Supplementary Material (ESI) for Chemical Science

In(III)-Pybox Complex Catalyzed Enantioselective Mukaiyama Aldol Reactions between Polymeric or Hydrated Glyoxylates and Enolsilanes Derived from Aryl Ketones

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Supporting Information

Table of Contents

General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditons.

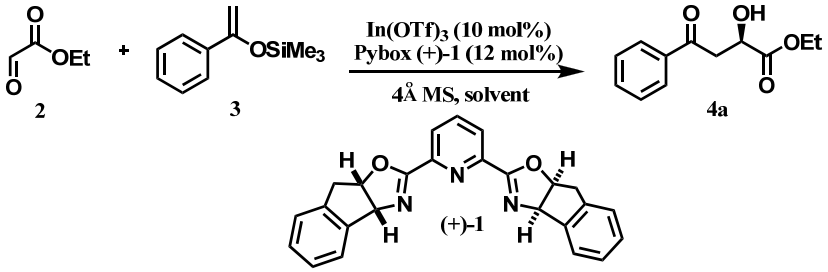
High Resolution Mass (HRMS) spectra were obtained using Waters Q-Tof Permies Mass Spectrometer.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dddd (doublets of doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet). Enantioselectivities were determined by HPLC analysis employing a Daicel Chiracel column at 25 ^oC and chiral GC. Optical rotation was measured using a JASCO P-1030 Polarimeter equipped with a sodium vapor lamp at 589 nm. Concentration is denoted as *c* and was calculated as grams per deciliters (g / 100mL). Absolute configuration of the products was determined by comparison with known compounds.

Preliminary studies of reaction conditions

Initially, we chose polymeric ethyl gloxylate (50% in toluene) and acetophenone-derived enolsilane as the model substrates to optimize reaction conditions (for details of condition optimization, see Tables 1-5 in the Supporting Information). The solvent, ligand, temperature, additive, catalyst loading and counterion effect were all evaluated. Polar solvents such as CH_3CN and THF proved to be better than non-polar solvents. Pybox (+)-**1** is the best choice of ligand and box ligands are ineffective for this transformation. With decreasing temperature, the enantioselectivity was favored to increase. Based on the optimization studies, we found that the combination of 5 mol% of $InBr_3$, 5 mol% of $AgSbF_6$ and 6 mol% of pybox (+)-**1** with CH_3CN as the solvent in the presence of 4 Å molecular sieves was the best catalytic system.

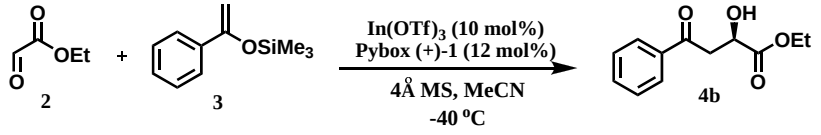
Table 1. Screening of solvents[a]

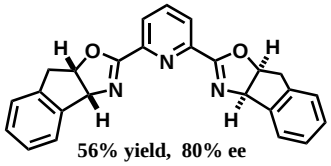
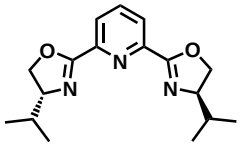
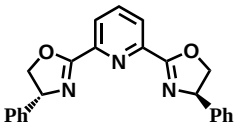
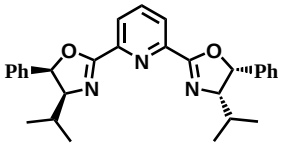
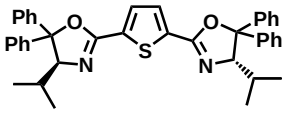
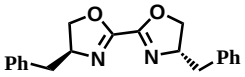
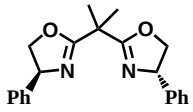
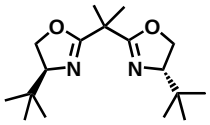
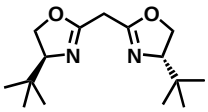
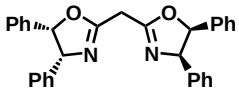
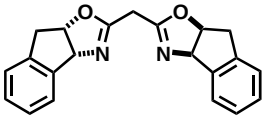
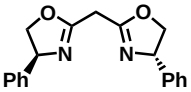


entry	solvent	temperature (^oC)	reaction time (h)	yield (%)[b]	ee (%)[c]
1	DCE	-20	28	60	51
2	$MeNO_2$	-20	27	68	74
3	Acetone	-40	35	63	11
4	Toluene	-40	35	22	11
5	MeOH	-40	39	46	15
6	CH_2Cl_2	-40	39	71	53
7	$CHCl_3$	-40	35	86	54
8	EtOAc	-40	35	49	69
9	THF	-40	39	34	71
10	$^iPrNO_2$	-40	35	42	76
11	MeCN	-40	39	56	80
12	EtCN	-40	39	71	78
13	EtCN	-60	90	42	70
14	EtCN	-78	90	31	66

[a] Unless noted otherwise, the reactions were carried out on a 0.50 mmol scale of **3** with 2 equiv of **2** (1 mmol).
[b] Isolated yield.
[c] Ee values were determined by chiral-phase HPLC analysis and the absolute configuration of the major products was *R*, assigned by comparing HPLC with the literature.

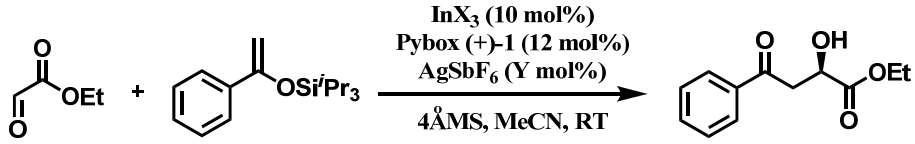
Table 2. Screening of chiral ligands[a]



 56% yield, 80% ee	 78% yield, 64% ee	 79% yield, 49% ee
 90% yield, -72% ee	 24% yield, 2% ee	 35% yield, 1% ee
 28% yield, 0% ee	 26% yield, 0% ee	 50% yield, 0% ee
 40% yield, 2% ee	 28% yield, 0% ee	 28% yield, 3% ee

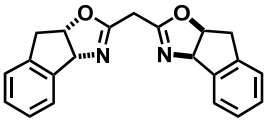
[a] Reactions were carried out with 0.75 mmol of ethyl glyoxylate and 0.50 mmol of enolsilane in the presence of 150 mg powdered activated 4Å molecular sieves in 2.0 mL of solvent.
[b] Isolated yield.
[c] *ee* values were determined by chiral stationary phase HPLC analysis. The absolute configuration of the major products was *R*, assigned by comparing the optical rotation with the literature.

Table 3. Investigation of different Lewis acid[a]

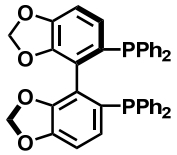


entry	LA	$AgSbF_6$	reaction time (h)	yield (%)[b]	ee (%)[c]
1	$In(OTf)_3$	--	2	97	77
2	$Sc(OTf)_3$	--	30	63	47
3	$Cu(OTf)_2$	--	48	7 conversion	0
4	$Zn(OTf)_2$	--	24	75 conversion	3
5[d]	$CuCl_2$	20%	72	82 conversion	-37
6	$CuCl_2$	20%	72	20 conversion	6
7[e]	$PdCl_2$	20%	4	54	-35
8[f,g]	$FeBr_3$	20%	2	30	49
9[d,g]	$SnCl_2$	20%	2	96	-16
10	$InBr_3$	10%	2	98	80

[a] Reactions were carried out with 0.75 mmol of ethyl glyoxylate and 0.50 mmol of enolsilane in the presence of 150 mg powdered activated 4Å molecular sieves in 2.0 mL of MeCN.
[b] Isolated yield.
[c] *ee* values were determined by chiral stationary phase HPLC analysis.
[d] BOX used as ligand.
[e] R-(+)-SEGPHOS used as ligand.
[f] Enol silane hydrolyzed product 45%.
[g] Dichloromethane used as solvent.

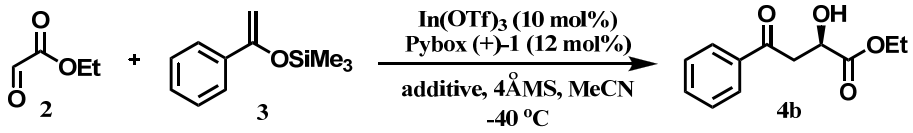


BOX



R-SEGPHOS

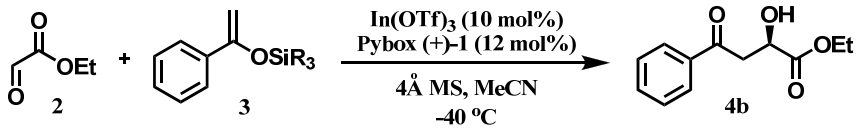
Table 4. Investigation of additive effect[a]



entry	additive	reaction time (h)	yield (%)[b]	ee (%)[c]
1	–	30	76	80
2	PhOH	35	47	67
3	$HOCH(CF_3)_2$	35	59	57
4	CF_3CH_2OH	54	20	79
5	PhCOOH	44	30	13
6[d]	Me_3SiBr	10	11	79

[a] Reactions were carried out with 0.75 mmol of ethyl glyoxylate and 0.50 mmol of enolsilane in the presence of 150 mg powdered activated 4Å molecular sieves in 2.0 mL of solvent.
[b] Isolated yield.
[c] *ee* values were determined by chiral stationary phase HPLC analysis. The absolute configuration of the major products was *R*, assigned by comparing the optical rotation with the literature.
[d] TLC showed that within 10 h of reaction, **7** was all consumed in which the majority was hydrolyzed to acetophenone.

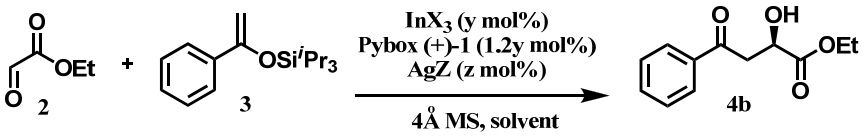
Table 5. Investigation of steric effect of silyl group[a]



entry	R_3	reaction time (h)	yield (%)[b]	ee (%)[c]
1	Me_3	30	76	80
2	$Me_2{}^tBu$	59	88	83
3	$^iPr_3$	46	76	85

[a] Reactions were carried out with 0.75 mmol of ethyl glyoxylate and 0.50 mmol of enolsilane in the presence of 150 mg powdered activated 4Å molecular sieves in 2.0 mL of solvent.
[b] Isolated yield.
[c] *ee* values were determined by chiral stationary phase HPLC analysis. The absolute configuration of the major products was *R*, assigned by comparing the optical rotation with the literature.

Table 6. Investigation of counterion effect of In(III)-pybox complex[a]



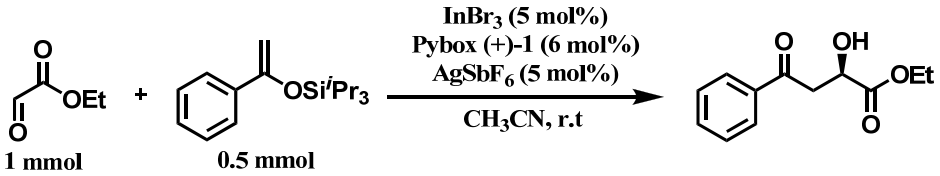
entry	InX_3 (mol%)	AgZ (mol %)	T (^oC)	solvent	reaction time (h)	yield (%)[b]	ee (%)[c]
1	$InCl_3$, 10	$AgSbF_6$, 20	-40	MeCN	20	70	85
2	$InCl_3$, 10	$AgSbF_6$, 20	-60	EtCN	60	63	87
3	$InCl_3$, 10	$AgSbF_6$, 20	-78	EtCN	60	54	88
4	$InCl_3$, 5	$AgSbF_6$, 10	-78	EtCN	63	37	86
5	$InBr_3$, 10	$AgSbF_6$, 20	-78	EtCN	48	53	89
6	$InBr_3$, 5	$AgSbF_6$, 15	-20	MeCN	19	48	84
7	$InBr_3$, 5	$AgSbF_6$, 10	-20	MeCN	19	71	85
8	$InBr_3$, 5	$AgSbF_6$, 5	-20	MeCN	19	89	87
9	$InBr_3$, 5	$AgSbF_6$, 5	-40	MeCN	36	91	89
10	$InBr_3$, 5	$AgSbF_6$, 5	25	MeCN	2	97	77
11	$InBr_3$, 5	$AgPF_6$, 5	25	MeCN	4	95	77
12	$InBr_3$, 5	$AgBF_4$, 5	25	MeCN	2	96	72
13	$InBr_3$, 5	$AgClO_4$, 5	25	MeCN	4	95	73
14	$InBr_3$, 5	AgOAc, 5	25	MeCN	24	-	nd

[a] Reactions were carried out with 0.75 mmol of ethyl glyoxylate and 0.50 mmol of enolsilane in the presence of 150 mg powdered activated 4Å molecular sieves in 2.0 mL of solvent.

[b] Isolated yield.

[c] *ee* values were determined by chiral stationary phase HPLC analysis. The absolute configuration of the major products was *R*, assigned by comparing the optical rotation with the literature.

Table **7**. The effect of 4 Å molecular sieves[a]

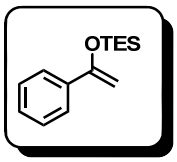


entry	4 Å MS	H_2O	yield (%)[b]	ee (%)[c]
1	**150 mg**	**–**	**97**	**77**
2	**–**	**–**	**96**	**77**
3[d]	**–**	**50 uL**	**75**	**76**

[a] Reactions were carried out with 1.0 mmol of ethyl glyoxylate and 0.50 mmol of enolsilane in the presence of 150 mg powdered activated 4Å molecular sieves in 2.0 mL of solvent.
[b] Isolated yield.
[c] *ee* values were determined by chiral stationary phase HPLC analysis.
[d] 20% of enolsilane was hydrolyzed.

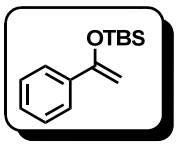
General procedure for the preparation of silyl enol ethers

To in a 50 mL round-bottom flask equipped with a stirring bar and filled with CH_2Cl_2 (20 mL), acetophenone (5.0 mmol) and triethylamine (1.3 mL, 9.0 mmol) were added. The solution was stirred at room temperature for 15 mins before cooling down to 0^oC. Triisopropylsilyl trifluoromethanesulfonate (1.7 mL, 6.0 mmol) was added by a syringe slowly over 2 min at 0^oC. The resulting mixture was stirred under N_2 atmosphere at 0 ^oC for 30 min. The reaction was quenched by saturated $NaHCO_3$ solution (20 mL) and diluted by cooled CH_2Cl_2 (10 mL). The organic layer was washed with cooled saturated $NaHCO_3$ solution twice, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on Et_3N-treated silica gel eluting with hexane to afford silyl enol ethers **3b-r** as colourless oils.



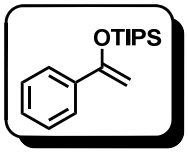
triethyl(1-phenylvinyloxy)silane (3b)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 62% yield (0.726g); R_f = 0.94 (ethyl acetate/hexane = 1/4); ^1H NMR (300 MHz, $CDCl_3$): δ 7.63–7.59 (m, 2H), 7.35 – 7.27(m, 3H), 4.87 (d, *J* = 1.7 Hz, 1H), 4.42 (d, *J* = 1.7 Hz, 1H), 1.01 (t, *J* = 7.8 Hz, 9H), 0.76 (q, *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.9, 137.7, 128.2, 128.1, 125.2, 90.4, 6.7, 5.0 ppm; FTIR (KBr, neat): *v* 2955, 2876, 1614, 1458, 1414, 1317, 1117, 1009, 737 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{22}OSiH^+$: 235.1518, found: 235.1517.



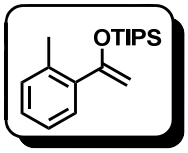
tert-butyldimethyl(1-phenylvinyloxy)silane (3c)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 64% yield (0.752g); R_f = 0.92 (ethyl acetate/hexane = 1/4); ^1H NMR (300 MHz, $CDCl_3$): δ 7.60–7.56 (m, 2H), 7.31 – 7.23 (m, 3H), 4.85 (d, *J* = 1.5 Hz, 1H), 4.39 (d, *J* = 1.6 Hz, 1H), 0.98 (s, 9H), 0.18 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.0, 137.9, 128.2, 128.1, 125.3, 90.9, 25.9, 18.4, -4.6 ppm; FTIR (KBr, neat): *v* 2957, 2930, 2859, 1614, 1472, 1315, 1256, 1117, 1013, 833, 772, 700 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{22}OSiH^+$: 235.1518, found: 235.1514.



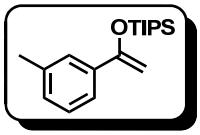
triisopropyl(1-phenylvinyloxy)silane (3d)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 83% yield (1.146g); R_f = 0.90 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 – 7.59 (m, 2H), 7.37 – 7.21 (m, 3H), 4.85 (d, *J* = 1.8 Hz, 1H), 4.41 (d, *J* = 1.7 Hz, 1H), 1.38 – 1.21 (m, 3H), 1.13 (d, *J* = 7.1 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 138.0, 128.11, 128.05, 125.3, 90.0, 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2945, 2866, 1612, 1464, 1385, 1317, 1117, 1015, 883, 772, 687 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{28}OSiH^+$: 277.1988, found: 277.1990.



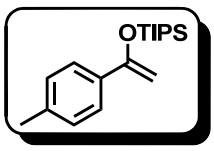
triisopropyl(1-o-tolylvinyloxy)silane (3e)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 77% yield (1.117g); R_f = 0.89 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.22 – 7.07 (m, 3H), 4.54 (d, *J* = 0.9 Hz, 1H), 4.35 (d, *J* = 0.9 Hz, 1H), 2.42 (s, 3H), 1.31 – 1.13 (m, 3H), 1.08 (d, *J* = 6.9 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 139.5, 135.8, 130.3, 128.6, 127.8, 125.3, 94.3, 20.6, 18.1, 12.7 ppm; FTIR (KBr, neat): *v* 2945, 2866, 1622, 1464, 1383, 1312, 1132, 1094, 1016, 883, 729, 687 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{18}H_{30}OSiH^+$: 291.2144, found: 291.2140.



triisopropyl(1-m-tolylvinyloxy)silane (3f)

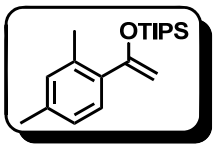
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 79% yield (1.146g); R_f = 0.91 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 4.83 (d, *J* = 1.4 Hz, 1H), 4.39 (d, *J* = 1.5 Hz, 1H), 2.34 (s, 3H), 1.37 – 1.21 (m, 3H), 1.13 (d, *J* = 7.1 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 138.0, 137.5, 128.9, 128.0, 126.1, 122.6, 89.9, 21.6, 18.2, 12.9 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1601, 1582, 1464, 1383, 1310, 1207, 1016, 883, 789, 685 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{18}H_{30}OSiH^+$: 291.2144, found: 291.2140.



triisopropyl(1-p-tolylvinyloxy)silane (3g)

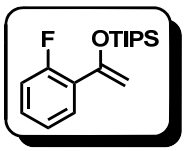
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 80% yield (1.161g); R_f = 0.90 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.80 (d, *J* = 1.6 Hz, 1H), 4.36 (d, *J* = 1.6 Hz, 1H), 2.36 (s, 3H), 1.38 – 1.20 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 137.9, 135.3, 128.8, 125.3, 89.2, 21.2,

18.2, 12.9 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1611, 1510, 1464, 1383, 1315, 1113, 1016, 883, 762, 681 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{18}H_{30}OSiH^+$: 291.2144, found: 291.2146.



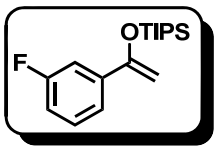
(1-(2,4-dimethylphenyl)vinyloxy)triisopropylsilane (3h)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 75% yield (1.145g); R_f = 0.92 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 4.51 (d, *J* = 0.7 Hz, 1H), 4.32 (d, *J* = 0.7 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 1.23 – 1.16 (m, 3H), 1.08 (d, *J* = 6.8 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 137.4, 136.7, 135.6, 131.1, 128.6, 125.9, 94.0, 21.1, 20.5, 18.1, 12.7 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1614, 1464, 1383, 1308, 1090, 1016, 883, 824, 683 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{19}H_{32}OSiH^+$: 305.2301, found: 305.2298.



(1-(2-fluorophenyl)vinyloxy)triisopropylsilane (3i)

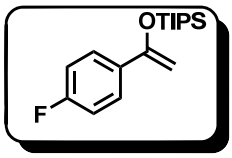
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 82% yield (1.206g); R_f = 0.93 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 – 7.63 (m, 1H), 7.27 – 6.99 (m, 3H), 4.99 – 4.94 (m, 1H), 4.70 – 4.67 (m, 1H), 1.34 – 1.21 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.01 (d, *J* = 250.9 Hz), 150.72 (d, *J* = 4.0 Hz), 129.2 (d, *J* = 8.7 Hz), 128.8 (d, *J* = 2.7 Hz), 126.0 (d, *J* = 11.1 Hz), 123.7 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 23.6 Hz), 96.0 (d, *J* = 11.4 Hz), 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2945, 2868, 1612, 1489, 1385, 1312, 1090, 1018, 883, 760, 685 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{27}FOSiH^+$: 295.1893, found: 295.1884.



(1-(3-fluorophenyl)vinyloxy)triisopropylsilane (3j)

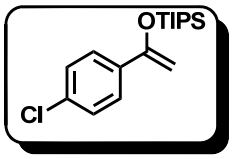
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 72% yield (1.059g); R_f = 0.90 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 – 7.22 (m, 3H), 7.01 – 6.92 (m, 1H), 4.86 (d, *J* = 2.0 Hz, 1H), 4.45 (d, *J* = 2.0 Hz, 1H), 1.36 – 1.22 (m, 3H), 1.13 (d, *J* = 7.0 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9 (d, *J* = 244.4 Hz), 155.0 (d, *J* = 2.6 Hz), 140.4 (d, *J* = 7.5 Hz), 129.4 (d, *J* = 8.2 Hz), 120.9 (d, *J* = 2.8 Hz), 114.8 (d, *J* = 21.4 Hz), 112.3 (d, *J* = 23.0 Hz), 90.8, 18.1, 12.8 ppm;

FTIR (KBr, neat): *v* 2945, 2868, 1614, 1582, 1464, 1385, 1315, 1308, 1207, 1016, 883, 787, 685 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{27}FOSiH^+$: 295.1893, found: 295.1910.



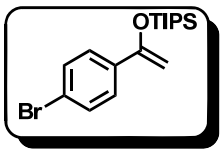
(1-(4-fluorophenyl)vinyloxy)triisopropylsilane (3k)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 74% yield (1.089g); R_f = 0.92 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.49 (m, 2H), 7.04 – 6.93 (m, 2H), 4.77 (d, *J* = 1.9 Hz, 1H), 4.39 (d, *J* = 1.9 Hz, 1H), 1.36 – 1.21 (m, 3H), 1.12 (d, *J* = 7.1 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8 (d, *J* = 247.1 Hz), 155.4, 134.1 (d, *J* = 3.2 Hz), 127.1 (d, *J* = 8.1 Hz), 114.9 (d, *J* = 21.5 Hz), 89.6 (d, *J* = 1.4 Hz), 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2945, 2868, 1607, 1508, 1464, 1385, 1314, 1115, 1015, 841, 762, 681 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{27}FOSiH^+$: 295.1893, found: 295.1937.



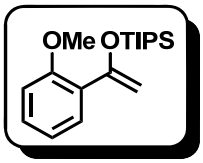
(1-(4-chlorophenyl)vinyloxy)triisopropylsilane (3l)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 71% yield (1.101g); R_f = 0.92 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.82 (d, *J* = 2.0 Hz, 1H), 4.42 (d, *J* = 2.0 Hz, 1H), 1.37 – 1.20 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 136.5, 133.9, 128.2, 126.6, 90.4, 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2945, 2866, 1612, 1489, 1396, 1314, 1117, 1013, 835, 741, 683 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{27}ClOSiH^+$: 311.1598, found: 311.1608.



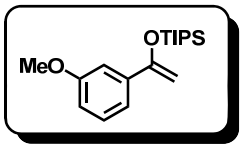
(1-(4-bromophenyl)vinyloxy)triisopropylsilane (3m)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 78% yield (1.369g); R_f = 0.88 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 2H), 7.45 – 7.42 (m, 2H), 4.83 (d, *J* = 2.0 Hz, 1H), 4.42 (d, *J* = 2.0 Hz, 1H), 1.37 – 1.21 (m, 3H), 1.12 (d, *J* = 7.1 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 136.9, 131.2, 126.9, 122.2, 90.4, 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2945, 2866, 1611, 1485, 1391, 1314, 1115, 1009, 831, 735, 657 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{27}BrOSiH^+$: 355.1093, found: 355.1111.



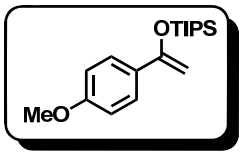
triisopropyl(1-(2-methoxyphenyl)vinyloxy)silane (3n)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 71% yield (1.087g); R_f = 0.89 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.59 (m, 1H), 7.26 – 7.20 (m, 1H), 6.95 – 6.86 (m, 2H), 5.01 (s, 1H), 4.65 (s, 1H), 3.84 (s, 3H), 1.31 – 1.17 (m, 3H), 1.10 (d, *J* = 6.9 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 153.2, 129.0, 128.9, 127.3, 120.1, 111.1, 95.5, 55.3, 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1612, 1489, 1464, 1383, 1277, 1018, 883, 752, 685 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{18}H_{30}O_2SiH^+$: 307.2093, found: 307.2097.



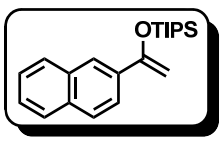
triisopropyl(1-(3-methoxyphenyl)vinyloxy)silane (3o)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 70% yield (1.072g); R_f = 0.91 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 – 7.16 (m, 3H), 6.85 – 6.82 (m, 1H), 4.85 (d, *J* = 1.2 Hz, 1H), 4.42 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 1.37 – 1.23 (m, 3H), 1.13 (d, *J* = 7.0 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 155.9, 139.5, 129.0, 117.9, 113.9, 110.8, 90.2, 55.1, 18.1, 12.8 ppm; FTIR (KBr, neat): *v* 2945, 2866, 1578, 1464, 1383, 1310, 1238, 1016, 883, 685 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{18}H_{30}O_2SiH^+$: 307.2093, found: 307.2095.



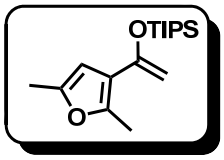
triisopropyl(1-(4-methoxyphenyl)vinyloxy)silane (3p)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 74% yield (1.133g); R_f = 0.89 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.80 (d, *J* = 1.6 Hz, 1H), 4.36 (d, *J* = 1.6 Hz, 1H), 2.34 (s, 3H), 1.45 – 1.19 (m, 3H), 1.12 (d, *J* = 7.2 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 137.9, 135.2, 128.8, 125.3, 89.2, 21.2, 18.2, 12.9 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1611, 1510, 1464, 1383, 1315, 1113, 1016, 883, 824, 762, 681 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{18}H_{30}O_2SiH^+$: 307.2093, found: 307.2094.



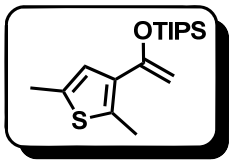
triisopropyl(1-(naphthalen-2-yl)vinyloxy)silane – (4q)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 81% yield (1.321g); R_f = 0.93 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.85 – 7.71 (m, 4H), 7.49 – 7.37 (m, 2H), 5.00 (d, *J* = 1.5 Hz, 1H), 4.52 (d, *J* = 1.5 Hz, 1H), 1.42 – 1.26 (m, 3H), 1.16 (d, *J* = 7.2 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 135.3, 133.34, 133.30, 128.6, 127.7, 127.6, 126.14, 126.11, 124.5, 123.6, 90.9, 18.2, 12.9 ppm; FTIR (KBr, neat): *v* 3059, 2943, 2866, 1611, 1464, 1385, 1364, 1310, 1094, 1015, 881, 748, 677 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{21}H_{30}OSiH^+$: 327.2144, found:327.2143.



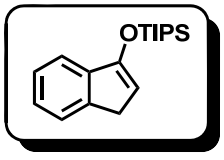
(1-(2,5-dimethylfuran-3-yl)vinyloxy)triisopropylsilane (3r)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 63% yield (0.927g); R_f = 0.9 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.97 (s, 1H), 4.32 (d, *J* = 1.3 Hz, 1H), 4.27 (d, *J* = 1.3 Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H), 1.33 – 1.19 (m, 3H), 1.12 (d, *J* = 6.8 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 148.9, 147.2, 119.7, 105.9, 90.0, 18.0, 13.6, 13.3, 12.9 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1651, 1570, 1464, 1412, 1383, 1290, 1215, 1080, 1013, 883, 799, 681 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{30}O_2SiH^+$: 295.2093, found: 295.2104.



(1-(2,5-dimethylthiophen-3-yl)vinyloxy)triisopropylsilane (3s)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 73% yield (1.132g); R_f = 0.89 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.70 (s, 1H), 4.43 (d, *J* = 1.1 Hz, 1H), 4.33 (d, *J* = 1.0 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 1.30 – 1.16 (m, 3H), 1.10 (d, *J* = 6.8 Hz, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4, 135.9, 134.3, 133.5, 126.1, 92.6, 18.1, 15.0, 14.9, 12.8 ppm; FTIR (KBr, neat): *v* 2943, 2866, 1614, 1464, 1385, 1337, 1269, 1015, 883, 752, 682 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{30}OSSiH^+$: 311.1865, found: 311.1873.



(1H-inden-3-yloxy)triisopropylsilane (5)

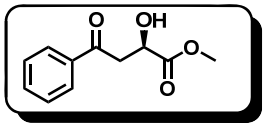
This compound was prepared by the General Procedure described above and was obtained as yellow oil in 85% yield (1.229g); R_f = 0.90 (ethyl acetate/hexane = 1/4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.21 – 7.16 (m, 1H), 5.40 (t, *J* = 2.4 Hz, 1H), 3.26 (d, *J* = 2.1 Hz,

2H), 1.36 – 1.27 (m, 3H), 1.14 (d, *J* = 7.2 Hz, 18H) ppm; ^{13}C NMR (75 MHz, CDCl3): δ 154.00, 142.8, 142.1, 126.1, 125.1, 123.8, 118.3, 105.2, 33.9, 18.1, 12.7 ppm; FTIR (KBr, neat): *v* 3072, 2943, 2866, 1603, 1576, 1464, 1362, 1308, 1248, 1180, 1126, 881, 850, 752 cm^{-1}; HRMS (ESI, m/z)

General procedure for In(III)-pybox complex catalyzed asymmetric Mukaiyama Aldol reactions of glyoxylates and enolsilanes derived from aryl ketones:

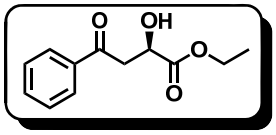
In a 5 mL round-bottom flask containing CH_3CN (1.5 ml) with a stirring bar, $InBr_3$ (8.9 mg, 0.025 mmol), pybox-**1** (11.8 mg, 0.03 mmol) and 4Å molecular sieves (150.0 mg) were added and stirred at room temperature for 30 minutes. To the above mixture, silver hexafluoroantimonate ($AgSbF_6$) (8.6 mg, 0.025 mmol) was added in one portion and stirred for another 30 minutes. To the pre-prepared catalyst in CH_3CN, the glyoxylate ester (1.0 mmol, 2 eq.) was added using a syringe sequentially under N_2 atmosphere. The resulting mixture was cooled to -20°C before enolsilane (0.5 mmol, 1 eq.) was added using syringe under N_2 atmosphere. It was stirred until the enolsilanes had undergone complete reaction using TLC to monitor its progress. The reaction was quenched by saturated $NaHCO_3$ solution (5 mL). The solution was extracted by ethyl acetate twice. The combined organic layer was washed with brine and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was loaded directly onto a silica gel column and purified by flash column chromatography to obtain the enantio-enriched β-hydroxy ketones.

Characterization data for enantioenriched *β*-hydroxy ketones



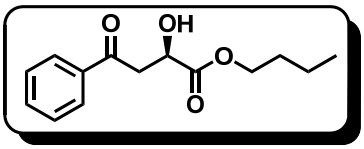
(*R*)-methyl 2-hydroxy-4-oxo-4-phenylbutanoate (4a)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 62% yield (0.064g, 43% *ee*): R_f = 0.24 (ethyl acetate : hexane = 1/4), [α]D^{21} = -3.8 (c = 1.72, $CHCl_3$, for 43% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.94 (m, 2H), 7.63 – 7.58 (m, 1H), 7.51 – 7.46 (m, 2H), 4.70 – 4.67 (m, 1H), 3.82 (s, 3H), 3.57 (dd, J = 17.6, 3.9 Hz, 1H), 3.47 (dd, *J* = 17.6, 5.9 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 174.2, 136.3, 133.7, 128.7, 128.2, 67.2, 52.7, 42.2 ppm; FTIR (KBr, neat): *v* 3503, 2956, 1744, 1685, 1598, 1581, 1450, 1369, 1220, 1108, 1041 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{11}H_{12}O_4H^+$: 209.0814, found: 209.0811; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 13.2 min (minor), t_2 = 15.6 min (major).



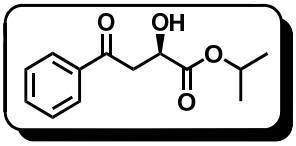
(*R*)-ethyl 2-hydroxy-4-oxo-4-phenylbutanoate (4b)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 88% yield (0.098g, 89% *ee*): R_f = 0.26 (ethyl acetate : hexane = 1/4), $[\alpha]D^{22}$ = -4.7 (c = 1.86, $CHCl_3$, for 89% *ee*); ^{1}H NMR (300 MHz, CDCl3): δ 7.97 – 7.94 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.44 (m, 2H), 4.69 – 4.65 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.55 (dd, J = 17.5, 4.0 Hz, 1H), 3.46 (dd, J = 17.5, 5.9 Hz, 1H), 3.43 (bs, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl3): δ 197.5, 173.8, 136.4, 133.6, 128.7, 128.2, 67.2, 61.9, 42.2, 14.1 ppm; FTIR (KBr, neat): ν 3485, 2982, 2934, 1736, 1686, 1597, 1580, 1449, 1368, 1273, 1215, 1101 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{12}H_{14}O_4H^+$: 223.0970, found: 223.0969; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 12.2 min (minor), t_2 = 14.7 min (major).



(*R*)-*n*-butyl 2-hydroxy-4-oxo-4-phenylbutanoate (4c)

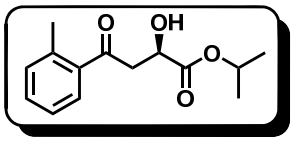
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 92% yield (0.115g, 73% *ee*): R_f = 0.28 (ethyl acetate : hexane = 1/4), $[\alpha]D^{21}$ = 3.78 (c = 1.72, $CHCl_3$, for 73% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.94 – 7.97 (m, 2H), 7.57 – 7.62 (m, 1H), 7.45 – 7.50 (m, 2H), 4.64 – 4.69 (m, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.54 (dd, *J* = 17.5, 4.0 Hz, 1H), 3.45 (dd, *J* = 17.5, 5.9 Hz, 1H), 3.31 (d, *J* = 5.8 Hz, 1H), 1.59 – 1.68 (m, 2H), 1.29 – 1.41 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 173.9, 136.4, 133.6, 128.7, 128.2, 67.2, 65.7, 42.2, 30.5, 19.0, 13.6 ppm; FTIR (KBr, neat): *ν* 3481, 2961, 2874, 1740, 1686, 1597, 1580, 1449, 1368, 1275, 1105 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_4H^+$: 251.1283, found: 251.1284; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.8 min (minor), t_2 = 11.4 min (major).



(*R*)-isopropyl 2-hydroxy-4-oxo-4-phenylbutanoate (4d)

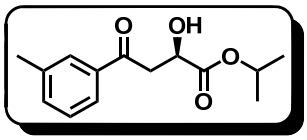
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 91% yield (0.107g, 96% *ee*): R_f = 0.27 (ethyl acetate : hexane = 1/4), $[\alpha]D^{22}$ = +2.6 (c = 1.59, $CHCl_3$, for 96% *ee*); ^{1}H NMR (300 MHz, CDCl3): δ 7.97 – 7.94 (m, 2H), 7.62 – 7.57 (m, 1H), 7.50 – 7.45 (m, 2H), 5.20 – 5.08 (m, 1H), 4.62 (dd, J = 9.5, 5.2 Hz, 1H), 3.53 (dd, J = 17.5, 4.1 Hz, 1H), 3.44 (dd, J = 17.4, 5.8 Hz, 1H), 3.36 (d, J = 5.5 Hz, 1H), 1.28 (d, J = 6.3 Hz, 3H), 1.24 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl3): δ 197.5, 173.4, 136.5, 133.6, 128.7, 128.2, 69.7, 67.3, 42.2, 21.72, 21.66 ppm; FTIR (KBr, neat): ν 3520, 3019, 2984, 1728, 1682, 1597, 1580, 1449, 1375, 1215, 1105 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{16}O_4H^+$:

237.1127, found: 237.1136; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.4 min (minor), t_2 = 12.0 min (major).



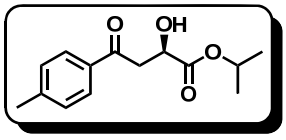
(*R*)-isopropyl 2-hydroxy-4-oxo-4-o-tolylbutanoate (4e)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 81% yield (0.101g, 94% *ee*): R_f = 0.26 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +2.7 (c = 1.69, $CHCl_3$, for 94% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.30 – 7.25 (m, 2H), 5.21 – 5.08 (m, 1H), 4.60 – 4.55 (m, 1H), 3.45 (dd, *J* = 17.5, 4.3 Hz, 1H), 3.37 (dd, *J* = 17.6, 5.8 Hz, 1H), 3.31 (d, *J* = 5.6 Hz, 1H), 2.51 (s, 3H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.0, 173.5, 138.7, 137.0, 132.1, 131.8, 128.8, 125.8, 69.7, 67.5, 44.8, 21.74, 21.70, 21.4 ppm; FTIR (KBr, neat): *v* 3489, 2980, 2930, 1732, 1686, 1600, 1570, 1456, 1375, 1265, 1215, 1107 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_4H^+$: 251.1283, found: 251.1290; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 8.7 min (minor), t_2 = 10.7 min (major).



(*R*)-isopropyl 2-hydroxy-4-oxo-4-m-tolylbutanoate (4f)

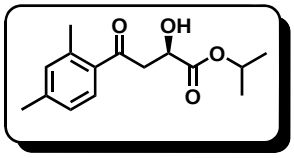
This compound was prepared by the General Procedure described above and was obtained as white solid in 88% yield (0.110g, 97% *ee*): R_f = 0.26 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +3.3 (c = 1.87, $CHCl_3$, for 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.31 (m, 2H), 5.21 – 5.01 (m, 1H), 4.62 (d, *J* = 4.2 Hz, 1H), 3.57 – 3.34 (m, 3H), 2.40 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.76 – 7.73 (m, 2H), 7.40 – 7.32 (m, 2H), 5.19 - 5.06 (m, 1H), 4.62 (d, J = 4.2 Hz, 1H), 3.54 – 3.39 (m, 3H), 2.40 (s, 3H), 1.27 (d, J = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; FTIR (KBr, neat): *v* 3499, 3019, 2982, 1732, 1684, 1605, 1585, 1215, 1105, 756 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_4H^+$: 251.1283, found: 251.1284; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.5 min (minor), t_2 = 12.0 min (major).



(*R*)-isopropyl 2-hydroxy-4-oxo-4-p-tolylbutanoate (4g)

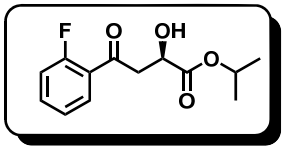
This compound was prepared by the General Procedure described above and was obtained as white solid in 94% yield (0.118g, 97% *ee*): R_f = 0.29 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +2.0 (c = 1.92, $CHCl_3$, for 97%

ee); ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.21 – 5.07 (m, 1H), 4.61 (dd, *J* = 10.0, 5.1 Hz, 1H), 3.49 (dd, *J* = 17.5, 4.2 Hz, 1H), 3.41 (dd, *J* = 17.9, 6.0 Hz, 1H), 3.37 – 3.34 (m, 1H), 2.42 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.2, 173.5, 144.6, 134.2, 129.4, 128.4, 69.7, 67.5, 42.1, 21.80, 21.76, 21.75 ppm; FTIR (KBr, neat): *v* 3676, 3019, 2934, 1728, 1684, 1607, 1215, 1105 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_4H^+$: 251.1283, found: 251.1287; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.3 min (minor), t_2 = 11.9 min (major).



(*R*)-isopropyl 4-(2,4-dimethylphenyl)-2-hydroxy-4-oxobutanoate (4h)

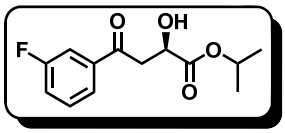
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 80% yield (0.106g, 95% *ee*): R_f = 0.27 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +1.3 (c = 2.10, $CHCl_3$, for 95% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 7.06 (s, 1H), 5.20 – 5.08 (m, 1H), 4.59 – 4.54 (m, 1H), 3.43 (dd, J = 17.5, 4.2 Hz, 1H), 3.36 (dd, J = 17.1, 5.5 Hz, 1H), 3.34 (d, *J* = 5.8 Hz, 1H), 2.50 (s, 3H), 2.36 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 173.6, 142.6, 139.2, 134.0, 133.0, 129.4, 126.4, 69.6, 67.5, 44.5, 21.72, 21.68, 21.63, 21.4 ppm; FTIR (KBr, neat): *v* 3676, 2980, 2926, 1732, 1682, 1611, 1566, 1267, 1213, 1107 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{15}H_{20}O_4H^+$: 265.1440, found: 265.1440; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 8.0 min (minor), t_2 = 10.1 min (major).



(*R*)-isopropyl 4-(2-fluorophenyl)-2-hydroxy-4-oxobutanoate (4i)

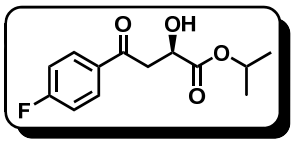
This compound was prepared by the General Procedure described above and was obtained as yellow oil in 60% yield (0.076g, 93% *ee*): R_f = 0.26 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +5.1 (c = 1.51, $CHCl_3$, for 93% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 1H), 7.59 – 7.51 (m, 1H), 7.28 –7.12 (m, 2H), 5.20 – 5.08 (m, 1H), 4.58 (dd, *J* = 9.7, 5.4 Hz, 1H), 3.59 – 3.41 (m, 2H), 3.31 (d, *J* = 5.6 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, DMSO): δ 195.3 (d, *J* = 3.9 Hz), 173.4, 162.1 (d, *J* = 255.0 Hz), 135.1 (d, *J* = 9.1 Hz), 130.6 (d, *J* = 2.4 Hz), 125.1 (d, *J* = 12.6 Hz), 124.6 (d, *J* = 3.4 Hz), 116.7 (d, *J* = 23.7 Hz), 69.7, 67.1 (d, *J* = 2.7 Hz), 47.1 (d, *J* = 8.1 Hz), 21.7, 21.6 ppm; FTIR (KBr, neat): *v* 3676, 3082, 3021, 1730, 1686, 1609, 1481, 1452, 1215, 1103cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{15}FO_4H^+$: 255.1033, found:

255.1033; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/ hexane/*i*-PrOH = 92.5:7.5, 0.75 mL/min): t_1 = 23.2 min (minor), t_2 = 26.9 min (major).



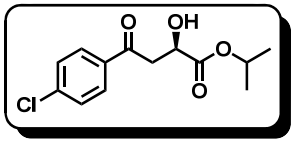
(*R*)-isopropyl 4-(3-fluorophenyl)-2-hydroxy-4-oxobutanoate (4j)

This compound was prepared by the General Procedure described above and was obtained as white solid in 85% yield (0.108g, 93% *ee*): R_f = 0.23 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +6.1 (c = 1.62, $CHCl_3$, for 93% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.72 (m, 1H), 7.66 – 7.61 (m, 1H), 7.50 – 7.42 (m, 1H), 7.32 – 7.26 (m, 1H), 5.20 – 5.07 (m, 1H), 4.63 (dd, *J* = 9.5, 5.1 Hz, 1H), 3.50 (dd, *J* = 17.4, 4.1 Hz, 1H), 3.41 (dd, *J* = 17.3, 5.8 Hz, 1H), 3.38 (bs, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 173.3, 162.8 (d, *J* = 248.3 Hz), 138.6 (d, *J* = 6.5 Hz), 130.4 (d, *J* = 7.6 Hz), 124.0 (d, *J* = 3.0 Hz), 120.6 (d, *J* = 21.5 Hz), 114.9 (d, *J* = 22.4 Hz), 69.8, 67.1, 42.3, 21.68, 21.64 ppm; FTIR (KBr, neat): *v* 3377, 3019, 2984, 1730, 1692, 1589, 1445, 1215, 1105 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{15}FO_4H^+$: 255.1033, found: 255.1039; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 8.6 min (minor), t_2 = 10.4 min (major).



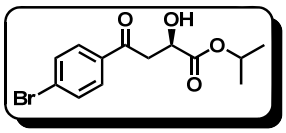
(*R*)-isopropyl 4-(4-fluorophenyl)-2-hydroxy-4-oxobutanoate (4k)

This compound was prepared by the General Procedure described above and was obtained as white solid in 71% yield (0.090g, 96% *ee*): R_f = 0.31 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +3.9 (c = 1.88, $CHCl_3$, for 96% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 – 7.95 (m, 2H), 7.17 – 7.11 (m, 2H), 5.20 – 5.07 (m, 1H), 4.64 – 4.59 (m, 1H), 3.49 (dd, J = 17.3, 4.0 Hz, 1H), 3.40 (dd, J = 17.3, 5.8 Hz, 1H), 3.32 (d, J = 5.6 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 173.3, 166.0 (d, *J* = 255.4 Hz), 133.1 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 9.4 Hz), 116.0 (d, *J* = 2.9 Hz), 115.7 (d, *J* = 2.9 Hz), 69.7 (d, *J* = 5.2 Hz), 67.2, 42.1, 21.7 (d, *J* = 2.8 Hz), 21.6 (d, *J* = 2.8 Hz) ppm; FTIR (KBr, neat): *v* 3198, 2984, 2938, 1802, 1732, 1686, 1599, 1468, 1375, 1231, 1103, 1049 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{15}FO_4H^+$: 255.1033, found: 255.1037; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 10.7 min (minor), t_2 = 12.2 min (major).



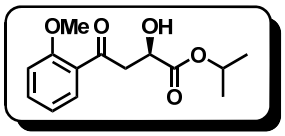
(*R*)-isopropyl 4-(4-chlorophenyl)-2-hydroxy-4-oxobutanoate (4l)

This compound was prepared by the General Procedure described above and was obtained as white solid in 82% yield (0.111g, 97% *ee*): R_f = 0.23 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +5.3 (c = 2.07, $CHCl_3$, for 97% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.19 – 5.07 (m, 1H), 4.64 – 4.59 (m, 1H), 3.48 (dd, J = 17.3, 4.1 Hz, 1H), 3.40 (dd, *J* = 17.2, 5.9 Hz, 1H), 3.39 (bs, 1H)., 1.28 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.2, 173.3, 140.1, 134.9, 129.6, 129.0, 69.8, 67.2, 42.1, 21.71, 21.67 ppm; FTIR (KBr, neat): *v* 3441, 3401, 3019, 2984, 1732, 1682, 1589, 1400, 1215, 816, 756 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{15}ClO_4H^+$: 271.0737, found: 271.0735; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.9 min (minor), t_2 = 11.0 min (major).



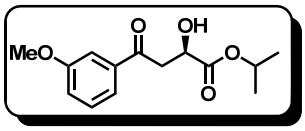
(*R*)-isopropyl 4-(4-bromophenyl)-2-hydroxy-4-oxobutanoate (4m)

This compound was prepared by the General Procedure described above and was obtained as white solid in 85% yield (0.134g, 98% *ee*): R_f = 0.26 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +3.1 (c = 1.67, $CHCl_3$, for 98% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 – 7.79 (m, 2H), 7.64 – 7.59 (m, 2H), 5.17 – 5.09 (m, 1H), 4.63 – 4.60 (m, 1H), 3.48 (dd, *J* = 17.3, 4.1 Hz, 1H), 3.39 (dd, *J* = 17.4, 5.8 Hz, 1H), 3.36 (bs, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 173.3, 135.3, 132.0, 129.7, 128.8, 69.8, 67.2, 42.1, 21.70, 21.66 ppm; FTIR (KBr, neat): *v* 3516, 3019, 2982, 1730, 1682, 1585, 1466, 1398, 1215, 1105, 752 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{15}BrO_4H^+$: 315.0232, found: 315.0250; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 10.2 min (minor), t_2 = 11.3 min (major).



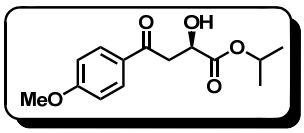
(*R*)-isopropyl 2-hydroxy-4-(2-methoxyphenyl)-4-oxobutanoate (4n)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 83% yield (0.111g, 92% *ee*): R_f = 0.14 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{22}$ = -1.0 (c = 1.57, $CHCl_3$, for 92% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 – 7.75 (m, 1H), 7.52 – 7.46 (m, 1H), 7.03 – 6.96 (m, 2H), 5.19 – 5.06 (m, 1H), 4.58 – 4.52 (m, 1H), 3.92 (s, 3H), 3.57 (dd, J = 18.0, 4.0 Hz, 1H), 3.46 (dd, J = 18.0, 6.0 Hz, 1H), 3.33 (d, J = 5.3 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.9, 173.7, 159.0, 134.3, 130.6, 127.1, 120.7, 111.6, 69.4, 67.6, 55.5, 47.7, 21.73, 21.65 ppm; FTIR (KBr, neat): *v* 3522, 2980, 2940, 1732, 1668, 1597, 1485, 1246, 1105, 1022 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_5H^+$: 267.1232, found: 267.1239; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 15.8 min (minor), t_2 = 22.1 min (major).



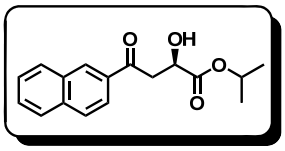
(*R*)-isopropyl 2-hydroxy-4-(3-methoxyphenyl)-4-oxobutanoate (4o)

This compound was prepared by the General Procedure described above and was obtained as colourless oil in 85% yield (0.113g, 95% *ee*): R_f = 0.14 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{22}$ = +2.9 (c = 1.54, $CHCl_3$, for 95% *ee*); ^{1}H NMR (300 MHz, CDCl3): δ 7.54 – 7.47 (m, 2H), 7.41 – 7.35 (m, 1H), 7.15 – 7.11 (m, 1H), 5.20 – 5.07 (m, 1H), 5.20 – 5.07 (m, 1H), 4.62 (dd, J = 9.5, 5.1 Hz, 1H), 3.85 (s, 3H), 3.51 (dd, *J* = 17.4, 4.0 Hz, 1H), 3.42 (dd, *J* = 17.4, 5.8 Hz, 1H), 3.37 (d, *J* = 4.4 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 173.4, 159.9, 137.9, 129.7, 120.8, 120.1, 112.3, 69.7, 67.3, 55.4, 42.3, 21.71, 21.66 ppm; FTIR (KBr, neat): *v* 3493, 2982, 2939, 1744, 1688, 1597, 1467, 1260, 1105, 1042 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_5H^+$: 267.1232, found: 267.1235; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 12.1 min (minor), t_2 = 15.5 min (major).



(*R*)-isopropyl 2-hydroxy-4-(4-methoxyphenyl)-4-oxobutanoate (4p)

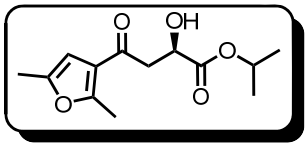
This compound was prepared by the General Procedure described above and was obtained as white solid in 88% yield (0.117g, 98% *ee*): R_f = 0.19 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{21}$ = +0.7 (c = 1.51, for 98% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 5.18 – 5.06 (m, 1H), 4.62 (dd, J = 9.5, 5.1 Hz, 1H), 3.52 – 3.37 (m, 3H), 2.40 (s, 3H), 1.27 (d, J = 6.3 Hz, 3H), 1.23 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 173.4, 144.4, 134.1, 129.3, 128.5, 128.3, 69.5, 67.3, 42.1, 21.7, 21.6 ppm; FTIR (KBr, neat): *v* 3566, 3019, 2984, 1730, 1680, 1607, 1215, 1105, 754 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{18}O_5H^+$: 267.1232, found: 267.1227; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.7 min (minor), t_2 = 12.4 min (major).



(*R*)-isopropyl 2-hydroxy-4-(naphthalen-2-yl)-4-oxobutanoate (4q)

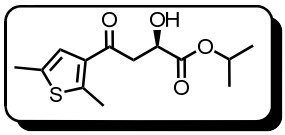
This compound was prepared by the General Procedure described above and was obtained as colourless oil in 89% yield (0.127g, 98% *ee*): R_f = 0.21 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{22}$ = -0.6 (c = 1.60, $CHCl_3$, for 98% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.02 – 7.94 (m, 2H), 7.89 – 7.85 (m, 2H), 7.63 – 7.52 (m,

2H), 5.21 – 5.10 (m, 1H), 4.72 – 4.67(m, 1H), 3.65 (dd, *J* = 17.4, 4.3 Hz, 1H), 3.58 (dd, *J* = 17.4, 5.9 Hz, 1H), 3.48 (d, *J* = 5.2 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 173.5, 135.8, 133.9, 132.4, 130.1, 129.6, 128.7, 128.6, 127.8, 126.9, 123.6, 69.7, 67.4, 42.3, 21.74, 21.69 ppm; FTIR (KBr, neat): *v* 3503, 3059, 2982, 2936, 1734, 1680, 1628, 1470, 1375, 1215, 1105 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_4H^+$: 287.1283, found: 287.1290; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0mL/min): t_1 = 11.2 min (minor), t_2 = 15.6 min (major).



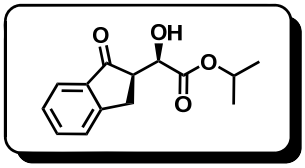
(*R*)-isopropyl 4-(2,5-dimethylfuran-3-yl)-2-hydroxy-4-oxobutanoate (4r)

This compound was prepared by the General Procedure described above and was obtained as yellow solid in 76% yield (0.097g, 90% *ee*): R_f = 0.22 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{22}$ = +1.2 (c = 1.89, $CHCl_3$, for 90% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (d, *J* = 0.7 Hz, 1H), 5.19 – 5.06 (m, 1H), 4.56 – 4.50 (m, 1H), 3.37 (d, J = 5.8 Hz, 1H), 3.20 (dd, J = 17.3, 4.2 Hz, 1H), 3.12 (dd, J = 17.4, 6.0 Hz, 1H), 2.54 (s, 3H), 2.26 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.5, 173.4, 157.7, 150.2, 121.4, 105.4, 69.5, 67.3, 44.4, 21.71, 21.66, 14.4, 13.2 ppm; FTIR (KBr, neat): *v* 3508, 2982, 2924, 1732, 1674, 1572, 1402, 1375, 1233, 1107 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{18}O_5H^+$: 255.1232, found: 255.1240; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 7.9 min (minor), t_2 = 9.4 min (major).



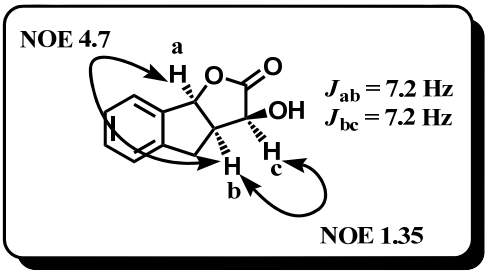
(*R*)-isopropyl 4-(2,5-dimethylthiophen-3-yl)-2-hydroxy-4-oxobutanoate (4s)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 92% yield (0.124g, 96% *ee)*: R_f = 0.24 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{22}$ = -0.8 (c = 1.62, $CHCl_3$, for 96% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 (d, *J* = 1.0 Hz, 1H), 5.19 – 5.07 (m, 1H), 4.57 – 4.52 (m, 1H), 3.37 (d, J = 5.8 Hz, 1H), 3.31 (dd, J = 17.5, 4.3 Hz, 1H), 3.24 (dd, *J* = 17.5, 5.7 Hz, 1H), 2.66 (s, 3H), 2.41 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.2, 173.5, 148.5, 135.4, 135.0, 125.8, 69.5, 67.4, 44.9, 21.72, 21.66, 16.09, 15.0 ppm; FTIR (KBr, neat): *v* 3505, 2980, 2922, 1732, 1670, 1549, 1481, 1373, 1265, 1225, 1107 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{13}H_{18}O_4SH^+$: 271.1004, found: 271.1005; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 85:15, 1.0 mL/min): t_1 = 9.9 min (minor), t_2 = 12.5 min (major).



(2*R*)-isopropyl 2-hydroxy-2-(1-oxo-2,3-dihydro-1H-inden-2-yl)acetate (6)

This compound was prepared by the General Procedure described above and was obtained as yellow oil in 94% yield (0.117g, 97:3 dr, 98% *ee* (major), 92% *ee* (minor)): R_f = 0.24 (ethyl acetate : hexane = 1/4), $[\alpha]_D^{22}$ = +65.8 (c = 1.51, $CHCl_3$, for 98% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 5.22 – 5.10 (m, 1H), 4.91 (dd, *J* = 4.4, 2.1 Hz, 1H), 3.18 – 3.08 (m, 3H), 2.98 (d, *J* = 4.4 Hz, 1H), 1.30 (d, *J* = 3.6 Hz, 3H), 1.28 (d, *J* = 3.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.1, 173.6, 154.0, 136.7, 135.0, 127.5, 126.5, 124.1, 70.1, 69.6, 50.0, 26.5, 21.74, 21.68 ppm; FTIR (KBr, neat): *v* 3503, 2982, 2936, 1712, 1609, 1466, 1281, 1105 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{14}H_{16}O_4H^+$: 249.1127, found: 249.1123; The enantiometric excess was determined by HPLC analysis employing Daicel Chiracel AS-H column (hexane/*i*-PrOH = 97:3, 1.25 mL/min): (major diastereomer) t_1 = 32.3 min (minor), t_2 = 49.5 min (major); (minor diastereomer) t_3 = 27.9 min (minor), t_4 = 40.4 min (major).



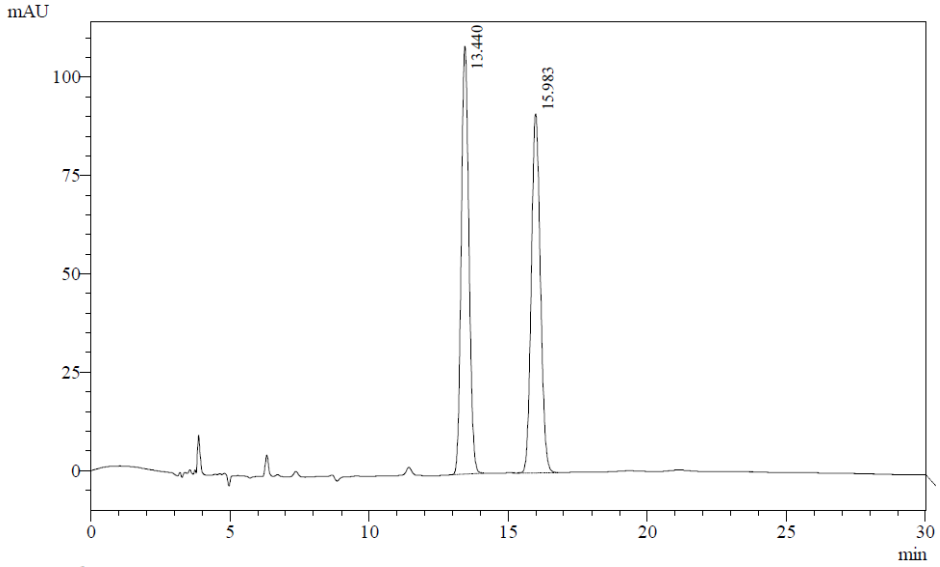
(3*S*)-3-hydroxy-3,3a,4,8b-tetrahydro-2H-indeno[1,2-b]furan-2-one (7)

To a solution of (2*R*)-isopropyl 2-hydroxy-2-(1-oxo-2,3-dihydro-1H-inden-2-yl)acetate (0.124 g, 0.5mmol) in MeOH (2 ml) was added $NaBH_4$ (0.038 g, 1.0 mmol) at -20 °C. The reaction mixture was stirred for 30 minutes, and the reaction was quenched by addition of acetone. The mixture was kept stirring for 10 minutes, and then saturated NH_4Cl aqueous solution was added. The mixture was extracted with CH_2Cl_2 three times, and the extract was dried over anhydrous $MgSO_4$. The solvents were evaporated to give a crude alcohol. To a solution of the crude product in CH_2Cl_2 (2 mL) was added $TsOH•H_2O$, and the reaction mixture was stirred for 16 h at room temperature. The reaction was quenched by addition of a saturated $NaHCO_3$ aqueous solution, and was extracted with CH_2Cl_2 three times. The extract was dried over anhydrous MgSO4. The solvents were evaporated to give a residue, followed by purification on silica gel chromatography to afford yellow oil in 67% yield (0.064g); R_f = 0.26 (ethyl acetate/hexane = 1/4); $[\alpha]D^{21}$ = 81.32 (c = 1.30, $CHCl_3$, for 98% *ee*) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.26 (m, 3H), 5.94 (d, *J* = 7.2 Hz, 1H), 4.12 (dd, *J* = 7.2, 3.4 Hz, 1H), 3.92 (d, *J* = 3.6 Hz, 1H), 3.31 – 3.23 (m, 2H), 3.16 –3.10 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.2, 141.7, 138.5, 130.0, 127.7, 125.81, 125.79, 85.2, 73.6, 46.1, 34.9 ppm; FTIR (KBr, neat): *v*

3429, 2928, 2857, 1769, 1609, 1462, 1317, 1182, 1119, 995, 743 cm^{-1}; HRMS (ESI, m/z) calcd for $C_{11}H_{10}O_3H^+$: 191.0708, found: 191.0712.

^{1}H-NMR, ^{13}C-NMR, HPLC and GC Chromatograms

(*R*)-methyl 2-hydroxy-4-oxo-4-phenylbutanoate



PDA Ch1 254nm 4nm

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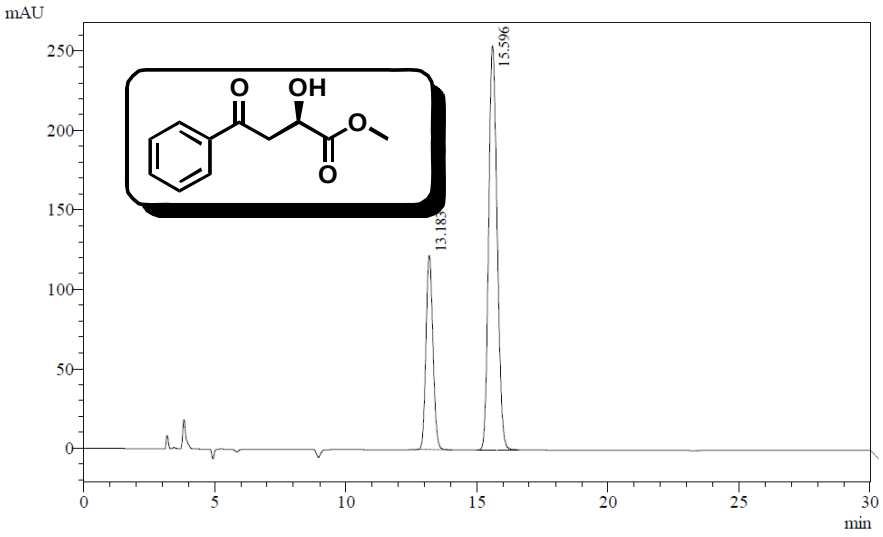

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
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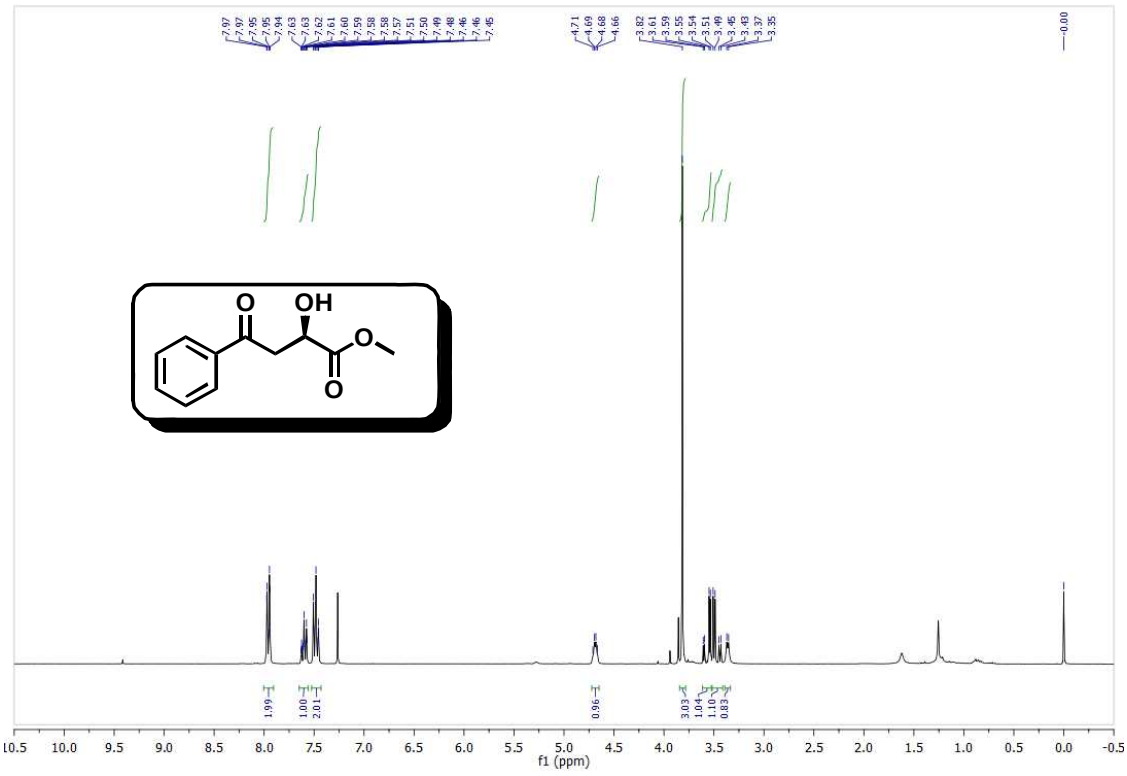
7.97
7.97
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7.95
7.94
7.63
7.62
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7.60
7.59
7.58
7.58
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7.51
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7.48
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3.51
3.49
3.45
3.43
3.37
3.35
0.00
O
OH
O
O
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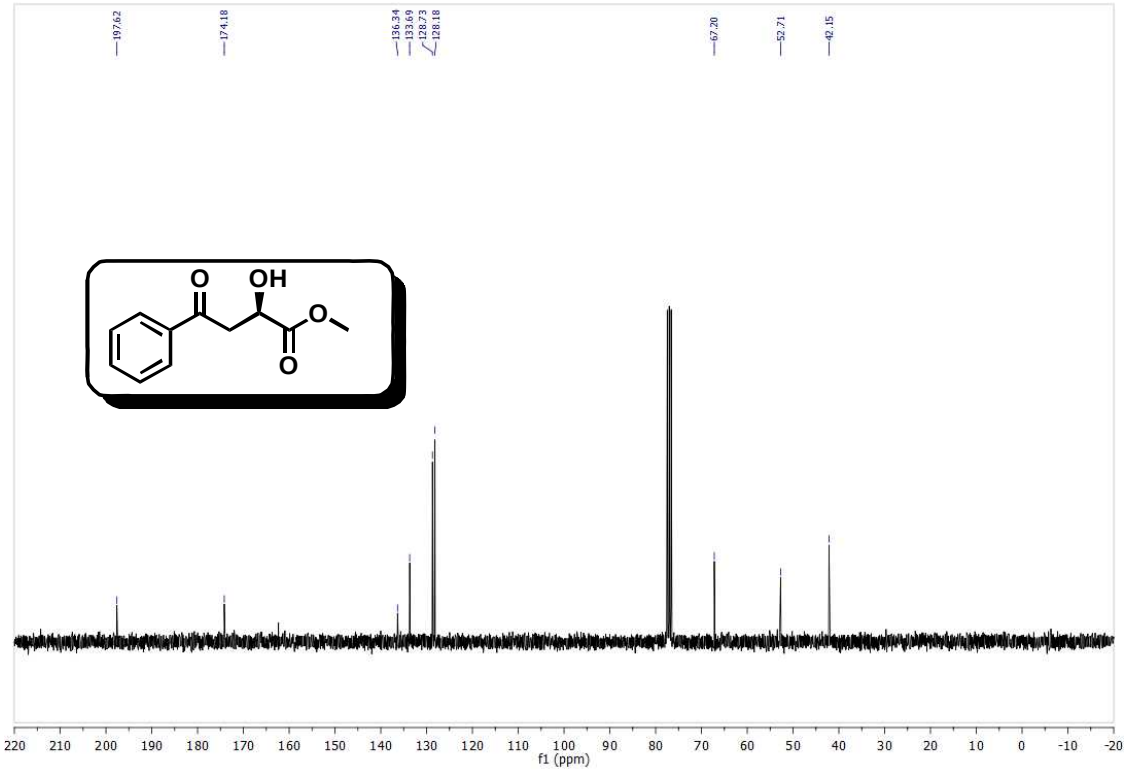
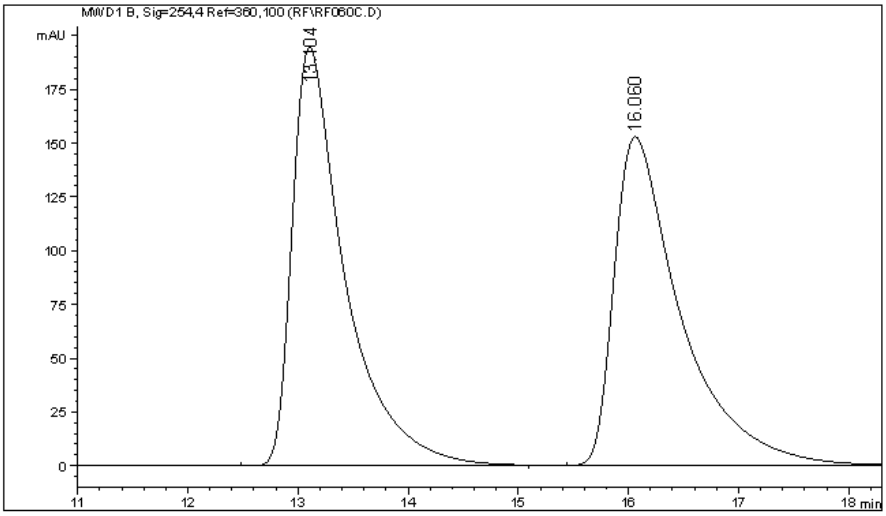
1.00
2.01
0.96
3.03
1.04
1.10
0.83
f1 (ppm)

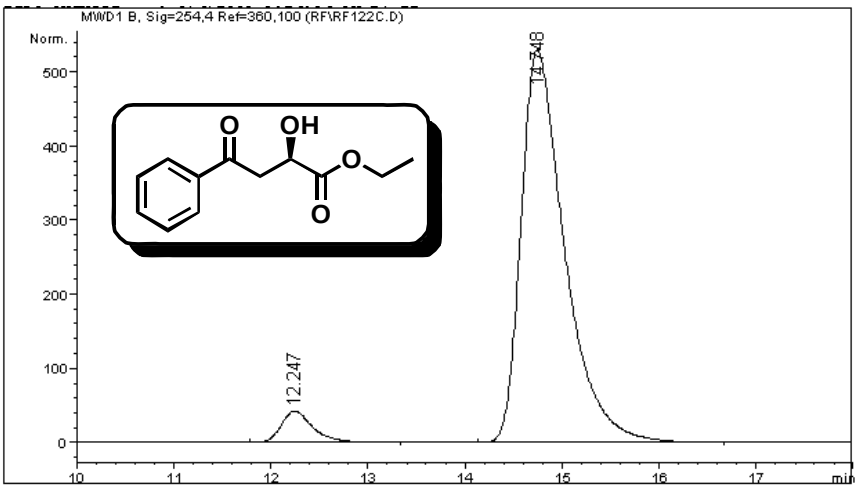

197.62
174.18
136.34
133.69
129.23
128.18
67.20
52.71
42.15
O
OH
O
O
f1 (ppm)

(*R*)-ethyl 2-hydroxy-4-oxo-4-phenylbutanoate



Signal 1: MWD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.104	VB	0.4867	6478.61621	194.45686	50.2475
2	16.060	BB	0.6160	6414.80615	152.72653	49.7525
Totals :				1.28934e4	347.18340	



Signal 1: MWD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.247	BB	0.3419	958.43781	42.06037	5.4860
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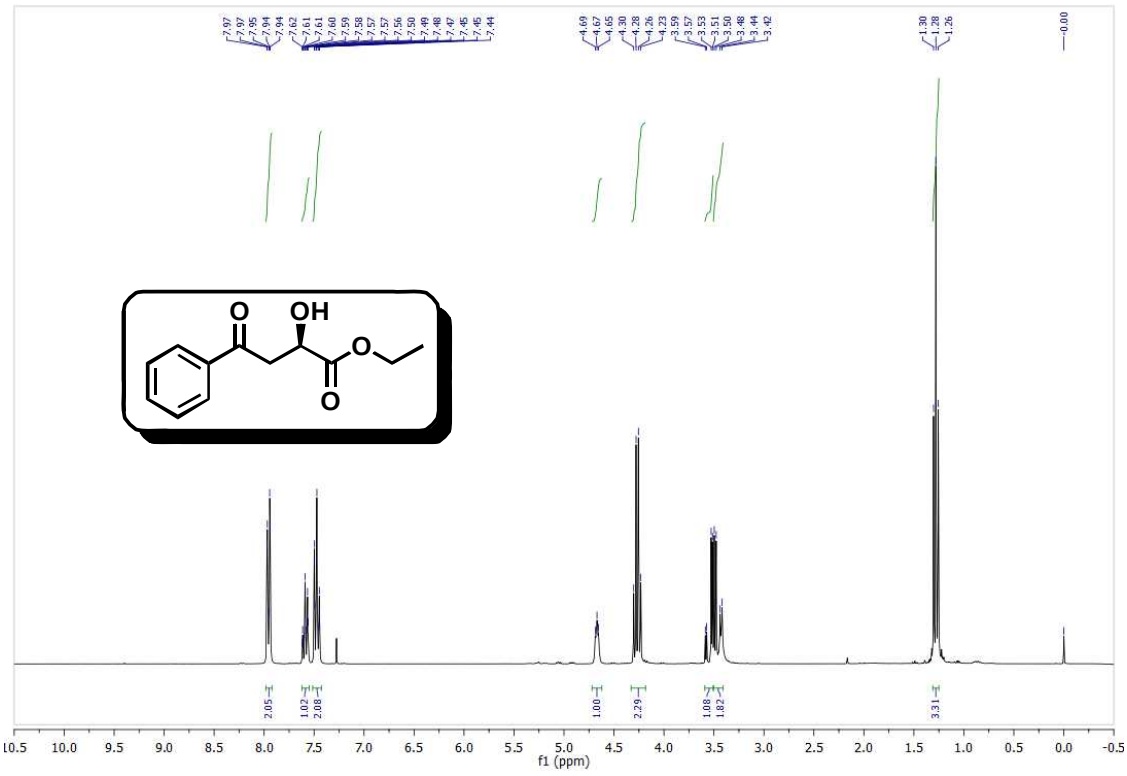
Totals :				1.74706e4	571.60541	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7.94
7.94
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7.58
7.57
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7.56
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7.49
7.48
7.47
7.45
7.45
7.44
4.69
4.67
4.65
4.30
4.28
4.26
4.23
3.59
3.57
3.53
3.51
3.50
3.48
3.44
3.42
1.30
1.28
1.26
0.00
O
OH
O
O
2.05
1.02
2.08
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1.08
1.82
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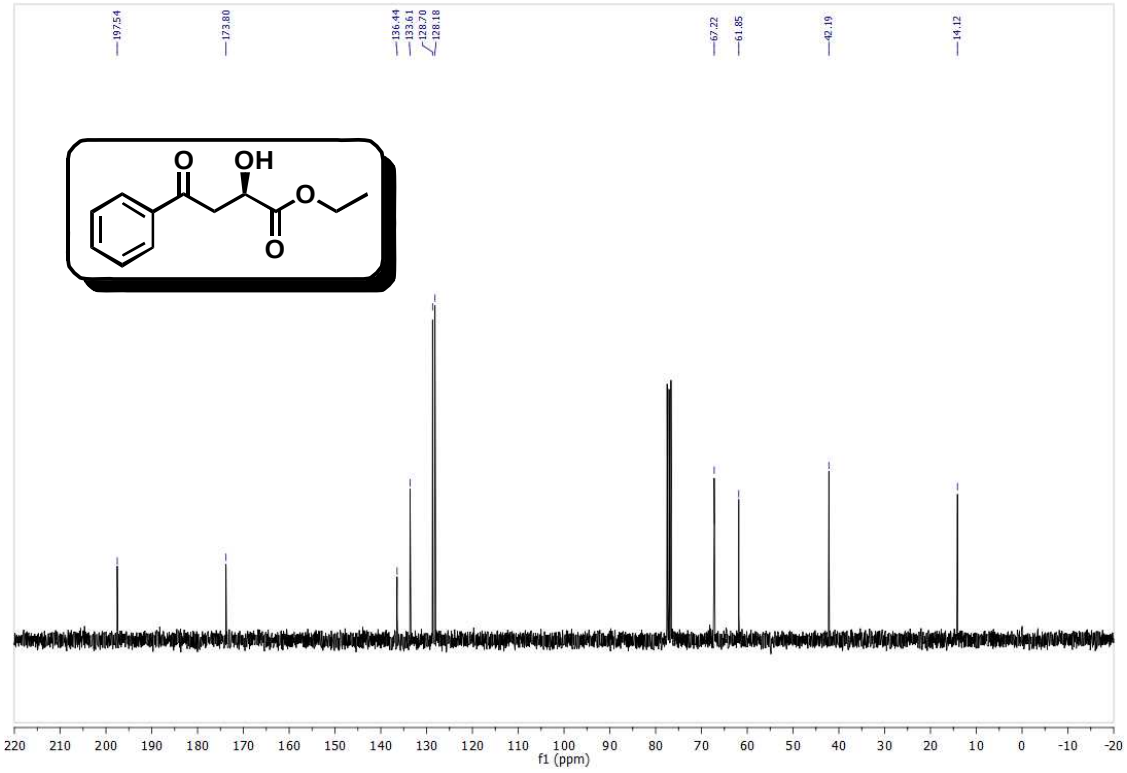
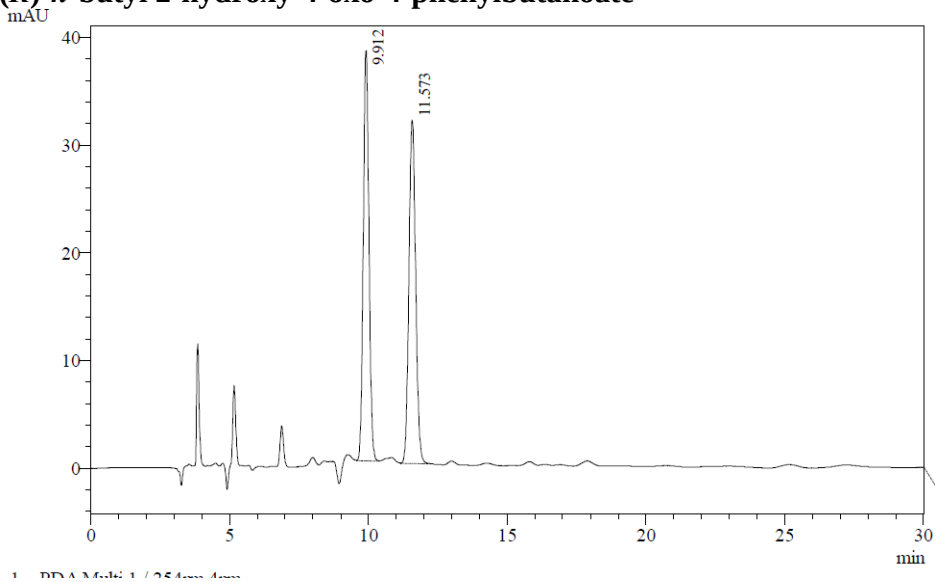
f1 (ppm)

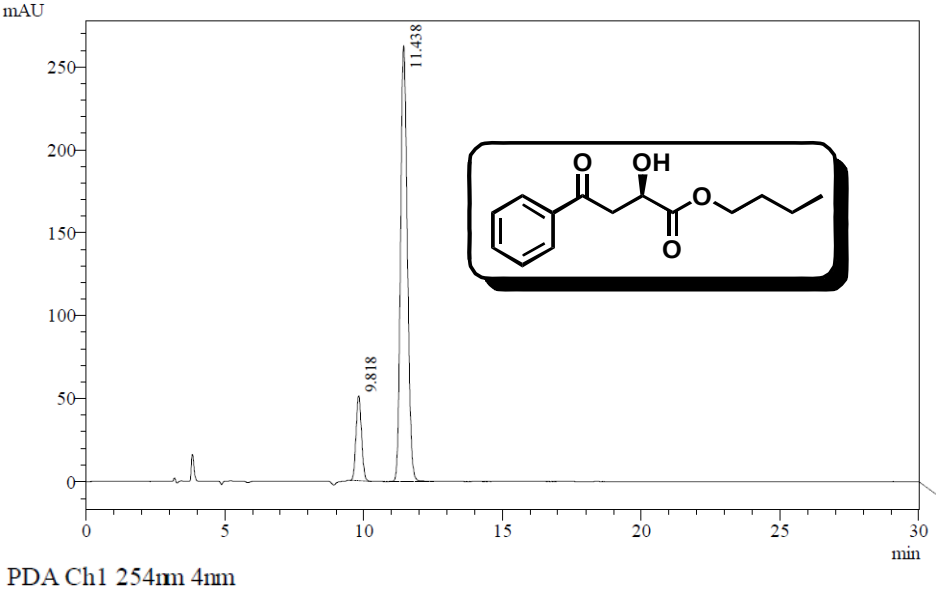

197.54
173.80
136.44
133.61
128.70
128.18
67.22
61.85
42.19
14.12
O
OH
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

(*R*)-*n*-butyl 2-hydroxy-4-oxo-4-phenylbutanoate



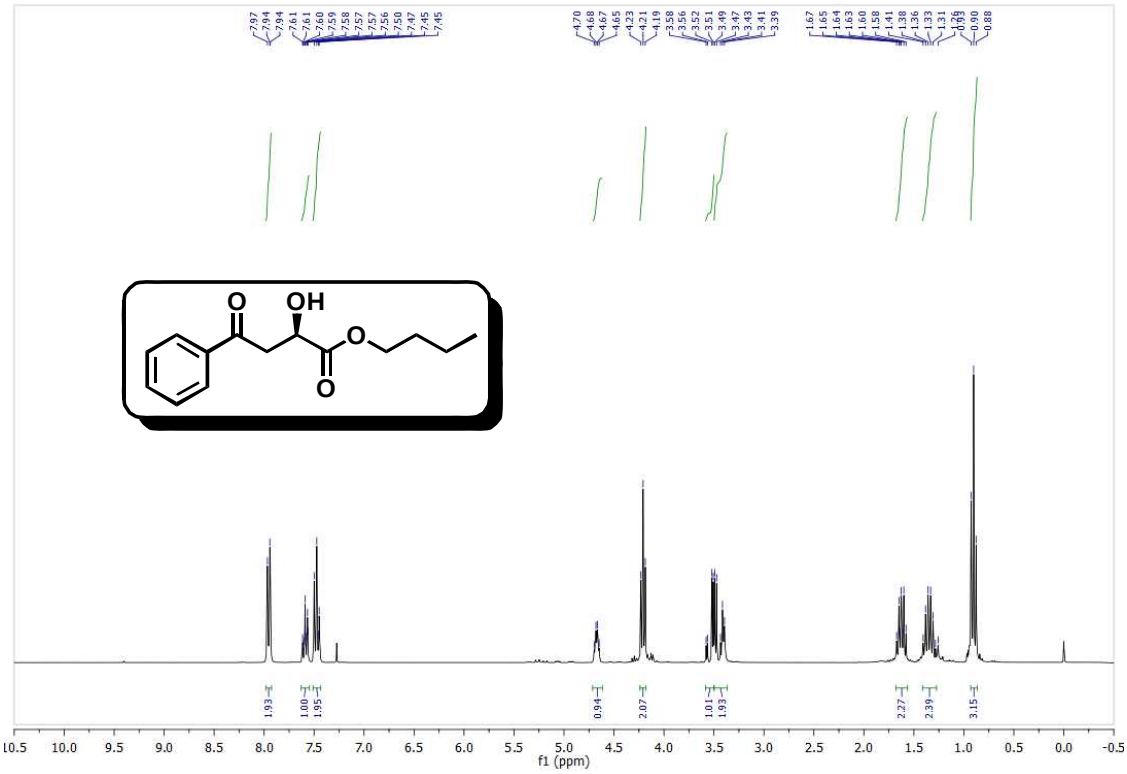
PDA Ch1 254nm 4nm

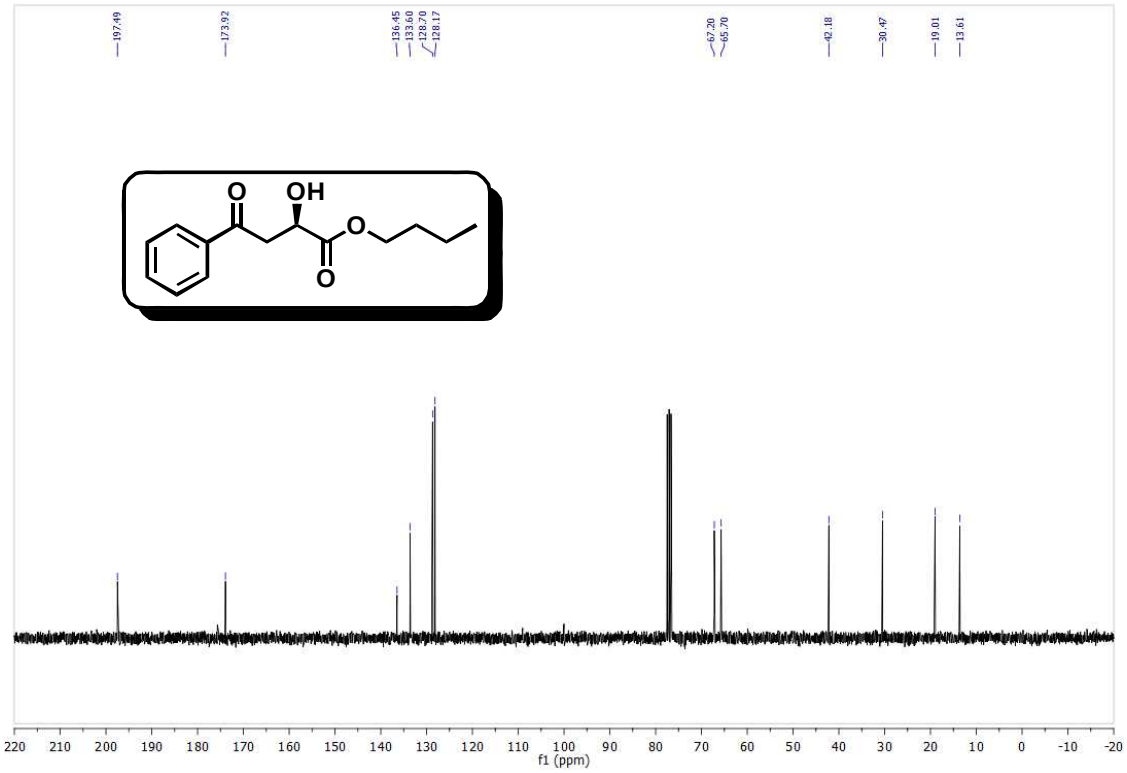
Peak#	Ret. Time	Area	Area %
1	9.912	541073	49.966
2	11.573	541811	50.034
Total		1082884	100.000



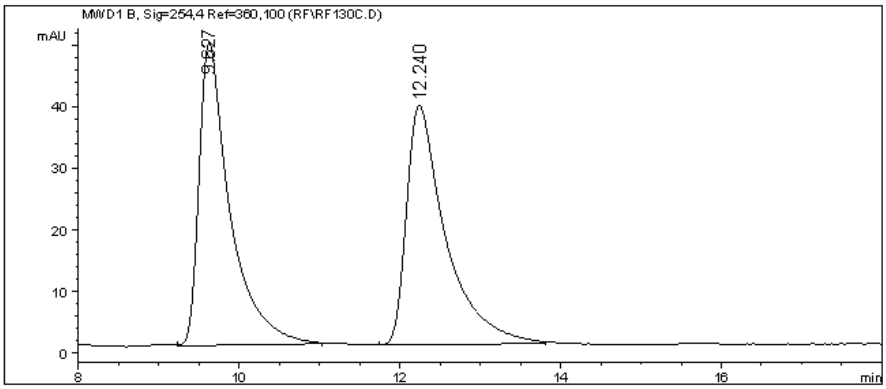
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.818	710667	13.601
2	11.438	4514339	86.399
Total		5225006	100.000


7.97
7.94
7.94
7.61
7.61
7.60
7.59
7.58
7.57
7.57
7.56
7.50
7.47
7.45
7.45
4.70
4.68
4.67
4.65
4.23
4.21
4.19
3.58
3.56
3.52
3.51
3.49
3.47
3.43
3.41
3.39
1.67
1.65
1.64
1.63
1.60
1.58
1.41
1.38
1.36
1.33
1.31
0.93
0.90
0.88
O
OH
O
O
1.93
1.00
1.95
0.94
2.07
1.01
1.93
2.27
2.39
3.15
f1 (ppm)

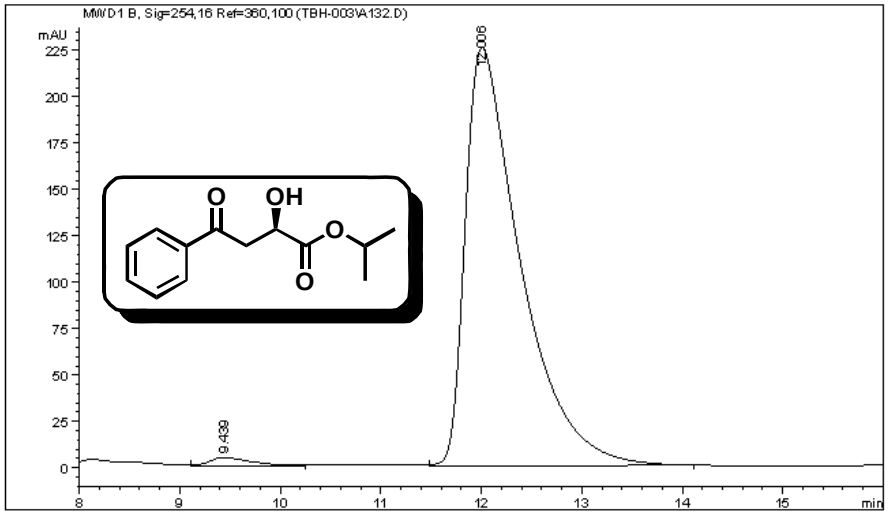

197.49
173.92
136.45
133.60
128.70
128.17
67.20
65.70
42.18
30.47
19.01
13.61
O
OH
O
O
f1 (ppm)

(*R*)-isopropyl 2-hydroxy-4-oxo-4-phenylbutanoate

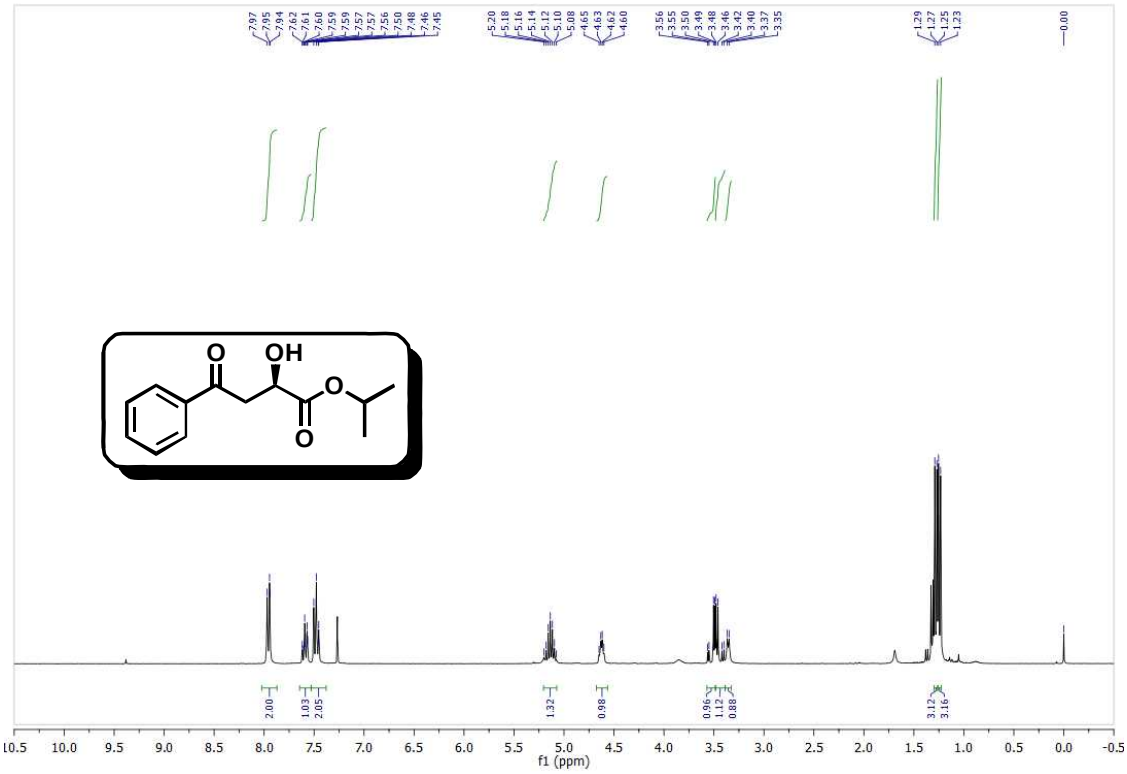


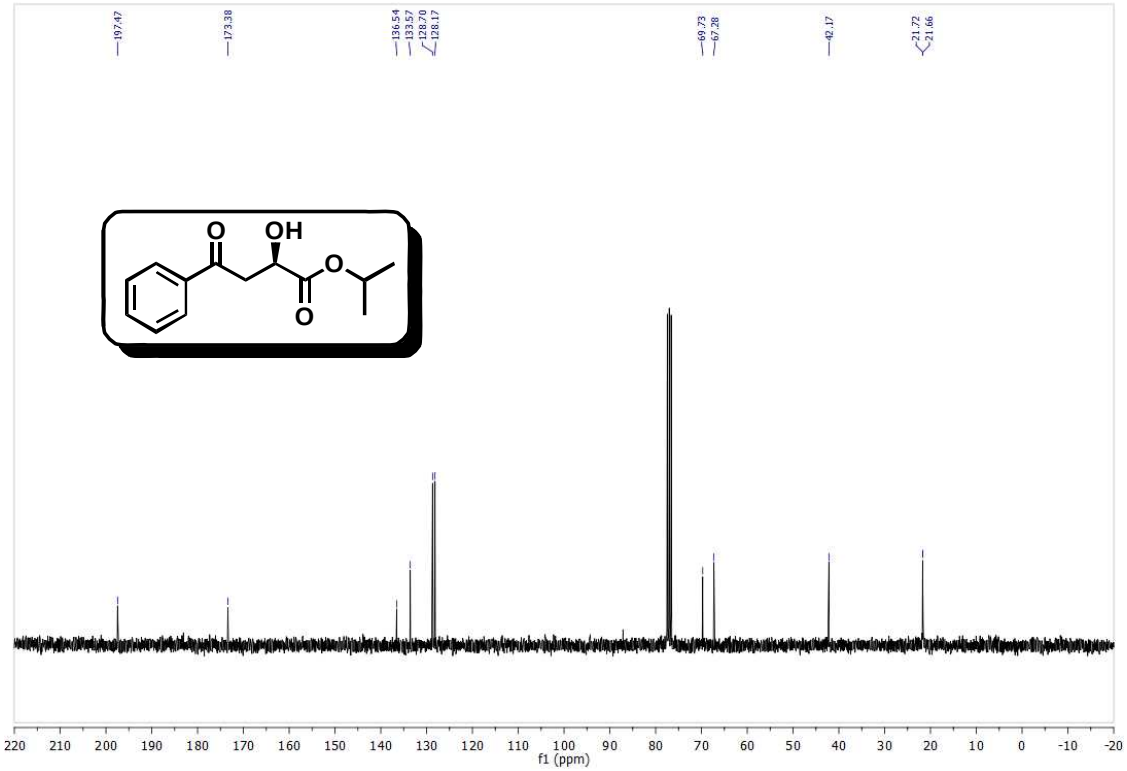
Signal 1: MWD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.627	BV	0.3833	1311.94666	49.16859	49.8901
2	12.240	VV	0.4816	1317.72925	38.85968	50.1099
Totals :				2629.67590	88.02828	

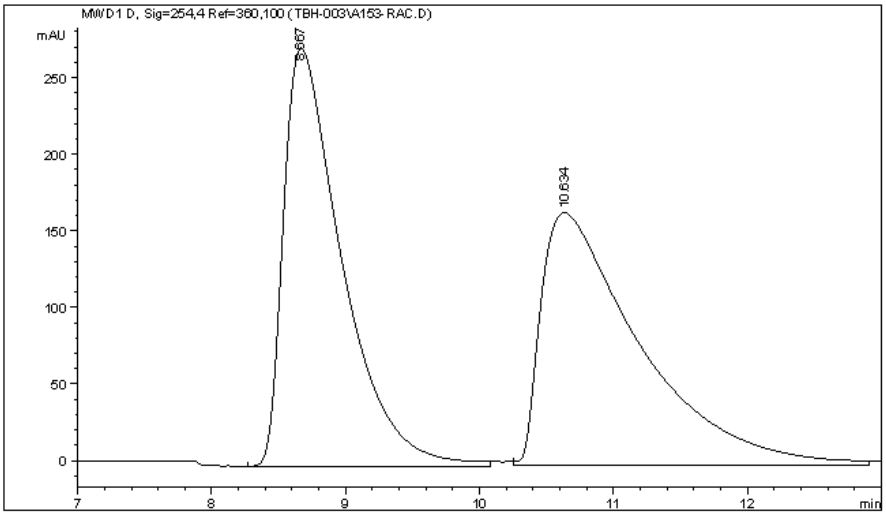


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.439	VV	0.4026	145.03171	4.71840	1.6593
2	12.006	VB	0.5489	8595.38086	225.38782	98.3407

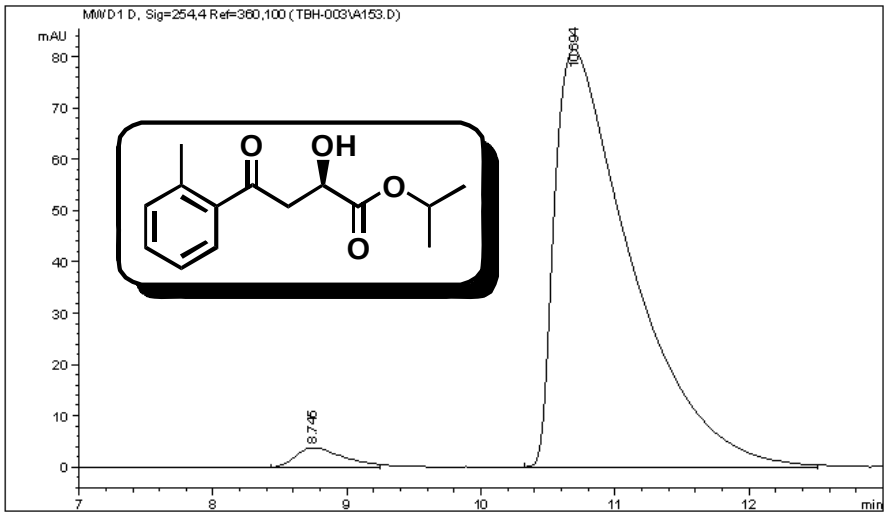

7.97
7.95
7.94
7.62
7.61
7.60
7.59
7.59
7.57
7.57
7.56
7.50
7.48
7.46
7.45
5.20
5.18
5.16
5.14
5.12
5.10
5.08
4.65
4.63
4.62
4.60
3.56
3.55
3.50
3.49
3.48
3.46
3.42
3.40
3.37
3.35
1.29
1.27
1.25
1.23
0.00
O
OH
O
O
2.00
1.03
2.05
1.32
0.98
0.96
1.12
0.88
3.12
3.16
f1 (ppm)


197.47
173.38
136.54
133.57
128.70
128.17
69.73
67.28
42.17
21.72
21.66
O
OH
O
O
f1 (ppm)

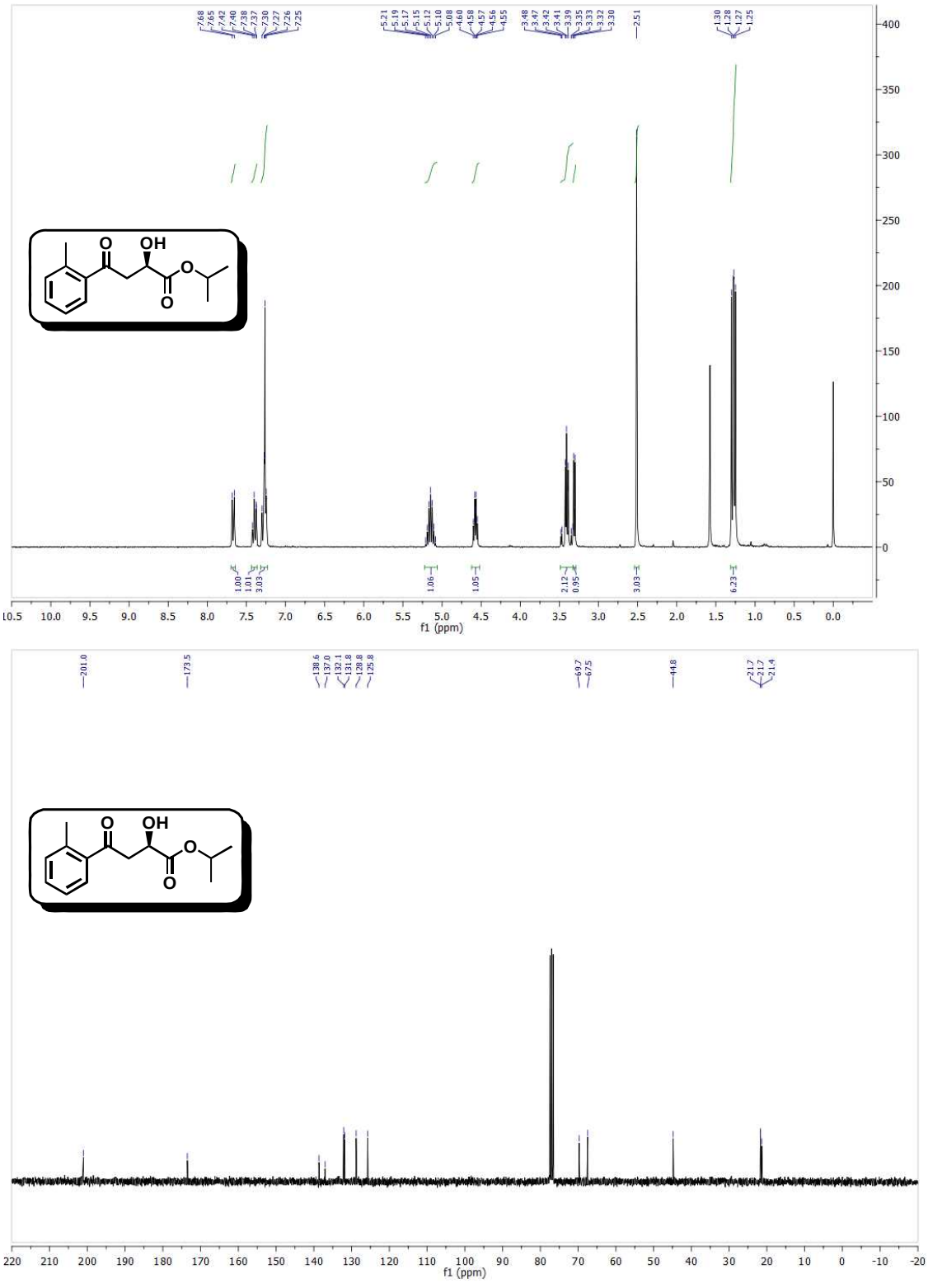
(*R*)-isopropyl 2-hydroxy-4-oxo-4-o-tolylbutanoate



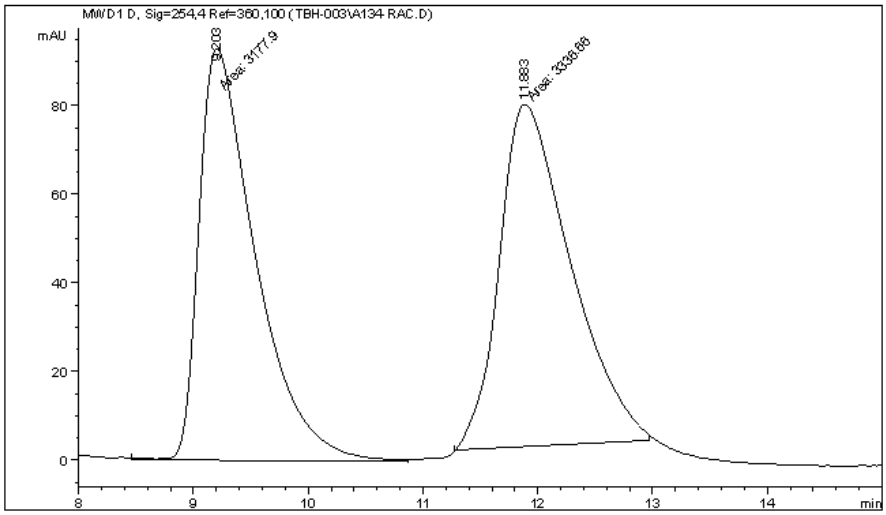
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.667	VV	0.4405	8249.48340	273.00421	49.3613
2	10.634	VV	0.7157	8462.95605	165.18712	50.6387



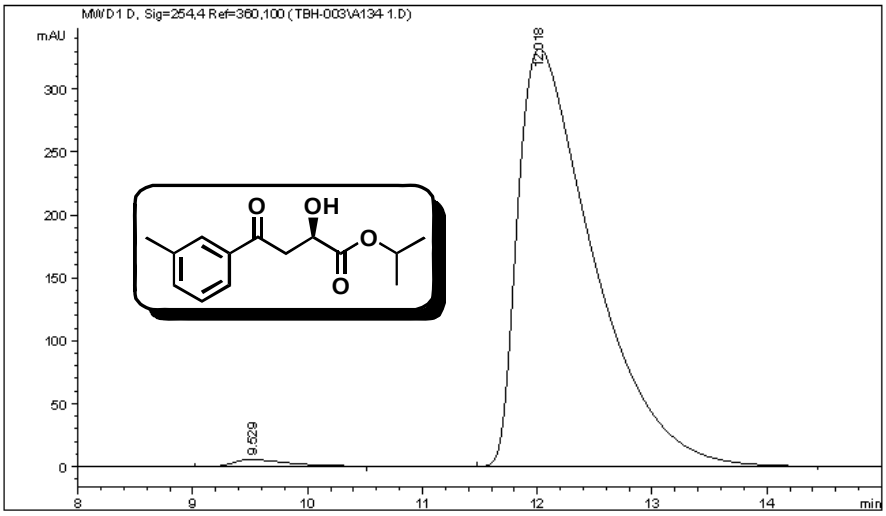
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.745	VV	0.3214	101.26785	3.94666	2.9958
2	10.694	VV	0.5818	3279.05957	81.77115	97.0042



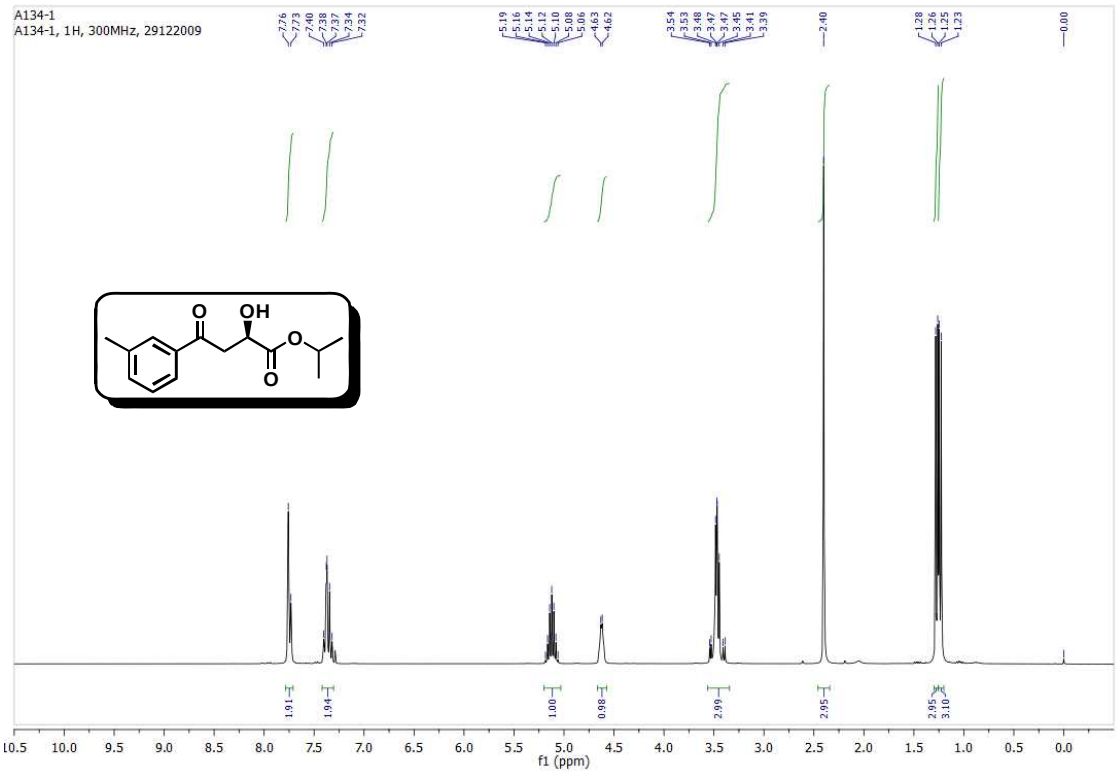
(*R*)-isopropyl 2-hydroxy-4-oxo-4-m-tolylbutanoate

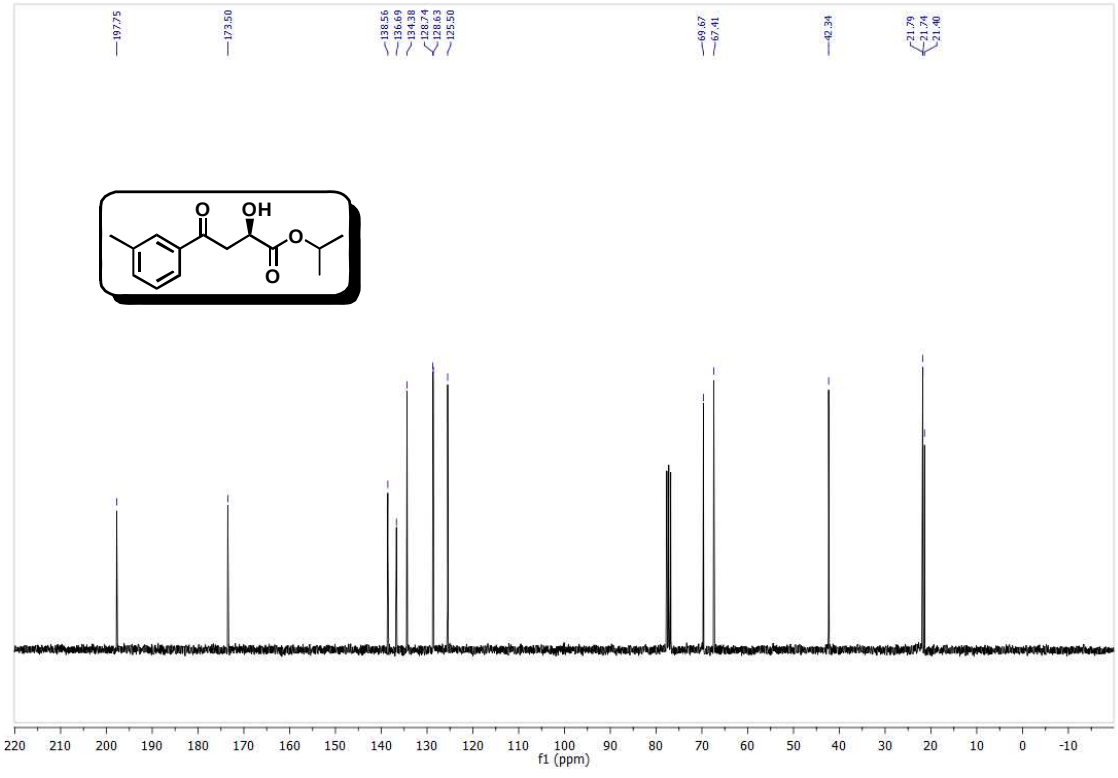


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.203	MM	0.5699	3177.89648	92.93600	48.7815
2	11.883	MM	0.7197	3336.65967	77.26497	51.2185

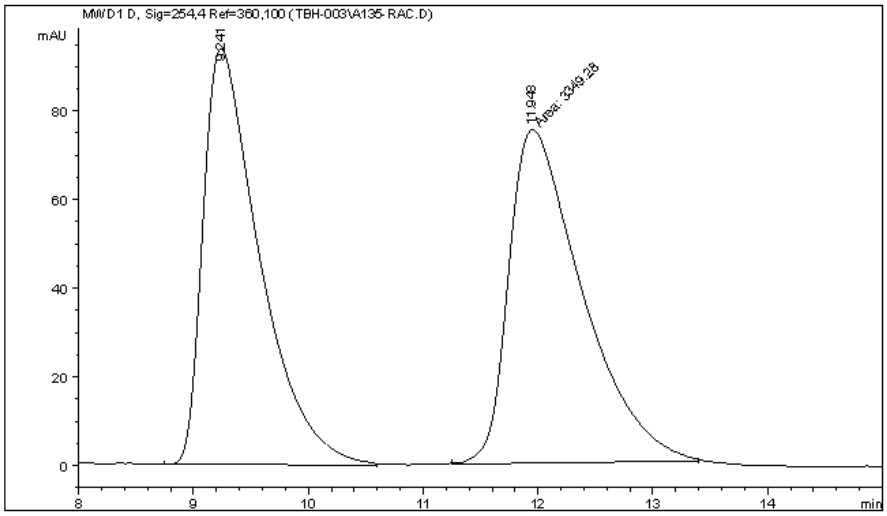


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.529	VV	0.4553	217.03958	5.89837	1.4030
2	12.018	VV	0.6757	1.52526e4	332.18802	98.5970

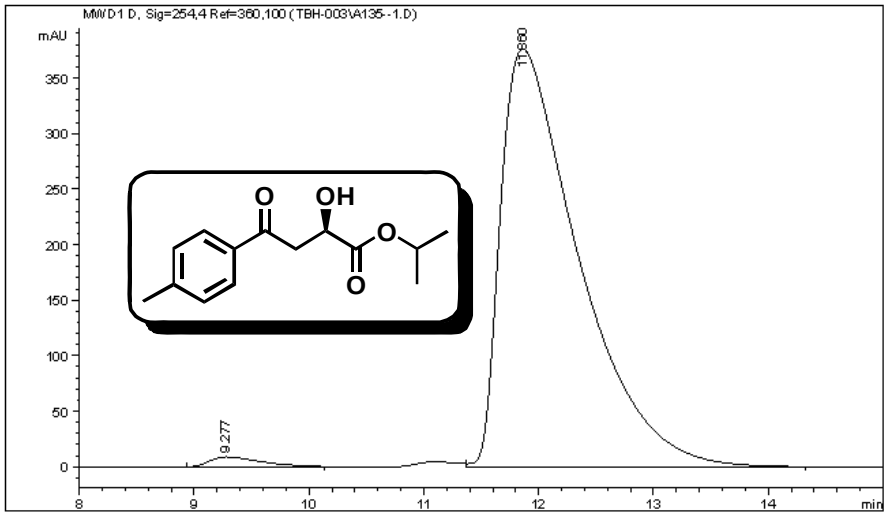




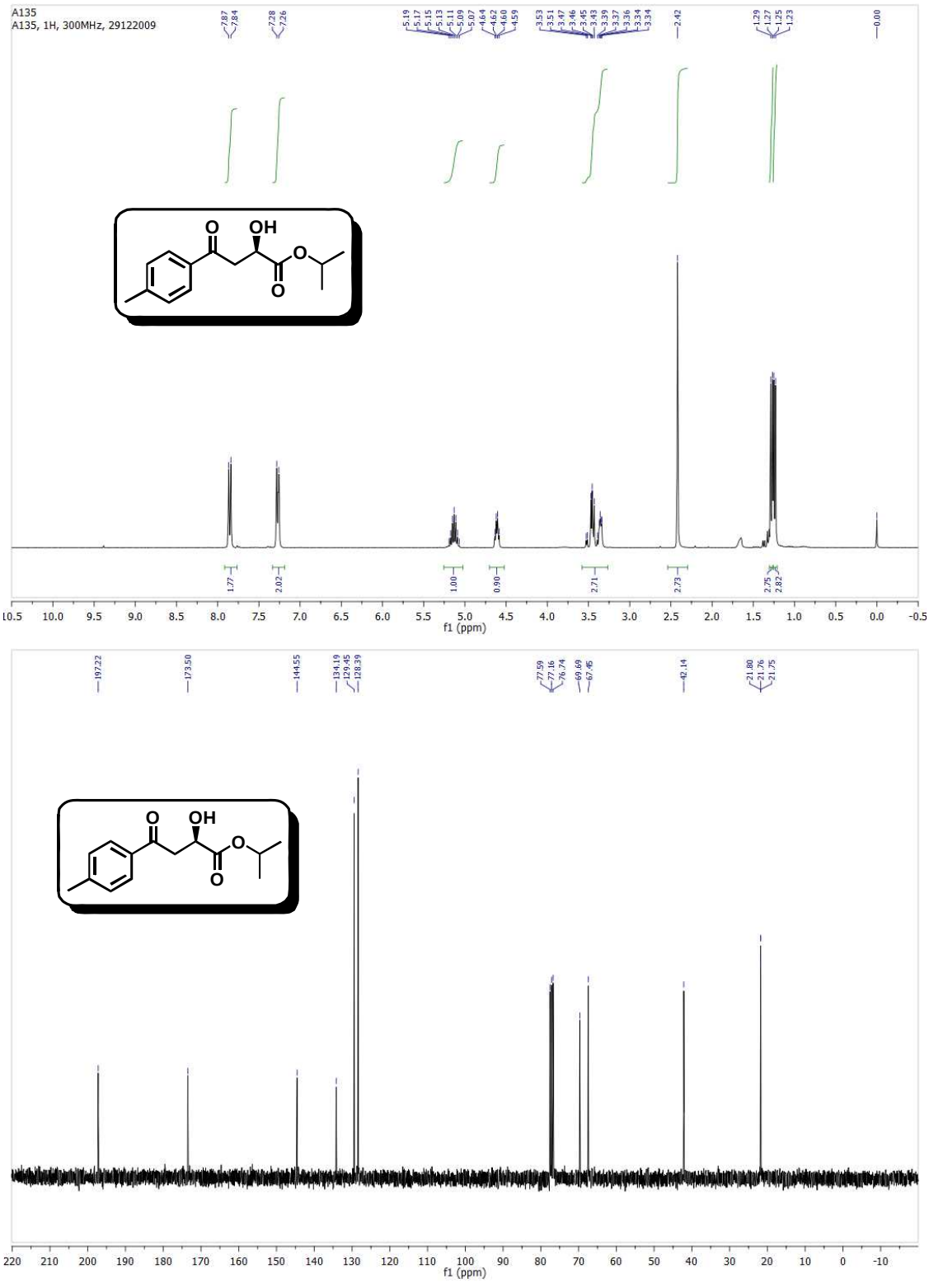
(*R*)-isopropyl 2-hydroxy-4-oxo-4-p-tolylbutanoate



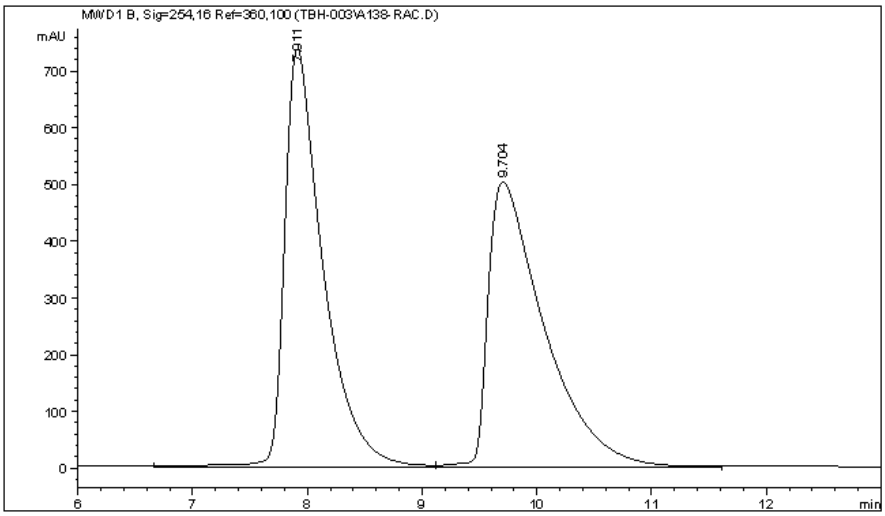
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.241	BV	0.4967	3206.66479	93.84001	48.9123
2	11.948	MM	0.7423	3349.28467	75.20341	51.0877



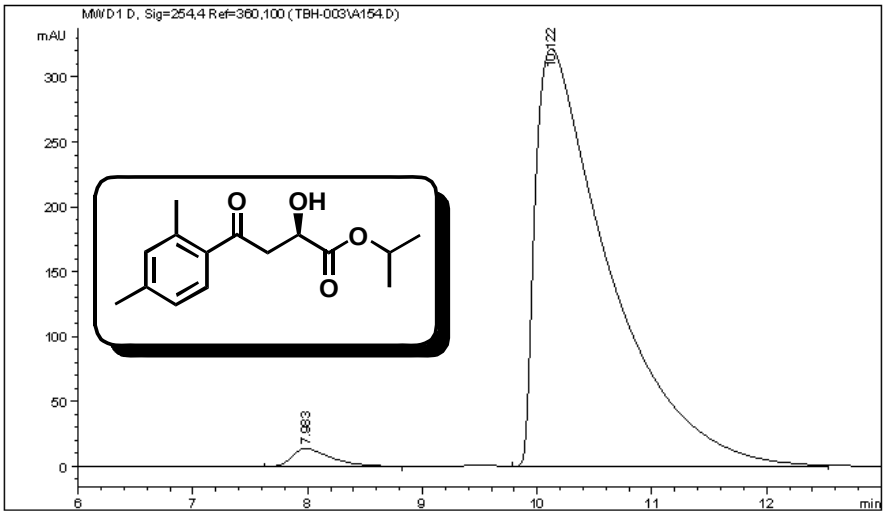
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.277	VV	0.4497	315.47281	9.44523	1.7345
2	11.860	VV	0.6933	1.78729e4	376.88269	98.2655



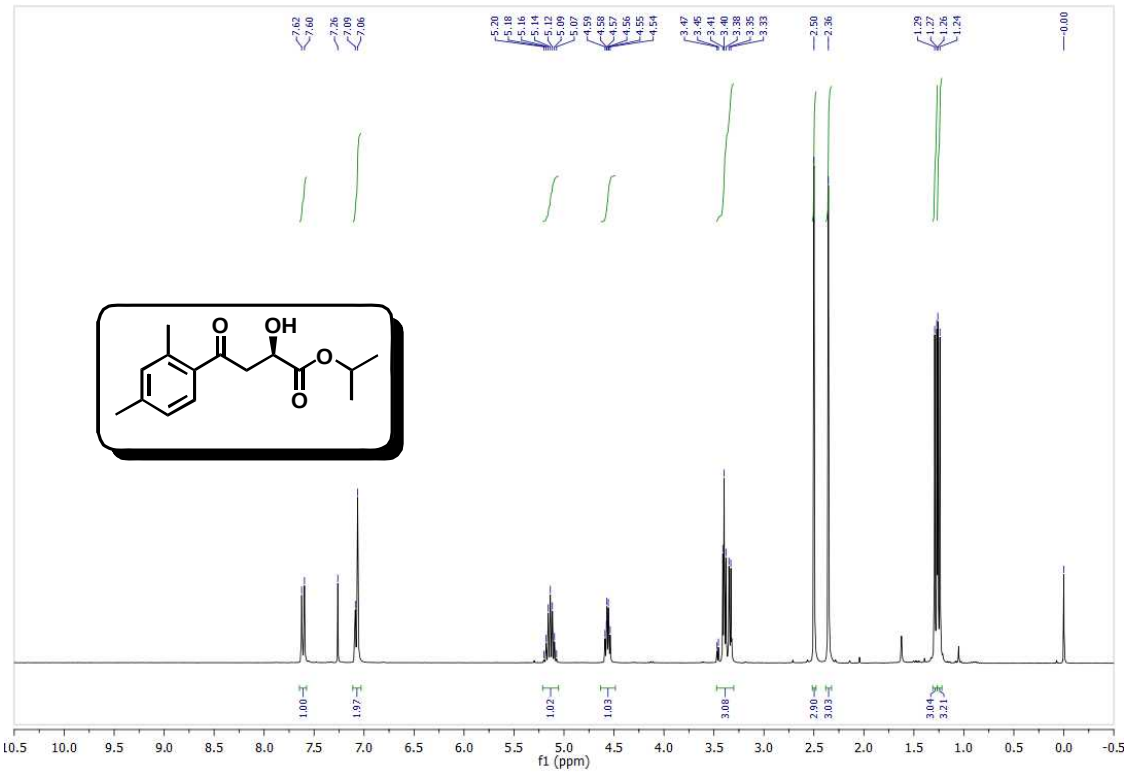
(*R*)-isopropyl 4-(2,4-dimethylphenyl)-2-hydroxy-4-oxobutanoate

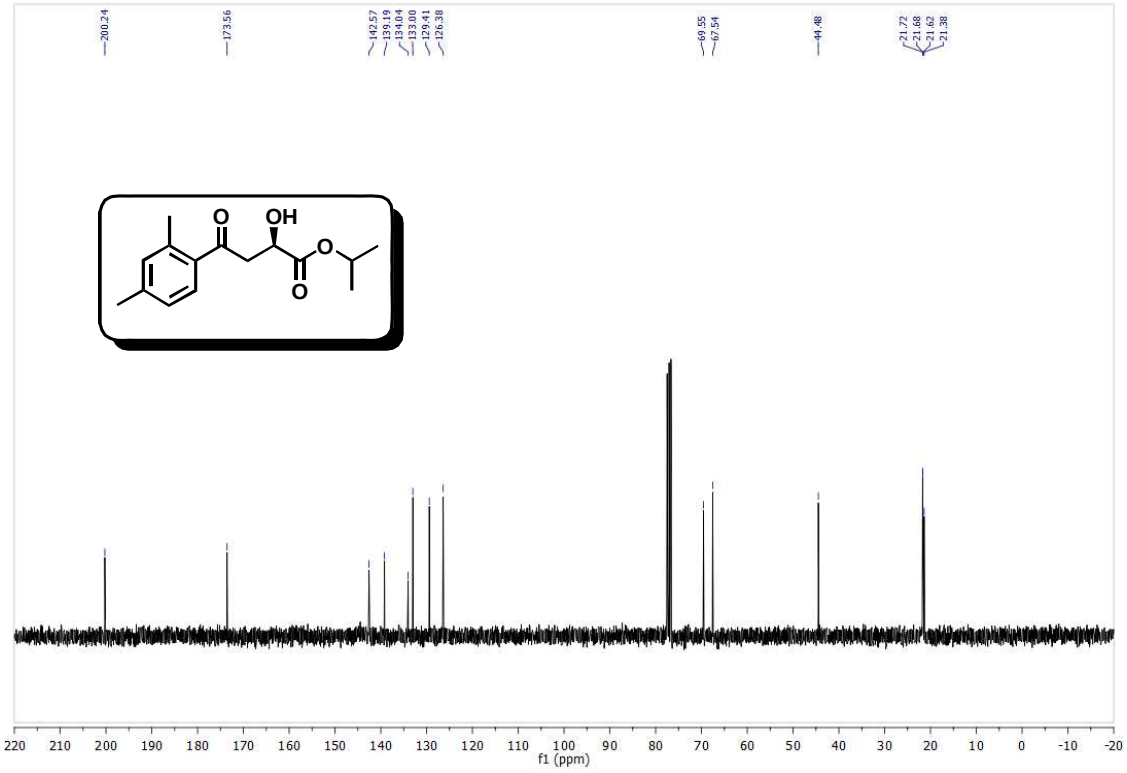


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.911	VV	0.3402	1.71972e4	737.16748	50.3130
2	9.704	VB	0.4943	1.69832e4	502.55173	49.6870

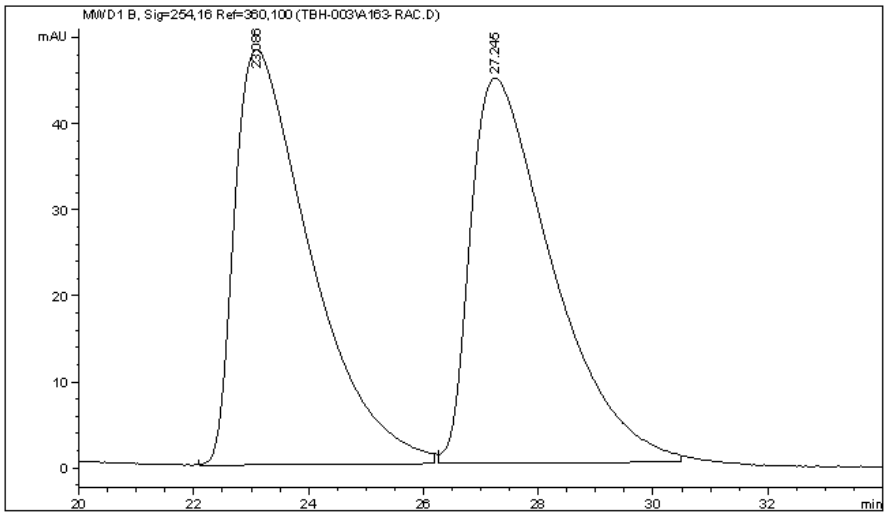


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.983	VV	0.3401	336.24344	14.00418	2.2734
2	10.122	VV	0.6354	1.44542e4	322.21100	97.7266

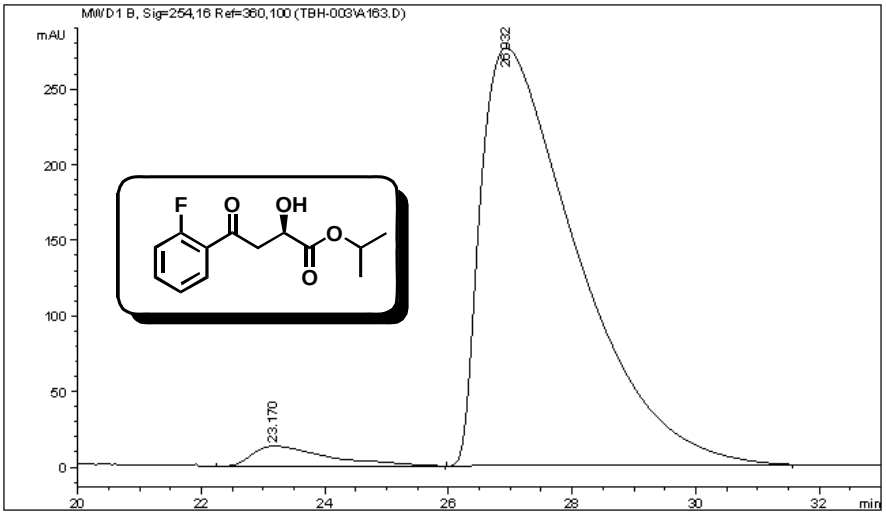




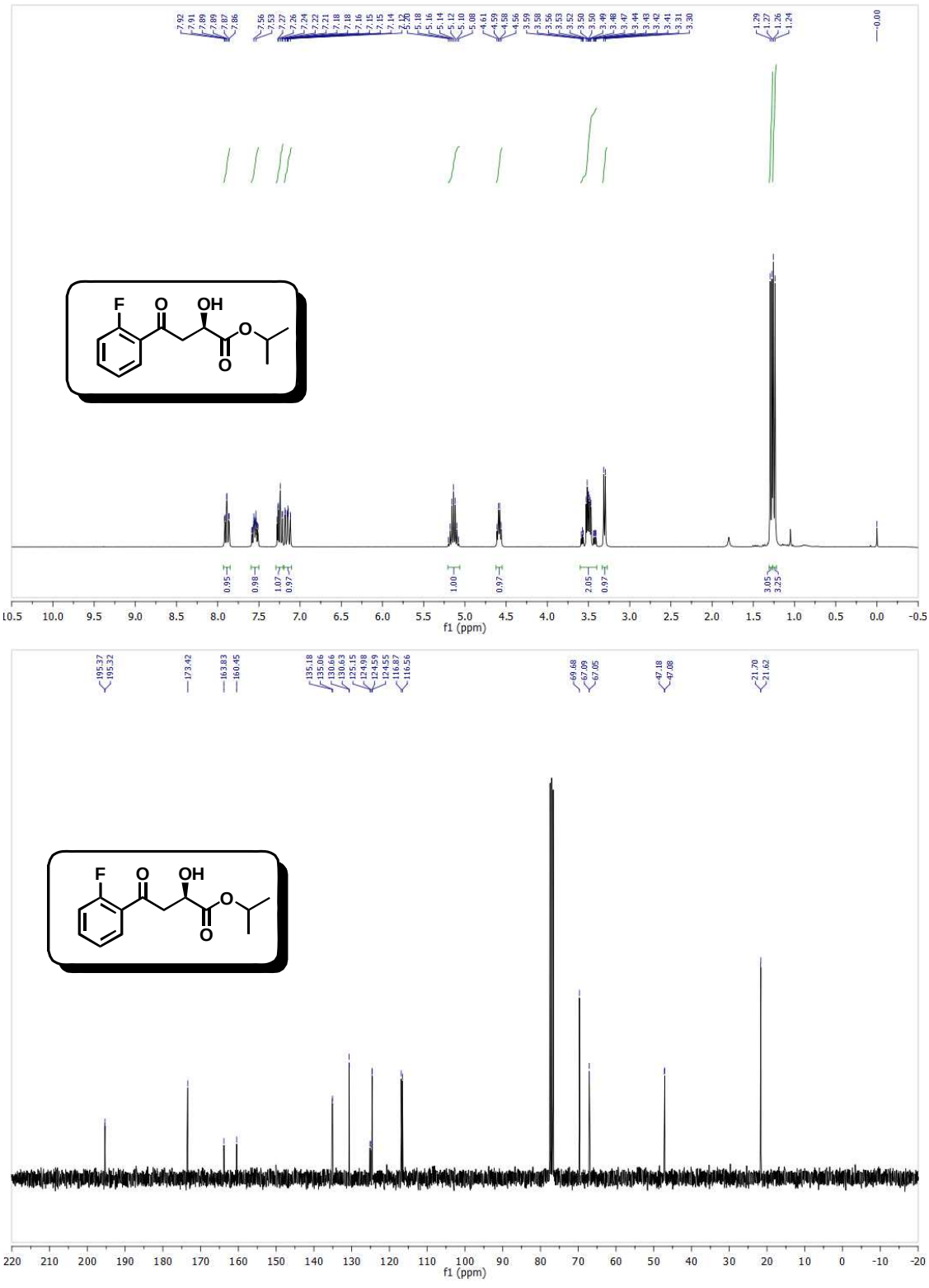
(*R*)-isopropyl 4-(2-fluorophenyl)-2-hydroxy-4-oxobutanoate



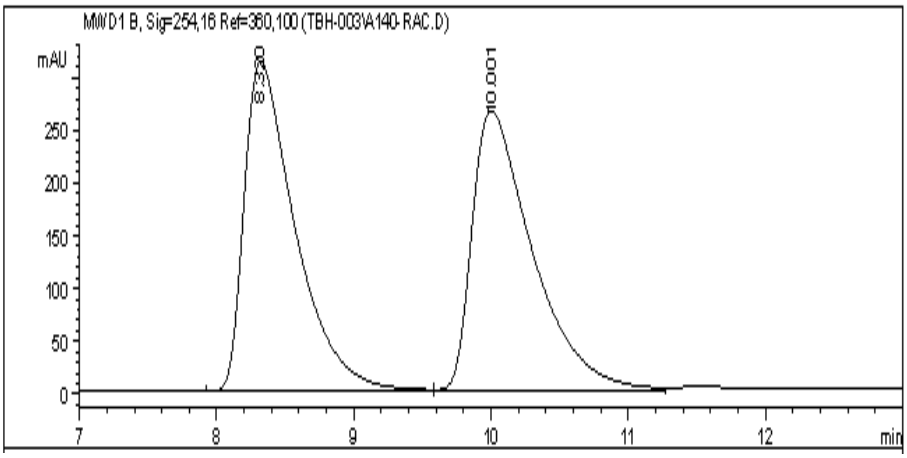
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.086	VB	1.0890	4444.06104	48.31876	49.9838
2	27.245	VV	1.1781	4446.94336	44.80021	50.0162



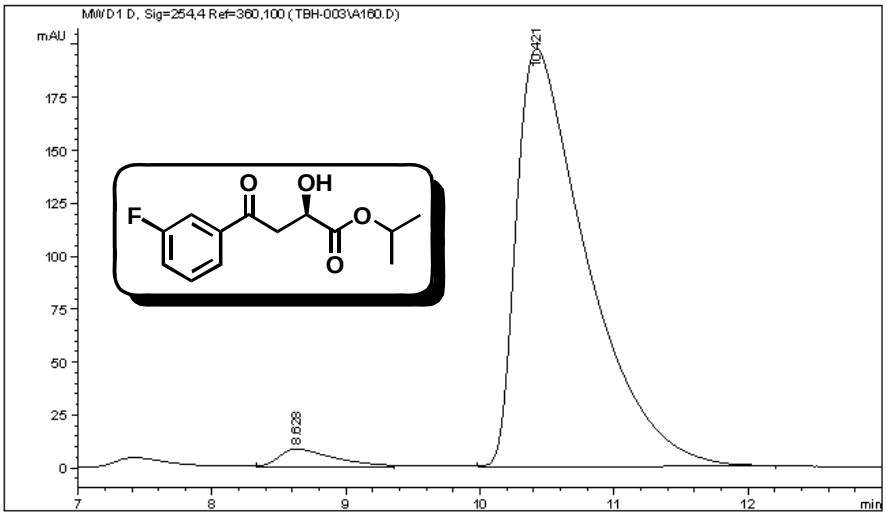
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.170	VB	1.0057	1146.05322	13.37496	3.6858
2	26.932	BB	1.4913	2.99479e4	276.13535	96.3142



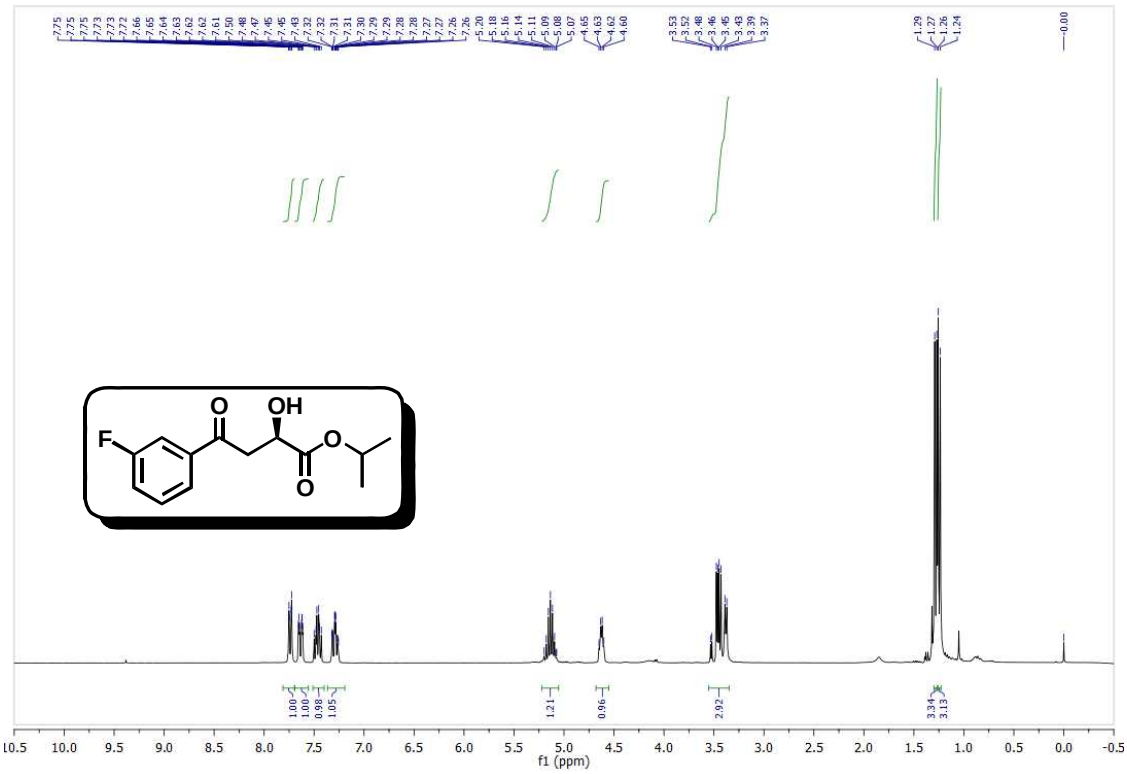
(*R*)-isopropyl 4-(3-fluorophenyl)-2-hydroxy-4-oxobutanoate

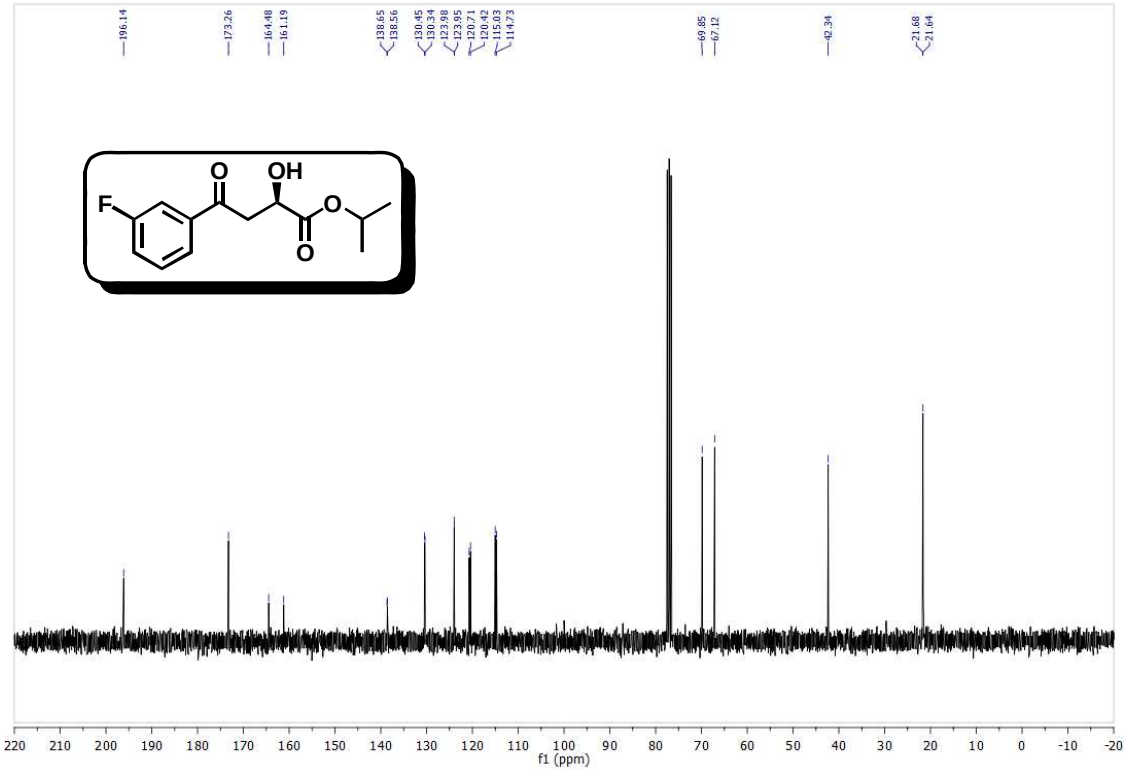


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.320	VV	0.3857	8083.31787	312.55811	49.9240
2	10.001	VV	0.4524	8107.93115	265.40823	50.0760

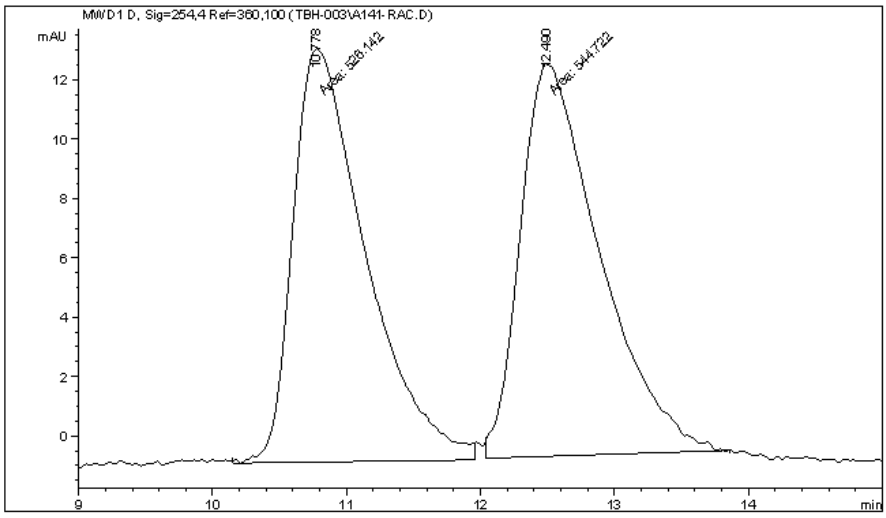


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.628	VV	0.3694	247.21349	8.60011	3.3026
2	10.421	VV	0.5380	7238.12500	197.31534	96.6974

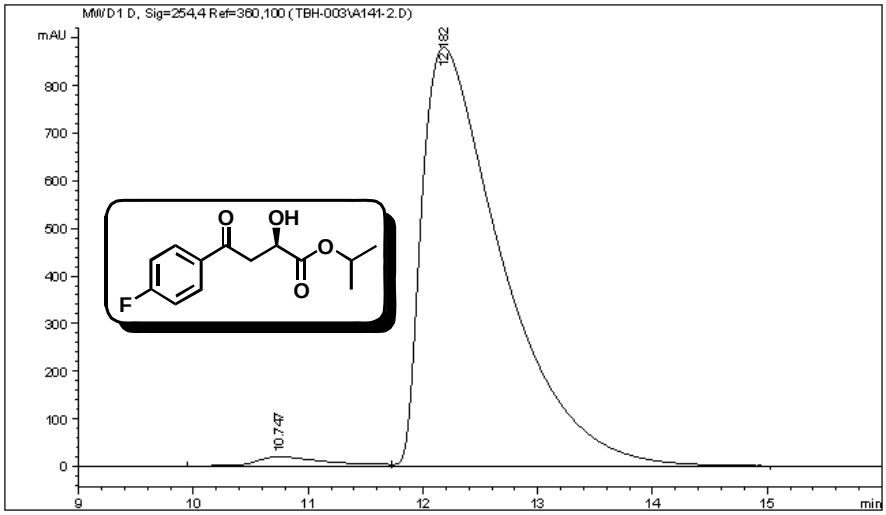




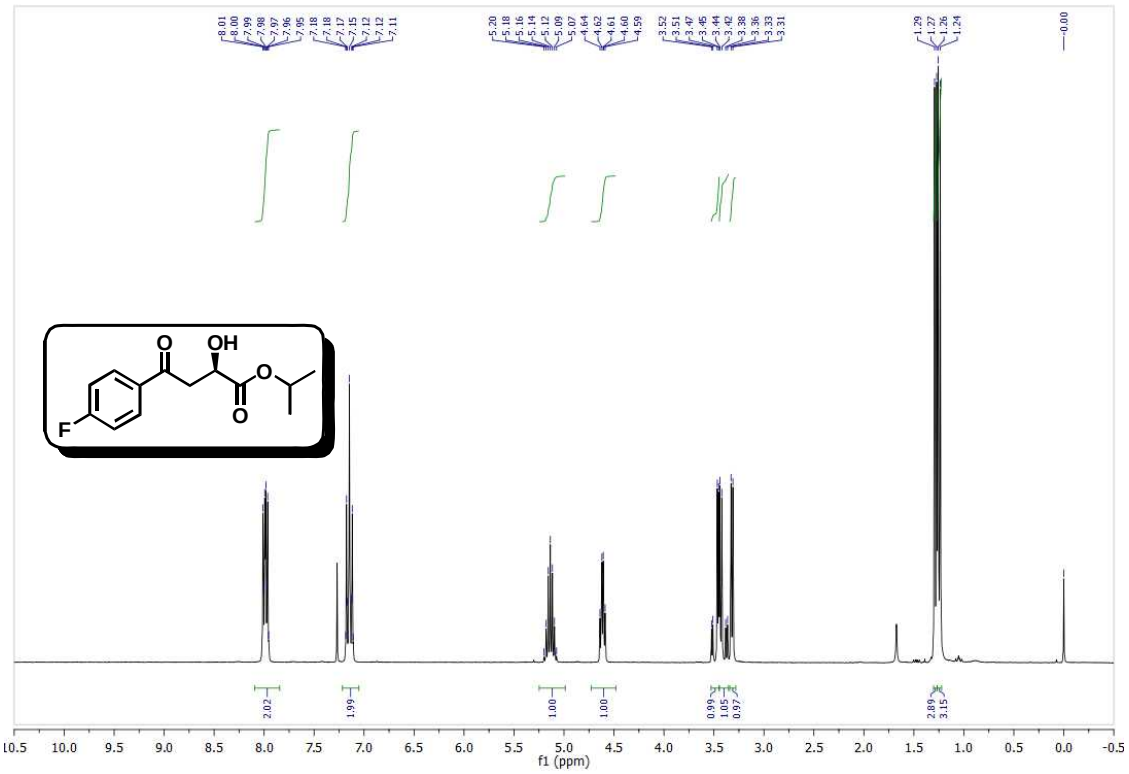
(*R*)-isopropyl 4-(4-fluorophenyl)-2-hydroxy-4-oxobutanoate

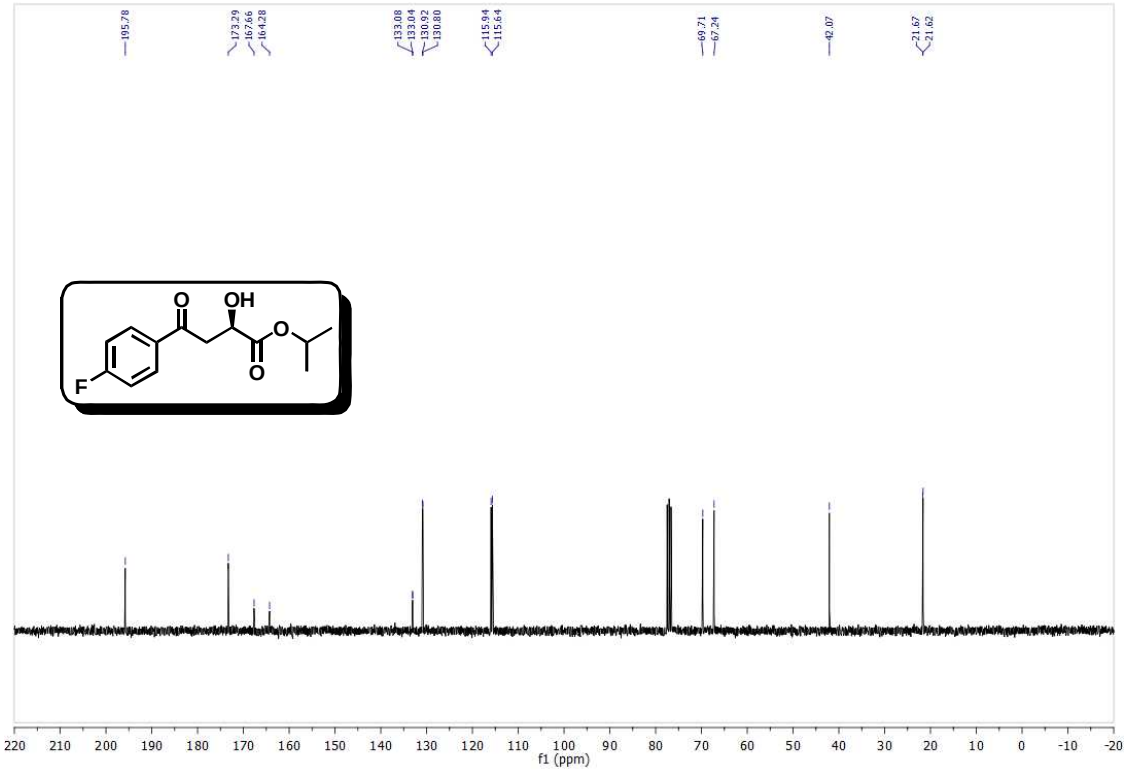


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.778	MM	0.6298	526.14166	13.92315	49.1325
2	12.490	MM	0.6864	544.72186	13.22623	50.8675

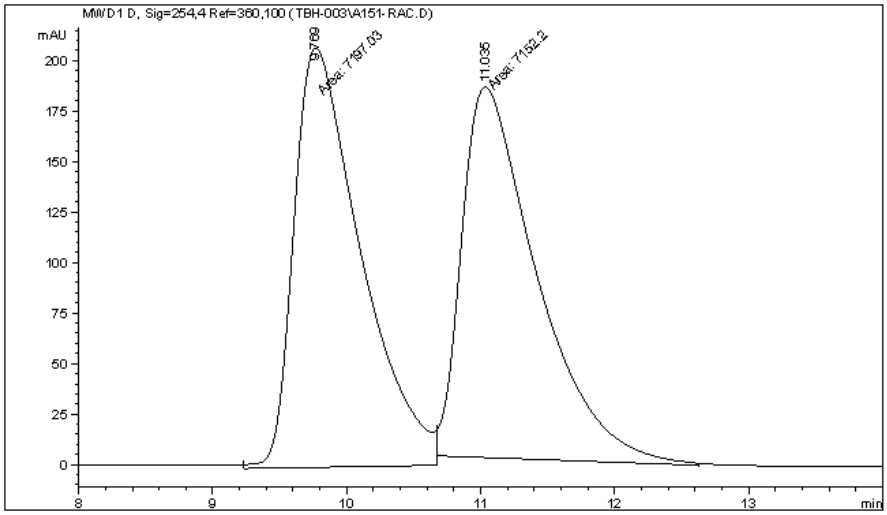


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.747	VV	0.5696	868.13147	19.87380	1.9869
2	12.182	VV	0.6897	4.28256e4	880.05719	98.0131

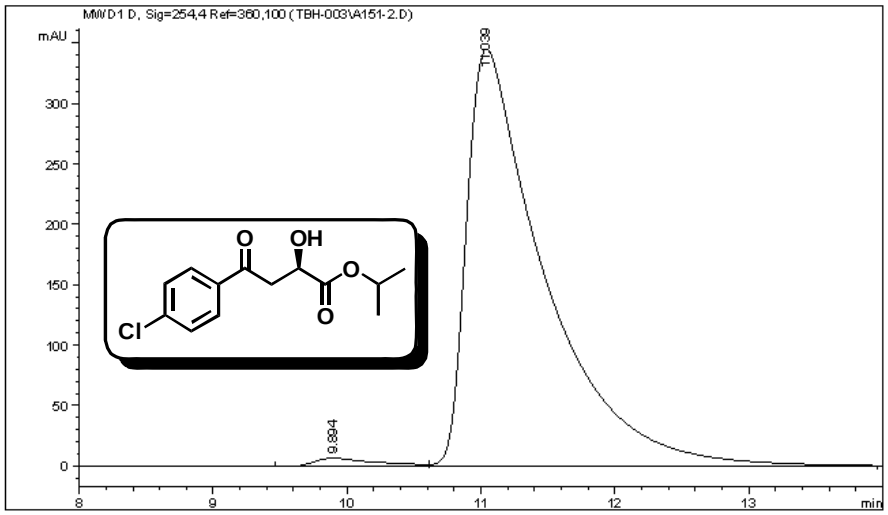




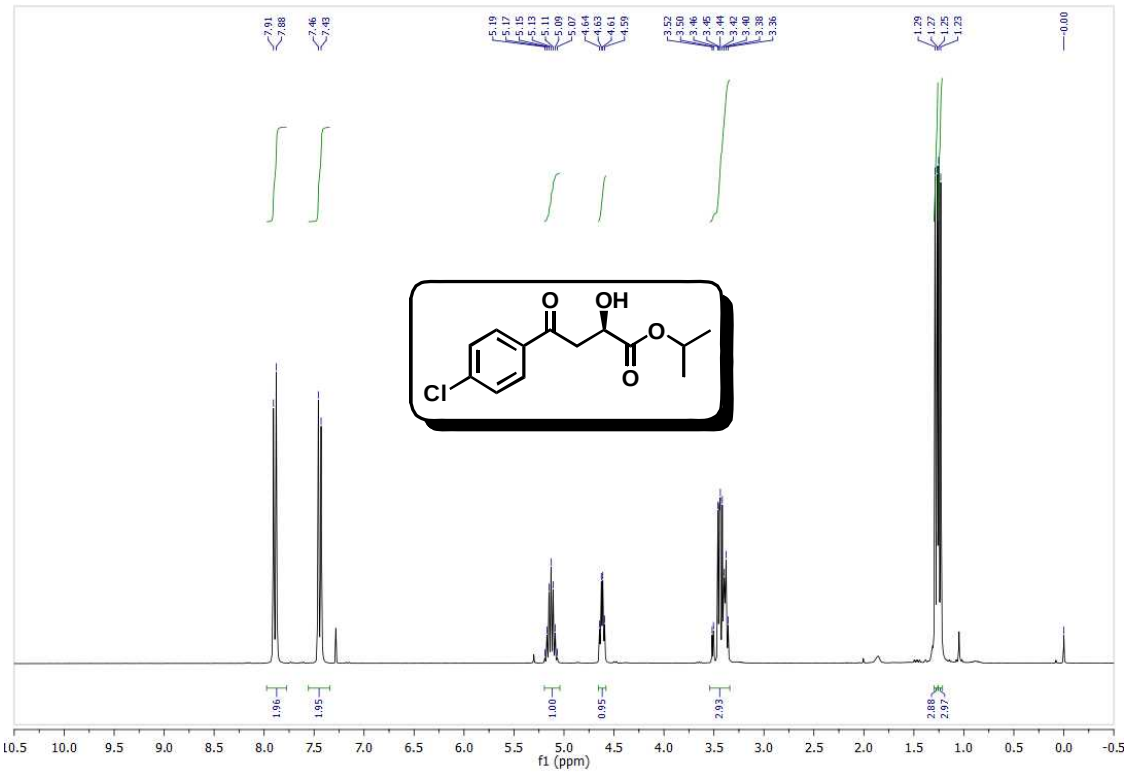
(*R*)-isopropyl 4-(4-chlorophenyl)-2-hydroxy-4-oxobutanoate

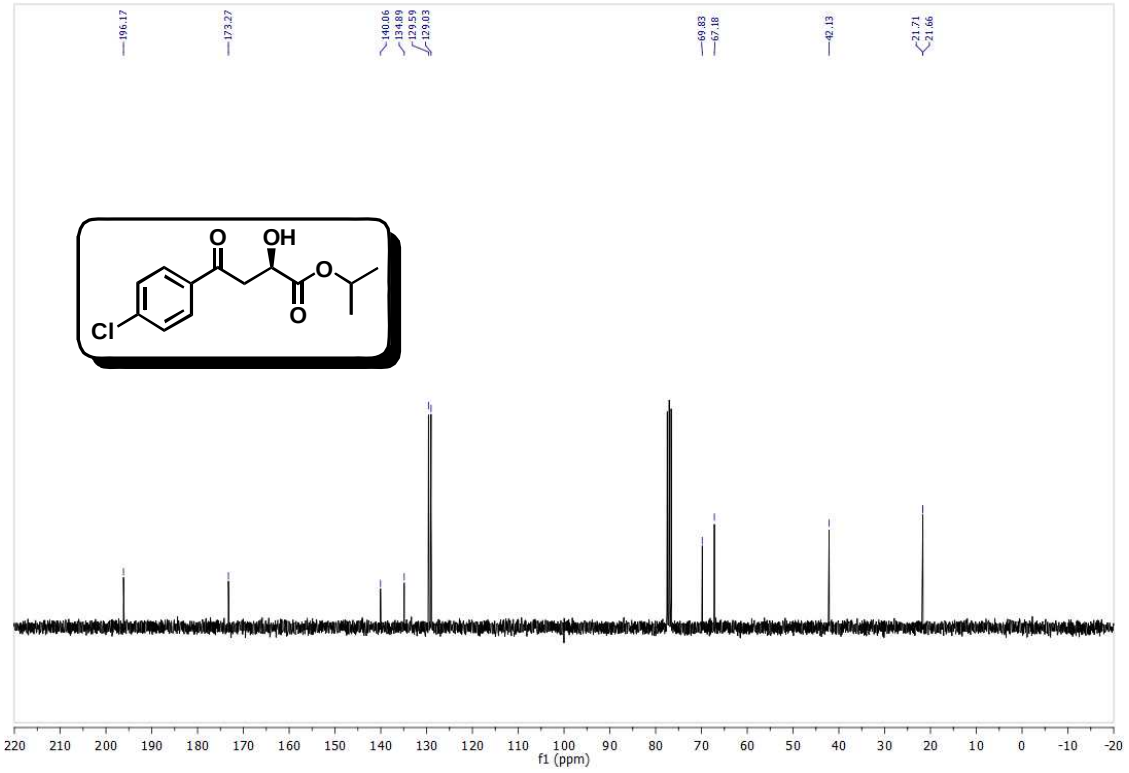


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.769	MM	0.5777	7197.03076	207.62784	50.1562
2	11.035	MM	0.6496	7152.19922	183.48976	49.8438

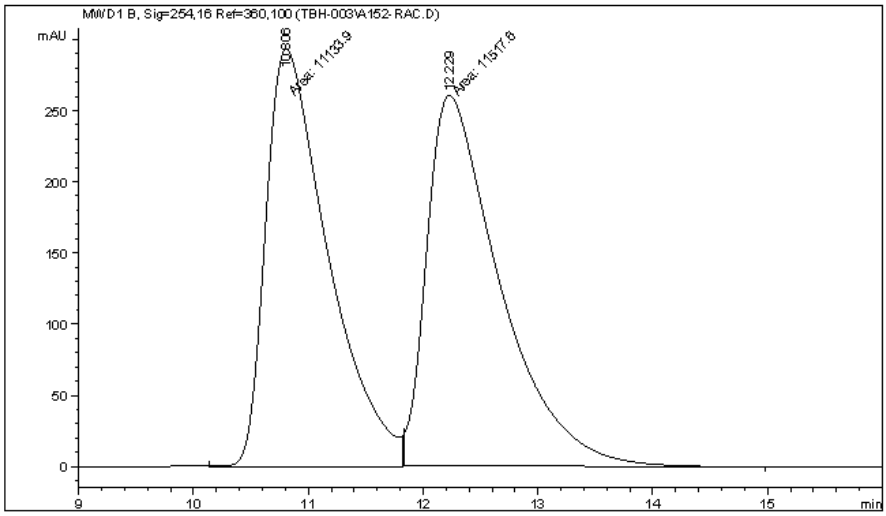


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.894	VV	0.3858	210.55847	6.78997	1.4873
2	11.039	VB	0.5672	1.39463e4	345.27692	98.5127

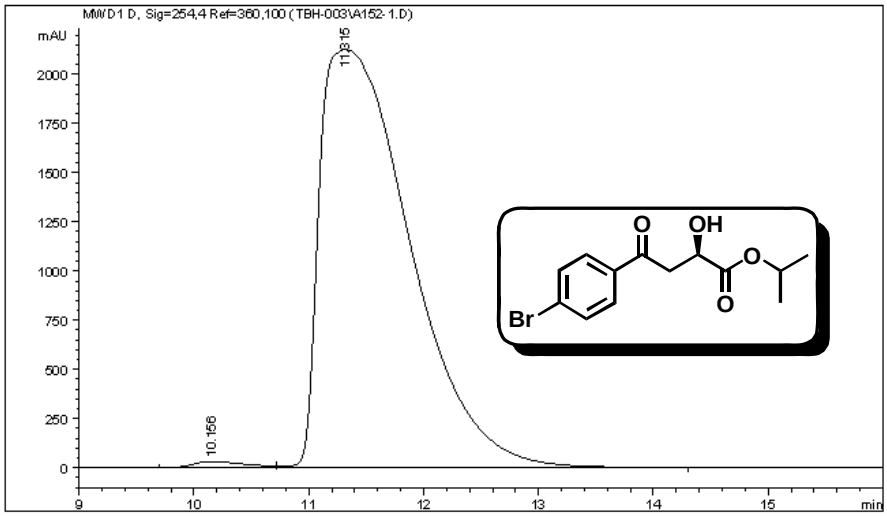




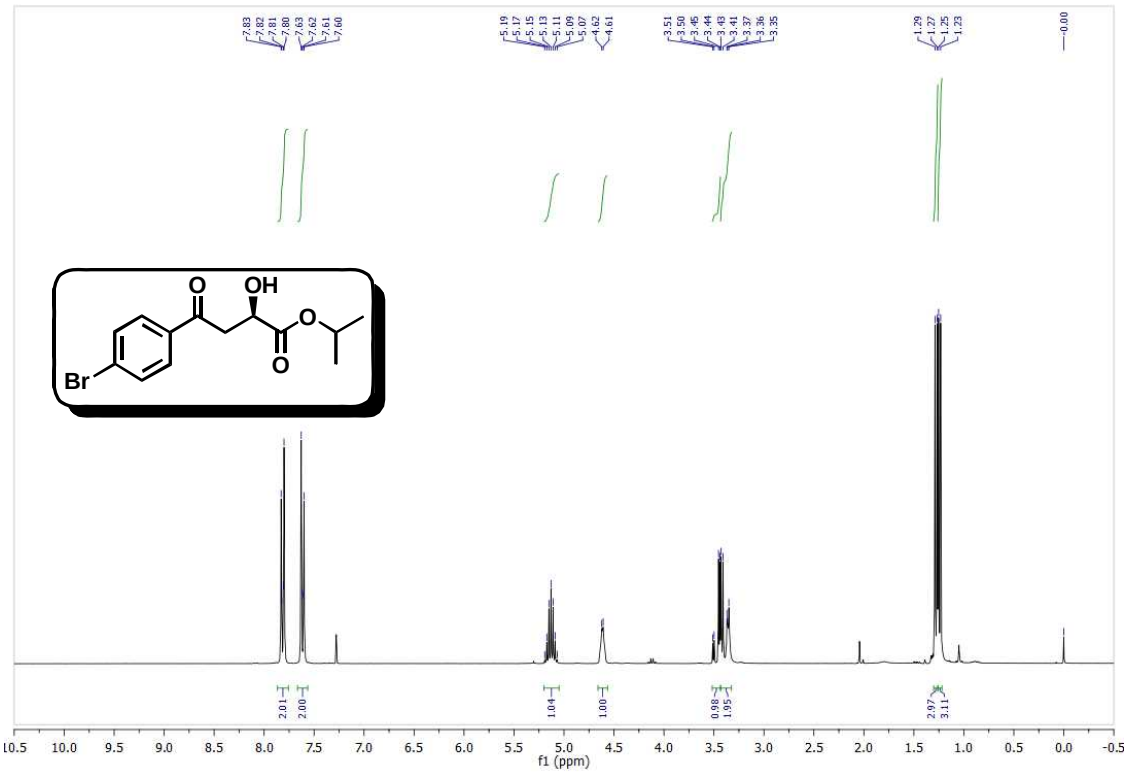
(*R*)-isopropyl 4-(4-bromophenyl)-2-hydroxy-4-oxobutanoate

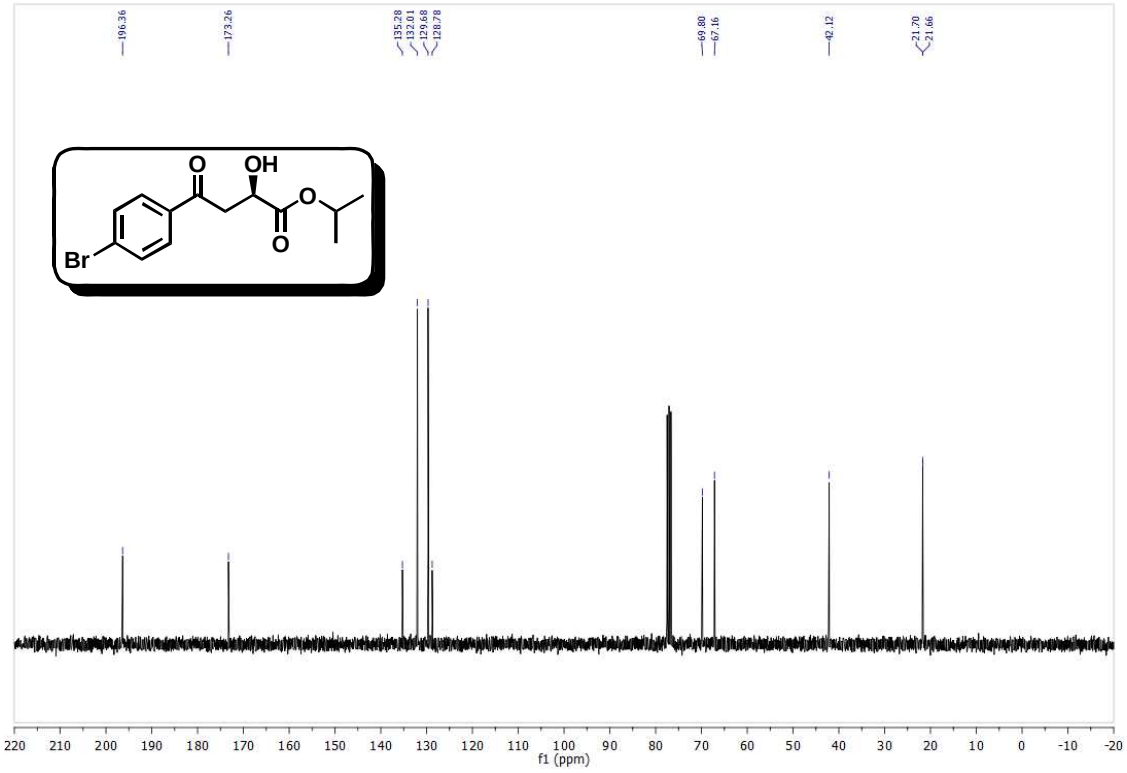


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.806	MM	0.6307	1.11339e4	294.24231	49.1532
2	12.229	MM	0.7377	1.15176e4	260.19601	50.8468

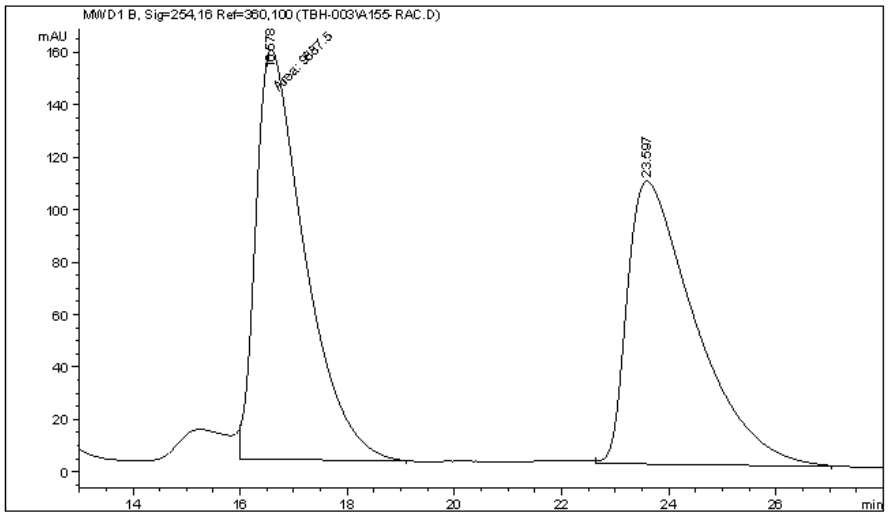


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.156	VV	0.4423	1014.92828	31.80775	0.8641
2	11.315	VV	0.6435	1.16435e5	2130.88379	99.1359

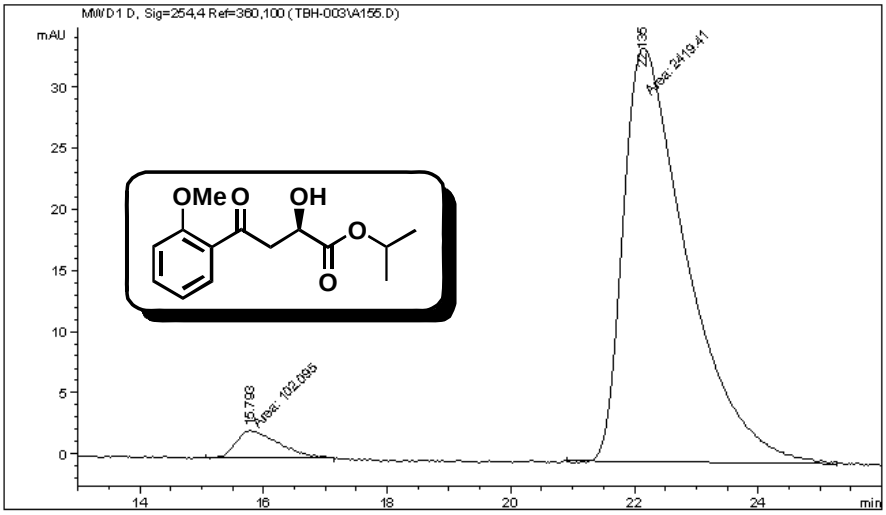




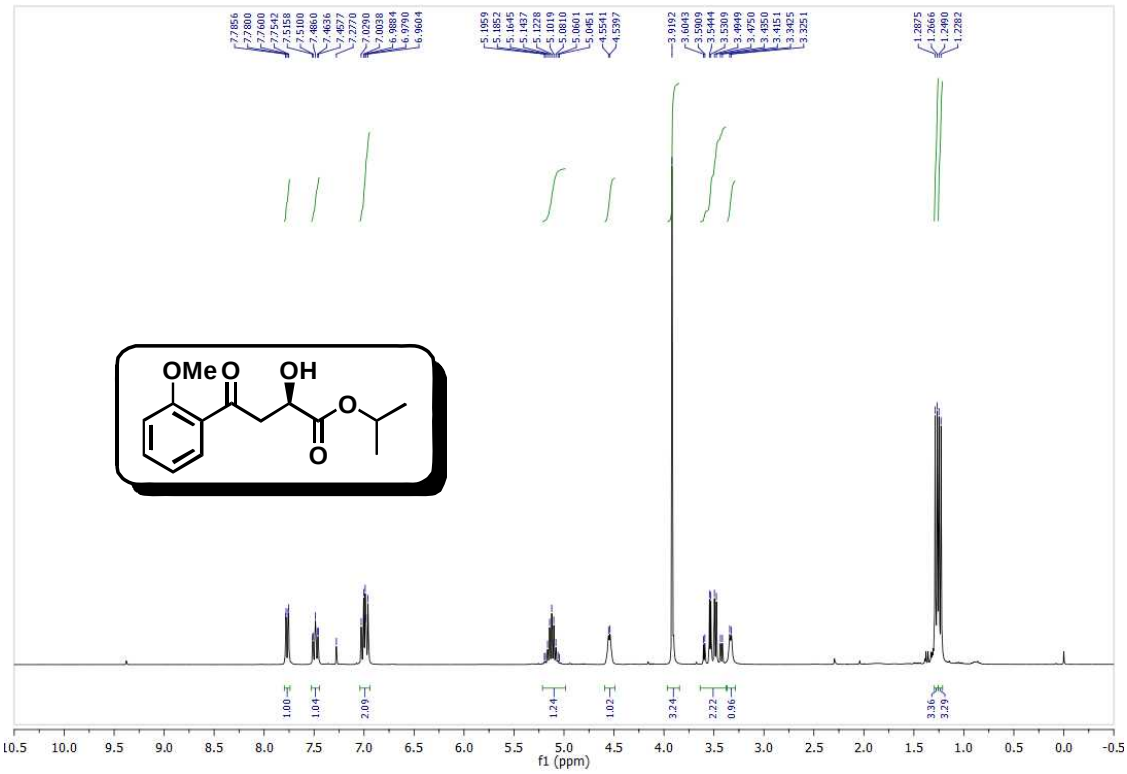
(*R*)-isopropyl 2-hydroxy-4-(2-methoxyphenyl)-4-oxobutanoate

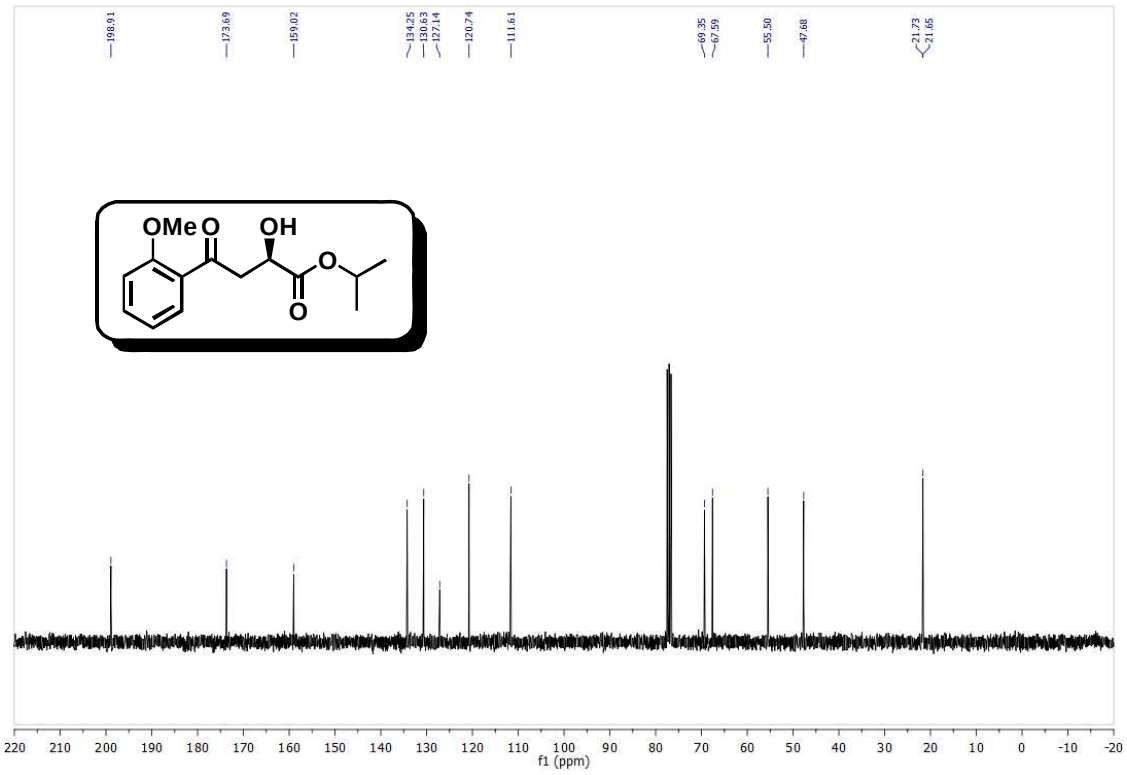


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.578	MM	1.0541	9887.50391	156.33430	50.9842
2	23.597	VV	1.2025	9505.77734	107.82711	49.0158

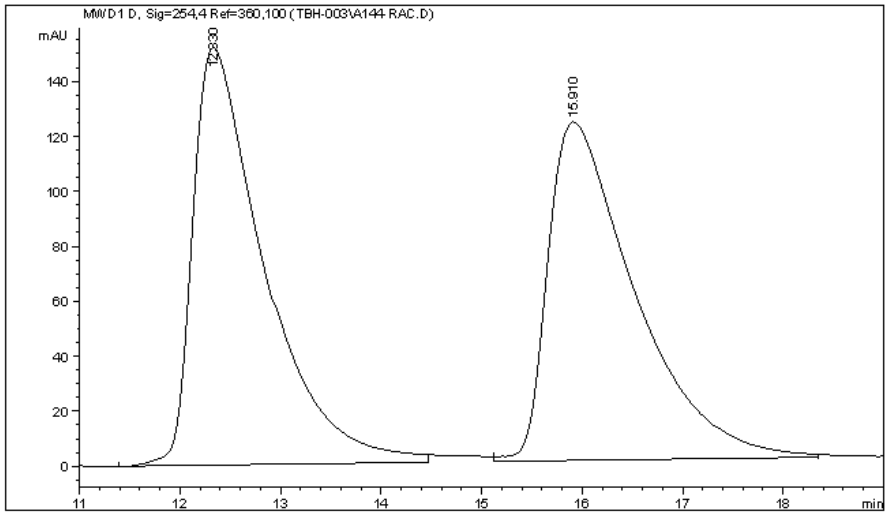


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.793	MM	0.7741	102.09519	2.19814	4.0490
2	22.135	MM	1.1928	2419.40942	33.80698	95.9510

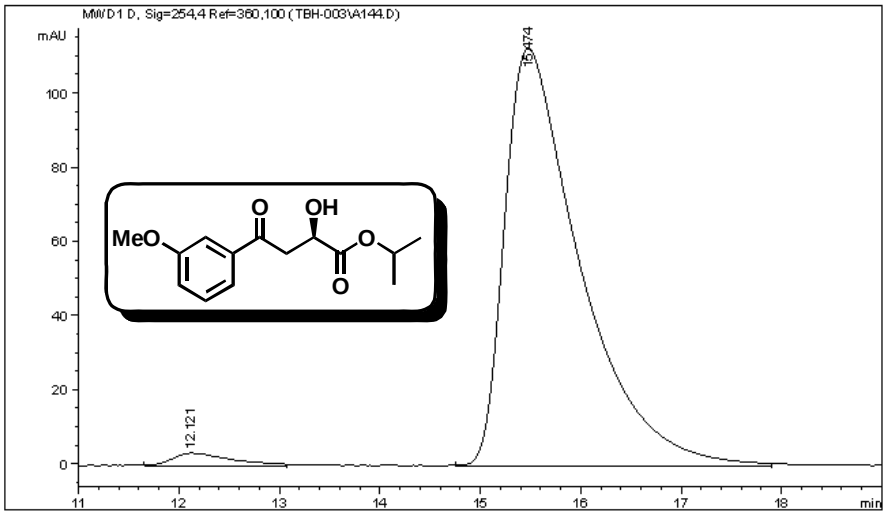




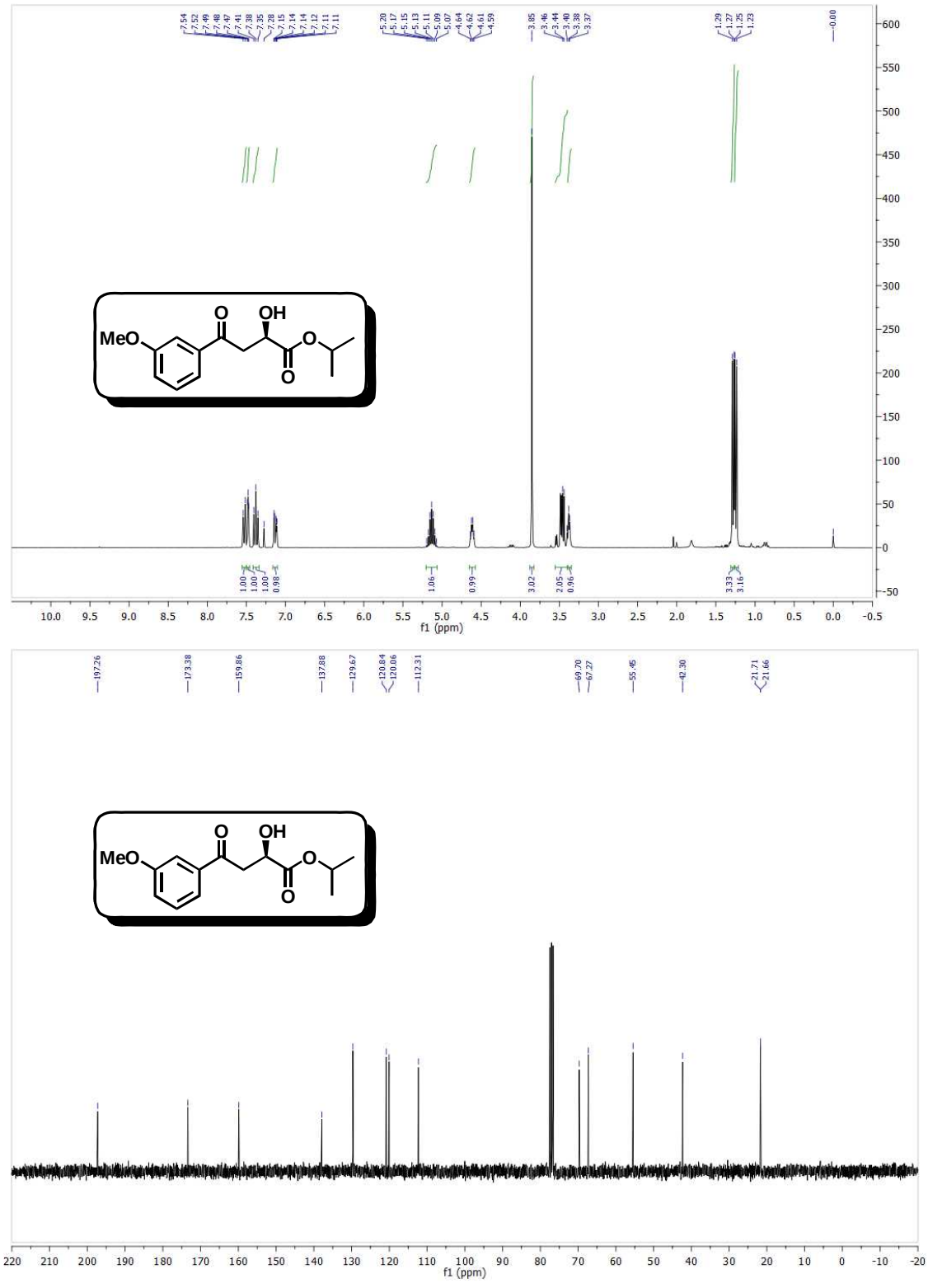
(*R*)-isopropyl 2-hydroxy-4-(3-methoxyphenyl)-4-oxobutanoate



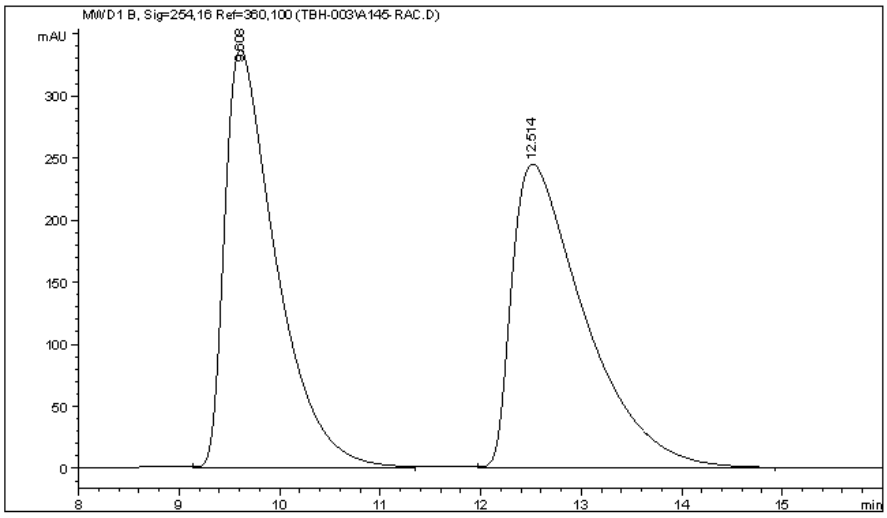
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.330	BV	0.7036	7511.45996	151.71510	50.3255
2	15.910	VV	0.8224	7414.30713	123.15359	49.6745



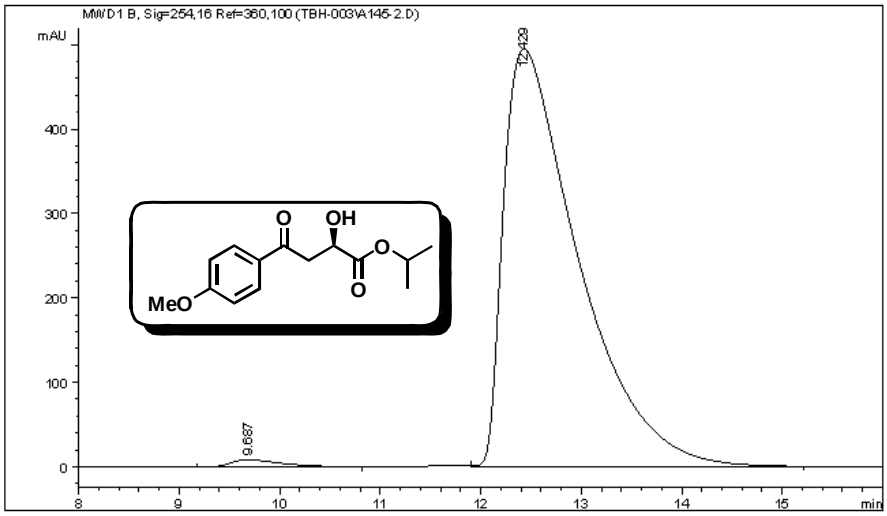
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.121	VV	0.4933	139.49068	3.40982	2.3205
2	15.474	VV	0.7345	5871.62500	112.57883	97.6795



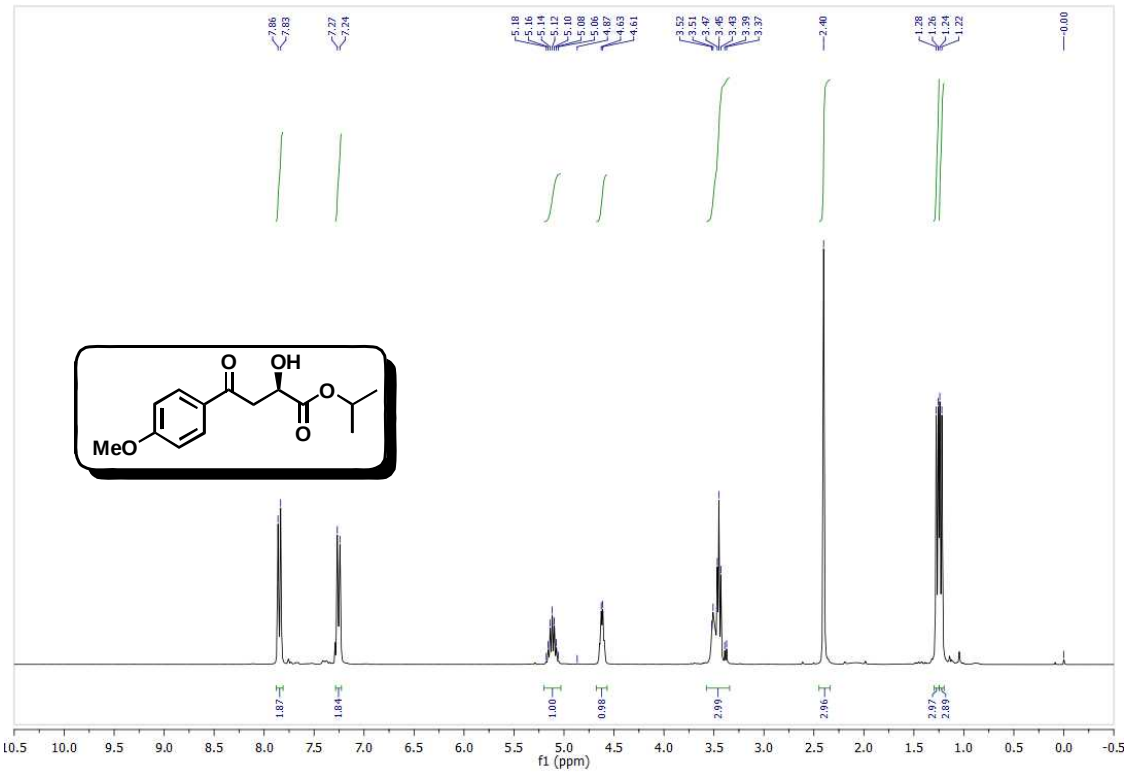
(*R*)-isopropyl 2-hydroxy-4-(4-methoxyphenyl)-4-oxobutanoate

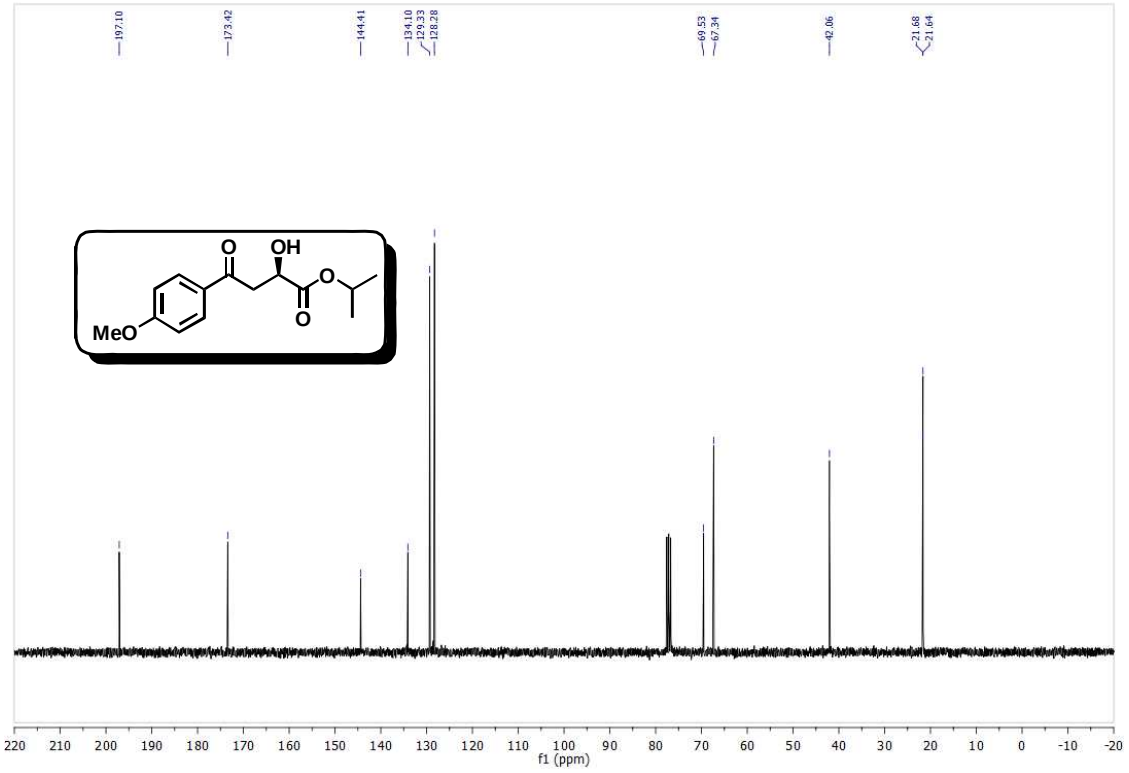


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.608	VB	0.5248	1.19906e4	337.22604	49.3060
2	12.514	VB	0.7195	1.23282e4	244.81075	50.6940

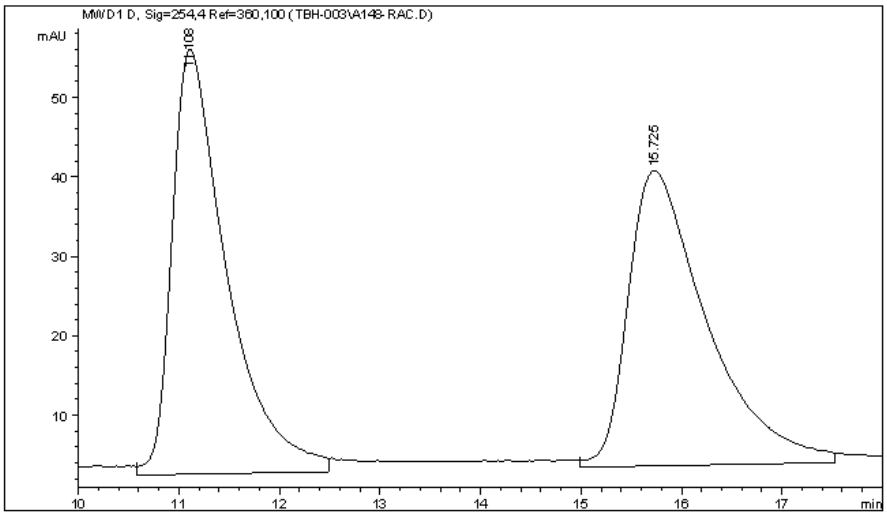


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.687	BV	0.4706	309.28354	8.74532	1.1911
2	12.429	VB	0.7466	2.56577e4	495.12180	98.8089

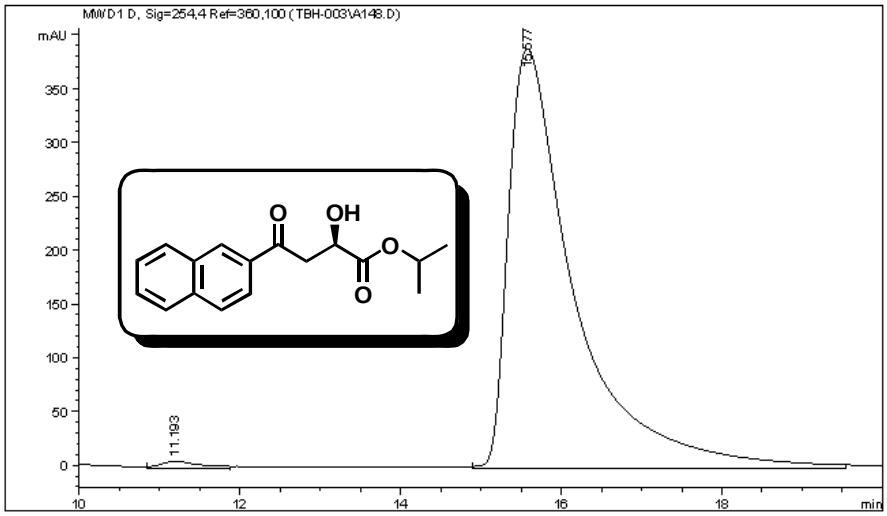




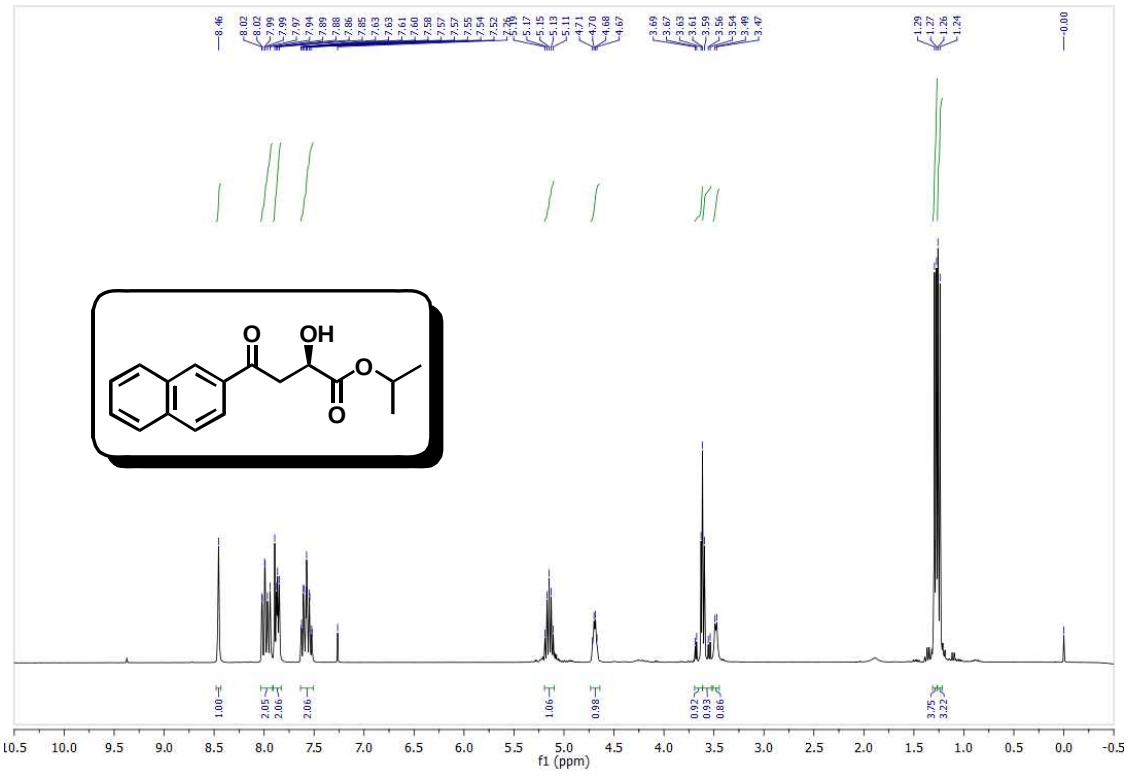
(*R*)-isopropyl 2-hydroxy-4-(naphthalen-2-yl)-4-oxobutanoate

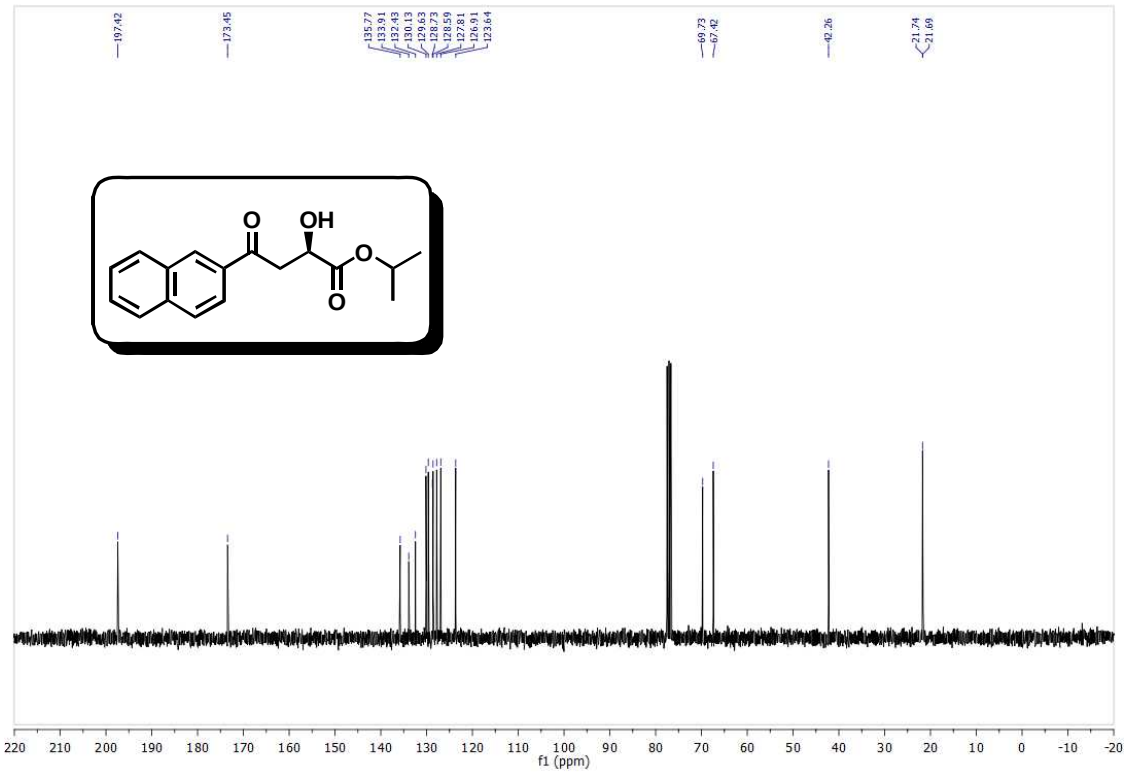


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.108	VV	0.5356	2025.58313	53.51257	49.9860
2	15.725	BV	0.7242	2026.71643	37.16394	50.0140

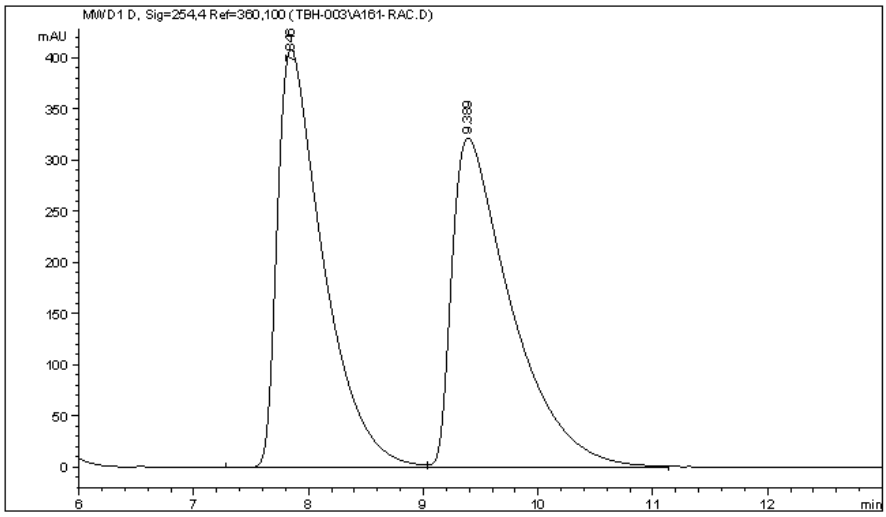


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.193	VV	0.4164	220.93372	6.53582	0.9807
2	15.577	VB	0.8136	2.23075e4	389.80887	99.0193

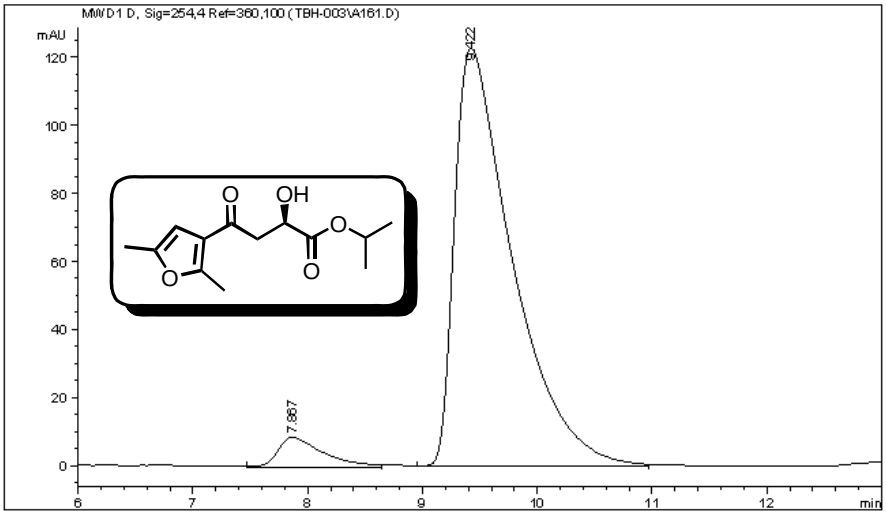




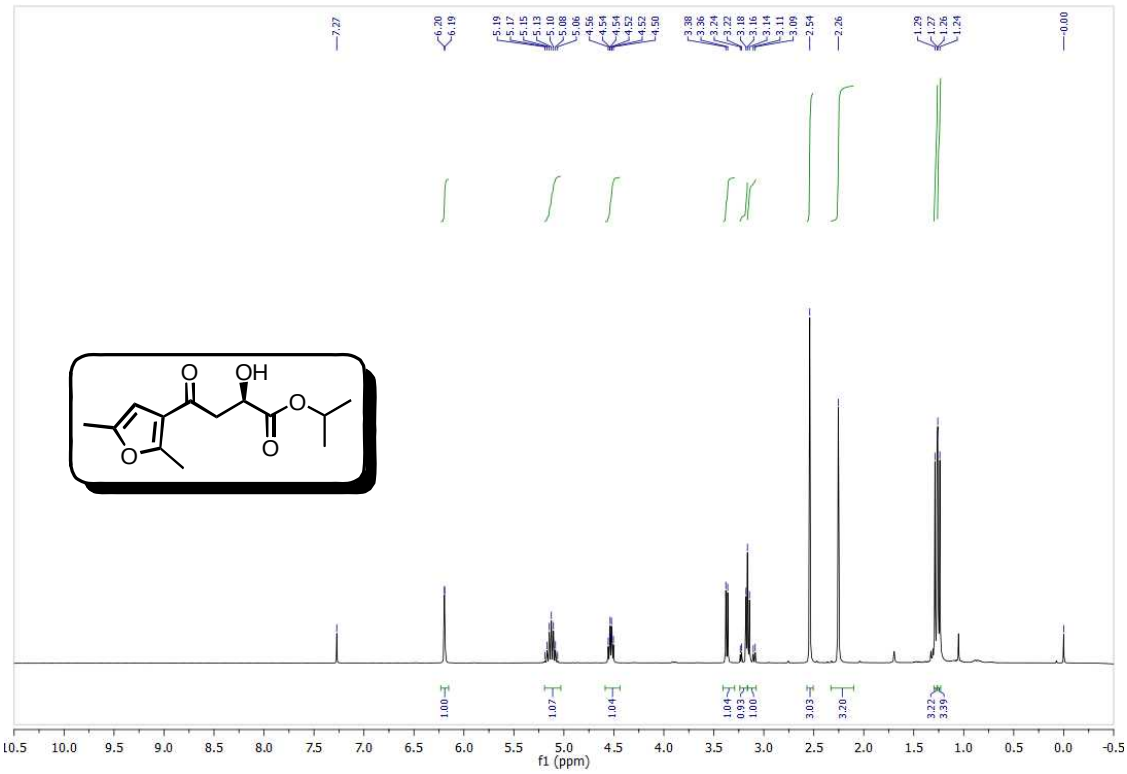
(*R*)-isopropyl 4-(2,5-dimethylfuran-3-yl)-2-hydroxy-4-oxobutanoate

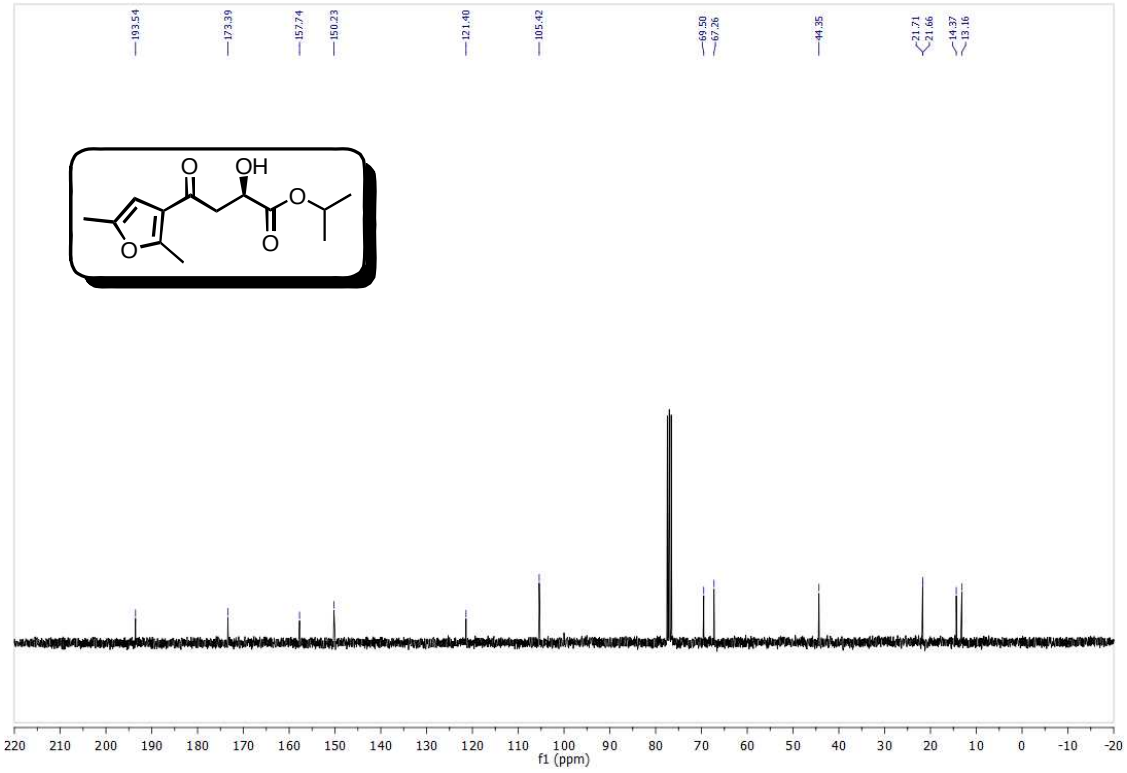


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.846	VV	0.4036	1.13255e4	408.29367	49.6027
2	9.389	VV	0.5078	1.15069e4	321.30951	50.3973

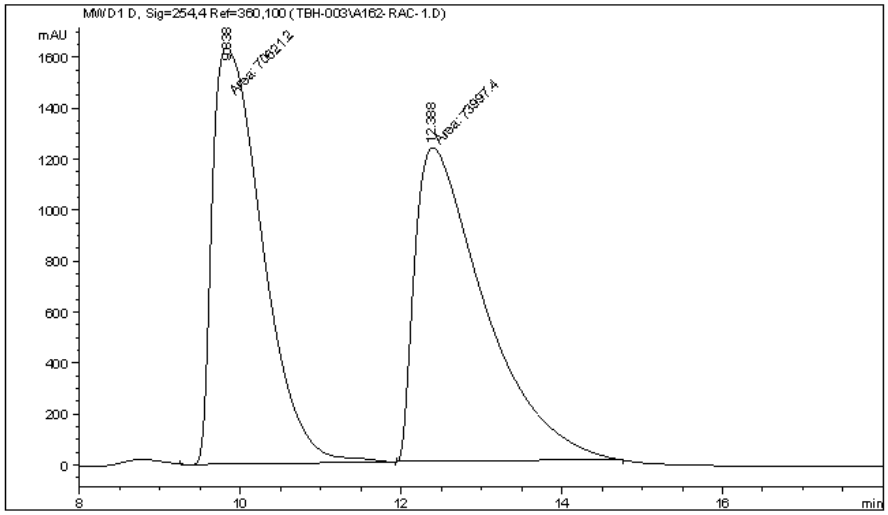


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.867	VV	0.3637	237.91139	8.73542	5.2142
2	9.422	VV	0.5060	4324.84033	123.07326	94.7858

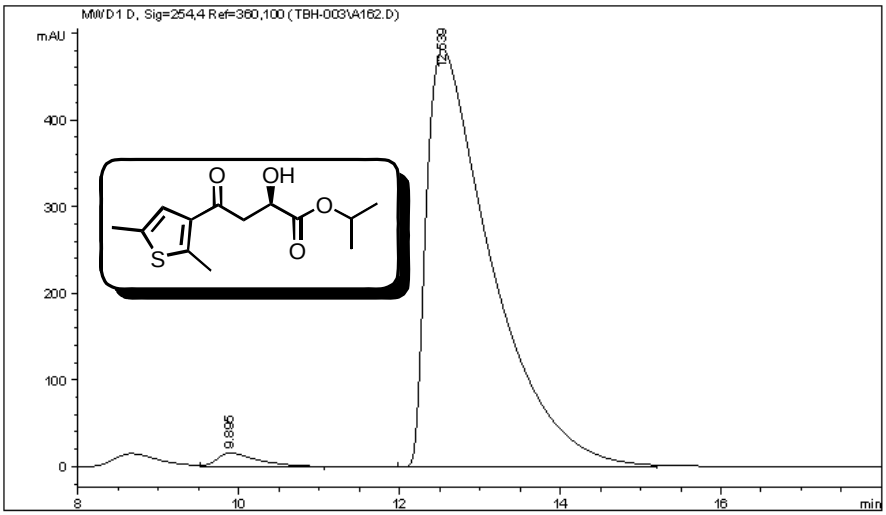




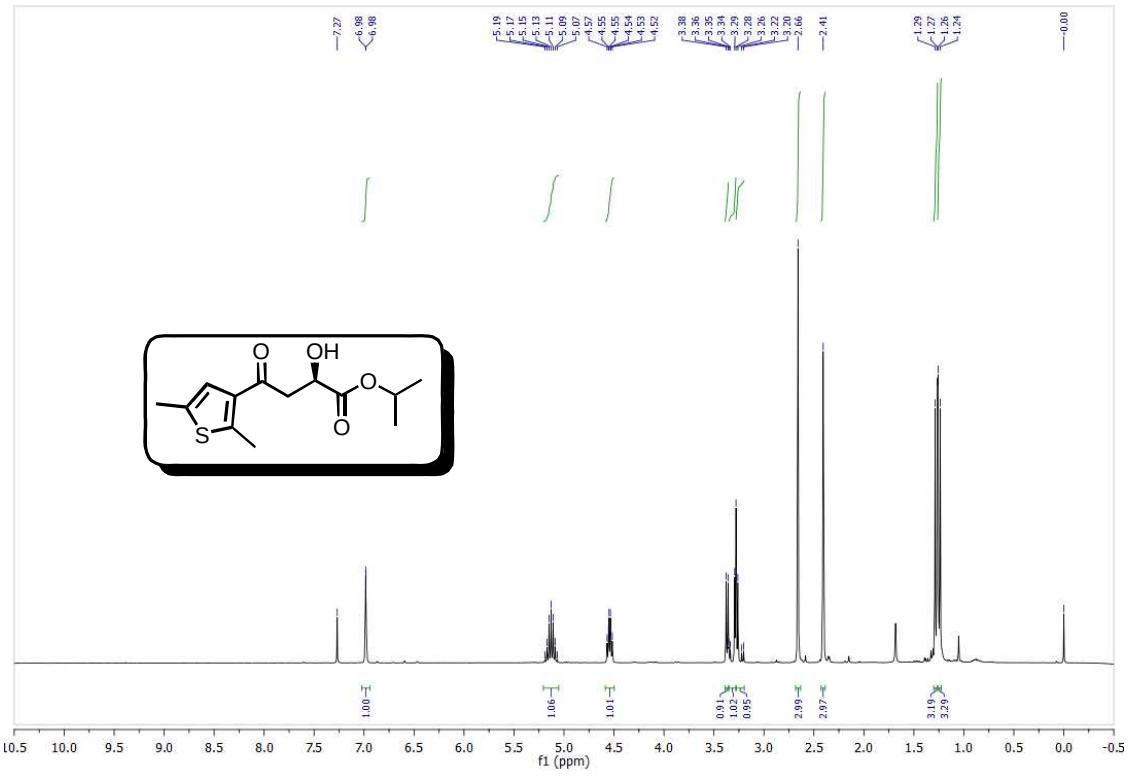
(*R*)-isopropyl 4-(2,5-dimethylthiophen-3-yl)-2-hydroxy-4-oxobutanoate

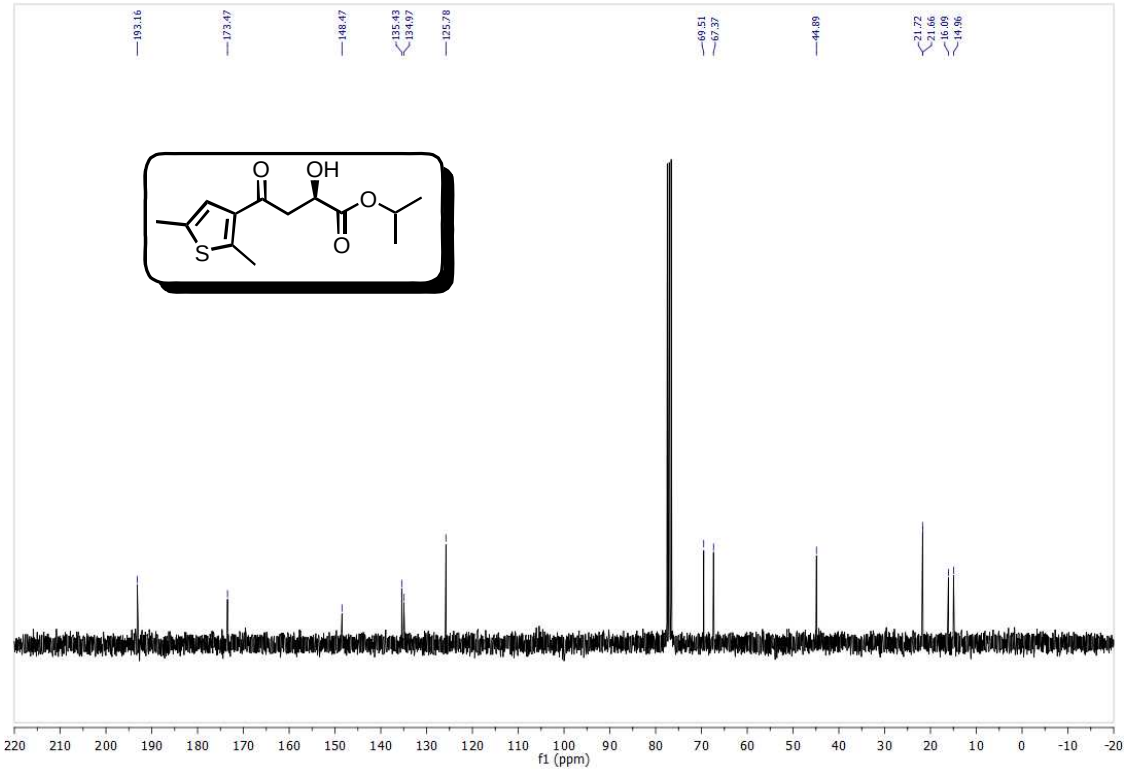


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.838	MM	0.7212	7.06212e4	1631.98828	48.8327
2	12.388	MM	1.0046	7.39974e4	1227.62646	51.1673

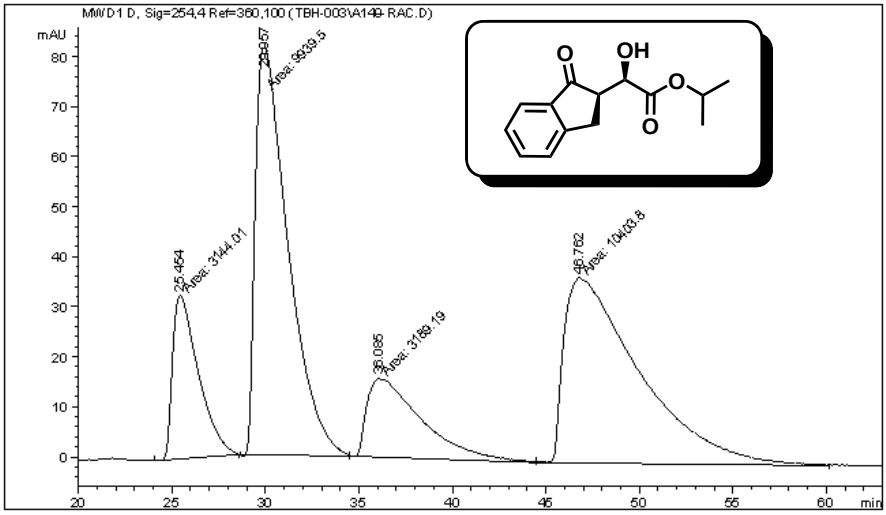


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.895	VV	0.4781	591.61829	16.43067	2.1344
2	12.539	VV	0.7863	2.71261e4	482.17899	97.8656

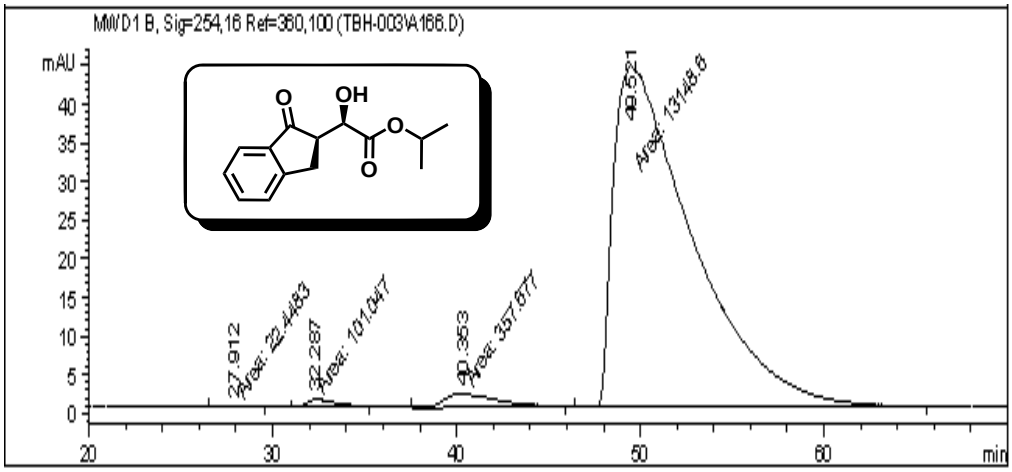




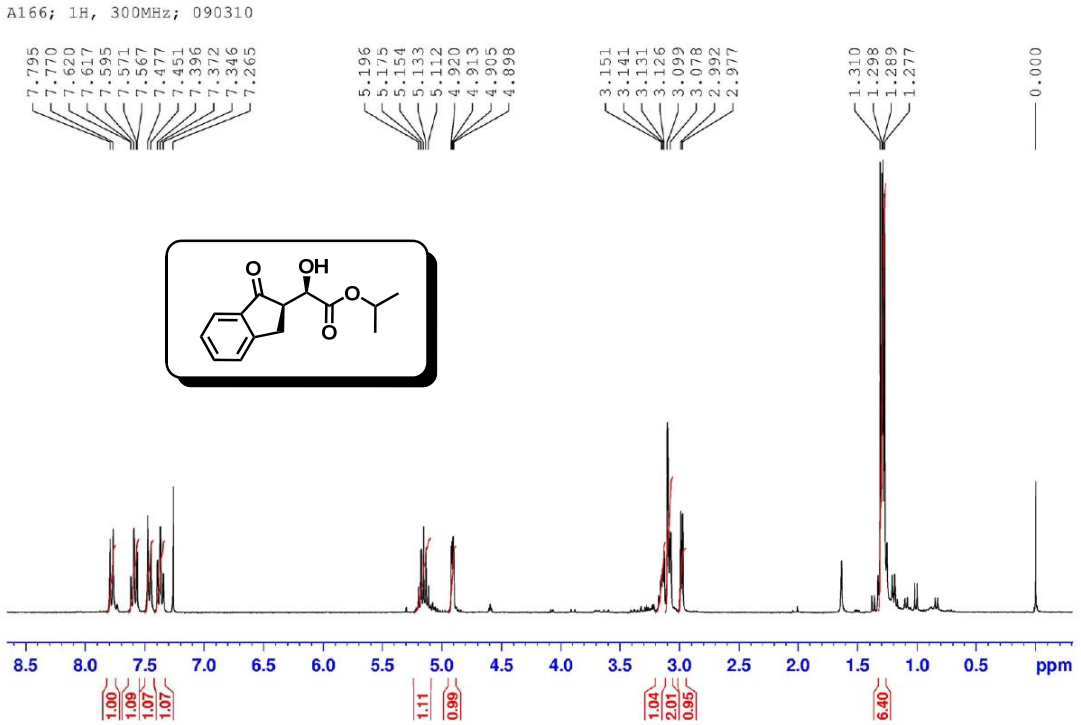
(2*R*)-isopropyl 2-hydroxy-2-(1-oxo-2,3-dihydro-1H-inden-2-yl)acetate

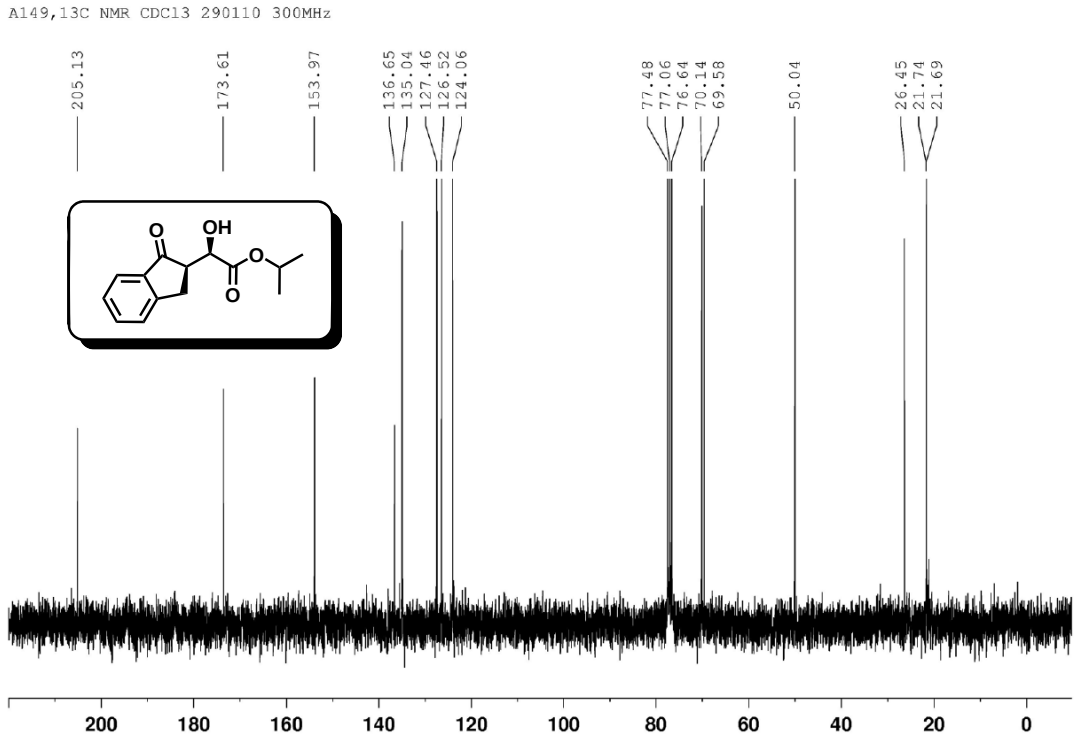


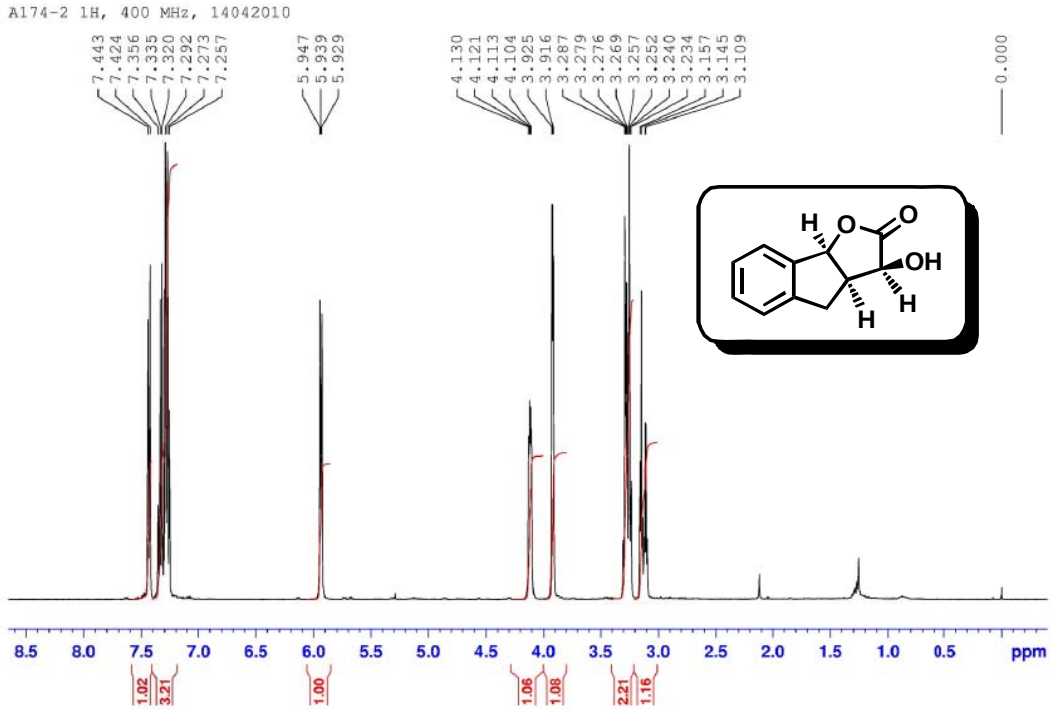
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.454	MM	1.6048	3144.01099	32.65192	11.7857
2	29.957	MM	2.0364	9939.49707	81.34872	37.2594
3	36.085	MM	3.3840	3189.19214	15.70726	11.9551
4	46.762	MM	4.6861	1.04038e4	37.00249	38.9998

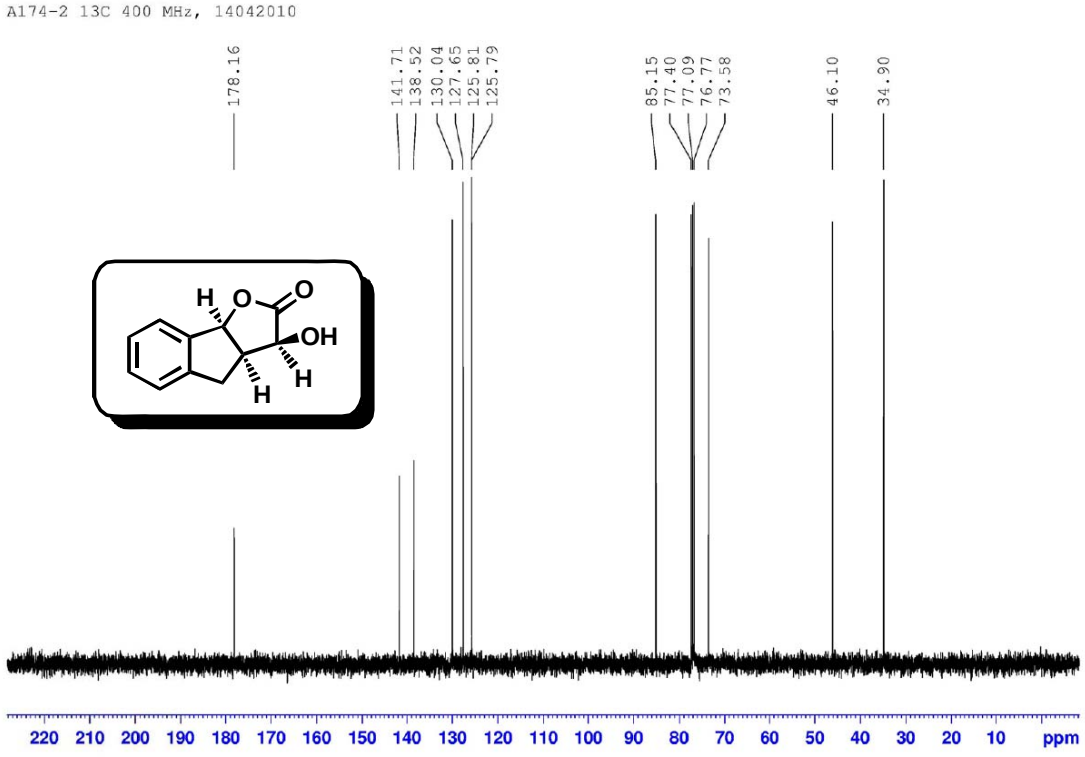


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.912	MM	1.5386	22.44826	2.43165e-1	0.1647
2	32.287	MM	1.7511	101.04681	9.61745e-1	0.7414
3	40.353	MM	3.2642	357.67703	1.82628	2.6242
4	49.521	MM	4.9573	1.31486e4	44.20634	96.4697


A166; 1H, 300MHz; 090310
7.795
7.770
7.620
7.617
7.595
7.571
7.567
7.477
7.451
7.396
7.372
7.346
7.265
5.196
5.175
5.154
5.133
5.112
4.920
4.913
4.905
4.898
3.151
3.141
3.131
3.126
3.099
3.078
2.992
2.977
1.310
1.298
1.289
1.277
0.000
O
OH
O
O
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
ppm
1.00
1.09
1.07
1.07
1.11
0.99
1.04
2.01
0.95
6.40


A149,13C NMR CDCl3 290110 300MHz
205.13
173.61
153.97
136.65
135.04
127.46
126.52
124.06
77.48
77.06
76.64
70.14
69.58
50.04
26.45
21.74
21.69
O
OH
O
O
200
180
160
140
120
100
80
60
40
20
0


A174-2 1H, 400 MHz, 14042010
7.443
7.424
7.356
7.335
7.320
7.292
7.273
7.257
5.947
5.939
5.929
4.130
4.121
4.113
4.104
3.925
3.916
3.287
3.279
3.276
3.269
3.257
3.252
3.240
3.234
3.157
3.145
3.109
0.000
H
O
O
OH
H
H
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
ppm
1.02
3.21
1.00
1.06
1.08
2.21
1.16


A174-2 13C 400 MHz, 14042010
178.16
141.71
138.52
130.04
127.65
125.81
125.79
85.15
77.40
77.09
76.77
73.58
46.10
34.90
H
O
O
OH
H
H
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm