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(1S,2S)-N-Benzyl-N-[(2,2-dimethyl-1,3-dioxolan-4-yl)-(2-benzothiazolyl)methyl] Hydroxylamine

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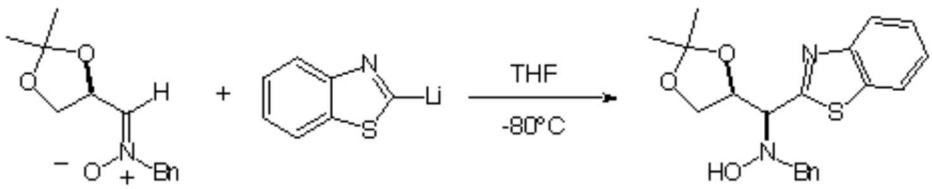

Scheme

A cooled solution (-90°C) of benzothiophene (0.402 g, 3 mmol) in THF (10 mL) was treated with butyllithium (2 mL of a 1.6 M solution in hexane, 3.2 mmol) under an inert atmopshere. The resulting solution was stirred at -80 °C for 15 min during which time the reaction mixture was cooled to -90 °C and treated with a solution of nitrone **1** (0.235 g, 1 mmol) in THF (10 mL) added drop by drop. The rate of addition was adjusted so as to keep the internal temperature below -80°C. The reaction mixture was stirred for 30 min at -80 °C and then quenched with saturated aqueous ammonium chloride (10 mL). The mixture was stirred at ambient temperature for 10 min and diluted with ethyl acetate (15 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 10 ml). The combined organic extracts were washed with brine and dried over magnesium sulfate, and the solvent was evaportaed under reduced pressure to give the crude mixture of diastereomeric hydroxylamines. The NMR analysis of this mixture revealed a diastereoselectivity of 94%, the absolute configuration of the major adduct being confirmed by X-ray crystallography [1]. Purification by column chromatography (hexane/diethyl ether 60:40) on silica gel afforded **3** as a white solid (0.289 g, 78%).

Mp 153-155°C

TLC (hexane/diethyl ether 60:40) R_f 0.48

$[a]_D^{20}$ = -25.7 (c 0.36, $CHCl_3$)

^{1}H NMR ($CDCl_3$) d 1.37 (s, 3H), 1.39 (s, 3H), 3.85 (dd, 1H, J = 6.5, 9.0 Hz), 4.00 (dd, 1H, J = 6.7, 9.0 Hz), 4.05 (d, 1H, J = 13.0 Hz), 4.12 (d, 1H, J = 13.0 Hz), 4.47 (d, 1H, J = 6.6 Hz), 4.83 (pseduo q, 1H, J = 6.5 Hz), 6.06 (bs, 1H, ex. D_2O), 7.20-7.42 (m, 7 H), 7.91 (d, 1H, J = 80 Hz), 8.03 (d, 1H, J = 8.0 Hz).

^{13}C NMR ($CDCl_3$) d 25.6, 26.7, 62.0, 67.3, 70.0, 76.2, 109.8, 119.8, 121.7, 123.4, 125.6, 126.2, 127.7, 128.5, 129.4, 135.3, 137.1, 170.7

Anal. Calcd. for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56. Found: C, 64.96; H, 5.73; N, 7.69.

References and Notes

1. Merino, P.; Franco, S.; Martinez, I.; Merchan, F. L.; Tejero, T. *Unpublished results*. Data is available from the authors.

Sample Availability: Available from the authors and MDPI: MDPI Reg. No. 15814.