Supporting Information

1. General methods.

**Chemicals.** β-ketophosphonates 1 were prepared according to the literature procedures.\textsuperscript{51} Dry dichloroethane was purchased from WAKO chemicals and used as received. MnO\textsubscript{2} was purchased from WAKO chemicals. All other chemicals were purchased from their commercial sources and used as it received.

**Analytics.** NMR spectra were recorded on a JEOL JNM LA-400 (400 MHz for \textsuperscript{1}H NMR and 100 MHz for \textsuperscript{13}C NMR). Chemical shifts were reported in ppm on the δ scale relative to Me\textsubscript{4}Si (δ = 0 for \textsuperscript{1}H NMR), CDCl\textsubscript{3} (δ = 77.2 for \textsuperscript{13}C NMR) as an internal reference. Multiplicities are indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), or m (multiplet). Coupling constants (J) are reported in Hertz (Hz). ESI mass spectra were measured on a Bruker Daltonics micrOTOF. High performance liquid chromatography (HPLC) was performed on Agilent Technologies 1220 Infinity LC instruments using Daicel Chiralpak AD-H, OD-H, OJ-H and AS-H 4.6 mm × 25 cm column. Optical rotations were measured on an ATAGO CO., LTD AP-300 polarimeter. Column chromatography was conducted with silica gel 60 N (KANTO CHEMICAL, spherical, neutral, 40-50 or 63-210 \textmu m). For thin-layer chromatography (TLC) analysis Merck precoated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), I\textsubscript{2}, anisaldehyde, KMnO\textsubscript{4}, and cerium molybdate.

2. \textit{O}-nitroso aldol reaction with \textit{in situ} generated nitrosocarbonyl compounds.**

**General procedure:**

To a dichloroethane solution (1 mL) of Cu(OTf)\textsubscript{2}/PhBox complex (prepared by mixing 0.01 mmol of Cu(OTf)\textsubscript{2} and 0.012 mmol of PhBox ligand at room temperature) was added a dichloroethane (1 mL) solution of the β-ketophosphonate (1, 0.1 mmol). Followed by solid N-protected hydroxamic acid (2, 0.12 mmol) and CuCl (1.0 mg, 0.01 mmol) were added. The reaction was placed under air using an air-baloon and was allowed to stir at room temperature (25 °C). After completion (monitored by TLC) it was directed loaded into a column packed with silica gel and purified using EtOAc/n-hexane (1:1 to 3:1) as eluent to afford the O-NA products 3.

All the recimic sample were similarly prepared using 10 mol% of Cu(OTf)\textsubscript{2} in combination with 20 mol% 2-ethyl oxazoline under same condition.
3a: Prepared according to general procedure. 40 mg, 97%. 97% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 13.0 min, t_R(major) = 19.0 min.

3b: Prepared according to general procedure. 30 mg, 75%, 94% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 245 nm, retention time; t_R(minor) = 25.4 min, t_R(major) = 29.0 min.

3c: Prepared according to general procedure. 35.1 mg, 93%. >99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AS-H, hexane/i-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 225 nm, retention time; t_R(minor) = 61.1 min, t_R(major) = 67.3 min.

3d: Prepared according to general procedure. 26.2 mg, 72%. 98% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak OD-H, hexane/i-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 230 nm, retention time; t_R(minor) = 33.8 min, t_R(major) = 39.6 min.

3e: Prepared according to general procedure. 32.9 mg, 90%. 99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak OJ-H, hexane/i-PrOH = 99.5/0.5, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 11.6 min, t_R(minor) = 15.4 min.

3f: Prepared according to general procedure. 33 mg, 94%. 97% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak OJ-H, hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 15.3 min, t_R(minor) = 18.0 min.

3g: Prepared according to general procedure. 29.9 mg, 88%. >99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AS-H, hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 26.1 min, t_R(minor) = 29.5 min.

3h: Prepared according to general procedure. 30 mg, 85%. 99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 50.2 min, t_R(minor) = 54.3 min.
3i: Prepared according to general procedure. 35.7 mg, 86%. >99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak OD-H, hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 18.3 min, t_R(minor) = 22.6 min.

3j: Prepared according to general procedure. 28.1 mg, 70%. 97% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 246 nm, retention time; t_R(major) = 25.2 min, t_R(minor) = 30.2 min.

3k: Prepared according to general procedure. 32.8 mg, 79%. 93% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AS-H, hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 14.1 min, t_R(minor) = 20.4 min.

3m: Prepared according to general procedure. 34.1 mg, 88%. >99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 220 nm, retention time; t_R(major) = 21.2 min, t_R(minor) = 23.9 min.

3n: Prepared according to general procedure. 35 mg, 75%. 99% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 222 nm, retention time; t_R(major) = 52.1 min, t_R(minor) = 65.0 min.

5x: Prepared according to general procedure. 33.3 mg, 76%. 98% ee. Analytical data is same as Ref S2. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 230 nm, retention time; t_R(major) = 36.1 min, t_R(minor) = 45.3 min.

3. References
4. Selected copies of HPLC chromatogram

HPLC chromatogram of 3a:

Daicel Chiralpak AD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 13.0 min, t_R(major) = 18.9 min.
HPLC chromatogram of 3e:
Daicel Chiralpak OJ-H, hexane/i-PrOH = 99.5/0.5, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 11.6 min, t_R(minor) = 15.4 min.
HPLC chromatogram of 3k:

Daicel Chiralpak AS-H, hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 215 nm, retention time; t_R(major) = 14.1 min, t_R(minor) = 20.4 min.