Supporting Information

Synthesis of Functionalized 2*H*-1-Benzopyrans by DBU-Catalyzed Reactions of Salicylic Aldehydes with Allenic Ketones and Esters

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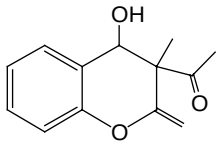
General Remarks. MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer or an Ion Spec 4.7 Tesla FTMS mass spectrometer. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer and some of the compounds reported in this paper gave satisfactory HRMS analytic data. 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 increased pressure. The starting materials such as 3-methylpenta-3,4-dien-2-one,[1] 3-benzylpenta-3,4-dien-2-one,[2,1c] and ethyl 2-methylbuta-2,3-dienoate[3] were prepared according to the literatures.

1) (a) Baumgarten, W. E., Ed. *Organic Synthesis*; Wiley: New York, **1973**, *5*, 785. (b) Ma, S.-M.; Li, L.-T.; Xie, H.-X. *J. Org. Chem*. **1999**, *64*, 5325-5328. (c) Buono, G. *Synthesis* **1981**, 272.
2) (a) Marquet, J.; Moreno-Mañas, M.; Pacheco, P.; Vallribera, A. *Tetrahedron Lett.* **1988**, *29*, 1465-1468. (b) Marquet, J.; Moreno-Mañas, M. *Synthesis* **1979**, 348-350.
3) (a) Anderson, J. C.; Cubbon, R. J.; Harling, J. D. *Tetrahedron: Asymmetry* **2001**, *12*, 923. (b) Jansch, H.; Kannenberg, S.; Boche, G. *Eur. J. Org. Chem.* **2001**, 2923.

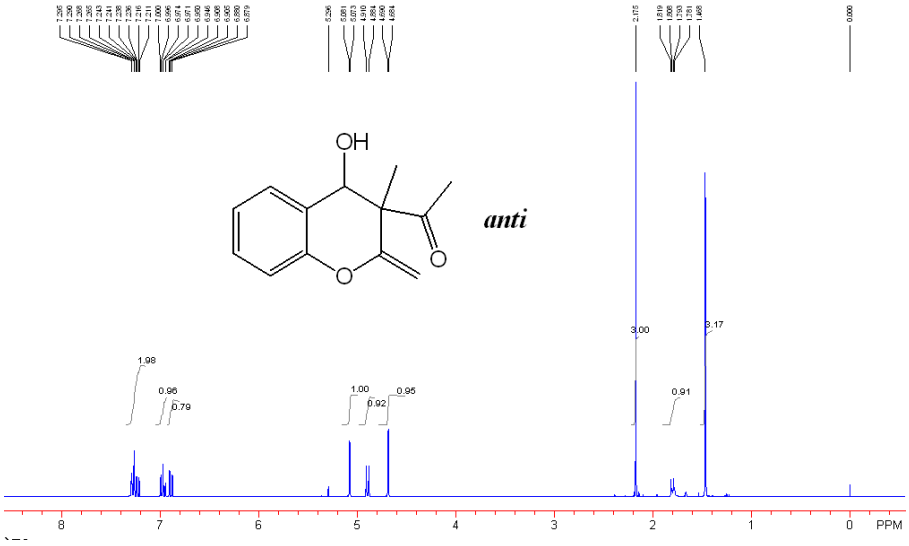
Reactions of salicylic aldehydes with 3-methylpenta-3,4-dien-2-one catalyzed by DBU.

Typical reaction procedure of salicylaldehyde with 3-methylpenta-3,4-dien-2-one in the presence of DBU in DMSO at room temperature.

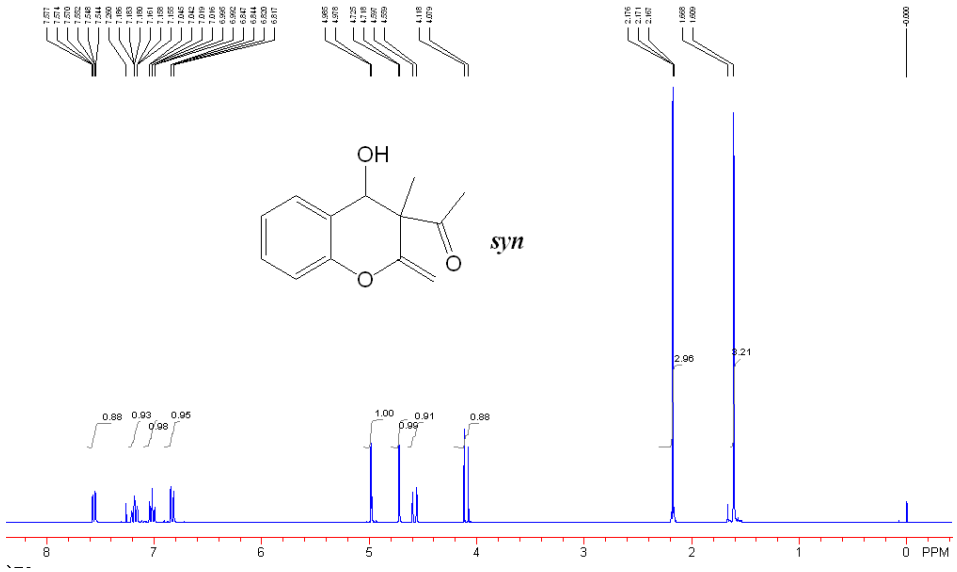
To a Schlenk tube with DMSO (0.5 mL) was added salicylaldehyde (61 mg, 0.5 mmol), 3-methylpenta-3,4-dien-2-one (96 mg, 1 mmol) and DBU (8 mg, 0.05 mmol). The solution was stirred for 24 h at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 15 mL) and extracted with dichloromethane (2 x 10 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 adduct *syn*-**3a** (eluent: EtOAc/petroleum= 1/10, 27 mg, yield 25%) as a pale yellow oil and the adduct *anti*-**3a** (eluent: EtOAc/petroleum= 1/4, 81 mg, yield 74%) as a pale yellow oil.

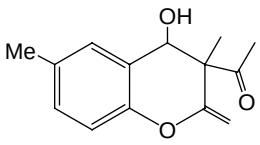


1-(4-Hydroxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone. ***anti*-3a**: a pale yellow oil; IR (CH_2Cl_2) ν 3416, 1712 (C=O), 1656, 1459, 1244, 1193 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.49 (3H, s, CH_3), 1.62 (1H, d, *J* = 7.8 Hz, OH), 2.19 (3H, s, CH_3), 4.70 (1H, d, *J* = 2.1 Hz, =CH), 4.92 (1H, d, *J* = 7.8 Hz, CH), 5.09 (1H, d, *J* = 2.1 Hz, =CH), 6.90 (1H, d, *J* = 7.5 Hz, ArH), 6.96-7.01 (1H, m, ArH), 7.22-7.31 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.9, 25.9, 56.1, 68.7, 95.6, 115.9, 122.0, 123.4, 129.6, 130.1, 151.4, 155.9, 208.2; MS (EI) *m/z* 218 (M^+, 11.61), 201 (M^+-17, 56.68), 200 (M^+-18, 25.99), 175 (M^+-43, 100), 159 (M^+-59, 49.96), 158 (M^+-60, 52.02), 43 (M^+-175, 76.62); HRMS (MALDI) calcd. for $C_{13}H_{14}O_3Na^{+1}$: 241.0835, Found: 241.0846.



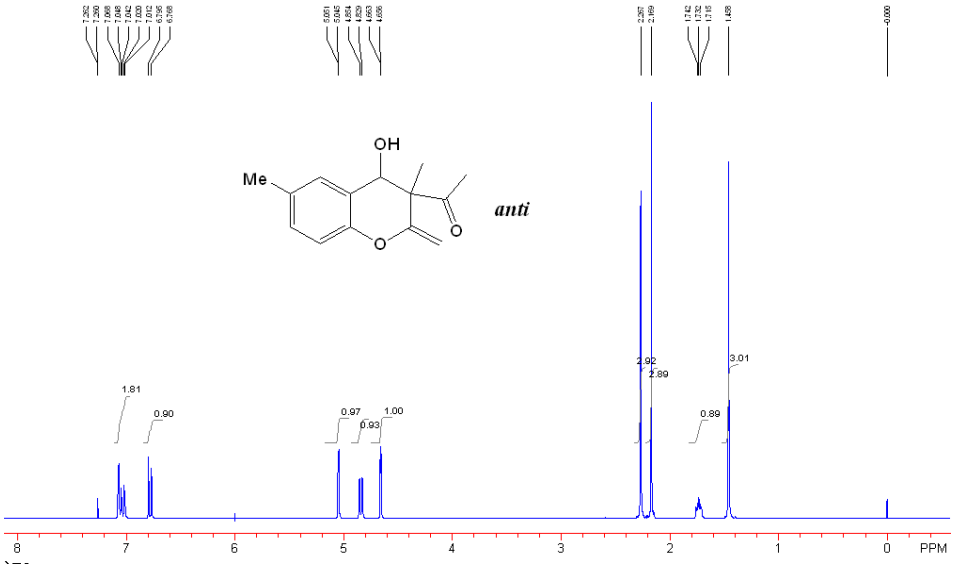
***syn*-3a**: a pale yellow oil; IR (CH_2Cl_2) ν 3487, 1702 (C=O), 1655, 1456, 1238, 1055 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.61 (3H, s, CH_3), 2.18 (3H, s, CH_3), 4.09 (1H, d, *J* = 11.7 Hz, OH), 4.58 (1H, d, *J* = 11.7 Hz, CH), 4.72 (1H, d, *J* = 2.1 Hz, =CH), 4.98 (1H, d, *J* = 2.1 Hz, =CH), 6.83 (1H, d, *J* = 7.5 Hz, ArH), 6.99-7.04 (1H, m, ArH), 7.16-7.19 (1H, m, ArH), 7.56 (1H, d, *J* = 7.5 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 26.6, 53.8, 72.6, 94.5, 115.1, 122.3, 126.0, 126.4, 128.9, 150.6, 158.2, 213.9; MS (EI) *m/z* 218 (M^+, 0.65), 201 (M^+-17, 0.80), 200 (M^+-18, 0.23), 175 (M^+-43, 1.46), 159 (M^+-59, 13.80), 158 (M^+-60, 100), 43 (M^+-175, 12.79); HRMS (EI) calcd. for $C_{13}H_{14}O_3$: 218.0943, Found: 218.0937.





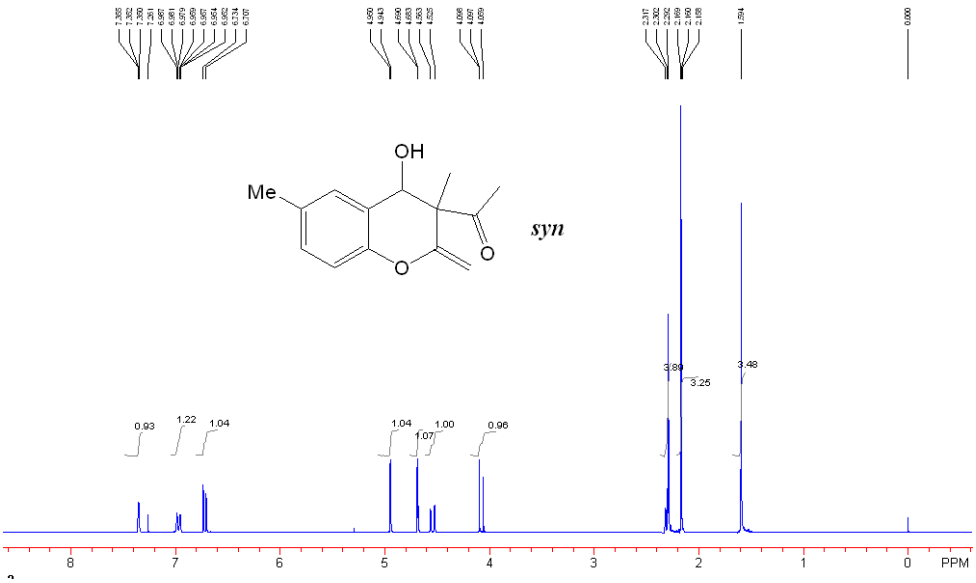
1-(4-Hydroxy-3,6-dimethyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone.

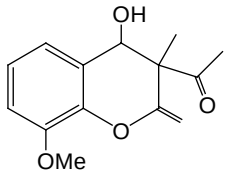
***anti*-3b**: a colorless crystal; mp. 133-136 ^{o}C; IR (CH_2Cl_2) ν 3326, 1709 (C=O), 1655, 1496, 1254, 1033 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.46 (3H, s, CH_3), 1.71-1.76 (1H, m, OH), 2.18 (3H, s, CH_3), 2.27 (3H, s, CH_3), 4.66 (1H, d, *J* = 1.8 Hz, =CH), 4.84 (1H, d, *J* = 7.5 Hz, CH), 5.05 (1H, d, *J* = 1.8 Hz, =CH), 6.78 (1H, d, *J* = 8.1 Hz, ArH), 7.01-7.07 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.0, 20.4, 26.0, 56.2, 68.9, 95.4, 115.7, 123.0, 129.8, 130.8, 131.4, 149.3, 156.1, 208.3; MS (EI) *m/z* 232 (M^+, 12.35), 215 (M^+-17, 28.07), 214 (M^+-18, 24.61), 189 (M^+-43, 100), 173 (M^+-59, 56.32), 172 (M^+-60, 69.81), 171 (M^+-61, 11.61), 43 (M^+-189, 26.18); Found: C, 72.57; H, 6.87%. $C_{14}H_{16}O_3$ requires C, 72.39; H, 6.94%.



***syn*-3b**: a pale yellow oil; IR (CH_2Cl_2) ν 3489, 2925, 2855, 1703 (C=O), 1654, 1492, 1258, 1054 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.59 (3H, s, CH_3), 2.17 (3H, s, CH_3), 2.29 (3H, s, CH_3), 4.08 (1H, d, *J* = 11.1 Hz, OH), 4.55 (1H, d, *J* = 11.1 Hz, CH), 4.69 (1H, d, *J* = 2.1 Hz, =CH), 4.95 (1H, d, *J* = 2.1 Hz, =CH), 6.72 (1H, d, *J* = 8.4 Hz, ArH), 6.95-6.99 (1H, m, ArH), 7.35-7.36 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 20.7, 26.7, 53.9, 72.6, 94.1, 114.8, 126.0, 126.3, 129.4, 131.6, 148.5, 158.4, 214.1; MS (EI) *m/z* 232 (M^+,

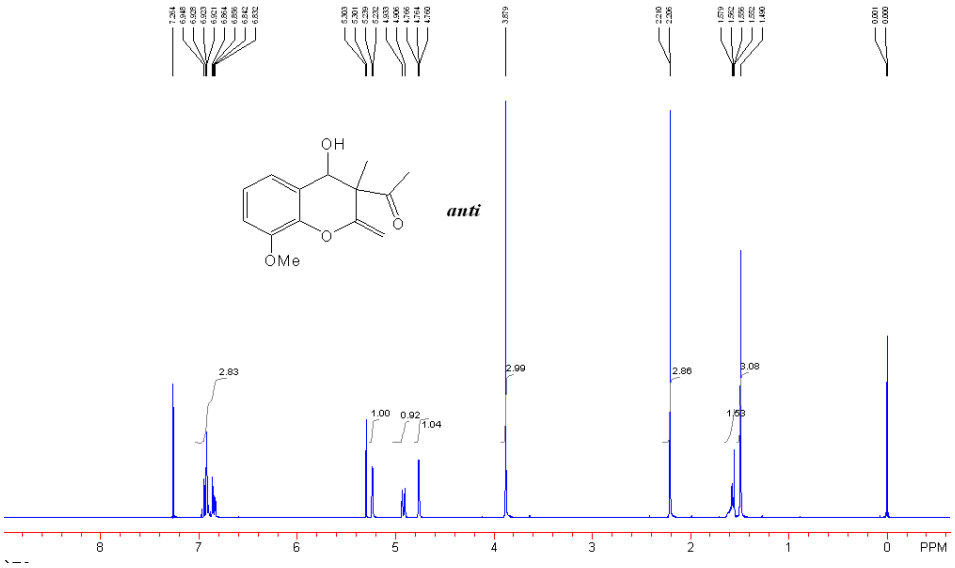
10.41), 215 (M^+-17, 10.96), 214 (M^+-18, 10.27), 189 (M^+-43, 57.06), 173 (M^+-59, 33.12), 172 (M^+-60, 100), 43 (M^+-189, 71.93); HRMS (EI) calcd. for $C_{14}H_{16}O_3$: 232.1099, Found: 232.1110. Found: C, 72.35; H, 6.83%. $C_{14}H_{16}O_3$ requires C, 72.39; H, 6.94%.



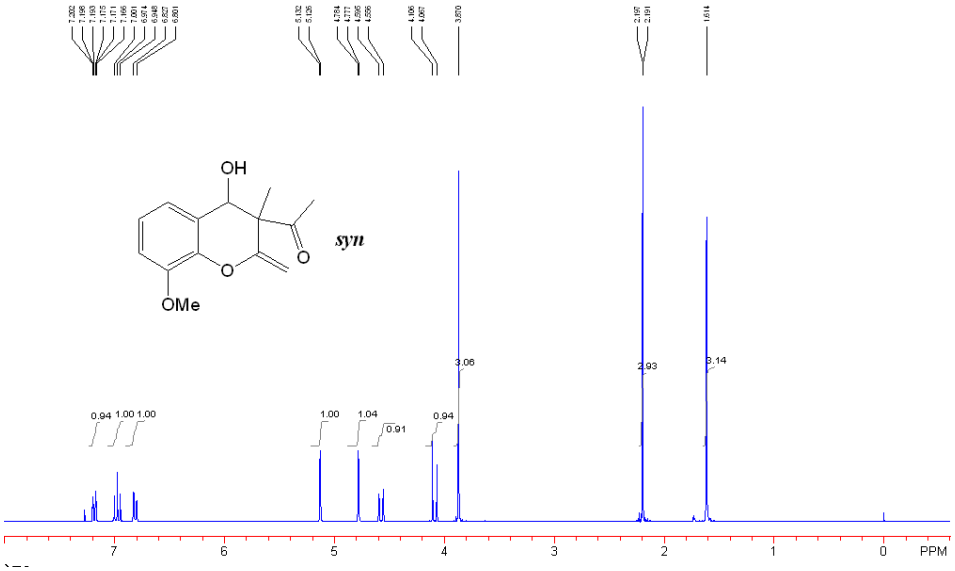


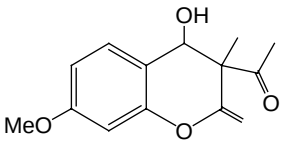
1-(4-Hydroxy-8-methoxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone

***anti*-3c**: a white solid; mp. 72-75 ^oC; IR (CH_2Cl_2) ν 3416, 1711 (C=O), 1655, 1488, 1270, 1229, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.42 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.39-2.43 (1H, m, OH), 3.84 (3H, s, OCH_3), 4.70 (1H, d, *J* = 1.8 Hz, =CH), 4.82 (1H, d, *J* = 8.1 Hz, CH), 5.17 (1H, d, *J* = 1.8 Hz, =CH), 6.80-6.93 (3H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.8, 25.9, 55.8, 55.9, 68.5, 96.3, 111.8, 121.1, 121.7, 124.3, 140.7, 147.0, 155.6, 208.1; MS (EI) *m/z* 248 (M^+, 24.50), 231 (M^+-17, 21.19), 230 (M^+-18, 14.18), 205 (M^+-43, 44.21), 189 (M^+-59, 46.10), 188 (M^+-60, 78.26), 43 (M^+-205, 100); Found: C, 67.88; H, 6.43%. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%.



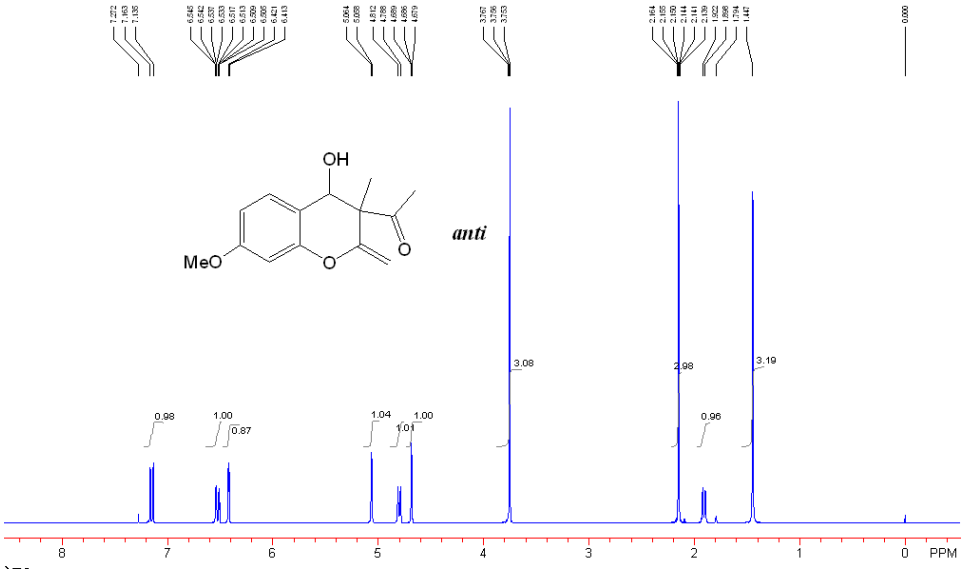
***syn*-3c**: a pale yellow oil; IR (CH_2Cl_2) ν 3488, 1702 (C=O), 1655, 1484, 1276, 1049 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.62 (3H, s, CH_3), 2.19 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 4.09 (1H, d, *J* = 11.4 Hz, OH), 4.58 (1H, d, *J* = 11.4 Hz, CH), 4.78 (1H, d, *J* = 2.1 Hz, =CH), 5.13 (1H, d, *J* = 2.1 Hz, =CH), 6.81 (1H, d, *J* = 8.4 Hz, ArH), 6.95-7.00 (1H, m, ArH), 7.17-7.20 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 26.6, 53.7, 56.0, 72.6, 95.3, 111.1, 117.6, 122.0, 127.4, 139.8, 146.6, 158.0, 213.7; MS (EI) *m/z* 248 (M^+, 3.85), 189 (M^+-59, 14.14), 188 (M^+-60, 100), 173 (M^+-75, 12.89), 43 (M^+-205, 11.61); Found: C, 67.80; H, 6.49%. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%.





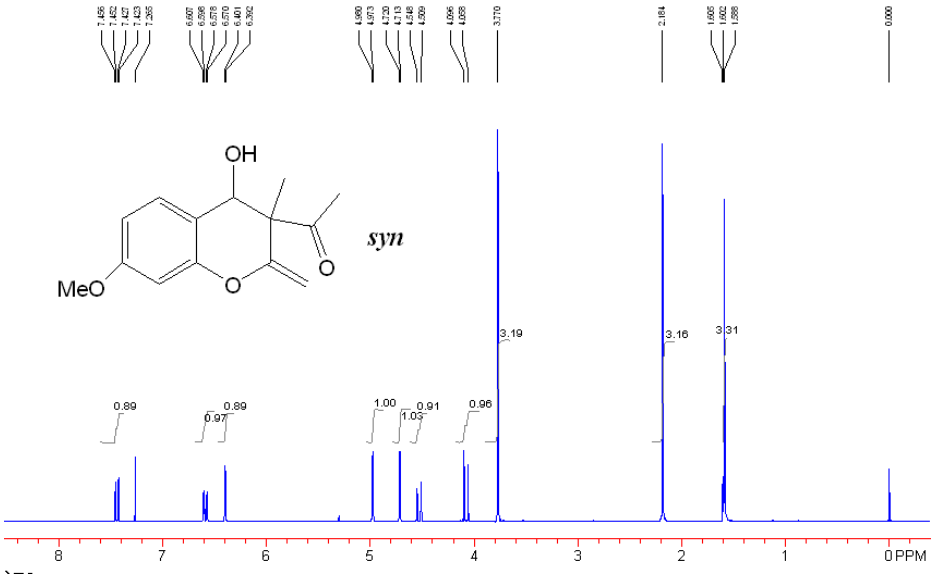
1-(4-Hydroxy-7-methoxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone

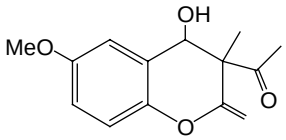
***anti*-3d**: a yellow oil; IR (CH_2Cl_2) ν 3411, 1710 (C=O), 1656, 1618, 1507, 1199, 1163 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.45 (3H, s, CH_3), 1.91 (1H, d, *J* = 7.5 Hz, OH), 2.16 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 4.68 (1H, d, *J* = 2.1 Hz, =CH), 4.80 (1H, d, *J* = 7.5 Hz, CH), 5.06 (1H, d, *J* = 2.1 Hz, =CH), 6.41-6.42 (1H, m, ArH), 6.51-6.55 (1H, m, ArH), 7.15 (1H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 25.9, 55.2, 56.3, 68.3, 95.7, 100.8, 108.7, 115.8, 130.4, 152.4, 156.0, 160.9, 208.1; MS (EI) *m/z* 248 (M^+, 5.38), 231 (M^+-17, 8.57), 230 (M^+-18, 14.87), 205 (M^+-43, 34.56), 189 (M^+-59, 23.88), 188 (M^+-60, 100), 43 (M^+-205, 33.24); Found: C, 67.79; H, 6.68%. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%.



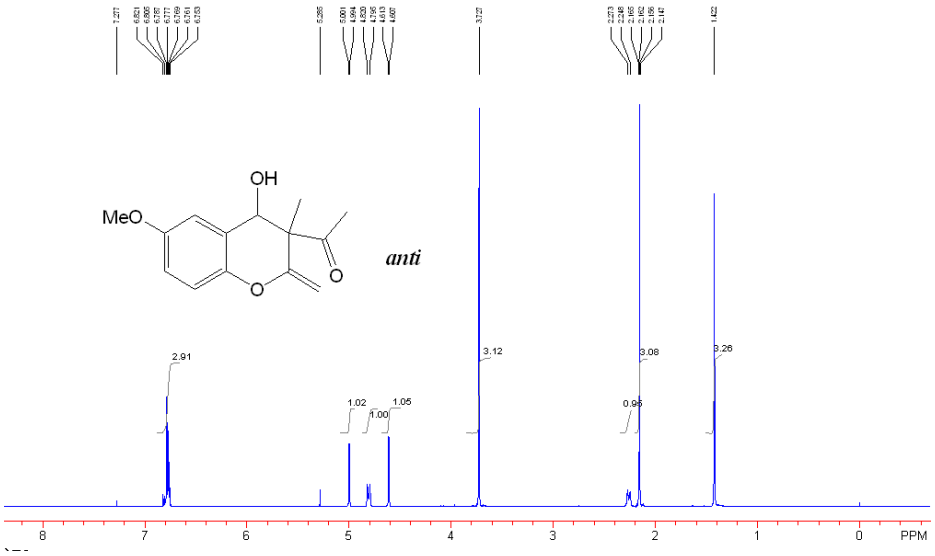
***syn*-3d**: a yellow oil; IR (CH_2Cl_2) ν 3487, 1702 (C=O), 1619, 1505, 1282, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.59 (3H, s, CH_3), 2.18 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 4.08 (1H, d, *J* = 11.4 Hz, OH), 4.53 (1H, d, *J* = 11.4 Hz, CH), 4.72 (1H, d, *J* = 2.1 Hz, =CH), 4.98 (1H, d, *J* = 2.1 Hz, =CH), 6.40 (1H, d, *J* = 2.7 Hz, ArH), 6.59 (1H, dd, *J* = 8.7, 2.7 Hz, ArH), 7.44 (1H, dd, *J* = 8.7, 1.2 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 26.7, 53.9, 55.3, 72.5, 94.7, 100.6, 108.4, 118.7, 126.9, 151.5, 158.4, 160.2, 213.9; MS (EI) *m/z* 248 (M^+, 8.57), 231 (M^+-17, 3.99), 230 (M^+-18, 8.87), 205 (M^+-43, 43.21), 189 (M^+-59, 20.78), 188 (M^+-60,

56.80), 151 (M^+-97, 100), 43 (M^+-205, 54.19); Found: C, 67.73; H, 6.47%. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%.

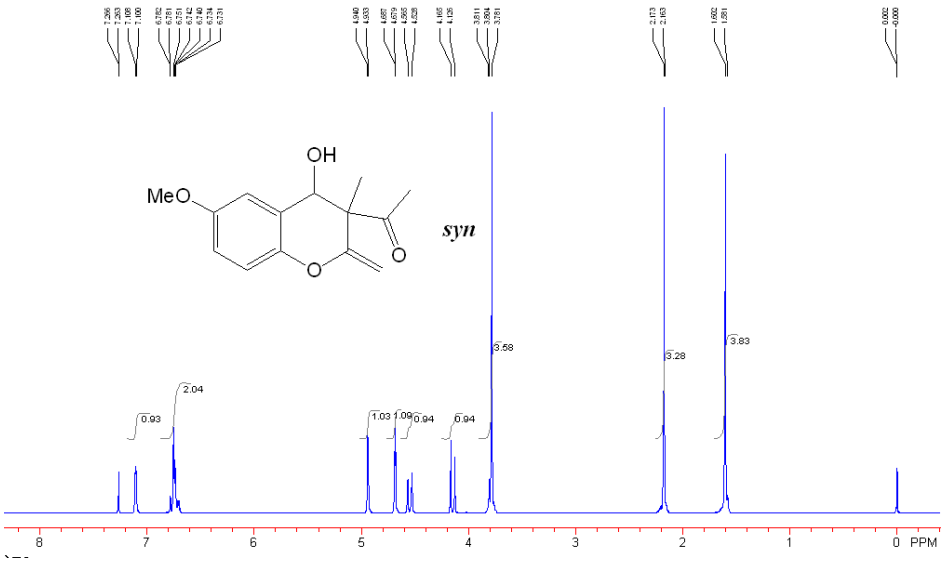


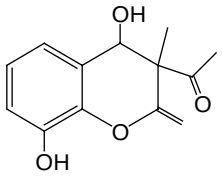


1-(4-Hydroxy-6-methoxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone ***anti*-3e**: a white solid; mp. 80-82 ^oC; IR (CH_2Cl_2) ν 3441, 1711 (C=O), 1655, 1492, 1226, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.42 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.26 (1H, d, *J* = 7.2 Hz, OH), 3.73 (3H, s, OCH_3), 4.61 (1H, d, *J* = 1.8 Hz, =CH), 4.80 (1H, d, *J* = 7.2 Hz, CH), 5.00 (1H, d, *J* = 1.8 Hz, =CH), 6.75-6.82 (3H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.9, 26.0, 55.5, 56.2, 69.0, 95.1, 113.3, 116.5, 116.7, 123.9, 145.4, 154.3, 156.1, 208.3; MS (EI) *m/z* 248 (M^+, 36.97), 231 (M^+-17, 20.59), 230 (M^+-18, 35.53), 205 (M^+-43, 53.30), 189 (M^+-59, 39.32), 188 (M^+-60, 31.19), 43 (M^+-205, 100); Found: C, 67.81; H, 6.49%. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%.

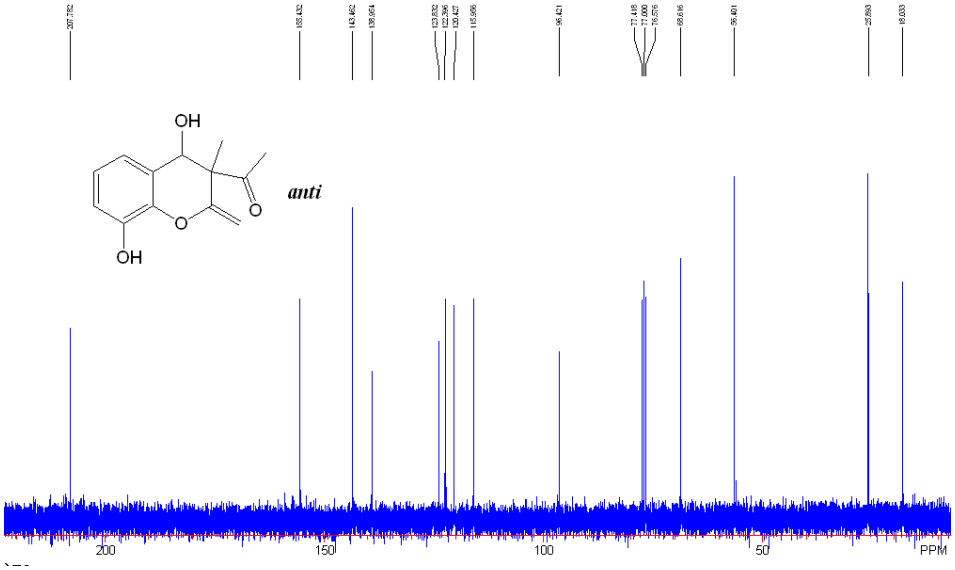


***syn*-3e:** a pale yellow oil; IR (CH_2Cl_2) ν 3504, 2932, 1702 (C=O), 1654, 1491, 1263, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.60 (3H, s, CH_3), 2.17 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 4.15 (1H, d, *J* = 11.4 Hz, OH), 4.55 (1H, d, *J* = 11.4 Hz, CH), 4.68 (1H, d, *J* = 2.1 Hz, =CH), 4.90 (1H, d, *J* = 2.1 Hz, =CH), 6.73-6.75 (1H, m, ArH), 7.10-7.11 (1H, m, ArH), 7.26-7.27 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 26.7, 53.8, 55.6, 72.7, 93.9, 110.2, 115.0, 115.9, 127.2, 144.5, 154.9, 158.4, 214.2; MS (EI) *m/z* 248 (M^+, 32.44), 231 (M^+-17, 11.57), 230 (M^+-18, 14.03), 205 (M^+-43, 54.35), 189 (M^+-59, 33.38), 188 (M^+-60, 100), 173 (M^+-75, 33.41), 152 (M^+-96, 96.10), 43 (M^+-205, 71.10); Found: C, 67.92; H, 6.40%. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%.



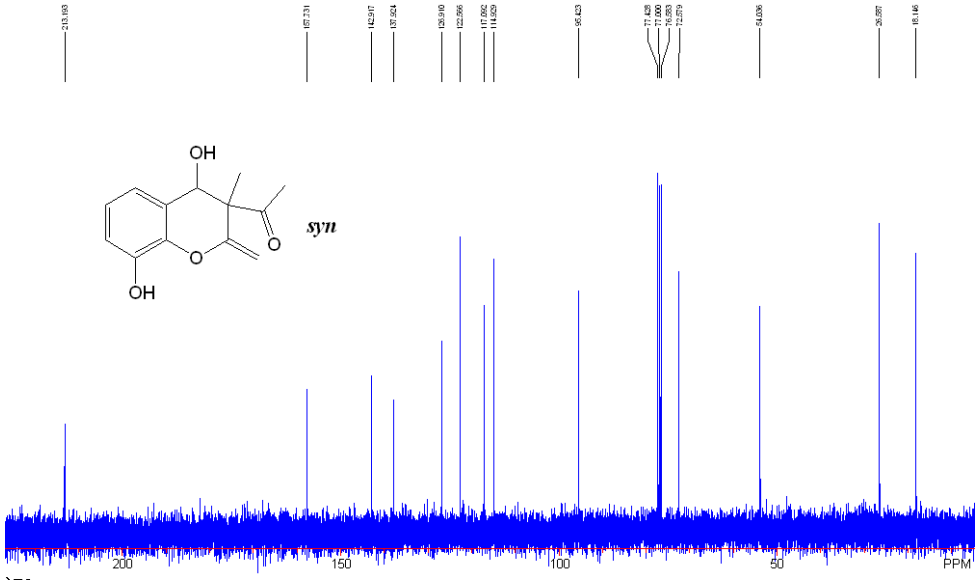


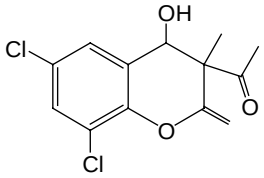
1-(4,8-Dihydroxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone *anti*-3f: a pale yellow oil; IR (CH_2Cl_2) ν 3404, 1708 (C=O), 1656, 1478, 1232, 1197 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.46 (3H, s, CH_3), 2.14 (3H, s, CH_3), 2.35 (1H, d, *J* = 6.9 Hz, OH), 4.72 (1H, d, *J* = 2.1 Hz, =CH), 4.88 (1H, d, *J* = 6.9 Hz, CH), 5.09 (1H, d, *J* = 2.1 Hz, =CH), 5.94 (1H, br s, OH), 6.79-6.85 (3H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.0, 25.9, 56.4, 68.6, 96.4, 116.0, 120.4, 122.4, 123.8, 139.0, 143.5, 155.4, 207.8; MS (EI) *m/z* 234 (M^+, 6.81), 163 (M^+-71, 100), 138 (M^+-96, 43.31), 137 (M^+-97, 18.03), 43 (M^+-191, 28.06); HRMS (EI) calcd. for $C_{13}H_{14}O_4$: 234.0892, Found: 234.0863.



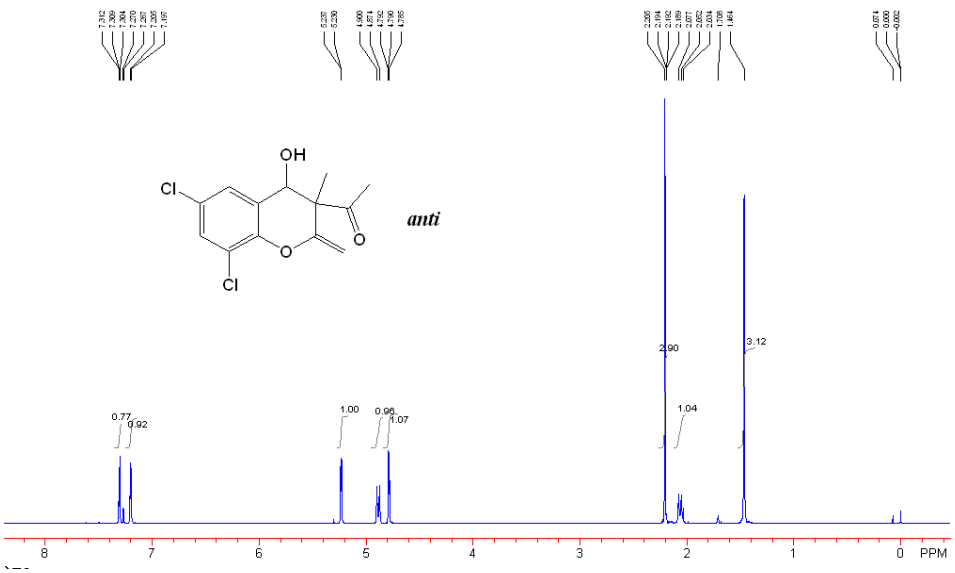
***syn*-3f**: a pale yellow oil; IR (CH_2Cl_2) ν 3459, 1702 (C=O), 1656, 1474, 1296, 1215, 1062 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.62 (3H, s, CH_3), 2.18 (3H, s, CH_3), 4.11 (1H, d, *J* = 12.0 Hz, OH), 4.59 (1H, d, *J* = 12.0 Hz, CH), 4.81 (1H, d, *J* = 2.4 Hz, =CH), 5.05 (1H, d, *J* = 2.4 Hz, =CH), 5.62 (1H, br s, OH), 6.83-6.86 (1H, m, ArH), 6.90-6.95 (1H, m, ArH), 7.08-7.11 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.1, 26.6, 54.0, 72.6, 95.4, 114.9, 117.1, 122.6, 126.9, 137.9, 142.9, 157.7, 213.2; MS (EI) *m/z* 234 (M^+, 8.08), 163 (M^+-71, 100), 138

(M^+-96, 25.12), 137 (M^+-97, 10.77), 43 (M^+-191, 28.38); HRMS (EI) calcd. for $C_{13}H_{14}O_4$: 234.0892, Found: 234.0885.

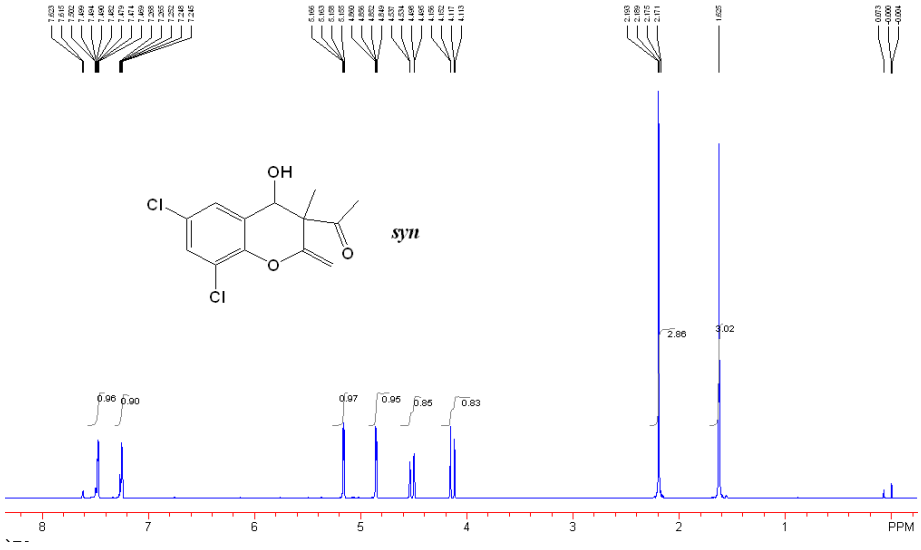


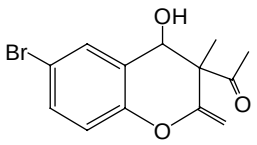


1-(6,8-Dichloro-4-hydroxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone *anti*-3g: a white solid; mp. 127-128 ^oC; IR (CH_2Cl_2) ν 3497, 3414, 1712 (C=O), 1660, 1459, 1259, 1190 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.46 (3H, s, CH_3), 2.06 (1H, d, *J* = 7.5 Hz, OH), 2.21 (3H, s, CH_3), 4.79 (1H, d, *J* = 2.1 Hz, =CH), 4.89 (1H, d, *J* = 7.5 Hz, CH), 5.23 (1H, d, *J* = 2.1 Hz, =CH), 7.20 (1H, d, *J* = 2.4 Hz, ArH), 7.31 (1H, d, *J* = 2.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.5, 26.0, 55.8, 68.3, 97.5, 121.5, 126.2, 126.7, 127.7, 130.1, 146.1, 155.0, 207.8; MS (EI) *m/z* 288 (M^++2, 5.88), 287 (M^++1, 2.51), 286 (M^+, 8.95), 269 (M^+-17, 8.76), 243 (M^+-43, 21.45), 228 (M^+-58, 40.52), 226 (M^+-60, 61.87), 43 (M^+-243, 100); Found: C, 54.30; H, 4.23%. $C_{13}H_{12}O_3Cl_2$ requires C, 54.38; H, 4.21%.



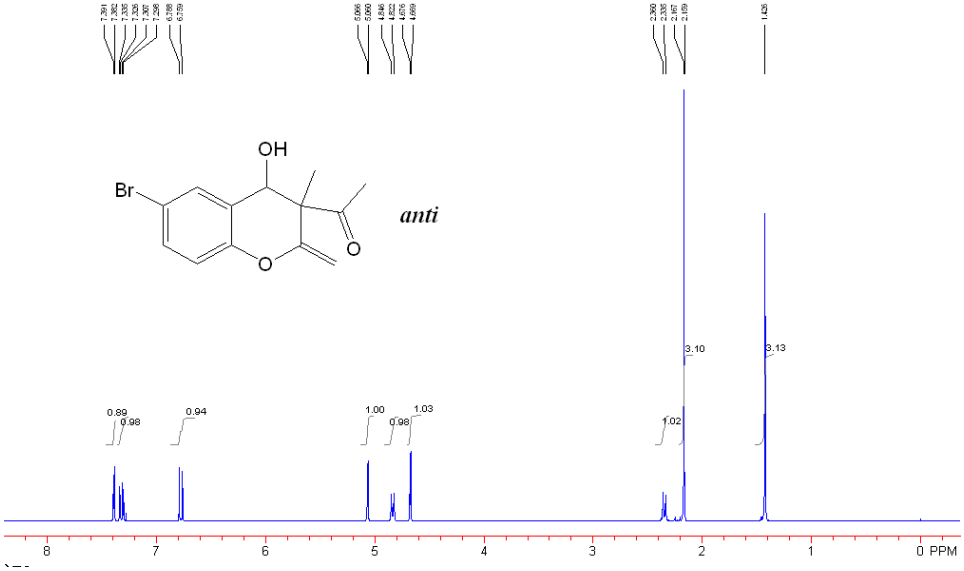
***syn*-3g**: a pale yellow oil; IR (CH_2Cl_2) ν 3488, 2927, 1704 (C=O), 1658, 1452, 1262, 1187 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.63 (3H, s, CH_3), 2.19 (3H, s, CH_3), 4.13 (1H, d, *J* = 11.7 Hz, OH), 4.52 (1H, d, *J* = 11.7 Hz, CH), 4.86 (1H, d, *J* = 2.4 Hz, =CH), 5.16 (1H, d, *J* = 2.4 Hz, =CH), 7.25-7.27 (1H, m, ArH), 7.47-7.48 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.0, 26.5, 53.5, 72.2, 96.6, 120.8, 124.7, 127.2, 129.1, 129.3, 145.2, 157.1, 213.3; MS (EI) *m/z* 288 (M^++2, 1.37), 287 (M^++1, 0.61), 286 (M^+, 2.39), 269 (M^+-17, 2.61), 243 (M^+-43, 7.63), 228 (M^+-58, 47.53), 226 (M^+-60, 100), 43 (M^+-243, 70.48); Found: C, 54.21; H, 4.25%. $C_{13}H_{12}O_3Cl_2$ requires C, 54.38; H, 4.21%.





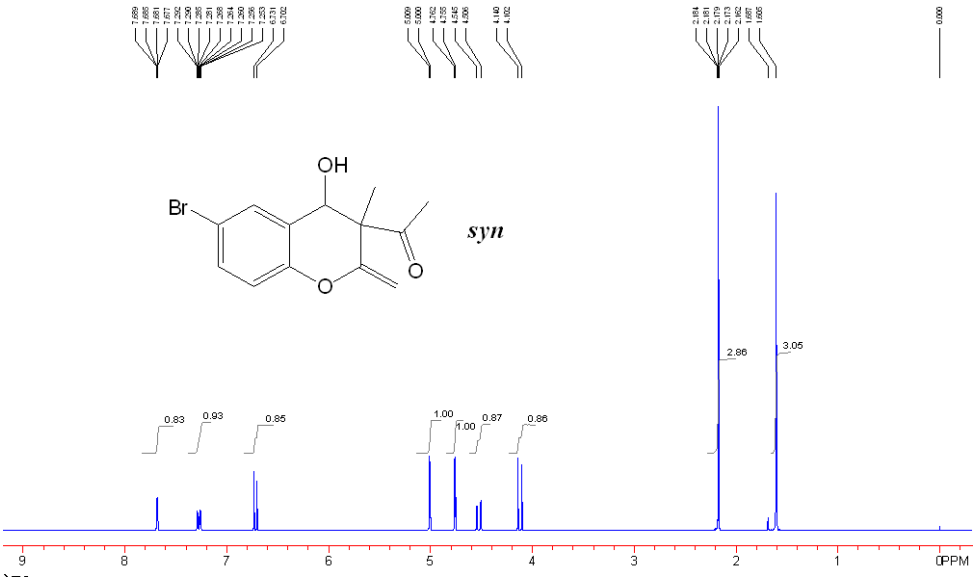
1-(6-Bromo-4-hydroxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone

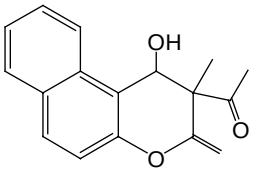
***anti*-3h**: a colorless needle crystal; mp. 118-122 ^{o}C; IR (CH_2Cl_2) ν 3407, 1712 (C=O), 1656, 1476, 1244, 1187 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.43 (3H, s, CH_3), 2.17 (3H, s, CH_3), 2.35 (1H, d, *J* = 7.5 Hz, OH), 4.67 (1H, d, *J* = 2.1 Hz, =CH), 4.82 (1H, d, *J* = 7.5 Hz, CH), 5.06 (1H, d, *J* = 2.1 Hz, =CH), 6.77 (1H, d, *J* = 8.7 Hz, ArH), 7.32 (1H, dd, *J* = 8.7, 2.4 Hz, ArH), 7.39 (1H, d, *J* = 2.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 17.7, 25.9, 55.9, 68.3, 96.3, 114.1, 117.8, 125.5, 132.1, 132.9, 150.6, 155.5, 208.0; MS (EI) *m/z* 298 (M^++2, 4.39), 296 (M^+, 4.96), 281 (M^+-15, 10.82), 279 (M^+-17, 8.72), 255 (M^+-41, 25.08), 253 (M^+-43, 22.57), 238 (M^+-58, 27.21), 236 (M^+-60, 26.06), 43 (M^+-253, 100); Found: C, 52.28; H, 4.42%. $C_{13}H_{13}O_3Br$ requires C, 52.55; H, 4.41%.



***syn*-3h**: a pale yellow solid; mp. 49-51 ^{o}C; IR (CH_2Cl_2) ν 3485, 1704 (C=O), 1652, 1472, 1260, 1189 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.61 (3H, s, CH_3), 2.17 (3H, s, CH_3), 4.12 (1H, d, *J* = 11.4 Hz, OH), 4.53 (1H, d, *J* = 11.4 Hz, CH), 4.76 (1H, d, *J* = 2.4 Hz, =CH), 5.00 (1H, d, *J* = 2.4 Hz, =CH), 6.72 (1H, d, *J* = 9.0 Hz, ArH), 7.23-7.26 (1H, m, ArH), 7.68-7.69 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.0, 26.5, 53.6, 72.2, 95.3, 114.8, 117.0, 128.5, 129.0, 131.7, 149.7, 157.7, 213.6; MS (EI) *m/z* 298 (M^++2, 5.23), 296 (M^+, 5.72), 281 (M^+-15,

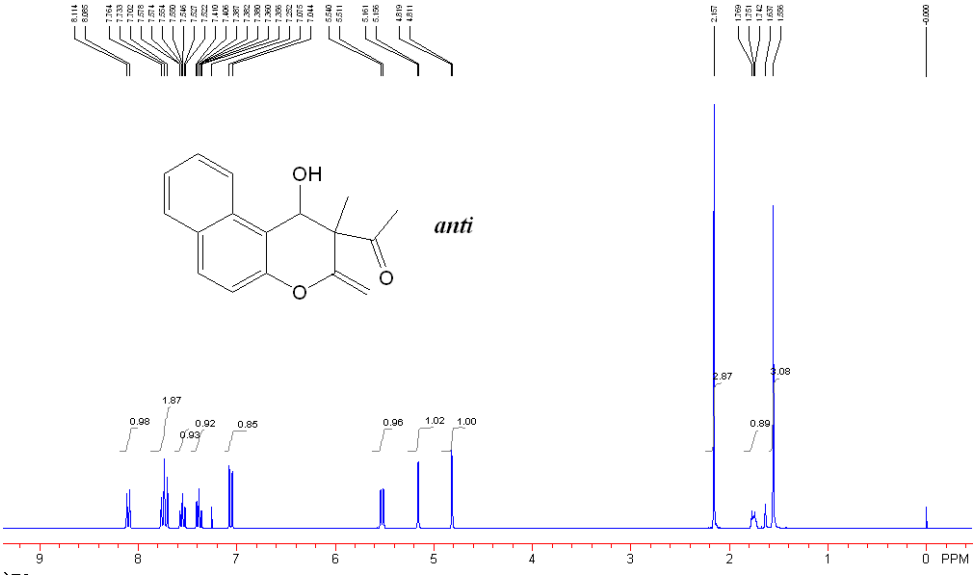
8.05), 279 (M^+-17, 7.09), 255 (M^+-41, 27.79), 253 (M^+-43, 31.35), 238 (M^+-58, 97.18), 236 (M^+-60, 100), 43 (M^+-253, 88.05); Found: C, 52.57; H, 4.38%. $C_{13}H_{13}O_3Br$ requires C, 52.55; H, 4.41%.



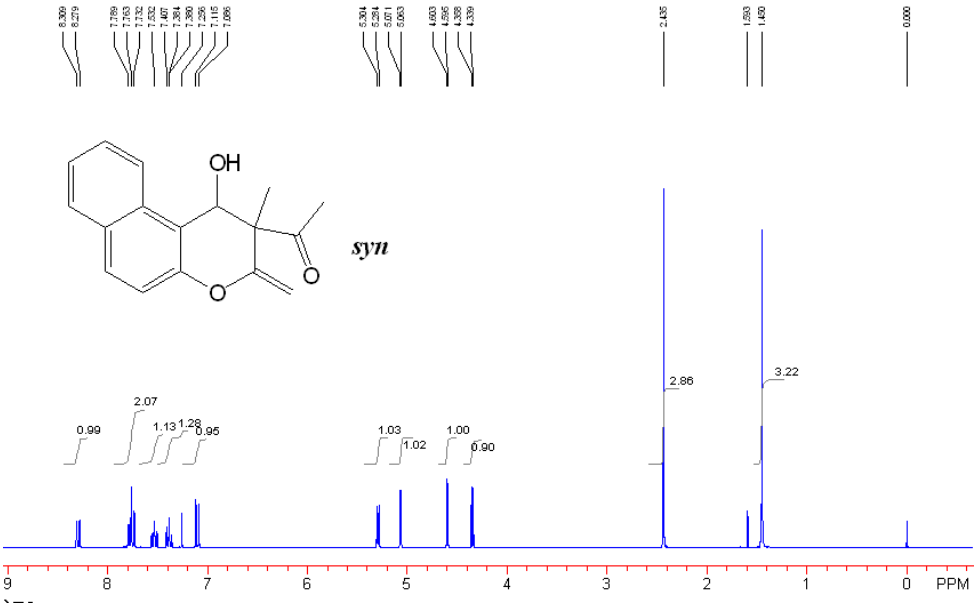


1-(1-Hydroxy-2-methyl-3-methylene-2,3-dihydro-1*H*-benzo[*f*]chromen-2-yl)ethanone

***anti*-3i**: a white solid; mp. 109-112 ^oC; IR (CH_2Cl_2) ν 3415, 1709 (C=O), 1655, 1516, 1356, 1237, 1202 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.56 (3H, s, CH_3), 1.76 (1H, d, *J* = 8.7 Hz, OH), 2.16 (3H, s, CH_3), 4.82 (1H, d, *J* = 2.1 Hz, =CH), 5.16 (1H, d, *J* = 2.1 Hz, =CH), 5.53 (1H, d, *J* = 8.7 Hz, CH), 7.06 (1H, d, *J* = 9.0 Hz, ArH), 7.36-7.41 (1H, m, ArH), 7.52-7.58 (1H, m, ArH), 7.70-7.76 (2H, m, ArH), 8.10 (1H, d, *J* = 9.0 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 18.2, 25.7, 56.0, 65.2, 96.3, 115.3, 117.2, 122.1, 124.2, 127.4, 128.3, 129.6, 130.9, 131.9, 149.5, 155.7, 207.7; MS (EI) *m/z* 268 (M^+, 21.79), 251 (M^+-17, 37.30), 250 (M^+-18, 36.35), 225 (M^+-43, 89.18), 209 (M^+-59, 61.63), 208 (M^+-60, 100), 165 (M^+-103, 41.56), 43 (M^+-225, 37.30); Found: C, 76.13; H, 6.07%. $C_{17}H_{16}O_3$ requires C, 76.10; H, 6.01%.



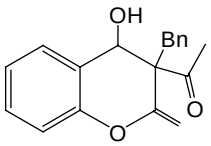
***syn*-3i**: a pale yellow oil; IR (CH_2Cl_2) ν 3481, 1701 (C=O), 1655, 1439, 1235, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.47 (3H, s, CH_3), 2.43 (3H, s, CH_3), 4.35 (1H, d, *J* = 5.7 Hz, OH), 4.60 (1H, d, *J* = 2.4 Hz, =CH), 5.07 (1H, d, *J* = 2.4 Hz, =CH), 5.29 (1H, d, *J* = 5.7 Hz, CH), 7.10 (1H, d, *J* = 9.0 Hz, ArH), 7.36-7.41 (1H, m, ArH), 7.50-7.56 (1H, m, ArH), 7.73-7.79 (2H, m, ArH), 8.29 (1H, d, *J* = 9.0 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 19.1, 27.5, 54.4, 69.7, 95.8, 114.7, 117.1, 123.3, 124.0, 127.0, 128.4, 129.9, 130.6, 132.4, 150.1, 155.2, 212.0; MS (EI) *m/z* 268 (M^+, 23.05), 251 (M^+-17, 37.99), 250 (M^+-18, 29.95), 225 (M^+-43, 100), 209 (M^+-59, 64.74), 208 (M^+-60, 72.92), 43 (M^+-225, 65.36); HRMS (EI) calcd. for $C_{17}H_{16}O_3$: 268.1099, Found: 268.1073.



Reactions of salicylic aldehydes with 3-benzylpenta-3,4-dien-2-one catalyzed by DBU.

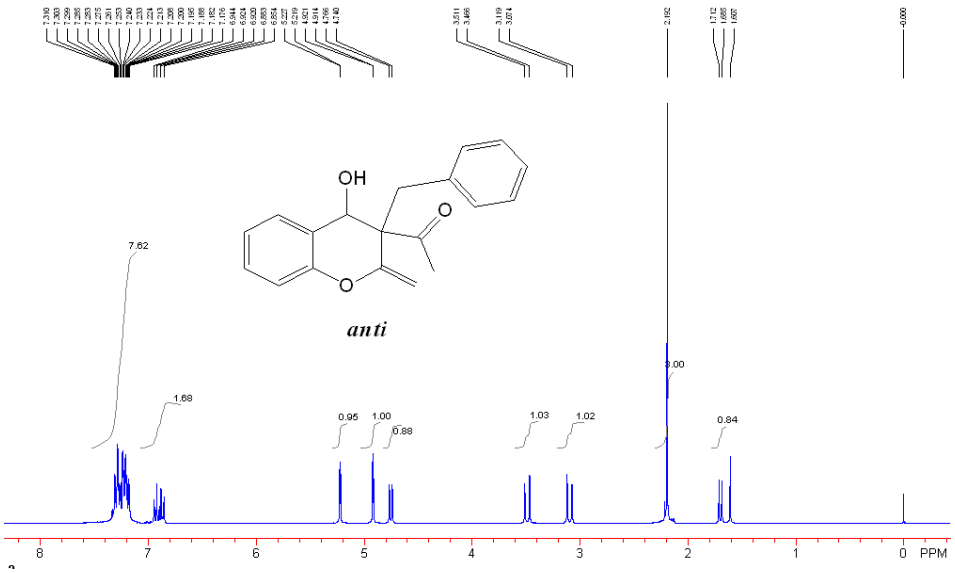
Typical reaction procedure of salicylaldehyde with 3-benzylpenta-3,4-dien-2-one in the presence of DBU in DMSO at room temperature.

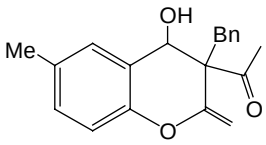
To a Schlenk tube with DMSO (0.5 mL) was added salicylaldehyde (61 mg, 0.5 mmol), 3-benzylpenta-3,4-dien-2-one (172 mg, 1.0 mmol) and DBU (8 mg, 0.05 mmol). The solution was stirred for 48 h at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 15 mL) and extracted with dichloromethane (2 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the adduct *anti*-**4a** (eluent: EtOAc/petroleum= 1/4, 123 mg, yield 84%) as a white solid. The configuration of **4a** was determined by comparison of ^{1}H-NMR spectroscopic data with those of adducts **3**.



1-(3-Benzyl-4-hydroxy-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone *anti*-4a: a white solid; mp. 107-110 ^{o}C; IR (CH_2Cl_2) ν 3464, 3030, 1712 (C=O), 1589, 1487, 1357, 1193, 1032 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.74 (1H, d, *J* = 7.8 Hz, OH), 2.19 (3H, s,

CH_3), 3.09 (1H, d, *J* = 13.5 Hz, CH_2), 3.49 (1H, d, *J* = 13.5 Hz, CH_2), 4.75 (1H, d, *J* = 7.8 Hz, CH), 4.91 (1H, d, *J* = 1.8 Hz, =CH), 5.22 (1H, d, *J* = 1.8 Hz, =CH), 6.85-6.94 (2H, m, ArH), 7.17-7.31 (7H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.4, 35.7, 60.8, 65.3, 96.7, 115.9, 122.1, 123.5, 127.1, 128.3, 129.8, 129.9, 130.2, 134.9, 151.6, 155.5, 205.5; MS (EI) *m/z* 294 (M^+, 2.71), 277 (M^+-17, 14.70), 276 (M^+-18, 27.45), 251 (M^+-43, 28.77), 235 (M^+-59, 26.58), 234 (M^+-60, 30.85), 233 (M^+-61, 100), 91 (M^+-203, 43.93); Found: C, 77.17; H, 6.11. $C_{19}H_{18}O_3$ requires C, 77.53; H, 6.16%.

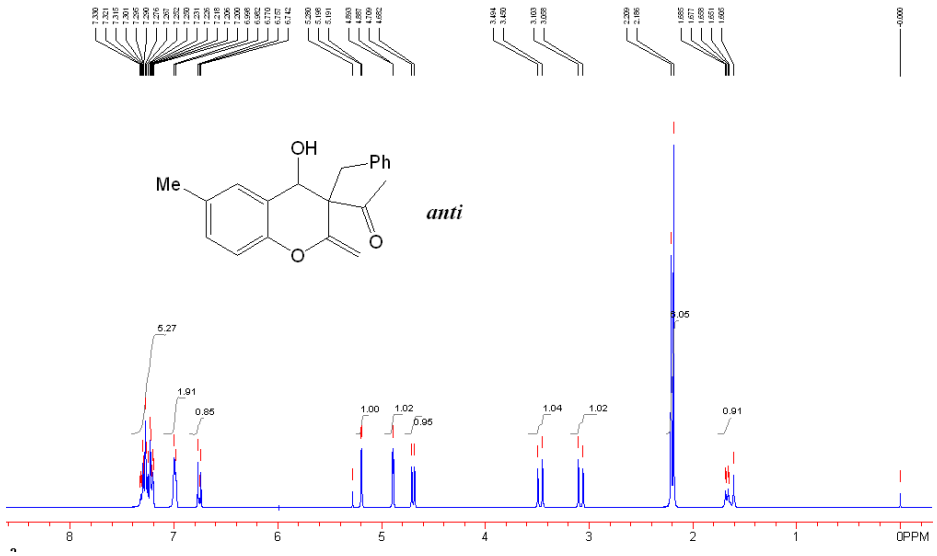


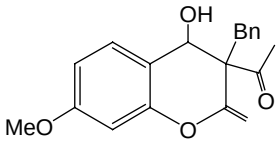


1-(3-Benzyl-4-hydroxy-6-methyl-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone

***anti*-4b**: **a** white solid; mp. 108-110 ^{o}C; IR (CH_2Cl_2) ν 3529, 3030, 1709 (C=O), 1655, 1498, 1199, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.67 (1H, d, *J* = 7.8 Hz, OH), 2.19 (3H, s, CH_3), 2.21 (3H, s, CH_3), 3.08 (1H, d, *J* = 13.5 Hz, CH_2), 3.47 (1H, d, *J* = 13.5 Hz, CH_2), 4.70 (1H, d, *J* = 7.8 Hz, CH), 4.89 (1H, d, *J* = 1.8 Hz, =CH), 5.19 (1H, d, *J* = 1.8 Hz, =CH), 6.76 (1H, d, *J* = 8.4 Hz, ArH), 6.98-7.00 (2H, m, ArH), 7.20-7.30 (5H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.3, 26.5, 35.8, 60.9, 65.4, 96.4, 115.6, 123.2, 127.0, 128.3, 130.0, 130.2, 130.6, 131.5, 134.9, 149.4, 155.7, 205.6; MS (EI) *m/z* 308 (M^+, 5.92), 290 (M^+-18, 31.71), 265 (M^+-43, 31.41), 249 (M^+-59, 30.23), 248 (M^+-60, 34.09), 247 (M^+-61, 100), 91

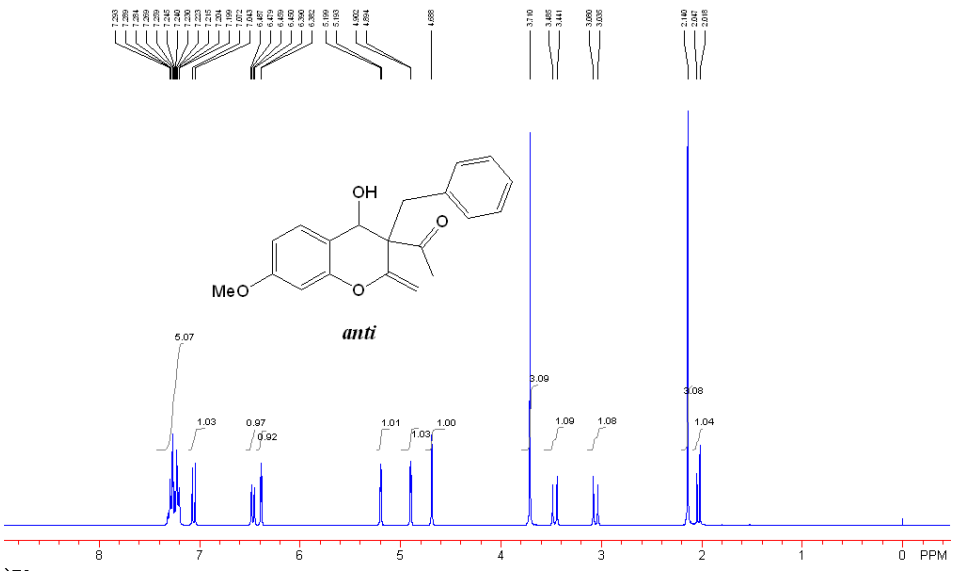
(M^+-217, 32.30); Found: C, 77.83; H, 6.60%. $C_{20}H_{20}O_3$ requires C, 77.90; H, 6.54%.

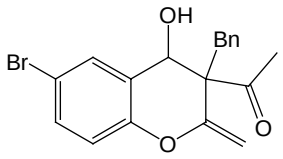




1-(3-Benzyl-4-hydroxy-7-methoxy-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone

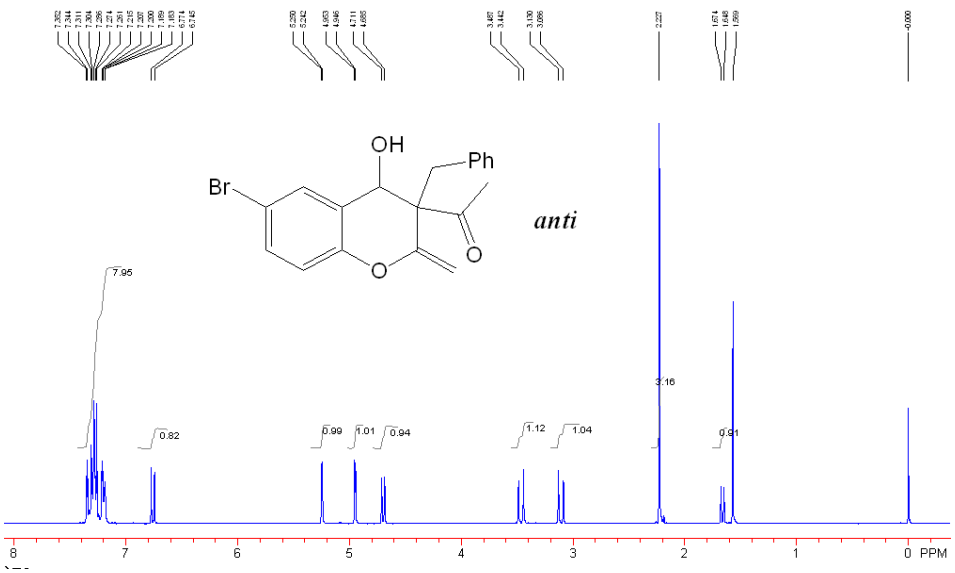
***anti*-4d**: a pale yellow oil; IR (CH_2Cl_2) ν 3504, 2961, 1711 (C=O), 1619, 1506, 1198, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.03 (1H, d, *J* = 8.7 Hz, OH), 2.16 (3H, s, CH_3), 3.09 (1H, d, *J* = 13.5 Hz, CH_2), 3.48 (1H, d, *J* = 13.5 Hz, CH_2), 3.74 (3H, s, OCH_3), 4.71 (1H, m, CH), 4.92 (1H, d, *J* = 1.8 Hz, =CH), 5.22 (1H, d, *J* = 1.8 Hz, =CH), 6.40-6.41 (1H, m, ArH), 6.48-6.52 (1H, m, ArH), 7.10 (1H, d, *J* = 8.4 Hz, ArH), 7.22-7.33 (5H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.6, 35.9, 55.2, 60.9, 64.8, 96.8, 100.8, 108.8, 116.0, 127.0, 128.3, 130.2, 130.6, 134.9, 152.6, 155.5, 160.9, 205.5; MS (EI) *m/e* 324 (M^+, 1.11), 306 (M^+-18, 21.82), 281 (M^+-43, 20.21), 265 (M^+-59, 26.30), 264 (M^+-60, 36.30), 263 (M^+-61, 100), 233 (M^+-91, 35.76), 91 (M^+-233, 47.49); HRMS (EI) calcd. for $C_{20}H_{20}O_4$: 324.1362, Found: 324.1332.



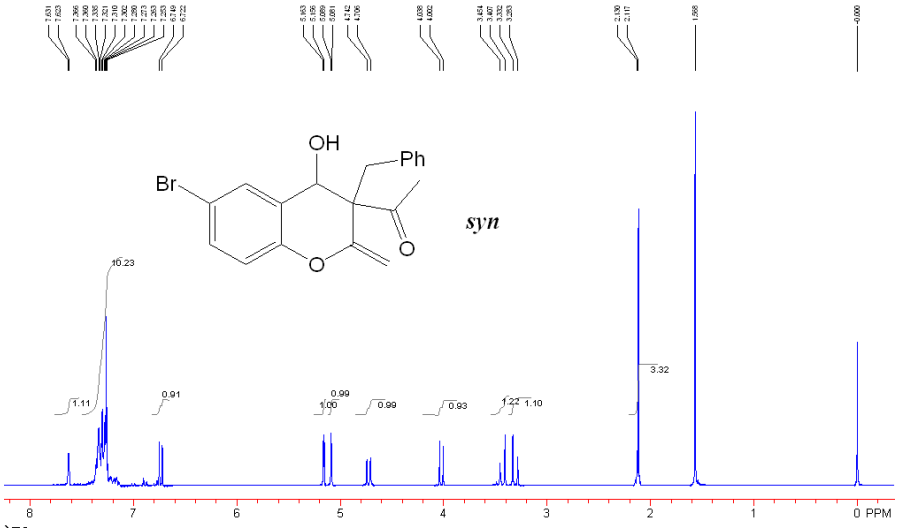


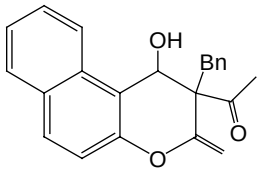
1-(3-Benzyl-6-bromo-4-hydroxy-2-methylene-3,4-dihydro-2*H*-chromen-3-yl)ethanone

***anti*-4h**: a colorless needle crystal; mp. 133-136 ^{o}C; IR (CH_2Cl_2) ν 3453, 3030, 1711 (C=O), 1655, 1477, 1247, 1187 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.66 (1H, d, *J* = 7.5 Hz, OH), 2.23 (3H, s, CH_3), 3.11 (1H, d, *J* = 13.5 Hz, CH_2), 3.46 (1H, d, *J* = 13.5 Hz, CH_2), 4.70 (1H, d, *J* = 7.5 Hz, CH), 4.95 (1H, d, *J* = 1.8 Hz, =CH), 5.25 (1H, d, *J* = 1.8 Hz, =CH), 6.76 (1H, d, *J* = 8.4 Hz, ArH), 7.18-7.35 (7H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.3, 35.6, 60.6, 64.9, 97.2, 114.1, 117.7, 125.6, 127.2, 128.4, 130.1, 132.3, 132.7, 134.5, 150.6, 155.0, 205.4; MS (EI) *m/z* 374 (M^++2, 3.12), 372 (M^+, 2.95), 356 (M^+-16, 18.60), 354 (M^+-18, 18.03), 331 (M^+-41, 12.98), 329 (M^+-43, 14.45), 313 (M^+-59, 100), 311 (M^+-61, 75.19), 91 (M^+-281, 52.15); Found: C, 61.20; H, 4.65%. $C_{19}H_{17}O_3Br$ requires C, 61.14; H, 4.59%.



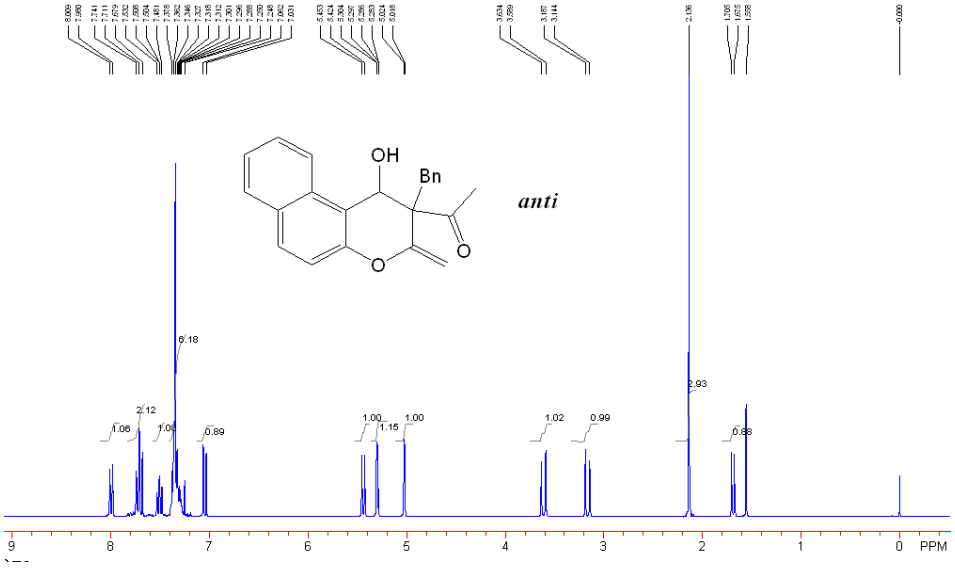
***syn*-4h**: a pale yellow oil; IR (CH_2Cl_2) ν 3470, 3029, 1703 (C=O), 1653, 1475, 1259, 1186, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.12 (3H, s, CH_3), 3.31 (1H, d, *J* = 14.4 Hz, CH_2), 3.43 (1H, d, *J* = 14.4 Hz, CH_2), 4.02 (1H, d, *J* = 10.5 Hz, OH), 4.72 (1H, d, *J* = 10.5 Hz, CH), 5.09 (1H, d, *J* = 2.4 Hz, =CH), 5.16 (1H, d, *J* = 2.4 Hz, =CH), 6.74 (1H, d, *J* = 8.4 Hz, ArH), 7.25-7.36 (6H, m, ArH), 7.62-7.63 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 28.8, 37.4, 58.6, 69.6, 97.5, 114.8, 117.0, 127.3, 127.8, 128.4, 129.6, 130.7, 132.0, 135.1, 149.7, 155.6, 212.9; MS (EI) *m/z* 374 (M^++2, 1.02), 372 (M^+, 0.87), 356 (M^+-16, 7.73), 354 (M^+-18, 7.27), 331 (M^+-41, 1.75), 329 (M^+-43, 2.36), 313 (M^+-59, 100), 311 (M^+-61, 82.59), 91 (M^+-281, 29.26); Found: C, 61.19; H, 4.82%. $C_{19}H_{17}O_3Br$ requires C, 61.14; H, 4.59%.





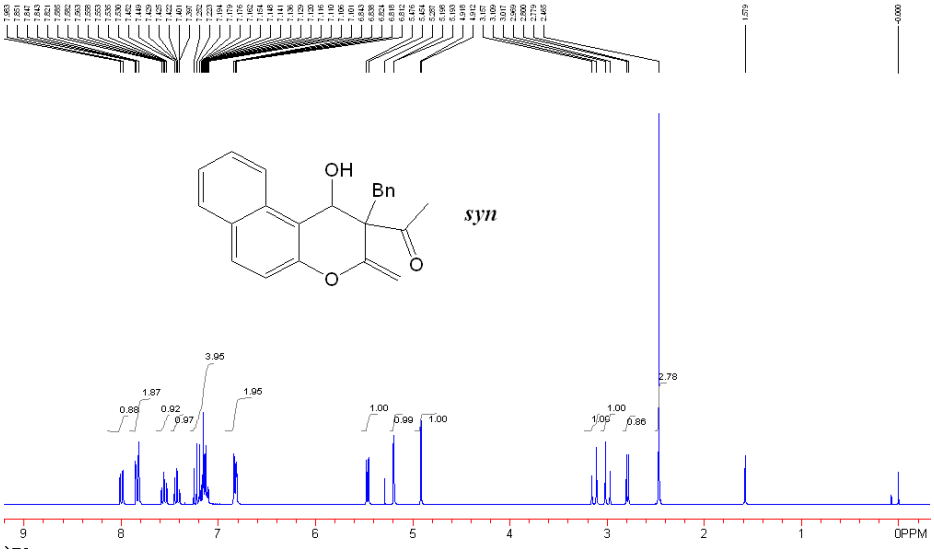
1-(2-Benzyl-1-hydroxy-3-methylene-2,3-dihydro-1*H*-benzo[*f*]chromen-2-yl)ethanone

***anti*-4i**: a white solid; mp. 146-148 ^{o}C; IR (CH_2Cl_2) ν 3552, 3030, 1713 (C=O), 1651, 1515, 1356, 1236 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.69 (1H, d, *J* = 9.0 Hz, OH), 2.14 (3H, s, CH_3), 3.17 (1H, d, *J* = 13.2 Hz, CH_2), 3.61 (1H, d, *J* = 13.2 Hz, CH_2), 5.02 (1H, d, *J* = 2.4 Hz, =CH), 5.30 (1H, d, *J* = 2.4 Hz, =CH), 5.44 (1H, d, *J* = 9.0 Hz, CH), 7.05 (1H, d, *J* = 9.0 Hz, ArH), 7.30-7.38 (6H, m, ArH), 7.48-7.53 (1H, m, ArH), 7.68-7.74 (2H, m, ArH), 8.00 (1H, d, *J* = 9.0 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.6, 35.9, 60.7, 61.8, 97.2, 115.4, 117.1, 122.1, 124.3, 127.2, 127.4, 128.3, 128.4, 129.7, 130.3, 130.7, 131.9, 135.0, 149.8, 155.4, 205.3; MS (EI) *m/z* 344 (M^+, 15.80), 327 (M^+-17, 34.05), 326 (M^+-18, 26.87), 301 (M^+-43, 35.21), 285 (M^+-59, 51.16), 284 (M^+-60, 75.86), 283 (M^+-61, 100), 91 (M^+-253, 41.20); Found: C, 80.04; H, 5.99. $C_{23}H_{20}O_3$ requires C, 80.21; H, 5.85%.



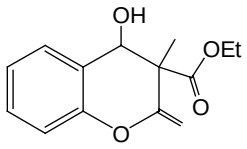
***syn*-4i**: a pale yellow oil; IR (CH_2Cl_2) ν 3542, 3030, 2927, 1713 (C=O), 1626, 1439, 1240, 1184 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.47 (3H, s, CH_3), 2.79 (1H, d, *J* = 6.3 Hz, OH), 2.99 (1H, d, *J* = 14.4 Hz, CH_2), 3.13 (1H, d, *J* = 14.4 Hz, CH_2), 4.91 (1H, d, *J* = 1.5 Hz,

=CH), 5.20 (1H, d, *J* = 1.5 Hz, =CH), 5.47 (1H, d, *J* = 6.3 Hz, CH), 6.81-6.84 (2H, m, ArH), 7.10-7.22 (4H, m, ArH), 7.40-7.45 (1H, m, ArH), 7.53-7.59 (1H, m, ArH), 7.82-7.85 (2H, m, ArH), 8.00 (1H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 29.6, 39.1, 60.3, 66.1, 99.2, 113.3, 117.2, 121.9, 124.3, 127.1, 127.5, 128.2, 128.6, 129.7, 129.8, 131.3, 132.1, 134.8, 150.5, 152.2, 208.2; MS (EI) *m/z* 344 (M^+, 7.30), 327 (M^+-17, 16.33), 326 (M^+-18, 11.65), 301 (M^+-43, 9.45), 285 (M^+-59, 31.89), 284 (M^+-60, 100), 283 (M^+-61, 78.96), 43 (M^+-301, 70.20); Found: C, 80.12; H, 5.94. $C_{23}H_{20}O_3$ requires C, 80.21; H, 5.85%.

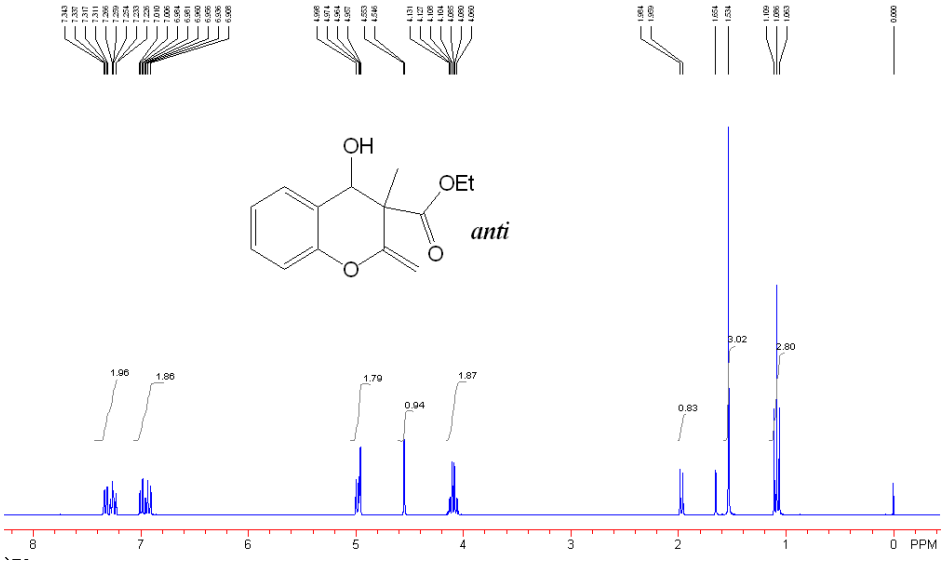


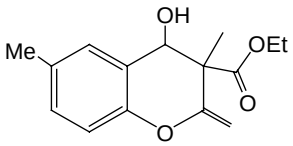
Reactions of salicylic aldehydes with ethyl 2-methylbuta-2,3-dienoate catalyzed by DBU. Typical reaction procedure of salicylaldehyde with ethyl 2-methylbuta-2,3-dienoate in the presence of DBU in DMSO at room temperature.

To a Schlenk tube with DMSO (0.5 mL) was added salicylaldehyde (61 mg, 0.5 mmol), ethyl 2-methylbuta-2,3-dienoate (126 mg, 1 mmol) and DBU (8 mg, 0.05 mmol). The solution was stirred for 48 h at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 15 mL) and extracted with dichloromethane (2 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give adduct the *anti*-**5a** (eluent: EtOAc/petroleum= 1/4, 73 mg, yield 59%) as a pale yellow oil. The configuration of **5a** was determined by comparison of ^{1}H-NMR spectroscopic data with those of adducts **3**.



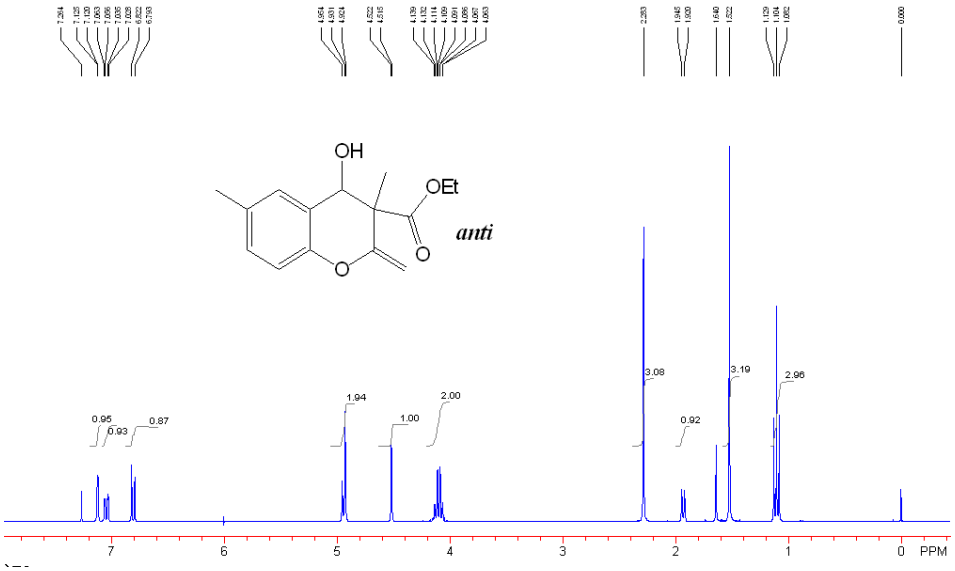
Ethyl 4-hydroxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromene-3-carboxylate *anti*-5a: a pale yellow oil; IR (CH_2Cl_2) ν 3473, 2983, 1728 (C=O), 1658, 1459, 1246, 1028 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.09 (3H, t, *J* = 7.2 Hz, CH_3), 1.54 (3H, s, CH_3), 1.90 (1H, d, *J* = 7.5 Hz, OH), 4.10 (2H, dq, *J* = 7.2, 1.5 Hz, CH_2), 4.55 (1H, d, *J* = 2.1 Hz, =CH), 4.96 (1H, d, *J* = 2.1 Hz, =CH), 4.99 (1H, d, *J* = 7.5 Hz, CH), 6.91-6.94 (1H, m, ArH), 6.96-7.01 (1H, m, ArH), 7.23-7.29 (1H, m, ArH), 7.32-7.35 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.7, 17.7, 50.8, 61.4, 69.4, 94.3, 115.8, 121.8, 123.1, 128.6, 130.0, 151.5, 155.1, 172.2; MS (EI) *m/z* 248 (M^+, 5.98), 230 (M^+-18, 5.86), 203 (M^+-45, 2.49), 175 (M^+-73, 100), 158 (M^+-90, 18.11), 121 (M^+-127, 19.31); HRMS (EI) calcd. for $C_{14}H_{16}O_4$: 248.1049, Found: 248.1048.

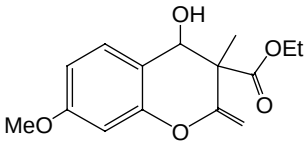




Ethyl 4-hydroxy-3,6-dimethyl-2-methylene-3,4-dihydro-2*H*-chromene-3-carboxylate *anti*-5b: a pale yellow oil; IR (CH_2Cl_2) ν 3464, 2989, 1718 (C=O), 1613, 1496, 1108, 1024 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.10 (3H, t, *J* = 7.2 Hz, CH_3), 1.52 (3H, s, CH_3),

1.93 (1H, d, *J* = 7.5 Hz, OH), 2.28 (3H, s, CH_3), 4.10 (2H, q, *J* = 7.2 Hz, CH_2), 4.52 (1H, d, *J* = 2.1 Hz, =CH), 4.93 (1H, d, *J* = 2.1 Hz, =CH), 4.94 (1H, d, *J* = 7.5 Hz, CH), 6.81 (1H, d, *J* = 8.7 Hz, ArH), 7.04 (1H, dd, *J* = 8.7, 1.8 Hz, ArH), 7.12 (1H, d, *J* = 1.8 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 17.7, 20.5, 50.9, 61.4, 69.5, 94.0, 115.6, 122.7, 128.8, 130.6, 131.1, 149.3, 155.3, 172.3; MS (EI) *m/z* 262 (M^+, 10.77), 244 (M^+-18, 3.99), 215 (M^+-47, 5.12), 189 (M^+-73, 100), 172 (M^+-90, 15.27), 135 (M^+-127, 15.74); HRMS (EI) calcd. for $C_{15}H_{18}O_4$: 262.1205, Found: 262.1202.



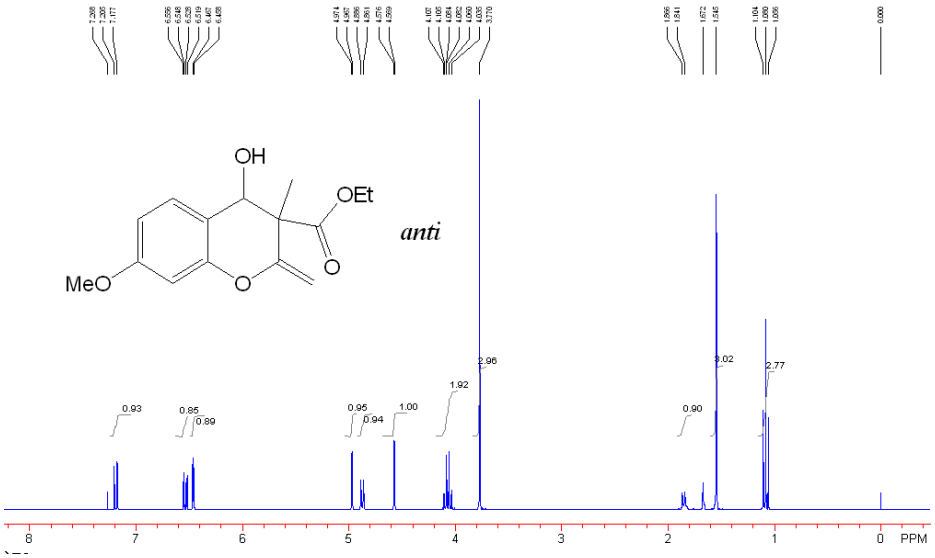


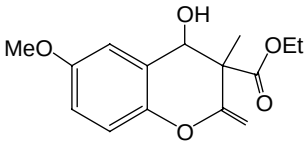
Ethyl

4-hydroxy-7-methoxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromene-3-carboxylate

***anti*-5d** : a pale yellow oil; IR (CH_2Cl_2) ν 3481, 2981, 1729 (C=O), 1619, 1507, 1201, 1027 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.08 (3H, t, *J* = 7.2 Hz, CH_3), 1.55 (3H, s, CH_3), 1.85 (1H, d, *J* = 7.5 Hz, OH), 3.77 (3H, s, OCH_3), 4.07 (2H, q, *J* = 7.2 Hz, CH_2), 4.57 (1H, d, *J* = 2.1 Hz, =CH), 4.87 (1H, d, *J* = 7.5 Hz, CH), 4.97 (1H, d, *J* = 2.1 Hz, =CH), 6.46 (1H, d, *J* = 2.4 Hz, ArH), 6.54 (1H, dd, *J* = 7.4, 2.4 Hz, ArH), 7.19 (1H, d, *J* = 7.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 18.1, 51.0, 55.3, 61.3, 69.2, 94.7, 100.7, 108.6, 115.5, 129.7, 152.6, 155.1, 161.1, 172.1; MS (EI) *m/z* 278 (M^+, 6.15), 260 (M^+-18, 11.64), 231 (M^+-47,

6.28), 205 (M^+-73, 100), 188 (M^+-90, 39.59), 151 (M^+-127, 63.20); HRMS (EI) calcd. for $C_{15}H_{18}O_5$: 278.1154, Found: 278.1168.

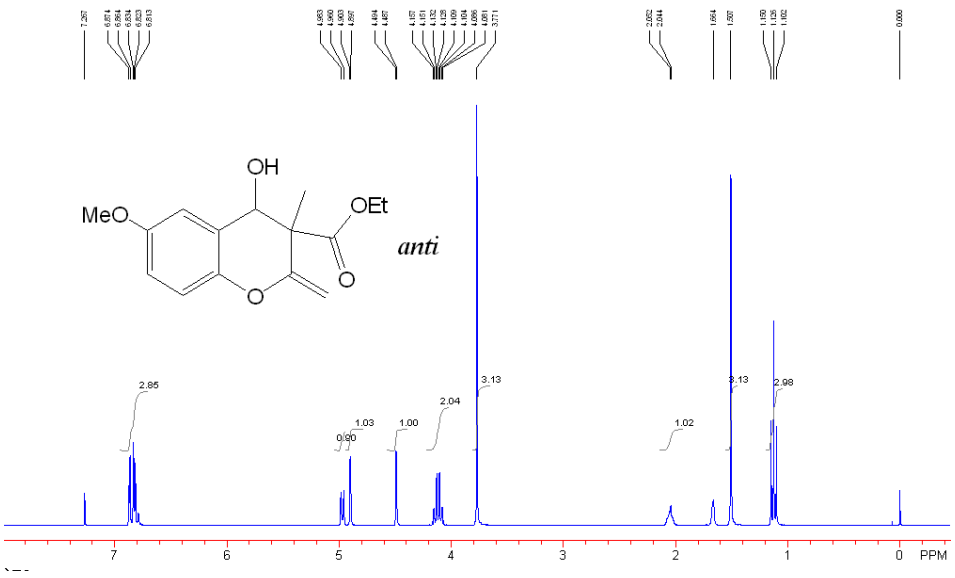




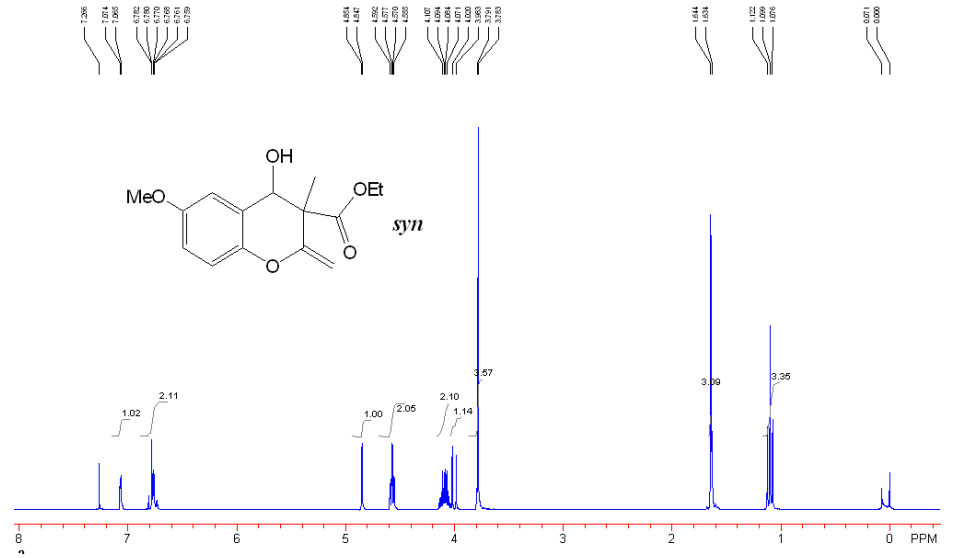
Ethyl

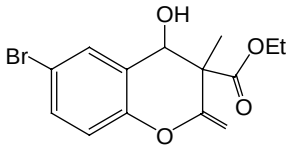
4-hydroxy-6-methoxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromene-3-carboxylate

***anti*-5e**: a yellow oil; IR (CH_2Cl_2) ν 3504, 2982, 1729 (C=O), 1655, 1493, 1217, 1036 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.13 (3H, t, *J* = 7.2 Hz, CH_3), 1.51 (3H, s, CH_3), 2.04 (1H, br s, OH), 3.77 (3H, s, OCH_3), 4.12 (2H, q, *J* = 7.2 Hz, CH_2), 4.49 (1H, d, *J* = 2.1 Hz, =CH), 4.90 (1H, d, *J* = 2.1 Hz, =CH), 4.97 (1H, d, *J* = 7.5 Hz, CH), 6.78-6.87 (3H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 17.6, 51.0, 55.7, 61.5, 69.7, 93.8, 112.5, 116.2, 116.7, 123.7, 145.5, 154.3, 155.4, 172.3; MS (EI) *m/z* 278 (M^+, 18.74), 260 (M^+-18, 2.02), 231 (M^+-47, 4.02), 206 (M^+-72, 8.09), 205 (M^+-73, 100), 188 (M^+-90, 12.32); HRMS (EI) calcd. for $C_{15}H_{18}O_5$: 278.1154, Found: 278.1151.



***syn*-5e**: a yellow oil; IR (CH_2Cl_2) ν 3489, 2960, 1709 (C=O), 1655, 1492, 1264, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.10 (3H, t, *J* = 7.2 Hz, CH_3), 1.64 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 4.01 (1H, d, *J* = 8.4 Hz, OH), 4.05-4.13 (2H, m, CH_2), 4.57 (1H, d, *J* = 2.1 Hz, =CH), 4.57 (1H, d, *J* = 8.4 Hz, CH), 4.85 (1H, d, *J* = 2.1 Hz, =CH), 6.76-6.82 (2H, m, ArH), 7.07 (1H, d, *J* = 2.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.8, 18.8, 49.3, 55.7, 61.7, 72.0, 92.9, 110.3, 115.3, 116.1, 126.2, 145.0, 154.6, 157.0, 174.2; MS (EI) *m/z* 278 (M^+, 97.44), 260 (M^+-18, 16.59), 232 (M^+-46, 10.55), 231 (M^+-47, 24.40), 215 (M^+-63, 19.84), 205 (M^+-73, 48.30), 190 (M^+-88, 19.21); HRMS (EI) calcd. for $C_{15}H_{18}O_5$: 278.1154, Found: 278.1154.

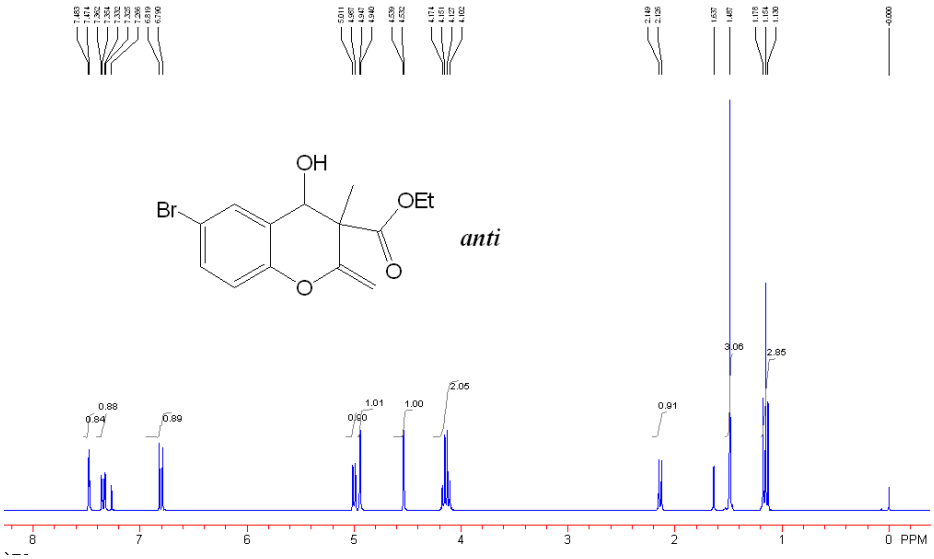


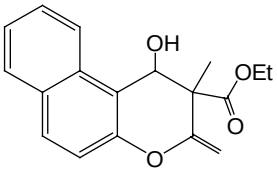


Ethyl

6-bromo-4-hydroxy-3-methyl-2-methylene-3,4-dihydro-2*H*-chromene-3-carboxylate

***anti*-5h**: a pale yellow oil; IR (CH_2Cl_2) ν 3489, 2982, 1729 (C=O), 1660, 1477, 1249, 1188 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.15 (3H, t, *J* = 7.2 Hz, CH_3), 1.49 (3H, s, CH_3), 2.14 (1H, d, *J* = 6.9 Hz, OH), 4.14 (2H, q, *J* = 7.2 Hz, CH_2), 4.54 (1H, d, *J* = 2.1 Hz, =CH), 4.94 (1H, d, *J* = 2.1 Hz, =CH), 5.00 (1H, d, *J* = 6.9 Hz, CH), 6.80 (1H, d, *J* = 8.7 Hz, ArH), 7.34 (1H, dd, *J* = 8.7, 2.7 Hz, ArH), 7.48 (1H, d, *J* = 2.7 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.9, 17.3, 50.7, 61.7, 69.0, 94.9, 114.0, 117.7, 125.2, 131.1, 132.8, 150.6, 154.9, 172.0; MS (EI) *m/z* 328 (M^++2, 8.50), 326 (M^+, 8.69), 281 (M^+-45, 5.58), 279 (M^+-47, 4.30), 254 (M^+-72, 25.08), 255 (M^+-71, 94.09), 253 (M^+-73, 100), 201 (M^+-125, 16.10); HRMS (EI) calcd. for $C_{14}H_{15}O_4Br$: 326.0154, Found: 326.0166.

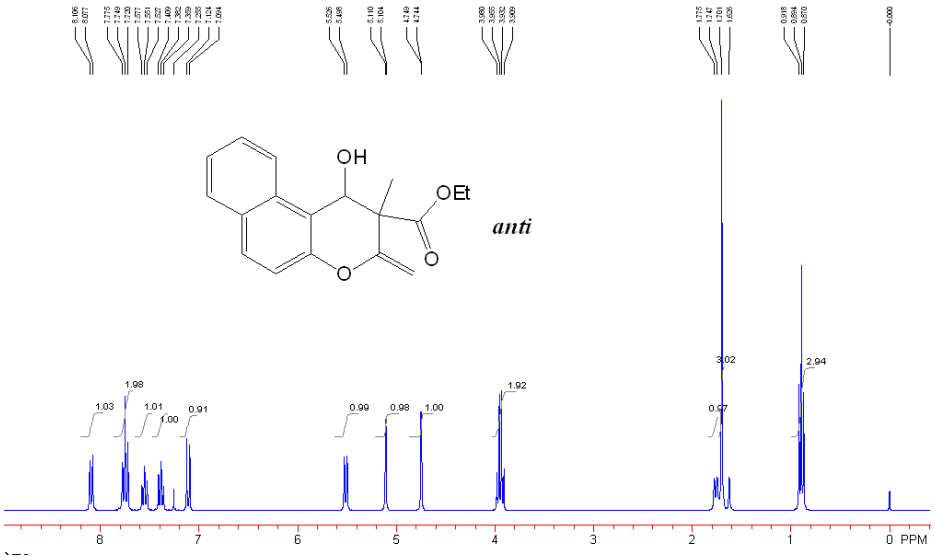




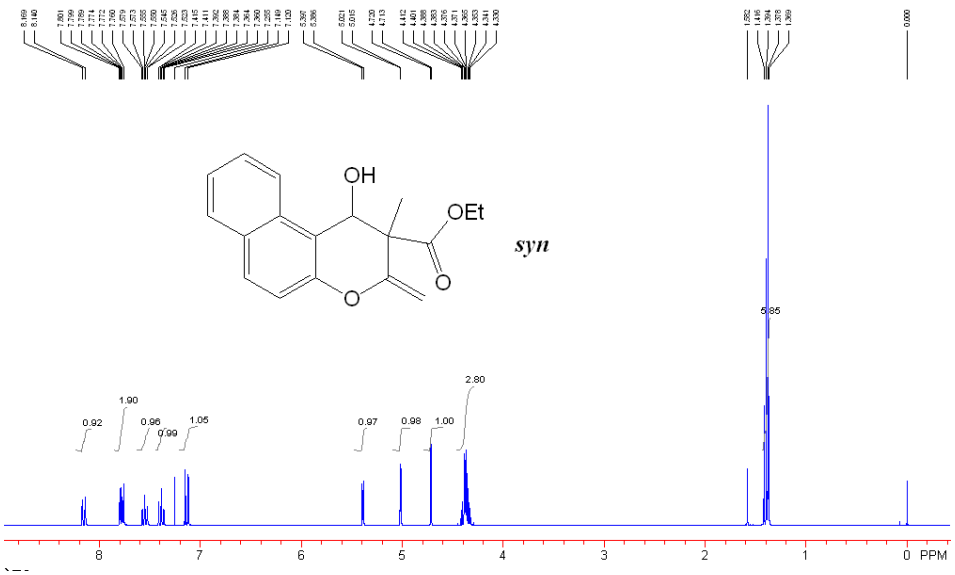
Ethyl

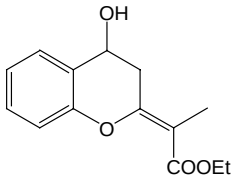
1-hydroxy-2-methyl-3-methylene-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carboxylate

***anti*-5i**: a pale yellow oil; IR (CH_2Cl_2) ν 3425, 2981, 1729 (C=O), 1627, 1466, 1243, 1024 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.89 (3H, t, *J* = 7.2 Hz, CH_3), 1.70 (3H, s, CH_3), 1.76 (1H, d, *J* = 8.4 Hz, OH), 3.94 (2H, q, *J* = 7.2 Hz, CH_2), 4.75 (1H, d, *J* = 1.8 Hz, =CH), 5.11 (1H, d, *J* = 1.8 Hz, =CH), 5.51 (1H, d, *J* = 8.4 Hz, CH), 7.11 (1H, d, *J* = 9.0 Hz, ArH), 7.36-7.41 (1H, m, ArH), 7.53-7.58 (1H, m, ArH), 7.72-7.78 (2H, m, ArH), 8.09 (1H, d, *J* = 9.0 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.7, 18.7, 50.5, 61.3, 65.9, 95.7, 114.9, 117.5, 121.9, 124.2, 127.4, 128.4, 129.5, 131.0, 131.9, 150.0, 154.3, 172.0; MS (EI) *m/z* 298 (M^+, 14.34), 280 (M^+-18, 4.46), 225 (M^+-73, 100), 208 (M^+-90, 32.12), 171 (M^+-127, 23.07), 115 (M^+-183, 19.34); HRMS (EI) calcd. for $C_{18}H_{18}O_4$: 298.1205, Found: 298.1216.

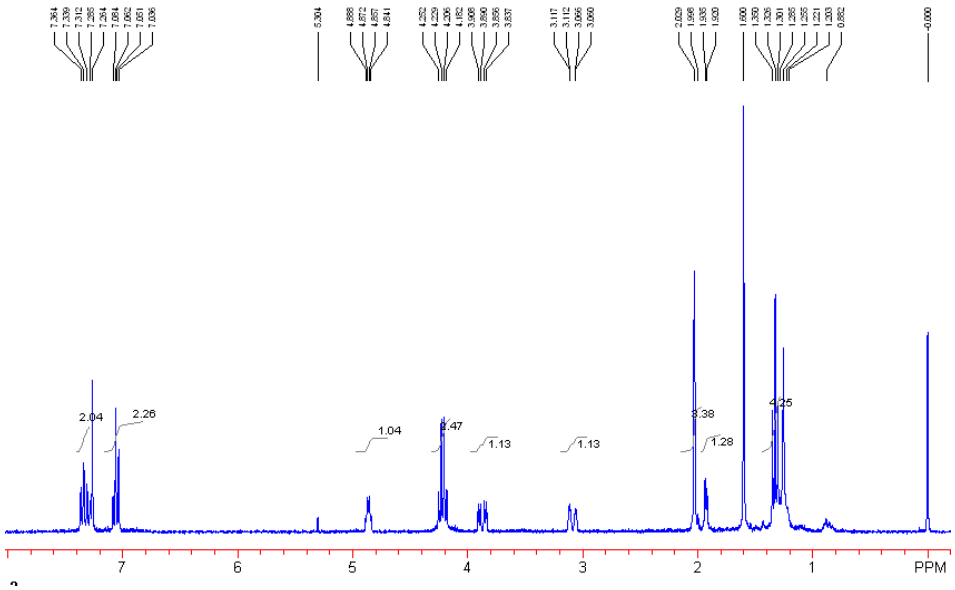


***syn*-5i**: a pale yellow oil; IR (CH_2Cl_2) ν 3485, 2982, 1707 (C=O), 1655, 1517, 1239, 1093, 1022 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.38 (3H, s, CH_3), 1.39 (3H, t, *J* = 7.2 Hz, CH_3), 4.33-4.41 (3H, m, CH_2, OH), 4.72 (1H, d, *J* = 1.8 Hz, =CH), 5.02 (1H, d, *J* = 1.8 Hz, =CH), 5.39 (1H, d, *J* = 3.6 Hz, CH), 7.14 (1H, d, *J* = 8.7 Hz, ArH), 7.37-7.42 (1H, m, ArH), 7.52-7.58 (1H, m, ArH), 7.76-7.80 (2H, m, ArH), 8.16 (1H, d, *J* = 8.7 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 20.6, 49.9, 61.9, 67.8, 94.7, 113.4, 117.2, 122.3, 124.0, 127.2, 128.4, 129.7, 130.7, 132.4, 149.7, 153.7, 174.1; MS (EI) *m/z* 298 (M^+, 59.16), 280 (M^+-18, 21.19), 251 (M^+-47, 13.64), 235 (M^+-63, 10.67), 225 (M^+-73, 100), 209 (M^+-89, 40.92); HRMS (EI) calcd. for $C_{18}H_{18}O_4$: 298.1205, Found: 298.1206.



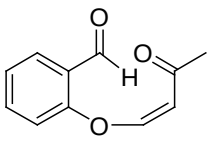


(Z)-ethyl 2-(4-hydroxy-3,4-dihydrochromen-2-ylidene)propanoate 6a: a pale yellow oil; IR (CH_2Cl_2) ν 3294, 2923, 1709 (C=O), 1646, 1276, 1225, 1112, 1065 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.33 (3H, t, *J* = 7.2 Hz, CH_3), 1.86 (1H, d, *J* = 5.1 Hz, OH), 2.03 (3H, s, CH_3), 3.09 (1H, dm, *J* = 16.5 Hz, CH_2), 3.87 (1H, dd, *J* = 16.5, 5.4 Hz, CH_2), 4.22 (2H, d, *J* = 7.2 Hz, CH_2), 4.86 (1H, m, CH), 7.03-7.09 (2H, m, ArH), 7.27-7.37 (2H, m, ArH); MS (EI) *m/z* 248 (M^+, 6.72), 230 (M^+-18, 100), 201 (M^+-47, 29.95), 185 (M^+-63, 36.67), 175 (M^+-73, 4.09), 158 (M^+-90, 64.18); HRMS (EI) calcd. for $C_{14}H_{16}O_4$: 248.1049, Found: 248.1046.



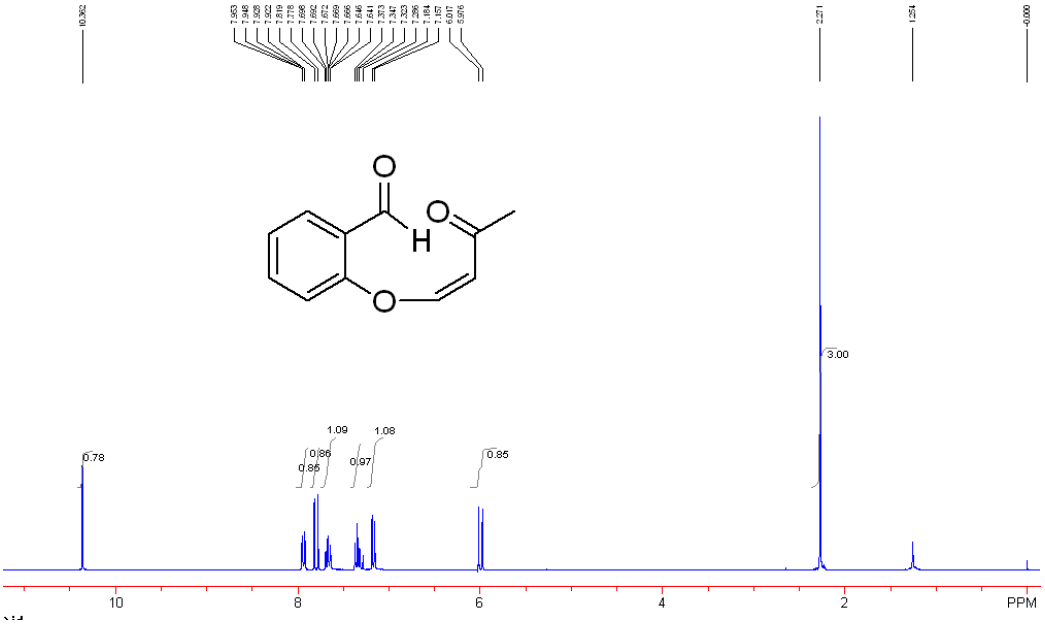
Typical reaction procedure of salicylaldehyde with but-3-yn-2-one in the presence of DABCO in THF at room temperature.

To a Schlenk tube with THF (1.0 mL) was added salicylaldehyde (61 mg, 0.5 mmol), ethyl but-3-yn-2-one (68 mg, 1.0 mmol) and DABCO (6.0 mg, 0.05 mmol). The solution was stirred for 15 min at room temperature (20 ^{o}C). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give adduct the **7a** (eluent: EtOAc/petroleum= 1/4, 81 mg, yield 85%). The pure *Z*-isomer of **7a** can be isolated by flash chromatography, but the pure *E*-isomer of **7a** is very difficult to be isolated and is obtained with small amount of the *Z*-isomer. The ratio of the two isomers is obtained based on ^{1}H NMR spectroscopic data of the crude product. The configuration of *Z*-isomer of **7a** is confirmed by its 2D NOESY spectrum.



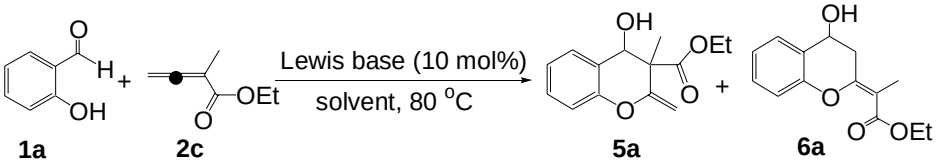
(*Z*)-**2-(3-oxobut-1-enyloxy)benzaldehyde 7a**: a colorless oil; IR (CH_2Cl_2) ν 2859, 1694,

1664, 1642, 1618, 1601, 1579, 1480, 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.27 (3H, S, CH_3), 6.00 (1H, d, *J* = 12.3 Hz, CH), 7.17 (1H, d, *J* = 8.1 Hz, Ar), 7.32-7.37 (1H, m, Ar), 7.64-7.70 (1H, m, Ar), 7.80 (1H, d, *J* = 12.3 Hz, CH), 7.92-7.95 (1H, m, Ar), 10.36 (1H, S, CHO); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 28.7, 112.8(2C), 118.3, 125.5, 126.5, 129.1, 136.0, 157.8, 188.0, 196.8; MS (EI) *m/z* 191 (M^++1, 14.9), 147 (M^+-43, 93.5), 121 (M^+-69, 91.9), 43 (M^+-147, 100); HRMS (MALDI) calcd. for $C_{11}H_{10}O_3Na^+$: 213.0522, Found: 213.0522.



(*E*)-**2-(3-oxobut-1-enyloxy)benzaldehyde 7a**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.50 (3H, S, CH_3), 5.50 (1H, d, *J* = 7.2 Hz, CH), 7.01 (1H, d, *J* = 7.2 Hz, CH), 7.16 (1H, d, *J* = 8.7 Hz, Ar), 7.29-7.37 (1H, m, Ar), 7.64-7.70 (1H, m, Ar), 7.93-7.97 (1H, m, Ar), 10.51 (1H, S, CHO).

The solvent and Lewis base effects on the reactions of salicylaldehydes 1a with ethyl 2-methylbuta-2,3-dienoate 2c which are not shown in main text due to the limited space.

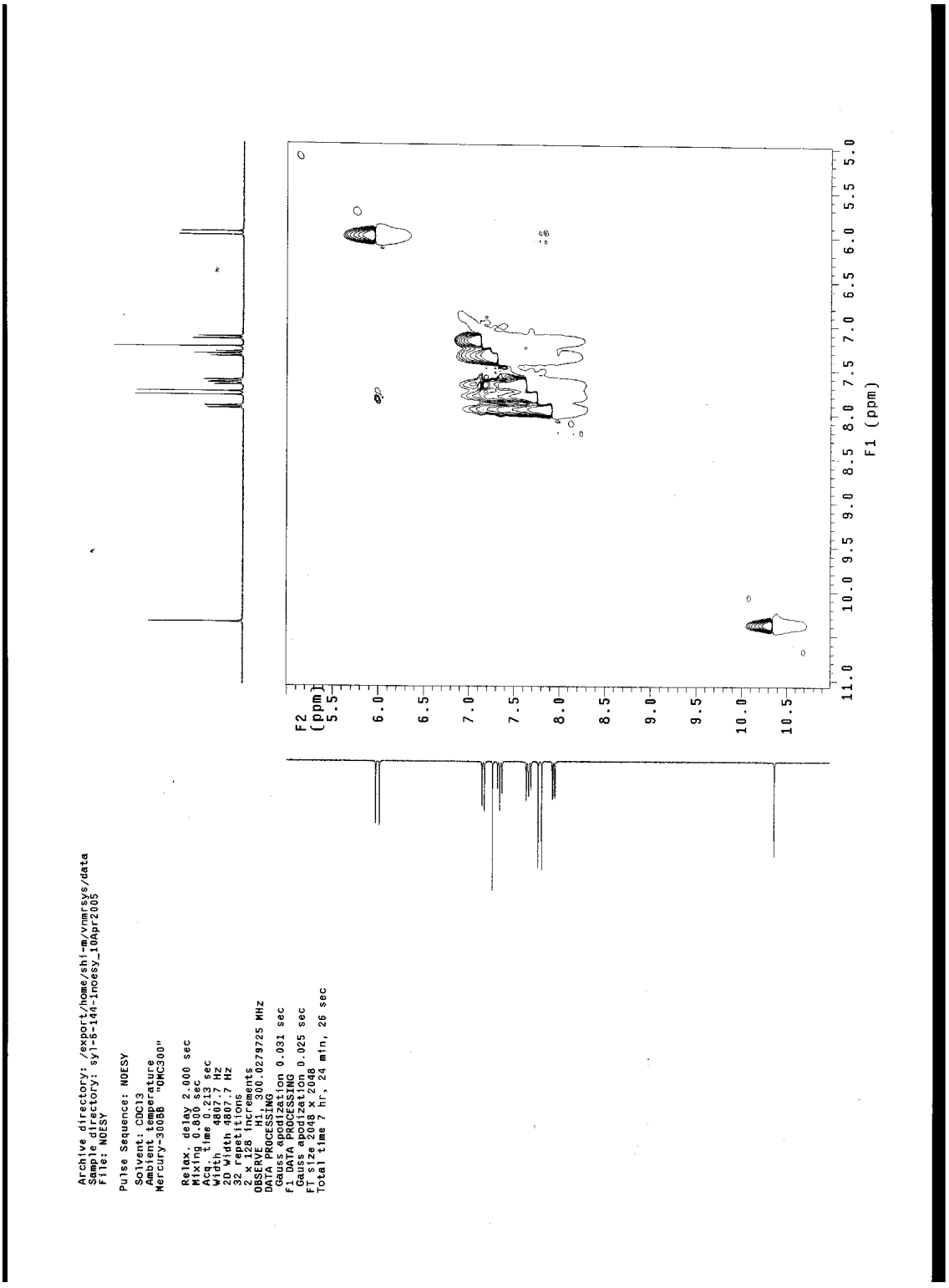


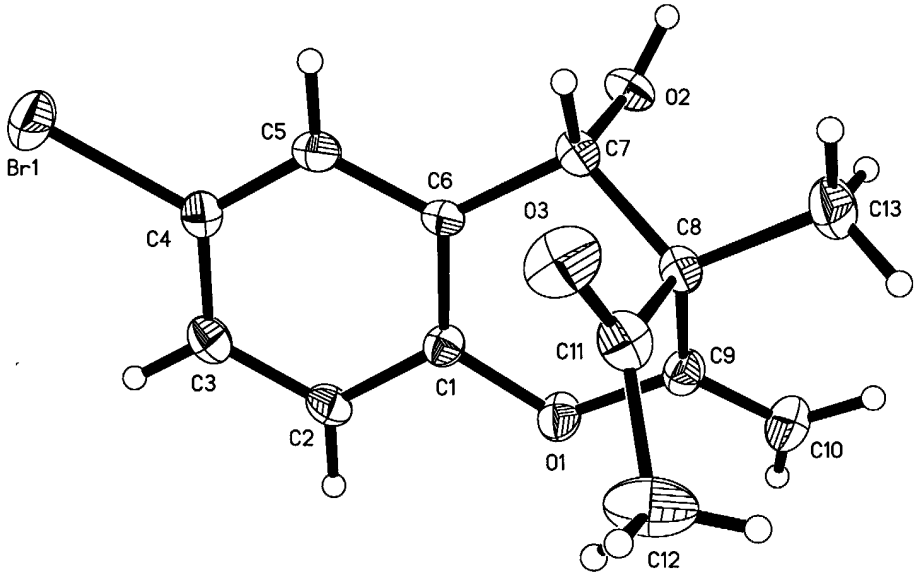
1a **2c** **5a** **6a**

entry	Lewis base	solvent	time/h	yield/[%][a]	
				5a (*anti*) +	**6a**
1	PPh_3	DMSO	24	trace	trace
2	PPh_2Me	DMSO	24	trace	trace
3	$PPhMe_2$	DMSO	24	35	trace
4	PBu_3	DMSO	24	50	6
5	PMe_3	DMSO	24	46	8
6	DMAP	DMSO	11	20	12
7	DBU	DMSO	6	61	trace
8	DBU	DMF	24	59	5
9	DBU	CH_3CN	24	trace	trace
10	DBU	DCE	24	trace	trace

[a]Isolated yields and the reaction time is determined by TLC on the basis of consuming the starting materials **1a**

The 2D NOESY spectrum of (*Z*)-2-(3-oxobut-1-enyloxy)benzaldehyde **7a**:





The crystal data of *anti*-**3h** has been deposited in CCDC with number 273551. Empirical Formula: $C_{13}H_{13}BrO_3$; Formula Weight: 297.14; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.401 x 0.357 x 0.338 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 13.9423(18)Å, b = 10.7041(14)Å, c = 17.044(2)Å, $\alpha = 90^o$, $\beta = 91.314(2)^o$, $\gamma = 90^o$, V = 2542.9(6)Å^3; Space group: P2(1)/c; Z = 8; D_{calc} = 1.552 g/cm^3; F_{000} = 1200; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0387, 0.0740.

Table 1. Crystal data and structure refinement for cd25164.

Identification code	cd25164
Empirical formula	C13 H13 Br O3
Formula weight	297.14
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.9423(18) A alpha = 90 deg. b = 10.7041(14) A beta = 91.314(2) deg. c = 17.044(2) A gamma = 90 deg.
Volume	2542.9(6) A^3
Z, Calculated density	8, 1.552 Mg/m^3
Absorption coefficient	3.226 mm^-1
F(000)	1200
Crystal size	0.401 x 0.357 x 0.338 mm
Theta range for data collection	2.25 to 27.00 deg.
Limiting indices	-17<=h<=17, -13<=k<=13, -8<=l<=21
Reflections collected / unique	14328 / 5525 [R(int) = 0.0835]
Completeness to theta = 27.00	99.5 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.54578
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5525 / 0 / 343
Goodness-of-fit on F^2	0.739
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0740
R indices (all data)	R1 = 0.1027, wR2 = 0.0827
Largest diff. peak and hole	0.589 and -0.562 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd25164.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9726(1)	468(1)	12473(1)	66(1)
Br(2)	8708(1)	3440(1)	11209(1)	65(1)
O(1)	7169(2)	-3413(2)	10997(1)	38(1)
O(2)	6377(2)	-605(2)	10383(1)	36(1)
O(3)	8793(2)	-1972(2)	9306(2)	59(1)
O(4)	7410(2)	1265(2)	8114(1)	49(1)
O(5)	5553(2)	1099(2)	9375(2)	50(1)
O(6)	6033(2)	4541(2)	8379(2)	62(1)
C(1)	7756(2)	-2492(3)	11297(2)	29(1)
C(2)	8229(2)	-2776(3)	12003(2)	37(1)
C(3)	8818(2)	-1894(3)	12348(2)	38(1)
C(4)	8925(2)	-751(3)	11994(2)	36(1)
C(5)	8458(2)	-475(3)	11293(2)	34(1)
C(6)	7848(2)	-1343(3)	10941(2)	27(1)
C(7)	7308(2)	-1091(3)	10189(2)	30(1)
C(8)	7203(2)	-2321(3)	9731(2)	32(1)
C(9)	6744(2)	-3268(3)	10254(2)	33(1)
C(10)	6017(3)	-4010(4)	10098(3)	47(1)
C(11)	8212(3)	-2744(4)	9484(2)	40(1)
C(12)	8424(3)	-4098(4)	9432(2)	70(1)
C(13)	6617(3)	-2122(4)	8967(2)	51(1)
C(14)	7660(2)	1775(3)	8833(2)	38(1)
C(15)	8632(2)	1752(4)	9040(2)	50(1)
C(16)	8939(3)	2232(4)	9744(2)	50(1)
C(17)	8284(3)	2731(3)	10241(2)	40(1)
C(18)	7323(2)	2747(3)	10053(2)	38(1)
C(19)	6995(2)	2246(3)	9339(2)	32(1)
C(20)	5953(2)	2247(3)	9101(2)	33(1)
C(21)	5863(2)	2345(3)	8205(2)	29(1)
C(22)	6464(2)	1348(3)	7845(2)	37(1)
C(23)	6212(4)	581(5)	7281(3)	66(1)
C(24)	6195(2)	3670(4)	7970(2)	38(1)
C(25)	6655(4)	3842(4)	7203(3)	104(2)
C(26)	4806(2)	2259(3)	7939(2)	42(1)

Table 3. Bond lengths [A] and angles [deg] for cd25164.

Br(1)-C(4)	1.891(3)
Br(2)-C(17)	1.898(3)
O(1)-C(1)	1.373(3)
O(1)-C(9)	1.394(3)
O(2)-C(7)	1.444(4)
O(2)-H(2A)	0.81(3)
O(3)-C(11)	1.202(4)
O(4)-C(14)	1.379(4)
O(4)-C(22)	1.389(4)
O(5)-C(20)	1.432(4)
O(5)-H(2A)	1.94(3)
O(5)-H(5A)	0.87(4)
O(6)-C(24)	1.190(4)
C(1)-C(6)	1.378(4)
C(1)-C(2)	1.392(4)
C(2)-C(3)	1.374(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.374(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.379(4)
C(5)-C(6)	1.386(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.496(4)
C(7)-C(8)	1.536(4)
C(7)-H(7)	0.97(3)
C(8)-C(9)	1.502(4)
C(8)-C(13)	1.535(4)
C(8)-C(11)	1.546(5)
C(9)-C(10)	1.310(5)
C(10)-H(9)	0.91(3)
C(10)-H(10)	0.93(3)
C(11)-C(12)	1.482(5)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(19)	1.376(4)
C(14)-C(15)	1.393(4)
C(15)-C(16)	1.366(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.368(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.371(4)
C(18)-C(19)	1.397(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.498(4)
C(20)-C(21)	1.534(4)
C(20)-H(20)	1.04(3)
C(21)-C(22)	1.497(4)
C(21)-C(26)	1.535(4)
C(21)-C(24)	1.547(5)
C(22)-C(23)	1.306(5)
C(23)-H(21)	0.83(4)
C(23)-H(22)	0.91(3)
C(24)-C(25)	1.480(5)
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(1)-O(1)-C(9)	119.7(2)
C(7)-O(2)-H(2A)	117(2)
C(14)-O(4)-C(22)	119.1(3)
C(20)-O(5)-H(2A)	125.8(10)

C(20)-O(5)-H(5A)	108(2)
H(2A)-O(5)-H(5A)	117(3)
O(1)-C(1)-C(6)	122.5(3)
O(1)-C(1)-C(2)	115.6(3)
C(6)-C(1)-C(2)	121.9(3)
C(3)-C(2)-C(1)	119.1(3)
C(3)-C(2)-H(2)	120.5
C(1)-C(2)-H(2)	120.5
C(4)-C(3)-C(2)	119.6(3)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	121.2(3)
C(3)-C(4)-Br(1)	119.6(2)
C(5)-C(4)-Br(1)	119.2(3)
C(4)-C(5)-C(6)	120.2(3)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(1)-C(6)-C(5)	118.0(3)
C(1)-C(6)-C(7)	119.2(3)
C(5)-C(6)-C(7)	122.8(3)
O(2)-C(7)-C(6)	107.8(3)
O(2)-C(7)-C(8)	110.4(3)
C(6)-C(7)-C(8)	108.8(3)
O(2)-C(7)-H(7)	110.2(15)
C(6)-C(7)-H(7)	109.8(15)
C(8)-C(7)-H(7)	109.8(16)
C(9)-C(8)-C(13)	111.8(3)
C(9)-C(8)-C(7)	108.3(3)
C(13)-C(8)-C(7)	110.8(3)
C(9)-C(8)-C(11)	111.5(3)
C(13)-C(8)-C(11)	106.3(3)
C(7)-C(8)-C(11)	108.2(3)
C(10)-C(9)-O(1)	115.3(4)
C(10)-C(9)-C(8)	128.8(4)
O(1)-C(9)-C(8)	115.9(3)
C(9)-C(10)-H(9)	118(2)
C(9)-C(10)-H(10)	123.0(19)
H(9)-C(10)-H(10)	119(3)
O(3)-C(11)-C(12)	121.3(3)
O(3)-C(11)-C(8)	119.4(3)
C(12)-C(11)-C(8)	119.2(3)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(8)-C(13)-H(13A)	109.5
C(8)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(8)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-O(4)	122.8(3)
C(19)-C(14)-C(15)	121.0(3)
O(4)-C(14)-C(15)	116.2(3)
C(16)-C(15)-C(14)	119.9(4)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	119.5(3)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
C(18)-C(17)-C(16)	121.5(3)
C(18)-C(17)-Br(2)	118.8(3)
C(16)-C(17)-Br(2)	119.7(3)
C(17)-C(18)-C(19)	119.9(3)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(14)-C(19)-C(18)	118.3(3)
C(14)-C(19)-C(20)	119.6(3)
C(18)-C(19)-C(20)	122.1(3)
O(5)-C(20)-C(19)	107.1(3)

O(5)-C(20)-C(21)	111.0(3)
C(19)-C(20)-C(21)	109.0(3)
O(5)-C(20)-H(20)	110.6(14)
C(19)-C(20)-H(20)	111.9(14)
C(21)-C(20)-H(20)	107.2(14)
C(22)-C(21)-C(20)	109.0(3)
C(22)-C(21)-C(26)	112.3(3)
C(20)-C(21)-C(26)	110.3(3)
C(22)-C(21)-C(24)	111.9(3)
C(20)-C(21)-C(24)	107.6(3)
C(26)-C(21)-C(24)	105.6(3)
C(23)-C(22)-O(4)	116.1(4)
C(23)-C(22)-C(21)	127.3(4)
O(4)-C(22)-C(21)	116.5(3)
C(22)-C(23)-H(21)	115(3)
C(22)-C(23)-H(22)	121(2)
H(21)-C(23)-H(22)	124(4)
O(6)-C(24)-C(25)	120.8(4)
O(6)-C(24)-C(21)	120.3(3)
C(25)-C(24)-C(21)	118.8(3)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(21)-C(26)-H(26A)	109.5
C(21)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(21)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd25164.
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
Br(1)	77(1)	54(1)	65(1)	-5(1)	-29(1)	-19(1)
Br(2)	65(1)	74(1)	54(1)	-4(1)	-20(1)	2(1)
O(1)	43(1)	38(1)	34(1)	7(1)	-3(1)	-14(1)
O(2)	32(1)	37(2)	39(2)	9(1)	2(1)	9(1)
O(3)	41(2)	60(2)	76(2)	-6(2)	25(2)	-8(1)
O(4)	36(1)	62(2)	48(2)	-15(1)	3(1)	16(1)
O(5)	25(1)	55(2)	71(2)	34(1)	7(1)	4(1)
O(6)	100(2)	33(2)	53(2)	0(2)	-2(2)	-5(2)
C(1)	28(2)	29(2)	29(2)	1(2)	3(2)	-4(2)
C(2)	44(2)	34(2)	33(2)	12(2)	-6(2)	1(2)
C(3)	39(2)	45(2)	31(2)	4(2)	-5(2)	4(2)
C(4)	32(2)	37(2)	38(2)	1(2)	-5(2)	-2(2)
C(5)	33(2)	29(2)	39(2)	5(2)	3(2)	2(2)
C(6)	27(2)	23(2)	30(2)	4(2)	2(2)	3(2)
C(7)	24(2)	37(2)	29(2)	7(2)	3(2)	-2(2)
C(8)	29(2)	37(2)	30(2)	4(2)	-2(2)	-2(2)
C(9)	32(2)	35(2)	33(2)	-7(2)	0(2)	0(2)
C(10)	45(3)	49(3)	46(3)	-7(2)	-3(2)	-11(2)
C(11)	38(2)	52(3)	30(2)	-1(2)	7(2)	4(2)
C(12)	68(3)	56(3)	88(3)	14(2)	39(3)	18(2)
C(13)	58(2)	60(3)	34(2)	2(2)	-11(2)	-1(2)
C(14)	28(2)	40(2)	45(2)	4(2)	-1(2)	5(2)
C(15)	32(2)	64(3)	56(3)	-6(2)	14(2)	8(2)
C(16)	32(2)	56(3)	62(3)	4(2)	-8(2)	0(2)
C(17)	37(2)	42(2)	42(2)	3(2)	-8(2)	1(2)
C(18)	40(2)	40(2)	34(2)	7(2)	8(2)	2(2)
C(19)	27(2)	33(2)	36(2)	7(2)	3(2)	6(2)
C(20)	29(2)	35(2)	35(2)	10(2)	6(2)	8(2)
C(21)	30(2)	27(2)	30(2)	2(2)	2(2)	2(2)
C(22)	32(2)	34(2)	44(2)	-3(2)	4(2)	-2(2)
C(23)	54(3)	57(3)	85(4)	-30(3)	-8(3)	3(3)
C(24)	37(2)	38(2)	38(2)	8(2)	2(2)	2(2)
C(25)	152(5)	63(3)	102(4)	35(3)	79(4)	10(3)
C(26)	37(2)	48(2)	41(2)	-2(2)	-4(2)	1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd25164.

	x	y	z	U(eq)
H(2)	8148	-3552	12238	45
H(3)	9142	-2070	12818	46
H(5)	8553	296	11055	41
H(12A)	9046	-4213	9212	105
H(12B)	7947	-4496	9102	105
H(12C)	8417	-4460	9947	105
H(13A)	6601	-2884	8671	77
H(13B)	6909	-1476	8663	77
H(13C)	5975	-1880	9090	77
H(15)	9072	1411	8698	61
H(16)	9587	2220	9885	60
H(18)	6890	3092	10399	45
H(25A)	6692	4718	7085	116
H(25B)	6282	3427	6801	116
H(25C)	7290	3495	7226	116
H(26A)	4753	2408	7384	63
H(26B)	4440	2875	8212	63
H(26C)	4564	1441	8054	63
H(7)	7655(18)	-490(20)	9879(15)	32(8)
H(9)	5720(20)	-3950(30)	9618(19)	42(11)
H(10)	5760(20)	-4540(30)	10469(18)	43(11)
H(21)	6640(30)	90(40)	7150(20)	71(16)
H(22)	5620(30)	640(30)	7040(20)	61(13)
H(2A)	6160(20)	-50(30)	10111(19)	48(12)
H(5A)	4940(30)	1210(30)	9410(20)	60(13)
H(20)	5592(18)	3010(20)	9333(14)	30(8)

Table 6. Torsion angles [deg] for cd25164.

C(9)-O(1)-C(1)-C(6)	9.0(4)
C(9)-O(1)-C(1)-C(2)	-173.4(3)
O(1)-C(1)-C(2)-C(3)	-178.9(3)
C(6)-C(1)-C(2)-C(3)	-1.2(5)
C(1)-C(2)-C(3)-C(4)	0.3(5)
C(2)-C(3)-C(4)-C(5)	-0.6(5)
C(2)-C(3)-C(4)-Br(1)	179.4(2)
C(3)-C(4)-C(5)-C(6)	1.7(5)
Br(1)-C(4)-C(5)-C(6)	-178.3(2)
O(1)-C(1)-C(6)-C(5)	179.8(3)
C(2)-C(1)-C(6)-C(5)	2.3(5)
O(1)-C(1)-C(6)-C(7)	-1.5(4)
C(2)-C(1)-C(6)-C(7)	-179.1(3)
C(4)-C(5)-C(6)-C(1)	-2.5(4)
C(4)-C(5)-C(6)-C(7)	178.9(3)
C(1)-C(6)-C(7)-O(2)	88.5(3)
C(5)-C(6)-C(7)-O(2)	-92.9(3)
C(1)-C(6)-C(7)-C(8)	-31.2(4)
C(5)-C(6)-C(7)-C(8)	147.4(3)
O(2)-C(7)-C(8)-C(9)	-63.3(3)
C(6)-C(7)-C(8)-C(9)	54.8(3)
O(2)-C(7)-C(8)-C(13)	59.6(3)
C(6)-C(7)-C(8)-C(13)	177.7(3)
O(2)-C(7)-C(8)-C(11)	175.7(3)
C(6)-C(7)-C(8)-C(11)	-66.2(3)
C(1)-O(1)-C(9)-C(10)	-163.1(3)
C(1)-O(1)-C(9)-C(8)	19.2(4)
C(13)-C(8)-C(9)-C(10)	9.3(5)
C(7)-C(8)-C(9)-C(10)	131.6(4)
C(11)-C(8)-C(9)-C(10)	-109.5(4)
C(13)-C(8)-C(9)-O(1)	-173.4(3)
C(7)-C(8)-C(9)-O(1)	-51.1(3)
C(11)-C(8)-C(9)-O(1)	67.8(4)
C(9)-C(8)-C(11)-O(3)	-154.8(3)
C(13)-C(8)-C(11)-O(3)	83.2(4)
C(7)-C(8)-C(11)-O(3)	-35.8(4)
C(9)-C(8)-C(11)-C(12)	28.5(4)
C(13)-C(8)-C(11)-C(12)	-93.5(4)
C(7)-C(8)-C(11)-C(12)	147.5(3)
C(22)-O(4)-C(14)-C(19)	7.3(5)
C(22)-O(4)-C(14)-C(15)	-174.9(3)
C(19)-C(14)-C(15)-C(16)	-1.7(5)
O(4)-C(14)-C(15)-C(16)	-179.6(3)
C(14)-C(15)-C(16)-C(17)	0.0(6)
C(15)-C(16)-C(17)-C(18)	0.8(6)
C(15)-C(16)-C(17)-Br(2)	-178.3(3)
C(16)-C(17)-C(18)-C(19)	0.1(5)
Br(2)-C(17)-C(18)-C(19)	179.2(2)
O(4)-C(14)-C(19)-C(18)	-179.7(3)
C(15)-C(14)-C(19)-C(18)	2.5(5)
O(4)-C(14)-C(19)-C(20)	-1.7(5)
C(15)-C(14)-C(19)-C(20)	-179.5(3)
C(17)-C(18)-C(19)-C(14)	-1.7(5)
C(17)-C(18)-C(19)-C(20)	-179.6(3)
H(2A)-O(5)-C(20)-C(19)	12.8(13)
H(2A)-O(5)-C(20)-C(21)	131.7(12)
C(14)-C(19)-C(20)-O(5)	91.2(4)
C(18)-C(19)-C(20)-O(5)	-90.9(4)
C(14)-C(19)-C(20)-C(21)	-29.0(4)
C(18)-C(19)-C(20)-C(21)	148.9(3)
O(5)-C(20)-C(21)-C(22)	-65.3(3)
C(19)-C(20)-C(21)-C(22)	52.5(4)
O(5)-C(20)-C(21)-C(26)	58.4(3)
C(19)-C(20)-C(21)-C(26)	176.2(3)
O(5)-C(20)-C(21)-C(24)	173.2(3)
C(19)-C(20)-C(21)-C(24)	-69.0(3)
C(14)-O(4)-C(22)-C(23)	-162.2(4)
C(14)-O(4)-C(22)-C(21)	20.8(4)

C(20)-C(21)-C(22)-C(23)	132.5(4)
C(26)-C(21)-C(22)-C(23)	10.0(5)
C(24)-C(21)-C(22)-C(23)	-108.6(4)
C(20)-C(21)-C(22)-O(4)	-50.9(4)
C(26)-C(21)-C(22)-O(4)	-173.4(3)
C(24)-C(21)-C(22)-O(4)	68.0(4)
C(22)-C(21)-C(24)-O(6)	-155.1(3)
C(20)-C(21)-C(24)-O(6)	-35.4(4)
C(26)-C(21)-C(24)-O(6)	82.4(4)
C(22)-C(21)-C(24)-C(25)	29.2(4)
C(20)-C(21)-C(24)-C(25)	148.8(3)
C(26)-C(21)-C(24)-C(25)	-93.4(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd25164 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)