Ni(II) Tol-BINAP-Catalyzed Enantioselective Orthoester Alkylations of *N*-Acylthiazolidinethiones

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Supporting Information

General Information. Reactions were carried out under a nitrogen atmosphere with a septum cap and magnetic stirring; no special precautions were taken to exclude water from the reaction vessel. CH₂Cl₂ was purified by passage through a bed of activated alumina.¹ All other reaction solvents were used as received. AgOTf was used as received from Aldrich Chemical Co. NiCl₂ was used as received from Alfa/Aesar Chemical Co. (*S*)-BINAP and (*S*)-Tol-BINAP were used as received from Strem Chemicals. Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.² Purification of 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 plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain, followed by heating. Optical rotations were measured on a Jasco DIP-0181 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]_{\lambda}^{T\text{ }^{\circ}\text{C}}$ (*c* = g/100 mL, solvent). Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ¹H NMR spectra were recorded on a Varian Inova-500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data are reported as (a = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hexet, sep = septet, o = octet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ¹³C NMR spectra were recorded on a Varian Mercury 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm). Low- and high-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers in the Harvard University Mass Spectrometry Laboratory.

General Procedure for Thiazoline Acylation. Prepared in analogy with the procedure of Mukaiyama and coworkers.³ To an oven-dried round-bottom flask under nitrogen atmosphere with a magnetic stirbar was added 2-mercaptothiazoline (1 g, 8.4 mmol), CH₂Cl₂ (50 mL) and Et₃N (1.4 mL, 10.1 mmol). The mixture was cooled to 0 °C and the acid chloride (9.2 mmol) was added drop wise over 5 min. The reaction mixture was allowed to gradually warm to room temperature. After 2 h, the reaction mixture was diluted with CH₂Cl₂ (50 mL) and washed with water (50 mL). The aqueous phase was extracted with CH₂Cl₂ (50 mL) and the combined organic layers washed with brine (100 mL) and dried (Na₂SO₄). Concentration in vacuo followed by flash chromatography on silica gel afforded the *N*-acylthiazolidinethione in >95% purity as determined by ¹H NMR spectroscopy.

1-(2-Thioxothiazolidin-3-yl)butan-1-one (1b): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (1.6 g, 100% yield): IR (film) 2961, 1699, 1464, 1363, 1279, 1156, 1050 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 4.57 (t, 2H, *J* = 7.7 Hz), 3.28 (t, 2H, *J* = 7.3 Hz), 3.21 (t, 2H, *J* = 7.3 Hz), 1.70 (h, 2H, *J* = 7.7 Hz), 0.96 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 174.7,

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 15, 1518-1520.

(2) Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford. 1988.

(3) Izawa, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1979**, 52, 555-558.

56.0, 40.3, 28.2, 18.1, 13.6; HRMS (CI, NH₃): Exact mass calcd for C₇H₁₅N₂OS₂ [M+NH₄]⁺, 207.0626. Found 207.0622.

1-(2-Thioxothiazolidin-3-yl)pentan-1-one (1c): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 10% EtOAc in hexanes as the eluant afforded the product as a yellow oil (1.5 g, 88% yield): IR (film) 2943, 1698, 1464, 1367, 1279, 1156, 1051 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 4.56 (t, 2H, *J* = 7.3 Hz), 3.27 (t, 2H, *J* = 7.3 Hz), 3.23 (t, 2H, *J* = 7.3 Hz), 1.65 (p, 2H, *J* = 7.8 Hz), 1.36 (h, 2H, 7.3 Hz), 0.91 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 174.9, 124.9, 56.0, 38.1, 28.2, 26.7, 22.1, 13.8; HRMS (ES⁺): Exact mass calcd for C₈H₁₄NOS₂ [M+H]⁺, 204.0517. Found 204.0524.

4-Methyl-1-(2-thioxothiazolidin-3-yl)pentan-1-one (1d): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 10% EtOAc in hexanes as the eluant afforded the product as a yellow oil (1.35 g, 74% yield): IR (film) 2956, 1700, 1466, 1365, 1280, 1157, 1052 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 4.56 (t, 2H, *J* = 7.7 Hz), 3.23 (m, 4H), 1.68-1.53 (m, 3H), 0.90 (d, 6H, *J* = 6.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 175.1, 56.0, 36.5, 33.4, 28.2, 27.6, 22.1; HRMS (ES⁺): Exact mass calcd for C₉H₁₆NOS₂ [M+H]⁺, 218.0673. Found 218.0670.

3-Methyl-1-(2-thioxothiazolidin-3-yl)butan-1-one (1e): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (1.55 g, 91% yield): IR (film) 2956, 1698, 1466, 1366, 1280, 1220, 1155 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 4.56 (t, 2H, *J* = 7.3 Hz), 3.27 (t, 2H, *J* = 7.7 Hz), 3.14 (d, 2H, *J* = 7.0 Hz), 2.21 (m, 1H), 0.96 (d, 6H, *J* = 6.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 174.1, 56.0, 46.9, 28.2, 25.3, 23.1; HRMS (ES⁺): Exact mass calcd for C₈H₁₄NOS₂ [M+H]⁺, 204.0517. Found 204.0526.

1-(2-Thioxothiazolidin-3-yl)pent-4-en-1-one (1f): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 10% EtOAc in hexanes as the eluant afforded the product as a yellow oil (1.4 g, 83% yield): IR (film) 2918, 1698, 1638, 1364, 1280, 1221, 1155, 1050 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 5.85 (m, 1H), 5.07 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.01 (dd, 1H, *J* = 10.3, 1.5 Hz), 4.57 (t, 2H, *J* = 7.8 Hz), 3.35 (t, 2H, *J* = 7.3 Hz), 3.29 (t, 2H, *J* = 7.3 Hz), 2.43 (q, 2H, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 174.0, 136.7, 129.9, 115.6, 55.9, 37.8, 28.6, 22.1; HRMS (ES⁺): Exact mass calcd for C₈H₁₂NOS₂ [M+H]⁺, 202.0360. Found 202.0369.

3-Phenyl-1-(2-thioxothiazolidin-3-yl)propan-1-one (1g): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (2.0 g, 95% yield): IR (film) 2939, 1697, 1603, 1495, 1366, 1278, 1221, 1156, 1049 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.31-7.19 (m, 5H), 4.54 (t, 2H, *J* = 7.7 Hz), 3.60 (t, 2H, *J* = 7.7 Hz), 3.24 (t, 2H, *J* = 7.7 Hz), 3.02 (t, 2H, *J* = 7.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 173.9, 140.4, 128.4, 126.2, 124.8, 55.9, 39.9, 30.7, 28.3; HRMS (ES⁺): Exact mass calcd for C₁₂H₁₄NOS₂ [M+H]⁺, 252.0517. Found 252.0512.

2-Phenyl-1-(2-thioxothiazolidin-3-yl)ethanone (1h): 2-Mercaptothiazoline (8.4 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 10% EtOAc in

hexanes as the eluant, increasing to 20% EtOAc in hexanes, afforded the product as a yellow solid (1.68 g, 84% yield): mp (EtOAc/Hex) 51-52 °C; IR (film) 2939, 1698, 1496, 1367, 1344, 1268, 1149, 1049 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.35-7.24 (m, 5H), 4.66 (s, 2H), 4.59 (t, 2H, *J* = 7.3 Hz), 3.28 (t, 2H, *J* = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 172.8, 133.8, 129.7, 129.3, 128.5, 127.1, 124.5, 56.2, 44.4. HRMS (ES+): Exact mass calcd for C₁₁H₁₂NOS₂ [M+H]⁺, 238.0360. Found 238.0357.

2-(4-Methoxyphenyl)-1-(2-thioxothiazolidin-3-yl)ethanone (1i): 2-Mercaptothiazoline (14.3 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 10% EtOAc in hexanes as the eluant, increasing to 20% EtOAc in

hexanes, afforded the product as a yellow oil (1.77 g, 46% yield): IR (film) 2960, 1706, 1614, 1574, 1386, 1269, 1155, 1028 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.16 (dt, 2H, *J* = 8.8, 2.2 Hz), 6.88 (dt, 2H, *J* = 8.8, 2.2 Hz), 4.58 (s, 2H), 4.57 (t, 2H, *J* = 7.7 Hz), 3.80 (s, 3H), 3.27 (t, 2H, *J* = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.7, 173.2, 158.6, 130.7, 125.7, 113.9, 56.3, 55.2. HRMS (ES+): Exact mass calcd for C₁₂H₁₄NO₂S₂ [M+H]⁺, 268.0466. Found 268.0467.

2-(4-Chlorophenyl)-1-(2-thioxothiazolidin-3-yl)ethanone (1j): 2-Mercaptothiazoline (11.7 mmol) was converted to the title compound according to the general procedure for thiazoline acylation. Purification by flash chromatography on silica gel using 20% EtOAc in hexanes as the eluant afforded the product as a yellow oil (0.6 g, 19% yield):

IR (film) 2915, 1711, 1490, 1372, 1281, 1226, 1155, 1043 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.09 (d, 2H, *J* = 8.4 Hz), 6.96 (d, 2H, *J* = 8.4 Hz), 4.41 (s, 2H), 4.37 (t, 2H, *J* = 7.7 Hz), 3.08 (t, 2H, *J* = 7.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 172.3, 133.0, 132.2, 131.1, 130.7, 128.7, 128.6, 56.2, 43.7. HRMS (ES+): Exact mass calcd for C₁₁H₁₁NOS₂ [M+H]⁺, 271.9970. Found 271.9969.

[Ni((S)-Tol-BINAP)]Cl₂: To a stirred suspension of (*S*)-Tol-BINAP (1.16 g, 1.71 mmol) in acetonitrile (30 mL) was added anhydrous NiCl₂ (221 mg, 1.71 mmol) and water (30 μL). The resulting mixture was heated at reflux for 16 h after which time a deep purple solution had formed. The reaction mixture was cooled to rt, filtered through a pad of dried celite and the solvent removed *in vacuo*. Drying overnight at 100 mtorr afforded a purple solid (1.3 g, 99%) which was stored in a dry box and could be used directly

without further purification: mp (decomp.) 237-240 °C; IR (film) 3050, 1598, 1499, 1189, 1097, 806 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 10.49 (br s, 4H), 9.48 (br s, 2H), 8.63 (d, 2H, *J* = 7.8 Hz), 8.44 (br s, 4H), 8.03 (t, 2H, *J* = 7.3 Hz), 6.96 (br s, 4H), 4.74 (s, 2H), 4.73 (s, 2H), 4.59 (br s, 2H), 4.55 (s, 6H), 2.39 (s, 6H).

[Ni((S)-Tol-BINAP)]OTf₂ (4): To a dried 50 mL round-bottomed flask was added [Ni((S)-Tol-BINAP)]NiCl₂ (1.3 g, 1.61 mmol), AgOTf (413 mg, 1.61 mmol) and CH₂Cl₂ (20 mL). The resulting mixture was stirred in the dark under an atmosphere of dry nitrogen for 5 h after which time the solution was filtered through oven-dried celite under an atmosphere of nitrogen. The solvent was removed under a stream of dry nitrogen to afford a dark brown, moisture sensitive residue (1.66 g, 100%) that could be stored in a

dry box and used directly without further purification: mp (decomp.) >230 °C; [α]_D²⁵ = -302° (*c* = 0.5, CHCl₃); IR (film) 3053, 1599, 1497, 1264, 1163, 1031, 806 cm⁻¹.

General procedure for the [Ni((S)-Tol-BINAP)]OTf₂ catalyzed trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones: To a dried 2 dram reaction vial in a glove box was added [Ni((S)-Tol-BINAP)]OTf₂ (25.9 mg, 0.025 mmol). The vial was fitted with a septum and removed to ambient atmosphere. Under an atmosphere of dry nitrogen the reaction vial was charged with CH₂Cl₂ (0.6 mL), *N*-acylthiazolidinethione (0.5 mmol) and trimethyl orthoformate (1.5 mmol). The resulting deep brown solution was cooled to -78 °C. 2,6-

Lutidine (1.5 mmol) was added drop wise, followed by $\text{BF}_3 \cdot \text{OEt}_2$ (1.5 mmol) and the reaction mixture placed in an ice bath. When the reaction was complete (0.5 to 1 h) as judged by tlc the mixture was diluted with CH_2Cl_2 (20 mL) and washed with 1.0 M HCl (20 mL). The aqueous layers were back extracted with CH_2Cl_2 (20 mL) and the combined organic layers washed with brine (40 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the residue purified by flash column chromatography to give the desired product in greater than 95% purity by ^1H NMR spectroscopy.

(R)-3,3-Dimethoxy-2-methyl-1-(2-thioxothiazolidin-3-yl)propan-1-one (3a): Prepared from **1a** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (91 mg, 73% yield):

$[\alpha]_{\text{D}}^{25} = -145.0^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2938, 1698, 1455, 1367, 1279, 1222, 1169, 1108 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 4.71 (m, 1H), 4.59 (d, 1H, $J = 8.1$ Hz), 4.60-4.56 (obs m, 1H), 4.40 (m, 1H), 3.38 (td, 1H, $J = 11.0, 7.7$ Hz), 3.32 (s, 3H), 3.29 (s, 3H), 3.19 (m, 1H), 1.20 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.6, 176.4, 106.0, 56.3, 55.0, 52.0, 42.2, 28.6, 13.0. HRMS (CI, NH_3): Exact mass calcd for $\text{C}_9\text{H}_{19}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M}+\text{NH}_4]^+$, 267.0844. Found 267.0837. Enantioselectivity determined by HPLC (Chiralcel ODH column, 5% *i*-PrOH/hexanes, 1.0 mL/min, 310 nm), $t_{\text{major}} = 11.7$ min, $t_{\text{minor}} = 12.7$ min; ee = 97%.

(R)-2-(Dimethoxymethyl)-1-(2-thioxothiazolidin-3-yl)butan-1-one (3b): Prepared from **1b** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (100 mg, 76% yield):

$[\alpha]_{\text{D}}^{25} = -92.1^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2934, 1697, 1459, 1365, 1277, 1221, 1160, 1109, 1056 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 5.15 (m, 1H), 4.70-4.62 (m, 1H), 4.65 (d, 1H, $J = 7.8$ Hz), 4.58 (m, 1H), 3.41-3.38 (m, 1H), 3.39 (s, 3H), 3.37 (s, 3H), 3.36-3.24 (m, 1H), 1.83 (m, 2H), 1.02 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.8, 175.3, 105.5, 56.4, 55.0, 52.2, 47.2, 28.3, 21.9. HRMS (ES+): Exact mass calcd for $\text{C}_{10}\text{H}_{18}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$, 264.0720. Found 264.0728. Enantioselectivity determined by HPLC (Chiralcel ODH column, 3% *i*-PrOH/hexanes, 1.0 mL/min, 310 nm), $t_{\text{major}} = 15.5$ min, $t_{\text{minor}} = 22.2$ min; ee = 95%.

(R)-2-(Dimethoxymethyl)-1-(2-thioxothiazolidin-3-yl)pentan-1-one (3c): Prepared from **1c** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (85 mg, 61% yield):

$[\alpha]_{\text{D}}^{25} = -98.1^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2957, 1650, 1464, 1362, 1280, 1156, 1059 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 5.16 (td, 1H, $J = 8.4, 4.4$ Hz), 4.65-4.46 (m, 2H), 4.56 (d, 1H, $J = 7.7$ Hz), 3.33 (s, 3H), 3.31 (s, 3H), 3.31 (obs m, 1H), 3.20 (m, 1H), 1.80-1.60 (m, 2H), 1.48-1.30 (m, 2H), 0.89 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.8, 175.5, 124.9, 105.8, 56.5, 55.1, 52.3, 46.3, 31.1, 28.3, 14.6. HRMS (CI, NH_3): Exact mass calcd for $\text{C}_{11}\text{H}_{23}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M}+\text{NH}_4]^+$, 295.1150. Found 295.1151. Enantioselectivity determined by HPLC (Chiralcel ODH column, 3% *i*-PrOH/hexanes, 1.0 mL/min, 310 nm), $t_{\text{major}} = 10.0$ min, $t_{\text{minor}} = 12.6$ min; ee = 94%.

(R)-2-(Dimethoxymethyl)-4-methyl-1-(2-thioxothiazolidin-3-yl)pentan-1-one (3d): Prepared from **1d** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (90 mg, 62% yield):

$[\alpha]_{\text{D}}^{25} = -63.6^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2955, 1697, 1467, 1365, 1266, 1221, 1110, 1061 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 5.28 (m, 1H), 4.63-4.50 (m, 2H), 4.56 (d, 1H, $J = 8.4$ Hz), 3.33 (s, 3H), 3.31 (s, 3H), 3.31-3.17 (obs m, 2H), 1.81 (ddd, 1H, $J = 13.5, 10.2, 5.1$ Hz), 1.61 (m, 1H), 1.46 (ddd, 1H, $J = 13.5, 8.4, 3.7$ Hz), 0.92 (d, 3H, $J = 6.6$ Hz), 0.89 (d, 3H, $J = 6.6$ Hz);

^{13}C NMR (100 MHz, CDCl_3) δ 201.9, 175.7, 106.3, 56.7, 55.5, 52.3, 45.0, 37.8, 28.3, 26.2, 23.5, 21.8. HRMS (ES+): Exact mass calcd for $\text{C}_{12}\text{H}_{22}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$, 292.1041. Found 292.1039. Enantioselectivity determined by HPLC (Chiralcel ODH column, 2% *i*-PrOH/hexanes, 0.8 mL/min, 310 nm), $t_{\text{major}} = 12.8$ min, $t_{\text{minor}} = 14.6$ min; ee = 93%.

(R)-2-(Dimethoxymethyl)-3-methyl-1-(2-thioxothiazolidin-3-yl)butan-1-one (3e):

Prepared from **1e** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones but using 10 mol% $[\text{Ni}((S)\text{-Tol-BINAP})]\text{OTf}_2$. After 1 h stirring at 0 °C and a further 1.5 mmol of 2,6-lutidine and $\text{BF}_3 \cdot \text{OEt}_2$ was added.

The reaction was complete after another 1 h and was quenched according to the general procedure. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (71 mg, 51% yield): $[\alpha]_{\text{D}}^{25} = -81.6^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2960, 1694, 1468, 1366, 1280, 1221, 1156, 1111, 1057 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 5.20 (dd, 1H, $J = 8.1, 5.5$ Hz), 4.69 (d, 1H, $J = 8.1$ Hz), 4.61–4.50 (m, 2H), 3.324 (s, 3H), 3.317 (s, 3H), 3.31–3.17 (m, 2H), 2.13 (o, 1H, $J = 7.0$ Hz), 1.04 (d, 3H, $J = 7.0$ Hz), 0.98 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.9, 174.3, 104.9, 56.4, 55.0, 52.5, 50.1, 28.8, 28.1, 20.0. HRMS (CI, NH_3): Exact mass calcd for $\text{C}_{11}\text{H}_{23}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M}+\text{NH}_4]^+$, 295.1150. Found 295.1157. Enantioselectivity determined by HPLC (Chiralcel ODH column, 2% *i*-PrOH/hexanes, 0.8 mL/min, 310 nm), $t_{\text{major}} = 15.7$ min, $t_{\text{minor}} = 19.5$ min; ee = 91%.

(R)-2-(Dimethoxymethyl)-1-(2-thioxothiazolidin-3-yl)pent-4-en-1-one (3f):

Prepared from **1f** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (127 mg, 92% yield): $[\alpha]_{\text{D}}^{25} = -78.4^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2936, 1697, 1441, 1366, 1279, 1225, 1159,

1112, 1059 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 5.85 (m, 1H), 5.25 (td, 1H, $J = 7.7, 5.9$ Hz), 5.07 (dd, 1H, $J = 17.2, 1.5$ Hz), 5.01 (dt, 1H, $J = 10.2, 1.1$ Hz), 4.63 (d, 1H, $J = 7.7$ Hz), 4.60–4.45 (m, 2H), 3.34 (s, 3H), 3.31–3.16 (m, 2H), 2.47 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.9, 174.5, 134.5, 124.9, 117.1, 105.1, 56.3, 55.2, 52.7, 46.2, 33.1. HRMS (ES+): Exact mass calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$, 276.0728. Found 276.0726. Enantioselectivity determined by HPLC (Chiralcel ODH column, 3% *i*-PrOH/hexanes, 1.0 mL/min, 310 nm), $t_{\text{major}} = 16.1$ min, $t_{\text{minor}} = 21.1$ min; ee = 94%.

(R)-2-Benzyl-3,3-dimethoxy-1-(2-thioxothiazolidin-3-yl)propan-1-one (3g):

Prepared from **1g** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (148 mg, 91% yield):

$[\alpha]_{\text{D}}^{25} = +11.7^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2934, 1698, 1456, 1363, 1279, 1223, 1156, 1118, 1057 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.28–7.20 (m, 5H), 5.59 (m, 1H), 4.69 (d, 1H, $J = 7.7$ Hz), 4.28 (m, 2H), 3.38 (s, 3H), 3.36 (s, 3H), 3.09 (dd, 1H, $J = 13.5, 5.5$ Hz), 3.01 (dt, 1H, $J = 11.0, 7.0$ Hz), 2.91 (dd, 1H, $J = 13.5, 9.9$ Hz), 2.77 (dt, 1H, $J = 10.6, 8.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.8, 174.5, 137.9, 129.0, 128.3, 126.5, 105.3, 56.2, 55.6, 52.7, 47.8, 35.6. HRMS (ES+): Exact mass calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$, 326.0884. Found 326.0880. Enantioselectivity determined by HPLC (Chiralcel ODH column, 5% *i*-PrOH/hexanes, 0.8 mL/min, 310 nm), $t_{\text{minor}} = 24.6$ min, $t_{\text{major}} = 34.5$ min; ee = 92%.

(R)-3,3-Dimethoxy-2-phenyl-1-(2-thioxothiazolidin-3-yl)propan-1-one (3h):

Prepared from **1h** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow solid (141 mg, 91%

yield). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a solution of **3h** in EtOAc: mp (EtOAc/Hex) 95–96 °C; $[\alpha]_{\text{D}}^{25} = +49.0^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2936, 1694, 1455,

1367, 1279, 1154, 1054 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.49 (d, 2H, $J = 7.0$ Hz), 7.35-7.26 (m, 3H), 6.33 (d, 1H, $J = 8.4$ Hz), 4.99 (d, 1H, $J = 8.4$ Hz), 4.64-4.58 (m, 1H), 4.48 (dt, 1H, $J = 12.1, 7.7$ Hz), 3.41 (s, 3H), 3.26 (dt, 1H, $J = 11.3, 7.7$ Hz), 3.15 (s, 3H), 3.17-3.11 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.6, 172.8, 134.1, 129.5, 128.4, 127.7, 106.5, 56.4, 55.1, 53.5, 52.4, 51.8, 51.1 (CI, NH_3): Exact mass calcd for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M}+\text{NH}_4]^+$, 329.0982. Found 329.0994. Enantioselectivity determined by HPLC (Chiralcel ODH column, 3% *i*-PrOH/hexanes, 1.0 mL/min, 310 nm), $t_{\text{minor}} = 21.8$ min, $t_{\text{major}} = 25.3$ min; ee = 98%.

(R)-3,3-Dimethoxy-2-(4-methoxyphenyl)-1-(2-thioxothiazolidin-3-yl)propan-1-one (3i):

Prepared from **1i** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (155 mg, 91% yield): $[\alpha]_{\text{D}}^{25} = -47.4^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2935, 1694, 1610, 1512, 1367, 1260, 1155, 1111, 1056 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.40 (d, 2H, $J = 8.8$ Hz), 6.86 (d, 2H, $J = 8.8$ Hz), 6.27 (d, 1H, $J = 8.4$ Hz), 4.96 (d, 2H, $J = 8.4$ Hz), 4.60 (dt, 1H, $J = 12.1, 7.3$ Hz), 4.47 (dt, 1H, $J = 12.1, 7.7$ Hz), 3.78 (s, 3H), 3.40 (s, 3H), 3.25 (dt, 1H, $J = 11.0, 7.7$ Hz), 3.16 (s, 3H), 3.14 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.5, 173.1, 159.0, 130.5, 126.1, 113.8, 106.4, 56.4, 55.12, 55.09, 54.85, 54.78, 54.61, 54.54, 54.47, 54.40, 54.33, 54.26, 54.19, 54.12, 54.05, 53.98, 53.91, 53.84, 53.77, 53.70, 53.63, 53.56, 53.49, 53.42, 53.35, 53.28, 53.21, 53.14, 53.07, 53.00, 52.93, 52.86, 52.79, 52.72, 52.65, 52.58, 52.51, 52.44, 52.37, 52.30, 52.23, 52.16, 52.09, 52.02, 51.95, 51.88, 51.81, 51.74, 51.67, 51.60, 51.53, 51.46, 51.39, 51.32, 51.25, 51.18, 51.11, 51.04, 50.97, 50.90, 50.83, 50.76, 50.69, 50.62, 50.55, 50.48, 50.41, 50.34, 50.27, 50.20, 50.13, 50.06, 49.99, 49.92, 49.85, 49.78, 49.71, 49.64, 49.57, 49.50, 49.43, 49.36, 49.29, 49.22, 49.15, 49.08, 49.01, 48.94, 48.87, 48.80, 48.73, 48.66, 48.59, 48.52, 48.45, 48.38, 48.31, 48.24, 48.17, 48.10, 48.03, 47.96, 47.89, 47.82, 47.75, 47.68, 47.61, 47.54, 47.47, 47.40, 47.33, 47.26, 47.19, 47.12, 47.05, 46.98, 46.91, 46.84, 46.77, 46.70, 46.63, 46.56, 46.49, 46.42, 46.35, 46.28, 46.21, 46.14, 46.07, 46.00, 45.93, 45.86, 45.79, 45.72, 45.65, 45.58, 45.51, 45.44, 45.37, 45.30, 45.23, 45.16, 45.09, 45.02, 44.95, 44.88, 44.81, 44.74, 44.67, 44.60, 44.53, 44.46, 44.39, 44.32, 44.25, 44.18, 44.11, 44.04, 43.97, 43.90, 43.83, 43.76, 43.69, 43.62, 43.55, 43.48, 43.41, 43.34, 43.27, 43.20, 43.13, 43.06, 42.99, 42.92, 42.85, 42.78, 42.71, 42.64, 42.57, 42.50, 42.43, 42.36, 42.29, 42.22, 42.15, 42.08, 42.01, 41.94, 41.87, 41.80, 41.73, 41.66, 41.59, 41.52, 41.45, 41.38, 41.31, 41.24, 41.17, 41.10, 41.03, 40.96, 40.89, 40.82, 40.75, 40.68, 40.61, 40.54, 40.47, 40.40, 40.33, 40.26, 40.19, 40.12, 40.05, 39.98, 39.91, 39.84, 39.77, 39.70, 39.63, 39.56, 39.49, 39.42, 39.35, 39.28, 39.21, 39.14, 39.07, 39.00, 38.93, 38.86, 38.79, 38.72, 38.65, 38.58, 38.51, 38.44, 38.37, 38.30, 38.23, 38.16, 38.09, 38.02, 37.95, 37.88, 37.81, 37.74, 37.67, 37.60, 37.53, 37.46, 37.39, 37.32, 37.25, 37.18, 37.11, 37.04, 36.97, 36.90, 36.83, 36.76, 36.69, 36.62, 36.55, 36.48, 36.41, 36.34, 36.27, 36.20, 36.13, 36.06, 35.99, 35.92, 35.85, 35.78, 35.71, 35.64, 35.57, 35.50, 35.43, 35.36, 35.29, 35.22, 35.15, 35.08, 35.01, 34.94, 34.87, 34.80, 34.73, 34.66, 34.59, 34.52, 34.45, 34.38, 34.31, 34.24, 34.17, 34.10, 34.03, 33.96, 33.89, 33.82, 33.75, 33.68, 33.61, 33.54, 33.47, 33.40, 33.33, 33.26, 33.19, 33.12, 33.05, 32.98, 32.91, 32.84, 32.77, 32.70, 32.63, 32.56, 32.49, 32.42, 32.35, 32.28, 32.21, 32.14, 32.07, 32.00, 31.93, 31.86, 31.79, 31.72, 31.65, 31.58, 31.51, 31.44, 31.37, 31.30, 31.23, 31.16, 31.09, 31.02, 30.95, 30.88, 30.81, 30.74, 30.67, 30.60, 30.53, 30.46, 30.39, 30.32, 30.25, 30.18, 30.11, 30.04, 29.97, 29.90, 29.83, 29.76, 29.69, 29.62, 29.55, 29.48, 29.41, 29.34, 29.27, 29.20, 29.13, 29.06, 28.99, 28.92, 28.85, 28.78, 28.71, 28.64, 28.57, 28.50, 28.43, 28.36, 28.29, 28.22, 28.15, 28.08, 28.01, 27.94, 27.87, 27.80, 27.73, 27.66, 27.59, 27.52, 27.45, 27.38, 27.31, 27.24, 27.17, 27.10, 27.03, 26.96, 26.89, 26.82, 26.75, 26.68, 26.61, 26.54, 26.47, 26.40, 26.33, 26.26, 26.19, 26.12, 26.05, 25.98, 25.91, 25.84, 25.77, 25.70, 25.63, 25.56, 25.49, 25.42, 25.35, 25.28, 25.21, 25.14, 25.07, 25.00, 24.93, 24.86, 24.79, 24.72, 24.65, 24.58, 24.51, 24.44, 24.37, 24.30, 24.23, 24.16, 24.09, 24.02, 23.95, 23.88, 23.81, 23.74, 23.67, 23.60, 23.53, 23.46, 23.39, 23.32, 23.25, 23.18, 23.11, 23.04, 22.97, 22.90, 22.83, 22.76, 22.69, 22.62, 22.55, 22.48, 22.41, 22.34, 22.27, 22.20, 22.13, 22.06, 21.99, 21.92, 21.85, 21.78, 21.71, 21.64, 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11.56, 11.49, 11.42, 11.35, 11.28, 11.21, 11.14, 11.07, 11.00, 10.93, 10.86, 10.79, 10.72, 10.65, 10.58, 10.51, 10.44, 10.37, 10.30, 10.23, 10.16, 10.09, 10.02, 9.95, 9.88, 9.81, 9.74, 9.67, 9.60, 9.53, 9.46, 9.39, 9.32, 9.25, 9.18, 9.11, 9.04, 8.97, 8.90, 8.83, 8.76, 8.69, 8.62, 8.55, 8.48, 8.41, 8.34, 8.27, 8.20, 8.13, 8.06, 7.99, 7.92, 7.85, 7.78, 7.71, 7.64, 7.57, 7.50, 7.43, 7.36, 7.29, 7.22, 7.15, 7.08, 7.01, 6.94, 6.87, 6.80, 6.73, 6.66, 6.59, 6.52, 6.45, 6.38, 6.31, 6.24, 6.17, 6.10, 6.03, 5.96, 5.89, 5.82, 5.75, 5.68, 5.61, 5.54, 5.47, 5.40, 5.33, 5.26, 5.19, 5.12, 5.05, 4.98, 4.91, 4.84, 4.77, 4.70, 4.63, 4.56, 4.49, 4.42, 4.35, 4.28, 4.21, 4.14, 4.07, 4.00, 3.93, 3.86, 3.79, 3.72, 3.65, 3.58, 3.51, 3.44, 3.37, 3.30, 3.23, 3.16, 3.09, 3.02, 2.95, 2.88, 2.81, 2.74, 2.67, 2.60, 2.53, 2.46, 2.39, 2.32, 2.25, 2.18, 2.11, 2.04, 1.97, 1.90, 1.83, 1.76, 1.69, 1.62, 1.55, 1.48, 1.41, 1.34, 1.27, 1.20, 1.13, 1.06, 1.09, 1.02, 1.05, 1.08, 1.11, 1.14, 1.17, 1.20, 1.23, 1.26, 1.29, 1.32, 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6.33, 6.36, 6.39, 6.42, 6.45, 6.48, 6.51, 6.54, 6.57, 6.60, 6.63, 6.66, 6.69, 6.72, 6.75, 6.78, 6.81, 6.84, 6.87, 6.90, 6.93, 6.96, 6.99, 7.02, 7.05, 7.08, 7.11, 7.14, 7.17, 7.20, 7.23, 7.26, 7.29, 7.32, 7.35, 7.38, 7.41, 7.44, 7.47, 7.50, 7.53, 7.56, 7.59, 7.62, 7.65, 7.68, 7.71, 7.74, 7.77, 7.80, 7.83, 7.86, 7.89, 7.92, 7.95, 7.98, 8.01, 8.04, 8.07, 8.10, 8.13, 8.16, 8.19, 8.22, 8.25, 8.28, 8.31, 8.34, 8.37, 8.40, 8.43, 8.46, 8.49, 8.52, 8.55, 8.58, 8.61, 8.64, 8.67, 8.70, 8.73, 8.76, 8.79, 8.82, 8.85, 8.88, 8.91, 8.94, 8.97, 9.00, 9.03, 9.06, 9.09, 9.12, 9.15, 9.18, 9.21, 9.24, 9.27, 9.30, 9.33, 9.36, 9.39, 9.42, 9.45, 9.48, 9.51, 9.54, 9.57, 9.60, 9.63, 9.66, 9.69, 9.72, 9.75, 9.78, 9.81, 9.84, 9.87, 9.90, 9.93, 9.96, 9.99, 10.02, 10.05, 10.08, 10.11, 10.14, 10.17, 10.20, 10.23, 10.26, 10.29, 10.32, 10.35, 10.38, 10.41, 10.44, 10.47, 10.50, 10.53, 10.56, 10.59, 10.62, 10.65, 10.68, 10.71, 10.74, 10.77, 10.80, 10.83, 10.86, 10.89, 10.92, 10.95, 10.98, 11.01, 11.04, 11.07, 11.10, 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15.42, 15.45, 15.48, 15.51, 15.54, 15.57, 15.60, 15.63, 15.66, 15.69, 15.72, 15.75, 15.78, 15.81, 15.84, 15.87, 15.90, 15.93, 15.96, 15.99, 16.02, 16.05, 16.08, 16.11, 16.14, 16.17, 16.20, 16.23, 16.26, 16.29, 16.32, 16.35, 16.38, 16.41, 16.44, 16.47, 16.50, 16.53, 16.56, 16.59, 16.62, 16.65, 16.68, 16.71, 16.74, 16.77, 16.80, 16.83, 16.86, 16.89, 16.92, 16.95, 16.98, 17.01, 17.04, 17.07, 17.10, 17.13, 17.16, 17.19, 17.22, 17.25, 17.28, 17.31, 17.34, 17.37, 17.40, 17.43, 17.46, 17.49, 17.52, 17.55, 17.58, 17.61, 17.64, 17.67, 17.70, 17.73, 17.76, 17.79, 17.82, 17.85, 17.88, 17.91, 17.94, 17.97, 18.00, 18.03, 18.06, 18.09, 18.12, 18.15, 18.18, 18.21, 18.24, 18.27, 18.30, 18.33, 18.36, 18.39, 18.42, 18.45, 18.48, 18.51, 18.54, 18.57, 18.60, 18.63, 18.66, 18.69, 18.72, 18.75, 18.78, 18.81, 18.84, 18.87, 18.90, 18.93, 18.96, 18.99, 19.02, 19.05, 19.08, 19.11, 19.14, 19.17, 19.20, 19.23, 19.26, 19.29, 19.32, 19.35, 19.38, 19.41, 19.44, 19.47, 19.50, 19.53, 19.56, 19.59, 19.62, 19.65, 19.68, 19.71, 19.74, 19.77, 19.80, 19.83, 19.86, 19.89, 19.92, 19.95, 19.98, 20.01, 20.04, 20.07, 20.10, 20.13, 20.16, 20.19, 20.22, 20.25, 20.28, 20.31, 20.34, 20.37, 20.40, 20.43, 20.46, 20.49, 20.52, 20.55, 20.58, 20.61, 20.64, 20.67, 20.70, 20.73, 20.76, 20.79, 20.82, 20.85, 20.88, 20.91, 20.94, 20.97, 21.00, 21.03, 21.06, 21.09, 21.12, 21.15, 21.18, 21.21, 21.24, 21.27, 21.30, 21.33, 21.36, 21.39, 21.42, 21.45, 21.48, 21.51, 21.54, 21.57, 21.60, 21.63, 21.66, 21.69, 21.72, 21.75, 21.78, 21.81, 21.84, 21.87, 21.90, 21.93, 21.96, 21.99, 22.02, 22.05, 22.08, 22.11, 22.14, 22.17, 22.20, 22.23, 22.26, 22.29, 22.32, 22.35, 22.38, 22.41, 22.44, 22.47, 22.50, 22.53, 22.56, 22.59, 22.62, 22.65, 22.68, 22.71, 22.74, 22.77, 22.80, 22.83, 22.86, 22.89, 22.92, 22.95, 22.98, 23.01, 23.04, 23.07, 23.10, 23.13, 23.16, 23.19, 23.22, 23.25, 23.28, 23.31, 23.34, 23.37, 23.40, 23.43, 23.46, 23.49, 23.52, 23.55, 23.58, 23.61, 23.64, 23.67, 23.70, 23.73, 23.76, 23.79, 23.82, 23.85, 23.88, 23.91, 23.94, 23.97, 24.00, 24.03, 24.06, 24.09, 24.12, 24.15, 24.18, 24.21, 24.24, 24.27, 24.30, 24.33, 24.36, 24.39, 24.42, 24.45, 24.48, 24.51, 24.54, 24.57, 24.60, 24.63, 24.66, 24.69, 24.72, 24.75, 24.78, 24.81, 24.84, 24.87, 24.90, 24.93, 24.96, 24.99, 25.02, 25.05, 25.08, 25.11, 25.14, 25.17, 25.20, 25.23, 25.26, 25.29, 25.32, 25.35, 25.38, 25.41, 25.44, 25.47, 25.50, 25.53, 25.56, 25.59, 25.62, 25.65, 25.68, 25.71, 25.74, 25.77, 25.80, 25.83, 25.86, 25.89, 25.92, 25.95, 25.98, 26.01, 26.04, 26.07, 26.10, 26.13, 26.16, 26.19, 26.22, 26.25, 26

acylthiazolidinethiones, using triethyl orthoformate. Purification by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant afforded the product as a yellow oil (90 mg, 68% yield): $[\alpha]_D^{25} = -16.2^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2975, 2882, 1702, 1455, 1371, 1278, 1221, 1169, 1058 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 4.70 (s, 1H, $J = 7.8$ Hz), 4.63 (m, 1H), 4.54 (m, 1H), 4.41 (td, 1H, $J = 11.7, 7.3$ Hz), 3.67 (m, 1H), 3.56 (m, 2H), 3.46 (m, 1H), 3.39 (td, 1H, $J = 11.7, 7.8$ Hz), 3.20 (m, 1H), 1.24 (d, 3H, $J = 6.8$ Hz), 1.20 (t, 3H, $J = 6.8$ Hz), 1.15 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.4, 177.0, 104.7, 63.2, 60.8, 56.4, 43.4, 29.0, 15.3; HRMS (ESI⁺): Exact mass calcd for $\text{C}_{11}\text{H}_{20}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$, 278.0947. Found 278.0948. Enantioselectivity determined by HPLC (Chiralcel ODH column, 2% *i*-PrOH/hexanes, 1.0 mL/min, 310 nm), $t_{\text{major}} = 9.9$ min, $t_{\text{minor}} = 10.6$ min; ee = 98%.

Double-stereodifferentiating Experiments using (S)- and (R)-1-(4-benzyl-2-thioxothiazolidin-3-yl)propan-1-one:

2(R),4'(S)-1-(4-benzyl-2-thioxothiazolidin-3-yl)-3,3-dimethoxymethyl propan-1-one:

Prepared from **5** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones to afford the product in 75% conversion as a 10:1 mixture of diastereomers as seen by ^1H NMR spectroscopy.

2(S),4'(R)-1-(4-benzyl-2-thioxothiazolidin-3-yl)-3,3-dimethoxymethyl propan-1-one:

Prepared from *ent*-**5** according to the general procedure for trimethyl orthoformate alkylation of *N*-acylthiazolidinethiones to afford the product in 10% conversion as a 5:1 mixture of diastereomers as seen by ^1H NMR spectroscopy. A pure sample was obtained by flash chromatography on silica gel using 30% EtOAc in hexanes as the eluant: $[\alpha]_D^{25} = -29.9^\circ$ ($c = 1.0$, CHCl_3); IR (film) 2934, 1698, 1455, 1364, 1342, 1257, 1164, 1057 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 7.36-7.25 (m, 5H), 5.43 (m, 1H), 5.20 (p, 1H, $J = 7.7$ Hz), 4.72 (d, 1H, $J = 8.1$ Hz), 3.37 (s, 3H), 3.34 (s, 3H), 3.31 (obs m, 1H), 3.18 (dd, 1H, $J = 13.2, 3.3$ Hz), 2.99 (dd, 1H, $J = 13.2, 10.6$ Hz), 2.86 (dd, 1H, $J = 11.3, 1.8$ Hz), 1.21 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 201.2, 175.4, 136.5, 129.3, 128.8, 127.1, 105.7, 68.5, 55.1, 52.2, 41.7, 37.1, 31.8; HRMS (ESI⁺): Exact mass calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$, 340.1041. Found 340.1038. Hydrolysis of a small portion to the corresponding carboxylic acid (LiOH in aqueous THF) confirmed the relative stereochemistry to be as shown.⁴

Product Elaboration:

(S)-3,3-dimethoxy-2-methylpropan-1-ol (7): To a stirred solution of **3a** (100 mg, 0.4 mmol) in Et_2O (4 mL) at 0°C was added solid LiBH_4 (26 mg, 1.2 mmol). After 10 min the yellow color had disappeared and the reaction was carefully quenched by the addition of water (5 mL). The mixture was diluted with 1.0 M NaOH (5 mL) and extracted with Et_2O (3

$\times$ 15 mL). The combined organic layers were washed with brine (20 mL) and dried (Na_2SO_4). Careful concentration at 200 mtorr afforded pure **7** as a clear colorless liquid (31 mg, 58%): $[\alpha]_D^{25} = -26.0$ ($c = 1.0$, CHCl_3), lit.⁵ $[\alpha]_D^{25} = -18.8$ ($c = 0.79$, CHCl_3); IR (film) 3446, 2936, 1457, 1384, 1109, 1052 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 4.21 (d, 1H, $J = 6.8$ Hz), 3.54 (br m, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 2.79 (br s, 1H), 2.01 (m, 1H), 0.89 (d, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 108.9, 65.0, 55.3, 52.9, 37.6, 12.1; HRMS (CI⁺): Exact mass calcd for $\text{C}_6\text{H}_{18}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$, 152.1287. Found 152.1294.

(4) Assigned by of comparison of the optical rotation to that of the acid derived by hydrolysis (LiOOH) of the corresponding oxazolidinone, which was prepared according to the procedure of Evans, see: Evans, D. A.; Urpi, F.; Somers, T. C.; Clark, J. S.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 8215-8216.

(5) Hosokawa, T.; Yamanaka, T.; Itotani, M.; Murahashi, S. *J. Org. Chem.* **1995**, *60*, 6159-6167.

(R)-N,3,3-trimethoxy-N,2-dimethylpropanamide (8): To a stirred solution of **3a** (100 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) was added $\text{Me}(\text{OMe})\text{NH}\cdot\text{HCl}$ (196 mg, 2.0 mmol), imidazole (137, 2.0 mmol) and Et_3N (279 μL , 2.0 mmol). After 2 h the yellow color had disappeared, and the reaction stirred at rt for 2 days. The solvent was removed in vacuo and the residue purified by flash chromatography on silica gel using 100% CH_2Cl_2 , increasing to 20% EtOAc in CH_2Cl_2 . Concentration in vacuo afforded the desired product as a clear colorless oil (70 mg, 92%): $[\alpha]_{\text{D}}^{25} = -31.7$ ($c = 0.75$, CHCl_3); IR (film) 2940, 1660, 1462, 1387, 1191, 1117, 1070 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 4.51 (d, 1H, $J = 8.4$ Hz), 3.71 (s, 3H), 3.38 (s, 3H), 3.376 (s, 3H), 3.25 (br m, 1H), 3.19 (s, 3H), 1.13 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) 106.5, 61.5, 56.1, 53.0, 38.6, 31.9, 13.5; HRMS (ES⁺): Exact mass calcd for $\text{C}_8\text{H}_{18}\text{NO}_4$ $[\text{M}+\text{H}]^+$, 192.1236. Found 192.1240.

(R)-Ethyl 5,5-dimethoxy-4-methyl-3-oxopentanoate (9): To a stirred solution of **3a** (100 mg, 0.4 mmol) in THF (1.0 mL) under an atmosphere of dry nitrogen was added ethyl malonate, K-salt (136 mg, 0.8 mmol) and anhydrous MgCl_2 (38 mg, 0.4 mmol). After 0.5 h imidazole (27 mg, 0.4 mmol) was added and the mixture stirred for 24 h. During this time the yellow color had faded. The reaction mixture was diluted with EtOAc (30 mL) and extracted with 1.0 M HCl (20 mL). The aqueous layer was extracted with EtOAc (15 mL) and the combined organic layers washed with saturated NaHCO_3 (10 mL) and brine (10 mL), and dried (Na_2SO_4). Concentration in vacuo followed by purification by flash chromatography on silica gel using 10% EtOAc in hexanes as the eluant afforded **9** (63 mg, 72%) as a 10:1 mixture of keto and enol tautomers: $[\alpha]_{\text{D}}^{25} = -91.3$ ($c = 1.0$, CHCl_3); IR (film) 2985, 2941, 1747, 1717, 1649, 1458, 1275 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) major tautomer: 4.32 (d, 1H, $J = 7.3$ Hz), 4.16 (q, 2H, $J = 7.0$ Hz), 4.50 (ABq, 2H, $J = 15.7$ Hz), 3.323 (s, 3H), 3.319 (s, 3H), 3.03 (p, 1H, $J = 7.0$ Hz), 1.25 (t, 3H, $J = 7.3$ Hz), 1.08 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) 204.2, 167.2, 106.1, 61.1, 55.8, 52.6, 50.0, 48.9, 14.0, 12.0; HRMS (ES⁺): Exact mass calcd for $\text{C}_{10}\text{H}_{18}\text{NO}_5$ $[\text{M}+\text{H}]^+$, 219.1232 Found 219.1235.

Stereochemical Proofs:

(R)-3,3-Dimethoxy-2-methylpropanoic acid: To a stirred solution of **3a** (100 mg, 0.4 mmol) in a 4:1 mixture of THF:water (2.0 mL) at 0 °C was added LiOH (19.1 mg, 0.8 mmol). After 10 min the yellow color had faded. The reaction mixture was acidified with 1.0 M HCl (10 mL) and extracted with EtOAc (2 $\times$ 20 mL). The combined organic layers were extracted with saturated aqueous NaHCO_3 (2 $\times$ 20 mL) and the combined aqueous layers acidified to pH 1 with concentrated HCl. Extraction of the aqueous layer with EtOAc (3 $\times$ 20 mL), and concentration in vacuo afforded the desired carboxylic acid (34 mg, 57%): $[\alpha]_{\text{D}}^{25} -16.0^\circ$ ($c = 0.5$, CHCl_3), compared to an authentic sample⁴ for (R) $[\alpha]_{\text{D}}^{25} = -19.4^\circ$ ($c = 0.5$, CHCl_3); IR (film) 2958, 1738, 1716, 1436, 1371, 1265, 1156, 1089 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.64 (s, 3H), 2.53–2.45 (m, 2H), 2.35–2.28 (m, 2H), 2.21 (dd, 1H, $J = 14.6$, 7.3 Hz), 2.11 (s, 3H), 0.95 (d, 3H, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 207.8, 172.9, 51.5, 49.9, 40.7, 30.3, 26.3, 20.0; HRMS (CI, NH_3) Exact mass calcd for $\text{C}_9\text{H}_{18}\text{O}_3\text{N}$ $[\text{M}+\text{NH}_4]^+$, 276.1288. Found 276.1287.

(R)-3,3-Dimethoxy-2-phenyl-1-(2-thioxothiazolidin-3-yl)propan-1-one (3h): X-ray Crystal Structure

3h

Table 1. Crystal data and structure refinement for **3h**.

Identification code	3h	
Empirical formula	C14 H17 N O3 S2	
Formula weight	311.41	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.5263(11) Å	a = 90°.
	b = 12.0867(11) Å	b = 90°.
	c = 16.312(2) Å	g = 90°.
Volume	1483.9(3) Å ³	
Z	4	
Density (calculated)	1.394 Mg/m ³	
Absorption coefficient	0.365 mm ⁻¹	
F(000)	656	
Crystal size	0.50 x 0.50 x 0.50 mm ³	
Theta range for data collection	2.10 to 25.00°.	
Index ranges	-6<=h<=8, -14<=k<=12, -18<=l<=19	
Reflections collected	7895	
Independent reflections	2597 [R(int) = 0.0219]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2597 / 0 / 183	
Goodness-of-fit on F ²	1.189	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0656	
R indices (all data)	R1 = 0.0287, wR2 = 0.0659	
Absolute structure parameter	0.02(7)	
Largest diff. peak and hole	0.175 and -0.143 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for **3h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-142(1)	771(1)	5146(1)	46(1)

S(2)	2960(1)	1199(1)	6147(1)	48(1)
O(1)	-1214(2)	3674(1)	7029(1)	37(1)
N(1)	-350(2)	2164(1)	6335(1)	29(1)
C(4)	-80(3)	2981(2)	6950(1)	28(1)
C(5)	1506(3)	2920(2)	7524(1)	27(1)
C(1)	846(3)	1456(2)	5965(1)	33(1)
C(12)	-272(4)	1380(2)	9756(1)	48(1)
C(9)	891(3)	2397(2)	8324(1)	28(1)
C(13)	786(3)	807(2)	9215(1)	45(1)
C(10)	-181(3)	2963(2)	8872(1)	36(1)
C(11)	-745(3)	2459(2)	9589(1)	45(1)
C(14)	1360(3)	1308(2)	8497(1)	35(1)
C(3)	-2071(3)	2269(2)	5896(1)	41(1)
C(2)	-2354(3)	1228(2)	5408(1)	45(1)
O(3)	3578(2)	4164(1)	8221(1)	33(1)
O(2)	2824(2)	4422(1)	6846(1)	35(1)
C(8)	5121(3)	3499(2)	8060(2)	47(1)
C(6)	2240(3)	4096(2)	7628(1)	28(1)
C(7)	3395(3)	5550(2)	6826(2)	43(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **3h**.

S(1)-C(1)	1.738(2)
S(1)-C(2)	1.805(3)
S(2)-C(1)	1.648(2)
O(1)-C(4)	1.203(2)
N(1)-C(1)	1.382(3)
N(1)-C(4)	1.422(2)
N(1)-C(3)	1.486(3)
C(4)-C(5)	1.519(3)
C(5)-C(9)	1.523(3)
C(5)-C(6)	1.534(3)
C(5)-H(5)	1.0000
C(12)-C(13)	1.377(3)
C(12)-C(11)	1.378(4)
C(12)-H(12)	0.9500
C(9)-C(10)	1.385(3)
C(9)-C(14)	1.390(3)

C(13)-C(14)	1.388(3)
C(13)-H(13)	0.9500
C(10)-C(11)	1.385(3)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(14)-H(14)	0.9500
C(3)-C(2)	1.504(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
O(3)-C(6)	1.400(2)
O(3)-C(8)	1.436(3)
O(2)-C(6)	1.405(2)
O(2)-C(7)	1.430(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(6)-H(6)	1.0000
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800

C(1)-S(1)-C(2)	93.84(10)
C(1)-N(1)-C(4)	130.22(18)
C(1)-N(1)-C(3)	114.19(16)
C(4)-N(1)-C(3)	113.92(16)
O(1)-C(4)-N(1)	117.21(18)
O(1)-C(4)-C(5)	121.72(17)
N(1)-C(4)-C(5)	120.89(17)
C(4)-C(5)-C(9)	108.06(15)
C(4)-C(5)-C(6)	107.80(15)
C(9)-C(5)-C(6)	113.60(16)
C(4)-C(5)-H(5)	109.1
C(9)-C(5)-H(5)	109.1
C(6)-C(5)-H(5)	109.1
N(1)-C(1)-S(2)	131.79(16)
N(1)-C(1)-S(1)	110.63(15)

S(2)-C(1)-S(1)	117.55(13)
C(13)-C(12)-C(11)	119.9(2)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(10)-C(9)-C(14)	119.01(19)
C(10)-C(9)-C(5)	121.63(18)
C(14)-C(9)-C(5)	119.32(18)
C(12)-C(13)-C(14)	120.1(2)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(11)-C(10)-C(9)	120.4(2)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(12)-C(11)-C(10)	120.3(2)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(13)-C(14)-C(9)	120.3(2)
C(13)-C(14)-H(14)	119.8
C(9)-C(14)-H(14)	119.8
N(1)-C(3)-C(2)	107.90(18)
N(1)-C(3)-H(3A)	110.1
C(2)-C(3)-H(3A)	110.1
N(1)-C(3)-H(3B)	110.1
C(2)-C(3)-H(3B)	110.1
H(3A)-C(3)-H(3B)	108.4
C(3)-C(2)-S(1)	104.51(16)
C(3)-C(2)-H(2A)	110.9
S(1)-C(2)-H(2A)	110.9
C(3)-C(2)-H(2B)	110.9
S(1)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	108.9
C(6)-O(3)-C(8)	115.02(15)
C(6)-O(2)-C(7)	112.52(15)
O(3)-C(8)-H(8A)	109.5
O(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
O(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5

H(8B)-C(8)-H(8C)	109.5
O(3)-C(6)-O(2)	112.67(16)
O(3)-C(6)-C(5)	112.91(15)
O(2)-C(6)-C(5)	105.85(15)
O(3)-C(6)-H(6)	108.4
O(2)-C(6)-H(6)	108.4
C(5)-C(6)-H(6)	108.4
O(2)-C(7)-H(7A)	109.5
O(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
O(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3h**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	57(1)	43(1)	37(1)	-12(1)	-7(1)	-5(1)
S(2)	43(1)	60(1)	40(1)	-17(1)	-4(1)	18(1)
O(1)	30(1)	39(1)	42(1)	-5(1)	-4(1)	8(1)
N(1)	29(1)	31(1)	28(1)	0(1)	-2(1)	-1(1)
C(4)	29(1)	28(1)	27(1)	2(1)	2(1)	-4(1)
C(5)	24(1)	29(1)	26(1)	-3(1)	0(1)	3(1)
C(1)	43(1)	29(1)	27(1)	3(1)	1(1)	-3(1)
C(12)	64(2)	51(1)	31(1)	6(1)	3(1)	-23(1)
C(9)	26(1)	30(1)	27(1)	-1(1)	-4(1)	-5(1)
C(13)	62(2)	34(1)	40(1)	8(1)	-9(1)	-9(1)
C(10)	40(1)	34(1)	34(1)	-1(1)	2(1)	-1(1)
C(11)	51(2)	52(1)	33(1)	-9(1)	10(1)	-9(1)
C(14)	40(1)	31(1)	34(1)	-1(1)	-4(1)	-2(1)
C(3)	33(1)	51(1)	37(1)	0(1)	-10(1)	-3(1)
C(2)	46(1)	47(1)	43(1)	2(1)	-11(1)	-13(1)
O(3)	27(1)	38(1)	33(1)	-7(1)	-2(1)	-2(1)
O(2)	39(1)	33(1)	31(1)	1(1)	3(1)	-7(1)

C(8)	30(1)	55(1)	55(1)	-12(1)	-10(1)	4(1)
C(6)	27(1)	29(1)	29(1)	-1(1)	3(1)	0(1)
C(7)	44(1)	38(1)	46(1)	6(1)	3(1)	-12(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3h**.

	x	y	z	U(eq)
H(5)	2442	2442	7271	32
H(12)	-676	1033	10244	58
H(13)	1125	66	9333	54
H(10)	-531	3701	8756	43
H(11)	-1461	2858	9967	54
H(14)	2076	906	8121	42
H(3A)	-2044	2919	5526	49
H(3B)	-3051	2370	6293	49
H(2A)	-3059	1381	4908	54
H(2B)	-2979	663	5739	54
H(8A)	4865	2725	8196	70
H(8B)	6115	3762	8396	70
H(8C)	5437	3556	7479	70
H(6)	1241	4593	7796	34
H(7A)	2435	6029	7023	64
H(7B)	3703	5755	6262	64
H(7C)	4440	5640	7178	64

Table 6. Torsion angles [$^\circ$] for **3h**.

C(1)-N(1)-C(4)-O(1)	161.87(19)
C(3)-N(1)-C(4)-O(1)	-2.3(3)
C(1)-N(1)-C(4)-C(5)	-22.9(3)
C(3)-N(1)-C(4)-C(5)	172.92(17)
O(1)-C(4)-C(5)-C(9)	77.1(2)
N(1)-C(4)-C(5)-C(9)	-97.9(2)
O(1)-C(4)-C(5)-C(6)	-46.1(2)
N(1)-C(4)-C(5)-C(6)	138.90(17)

C(4)-N(1)-C(1)-S(2)	6.8(3)
C(3)-N(1)-C(1)-S(2)	170.99(17)
C(4)-N(1)-C(1)-S(1)	-171.09(15)
C(3)-N(1)-C(1)-S(1)	-6.9(2)
C(2)-S(1)-C(1)-N(1)	-10.67(16)
C(2)-S(1)-C(1)-S(2)	171.09(13)
C(4)-C(5)-C(9)-C(10)	-72.3(2)
C(6)-C(5)-C(9)-C(10)	47.3(2)
C(4)-C(5)-C(9)-C(14)	105.3(2)
C(6)-C(5)-C(9)-C(14)	-135.19(19)
C(11)-C(12)-C(13)-C(14)	-0.8(4)
C(14)-C(9)-C(10)-C(11)	1.4(3)
C(5)-C(9)-C(10)-C(11)	178.88(19)
C(13)-C(12)-C(11)-C(10)	1.0(4)
C(9)-C(10)-C(11)-C(12)	-1.3(3)
C(12)-C(13)-C(14)-C(9)	0.9(3)
C(10)-C(9)-C(14)-C(13)	-1.2(3)
C(5)-C(9)-C(14)-C(13)	-178.76(19)
C(1)-N(1)-C(3)-C(2)	25.5(2)
C(4)-N(1)-C(3)-C(2)	-167.68(17)
N(1)-C(3)-C(2)-S(1)	-30.6(2)
C(1)-S(1)-C(2)-C(3)	24.04(16)
C(8)-O(3)-C(6)-O(2)	-59.4(2)
C(8)-O(3)-C(6)-C(5)	60.4(2)
C(7)-O(2)-C(6)-O(3)	-61.7(2)
C(7)-O(2)-C(6)-C(5)	174.40(17)
C(4)-C(5)-C(6)-O(3)	172.90(16)
C(9)-C(5)-C(6)-O(3)	53.2(2)
C(4)-C(5)-C(6)-O(2)	-63.39(19)
C(9)-C(5)-C(6)-O(2)	176.91(16)

Symmetry transformations used to generate equivalent atoms:

[Ni(δ -BINAP)]Cl₂: To a stirred suspension of (*S*)-BINAP (1.0 g, 1.61 mmol) in acetonitrile (20 mL) was added anhydrous NiCl₂ (208 mg, 1.61 mmol) and water (150 μ L). The resulting mixture was heated at reflux for 16 h after which time a deep purple solution had formed. The reaction mixture was cooled to rt, filtered through a pad of dried celite and the solvent removed *in vacuo*. Drying overnight at 100 mtorr afforded a purple-black solid (1.2 g, 100%) which was stored in a dry box and could be used directly

without further purification. A small portion was crystallized for X-ray analysis by layering of diethyl ether onto a solution of the complex in CH_2Cl_2 : mp ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$) 250-255 °C; IR (film) 3054, 1501, 1480, 1436, 1312, 1098, 734, 696 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) 10.90 (s, 4H), 9.59 (s, 2H), 8.72 (d, 2H, $J = 8.1$ Hz), 8.64 (br s, 4H), 8.10 (t, 2H, $J = 7.3$ Hz), 7.10 (br, 8H), 6.31 (t, 2H, $J = 6.96$ Hz), 6.02 (t, 2H, 7.0 Hz), 4.62 (d, 2H, $J = 8.4$ Hz), 4.52 (t, 2H, $J = 7.3$ Hz), 4.38 (br s, 2H).

X-Ray Crystal Structure: $[\text{Ni}((S)\text{-BINAP})]\text{Cl}_2$ (X-ray)

Table 2. Crystal data and structure refinement for $[\text{Ni}((S)\text{-BINAP})]\text{Cl}_2$.

Identification code	$[\text{Ni}((S)\text{-BINAP})]\text{Cl}_2$	
Empirical formula	$\text{C}_{44} \text{H}_{32} \text{Cl}_2 \text{Ni P}_2$	
Formula weight	752.25	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4(3)2(1)2$	
Unit cell dimensions	$a = 11.647(3)$ Å	$a = 90^\circ$.
	$b = 11.647(3)$ Å	$b = 90^\circ$.
	$c = 26.381(8)$ Å	$g = 90^\circ$.
Volume	$3578.5(15)$ Å ³	
Z	4	
Density (calculated)	1.396 Mg/m^3	
Absorption coefficient	0.813 mm^{-1}	
$F(000)$	1552	
Crystal size	$0.2 \times 0.2 \times 0.3 \text{ mm}^3$	
Theta range for data collection	1.91 to 27.74° .	
Index ranges	$-15 \leq h \leq 14$, $-15 \leq k \leq 14$, $-12 \leq l \leq 34$	
Reflections collected	22367	

Independent reflections	3907 [R(int) = 0.0539]
Completeness to theta = 27.74°	94.1 %
Absorption correction	Empirical
Max. and min. transmission	1.000000 and 0.639095
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3907 / 0 / 222
Goodness-of-fit on F ²	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0686
R indices (all data)	R1 = 0.0502, wR2 = 0.0732
Absolute structure parameter	-0.009(13)
Largest diff. peak and hole	0.236 and -0.239 e.Å ⁻³

Table 8. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³)
For **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	5278(1)	5278(1)	0	30(1)
P(1)	3673(1)	5075(1)	407(1)	26(1)
Cl(1)	7160(1)	5177(1)	-70(1)	52(1)
C(1)	2343(2)	6133(2)	-332(1)	40(1)
C(2)	3456(2)	3582(2)	606(1)	24(1)
C(3)	2801(2)	6395(2)	1216(1)	42(1)
C(4)	3760(2)	5869(2)	1001(1)	35(1)
C(5)	2337(2)	5502(2)	114(1)	31(1)
C(6)	3802(2)	3236(2)	1099(1)	35(1)
C(7)	1291(2)	5156(2)	320(1)	38(1)
C(8)	3004(2)	1574(2)	416(1)	33(1)
C(9)	3072(2)	2748(2)	266(1)	25(1)
C(10)	2897(3)	7007(2)	1667(1)	59(1)
C(11)	3368(2)	1256(2)	915(1)	44(1)
C(12)	3751(3)	2115(2)	1245(1)	44(1)
C(13)	4817(3)	5971(3)	1243(1)	57(1)
C(14)	283(3)	6034(3)	-365(1)	58(1)
C(15)	1307(3)	6396(3)	-571(1)	58(1)
C(16)	272(2)	5435(2)	83(1)	50(1)
C(17)	3352(3)	80(3)	1052(1)	67(1)
C(18)	2662(3)	-434(2)	234(1)	66(1)
C(19)	4885(4)	6590(3)	1699(1)	78(1)

C(20)	3026(4)	-737(3)	718(1)	78(1)
C(22)	2646(3)	685(2)	85(1)	45(1)
C(25)	3921(4)	7090(3)	1904(1)	72(1)

Table 9. Bond lengths [Å] and angles [°] for [Ni((*S*)-BINAP)]Cl₂.

Ni(1)-P(1)#1	2.1697(7)
Ni(1)-P(1)	2.1697(7)
Ni(1)-Cl(1)#1	2.2022(8)
Ni(1)-Cl(1)	2.2022(8)
P(1)-C(5)	1.807(2)
P(1)-C(4)	1.822(2)
P(1)-C(2)	1.834(2)
C(1)-C(5)	1.388(3)
C(1)-C(15)	1.395(4)
C(2)-C(9)	1.394(3)
C(2)-C(6)	1.420(3)
C(3)-C(10)	1.390(3)
C(3)-C(4)	1.395(4)
C(4)-C(13)	1.391(4)
C(5)-C(7)	1.393(3)
C(6)-C(12)	1.363(3)
C(7)-C(16)	1.380(3)
C(8)-C(22)	1.417(3)
C(8)-C(9)	1.426(3)
C(8)-C(11)	1.433(3)
C(9)-C(9)#1	1.502(4)
C(10)-C(25)	1.350(5)
C(11)-C(12)	1.398(4)
C(11)-C(17)	1.417(4)
C(13)-C(19)	1.406(4)
C(14)-C(16)	1.371(4)
C(14)-C(15)	1.377(4)
C(17)-C(20)	1.353(4)
C(18)-C(22)	1.362(4)
C(18)-C(20)	1.391(5)
C(19)-C(25)	1.374(5)

P(1)#1-Ni(1)-P(1)	93.28(3)
P(1)#1-Ni(1)-Cl(1)#1	153.27(3)
P(1)-Ni(1)-Cl(1)#1	91.20(2)
P(1)#1-Ni(1)-Cl(1)	91.19(2)
P(1)-Ni(1)-Cl(1)	153.27(3)
Cl(1)#1-Ni(1)-Cl(1)	96.55(4)
C(5)-P(1)-C(4)	106.04(11)
C(5)-P(1)-C(2)	105.34(10)
C(4)-P(1)-C(2)	104.06(10)
C(5)-P(1)-Ni(1)	120.04(8)
C(4)-P(1)-Ni(1)	108.81(9)
C(2)-P(1)-Ni(1)	111.31(7)
C(5)-C(1)-C(15)	119.6(3)
C(9)-C(2)-C(6)	118.8(2)
C(9)-C(2)-P(1)	121.39(15)
C(6)-C(2)-P(1)	119.42(17)
C(10)-C(3)-C(4)	120.5(3)
C(13)-C(4)-C(3)	119.0(2)
C(13)-C(4)-P(1)	119.2(2)
C(3)-C(4)-P(1)	121.9(2)
C(1)-C(5)-C(7)	119.3(2)
C(1)-C(5)-P(1)	120.24(19)
C(7)-C(5)-P(1)	120.43(17)
C(12)-C(6)-C(2)	121.2(2)
C(16)-C(7)-C(5)	120.4(2)
C(22)-C(8)-C(9)	123.1(2)
C(22)-C(8)-C(11)	117.7(2)
C(9)-C(8)-C(11)	119.1(2)
C(2)-C(9)-C(8)	120.51(19)
C(2)-C(9)-C(9)#1	120.43(16)
C(8)-C(9)-C(9)#1	119.05(17)
C(25)-C(10)-C(3)	120.3(3)
C(12)-C(11)-C(17)	122.5(2)
C(12)-C(11)-C(8)	118.8(2)
C(17)-C(11)-C(8)	118.7(3)
C(6)-C(12)-C(11)	121.6(2)
C(4)-C(13)-C(19)	119.1(3)
C(16)-C(14)-C(15)	120.2(3)

C(14)-C(15)-C(1)	120.3(3)
C(14)-C(16)-C(7)	120.2(3)
C(20)-C(17)-C(11)	121.1(3)
C(22)-C(18)-C(20)	120.8(3)
C(25)-C(19)-C(13)	120.5(3)
C(17)-C(20)-C(18)	120.4(3)
C(18)-C(22)-C(8)	121.2(3)
C(10)-C(25)-C(19)	120.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 y,x,-z

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ni}((S)\text{-BINAP})]\text{Cl}_2$. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<hr/>						
Ni(1)	26(1)	26(1)	38(1)	-4(1)	4(1)	-5(1)
P(1)	25(1)	23(1)	30(1)	-2(1)	1(1)	0(1)
Cl(1)	26(1)	58(1)	71(1)	-10(1)	6(1)	-10(1)
C(1)	45(2)	29(1)	46(1)	6(1)	0(1)	3(1)
C(2)	21(1)	26(1)	26(1)	1(1)	2(1)	3(1)
C(3)	58(2)	25(1)	43(1)	-4(1)	16(1)	-5(1)
C(4)	44(2)	27(1)	34(1)	-5(1)	5(1)	-10(1)
C(5)	32(1)	24(1)	36(1)	-1(1)	1(1)	7(1)
C(6)	42(2)	36(1)	26(1)	-2(1)	-7(1)	6(1)
C(7)	32(1)	38(1)	44(1)	1(1)	4(1)	9(1)
C(8)	37(2)	27(1)	35(1)	0(1)	9(1)	-3(1)
C(9)	21(1)	26(1)	29(1)	0(1)	3(1)	3(1)
C(10)	94(3)	34(2)	49(2)	-11(1)	32(2)	-17(2)
C(11)	61(2)	31(1)	40(1)	10(1)	9(1)	8(1)
C(12)	60(2)	43(2)	30(1)	8(1)	-6(1)	13(2)
C(13)	55(2)	67(2)	49(2)	-16(1)	-1(2)	-13(2)
C(14)	46(2)	59(2)	71(2)	4(2)	-11(2)	26(2)
C(15)	71(2)	47(2)	56(2)	17(1)	-11(2)	13(2)
C(16)	30(1)	54(2)	66(2)	-3(2)	2(1)	14(1)
C(17)	111(3)	38(2)	50(2)	16(2)	11(2)	8(2)
C(18)	109(3)	27(2)	61(2)	-4(1)	24(2)	-18(2)
C(19)	90(3)	92(3)	54(2)	-19(2)	-17(2)	-43(2)

C(20)	137(4)	26(2)	70(2)	13(2)	31(2)	-1(2)
C(22)	61(2)	32(1)	42(1)	-2(1)	10(1)	-11(1)
C(25)	113(3)	61(2)	42(2)	-21(2)	20(2)	-41(2)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $[\text{Ni}((S)\text{-BINAP})]\text{Cl}_2$.

	x	y	z	U(eq)
H(1A)	3042	6383	-473	48
H(3A)	2083	6336	1055	51
H(6A)	4072	3791	1328	41
H(7A)	1279	4730	623	46
H(10A)	2247	7365	1807	71
H(12A)	3979	1914	1575	53
H(13A)	5476	5630	1103	69
H(14A)	-411	6197	-531	70
H(15A)	1308	6821	-873	70
H(16A)	-430	5214	228	60
H(17A)	3571	-136	1382	80
H(18A)	2423	-1009	7	79
H(19A)	5595	6663	1866	94
H(20A)	3047	-1515	812	94
H(22A)	2394	872	-244	54
H(25A)	3976	7493	2212	86