

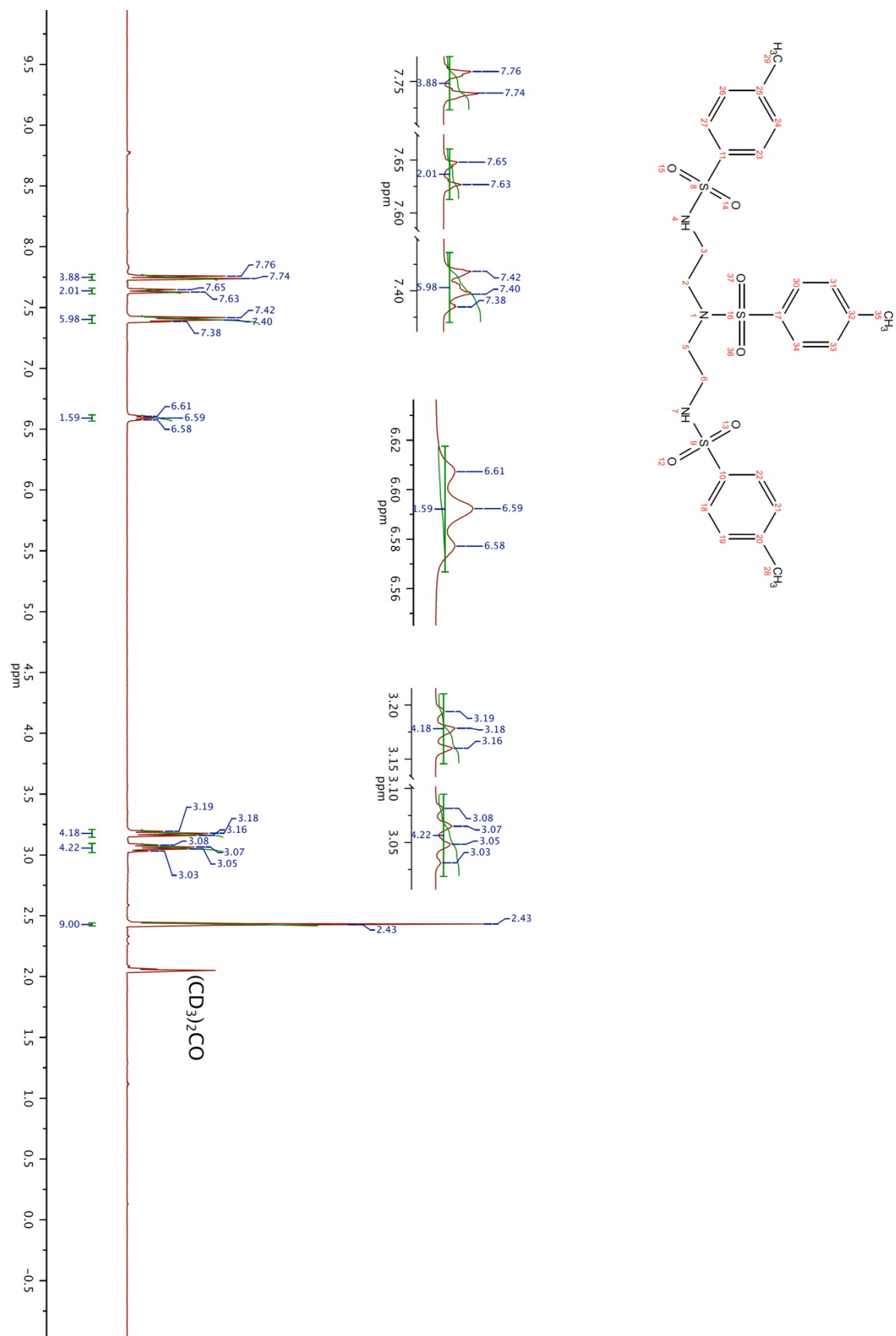
Anhang für das Buch

Cyclen-basierte Metallonucleasen
Synthese und biochemische Evaluation

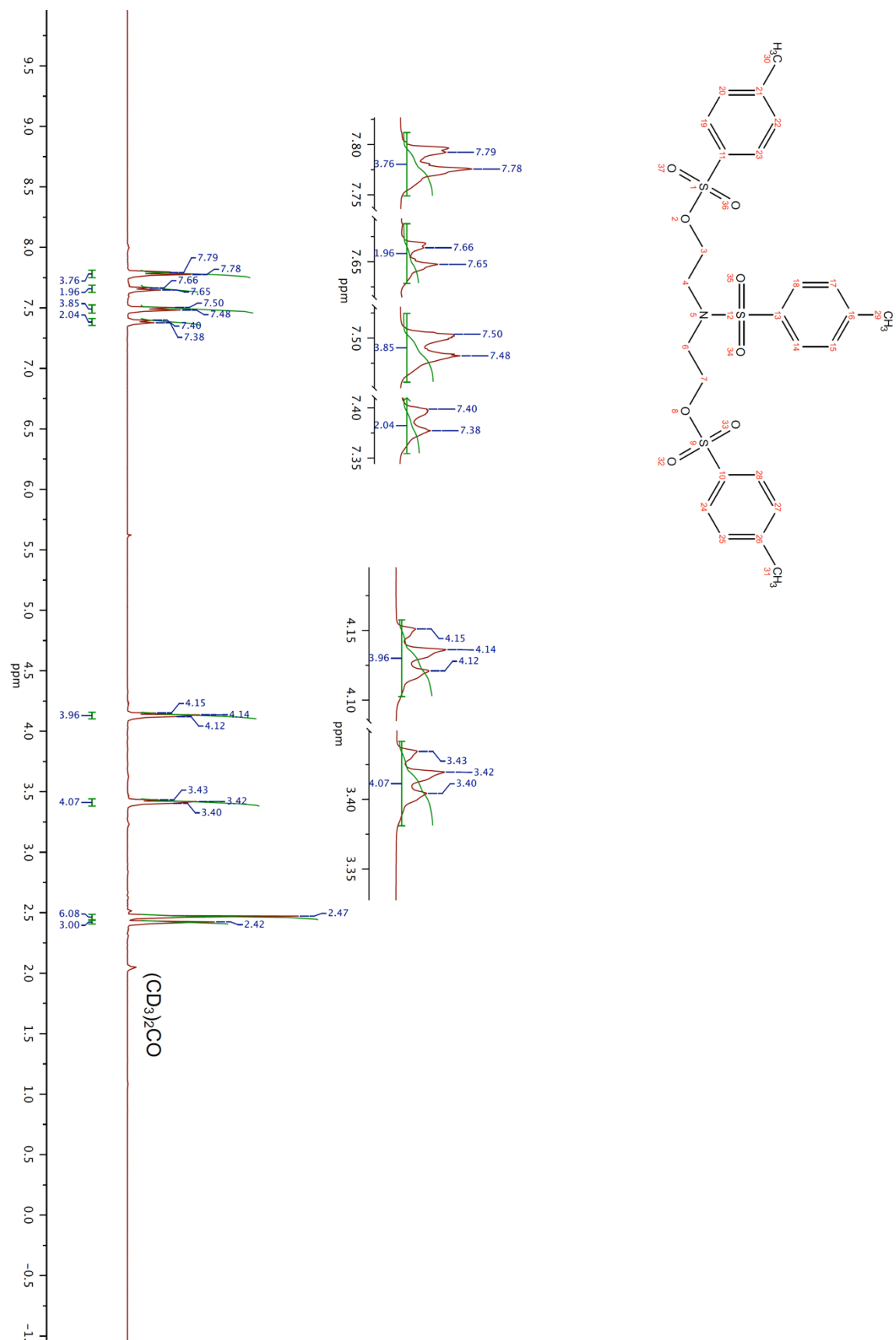
von

Jan Hormann

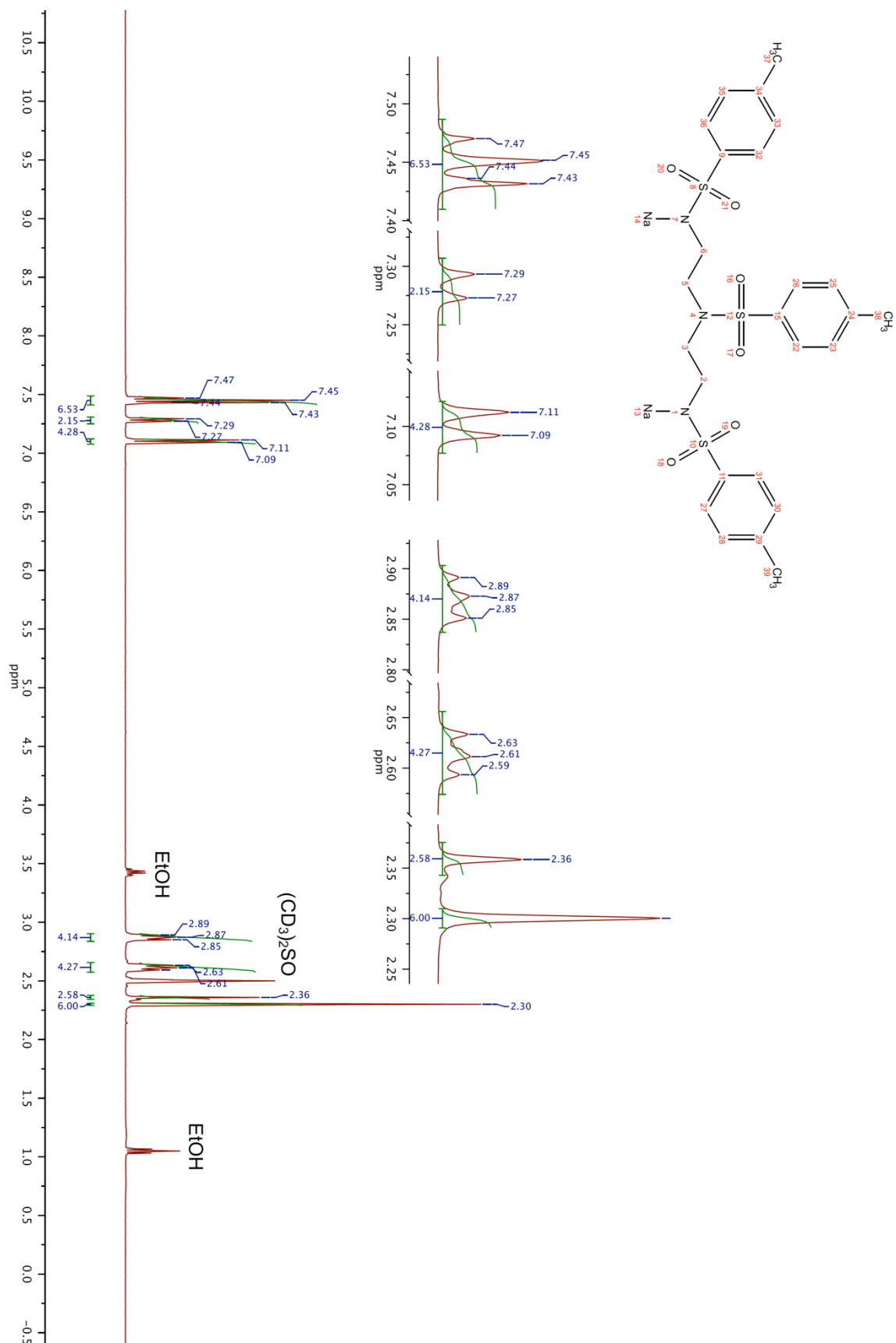
N,N',N'' -Tris(*p*-tolylsulfonyl)diethylentriamin (**3**) - ^1H -NMR



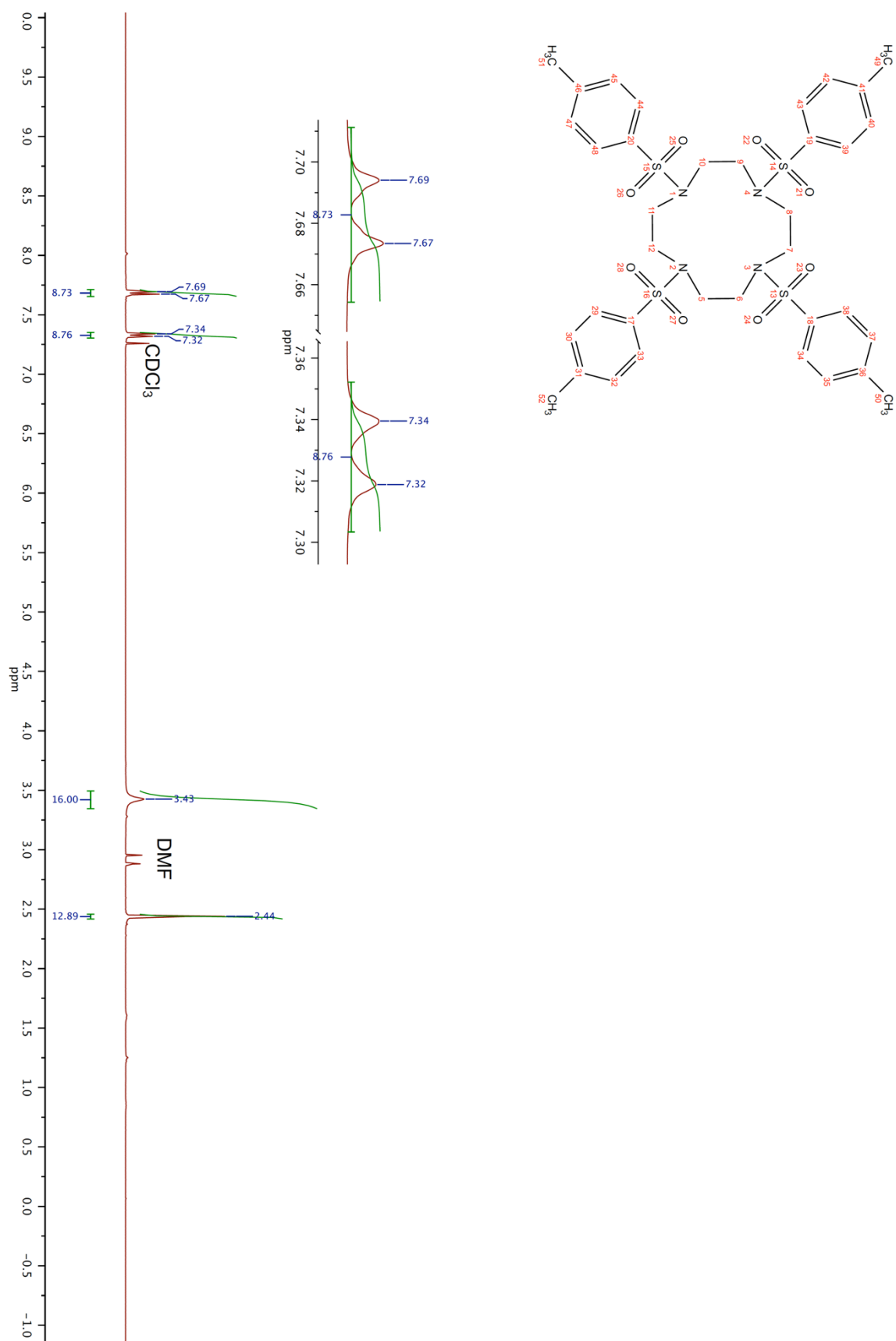
N,O,O'-Tris(*p*-tolylsulfonyl)diethanolamin (**5**) - ^1H -NMR



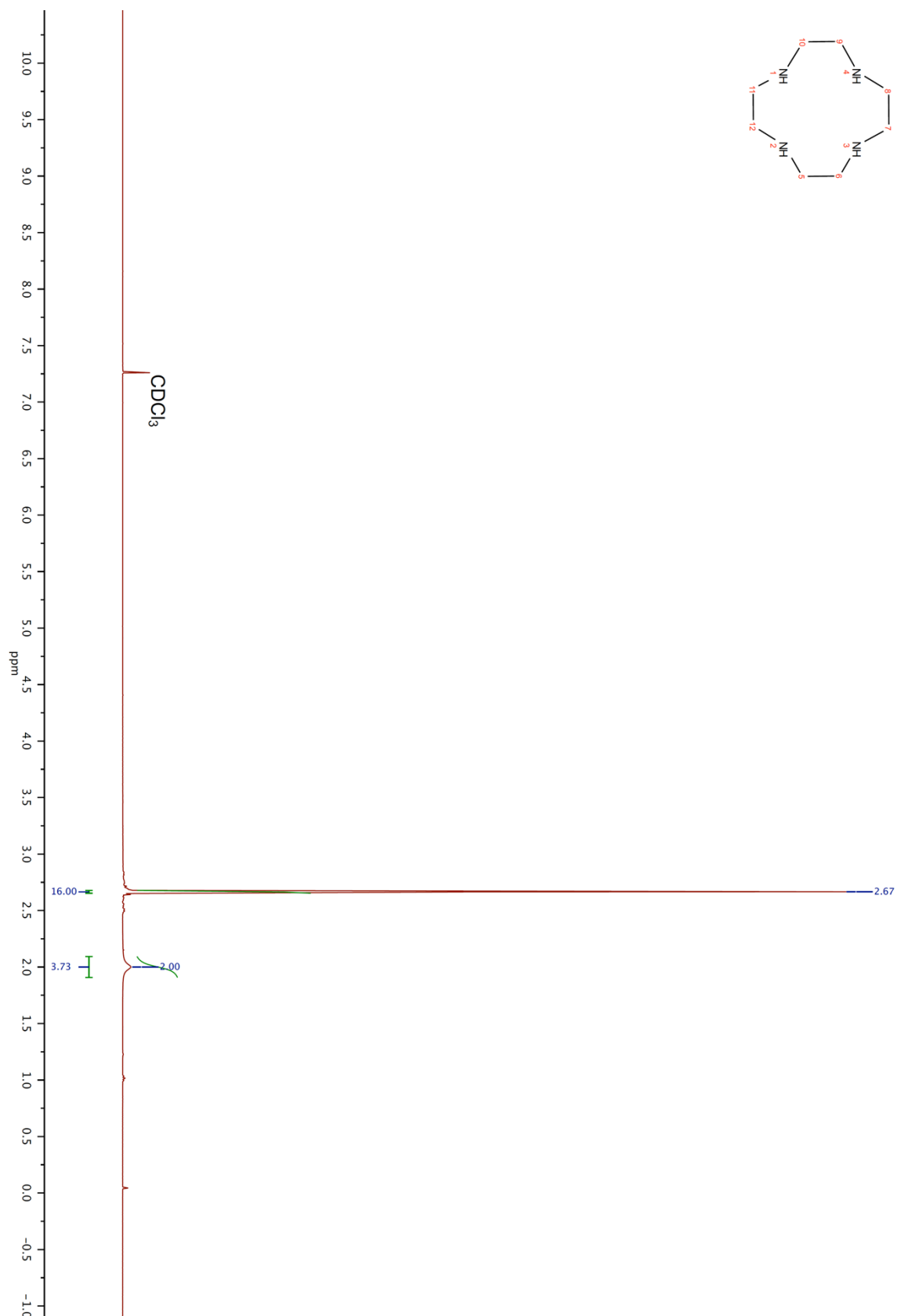
N,N',N'' -Tris(*p*-tolylsulfonyl)diethylentriamin- N,N''' -Dinatriumsalz (**6**) - ^1H -NMR



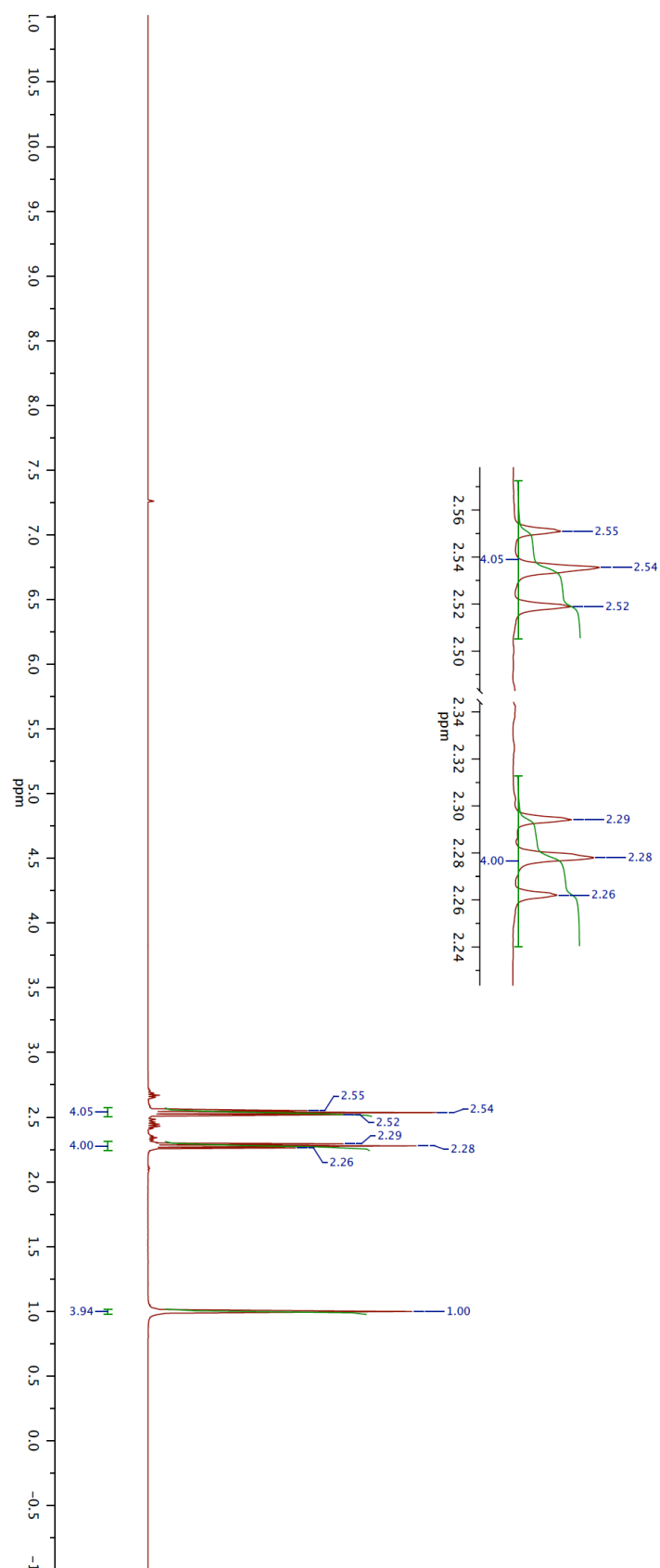
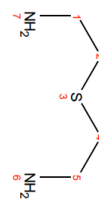
1,4,7,10-Tetrakis(*p*-tolylsulfonyl)1,4,7,10-tetraazacyclododecan (7) - ^1H -NMR



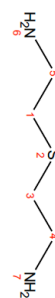
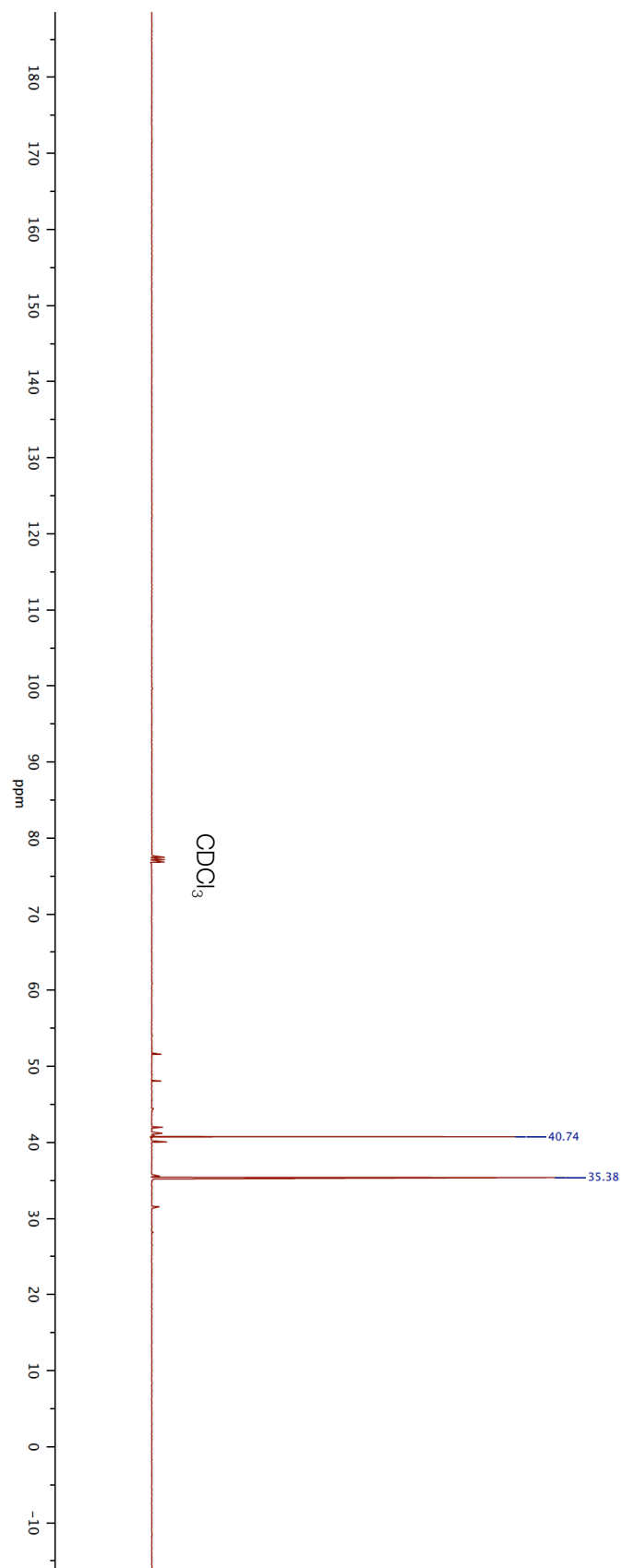
1,4,7,10-Tetraazacyclododecan (**8**) - ^1H -NMR



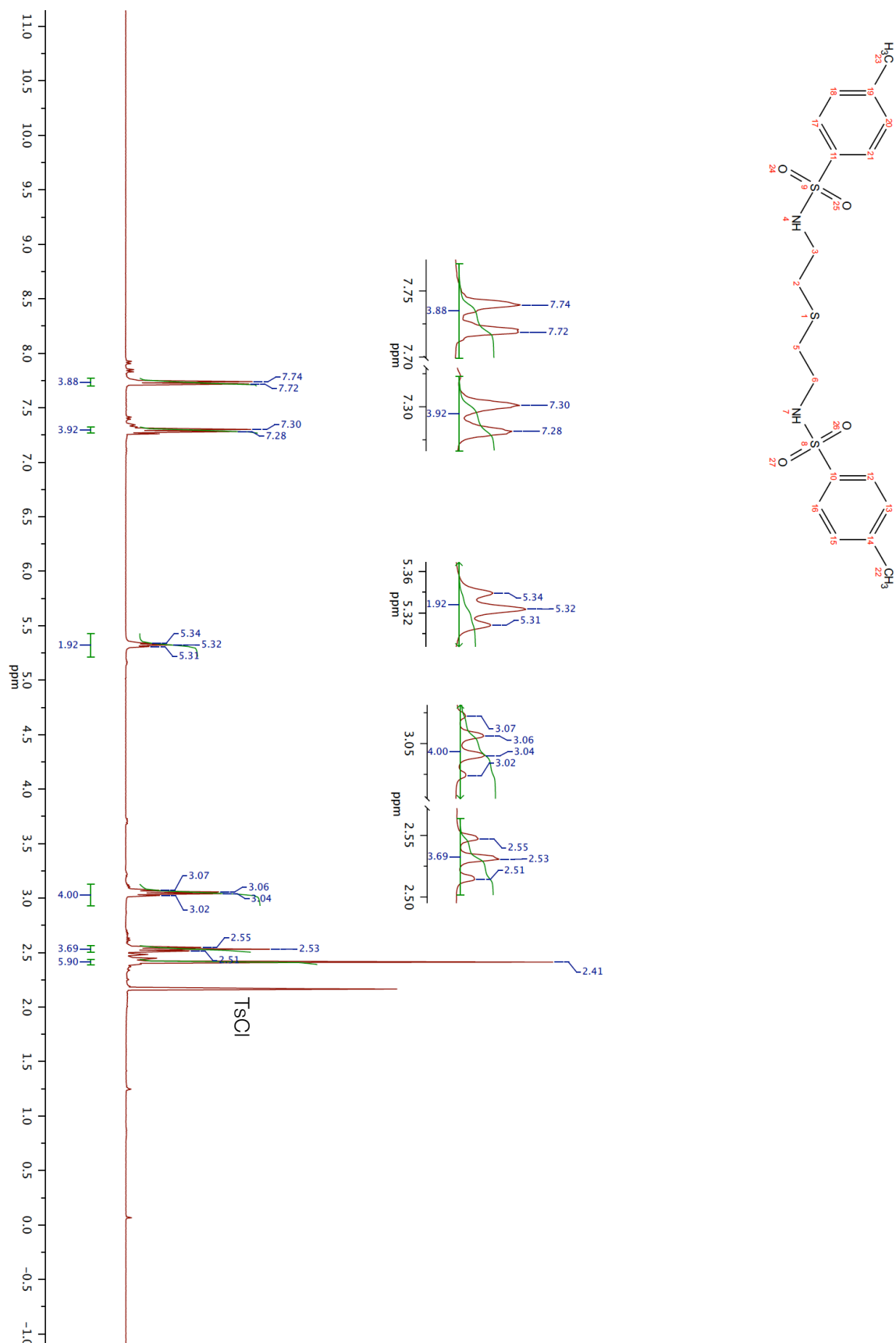
Bis(2-aminoethyl)sulfid (**11**) - ^1H -NMR



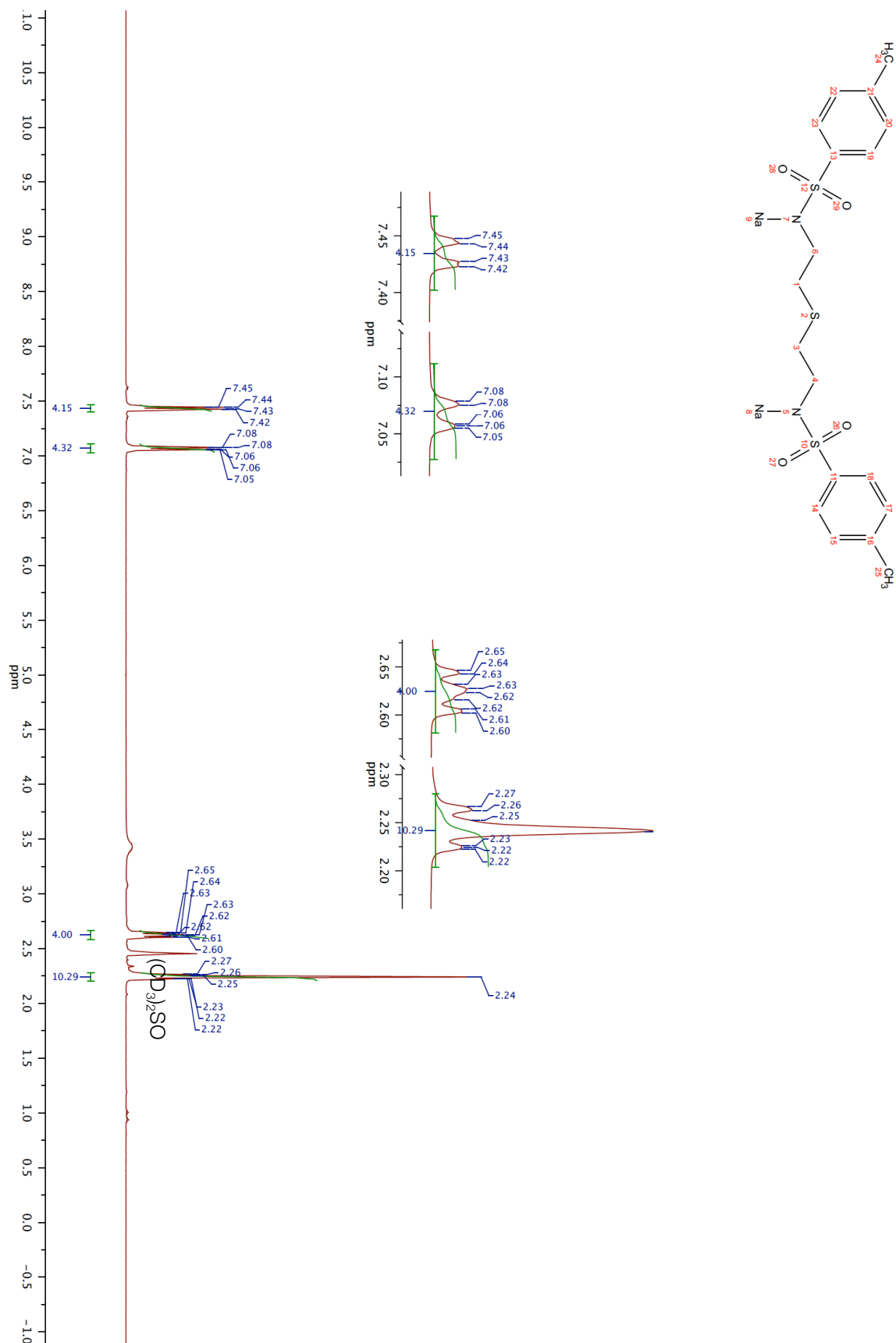
Bis(2-aminoethyl)sulfid (**11**) - ^{13}C -NMR



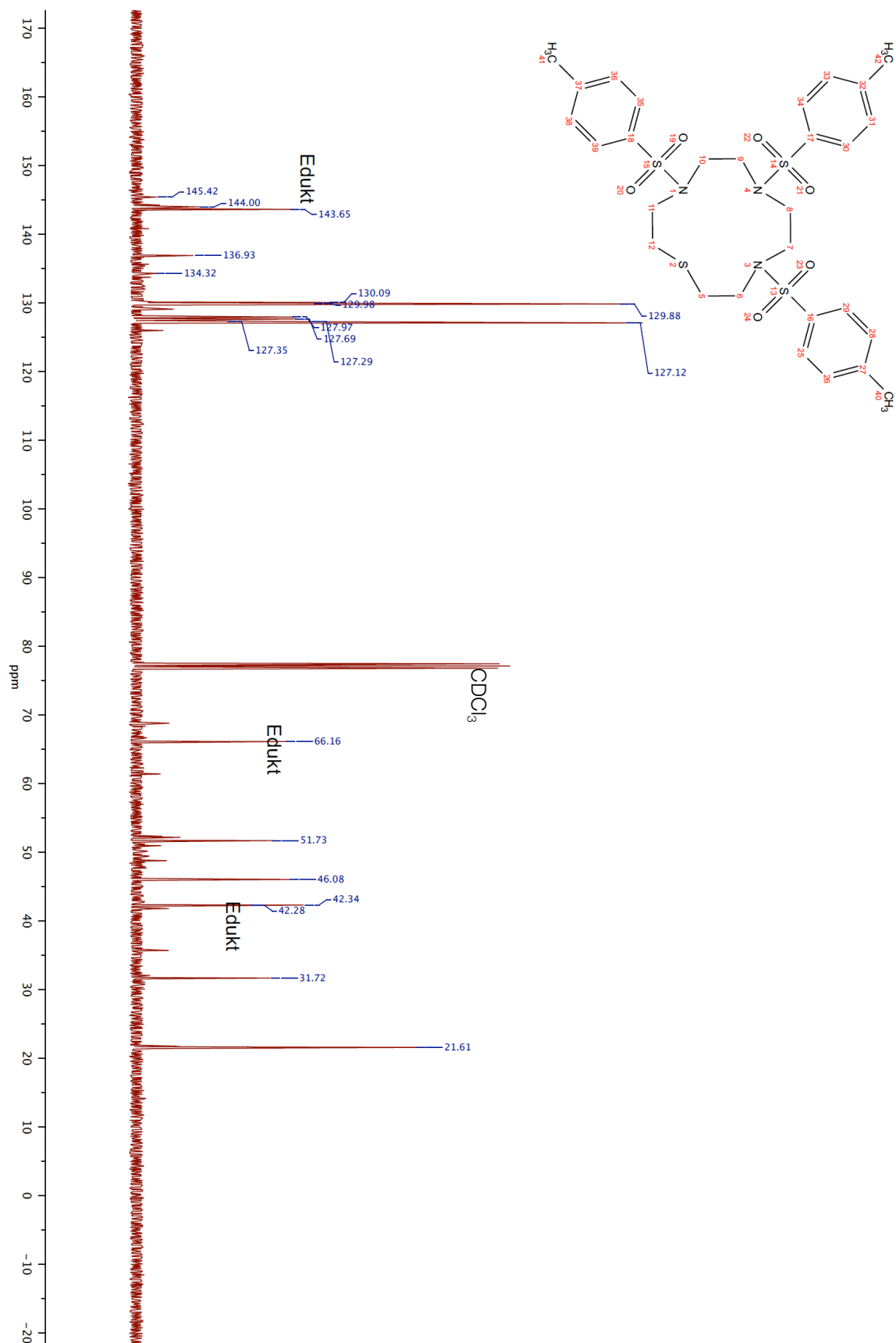
Bis[(*p*-tolylsulfonylamino)ethyl]sulfid (**12**) - ^1H -NMR



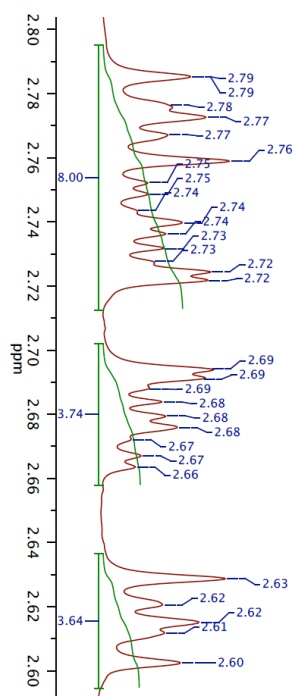
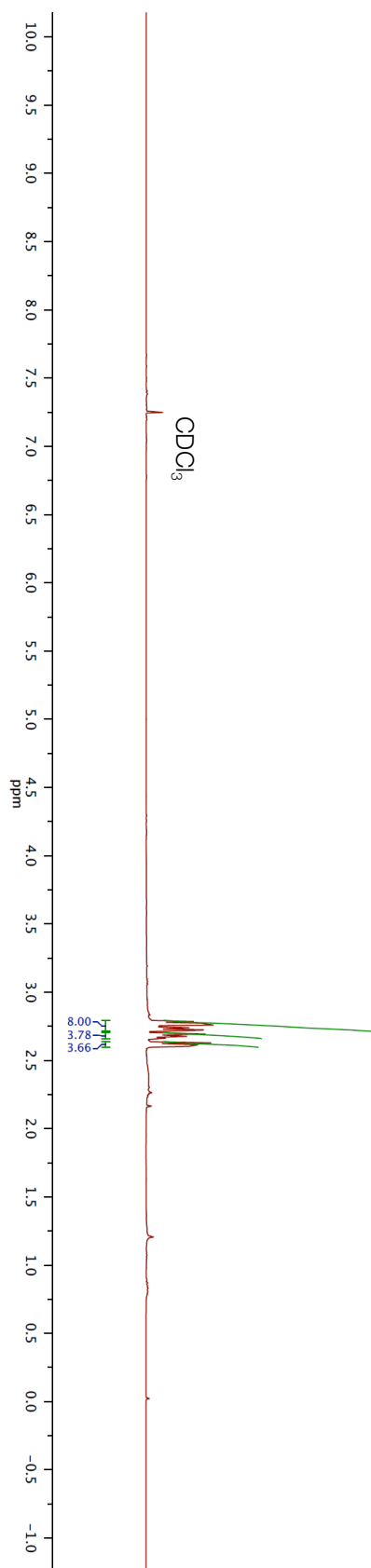
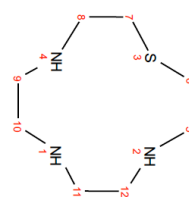
Bis[(*p*-tolylsulfonylamino)ethyl]sulfid-Dinatriumsalz (**13**) - ^1H -NMR



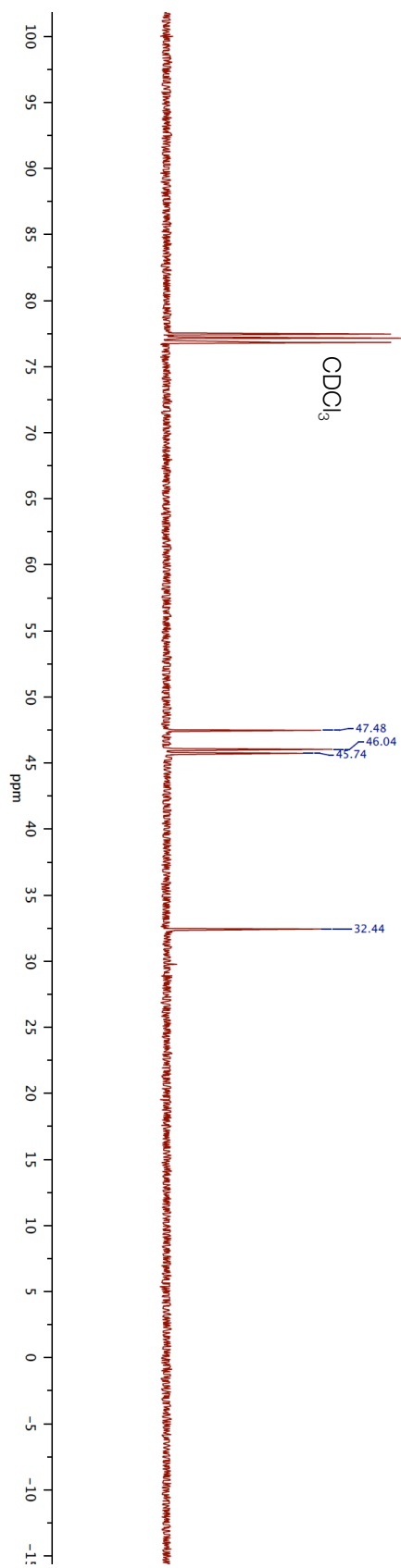
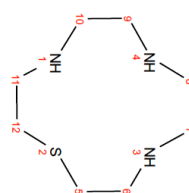
4,7,10-Tris(*p*-tolylsulfonyl)-1-thia-4,7,10-triazacyclododecan (**14**) - ¹³C-NMR



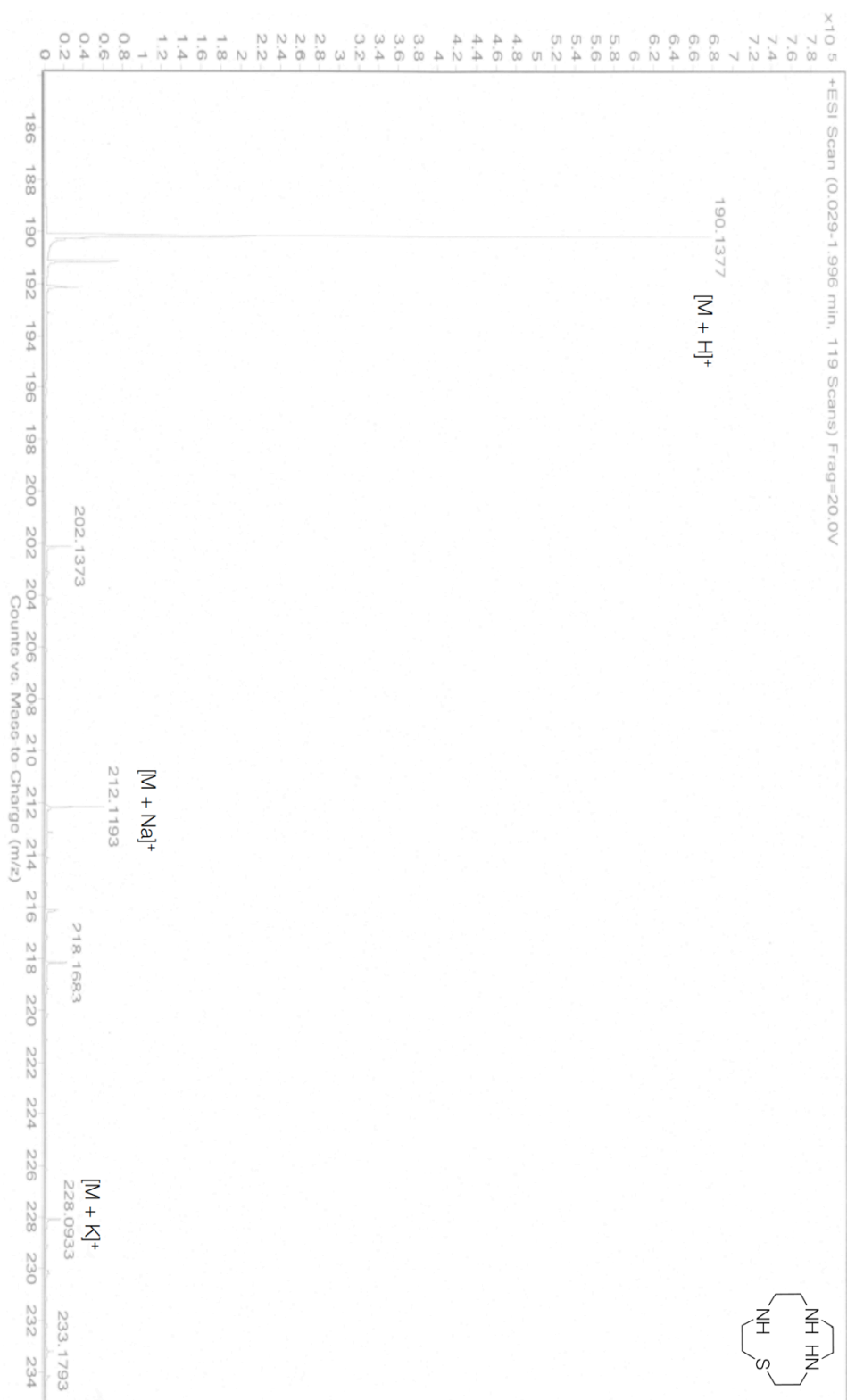
1-Thia-4,7,10-triazacyclododecan (**15**) - H-NMR



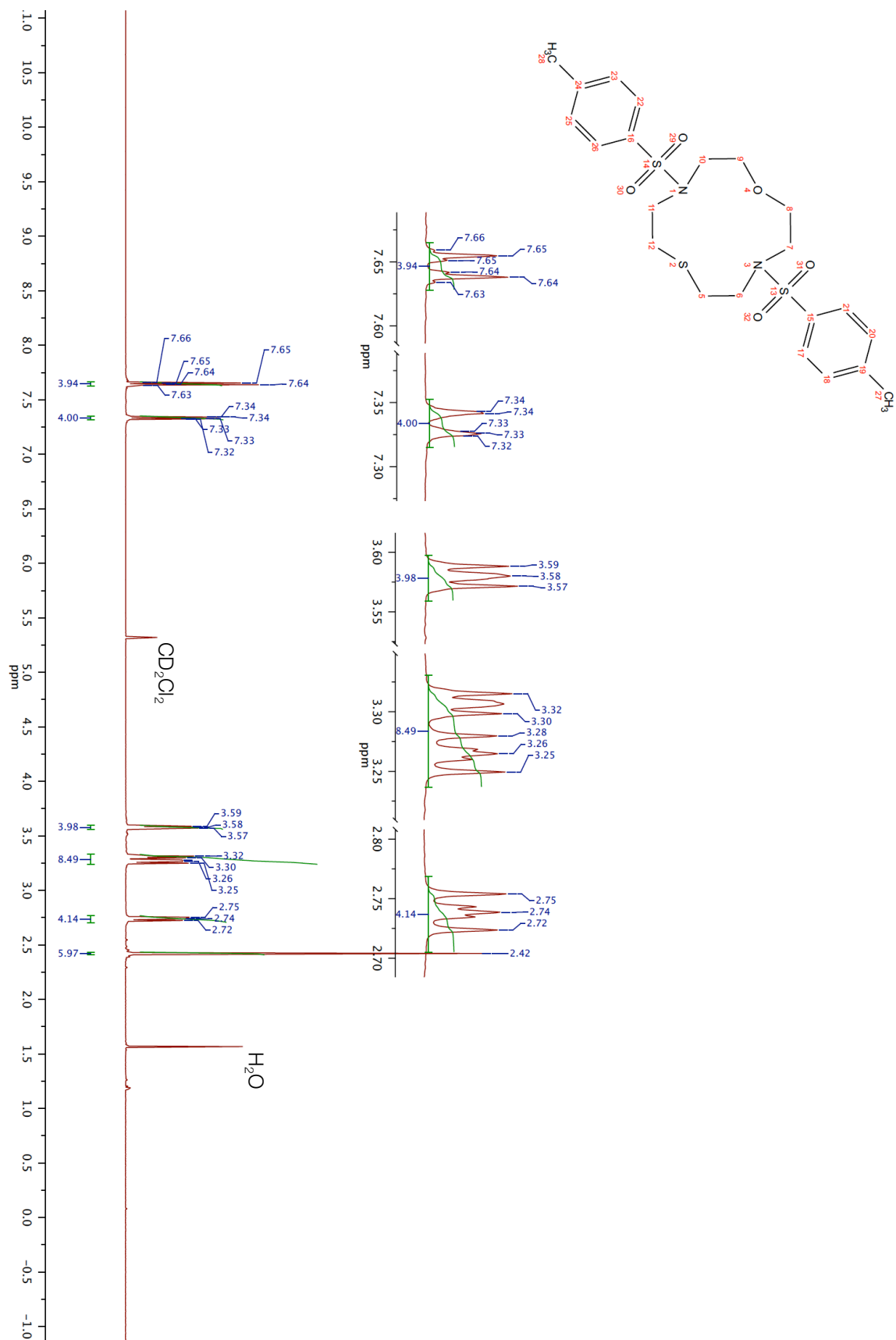
1-Thia-4,7,10-triazacyclododecan (**15**) - ^{13}C -NMR



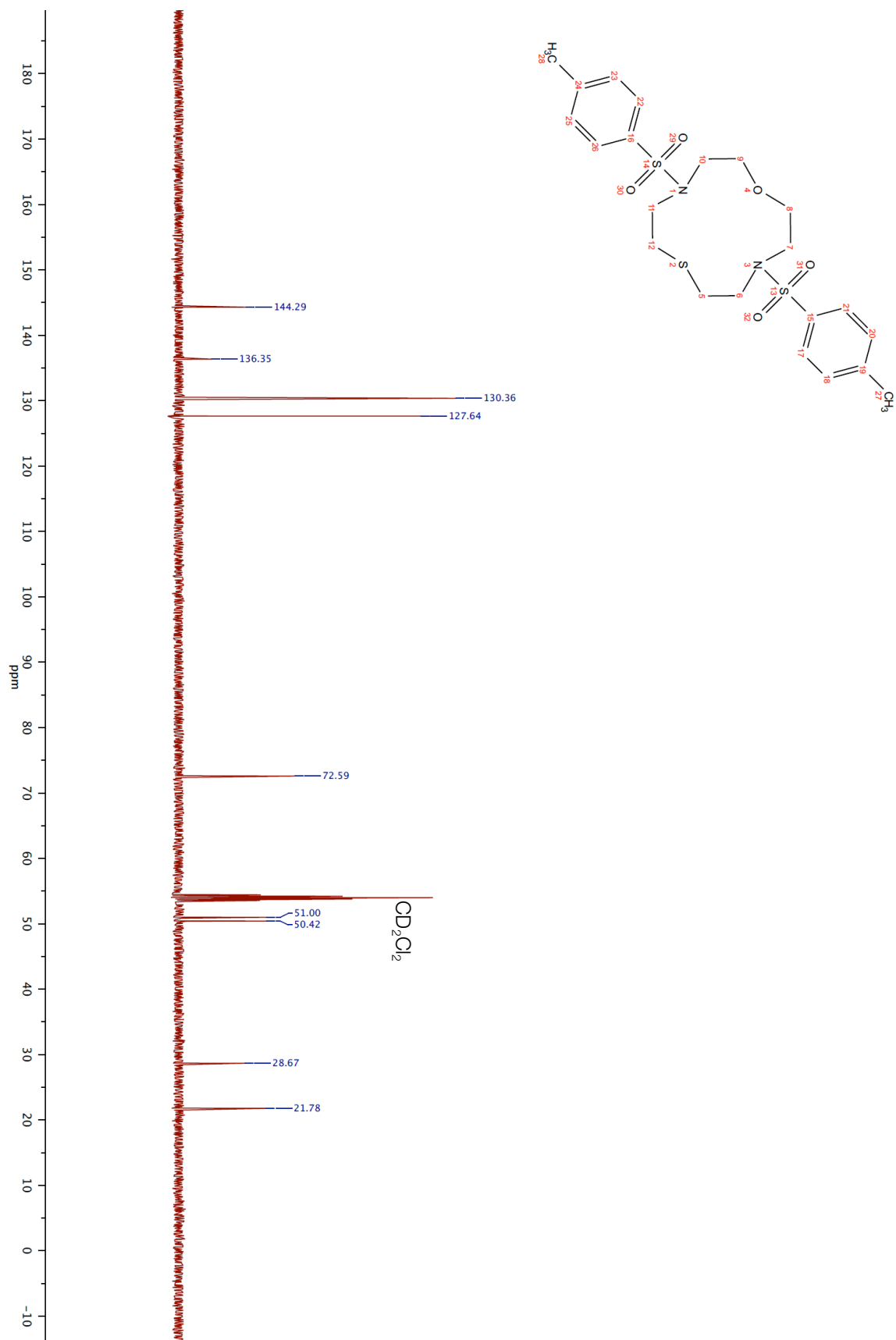
1-Thia-4,7,10-triazacyclododecan (**15**) - ESI-MS



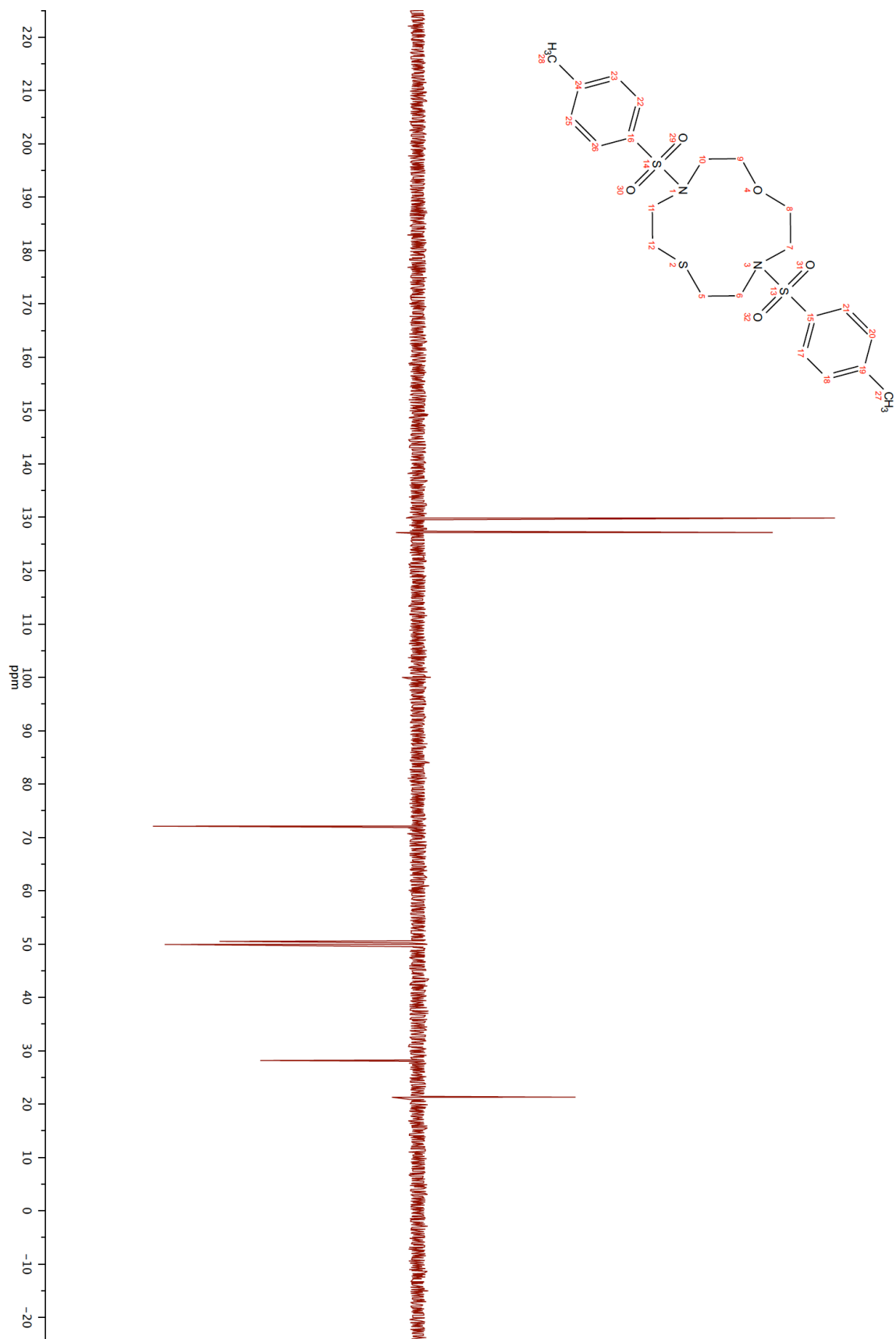
4,10-Bis(*p*-tolylsulfonyl)-1-oxa-7-thia-4,10-diazacyclododecan (**17**) - ¹H-NMR



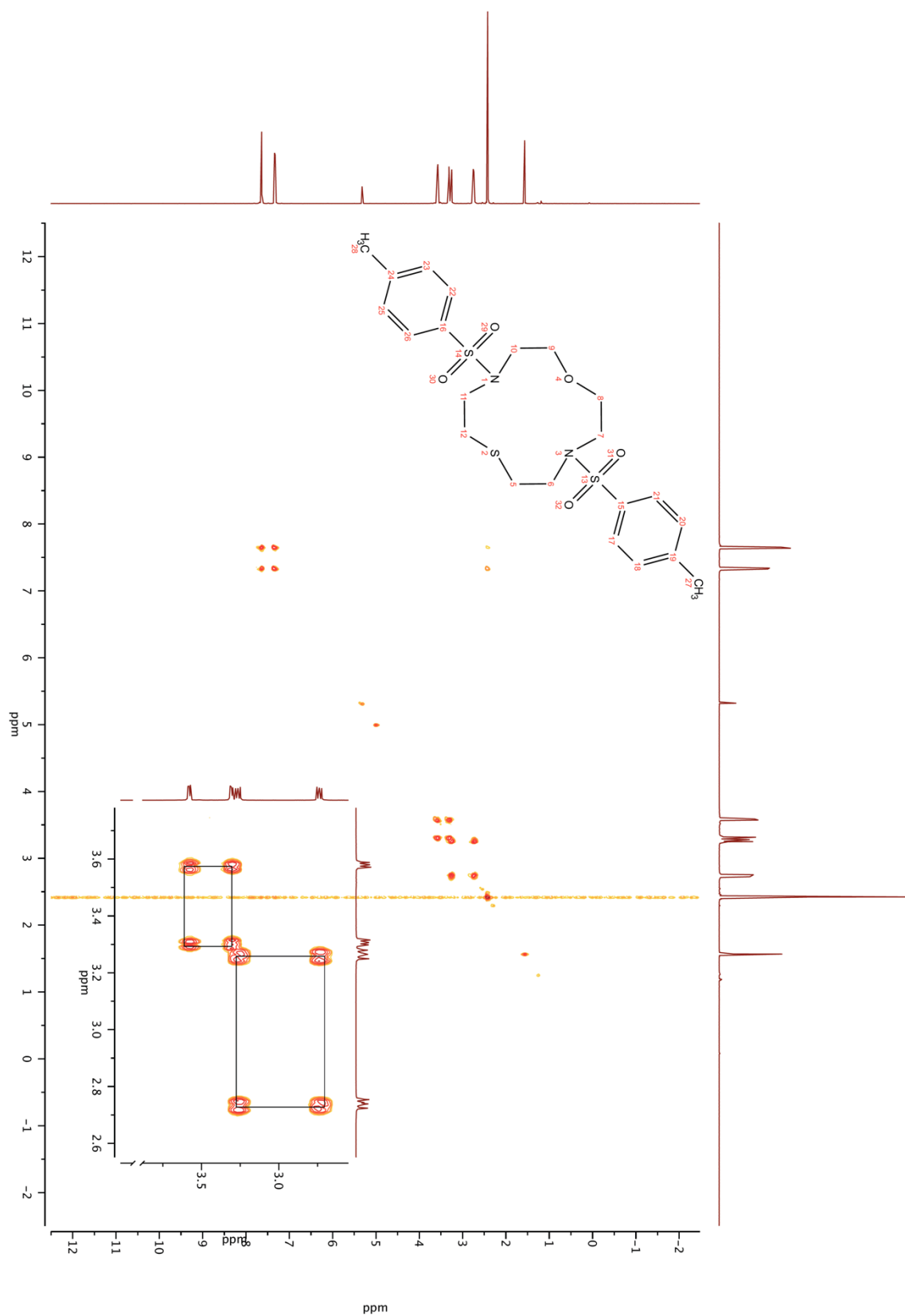
4,10-Bis(*p*-tolylsulfonyl)-1-oxa-7-thia-4,10-diazacyclododecan (**17**) - ¹³C-NMR



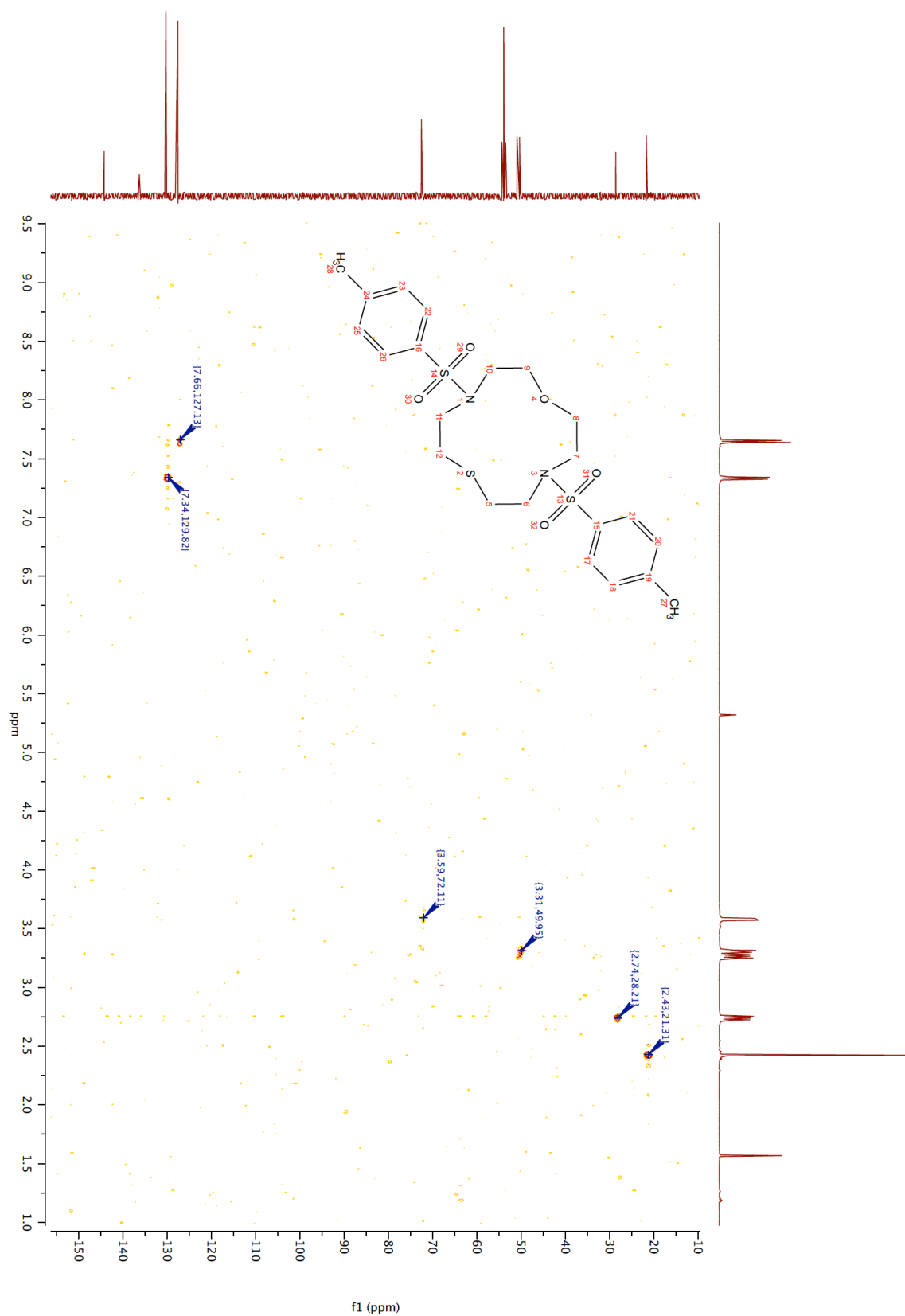
4,10-Bis(*p*-tolylsulfonyl)-1-oxa-7-thia-4,10-diazacyclododecan (**17**) - DEPT-NMR



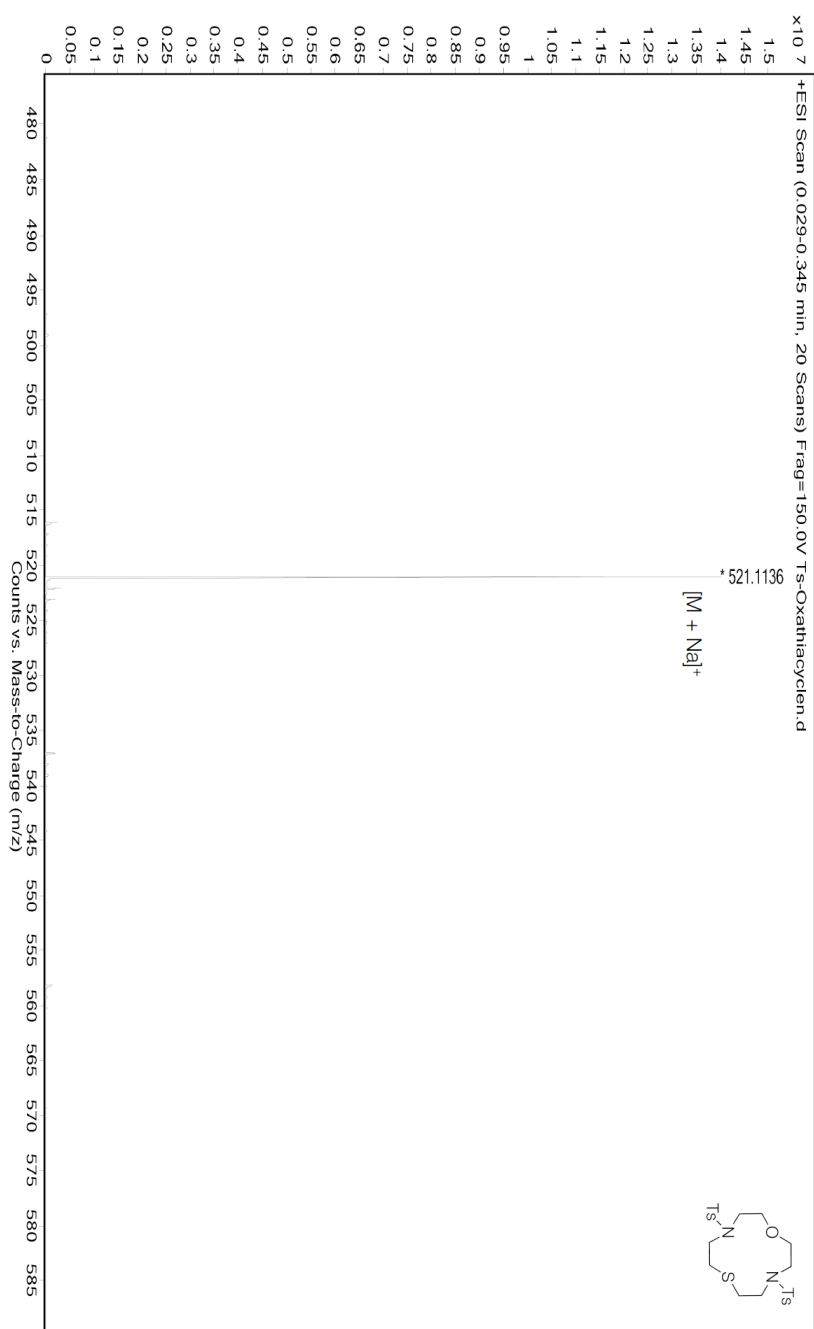
4,10-Bis(*p*-tolylsulfonyl)-1-oxa-7-thia-4,10-diazacyclododecan (**17**) - COSY-NMR



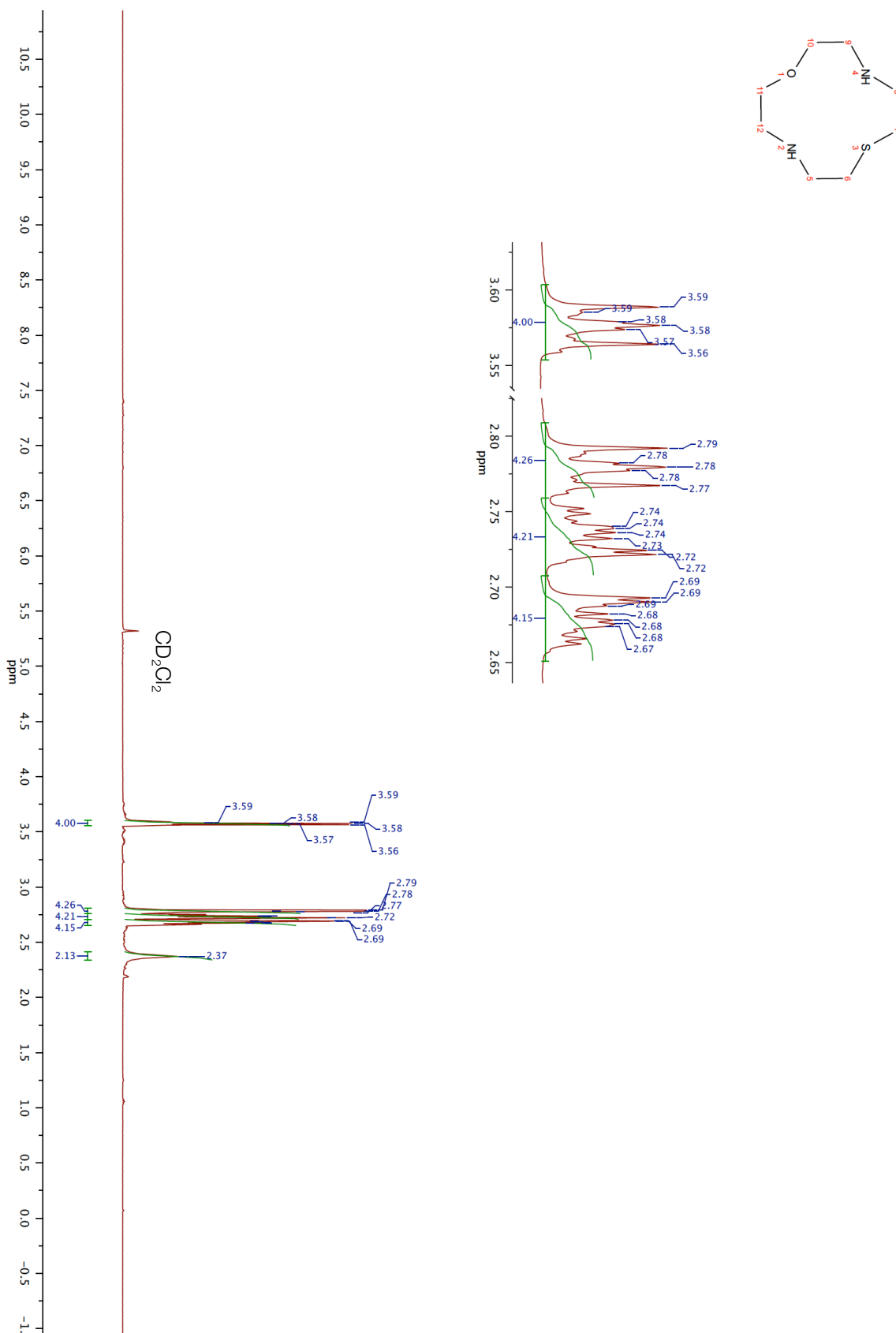
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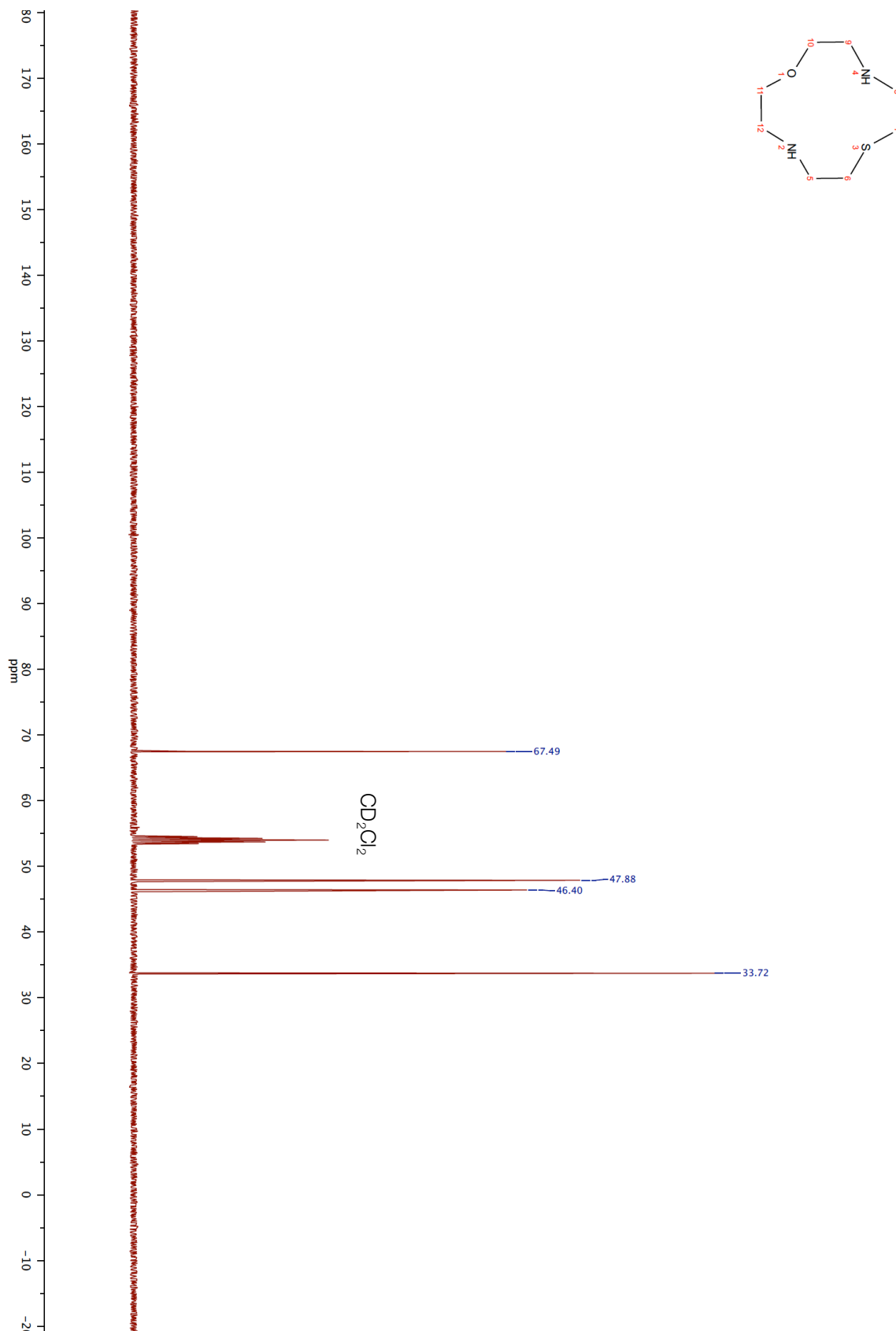
4,10-Bis(*p*-tolylsulfonyl)-1-oxa-7-thia-4,10-diazacyclododecan (**17**) - ESI-MS



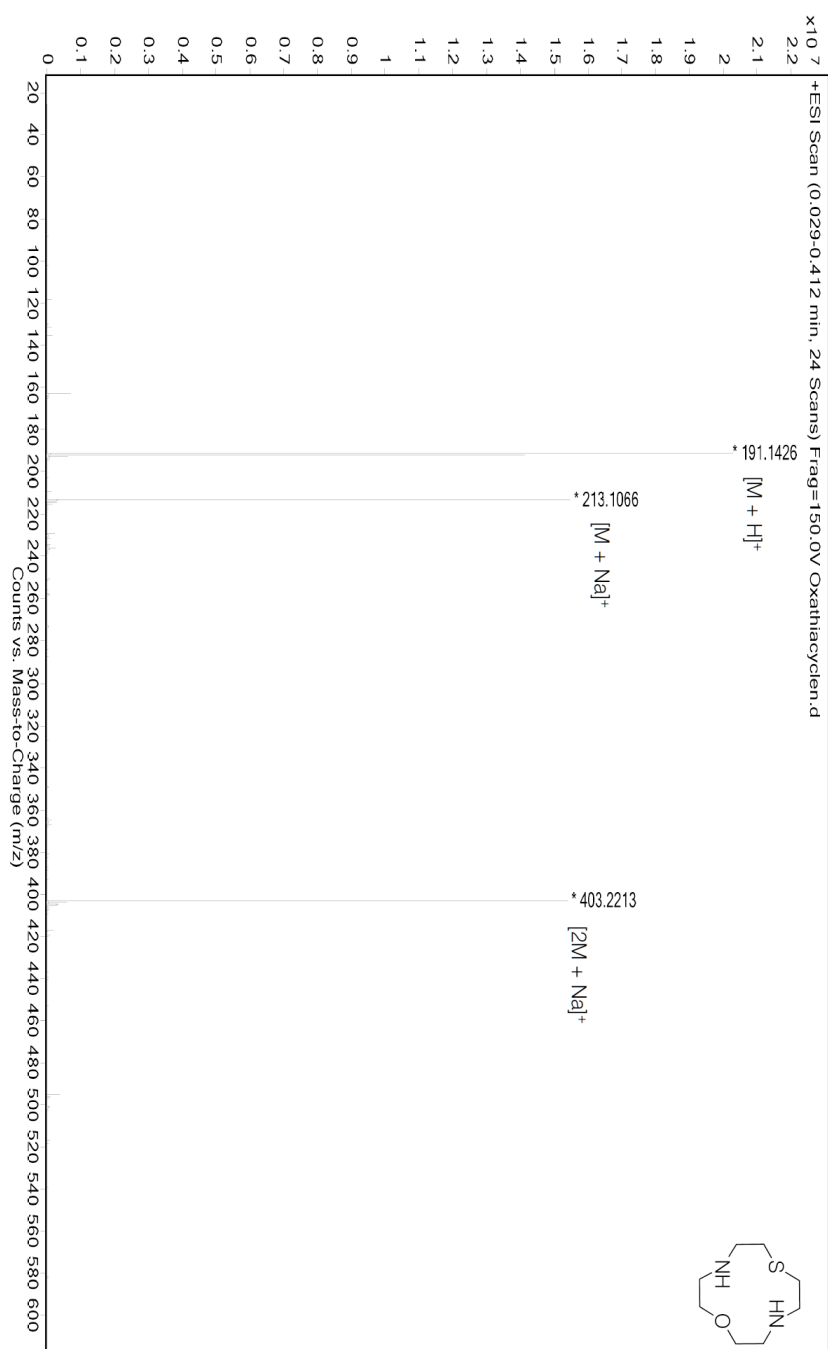
1-Oxa-7-thia-4,10-diazacyclododecan (**18**) - ¹H-NMR



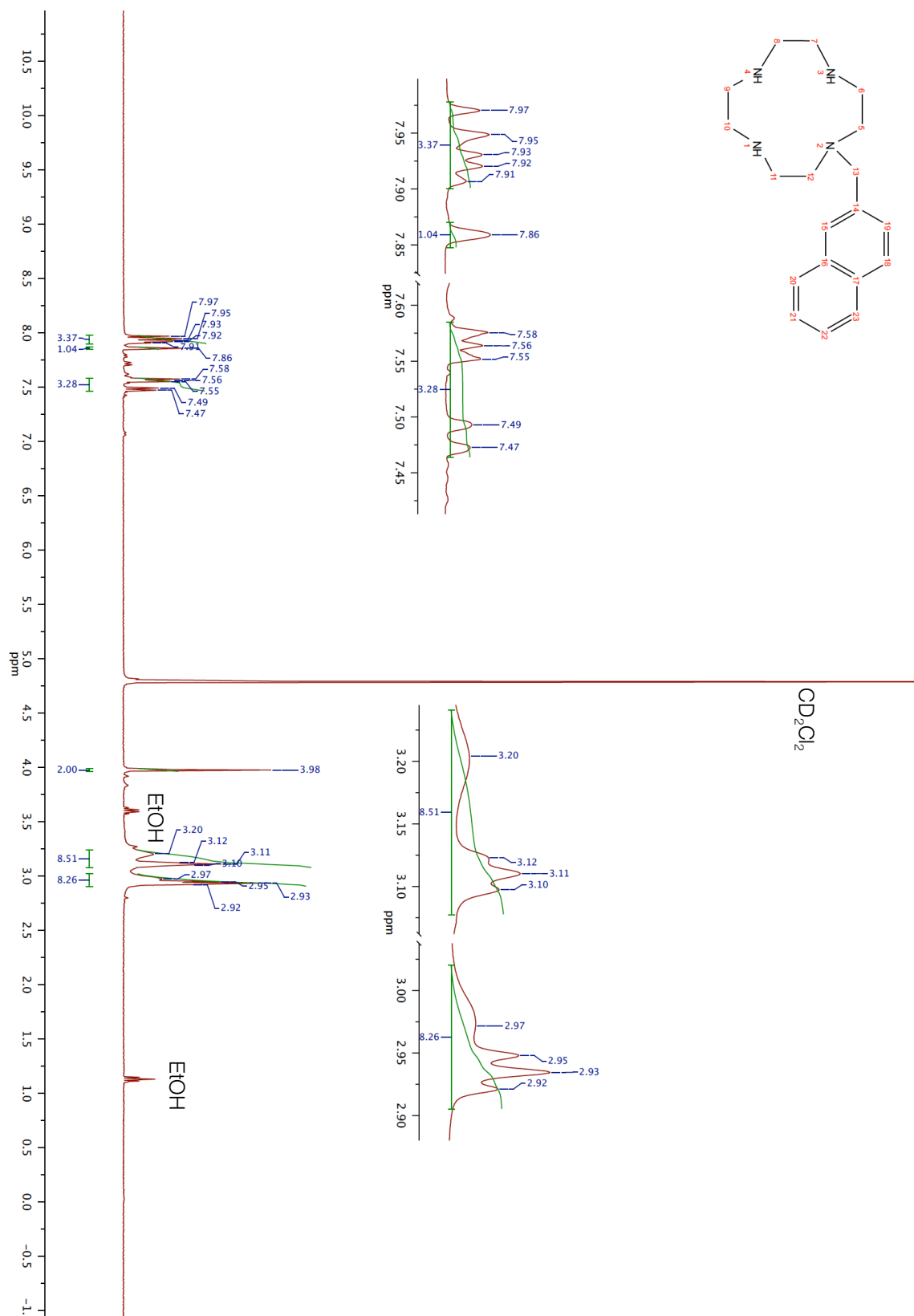
1-Oxa-7-thia-4,10-diazacyclododecan (**18**) - ¹³C-NMR



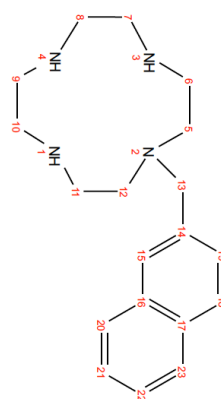
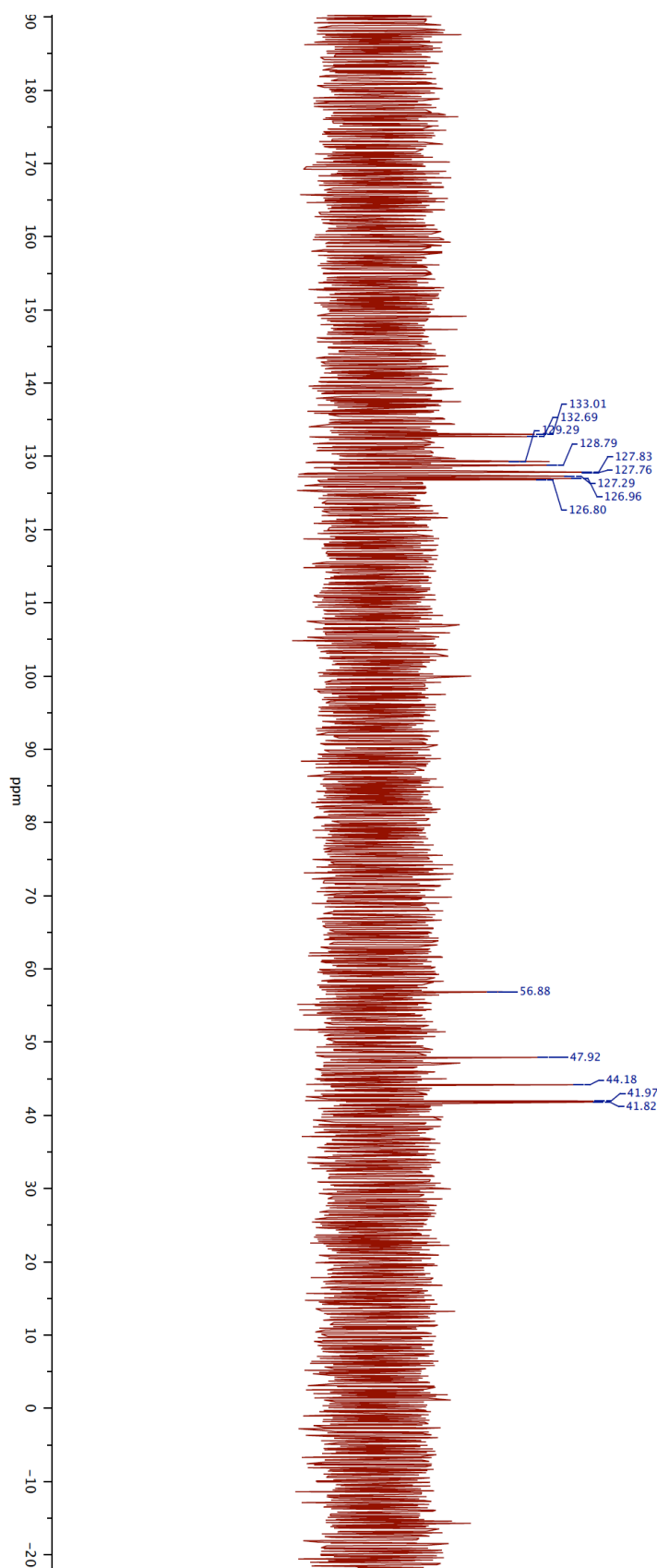
1-Oxa-7-thia-4,10-diazacyclododecan (**18**) - ESI-MS



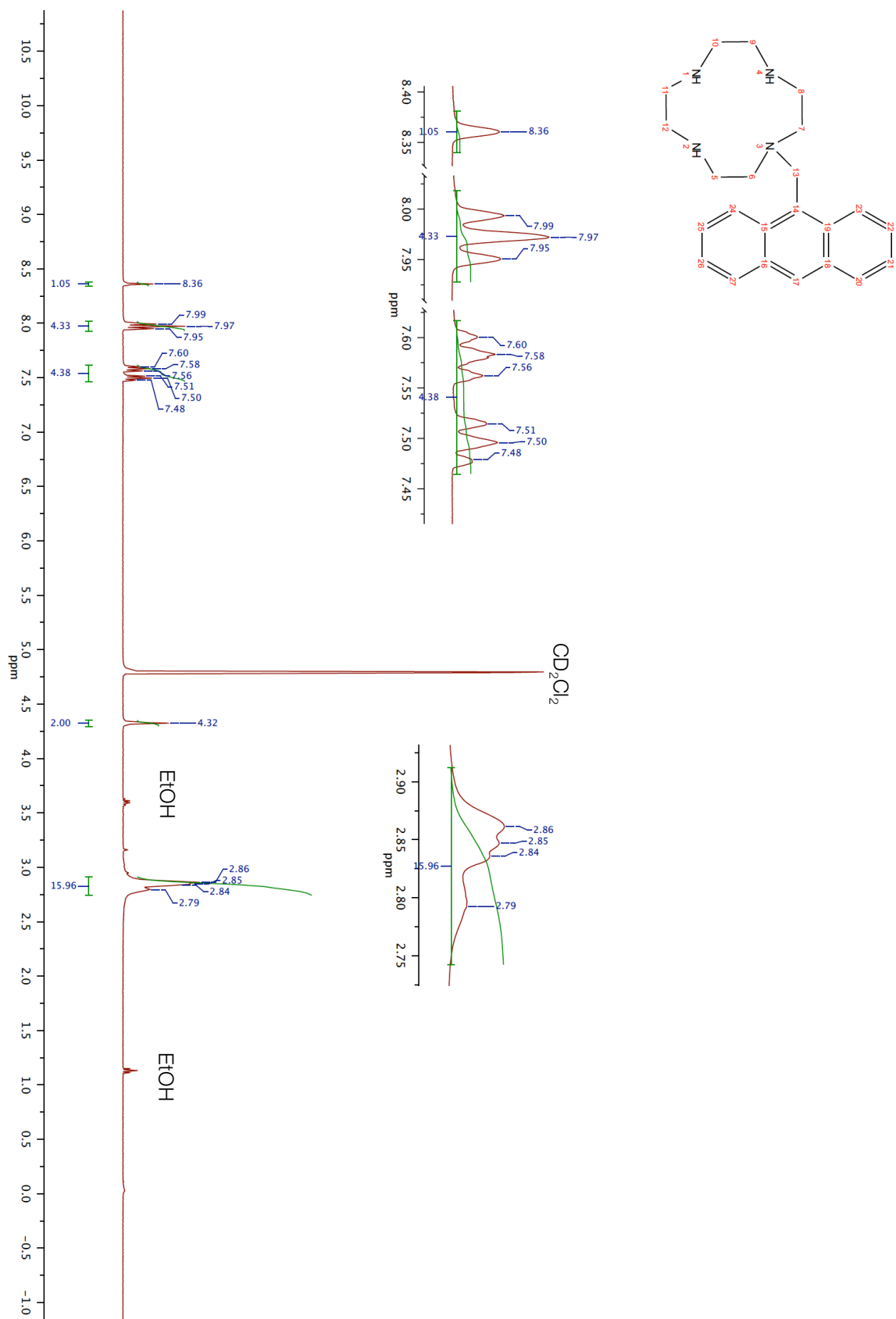
1-(2-Naphthalinmethyl)-1,4,7,10-tetraazacyclododecan (**20**) - H-NMR



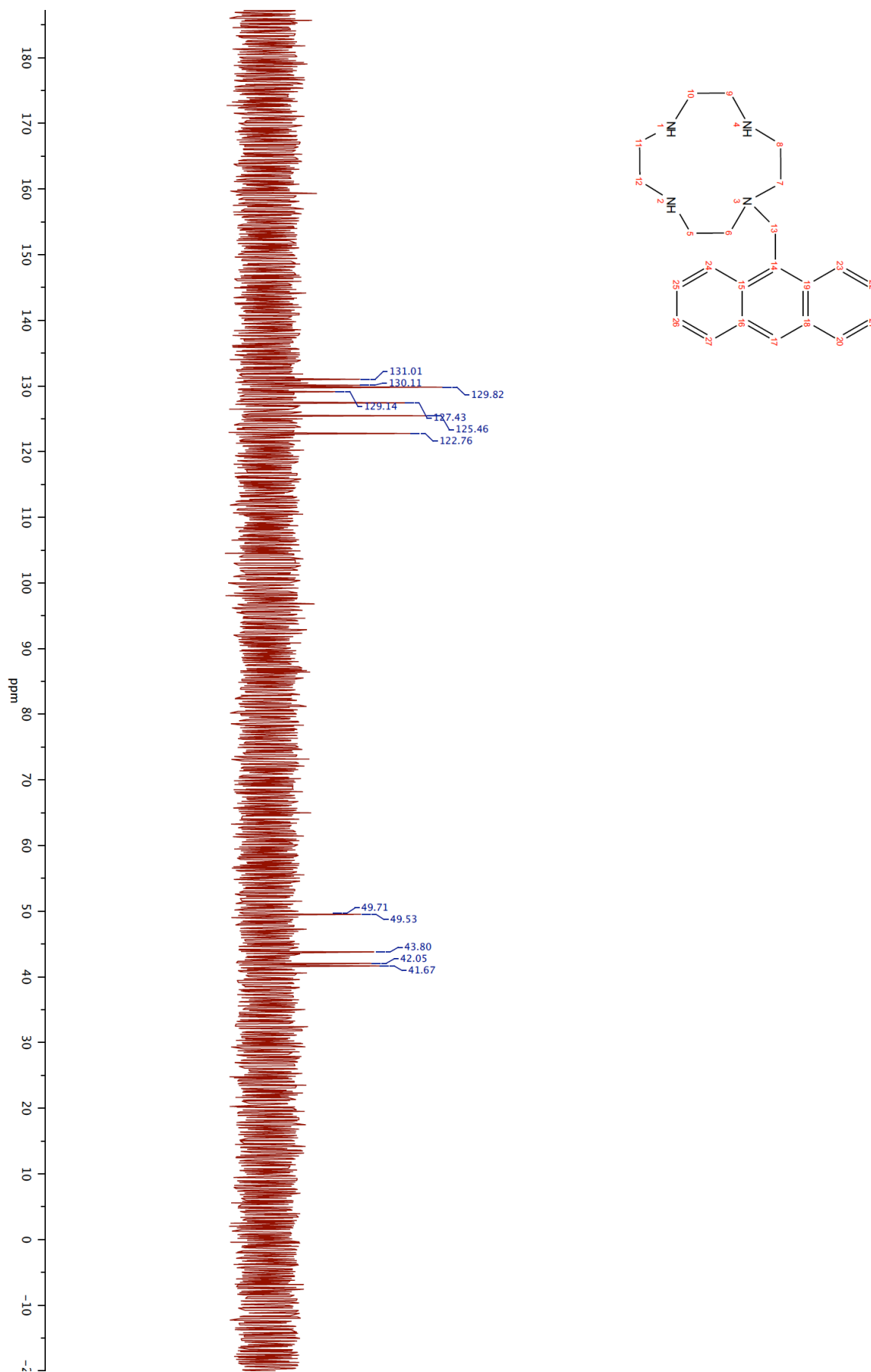
1-(2-Naphthalinmethyl)-1,4,7,10-tetraazacyclododecan (**20**) - ¹³C-NMR



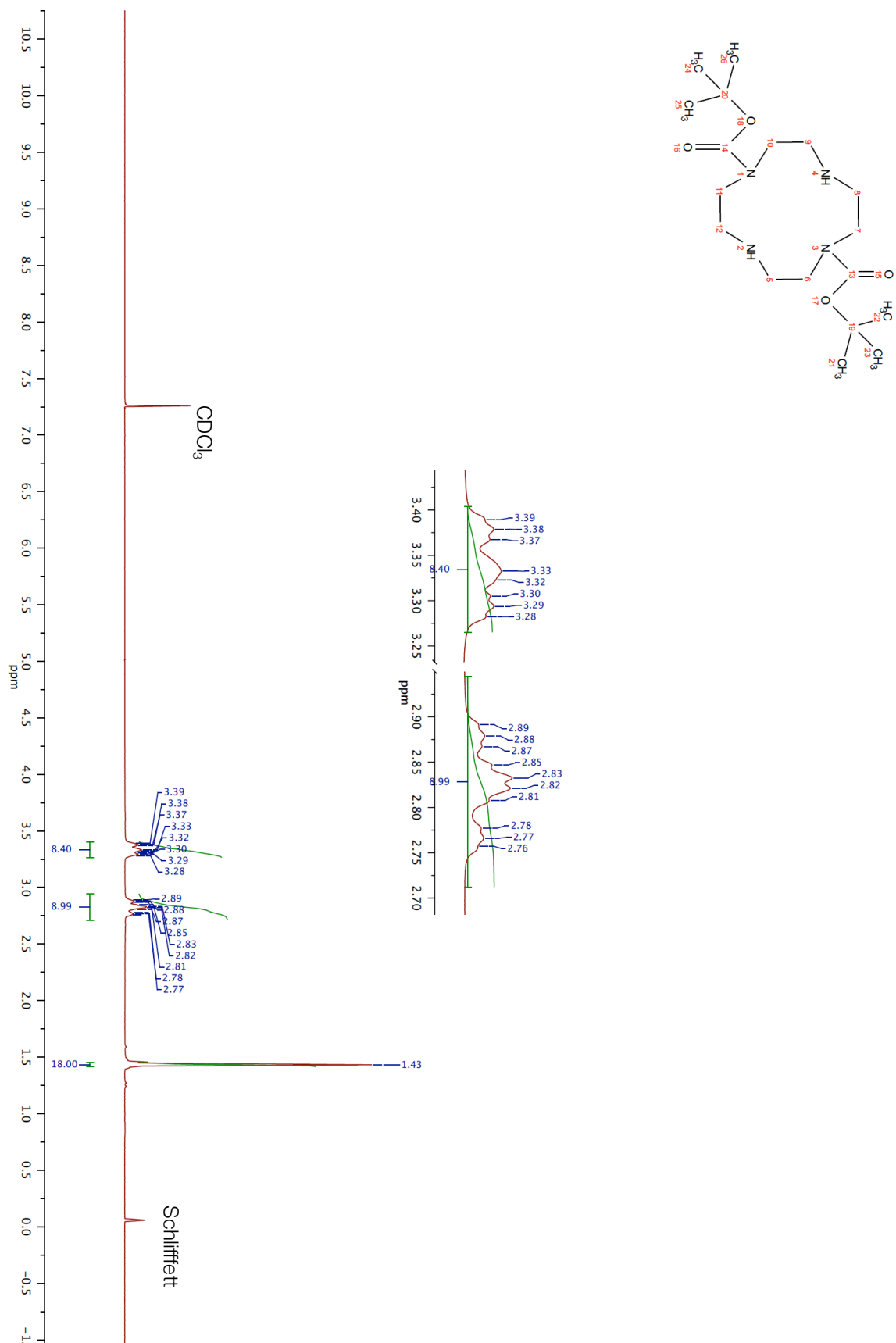
1-(9-Anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**22**) - ¹H-NMR



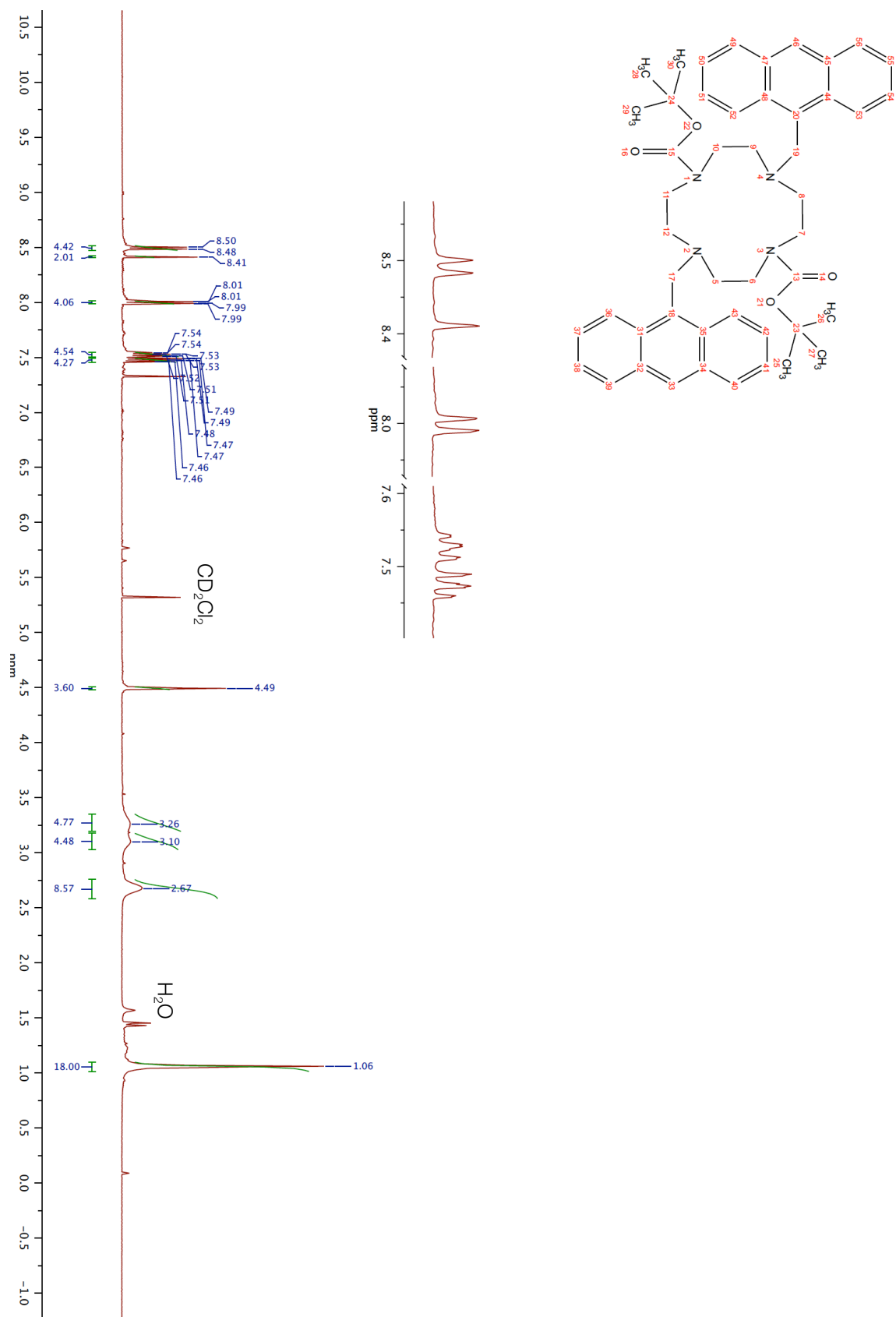
1-(9-Anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**22**) - ^{13}C -NMR



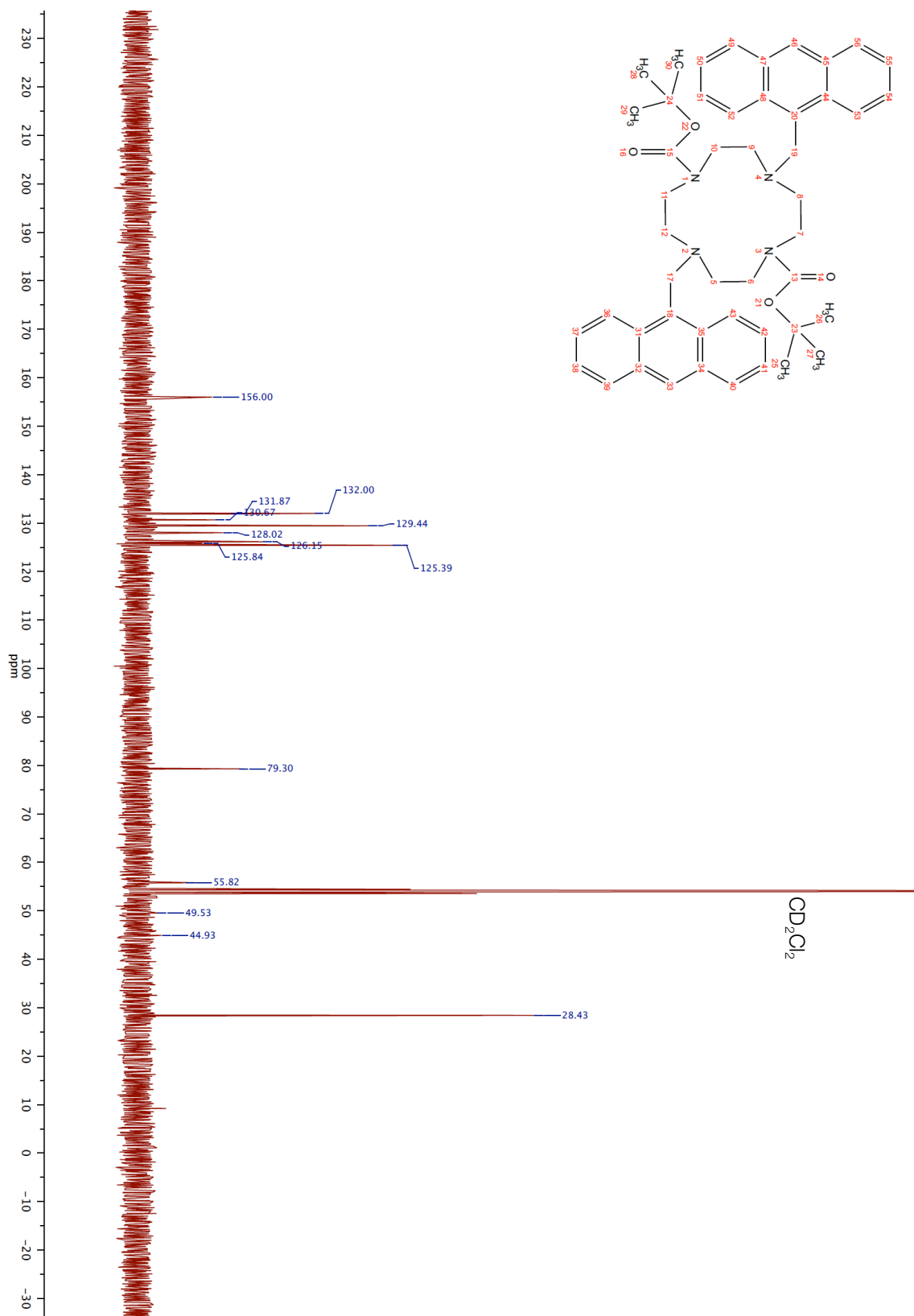
1,7-Bis(*tert*-butoxycarbonyl)-1,4,7,10-tetraazacyclododecan (**24**) - ¹H-NMR



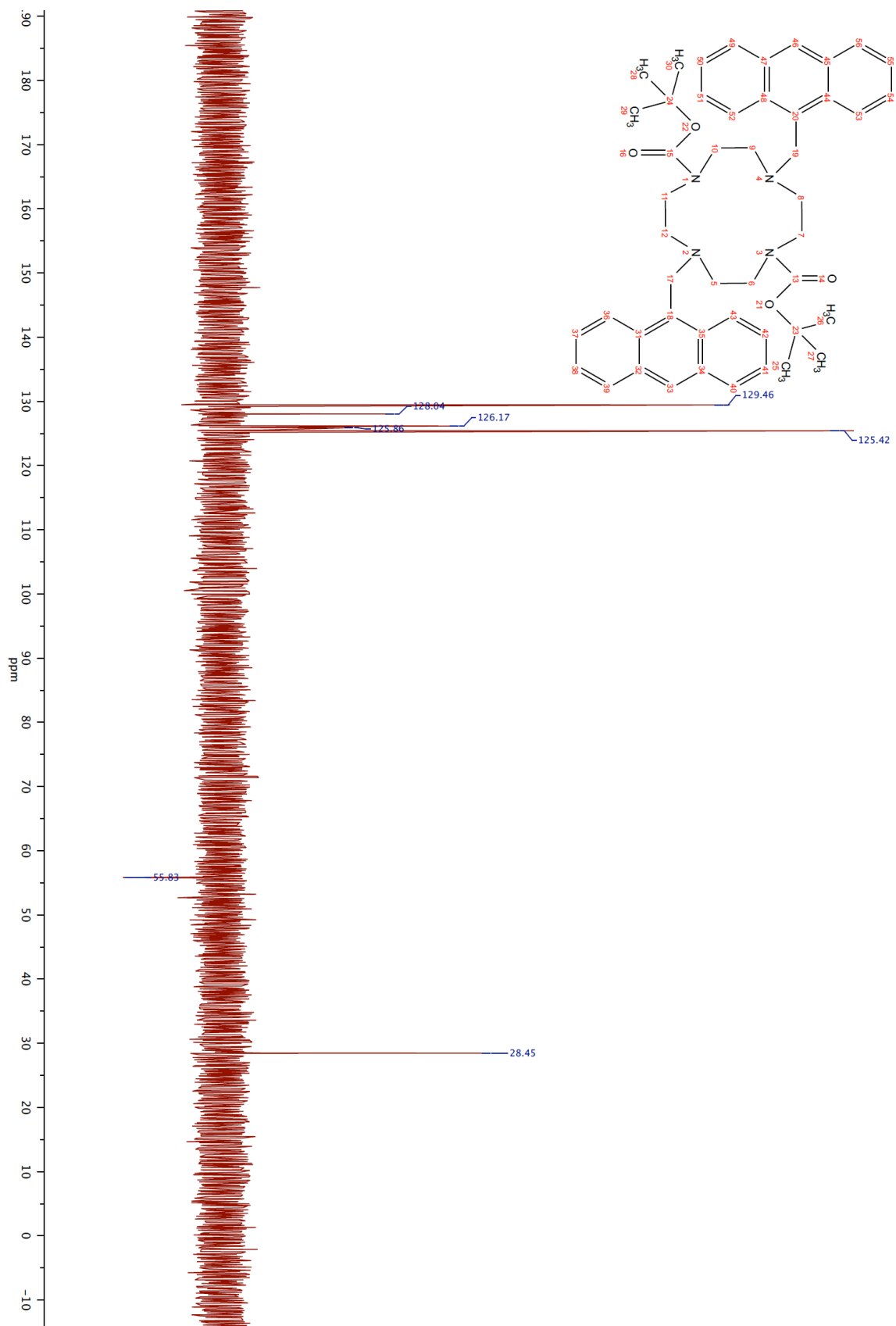
1,7-Bis(9-anthracenmethyl)-4,10-bis(*tert*-butoxycarbonyl)-1,4,7,10-tetraazacyclododecan (**25**) - ¹H-NMR



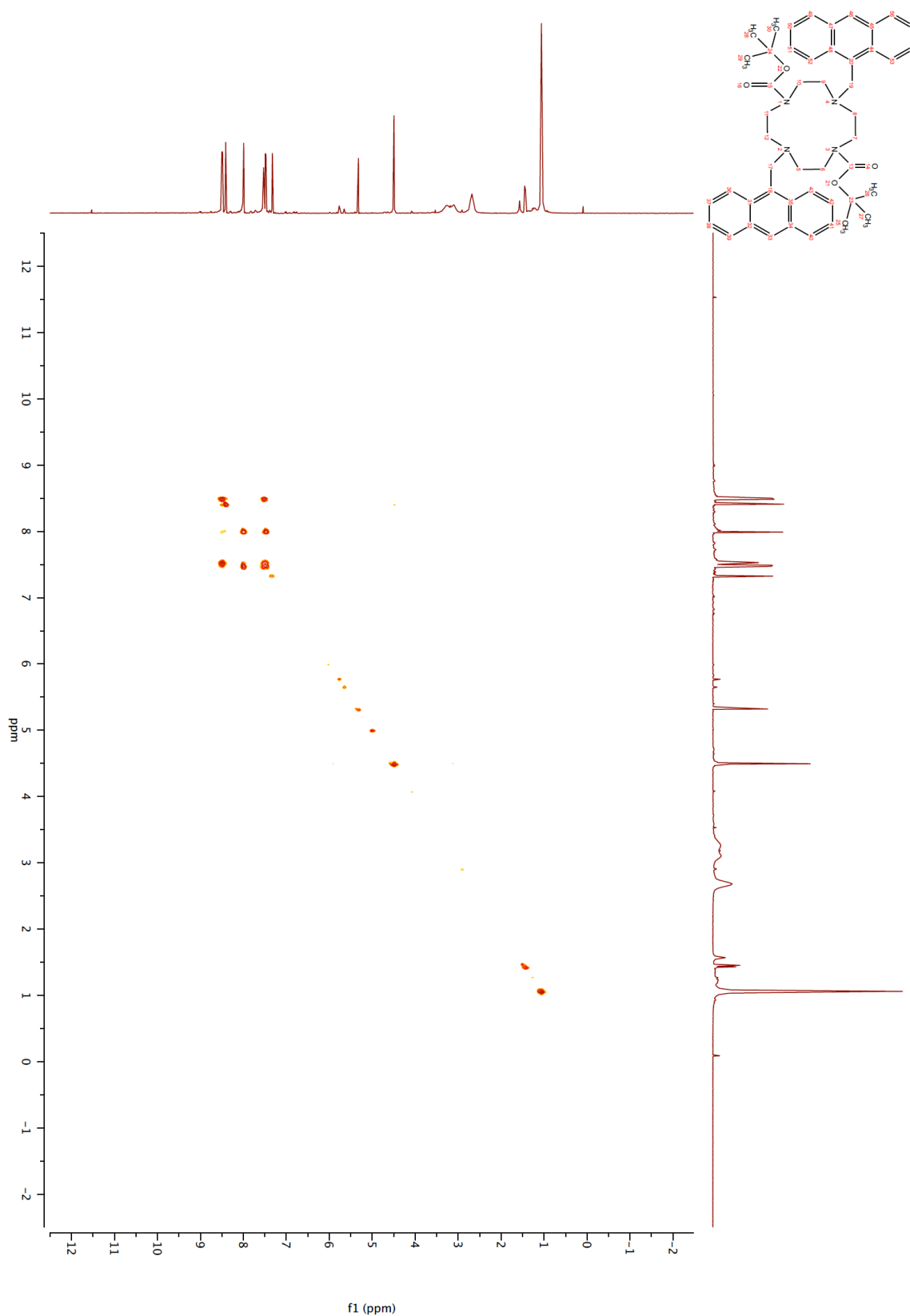
1,7-Bis(9-anthracenmethyl)-4,10-bis(*tert*-butyloxycarbonyl)-1,4,7,10-tetraazacyclododecan (**25**) - ¹³C-NMR



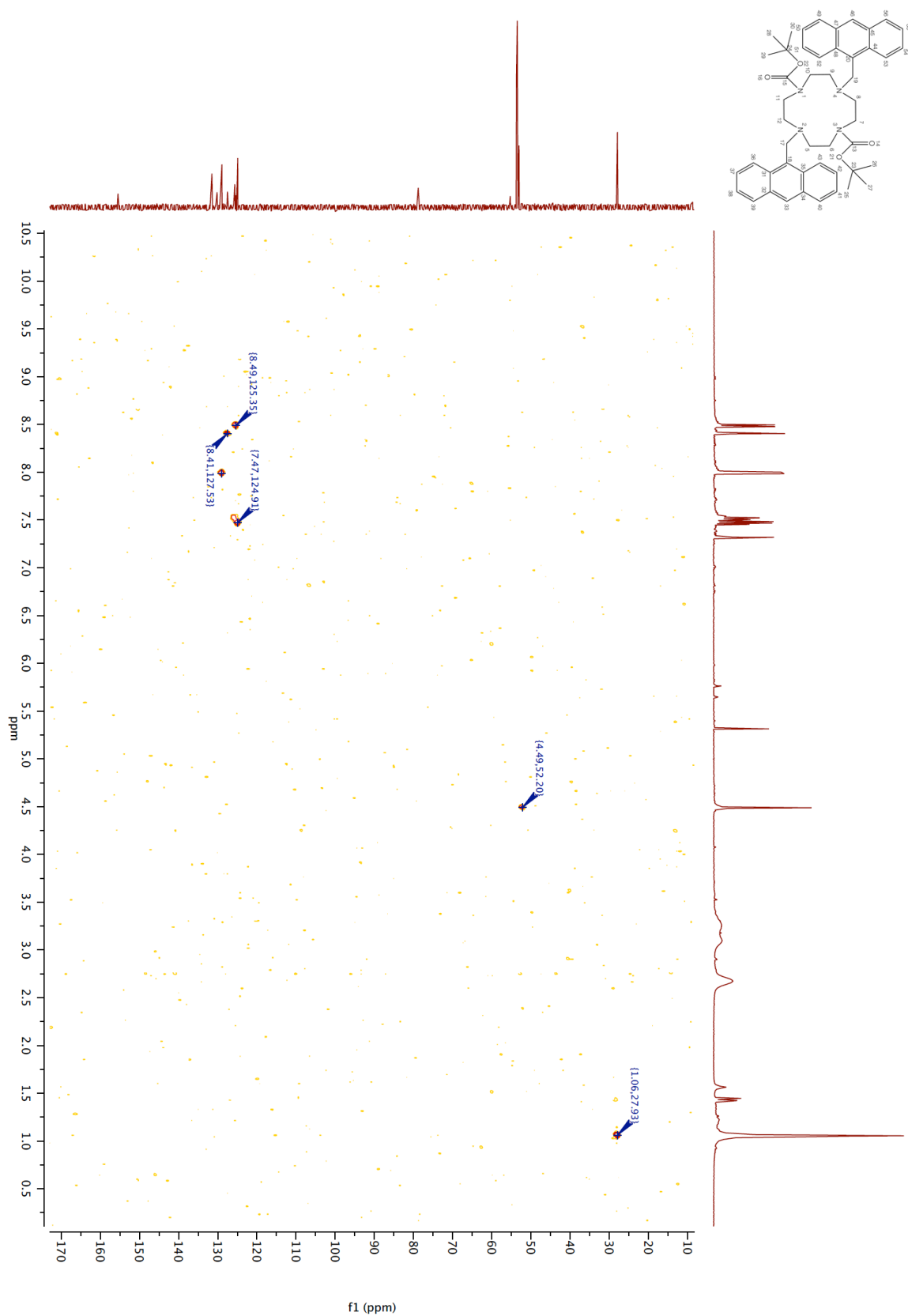
1,7-Bis(9-anthracenmethyl)-4,10-bis(*tert*-butoxycarbonyl)-1,4,7,10-tetraazacyclododecan (**25**) - DEPT-NMR



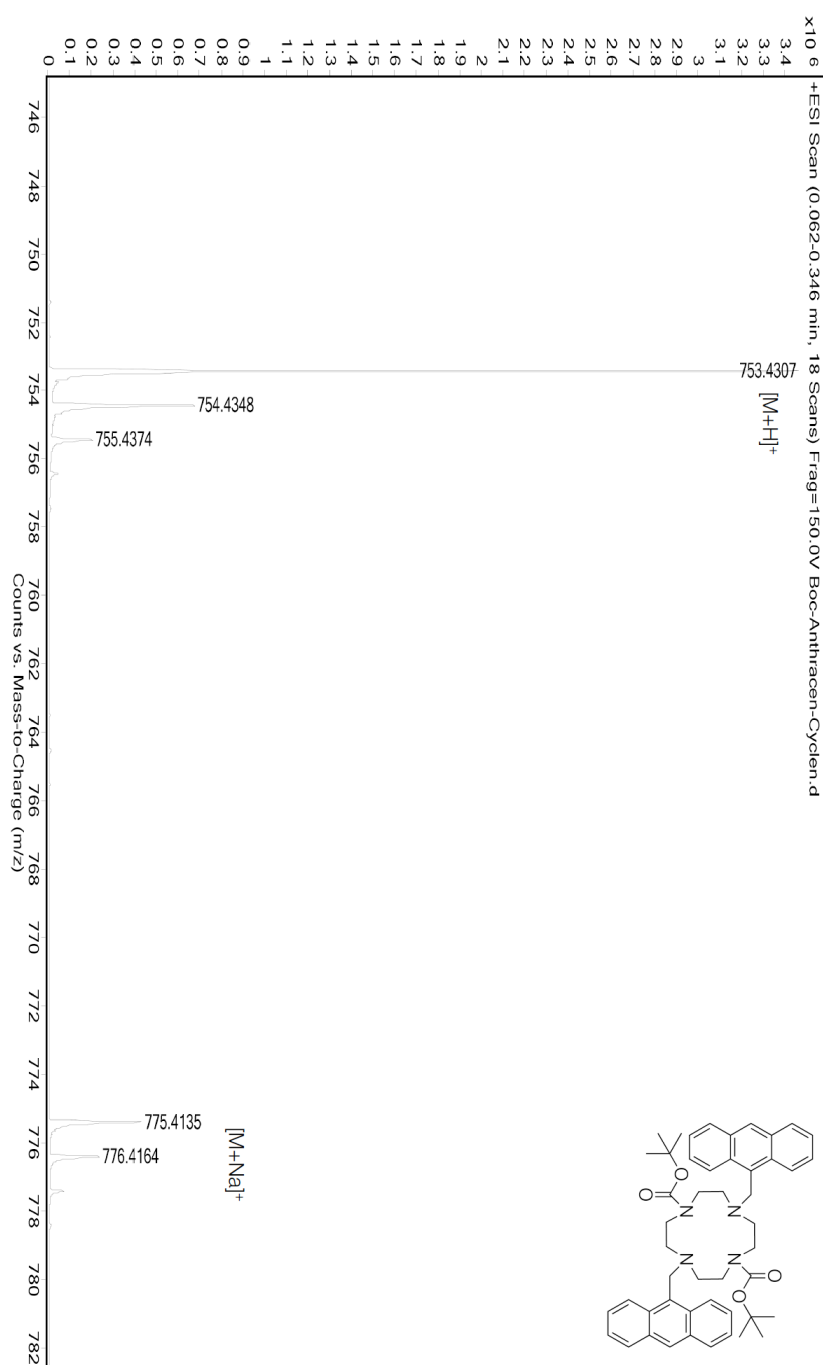
1,7-Bis(9-anthracenmethyl)-4,10-bis(*tert*-butyloxycarbonyl)-1,4,7,10-tetraazacyclododecan (**25**) - COSY-NMR



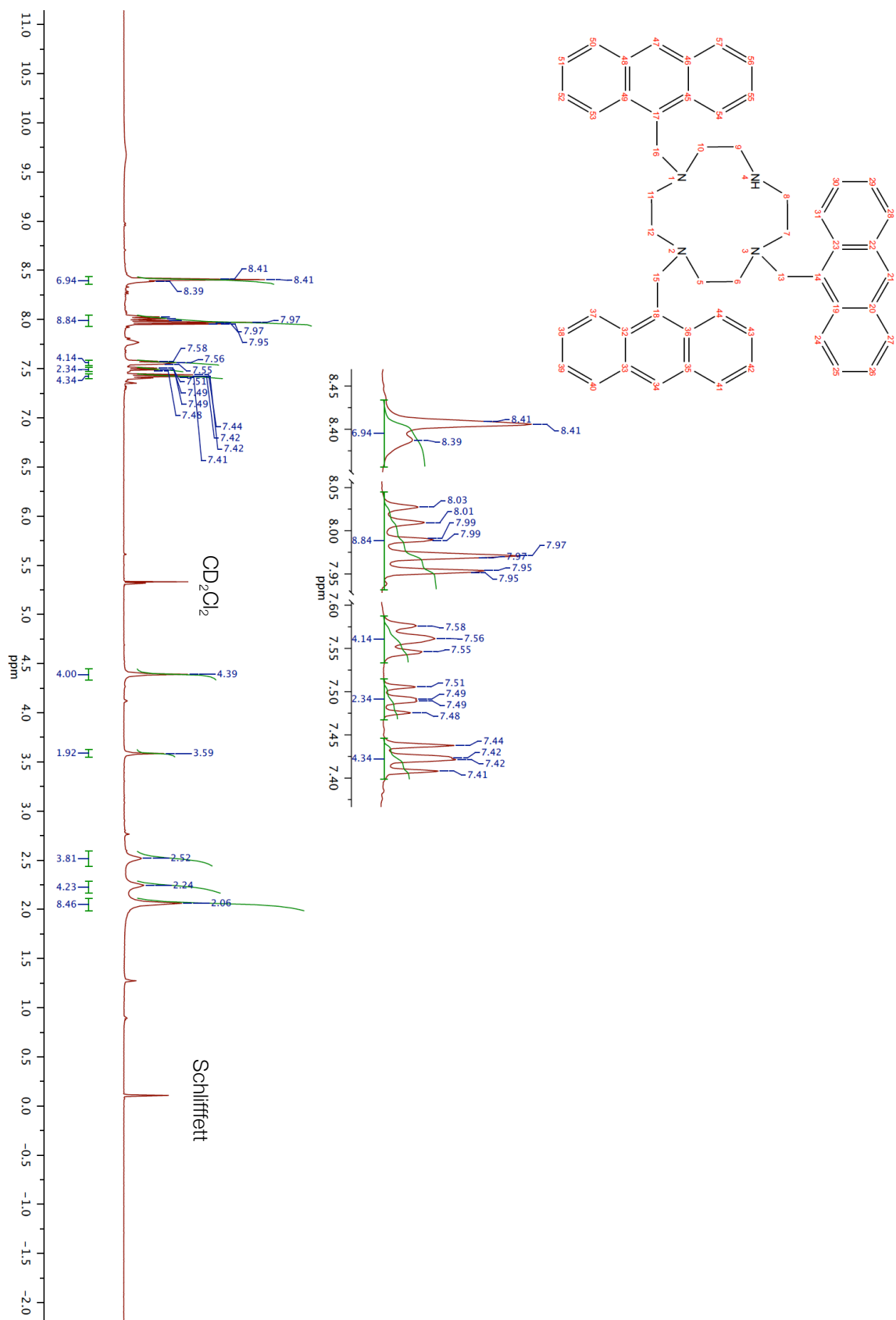
1,7-Bis(9-anthracenmethyl)-4,10-bis(*tert*-butoxycarbonyl)-1,4,7,10-tetraazacyclododecan (**25**) - HMQC-NMR



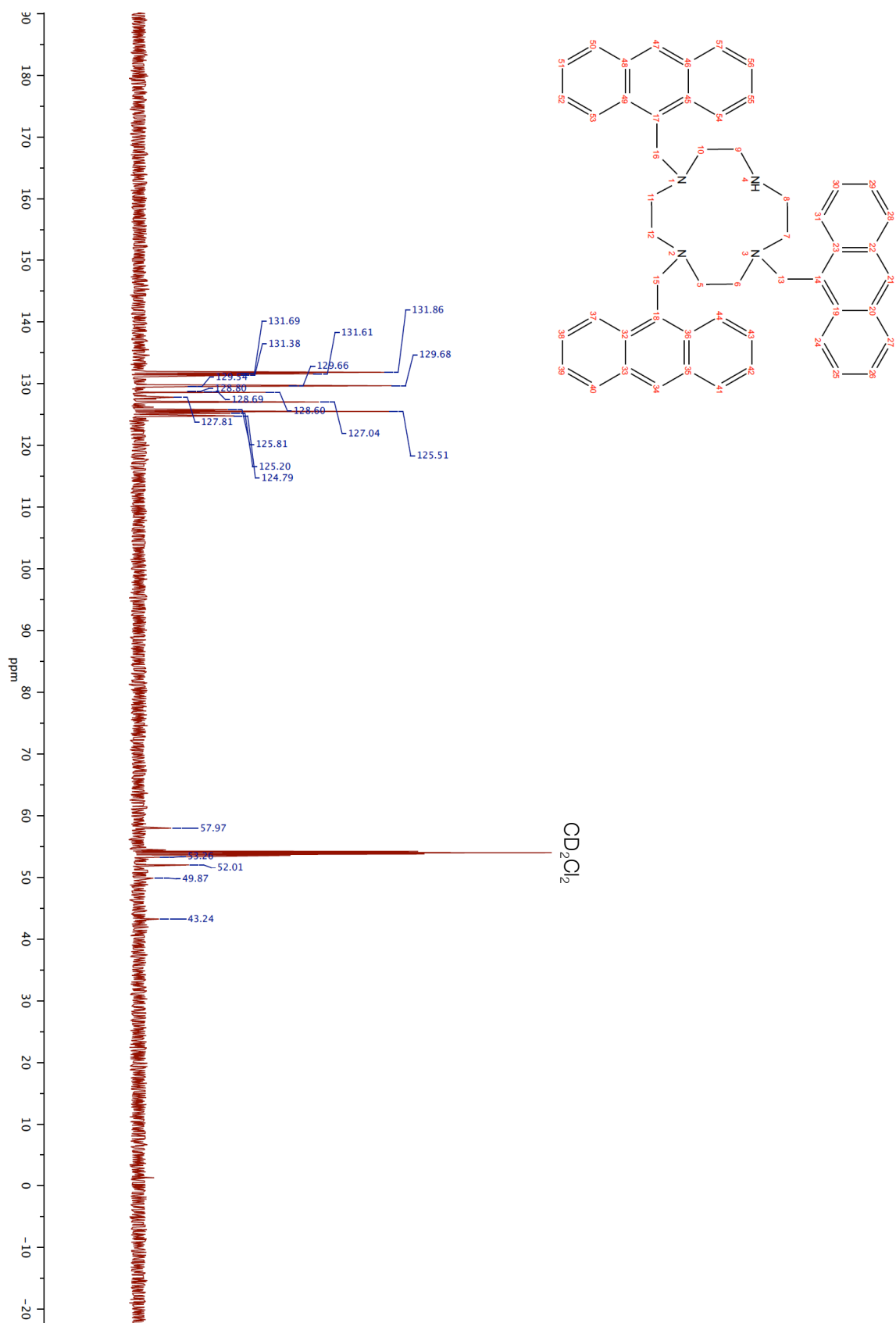
1,7-Bis(9-anthracenmethyl)-4,10-bis(*tert*-butyloxycarbonyl)-1,4,7,10-tetraazacyclododecan (**25**) - ESI-MS



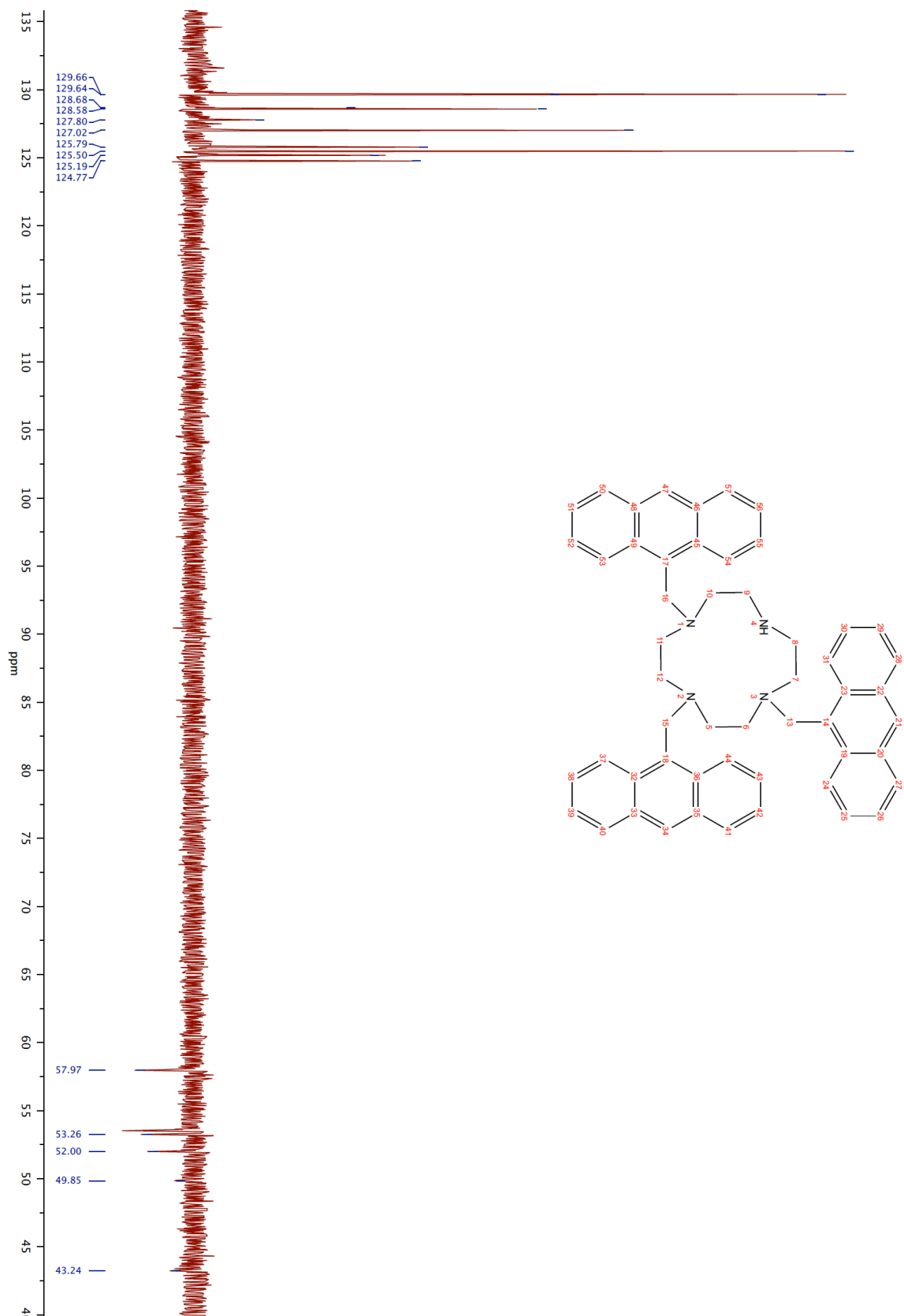
1,4,7-Tris(9-anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**27**) - ¹H-NMR



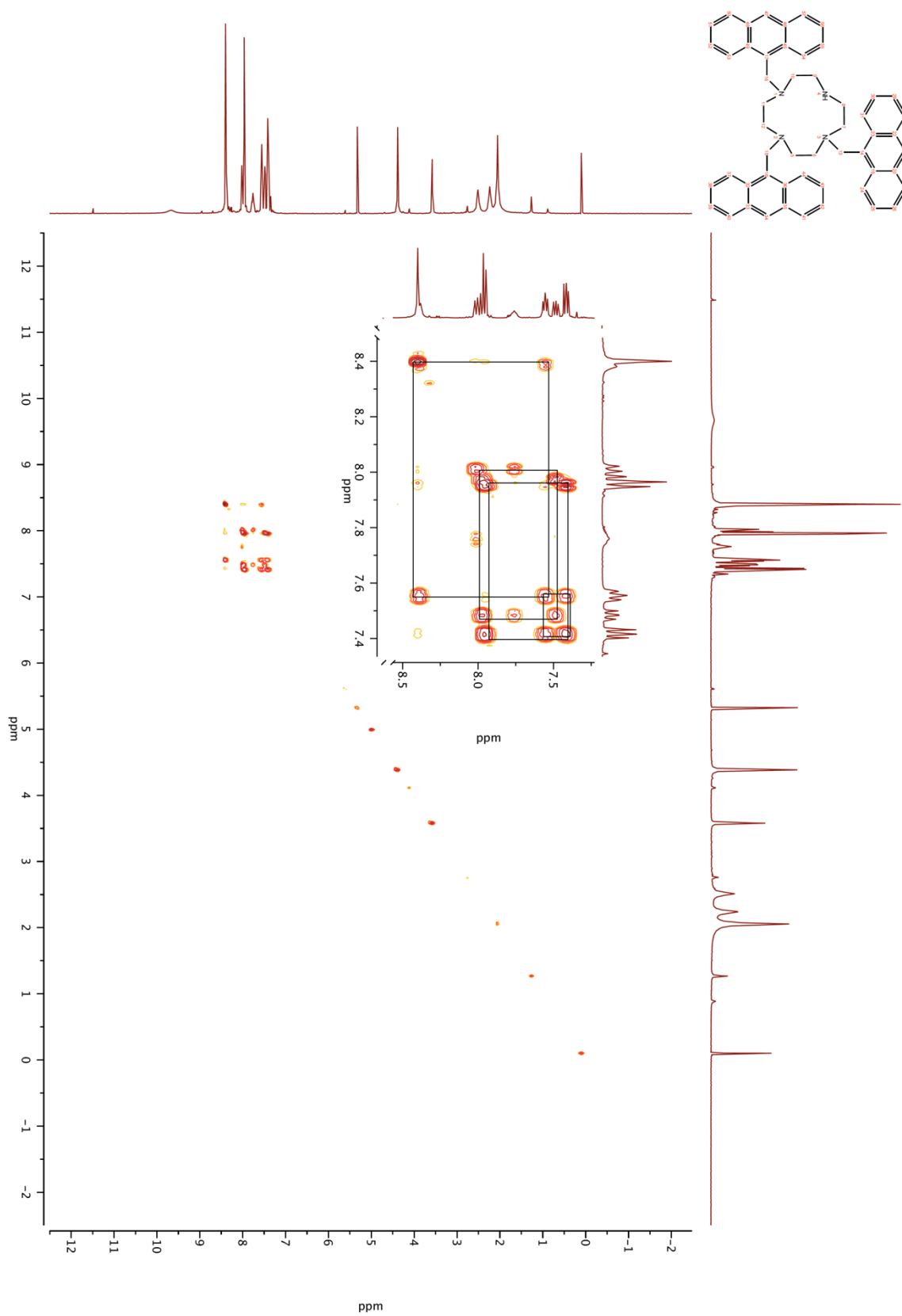
1,4,7-Tris(9-anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**27**) - ^{13}C -NMR



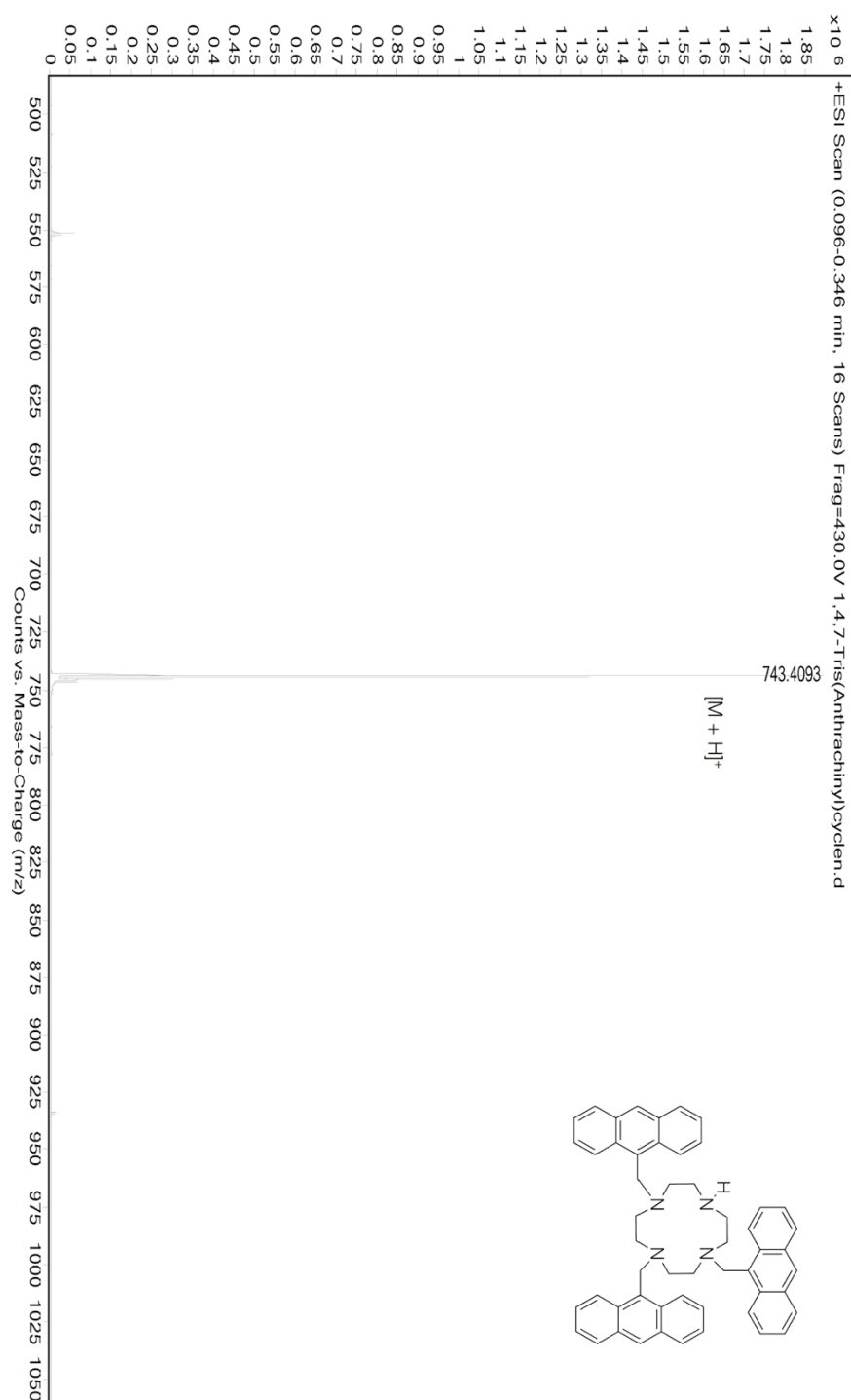
1,4,7-Tris(9-anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**27**) - DEPT-NMR



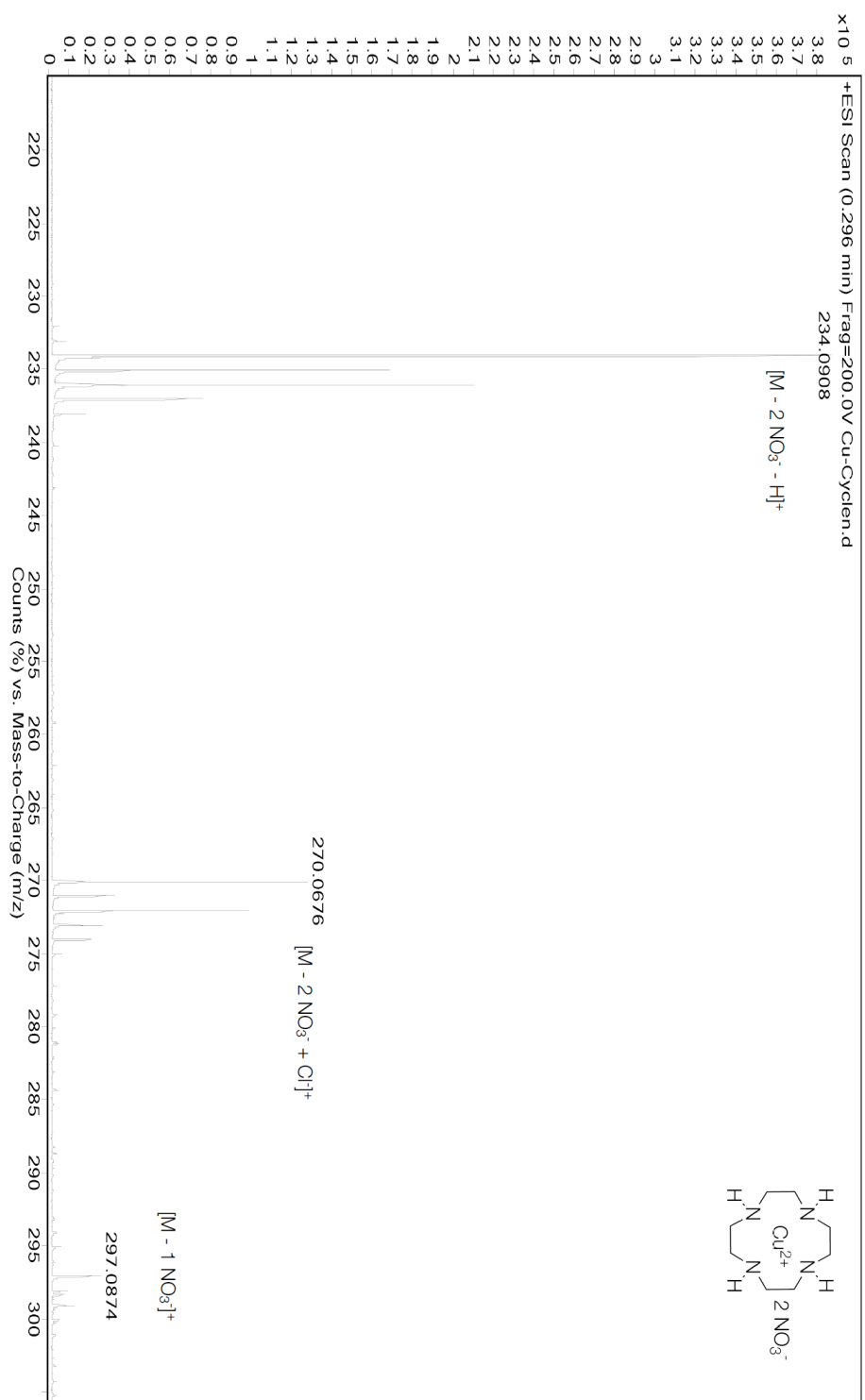
1,4,7-Tris(9-anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**27**) - COSY-NMR



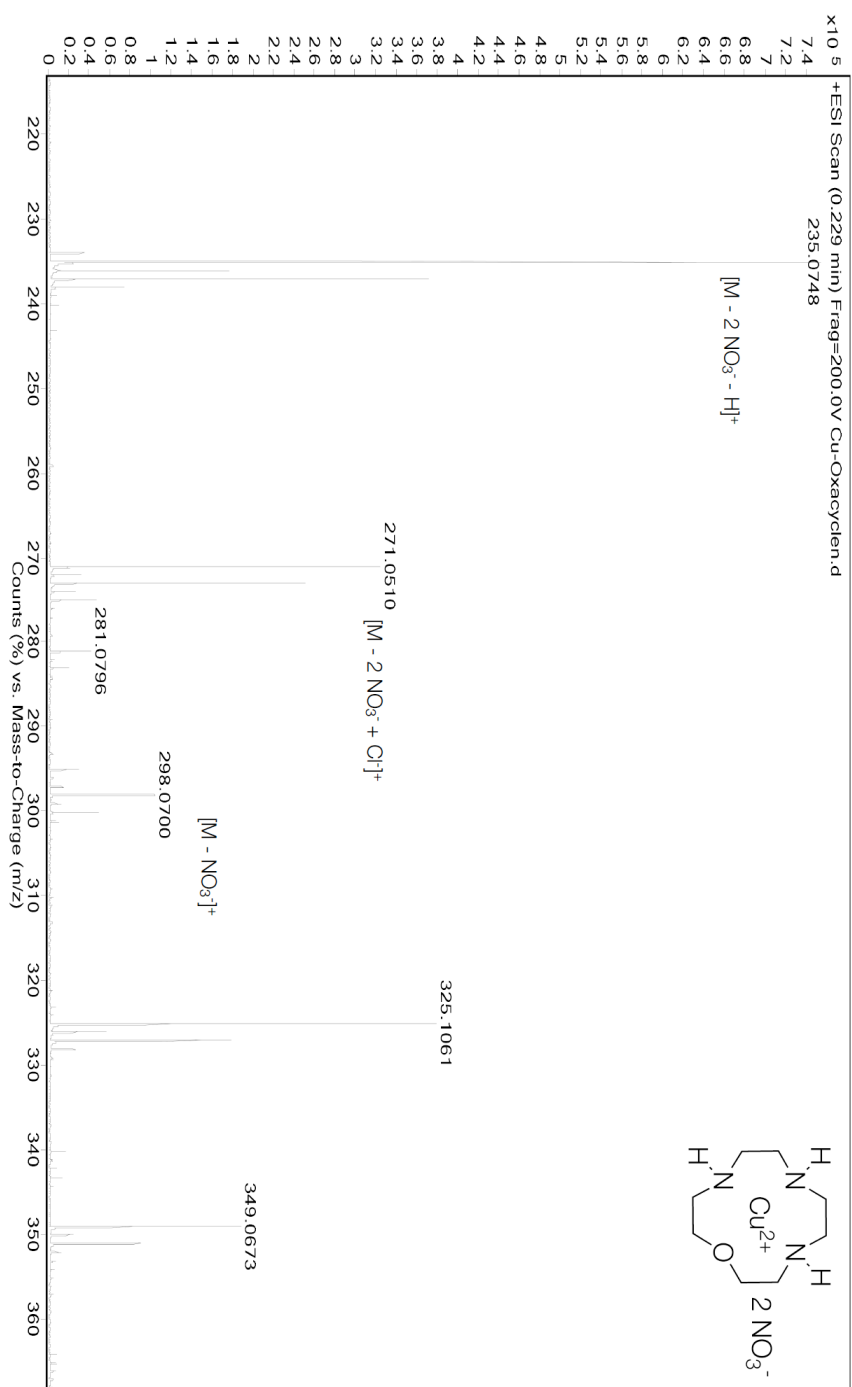
1,4,7-Tris(9-anthracenmethyl)-1,4,7,10-tetraazacyclododecan (**27**) - ESI-MS



[Cu([12]aneN)(NO₃)] (**29**)



[Cu([12]aneNO)(NO)] (31)



Crystal data and structure refinement for [Cu([12]aneNO)(NO)]

Identification code	oxaa	
Empirical formula	C ₈ H ₁₉ Cu N ₅ O ₇	
Formula weight	360.82	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.9211(19) Å	α = 90°.
	b = 11.979(3) Å	β = 92.587(5)°.
	c = 14.757(3) Å	γ = 90°.
Volume	1398.9(6) Å ³	
Z	4	
Density (calculated)	1.713 Mg/m ³	
Absorption coefficient	1.604 mm ⁻¹	
F(000)	748	
Crystal size	0.40 x 0.15 x 0.07 mm ³	
Theta range for data collection	2.19 to 30.56°.	
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 13, -21 ≤ l ≤ 19	
Reflections collected	17378	
Independent reflections	4238 [R(int) = 0.0253]	
Completeness to theta = 30.56°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.54	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4238 / 0 / 202	
Goodness-of-fit on F ²	1.089	
Final R indices [I > 2σ(I)]	R1 = 0.0290, wR2 = 0.0683	
R indices (all data)	R1 = 0.0399, wR2 = 0.0731	
Largest diff. peak and hole	0.597 and -0.399 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for oxaa. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Cu(01)	8860(1)	10268(1)	7106(1)	13(1)
C(1)	6698(2)	9853(2)	8649(1)	18(1)
C(2)	8387(2)	10264(2)	9047(1)	17(1)
C(3)	10771(2)	9112(2)	8475(1)	18(1)
C(4)	9937(2)	8207(1)	7893(1)	18(1)
C(5)	8257(2)	8099(2)	6411(1)	20(1)
C(7)	7687(2)	8876(2)	5647(1)	22(1)
C(8)	5529(2)	10221(2)	6233(1)	20(1)
C(9)	5170(2)	9867(2)	7193(1)	19(1)
N(1)	9782(2)	10166(1)	8407(1)	15(1)
N(2)	9555(2)	8686(1)	6983(1)	16(1)
N(3)	7309(2)	10013(1)	5999(1)	17(1)
N(4)	10573(2)	11972(1)	6504(1)	17(1)
N(5)	2880(2)	7603(1)	5688(1)	21(1)
O(1)	6410(1)	10394(1)	7788(1)	16(1)
O(2)	9138(1)	11931(1)	6891(1)	18(1)
O(3)	11417(2)	11096(1)	6481(1)	23(1)
O(4)	11038(2)	12848(1)	6171(1)	31(1)
O(5)	2070(2)	8503(1)	5578(1)	27(1)
O(6)	2594(2)	7002(2)	6353(1)	45(1)
O(7)	3954(2)	7328(1)	5145(1)	36(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for oxaa.

Cu(01)-N(2)	1.9837(15)
Cu(01)-N(3)	2.0224(15)
Cu(01)-N(1)	2.0267(14)
Cu(01)-O(2)	2.0312(13)
Cu(01)-O(1)	2.2310(12)
C(1)-O(1)	1.4347(19)
C(1)-C(2)	1.518(2)

[Cu([12]aneNO)(NO)] (**31**)- Röntgenstrukturanalyse

C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-N(1)	1.491(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-N(1)	1.487(2)
C(3)-C(4)	1.516(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-N(2)	1.478(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-N(2)	1.478(2)
C(5)-C(7)	1.515(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(7)-N(3)	1.493(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(3)	1.488(2)
C(8)-C(9)	1.518(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-O(1)	1.4348(19)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
N(1)-H(1)	0.80(2)
N(2)-H(2)	0.86(2)
N(3)-H(3)	0.81(2)
N(4)-O(4)	1.2227(19)
N(4)-O(3)	1.2457(19)
N(4)-O(2)	1.2955(17)
N(5)-O(7)	1.2390(19)
N(5)-O(6)	1.245(2)
N(5)-O(5)	1.261(2)
N(2)-Cu(01)-N(3)	86.73(6)

N(2)-Cu(01)-N(1)	86.54(6)
N(3)-Cu(01)-N(1)	159.40(6)
N(2)-Cu(01)-O(2)	152.88(5)
N(3)-Cu(01)-O(2)	95.04(5)
N(1)-Cu(01)-O(2)	99.78(5)
N(2)-Cu(01)-O(1)	110.88(5)
N(3)-Cu(01)-O(1)	82.29(5)
N(1)-Cu(01)-O(1)	81.97(5)
O(2)-Cu(01)-O(1)	96.15(4)
O(1)-C(1)-C(2)	107.37(13)
O(1)-C(1)-H(1A)	110.2
C(2)-C(1)-H(1A)	110.2
O(1)-C(1)-H(1B)	110.2
C(2)-C(1)-H(1B)	110.2
H(1A)-C(1)-H(1B)	108.5
N(1)-C(2)-C(1)	113.26(13)
N(1)-C(2)-H(2A)	108.9
C(1)-C(2)-H(2A)	108.9
N(1)-C(2)-H(2B)	108.9
C(1)-C(2)-H(2B)	108.9
H(2A)-C(2)-H(2B)	107.7
N(1)-C(3)-C(4)	110.72(13)
N(1)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3A)	109.5
N(1)-C(3)-H(3B)	109.5
C(4)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	108.1
N(2)-C(4)-C(3)	107.68(13)
N(2)-C(4)-H(4A)	110.2
C(3)-C(4)-H(4A)	110.2
N(2)-C(4)-H(4B)	110.2
C(3)-C(4)-H(4B)	110.2
H(4A)-C(4)-H(4B)	108.5
N(2)-C(5)-C(7)	107.96(14)
N(2)-C(5)-H(5A)	110.1
C(7)-C(5)-H(5A)	110.1
N(2)-C(5)-H(5B)	110.1

C(7)-C(5)-H(5B)	110.1
H(5A)-C(5)-H(5B)	108.4
N(3)-C(7)-C(5)	111.10(13)
N(3)-C(7)-H(7A)	109.4
C(5)-C(7)-H(7A)	109.4
N(3)-C(7)-H(7B)	109.4
C(5)-C(7)-H(7B)	109.4
H(7A)-C(7)-H(7B)	108.0
N(3)-C(8)-C(9)	112.92(13)
N(3)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8A)	109.0
N(3)-C(8)-H(8B)	109.0
C(9)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
O(1)-C(9)-C(8)	107.24(13)
O(1)-C(9)-H(9A)	110.3
C(8)-C(9)-H(9A)	110.3
O(1)-C(9)-H(9B)	110.3
C(8)-C(9)-H(9B)	110.3
H(9A)-C(9)-H(9B)	108.5
C(3)-N(1)-C(2)	115.28(13)
C(3)-N(1)-Cu(01)	106.34(10)
C(2)-N(1)-Cu(01)	110.47(10)
C(3)-N(1)-H(1)	107.9(17)
C(2)-N(1)-H(1)	107.2(16)
Cu(01)-N(1)-H(1)	109.6(17)
C(5)-N(2)-C(4)	116.26(13)
C(5)-N(2)-Cu(01)	108.56(10)
C(4)-N(2)-Cu(01)	109.51(10)
C(5)-N(2)-H(2)	108.1(15)
C(4)-N(2)-H(2)	107.4(15)
Cu(01)-N(2)-H(2)	106.6(16)
C(8)-N(3)-C(7)	116.14(14)
C(8)-N(3)-Cu(01)	109.56(10)
C(7)-N(3)-Cu(01)	107.12(10)
C(8)-N(3)-H(3)	107.5(14)
C(7)-N(3)-H(3)	105.9(14)

[Cu([12]aneNO)(NO)] (**31**)- Röntgenstrukturanalyse

Cu(01)-N(3)-H(3)	110.5(15)
O(4)-N(4)-O(3)	122.78(13)
O(4)-N(4)-O(2)	119.69(14)
O(3)-N(4)-O(2)	117.52(13)
O(7)-N(5)-O(6)	120.67(16)
O(7)-N(5)-O(5)	120.30(15)
O(6)-N(5)-O(5)	119.03(14)
C(1)-O(1)-C(9)	114.87(13)
C(1)-O(1)-Cu(01)	105.20(8)
C(9)-O(1)-Cu(01)	106.23(9)
N(4)-O(2)-Cu(01)	102.11(9)

Symmetry transformations used to generate equivalent atoms:

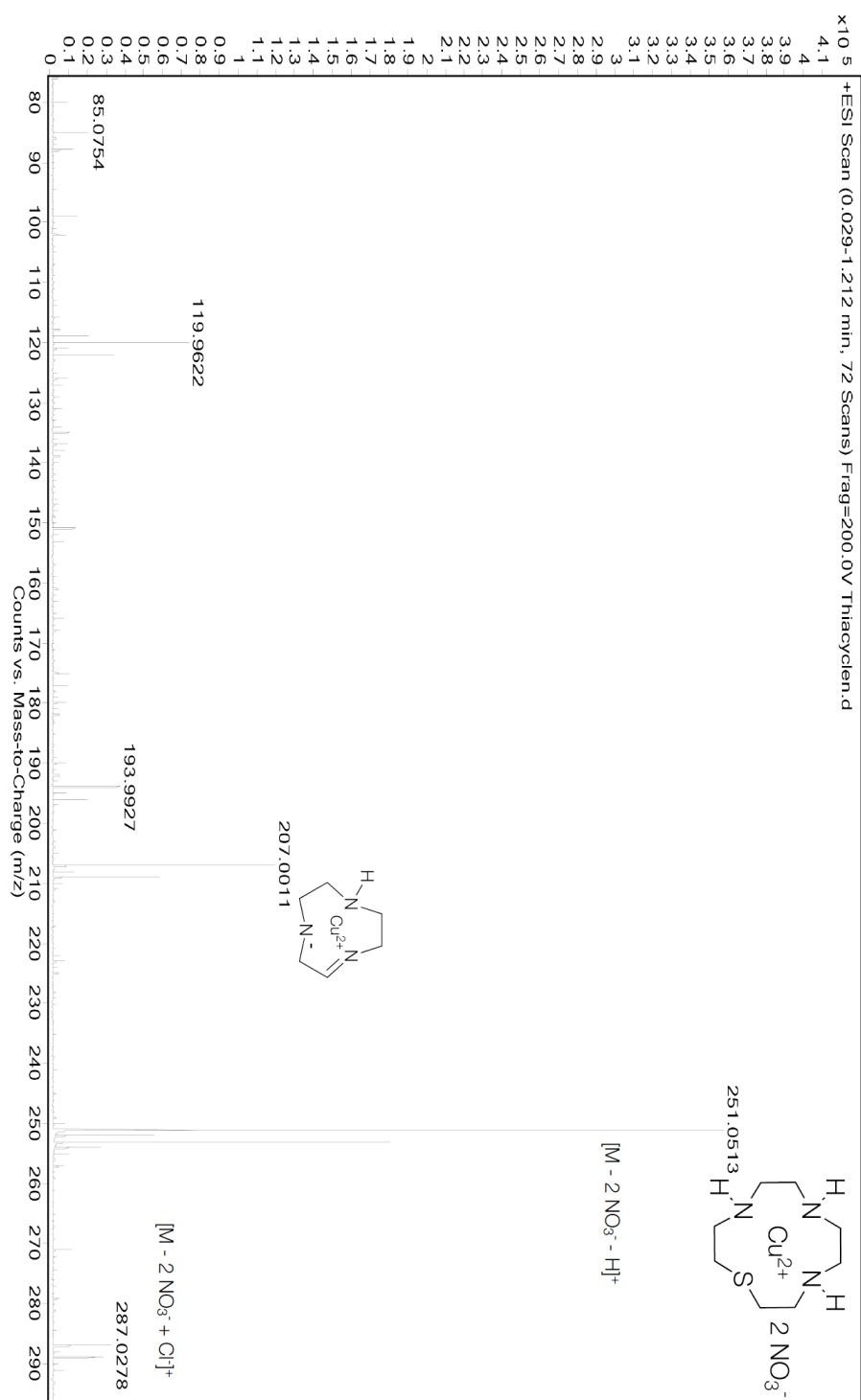


Table 1. Crystal data and structure refinement for [Cu([12]aneN3S) (NO3)2]

Identification code	thiaa	
Empirical formula	C8 H19 Cu N5 O6 S	
Formula weight	376.88	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.5321(16) Å	$\alpha = 90^\circ$.
	b = 11.903(2) Å	$\beta = 94.368(4)^\circ$.
	c = 14.168(3) Å	$\gamma = 90^\circ$.
Volume	1434.7(5) Å ³	
Z	4	
Density (calculated)	1.745 Mg/m ³	
Absorption coefficient	1.703 mm ⁻¹	
F(000)	780	
Crystal size	0.50 x 0.12 x 0.07 mm ³	
Theta range for data collection	2.24 to 30.56°.	
Index ranges	-11 ≤ h ≤ 12, -15 ≤ k ≤ 16, -19 ≤ l ≤ 20	
Reflections collected	17105	
Independent reflections	4381 [R(int) = 0.0143]	
Completeness to theta = 30.56°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4381 / 0 / 202	
Goodness-of-fit on F ²	1.129	
Final R indices [I > 2σ(I)]	R1 = 0.0241, wR2 = 0.0639	
R indices (all data)	R1 = 0.0264, wR2 = 0.0649	
Largest diff. peak and hole	0.619 and -0.288 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for thiaa. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	2037(1)	8353(1)	582(1)	13(1)
S(2)	1437(1)	6587(1)	-55(1)	18(1)
C(1)	309(2)	6253(1)	947(1)	19(1)
C(2)	-876(2)	7197(1)	1031(1)	19(1)
C(3)	392(2)	8546(1)	2188(1)	19(1)
C(4)	1375(2)	9606(1)	2219(1)	21(1)
C(5)	4147(2)	9035(1)	2088(1)	19(1)
C(6)	5200(2)	8651(1)	1335(1)	20(1)
C(7)	4333(2)	6680(1)	995(1)	21(1)
C(8)	3364(2)	5980(1)	263(1)	23(1)
N(1)	-71(2)	8297(1)	1173(1)	16(1)
N(2)	2676(2)	9469(1)	1597(1)	16(1)
N(3)	4308(2)	7865(1)	681(1)	16(1)
N(4)	2418(2)	9037(1)	-1412(1)	17(1)
O(1)	1816(1)	9400(1)	-666(1)	20(1)
O(2)	3121(2)	8124(1)	-1394(1)	26(1)
O(3)	2279(2)	9621(1)	-2139(1)	24(1)
N(5)	3232(2)	2314(1)	1230(1)	20(1)
O(4)	3276(2)	1539(1)	623(1)	26(1)
O(5)	3533(2)	3293(1)	995(1)	34(1)
O(6)	2905(2)	2076(1)	2043(1)	38(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for thiaa.

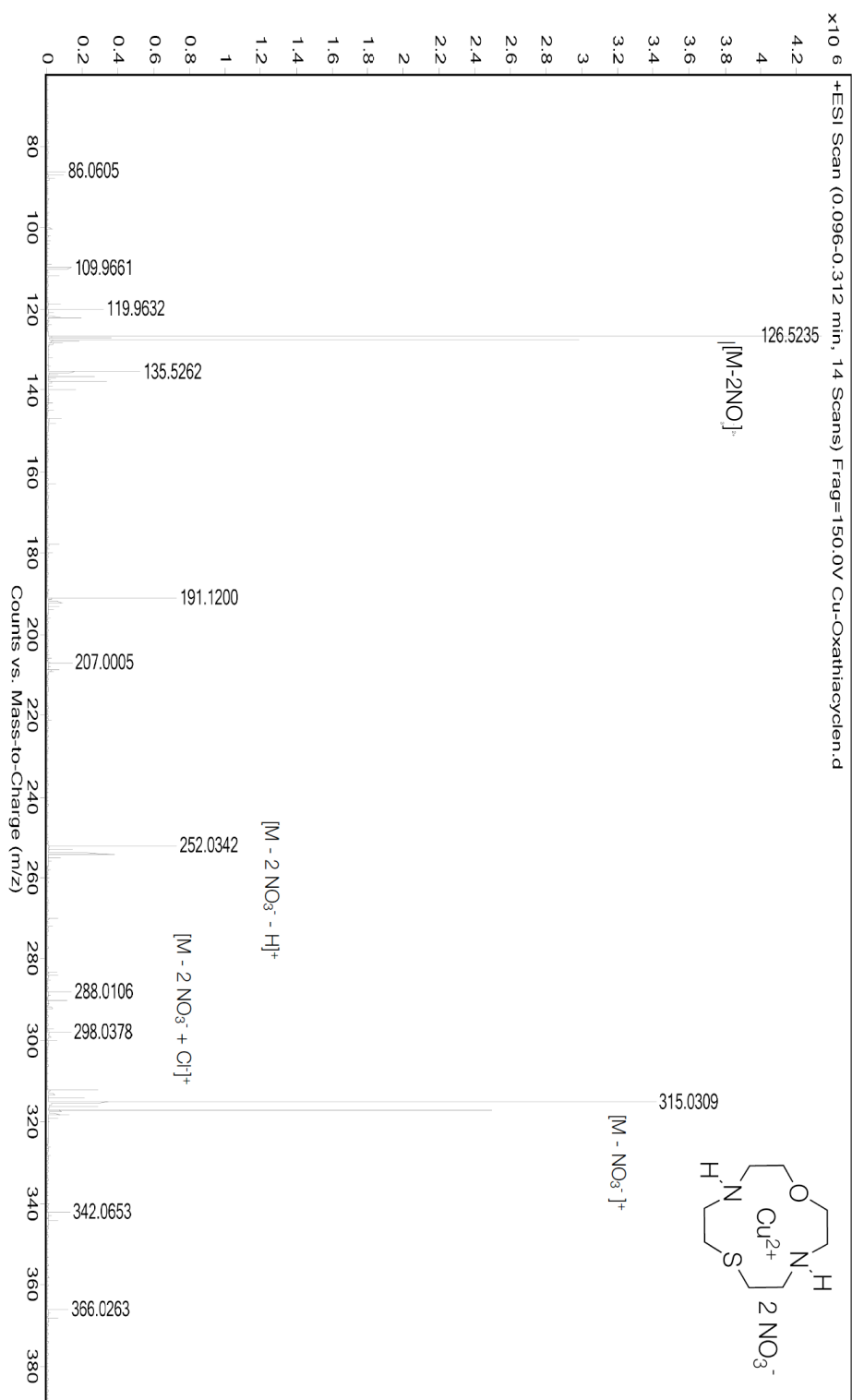
Cu(1)-N(2)	2.0027(13)
Cu(1)-N(3)	2.0176(13)
Cu(1)-N(1)	2.0423(13)
Cu(1)-O(1)	2.1596(11)
Cu(1)-S(2)	2.3283(5)
S(2)-C(1)	1.8184(16)
S(2)-C(8)	1.8211(17)

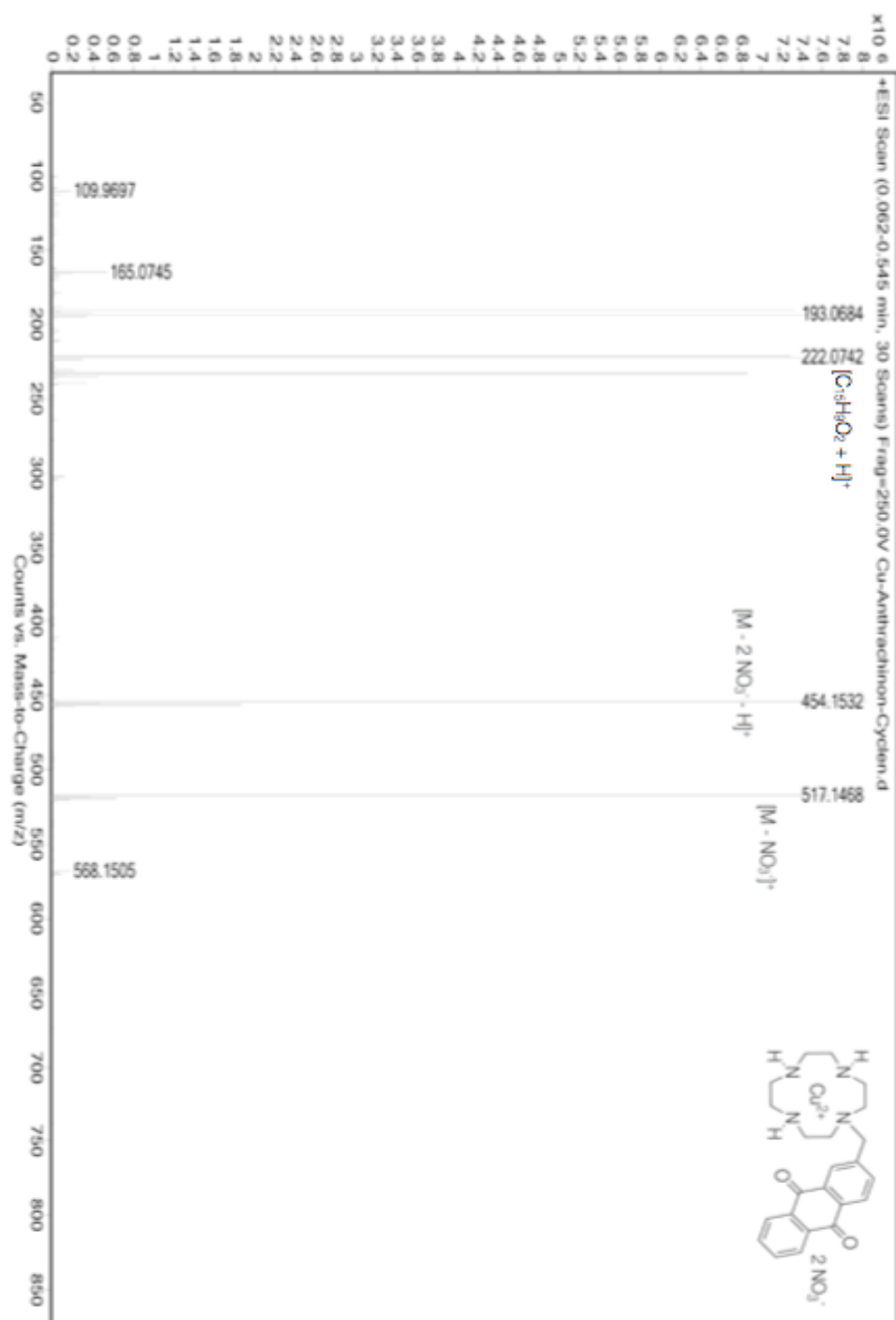
C(1)-C(2)	1.523(2)
C(2)-N(1)	1.485(2)
C(3)-N(1)	1.492(2)
C(3)-C(4)	1.515(2)
C(4)-N(2)	1.4782(19)
C(5)-N(2)	1.481(2)
C(5)-C(6)	1.516(2)
C(6)-N(3)	1.485(2)
C(7)-N(3)	1.478(2)
C(7)-C(8)	1.524(2)
N(4)-O(3)	1.2406(17)
N(4)-O(2)	1.2408(18)
N(4)-O(1)	1.2848(16)
N(5)-O(6)	1.2383(18)
N(5)-O(5)	1.2442(18)
N(5)-O(4)	1.2640(17)

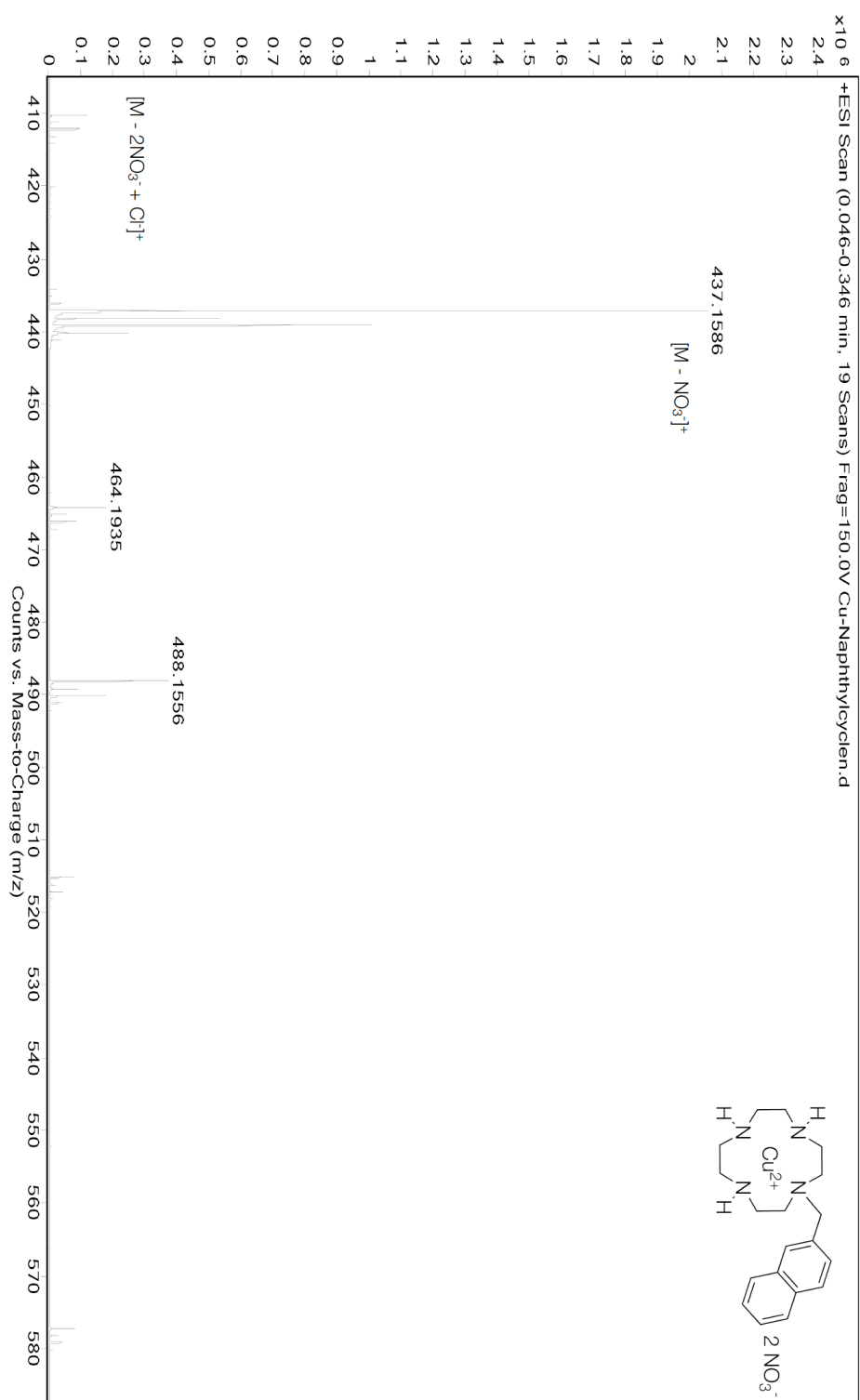
N(2)-Cu(1)-N(3)	86.19(5)
N(2)-Cu(1)-N(1)	85.81(5)
N(3)-Cu(1)-N(1)	146.42(5)
N(2)-Cu(1)-O(1)	101.94(5)
N(3)-Cu(1)-O(1)	104.32(5)
N(1)-Cu(1)-O(1)	109.24(5)
N(2)-Cu(1)-S(2)	156.44(4)
N(3)-Cu(1)-S(2)	87.07(4)
N(1)-Cu(1)-S(2)	87.42(4)
O(1)-Cu(1)-S(2)	101.60(3)
C(1)-S(2)-C(8)	103.98(8)
C(1)-S(2)-Cu(1)	90.53(5)
C(8)-S(2)-Cu(1)	95.44(5)
C(2)-C(1)-S(2)	107.06(10)
N(1)-C(2)-C(1)	110.99(12)
N(1)-C(3)-C(4)	107.38(12)
N(2)-C(4)-C(3)	109.26(12)
N(2)-C(5)-C(6)	107.51(12)
N(3)-C(6)-C(5)	109.06(12)
N(3)-C(7)-C(8)	108.85(13)

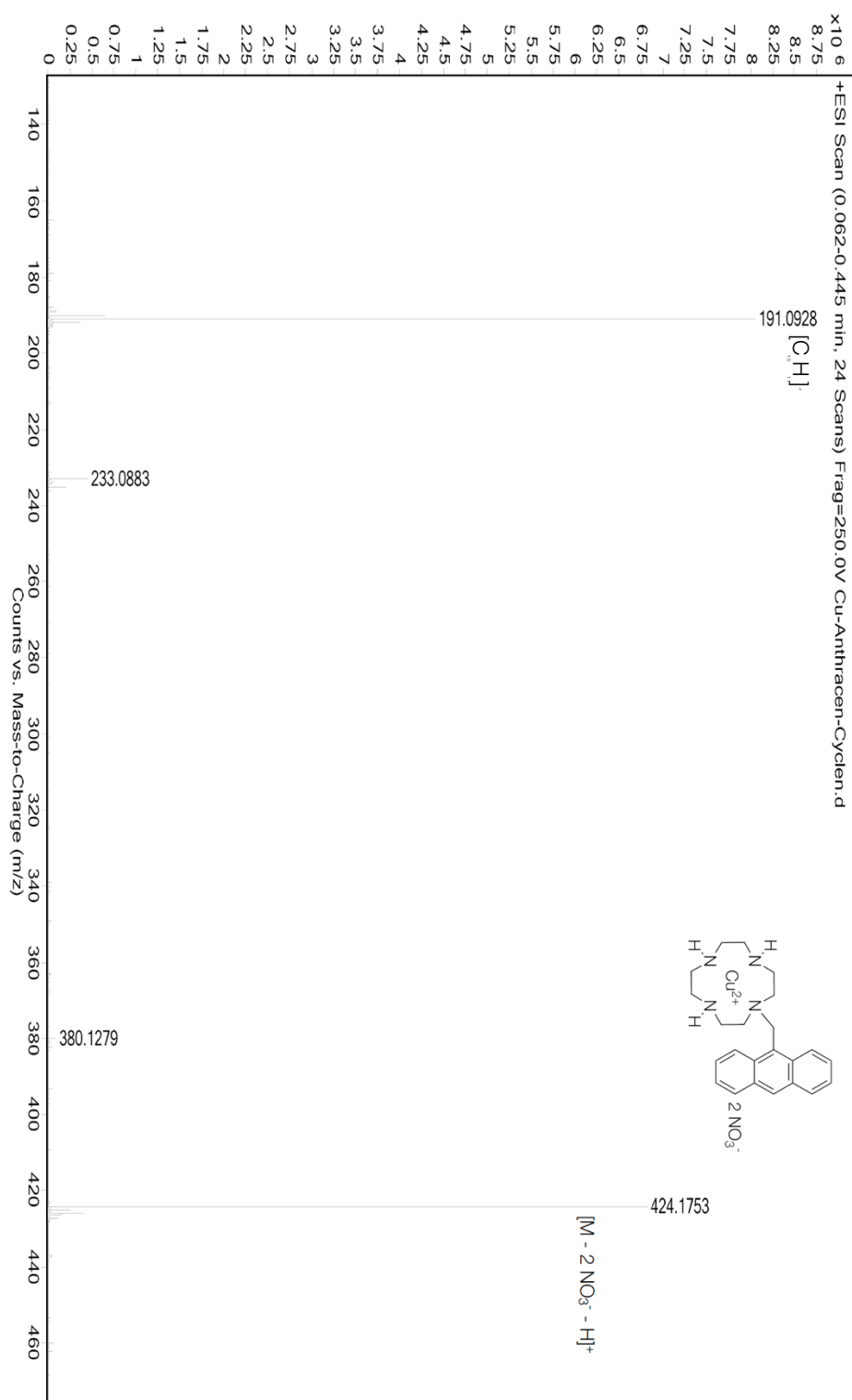
C(7)-C(8)-S(2)	112.58(11)
C(2)-N(1)-C(3)	113.02(12)
C(2)-N(1)-Cu(1)	112.70(9)
C(3)-N(1)-Cu(1)	102.27(9)
C(4)-N(2)-C(5)	113.93(12)
C(4)-N(2)-Cu(1)	109.05(10)
C(5)-N(2)-Cu(1)	106.30(9)
C(7)-N(3)-C(6)	114.75(12)
C(7)-N(3)-Cu(1)	106.71(9)
C(6)-N(3)-Cu(1)	107.80(9)
O(3)-N(4)-O(2)	121.54(13)
O(3)-N(4)-O(1)	118.42(13)
O(2)-N(4)-O(1)	120.04(13)
N(4)-O(1)-Cu(1)	117.63(9)
O(6)-N(5)-O(5)	121.96(15)
O(6)-N(5)-O(4)	119.11(14)
O(5)-N(5)-O(4)	118.93(14)

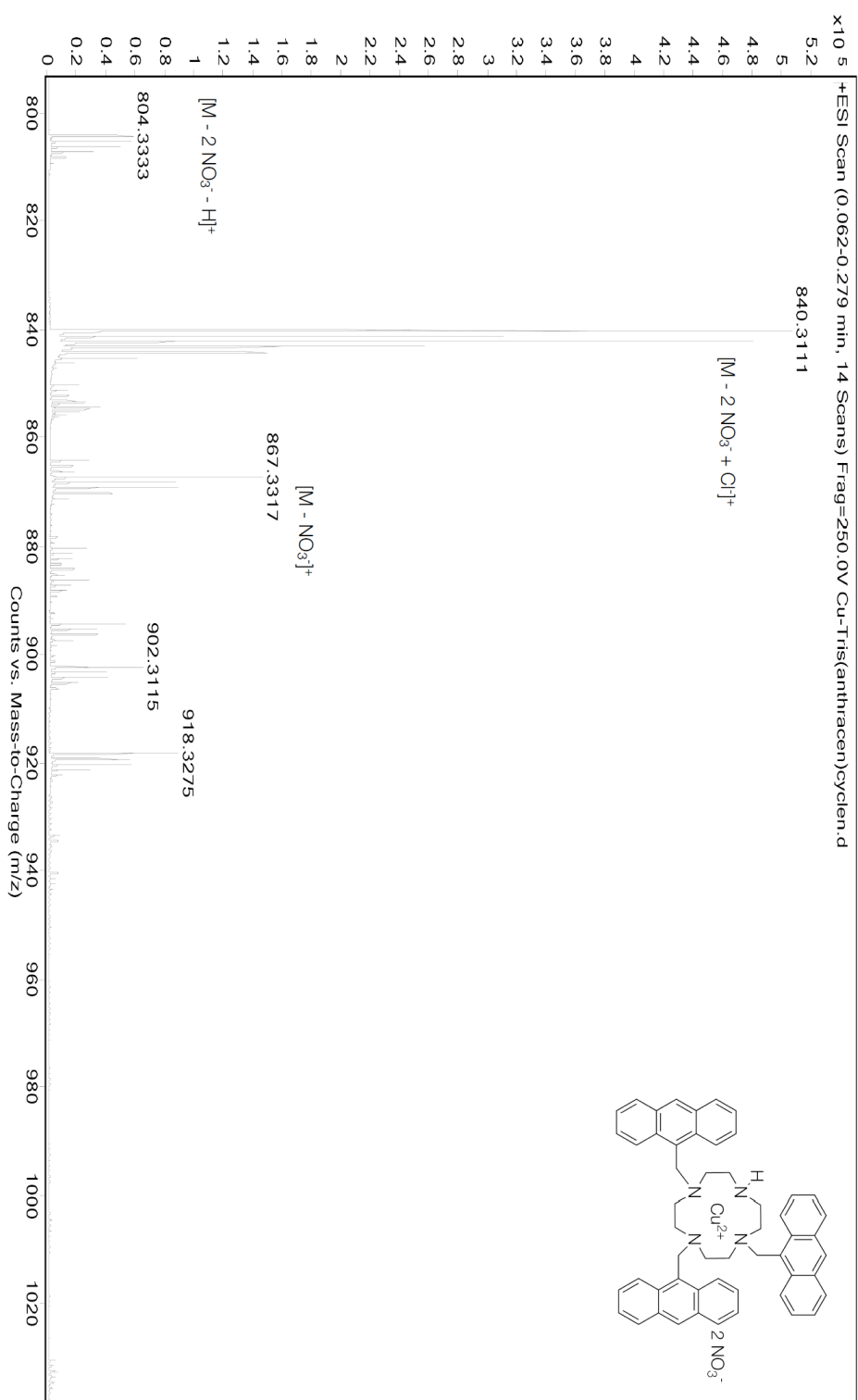
Symmetry transformations used to generate equivalent atoms:

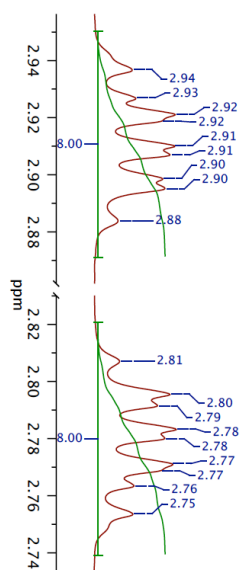
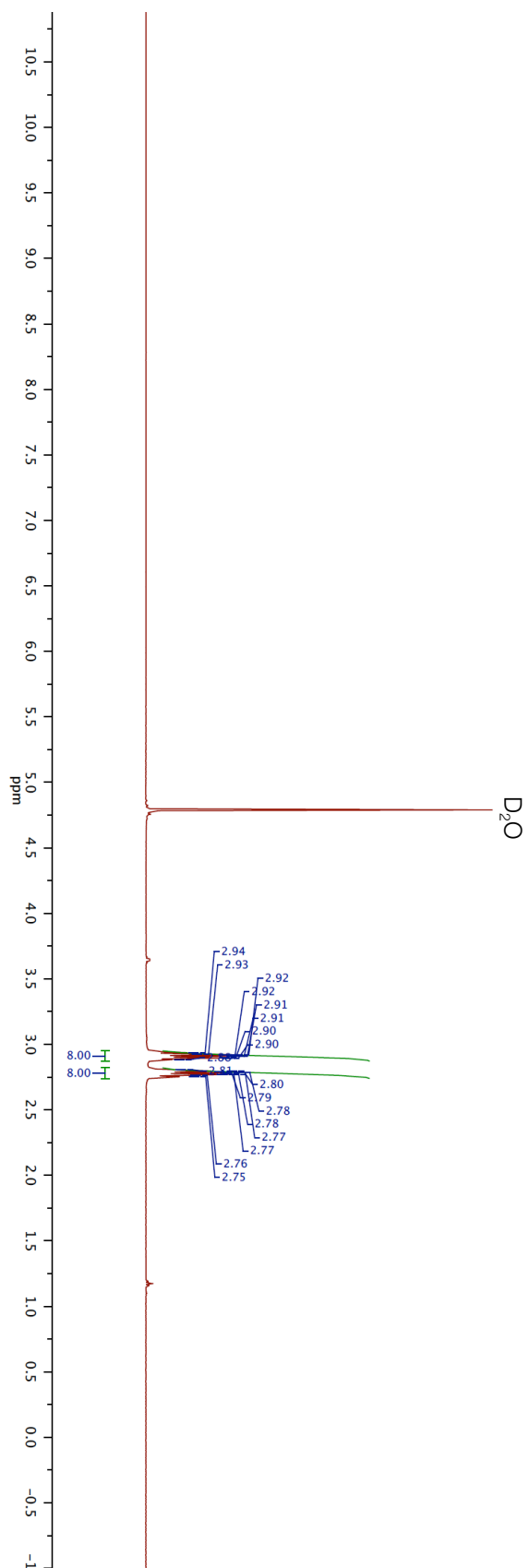
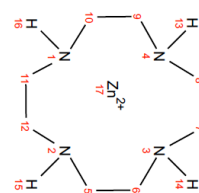




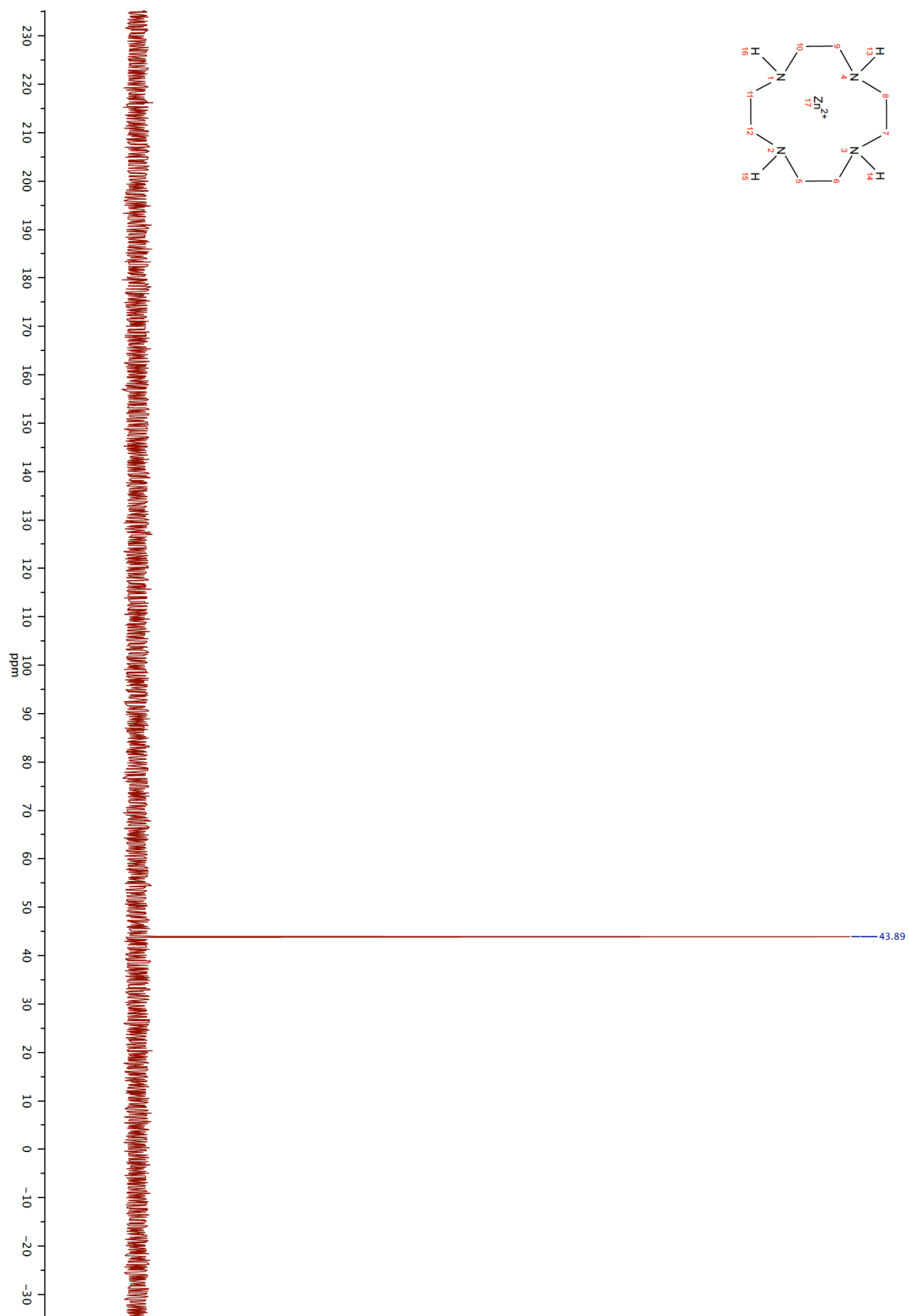


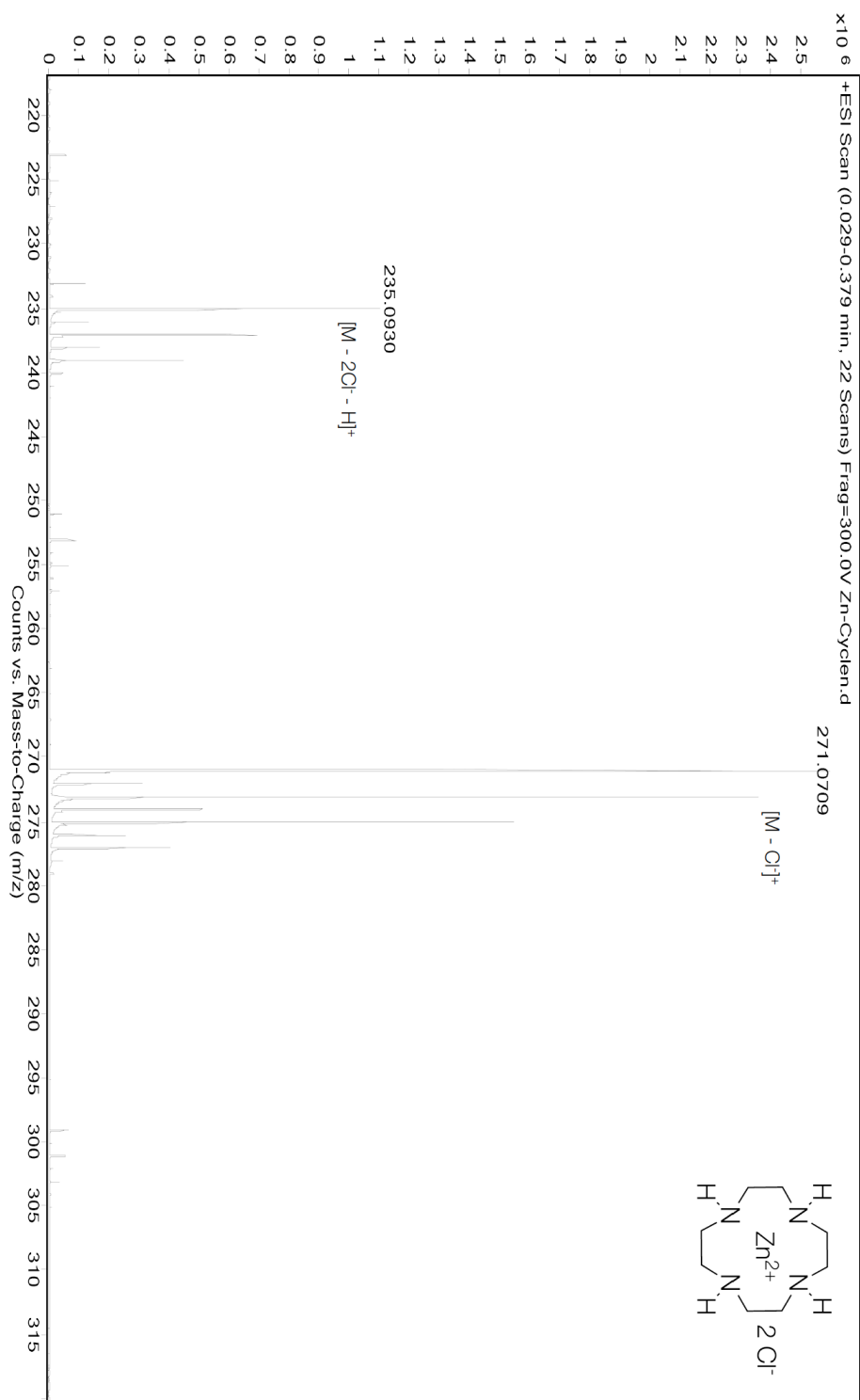


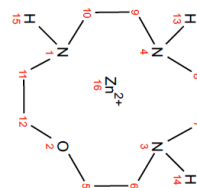
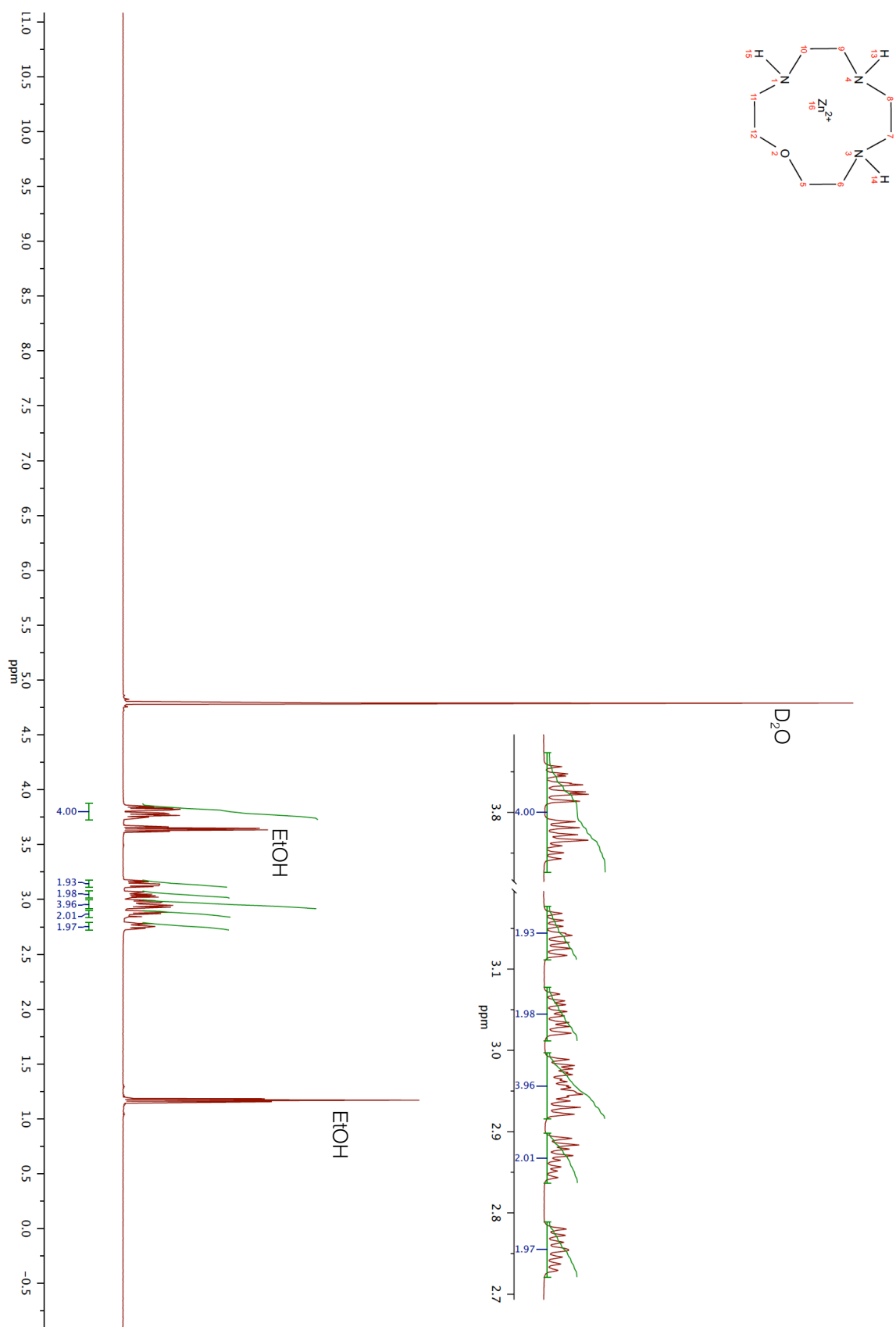




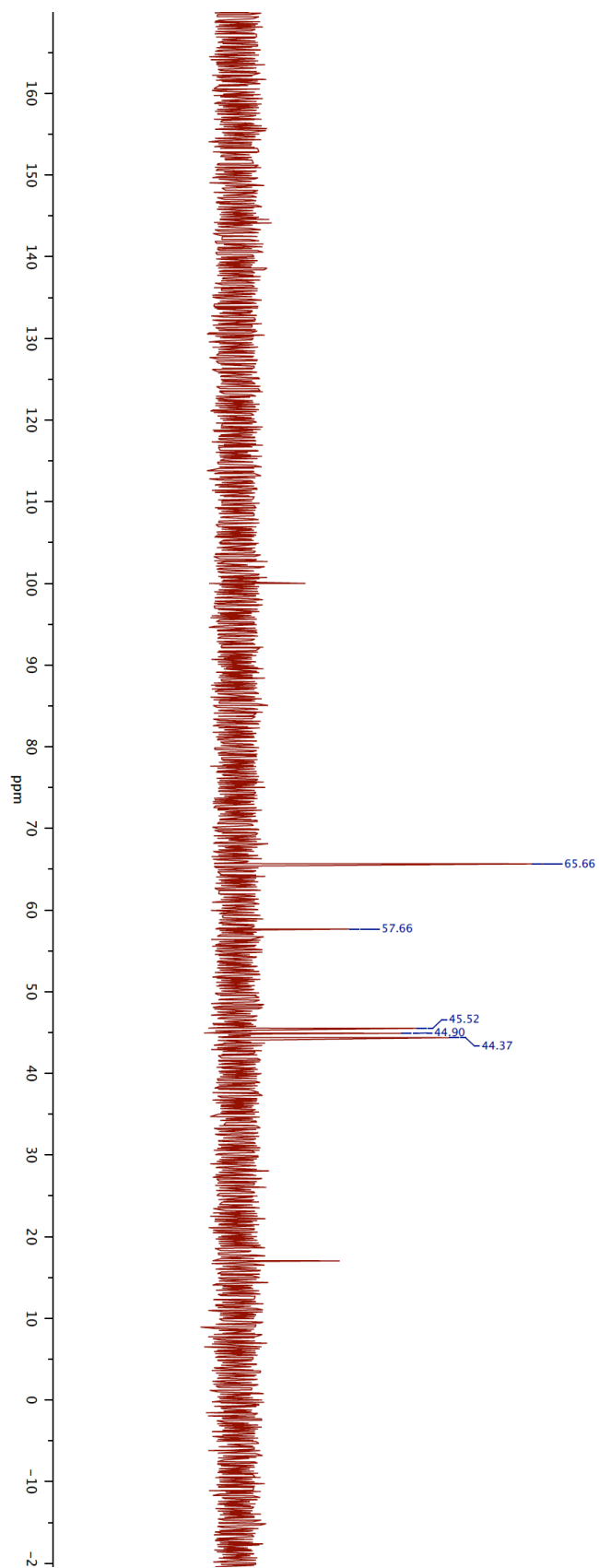
[Zn([12]aneN)Cl] (**40**) - ¹³C-NMR

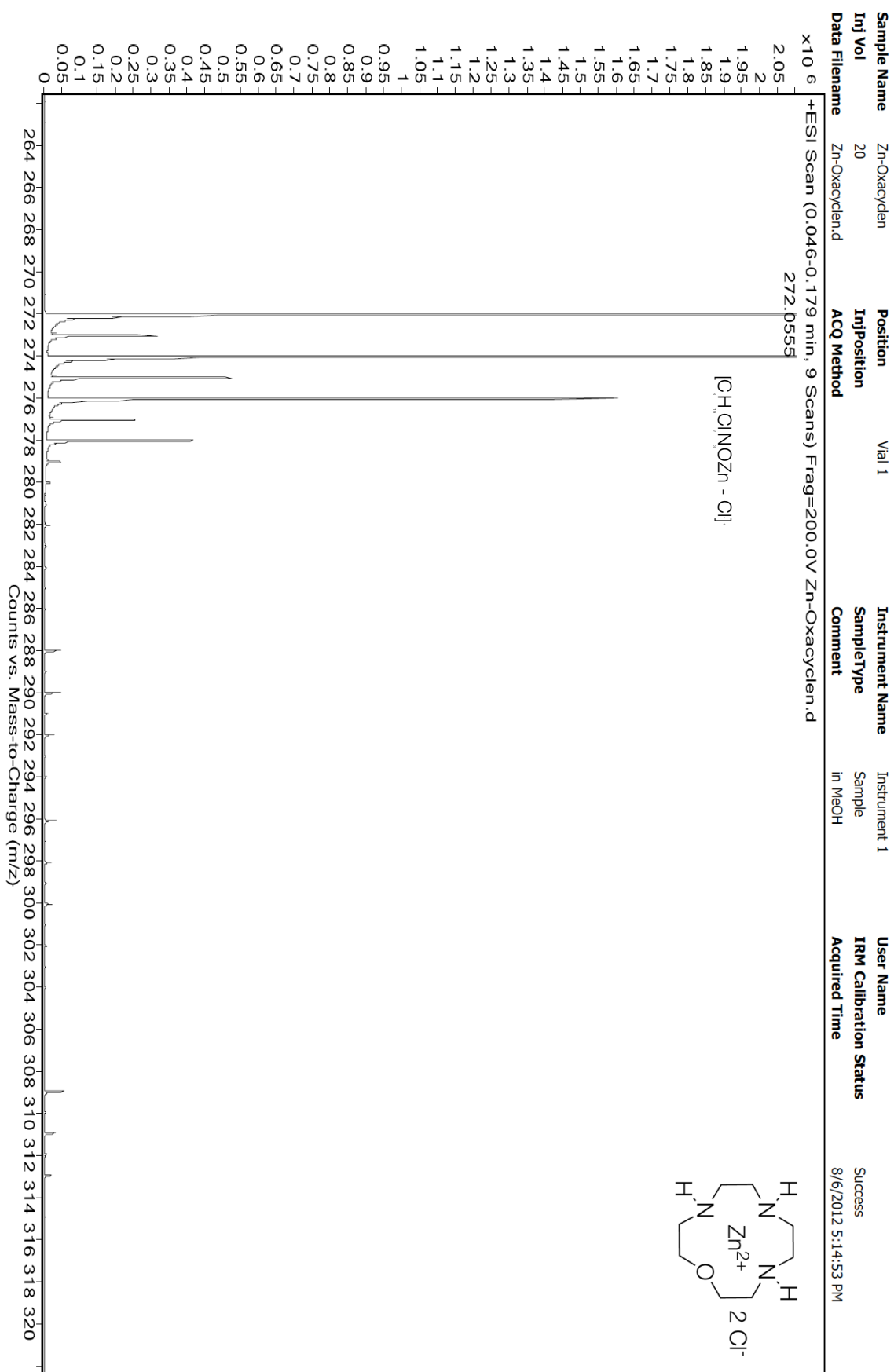




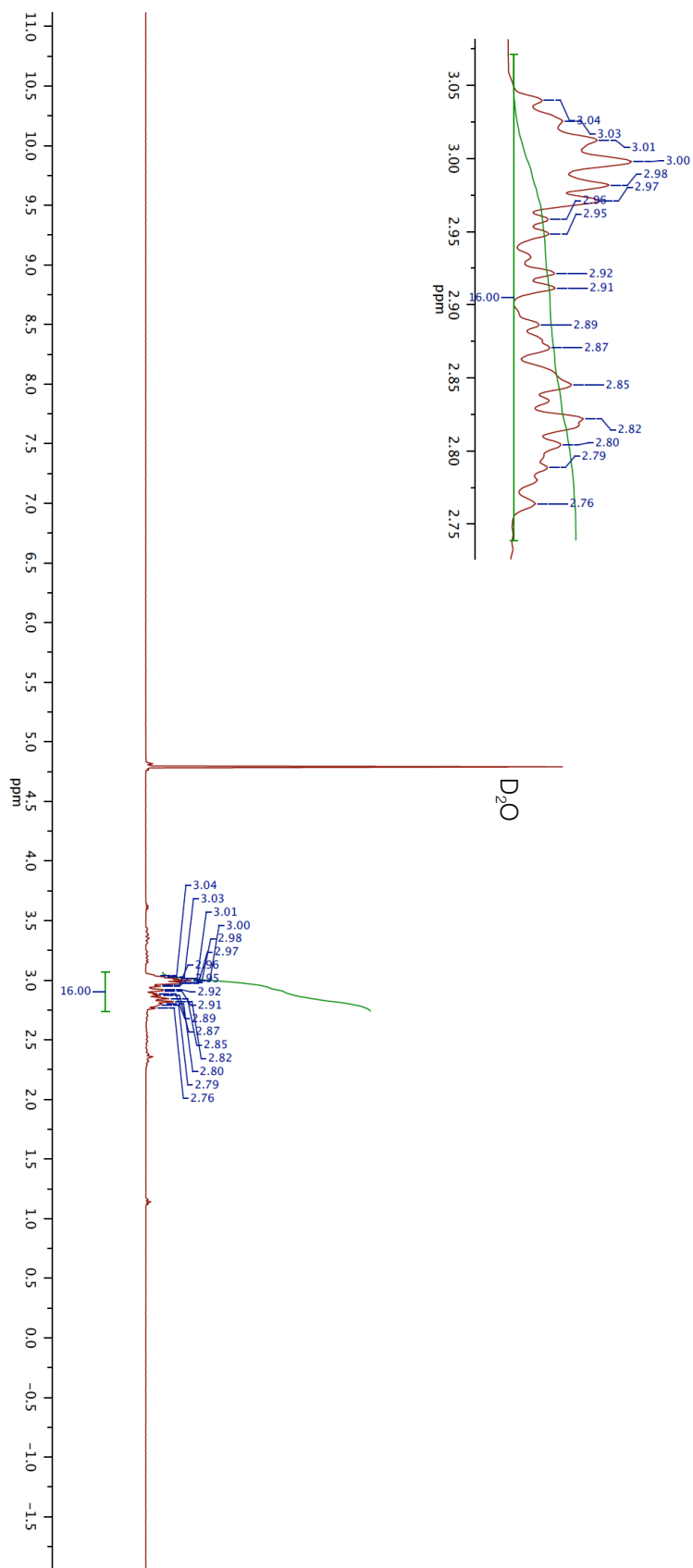
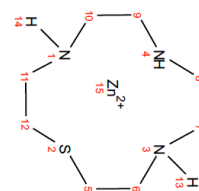


[Zn([12]aneNO)Cl] (**41**) - ¹³C-NMR

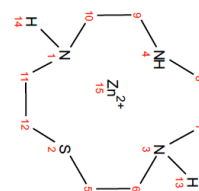
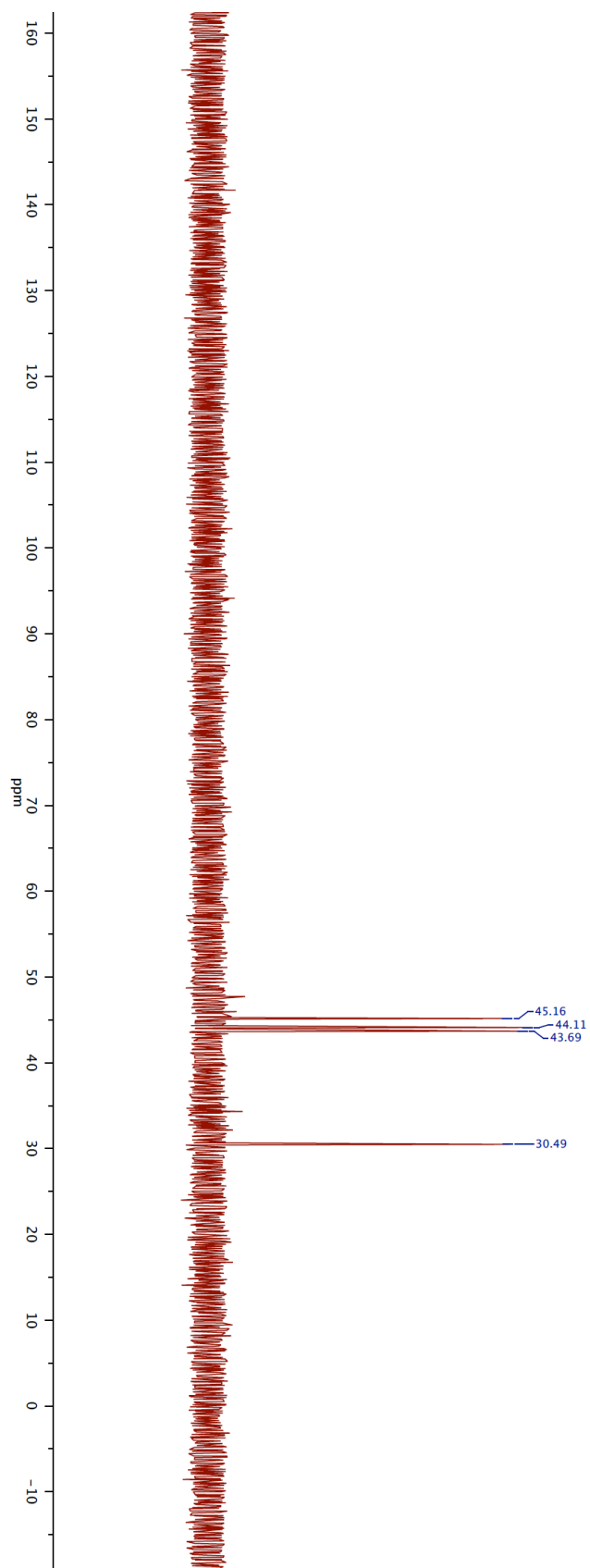


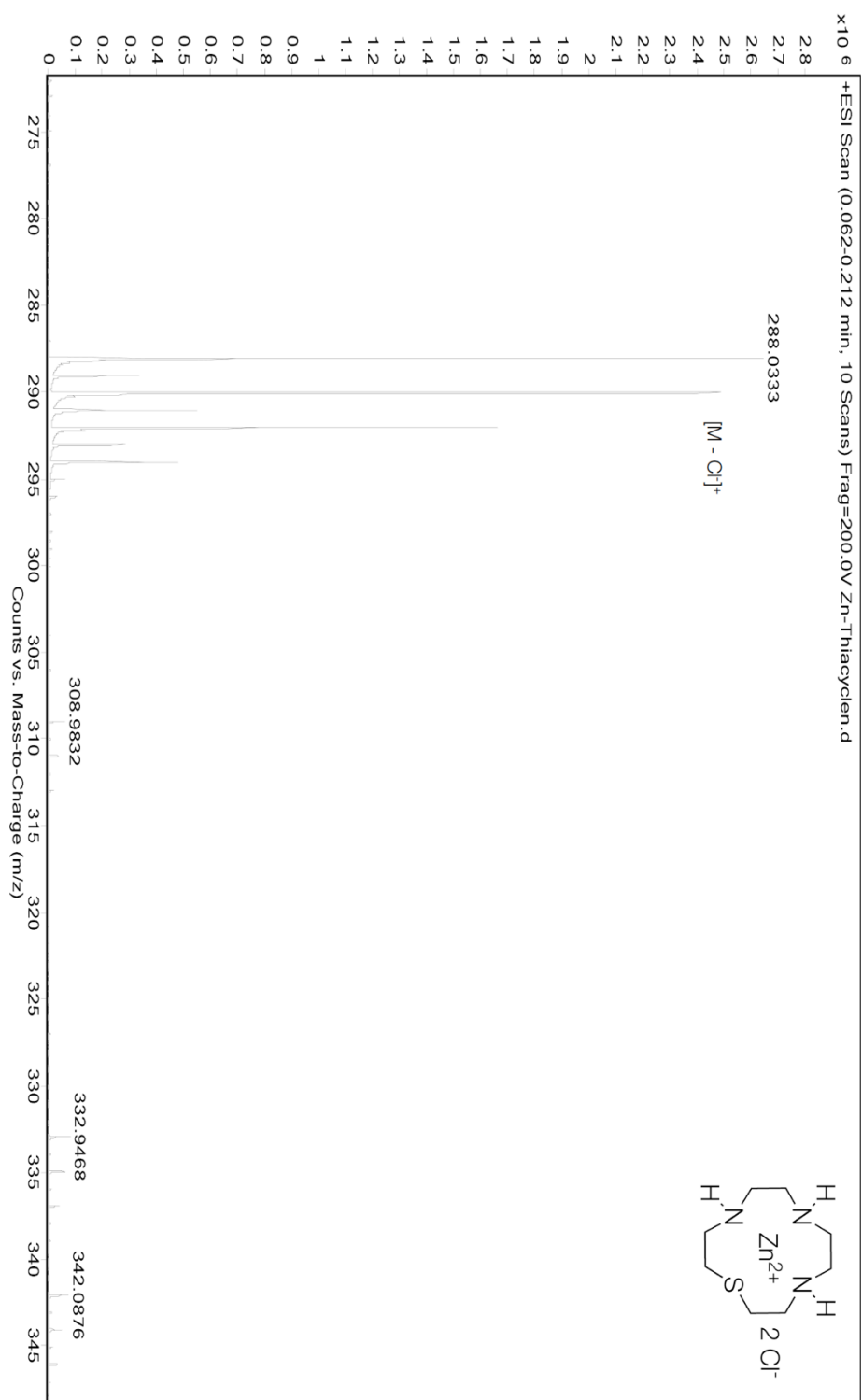


[Zn([12]aneNS)Cl] (**42**) - ¹H-NMR

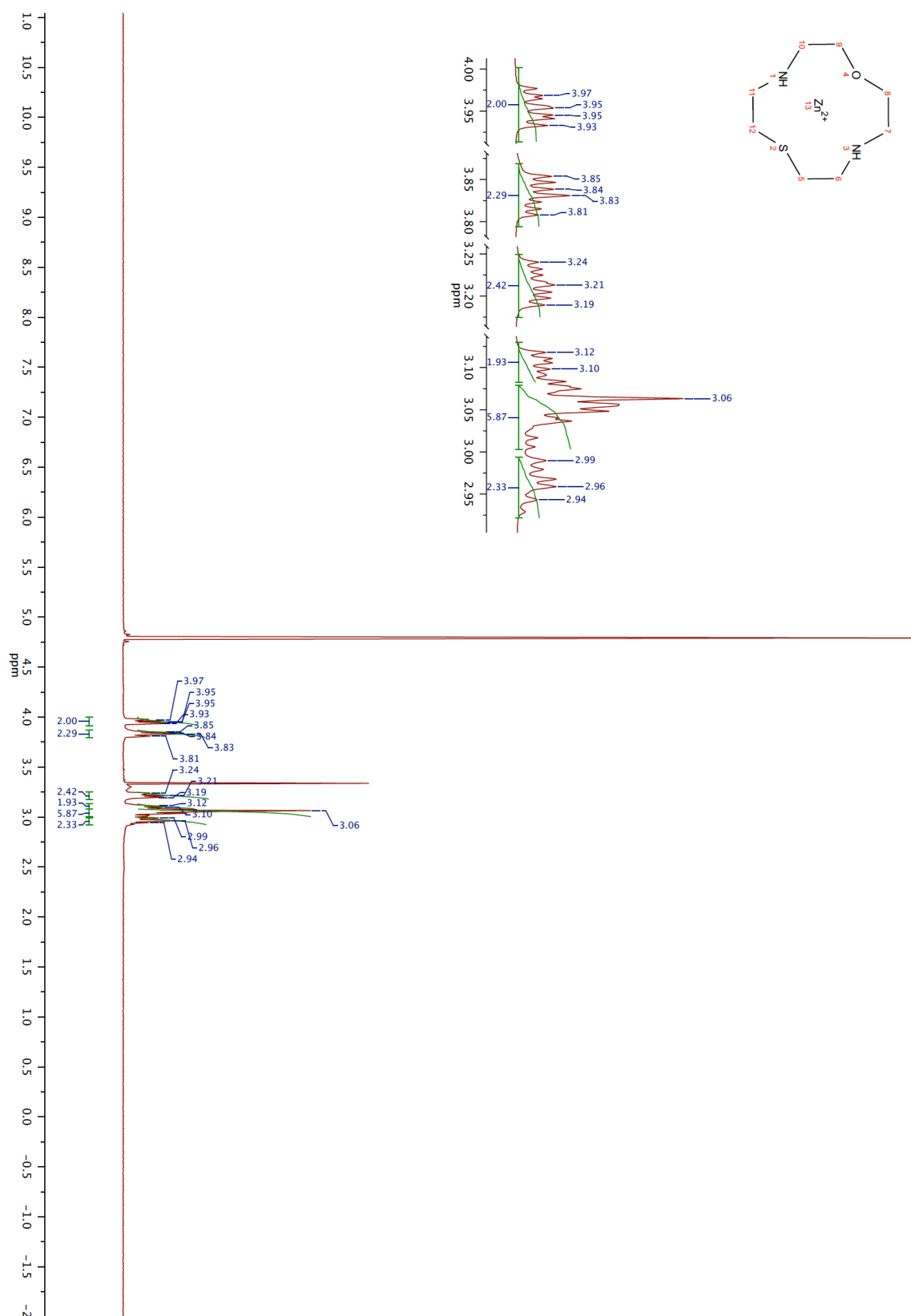


[Zn([12]aneN₃S)Cl] (**42**) - ¹³C-NMR

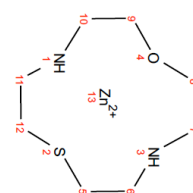
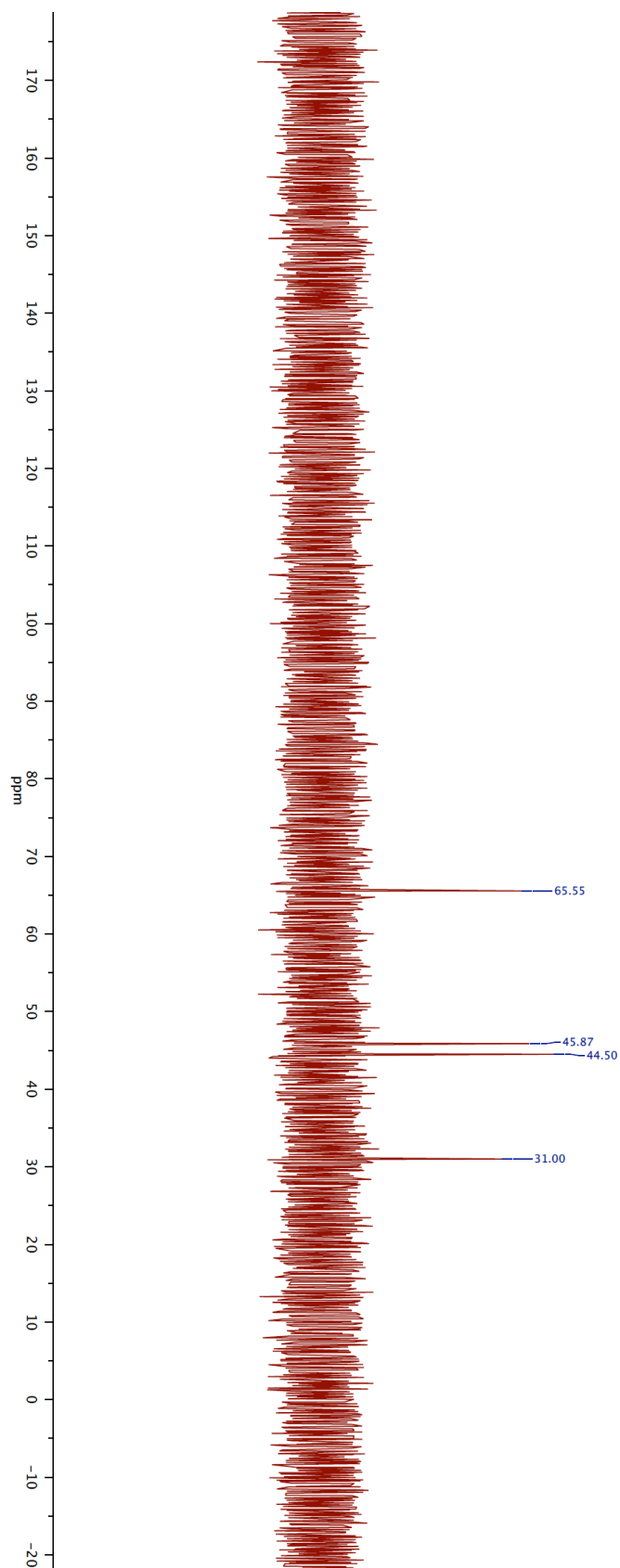


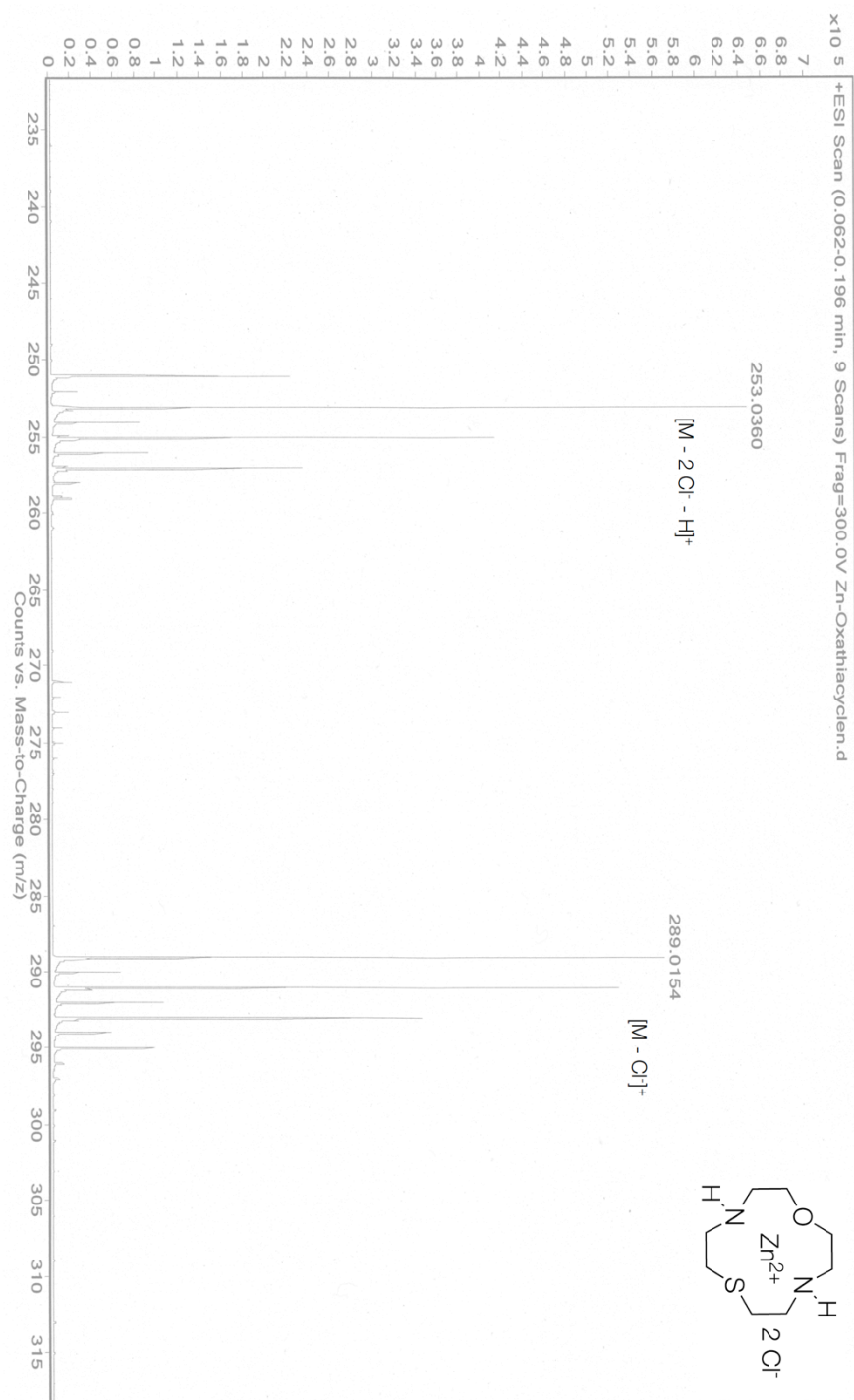


[Zn([12]aneN₂SO)Cl] (**43**) - H-NMR



[Zn([12]aneN₂SO)Cl] (**43**) - ¹³C-NMR





Cyclen-basierte Metallonucleasen
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