Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

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

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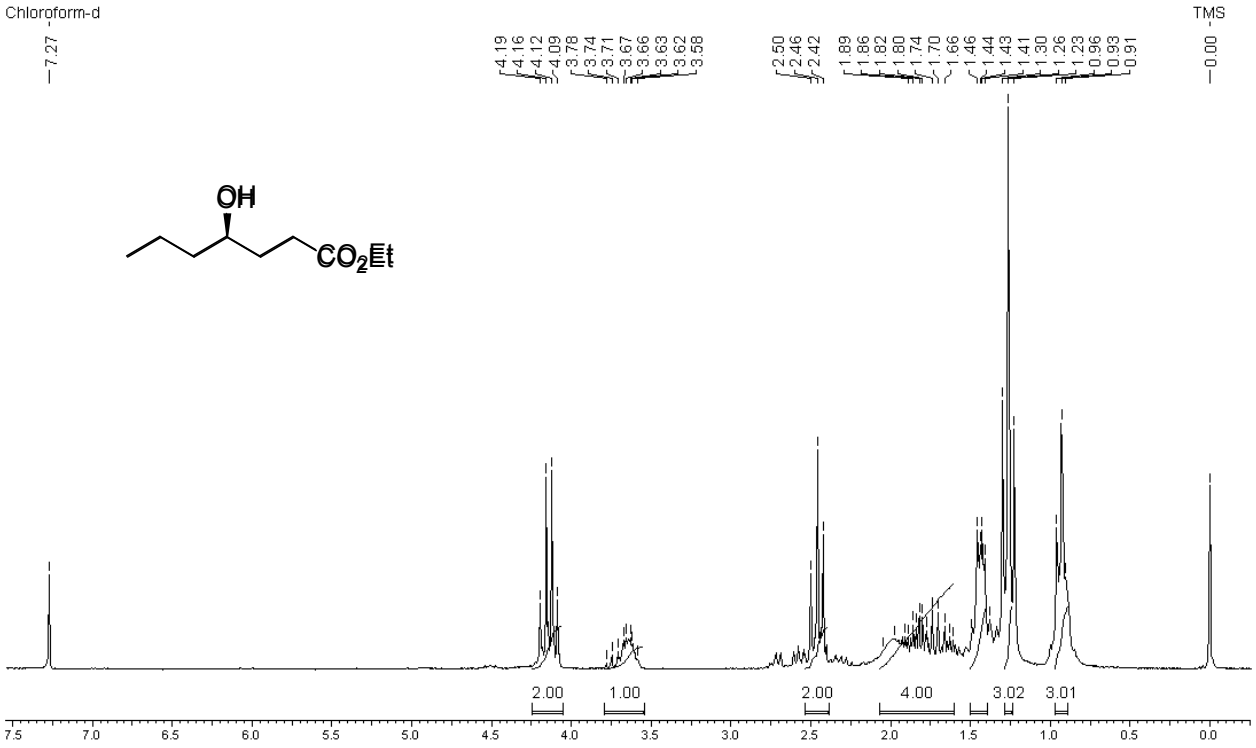
General Methods :

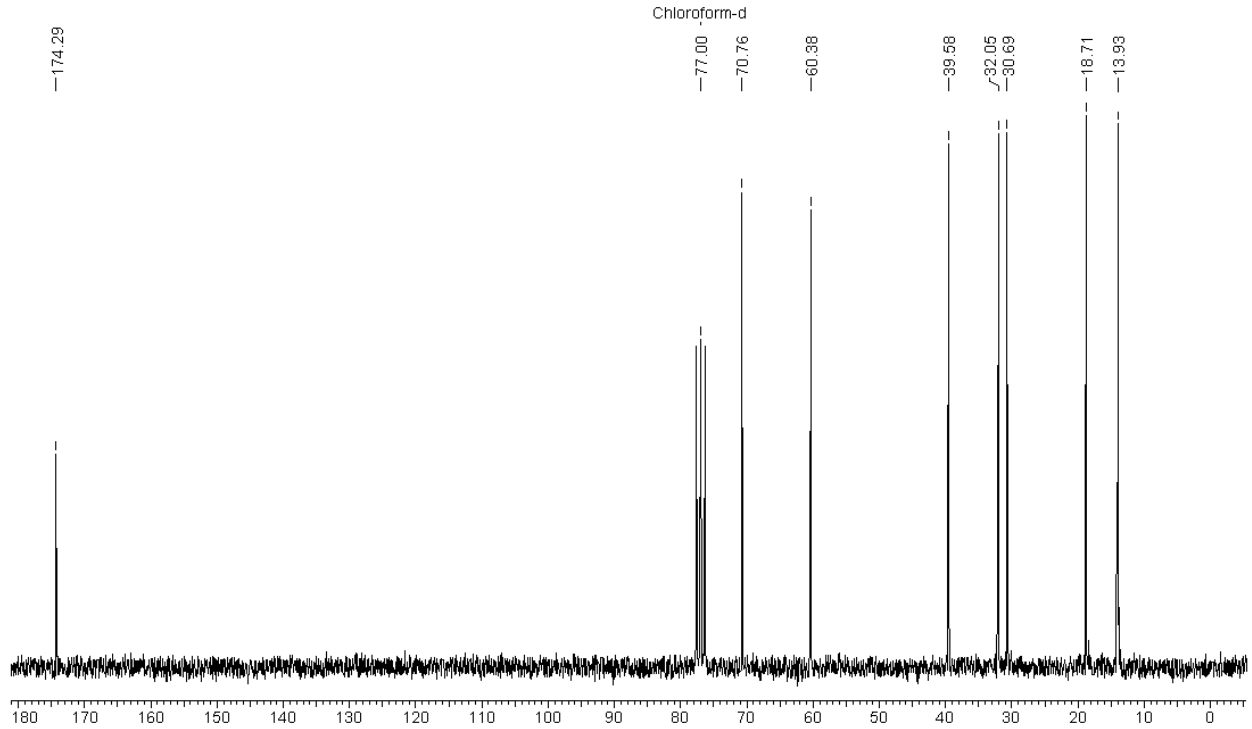
All reactions requiring anhydrous conditions were performed under a positive pressure of argon using oven-dried glassware (110 °C), which was cooled under argon. Solvents used for chromatography were distilled at respective boiling points using known procedures.

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.

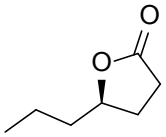
IR spectra were recorded on a Perkin–Elmer infrared spectrometer model 599-B and model 1620 FT-IR. ^{1}H NMR spectra were recorded on Bruker AC-200, Bruker AV-400, Jeol-400 and Bruker DRX – 500 instruments using deuterated solvent. Chemical shifts are reported in ppm. Proton coupling constants (*J*) 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 $CDCl_3$ (δ 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 caliberated with sample of the racemate.

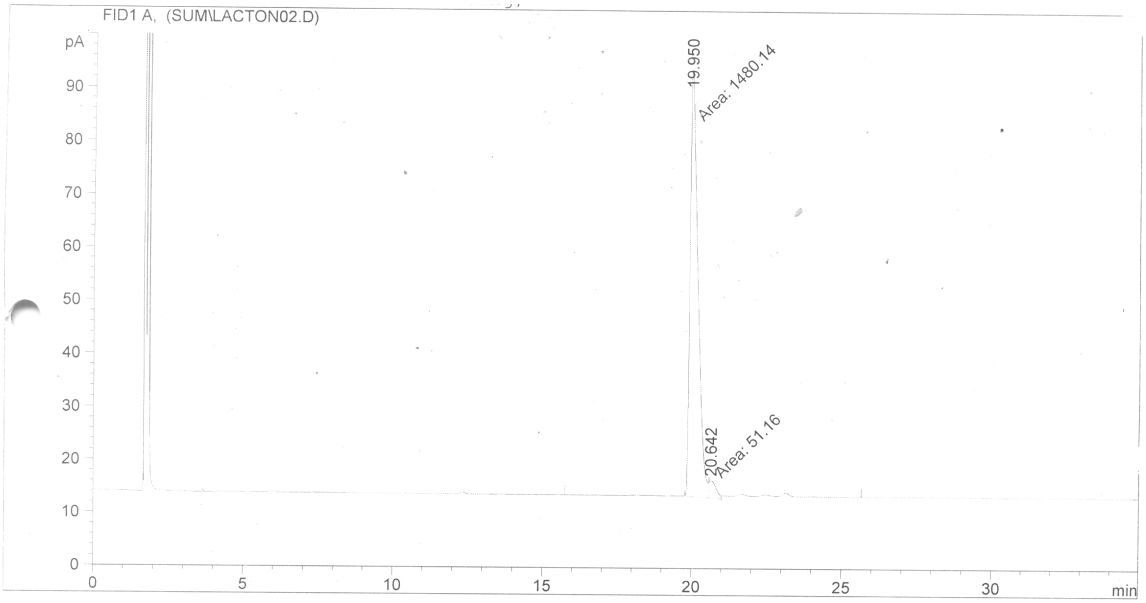
Ethyl (*R*)-4-hydroxyheptanoate (9):





Enantiomeric excess:



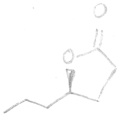


Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.950	MF	0.3058	1480.13977	80.67734	96.65905
2	20.642	FM	0.2582	51.16001	3.30218	3.34095



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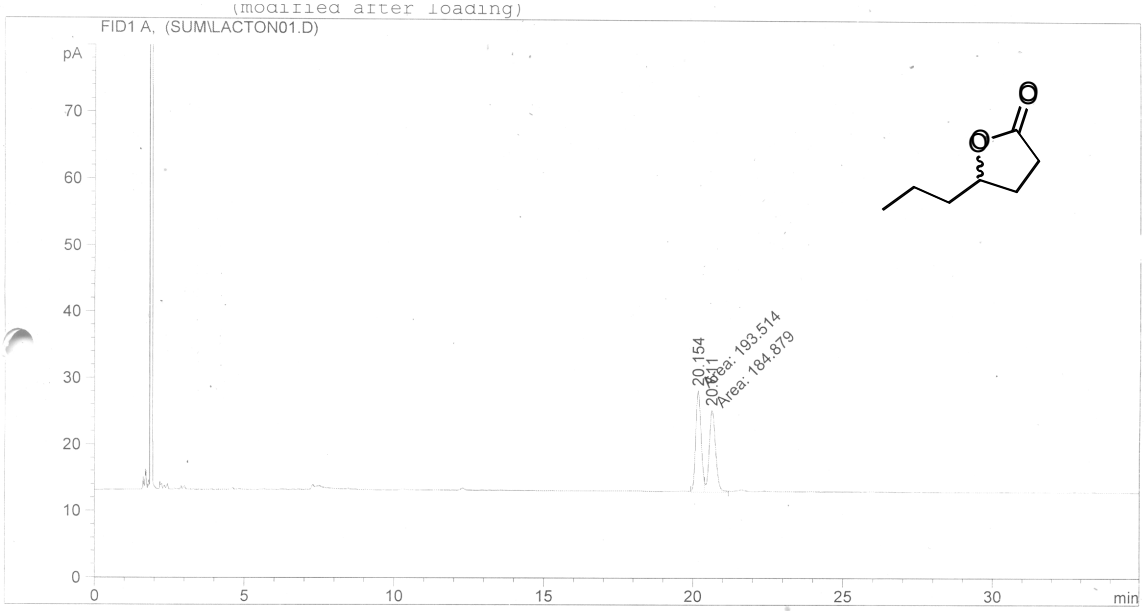

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Area Percent Report

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Dilution : 1.0000
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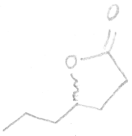
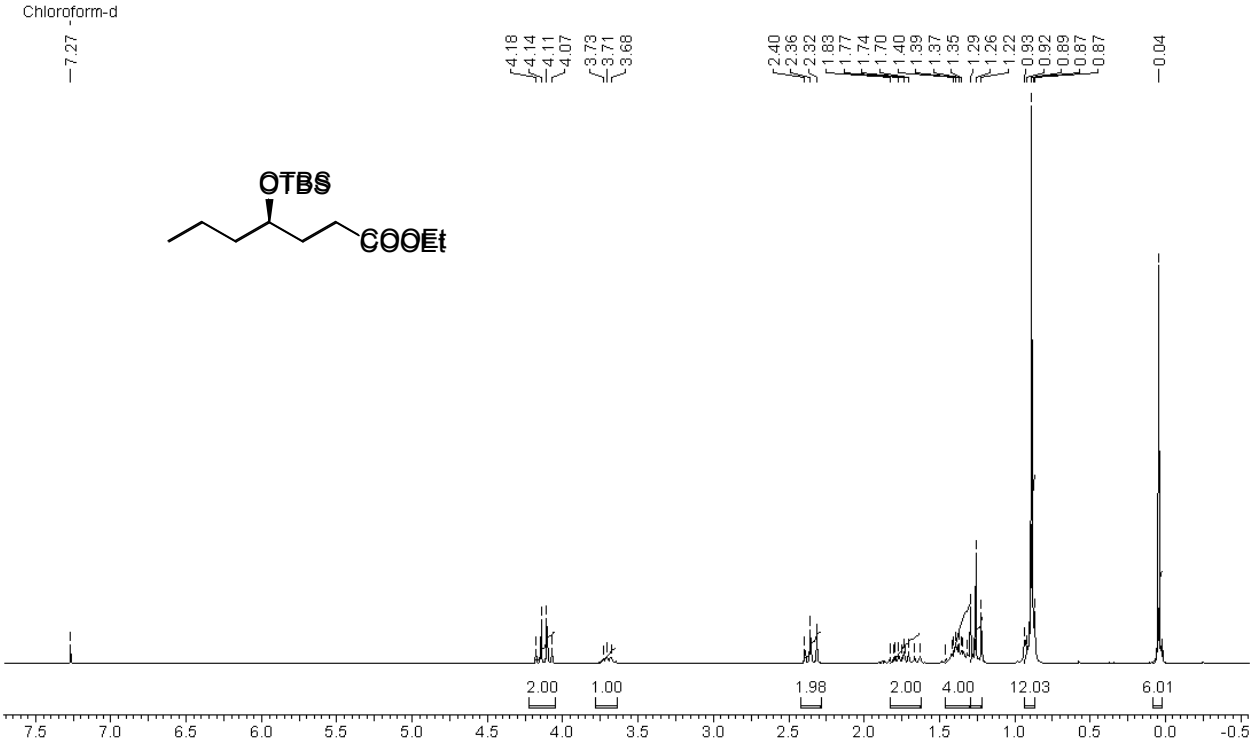
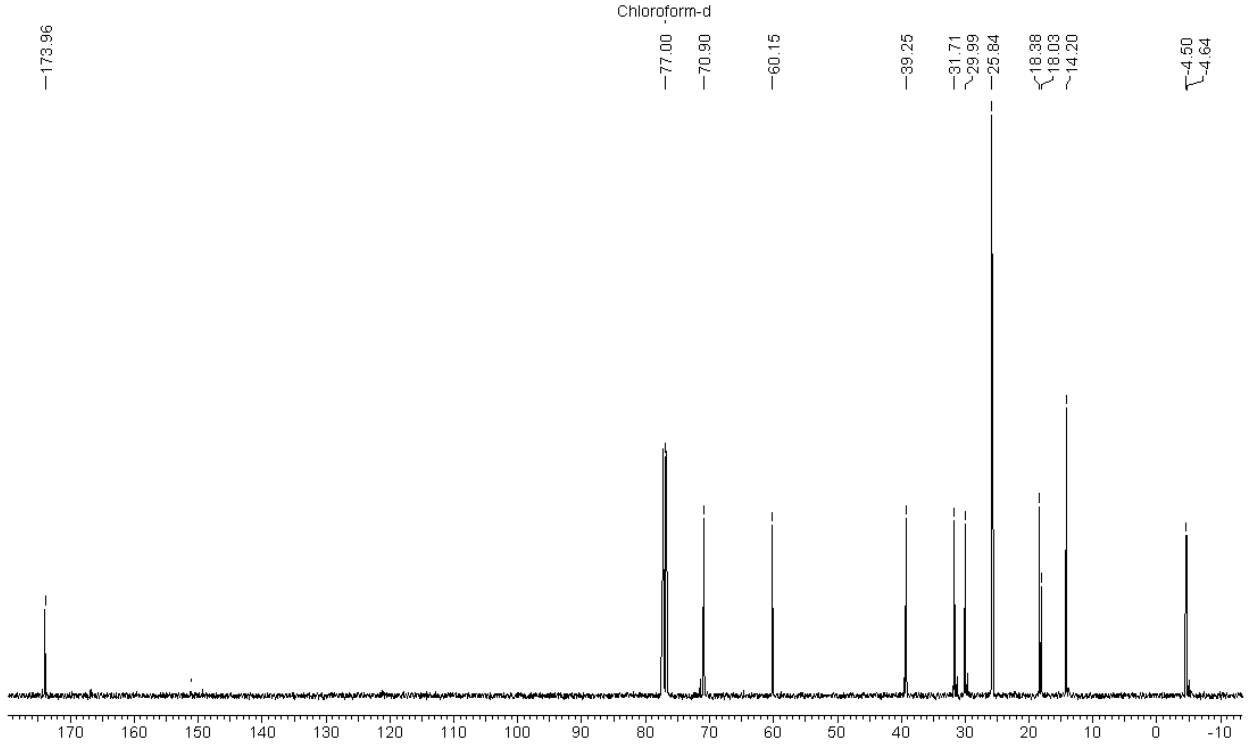


Signal 1: FID1 A,

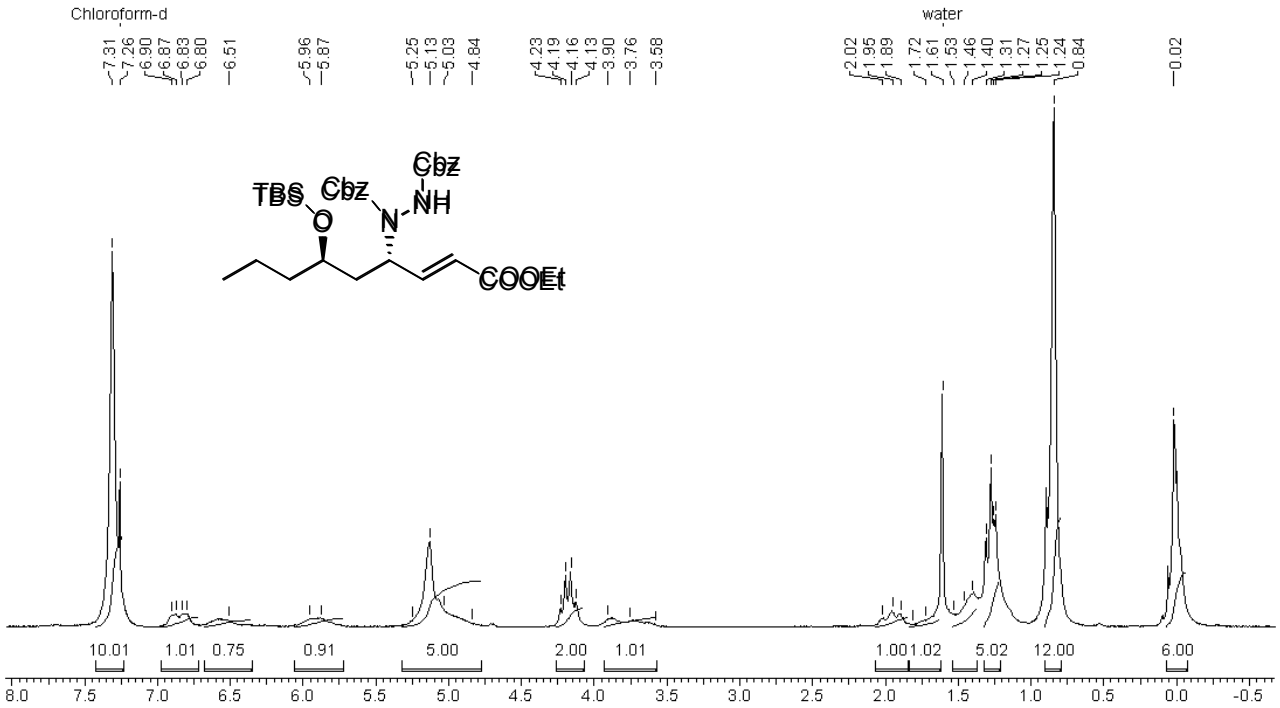
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.154	MF	0.2097	193.51364	15.37672	51.14102
2	20.611	FM	0.2495	184.87860	12.35137	48.85898

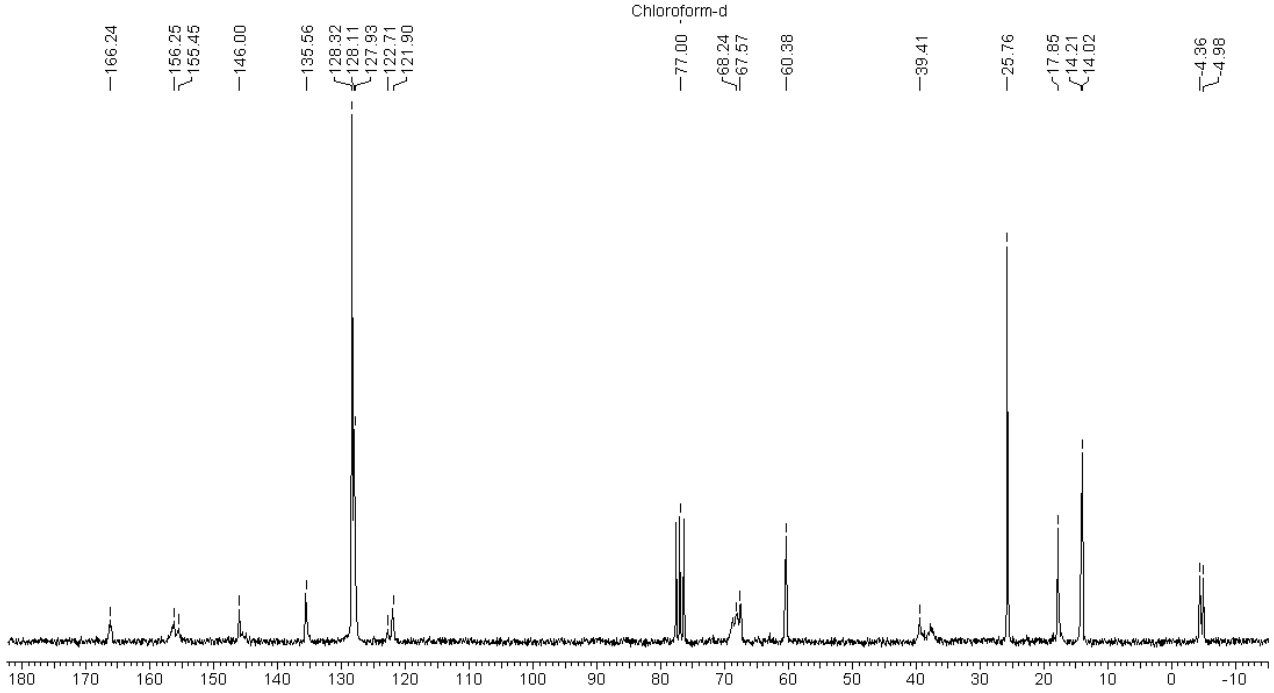
Ethyl (*R*)-4-((*tert*-butyldimethylsilyl)oxy)heptanoate (11):





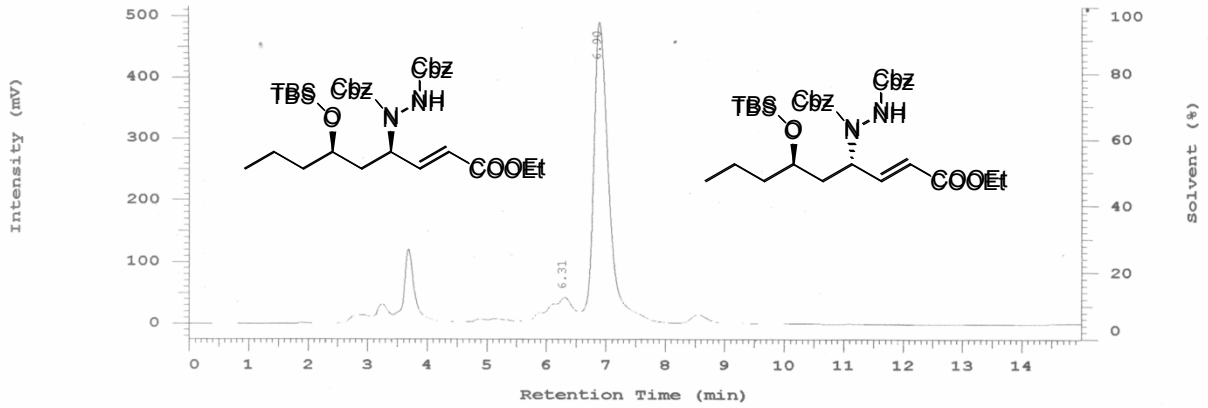
Dibenzyl 1-((4S,6R,E)-6-((*tert*-butyldimethylsilyl)oxy)-1-ethoxy-1-oxonon-2-en-4-yl)hydrazine-1,2-dicarboxylate (8):





Volume: 10.0 ul

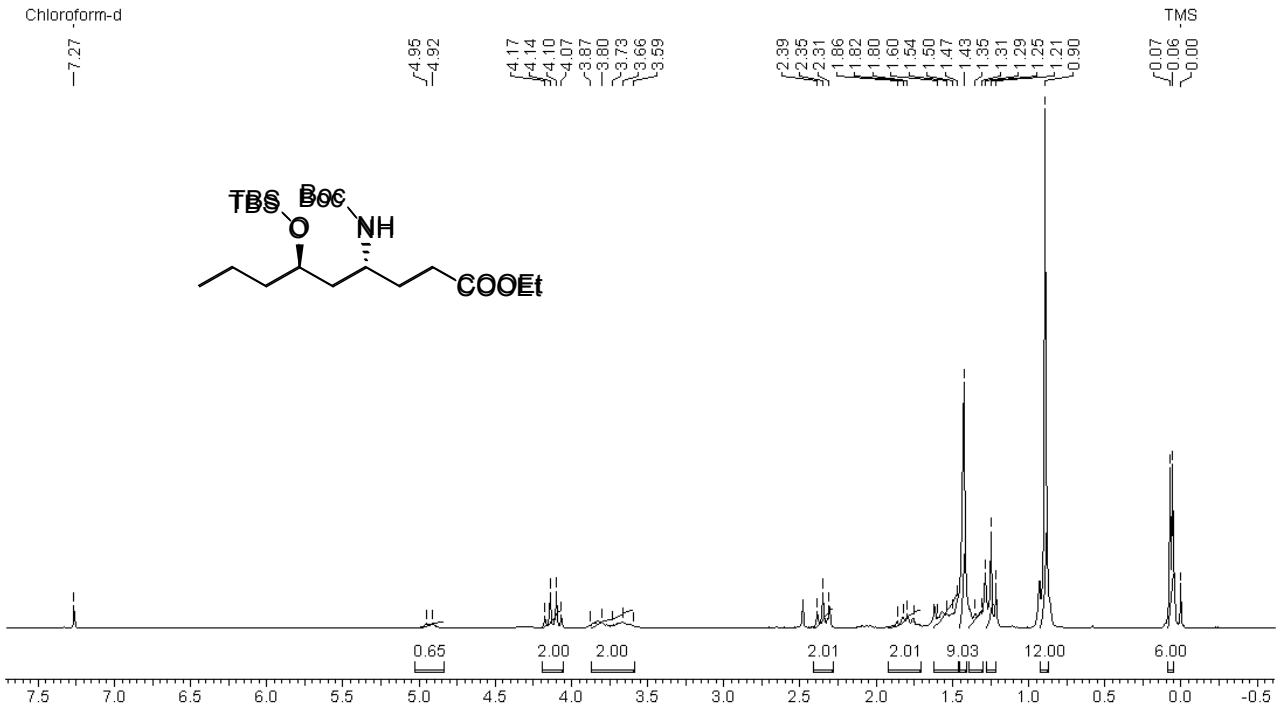
Chrom Type: HPLC Channel : 1

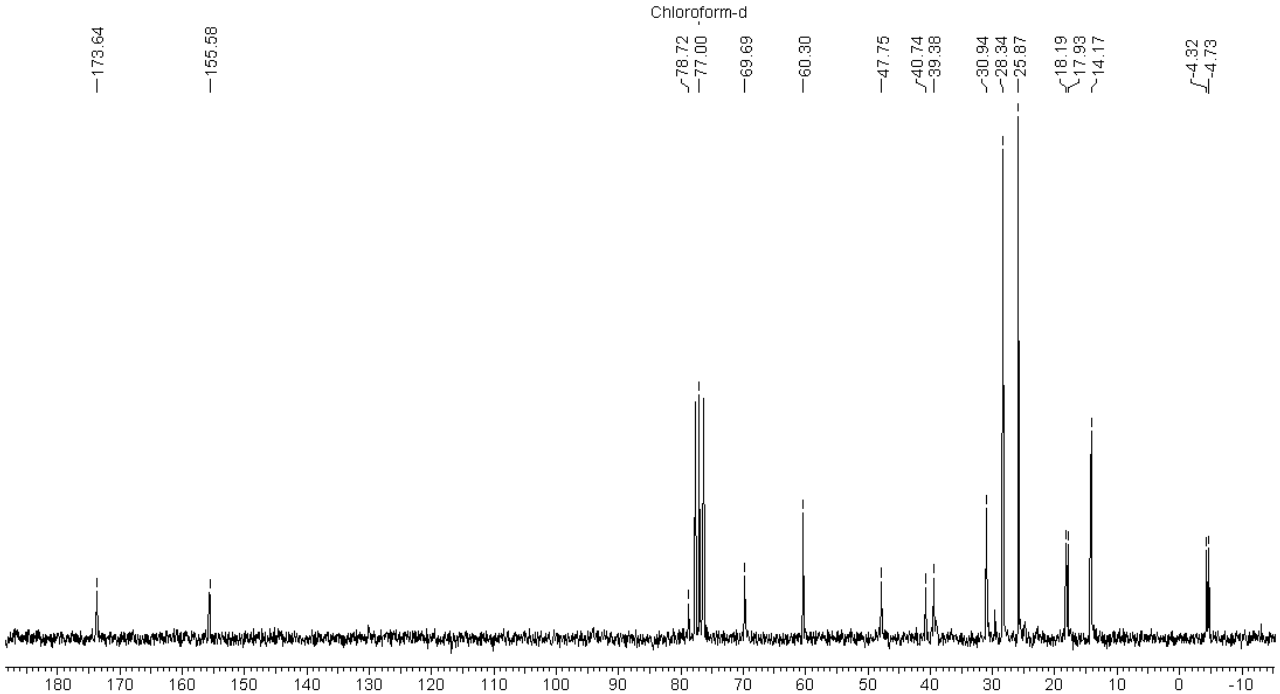


Peak Quantitation: AREA Calculation Method: AREA%

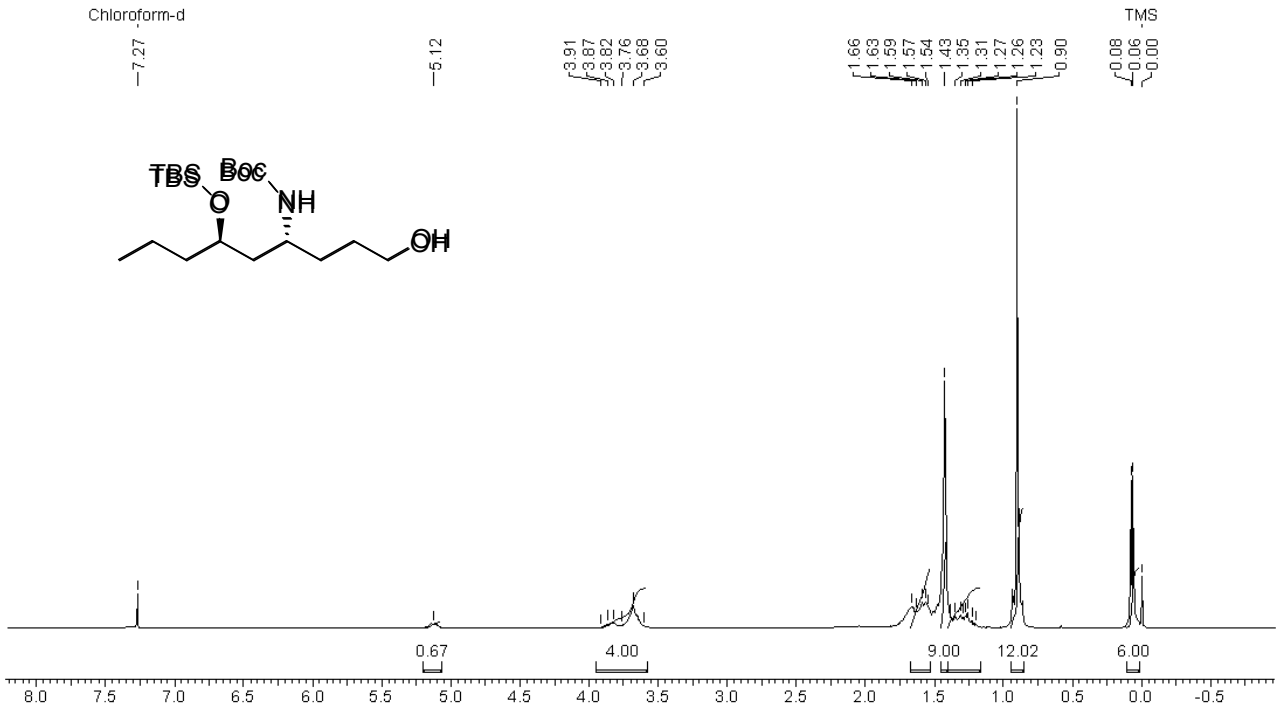
No.	RT	Height	Area	Area %
1	6.31	15473	153762	1.940
2	6.90	474211	7773316	98.060
		489684	7927078	100.000

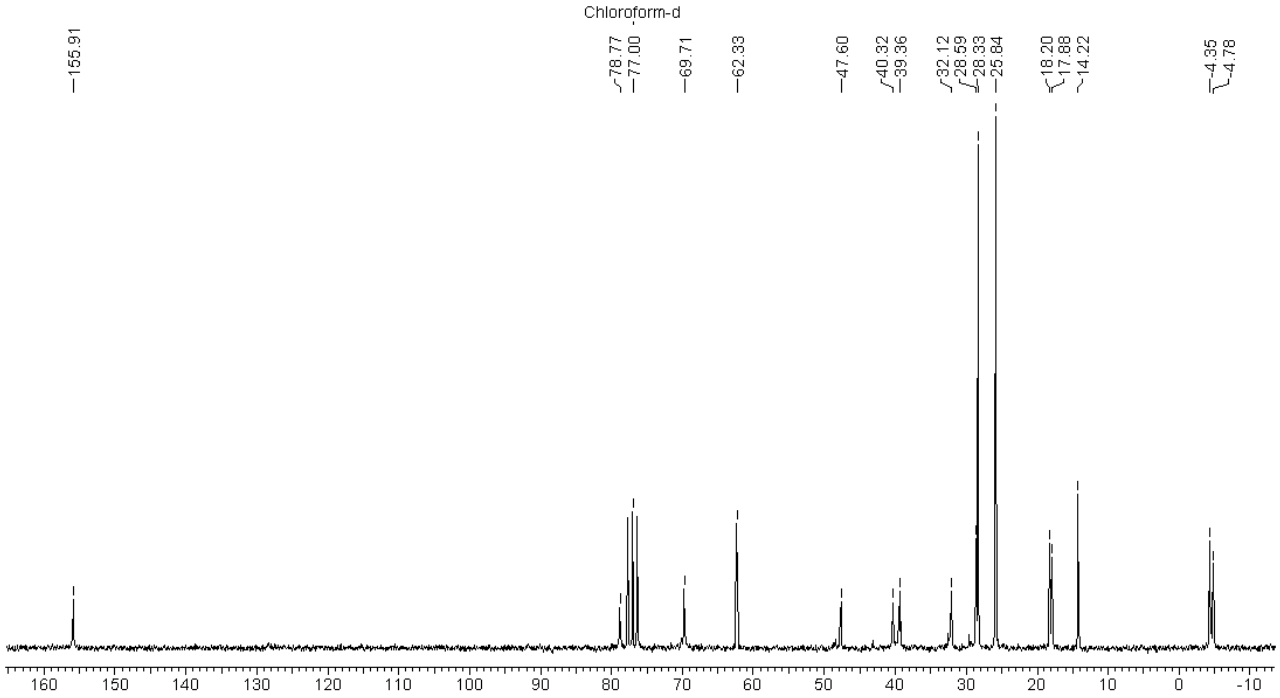
Ethyl (4*R*,6*R*)-4-((*tert*-butoxycarbonyl)amino)-6-((tert-butyldimethylsilyl)oxy)nonanoate (12):



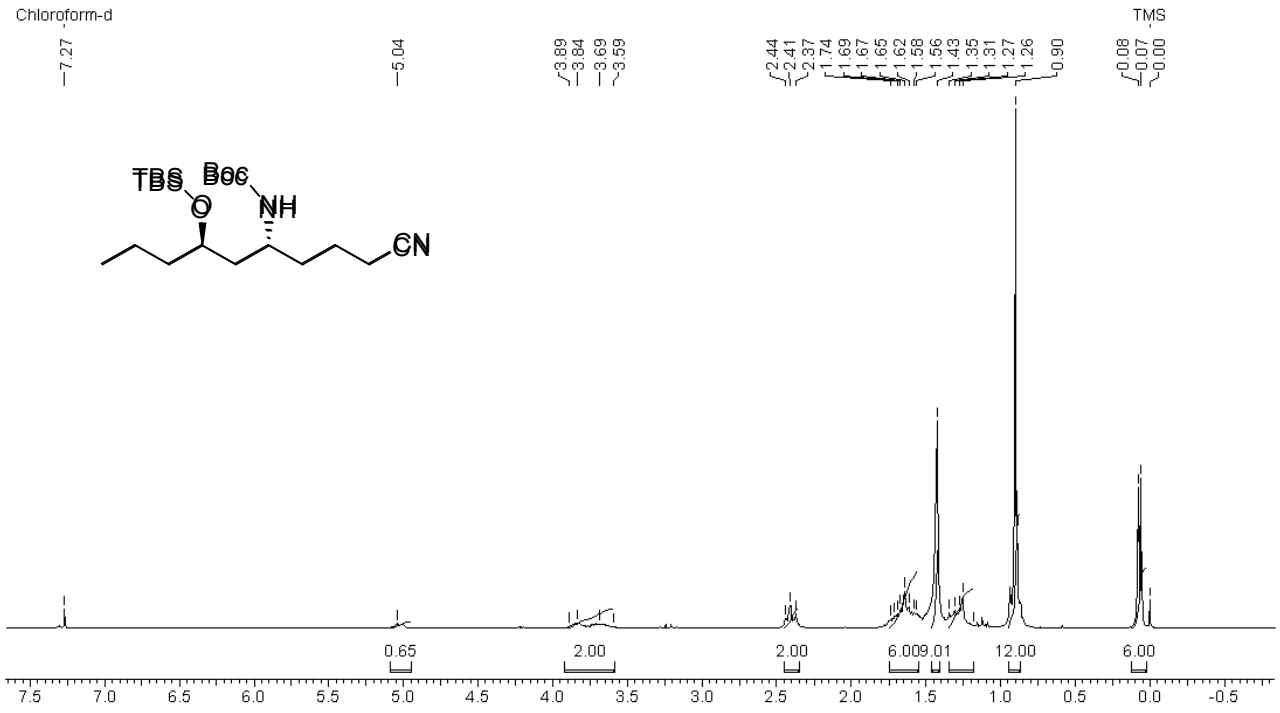


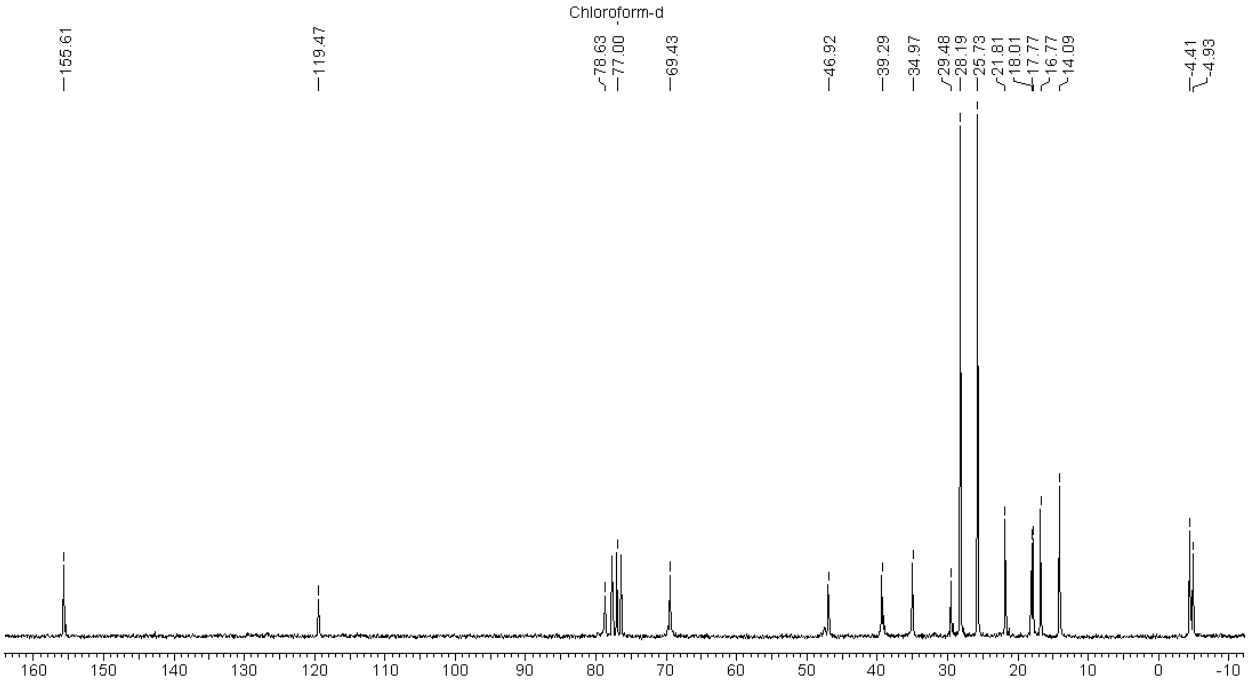
tert-Butyl ((4_R_,6_R_)-6-((_tert_-butyldimethylsilyl)oxy)-1-hydroxynonan-4-yl)carbamate (13):



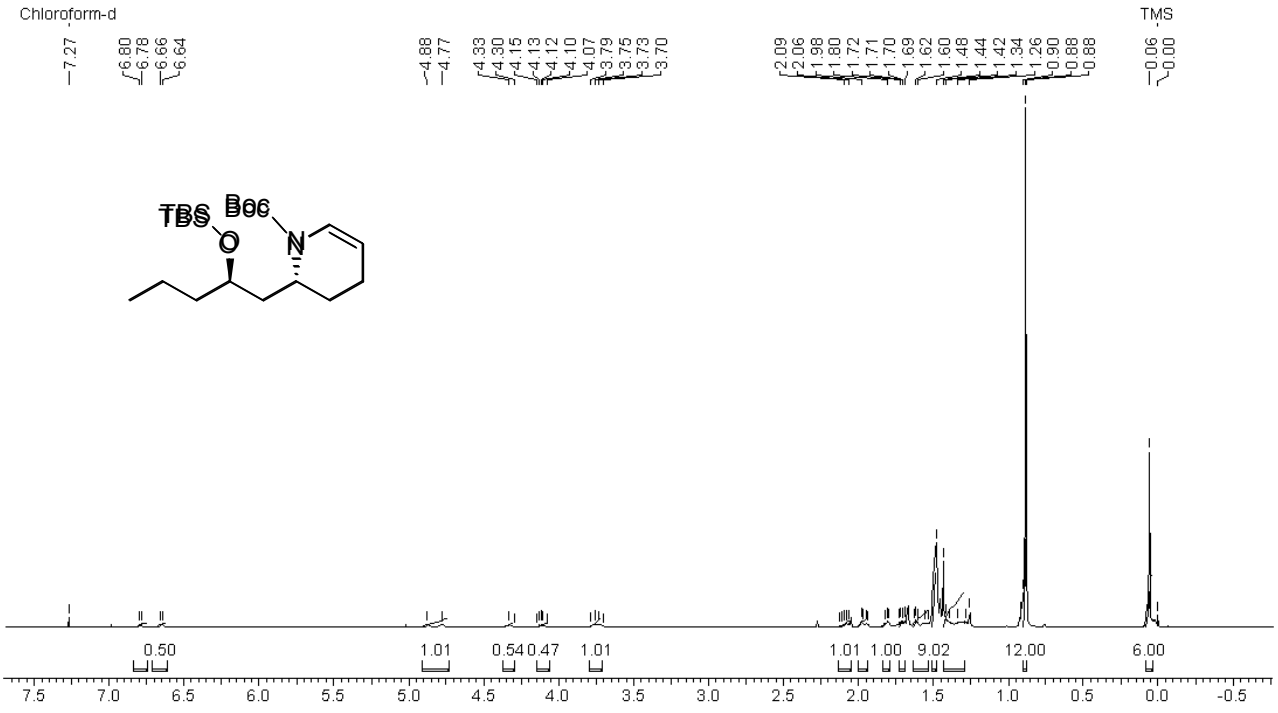


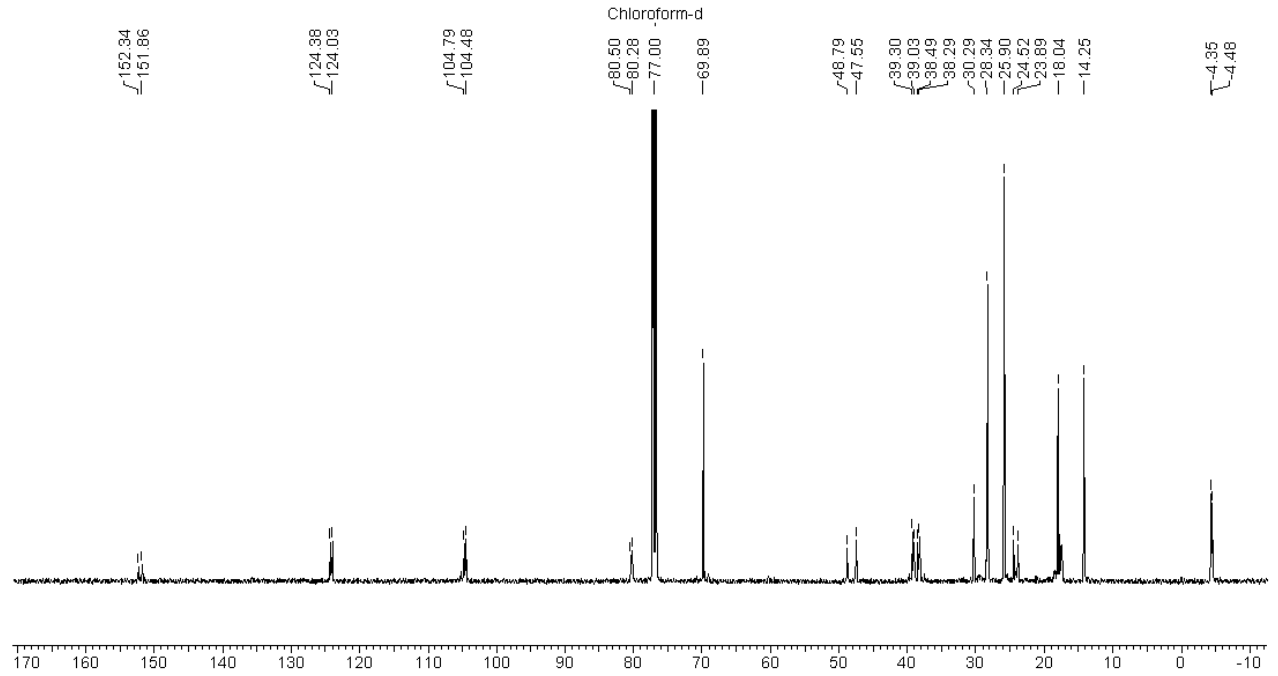
tert-Butyl ((4*R*,6*R*)-6-((_tert_-butyldimethylsilyl)oxy)-1-cyanononan-4-yl)carbamate (18):



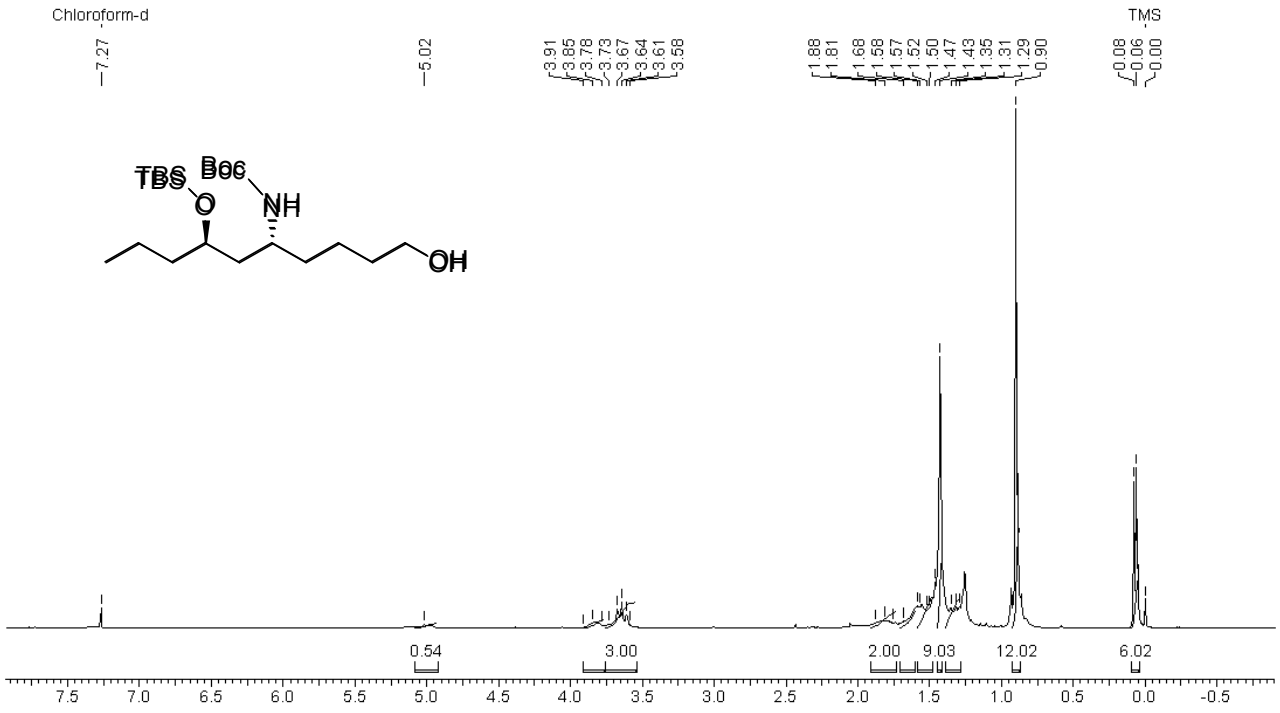


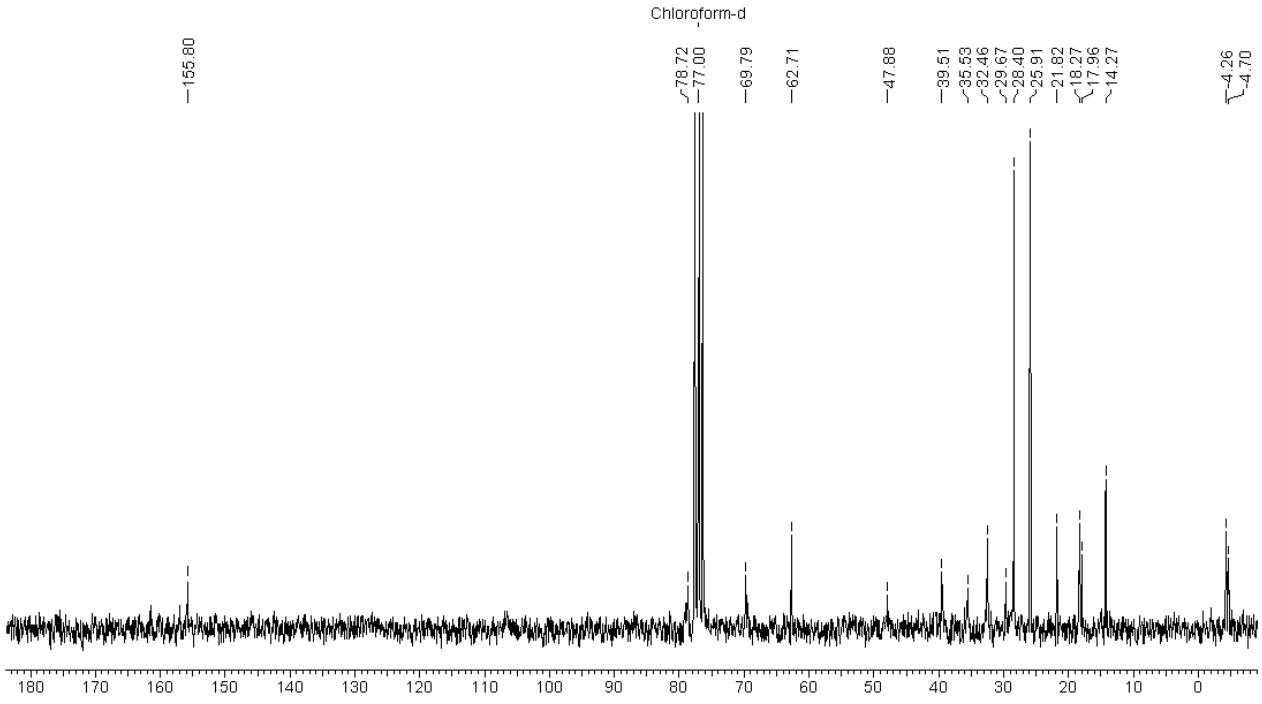
tert-Butyl (_R_)-2-((_R_)-2-((_tert_-butyldimethylsilyl)oxy)pentyl)-3,4-dihydropyridine-1(2H)-carboxylate (19):



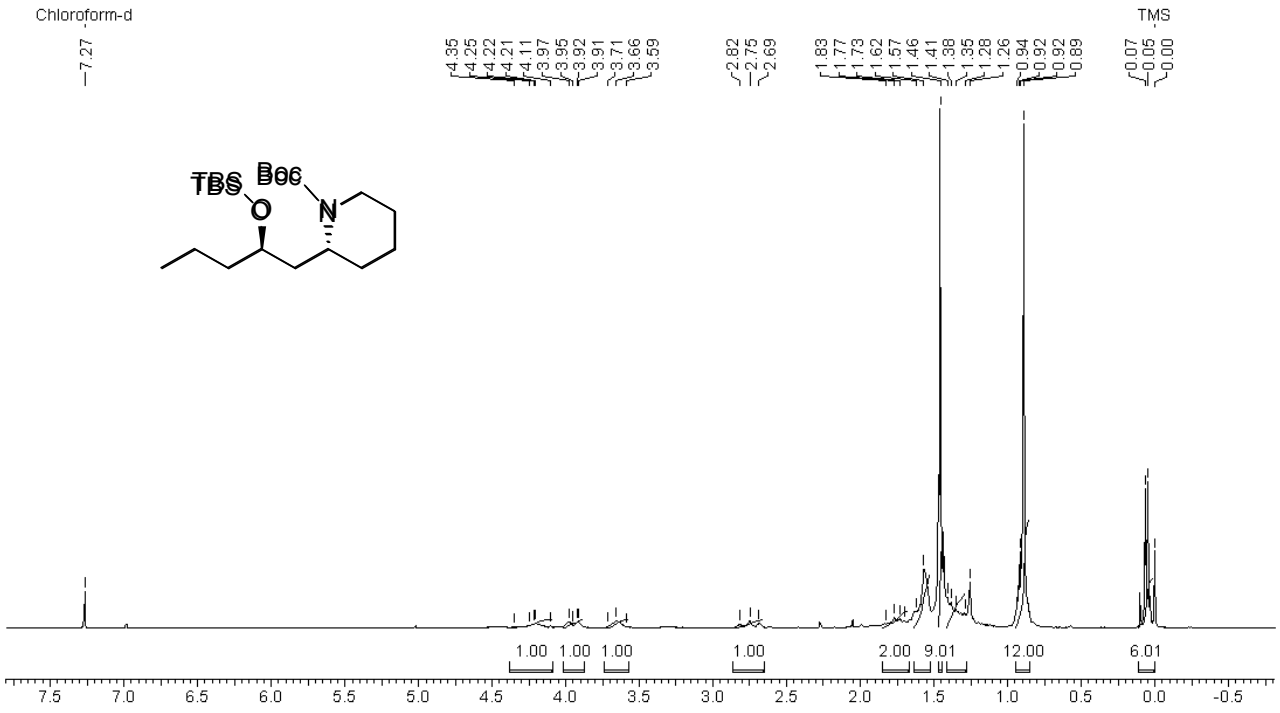


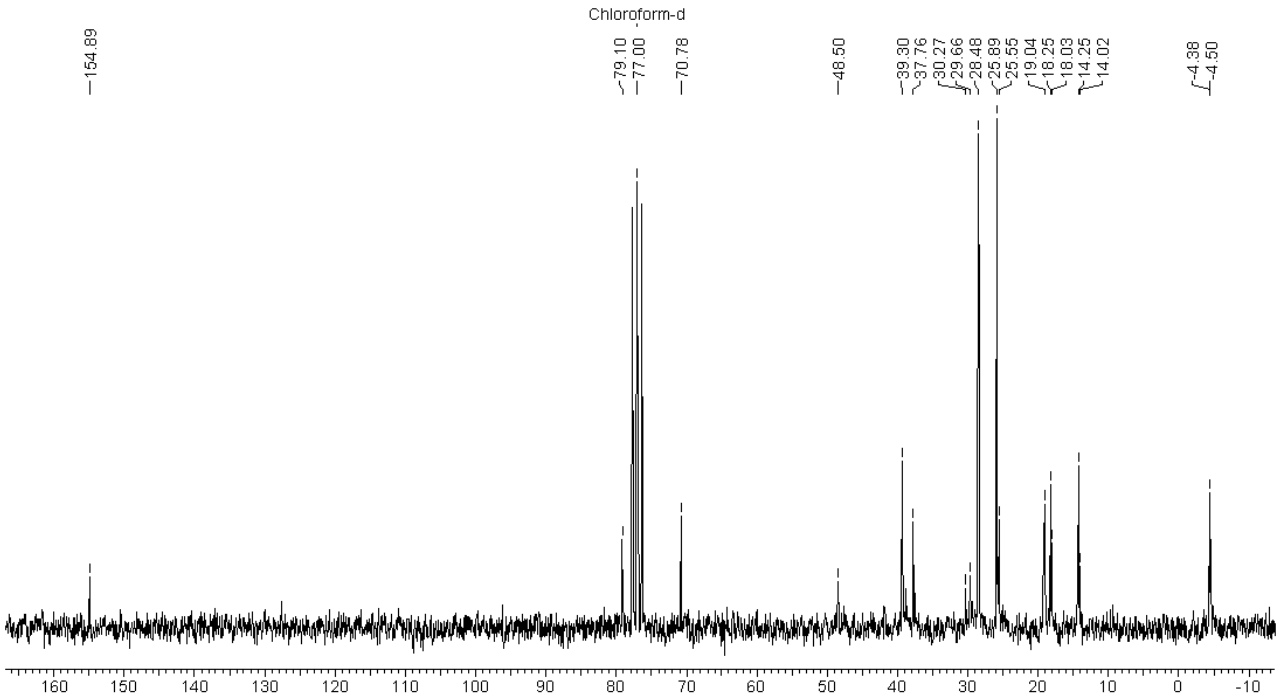
tert-Butyl ((5_R_,7_R_)-7-((_tert_-butyldimethylsilyl)oxy)-1-hydroxydecan-5-yl)carbamate (20):



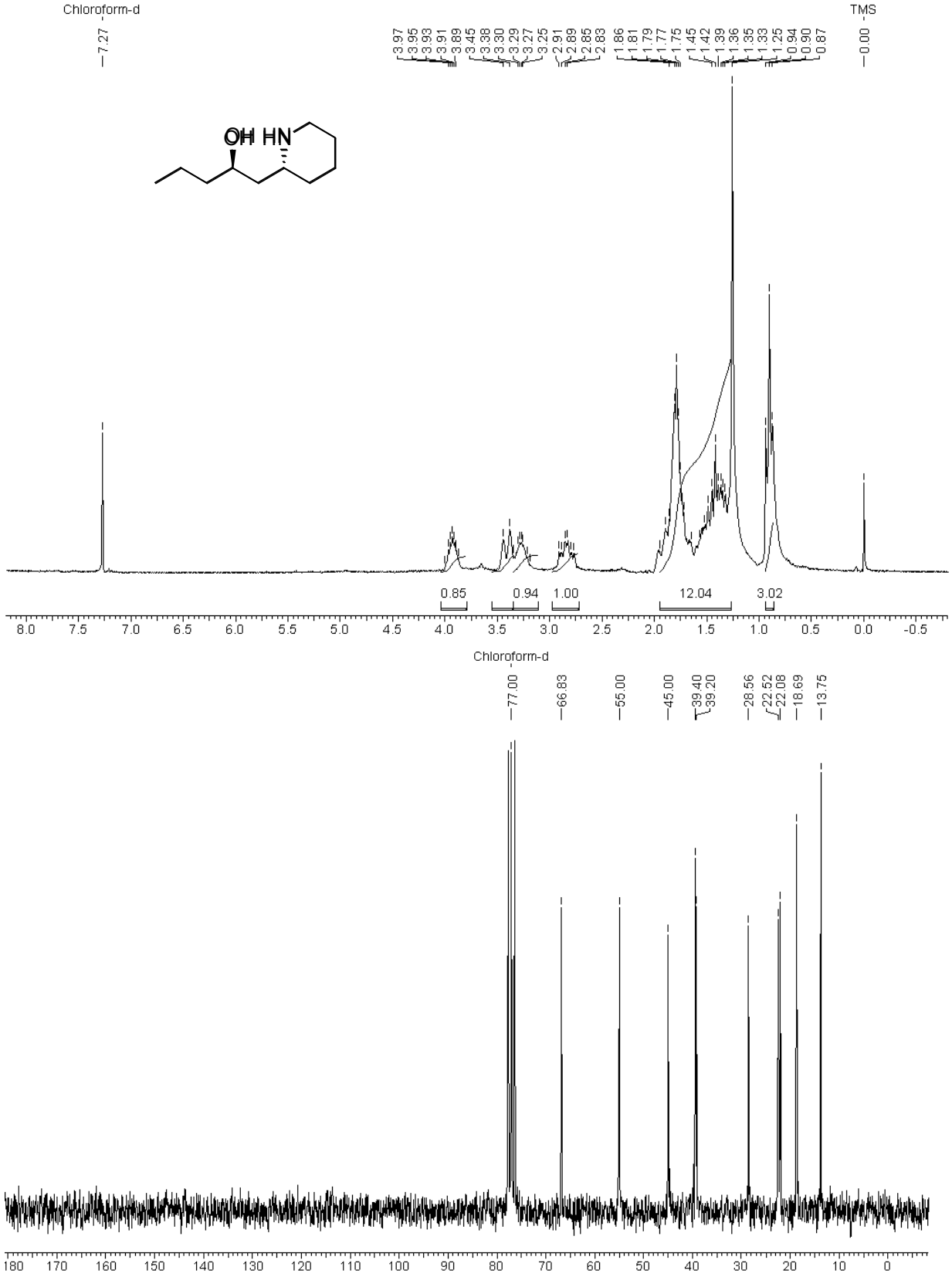


tert-Butyl (_R_)-2-((_R_)-2-((_tert_-butyldimethylsilyl)oxy)pentyl)piperidine-1-carboxylate (21):

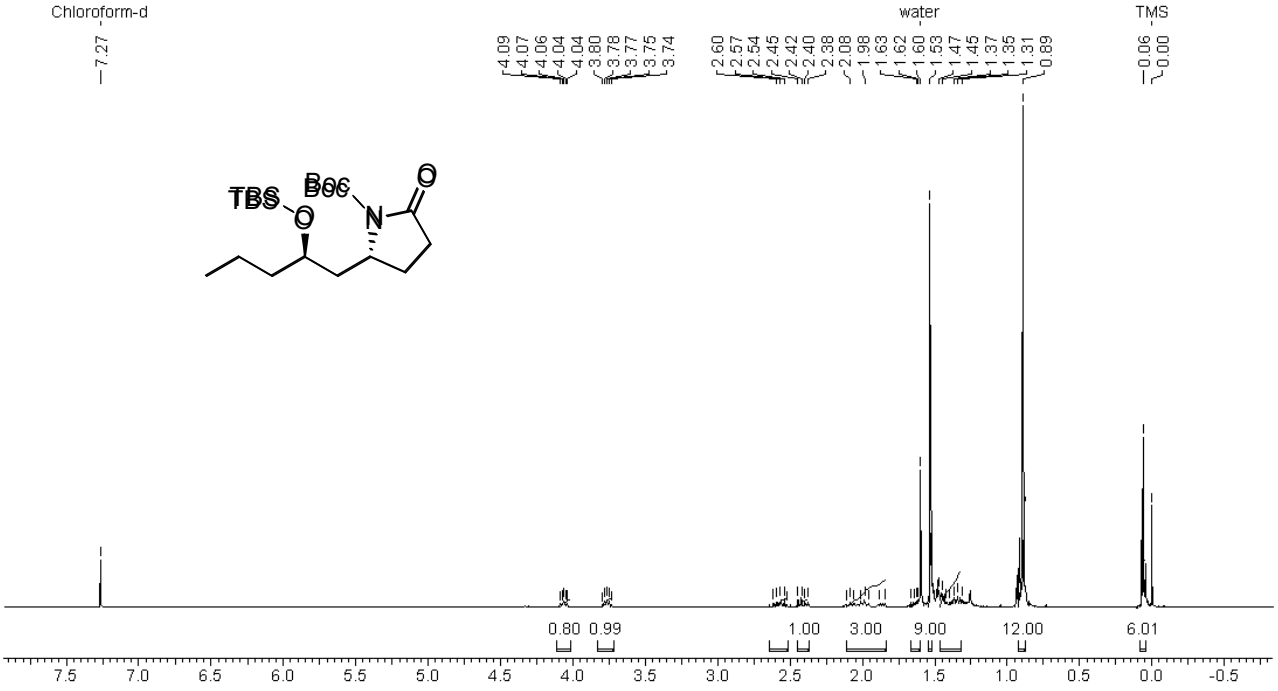


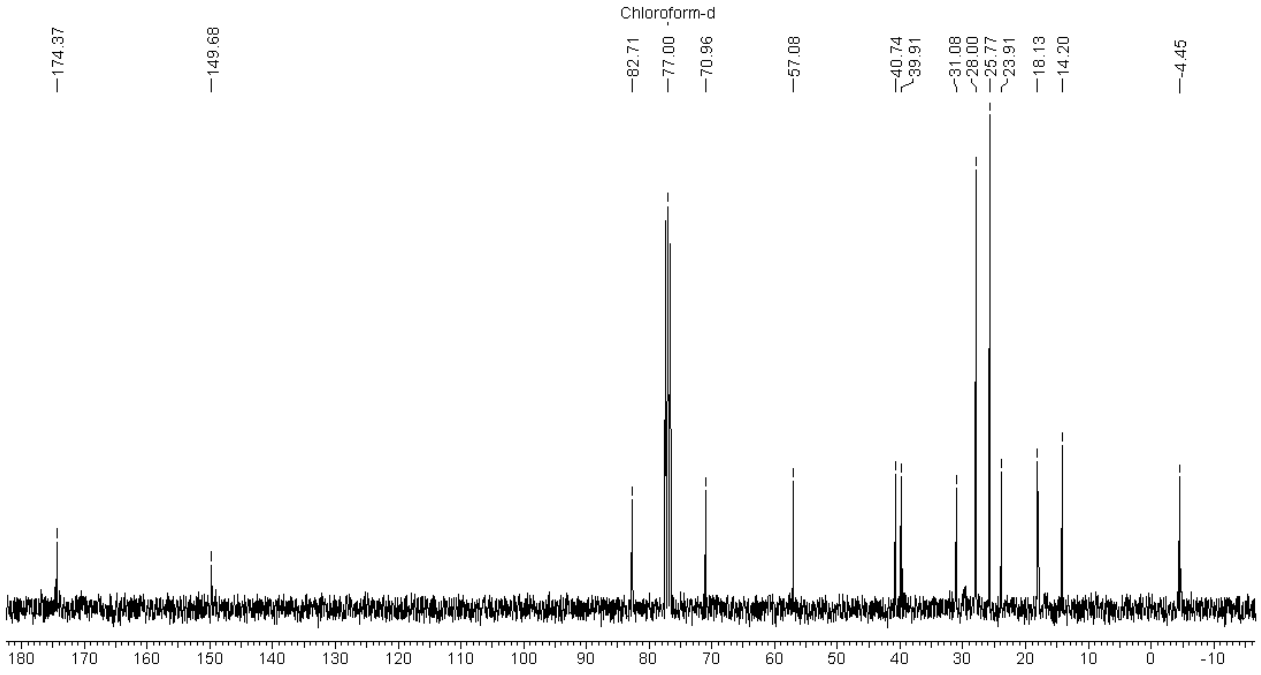


(-)-Halosaline (1):



***tert*-Butyl (*R*)-2-((*R*)-2-((*tert*-butyldimethylsilyl)oxy)pentyl)-5-oxopyrrolidine-1-carboxylate (17):**





tert-Butyl (_R_)-2-((_R_)-2-hydroxypentyl)pyrrolidine-1-carboxylate (15):