Supporting Information

Catalytic Asymmetric Cyano-ethoxycarbonylation Reaction of Aldehydes Using a $\text{YLi}_3\text{tris}(\text{binaphthoxide})$ (YLB) Complex: Mechanism and Roles of Achiral Additives

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Apparatus: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. *In situ*-IR spectra of reaction mixture were recorded on a METTLER TOLEDO ReactIR 4000. NMR spectra were recorded on a JEOL JNM-LA500 and JEOL ECX-500 spectrometers, operating at 500 MHz for ^1H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in CDCl_3 were reported downfield from TMS (= 0) or in the scale relative to CHCl_3 (7.24 ppm for ^1H NMR) and CDCl_3 (77.0 ppm for ^{13}C NMR) as internal references. Chemical shifts in d_8 -THF were reported in the scale relative to d_8 -THF residual peak (1.73 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to d_8 -THF (25.5 ppm and/or 67.7 ppm) as internal references. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra (for LRMS) were measured on a Waters ZQ4000 spectrometer. FAB mass spectra (for HRMS) were measured on a JEOL JMS-700 spectrometer. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC analysis (JASCO HPLC systems consisting of the following: pump, 880-PU, PU-980, or PU-2080plus; detector, 875-UV, UV-970, or UV-2075plus, measured at 254 nm; column, DAICEL CHIRALCEL OD, OD-H) and Gas Chromatography (Shimadzu GC-14A with Varian Chirasil DEX CB column (0.25 mm x 25 m); carrier gas, nitrogen (4 kPa)). Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. $\text{Y}[\text{N}\{\text{Si}(\text{CH}_3)_2\}_2]_3$ was purchased from Aldrich Co. Ltd and used as received. (*S*)-1,1'-Bi-2-naphthol [(*S*)-BINOL] was recrystallized from diethylether and hexane. A hexanes solution of *n*-BuLi (1.6 M) was purchased from Aldrich Co. Ltd. Acetone cyanohydrin (**8**) was purchased from TCI and used without any purification.

S1: Preparation of YLB complex

Procedure for preparation of (*S*)- $\text{YLi}_3[\text{tris}(\text{binaphthoxide})]$ complex [(*S*)-YLB **1**]:

To a stirred solution of (*S*)-BINOL (1.237 g, 4.32 mmol) in THF (20 mL) at 0 °C, was added BuLi (2.72 mL, 4.32 mmol, 1.59 M in hexanes). To the resulting suspended mixture was added a solution of $\text{Y}[\text{N}\{\text{Si}(\text{CH}_3)_2\}_2]_3$ (820 mg, 1.44 mmol) in THF (20 mL). After stirring for 10 min at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in THF (24 mL) to give (*S*)-anhydrous-YLB solution (60 mM, in THF). 30 mM YLB-90 mM H_2O in THF solution was prepared in a similar manner just by changing the amount of THF in the last step. [The residue was dissolved in THF (48 mL), and H_2O (78 μL , 4.32 mmol) was added to give (*S*)-YLB **1**- H_2O solution (30 mM, in THF). See, Scheme below] YLB solution was stored at room temperature under Ar either as anhydrous solution or as YLB- H_2O .

S2: Preparation of Lithium Cyanide

To acetone cyanohydrin (**8**) (0.10 mL, 1.09 mmol) in dry THF (1.0 mL), a THF solution of lithium hexamethyldisilazide (1.0 M, 1.09 mL, 1.09 mmol) was added at 0 °C. Colorless solid was immediately precipitated. After stirring for 30 min, solvent was removed under reduced pressure to give a colorless powder of lithium cyanide. Because lithium cyanide is hygroscopic, lithium cyanide was used immediately after preparation and drying in vacuo. [Lit. Livinghouse, T. *Org. Synth.* **1984**, 60, 126. In the original report, LiH was used as a base.]

S3: Preparation of Phosphine Oxides

Phosphine oxides (**3a**, **3c–3k**) were prepared from corresponding phosphines. Phosphine oxides (**3a**, **3c–3k**) are known compound. **Registry number:** **3a** (120933-27-9), **3c** (803-17-8), **3d** (797-70-6), **3e** (4576-56-1), **3f** (148345-92-0), **3g** (23897-17-8), **3h** (847467-89-0), **3i** (51008-47-0), **3j** (149639-58-7), **3k** (51986-54-0). Spectra data of phosphine oxides synthesized are shown below.

S 3-1: Procedure of oxidation of phosphine to phosphine oxides 3

Tris(2,6-dimethoxyphenyl)phosphine oxide (**3a**):

To a stirred solution of tris(2,6-dimethoxyphenyl)phosphine (12.1 g, 27.3 mmol) and Na₂HPO₄ (11.6 g, 81.9 mmol) in CH₂Cl₂ (300 mL) at 0 °C was added *m*CPBA (7.1 g, 60-70% purity, 28.8 mmol). The mixture was stirred at 0 °C for 30 min and, then *sat. aq.* Na₂S₂O₃ solution and *sat. aq.* NaHCO₃ solution were added. Organic layer was separated, washed with brine, and was dried over MgSO₄. After evaporation, the residue was purified by flash column chromatography (silica gel, acetone/2-propanol = 10/1) to give **3a** as colorless solid (10.6 g, y. 85%). **3a** was used for cyanation reaction after recrystallization from acetone; colorless solid; IR (KBr) ν 2935, 1586, 1465, 1249, 1184, 1098 cm⁻¹; ¹H NMR (CDCl₃) δ 3.52 (s, 18H), 6.49 (dd, *J* = 8.3, *J*_(C-P) = 6.4 Hz, 6H), 7.21 (t, *J* = 8.3 Hz, 3H); ¹³C NMR (CDCl₃) δ 56.1, 105.0 (d, *J*_(C-P) = 7.3 Hz), 116.7 (d, *J*_(C-P) = 116 Hz), 131.3, 162.5; LRMS (ESI, methanol) *m/z* 481 [M+Na⁺], 459 [M⁺+1]; HRMS (FAB) *m/z* 459.1569 [M+H⁺] calcd. for C₂₄H₂₉O₇P = 459.1567.

Tris(4-methoxyphenyl)phosphine oxide (**3c**):

colorless solid; IR (KBr) ν 544, 666, 803, 830, 1025, 1119, 1178, 1254, 1293, 1503, 1596, 3420 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.82 (s, 9H), 6.92 (dd, $J = 8.9$ Hz, $J_{(\text{C-P})} = 11.3$ Hz, 6H), 7.54 (dd, $J = 8.9$ Hz, $J_{(\text{C-P})} = 2.1$ Hz, 6H); ^{13}C NMR (CDCl_3) δ 55.30, 113.9 (d, $J_{(\text{C-P})} = 13.4$ Hz), 124.7 (d, $J_{(\text{C-P})} = 111$ Hz), 133.9 (d, $J_{(\text{C-P})} = 11.3$ Hz), 162.3 (d, $J_{(\text{C-P})} = 2.0$ Hz); ^{31}P NMR (CDCl_3) δ 28.58; LRMS (ESI, methanol) m/z 391 $[\text{M}+\text{Na}^+]$; HRMS (FAB) m/z 369.1252 $[\text{M}+\text{H}^+]$ calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{P} = 369.1250$.

Tris(4-methylphenyl)phosphine oxide (3d):

colorless solid; IR (KBr) ν 527, 634, 659, 714, 808, 1116, 1182, 1397, 1456, 1500, 1601, 2920, 3021, 3445 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.37 (s, 9H), 7.22 (dd, $J_{(\text{C-P})} = 2.4$ Hz, $J = 8.0$ Hz, 6H), 7.51 (dd, $J = 8.0$ Hz, $J_{(\text{C-P})} = 11.6$ Hz, 6H); ^{13}C NMR (CDCl_3) δ 21.6, 129.1 (d, $J_{(\text{C-P})} = 12.3$ Hz), 129.8 (d, $J_{(\text{C-P})} = 106$ Hz), 132.1 (d, $J_{(\text{C-P})} = 10.3$ Hz), 142.2 (d, $J_{(\text{C-P})} = 3.0$ Hz); ^{31}P NMR (CDCl_3) δ 29.32; LRMS (ESI, methanol) m/z 343 $[\text{M}+\text{Na}^+]$; HRMS (FAB) m/z 321.1405 $[\text{M}+\text{H}^+]$ calcd. for $\text{C}_{21}\text{H}_{22}\text{OP} = 321.1403$.

Tris(4-chlorophenyl)phosphine oxide (3e):

colorless solid; IR (KBr) ν 589, 757, 821, 1013, 1092, 1121, 1389, 1481, 1580, 3446 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.44-7.46 (m, 6H), 7.53-7.57 (m, 6H); ^{13}C NMR (CDCl_3) δ 129.1 (d, $J_{(\text{C-P})} = 12.3$ Hz), 130.3 (d, $J_{(\text{C-P})} = 106$ Hz), 133.3 (d, $J_{(\text{C-P})} = 11.4$ Hz), 139.1; ^{31}P NMR (CDCl_3) δ 26.88; LRMS (ESI, methanol) m/z 403 $[\text{M}+\text{Na}^+]$; HRMS (FAB) m/z 380.9766 $[\text{M}+\text{H}^+]$ calcd. for $\text{C}_{18}\text{H}_{13}\text{Cl}_3\text{OP} = 380.9764$.

Tris(2,4,6-trimethoxyphenyl)phosphine oxide (3f):

colorless solid; IR (KBr) ν 490, 812, 921, 951, 1031, 1097, 1123, 1160, 1205, 1227, 1408, 1456, 1579, 1596, 3397 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.49 (s, 18H), 3.76 (s, 9H), 6.00 (s, 3H), 6.01 (s, 3H); ^{13}C NMR (CDCl_3) δ 55.1, 56.1, 91.5 (d, $J_{(\text{C-P})} = 6.3$ Hz), 109.4 (d, $J_{(\text{C-P})} = 122$ Hz), 162.6, 163.6; ^{31}P NMR (CDCl_3) δ 9.28; LRMS (ESI, methanol) m/z 571 $[\text{M}+\text{Na}^+]$; HRMS (FAB) m/z 549.1886 $[\text{M}+\text{H}^+]$ calcd. for $\text{C}_{27}\text{H}_{34}\text{O}_{11}\text{P} = 549.1884$.

Tris(2-methoxyphenyl)phosphine oxide (3h):

colorless solid; IR (KBr) ν 512, 531, 553, 582, 697, 765, 801, 1023, 1046, 1084, 1138, 1162, 1186, 1253, 1278, 1430, 1462, 1477, 1574, 1589, 2835, 2936, 3065, 3502 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.55 (s, 9H), 6.87 (dd, $J = 5.5$ Hz, 8.3 Hz, 3H), 6.93-6.97 (m, 3H), 7.41-7.44 (m, 3H), 7.49 (dd, $J = 7.7$ Hz, 14.7 Hz, 3H); ^{13}C NMR (CDCl_3) δ 55.5, 111.2 (d, 6.3 Hz), 120.3 (d, $J_{(\text{C-P})} = 12.4$ Hz), 121.5 (d, $J_{(\text{C-P})} = 111$ Hz), 133.0, 134.5 (d, $J_{(\text{C-P})} = 8.3$ Hz), 161.5; ^{31}P NMR (CDCl_3) δ 26.06; LRMS (ESI, methanol) m/z 391 $[\text{M}+\text{Na}^+]$;

HRMS (FAB) m/z 390.3704 $[M+H]^+$ calcd. for $C_{21}H_{22}O_4P^+ = 390.3702$.

Tris(2-ethylphenyl)phosphine oxide (3i):

colorless solid; IR (KBr) ν 577, 685, 769, 786, 1181, 1435, 1471, 1564, 1591, 2869, 2930, 2972, 3004 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.03 (t, $J = 7.5$ Hz, 9H), 2.94-2.96 (m, 6H), 7.06 (dd, $J = 7.7$ Hz, 13.7 Hz, 3H), 7.10-7.13 (m, 3H), 7.37-7.39 (m, 3H), 7.44-7.47 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 15.1, 27.6 (d, $J = 4.1$ Hz), 125.2 (d, $J = 12$ Hz), 130.1 (d, $J = 10$ Hz), 131.3 (d, $J = 101$ Hz), 131.8 (d, $J = 3.0$ Hz), 133.0 (d, $J = 13$ Hz), 149.7 (d, $J = 8.3$ Hz); ^{31}P NMR ($CDCl_3$) δ 37.15; LRMS (ESI, methanol) m/z 385 $[M+Na^+]$.

(2,6-dimethoxyphenyl)diphenylphosphine oxide (3j):

colorless solid; IR (KBr) ν 539, 698, 717, 752, 784, 1026, 1103, 1181, 1254, 1292, 1428, 1469, 1586, 2838, 2940, 3055, 3422 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.32 (s, 6H), 6.48-6.50 (m, 2H), 7.34-7.42 (m, 7H), 7.68-7.72 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.4, 104.7 (d, $J_{(C-P)} = 6.3$ Hz), 108.7 (d, $J_{(C-P)} = 103$ Hz), 127.7 (d, $J_{(C-P)} = 13$ Hz), 130.2 (d, $J_{(C-P)} = 2.0$ Hz), 130.5 (d, $J_{(C-P)} = 9.3$ Hz), 134.7, 136.4 (d, $J_{(C-P)} = 107$ Hz), 163.1; ^{31}P NMR ($CDCl_3$) δ 21.84; LRMS (ESI, methanol) m/z 361 $[M+Na^+]$; HRMS (FAB) m/z 339.1146 $[M+H]^+$ calcd. for $C_{20}H_{20}O_3P^+ = 339.1145$.

(2-methoxyphenyl)diphenylphosphine oxide (3k):

colorless solid; IR (KBr) ν 523, 543, 695, 710, 756, 1137, 1180, 1276, 1436, 1477, 1589, 3435 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.53 (s, 3H), 6.89 (dd, $J = 5.2$ Hz, 7.9 Hz, 1H), 7.04-7.07 (m, 1H), 7.38-7.52 (m, 7H), 7.66-7.70 (m, 4H), 7.75 (dd, $J = 7.3$ Hz, 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.2, 111.4 (d, $J_{(C-P)} = 7.2$ Hz), 120.3 (d, $J_{(C-P)} = 105$ Hz), 120.9 (d, $J_{(C-P)} = 11$ Hz), 128.1 (d, $J_{(C-P)} = 12$ Hz), 131.4 (d, $J_{(C-P)} = 3.6$ Hz), 131.8 (d, $J_{(C-P)} = 9.6$ Hz), 133.2 (d, $J_{(C-P)} = 108$ Hz), 134.2 (d, $J_{(C-P)} = 2.4$ Hz), 135.0 (d, $J_{(C-P)} = 7.2$ Hz), 160.8 (d, $J_{(C-P)} = 3.6$ Hz); ^{31}P NMR ($CDCl_3$) δ 27.37; LRMS (ESI, methanol) m/z 331 $[M+Na^+]$; HRMS (FAB) m/z 309.1039 $[M+H]^+$ calcd. for $C_{19}H_{18}O_2P^+ = 309.1039$.

S4: General Procedure for Catalytic Asymmetric Cyano-ethoxycarbonylation Reaction of Aldehydes:

To tris(2,6-dimethoxyphenyl)phosphine oxide (**3a**) (27.5 mg, 0.06 mmol) in a test tube was added (S)-YLB **1**- H_2O solution (2.0 mL, 0.06 mmol, 30 mM of YLB in THF, containing 0.18 mmol of H_2O). The solution was stirred at room temperature. After completely dissolving **3a**, BuLi (0.06 mmol, 1.6 M in hexanes) was added to the mixture. The mixture solution was cooled down to $-78^\circ C$, aldehyde (0.6 mmol) and ethyl cyanofomate (**2**) (0.72 mmol) was added and stirred at $-78^\circ C$. After stirring

for indicated time in Tables and Schemes a cold HCl/THF ($-78\text{ }^{\circ}\text{C}$, 1.0 M, 2 mL) and water (5 mL) was added to the solution and organic component was extracted with diethyl ether. Organic layer was washed with brine, dried over Na_2SO_4 . After evaporating solvent, the residue was purified by silica gel flash column chromatography to give product.

General Procedure for Catalytic Asymmetric Cyano-ethoxycarbonylation Reaction of Aldehydes Using YLB and Acetonecyanohydrin (8) as an Initiator:

To tris(2,6-dimethoxyphenyl)phosphine oxide (**3a**) (27.5 mg, 0.06 mmol) in a test tube was added (S)-YLB 1- H_2O solution (2.0 mL, 0.06 mmol, 30 mM of YLB in THF, containing 0.18 mmol of H_2O). The solution was stirred at room temperature. After completely dissolving **3a**, BuLi (0.06 mmol, 1.6 M in hexanes) and acetone cyanohydrin (**8**) (0.06 mmol, neat) were added to the mixture. The mixture solution was cooled down to $-78\text{ }^{\circ}\text{C}$, aldehyde (0.6 mmol) and ethyl cyanoformate (**2**) (0.72 mmol) was added and stirred at $-78\text{ }^{\circ}\text{C}$. After stirring for indicated time in Tables and Schemes, a cold HCl/THF ($-78\text{ }^{\circ}\text{C}$, 1.0 M, 2 mL) and water (5 mL) was added to the solution and organic component was extracted with diethyl ether. Organic layer was washed with brine, dried over Na_2SO_4 . After evaporating solvent, the residue was purified by silica gel flash column chromatography to give product.

(R)-2-Ethoxycarboxy-2-phenylacetonitrile (**5a**):

colorless oil; IR (neat) ν 1757, 1249 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.34 (dd, $J = 7.2, 7.2$ Hz, 3H), 4.24-4.34 (m, 2H), 6.27 (s, 1H), 7.44-7.56 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.1, 65.6, 66.4, 115.7, 127.9, 129.27, 130.63, 131.22, 153.42; LRMS (EI-MS) m/z 205 $[\text{M}]^+$; $[\alpha]_{\text{D}}^{21.7} +16.2$ (c 2.8, CH_3Cl) (94% ee), [lit. $[\alpha]_{\text{D}}^{16} +13.7$ (c 2.8, CHCl_3) for *R* enantiomer in 75% ee]; Anal. Calcd for $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$; C, 64.38; H, 5.40; N, 6.83; O, 24.39. Found: C, 64.34; H, 5.59; N, 6.64; HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 1/99, flow 1.0 mL/min, detection at 254 nm) t_{R} 12.4 min (*R*) and 16.2 min (*S*). Absolute configuration was determined by from the sign of optical rotation. Lit. Hamashima, Y.; Sawada, D.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1999**, *121*, 2641.

(R)-2-Ethoxycarboxy-2-(1-naphthyl)acetonitrile (**5b**):

colorless oil; IR (neat) ν 1755, 1248 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.31 (dd, $J = 7.5, 7.5$ Hz, 3H), 4.23-4.34 (m, 2H), 6.87 (s, 1H), 7.49-8.07 (m, 7H); ^{13}C NMR (CDCl_3) δ 13.3, 64.1, 64.9, 115.0, 121.84, 124.25, 125.76, 126.91, 127.03, 128.34, 129.24, 130.94, 133.15, 152.73.; LRMS (EI-MS) m/z 255 $[\text{M}]^+$, 165 $[\text{M}-\text{HCO}_2\text{Et}]^+$; $[\alpha]_{\text{D}}^{23.0} +36.2$ (c 2.00, CHCl_3) (90% ee); HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 1/99, flow 1.0 mL/min, detection at 254 nm) t_{R} 12.4 min (*R*) and 16.2 min (*S*). Absolute configuration was determined after converting into corresponding 2-hydroxyacid methyl ester. **Methyl (R)-2-hydroxy-2-(1-naphthyl)acetate**; colorless oil; ^1H NMR (CDCl_3) δ 3.72 (s, 3H), 5.81 (s, 1H), 7.43-7.56 (m, 4H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 53.0, 71.4, 123.6, 125.2,

125.9, 126.6, 128.8, 129.5, 131.0, 133.9, 134.0, 174.7; $[\alpha]_{435}^{25.9} -223$ (c 1.25, acetone). [lit. $[\alpha]_{435}^{16} +319$ (c 1.5816, acetone) for *S* enantiomer]. Lit. McKenzie, A.; Dennler, W. S. *Ber.* **1937**, *60*, 220.

(*R*)-2-Ethoxycarboxy-3-heptenenitrile (5c):

colorless oil; IR (neat) ν 1757, 1251 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.90 (t, $J = 7.3$ Hz, 3H), 1.32 (dd, $J = 7.2, 7.2$ Hz, 3H), 1.40-1.47 (m, 2H), 2.07-2.12 (m, 2H), 4.21-4.30 (m, 2H), 5.54-5.59 (m, 1H), 5.65 (dd, $J = 6.7, 0.9$ Hz, 1H), 6.16 (ddt, $J = 15.3, 6.7, 0.9$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.7, 14.3, 21.6, 34.1, 65.1, 65.5, 115.5, 119.9, 141.3, 153.5; LRMS (EI-MS) m/z 197 $[\text{M}]^+$, 169 $[\text{M}-\text{CH}_2\text{CH}_2]^+$; $[\alpha]_{\text{D}}^{23} -11.5$ (c 2.17, CHCl_3) (92% ee); Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$; C, 60.90; H, 7.67; N, 7.10; O, 24.33. Found: C, 60.88; H, 7.78; N, 7.07; GC, injection temp. 120 $^\circ\text{C}$; initial column temp. 230 $^\circ\text{C}$; detection temp. 250 $^\circ\text{C}$; retention time (t_{R}) of 14.4 min (major), 15.9 min (minor). Absolute configuration was determined after converting into **5f** by hydrogenation.

(2*R*,3*E*)-2-(Ethoxycarboxy)-4-cyclohexyl-3-butenenitrile (5d):

colorless oil; IR (neat) ν 2927, 2853, 1757, 1261 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.04-1.29 (m, 6H), 1.32 (dd, $J = 7.0, 7.0$ Hz, 3H), 1.63-1.74 (m, 4H), 2.00-2.08 (m, 1H), 4.21-4.30 (m, 2H), 5.51 (ddd, $J = 1.5, 6.7, 15.6$ Hz, 1H), 5.64 (d, $J = 6.7$ Hz, 1H), 6.10 (dd, $J = 6.7, 15.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 14.1, 25.7, 25.9, 31.9, 40.2, 65.2, 65.4, 115.4, 117.3, 146.5, 153.0; LRMS (ESI, methanol) (m/z) 260; $[\text{M}+\text{Na}]^+$; HRMS (FAB) m/z 238.1443 $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{13}\text{H}_{20}\text{NO}_3 = 238.1434$; $[\alpha]_{\text{D}}^{24.3} -12.6$ (c 1.24, CHCl_3) (93% ee); GC (injection temp. 250 $^\circ\text{C}$; column temp. 150 $^\circ\text{C}$; detection temp. 250 $^\circ\text{C}$) t_{R} 39.2 min (major), 40.7 min (minor).

(*R*)-2-Ethoxycarboxy-4-phenyl-3-butenenitrile (5e):

colorless oil; IR (neat) ν 1756, 1250 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.34 (dd, $J = 7.0, 7.0$ Hz, 3H), 4.24-4.33 (m, 2H), 5.88 (dd, $J = 6.8, 1.3$ Hz, 1H), 6.22 (dd, $J = 15.9, 6.8$, 1H), 6.98 (d, $J = 15.9$ Hz, 1H), 7.31-7.37 (m, 3H) 7.41-7.42 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.1, 65.0, 65.1, 115.1, 117.8, 127.2, 128.9, 129.5, 134.2, 138.4, 153.4.; $[\alpha]_{\text{D}}^{22.4} -17.2$ (c 2.02, CHCl_3) (88% ee); Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$; C, 67.52; H, 5.67; N, 6.06; O, 20.75. Found: C, 67.25; H, 5.83; N, 5.96; HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 1/99, flow 1.0 mL/min, detection at 254 nm) t_{R} 52.0 min (*S*) and 68.7 min (*R*). Absolute configuration was determined after converting into corresponding 2-hydroxyacid methyl ester; **Methyl (*R*)-2-hydroxy-4-phenyl-3-butenate**: colorless oil; ^1H NMR (CDCl_3) δ 3.72 (brs, 1H), 3.82 (s, 3H), 4.83 (dd, $J = 5.6, 1.6$ Hz, 1H), 6.22 (dd, $J = 15.6, 5.6$, 1H), 6.79 (dd, $J = 15.6, 1.6$ Hz, 1H), 7.23-7.26 (m, 1H) 7.29-7.32 (m, 2H), 7.37-7.38 (m, 2H); ^{13}C NMR (CDCl_3) δ 53.0, 71.28, 125.2, 126.7, 128.1, 128.6, 132.4, 136.0, 173.8.; $[\alpha]_{\text{D}}^{24.4} -32.8$ (c 0.9, CHCl_3), [lit. $[\alpha]_{\text{D}}^{24.4} -67.7$ (c 0.05 M, CHCl_3 for *R* enantiomer). Lit. Yu, H.-T.; Simon, H. *Tetrahedron*, **1991**, *47*, 9035.]

(R)-2-Ethoxycarboxyheptanenitrile (5f):

colorless oil; IR (neat) ν 2959, 1758, 1256 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87-0.90 (m, 3H), 1.31-1.32 (m, 7H), 1.46-1.54 (m, 2H), 1.89-1.94 (m, 2H), 4.22-4.29 (m, 2H), 5.17 (dd, $J = 6.7, 6.7$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.8, 14.1, 22.3, 24.1, 30.9, 32.3, 64.7, 65.4, 116.6, 153.6; LRMS (EI-MS) m/z 200 $[\text{M}+\text{H}]^+$;

HRMS (FAB) m/z 200.1286 $[\text{M}+\text{H}^+]$ calcd. for $\text{C}_{10}\text{H}_{18}\text{NO}_3 = 200.1282$; $[\text{M}+\text{H}^+]$; $[\alpha]_{\text{D}}^{23} +61.7$ (c 2.02, CHCl_3) (94% ee); GC, injection temp. 110 $^{\circ}\text{C}$; initial column temp. 230 $^{\circ}\text{C}$; detection temp. 250 $^{\circ}\text{C}$; retention time (t_{R}) of 20.0 min (major), 23.1 min (minor). Absolute configuration was determined after converting into corresponding 2-hydroxyacid methyl ester; **Methyl (R)-2-hydroxyheptanoic acid**: colorless oil; ^1H NMR (C_6D_6) δ 0.83 (t, $J = 7.0$ Hz, 3H), 1.12-1.27 (m, 4 H), 1.37-1.47 (m, 2H), 1.49-1.56 (m, 1H), 1.65-1.72 (m, 1H) 2.64 (brs, 1H), 3.05 (s, 3H), 4.03 (br, 1H); ^{13}C NMR (C_6D_6) δ 14.1, 22.8, 24.8, 31.8, 34.7, 51.7, 70.5, 175.8; $[\alpha]_{\text{D}}^{27.4} -7.12$ (c 2.21, CHCl_3), [lit. $[\alpha]_{\text{D}}^{24} +12.8$ (c 2.35, CHCl_3 for *S* enantiomer), Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1992**, 33, 3431]

(R)-2-Ethoxycarboxybutanenitrile (5g):

colorless oil; IR (neat) ν 1758, 1257 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.11 (dd, $J = 7.3, 7.3$ Hz, 3H), 1.33 (dd, $J = 7.0, 7.0$ Hz, 3H), 1.90-2.03 (m, 2H), 4.23-4.29 (m, 2H), 5.13 (dd, $J = 6.6, 6.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 8.2, 13.5, 25.3, 64.7, 65.1, 115.7, 153.0; LRMS (ESI-MS) m/z 180 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{23} +87.0$ (c 1.0, CHCl_3) (92% ee); GC, injection temp. 80 $^{\circ}\text{C}$; initial column temp. 200 $^{\circ}\text{C}$; detection temp. 250 $^{\circ}\text{C}$; retention time (t_{R}) of 13.1 min (major), 17.8 min (minor).

(R)-2-Ethoxycarboxy-3-methylbutanenitrile (5h):

colorless oil; IR (neat) ν 1758, 1254 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.08 (d, $J = 6.7$ Hz, 3H), 1.11 (d, $J = 7.0$ Hz, 3H), 1.32 (dd, $J = 7.0, 7.0$ Hz, 3H), 2.13-2.22 (m, 1H), 4.20-4.29 (m, 2H), 5.01 (d, $J = 5.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.1, 16.2, 16.6, 30.2, 64.3, 68.9, 114.6, 152.7; LRMS (EI-MS) m/z 171 $[\text{M}]^+$; $[\alpha]_{\text{D}}^{24.9} +80.9$ (c 2.210, CHCl_3) (98% ee); Anal. Calcd for $\text{C}_8\text{H}_{13}\text{O}_3\text{N}$; C, 56.13; H, 7.65; N, 8.18; O, 28.04. Found: C, 55.91; H, 7.71; N, 7.98; GC, injection temp. 80 $^{\circ}\text{C}$; initial column temp. 200 $^{\circ}\text{C}$; detection temp. 250 $^{\circ}\text{C}$; retention time (t_{R}) of 16.2 min (*R*), 20.4 min (*S*). Absolute configuration was determined after converting into corresponding 2-hydroxyacid. **(R)-2-hydroxy-3-methylbutanoic acid**; ^1H NMR (CDCl_3) δ 0.90 (d, $J = 7.0$ Hz, 3H), 1.04 (d, $J = 7.0$ Hz, 3H), 2.10-2.19 (ttd, $J = 7.0, 7.0, 3.4$ Hz, 1H), 4.13 (d, $J = 3.4$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 15.8, 18.7, 32.0, 74.8; $[\alpha]_{\text{D}}^{22.4} -13.7$ (c 1.11, CHCl_3) [lit. $[\alpha]_{\text{D}}^{18} +19$ (c 1.0, CHCl_3 for *S* enantiomer)]

(R)-2-Ethoxycarboxy-2-cyclohexylacetonitrile (5i):

colorless oil; IR (neat) ν 1757, 1254 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.04-1.28 (m, 5H), 1.26 (dd, $J = 7.2$, 7.2 Hz, 3H), 1.61-1.64 (m, 1H), 1.72-1.86 (m, 5H), 4.16 (dq, $J = 7.2$, 10.4, 1H), 4.20 (dq, $J = 7.2$, 10.4 Hz, 1H), 4.95 (d, $J = 6.1$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 14.1, 25.2, 25.3, 25.7, 27.8, 28.0, 40.2, 65.4, 69.3, 115.8, 153.8; LRMS (EI-MS) m/z 211 $[\text{M}]^+$; HRMS (FAB) m/z 212.1286 $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{11}\text{H}_{18}\text{NO}_3 = 212.1284$; $[\text{M}]^+$; $[\alpha]_{\text{D}}^{24.9} +53.4$ (c 2.02, CHCl_3) (96% ee); GC, injection temp. 130 $^\circ\text{C}$; initial column temp. 250 $^\circ\text{C}$; detection temp. 250 $^\circ\text{C}$; retention time (t_{R}) of 20.2 min (*R*), 21.3 min (*S*). Absolute configuration was determined after converting into corresponding 2-hydroxyacid. **(*R*)-2-hydroxy-2-cyclohexylacetic acid**; ^1H NMR (CDCl_3) δ 1.04-1.40 (m, 6H), 1.50-1.51 (m, 1H), 1.64-1.81 (m, 5H), 4.10 (d, $J = 3.4$ Hz, 1H); $[\alpha]_{\text{D}} -18.7$ (c 1.6, CH_3COOH), [lit. $[\alpha]_{\text{D}}^{18} +23$ (c 1.0, CH_3COOH for *S* enantiomer)]

(*R*)-2-Ethoxycarboxy-3,3-dimethylbutanenitrile (5j):

colorless oil; IR (neat) ν 2972, 1758, 1258 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.09 (s, 9H), 1.32 (dd, $J = 7.2$, 7.2 Hz, 3H), 4.25 (m, 2H), 4.89 (s, 1H); ^{13}C NMR (CDCl_3) δ 13.0, 24.0, 33.8, 64.2, 72.1, 114.6, 152.8; $[\alpha]_{\text{D}}^{23.1} +75.6$ (c 2.2, CHCl_3) (87% ee); Anal. Calcd for $\text{C}_9\text{H}_{15}\text{O}_3\text{N}$; C, 58.36; H, 8.16; N, 7.56; O, 25.92. Found: C, 58.20; H, 8.12; N, 7.36; GC, injection temp. 80 $^\circ\text{C}$; initial column temp. 200 $^\circ\text{C}$; detection temp. 250 $^\circ\text{C}$; retention time (t_{R}) of 16.9 min (*R*), 18.5 min (*S*). Absolute configuration was determined after converting into corresponding cyanohydrin. **(*R*)-2-hydroxy-3,3-dimethylbutanenitrile**; ^1H NMR (CDCl_3) δ 1.05 (s, 9H), 4.10 (s, 1H); ^{13}C NMR (CDCl_3) δ 25.1, 35.6, 70.7, 119.3; $[\alpha]_{\text{D}}^{25.1} +17.3$ (c 1.25, CHCl_3), [lit. $[\alpha]_{\text{D}}^{24} +14.5$ (c 1.0, CHCl_3) for *R* enantiomer in 70% ee]. [Lit. Hayashi, M.; Miyamoto, Y.; Inoue, T.; Oguni, N. *J. Org. Chem.* **1993**, 58, 1515.]

S5: General Procedure for Kinetics Studies Using *in situ* IR analysis

Reaction profiles were recorded using ReactIR apparatus, which was shown in Figure S-1. To a Schlenk tube with two-way cock, a catalyst solution including additives was added. A probe rod of ReactIR was inserted into the solution. The catalyst solution was cooled to $-78\text{ }^{\circ}\text{C}$, and back ground spectrum was collected. The scanning started and aldehyde **4a** was slowly added over 10–20 seconds by syringe into the catalyst mixture. Signals of aldehyde **4a** gradually increased (over ca. 1 min). After five minutes, ethyl cyanoformate **2** was slowly added over 10–20 seconds. The signals from aldehyde **4a** (1700 cm^{-1}) and **2** (1750 cm^{-1}) gradually decreased and a signal of product **5a** (1760 cm^{-1}) increased. The profile of reaction was recorded. Representative IR spectra profile of kinetic experiments are shown in Figure S-2. Peaks of **2**, **4a**, and **5a** were monitored.

Figure S-1. Apparatus for React IR experiment

Figure S-2. *in-situ* IR experiment for initial rate kinetics

S5-1: Experiments in Figure 5 and Figure 9

Reactions were performed and monitored by following the general procedure for *in-situ* IR analysis. Detailed reaction conditions in Figure 5a-c and Figure 9 are as follows.

Conditions for Figure 5a: Total THF 2.0 mL; YLB [15 mM THF solution {including additives, H₂O (45 mM), Ar₃P=O **3a** (15 mM)} 2 mL (0.030 mmol)], benzaldehyde (**4a**) (0.060 mL, 0.60 mmol), ethyl cyanoformate (**2**) (0.070 mL, 0.73 mmol, 1.2 mol equiv), -78 °C.

Conditions for Figure 5b: Total THF 2.0 mL; YLB [15 mM THF solution {including additives, H₂O (45 mM), Ar₃P=O **3a** (15 mM), BuLi (15 mM)} 2 mL (0.030 mmol)], benzaldehyde (**4a**) (0.060 mL, 0.60

mmol), ethyl cyanoformate (**2**) (0.070 mL, 0.73 mmol, 1.2 mol equiv), $-78\text{ }^{\circ}\text{C}$.

Conditions for Figure 5c: Total THF 2.0 mL; YLB [15 mM THF solution {including additives, H_2O (45 mM), $\text{Ar}_3\text{P}=\text{O}$ **3a** (15 mM)} 2 mL (0.030 mmol)], LiCN (0.99 mg, 0.030 mmol), benzaldehyde (**4a**) (0.060 mL, 0.60 mmol), ethyl cyanoformate (**2**) (0.070 mL, 0.73 mmol, 1.2 mol equiv), $-78\text{ }^{\circ}\text{C}$.

Conditions for Figure 9: Total THF 2.0 mL; YLB [15 mM THF solution {including additives, H_2O (45 mM), $\text{Ar}_3\text{P}=\text{O}$ **3a** (15 mM), BuLi (15 mM)} 2 mL (0.030 mmol)], acetone cyanohydrin (**8**) (0.030 mmol), benzaldehyde (**4a**) (0.060 mL, 0.60 mmol), ethyl cyanoformate (**2**) (0.070 mL, 0.73 mmol, 1.2 mol equiv), $-78\text{ }^{\circ}\text{C}$.

S5-2: Experiments in Figure 6

In experiments in Figure 6b and Figure 6c, peaks corresponding to ethyl cyanoformate (1750 cm^{-1}) and **7** (1740 cm^{-1}) were overlapped. Thus, the profiles of the two peaks were separated mathematically using ConcIRT AF version 3.5.0.4 software as shown in Figure 6a (METTLER TOLEDO Autochem).

Conditions: total THF 2.0 mL; (*S*)-YLB [THF solution (60 mM) including H_2O (180 mM), $\text{Ar}_3\text{P}=\text{O}$ **3a** (60 mM), BuLi (60 mM), 2 mL, 0.12 mmol], ethyl cyanoformate (**2**) (0.12 mmol), $-78\text{ }^{\circ}\text{C}$. In Figure 6c, 0.12 mmol of BuLi in hexanes was added after 50 min.

S5-3: Experiments in Figure 13a, b, and c:

Initial rate kinetics with phosphine oxide (3a)

Data of Figure 13a: Initial rate kinetics for YLB 1 catalyst including additives

Conditions: Total THF (2.0 mL); catalyst mixture [YLB **1** (30 mM THF solution) including additives H₂O (90 mM), Ar₃P=O **3a** (30 mM), BuLi (30 mM)], (a) 2 mL (0.060 mmol) (b) 1.4 mL (0.042 mmol) (c) 1.0 mL (0.030 mmol) (d) 0.8 mL (0.024 mmol) (e) 0.6 mL (0.018 mmol) (f) 0.4 mL (0.012 mmol)], THF [(a) 0 mL (b) 0.6 mL (c) 1.0 mL (d) 1.2 mL (e) 1.4 mL (f) 1.6 mL], benzaldehyde (**4a**) (0.060 mL,

0.60 mmol), ethyl cyanoformate (**2**) (0.070 mL, 0.73 mmol, 1.2 mol equiv), $-78\text{ }^{\circ}\text{C}$, 20–60 min.

Data of Figure 13b: Initial rate kinetics for benzaldehyde (4a**)**

4a [mM]	log [4a (mM)]	relative rate	log [relative rate]
1200	0.77	1.10	0.04
900	0.65	1.11	0.05
750	0.57	1.24	0.10
600	0.47	1.14	0.06
450	0.35	1.10	0.04
300	0.17	1.00	0.00

Conditions: total THF (2.0 mL); [YLB **1** 15 mM THF solution including additives, H_2O (45 mM), $\text{Ar}_3\text{P}=\text{O}$ **3a** (15 mM), BuLi (15 mM), and acetone cyanohydrin (**2**) (15 mM), 2.0 mL, 0.03 mmol of YLB], benzaldehyde (**4a**) [(a) 0.060 mL (0.06 mmol) (b) 0.090 mL (0.90 mmol) (c) 0.120 mL (1.20 mmol) (d) 0.150 mL (1.50 mmol) (e) 0.180 mL (1.80 mmol) (f) 0.240 mL (2.40 mmol)], ethyl cyanoformate (**2**) (0.070 mL, 0.73 mmol), $-78\text{ }^{\circ}\text{C}$, 25 min.

Data of Figure 13c: Initial rate kinetics for ethyl cyanoformate (2)

2 [mM]	log [2 (mM)]	relative rate	log [relative rate]
1080	0.75	4.45	0.65
900	0.67	3.71	0.57
720	0.57	2.78	0.44
490	0.41	2.23	0.35
360	0.27	1.48	0.17
260	0.13	1.00	0.00

Conditions: total THF (2.0 mL); YLB **1** [30 mM THF solution, including additives, H₂O (90 mM), Ar₃P=O **3a** (30 mM), BuLi (30 mM), 0.5 mL, 0.015 mmol], THF (1.5 mL), benzaldehyde (**4a**) (0.060 mL, 0.60 mmol), ethyl cyanoformate (**2**) [(a) 0.050 mL (0.53 mmol) (b) 0.070 mL (0.72 mmol) (c) 0.095 mL (1.00 mmol) (d) 0.140 mL (1.44 mmol) (e) 0.175 mL (1.85 mmol) (f) 0.210 mL (2.22 mmol)], -78 °C, 20–60 min.

S5-4: Experiments in Figure 13d, e, and f:

Initial rate kinetics without phosphine oxide (3a)

Data of Figure 13d: Initial rate kinetics for YLB catalyst solution (1)

catalyst [mM]	log [catalyst]	relative rate	log [relative rate]
60	-0.74	3.99	0.60
45	-0.87	2.94	0.47
30	-1.05	1.79	0.25
15	-1.35	1.00	0.00

Conditions: total THF (2.0 mL); YLB **1** [60 mM THF solution, including additives, H₂O (180 mM), BuLi (60 mM), acetone cyanohydrin (**8**) (60 mM), (a) 2.0 mL (0.120 mmol) (b) 1.5 mL (0.090 mmol) (c) 1.0 mL (0.060 mmol) (d) 0.5 mL (0.030 mmol)], THF [(a) 0 mL (b) 0.5 mL (c) 1.0 mL (d) 1.5 mL]. benzaldehyde (**4a**) (0.120 mL, 1.20 mmol), ethyl cyanoformate (**2**) (0.140 mL, 1.46 mmol, 1.2 mol equiv), -78 °C.

Data of Figure 13e: Initial rate kinetics for benzaldehyde (4a)

4a [mM]	log [4a (mM)]	relative rate	log [relative rate]
750	2.88	0.84	-0.07
600	2.78	0.86	-0.06
525	2.72	1.00	0.00
450	2.65	1.03	0.01
400	2.60	1.07	0.03
350	2.54	0.94	-0.03
300	2.48	0.89	-0.05
250	2.40	1.00	0.00

Conditions: total THF (2.0 mL); YLB **1** [15 mM THF solution, including additives, H₂O (45 mM), BuLi (15 mM), acetone cyanohydrin (**8**) (15 mM) 2 mL, 0.030 mmol], benzaldehyde (**4a**) [(a) 0.050 mL (0.50 mmol) (b) 0.060 mL (0.60 mmol) (c) 0.070 mL (0.70 mmol) (d) 0.080 mL (0.80 mmol) (e) 0.090 mL (0.90 mmol) (f) 0.105 mL (1.05 mmol) (g) 0.120 mL (1.20 mmol) (h) 0.150 mL (1.50 mmol)], ethyl cyanoformate (**2**) [0.070 mL (0.73 mmol)], -78 °C.

Data of Figure 13f: Initial rate kinetics for ethyl cyanoformate (2)

Conditions: total THF (2.0 mL); YLB **1** [15 mM THF solution, including additives, H₂O (45 mM), BuLi (15 mM), acetone cyanohydrin (**8**) (15 mM) 2 mL, 0.030 mmol], benzaldehyde (**4a**) (0.060 mL, 0.60 mmol), ethyl cyanoformate (**2**) [(a) 0.070 mL (0.73 mmol) (b) 0.090 mL (0.94 mmol) (c) 0.105 mL (1.09 mmol) (d) 0.140 mL (1.46 mmol)], -78 °C.

S5-5: Experiments in Figure 15 and Scheme 5

Reversibility of C-C bond formation step

Reaction procedure: To the Schlenk tube equipped with probe of the ReactIR apparatus, the catalyst mixture including (S)-YLB **1** [THF solution (60 mM), H₂O (180 mM), Ar₃P=O **3a** (60 mM), *n*-BuLi (60 mM), acetone cyanohydrin (60 mM)] was added. After recording background spectrum at indicated temperature (-45 °C or -78 °C), profiles of reactions were monitored. Benzaldehyde (**4a**, 60 mM) was slowly added at the same temperature (-45 °C or -78 °C). The absorption of benzaldehyde **4a** ($\nu = 1700$

cm^{-1}) appeared and then gradually disappeared. After **4a** disappeared completely, the monitoring was stopped. The background spectrum was collected again, and then the monitoring of the profile was restarted. The isobutyraldehyde (**4h**, 60 mM) was added at the same temperature ($-45\text{ }^{\circ}\text{C}$ or $-78\text{ }^{\circ}\text{C}$) and the mixture was monitored. The results are summarized in the Figures below.

condition A: at $-45\text{ }^{\circ}\text{C}$

condition B: at $-78\text{ }^{\circ}\text{C}$

S6: ESI-Mass analysis of YLB 1 complex with and without additives

ESI mass spectra (for LRMS) of YLB solution in THF were measured on a Waters ZQ4000 spectrometer under following conditions. ESI-MS charts are shown below.

ESI-MS conditions:

Source (ES+), Capillary 4.0 kV, Cone 165 V, Extractor 5.5 V, RF lens 0.5 V, Source Temperature 88 °C, Cone Temperature 20 °C, Desolvation Temperature 99 °C, Cone Gas Flow 60 L/h, Desolvation Gas Flow 359 L/h

Chart A: YLB + H₂O (3 mol equiv to YLB) in THF

Chart B: YLB in THF

Chart C: YLB + Drierite (CaSO₄) in THF

Chart D: YLB + H₂O (3 mol equiv to YLB) + Ar₃P=O **3a** (1 mol equiv to YLB) in THF

Chart E: YLB + H₂O (3 mol equiv to YLB) + Ar₃P=O **3a** (1 mol equiv to YLB) + BuLi (1 mol equiv to YLB) in THF

Chart F: YLB + H₂O (3 mol equiv to YLB) + Ar₃P=O **3a** (1 mol equiv to YLB) + BuLi (1 mol equiv to YLB) + acetone cyanohydrin **8** (1 mol equiv to YLB) in THF