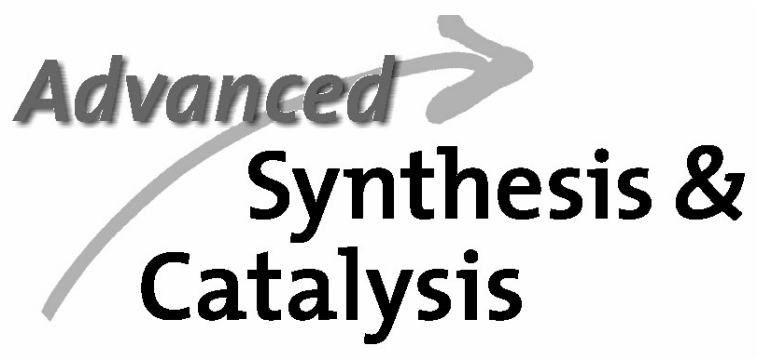

Supporting Information

Supporting information for:

Dimethylzinc mediated, oxidatively promoted Reformatsky reaction of ethyl iodoacetate with aldehydes and ketones

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1. General Information

General: ^{1}H NMR spectra were recorded on Varian 200 MHz or Varian 300 MHz spectrometers. Chemical Shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.27 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian 50 MHz or Varian 75 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). Mass spectra were performed at an ionising voltage of 70 eV. Chromatographic purification was done with 240-400 mesh silica gel. Analytical gas chromatography (GC) was performed on a Hewlett-Packard HP 6890 gas chromatograph with a flame ionization detector and split mode capillary injection system, using a Crosslinked 5% PH ME Siloxane (30 m) column or a Megadex5 chiral (25 m) column. Analytical high performance liquid chromatograph (HPLC) was performed on a HP 1090 liquid chromatograph equipped with a variable wavelength UV detector (deuterium lamp 190-600 nm), using a Daicel Chiralcel^{TM} OD column (0.46 cm I.D. x 25 cm) (Daicel Inc.) and AD. Column. HPLC grade isopropanol and hexane were used as the eluting solvents. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. All the reactions were carried out under a nitrogen atmosphere in flame-dried glassware using standard inert techniques for introducing reagents and solvents. All commercially available aldehydes were purified before use.

Me_2Zn 2M in toluene was purchased by Fluka. Anhydrous Et_2O, THF, and CH_2Cl_2 were purchased by Fluka.

All aldehydes and ketones were commercially available, and carefully purified by crystallization of distillation before their use.

General procedures for the Reformatsky reaction:

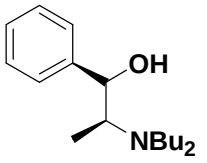
Method A. (For aromatic aldehydes and not enolizable aldehydes).

A flame-dried, 25 mL, two necked round-bottom flask, equipped with magnetic stirring bar and nitrogen inlet is charged with Et_2O (3 mL) and Me_2Zn (200 µL, 0.4 mmol, 2 equiv). The solution is then cooled to 0°C in an ice-water bath and the ethyl iodoacetate (50 µL, 0.4 mmol, 2 equiv) is added. The flask is connected to air through a calcium chloride drying tube. After 30 min the aldehyde or ketone (0.2 mmol) and Ph_3PO (30 mol%, 17 mg) are added. The mixture is stirred for 1-3 hours then quenched with HCl 1N and diluted with Et_2O. The phases are separated, and the aqueous phase is extracted with Et_2O. The organic phases is collected, dried over Na_2SO_4 and evaporated under reduced pressure to give an yellow pale oil purified by chromatography (Et_2O:cyclohexane).

Method B (For enolizable aldehydes and ketones).
Catalytic enantioselective Reformatsky reaction with benzaldehyde or acetophenone:

A flame-dried, 25 mL, two necked round-bottom flask, equipped with magnetic stirring bar and nitrogen inlet is charged with Et_2O (3 mL), THF (2 mL), Me_2Zn (150 µL, 1,5 equiv.) The mixture is then cooled to 0°C in an ice-water bath and aldehyde or ketone (0.2 mmol), ethyl iodoacetate (50 µL, 0.4 mmol, 2 equiv) and Ph_3PO (20 mol%, 11.2 mg) are added in sequence. The flask is connected to air through a calcium chloride drying tube and the mixture is stirred for 24 hours, then quenched with HCl 1N and diluted with Et_2O. The phases are separated, and the aqueous phase is extracted with Et_2O (3 x 3 mL). The organic phases were reunited, dried over Na_2SO_4 and evaporated under reduced pressure to give an yellow pale oil purified by chromatography (Et_2O:cyclohexane).

Ligands tested in the catalytic enantioselective reaction with Benzaldehyde



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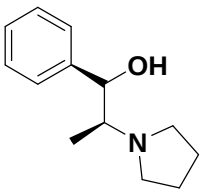

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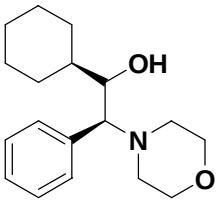

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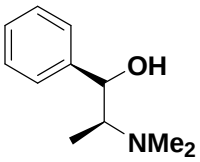

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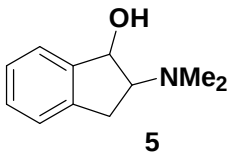

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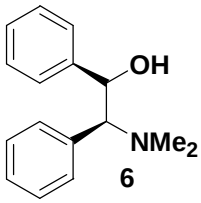

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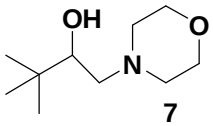

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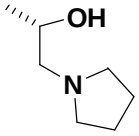

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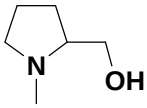

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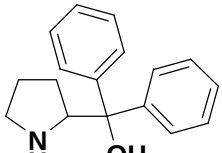

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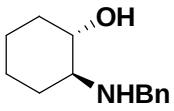

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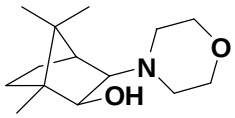
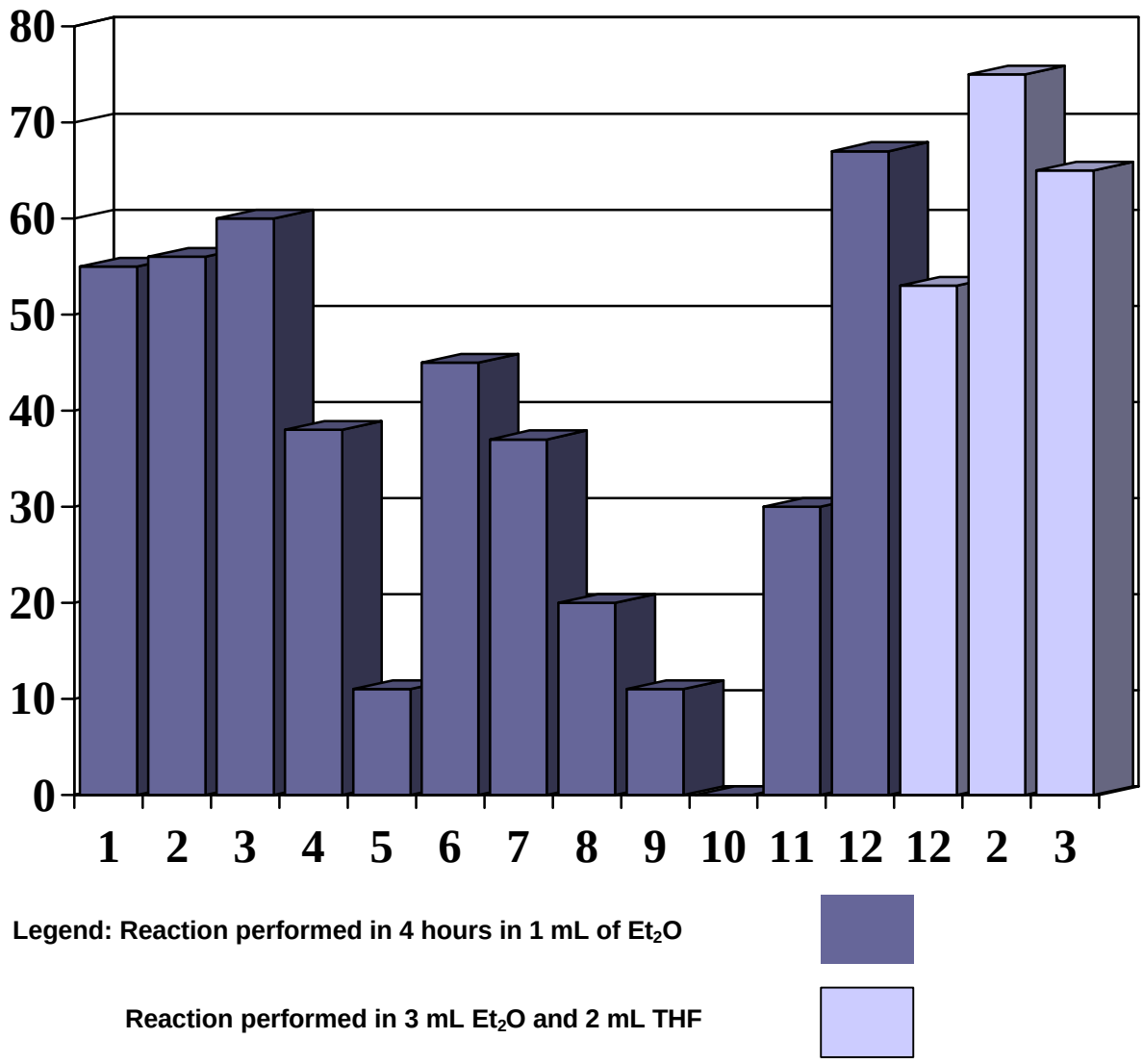


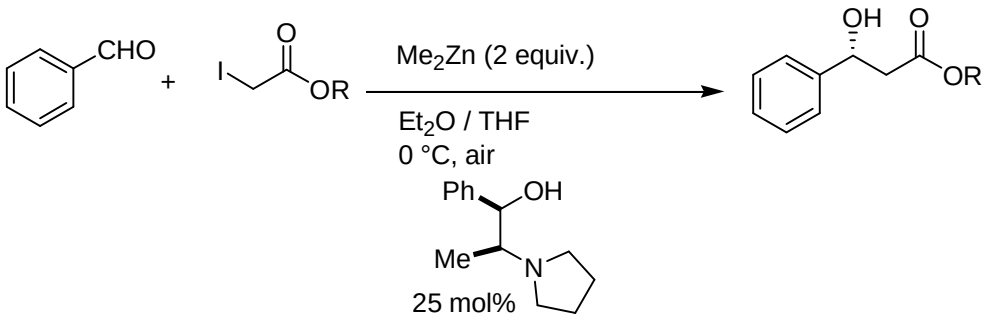
12

Results obtained.

In the graph are reported the enantiomeric excesses obtained with the ligands **1**-**12**, performing the reaction in Et_2O, and in Et_2O/THF. In more concentrate conditions the enantiomeric excesses are decreased. Performing the reaction by slow addition with a syringe pump (adding the iodoacetate) does not improve the enantiomeric excess obtained in the model reaction.



Enantioselective Reformatsky reaction with PhCHO performed with different iodo esters.

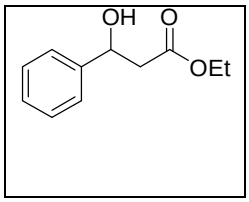


Entry	R	E.e %[a]
1	**Ethyl**	**73**
2	***t*Butyl**	40
3	**Methyl**	63
4	**Benzyl**	67
5	***o*MethoxyBenzyl**	60

Catalytic enantioselective Reformatsky reaction with benzaldehyde or acetophenone:

A flame-dried, 25 mL, two necked round-bottom flask, equipped with magnetic stirring bar and nitrogen inlet is charged with Et_2O (3 mL), THF (2 mL), Me_2Zn (150 µL, 1,5 equiv.) and (1*R*, 2*S*)-N-pyrrolydinephedrine (25% mol, 10.3 mg). The mixture is then cooled to 0°C in an ice-water bath and aldehyde or ketone(0.2 mmol), ethyl iodoacetate (50 µL, 0.4 mmol, 2 equiv), Ph_3PO (20 %mol, 11.2 mg) are added in sequence. The flask is connected to air through a calcium chloride drying tube and the mixture is stirred for 87 hours then quenched with HCl 1N and diluted with Et_2O. The phases are separated, and the aqueous phase is extracted with Et_2O. The organic phases is collected, dried over Na_2SO_4 and evaporated under reduced pressure to give an yellow pale oil purified by chromatography (Et_2O:cyclohexane 8:2).

Ethyl 3-hydroxy-3-phenyl-propanoate



$C_{11}H_{14}O_3$ Fw = 194.22

Colourless oil.

$[a]_D$ = +38 (c 1, $CHCl_3$). Lit.[1] (S)-Methyl-3-phenyl-3-hydroxypropanoate $[a]_D$ = -17 (c 1, MeOH).

IR (film): 3444 (s), 3086 (w), 3063 (w), 3032 (w), 2982 (m), 2920 (m), 1724 (s), 1493 (w), 1454 (m), 1396 (w), 1373 (m), 1296 (w), 1269 (m), 1195 (m), 1161(m), 1038 (m), 914 (w), 871 (w), 760 (m), 737 (m), 702 (m), 604 (w) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.27 (3H, t, J = 7.3 Hz); 2.70 (1H, ABX, *J* = 4.5, 16.5 Hz); 2.78 (1H, ABX, J = 8.4, 16.5 Hz); 4.19 (2H, q, *J* = 7.3 Hz); 5.15 (1H, dd, *J* = 4.5, 8.4 Hz); 7.28-7.41 (5H, m).

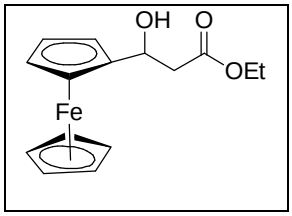
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1; 43.3; 60.8; 70.3; 125.6(2); 127.7; 128.5(2); 142.5; 172.4.

GC MS: 194(31); 176(5); 165(5); 147(10); 131(10); 120(19); 107(100); 88(17); 79(70); 60(11); 51(19).

ESI-MS: rt 5.4 min *m/z*: 195.1 (M+H); 412.2 (2M + Na).

HPLC analysis OD: isocratic, flux 0.5mL/min (hexane: *i*-PrOH) 90:10. tm 15 min; TM: 20 min.

Ethyl 3-hydroxy-3-ferrocenyl-propanoate



$C_{15}H_{18}O_3$ Fw = 302.06

Red oil.

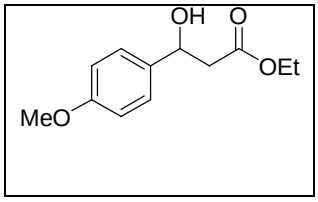
IR (film): 3460 (s), 3093 (m), 2982 (m), 2927 (m), 2854 (m), 2360 (w), 2341 (w), 1732 (s), 1627 (w), 1373 (m), 1273 (m), 1196 (m), 1161 (m), 1026 (s), 818 (m) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.30 (3H, t, *J* = 6.9 Hz); 1.60 (1H, brs); 2.68-2.78 (2H, m); 4.17-4.27 (11H, m); 4.87 (1H, t, *J* = 6.6 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.2; 42.7; 60.7; 66.0; 66.4; 66.5; 68.0; 68.1; 68.5(5); 91.5; 172.0.

GC MS: 302(9), 284(100), 256(34), 239(8), 219(28), 191(16), 175(25), 147(17), 121(35), 89(13), 56(12).

Ethyl 3-hydroxy-3(4-methoxyphenyl)-propanoate



$C_{12}H_{16}O_4$ Fw = 224.10

Yellow oil.

IR (film): 3452 (m); 2982 (m); 2962 (m); 2935 (m); 2839 (m); 1731 (s); 1621 (m);1512 (s); 1373 (m); 1304 (w); 1250 (m); 1176 (m); 1034 (m); 833 (m) cm^{-1}.

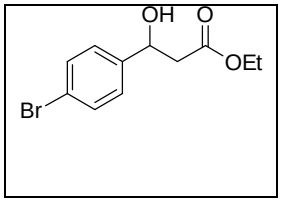
^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.27 (3H, t, J = 7 Hz); 2.68 (ABX, 1H, J = 4.0, 16.5 Hz); 2.77 (ABX, 1H, J = 9, 16.5 Hz); 3.19 (1H, brs); 3.81 (3H, s); 4.19 (2H, q, J = 7.0 Hz); 5.10 (1H, dd, J = 4.0, J = 9.0 Hz); 6.89 (2H, d, J = 9.0 Hz); 7.31 (2H, d, J = 9 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1; 43.3; 55.2; 60.8; 69.9; 113.8(2); 126.9(2); 134.7; 159.2; 172.4.

GC MS: 224(9); 206(28); 191(1); 178(4); 161(40); 137(100); 109(20); 94(12); 77(17).

ESI-MS: rt 5.3 min *m/z*: 471.0 (2M + Na).

Ethyl 3-hydroxy-3-(4-bromophenyl)-propanoate



$C_{11}H_{13}BrO_3$ Fw = 272.12

Yellow pale oil

IR (film): 3460 (m); 3063 (w); 2981 (m); 2931 (w); 1728 (s); 1597 (w); 1570 (m); 1473 (m); 1373 (m); 1296 (m); 1192 (s); 1095 (m); 1074 (m); 1037 (m); 891 (w); 787 (m); 694 (m); 667 (w) cm^{-1}.

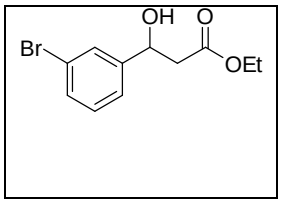
^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.28 (3H, t, J = 10.5 Hz); 2.71 (2H, d, J = 6.0 Hz); 4.20 (2H, q, J = 10.5 Hz); 5.10 (1H, t, J = 6 Hz); 7.27 (2H, d, J = 12.6 Hz); 7.50 (2H, d, J = 12.6 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1; 43.1; 61.0; 69.6; 121.6; 127.4(2); 131.6(2); 141.5; 172.2.

GC MS: 274(18) [M^+; ^{81}Br]; 272(18) [M^+; ^{79}Br]; 254(2); 227(8); 211(5); 198(6); 185(100); 157(20); 105(17); 88(40); 77(56).

ESI-MS: rt: 10.9 min. *m/z:* 275.9 ($M+H^+$; ^{81}Br); 292.1 ($M+H_2O$; ^{81}Br); 296.9 ($M+Na^+$; ^{81}Br); 313.1 ($M+K^+$; ^{81}Br).

Ethyl 3-hydroxy-3-(3-bromophenyl)-propionate



$C_{11}H_{13}BrO_3$ Fw = 272.12

Yellow oil

IR (film): 3440 (m); 3063 (w); 2982 (m); 2935 (w); 2905 (w); 1727 (s); 1523 (w); 1570 (w); 1473 (m); 1373 (m); 1191 (m); 1161 (m); 1095 (m); 1072 (m); 1037 (m); 825 (w); 787 (w); 698 cm^{-1}.

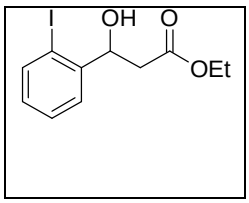
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.29 (3H, t, J = 7 Hz); 2.73 (2H, d, J = 6.0 Hz); 4.21 (2H, q, J = 7.0 Hz), 5.12 (1H, t, J = 6.0 Hz); 7.22-7.34 (2 H, m); 7.44 (1H, dt, J = 1.5, J = 7.8 Hz); 7.58 (1H, J = 1.5 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1; 43.1; 61.0; 122.6; 124.3; 128.8; 130.8; 130.1; 130.8; 144.8; 172.2.

GC MS: 274(37) (M^+; ^{81}Br); 272(37) (M^+; ^{79}Br); 256(2); 245(3); 227(17); 209(5); 198(18); 185(100); 157(38); 105(23); 88(46); 77(42); 70(14); 60(23); 51(22).

ESI-MS: rt: 7.8 *m/z:* 275.9 ($M+H^+$; ^{81}Br); 292.1 ($M+H_2O$; ^{81}Br); 296.9 ($M+Na^+$; ^{81}Br); 313.1 ($M+K^+$; ^{81}Br).

Ethyl 3-hydroxy-3-(2-iodophenyl)-propionate



$C_{11}H_{13}IO_3$ Fw = 320.12

Pink oil.

IR (film): 3475 (s); 3059 (w); 2982 (m); 2931 (w); 1724 (s); 1585 (w); 1562 (w); 1461 (m); 1434 (m); 1373 (m); 1292 (m); 1196 (m); 1115 (m); 1072 (m); 1011 (m); 867 (w); 756 (m); 652 (w); 609 (w) cm^{-1}.

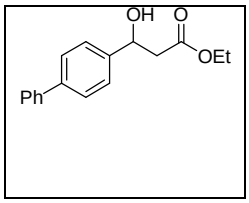
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.29 (3H, t, J = 7.2 Hz); 2.53 (1H, dd, J = 2.4, 16.8 Hz); 2.85 (1H, dd, J = 2.4, 16.8 Hz); 4.22 (2H, q, J = 7.2 Hz); 5.29 (1H, d, J = 9.6 Hz); 6.99 (1H, dt, J = 1.8, 7.8 Hz); 7.39 (1H, dt, J = 1.2, 7.5 Hz); 7.59 (1H, dd, J = 1.8, 7.8 Hz); 7.80 (1H, dd, J = 1.2, 7.8 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1; 41.6; 61.0; 73.7; 96.8; 127.0; 128.6; 129.4; 139.3; 144.23; 172.3.

GC MS: 320(1); 303(1); 275(3); 233(81); 193(100); 165(18); 147(56); 123(9); 105(56); 91(21); 78(56).

ESI-MS: rt: 9.0 min; *m/z:* 293.1 ($M+Na^+$); 563.0 ($2M+Na^+$).

Ethyl 3-hydroxy-3(4-phenylphenyl)-propionate



$C_{17}H_{18}O_3$ Fw = 270.32

White solid.

m.p.:79-81 °C

IR (film): 3437 (m); 3076 (w); 3032 (w); 2982 (w); 2916 (w); 1728 (m); 1485 (w); 1373 (w); 1157 (m); 1038 (m); 833 (m); 764 (m); 698 (m) cm^{-1}.

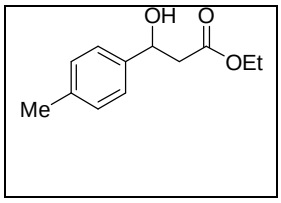
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.29 (3H, t, J = 7.2 Hz); 2.78 (1H, ABX, J =4.5, 16.5 Hz); 2.80 (1H, ABX, J =8.4, 16.5 Hz); 4.22 (2H, q, J = 7.2 Hz); 5.20 (1H, dd, J = 4.5 Hz; J = 8.4 Hz); 7.33-7.39 (1H, m); 7.42-7.50 (4H, m); 7.58-7.62 (4H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1; 43.2; 60.9; 70.0; 126.1(2); 127.0(2); 127.2(2); 127.3(2); 128.7(2); 140.7; 141.5; 172.4.

GC MS: 270(22); 252(43); 224(7); 207(28); 183(100); 165(16); 152(42); 77(5).

ESI-MS: rt: 9.0 min; *m/z:* 293.1 ($M+Na^+$); 563.0 ($2M+Na^+$).

Ethyl 3-hydroxy-3-(4-methylphenyl)-propionate



$C_{12}H_{16}O_3$ Fw = 208.25

Colorless oil

IR (film): 3460 (s); 2982 (m); 2924 (m); 2874 (m); 1731 (s); 1516 (w); 1446 (m); 1373 (m); 1265 (m); 1196 (s); 1161 (s); 1038 (s); 818 (m) cm^{-1}.

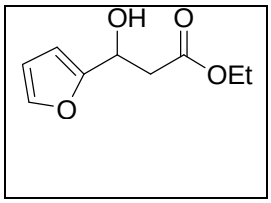
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.27 (3H, t, J = 7 Hz); 2.35 (3H, s); 1.62 (1H, ABX, J = 4.2, 16.5 Hz); 2.77 (1H, ABX, J = 9, 16.5 Hz); 4.21 (2H, q, J = 7 Hz); 5.11 (1H, J = 4.2, 9.0 Hz); 7.18 (2H, J = 8.1 Hz); 7.28 (2H, d, J = 8.1 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1; 21.1; 43.3; 60.8; 70.2; 125.6(2); 129.2(2); 137.5; 139.6; 172.4.

GC MS: 208(20); 193(13); 163(4); 145(14); 134(6); 121(100); 105(11); 91(51); 77(21); 65(12).

ESI-MS: rt: 6.8 min; *m/z:* 231.1 ($M+Na^+$); 439.1 ($2M+Na^+$).

Ethyl 3-hydroxy-3-(2-furyl)-propionate



$C_9H_{12}O_4$ Fw = 184.18

dark yellow oil

IR (film): 3441 (m); 3059 (w); 2982 (m); 2935 (w); 1732 (s); 1632 (w); 1504 (w); 1373 (m); 1265 (m); 1165 (m); 1018 (m); 814 (w); 737 (m) cm^{-1}.

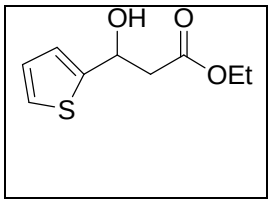
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.28 (3H, t, J = 7.2 Hz); 2.83 (1H, ABX, J = 4.2, 16.8 Hz); 2.92 (1H, ABX, J = 8.2, 16.8 Hz); 3.25 (1H, brs); 4.20 (2H, q, J = 7.2 Hz); 5.15 (1H, dd, J = 4.2, 8.2 Hz); 6.28 (1H, d, J = 3.3 Hz); 6.34 (1H, dd, J = 1.8, 3.3 Hz); 7.38 (1H, d, J = 1.8 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1; 39.86; 60.9; 64.2; 106.3; 110.3; 142.2; 154.7; 171.9.

GC MS: 184(18); 166(14); 155(4); 137(16); 121(26); 110(21); 97(100); 81(4); 65(18).

ESI-MS: rt: 6.8 min; *m/z:* 231.1 ($M+Na^+$); 439.1 ($2M+Na^+$).

Ethyl 3-hydroxy-3-(2-thienyl)-propanoate



$C_9H_{12}O_3S$ Fw = 200.25

dark yellow oil

IR (film): 3440 (m); 3105 (w); 2982 (m); 2931 (w); 1728 (s); 1419 (m); 1373 (m); 1277 (m); 1165 (m); 1038 (m); 852 (w); 791 (m); 737 (w); 679 (w) cm^{-1}.

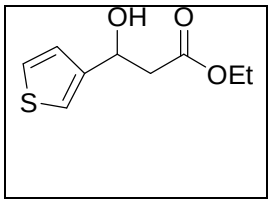
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.27 (3H, t, J = 7.2Hz); 2.80-2.83 (2H, m); 3.32 (1H, brs); 4.19 (2H, q, J = 7.2 Hz); 5.21 (1H, t, J = 6.3 Hz); 7.08 (1H, dd, J = 1.5, 5.1 Hz); 7.23-7.25 (1H, m); 7.31 (1H, dd; J = 3, 5.1 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1; 42.5; 60.8; 66.7; 120.9; 125.4; 126.2; 143.9; 172.2.

GC MS: 200(46); 184(14); 154(14); 137(31); 113(100); 97(10); 85(95); 65(13).

ESI-MS: rt: 4.4 min; *m/z*: 223.6 ($M+Na^+$); 239.1 ($M+K^+$).

Ethyl 3-hydroxy-3-(3-thienyl)-propanoate



$C_9H_{12}O_3S$ Fw = 200.25

dark yellow oil

IR (film): 3441 (m); 3105 (w); 2982 (w); 2935 (w); 2905 (w); 1728 (s); 1416 (m); 1373 (m); 1277 (m); 1173 (m); 1038 (m); 852 (w); 791 (m); 737 (w); 679 (w); 652 (w) cm^{-1}.

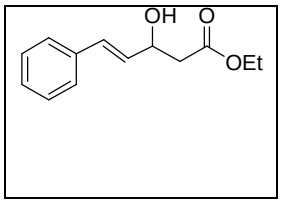
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.27 (3H, t, J = 7.2 Hz); 2.78-2.80 (2H, m); 3.31 (1H, brs); 4.19 (2H, t, J = 7.2 Hz); 5.22 (1H, t, J = 6 Hz); 7.09 (1H, dd, J = 1.2, 4.8 Hz); 7.24-7.25 (1H, m); 7.32 (1H, dd, J = 3, 4.8 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1; 42.5; 60.9; 66.7; 120.9; 125.5; 126.3; 143.9; 172.3.

GC MS: 200(46); 184(14); 154(14); 137(31); 113(100); 97(10); 85(95); 65(13).

ESI-MS: rt: 4.4 min; *m/z*: 223.6 ($M+Na^+$); 239.1 ($M+K^+$).

Ethyl 3-hydroxy-5-phenyl-pent-4-enoate



$C_{13}H_{16}O_3$ Fw = 220.11

yellow oil

IR (film): 3433 (m); 3082 (w); 3059 (w); 3028 (w); 2982 (w); 2931 (w); 1736 (s); 1493 (w); 1450 (w); 1373 (m); 1284 (w); 1161 (m); 1030 (m); 968 (w); 752 (m); 694 (m) cm^{-1}.

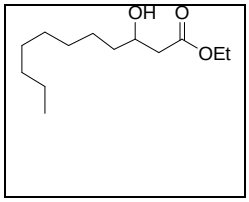
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.31 (3H, t, J = 7.2 Hz); 2.63 (1H, ABX, J = 7.5, 16.5 Hz); 2.71 (1H, ABX, J = 5.0, 16.5 Hz); 4.22 (2H, q, J = 7.2 Hz); 4.72-4.79 (1H, m); 6.26 (1H, dd, J = 6.0, 16.0 Hz); 6.69 (1H, J = 1.2, 16.0 Hz); 7.25-7.43 (5H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1; 41.5; 60.8; 68.9; 126.5, 127.8; 128.5(2); 129.5; 129.90; 130.7; 136.4; 178.2.

GC MS: 220(5); 202(23); 174(15); 157(17); 146(6); 129(100); 115(37); 104(73); 91(23); 77(32); 55(17).

ESI-MS: rt: 7.14 min; *m/z*: 243.2 ($M+H^+$); 441.6 ($2M+H^+$).

Ethyl 3-hydroxy-undecanoate



$C_{13}H_{26}O_3$ Fw = 230.34

Colourless oil

IR (film): 3444 (m); 2954 (s); 2928 (s); 2854 (s); 1736 (s); 1466 (m); 1408 (w); 1373 (m); 1300 (m); 1180 (m); 1119 (w); 1030 (m); 721 (w) cm^{-1}.

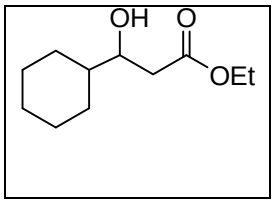
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.87 (3H, t, J = 6.3 Hz); 1.25-1.51 (17H, m); 2.39 (1H, dd, J = 8.7, 16.5 Hz); 2.50 (1H, dd, J = 3.0, 16.5 Hz); 2.97 (1H, J = 3 Hz); 3.95-4.05 (1H, m); 4.17 (2H, q, J = 7.2 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.0; 14.1; 22.6; 25.4; 29.2; 29.5(2); 31.8; 36.5; 41.3; 60.6; 68.0; 173.1.

GC MS: 229(1); 212(1); 185(1); 141(7); 117(100); 89(18); 71(32); 55(14).

ESI-MS: rt: 11.1 min; *m/z*: 231.1 ($M+Na^+$); 478.7 ($2M+H_2O$).

Ethyl 3-Cyclohexyl-hydroxy-propanoate



$C_{11}H_{20}O_3$ Fw = 200.27

Yellow oil

IR (film): 3491 (m); 2958 (s); 2876 (m); 1724 (s); 1465 (m); 1369 (m); 1304 (m); 1261 (m); 1165 (m); 1030 (m); 914 (w); 802 (w) cm^{-1}.

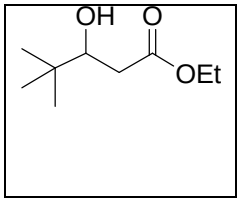
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.99-1.12 (8H, m); 1.65-1.89 (5H, m); 2.40 (1H, dd, J = 9.3, 15.6 Hz); 2.53 (1H, dd, J = 3, 15.6 Hz); 2.87-2.90 (1H, m); 3.71 (1H, dt, J = 2.4, 10.5 Hz), 4.18 (2H, q, J = 7.2 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.2; 26.0; 26.1; 26.4; 28.2; 28.8; 38.6; 43.1; 60.7; 72.1; 173.5.

GC MS: 199(1); 182(2); 155(1); 136(16); 117(100); 95(17); 83(8); 71(19); 55(16).

ESI-MS: rt: 7.8 min; *m/z*: 201.1 ($M+H^+$).

Ethyl 3-hydroxy-4,4-dimethyl-pentanoate



$C_9H_{18}O_3$ Fw = 174.23

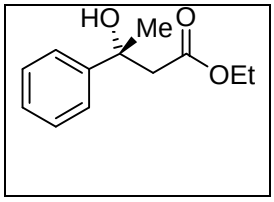
IR (film): 3491 (m); 2958 (s); 2876 (m); 1724 (s); 1465 (m); 1369 (m); 1304 (m); 1261 (m); 1165 (m); 1030 (m); 914 (w); 802 (w) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.93 (9H, s); 1.29 (3H, t, J = 6.9 Hz); 2.35 (1H, dd, J = 10.5, 16.2 Hz); 2.53 (1H, dd, J = 2.4, 16.2 Hz); 2.87-2.90 (1H, m); 3.71 (1H, dt; J = 2.4, 10.5 Hz); 4.18 (2H, q, J = 6.9 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.2; 25.6(3); 34.3; 36,6; 60.7; 75.4; 173.9.

GC MS: 173(1); 155(1); 141(3); 129(6); 117(100); 111(24); 89(34); 83(9); 75(13); 71(81); 57(33).

(*R*) Ethyl 3-hydroxy-3-phenyl-butyrate



$C_{12}H_{16}O_3$ Fw = 208.25

$[a]_D$ = -10.1 (c 0.5, EtOH). Lit.[2] (*S*) Methyl-3-phenyl-3-hydroxypropanoate $[a]_D$ = +3.05 (neat)

IR (film): 3495 (m); 3090 (w); 3059 (w); 3028 (w); 2978 (m); 2931 (m); 1716 (s); 1492 (w); 1446 (w); 1373 (m); 1335 (m) 1277 (m); 1192 (m); 1026 (m); 957 (w); 768 (w); 736 (w); 702 (m) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.17 (3H, t, J = 6.9 Hz); 1.58 (3H, s); 2.83 (1H, d, J = 15.6 Hz); 3.02 (1H, d, J = 15.6 Hz); 4.10 (2H, q, J = 6.9 Hz); 4.43 (1H, s); 7.24-7.30 (1H, m); 7.34-7.40 (2H, m); 7.47-7.51 (2H, m).

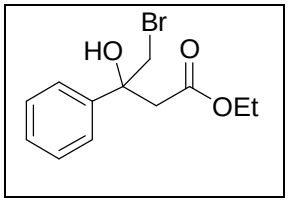
^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.0; 30.6; 46.4; 60.7; 72.7; 124.5(2); 126.8; 128.2(2); 146.8; 172.7.

GC MS: 208(1); 193(46); 163(2); 147(8); 121(100); 105(72); 91(14); 77(28); 65(5); 51(9).

ESI-MS: rt: 6.9 min; *m/z*: 231.1 ($M+Na^+$); 439.4 ($2M+Na^+$).

CHIRAL GC analysis: initial temperature 105°C, slope 0.5°C/min. tm: 28.6 min; TM: 29 min.

Ethyl 4-Bromo-3-hydroxy-3-phenyl-butyrate



$C_{12}H_{15}BrO_3$ Fw = 287.14

IR (film): 3479 (m); 3086 (w); 3062 (w); 3028 (w); 2982 (m); 2928 (m); 1712 (s); 1492 (w); 1446 (m); 1373 (m); 1338 (m); 1200 (m); 1095 (w); 1068 (w); 1022 (m); 854 (w); 772 (w); 706 (m) cm^{-1}.

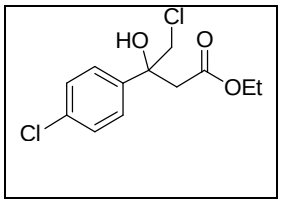
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.13 (3H, t, J = 7.2 Hz); 3.05 (1H, d, J = 16.2 Hz); 3.21 (1H, AB, J = 16.2 Hz); 3.64 (1H, AB, J = 10.8 Hz); 4.06 (2H, q, J = 7.5 Hz); 4.59 (1H, d, J = 1.5 Hz); 7.30-7.40 (3H, m); 7.46-7.50 (2H, m).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.9; 42.6; 42.8; 61.1; 74.0; 125.3(2); 128.0; 128.5(2); 142.5; 172.2.

GC-MS: 270(1); 201(11); 193(84); 147(14); 121(9); 105(100); 91(19); 77(19); 65(4); 51(5).

ESI-MS: rt: 7.8 min; *m/z*: 288.0 ($M+H^+$; ^{79}Br), 305.0 ($M+H_2O$; ^{79}Br).

Ethyl 4-Chloro-3-(4-chlorophenyl)-3-hydroxy-butyrate



$C_{12}H_{14}Cl_2O_3$ Fw = 277.14

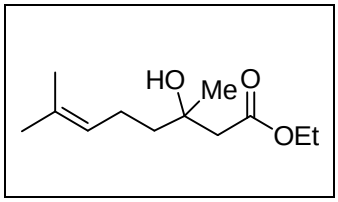
IR (film): 3475 (m); 2982 (w); 2935 (w); 1713 (m); 1597 (w); 1489 (m); 1373 (m); 1332 (m); 1201 (m); 1086 (m); 1017 (w); 829 (w); 756 (w) cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.16 (3H, t, J = 7.2 Hz); 3.07 (2H, AB, J = 16.5 Hz); 3.68 (2H, AB, J = 11.4 Hz); 4.08 (2H, q, J = 7.2 Hz); 4.62 (1H, d, J = 1.2 Hz); 7.34 (2H, AA',BB', J = 9 Hz); 7.43 (2H, AA',BB', J = 9 Hz).

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.9; 41.7; 52.6; 61.2; 74.4; 127.0(2); 128.6(2); 133.9; 141.1 172.1.

GC-MS: 276(1); 258(1); 227(59); 189(17); 181(17); 139(100); 125(10); 111(10); 89(4); 77(13).

Ethyl 3-hydroxy-3,7-dimethyl-oct-6-enoate



$C_{12}H_{22}O_3$ Fw = 214.30

colourless oil

IR (film): 3518 (m); 2973 (s); 2928 (s); 2858 (m); 1716 (s); 1450 (m); 1377 (m); 1331 (m); 1200 (m); 1115 (w); 922 (w); 837 (w) cm^{-1}.

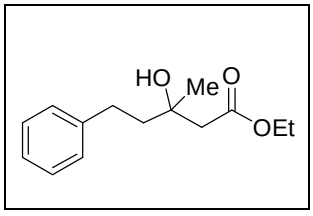
^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24-1.30 (6H, m); 1.61 (3H, s); 1.68 (3H, d, J = 1.2 Hz); 2.01-2.10 (2H, m); 2.48 (2H, *J* = 15.6 Hz); 3.54 (1H, brs); 4.18 (2H, q, J = 7.2 Hz); 5.06-5.13 (1H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1; 17.6; 22.7; 25.6; 26.6; 41.8; 44.9; 60.6; 70.9; 124.1; 131.8; 173.0.

GC-MS: 212(1); 196(37); 181(4); 167(4); 151(12); 131(19); 122(61); 109(100); 93(22); 85(34); 69(52); 55(19).

ESI-MS: rt: 8.8 min; *m/z*: 215.1 ($M+H^+$); 237.1 ($M+Na^+$); 451.2 ($2M+Na^+$).

Ethyl 3-hydroxy-3-methyl-5-phenyl-pentenoate



$C_{14}H_{20}O_3$ Fw = 236.30

IR (film): 3510 (s); 3089 (w); 3064 (w); 3032 (m); 2974 (s); 2935 (s); 2856 (m); 1728 (s); 1716 (s); 1605 (w); 1497 (m); 1450 (m); 1373 (m); 1335 (m); 1211 (s); 1188 (s); 1030 (m); 922 (m); 741 (m); 698 (m) cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30-1.31 (6H, m); 1.94 (dt, *J* = 2.7, 14.1 Hz); 2.55 (2H, AB, J = 15.6 Hz); 3.67 (1H, s, OH); 4.20 (2H, q, J = 7.2 Hz); 7.17-7.22 (3H, m); 7.28-7.32 (2H, m).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.5; 26.7; 30.3; 43.8; 44.9; 60.7; 70.8; 125.8; 128.3(2); 128.4(2); 142.2; 173.0.

GC MS: 236(1); 218(32); 172(4); 144(69); 131(84); 105(28); 91(100); 85(32); 77(14); 65(13); 51(5).

ESI-MS: rt 8.4 min *m/z*: 259.1 ($M+Na^+$)

[1] R. J. Kloetzing, T. Thaler, P. Knochel, *Org. Lett.* **2006**, *8*, 1125.
[2] M. Guetté, J. Capillon, J.-P. Guettè, *Tetrahedron*, **1973**, *29*, 3659-3667.