Supporting information for:

Enantioselective Addition of a Chiral Thiazolidinethione-derived Titanium Enolate to Acetals

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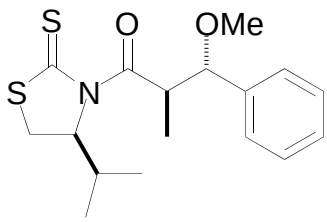
Characterisation data of compounds **2a-g, i-j.**

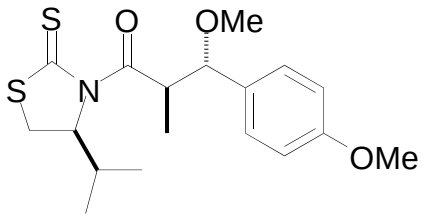
(4*S*)-4-Isopropyl-*N*-[(2*R*,3*S*)-3-methoxy-2-methyl-3-phenylpropanoyl]-1,3-thiazolidine-2-thione.



2a

Yellow solid; m.p. 82.1–83.0 °C; R_f (CH_2Cl_2) = 0.60; HPLC (hexanes/EtOAc 97:3) t_R = 17.1 min; $[\alpha]_D$ = +120.2 (*c* = 1.96 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.22 (m, 5H; ArH), 5.36 (ddd, *J* = 8.9 Hz, *J* = 5.5 Hz, *J* = 2.1 Hz, 1H; NCH), 5.26 (dq, *J* = 9.8 Hz, *J* = 7.0 Hz, 1H; COC*H*CH_3), 4.35 (d, *J* = 9.8 Hz, 1H; C*H*OCH_3), 3.46 (dd, *J* = 11.5 Hz, *J* = 8.9 Hz, 1H; SC$H_a$$H_b$), 3.08 (s, 3H; OCH_3), 3.01 (dd, *J* = 11.5 Hz, *J* = 2.1 Hz; SCH_aH_b), 2.40 (heptd, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H; C*H*$(CH_3)_2$), 1.11 (d, *J* = 8.0 Hz, 3H; C$H_3$$CHCH_3$), 1.03(d, *J* = 8.0 Hz, 3H; CH_3CHCH_3), 0.86 (d, *J* = 7.0 Hz, 3H; $COCHCH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.6, 177.7, 139.1, 128.3, 128.2, 128.1, 87.7, 71.9, 56.4, 45.1, 30.4, 28.8, 19.0, 17.0, 14.3; IR (KBr): ν = 2927, 1670, 1154 cm^{-1}; HRMS (+FAB): calcd. for $[M+H]^+$ $C_{17}H_{24}NO_2S_2$ 338.1249, found 338.1251.

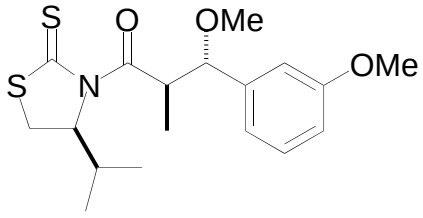
(4*S*)-4-Isopropyl-*N*-[(2*R*,3*S*)-3-methoxy-3-(*p*-methoxyphenyl)-2-methylpropanoyl]-1,3-thiazolidine-2-thione.



2b

Yellow oil; R_f (CH_2Cl_2) = 0.70; HPLC (hexanes/EtOAc 97:3) t_R = 21.1 min; $[\alpha]_D$ = +79.3 (*c* = 1.2 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.7 Hz, 2H; ArH), 6.89 (d, *J* = 8.7 Hz, 2H; ArH), 5.37 (ddd, *J* = 8.5 Hz, *J* = 5.5 Hz, *J* = 2.1 Hz, 1H; NCH), 5.24 (dq, *J* = 10.0 Hz, *J* = 7.0 Hz, 1H; COC*H*CH_3), 4.30 (d, *J* = 10.0 Hz, 1H; C*H*OCH_3), 3.82 (s, 3H; OCH_3), 3.45 (dd, *J* = 11.3 Hz, *J* = 8.5 Hz, 1H; SC$H_a$$H_b$), 3.06 (s, 3H; OCH_3), 3.00 (dd, *J* = 11.3 Hz, *J* = 2.1 Hz, 1H; SC$H_a$$H_b$), 2.45–2.30 (m, 1H; C*H*$(CH_3)_2$), 1.10 (d, *J* = 6.7 Hz, 3H; C$H_3$$CHCH_3$), 1.03 (d, *J* = 7.0 Hz, 3H; $CH_3$$CHCH_3$), 0.85 (d, *J* = 7.0 Hz, 3H; $COCHCH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.6, 177.8, 159.5, 131.2, 129.3, 113.8, 87.3, 71.9, 56.2, 55.2, 45.1, 30.4, 28.8, 19.1, 17.0, 14.4; IR (film): ν = 2964, 1698, 1513, 1252, 1156 cm^{-1}; HRMS (+FAB): calcd. for $[M+H]^+$ $C_{18}H_{26}NO_3S_2$ 368.1354, found 368.1360.

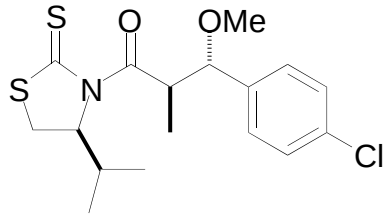
(4*S*)-4-Isopropyl-*N*-[(2*R*,3*S*)-3-methoxy-3-(*m*-methoxyphenyl)-2-methylpropanoyl]-1,3-thiazolidine-2-thione.



2c

Yellow oil; R_f (CH_2Cl_2) = 0.80; HPLC (hexanes/EtOAc 97:3) t_R = 21.2 min; $[\alpha]_D$ = +118.7 (*c* = 1.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.23 (m, 1H; ArH), 6.95–6.90 (m, 2H; ArH), 6.87–6.83 (m, 1H; ArH), *5*.36 (ddd, *J* = 8.7 Hz, *J* = 5.5 Hz, *J* = 2.0 Hz, 1H; NCH), 5.27 (dq, *J* = 9.8 Hz, *J* = 6.8 Hz, 1H; COC*H*CH_3), 4.32 (d, *J* = 9.8 Hz, 1H; C*H*OCH_3), 3.82 (s, 3H; OCH_3), 3.46 (dd, *J* = 11.4 Hz, *J* = 8.7 Hz, 1H; SC$H_a$$H_b$), 3.09 (s, 3H; OCH_3), 3.00 (dd, *J* = 11.4 Hz, *J* = 2.0 Hz, 1H; $SCH_a$$H_b$), 2.45–2.30 (m, 1H; C*H*$(CH_3)_2$), 1.11 (d, *J* = 6.7 Hz, 3H; C$H_3$$CHCH_3$), 1.03 (d, *J* = 7.0 Hz, 3H; CH_3CHCH_3), 0.87 (d, *J* = 6.8 Hz, 3H; $COCHCH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.6, 177.6, 159.8, 140.8, 129.3, 120.6, 113.8, 113.1, 87.6, 71.9, 56.5, 55.2, 45.0, 30.4, 28.9, 19.0, 17.0, 14.4; IR (film): ν = 2966, 1698, 1372, 1258, 1156 cm^{-1}; HRMS (+FAB): calcd. for $[M+H]^+$ $C_{18}H_{26}NO_3S_2$ 368.1354, found 368.1338.

(4*S*)-*N*-[(2*R*,3*S*)-3-(*p*-Chlorophenyl)-3-methoxy-2-methylpropanoyl]-4-isopropyl-1,3-thiazolidine-2-thione.

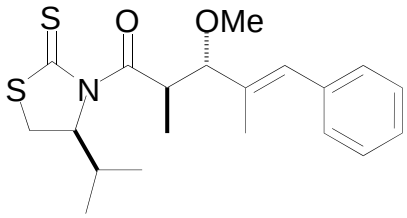


2d

Yellow solid; m.p. 66.0–68.0 °C; R_f (CH_2Cl_2/hexanes 1:1) = 0.35; HPLC (hexanes/EtOAc 97:3) t_R = 18.0 min; $[\alpha]_D$ = +95.7 (*c* = 2.4 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.25 (m, 4H; ArH), 5.35 (ddd, *J* = 8.9 Hz, *J* = 5.8 Hz, *J* = 1.8 Hz, 1H; NCH), 5.25 (dq, *J* = 9.8 Hz, *J* = 7.0 Hz, 1H; COC*H*CH_3), 4.34 (d, *J* = 9.8 Hz, 1H; C*H*OCH_3), 3.46 (dd, *J* = 11.6 Hz, *J* = 8.9 Hz, 1H; SC$H_a$$H_b$), 3.07 (s, 3H; OCH_3), 3.01 (dd, *J* = 11.6 Hz, *J* = 1.8 Hz, 1H; $SCH_a$$H_b$), 2.45–2.30 (m, 1H; C*H*$(CH_3)_2$), 1.10 (d, *J* = 6.7 Hz, 3H; C$H_3$$CHCH_3$), 1.02 (d, *J* = 7.0 Hz, 3H; CH_3CHCH_3), 0.85 (d, *J* = 7.0 Hz, 3H; $COCHCH_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.7, 177.2, 137.8, 134.0, 129.4, 128.6, 86.9, 71.9, 56.5, 44.9, 30.4, 28.9, 19.0, 17.0, 14.2; IR (KBr): ν = 2966, 1698, 1374, 1156,

1092 cm^{-1}; Anal.: calcd. for $C_{17}H_{22}ClNO_2S_2$ C 54.90%, H 5.97%, N 3.77%, found C 55.10%, H 6.01%, N 3.80%.

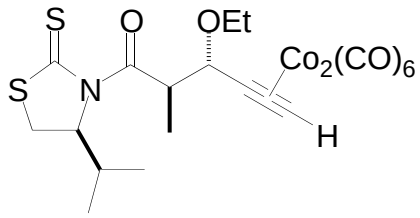
(4*S*)-*N*-[(2*R*,3*S*,4*E*)-2,4-Dimethyl-3-methoxy-5-phenyl-4-pentenoyl]-4-isopropyl-1,3-thiazolidine-2-thione.



2e

Yellow oil; R_f (CH_2Cl_2/hexanes 1:1) = 0.40; HPLC (hexanes/EtOAc 97:3) t_R = 15.8 min; $[\alpha]_D$ = +175.5 (*c* = 1.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.15 (m, 5H; ArH), 6.52 (br s, 1H; C=CHPh), 5.34 (ddd, *J* = 8.9 Hz, *J* = 5.5 Hz, *J* = 2.1 Hz, 1H; NCH), 5.21 (dq, *J* = 9.9 Hz, *J* = 7.0 Hz, 1H; COC*H*CH_3), 3.93 (d, *J* = 9.9 Hz, 1H; C*H*OCH_3), 3.44 (dd, *J* = 11.3 Hz, *J* = 8.9 Hz, 1H; SC$H_a$$H_b$), 3.17 (s, 3H; OCH_3), 2.98 (dd, *J* = 11.3 Hz, *J* = 2.1 Hz, 1H; SC$H_a$$H_b$), 2.45–2.30 (m, 1H; C*H*$(CH_3)_2$), 1.82 (d, *J* = 1.2 Hz, 3H; C(CH_3)=CHPh), 1.08 (d, *J* = 6.7 Hz, 3H; C$H_3$$CHCH_3$), 1.03 (d, *J* = 7.0 Hz, 3H; COCHCH_3), 1.01 (d, *J* = 7.0 Hz, 3H; CH_3CHCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.6, 177.8, 137.0, 135.0, 131.2, 129.0, 128.1, 126.7, 91.8, 71.9, 55.9, 41.3, 30.4, 28.7, 19.0, 16.9, 14.3, 12.1; IR (film): ν = 2940, 1690, 1440, 1365, 1240, 1150 cm^{-1}; HRMS (+FAB): calcd. for $[M+H]^+$ $C_{20}H_{28}NO_2S_2$ 378.1561, found 378.1544.

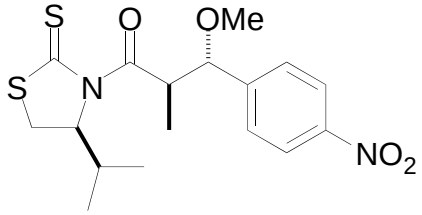
(4*S*)-*N*-[(2*R*,3*S*)-Hexacarbonyl{μ-η^4-(3-ethoxy-2-methyl-4-pentynoyl) dicobalt (*Co*-*Co*)]-4-isopropyl-1,3-thiazolidine-2-thione.



2f

Red oil; R_f (hexanes/EtOAc 9:1) = 0.35; HPLC (hexanes/EtOAc 93:7) t_R = 7.2 min; $[\alpha]_D$ = +849.0 (*c* = 0.01 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.05 (br s, 1H; C[$Co_2(CO)_6$]H), 5.35–5.25 (m, 1H; NCH), 5.08–4.98 (m, 1H; COC*H*CH_3), 4.67 (d, *J* = 9.6 Hz, 1H; CHOEt), 3.82 (m, 1H; OC*H*$_a$H$_b$$CH_3$), 3.62 (m, 1H; OCH$_a$*H*$_b$$CH_3$), 3.47 (dd, *J* = 11.5 Hz, *J* = 8.5 Hz, 1H; SC*H*$_a$H$_b$), 2.98 (d, *J* = 11.5 Hz, 1H; SCH$_a$*H*$_b$), 2.42–2.30 (m, 1H; CH_3C*H*CH_3), 1.22 (d, *J* = 6.7 Hz, 3H; C*H*$_3$CHCH_3)), 1.10 (t, *J* = 6.5 Hz, 3H; OCH_2C*H*$_3$), 1.02 (d, *J* = 6.9 Hz, 3H; CH_3CHC*H*$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.4, 199.5 (broad peak), 175.7, 93.4, 82.3, 73.0, 71.6, 66.6, 45.7, 30.6, 29.0, 19.1, 17.3, 14.9, 14.7; IR (film): ν = 2920, 2070, 2030, 2000, 1680, 1340, 1240, 1140 cm^{-1}.

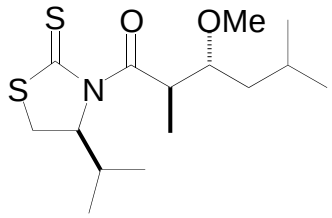
(4*S*)-4-Isopropyl-*N*-[(2*R*,3*S*)-3-methoxy-2-methyl-3-(*p*-nitrophenyl) propanoyl]-1,3-thiazolidine-2-thione.



2g

Yellow solid; m.p. 97.0–98.0 °C; R_f (CH_2Cl_2/hexanes 7:3) = 0.70; HPLC (hexanes/EtOAc 97:3) t_R = 60.0 min; $[\alpha]_D$ = +109.6 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.7 Hz, 2H; ArH), 7.56 (d, *J* = 8.7 Hz, 2H; ArH), 5.40–5.25 (m, 2H; NCH and COC*H*CH_3), 4.50 (d, *J* = 9.8 Hz, 1H; C*H*OCH_3), 3.49 (dd, *J* = 11.3 Hz, *J* = 8.5 Hz, 1H; SC*H*$_a$H$_b$), 3.12 (s, 3H; OCH_3), 3.03 (dd, *J* = 11.3 Hz, *J* = 1.8 Hz, 1H; SCH$_a$*H*$_b$), 2.45–2.30 (m, 1H; C*H*$(CH_3)_2$), 1.12 (d, *J* = 6.7 Hz, 3H; C*H*$_3$CHCH_3), 1.04 (d, *J* = 7.0 Hz, 3H; CH_3CHC*H*$_3$), 0.88 (d, *J* = 7.0 Hz, 3H; COCHC*H*$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.9, 176.4, 147.9, 146.9, 128.9, 123.6, 86.4, 71.9, 57.0, 44.7, 30.4, 29.1, 18.9, 17.1, 14.1; IR (KBr): ν = 2968, 1698, 1524, 1347, 1160 cm^{-1}; Anal.: calcd. for $C_{17}H_{22}N_2O_4S_2$ C 53.38%, H 5.80%, N 7.32%, found C 53.43%, H 5.91%, N 7.25%.

(4*S*)-*N*-[(2*R*,3*R*)-2,5-Dimethyl-3-methoxyhexanoyl]-4-isopropyl-1,3-thiazolidine-2-thione.

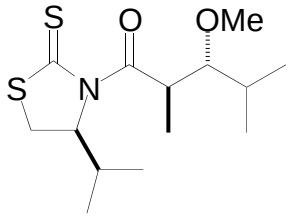


2i

Yellow oil; R_f (CH_2Cl_2) = 0.70; HPLC (hexanes/EtOAc 98:2) t_R = 20.0 min; $[\alpha]_D$ = +234.6 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (ddd, *J* = 8.4 Hz, *J* =5.6 Hz, *J* = 1.7 Hz, 1H; NCH), 5.09–4.97 (m, 1H; COC*H*CH_3), 3.76 (ddd, *J* = 9.1 Hz, *J* = 6.8 Hz, *J* = 2.8 Hz, 1H; C*H*OCH_3), 3.46 (dd, *J* = 11.4 Hz, *J* = 8.4 Hz, 1H; SC*H*$_a$H$_b$), 3.35 (s, 3H; OCH_3), 2.98 (dd, *J* = 11.4 Hz, *J* = 1.7 Hz, 1H; SCH$_a$*H*$_b$), 2.37–2.23 (m, 1H; NCHC*H*$(CH_3)_2$), 1.87–1.67 (m, 1H; CH(OCH_3)CH_2C*H*$(CH_3)_2$), 1.47 (ddd, *J* = 14.4 Hz, *J* = 9.1 Hz, *J* = 4.1 Hz, 1H;

$CH(OCH_3)CH_aH_b$), 1.25 (ddd, *J* = 14.4 Hz, *J* = 9.4 Hz, *J* = 2.8 Hz, 1H; $CH(OCH_3)CH_aH_b$), 1.10 (d, *J* = 6.9 Hz, 3H; $COCHCH_3$), 1.06 (d, *J* = 6.8 Hz, 3H ; $NCH(CH_3CHCH_3)$), 0.98 (d, *J* = 6.9 Hz, 3H; $NCH(CH_3CHCH_3)$), 0.93 (d, *J* = 6.6 Hz, 3H; $CH(OCH_3)CH_2(CH_3CHCH_3)$), 0.91 (d, *J* = 6.5 Hz, 3H; $CH(OCH_3)CH_2(CH_3CHCH_3)$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.6, 176.4, 80.1, 71.8, 57.6, 42.0, 39.8, 30.7, 29.2, 24.6, 24.0, 22.0, 19.1, 17.2, 12.7; IR (film): ν = 2960, 1696, 1466, 1256, 1158 cm^{-1}; HRMS (+FAB): calcd. for $[M+H]^+$ $C_{15}H_{28}NO_2S_2$ 318.1561, found 318.1571.

(4*S*)-*N*-[(2*R*,3*R*)-2,4-Dimethyl-3-methoxypentanoyl]-4-isopropyl-1,3-thiazolidine-2-thione.



2j

Yellow solid; m.p. 49.0–50.0 °C; R_f (CH_2Cl_2) = 0.60; HPLC (hexanes/EtOAc 97:3) t_R = 11.2 min; $[\alpha]_D$ = +172.8 (*c* = 0.1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.27 (ddd, *J* = 8.2 Hz, *J* = 6.1 Hz, *J* = 1.4 Hz, 1H; NCH), 5.09 (dq, *J* = 9.6 Hz, *J* = 7.0 Hz, 1H; $COCHCH_3$), 3.45 (dd, *J* = 9.6 Hz, *J* = 2.4 Hz, 1H; $CHOCH_3$), 3.40 (dd, *J* = 11.4 Hz, *J* = 8.2 Hz, 1H; SCH_aH_b), 3.39 (s, 3H; OCH_3), 2.97 (dd, *J* = 11.4 Hz, *J* = 1.4 Hz, 1H; SCH_aH_b), 2.40–2.25 (m, 1H; $NCHCH(CH_3)_2$), 1.95–1.80 (m, 1H; $CH(OCH_3)CH(CH_3)_2$), 1.07 (d, *J* = 6.6 Hz, 3H; $NCH(CH_3CHCH_3)$), 1.05 (d, *J* = 7.0 Hz, 3H; CH_3), 1.04 (d, *J* = 6.9 Hz, 3H ; CH_3), 1.00 (d, *J* = 6.9 Hz, 3H; $NCH(CH_3CHCH_3)$), 0.89 (d, *J* = 6.9 Hz, 3H; $CH(OCH_3)CH(CH_3CHCH_3)$; ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 202.7, 177.2, 88.1, 71.7, 61.3, 41.6, 30.6, 29.7, 29.3, 20.6, 19.1, 17.4, 15.6, 15.0; IR (KBr): ν = 2966, 1700, 1254, 1158, 1092 cm^{-1}; HRMS (+FAB): calcd. for $[M+H]^+$ $C_{14}H_{26}NO_2S_2$ 304.1405, found 304.1400.