

Supplementary information for

Eco-friendly synthesis of fused pyrano[2,3-*b*]pyrans via ammonium acetate-mediated formal oxa-[3 + 3] cycloaddition of 4*H*-chromene-3-carbaldehydes and cyclic 1,3-dicarbonyl compounds

Vitaly A. Osyanin,^{*,†} Dmitry V. Osipov,[†] Irina A. Semenova,[†] Kirill S. Korzhenko,[†] Anton V. Lukashenko,[†] Oleg P. Demidov,[‡] and Yuri N. Klimochkin[†]

[†]Department of Organic Chemistry, Chemical Technological Faculty, Samara State Technical University, 244 Molodogvardeyskaya St., Samara 443100, Russia.

[‡]Department of Chemistry, North Caucasus Federal University, 1 Pushkin St., Stavropol 355009, Russia.

Table of Contents

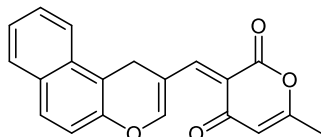
I.	Raw thermodynamic data used to calculate Gibbs free energies for 1-oxatriene – 2 <i>H</i> -pyran equilibrium	S1
II.	Cartesian coordinates of the geometries optimized in acetic acid at the B3LYP/cc-pVDZ level for 3ab	S2
	for 3ad	S3
	for 3ca	S5
	for 3ai	S6
	for 3aj	S8
	for 3ak	S10
	for Z-5al	S11
III.	Copies of NMR spectra for type 3 series	S13
	for 5ak	S63
	for 6ak	S65
	for 5al	S67

I. Raw thermodynamic data used to calculate Gibbs free energies for 1-oxatriene – 2*H*-pyran equilibrium.

Compound	Total electronic energy (<i>E</i> , a.u.)		Total Gibbs free energy (<i>G</i> , a.u.)	
	1-oxatriene form	2 <i>H</i> -pyran form	1-oxatriene form	2 <i>H</i> -pyran form
3ab	-1071.521532	-1071.531084	-1071,280270	-1071,285621
3ad	-1051.668501	-1051.681065	-1051,414286	-1051,422182
3ca	-1185.863709	-1185.871707	-1185,604018	-1185,607718
3ai	-1076.122537	-1076.128937	-1075,808558	-1075,810646
3aj	-1228.766708	-1228.772292	-1228,421632	-1228,422259
5ak	-1110.628821	-1110.613306	-1110,372219	-1110,353547
Z-5al	-1052.662513	-1052.644851	-1052,398729	-1052,376779

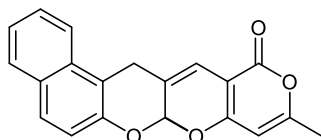
All minima had no imaginary frequencies. Rate constants was defined as: $K_{eq} = e^{\frac{-\Delta G}{RT}}$

II. Cartesian coordinates of the geometries optimized in acetic acid at the B3LYP/cc-pVDZ level



3ab (1-oxatriene form)

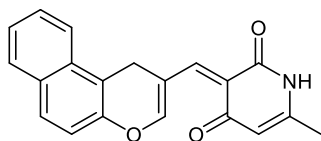
C	-4.76303600	-0.35044600	0.00044000
C	-4.62649700	-1.76823900	0.00029200
C	-3.38224700	-2.35108300	-0.00015800
C	-2.23266500	-1.52684400	-0.00045900
C	-2.28963100	-0.15000500	-0.00034200
C	-3.58199600	0.46877300	0.00010500
O	-1.02635800	-2.22390100	-0.00088100
C	0.13112800	-1.54904000	-0.00079200
C	0.23811400	-0.18565100	-0.00063800
C	-1.02062900	0.67232300	-0.00070400
O	2.90042200	-2.14651800	-0.00048500
C	3.50463000	-1.06301000	-0.00061300
C	2.83767000	0.25684800	-0.00038300
C	1.47743700	0.53349100	-0.00044000
C	4.96202500	-1.03964600	0.00010400
C	5.66513700	0.11230700	0.00046300
H	-5.52480900	-2.38916900	0.00053000
H	-3.24932500	-3.43375500	-0.00028100
H	1.00426100	-2.19972300	-0.00088100
H	-1.01139100	1.34164400	-0.87995100
H	-1.01116700	1.34208700	0.87818500
H	1.31083400	1.61689600	-0.00028300
C	-3.74252100	1.88448000	0.00020700
H	-2.86285900	2.52862700	-0.00005400
C	-6.04116600	0.27241800	0.00089500
C	-6.16125400	1.64706900	0.00099500
H	-7.14875800	2.11311900	0.00134600
C	-4.99945200	2.45730200	0.00063900
H	-5.09881800	3.54490100	0.00070500
H	-6.93152100	-0.36124500	0.00115600
C	3.67486500	1.48299300	-0.00007800
O	3.27425800	2.62728000	0.00008300
O	5.05776100	1.33684100	0.00033100
C	7.15065400	0.24171300	0.00102600
H	7.48110700	0.80781600	-0.88523200
H	7.48041400	0.80789200	0.88749000
H	7.63126700	-0.74458800	0.00125100
H	5.47870000	-1.99863000	0.00027900



3ab (2H-pyran form)

C	-4.27785800	-0.71313500	-0.48685500
C	-3.69745600	-1.96917200	-0.82692200
C	-2.36529300	-2.21042300	-0.60145100
C	-1.54243100	-1.19802900	-0.03839000
C	-2.04611200	0.05594200	0.28600800
C	-3.44281300	0.30997400	0.07787600
O	-0.22827700	-1.56306300	0.15318100
C	0.49557900	-0.73378100	1.08134300
C	0.31169400	0.70305200	0.70206100
C	-1.11967700	1.14042700	0.81696000

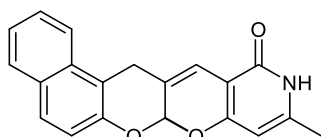
O	1.82810700	-1.22266200	1.06827600
C	2.81659000	-0.51916100	0.47061100
C	2.63671100	0.77669400	0.03242900
C	1.33262700	1.39921500	0.17252900
C	4.07387700	-1.17902200	0.35511500
C	5.10742000	-0.49727700	-0.20974600
H	-4.33094900	-2.74627400	-1.26095800
H	-1.90588400	-3.17079300	-0.84116300
H	0.10813300	-0.95709900	2.09064100
H	-1.26383800	2.07952400	0.26147500
H	-1.37111800	1.36051500	1.87297400
H	1.20966600	2.42545700	-0.17794100
C	-4.04687400	1.55670600	0.41206800
H	-3.44047000	2.35200800	0.84708300
C	-5.65961800	-0.45233000	-0.69502400
C	-6.21271900	0.76698200	-0.35954700
H	-7.27591200	0.95472000	-0.52363200
C	-5.39449800	1.77783900	0.20034000
H	-5.83259900	2.74213000	0.46779600
H	-6.28008600	-1.24157100	-1.12753200
C	3.74334700	1.48755800	-0.56016900
O	3.74715900	2.62452400	-0.98649800
O	4.95696800	0.77489600	-0.65153500
C	6.48925000	-1.01707000	-0.42027500
H	6.74715700	-0.98819800	-1.49149300
H	7.21939000	-0.38154800	0.10689700
H	6.57933500	-2.04826900	-0.05581300
H	4.19505000	-2.20009300	0.71051800



3ad (1-oxatriene form)

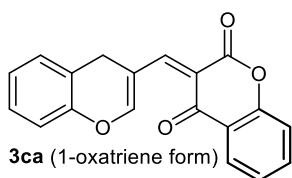
C	-4.76780400	-0.35350800	0.00019700
C	-4.63162900	-1.77136900	0.00008500
C	-3.38750900	-2.35424100	-0.00014700
C	-2.23597400	-1.53172700	-0.00027100
C	-2.29363000	-0.15439300	-0.00017400
C	-3.58604200	0.46462600	0.00005900
O	-1.03264200	-2.22912400	-0.00049500
C	0.12815800	-1.55065700	-0.00044200
C	0.23415800	-0.18975700	-0.00032300
C	-1.02451300	0.66787600	-0.00032600
O	2.89328300	-2.13715500	-0.00032800
C	3.50815200	-1.05488000	-0.00017800
C	2.83308100	0.26802300	-0.00012700
C	1.47501800	0.53446200	-0.00020500
C	4.96261900	-1.04802800	0.00006600
C	5.68811000	0.10228000	0.00024200
H	-5.53018100	-2.39209500	0.00018500
H	-3.25526200	-3.43708600	-0.00023600
H	1.00229700	-2.19990800	-0.00050600
H	-1.01492300	1.33823000	-0.87911800
H	-1.01481300	1.33839200	0.87833300
H	1.30823700	1.61881400	-0.00013500
C	-3.74621100	1.88046000	0.00015000
H	-2.86604200	2.52396000	0.00003600
C	-6.04555200	0.27001900	0.00043400
C	-6.16519600	1.64480500	0.00052500
H	-7.15252300	2.11134100	0.00070800
C	-5.00285600	2.45418000	0.00037800

H	-5.10146300	3.54191200	0.00044300
H	-6.93623400	-0.36331400	0.00054200
C	3.66841000	1.50860200	0.00004500
O	3.22652100	2.65758700	0.00001000
C	7.18599500	0.15376600	0.00046500
H	7.55544200	0.69330000	-0.88771900
H	7.55517200	0.69324700	0.88879200
H	7.61153300	-0.85743900	0.00049900
H	5.46260700	-2.01583700	0.00008100
N	5.04411600	1.32195000	0.00022000
H	5.58932700	2.17914600	0.00032800

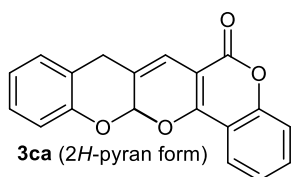


3ad (2H-pyran form)

C	-4.27092700	-0.71859600	-0.49934300
C	-3.68330900	-1.96907200	-0.84735300
C	-2.35129900	-2.20615100	-0.61698300
C	-1.53400600	-1.19599600	-0.04048300
C	-2.04582900	0.05348900	0.29161300
C	-3.44253100	0.30286000	0.07833700
O	-0.22189900	-1.55833200	0.15574400
C	0.49763100	-0.72956700	1.09692600
C	0.30674100	0.70700800	0.72357100
C	-1.12676400	1.13810600	0.83594600
O	1.82683800	-1.20897000	1.09664900
C	2.81926500	-0.50928100	0.47959100
C	2.63078400	0.79007900	0.04095500
C	1.32639200	1.40496600	0.19221900
C	4.06385900	-1.18004900	0.35863500
C	5.11449300	-0.51068700	-0.21904400
H	-4.31118000	-2.74518100	-1.29137900
H	-1.88664600	-3.16258500	-0.86261800
H	0.09612900	-0.96200000	2.09894700
H	-1.27296900	2.08064500	0.28654200
H	-1.38636300	1.34918100	1.89202600
H	1.20185800	2.43177500	-0.15708300
C	-4.05392800	1.54419600	0.41999300
H	-3.45285000	2.33817700	0.86470200
C	-5.65270300	-0.46174500	-0.71205500
C	-6.21280900	0.75229300	-0.36891700
H	-7.27601400	0.93693100	-0.53660600
C	-5.40143300	1.76164900	0.20358400
H	-5.84480300	2.72186200	0.47713600
H	-6.26768700	-1.24991300	-1.15438700
C	3.73173900	1.51071900	-0.56653800
O	3.69369800	2.67017100	-0.99066700
C	6.47892300	-1.10098500	-0.41341400
H	6.74811300	-1.11953500	-1.48263700
H	7.24293300	-0.50126200	0.10869200
H	6.51615800	-2.12731700	-0.02671600
H	4.17179200	-2.20109000	0.71847200
N	4.92402300	0.77323100	-0.65313700
H	5.69853200	1.27531100	-1.08038200

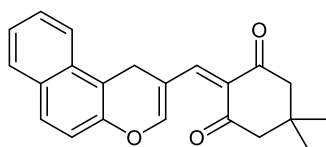


C	5.40157453	-0.55686882	0.00001475
C	5.16439853	-1.96129982	0.00000875
C	3.88176353	-2.45411482	-0.00002325
C	2.79470353	-1.54932482	-0.00004825
C	2.94916953	-0.18033182	-0.00004325
C	4.28222153	0.34481018	-0.00001325
O	1.54049953	-2.15779482	-0.00007625
C	0.43494553	-1.40384482	-0.00005025
C	0.42376553	-0.03511082	-0.00003725
C	1.74181953	0.72982718	-0.00007725
O	-2.36820847	-1.77700982	-0.00011425
C	-2.89282147	-0.65632682	0.00003175
C	-2.13787747	0.60732818	0.00003875
C	-0.75768047	0.77333918	0.00000675
H	6.01640653	-2.64437782	0.00002875
H	3.67189553	-3.52451682	-0.00002825
H	-0.47933247	-1.99346882	-0.00003725
H	1.78038753	1.39803418	0.87897175
H	1.78038153	1.39795318	-0.87919125
H	-0.50947747	1.84074718	0.00002175
C	-2.87203447	1.90359918	0.00007775
O	-2.36063947	3.00394918	0.00011875
O	-4.25153047	1.88753618	0.00009975
C	-4.97754047	0.72270118	0.00005775
C	-6.36969647	0.85624718	0.00005575
C	-7.16017247	-0.29133582	-0.00000125
H	-8.24768347	-0.19251082	-0.00000425
C	-4.36752547	-0.53681882	0.00000875
C	-5.18468347	-1.68288882	-0.00005125
C	-6.56978847	-1.56649982	-0.00005525
H	-7.19655547	-2.45987782	-0.00009925
H	-6.80644447	1.85565518	0.00009475
H	-4.69307447	-2.65634782	-0.00008825
H	4.44668264	1.42263514	-0.00001167
H	6.42066344	-0.17014179	0.00004029



C	-4.73439760	-0.90605194	-0.52033527
C	-4.03499160	-2.07195594	-0.94651527
C	-2.68109460	-2.18785794	-0.75349227
C	-1.95668460	-1.13251494	-0.13728727
C	-2.57964160	0.03953306	0.27365773
C	-3.99854460	0.16089206	0.09851973
O	-0.60726060	-1.36926694	0.01337473
C	0.04052740	-0.53474894	0.98815873
C	-0.29365260	0.89795506	0.70790673
C	-1.75992060	1.17833206	0.86321473
O	1.41757640	-0.87732394	0.92983473
C	2.31621040	-0.03812294	0.37021673
C	2.00261640	1.25241406	0.02654573
C	0.64363540	1.72898906	0.22074873
H	-4.59368360	-2.88191294	-1.42124227

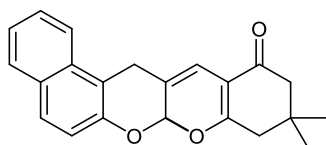
H	-2.13020960	-3.07858994	-1.05981727
H	-0.30321360	-0.86198094	1.98454273
H	-2.00708060	2.13070406	0.37028673
H	-2.01426760	1.30508306	1.93367873
H	0.41474840	2.75856706	-0.05830227
C	3.01739740	2.13239106	-0.53000727
O	2.85143240	3.28793106	-0.86163827
O	4.29328940	1.60191506	-0.69405527
C	4.60522340	0.31562806	-0.35093427
C	5.92297940	-0.10108594	-0.56123827
C	6.28523140	-1.40431394	-0.22778027
H	7.31351240	-1.73267494	-0.39127327
C	3.64668340	-0.56340594	0.19137173
C	4.03256540	-1.87898294	0.52154073
C	5.34163740	-2.29516094	0.31342673
H	5.63690840	-3.31405494	0.56903573
H	6.63901240	0.60500206	-0.98316127
H	3.28644940	-2.55582594	0.93762273
H	-4.51710761	1.06124823	0.43454826
H	-5.81311447	-0.82496310	-0.66202336



3ai (1-oxatriene form)

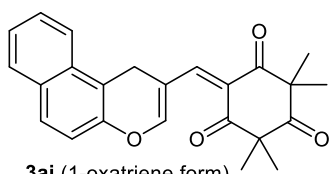
C	5.10458100	-0.36442900	0.03493800
C	4.96299500	-1.78139300	0.06675400
C	3.71673300	-2.35981900	0.06634200
C	2.56880700	-1.53310300	0.03355800
C	2.63153200	-0.15653100	0.00142500
C	3.92612800	0.45779300	0.00209600
O	1.36212500	-2.22556900	0.03906200
C	0.20485300	-1.54300400	0.00605200
C	0.10271000	-0.18229500	-0.03287300
C	1.36567300	0.66975700	-0.03390400
O	-2.57343100	-2.08310600	-0.18117400
C	-3.16505400	-1.00532400	-0.27456600
C	-2.49387900	0.30566700	-0.15120600
C	-1.13380500	0.54881000	-0.05059700
C	-4.66068100	-1.02735300	-0.55759800
C	-5.47024500	0.11372500	0.08443800
C	-4.83006200	1.43337700	-0.37818200
H	5.85913000	-2.40509800	0.09175500
H	3.58042100	-3.44187000	0.09090400
H	-0.66679700	-2.19301500	0.01788400
H	1.34572600	1.36041000	0.82891100
H	1.37102200	1.31945800	-0.92784500
H	-0.96038100	1.63107200	0.01443100
H	-4.77114700	-0.97047600	-1.65767100
H	-5.03292500	-2.01694200	-0.25318400
H	-4.96387300	1.53334300	-1.47265400
H	-5.31197900	2.31090100	0.07838100
C	-5.43790500	0.00461200	1.62144300
H	-6.01193900	0.82533400	2.08145700
H	-5.88259900	-0.94746700	1.95393200
H	-4.41166600	0.05104100	2.02133700
C	-6.92759600	0.04735200	-0.39846400
H	-7.39890100	-0.90155800	-0.09450700
H	-7.52080100	0.87180100	0.02976000
H	-6.98932500	0.12020700	-1.49663000
C	-3.33590100	1.55267400	-0.12657000

O	-2.84633200	2.66240900	0.06309900
C	4.09155600	1.87265600	-0.02917400
H	3.21390700	2.51912800	-0.05404600
C	6.38464100	0.25439200	0.03487800
C	6.50943100	1.62835800	0.00404400
H	7.49845000	2.09129600	0.00440500
C	5.35029300	2.44169000	-0.02817900
H	5.45310000	3.52876200	-0.05238600
H	7.27286200	-0.38187600	0.05995300



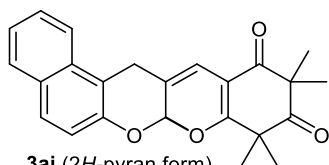
3ai (2H-pyran form)

C	-4.62286500	-0.71736800	-0.41932700
C	-4.05262200	-1.97374100	-0.77482400
C	-2.71354100	-2.21279500	-0.59233000
C	-1.87271600	-1.19868400	-0.05897100
C	-2.36740500	0.05592100	0.27914400
C	-3.77051000	0.30757500	0.11559700
O	-0.55367900	-1.56368900	0.08983200
C	0.20275100	-0.72570300	0.98734600
C	0.00127400	0.70756100	0.60954500
C	-1.42573300	1.14334600	0.77706300
O	1.53721300	-1.20430300	0.92562100
C	2.50154200	-0.50454000	0.27997900
C	2.30257700	0.76853500	-0.16546000
C	1.00197100	1.39446500	0.03516400
C	3.78005700	-1.26986500	0.14627800
C	5.01618400	-0.35903200	-0.04441700
C	4.67384300	0.71003400	-1.10622000
H	-4.69904900	-2.75270500	-1.18590900
H	-2.26129000	-3.17341300	-0.84456000
H	-0.14630300	-0.94969900	2.01055400
H	-1.59179000	2.08151900	0.22607100
H	-1.64093000	1.36340300	1.84106100
H	0.87272600	2.41968500	-0.31685800
C	3.39581300	1.49082600	-0.83338200
H	3.67628400	-1.94972300	-0.72050800
H	3.89650600	-1.91830300	1.02970700
H	5.49416800	1.43296300	-1.23017700
H	4.53361400	0.21558500	-2.08646500
C	5.39517000	0.31510700	1.28907400
H	5.66067400	-0.44140200	2.04535200
H	6.26649100	0.97586400	1.15282000
H	4.57270600	0.92421800	1.69580100
C	6.19982300	-1.21023800	-0.53052400
H	7.09733700	-0.58665100	-0.67077700
H	6.44620500	-1.99598000	0.20243600
H	5.97400900	-1.70091600	-1.49124600
O	3.26930900	2.66020400	-1.18923100
C	-4.36477200	1.55470900	0.46601100
H	-3.74524700	2.35138200	0.87942900
C	-6.01078100	-0.45796400	-0.58367900
C	-6.55379800	0.76185300	-0.23380100
H	-7.62183400	0.94853600	-0.36425200
C	-5.71863400	1.77455500	0.29704100
H	-6.14855700	2.73928100	0.57602600
H	-6.64424800	-1.24869400	-0.99411600



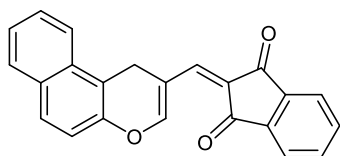
3aj (1-oxatriene form)

C	-5.58602200	-0.31888100	0.07029400
C	-5.46519900	-1.70432800	-0.23768900
C	-4.23359700	-2.26154200	-0.48296900
C	-3.07907600	-1.44515600	-0.42546000
C	-3.12209600	-0.09891000	-0.13112600
C	-4.40172600	0.49359200	0.12382700
O	-1.89028200	-2.11259900	-0.70154100
C	-0.72842200	-1.43629900	-0.66373700
C	-0.60846700	-0.11035500	-0.36993300
C	-1.85101900	0.71877700	-0.07899500
O	2.04659600	-2.07320100	-0.43111600
C	2.57583700	-1.02191700	-0.07692900
C	1.97949900	0.31072300	-0.30531700
C	0.63494500	0.61170500	-0.39193100
C	3.87130400	-1.08819600	0.75384500
C	4.41451800	1.20196800	-0.45148200
H	-6.36584900	-2.32070700	-0.27780900
H	-4.11377200	-3.31884600	-0.72327000
H	0.12307400	-2.06345800	-0.91538100
H	-1.91141200	1.55917400	-0.79511200
H	-1.75420500	1.18996800	0.91574600
H	0.48597700	1.69878700	-0.43733400
C	2.90077400	1.48604600	-0.38483800
O	2.49246700	2.63728500	-0.46620500
C	4.78649200	0.13855900	0.58519400
O	5.79582400	0.23579200	1.25734000
C	4.71546600	0.60970800	-1.86262400
H	5.79319400	0.40583000	-1.95532000
H	4.16877300	-0.32273200	-2.06688100
H	4.43190000	1.34348200	-2.63266300
C	5.22500600	2.48276400	-0.24085700
H	6.29937700	2.26283700	-0.30037000
H	4.96306700	3.22582000	-1.00576600
H	5.02104600	2.92353200	0.74568600
C	4.67618200	-2.35848700	0.41634800
H	4.05862400	-3.24976000	0.58902800
H	4.99592700	-2.36643800	-0.63728700
H	5.57132500	-2.40372700	1.05186900
C	3.42689700	-1.13358000	2.24251100
H	2.81755200	-2.03189700	2.42121400
H	4.31930800	-1.16698600	2.88344000
H	2.83313700	-0.24847100	2.51938700
C	-4.54624600	1.87688900	0.43305500
H	-3.66384100	2.51568800	0.47965200
C	-6.85097800	0.27773600	0.32567700
C	-6.95576500	1.62142900	0.62209700
H	-7.93339400	2.06767100	0.81590100
C	-5.79083500	2.42521800	0.67525700
H	-5.87775800	3.48833500	0.90994000
H	-7.74372800	-0.35110600	0.28219300



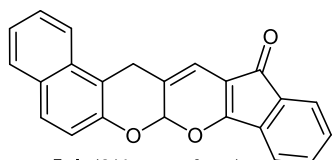
3aj (2H-pyran form)

C	5.03147500	-0.56050000	0.64575300
C	4.42832700	-1.72912400	1.19393800
C	3.10020700	-1.99981700	0.97847800
C	2.30400200	-1.10366300	0.21567000
C	2.83019400	0.06616400	-0.32012300
C	4.22355400	0.34577300	-0.12164200
O	0.99107900	-1.49114700	0.05771100
C	0.30318200	-0.83869600	-1.02594500
C	0.49385300	0.63911300	-0.91068800
C	1.93154900	1.04043300	-1.06920500
O	-1.03853900	-1.29286900	-0.95876200
C	-2.03698300	-0.49789000	-0.50520000
C	-1.85068900	0.83392900	-0.28774000
C	-0.53355900	1.41477300	-0.53232900
C	-3.33326200	-1.26035400	-0.38095100
C	-4.23611900	1.02774100	0.69010400
H	5.04109600	-2.41689500	1.78135700
H	2.62399800	-2.89708100	1.37716500
H	0.70861800	-1.25045200	-1.96634500
H	2.07247600	2.06552700	-0.69451100
H	2.21143300	1.05715800	-2.14054400
H	-0.41997300	2.48782700	-0.36981900
C	-2.94700800	1.69239800	0.17652600
O	-2.81887000	2.91167000	0.22543800
C	-4.50018600	-0.34121300	0.04726100
O	-5.64024900	-0.74253900	-0.09102000
C	-5.44254700	1.95414300	0.47760600
H	-5.63856900	2.11001900	-0.59429000
H	-6.34238200	1.51609100	0.92840900
H	-5.24040500	2.93149300	0.93439200
C	-4.02486700	0.79532900	2.21796500
H	-3.89627100	1.77025300	2.71184200
H	-4.90690800	0.29548400	2.64631200
H	-3.13465300	0.18542700	2.43034400
C	-3.68959600	-1.89913700	-1.74697000
H	-3.77595200	-1.13216600	-2.53220200
H	-2.91412900	-2.61792200	-2.04331400
H	-4.65348600	-2.41702500	-1.66133800
C	-3.18850600	-2.38267700	0.68390500
H	-4.13820500	-2.93063800	0.76443300
H	-2.39584000	-3.08086400	0.37985200
H	-2.93005500	-1.98038400	1.67437100
C	4.85033200	1.50616000	-0.66168100
H	4.26511100	2.21104900	-1.25334400
C	6.40972700	-0.27365500	0.84268600
C	6.98513500	0.86001200	0.30530500
H	8.04532600	1.06877400	0.46320600
C	6.19384700	1.75502200	-0.45468400
H	6.64965700	2.65113700	-0.88190200
H	7.00938200	-0.97330600	1.43074900



5ak (1-oxatriene form)

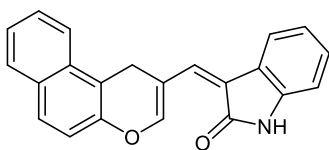
C	-5.22679200	-0.43426500	-0.00011500
C	-5.01999900	-1.84349300	-0.00023800
C	-3.74846900	-2.36364600	-0.00025700
C	-2.63899000	-1.48513700	-0.00015100
C	-2.76553700	-0.11167000	-0.00003000
C	-4.08738400	0.44171500	-0.00000900
O	-1.40315200	-2.12441900	-0.00018500
C	-0.28045100	-1.38381500	-0.00012400
C	-0.24785700	-0.02137600	-0.00000700
C	-1.54064300	0.77635600	0.00007700
O	2.62096800	-2.03309100	0.00021000
C	3.05334400	-0.88180000	-0.00003200
C	2.31443500	0.40248100	0.00002900
C	0.98029400	0.72539000	0.00003900
H	-5.88659100	-2.50807600	-0.00032100
H	-3.56252000	-3.43854900	-0.00035300
H	0.62067600	-1.99834100	-0.00019900
H	-1.56336000	1.44638800	-0.87878000
H	-1.56336900	1.44618500	0.87908800
H	0.83194200	1.81439000	0.00009900
C	3.32320700	1.50546500	0.00012700
O	3.09705000	2.70841500	-0.00016700
C	5.61158700	-1.38607800	0.00018600
C	6.88685700	-0.80740100	0.00017500
C	7.04757800	0.58951100	0.00008600
C	5.93634300	1.44176700	0.00002400
C	4.66965500	0.86034800	0.00005800
C	4.50900200	-0.53323100	0.00010500
H	5.47614200	-2.46895800	0.00021500
H	7.77175900	-1.44735200	0.00021800
H	8.05454500	1.01203800	0.00008100
H	6.05021200	2.52718800	-0.00000900
C	-4.31800700	1.84780600	0.00011600
H	-3.47114800	2.53458500	0.00020300
C	-6.53408200	0.12452500	-0.00009300
C	-6.72222000	1.49161000	0.00003000
H	-7.73156800	1.90831300	0.00004700
C	-5.60175600	2.35798800	0.00013600
H	-5.75456700	3.43941700	0.00023400
H	-7.39177500	-0.55276900	-0.00017500



5ak (2H-pyran form)

C	-4.63669300	-0.82179000	-0.49307100
C	-3.97713200	-2.03044300	-0.85954800
C	-2.62867300	-2.18376100	-0.65466600
C	-1.87008700	-1.12543300	-0.08667100
C	-2.45219200	0.08655800	0.26307900
C	-3.86570500	0.24781200	0.07657500
O	-0.53070000	-1.40193400	0.08388100
C	0.14335900	-0.54283300	1.01645900
C	-0.13500500	0.89193400	0.65910900
C	-1.59352000	1.22254900	0.79953700

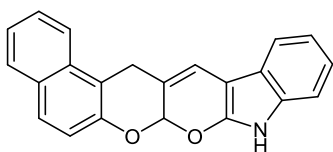
O	1.51252600	-0.96383400	0.98240900
C	2.40727800	-0.14825600	0.41538000
C	2.15510500	1.12936900	-0.00063500
C	0.82708400	1.67852600	0.13414100
H	-4.56229600	-2.84257500	-1.29724400
H	-2.10826400	-3.10695400	-0.91471200
H	-0.21805400	-0.80170300	2.02670500
H	-1.81001700	2.15819100	0.26184500
H	-1.84581400	1.40862700	1.86212300
H	0.61891500	2.69975900	-0.19255600
C	3.41659200	1.69321000	-0.52694000
O	3.60921500	2.80812900	-0.98784900
C	4.51723000	-1.69716300	0.46970600
C	5.88816900	-1.72580800	0.13696400
C	6.51471600	-0.61858100	-0.43703100
C	5.78921500	0.56403700	-0.70059200
C	4.44682400	0.59172000	-0.37293500
C	3.81447400	-0.53022500	0.20759500
H	4.03028300	-2.56526900	0.91661000
H	6.46667600	-2.63104200	0.33241600
H	7.57689700	-0.66740700	-0.68498900
H	6.27073500	1.43481900	-1.14992900
C	-4.54843400	1.44552900	0.43724400
H	-3.99159700	2.27389700	0.87673100
C	-6.03571700	-0.65285800	-0.67985300
C	-6.66577700	0.52097000	-0.31893400
H	-7.74141000	0.63809000	-0.46669700
C	-5.91073100	1.57720100	0.24592600
H	-6.40977400	2.50537700	0.53359900
H	-6.60690100	-1.47628400	-1.11645600



Z-5al (1-oxatriene form)

C	-4.93913300	-0.10355100	-0.00005400
C	-4.92606800	-1.52807400	-0.00004700
C	-3.73747800	-2.21641200	-0.00003900
C	-2.51546000	-1.50020400	-0.00003600
C	-2.45621800	-0.12138500	-0.00004000
C	-3.69015300	0.60755700	-0.00005000
O	-1.38356800	-2.29889200	-0.00003000
C	-0.16154700	-1.71291300	-0.00002000
C	0.05453100	-0.37167800	-0.00002100
C	-1.12213200	0.59105500	-0.00003500
C	2.65890400	-0.21627500	-0.00001900
C	1.36651200	0.23919800	-0.00001400
H	-5.87511400	-2.06861700	-0.00005100
H	-3.70066100	-3.30677500	-0.00003600
H	0.64518800	-2.44475300	-0.00001700
H	-1.05406100	1.25923900	-0.87883900
H	-1.05407400	1.25924800	0.87876300
H	1.30108300	1.33432300	-0.00002000
C	6.28230500	0.33791300	0.00020900
C	4.98903200	-0.17720100	0.00011200
C	3.84434600	0.65414900	-0.00001300
C	4.01157800	2.04152800	-0.00004600
C	5.30729000	2.57593800	0.00002500
C	6.42741500	1.73332200	0.00015100
H	7.15271200	-0.32081600	0.00031900
H	3.14687400	2.70919200	-0.00012300

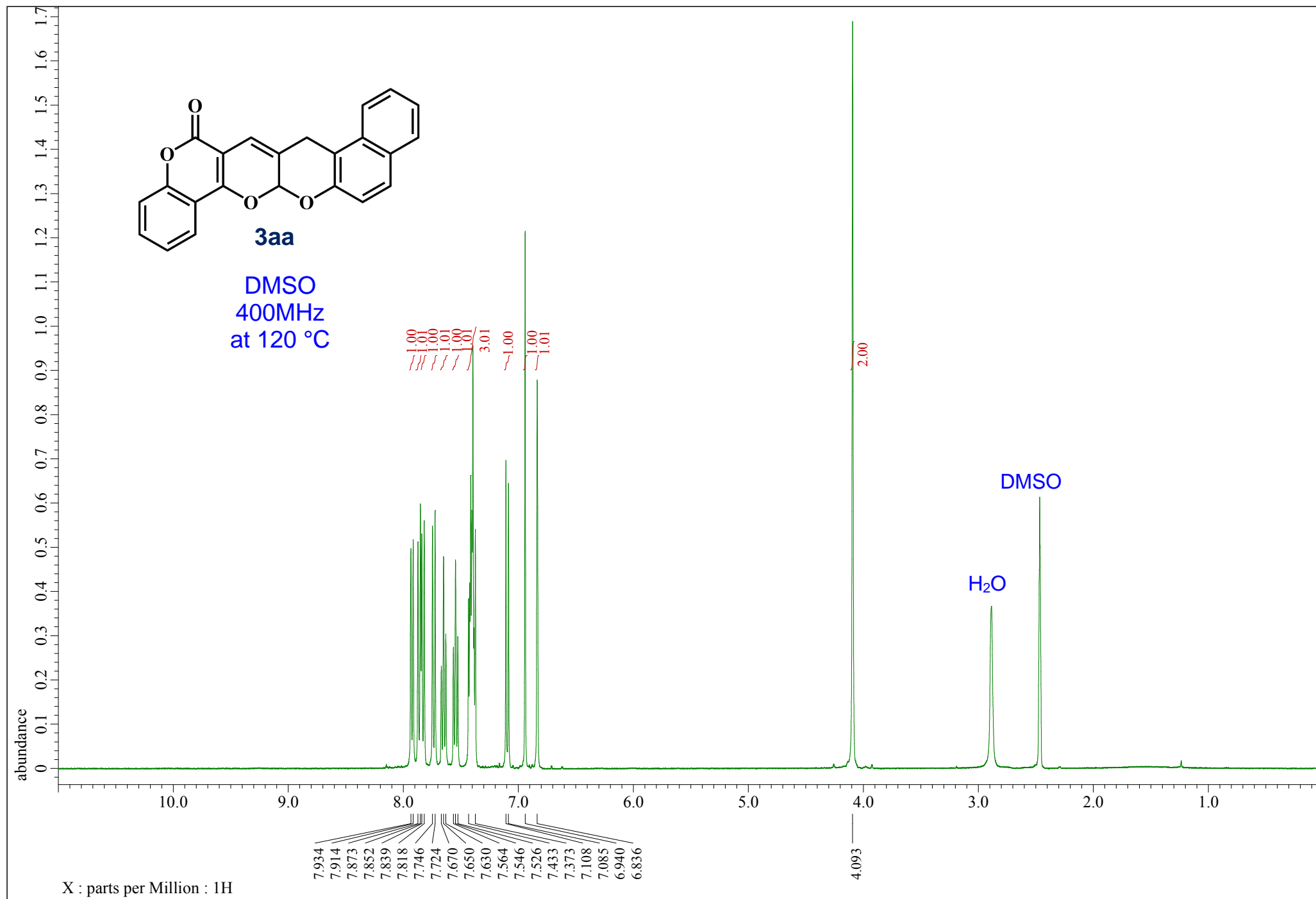
H	5.44423000	3.65907200	-0.00000400
H	7.43033800	2.16555700	0.00021800
C	3.18737500	-1.61991300	-0.00007300
O	2.59536000	-2.70002100	0.00009100
N	4.56698800	-1.50706800	0.00014900
H	5.17207100	-2.31958200	0.00028700
C	-3.72730300	2.03210000	-0.00005900
H	-2.79458500	2.59681300	-0.00005000
C	-6.15754800	0.62868700	-0.00006700
C	-6.15769200	2.00891600	-0.00007900
H	-7.10071500	2.55951100	-0.00009000
C	-4.92925400	2.71350600	-0.00007400
H	-4.93247400	3.80573600	-0.00008400
H	-7.09989400	0.07506800	-0.00006900

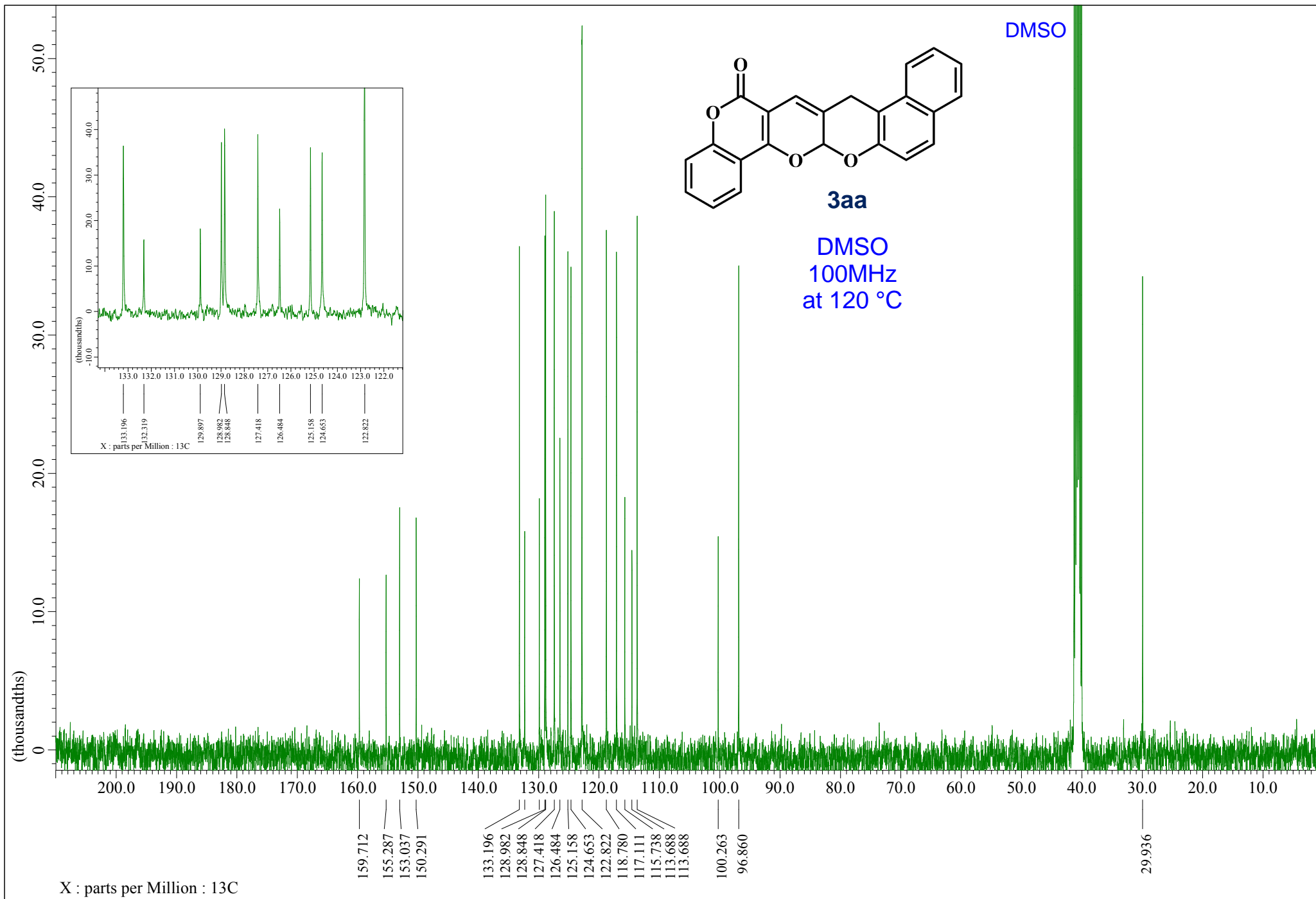


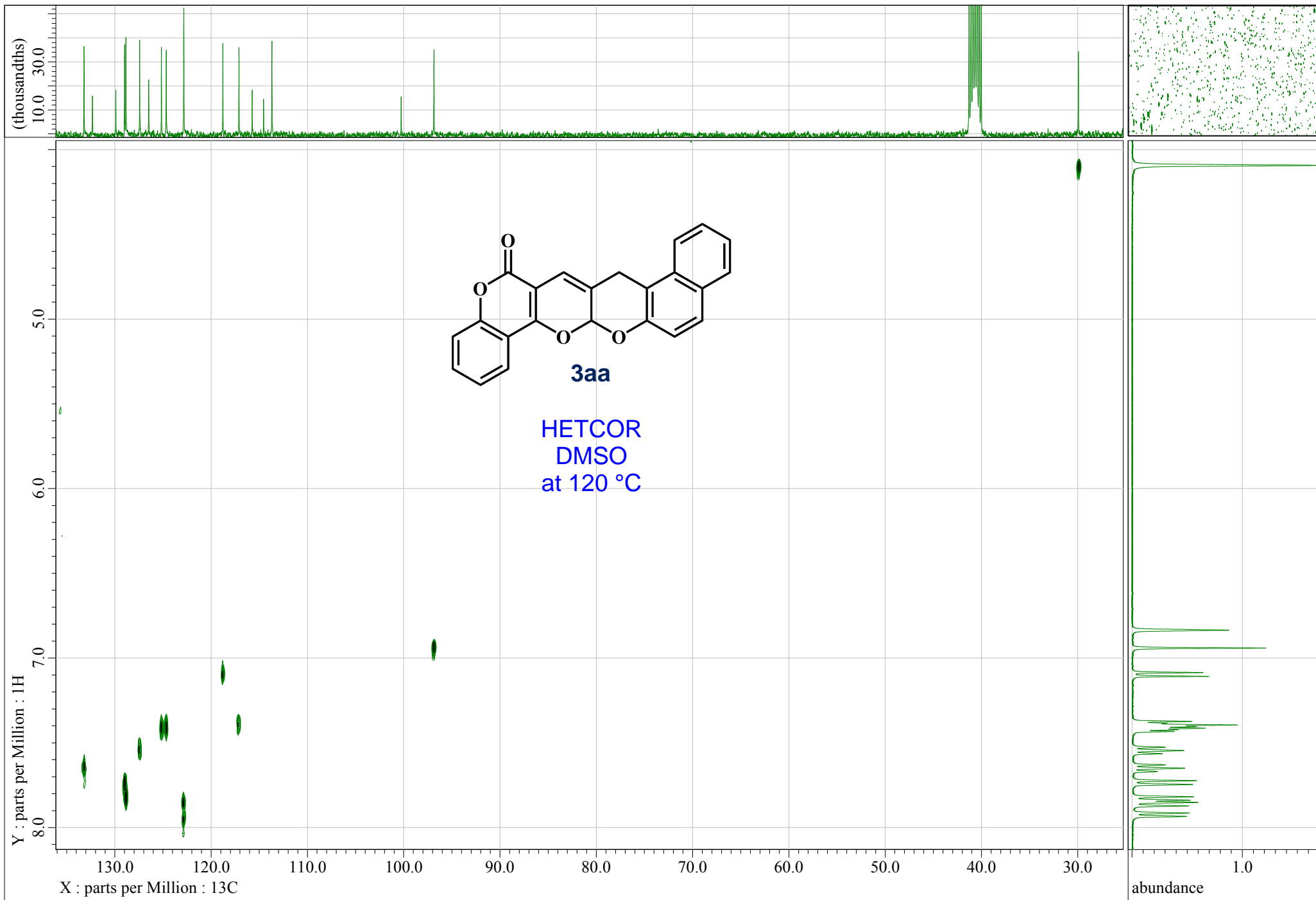
Z-5al (2H-pyran form)

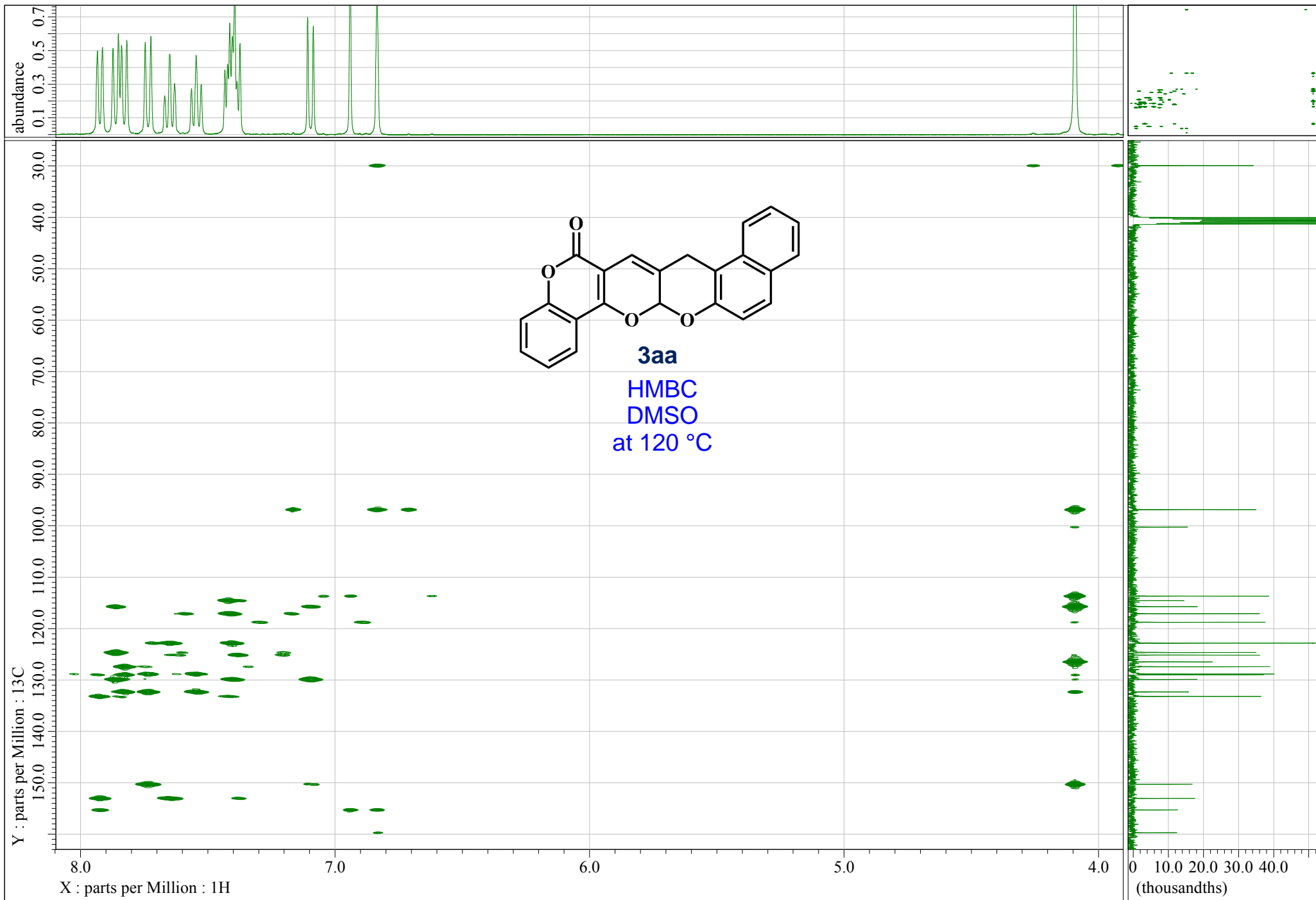
C	-4.49482800	-0.43254800	-0.67480400
C	-3.98836200	-1.67489100	-1.15442100
C	-2.69420800	-2.05116400	-0.89520900
C	-1.83421500	-1.19426600	-0.15571800
C	-2.26346000	0.04368000	0.31023400
C	-3.62254000	0.43445400	0.06744900
O	-0.56916900	-1.69159900	0.05552300
C	0.16260700	-1.04074900	1.11889700
C	0.11120000	0.44682000	0.91058000
C	-1.29282100	0.96937000	1.03094000
C	2.43988700	0.41997400	0.29611900
C	1.19294600	1.12928300	0.47509800
H	-4.64894300	-2.33303000	-1.72384400
H	-2.29295900	-3.00543100	-1.24077600
H	-0.30985900	-1.34876900	2.06747900
H	-1.34418900	1.98373200	0.60632100
H	-1.59098000	1.06228500	2.09415700
H	1.12376800	2.19676700	0.25034200
C	5.87601700	-0.54461100	-0.45182500
C	4.53122500	-0.47647900	-0.08326100
C	3.77457300	0.73412300	-0.16042800
C	4.41240800	1.89768800	-0.62606200
C	5.75702400	1.83374000	-0.99393300
C	6.48225500	0.62834500	-0.90936600
H	6.43303600	-1.48166800	-0.38526000
H	3.86332200	2.83929800	-0.69844700
H	6.25830200	2.73463600	-1.35532400
H	7.53321200	0.60808000	-1.20533600
C	2.46010100	-0.92359100	0.61161100
O	1.44944800	-1.65032100	1.12534000
N	3.68825700	-1.47729800	0.39973300
H	3.92983700	-2.44711500	0.56077700
C	-4.15360400	1.67033800	0.53904800
H	-3.51824600	2.34803200	1.11048400
C	-5.83815400	-0.03482300	-0.91544000
C	-6.32013400	1.16950900	-0.44361600
H	-7.35462000	1.46303900	-0.63417800
C	-5.46576500	2.02652400	0.29161300
H	-5.84757300	2.97863100	0.66736000
H	-6.48705700	-0.70639100	-1.48381100

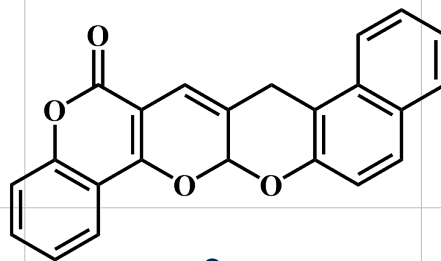
III. Copies of NMR spectra



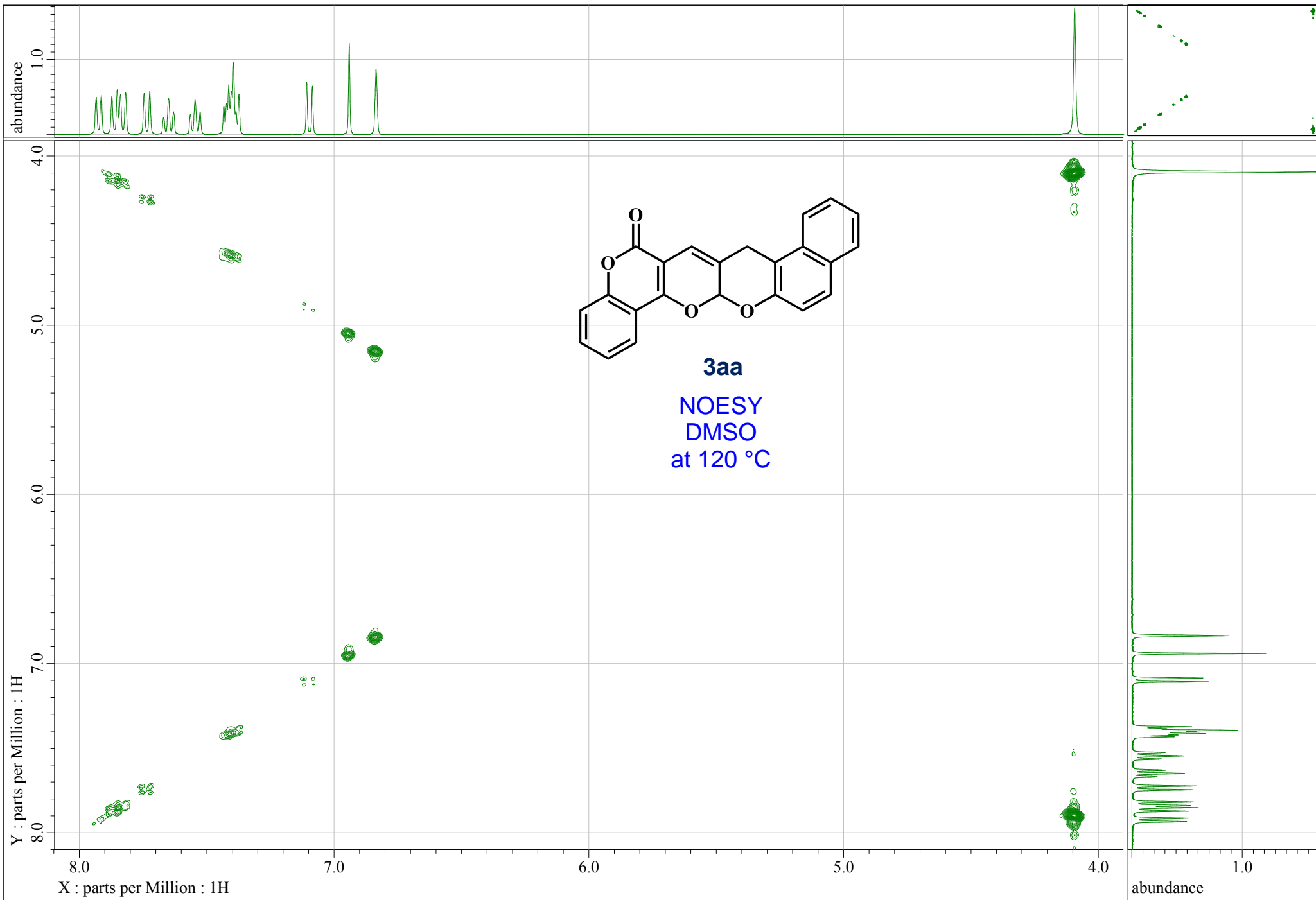


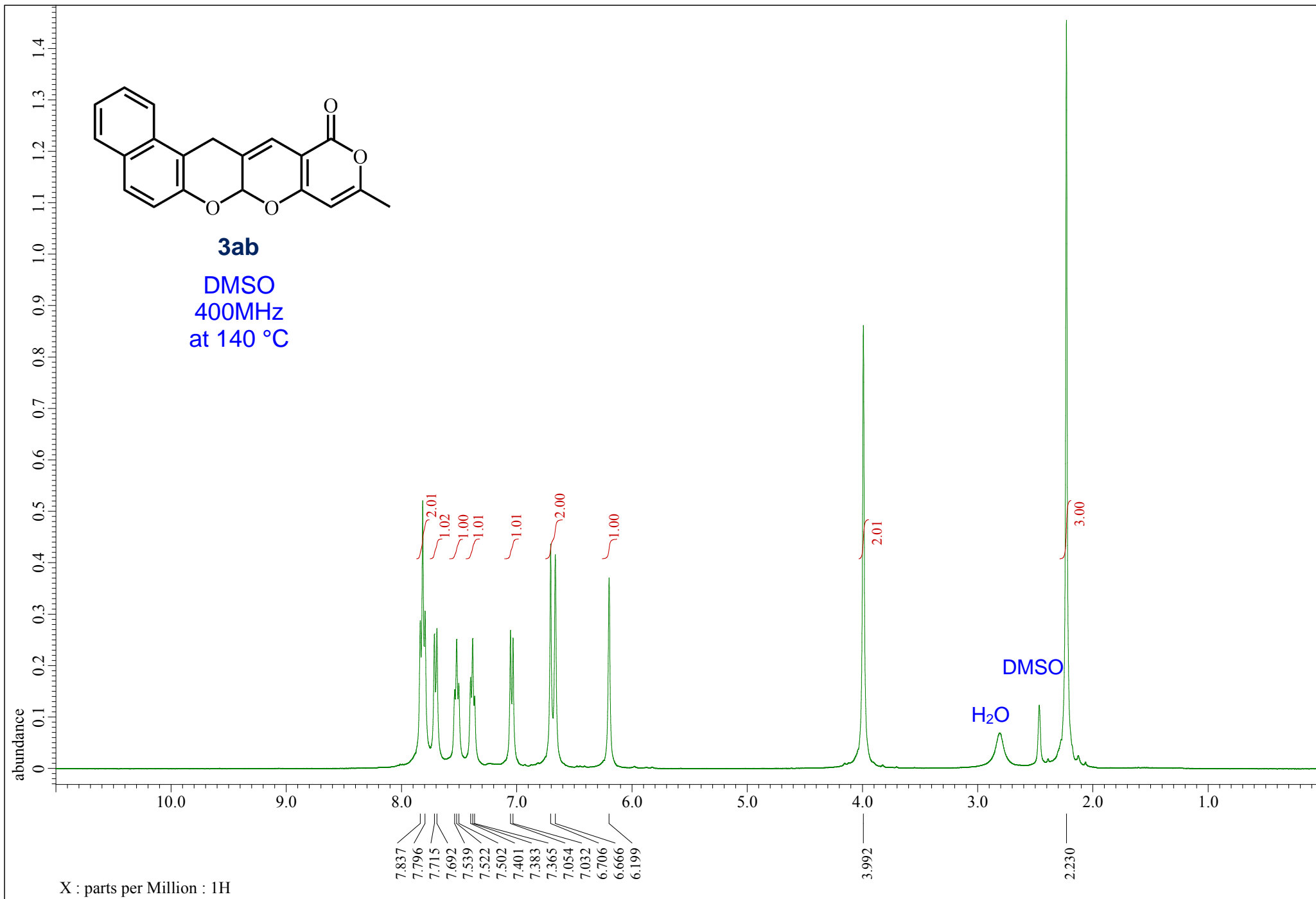


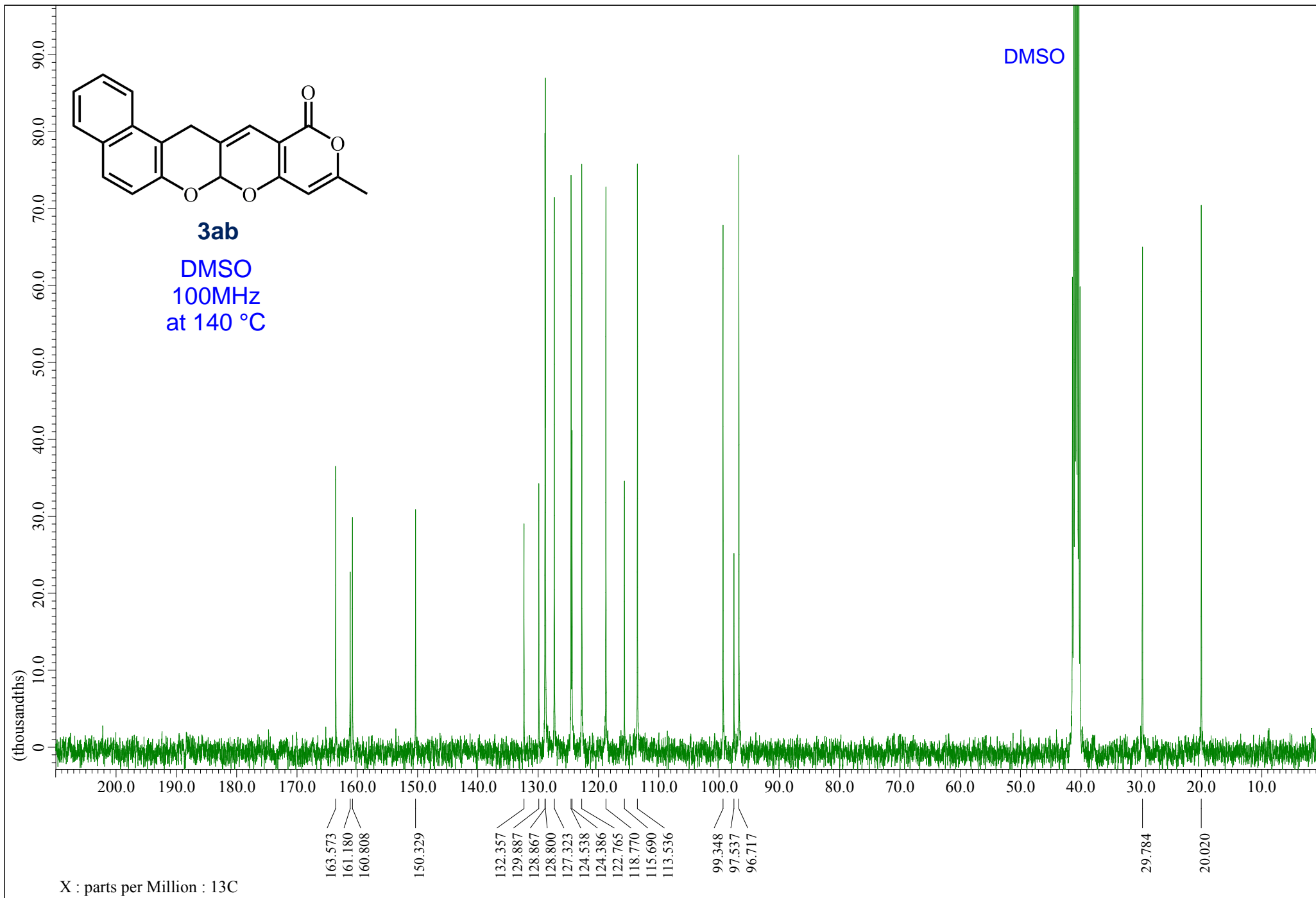


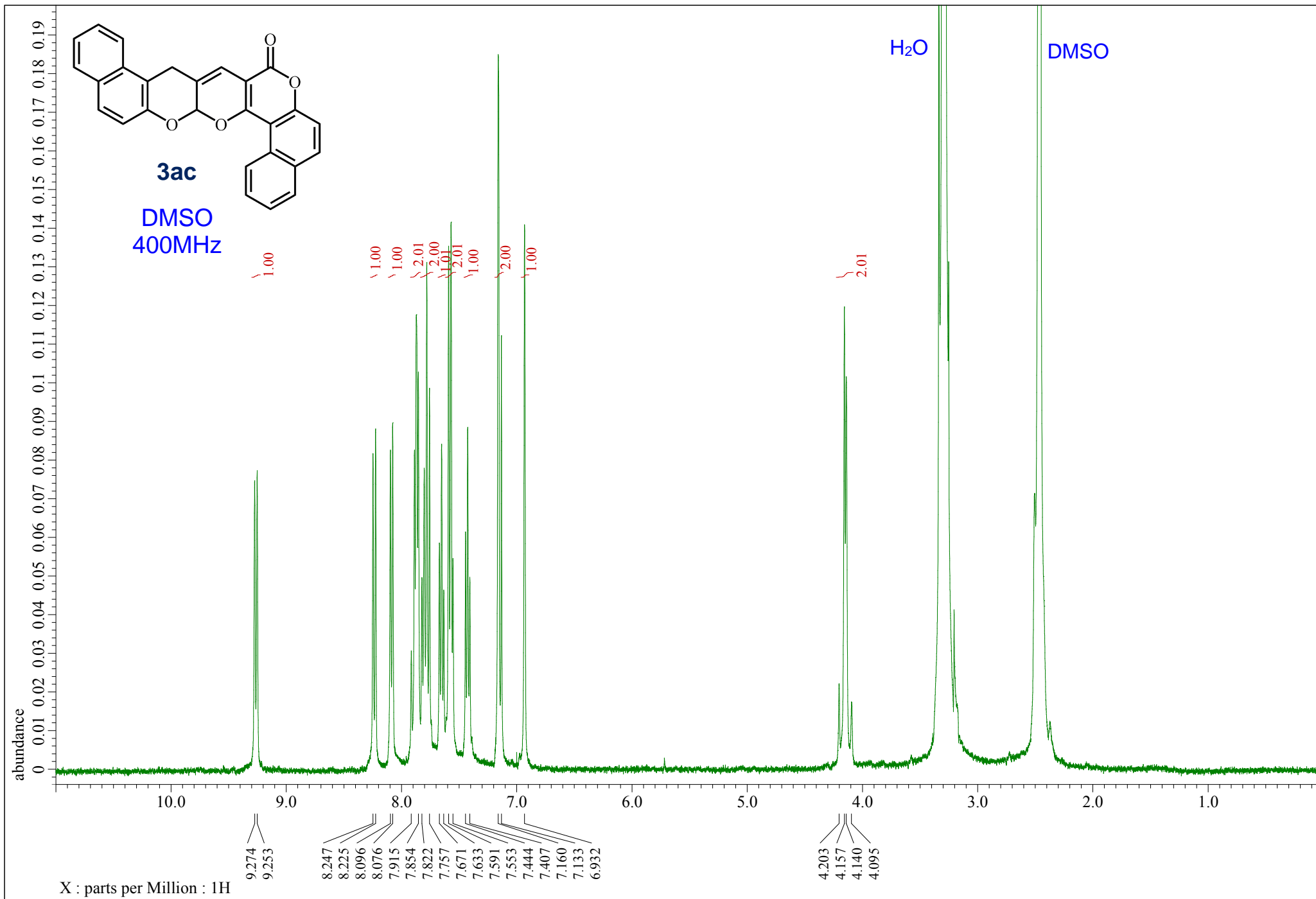


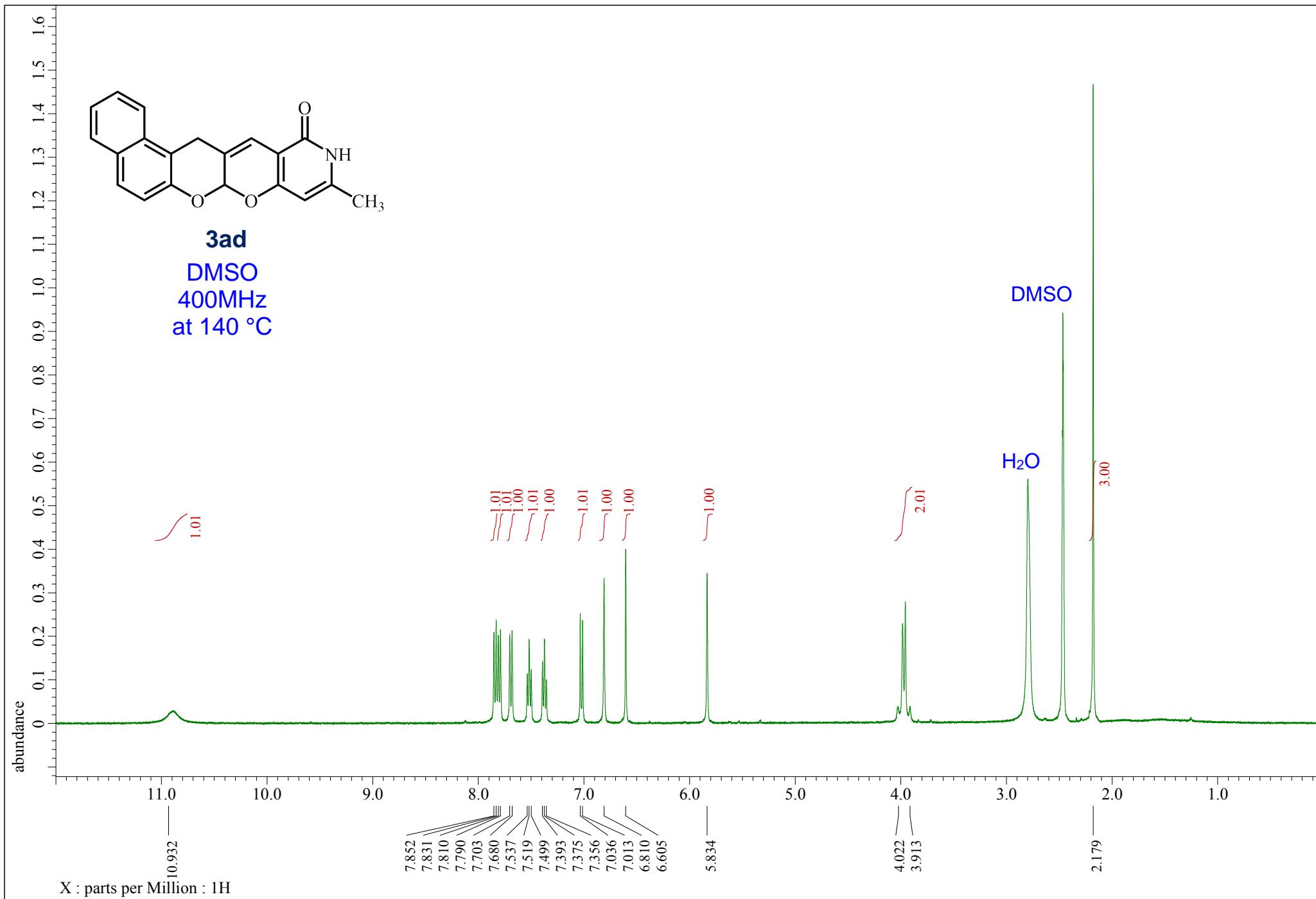
3aa
NOESY
DMSO
at 120 °C

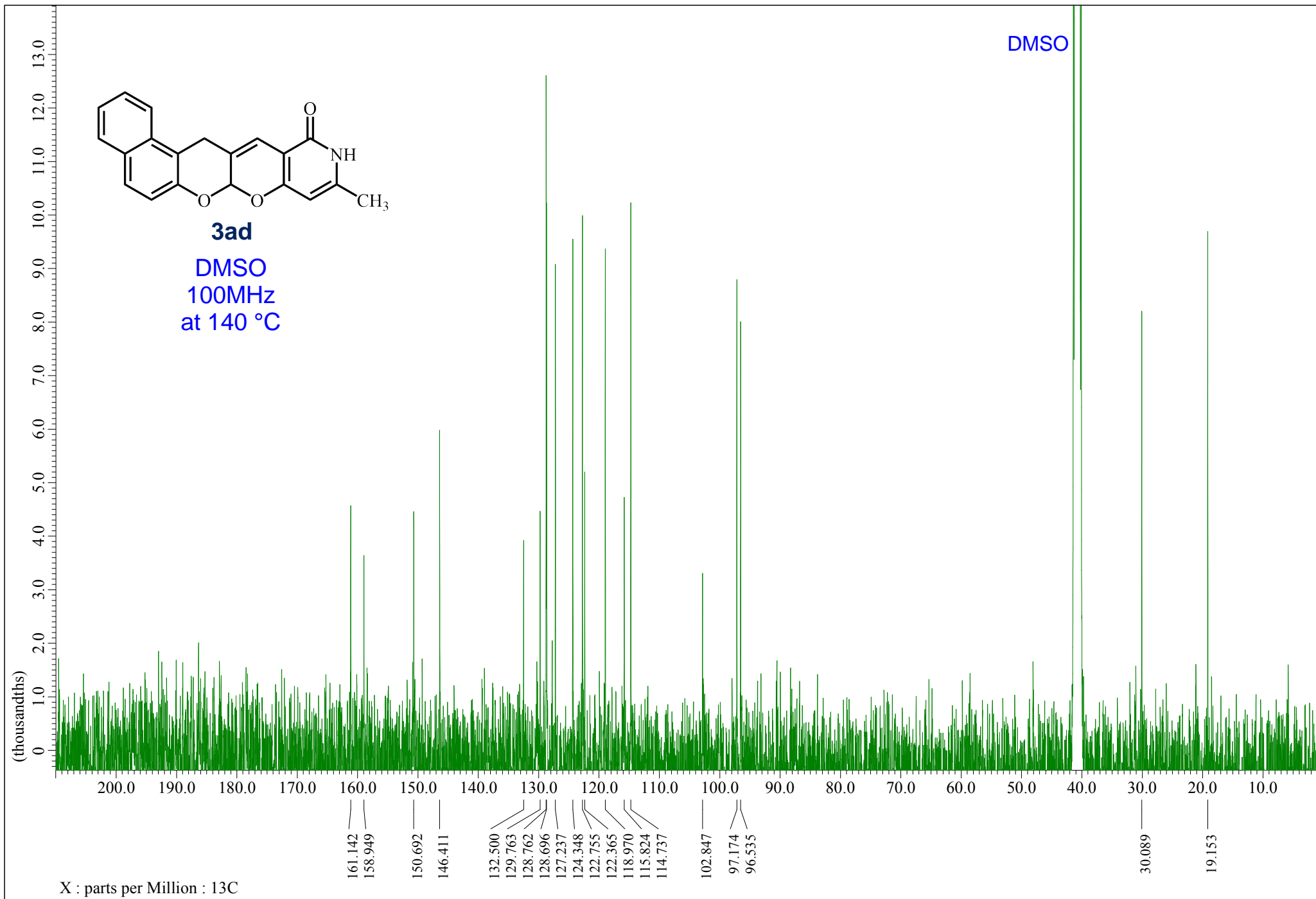


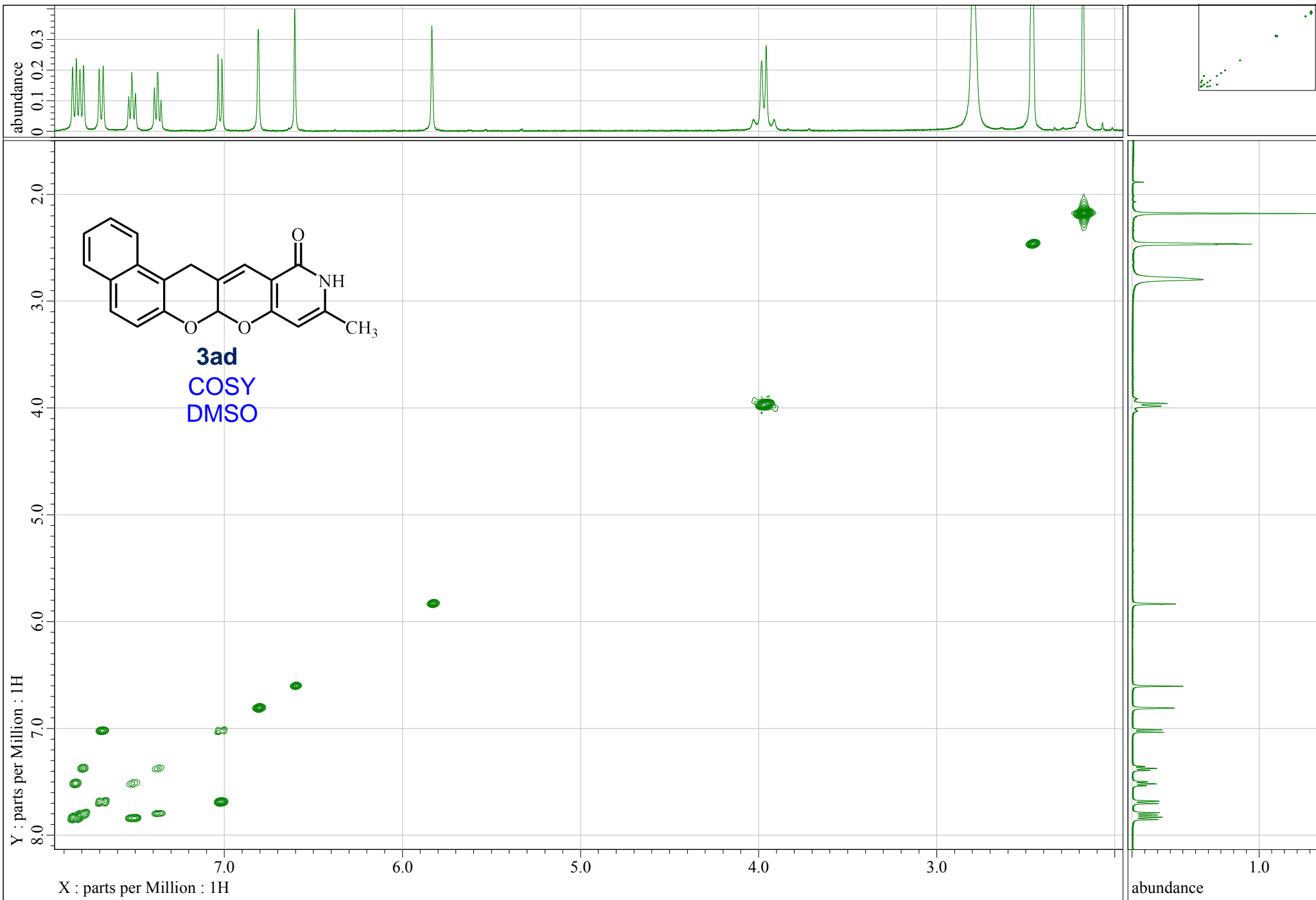


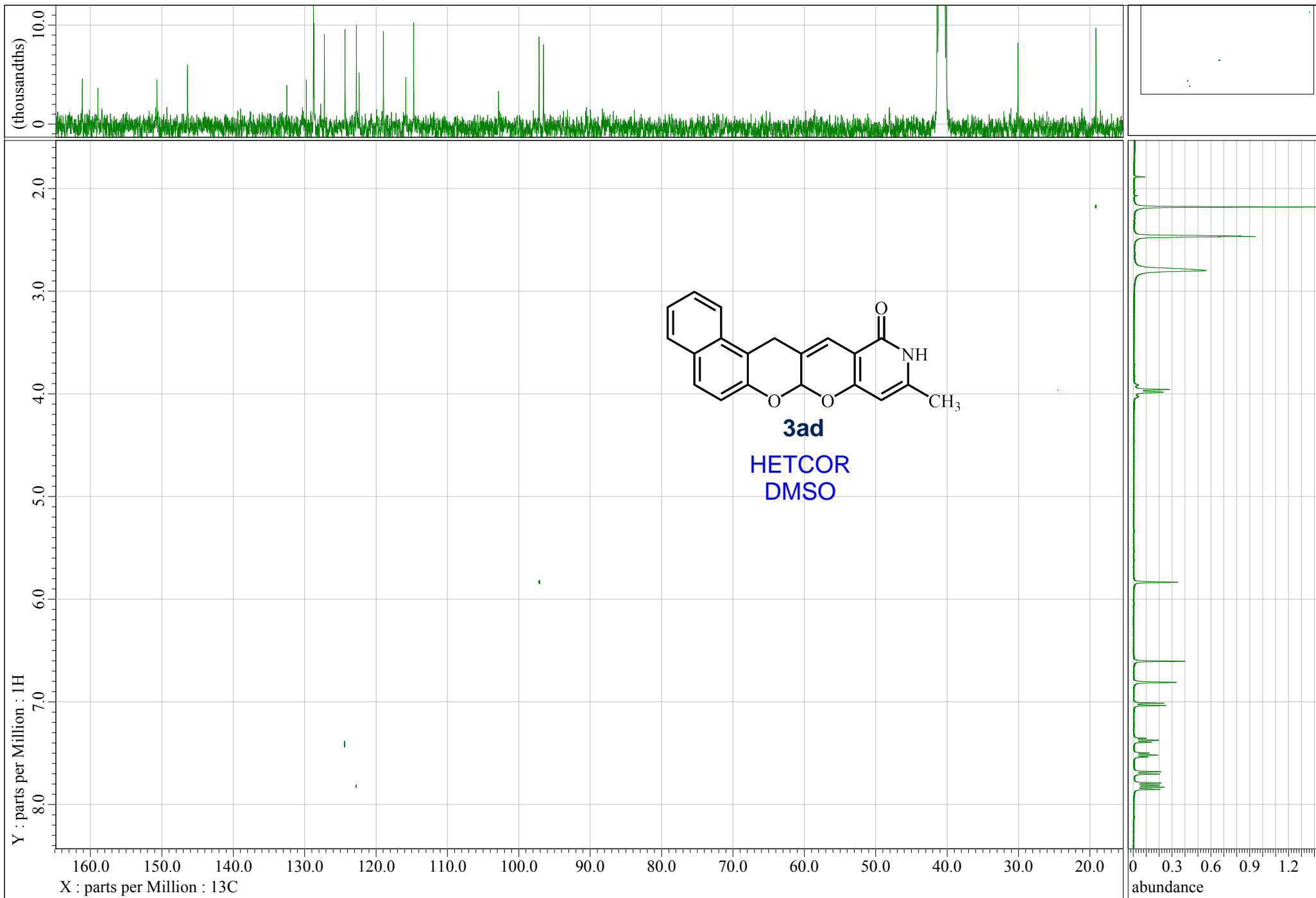


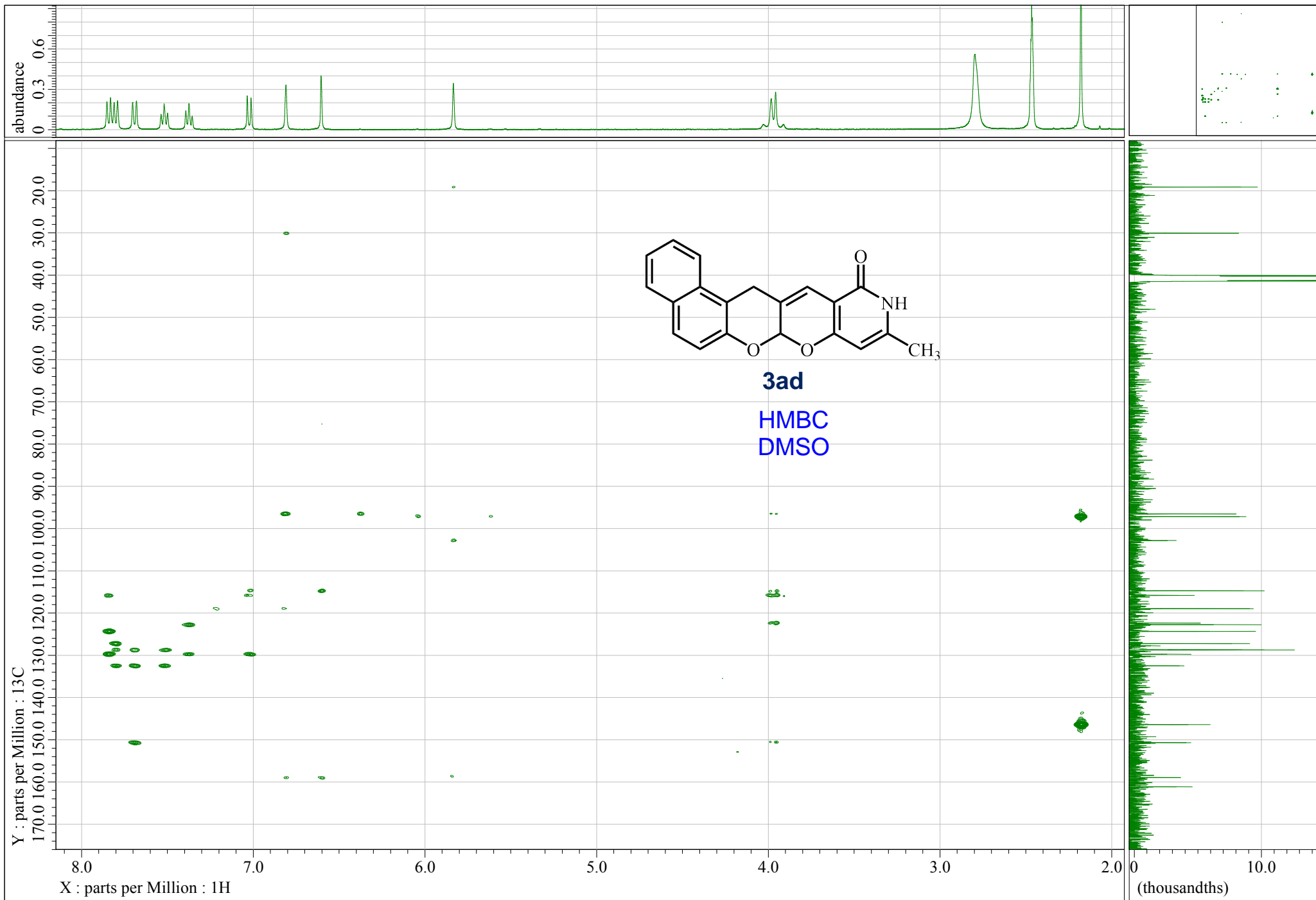


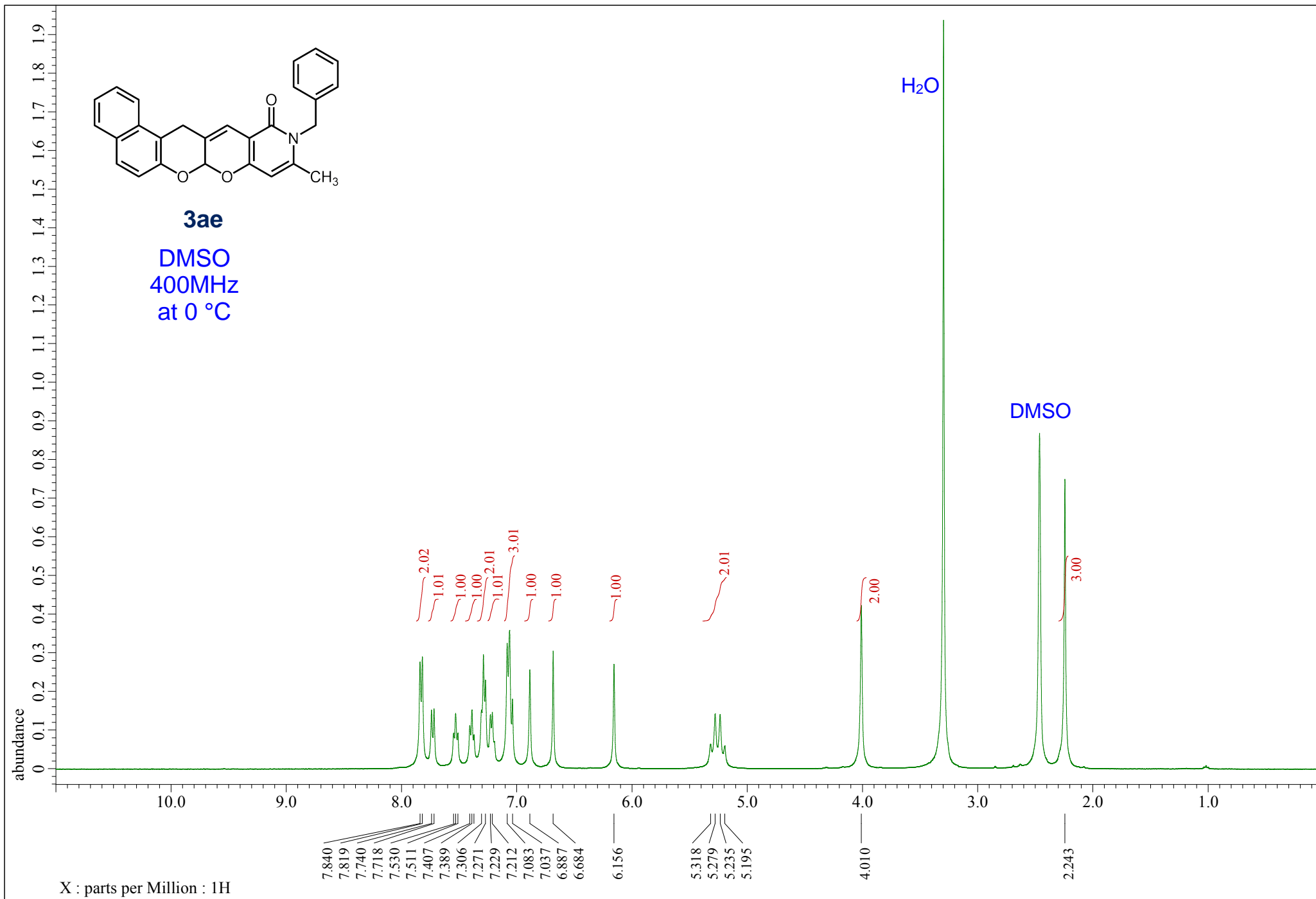


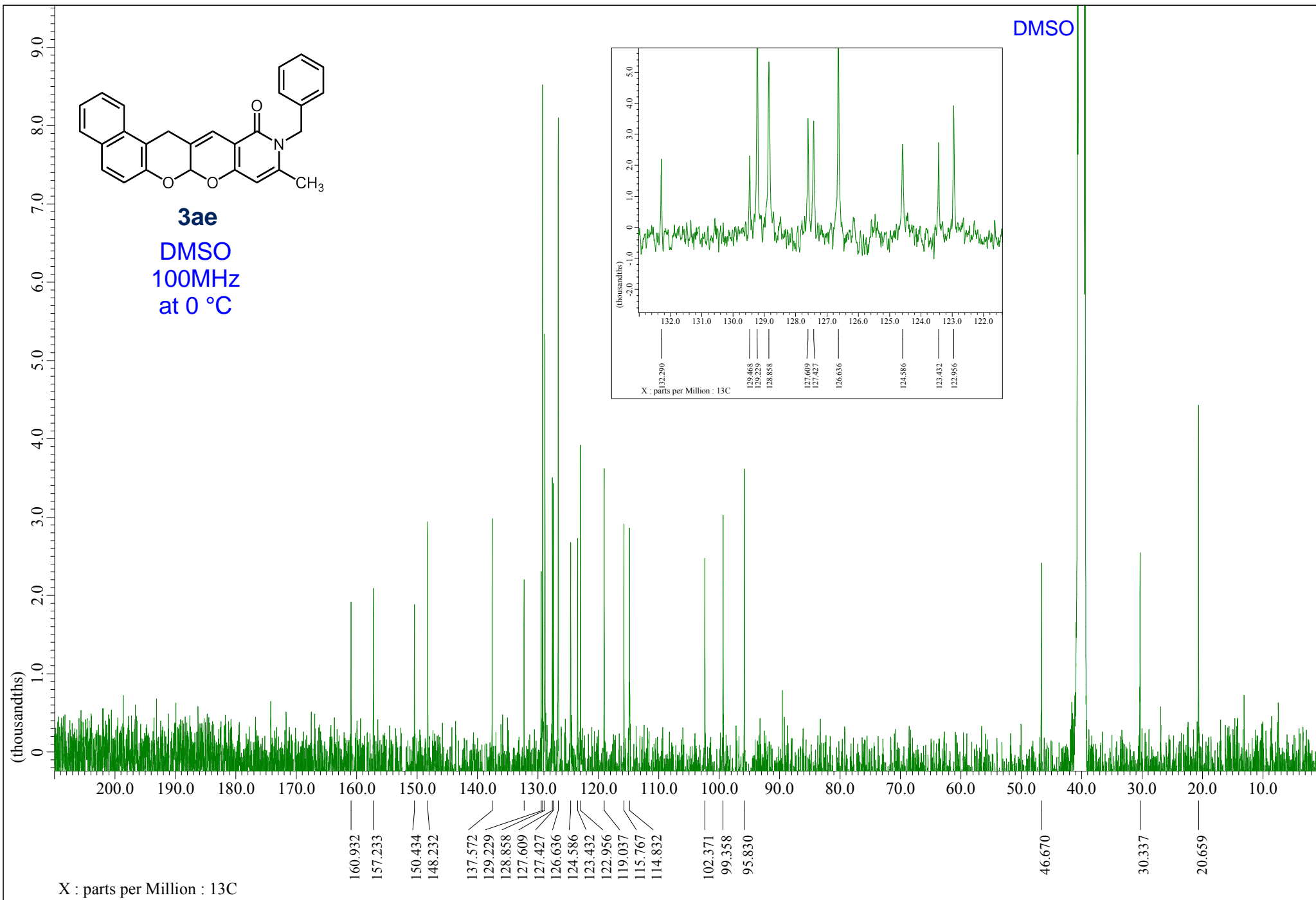


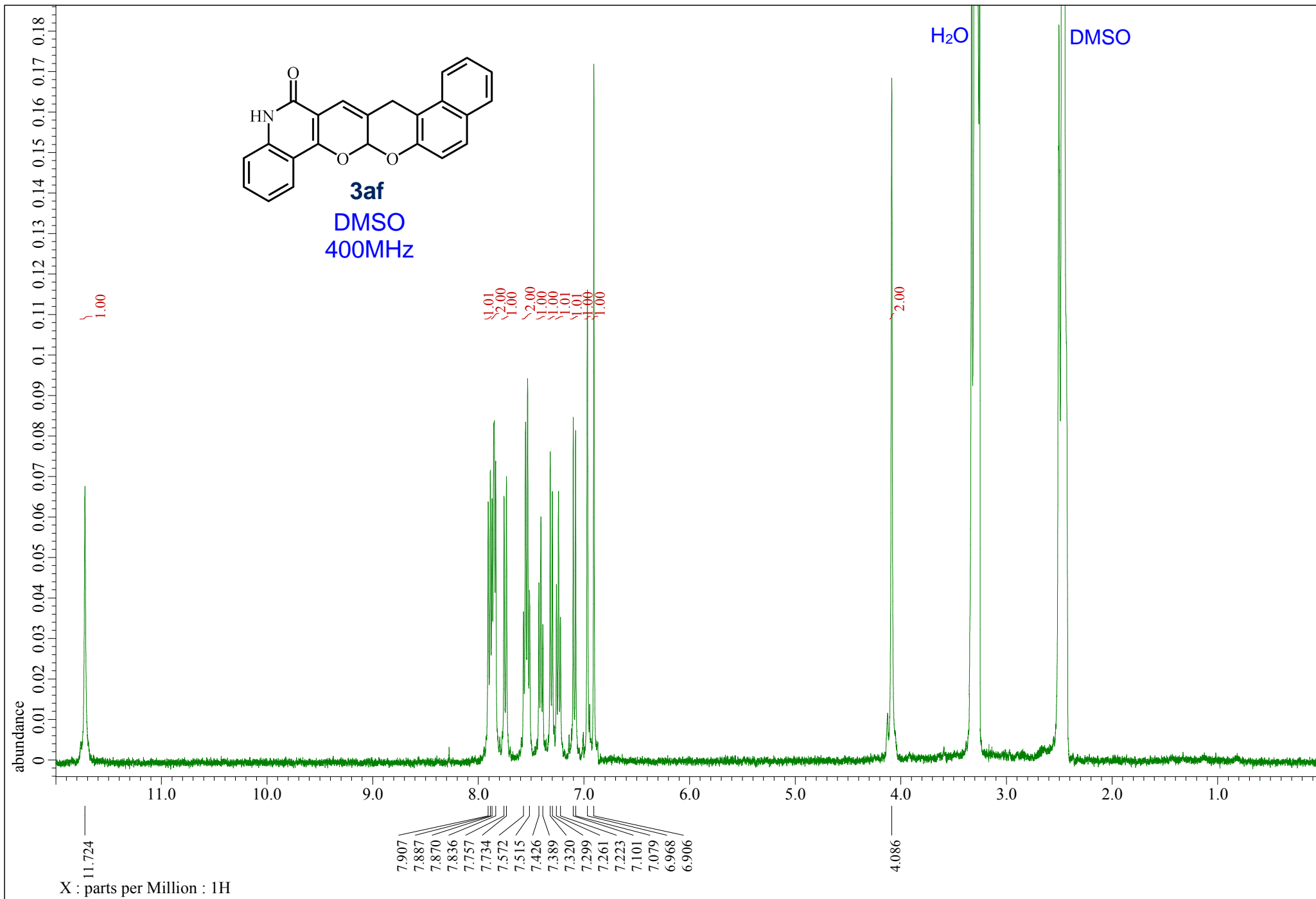


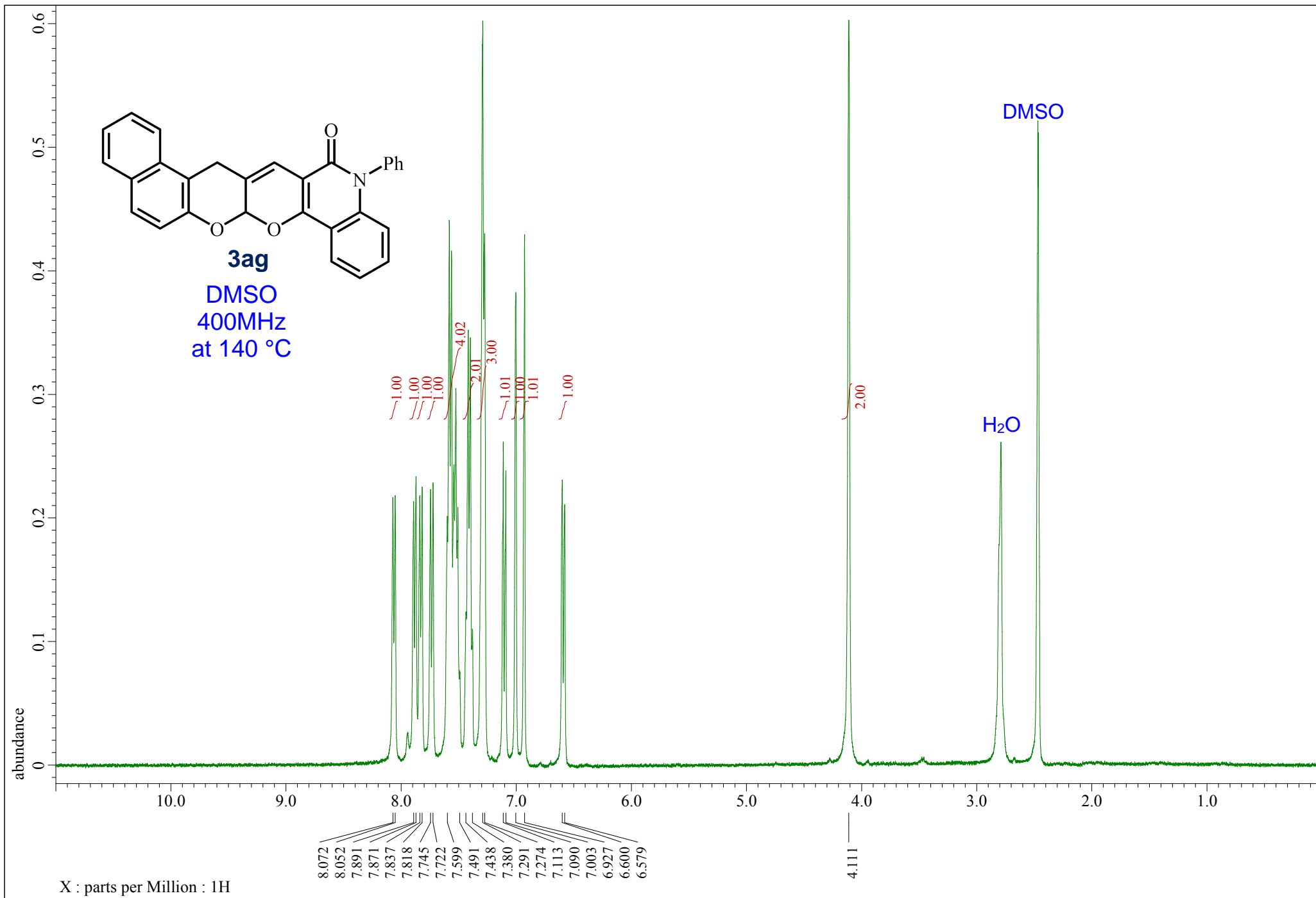


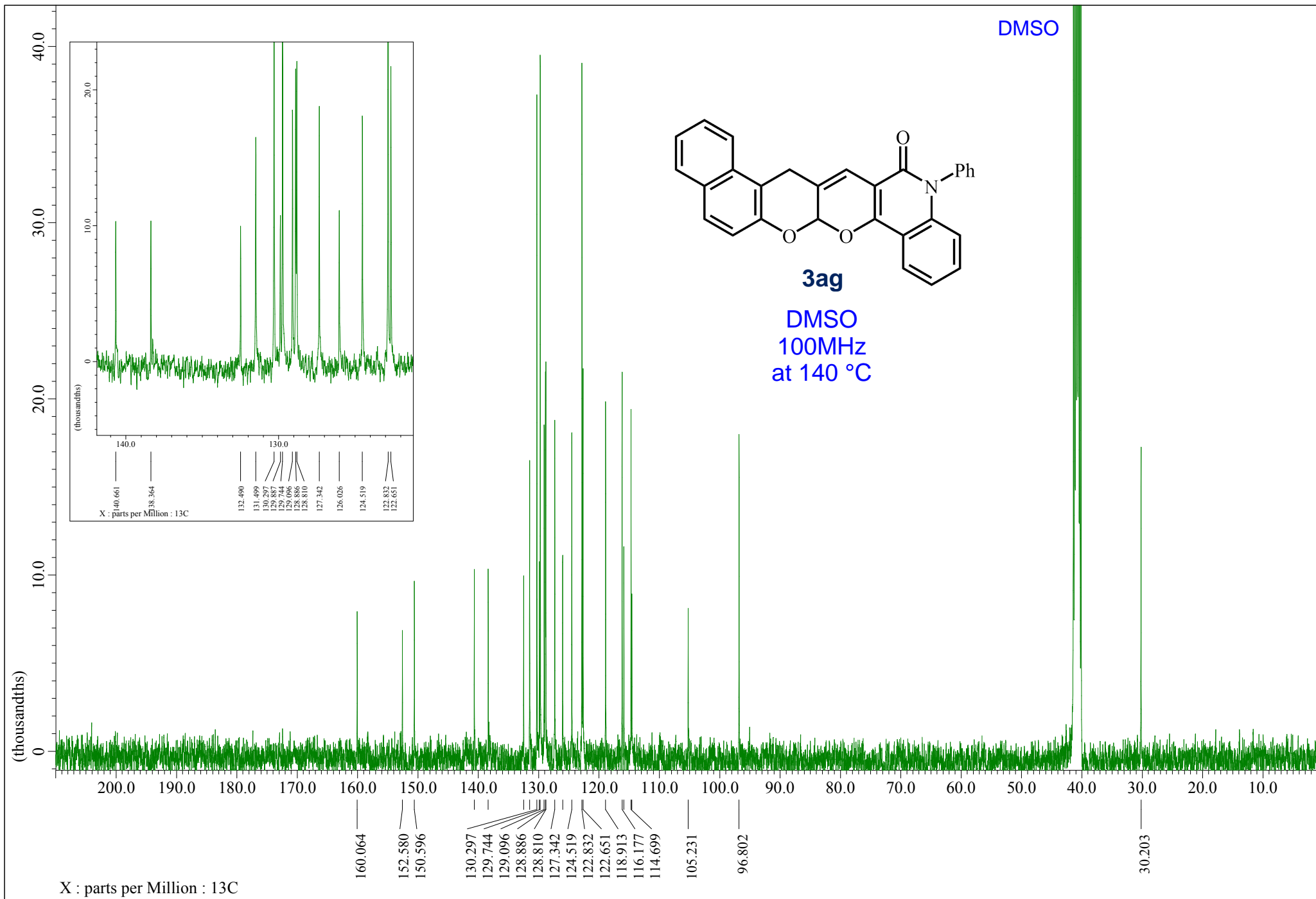


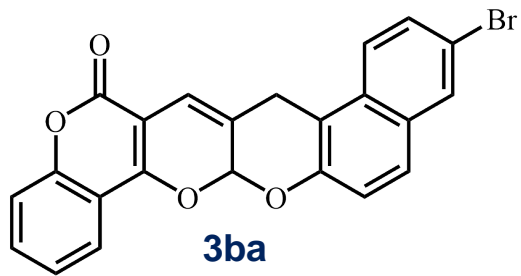




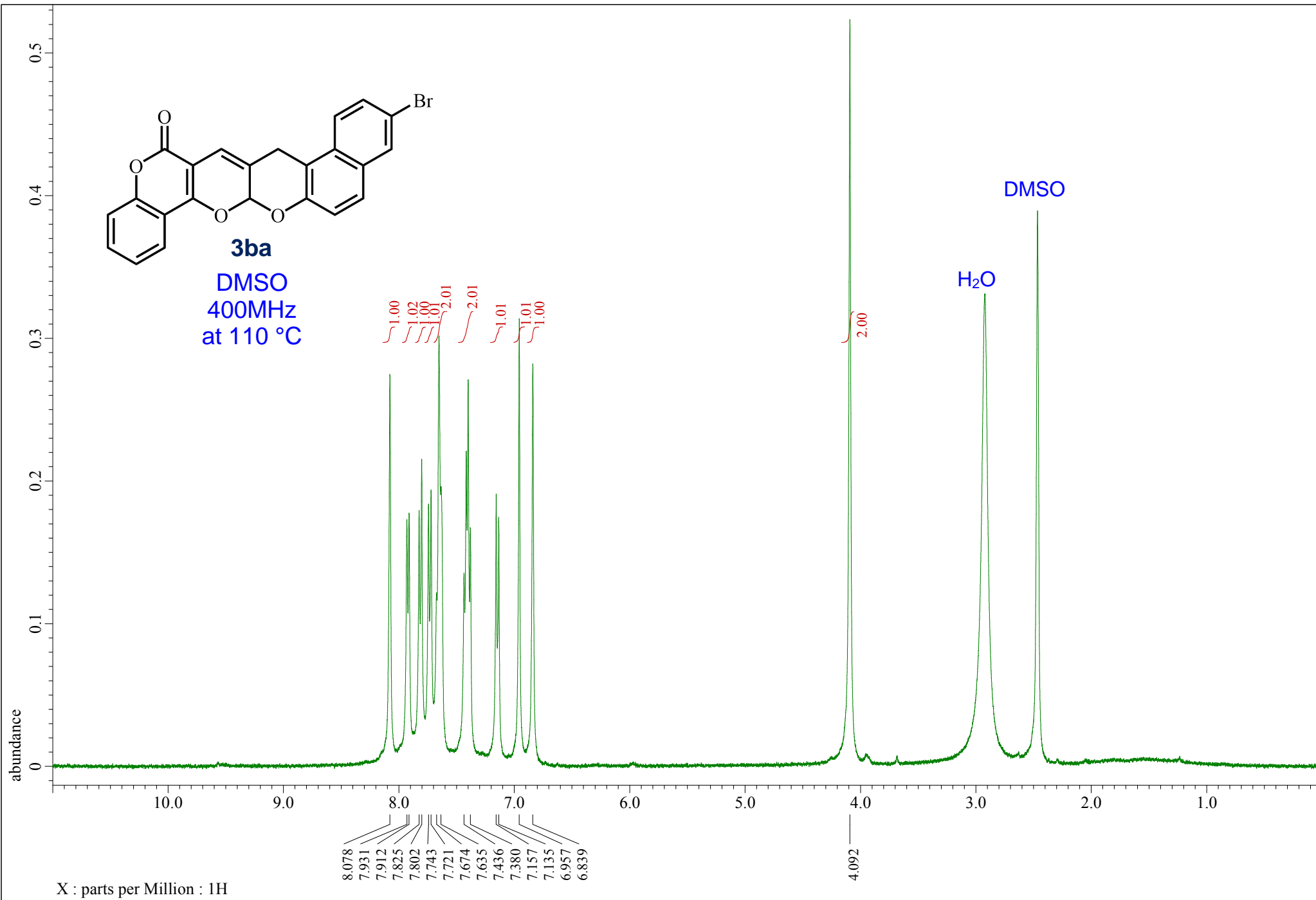


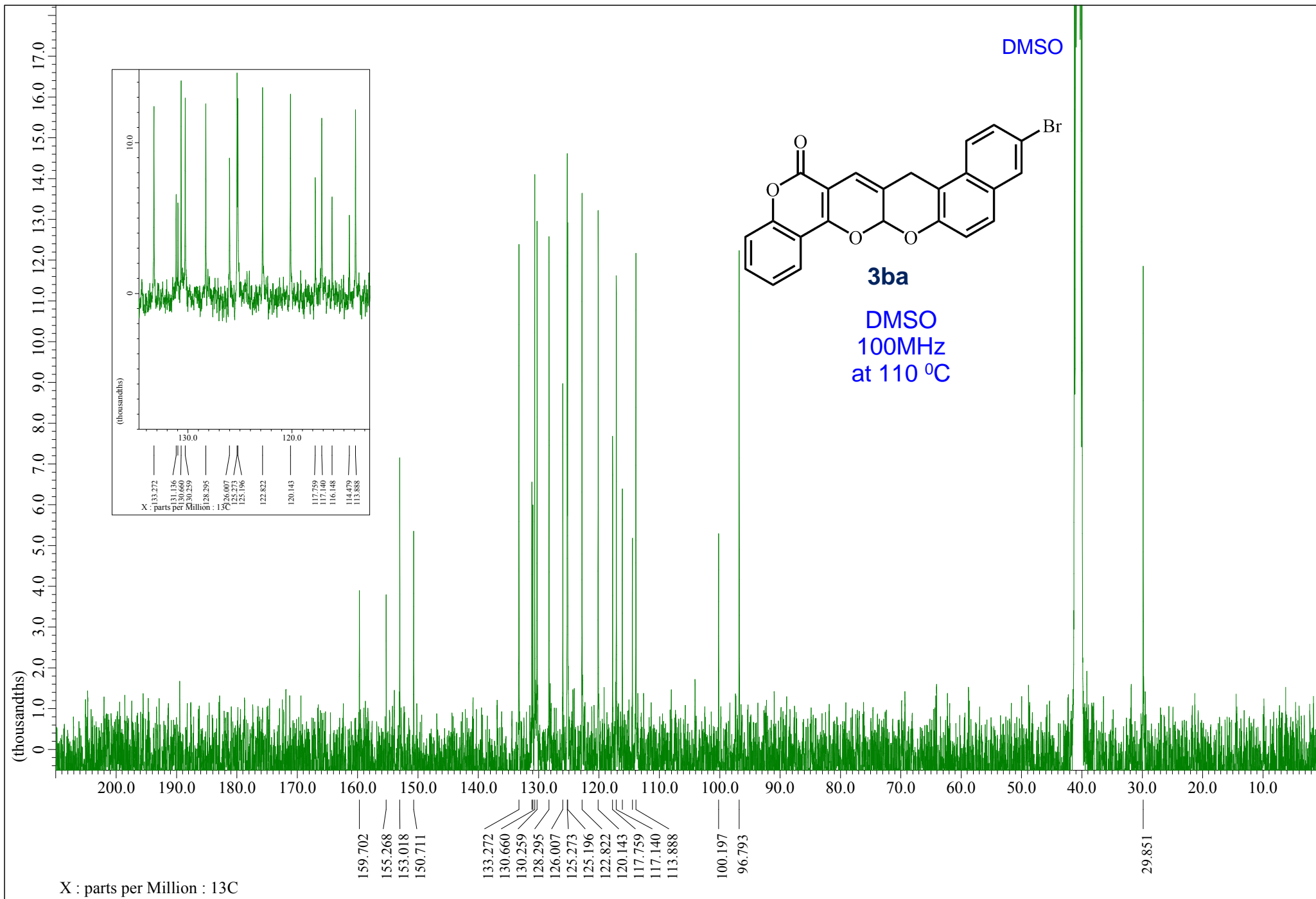


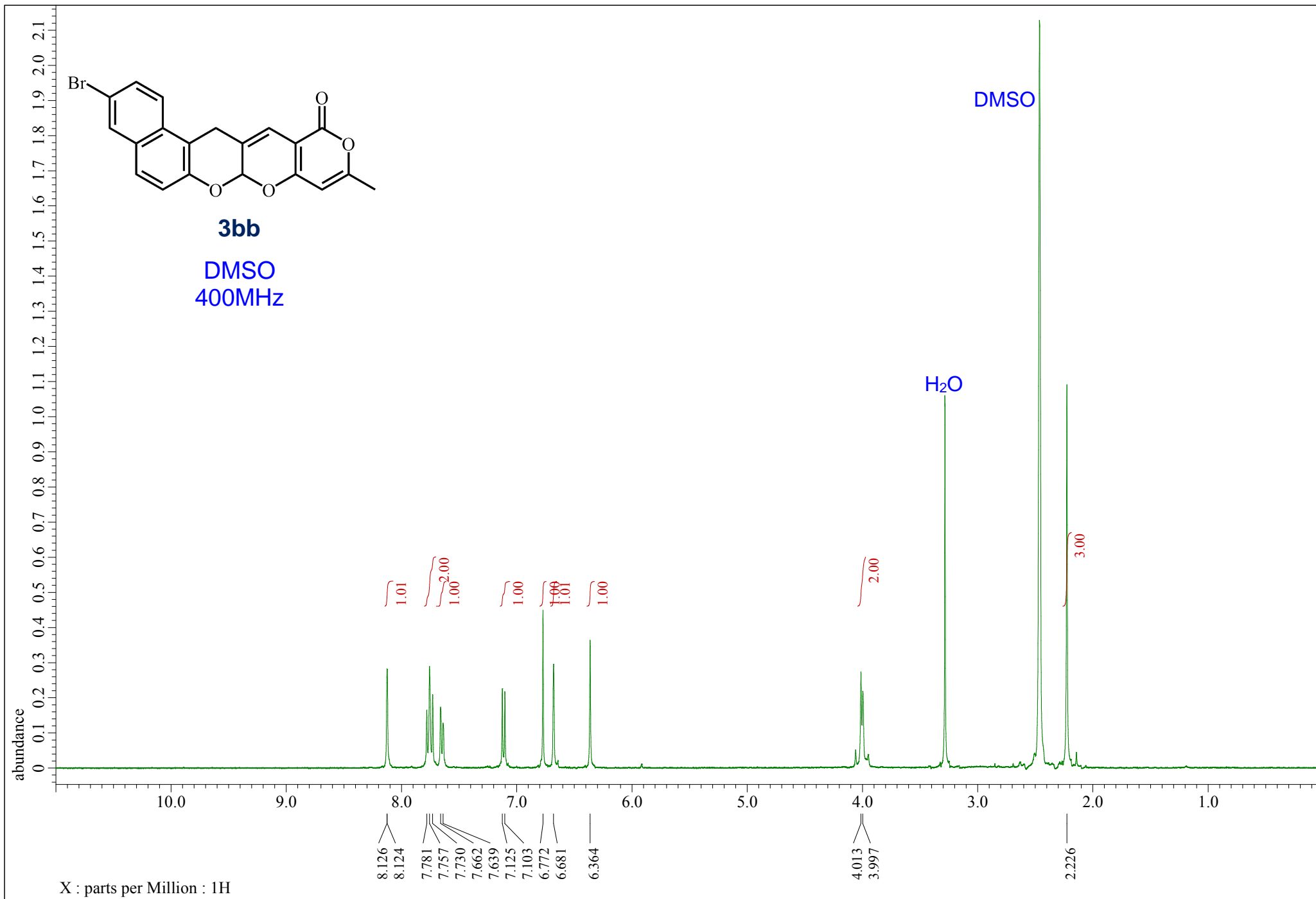


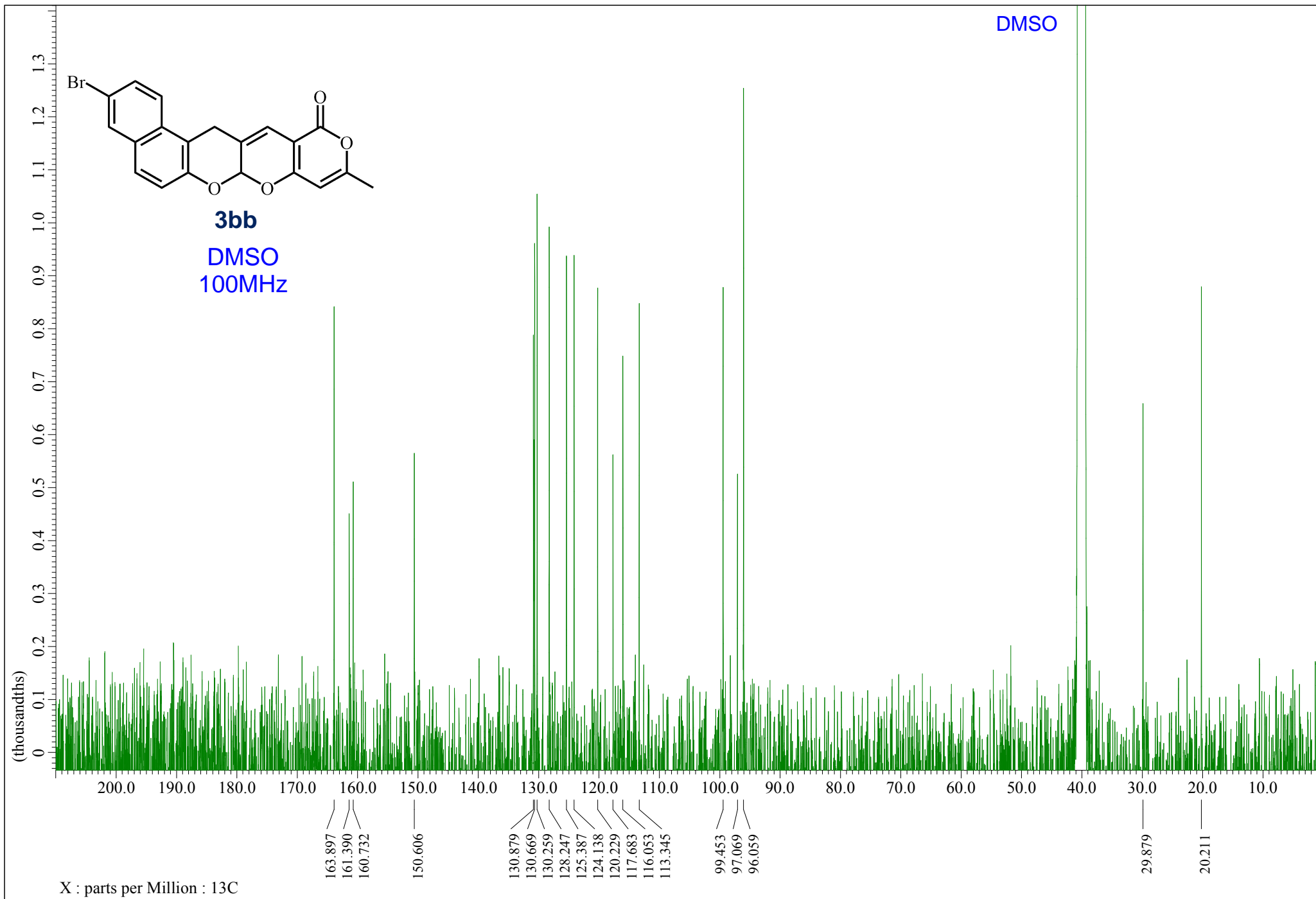


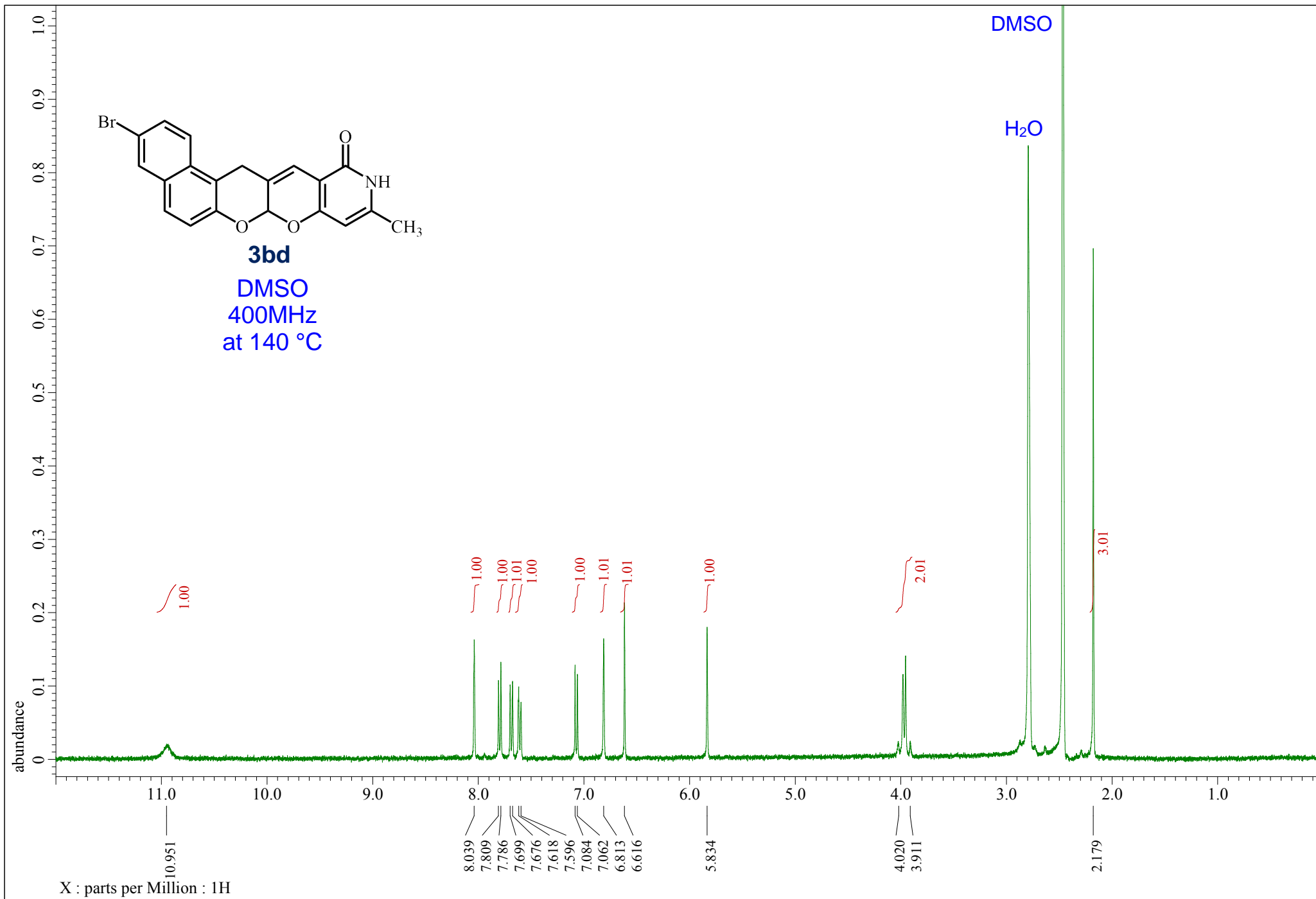
DMSO
400MHz
at 110 °C

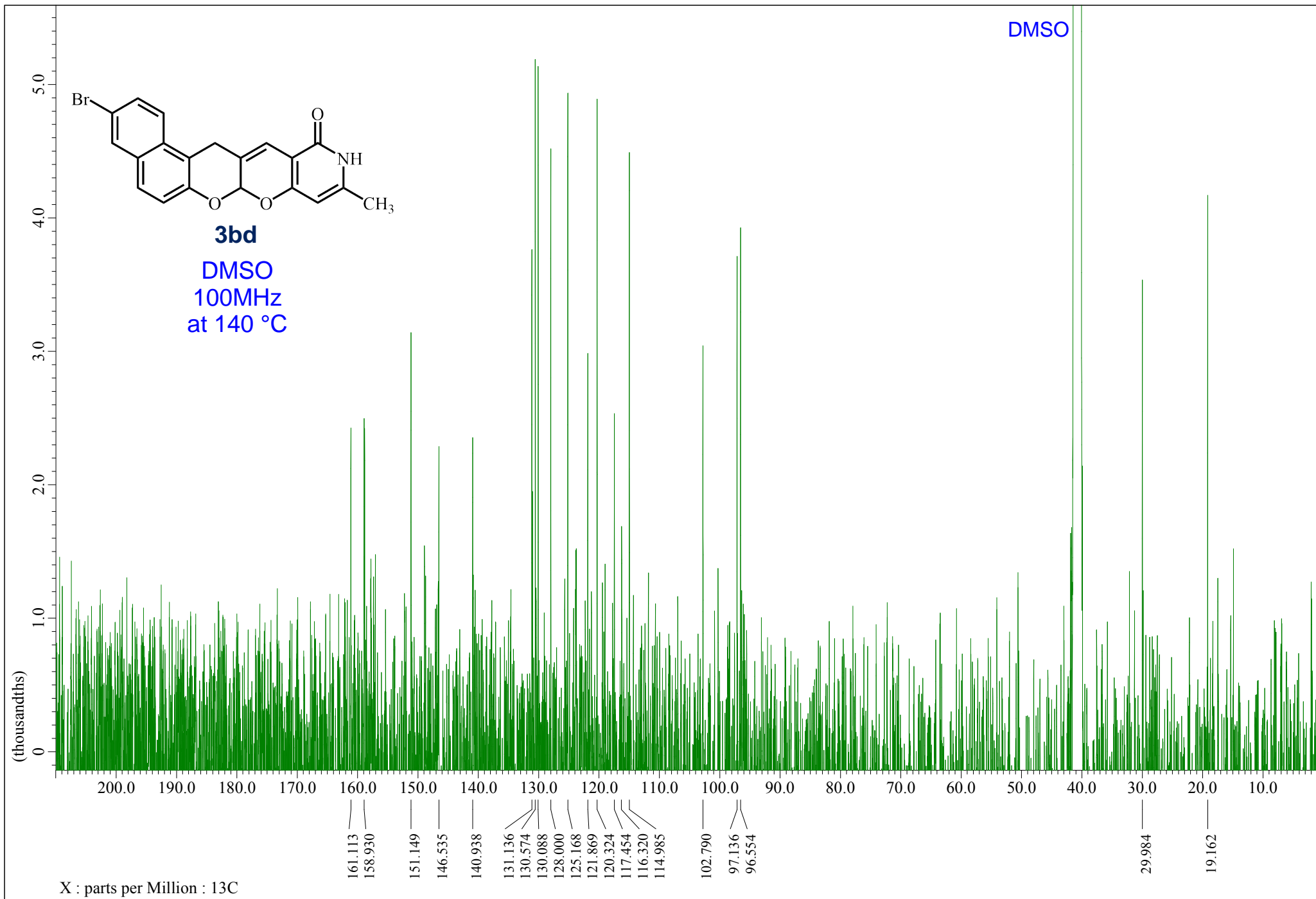


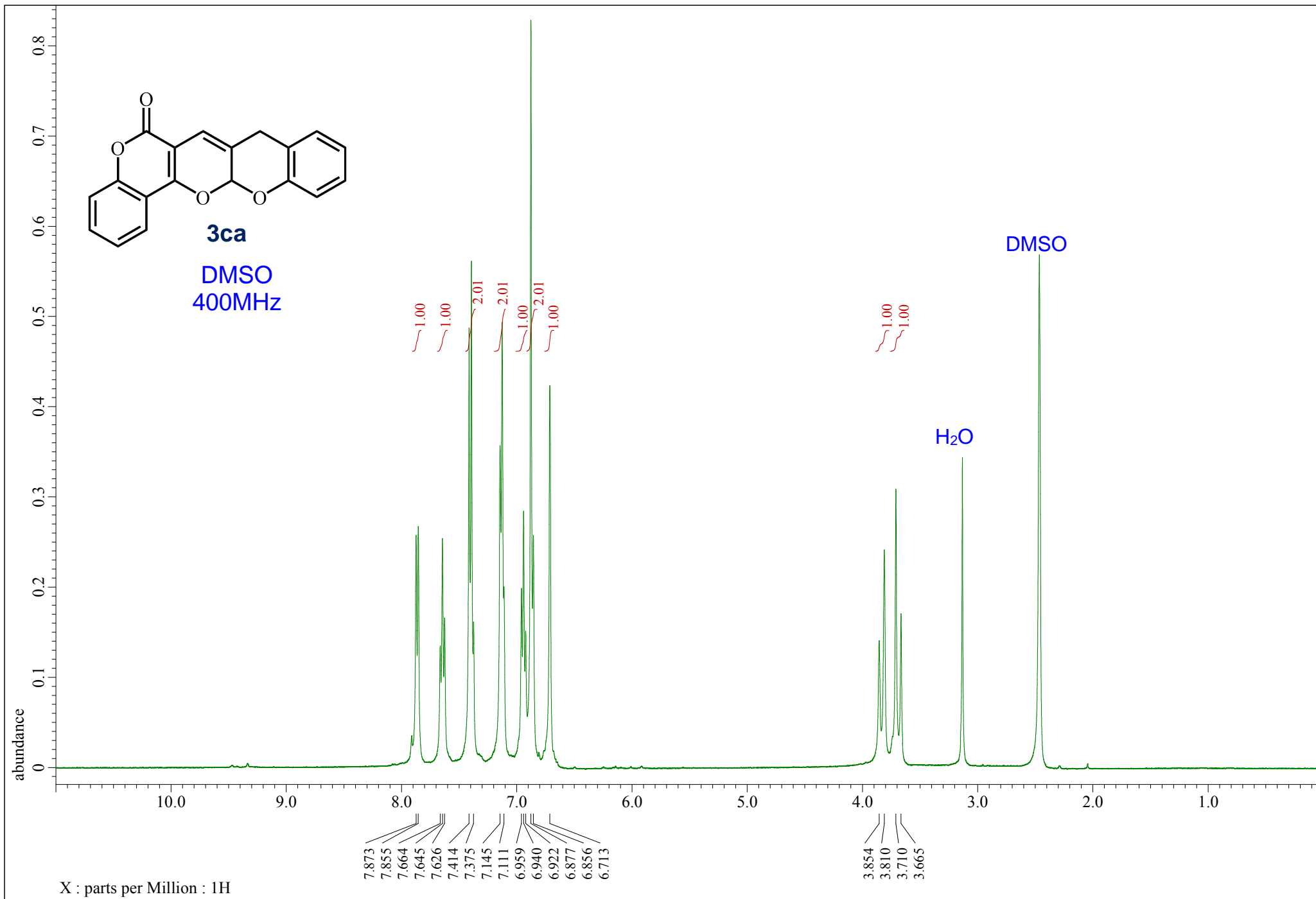


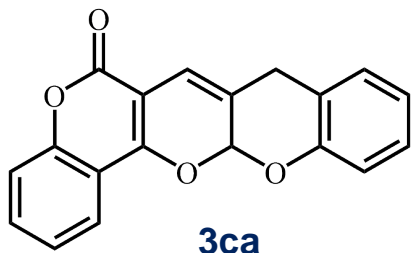






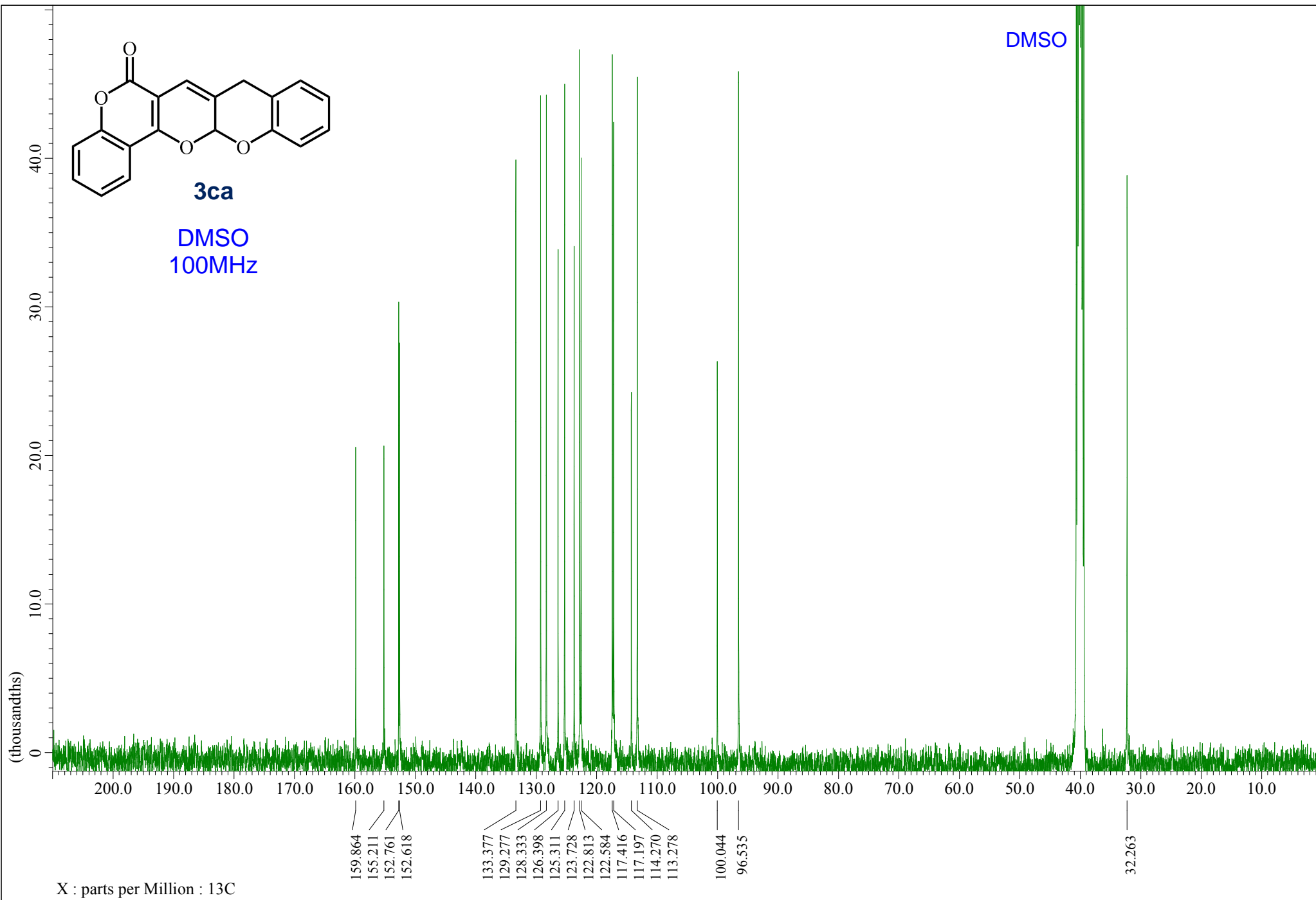


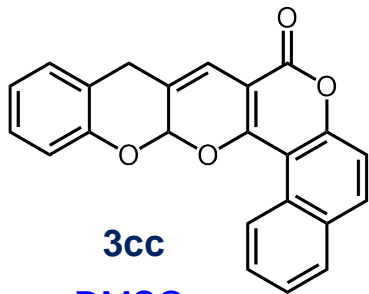




DMSO
100MHz

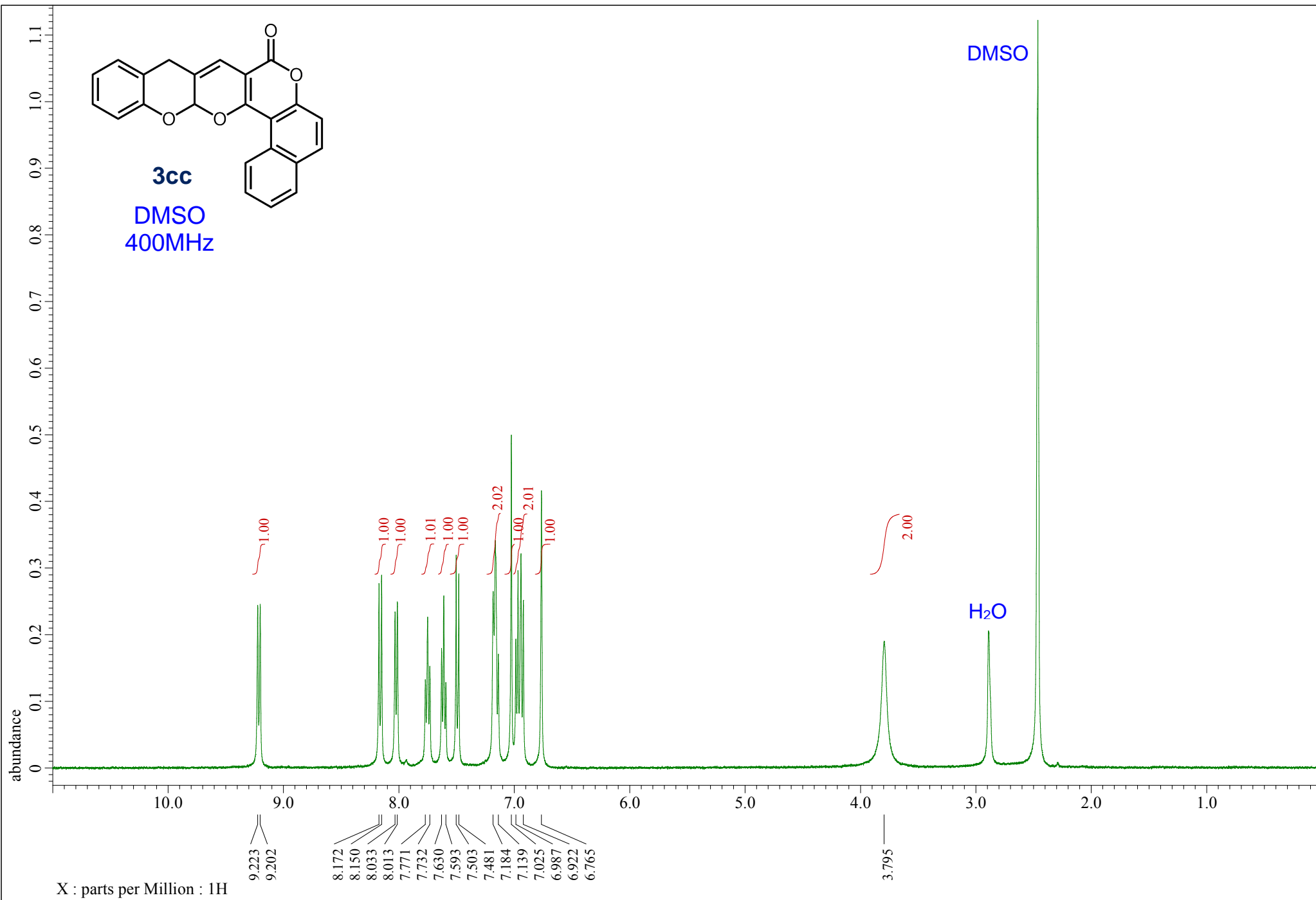
DMSO

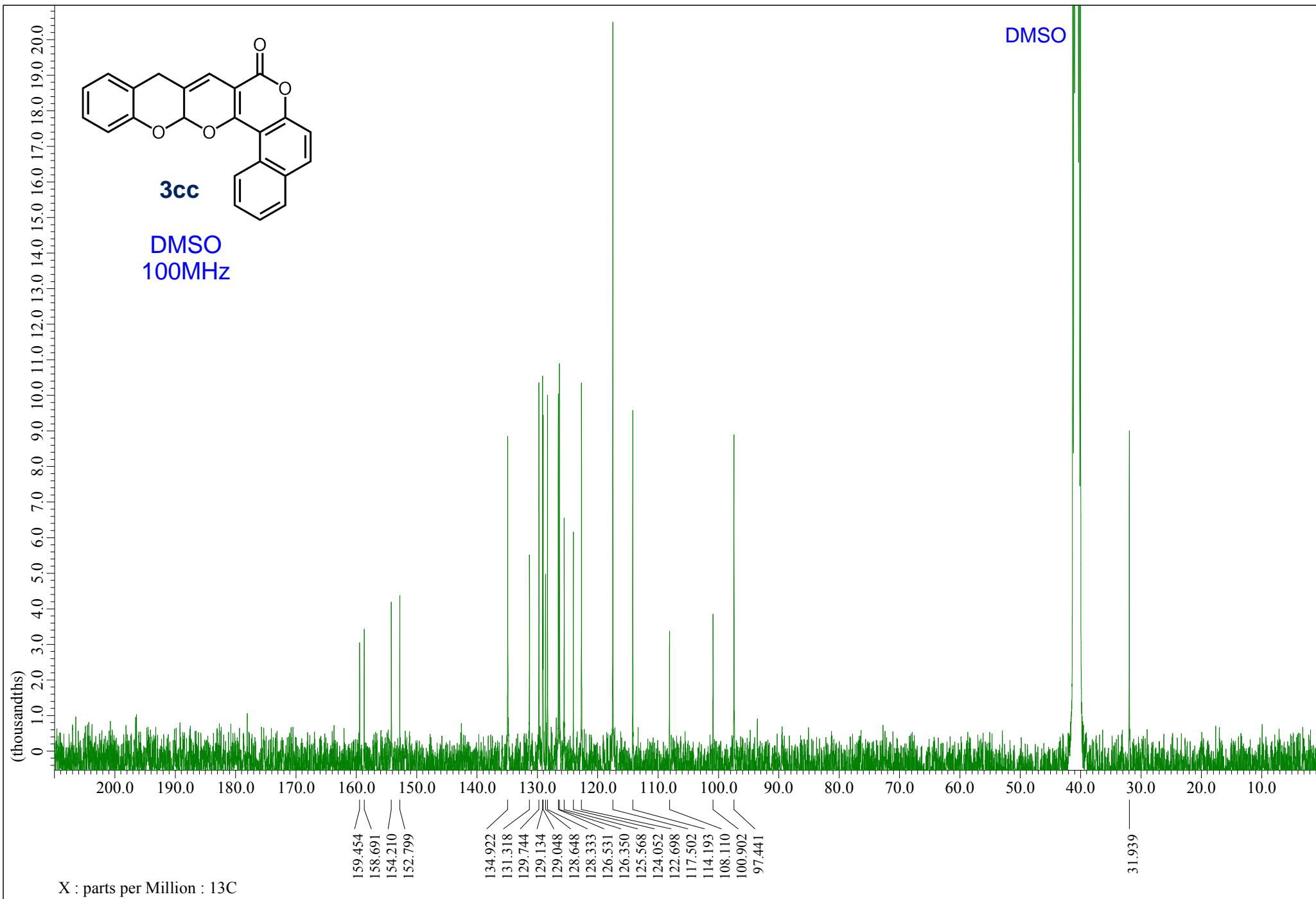


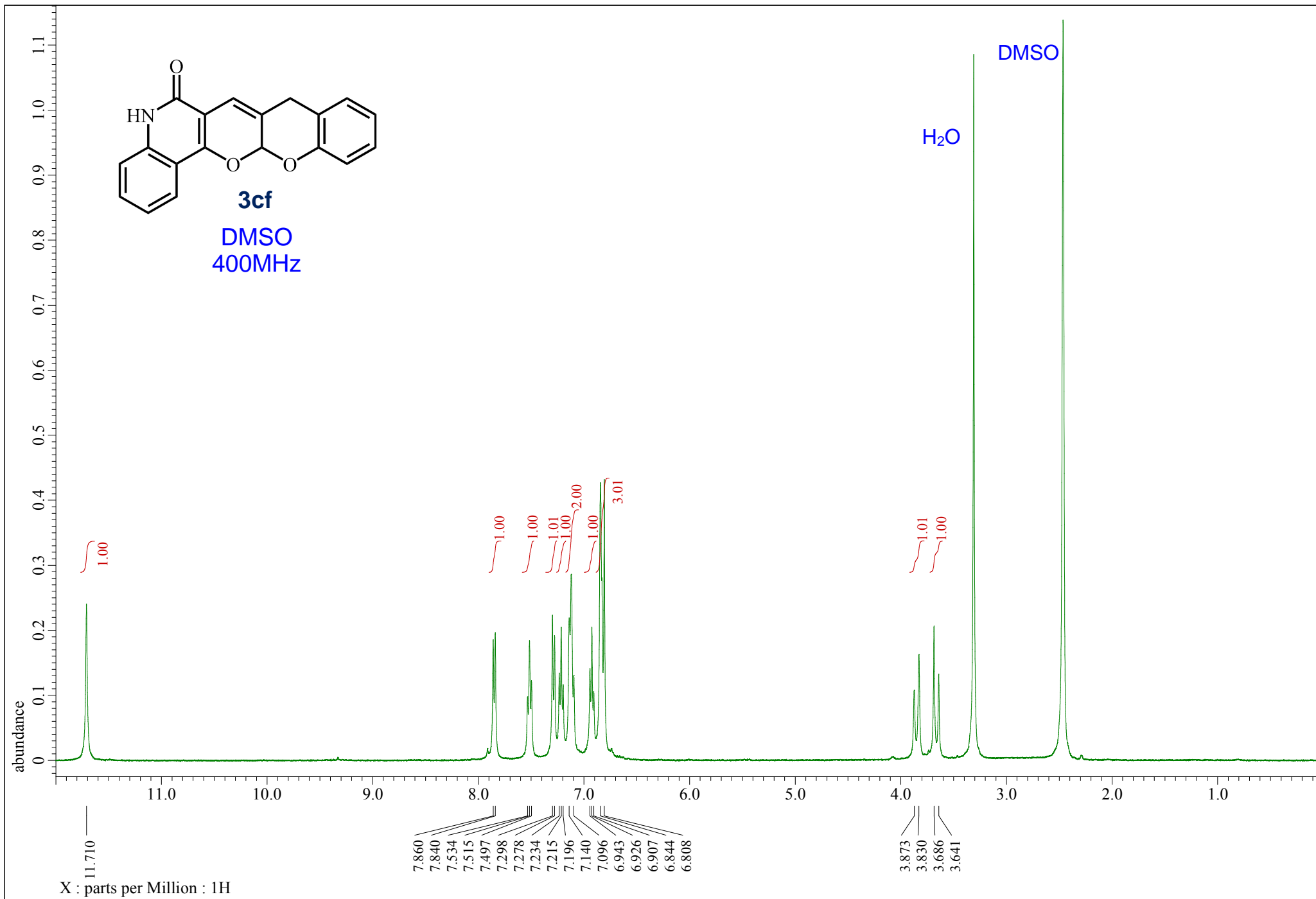


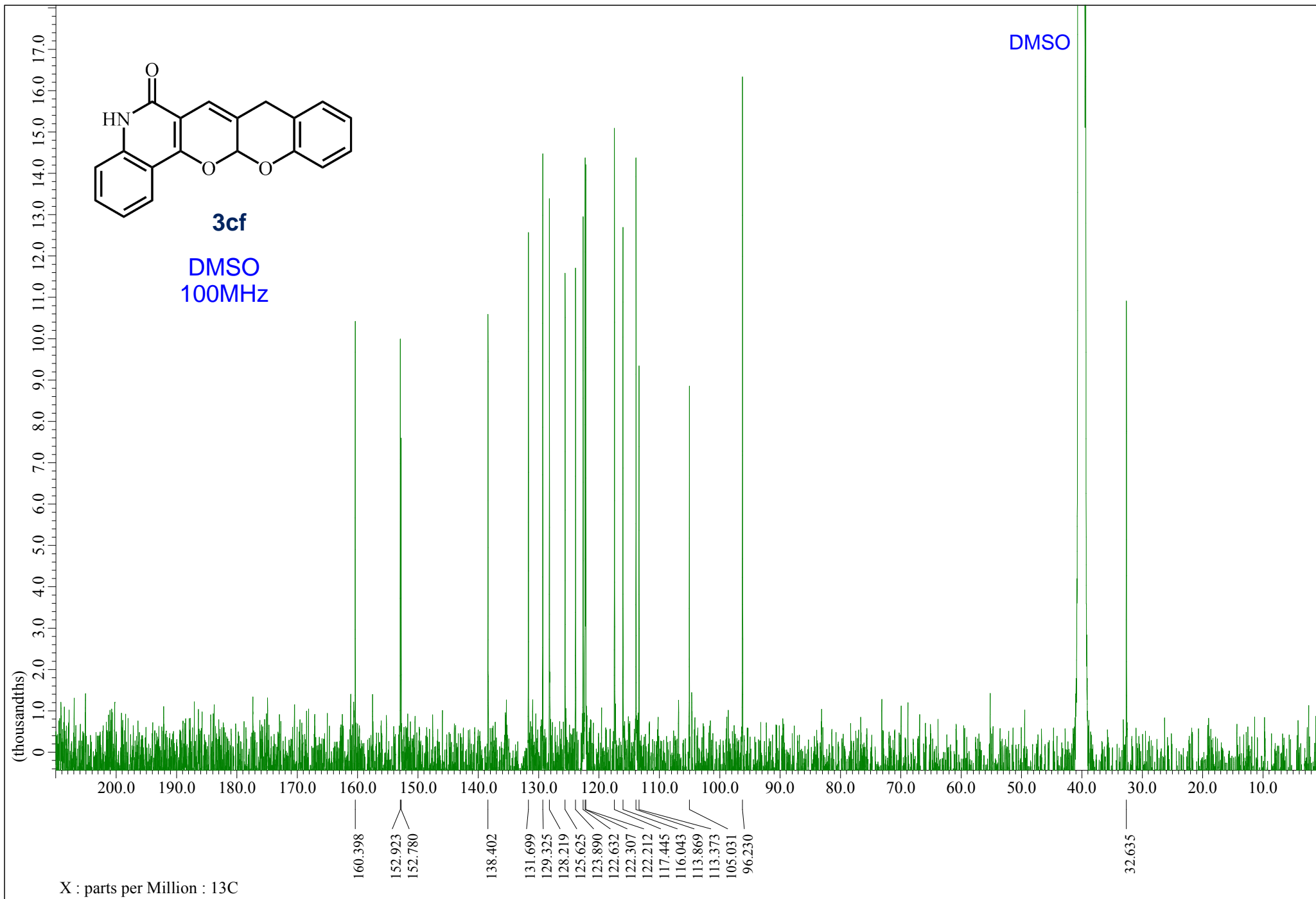
3cc

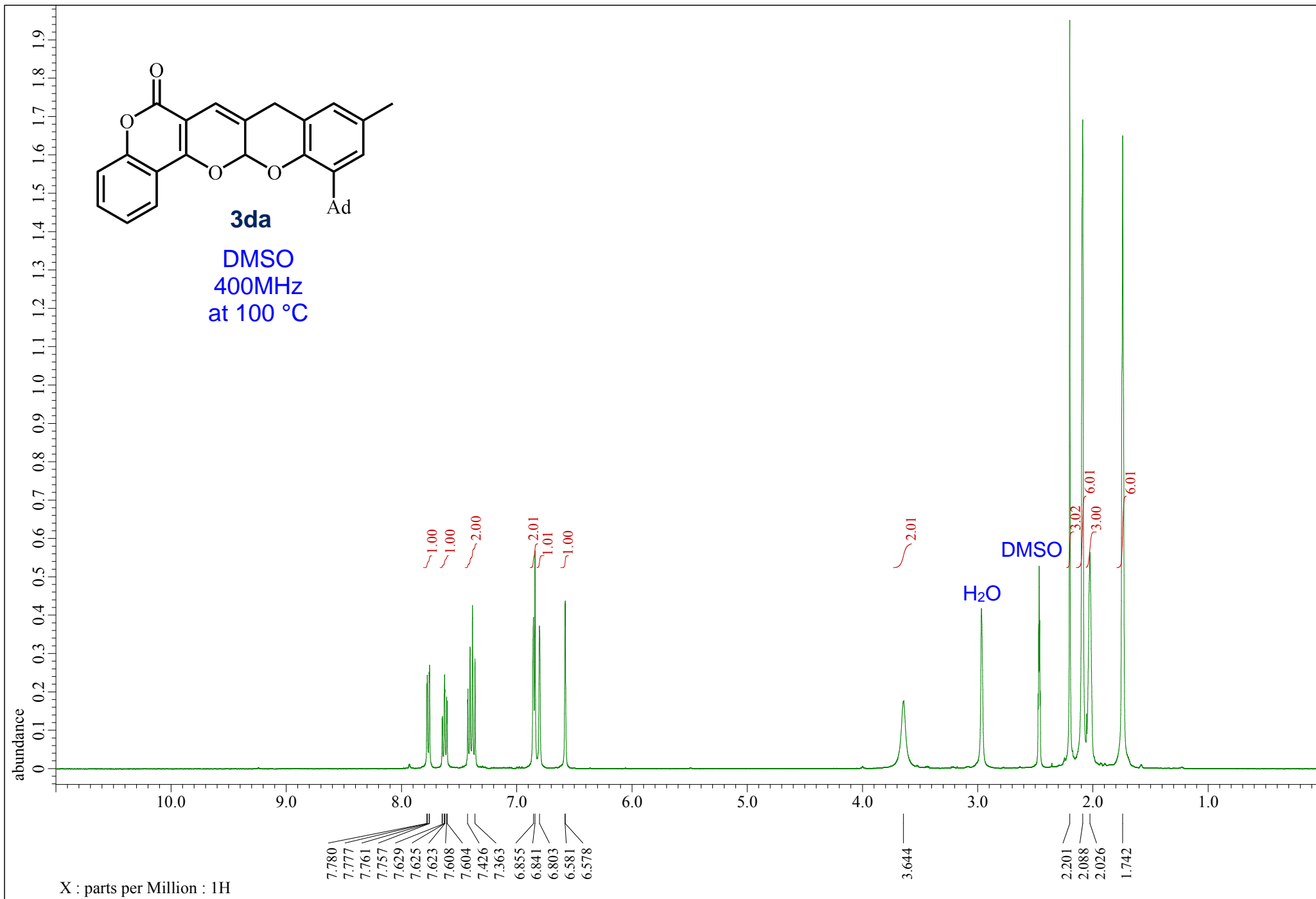
DMSO
400MHz

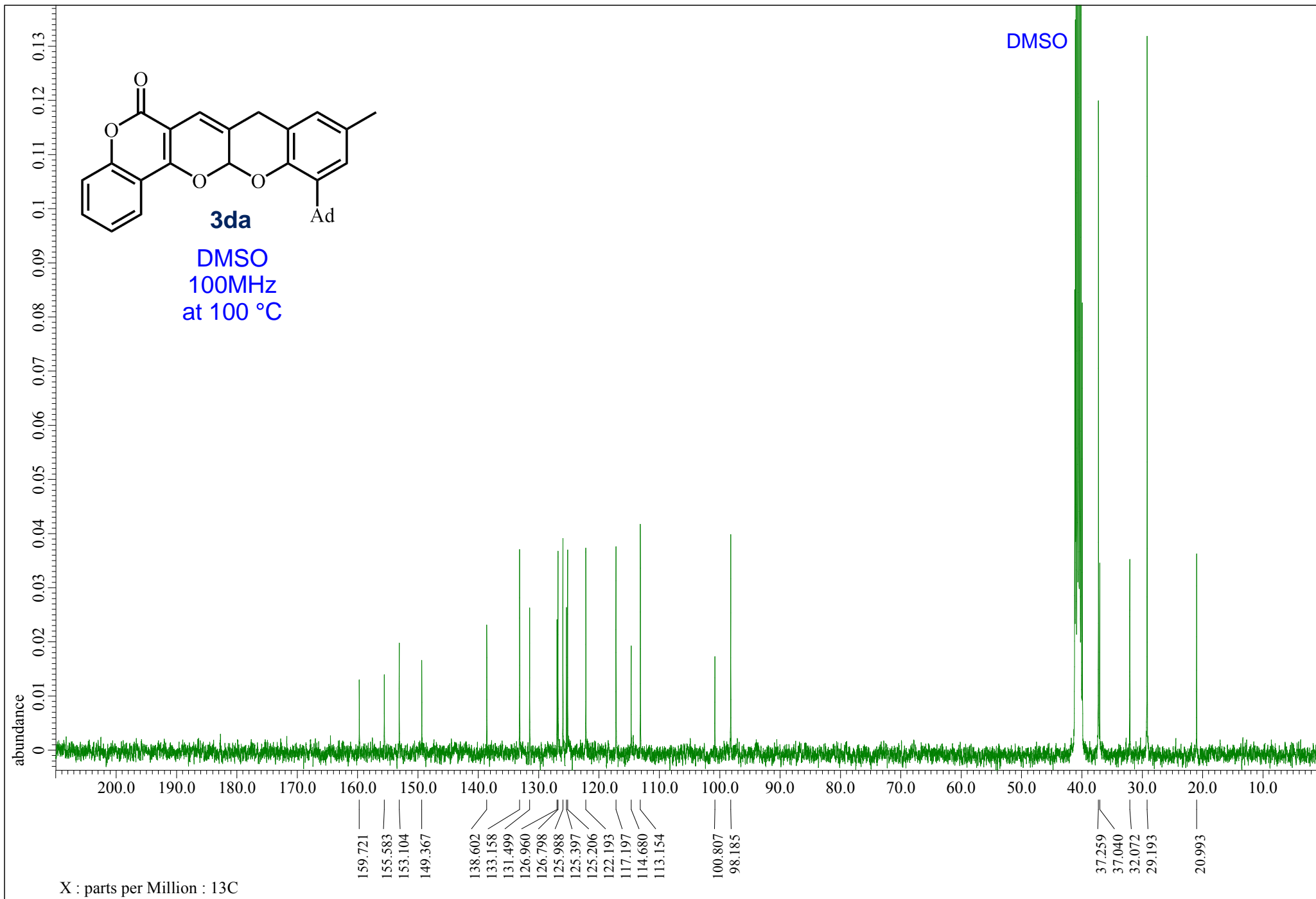


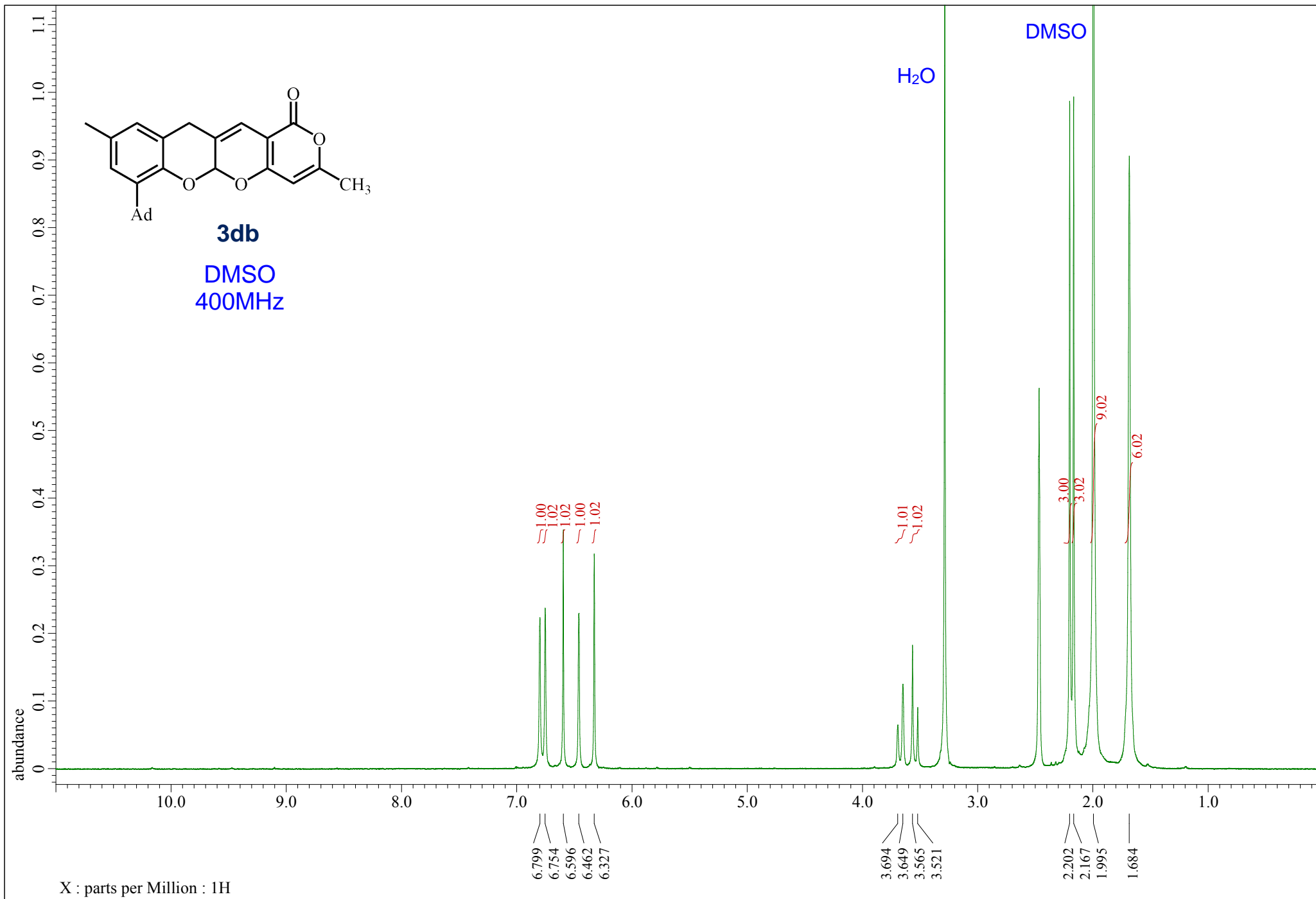


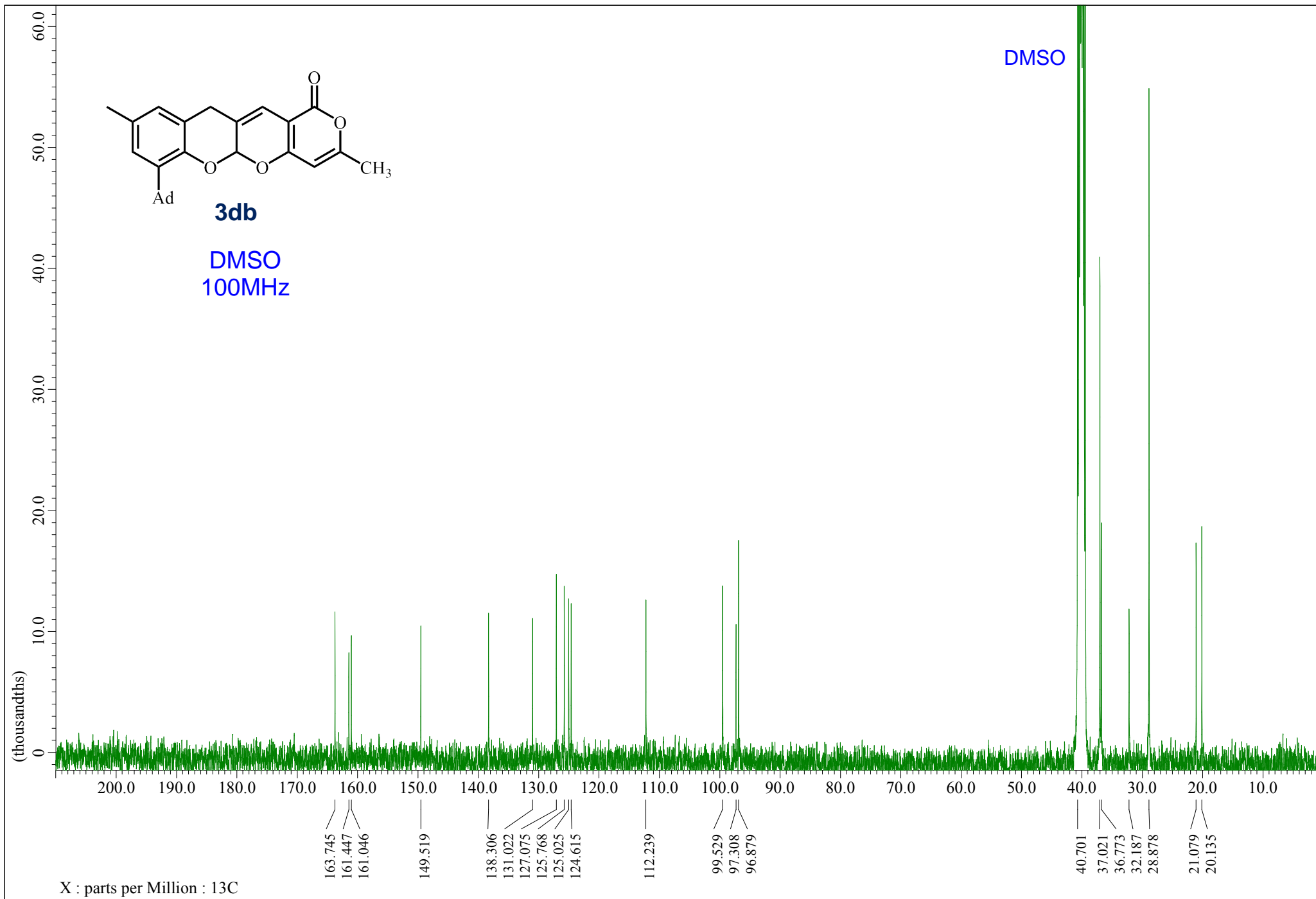


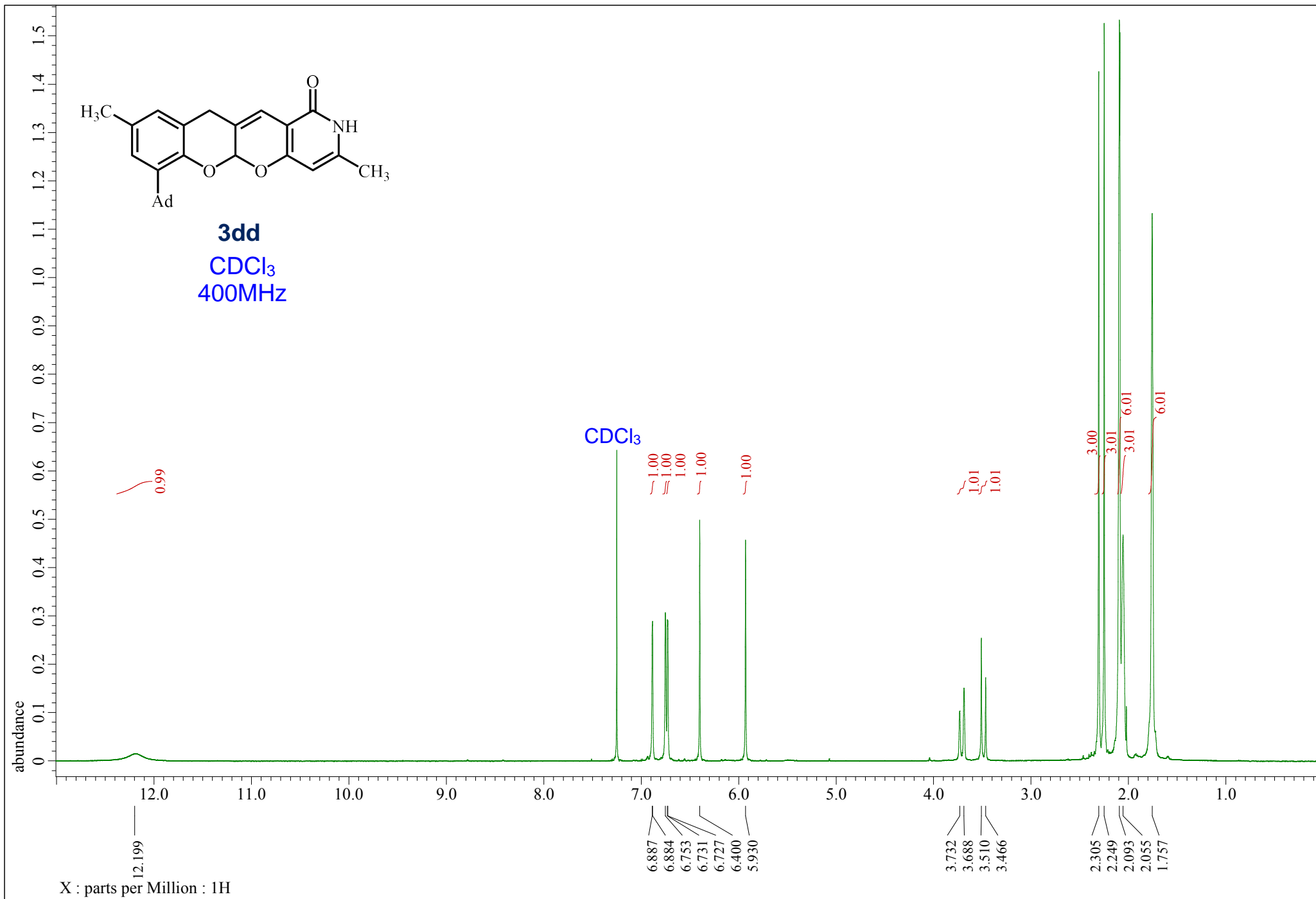


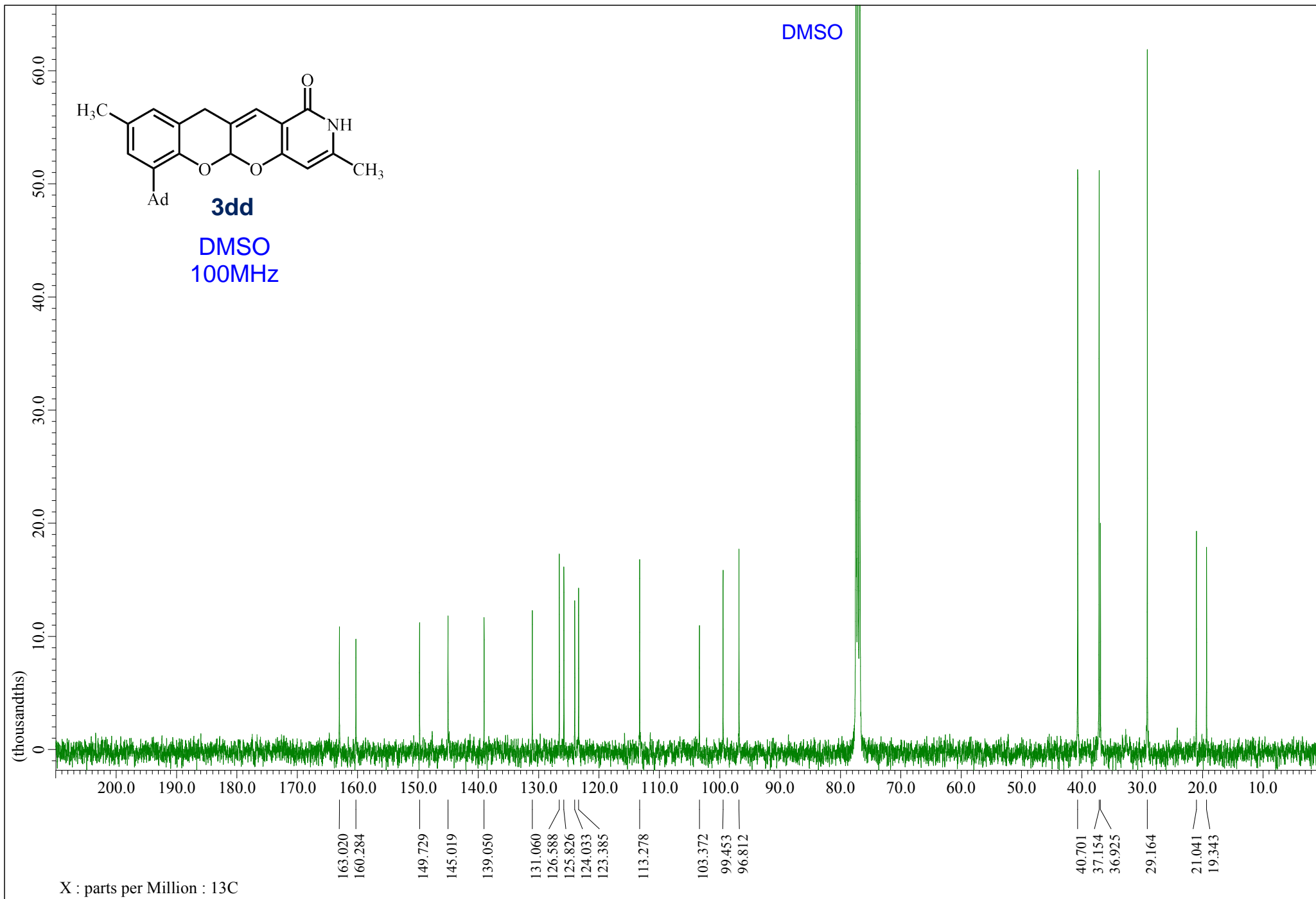


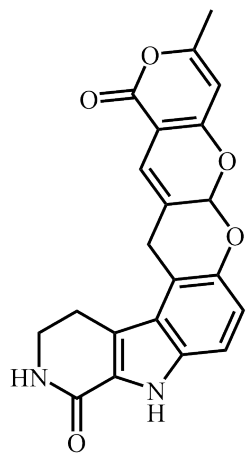






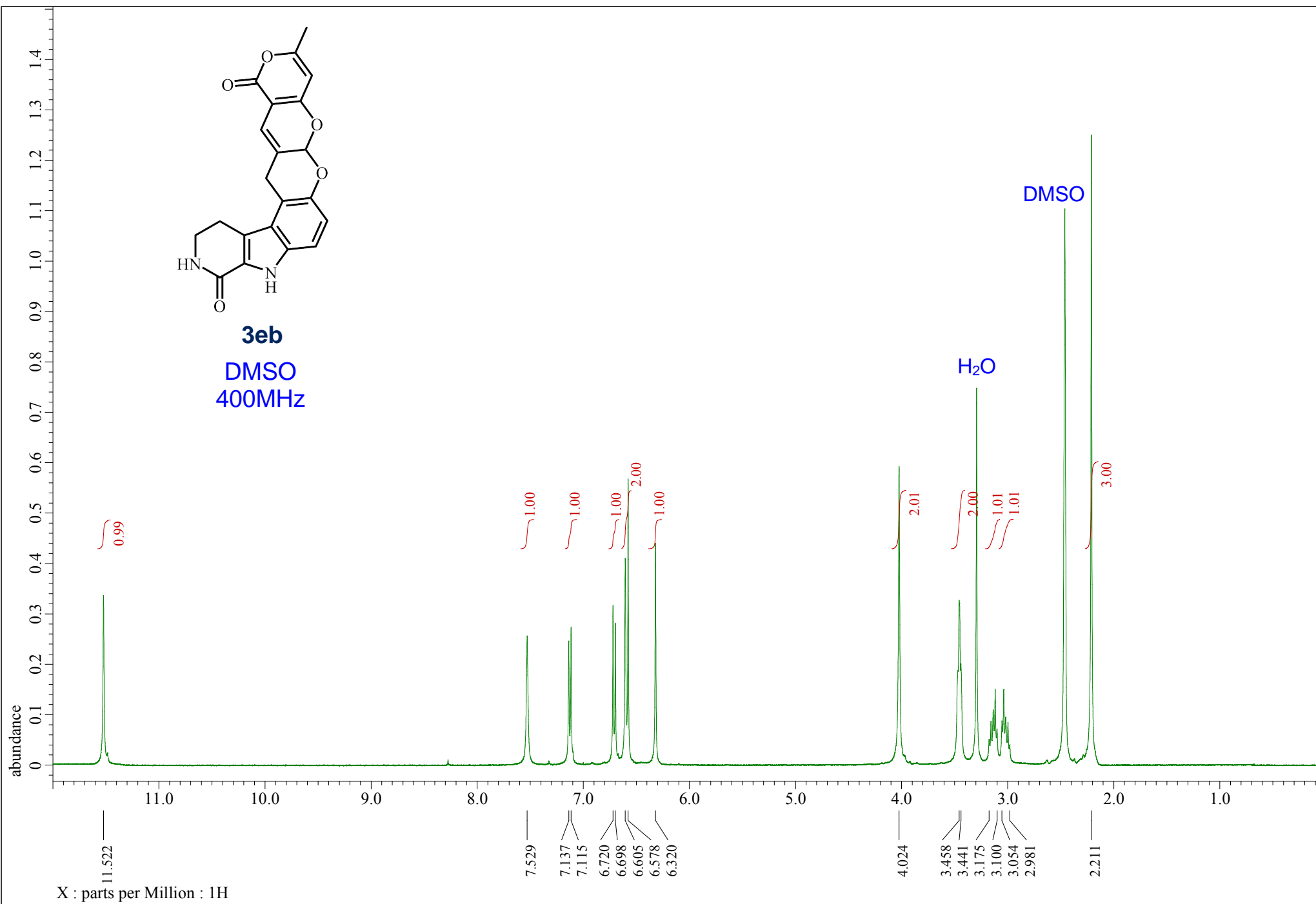


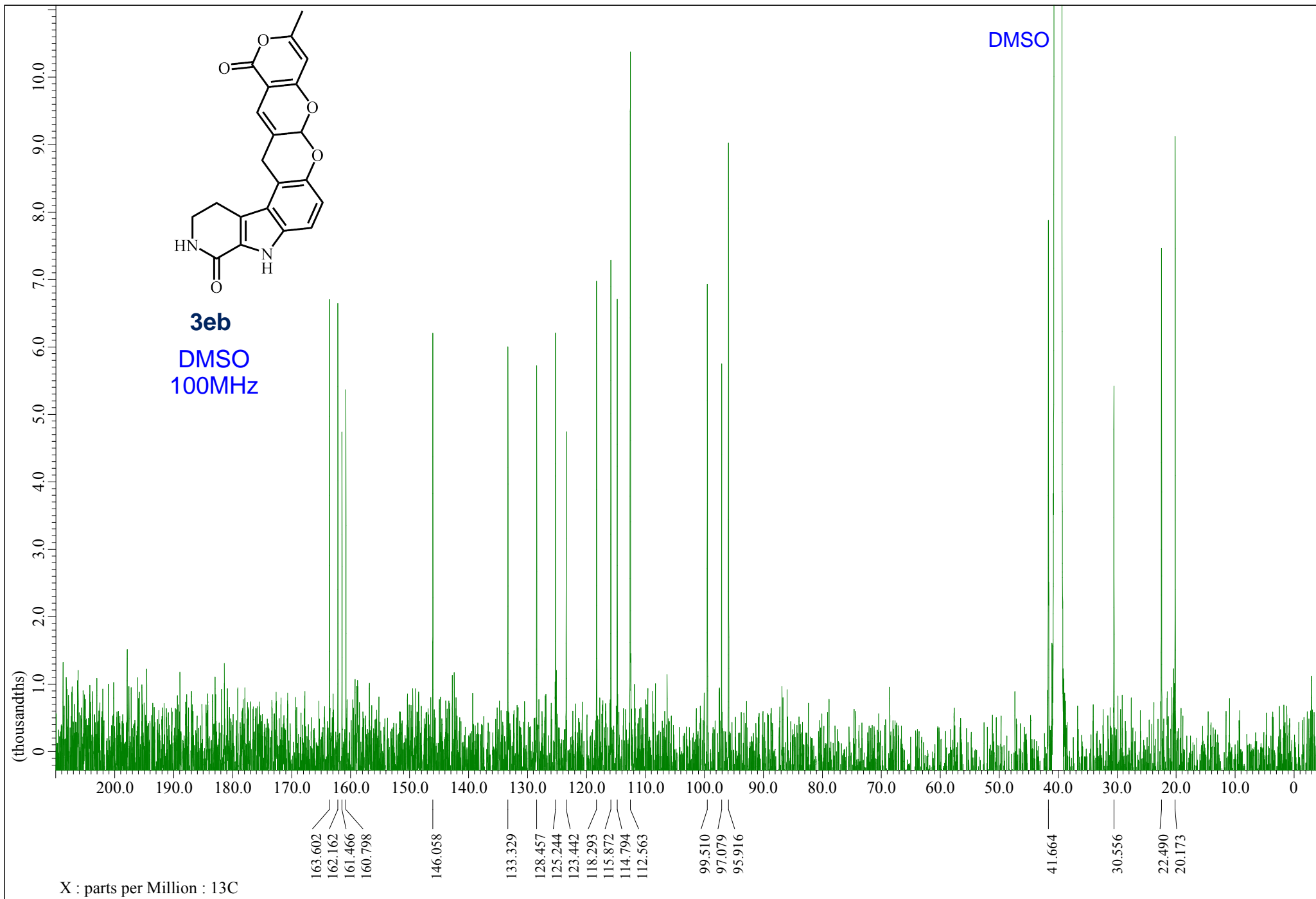


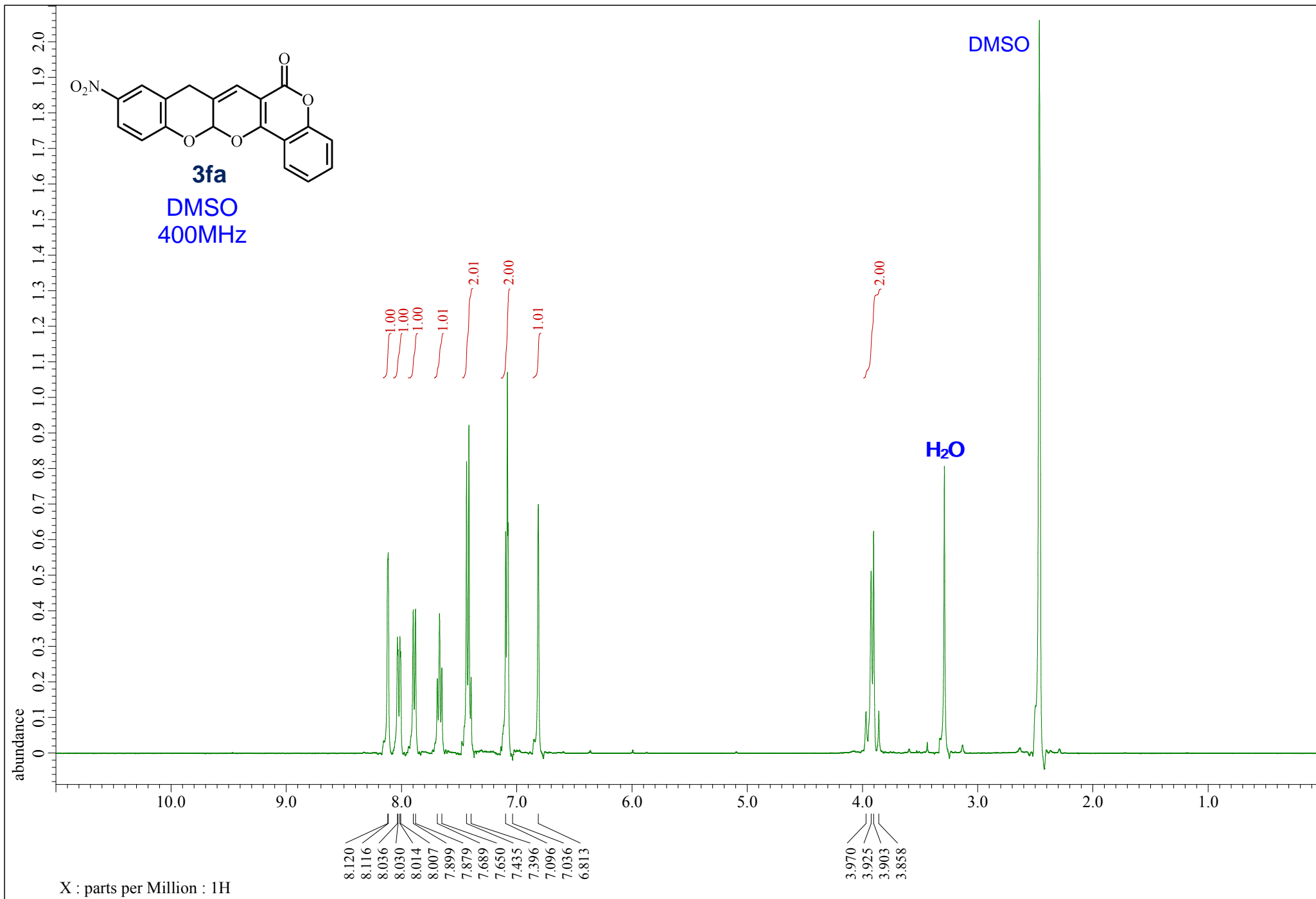


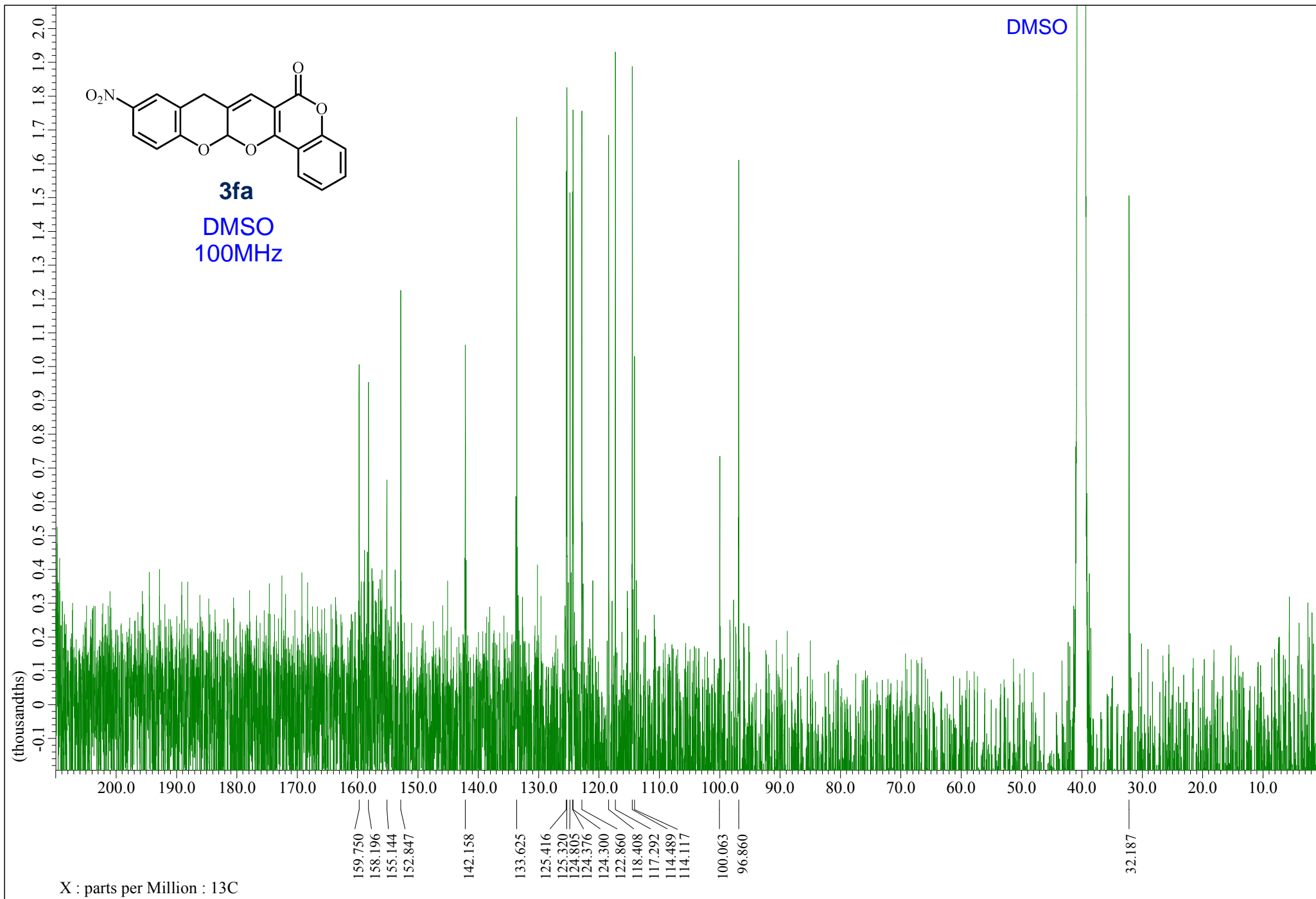
3eb

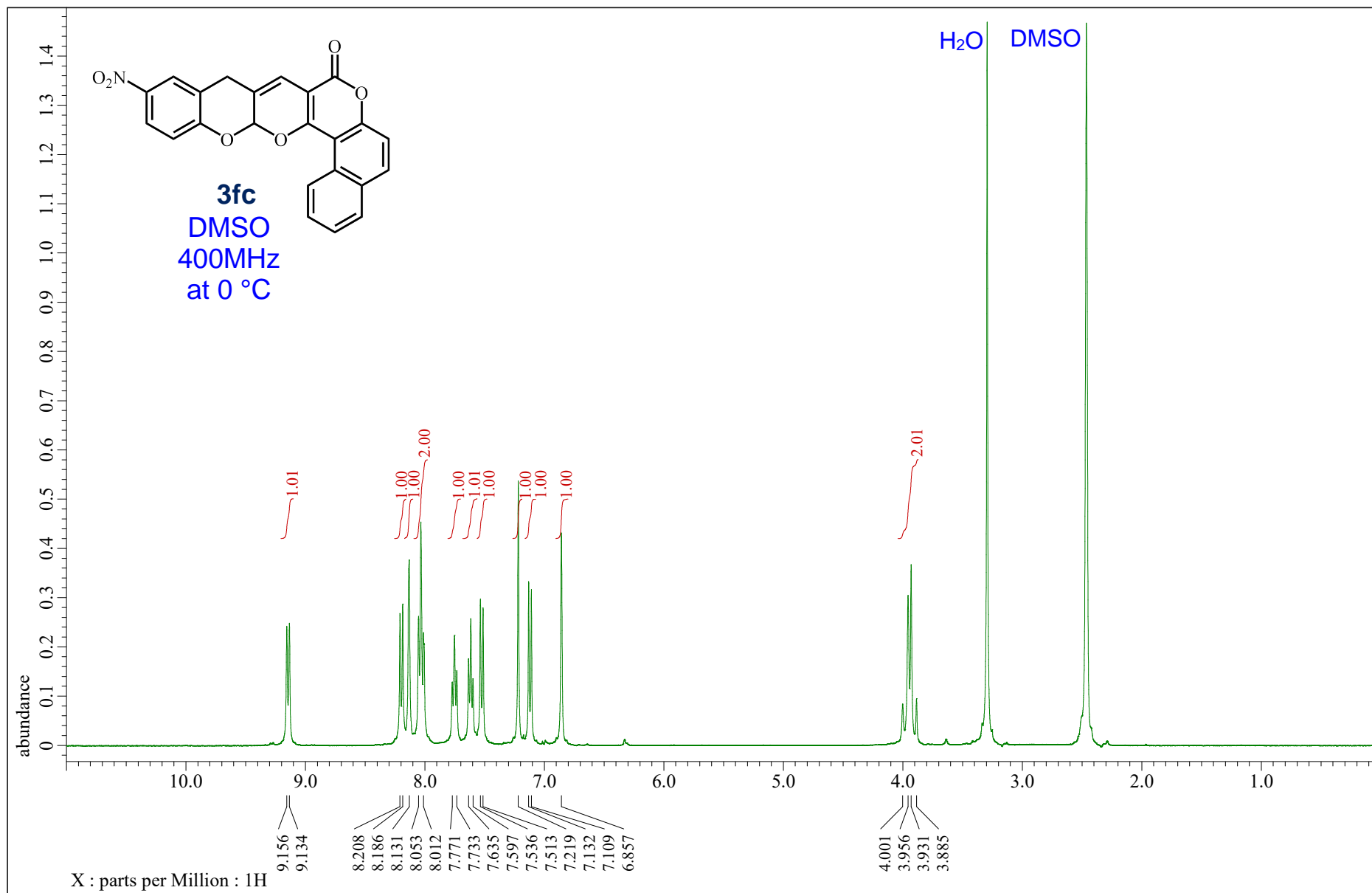
DMSO
400MHz

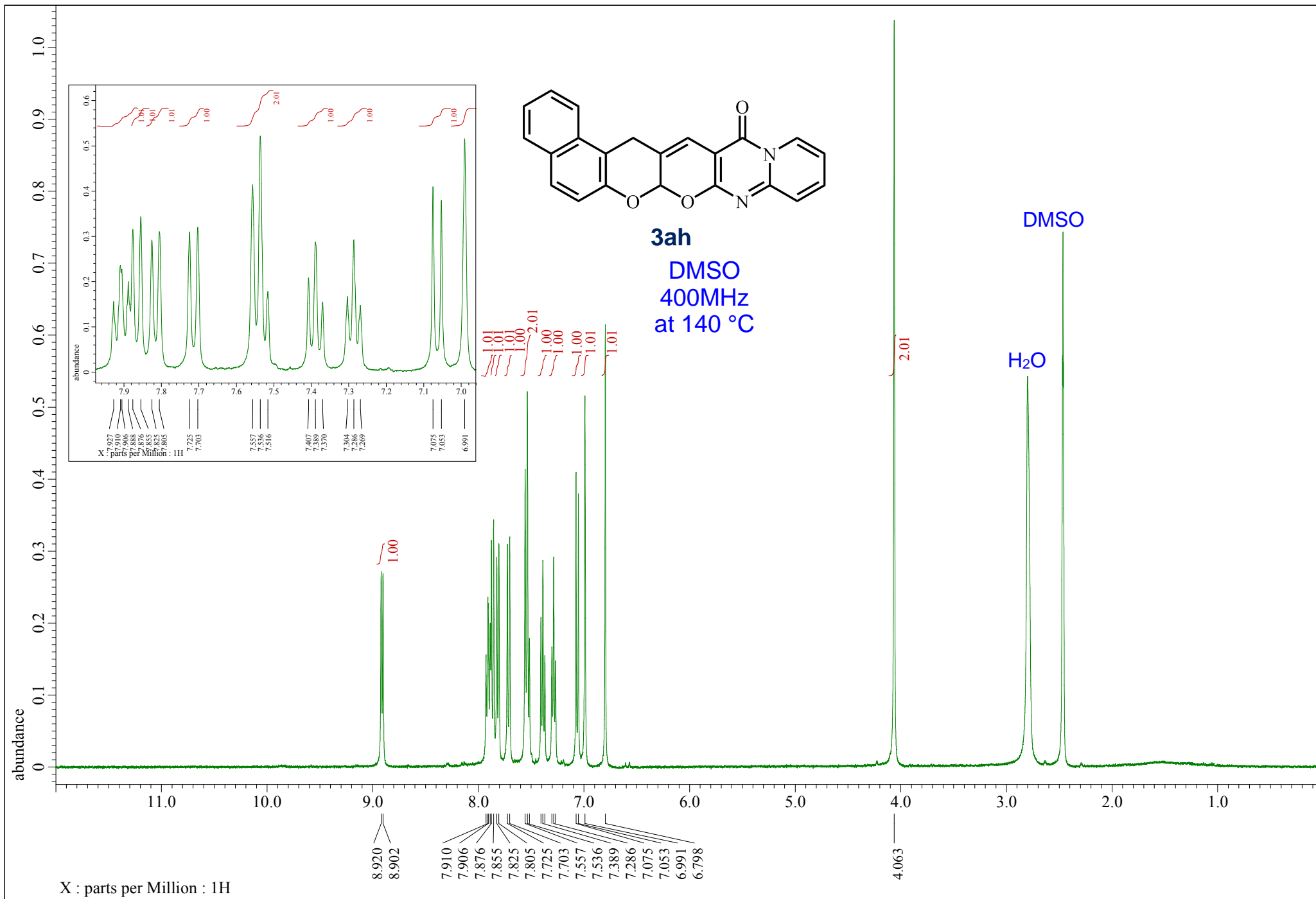


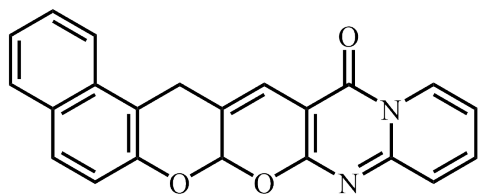












3ah

DMSO
100MHz
at 140 °C

