

Supporting Information

Modular access to N-substituted *cis*-3,5-diaminopiperidines

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Supporting Material

A. General	S2
B. ¹ H and ¹³ C spectra	S3
C. Chiral HPLC Data of 7k and 7l	S67

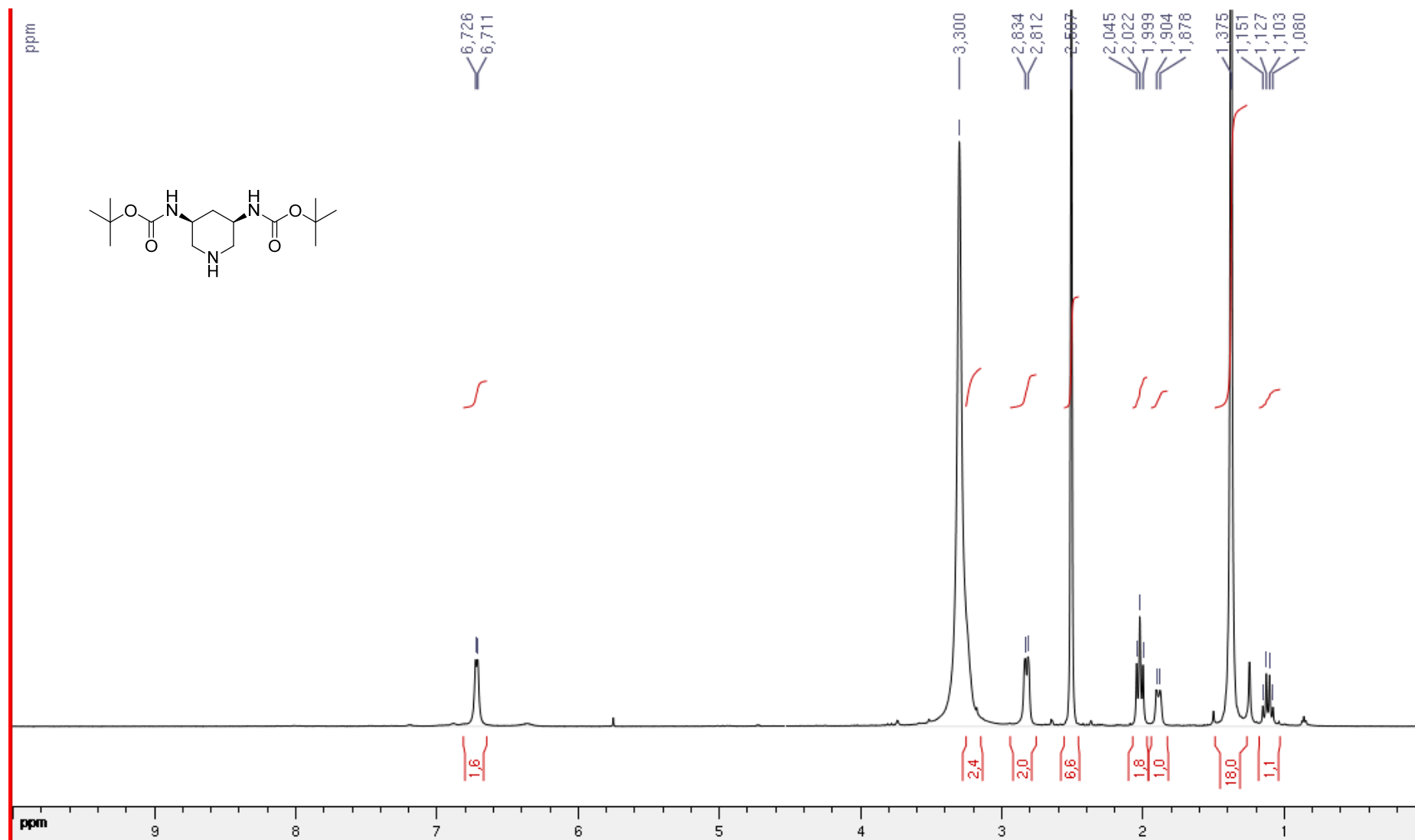
A. General

All reagents and solvents were obtained from commercial suppliers and used as such without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm silica-gel (60-F254) with visualization by UV-light or staining with phosphomolybdic acid, ninhydrin or Dragendorff's reagent. Column chromatography was performed on silica gel 60 Å (40-63 µm). All ^1H NMR and ^{13}C NMR spectra were recorded on spectrometers operating at 250, 300, 400 or 500 MHz and at 75, 100 or 125 MHz, respectively. HRMS spectra were recorded on a Orbitrap Mass Spectrometer or on a ESI-QToF II instrument.

B. ^1H and ^{13}C spectra

Di-tert-butyl (3S,5R)-piperidine-3,5-diylldicarbamate

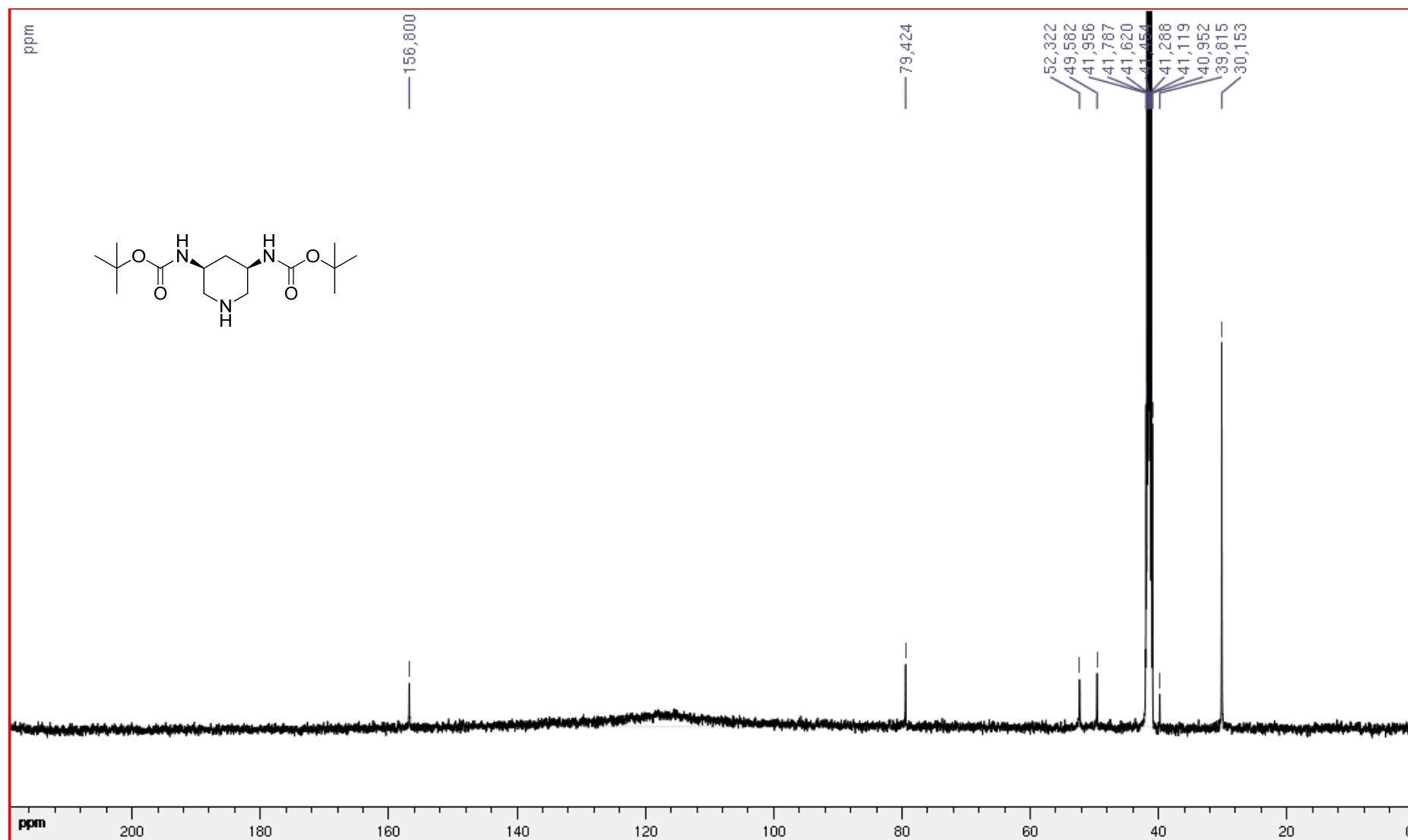
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S3

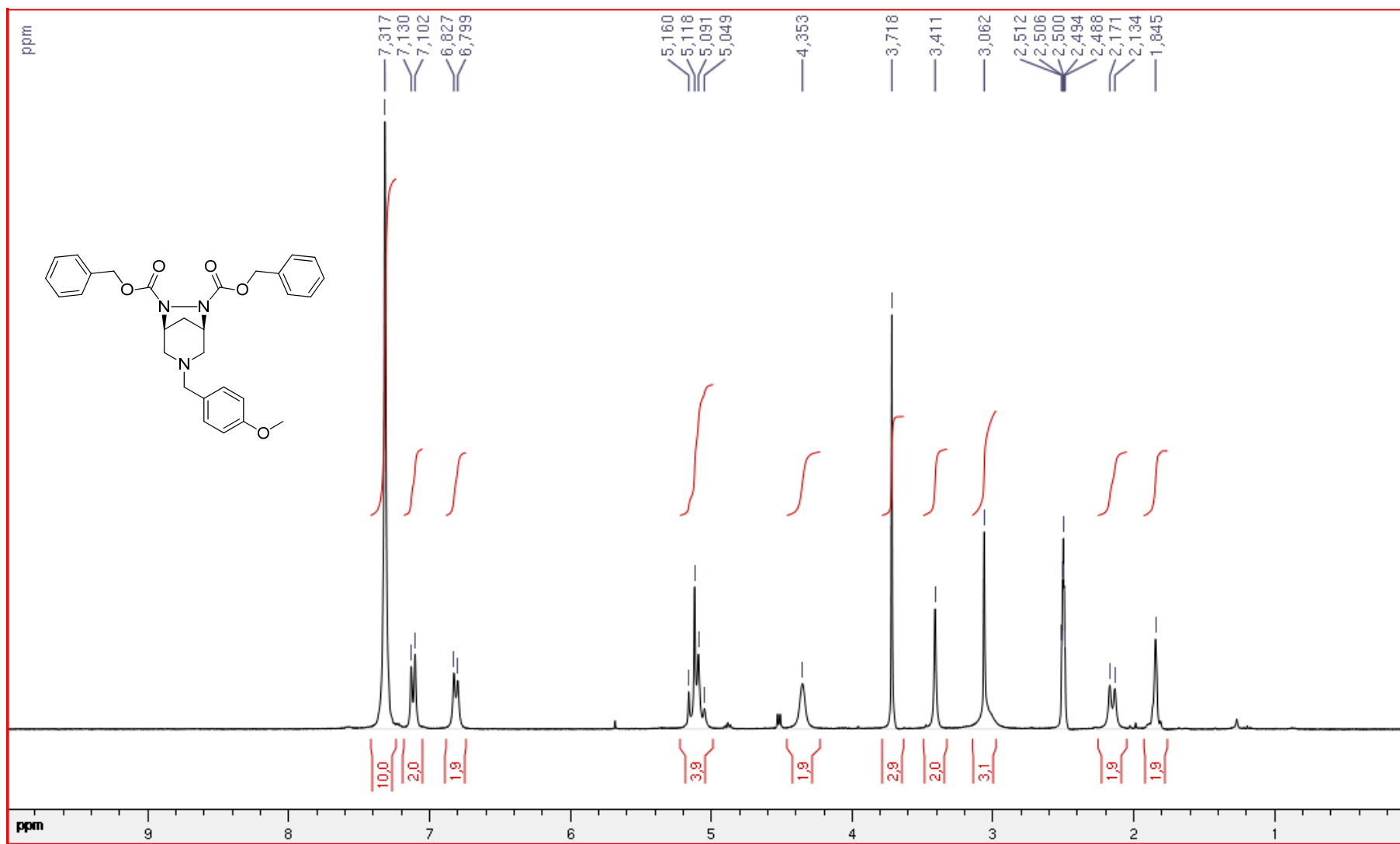
Di-tert-butyl (3S,5R)-piperidine-3,5-diylldicarbamate

4



Dibenzyl 3-(4-methoxybenzyl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

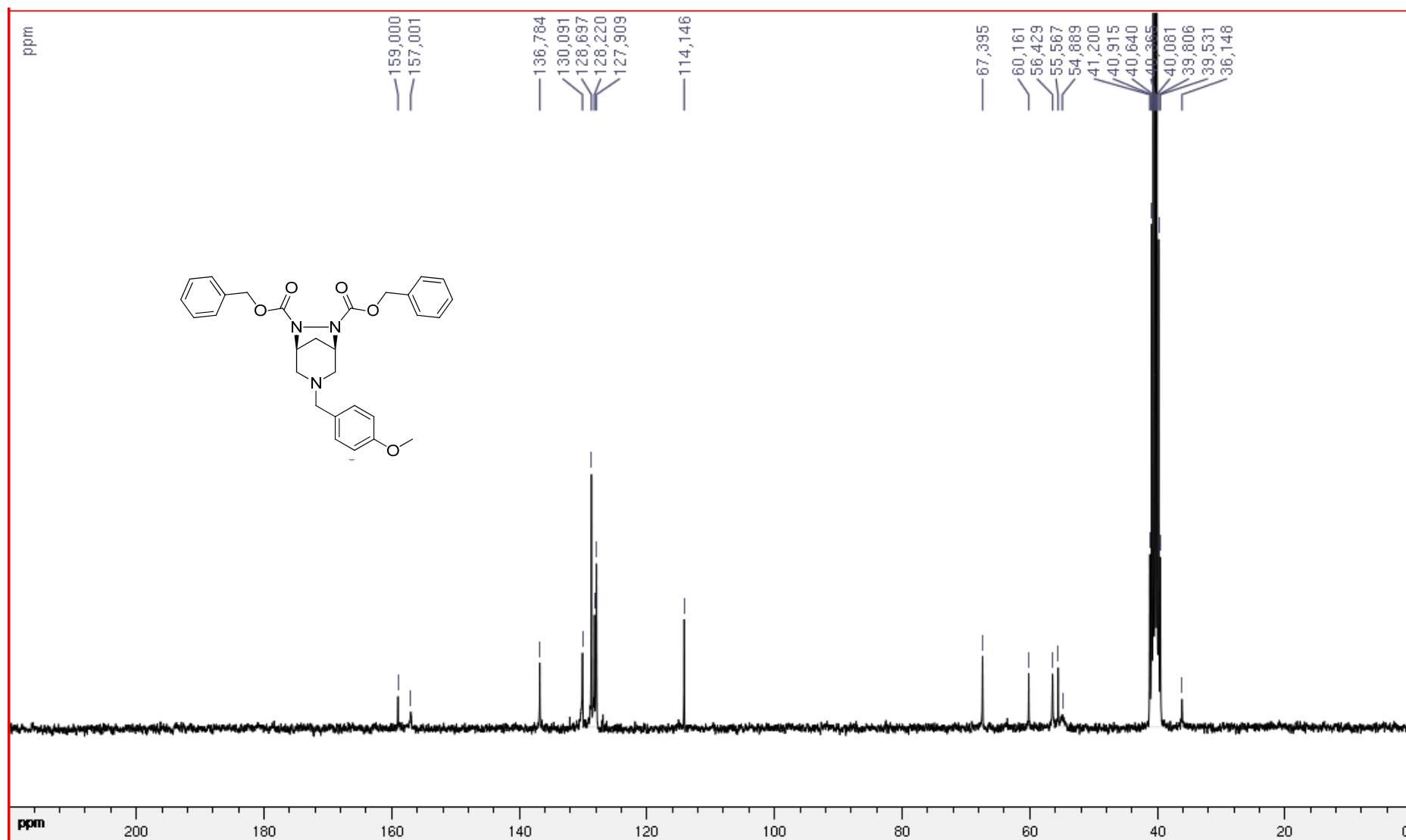
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S5

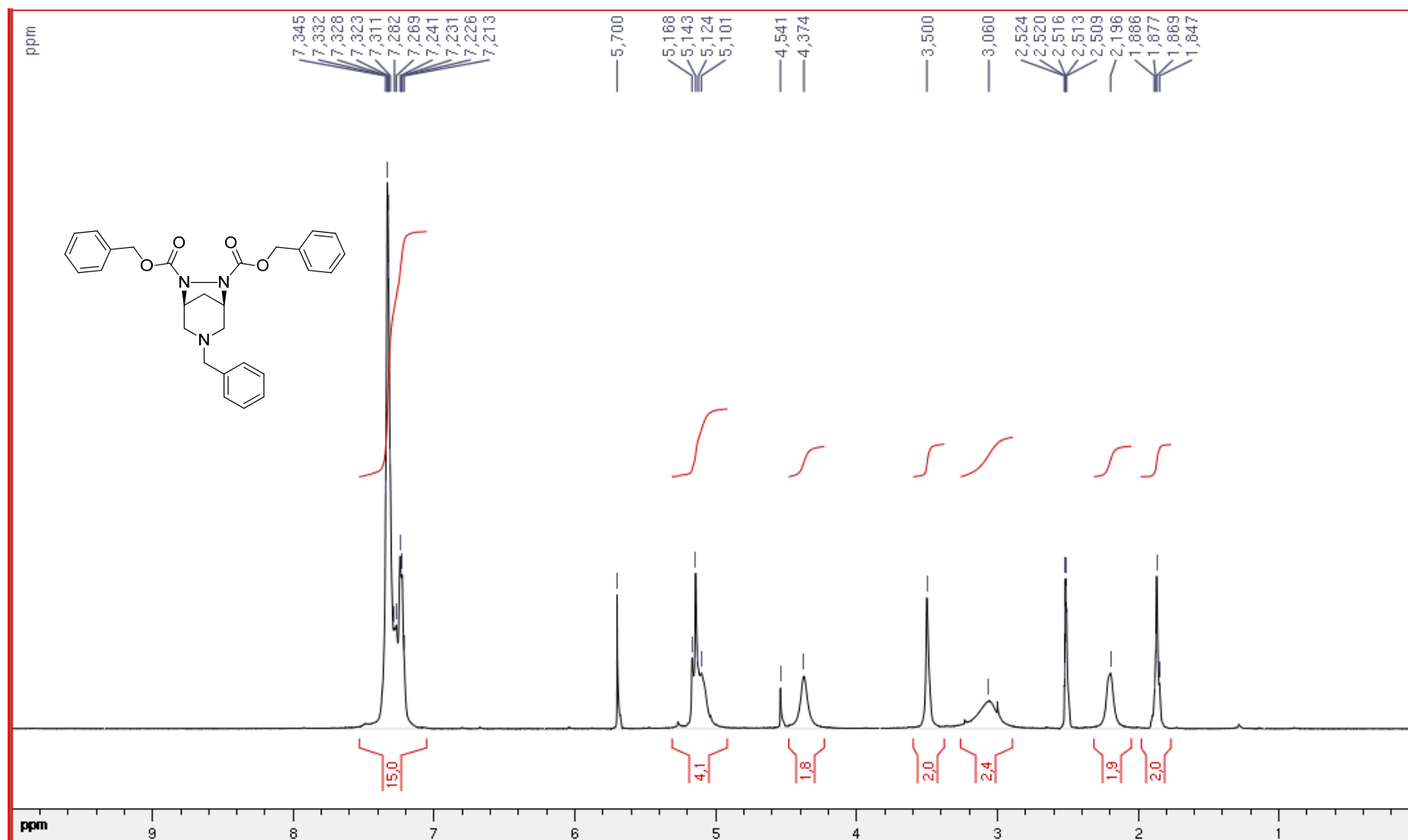
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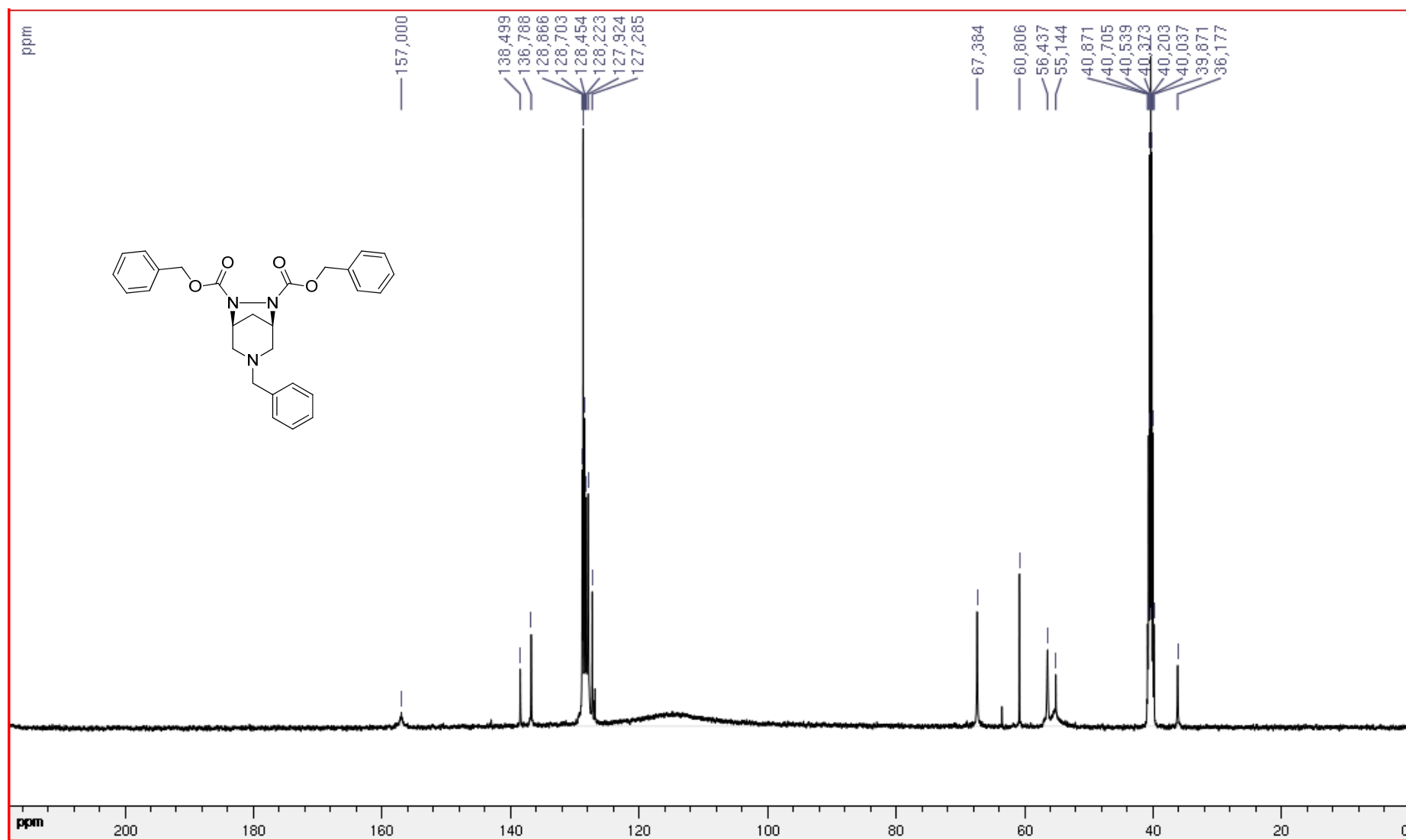
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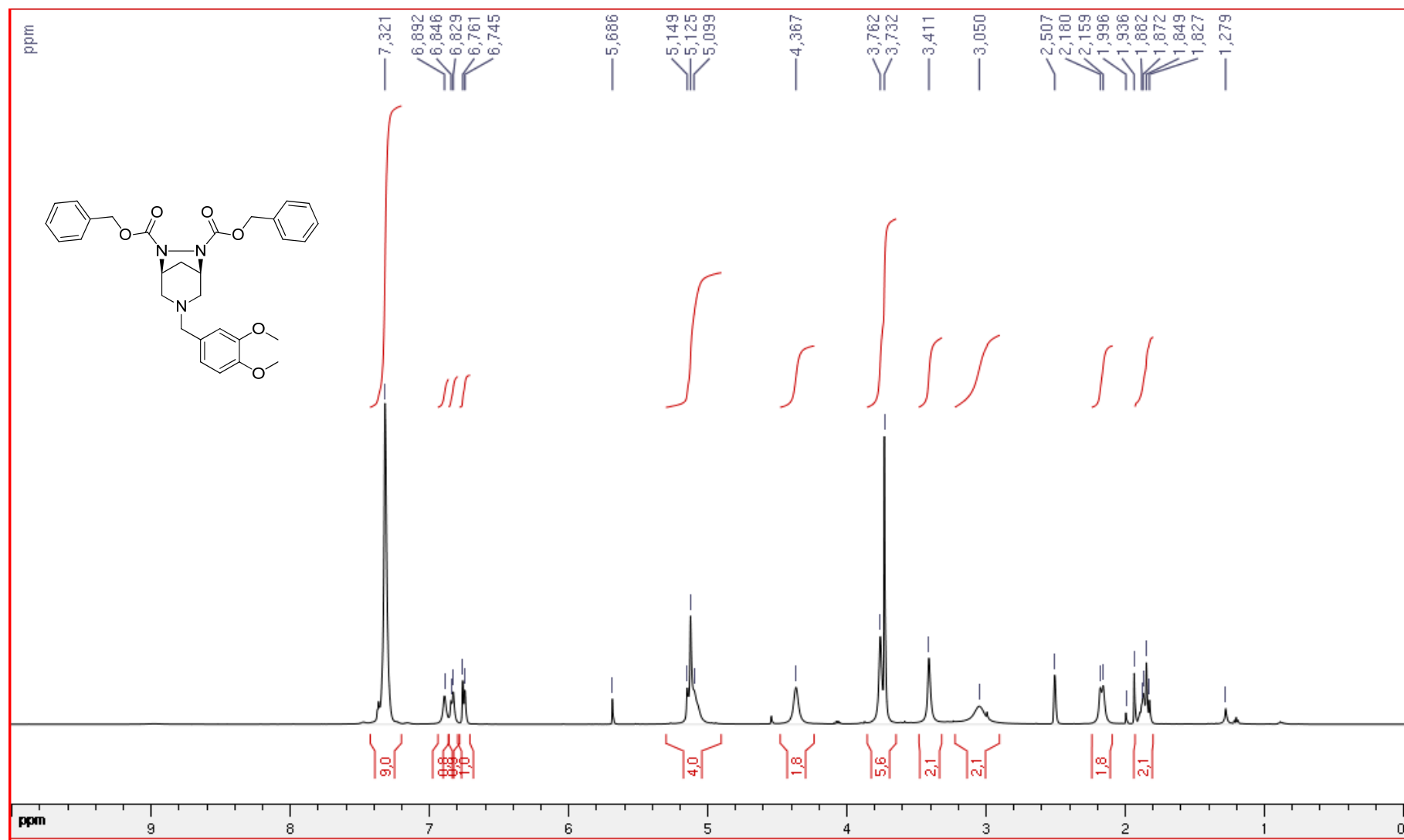
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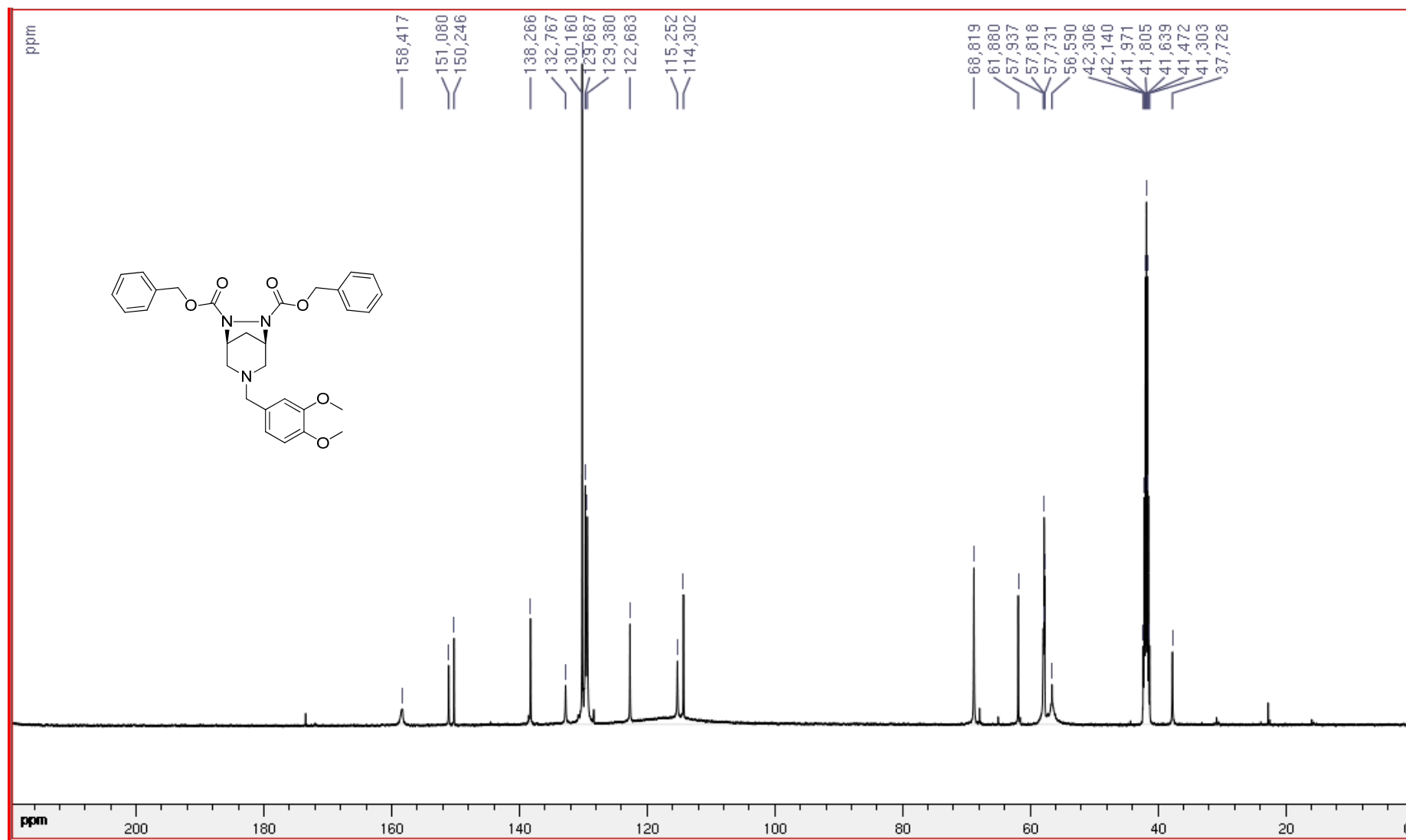
Dibenzyl 3-(3,4-dimethoxybenzyl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7c



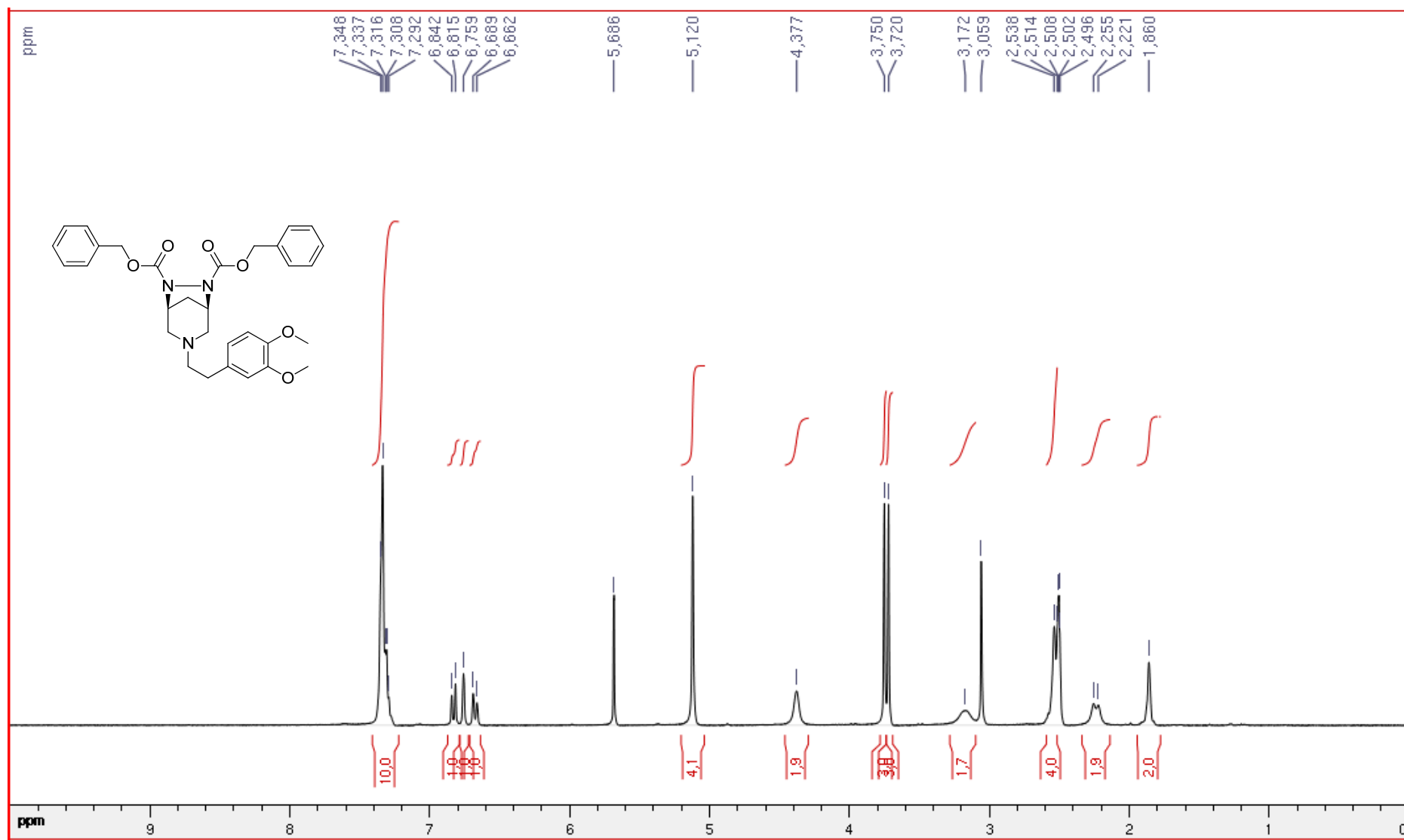
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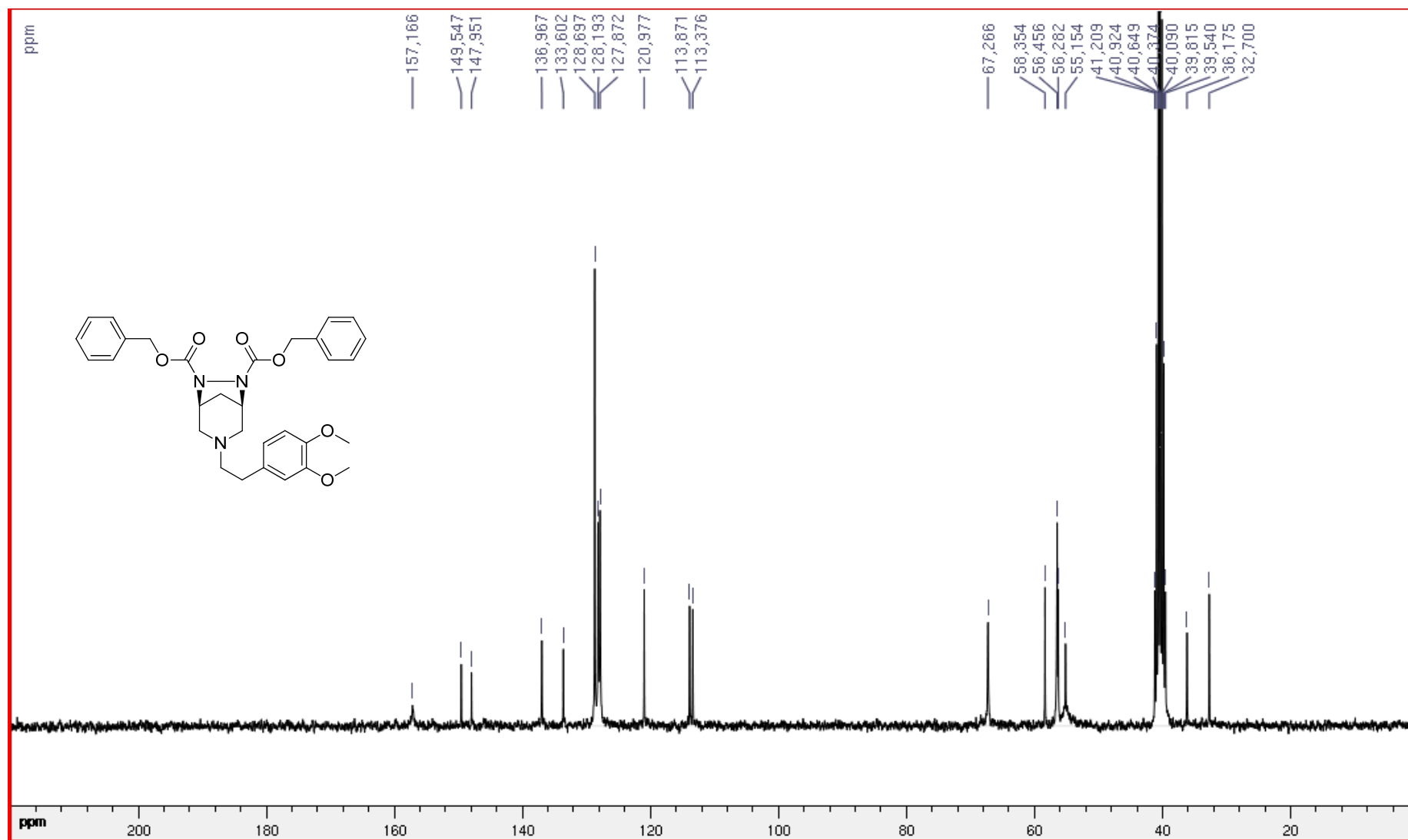
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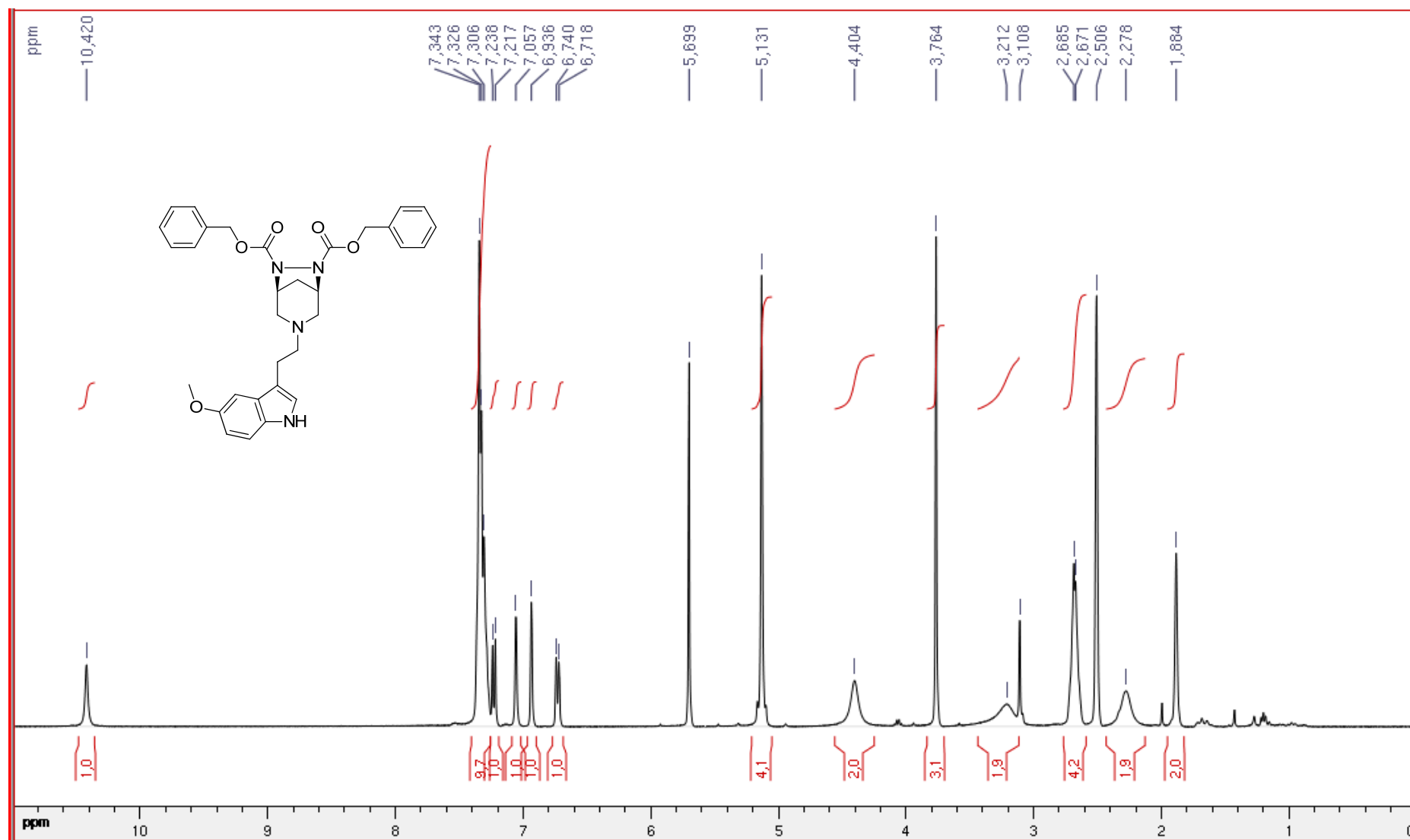
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7d



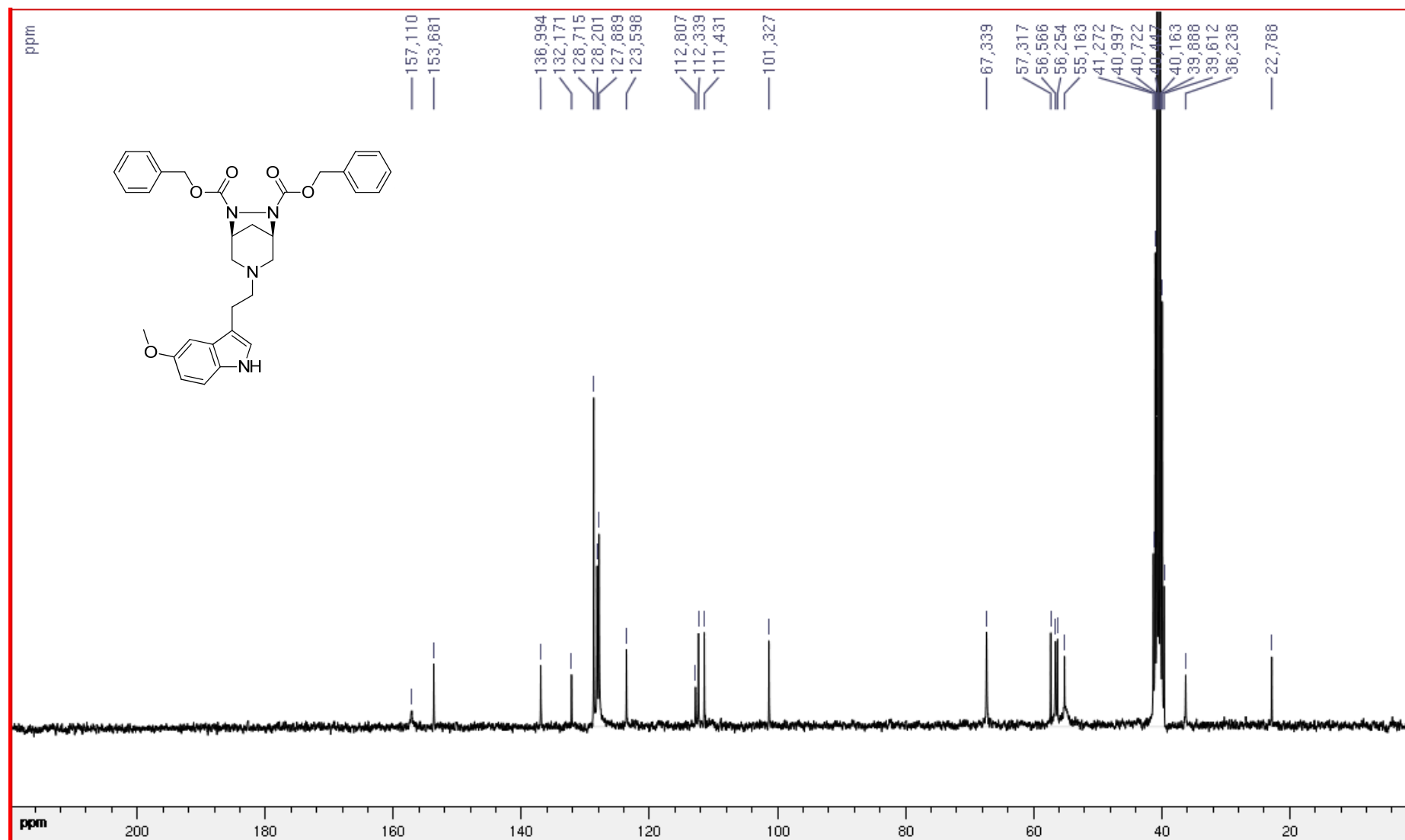
Dibenzyl 3-(2-(5-methoxy-1H-indol-3-yl)ethyl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

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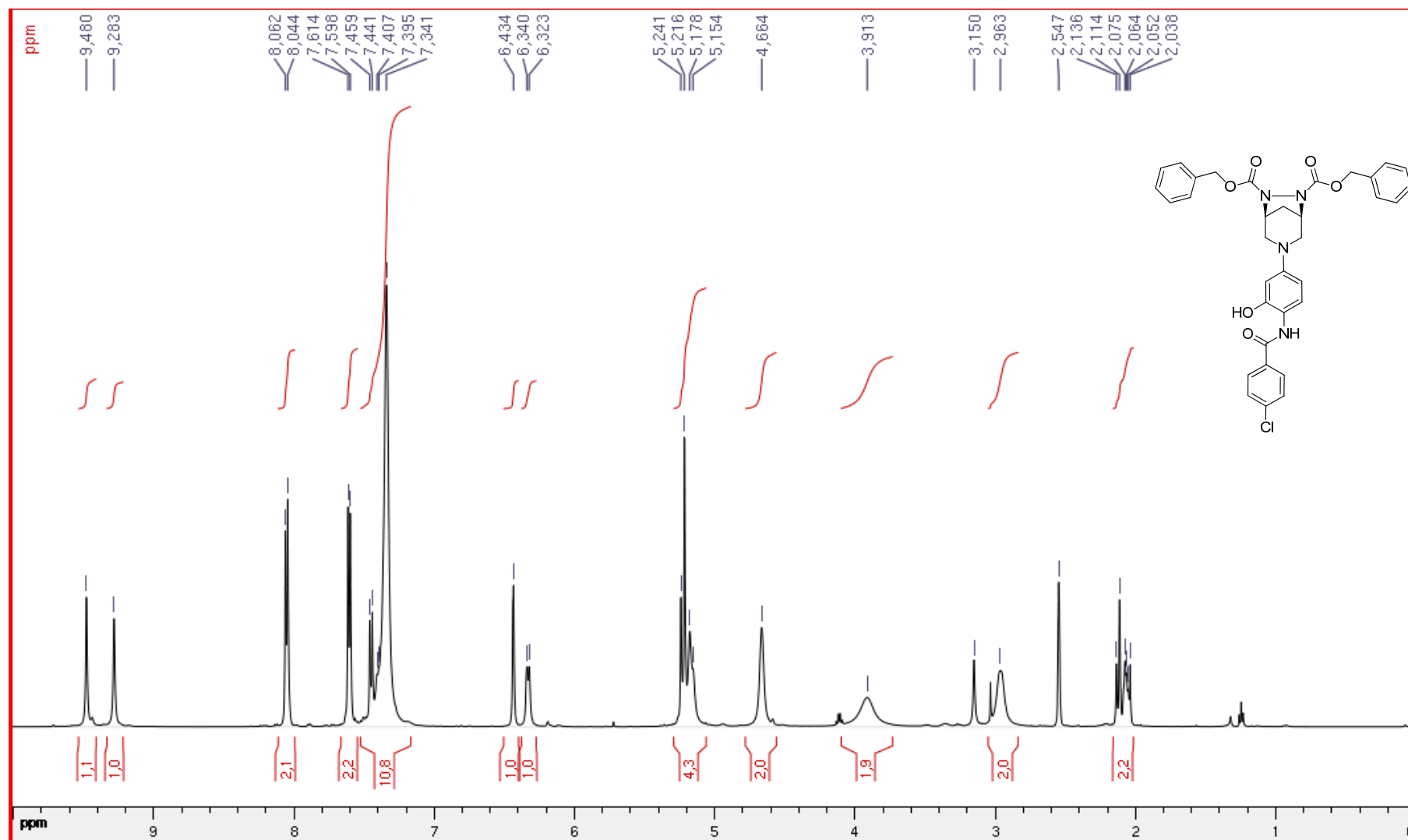
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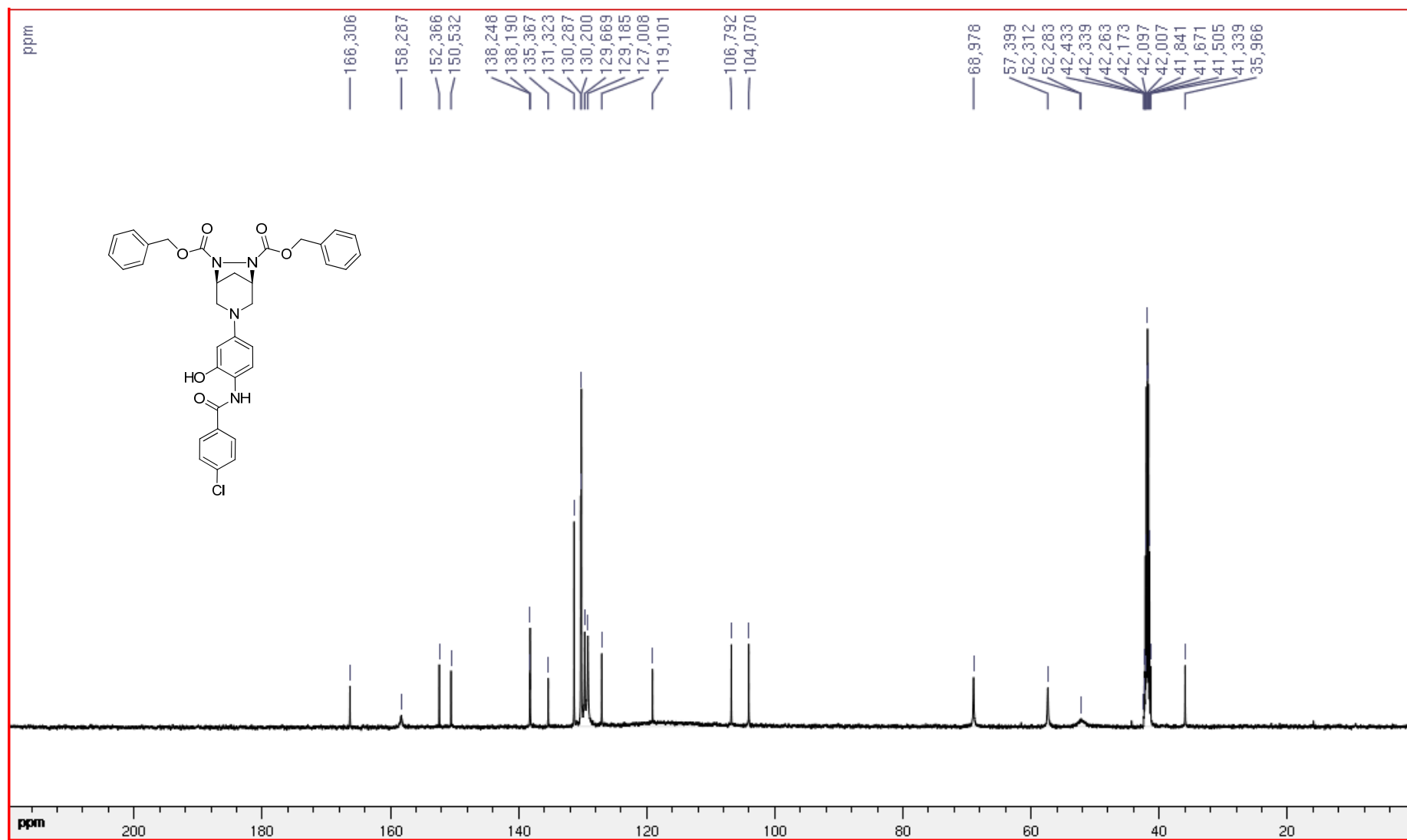
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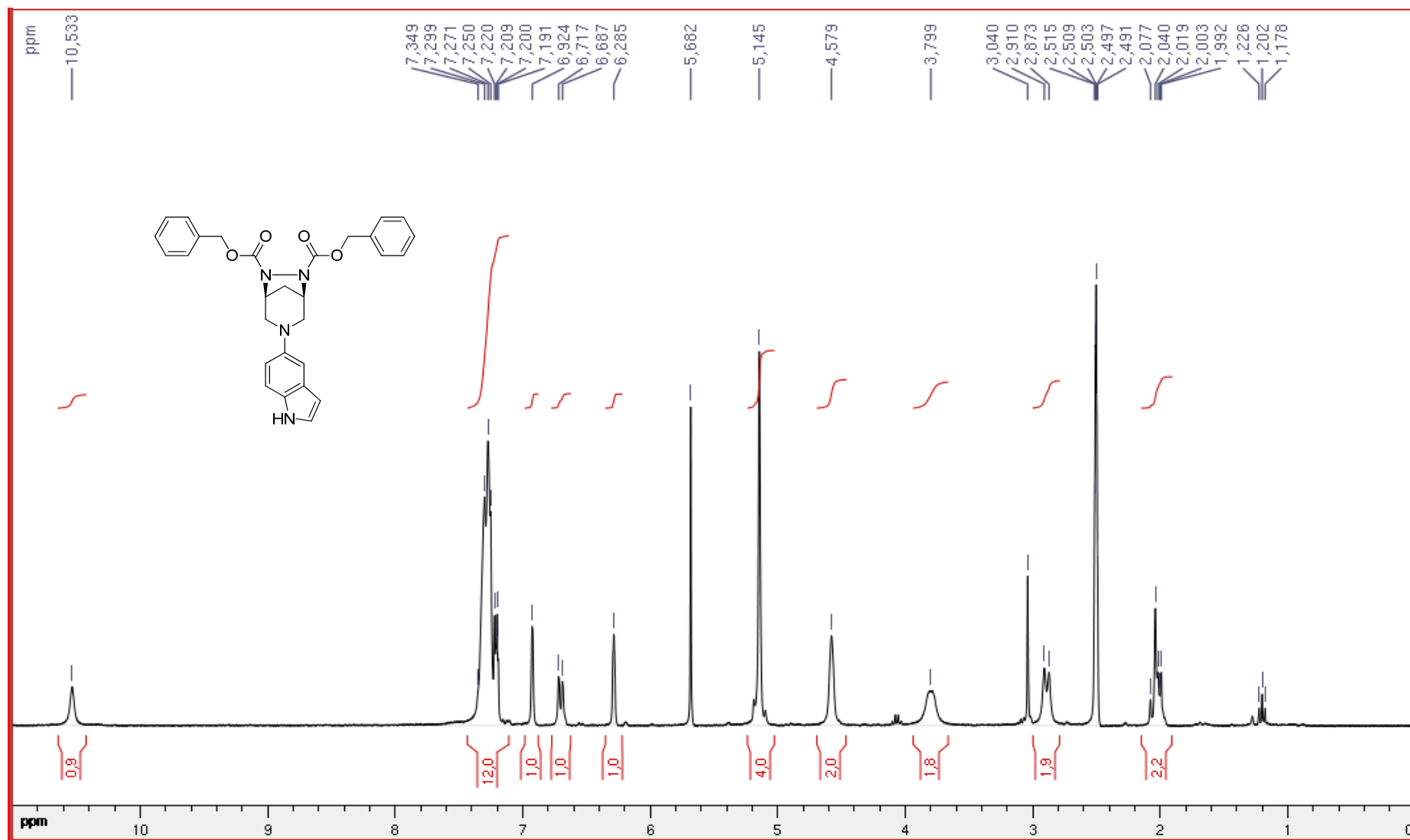
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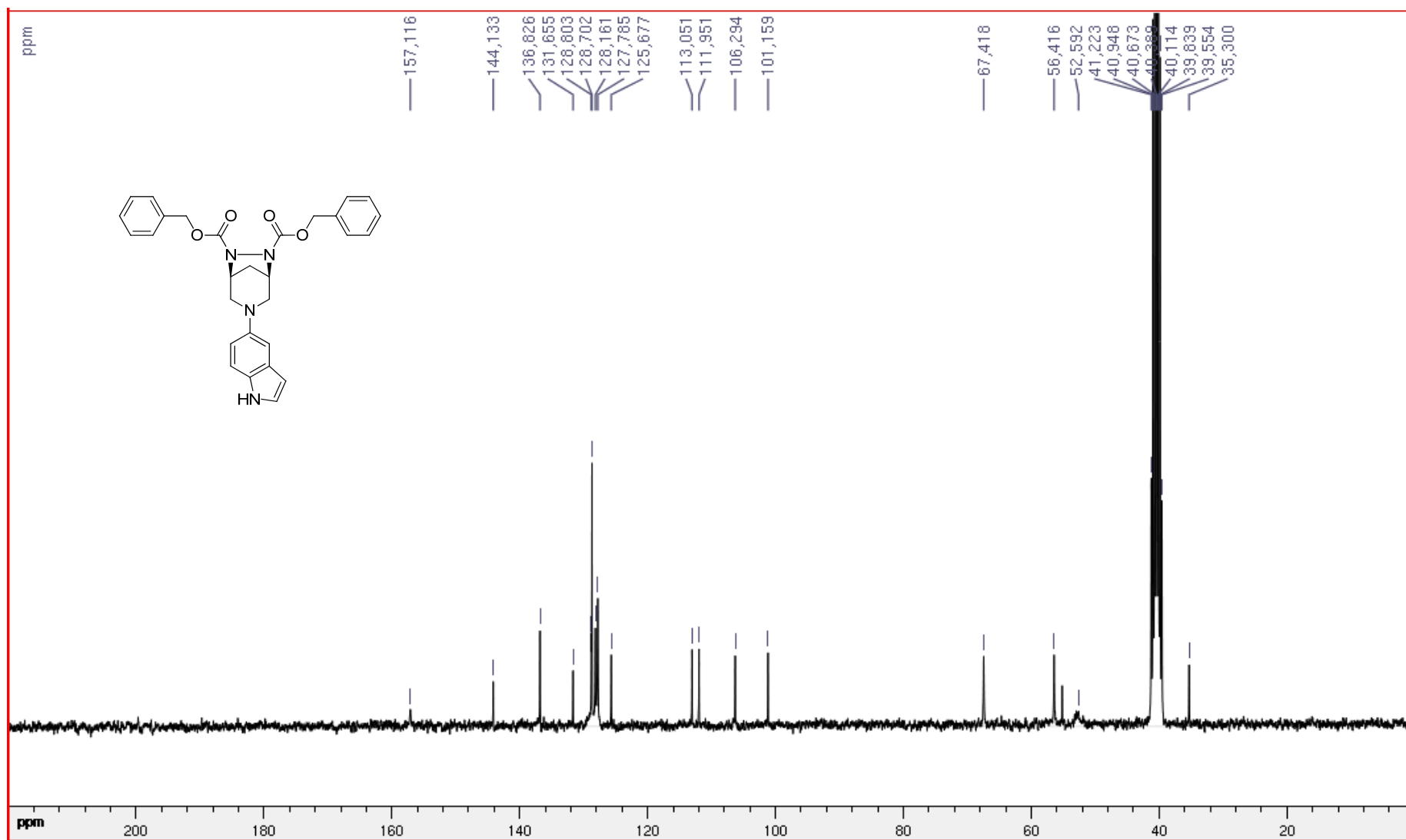
Dibenzyl 3-(1H-indol-5-yl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7g



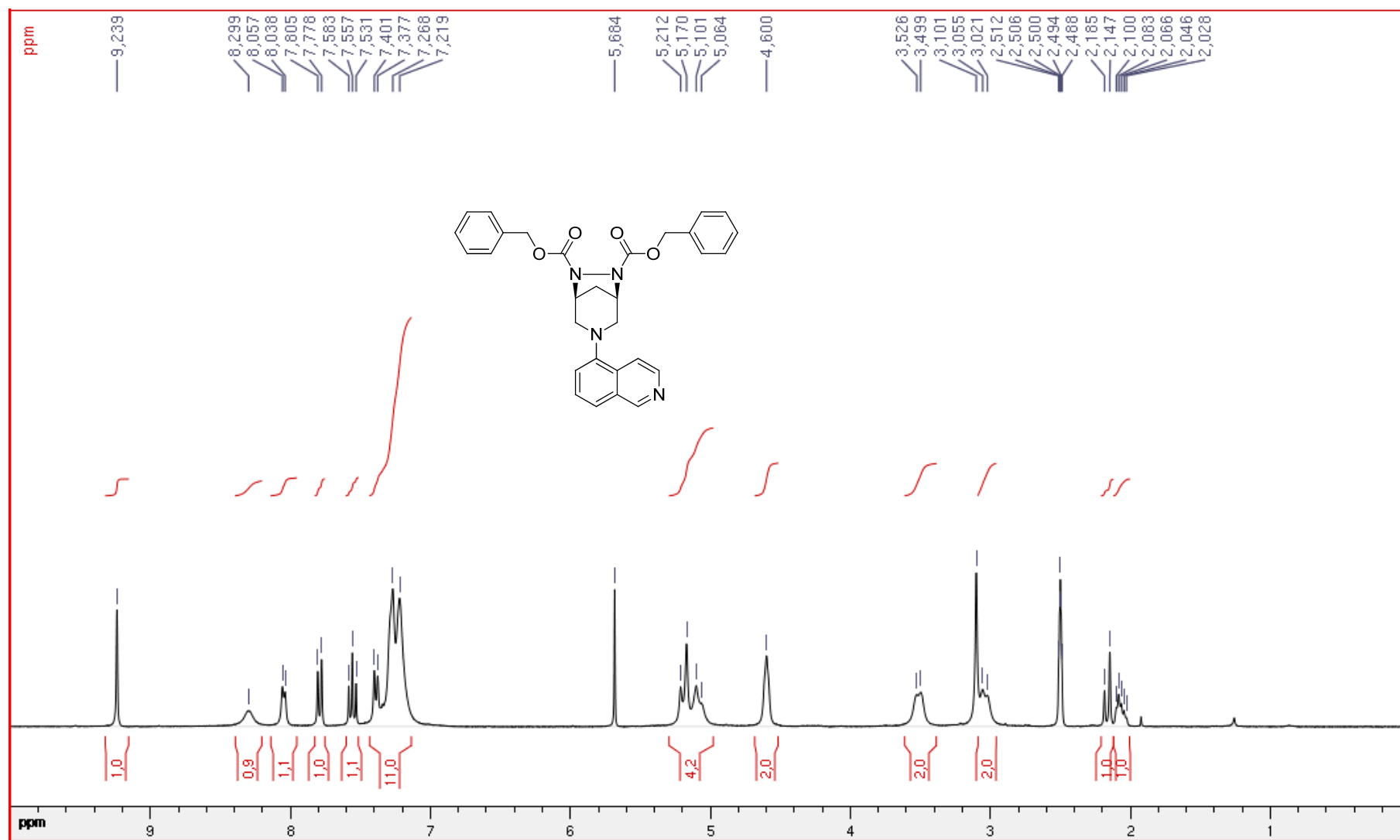
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7g



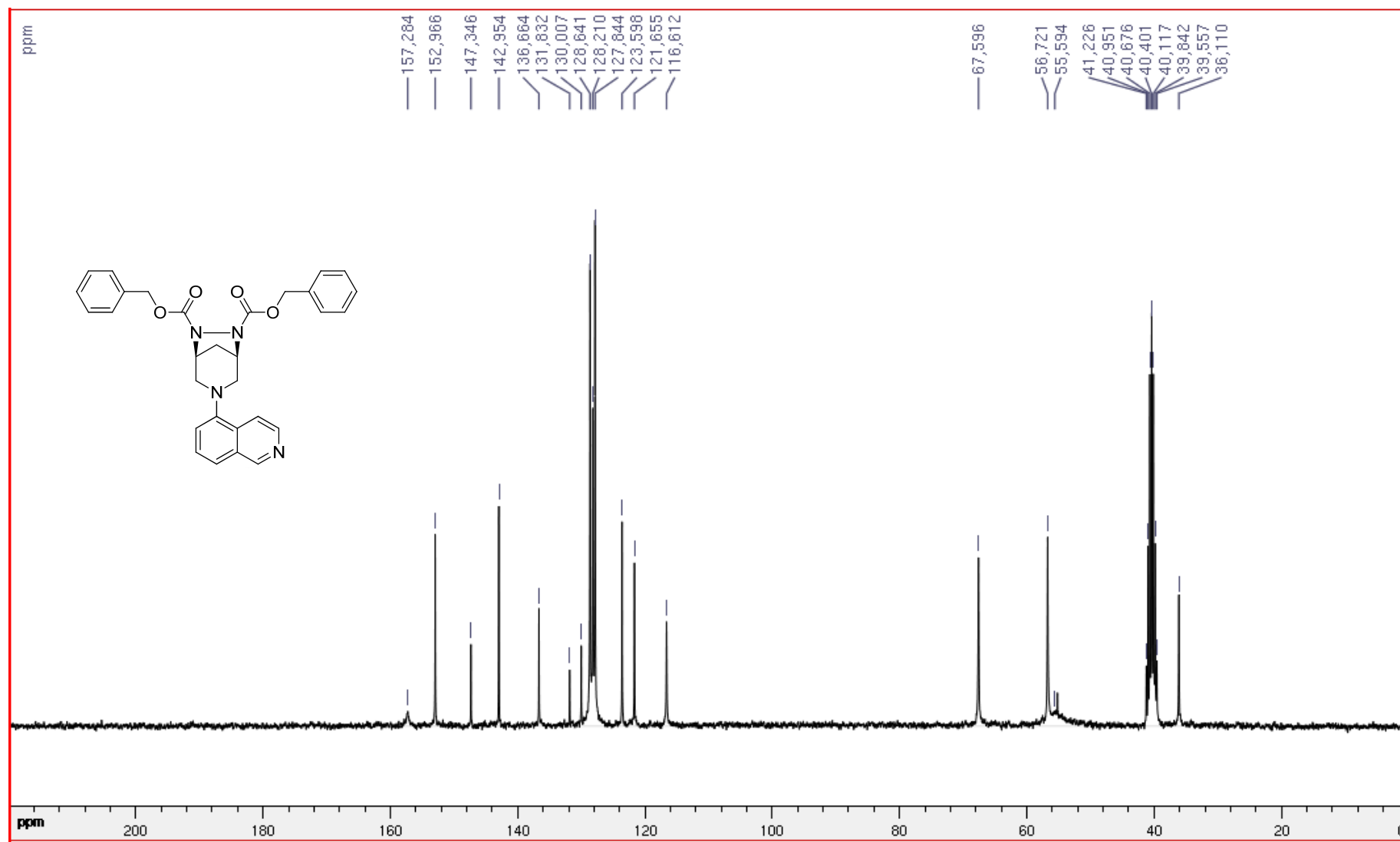
Dibenzyl 3-(isoquinolin-5-yl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7h



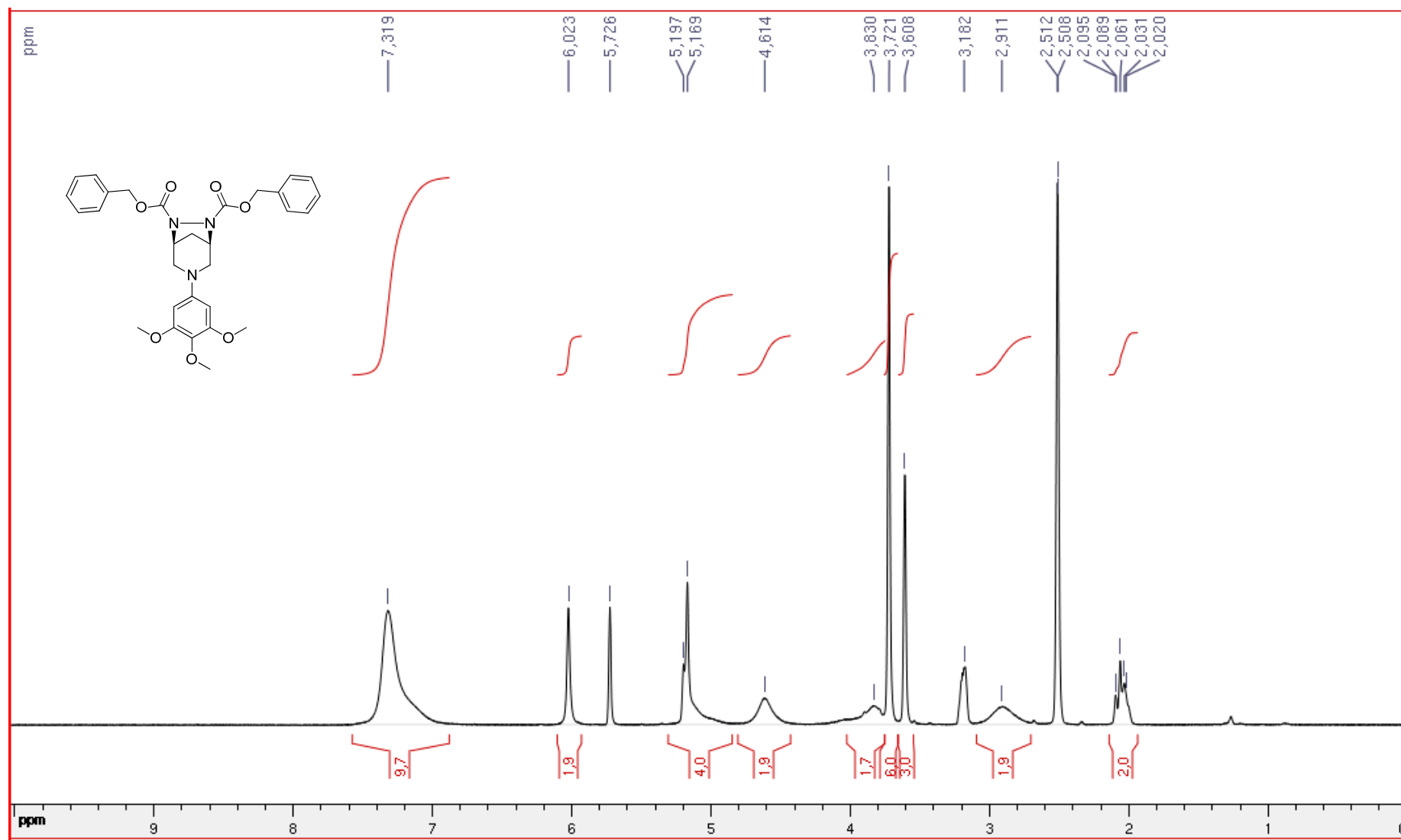
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7h



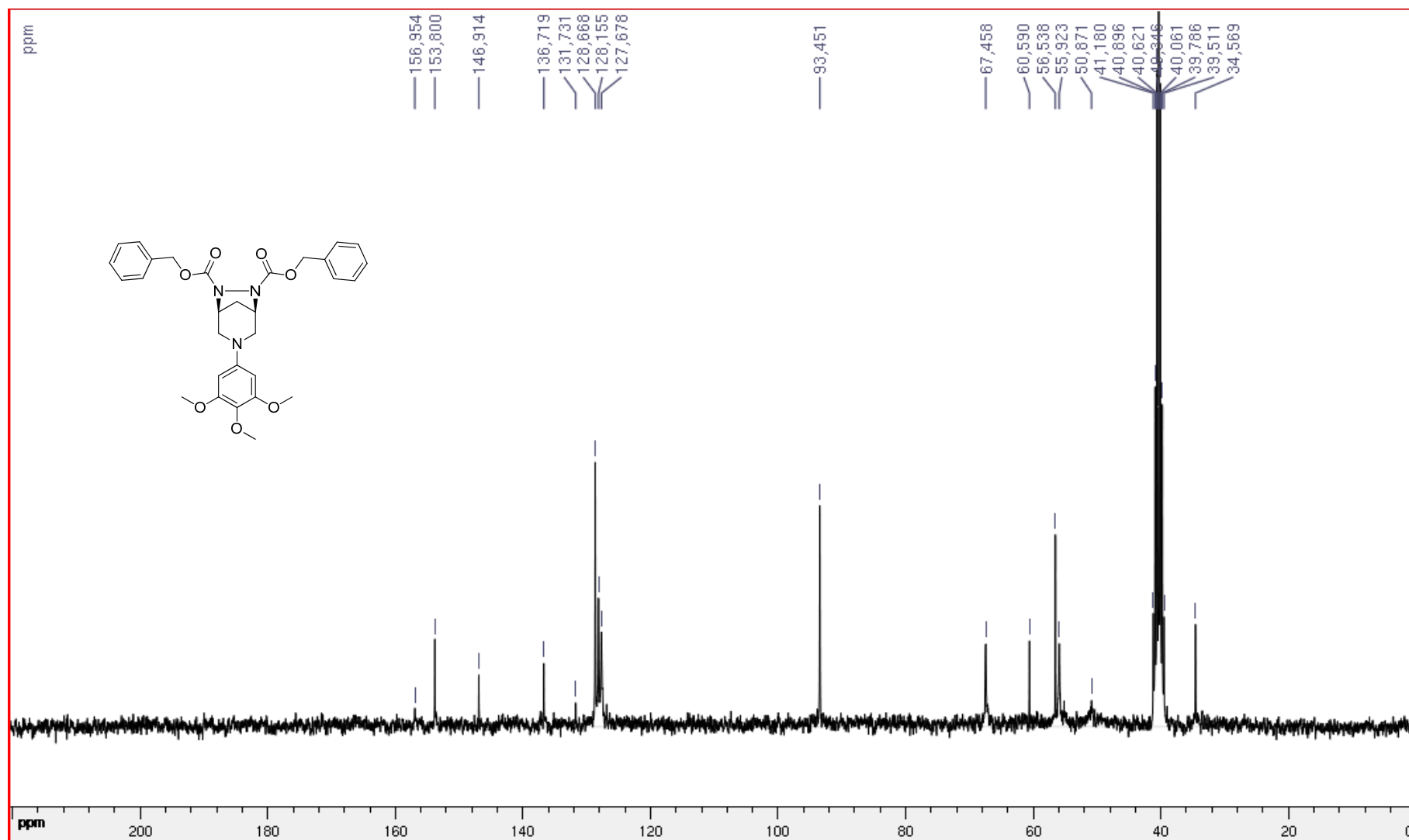
Dibenzyl 3-(3,4,5-trimethoxyphenyl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7i



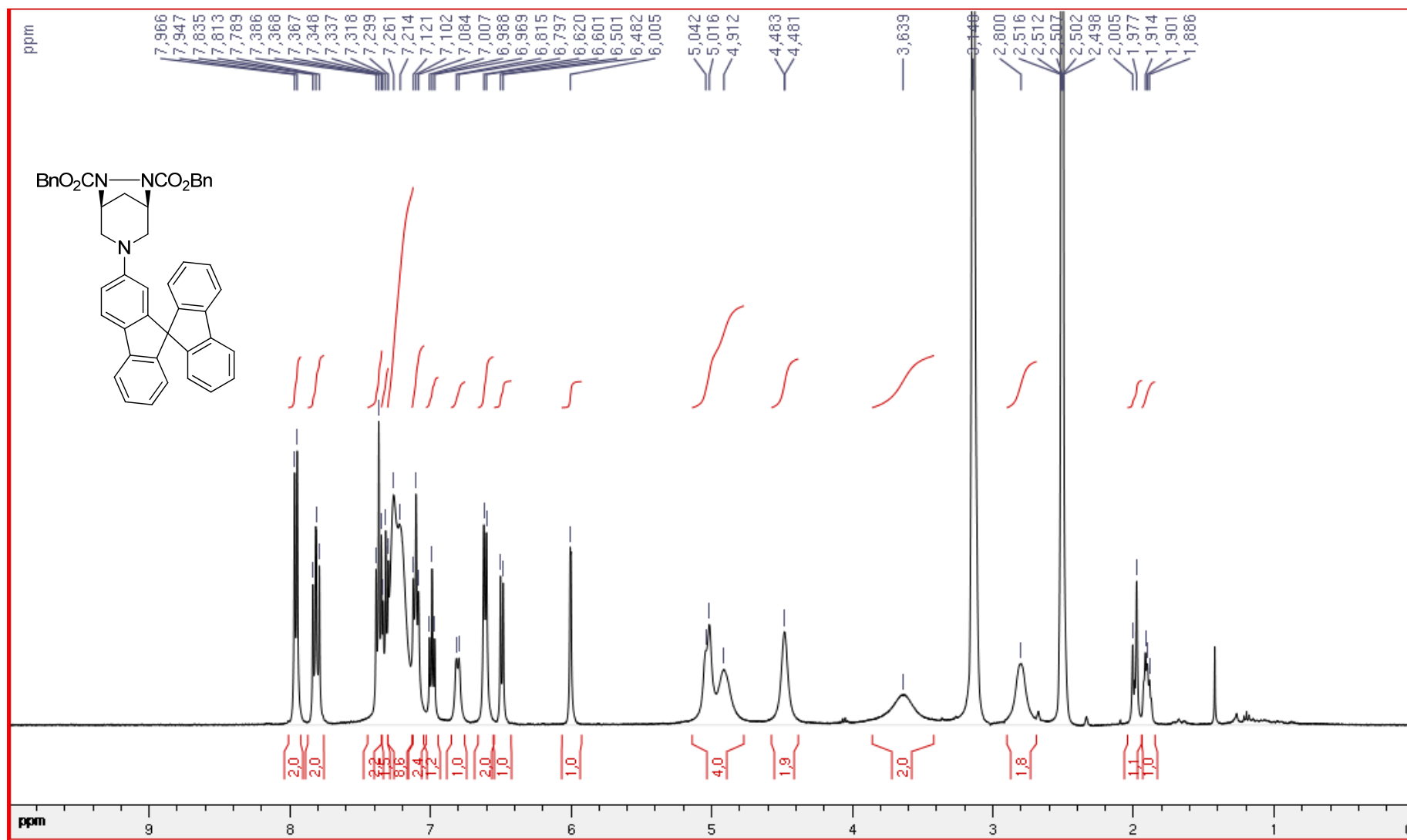
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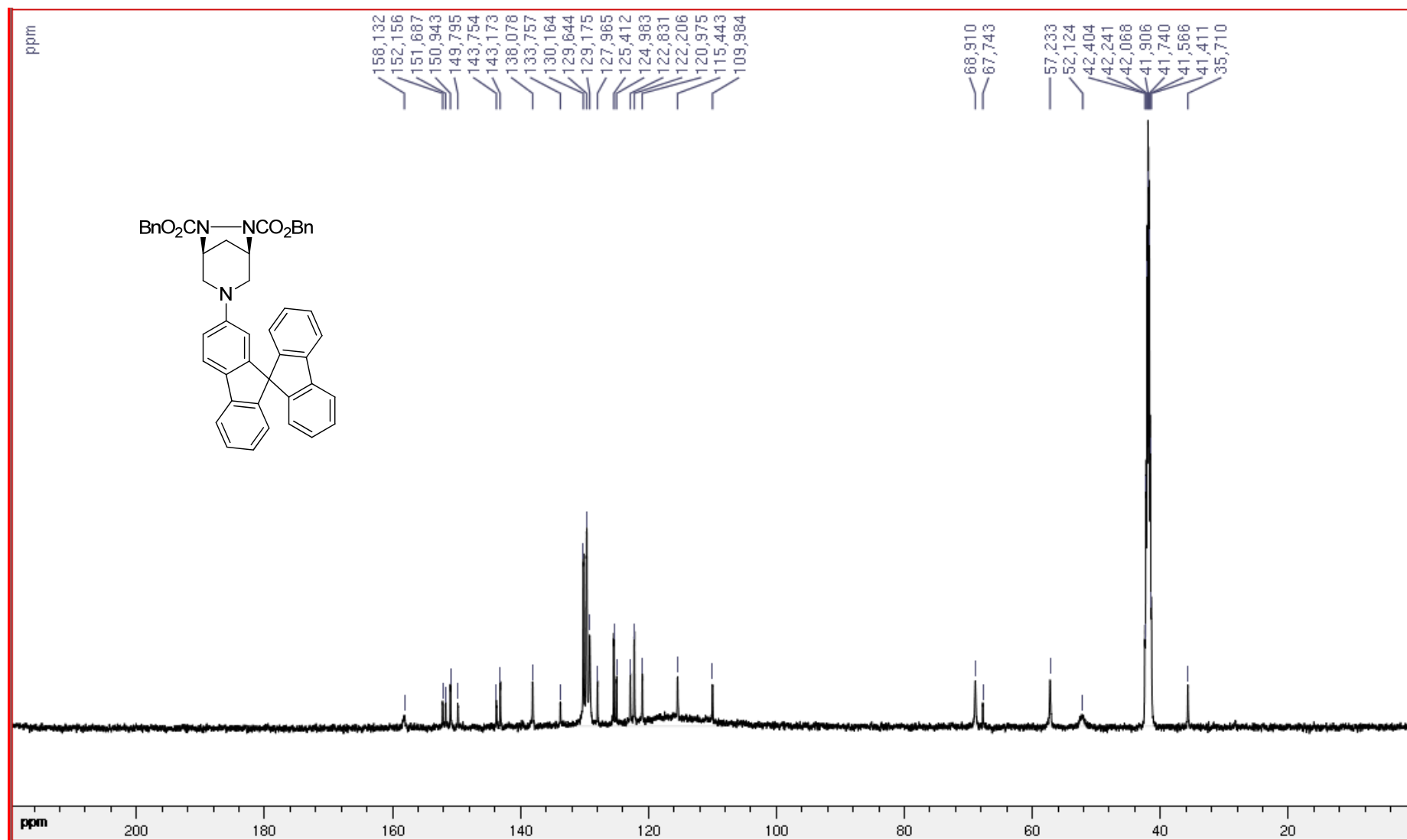
(1R,5S)-dibenzyl 3-(9,9'-spirobi[fluoren]-2-yl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7j



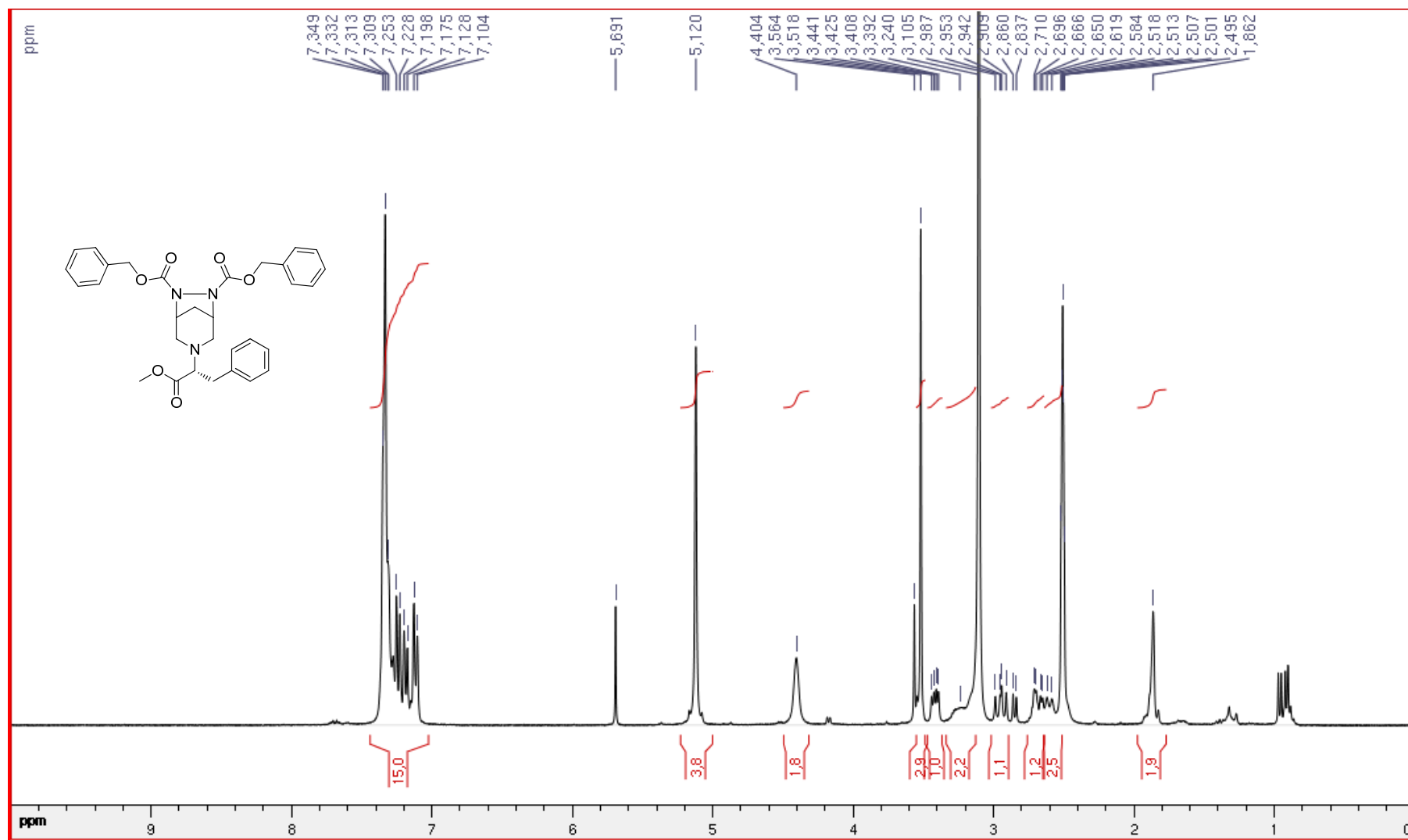
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7j



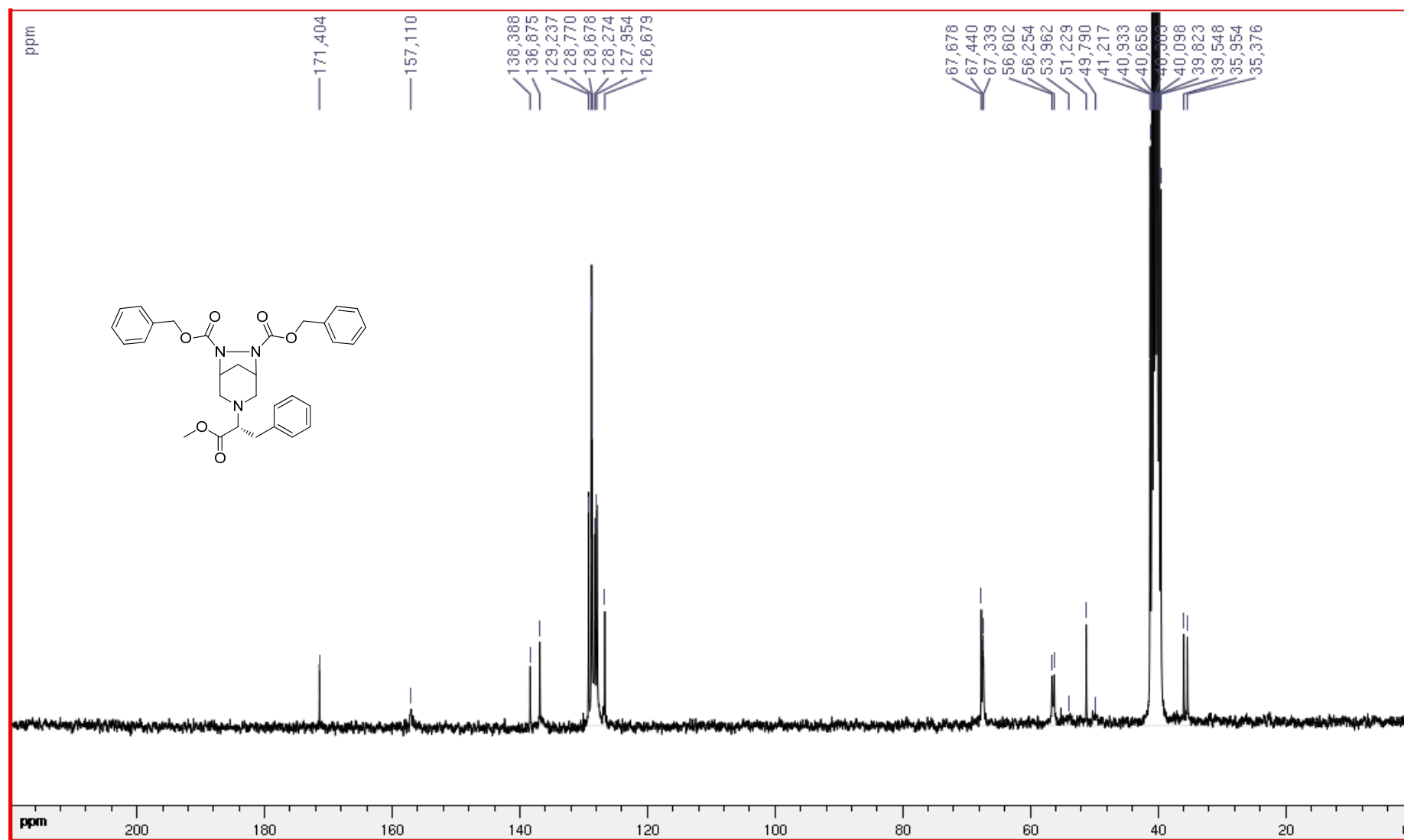
Dibenzyl 3-((R)-1-methoxy-1-oxo-3-phenylpropan-2-yl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7k



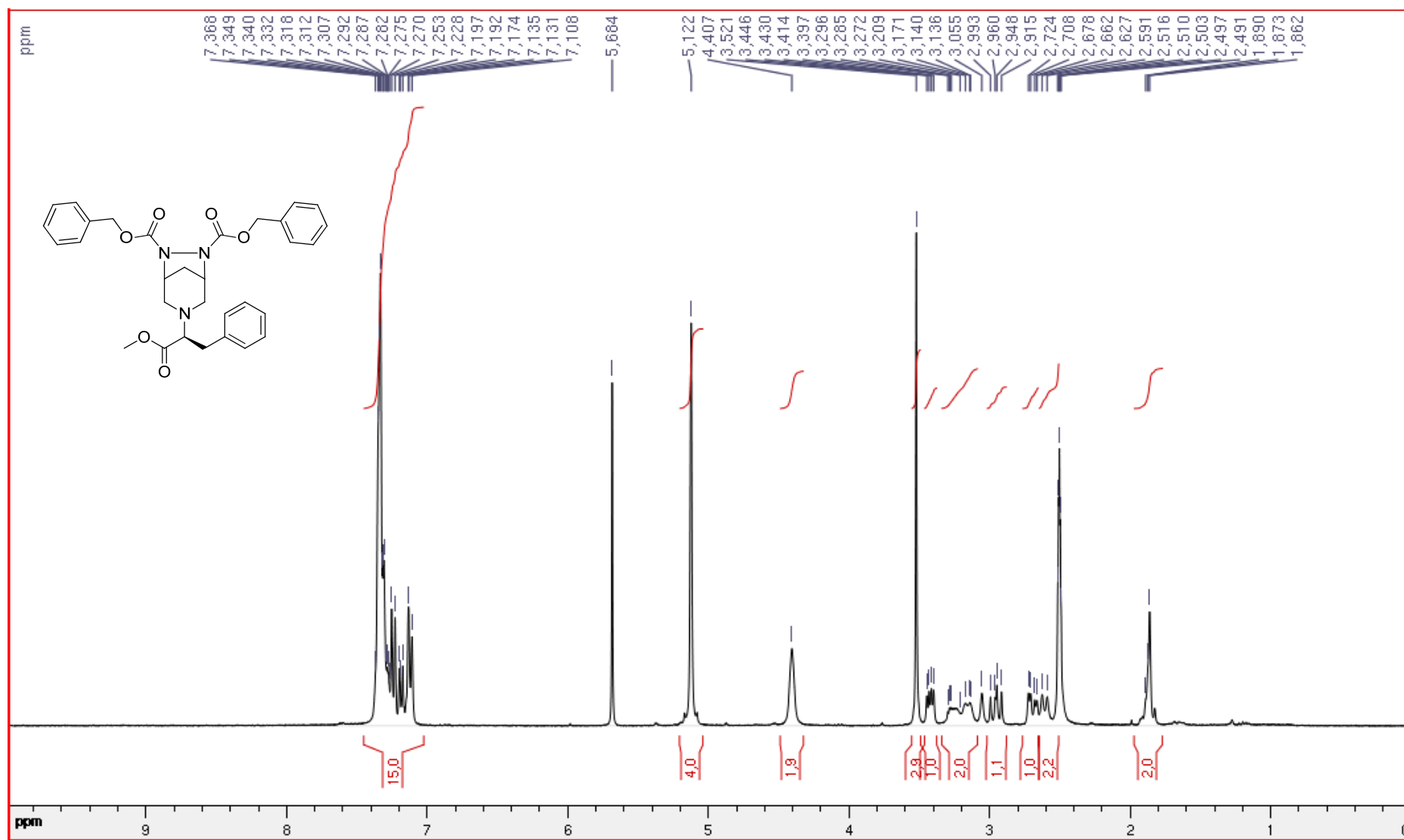
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7k



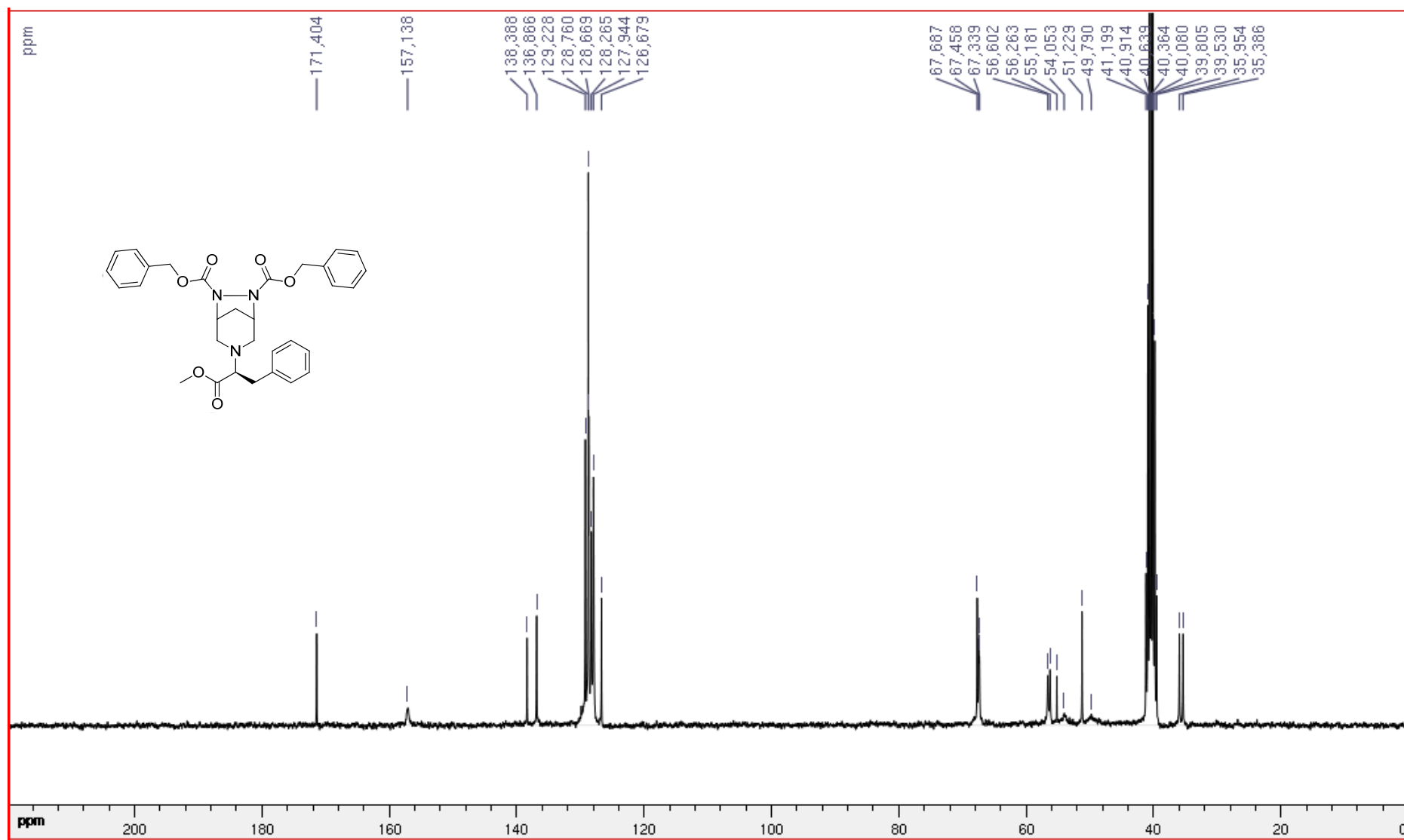
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71



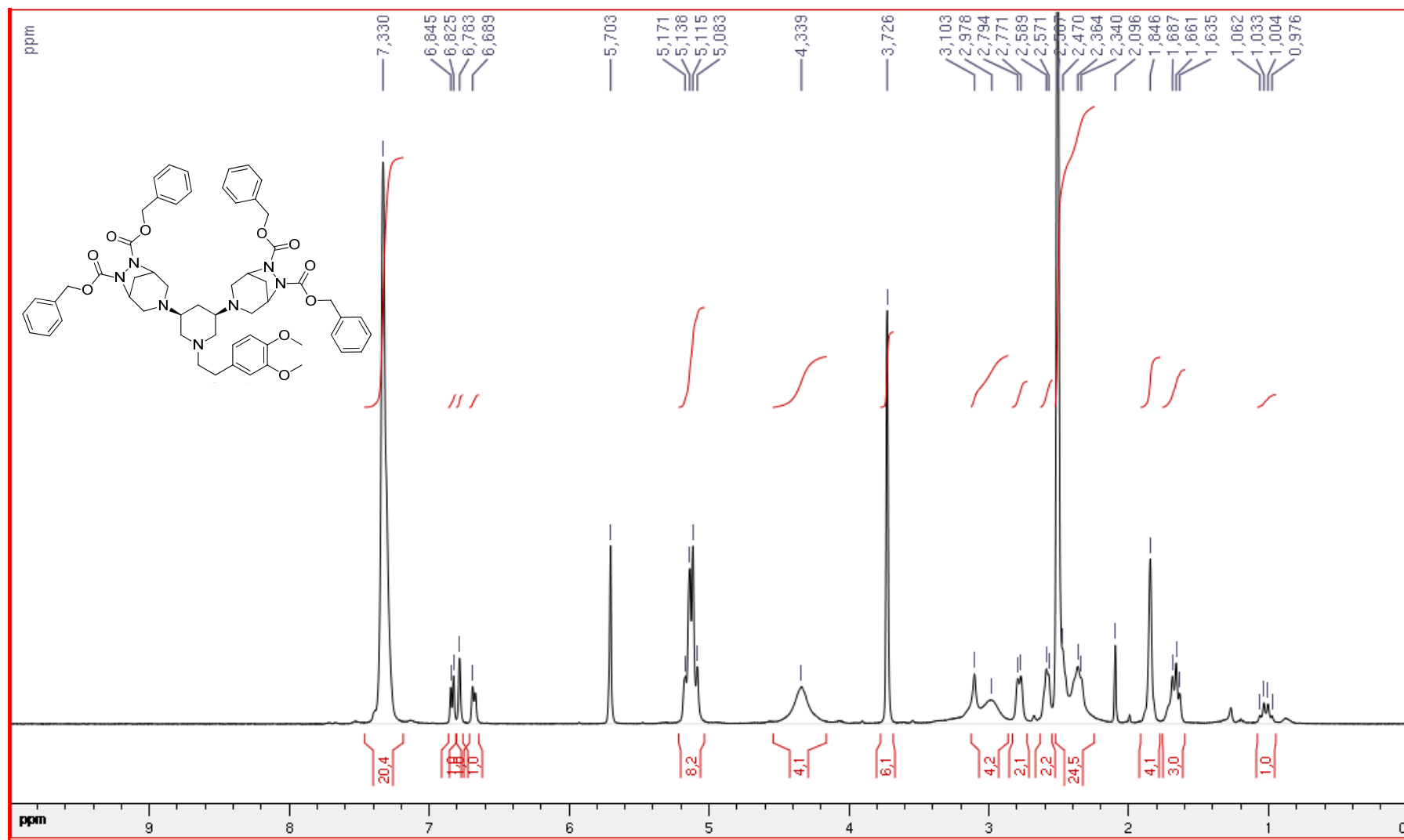
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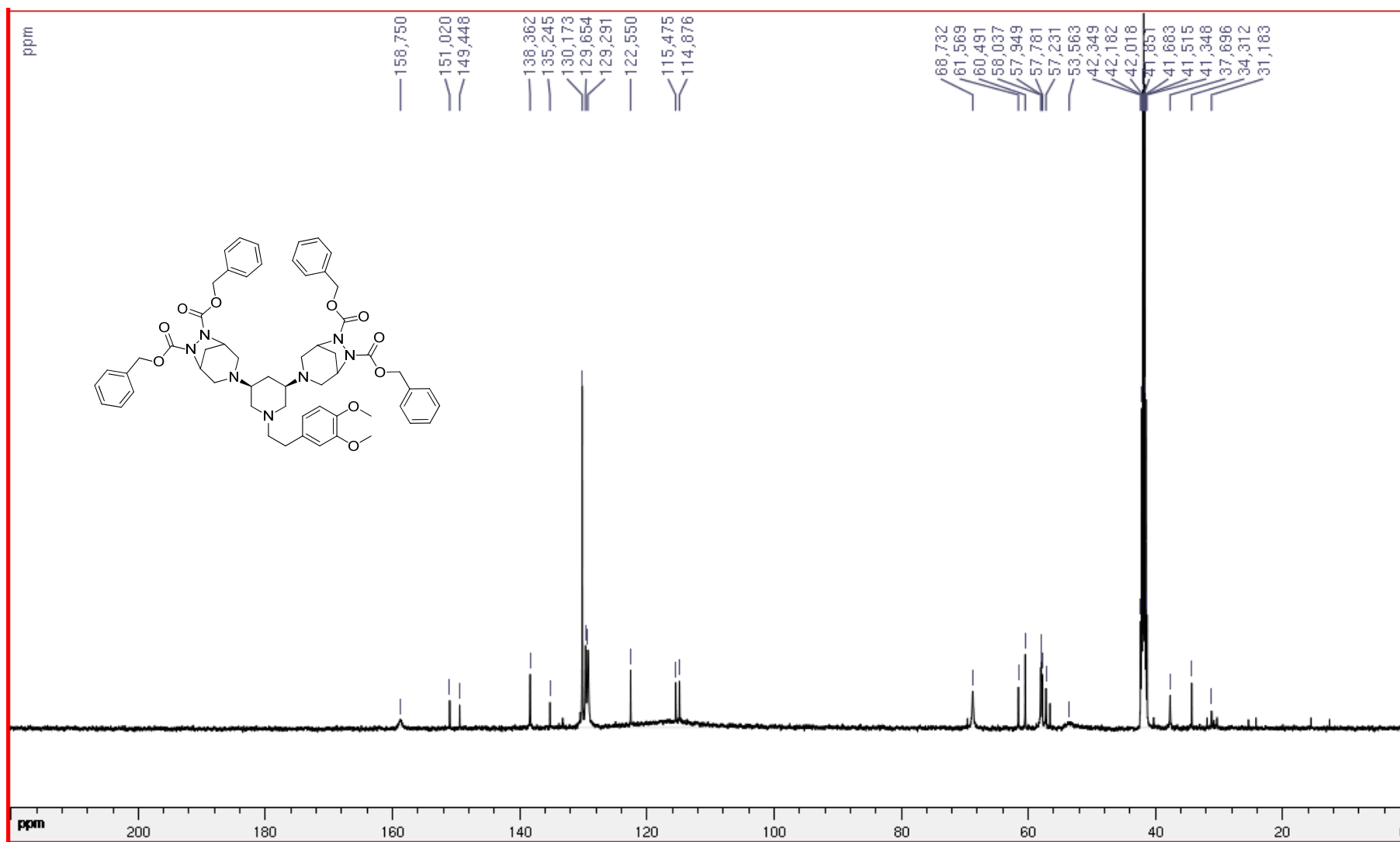
Tetrabenzyl 3,3'-((3S,5R)-1-(3,4-dimethoxyphenethyl)piperidine-3,5-diyl)bis(3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate)

7m



Tetrabenzyl 3,3'-((3S,5R)-1-(3,4-dimethoxyphenethyl)piperidine-3,5-diyl)bis(3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate)

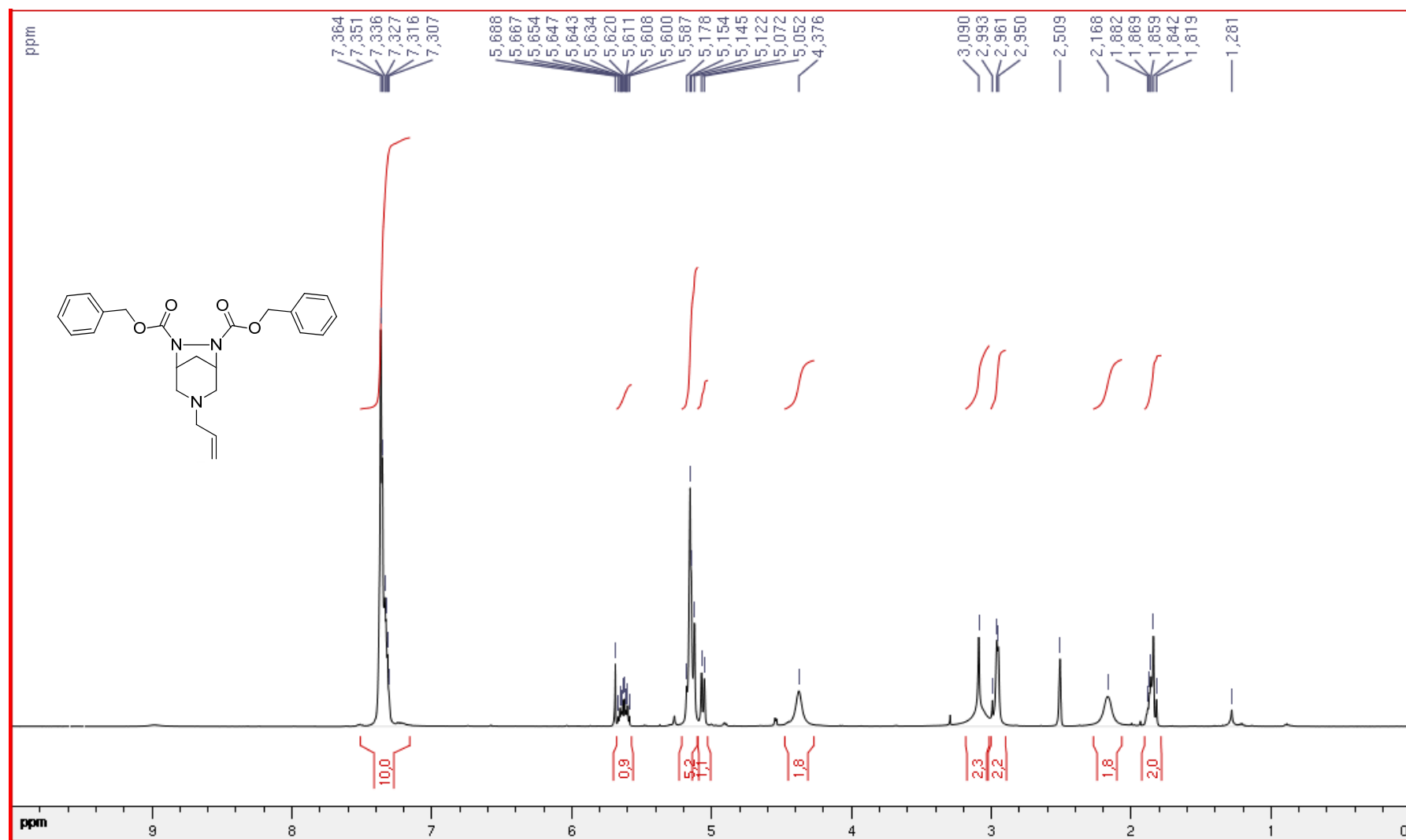
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S30

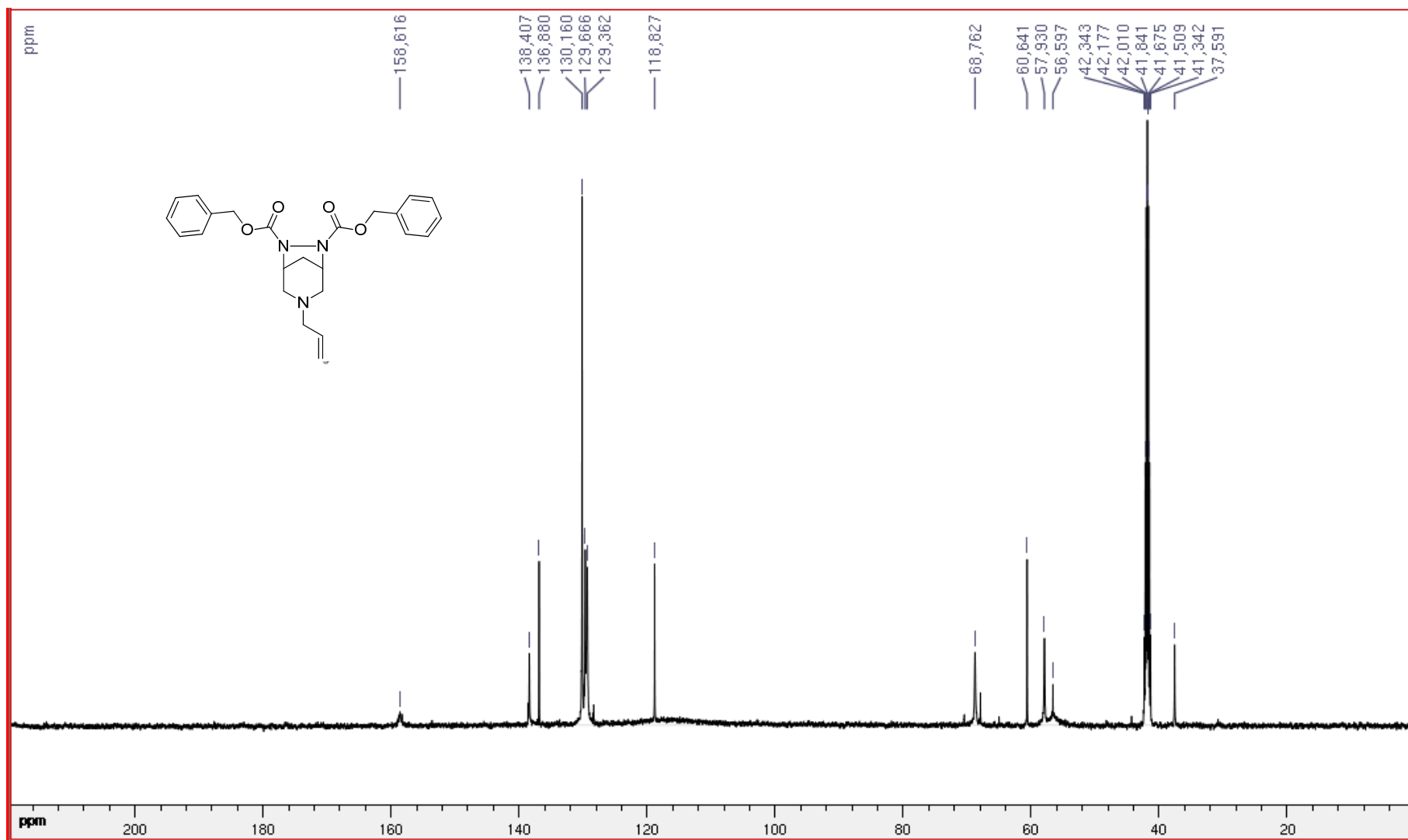
Dibenzyl 3-allyl-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

7n



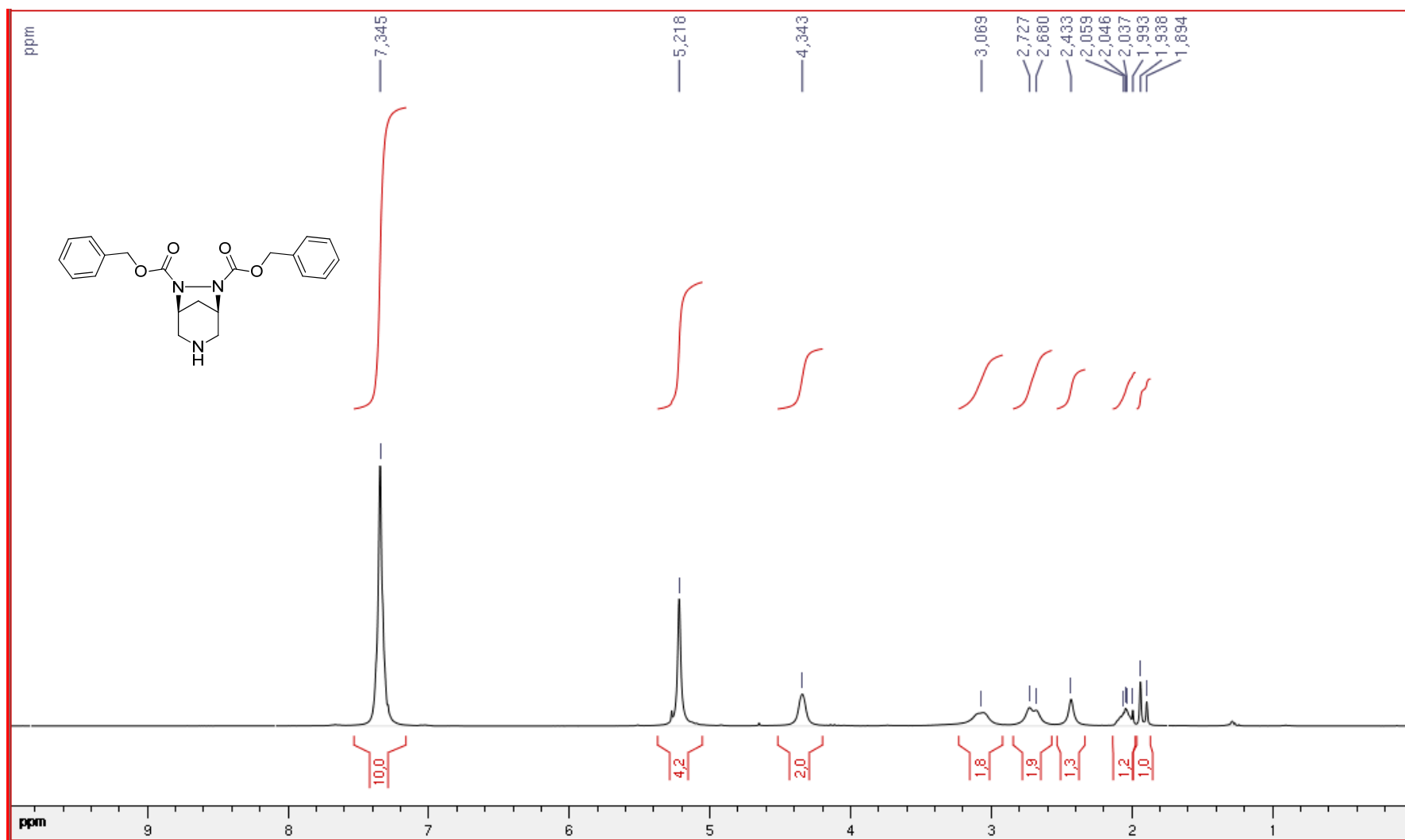
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7n



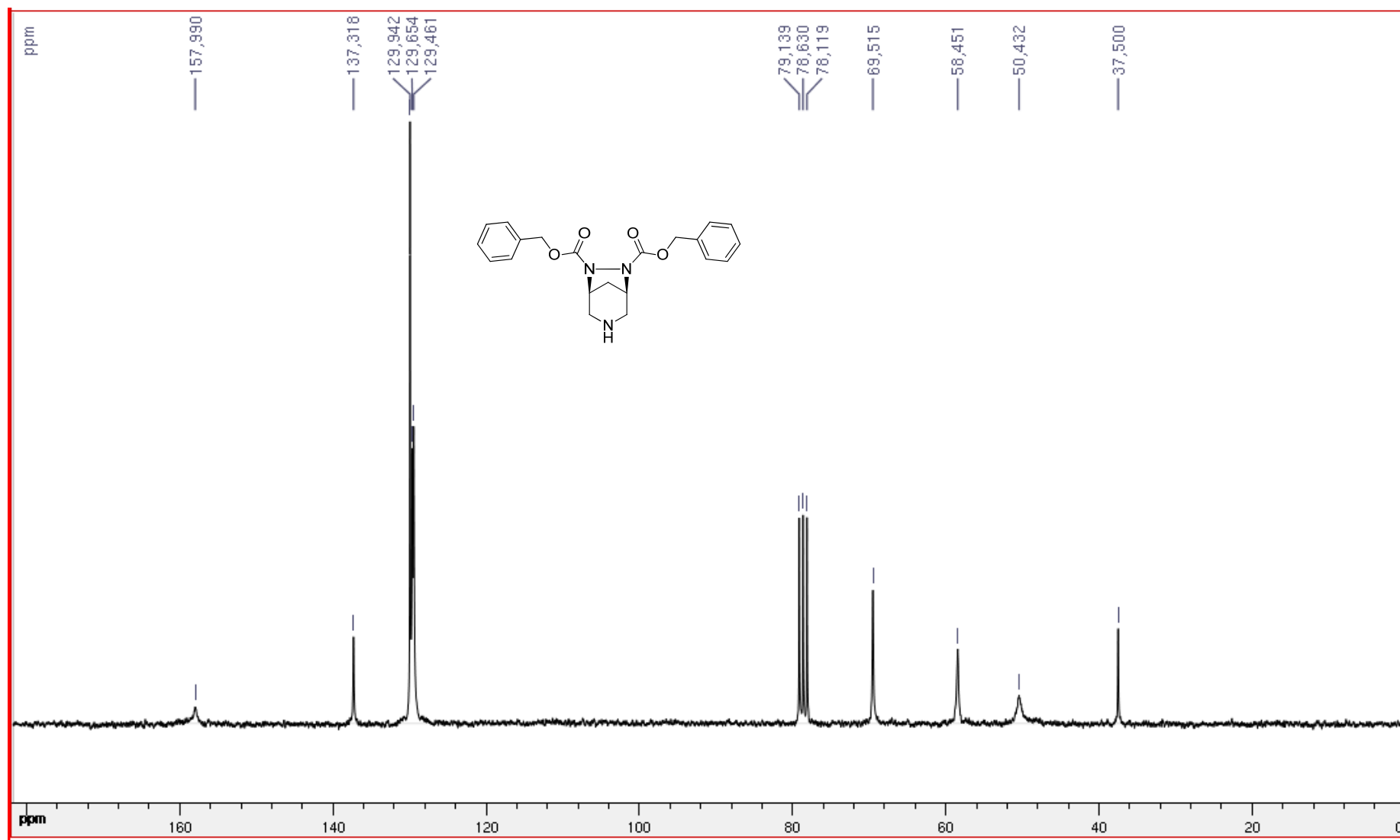
Dibenzyl 3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

8



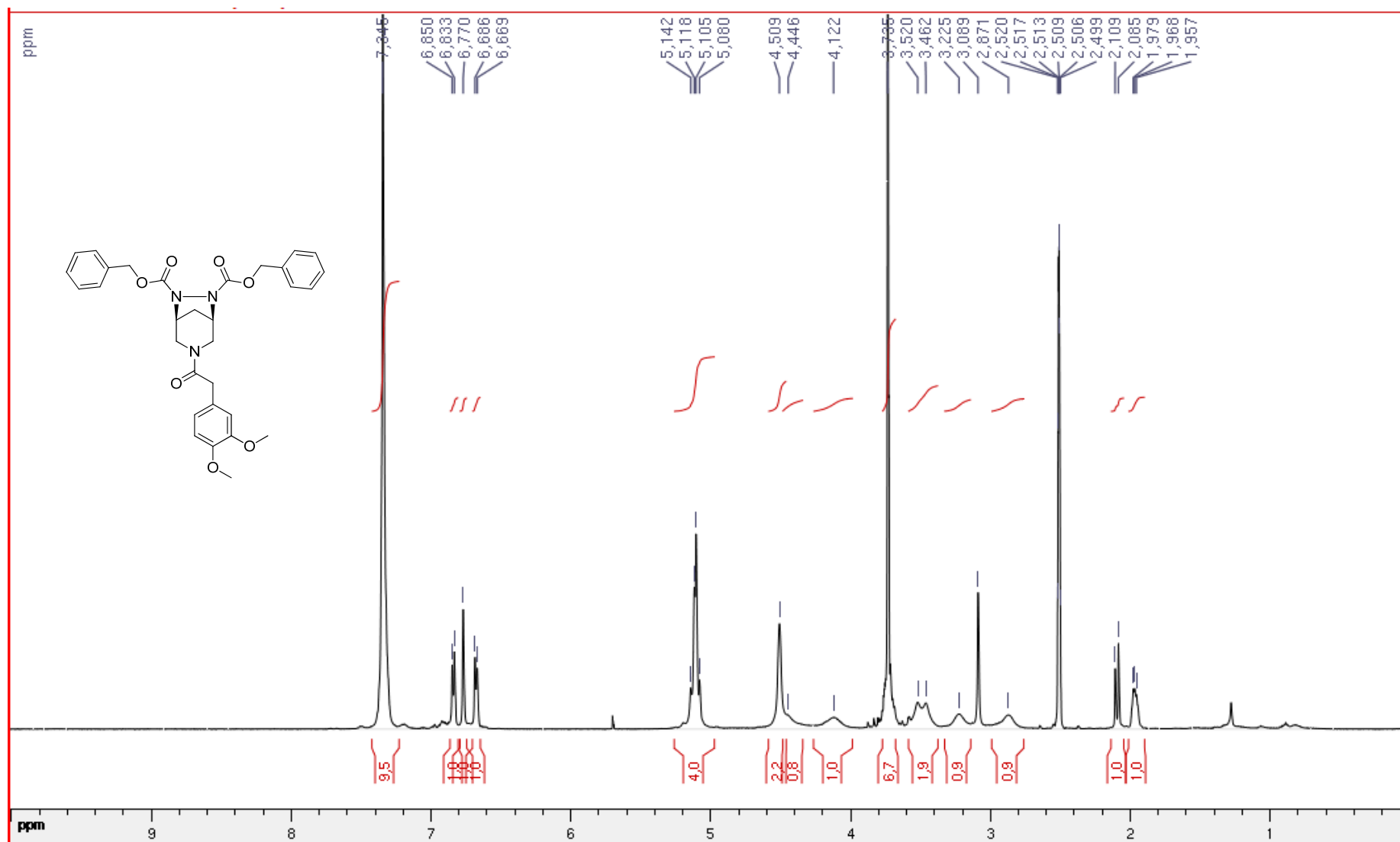
Dibenzyl 3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

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Dibenzyl 3-(2-(3,4-dimethoxyphenyl)acetyl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

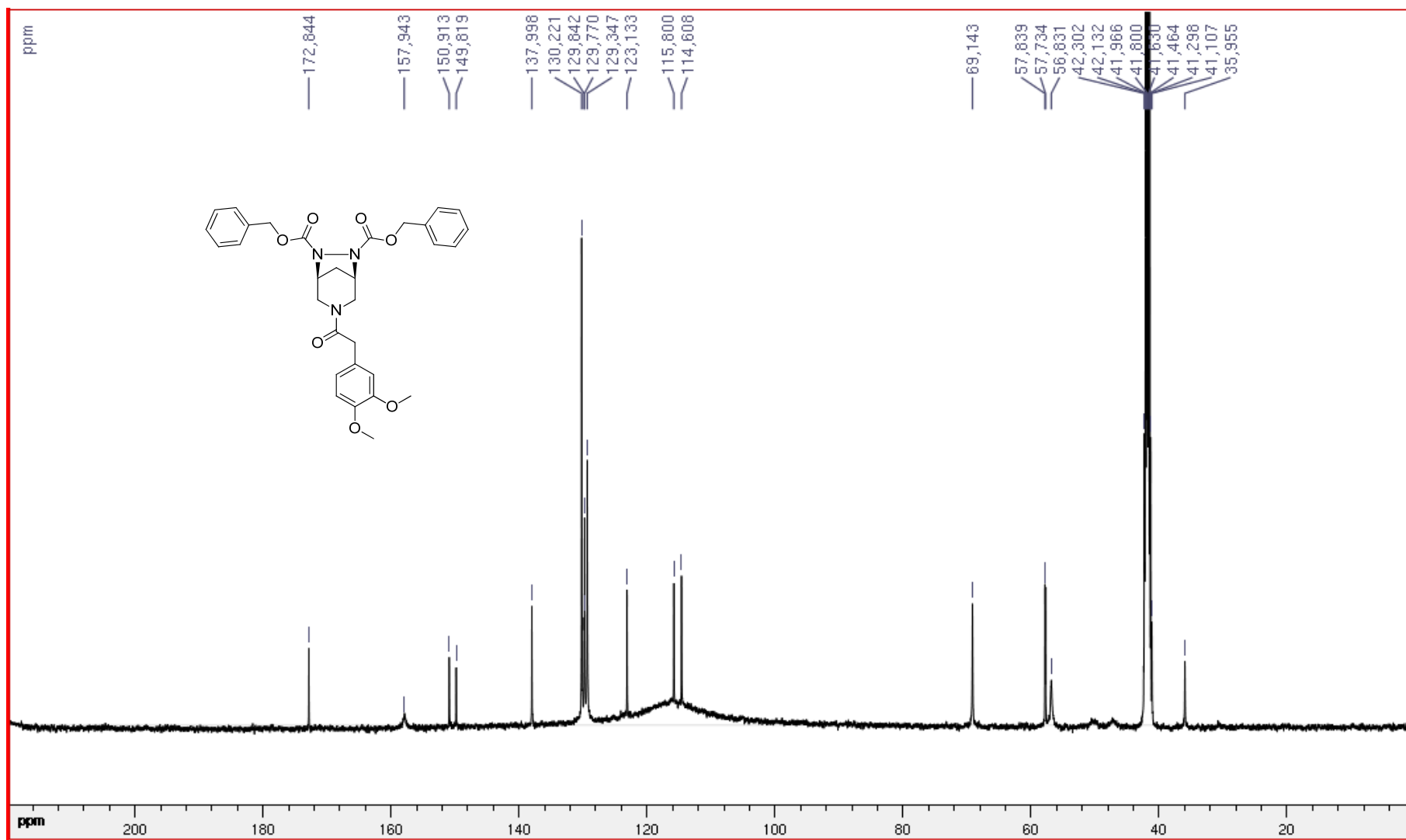
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S35

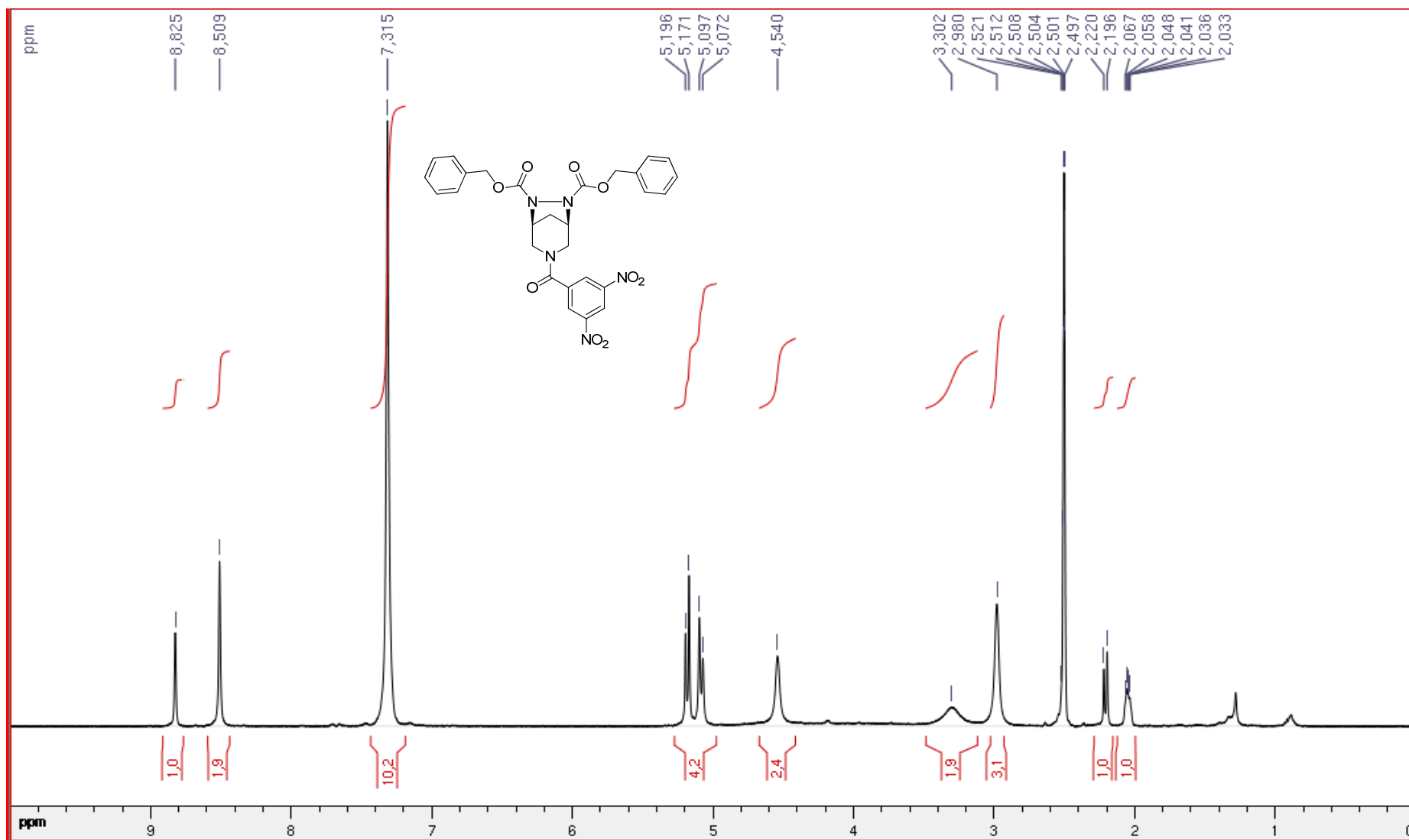
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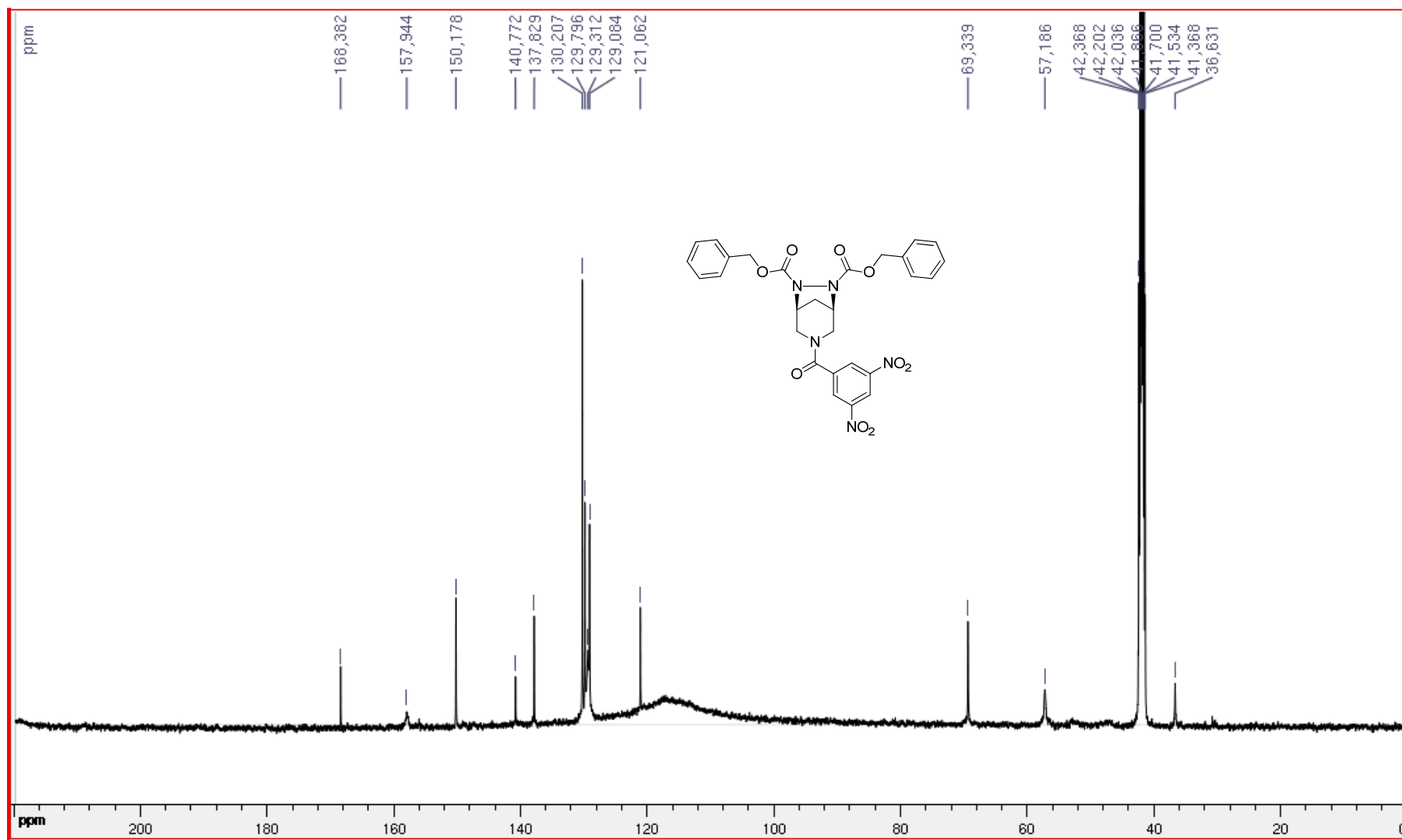
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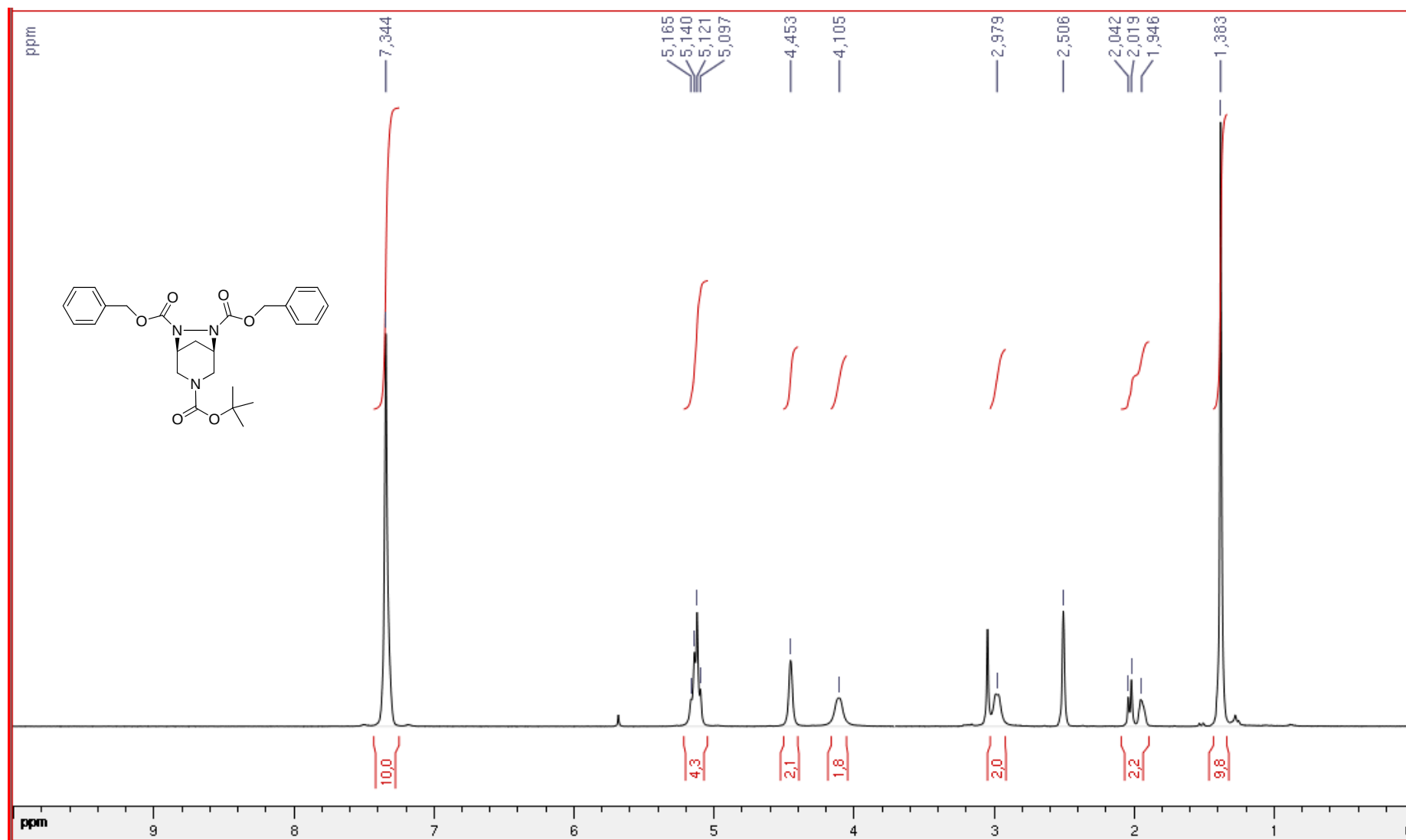
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6,7-dibenzyl 3-tert-butyl 3,6,7-triazabicyclo[3.2.1]octane-3,6,7-tricarboxylate

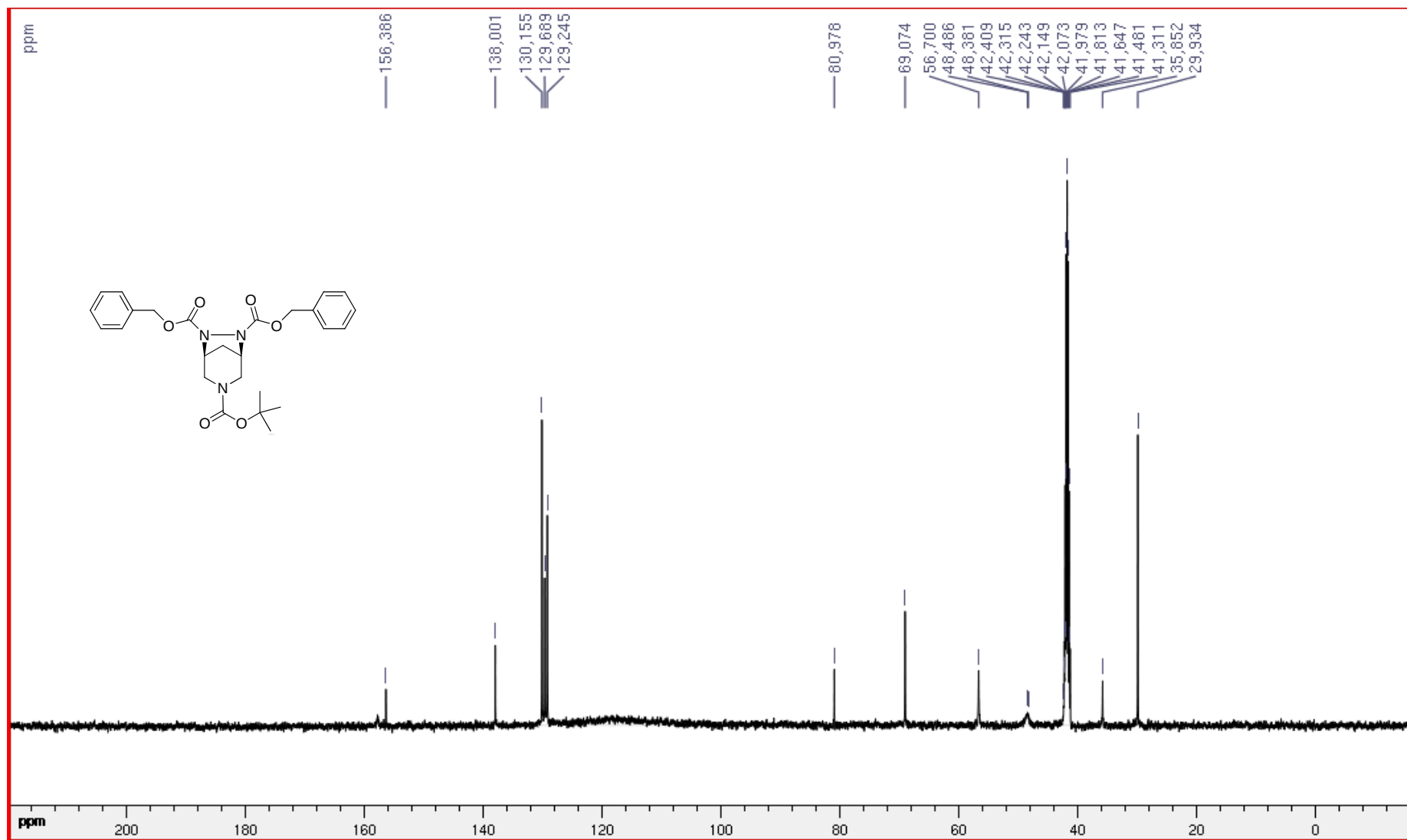
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S39

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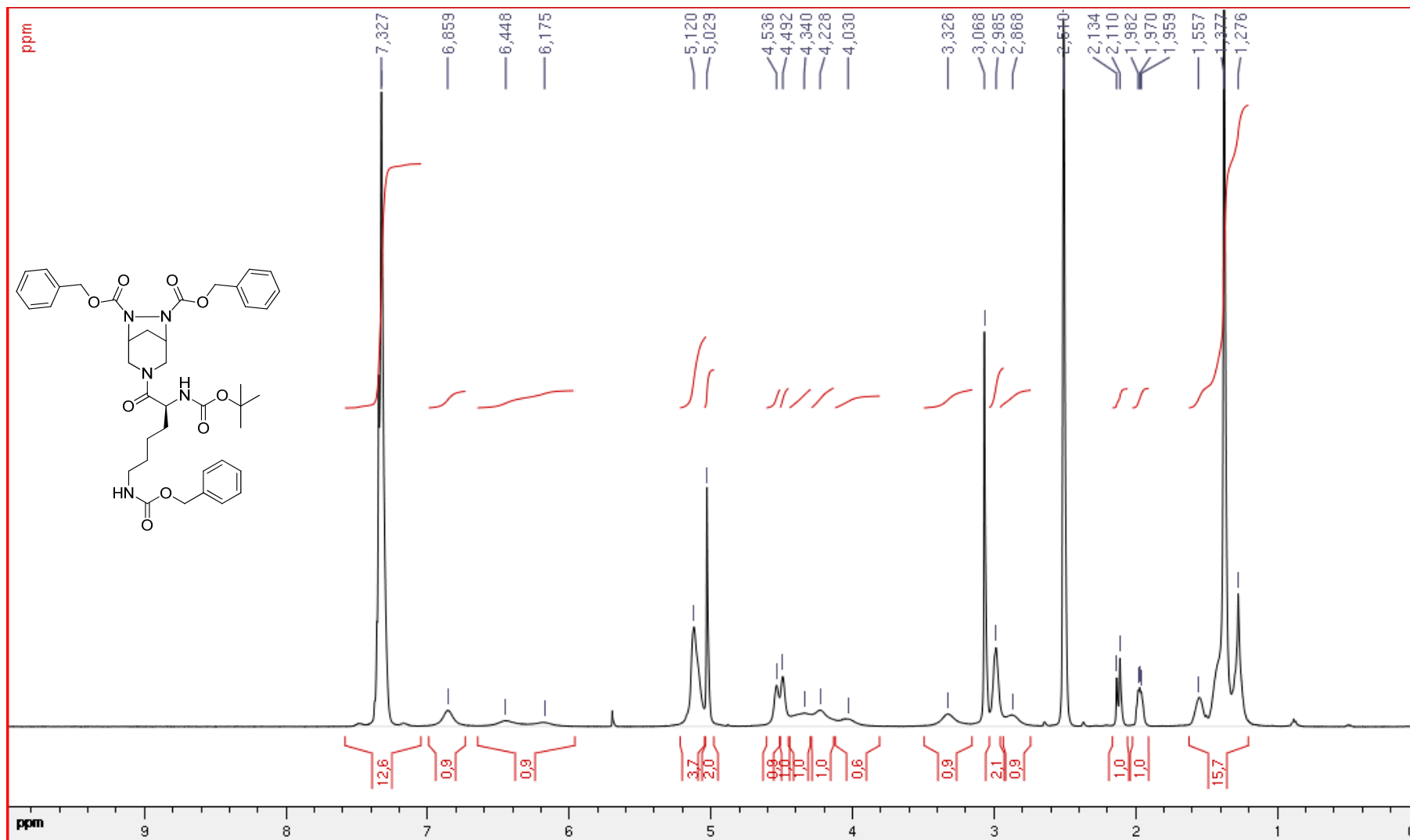
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S40

Dibenzyl 3-(6-(((benzyloxy)carbonyl)amino)-2-((tert-butoxycarbonyl)amino)hexanoyl)-3,6,7-triazabicyclo[3.2.1]octane-6,7-dicarboxylate

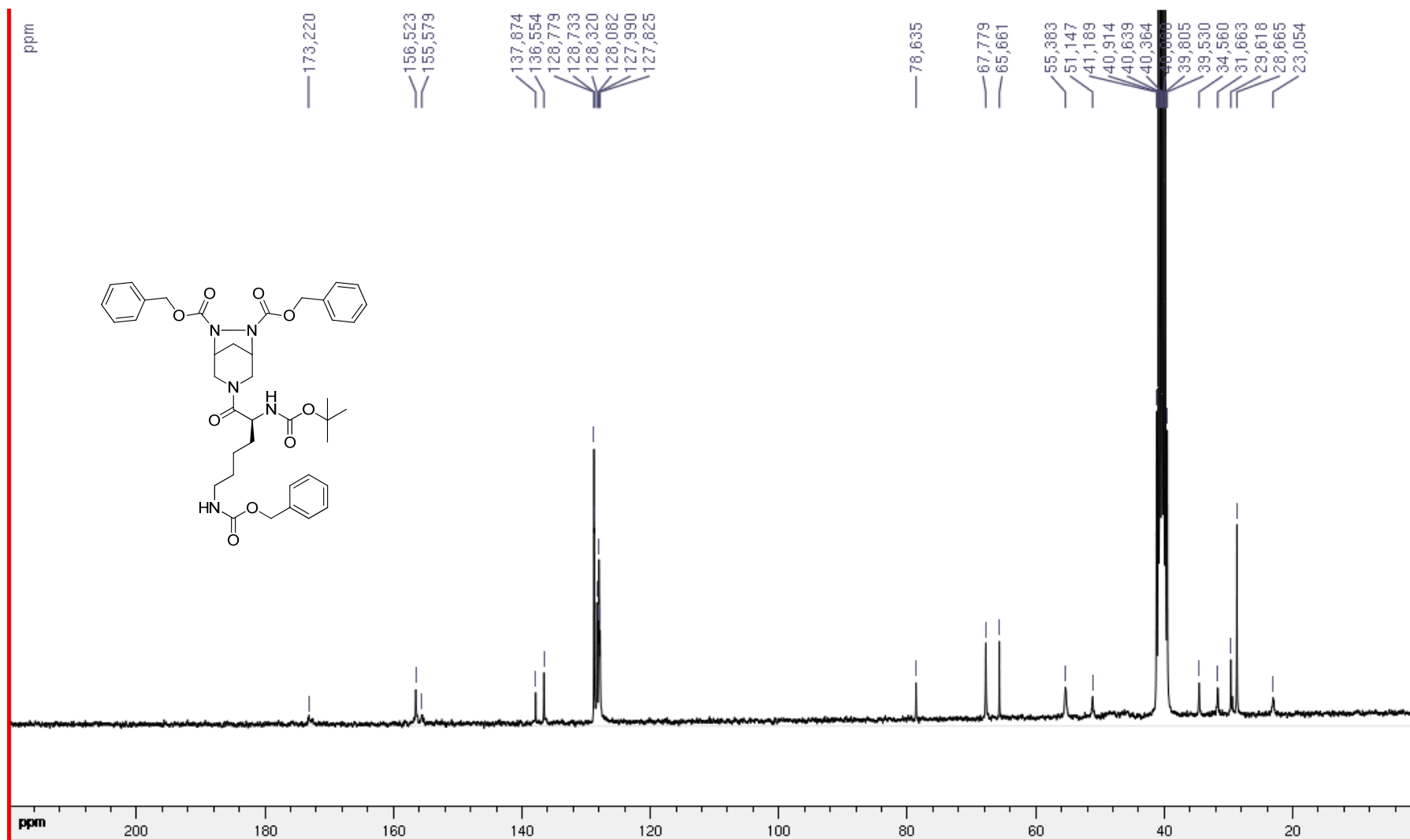
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S41

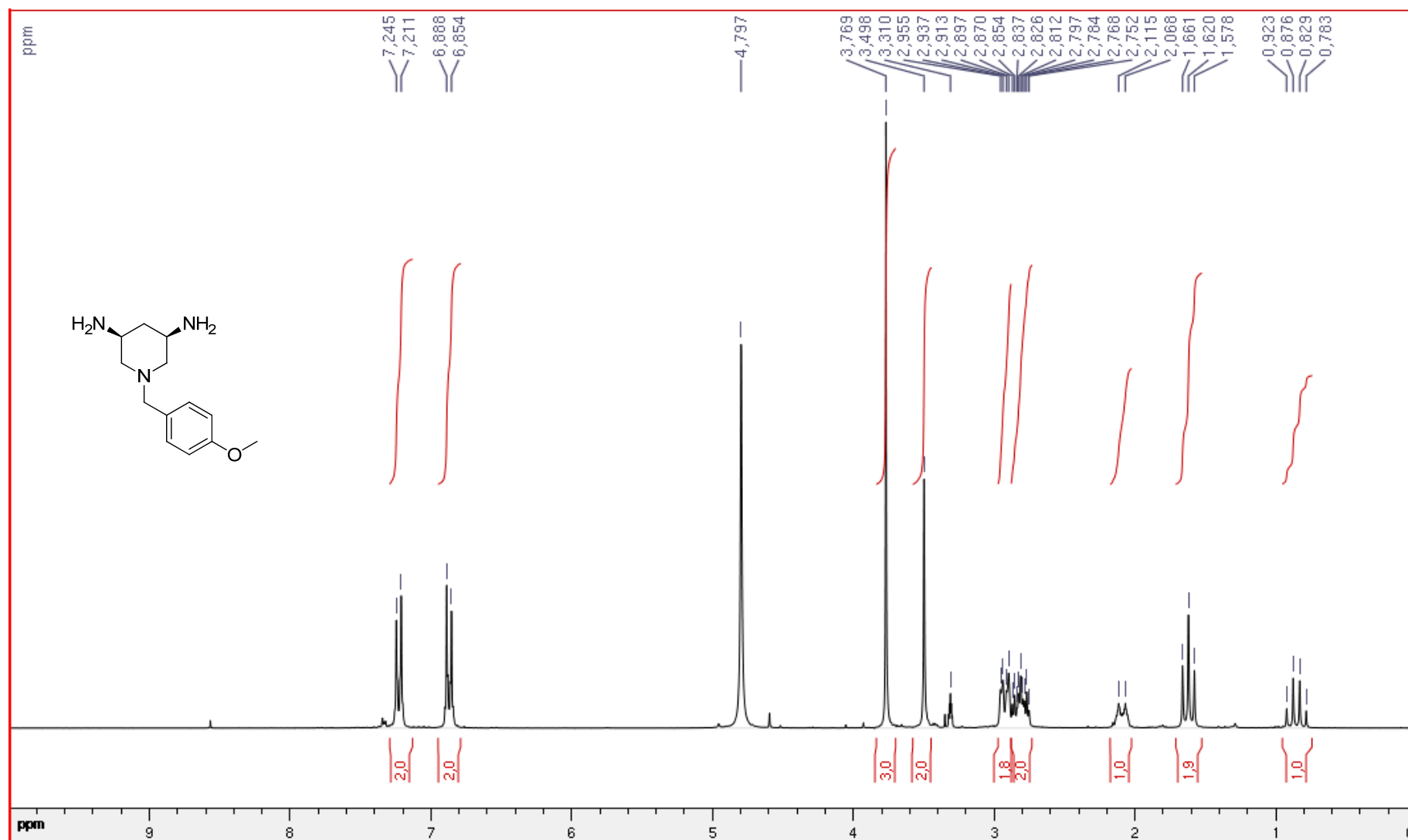
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12



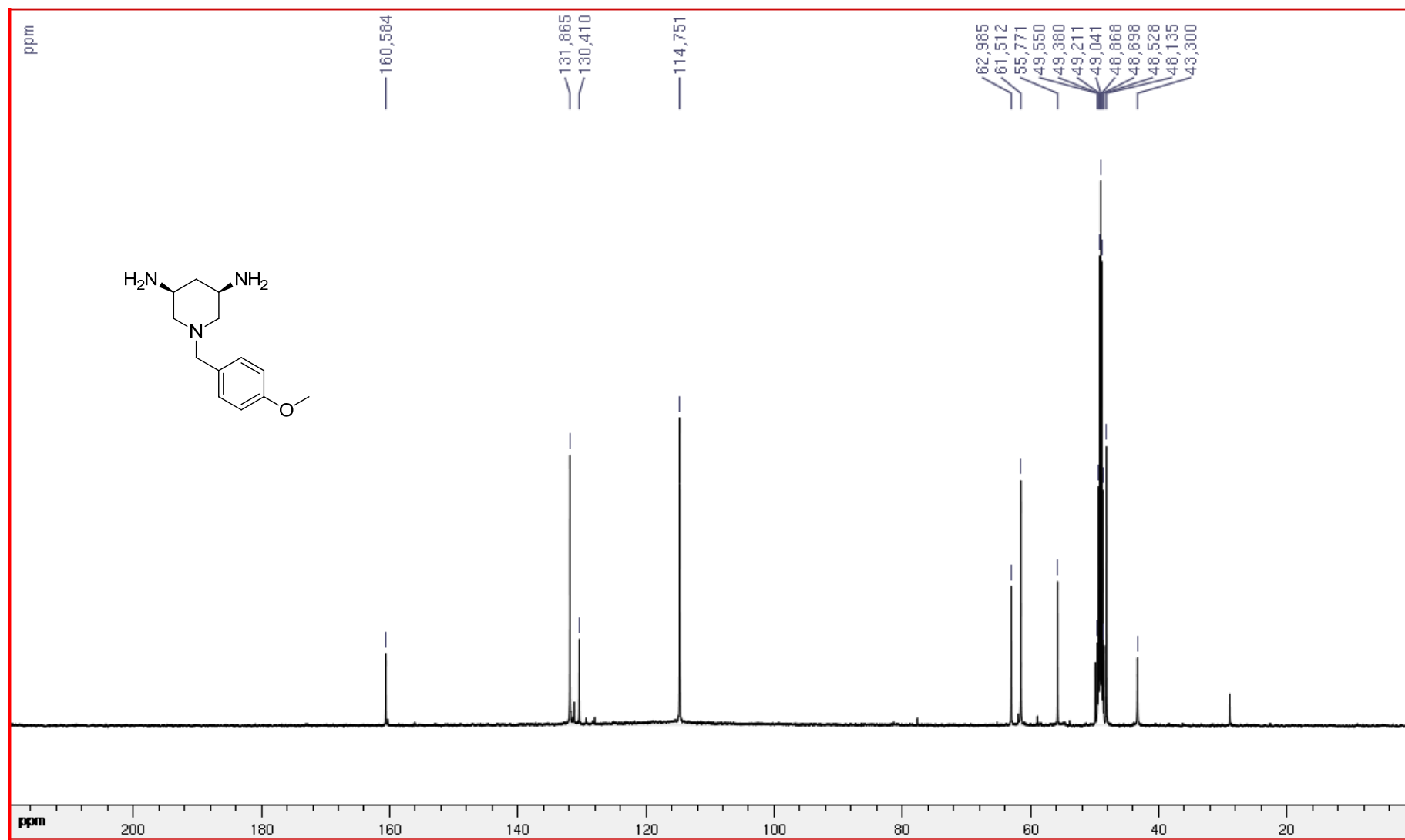
(3S,5R)-1-(4-methoxybenzyl)piperidine-3,5-diamine

13a



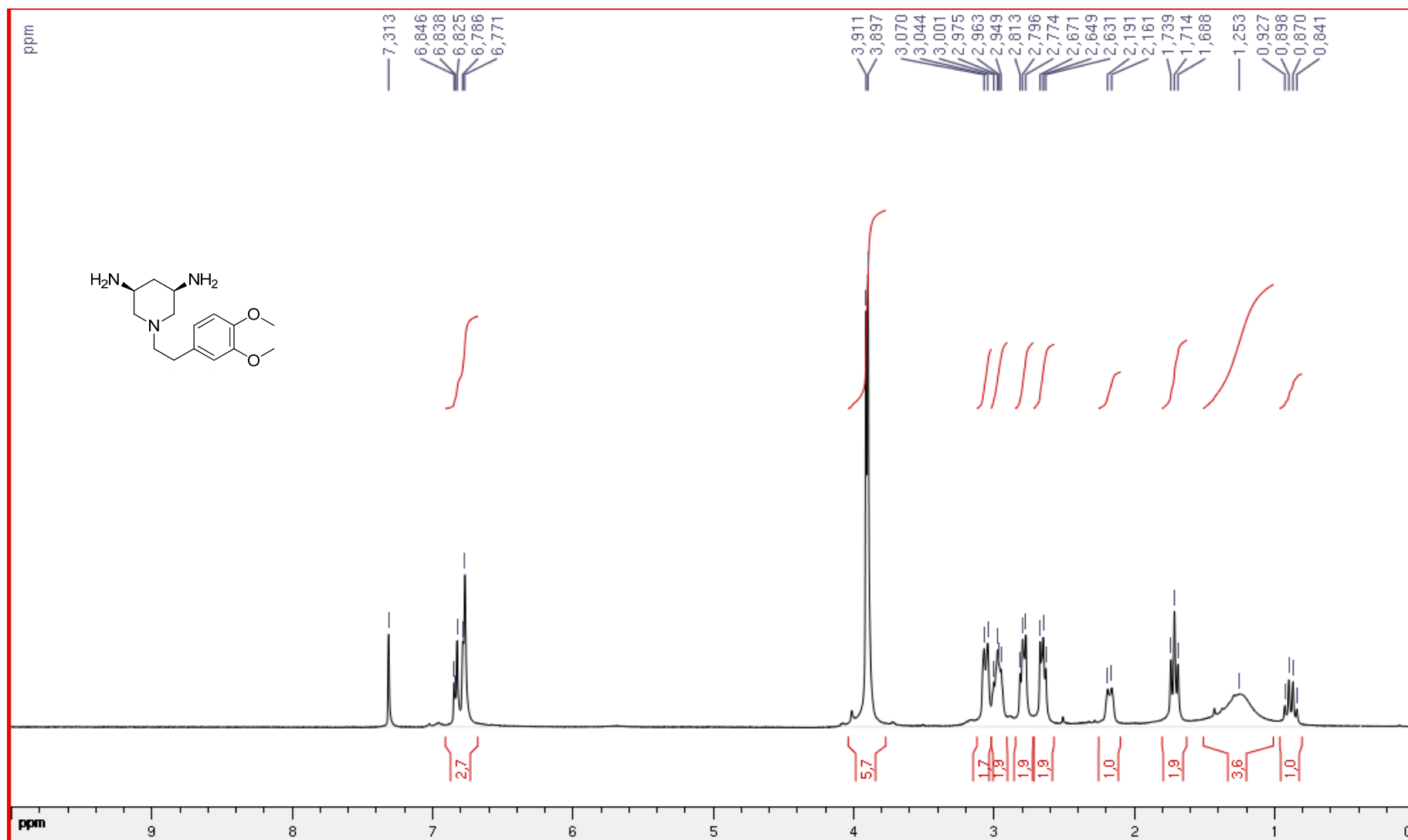
(3S,5R)-1-(4-methoxybenzyl)piperidine-3,5-diamine

13a



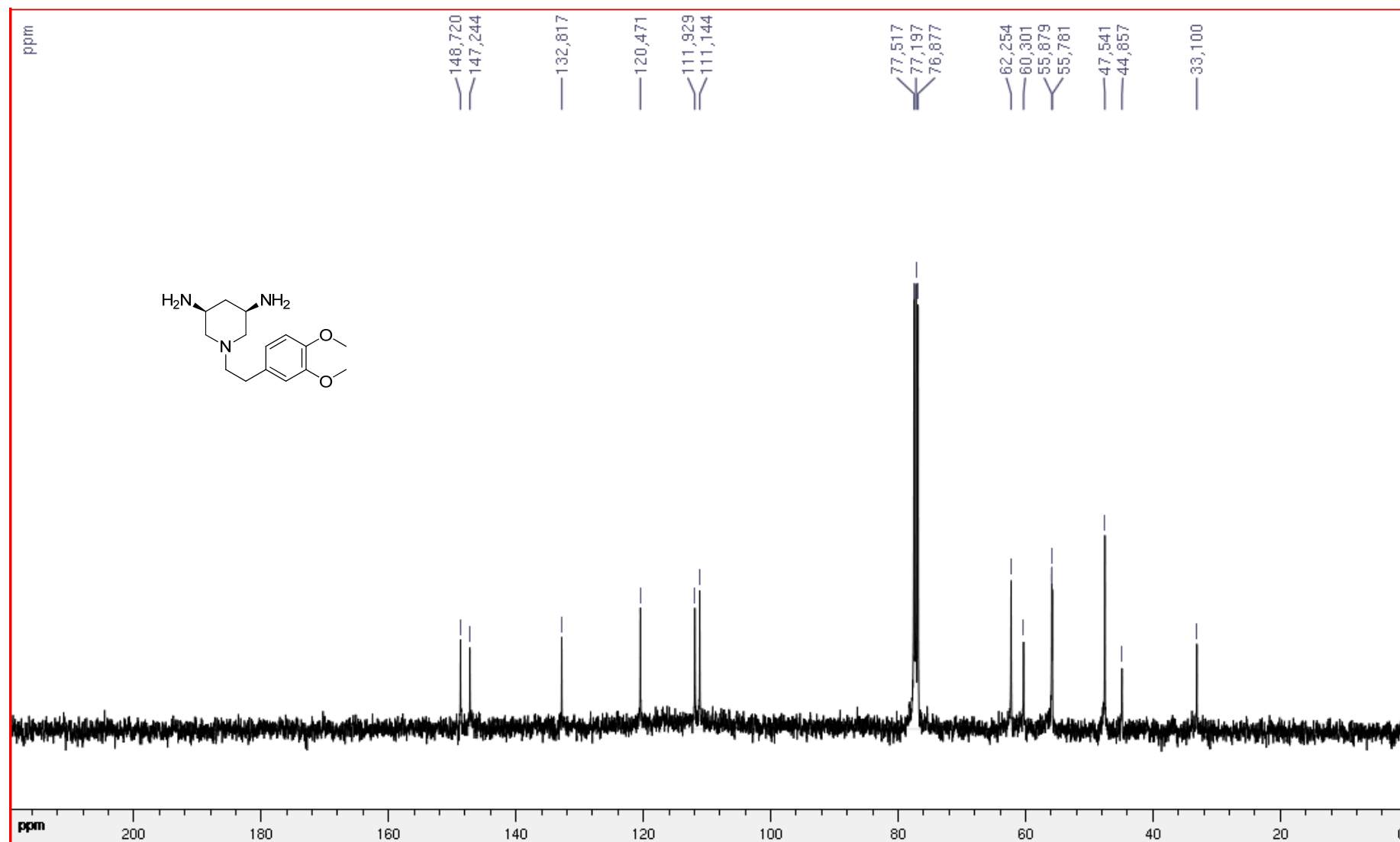
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13b



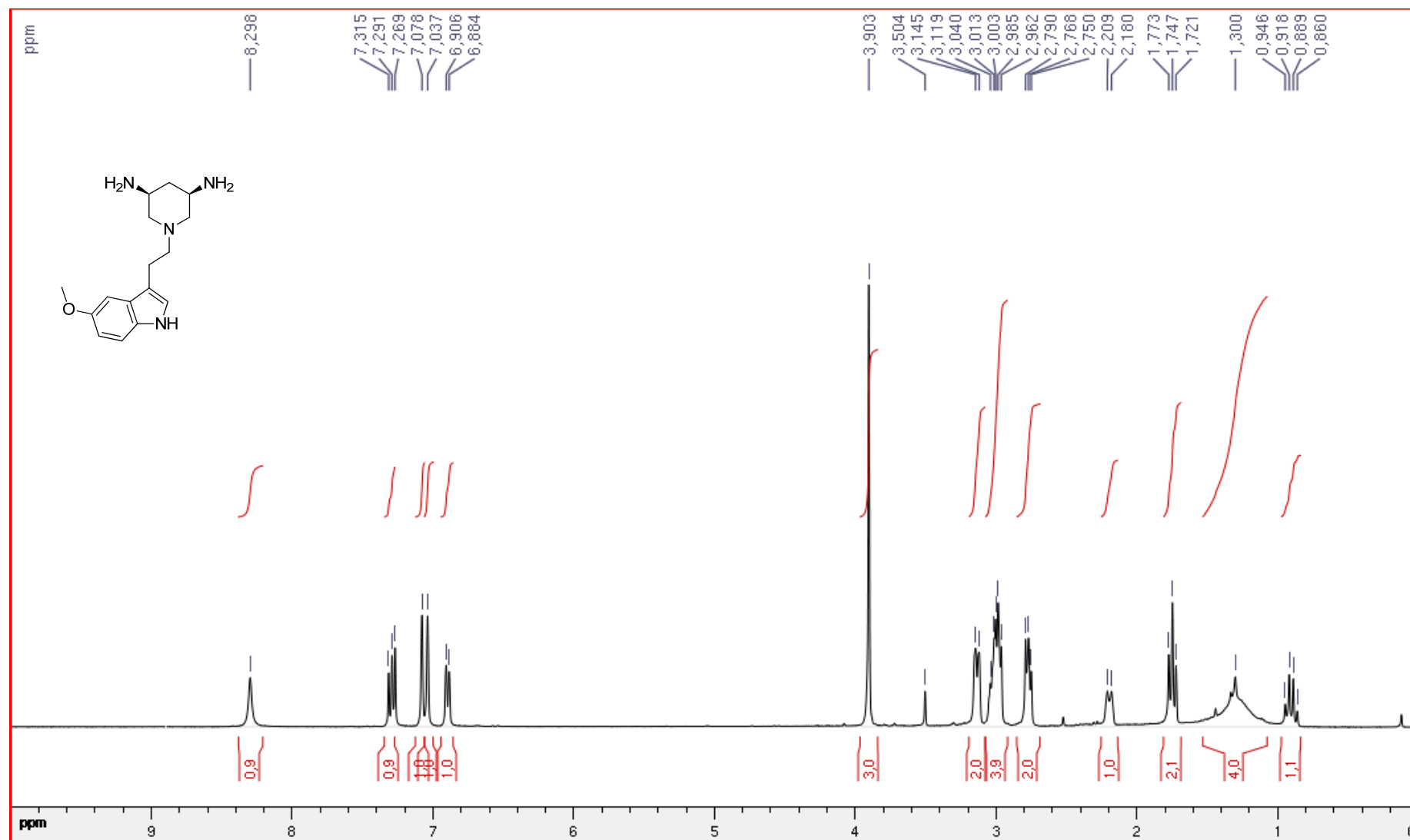
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13b



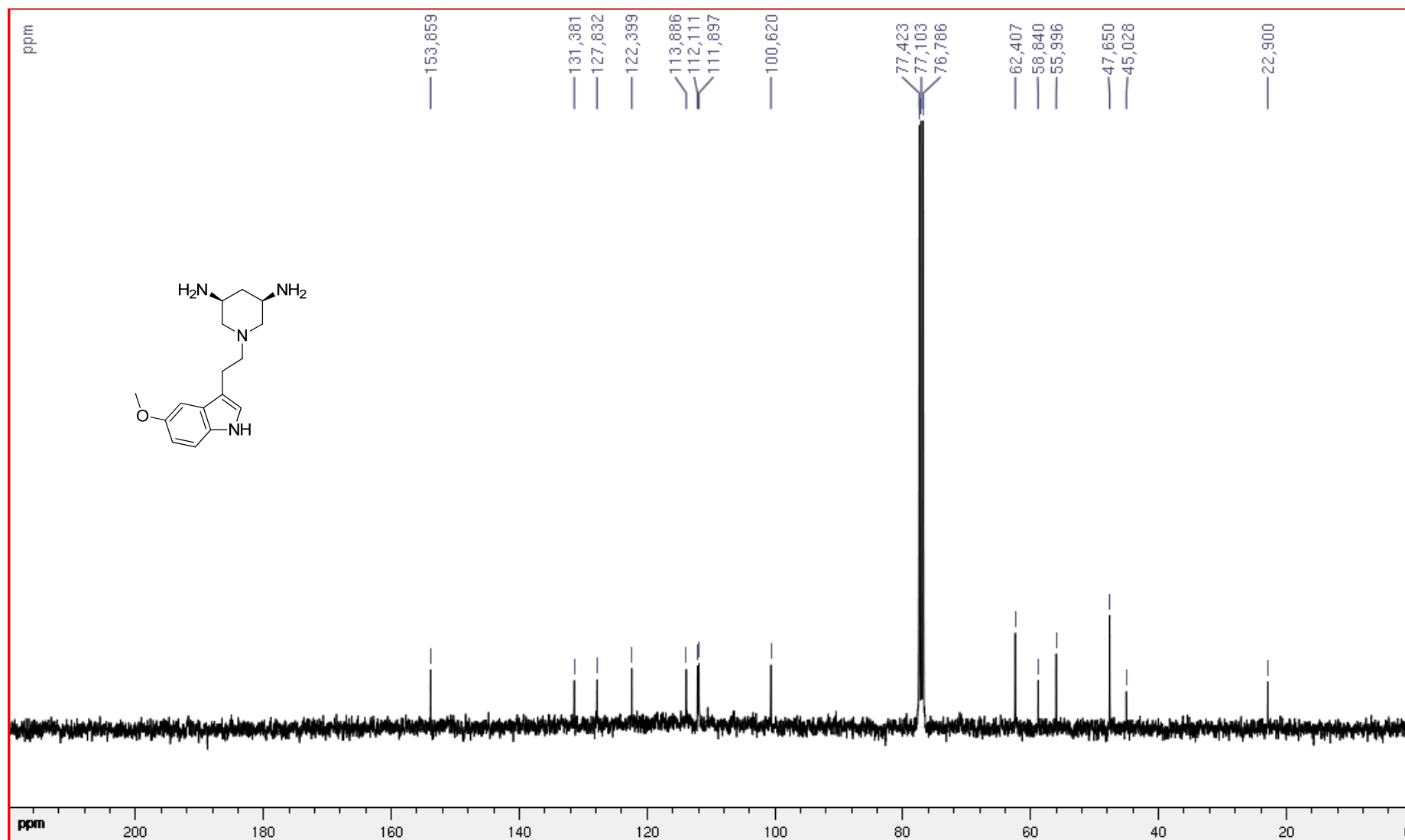
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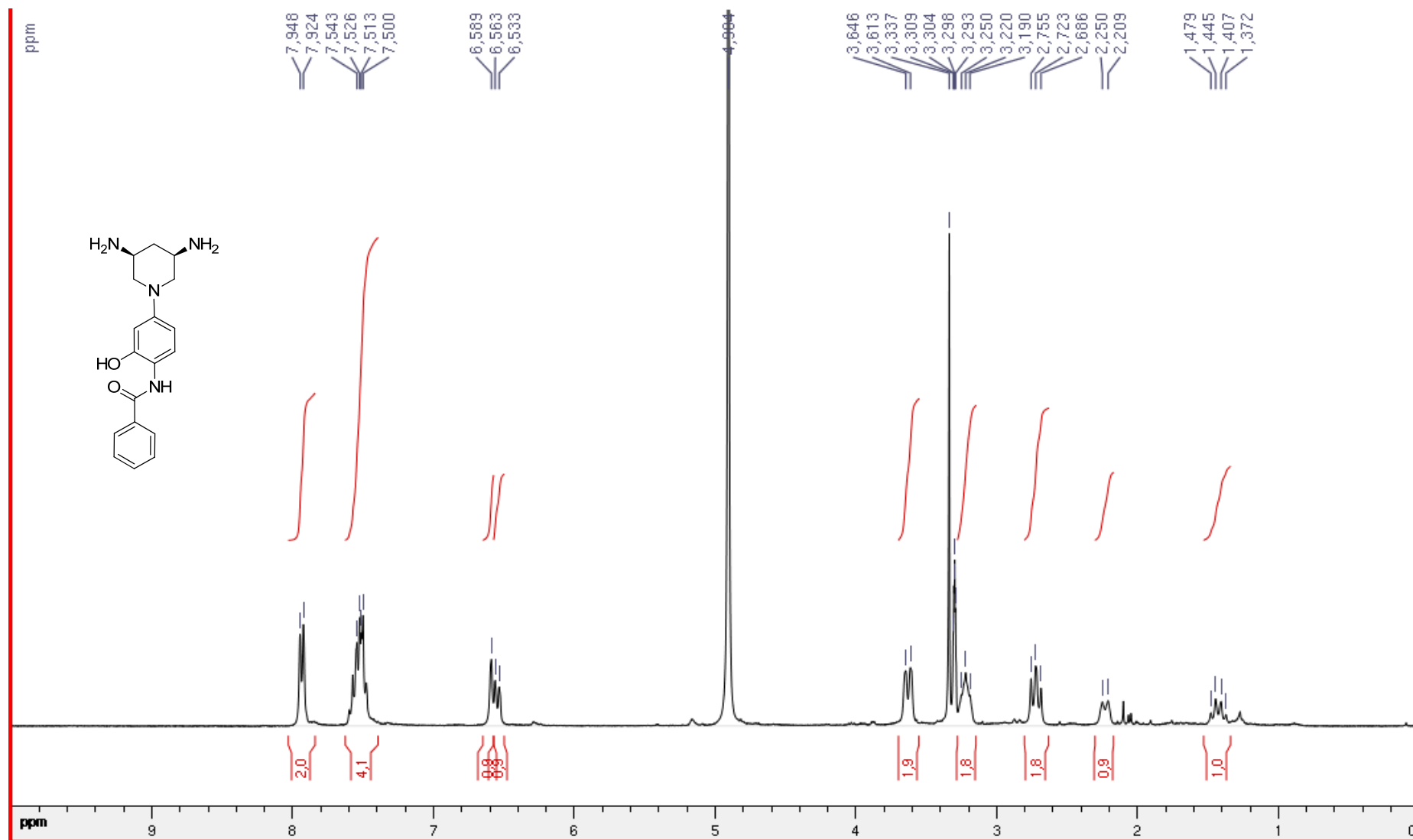
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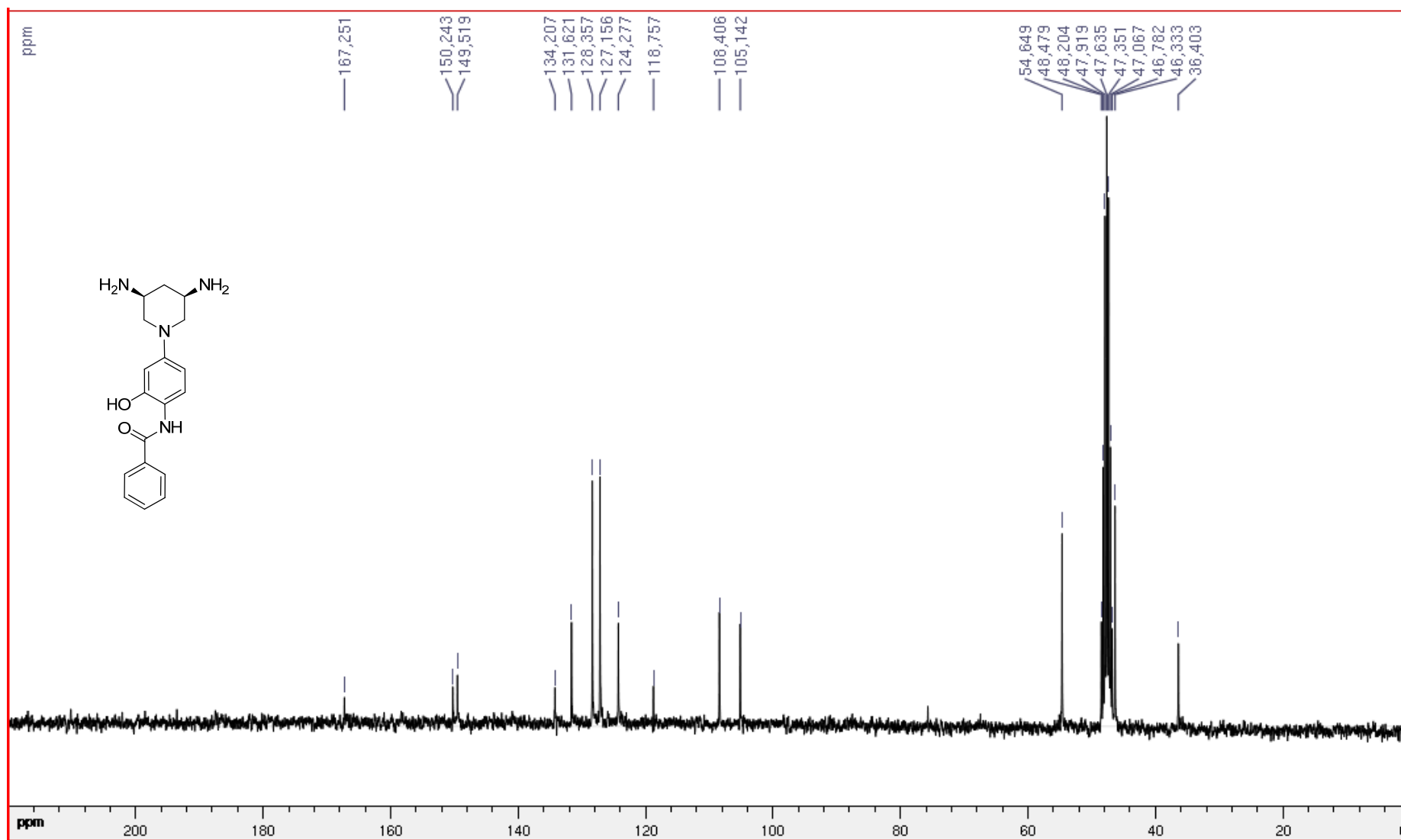
N-(4-((3S,5R)-3,5-diaminopiperidin-1-yl)-2-hydroxyphenyl)benzamide

13d



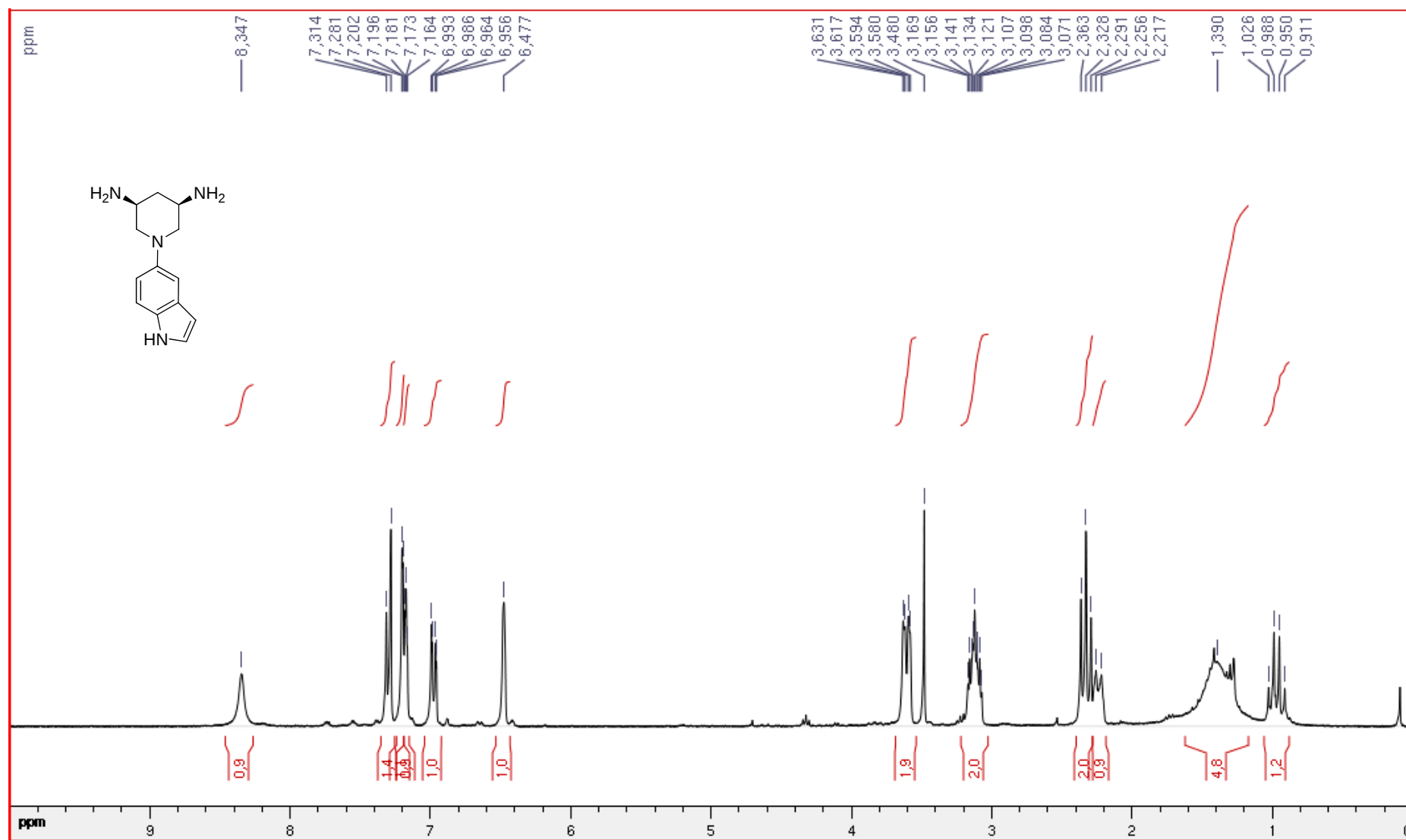
N-(4-((3S,5R)-3,5-diaminopiperidin-1-yl)-2-hydroxyphenyl)benzamide

13d



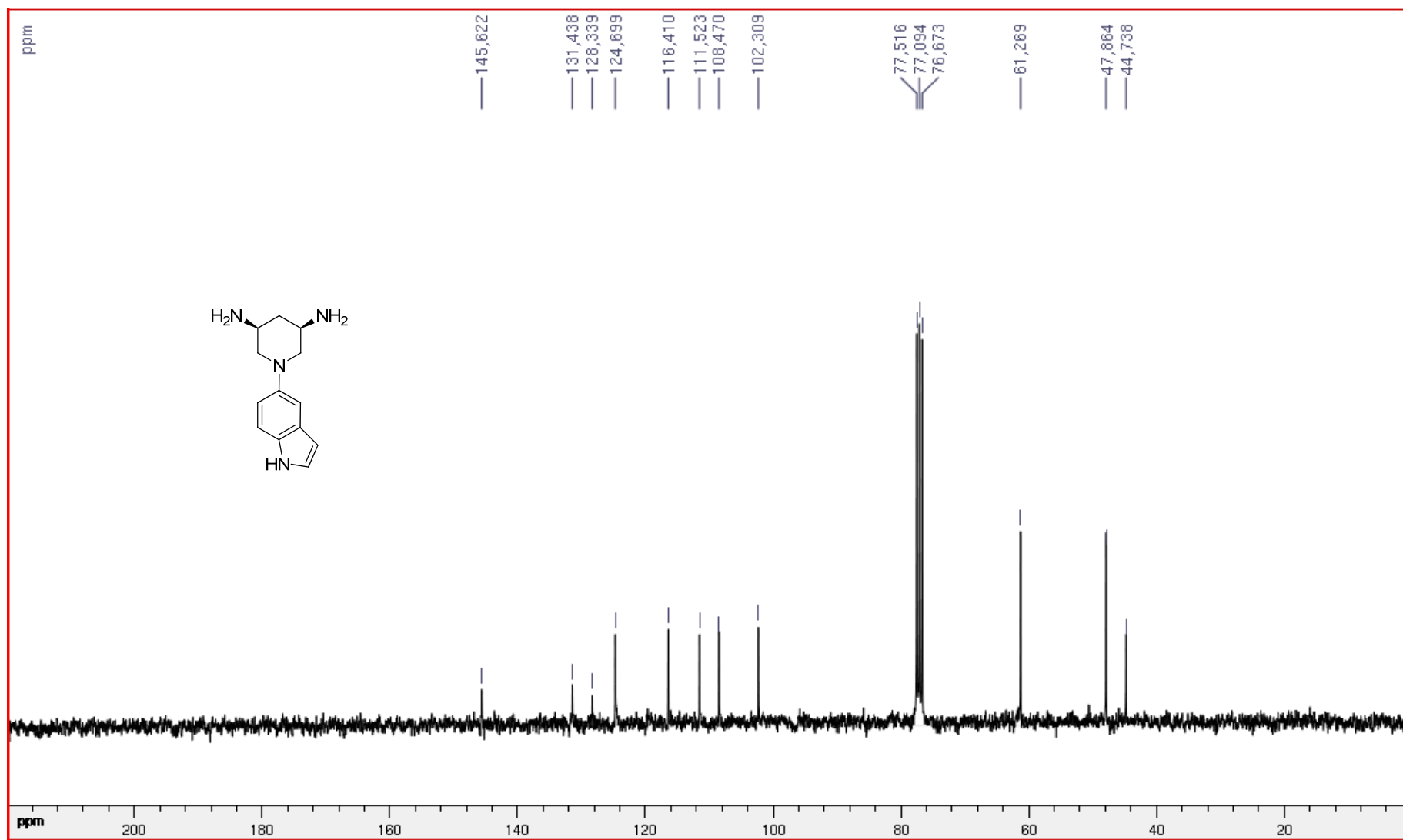
(3S,5R)-1-(1H-indol-5-yl)piperidine-3,5-diamine

13e



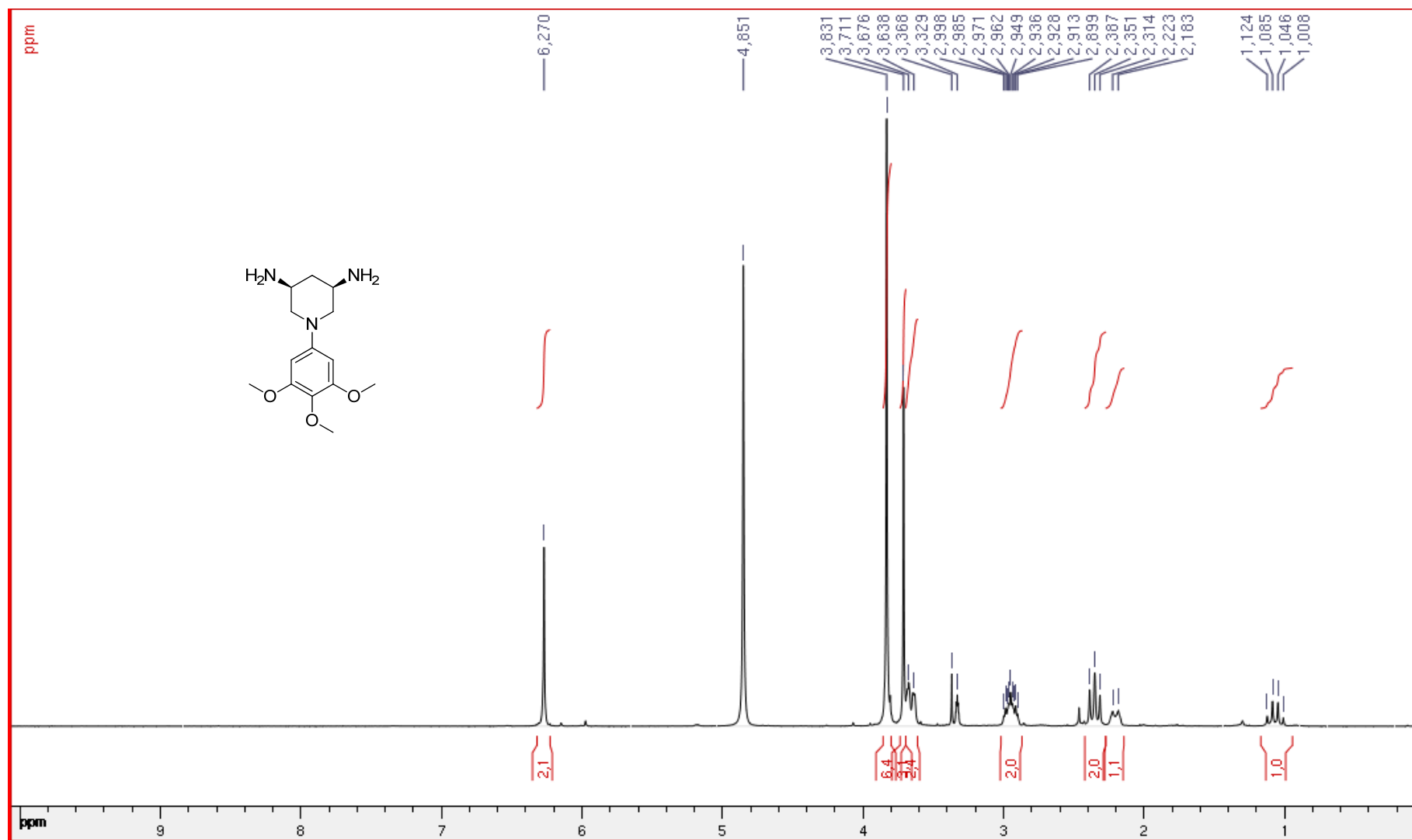
(3S,5R)-1-(1H-indol-5-yl)piperidine-3,5-diamine

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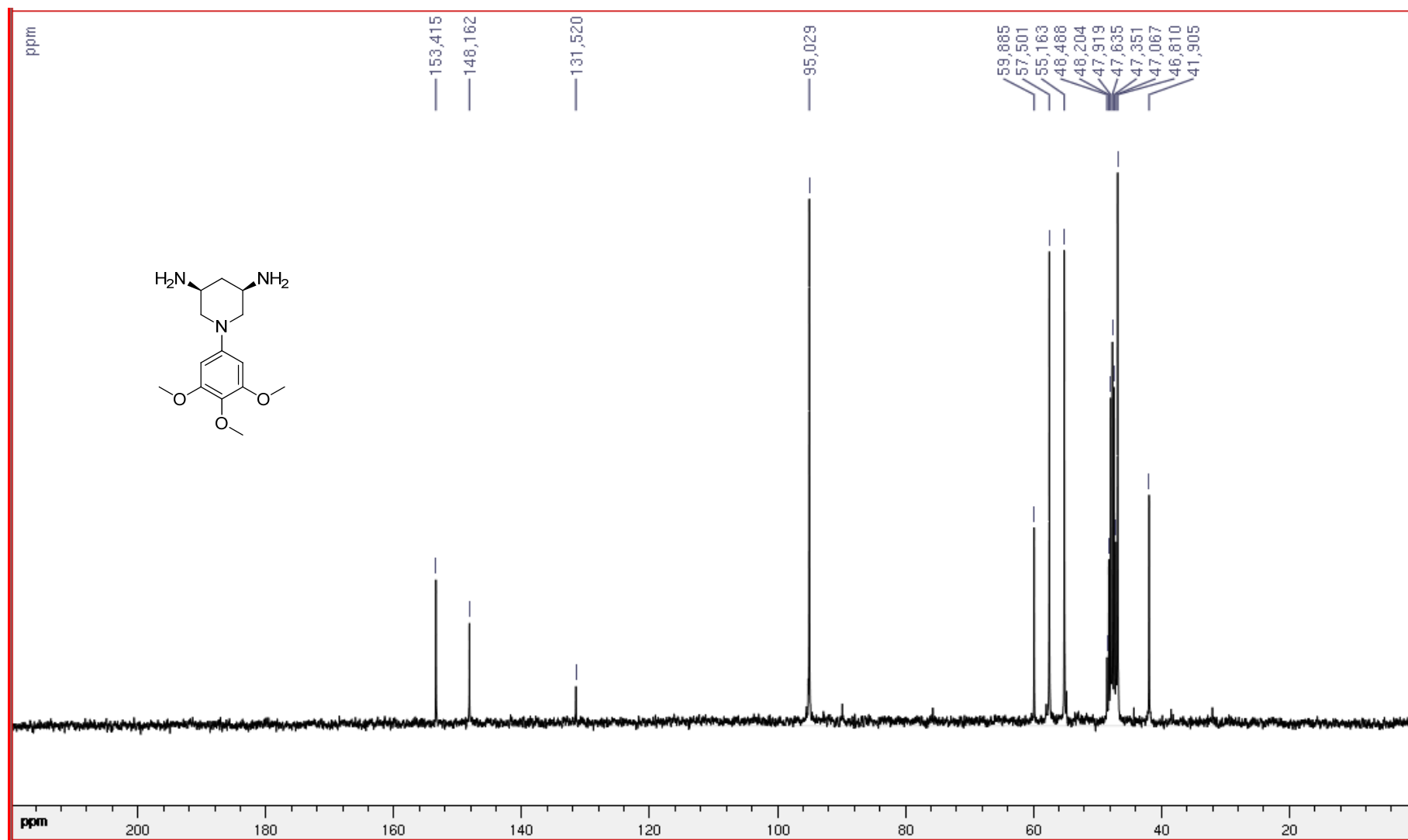
(3S,5R)-1-(3,4,5-trimethoxyphenyl)piperidine-3,5-diamine

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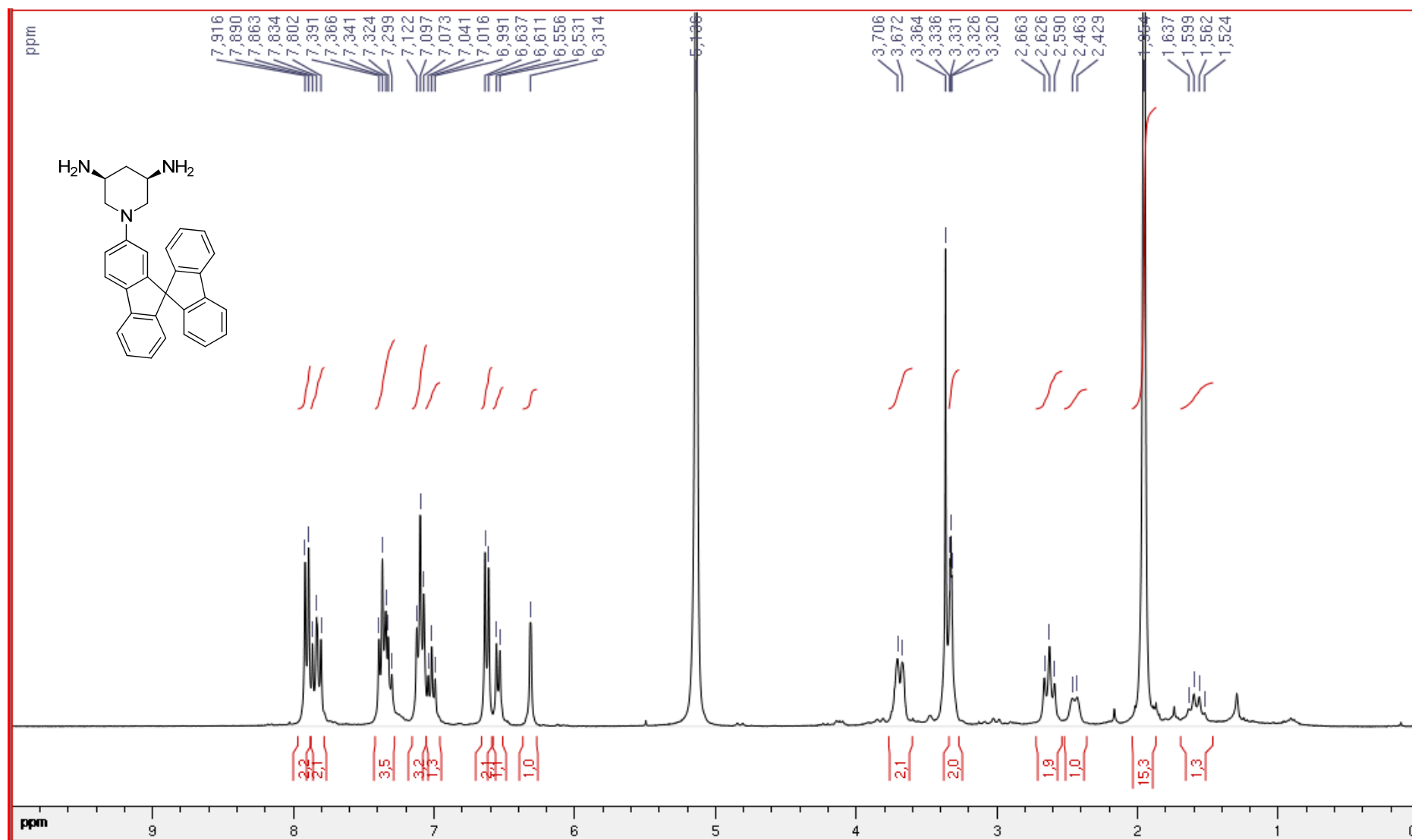
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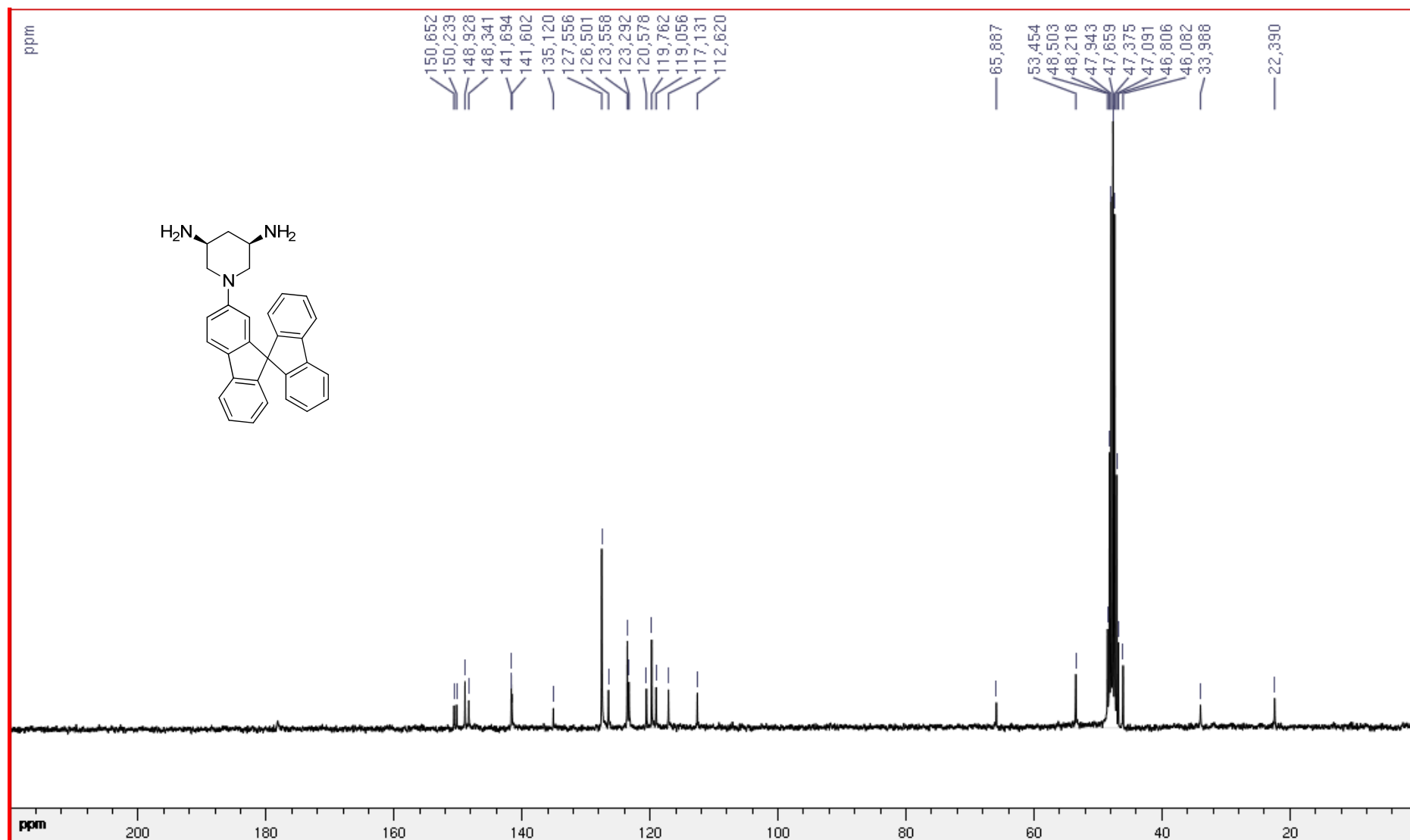
(3S,5R)-1-(9,9'-spirobi[fluoren]-2-yl)piperidine-3,5-diamine

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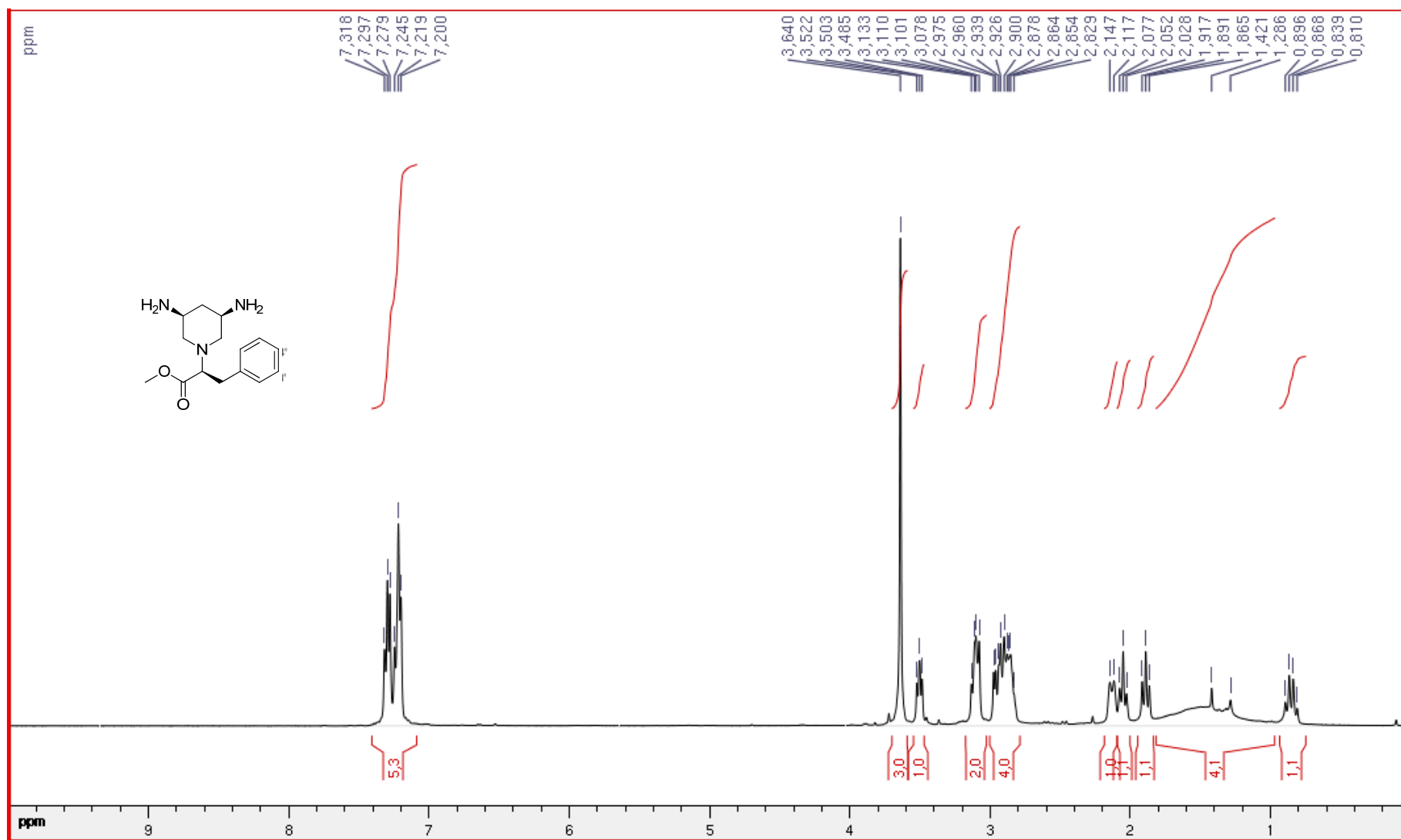
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13g



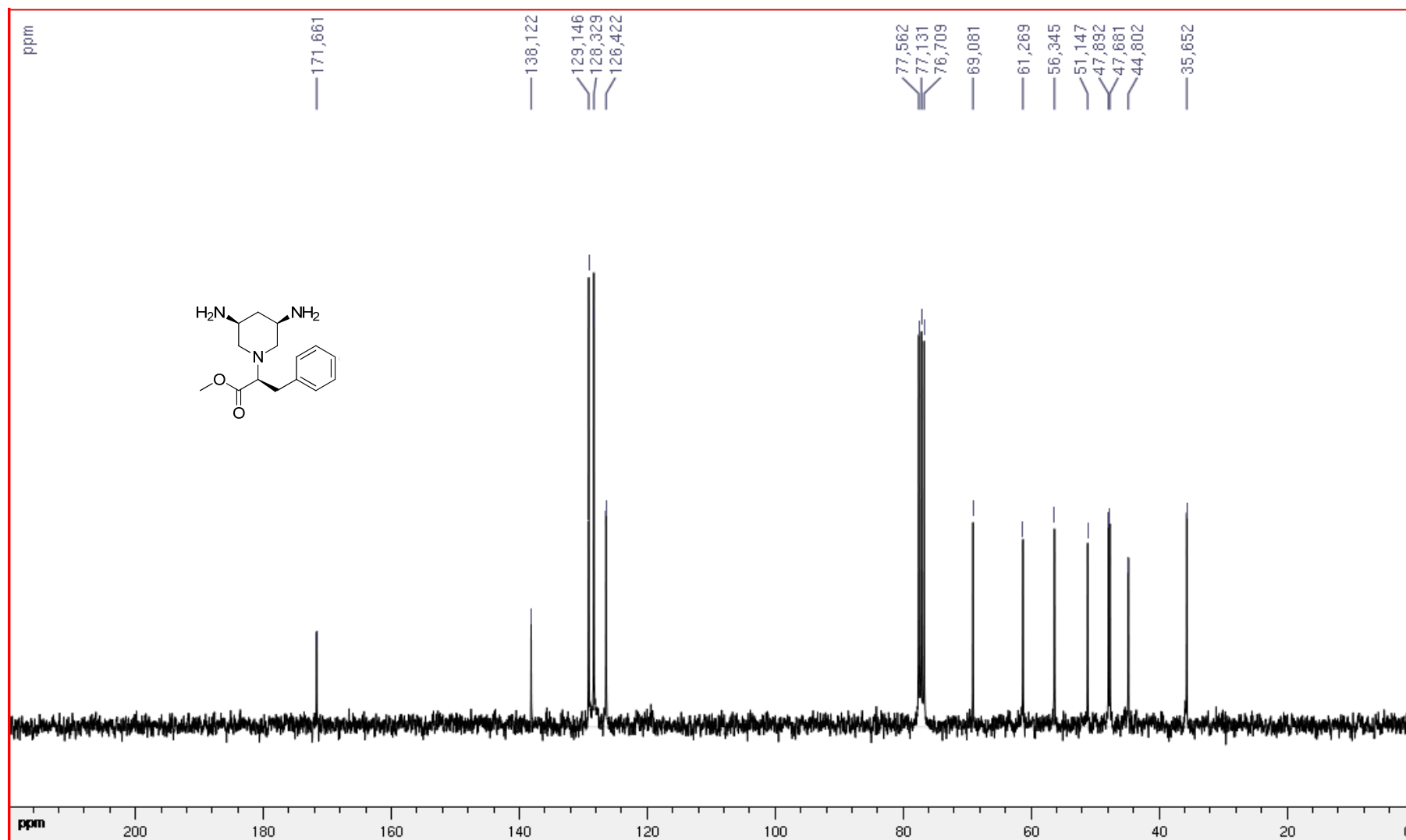
(R)-methyl 2-((3S,5R)-3,5-diaminopiperidin-1-yl)-3-phenylpropanoate

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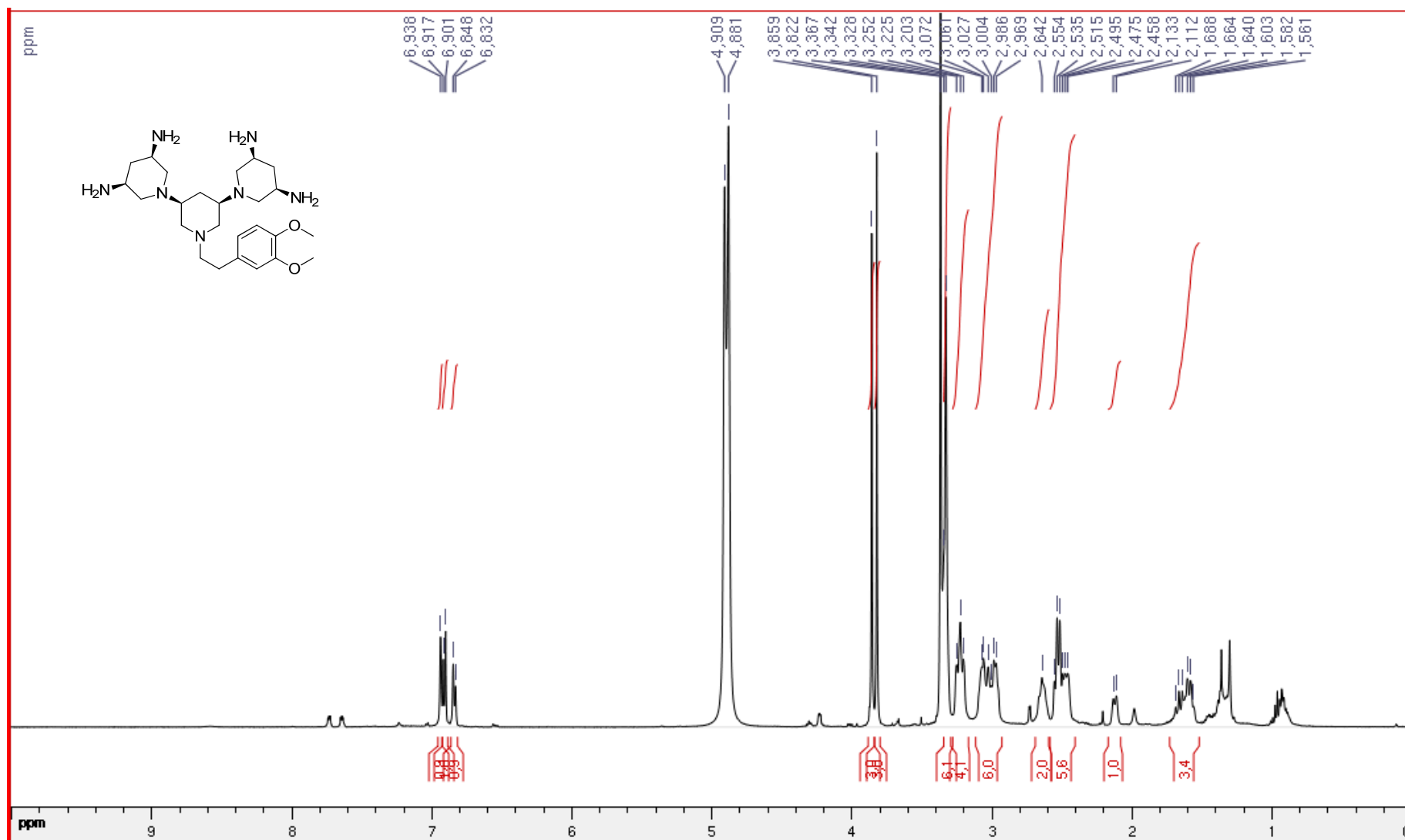
(R)-methyl 2-((3S,5R)-3,5-diaminopiperidin-1-yl)-3-phenylpropanoate

13h



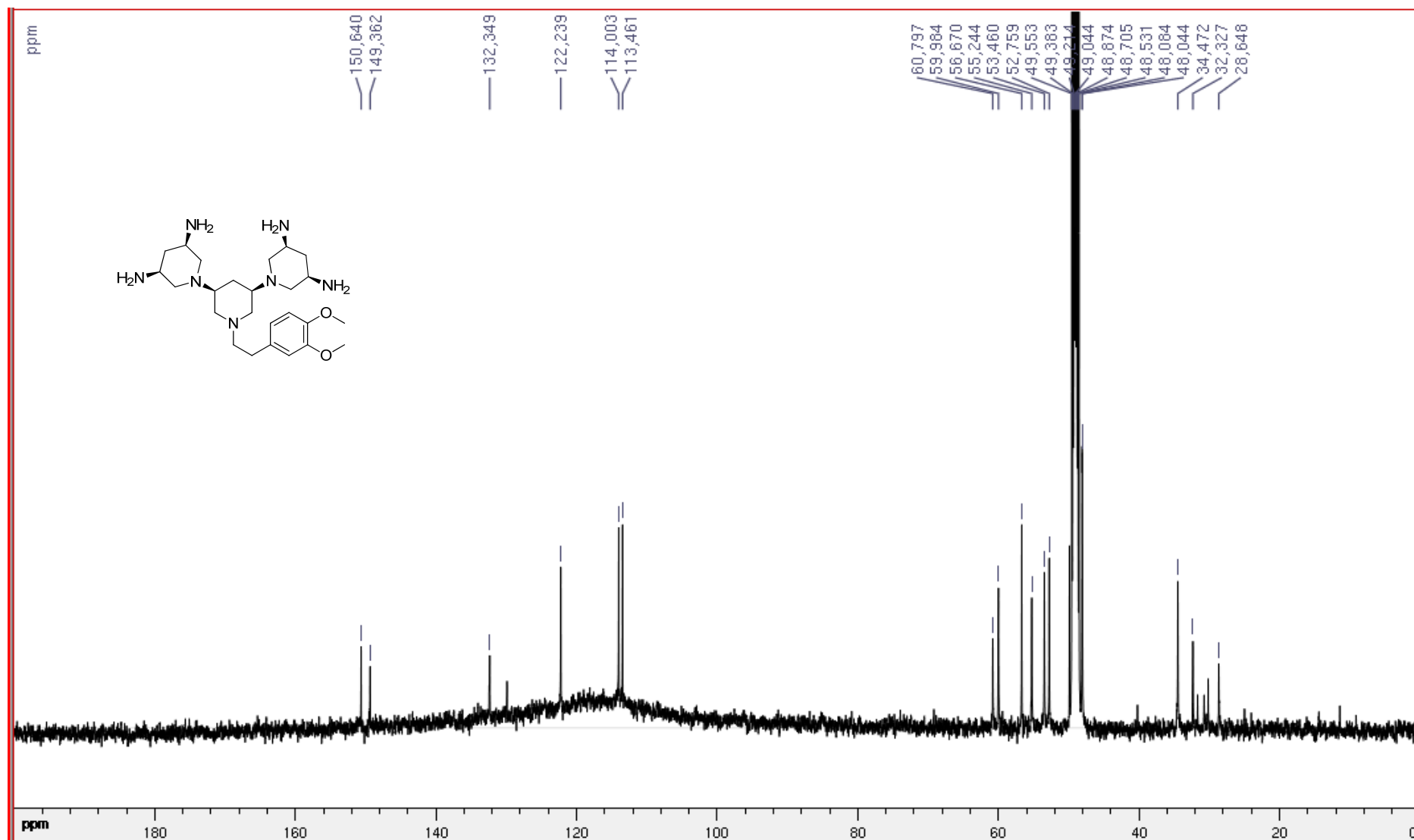
(3S,3'R,3''S,5R,5'S,5''R)-1'-(3,4-dimethoxyphenethyl)-[1,3':5',1''-terpiperidine]-3,3'',5,5''-tetraamine

13i



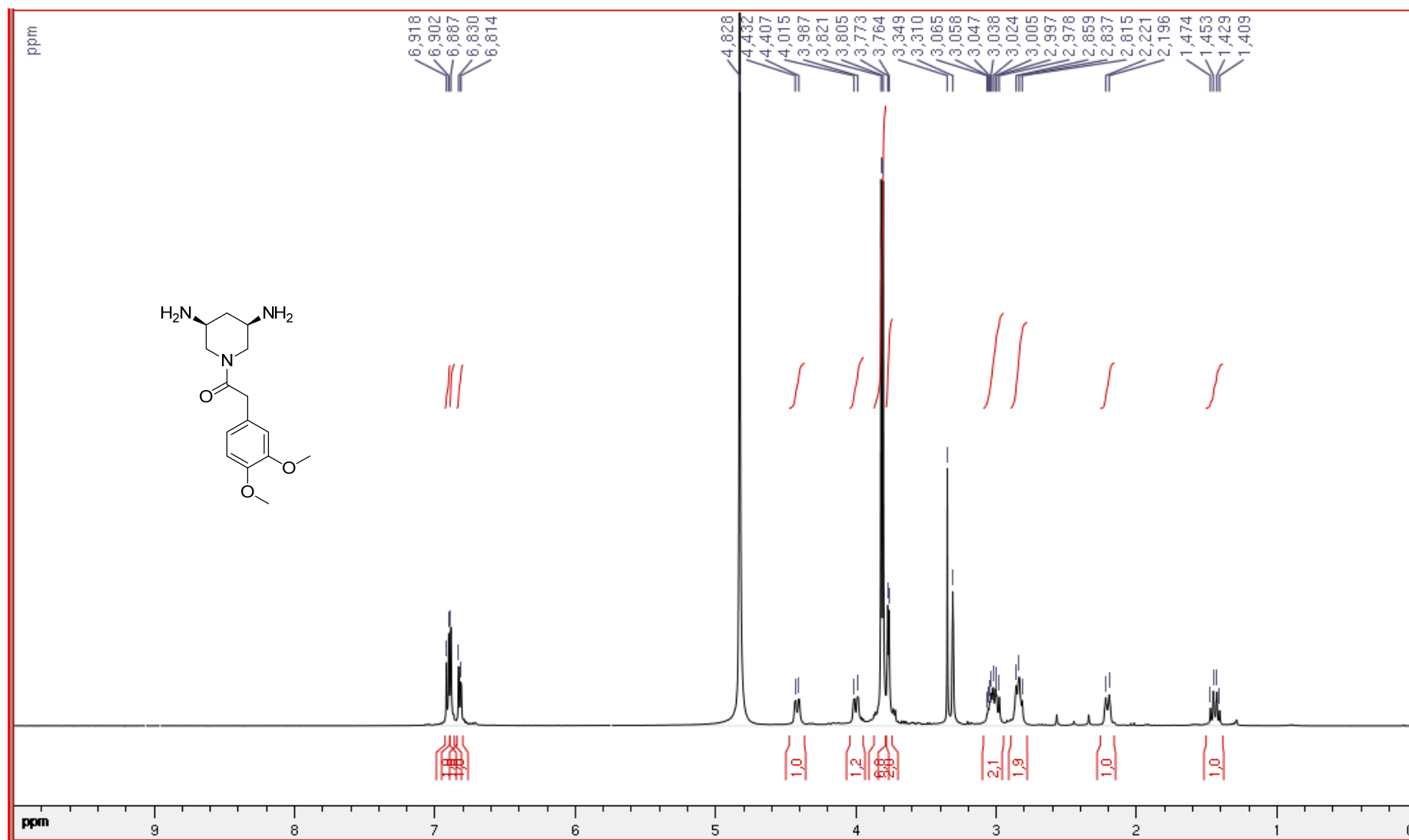
(3S,3'R,3''S,5R,5'S,5''R)-1'-(3,4-dimethoxyphenethyl)-[1,3':5',1''-terpiperidine]-3,3'',5,5''-tetraamine

13i



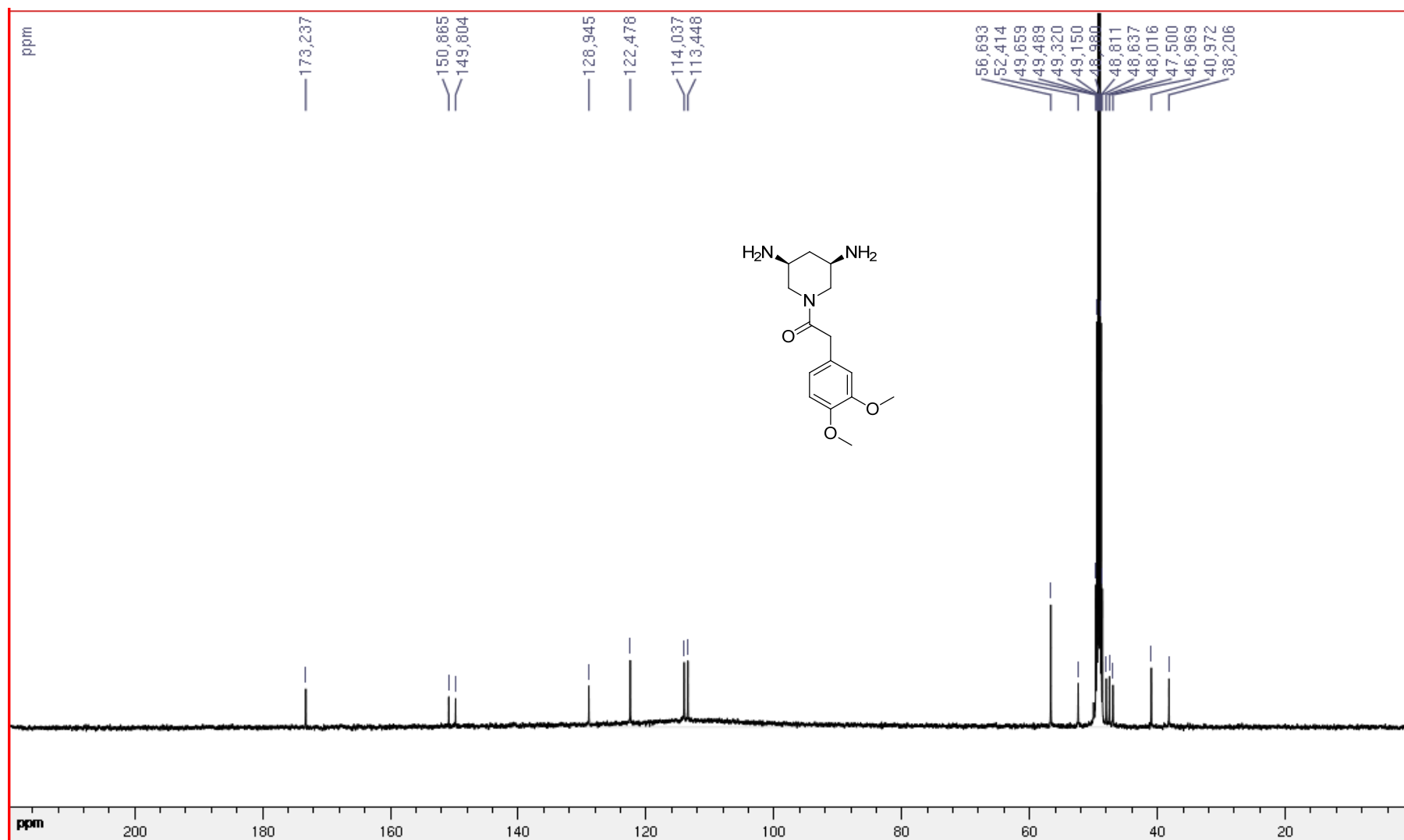
1-((3S,5R)-3,5-diaminopiperidin-1-yl)-2-(3,4-dimethoxyphenyl)ethanone

13j



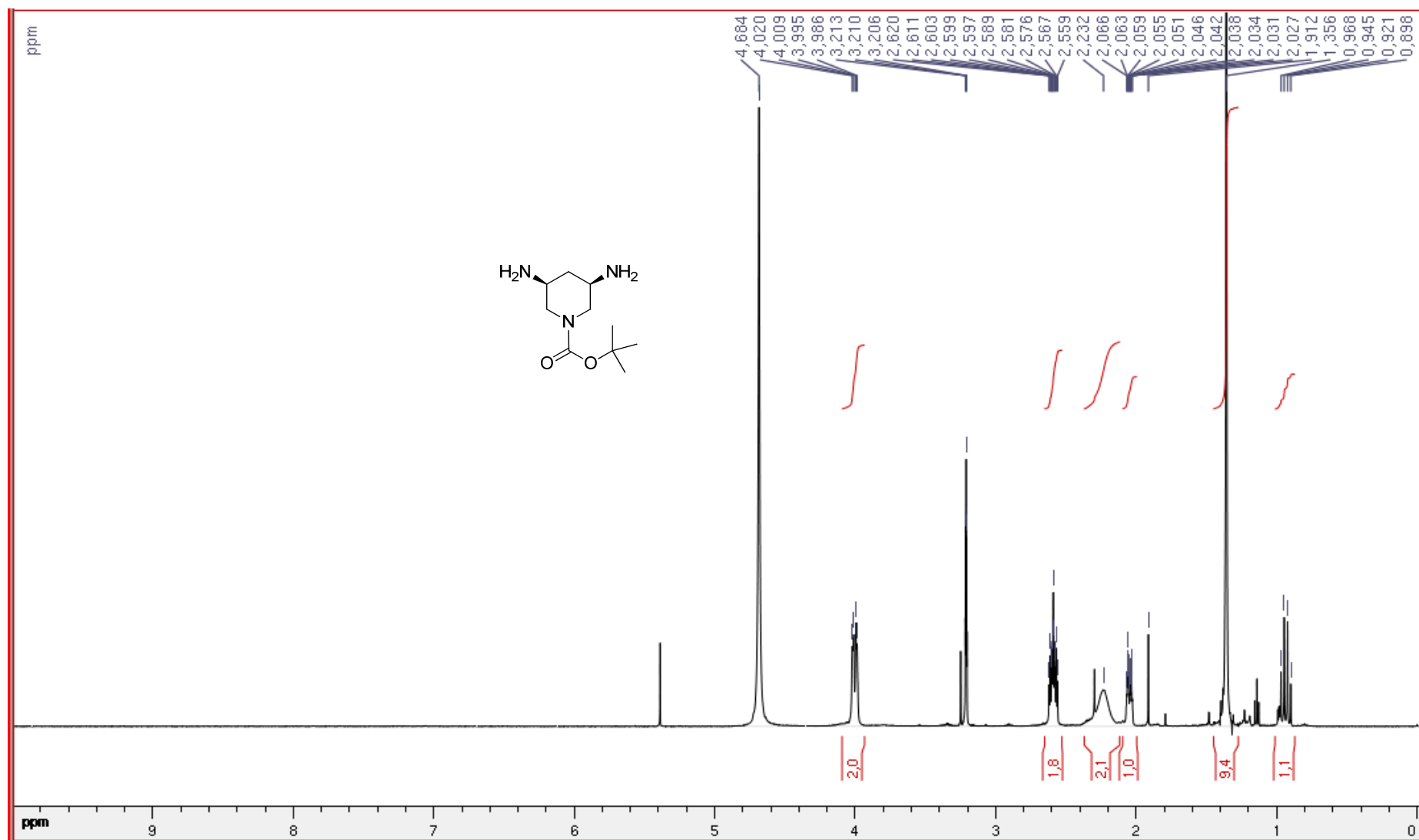
1-((3S,5R)-3,5-diaminopiperidin-1-yl)-2-(3,4-dimethoxyphenyl)ethanone

13j



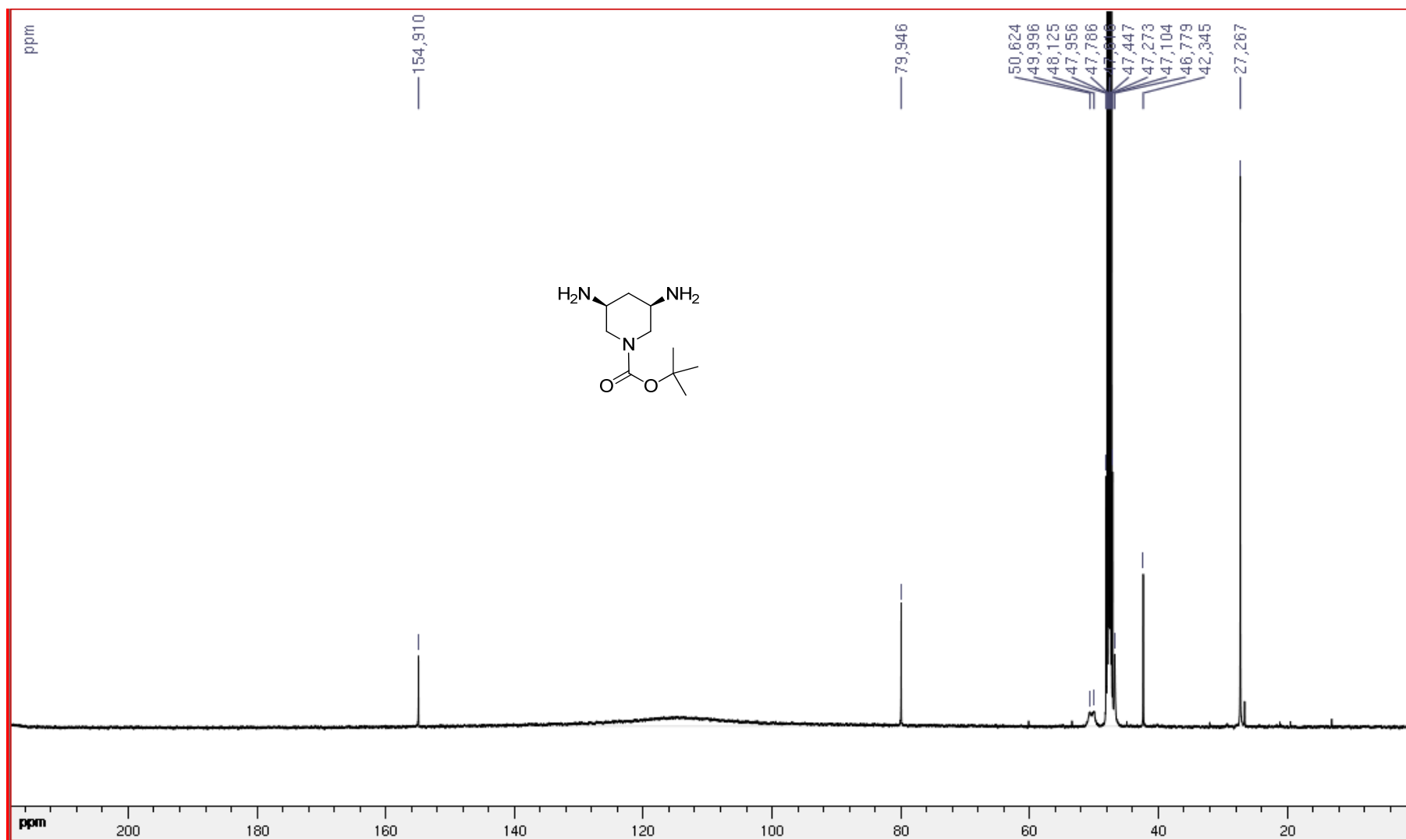
(3S,5R)-tert-butyl 3,5-diaminopiperidine-1-carboxylate

13k



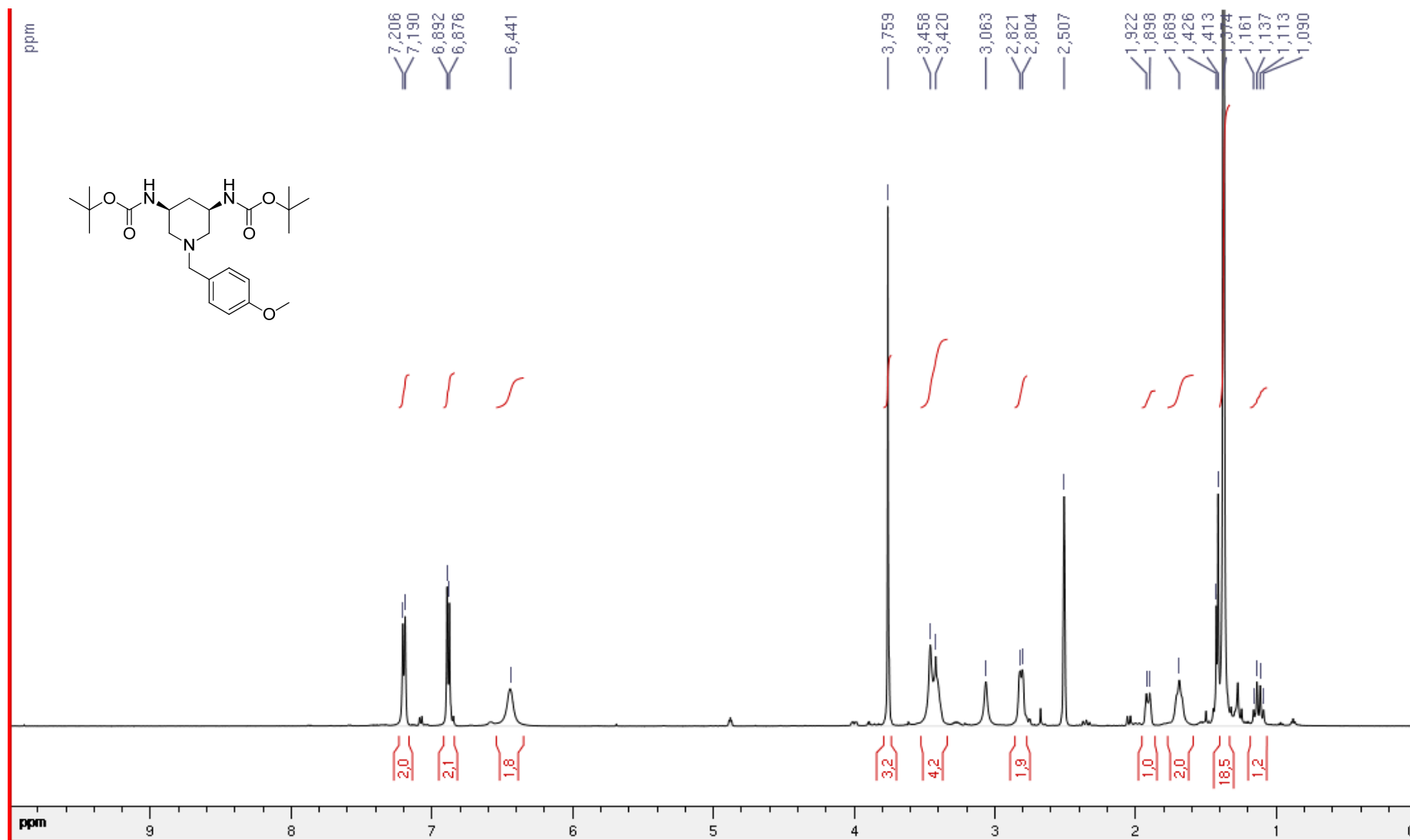
(3S,5R)-tert-butyl 3,5-diaminopiperidine-1-carboxylate

13k



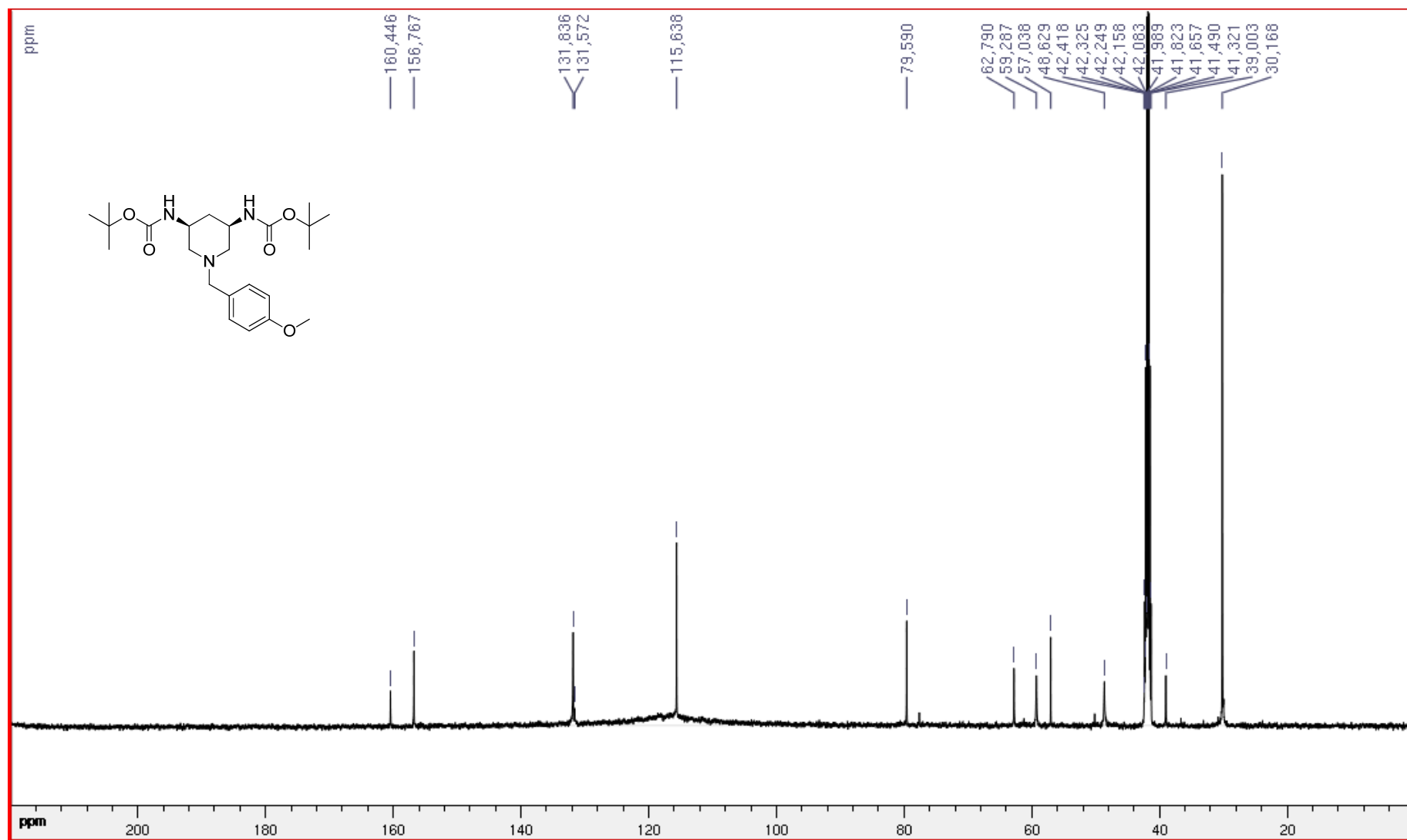
Di-tert-butyl ((3S,5R)-1-(4-methoxybenzyl)piperidine-3,5-diyl)dicarbamate

14



Di-tert-butyl ((3S,5R)-1-(4-methoxybenzyl)piperidine-3,5-diyl)dicarbamate

14



C. Chiral HPLC Data of 7k and 7l

HPLC analysis using Chiralcel[®] OD-H Column (n-hexane/i-PrOH 80:20, 1.0 mL/min)

