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Supporting Information

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Enantioselective Michael Addition to α,β-Unsaturated Imides Catalyzed by a Bifunctional Organocatalyst

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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. ^{1}H NMR and ^{13}C NMR 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 $CHCl_3$ unless otherwise noted with a JASCO DIP-360 digital polarimeter. For column chromatography, Kanto Silica gel 60 (spherical, 63-210 mm) 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-H (0.46cm x 25 cm), Chiralpak OJ-H (0.46cm x 25 cm) or Chiralpak OD-H (0.46cm x 25 cm), Chiralpak AS-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. **3A, 3B, 3D, 3E, 3G, 5a, 5c, 5e, 5g** were prepared according to literatures[1].

1-methyl-3-[(E)-3-phenylacryloyl]imidazolidin-2-one (3C): To a stirred solution of 1-methyl-2-imidazolidinone[2] (500 mg, 5 mmol), cinnamoyl chloride (916 mg, 5.5 mmol) and CuCl (49.5 mg, 0.5 mmol) in dry CH_2Cl_2 (5 mL) was added diisopropyl ethyl amine (948 μL, 5.5 mmol). After 1 h, water was added and the mixture extracted three times with $CHCl_3$. The combined organic layers were dried over Na_2SO_4 and solvent evaporated at reduced pressure. Purification over silica gel with AcOEt afforded **3C** (1.10 g, 96%). Colorless solid; M.p. 146-148 °C (Hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.7 Hz, 1H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.65-7.58 (m, 2H), 7.40-7.33 (m, 3H), 4.00-3.93 (m, 2H), 3.51-3.43 (m, 2H), 2.93 (s, 3H) ppm; ^{13}C NMR (126 MHz, CD_3OD) δ 167.5, 156.7, 144.8, 136.5, 131.4, 130.1, 129.3, 119.7, 44.1, 41.0, 30.8 ppm; IR ($CHCl_3$) ν 3014, 1725, 1661, 1617 cm^{-1}; MS (EI^{+}) 230 (M^{+}, 41), 131 (100); *Anal*. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; Found: C, 67.79; H, 6.12; N, 12.14.

(E)-N-acetyl-N-methylcinnamamide (3F): A procedure similar to that described for the preparation

of the **3d** afforded **3f** (475 mg, 47%). Colorless solid; M.p. 75-76 °C (Hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 15.6 Hz, 1H), 7.58-7.50 (m, 2H), 7.41-7.33 (m, 3H), 7.07 (d, *J* = 15.6 Hz, 1H), 3.30 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 169.3, 145.1, 134.7, 130.5, 129.0, 128.3, 120.2, 32.0, 26.1 ppm; IR ($CHCl_3$) ν 3031, 1684, 1619 cm^{-1}; MS (EI$^+$) 203 (M^+, 39), 131 (100); *Anal.* Calcd. for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89; Found: C, 70.92; H, 6.16; N, 6.88.

General procedure for the preparation of imides 5b, d, f, h. To a solution of 2-pyrrolidinone (536 mg, 6.30 mmol) and pyridine (1 mL, 12.6 mmol) in MeCN (12 mL) at 0 ºC was added dropwise bromoaceetyl bromide (25.4 g, 12.6 mmol), then warmed to room temperature and stirred for 2 days. The solvent was removed in vacuo, diluted with AcOEt, washed with brine, dried over Na_2SO_4, and evaporated to afford 1-bromoacetylpyrrolidin-2-one. Triethylphosphite (1.3 mL, 7.5 mmol) was added to 1-bromoacetylpyrrolidin-2-one dropwise, and the reaction mixture was stirred for 8 h at 50 ºC. Purification over silica gel with $CHCl_3$/MeOH (20/1) afforded diethyl 2-oxo-2-(2-oxopyrrolidin-1-yl)ethylphosphonate. To a suspension of NaH (60%, 176 mg, 4.4 mmol) in THF (4 mL) was added diethyl 2-oxo-2-(2-oxopyrrolidin-1-yl)ethylphosphonate in THF (4 mL) 0 ºC. After stirring for 30 min at room temperature, corresponding aldehyde in THF (8 mL) was added. After 30 min, the reaction mixture was diluted with H_2O, evaporated, extracted with Et_2O, dried over $MgSO_4$ and evaporated. Purification over silica gel with Hexane/AcOEt (1/1) afforded desired product.

1-[(E)-3-(4-fluorophenyl)acryloyl]pyrrolidin-2-one (5b): Colorless solid; M.p. 122-124 °C (Hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.8 Hz, 1H), 7.79 (d, *J* = 15.8 Hz, 1H), 7.65-7.56 (m, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 3.93 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 8.1 Hz, 2H), 2.14-2.03 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 166.1, 164.9, 162.9, 144.0, 131.11, 131.08, 130.4, 130.3, 118.7, 115.8, 45.7, 33.8, 17.0 ppm; IR ($CHCl_3$) ν 3026, 1734, 1672, 1619, 1600, 1510 cm^{-1}; MS (EI$^+$) 233 (M^+, 35), 131 (149); HRMS (EI$^+$) Calcd for $[C_{13}H_{12}FNO_2]^+$: 233.0852; Found: 233.0855.

1-[(E)-3-(naphthalen-4-yl)acryloyl]pyrrolidin-2-one (5d): Colorless solid; M.p. 130-140 °C (Hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 15.6 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 15.6 Hz, 1H), 7.93-7.83 (m, 3H), 7.61-7.46 (m, 3H), 3.96 (t, *J* = 7.3 Hz, 2H), 2.67 (t, *J* = 8.1 Hz, 2H), 2.15-2.14 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 166.4, 142.2, 133.7, 132.1, 131.6, 130.7, 128.7, 126.8, 126.1, 125.6, 125.5, 123.5, 121.5, 45.8, 33.9, 17.2 ppm; IR ($CHCl_3$) ν 3015, 1734, 1670, 1611 cm^{-1}; MS (EI$^+$) 265 (M^+, 20), 180 (100); *Anal.* Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28; Found: C, 77.08; H, 5.73; N, 5.28.

1-[(E)-5-phenylpent-2-enoyl]pyrrolidin-2-one (5f): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 3H), 7.23-7.12 (m, 4H), 3.85 (t, *J* = 7.0 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.64-2.56 (m, 4H), 2.04 (q, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 166.2, 149.4, 141.0, 128.5, 128.4, 126.1, 122.6, 45.7, 34.4, 34.3, 33.9, 17.1 ppm; IR ($CHCl_3$) ν 3025, 1735, 1676, 1632 cm^{-1}; MS (EI^{+}) 243 (M^{+}, 22), 91 (100); *Anal*. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76; Found: C, 74.20; H, 6.87; N, 5.61.

1-[(E)-4,4-dimethylpent-2-enoyl]pyrrolidin-2-one (5h): Colorless solid; M.p. 62-63 °C (Hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 15.6 Hz, 1H), 7.12 (d, *J* = 15.6 Hz, 1H), 3.86 (t, *J* = 7.0 Hz, 2H), 2.61 (t, *J* = 8.1 Hz, 2H), 2.08-2.00 (m, 2H), 1.11 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 166.9, 160.3, 117.7, 45.7, 34.1, 33.9, 28.6, 17.1 ppm; IR ($CHCl_3$) ν 3018, 2965, 1734, 1676, 1629 cm^{-1}; MS (EI^{+}) 196 (M^{+}), 131 (138); *Anal*. Calcd. for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17; Found: C, 67.57; H, 8.61; N, 7.17.

Typical procedure for enantioselective Michael addition of malononitrile to α,β-unsaturated imides catalyzed by thiourea. A solution of **3d** (43.1 mg, 0.20 mmol), malononitrile (2.0 equiv., 226.4 mg) and thiourea-catalyst **1** (0.1 equiv., 8.2 mg) in dry toluene (0.40 ml) was stirred for 2.5 days at room temperature. The reaction mixture was purified by preparative TLC (Et_2O as eluent) to afford desired Michael adduct **4d** (52.3 mg, 93%).

(R)-3-(4,4-dicyano-3-phenylbutanoyl)oxazolidin-2-one (4B): Yellow amorphous; $[\alpha]_D^{28}$ +10.9 (*c* 0.95, $CHCl_3$, 83% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.35 (m, 5H), 4.51 (d, *J* = 6.1 Hz, 1H), 4.49-4.37 (m, 2H),4.06-3.93 (m, 2H), 3.86 (ddd, *J* = 8.4, 6.0, 5.8 Hz, 1H), 3.70 (dd, *J* = 18.4, 5.8 Hz, 1H), 3.60 (dd, *J* = 18.4, 8.4 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 153.4, 136.0, 129.4, 129.3, 128.0, 111.7, 111.5, 62.3, 42.3, 41.6, 37.3, 28.8 ppm; IR ($CHCl_3$) ν 3030, 1786, 1698 cm^{-1}; MS (EI^{+}) 283 (M^{+}, 6), 131 (100); HRMS (EI^{+}) Calcd for $[C_{15}H_{13}N_3O_3]^{+}$: 283.0957; Found: 283.0960; HPLC [Chiralcel OD-H, hexane/2-propanol = 70/30, 0.5 mL/min, λ = 210 nm, retention times: (major) 60.4 min, (minor) 75.6 min].

(R)-1-(4,4-dicyano-3-phenylbutanoyl)-3-methylimidazolidin-2-one (4C): Colorless solid; $[\alpha]_D^{26}$ +6.25 (*c* 0.96, $CHCl_3$, 81% ee); M.p. 139-141 °C (Hexane/ AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.30 (m, 5H), 4.63 (d, *J* = 5.8 Hz, 1H), 3.90-3.75 (m, 3H), 3.70 (dd, *J* = 18.0, 5.2 Hz, 1H), 3.62 (dd, *J* = 18.0, 8.9 Hz, 1H), 3.47-3.37 (m, 2H), 2.88 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 154.5, 136.5, 129.1, 128.9, 128.1, 112.0, 111.7, 43.0, 41.8, 39.2, 37.1, 30.5, 28.8 ppm; IR ($CHCl_3$) ν 3030, 1736, 1672 cm^{-1}; MS (EI^{+}) 296 (M^{+}, 20), 131 (100); *Anal*. Calcd. for $C_{16}H_{16}N_4O_2$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.72; H, 5.42; N, 18.86; HPLC [Chiralcel AD-H, hexane/2-

propanol = 80/20, 0.5 mL/min, λ = 210 nm, retention times: (major) 48.1 min, (minor) 55.5 min].

(R)-1-(4,4-dicyano-3-phenylbutanoyl)pyrrolidin-2-one (4D): Colorless solid; $[\alpha]_D^{26}$ +8.64 (*c* 1.00, $CHCl_3$, 93% ee); M.p. 103-105 °C (Hexane/ AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.35 (m, 5H), 4.57 (d, *J* = 5.8 Hz, 1H), 3.86-3.74 (m, 3H), 3.63-3.58 (m, 2H), 2.68-2.55 (m, 2H), 2.13-2.00 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 170.9, 136.3, 129.3, 129.1, 128.1, 111.9, 111.6, 45.3, 41.6, 38.8, 33.3, 28.8, 17.1 ppm; IR ($CHCl_3$) ν 3030, 1742, 1688 cm^{-1}; MS (EI$^+$) 281 (M^+, 12), 131 (100); *Anal.* Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.94. Found: C, 68.37; H, 5.66; N, 15.02; HPLC [Chiralcel AS-H, hexane/ethanol = 80/20, 0.5 mL/min, λ = 210 nm, retention times: (major) 50.8 min, (minor) 47.0 min].

(R)-1-[4,4-dicyano-3-phenylbutanoyl]piperidin-2-one (4E): Colorless oil; $[\alpha]_D^{28}$ +6.17 (*c* 0.67, $CHCl_3$, 59% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.33 (m, 5H), 4.54 (d, *J* = 5.5 Hz, 1H), 3.83 (dt, *J* = 8.5, 5.5 Hz, 1H), 3.76-3.56 (m, 4H), 2.64-2.50 (m, 2H), 1.92-1.75 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 173.6, 136.6, 129.2, 129.0, 128.1, 112.0, 111.7, 44.3, 42.2, 41.7, 34.7, 28.8, 22.2, 20.0 ppm; IR ($CHCl_3$) ν 3027, 2957, 1737, 1692 cm^{-1}; MS (EI$^+$) 295 (M^+, 8), 131 (100); HRMS (EI$^+$) Calcd for $[C_{17}H_{17}N_3O_2]^+$: 295.1321; Found: 295.1314**;** HPLC [Chiralcel AS-H, hexane/EtOH = 80/20, 0.5 mL/min, λ = 210 nm, retention times: (major) 41.7 min, (minor) 36.4 min].

(R)-N-acetyl-4,4-dicyano-N-methyl-3-phenylbutanamide (4F): Colorless oil; $[\alpha]_D^{26}$ +8.98 (*c* 0.72, $CHCl_3$, 56% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.31 (m, 5H), 4.56 (d, *J* = 5.5 Hz, 1H), 3.88-3.77 (m, 1H), 3.54 (dd, *J* = 18.5, 8.5 Hz, 1H), 3.47 (dd, *J* = 18.5, 5.3 Hz, 1H), 3.24 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 173.1, 136.5, 129.3, 129.1, 128.0, 111.9, 111.6, 42.1, 40.7, 31.9, 28.7, 26.1 ppm; IR ($CHCl_3$) ν 3030, 1737, 1700 cm^{-1}; MS (EI$^+$) 269 (M^+, 14), 131 (100); HRMS (EI$^+$) Calcd for $[C_{15}H_{15}N_3O_2]^+$: 269.1164; Found: 269.1155**;** HPLC [Chiralcel OJ-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 56.4 min, (minor) 79.0 min].

(R)-N-(4,4-dicyano-3-phenylbutanoyl)benzamide (4G): Colorless solid; $[\alpha]_D^{26}$ –16.5 (*c* 1.25, $CHCl_3$, 84% ee); M.p. 150-155 °C (Hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (br s, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.48-7.37 (m, 5H), 4.59 (d, *J* = 5.5 Hz, 1H), 3.93-3.86 (m, 1H), 3.79-3.71 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 165.6, 136.1, 133.8, 132.0, 129.3, 129.24, 129.19, 128.1, 127.7, 111.8, 111.5, 41.4, 39.6, 28.9 ppm; IR ($CHCl_3$) ν 3396, 3018, 1701 cm^{-1}; MS (EI$^+$) 317 (M^+, 4), 105 (100); HRMS (EI$^+$) Calcd for $[C_{19}H_{15}N_3O_2]^+$: 317.1164; Found: 317.1160; HPLC [Chiralcel AD-H, hexane/2-propanol = 70/30, 0.5 mL/min, λ = 210 nm, retention times: (major) 62.8 min, (minor) 33.9 min].

(R)-1-[3-(4-chlorophenyl)-4,4-dicyanobutanoyl]pyrrolidin-2-one (6a): Colorless amorphous; $[\alpha]_D^{28}$ +4.86 (*c* 0.85, $CHCl_3$, 93% ee); ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.56 (d, *J* = 5.8 Hz, 1H), 3.87-3.42 (m, 3H), 3.63-3.50 (m, 2H), 2.69-2.55 (m, 2H), 2.13-2.00 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 170.5, 135.1, 134.7, 129.47, 129.46, 111.7, 111.4, 45.3, 40.9, 38.7, 33.2, 28.6, 17.1 ppm; IR ($CHCl_3$) ν 2976, 1743, 1687 cm^{-1}; MS (EI^+) 315 (M^+, 5), 165 (100); HRMS (EI^+) Calcd for $[C_{16}H_{14}ClN_3O_2]^+$: 315.0775; Found: 315.0770**;** HPLC [Chiralcel AD-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 19.3 min, (minor) 24.9 min].

(R)-1-[4,4-dicyano-3-(4-fluorophenyl)butanoyl]pyrrolidin-2-one (6b): Colorless amorphous; $[\alpha]_D^{23}$ +10.3 (*c* 0.78, $CHCl_3$, 93% ee); ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.0, 8.4 Hz, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 4.57 (d, *J* = 5.5 Hz, 1H), 3.90-3.72 (m, 3H), 3.64-3.51 (m, 2H), 2.69-2.54 (m, 2H), 2.15-1.99 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 170.6, 164.0, 162.0, 132.10, 132.08, 129.93, 129.86, 116.3, 116.1, 111.8, 111.4, 45.3, 40.8, 38.8, 33.2, 28.8, 17.1 ppm; IR ($CHCl_3$) ν 3018, 2976, 1743, 1686 cm^{-1}; MS (EI^+) 299 (M^+, 6), 149 (100); HRMS (EI^+) Calcd for $[C_{16}H_{14}FN_3O_2]^+$: 299.1070; Found: 299.1077**;** HPLC [Chiralcel AD-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 16.0 min, (minor) 19.3 min].

(R)-1-[4,4-dicyano-3-(4-methoxyphenyl)butanoyl]pyrrolidin-2-one (6c): Yellow amorphous; $[\alpha]_D^{28}$ +6.09 (*c* 1.04, $CHCl_3$, 85% ee); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.52 (d, *J* = 5.5 Hz, 1H), 3.87-3.71 (m, 6H), 3.61-3.52 (m, 2H), 2.69-2.55 (m, 2H), 2.13-2.00 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 171.0, 160.0, 129.2, 128.2, 114.6, 112.0, 111.7, 55.2, 45.3, 40.9, 38.9, 33.3, 29.1, 17.1 ppm; IR ($CHCl_3$) ν 2974, 1742, 1686 cm^{-1}; MS (EI^+) 311 (M^+, 2), 161 (100); HRMS (EI^+) Calcd for $[C_{17}H_{17}N_3O_3]^+$: 311.1270; Found: 311.1270**;** HPLC [Chiralcel AD-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 18.9 min, (minor) 24.2 min].

(R)-1-[4,4-dicyano-3-(naphthalen-4-yl)butanoyl]pyrrolidin-2-one (6d): Colorless amorphous; $[\alpha]_D^{28}$ +12.2 (*c* 0.97, $CHCl_3$, 94% ee); ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.70-7.43 (m, 4H), 4.97-4.84 (m, 1H), 4.62 (d, *J* = 6.1 Hz, 1H), 3.85-3.67 (m, 4H), 2.68-2.51 (m, 2H), 2.11-1.94 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 170.7, 134.1, 132.6, 130.9, 129.6, 129.5, 127.2, 126.3, 125.4, 124.6, 121.8, 112.0, 111.7, 45.4, 39.3, 35.2, 33.3, 28.1, 17.1 ppm; IR ($CHCl_3$) ν 3018, 1742, 1689 cm^{-1}; MS (FAB^+) 332 (MH^+, 100); HRMS (FAB^+) Calcd for $[C_{20}H_{18}N_3O_2]^+$: 332.1399; Found: 314.1402**;** HPLC [Chiralcel AD-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 24.0 min, (minor)

21.1 min].

(R)-1-[4,4-dicyano-3-(furan-2-yl)butanoyl]pyrrolidin-2-one (6e): Colorless oil; $[\alpha]_D^{28}$ –10.9 (*c* 0.84, $CHCl_3$, 85% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.42 (m, 1H), 6.47-6.36 (m, 2H), 4.57 (d, *J* = 5.8 Hz, 1H), 4.02 (dt, *J* = 8.2, 5.7 Hz, 1H), 3.81 (t, *J* = 7.2 Hz, 2H), 3.62 (d, *J* = 18.9, 5.7 Hz, 1H), 3.52 (d, *J* = 18.9, 8.2 Hz, 1H), 2.68-2.58 (m, 2H), 2.14-2.02 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 170.3, 149.4, 143.4, 111.6, 111.2, 110.7, 109.1, 45.3, 37.4, 35.9, 33.2, 27.0, 17.1 ppm; IR ($CHCl_3$) ν 3018, 2976, 1743, 1688 cm^{-1}; MS (EI$^+$) 271 (M^+, 8), 121 (100); HRMS (EI$^+$) Calcd for $[C_{14}H_{13}N_3O_3]^+$: 271.0957; Found: 271.0959**;** HPLC [Chiralcel OJ-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 46.3 min, (minor) 52.3 min].

(R)-1-[3-(dicyanomethyl)-5-phenylpentanoyl]pyrrolidin-2-one (6f): Colorless oil; $[\alpha]_D^{28}$ –35.1 (*c* 1.10, $CHCl_3$, 94% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.16 (m, 5H), 4.44 (d, *J* = 4.9 Hz, 1H), 3.82-3.77 (m, 2H), 3.35 (dd, *J* = 18.6, 4.0 Hz, 1H), 3.10 (dd, *J* = 18.6, 9.0 Hz, 1H), 2.84 (ddd, *J* = 14.2, 9.3, 5.5 Hz, 1H), 2.73-2.55 (m, 4H), 2.19-2.03 (m, 3H), 2.02-1.97 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 171.4, 139.8, 128.8, 128.3, 126.6, 112.3, 111.7, 45.3, 37.1, 35.7, 33.3, 32.7, 32.6, 26.9, 17.1 ppm; IR ($CHCl_3$) ν 3028, 1742, 1686 cm^{-1}; MS (EI$^+$) 309 (M^+, 4), 127 (100); HRMS (EI$^+$) Calcd for $[C_{18}H_{19}N_3O_2]^+$: 309.1477; Found: 309.1480; HPLC [Chiralcel AD-H, hexane/2-propanol = 50/50, 0.5 mL/min, λ = 210 nm, retention times: (major) 14.2 min, (minor) 19.7 min].

(R)-1-[4,4-dicyano-3-methylbutanoyl]pyrrolidin-2-one (6g): Colorless oil; $[\alpha]_D^{25}$ –23.5 (*c* 0.74, $CHCl_3$, 93% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41 (d, *J* = 4.9 Hz, 1H), 3.80 (t, *J* = 7.2 Hz, 2H), 3.18 (dd, *J* = 18.6, 4.9 Hz, 1H), 3.08 (dd, *J* = 18.6, 8.7 Hz, 1H), 2.77-2.67 (m, 1H), 2.62 (t, *J* = 8.1 Hz, 2H), 2.14-2.04 (m, 2H), 1.36 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 171.2, 112.4, 111.4, 45.2, 39.7, 33.3, 31.6, 27.7, 17.1, 17.0 ppm; IR ($CHCl_3$) ν 3024, 1742, 1688 cm^{-1}**;** MS (FAB$^+$) 220 (MH^+, 46), 69 (100); *Anal*. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.08; H, 5.97; N, 19.14**;** HPLC [Chiralcel OD-H, hexane/2-propanol = 70/30, 0.5 mL/min, λ = 210 nm, retention times: (major) 30.9 min, (minor) 41.5 min].

(R)-1-[3-dicyanomethyl-4,4-dimethylpentanoyl]pyrrolidin-2-one (6h): Colorless solid; $[\alpha]_D^{26}$ –25.1 (*c* 0.96, $CHCl_3$, 92% ee); M.p. 127-129 °C (Hexane/ AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.07 (d, *J* = 3.4 Hz, 1H), 3.94-3.76 (m, 2H), 3.39 (dd, *J* = 18.5, 3.1 Hz, 1H), 3.12 (dd, *J* = 18.5, 9.6 Hz, 1H), 2.74-2.55 (m, 3H), 2.17-2.00 (m, 2H), 1.04 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 172.0, 113.3, 112.7, 45.6, 45.2, 35.8, 34.2, 33.4, 27.5, 23.3, 17.1 ppm; IR ($CHCl_3$) ν 3029, 2969, 1740, 1691 cm^{-1}; MS (EI$^+$) 261 (M^+), 86 (100); *Anal*. Calcd. for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found C, 64.28; H, 7.45; N, 16.04**;** HPLC [Chiralcel AD-H, hexane/2-propanol =

90/10, 0.5 mL/min, λ = 210 nm, retention times: (major) 42.2 min, (minor) 47.8 min].

(R)-methyl 4,4-dicyano-3-(4-fluorophenyl)butanoate (7): To a stirred solution of **6b** (0.136 mmol, 40.6 mg) in MeOH/MeCN (0.16 ml/0.11 ml) was added $Er(OTf)_3$ (0.0068 mmol, 4.2 mg) at rt. After 21 h, the reaction mixture was evaporated and purified by column chromatography (Hexane/AcOEt = 2/1) to afford desired Michael adduct **7** (29.8 mg, 89%). Colorless oil; $[a]_D^{24}$ +21.8 (*c* 0.71, $CHCl_3$, 93% ee); ^1H NMR (500 MHz, $CDCl_3$) d 7.39-7.32 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 4.49 (d, *J* = 5.2 Hz, 1H), 3.76-3.67 (m, 4H), 3.05 (dd, *J* = 17.2, 8.7 Hz, 1H), 2.93 (dd, *J* = 17.2, 6.4 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) d 170.7, 164.1, 162.1, 131.5, 129.7, 129.6, 116.5, 116.3, 111.5, 111.2, 52.4, 41.4, 35.9, 28.8 ppm; IR ($CHCl_3$) n 3026, 1734, 1607, 1513 cm^{-1}**;** MS (EI^+) 246 (M^+, 10), 139 (100)**;** *Anal*. Calcd. for $C_{13}H_{11}FN_2O_2$: C, 63.41; H, 4.50; N, 11.38. Found: C, 63.56; H, 4.70; N, 11.49**;** HPLC [Chiralcel AD-H, hexane/2-propanol = 90/10, 0.5 mL/min, 1 = 210 nm, retention times: (major) 34.8 min, (minor) 31.8 min].

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