

**Electronic Supplementary Information for**

**Total Synthesis of Haliclamide**

Suraksha Gahalawat and Satyendra Kumar Pandey\*

*School of Chemistry and Biochemistry, Thapar University, Patiala 147001, India*

\*Corresponding Author: Phone: +91-175-239-3832, Fax No. +91-175-236-4498

E-mail address: [skpandey@thapar.edu](mailto:skpandey@thapar.edu)

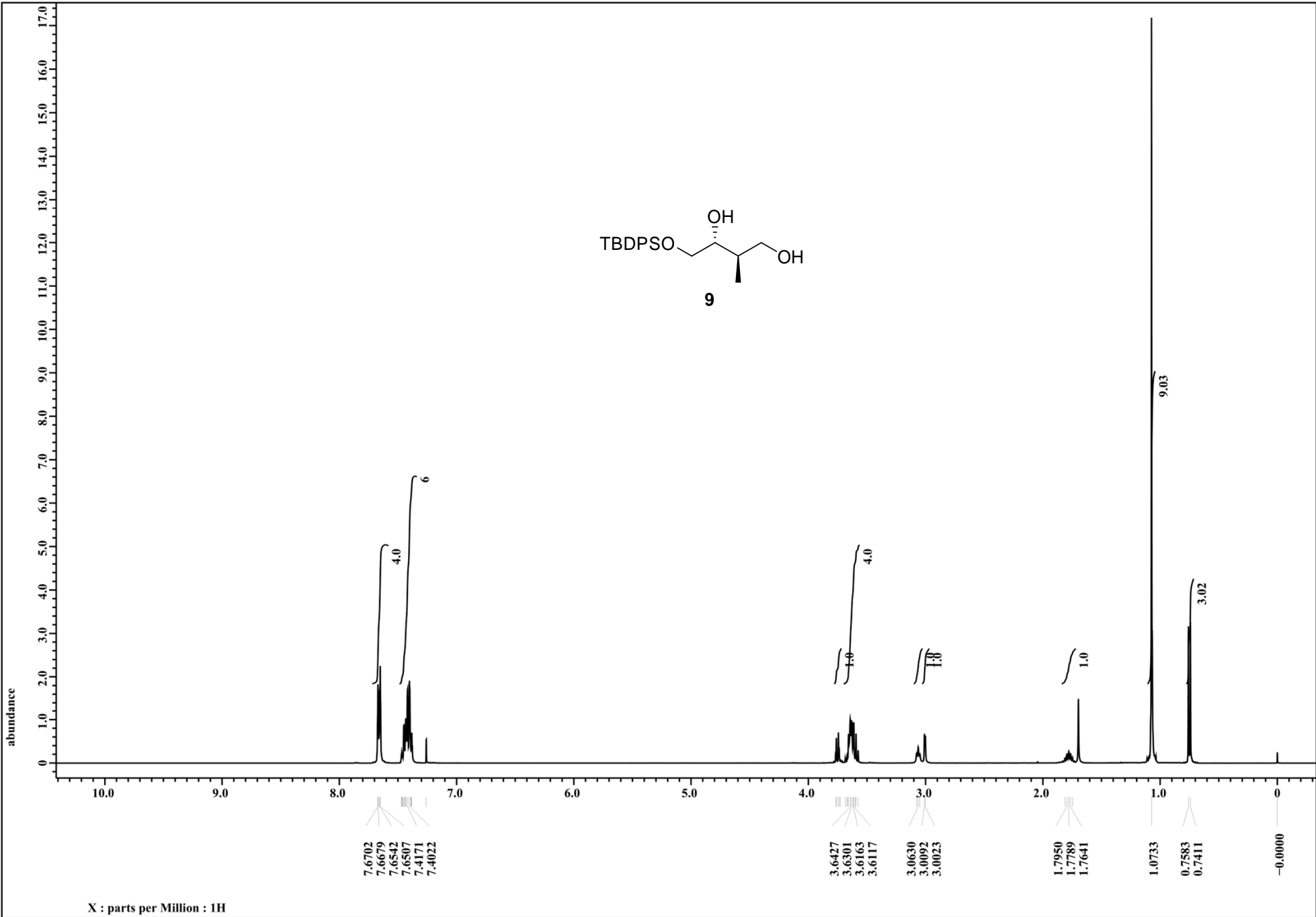
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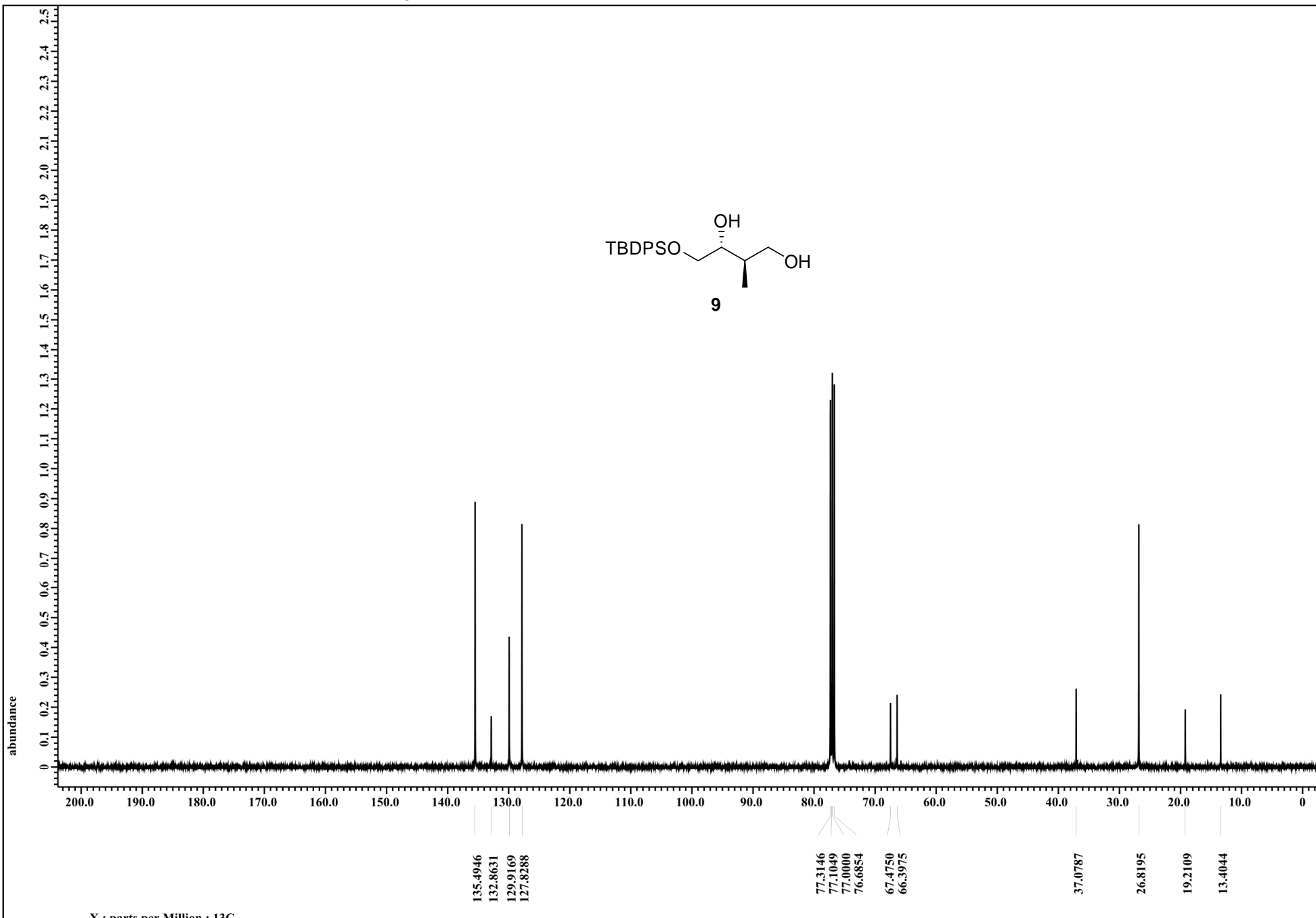
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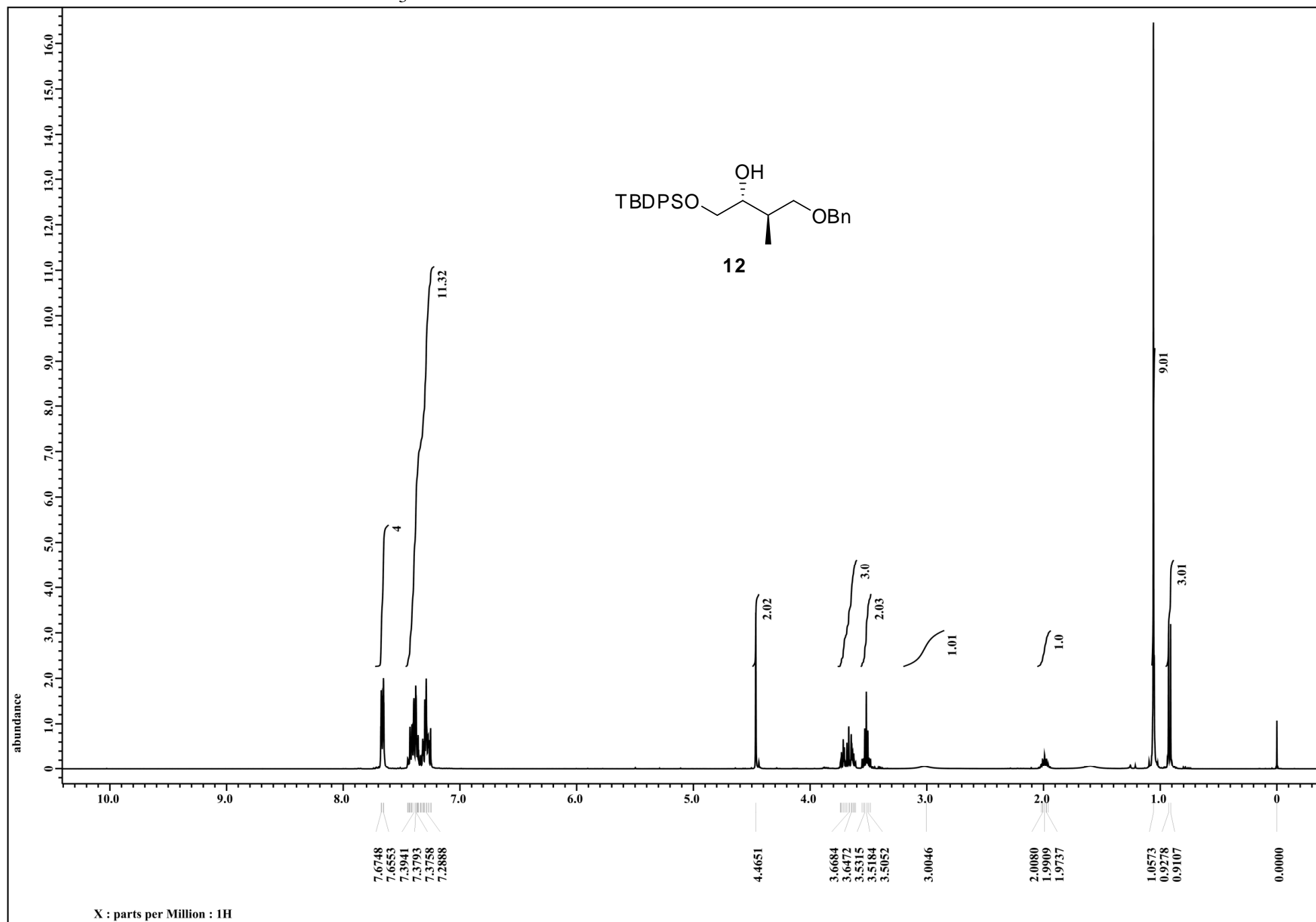
**General Information**

All reactions sensitive to air or moisture were carried out under nitrogen or argon atmosphere with anhydrous solvents. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR (400 and 100 MHz, respectively) spectra were recorded and chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, td = triplet of doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ESI-HRMS spectra were recorded on Mass Q-TOF.

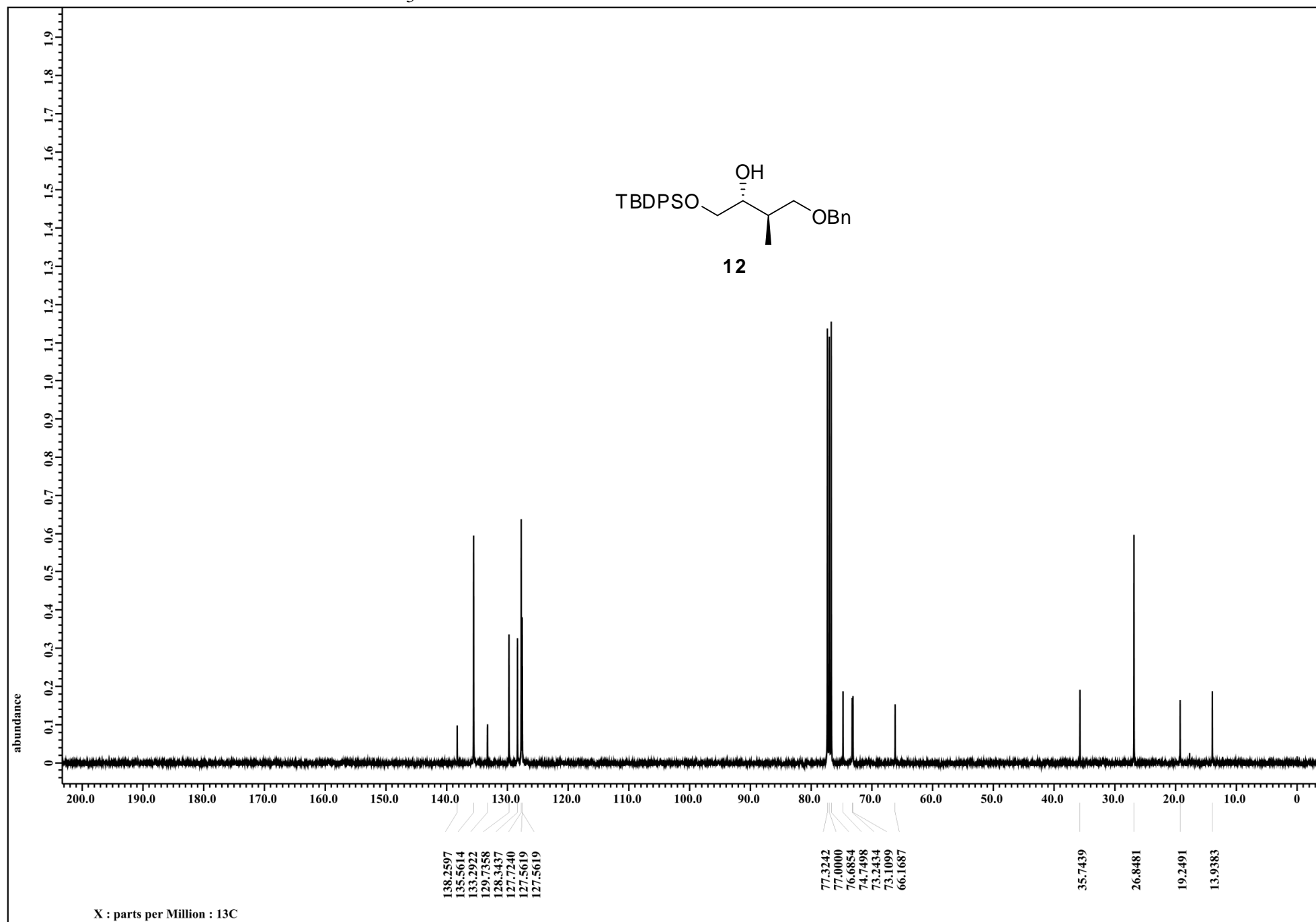
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

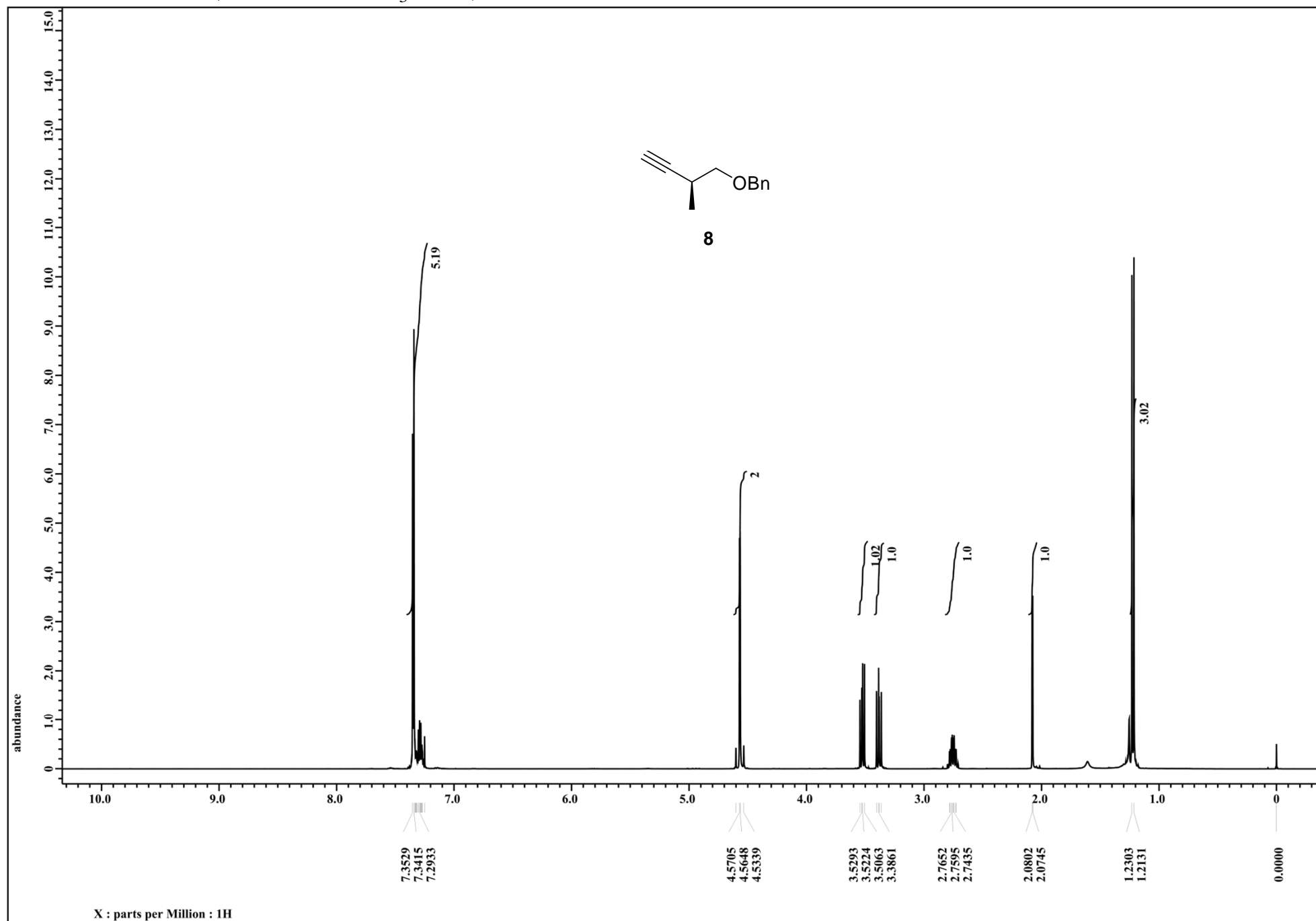
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )



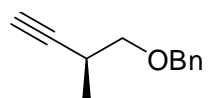
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



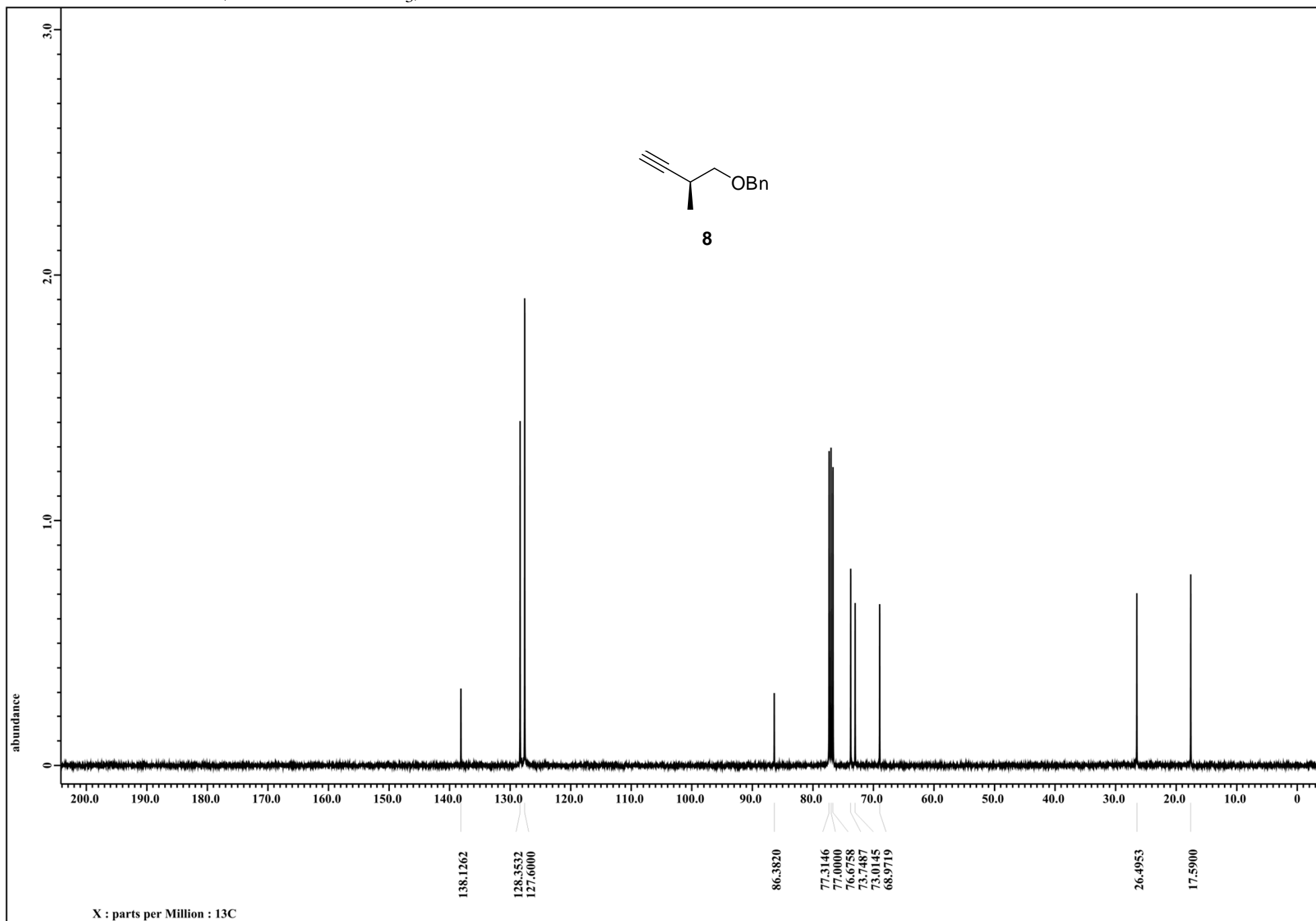
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



**8**



# Racemic 8

## D-7000 HPLC System Manager Report

Analyzed: 07/15/16 12:40 PM

Reported: 07/15/16 01:56 PM

Processed: 07/15/16 01:56 PM

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Processing Method: SANTOSHH

System(acquisition): Sys 1

Series:8991

Application: HPLC

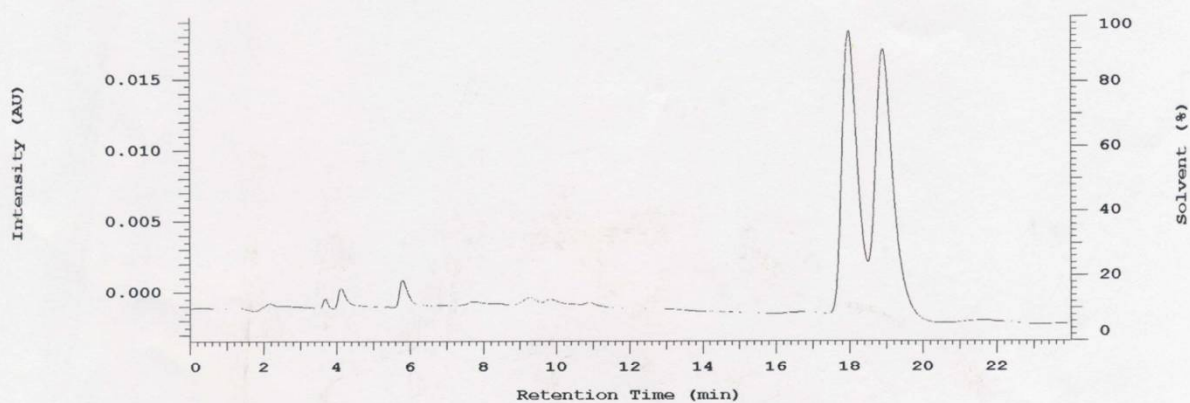
Volume: 10.0 ul

Sample Name: BENZYL-Rac

Injection from this vial: 1 of 1

Sample Description: MEOH:H2O (85:15)

Chrom Type: HPLC Channel : 1



No.	RT	Height	Area	Area %
1	17.97	9911	287710	48.144
2	18.90	9294	309894	51.856
		19205	597604	100.000

Peak rejection level: 0

COLUMN :chiralcel OJ-RH(150 X 4.6mm)  
MOBILE PHASE :-MEOH:H2O(85:15)  
WAVELENGTH :- 254nm  
FLOW RATE :- 0.5 ml/min (880 psi)  
SAMPLE CONC :-1 mg/1 ml Injection vol: 2 ul



# Chiral 8

## D-7000 HPLC System Manager Report

Analyzed: 07/15/16 01:09 PM

Reported: 07/15/16 01:55 PM

Processed: 07/15/16 01:55 PM

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Processing Method: SANTOSHH

System(acquisition): Sys 1

Series:8992

Application: HPLC

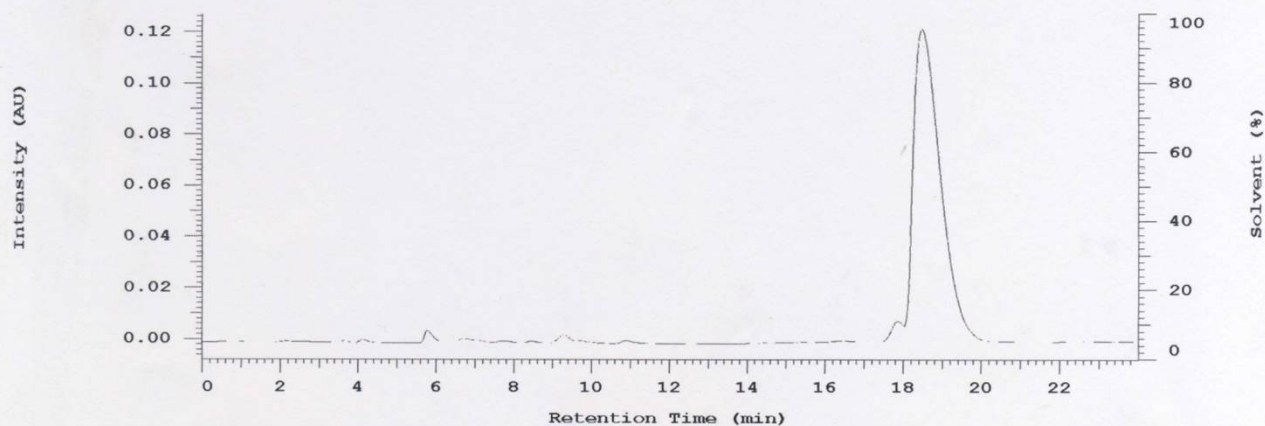
Volume: 10.0 ul

Sample Name: BENZYL-Chiral

Injection from this vial: 1 of 1

Sample Description: MEOH:H2O(85:15)

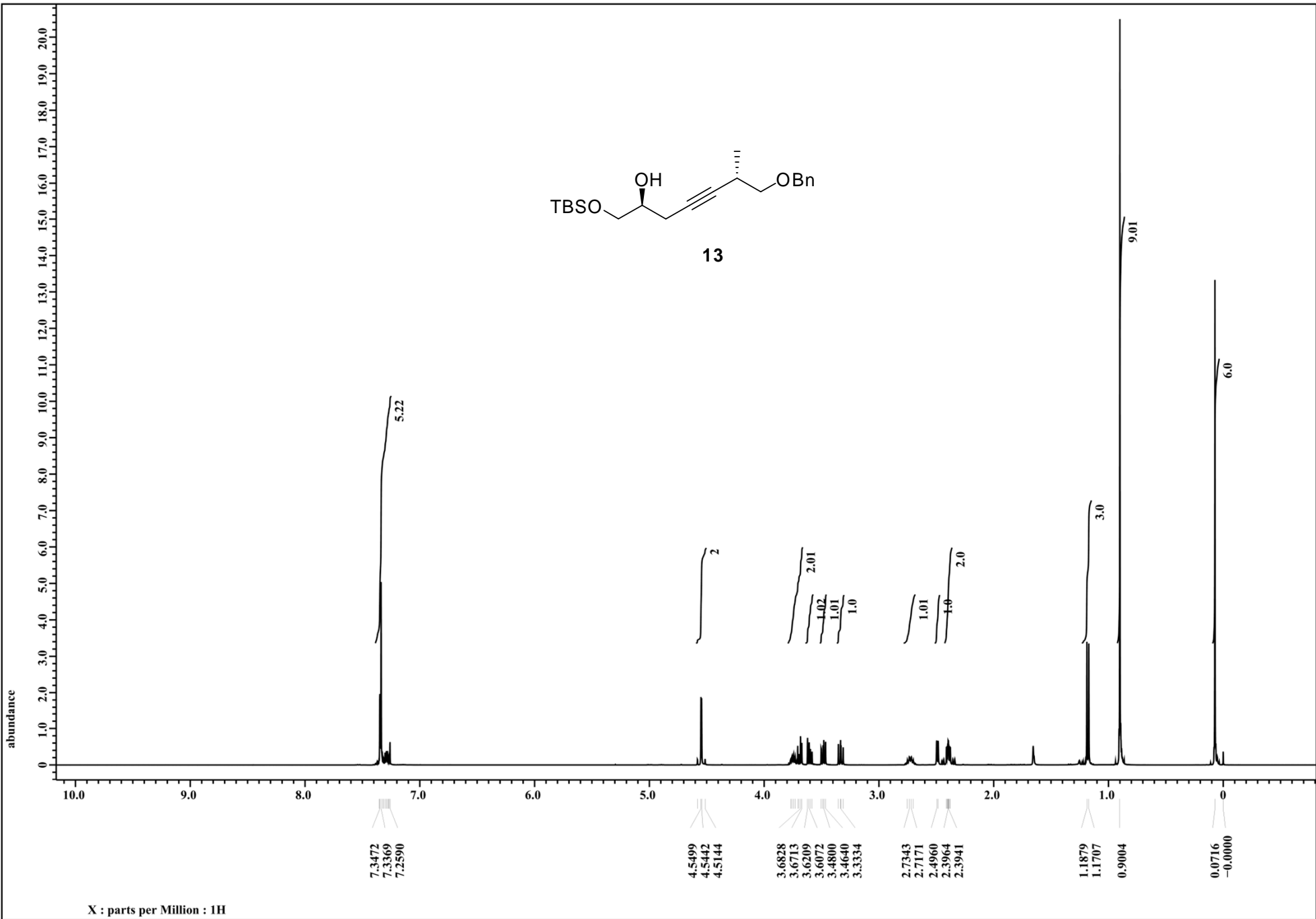
Chrom Type: HPLC Channel : 1



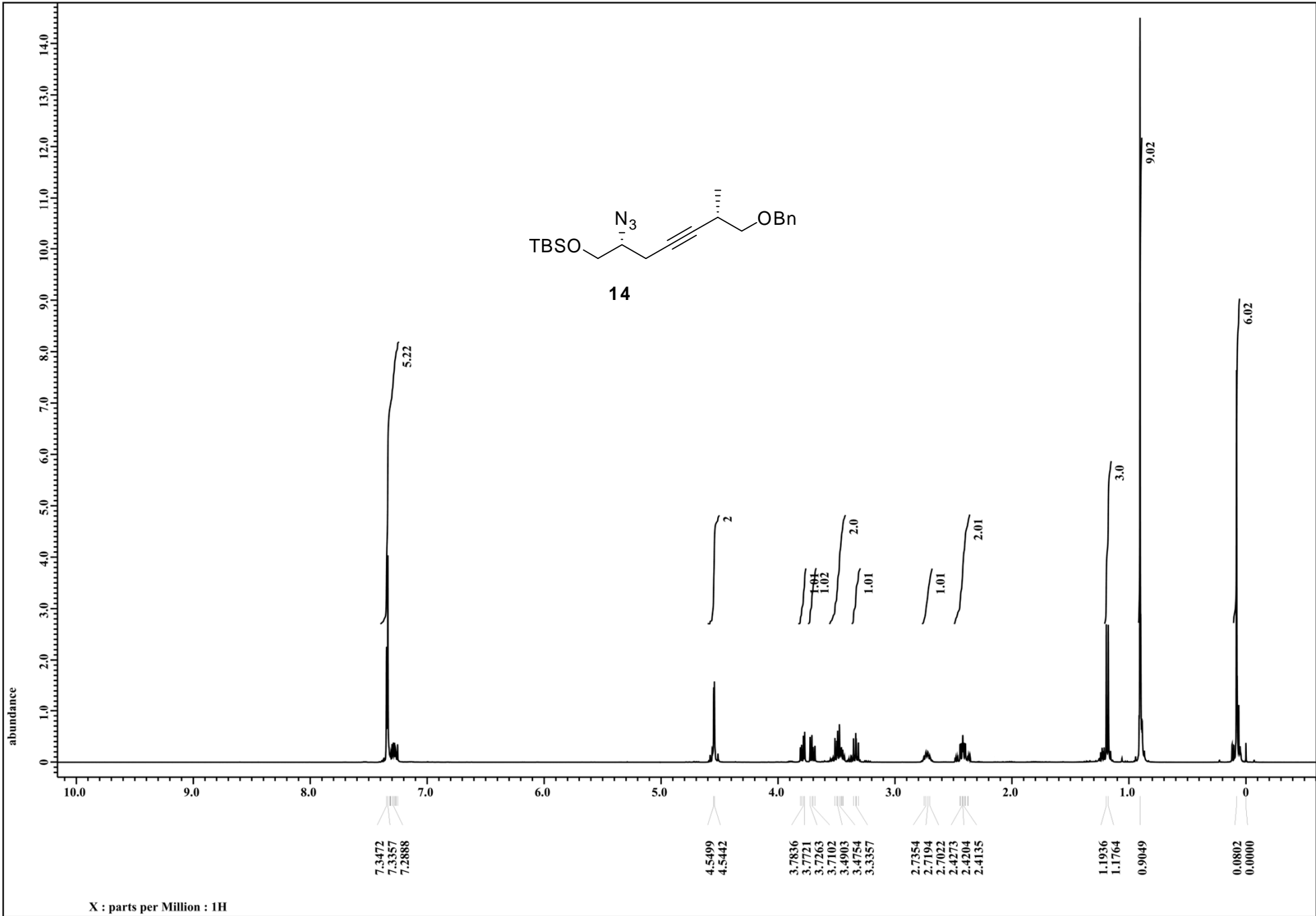
No.	RT	Height	Area	Area %
1	17.87	3947	76375	2.565
2	18.48	60703	2900988	97.435
		64650	2977363	100.000

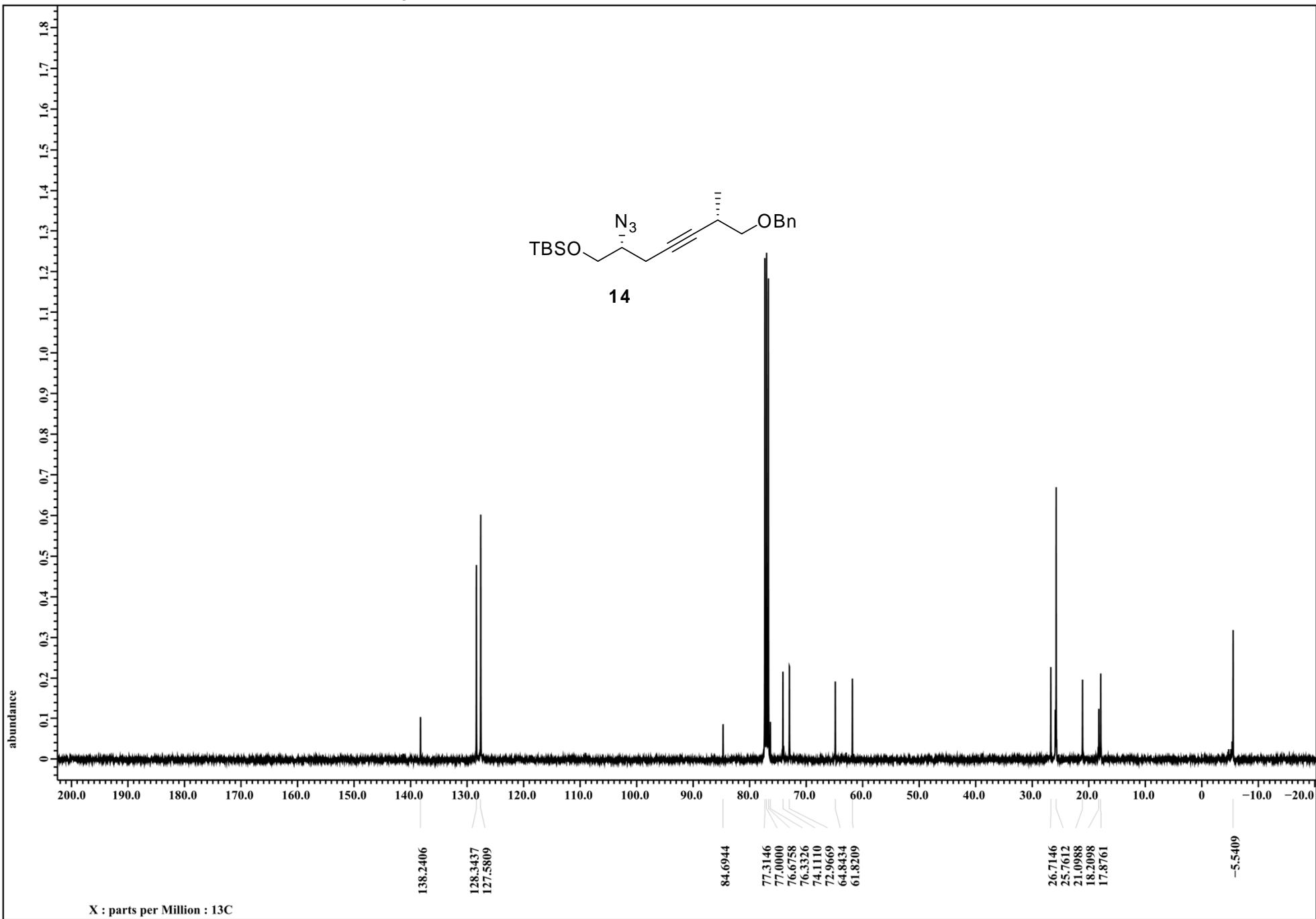
Peak rejection level: 0

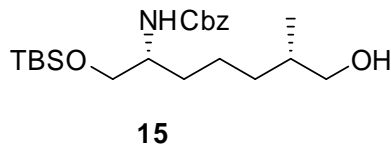
COLUMN :chiralcel OJ-RH(150 X 4.6mm)  
MOBILE PHASE :-MEOH:H2O(85:15)  
WAVELENGTH :- 254nm  
FLOW RATE :- 0.5 ml/min (880 psi)  
SAMPLE CONC :-1 mg/1 ml Injection vol: 2 ul

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

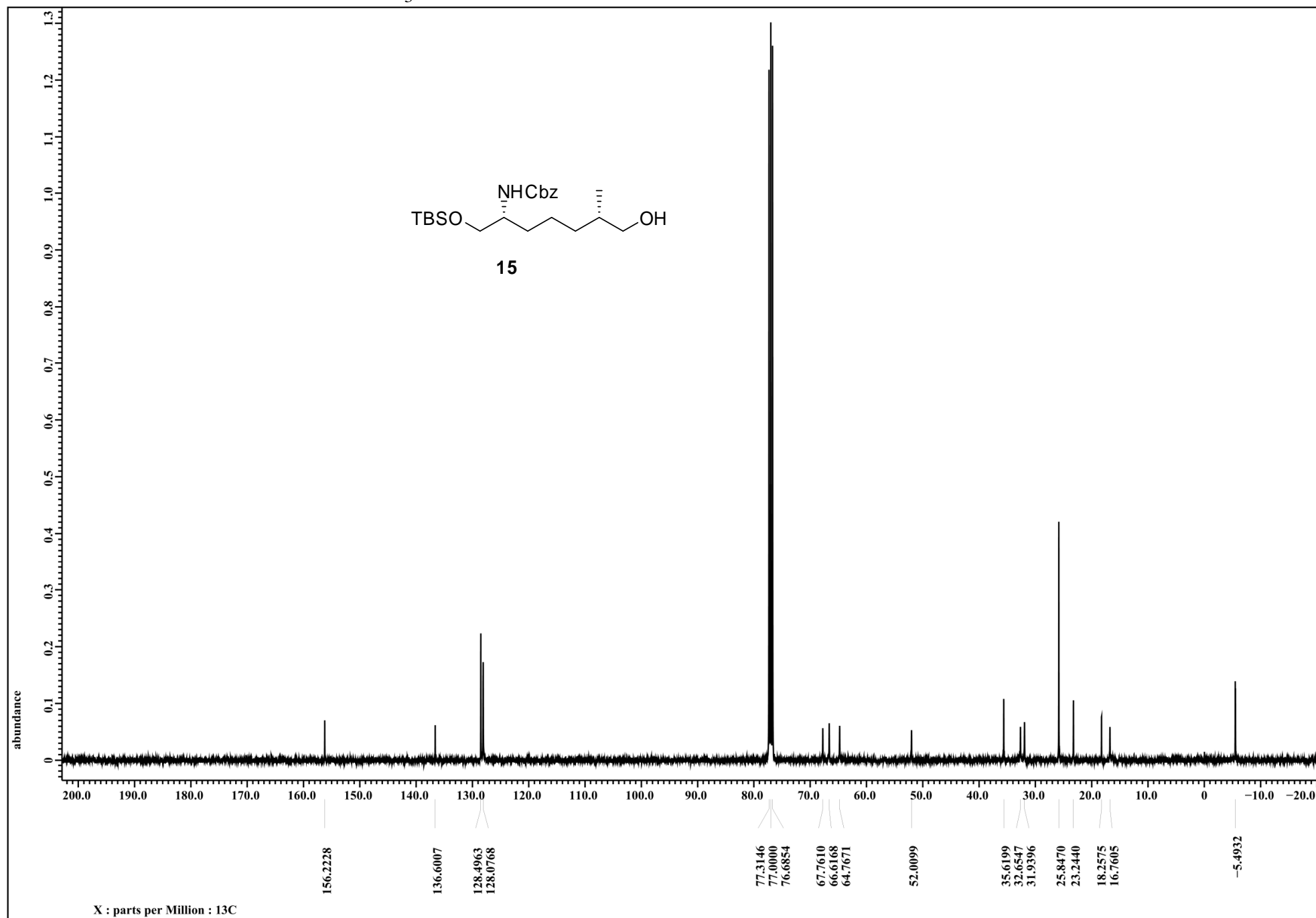
[illegible]

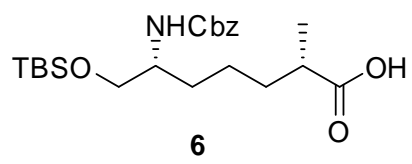
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

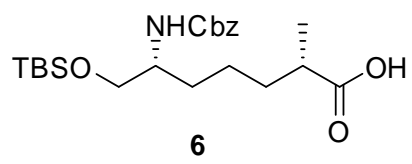
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

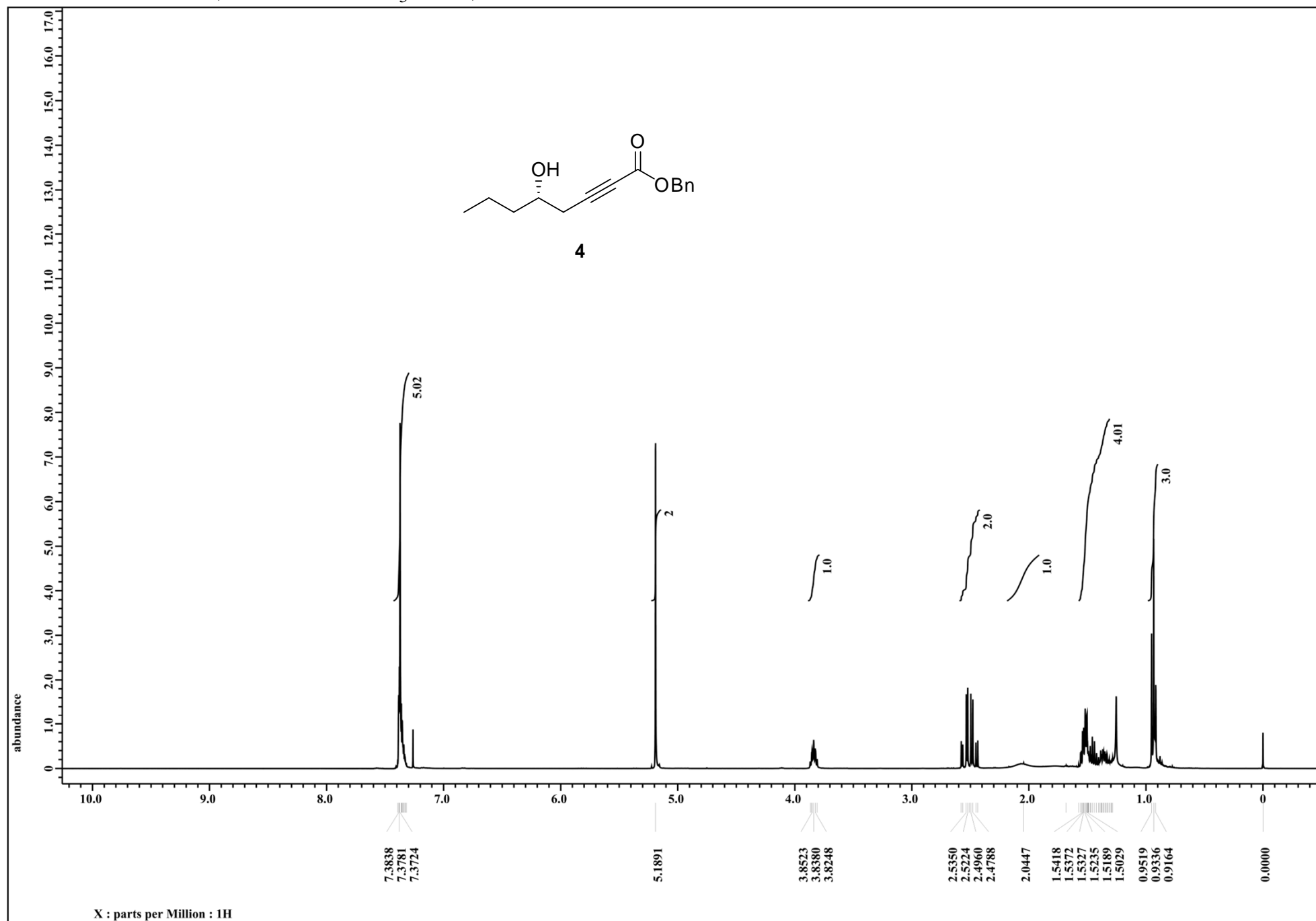


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

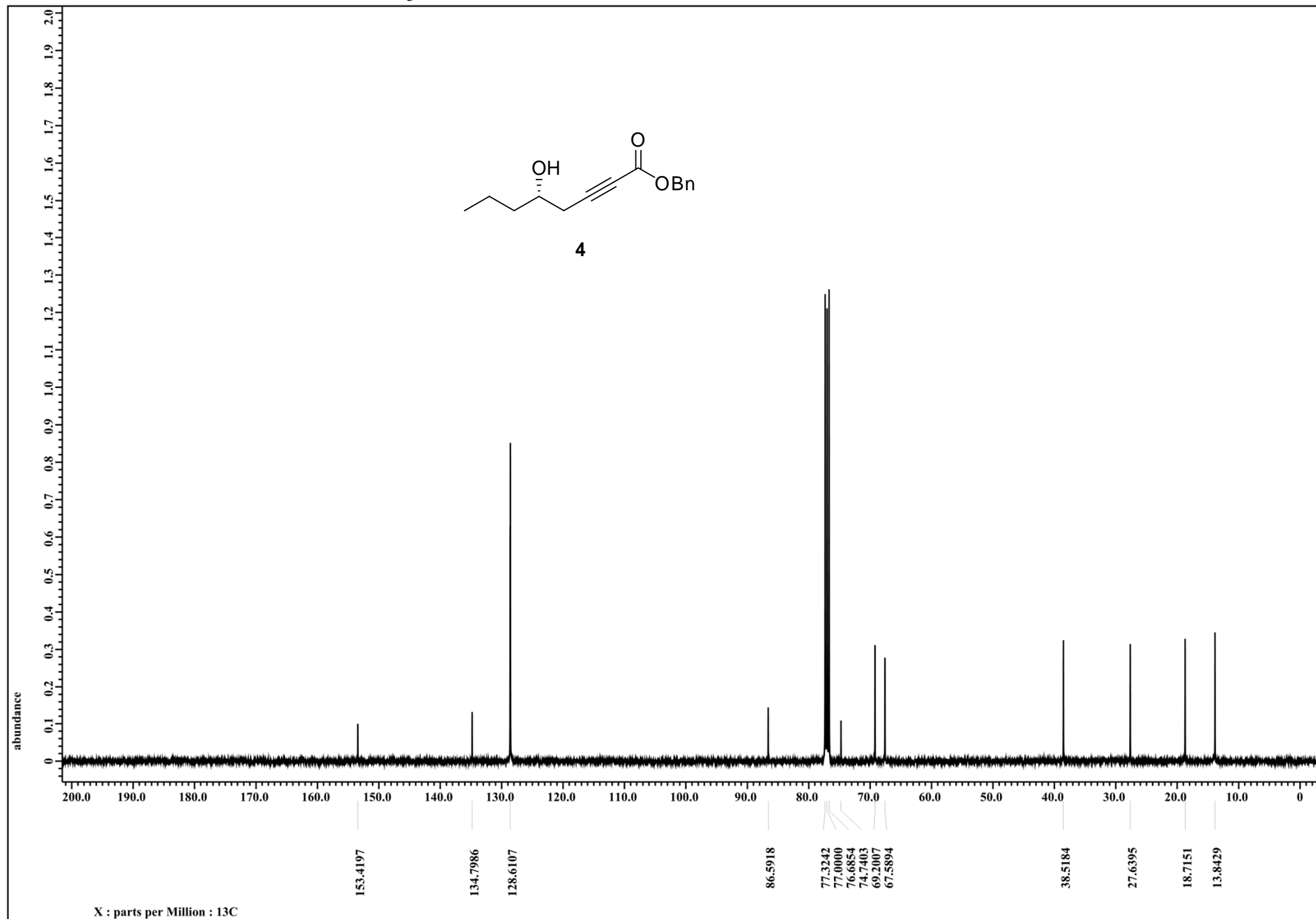


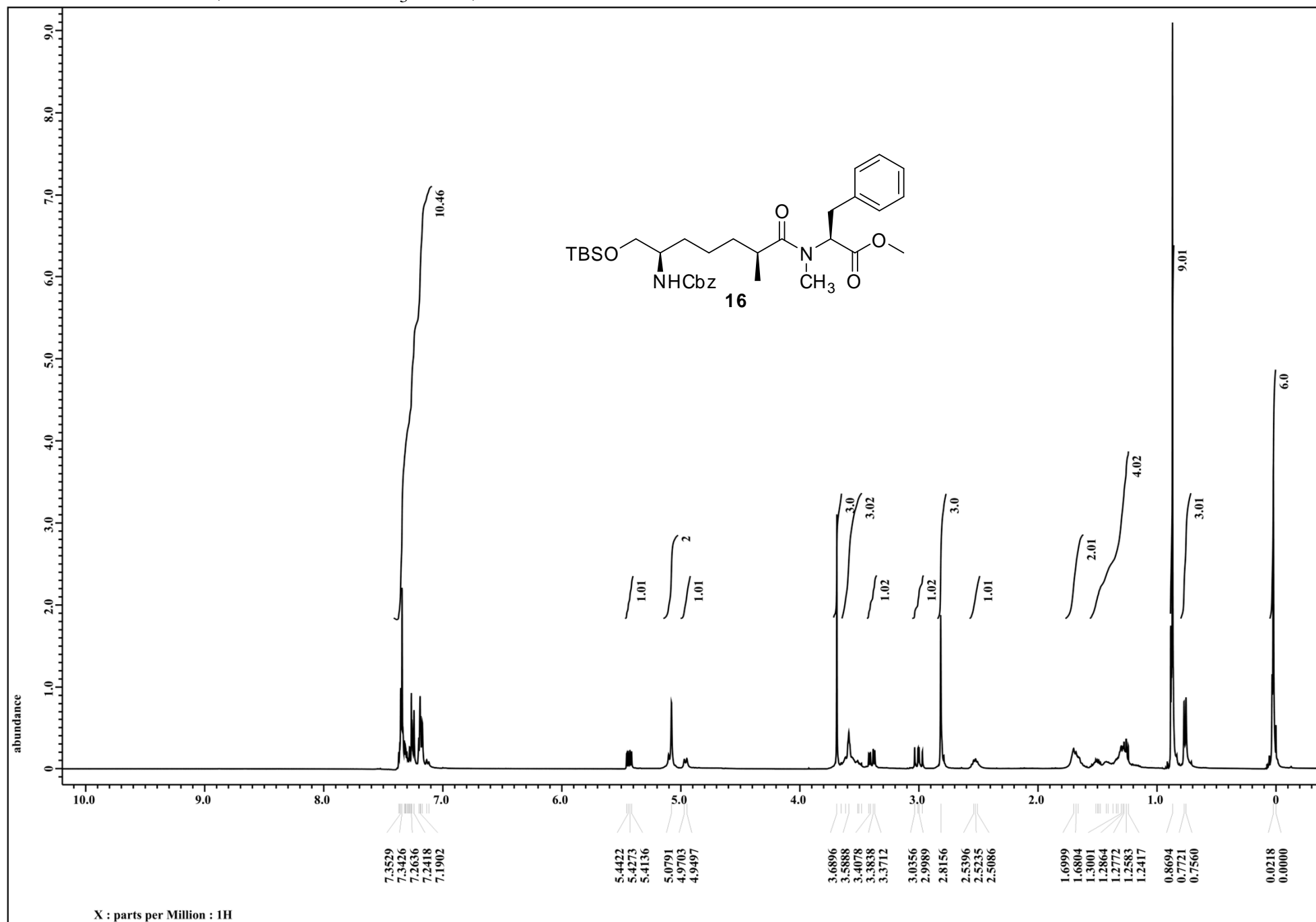
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

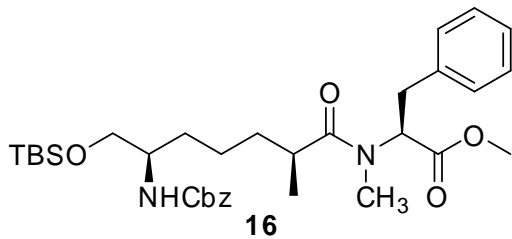
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )

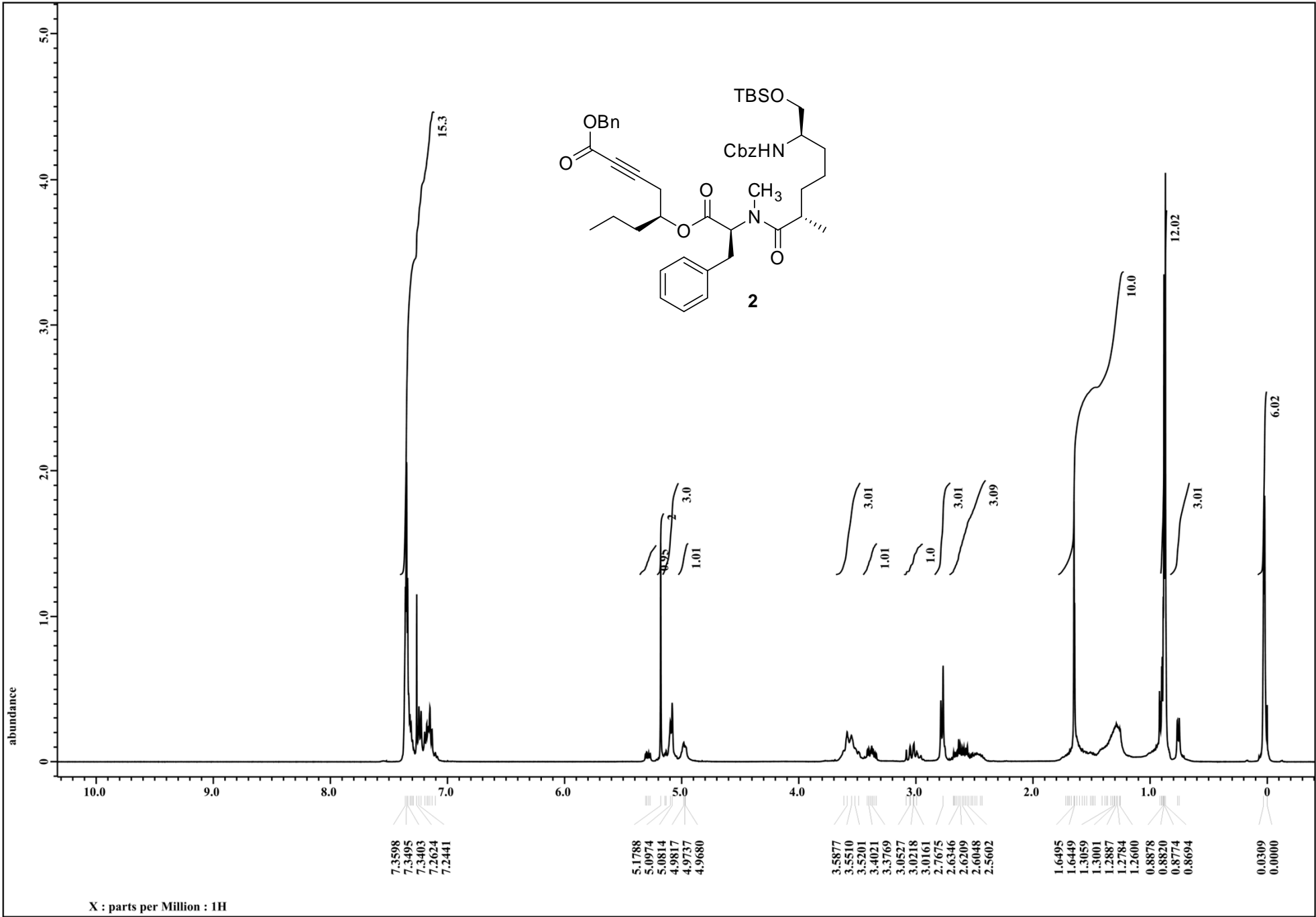


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

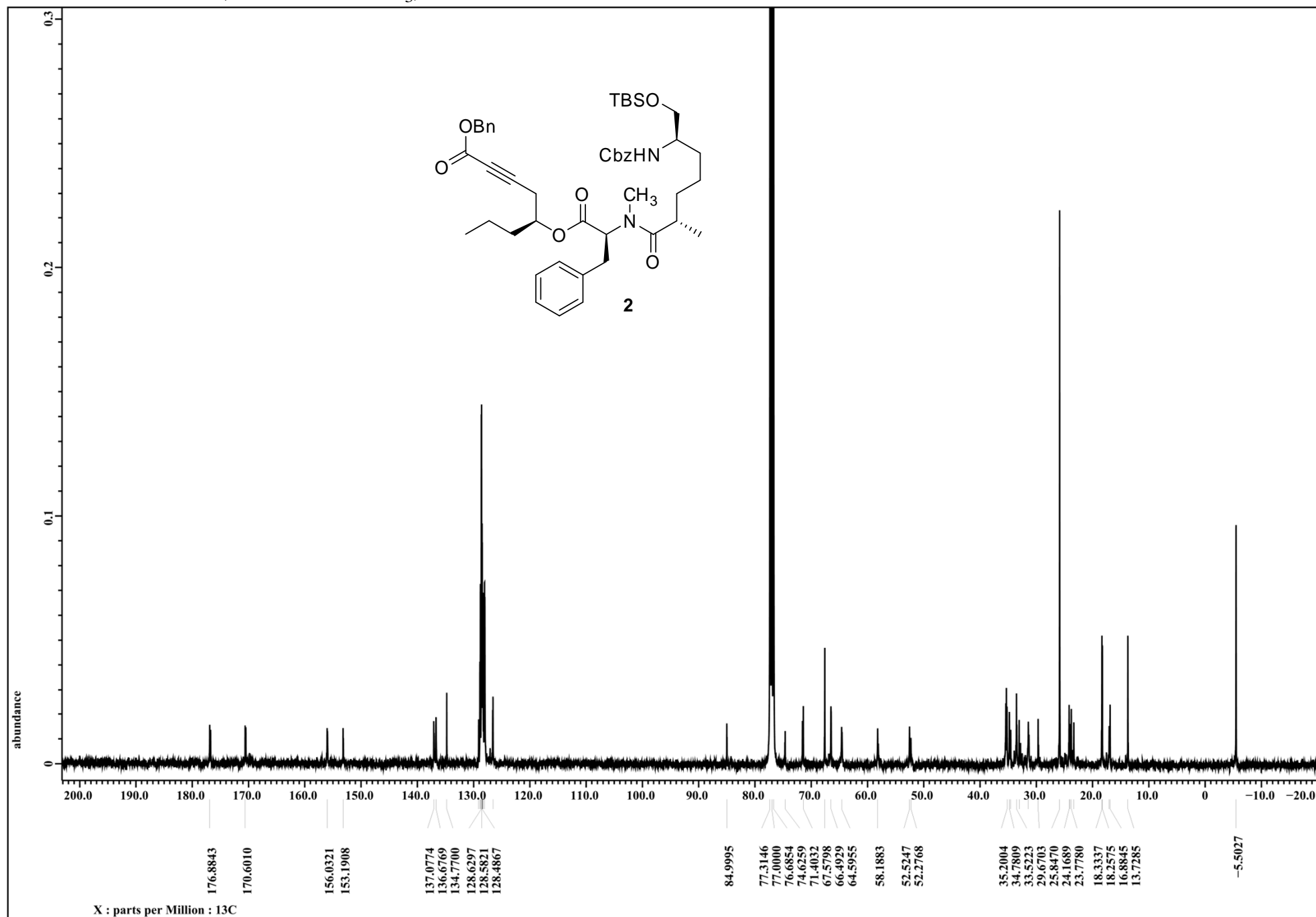


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

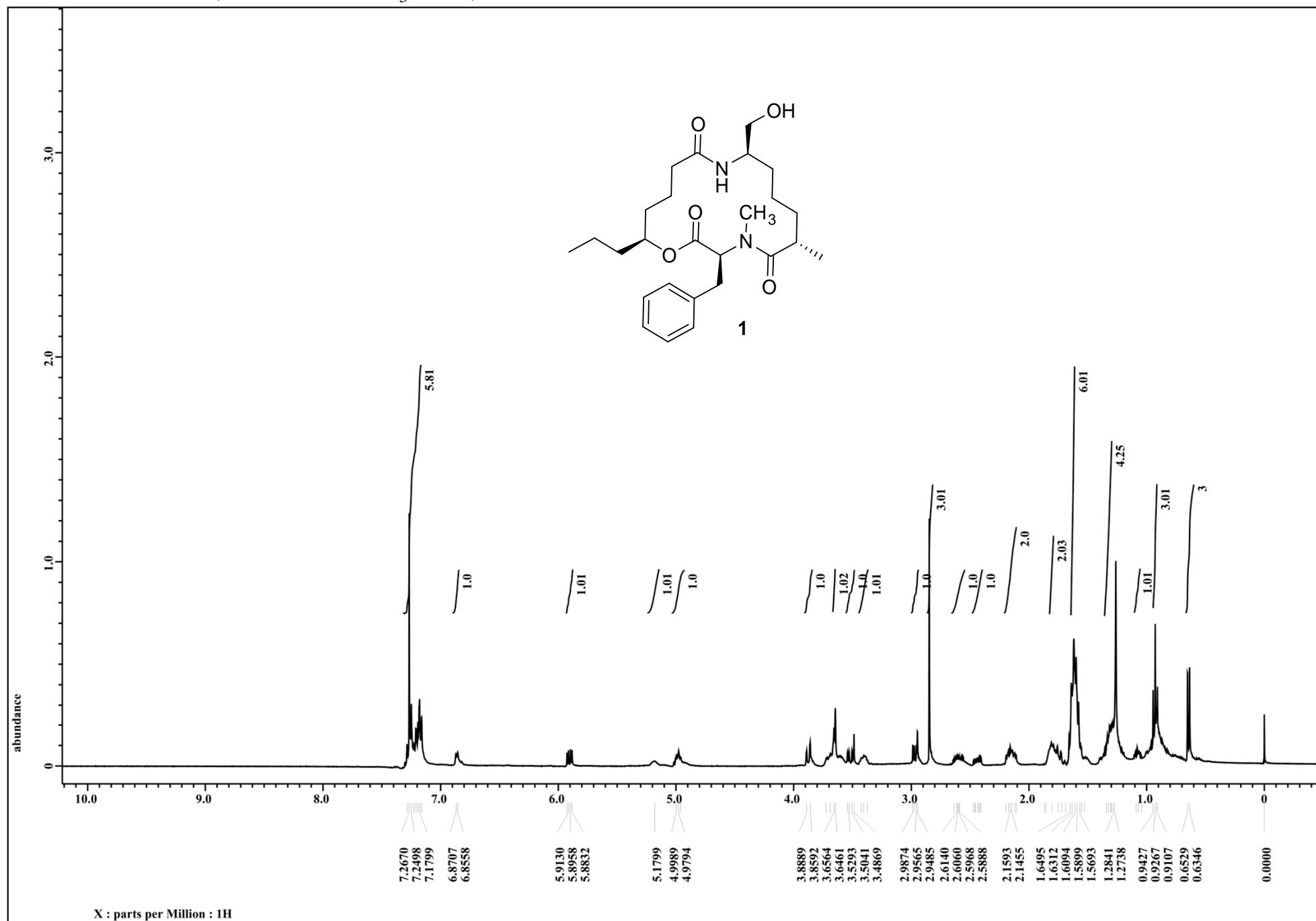
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

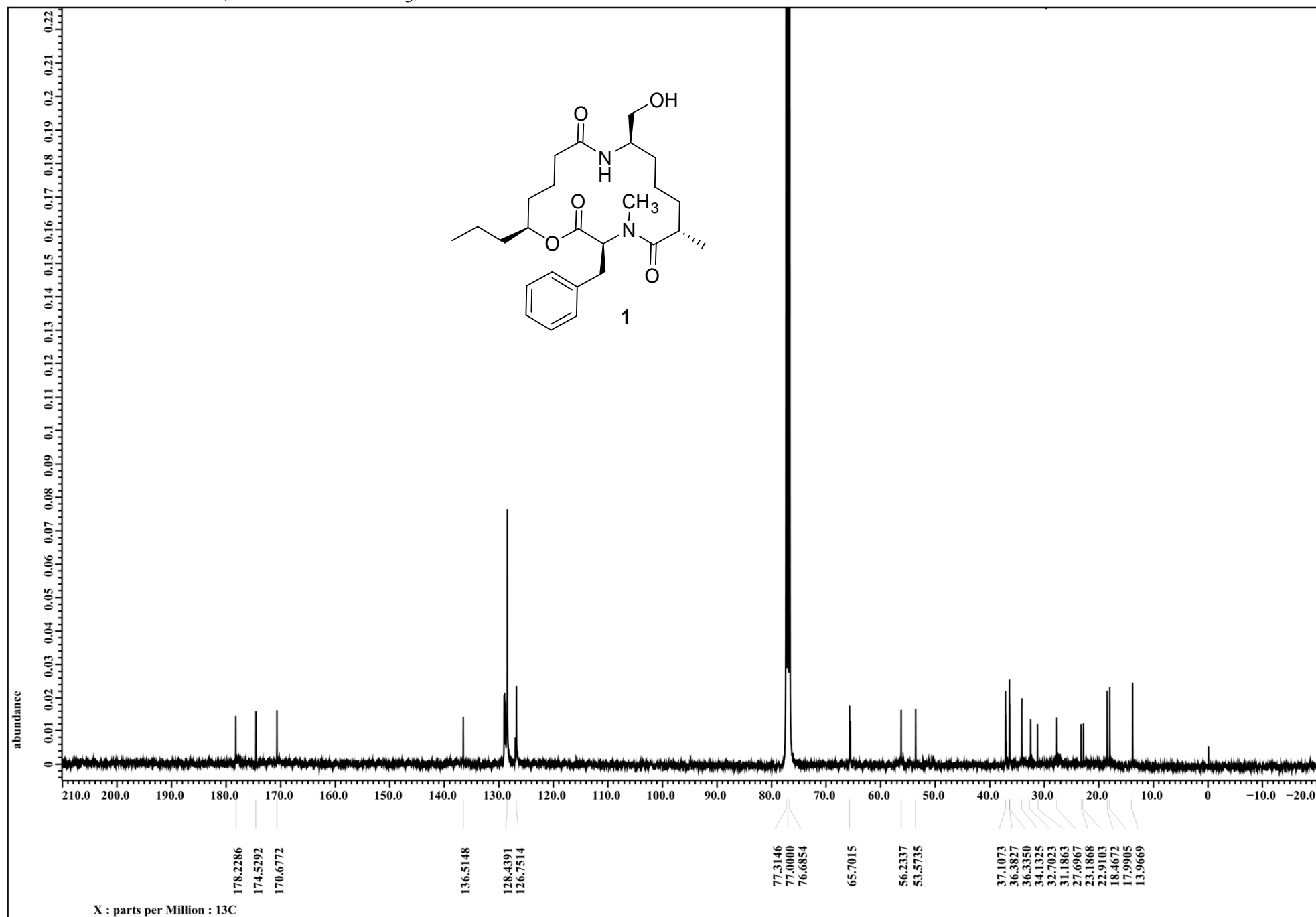


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ )





$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



Synthetic Haliclamide <b>1</b>			Natural Haliclamide	
Atom no.	$\delta_C$ (ppm)	$\delta_H$ (ppm, <i>J</i> in Hz )	$\delta_C$ (ppm)	$\delta_H$ (ppm, <i>J</i> in Hz )
1	170.7		170.7	
2	56.2	5.90, dd (11.9, 5.06)	56.2	5.90, dd (12.4, 5.6)
3	34.1	2.96, dd (15.5, 12.4) 3.51, dd (15.1, 5.04)	34.1	2.94, dd (14.6, 12.4) 3.51, dd (14.6, 5.6)
4	136.5		136.5	
5/5'	128.5	7.27, m	128.4	7.27, t (7.7)
6/6'	128.4	7.18, m	128.4	7.18, t (7.7)
7	126.8	7.20, m	126.7	7.20, t (7.7)
NMe	31.2	2.84, s	31.2	2.83, s
8	178.2		178.2	
9	36.4	2.60, m	36.4	2.60, m
10	18.0	0.65, d (7.0)	18.0	0.63, d (6.8)
11	31.2	1.74, m 1.29, m	31.3	1.72, m 1.20, m
12	23.2	1.55, m 1.07, m	23.2	1.45, m 1.02, m
13	27.7	2.15, m 1.26, m	27.7	2.14, m 1.25, m
14	53.6	3.41, br m	53.6	3.40, br m
15	65.7	3.68, brd (4.12)	65.7	3.68, br dd (11.6, 4.3) 3.87, d (11.6)
OH		3.87, d (11.8)		
NH		5.17 br s		
16	174.5	6.86 br d (5.96)	174.5	6.82, br d (5.6)
17	36.3	2.43, m 2.18, m	36.0	2.43, m 2.18, m
18	22.9	1.77, m	22.9	1.77, m 1.60, m
19	32.7	1.62, m 1.45, m	31.9	1.62, m 1.45, m
20	77.0	4.98, m	77.0	4.98, m
21	37.1	1.55, m 1.48, m	37.1	1.55, m 1.50, m
22	18.5	1.32, m	18.5	1.32, m
23	14.0	0.93, t (7.3)	13.9	0.92, t (7.3)