General Methods. All reactions were carried out under nitrogen in oven-dried or flame-dried glassware. Tetrahydrofuran was purified using a Solv-Tek purification system employing activated Al₂O₃. Triphenylphosphine was recrystallized from hexane prior to use. Other commercially available reagents were used as received. All reactions were monitored by TLC analysis using GF254 silica gel coated plates. Column chromatography was carried out using silica gel (300-400 mesh) at increased pressure. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ on a Bruker DRX-400 spectrometer operating at 400 MHz for ¹H analyses and at 75 MHz for ¹³C analyses. Chemical shift data is expressed in ppm with reference to TMS. HR EIMS data was recorded on a Finnigan MAT 96 mass spectrometer. Optical rotation data were recorded in CHCl₃ or EtOH on a Perkin Elmer Polarimeter 343 operating at 20 °C for 589 nm. HPLC analyses were carried out using a Waters Delta Prep 4000 chromatography system with the indicated columns.
General procedure for catalytic Mitsunobu reactions. Procedure A.  To 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and 2-phenylethanol (0.21 mL, 1.8 mmol) in anhydrous THF (15 mL), was added triphenylphosphine (0.94 g, 3.6 mmol), diethyl azodicarboxylate (0.028 mL, 0.18 mmol), and iodosobenzene diacetate (1.16 g, 3.6 mmol).  The reaction was stirred at rt for 16 h and then the reaction mixture was diluted with diethyl ether (30 mL).  The organic phase was washed with saturated aq. NaHCO₃ (2 x 20 mL) and brine (20 mL).  The organic layer was dried with Na₂SO₄, filtered and evaporated.  The residue was purified by column chromatography to afford 2-phenylethyl 4-nitrobenzoate¹ as yellow solid: TLC (1:4 EA/hexane) Rₛ 0.55; ¹H-NMR (400 MHz, CDCl₃) δ 3.10 (t, 2H, J = 6.9 Hz), 4.59 (t, 2H, J = 6.9 Hz), 7.20-7.36 (m, 5H), 8.16 (d, 2H, J = 8.8 Hz), 8.28 (d, 2H, J = 8.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 55.2, 67.5, 114.0, 123.4, 127.3, 130.3, 130.7, 135.6, 150.5, 164.5.  The yield for the background reaction was determined by ¹H-NMR since the desired product was mixed with 2-phenylethyl acetate.

General procedure for slow addition of PPh₃ catalytic Mitsunobu reactions. Procedure B.  To 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and 2-phenylethanol (0.21 mL, 1.8 mmol) in anhydrous THF (11 mL), was added diethyl azodicarboxylate (0.028 mL, 0.18 mmol), and iodosobenzene diacetate (1.16 g, 3.6 mmol), then triphenylphosphine (0.94 g, 3.6 mmol) in 4 mL anhydrous THF was added slowly by syringe pump.  The reaction was stirred at rt for 16 h and then the reaction mixture was diluted with diethyl ether (30 mL).  The organic phase was washed with saturated aq. NaHCO₃ (2 x 20 mL) and brine (20 mL).  The organic layer was dried with Na₂SO₄, filtered and evaporated.  The residue was purified by column chromatography.
4-Phenylbutyl 4-nitrobenzoate. General procedure A was followed using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and 4-phenylbutanol (0.27 mL, 1.8 mmol), to afford a yellow oil: TLC (1:4 EA/hexane) R_f = 0.62; 1H-NMR (400 MHz, CDCl_3) δ 1.81 (m, 4H), 2.70 (t, 2H, J = 7.3 Hz), 4.39 (t, 2H, J = 6.1 Hz), 7.18-7.29 (m, 5H), 8.27 (d, 2H, J = 1.9 Hz), 8.29 (d, 2H, J = 1.9 Hz); 13C-NMR (100 MHz, CDCl_3) δ 27.6, 28.1, 35.3, 65.7, 123.4, 125.9, 128.3, 130.6, 135.7, 141.7, 150.4, 164.6; HRMS for C_{17}H_{17}NO_{4}: calcd 299.1158, found 299.1158.

Benzyl 4-nitrobenzoate. General procedure A was followed using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and benzyl alcohol (0.18 mL, 1.8 mmol), to afford a yellow solid: TLC (1:4 EA/hexane) R_f = 0.58; 1H-NMR (400 MHz, CDCl_3) δ 5.40 (s, 2H), 7.26-7.39 (m, 5H), 8.16 (d, 2H, J = 9 Hz), 8.28 (d, 2H, J = 9 Hz); 13C-NMR (100 MHz, CDCl_3) δ 67.7, 123.5, 128.4, 128.5, 128.6, 128.7, 130.8, 135.2, 135.4, 150.3, 164.5; HRMS for C_{14}H_{11}NO_{4}: calcd 257.0688, found 257.0688.

4-Bromobenzyl 4-nitrobenzoate. General procedure A was followed using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and 4-bromobenzyl alcohol (0.33 g, 1.8 mmol), to afford a pale yellow solid: TLC (1:4 EA/hexane) R_f = 0.58; 1H-NMR (400 MHz, CDCl_3) δ 5.34 (s, 2H), 7.32 (d, 2H, J = 8.1 Hz), 7.53 (d, 2H, J = 8.1 Hz), 8.23 (d, 2H, J = 12 Hz), 8.27 (d, 2H, J = 12 Hz); 13C-NMR (100 MHz, CDCl_3) δ 66.8, 123.5, 130.1, 130.8, 131.9, 162.3; HRMS for C_{14}H_{10}BrNO_{4}: calcd 334.9793, found 334.9793.
4-Methoxybenzyl 4-nitrobenzoate. Procedure A was followed using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and 4-methoxybenzyl alcohol (0.22 mL, 1.8 mmol), to afford a pale yellow solid: TLC (1:4 EA/hexane) R_f = 0.45; ^1H-NMR (400 MHz, CDCl_3) δ 3.82 (s, 3H), 5.33 (s, 2H), 6.92 (d, 2H, J = 8.7 Hz), 7.39 (d, 2H, J = 8.7 Hz), 8.22 (d, 2H, J = 9 Hz), 8.25 (d, 2H, J = 9 Hz); ^13C-NMR (100 MHz, CDCl_3) δ 55.2, 67.5, 114.0, 123.4, 127.3, 130.3, 130.7, 135.6, 150.3, 159.9, 164.5; HRMS for C_{15}H_{13}NO_5: calcd 287.0794, found 287.0793.

Benzyl phenylacetate. Procedure A was followed using phenyl acetic acid (0.33 g, 1.98 mmol) and benzyl alcohol (0.18 mL, 1.8 mmol), to afford a colorless oil: TLC (1:4 EA/Hexane) R_f 0.61; ^1H-NMR (400 MHz, CDCl_3) δ 3.67 (s, 2H), 5.13 (s, 3H), 7.25-7.35 (m, 10H); ^13C-NMR (100 MHz, CDCl_3) δ 41.2, 66.4, 127.0, 128.0, 128.1, 128.43, 128.47, 129.2, 133.8, 135.7, 171.2; HRMS for C_{15}H_{14}O_2: calcd 226.0993, found 226.0994.

2-Phenylethyl N-Boc-2-aminoacetate. Procedure A was followed using Boc-glycine (0.34 g, 1.98 mmol) and 2-phenylethanol (0.21 mL, 1.8 mmol), to afford a colorless oil: TLC (1:4 EA/Hexane) R_f = 0.33; ^1H-NMR (400 MHz, CDCl_3) δ 1.45 (s, 9H), 2.95 (t, 2H, J = 7.2 Hz), 3.89 (d, 2H, J = 5.2 Hz), 4.35 (t, 2H, J = 7.2 Hz), 4.93 (s, 1H) 7.19-7.30 (m, 5H); ^13C-NMR (100 MHz, CDCl_3) δ 82.2, 34.9, 42.3, 65.5, 79.8, 126.5, 128.4, 128.7, 137.3, 155.6, 170.2.
(R)-1-Phenylethyl 4-nitrobenzoate. Procedure B was followed, using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and (S)-1-phenylethanol (0.21 mL, 1.8 mmol), to afford a yellow oil: TLC (1:4 EA/Hexane) Rf = 0.61; 1H-NMR (400 MHz, CDCl3) δ 1.71 (d, 3H, J = 6.8 Hz), 6.15 (q, 1H, J = 6.8 Hz), 7.32-7.45 (m, 5H) 8.22 (d, 2H, J = 8.8 Hz), 8.26 (d, 2H, J = 8.8 Hz); 13C-NMR (100 MHz, CDCl3) δ 22.1, 74.1, 123.4, 126.0, 128.2, 128.6, 130.6, 135.8, 140.9, 150.4, 163.8; HRMS for C15H13NO4: calcd 271.0844, found 271.0844.

Ethyl (R)-2-((4-nitrobenzoyl)oxy)propionate. Procedure B was followed, using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and L-ethyl lactate (0.20 mL, 1.8 mmol), to afford a yellow solid: TLC (1:4 EA/Hexane) Rf = 0.46; 1H-NMR (300 MHz, CDCl3) δ 1.29 (t, 3H, J = 7.1 Hz), 1.66 (d, 3H, J = 7.0 Hz), 4.23 (q, 2H, J = 7.1 Hz), 5.35 (q, 1H, J = 7.0 Hz), 8.27 (d, 2H, J = 1.2 Hz), 8.29 (d, 2H, J = 1.2 Hz); 13C-NMR (100 MHz, CDCl3) δ 14.0, 16.9, 61.6, 69.9, 123.5, 130.9, 134.8, 150.7, 164.0, 170.1; HRMS for C12H13NO6: calcd 267.0743, found 267.0743.

(S)-2-Butyl 4-nitrobenzoate. Procedure B was followed, using 4-nitrobenzoic acid (0.33 g, 1.98 mmol) and (R)-2-butanol (0.27 mL, 1.8 mmol), to afford a yellow liquid: TLC (1:4 EA/Hexane) Rf = 0.64; 1H-NMR (400 MHz, CDCl3) δ 0.98 (t, 3H, J = 7.4 Hz), 1.36 (d, 3H, J = 6.2 Hz), 1.75 (m, 1H), 5.13 (m, 1H), 8.21 (d, 2H, J = 8.9 Hz), 8.29 (d, 2H, J = 8.9 Hz); 13C-NMR (100 MHz, CDCl3) δ 9.6, 19.3, 28.7, 74.1, 123.4, 130.5, 136.2, 150.3, 164.2; HRMS for C11H13NO4: calcd 223.0844, found 223.0844.
Characterization data of the products prepared from chiral secondary alcohols:

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<th>Yield (%)</th>
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Average ee = 68%

HPLC traces:
OJ column, 0.5mL/min, 50% IPA in hexane

From racemic 1-phenylethanol
Graph A-1, $ee = 93 - 7 = 86\%$

Graph A-2, $ee = 82.71 - 17.29 = 65\%$

Graph A-3, $ee = 82.62 - 17.38 = 65\%$
Graph A-4, ee = 85.92 – 14.08 = 72%

Graph A-5, ee = 86.03 – 13.97 = 72%
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<thead>
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<th>HPLC</th>
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HPLC traces:

OD column, 0.5mL/min, 50% EtOH in hexane

![HPLC trace 1](image1)

OD column, 0.7mL/min, 50% IPA in hexane

![HPLC trace 2](image2)
OD column, 0.4mL/min, 50% IPA in hexane

OT column, 0.5mL/min, 10% MeOH in CH₂Cl₂

OJ column, 0.7mL/min, 50% IPA in hexane

OJ column, 0.5mL/min, 50% IPA in hexane
OJ column, 0.5mL/min, 30% IPA in hexane

OJ column, 0.7mL/min, 4% IPA in hexane

OJ column, 0.7mL/min, 2% IPA in hexane

OJ column, 0.5mL/min, 1% IPA in hexane
<table>
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<th>HPLC</th>
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<td><strong>Third</strong> Set</td>
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Average ee = 87%

HPLC traces:
OJ column, 0.5mL/min, 1% IPA in hexane

From racemic 2-butanol
Graph B-1, $ee = 94 - 6 = 88\%$

Graph B-2, $ee = 93.59 - 6.41 = 87\%$

Graph B-3, $ee = 93.60 - 6.40 = 87\%$
Graph B-4, ee = 93.67 – 6.33 = 87%
References:
