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Asymmetric Synthesis of Enantioenriched α-Allyl Esters through Pd(BINAPHANE)-Catalysed Allylation of Disubstituted Ketenes

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Experimental Procedures & Characterization Data

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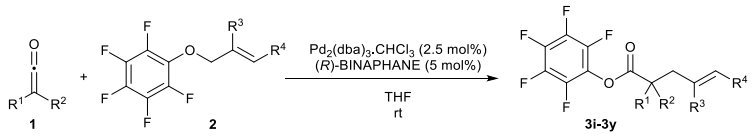
General Information:

THF was freshly distilled from benzophenone ketyl radical under nitrogen prior to use, while Hünig's base (diisopropylethylamine) was distilled from calcium hydride.[1] Most anhydrous solvents (dichloromethane and diethyl ether) were obtained by passing through activated alumina columns on a solvent purification system or distilled from calcium hydride. All chemicals were purchased from Sigma Aldrich (Merck Life Sciences) or Fisher Scientific and used as received from the supplier without further purification unless mentioned otherwise. All ketenes and allyl aryl ethers were synthesised according to reported literature procedures.[2,3]

NMR spectra were recorded on a Bruker DPX Avance 200 spectrometer (200 MHz for ^{1}H and 50 MHz for ^{13}C), on a Bruker Biospin AG 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) or on a Bruker 600 MHz spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C). NMR chemical shifts were reported relative to TMS (0 ppm) or $CHCl_3$ (7.26 ppm) for ^{1}H and to $CDCl_3$ (77.23 ppm) for ^{13}C spectra. High resolution mass spectra were recorded on Agilent Technologies 6520 Accurate Mass Q-TOF LC-MS instrument at Oakland University or at Trinity College Dublin using ESI or APCI. Low resolution mass spectra were recorded on a GC/MS Hewlett Packard HP 6890 GC instrument with a 5973 mass selective detector. IR spectra were recorded on a Bio Rad FTS-175C spectrometer. Optical rotations were measured on a Rudolph DigiPol 781 TDV automatic polarimeter.

Chiral high-performance liquid chromatography analysis (HPLC) was performed using Daicel Chiralcel OD-H, Chiralpak AD, and Chiralpak AD-H (Daicel chemical Ind., Ltd.) on a Perkin Elmer Flexar or on an Agilent 1200 series instrument attached with diode array detector (deuterium lamp, 190-600 nm) with HPLC-grade isopropanol and hexanes as the eluting solvents. Enantiomeric excesses were determined at λ = 254, 225 nm or 210 nm (details given for each compound).

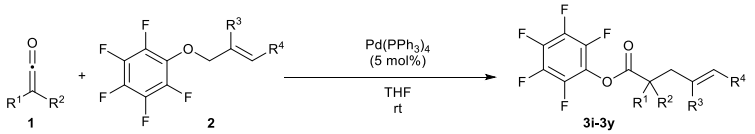
General Procedure A for catalytic enantioselective allylation reaction:



A solution of BINAPHANE (0.008 mmol, 0.05 equiv) in THF (0.4 mL) was added to a solution of $Pd_2dba_3.CHCl_3$ (0.004 mmol, 0.025 equiv) in THF (0.4 mL). The reaction solution was stirred for 10 min. Allyl ether **2** (0.16 mmol, 1.0 equiv-1.5 equiv) in THF (0.4 mL) was then added. Ketene **1** (0.16 mmol, 1.0 equiv) in THF (0.4 mL) was added in one portion to the reaction solution. The reaction was stirred at room temperature overnight (total reaction time: 16-20 h) and then neutral silica (0.5 g) was added to the reaction solution and the solvent was evaporated. The preabsorbed crude/silica was loaded onto a neutral silica column (20 cm × 1 cm), and eluted with a gradient solvent system (0-3% EtOAc/hexanes) to afford the desired product as a solid or oil in *ca.* 80->95% purity as determined by GC-MS and ^{1}H NMR analysis.

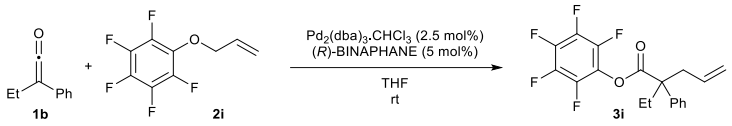
For racemic or achiral sample generation, General Procedure B was followed.

General Procedure B for non-enantioselective catalytic allylation reaction:

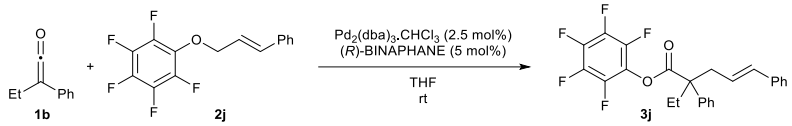


A solution of allyl ether **2** (0.17 mmol, 1.0-1.2 equiv) in THF (0.4 mL) was added to $Pd(PPh_3)_4$ (0.0085 mmol, 0.05 equiv) in THF (0.5 mL). Ketene **1** (0.17 mmol, 1.0-1.2 equiv) in THF (0.8 mL)

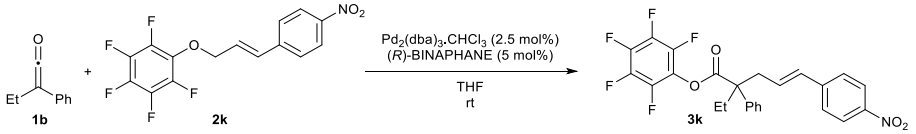
was then added in one portion to the reaction solution and the resulting solution was stirred overnight (total reaction time: 16-20 h). Neutral silica (0.5 g) was then added to the reaction solution and the solvent was evaporated. The preabsorbed crude/silica was loaded onto a neutral silica column (20 cm × 1 cm), and eluted with a gradient solvent system (0-3% EtOAc/hexanes) to afford the desired product as a solid or oil in *ca.* 80->95% purity as determined by GC-MS and ^{1}H NMR analysis.



Perfluorophenyl 2-ethyl-2-phenylpent-4-enoate (3i): Following General Procedure A, a solution of BINAPHANE (7 mg, 0.010 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (5 mg, 0.005 mmol). A solution of allyl ether **2i** (71 mg, 0.32 mmol, 1.5 equiv) and solution of ketene **1b** (31 mg, 0.21 mmol) were then added. Product **3i** was isolated as a pale yellow oil (70 mg, 90%). HPLC analysis: 34% ee [Daicel Chiralcel OD-H column; 1.0 mL/min; solvent system: 100% hexanes; retention times: 8.1 min (major), 9.6 min (minor)]; $[\alpha]_D^{24}$ = 71.2 (c = 1.65, $CHCl_3$); IR (thin film) 1777, 1519 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.41-7.28 (m, 5H), 5.61-5.49 (m, 1H), 5.15 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.10 (*app* dt, *J* = 10.2, 0.9 Hz, 1H), 2.96 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.87 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.30-2.12 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.0, 142.6 (m), 140.5, 140.1 (m), 139.3 (m), 136.8 (m), 132.5, 128.8, 127.6, 126.8, 119.4, 55.1, 38.8, 27.2, 8.3; $(M + H)^+$ HRMS m/z calcd for $(C_{19}H_{16}F_5O_2)^+$: 371.1061; found: 371.1065.

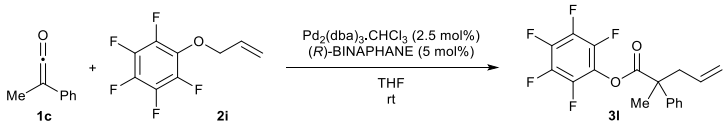


Perfluorophenyl (*E*)-2-ethyl-2,5-diphenylpent-4-enoate (3j): Following General Procedure A, a solution of BINAPHANE (7 mg, 0.010 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (5 mg, 0.005 mmol). A solution of allyl ether **2j** (58 mg, 0.20 mmol) and a solution of ketene **1b** (28 mg, 0.20 mmol) were then added. Product was isolated as an off-white solid (71 mg, 82%), which was composed of an inseparable mixture of linear isomer **3j** (96%) and branched isomer **3j′** (4%). mp 84-85 °C; HPLC analysis: 70% ee [Daicel Chiralcel OD-H column; 0.5 mL/min; solvent system: 1% isopropanol in hexane; retention times: 12.4 min (major), 13.2 min (minor)]; IR (thin film) 1774, 1520 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.43-7.18 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 5.93 (*app* quint, *J* = 7.9 Hz, 1H), 3.11 (dd, *J* = 14.2, 8.0 Hz, 1H), 3.02 (dd, *J* = 14.1, 6.8 Hz, 1H), 2.33-2.16 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.1, 142.7 (m), 140.5, 140.1 (m), 139.3 (m), 137.3, 136.9 (m), 134.3, 128.8, 128.7, 127.7, 127.6, 126.8, 126.4, 124.1, 55.5, 38.1, 27.4, 8.4; $(M + Na)^+$ HRMS m/z calcd for $(C_{25}H_{19}F_5NaO_2)^+$: 469.1197; found: 469.1191.

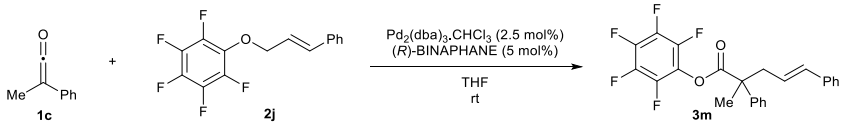


Perfluorophenyl (*E*)-2-ethyl-5-(4-nitrophenyl)-2-phenylpent-4-enoate (3k): Following General Procedure A, a solution of BINAPHANE (6 mg, 0.008 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (4 mg, 0.004 mmol). A solution of allyl ether **2k** (57 mg, 0.16 mmol) and a solution of ketene **1b** (24 mg, 0.16 mmol) were then added. Product was isolated as an oily solid (72 mg, 89%), which was composed of an inseparable mixture of linear isomer **3k** (88%) and branched isomer **3k′**

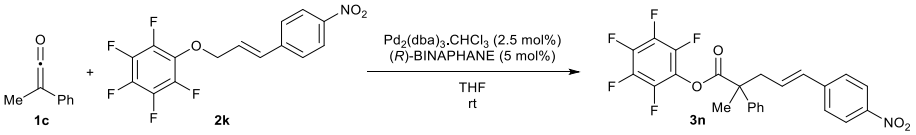
(12%). HPLC analysis: 75% ee [Daicel Chiralcel OD-H column; 1.0 mL/min; solvent system: 2% isopropanol in hexane; retention times: 11.1 min (minor), 14.8 min (major)]; $[\alpha]_D^{24}$ = –6.1 (c = 1.72, $CHCl_3$); IR (thin film) 1775, 1597, 1519 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 8.14 (d, J = 7.0 Hz, 2H), 7.45-7.31 (m, 7H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.14 (*app* quint, *J* = 7.3 Hz, 1H), 3.16-3.05 (m, 2H), 2.34-2.19 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 171.8, 147.1, 143.6, 142.6 (m), 140.9 (m), 140.2 (m), 140.1, 139.3 (m), 138.4 (m), 136.7 (m), 132.4, 129.6, 129.0, 127.9, 126.9, 126.8, 124.2, 55.4, 38.5, 27.7, 8.5; $(M + H)^+$ HRMS m/z calcd for $(C_{25}H_{19}F_5NO_4)^+$: 492.1229; found: 492.1226.



Perfluorophenyl 2-methyl-2-phenylpent-4-enoate (3l): Following General Procedure A, a solution of BINAPHANE (9.5 mg, 0.014 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (7 mg, 0.007 mmol). A solution of allyl ether **2i** (91 mg, 0.41 mmol, 1.5 equiv) and a solution of ketene **1c** (36 mg, 0.27 mmol) were then added. Product **3l** was isolated as a clear oil (63 mg, 65%). ee determination: 34% ee [determined by GC-MS analysis of diastereomeric mixture formed from reaction with (*S*)-α-methylbenzylamine]; $[\alpha]_D^{24}$ = –13.4 (c = 3.23, $CHCl_3$); IR (thin film) 1777, 1520 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.43-7.28 (m, 5H), 5.68 (m, 1H), 5.73-5.62 (m, 1H), 5.18-5.12 (m, 2H), 2.97 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.78 (dd, *J* = 13.8, 7.1 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.4, 142.7 (m), 141.7, 140.0 (m), 139.3 (m), 136.8 (m), 132.9, 128.9, 127.7, 126.2, 119.7, 50.9, 43.7, 22.9; $(M + H)^+$ HRMS m/z calcd for $(C_{19}H_{17}F_4O_2)^+$: 357.0908; found: 357.0908.

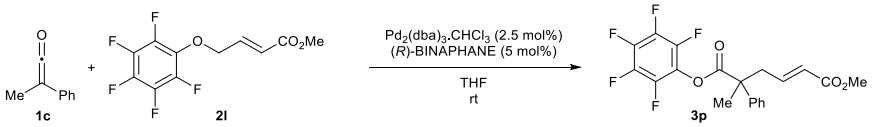


Perfluorophenyl (*E*)-2-methyl-2,5-diphenylpent-4-enoate (3m): Following General Procedure A, a solution of BINAPHANE (8.5 mg, 0.012 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (6 mg, 0.006 mmol). A solution of allyl ether **2j** (72 mg, 0.24 mmol) and a solution of ketene **1c** (32 mg, 0.24 mmol) were then added. Product was isolated as an oily solid (45 mg, 43%), which was composed of an inseparable mixture of linear isomer **3m** (92%), **2j** (2%) and methylphenylketene dimer (6%). HPLC analysis: 70% ee [Daicel Chiralcel OD-H column; 0.5 mL/min; solvent system: 1% isopropanol in hexane; retention times: 12.2 min (major), 12.8 min (minor)]; $[\alpha]_D^{24}$ = 5.1 (c = 1.26, $CHCl_3$); IR (thin film) 1776, 1521 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.45-7.18 (m, 10H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.07 (*app* quint, *J* = 7.4 Hz, 1H), 3.12 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.92 (dd, *J* = 13.8, 7.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, Major isomer): δ 172.4, 142.2 (m), 141.6, 140.5 (m), 138.9 (m), 137.3, 137.2 (m), 134.7, 129.0, 128.8, 127.8, 127.7, 126.4, 126.2, 124.5, 51.3, 43.0, 23.1; $(M + H)^+$ HRMS m/z calcd for $(C_{24}H_{18}F_5O_2)^+$: 433.1221; found: 433.1227.

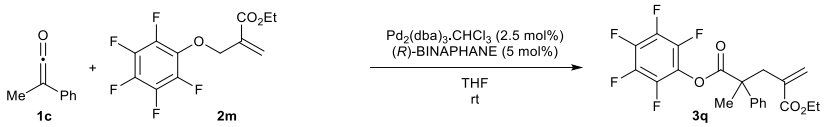


Perfluorophenyl (*E*)-2-methyl-5-(4-nitrophenyl)-2-phenylpent-4-enoate (3n): Following General Procedure A, a solution of BINAPHANE (7 mg, 0.010 mmol) was added to a solution of

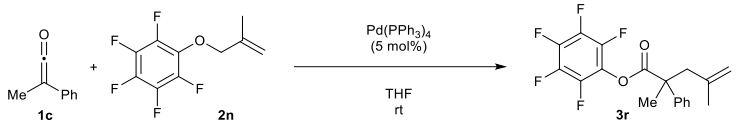
$Pd_2dba_3.CHCl_3$ (5 mg, 0.005 mmol). A solution of allyl ether **2k** (69 mg, 0.20 mmol) and a solution of ketene **1c** (26 mg, 0.20 mmol) were then added. Product was isolated as an off-white oil (81 mg, 85%) which was composed of an inseparable mixture of linear isomer **3n** (79%), **2k** (12%), and branched isomer **3n′** (9%). HPLC analysis: 80% ee [Daicel Chiralcel OD-H column; 1.0 mL/min; solvent system: 2% isopropanol in hexane; retention times: 16.7 min (minor), 17.8 min (major)]; $[\alpha]_D^{24}$ = 17.0 (c = 1.17, $CHCl_3$); IR (thin film) 1775, 1518, 1343 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.55-7.32 (m, 7H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.27 (*app* quint, *J* = 7.4 Hz, 1H), 3.15 (dd, *J* = 14.0, 7.7 Hz, 1H), 2.98 (dd, *J* = 14.0, 7.3 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.2, 147.1, 143.6, 142.6 (m), 141.2, 141.0 (m), 140.2 (m), 139.4 (m), 138.4 (m), 136.8 (m), 132.8, 129.9, 129.1, 128.0, 126.9, 126.1, 124.2, 51.2, 43.2, 23.2; $(M + Na)^+$ HRMS m/z calcd for carboxylic acid derivative $(C_{18}H_{17}NNaO_4)^+$: 334.1050; found: 334.1053.



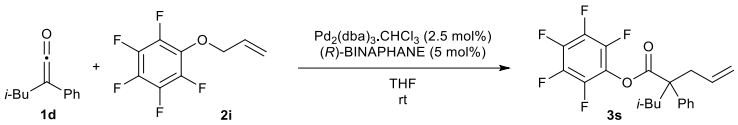
1-Methyl 6-(perfluorophenyl) (*E*)-5-methyl-5-phenylhex-2-enedioate (3p): Following General Procedure A, a solution of BINAPHANE (6 mg, 0.009 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (6 mg, 0.006 mmol). A solution of allyl ether **2l** (49 mg, 0.17 mmol) and a solution of ketene **1c** (23 mg, 0.17 mmol) were then added. Product was isolated as a clear oil (53 mg, 75%) which was composed of an inseparable mixture of linear isomer **3p** (84%), **2l** (12%), and branched isomer **3p′** (4%). HPLC analysis: 79% ee [Daicel Chiralpak AD column; 1.0 mL/min; solvent system: 1% isopropanol in hexane; retention times: 7.2 min (major), 8.1 min (minor)]; $[\alpha]_D^{24}$ = 17.8 (c = 1.97, $CHCl_3$); IR (thin film) 1777, 1727, 1521 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.44-7.31 (m, 5H), 6.79 (*app* quint, *J* = 7.5 Hz, 1H), 5.91 (dt, *J* = 15.5, 1.2 Hz, 1H), 3.71 (s, 3H), 3.06 (ddd, *J* = 14.3, 7.8, 1.2 Hz, 1H), 2.93 (ddd, *J* = 14.2, 7.3, 1.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.0, 166.5, 143.2, 142.5 (m), 140.6, 140.1 (m), 139.4 (m), 138.5 (m), 136.8 (m), 129.2, 128.6, 128.1, 126.1, 125.4 (m), 51.8, 50.7, 42.3, 22.8; $(M + H)^+$ HRMS m/z calcd for $(C_{20}H_{16}F_5O_4)^+$: 415.0963; found: 415.0960.



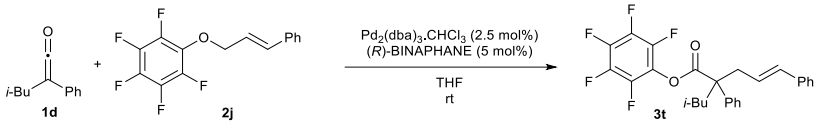
5-Ethyl 1-(perfluorophenyl) 2-methyl-4-methylene-2-phenylpentanedioate (3q): Following General Procedure A, a solution of BINAPHANE (5 mg, 0.008 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (4 mg, 0.004 mmol). A solution of allyl ether **2m** (46 mg, 0.16 mmol) and a solution of ketene **1c** (20 mg, 0.16 mmol) were then added. Product **3q** was isolated as a clear oil (45 mg, 68%). HPLC analysis: 44% ee [Daicel Chiralcel OD-H column; 0.5 mL/min; solvent system: 1% isopropanol in hexane; retention times: 12.8 min (major), 13.3 min (minor)]; $[\alpha]_D^{24}$ = 18.5 (c = 1.00, $CHCl_3$); IR (thin film) 1777, 1727, 1521 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.40-7.28 (m, 5H), 6.20 (d, *J* = 1.3 Hz, 1H), 5.37 (d, *J* = 1.0 Hz, 1H), 4.11-3.96 (m, 2H), 3.19 (s, 2H), 1.75 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.4, 167.5, 142.5 (m), 140.6, 140.1 (m), 139.3 (m), 138.4 (m), 136.7 (m), 136.5, 129.3, 128.7, 127.8, 126.7, 125.5 (m), 61.1, 51.8, 39.8, 21.8, 14.3; $(M + H)^+$ HRMS m/z calcd for $(C_{21}H_{18}F_5O_4)^+$: 429.1120; found: 429.1120.



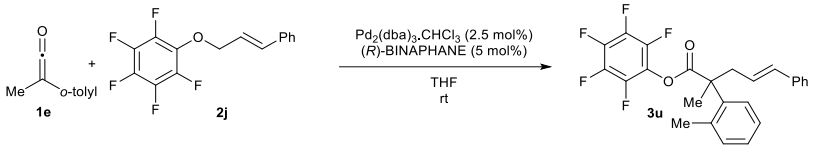
Perfluorophenyl 2,4-dimethyl-2-phenylpent-4-enoate (3r): Following General Procedure B, a solution of allyl ether **2n** (45 mg, 0.19 mmol) was added to $Pd(PPh_3)_4$ (11 mg, 0.0094 mmol) solution. A solution of ketene **1c** (25 mg, 0.19 mmol) was then added. Product **3r** was isolated as a clear oil (55 mg, 72%). IR (thin film) 1776, 1520 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, Major isomer): δ 7.46-7.29 (m, 5H), 4.89 (*app* t, *J* = 1.7 Hz, 1H), 4.72 (*app* d, *J* = 0.8 Hz, 1H), 3.03 (d, *J* = 13.8 Hz, 1H), 2.78 (d, *J* = 13.7 Hz, 1H), 1.78 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, Major isomer): δ 172.8, 142.2 (m), 141.8, 141.3, 140.5 (m), 138.8 (m), 137.2 (m), 128.8, 127.7, 126.5, 125.5 (m), 116.3, 50.3, 47.1, 24.0, 22.1; $(M + H)^+$ HRMS m/z calcd for $(C_{19}H_{16}F_5O_2)^+$: 371.1065; found: 371.1055.



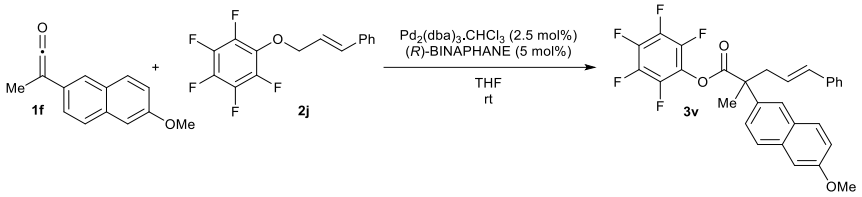
Perfluorophenyl 2-isobutyl-2-phenylpent-4-enoate (3s): Following General Procedure A, a solution of BINAPHANE (8 mg, 0.011 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (6 mg, 0.006 mmol). A solution of allyl ether **2i** (74 mg, 0.33 mmol, 1.5 equiv) and a solution of ketene **1d** (38 mg, 0.22 mmol) were then added. Product **3s** was isolated as a clear oil (47 mg, 54%). HPLC analysis: 41% ee [Daicel Chiralcel OD-H column; 0.5 mL/min; solvent system: 100% hexane; retention times: 13.3 min (minor), 14.1 min (major)]; $[\alpha]_D^{24}$ = –17.7 (c = 0.64, $CHCl_3$); IR (thin film) 1775, 1518 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.42-7.28 (m, 5H), 5.68-5.57 (m, 1H), 5.17 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.13 (*app* d, *J* = 10.2 Hz, 1H), 3.04 (*app* sept, *J* = 7.3 Hz, 2H), 2.13 (dq, *J* = 14.3, 5.7 Hz, 2H), 1.70 (sept, *J* = 6.5 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.2, 142.6 (m), 141.0, 140.1 (m), 139.4 (m), 138.3 (m), 136.8 (m), 132.7, 128.7, 127.6, 126.9, 119.6, 54.6, 43.2, 39.3, 24.6, 24.5, 24.2; $(M + H)^+$ HRMS m/z calcd for $(C_{21}H_{20}F_5O_2)^+$: 399.1378; found: 399.1375.



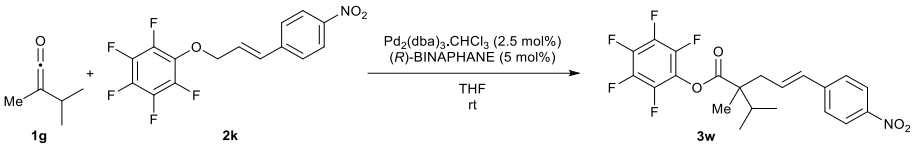
Perfluorophenyl (*E*)-2-isobutyl-2,5-diphenylpent-4-enoate (3t): Following General Procedure A, a solution of BINAPHANE (9 mg, 0.013 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (7 mg, 0.006 mmol). A solution of allyl ether **2j** (77 mg, 0.26 mmol) and a solution of ketene **1d** (45 mg, 0.26 mmol) were then added. Product was isolated as a cloudy oil (112 mg, 92%) which was composed of an inseparable mixture of linear isomer **3t** (91%) and branched isomer **3t′** (9%). HPLC analysis: 68% ee [Daicel Chiralcel OD-H column; 0.5 mL/min; solvent system: 100% hexane; retention times: 30.7 min (major), 34.1 min (minor)]; $[\alpha]_D^{24}$ = 4.46 (c = 1.54, $CHCl_3$); IR (thin film) 1774, 1517 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.35-7.09 (m, 10H), 6.41 (d, *J* = 15.8 Hz, 1H), 5.91 (*app* quint, *J* = 7.3 Hz, 1H), 3.16-3.04 (m, 2H), 2.13-2.02 (m, 2H), 1.66 (m, 1H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.2, 142.7 (m), 141.0, 140.8 (m), 140.2 (m), 139.3 (m), 137.8 (m), 137.4, 136.8 (m), 134.6, 128.8, 128.7, 127.7, 127.6, 126.9, 126.4, 124.3, 55.0, 43.4, 38.7, 24.7, 24.5, 24.3; $(M + H)^+$ HRMS m/z calcd for $(C_{27}H_{24}F_5O_2)^+$: 475.1691; found: 475.1666.



Perfluorophenyl (*E*)-2-methyl-5-phenyl-2-(*o*-tolyl)pent-4-enoate (3u): Following General Procedure A, a solution of BINAPHANE (9 mg, 0.013 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (7 mg, 0.006 mmol). A solution of allyl ether **2j** (76 mg, 0.25 mmol) and a solution of ketene **1e** (45 mg, 0.25 mmol) were then added. Product was isolated as an off-white oily solid (86 mg, 77%) which was composed of an inseparable mixture of linear isomer **3u** (82%), branched isomer **3u′** (12%) and methyl-*o*-tolylketene dimer (6%). HPLC analysis: 14% ee [Daicel Chiralpak AD-H column; 0.5 mL/min; solvent system: 1% isopropanol in hexane; retention times: 8.4 min (major), 9.0 min (minor)]; IR (thin film) 1768, 1511 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.30-7.08 (m, 9H), 6.36 (d, *J* = 19.4 Hz, 1H), 5.77 (m, 1H), 3.03 (ddd, *J* = 14.1, 6.7, 1.2 Hz, 1H), 2.93 (ddd, *J* = 14.0, 8.2, 0.9 Hz, 1H), 2.34 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 173.7, 140.1 (m), 138.9, 137.3, 136.5, 134.4, 132.4, 128.7, 127.8, 127.6, 126.5, 126.4, 126.3, 124.4, 50.6, 41.2, 24.6, 20.5; $(M + Na)^+$ HRMS m/z calcd for carboxylic acid derivative $(C_{19}H_{20}NaO_2)^+$: 303.1356; found: 303.1366.

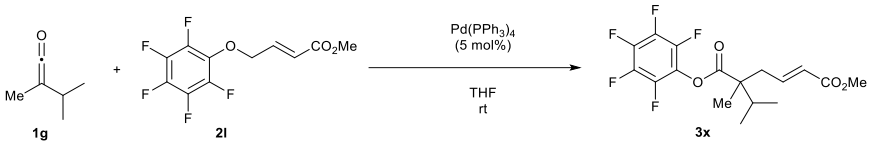


Perfluorophenyl (*E*)-2-(6-methoxynaphthalen-2-yl)-2-methyl-5-phenylpent-4-enoate (3v): Following General Procedure A, a solution of BINAPHANE (8 mg, 0.011 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (6 mg, 0.006 mmol). A solution of allyl ether **2j** (66 mg, 0.22 mmol) and a solution of ketene **1f** (47 mg, 0.22 mmol) were then added. Product was isolated as a yellow oily solid (79 mg, 77%) which was composed of an inseparable mixture of linear isomer **3v** (78%), **2j** (6%), ketene dimer (10%) and branched isomer **3v′** (6%). HPLC analysis: 69% ee [Daicel Chiralpak AD-H column; 1.0 mL/min; solvent system: 1% isopropanol in hexane; retention times: 7.3 min (minor), 8.5 min (major)]; $[\alpha]_D^{24}$ = 7.33 (c = 1.31, $CHCl_3$); IR (thin film) 1774, 1520, 1382 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 7.81-7.14 (m, 11H), 6.54 (t, *J* = 16.0 Hz, 1H), 6.10 (*app* quint, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.21 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.04 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.5, 158.3, 137.3, 136.7, 134.7, 134.0, 129.9, 129.0, 128.7, 127.6, 127.6, 126.4, 125.0, 124.8, 124.5, 119.5, 105.8, 55.6, 51.2, 43.0, 23.2; $(M + H)^+$ HRMS m/z calcd for $(C_{29}H_{22}F_5O_3)^+$: 513.1484; found: 513.1499.

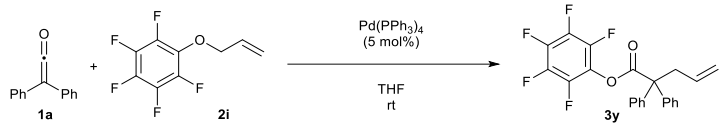


Perfluorophenyl (*E*)-2-isopropyl-2-methyl-5-(4-nitrophenyl)pent-4-enoate (3w): Following General Procedure A, a solution of BINAPHANE (7 mg, 0.010 mmol) was added to a solution of $Pd_2dba_3.CHCl_3$ (5 mg, 0.005 mmol). A solution of allyl ether **2k** (70 mg, 0.20 mmol) and a solution of ketene **1g** (20 mg, 0.20 mmol) were then added. Product **3w** was isolated as a brown oil (84 mg, 93%) which was composed of an inseparable mixture of (*E*)-**3w** (85%) and (*Z*)-**3w** (15%). HPLC analysis:

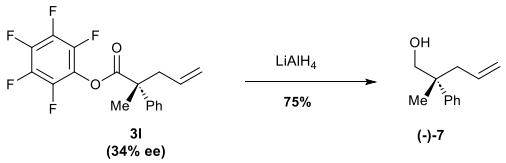
3% ee [Daicel Chiralpak AD-H column; 1.0 mL/min; solvent system: 1% isopropanol in hexane; retention times: 9.3 min (major), 11.9 min (minor)]; IR (thin film) 1772, 1597, 1519, 1344 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, Major isomer): δ 8.17 (*app* d, *J* = 9 Hz, 2H), 7.46 (*app* d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.44-6.39 (m, 1H), 2.81 (dd, J = 13.8, 6.6 Hz, 1H), 2.50 (ddd, *J* = 13.8, 7.8, 0.6 Hz, 1H), 2.25 (quint, *J* = 7.2 Hz, 1H), 1.25 (s, 3H), 1.04 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 173.0, 147.1, 143.7, 142.7 (m), 140.2 (m), 139.4 (m), 136.9 (m), 132.3, 130.4, 126.9, 124.2, 51.4, 41.2 35.3, 18.3, 17.1, 16.7; $(M + H)^+$ HRMS m/z calcd for $(C_{21}H_{19}F_5NO_4)^+$: 444.1229; found: 444.1218.



1-methyl 6-(perfluorophenyl) (*E*)-5-isopropyl-5-methylhex-2-enedioate (3x): Following General Procedure B, a solution of allyl ether **2l** (52 mg, 0.18 mmol) was added to $Pd(PPh_3)_4$ (11 mg, 0.009 mmol) solution. A solution of ketene **1g** (18 mg, 0.18 mmol) was then added. Product was isolated as a yellow oily solid (27 mg, 39%) which was composed of an inseparable mixture of linear isomer **3x** (97%) and branched isomer **3x′** (3%). IR (thin film) 1775, 1727, 1519 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, Major isomer): δ 6.95 (*app* quint, *J* = 8.1 Hz, 1H), 5.93 (d, *J* = 15.5 Hz, 1H), 3.74 (s, 3H), 2.72 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.45 (*app* dd, *J* = 14.1, 8.2 Hz, 1H), 2.20 (sept, *J* = 6.9 Hz, 1H), 1.24 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Major isomer): δ 172.5, 166.6, 143.7, 142.5 (m), 140.2 (m), 139.4 (m), 136.9 (m), 125.0, 51.8, 50.9, 39.8, 35.2, 18.2, 17.2, 17.2; $(M - H)^-$ HRMS m/z calcd for $(C_{17}H_{16}F_5O_4)^-$: 379.0974; found: 379.0981.



Perfluorophenyl 2,2-diphenylpent-4-enoate (3y): Following General Procedure B, a solution of allyl ether **2i** (71 mg, 0.32 mmol) was added to $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) solution. A solution of ketene **1a** (52 mg, 0.27 mmol) was then added. Product **3y** was isolated as a clear oil (68 mg, 61%). IR (thin film) 1776, 1520 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.40-7.30 (m, 10H), 5.67-5.60 (m, 1H), 5.04-5.01 (m, 2H), 3.31 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.5, 142.1 (m), 141.0, 140.5 (m), 138.9 (m), 137.3 (m), 133.1, 129.1, 128.4, 127.7, 119.5, 61.0, 43.0; $(M + H)^+$ HRMS m/z calcd for $(C_{23}H_{16}F_5O_2)^+$: 419.1065; found: 419.1070.

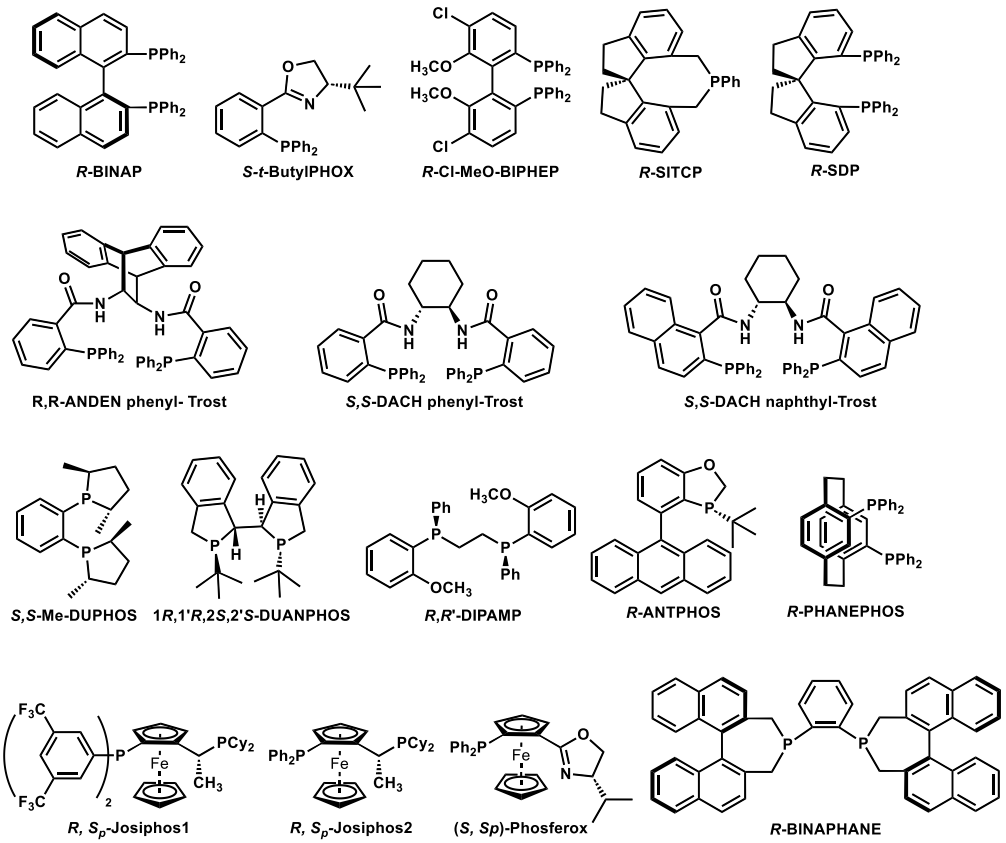


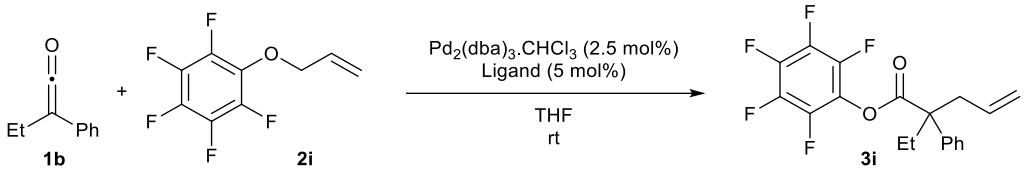
(*R*)-2-methyl-2-phenylpent-4-en-1-ol ((–)-7)): 3l (38 mg, 0.11 mmol) was dissolved in THF (1 mL) and the solution cooled to 0 °C. $LiAlH_4$ (2.4 M in THF, 0.1 mL, 0.24 mmol) was then added at 0 °C and the reaction was stirred for 1 h before being quenched with Rochelle's salt. Extraction with EtOAc and drying of organics over anhydrous Na_2SO_4, followed by concentration *in vacuo* afforded **7** (14.5 mg, 75%), isolated as a colourless oil. $[\alpha]_D^{24} = -78.4$ (c = 0.59, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4H), 7.25-7.22 (m, 1H), 5.63-5.56 (m, 1H), 5.05 (*app* dq, *J* = 16.8, 1.8 Hz, 1H), 4.99 (*app* dt, *J* = 10.2, 1.2 Hz, 1H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.63 (d, *J* = 11.4 Hz, 1H), 2.56 (dd, *J* = 14.4,

6.6 Hz, 1H), 2.36 (dd, J = 13.8, 8.4 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 134.6, 128.7, 126.9, 126.6, 117.9, 72.0, 43.4, 43.2, 22.0.

Determination of absolute stereochemistry of allyl esters: The absolute stereochemistry of the major enantiomer of allyl ester **3l** was deduced by comparison of the specific rotation value for derived alcohol **7** with the literature value for that compound.[4] The major enantiomer for **7** was determined to possess (*R*)-configuration, and by analogy all enantioenriched allyl ester examples (**3i**-**3w**) were deduced to possess (*R*) absolute stereochemistry for the major enantiomer.

General ligand screening:

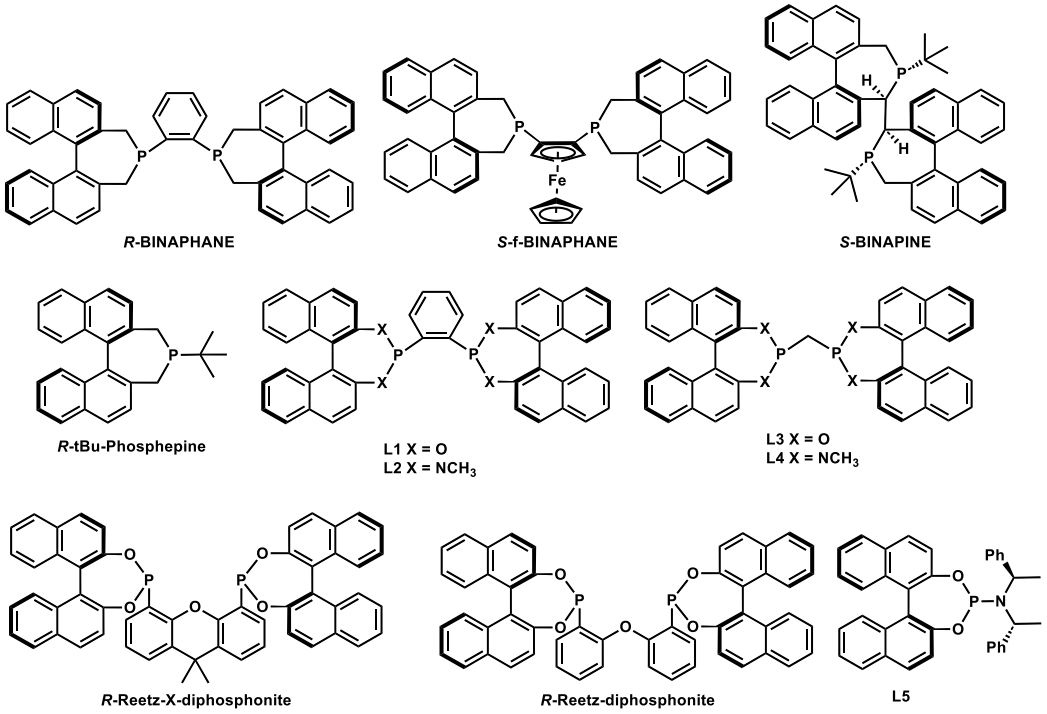


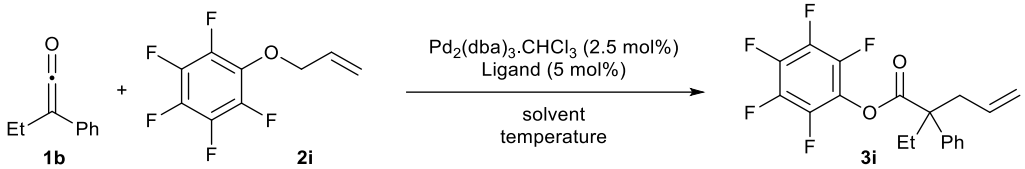


Ligand	Temperature (˚C)	Additive	Yield(%)	ee(%)
R-BINAP	rt		98	4
R-BINAP	–25		>99	0
R-BINAP	rt	LiCl	54	6
S,S-DACH naphthyl-Trost	rt		93	5
R,R-ANDEN phenyl- Trost	rt		91	0
R,R-ANDEN phenyl- Trost	–25		73	5
R,R-ANDEN phenyl- Trost	–78		74	5
S-t-ButylPHOX	rt		80	0
S,S-Me-DUPHOS	rt		76	0
1*R*,1'*R*,2*S*,2'*S*-DUANPHOS	rt		80	3
R,*R*'-DIPAMP	rt		71	8
R-SITCP	rt		90	3
R-SDP	rt		68	3
R-ANTPHOS	rt		91	1
R-Cl-MeO-BIPHEP	rt		96	7
R-PHANEPHOS	rt		88	7
(*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino) ferrocenyl]ethyldiphenylphosphine (JOSIPHOS2)	–25		74	1
(R)-(-)-1-{(S)-2-[Bis(3,5-di-trifluoromethylphenyl)phosphino] ferrocenyl}ethyldicyclohexylphosphine (JOSIPHOS1)	–25		83	1

(*S*, S_p)-Phosferox	rt		91	3
R-BINAPHANE	rt		90	34

Phosphepine and related ligand screening:





Ligand	Solvent	Temperature (°C)	Additive	Yield (%)	ee (%)
R-BINAPHANE	THF	rt		90	34
S-f-BINAPHANE	THF	rt		79	-27
S-BINAPINE	THF	rt		86	-34
S-BINAPINE (using pentachlorophenyl allyl ether)	THF	rt		57	-5
R-tBu-Phosphepine	THF	rt		87	20
L1	THF	rt		29	5
L2	THF	rt		81	20
L3	THF	rt		42	20
L4	THF	rt		80	9
R-Reetz-X-diphosphonite	THF	rt		90	3
R-Reetz-diphosphonite	THF	rt		<1	nd
L5	THF	rt		94	20
R-BINAPHANE	THF	–25		75	37
R-BINAPHANE	THF	–78		13	-35
R-BINAPHANE	THF	rt	TBAI	49	26
R-BINAPHANE	THF	rt	LiCl	<1	nd
R-BINAPHANE	THF	rt	LiI	<1	nd
R-BINAPHANE	CH_2Cl_2	rt		72	32
R-BINAPHANE	toluene	rt		70	32
R-BINAPHANE	DMF	rt		<1	nd

References:

1) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th Ed. Butterworth Heinemann, 2002.
2) (a) B. L. Hodous and G. C. Fu, *J. Am. Chem. Soc*., 2002, **124**, 10006. (b) S. L. Wiskur and G. C. Fu, *J. Am. Chem. Soc*., 2005, **127**, 6176. (c) A. D. Allen, L. M. Baigrie, L. Gong and T. T. Tidwell, *Can. J. Chem*., 1991, **69**, 138. (d) J. E. Wilson, and G. C. Fu, *Angew. Chem. Int. Ed*., 2004, **43**, 6358. (e) R. A. Ruden, *J. Org. Chem*., 1974, **39**, 3607. (f) S. Chen, A. A. Ibrahim, N. J. Peraino, D. Nalla, M. Mondal, M. V. Raaphorst, N. J. Kerrigan, *J. Org. Chem.*, 2016, **81**, 7824. (g) J. J. Douglas, G. Churchill, A. M. Z. Slawin, D. J. Fox and A. D. Smith, *Chem. Eur. J*., 2015, **21**, 16354. (h) M. Panda, M. Mondal, S. Chen, A. A. Ibrahim, D. J. Twardy and N. J. Kerrigan, *Eur. J. Org. Chem.*, 2020, 5752.
3) (a) X. Wang, Q. Ye, J. Song, C. M. Cho, C. Heab and J. Xu, *RSC Adv.*, 2015, **5**, 4547. (b) S. Priya and J. D. Weaver, III, *J. Am. Chem. Soc.*, 2018, **140**, 16020.
4) T. Fujita, T. Yamamoto, Y. Morita, H. Chen, Y. Shimizu and M. Kanai, *J. Am. Chem. Soc.*, 2018, **140**, 5899.