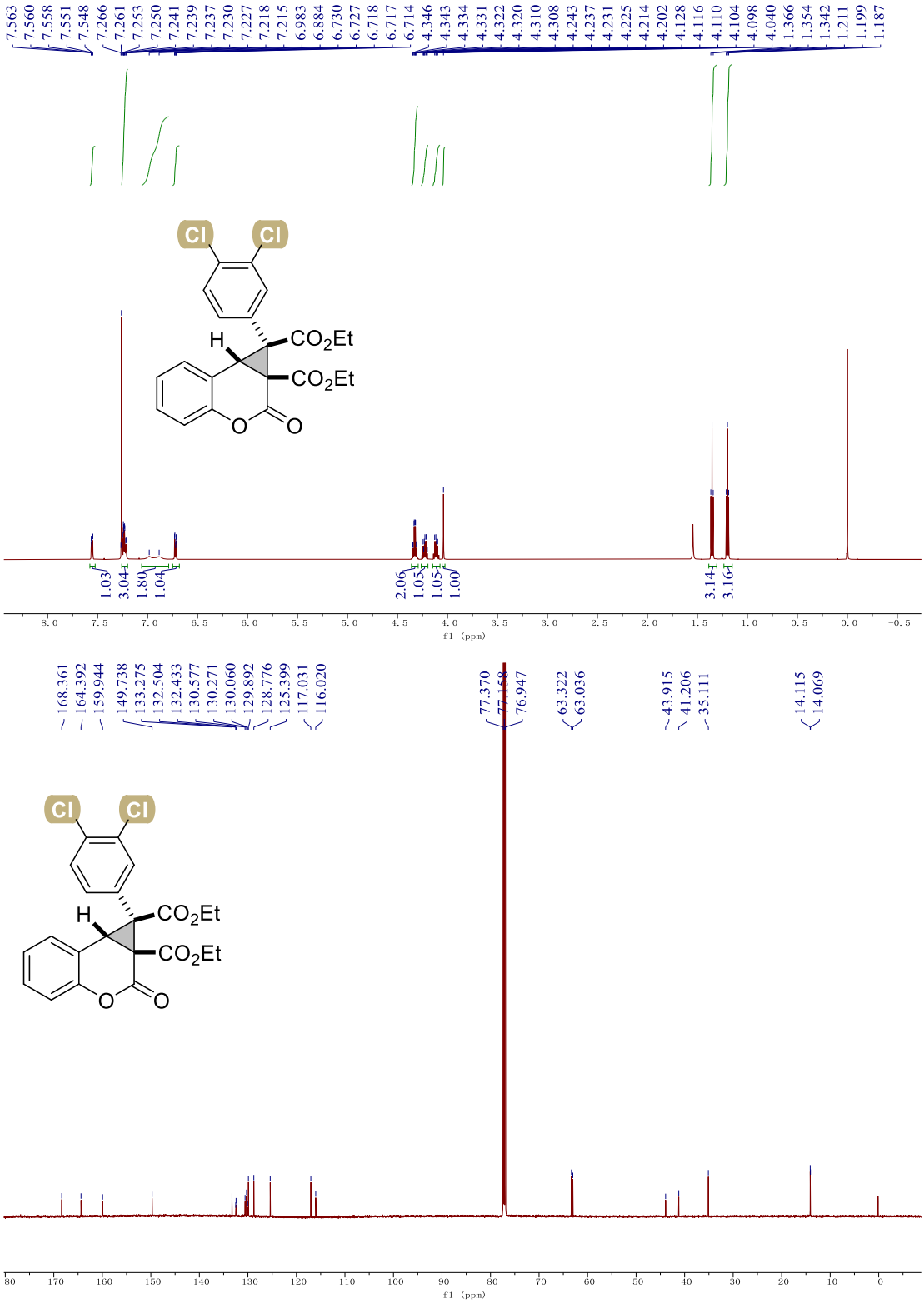




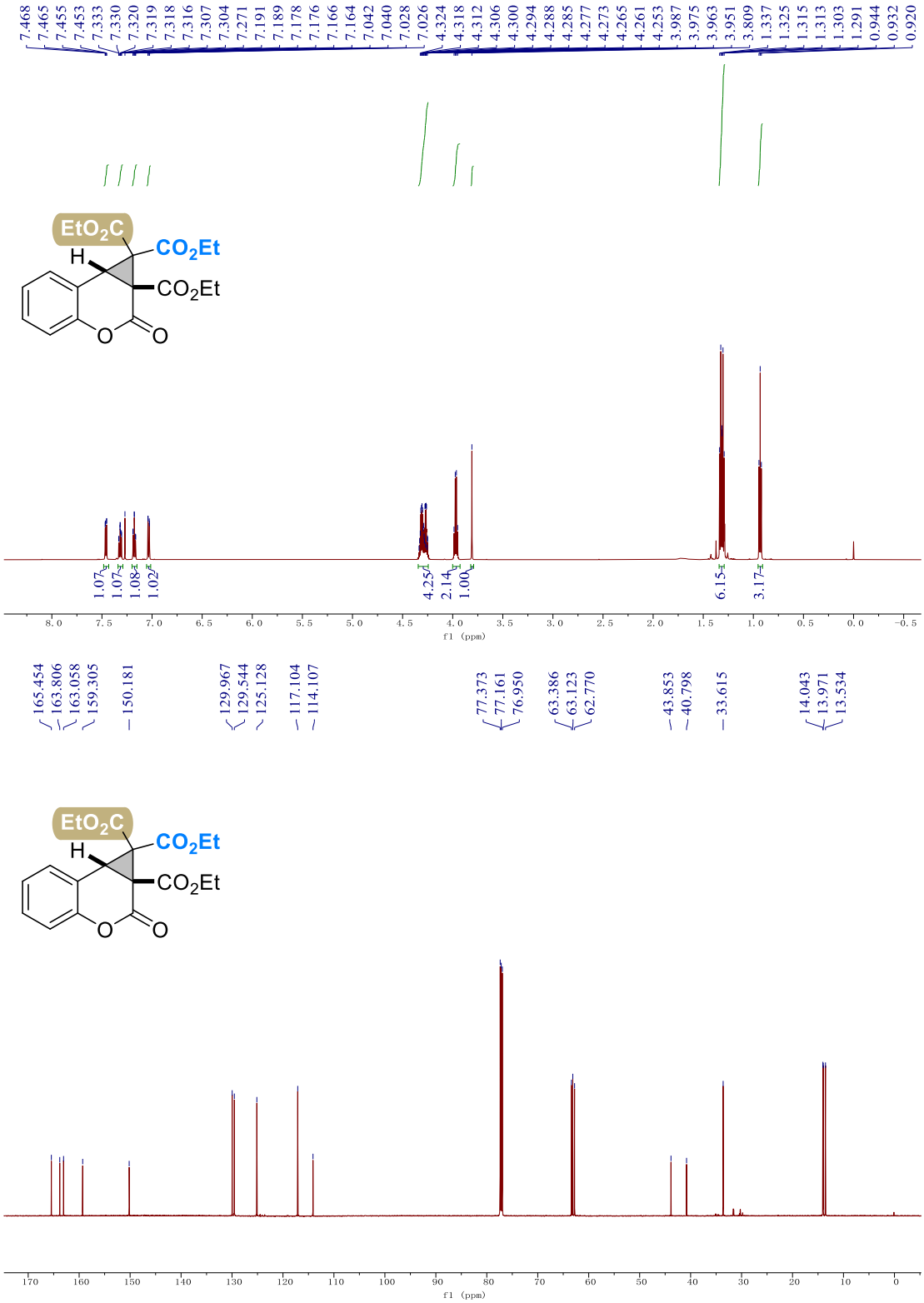
diethyl 1-(4-bromophenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3s)



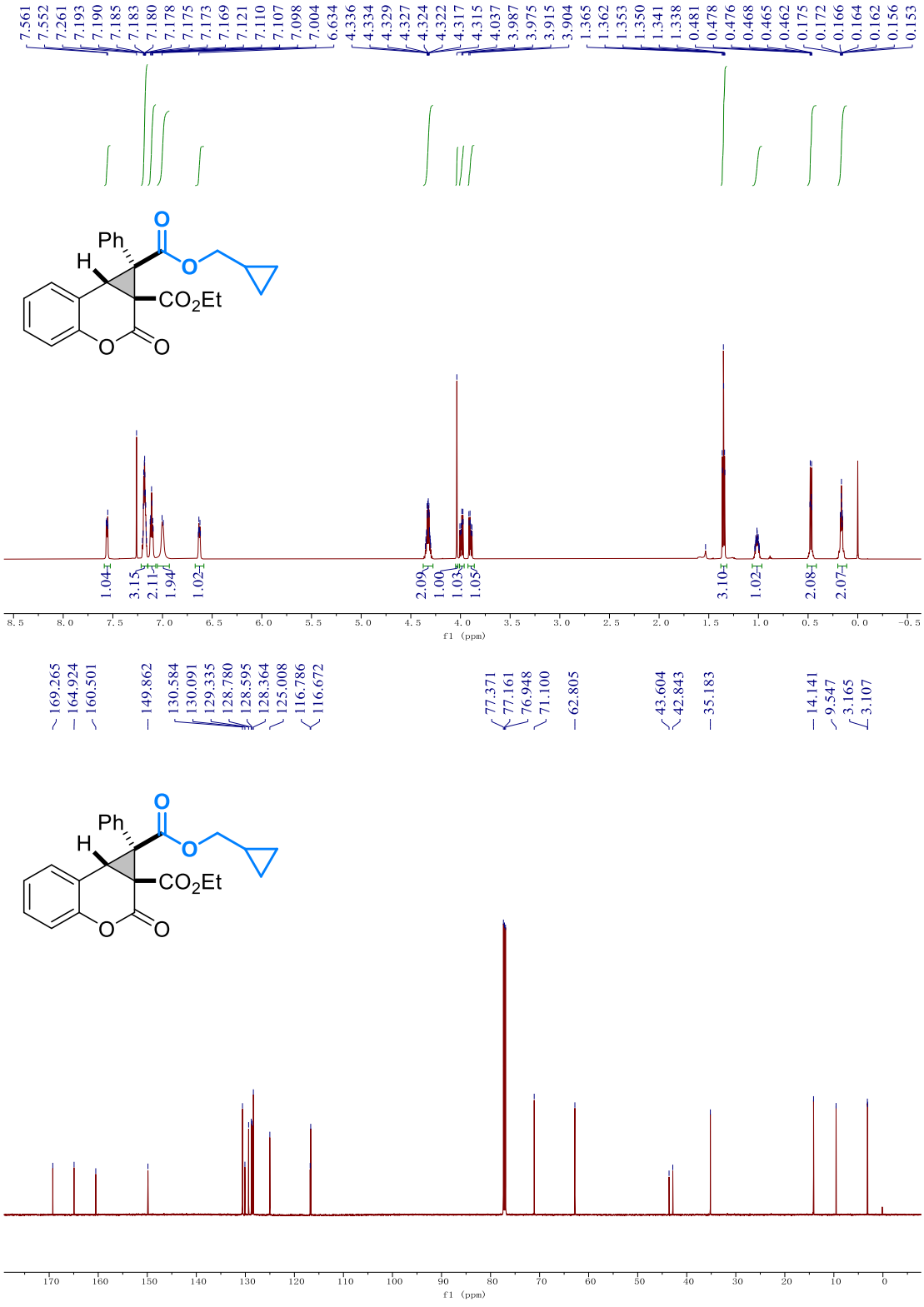
diethyl 1-(3,4-dichlorophenyl)-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3t)



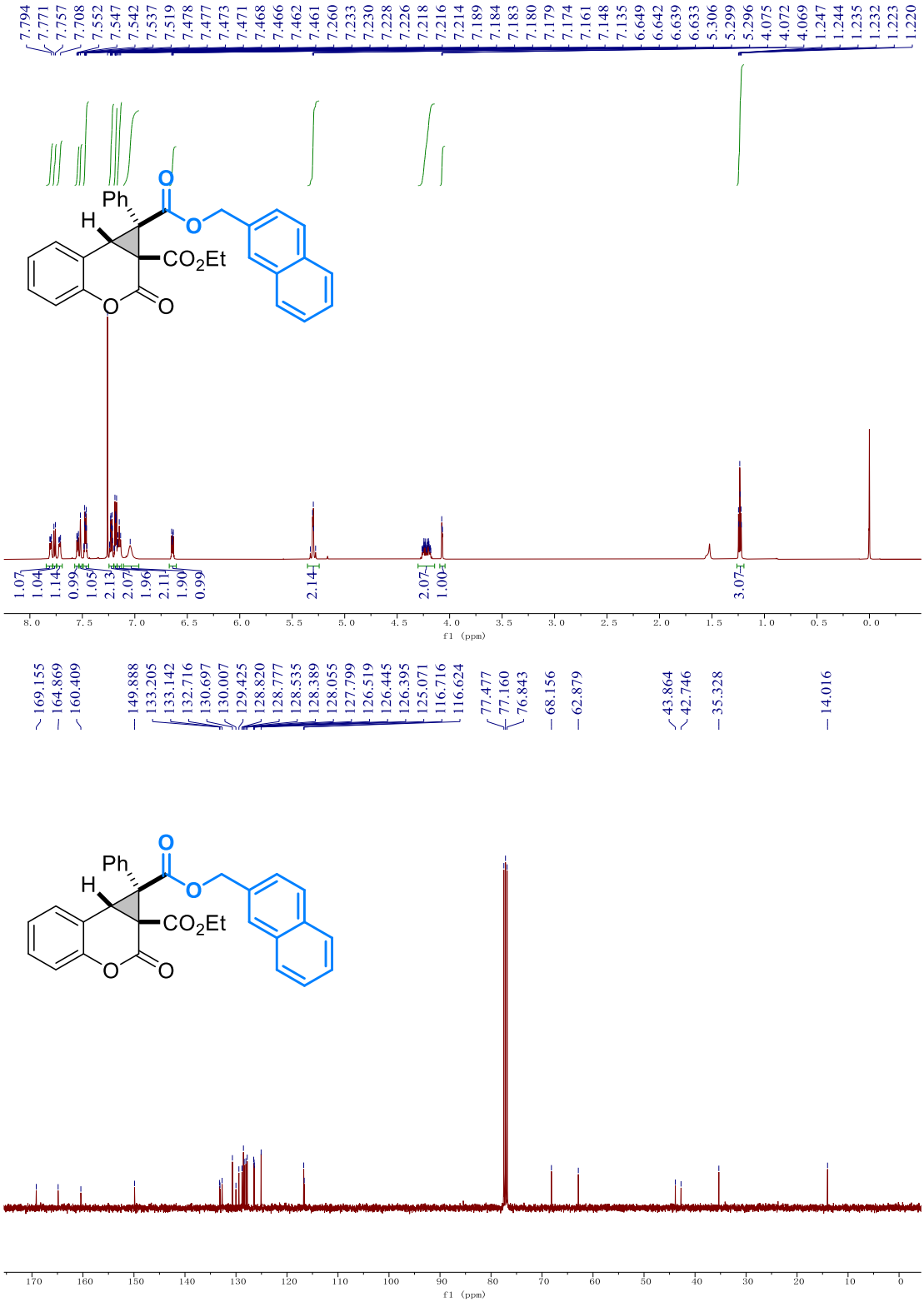
triethyl 2-oxocyclopropa[*c*]chromene-1,1,1a(2*H*,7b*H*)-tricarboxylate (3u)



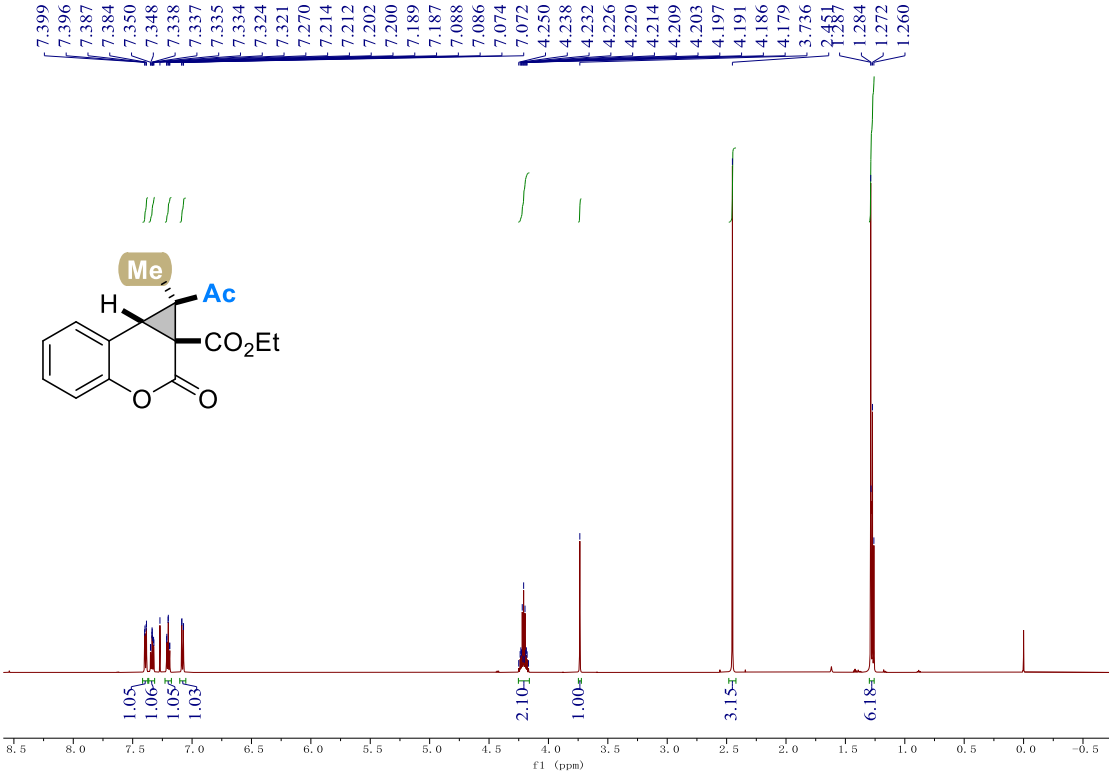
1-(cyclopropylmethyl) 1a-ethyl 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3v)

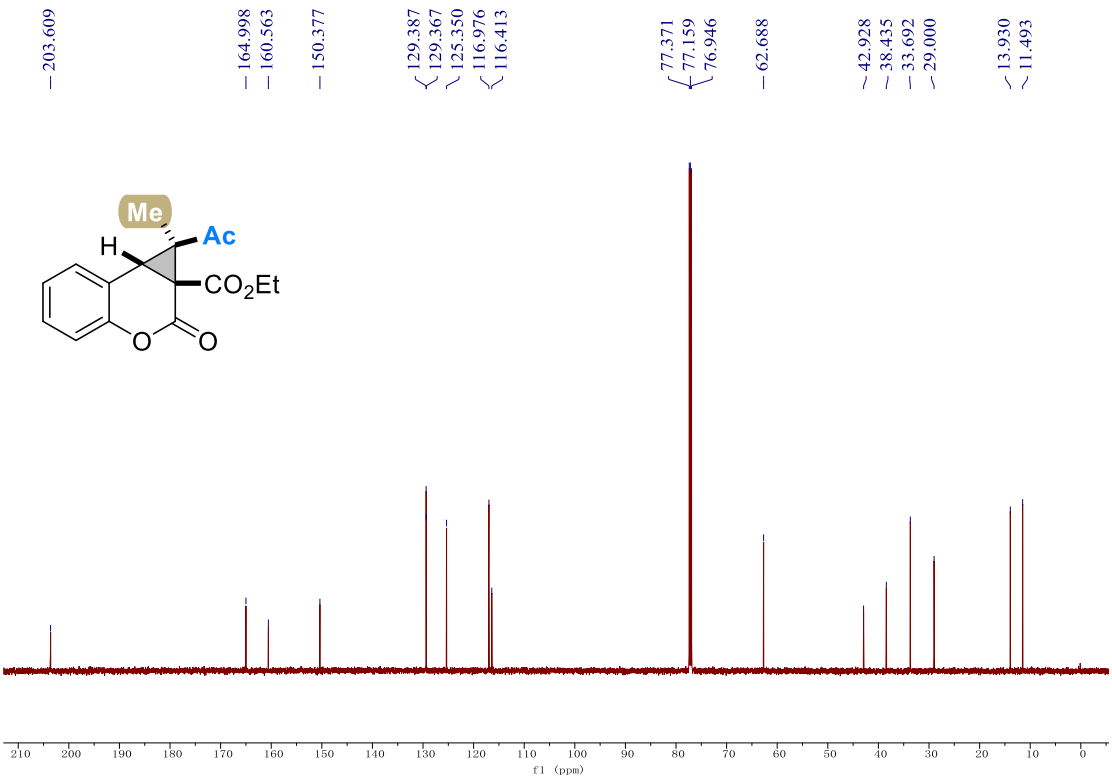


1a-ethyl 1-(naphthalen-2-ylmethyl) 2-oxo-1-phenyl-1,7b-dihydrocyclopropa[*c*]chromene-1,1a(2*H*)-dicarboxylate (3w)

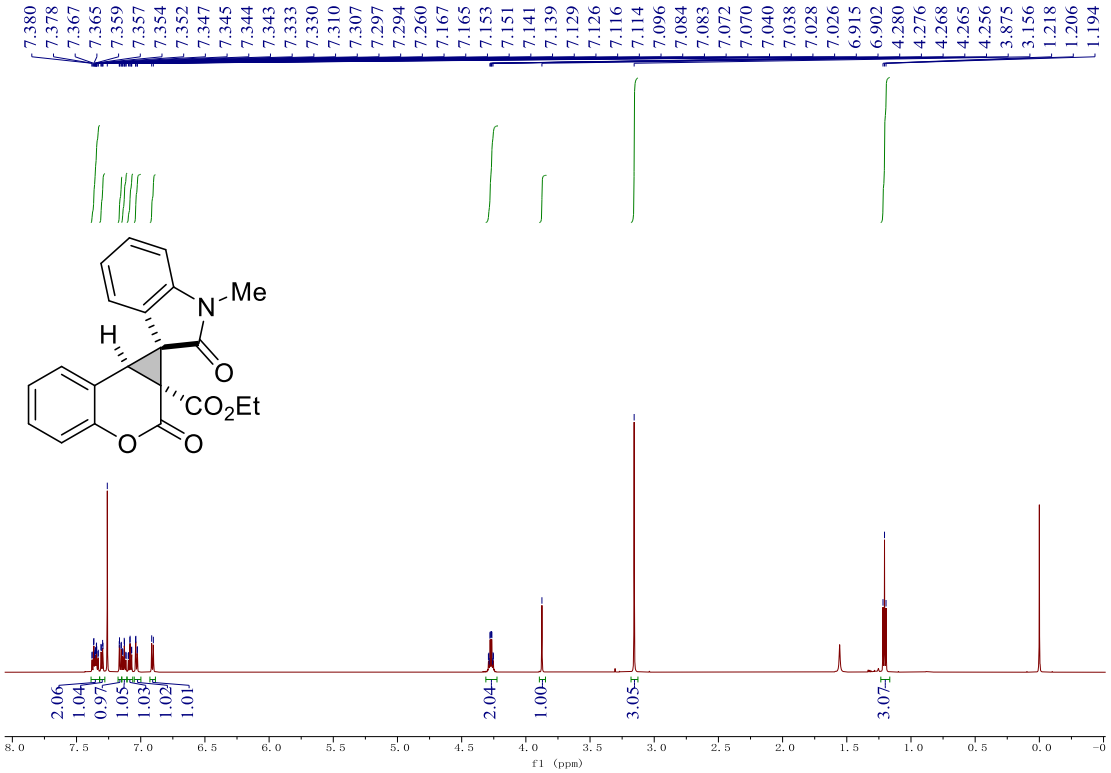


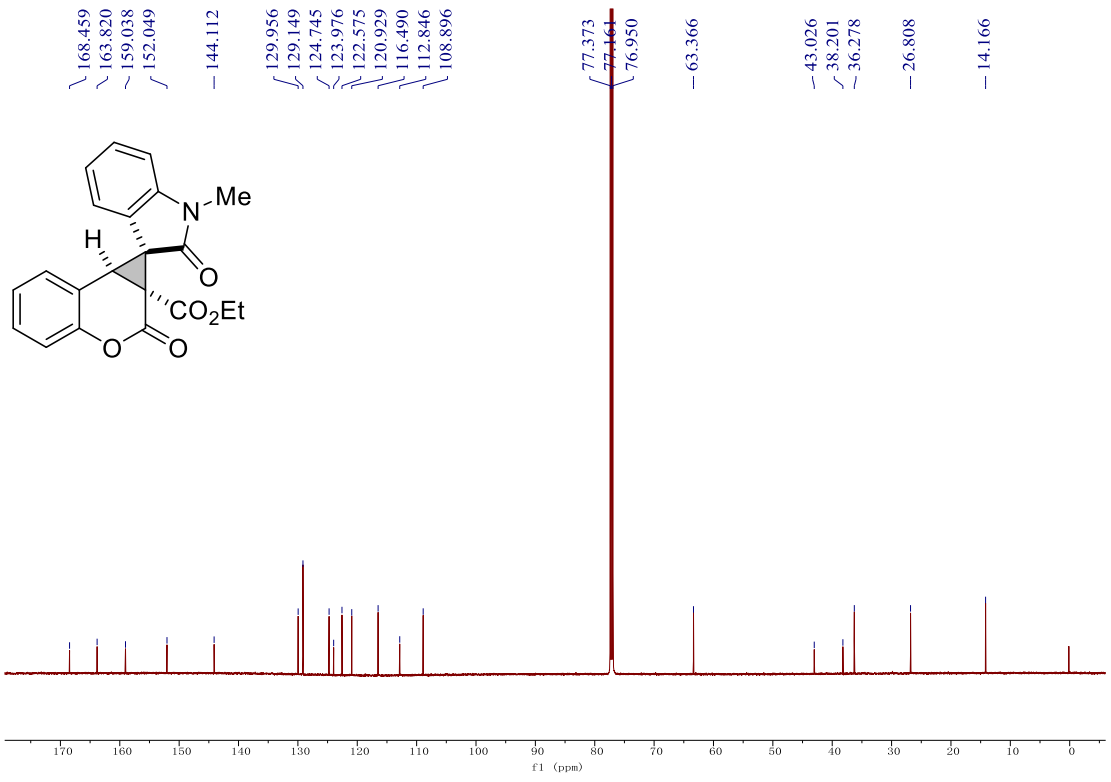
ethyl 1-acetyl-1-methyl-2-oxo-1,7b-dihydrocyclopropa[*c*]chromene-1a(2*H*)-carboxylate (3x)



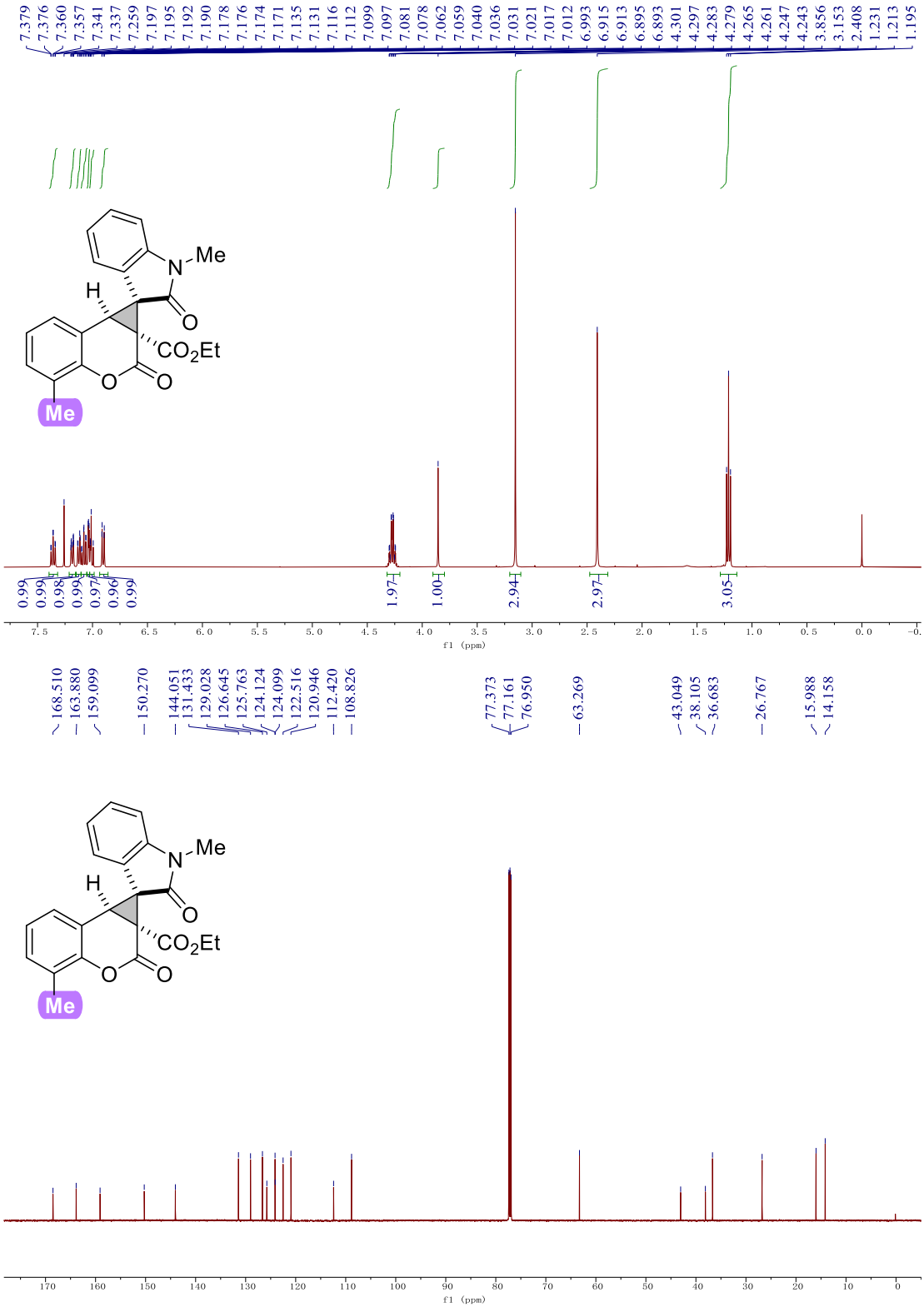


ethyl 1'-methyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5a)

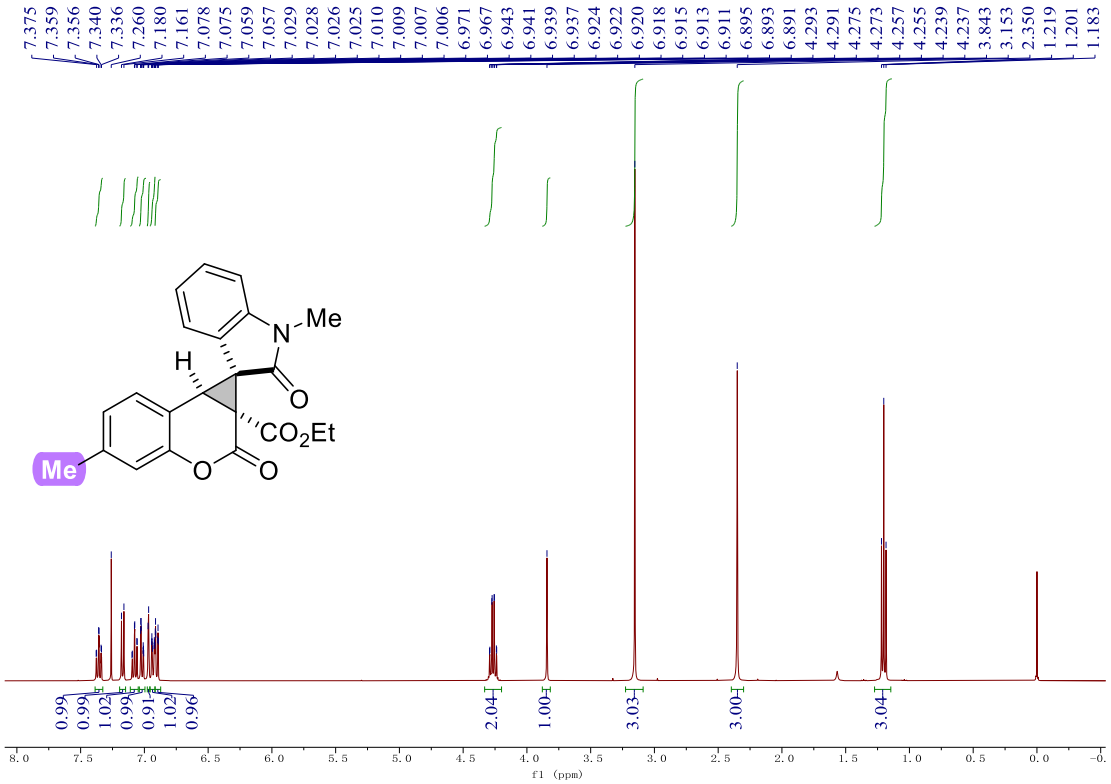


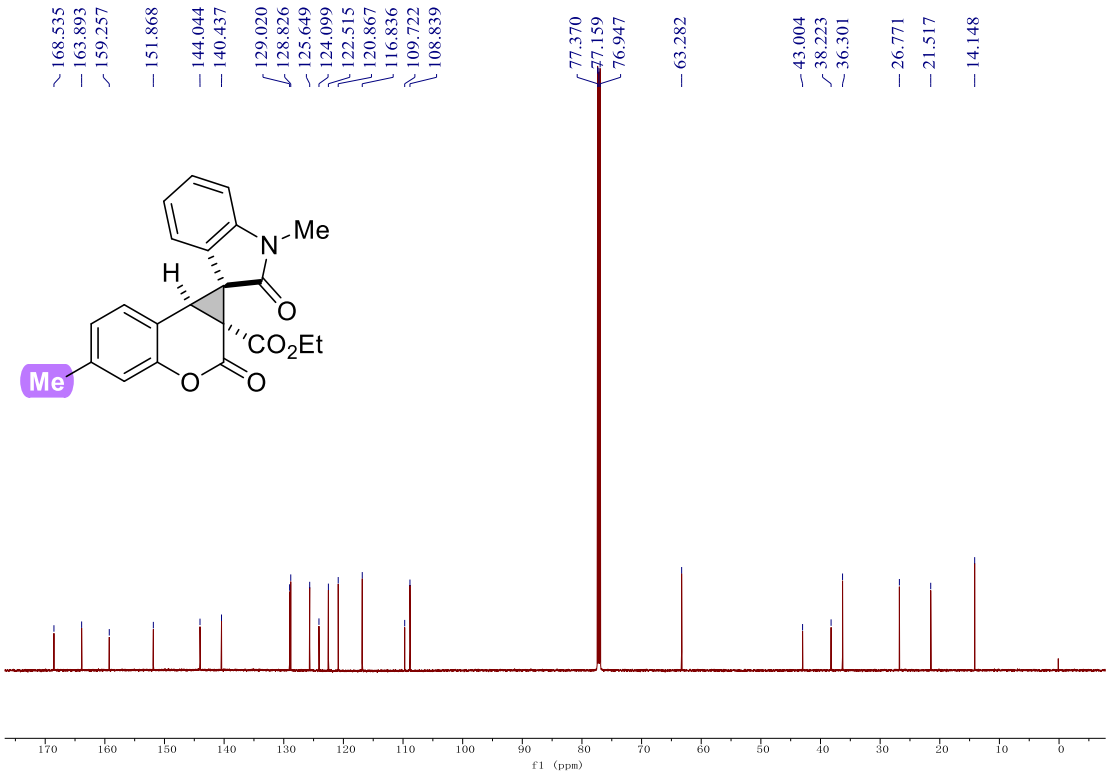


ethyl 1',4-dimethyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5b)

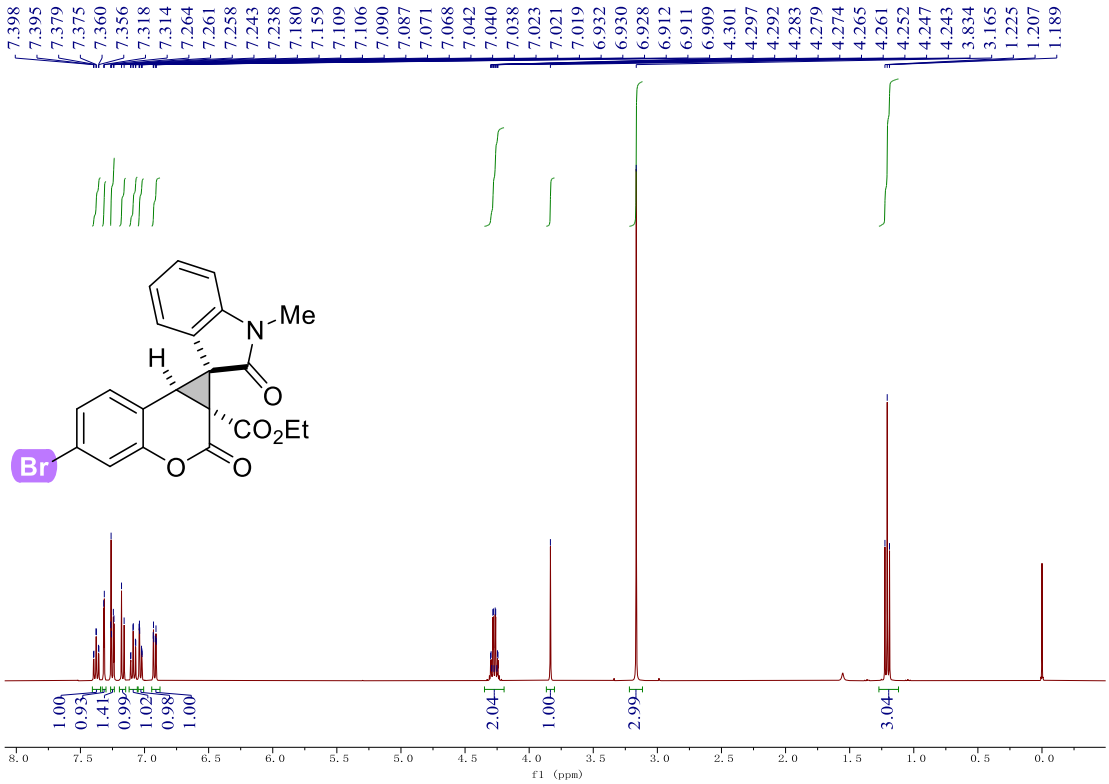


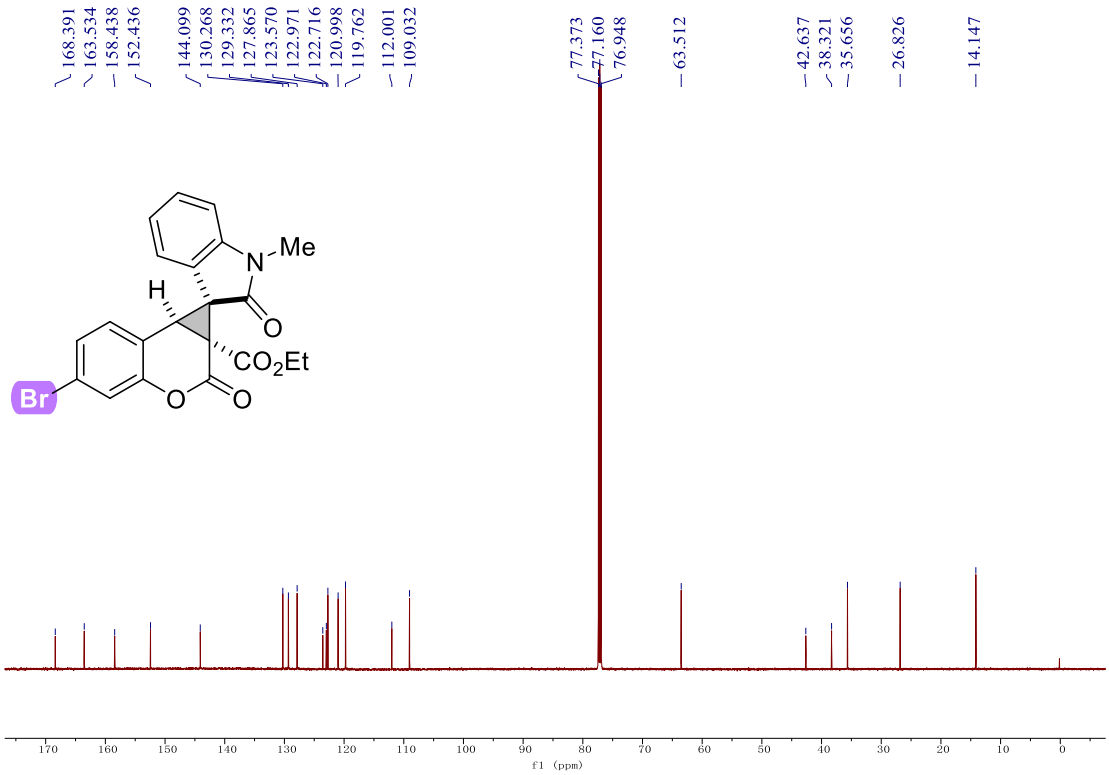
ethyl 1',5-dimethyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5c)



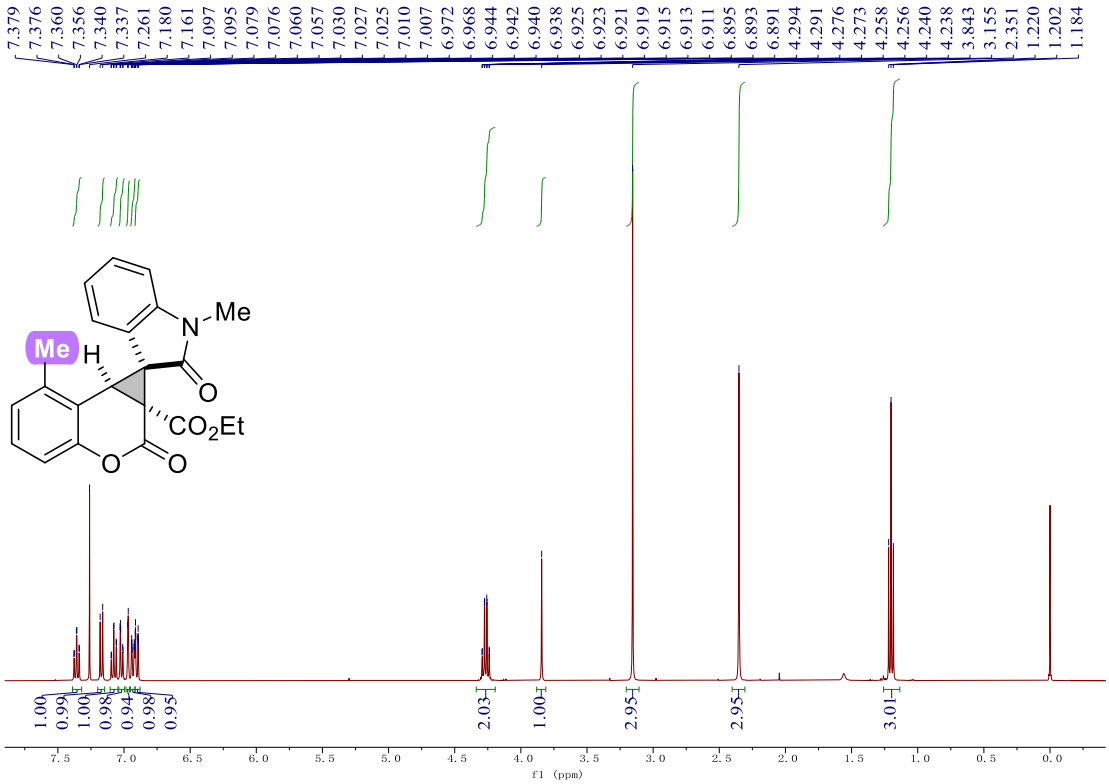


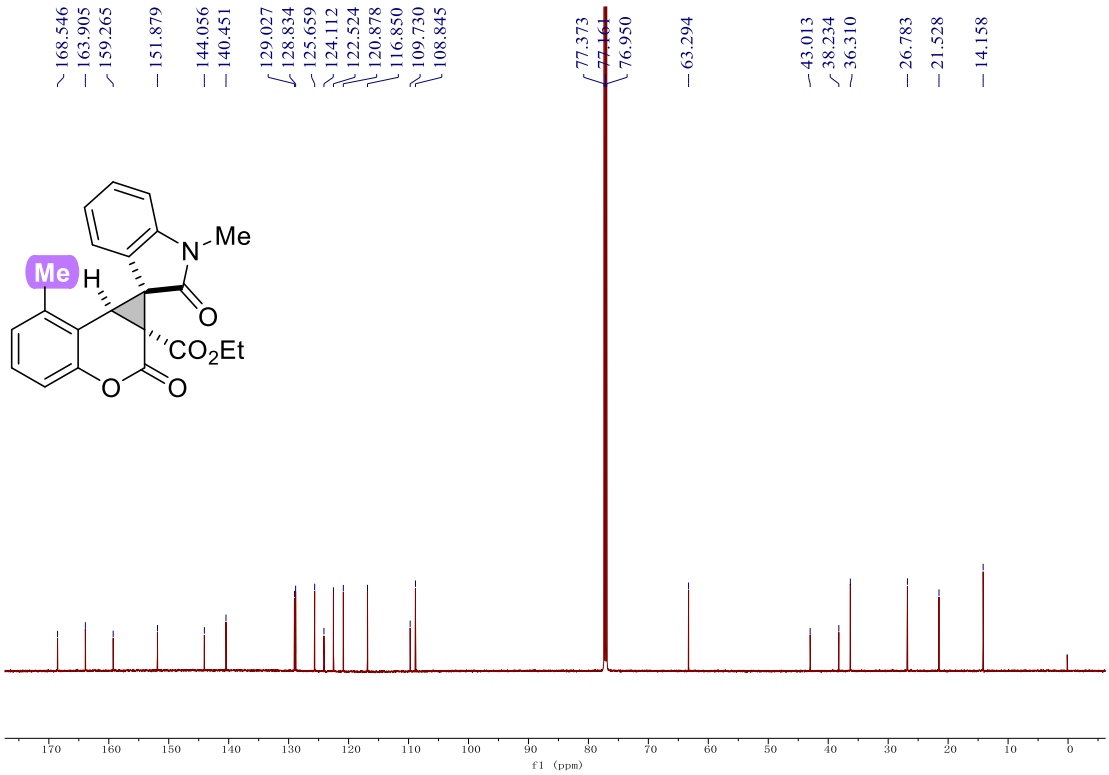
ethyl 5-bromo-1'-methyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5d)



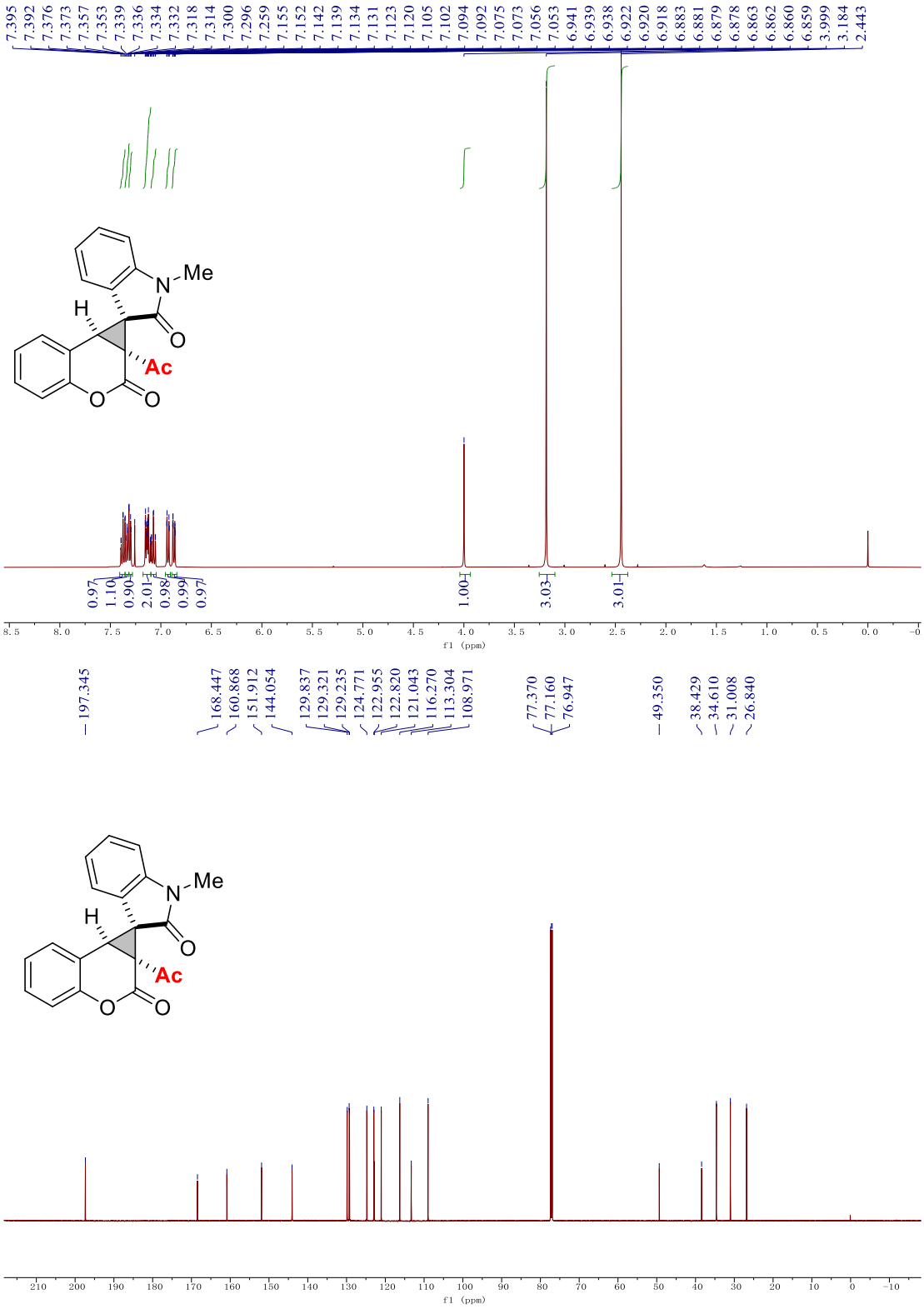


ethyl 1',7-dimethyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5e)

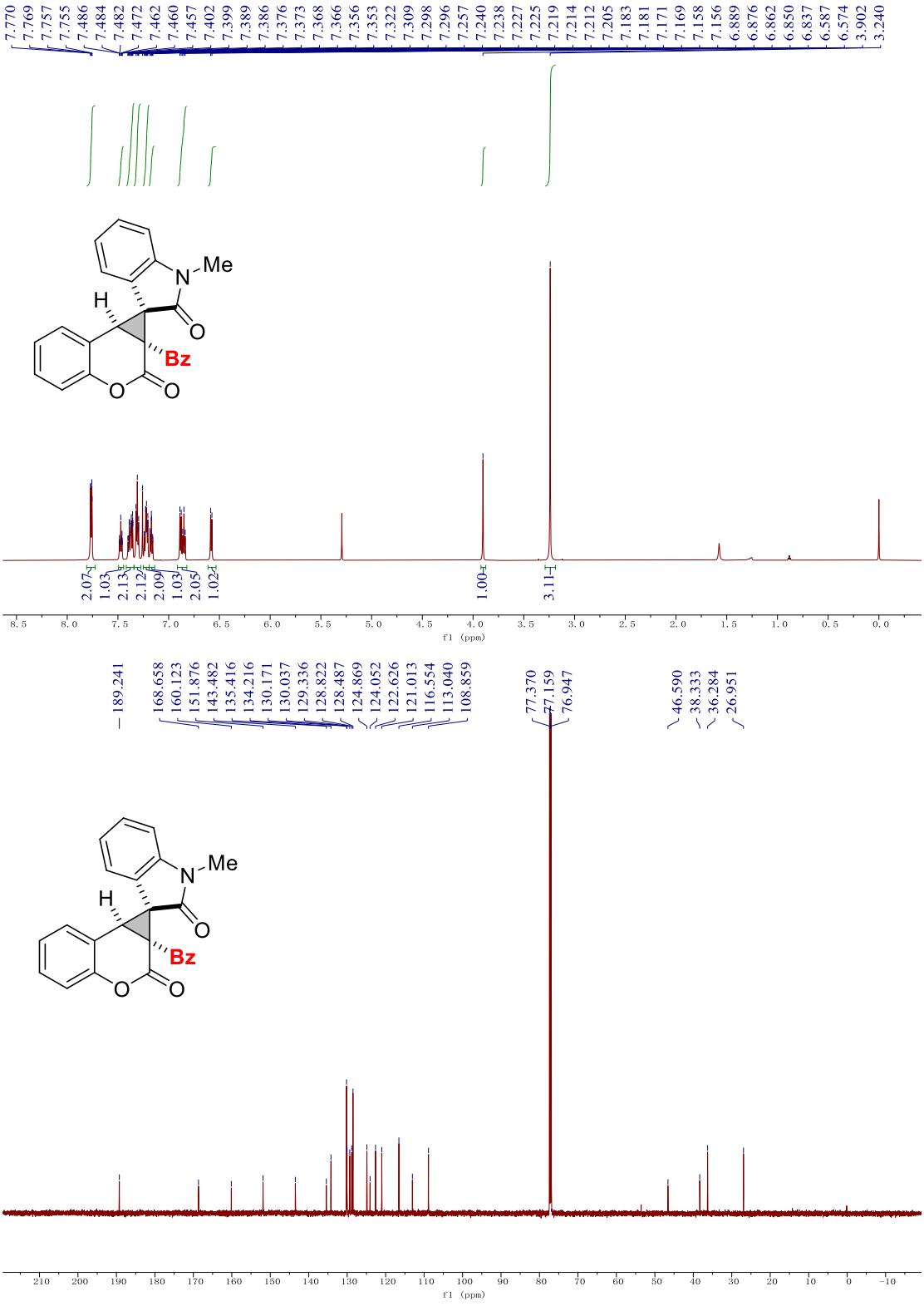




1a-acetyl-1'-methyl-1a,7b-dihydro-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-2,2'-dione (5f)



1a-benzoyl-1'-methyl-1a,7b-dihydro-2H-spiro[cyclopropa[c]chromene-1,3'-indoline]-2,2'-dione (5g)



tert-butyl 5'-bromo-1'-methyl-2,2'-dioxo-2*H*-spiro[cyclopropa[*c*]chromene-1,3'-indoline]-1a(7b*H*)-carboxylate (5h)