SUPPORTING INFORMATION

for

Chiral Cobalt-Catalyzed Enantioselective Aerobic Oxidation of α–Hydroxy Esters

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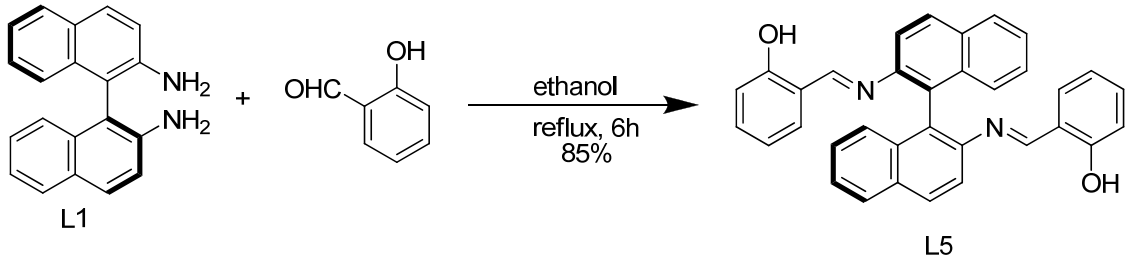
General considerations

Cobalt(II) acetate tetrahydrate and 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) were purchased from Sigma-Aldrich chemical company and used as received. (*S*)-BINAM purchased from Gerchem Labs Pvt. Ltd. Hyderabad, India. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching. Silica gel for column chromatography (particle size 100-200 mesh) purchased from SRL India. Optical rotations were measured with Autopol IV - Rudolph Research Analytical Polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. ^{1}H NMR spectra were reported relative to Me_4Si (δ 0.0 ppm) or residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. The enantiomeric excess (%*ee*) of α-hydroxy esters were determined by JASCO uv-2070 plus HPLC and Shimadzu UFLC systems using Daicel chemical industries, Ltd ChiralPAK AS-H (0.46cm ϕ x 25cm) column. ^{1}H and ^{13}C NMR and HRMS Spectral data have been included for all compounds. HPLC spectra for the %*ee* determination of all optically active α-hydroxy esters are given in this supporting information.

Synthesis of Ligand L5

Scheme 1



Experimental Procedure

Synthesis of L5[1]**:** In a 50 mL two neck round bottom flask equipped with reflux condenser, a mixture of **L1 (**502.7 mg, 1.77 mmol) and salicylaldehyde (0.38 mL, 3.54 mmol) in ethanol (20 mL) was taken and refluxed for 6 hours. The reaction mixture was cooled to room temperature, the solution was filtered off. The solvent was removed under reduced pressure and the residue was recrystallizd from benzene : heaxane (1:3, V/V) to give **L5** (740 mg, 85%) as a yellow compound. Mp 181 ^{o}C (lit.[1] 181-183 ^{o}C); R_f 0.41 (in hexanes : ethyl acetate, 80:20 V/V); $[\alpha]^{D}_{25}$ = 509.2 (*c* = 0.5 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.12 (s, 2H), 8.69 (s, 2H), 8.13 (d, *J* = 9.2 Hz, 2H), 8.00 (d, *J* = 8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.46-7.50 (m, 2H), 7.27-7.33 (m, 4H), 7.19-7.23 (m, 4H), 6.78-6.82 (m, 2H), 6.73 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 160.8, 143.8, 133.2, 132.8, 132.5, 132.2, 130.0, 129.5, 128.3, 127.0, 126.5, 125.9, 119.3, 118.7, 117.1, 116.9; IR (Neat) 3056, 1608, 1282, 750 cm^{-1}; HRMS (*m*/*z*): $[M+1]^{+}$calcd for $C_{34}H_{25}N_2O_2$, 493.1916; found, 493.1917.

General experimental procedure for oxidative kinetic resolution

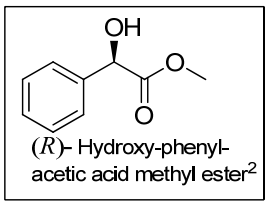
A mixture of **L5** (49.2 mg, 0.1 mmol) and Cobalt(II) acetate tetrahydrate (25 mg, 0.1mmol) in 8 mL of toluene was stirred at room temperature for 10 min, TEMPO (7.82 mg, 0.05 mmol) was then added to the reaction mixture. After stirring for 5 min, (±)-Hydroxy-phenyl-acetic acid methyl ester (166 mg, 1 mmol) was added and then reaction stirred under an O_2 atmosphere (using O_2 balloon) for 11 hours at 90 ^{o}C. The reaction mixture was concentrated and the resulting residue was purified by silica gel column chromatography (eluents: hexanes-ethylacetate) to give the Methyl phenylglyoxylate (75.5 mg, yield 46%) and unreacted Hydroxy-phenyl-acetic acid methyl ester (78 mg, yield 47%).

Hydroxy-phenyl-acetic acid methyl ester: Colorless oil; R_f 0.33; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -108.7 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.40-7.33 (m, 3H), 5.18 (d, *J* = 5.6 Hz, 1H),3.77 (s, 3H), 3.14 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 138.4, 128.8, 128.7, 126.7, 73.0, 53.2; IR

(Neat) 3457, 2954, 1735, 1221, 1071 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_9H_{10}O_3Na_1$, 189.0528; found, 189.0526. The enantiomeric excess (%*ee*) was determined to be 78% by HPLC using ChiralPAK AS-H column (25% *i*-PrOH/ hexanes, 1 mL/min, 220 nm): t_R (minor, 5.1 min), t_R (major, 5.6 min).

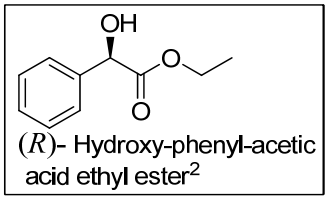
Methyl phenylglyoxylate: Colorless oil; R_f 0.63; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 164.1, 135.0, 132.4, 130.1, 128.9, 52.8 ; IR (Neat) 2963, 1741, 1688, 1208, 1003 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_9H_8O_3Na_1$, 187.0371; found, 187.0374.

Spectral data for all α-hydroxy esters and α-keto esters



(*R*)- Hydroxy-phenyl-acetic acid methyl ester[2]

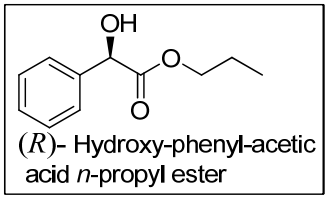
Colorless oil; R_f 0.33; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -108.7 (*c* = 1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.40-7.33 (m, 3H), 5.18 (d, J = 5.6 Hz, 1H), 3.77 (s, 3H), 3.14 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 138.4, 128.8, 128.7, 126.7, 73.0, 53.2; IR (Neat) 3457, 2954, 1735, 1221, 1071 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_9H_{10}O_3Na_1$, 189.0528; found, 189.0526. The enantiomeric excess (%*ee*) was determined to be 78% by HPLC using ChiralPAK AS-H column (25% *i*-PrOH/ hexanes, 1 mL/min, 220 nm): t_R (minor, 5.1 min), t_R (major, 5.6 min).



(*R*)- Hydroxy-phenyl-acetic acid ethyl ester[2]

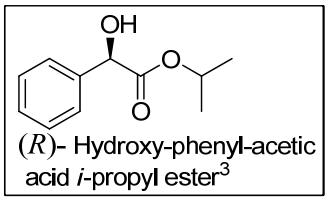
Colorless oil; R_f 0.38; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -127.7 (*c* = 1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.45 (m, 2H),

7.30-7.39 (m, 3H), 5.16 (d, J = 5.6 Hz, 1H), 4.13-4.32 (m, 2H), 3.46 (d, J = 5.6 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 138.5, 128.6, 128.4, 126.6, 73.0, 62.2, 14.0; IR (Neat) 3460, 2982, 1728, 1182, 1065 cm^{-1}; HRMS (m/z): $[MNa]^+$ calcd for $C_{10}H_{12}O_3Na_1$, 203.0684; found, 203.0687. The enantiomeric excess (%*ee*) was determined to be 97% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (minor, 8.7 min), t_R (major, 9.2 min).



(*R*)- Hydroxy-phenyl-acetic acid *n*-propyl ester

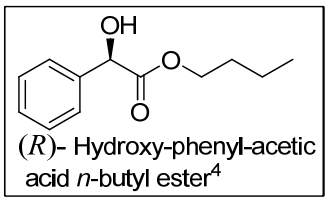
Colorless oil; R_f 0.35; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -67.9 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.45 (m, 2H), 7.29-7.38 (m, 3H), 5.17 (d, J = 6 Hz, 1H), 4.06-4.17 (m, 2H), 3.48-3.56 (m, 1H), 1.60 (sextet, J = 7.2 Hz, 2H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 138.6, 128.6, 128.4, 126.6, 72.9, 67.7, 21.9, 10.2; IR (Neat) 3453, 2968, 1730, 1180, 1064 cm^{-1}; HRMS (m/z): $[MNa]^+$ calcd for $C_{11}H_{14}O_3Na_1$, 217.0841; found, 217.0843. The enantiomeric excess (%*ee*) was determined to be 91% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 220 nm): t_R (minor, 7.4 min), t_R (major, 8.5 min).



(*R*)- Hydroxy-phenyl-acetic acid *i*-propyl ester[3]

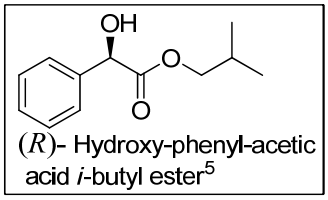
Colorless oil; R_f 0.49; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -173.5 (c = 2 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.34 (m, 2H), 7.15-7.25 (m, 3H), 5.02 (d, J = 6 Hz, 1H), 4.94 (septet, J = 6 Hz, 1H), 3.77 (d, J = 4.4 Hz, 1H), 1.15 (d, J = 6 Hz, 3H), 0.98 (d, J = 6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 138.6, 128.6, 128.4, 126.5, 73.0, 70.2, 21.8, 21.5; IR (Neat) 3458, 2982, 1726, 1181, 1098 cm^{-1}; HRMS (m/z): $[MNa]^+$ calcd for $C_{11}H_{14}O_3Na_1$, 217.0841; found, 217.0845. The enantiomeric excess (%*ee*) was determined to be 84% by HPLC using ChiralPAK

AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 220 nm): t_R (major, 6.7 min), t_R (minor, 7.2 min).



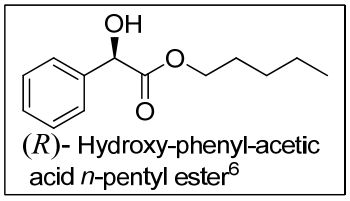
(*R*)- Hydroxy-phenyl-acetic acid *n*-butyl ester[4]

Colorless oil; R_f 0.32; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -62.9 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.44 (m, 2H), 7.28-7.38 (m, 3H), 5.16 (d, *J* = 5.2 Hz, 1H), 4.10-4.22 (m, 2H), 3.53 (d, *J* = 3.6 Hz, 1H), 1.51-1.60 (m, 2H), 1.24 (sextet, *J* = 7.6 Hz, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 138.5, 128.6, 128.4, 126.6, 72.9, 66.0, 30.4, 18.9, 13.6; IR (Neat) 3469, 2959, 1731, 1180, 1066 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{12}H_{16}O_3Na_1$, 231.0997; found, 231.0996. The enantiomeric excess (%*ee*) was determined to be 90% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 220 nm): t_R (minor, 6.2 min), t_R (major, 8.3 min).



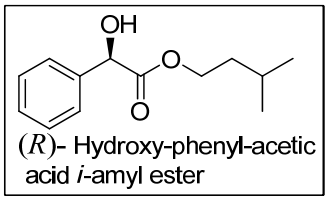
(*R*)- Hydroxy-phenyl-acetic acid *i*-butyl ester[5]

Colorless oil; R_f 0.54; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -118.7 (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.28-7.39 (m, 3H), 5.18 (d, *J* = 5.2 Hz, 1H), 3.98-4.00 (m, 2H), 3.53 (d, *J* = 5.6 Hz, 1H), 1.87 (septet, *J* = 6.4 Hz, 1H), 0.81 (dd, *J* = 6.8 Hz, 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 138.6, 128.6, 128.5, 126.6, 72.9, 72.2, 27.8, 18.9; IR (Neat) 3482, 2962, 1735, 1183, 1099 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{12}H_{16}O_3Na_1$, 231.0997; found, 231.0995. The enantiomeric excess (%*ee*) was determined to be 84% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 220 nm): t_R (minor, 5.7 min), t_R (major, 7.2 min).



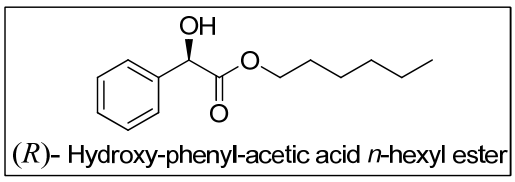
(*R*)- Hydroxy-phenyl-acetic acid *n*-pentyl ester[6]

Colorless oil; R_f 0.42; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -88.2 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.45 (m, 2H), 7.29-7.39 (m, 3H), 5.16 (d, *J* = 5.6 Hz, 1H), 4.12-4.18 (m, 2H), 3.49 (d, *J* = 5.6 Hz, 1H), 1.53-1.62 (m, 2H), 1.12-1.28 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 138.6, 128.7, 128.5, 126.7, 73.0, 66.4, 28.2, 27.9, 22.3, 14.0; IR (Neat) 3446, 2957, 2872, 1731, 1183, 1067 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{13}H_{18}O_3Na_1$, 245.1154; found, 245.1157. The enantiomeric excess (%*ee*) was determined to be 94% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (minor, 6.5 min), t_R (major, 8.5 min).



(*R*)- Hydroxy-phenyl-acetic acid *i*-amyl ester

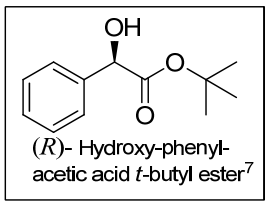
Colorless oil; R_f 0.35; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -80.7 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.44 (m, 2H),7.30-7.38 (m, 3H), 5.15 (d, *J* = 5.6 Hz, 1H), 4.12-4.25 (m, 2H), 3.49 (d, *J* = 5.6 Hz, 1H), 1.43-1.56 (m, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 138.6, 128.7, 128.5, 126.6, 73.0, 65.0, 37.2, 25.0, 22.5, 22.4; IR (Neat) 3445, 2958, 1731, 1183, 1067 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{13}H_{18}O_3Na_1$, 245.1154; found, 245.1157. The enantiomeric excess (%*ee*) was determined to be 98% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (minor, 5.9 min), t_R (major, 8.4 min).



(*R*)- Hydroxy-phenyl-acetic acid *n*-hexyl ester

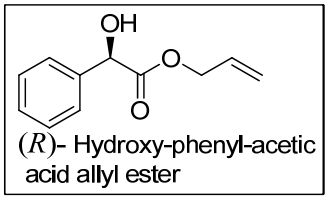
Colorless oil; R_f 0.47; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -70.3 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* =

7.2 Hz, 2H), 7.29-7.39 (m, 3H), 5.16 (d, J = 5.6 Hz, 1H), 4.15 (t, J = 6.8 Hz, 2H), 3.50 (d, J = 5.6 Hz, 1H), 1.52-1.60 (m, 2H), 1.15-1.28 (m, 6H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 138.6, 128.7, 128.5, 126.6, 73.0, 66.5, 31.3, 28.5, 25.4, 22.6, 14.0; IR (Neat) 3464, 2956, 2930, 2858, 1731, 1455, 1182, 1067 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{14}H_{20}O_3Na_1$, 259.1310; found, 259.1310. The enantiomeric excess (%*ee*) was determined to be 98% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (minor, 6.1 min), t_R (major, 8.2 min).



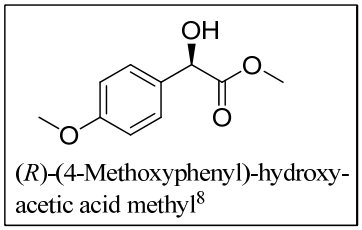
(*R*)- Hydroxy-phenyl-acetic acid *t*-butyl ester[7]

White solid; mp = 56 °C (lit. 53-54 °C,); R_f 0.48; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -86.7 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 7.2 Hz, 2H), 7.28-7.38 (m, 3H), 5.04 (s, 1H), 3.52 (bs, 1H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 139.1, 128.5, 128.2, 126.5, 83.2, 73.1, 27.9; IR (Neat) 3476, 2977, 2930, 1729, 1157, 912 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{12}H_{16}O_3Na_1$, 231.0997; found, 231.0997. The enantiomeric excess (%*ee*) was determined to be 98% by HPLC using ChiralPAK OD-H column (25% *i*-PrOH/ hexanes, 0.5 mL/min, 200 nm): t_R (minor, 8.0 min), t_R (major, 11.3 min).



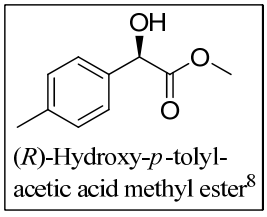
(*R*)- Hydroxy-phenyl-acetic acid allyl ester

Colorless oil; R_f 0.32; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^D_{30}$ = -90.5 (*c* = 0.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.46 (m, 2H), 7.30-7.40 (m, 3H), 5.78-5.89 (m, 1H), 5.21 (s, 2H), 5.15-5.19 (m, 1H), 4.60-4.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 138.4, 131.2, 128.6, 128.5, 126.6, 118.7, 73.0, 66.4; IR (Neat) 3442, 2932, 1731, 1596, 1454, 1212, 1164 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{11}H_{12}O_3Na_1$, 215.0684; found, 215.0686. The enantiomeric excess (%*ee*) was determined to be 99.9% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (major, 5.1 min),



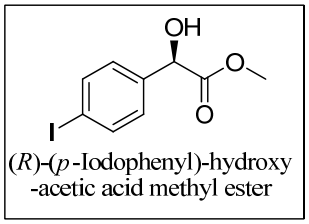
(*R*)-(4-Methoxyphenyl)-hydroxy-acetic acid methyl[8]

White solid; mp = 62 ^{o}C (lit. 63-64 ^{o}C,); R_f 0.30; (hexanes : ethyl acetate, 70:30 v/v): $[\alpha]^{D}_{30}$ = -129.1 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 2.0 Hz, 6.8 Hz, 2H), 6.90 (dd, *J* = 2.0 Hz, 6.8 Hz, 2H), 5.13 (d, *J* = 5.6 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.39 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 159.9, 130.6, 128.1, 114.2, 72.6, 55.4, 53.1; IR (Neat) 3452, 2948, 1738, 1248, 913 cm^{-1}; HRMS (*m*/*z*): $[MNa]^{+}$ calcd for $C_{10}H_{12}O_4Na_1$, 219.0997; found, 219.0995. The enantiomeric excess (%*ee*) was determined to be 90% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (major, 21.5 min), t_R (minor, 24.8 min).



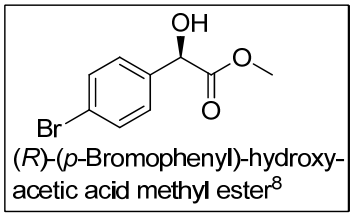
(*R*)-Hydroxy-*p*-tolyl-acetic acid methyl ester[8]

Colorless oil; R_f 0.35; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -82.6 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 5.15 (d, *J* = 5.6 Hz, 1H), 3.76 (s, 3H), 3.40 (d, *J* = 5.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 138.4, 135.5, 129.4, 126.6, 72.9, 53.0, 21.3; IR (Neat) 3477, 2952, 1738, 1081, 921 cm^{-1}; HRMS (*m*/*z*): $[MNa]^{+}$ calcd for $C_{10}H_{12}O_3Na_1$, 203.1048; found, 203.1043. The enantiomeric excess (%*ee*) was determined to be 90% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (major, 10.3 min), t_R (minor, 12.1 min).



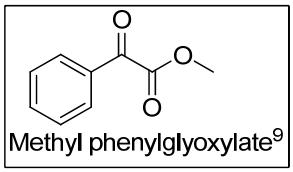
(*R*)-(*p*-Iodophenyl)-hydroxy -acetic acid methyl ester

White solid; mp = 64 ^{o}C; R_f 0.29; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -55.8 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 5.12 (s, 1H), 3.76 (s, 3H), 3.47 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 138.0, 137.8, 128.6, 94.4, 72.4, 53.3; IR (Neat) 3443, 2937, 1737, 1224, 1180, 1077 cm^{-1}; HRMS (*m*/*z*): $[MHNa]^+$ calcd for $C_9H_{10}O_3I_1Na_1$, 315.9570; found, 315.9572. The enantiomeric excess (%*ee*) was determined to be 99.64% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (major, 11.0 min), t_R (minor, 12.4 min).



(*R*)-(*p*-Bromophenyl)-hydroxy-acetic acid methyl ester[8]

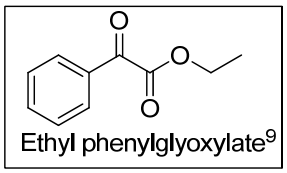
Colorless oil; R_f 0.25; (hexanes : ethyl acetate, 80:20 v/v): $[\alpha]^{D}_{30}$ = -83.0 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2H), 5.14 (d, *J* = 4.4 Hz, 1H), 3.77 (s, 3H), 3.47 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 137.3, 131.9, 128.4, 122.7, 72.4, 53.3; IR (Neat) 3401, 2952, 1739, 1252, 913 cm^{-1}; HRMS (*m*/*z*): $[MHNa]^+$ calcd for $C_9H_{10}O_3Br_1Na_1$, 267.9711; found, 267.9713. The enantiomeric excess (%*ee*) was determined to be 85% by HPLC using ChiralPAK AS-H column (10% *i*-PrOH/ hexanes, 1 mL/min, 190 nm): t_R (minor, 8.9 min), t_R (major, 10.4 min).



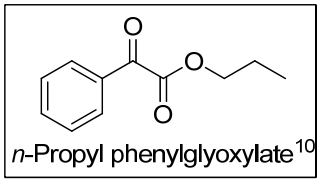
Methyl phenylglyoxylate[9]

Colorless oil; R_f 0.63; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 164.1, 135.0, 132.4,

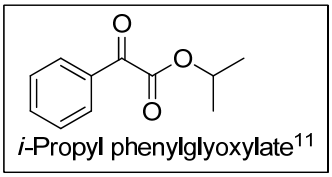
130.1, 128.9, 52.8 ; IR (Neat) 2963, 1741, 1688, 1208, 1003 cm^{-1}; HRMS (*m*/*z*): $[MH]^+$ calcd for $C_9H_9O_3$, 165.0552; found, 165.0547.



Colorless oil; R_f 0.69; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.99-8.04 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.4, 163.8, 134.9, 132.4, 130.0, 128.9, 62.3, 14.1; IR (Neat) 2984, 2920, 1732, 1686, 1196, 1175 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{10}H_{10}O_3Na_1$, 201.0528; found, 201.0528.

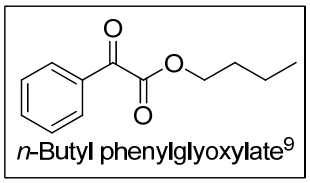


Colorless oil; R_f 0.76; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.03 (m, 2H), 7.63-7.68 (m, 1H), 7.51 (t, *J* = 8 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 1.81 (Sextet, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 164.1, 135.0, 132.6, 130.1, 129.0, 67.9, 22.0, 10.4; IR (Neat) 2970, 1736, 1690, 1199, 1177, 991 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{11}H_{12}O_3Na_1$, 215.0684; found, 215.0683.



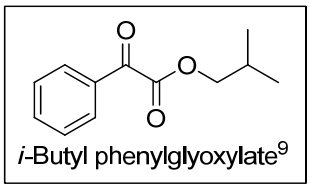
Colorless oil; R_f 0.75; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.02 (m, 2H), 7.63-7.68 (m, 1H), 7.51 (t, *J* = 8 Hz, 2H), 5.33 (Septet, *J* = 6 Hz, 1H), 1.41 (d, *J* = 6 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8, 163.7, 134.9, 132.5, 130.0, 128.9, 70.7, 21.8; IR (Neat) 2984, 2920, 1728, 1687,

1201, 1176, 1101, 986 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{11}H_{12}O_3Na_1$, 215.0684; found, 215.0681.



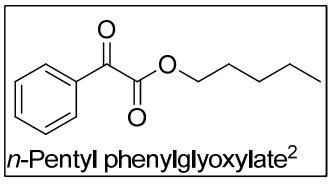
n-Butyl phenylglyoxylate[9]

Colorless oil; R_f 0.74; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.03 (m, 2H), 7.63-7.69 (m, 1H), 7.48-7.54 (m, 2H), 4.40 (t, *J* = 6.8 Hz, 2H), 1.77 (Quintet, *J* = 6.8 Hz, 2H), 1.45 (Sextet, *J* = 7.6 Hz, 2H), 0.94-1.0 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 164.1, 135.0, 132.6, 130.1, 129.0, 66.2, 30.6, 19.1, 13.7; IR (Neat) 2961, 2875, 1733, 1687, 1196, 1175 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{12}H_{14}O_3Na_1$, 229.0841; found, 229.0845.



i-Butyl phenylglyoxylate[9]

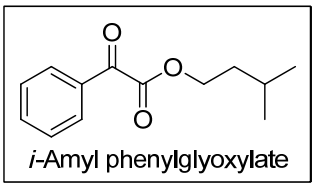
Colorless oil; R_f 0.74; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.03 (m, 2H), 7.64-7.69 (m, 1H), 7.49-7.55 (m, 2H), 4.18 (d, *J* = 6.8 Hz, 2H), 2.09 (Septet, *J* = 7.2 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7, 164.2, 135.0, 132.6, 130.1, 129.0, 72.2, 27.8, 19.1; IR (Neat) 2964, 1733, 1687, 1196, 1174, 995 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{12}H_{14}O_3Na_1$, 229.0841; found, 229.0839.



n-Pentyl phenylglyoxylate[2]

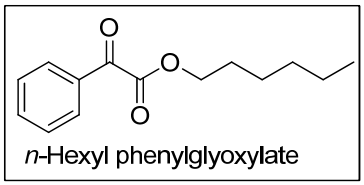
Colorless oil; R_f 0.67; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.02 (m, 2H), 7.63-7.68 (m, 1H), 7.51 (t, *J* = 8 Hz, 2H), 4.38 (t, *J* = 6.8 Hz, 2H), 1.78 (Quintet, *J* = 7.2 Hz, 2H), 1.30-1.45(m, 4H), 0.914 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 164.1, 135.0, 132.6, 130.1, 129.0,

66.5, 28.3, 28.0, 22.4, 14.0; IR (Neat) 2958, 2934, 2872, 1733, 1687, 1196, 1175 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{13}H_{16}O_3Na_1$, 243.0997; found, 243.0994.



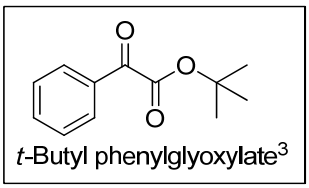
i-Amyl phenylglyoxylate

Colorless oil; R_f 0.71; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.02 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 4.42 (t, *J* = 7.2 Hz, 2H), 1.75 (q, *J* = 6.8 Hz, 1H), 1.67 (q, *J* = 6.8 Hz, 2H), 0.96 (d, *J* = 6.4 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 164.1, 135.0, 132.5, 130.1, 129.0, 65.0, 37.1, 34.2, 25.0, 22.5; IR (Neat) 2959, 1732, 1687, 1196, 1174, cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{13}H_{16}O_3Na_1$, 243.0997; found, 243.0992.



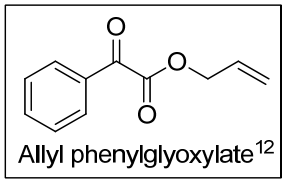
n-Hexyl phenylglyoxylate

Colorless oil; R_f 0.65; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-8.02 (m, 2H), 7.62-7.68 (m, 1H), 7.48-7.54 (m, 2H), 4.35-4.41 (m, 2H), 1.77 (Quintet, *J* = 7.2 Hz, 2H), 1.37-1.44(m, 2H), 1.26-1.34 (m, 4H), 0.85-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5, 164.1, 134.9, 132.5, 130.0, 128.9, 66.4, 31.3, 28.4, 25.5, 22.5, 14.0; IR (Neat) 2957, 2931, 2860, 1733, 1687, 1194, 1174 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{14}H_{18}O_3Na_1$, 257.1154; found, 257.1155.

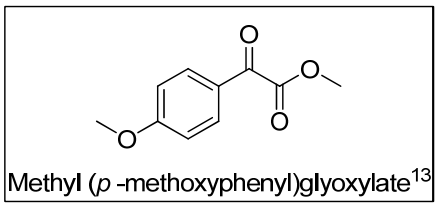


t-Butyl phenylglyoxylate[3]

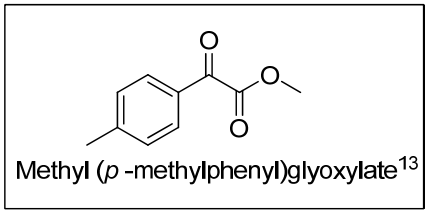
Colorless oil; R_f 0.61; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$): δ 7.99-7.95 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 1.61 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 163.9, 134.8, 132.7, 130.0, 129.0, 84.9, 28.2; IR (Neat) 2927, 2861, 1730,1688,1211, 1149,985 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_{12}H_{14}O_3Na_1$, 229.0841; found, 229.0836.


Allyl phenylglyoxylate[12]

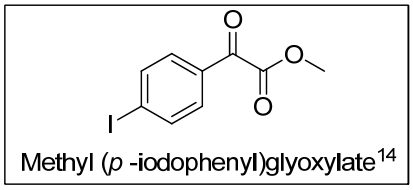
Colorless oil; R_f 0.68; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-8.04 (m, 2H), 7.64-7.69 (m, 1H), 7.52 (t, J = 8 Hz, 2H), 5.97-6.08 (m, 2H),5.32-5.49 (m, 1H), 4.88 (dt, J = 6 Hz, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 163.5, 135.0, 132.5, 130.8, 130.0, 128.9, 120.0, 66.6; IR (Neat) 3067, 1738, 1687, 1599, 1451, 1194, cm^{-1}; HRMS (m/z): $[MNa]^+$ calcd for $C_{11}H_{10}O_3Na_1$, 213.0528; found, 213.0532.


Methyl (*p* -methoxyphenyl)glyoxylate[13]

White solid; mp = 52 ^{o}C (lit. 51-49 ^{o}C,) R_f 0.54; (hexanes : ethyl acetate, 70:30 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.96 (s, 3H), 3.89 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.6, 165.2, 132.8, 125.6, 114.4, 55.8, 52.8; IR (Neat) 2936, 2859, 1730, 1682, 1213, 1155, 993 cm^{-1}; HRMS (m/z): $[MNa]^+$ calcd for $C_{10}H_{11}O_4$, 195.0657; found, 195.0661.

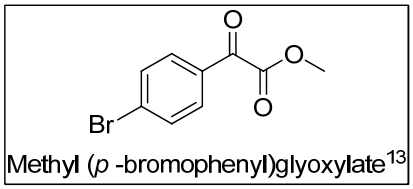

Methyl (*p* -methylphenyl)glyoxylate[13]

light yellow oil; R_f 0.70; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8 Hz, 2H), 4.02 (s, 3H), 2.49 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 163.5, 129.5, 129.2, 128.9, 53.1, 21.2; IR (Neat) 1739, 1686, 1210, 1172, 913 cm^{-1}; HRMS (m/z): $[MNa]^+$ calcd for $C_{10}H_{11}O_3Na_1$, 202.0606; found, 202.0597.



Methyl (*p* -iodophenyl)glyoxylate[14]

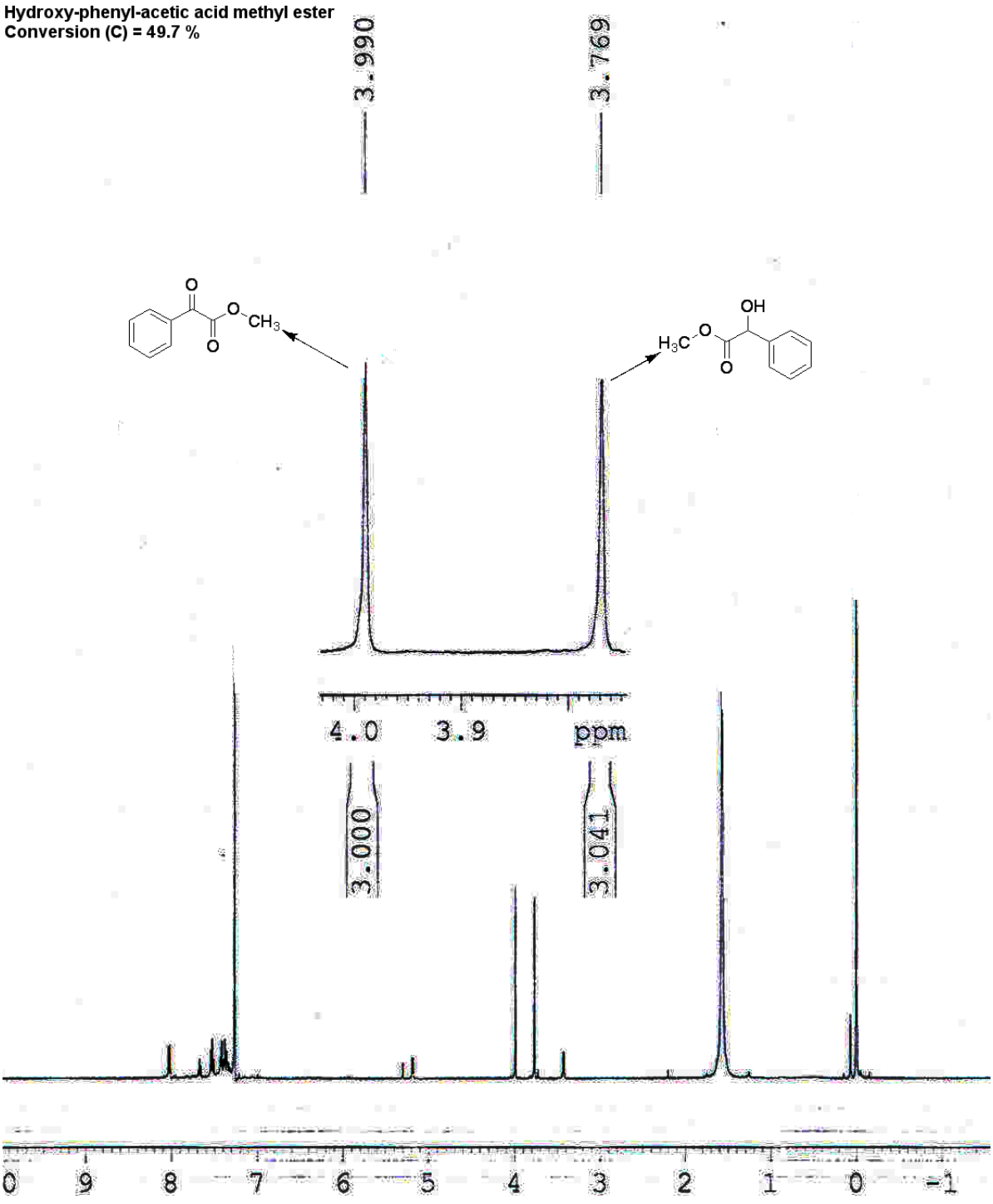
White solid; mp = 58-60 ^{o}C; R_f 0.61; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.91 (m, 2H), 7.74 (dd, J = 1.6 Hz, 8.4 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.2, 163.5, 138.4, 131.8, 131.3, 104.0, 53.1; IR (Neat) 1739, 1689, 1209, 1173, 1002, 912 cm^{-1}; HRMS (*m*/*z*): $[MHNa]^+$ calcd for $C_9H_8O_3I_1Na_1$, 313.9416; found, 313.9428.

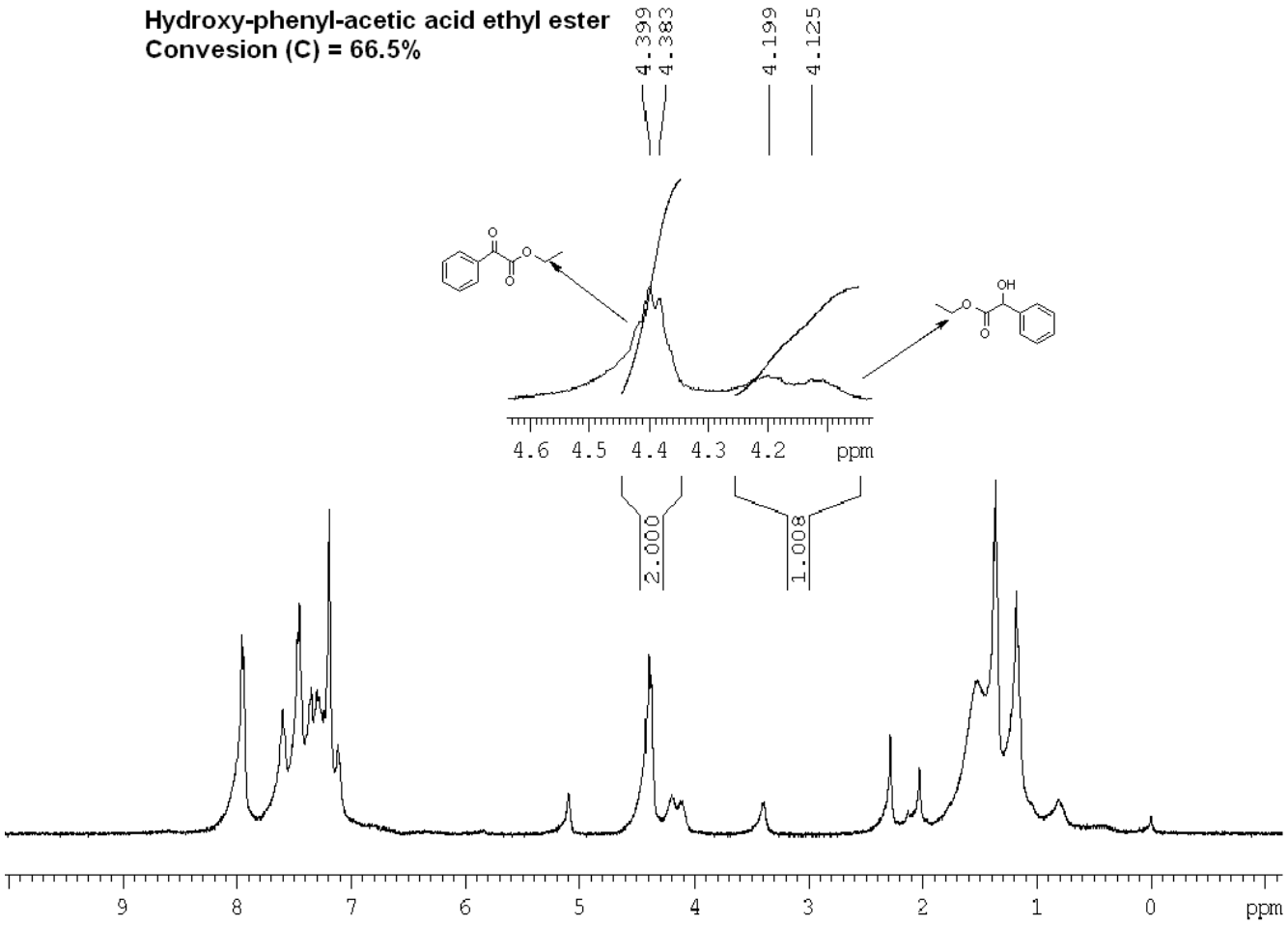


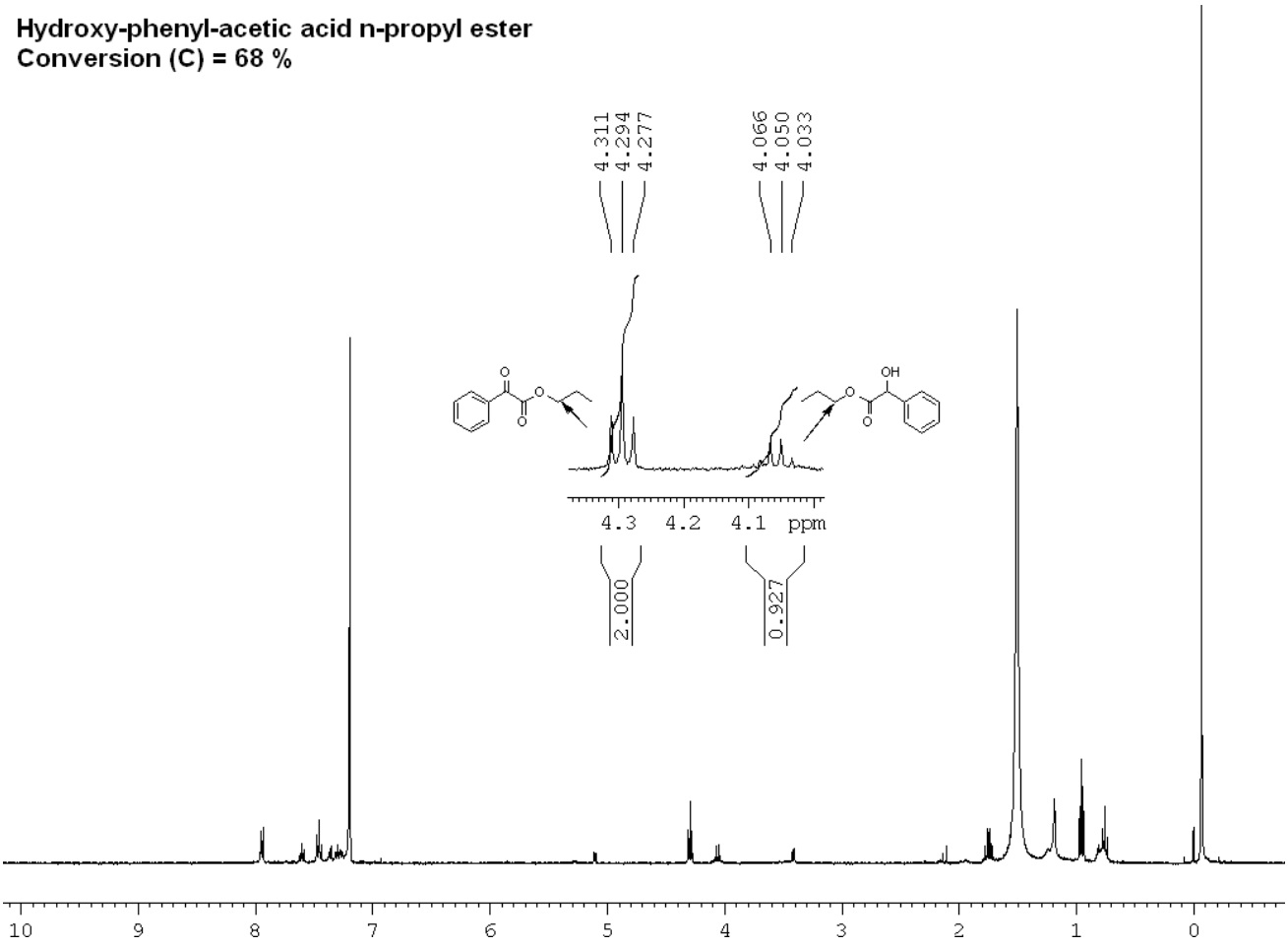
Methyl (*p* -bromophenyl)glyoxylate[13]

White solid; mp = 62 ^{o}C (lit. 63 ^{o}C,) R_f 0.53; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (J = 8.8 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.8, 163.5, 132.5, 131.6, 131.4, 130.8, 53.1; IR (Neat) 1737, 1689, 1209, 1171, 1003, 907 cm^{-1}; HRMS (*m*/*z*): $[MNa]^+$ calcd for $C_9H_7O_3Br_1Na_1$, 264.9476; found, 264.9473.

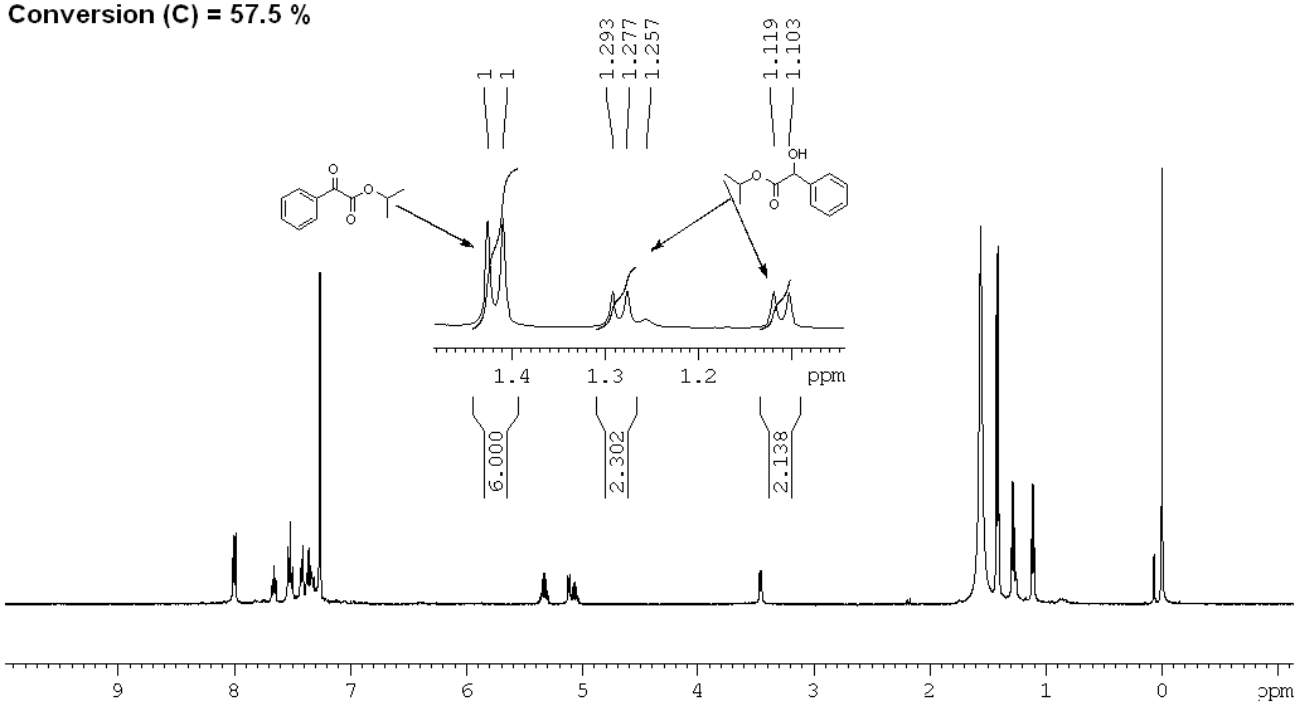
Calculation of conversion C (%) using ^{1}H NMR

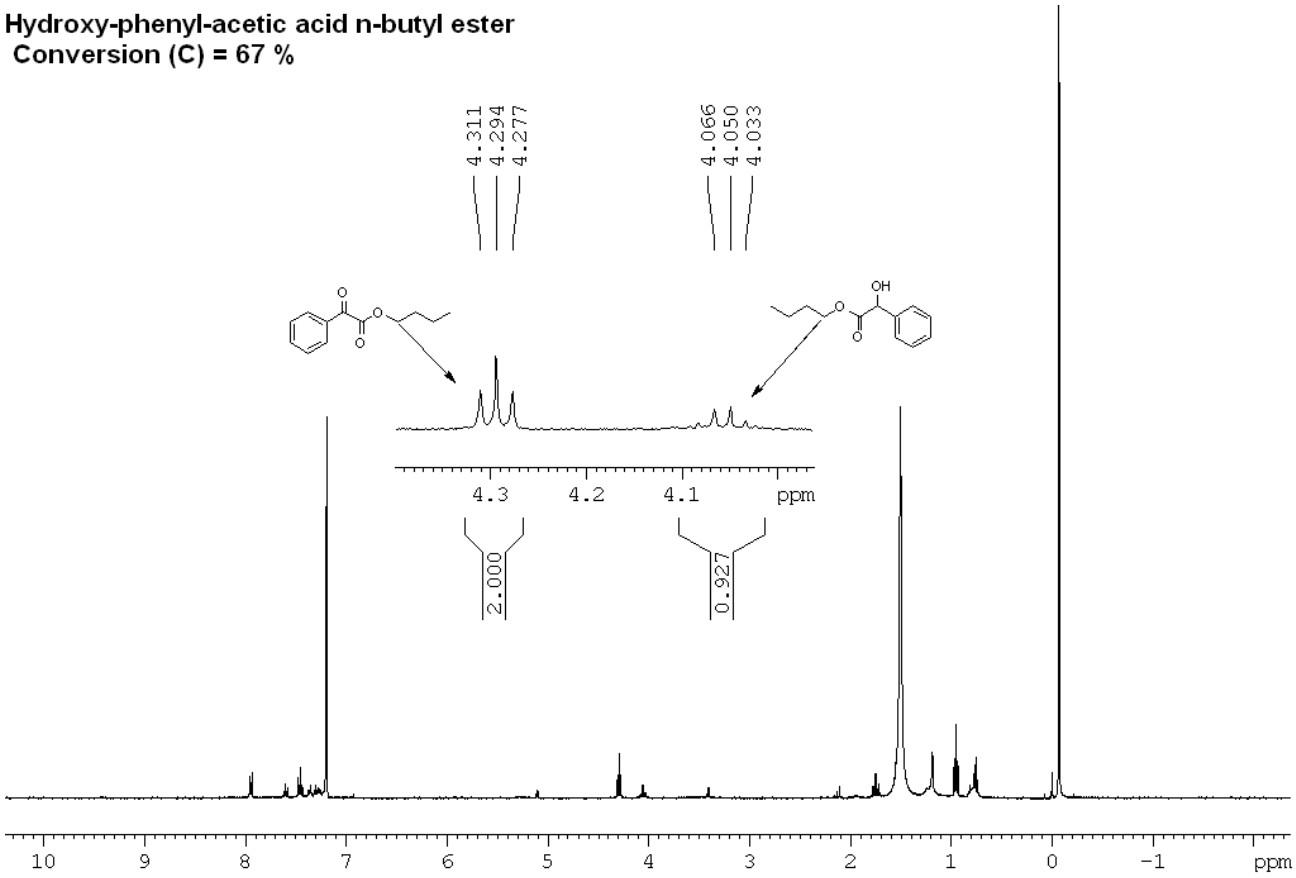


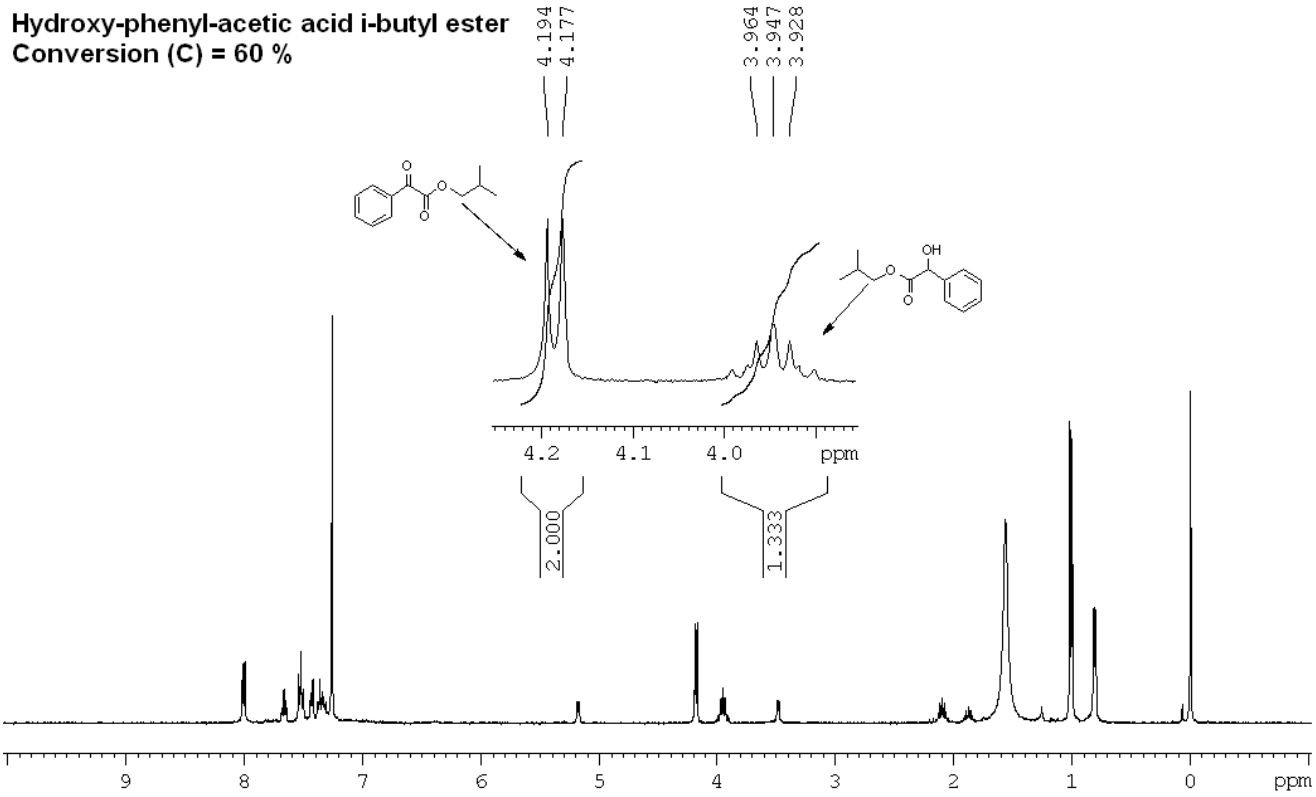

Hydroxy-phenyl-acetic acid ethyl ester
Convesion (C) = 66.5%
4.399
4.383
4.199
4.125
OH
4.6 4.5 4.4 4.3 4.2 ppm
2.000
1.008
9 8 7 6 5 4 3 2 1 0 ppm

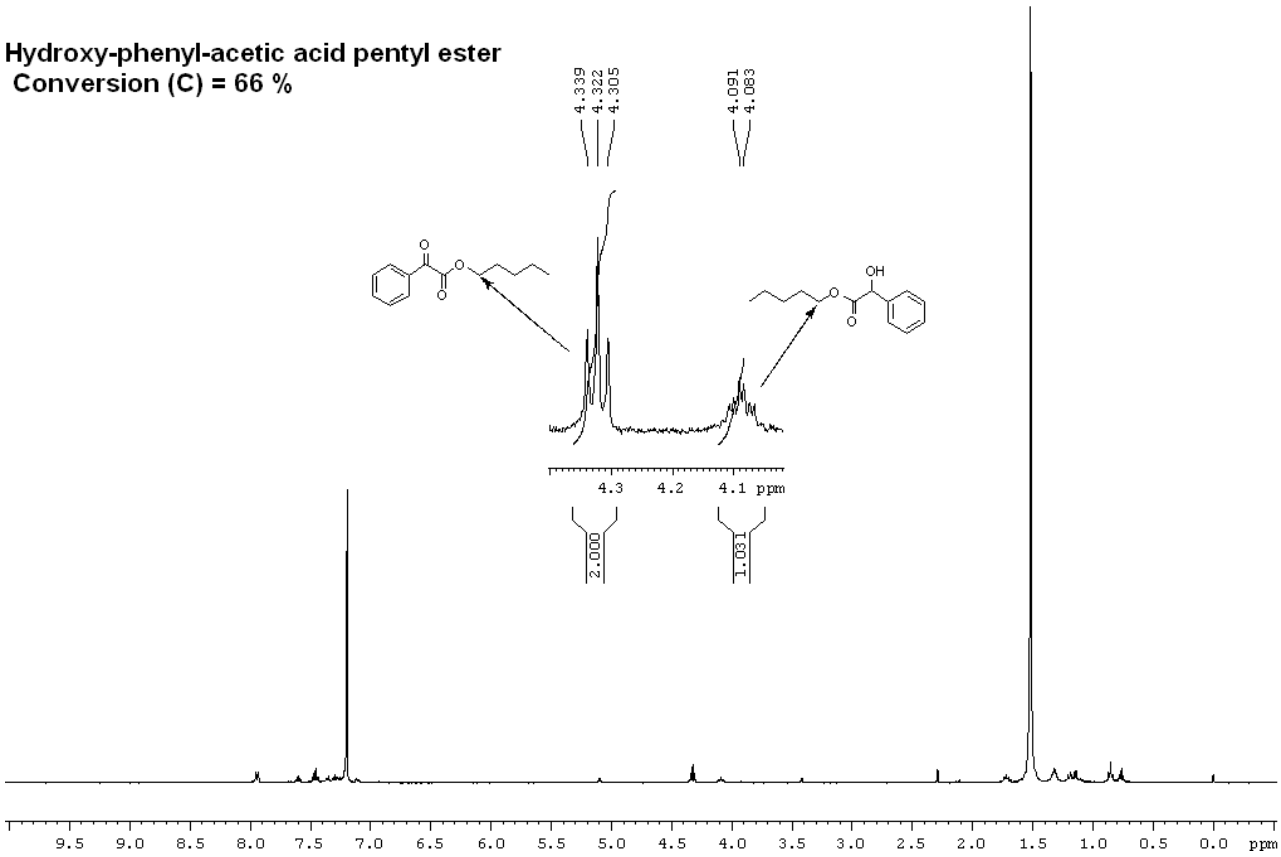

Hydroxy-phenyl-acetic acid n-propyl ester
Conversion (C) = 68 %
4.311
4.294
4.277
4.066
4.050
4.033
OH
4.3
4.2
4.1
ppm
2.000
0.927
10
9
8
7
6
5
4
3
2
1
0

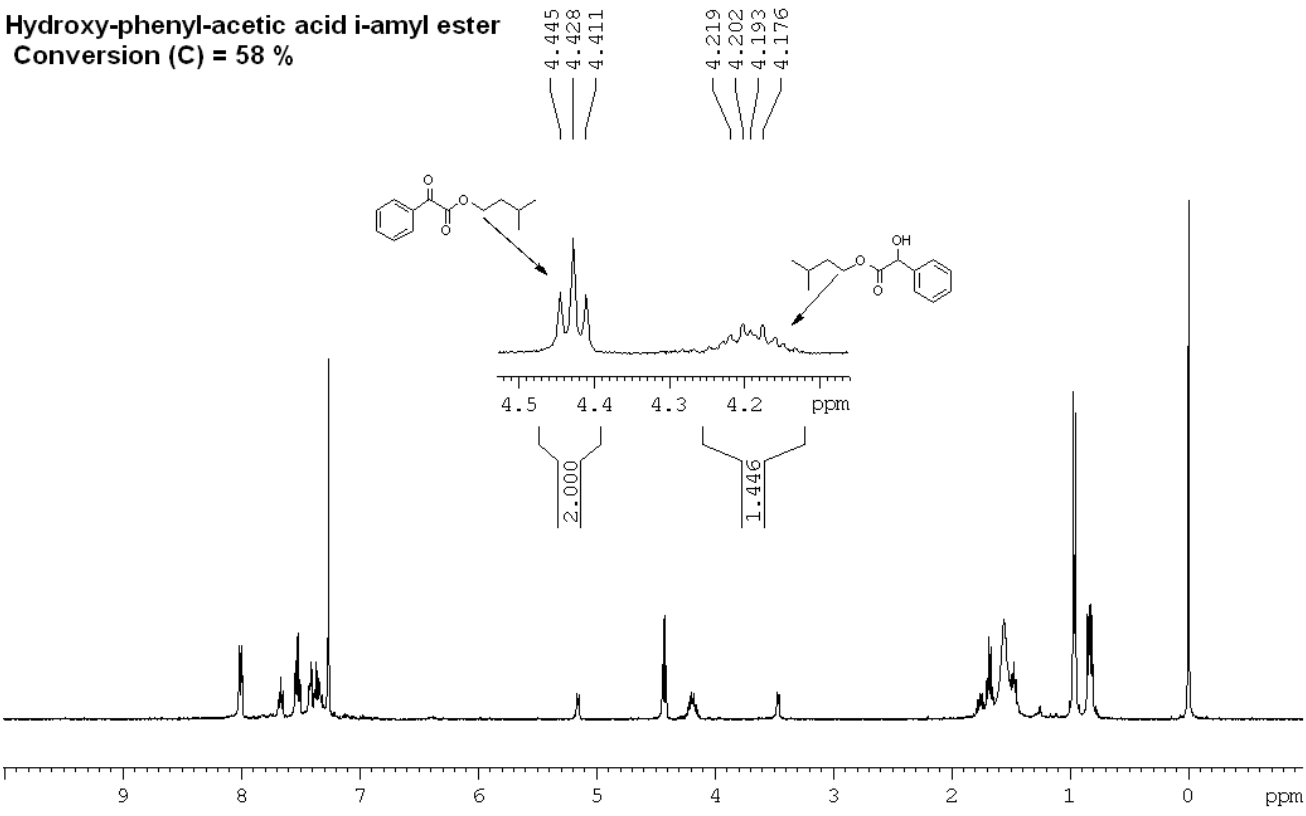
Hydroxy-phenyl-acetic acid i-propyl ester
Conversion (C) = 57.5 %

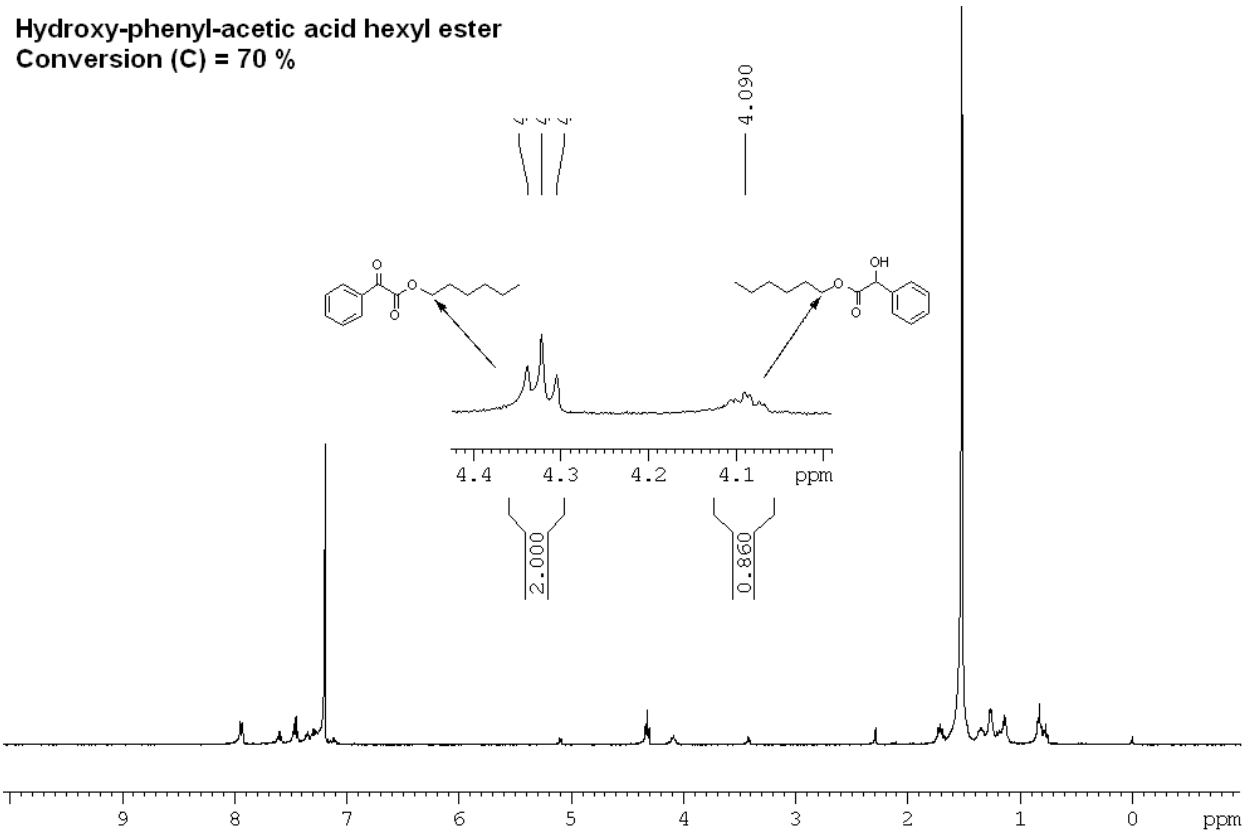


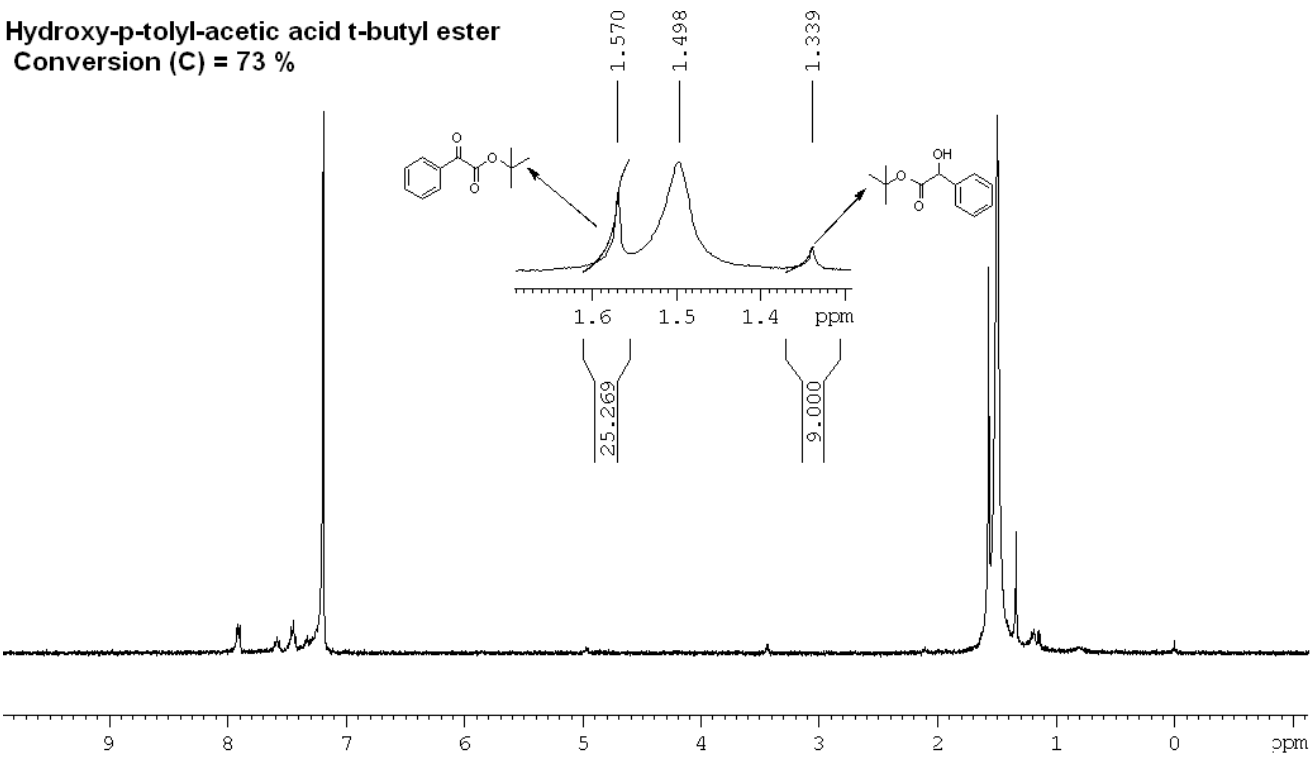

Hydroxy-phenyl-acetic acid n-butyl ester
Conversion (C) = 67 %
4.311
4.294
4.277
4.066
4.050
4.033
OH
4.3
4.2
4.1
ppm
2.000
0.927
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

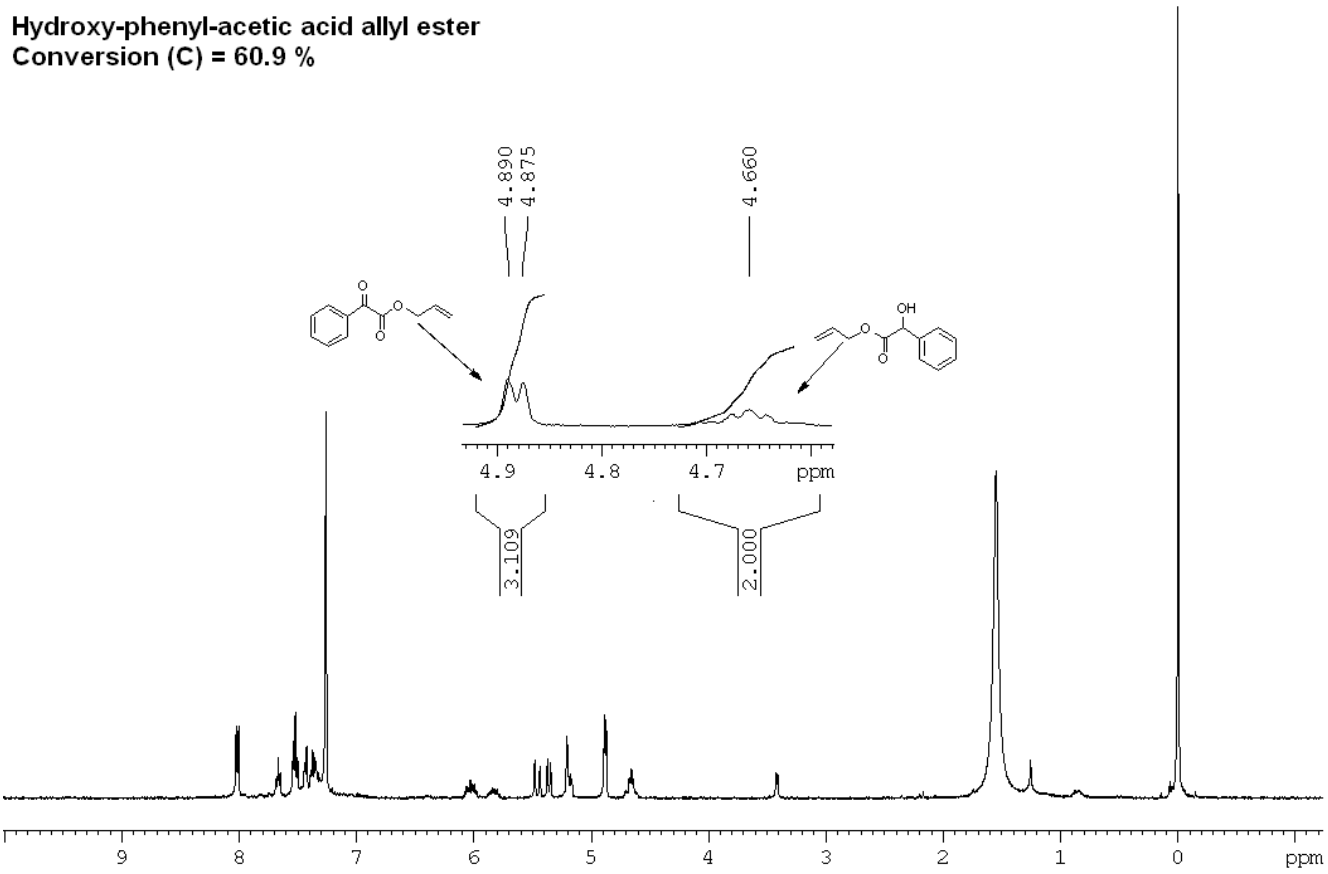

Hydroxy-phenyl-acetic acid i-butyl ester
Conversion (C) = 60 %
4.194
4.177
3.964
3.947
3.928
OH
4.2
4.1
4.0
ppm
2.000
1.333
9
8
7
6
5
4
3
2
1
0
ppm

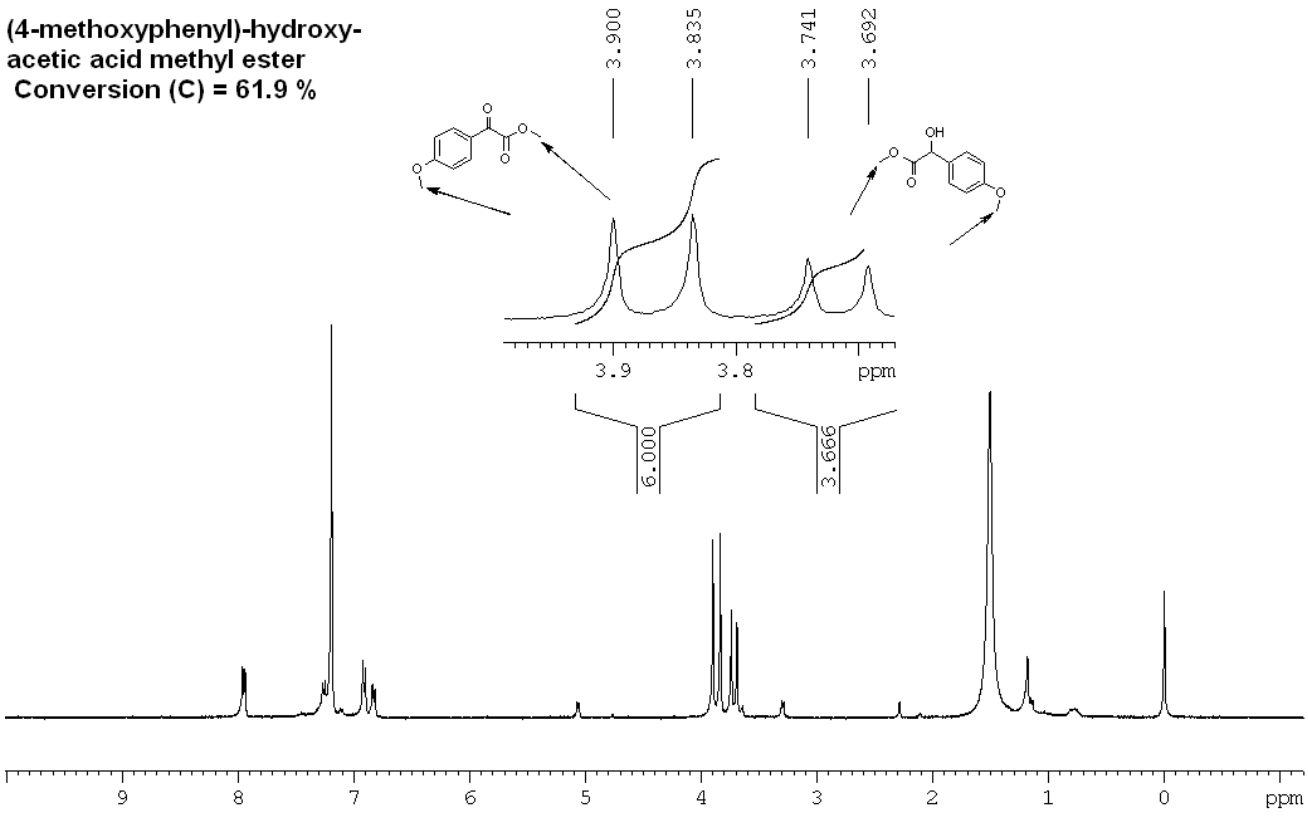

Hydroxy-phenyl-acetic acid pentyl ester
Conversion (C) = 66 %
4.339
4.322
4.305
4.091
4.083
OH
4.3
4.2
4.1 ppm
2.000
1.031
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Hydroxy-phenyl-acetic acid i-amyl ester
Conversion (C) = 58 %
4.445
4.428
4.411
4.219
4.202
4.193
4.176
OH
4.5
4.4
4.3
4.2
ppm
2.000
1.446
9
8
7
6
5
4
3
2
1
0
ppm

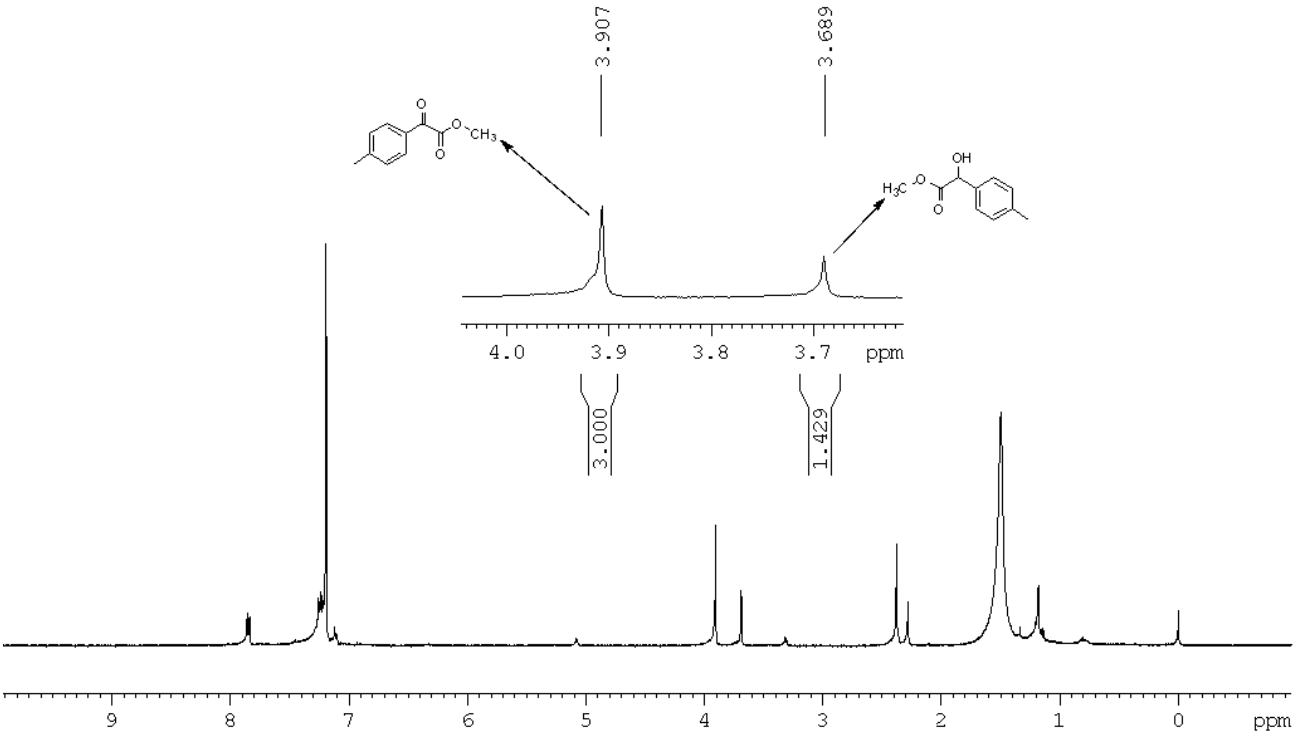

Hydroxy-phenyl-acetic acid hexyl ester
Conversion (C) = 70 %
4.090
OH
4.4
4.3
4.2
4.1
ppm
2.000
0.860
9
8
7
6
5
4
3
2
1
0
ppm

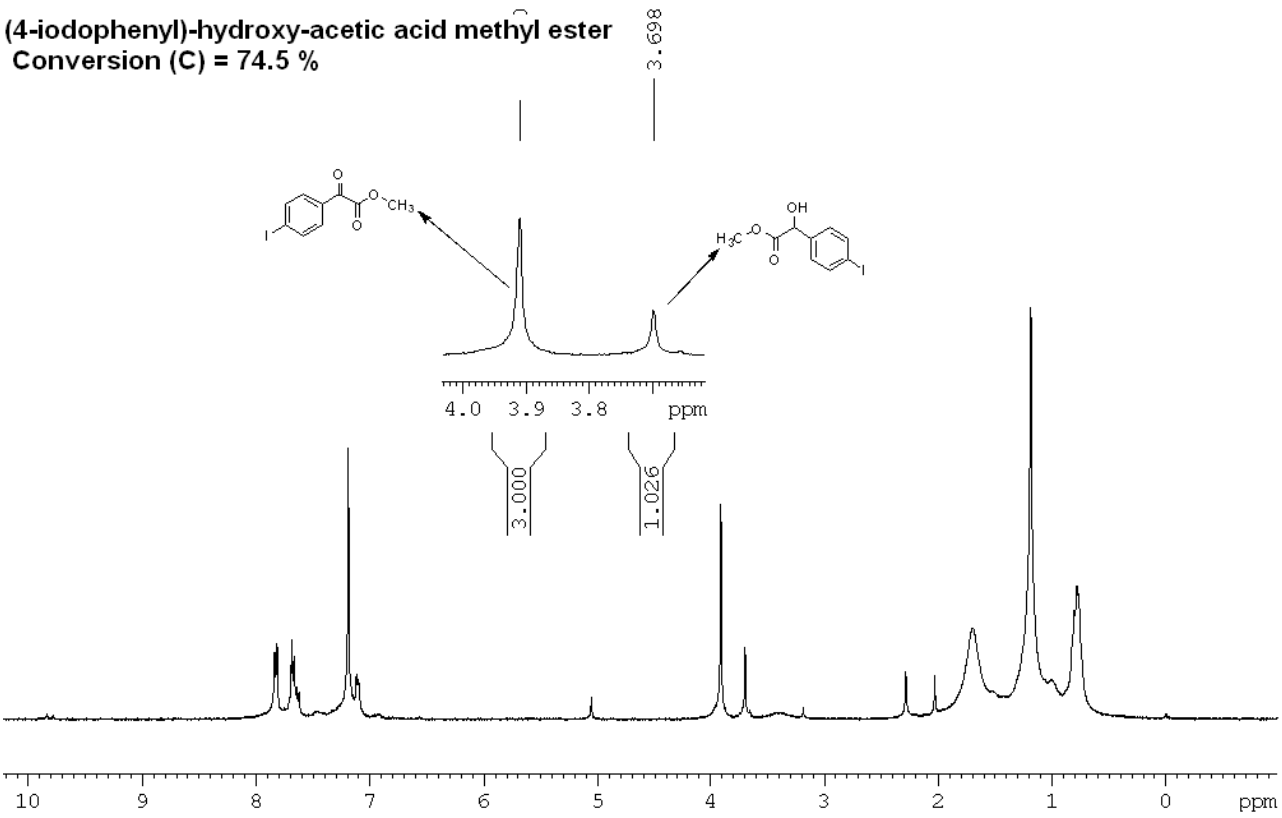

Hydroxy-p-tolyl-acetic acid t-butyl ester
Conversion (C) = 73 %
1.570
1.498
1.339
OH
1.6
1.5
1.4
ppm
25.269
9.000
9
8
7
6
5
4
3
2
1
0
ppm


Hydroxy-phenyl-acetic acid allyl ester
Conversion (C) = 60.9 %
4.890
4.875
4.660
OH
4.9
4.8
4.7
ppm
3.109
2.000
9
8
7
6
5
4
3
2
1
0
ppm

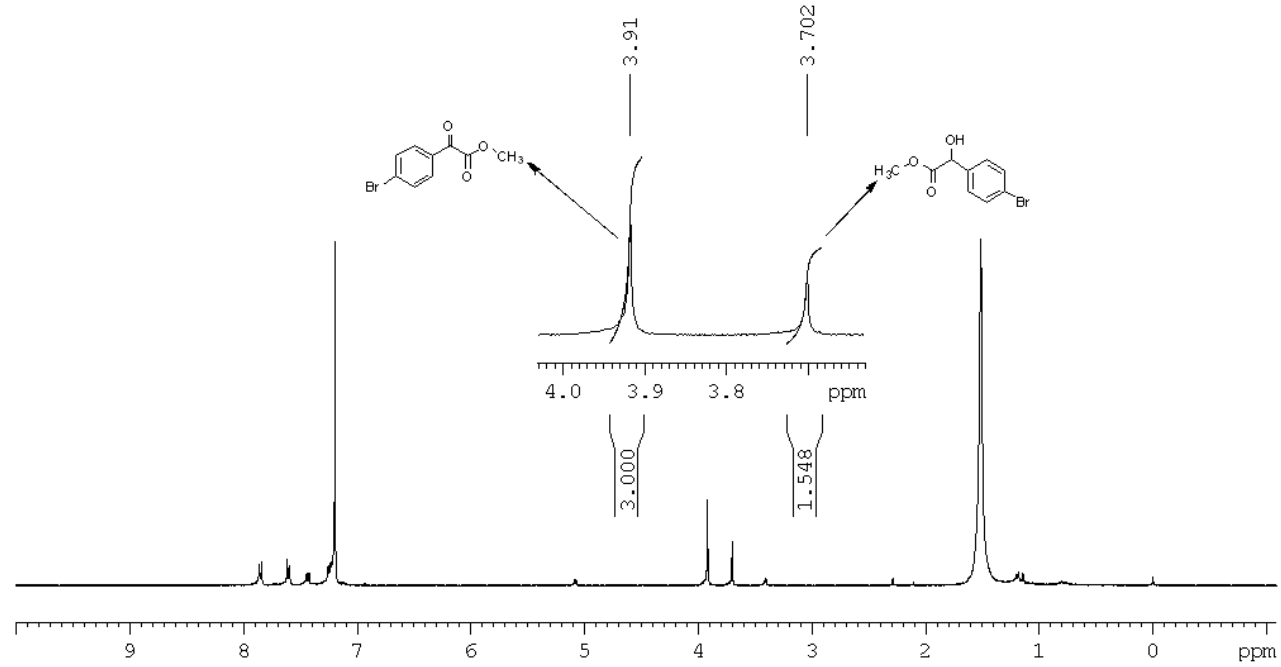

(4-methoxyphenyl)-hydroxy-
acetic acid methyl ester
Conversion (C) = 61.9 %
3.900
3.835
3.741
3.692
OH
3.9
3.8
ppm
6.000
3.666
9
8
7
6
5
4
3
2
1
0
ppm

Hydroxy-p-tolyl-acetic acid methyl ester
Conversion (C) = 67.7 %

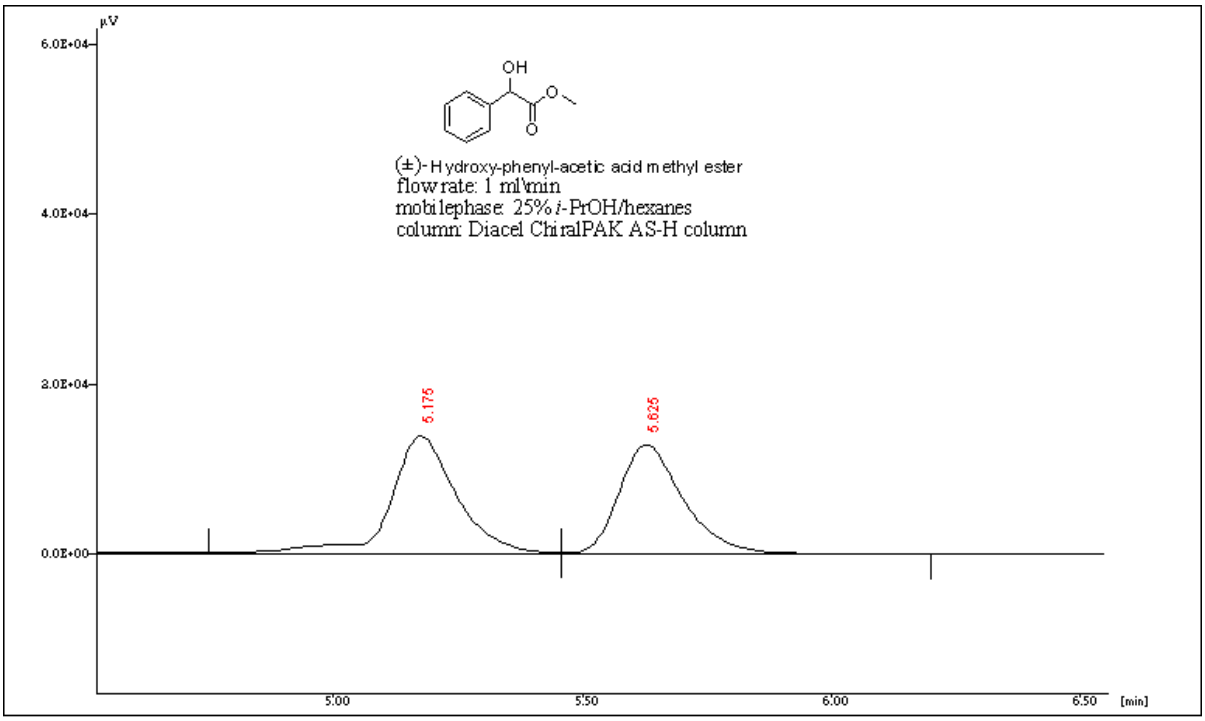


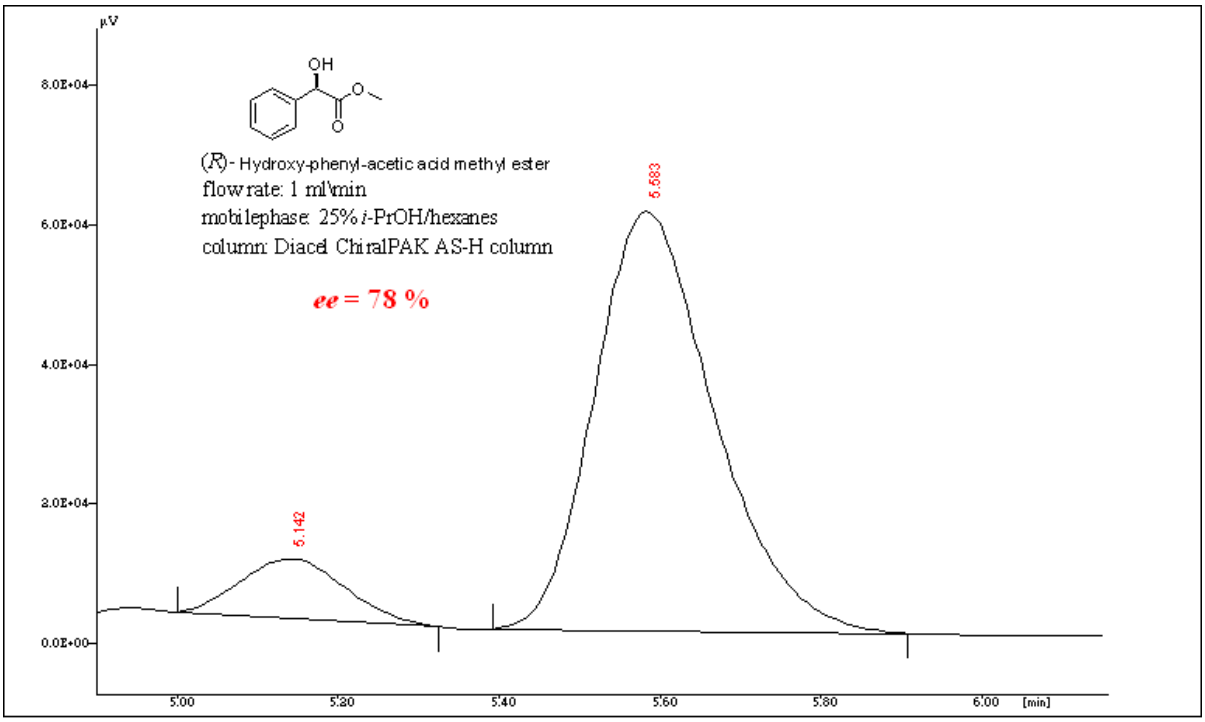

(4-iodophenyl)-hydroxy-acetic acid methyl ester
Conversion (C) = 74.5 %
3.698
4.0
3.9
3.8
ppm
3.000
1.026
10
9
8
7
6
5
4
3
2
1
0
ppm

(4-bromophenyl)-hydroxy-acetic acid methyl ester
COnversion (C) = 66 %

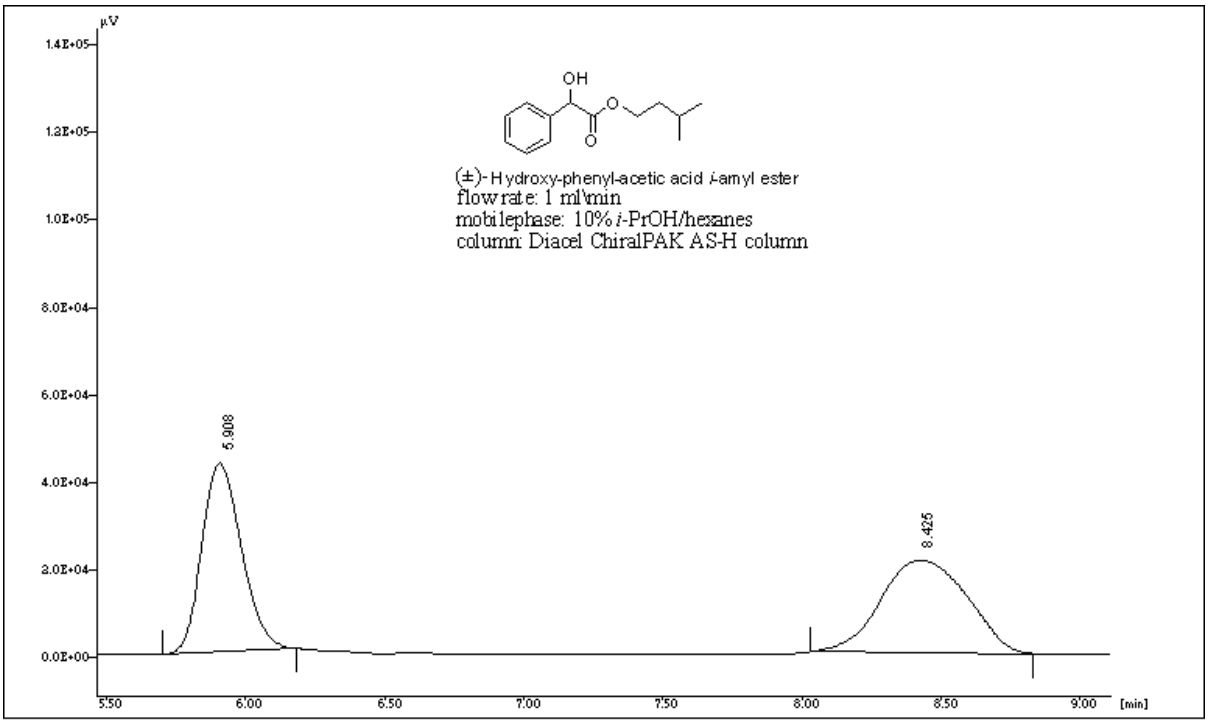


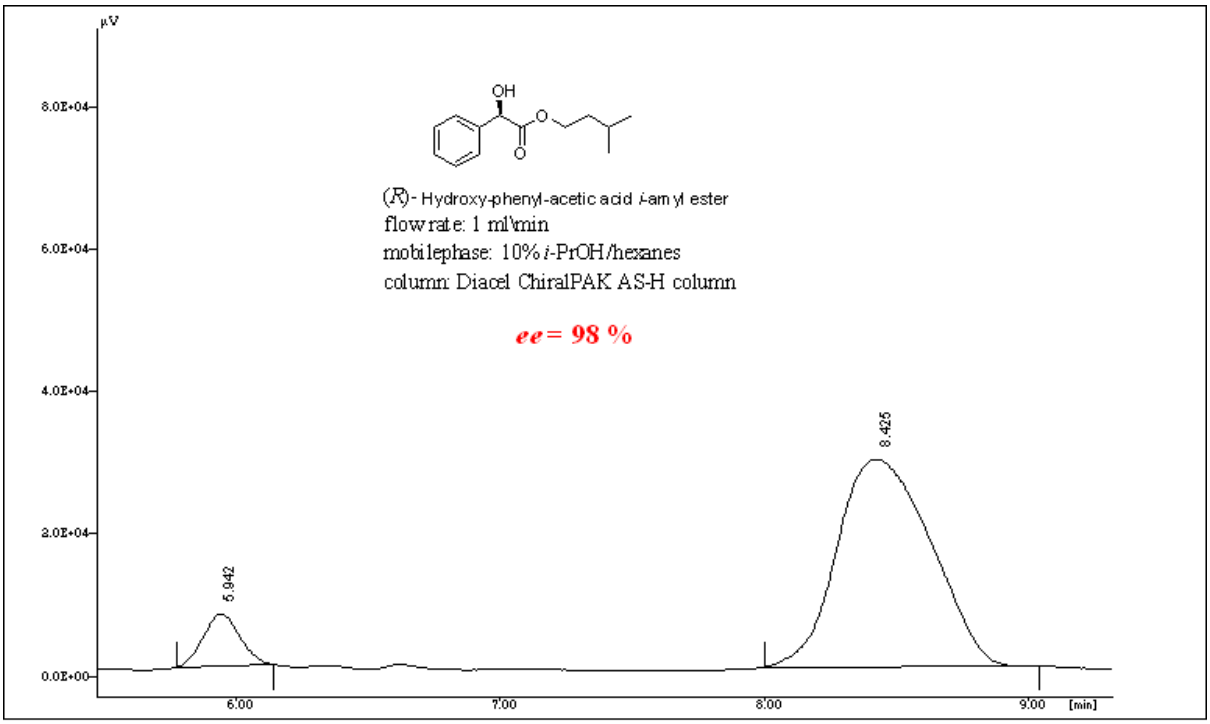
Hydroxy-phenyl-acetic acid methyl ester



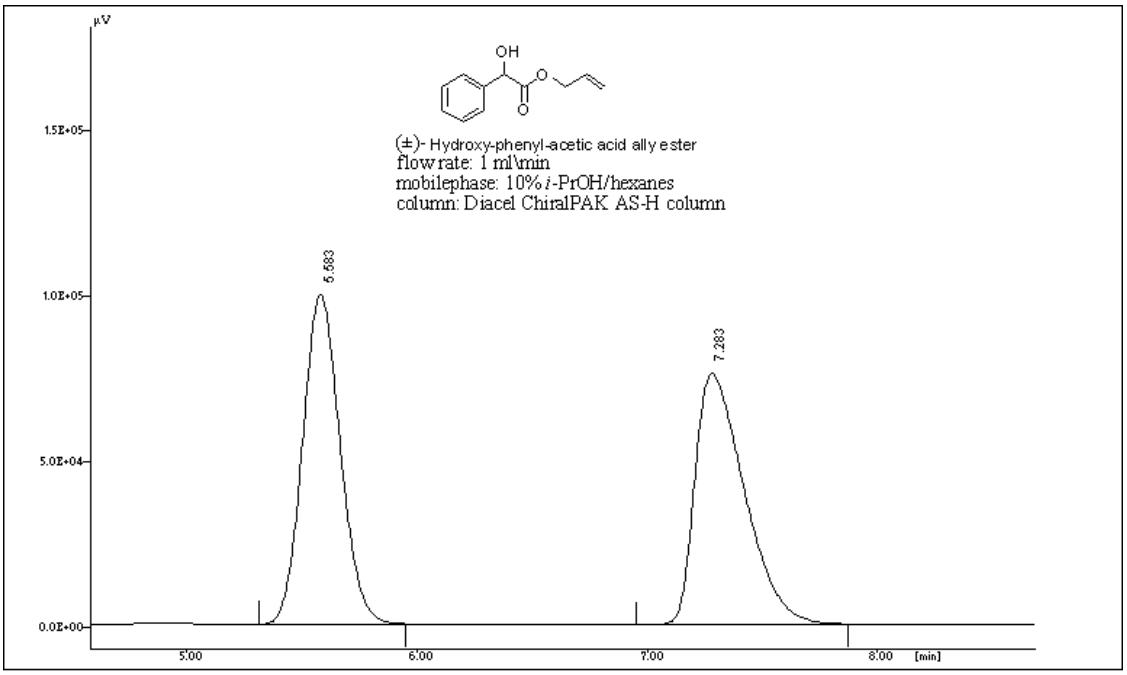


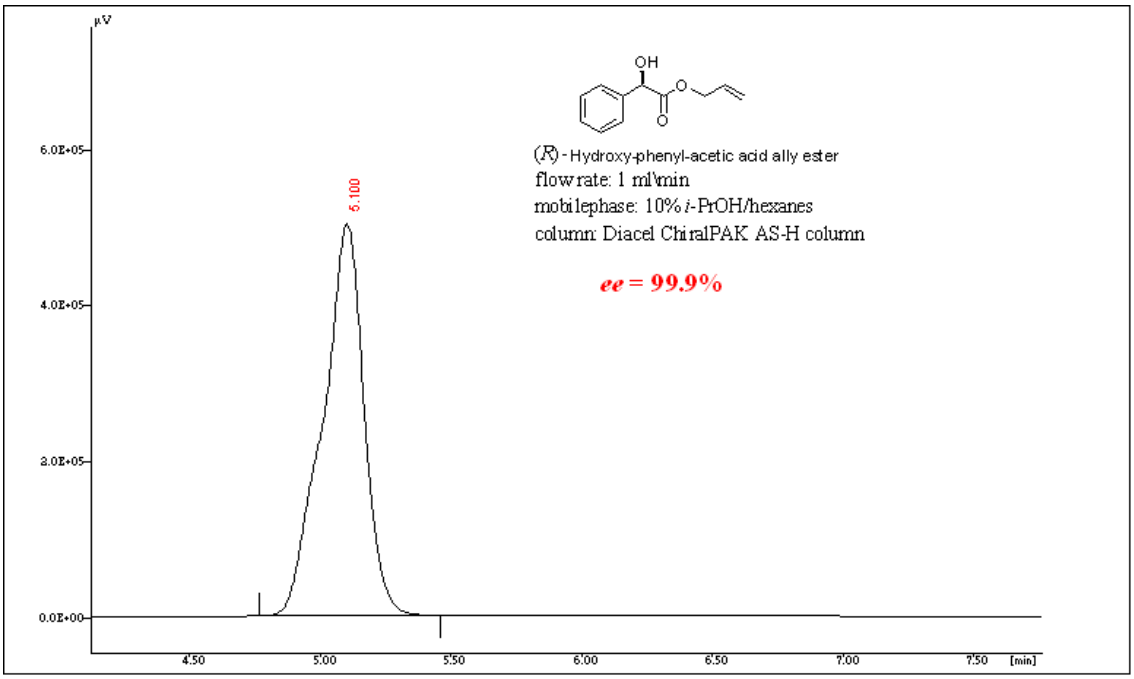
Hydroxy-phenyl-acetic acid *i*-amyl ester



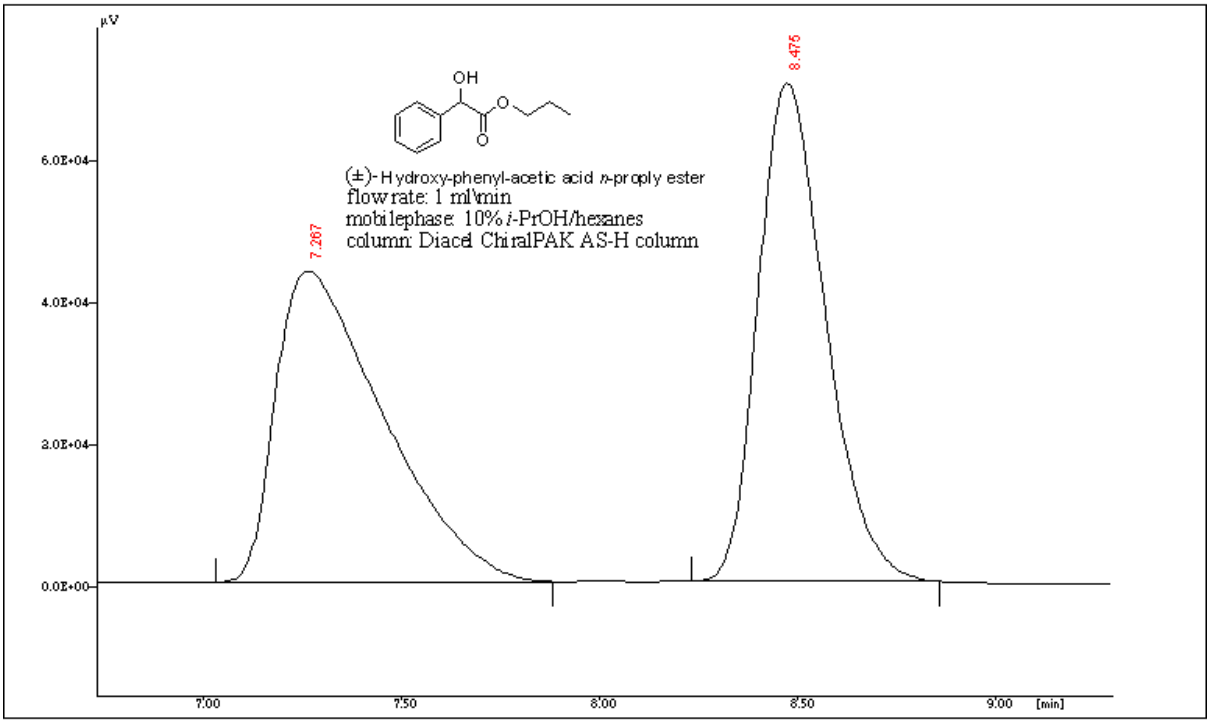


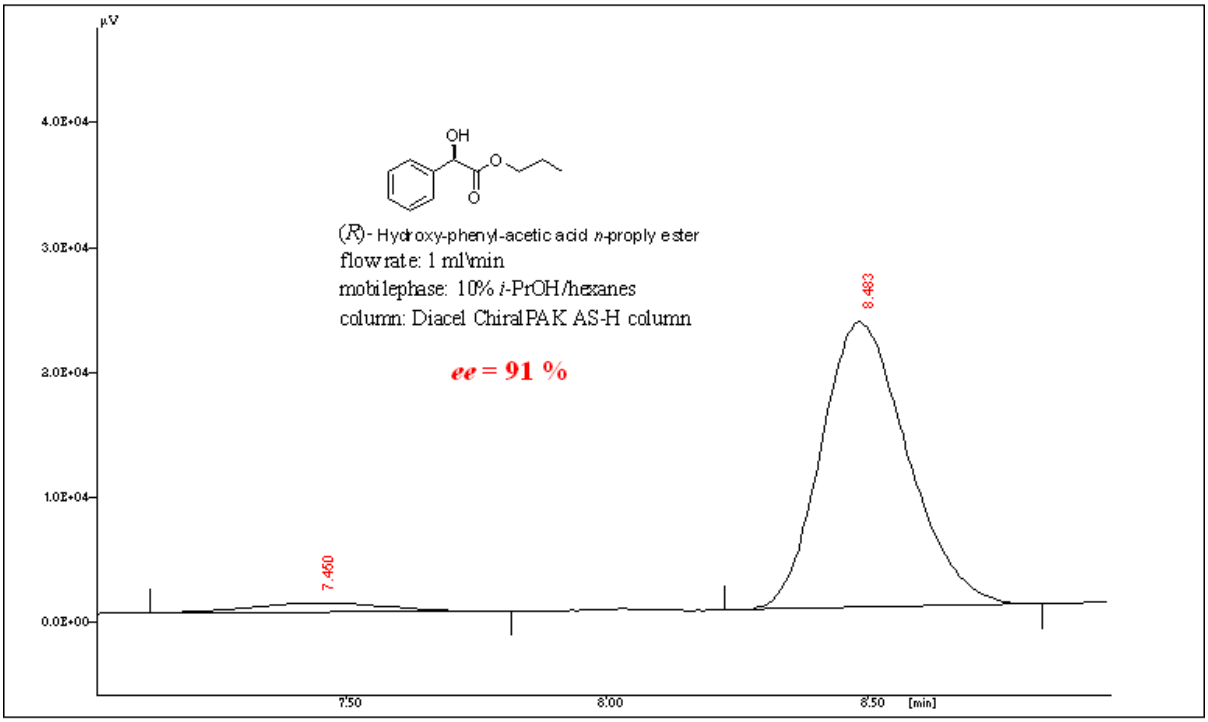
Hydroxy-phenyl-acetic acid allyl ester



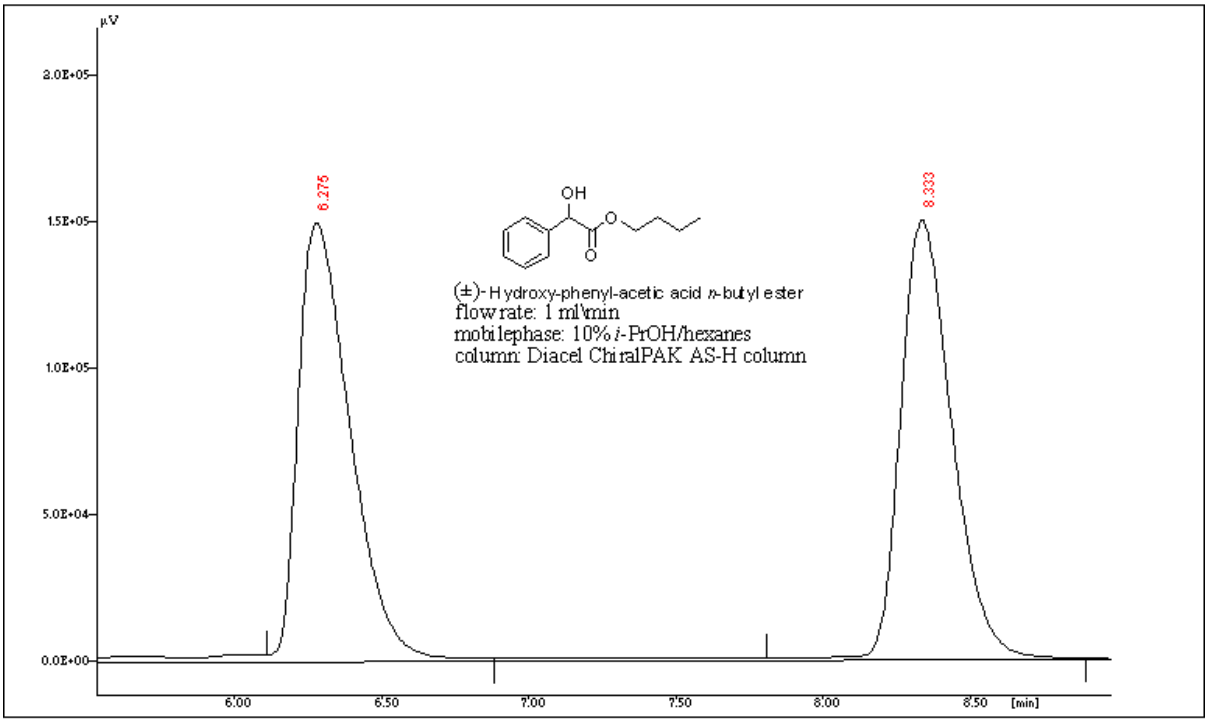


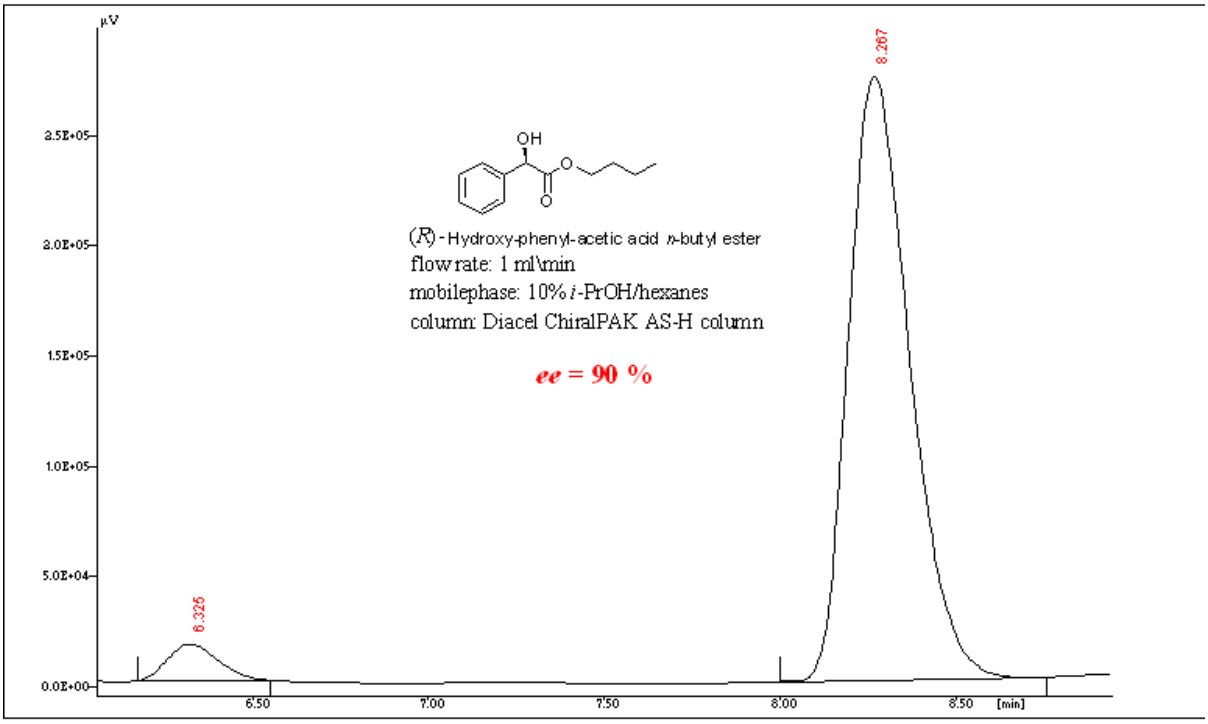
Hydroxy-phenyl-acetic acid *n*-propyl ester



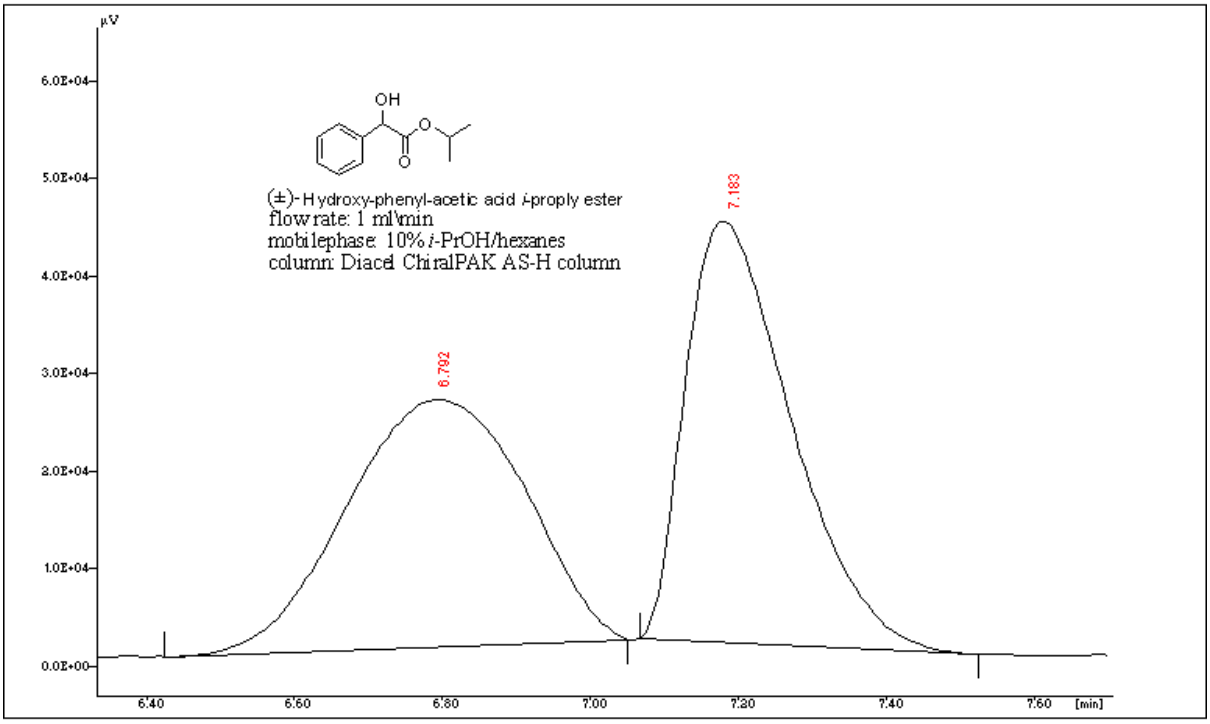


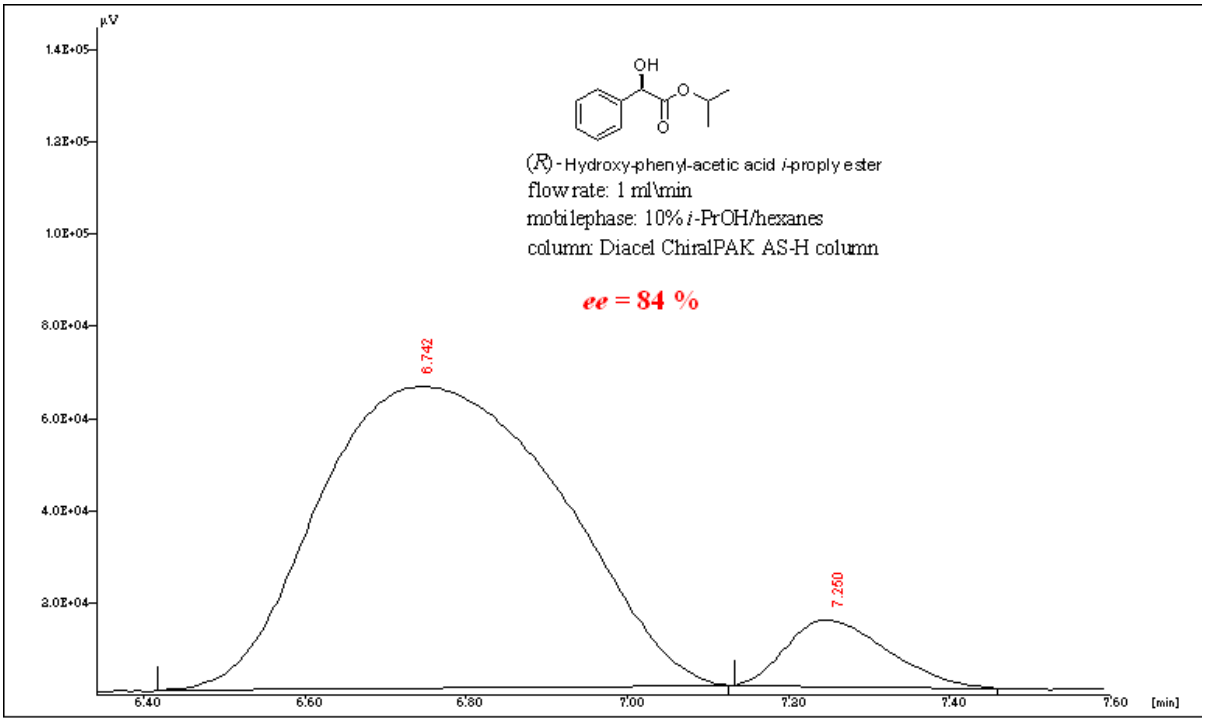
Hydroxy-phenyl-acetic acid *n*-butyl ester



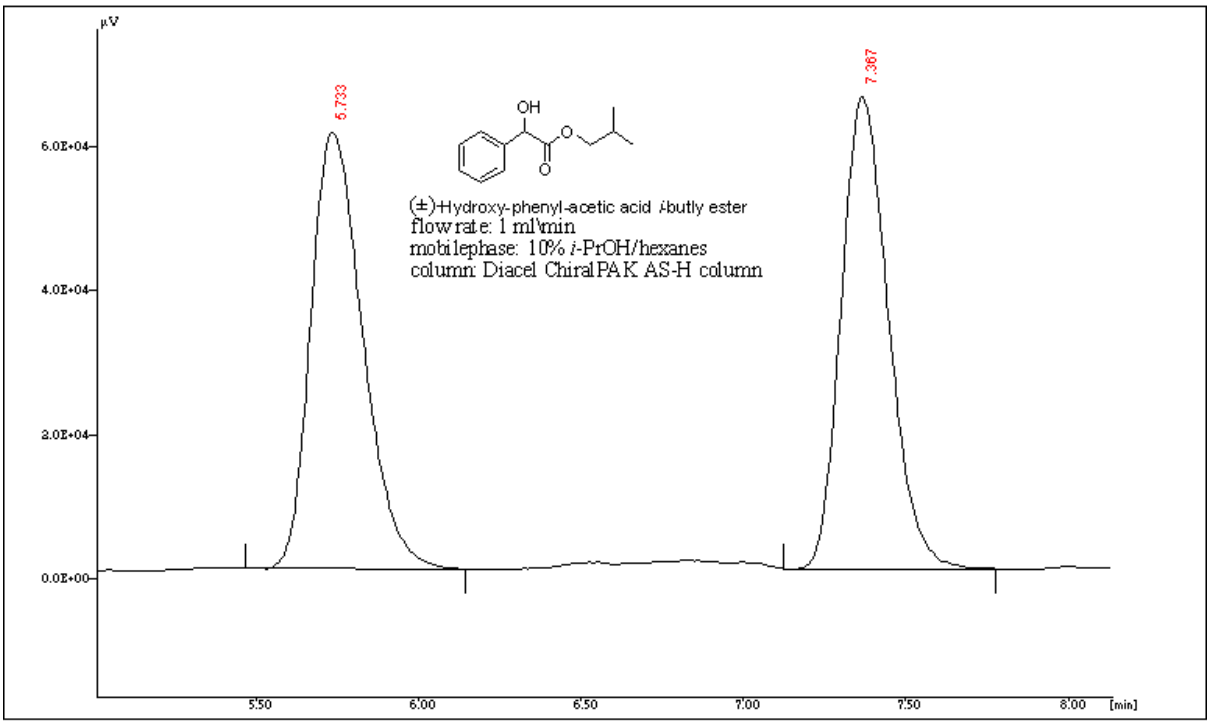


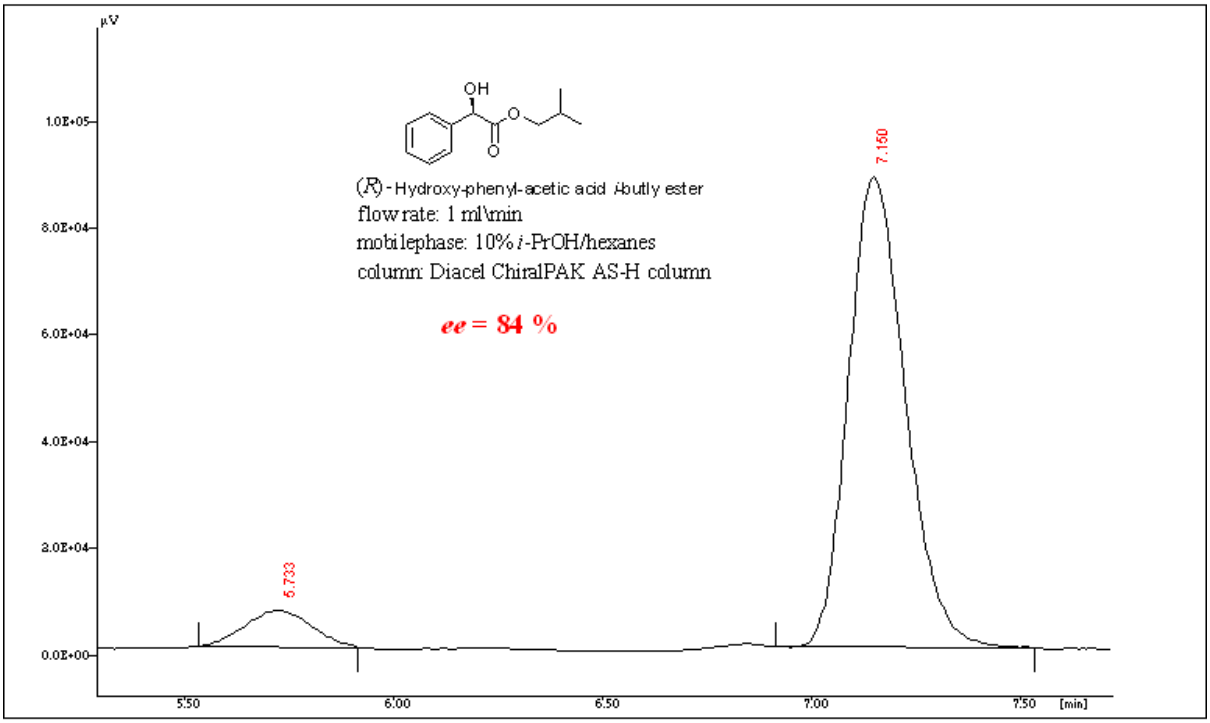
Hydroxy-phenyl-acetic acid *i*-propyl ester



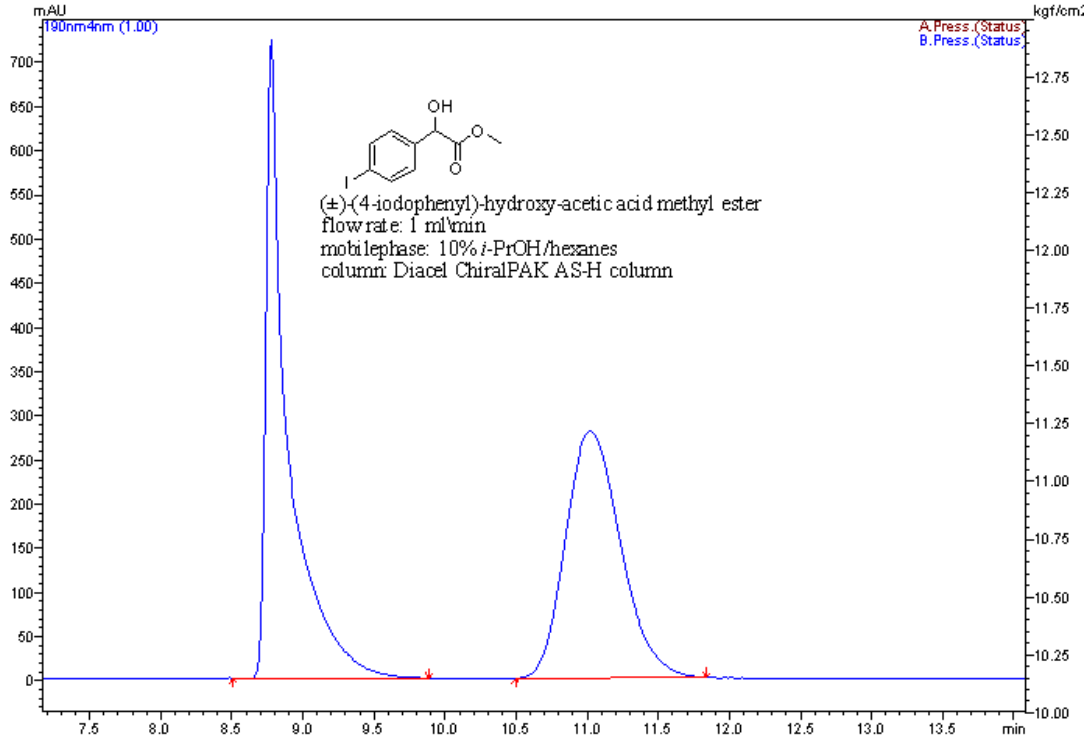


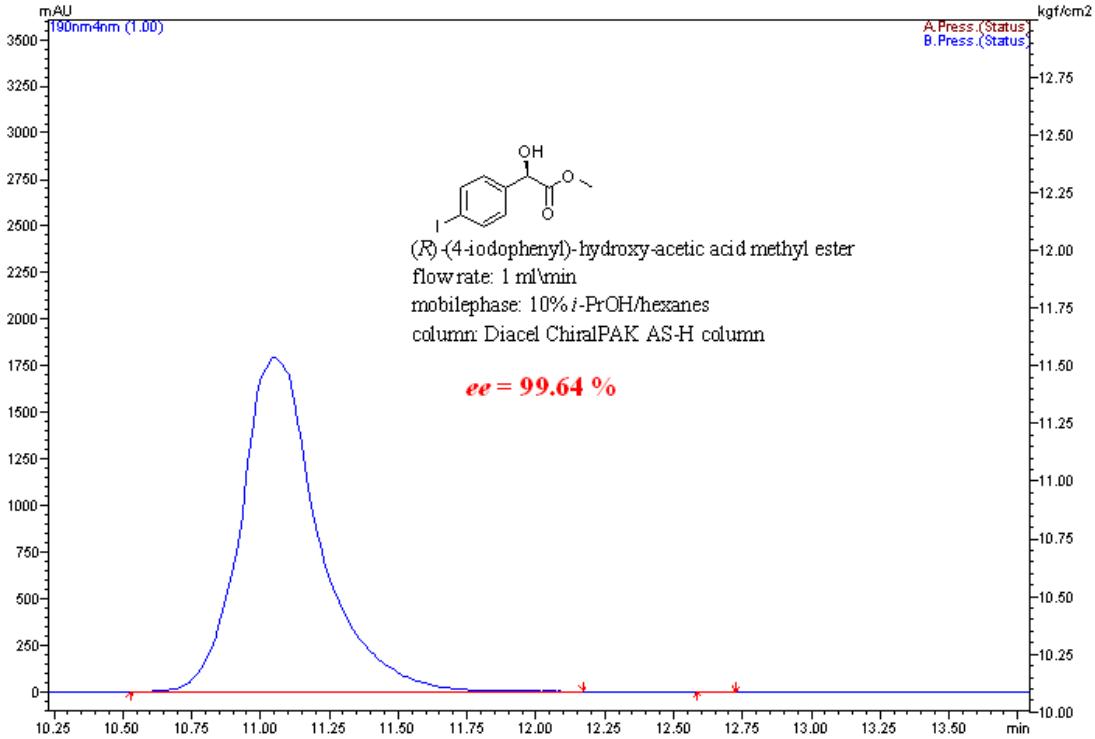
Hydroxy-phenyl-acetic acid *i*-butyl ester



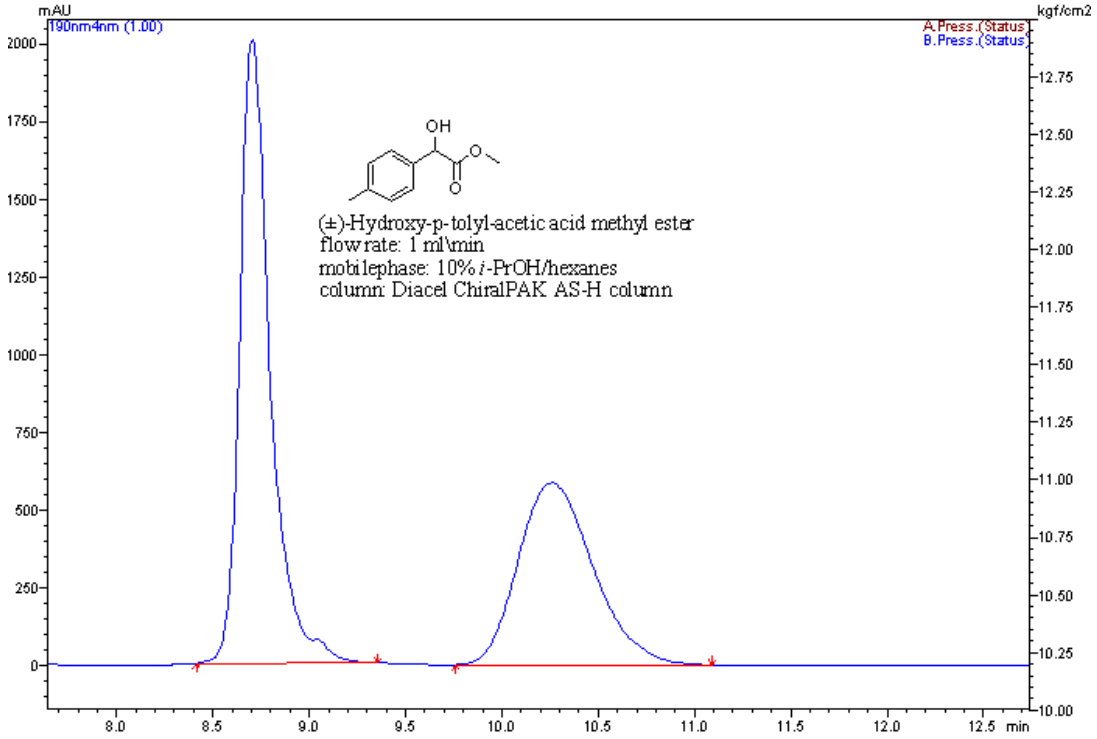


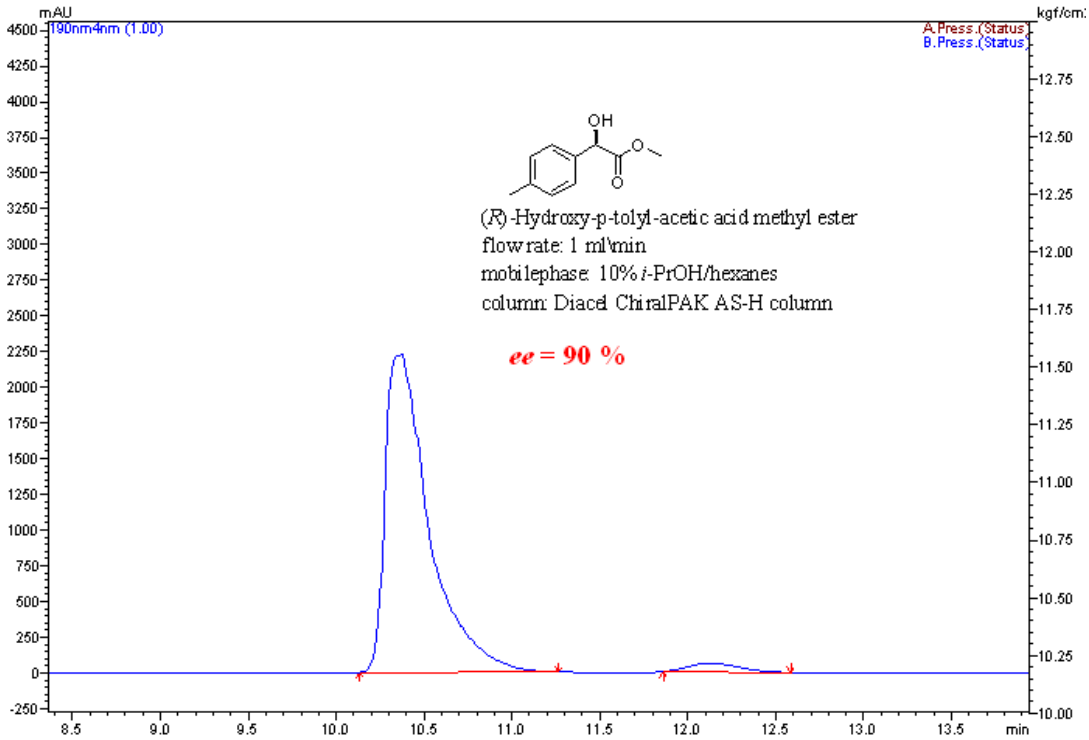
p-Iodophenyl-hydroxy-acetic acid methyl ester



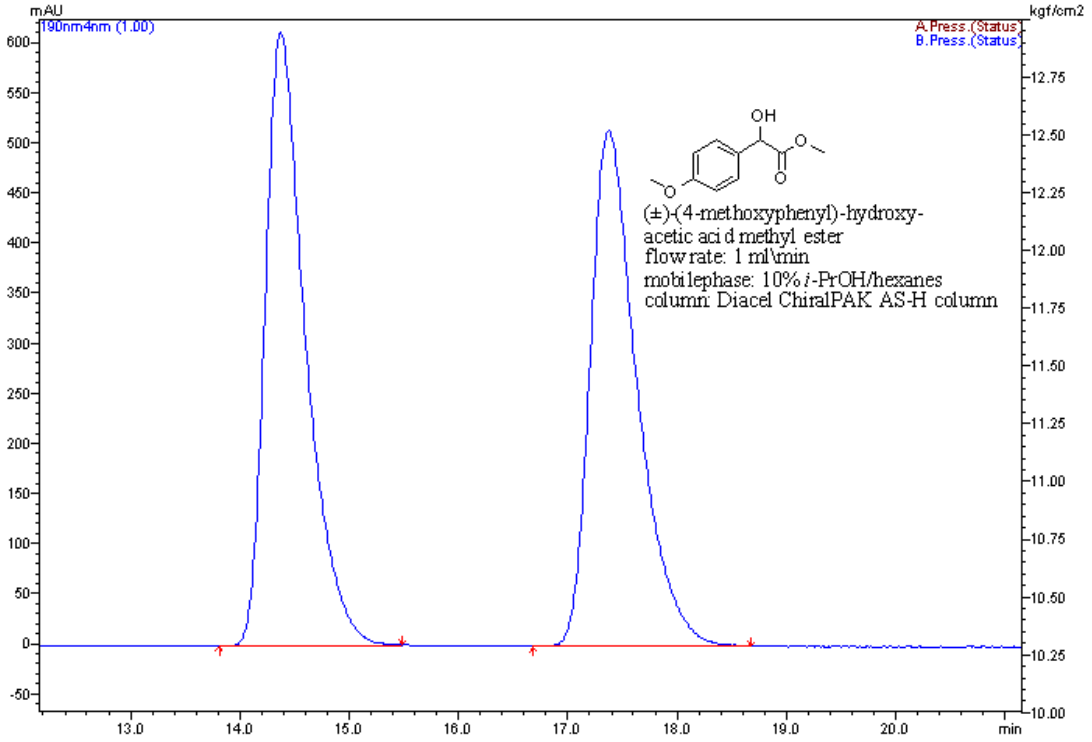


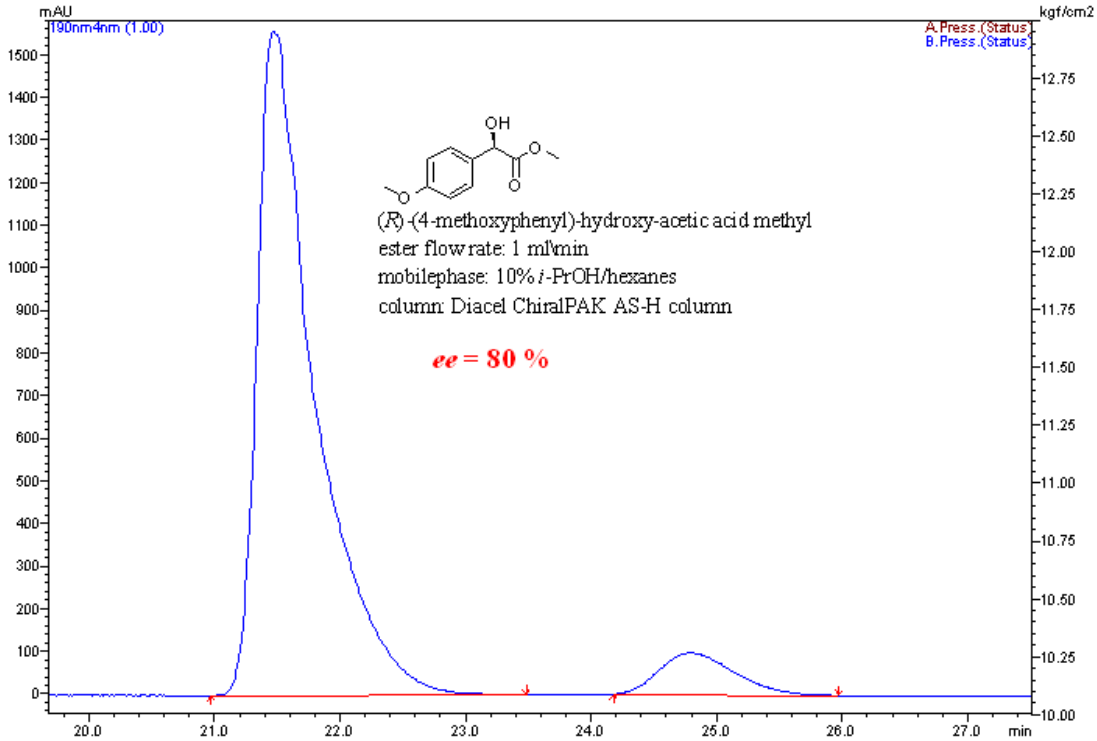
Hydroxy-*p*-tolyl-acetic acid methyl ester



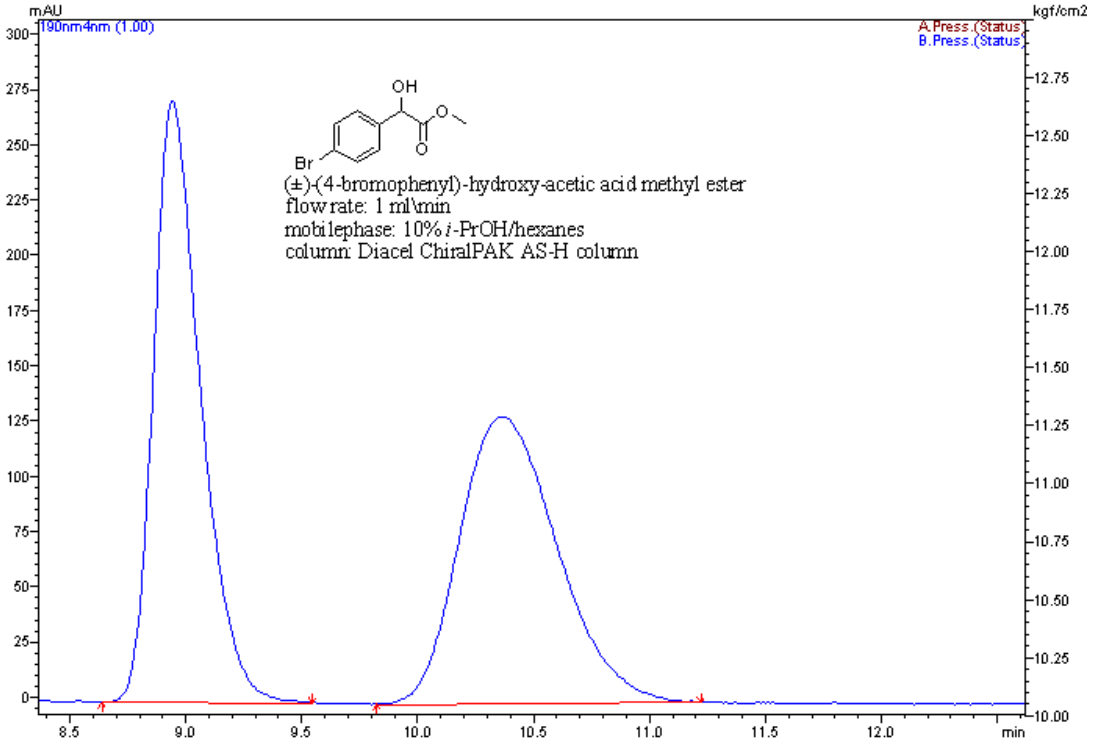


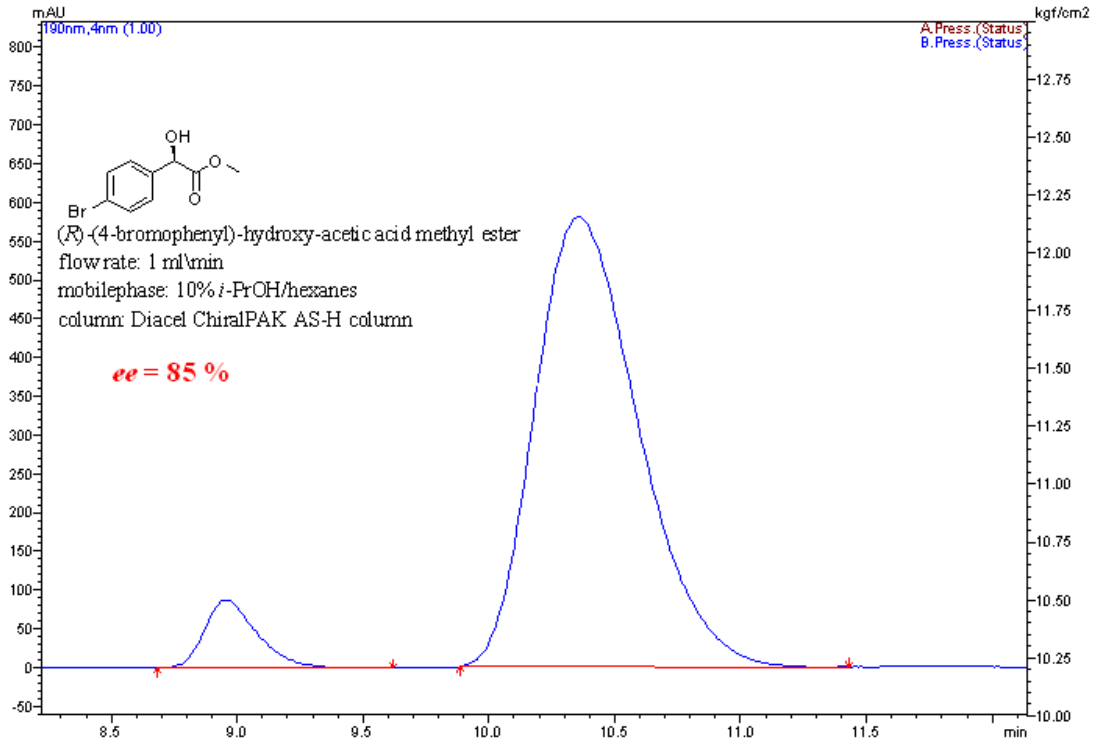
p-Methoxyphenyl-hydroxy-acetic acid methyl



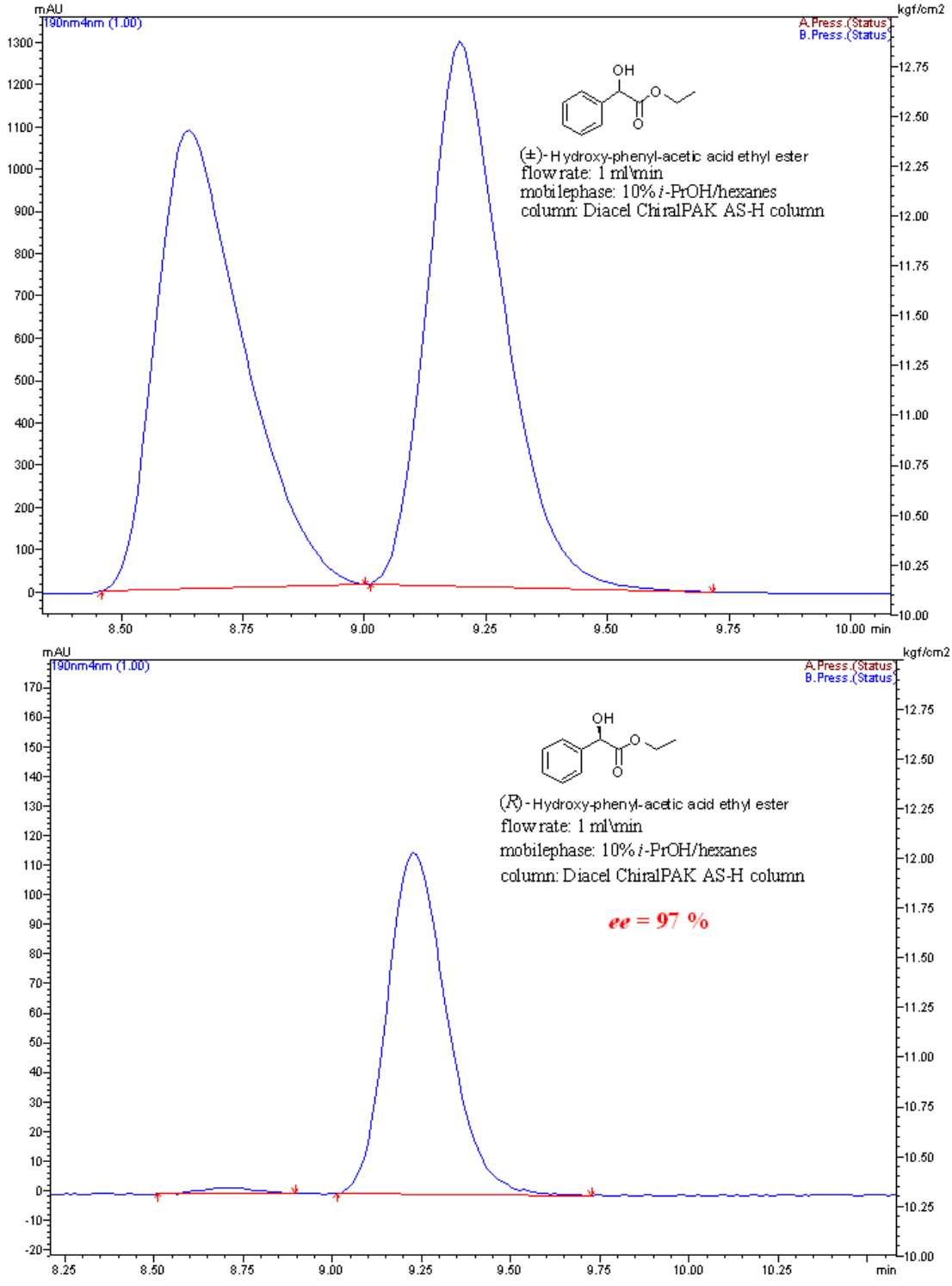


p-Bromophenyl-hydroxy-acetic acid methyl ester

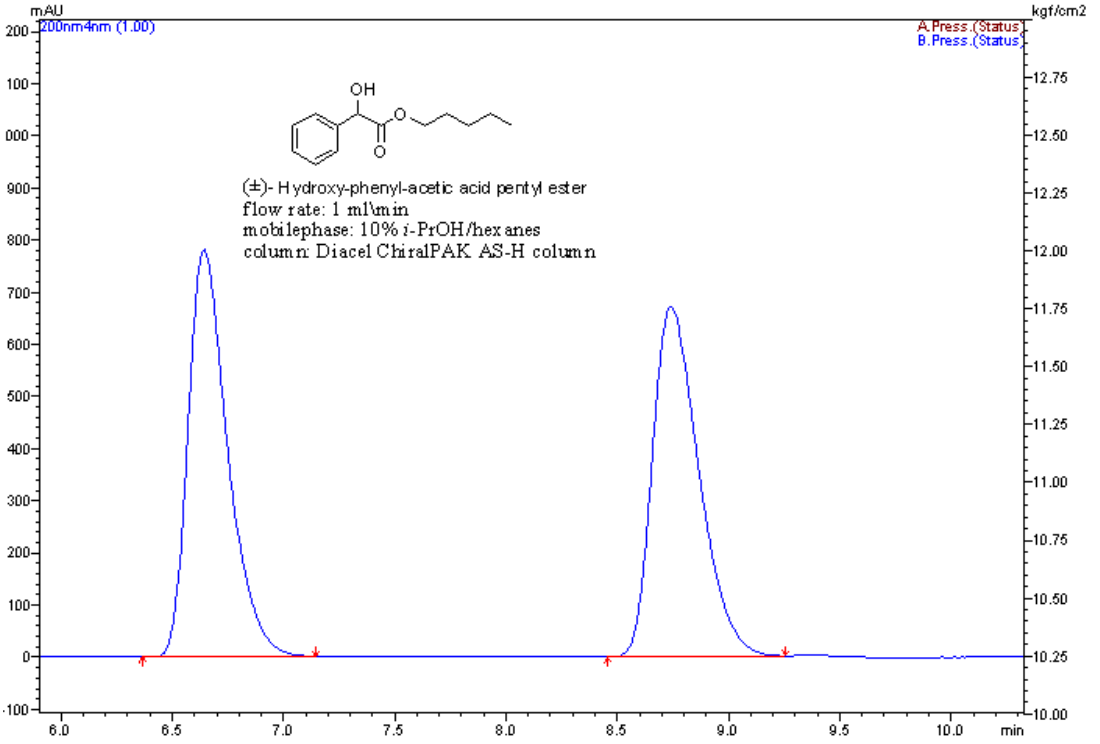


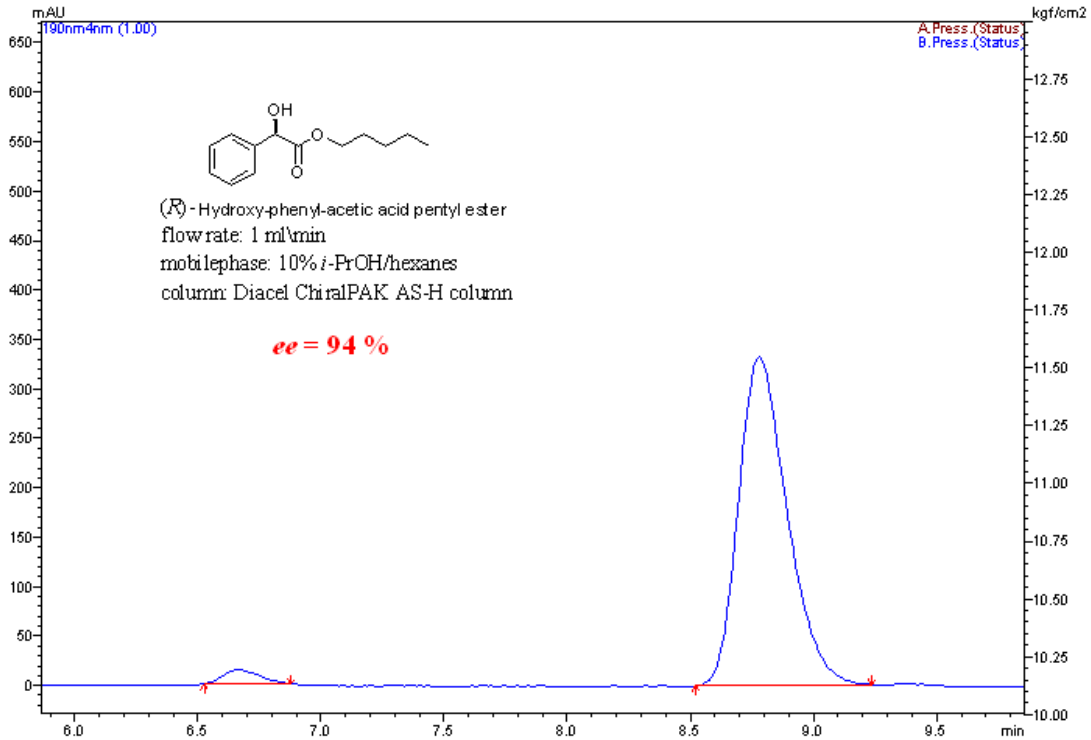


Hydroxy-phenyl-acetic acid ethyl ester

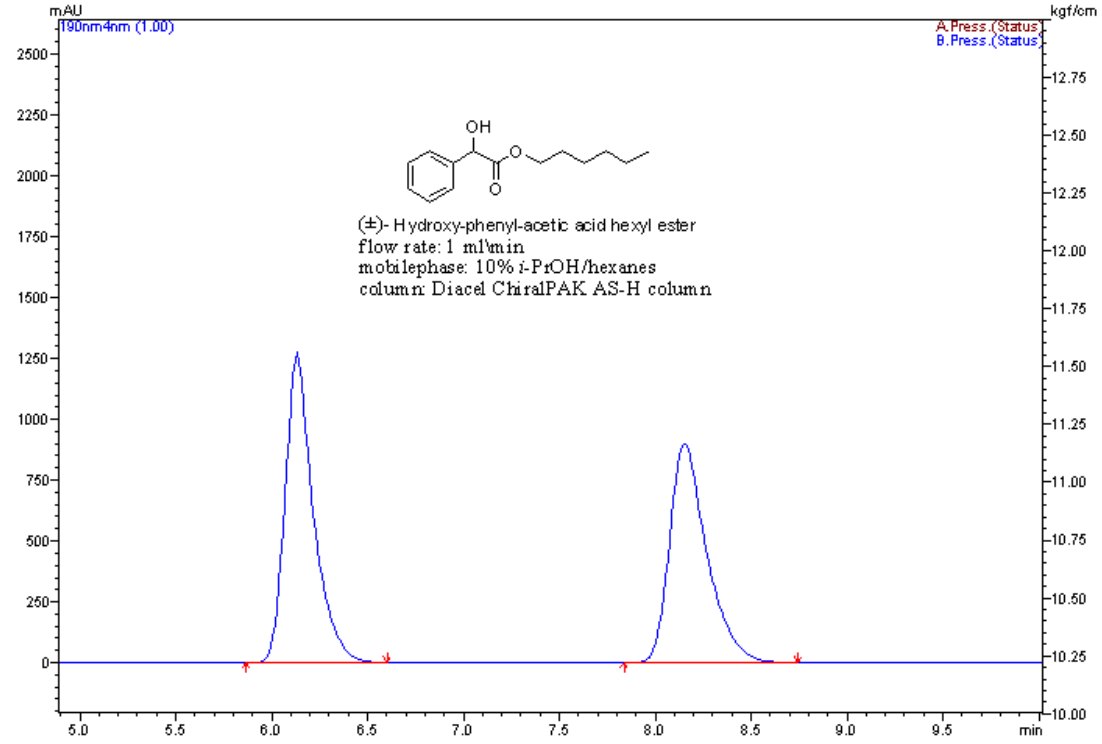


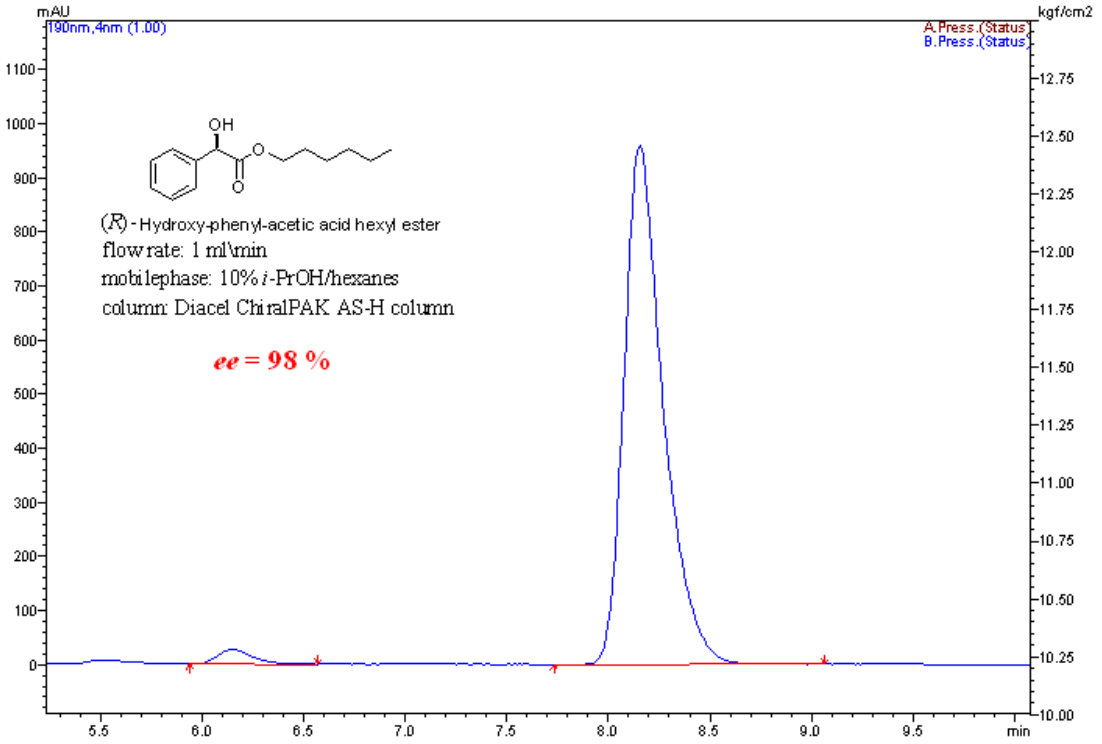
Hydroxy-phenyl-acetic acid *n*-pentyl ester



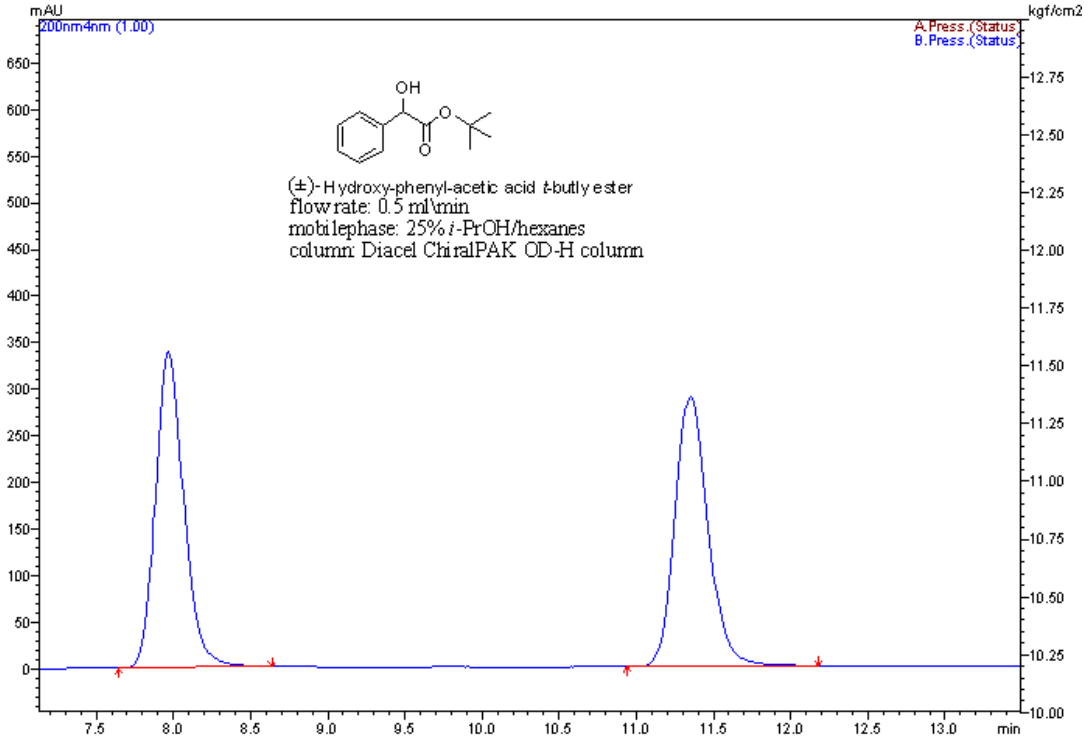


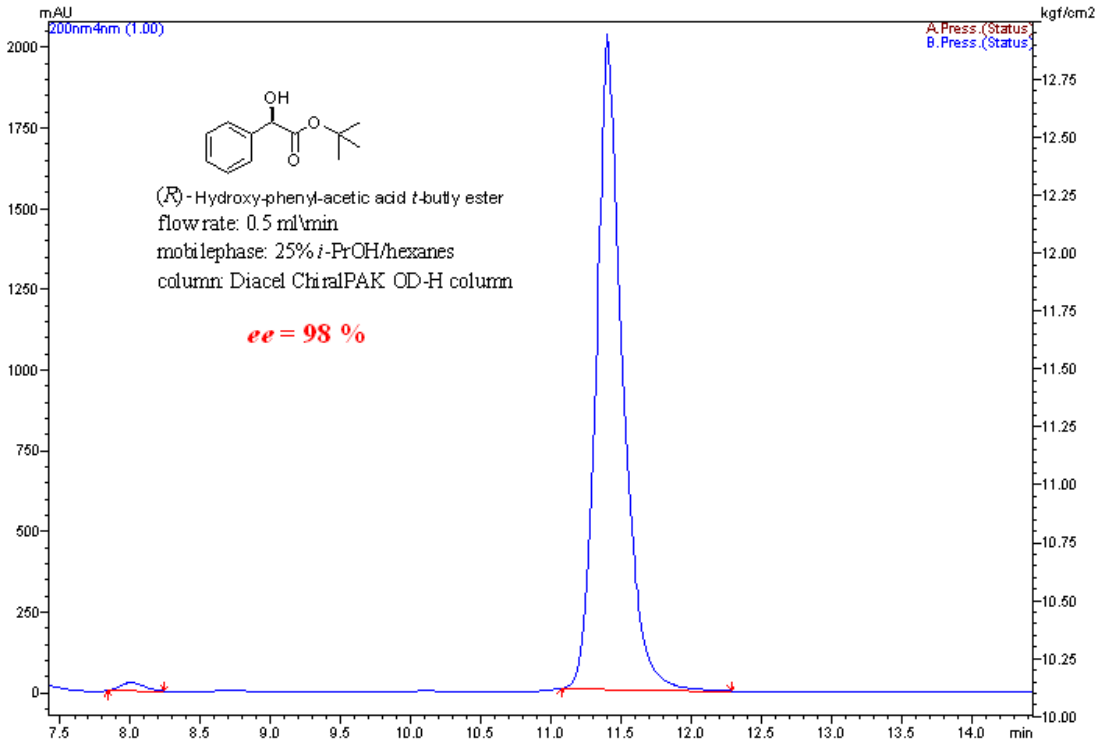
Hydroxy-phenyl-acetic acid *n*-hexyl ester

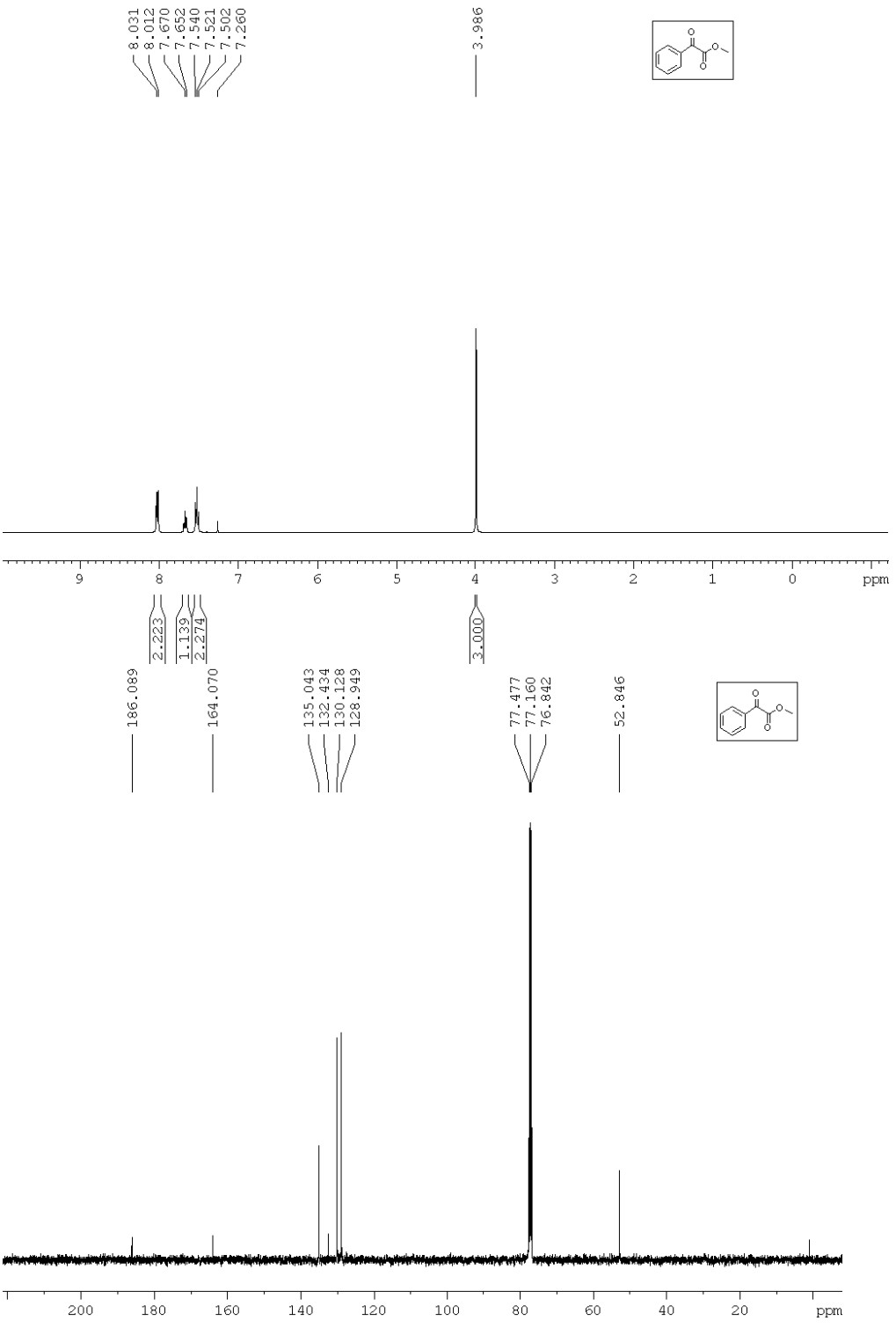


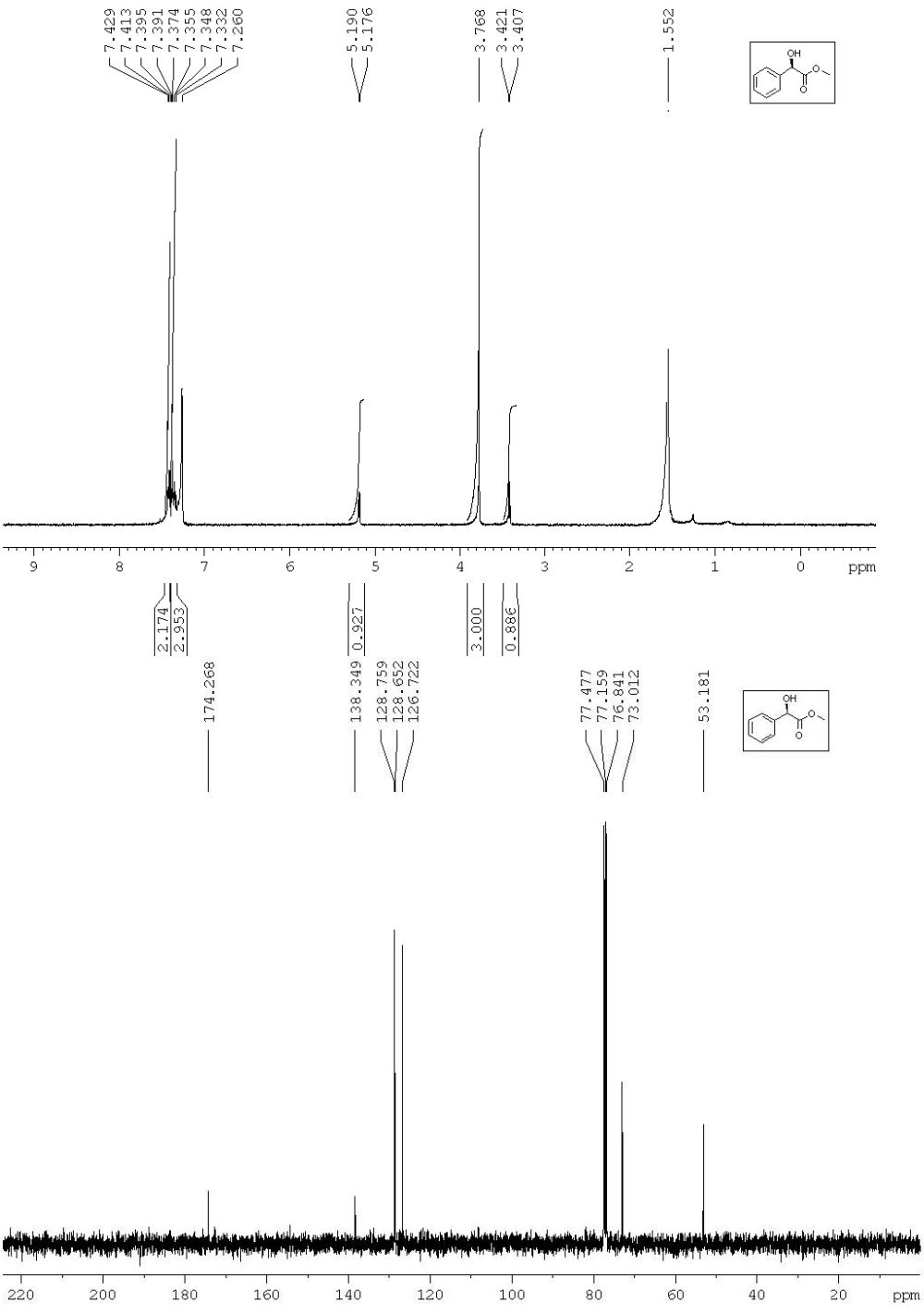


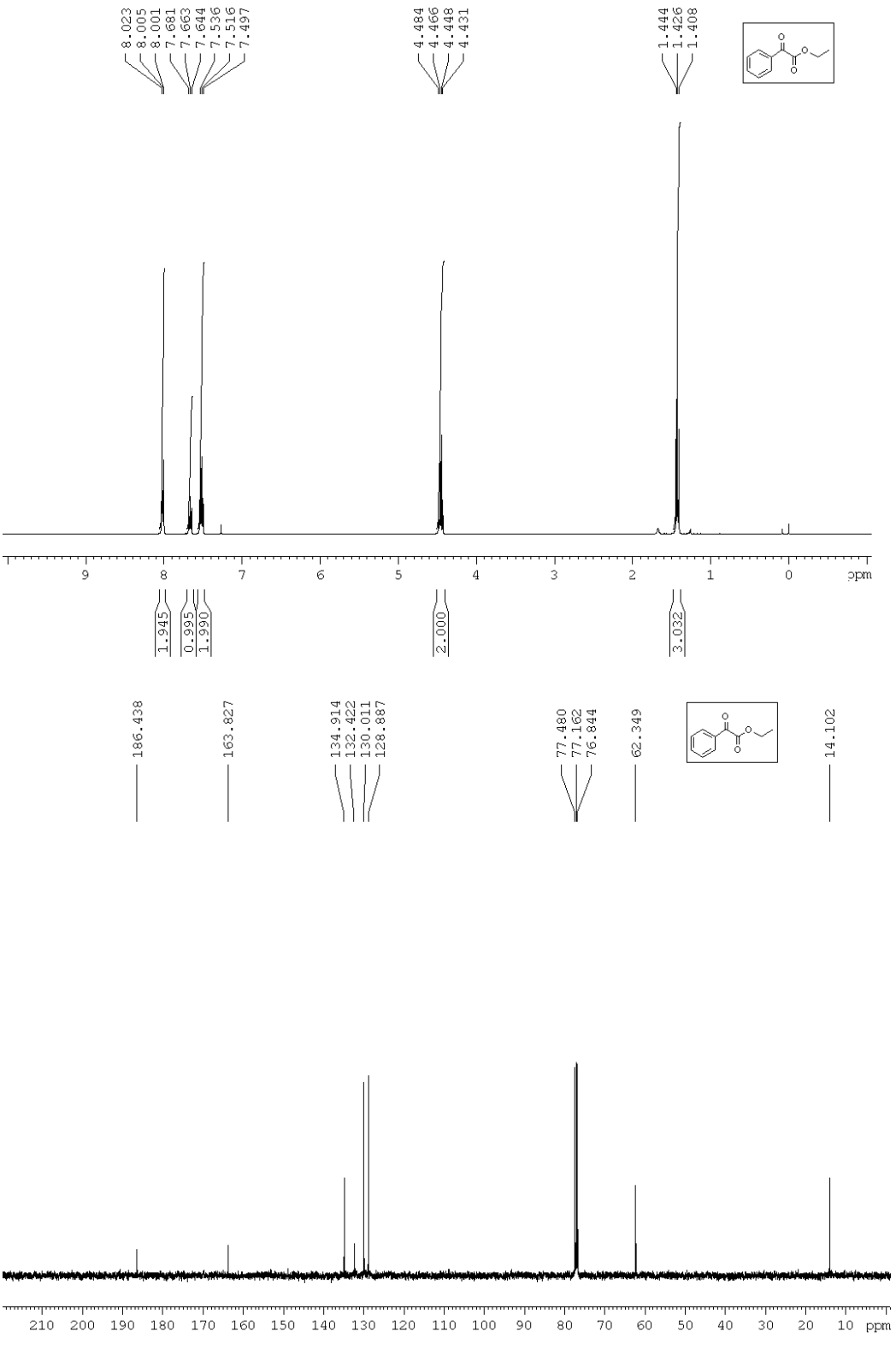
Hydroxy-phenyl-acetic acid *t*-butyl ester

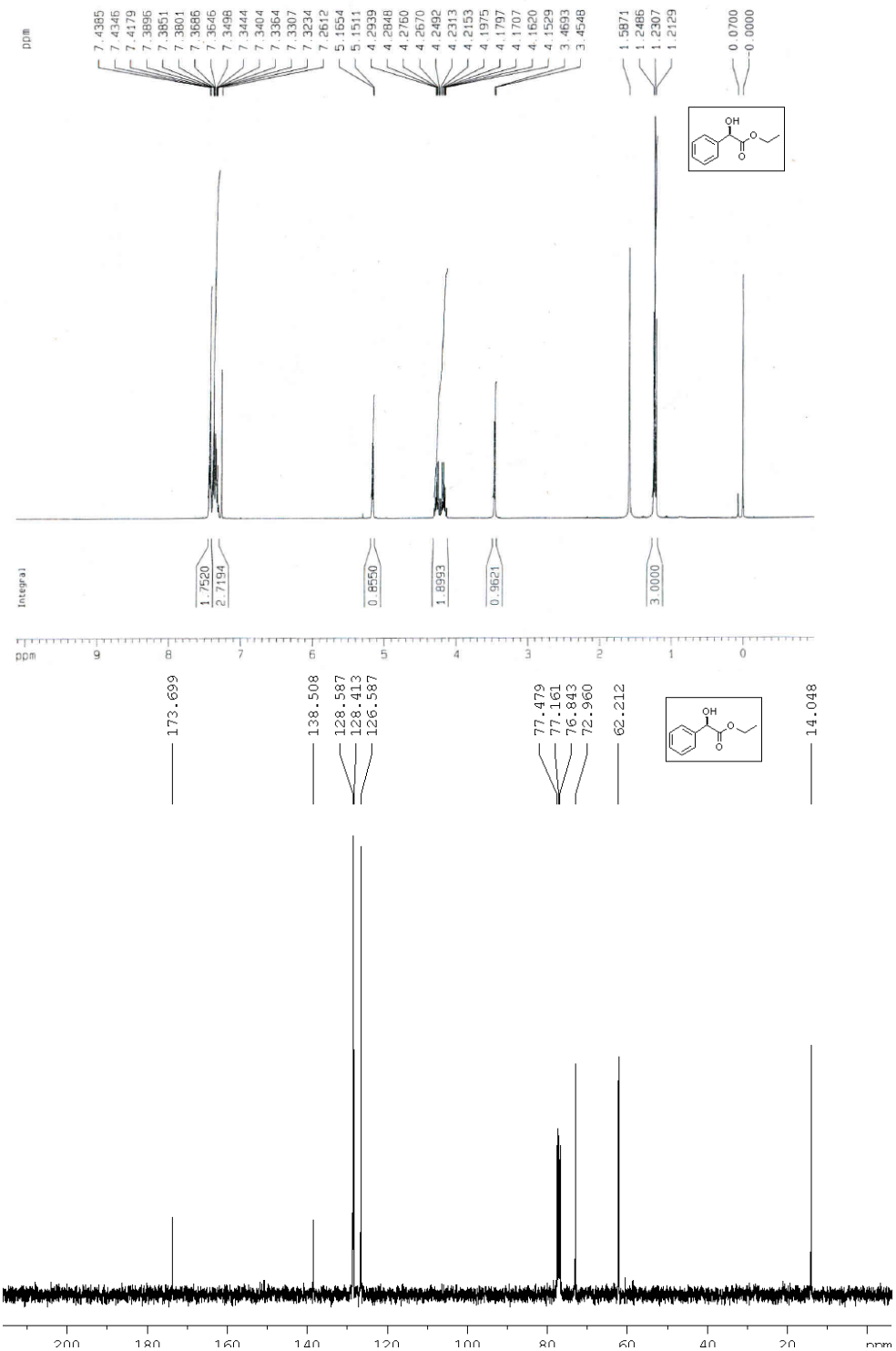


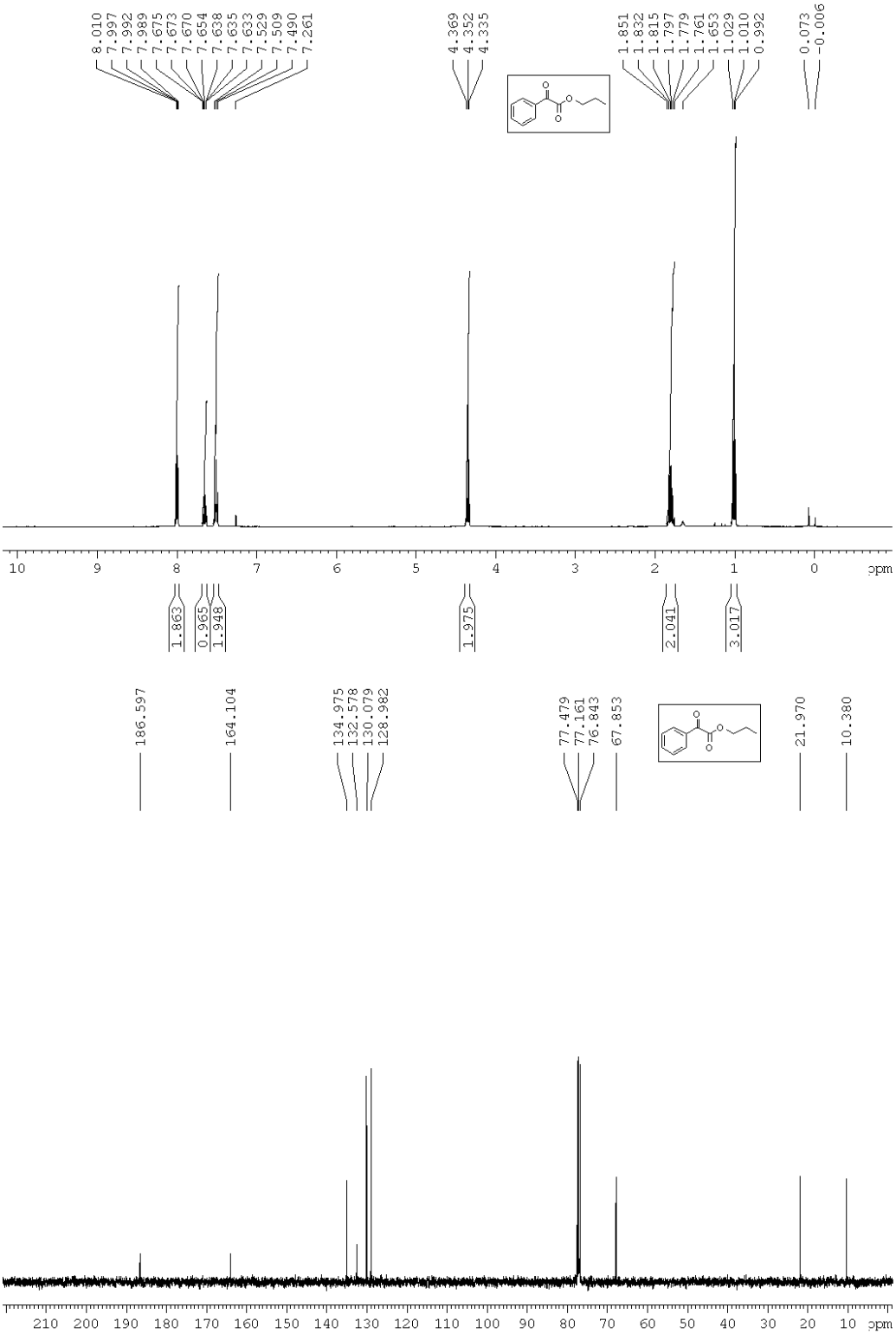



8.031
8.012
7.670
7.652
7.540
7.521
7.502
7.260
3.986
9
8
7
6
5
4
3
2
1
0
ppm
2.223
1.139
2.274
3.000
186.089
164.070
135.043
132.434
130.128
128.949
77.477
77.160
76.842
52.846
200
180
160
140
120
100
80
60
40
20
ppm


7.429
7.413
7.395
7.391
7.374
7.355
7.348
7.332
7.260
5.190
5.176
3.768
3.421
3.407
1.552
OH
O
O
9
8
7
6
5
4
3
2
1
0
ppm
2.174
2.953
0.927
3.000
0.886
174.268
138.349
128.759
128.652
126.722
77.477
77.159
76.841
73.012
53.181
220
200
180
160
140
120
100
80
60
40
20
ppm


8.023
8.005
8.001
7.681
7.663
7.644
7.536
7.516
7.497
4.484
4.466
4.448
4.431
1.444
1.426
1.408
ppm
1.945
0.995
1.990
2.000
3.032
186.438
163.827
134.914
132.422
130.011
128.887
77.480
77.162
76.844
62.349
14.102
ppm


ppm
7.4385
7.4346
7.4179
7.3996
7.3851
7.3801
7.3686
7.3646
7.3498
7.3444
7.3404
7.3364
7.3307
7.3234
7.2612
5.1654
5.1511
4.2939
4.2848
4.2760
4.2670
4.2492
4.2313
4.2153
4.1975
4.1797
4.1707
4.1620
4.1529
3.4693
3.4548
1.5871
1.2486
1.2307
1.2129
0.0700
-0.0000
OH
O
O
Integral
1.7520
2.7194
0.8550
1.8993
0.9621
3.0000
ppm
9
8
7
6
5
4
3
2
1
0
173.699
138.508
128.587
128.413
126.587
77.479
77.161
76.843
72.960
62.212
14.048
200
180
160
140
120
100
80
60
40
20
ppm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7.992
7.989
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7.670
7.654
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7.635
7.633
7.529
7.509
7.490
7.261
4.369
4.352
4.335
1.851
1.832
1.815
1.797
1.779
1.761
1.653
1.029
1.010
0.992
0.073
-0.006
10
9
8
7
6
5
4
3
2
1
0
ppm
1.863
0.965
1.948
1.975
2.041
3.017
186.597
164.104
134.975
132.578
130.079
128.982
77.479
77.161
76.843
67.853
21.970
10.380
210
200
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180
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150
140
130
120
110
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70
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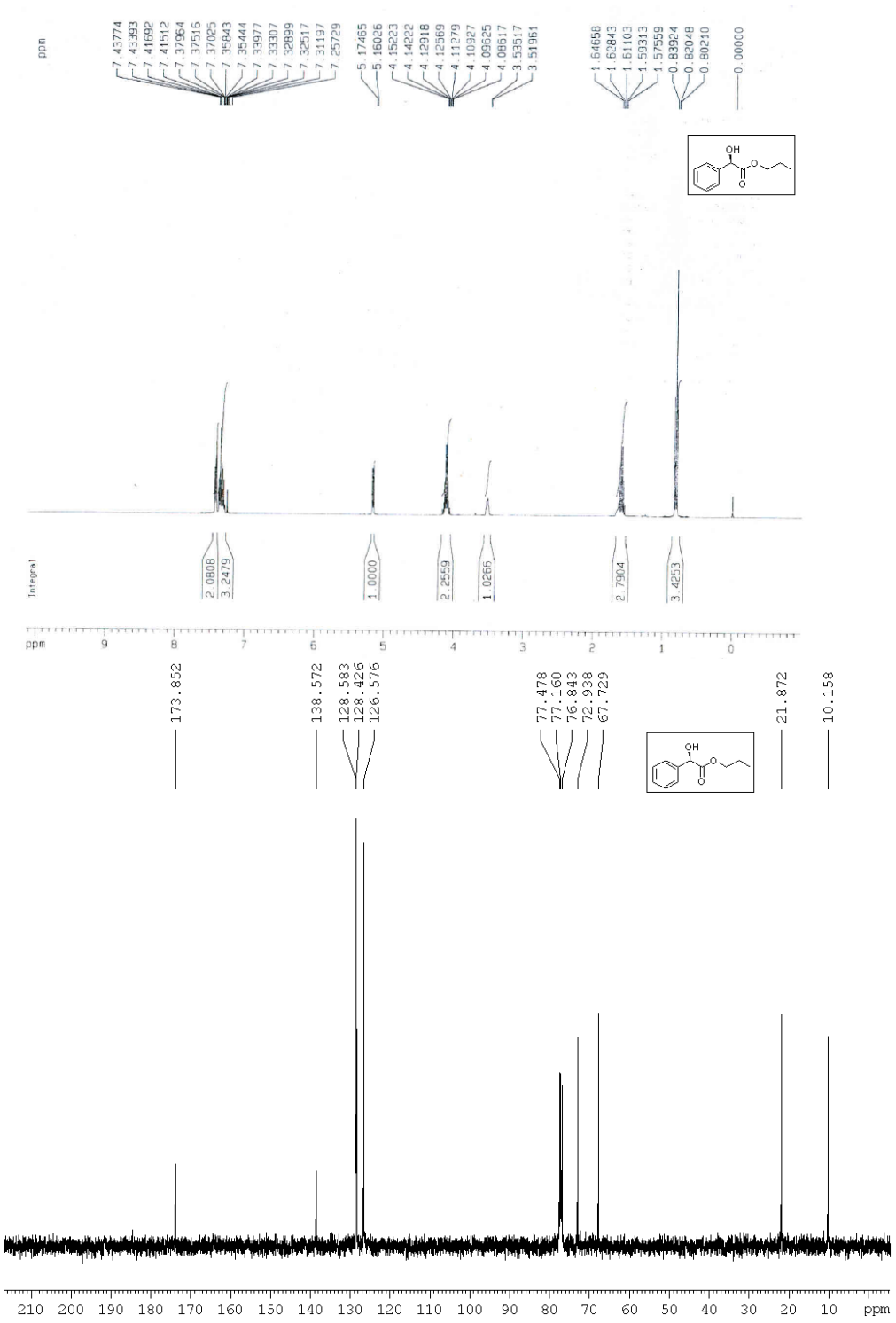
30
20
10
ppm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7.33307
7.32899
7.32517
7.31197
7.25729
5.17465
5.16026
4.15223
4.14222
4.12918
4.12569
4.11279
4.10927
4.09625
4.08617
3.53517
3.51961
1.64658
1.62843
1.61103
1.59313
1.57559
0.83924
0.82048
0.80210
0.00000
OH
O
O
Integral
2.0808
3.2479
1.0000
2.2559
1.0266
2.7904
3.4253
ppm
9
8
7
6
5
4
3
2
1
0
173.852
138.572
128.583
128.426
126.576
77.478
77.160
76.843
72.938
67.729
21.872
10.158
OH
O
O
210
200
190
180
170
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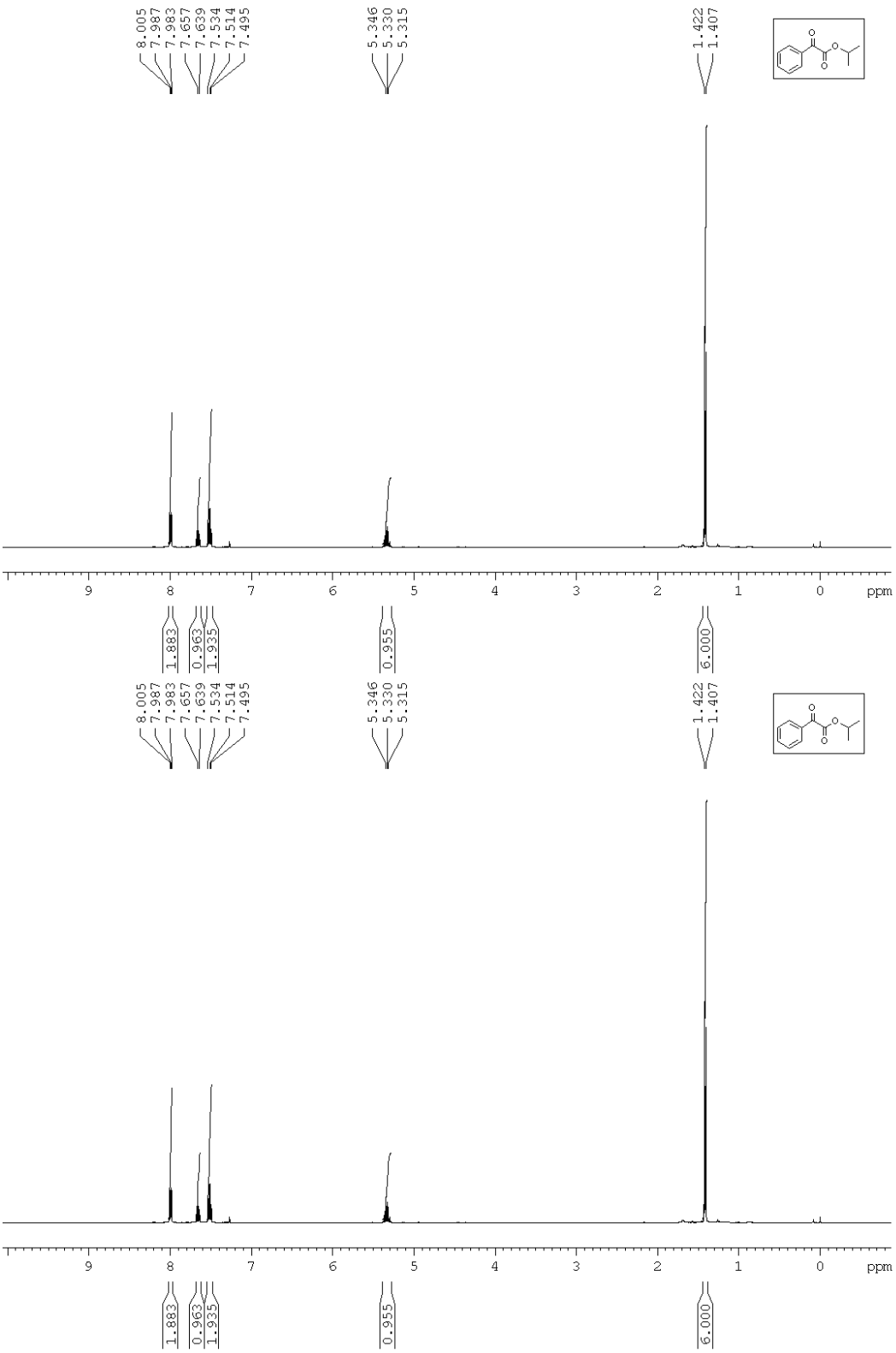
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.987
7.983
7.657
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7.534
7.514
7.495
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5.330
5.315
1.422
1.407
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0.963
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6.000
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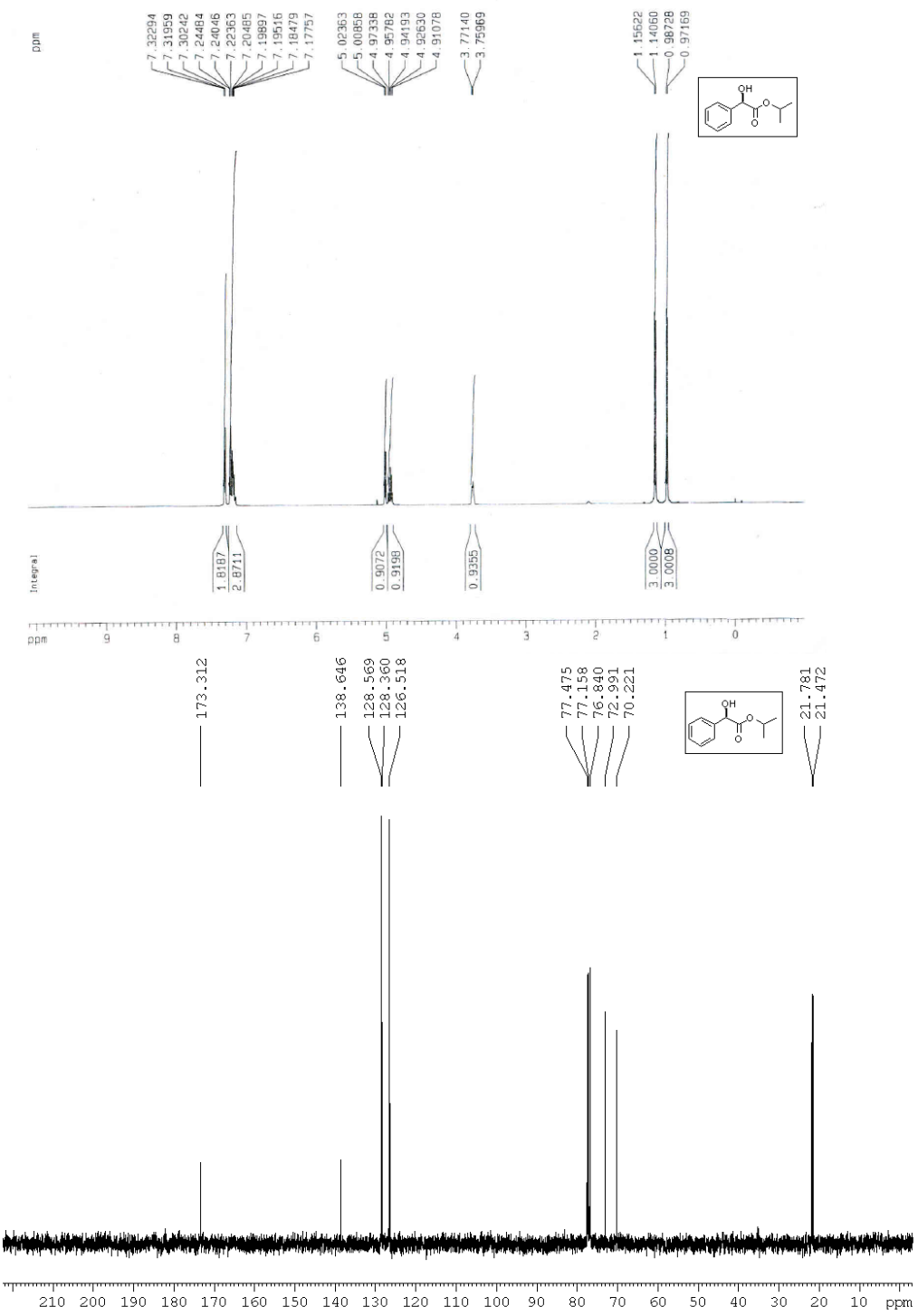
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7.30242
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7.24046
7.22363
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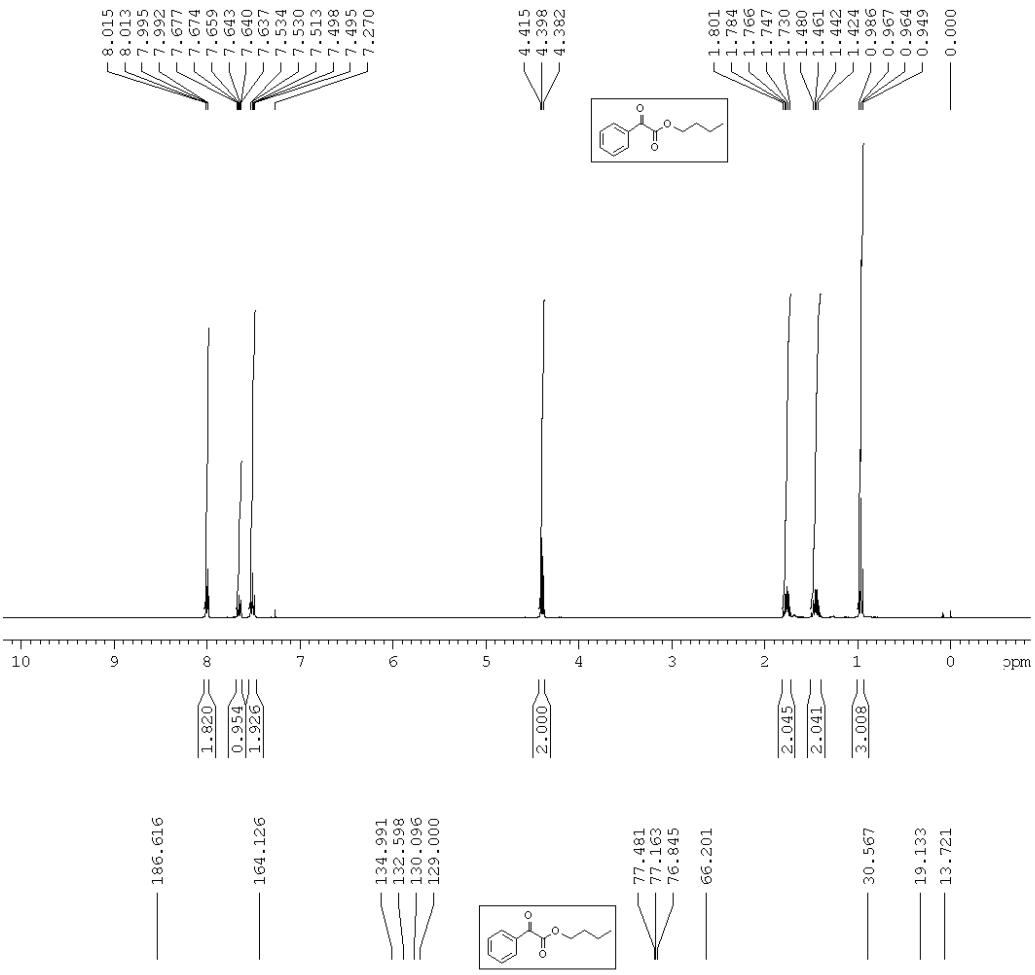
7.19897
7.19516
7.18479
7.17757
5.02363
5.00858
4.97338
4.95782
4.94193
4.92630
4.91078
3.77140
3.75969
1.15622
1.14060
0.98728
0.97169
OH
O
O
Integral
1.8187
2.8711
0.9072
0.9198
0.9355
3.0000
3.0008
ppm
9
8
7
6
5
4
3
2
1
0
173.312
138.646
128.569
128.360
126.518
77.475
77.158
76.840
72.991
70.221
21.781
21.472
OH
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.013
7.995
7.992
7.677
7.674
7.659
7.643
7.640
7.637
7.534
7.530
7.513
7.498
7.495
7.270
4.415
4.398
4.382
1.801
1.784
1.766
1.747
1.730
1.480
1.461
1.442
1.424
0.986
0.967
0.964
0.949
0.000
10 9 8 7 6 5 4 3 2 1 0 ppm
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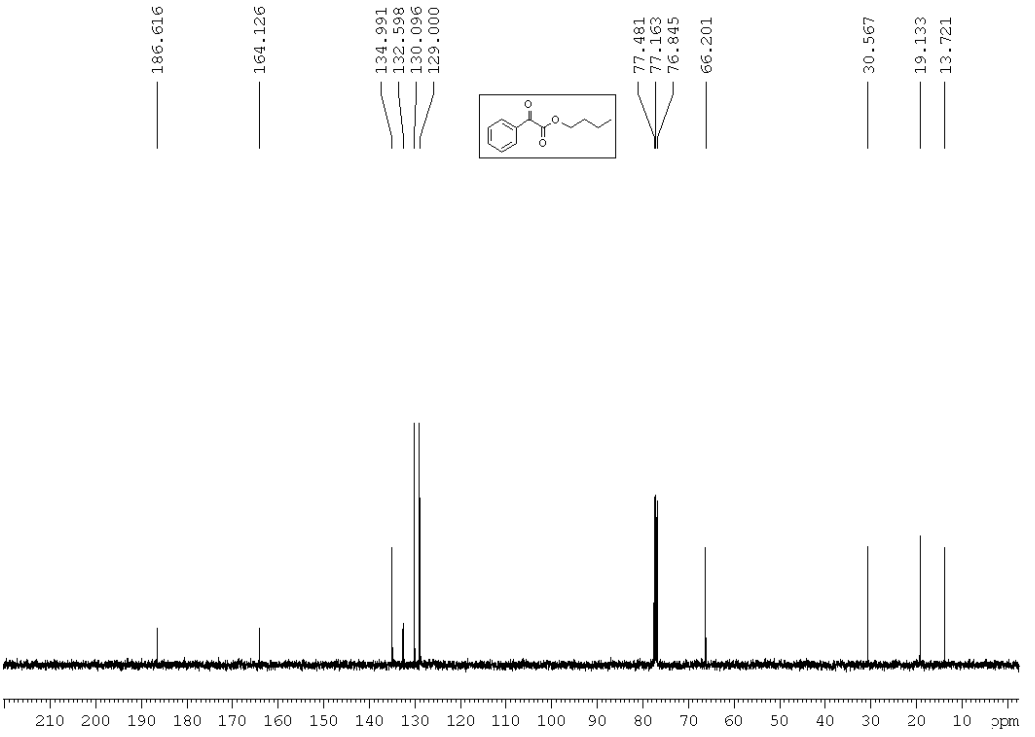
0.954
1.926
2.000
2.045
2.041
3.008


186.616
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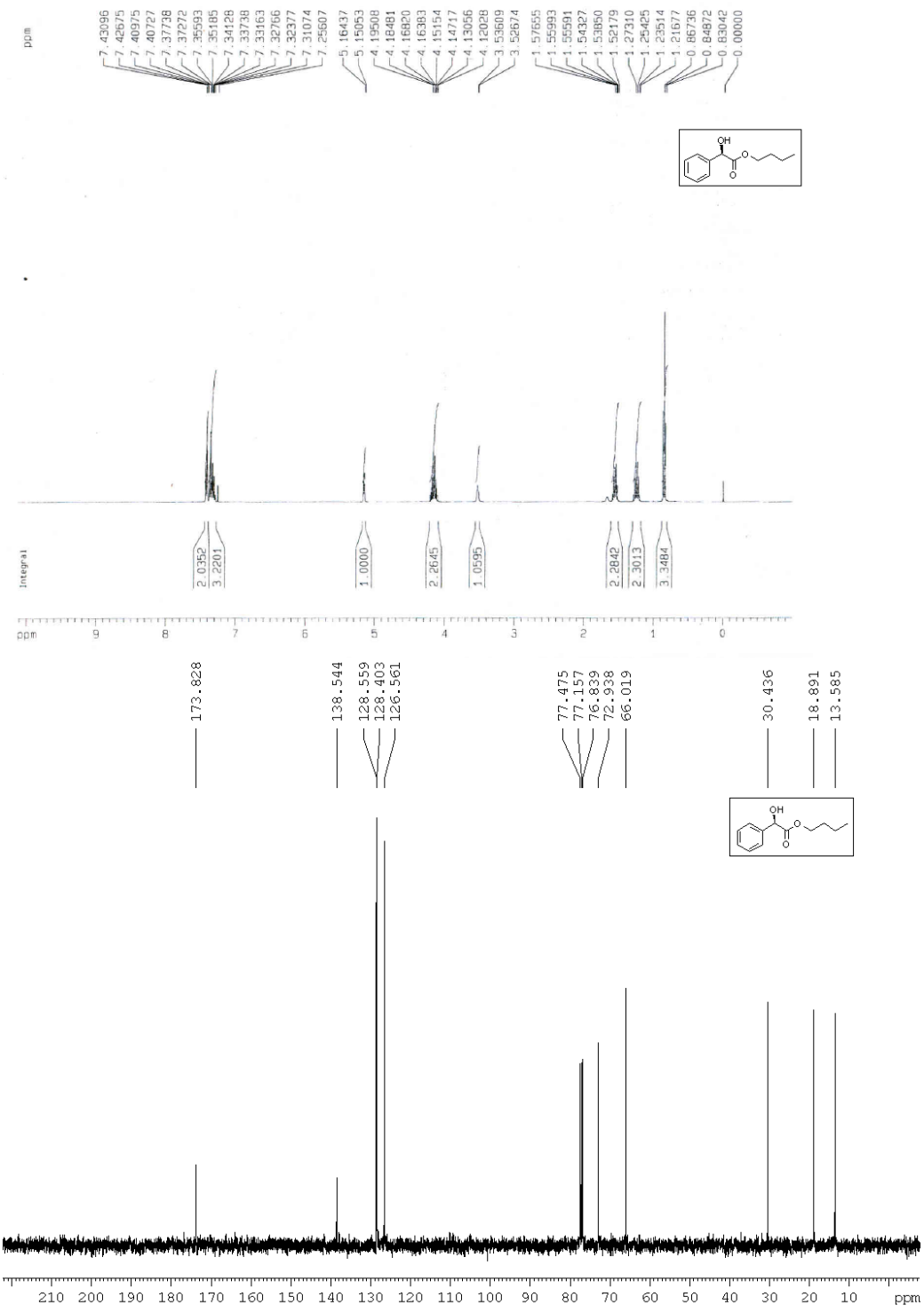
134.991
132.598
130.096
129.000
77.481
77.163
76.845
66.201
30.567
19.133
13.721
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


ppm
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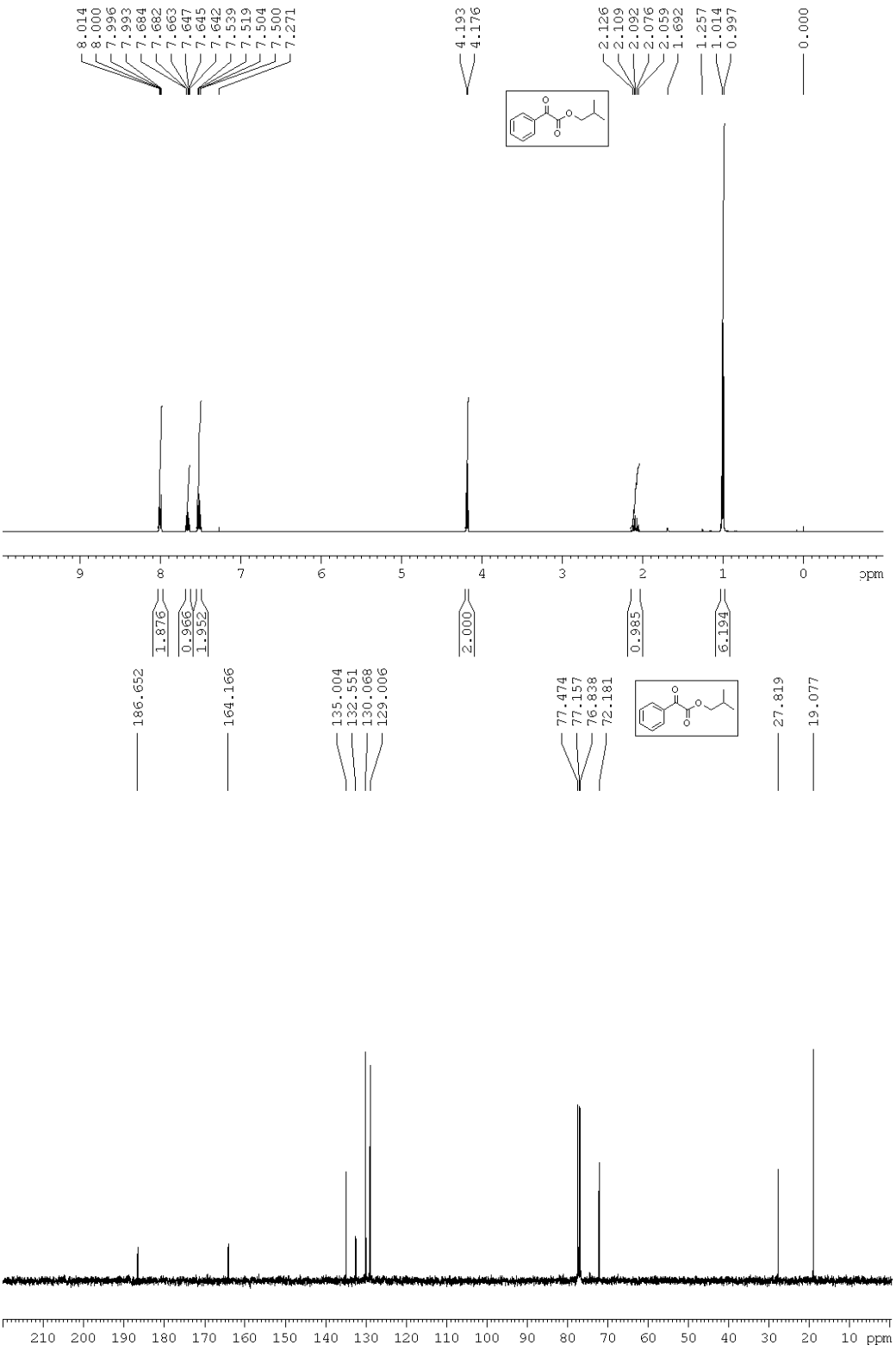
7.42675
7.40975
7.40727
7.37738
7.37272
7.35593
7.35185
7.34128
7.33738
7.33163
7.32766
7.32377
7.31074
7.25607
5.16437
5.15053
4.19508
4.18481
4.16820
4.16383
4.15154
4.14717
4.13056
4.12028
3.53609
3.52674
1.57655
1.55993
1.55591
1.54327
1.53850
1.52179
1.27310
1.25425
1.23514
1.21677
0.86736
0.84872
0.83042
0.00000
OH
O
O
Integral
2.0352
3.2201
1.0000
2.2645
1.0595
2.2842
2.3013
3.3484
ppm
9
8
7
6
5
4
3
2
1
0
173.828
138.544
128.559
128.403
126.561
77.475
77.157
76.839
72.938
66.019
30.436
18.891
13.585
OH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.996
7.993
7.684
7.682
7.663
7.647
7.645
7.642
7.539
7.519
7.504
7.500
7.271
4.193
4.176
2.126
2.109
2.092
2.076
2.059
1.692
1.257
1.014
0.997
0.000
ppm
1.876
0.966
1.952
2.000
0.985
6.194
186.652
164.166
135.004
132.551
130.068
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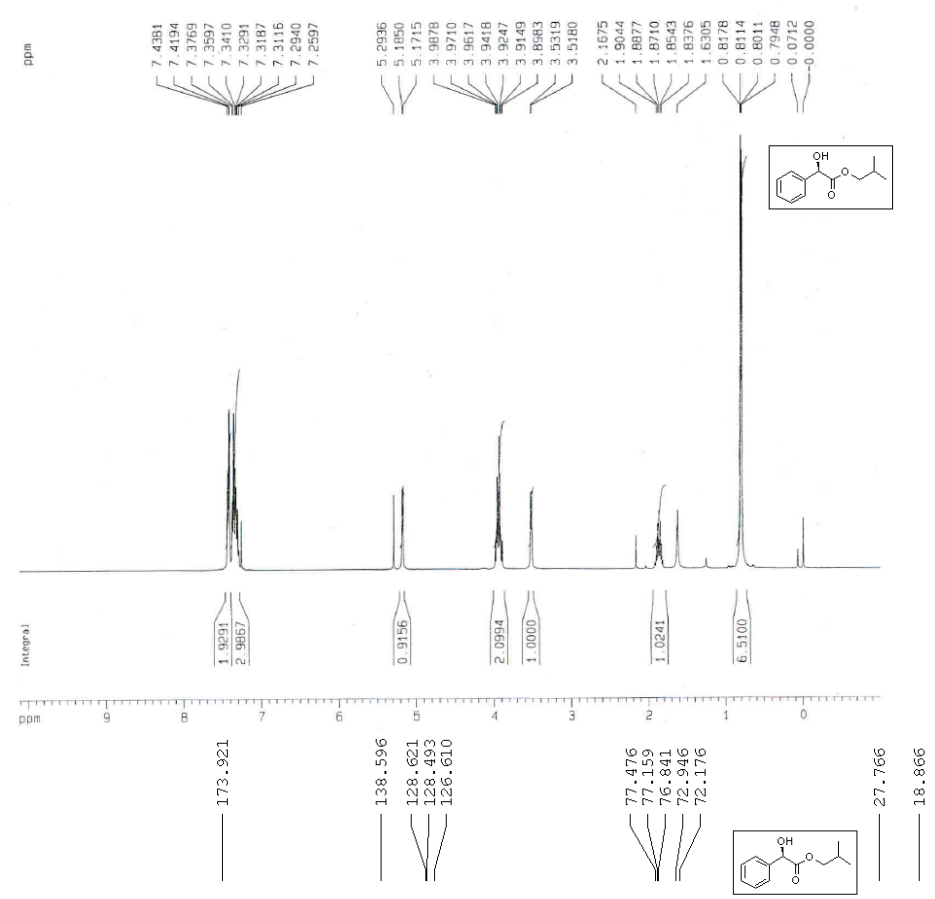
76.838
72.181
27.819
19.077
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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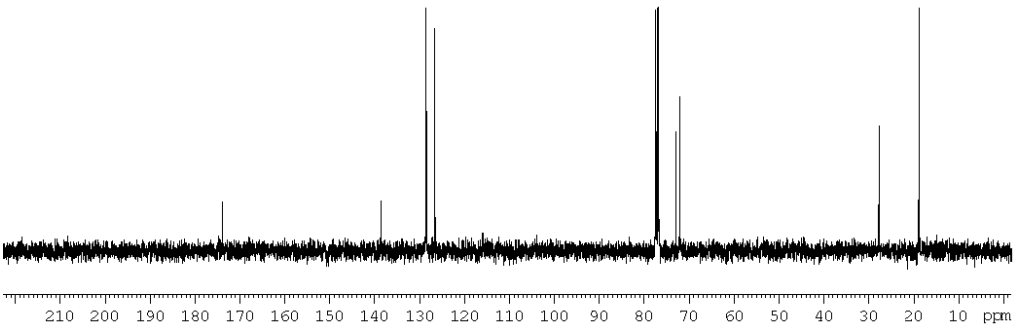
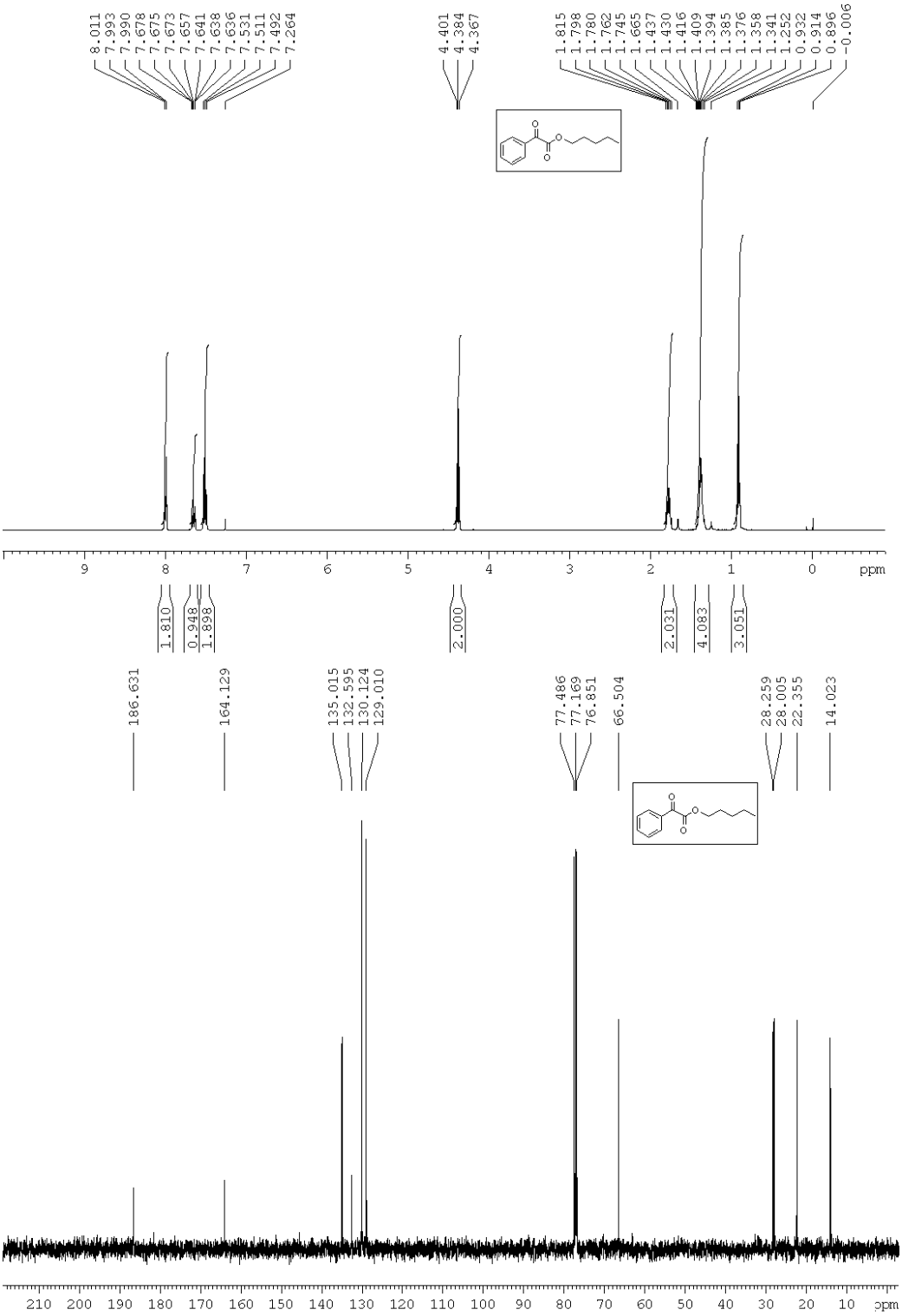
7.3769
7.3597
7.3410
7.3291
7.3187
7.3116
7.2940
7.2597
5.2936
5.1850
5.1715
3.9878
3.9710
3.9617
3.9418
3.9247
3.9149
3.8683
3.5319
3.5180
2.1675
1.9044
1.8877
1.8710
1.8543
1.8376
1.6305
0.8178
0.8114
0.8011
0.7948
0.0712
-0.0000
OH
O
O
Integral
1.9291
2.9867
0.9156
2.0994
1.0000
1.0241
6.5100
ppm
9
8
7
6
5
4
3
2
1
0
173.921
138.596
128.621
128.493
126.610
77.476
77.159
76.841
72.946
72.176
27.766
18.866
OH
O
O


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.993
7.990
7.678
7.675
7.673
7.657
7.641
7.638
7.636
7.531
7.511
7.492
7.264
4.401
4.384
4.367
1.815
1.798
1.780
1.762
1.745
1.665
1.437
1.430
1.416
1.409
1.394
1.385
1.376
1.358
1.341
1.252
0.932
0.914
0.896
-0.006
ppm
1.810
0.948
1.898
2.000
2.031
4.083
3.051
186.631
164.129
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129.010
77.486
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76.851
66.504
28.259
28.005
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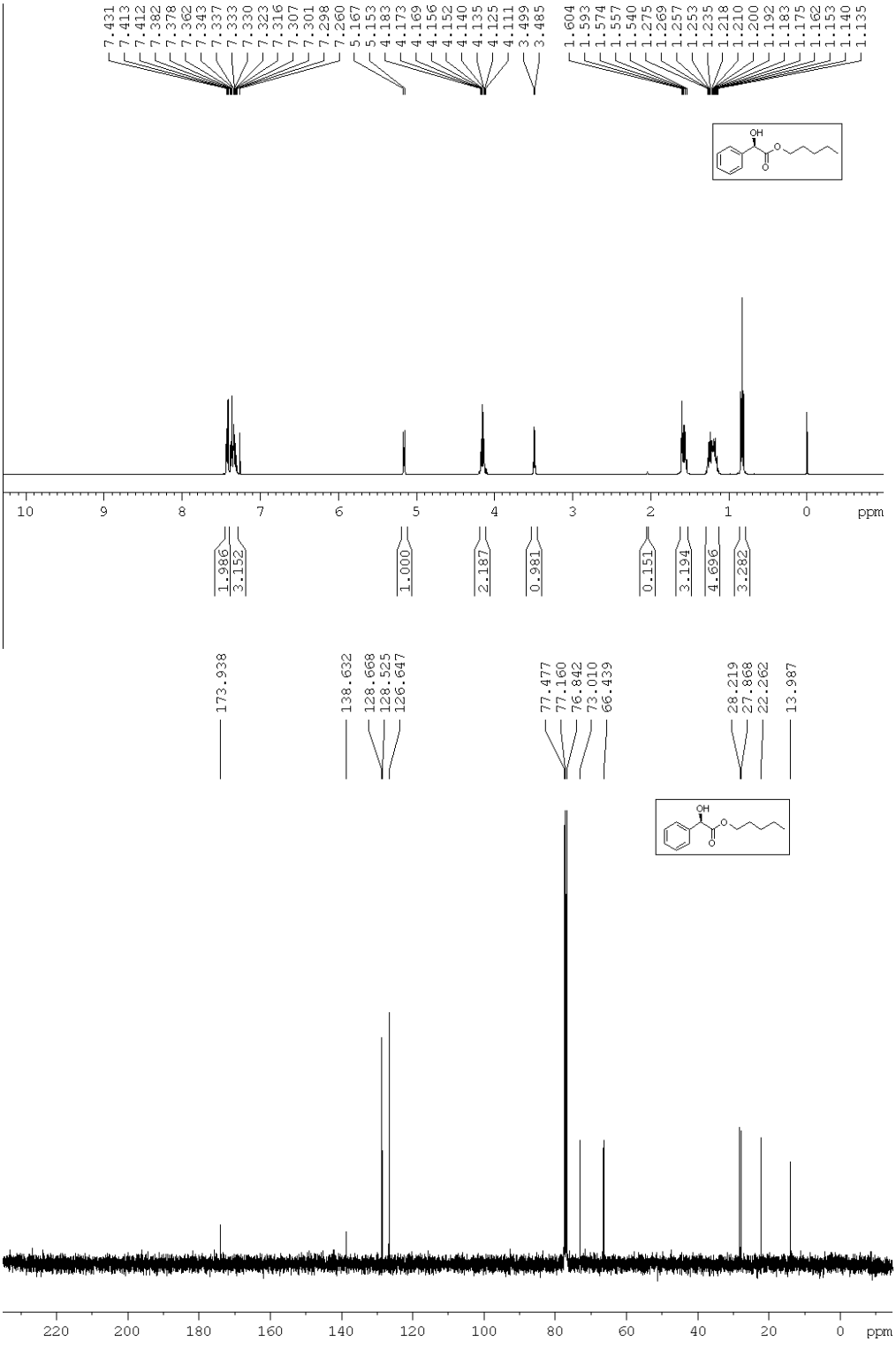
ppm


7.431
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7.412
7.382
7.378
7.362
7.343
7.337
7.333
7.330
7.323
7.316
7.307
7.301
7.298
7.260
5.167
5.153
4.183
4.173
4.169
4.156
4.152
4.140
4.135
4.125
4.111
3.499
3.485
1.604
1.593
1.574
1.557
1.540
1.275
1.269
1.257
1.253
1.235
1.218
1.210
1.200
1.192
1.183
1.175
1.162
1.153
1.140
1.135
OH
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.986
3.152
1.000
2.187
0.981
0.151
3.194
4.696
3.282
173.938
138.632
128.668
128.525
126.647
77.477
77.160
76.842
73.010
66.439
28.219
27.868
22.262
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OH
O
O
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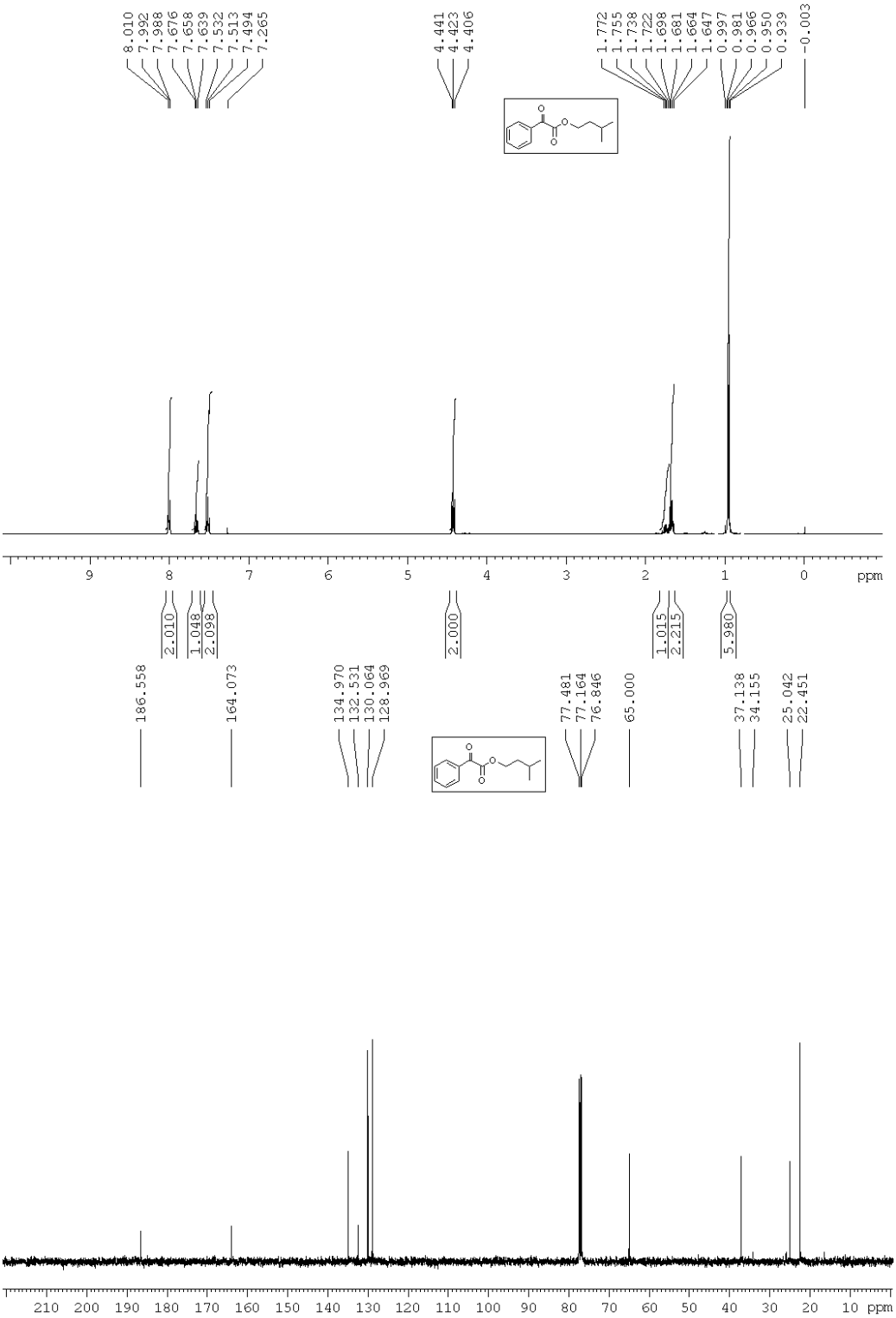
160
140
120
100
80
60
40
20
0
ppm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7.532
7.513
7.494
7.265
4.441
4.423
4.406
1.772
1.755
1.738
1.722
1.698
1.681
1.664
1.647
0.997
0.981
0.966
0.950
0.939
-0.003
ppm
2.010
1.048
2.098
2.000
1.015
2.215
5.980
186.558
164.073
134.970
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130.064
128.969
77.481
77.164
76.846
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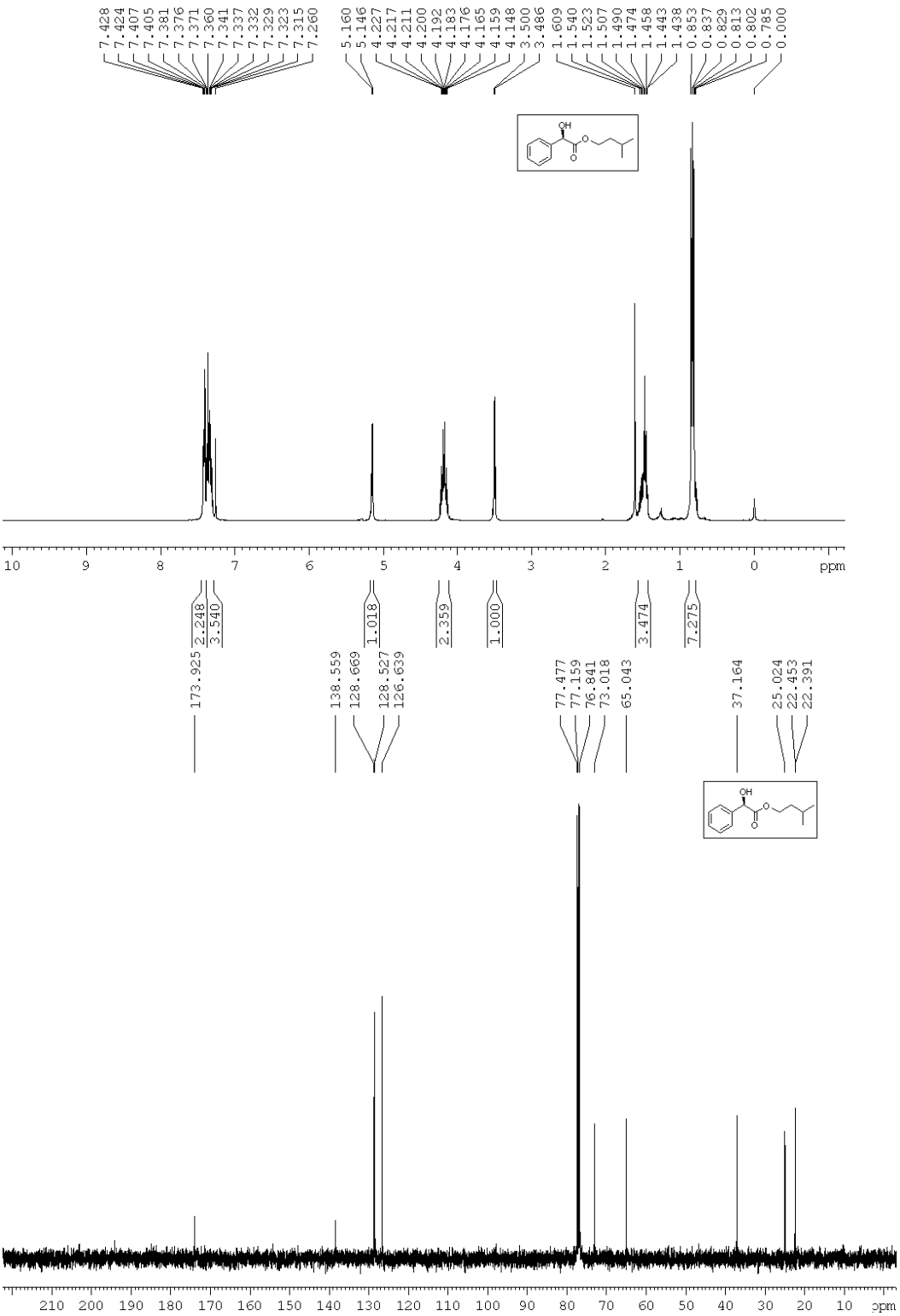
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7.407
7.405
7.381
7.376
7.371
7.360
7.341
7.337
7.332
7.329
7.323
7.315
7.260
5.160
5.146
4.227
4.217
4.211
4.200
4.192
4.183
4.176
4.165
4.159
4.148
3.500
3.486
1.609
1.540
1.523
1.507
1.490
1.474
1.458
1.443
1.438
0.853
0.837
0.829
0.813
0.802
0.785
0.000
OH
O
O
10 9 8 7 6 5 4 3 2 1 0 ppm
2.248
3.540
1.018
2.359
1.000
3.474
7.275
173.925
138.559
128.669
128.527
126.639
77.477
77.159
76.841
73.018
65.043
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25.024
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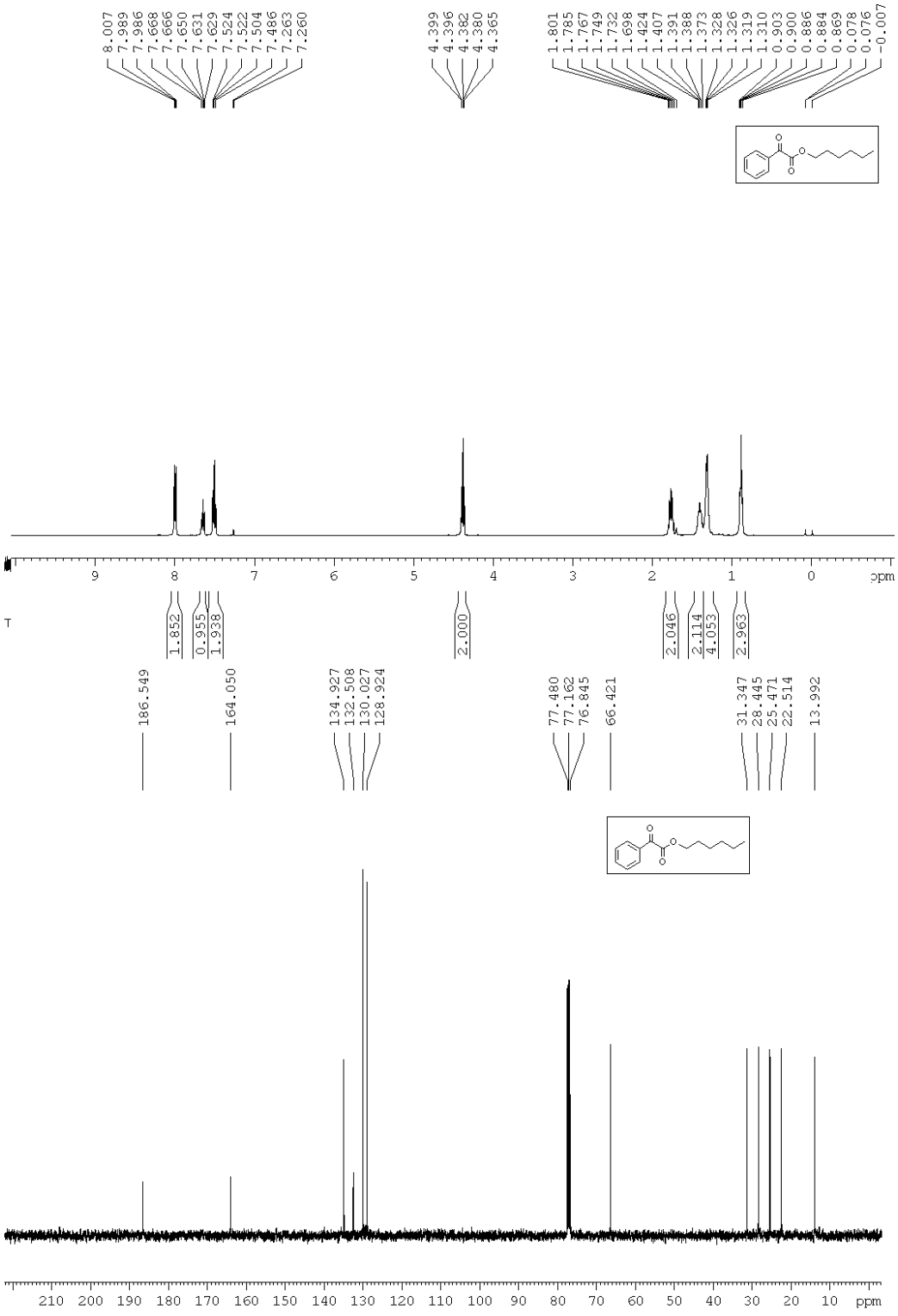
22.391
OH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.986
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7.666
7.650
7.631
7.629
7.524
7.522
7.504
7.486
7.263
7.260
4.399
4.396
4.382
4.380
4.365
1.801
1.785
1.767
1.749
1.732
1.698
1.424
1.407
1.391
1.388
1.373
1.328
1.326
1.319
1.310
0.903
0.900
0.886
0.884
0.869
0.078
0.076
-0.007
ppm
1.852
0.955
1.938
2.000
2.046
2.114
4.053
2.963
186.549
164.050
134.927
132.508
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77.162
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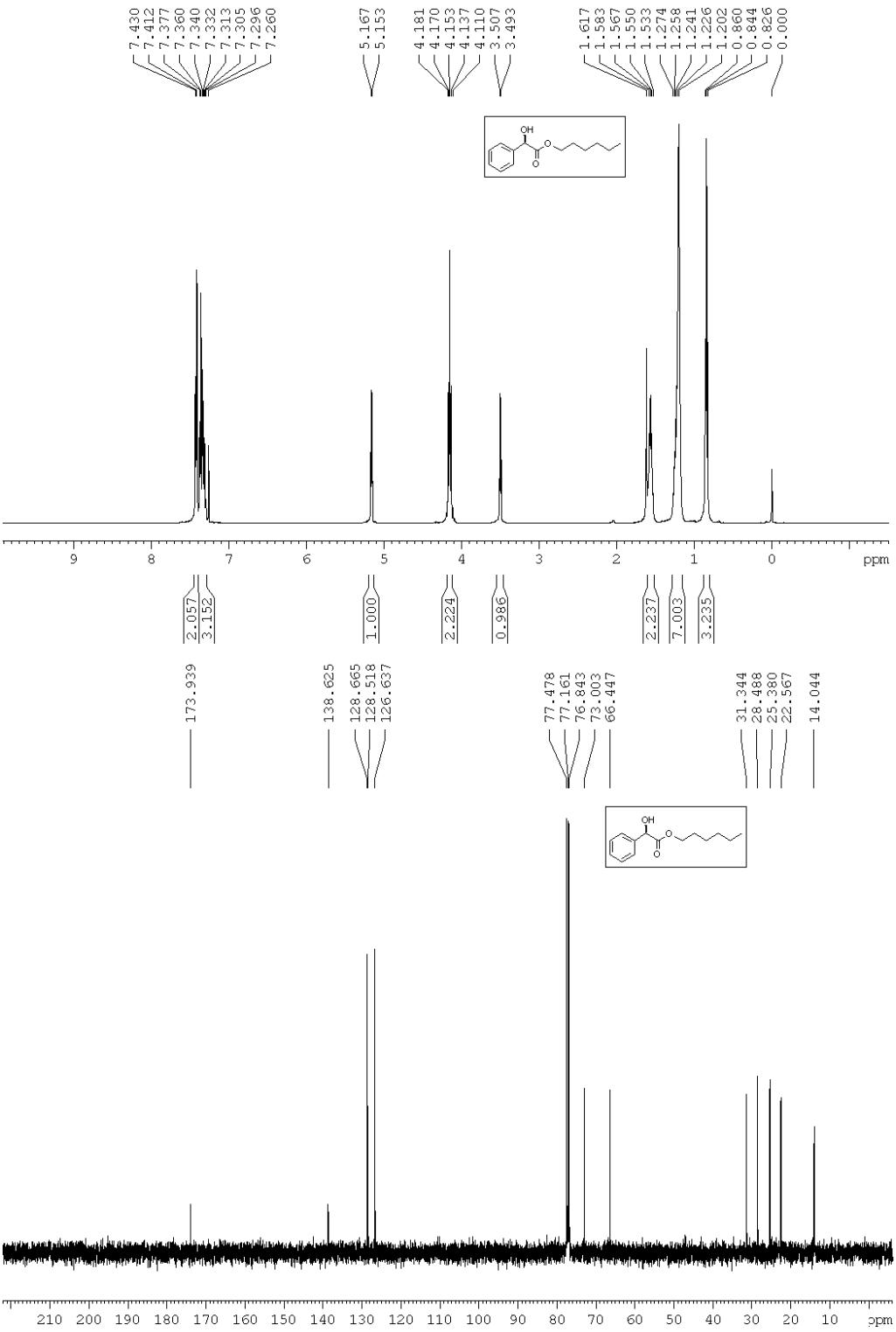
22.514
13.992
ppm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7.360
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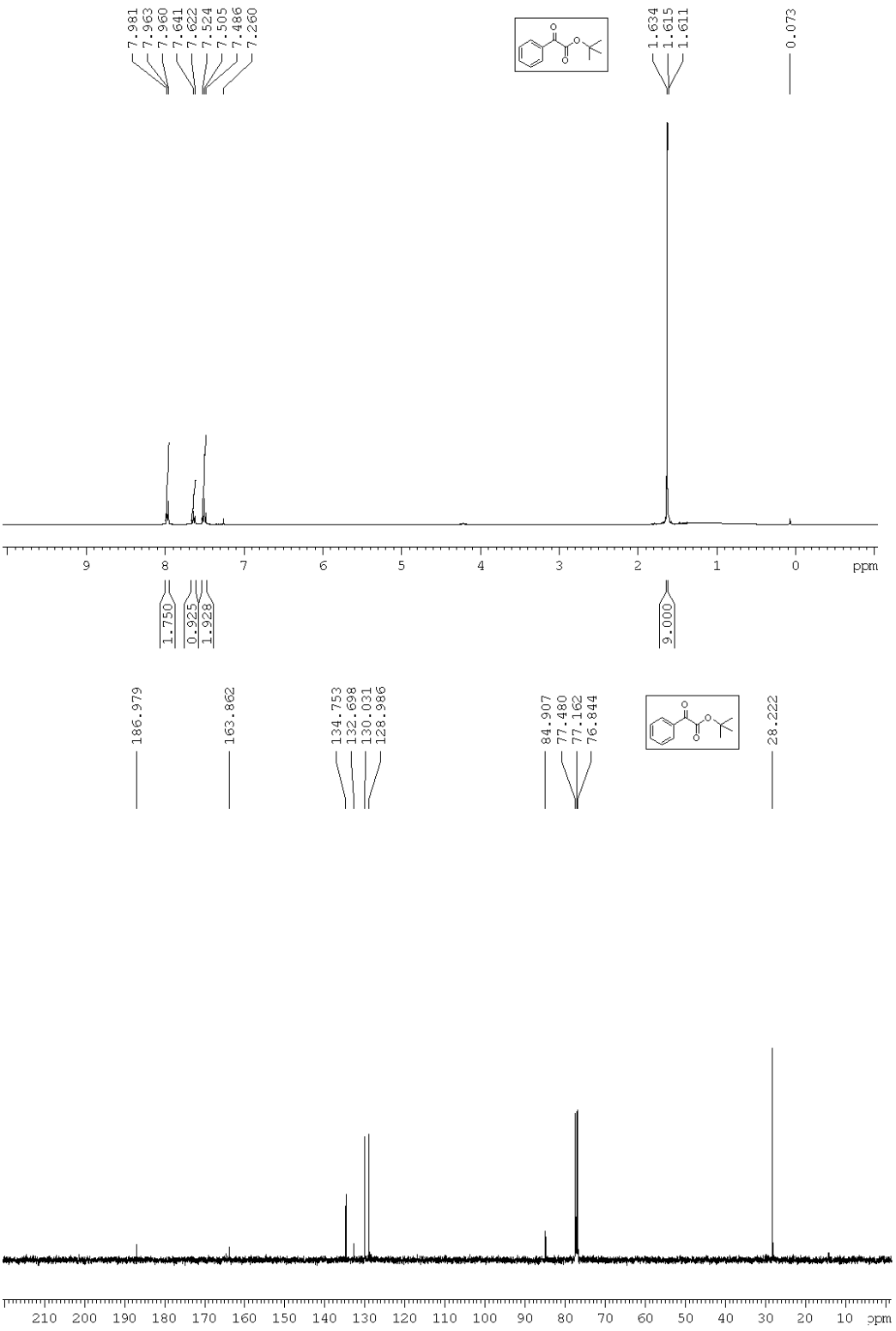
7.332
7.313
7.305
7.296
7.260
5.167
5.153
4.181
4.170
4.153
4.137
4.110
3.507
3.493
1.617
1.583
1.567
1.550
1.533
1.274
1.258
1.241
1.226
1.202
0.860
0.844
0.826
0.000
OH
O
O
9
8
7
6
5
4
3
2
1
0
ppm
2.057
3.152
1.000
2.224
0.986
2.237
7.003
3.235
173.939
138.625
128.665
128.518
126.637
77.478
77.161
76.843
73.003
66.447
31.344
28.488
25.380
22.567
14.044
OH
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.960
7.641
7.622
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7.505
7.486
7.260
1.634
1.615
1.611
0.073
9
8
7
6
5
4
3
2
1
0
ppm
1.750
0.925
1.928
9.000
186.979
163.862
134.753
132.698
130.031
128.986
84.907
77.480
77.162
76.844
28.222
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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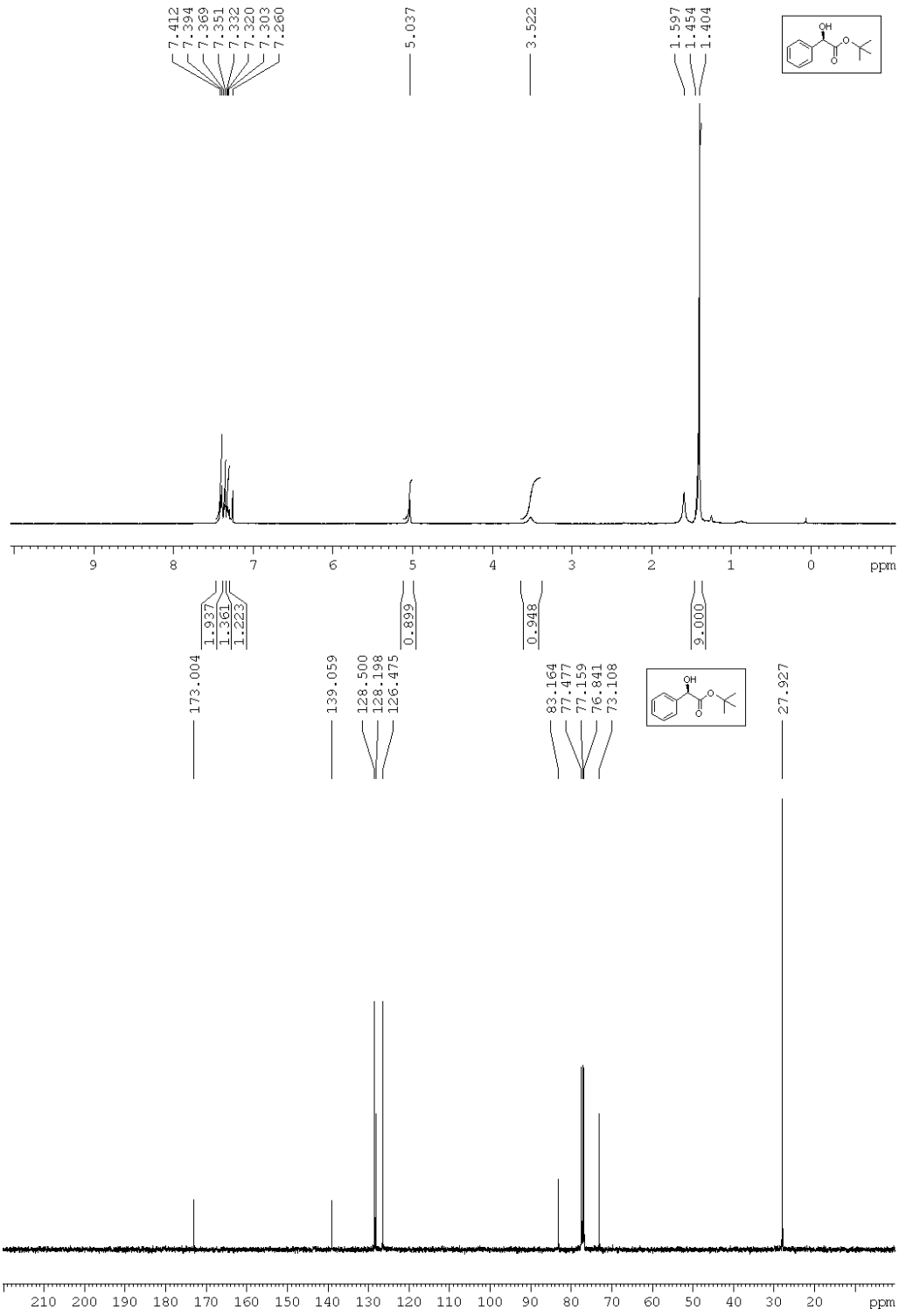
30
20
10
ppm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7.332
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7.260
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3.522
1.597
1.454
1.404
ppm
1.937
1.361
1.223
0.899
0.948
9.000
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128.198
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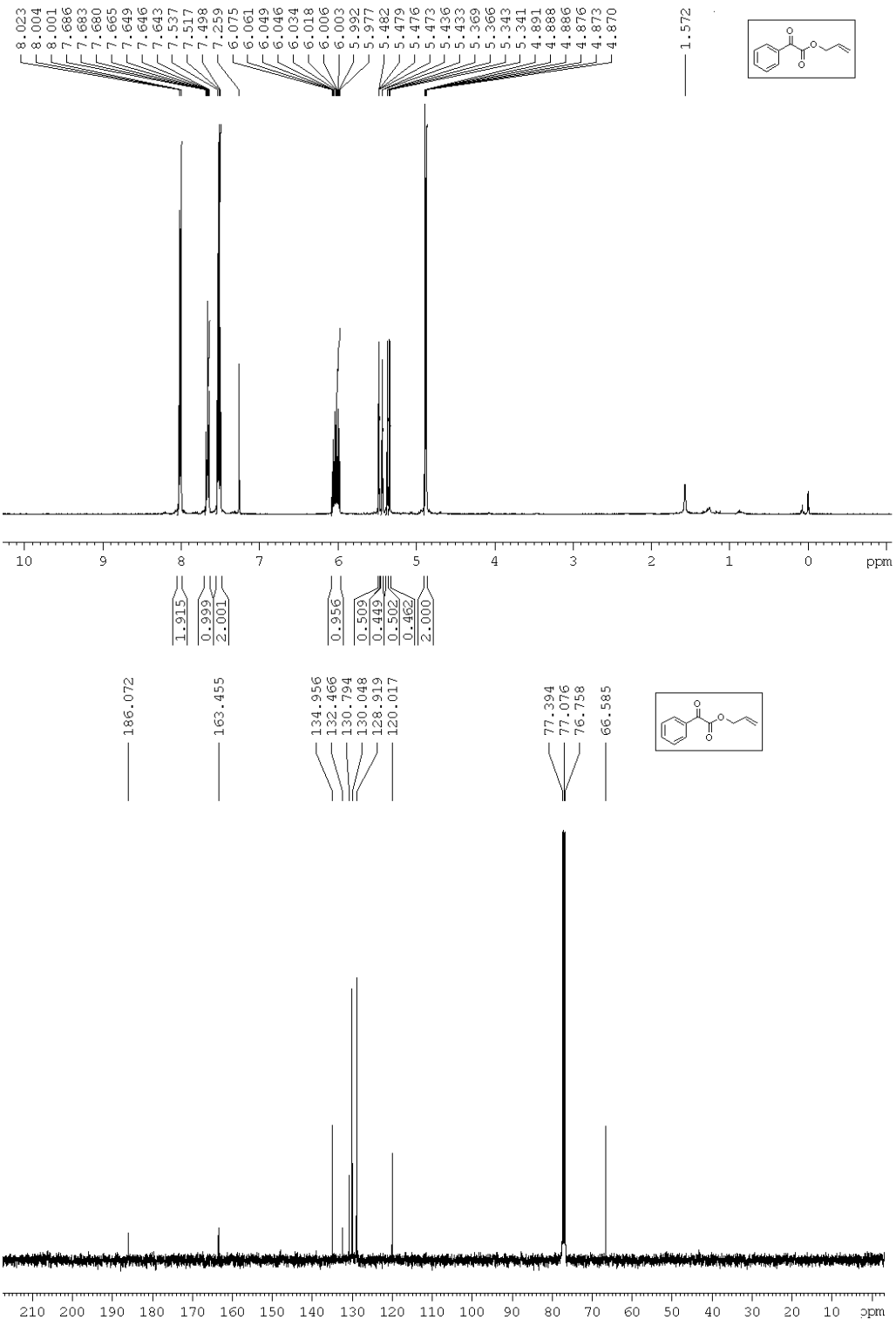
77.159
76.841
73.108
27.927
ppm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8.004
8.001
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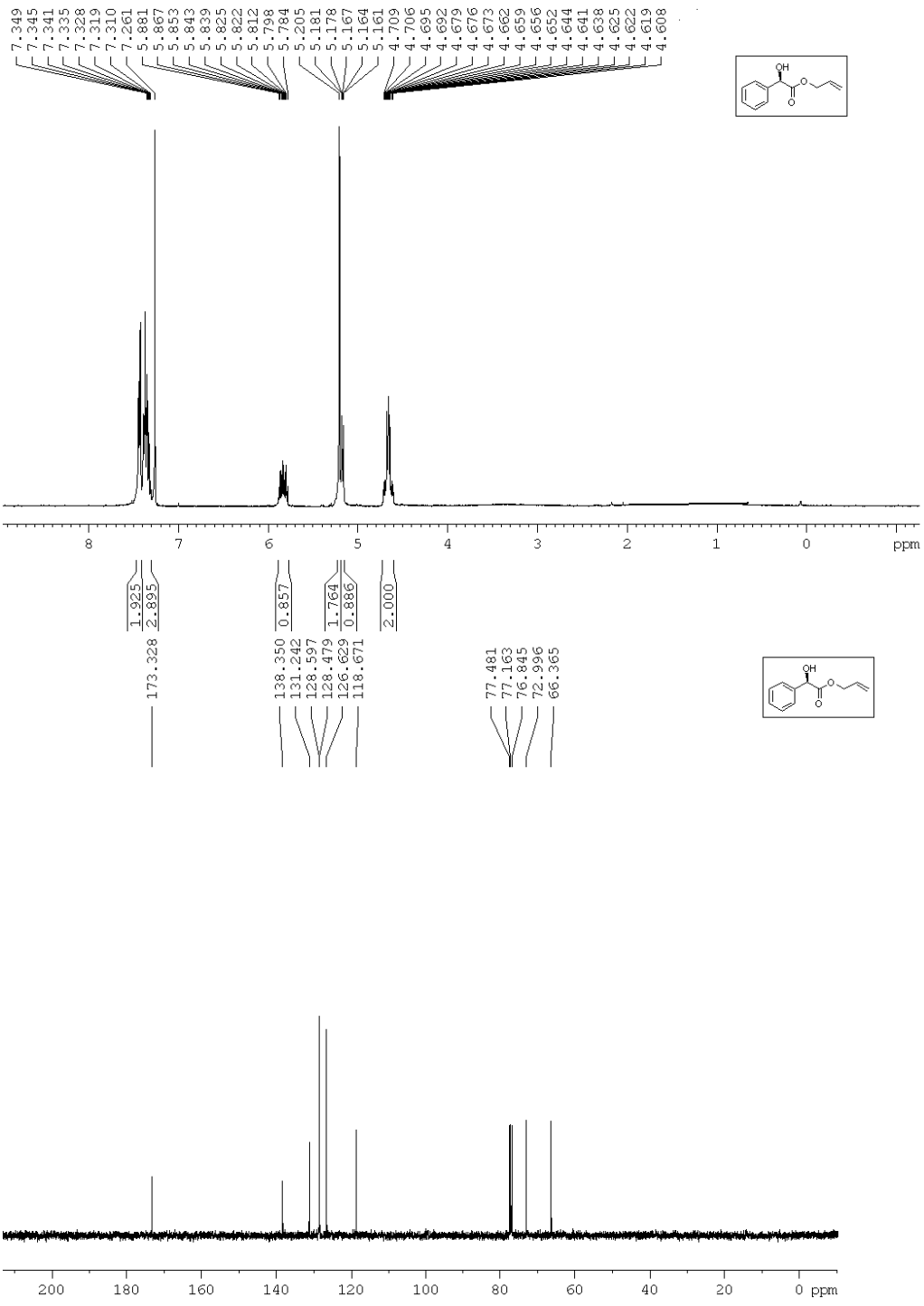
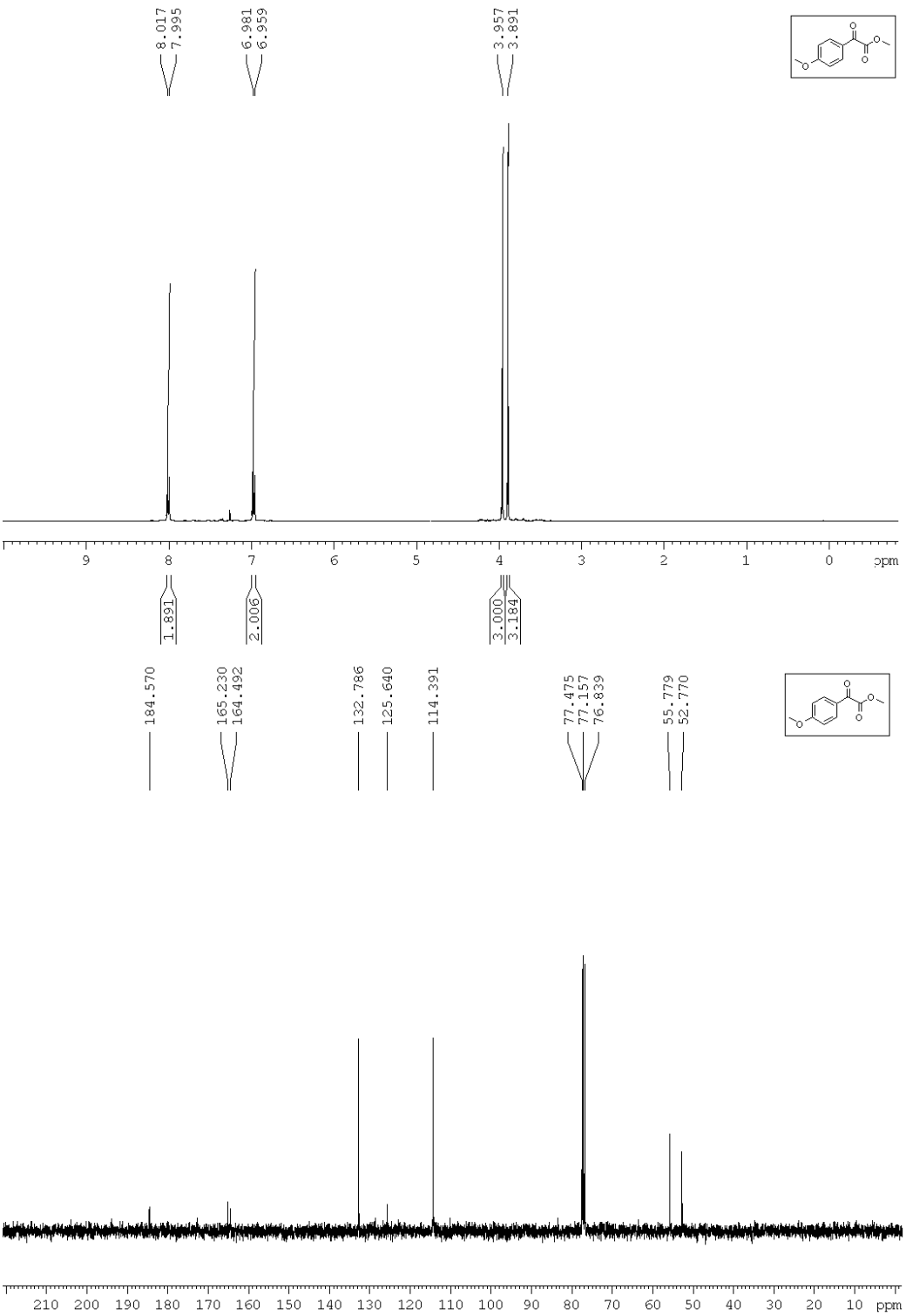
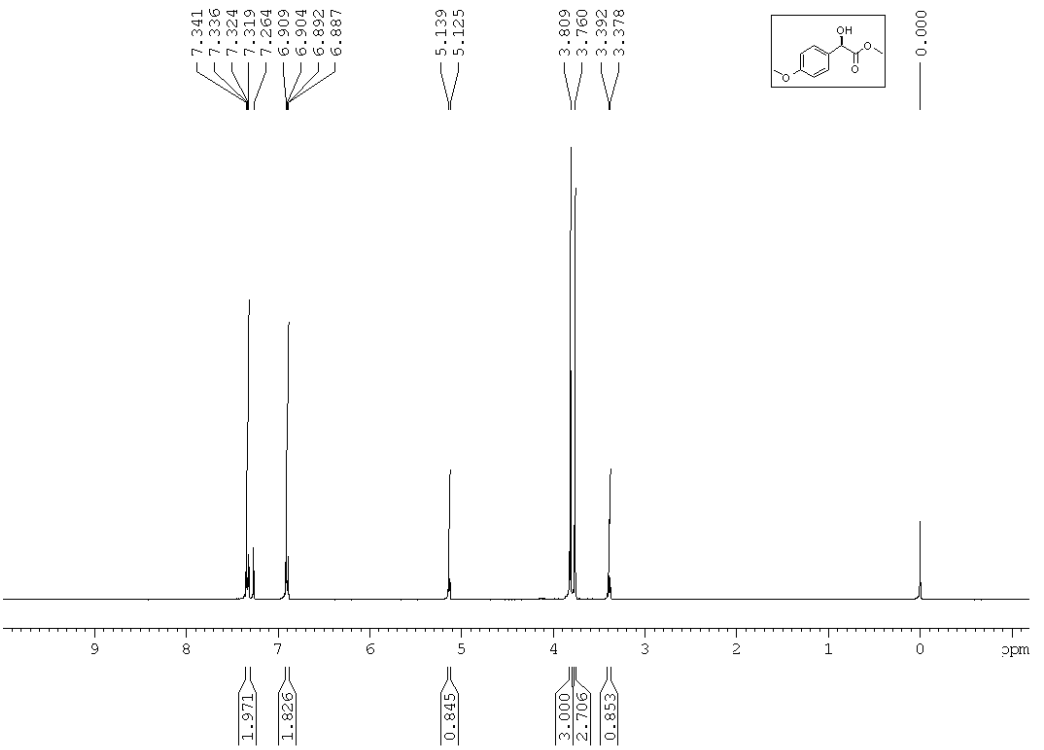
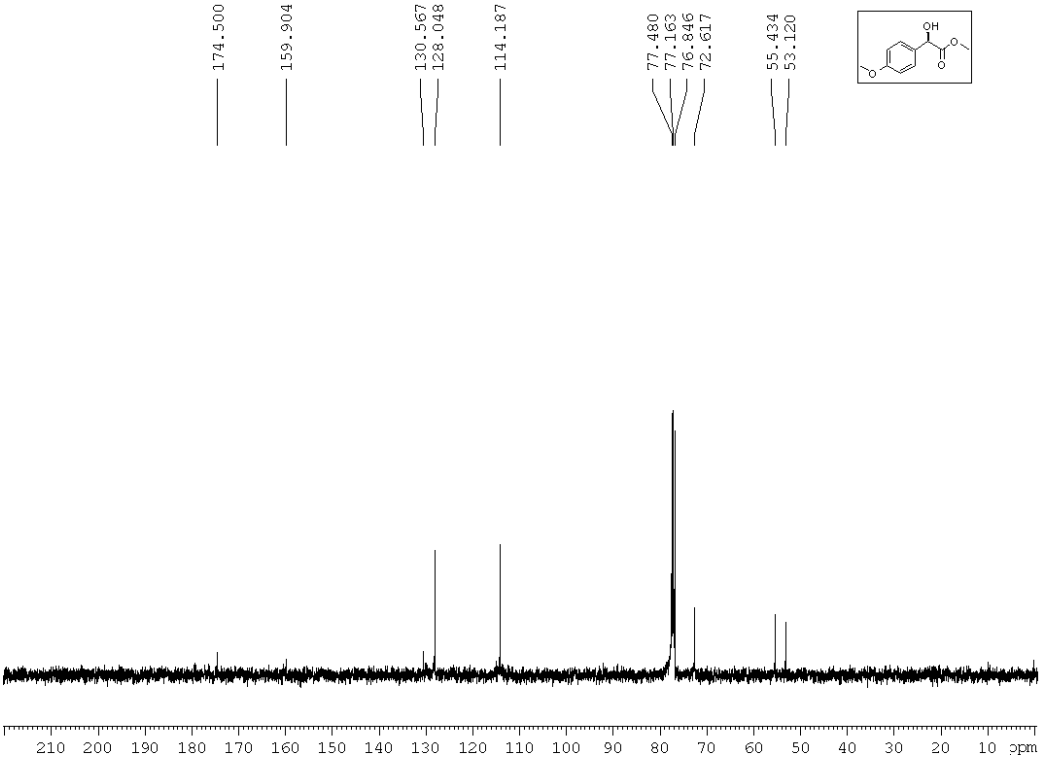
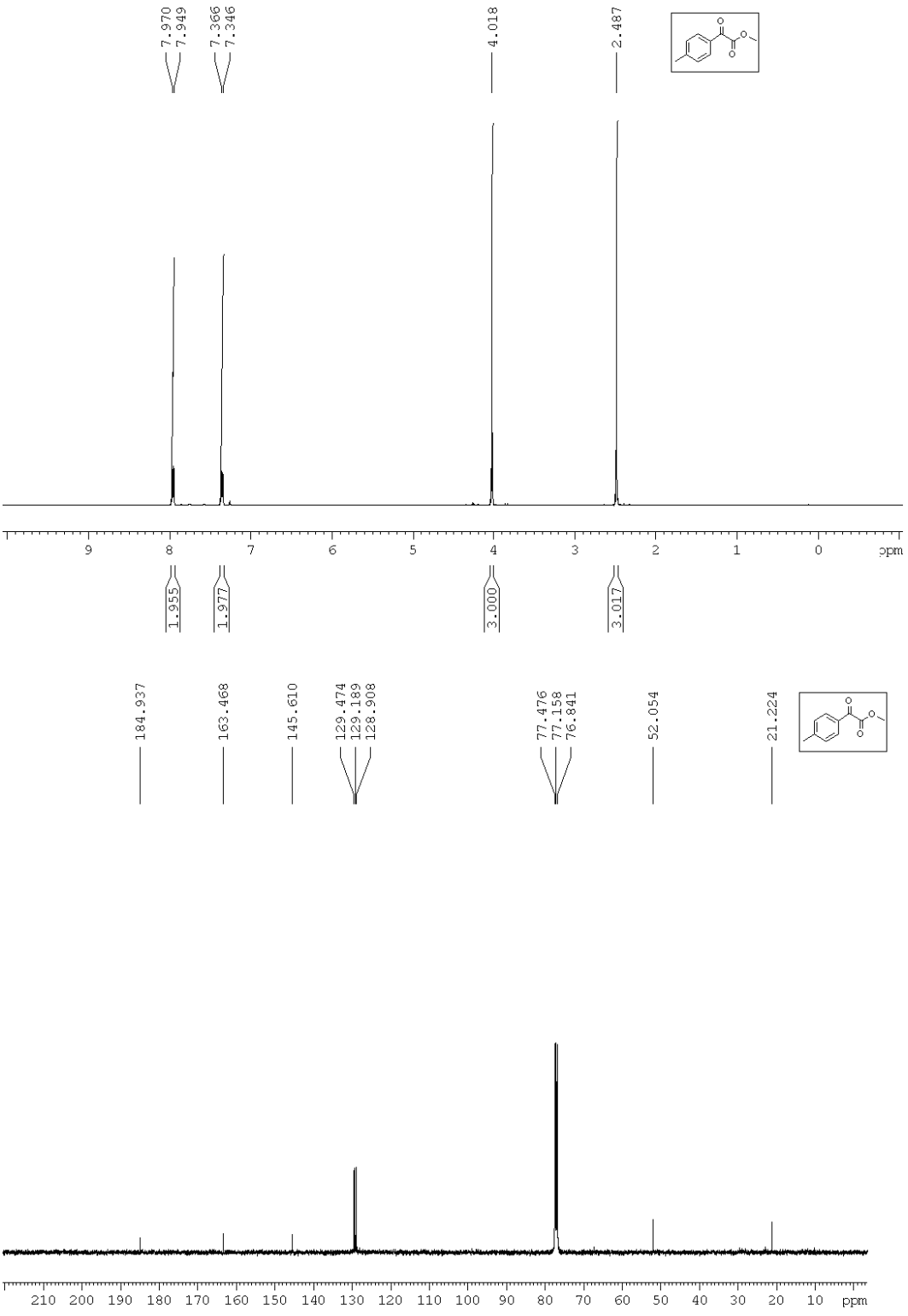
7.680
7.665
7.649
7.646
7.643
7.537
7.517
7.498
7.259
6.075
6.061
6.049
6.046
6.034
6.018
6.006
6.003
5.992
5.977
5.482
5.479
5.476
5.473
5.436
5.433
5.369
5.366
5.343
5.341
4.891
4.888
4.886
4.876
4.873
4.870
1.572
10 9 8 7 6 5 4 3 2 1 0 ppm
1.915
0.999
2.001
0.956
0.509
0.449
0.502
0.462
2.000
186.072
163.455
134.956
132.466
130.794
130.048
128.919
120.017
77.394
77.076
76.758
66.585
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

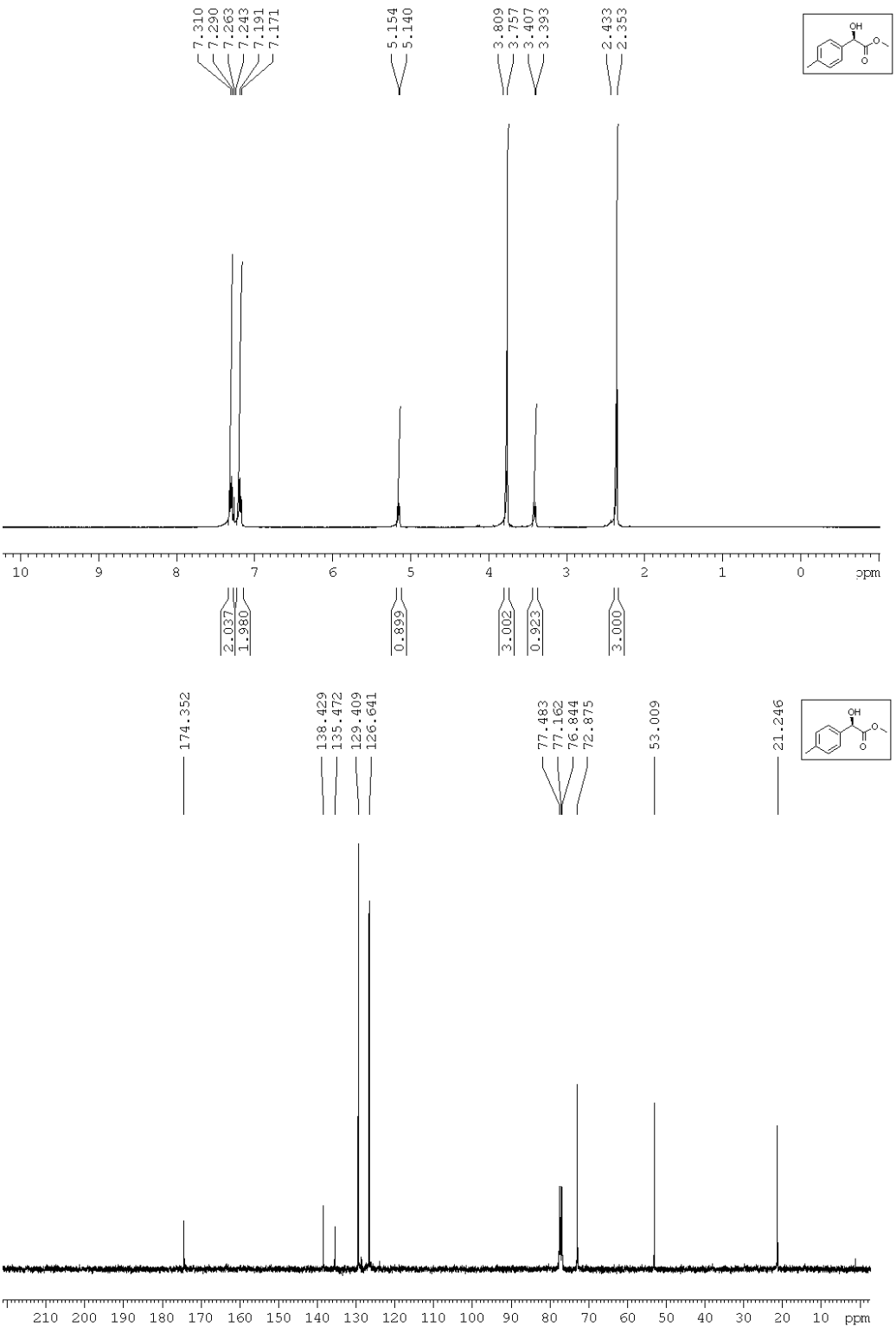

7.349
7.345
7.341
7.335
7.328
7.319
7.310
7.261
5.881
5.867
5.853
5.843
5.839
5.825
5.822
5.812
5.798
5.784
5.205
5.181
5.178
5.167
5.164
5.161
4.709
4.706
4.695
4.692
4.679
4.676
4.673
4.662
4.659
4.656
4.652
4.644
4.641
4.638
4.625
4.622
4.619
4.608
OH
O
O
8
7
6
5
4
3
2
1
0
ppm
1.925
2.895
0.857
1.764
0.886
2.000
173.328
138.350
131.242
128.597
128.479
126.629
118.671
77.481
77.163
76.845
72.996
66.365
OH
O
O
200
180
160
140
120
100
80
60
40
20
0 ppm

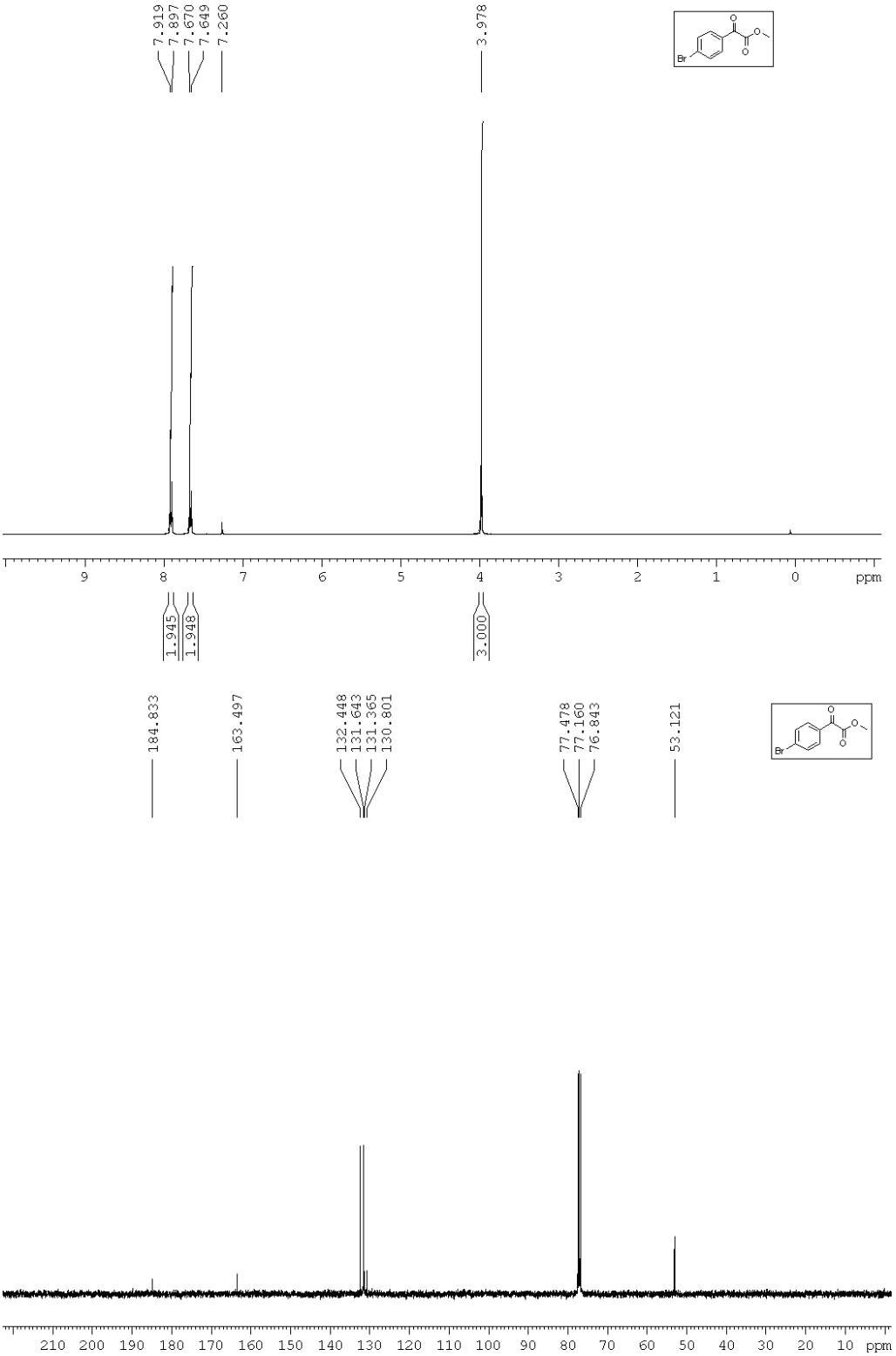

8.017
7.995
6.981
6.959
3.957
3.891
9
8
7
6
5
4
3
2
1
0
ppm
1.891
2.006
3.000
3.184
184.570
165.230
164.492
132.786
125.640
114.391
77.475
77.157
76.839
55.779
52.770
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

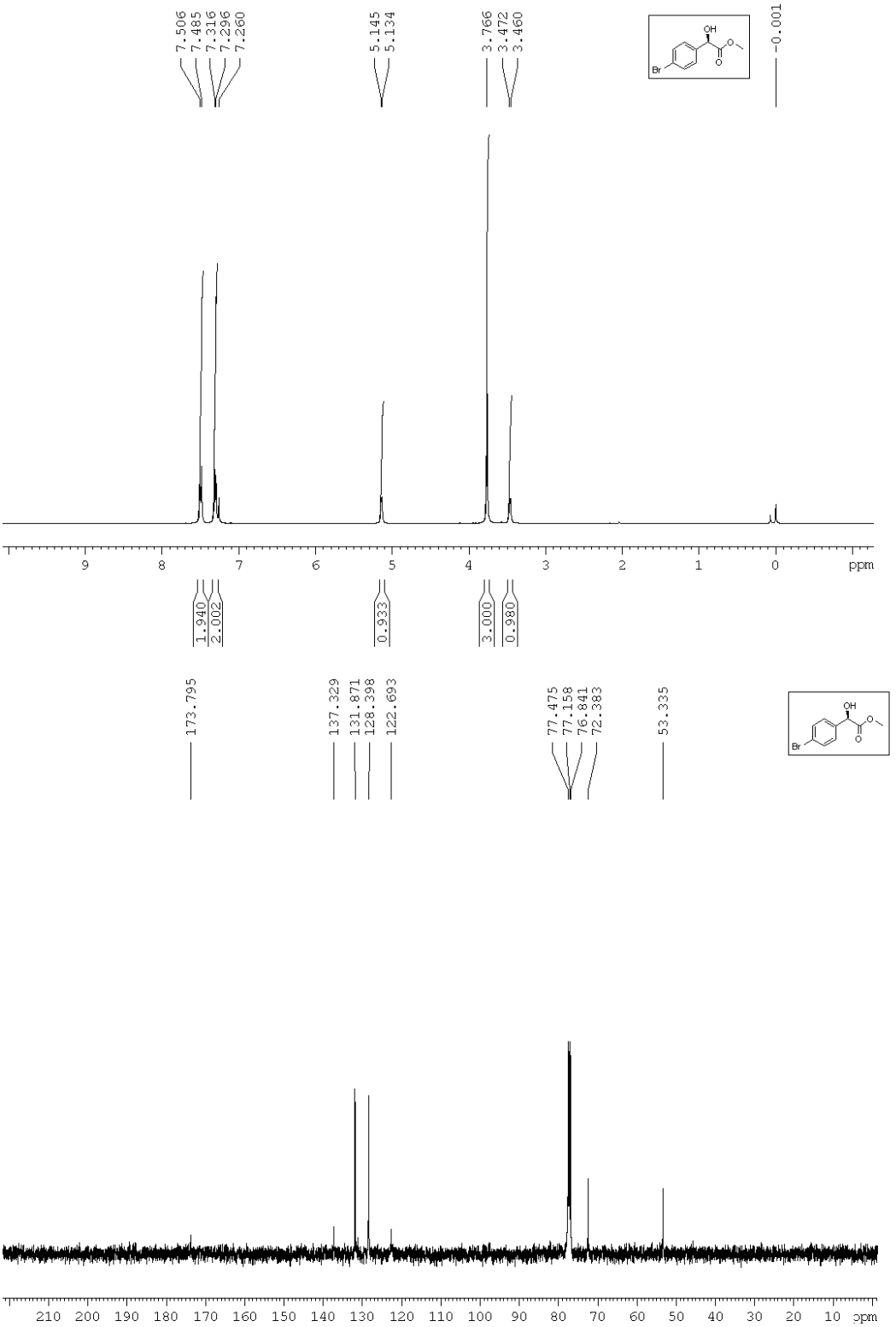

7.341
7.336
7.324
7.319
7.264
6.909
6.904
6.892
6.887
5.139
5.125
3.809
3.760
3.392
3.378
0.000
OH
O
O
O
9
8
7
6
5
4
3
2
1
0
ppm
1.971
1.826
0.845
3.000
2.706
0.853

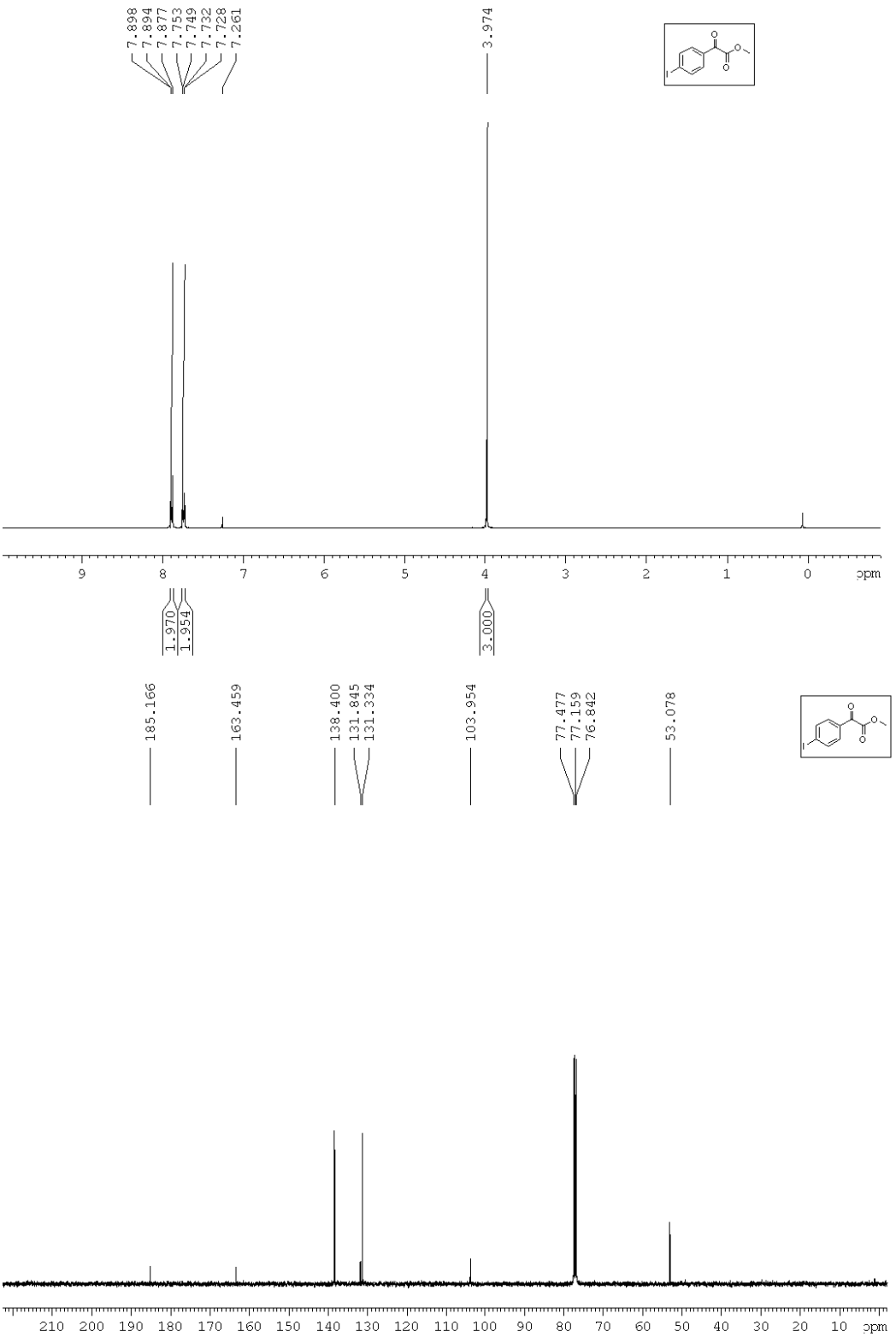

174.500
159.904
130.567
128.048
114.187
77.480
77.163
76.846
72.617
55.434
53.120
OH
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

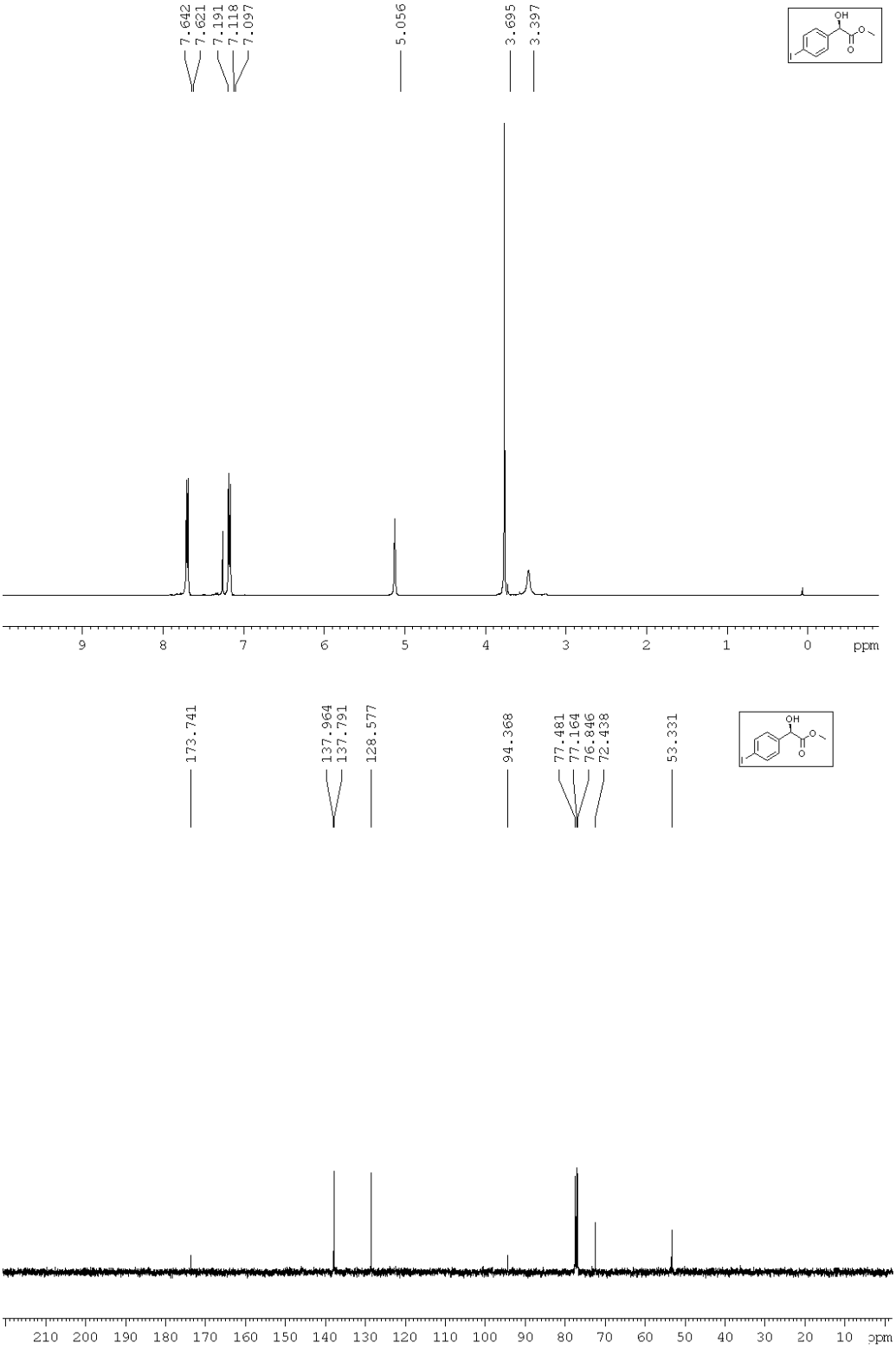

7.970
7.949
7.366
7.346
4.018
2.487
9
8
7
6
5
4
3
2
1
0
ppm
1.955
1.977
3.000
3.017
184.937
163.468
145.610
129.474
129.189
128.908
77.476
77.158
76.841
52.054
21.224
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.310
7.290
7.263
7.243
7.191
7.171
5.154
5.140
3.809
3.757
3.407
3.393
2.433
2.353
OH
O
O
10 9 8 7 6 5 4 3 2 1 0 ppm
2.037
1.980
0.899
3.002
0.923
3.000
174.352
138.429
135.472
129.409
126.641
77.483
77.162
76.844
72.875
53.009
21.246
OH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.919
7.897
7.670
7.649
7.260
3.978
Br
9
8
7
6
5
4
3
2
1
0
ppm
1.945
1.948
3.000
184.833
163.497
132.448
131.643
131.365
130.801
77.478
77.160
76.843
53.121
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.506
7.485
7.316
7.296
7.260
5.145
5.134
3.766
3.472
3.460
-0.001
OH
Br
O
ppm
1.940
2.002
0.933
3.000
0.980
173.795
137.329
131.871
128.398
122.693
77.475
77.158
76.841
72.383
53.335
ppm


7.898
7.894
7.877
7.753
7.749
7.732
7.728
7.261
3.974
9
8
7
6
5
4
3
2
1
0
ppm
1.970
1.954
3.000
185.166
163.459
138.400
131.845
131.334
103.954
77.477
77.159
76.842
53.078
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.642
7.621
7.191
7.118
7.097
5.056
3.695
3.397
OH
O
O
I
9
8
7
6
5
4
3
2
1
0
ppm
173.741
137.964
137.791
128.577
94.368
77.481
77.164
76.846
72.438
53.331
OH
O
O
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

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