Supplementary Experimental Information.

Dimethylmalonyltrialkylphosphoranes: New General Reagents for Esterification Reactions Allowing Controlled Inversion or Retention of Configuration on Chiral Alcohols.

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General details: Dry THF was obtained by distillation from sodium-benzophenone, anhydrous DMF used directly (Aldrich *Sure/Seal^{TM}*) and triethylamine distilled over calcium hydride. Methanol, ethanol and isopropanol were redistilled from magnesium turnings before use. Esterification reactions were performed individually or in parallel on the Quest 210 Organic Synthesizer. ¹H-NMR, ¹³C-NMR were recorded at 300 and 75 MHz in CDCl₃. MS analysis was performed on a Kratos Concept 1S spectrometer. FTIR spectra (KBr) were recorded on a Mattson Research Series spectrophotometer. Chiral GC analysis was performed on the HP-6890 with FID and chiral HPLC performed on a Waters 600 series system under the individual conditions described below.

Synthesis of Phosphorane 6a: Into a flame-dried round-bottom flask containing dry EtOAc (50.0 ml) was added dimethyl-2-chloromalonate (5.113 ml, 40.0 mmol, 1.0 eq.) and tributylphosphine (10.0 ml, 40.0 mmol, 1.0 eq.) was injected via syringe under argon. The phosphonium salt occasionally crystallizes at this point with no deleterious effects on the reaction. The mixture was cooled in an ice bath while dry Et₃N (5.575 ml, 40.0 mmol, 1.0 eq.) was added dropwise (mild exotherm) to the mixture via syringe. Upon the addition of base the solution becomes a viscous white slurry. The reaction mixture was stirred at room temperature for one hour under argon. The slurry was filtered under positive argon through a short column containing a cotton plug and the precipitated Et₃N-HCl washed thoroughly with EtOAc. The clear filtrate was concentrated by removing the solvent under reduced pressure to give **6a** as a colourless oil, 13.105 g, 98.6%. The yield ranged from 98-100% over many runs. ¹H-NMR: δ 0.75 (t, 3H, *J*=6.75), 1.21-1.28 (m, 12H), 1.91-1.98 (m, 6H), 3.47 (s, 6H). ¹³C-NMR: δ 13.2, 21.8 (d, *J*=55 Hz), 23.6 (d, *J*=15.4 Hz), 23.9 (d, *J*=3.8 Hz), 49.9, 168.8 (d, *J*=14.5 Hz). ³¹P-NMR: δ 27.8. MS: *m/z* (% rel.): 332 (24.3), 303 (53.4), 301 (100), 276 (30.1), 261 (31.1), 219 (22.0), 206 (25.8), 177 (22.8). HREIMS: calcd. for C₁₇H₃₃PO₄ 332.2116; found 332.2112. FTIR: 2958, 2936, 2872, 1678, 1640, 1605, 1433, 1312 (P=C), 1076 cm⁻¹.

Typical esterification procedure: Synthesis of methyl 4-nitrobenzoate.

4-Nitrobenzoic acid (109 mg, 0.652 mmol, 1.87 eq.) was weighed into a dried reaction vessel, sealed and purged with argon. A solution of the phosphorane **6a** in PhMe (0.5 ml, ~0.43 mmol, 1.24 eq.) was then added via syringe followed by methanol (14.0 μL, 0.347 mmol, 1.00 eq.) under argon. The clear yellow solution was stirred at 70 °C for 24 hours. The solution was cooled to room temperature and diluted with 5 ml of EtOAc. The organic layer was washed with 0.2N Na₂CO₃ (aq.) (3 x 2 ml) and dried with Na₂SO₄. The solution was gravity filtered and the drying agent was washed thoroughly (4 x 2 ml) with EtOAc. The solvent was removed under reduced pressure to afford a yellow crystalline mass as the crude product. The product was purified on a silica gel column (31 x 1 cm) with Hexane/CH₂Cl₂ 50/50 to give methyl 4-nitrobenzoate as white fine crystals (59 mg, 94%), see below.

Table 1, Entry 1: Methyl 4-nitrobenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.90 (s, 3H), 8.23 (d, 2H, $J=8.9$ Hz), 8.31 (d, 2H, $J=8.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 53.2, 123.9, 131.1, 135.9, 150.9, 165.6.

Table 1, Entry 2: Ethyl 4-nitrobenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 1.45 (t, 3H, $J=7.1$ Hz), 4.46 (q, 2H, $J=7.2$ Hz), 8.23 (d, 2H, $J=8.9$ Hz), 8.31 (d, 2H, $J=8.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 14.6, 62.4, 123.9, 131.1, 136.2, 150.9, 165.1.

Table 1, Entry 3: Isopropyl 4-nitrobenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 1.40 (d, 6H, $J=6.9$ Hz), 5.29 (septet, 1H, $J=6.4$ Hz), 8.20 (d, 2H, $J=9.0$ Hz), 8.27 (d, 2H, $J=9.0$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 22.2, 70.1, 123.9, 131.0, 136.6, 150.8, 164.6.

Table 1, Entry 4: N/A

Table 1, Entry 5: Phenethyl-4-nitrobenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.13 (t, 2H, $J=6.9$ Hz), 4.62 (t, 2H, $J=6.9$ Hz), 7.05-7.44 (m, 5H), 8.18 (d, 2H, $J=8.3$ Hz), 8.29 (d, 2H, $J=8.3$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 35.5, 66.7, 123.9, 127.2, 129.05, 129.3, 131.1, 136.0, 137.8, 150.9, 164.97.

Table 1, Entry 6: Methyl benzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.49 (s, 3H), 7.46 (t, 2H, $J=7.6$ Hz), 7.58 (t, 1H, $J=7.3$ Hz), 8.07 (d, 2H, $J=7.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 52.4, 128.7, 129.9, 130.6, 133.3, 167.5.

Table 1, Entry 7: Methyl 4-chlorobenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.83 (s, 3H), 7.33 (d, 2H, $J=8.5$ Hz), 7.89 (d, 2H, $J=8.3$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 52.6, 129.0, 129.1, 131.3, 139.8, 166.6.

Table 1, Entry 8: Methyl 4-hydroxybenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.68 (s, 3H), 6.82 (d, 2H, $J=8.8$ Hz), 7.87 (d, 2H, $J=8.8$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 53.0, 115.6, 122.4, 132.3, 161.0, 167.8.

Table 1, Entry 9: Methyl 4-methoxybenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.77 (s, 3H), 3.80 (s, 3H), 6.83 (d, 2H, $J=8.8$ Hz), 7.91 (d, 2H, $J=8.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 52.2, 55.7, 113.9, 123.0, 131.9, 163.7, 167.2.

Table 1, Entry 10: Methyl 2,6-dimethoxybenzoate: $^1\text{H-NMR}$ (CDCl_3) δ 3.74 (s, 6H), 3.83 (s, 3H), 6.48 (d, 2H, $J=8.4$ Hz), 7.21 (t, 1H, $J=8.3$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 52.7, 56.4, 104.3, 113.4, 131.5, 157.7, 167.4.

Table 1, Entry 11: Methyl 4-chlorocinnamate: $^1\text{H-NMR}$ (CDCl_3) δ 3.51 (s, 3H), 6.13 (d, 1H, $J=16.0$ Hz), 7.07 (d, 2H, $J=8.2$ Hz), 7.18 (d, 2H, $J=8.4$ Hz), 7.34 (d, 1H, $J=16.0$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 52.2, 118.8, 129.56, 129.61, 133.2, 136.6, 143.8, 167.6.

Table 1, Entry 12: Methyl 4-methoxycinnamate: $^1\text{H-NMR}$ (CDCl_3) δ 3.61 (s, 3H), 3.65 (s, 3H), 6.14 (d, 1H, $J=15.9$ Hz), 6.73 (d, 2H, $J=8.8$ Hz), 7.30 (d, 2H, $J=8.7$ Hz), 7.47 (d, 1H, $J=15.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 51.7, 55.4, 114.4, 116.4, 128.1, 130.9, 145.5, 160.3, 167.1.

Table 1, Entry 13: Ethyl cyclohexanecarboxylate: $^1\text{H-NMR}$ (CDCl_3) δ 1.26 (t, 3H, $J=7.0$ Hz), 1.48-1.92 (m, 10H), 2.21 (m, 1H), 4.04 (q, 2H, $J=7.1$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 14.5, 26.0, 26.4, 29.4, 44.3, 59.8, 176.7.

Table 2, Entry 1: (1*R/S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-nitrobenzoate) was obtained as white solid 86 mg (82%): (1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-nitrobenzoate) (retention): $^1\text{H-NMR}$ (CDCl_3) δ 0.80-2.2 (m, 17H), 4.98 (m, 1H), 8.21 (d, 2H, $J=9.0$ Hz), 8.29 (d, 2H, $J=9.0$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 16.85, 21.1, 22.4, 23.9, 26.9, 31.8, 34.5, 41.2, 47.5, 76.5, 123.9, 131.0, 136.6, 150.8, 164.6. (1*S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-nitrobenzoate) (inversion) had similar chemical shifts except for the C-1 proton $^1\text{H-NMR}$ δ 5.51 (broad s). The integration ratio of the C-1 protons corresponded to a retention : inversion ratio of 95 : 5. Standard samples of each

ester were prepared from L-menthol and neomenthol (1-epimer) and 4-nitrobenzoyl chloride for direct confirmation of the chemical shifts reported. See: J.A. Dodge et al, *J. Org. Chem.*, **1994**, 59, 234 (inversion); and R.B. Silverman et al, *Org. Lett.*, **2001**, 3, 2477 (retention).

Table 2, Entry 2: (*1R/S*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-methylbenzoate) was obtained as colourless oil (53%): (*1R*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-methylbenzoate) (retention): $^1\text{H-NMR}$ (CDCl_3) δ 0.7-2.2 (m, 17H), 2.43 (s, 3H), 4.94 (m, 1H), 7.26 (d, 2H, $J=8.0$ Hz), 7.97 (d, 2H, $J=8.1$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 16.9, 21.2, 22.0, 22.4, 24.1, 26.9, 31.8, 34.7, 41.4, 47.7, 74.9, 128.5, 129.9, 131.9, 143.7, 166.5. (*1S*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-methylbenzoate) (inversion): had similar chemical shifts except for the C-1 proton $^1\text{H-NMR}$ δ 5.44 (broad s). The integration ratio of the C-1 protons corresponded to a retention : inversion ratio of 63 : 37.

Table 2, Entry 3: (*1R/S*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-methoxybenzoate) was obtained as colourless oil 52 mg (52%): (*1R*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-methoxybenzoate) (retention): $^1\text{H-NMR}$ (CDCl_3) δ 0.65-2.2 (m, 17H), 3.87 (s, 3H), 4.92 (m, 1H), 6.94 (m, 2H), 8.02 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3) δ 16.95, 21.2, 22.4, 24.1, 26.9, 31.8, 34.7, 41.4, 47.7, 55.8, 74.8, 113.9, 123.9, 131.9, 163.6, 166.0. (*1S*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(4'-methoxybenzoate) (inversion): had similar chemical shifts except for the C-1 proton $^1\text{H-NMR}$ δ 5.44 (broad s). The integration ratio of the C-1 protons corresponded to a retention : inversion ratio of 33 : 67.

Table 2, Entry 4: (*1R/S*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(2'-methoxybenzoate) was obtained as colourless oil (28%): (*1S*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(2'-methoxybenzoate) (inversion): $^1\text{H-NMR}$ (CDCl_3) δ 0.65-2.2 (m, 17H), 3.87 (s, 3H), 5.43 (broad s, 1H), 6.95-7.10 (m, 2H), 7.45-7.50 (m, 2H), 7.75-7.91 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3) δ 21.2, 21.4, 22.6, 25.7, 26.5, 29.6, 35.4, 39.6, 56.2, 71.9, 112.4, 120.4, 121.1, 132.1, 133.7, 159.8, 165.9. (*1R*, *2S*, *5R*)-2-isopropyl-5-methylcyclohexyl-1-(2'-methoxybenzoate) (retention): had similar chemical shifts except for the C-1 proton $^1\text{H-NMR}$ δ 4.92 (m). The integration ratio of the C-1 protons corresponded to a retention : inversion ratio of 2 : 98.

Table 2, Entry 5: *(1R/S, 2S, 5R)*-2-isopropyl-5-methylcyclohexyl-1-(2'-methylbenzoate) was obtained as a colourless oil (27%): *(1S, 2S, 5R)*-2-isopropyl-5-methylcyclohexyl-1-(2'-methylbenzoate) (inversion): ^1H -NMR (CDCl_3) δ 0.60-2.2 (m, 17H), 2.56 (s, 3H), 5.40 (broad s, 1H), 6.95-7.35 (m, 3H), 7.85(d, 2H, $J=8.0$ Hz); ^{13}C -NMR (CDCl_3) δ 21.2, 21.4, 22.5, 22.6, 25.9, 27.2, 29.7, 35.3, 39.6, 47.4, 71.9, 126.1, 130.7, 131.0, 132.10, 132.13, 140.6, 167.3. *(1R, 2S, 5R)*-2-isopropyl-5-methylcyclohexyl-1-(2'-methylbenzoate) (retention) had similar chemical shifts except the C-1 proton ^1H -NMR δ 4.92 (m). The integration ratios of the C-1 protons corresponded to a retention : inversion ratio of 5 : 95.

Table 2, Entry 6: (1*R/S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(2,6-dimethoxybenzoate) was obtained as a white solid (56%): (1*S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(2',6'-dimethoxybenzoate) (inversion): $^1\text{H-NMR}$ (CDCl_3) δ 0.80-2.3 (m, 17H), 3.80 (s, 6H), 5.44 (broad s, 1H), 6.55 (d, 2H, J = 8.4 Hz), 7.27 (t, 2H, J = 8.4 Hz); $^{13}\text{C NMR}$ (CDCl_3) δ 20.9, 21.5, 22.7, 25.6, 26.7, 29.5, 35.2, 39.5, 47.25, 56.2, 72.7, 104.3, 114.8, 130.8, 157.5, 166.7. (1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(2',6'-dimethoxybenzoate) (retention) has similar chemical shifts except ester proton $^1\text{H-NMR}$ δ 4.75 (m). The integration ratio of the C-1 protons corresponded to a retention : inversion ratio of 4 : 96.

Table 2, Entry 7: (1*R/S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(2,4,6-trimethylbenzoate) was obtained as colourless oil (78%): (1*S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(2',4',6'-trimethylbenzoate) (inversion): ^1H -NMR (CDCl_3) δ 0.80-2.34 (m, 17H), 2.31 (s, 3H), 2.33 (s, 6H), 5.54 (broad s, 1H), 6.88 (s, 2H); ^{13}C -NMR (CDCl_3) δ 19.9, 21.3, 21.5, 22.6, 23.1, 25.5, 27.2, 29.3, 35.2, 39.7, 47.5, 72.4, 128.6, 132.6, 134.7, 139.1, 170.5. The minor diastereomer (1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl-1-(2',4',6'-trimethylbenzoate) (retention) was not observed in ^1H -NMR spectra.

Table 2, Entry 8: The NMR data were identical to Table 2, Entry 1 except the ratio of the C-1 protons at δ 4.98 (m, 1H) and 5.51 (broad s, 1H). The integration ratio of the C-1 protons corresponded to a retention : inversion ratio of 99.2 : 0.8.

Table 2, Entries 9 and 10: 1-Phenyl-1-propyl 4'-nitrobenzoate was obtained as a colourless oil 60.6 mg (61%) Entry 9, and 26.3 mg (27%) Entry 10: ^1H -NMR (CDCl_3) δ 0.99 (t, 3H, $J=7.4$ Hz), 1.9-2.25 (m, 2H, $J=7.0$ Hz), 5.95 (t, 1H, $J=6.8$ Hz), 7.1-7.52 (m, 5H), 8.29 (AB, 4H, $J=8.8$ Hz); ^{13}C -NMR (CDCl_3) δ 10.4, 29.7, 79.6, 123.9, 126.9, 128.6, 129.0, 131.1, 136.3, 140.2, 150.9, 164.4. Enantiomeric purity was determined by chiral HPLC on an Astec chirobiotic V column (hexane/iPrOH 98/2, flow rate 1 ml/min, 254nm). Standards were prepared from racemic 1-phenyl-1-propanol and enantiomerically pure (*1R*)-1-phenyl-1-propanol by reaction with 4-nitrobenzoyl chloride for confirmation of baseline separation and unambiguous enantiomeric assignment.

Standard retention times were: 6.00 min for (1*R*)-1-phenyl-1-propyl 4'-nitrobenzoate and 6.34 min for (1*S*)-1-phenyl-1-propyl 4'-nitrobenzoate.

1-phenylpropyl 4-nitrobenzoate

Table 2, Entry 11: 1-Phenyl-1-propyl 2',4',6'-trimethylbenzoate was obtained as a colourless oil (83%): $^1\text{H-NMR}$ (CDCl_3) δ 1.05 (t, 3H, $J=7.4$ Hz), 2.01 (m, 1H), 2.15 (m, 1H), 2.27 (s, 6H), 2.34 (s, 3H), 6.02 (t, 1H, $J=6.9$ Hz), 6.91 (s, 2H), 7.30-7.58 (m, 5H); $^{13}\text{C-NMR}$ (CDCl_3) δ 10.6, 20.0, 21.5, 29.6, 78.8, 127.2, 127.5, 128.4, 128.8, 131.8, 135.3, 139.5, 140.6, 170.5. The enantiomeric purity was determined on the alcohol liberated by reduction of the scalemic ester. Thus, a 1M solution of LiAlH_4 in THF (0.1 ml) was added to a solution of 5 mg of the scalemic ester in 0.1 ml THF. After 8 h the reaction mixture was decomposed with 0.05 ml of water. The crude alcohol mixture was extracted with 2 ml of CH_2Cl_2 and dried with Na_2SO_4 . The solution of 1-phenyl-1-propanol so obtained was analyzed by chiral GC on an Astec β -PM capillary column (30m x 0.25mm, flow rate=0.5 ml/min, temperature 120 $^\circ\text{C}$). Standard retention times were 7.10 min for (1*R*)-1-phenyl-1-propanol and 7.25 min for (1*S*)-1-phenyl-1-propanol.

Table 2, Entries 12 and 13: 2-Hexyl 4'-nitrobenzoate was obtained as a white solid in 71% (Entry 12) and 34 % (Entry 13) yield : ¹H-NMR (CDCl₃) δ 0.83 (t, 3H, *J*= 6.7 Hz), 1.25-1.32(m, 4H), 1.29 (d, 3H, *J*= 6.2 Hz), 1.33-1.80(m, 2H), 5.11 (m, 1H), 8.17(AB, 4H, *J*= 8.7 Hz); ¹³C-NMR (CDCl₃) δ 14.4, 20.4, 22.9, 27.9, 36.0, 73.5, 123.85, 131.0, 136.7, 150.8, 164.7. Enantiomeric purity of the esters was determined by direct chiral GC on an Astec β-PM capillary column (30m x0.25mm, flow rate=0.5 ml/min, temperature 130 °C) Standard retention times were 106.4 min for (2*S*)-2-hexyl 4'-nitrobenzoate, 107.7 min for (2*R*)-2-hexyl 4'-nitrobenzoate.

Table 2, Entry 14: 2-Hexyl 2',6'-dimethoxybenzoate was obtained as colourless oil (85 %): $^1\text{H-NMR}$ (CDCl_3) δ 0.93 (t, 3H, J = 6.9 Hz), 1.20-1.50 (m, 4H), 1.34 (d, 3H, J = 6.1 Hz), 1.51-1.80 (m, 2H), 3.80 (s, 6H), 5.20 (m, 1H), 6.55 (d, 4H, J = 8.4 Hz), 7.28 (t, 1H, J = 8.4 Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ 14.5, 20.5, 22.9, 27.9, 36.1, 56.3, 72.3, 104.3, 114.3, 131.0, 157.5, 166.6. The enantiomeric purity was determined by reductive liberation of the scalemic alcohol and conversion to the 2-hexyl 4'-nitrobenzoate derivative. Thus, a 1M solution of LiAlH_4 in THF (0.1 ml) was added to a solution of 5 mg of scalemic ester in 0.1 ml THF. After 24 h the reaction mixture was decomposed with 0.05 ml of 4N HCl followed by extraction into CH_2Cl_2 . The organic phase was dried with Na_2SO_4 , filtered and solutions of 4-nitrobenzoyl chloride (2 mg in 50 μL) and 4-dimethylaminopyridine (1.5 mg in 50 μL) were injected sequentially. After 2h the reaction mixture was diluted with CH_2Cl_2 (5 ml) and washed with 0.2M Na_2CO_3 (3 x 1ml), dried with Na_2SO_4 and

evaporated. The white solid so obtained was dissolved in 0.5 ml of CH₂Cl₂ and analyzed by chiral GC on Astec β -PM capillary column as reported in Entries 12 and 13.

1-methylpentyl 2,6-dimethoxybenzoate

Table 2, Entry 15: 2-Hexyl 2', 4', 6'-trimethylbenzoate was obtained as colourless oil (84 %): ¹H-NMR (CDCl₃) δ 0.95 (t, 3H, J = 6.7 Hz), 1.22-1.49 (m, 4H), 1.39 (d, 3H, J = 6.4 Hz), 1.50-1.85 (m, 2H), 2.31 (s, 3H), 2.34 (s, 6H), 5.25 (m, 1H), 6.91 (s, 2H); ¹³C-NMR (CDCl₃) δ 14.4, 19.9, 20.4, 21.5, 22.9, 28.0, 36.0, 72.2, 128.7, 132.1, 135.0, 139.3, 170.3. The enantiomeric purity was determined by reductive liberation of the alcohol, conversion to the scalemic 4-nitrobenzoate esters and chiral GC analysis as described in Entry 14.

Esterification of L-menthol with tributylphosphine and benzoyl peroxide:

A solution of benzoyl peroxide (185 mg, 0.64 mmol) in dry THF (0.5 mL) was added dropwise to a stirring mixture of L-menthol (100 mg, 0.64 mmol) and tributylphosphine (160 μ L, 0.64 mmol) in 0.5 ml of dry THF at 70 °C for 2h. The reaction mixture was then diluted with EtOAc (3.0mL), washed with 0.2N $\text{Na}_2\text{CO}_3(\text{aq.})$ (2 x 2 ml), dried with Na_2SO_4 , filtered and concentrated. The ^1H -NMR spectra of the product showed that (1*R/S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl benzoate was formed in approximately 53% conversion leaving 47% unreacted L-menthol. The integration ratio for the C-1 protons for retention : inversion in the ester products was 80 : 20.

Esterification of L-menthol with tributylphosphine and benzoyl peroxide in the presence of diisopropylamine:

A solution of benzoyl peroxide (232.6 mg, 0.96 mmol) in dry THF (1 mL) was added dropwise to a stirring mixture of L-menthol (100 mg, 0.64 mmol), tributylphosphine (240 μ L, 0.96 mmol) and diisopropylamine (0.45 mL, 3.2 mmol) in 0.5 mL of dry THF at 70 °C for 2h. The reaction mixture was then diluted with EtOAc (3.0 mL), washed with 2N HCl (2 x 2 mL) then 0.2N Na₂CO₃(aq.) (2 x 2 mL), dried with Na₂SO₄, filtered and concentrated. The ¹H-NMR spectra of the product showed that (1*R*/*S*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl benzoate was formed in approximately 47% conversion leaving 53% unreacted L-menthol. The integration ratio for the C-1 protons for retention : inversion in the ester products was 40 : 60.