

Manuscript OB-ART-02-2012-025245

Supplementary Information

A Convenient Biomimetic Synthesis of Optically Active Putative Neurotoxic Metabolites of MDMA (“Ecstasy”) from *R*-(-)- and *S*-(+)-*N*-Methyl- α -Methyldopamine Precursors

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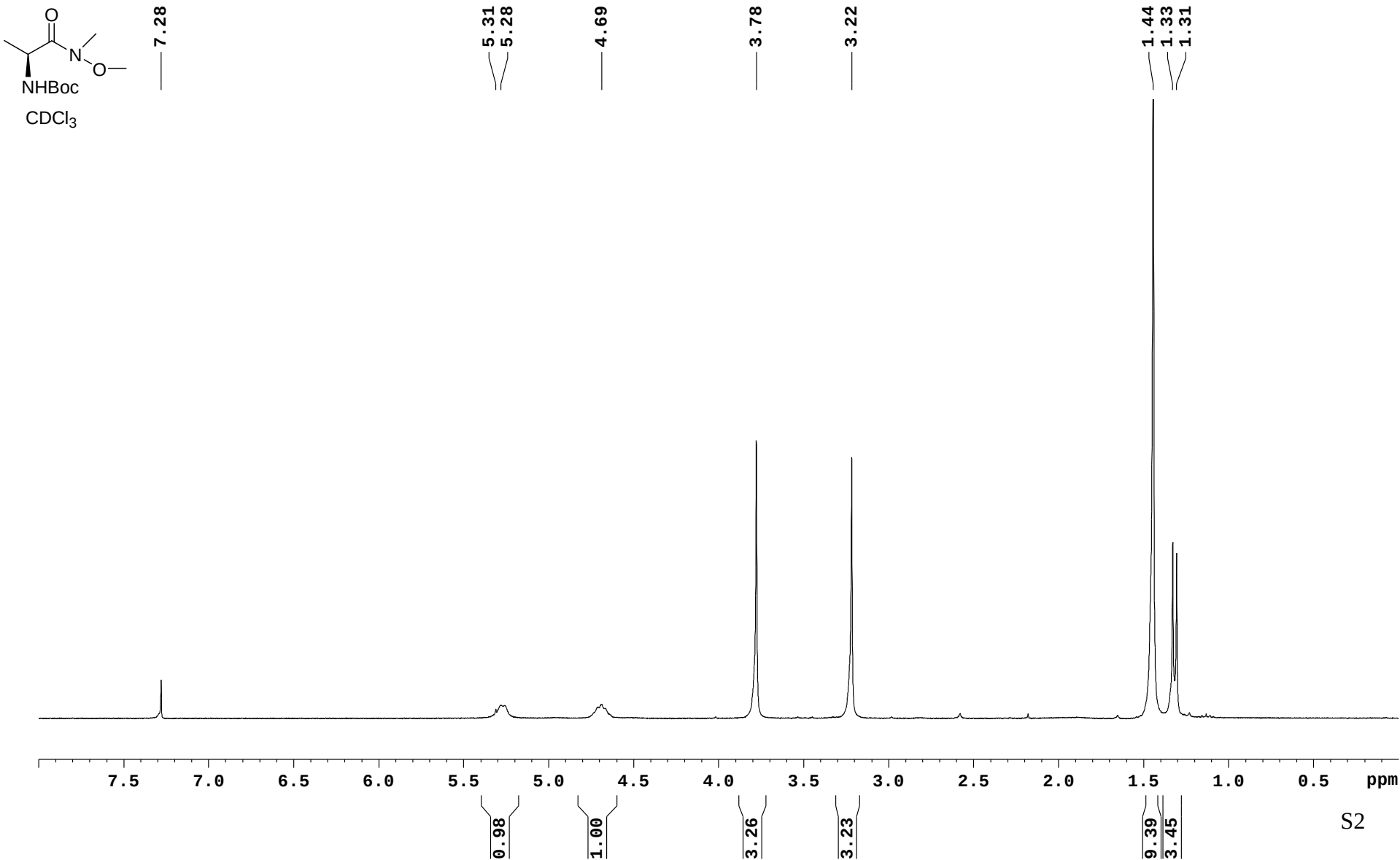
E-mail: martine.largeron@parisdescartes.fr

Table of Contents

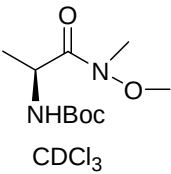
- I. ^1H and ^{13}C NMR spectra of *S*-(+)-HHMA **7** and its synthetic intermediates **1-6**
- II. ^1H and ^{13}C NMR spectra of optically active catechol-thioether conjugates **8-15**
- III. Analytical HPLC chromatograms of *S*-(+)-HHMA **7** and of optically active catechol-thioether conjugates **8-15**

I. ¹H and ¹³C NMR spectra of S-(+)-HHMA 7 and its synthetic intermediates 1-6

Compound 1



Compound 1



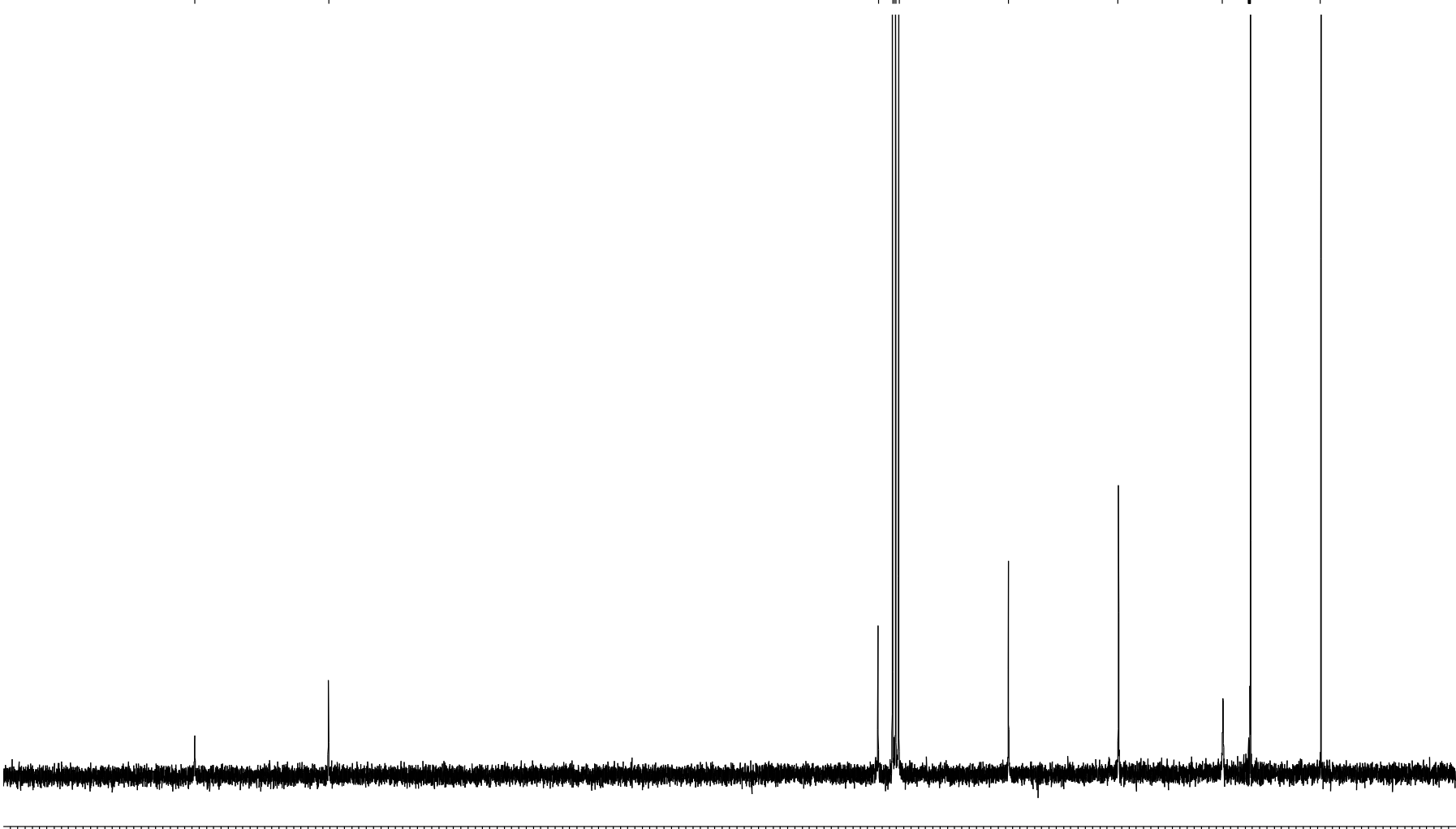
173.6

155.2

79.5
77.5
77.3
77.1
76.6

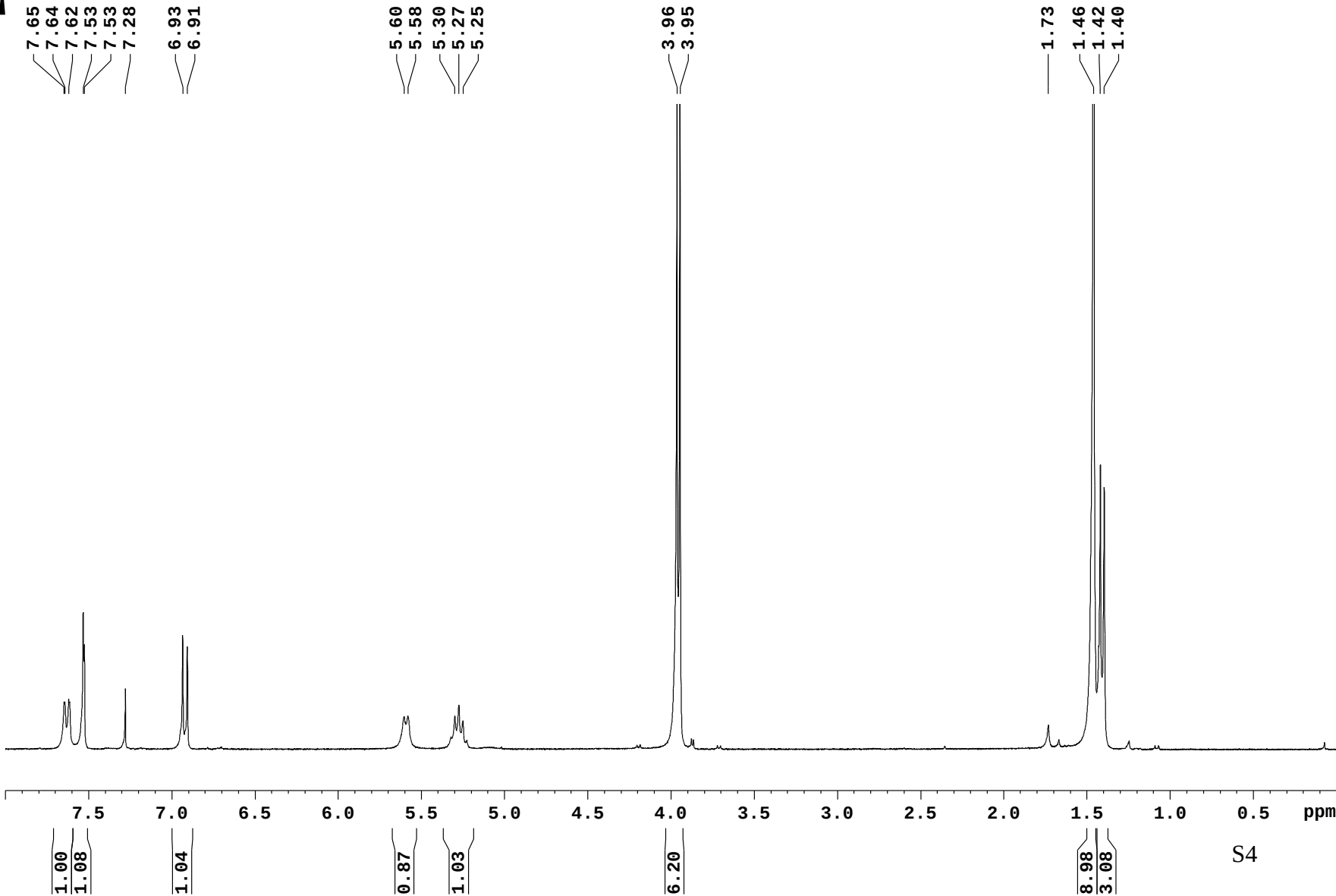
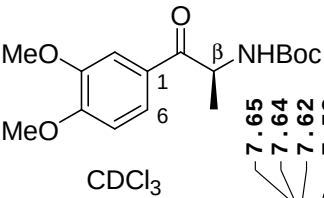
61.6

46.5
32.1
28.6
28.5
28.5
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28.4
28.4
28.4
28.4
28.3
28.3
18.6

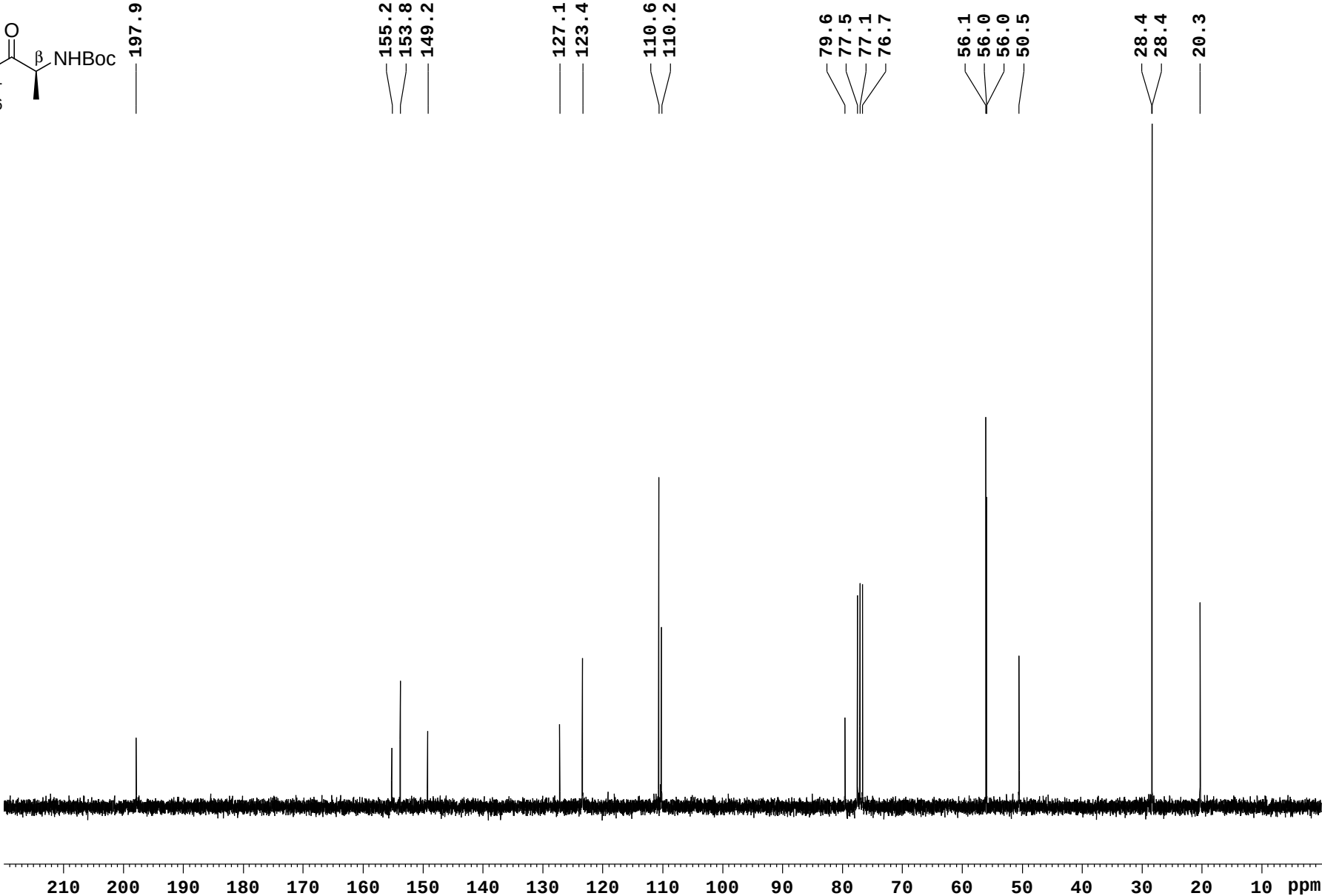
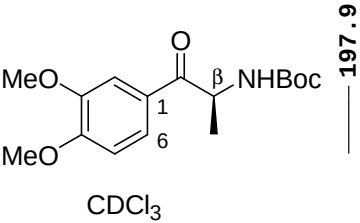


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm S3

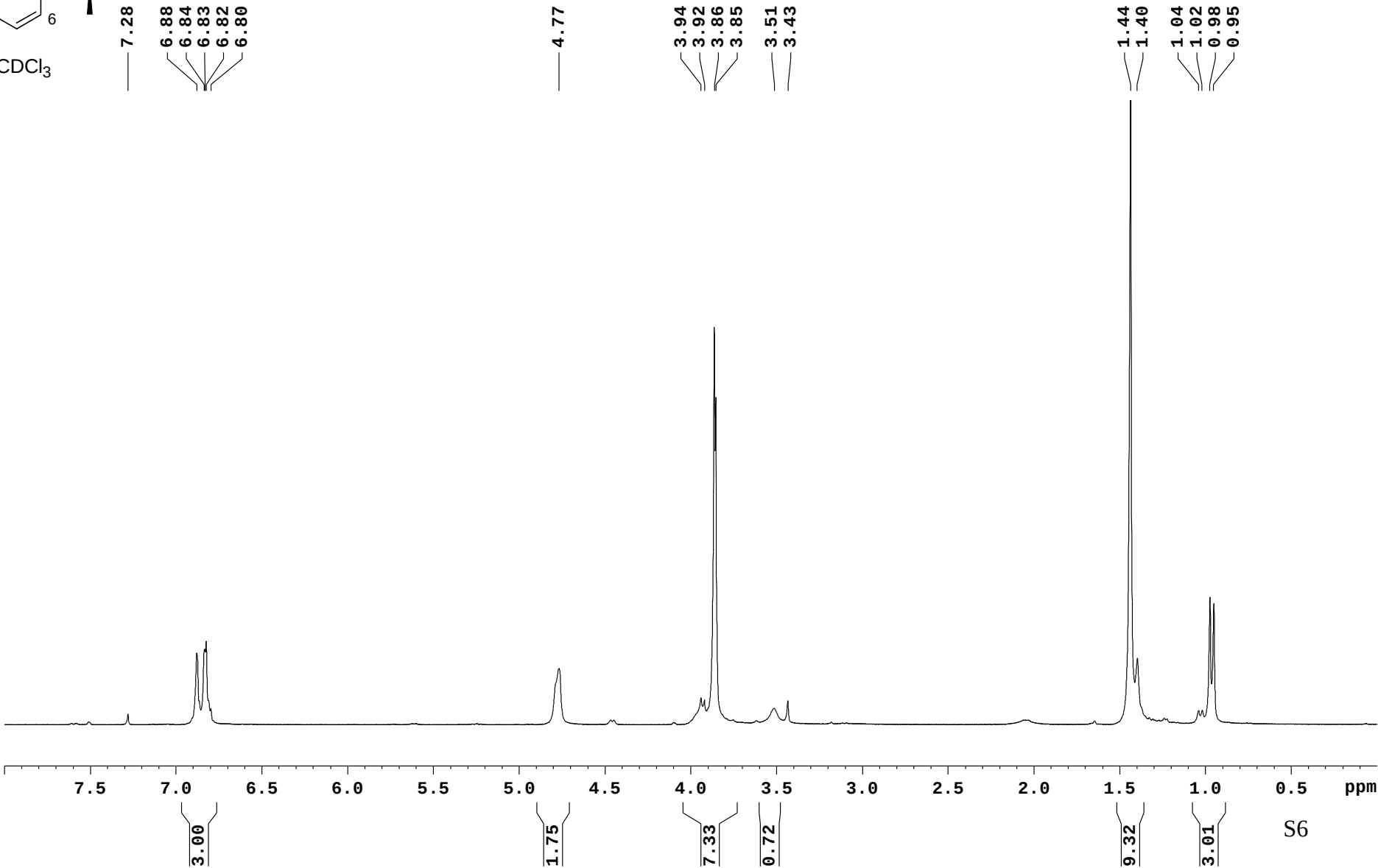
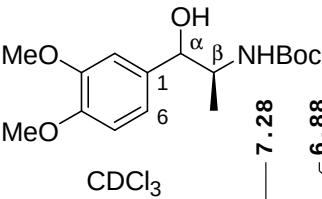
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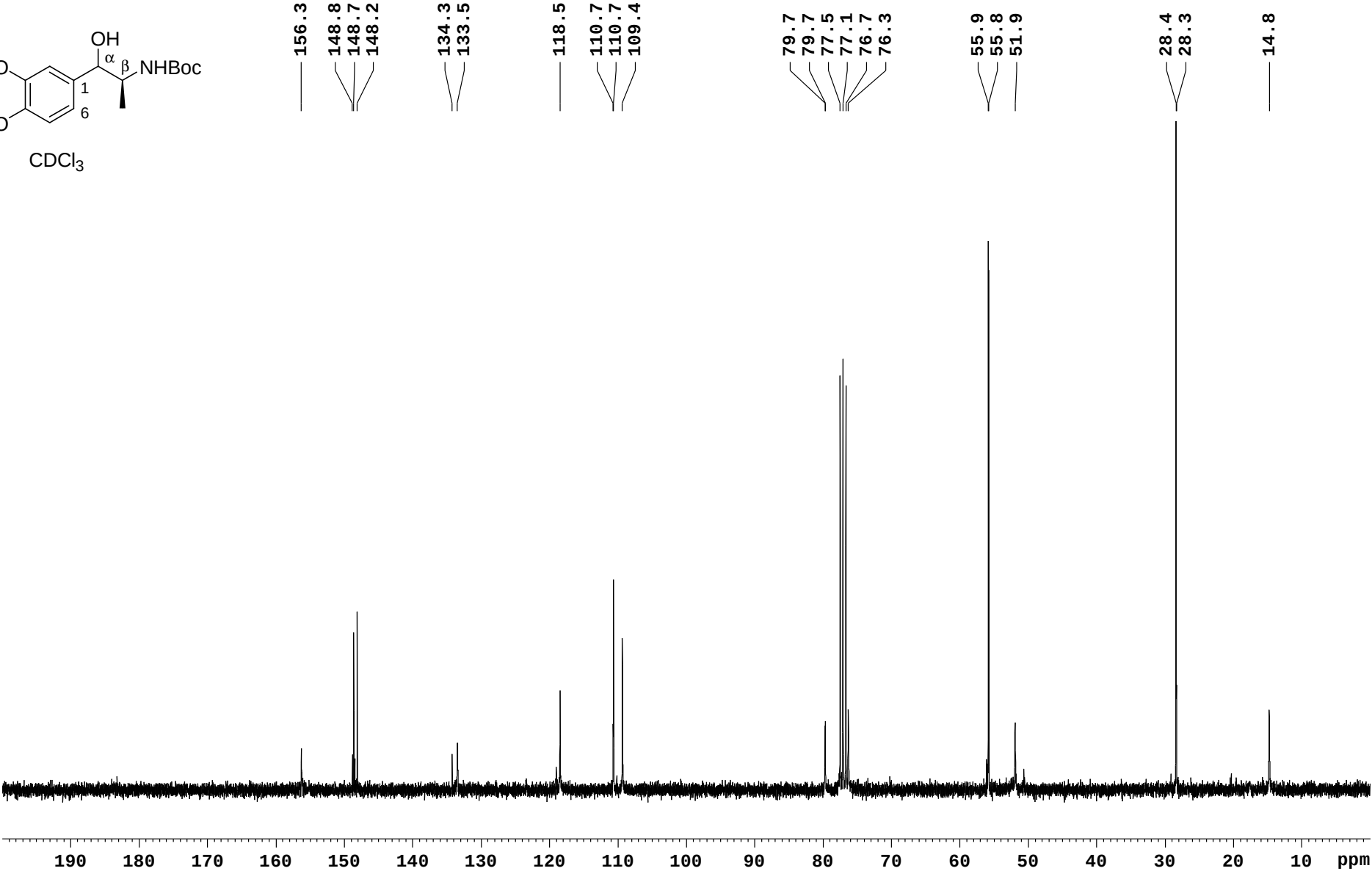
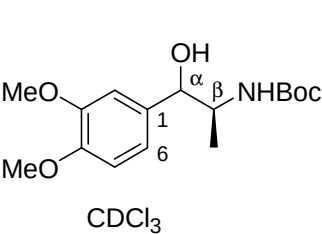
Compound 2



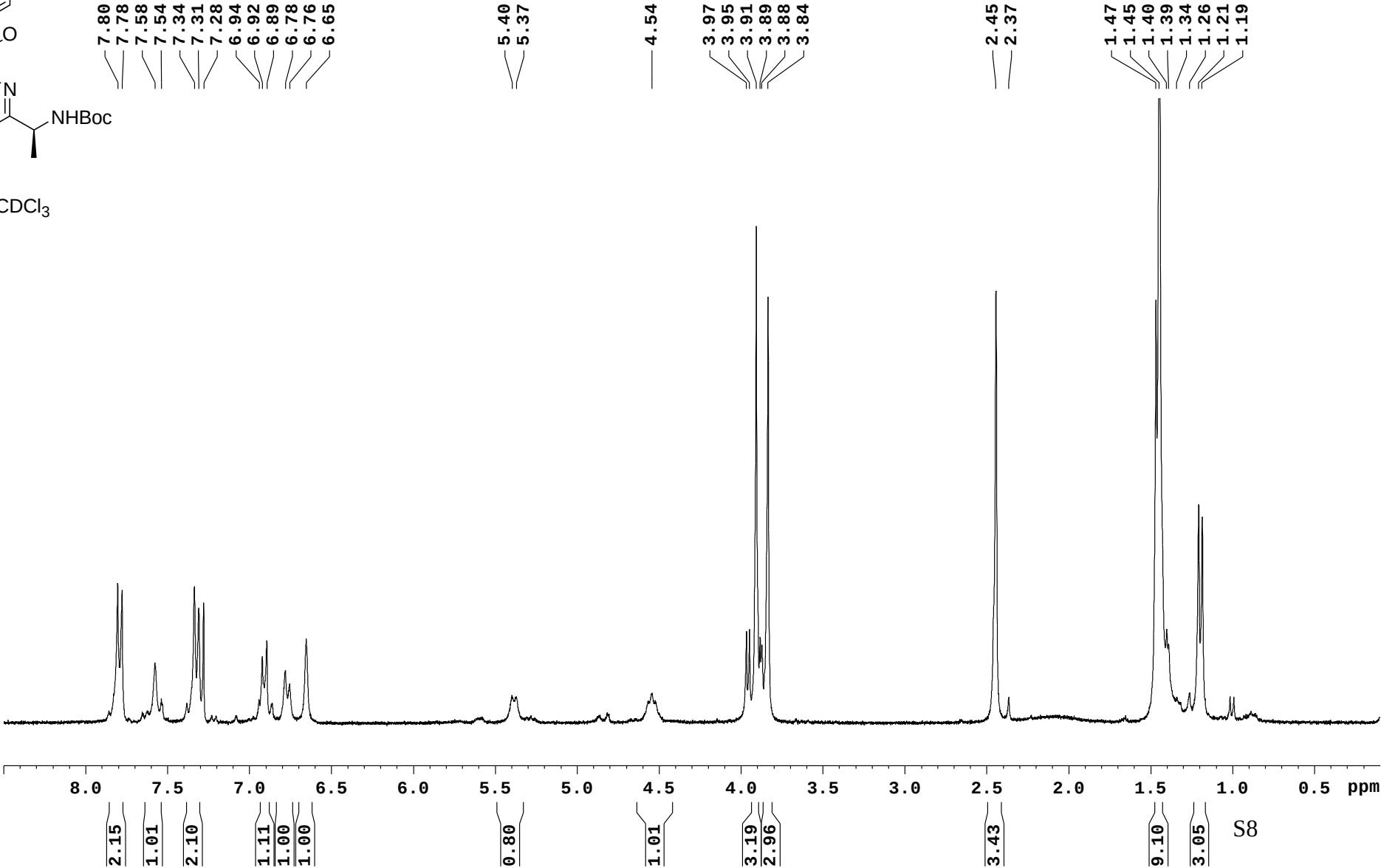
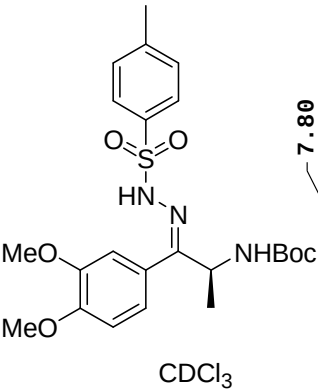
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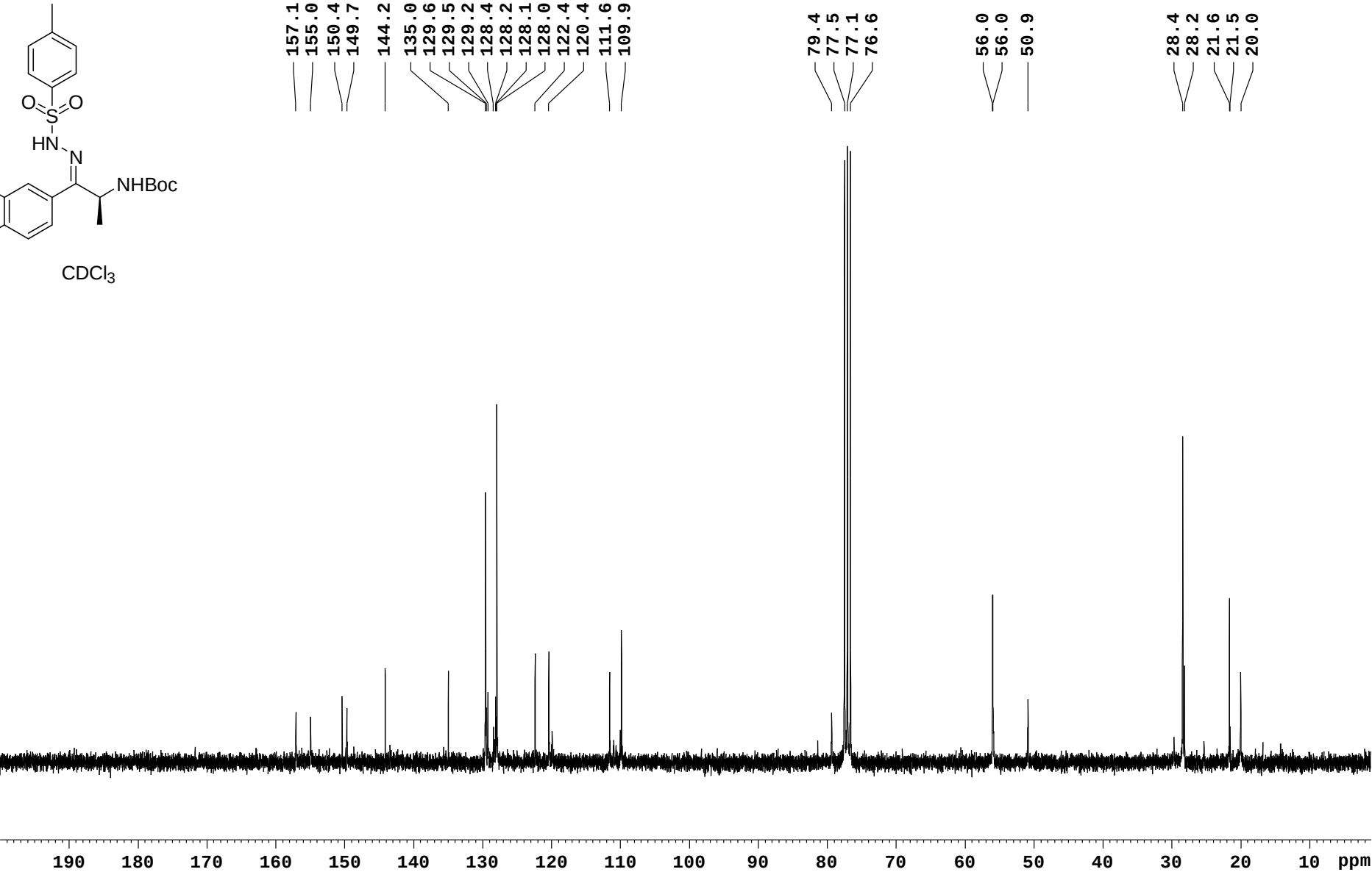
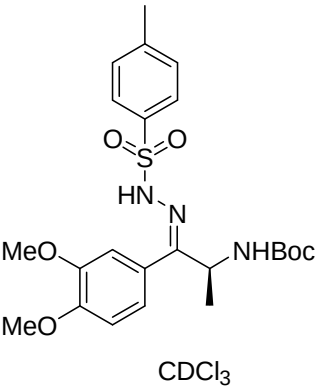
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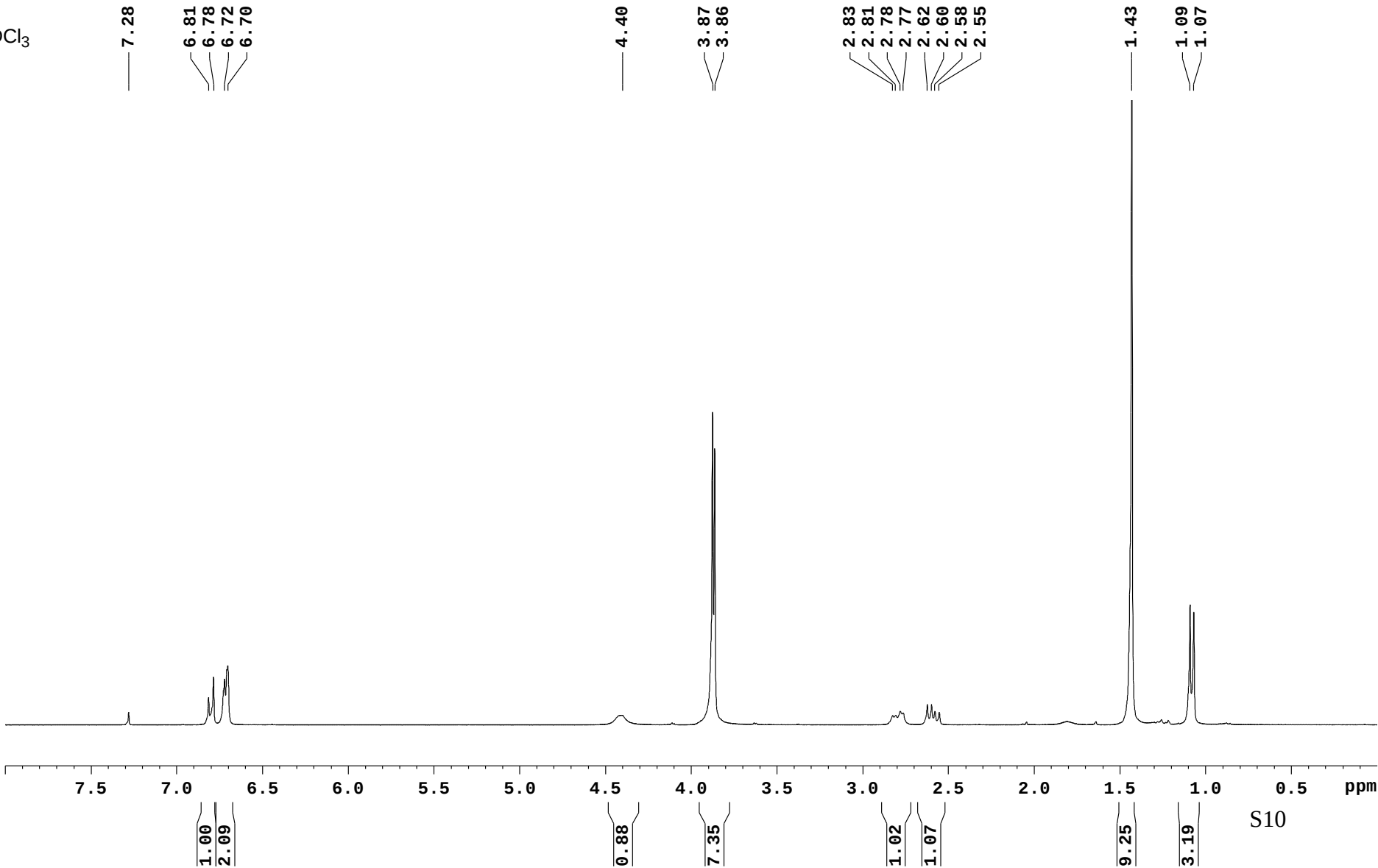
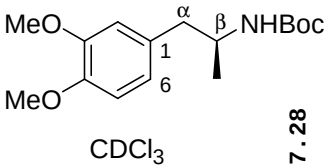
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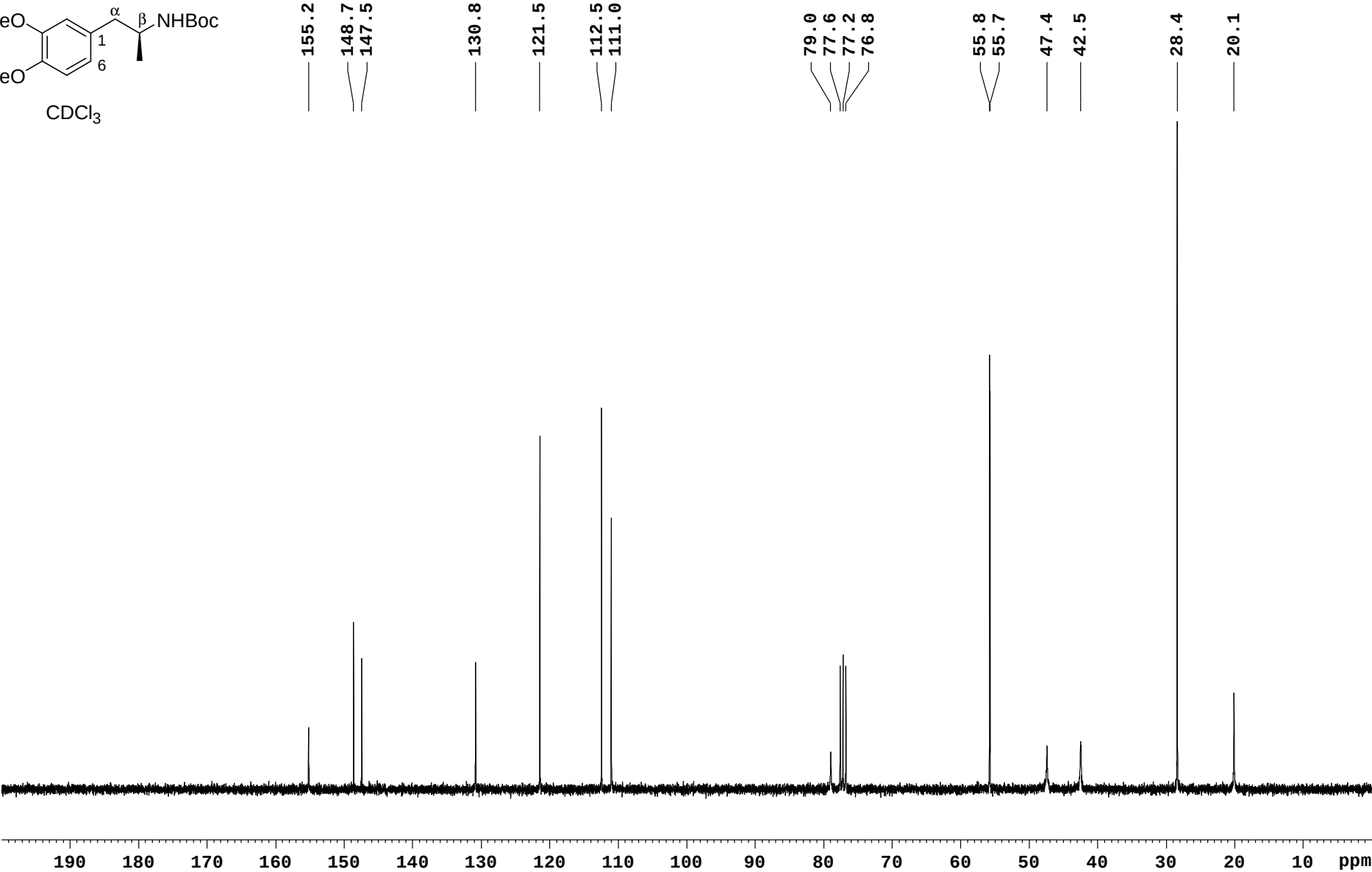
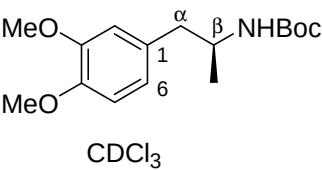
Compound 4



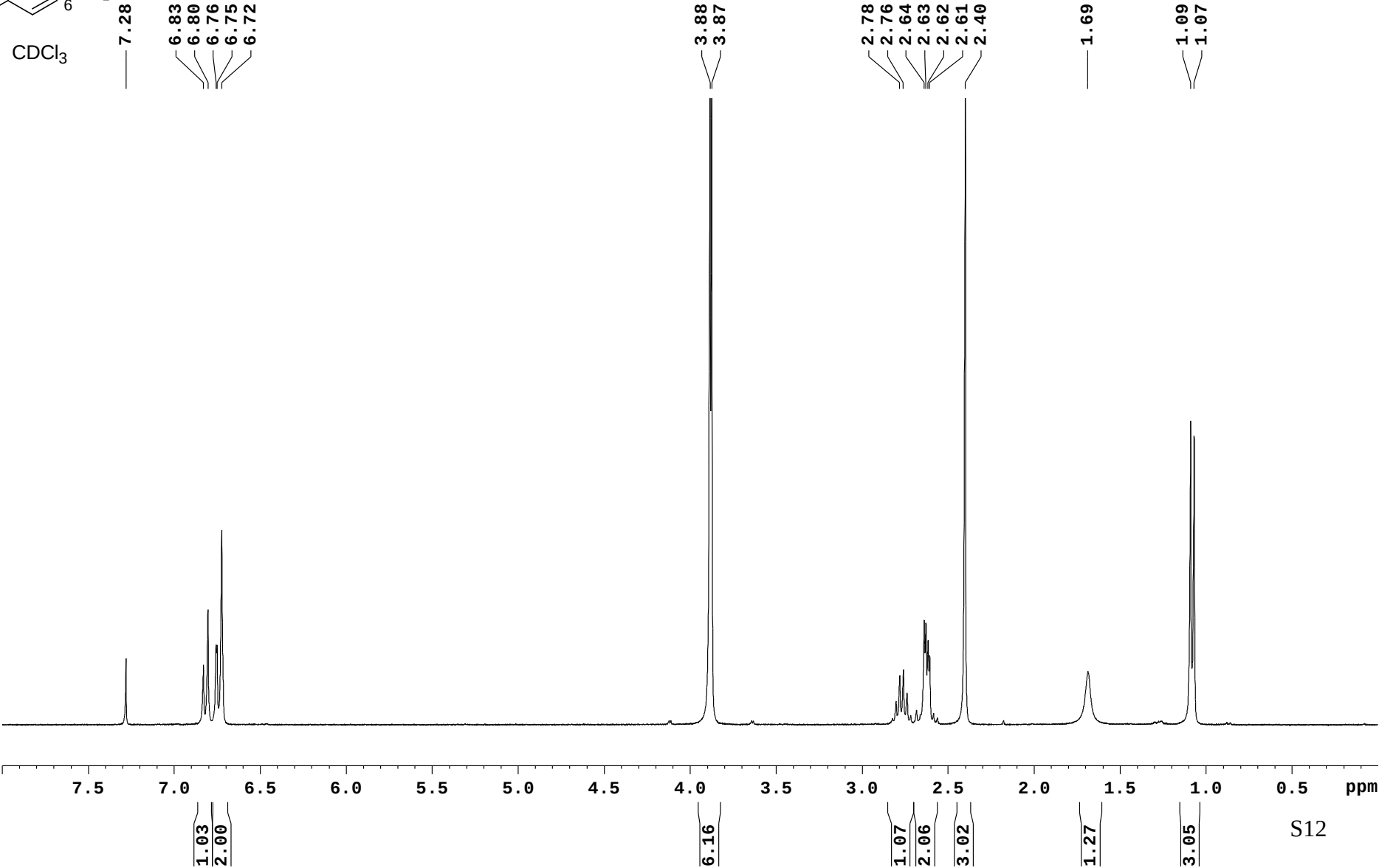
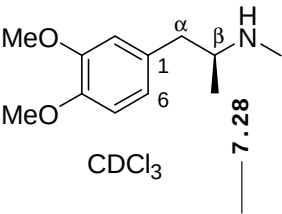
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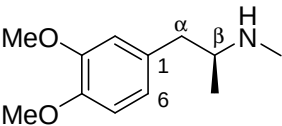
Compound 5



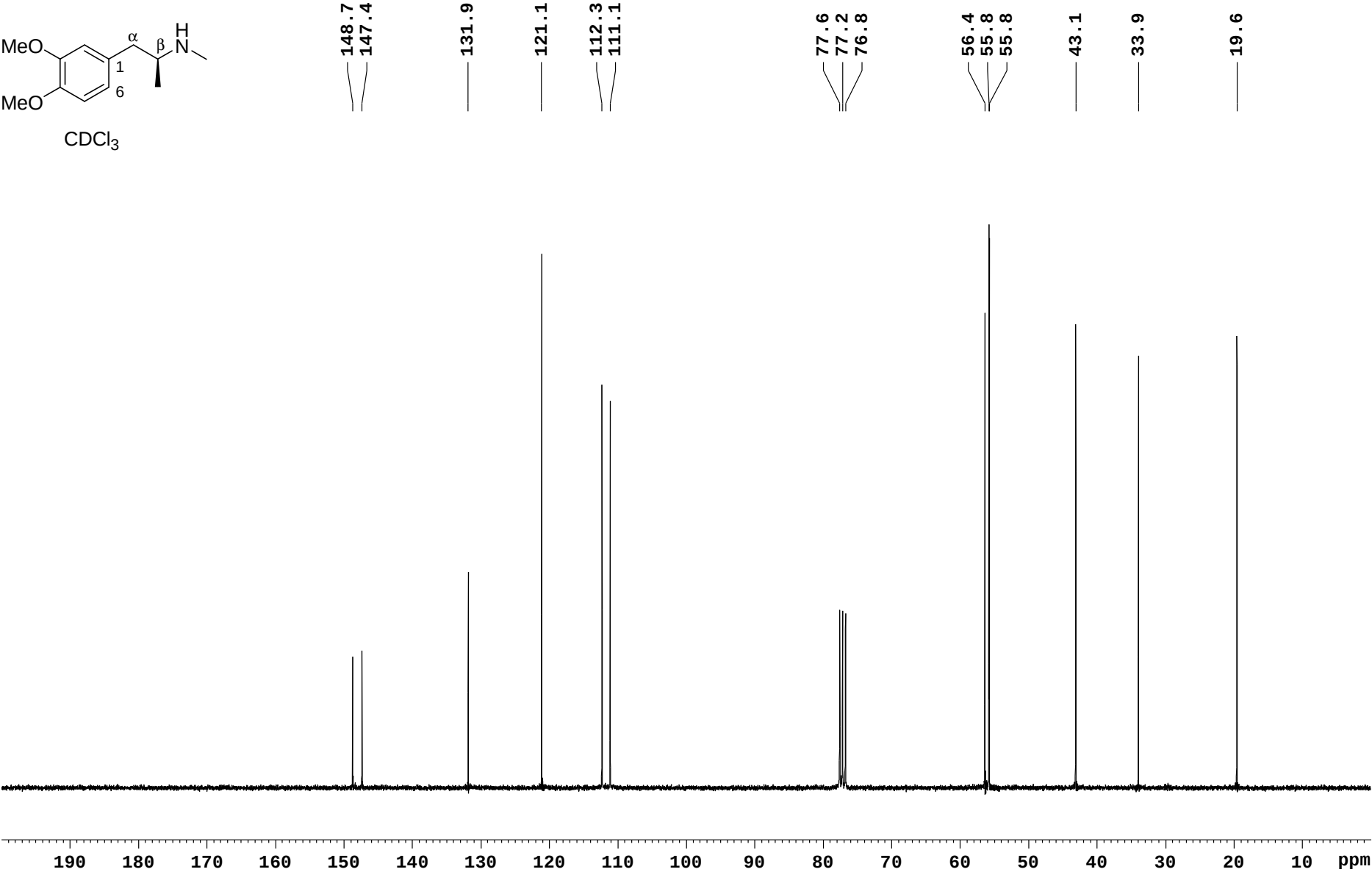
Compound 6



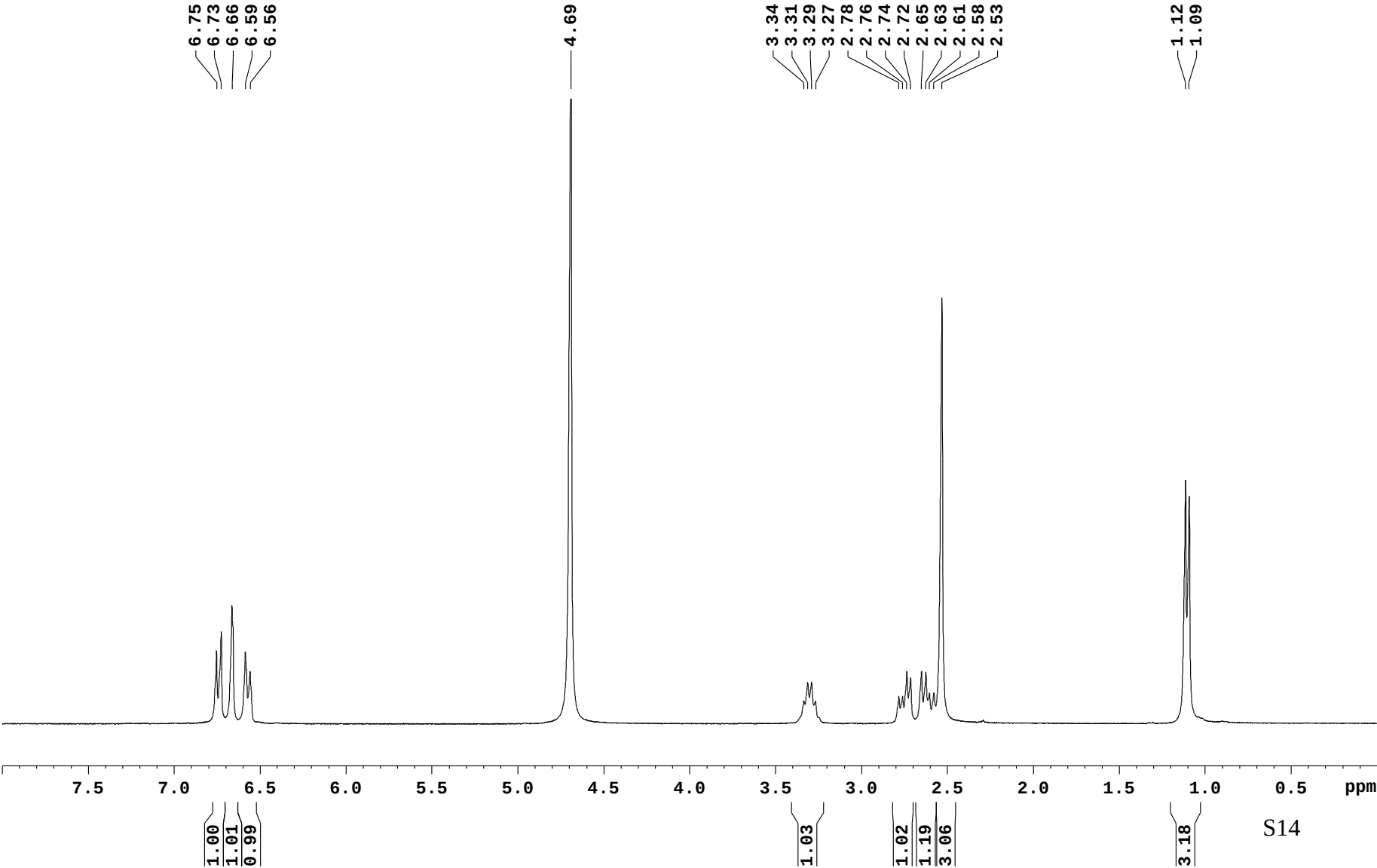
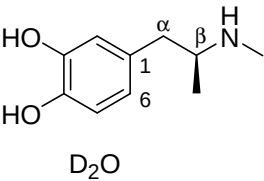
Compound 6



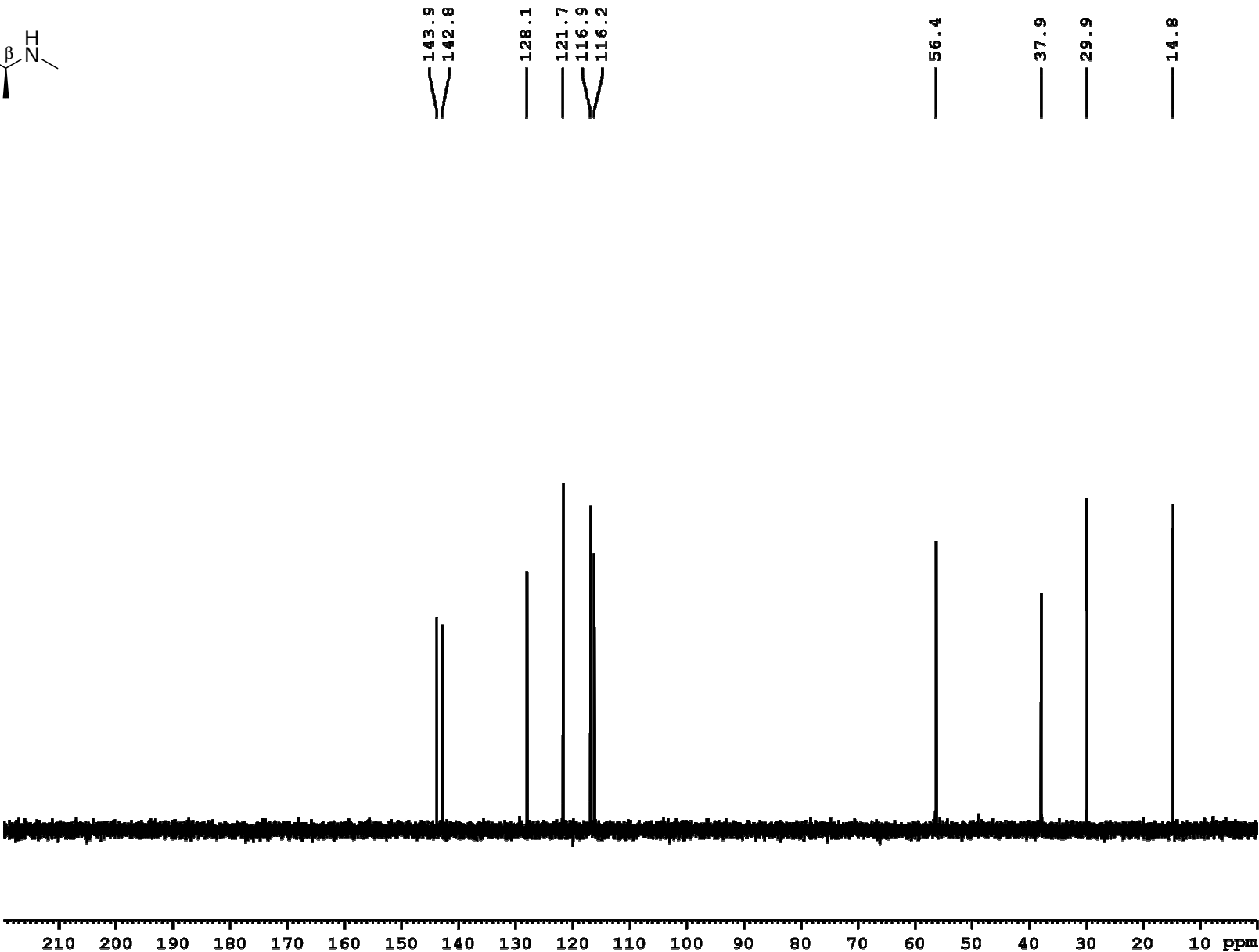
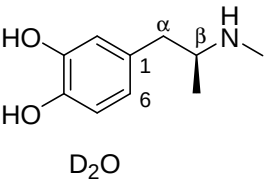
CDCl₃



Compound 7

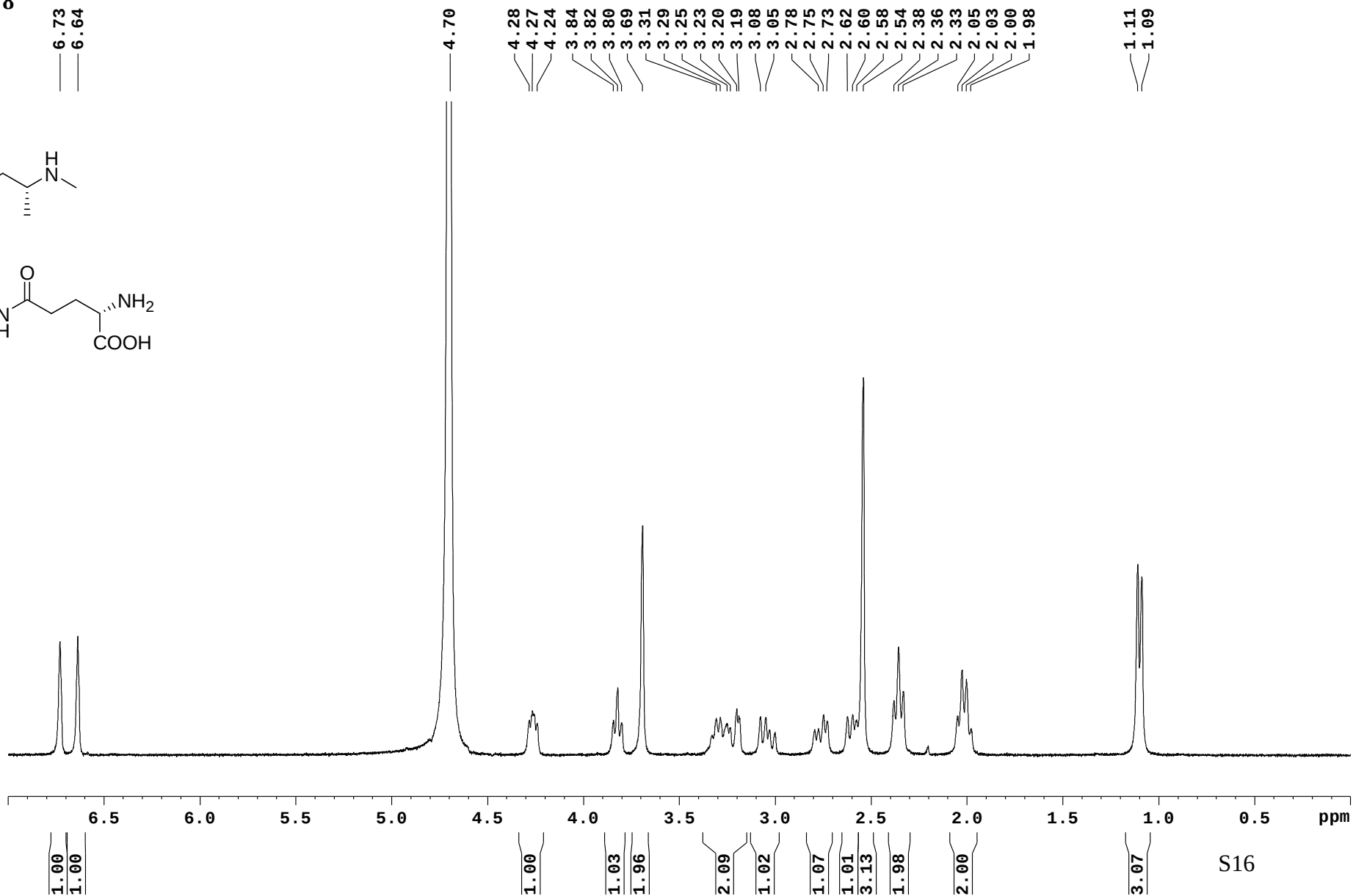
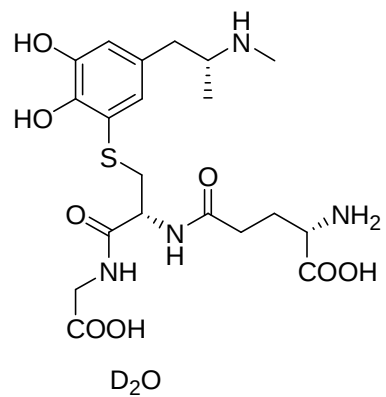


Compound 7

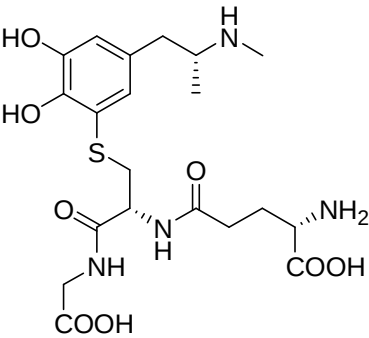


II. ^1H and ^{13}C NMR spectra of optically active catechol-thioether conjugates 8-15

Compound 8



Compound 8



D₂O

174.2
172.8
172.3
172.1

144.4
143.9

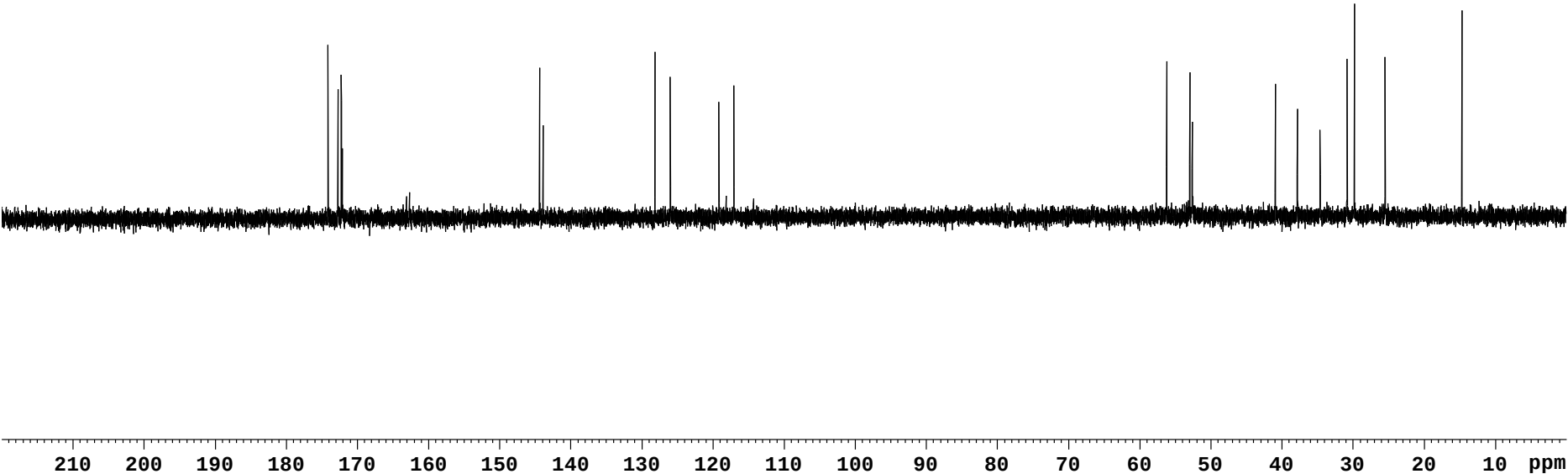
128.2
126.0

119.2
117.1

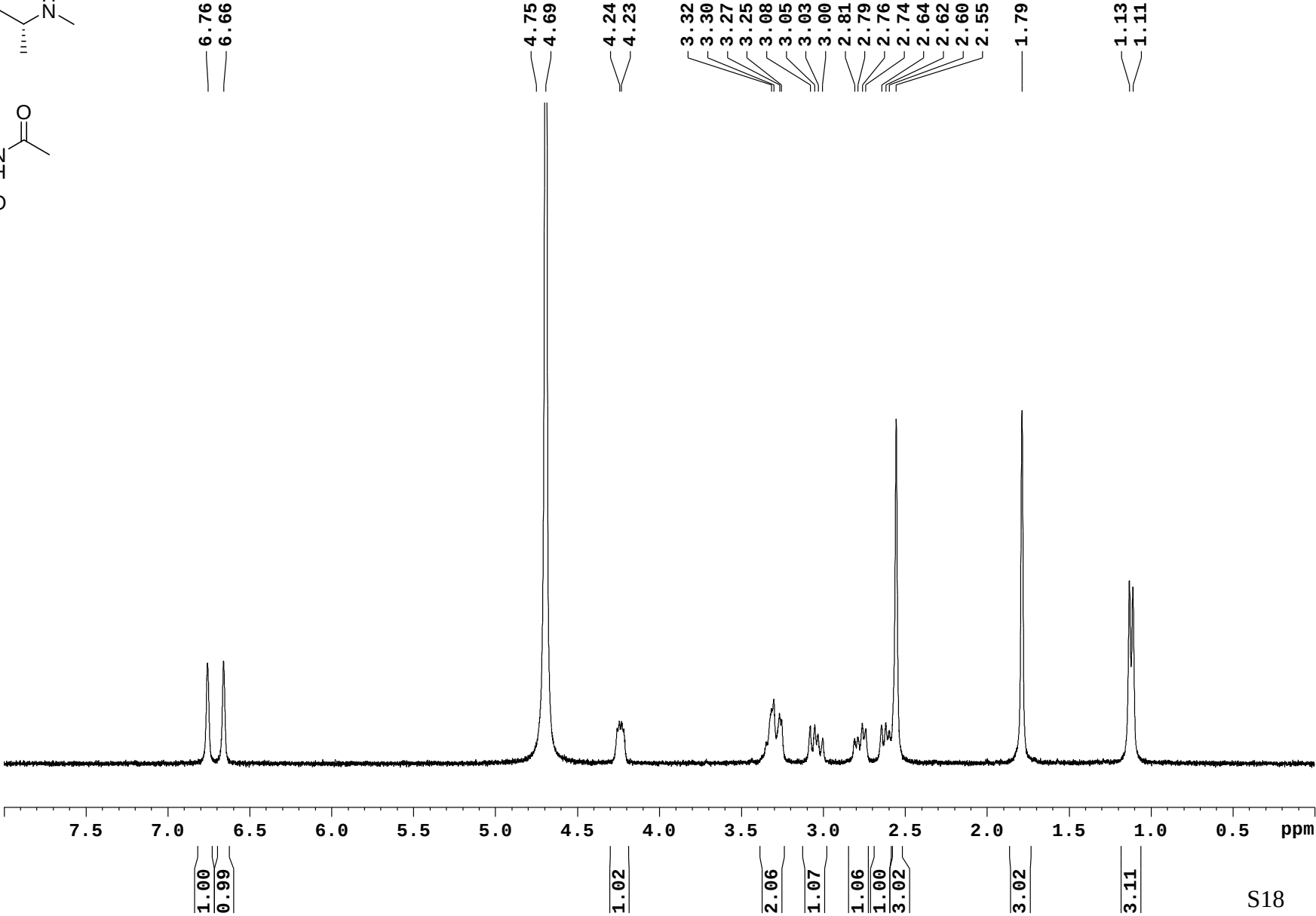
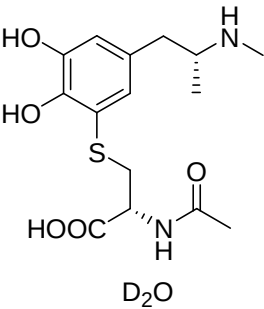
56.2
53.0
52.6

40.9
37.8
34.6
30.9
29.8
25.5

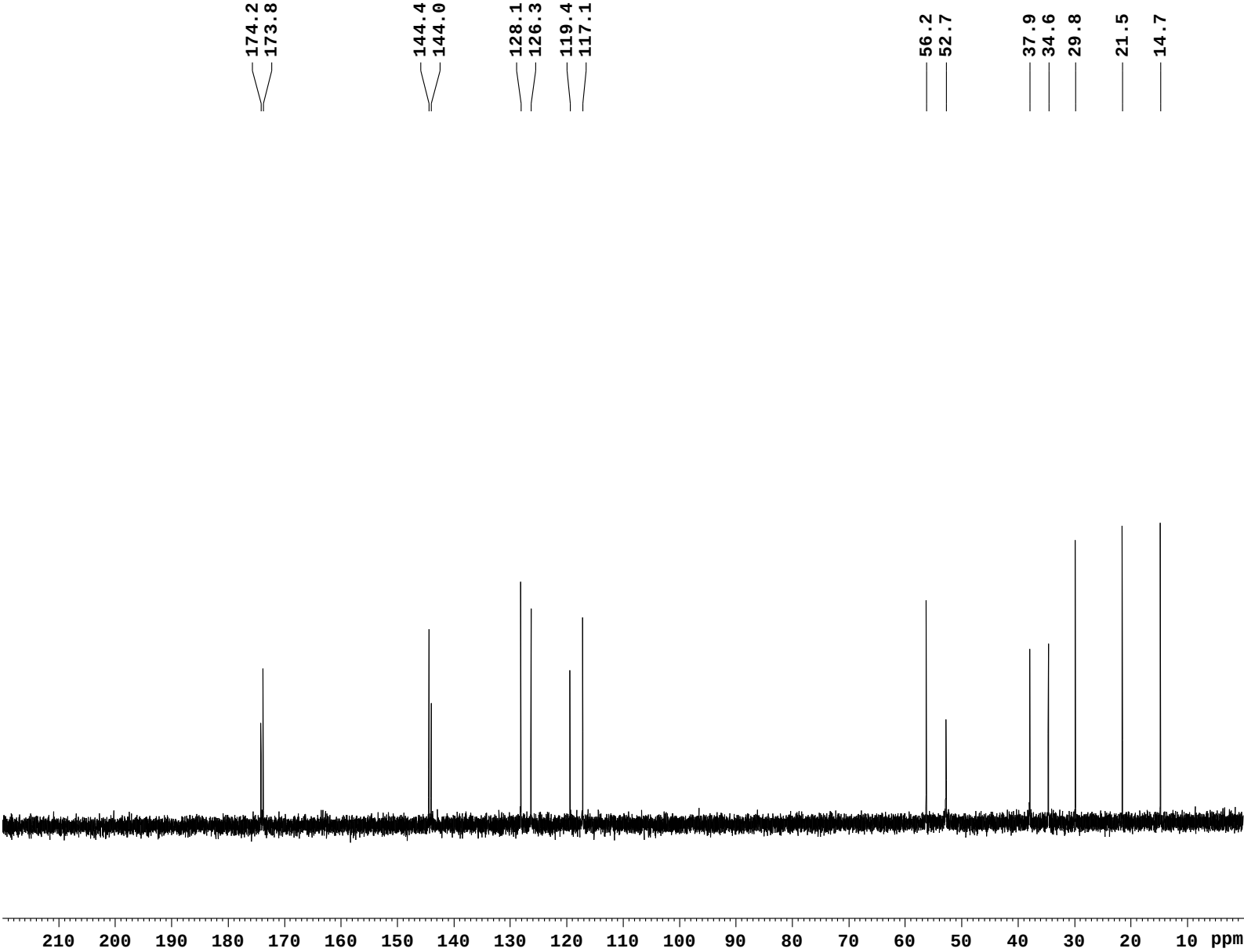
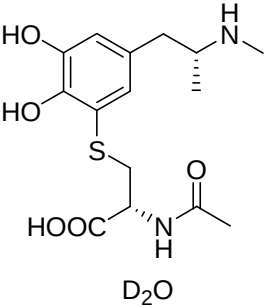
14.7



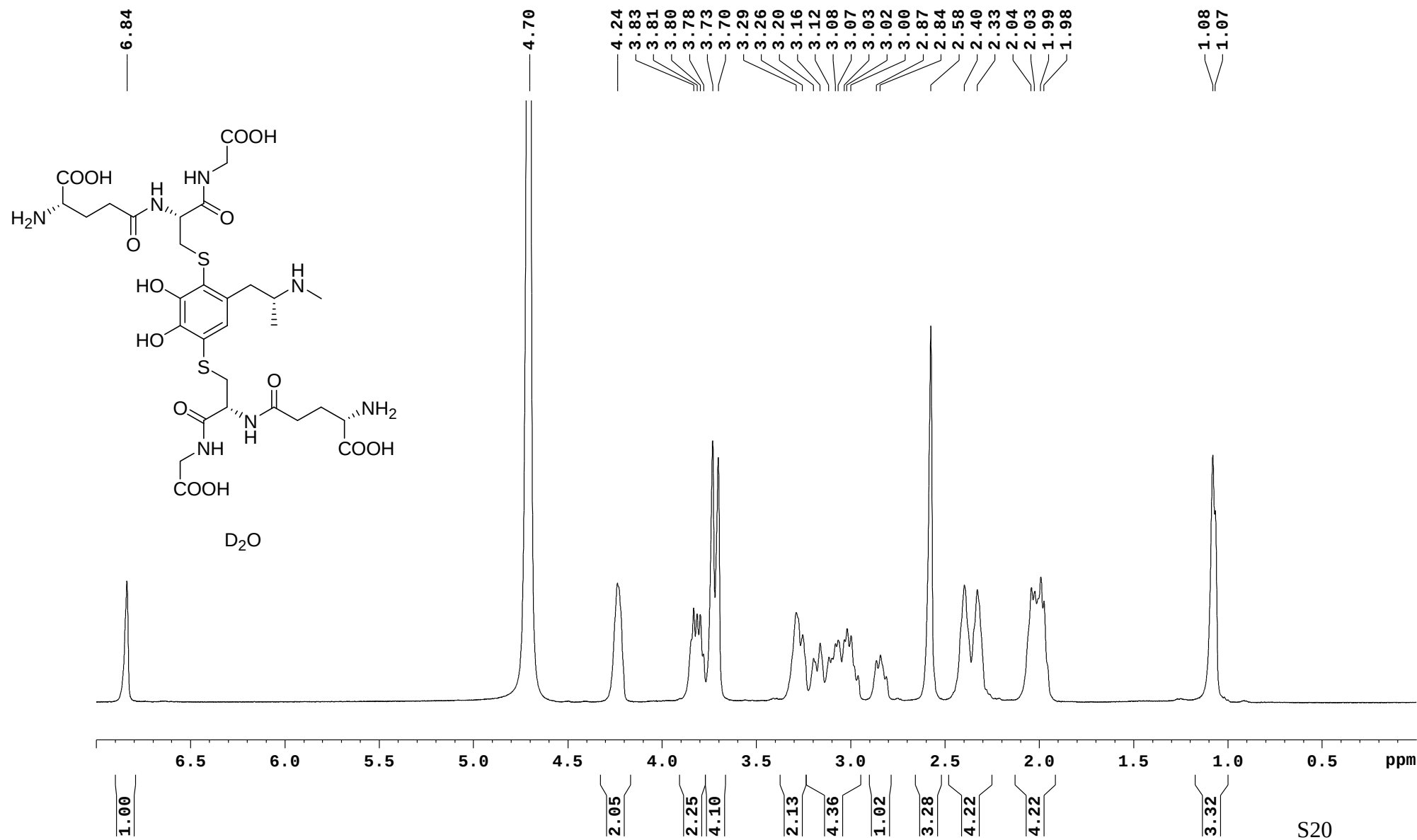
Compound 9



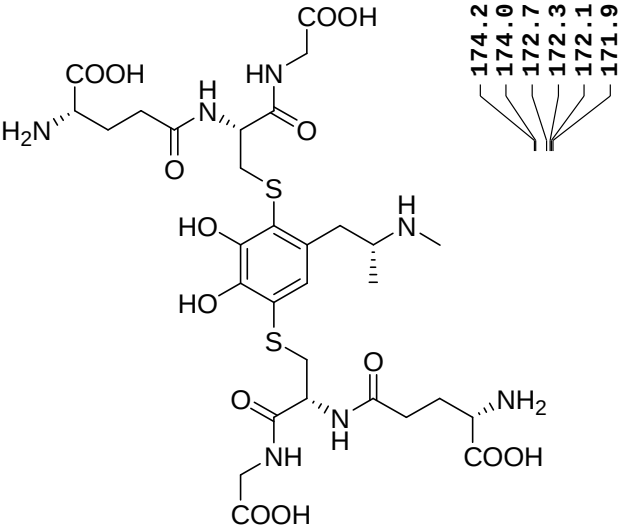
Compound 9



Compound 10



Compound 10



D₂O

174.2
174.0
172.7
172.3
172.1
171.9

146.7
143.8

131.8

126.0

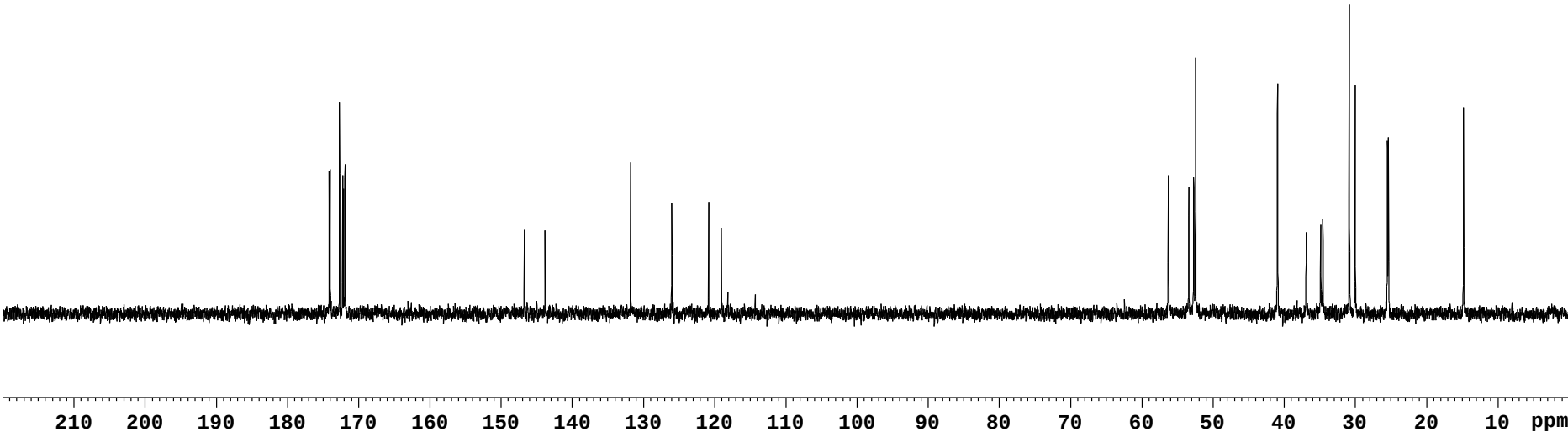
120.8

119.1

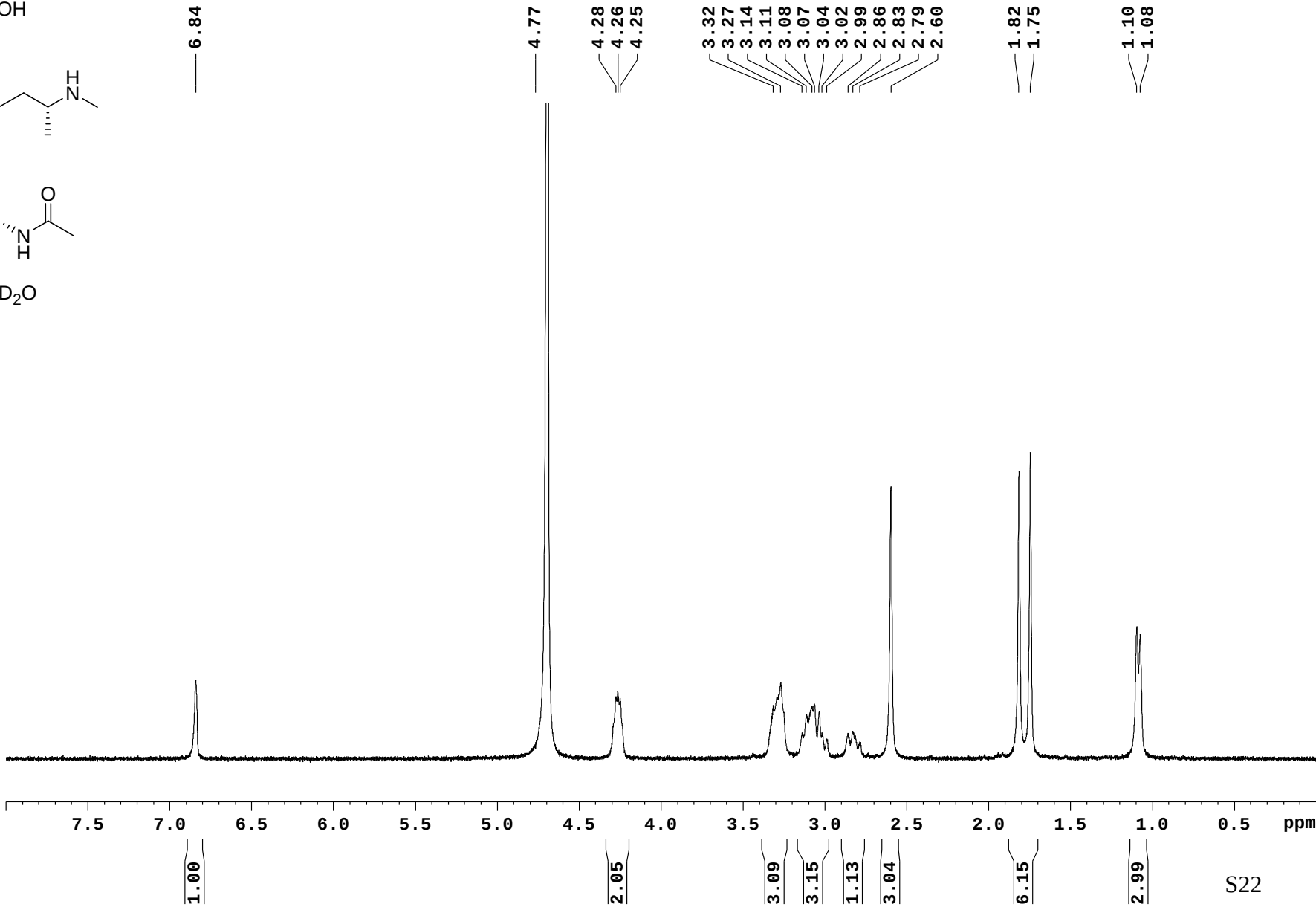
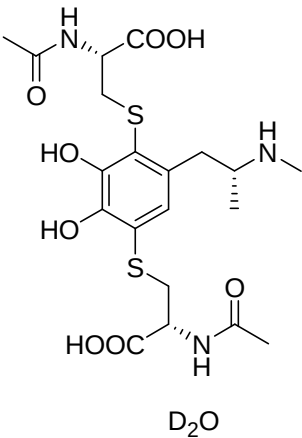
56.3
53.4
52.7
52.4

40.9
36.9
34.9
34.6
30.9
30.0
25.5
25.4

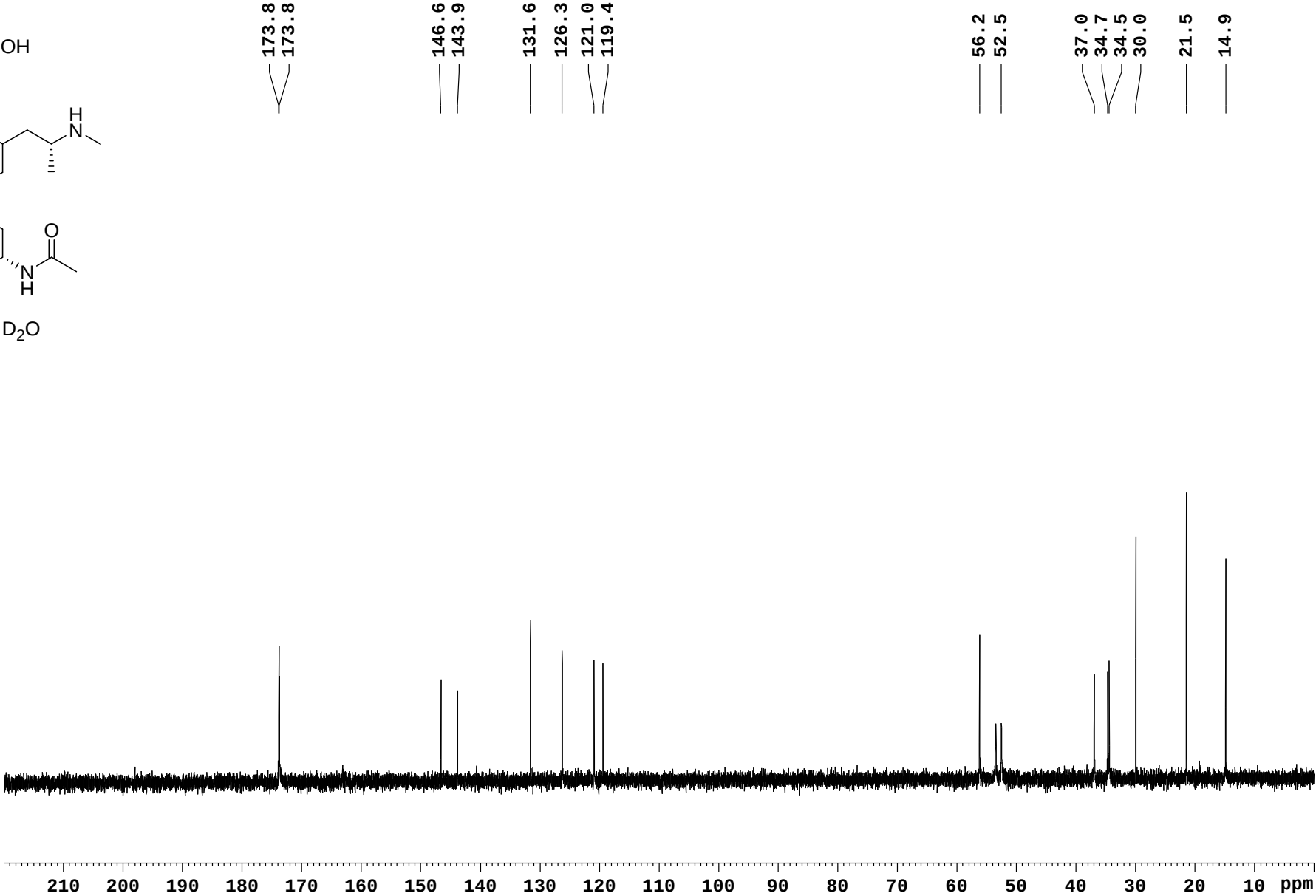
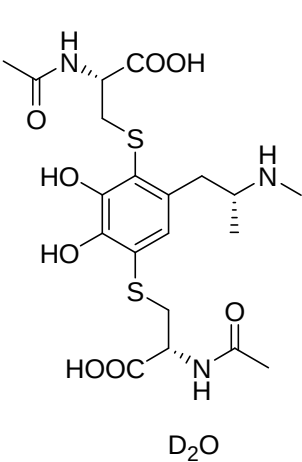
14.8



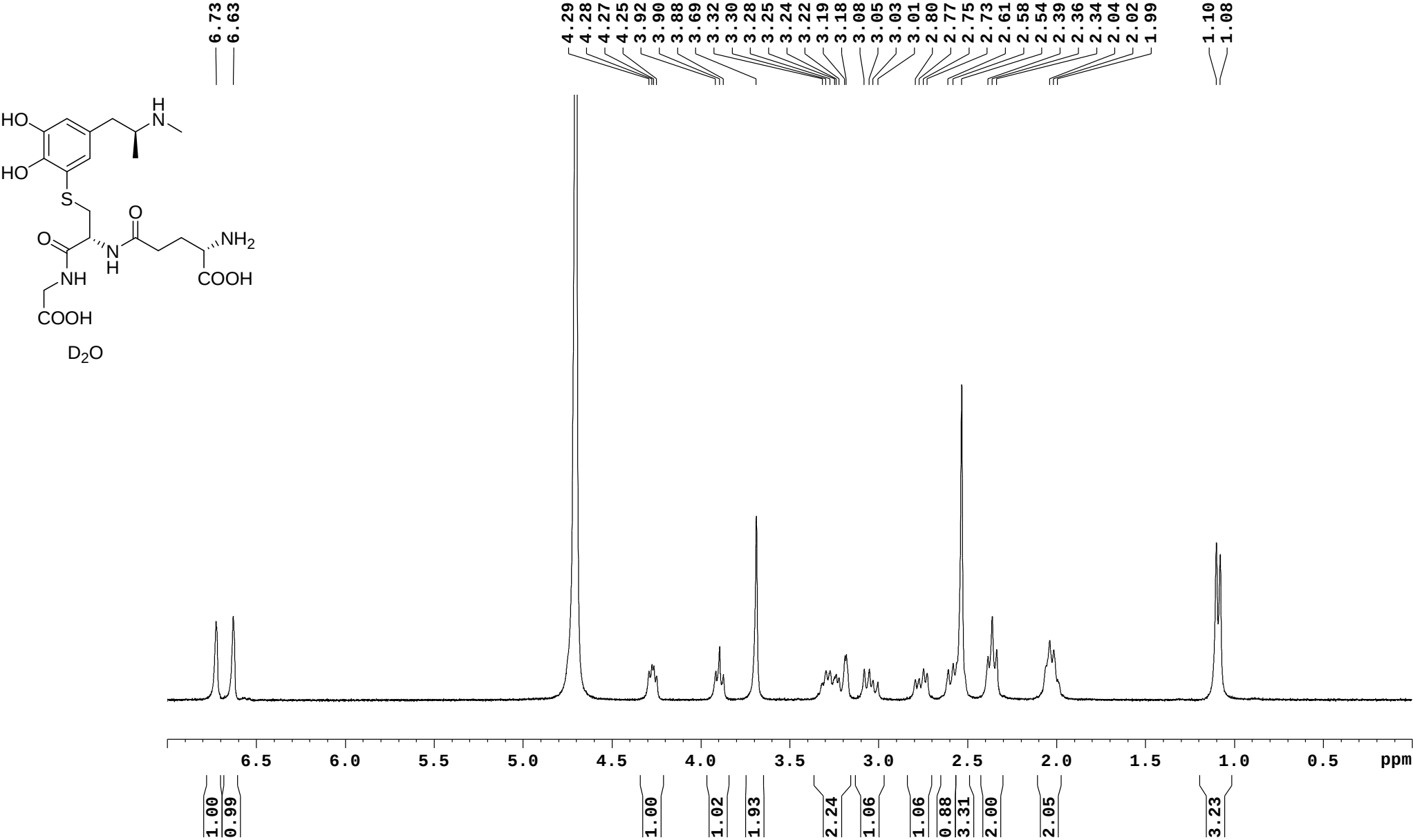
Compound 11



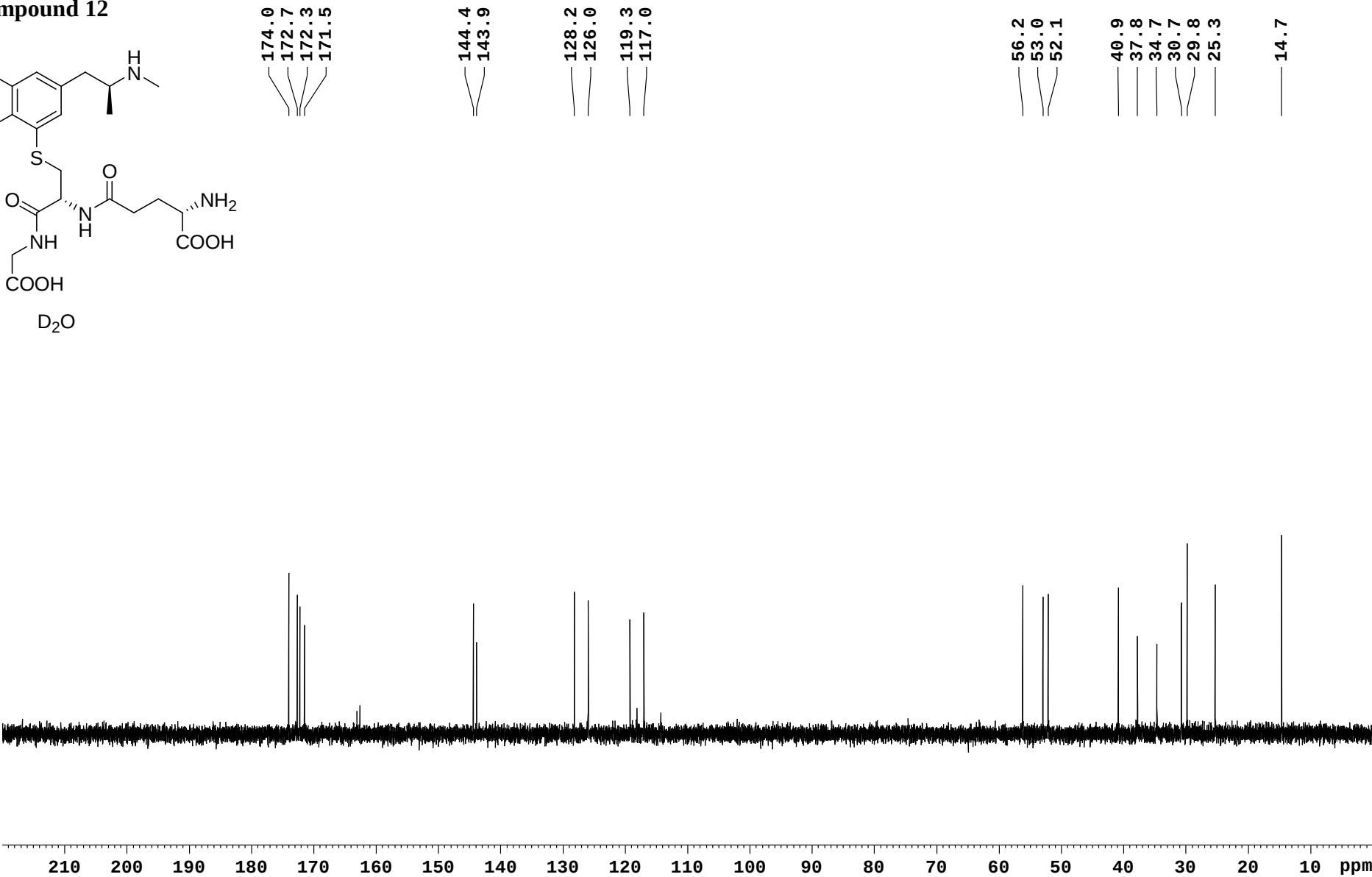
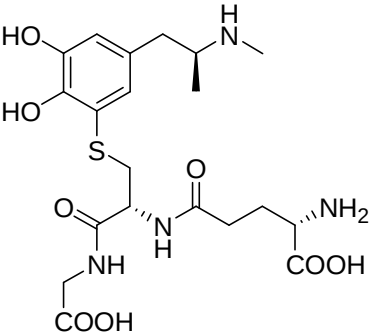
Compound 11



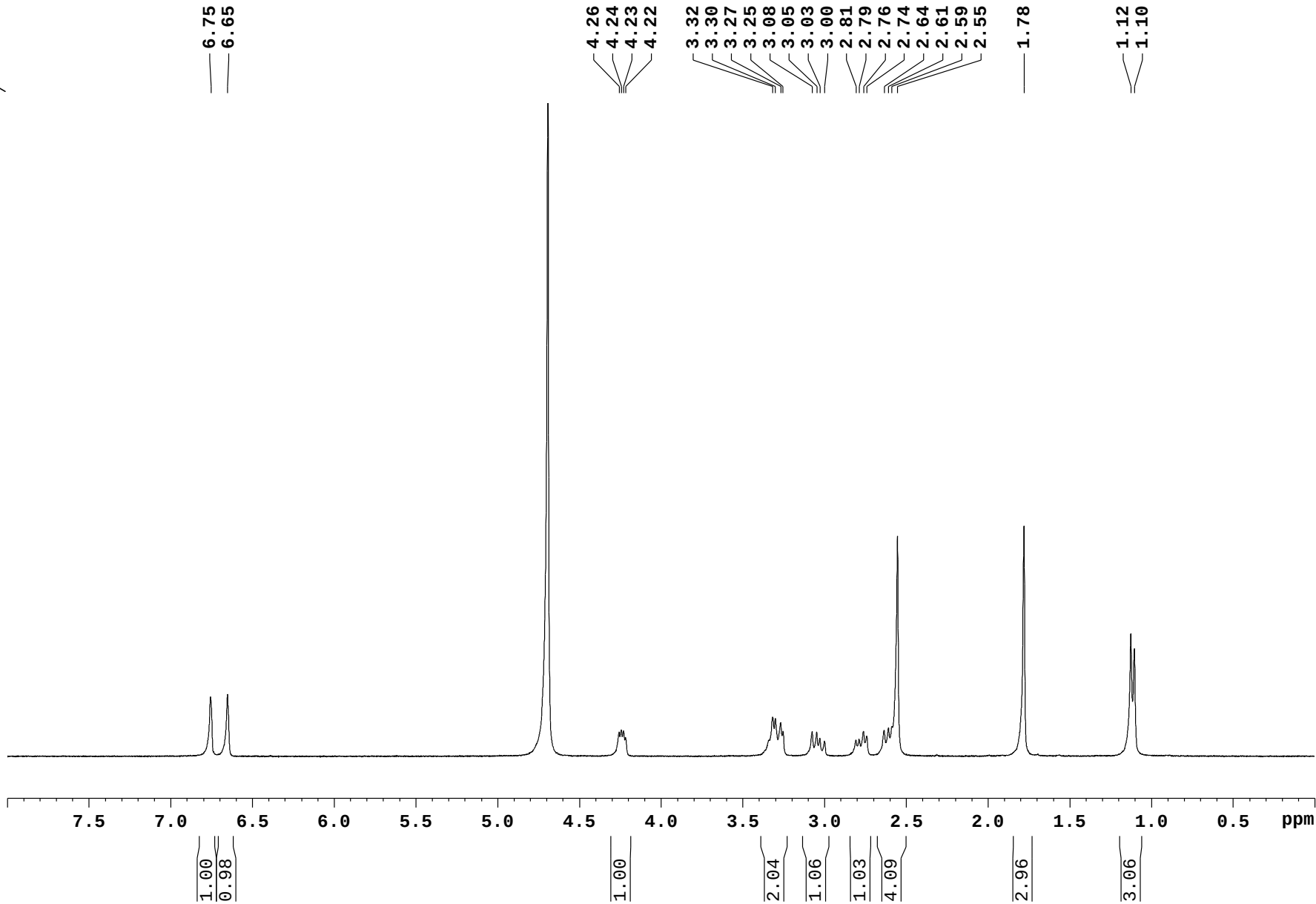
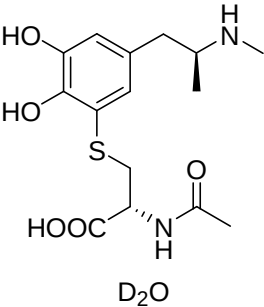
Compound 12



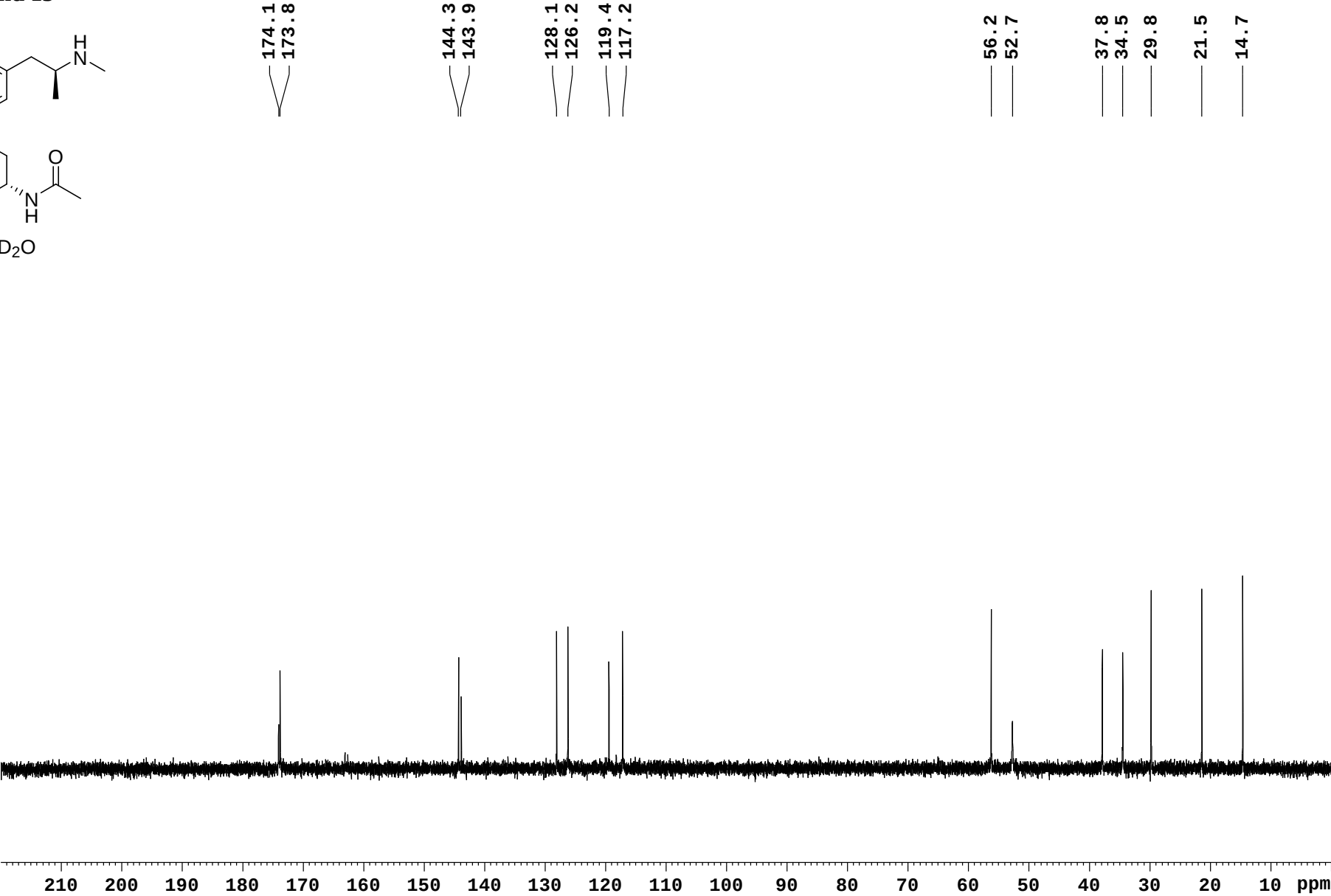
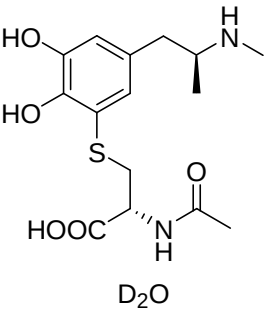
Compound 12



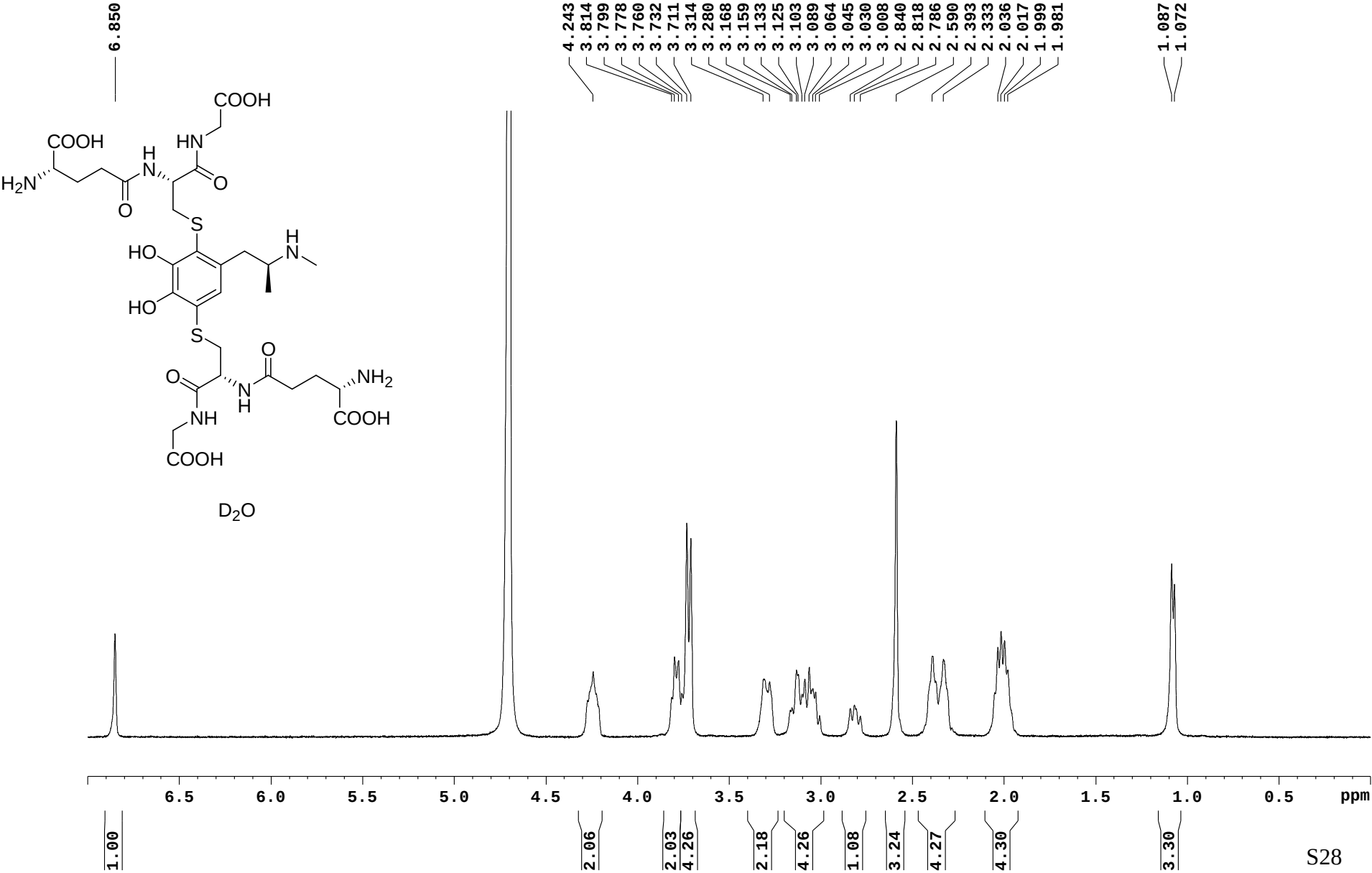
Compound 13



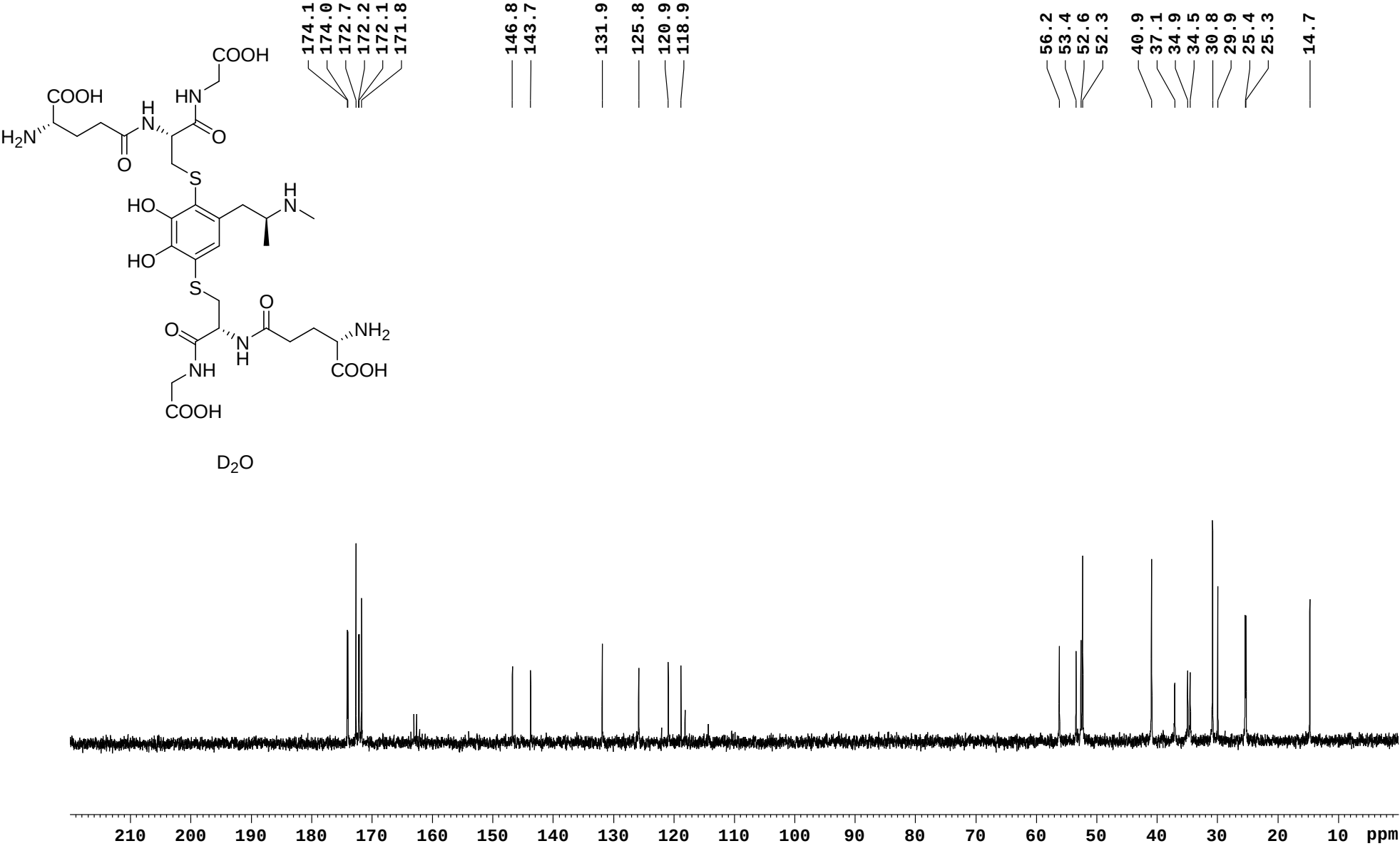
Compound 13



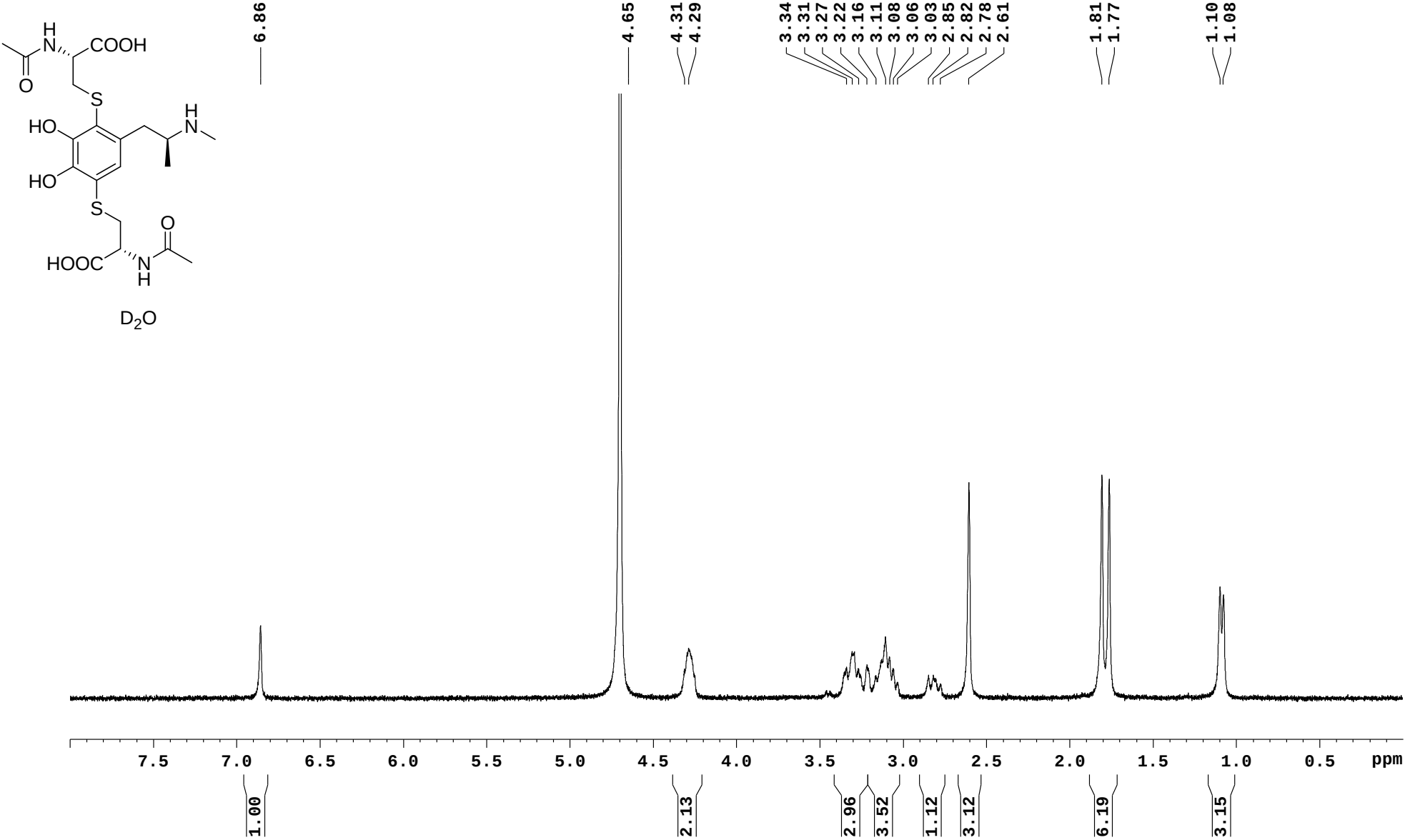
Compound 14



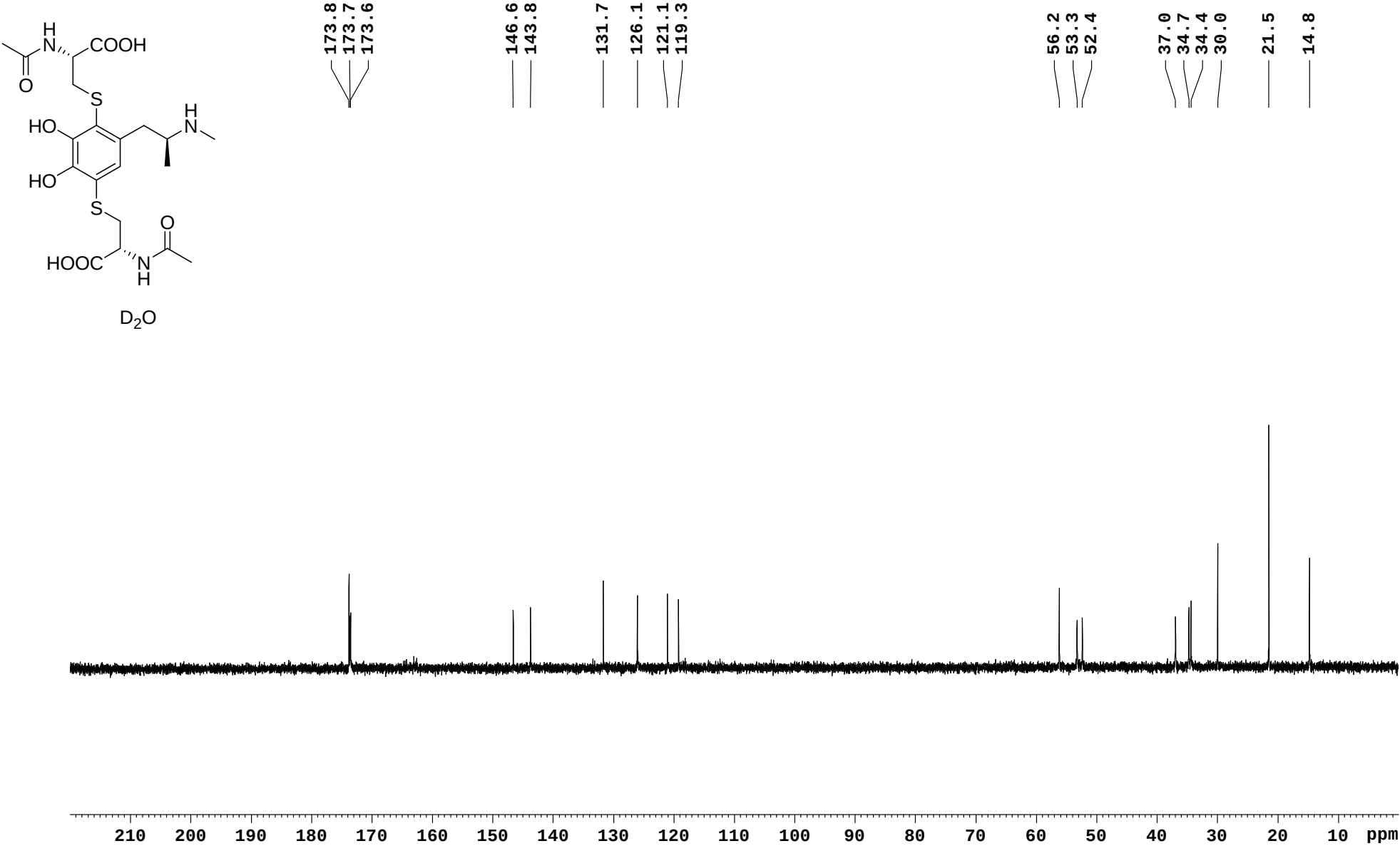
Compound 14



Compound 15

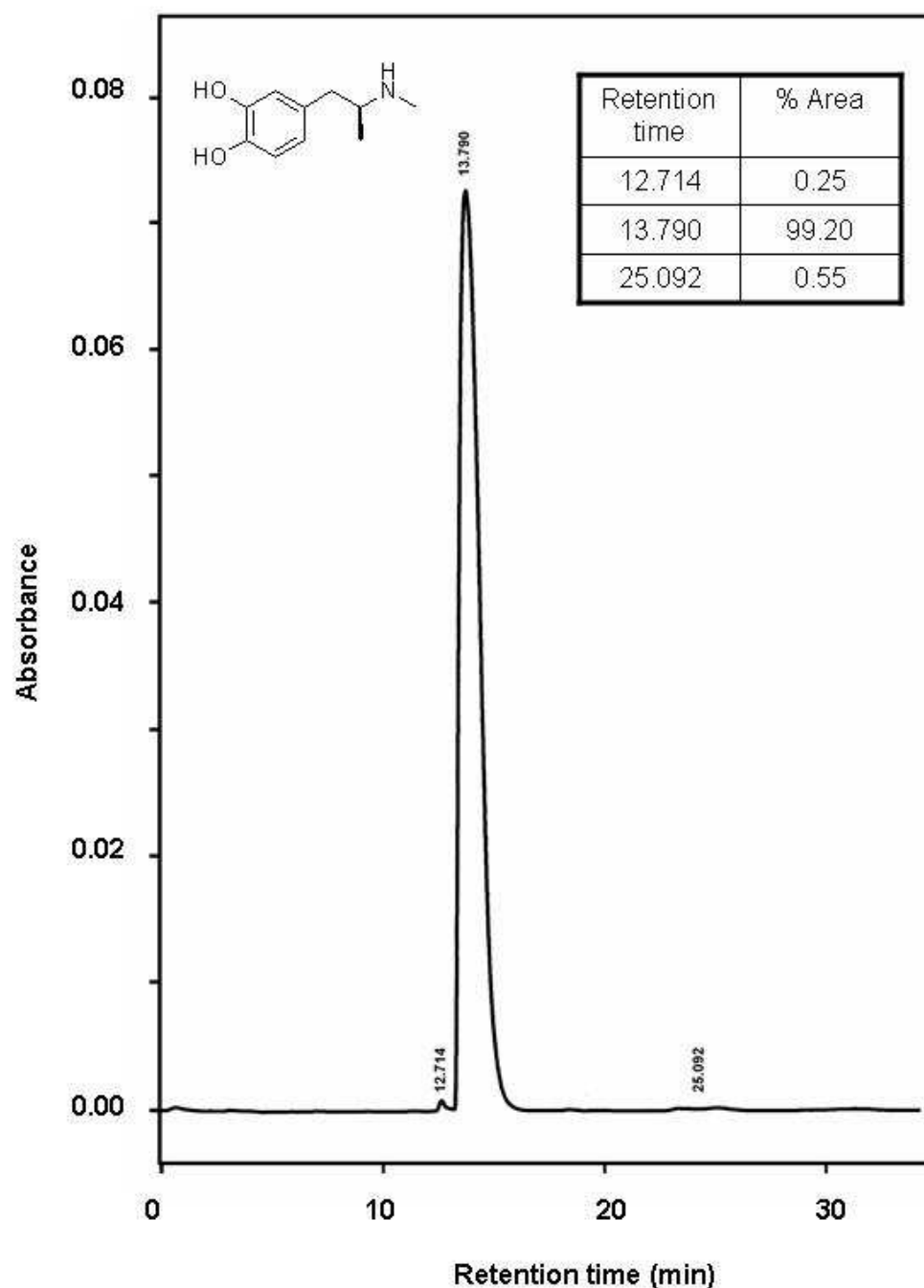


Compound 15



III. Analytical HPLC chromatograms of *S*-(+)-HHMA 7 and of optically active catechol-thioether conjugates 8-15

Compound 7



Conditions of HPLC analysis:

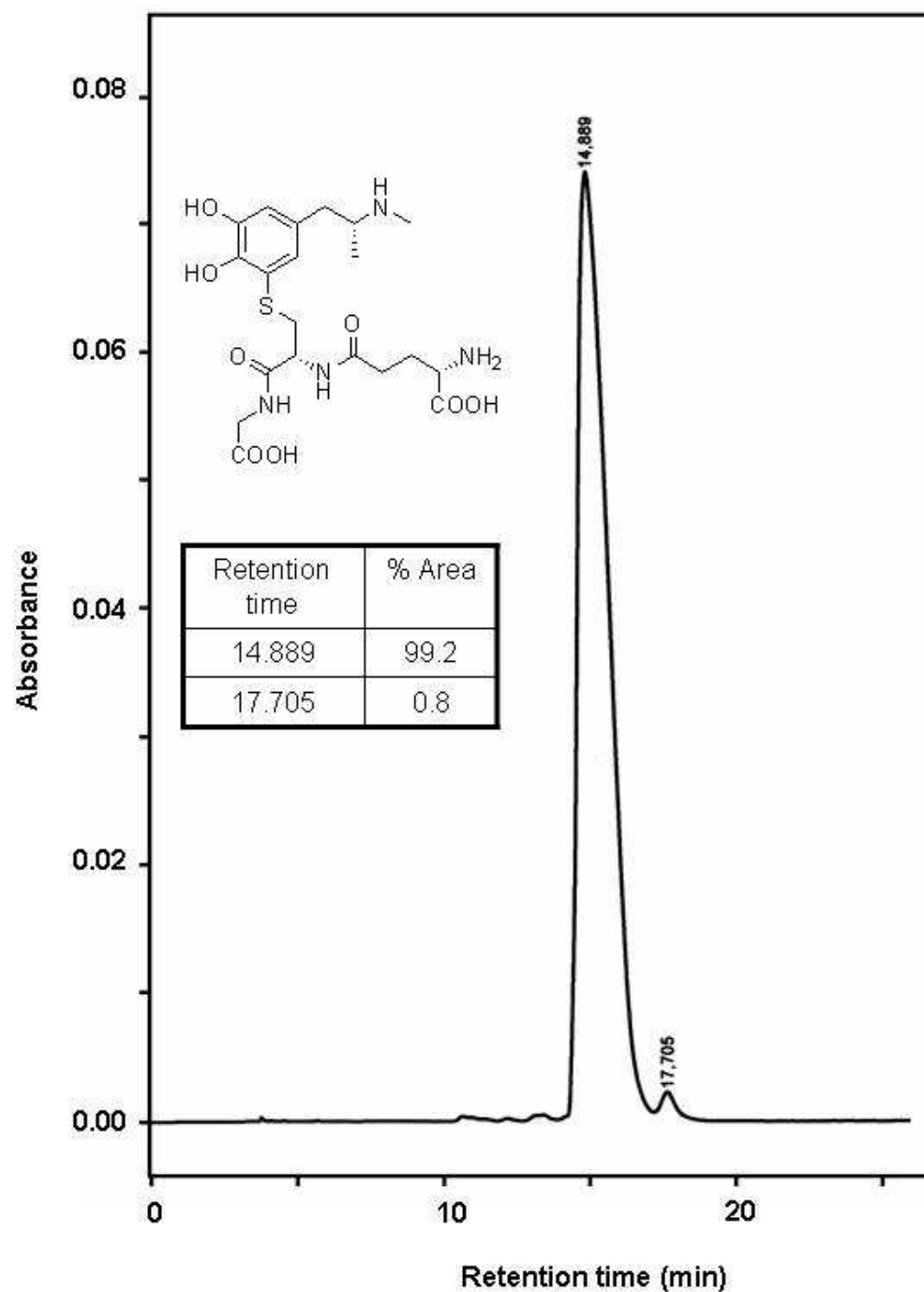
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 94/6;

Flow rate: 0.8 mL min⁻¹;

UV detector wavelength: 278 nm

Compound 8



Conditions of HPLC analysis:

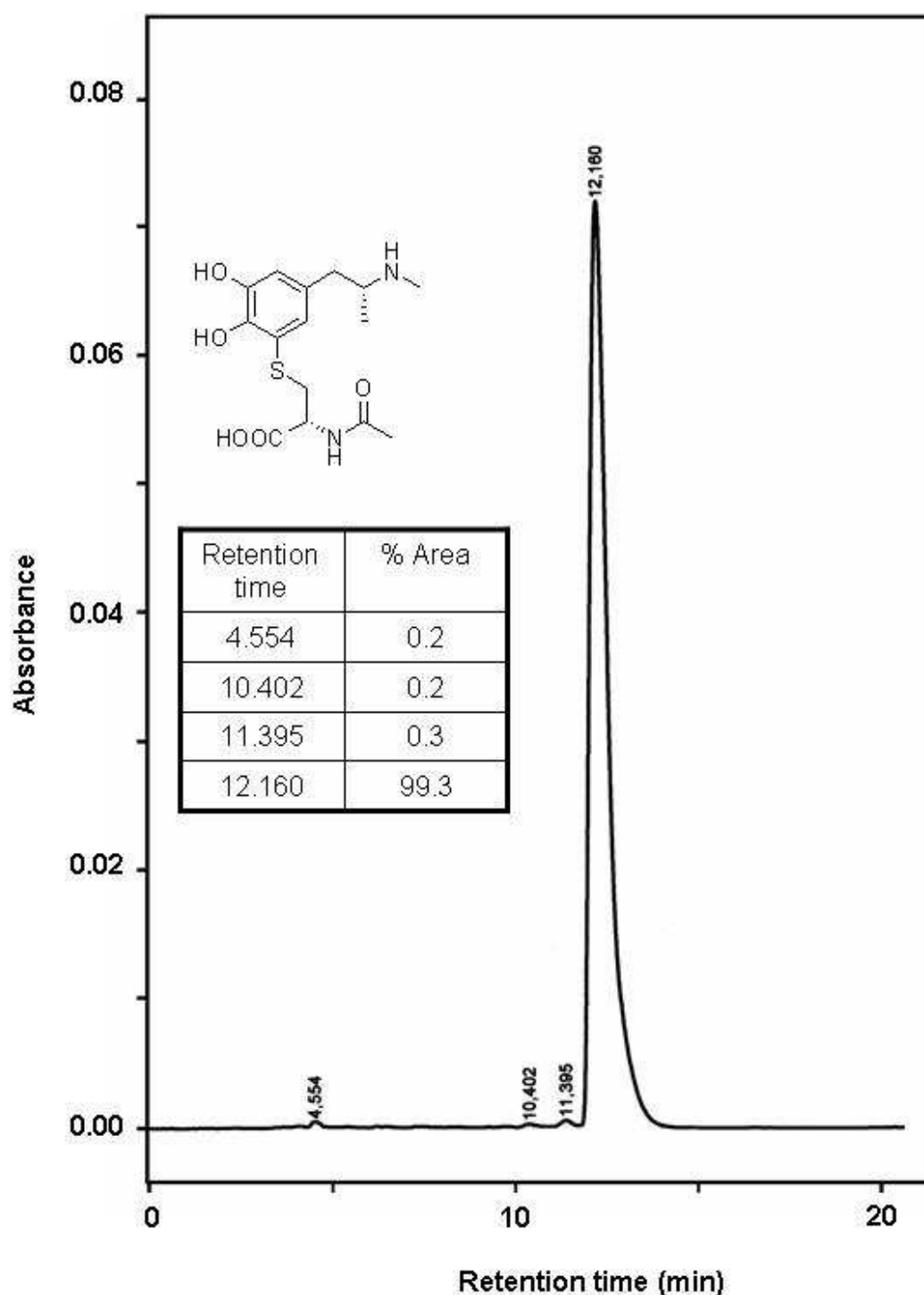
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 93/7;

Flow rate: 1.0 mL min⁻¹;

UV detector wavelength: 254 nm

Compound 9



Conditions of HPLC analysis:

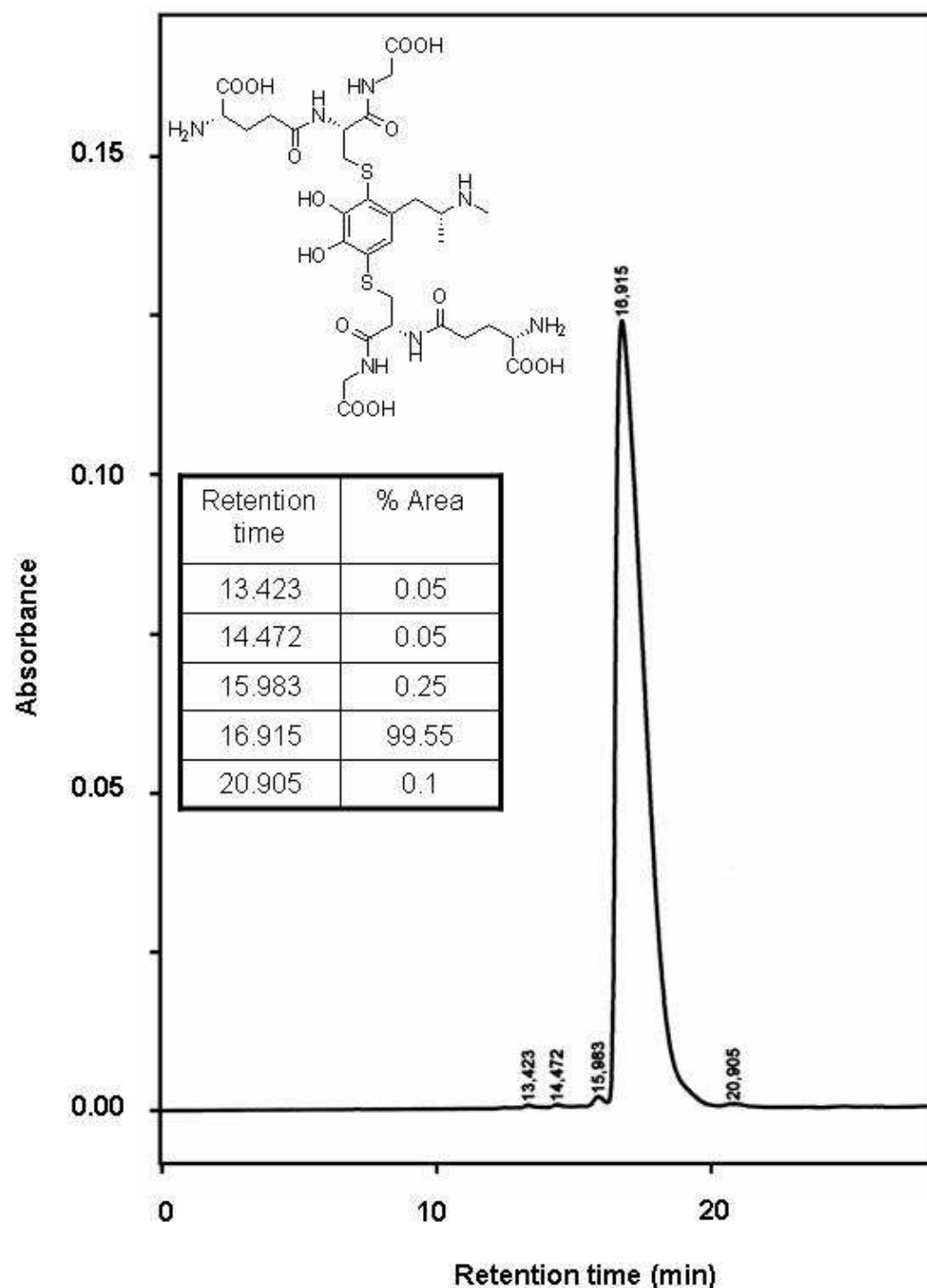
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 93/7;

Flow rate: 0.8 mL min⁻¹;

UV detector wavelength: 254 nm

Compound 10



Conditions of HPLC analysis:

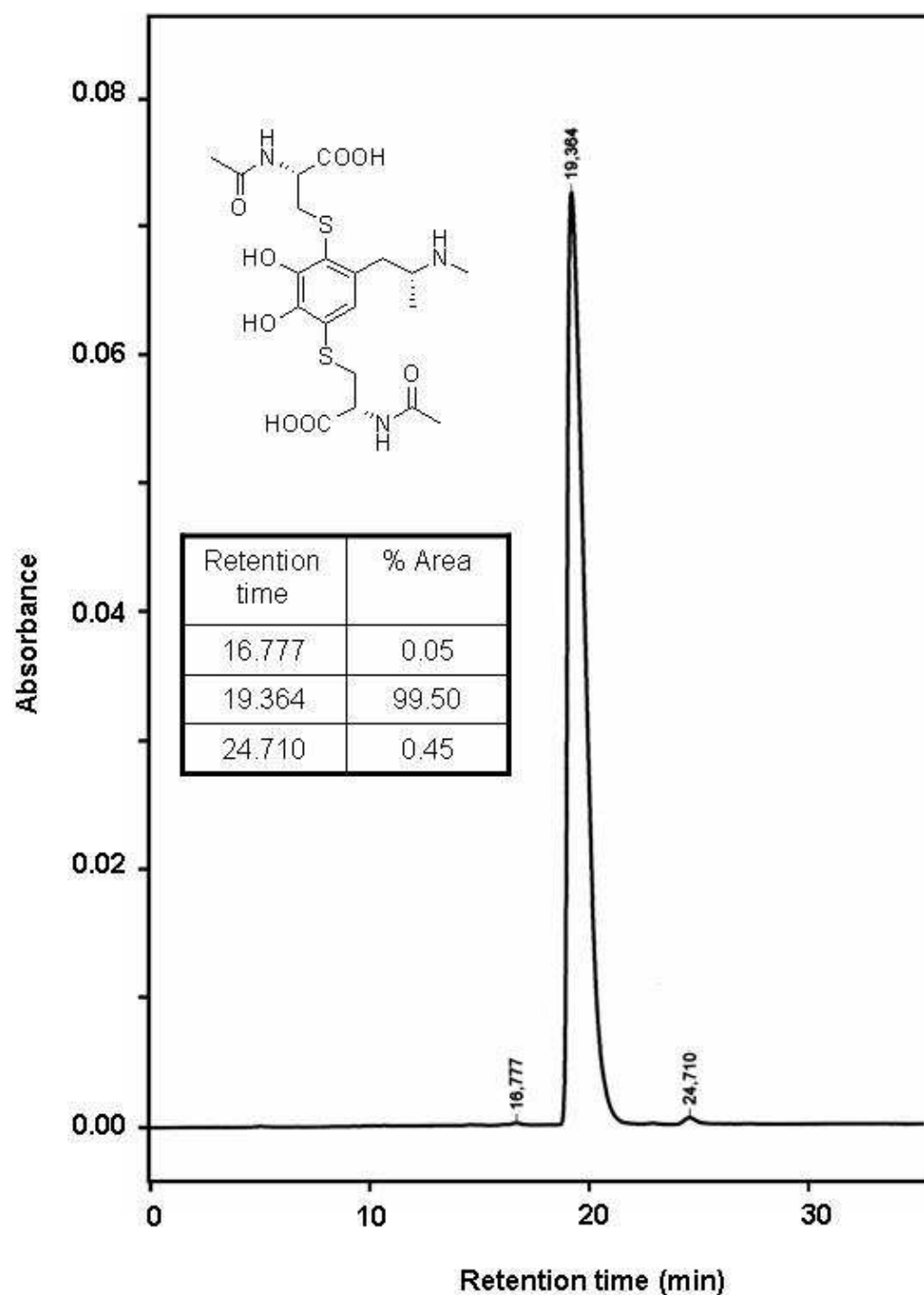
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 95/5;

Flow rate: 0.6 mL min⁻¹;

UV detector wavelength: 278 nm

Compound 11



Conditions of HPLC analysis:

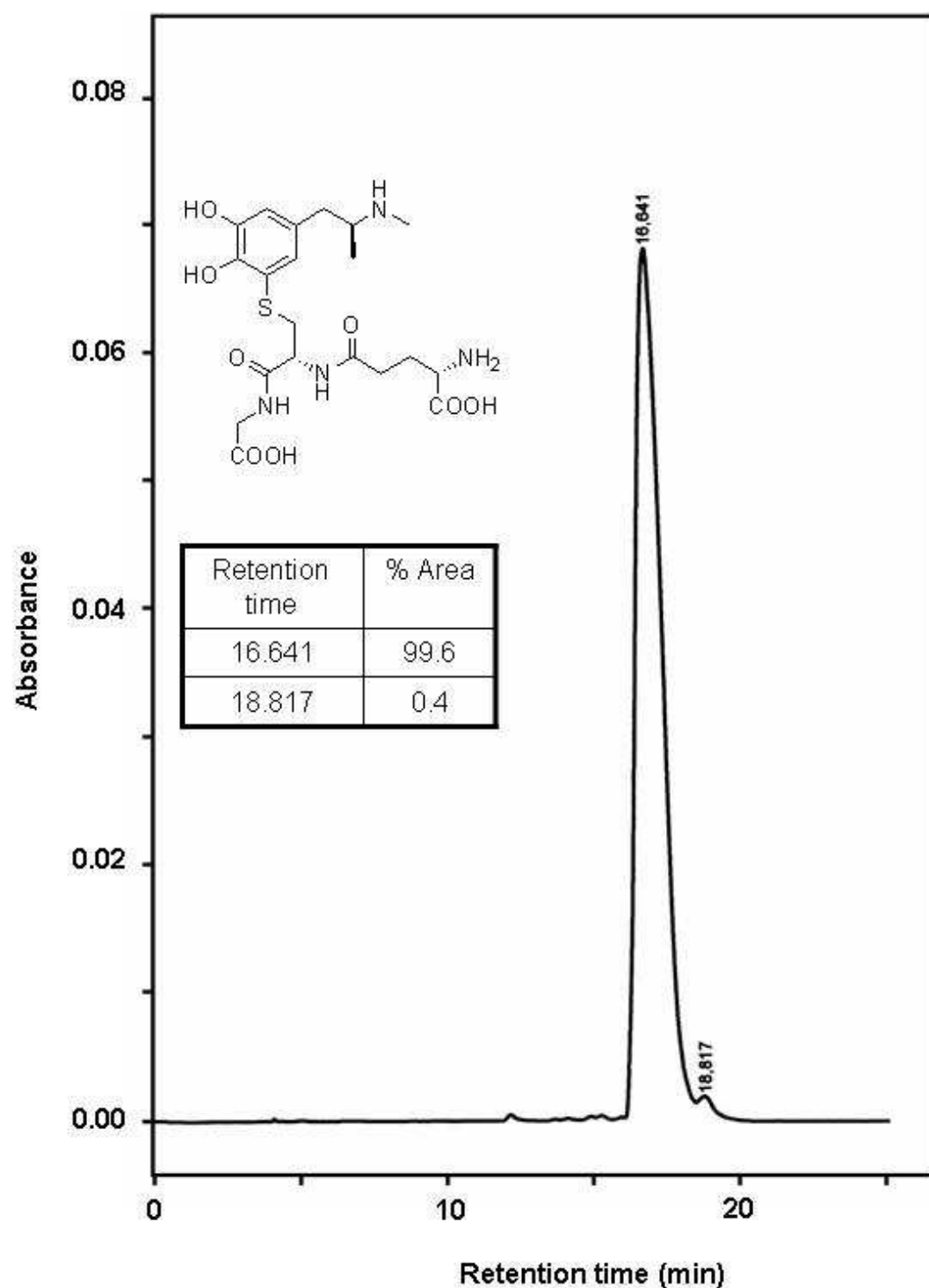
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 92/8;

Flow rate: 0.8 mL min⁻¹;

UV detector wavelength: 278 nm

Compound 12



Conditions of HPLC analysis:

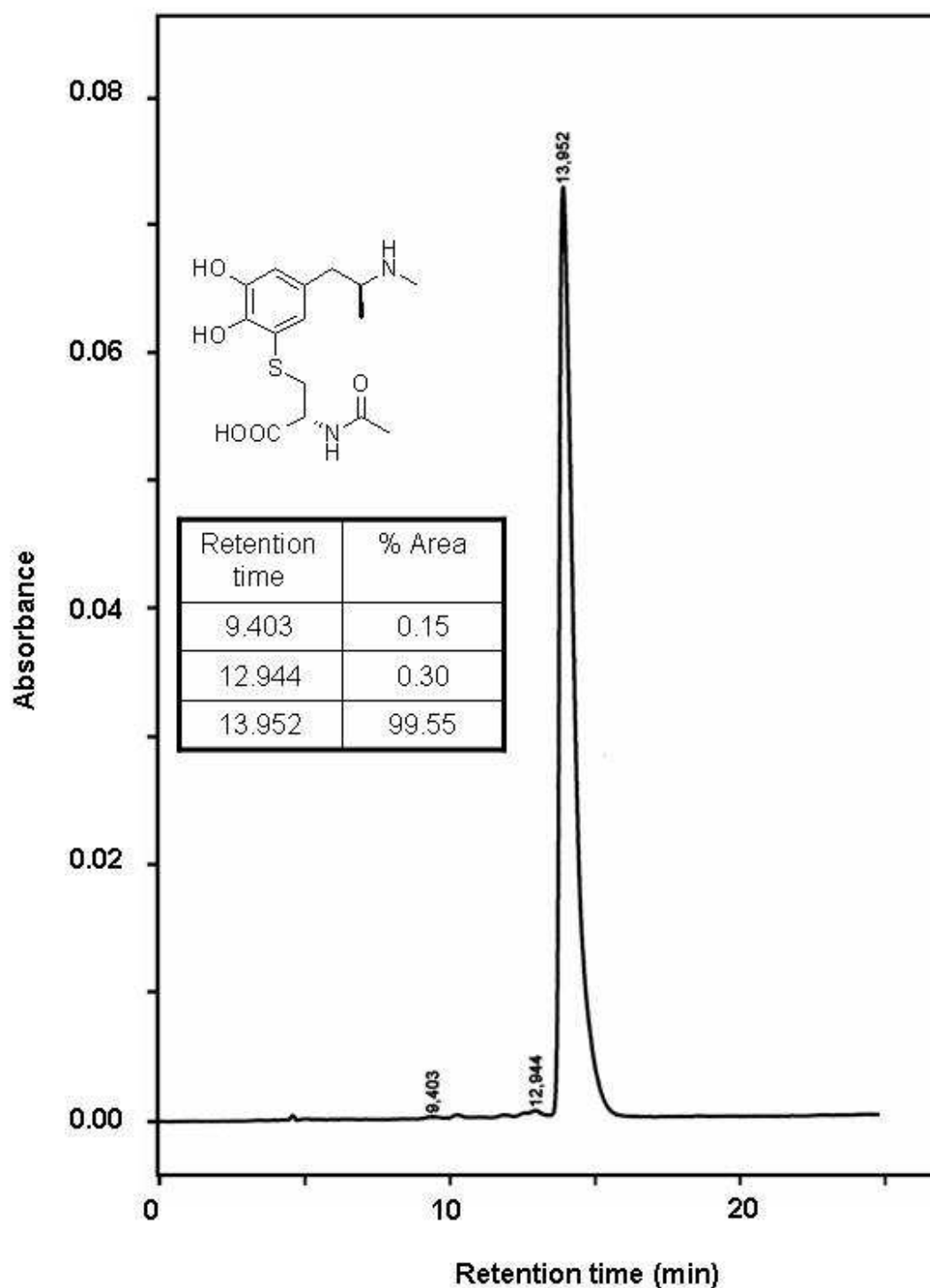
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 93/7;

Flow rate: 1.0 mL min⁻¹;

UV detector wavelength: 254 nm

Compound 13



Conditions of HPLC analysis:

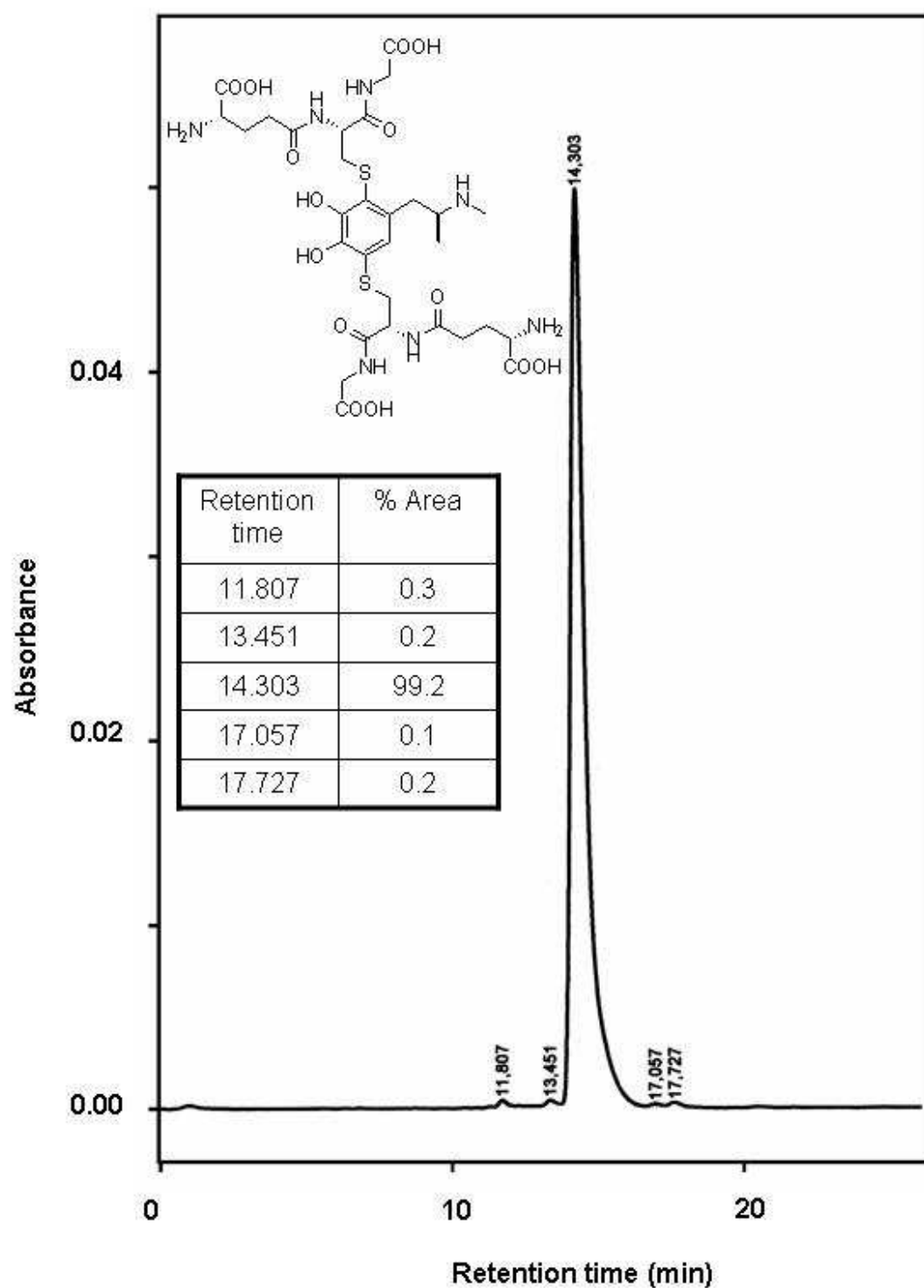
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 93/7;

Flow rate: 0.8 mL min⁻¹;

UV detector wavelength: 254 nm

Compound 14



Conditions of HPLC analysis:

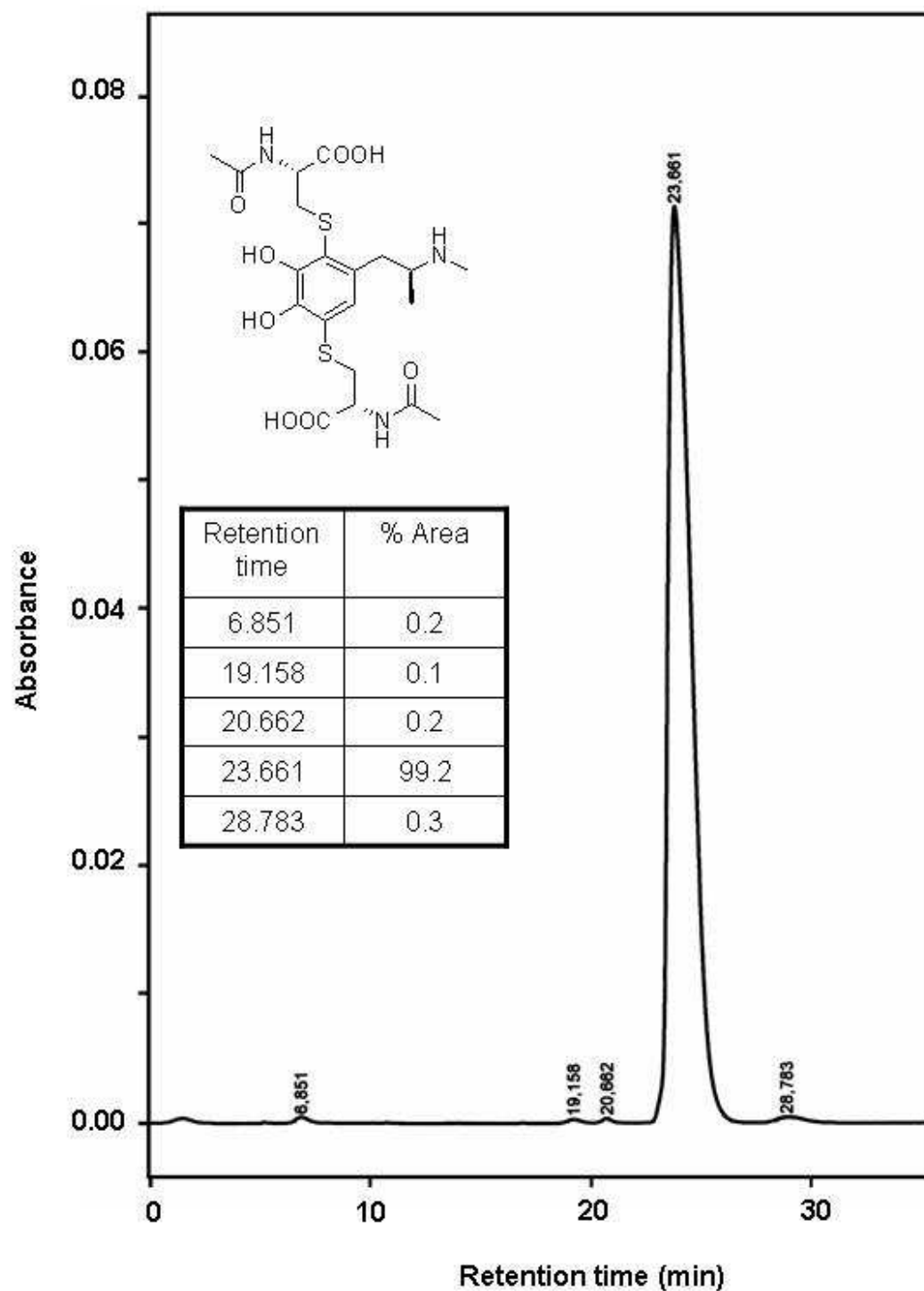
Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 95/5;

Flow rate: 0.6 mL min⁻¹;

UV detector wavelength: 278 nm

Compound 15



Conditions of HPLC analysis:

Column Kromasil C18, 250 × 4.6 mm – 5 μm

Mobile phase: (H₂O + 1% TFA)/ MeCN 92/8;

Flow rate: 0.8 mL min⁻¹;

UV detector wavelength: 278 nm