Supporting Information

Enantioselective Total Synthesis of Lycoposerramine-Z using Chiral Phosphoric Acid-catalyzed Intramolecular Michael Addition

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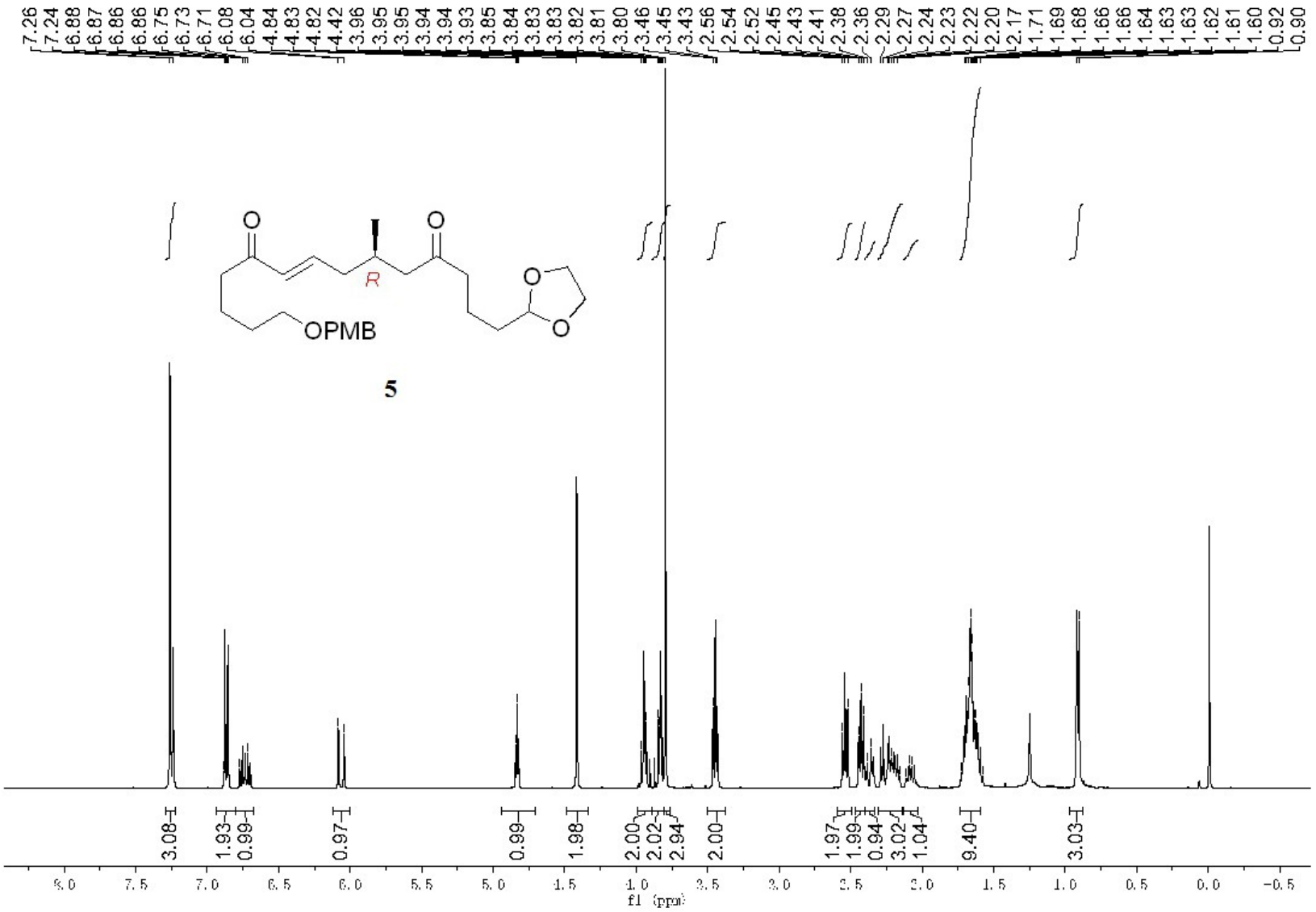
1. General

Reagents were used as received from commercial suppliers unless otherwise indicated. All reactions were carried out under an atmosphere of N_2 unless otherwise indicated using over-dried glassware (120 °C), which was cooled under atmosphere. THF, Et_2O and toluene were distilled from sodium/benzophenone prior to use. CH_2Cl_2 and DMF were distilled from calcium hydride prior to use and *t*-BuOH was distilled from calcium oxide prior to use. Alternatively, acetone and MeOH were purchased as dehydrated solvents and stored with active molecular sieves 4A prior to use for reactions. All solvents for work-up procedure were used as received. All inorganic salt solutions are aqueous unless otherwise stated. "Evaporation" refers to removal of solvent under reduced pressure (10-100 mmHg) with a rotary evaporator, followed by a period under high vacuum (< 1 mmHg) unless otherwise indicated. Silica gel (300~400 mesh) and *n*-hexane, ethyl acetate are used for product purification by flash column chromatography. Analytical thin-layer chromatography (TLC) was performed with glass TLC plates. Visualization was accomplished with UV light, phosphomolybdic acid staining and subsequent heating.

IR spectra were recorded on Fourier Transform infrared spectrometer and listed in cm^{-1}. ^1H, ^{13}C and 2D NMR spectra were recorded in $CDCl_3$ solution on 300, 400 or 600 MHz instruments. Mass spectra were electrospray ionization mass spectrome (ESI) and were recorded on a LCQ Fleet spectrometer. High-resolution mass spectral analyses (HRMS) were determined on a Q-TOF-MS spectrometer. Optical rotations were measured with a polarimeter with a sodium lamp.

2. Copies of ^{1}H, ^{13}C and 2D NMR spectra

(see below pages)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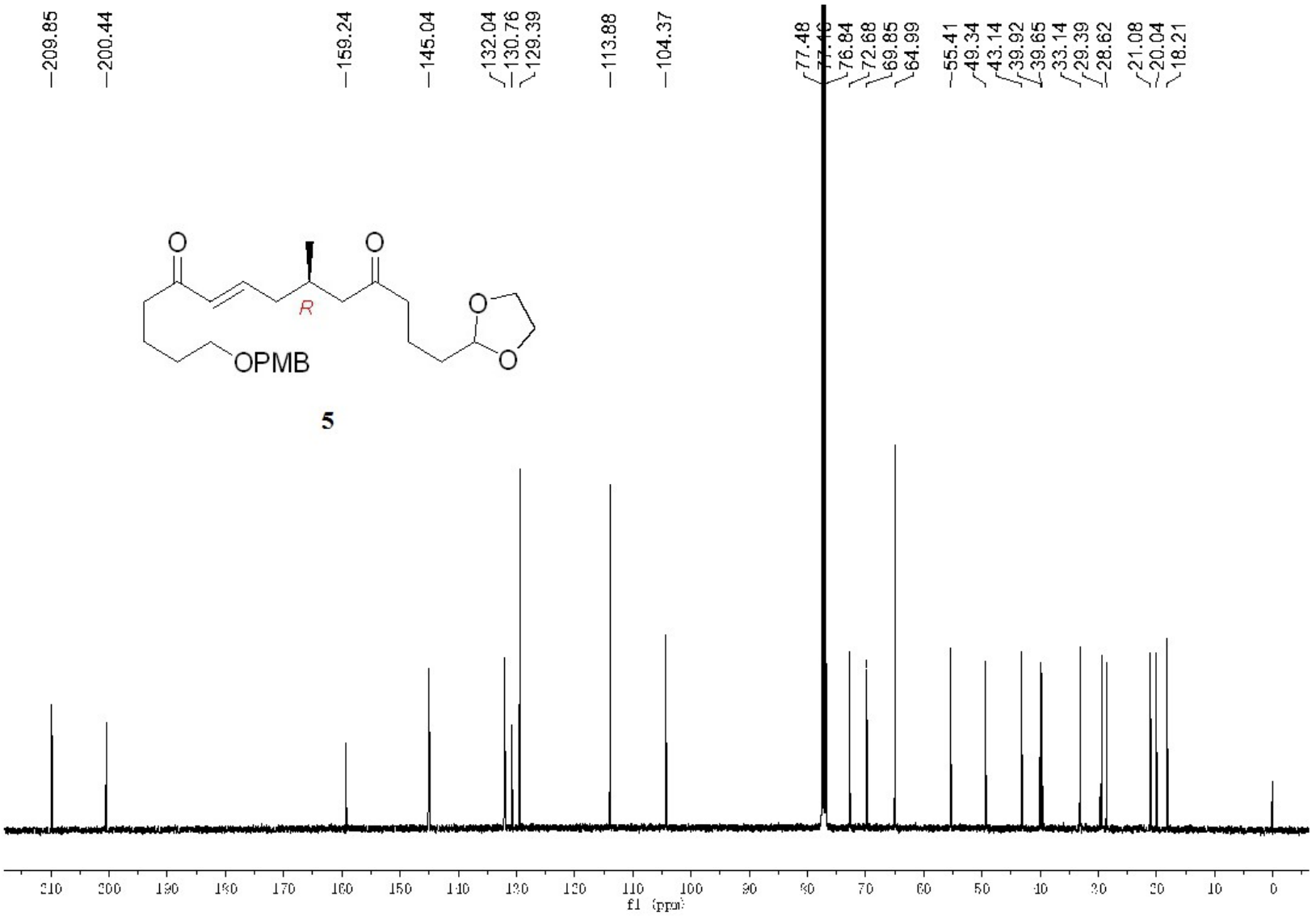
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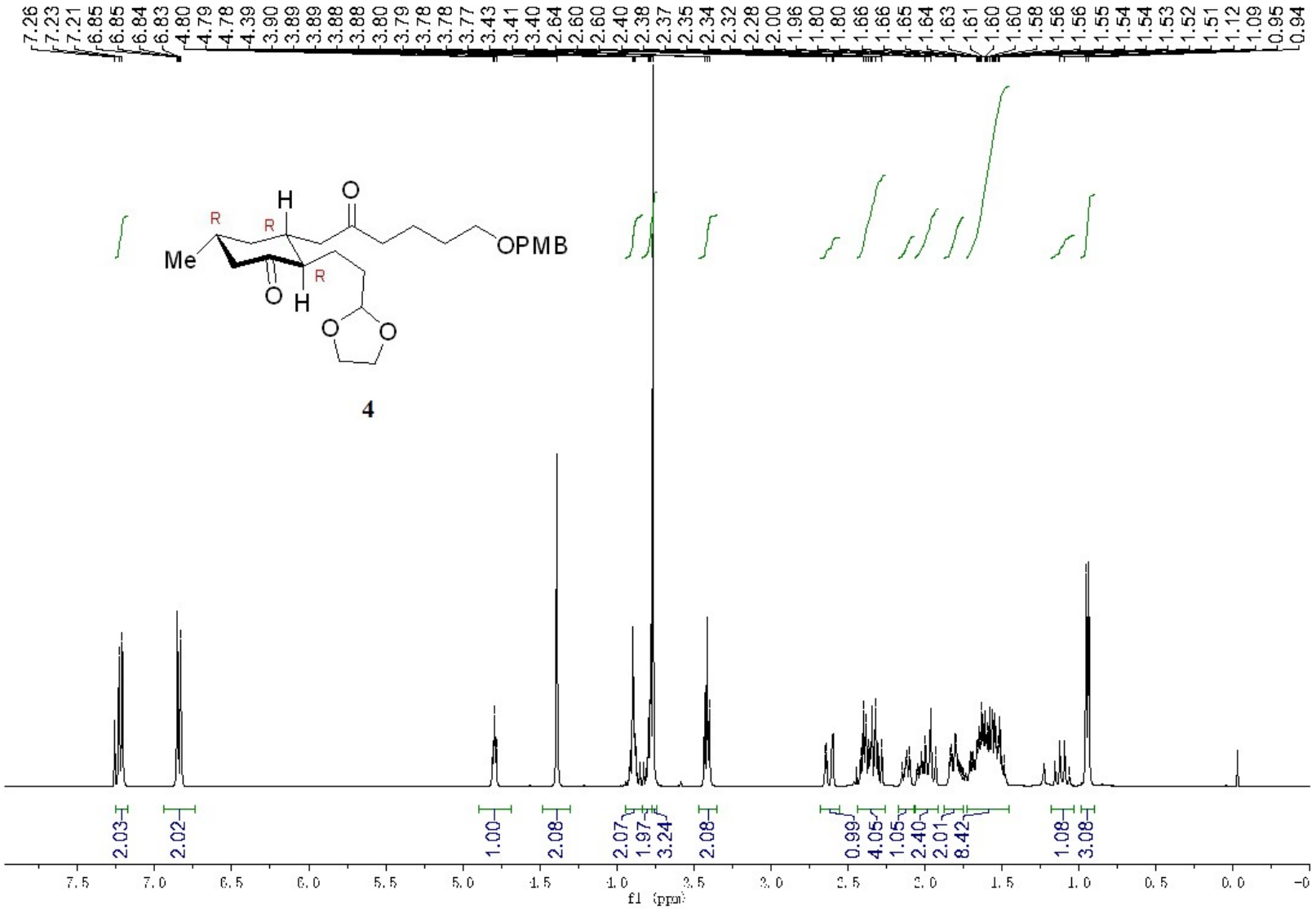
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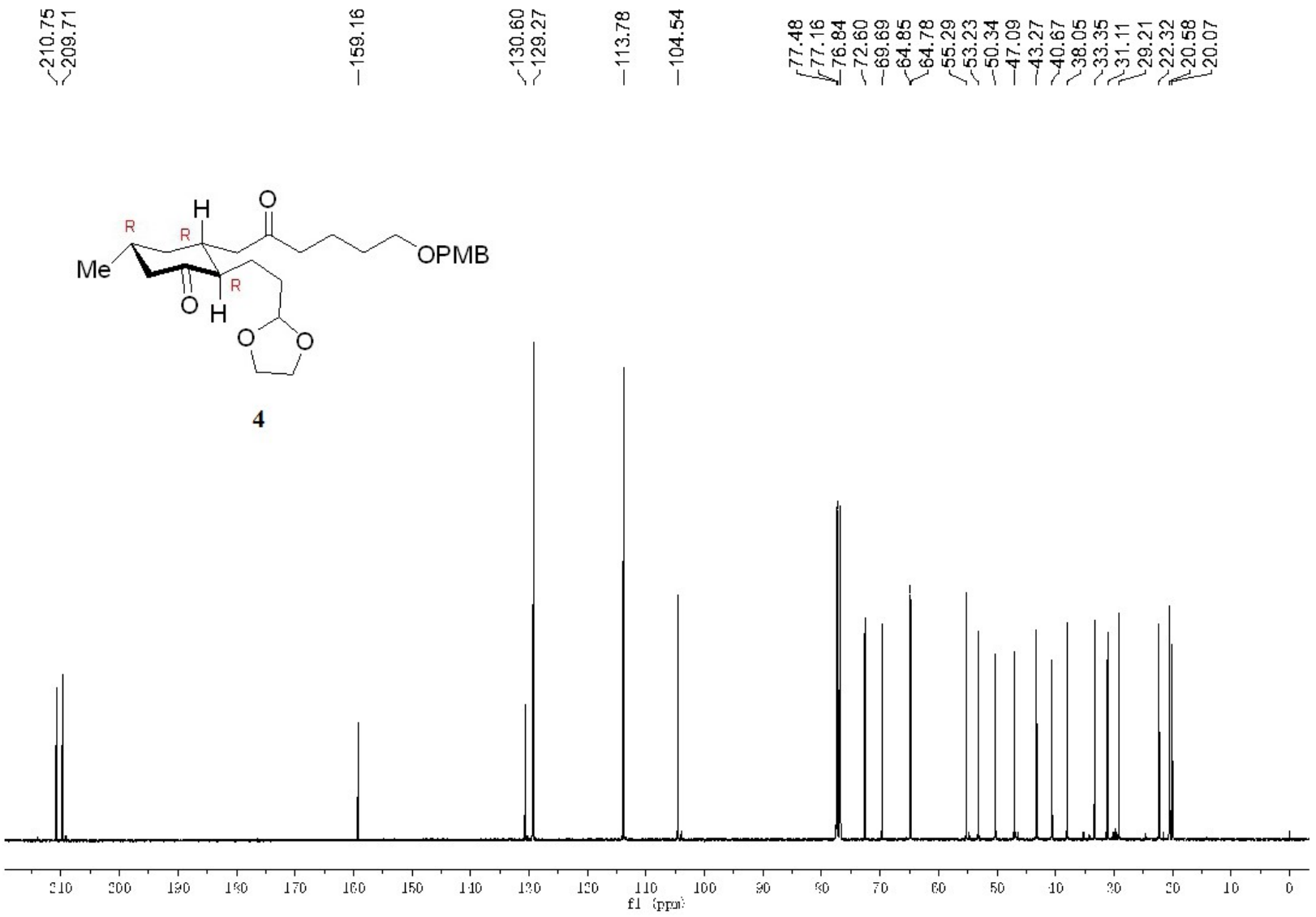
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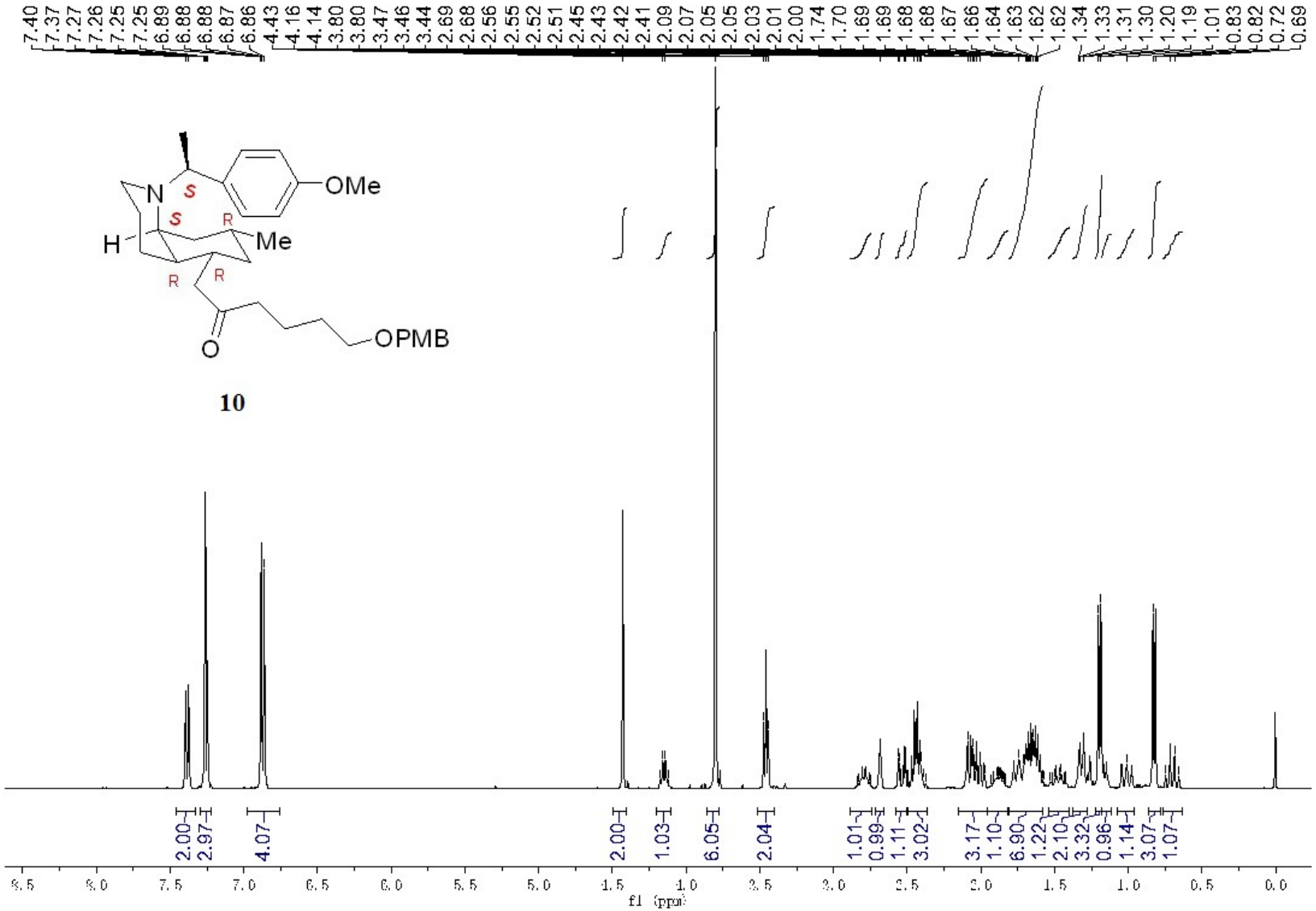
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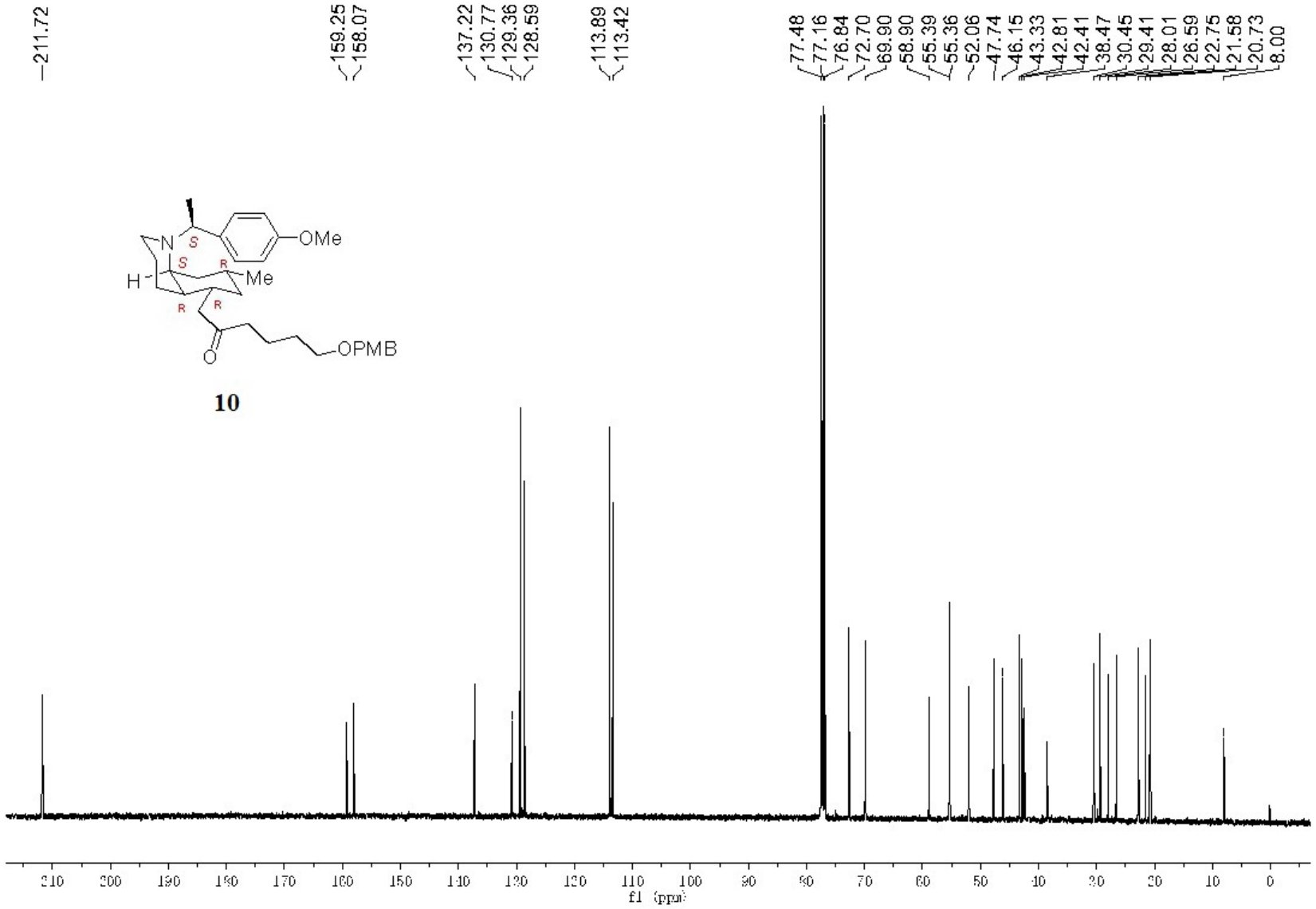
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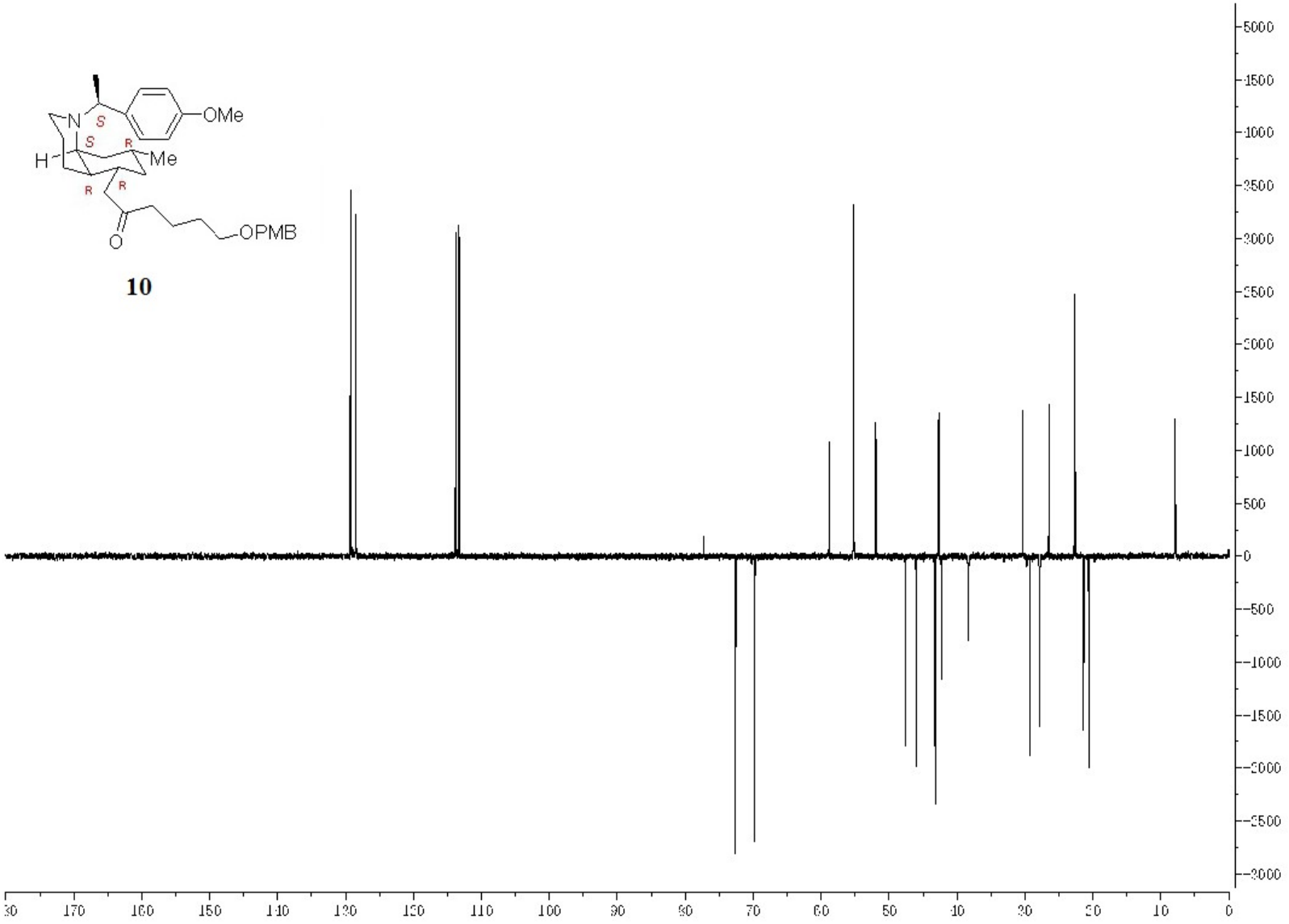
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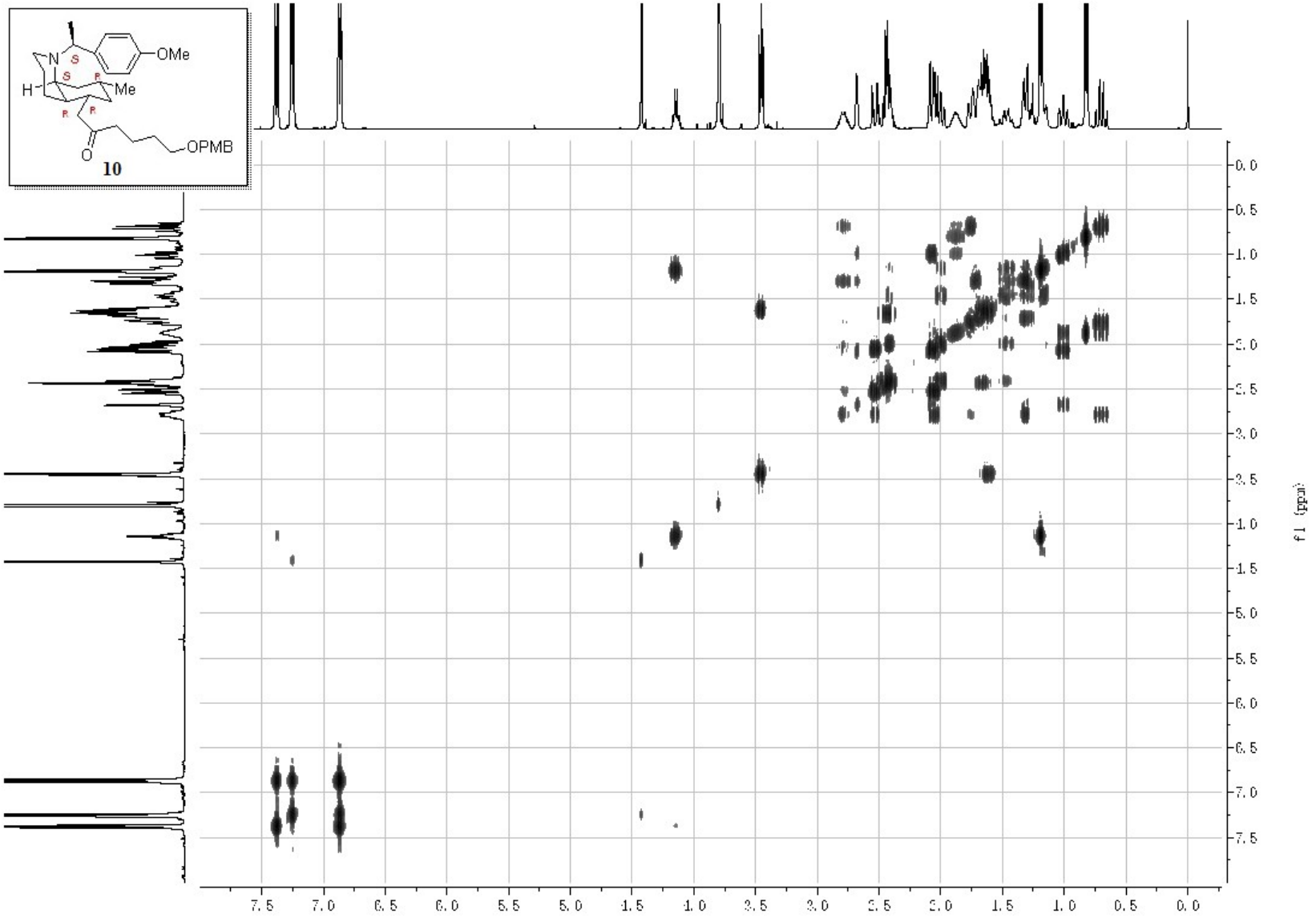
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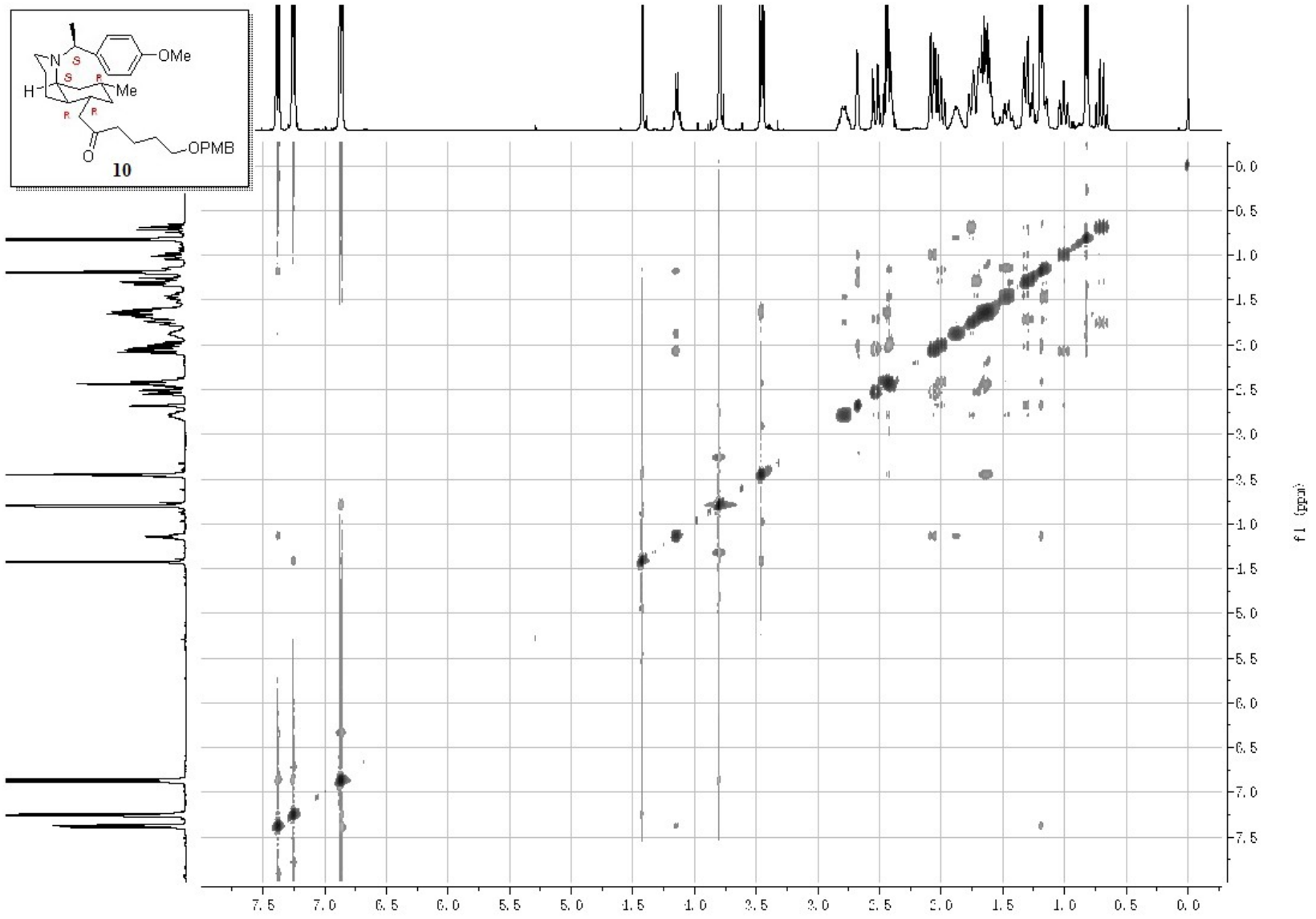
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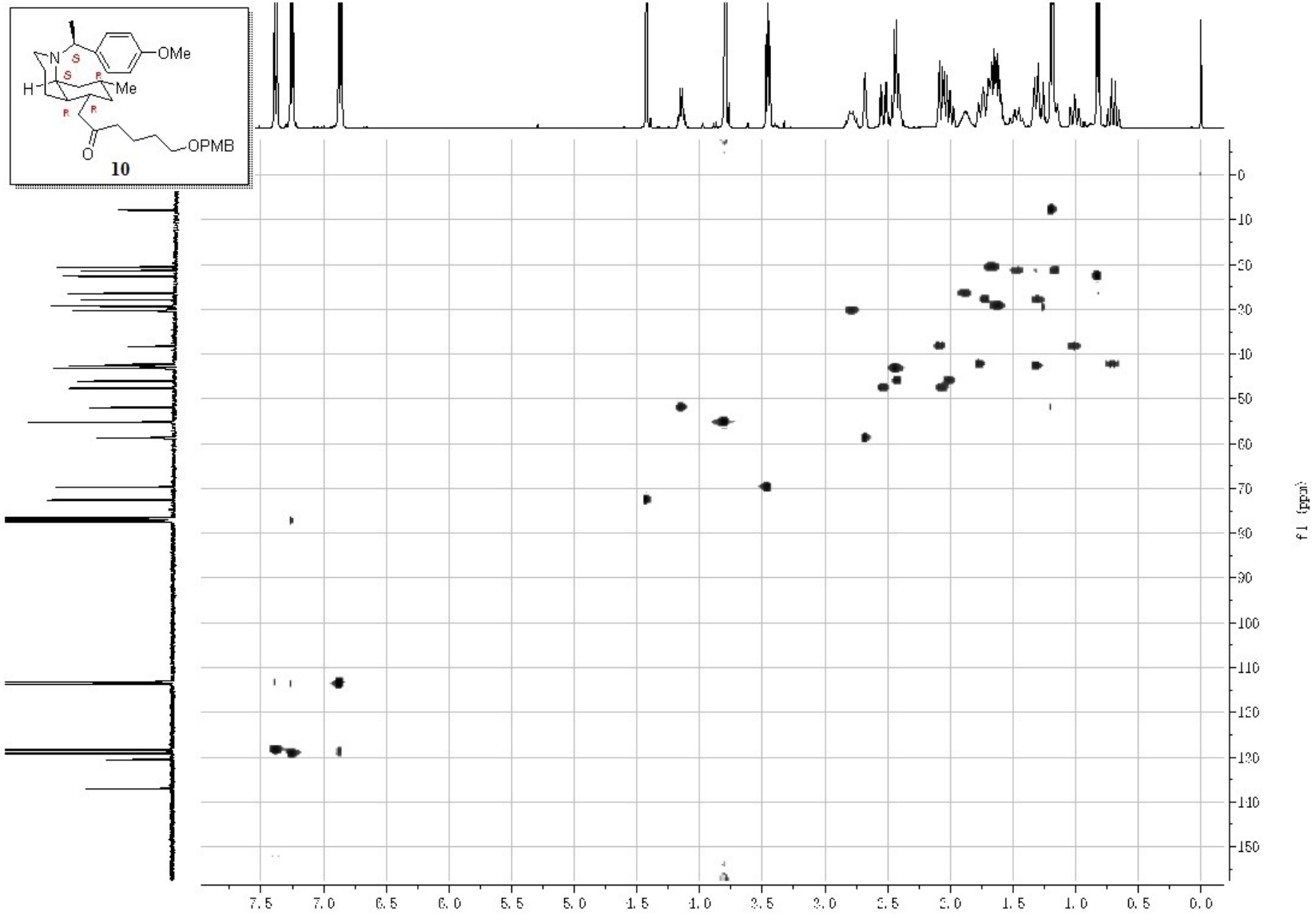
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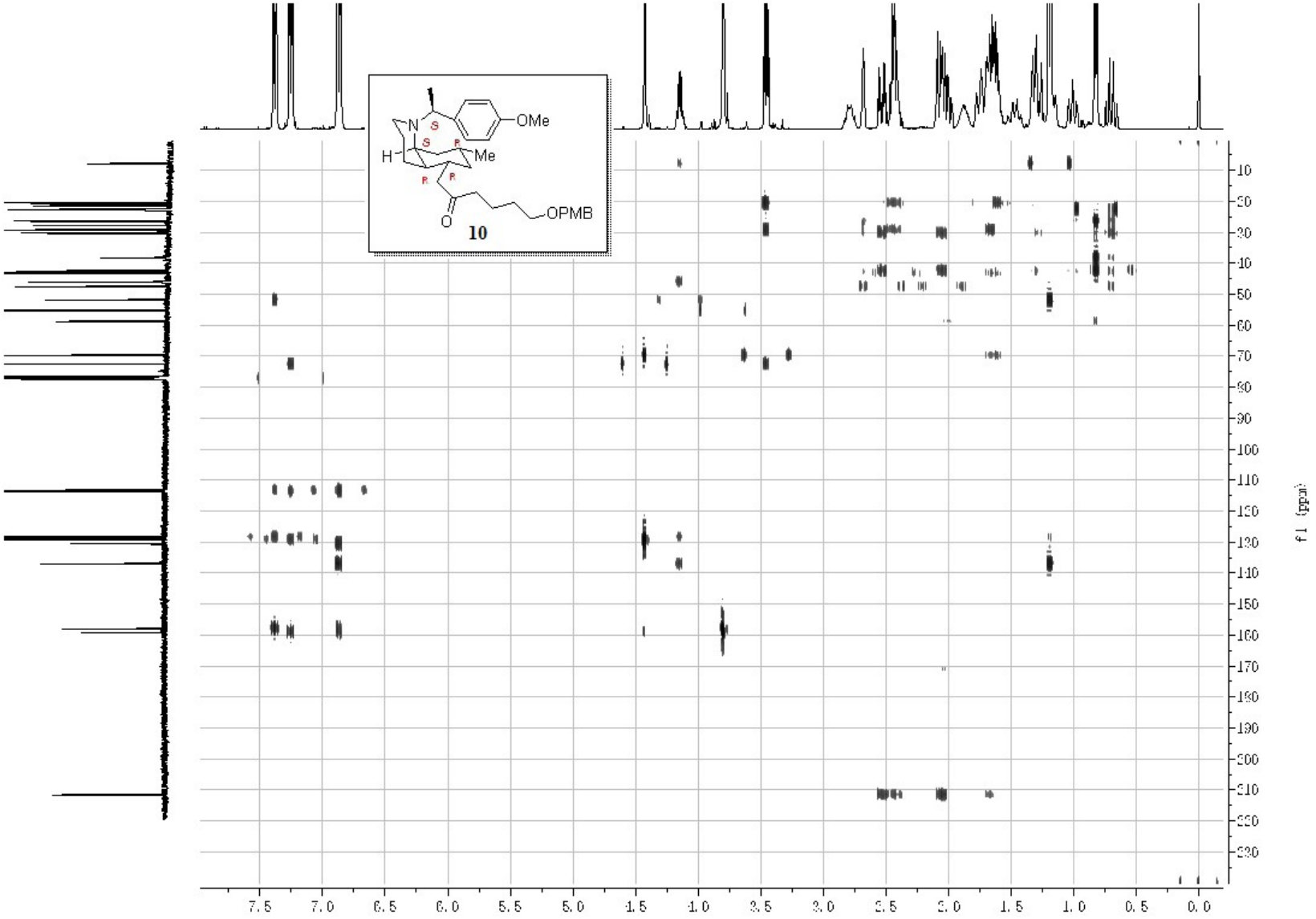
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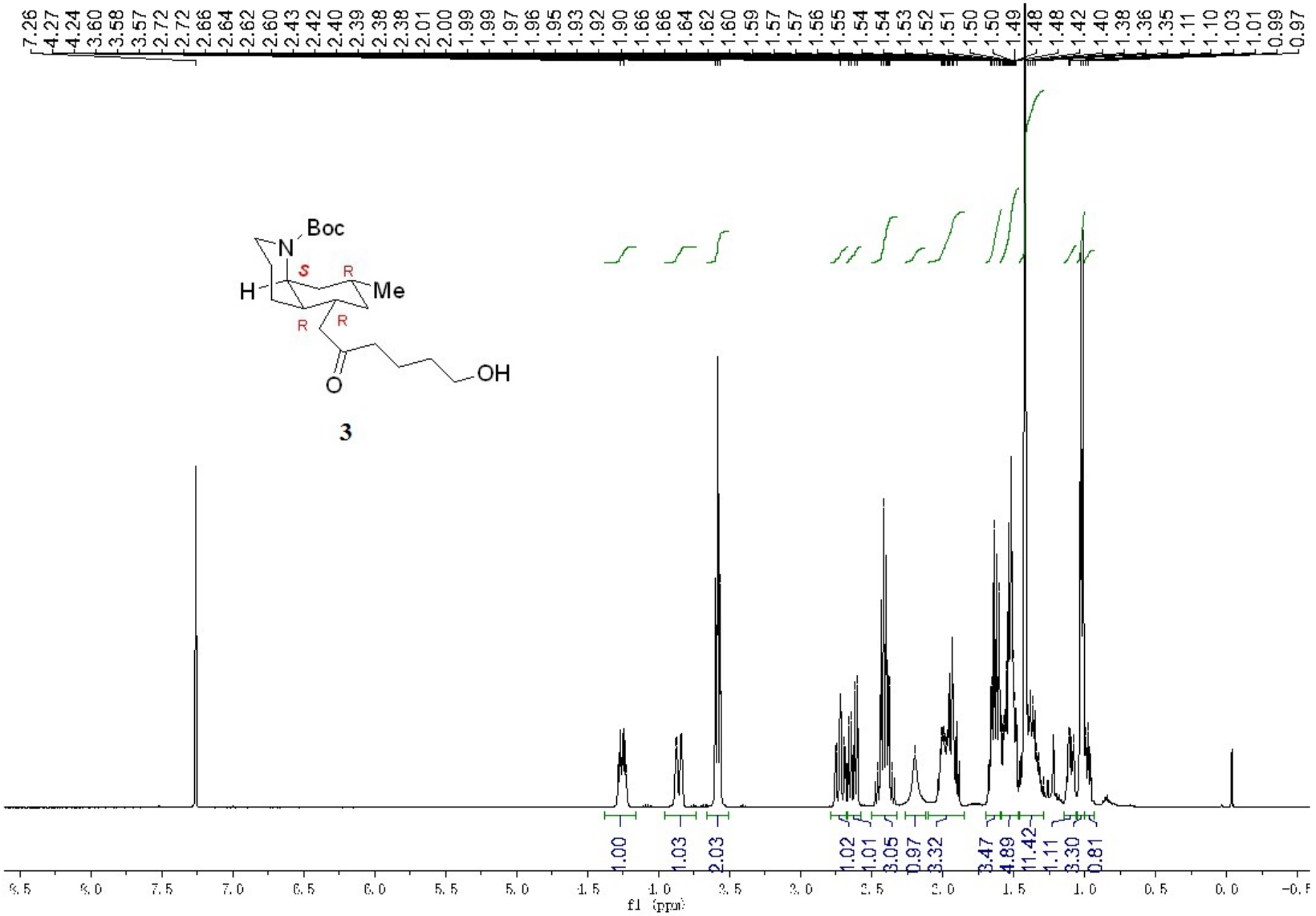
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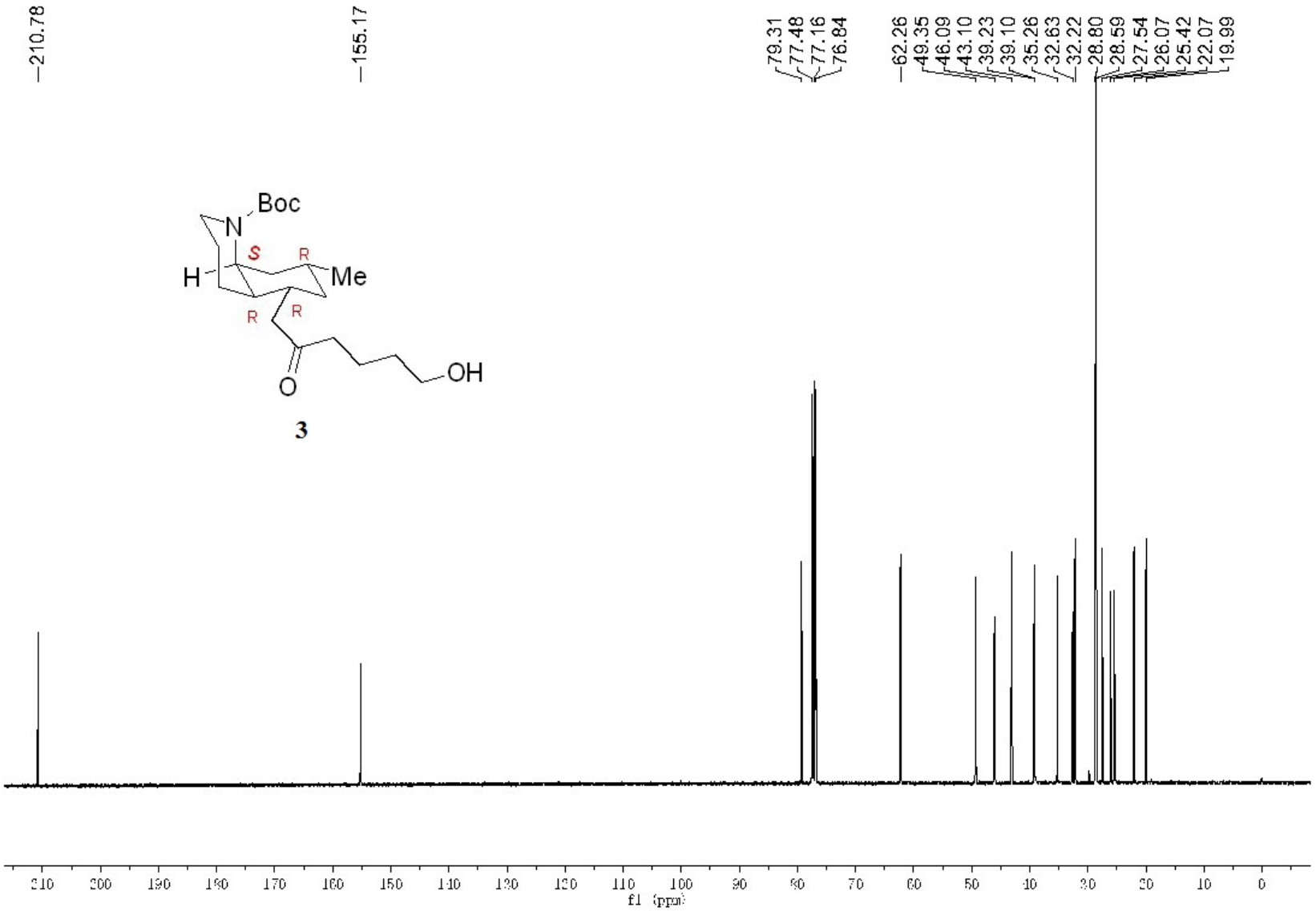
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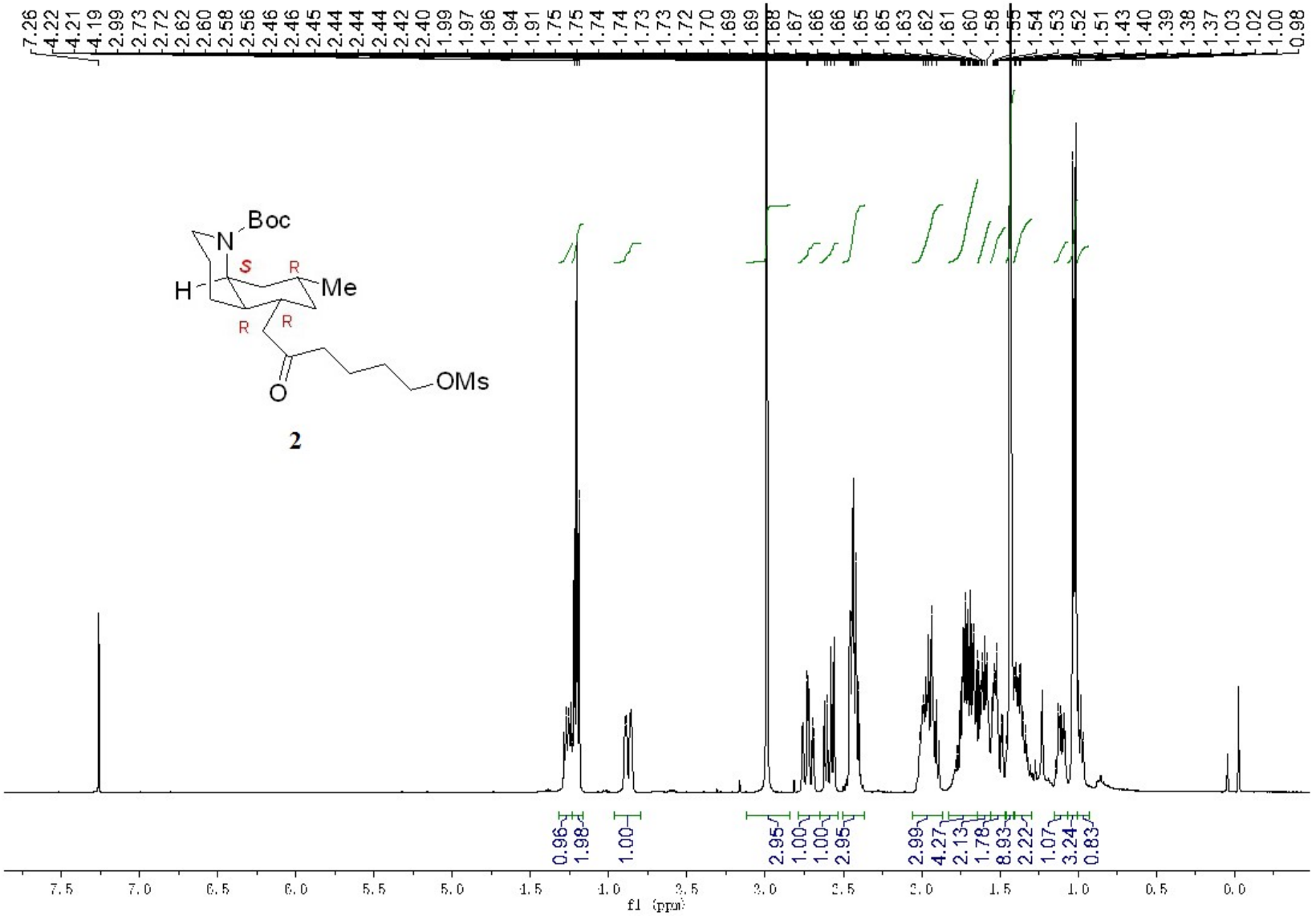
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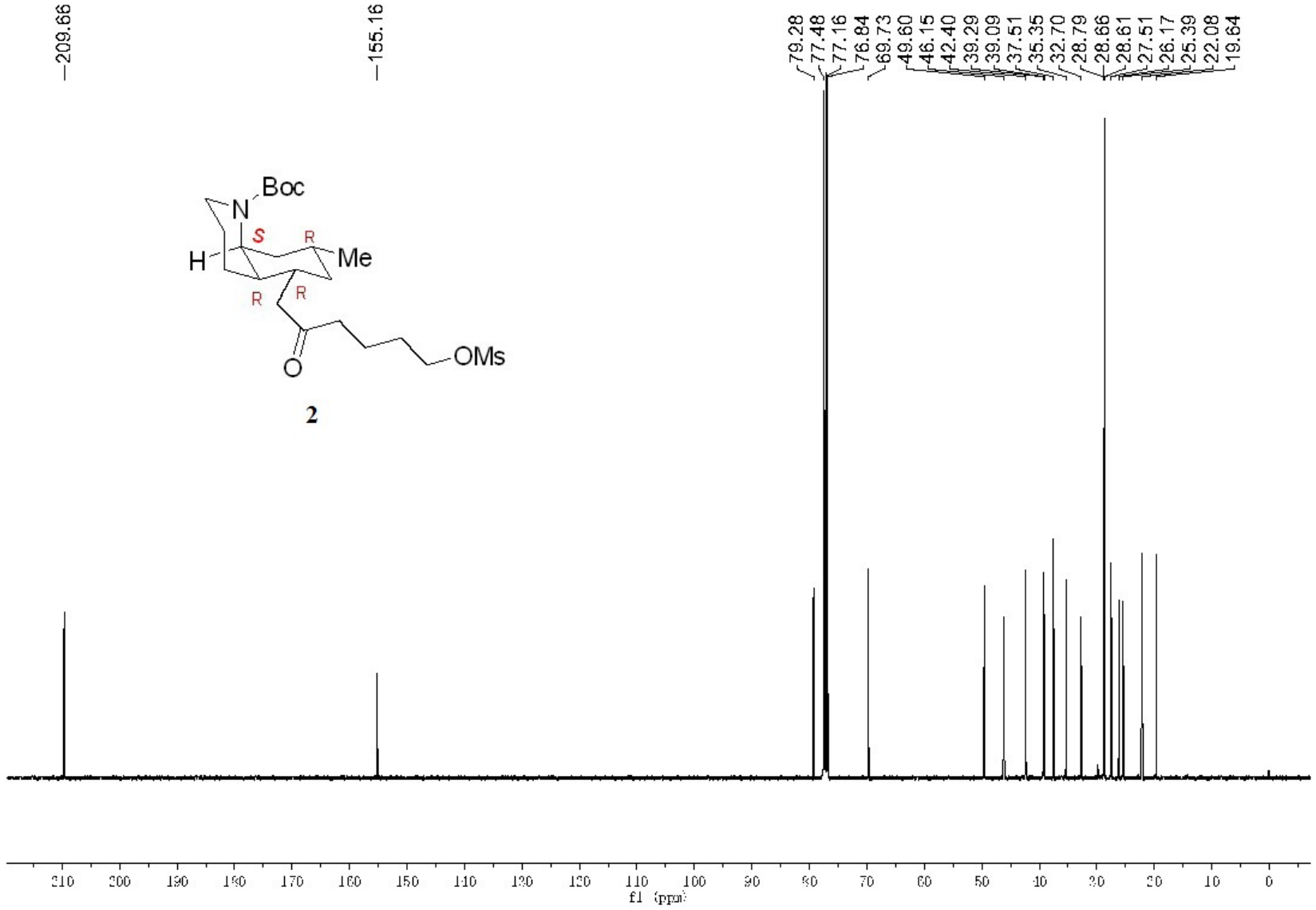
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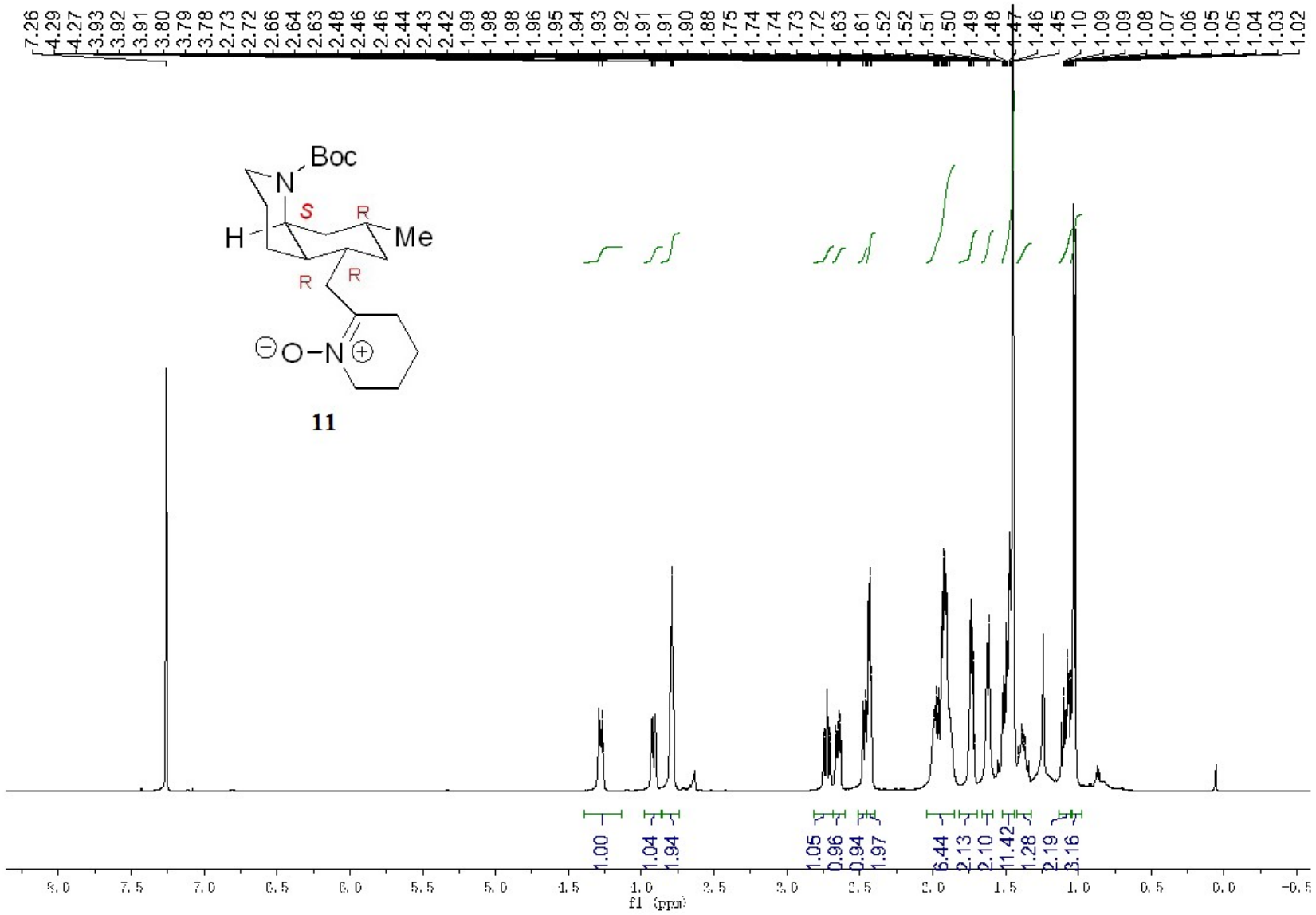
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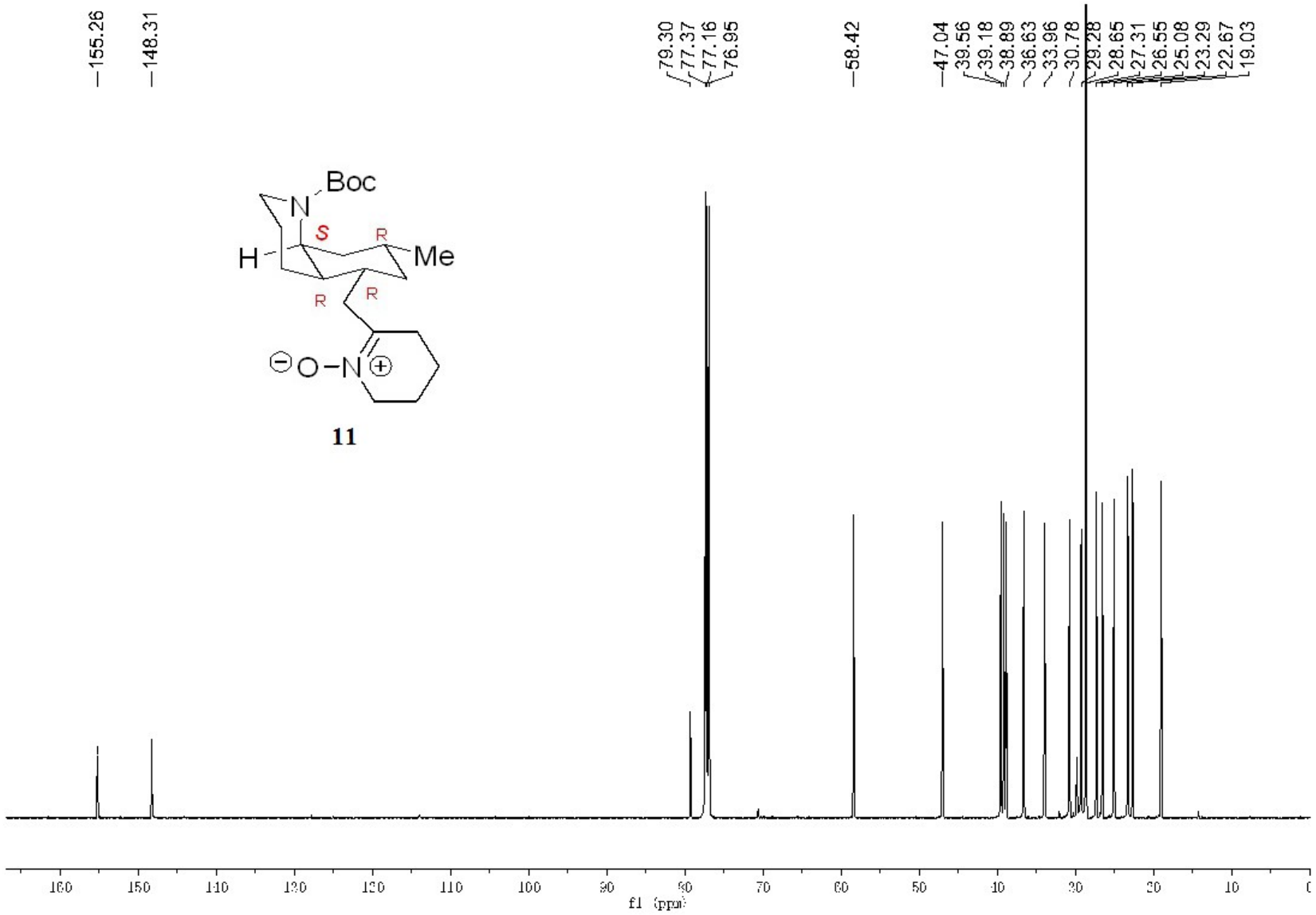
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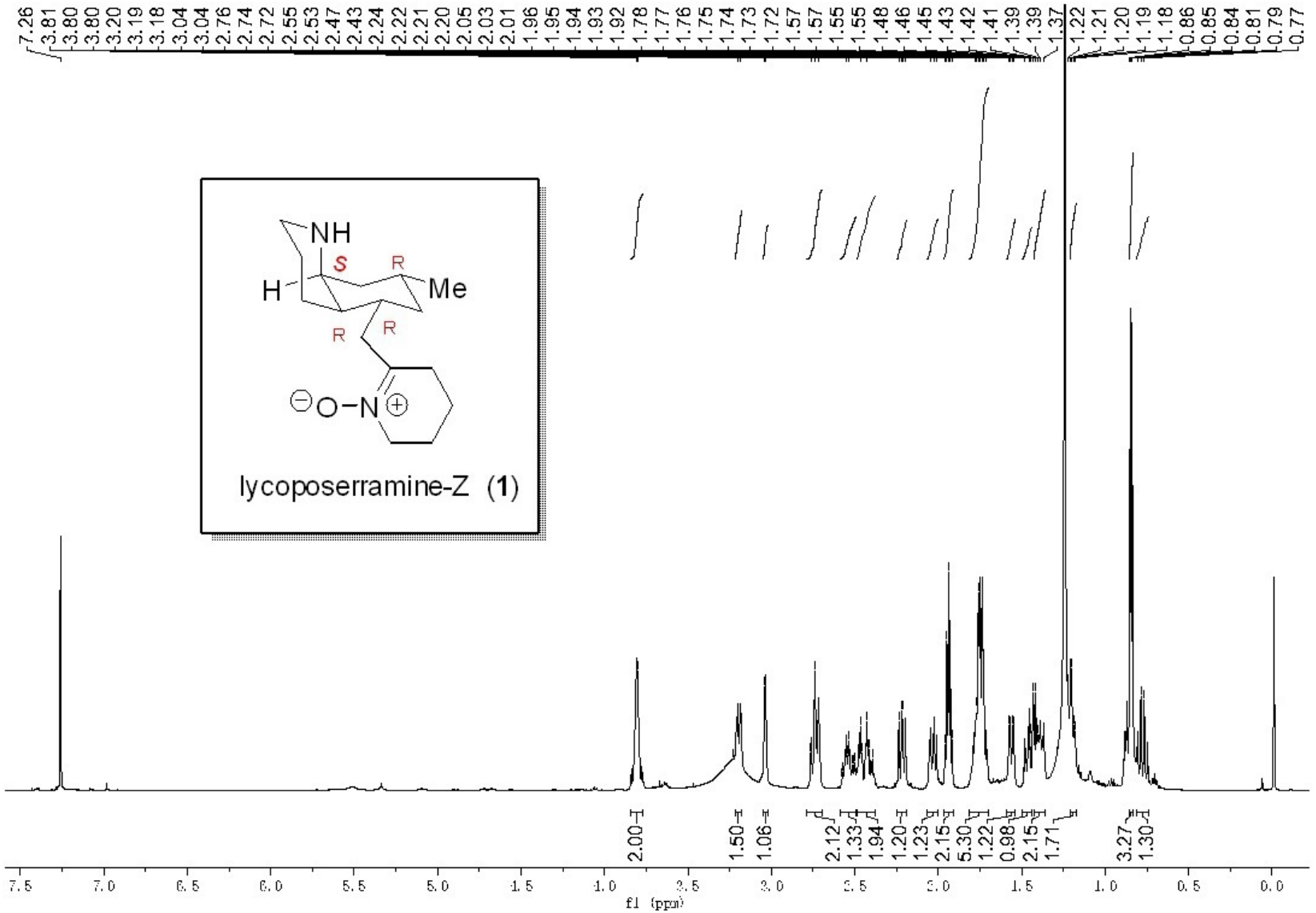
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lycoposerramine-Z (1)
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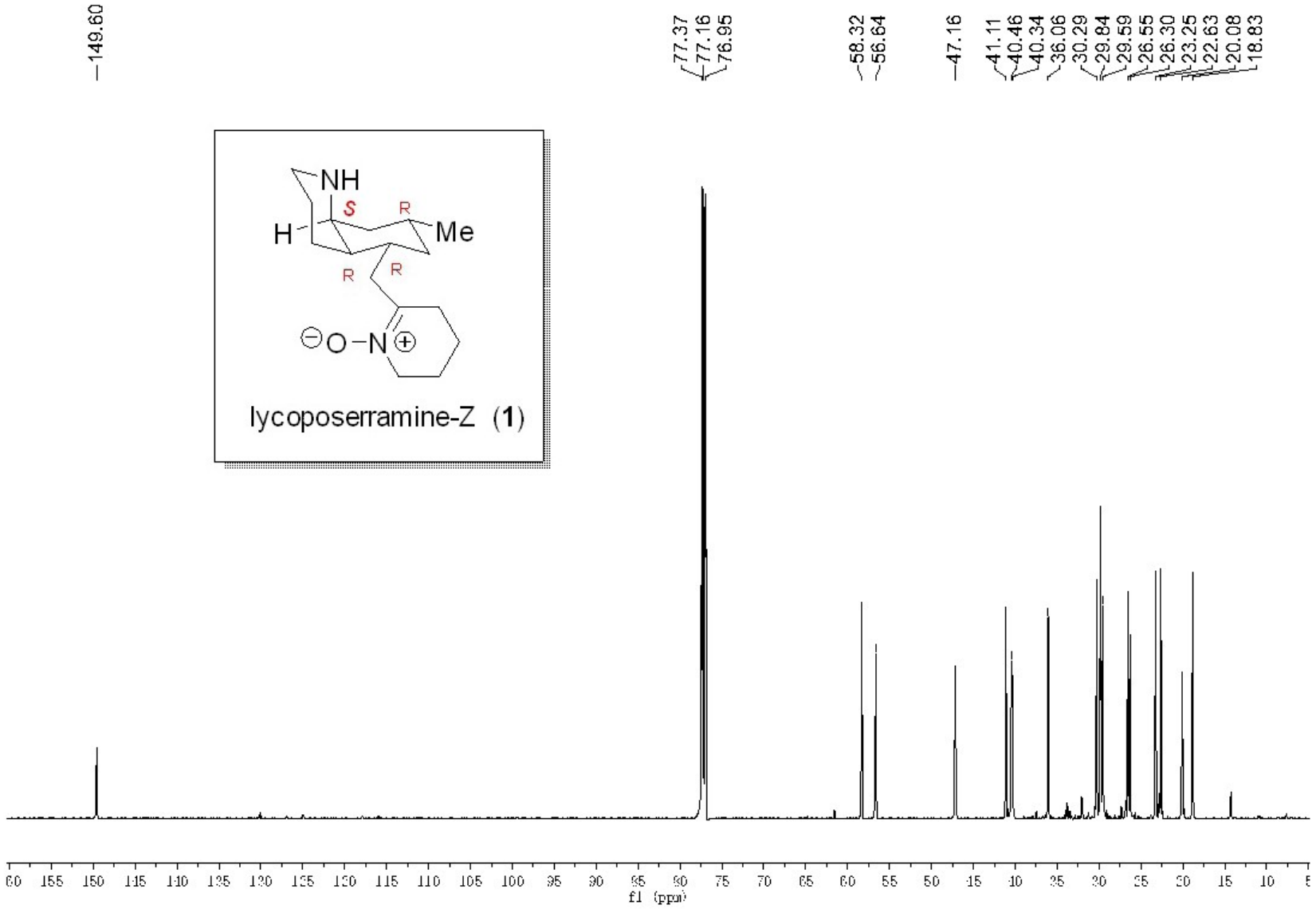
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20.08
18.83
NH
S
R
H
Me
R
R
O
N
lycoposerramine-Z (1)
f1 (ppm)

3. Comparison of ^{1}H and ^{13}C NMR data for natural and synthetic lycoposerramine-Z

Lycoposerramine-Z (1)			
^{1}H NMR (nature)[1]	**^{1}H NMR (synthetic)**	**^{13}C NMR (nature)[1]**	**^{1}H NMR (synthetic)**
0.79 (ddd, *J*=12.3, 12.3, 12.3 Hz, 1H)	0.78 (q, *J* = 12.2 Hz, 1H)	18.8 (CH_2)	18.8 (CH_2)
0.85 (d, *J*=6.1 Hz, 3H)	0.84 (d, *J* = 6.3 Hz, 3H)	20.3 (CH_2)	20.1 (CH_2)
1.22 (ddd, *J*=3.8, 13.9, 13.9 Hz, 1H)	1.21–1.17 (m, 1H)	22.5 (CH_3)	22.6 (CH_3)
1.40 (m, 1H)	1.43–1.36 (m, 2H)	23.2 (CH_2)	23.2 (CH_2)
1.42 (m, 1H)		26.4 (CH_2)	26.3 (CH_2)
1.47 (m, 1H)	1.47 (dt, J_1 = 13.8 Hz, J_2 = 4.0 Hz, 1H)	26.5 (CH)	26.6 (CH)
1.58 (br d, *J*=13.1 Hz, 1H)	1.56 (br dd, J_1 = 13.2 Hz, J_2 = 1.8 Hz, 1H)	29.6 (CH)	29.6 (CH)
1.76 (m, 5H)	1.75 (m, 5H)	30.0 (CH_2)	30.3 (CH_2)
1.95 (m, 2H)	1.94 (p, *J* = 6.1 Hz, 2H)	35.9 (CH_2)	36.1 (CH_2)
2.06 (br d, *J*=15.6 Hz, 1H)	2.04 (m, 1H)	40.6 (CH)	40.3 (CH)
2.26 (dd, *J*=10.4, 13.1 Hz, 1H)	2.22 (dd, J_1 = 12.9 Hz, J_2 = 10.8 Hz, 1H),	40.6 (CH_2)	40.5 (CH_2)
2.46 (m, 2H)	2.48-2.40 (m, 2H),	41.1 (CH_2)	41.1 (CH_2)
2.55 (m, 1H)	2.58–2.49 (m, 1H)	47.4 (CH_2)	47.2 (CH_2)
2.72 (br d, *J*=12.2 Hz, 1H)	2.77-2.72 (m, 2H)	56.6 (CH)	56.6 (CH)

2.76 (ddd, *J*=3.2, 12.4, 12.4 Hz, 1H)		58.3 (CH_2)	58.3 (CH_2)
3.05 (br s, 1H)	3.05–3.02 (m, 1H)	149.0 (C)	149.6 (C)
3.21(br d, *J*=11.3 Hz, 1H)	3.20 (br d, *J* = 11.4 Hz, 1H)		
3.82(ddd like, *J*=5.3, 5.3, 5.3 Hz, 2H)	3.84–3.77 (m, 2H)		

4. Reference

[1] Katakawa, K.; Kitajima, K.; Yamaguchi, K.; Takayama, H. *Heterocycles* **2006**, *69*, 223-229.