Supplementary Material (ESI) for Chemical Communications

Catalytic Enantioselective Aldol Additions of α-Isothiocyanato Imides to α-Ketoesters

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Electronic Supplementary Information

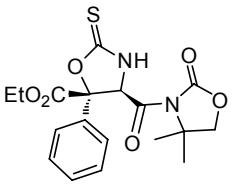
General information: Starting materials, reagents and solvents were purchased from commercial sources and were used as received. Anhydrous methyl *t*-butyl ether was purchased from commercial sources and used without further purification. Toluene was distilled from sodium prior to use. Reactions were run in medium sized screw-capped vials. Purification of the reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60 F_{254} plates. Visualization was accomplished with UV light and permanganate stain followed by heating. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on an ATI Mattson Genesis Series FT-Infrared spectrophotometer. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian VNMRS 500 and 400 MHz instrument and chemical shifts are reported in parts per million (ppm) downfield from TMS, using residual $CDCl_3$ (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex; br = broad), coupling constant(s) in Hz and integration. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) spectra were recorded on a Varian VNMRS 500 and 400 MHz instrument and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer. Optical rotation was recorded on Perkin-Elmer 343 polarimeter at 589 nm and 293 K. HPLC analysis was carried out on an Agilent 1100 series HPLC with auto sampler and a multiple wavelength detector. Racemic products were prepared using DABCO in toluene.[1]

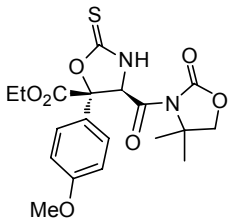
Preparation of Substrates

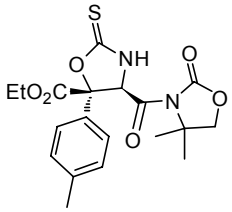
The α-ketoesters were prepared according to literatures procedures.[2]

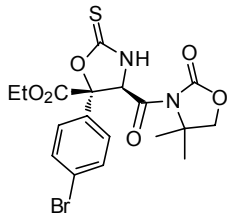
General Procedure for catalytic aldol reaction between isothiocyanates and α-ketoesters

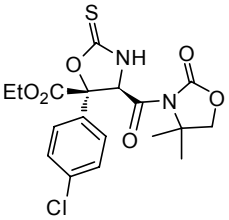
α-Ketoesters (1.1 equiv) and catalyst (0.05 equiv) were dissolved in anhydrous methyl *t*-butyl ether followed by addition of the isothiocyanato imide (1.0 equiv). Reactions were run on a 0.5 mmol scale. The reaction progress was monitored by TLC analysis. Upon consumption of the isothiocyanato imide, the solvent was removed in vacuo and the crude product was purified by silica gel flash chromatography. The diastereomers were separable in all cases. Racemic samples were prepared using 1.1 eq of α-ketoesters, 1.0 eq isothiocyanato imide, and 0.30 eq of DABCO in toluene.[1]

(4S,5R)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-5-phenyl-2-thioxooxazolidine-5-carboxylate (5a). 
mp = 172–173 °C (EtOAc/DCM); R_f = 0.3 (EtOAc/DCM 19:1 v/v); $[\alpha]_D^{20}$ –9.5 (*c* 1.0, $CHCl_3$, 95% ee); IR (KBr) 3334, 2970, 2932, 1814, 1783, 1740, 1681, 1506, 1473, 1451, 1387, 1339, 1300 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 – 7.69 (d, *J* = 8.1, 2H), 7.58 (br, s, 1H), 7.38 – 7.44 (comp, 3H), 5.93 (s, 1H), 4.20 – 4.26 (m, 1H), 4.10 – 4.17 (m, 1H), 4.15 (app s, 2H), 1.63 (s, 3H), 1.61 (s, 3H), 1.22 (app t, *J* = 7.3 MHz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.6, 169.1, 167.5, 154.5, 136.1, 129.9, 129.2, 125.2, 92.6, 76.2, 66.0, 64.7, 63.1, 61.6, 25.5, 24.9, 24.0, 14.0; *m/z* (ESI-MS) 415.1 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 16.48 min (major) and t_r = 22.54 min.

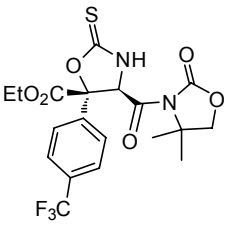
(4R,5S)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-5-(4-methoxyphenyl)-2-thioxooxazolidine-5-carboxylate (5b). 
Yellow oil; R_f = 0.25 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{20}$ –15.7 (*c* 1.0, $CHCl_3$, 94% ee); IR (KBr) 3426, 1775, 1736, 1704, 1646, 1610, 1513, 1381, 1306, 1257 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (br, s, 1H), 7.58 – 7.60 (d, *J* = 8.9 Hz, 2H), 6.91 – 6.93 (d, *J* = 8.9 Hz, 2H), 5.91 (s, 1H), 4.19 – 4.25 (m, 1H), 4.14 (comp, 3H), 3.81 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H), 1.21 (app t, *J* = 5.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.7, 169.2, 167.7, 160.8, 154.6, 128.0, 126.7, 114.6, 92.6, 76.2, 66.0, 64.7, 63.0, 61.6, 55.6, 25.6, 25.0, 24.0, 14.0; *m/z* (ESI-MS) 445.0 $[MNa]^+$; HPLC: Daicel (Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 20.91 min and t_r = 23.35 min (major).

(4R,5S)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxo-5-(p-tolyl)oxazolidine-5-carboxylate (5c). 
Yellow oil; R_f = 0.25 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{20}$ –22.0 (*c* 1.0, $CHCl_3$, 92% ee); IR (KBr) 3441, 1775, 1703, 1646, 1495, 1381, 1303, 1275, 1238, 1201 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 4.1 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 5.9 (s, 1H), 4.19 – 4.26 (m, 1H), 4.10 – 4.17 (comp, 3H), 2.35 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H), 1.23 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.7, 169.2, 167.6, 154.5, 140, 133.2, 129.9, 125.1, 92.7, 76.2, 66.1, 64.7, 63.1, 61.6, 25.6, 25.0, 24.0, 21.3, 14.1; *m/z* (ESI-MS) 429.1 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 13.70 min and t_r = 18.31 min (major).

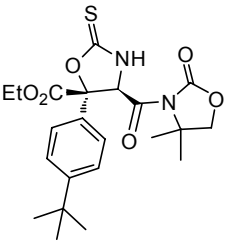
(4R,5S)-ethyl 5-(4-bromophenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5d). 
mp = 165–166 °C (EtOAc/DCM); R_f = 0.25 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{20}$ –15.2 (*c* 1.0, $CHCl_3$, 97% ee); IR (KBr) 3334, 2977, 2932, 1777, 1705, 1490, 1382, 1304 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (app t, *J* = 9.9Hz, 4H), 7.43 (br, s, 1H), 4.20 – 4.26 (m, 1H), 4.12 – 4.18 (comp, 3H), 1.62 (s, 3H), 1.61 (s, 3H), 1.23 (app t, *J* = 7.1 Hz, 3H; ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5, 168.9, 167.0, 154.6, 135.3, 132.4, 127.1, 124.4, 92.2, 76.2, 65.9, 63.4, 61.7, 25.6, 24.9, 24.1, 14.0; *m/z* (ESI-MS) 493.0 (^{79}Br) 494.9 (^{81}Br) $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, F1ow rate = 1 mL/min, UV = 254 nm, t_r = 12.60 min and t_r = 18.23 min (major).

(4R,5S)-ethyl 5-(4-chlorophenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5e). 

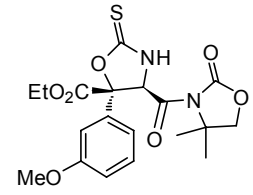
mp = 182–183 °C (EtOAc/DCM); R_f = 0.25 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{20}$ –7.0 (*c* 1.0, $CHCl_3$, 98% ee); IR (KBr) 3334, 2970, 2932, 1814, 1783, 1740, 1681, 1506, 1473, 1451, 1387, 1339, 1300 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.64 (d, *J* = 8.7 Hz, 2H), 7.47 (br, s, 1H), 7.38 – 7.40 (d, *J* = 8.7 Hz, 2H), 5.86, (s, 1H), 4.10 – 4.27 (comp, 4H), 1.62 (s, 3H), 1.60 (s, 3H), 1.22 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.4, 168.9, 167.2, 154.6, 136.2, 134.7, 129.5, 126.8, 92.1, 76.2, 66.1, 63.4, 61.7, 25.0, 24.0, 14.0; *m/z* (ESI-MS) 449.3 (^{35}Cl) 451.3 (^{37}Cl) $[MNa]^+$; Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 12.05 min and t_r = 17.49 min (major).

(4R,5S)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxo-5-(4-(trifluoromethyl)phenyl)oxazolidine-5-carboxylate (5f). 

mp = 157–158 °C (EtOAc/DCM); R_f = 0.20 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{20}$ –3.1 (*c* 1.0, $CHCl_3$, 97% ee); IR (KBr) 3231, 2974, 2942, 2915, 2360, 1771, 1753, 1706, 1683, 1618, 1500, 1413, 1382, 1328, 1308 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.83 – 7.85 (d, *J* = 8.1 Hz, 2H, 7.68 – 7.72 (comp, 3H), 5.92 (s, 1H), 4.20 – 4.27 (m, 1H), 4.13 – 4.18 (comp, 3H), 1.63 (s, 3H), 1.61 (s, 3H), 1.23 (app t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5, 168.8, 166.8, 154.6, 132.1 (q, $J_{C\text{-}F}$ = 32.8 Hz), 126.2 (q, $J_{C\text{-}F}$, 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 273.1 Hz), 92.1, 77.5, 77.3, 77.0, 76.2, 66.0, 63.6 61.7, 24.8, 24.1, 14.0; *m/z* (ESI-MS) 483.2 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 8.63 min and t_r = 11.42 min (major).

(4R,5S)-ethyl 5-(4-(tert-butyl)phenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5g). 

mp = 182–183 °C (EtOAc/DCM); R_f = 0.25 (EtOAc/DCM 2:98 v/v); $[\alpha]_D^{20}$ –17.7 (c 1.0, $CHCl_3$, 96% ee); IR (KBr) 3378, 2966, 2870, 1778, 1737, 1708, 1491, 1382, 1304, 1273, 1238, 1175, 1098, 1067, 1033, 927, 762, 711, 671, 564 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (br, s, 1H), 7.58, (d, *J* = 4.1 Hz, 2H), 7.42, (d, *J* = 4.1 Hz, 2H), 5.93 (s, 1H), 4.20 – 4.28 (m, 1H), 4.08 – 4.18 (comp, 3H), 1.62 (s, 3H), 1.60 (s, 3H), 1.30 (app t, 9H), 1.23 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.7, 169.1, 167.6, 154.5, 153.0, 133.1, 126.3, 124.9, 92.6, 76.2, 66.1, 63.1, 61.6, 34.9, 31.4, 24.9, 24.1, 14.1; *m/z* (ESI-MS) 471.2 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 871 min and t_r = 11.51 min (major).

(4R,5S)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-5-(3-methoxyphenyl)-2-thioxooxazolidine-5-carboxylate (5h). 

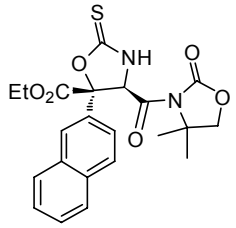
Yellow oil; R_f = 0.25 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{22}$ –22 (*c* 1.0 $CHCl_3$, 96% ee); IR (KBr) 3403, 1775, 1739, 1705, 1602, 1493, 1381, 1303, 1259 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (br, s, 1H), 7.30 (app t, *J* = 7.3, 1H), 7.23 – 7.26 (comp, 2H), 6.90 – 6.92 (m, 1H), 4.19 – 4.26 (m, 1H), 4.09 – 4.15 (comp, 3H), 3.81 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H), 1.21 (app t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.7, 169.1, 167.3, 160.2, 154.5, 137.7, 130.3, 117.2, 116.0, 110.5,

92.6, 76.1, 65.9, 63.2, 61.6, 24.9, 24.1, 14.1 ; *m/z* (ESI-MS) 445.2 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 18.78 min (major) and t_r = 27.54 min.

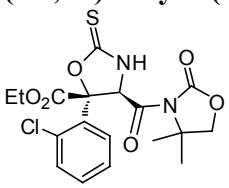
(4R,5S)-ethyl 5-(3,4-dichlorophenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5i). mp = 161–162 °C (EtOAc/DCM); R_f = 0.25 (EtOAc/DCM 2:98 v/v); $[\alpha]_D^{20}$ –9.2 (c, 1.0, $CHCl_3$, 98% ee); IR (KBr) 3340, 2979, 2936, 1777, 1707, 1574, 1382, 1306, 1240, 1175, 1100, 1071, 1031, 925, 853, 823, 806, 763, 713, 683, 666, 635, 613, 572, 513, 441 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.2 Hz, 1H), 7.56 (dd, *J* = 2.2 and 2.3 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 5.79 (s, 1H), 4.21 – 4.28 (m, 1H), 4.14 – 4.20 (comp, 3H), 1.62 (s, 3H), 1.61 (s, 3H), 1.25 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 168.6, 166.8, 154.6, 136.4, 134.5, 133.7, 131.2, 127.6, 124.9, 76.3, 66.1, 63.6, 61.7, 24.8, 24.1, 14.0; *m/z* (ESI-MS) 481.1 (2 ^{35}Cl) 483.1 ($^{35,37}Cl$) 485.1 (2 ^{37}Cl) $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 10.2 min and t_r = 14.3 min (major).

(4R,5S)-ethyl 5-(3,5-difluorophenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5j). mp = 155–156°C (EtOAc/DCM); R_f = 0.2 (EtOAc/DCM 2:98 v/v); $[\alpha]_D^{20}$ –5.1 (c, 1.0, $CHCl_3$, 97% ee); IR (KBr) 3332, 3103, 2972, 2937, 1770, 1729, 1707, 1627, 1601, 1513, 1477, 1443, 1397, 1382, 1354, 1309, 1274, 1251, 1189, 1158, 1122, 1105, 1079, 1050, 1026, 984, 942, 922, 861, 842, 761, 746, 713, 681, 668, 658, 638, 613, 599, 574, 532, 511 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.8 (br, s, 1H), 7.26 – 7.27 (comp, 2H), 6.82 – 6.87 (m, 1H), 5.85 (s, 1H), 4.21 – 4.28 (m, 1H), 4.10 – 4.20 (comp, 3H), 1.63 (s, 3H), 1.60 (s, 3H), 1.24 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 168.5, 166.6, 163.3 (dd, $J_{C\text{-}F}$, 252.3 and 13.1 Hz), 154.6, 140.1 (t, $J_{C\text{-}F}$ = 9.0 Hz), 109.1 (dd, $J_{C\text{-}F}$ = 21.0 and 7.3 Hz), 105.5 (t, $J_{C\text{-}F}$ = 24.9 Hz), 91.5, 76.3, 66.2, 63.6, 61.7, 24.9, 24.1, 14.0; *m/z* (ESI-MS) 451.2 $[MNa]^+$; Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 10.5 min and t_r = 12.5 min (major).

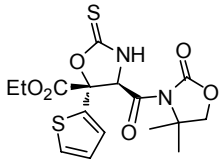
(4R,5S)-ethyl 5-(2,4-dichlorophenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5k). mp = 186–187°C (EtOAc/DCM); R_f = 0.2 (EtOAc/DCM 2:98 v/v); $[\alpha]_D^{20}$ 18.1 (c 1.0, $CHCl_3$, 93% ee); IR (KBr) 3338, 2980, 1778, 1711, 1587, 1475, 1381, 1308, 1242, 1176, 1099, 1057, 1031, 970, 924, 866, 815, 763, 710, 606, 574, 486 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 4.2 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.41 (br, s, 1H), 7.34 (dd, *J* =4.2 Hz, 1H), 6.24 (s, 1H), 4.18 – 4.26 (m, 1H), 4.10 – 4.16 (comp, 3H), 1.65 (app s, 3H), 1.60 (app s, 3H), 1.23 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 167.9, 165.2, 154.3, 136.7, 132.5, 132.3, 131.6, 129.3, 128.0, 91.8, 76.1, 63.6, 63.6, 61.9, 25.0, 23.6, 14.0; *m/z* (ESI-MS) 481.1 (2 ^{35}Cl) 483.1 ($^{35,37}Cl$) 485.1 (2 ^{37}Cl) $[MNa]^+$; Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 11.8 min and t_r = 25.4 min (major).

(4R,5S)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-5-(naphthalen-2-yl)-2-oxooxazolidine-5-carboxylate (5l). 

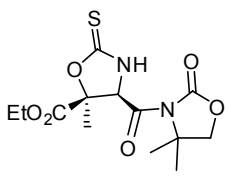
Colorless oil; R_f = 0.20 (EtOAc/DCM 2:98 v/v); $[\alpha]_D^{20}$ –18.5 (c 1.0, $CHCl_3$, 97% ee); IR (KBr) 3332, 3103, 2972, 2937, 1770, 1729, 1707, 1627, 1601, 1513, 1477, 1443, 1397, 1382, 1354, 1309, 1274, 1251, 1189, 1158, 1122, 1105, 1079, 1050, 1026, 984, 942, 922, 861, 842, 761, 746, 713, 681, 668, 658, 638, 613m, 599, 574, 532, 511 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.2 (br, s, 1H), 7.89 – 7.93 (comp, 2H), 7.84 – 7.85 (m, 1H), 7.76 (dd, 1.8 and 1.9 Hz, 1H), 7.21 (br, s, 1H), 6.0 (s, 1H), 4.22 – 4.28 (m, 1H), 4.12 – 4.20 (comp, 3H), 1.64 (app s, 6H), 1.23 (app t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.8, 169.2, 167.4, 154.6, 133.8, 133.3, 133.0, 129.3, 129.0, 127.8, 127.4, 127.0, 125.1, 122.3, 92.8, 76.2, 65.8, 63.2, 61.7, 24.9, 24.2, 14.1; *m/z* (ESI-MS) 465.2 $[MNa]^+$; Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 20.0 min and t_r = 26.1 min (major).

(4R,5S)-ethyl5-(2-chlorophenyl)-4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-2-thioxooxazolidine-5-carboxylate (5m). 

Colorless oil, R_f = 0.30 (EtOAc/DCM 3:97 v/v); $[\alpha]^{20}_D$ 22.1 (*c* 1.0, $CHCl_3$, 87% ee); IR (KBr) 2980, 1774, 1710, 1506, 1382, 1309, 1248, 1176, 1097, 1030, 913, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.72 (m, 1H), 7.41 – 7.44 (m, 1H), 7.34 – 7.39 (comp, 2H), 6.27 (s, 1H), 4.19 – 4.27 (comp, 2H), 4.10 – 4.15 (comp, 2H), 1.67 (s, 3H), 1.61 (s, 3H), 1.23 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.2, 168.1, 165.5, 154.3, 133.7, 131.8, 131.6, 131.1, 128.2, 127.8, 76.2, 63.7, 63.4, 61.9, 25.0, 23.6, 14.0; *m/z* (ESI-MS) 449.3 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 22.91 min and t_r = 31.25 min (major).

(4R,5S)-ethyl 4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-5-(thiophen-2-yl)-2-thioxooxazolidine-5-carboxylate (5n). 

Pale Yellow oil; R_f = 0.30 (EtOAc/DCM 1:19 v/v); $[\alpha]^{20}_D$ –44.5 (*c* 1.0, $CHCl_3$, 92% ee); IR (KBr) 3434, 1773, 1705, 1650, 1496, 1382, 1306, 1275, 1240 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.75 (br, s, 1H), 7.28 – 7.30 (comp, 2H), 7.2 (d, *J* = 1.2Hz, 1H), 5.80 (s, 1H), 4.12 – 4.25 (comp, 2H), 4.06 (app s, 2H), 1.55 (s, 3H), 1.57 (s, 3H), 1.21 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.1, 168.1, 166.7, 154.6, 138.9, 127.6, 127.6, 126.8, 90.5, 76.3, 67.1, 63.4, 61.6, 24.9, 24.1, 14.1; *m/z* (ESI-MS) 420.9 $[MNa]^+$; HPLC: (Chiracel AD-H, Hexane/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r = 28.07 min (major) and t_r = 31.19 min.

(4R,5S)-ethyl4-(4,4-dimethyl-2-oxooxazolidine-3-carbonyl)-5-methyl-2-thioxooxazolidine-5-carboxylate (5o). 

Colorless oil; R_f = 0.40 (EtOAc/DCM 3:97 v/v); $[\alpha]_D^{20}$ –17.1 (*c* 1.0, $CHCl_3$, 79% ee); IR (KBr) 3405, 2883, 1773, 1709, 1643, 1505, 1383, 1318, 1248, 1191, 1134, 1088, 1023, 942, 854, 764, 735, 711 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (br, s, 1H), 5.23, (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.11 (app s, 2H), 1.87 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H), 1.30 (app t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 168.3, 167.7, 154.8, 90.8, 76.4, 66.4, 63.0, 61.5, 24.9, 24.0, 17.1, 14.1; *m/z* (ESI-MS) 353.6 $[MNa]^+$; HPLC: Daicel Chiralpak AD-H, hexanes/*i*- PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_r= 8.54 min and t_r = 10.72 min (major).

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(2) (a) Q. Meng, Y. Sun, V. Ratovelomanana-Vidal, J. P. Genêt, Z. Zhang. *J. Org. Chem*. 2008, **73**, 3842. (b) J. Zhuang, C. Wang, F. Xie, W. Zhang. *Tetrahedron*. 2009, **65**, 9797.