

Supporting Information

An Unusual Me₃SiI-Promoted [4+2] Annulation and Reduction: An Efficient Approach to Construct 4*H*-Benzopyrans

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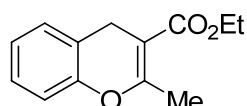
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General remarks. Dichloromethane was freshly distilled from calcium hydride; THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF₂₅₄) were used. Mass spectra were recorded by EI and ESI, and HRMS were measured on a HP-5989 instrument.

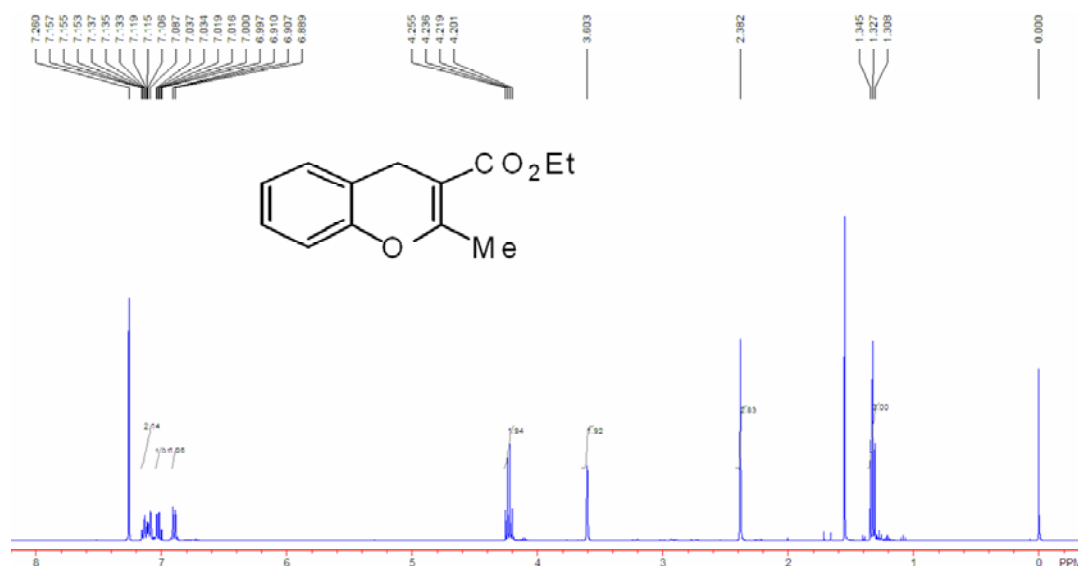
General procedure for the Me₃SiI-promoted reaction of salicylic aldehyde with β -dicarbonyl compound.

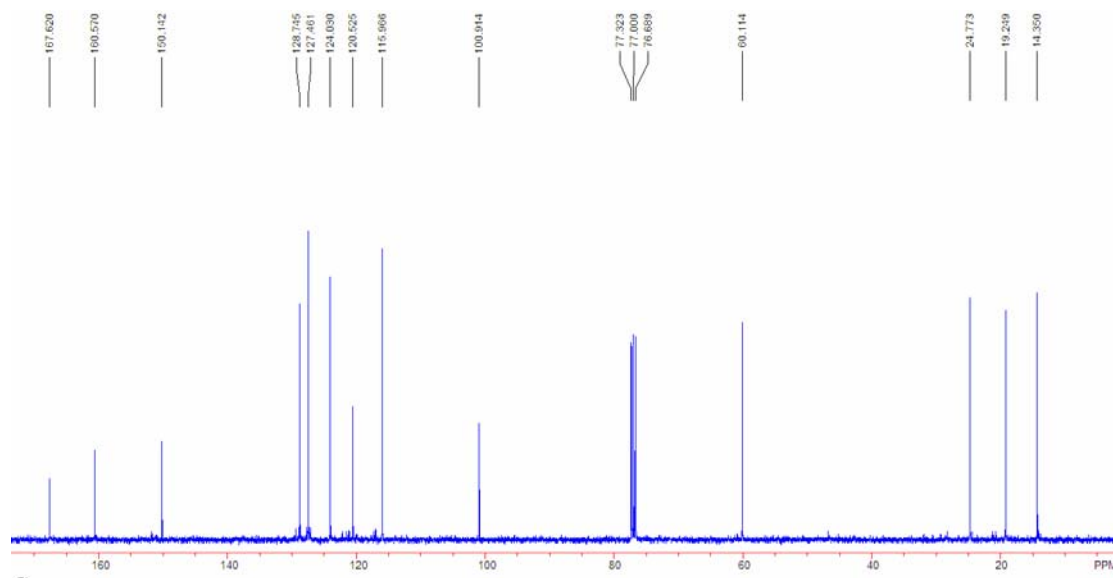
To a stirred mixture of Me₃SiCl (5.0 mmol), NaI (5.0 mmol), β -dicarbonyl compound **1** (1.0 mmol) and CH₃CN (5 mL) was added salicylic aldehyde **2** (1.0 mmol) at ice-bath temperature. The reaction mixture was stirred at room temperature for 24 h. After addition of aqueous Na₂S₂O₄ to the reaction mixture, the organic layer was extracted with dichloromethane, washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to obtain the 4*H*-benzopyran **3**.

Ethyl 2-methyl-4*H*-chromene-3-carboxylate **3aa**.¹

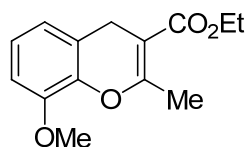


Yellow liquid; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.33 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 3.60 (s, 2H), 4.23 (dd, *J* = 7.6, 14.4 Hz, 2H), 6.90 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.02 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.09-7.16 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 14.4, 19.2, 24.8, 60.1, 100.9, 116.0, 120.5, 124.0, 127.5, 128.7, 150.1, 160.6, 167.6; MS (ESI) *m/z* (%): 219.1 (M + H, 100); HRMS (Micromass LCT) Calcd. for C₁₃H₁₅O₃: 219.1021; Found: 219.1023.

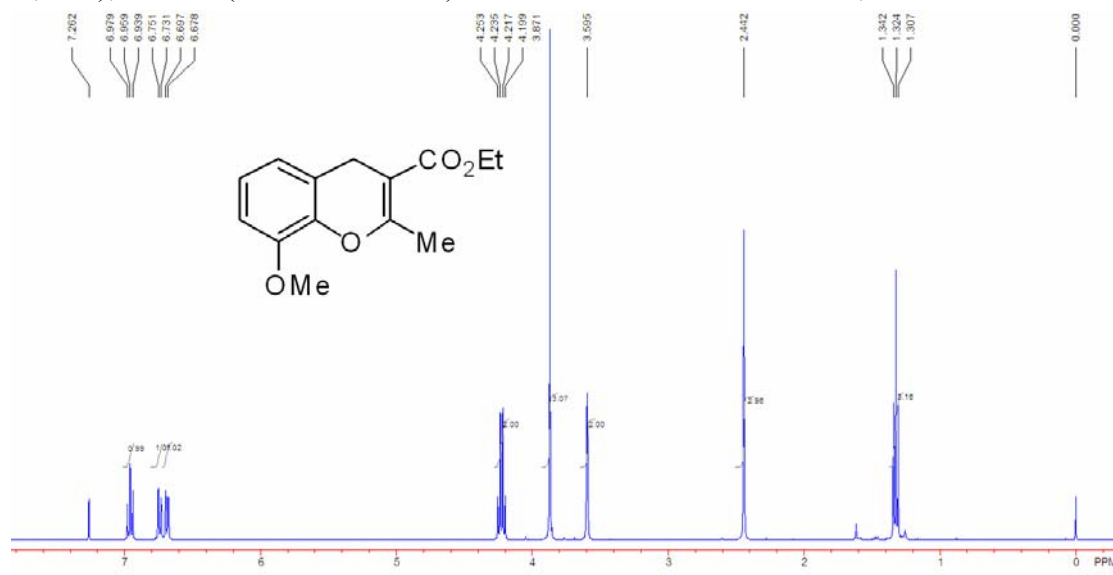


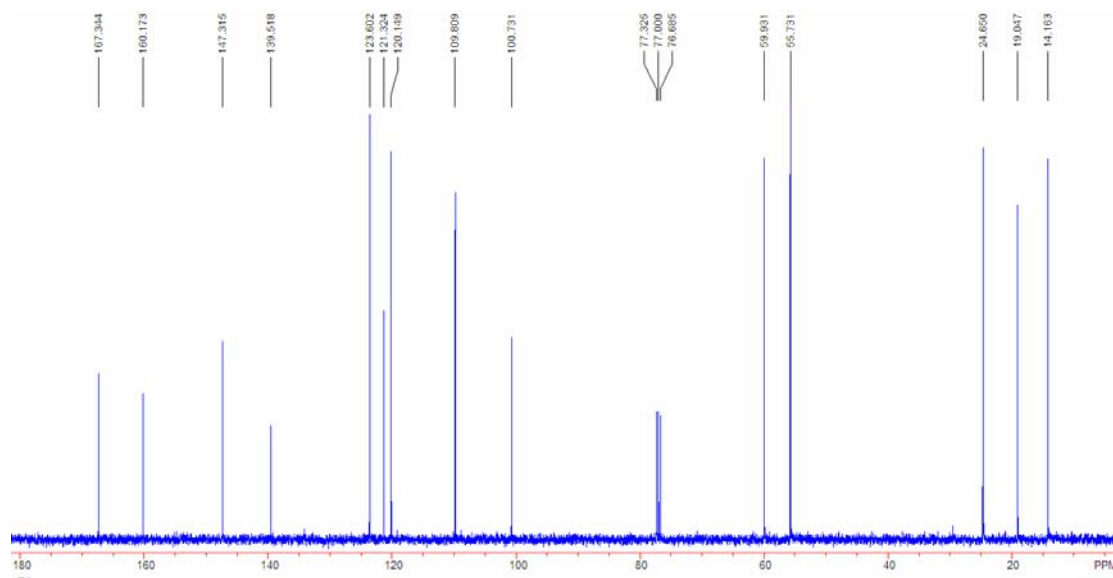


Ethyl 8-methoxy-2-methyl-4*H*-chromene-3-carboxylate **3ab**.

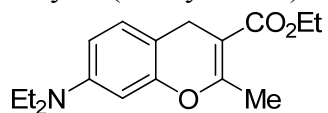


Yellow solid; Mp. 95.3-995.8 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.32 (t, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 3.60 (s, 2H), 3.87 (s, 3H), 4.23 (dd, *J* = 7.2, 14.4 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 14.2, 19.0, 24.7, 55.7, 59.9, 100.7, 109.8, 120.1, 121.3, 123.6, 139.5, 147.3, 160.2, 167.3; MS (ESI) *m/z* (%): 249.1 (M + H, 100); HRMS (Micromass LCT) Calcd. for C₁₄H₁₇O₄: 249.1127; Found: 249.1135.

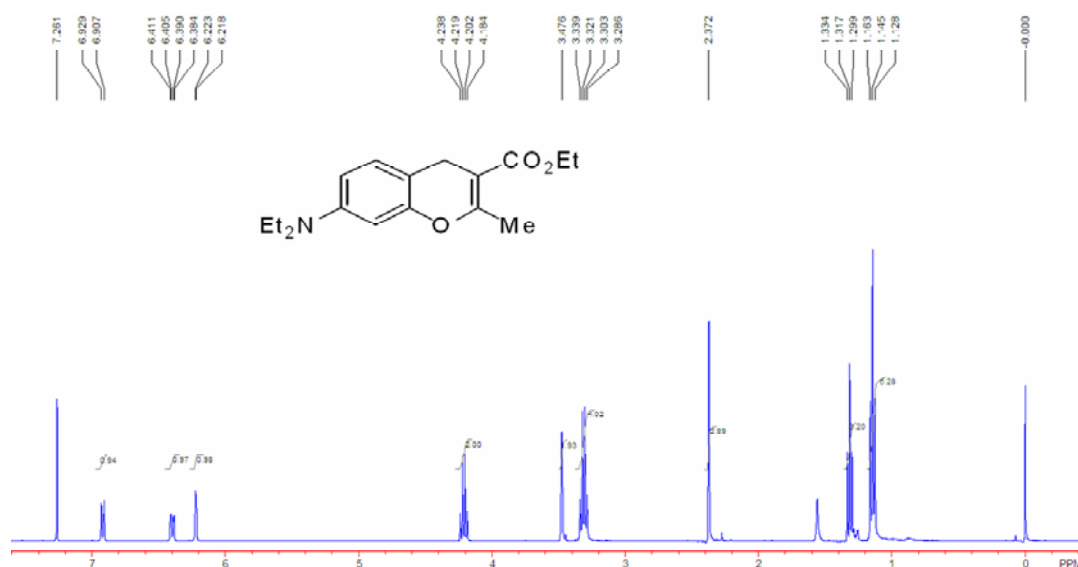


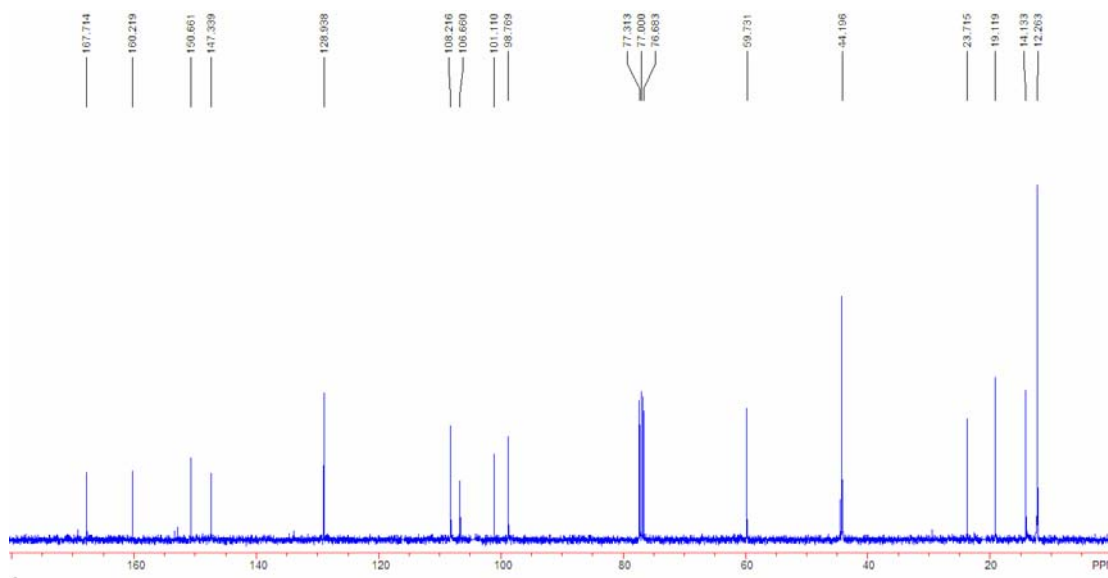


Ethyl 7-(diethylamino)-2-methyl-4*H*-chromene-3-carboxylate **3ac**.

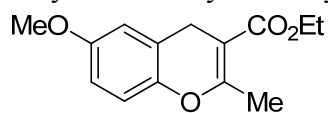


Yellow liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.15 (t, $J = 7.2$ Hz, 6H), 1.32 (t, $J = 6.8$ Hz, 3H), 2.37 (s, 3H), 3.31 (t, $J = 7.2$ Hz, 4H), 3.48 (s, 2H), 4.21 (dd, $J = 7.6, 14.4$ Hz, 2H), 6.22 (t, $J = 2.0$ Hz, 1H), 6.40 (dd, $J = 2.4, 8.4$ Hz, 1H), 6.92 (t, $J = 8.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 12.3, 14.1, 19.1, 23.7, 44.2, 59.7, 98.8, 101.1, 106.7, 108.2, 128.9, 147.3, 150.7, 160.2, 167.7; MS (ESI) m/z (%): 290.2 (M + H, 78); HRMS (Micromass LCT) Calcd. for $\text{C}_{17}\text{H}_{24}\text{NO}_3$: 290.1756; Found: 290.1752.

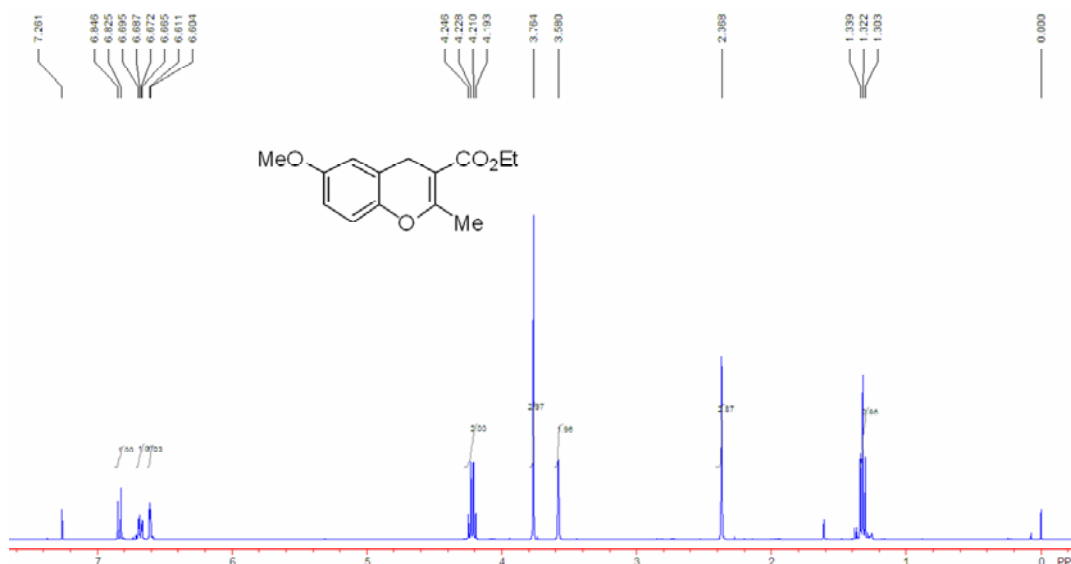


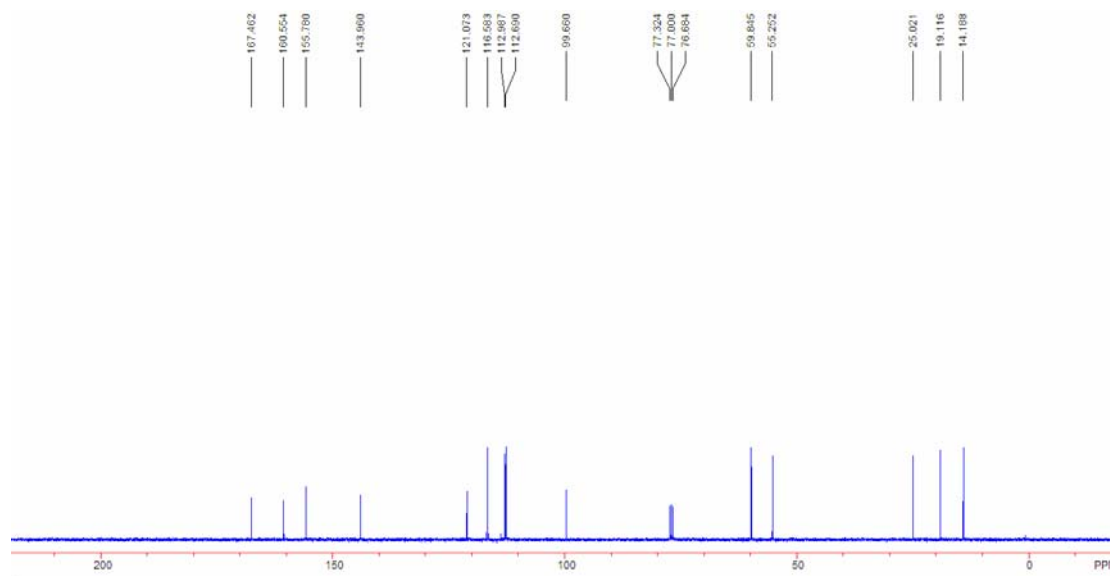


Ethyl 6-methoxy-2-methyl-4*H*-chromene-3-carboxylate **3ad**.

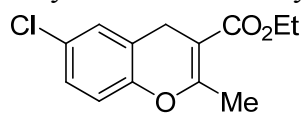


Yellow liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.32 (t, $J = 6.8$ Hz, 3H), 2.37 (s, 3H), 3.58 (s, 2H), 3.76 (s, 3H), 4.22 (dd, $J = 7.2, 14.4$ Hz, 2H), 6.61 (d, $J = 2.8$ Hz, 1H), 6.68 (dd, $J = 2.8, 9.2$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 14.2, 19.1, 25.0, 55.3, 59.8, 99.7, 112.7, 113.0, 116.6, 121.1, 144.0, 155.8, 160.6, 167.5; MS (ESI) m/z (%): 249.1 (M + H, 100); HRMS (Micromass LCT) Calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_4$: 249.1127; Found: 249.1130.

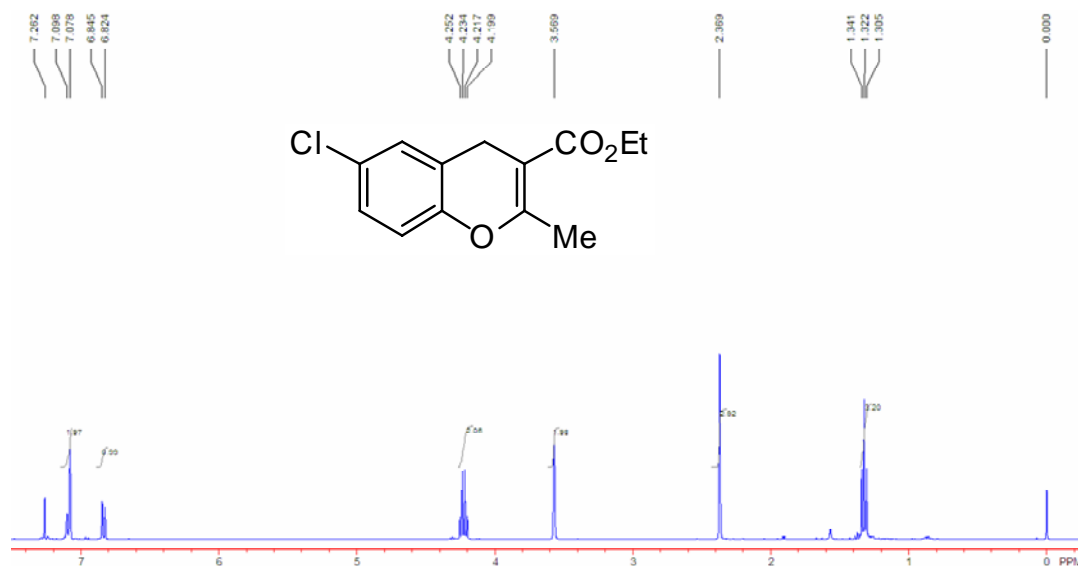


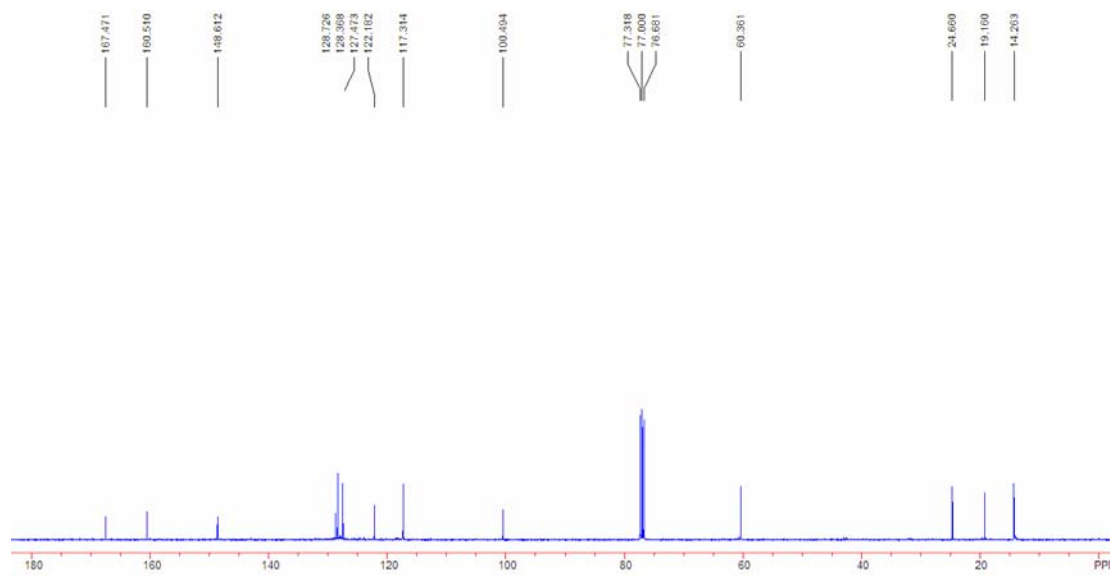


Ethyl 6-chloro-2-methyl-4*H*-chromene-3-carboxylate **3ae**.

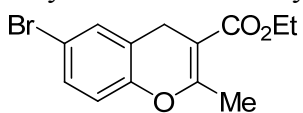


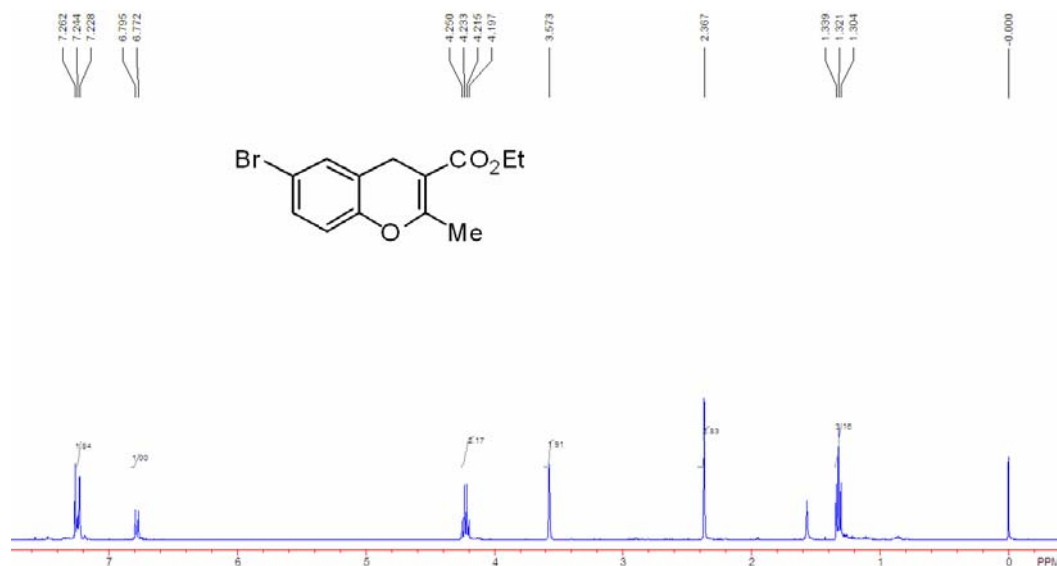
Yellow liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.32 (t, J = 7.6 Hz, 3H), 2.37 (s, 3H), 3.57 (s, 2H), 4.23 (dd, J = 7.2, 14.0 Hz, 2H), 6.83 (d, J = 8.4 Hz, 1H), 7.08-7.10 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 14.3, 19.2, 24.7, 60.4, 100.5, 117.3, 122.2, 127.5, 128.4, 128.7, 148.6, 160.5, 167.4; MS (ESI) m/z (%): 253.1 (M + H, 65); HRMS (Micromass LCT) Calcd. for $\text{C}_{13}\text{H}_{14}\text{ClO}_3$: 253.0631; Found: 253.0632.

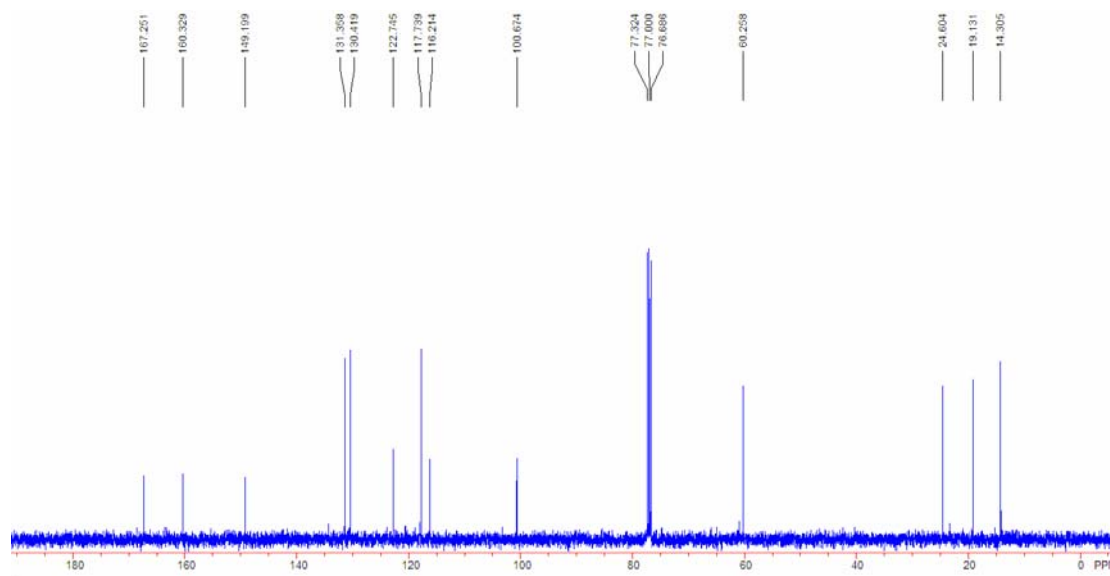




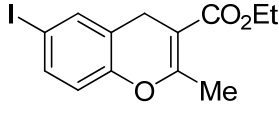
Ethyl 6-bromo-2-methyl-4*H*-chromene-3-carboxylate **3af**.

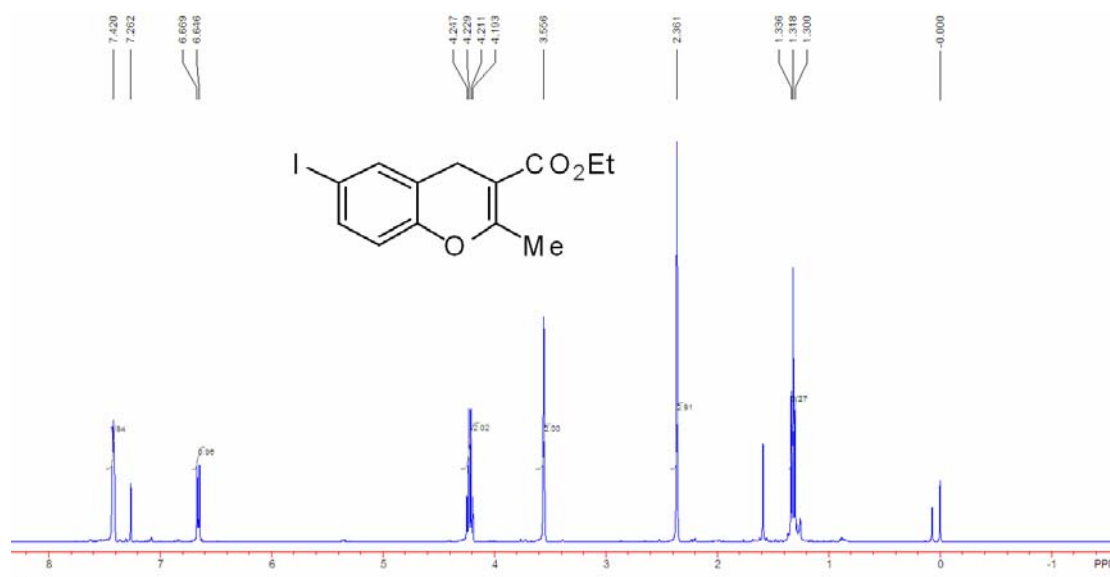
 Red liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.32 (t, J = 7.2 Hz, 3H), 2.37 (s, 3H), 3.57 (s, 2H), 4.22 (dd, J = 6.8, 14.0 Hz, 2H), 6.78 (d, J = 9.2 Hz, 1H), 7.23-7.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 14.3, 19.1, 24.6, 60.3, 100.7, 116.2, 117.7, 122.7, 130.4, 131.4, 149.3, 160.3, 167.3; MS (ESI) m/z (%): 297.0 (M + H, 89); HRMS (Micromass LCT) Calcd. for $\text{C}_{13}\text{H}_{14}\text{BrO}_3$: 297.0126; Found: 297.0133.

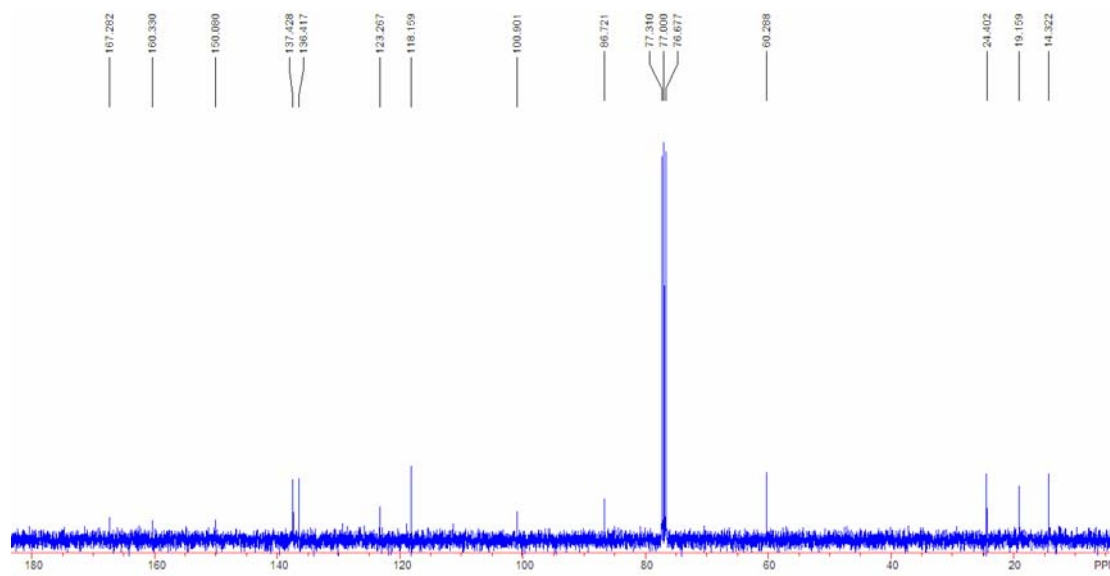




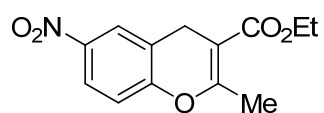
Ethyl 6-iodo-2-methyl-4*H*-chromene-3-carboxylate **3ag**.

 Yellow liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.32 (t, J = 7.2 Hz, 3H), 2.36 (s, 3H), 3.56 (s, 2H), 4.23 (dd, J = 7.2, 14.4 Hz, 2H), 6.66 (d, J = 9.2 Hz, 1H), 7.42 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 14.3, 19.2, 24.4, 60.3, 68.7, 100.9, 118.2, 123.3, 136.4, 137.4, 150.1, 160.3, 167.3; MS (ESI) m/z (%): 345.0 (M + H, 100); HRMS (Micromass LCT) Calcd. for $\text{C}_{13}\text{H}_{14}\text{IO}_3$: 344.9988; Found: 344.9995.

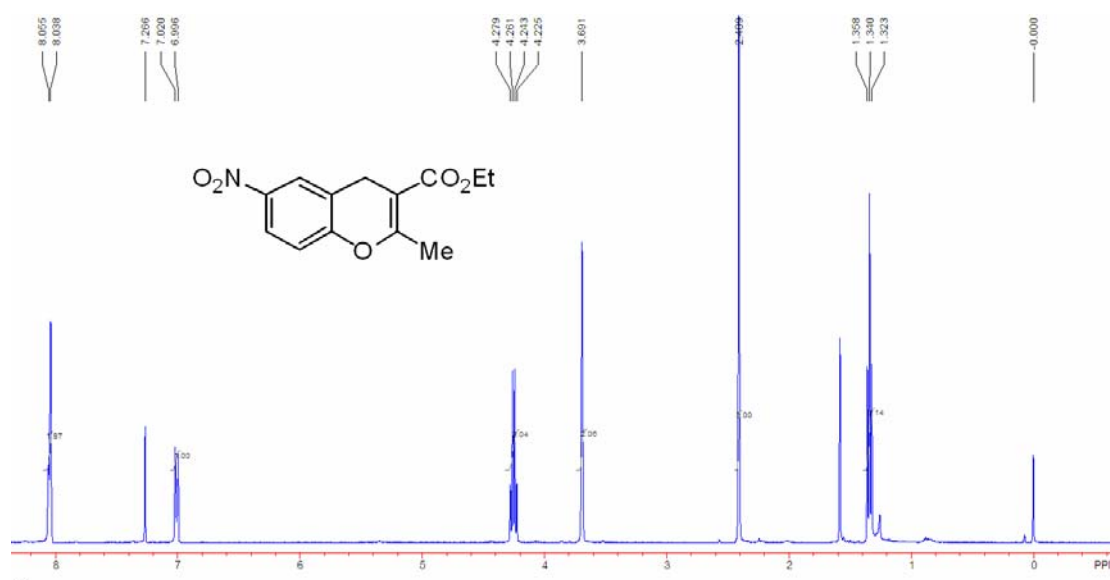


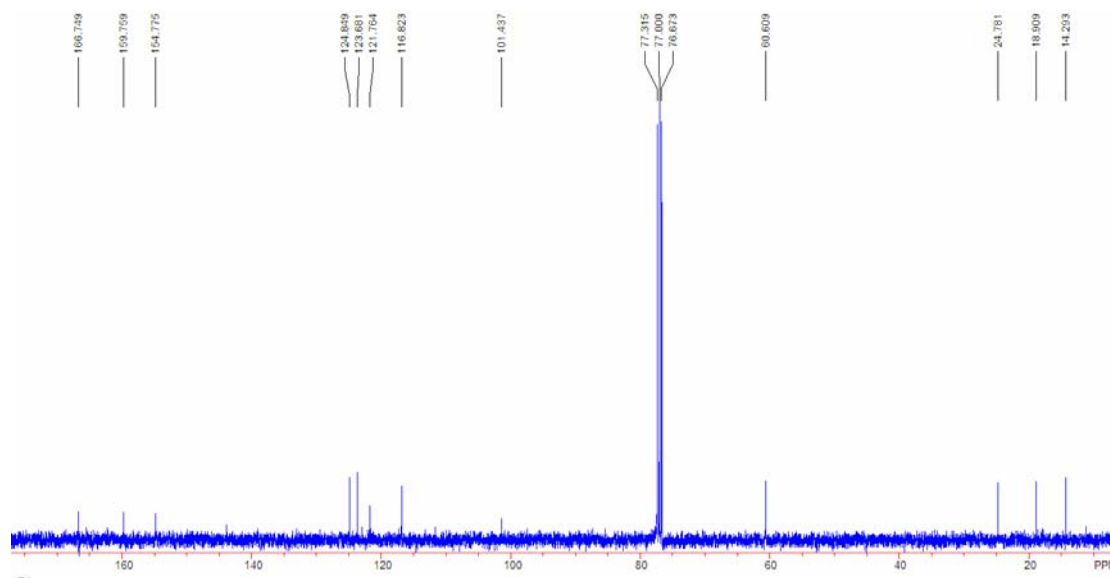


Ethyl 2-methyl-6-nitro-4*H*-chromene-3-carboxylate **3ah**.

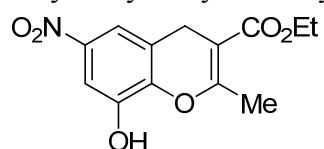


White solid; Mp. 110.5-111.2 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.34 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 3.69 (s, 2H), 4.25 (dd, *J* = 7.2, 14.4 Hz, 2H), 7.01 (d, *J* = 9.6 Hz, 1H), 8.04-8.06 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 14.3, 18.9, 24.8, 60.6, 101.4, 116.8, 121.8, 123.7, 124.8, 154.8, 159.8, 166.7; MS (ESI) *m/z* (%): 264.1 (M + H, 90); HRMS (Micromass LCT) Calcd. for C₁₃H₁₄NO₅: 264.0872; Found: 264.0874.

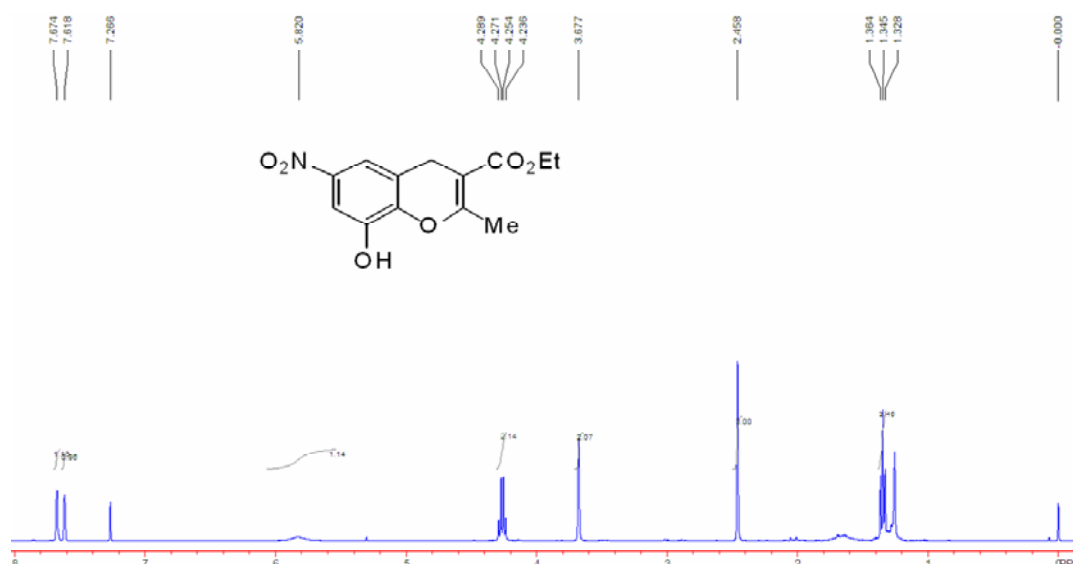


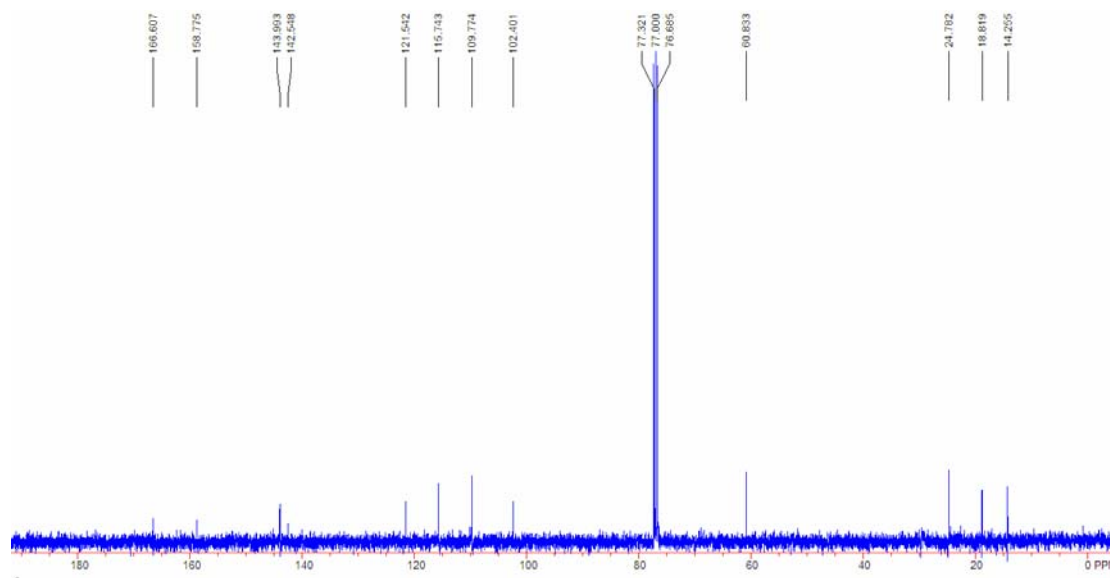


Ethyl 8-hydroxy-2-methyl-6-nitro-4*H*-chromene-3-carboxylate **3ai**.

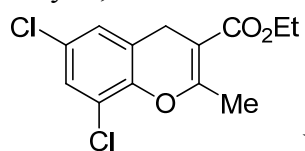


White solid; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.35 (t, *J* = 7.6 Hz, 3H), 2.46 (s, 3H), 3.68 (s, 2H), 4.26 (dd, *J* = 7.2, 14.0 Hz, 2H), 5.82 (br s, 1H), 7.62 (s, 1H), 7.67 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 14.3, 18.8, 24.8, 60.8, 102.4, 109.8, 115.7, 121.5, 142.5, 144.0, 158.8, 166.6; MS (ESI) *m/z* (%): 280.1 (M + H, 56); HRMS (Micromass LCT) Calcd. for C₁₃H₁₄NO₆: 280.0821; Found: 280.0823.

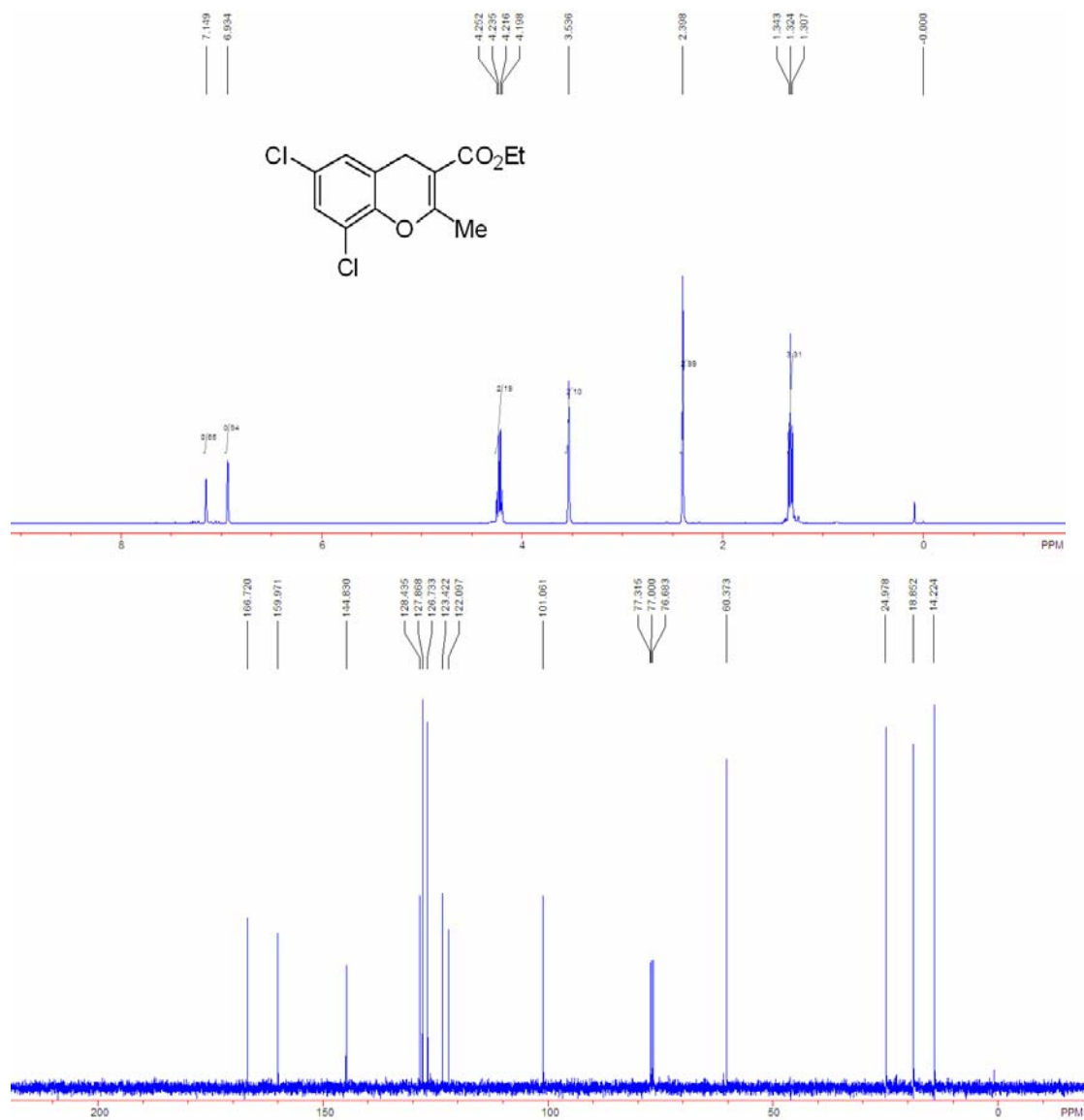




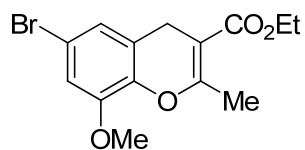
Ethyl 6,8-dichloro-2-methyl-4*H*-chromene-3-carboxylate **3aj**.



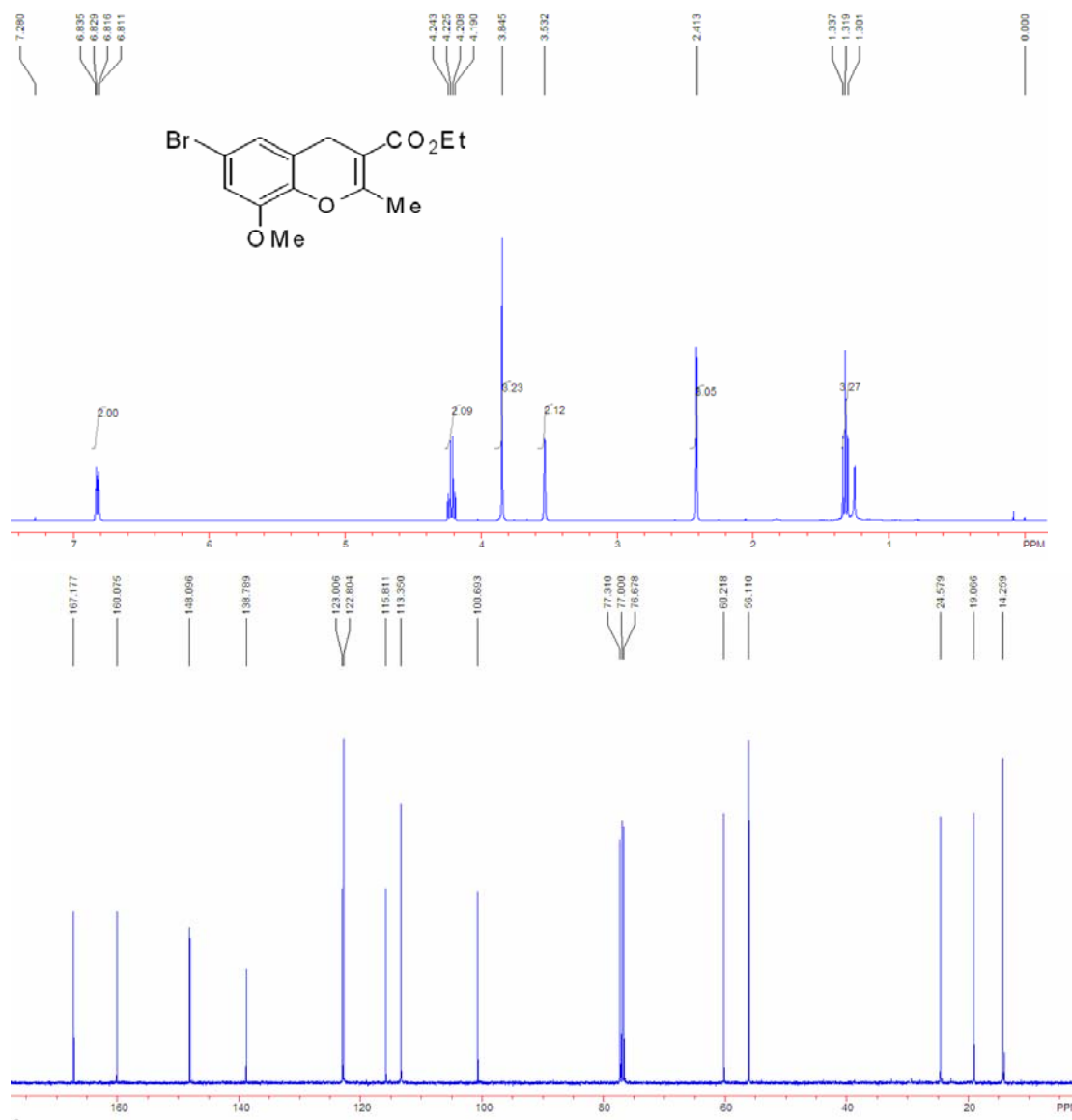
Yellow solid; Mp. 120.5-121.1 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.32 (t, *J* = 7.6 Hz, 3H), 2.40 (s, 3H), 3.54 (s, 2H), 4.23 (dd, *J* = 6.8, 14.4 Hz, 2H), 6.93 (s, 1H), 7.15 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 14.2, 18.9, 25.0, 60.4, 101.1, 122.1, 123.4, 126.7, 127.9, 128.4, 144.8, 160.0, 166.7; MS (ESI) *m/z* (%): 287.0 (M + H, 100); HRMS (Micromass LCT) Calcd. for C₁₃H₁₃Cl₂O₃: 287.0242; Found: 287.0244.



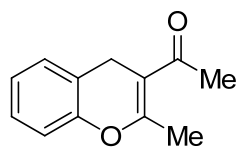
Ethyl 6-bromo-8-methoxy-2-methyl-4H-chromene-3-carboxylate **3ak**.



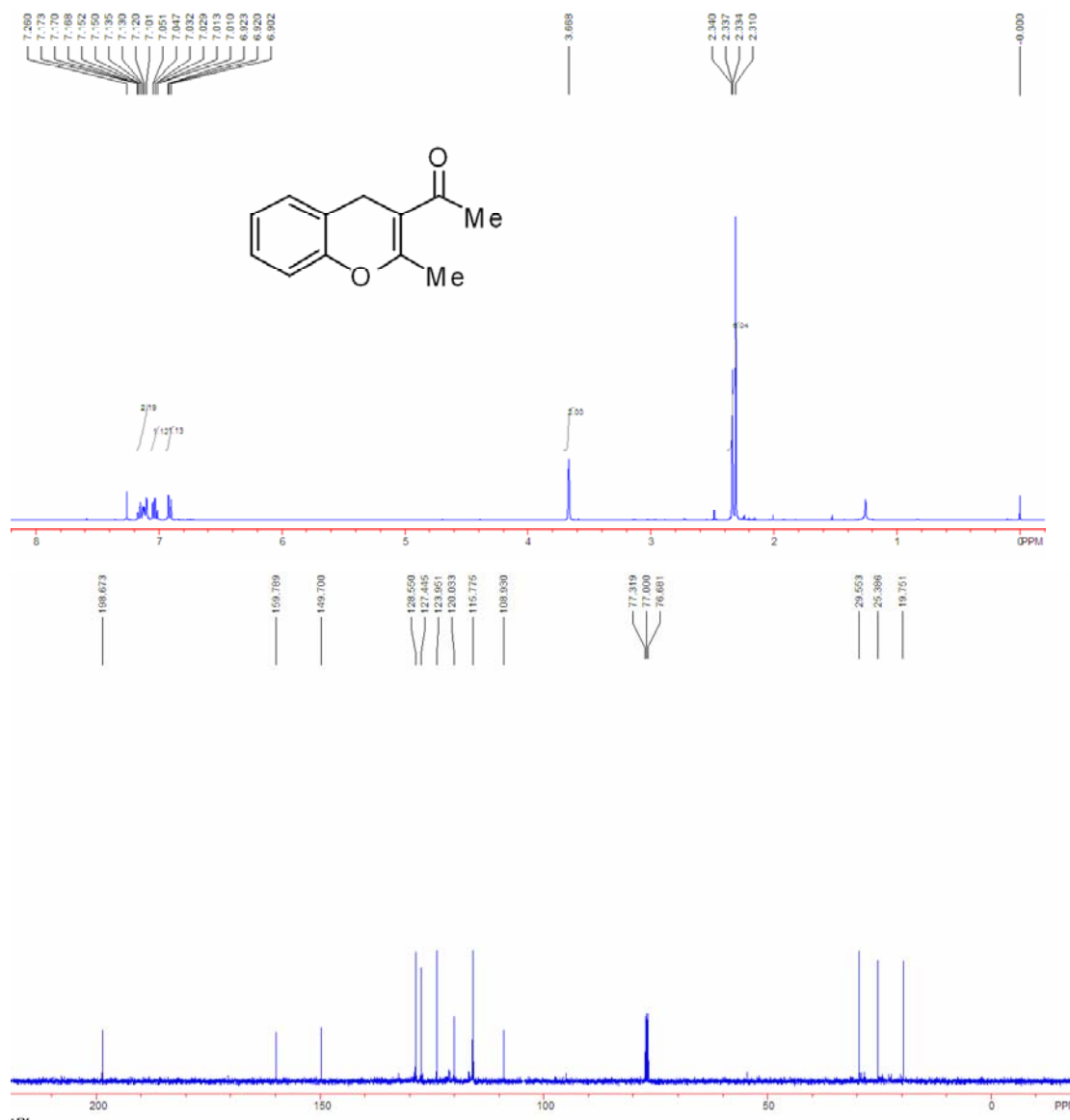
Red solid; Mp. 187.1-187.6 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.32 (t, $J = 7.2$ Hz, 3H), 2.41 (s, 3H), 3.53 (s, 2H), 3.84 (s, 3H), 4.22 (dd, $J = 7.2, 14.8$ Hz, 2H), 6.81 (d, $J = 2.0$ Hz, 1H), 6.83 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 14.3, 19.1, 24.6, 56.1, 60.2, 100.7, 113.4, 115.8, 122.8, 123.0, 138.8, 148.1, 160.1, 167.2; MS (ESI) m/z (%): 327.0 (M + H, 90); HRMS (Micromass LCT) Calcd. for $\text{C}_{14}\text{H}_{16}\text{BrO}_4$: 327.0232; Found: 327.0239.



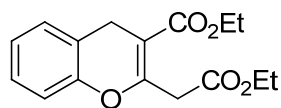
1-(2-Methyl-4H-chromen-3-yl)ethanone **3ba**.²



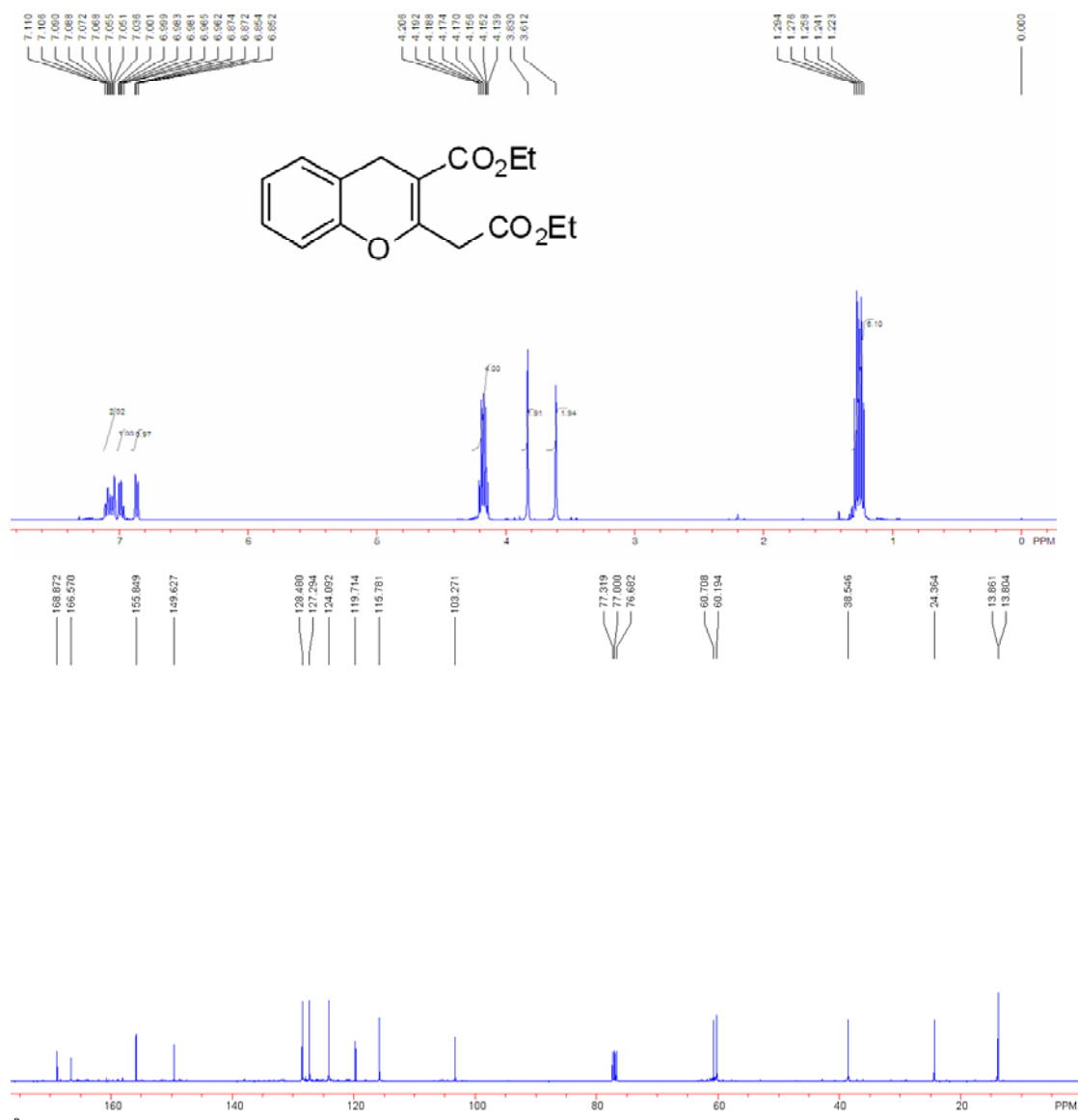
Yellow liquid; ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.31 (s, 3H), 2.34 (t, *J* = 1.2 Hz, 3H), 3.67 (s, 2H), 6.91 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.03 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.10-7.17 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 19.8, 25.4, 29.6, 108.9, 115.8, 120.0, 124.0, 127.4, 128.6, 149.7, 159.8, 198.7; MS (ESI) *m/z* (%): 189.1 (M + H, 80); HRMS (Micromass LCT) Calcd. for C₁₂H₁₃O₂: 189.0916; Found: 189.0920.



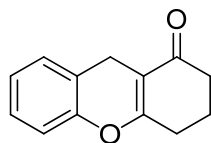
Ethyl 2-(2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate **3ca**.



Yellow liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.24 (t, $J = 7.2$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 3.61 (s, 2H), 3.83 (s, 2H), 4.14-4.21 (m, 4H), 6.86 (dd, $J = 0.8, 8.0$ Hz, 1H), 6.98 (dt, $J = 0.8, 7.2$ Hz, 1H), 7.04-7.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 13.8, 13.9, 24.4, 38.5, 60.2, 60.7, 103.3, 115.8, 119.7, 124.1, 127.3, 128.5, 149.6, 155.8, 166.6, 168.9; MS (ESI) m/z (%): 291.1 (M + H, 72); HRMS (Micromass LCT) Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_5$: 291.1232; Found: 291.1235.

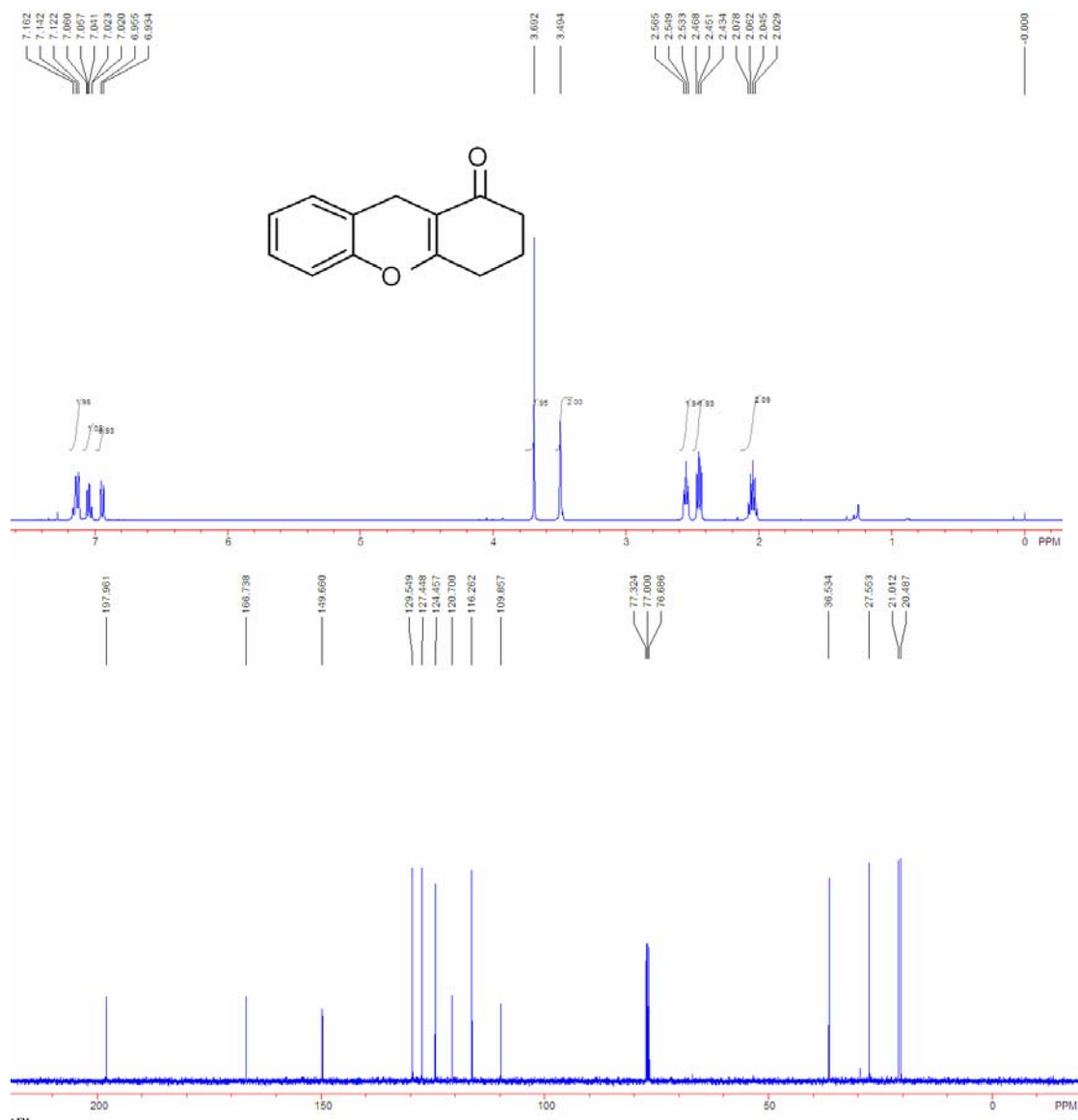


2,3,4,9-Tetrahydro-1*H*-xanthen-1-one **3da**.³

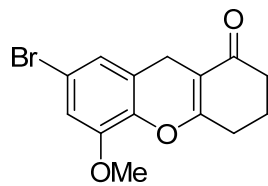


Red solid; Mp. 131.2-131.9 °C; ¹H NMR (400 MHz, CDCl₃, TMS)

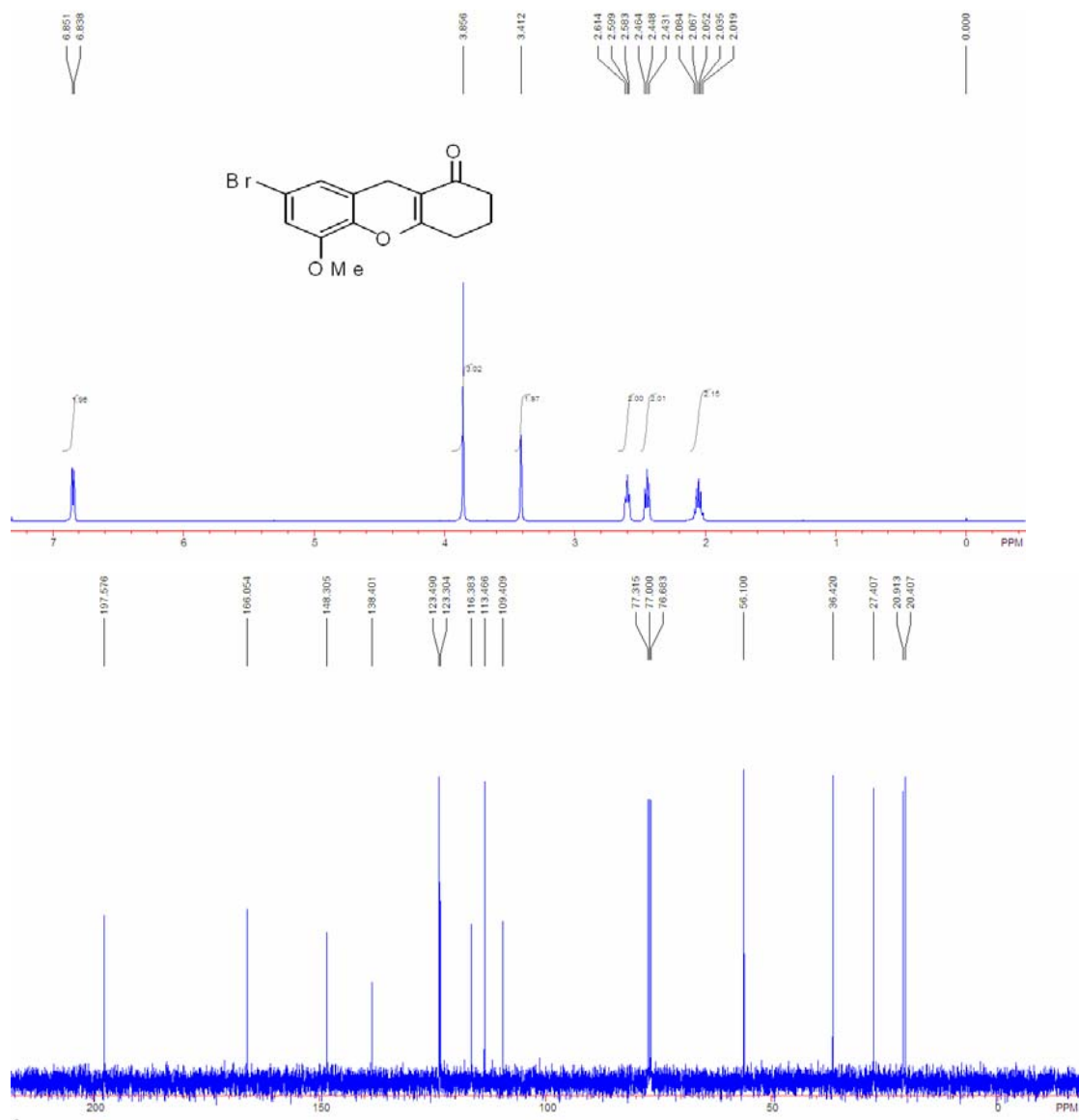
δ 2.03-2.08 (m, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 5.6 Hz, 2H), 3.49 (s, 2H), 3.69 (s, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.04 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.12-7.16 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 20.5, 21.0, 27.6, 36.5, 109.9, 116.3, 120.7, 124.5, 127.4, 129.5, 149.7, 166.7, 198.0; MS (ESI) *m/z* (%): 201.1 (M + H, 21); HRMS (Micromass LCT) Calcd. for C₁₃H₁₃O₂: 201.0916; Found: 201.0917.



7-Bromo-5-methoxy-2,3,4,9-tetrahydro-1H-xanthen-1-one **3dk**.



Red solid; Mp. 187.0-188.0 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.02-2.08 (m, 2H), 2.45 (t, *J* = 5.6 Hz, 2H), 2.60 (t, *J* = 5.6 Hz, 2H), 3.41 (s, 2H), 3.86 (s, 3H), 6.84 (s, 1H), 6.85 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 20.4, 20.9, 27.4, 36.4, 56.1, 109.4, 113.5, 116.4, 123.3, 123.5, 138.4, 148.3, 166.1, 197.6; MS (ESI) *m/z* (%): 309.0 (M + H, 71); HRMS (Micromass LCT) Calcd. for C₁₄H₁₄BrO₃: 309.0126; Found: 309.0130.



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