SUPPORTING INFORMATION

Intermolecular C-H amination of complex molecules: insights into the factors governing the selectivity

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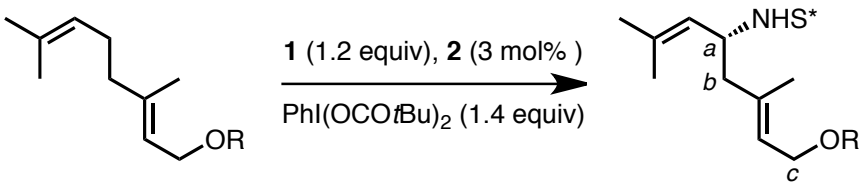
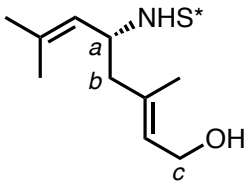
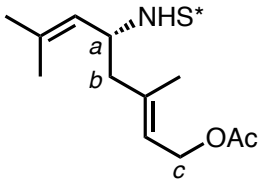
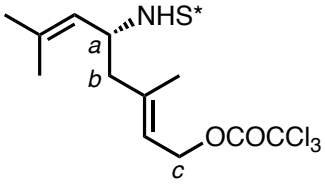
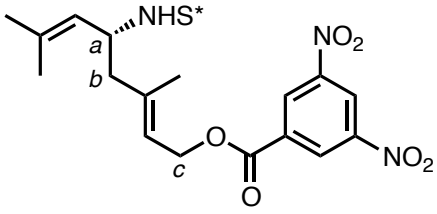
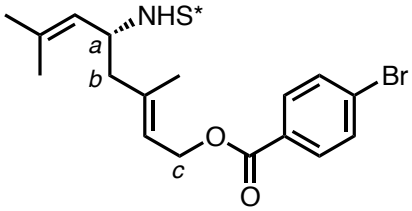
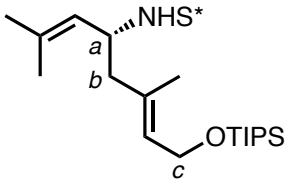
Table 1. Allylic amination of geraniol derivatives.[a]



Entry	Product	Yield (%)[b]	d.r. (%)[c]
1		66	>20:1
2		90	19 :1
3		89	>20:1
4		91	15 :1
5		98	18 :1
6		76	18 :1

[a] *Reaction conditions*: Geraniol derivative (0.2 mmol) in a 3:1 mixture of $(Cl_2CH)_2$:MeOH at -35 °C. [b] Isolated yields. [c] The diastereomeric ratios have been determined by ^{1}H NMR.

Crystallographic data

Identification code	**3a**	**3e**	**3g**	**3i**
CCDC deposit number	857497	857498	857499	857500
Empirical formula	$C_{24}H_{30}N_2O_3S_2$	$C_{24}H_{30}N_2O_3S_2$	$C_{29}H_{38}N_2O_3S_2$	$C_{26}H_{31}Cl_3N_2O_5S_2$
Formula weight	458.62	458.62	526.73	622.00
Temperature (K)	203(2)	293(2)	203(2)	293(2)
Diffractometer	Rapid II mm007HF – CMF optics (*)			Enraf-Nonius FR590 KappaCCD (†)
Wavelength (Å)	1.54187	1.54187	1.54187	0.71069
Crystal system	Monoclinic,	Monoclinic,	Orthorhombic,	Orthorhombic,
Space group	$P\,2_1$	$C\,2$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$
a (Å)	11.5299 (8)	21.3898 (14)	5.8634 (1)	6.2850 (10)
Unit cell dimensions *b* (Å)	10.2662 (4)	9.7688 (8)	16.1936 (4)	17.836 (3)
c (Å)	11.8713 (8)	12.5363 (9)	29.1960 (2)	27.578(3)
β (°)	119.144 (8)	109.462(5)	90	90
Volume (Å^3)	1227.29 (13)	2469.8 (3)	2772.15 (9)	3091.5 (8)
Z, Z'	2, 1	4, 1	4, 1	4, 1
*Calcd density (*Mg/m^3)	1.241	1.233	1.262	1.336
Abs. coefficient (mm^{-1})	2.180	2.166	1.996	0.468
F(000)	488	976	1128	1296
Crystal size (mm)	0.31 x 0.16 x 0.12	0.26 x 0.18 x 0.04	0.50 x 0.06 x 0.05	0.39 x 0.15 x 0.10
θ range (°) for data collection	7.47 to 68.23	6.65 to 60.49	6.65 to 68.25	2.40 to 24.41
Limiting indices	$-13 \le h \le 13$ $-11 \le k \le 12$ $-14 \le l \le 13$	$-24 \le h \le 24$ $-10 \le k \le 11$ $-14 \le l \le 12$	$-6 \le h \le 4$ $-19 \le k \le 18$ $-35 \le l \le 34$	$-7 \le h \le 7$ $-20 \le k \le 20$ $-31 \le l \le 32$
Reflect° collected / unique	12675 / 3924	10068 / 3607	19671 / 4989	28620 / 5073
R(int)	0.0433	0.0707	0.0359	0.0276
Completeness to θ_{max}	99.1 %	99.7 %	98.8 %	99.5 %
Absorption correction	Semi-empirical from equivalents			
Max. and min. T	1.000 and 0.761	1.000 and 0.728	1.000 and 0.726	0.97 and 0.84
Refinement method	Full-matrix least-squares on F^2			
Data / restraints / parameters	3924 / 1 / 285	3607 / 1 / 285	4989 / 94 / 346	5066 / 3 / 367
Goodness-of-fit on F^2	1.007	1.033	1.181	1.040
Final R indices [I>2σ(I)]	R1 = 0.0336 wR2 = 0.0839	R1 = 0.0663 wR2 = 0.1291	R1 = 0.0424 wR2 = 0.0790	R1 = 0.0798 wR2 = 0.2019
R indices (all data)	R1 = 0.0362 wR2 = 0.0858	R1 = 0.1331 wR2 = 0.1847	R1 = 0.0650 wR2 = 0.1056	R1 = 0.1087 wR2 = 0.2292
Flack parameter	0.006 (13)	0.01 (3)	-0.01(2)	-0.05 (14)
Extinction coefficient	-	-	-	0.046(4)
Largest diff. peak and hole (e. Å3)	0.157 and -0.267	0.321 -0.444	0.395 -0.555	0.505 -0.426

Identification code	**4**	**5e**	**8c**
CCDC deposit number	857501	857503	857504
Empirical formula	$C_{29}\ H_{38}\ N_2\ O_3\ S_2$	$C_{22}\ H_{23}\ N_3\ O_8\ S_2$	$C_{28}\ H_{34}\ N_2\ O_3\ S_2$
Formula weight	526.73	521.55	510.69
Temperature (K)	293 (2) K	173 (2) K	293 (2) K
Diffractometer	Rapid II mm007HF – CMF optics (*)		Enraf-Nonius FR590 KappaCCD (†)
Wavelength (Å)	1.54187	1.54187	0.71069
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 2_1	P $2_1\ 2_1\ 2_1$	P 2_1
Unit cell dimensions *a* (Å)	13.0891 (4)	5.7918 (1)	10.505 (2)
b (Å)	9.7802 (3)	17.1657 (5)	24.665 (4)
c (Å)	22.7700 (16)	25.0580 (17)	11.273 (2)
β (°)	96.735 (7)	90	116.31 (6)
Volume ($Å^3$)	2894.8 (2)	2491.27 (19)	2618.32 (8)
Z, Z'	4, 2	4, 1	4, 2
Calcd density (Mg/m^3)	1.209	1.391	1.296
Abs. coefficient (mm^{-1})	1.911	2.390	0.236
F(000)	1128	1088	1088
Crystal size (mm)	0.60 x 0.20 x 0.08	0.52 x 0.06 x 0.04	0.33 x 0.28 x 0.22
θ range for data collection (°)	6.66 to 68.24	7.07 to 49.99	2.02 to 27.48
Limiting indices	$-15 \le h \le 15$, $-11 \le k \le 10$, $-27 \le l \le 25$	$-5 \le h \le 4$, $-14 \le k \le 17$, $-17 \le l \le 24$	$-13 \le h \le 13$, $-31 \le k \le 32$, $-14 \le l \le 14$
Reflect° collected / unique	25101 / 9825	10781 / 2542	26840 / 11154
R(int)	0.0388	0.0390	0.0274
Completeness to θ_{max}	99.3 %	99.5 %	99.5 %
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.000 and 0.695	1.000 and 0.747	0.94 and 0.82
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	9817 / 1 / 659	2542 / 66 / 327	11144 / 1 / 635
Goodness-of-fit on F^2	1.100	1.215	1.020
Final R indices [I>2σ(I)]	R1 = 0.0408, wR2 = 0.0811	R1 = 0.0516, wR2 = 0.1204	R1 = 0.0414, wR2 = 0.0923
R indices (all data)	R1 = 0.1101, wR2 = 0.1173	R1 = 0.0895, wR2 = 0.1695	R1 = 0.0551, wR2 = 0.1008
Flack parameter	0.015 (13)	0.02 (5)	-0.01 (4)
Largest diff. peak and hole (e. Å3)	0.241 and -0.305	0.357 and -0.296	0.211 and -0.256

Computing Software for :

- Data Collection, Cell Refinement and Data Reduction: CrystalClear-SM Expert 2.0 r4 *(Rigaku, 2009) (*) ;*

HKL2000 (*Otwinowski & Minor, 1997*); COLLECT (*Nonius B.V., 1999*) (†).

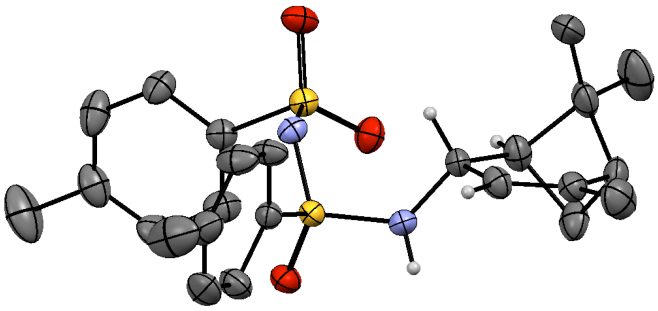
- Structure solution : 'SHELXS97 (Sheldrick, 2008).

- Structure refinement : 'SHELXL97 (Sheldrick, 2008); CRYSTALBUILDER (Welter, 2006)'

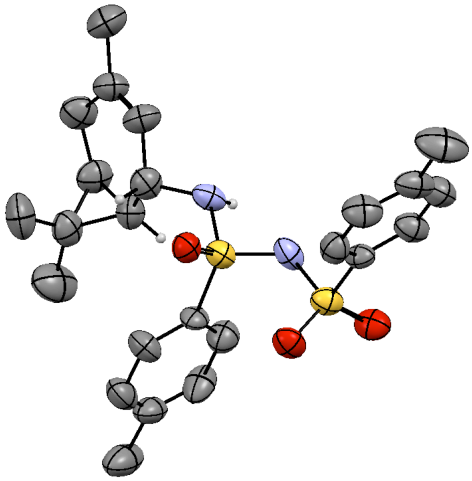
- Computing molecular graphics 'PLATON (Spek, 2003)' computing publication material 'SHELXL97 (Sheldrick, 2008)'

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115-119.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). Mercury: visualization and analysis of crystal structures. *J.Appl. Cryst.* **39**, 453-457.
Nonius, B. V. (1999). *COLLECT*, data collection software.
Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Volume 276, Macromolecular Crystallography, part A, edited by C.W. Carter, Jr. & R.M. Sweet, 307-326, 1997, New York: Academic Press.
Sheldrick, G.M. (2008). *Acta Cryst.* A **64**, 112-122.
Spek, A. L. (2003). *J.Appl. Cryst.* **36**, 7-13.
Welter, R. (2006). The Crystalbuilder Project *Acta Cryst.* A **62**, s252.

X-ray structure of compound 3a



X-ray structure of compound 3e



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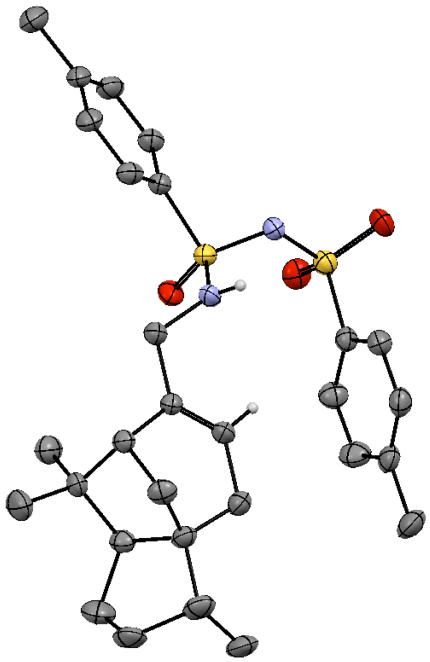

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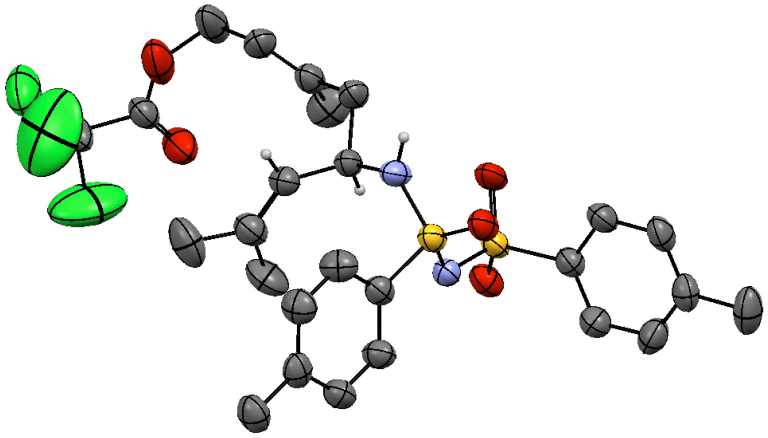

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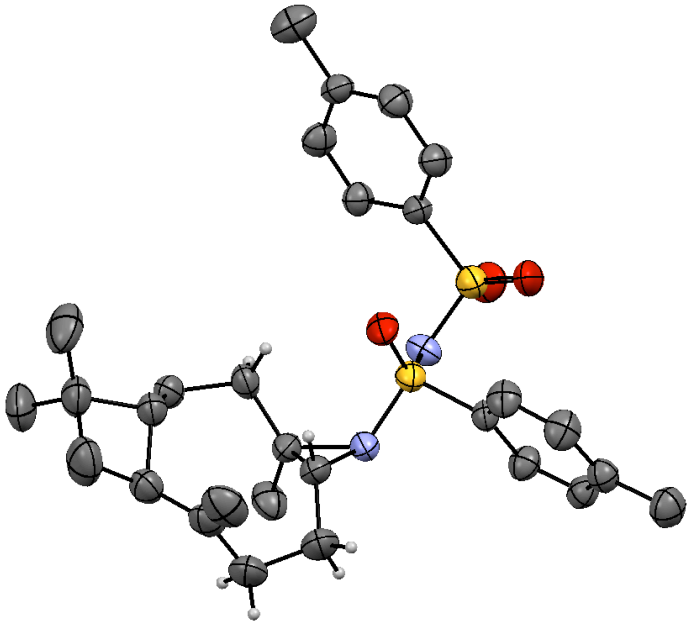

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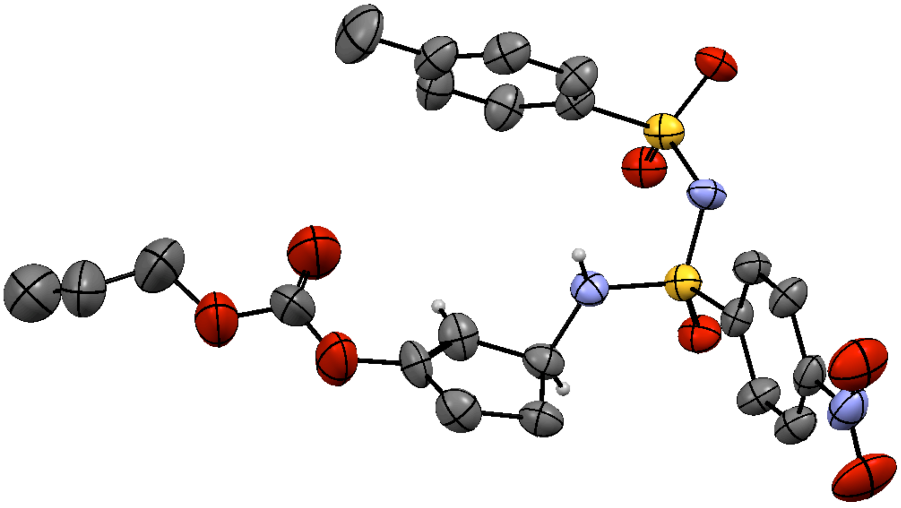

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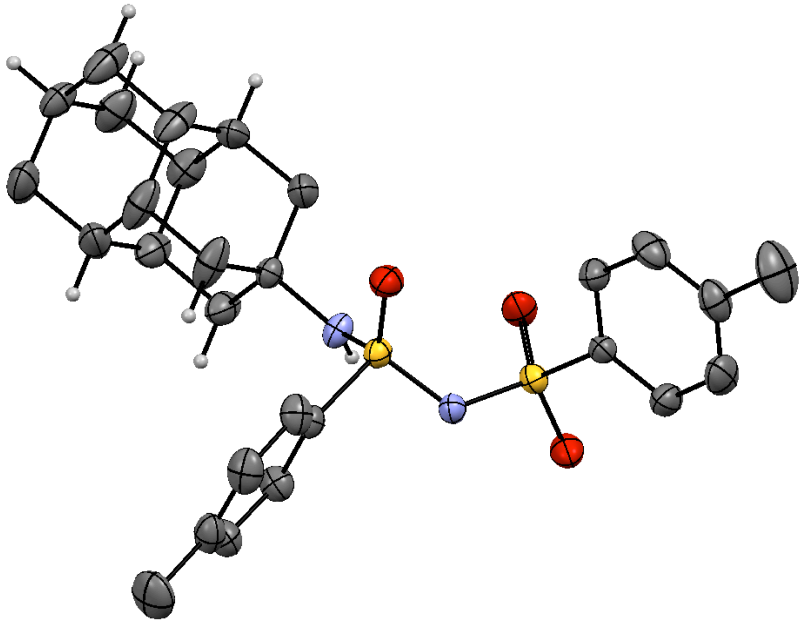

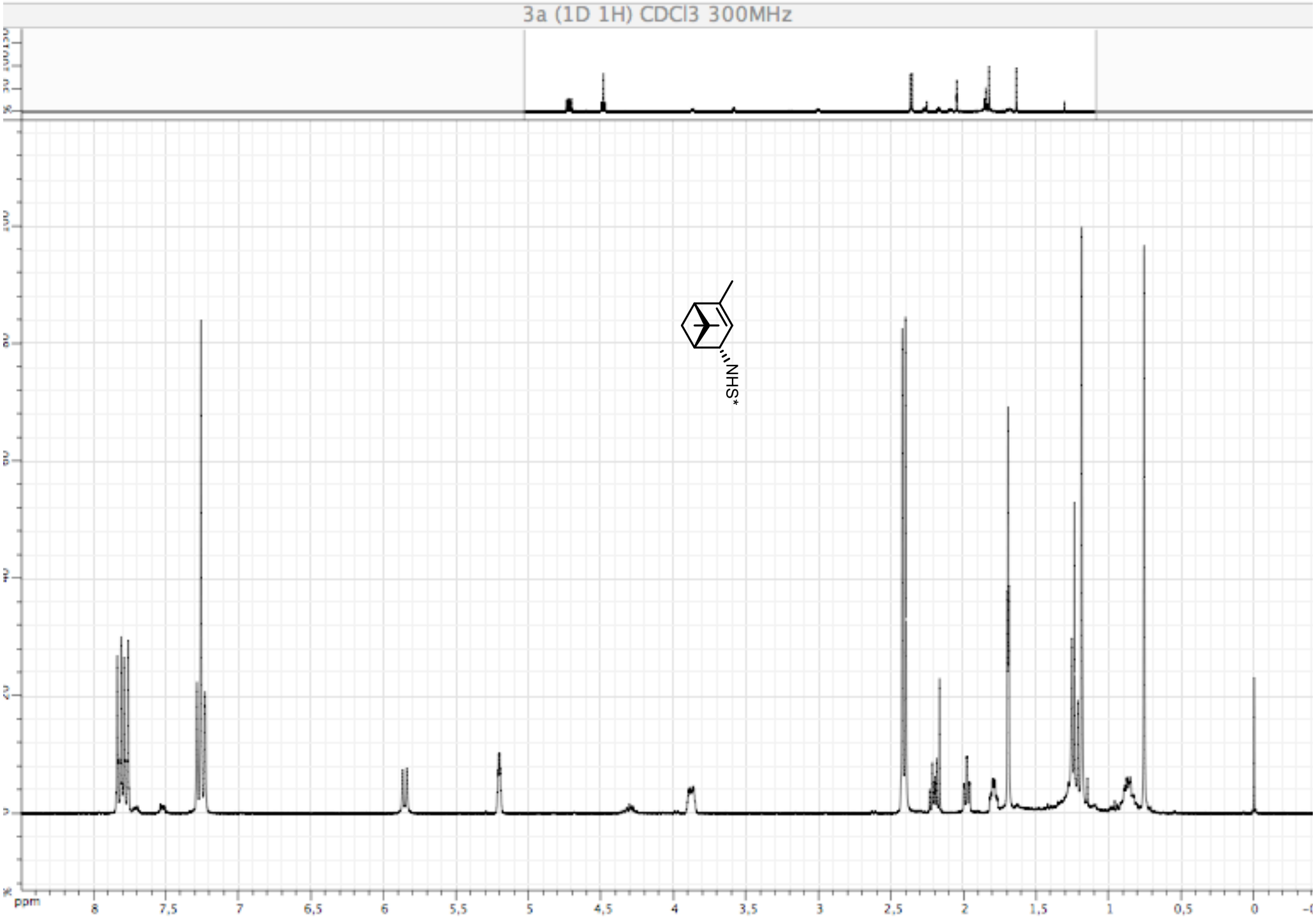
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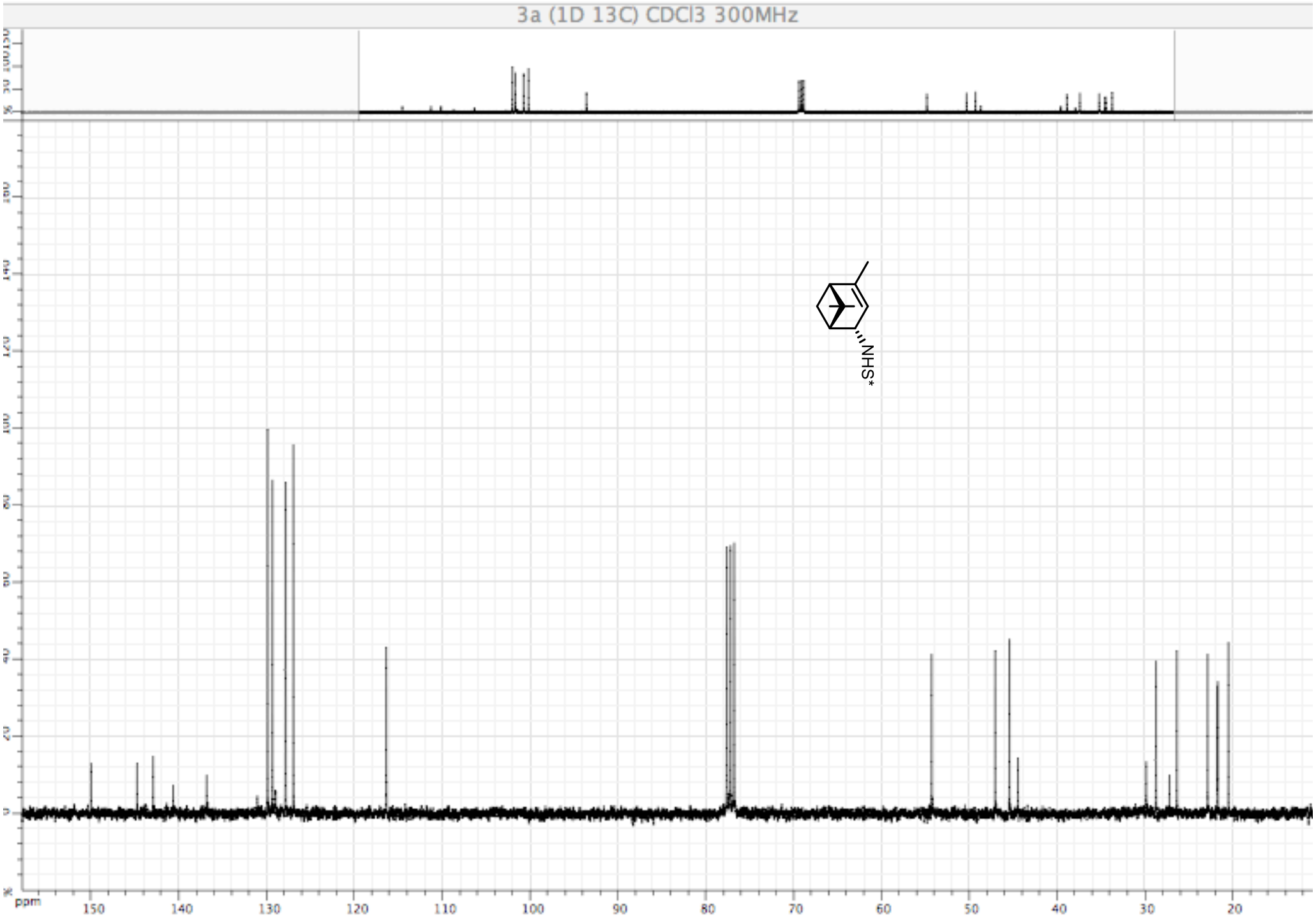
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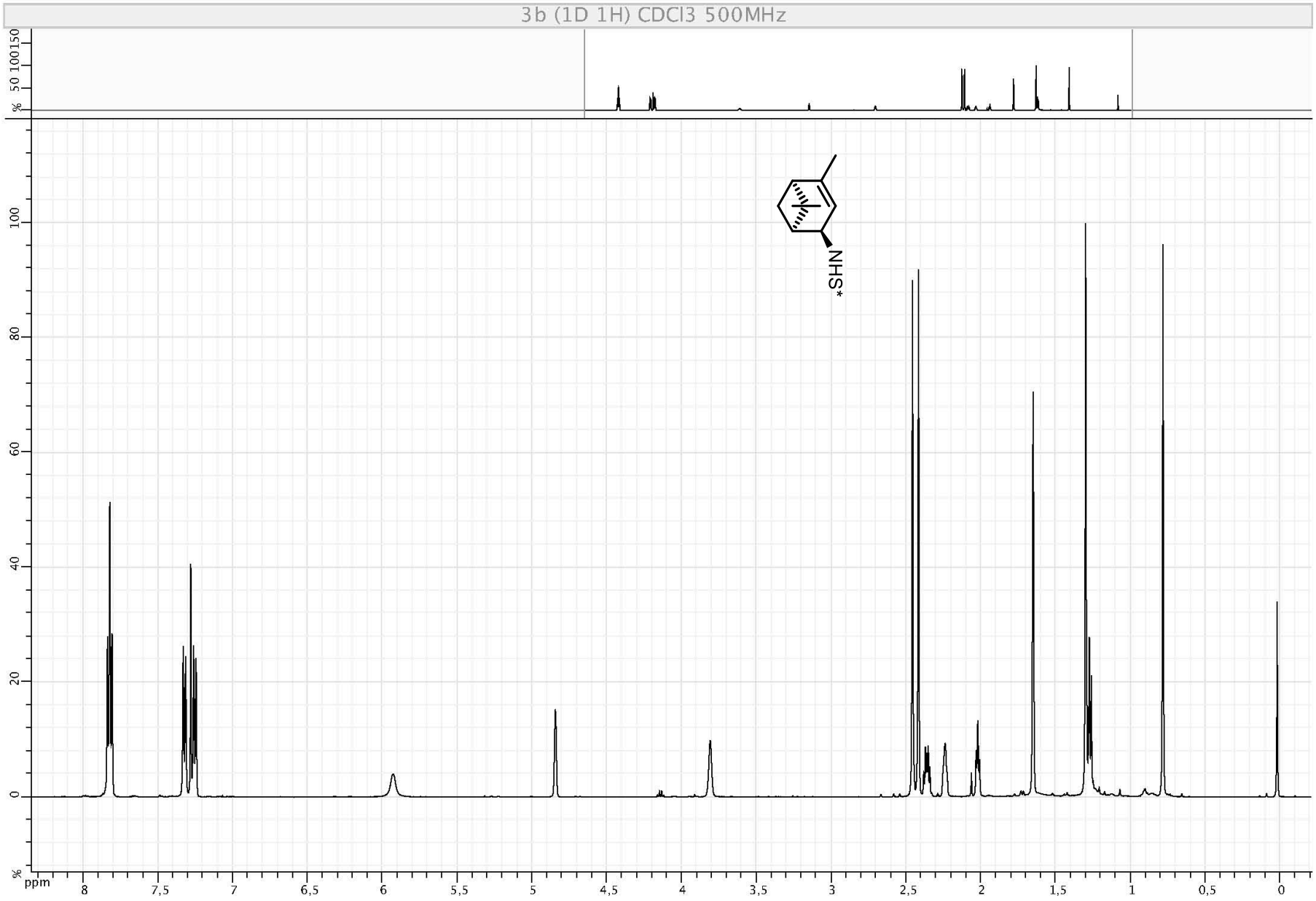
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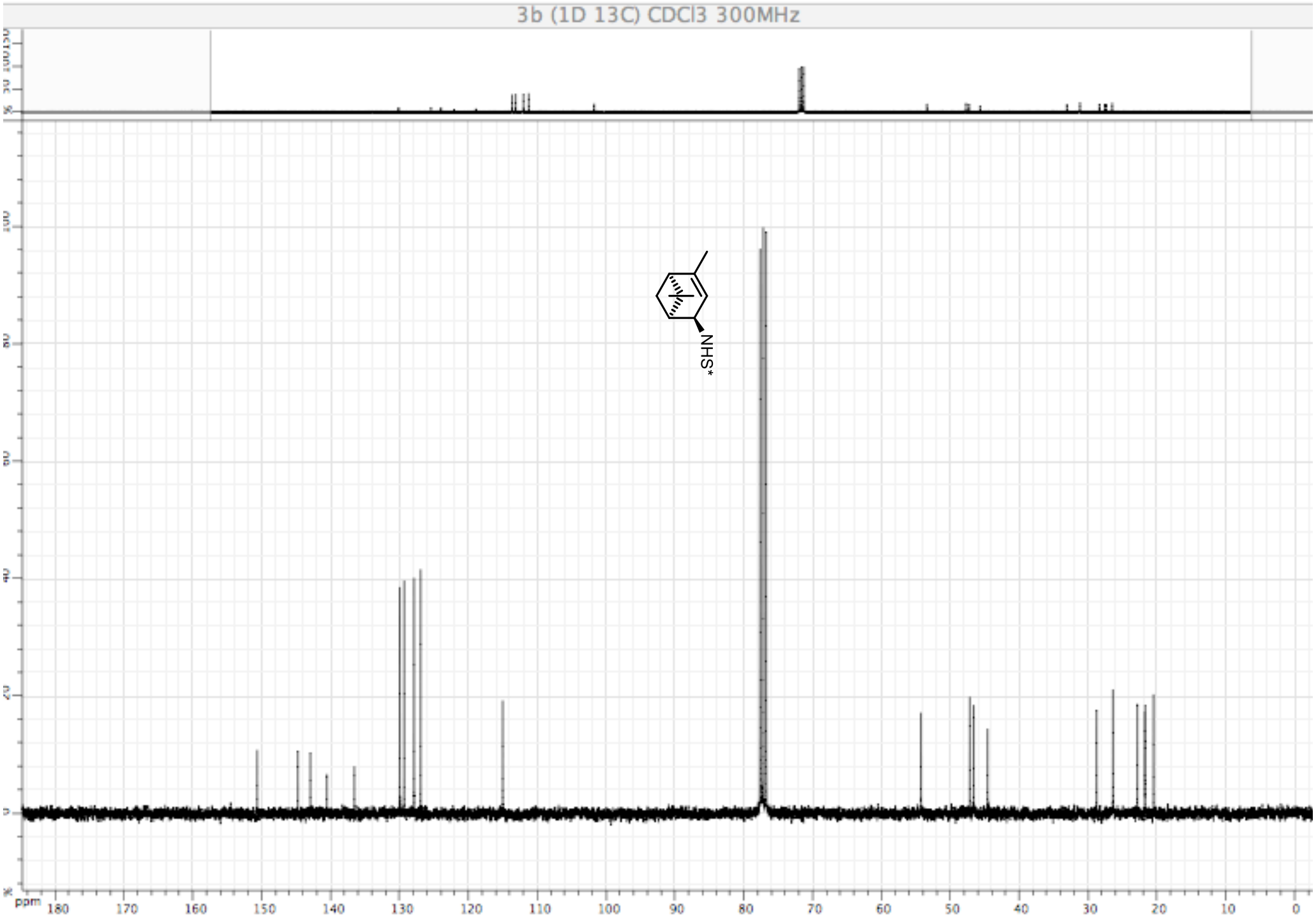
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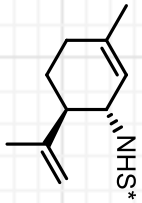

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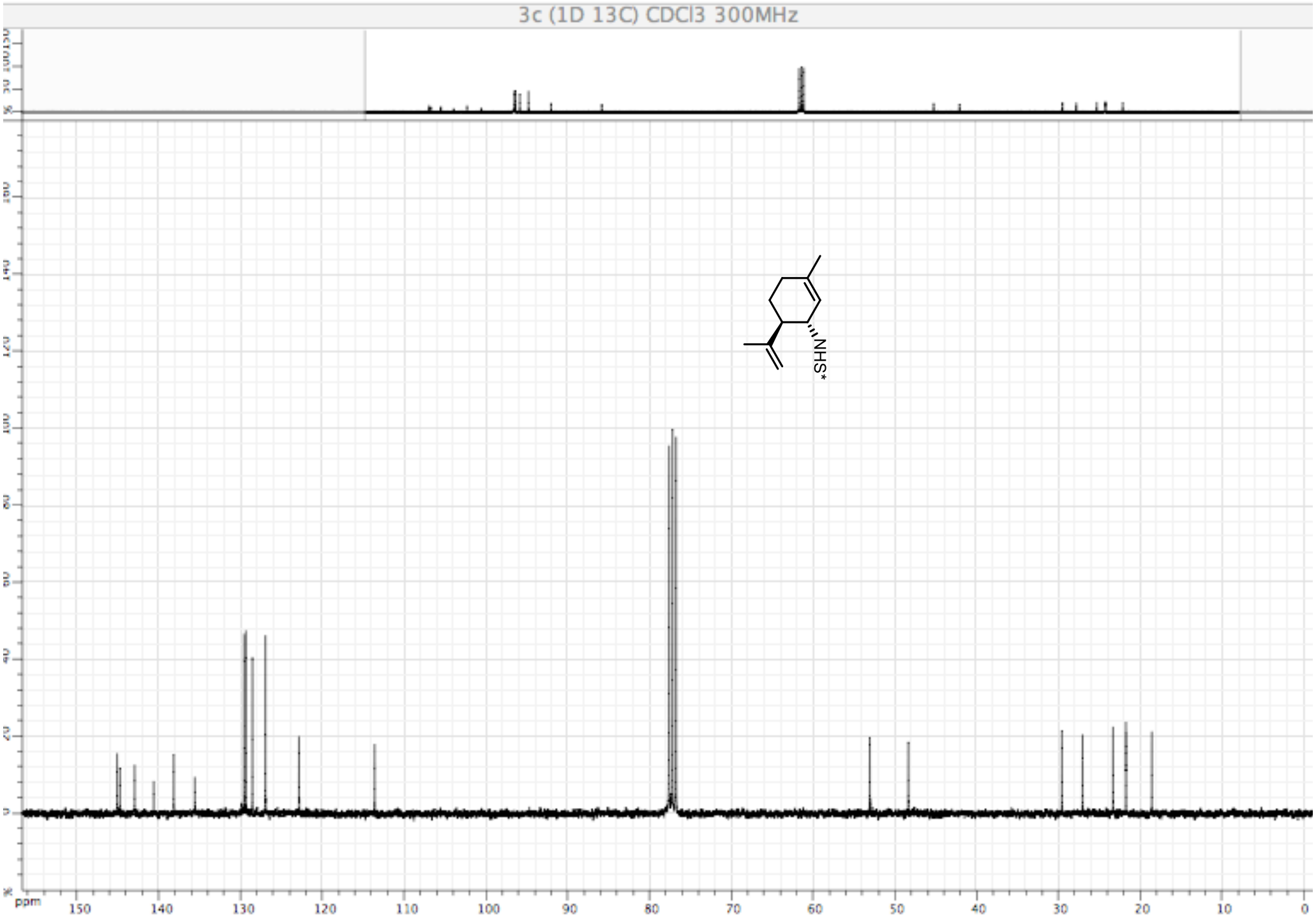
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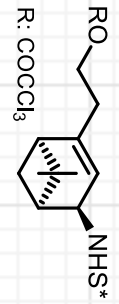

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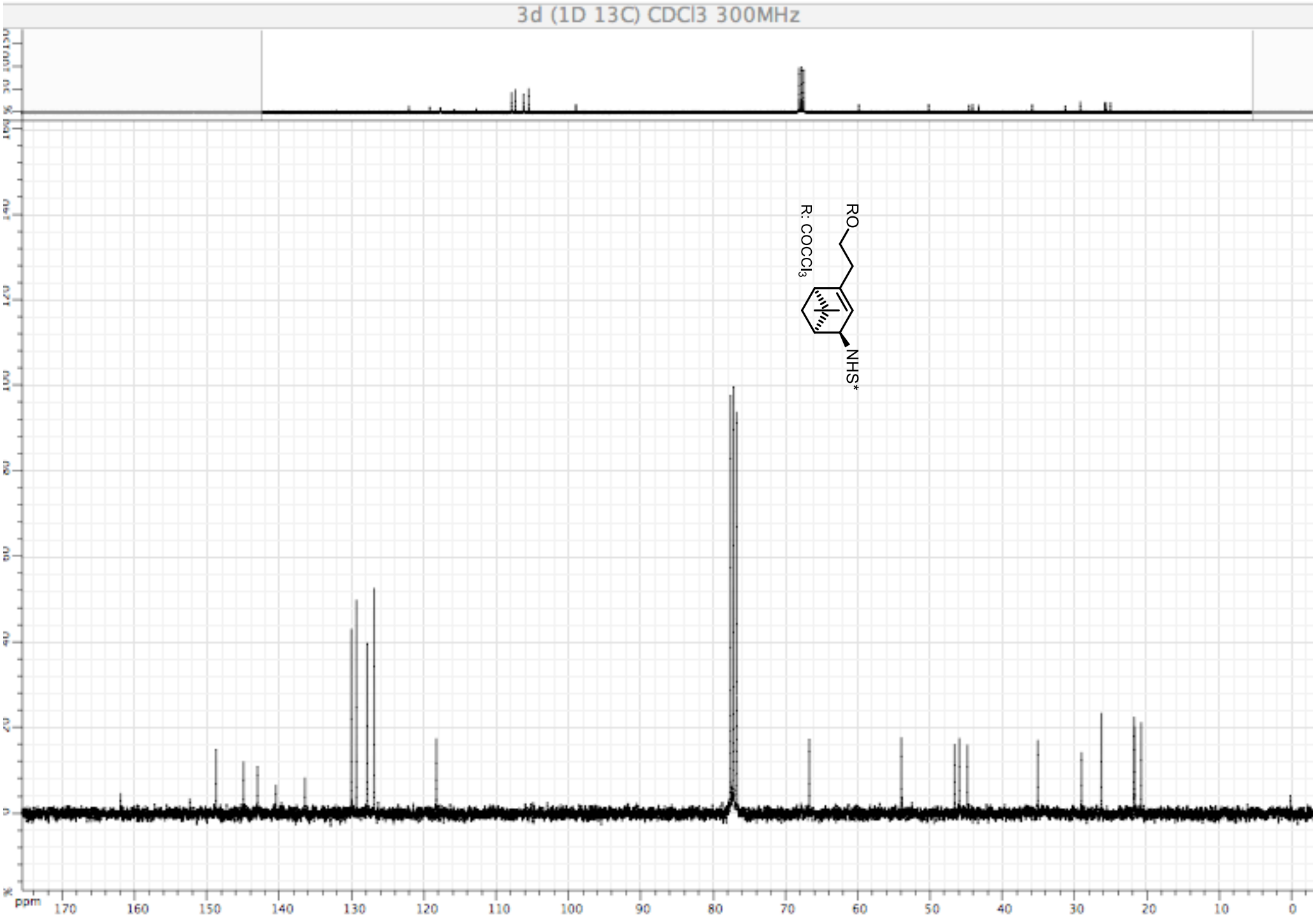
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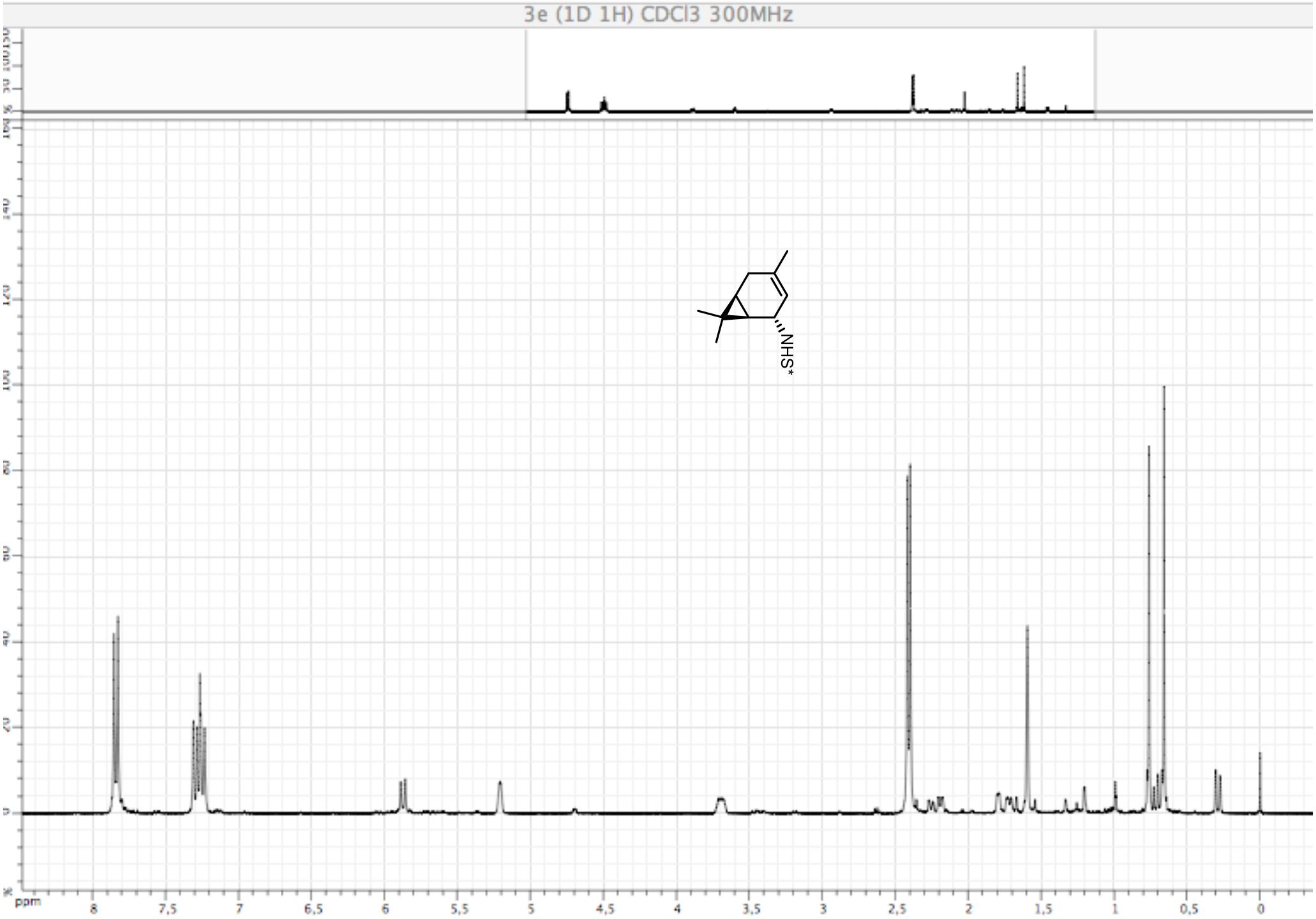
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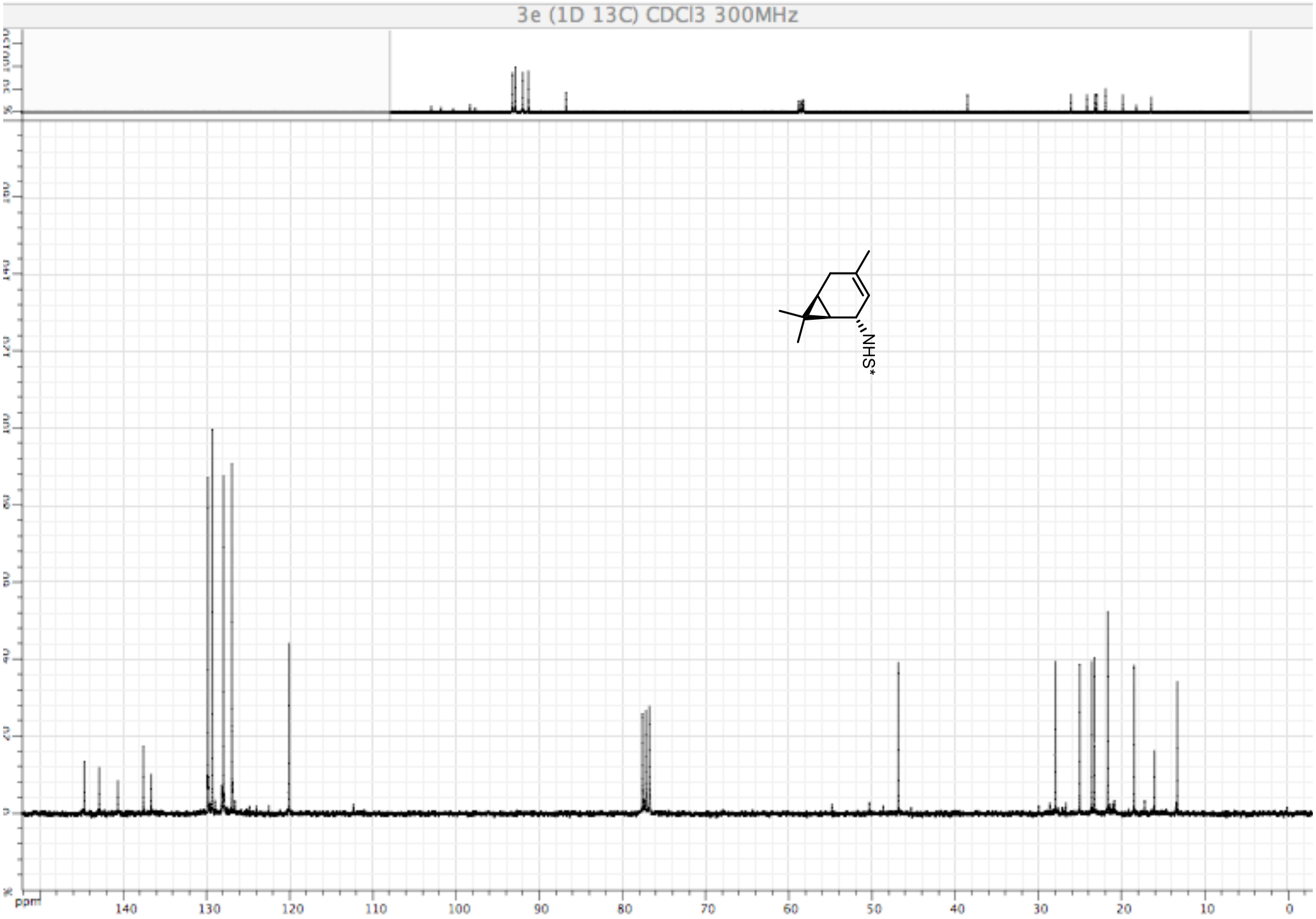
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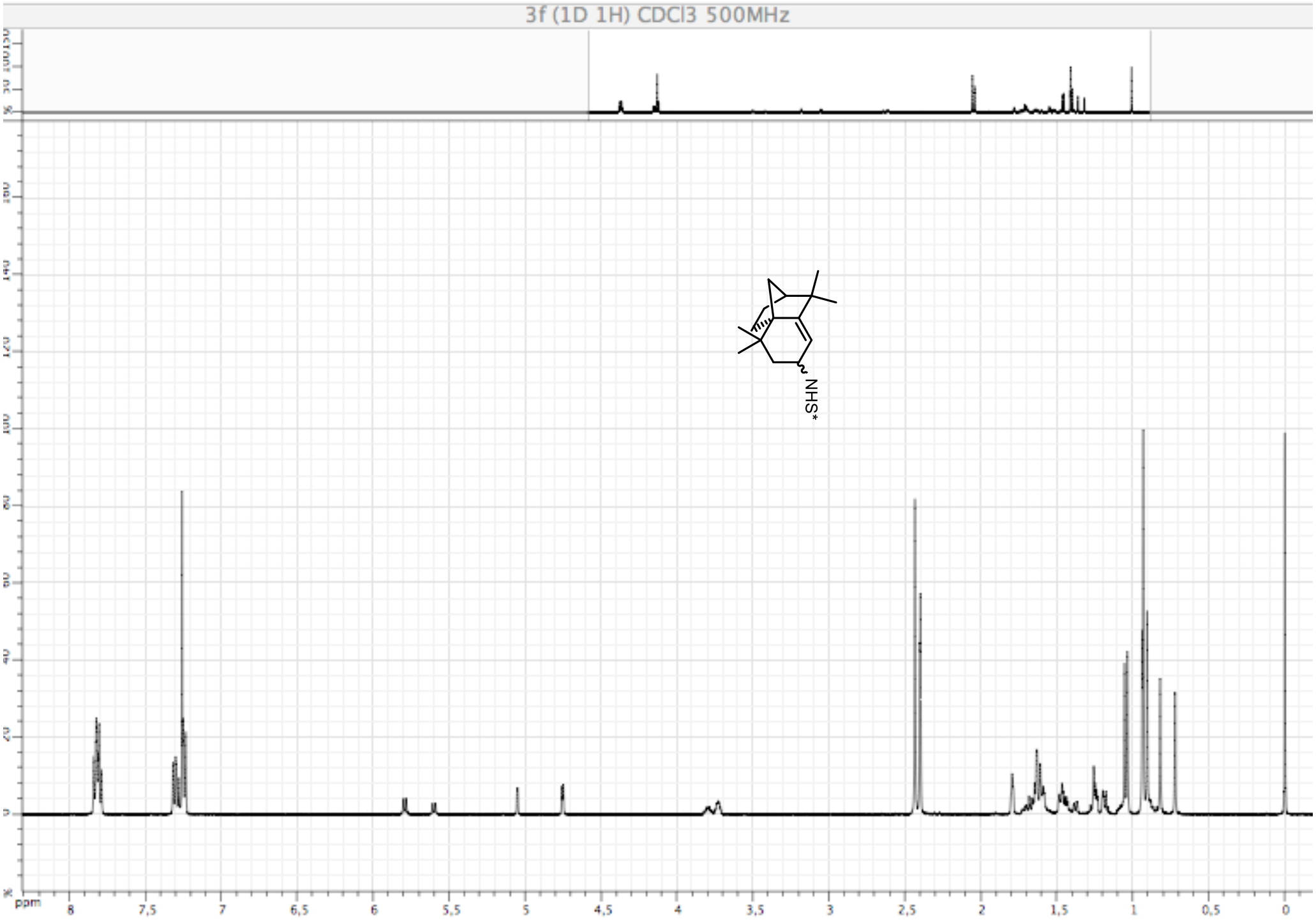
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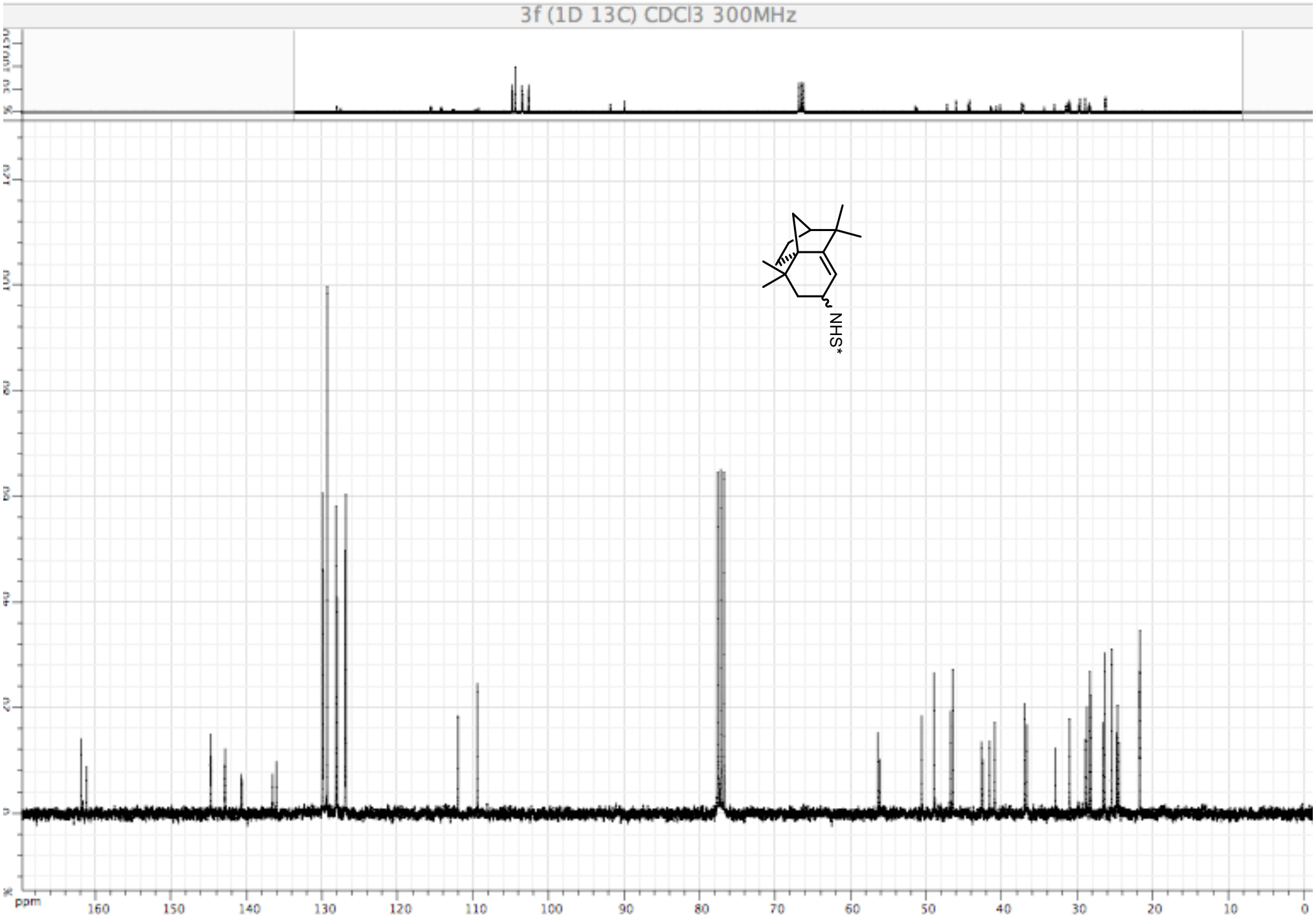
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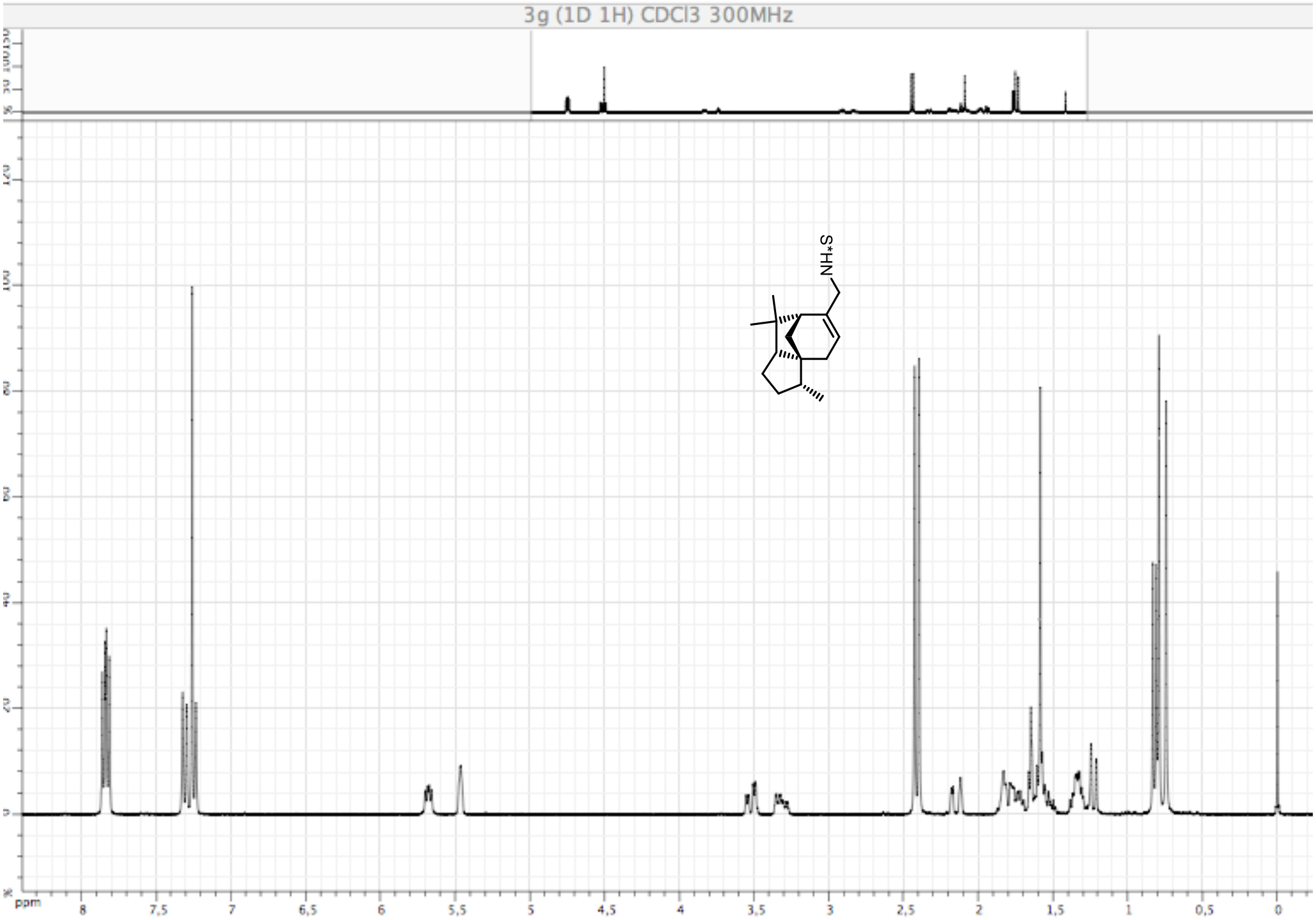
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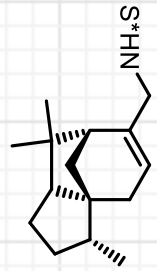

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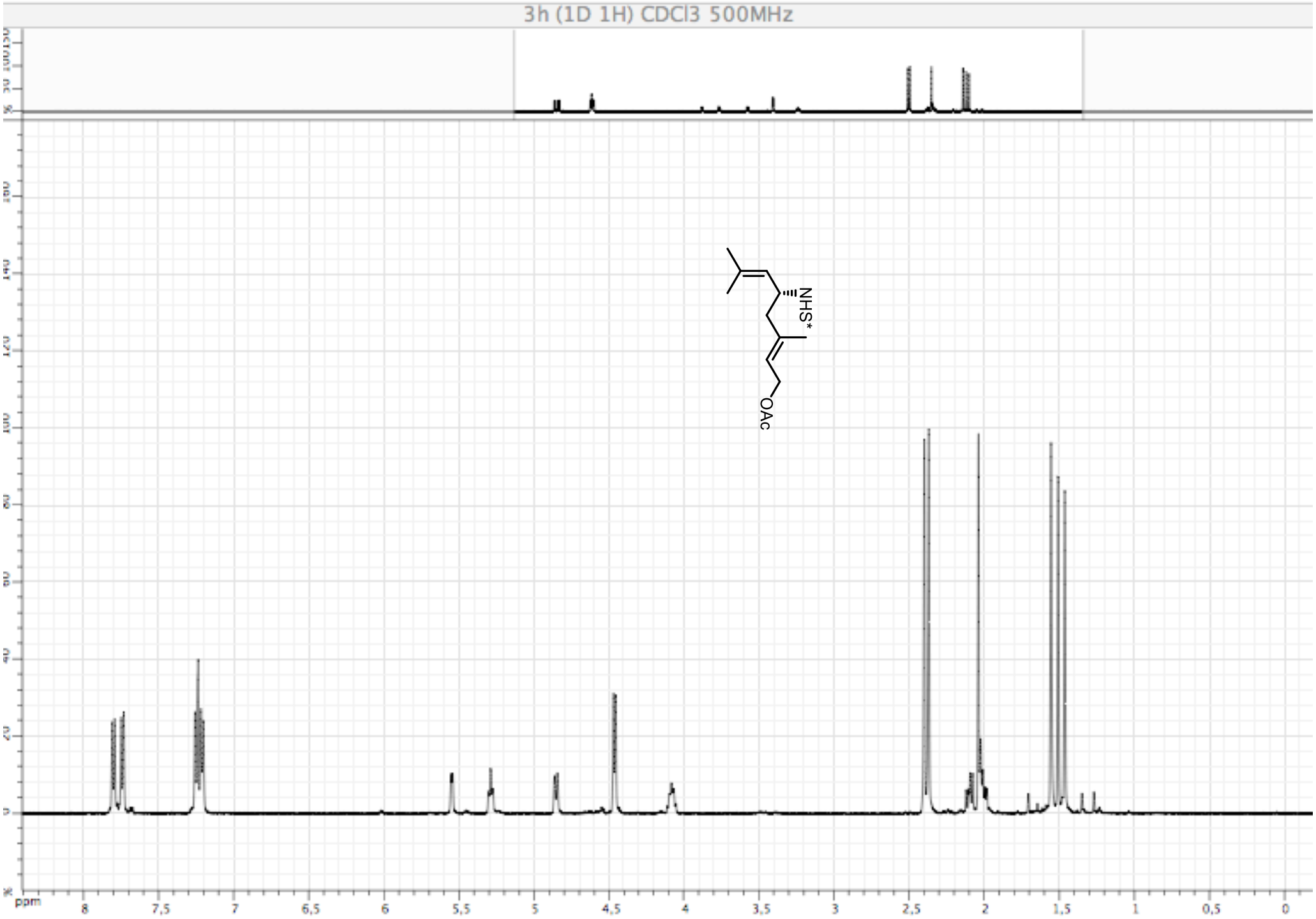
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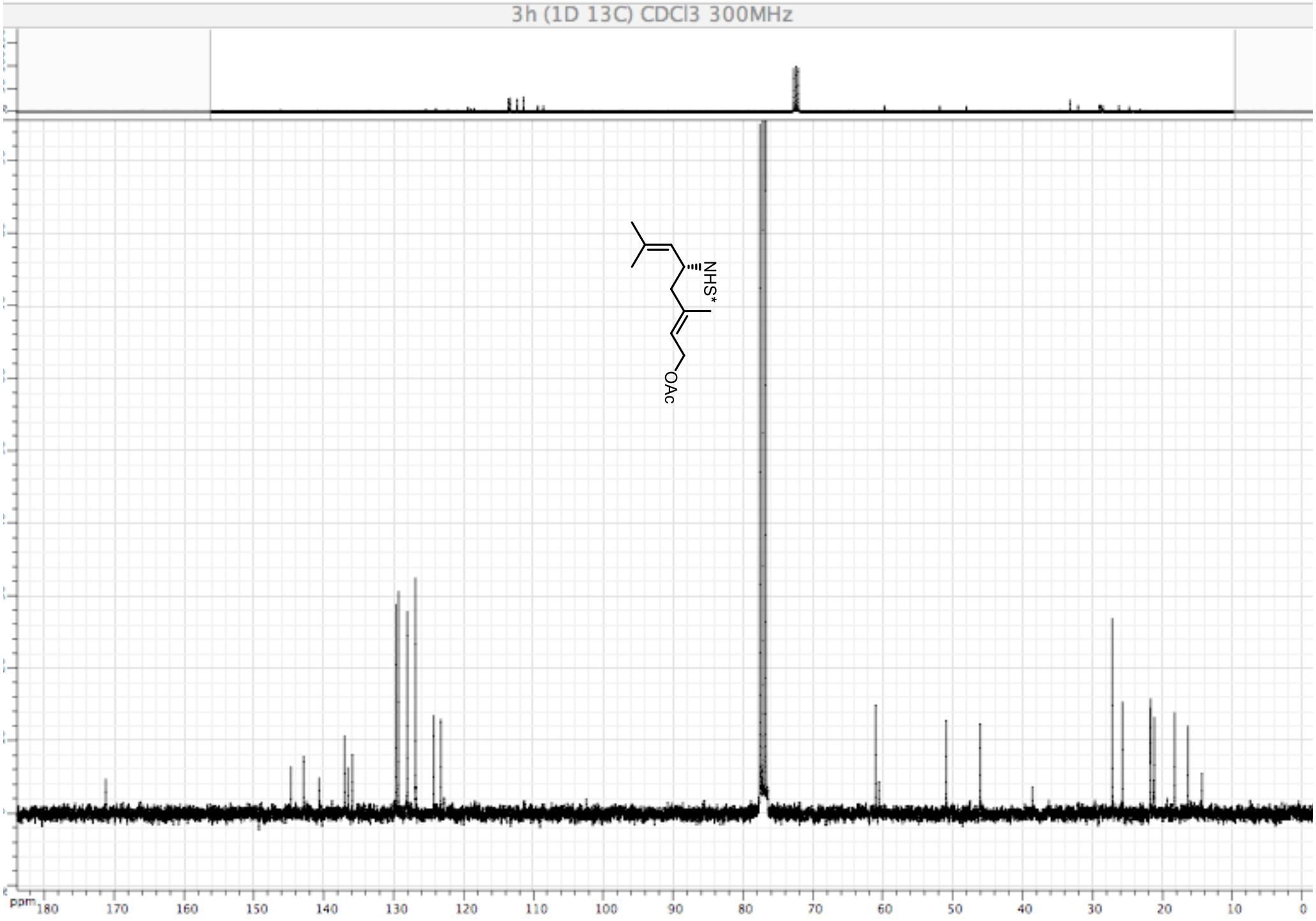
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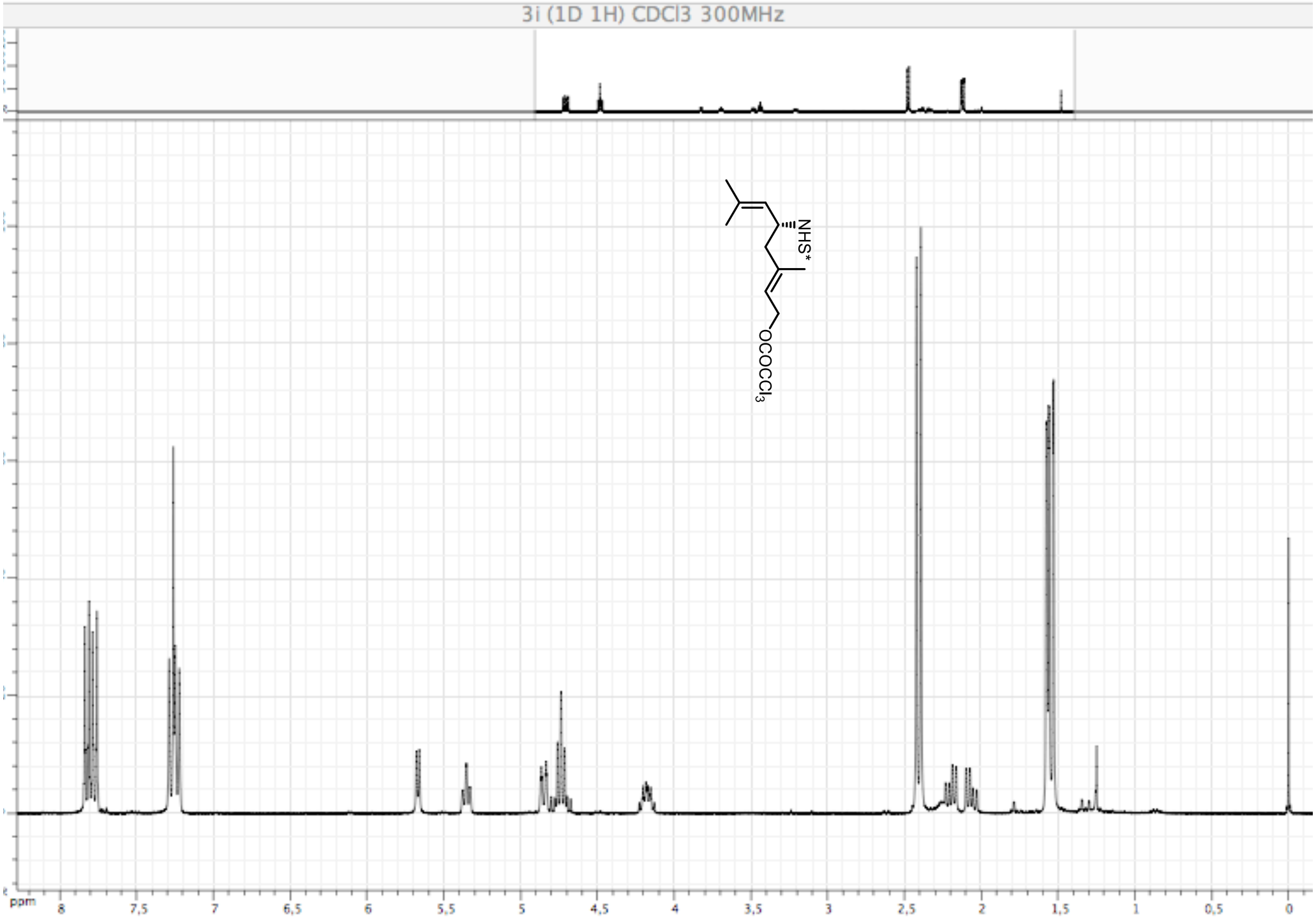
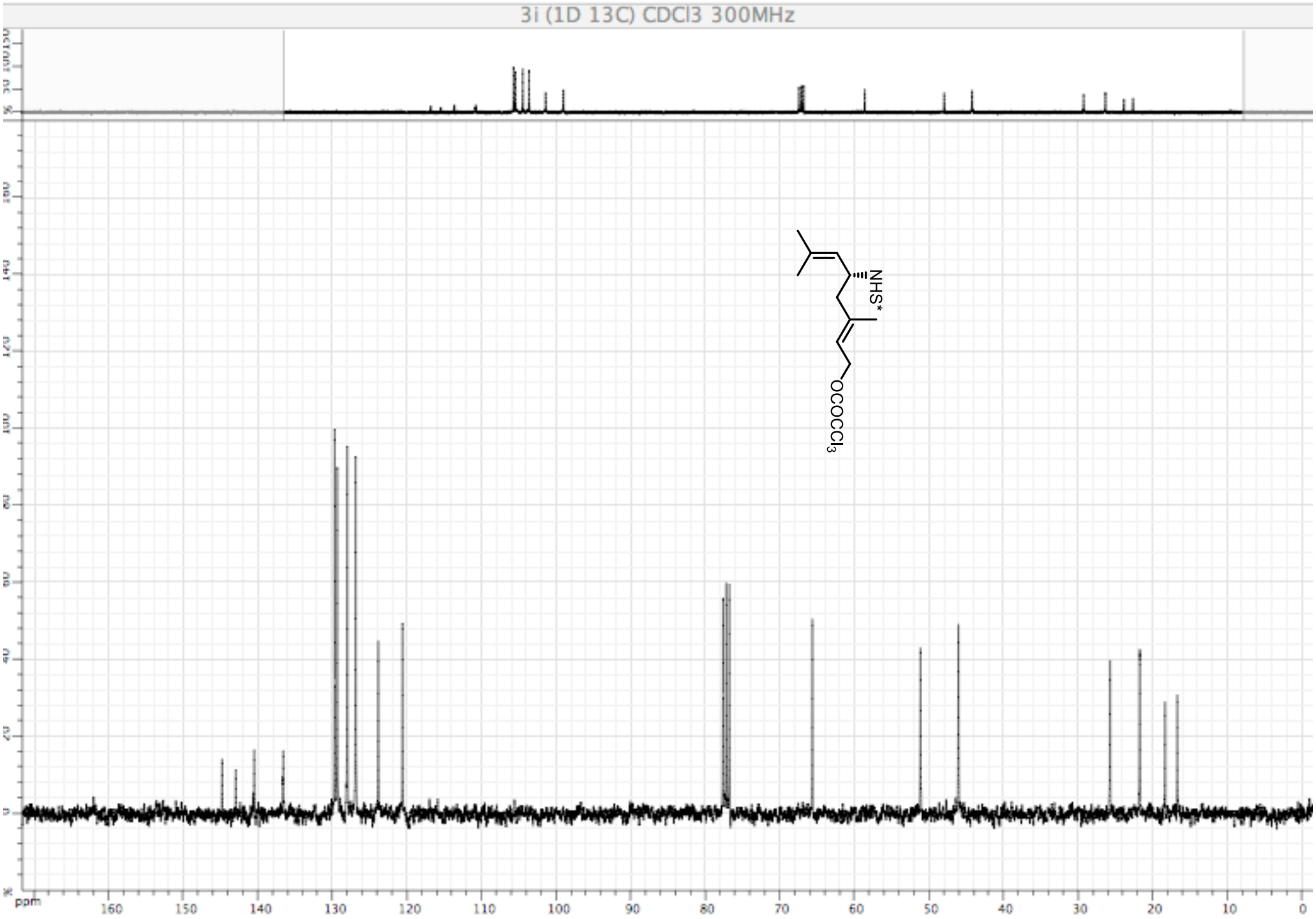
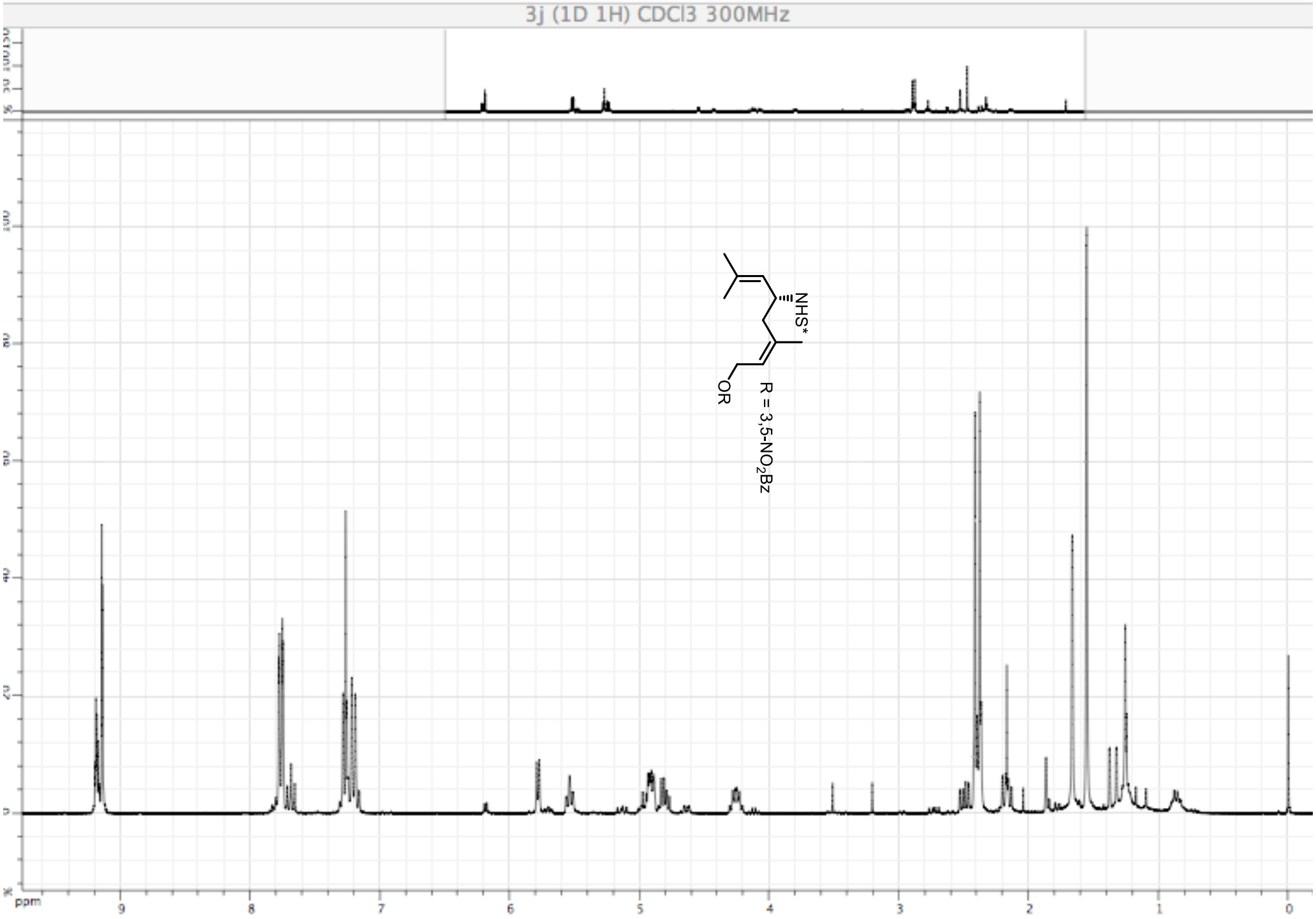
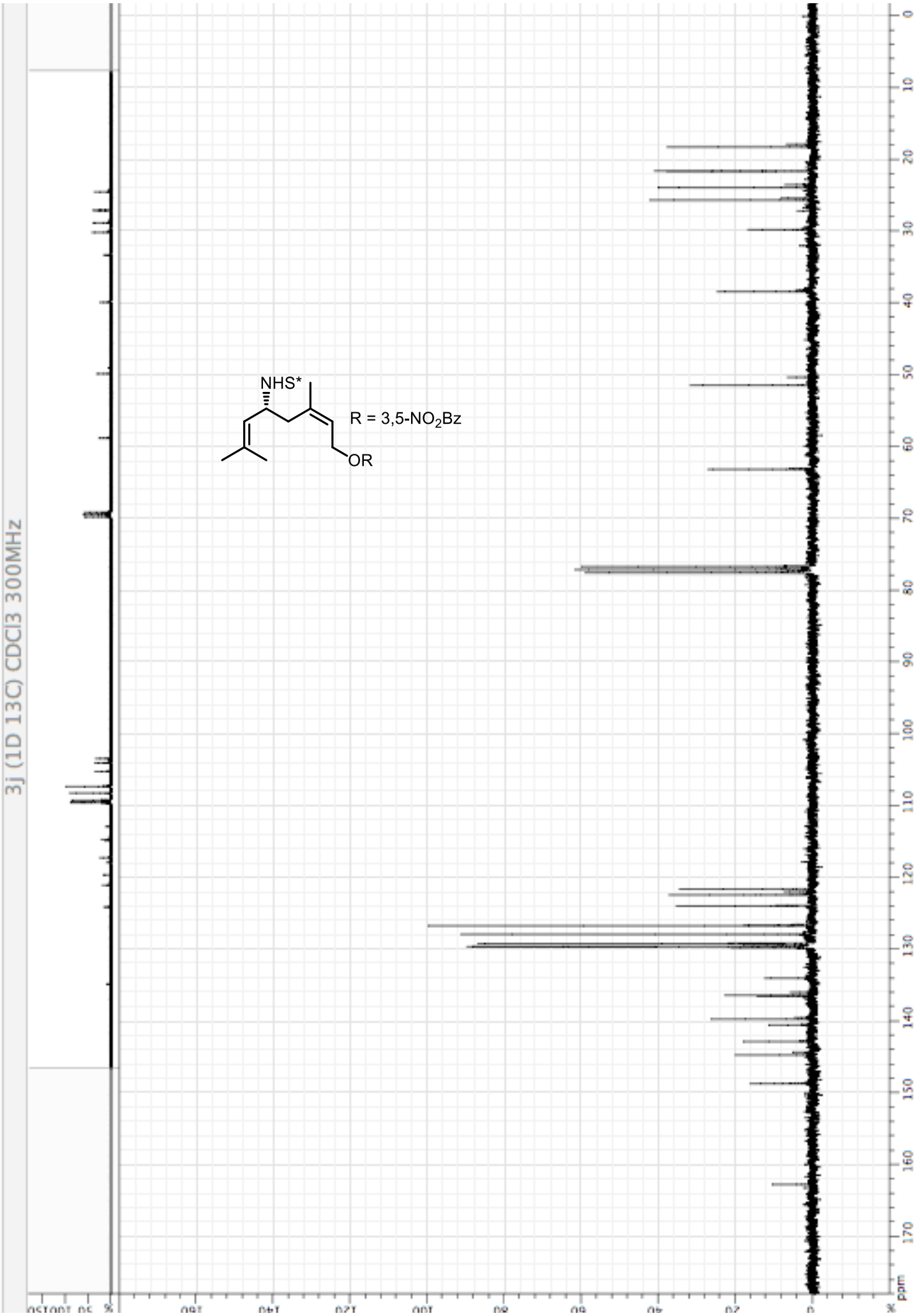
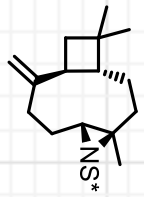

3i (1D 1H) CDCl3 300MHz
NHS*
OCOCCl3
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


3i (1D 13C) CDCl3 300MHz
NHS*
OCOCCl3
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

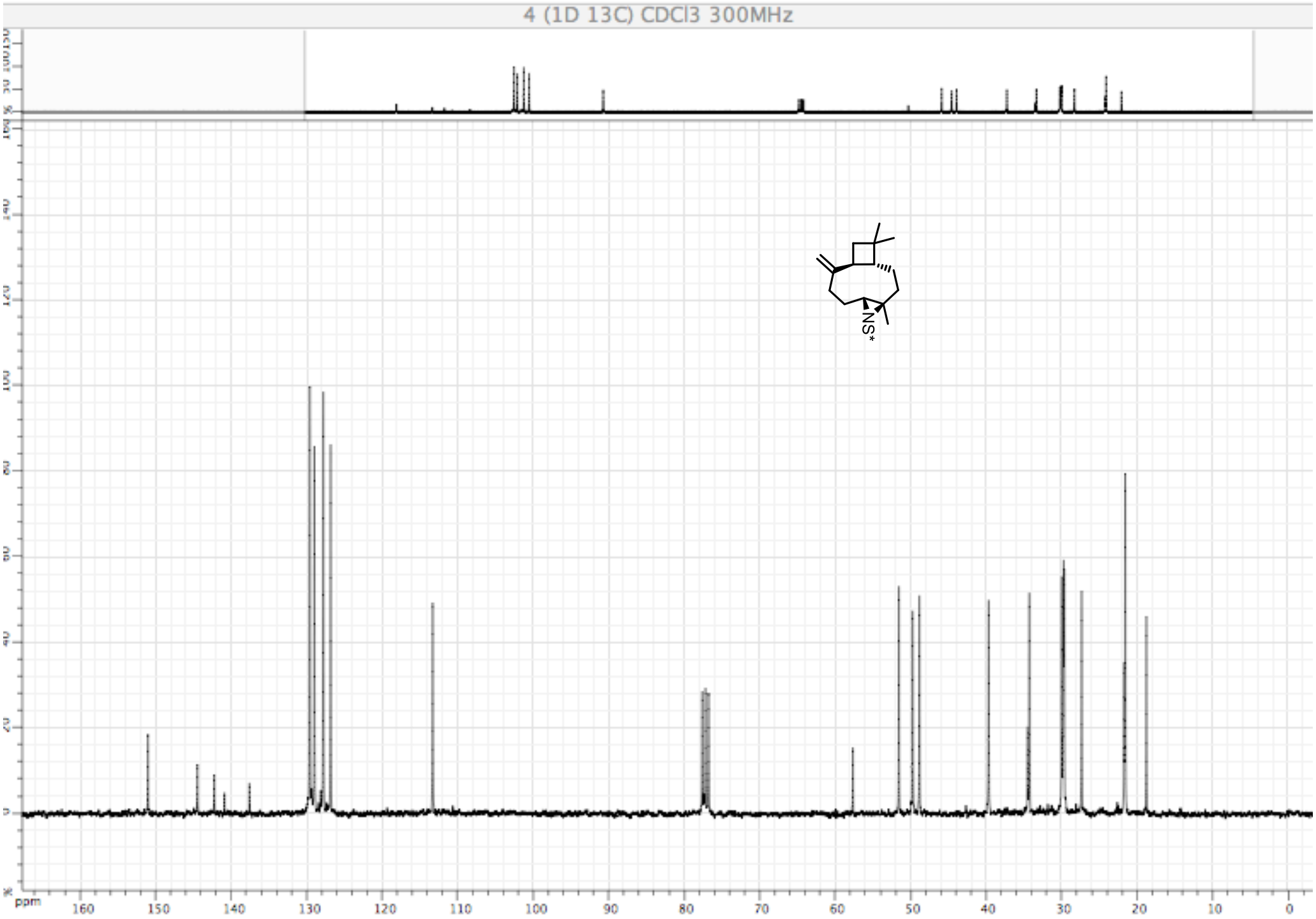

3j (1D 1H) CDCl3 300MHz
NHS*
OR
R = 3,5-NO2Bz
ppm
9
8
7
6
5
4
3
2
1
0

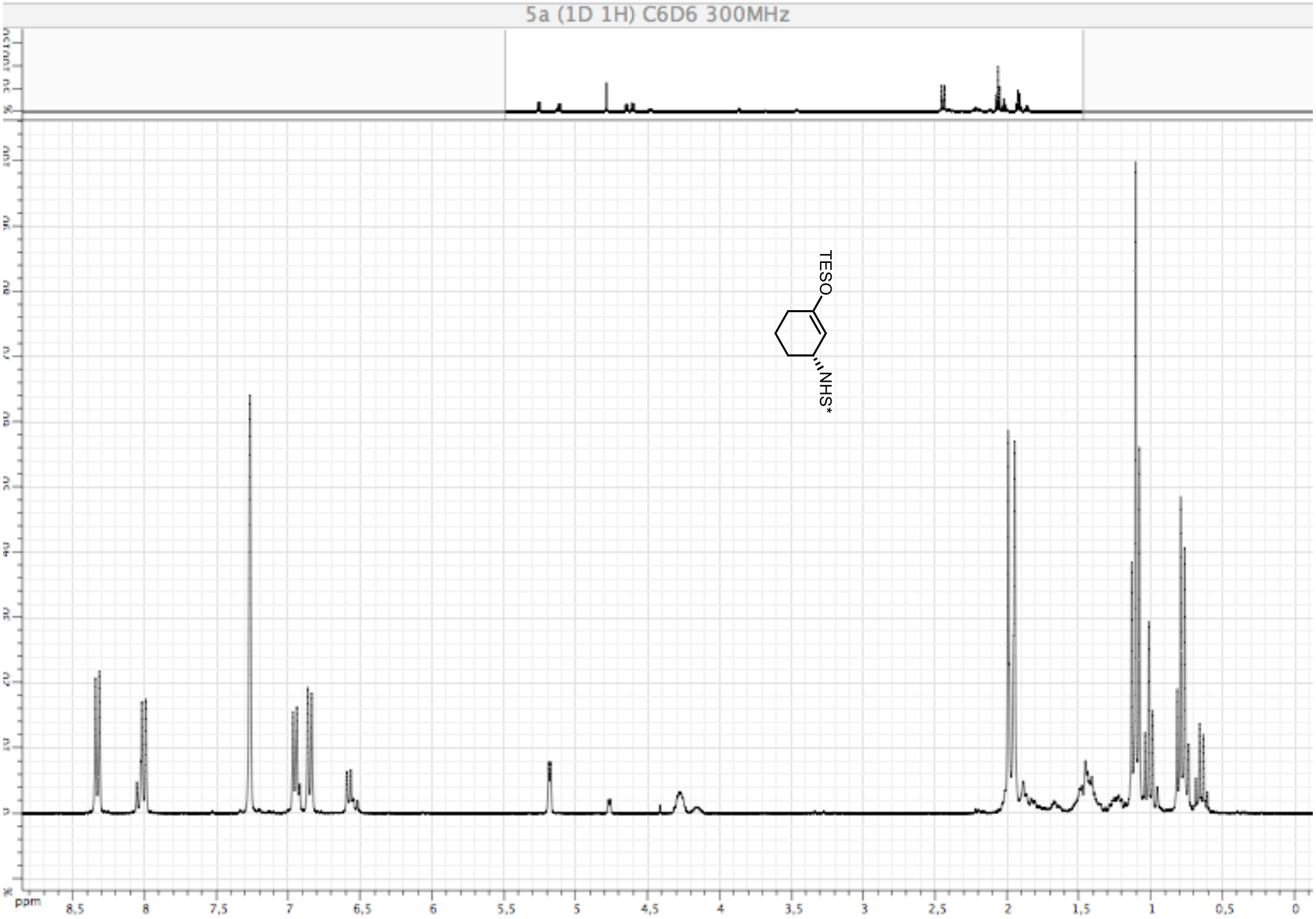

3j (1D 13C) CDCl3 300MHz
NHS*
R = 3,5-NO2Bz
OR
ppm

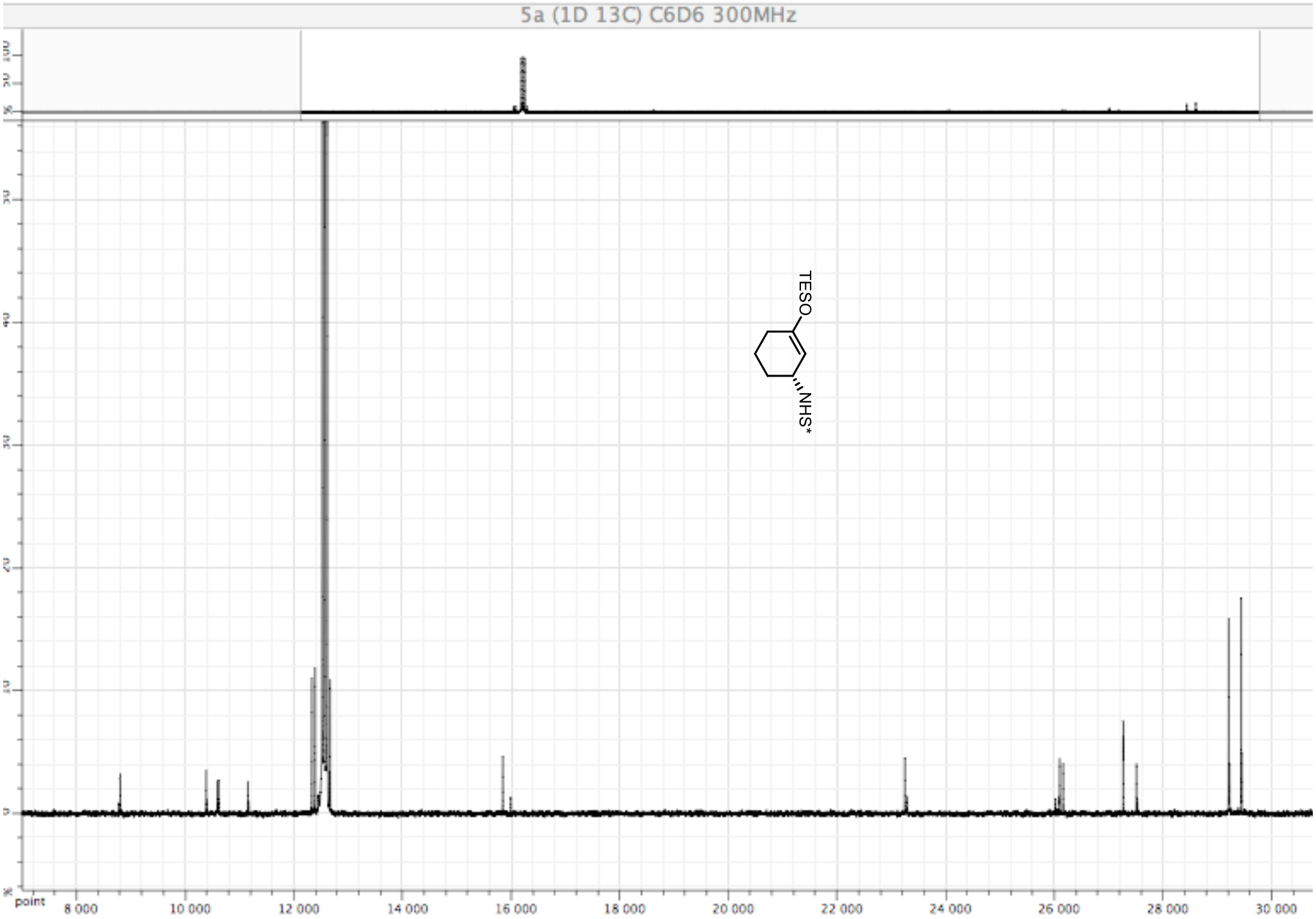
4 (1D 1H) CDCl3 300MHz

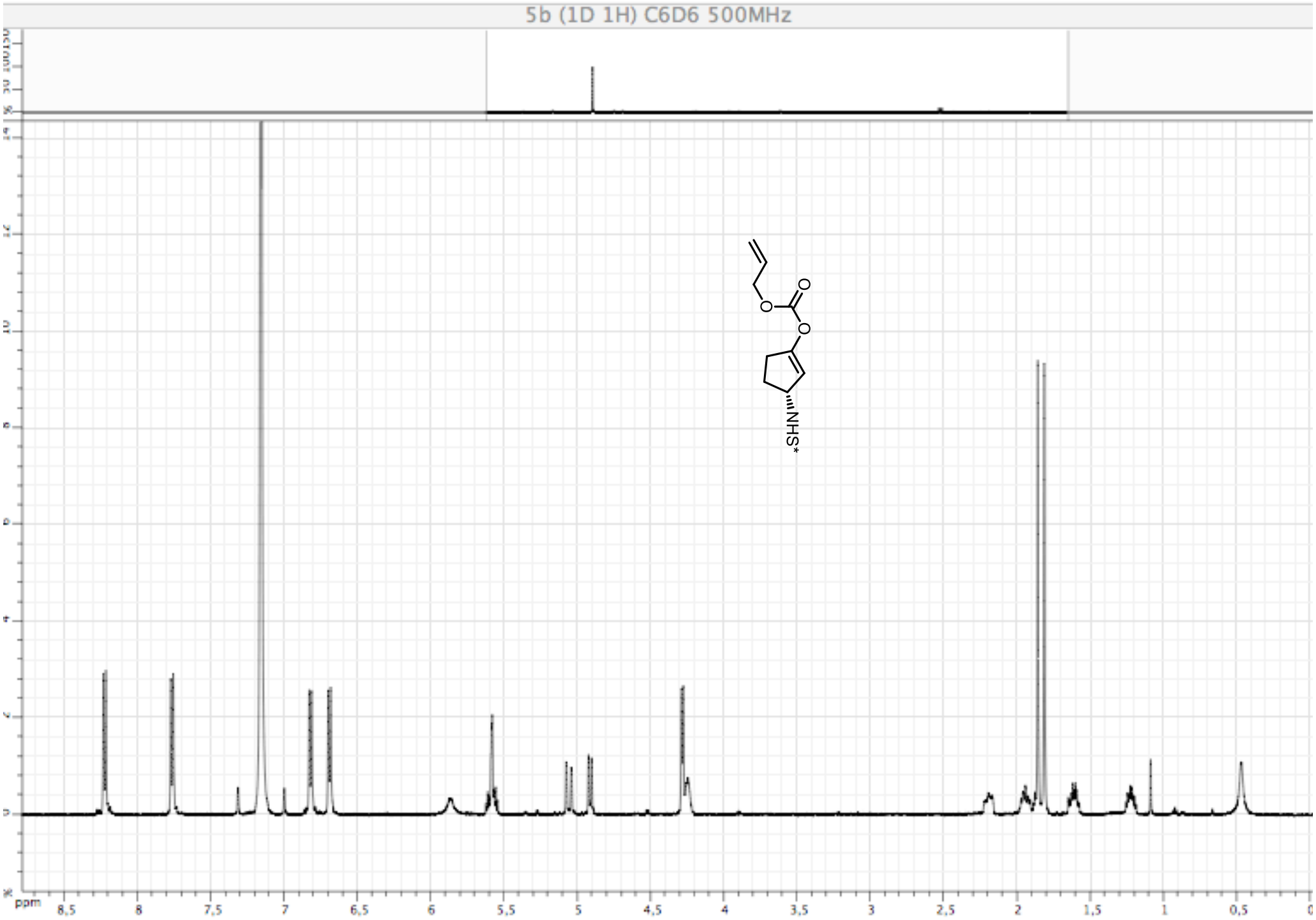


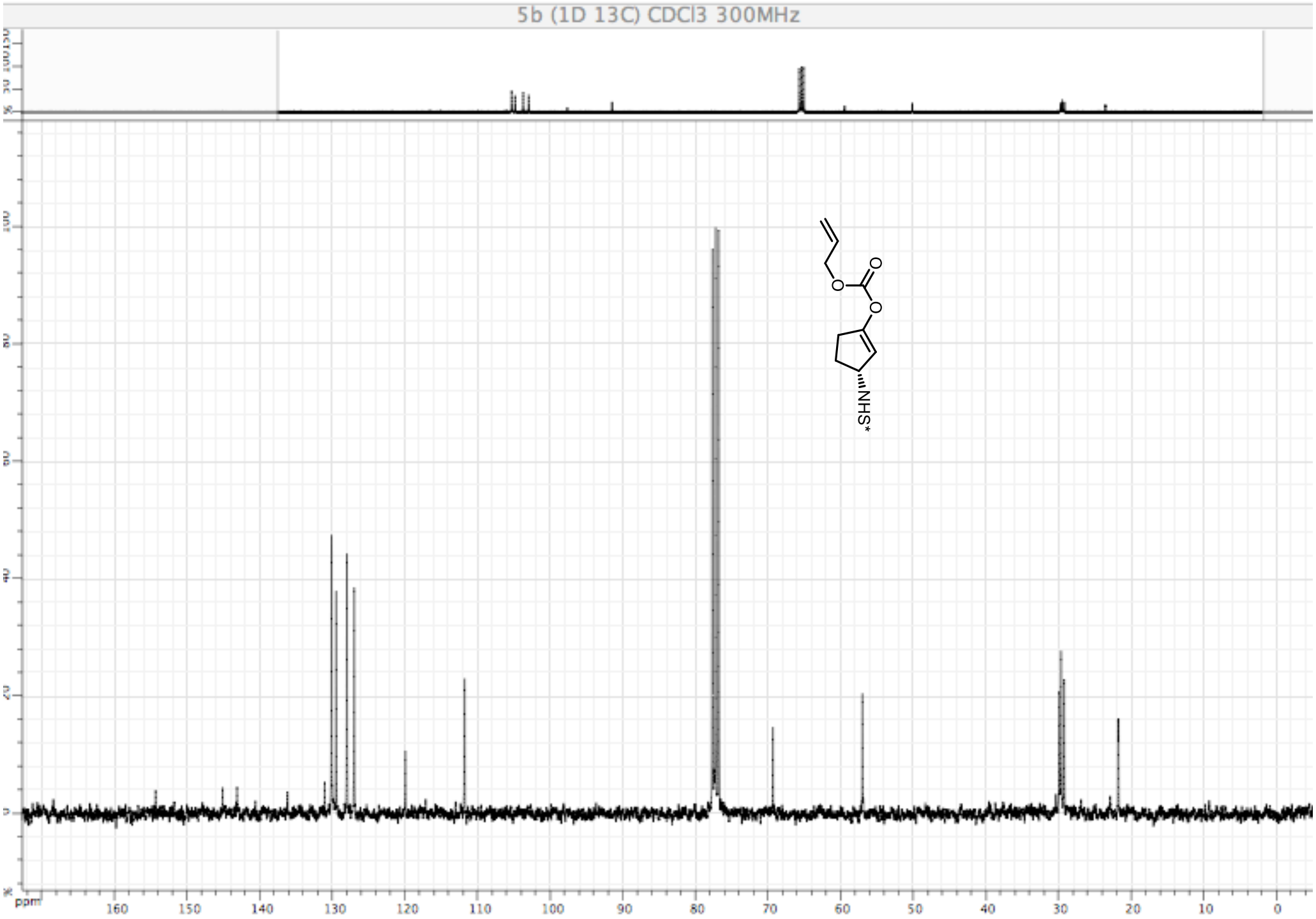
ppm 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0

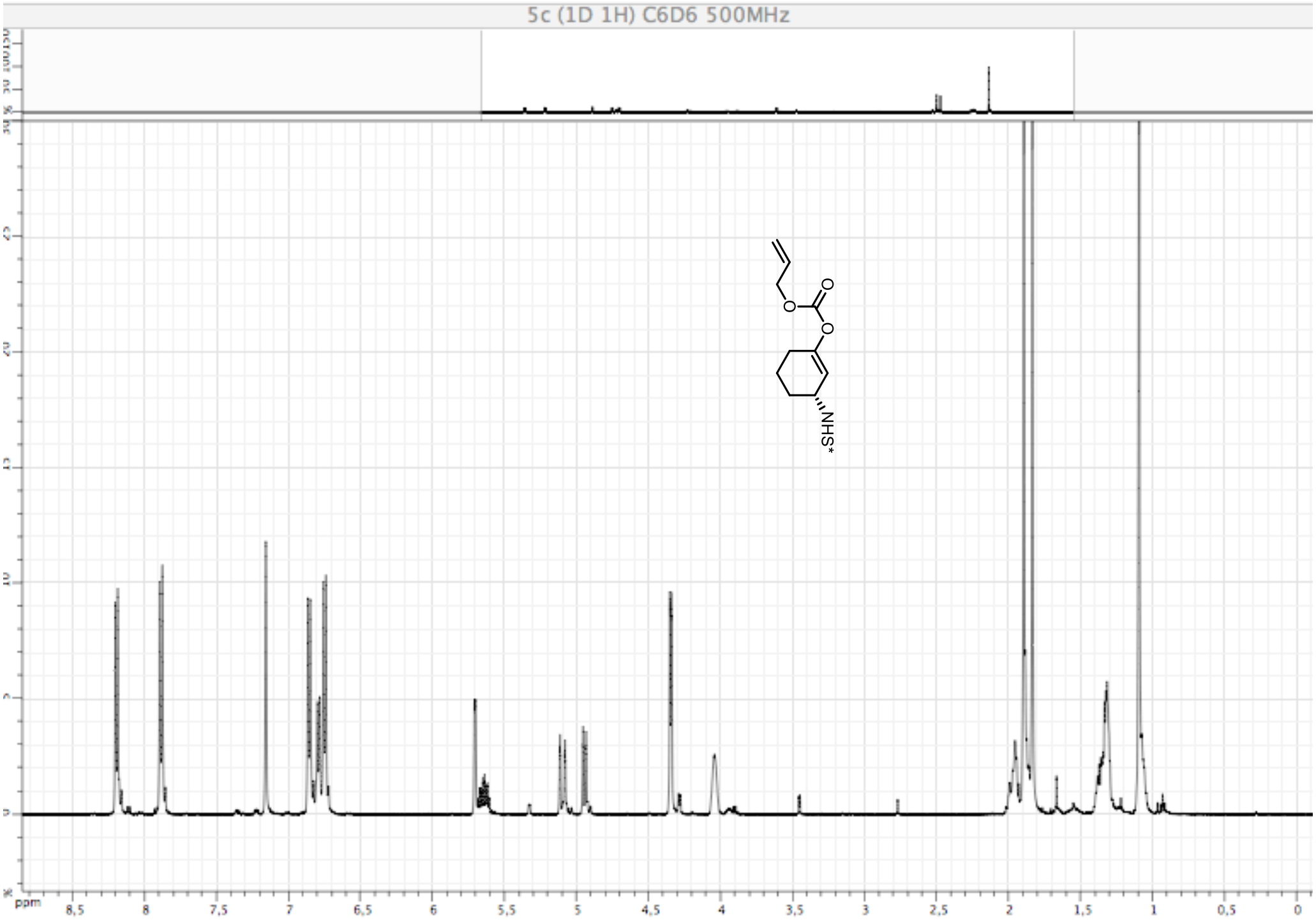

4 (1D 13C) CDCl3 300MHz
NS*
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

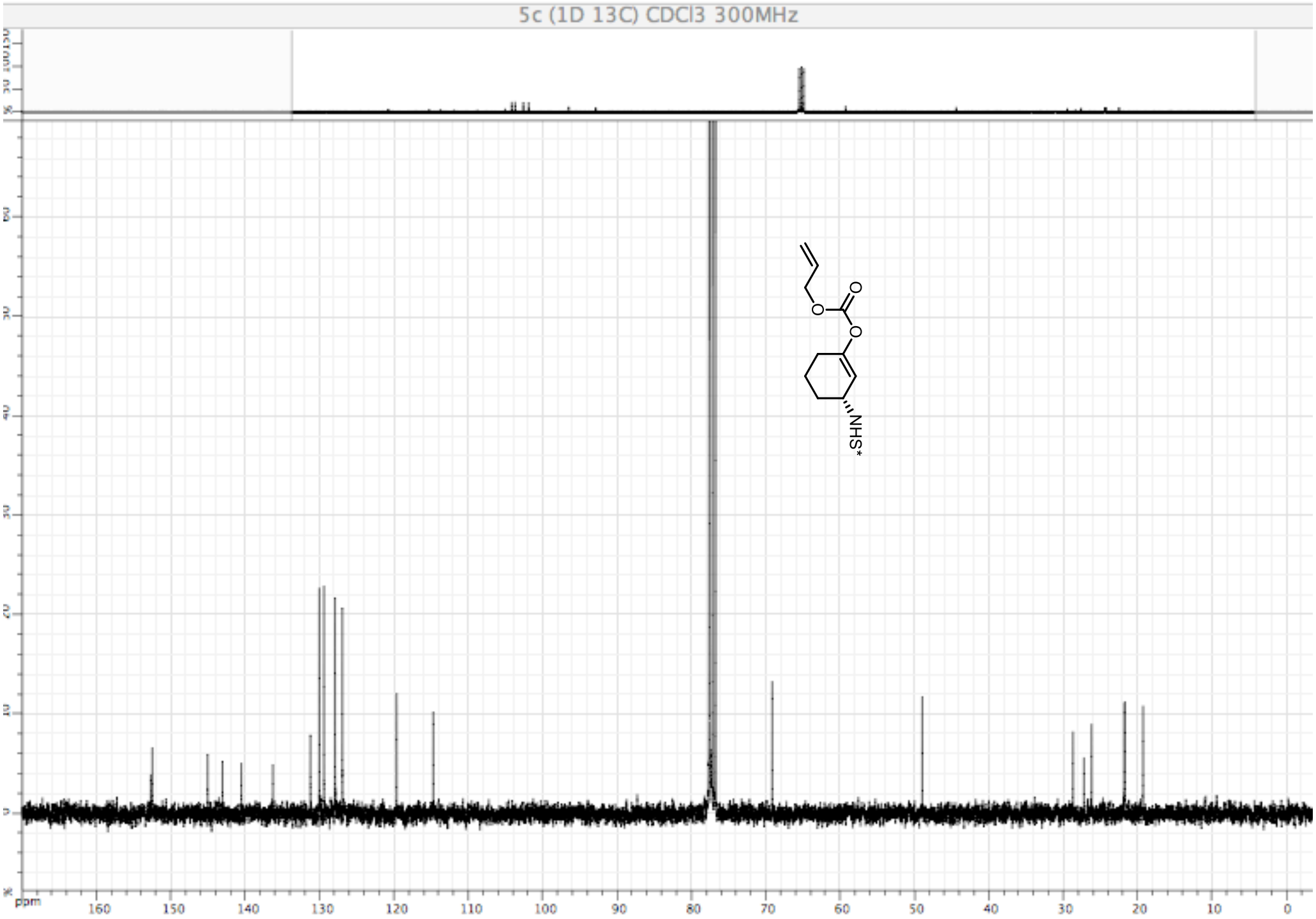

5a (1D 1H) C6D6 300MHz
TESO
NHS*
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


5a (1D 13C) C6D6 300MHz
TESO
NHS*
point
8 000
10 000
12 000
14 000
16 000
18 000
20 000
22 000
24 000
26 000
28 000
30 000

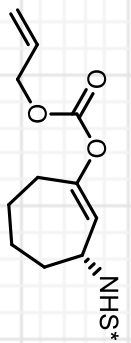

5b (1D 1H) C6D6 500MHz
O
O
O
NHS*
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5


5b (1D 13C) CDCl3 300MHz
O
O
O
NHS*
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

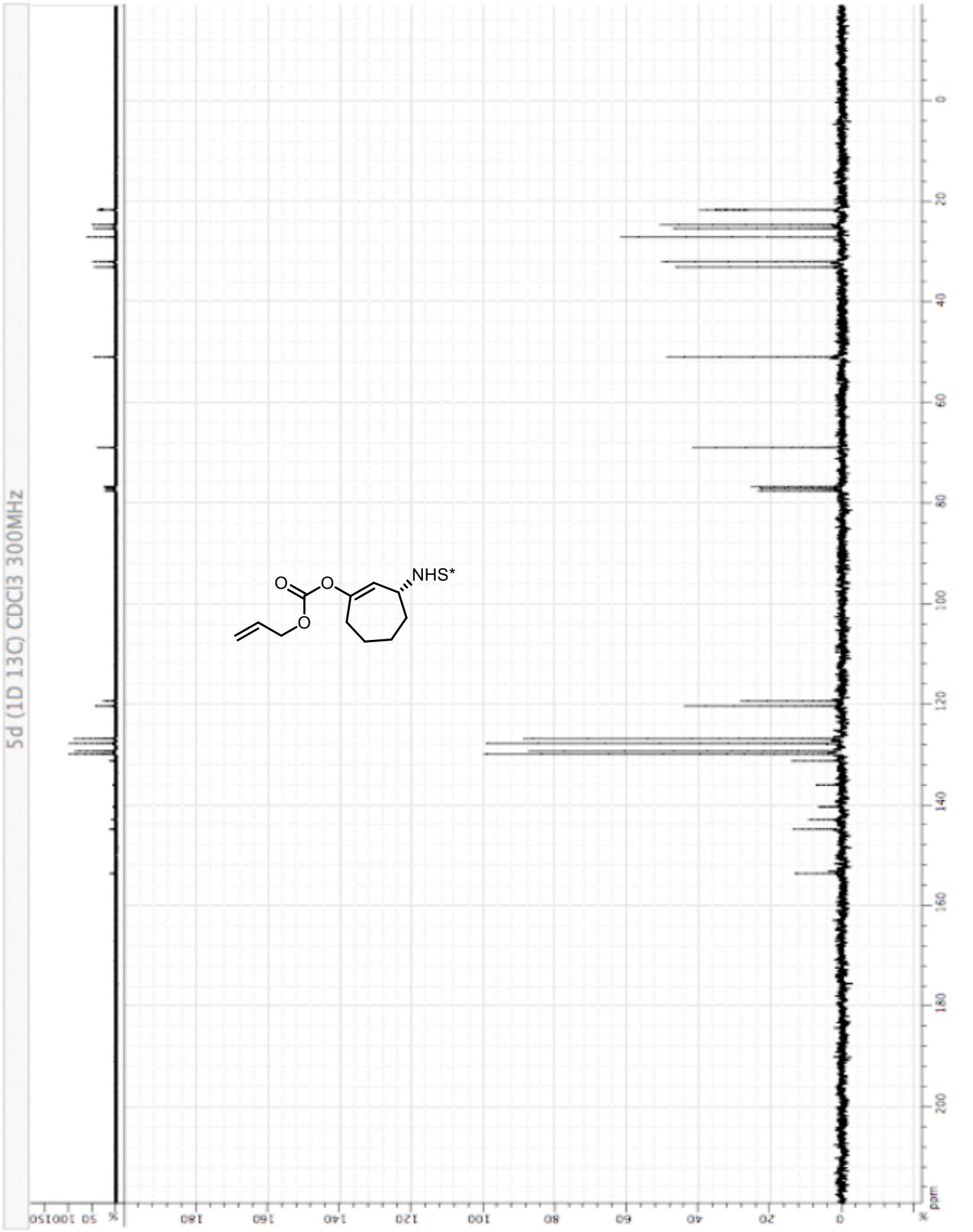

5c (1D 1H) C6D6 500MHz
NHS*
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

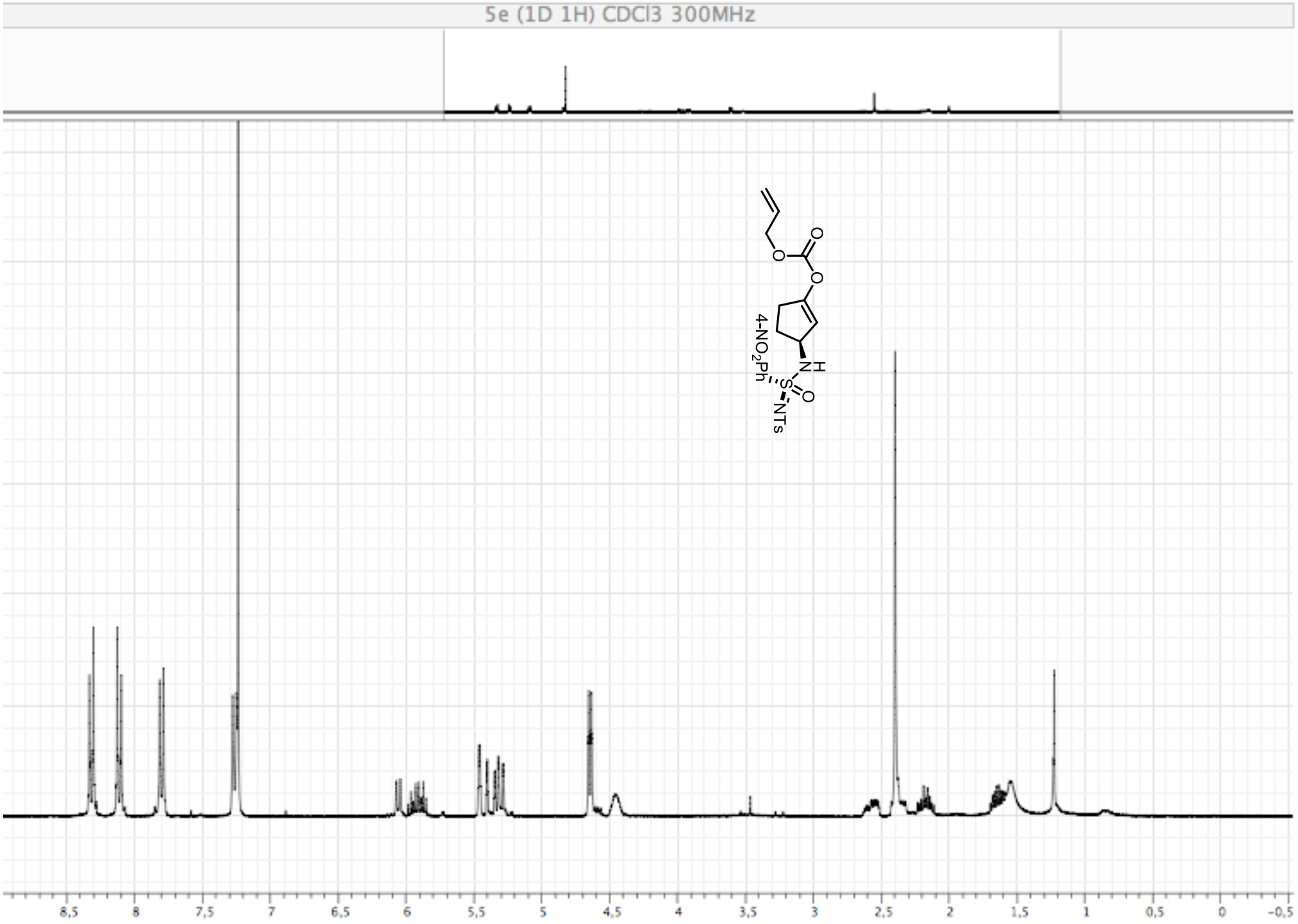

5c (1D 13C) CDCl3 300MHz
NHS*
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

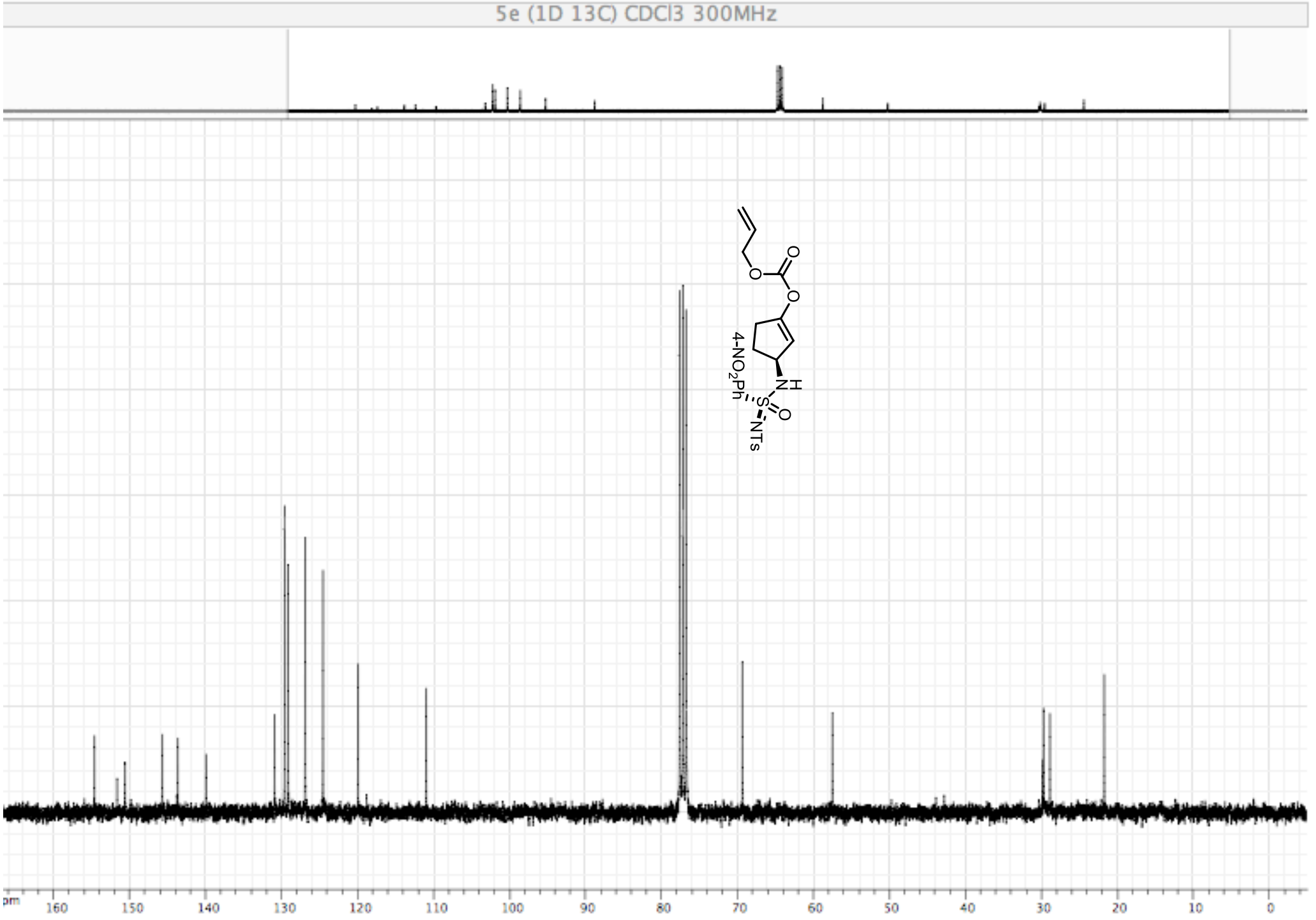
5d (1D 1H) C6D6 300MHz

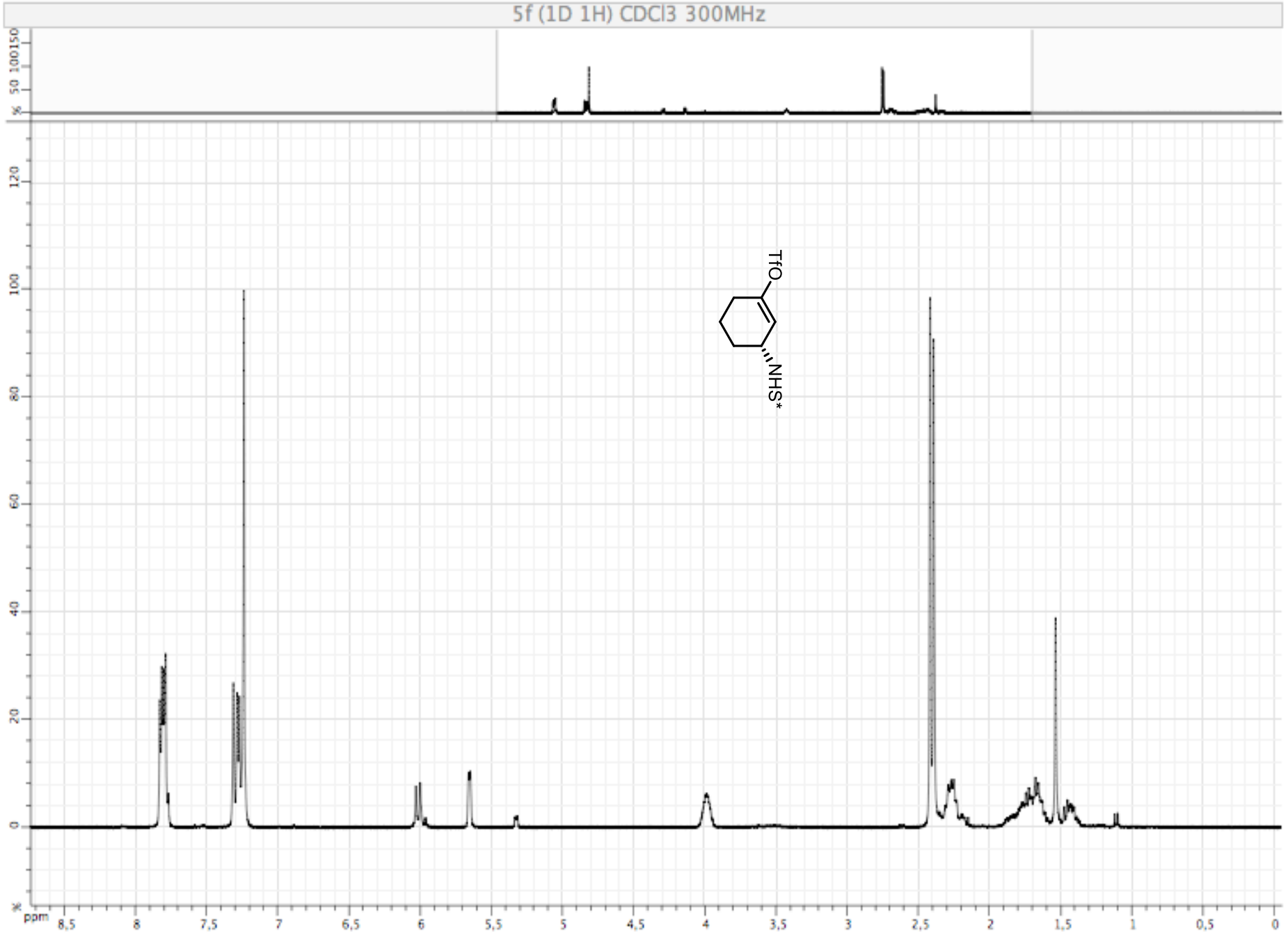


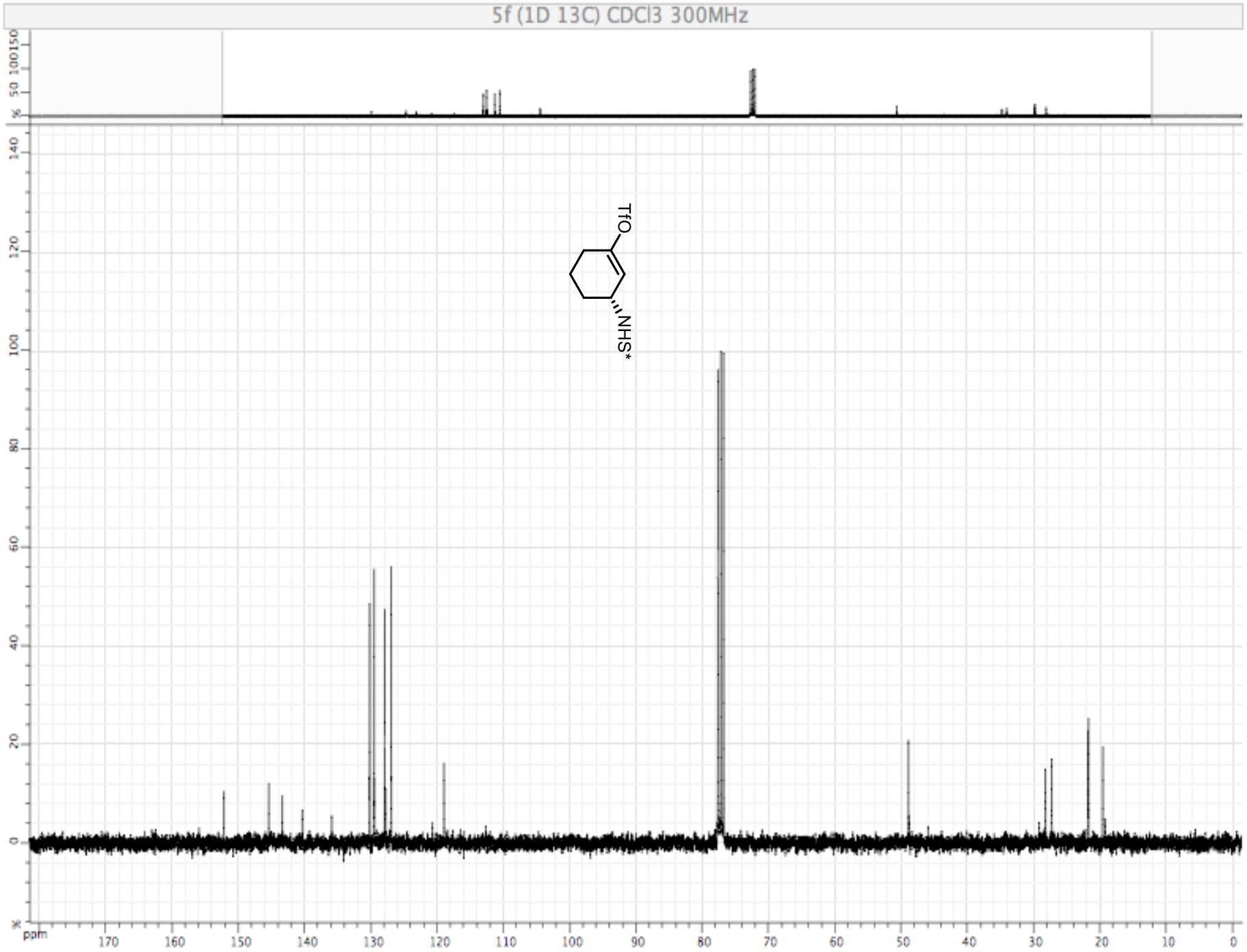
ppm
8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0

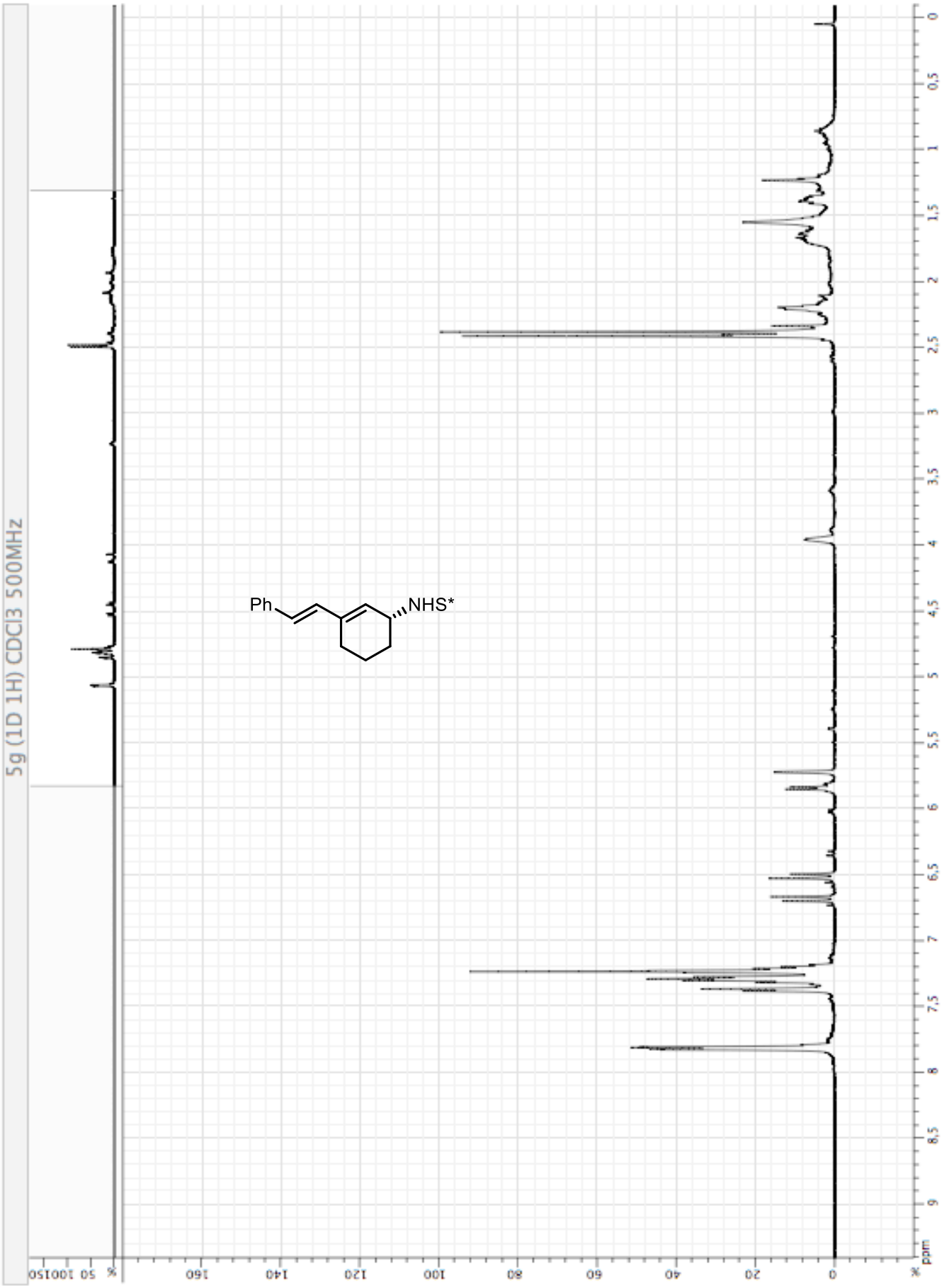

5d (1D 13C) CDCl3 300MHz
NHS*
O
O
O
O
ppm

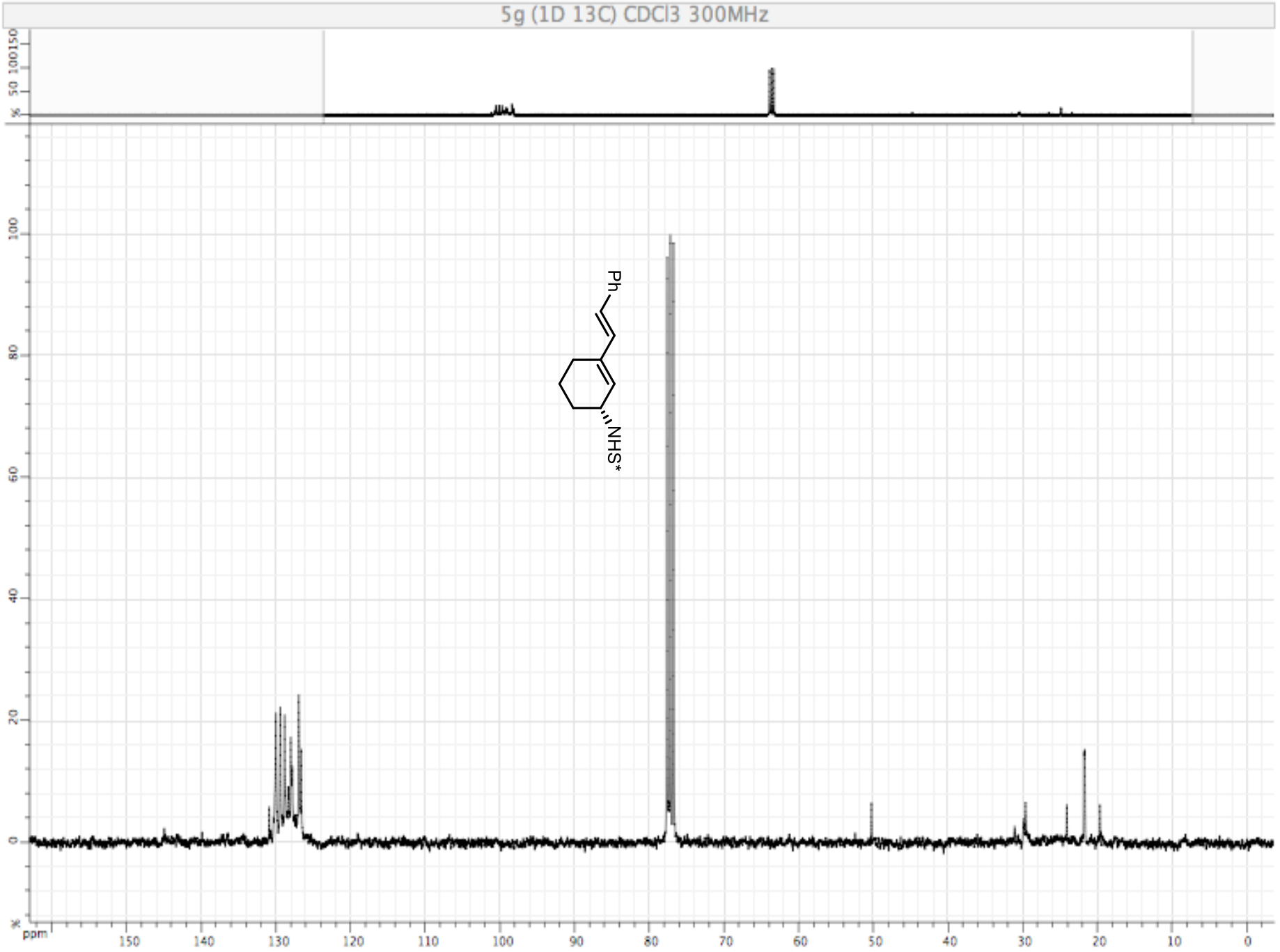

5e (1D 1H) CDCl3 300MHz
4-NO2Ph
NTs
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
-0,5

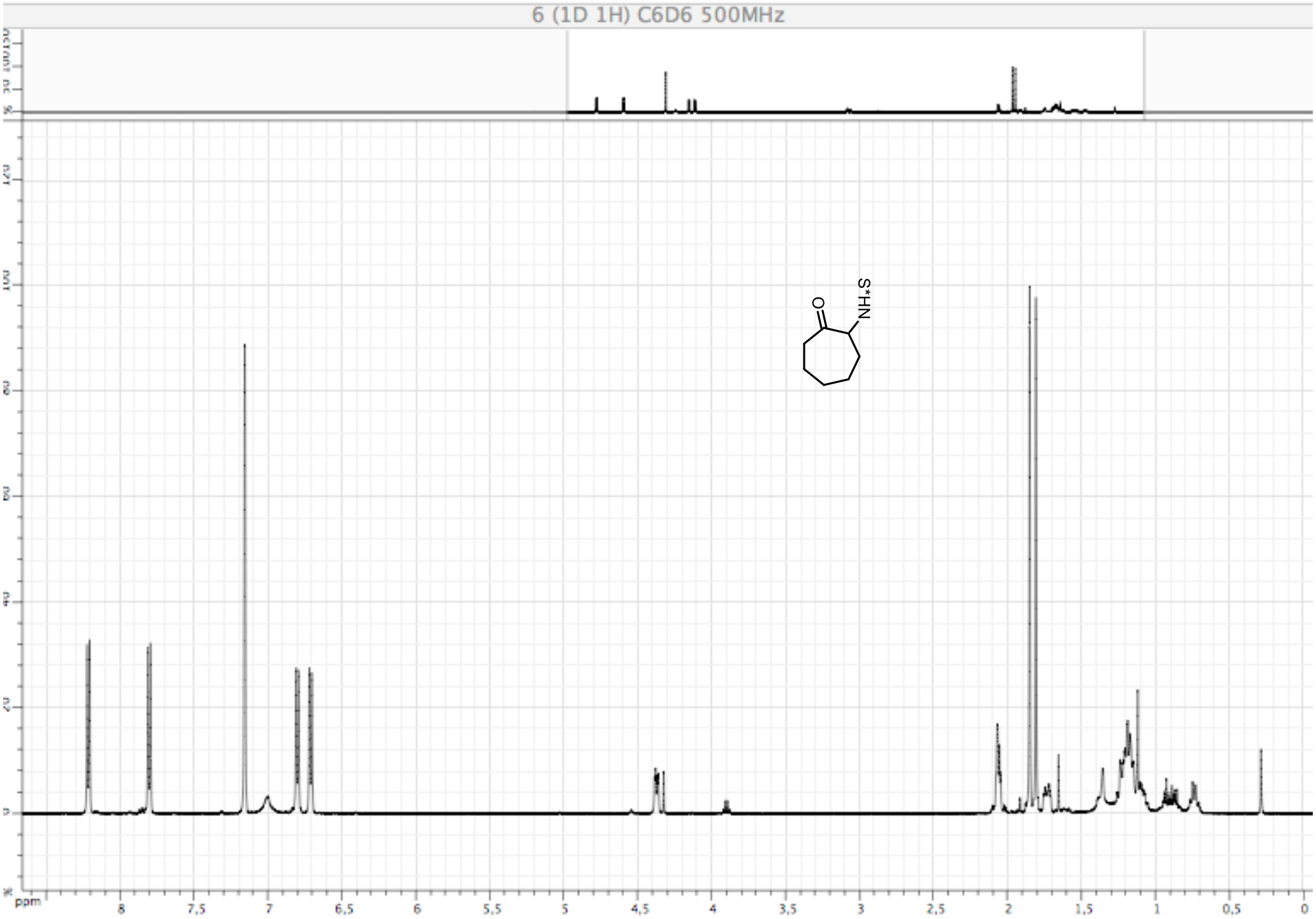

5e (1D 13C) CDCl3 300MHz
4-NO2Ph
NTs
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

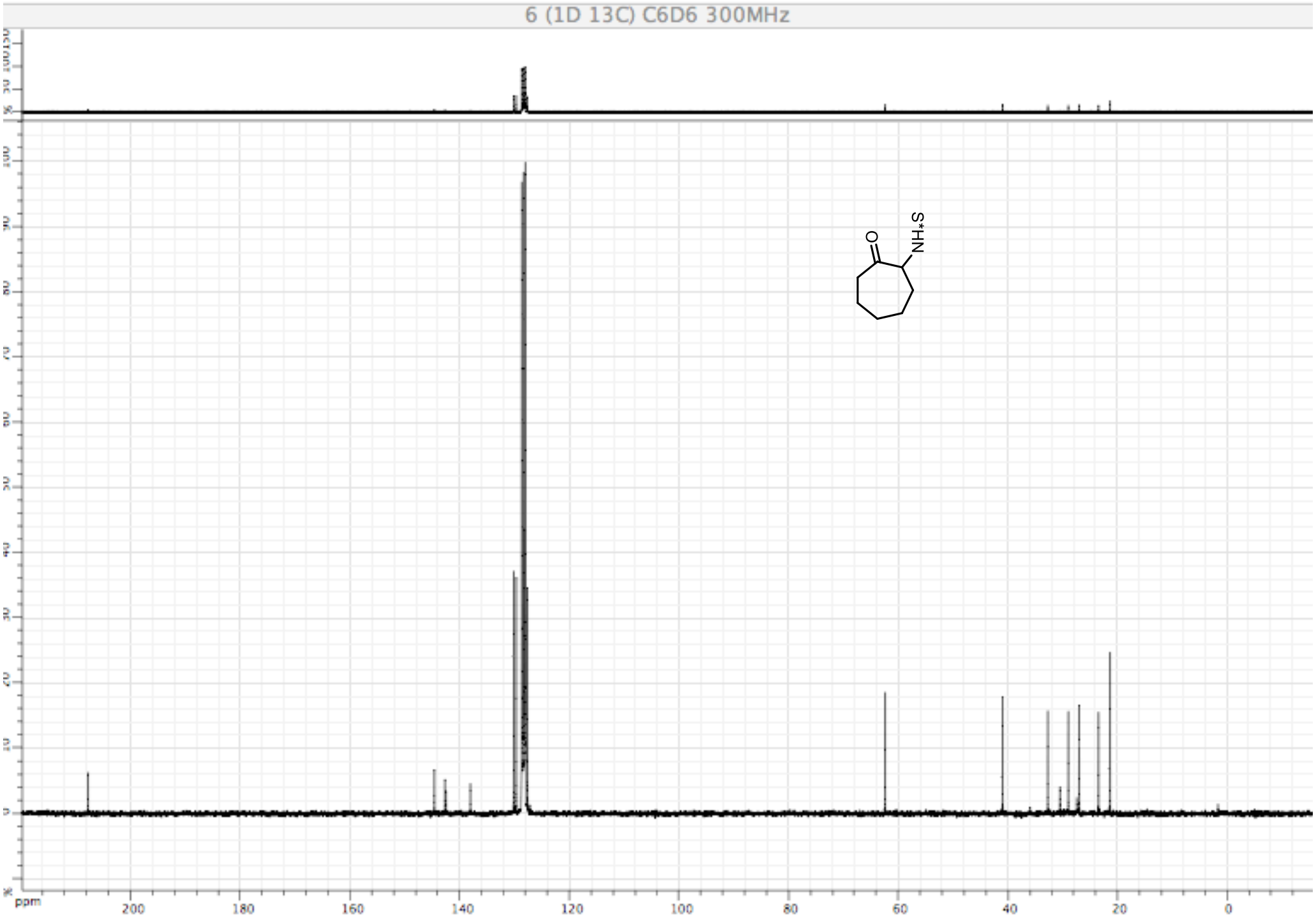

5f (1D 1H) CDCl3 300MHz
TfO
NHS*
ppm

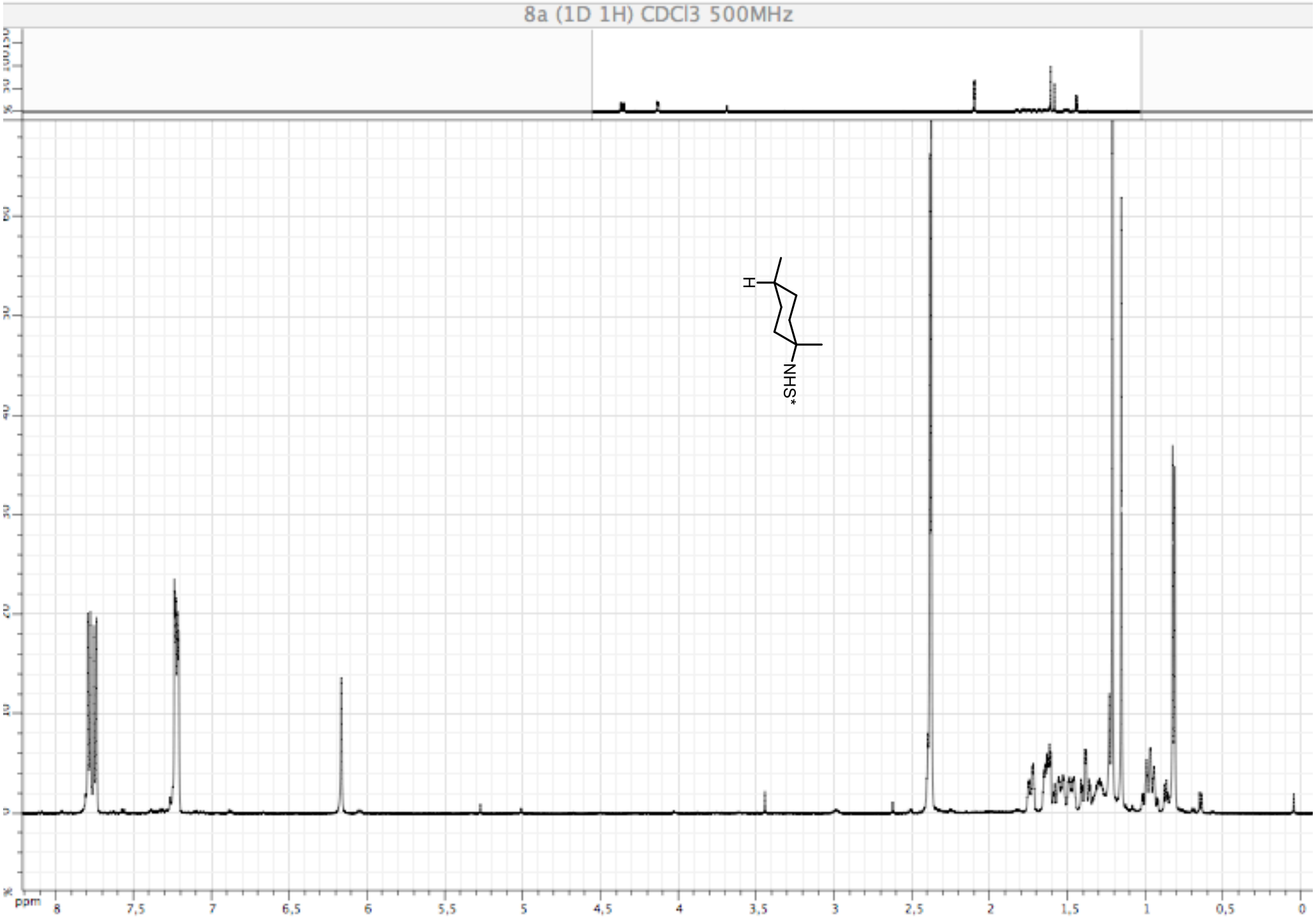

5f (1D 13C) CDCl3 300MHz
TfO
NHS*
ppm

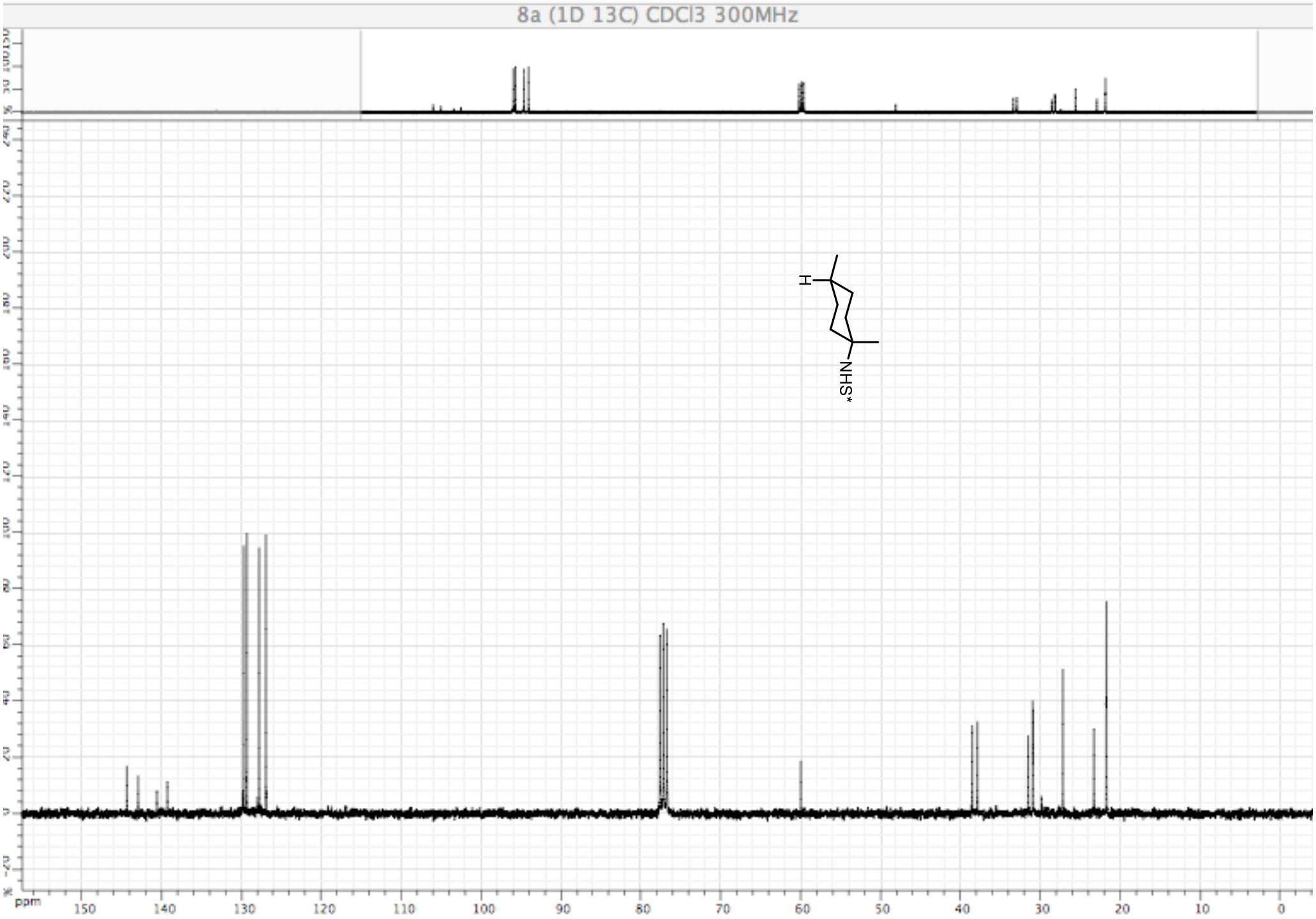

5g (1D 1H) CDCl3 500MHz
Ph
NHS*
ppm

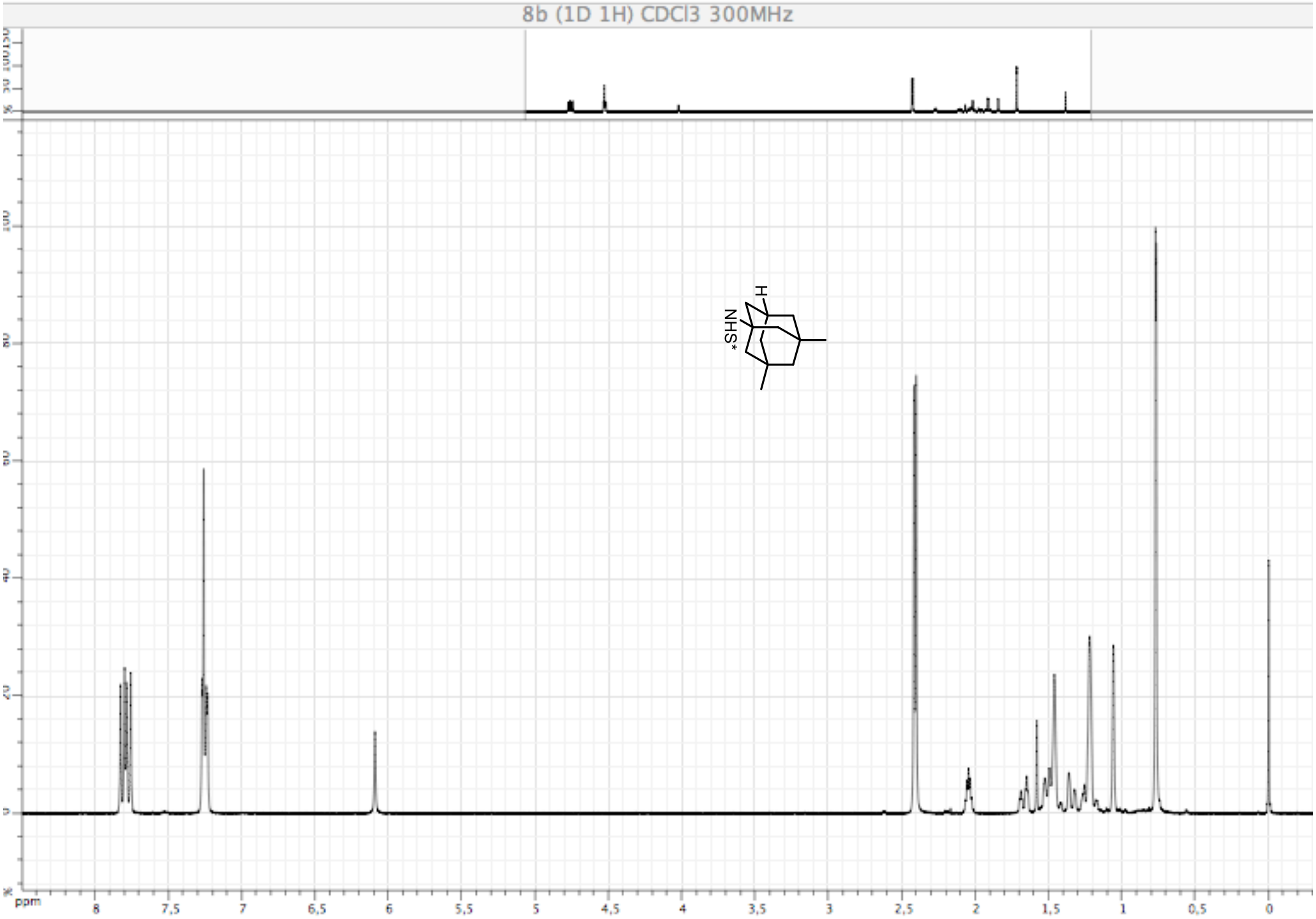

5g (1D 13C) CDCl3 300MHz
Ph
NHS*
ppm


6 (1D 1H) C6D6 500MHz
O
NH
S
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

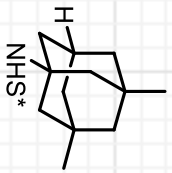

6 (1D 13C) C6D6 300MHz
O
NH*S
ppm
200
180
160
140
120
100
80
60
40
20
0


8a (1D 1H) CDCl3 500MHz
H
*SHN
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


8a (1D 13C) CDCl3 300MHz
H
NHS*
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

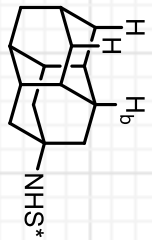

8b (1D 1H) CDCl3 300MHz
H
NHS*
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

8b (1D 13C) CDCl3 300MHz

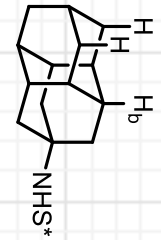


ppm 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

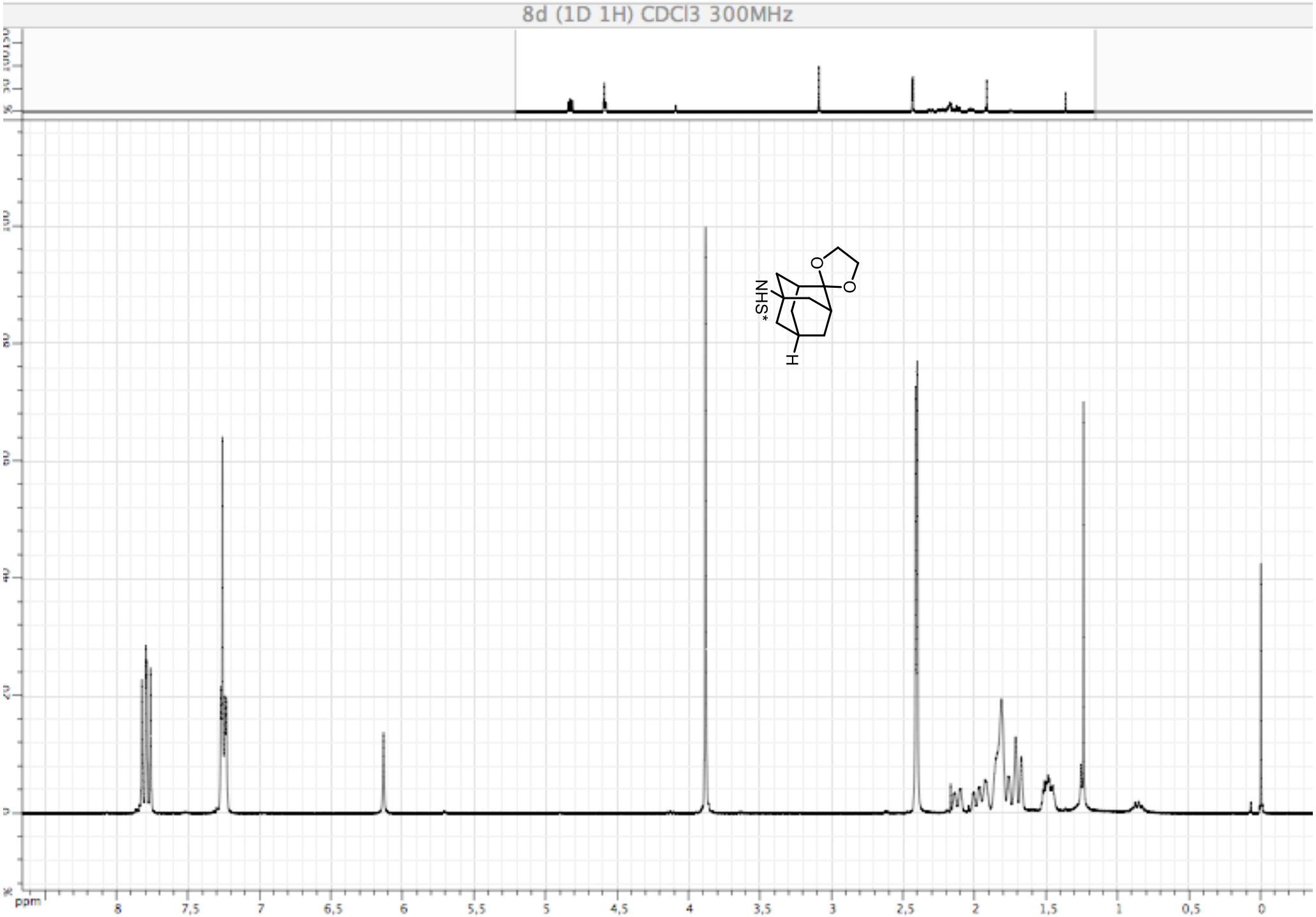
8c (1D 1H) CDCl3 300MHz



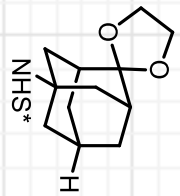
8c (1D 13C) CDCl3 300MHz



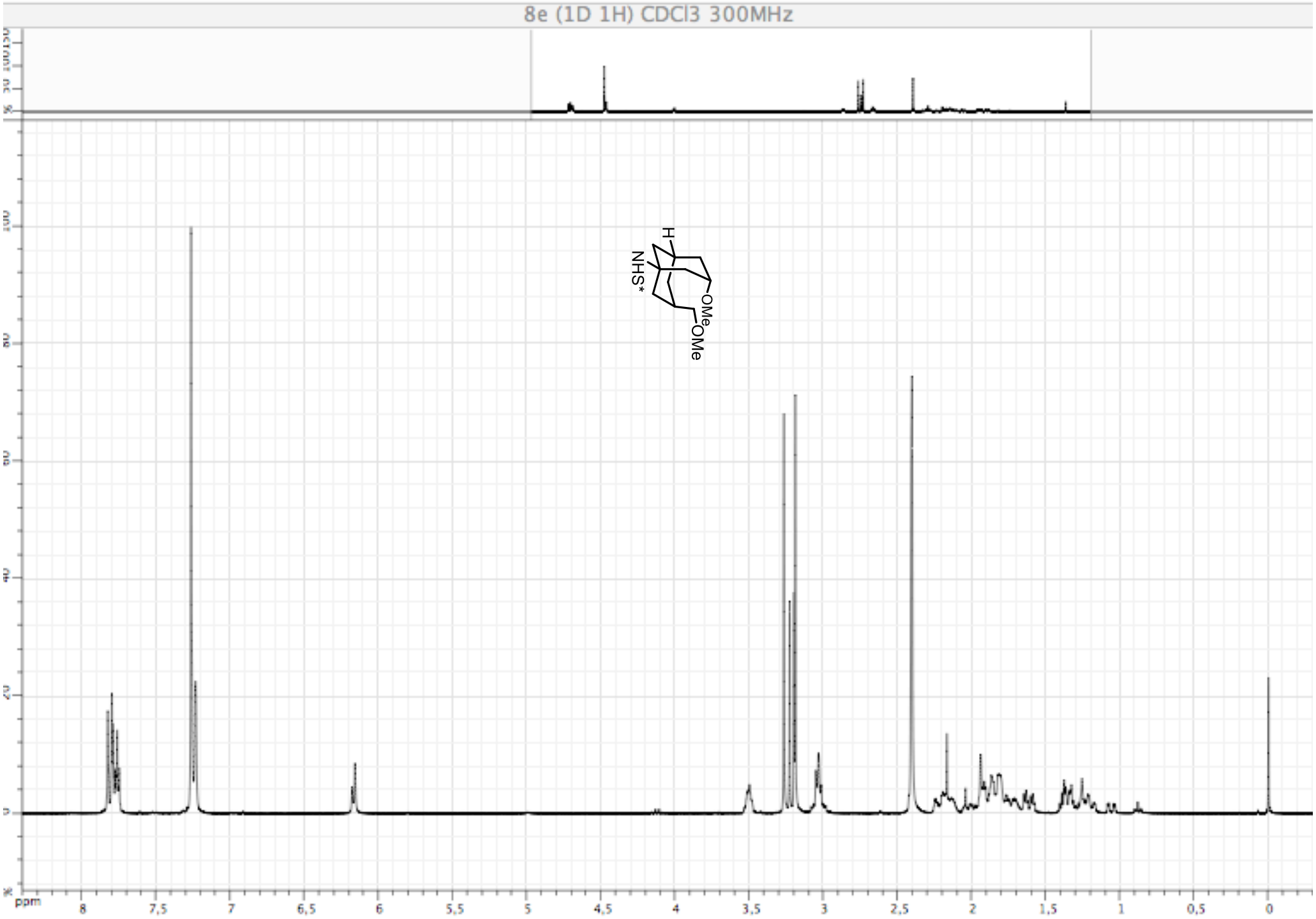
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

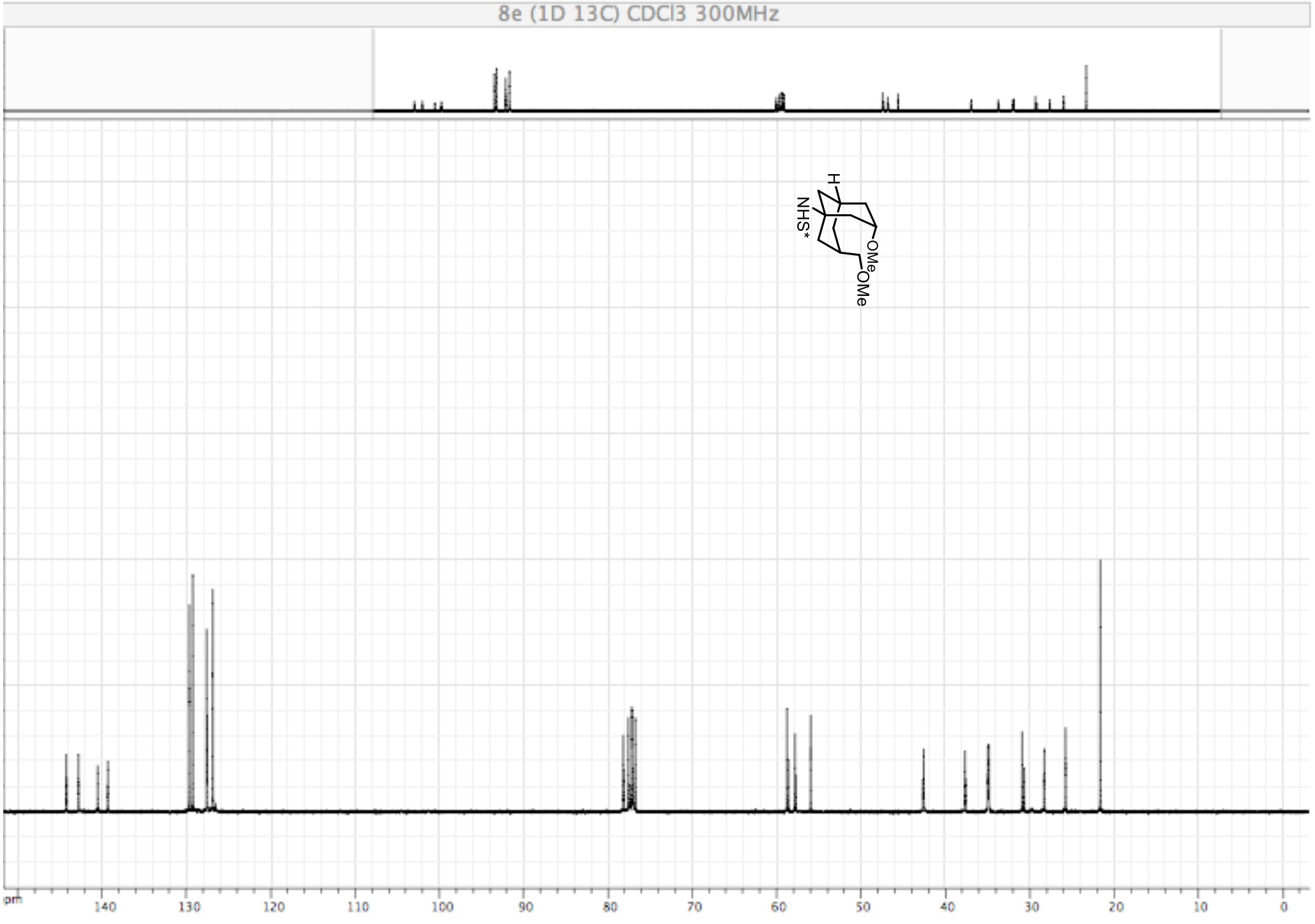

8d (1D 1H) CDCl3 300MHz
NHS*
H
O
O
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

8d (1D 13C) CDCl3 300MHz



ppm 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8e (1D 1H) CDCl3 300MHz
H
NHS*
OMe
OMe
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


8e (1D 13C) CDCl3 300MHz
H
NHS*
OMe
OMe
ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0