

Titanium Enolates of Thiazolidinethione Chiral Auxiliaries:

Versatile Tools for Asymmetric Aldol Additions

Michael T. Crimmins* and Kleem Chaudhary

Venable and Kenan Laboratories of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599.

Supporting Information:

Evans syn products:

(2S, 3S)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-5-phenyl-pent-4-en-1-one (4a): ^1H NMR (400 MHz, CDCl_3) δ 0.96 (d, $J=6.3$ Hz, 6H), 1.28 (d, $J=6.7$ Hz, 3H), 1.52-1.61 (m, 2H), 1.86 (m, 1H), 2.65 (s, 1H), 2.8 (d, $J=10.8$, 1H), 3.3 (dd, $J=4.3$, 7.0, 1H), 4.5-4.63 (m, 2H), 5.11 (m, 1H), 6.15 (dd, $J=6.2$, 9.7, 1H), 6.60 (dd, $J=0.9$, 15.0, 1H), 7.20-7.38 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 202.2, 177.8, 136.8, 132, 129.3, 129.1, 128.9, 128.3, 126.9, 74.4, 67, 44.8, 39.9, 33.7, 25.8, 24, 21.7, 12. IR (neat): 3450, 2980, 1700, 1455, 1350, 1250, 1155 cm^{-1} . $[\alpha]_D^{24} = +286.5^\circ$ ($c=0.23$, CH_2Cl_2). Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2\text{S}_2$: C, 62.77; H, 6.93; N, 3.85. Found: C, 62.19; H, 7.13; N, 4.01.

(2S, x3S)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-hex-4-en-1-one (4b): ^1H NMR (400 MHz, CDCl_3) δ 0.96 (dd, $J=1.3$, 5.2, 6H), 1.19 (d, $J=6.7$, 3H), 1.51-1.68 (m, 5H), 1.86 (m, 1H), 2.5 (s, 1H), 1.9 (d, $J=11.3$, 1H), 3.5 (dd, $J=3.1$, 8.0, 1H), 4.3, (s, 1H), 4.45 (m, 1H), 5.11 (m, 1H), 5.45 (m, 1H), 5.7 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 202.1, 177.9, 177.7, 130.9, 128.6, 74, 69.3, 67, 44.5, 39.9, 33.8, 25.9, 24, 21.7, 18.2, 11.8. IR (neat): 3440, 2980, 2010, 1710, 1525, 1350, 1275, 1175, 1100, 1035, 955 cm^{-1} . $[\alpha]_D^{24} = +283.7^\circ$ ($c=1.04$, CH_2Cl_2). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_2\text{S}_2$: C, 55.78; H, 7.69; N, 4.65. Found: C, 55.93; H, 7.65; N, 4.74.

(2S, 3S)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-pent-4-en-1-one (4c): ^1H NMR (400 MHz, CDCl_3) δ 0.97 (dd, $J=1.1$, 5.3, 6H), 1.2 (d, $J=6.8$, 3H), 1.5 (m, 1H), 1.6 (m, 1H), 1.9 (m, 1H), 2.65 (s, 1H), 2.9 (d, $J=11.3$, 1H), 3.5 (dd, $J=7.1$, 1H), 4.4 (m, 1H), 4.5 (m, 1H), 5.17 (m, 2H), 5.3 (d, $J=17.2$, 1H), 5.8 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 202.1, 177.8, 138, 116.7, 73.8, 66.9, 44, 39.9, 33.7, 25.9, 24, 21.7, 11.4. IR (neat): 3460, 2980, 1700, 1470, 1350, 1275, 1230, 1175, 1110, 1030, 1000, 940 cm^{-1} . $[\alpha]_D^{24} = +263.3^\circ$ ($c=1.39$, CH_2Cl_2). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{S}_2$: C, 54.31; H, 7.36; N, 4.89. Found: C, 54.52; H, 7.50; N, 4.94.

(2S, 3R)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2,4-dimethyl-pentan-1-one (4d): ^1H NMR (300 MHz, CDCl_3) δ 0.84 (d, $J=6.8$, 3H), 1.1 (m, 9H), 1.19 (d, $J=6.9$, 3H), 1.60 (m, 3H), 1.88 (m, 1H), 2.89 (d, $J=11.2$, 1H), 3.50 (m, 2H), 4.63 (m, 1H), 5.24 (m, 1H). ^{13}C NMR (300 MHz, CDCl_3) δ 201.8, 178.3, 66.6, 41, 39.7, 33.3, 31.3, 25.7, 23.8, 21.5, 19.2, 10.5. IR (neat): 390, 2980, 1685, 1475, 1350, 1275, 1225, 1150, 1100, 1025, 880 cm^{-1} . $[\alpha]_D^{24} = +222.7^\circ$ ($c=0.67$, CH_2Cl_2). Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_2\text{S}_2$: C, 55.41; H, 8.30; N, 4.62. Found: C, 55.46; H, 8.27; N, 4.65.

(2S, 3S)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidine-3-yl]-2-methyl-3-phenyl-propan-1-one (4e): ^1H NMR (400 MHz, CDCl_3) δ 0.92 (dd, $J=3.2$, 3.0, 6H), 1.29 (d, $J=6.7$, 3H), 1.49 (m, 2H), 1.75 (m, 1H), 2.68 (d, $J=10.9$, 1H), 2.90 (dd, $J=0.7$, 6.6, 1H), 4.63-4.71 (m, 2H), 4.83 (d,

J=6.4, 1H), 7.25-7.33 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 202.1, 177.7, 142.2, 128.8, 128.3, 126.8, 76.5, 67, 47, 39.7, 33.9, 25.8, 23.9, 21.7, 12.8. IR (neat): 3780, 2980, 1700, 1460, 1350, 1275, 1175, 1100, 1050, 910 cm^{-1} . $[\alpha]^{24}_{\text{D}} = +231.9^\circ$ (c=0.995, CH_2Cl_2). Anal Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{S}_2$: C, 60.50; H, 6.87; N, 4.15. Found: C, 60.33; H, 7.00; N, 4.02.

(2S, 3R)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidine-3-yl]-2,5-dimethyl-hexan-1-one (4f): ^1H NMR (400 MHz, CDCl_3) δ 0.88 (dd, J=1.3, 5.3, 6H), 0.95 (d, J=1.9, 6H), 1.08 (m, 1H), 1.19 (d, J=7.0, 3H), 1.45 (m, 1H), 1.65 (m, 1H), 1.74 (m, 1H), 1.87 (m, 1H), 2.74 (s, 1H), 2.9 (d, J=11.0, 1H), 3.5 (dd, J=1.0), 3.95 (m, 1H), 4.35 (m, 1H), 5.25 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 202, 178.9, 70.4, 66.7, 43.7, 40, 33.5, 25.8, 25, 24, 22.4, 21.7, 10.8. IR (neat): 3780, 2980, 1700, 1475, 1350, 1275, 1225, 1175, 1100, 1030 cm^{-1} . $[\alpha]^{24}_{\text{D}} = +216.6^\circ$ (c=1.40, CH_2Cl_2). Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{NO}_2\text{S}_2$: C, 56.74; H, 8.57; N, 4.41. Found: C, 56.66; H, 8.59; N, 4.52.

(2S, 3S)-1-[(4S)-4-Benzyl-2-thioxo-thiazolidin-3-yl]-3-hydroxy-2-methyl-5-phenyl-pent-4-en-1-one (4g): ^1H NMR (400 MHz, CDCl_3) δ 1.3 (d, 3H, J=6.7 Hz), 2.8 (d, 1H, J=11.5 Hz), 3.0 (m, 1H), 3.2 (m, 2H), 4.63 (m, 1H), 4.67 (m, 1H), 5.2 (m, 1H), 6.17 (dd, 1H, J=6.3, 9.7 Hz), 6.62 (dd, 1H, J=0.7, 15.2 Hz), 7.19-7.40 (m, 10H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.9, 177.8, 136.7, 132.1, 129.8, 129.7, 129.3, 129.2, 129.1, 128.3, 127.7, 126.9, 74.5, 69.3, 44.9, 37.1, 32.6, 12.

(2S, 3S)-1-[(4S)-4-Benzyl-2-thioxo-thiazolidin-3-yl]-3-hydroxy-2-methyl-hex-4-en-1-one (4h): ^1H NMR (400 MHz, CDCl_3) δ 1.24 (d, 3H, J=6.8 Hz), 1.69 (d, 3H, J=1.0 Hz), 2.88 (d, 1H, J=11.3 Hz), 3.03 (dd, 1H, J=10.6, 2.6 Hz), 3.21 (dd, 1H, J=3.6, 9.4 Hz), 3.3 (m, 1H), 4.35 (m, 1H), 4.49 (m, 1H), 5.2 (m, 1H), 5.50 (dd, 1H, J=1.6, 5.0 Hz), 5.74 (m, 1H), 7.18-7.50 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.7, 178, 136.8, 130.9, 129.9, 129.3, 128.8, 127.7, 74.2, 69.4, 44.7, 37.1, 32.7, 18.2, 11.8.

(2S, 3S)-1-[(4S)-4-Benzyl-2-thioxo-thiazolidin-3-yl]-3-hydroxy-2-methyl-pent-4-en-1-one (4i): ^1H NMR (400 MHz, CDCl_3) δ 1.13 (d, 3H, J=6.9 Hz), 2.51 (s, 1H), 2.78 (d, 1H, J=11.5 Hz), 2.92 (dd, 1H, J=10.5, 2.7 Hz), 3.10 (dd, 1H, J=3.8, 9.3 Hz), 3.26 (m, 1H), 4.35 (m, 1H), 4.45 (m, 1H), 5.06-5.24 (m, 3H), 5.66-5.76 (m, 1H), 7.14-7.25 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 177.4, 137.7, 136.4, 129.5, 129, 127.4, 116.5, 73.7, 69.1, 44, 36.9, 32.5, 11.3. $[\alpha]^{24}_{\text{D}} = +69.7^\circ$ (c=5.94, CH_2Cl_2).

(2S, 3R)-1-[(4S)-4-Benzyl-2-thioxo-thiazolidin-3-yl]-3-hydroxy-2,4-dimethyl-pentan-1-one (4j): ^1H NMR (400 MHz, CDCl_3) δ 0.76 (d, 3H, J=6.9 Hz), 0.88 (d, 3H, J=6.6 Hz), 1.12 (d, 3H, J=6.1 Hz), 1.51 (m, 1H), 2.77 (d, 1H, J=11.6 Hz), 2.92 (m, 1H), 3.12 (m, 1H), 3.27 (dd, 1H, J=6.5, 4.2 Hz), 3.43 (m, 1H), 4.56 (m, 1H), 5.22 (m, 1H), 7.13-7.25 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.2, 178.6, 136.4, 129.4, 128.9, 127.2, 68.9, 41, 36.7, 32, 31.1, 18.9, 10.2. $[\alpha]^{24}_{\text{D}} = +39.1^\circ$ (c=8.29, CH_2Cl_2).

(2S, 3S)-1-[(4S)-4-Benzyl-2-thioxo-thiazolidin-3-yl]-3-hydroxy-2-methyl-3-phenyl-propan-1-one (4k): ^1H NMR (400 MHz, CDCl_3) δ 1.08 (d, 3H, J=7.1 Hz), 1.33 (d, 3H, J=6.6 Hz), 3.18 (m, 1H), 3.36 (m, 1H), 5.04 (m, 1H), 5.27 (m, 1H), 5.36 (m, 1H), 7.17-7.50 (m, 10H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.9, 178.8, 141.6, 136.8, 129.8, 129.3, 128.7, 127.7, 127.6, 126.7, 126.5, 72.9, 69.3, 45.2, 37.3, 32.3, 11.3.

(2S, 3R)-1-[(4S)-4-Benzyl-2-thioxo-thiazolidin-3-yl]-3-hydroxy-2,5-dimethyl-hexan-1-one (4l): ^1H NMR (300 MHz, CDCl_3) δ 0.8 (dd, 6H, J=3.8, 2.7 Hz), 1.1 (d, 3H, J=6.9 Hz), 1.38 (m, 1H), 1.65 (m, 2H), 2.77 (d, 1H, J=11.6 Hz), 2.91 (dd, 1H, J=10.4, 2.7 Hz), 3.08 (dd, 1H, J=3.8, 9.3 Hz), 3.28 (dd, 1H, J=7.2, 4.3 Hz), 3.89 (m, 1H), 4.3 (m, 1H), 5.25 (m, 1H), 7.13-7.25 (m, 5H). ^{13}C NMR (300 MHz, CDCl_3) δ 178.5, 136.4, 129.5, 129, 127.4, 70.3, 68.9, 43.8, 43.5, 37, 32.3, 24.8, 23.8, 22.2, 10.7. $[\alpha]^{24}_{\text{D}} = +50.0^\circ$ (c=8.44, CH_2Cl_2).

Non-Evans syn:

(2R, 3R)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-5-phenyl-pent-4-en-1-one (3a): ^1H NMR (400 MHz, CDCl_3) δ 0.95 (dd, 6H, $J=6.4, 5.0$ Hz), 1.20 (d, 3H, $J=6.9$ Hz), 1.40-1.64 (m, 3H), 1.86 (m, 1H), 2.89 (dd, 1H, $J=0.6, 10.7$ Hz), 3.52 (m, 1H), 4.76 (m, 1H), 4.87 (m, 1H), 5.28 (m, 1H), 6.20 (dd, 1H, $J=5.6, 10.3$), 6.66 (dd, 1H, $J=1.3, 14.7$), 7.19-7.38 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 202.5, 177.7, 131.7, 129, 128.9, 128, 127, 72.8, 67, 43.7, 40.1, 33.2, 25.8, 23.9, 21.7, 11.9. $[\alpha]^{24}_{\text{D}} = +169.3^\circ$ ($c=2.46$, CH_2Cl_2).

(2R, 3R)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-hex-4-en-1-one (3b): ^1H NMR (400 MHz, CDCl_3) δ 0.97 (dd, 6H, $J=2.1, 4.3$ Hz), 1.13 (d, 3H, $J=7.0$ Hz), 1.51-1.70 (m, 6H), 1.85 (m, 1H), 2.79 (s, 1H), 2.9 (dd, 1H, $J=0.67, 10.7$ Hz), 3.50 (m, 1H), 4.50 (s, 1H), 4.74 (m, 1H), 5.25 (m, 1H), 5.47 (m, 1H), 5.73 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 202, 177.4, 130.1, 128, 72.5, 66.6, 43.1, 39.7, 32.8, 25.4, 23.5, 21.3, 17.8, 11.4. $[\alpha]^{24}_{\text{D}} = +152.0^\circ$ ($c=4.21$, CH_2Cl_2).

(2R, 3R)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-pent-4-en-1-one (3c): ^1H NMR (400 MHz, CDCl_3) δ 0.95 (dd, 6H, $J=2.2, 4.2$ Hz), 1.10 (d, 3H, $J=7.1$ Hz), 1.51-1.62 (m, 2H), 1.88 (m, 1H), 2.9 (d, 1H, $J=10.8$ Hz), 3.52 (m, 1H), 4.58 (m, 1H), 4.74 (m, 1H), 5.16 (d, 1H, $J=10.6$ Hz), 5.22 (m, 1H), 5.3 (d, 1H, $J=17.2$ Hz), 5.8 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 202, 177.3, 137.1, 116, 72.1, 66.5, 44, 39.6, 29.7, 25.4, 23.5, 21.2, 10.9. $[\alpha]^{24}_{\text{D}} = +177.9^\circ$ ($c=1.31$, CH_2Cl_2).

(2R, 3S)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidin-3-yl]-2,4-dimethyl-pentan-1-one (3d): ^1H NMR (400 MHz, CDCl_3) δ 0.84 (d, 3H, $J=6.8$ Hz), 0.98 (dd, 6H, $J=1.9, 4.4$), 1.0 (d, 3H, $J=6.5$ Hz), 1.13 (d, 3H, $J=7.1$), 1.51-1.70 (m, 3H), 1.91 (m, 1H), 2.89 (dd, 1H, $J=0.7, 10.6$ Hz), 3.50 (m, 1H), 3.60 (dd, 1H, $J=2.1, 6.8$ Hz), 4.88 (m, 1H), 5.22 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.8, 179.1, 66.6, 40.2, 32.7, 30.7, 25.5, 23.6, 21.2, 19.7, 18.7, 10.2. $[\alpha]^{24}_{\text{D}} = +159.7^\circ$ ($c=3.07$, CH_2Cl_2).

(2R, 3R)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidine-3-yl]-2-methyl-3-phenyl-propan-1-one (3e): ^1H NMR (400 MHz, CDCl_3) δ 0.96 (dd, 6H, $J=3.6, 2.9$ Hz), 1.07 (d, 3H, $J=7.0$ Hz), 1.23-1.61 (m, 3H), 1.84 (m, 1H), 2.88 (dd, 1H, $J=0.6, 10.7$ Hz), 3.51 (m, 1H), 5.03 (m, 1H), 5.24 (m, 2H), 7.21-7.41 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 205, 178.2, 128.2, 127.3, 126.1, 72.7, 66.5, 44.6, 39.6, 32.8, 25.4, 23.5, 21.2, 10.9. $[\alpha]^{24}_{\text{D}} = +190.8^\circ$ ($c=2.19$, CH_2Cl_2).

(2R, 3S)-3-Hydroxy-1-[(4S)-4-isobutyl-2-thioxo-thiazolidine-3-yl]-2,5-dimethyl-hexan-1-one (3f): ^1H NMR (400 MHz, CDCl_3) δ 0.89 (dd, 6H, $J=4.9, 1.7$ Hz), 0.96 (d, 6H, $J=2.3$ Hz), 1.13 (d, 3H, $J=7.1$ Hz), 1.44-1.93 (m, 5H), 1.9 (m, 1H), 2.89 (dd, 1H, $J=0.6, 10.7$ Hz), 3.50 (m, 1H), 4.11 (m, 1H), 4.57 (m, 1H), 5.2 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.9, 178.5, 66.9, 66.6, 42.7, 39.6, 32.8, 25.4, 24.5, 23.5, 21.9, 21.2, 10.4. $[\alpha]^{24}_{\text{D}} = +156.1^\circ$ ($c=3.31$, CH_2Cl_2).

Cleaved products:

(1S, 2R)-2-methyl-1-phenyl-propane-1,3-diol (5): ^1H NMR (400 MHz, CDCl_3) δ 0.82 (d, $J=7.1$, 3H), 1.03 (m, 1H), 2.63 (s, 2H), 3.64 (dd, $J=1.8, 3.6$, 2H), 4.9 (d, $J=3.9$, 1H), 7.23-7.35 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 143, 128.6, 127.7, 126.5, 66.8, 41.8, 11.2. IR (neat): 3680, 2975, 1460, 1040 cm^{-1} . $[\alpha]^{24}_{\text{D}} = -51.6^\circ$ ($c=0.15$, CHCl_3).

(2S, 3S)-1-[(4S)-4-Isobutyl-2-thioxo-thiazolidin-3-yl]-2-methyl-3-phenyl-3-triethylsilanyloxy-propan-1-one (6): ^1H NMR (400 MHz, CDCl_3) δ 0.36-0.49 (m, 6H), 0.76-0.91 (m, 16H), 1.36 (d, $J=6.1$, 3H), 1.44 (m, 1H), 1.60-1.67 (m, 1H), 2.43-2.50 (m, 2H), 4.16 (m, 1H), 4.58 (m, 2H), 7.24-7.38 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 201.4, 176.9, 143.3, 128, 127.7, 126.9, 78.6, 66.7, 49, 47, 39, 33.6, 31.5, 25.2, 23.4, 21.3, 14.3, 6.7, 6.5, 4.7. IR (neat): 2980, 1700, 1470, 1350, 1275, 1175, 1080, 1025, 910, 820 cm^{-1} . $[\alpha]^{24}_{\text{D}} = +179.2^\circ$ ($c=2.30$, CH_2Cl_2).

(2S, 3R)-3-Hydroxy-2,5-dimethyl-hexanoic acid methyl ester (7): ^1H NMR (300 MHz, CDCl_3) δ 0.90 (dd, $J=0.7$, 5.9, 6H), 1.16 (d, $J=7.1$, 3H), 1.40 (m, 1H), 1.5 (m, 1H), 2.40 (d, $J=4.8$, 1H), 2.49 (m, 1H), 3.69 (s, 3H), 3.95 (m, 1H). ^{13}C NMR (300 MHz, CDCl_3) δ 176.7, 69.9, 52, 44.7, 43, 24.9, 23.7, 22.1, 10.9. IR (neat): 3450, 2943, 1716, 1460, 1186 cm^{-1} . $[\alpha]^{24}_{\text{D}} = +67.8^\circ$ ($c=0.215$, CH_2Cl_2).

(2S, 3R)-3-Hydroxy-2,5-dimethyl-hexanoic acid methoxy-methyl-amide (8): ^1H NMR (400 MHz, CDCl_3) δ 0.90 (dd, $J=2.5$, 4.15, 6H), 1.10 (m, 1H), 1.4 (d, $J=7.1$, 3H), 1.48 (m, 1H), 1.77 (m, 1H), 2.80 (s, 1H), 3.17 (s, 3H), 3.68 (s, 3H), 3.94 (m, 1H). ^{13}C NMR (400 MHz, CDCl_3) δ 178.5, 69.2, 61.5, 42.9, 38.9, 24.5, 23.3, 22.1, 10. IR (neat): 3429, 2950, 2871, 2360, 1643, 1463, 1387, 1177, 1150, 1085, 1035, 992 cm^{-1} . $[\alpha]^{24}_{\text{D}} = +22.7^\circ$ ($c=0.725$, CH_2Cl_2).

(2S, 3R)-3-Hydroxy-2,5-dimethyl-hexanoic acid benzylamide (9): ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, $J=6.75$, 6H), 1.09 (m, 1H), 1.16 (d, $J=7.2$, 3H), 1.44 (m, 1H), 1.74 (m, 1H), 2.30 (m, 1H), 3.25 (s, 1H), 3.95 (m, 1H), 4.41 (d, $J=5.7$, 2H), 6.19 (s, 1H), 7.24-7.34 (m, 5H). ^{13}C NMR (400 MHz, CDCl_3) δ 176.4, 128.8, 127.8, 127.7, 70.1, 45.3, 43.6, 42.8, 24.8, 23.8, 22.2, 11.6. IR (neat): 3402, 3285, 2955, 2923, 2360, 2339, 1632, 1536, 1454, 1363, 1075, 1048, 983 cm^{-1} . $[\alpha]^{24}_{\text{D}} = +4.6^\circ$ ($c=0.635$, CH_2Cl_2).