Supporting Information For:
Enantioselective Michael Reaction of Malonates to Nitroolefins Catalyzed by
Bifunctional Organocatalysts

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General. Nominal (LR-MS) and exact mass (HR-MS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ¹H NMR and ¹³CNMR spectra were registered on JEOL JNM-LA500 using TMS as an internal standard. (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublets, t = triplet, q = quartet, m = multiplet, br = broad). Optical rotations were measured in CHCl₃ unless otherwise noted with a JASCO DIP-360 digital polarimeter. For column chromatography, Kanto Silica gel 60 (spherical, 63-210 μm) was employed and preparative thin-layer chromatography (PTLC) was carried out using Silica gel 60 (Merck). Enantiomer ratios were determined by chiral HPLC using a Shimadzu SPD-10A with Daicel Chemical Industries, LTD. Chiralpak AD (0.46cm x 25 cm) or Chiralpak OD-H (0.46cm x 25 cm).

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used without purification. The *trans*-β-substituted nitroolefins **2b-2g** were prepared according to literatures.¹

General Procedure for preparing catalysts

Under an argon atmosphere, to a solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (1.0 eq, 605 mg) in dry THF (1.0 ml) was added (*R,R*)-*N,N*-dimethyl-*trans*-diaminocyclohexane (317 mg, 2.23 mmol). After the reaction mixture was stirred for 3 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (CHCl₃/MeOH/TEA = 100/5/1 as eluant) gave the desired thiourea **1a** (597 mg, 65 %) as white amorphous solid. $[\alpha]_D^{16} -32.7$ (c 0.99, CHCl₃); ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.0 (s, 1H), 8.21 (s, 1H), 8.17 (s, 2H), 7.66 (s, 1H), 4.09 (br s, 1H), 2.54 (br s, 1H), 2.21 (s, 7H), 1.82 (br s, 1H), 1.74 (br s, 1H), 1.63 (br d, *J* = 11.0 Hz, 1H), 1.31-1.01 (m, 4H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆) δ 178.6, 142.0, 130.8, 130.5, 130.3, 130.0, 126.5, 124.3, 122.2, 120.9, 120.0, 115.3, 65.0, 55.3, 45.7, 31.6, 24.6, 24.5, 21.0 ppm; IR (CHCl₃) ν 3402, 3200, 2942, 2865, 1528, 1469, 1383, 1278 cm⁻¹; MS (FAB⁺) 414 (MH⁺, 100); *Anal.* Calcd. for

C₁₇H₂₁F₆N₃S: C, 49.39; H, 5.12; N, 10.16; F, 27.57. Found: C, 49.36; H, 5.28; N, 10.11; F, 27.71.

1d. $[\alpha]_D^{17} -18.1$ (*c* 1.01, CHCl₃); m.p. 154-156 °C. (Hexane/AcOEt); ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.00 (s, 1H), 8.30 (d, *J* = 7.0 Hz, 1H), 8.15 (s, 2H), 7.67 (s, 1H), 7.24 (dd, *J* = 3.4, 5.2 Hz, 2H), 7.18 (dd, *J* = 3.2, 5.3 Hz, 2H), 4.31 (br s, 1H), 4.04 (d, *J* = 11.6 Hz, 2H), 3.99 (d, *J* = 11.9 Hz, 2H), 2.87 (dt, *J* = 2.7, 9.8 Hz, 1H), 2.18 (br d, *J* = 8.2 Hz, 1H), 1.88 (br d, *J* = 11.6 Hz, 1H), 1.76 (br d, *J* = 7.9 Hz, 1H), 1.65 (m, 1H), 1.44 (m, 1H), 1.30 (m, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 184.1, 147.0, 144.9, 135.6, 135.3, 131.6, 129.5, 127.5, 127.3, 126.4, 120.8, 65.6, 60.5, 58.3, 29.0, 28.82, 28.77, 28.1 ppm; IR (CHCl₃) ν 3402, 2941, 2862, 1539, 1495, 1470, 1382, 1279, 1179, 1140 cm⁻¹; MS (FAB⁺) 488 (MH⁺, 100); *Anal.* Calcd. for C₂₃H₂₃F₆N₃S: C, 56.67; H, 4.76; N, 8.62; F, 23.38. Found: C, 56.66; H, 4.74; N, 8.46; F, 23.45.

1e. $[\alpha]_D^{26} +51.3$ (*c* 0.98, CHCl₃); ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.10 (s, 1H), 8.21 (s, 2H), 7.87 (s, 1H), 7.69 (s, 1H), 4.08 (br s, 1H), 2.96-2.78 (m, 1H), 2.62 (br s, 1H), 2.37-2.07 (m, 4H), 1.82 (br d, *J* = 10.7 Hz, 1H), 1.71 (br d, *J* = 6.7 Hz, 1H), 1.61 (br d, *J* = 7.7 Hz, 1H), 1.31-1.07 (m, 4H), 0.98 (d, *J* = 6.1 Hz, 6H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆) δ 179.2, 142.0, 130.7, 130.5, 130.2, 129.9, 126.6, 124.4, 122.2, 121.4, 120.1, 115.6, 63.6, 55.0, 31.8, 31.3, 25.6, 25.0, 24.5, 21.4, 20.1 ppm; IR (CHCl₃) ν 3402, 2943, 2863, 1496, 1470, 1384, 1279, 1179, 1141 cm⁻¹; MS (FAB⁺) 442 (MH⁺, 100); HRMS (FAB⁺) Calcd for [C₁₉H₂₆F₆N₃S]⁺: 442.1752; Found: 442.1743.

1f. $[\alpha]_D^{21} -112$ (*c* 0.98, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.30-7.14 (m, 4H), 6.79 (s, 1H), 3.86 (br s, 1H), 2.73 (br s, 1H), 2.33 (dt, *J* = 2.9, 11.1 Hz, 1H), 2.24 (s, 6H), 1.93-1.75 (m, 2H), 1.70 (br d, *J* = 13.7 Hz, 1H), 1.42-1.28 (m, 1H), 1.28-1.11 (m, 2H), 1.10-0.96 (m, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 179.1, 137.4, 128.9, 125.5, 124.3, 66.0, 55.4, 39.4, 32.4, 24.6, 24.2, 21.0 ppm; IR (CHCl₃) ν 3411, 2939, 2864, 2790, 1529, 1500 cm⁻¹; MS (FA B⁺) 278 (MH⁺, 100); HRMS (FAB⁺) Calcd for [C₁₅H₂₄N₃S]⁺: 278.1691; Found: 278.1692.

1g. $[\alpha]_D^{19} -116$ (*c* 1.10, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.19 (s, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.15-6.92 (m, 2H), 6.89-6.69 (m, 2H), 3.79 (br s, 1H), 3.67 (s, 3H), 2.60 (d, *J* = 10.7 Hz, 1H), 2.35-2.22 (m, 1H), 2.09 (s, 6H), 1.83-1.60 (m, 2H), 1.54 (d, *J* = 13.7 Hz, 1H), 1.20 (q, *J* = 13.0 Hz, 1H), 1.15-0.97 (m, 2H), 0.96-0.81 (m, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 179.5, 151.5, 126.3, 125.0, 124.1, 120.2, 111.1, 66.3, 55.9, 55.3, 39.5, 32.3, 24.8, 24.3, 21.2 ppm; IR (CHCl₃) ν 3406, 2939, 2863, 1600, 1512 cm⁻¹; MS (FAB⁺) 308 (MH⁺, 100); HRMS (FAB⁺) Calcd for [C₁₆H₂₆N₃OS]⁺: 308.1757; Found: 308.1790.

Typical procedure for enantioselective Michael addition of malonates to nitroolefins

Under an argon atmosphere, to a stirred solution of *trans*- β -nitrostyrene **2a** (29.8 mg, 0.20 mmol) and

diethyl malonate **3a** (2.0 equiv., 0.061 ml) in dry toluene (0.40 ml) was added thiourea-catalyst **1a** (0.1 equiv., 8.2 mg). After being stirred for 24 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by preparative TLC (hexane/Et₂O = 5/1 as eluent) to afford desired Michael adduct **4a** (53.3 mg, 86%).

Ethyl 2-carboethoxy-4-nitro-3-phenylbutyrate, 4a: colorless needle; $[\alpha]_D^{30} = -6.00$ (*c* 1.00, CHCl₃, 93% ee (*S*)); m.p. 45-47 °C; (Hexane/Et₂O); ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.10 (m, 5H), 4.93 (dd, *J* = 4.6, 13.1 Hz, 1H), 4.86 (dd, *J* = 9.2, 13.1 Hz, 1H), 4.33-4.15 (m, 3H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.82 (d, *J* = 9.5 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 167.4, 166.7, 136.2, 128.8, 128.2, 127.9, 77.6, 62.0, 61.8, 54.9, 42.9, 13.9, 13.6 ppm; IR (CHCl₃) ν 2989, 2938, 1731, 1557 cm⁻¹; MS (FAB⁺) 310 (MH⁺, 100); *Anal.* Calcd. for C₁₅H₁₉NO₆: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.43; H, 6.20; N, 4.56; HPLC (Chiralcel AD, hexane/ethanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (*S*) (major) 11.1 min, (*R*) (minor) 13.9 min).

Ethyl 2-carboethoxy-4-nitro-3-(2,6-dimethoxyphenyl)butyrate, 4b: colorless oil; $[\alpha]_D^{24} = -11.4$ (*c* 1.03, CHCl₃, 93% ee (*S*)); ¹H NMR (500 MHz, CDCl₃) δ 7.18 (t, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.2 Hz, 2H), 5.08-4.99 (m, 1H), 4.93 (dd, *J* = 12.1, 9.0 Hz, 1H), 4.85 (dd, *J* = 12.1, 4.7 Hz, 1H), 4.32-4.15 (m, 3H), 3.92-3.80 (m, 2H), 3.82 (s, 6H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 168.4, 167.3, 158.9, 129.6, 112.5, 104.3, 76.6, 61.8, 61.2, 55.8, 52.5, 33.2, 13.9, 13.5 ppm; IR (CHCl₃) ν 3030, 2985, 2842, 1730, 1555 cm⁻¹; MS (EI⁺) 369 (M⁺), 249 (100); *Anal.* Calcd. for C₁₇H₂₃NO₈: C, 55.28; H, 6.28; N, 3.79. Found: C, 55.31; H, 6.13; N, 3.55; HPLC (Chiralcel AD, hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (*S*) (major) 12.8 min, (*R*) (minor) 15.7 min).

Ethyl 2-carboethoxy-4-nitro-3-(4-fluorophenyl)butyrate, 4c: colorless oil; $[\alpha]_D^{28} = -7.20$ (*c* 1.00, CHCl₃, 92% ee (*S*)); ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.18 (m, 2H), 7.05-6.96 (m, 2H), 4.91 (dd, *J* = 13.1, 4.6 Hz, 1H), 4.83 (dd, *J* = 13.1, 9.5 Hz, 1H), 4.30-4.15 (m, 3H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.78 (d, *J* = 9.2 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 167.4, 166.8, 163.6, 161.6, 132.02, 131.99, 129.9, 129.8, 116.0, 115.9, 77.6, 62.2, 61.9, 54.9, 42.2, 13.9, 13.7 ppm; IR (CHCl₃) ν 3031, 2987, 1733, 1558 cm⁻¹; MS (EI⁺) 327 (M⁺), 207 (100); *Anal.* Calcd. for C₁₅H₁₈FNO₆: C, 55.04; H, 5.54; N, 4.28; F, 5.80. Found: C, 55.24; H, 5.46; N, 4.15; F, 5.67; HPLC (Chiralcel AD, hexane/ethanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (*S*) (major) 16.3 min, (*R*) (minor) 23.9 min).

Ethyl 2-carboethoxy-4-nitro-3-(1-naphthyl)butyrate, 4d: colorless oil; $[\alpha]_D^{32} = +1.60$ (*c* 1.14, CHCl₃, 92% ee); ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.65-7.56 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.47-7.34 (m, 2H), 5.29-5.18 (m, 1H),

5.18-5.10 (m, 1H), 5.06 (dd, $J = 4.7, 13.3$ Hz, 1H), 4.28-4.12 (m, 2H), 4.07 (d, $J = 8.6$ Hz, 1H), 4.01-3.88 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 3H), 0.93 (t, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 167.7, 167.0, 134.1, 132.4, 131.1, 129.2, 128.9, 127.0, 126.1, 125.1, 124.3, 122.4, 77.0, 62.0, 61.9, 54.7, 36.7, 13.8, 13.5 ppm; IR (CHCl_3) ν 3025, 2987, 1732, 1557 cm^{-1} ; MS (EI^+) 359 (M^+), 152 (100); *Anal.* Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.58; H, 5.96; N, 3.76; HPLC (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min, $\lambda = 254$ nm, retention times: (minor) 14.6 min, (major) 16.7 min.)

Ethyl 2-carboethoxy-4-nitro-3-(2-thienyl)butyrate, 4e: colorless oil; $[\alpha]_{\text{D}}^{32} = +4.28$ (c 0.90, CHCl_3 , 90% ee); ^1H NMR (500 MHz, CDCl_3) δ 7.22 (d, $J = 4.9$ Hz, 1H), 7.01-6.85 (m, 2H), 5.01-4.81 (m, 2H), 4.62-4.47 (m, 1H), 4.30-4.16 (m, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.87 (d, $J = 8.2$ Hz, 1H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 167.3, 166.8, 138.6, 127.0, 126.8, 125.6, 78.0, 62.2, 62.1, 55.5, 38.3, 13.9, 13.7 ppm; IR (CHCl_3) ν 3031, 2988, 1733, 1558 cm^{-1} ; MS (EI^+) 315 (M^+), 195 (100); *Anal.* Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_6\text{S}$: C, 49.51; H, 5.43; N, 4.44; S, 10.17. Found: C, 49.67; H, 5.43; N, 4.23; S, 10.32; HPLC (Chiralcel AD, hexane/2-propanol = 90/10, 1.0 mL/min, $\lambda = 254$ nm, retention times: (major) 12.0 min, (minor) 21.9 min).

Ethyl 2-carboethoxy-3-nitromethyloctanoate, 4f: colorless oil; $[\alpha]_{\text{D}}^{30} = -4.87$ (c 1.00, CHCl_3 , 81% ee (*S*)); ^1H NMR (500 MHz, CDCl_3) δ 4.71 (dd, $J = 13.4, 4.9$ Hz, 1H), 4.54 (dd, $J = 13.3, 6.9$ Hz, 1H), 4.30-4.10 (m, 4H), 3.63 (d, $J = 5.8$ Hz, 1H), 3.02-2.76 (m, 1H), 1.51-1.42 (m, 2H), 1.53-1.19 (m, 12H), 0.88 (t, $J = 6.9$ Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 168.1, 167.9, 76.7, 61.9, 61.7, 52.6, 36.9, 31.4, 29.9, 26.2, 22.3, 14.0, 13.9, 13.8 ppm; IR (CHCl_3) ν 3030, 2960, 2932, 2865, 1730, 1553 cm^{-1} ; MS (FAB^+) 304 (MH^+ , 100); HRMS (FAB^+) Calcd for $[\text{C}_{14}\text{H}_{26}\text{NO}_6]^+$: 304.1760; Found: 304.1762; HPLC (Chiralcel OD, hexane/2-propanol = 98/2, 0.5 mL/min, $\lambda = 210$ nm, retention times: (*R*) (minor) 12.7 min, (*S*) (major) 16.3 min).

Ethyl 2-carboethoxy-5-methyl-3-nitromethylhexanoate, 4g: colorless oil; $[\alpha]_{\text{D}}^{24} = -6.92$ (c 1.04, CHCl_3 , 81% ee (*S*)); ^1H NMR (500 MHz, CDCl_3) δ 4.71 (dd, $J = 13.3, 5.0$ Hz, 1H), 4.53 (dd, $J = 13.3, 6.6$ Hz, 1H), 4.31-4.14 (m, 4H), 3.62 (d, $J = 5.5$ Hz, 1H), 3.07-2.82 (m, 1H), 1.73-1.57 (m, 1H), 1.36-1.25 (m, 8H), 0.95-0.89 (m, 6H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 168.0, 167.9, 76.8, 61.8, 61.7, 52.6, 38.9, 34.8, 25.0, 22.3, 22.1, 13.93, 13.90 ppm; IR (CHCl_3) ν 3030, 2962, 2873, 1730, 1553 cm^{-1} ; MS (EI^+) 290 (MH^+), 160 (100); *Anal.* Calcd. for $\text{C}_{13}\text{H}_{23}\text{NO}_6$: C, 53.97; H, 8.01; N, 4.84. Found: C, 54.20; H, 7.95; N, 4.85; HPLC (Chiralcel OD, hexane/2-propanol = 98/2, 0.5 mL/min, $\lambda = 210$ nm, retention times: (*R*) (minor) 12.1 min, (*S*) (major) 16.2 min).

Methyl 2-carbomethoxy-2-methyl-4-nitro-3-phenylbutyrate, 4h: colorless needle; $[\alpha]_{\text{D}}^{32} = +32.3$ (c 1.06, CHCl_3 , 93% ee); m.p. 130-132 $^{\circ}\text{C}$ (Hexane/AcOEt); ^1H NMR (500 MHz, CDCl_3) δ 7.39-7.23 (m,

3H), 7.21-7.09 (m, 2H), 5.12-4.95 (m, 2H), 4.18 (dd, $J = 9.9, 4.4$ Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 1.35 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.4, 170.8, 135.0, 129.0, 128.8, 128.5, 77.5, 56.7, 53.0, 52.8, 48.3, 20.2 ppm; IR (CHCl_3) ν 3032, 2955, 1735, 1557 cm^{-1} ; MS (EI^+) 295 (M^+), 189 (100); *Anal.* Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_6$: C, 56.94; H, 5.80; N, 4.74. Found: C, 56.92; H, 5.82; N, 4.64; HPLC (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min, $\lambda = 254$ nm, retention times: (minor) 8.9 min, (major) 13.9 min).

Reference: ¹ (a) Fujii, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4029-4035. (b) Denmark, S. E.; Marcin, L. *R. J. Org. Chem.* **1993**, *58*, 3850-3856.