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Supporting Information

A Facile Way to Synthesize 2H-Chromenes: Reconsideration of the Reaction Mechanism between Salicylic Aldehyde and Ethyl 2-Methylbuta-2,3-dienoate Catalyzed by DBU

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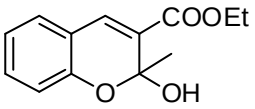
Contents

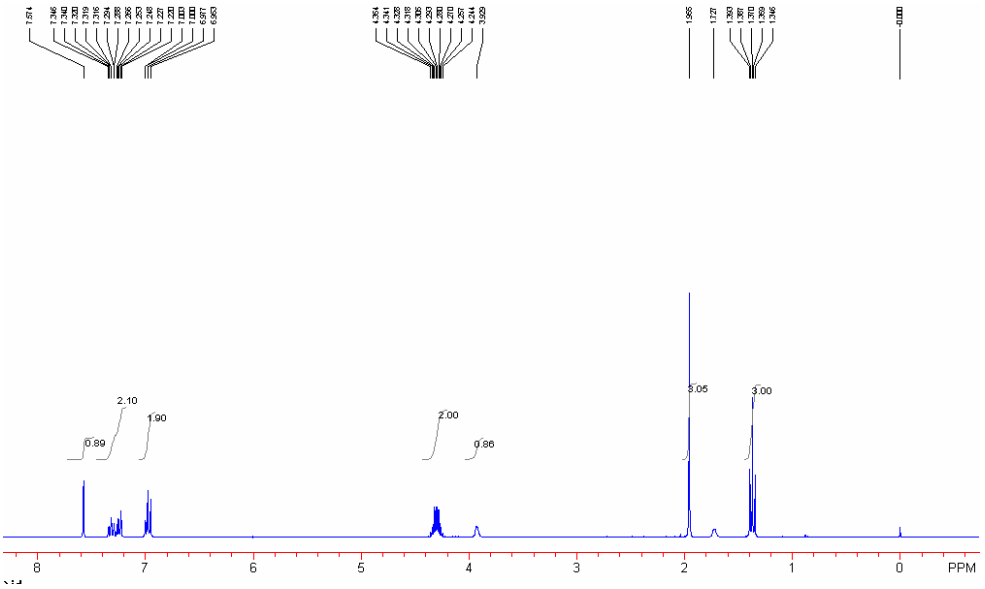
General Remarks. MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at medium pressure.

Reactions of salicylic aldehydes with ethyl buta-2,3-dienoate catalyzed by K_2CO_3. Typical reaction procedure of salicylaldehyde with ethyl buta-2,3-dienoate in the presence of K_2CO_3 in DMSO at room temperature.

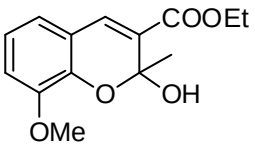
To a Schlenk tube with DMSO (1.0 mL) was added salicylaldehyde **1a** (61 mg, 0.5 mmol), ethyl buta-2,3-dienoate **2a** (84 mg, 0.75 mmol) and K_2CO_3 (7.0 mg, 0.05 mmol). The solution was stirred for 4 h at room temperature (25 ^{o}C). The reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (3 x 15 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give the corresponding product **3a** (eluent: EtOAc/petroleum ether = 1/4, 74 mg, yield 64%) as a yellow solid.



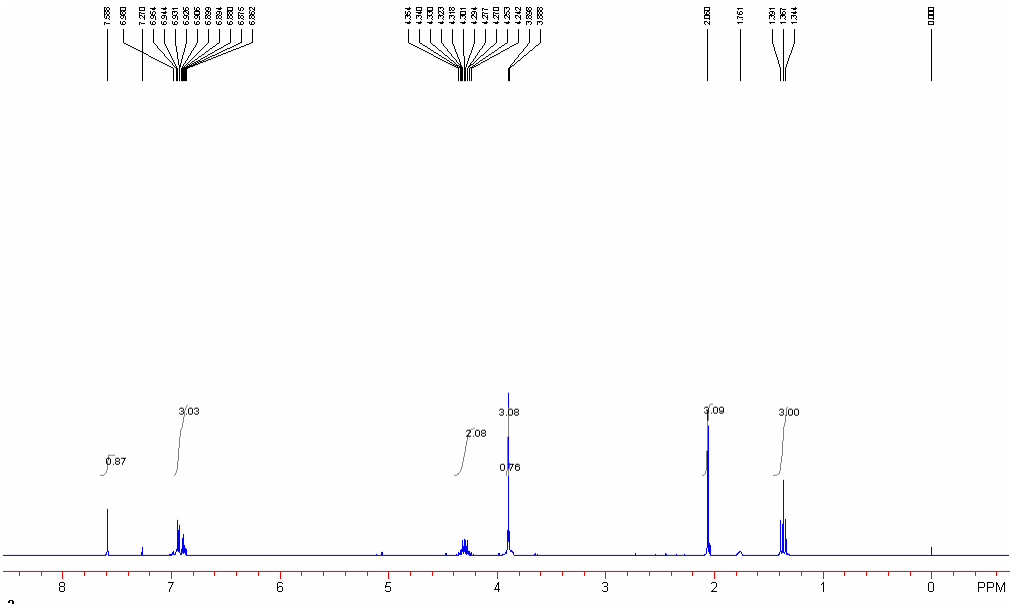
3a



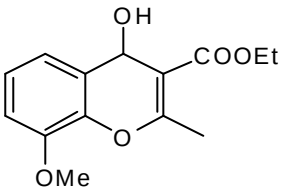
Ethyl 2-hydroxy-2-methyl-2H-chromene-3-carboxylate 3a: a pale yellow solid; mp. 88-90 ^{o}C; IR (CH_2Cl_2): ν bar = 3429, 2984, 2939, 1712, 1629, 1486, 1458, 1214 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.1 Hz, CH_3), 1.96 (3H, s, CH_3), 3.93 (1H, s, OH), 4.24-4.35 (2H, m, CH_2), 6.95-7.00 (2H, m, ArH), 7.22-7.35 (2H, m, ArH), 7.57 (1H, s, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.6, 61.0, 97.7, 116.6, 118.7, 121.5, 125.5, 128.6, 132.2, 134.2, 152.5, 165.1; MS (EI) *m/z* 216 (49) [M^+-18], 187 (32) [M^+-47], 173 (54) [M^+-61], 144 (100) [M^+-90], 115 (73) [M^+-119], 89 (40) [M^+-145], 63 (29) [M^+-171], 43 (40) [M^+-191]; HRMS Calcd. for $C_{13}H_{14}O_4$ (-H_2O) requires 216.0786, Found: 216.0796.



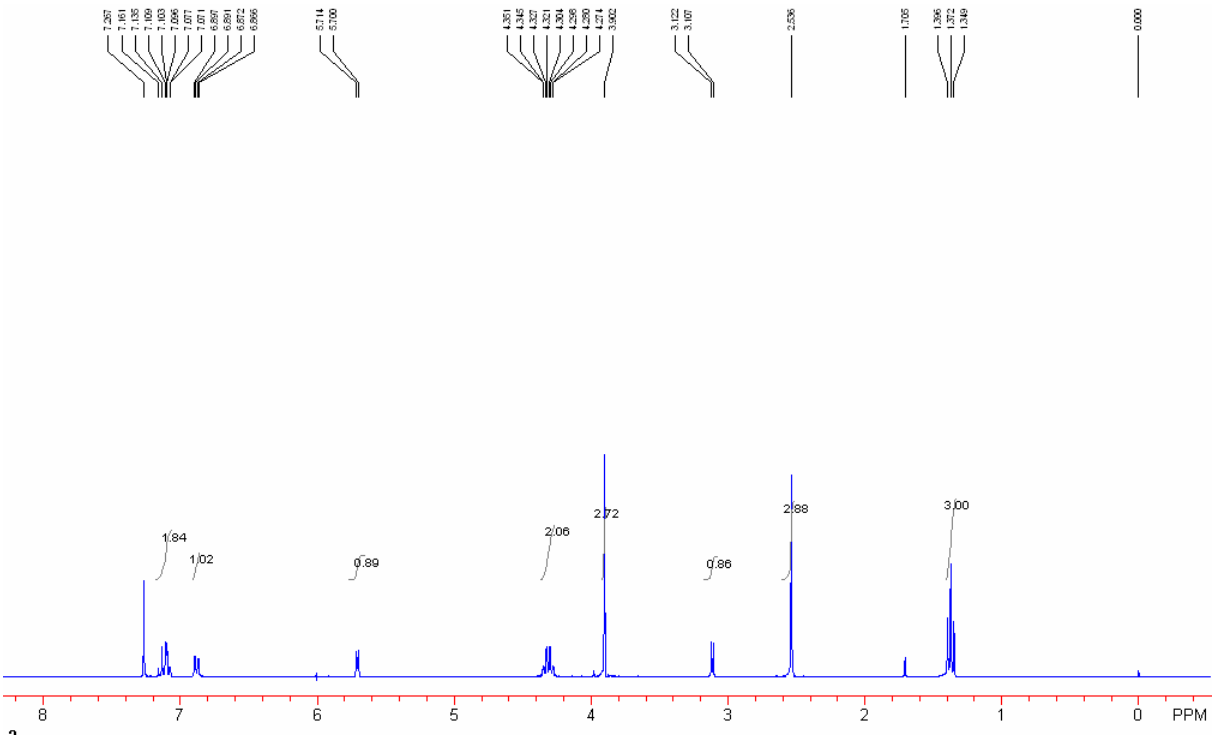
3b



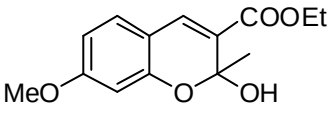
Ethyl 2-hydroxy-8-methoxy-2-methyl-2H-chromene-3-carboxylate 3b: a colorless solid; mp. 110-112 ^{o}C; IR (CH_2Cl_2): ν bar = 3465, 3000, 2937, 2896, 1708, 1478, 1112 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.1 Hz, CH_3), 2.06 (3H, s, CH_3), 3.89 (1H, s, OH), 3.90 (3H, s, CH_3), 4.24-4.35 (2H, m, CH_2), 6.86-6.99 (3H, m, ArH), 7.59 (1H, s, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.2, 27.6, 56.1, 61.0, 97.9, 114.4, 119.5, 120.6, 121.4, 125.8, 134.4, 141.8, 148.0, 165.0; MS (EI) *m/z* 246 (65) [M^{+}-18], 218 (63) [M^{+}-46], 217 (52) [M^{+}-47], 203 (90) [M^{+}-61], 175 (33) [M^{+}-89], 174 (100) [M^{+}-90], 102 (33) [M^{+}-162], 43 (73) [M^{+}-221]; Found: C, 63.52; H, 6.17%. $C_{14}H_{16}O_5$ requires C, 63.63; H, 6.10%.



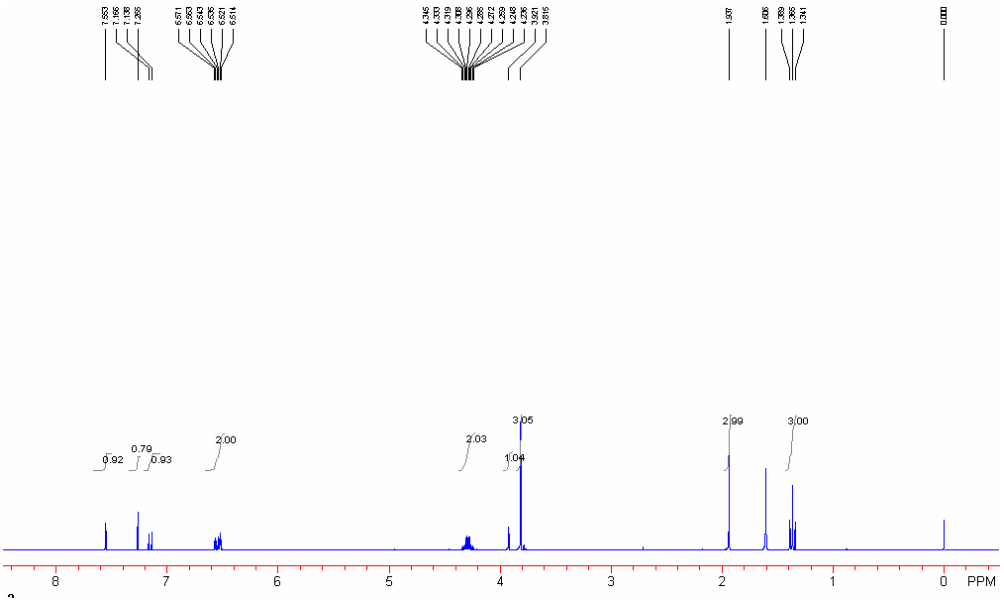
4b



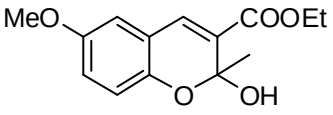
Ethyl 4-hydroxy-8-methoxy-2-methyl-4H-chromene-3-carboxylate 4b: a pale yellow oil; IR (CH_2Cl_2): ν bar = 3467, 2982, 2932, 2840, 1712, 1481, 1265, 1212 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.1 Hz, CH_3), 2.54 (3H, s, CH_3), 3.11 (1H, d, *J* = 4.4 Hz, OH), 3.90 (3H, s, CH_3), 4.31 (2H, qd, *J* = 7.2 Hz, *J* = 1.8 Hz, CH_2), 5.71 (1H, d, *J* = 4.4 Hz, CH), 7.38 (1H, dd, *J* = 7.5 Hz, *J* = 1.8 Hz, ArH), 7.07-7.16 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.3, 19.8, 56.1, 60.7, 61.2, 77.0, 105.6, 111.1, 121.0, 122.4, 124.5, 127.3, 161.8, 167.7; MS (EI) *m/z* 264 (4) [M^+], 218 (39) [M^+-46], 203 (100) [M^+-61], 175 (15) [M^+-89], 148 (5) [M^+-118], 89 (5) [M^+-175], 77 (5) [M^+-187], 43 (16) [M^+-221]; HRMS Calcd. for $C_{14}H_{16}O_5$ requires 264.0998, Found: 264.1014.



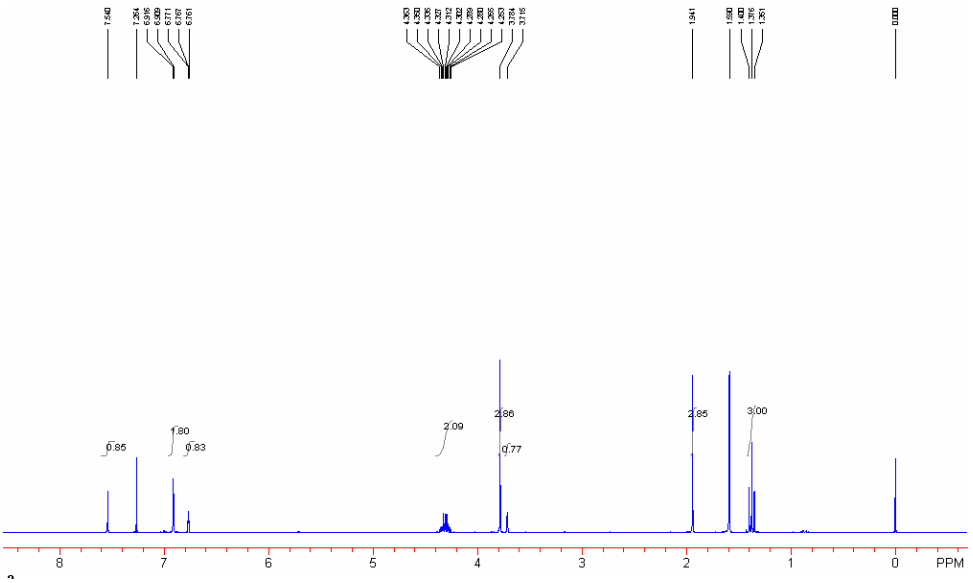
3c



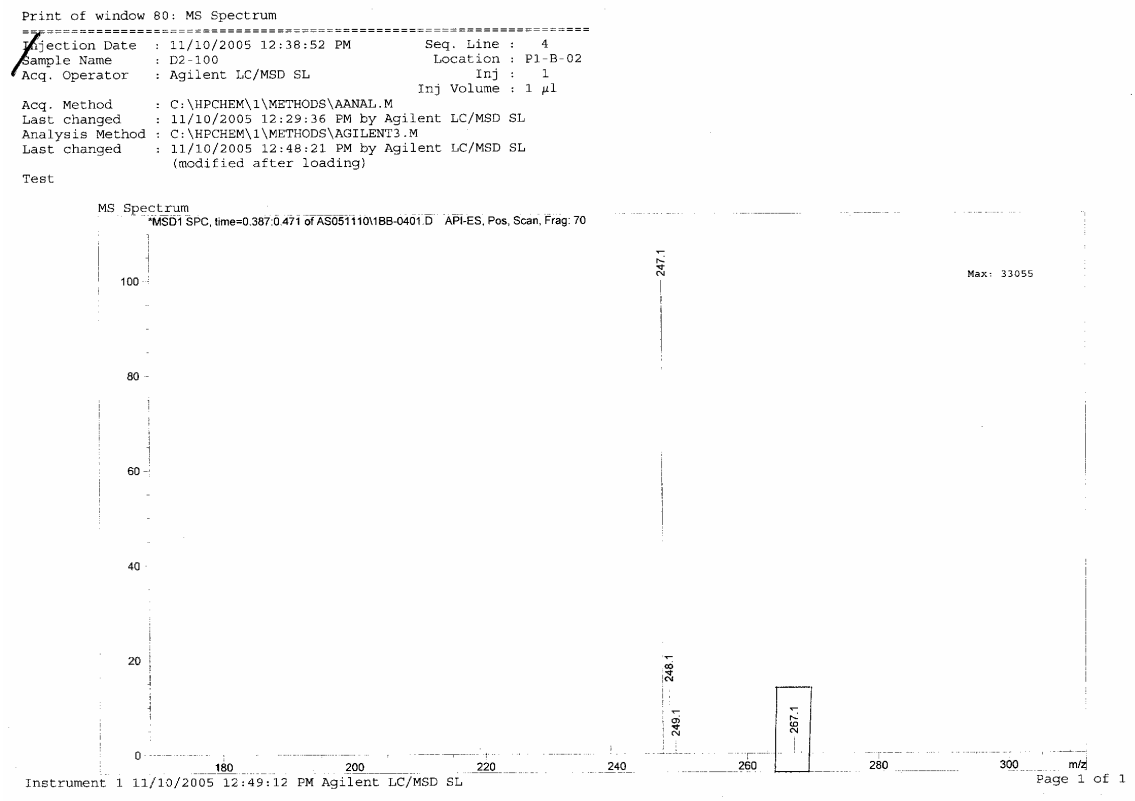
Ethyl 2-hydroxy-7-methoxy-2-methyl-2H-chromene-3-carboxylate 3c: a yellow oil; IR (CH_2Cl_2) ν bar = 3047, 3059, 3004, 1714, 1423, 1363, 1222 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.2 Hz, CH_3), 1.94 (3H, s, CH_3), 3.82 (3H, s, CH_3), 3.92 (1H, s, OH), 4.24-4.35 (2H, m, CH_2), 6.51-6.57 (2H, m, ArH), 7.15 (1H, d, *J* = 8.4 Hz, ArH), 7.55 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.5, 55.4, 60.7, 98.2, 101.3, 108.8, 112.1, 122.3, 129.6, 134.3, 154.2, 163.2, 165.4; MS (EI) *m/z* 246 (24) [M^+-18], 218 (27) [M^+-46], 203 (100) [M^+-61], 174 (53) [M^+-90], 159 (50) [M^+-105], 119 (27) [M^+-145], 84 (43) [M^+-180], 43 (78) [M^+-221]; HRMS Calcd. for $C_{14}H_{16}O_5$ (-H_2O) requires 246.0892, Found: 246.0902.



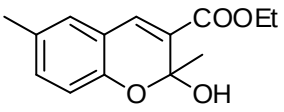
3d



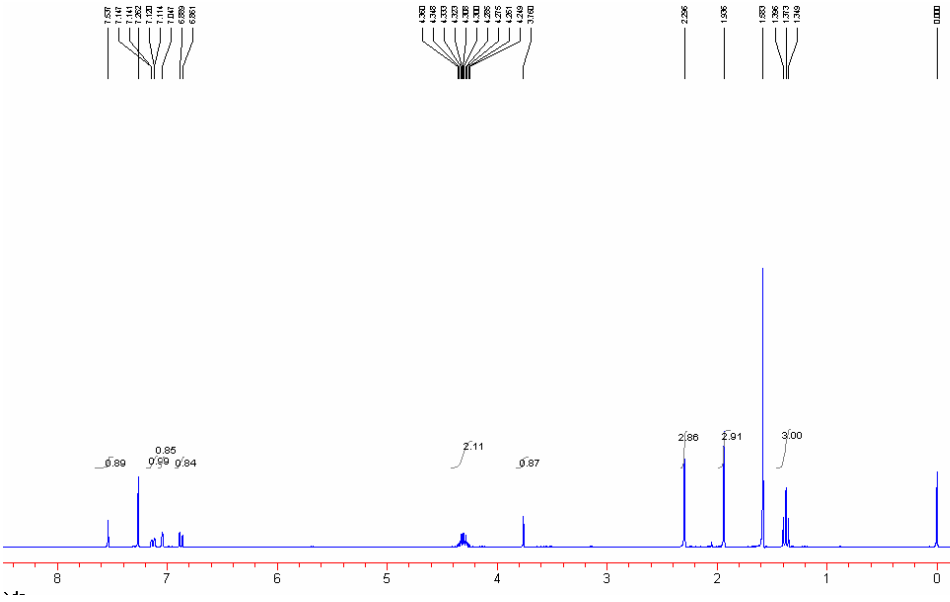
Ethyl 2-hydroxy-6-methoxy-2-methyl-2H-chromene-3-carboxylate 3d: a yellow oil; IR (CH_2Cl_2) ν bar = 3417, 3059, 2982, 2926, 1712, 1494, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.38 (3H, t, *J* = 7.4 Hz, CH_3), 1.94 (3H, s, CH_3), 3.72 (1H, s, OH), 3.78 (3H, s, CH_3), 4.25-4.35 (2H, m, CH_2), 6.76-6.77 (1H, m, ArH), 6.91-6.92 (2H, m, ArH), 7.54 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.3, 55.6, 61.0, 97.5, 112.0, 117.5, 118.7, 119.0, 126.2, 134.1, 146.6, 154.0, 165.1; MS (EI) *m/z* 264 (13) [M^+], 246 (34) [M^+-18], 218 (52) [M^+-46], 203 (100) [M^+-61], 174 (52) [M^+-90], 84 (33) [M^+-180], 49 (59) [M^+-115], 43 (82) [M^+-221]; HRMS Calcd. for $C_{14}H_{16}O_5$ requires 264.0998, Found: 264.0996.



ESI-MS of **3d**-^{18}O from which a Mass peak at 267 can be realized.

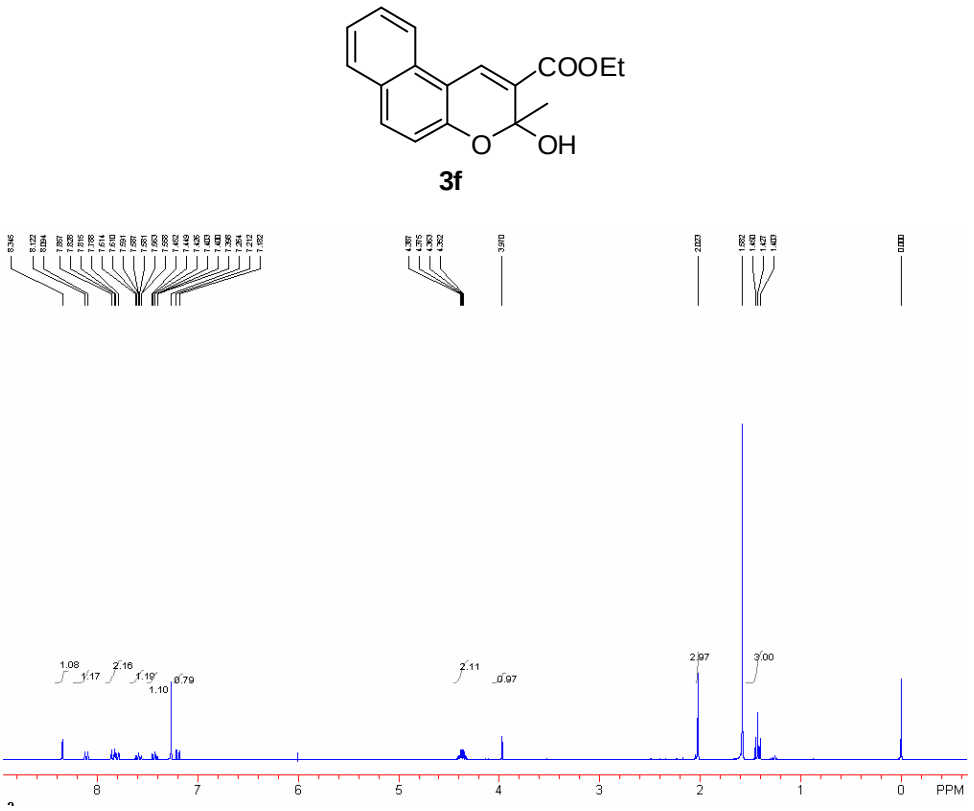


3e



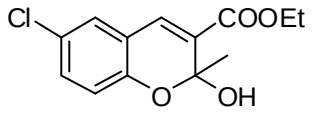
Ethyl 2-hydroxy-2,6-dimethyl-2H-chromene-3-carboxylate 3e: a yellow oil; IR (CH_2Cl_2) ν

bar = 3430, 2982, 2928, 1711, 1630, 1370, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.1 Hz, CH_3), 1.94 (3H, s, CH_3), 2.30 (3H, s, CH_3), 3.76 (1H, s, OH), 4.25-4.35 (2H, m, CH_2), 6.87 (1H, d, *J* = 8.4 Hz, ArH), 7.05 (1H, s, ArH), 7.13 (1H, dd, *J* = 8.4 Hz, *J* = 1.5 Hz, ArH), 7.54 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 20.4, 27.5, 61.0, 97.7, 116.5, 118.5, 125.5, 128.7, 130.9, 133.0, 134.4, 150.4, 165.3; MS (EI) *m/z* 248 (2) [M^+], 233 (33) [M^+-15], 230 (13) [M^+-18], 187 (100) [M^+-61], 159 (16) [M^+-89], 158 (21) [M^+-90], 77 (18) [M^+-171], 43 (49) [M^+-105]; HRMS Calcd. for $C_{14}H_{16}O_4$(-CH_3) requires 233.0814, Found: 233.0819.

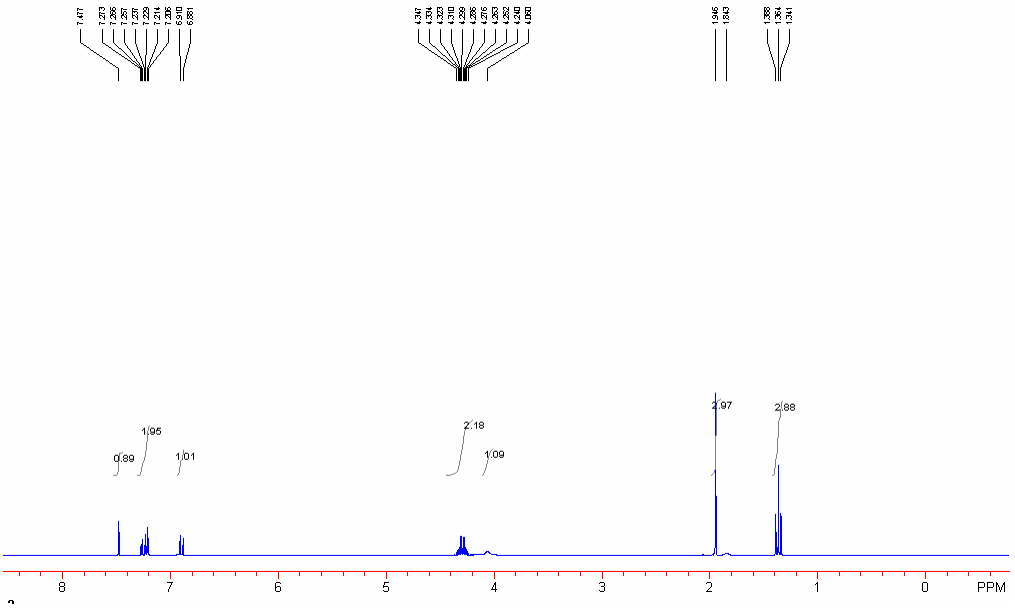


Ethyl 3-hydroxy-3-methyl-3H-benzo[f]chromene-2-carboxylate 3f: a yellow solid; mp. 107-109 °C; IR (CH_2Cl_2) ν bar = 3429, 2985, 2941, 1710, 1567, 1261 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.43 (3H, t, *J* = 7.1 Hz, CH_3), 2.02 (3H, s, CH_3), 3.97 (1H, s, OH), 4.32-4.42 (2H, m, CH_2), 7.20 (1H, d, *J* = 8.7 Hz, ArH), 7.40-7.45 (1H, m, ArH), 7.56-7.61 (1H, m, ArH), 7.80 (1H, d, *J* = 7.8 Hz, ArH), 7.84 (1H, d, *J* = 9.3 Hz, ArH), 8.11 (1H, d, *J* = 8.1 Hz, ArH), 8.35 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.3, 27.4, 61.1,

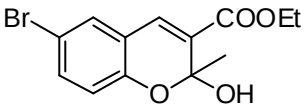
98.1, 111.5, 118.0, 121.0, 123.3, 124.3, 127.6, 128.7, 129.2, 130.0, 130.2, 133.1, 151.8, 165.4; MS (EI) *m/z* 284 (1) [M^+], 266 (49) [M^+-18], 238 (35) [M^+-46], 223 (61) [M^+-61], 194 (100) [M^+-90], 165 (39) [M^+-119], 139 (58) [M^+-145], 43 (42) [M^+-241]; Found: C, 71.98; H, 5.59%. $C_{17}H_{16}O_4$ requires C, 71.82; H, 5.67%.



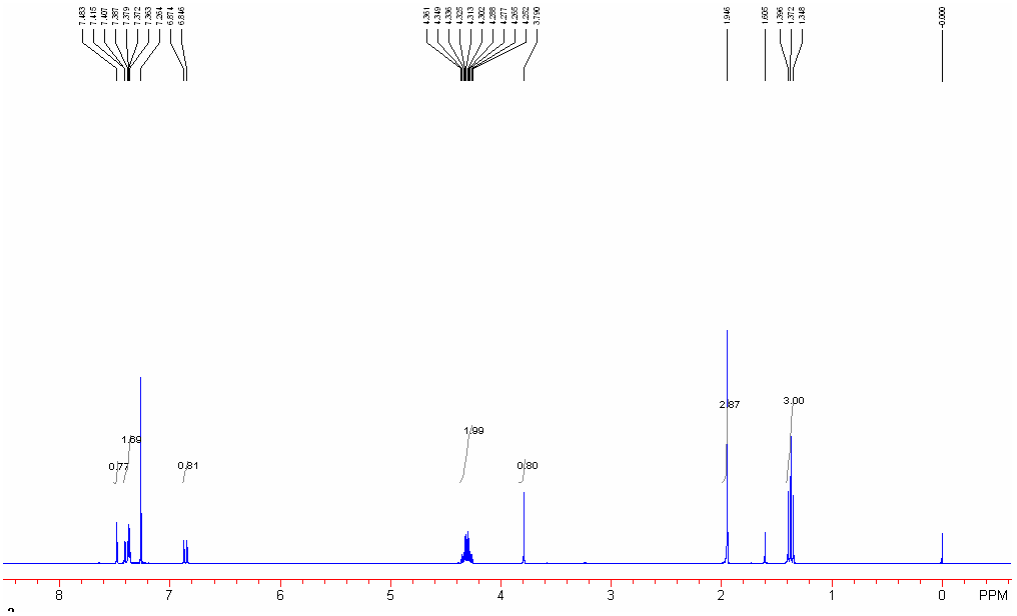
3g



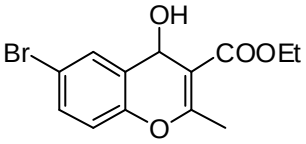
Ethyl 6-chloro-2-hydroxy-2-methyl-2H-chromene-3-carboxylate 3g: a pale yellow solid; mp. 89-91 ^oC; IR (CH_2Cl_2) ν bar = 3430, 2985, 2926, 2896, 1713, 1479, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.36 (3H, t, *J* = 7.1 Hz, CH_3), 1.95 (3H, s, CH_3), 4.06 (1H, s, OH), 4.24-4.35 (2H, m, CH_2), 6.90 (1H, d, *J* = 8.7 Hz, ArH), 7.21-7.27 (2H, m, ArH), 7.48 (1H, s, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.6, 61.3, 98.0, 118.1, 119.9, 126.4, 126.7, 127.8, 131.8, 132.9, 151.0, 164.8; MS (EI) *m/z* 250 (55) [M^+-18], 221 (46) [M^+-47], 207 (83) [M^+-61], 180 (44) [M^+-88], 178 (97) [M^+-90], 149 (36) [M^+-119], 115 (45) [M^+-153], 43 (100) [M^+-223]; HRMS Calcd. for $C_{13}H_{13}O_4Cl$ (-H_2O) requires 250.0397, Found: 250.0406.



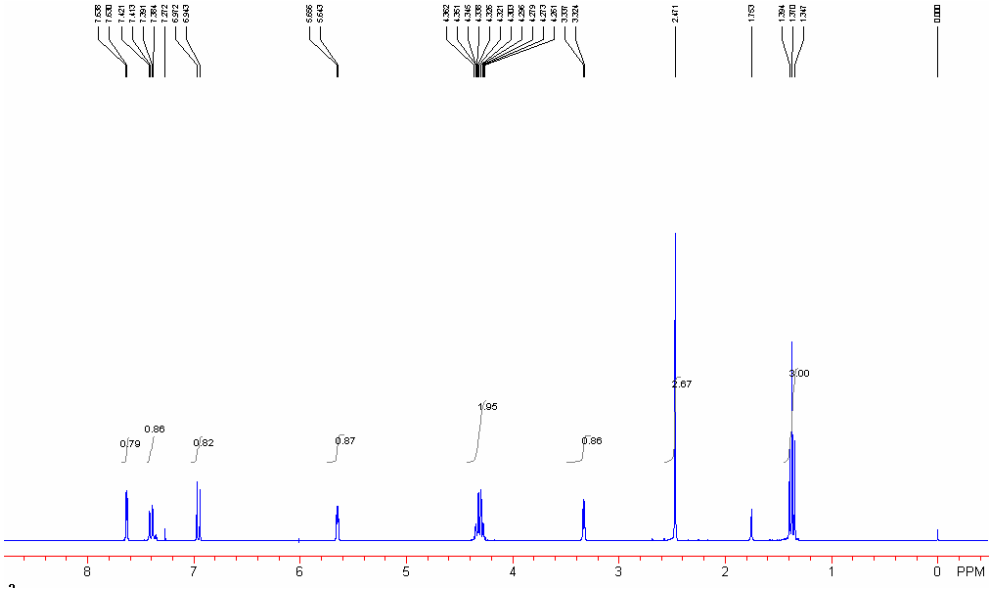
3h



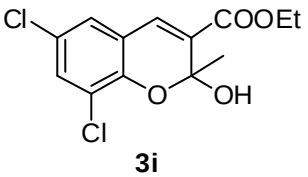
Ethyl 6-bromo-2-hydroxy-2-methyl-2H-chromene-3-carboxylate 3h: a pale yellow solid; mp. 117-119 ^{o}C; IR (CH_2Cl_2) ν bar = 3420, 2978, 2919, 2296, 1714, 1208 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.4 Hz, CH_3), 1.95 (3H, s, CH_3), 3.79 (1H, s, OH), 4.25-4.36 (2H, m, CH_2), 6.86 (1H, d, *J* = 8.4 Hz, ArH), 7.36-7.42 (2H, m, ArH), 7.48 (1H, s, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.6, 61.2, 98.0, 113.5, 118.5, 120.5, 126.7, 130.7, 132.7, 134.6, 151.5, 164.8; MS (EI) *m/z* 314 (4) [M^++2], 312 (4) [M^+], 298 (26) [M^+-14], 296 (30) [M^+-16], 252 (91) [M^+-60], 250 (100) [M^+-62], 89 (8) [M^+-223], 43 (30) [M^+-269]; HRMS Calcd. for $C_{13}H_{13}O_4Br$ requires 311.9997, Found: 312.0005.



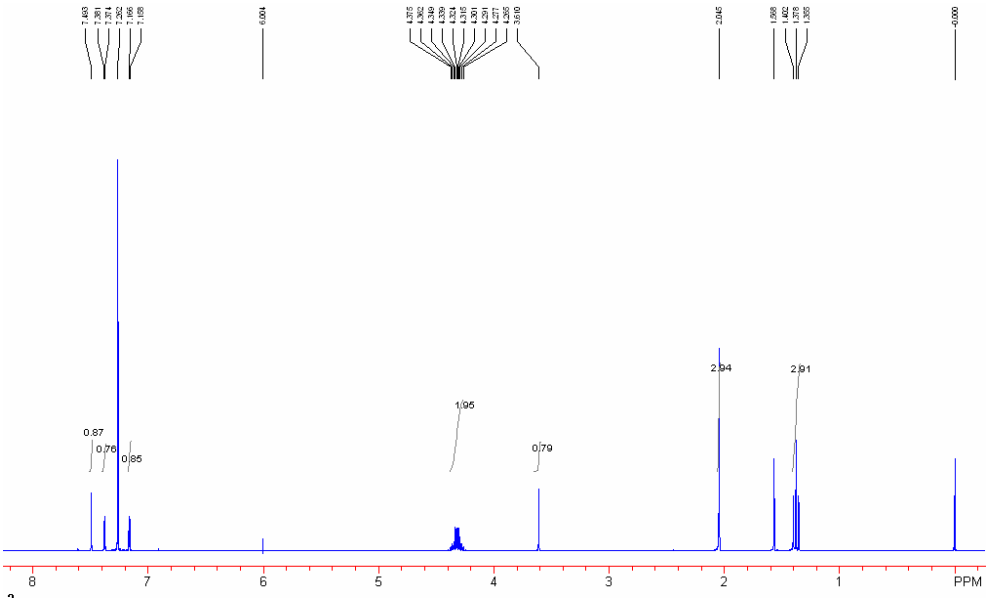
4h



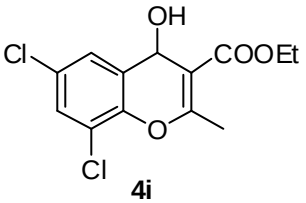
Ethyl 6-bromo-4-hydroxy-2-methyl-4H-chromene-3-carboxylate 4h: a pale yellow solid; mp. 115-117 ^{o}C; IR (CH_2Cl_2) ν bar = 3437, 2984, 2940, 2904, 1712, 1477, 1209 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.37 (3H, t, *J* = 7.1 Hz, CH_3), 2.47 (3H, s, CH_3), 3.33 (1H, d, *J* = 4.1 Hz, OH), 4.26-4.35 (2H, m, CH_2), 5.65 (1H, d, *J* = 4.1 Hz, CH), 6.96 (1H, d, *J* = 8.9 Hz, ArH), 7.40 (1H, dd, *J* = 8.9 Hz, *J* = 2.4 Hz, ArH), 7.63 (1H, d, *J* = 2.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.5, 61.2, 97.9, 113.4, 118.5, 120.5, 126.6, 130.6, 132.7, 134.6, 151.5, 164.7; MS (EI) *m/z* 312 (1) [M^+], 266 (14) [M^+-46], 253 (48) [M^+-59], 251 (63) [M^+-61], 89 (19) [M^+-223], 88 (15) [M^+-224], 43 (100) [M^+-269]; Found: C, 50.10; H, 4.18%. $C_{13}H_{13}BrO_4$ requires C, 49.86; H, 4.18%.



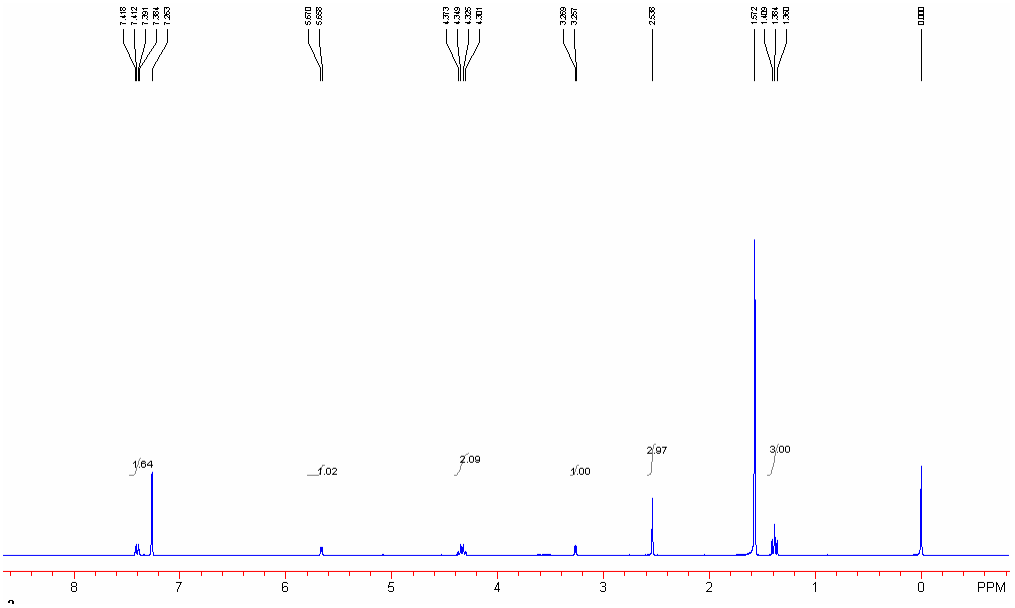
3i



Ethyl 6,8-dichloro-2-hydroxy-2-methyl-2H-chromene-3-carboxylate 3i: a pale yellow solid; mp. 90-92 ^{o}C; IR (CH_2Cl_2) ν bar = 3421, 2984 2941, 1716, 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.38 (3H, t, *J* = 7.1 Hz, CH_3), 2.05 (3H, s, CH_3), 3.61 (1H, s, OH), 4.27-4.38 (2H, m, CH_2), 7.16 (1H, d, *J* = 2.3 Hz, ArH), 7.38 (1H, d, *J* = 2.3 Hz, ArH), 7.49 (1H, s, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 27.6, 61.4, 98.8, 121.0, 122.5, 126.2, 126.3, 127.5, 131.6, 132.4, 147.1, 164.4; MS (EI) *m/z* 306 (1) [M^++4], 304 (3) [M^++2], 302 (4) [M^+], 255 (32) [M^+-47], 244 (6) [M^+-58], 242 (60) [M^+-60], 240 (100) [M^+-62], 43 (55.10) [M^+-259]; HRMS Calcd. for $C_{13}H_{12}O_4Cl_2$ requires 302.0113, Found: 302.0113.



4i

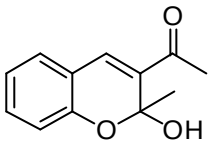


Ethyl 6,8-dichloro-4-hydroxy-2-methyl-4H-chromene-3-carboxylate 4i: a pale yellow solid; mp. 88-90 ^{o}C; IR (CH_2Cl_2) ν bar = 3429, 2982, 2933, 2896, 1714, 1454, 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.38 (3H, t, *J* = 7.4 Hz, CH_3), 2.54 (3H, s, CH_3), 3.26 (1H, d, *J* = 3.6 Hz, OH), 4.34 (2H, q, *J* = 14.4 Hz, *J* = 7.2 Hz, CH_2), 5.66 (1H, d, *J* = 3.6 Hz, CH), 7.38 (1H, d, *J* = 2.1 Hz, ArH), 7.42 (1H, d, *J* = 2.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.3, 19.5, 60.9, 61.0, 105.8, 122.2. 124.0, 127.9, 129.1, 129.6, 144.4, 161.3, 167.1; MS (EI) *m/z* 302 (3) [M^+], 287 (30) [M^+-15], 285 (21) [M^+-17], 257 (12) [M^+-45], 256 (15) [M^+-46], 241 (43) [M^+-61], 123 (15.86) [M^+-179], 43 (100) [M^+-259]; Found: C, 51.49; H, 3.96%. $C_{13}H_{12}Cl_2O_4$ requires C, 51.51; H, 3.99%.

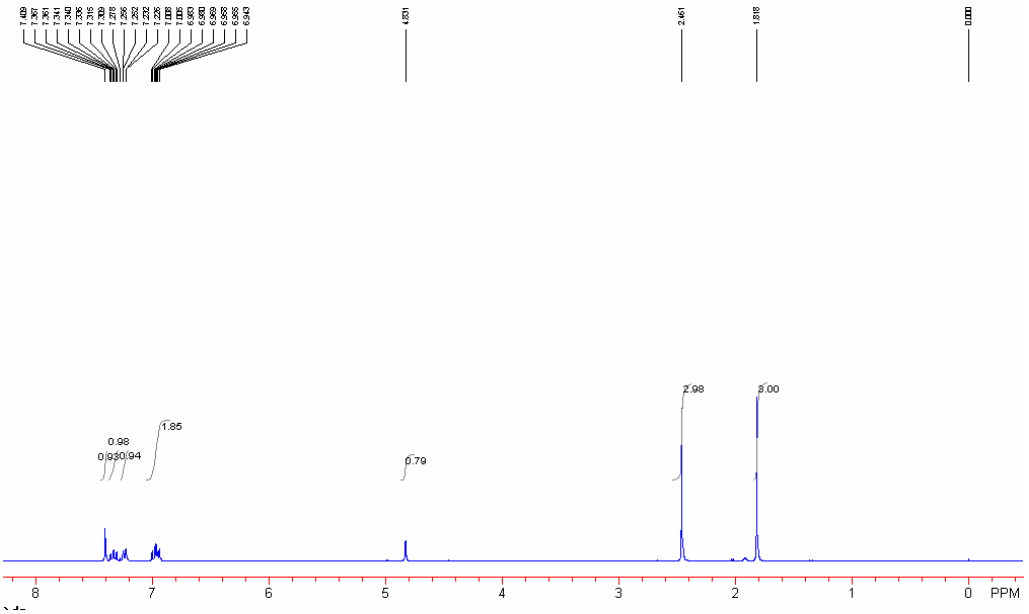
Reactions of salicylic aldehydes with penta-3,4-dien-2-one catalyzed by K_2CO_3. Typical reaction procedure of salicylaldehyde with penta-3,4-dien-2-one in the presence of K_2CO_3 in ethanol at room temperature.

To a Schlenk tube with ethanol (1.0 mL) was added salicylaldehyde **1a** (61 mg, 0.5 mmol), penta-3,4-dien-2-one **2b** (62 mg, 0.75 mmol) and K_2CO_3 (7 mg, 0.05 mmol). The solution was stirred for 3 h at room temperature (25 ^{o}C). The reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (3 x 15 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was

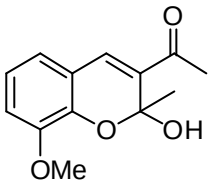
purified by a silica gel column chromatography to give the corresponding product **5a** (eluent: EtOAc/petroleum ether = 1/4, 68 mg, yield 64%) as a yellow liquid.



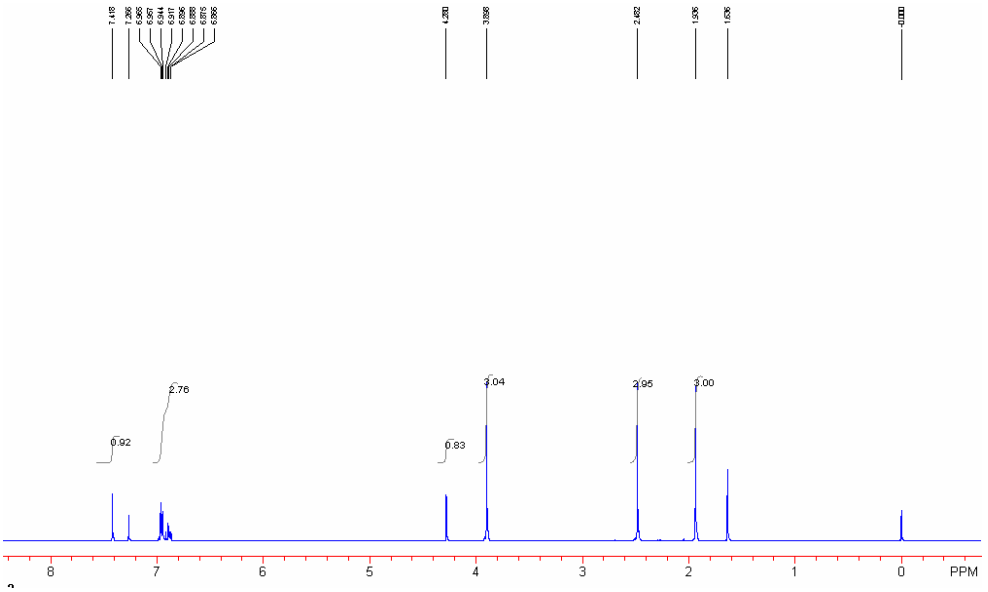
5a



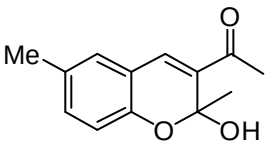
1-(2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone 5a: a pale yellow oil; IR (CH_2Cl_2) ν bar = 3384, 3059, 2993, 2924, 1667, 1486, 1214, 937, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.82 (3H, s CH_3), 2.46 (3H, s, CH_3), 4.83 (1H, s OH), 6.94-7.00 (2H, m, ArH), 7.23-7.26 (1H, m, ArH), 7.31-7.37 (1H, m, ArH), 7.41 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 26.4, 27.6, 98.7, 116.8, 118.7, 121.6, 128.9, 132.86, 132.95, 135.1, 152.9, 198.3; MS (EI) *m/z* 186 (88) [M^+-18], 185 (30) [M^+-19], 171 (23) [M^+-33], 158 (19) [M^+-46], 144 (66) [M^+-58], 115 (100) [M^+-87], 63 (27) [M^+-141], 43 (55) [M^+-161]; HRMS Calcd. for $C_{12}H_{12}O_3$ requires 204.0786, Found: 204.0792.



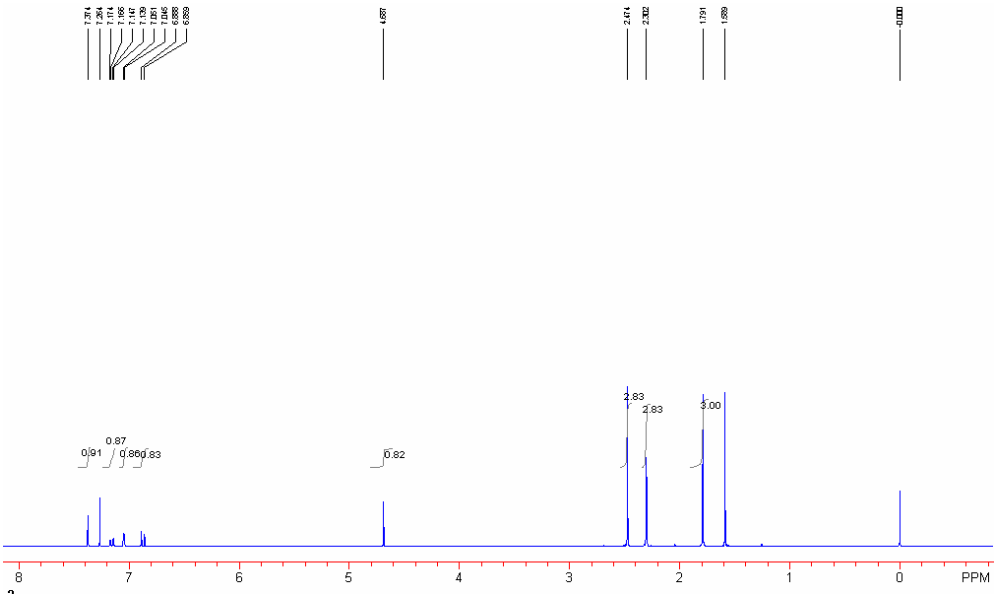
5b



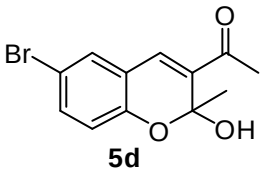
1-(2-hydroxy-8-methoxy-2-methyl-2H-chromen-3-yl)ethanone 5b: a pale yellow solid; mp. 155-157 ^{o}C; IR (CH_2Cl_2) ν bar = 3463, 3007, 3000, 2941, 1664, 1482, 1275, 1257, 926, 777 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.94 (3H, s CH_3), 2.48 (3H, s, CH_3), 3.90 (3H, s, CH_3); 4.28 (1H, s OH), 6.87-6.97 (3H, m, ArH), 7.42 (1H, s, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 26.6, 27.6, 56.1, 98.8, 115.0, 119.4, 120.7, 121.4, 133.2, 135.0, 142.2, 148.1, 197.7; MS (EI) *m/z* 234 (7) [M^+], 219 (28) [M^+-15], 216 (37) [M^+-18], 215 (15) [M^+-19], 201(19) [M^+-33], 115 (15) [M^+-119], 44 (29) [M^+-190], 43 (100) [M^+-191]; Found: C, 66.73; H, 6.32%. $C_{13}H_{14}O_4$ requires C, 66.66; H, 6.02%.



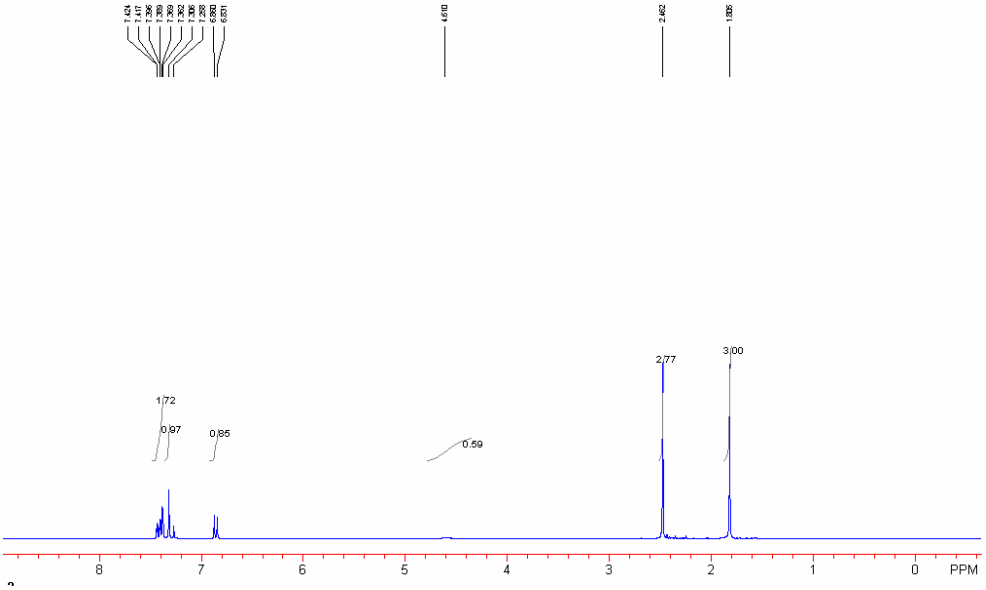
5c



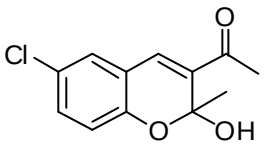
1-(2-hydroxy-2,6-dimethyl-2H-chromen-3-yl)ethanone 5c: a pale yellow oil; IR CH_2Cl_2) ν bar = 3385, 2984, 2925, 2865, 1708, 1666, 1627, 1574, 1375, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.79 (3H, s CH_3), 2.30 (3H, s, CH_3), 2.47 (3H, s, CH_3), 4.69 (1H, s OH), 6.87 (2H, d, *J* = 8.4 Hz, ArH), 7.05 (1H, d, *J* = 1.5 Hz, ArH), 7.16 (1H, dd, *J* = 8.4 Hz, *J* = 2.3 Hz, ArH), 7.37 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 20.4, 26.4, 27.6, 98.8, 116.6, 118.5, 129.0, 131.0, 132.9, 133.8, 135.3, 150.9, 198.4; MS (EI) *m/z* 200 (75) [M^+-18], 199 (24) [M^+-19], 158 (30) [M^+-60], 157 (40) [M^+-61], 128 (33) [M^+-90], 129 (32) [M^+-89], 115 (23) [M^+-103], 43 (100) [M^+-175]; HRMS Calcd. for $C_{13}H_{14}O_3$(-H_2O) requires 200.0837, Found: 200.0841.



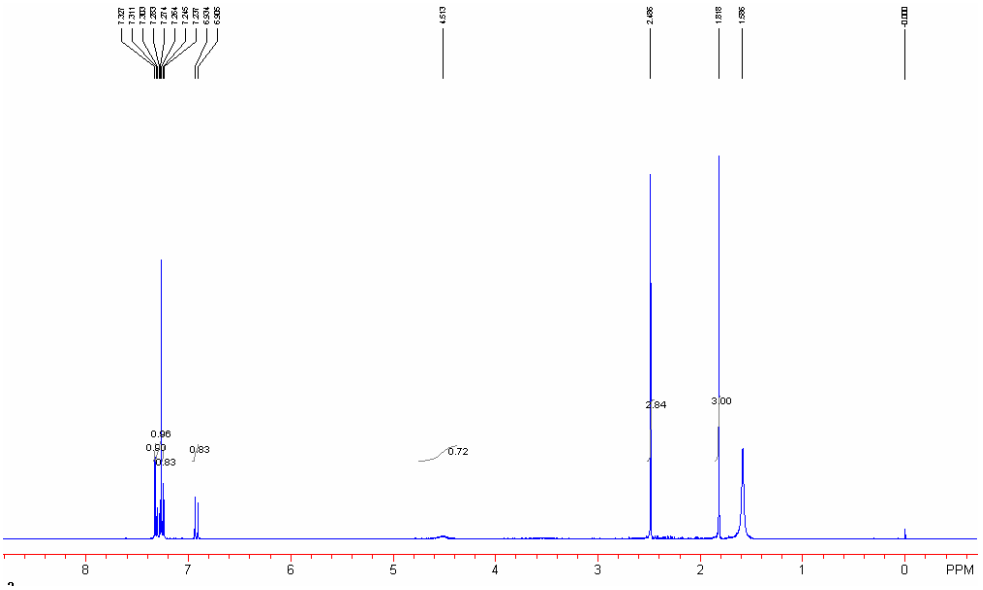
5d



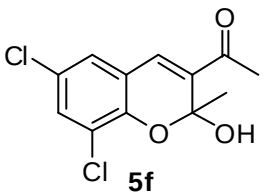
1-(6-bromo-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone 5d: a pale yellow solid; mp. 106-108 ^{o}C; IR (CH_2Cl_2) ν bar = 3400, 2911, 2844, 1668, 1476, 1210 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.81 (3H, s CH_3), 2.46 (3H, s, CH_3), 4.61 (1H, s OH), 6.85 (1H, d, *J* = 8.7 Hz, ArH), 7.31 (1H, s, =CH_2), 7.36-7.42 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 26.5, 27.8, 99.0, 113.6, 118.7, 120.5, 131.0, 133.4, 133.8, 135.4, 151.9, 198.1; MS (EI) *m/z* 266 (48) [M^+-16], 265 (27) [M^+-17], 264 (55) [M^+-18], 224 (26) [M^+-58], 142 (33) [M^+-140], 115 (53) [M^+-167], 44 (42) [M^+-238], 43 (100) [M^+-239]; HRMS Calcd. for $C_{12}H_{12}O_3Br(-H_2O)$ requires 264.9864, Found: 264.9858.



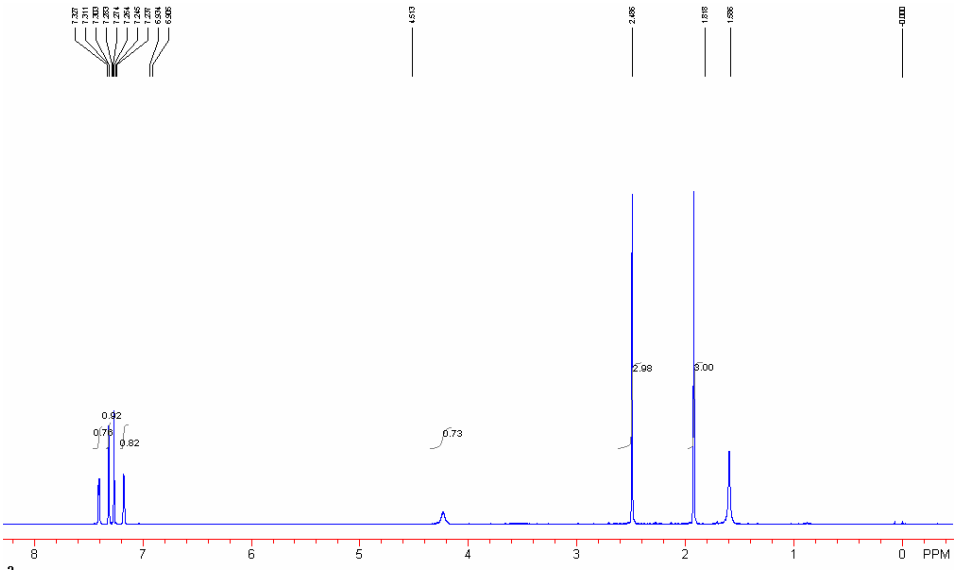
5e



1-(6-chloro-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone 5e: a pale yellow oil; IR (CH_2Cl_2) ν bar = 3377, 3062, 2990, 2942, 1666, 1479, 1211 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.82 (3H, s CH_3), 2.49 (3H, s, CH_3), 4.52 (1H, s OH), 6.92 (1H, d, *J* = 8.4 Hz, ArH), 7.24 (1H, d, *J* = 2.1 Hz, ArH), 7.29 (1H, dd, *J* = 8.4 Hz, *J* = 2.1 Hz, ArH), 7.33 (1H, s, $=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 26.5, 27.6, 98.9, 118.2, 119.9, 126.4, 127.9, 132.4, 133.4, 133.8, 151.3, 198.0; MS (EI) *m/z* 223 (12) [M^+-15], 220 (37) [M^+-18], 178 (18) [M^+-60], 149 (14) [M^+-89], 115 (28) [M^+-123], 63 (15) [M^+-175], 43 (100) [M^+-195], 42 (27) [M^+-196]; HRMS Calcd. for $C_{12}H_{11}Cl_2O_3$ requires 238.0397, Found: 238.0407.



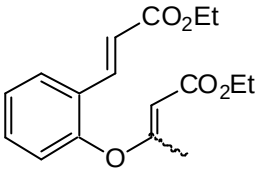
5f



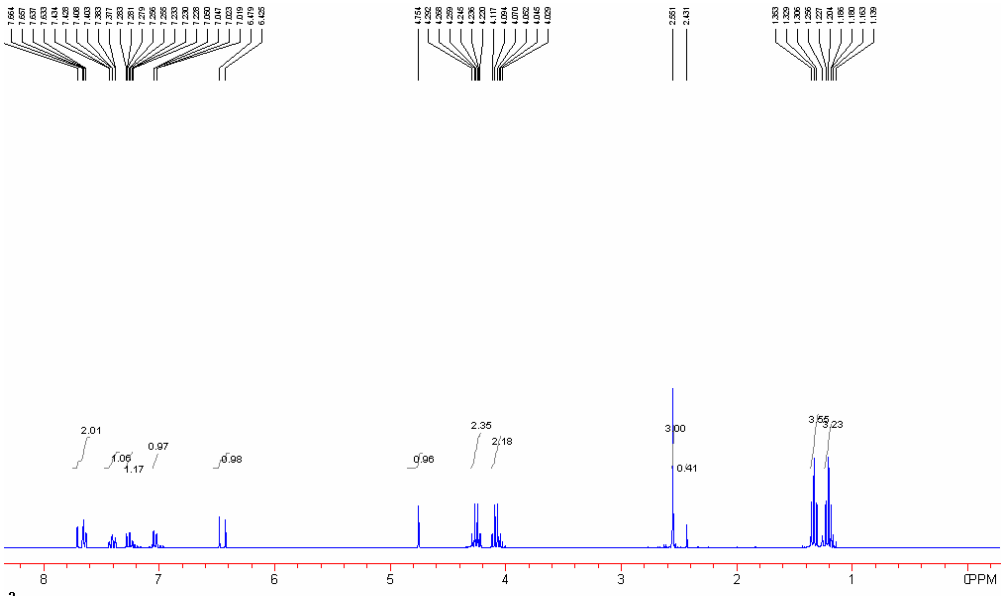
1-(6,8-dichloro-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone 5f: a pale yellow solid; mp. 128-130 ^{o}C; IR (CH_2Cl_2) ν bar = 3347, 3074, 2995, 2944, 1666, 1627, 1455, 1223, 1048 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.93 (3H, s CH_3), 2.49 (3H, s, CH_3), 4.23 (1H, s, OH), 7.17 (1H, d, *J* = 2.2 Hz, ArH), 7.32 (1H, s, =CH_2), 7.40 (1H, d, *J* = 2.2 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 26.8, 27.6, 99.6, 120.9, 122.6, 126.2, 126.5, 132.1, 132.8, 134.6, 147.4, 197.4; MS (EI) *m/z* 259 (14) [M^+-14], 257 (20) [M^+-16], 241 (6) [M^+-32], 239 (8) [M^+-34], 215 (7) [M^+-58], 63 (6) [M^+-210], 44 (6) [M^+-229], 43 (100) [M^+-230]; Found: C, 52.88; H, 3.52%. $C_{12}H_{10}Cl_2O_3$ requires C, 52.77; H, 3.69%.

Reaction procedure of (E)-ethyl 3-(2-hydroxyphenyl)acrylate with ethyl buta-2,3-dienoate in the presence of K_2CO_3 in DMSO at room temperature.

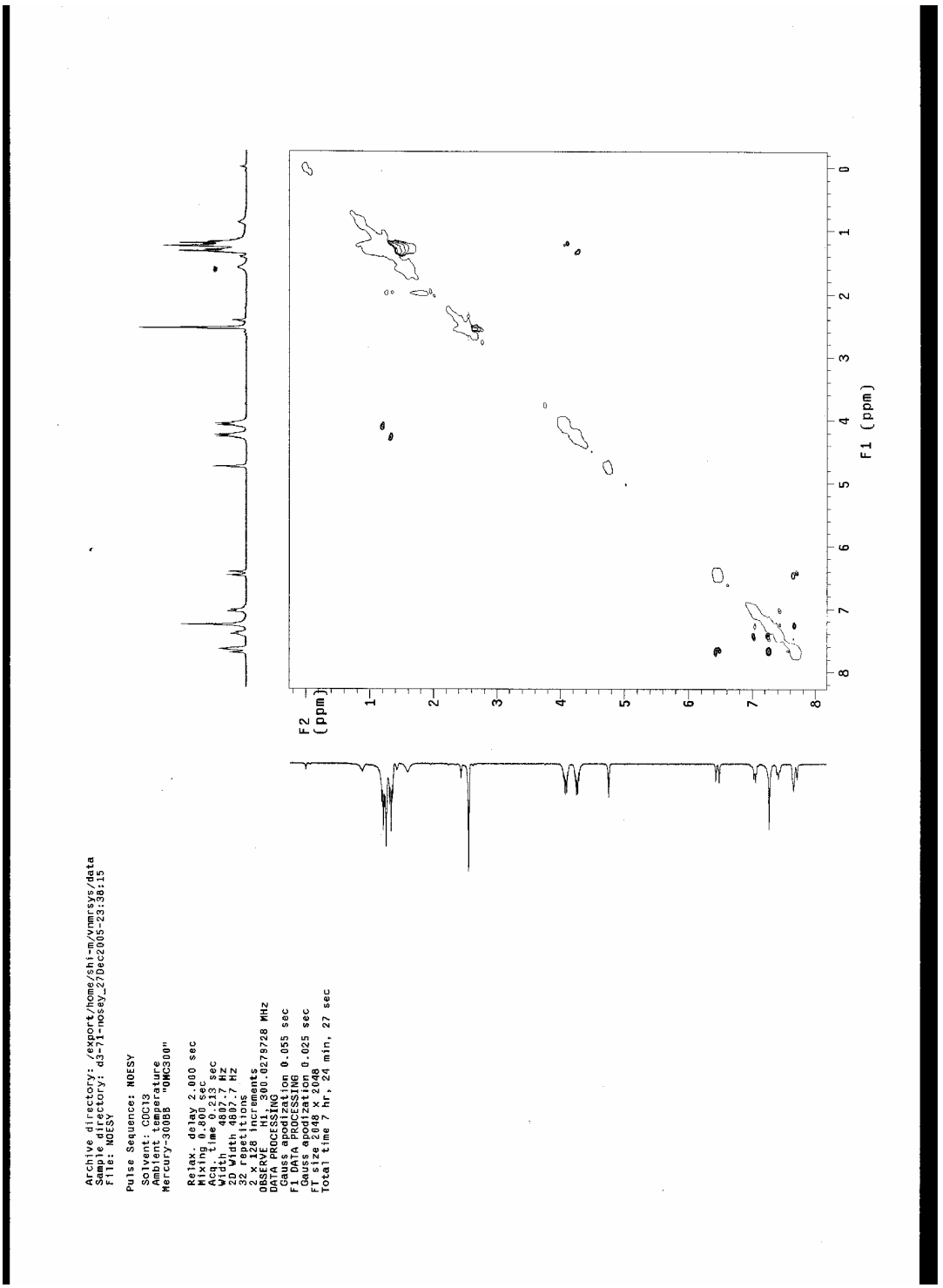
To a Schlenk tube with DMSO (1.0 mL) was added (E)-ethyl 3-(2-hydroxyphenyl)acrylate **1j** (58 mg, 0.3 mmol), ethyl buta-2,3-dienoate **2a** (50 mg, 0.45 mmol) and K_2CO_3 (5 mg, 0.03 mmol). The solution was stirred for 4 h at room temperature (25 ^{o}C). The reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (3 x 15 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give the corresponding product **6a** (eluent: EtOAc/petroleum ether = 1/10, 70 mg, yield 78%, E/Z = 8/1) as a colorless oil.



6a



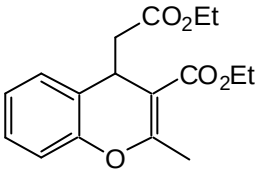
(*E*)-ethyl 3-(2-(3-ethoxy-3-oxoprop-1-enyl)phenoxy)but-2-enoate 6a: a colorless oil; IR (CH_2Cl_2) ν bar = 2981, 2927, 2852, 1716, 1638, 1485, 1454 cm^{-1}; **(*E*)-ethyl 3-(2-((E)-3-ethoxy-3-oxoprop-1-enyl)phenoxy)but-2-enoate:** ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.21 (3H, t, *J* = 7.2 Hz, CH_3), 1.33 (3H, t, *J* = 7.2 Hz, CH_3), 2.55 (3H, s, CH_3), 4.08 (2H, q, *J* = 7.2 Hz, CH_2), 4.26 (2H, q, *J* = 7.2 Hz, CH_2), 4.75 (1H, s, =CH_2), 6.45 (1H, d, *J* = 15.4 Hz, =CH_2), 7.04 (1H, dd, *J* = 8.7 Hz, *J* = 1.2 Hz, ArH), 7.24-7.29 (1H, m, ArH), 7.38-7.44 (1H, m, ArH), 7.63-7.66 (1H, m, ArH), 6.45 (1H, d, *J* = 15.4 Hz, =CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.2, 18.2, 59.6, 60.2, 60.6, 97.0, 120.4, 122.7, 126.1, 127.3, 128.1, 131.5, 137.6, 151.8, 166.6, 167.2, 172.1; MS (EI) *m/z* 230 (93) [M^+-74], 217 (100) [M^+-87], 201 (54) [M^+-103], 158 (72) [M^+-146], 132 (64) [M^+-172], 118 (82) [M^+-186], 91 (55) [M^+-213], 43 (85) [M^+-261]; HRMS Calcd. for $C_{17}H_{20}O_5$ requires 304.1311, Found: 304.1311.



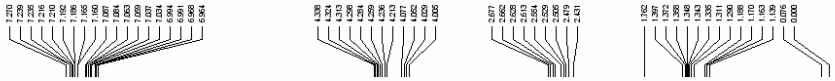
Reaction procedure of (E)-ethyl 3-(2-hydroxyphenyl)acrylate with ethyl buta-2,3-dienoate in the presence of K_2CO_3 in DMSO at 120 ^oC.

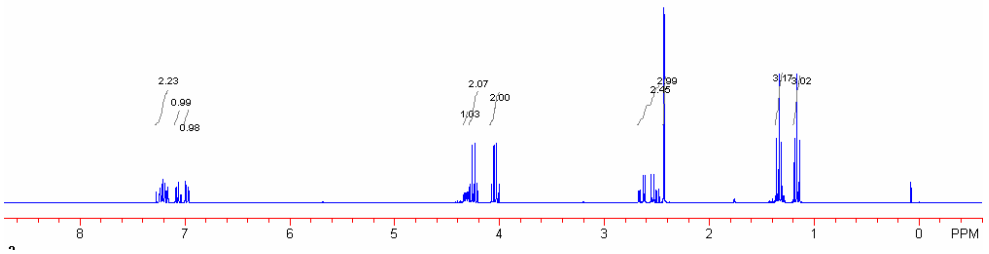
To a Schlenk tube with DMSO (1.0 mL) was added (E)-ethyl 3-(2-hydroxyphenyl)acrylate **1j** (58 mg, 0.3 mmol), ethyl buta-2,3-dienoate **2a** (50 mg, 0.45 mmol) and K_2CO_3 (5 mg, 0.03 mmol). The solution was stirred for 2 h at 120 ^oC. The reaction mixture was diluted with ethyl

acetate (20 mL) and washed with water (3 x 15 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography to give the corresponding product **7a** (eluent: EtOAc/petroleum ether = 1/10, 70 mg, yield 78%) as a pale yellow oil.



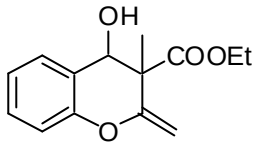
7a



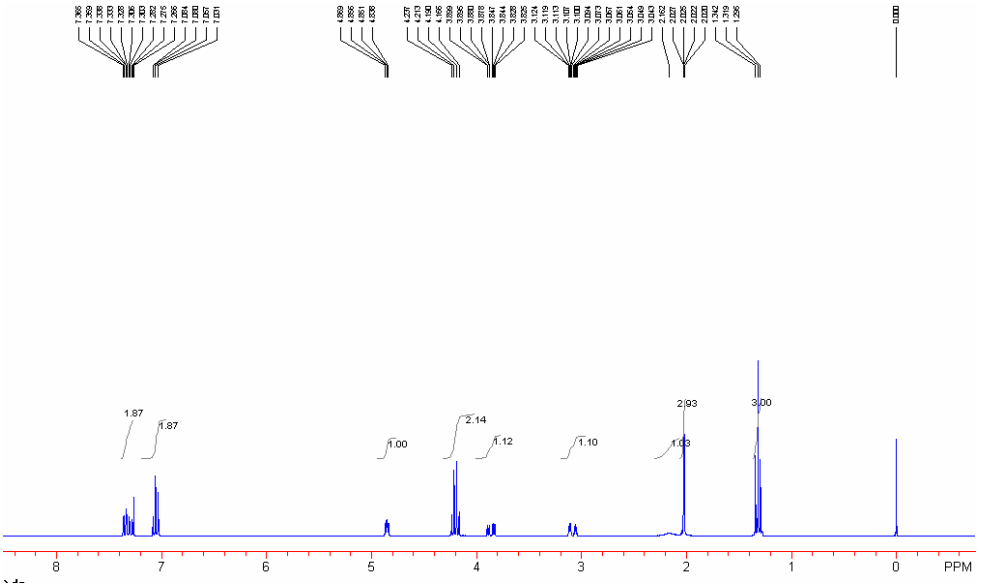


Ethyl 4-(2-ethoxy-2-oxoethyl)-2-methyl-4H-chromene-3-carboxylate 7a: a pale yellow oil; IR (CH_2Cl_2) ν bar = 2981, 2935, 2906, 2873, 1765, 1642, 1585, 1489, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.16 (3H, t, *J* = 7.3 Hz, CH_3), 1.34 (3H, t, *J* = 7.2 Hz, CH_3), 2.43 (3H, s, CH_3), 2.52 (1H, dd, *J* = 14.9 Hz, *J* = 7.5 Hz, CH_2), 2.65 (1H, dd, *J* = 14.9 Hz, *J* = 4.5 Hz, CH_2), 4.04 (2H, q, *J* = 7.3 Hz, CH_2), 4.25 (2H, q, *J* = 7.2 Hz, CH_2), 4.75 (1H, dd, *J* = 7.5 Hz, *J* = 4.5 Hz, CH), 6.98 (1H, dd, *J* = 7.7 Hz, *J* = 1.2 Hz, ArH), 7.06 (1H, td, *J* = 7.7 Hz, *J* = 1.2 Hz, ArH), 7.16-7.24 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.0, 14.2, 19.6, 32.2, 43.5, 60.2, 60.2 104.6, 115.9, 124.1, 124.3, 127.7, 128.1, 150.5,. 162.5, 166.8, 171.3; MS (EI) *m/z* 230 (38) [M^+-74], 217 (100) [M^+-87], 201 (16) [M^+-103], 189 (49)

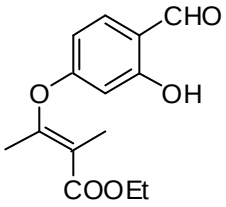
[M^+-115], 171 (39) [M^+-133], 158 (20) [M^+-146], 115 (38) [M^+-189], 43 (18) [M^+-261]; HRMS Calcd. for $C_{17}H_{20}O_5$ requires 304.1311, Found: 304.1321.



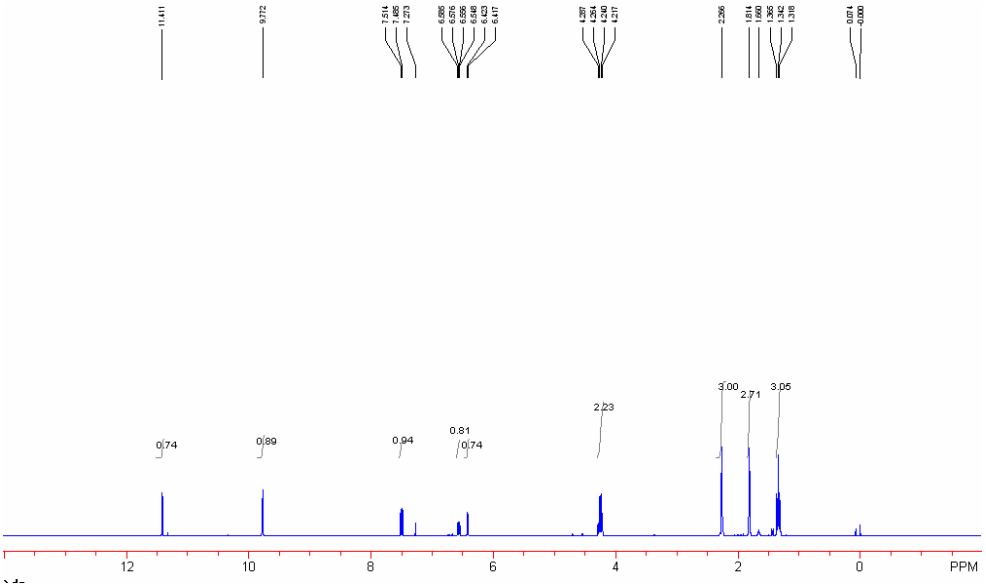
8a



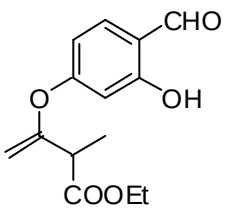
(Syn)-ethyl 4-hydroxy-3-methyl-2-methylene-3,4-dihydro-2H-chromene-3-carboxylate 8a: a pale yellow solid; mp. 87-89 ^oC; IR (CH_2Cl_2) ν bar = 3294, 3198, 2975, 2926, 2870, 1709, 1647, 1606, 1486, 1453, 1276, 1224, 1112, 1065, 766, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.32 (3H, t, *J* = 6.9 Hz, CH_3), 2.02 (3H, dd, *J* = 1.5 Hz, *J* = 0.6 Hz, CH_3), 2.16 (3H, s, OH), 3.08 (1H, m, $=CH_2$), 3.86 (1H, ddd, *J* = 15.6 Hz, *J* = 2.7 Hz, *J* = 0.9 Hz, $=CH_2$), 4.20 (2H, q, J = 6.9 Hz, CH_2), 4.85 (1H, dd, *J* = 5.4 Hz, *J* = 0.9 Hz, CH), 7.03-7.08 (2H, m, ArH); 7.28-7.37 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 11.8, 14.3, 32.5, 60.3, 63.6, 109.0, 116.6, 122.7, 124.9, 127.8, 129.9, 151.4, 157.0, 168.9; MS (EI) *m/z* 248 (M^+, 5.05,), 230 (M^+-18 73.81), 201 (35) [M^+-47], 185 (38) [M^+-63], 158 (100) [M^+-90], 157 (54) [M^+-91], 121 (59) [M^+-127], 77 (35) [M^+-171], 53 (62) [M^+-195]; HRMS Calcd. for $C_{14}H_{16}O_4$ requires 248.1049, Found: 248.1060.



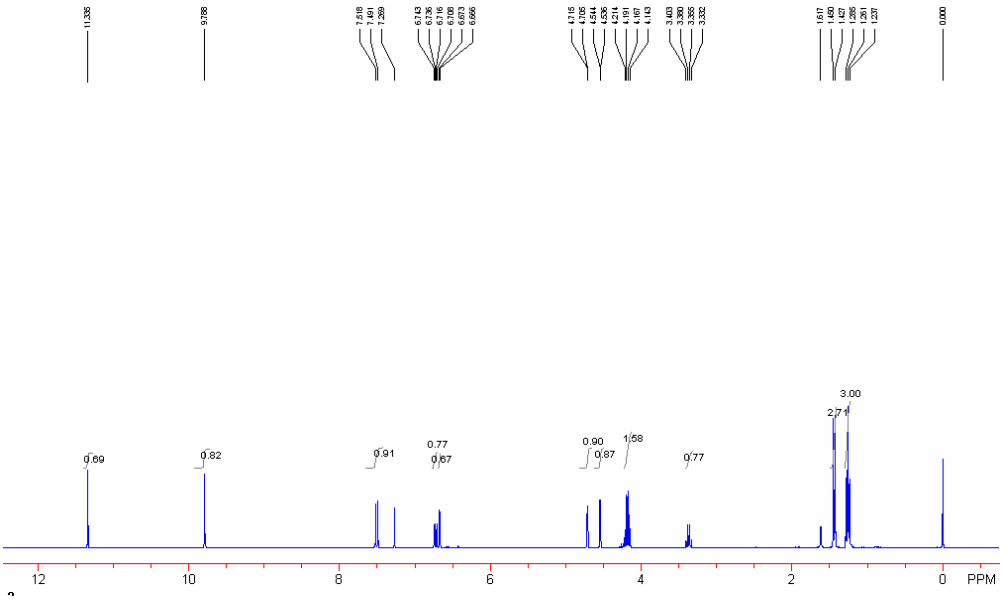
10a



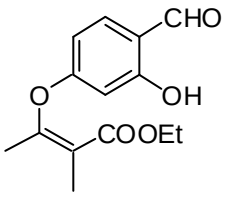
(*E*)-ethyl 3-(4-formyl-3-hydroxyphenoxy)-2-methylbut-2-enoate 10a: a colorless oil; IR (CH_2Cl_2) ν bar = 2987, 2932, 2845, 2747, 1715, 1654, 1578, 1500 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.34 (3H, t, *J* = 7.2 Hz, CH_3), 1.81 (3H, s, CH_3), 2.27 (3H, s, CH_3), 4.25 (2H, q, *J* = 7.2 Hz, CH_2), 6.42 (1H, d, *J* = 1.8 Hz, ArH), 6.57 (1H, dd, *J* = 8.6 Hz, *J* = 2.6 Hz, ArH), 7.50 (1H, d, *J* = 8.6 Hz, ArH); 9.77 (1H, s, OH); 11.41 (1H, s, CHO); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 12.4, 14.1, 18.1, 60.6, 103.6, 109.1, 116.3, 118.0, 135.7, 157.7, 162.3, 164.1, 167.9, 194.6; MS (EI) *m/z* 264 (20) [M^+], 191 (60) [M^+-73], 137 (70.63) [M^+-127], 99 (100) [M^+-165], 81 (35) [M^+-183], 65 (40) [M^+-199], 53 (64) [M^+-211], 43 (75) [M^+-221]; HRMS Calcd. for $C_{14}H_{16}O_5$ (-CH_3) requires 249.0763, Found: 249.0766.



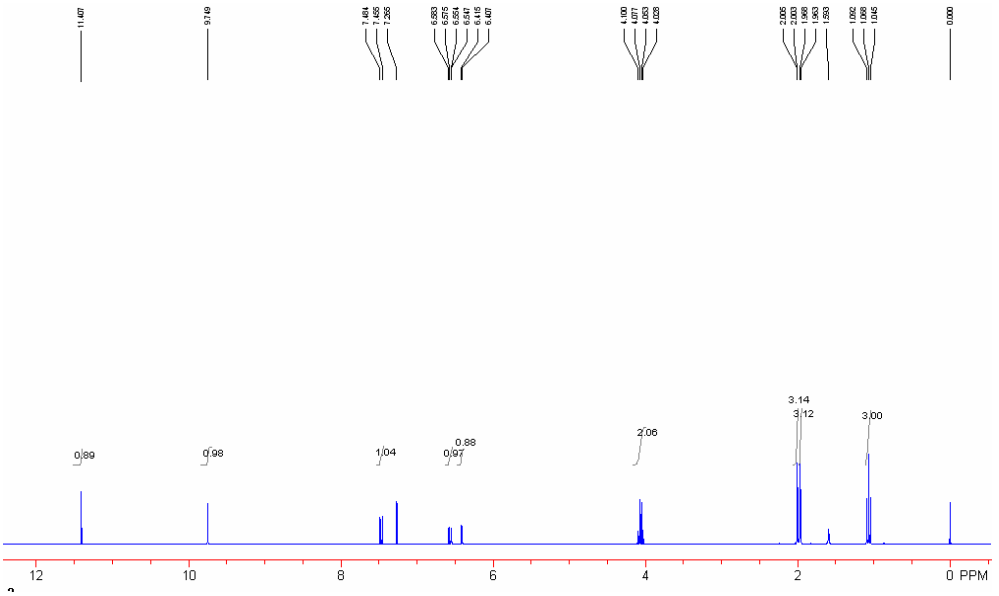
10b



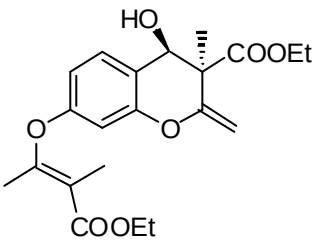
Ethyl 3-(4-formyl-3-hydroxyphenoxy)-2-methylbut-3-enoate 10b: a colorless oil; IR (CH_2Cl_2) ν bar = 2982, 2925, 2851, 1736, 1653, 1623, 1214, 1159 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.26 (3H, t, *J* = 7.1 Hz, CH_3), 1.44 (3H, d, *J* = 7.2Hz, CH_3), 3.37 (1H, q, *J* = 7.2 Hz, CH), 4.18 (2H, q, *J* = 7.1 Hz, CH_2), 4.54 (1H, d, *J* = 2.7 Hz, CH_2), 4.71 (1H, d, *J* = 2.7 Hz, CH_2), 6.67 (1H, d, *J* = 2.1 Hz, ArH), 6.72 (1H, dd, *J* = 8.4 Hz, *J* = 2.1 Hz, ArH), 7.50 (1H, d, *J* = 8.4 Hz, ArH); 9.79 (1H, s, OH); 11.33 (1H, s, CHO). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.1, 15.1, 44.3, 61.2, 96.3, 106.7, 111.4, 116.9, 135.5, 158.95, 163.3, 163.8, 172.4, 194.9; MS (EI) *m/z* 264 (4) [M^+], 163 (100) [M^+-101], 137 (70) [M^+-127], 102 (75) [M^+-162], 74 (46) [M^+-190], 65 (27) [M^+-199], 53 (82) [M^+-211], 43 (45) [M^+-22]; HRMS Calcd. for $C_{14}H_{16}O_5$ (-CH_3) requires 249.0763, Found: 249.0769.



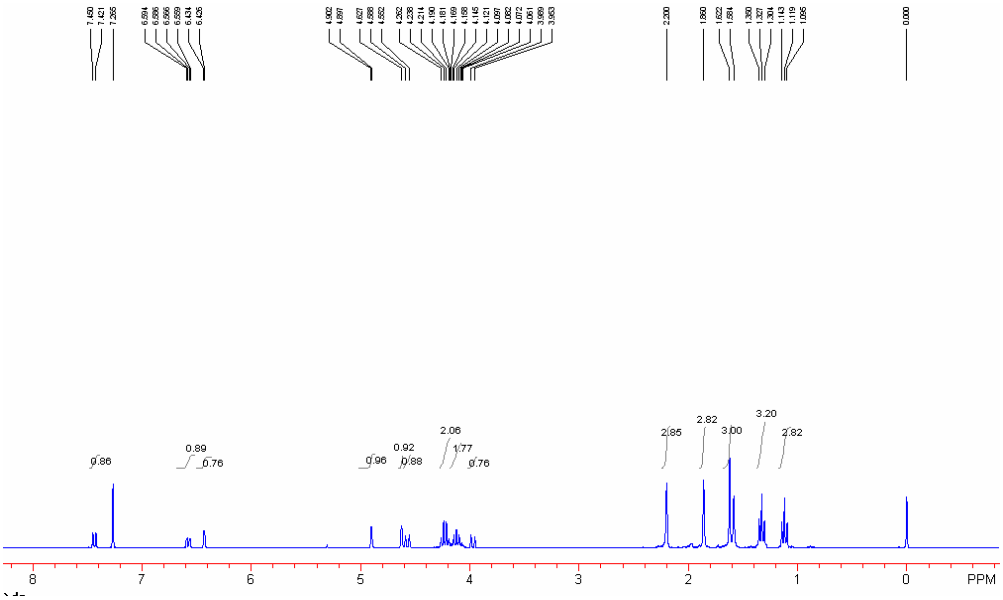
10c



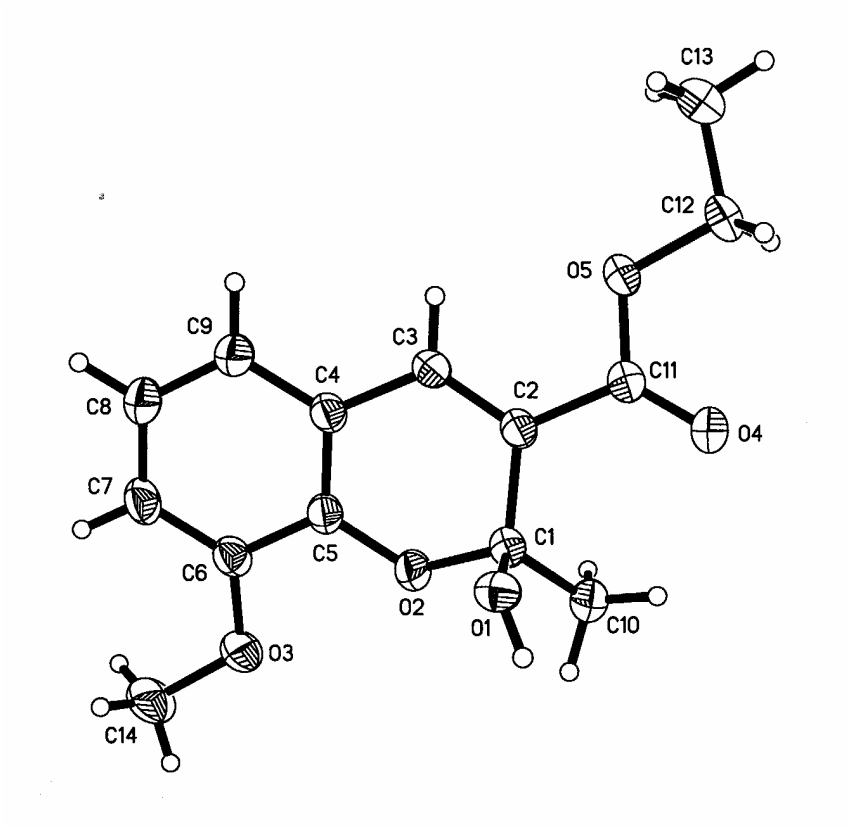
(*Z*)-ethyl 3-(4-formyl-3-hydroxyphenoxy)-2-methylbut-2-enoate 10c: a colorless oil; IR (CH_2Cl_2) ν bar = 2983, 2933, 2851, 1720, 1647, 1625, 1501, 1308, 1289 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.07 (3H, t, *J* = 7.1 Hz, CH_3), 1.97 (3H, d, *J* = 0.9 Hz, CH_3), 2.00 (3H, d, *J* = 0.9 Hz, CH_3), 4.07 (2H, q, *J* = 7.2 Hz, CH_2), 6.41 (1H, d, *J* = 2.2 Hz, ArH), 6.57 (1H, dd, *J* = 8.6 Hz, *J* = 2.2 Hz, ArH), 7.47 (1H, d, *J* = 8.6 Hz, ArH); 9.75 (1H, s, OH); 11.41 (1H, s, CHO). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 13.9, 14.5, 17.0, 60.5, 103.3, 109.1, 115.9, 117.6, 135.5, 152.1, 163.7, 164.1, 166.8, 194.6; MS (EI) *m/z* 264 (15) [M^+], 191 (51) [M^+-73], 137 (61) [M^+-127], 99 (100) [M^+-165], 81 (35) [M^+-163], 65 (36) [M^+-199], 53 (66) [M^+-211], 43 (81) [M^+-221]; HRMS Calcd. for $C_{14}H_{16}O_5$ (-CH_3) requires 249.0763, Found: 249.0756.



10d



(3*R*,4*R*,*E*)-ethyl7-(4-ethoxy-3-methyl-4-oxobut-2-en-2-yloxy)-4-hydroxy-3-methyl-2-methylene-3,4-dihydro-2H-chromene-3-carboxylate 10d: a colorless oil; IR (CH_2Cl_2) ν bar = 3491, 2982, 2932, 1712, 1658, 1613, 1496, 1261, 1155, 1098, 1005 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.12 (3H, t, *J* = 7.2 Hz, CH_3), 1.33 (3H, t, *J* = 6.9 Hz, CH_3), 1.62 (3H, s, CH_3), 1.86 (3H, s, CH_3), 3.20 (3H, s, CH_3), 3.96 (1H, d, *J* = 10.5 Hz, OH), 4.12 (2H, m, CH_2), 4.23 (2H, q, *J* = 7.2 Hz, CH_2), 4.57 (1H, dd, *J* = 10.5 Hz, *J* = 0.9 Hz, CH), 4.62 (1H, d, *J* = 2.1 Hz, =CH_2), 4.95 (1H, d, *J* = 2.1 Hz, =CH_2), 6.43 (1H, d, *J* = 2.4 Hz, ArH); 6.58 (1H, dd, *J* = 8.4 Hz, *J* = 2.4 Hz, ArH); 7.43 (1H, dd, *J* = 8.4 Hz, *J* = 0.8 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 12.3, 13.8, 14.2, 17.9, 18.8, 49.3, 60.3, 61.7, 71.6, 93.98, 104.4, 111.4, 115.5, 120.0, 127.4, 152.0, 155.8, 156.5, 159.5, 168.6, 173.97; MS (EI) *m/z* 390 (26) [M^+], 371 (41) [M^+-19], 317 (68) [M^+-73], 137 (40) [M^+-253], 99 (74) [M^+-291], 81 (61) [M^+-309], 53 (82) [M^+-337], 43 (100) [M^+-347]; HRMS Calcd. for $C_{21}H_{26}O_7$ requires 390.1679, Found: 390.1681.



The crystal data of **3b** has been deposited in CCDC with number 283692. Empirical Formula: $C_{14}H_{16}O_5$; Formula Weight: 264.27; Crystal size: 0.506 x 0.279 x 0.237; Crystal Color, Habit: colorless, prismatic; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a = 8.5461(11)Å, b = 8.9372(4)Å, c = 11.0662(14)Å, α = 111.524(2)^o, β = 92.403(3)^o, γ = 117.794(2)^o, V = 671.86(15)Å^3; Space group: P-1; Z = 2; D_{calc} = 1.306 g/cm^3; F_{000} = 280; R1 = 0.0477, wR2 = 0.1138. Diffractometer: Rigaku AFC7R.

Table 1. Crystal data and structure refinement for cd25410.

Identification code	cd25410
Empirical formula	C14 H16 O5
Formula weight	264.27
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.5461(11) A alpha = 111.524(2) deg. b = 8.9372(11) A beta = 92.403(3) deg. c = 11.0662(14) A gamma = 117.794(2) deg.
Volume	671.86(15) A^3
Z, Calculated density	2, 1.306 Mg/m^3
Absorption coefficient	0.099 mm^-1
F(000)	280
Crystal size	0.506 x 0.279 x 0.237 mm
Theta range for data collection	2.05 to 26.99 deg.
Limiting indices	-10<=h<=7, -11<=k<=11, -10<=l<=14
Reflections collected / unique	3967 / 2846 [R(int) = 0.0543]
Completeness to theta = 26.99	97.2 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.69338
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2846 / 0 / 237
Goodness-of-fit on F^2	0.946
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1138
R indices (all data)	R1 = 0.0635, wR2 = 0.1223
Extinction coefficient	0.017(5)
Largest diff. peak and hole	0.174 and -0.241 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd25410.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5416(2)	2427(2)	5968(1)	51(1)
O(2)	6232(2)	1417(1)	3984(1)	50(1)
O(3)	4045(2)	-1574(2)	1753(1)	60(1)
O(4)	9502(2)	6361(2)	7766(1)	72(1)
O(5)	9582(2)	8009(1)	6645(1)	55(1)
C(1)	6903(2)	2790(2)	5398(1)	45(1)
C(2)	7657(2)	4755(2)	5499(1)	44(1)
C(3)	6951(2)	4984(2)	4528(2)	46(1)
C(4)	5635(2)	3400(2)	3302(1)	44(1)
C(5)	5334(2)	1647(2)	3078(1)	44(1)
C(6)	4170(2)	65(2)	1875(2)	48(1)
C(7)	3276(2)	254(3)	932(2)	57(1)
C(8)	3548(3)	2013(3)	1171(2)	62(1)
C(9)	4717(2)	3572(3)	2331(2)	54(1)
C(10)	8241(3)	2409(3)	5969(2)	52(1)
C(11)	8992(2)	6405(2)	6760(2)	50(1)
C(12)	10904(3)	9721(2)	7806(2)	57(1)
C(13)	11334(5)	11309(3)	7472(3)	88(1)
C(14)	2733(4)	-3266(3)	611(2)	79(1)

Table 3. Bond lengths [A] and angles [deg] for cd25410.

O(1)-C(1)	1.3969(19)
O(1)-H(1)	0.84(2)
O(2)-C(5)	1.3682(18)
O(2)-C(1)	1.4638(17)
O(3)-C(6)	1.3722(19)
O(3)-C(14)	1.428(2)
O(4)-C(11)	1.1987(19)
O(5)-C(11)	1.3388(19)
O(5)-C(12)	1.4465(18)
C(1)-C(10)	1.512(2)
C(1)-C(2)	1.518(2)
C(2)-C(3)	1.336(2)
C(2)-C(11)	1.487(2)
C(3)-C(4)	1.444(2)
C(3)-H(3)	0.928(16)
C(4)-C(5)	1.384(2)
C(4)-C(9)	1.399(2)
C(5)-C(6)	1.399(2)
C(6)-C(7)	1.373(2)
C(7)-C(8)	1.394(3)
C(7)-H(7)	0.914(18)
C(8)-C(9)	1.367(2)
C(8)-H(8)	0.95(2)
C(9)-H(9)	0.964(16)
C(10)-H(10A)	0.93(2)
C(10)-H(10B)	0.951(19)
C(10)-H(10C)	0.968(17)
C(12)-C(13)	1.481(3)
C(12)-H(12A)	0.969(19)
C(12)-H(12B)	1.00(2)
C(13)-H(13A)	0.92(3)
C(13)-H(13B)	0.96(2)
C(13)-H(13C)	0.92(3)
C(14)-H(14A)	0.96(2)
C(14)-H(14B)	0.99(3)
C(14)-H(14C)	0.91(2)

C(1)-O(1)-H(1)	111.5(16)
C(5)-O(2)-C(1)	118.81(11)
C(6)-O(3)-C(14)	117.30(16)
C(11)-O(5)-C(12)	116.32(12)
O(1)-C(1)-O(2)	108.39(12)
O(1)-C(1)-C(10)	112.72(14)
O(2)-C(1)-C(10)	102.61(13)
O(1)-C(1)-C(2)	106.01(13)
O(2)-C(1)-C(2)	109.92(11)
C(10)-C(1)-C(2)	116.96(13)
C(3)-C(2)-C(11)	120.80(14)
C(3)-C(2)-C(1)	119.52(13)
C(11)-C(2)-C(1)	119.17(13)
C(2)-C(3)-C(4)	121.68(15)
C(2)-C(3)-H(3)	121.7(10)
C(4)-C(3)-H(3)	116.6(10)
C(5)-C(4)-C(9)	119.37(14)
C(5)-C(4)-C(3)	117.37(14)
C(9)-C(4)-C(3)	123.23(14)
O(2)-C(5)-C(4)	121.44(13)
O(2)-C(5)-C(6)	117.79(14)
C(4)-C(5)-C(6)	120.68(14)
O(3)-C(6)-C(7)	125.73(14)
O(3)-C(6)-C(5)	115.00(14)
C(7)-C(6)-C(5)	119.28(15)
C(6)-C(7)-C(8)	120.04(15)
C(6)-C(7)-H(7)	121.3(11)
C(8)-C(7)-H(7)	118.5(11)
C(9)-C(8)-C(7)	120.89(16)
C(9)-C(8)-H(8)	119.6(11)
C(7)-C(8)-H(8)	119.5(11)

C(8)-C(9)-C(4)	119.71(16)
C(8)-C(9)-H(9)	120.4(9)
C(4)-C(9)-H(9)	119.9(10)
C(1)-C(10)-H(10A)	108.6(13)
C(1)-C(10)-H(10B)	111.2(11)
H(10A)-C(10)-H(10B)	110.4(16)
C(1)-C(10)-H(10C)	108.7(10)
H(10A)-C(10)-H(10C)	106.6(16)
H(10B)-C(10)-H(10C)	111.2(15)
O(4)-C(11)-O(5)	122.81(14)
O(4)-C(11)-C(2)	126.19(15)
O(5)-C(11)-C(2)	110.99(13)
O(5)-C(12)-C(13)	107.33(16)
O(5)-C(12)-H(12A)	110.3(11)
C(13)-C(12)-H(12A)	110.3(11)
O(5)-C(12)-H(12B)	110.4(10)
C(13)-C(12)-H(12B)	110.5(10)
H(12A)-C(12)-H(12B)	108.2(15)
C(12)-C(13)-H(13A)	105.3(19)
C(12)-C(13)-H(13B)	110.8(15)
H(13A)-C(13)-H(13B)	104(2)
C(12)-C(13)-H(13C)	110.4(14)
H(13A)-C(13)-H(13C)	113(2)
H(13B)-C(13)-H(13C)	113(2)
O(3)-C(14)-H(14A)	112.0(13)
O(3)-C(14)-H(14B)	109.8(14)
H(14A)-C(14)-H(14B)	106(2)
O(3)-C(14)-H(14C)	104.7(13)
H(14A)-C(14)-H(14C)	115.8(19)
H(14B)-C(14)-H(14C)	109(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd25410.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	50(1)	45(1)	57(1)	26(1)	16(1)	22(1)
O(2)	56(1)	42(1)	41(1)	11(1)	0(1)	24(1)
O(3)	71(1)	39(1)	48(1)	10(1)	3(1)	21(1)
O(4)	87(1)	53(1)	48(1)	17(1)	-14(1)	21(1)
O(5)	58(1)	39(1)	42(1)	12(1)	-4(1)	11(1)
C(1)	43(1)	41(1)	40(1)	15(1)	5(1)	17(1)
C(2)	42(1)	40(1)	39(1)	15(1)	5(1)	15(1)
C(3)	47(1)	37(1)	42(1)	16(1)	6(1)	14(1)
C(4)	42(1)	41(1)	38(1)	14(1)	6(1)	16(1)
C(5)	40(1)	45(1)	38(1)	16(1)	7(1)	18(1)
C(6)	48(1)	43(1)	40(1)	14(1)	9(1)	18(1)
C(7)	56(1)	52(1)	37(1)	9(1)	-2(1)	17(1)
C(8)	68(1)	60(1)	45(1)	19(1)	-3(1)	29(1)
C(9)	61(1)	49(1)	45(1)	18(1)	4(1)	26(1)
C(10)	52(1)	53(1)	48(1)	21(1)	5(1)	26(1)
C(11)	49(1)	44(1)	43(1)	17(1)	3(1)	17(1)
C(12)	50(1)	43(1)	48(1)	8(1)	-4(1)	13(1)
C(13)	99(2)	45(1)	81(2)	17(1)	-14(2)	21(1)
C(14)	95(2)	45(1)	55(1)	7(1)	4(1)	20(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd25410.

	x	y	z	U(eq)
H(1)	5260(30)	1680(30)	6310(20)	99(8)
H(3)	7300(20)	6170(20)	4599(16)	51(4)
H(7)	2430(20)	-770(30)	169(18)	66(5)
H(8)	2910(30)	2130(20)	518(19)	71(5)
H(9)	4900(20)	4780(20)	2490(16)	54(5)
H(10A)	9180(30)	2640(30)	5532(19)	77(6)
H(10B)	8730(20)	3170(30)	6910(20)	65(5)
H(10C)	7620(20)	1080(20)	5756(17)	60(5)
H(12A)	10400(20)	9850(20)	8581(19)	64(5)
H(12B)	12040(30)	9700(20)	8025(18)	65(5)
H(13A)	10240(40)	11250(40)	7310(30)	133(11)
H(13B)	11650(30)	11090(30)	6630(30)	105(9)
H(13C)	12220(30)	12430(30)	8170(20)	90(7)
H(14A)	3010(30)	-3250(30)	-220(20)	89(7)
H(14B)	1510(40)	-3410(30)	560(30)	115(10)
H(14C)	2700(30)	-4200(30)	770(20)	78(6)

Table 6. Torsion angles [deg] for cd25410.

C(5)-O(2)-C(1)-O(1)	76.47(15)
C(5)-O(2)-C(1)-C(10)	-164.09(13)
C(5)-O(2)-C(1)-C(2)	-38.97(18)
O(1)-C(1)-C(2)-C(3)	-86.74(17)
O(2)-C(1)-C(2)-C(3)	30.2(2)
C(10)-C(1)-C(2)-C(3)	146.61(17)
O(1)-C(1)-C(2)-C(11)	85.18(16)
O(2)-C(1)-C(2)-C(11)	-157.88(13)
C(10)-C(1)-C(2)-C(11)	-41.5(2)
C(11)-C(2)-C(3)-C(4)	-179.23(14)
C(1)-C(2)-C(3)-C(4)	-7.4(2)
C(2)-C(3)-C(4)-C(5)	-9.5(2)
C(2)-C(3)-C(4)-C(9)	172.71(16)
C(1)-O(2)-C(5)-C(4)	25.4(2)
C(1)-O(2)-C(5)-C(6)	-158.09(13)
C(9)-C(4)-C(5)-O(2)	178.47(14)
C(3)-C(4)-C(5)-O(2)	0.5(2)
C(9)-C(4)-C(5)-C(6)	2.1(2)
C(3)-C(4)-C(5)-C(6)	-175.85(14)
C(14)-O(3)-C(6)-C(7)	-6.8(3)
C(14)-O(3)-C(6)-C(5)	173.62(18)
O(2)-C(5)-C(6)-O(3)	0.9(2)
C(4)-C(5)-C(6)-O(3)	177.45(14)
O(2)-C(5)-C(6)-C(7)	-178.69(15)
C(4)-C(5)-C(6)-C(7)	-2.2(2)
O(3)-C(6)-C(7)-C(8)	-178.87(16)
C(5)-C(6)-C(7)-C(8)	0.7(3)
C(6)-C(7)-C(8)-C(9)	0.8(3)
C(7)-C(8)-C(9)-C(4)	-0.9(3)
C(5)-C(4)-C(9)-C(8)	-0.5(3)
C(3)-C(4)-C(9)-C(8)	177.28(16)
C(12)-O(5)-C(11)-O(4)	0.7(3)
C(12)-O(5)-C(11)-C(2)	-179.48(14)
C(3)-C(2)-C(11)-O(4)	168.33(18)
C(1)-C(2)-C(11)-O(4)	-3.5(3)
C(3)-C(2)-C(11)-O(5)	-11.5(2)
C(1)-C(2)-C(11)-O(5)	176.68(14)
C(11)-O(5)-C(12)-C(13)	-178.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd25410 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(3)#1	0.84(2)	2.25(2)	2.9650(17)	143(2)
O(1)-H(1)...O(2)#1	0.84(2)	2.33(2)	3.0686(16)	147(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1