An Efficient, Stereocontrolled, Total Synthesis of the Orchidaceae Alkaloid (±)-Dendrobine

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1) LiCH₂NC, HMPA, THF, *then* TBSCI

2) SOCl₂, CH₂OH

3) MS, CH₂Cl₂, reflux, *then* AgBF₄, DCE, –78 °C to –20 °C
4) MeOTf
5) K[HB(O-‡Bu)₃], –78 °C
6) SmI₂, THF, 25 °C

How would you prepare the diacid?

Hint: methanolysis at only one position

Step 3: Please provide a mechanism.

Step 6: A different main product is observed with HMPA at –78 °C, which?

(-)-dendrobine
7) {\text{SOCl}_2}, \text{NEt}_3, \text{EtOAc}, 0 \degree \text{C to 25 \degree C}
8) \text{DBU}, 1,4-\text{dioxane}, \text{reflux}
9) \text{PtO}_2, \text{H}_2, \text{AcOH}, 25 \degree \text{C}
10) \text{NaBH}_4, \text{PrOH}

Step 9: Hint: Two reactions occur.

(-)-dendrobine