

## Supporting Information

# Efficient and Selective Multicomponent Oxidative Coupling of Two Different Aliphatic Primary Amines into Thioamides by Elemental Sulfur

Thanh Binh Nguyen,\* Ludmila Ermolenko and Ali Al-Mourabit

### General information

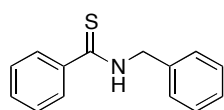
Reagents were obtained from commercial supplier and used without further purification. Analytical thinlayer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70  $\mu\text{m}$  particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in ( $\delta$ ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ( $\text{CDCl}_3$ ,  $\delta$  7.26 ppm for  $^1\text{H}$  and  $\delta$  77.0 ppm for  $^{13}\text{C}$ ). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

### General procedure

A mixture of **amine 1** (5 mmol), **amine 2** (6 mmol) and elemental sulfur (15 mmol) was stirred under argon in a pressure equalization tubes at indicated temperature for indicated reaction time (See Tables 1-2). After being cooled to room temperature, the crude reaction mixture was purified by silica gel column chromatography. The yields are given in Tables 1-2.

### Characterizations of Products

#### *N*-Benzylbenzothioamide (3a)

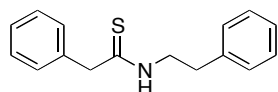


Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 2 : 1 to 1 : 2) afforded the product as pale yellow crystals. Mp 83 °C (Lit.<sup>1</sup> 84-85).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.75-7.72 (m, 3H), 7.46-7.32 (m, 8H), 4.97 (d, *J* = 5.0 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 199.3, 141.8, 136.4, 131.3, 129.2, 128.7, 128.5, 128.4, 126.9, 51.2.

### ***N*-Phenethyl-2-phenylethanethioamide (3b)**

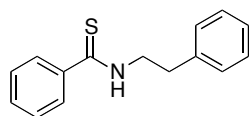


Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 2 : 1 to 1 : 2) afforded the product as pale yellow crystals. Mp 83 °C (Lit.<sup>2</sup> 73.5-74.5).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32-7.27 (m, 3H), 7.22-7.17 (m, 3H), 7.12-7.98 (m, 2H), 6.97-6.94 (m, 2H), 6.93 (broad s, 1H), 4.07 (s, 2H), 3.86 (q, *J* = 6.8 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 202.1, 138.1, 134.6, 129.8, 129.5, 129.0, 128.7, 128.0, 126.9, 53.4, 47.1, 33.8.

### ***N*-Phenethylbenzothioamide (3c)<sup>3</sup>**



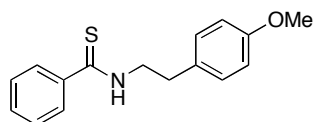
Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 2 : 1 to 1 : 2) afforded the product as pale yellow crystals. Mp 95 °C. (Lit.<sup>3</sup> 95-97 °C).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.68-7.30 (m, 11H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.12 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 199.4, 142.0, 138.4, 131.2, 129.0, 128.9, 128.6, 127.0, 126.7, 47.6, 34.0.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>NS 242.1003. Found 242.0994.

### ***N*-(4-Methoxyphenethyl)benzothioamide (3d)**



<sup>1</sup> McMillan, F. H. *J. Am. Chem. Soc.* **1948**, *70*, 868.

<sup>2</sup> Kornfeld, E. C. *J. Org. Chem.* **1951**, *16*, 131.

<sup>3</sup> Bowman, W. R.; Fletcher, A. J.; Pedersen, J. M.; Lovell, P. J.; Elsegood, M. R. J.; López, E. H.; McKee V.; Potts, G. B. S. *Tetrahedron* **2007**, *63*, 191.

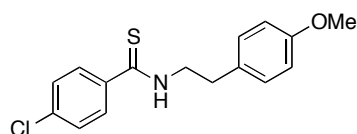
Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 1 : 1) afforded the product as pale yellow crystals. Mp 110 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.63-7.60 (m, 2H), 7.51 (broad s, 1H), 7.41-7.30 (m, 3H) 7.18-7.15 (m, 2H), 6.88-6.85 (m, 2H), 4.06 (q, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 3.01 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 199.4, 158.6, 142.1, 131.2, 130.3, 129.9, 128.7, 126.7, 114.5, 55.5, 47.8, 33.2.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>18</sub>NOS 272.1109. Found 272.1098.

#### 4-Chloro-*N*-(4-methoxyphenethyl)benzothioamide (3e)



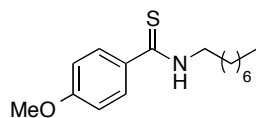
Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 1 : 1) afforded the product as pale yellow crystals. Mp 108 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.56-7.53 (m, 2H), 7.47 (broad s, 1H), 7.30-7.28 (m, 2H), 7.16-7.14 (m, 2H), 6.87-6.84 (m, 2H), 4.04 (q, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 3.00 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.8, 158.8, 140.3, 137.5, 130.2, 129.9, 128.9, 128.1, 114.5, 55.5, 47.9, 33.1.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>17</sub>ClNOS 306.0719. Found 306.0704.

#### 4-Methoxy-*N*-octylbenzothioamide (3f)



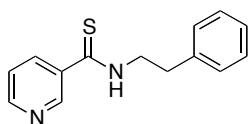
Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 1 : 1) afforded the product as pale yellow amorphous solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.74-7.70 (m, 2H), 7.48 (broad s, 1H), 6.87-6.83 (m, 2H), 3.80 (s, 3H), 3.79-3.74 (m, 2H), 1.74-1.70 (m, 2H), 1.41-1.26 (m, 10 H), 0.88-0.83 (m, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.1, 162.3, 134.6, 128.6, 113.8, 55.7, 47.1, 32.0, 29.5, 29.4, 28.5, 27.3, 22.8, 14.3.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>26</sub>NOS 280.1735. Found 280.1730.

#### *N*-Phenethylpyridine-3-carbothioamide (3g)



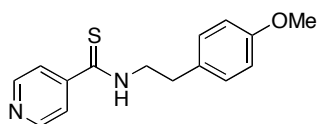
Purification of the crude mixture by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> : AcOEt 4 : 1) afforded the product as pale yellow crystals. Mp 110 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.70 (d, *J* = 1.3 Hz, 1H), 8.58 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.07 (dt, *J* = 8.1, 4.7 Hz, 1H), 7.99 (broad s, 1H), 7.41- 7.27 (m, 6H), 4.15 (q, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.4, 151.6, 146.2, 138.2, 137.8, 135.6, 129.1, 128.9, 127.2, 123.5, 47.8, 33.9.

HRMS-ESI (m/z) [M-H]<sup>-</sup> calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>S 241.0799. Found 241.0805.

### ***N*-(4-Methoxyphenethyl)pyridine-4-carbothioamide (3h)**



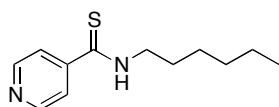
Purification of the crude mixture by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> : AcOEt 4 : 1) afforded the product as pale yellow crystals. Mp 130 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.46-8.44 (m, 2H), 8.15 (broad s, 1H), 7.39-7.38 (m, 2H), 7.15-7.12 (m, 2H), 6.86-6.83 (m, 2H), 4.02 (q, *J* = 6.8 Hz, 2H), 3.77 (s, 3H), 3.00 (t, *J* = 6.8 Hz, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.6, 158.8, 150.2, 148.7, 130.1, 129.9, 120.7, 114.5, 77.4, 55.5, 47.9, 32.8.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>OS 273.1062. Found 273.1057.

### ***N*-Hexylpyridine-4-carbothioamide (3i)**



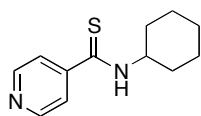
Purification of the crude mixture by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> : AcOEt 4 : 1) afforded the product as pale yellow viscous oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.56-8.54 (m, 2H), 8.03 (broad s), 7.50-7.48 (m, 2H), 3.81-3.74 (m, 2H), 1.78-1.68 (m, 2H), 1.44-1.27 (m, 6H), 0.90-0.85 (m, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.6, 150.3, 148.9, 120.8, 47.2, 31.6, 28.1, 26.9, 22.7, 14.2.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>S 223.1269. Found 223.1246.

### ***N*-Cyclohexylpyridine-4-carbothioamide (3j)**



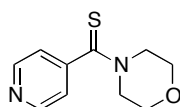
Purification of the crude mixture by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> : AcOEt 4 : 1) afforded the product as pale yellow crystals. Mp 175 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.52-8.50 (m, 2H), 7.99 (broad s, 1H), 7.47-7.45 (m, 2H), 4.52-4.42 (m, 1H), 2.18-2.13 (m, 2H), 1.80-1.64 (m, 3H), 1.50-1.14 (m, 5H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.2, 150.1, 149.2, 120.9, 77.4, 55.3, 31.7, 25.6, 24.9.

HRMS-ESI (m/z) [M-H]<sup>-</sup> calcd for C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>S 220.1077. Found 220.1034.

### Morpholino(pyridin-4-yl)methanethione (3k)



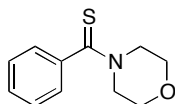
Purification of the crude mixture by column chromatography (CH<sub>2</sub>Cl<sub>2</sub> : AcOEt 4 : 1) afforded the product as pale yellow crystals. Mp 151 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.62-8.60 (m, 2H), 7.14-7.12 (m, 2H), 4.39-4.36 (m, 2H), 3.87-3.83 (m, 2H), 3.64-3.59 (m, 2H), 3.54-3.49 (m, 2H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.2, 150.4, 149.6, 120.2, 66.8, 66.6, 52.6, 49.2.

HRMS-ESI (m/z) [M-H]<sup>-</sup> calcd for C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>OS 209.0749. Found 209.0741.

### Morpholino(phenyl)methanethione (3l)



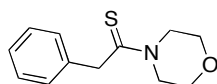
Purification of the crude mixture by column chromatography (heptane : CH<sub>2</sub>Cl<sub>2</sub> 2 : 1 to 1 : 2) afforded the product as pale yellow crystals. Mp 138 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.43-7.26 (m, 5H), 4.45 (t, *J* = 5.1 Hz, 2H), 3.90 (t, *J* = 5.1 Hz, 2H), 3.68-3.59 (m, 4H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 201.3, 142.7, 129.1, 128.7, 126.1, 66.9, 66.7, 52.7, 49.8.

HRMS-ESI (m/z) [M-H]<sup>-</sup> calcd for C<sub>11</sub>H<sub>14</sub>NOS 208.0796. Found 208.0784.

### 1-Morpholino-2-phenylethanethione (3m)



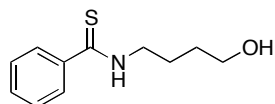
Purification of the crude mixture by column chromatography (heptane : AcOEt 3 : 1) afforded the product as pale yellow crystals.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.23 (m, 5H), 4.35-4.32 (m, 2H), 4.33 (s, 2H), 3.73-3.70 (m, 2H), 3.62-3.59 (m, 2H), 3.38-3.35 (m, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.2, 136.0, 129.2, 127.9, 127.3, 66.5, 66.3, 51.0, 50.8, 50.4.

HRMS-ESI (m/z)  $[\text{M}-\text{H}]^-$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NOS}$  222.0953. Found 222.0928.

***N*-(4-Hydroxybutyl)benzothioamide (3n)**



Purification of the crude mixture by column chromatography ( $\text{CH}_2\text{Cl}_2$  : MeOH 95 : 5) afforded the product as pale yellow crystals.

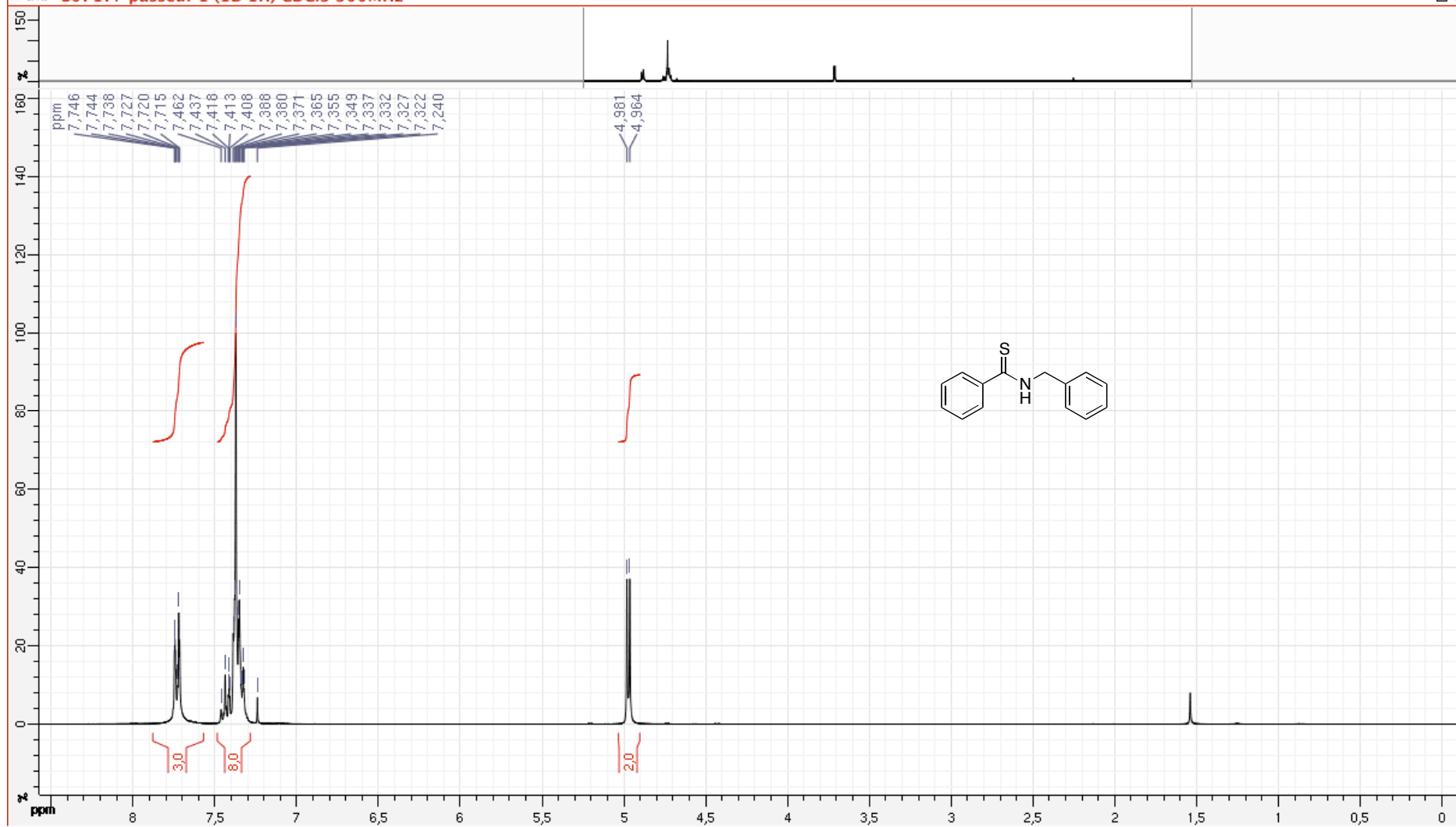
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (broad s, 1H), 7.73-7.68 (m, 2H), 7.42-7.27 (m, 3H), 3.79-3.72 (m, 2H), 3.62 (t,  $J = 6.0$  Hz, 2H) 2.29 (broad s, 1H), 1.85-1.75 (m, 2H), 1.66-1.58 (m, 2H).

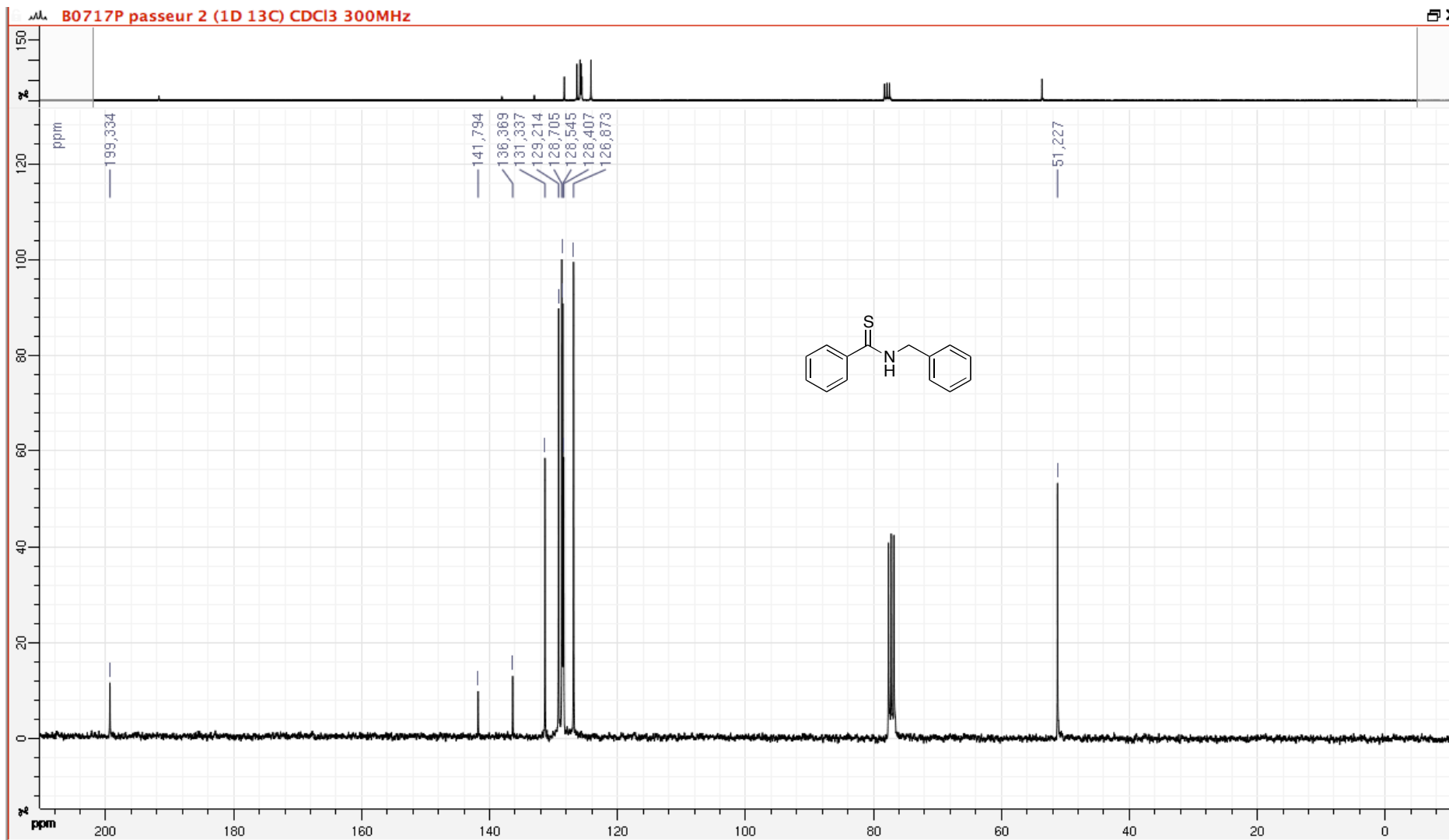
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 141.9, 131.1, 128.5, 126.9, 62.2, 46.9, 29.8, 24.8.

HRMS-ESI (m/z)  $[\text{M}-\text{H}]^-$  calcd for  $\text{C}_{11}\text{H}_{16}\text{NOS}$  210.0953. Found 222.0943.

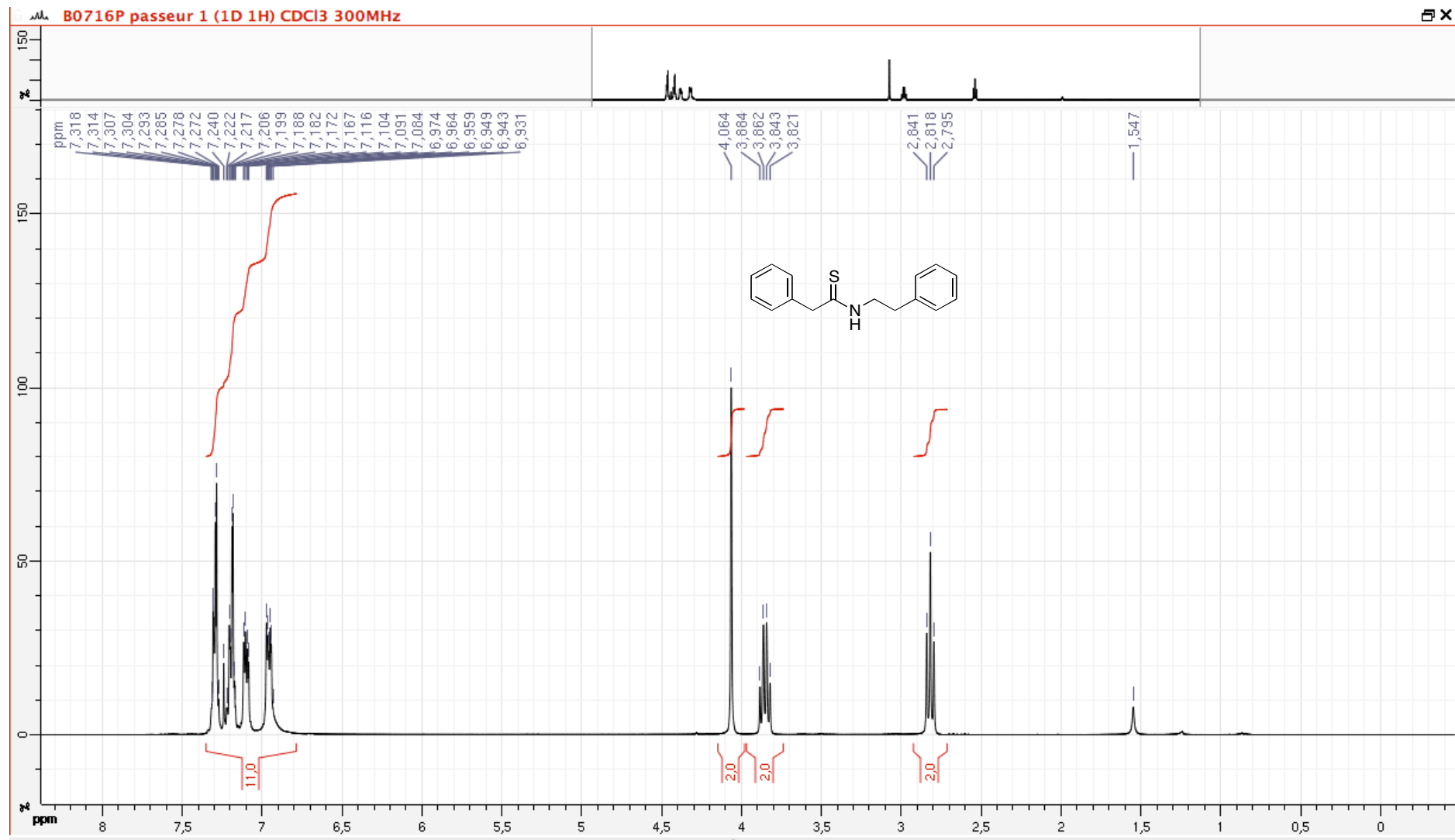
# N-benzylbenzothioamide (3a)

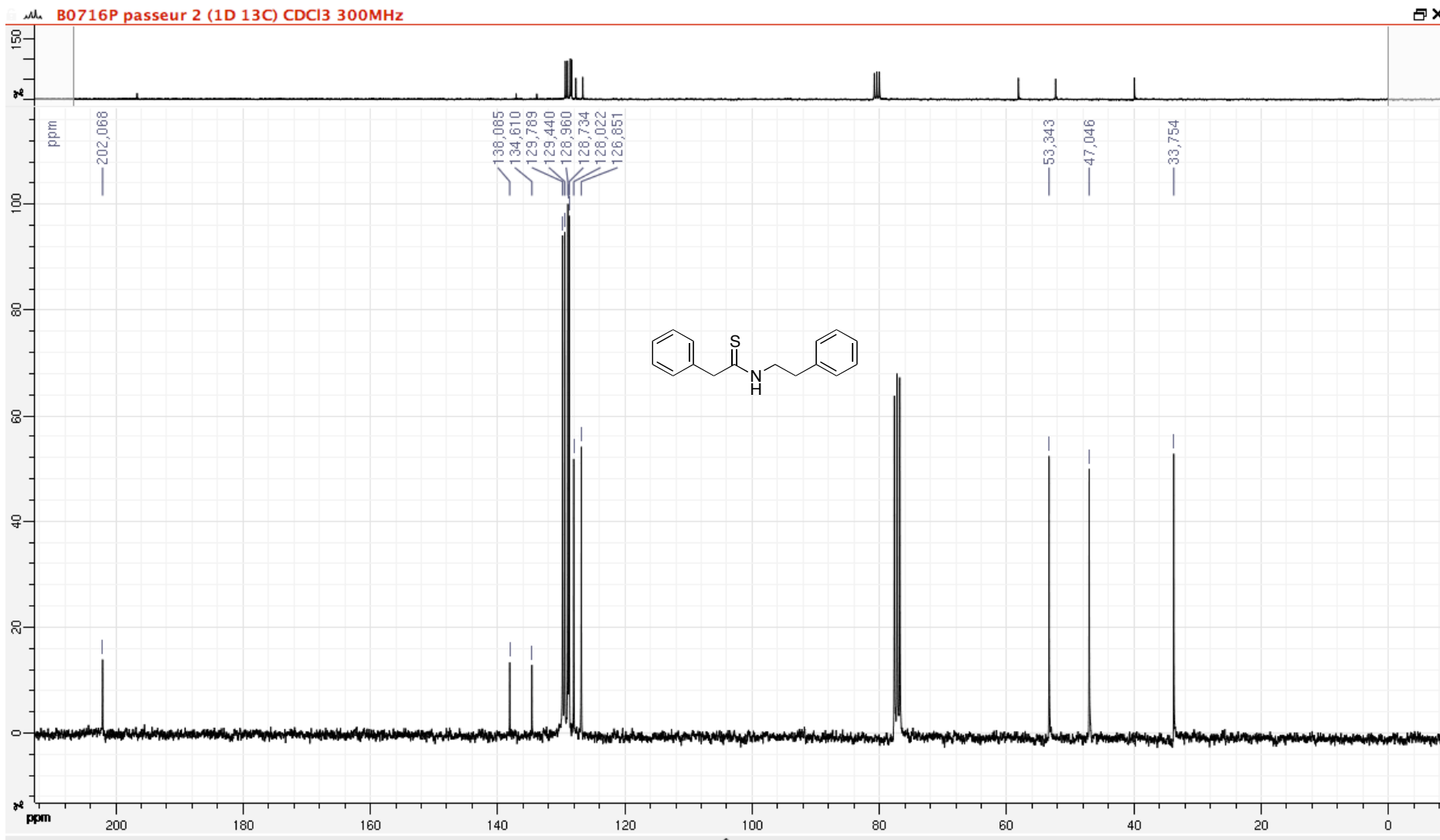
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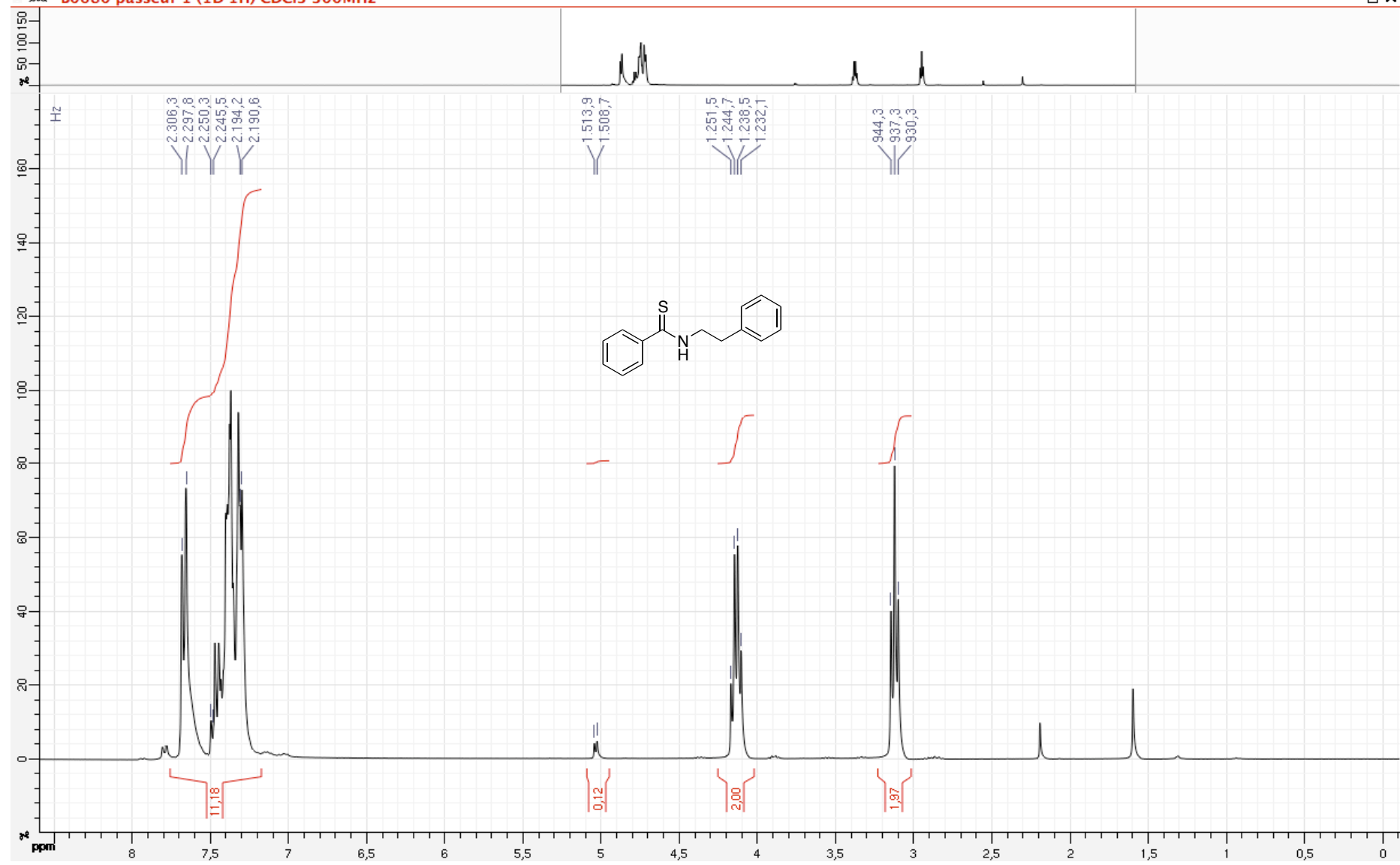
***N*-phenethyl-2-phenylethanethioamide (3b)**

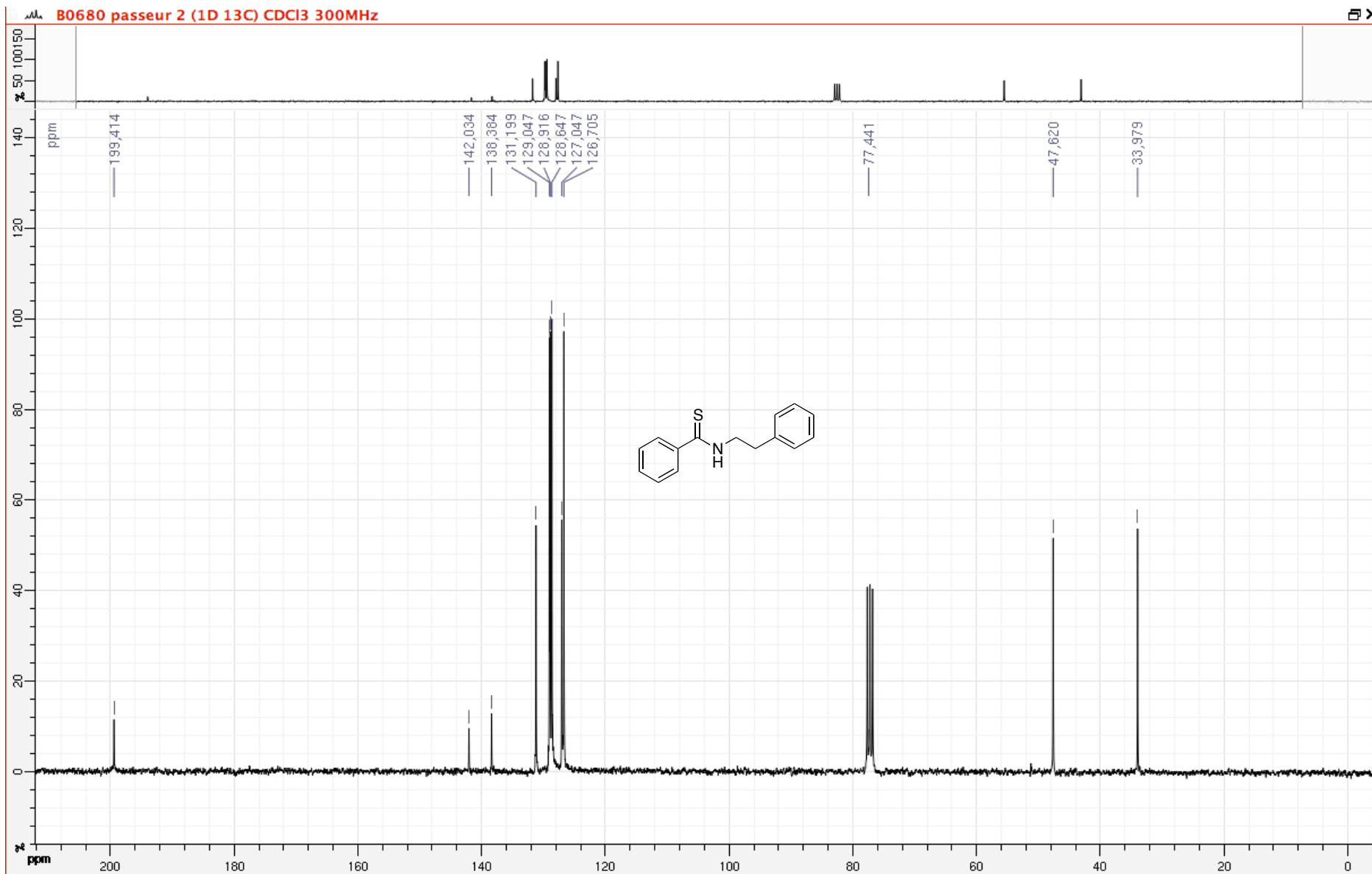




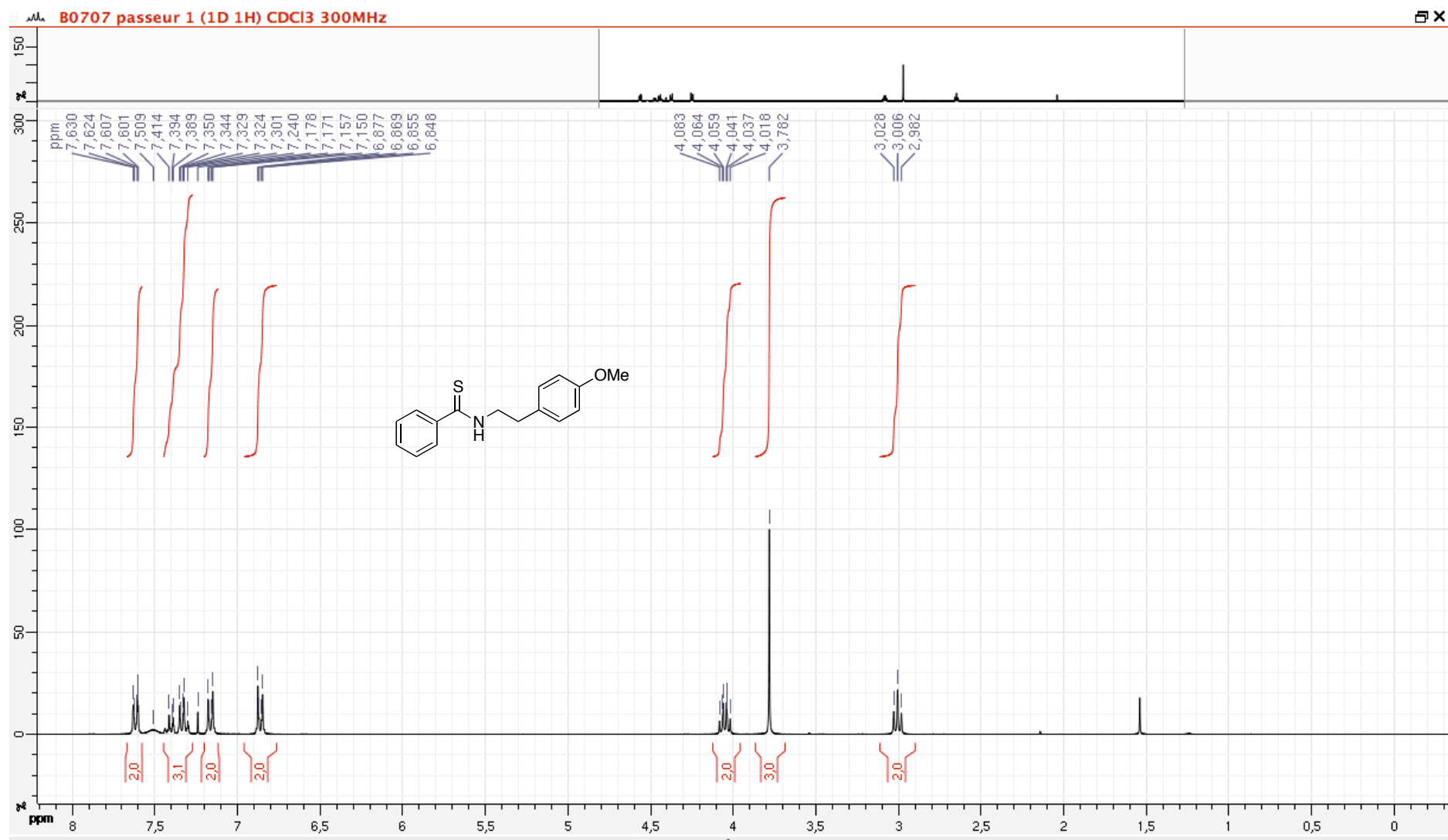
# N-Phenethylbenzothioamide (3c)

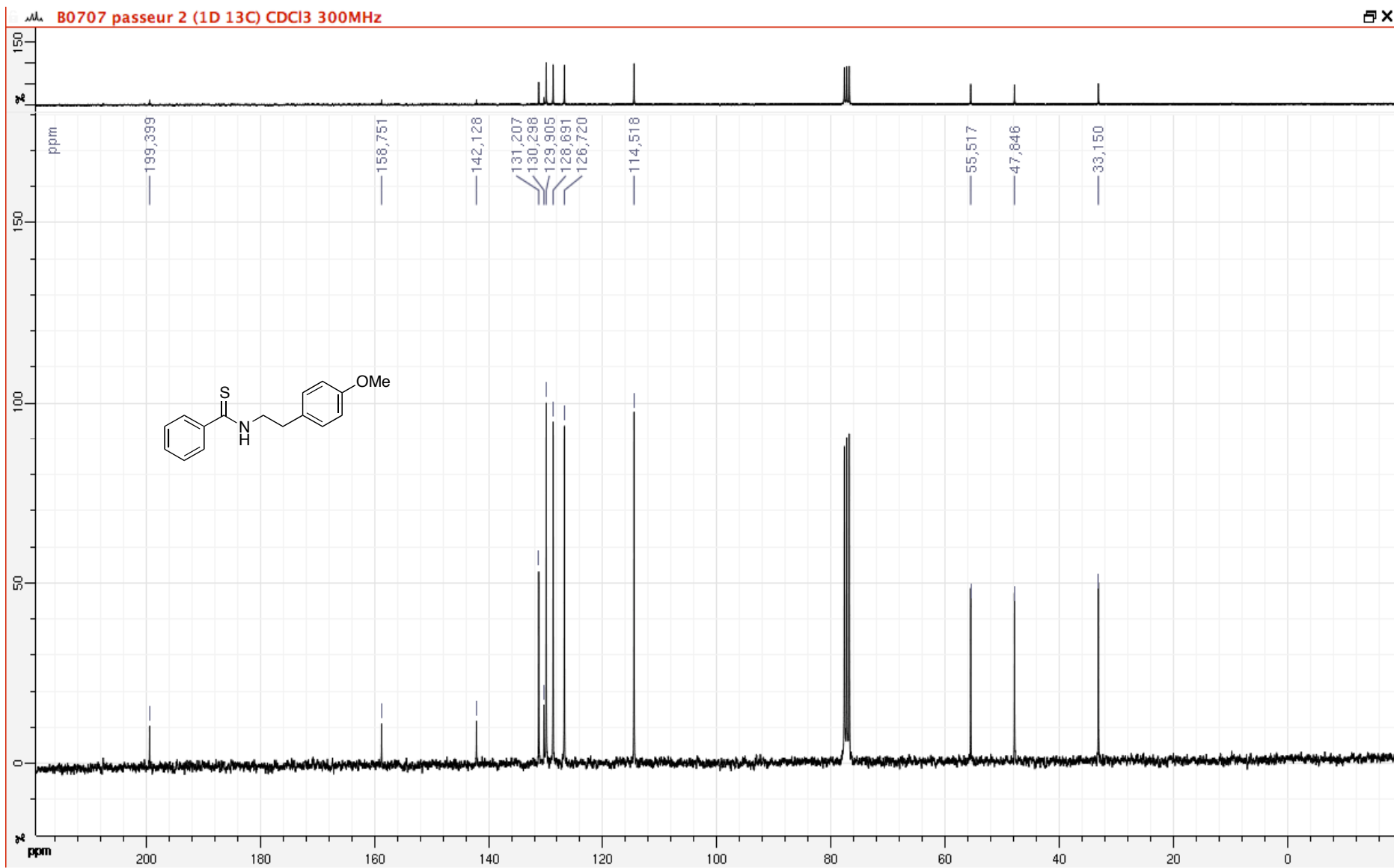
B0680 passeur 1 (1D 1H) CDCl3 300MHz



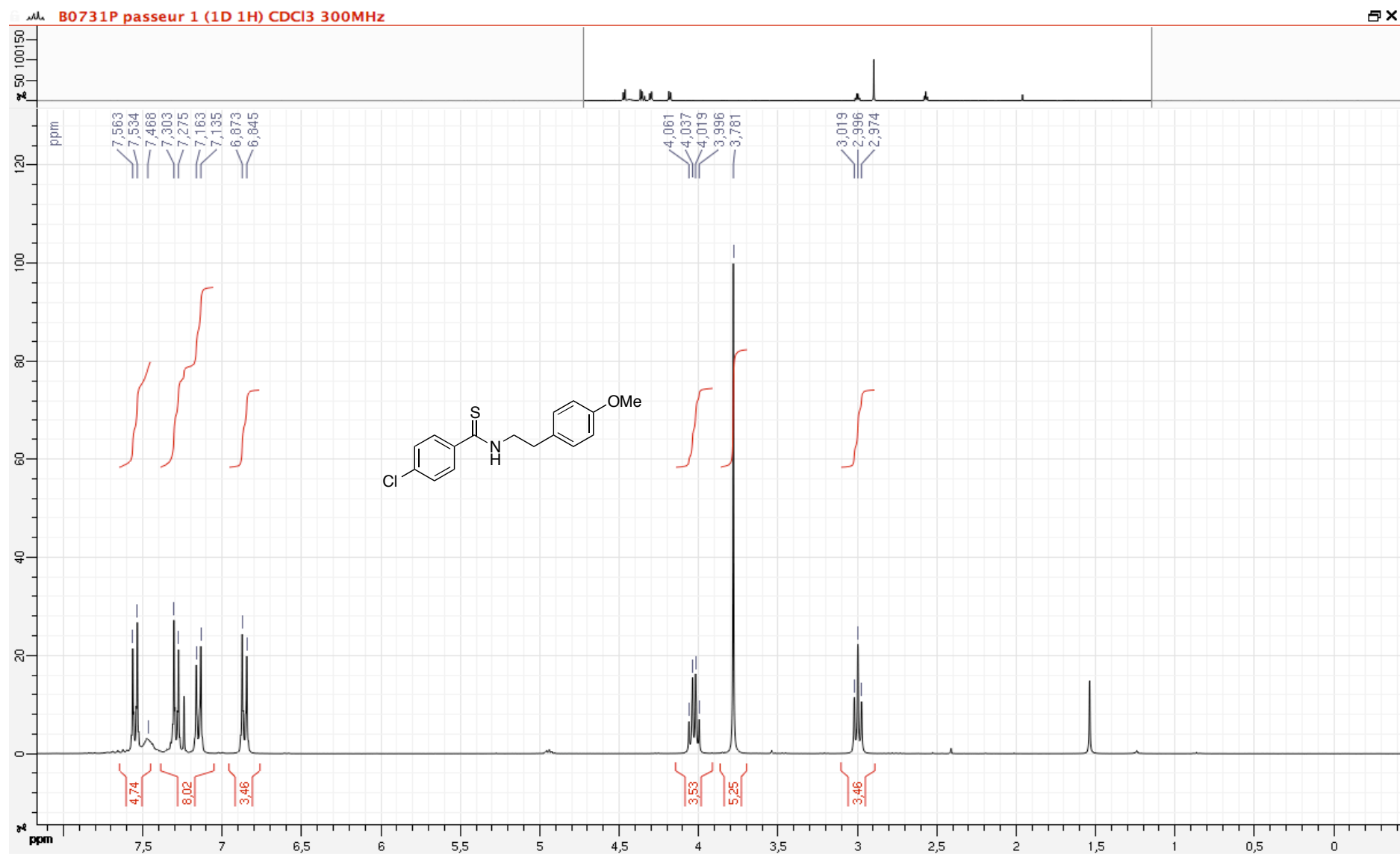


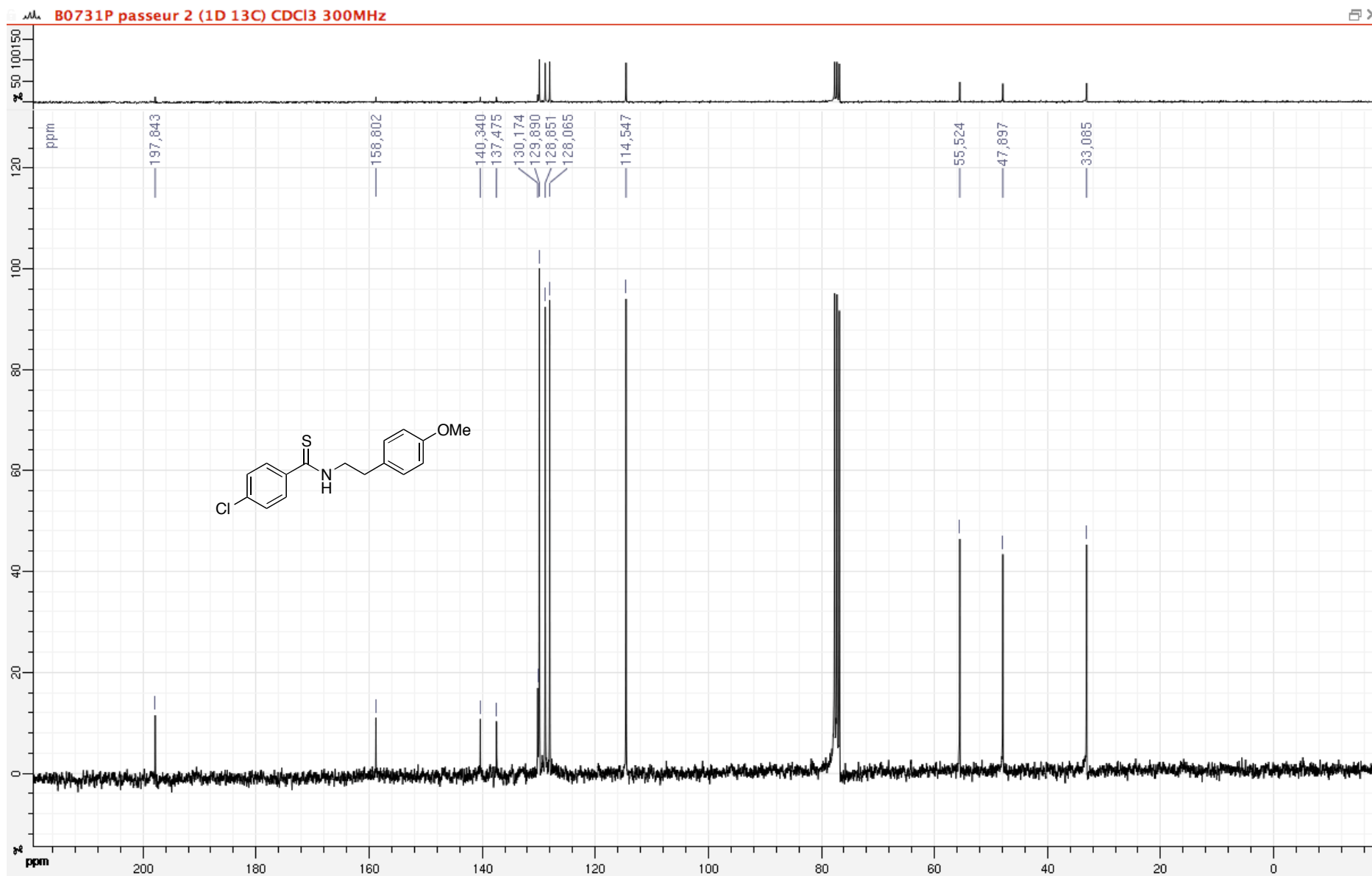
# *N*-(4-Methoxyphenethyl)benzothioamide (3d)





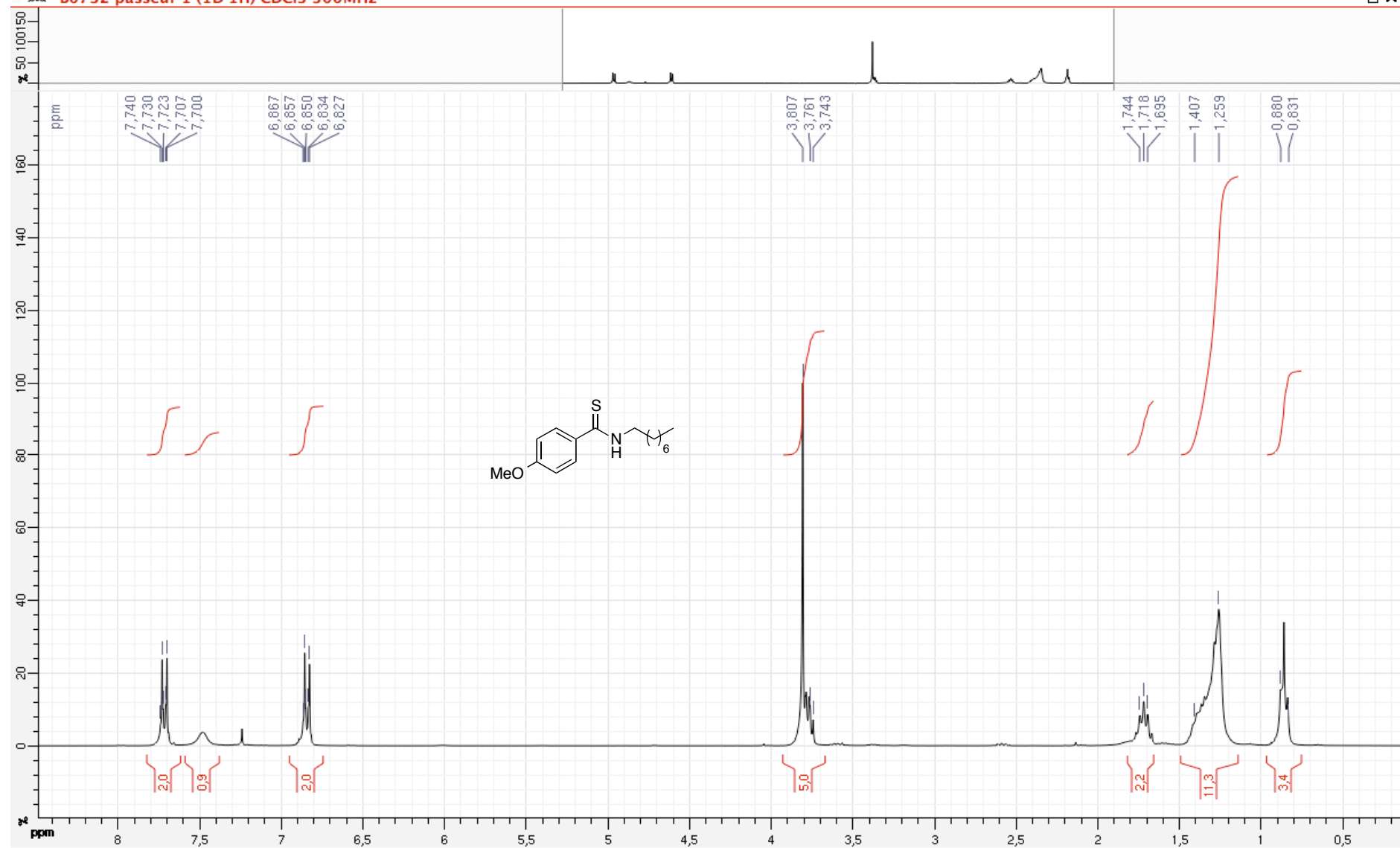
### 4-Chloro-N-(4-methoxyphenethyl)benzothioamide (3e)

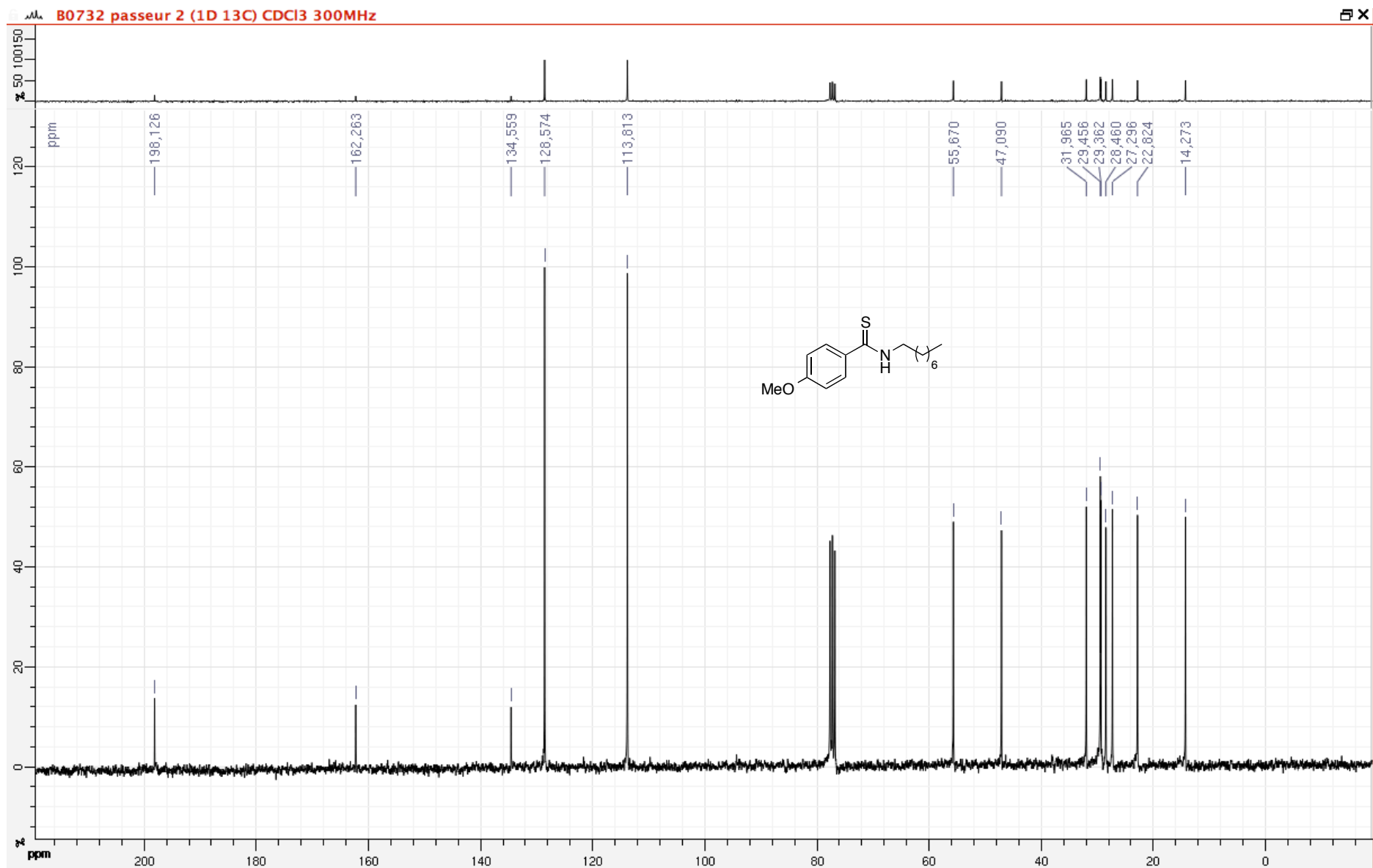




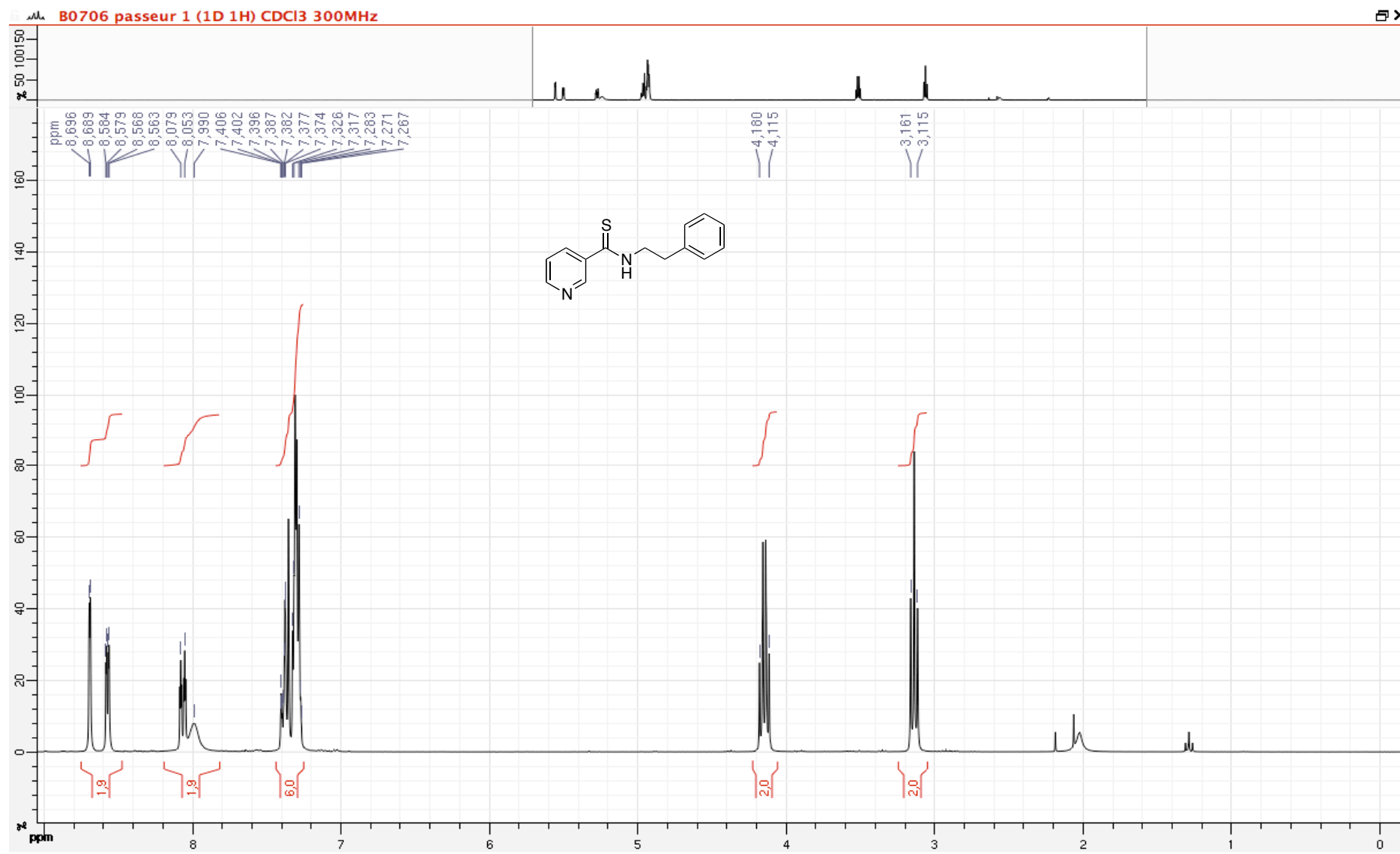
# 4-Methoxy-N-octylbenzothioamide (3f)

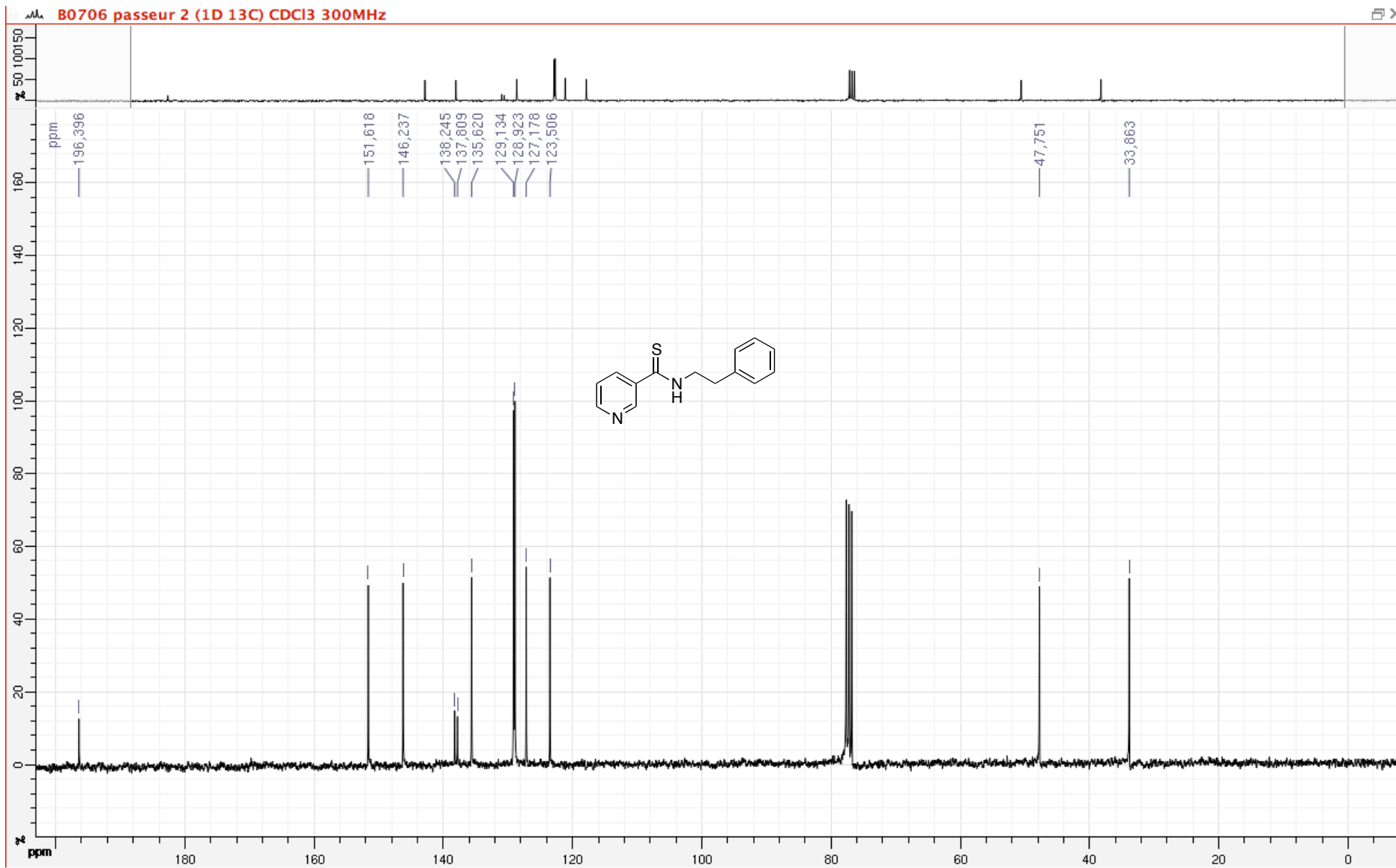
B0732 passeur 1 (1D 1H) CDCl3 300MHz



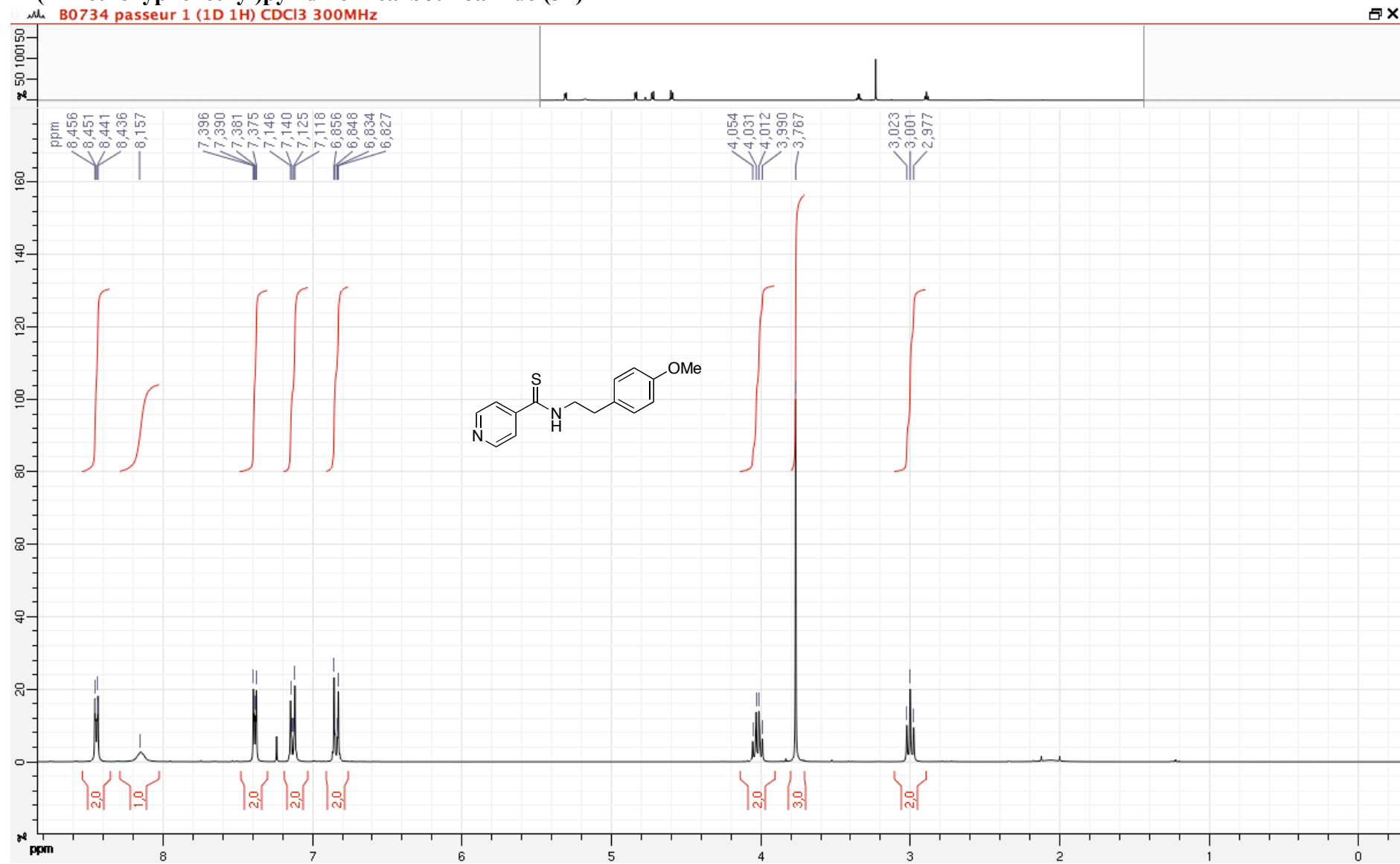


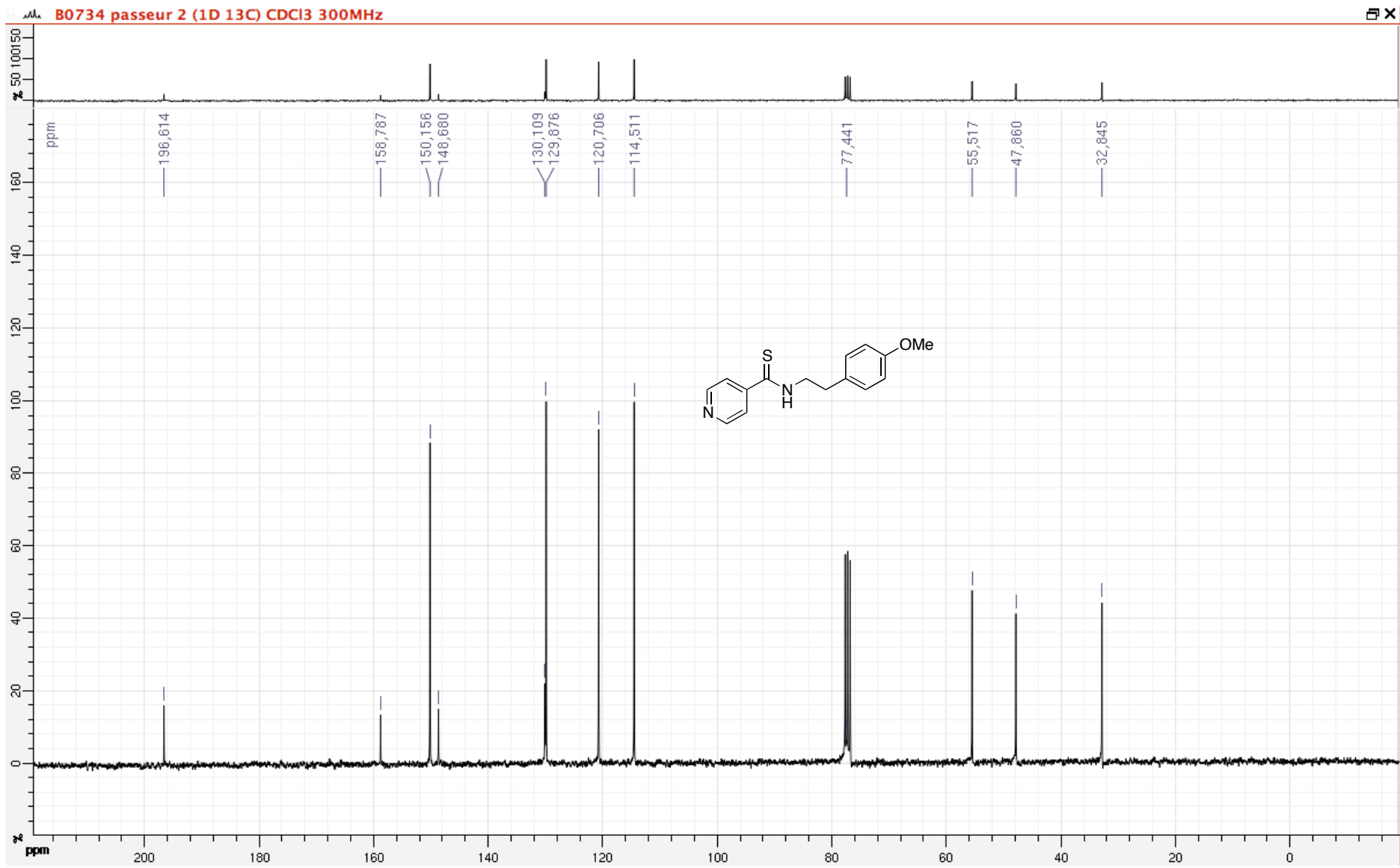
**N-phenethylpyridine-3-carbothioamide (3g)**



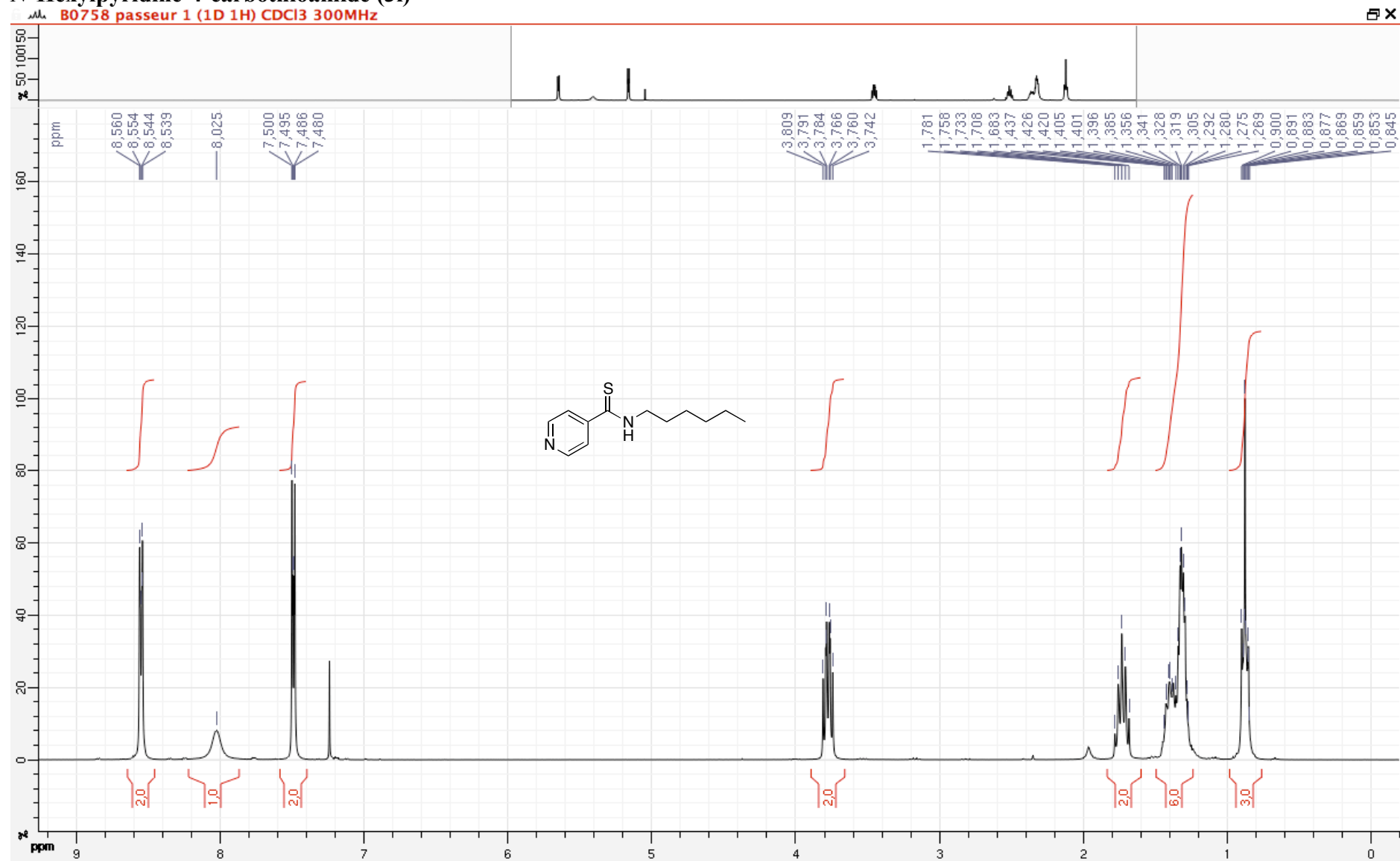


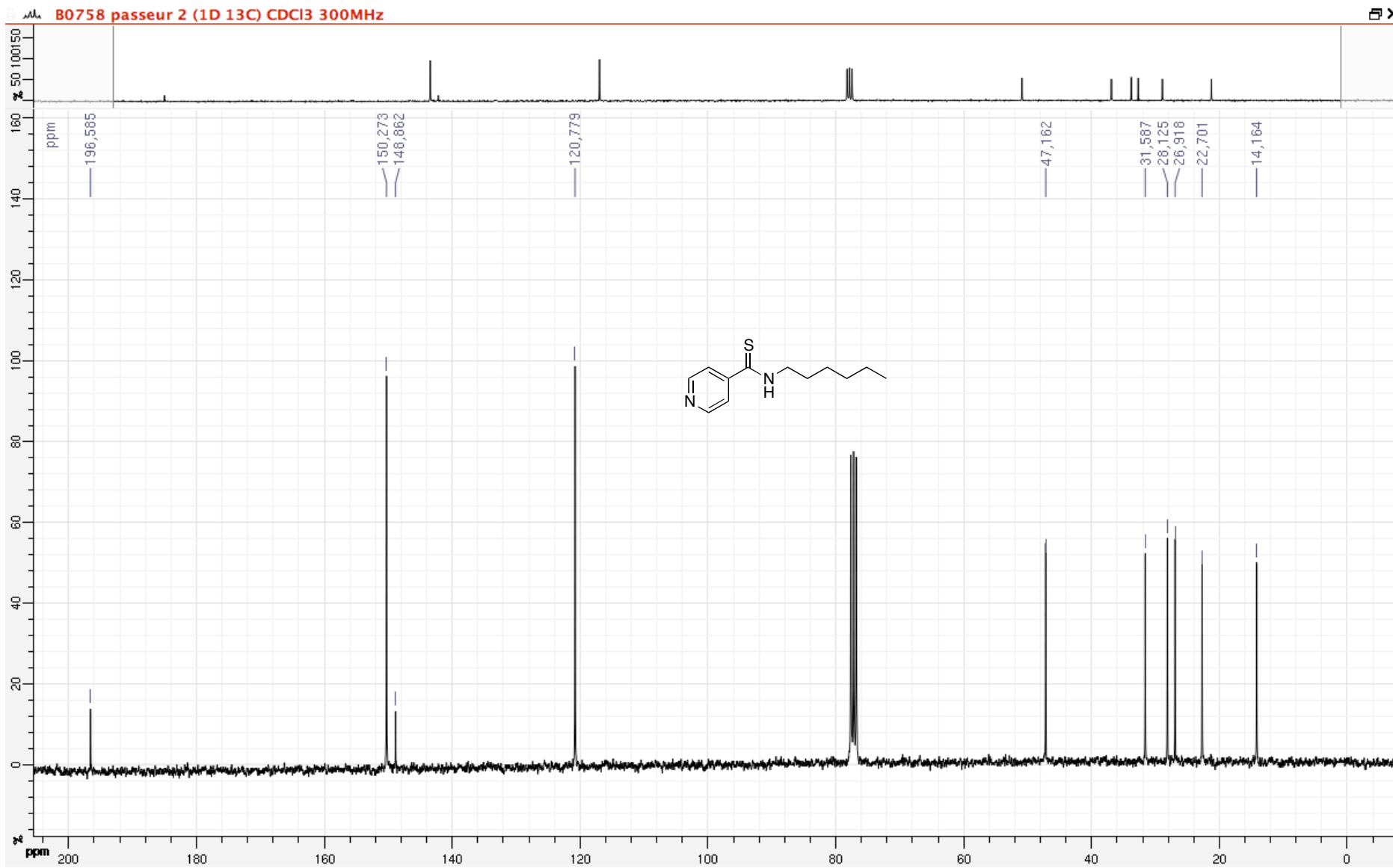
# *N*-(4-Methoxyphenethyl)pyridine-4-carbothioamide (3h)





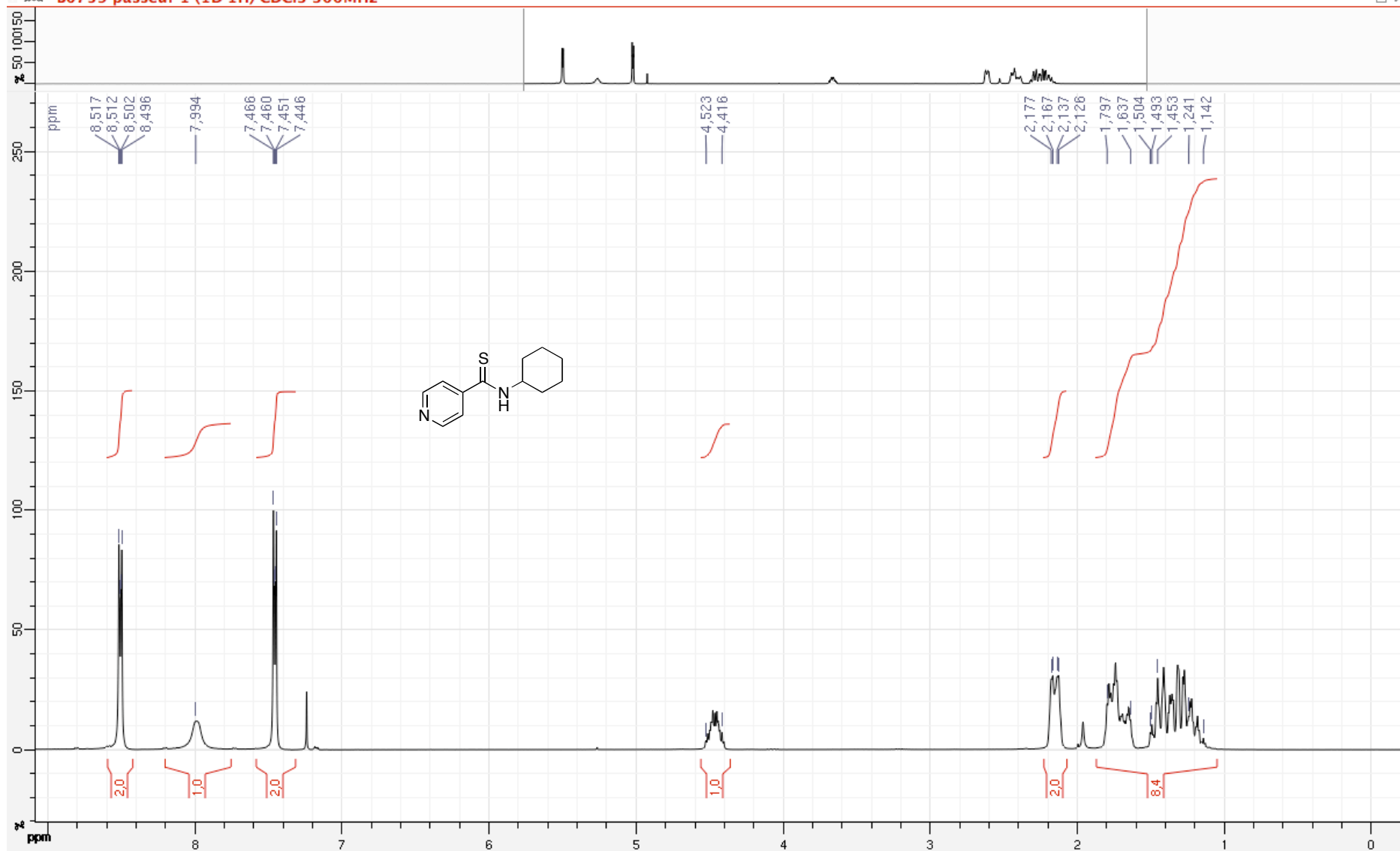
# N-Hexylpyridine-4-carbothioamide (3i)

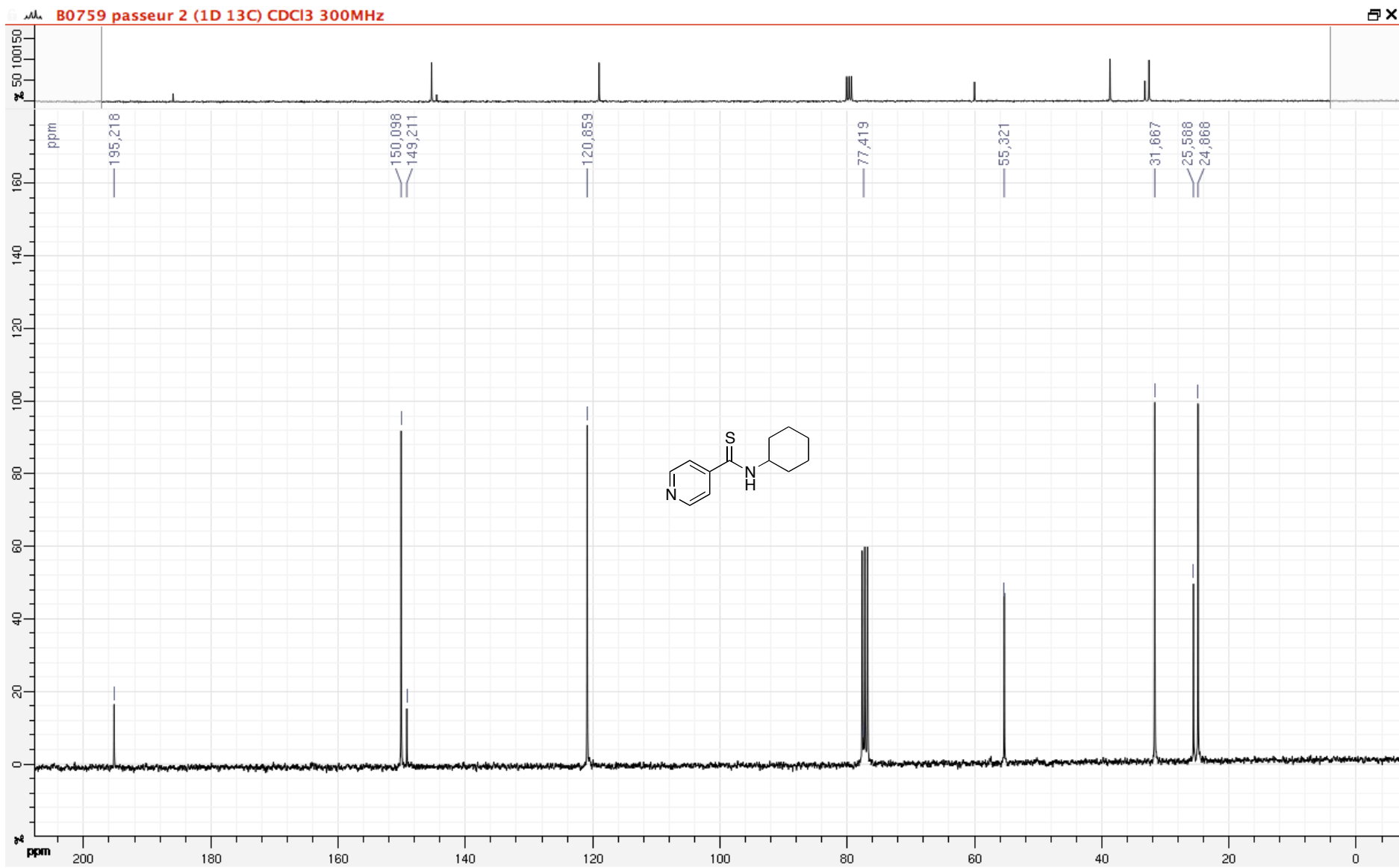




# N-Cyclohexylpyridine-4-carbothioamide (3j)

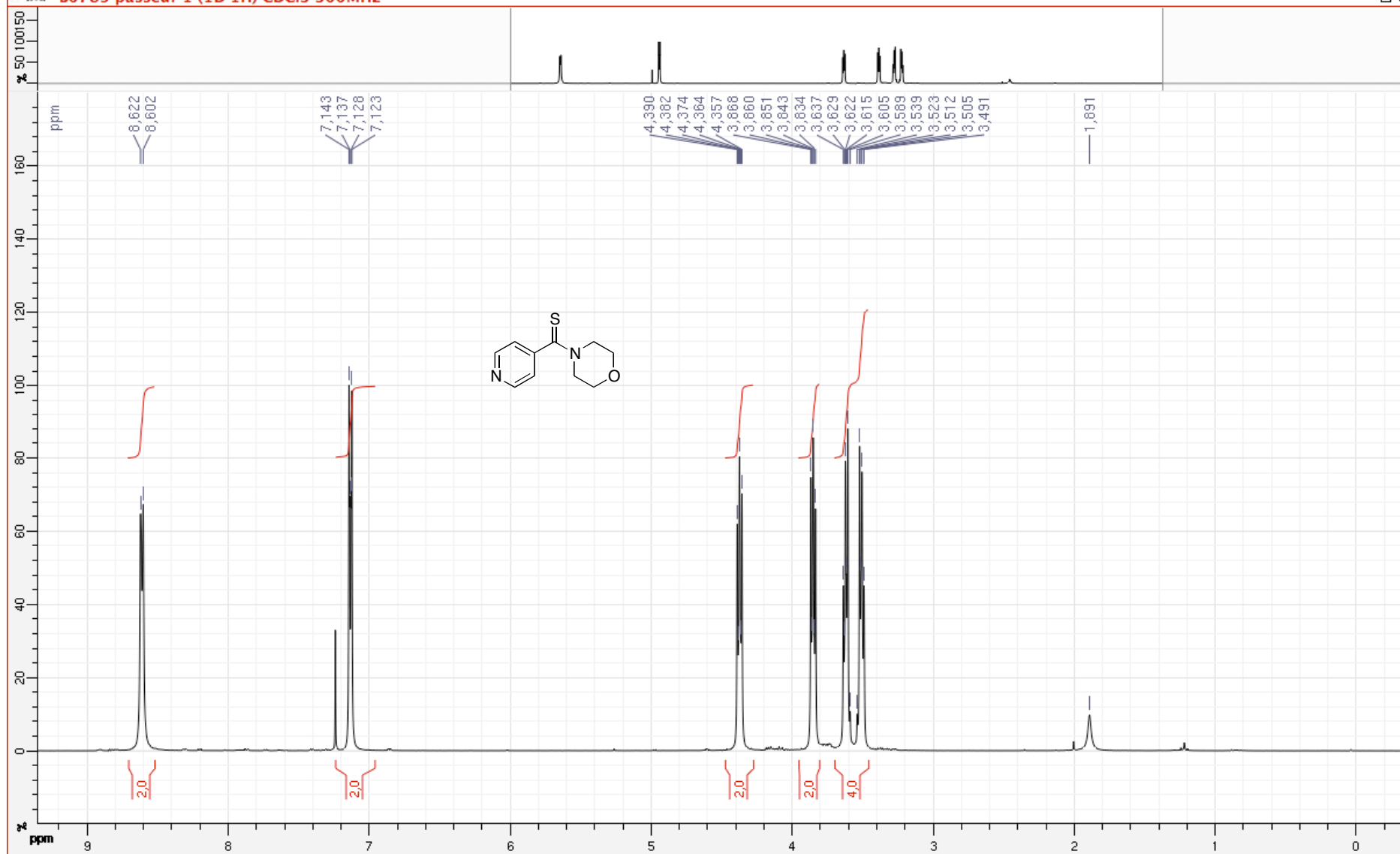
B0759 passeur 1 (1D 1H) CDCl3 300MHz

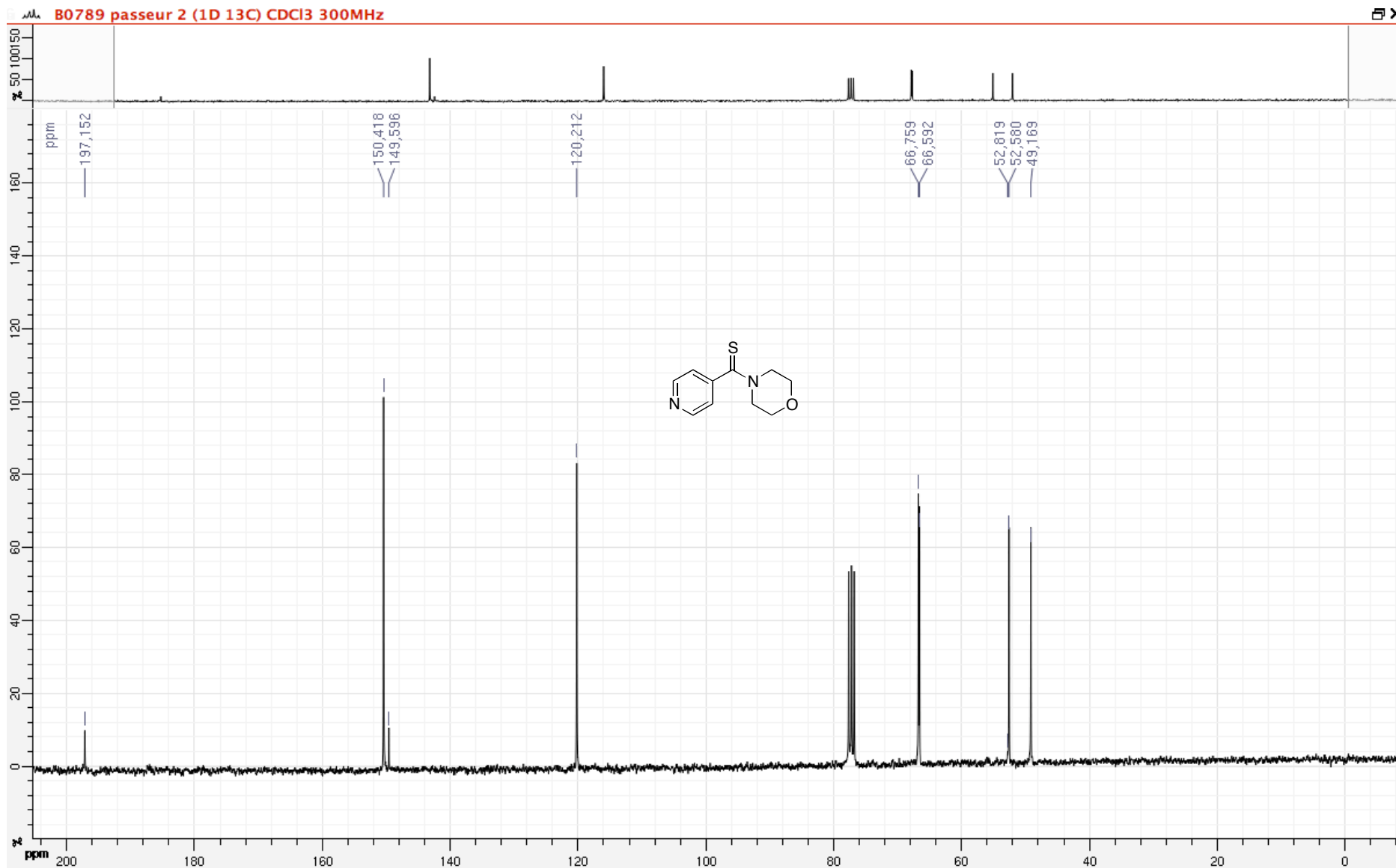




# Morpholino(pyridin-4-yl)methanethione

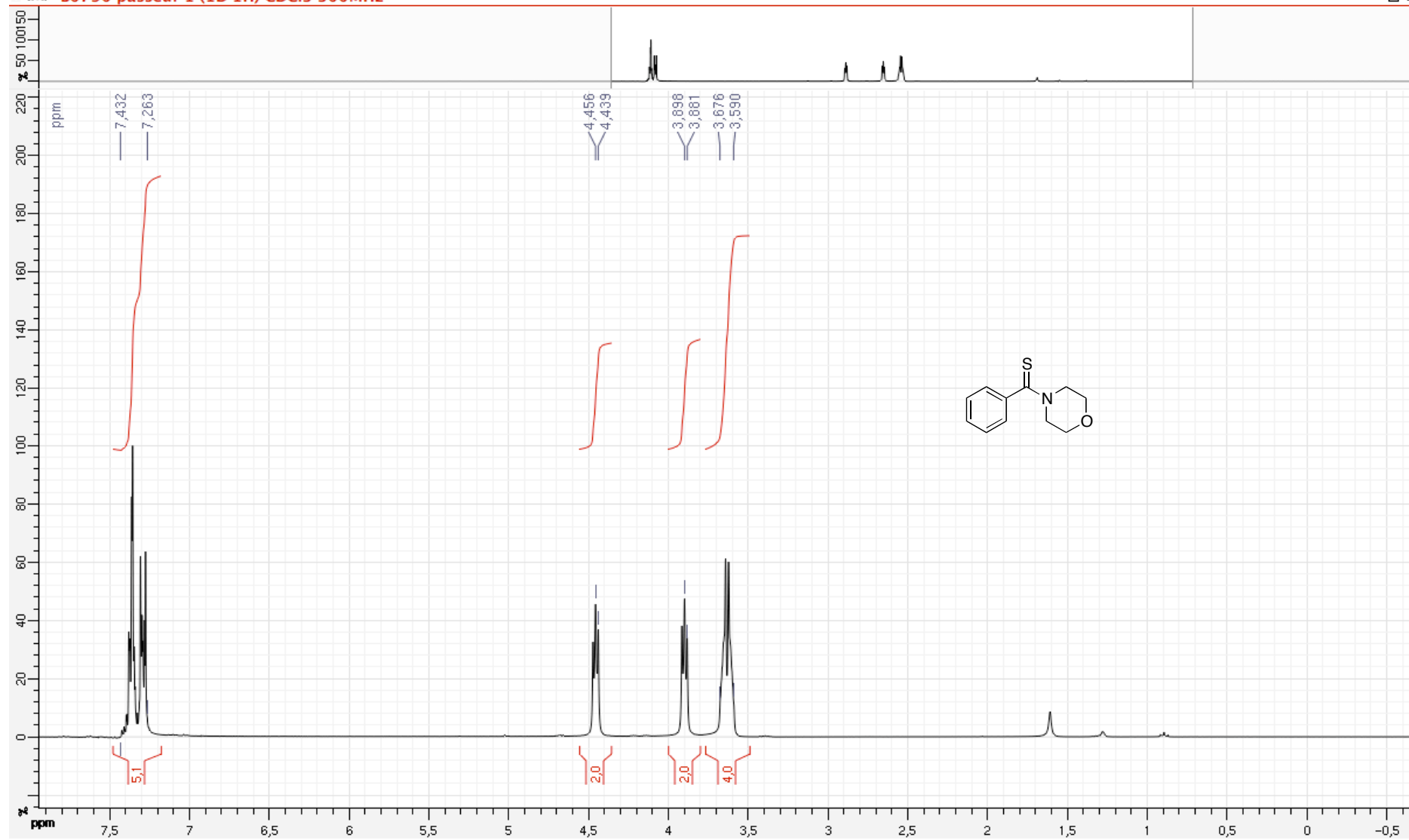
B0789 passeur 1 (1D 1H) CDCl3 300MHz

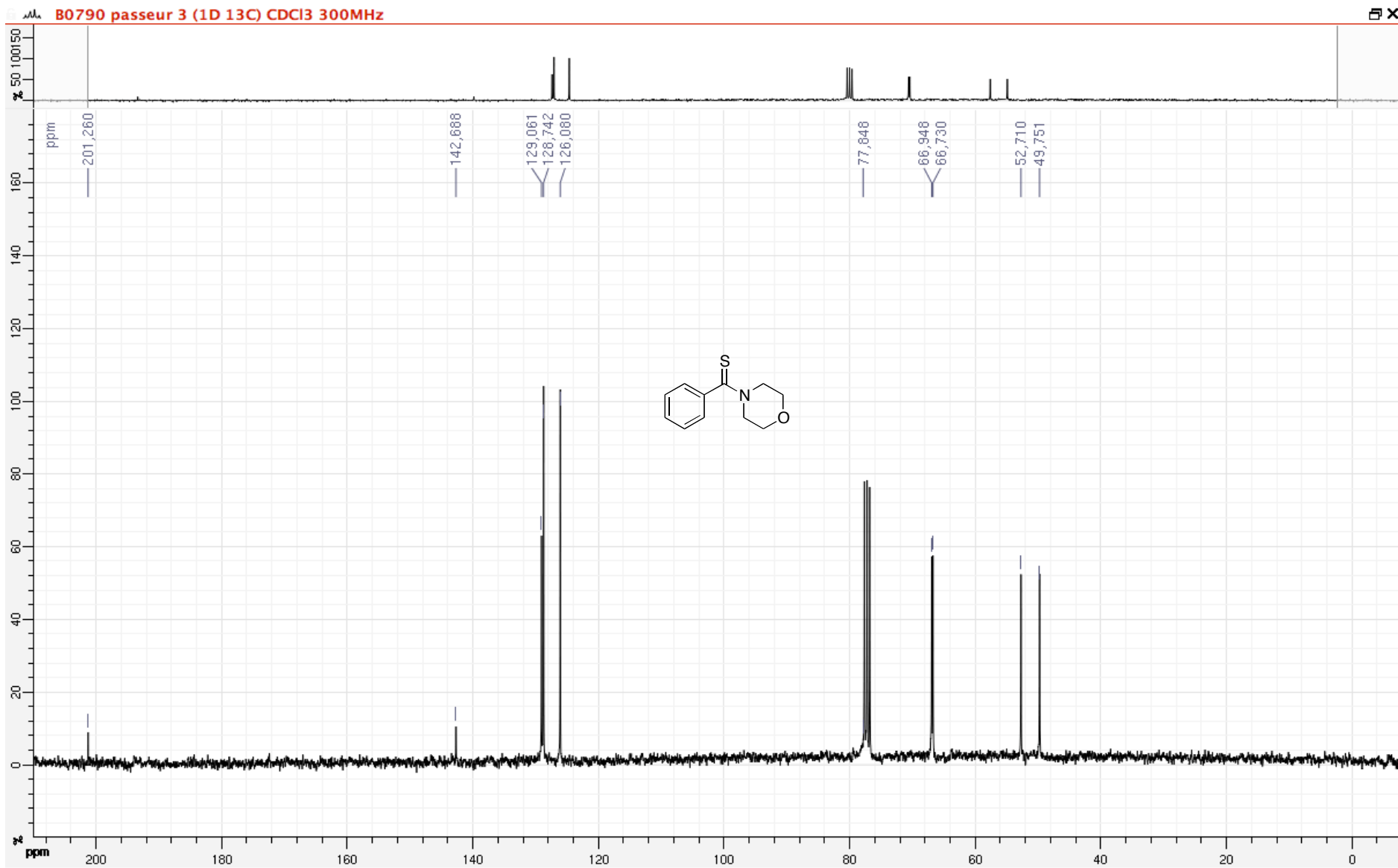




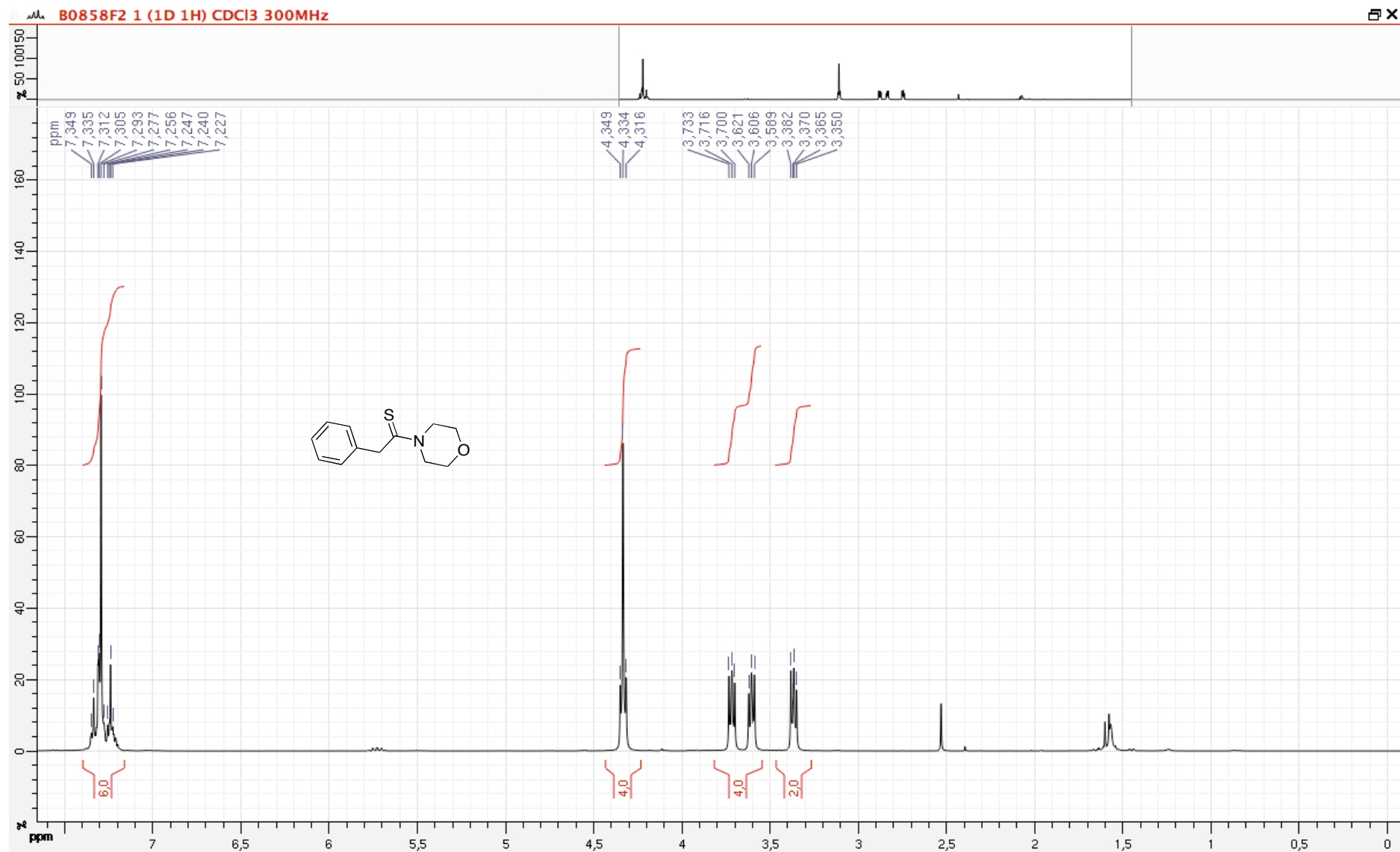
# Morpholino(phenyl)methanethione (3l)

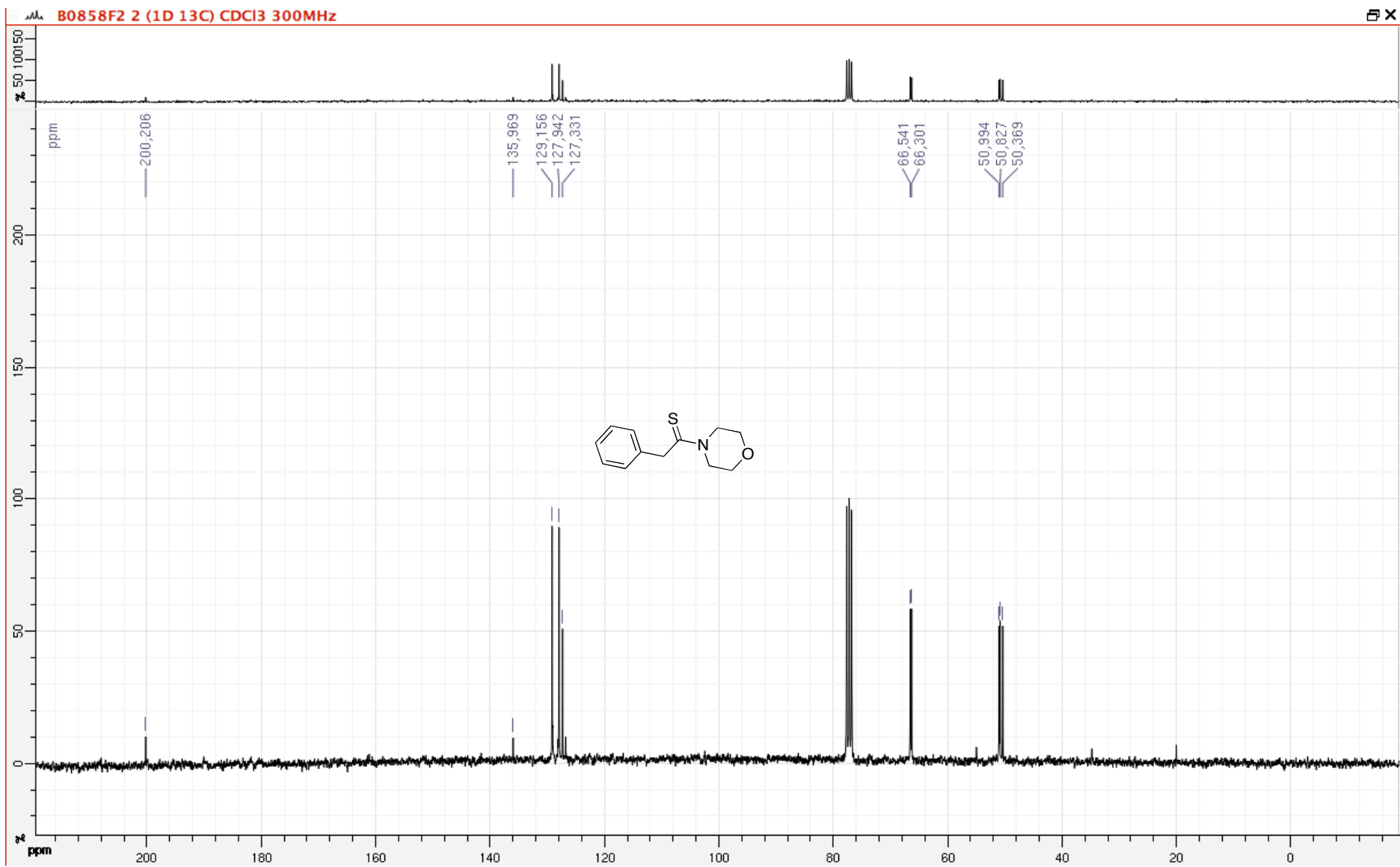
B0790 passeur 1 (1D 1H) CDCl3 300MHz





# 1-Morpholino-2-phenylethanethione (3m)





# N-(4-Hydroxybutyl)benzothioamide (3n)

