Supporting Information

Diastereoselective Addition of Chlorotitanium Enolate of N-Acyl Thiazolidinethione to O-Methyl Oximes: A Novel, Stereoselective Synthesis of α,β -Disubstituted β -Amino Carbonyl Compounds via Chiral Auxiliary Mediated Azetine Formation

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Representative Examples of Azetine Synthesis and Hydrolytic Opening

Aldoxime 1 (R = Phenyl)

Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.08, 7.58 (m, 2H), 7.38 (m, 3H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.80, 132.02, 130.02, 128.90, 127.22, 62.22. EIMS m/z 135.20 (M^+ , $\text{C}_8\text{H}_9\text{NO}$ requires 135.06).

Procedure for the Synthesis of Azetines

To a solution of **2** (1.15 mM) in 7.5 ml of anhydrous dichloromethane at 0 °C was added titanium tetrachloride (4.60 mM, neat) dropwise under argon. The resulting thick yellow complex was stirred for 5 min and (-)-sparteine (2.87 mM, neat) was then slowly added to it. The brown mixture was stirred for 40 min at 0 °C. With constant stirring the mixture became homogeneous. It was then cooled to -78 °C and the O-alkyl oxime ether (3.45 mM, neat) was added. The temperature was slowly raised to 0 °C. The reaction mixture stirred for about 12 - 14 hr, quenched with 20 ml of saturated aqueous ammonium chloride solution and treated with dichloromethane (30 ml) and distilled water (30 ml). The organic phase was separated and washed with saturated aqueous sodium bicarbonate solution, then brine, dried with anhydrous magnesium sulfate and finally concentrated under vacuum. The impure product mixture was purified by flash column chromatography (EtOAc / Hexanes: 10/1).

Compound 3 (R = Phenyl)

Pale yellow crystalline solid. Melting point: 116-118 °C Stereochemistry established by X-ray crystallography. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 5H), 4.99 (dd, 1H, J = 4.81 Hz, J = 7.9 Hz), 4.44 (d, 1H, J = 1.4 Hz), 3.96 (q, 1H, J = 1.71 Hz, J = 7.21 Hz), 3.69 (dd, 1H, J = 8.59 Hz, J = 11.3 Hz), 3.19 (d, 1H, J = 0.7 Hz, J = 11.7 Hz), 2.82 (m, 1H), 1.58 (d, 3H, J = 7.27 Hz), 1.13 (d, 3H, J = 6.9 Hz), 1.08 (d, 3H, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 199.46, 173.50, 140.51, 128.64, 127.66, 126.38, 71.03, 69.86, 52.09, 30.68, 19.67, 16.90, 16.31. FABMS m/z 311.2841 ($\text{C}_{16}\text{H}_{20}\text{N}_2\text{S}_2\text{Li}$ requires 311.1228).

Procedure for 'Hydrolytic' Opening of Azetines

Excess benzoyl chloride (~0.5 ml, neat) was added to a solution of azetine (0.33 mM) in CH_2Cl_2 (10 ml) open to the atmosphere. The mixture was stirred vigorously for 5 min, and the reaction mixture purified by flash column chromatography (Hexanes/EtOAc 8/1). The product fraction was concentrated under aspirator vacuum and subsequently under high vacuum to afford a yellow solid.

Compound 5 (*R* = Phenyl)

X-Ray Crystal Structure of 5 with R = Phenyl

Pale yellow crystalline solid. Melting point: 130-134 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, 2H, J = 7.0 Hz), 7.67 (d, 1H, J = 9.2 Hz), 7.47 (m, 3H), 7.26 (m, 2H), 7.18 (m, 2H), 5.46 (m, 2H), 5.11 (t, 1H, J = 6.9 Hz), 3.48 (dd, 1H, J = 7.9 Hz, J = 11.5 Hz), 2.99 (d, J = 11.7 Hz), 2.11 (m, 1H, J = 6.9 Hz, J = 6.6 Hz), 1.16 (d, 3H, J = 6.3 Hz), 0.80 (d, 1H, J = 6.6 Hz), 0.75 (d, 3H, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 205.19, 176.64, 166.284, 140.69, 134.11, 131.68, 128.86, 128.68, 127.80, 127.42, 127.33, 72.69, 57.82, 41.95, 31.03, 30.57, 19.02, 17.74, 16.91. HRFABMS m/z 433.1588 (M^+ , $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2\text{Li}$ requires 433.1596).