Supporting information for full characterization of compounds

General. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on 300 MHz and 75 MHz, respectively. Mass spectra were recorded by EI method and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $60F_{254}$ silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Preparation of 3-(chloromethyl)-4-hydroxy-4-(3'-nitrophenyl)-2-butanone (1b).

This compound was prepared in the same manner as that described above. 113 mg, 88%; a colorless oil; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.20 (3H, s, Me), 2.95 (1H, br. s, OH), 3.20-3.35 (1H, m), 3.66 (1H, dd, *J* 11.3, 3.9 Hz), 3.89 (1H, dd, *J* 11.3, 9.3 Hz), 5.13 (1H, d, *J* 5.6 Hz), 7.54 (1H, t, *J* 7.9 Hz, Ar), 7.69 (1H, d, *J* 7.6 Hz, Ar), 8.2 (1H, d, *J* 7.6 Hz, Ar), 8.25 (1H, s, Ar); MS (EI) m/e 257 (M^+, 0.60), 208 (M^+-49, 60), 71(M^+-186, 100); [HRMS (EI) *m/z* 239.0353 (M^+-H_2O). $C_{11}H_{10}O_3NCl$ requires *M-H2O*, 239.0349].

Preparation of 3-(chloromethyl)-4-hydroxy-4-(4'-trifluoromethylphenyl)-2-butanone (1c).

This compound was prepared in the same manner as that described above. 112 mg, 80%; a colorless oil; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.13 (3H, s, Me), 2.65 (1H, br. s, OH), 3.22-3.37 (1H, m), 3.70 (1H, dd, *J* 10.2, 3.9 Hz), 3.89 (1H, dd, *J* 10.2, 10.2 Hz), 5.02 (1H, d, *J* 6.1 Hz), 7.37 (2H, d, *J* 8.0 Hz, Ar), 7.64 (2H, d, *J* 8.0 Hz, Ar); MS (EI) m/e 280 (M^+, 0.45), 243 (M^+-37, 40), 43 (M^+-237, 100); [HRMS (EI) *m/z* 262.0377 (M^+-H_2O). $C_{12}H_{10}OClF_3$ requires *M-H2O*, 262.0372].

Preparation of 3-(chloromethyl)-4-hydroxy-4-phenyl-2-butanone (1d).

This compound was prepared in the same manner as that described above. 85 mg, 80%; a colorless oil; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.02 (3H, s, Me), 2.45 (1H, br. s, OH), 3.22-3.37 (1H, m), 3.78 (1H, dd, *J* 10.7, 3.8 Hz), 3.90 (1H, dd, *J* 10.4, 10.4 Hz), 4.84 (1H, d, *J* 6.9 Hz), 7.10-7.32 (5H, m, Ar); MS (EI) m/e 212 (M^+, 1.05), 163 (M^+-49, 60), 107 (M^+-105, 100); [HRMS (EI) *m/z* 212.0594 (M^+). $C_{11}H_{13}O_2Cl$ requires *M*, 212.0604].

Preparation of 3-(chloromethyl)-4-hydroxy-4-(4'-ethylphenyl)-2-butanone (1e).

This compound was prepared in the same manner as that described above. 87 mg, 72%; a colorless solid; mp 69-71 °C; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21 (3H, t, *J* 7.7 Hz), 2.02 (3H, s, Me), 2.15 (1H, br. s, OH), 2.63 (2H, q, *J* 7.7 Hz), 3.22-3.37 (1H, m), 3.80 (1H, dd, *J* 10.7, 3.8 Hz), 3.90 (1H, dd, *J* 10.7, 10.7 Hz), 4.82 (1H, d, *J* 7.2 Hz), 7.10-7.32 (4H, m, Ar); MS (EI) m/e 222 (M^+-18, 1.20), 191 (M^+-49, 20), 135 (M^+-105, 100); [HRMS (EI) *m/z* 240.0908 (M^+). $C_{13}H_{17}O_2Cl$ requires *M*, 240.0917].

Preparation of 3-(chloromethyl)-4-hydroxy-4-(4'-chlorophenyl)-2-butanone (1f).

This compound was prepared in the same manner as that described above. 86 mg, 70%; a colorless oil; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.0 (3H, s, Me), 2.50 (1H, br. s, OH), 3.20-3.32 (1H, m), 3.75 (1H, dd, *J* 10.7, 3.8 Hz), 3.87 (1H, dd, *J* 10.7, 10.7 Hz), 4.82 (1H, d, *J* 6.7 Hz), 7.10-7.32 (4H, m, Ar); MS (EI) m/e 246 (M^+, 1.20), 121 (M^+-125, 20), 91 (M^+-155, 100); [HRMS (EI) *m/z* 246.0210 (M^+). $C_{11}H_{12}O_2Cl_2$ requires *M*, 246.0214].

Preparation of 3-(chloromethyl)-4-hydroxy-4-butyl-2-butanone (1g).

This compound was prepared in the same manner as that described above. 43 mg, 45%; a colorless oil; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (3H, t, *J* 7.1 Hz), 1.10-1.60 (6H, m), 2.08 (1H, s, OH), 2.34 (3H, s, Me), 3.0-3.10 (1H, m), 3.60-3.85 (3H, m); MS (EI) m/e 192 (M^+, 0.80), 155 (M^+-37, 30), 43 (M^+-149, 100); [HRMS (EI) *m/z* 192.0908 (M^+). $C_9H_{17}O_2Cl$ requires *M*, 192.0917].

Preparation of 2-(chloromethyl)-3-hydroxy-3-(4'-nitrophenyl)-propionitrile (1h).

This compound was prepared in the same manner as that described above. 45 mg, 37%; a colorless oil; IR(KBr) ν 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.50 (1H, s, OH), 3.28 (1H, q, *J* 6.1 Hz), 3.70 (1H, dd, *J* 11.3, 4.5 Hz), 3.96 (1H, dd, *J* 11.3, 5.8 Hz), 7.67 (2H, d, *J* 8.3 Hz), 8.28 (2H, d, *J* 8.3 Hz); MS (EI) m/e 240 (M^+, 38.75), 205 (M^+-35, 30), 152 (M^+-149, 100); [HRMS (EI) *m/z* 240.0310 (M^+). $C_{10}H_9ClN_2O_3$ requires *M*, 240.0302].

The physical data of the known product 3-[(4'-nitrophenyl)hydroxymethyl]-3-buten-2-one

(2a)[9]: this is a known compound. Please compare its physical with that reported in literature. mp 66-68 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) d 2.36 (3H, s, Me), 3.26 (1H, br. s, OH), 5.68 (1H, s), 6.05 (1H, s), 6.28 (1H, s), 7.56 (2H, d, *J* 8.6 Hz, Ar), 8.19 (2H, d, *J* 8.6 Hz, Ar).

Reference:

9). Iwama, T.; Tsujiyama, S.-I.; Kinoshita, H.; Kanamatsu, K.; Tsurukami, Y.; Iwamura, T.; Watanabe, S.-I.; Kataoka, T. *Chem. Pharm. Bull.* **1999**, *47*, 956.