Electric Supporting Information

Methyl 3-hydroxy-2-methyl-3-phenylpropanoate (1a)[18]

syn- and *anti*-Mixture; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (*anti*, 3H x 1/3, d, *J* = 7.2 Hz), 1.13 (*syn*, 3H x 2/3, d, *J* = 7.2 Hz), 2.72 (1H, br s), 2.73-2.89 (1H, m), 3.67 (*syn*, 3H x 2/3, s), 3.72 (*anti*, 3H x 1/3, s), 4.74 (*anti*, 1H x 1/3, d, *J* = 8.6 Hz), 5.10 (*syn*, 1H x 2/3, d, *J* = 4.5 Hz), 7.23-7.39 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.69, 14.44, 15.20, 46.35, 47.08, 51.84, 51.89, 73.58, 76.41, 125.91, 126.64, 127.46, 128.07, 128.23, 128.47, 141.38, 141.50, 176.16, 176.24; IR (neat) 3468, 2978, 2951, 1730, 1456, 1200, 910, 733 cm^{-1}.

Methl 3-hydroxy-2,4,4-trimethylpentanoate (1b)[19]

syn- and *anti*-Mixture; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (*anti*, 9H x 1/5), 0.95 (*syn*, 9H x 4/5), 1.24 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 1.36 (*anti*, 3H x 1/5, d, *J* = 7.2 Hz), 1.86 (1H, br s), 2.72 (*syn*, 1H x 4/5, dq, *J* = 4.5, 7.2 Hz), 2.76 (*anti*, 1H x 1/5, dq, *J* = 2.1, 7.2 Hz), 3.18 (*anti*, 1H x 1/5, d, *J* = 2.1 Hz), 3.64 (*syn*, 1H x 4/5, d, *J* = 4.5 Hz), 3.69 (*syn*, 3H x 4/5, s), 3.69 (*anti*, 3H x 1/5, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.92, 18.01, 26.08, 26.42, 35.53, 35.93, 38.28, 41.03, 51.74, 78.15, 82.60, 177.48, 177.92; IR (neat) 3493, 2957, 2876, 1721, 1460, 1368, 1198, 1167, 1049, 1011 cm^{-1}.

Phenyl 3-hydroxy-2-methyl-3-phenylpropanoate (3a)[20]

syn- and *anti*-Mixture; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (*anti*, 3H x 1/7, d, *J* = 7.2 Hz), 1.33 (*syn*, 3H x 6/7, d, *J* = 7.2 Hz), 2.29 (1H, br s), 3.05 (*syn*, 1H x 6/7, dq, *J* = 5.2, 7.2 Hz), 4.87 (*anti*, 1H x 1/7, d, *J* = 8.6 Hz), 5.17 (*syn*, 1H x 6/7, d, *J* = 5.2 Hz), 6.87-6.94 (2H, m), 7.02-7.09 (*anti*, 2H x 1/7, m), 7.17-7.27 (*syn*, 2H x 6/7, m), 7.28-7.47 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.49, 46.90, 74.15, 121.36, 121.50, 125.91, 126.20, 126.68, 127.82, 128.42, 128.59, 129.37, 141.34, 150.39, 173.96; IR (neat) 3484, 3065, 3032, 2983, 2940, 2882, 1753, 1493, 1196, 1163, 702 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29, found: C, 75.1; H, 6.4.

Phenyl 3-hydroxy-2-methylhexanoate (3b)[20]

syn-Isomer; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (3H, t, *J* = 7.2 Hz), 1.31-1.65 (4H, m), 1.34 (3H, d, *J* = 7.2 Hz), 2.17 (1H, br s), 2.78 (1H, dq, *J* = 3.8, 7.2 Hz), 4.06 (1H, dt, *J* = 3.8, 8.6 Hz), 7.05-7.11 (2H, m), 7.20-7.27 (1H, m), 7.34-7.42 (2H, m); ^{13}C NMR (75

MHz, $CDCl_3$) δ 10.71, 13.98, 19.16, 36.16, 44.57, 71.49, 121.42, 125.91, 129.43, 150.48, 174.63; IR (neat) 3459, 2959, 1753, 1593, 1493, 1196 cm^{-1}.

Phenyl 3-hydroxy-2,4-dimethylpentanoate (3c)[20]

syn-Isomer; Pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (3H, d, *J* = 6.9 Hz), 1.07 (3H, d, *J* = 6.9 Hz), 1.34 (3H, d, *J* = 7.2 Hz), 1.70-1.88 (1H, m), 2.10 (1H, br s), 2.92 (1H, dq, *J* = 3.8, 7.2 Hz), 3.73 (1H, dd, *J* = 3.8, 7.9 Hz), 7.04-7.12 (2H, m), 7.20-7.27 (1H, m), 7.34-7.44 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.27, 18.55, 19.11, 30.84, 42.18, 76.87, 121.44, 125.91, 129.43, 150.56, 174.94; IR (neat) 3515, 2965, 2878, 1753, 1595, 1493, 1196 cm^{-1}.

Phenyl 2-butyl-3-hydroxy-3-phenylpentanoate (3h)

syn-Isomer; Colorless crystals; mp 79 – 81 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.71 (3H, t, *J* = 7.2 Hz), 0.79 (3H, t, *J* = 6.9 Hz), 1.10-1.40 (4H, m), 1.86 (1H, dq, *J* = 7.2 Hz, *Jgem* = 14.5 Hz), 2.09 (1H, dq, *J* = 7.2 Hz, *Jgem* = 14.5 Hz), 3.04 (1H, dd, *J* = 2.8, 11.7 Hz), 3.29 (1H br s), 7.07-7.15 (2H, m), 7.22-7.31 (2H, m), 7.33-7.51 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.77, 13.80, 22.27, 27.47, 29.86, 34.87, 55.48, 77.72, 121.51, 125.54, 126.25, 126.59, 128.09, 129.56, 142.48, 150.21, 175.83; IR (KBr) 3534, 2971, 1725, 1364, 1190, 1159, 1142, 1123, 747, 702 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03, found: C, 77.0; H, 7.9.

anti-Isomer;Yellow crystals; mp 38 – 40 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.70 (3H, t, *J* = 7.2 Hz), 0.97 (3H, t, *J* = 7.2 Hz), 1.37-1.57 (4H, m), 1.75 (1H, dq, *J* = 7.2 Hz, *Jgem* = 13.8 Hz), 1.87-2.05 (2H, m), 2.09 (1H, dq, *J* = 7.2 Hz, *Jgem* = 13.8 Hz), 3.19 (1H, dd, *J* = 4.5 11.0 Hz), 3.72 (1H, br s), 6.32-6.42 (2H, m), 7.07-7.52 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.60, 13.95, 22.71, 26.82, 30.09, 31.90, 54.62, 77.62, 121.26, 125.86, 125.98, 126.88, 128.04, 129.27, 144.93, 149.86, 175.50; IR (KBr) 3515, 2967, 1730, 1495, 1358, 1188, 1154, 1111, 750, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71, found: C, 75.2; H, 6.4.

Phenyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (3i)[22]

Colorless crystals; mp 84 – 85 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (3H, s), 1.29 (3H, s), 2.80 (1H, br s), 5.06 (1H, s), 7.01-7.09 (2H, m), 7.19-7.27 (1H, m), 7.28-7.42 (7H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.04, 22.85, 48.13, 78.57, 121.44, 125.82, 127.73, 127.84, 127.92, 129.39, 139.81, 150.81, 176.20; IR (KBr) 3472, 2976, 1721, 1491, 1258, 1188, 1128, 1047, 740, 704 cm^{-1}.

Phenyl 3-hydroxy-2,2,4-trimethylpentanoate (3k)

Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, d, *J* = 6.9 Hz), 1.04 (3H, d, *J* = 6.9 Hz), 1.35 (3H, s), 1.40 (3H, s), 1.86-2.01 (1H, m), 2.67 (1H, br s), 3.58 (1H, d, *J* = 4.1 Hz), 7.01-7.12 (2H, m), 7.18-7.28 (1H, m), 7.31-7.45 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.06, 21.59, 22.60, 22.72, 30.29, 46.58, 81.11, 121.27, 125.82, 129.35, 150.52, 176.60; IR (neat) 3520, 2969, 1746, 1595, 1491, 1194, 1111, 745, 691 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53, found: C, 70.7; H, 8.3.

Phenyl 3-ethyl-3-hydroxy-2,2-dimethylpentanoate (3m)

Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (6H, t, *J* = 7.6 Hz), 1.40 (6H, s), 1.60-1.78 (4H, m), 3.47 (1H, br s), 7.02-7.09 (2H, m), 7.21-7.29 (1H, m), 7.35-7.44 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.97, 21.76, 28.24, 50.88, 76.43, 121.38, 126.05, 129.05, 129.49, 150.46, 177.75; IR (neat) 3513, 2980, 2944, 1746, 1723, 1593, 1493, 1472, 1190, 1098, 747 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86, found: C, 71.7; H, 8.5.

Phenyl 2-chloro-3-hydroxy-2-methyl-3-phenylpentanoate (5d)

Diastereomixture; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (3H, t, *J* = 7.6 Hz), 1.86 (3H x 7/10, s), 1.87 (3H x 3/10, s), 2.07-2.30 (1H, m), 2.44-2.62 (1H, m), 3.80 (1H, br s), 6.89-6.97 (2H, m), 7.21-7.42 (6H, m), 7.52-7.61 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.72, 8.07, 24.95, 25.03, 28.16, 28.97, 75.51, 80.75, 121.04, 121.07, 126.41, 127.71, 127.77, 127.98, 129.49, 138.44, 138.76, 150.20, 170.45; IR (neat) 3530, 2976, 2942, 1752, 1593, 1493, 1449, 1242, 1190, 752, 704 cm^{-1}. Anal. Calcd for $C_{18}H_{19}ClO_3$: C, 67.82; H, 6.01, found: C, 6176.6; H, 5.9.

***S*-Phenyl 3-hydroxy-2-methyl-3-phenylpropanethioate (8a)**[23]

syn- and *anti*-Mixture; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (*anti*, 3H x 1/5, d, *J* = 7.2 Hz), 1.26 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 2.50 (1H, br s), 3.05 (*syn*, 1H x 4/5, dq, *J* = 4.1, 7.2 Hz), 3.12 (*anti*, 1H x 1/5, dq, *J* = 7.2, 8.3 Hz), 4.84 (*anti*, 1H x 1/5, d, *J* = 8.3 Hz), 5.14 (*syn*, 1H x 4/5, d, *J* = 4.1 Hz), 7.30-7.43 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.63, 15.46, 54.89, 55.25, 73.77, 126.09, 126.59, 127.65, 128.31, 129.22, 129.57, 141.06, 141.46, 201.66, 202.04; IR (neat) 3542, 3495, 3405, 3378, 1692, 955, 748, 702 cm^{-1}.

***S*-Phenyl 3-hydroxy-2-methylhexanethioate (8b)**[24]

syn- and *anti*-Mixture; Colorless crystals; mp 35 – 37 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (3H, t, *J* = 6.9 Hz), 1.30 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 1.32 (*anti*, 3H x 1/5, d, *J* = 7.2 Hz), 1.34-1.60 (4H, m), 2.29 (1H br s), 2.80 (*syn*, 1H x 4/5, dq, *J* = 3.8, 7.2 Hz), 2.85 (*anti*, 1H x 1/5, dq, *J* = 5.9, 7.2 Hz), 3.70-3.79 (*anti*, 1H x 1/5, m), 3.98 (*syn*, 1H x 4/5, dt, *J* = 3.8, 7.6 Hz), 7.37-7.45 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.51, 13.92, 15.24, 18.79, 19.12, 36.20, 37.02, 52.85, 53.48, 71.59, 73.62, 127.23, 129.18, 129.49, 134.40, 134.44, 202.19, 202.23; IR (KBr) 3409, 2963, 2926, 1680, 1456, 1441, 1144, 951, 754, 689 cm^{-1}.

_S_-Phenyl 3-hydroxy-2,4-dimethylpentanethioate (8c)[23]

syn- and *anti*-Mixture; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (*syn*, 3H x 4/5, d, *J* = 6.9 Hz), 0.96 (*anti*, 3H x 1/5, d, *J* = 6.9 Hz), 1.01 (*anti*, 3H x 1/5, d, *J* = 6.9 Hz), 1.04 (*syn*, 3H x 4/5, d, *J* = 6.9 Hz), 1.29 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 1.33 (*anti*, 3H x 1/5, d, *J* = 7.2 Hz), 1.66-1.86 (1H, m), 2.18 (1H, br s), 2.96 (*syn*, 1H x 4/5, dq, *J* = 3.8, 7.2 Hz), 2.99 (*anti*, 1H x 1/5, dq, *J* = 5.9, 7.2 Hz), 3.45 (*anti*, 1H x 1/5, t, *J* = 5.9 Hz), 3.64 (*syn*, 1H x 4/5, dd, *J* = 3.8, 7.6 Hz), 7.38-7.45 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.28, 15.87, 16.60, 18.45, 19.16, 19.87, 30.73, 31.26, 50.31, 50.78, 76.90, 78.87, 127.23, 129.20, 129.51, 134.42, 134.48, 202.49; IR (neat) 3457, 2965, 1703, 1478, 1441, 1065, 961, 947, 747, 689 cm^{-1}.

_S_-Phenyl 3-hydroxy-2-methyl-5-phenylpentanethioate (8d)[23]

syn- and *anti*-Mixture; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 1.32 (*anti*, 3H x 1/5, d, *J* = 7.2 Hz), 1.64-1.79 (1H, m), 1.79-1.95 (1H, m), 2.32 (1H br s), 2.59-2.74 (1H, m), 2.75-2.94 (2H, m), 3.74 (*anti*, 1H x 1/5, ddd, *J* = 3.8, 5.9, 9.3 Hz), 3.99 (*syn*, 1H x 4/5, dt, *J* = 3.8, 9.3 Hz), 7.15-7.24 (3H, m), 7.25-7.33 (2H, m), 7.36-7.44 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.64, 15.33, 31.97, 32.22, 35.81, 36.79, 52.83, 53.44, 71.09, 73.19, 125.93, 127.08, 128.44, 129.22, 129.56, 134.42, 134.48, 141.63, 202.34; IR (neat) 3314, 2932, 1692, 1478, 1454, 1441, 953, 748, 700, 691 cm^{-1}.

_S_-Phenyl 3-hydroxy-2-methyl-3-phenylpentanethioate (8f)

syn-Isomer; Colorless crystals; mp 66 – 67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (3H, t, *J* = 7.2 Hz), 1.04 (3H, d, *J* = 7.2 Hz), 1.91 (1H, dq, *J* = 7.6 Hz, *Jgem* = 13.8 Hz), 2.05 (1H, dq, *J* = 7.6 Hz, *Jgem* = 13.8 Hz), 3.08 (1H, br s), 3.15 (1H, q, *J* = 7.2 Hz), 7.20-7.27 (1H, m), 7.31-7.42 (4H, m), 7.43-7.47 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.86, 13.65, 34.34, 57.13,

78.42, 125.47, 126.54, 127.02, 128.03, 129.32, 129.76, 134.34, 142.32, 204.73; IR (KBr) 3513, 2924, 1672, 1449, 1391, 972, 934, 905, 745, 694 cm^{-1}.

anti-Isomer; Yellow crystals; mp 54 – 55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.67 (3H, t, *J* = 7.2 Hz), 1.46 (3H, d, *J* = 7.2 Hz), 1.71 (1H, dq, *J* = 7.2 Hz, *Jgem* = 13.4 Hz), 1.97 (1H, dq, *J* = 7.2 Hz, *Jgem* = 13.4 Hz), 3.32 (1H, q, *J* = 7.2 Hz), 3.76 (1H, br s), 6.98-7.04 (2H, m), 7.23-7.44 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.42, 12.75, 31.61, 55.99, 78.07, 125.80, 126.70, 127.96, 129.09, 129.53, 134.31, 144.52, 204.25; IR (KBr) 3476, 2975, 1667, 1439, 1373, 1321, 955, 762, 741, 702 cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71, found: C, 72.1; H, 6.8

_S_-Phenyl 2-butyl-3-ethyl-3-hydroxypentanethioate (8h)

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, t, *J* = 7.6 Hz), 0.94 (6H, t, *J* = 7.6 Hz), 1.25-1.72 (9H, m), 1.78-1.95 (1H, m), 2.40 (1H, br s), 2.80 (1H, dd, *J* = 3.8, 11.0 Hz), 7.37-7.47 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.74, 7.90, 13.90, 22.89, 26.63, 27.23, 30.10, 59.16, 76.37, 127.54, 129.24, 129.62, 134.21, 204.00; IR (neat) 3534, 2965, 1684, 1462, 1022, 995, 976, 924, 745, 689 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_2S$: C, 69.34; H, 8.90, found: C, 69.1; H, 8.79.

_S_-Phenyl 3-hydroxy-2,2-dimethyl-3-phenylpropanethioate (8i)[25]

Colorless crystals; mp 92 – 93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (3H, s), 1.33 (3H, s), 2.56 (1H, br s), 4.98 (1H, s), 7.27-7.47 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.16, 23.52, 55.01, 78.84, 127.50, 127.79, 127.82, 127.90, 129.20, 129.43, 134.92, 139.68, 205.95; IR (KBr) 3572, 2973, 1678, 1441, 1044, 999, 932, 748, 700, 689 cm^{-1}.

_S_-Phenyl 2-chloro-3-hydroxy-2-methylhexanethioate (8l)

Diastereomixture; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (3H x 5/7, t, *J* = 6.9 Hz), 0.96 (3H x 2/7, t, *J* = 6.9 Hz), 1.22-1.69 (4H, m), 1.78 (3H x 2/7, s), 1.84 (3H x 5/7, s), 2.26 (1H, br s), 3.91-4.00 (1H, m), 7.35-7.49 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.80, 19.24, 19.31, 25.11, 25.53, 33.58, 34.49, 76.10, 76.90, 81.30, 127.58, 127.65, 129.28, 129.68, 134.61, 199.95, 200.43; IR (neat) 3441, 2963, 1684, 1443, 972, 747, 689 cm^{-1}. Anal. Calcd for $C_{13}H_{17}ClO_2S$: C, 57.24; H, 6.28, found: C, 57.2; H, 6.2.

_S_-(4-Methoxyphenyl) 3-hydroxy-2-methyl-3-phenylpropanethioate (10a)

syn- and *anti*-Mixture; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (*anti*, 3H x 1/5, d, *J* = 7.2 Hz), 1.24 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 2.55 (1H br s), 3.03 (*syn*, 1H x 4/5, dq, *J* = 4.1, 7.2 Hz), 3.10 (*anti*, 1H x 1/5, dq, *J* = 7.2, 8.3 Hz), 3.81 (*syn*, 3H x 4/5, s), 3.82 (*anti*, 3H x 1/5, s), 4.82 (*anti*, 1H x 1/5, d, *J* = 8.3 Hz), 5.12 (*syn*, 1H x 4/5, d, *J* = 4.1 Hz), 6.89-6.96 (2H, m), 7.20-7.40 (7H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.59, 15.45, 54.53, 54.88, 55.32, 73.73, 114.88, 117.67, 126.07, 126.56, 127.60, 128.11, 128.26, 128.49, 136.05, 141.08, 141.52, 160.75, 203.14; IR (neat) 3493, 2932, 1696, 1593, 1495, 1290, 1250, 1030, 957, 828 cm^{-1}.

_S_-(4-*tert*-Buthylphenyl) 3-hydroxy-2-methyl-3-phenylpropanethioate (10b)

syn- and *anti*-Mixture; Colorless crystals; mp 58 – 60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (*anti*, 1H x 1/5, d, *J* = 7.2 Hz), 1.25 (*syn*, 1H x 4/5, d, *J* = 7.2 Hz), 1.320 (*anti*, 9H x 1/5, s), 1.322 (*syn*, 9H x 4/5, s), 2.81 (1H br s), 3.05 (*syn*, 1H x 4/5, dq, *J* = 4.1, 7.2 Hz), 3.11 (*anti*, 1H x 1/5, dq, *J* = 7.2, 7.9 Hz), 4.83 (*anti*, 1H x 1/5, d, *J* = 7.9 Hz), 5.14 (syn, 1H x 4/5, d, *J* = 4.1 Hz), 7.23-7.45 (9H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.55, 15.51, 31.17, 34.76, 54.70, 55.13, 73.71, 123.56, 126.07, 126.39, 126.58, 127.61, 128.13, 128.30, 128.51, 134.12, 141.04, 152.91, 202.74; IR (KBr) 3478, 2963, 1678, 1493, 1454, 1042, 963, 833, 768, 706 cm^{-1}.

_S_-(2-Chlorophenyl) 3-hydroxy-2-methyl-3-phenylpropanethioate (10c)

syn- and *anti*-Mixture; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (*anti*, 3H x 1/10, d, *J* = 7.2 Hz), 1.28 (*syn*, 3H x 9/10, d, *J* = 7.2 Hz), 3.09 (*syn*, 1H x 9/10, dq, *J* = 4.1, 7.2 Hz), 3.15 (*anti*, 1H x 1/10, dq, *J* = 7.2, 8.3 Hz), 4.85 (*anti*, 1H x 1/10, d, *J* = 8.3 Hz), 5.16 (*syn*, 1H x 9/10, d, *J* = 4.1 Hz), 7.24-7.45 (8H, m), 7.47-7.54 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.53, 54.99, 73.71, 126.12, 126.64, 126.68, 127.31, 127.69, 128.36, 130.25, 131.30, 137.04, 138.59, 140.94, 199.93; IR (neat) 3468, 2980, 1703, 1453, 1433, 1038, 953, 758, 700 cm^{-1}.

_S_-(3-Chlorophenyl) 3-hydroxy-2-methyl-3-phenylpropanethioate (10d)

syn- and *anti*-Mixture; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (*anti*, 3H x 1/7, d, *J* = 6.9 Hz), 1.27 (*syn*, 3H x 6/7, d, *J* = 6.9 Hz), 2.45 (1H br s), 3.03 (*syn*, 1H x 6/7, dq, *J* = 4.5, 6.9 Hz), 3.10 (*anti*, 1H x 1/7, dq, *J* = 6.9, 8.3 Hz), 4.83 (*anti*, 1H x 1/7, d, *J* = 8.3 Hz), 5.10 (*syn*, 1H x 6/7, d, *J* = 4.5 Hz), 7.16-7.22 (1H, m), 7.26-7.44 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.80, 15.31, 55.26, 55.47, 73.96, 126.10, 126.58, 127.79, 128.36, 128.59, 128.80, 129.62, 129.72, 130.14, 132.55, 134.10, 134.15, 134.71, 141.00, 141.30, 200.58, 200.77; IR (neat) 3468, 2982, 1698, 1568, 1456, 951, 781, 764, 702, 679 cm^{-1}.

***S*-(4-Chlorophenyl) 3-hydroxy-2-methyl-3-phenylpropanethioate (10e)**

syn- and *anti*-Mixture; Colorless crystals; mp 56 – 58 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (*anti*, 3H x 1/7, d, *J* = 7.2 Hz), 1.27 (*syn*, 3H x 6/7, d, *J* = 6.9 Hz), 2.52 (1H br s), 3.03 (*syn*, 1H x 6/7, dq, *J* = 4.5, 6.9 Hz), 3.09 (*anti*, 1H x 1/7, dq, *J* = 7.2, 8.3 Hz), 4.82 (*anti*, 1H x 1/7, d, *J* = 8.3 Hz), 5.09 (*syn*, 1H x 6/7, d, *J* = 4.5 Hz), 7.19-7.25 (1H, m), 7.26-7.41 (7H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.80, 15.35, 55.16, 55.37, 73.94, 76.58, 125.53, 126.10, 126.58, 127.75, 128.34, 128.57, 129.43, 135.66, 135.95, 141.04, 141.36, 201.15; IR (KBr) 3463, 3029, 1678, 1478, 1453, 1088, 968, 824, 768, 696 cm^{-1}.

***S*-(4-Nitrophenyl) 3-hydroxy-2-methyl-3-phenylpropanethioate (10f)**

syn-Isomer; Yellow crystals; mp 80 – 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (3H, d, *J* = 6.9 Hz), 2.34 (1H, br s), 3.08 (1H, dq, *J* = 5.2, 6.9 Hz), 1.32 (1H, d, *J* = 5.2 Hz), 7.27-7.42 (4H, m), 7.44-7.52 (2H, m), 8.18-8.27 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.01, 55.89, 74.19, 123.90, 126.14, 127.98, 128.46, 134.77, 135.66, 140.96, 148.15, 199.01; IR (KBr) 3522, 2976, 1676, 1516, 1345, 984, 949, 853, 750, 702 cm^{-1}.

***S*-(4-Nitrophenyl) 3-hydroxy-2-methylhexanethioate (10g)**

syn- and *anti*-Mixture; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 6.9 Hz), 1.28-1.62 (4H, m), 1.33 (3H, d, *J* = 6.9 Hz), 1.99 (1H br s), 2.79-2.93 (1H, m), 3.81 (*anti*, 1H x 3/10, dt, *J* = 3.1, 7.2 Hz), 4.01 (*syn*, 1H x 7/10, dt, *J* = 4.1, 8.3 Hz), 7.55-7.65 (2H, m), 8.21-8.30 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.49, 13.90, 14.99, 18.66, 19.14, 36.37, 36.85, 53.73, 54.53, 71.70, 73.48, 123.94, 134.67, 134.75, 136.87, 148.15, 199.53; IR (neat) 3426, 2961, 1707, 1599, 1521, 1458, 1345, 943, 853, 745 cm^{-1}.

***S*-(4-Nitrophenyl) 3-hydroxy-2,4-dimethylpentanethioate (10h)**

syn- and *anti*-Mixture; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (*syn*, 3H x 3/5, d, *J* = 6.5 Hz), 0.95 (*anti*, 3H x 2/5, d, *J* = 6.5 Hz), 1.02 (*anti*, 3H x 2/5, d, *J* = 6.5 Hz), 1.04 (*syn*, 3H x 3/5, d, *J* = 6.5 Hz), 1.316 (*anti*, 3H x 2/5, d, *J* = 7.2 Hz), 1.322 (*syn*, 3H x 3/5, d, *J* = 7.2 Hz), 1.67-1.88 (1H, m), 2.04 (1H, br s), 2.92-3.05 (1H, m), 3.56 (*anti*, 1H x 2/5, dd, *J* = 4.8, 6.9 Hz), 3.69 (*syn*, 1H x 3/5, dd, *J* = 4.1, 7.6 Hz), 7.56-7.64 (2H, m), 8.21-8.27 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.20, 15.37, 15.77, 18.22, 19.21, 19.83, 30.67, 30.92, 51.28, 51.95, 77.00,

78.36, 123.90, 134.65, 134.75, 135.89, 148.11, 199.64, 199.85; IR (neat) 3551, 2965, 1711, 1599, 1522, 1370, 1345, 947, 853, 745 cm^{-1}.

_S_-(4-Nitrophenyl) 3-hydroxy-3-methyl-3-phenylpentanethioate (10i)

syn- and *anti*-Mixture; Pale yellow crystals; mp 76 – 78 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.67 (*anti*, 3H x 1/5, t, *J* = 7.2 Hz), 0.69 (*syn*, 3H x 4/5, t, *J* = 7.2 Hz), 1.08 (*syn*, 3H x 4/5, d, *J* = 7.2 Hz), 1.47 (*anti*, 3H x 1/5, d, J = 7.2 Hz), 1.74 (*anti*, 1H x 1/5, dq, *J* = 7.2 Hz, *Jgem* = 13.8 Hz), 1.82-2.03 (1H, m), 2.08 (*syn*, 1H x 4/5, dq, *J* = 7.2Hz, *Jgem* = 13.8 Hz), 2.99 (1H, br s), 3.16 (*syn*, 1H x 4/5, q, *J* = 7.2 Hz), 3.34 (*anti*, 1H x 1/5, q, *J* = 7.2 Hz), 7.13-7.43 (5H, m), 7.56-7.68 (2H, m), 8.09-8.33 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.34, 7.80, 12.62, 13.54, 31.49, 34.23, 57.06, 58.15, 78.11, 78.40, 123.79, 124.00, 125.43, 125.68, 126.75, 126.89, 128.11, 134.65, 135.43, 141.92, 144.17, 148.09, 148.27, 201.65, 201.94; IR (KBr) 3567, 2976, 1688, 1516, 1451, 1343, 1171, 957, 928, 853 cm^{-1}.

4-Methyl-3-pentyl-2(*5H*)-furanone (11)[15]

1.0 M KOH aqueous solution (2.5 mL) was added to a stirred solution of phenyl 4-acetoxy-3-hydroxy-3-methylheptanoate (**14**; 322 mg, 1.0 mmol) in MeOH – THF (7.8 mL, v/v = 2/1) at 20 – 25 °C, and the mixture was stirred at the same temp. for 10 h. 1.0 M HCl aqueous solution (3.0 mL) was added to the mixture, followed by being stirred at the same temp. for 2 h. The mixture was concentrated under reduced pressure, which was extracted twice with Et_2O. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. Obtained crude product was purified by SiO_2-column chromatography (hexane : AcOEt = 8 : 1) to give the desired product **11** (117 mg, 70%).

Yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.2 Hz), 1.21-1.40 (4H, m), 1.50 (2H, quint, *J* = 7.6 Hz), 2.02 (3H, s), 2.25 (t, *J* = 7.6 Hz), 4.61 (2H, d, *J* = 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.20, 13.96, 22.37, 23.29, 27.57, 31.51, 72.35, 127.40, 156.32, 175.05 ; IR (neat) 2930, 1752, 1678, 1451, 1391, 1090, 1040 cm^{-1}.

Dimethyl 2-[(*Z*)-pent-2-enyl]malonate (19)

A solution of Et_3N (4.55 g, 45.0 mmol) in Et_2O (10.0 mL) was added slowly to a stirred solution of *cis*-2-penten-1-ol (**14**; 2.58 g, 30.0 mmol) and $MeSO_2Cl$ (5.15 g, 45.0 mmol) in Et_2O (80 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at the same temp. for 1 h. Using an alternative safe method,[14] also gave successful results [CH_3SO_2Cl (1.5

equiv) – Et_3N (2.0 equv) – Me_3N•HCl (0.1 equiv) in toluene at 0 – 5 °C for 1 h]. Water was added to the mixture, which was extracted twice with Et_2O. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated to give crude oil of *cis*-2-pentyl methanesulfonate **17**. This was immediately used for the next reaction, because **17** is somewhat unstable. A solution of dimethyl malonate (5.55 g, 42.0 mmol) in DMF (10 mL) was added to a stirred suspension of NaH (1.44 g, 60% in oil, 36.0 mmol) in DMF (40 mL) at 20 – 25 °C under an Ar atmosphere, and the mixture was stirred at the same temp. for 30 min. To the mixture, a solution of **17** in DMF (10 mL) was added at 20 – 25 °C, which was stirred at same temp. for 10 h. Water was added to the mixture, which was extracted twice with Et_2O. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane : AcOEt = 10 : 1) to give the desired product **19** (4.76 g, 79% in 2 steps).

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 7.6 Hz), 2.07 (2H, dquint., *J* = 1.4, 7.6 Hz), 2.65 (2H, tt, *J* = 0.7, 7.6 Hz), 3.40 (2H, t, *J* = 7.6 Hz), 3.74 (3H, s), 5.26 (1H, dtt, *J* = 1.4, 7.2, 10.7 Hz), 5.49 (1H, dtt, *J* = 1.4, 7.2, 10.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07, 20.49, 26.63, 51.76, 52.41, 123.71, 134.96, 169.43; IR (neat) 2959, 1738, 1437, 1332, 1283, 1267, 1250, 1206, 1194, 1155 cm^{-1}.

(*Z*)-Hept-4-enoic acid (21)[25]

5.0 M KOH aqueous solution (10 mL) was added to a stirred solution of dimethyl 2-[(*Z*)-pent-2-enyl]malonate (**19**; 4.00 g, 20.0 mmol) in MeOH – THF (30 mL, v/v = 2/1) at 20 – 25 °C, and the mixture was heated under reflux for 2 h. The mixture was concentrated under reduced pressure, which was extracted twice with Et_2O. Aqueous layer was acidified using conc. HCl (15 mL) and then re-extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude oil of 2-[(*Z*)-pent-2-enyl]malonic acid was heating at 150 °C for 2 h to give the desired product **20** (2.45 g, 96% in 2 steps), which was used for the next reaction without purification.

Orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 7.6 Hz), 2.07 (2H, quint, *J* = 7.6 Hz), 2.30-2.48 (4H, m), 5.25-5.37 (1H, m), 5.39-5.53 (1H, m), 10.7 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.20, 20.49, 22.38, 34.18, 126.32, 133.48, 179.65; IR (neat) 2967, 1713, 1414, 1281, 1211 cm^{-1}.

(*Z*)-Phenyl hept-4-enoate (23)

$SOCl_2$ (3.0 mL) and catalytic amount of DMF (5 μL) were added to a stirred solution of (*Z*)-hept-4-enoic acid (**21**; 1.92 g, 15.0 mmol) in hexane (15 mL) at 20 – 25 °C, and the mixture was heated under reflux for 2 h. The mixture was concentrated under reduced pressure to give crude oil of (*Z*)-hept-4-enoyl chloride (2.16 g, 14.7 mmol). This was dissolved in CH_3CN (5 mL) and the solution was added to a stirred solution of PhOH (1.66 g, 17.6 mmol) and Et_3N (2.08 g, 20.6 mmol) in CH_3CN (25 mL) at 0 – 5 °C under an Ar atmosphere, and the mixture was stirred at 20 – 25 °C for 4 h. Water was added to the mixture, which was extracted twice with Et_2O. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2-column chromatography (hexane : AcOEt = 20 : 1) to give the desired product **22** (2.61 g, 85% in 2 steps).

Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (3H, t, *J* = 7.6 Hz), 2.11 (2H, quint, *J* = 7.6 Hz), 2.44-2.54 (2H, m), 2.57-2.65 (2H, m), 5.33-5.54 (2H, m), 7.04-7.10 (2H, m), 7.18-7.27 (1H, m), 7.33-7.41 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.22, 20.53, 22.70, 34.46, 121.53, 125.70, 126.35, 129.35, 133.52, 150.71, 171.69; IR (neat) 2964, 2934, 1763, 1595, 1493, 1362, 1198, 1143, 752, 691 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90, found: C, 76.2; H, 7.8.

Dimethyl 2-[(*E*)-pent-2-enyl]malonate (20)

Following the procedure for the preparation of **19**, the reaction of *trans*-2-penten-1-ol (**16**; 2.58 g, 30.0 mmol) gave the desired product **19** (2.53 g, 42% in 2 steps).

Pale yellow oil; ^{1}H NMR (300 MHz,$CDCl_3$) δ 0.94 (3H, t, *J* = 7.6 Hz), 1,.99 (2H, dquint, *J* = 1.0, 7.1 Hz), 3.41 (1H, t, *J* = 7.6 Hz), 3.73 (6H, s), 5.34 (1H, dtt, *J* = 1.4, 6.9, 15.5 Hz), 5.57 (1H, dtt, *J* = 1.0, 6.2, 15.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.65, 25.49, 31.87, 51.99, 52.35, 52.41, 124.06, 135.64, 169.41; IR (neat) 2961, 1740, 1437, 1341, 1231, 1155, 1028, 970 cm^{-1}.

(*E*)-Hept-4-enoic acid (22)

Following the procedure for the preparation of **21**, the reaction of **20** (2.00 g, 10.0 mmol) gave the desired product **21** (1.23 g, 96% in 2 steps).

Light brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 7.6 Hz), 2.00 (2H, dquint. *J* = 1.0, 7.6 Hz), 2.26-2.37 (2H, m), 2.38-2.46 (2H, m), 5.40 (1H, dtt, *J* = 1.0, 6.2, 15.5 Hz), 5.53 (1H, dtt, *J* = 1.0, 6.2, 15.5 Hz), 11.0 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.73, 25.49,

27.49, 34.11, 126.52, 133.62, 179.53; IR (neat) 29656, 1713, 1414, 1319, 1294, 1281, 1269, 1204, 1159, 966 cm^{-1}.

(*E*)-Phenyl hept-4-enoate (24)

Following the procedure for the preparation of **22**, the reaction of **21** (1.11 g, 8.66 mmol) gave the desired product **23** (1.44 g, 83% in 2 steps).

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (3H, t, *J* = 7.6 Hz), 1.97-2.09 (2H, m), 2.39-2.49 (2H, m), 2.62 (2H, dt, *J* = 1.0, 7.2 Hz), 5.41-5.53 (1H, m), 5.54-5.66 (1H, m), 7.03-7.10 (2H, m), 7.18-7.26 (1H, m), 7.33-7.41 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.77, 25.54, 27.92, 34.44, 121.55, 125.70, 126.54, 129.37, 133.77, 150.69, 171.75; IR (neat) 2965, 1763, 1593, 1493, 1198, 1163, 1140, 1071, 968, 691 cm^{-1}.

Phenyl 4-acetoxy-3-hydroxy-3-methyl-2-[(*E*)-pent-2-enyl]butanoate (26)

Following the procedure for the preparation of **25**, the reaction of (*E*)-phenyl hept-4-enoate (**24**; 613 mg, 3.0 mmol) with acetoxy acetone (418 mg, 3.6 mmol) using $TiCl_4$ (396 μL, 3.6 mmol) and Et_3N (425 mg, 4.2 mmol) gave the desired product **26** (677 mg, 70%).

Diastereomixture; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (3H, t, *J* = 7.2 Hz), 1.34 (3H x 7/10, s), 1.38 (3H x 3/10, s) 2.05 (2H, quint., *J* = 7.2 Hz), 2.10 (3H x 7/10, s) 2.13 (3H x 3/10, s), 2.37-2.61 (2H, m), 2.88 (1H x 7/10, dd, *J* = 4.5, 11.01 Hz), 2.90 (1H x 3/10, dd, *J* = 4.8, 9.6 Hz), 3.11 (1H, br s), 4.08 (1H x 7/10, d, *Jgem* = 11.4 Hz), 4.10 (1H x 3/10, d, *Jgem* = 11.4 Hz), 4.14 (1H x 7/10, d, *Jgem* = 11.4 Hz), 4.19 (1H x 3/10, *Jgem* = 11.4 Hz), 5.39-5.53 (1H, m), 5.65 (1H, dt, *J* = 6.2, 15.5 Hz), 6.99-7.11 (2H, m), 7.19-7.28 (1H, m), 7.32-7.43 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.57, 20.84, 21.74, 23.14, 25.53, 30.32, 30.86, 51.74, 52.62, 68.95, 70.02, 72.20, 72.35, 121.44, 121.48, 124.80, 125.07, 126.07, 129.43, 135.32, 135.45, 150.29, 170.73, 173.20; IR (neat) 3497, 2965, 1734, 1493, 1373, 1238, 1194, 1163, 1047, 970 cm^{-1}.

4-Methyl-3-[(*E*)-pent-2-enyl]-2(*5H*)-furanone (13)

Following the procedure for the preparation of **12**, the reaction of (**26**; 320 mg, 1.0 mmol) gave the desired product **13** (108 mg, 65%).

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (3H, t, *J* = 7.2 Hz), 1.94-2.06 (2H, m), 2.03 (3H, s), 2.97 (2H, d, *J* = 6.2 Hz), 4.62 (2H, d, *J* = 1.0 Hz), 5.41 (1H, dtt, *J* = 1.4, 6.2, 15.1 Hz), 5.55 (1H, dtt, *J* = 1.4, 6.2, 15.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.14, 13.46, 25.26, 26.39,

72.37, 123.60, 125.68, 133.96, 157.04, 174.69; IR (neat) 3418, 2973, 1740, 1676, 1443, 1389, 1343, 1188, 1101, 1038 cm^{-1}.