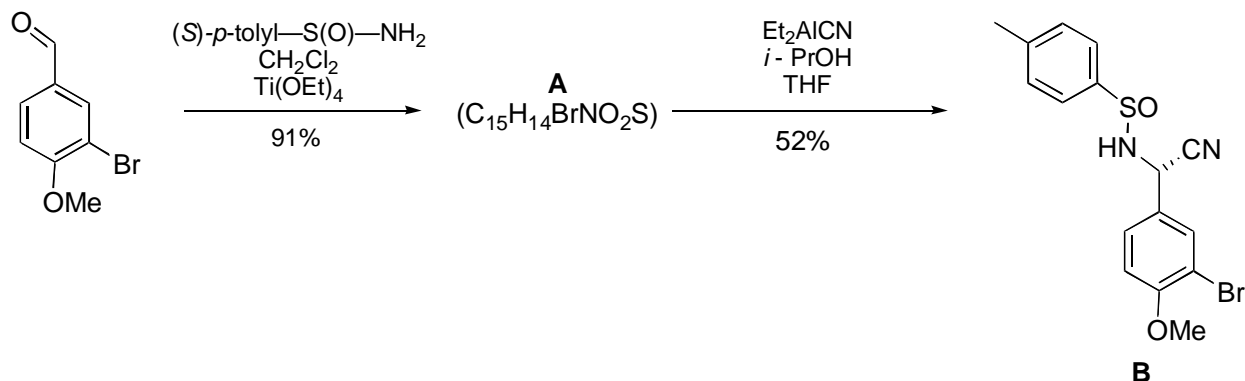


2nd Year Synoptic Organic Problem Sheets 2005-6

Set 2

The following sequence is the start of an asymmetric synthesis of a natural product.



Ti(OEt)_4 is effectively a dehydrating agent (TiO_2 , the Ti containing product is very stable) and Et_2AlCN can be considered to be a more electrophilic version of HCN. *p*-Tolyl is 4-methylphenyl.

- i. Draw a full stereostructure of the reagent (*S*)-*p*-tolyl—S(O)—NH₂.
- ii. Suggest a structure for **A**, paying particular attention to the stereochemistries involved and justify your proposal.
- iii. By careful consideration of the chemical shifts, multiplicities and coupling constants, assign the proton nmr spectrum (given below) of **A**.

A: δ_{H} (270 Mz) 8.60 (1H, s), 8.09 (1H, d, *J* 2.2 Hz), 7.69 (2H, dd, *J* 8.6, 2.2 Hz), 7.60 (2H, d, *J* 8.1 Hz), 7.30 (2H, d, *J* 8.1 Hz), 6.92 (1H, d, *J* 8.6 Hz), 3.93 (3H, s), 2.38 (3H, s).
- iv. Suggest a mechanism for the formation of **A**.
- v. Draw a full stereostructure of **B**.
- vi. By use of a suitable transition state model (use your molecular models and try a Felkin-Ahn type rationale), propose a mechanism for the formation of **B**.