Supporting Information

Organocatalytic stereoselective approach to the total synthesis of (-)-halosaline

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General Methods:

All reactions requiring anhydrous conditions were performed under a positive pressure of argon using oven-dried glassware (110 °C), which was cooled under argon. Solvents used for chromatography were distilled at respective boiling points using known procedures.

All commercial reagents were obtained from Sigma-Aldrich Chemical Co. and Alfa Aesar. Progress of the reactions was monitored by TLC using precoated aluminium plates (Merck kieselgel 60 F 254). Column chromatographies were performed on silica gel 60-120/ 100-200/ 230-400 mesh obtained from S. D. Fine Chemical Co. India or Spectrochem India. Typical syringe and cannula techniques were used to transfer air- and moisture-sensitive reagents.

IR spectra were recorded on a Perkin–Elmer infrared spectrometer model 599-B and model 1620 FT-IR. $^1$H NMR spectra were recorded on Bruker AC-200, Bruker AV-400, Jeol-400 and Bruker DRX – 500 instruments using deuterated solvent. Chemical shifts are reported in ppm. Proton coupling constants ($J$) are reported as absolute values in Hz and multiplicity (br, broadened; s, singlet; d, douplet; t, triplet; m, multiplet). $^{13}$C NMR spectra were recorded on Bruker AC-200, Bruker AV- 400, Jeol-400 and Bruker DRX-500 instruments operating at 50 MHz, 100 MHz, and 125 MHz, respectively. $^{13}$C NMR chemical shifts are reported in ppm relative to the central line of CDCl$_3$ ($\delta$ 77.0). Elemental analyses were determined at Central Elemental Analysis Facility division at National Chemical Laboratory. All HPLC analyses used to determine enantiomeric purity were calibrated with sample of the racemate.
Ethyl (R)-4-hydroxyheptanoate (9):
Enantiomeric excess:

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Volume: 1.0000
Sample Amount: 2.00000 ng/ul (not used in calc.)

Signal 1: FID1 A

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Ethyl (R)-4-((tert-butyldimethylsilyl)oxy)heptanoate (11):
Dibenzyl 1-((4S,6R,E)-6-((tert-butyldimethylsilyl)oxy)-1-ethoxy-1-oxonon-2-en-4-yl)hydrazine-1,2-dicarboxylate (8):
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Peak Quantitation: AREA
Calculation Method: AREA%
Ethyl (4R,6R)-4-((tert-butoxycarbonyl)amino)-6-((tert-butyldimethylsilyl)oxy)nonanoate (12):
**tert-Butyl ((4R,6R)-6-((tert-butyldimethylsilyl)oxy)-1-hydroxynonan-4-yl)carbamate (13):**

[Chemical structure diagram]

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tert-Butyl ((4R,6R)-6-((tert-butyldimethylsilyl)oxy)-1-cyanononan-4-yl)carbamate (18):
tert-Butyl (R)-2-((R)-2-((tert-butyldimethylsilyl)oxy)pentyl)-3,4-dihydropyridine-1(2H)-carboxylate (19):
tert-Butyl ((5R,7R)-7-((tert-butyldimethylsilyl)oxy)-1-hydroxydecan-5-yl)carbamate (20):
tert-Butyl \((R)\)-2-\((R)\)-2-\((\text{tert-butyl} \text{dimethylsilyl})\text{oxy})\text{pentyl}\text{piperidine-1-carboxylate} (21):
(-)-Halosaline (1):
**tert-Butyl (R)-2-((R)-2-((tert-butyl dimethylsilyl)oxy)pentyl)-5-oxopyrrolidine-1-carboxylate (17):**
**tert-Butyl (R)-2-((R)-2-hydroxypentyl)pyrrolidine-1-carboxylate (15):**

Chloroform-d

![Chemical structure](image)

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