

Supplementary Information

Stereoselective Oxidation of Phenoxathiin-Based Thiacalix[4]arenes – Stereomutation of Sulfoxide groups

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1. Spectral characterization of compounds

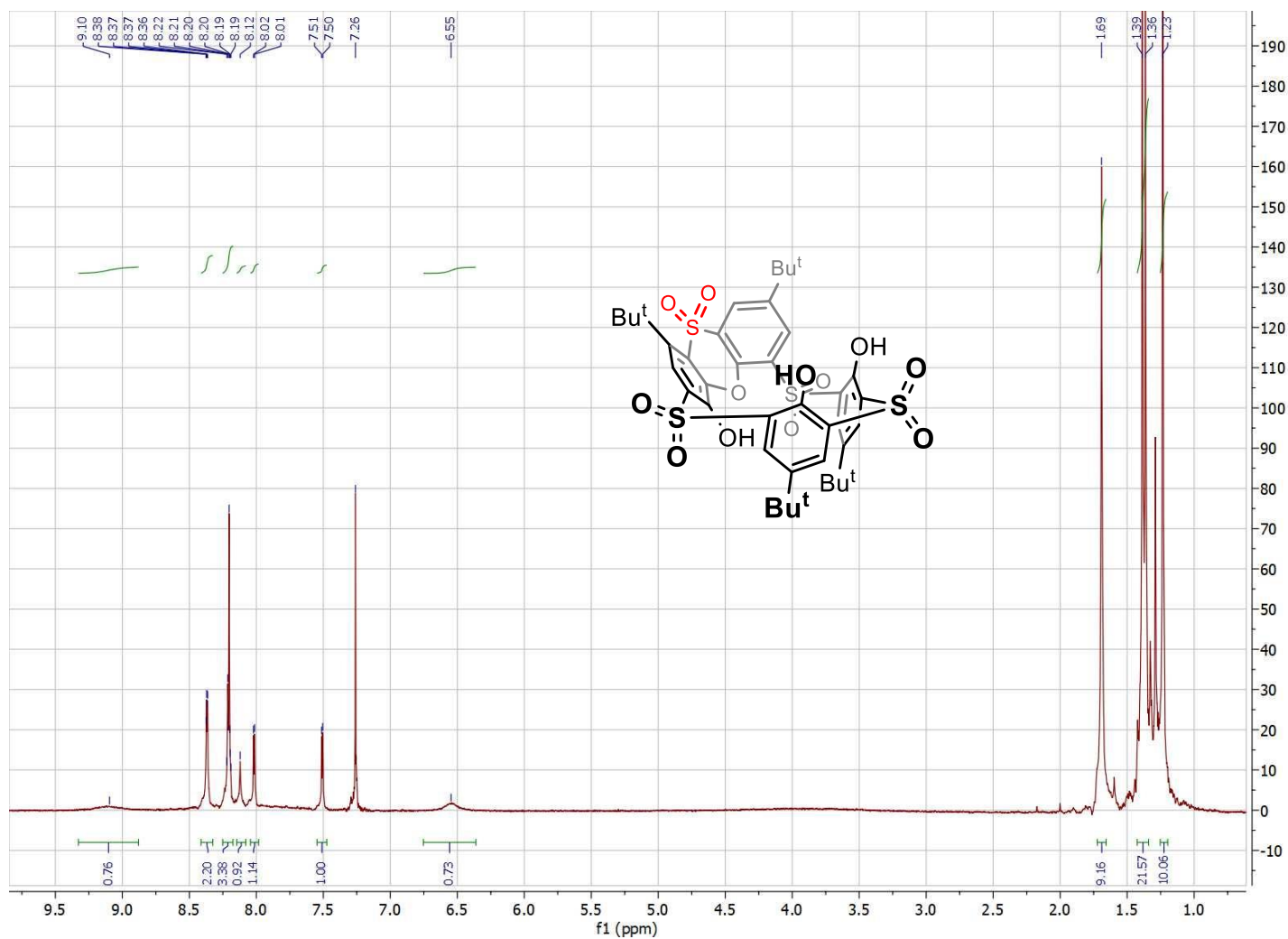


Figure 1: ¹H NMR (300 MHz, CDCl₃, 298 K) spectrum of compound 4

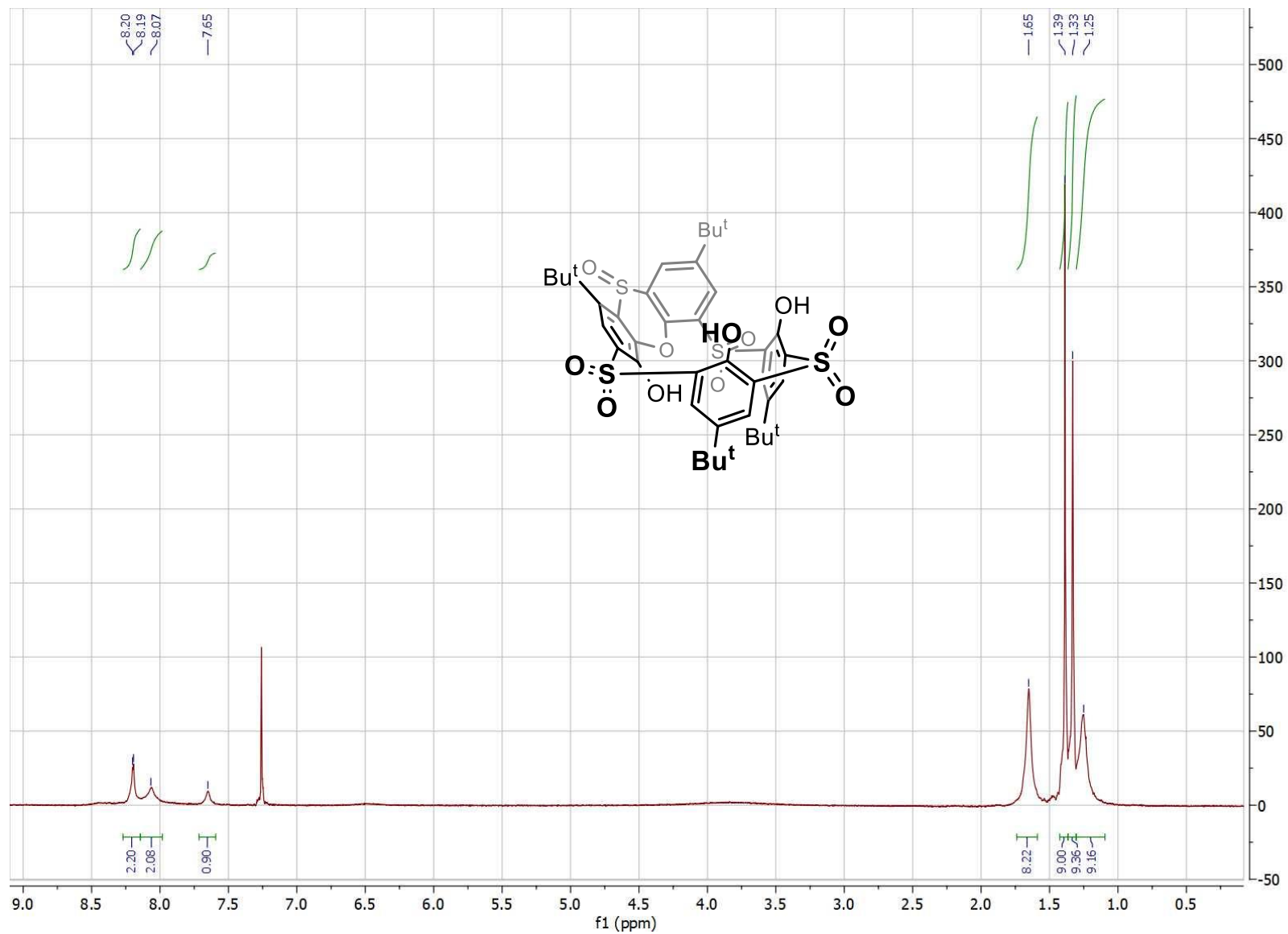


Figure 2: ¹H NMR (300 MHz, CDCl₃, 298 K) spectrum of compound 8

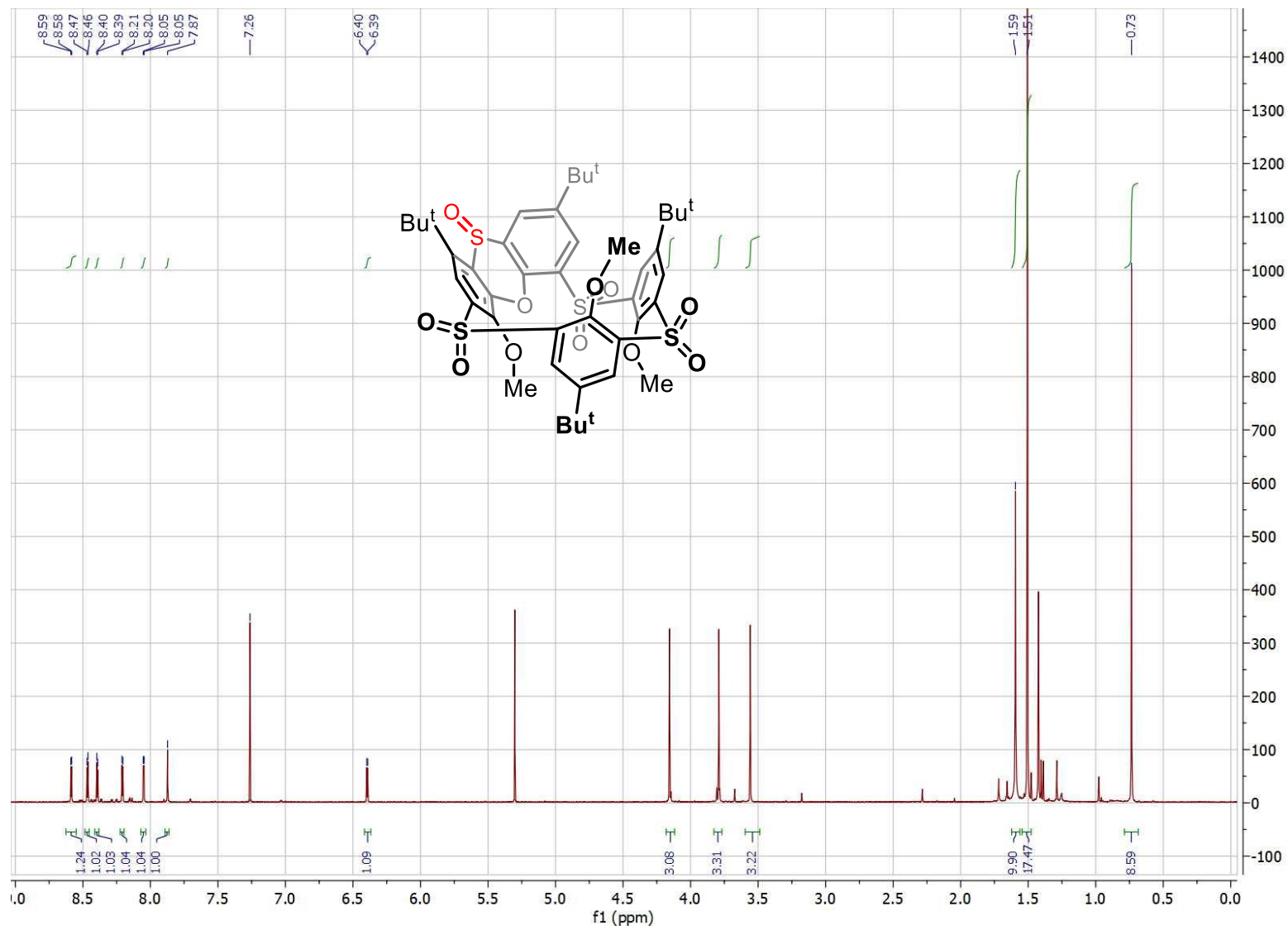


Figure 3: ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **9a**

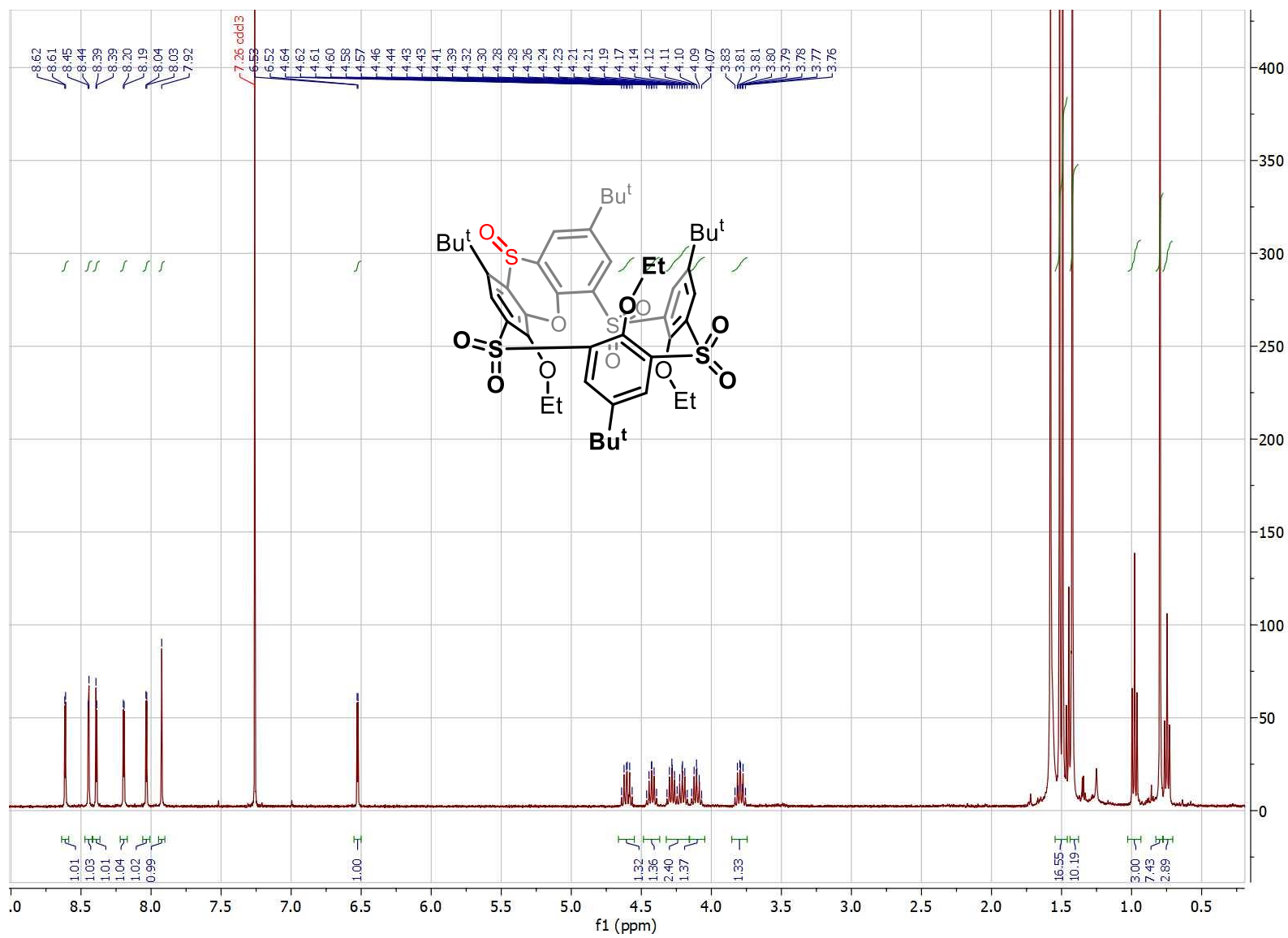


Figure 4: ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of compound **9b**

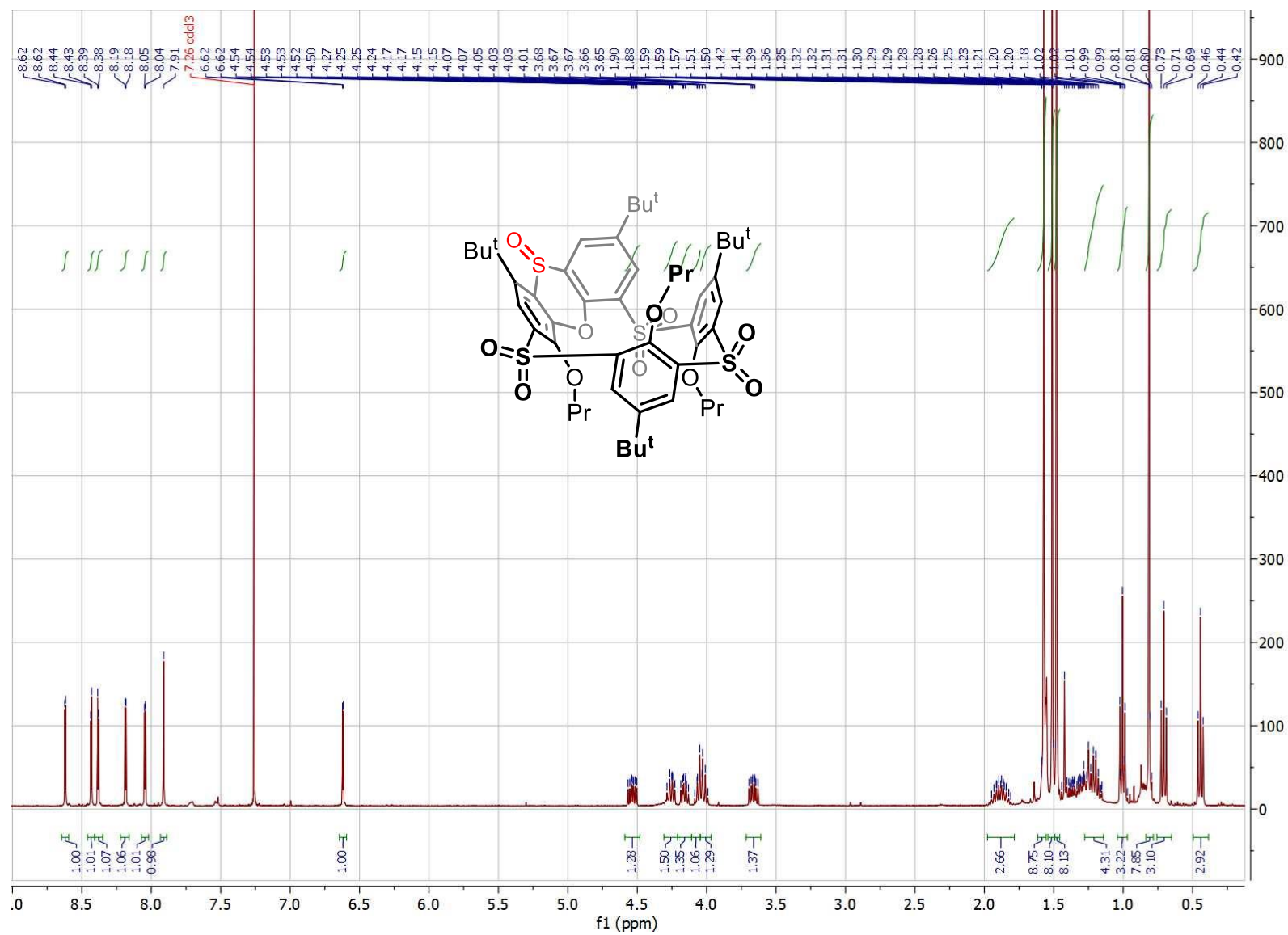


Figure 5: ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **9c**

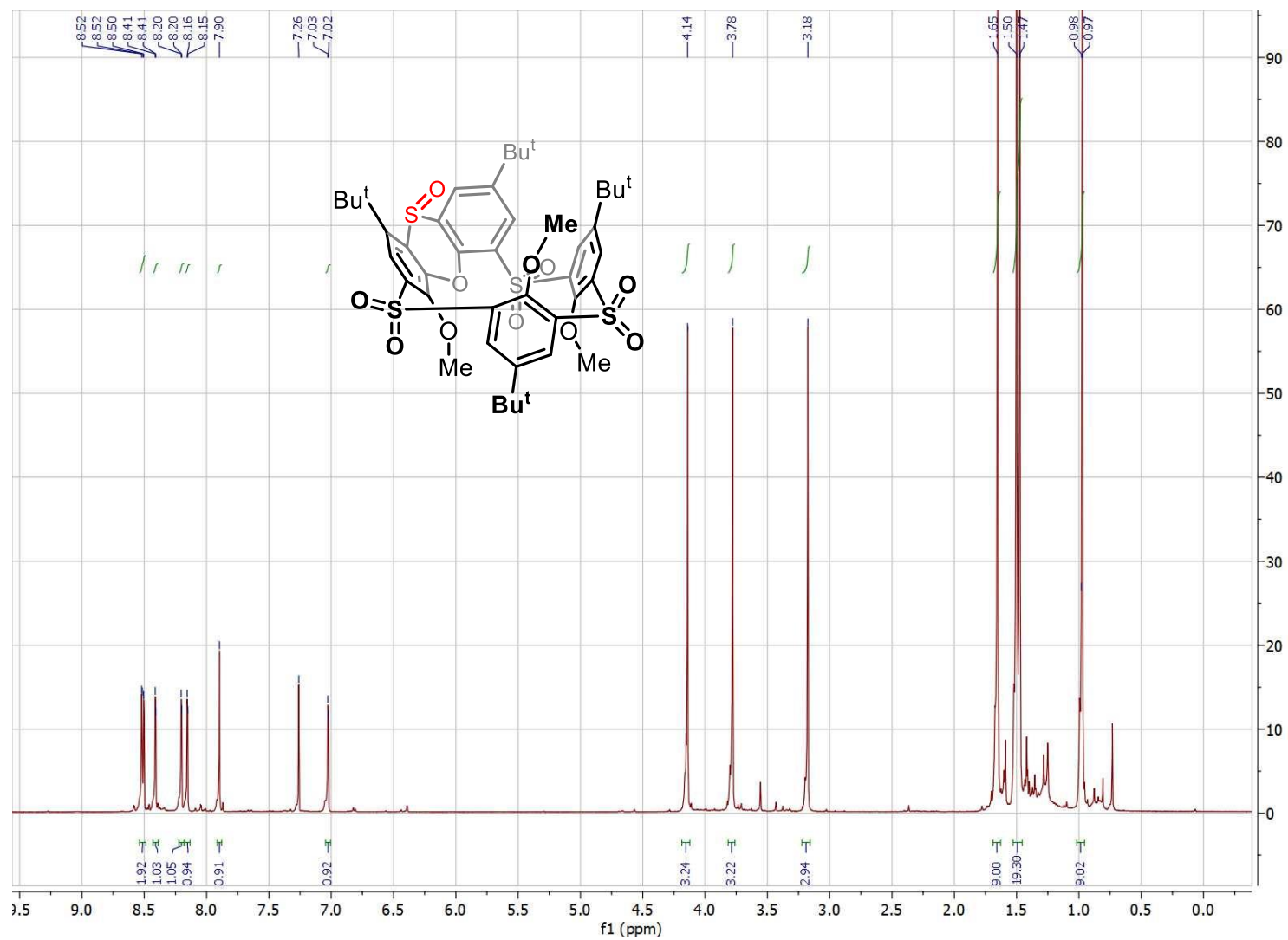


Figure 6: ^1H NMR (500 MHz, CDCl_3 , 298 K) spectrum of compound **10a**

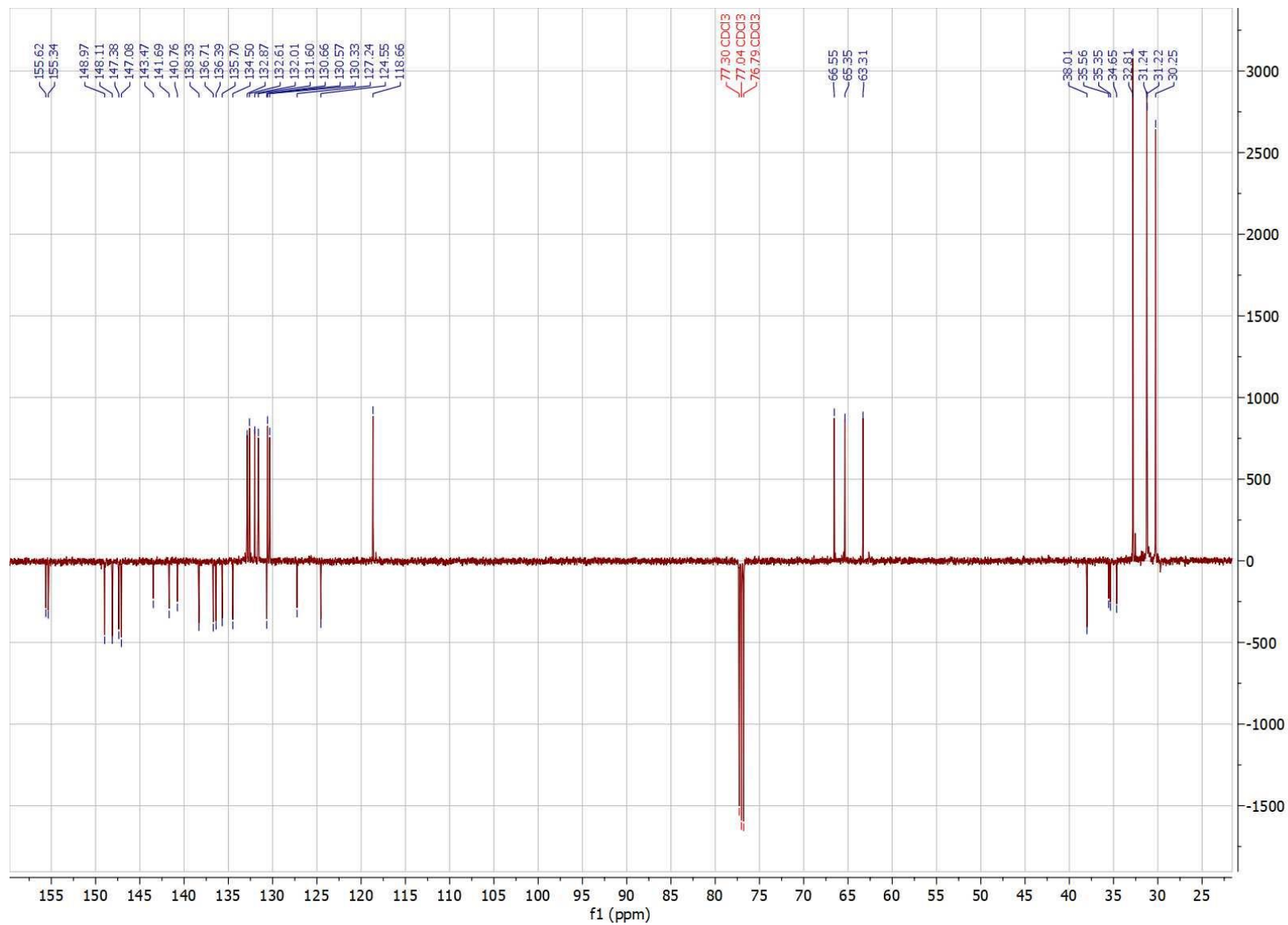


Figure 7: ^{13}C NMR (APT, 126 MHz, CDCl_3 , 298 K) spectrum of compound **10a**

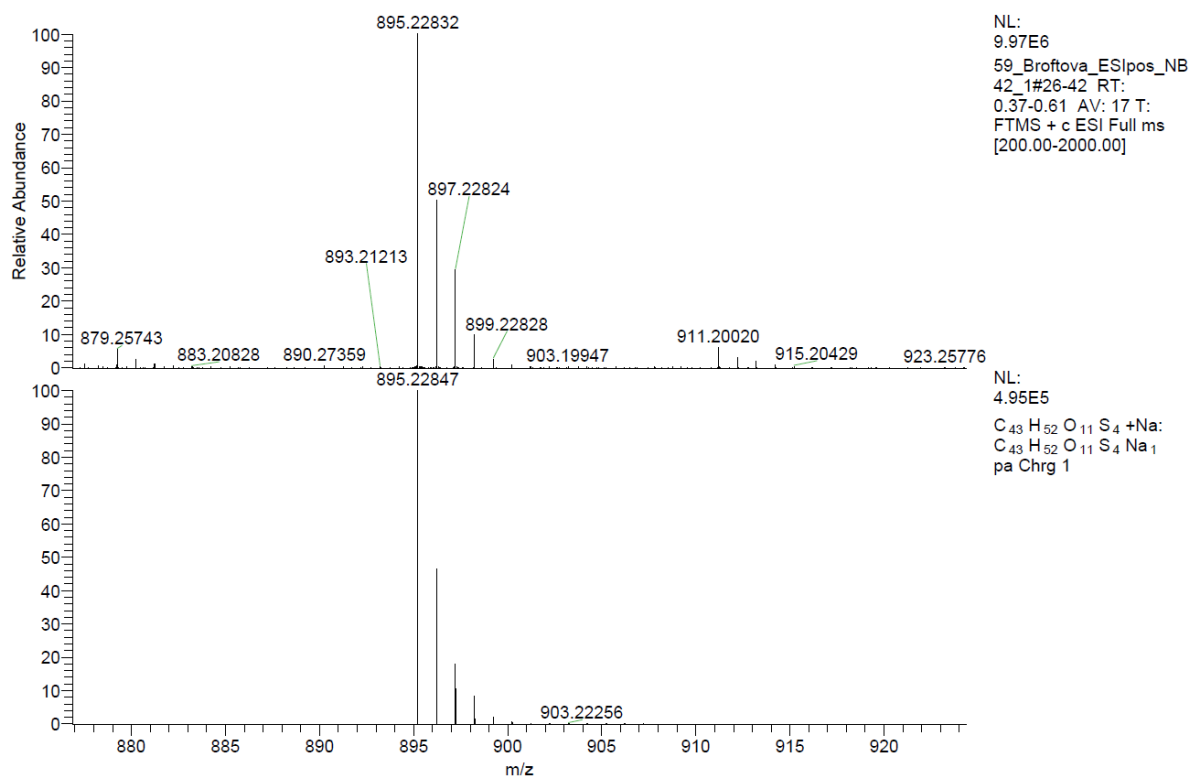


Figure 8: HRMS ESI+ spectrum of compound 10a

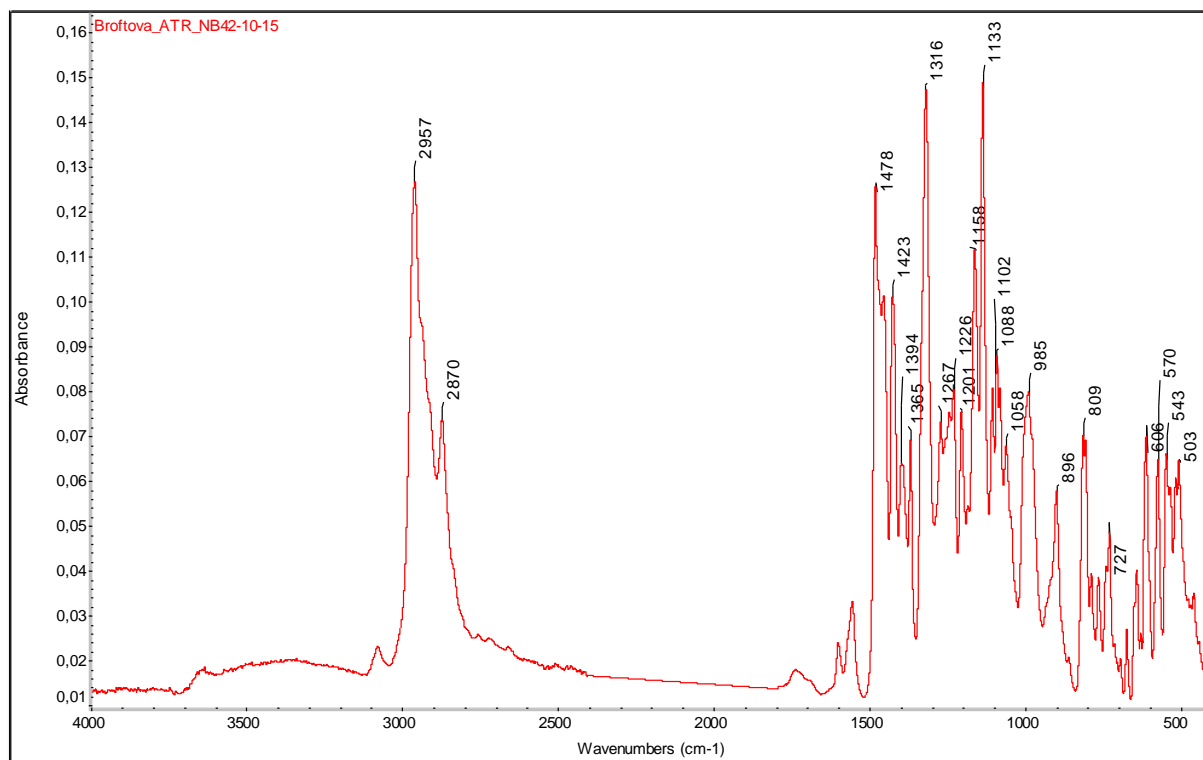


Figure 9: IR spectrum of compound 10a

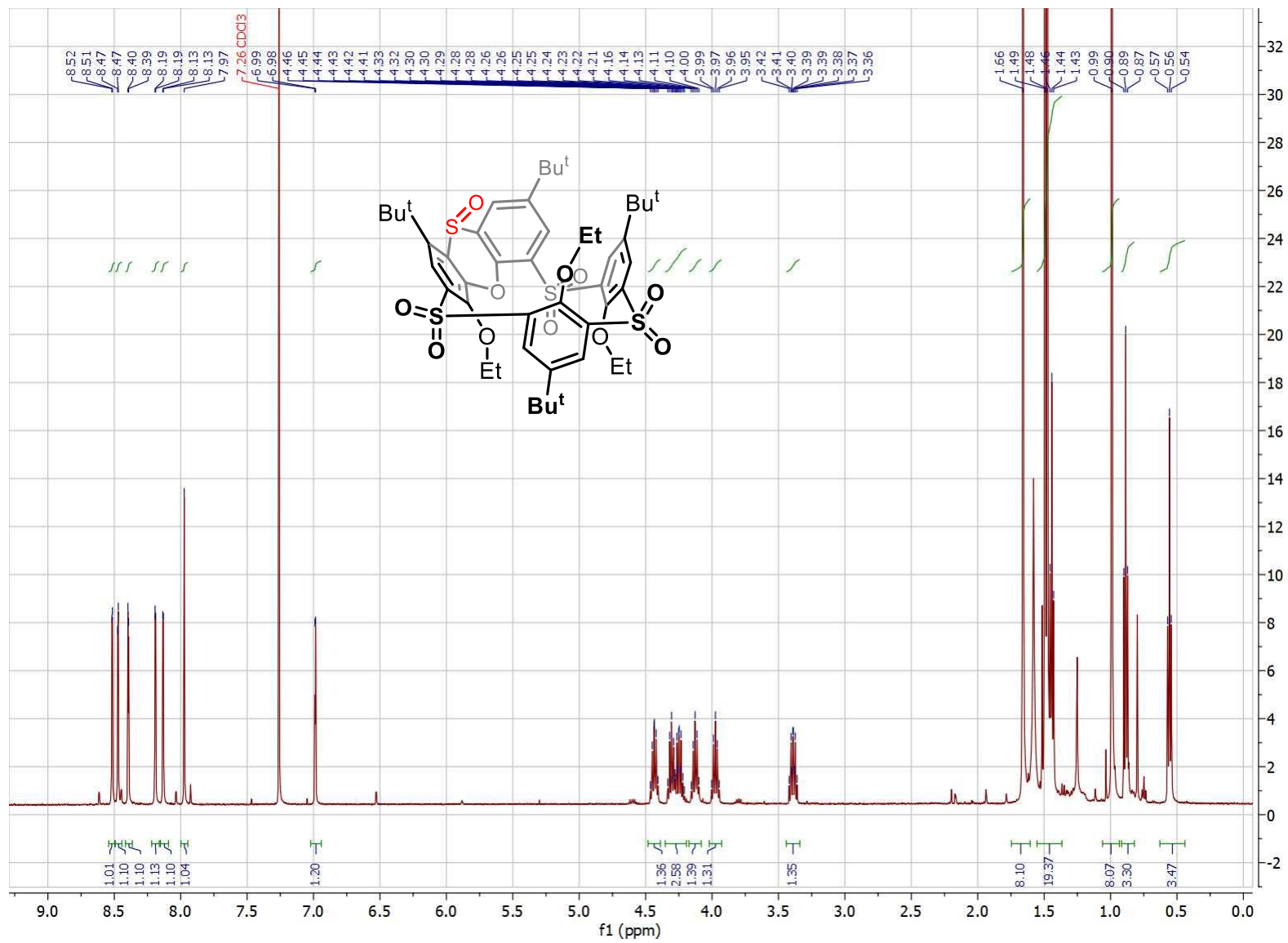


Figure 10: ¹H NMR (500 MHz, CDCl₃, 298 K) spectrum of compound **10b**

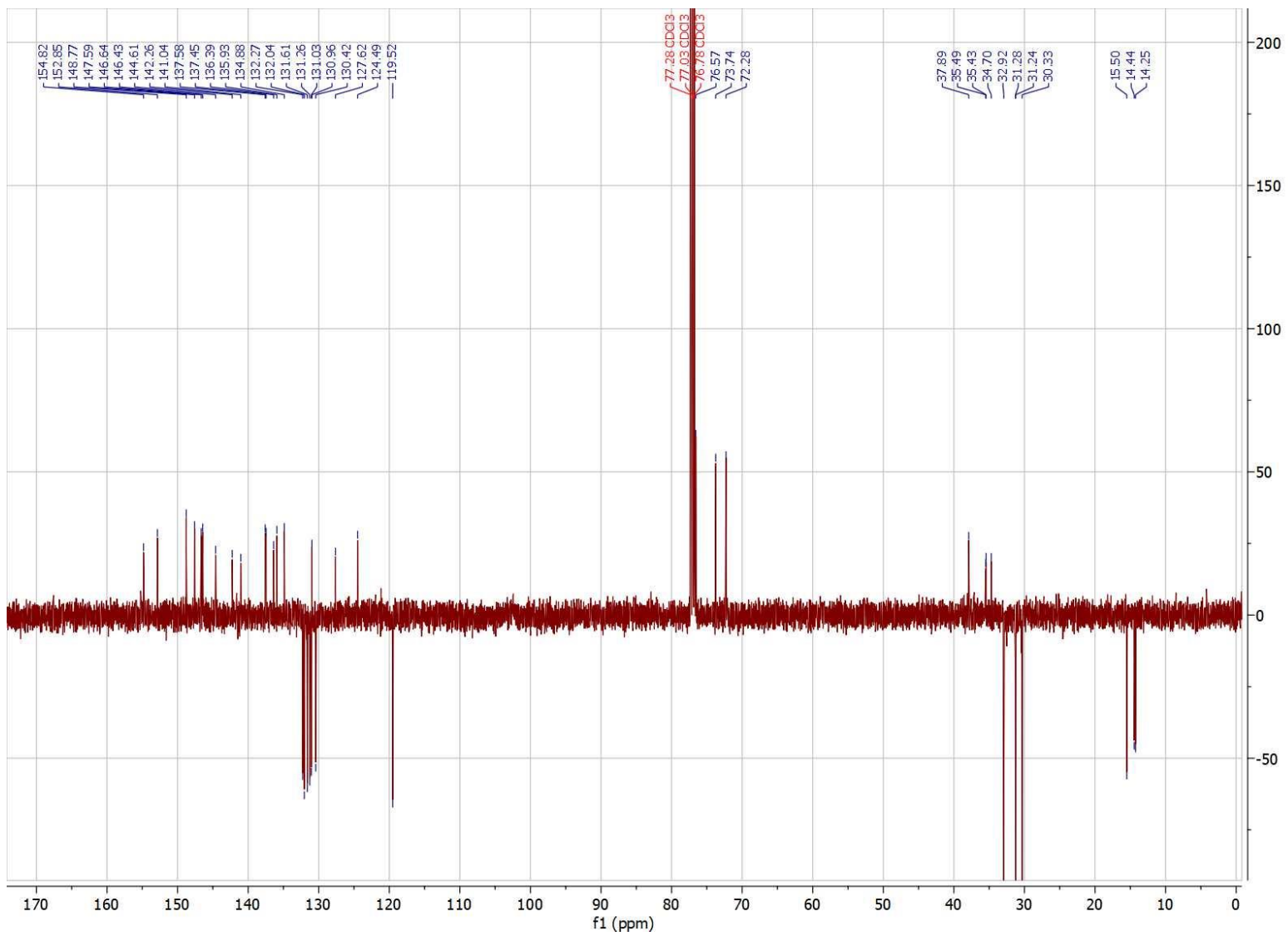


Figure 11: ^{13}C NMR (APT, 126 MHz, CDCl_3 , 298 K) spectrum of compound **10b**

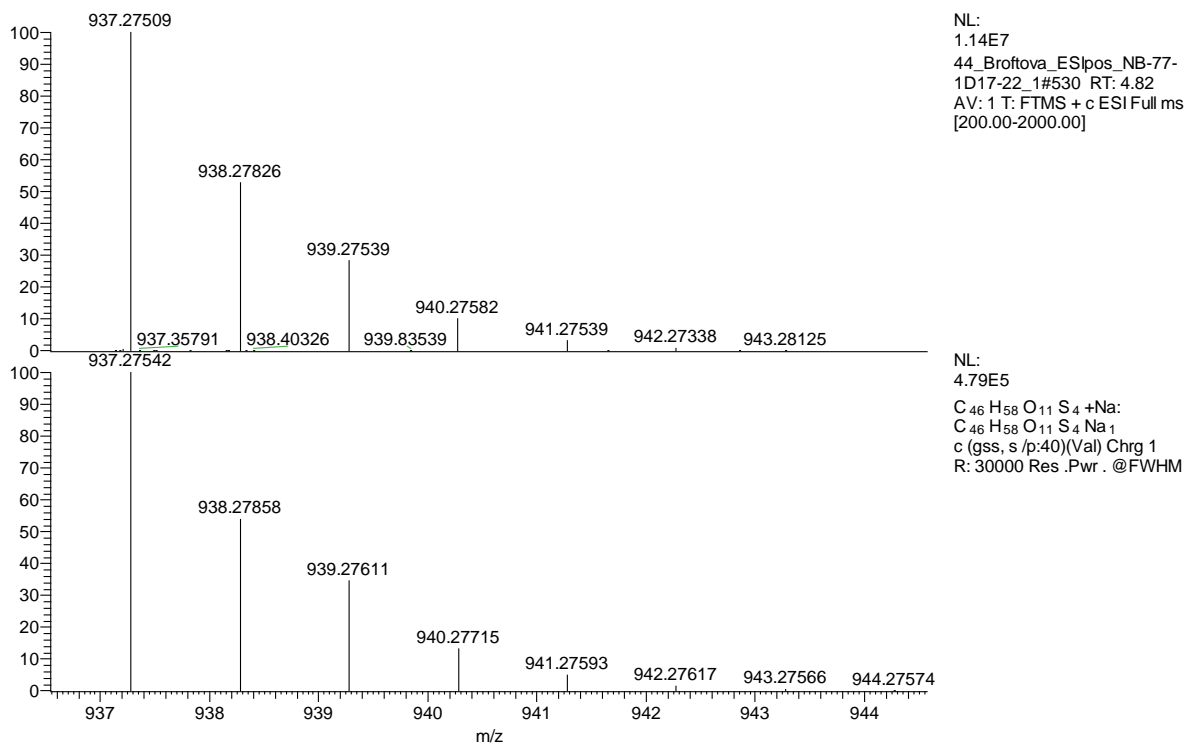


Figure 12: HRMS ESI+ spectrum of compound 10b

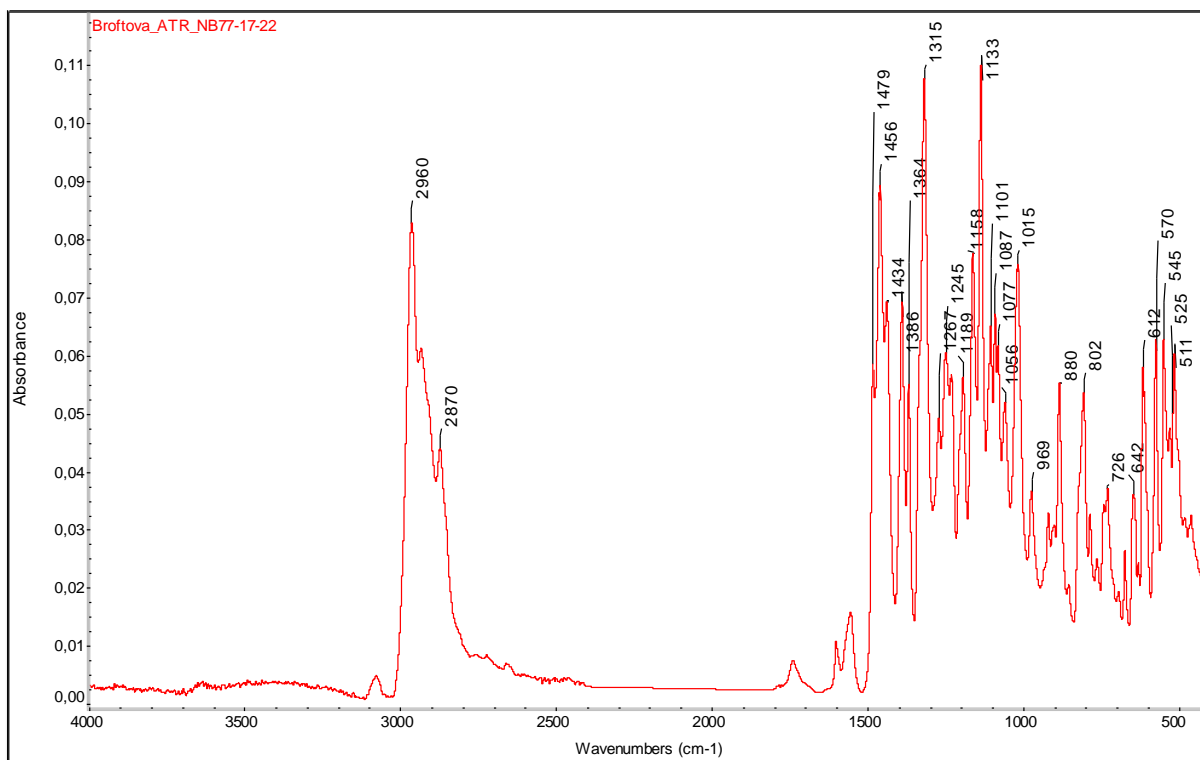


Figure 13: IR spectrum of compound 10b

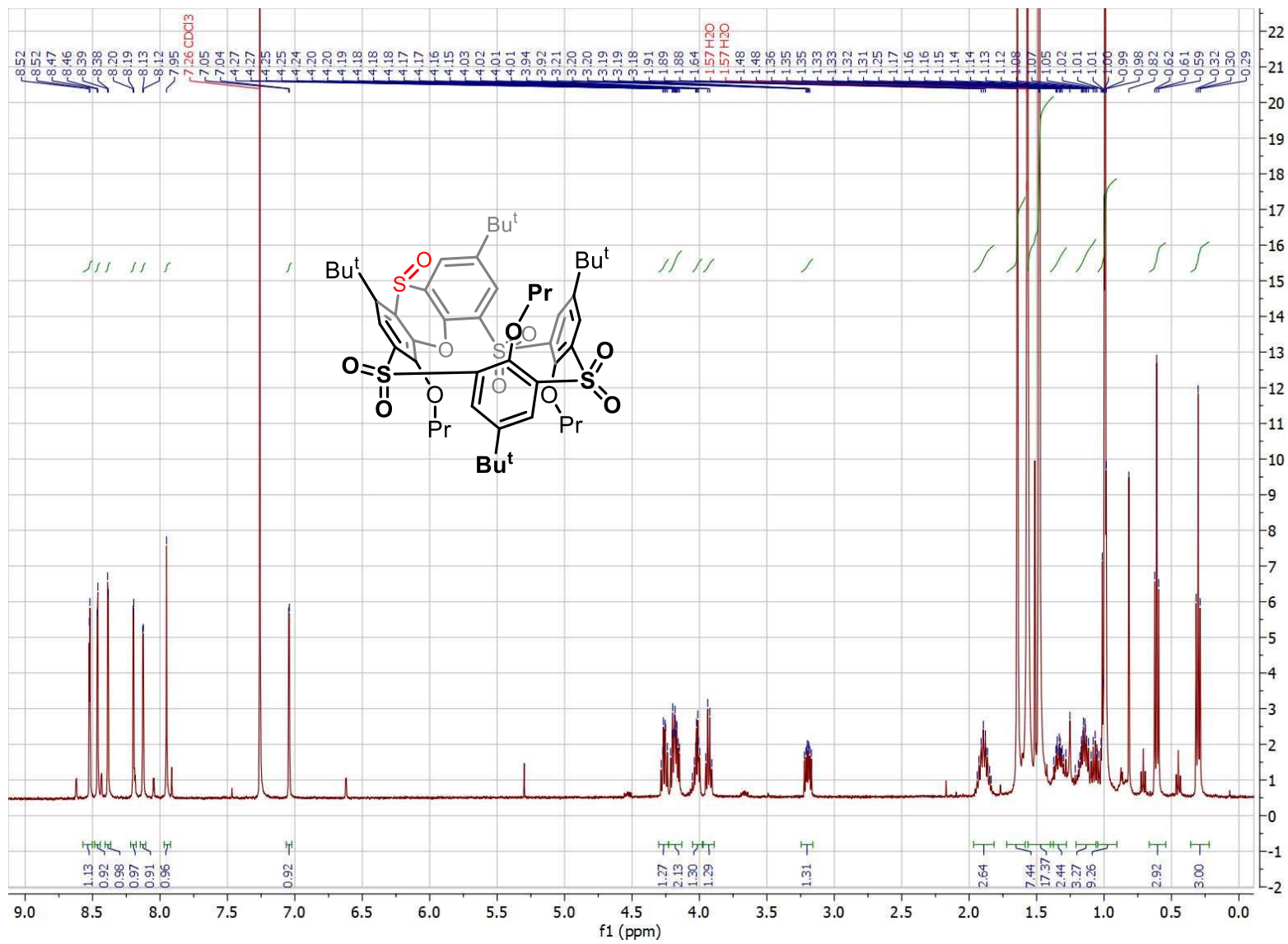


Figure 14: ¹H NMR (500 MHz, CDCl₃, 298 K) spectrum of compound 10c

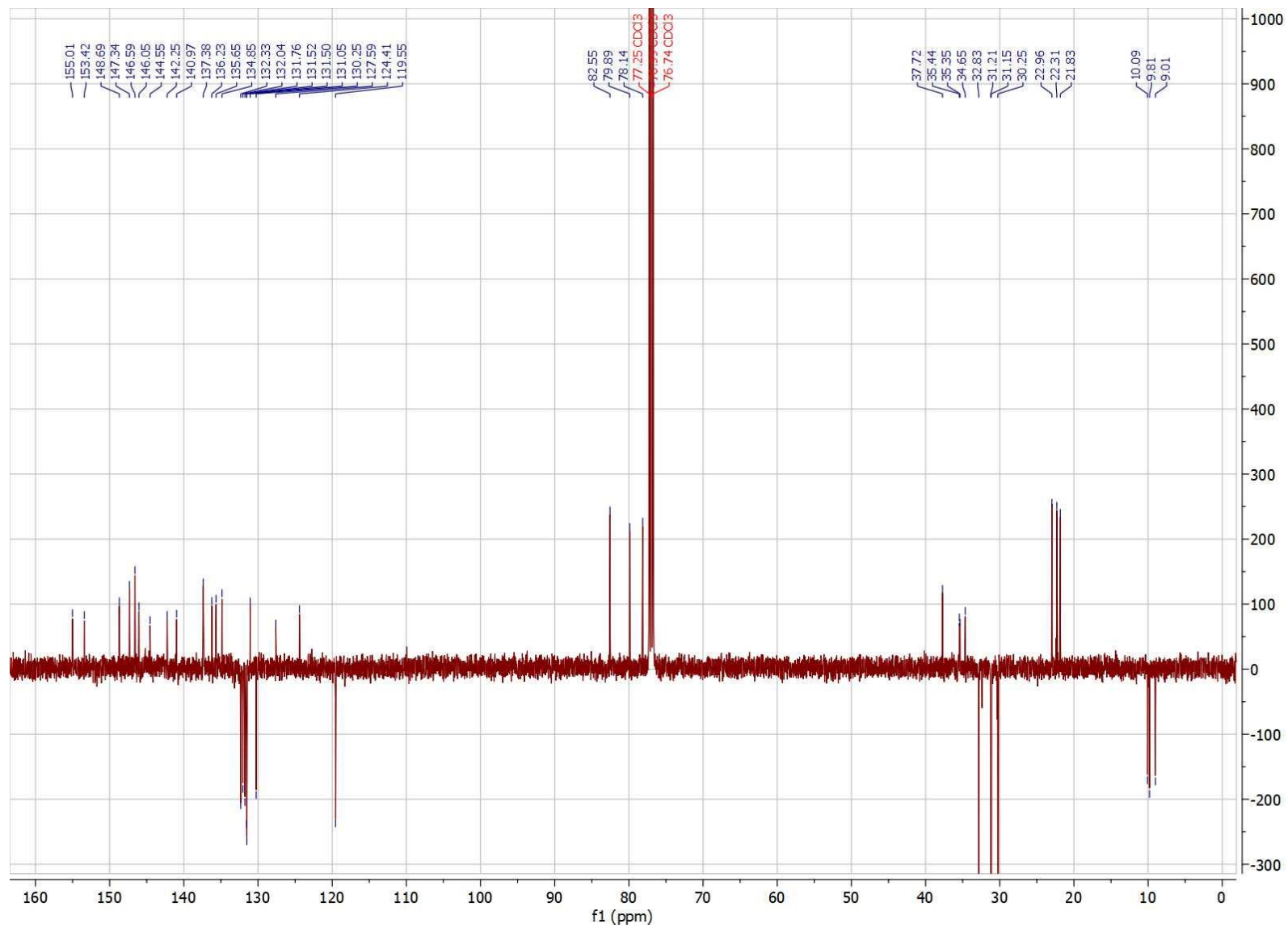


Figure 15: ^{13}C NMR (APT, 126 MHz, CDCl₃, 298 K) spectrum of compound **10c**

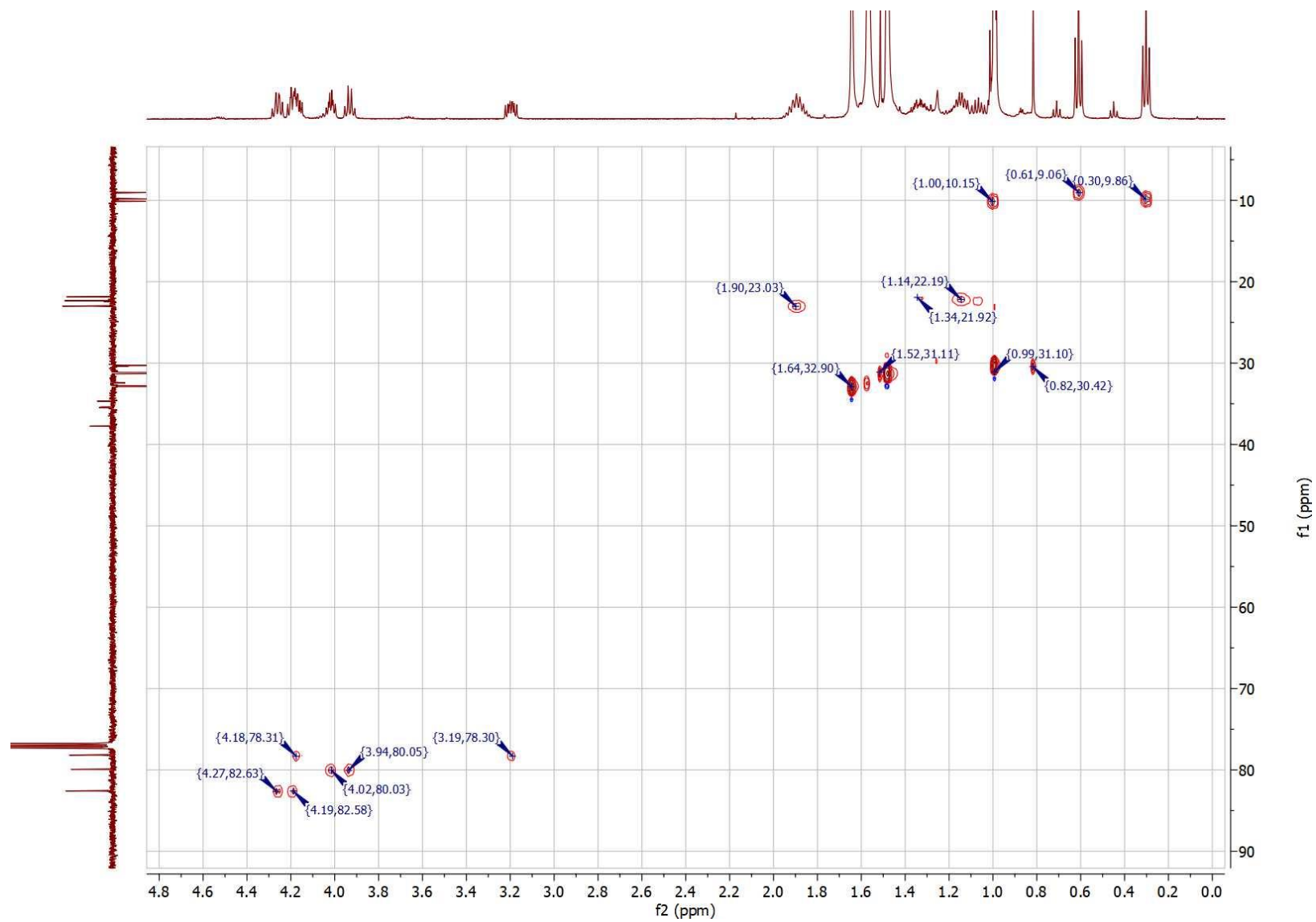


Figure 16: HSQC spectrum of compound **10c** – aliphatic region

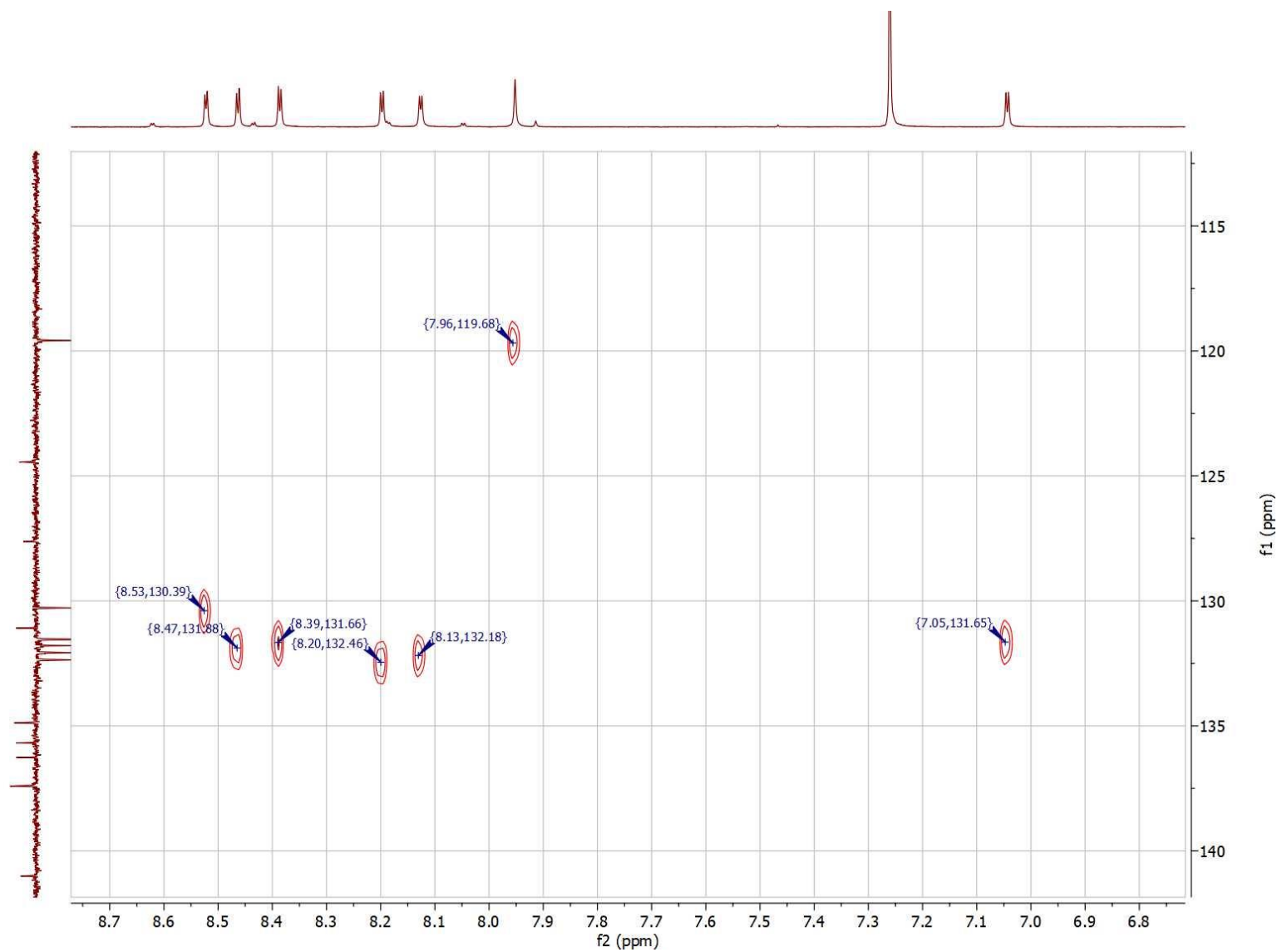


Figure 17: HSQC spectrum of compound **10c** – aromatic region

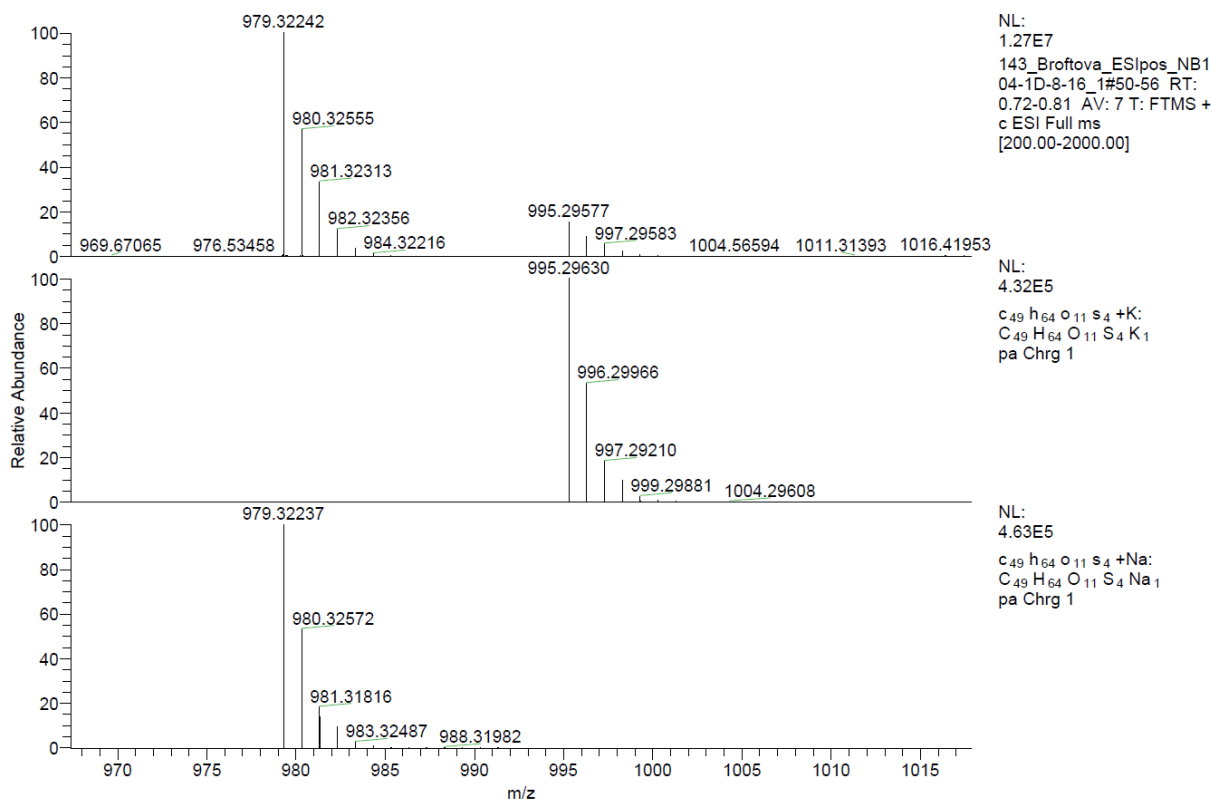


Figure 18: HRMS ESI+ spectrum of compound 10c

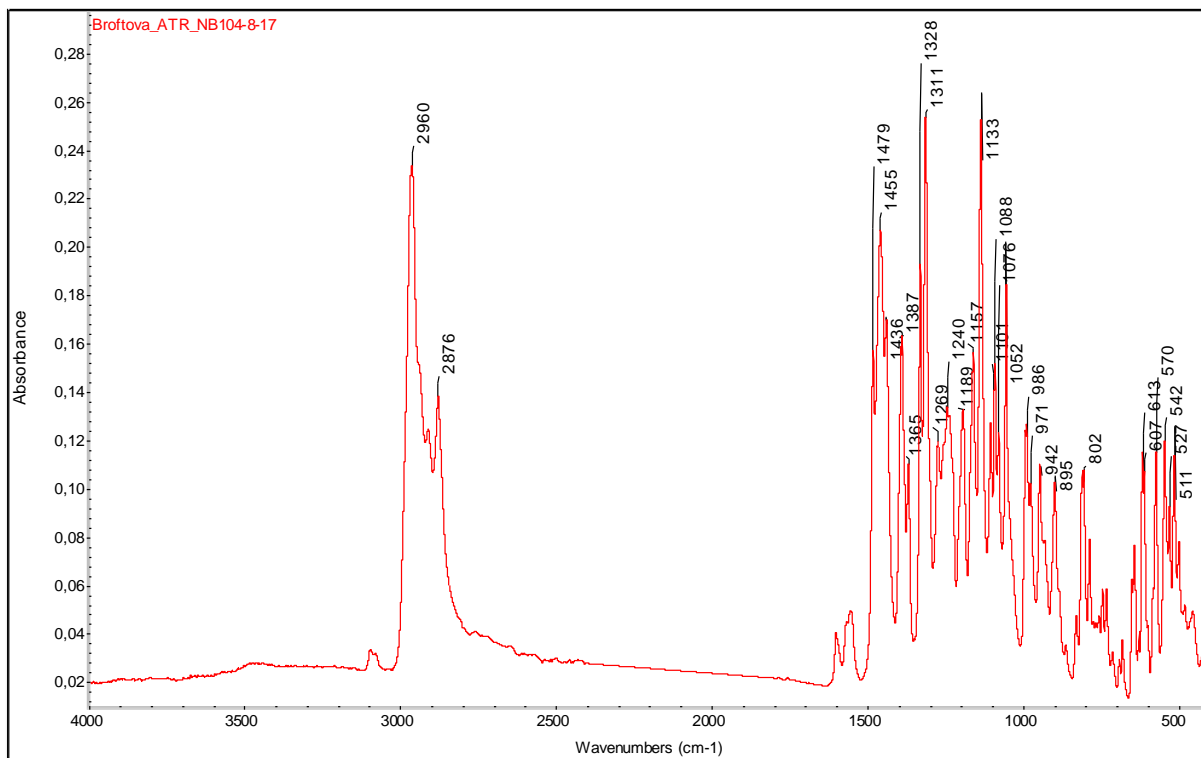


Figure 19: IR spectrum of compound 10

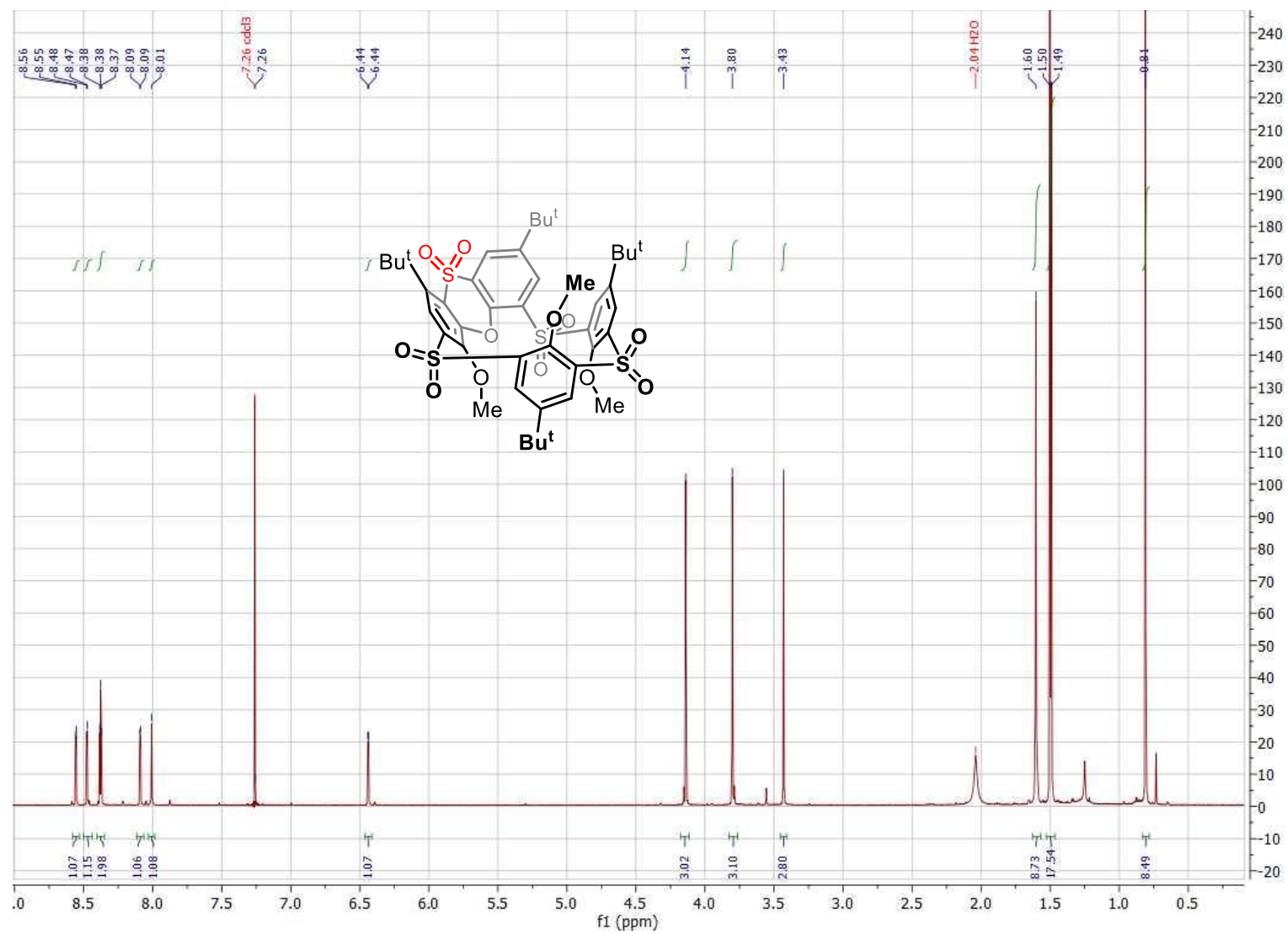


Figure 20: ¹H NMR (500 MHz, CDCl₃, 298 K) spectrum of compound **11a**

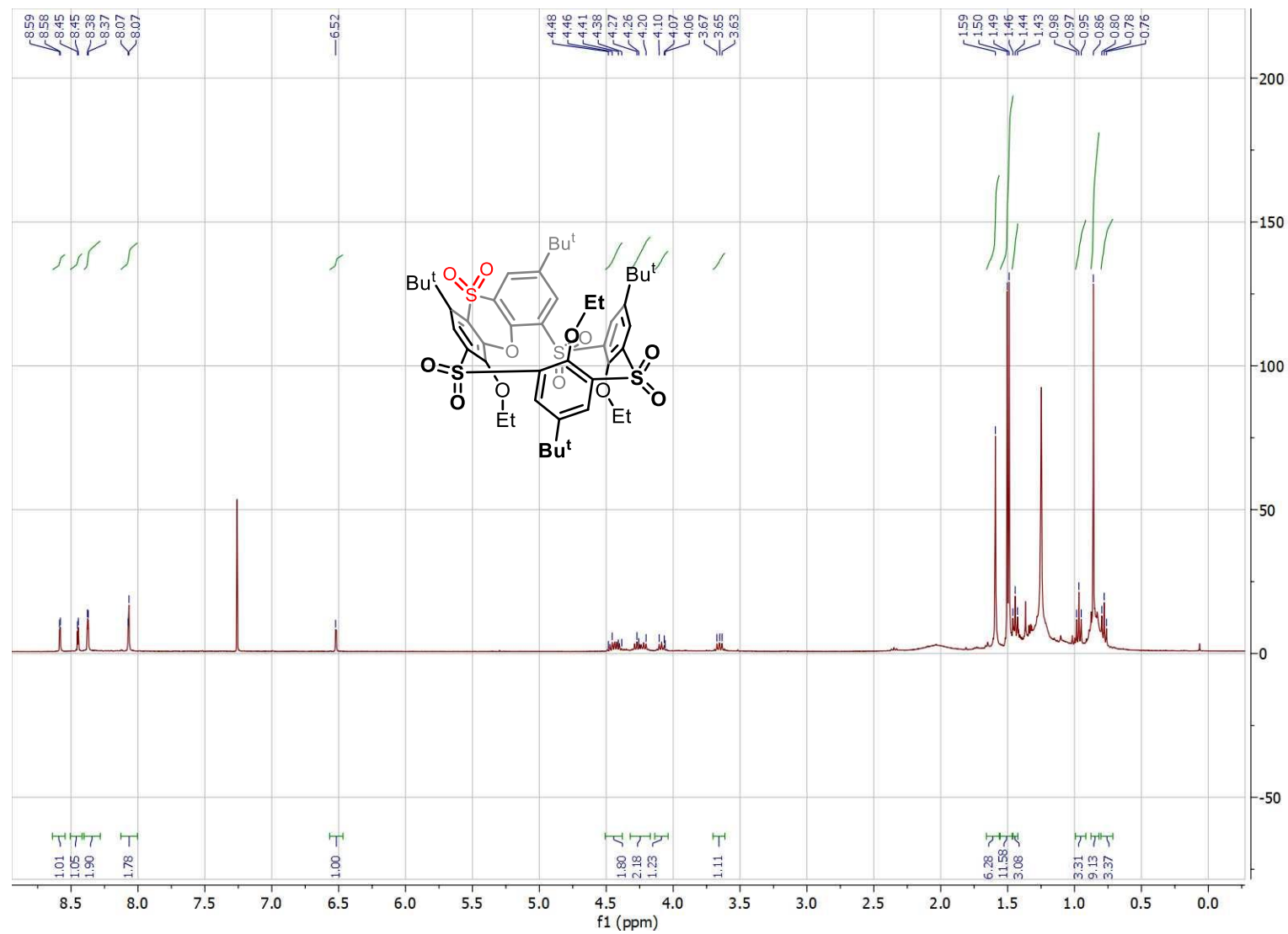


Figure 21: ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of compound **11b**

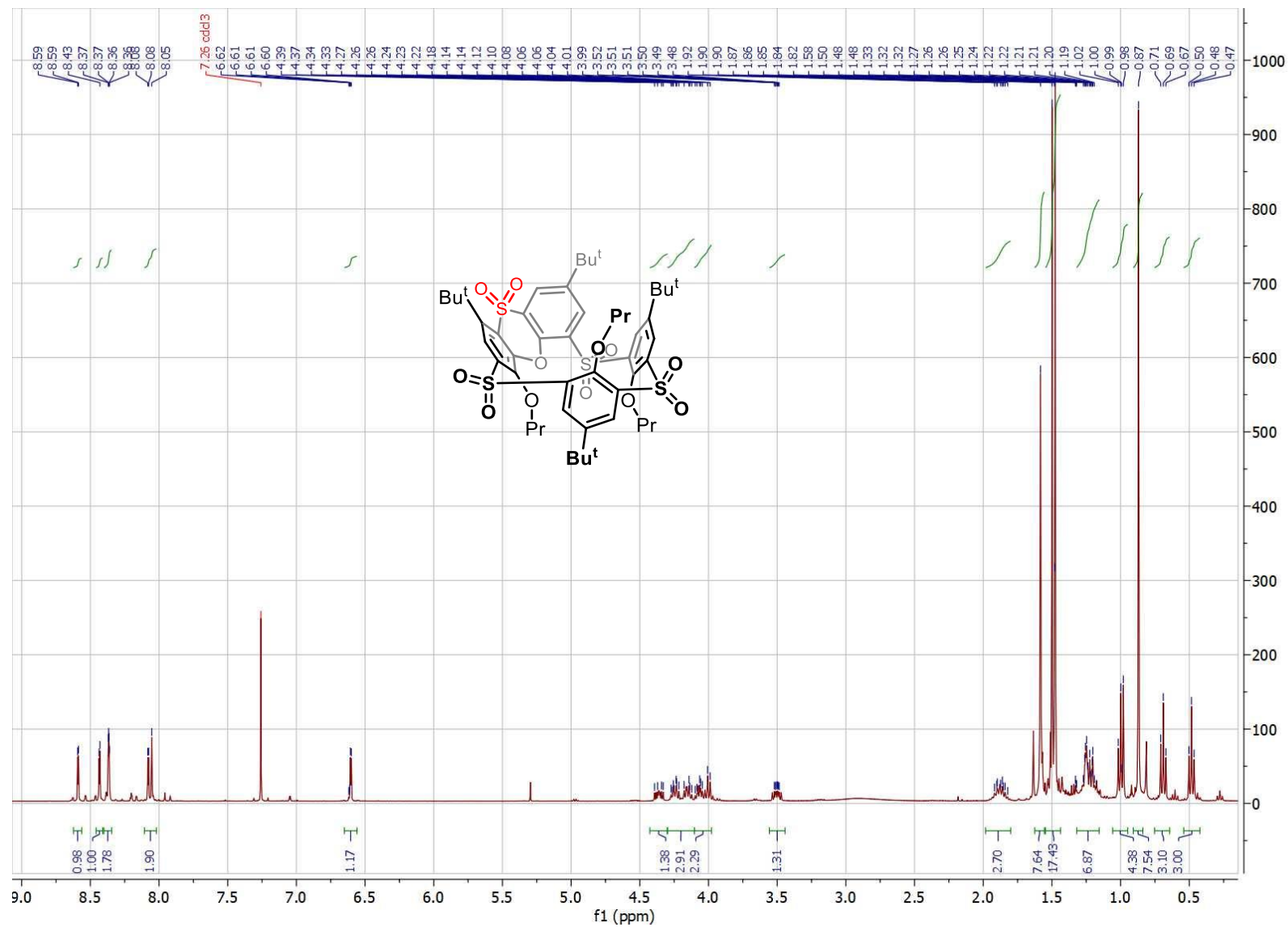


Figure 22: ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of compound **11c**

roftova_nb_6b, !H, CD2Cl2

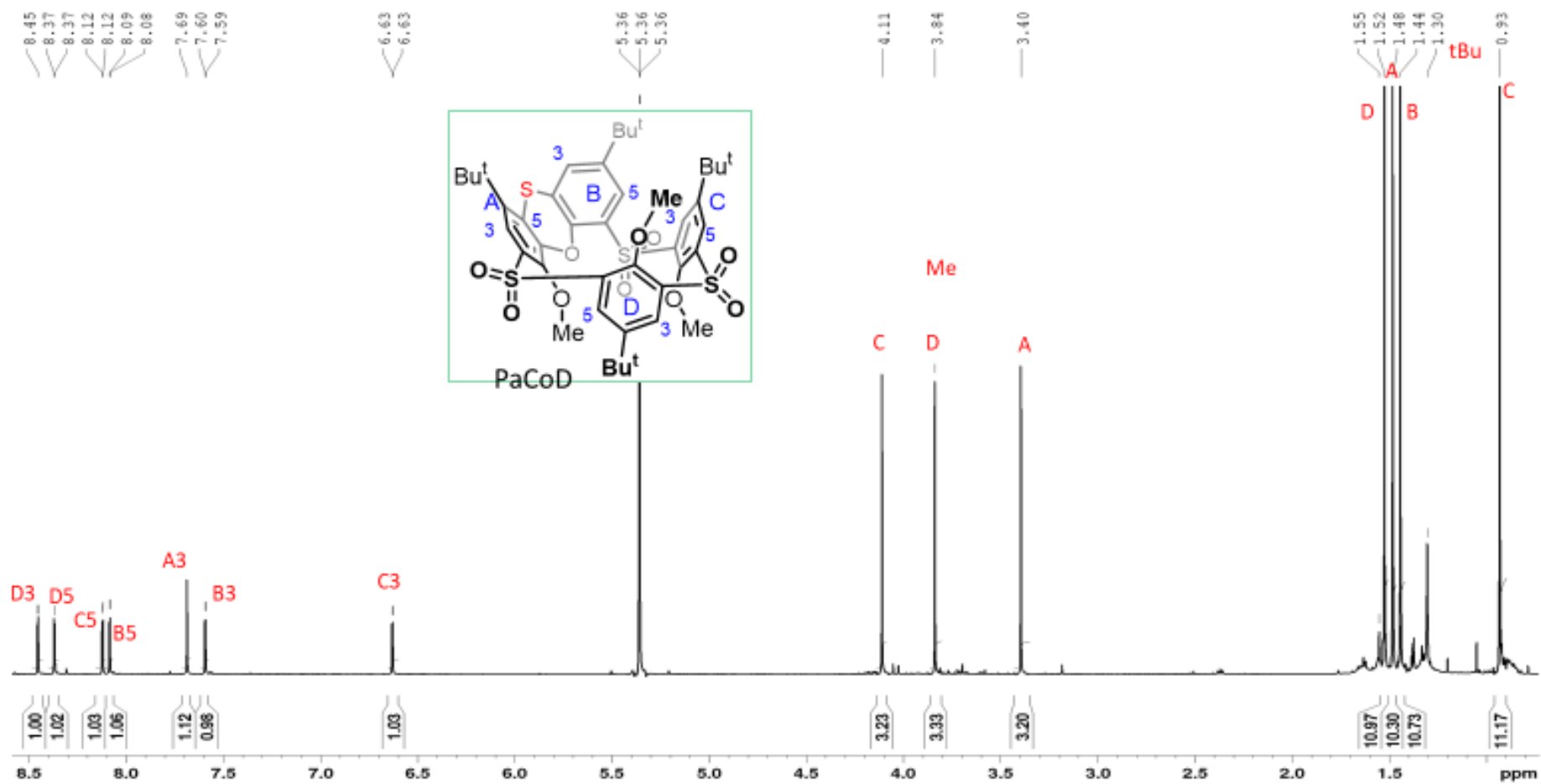


Figure 23: ^1H NMR (600 MHz, CD_2Cl_2 , 298 K) spectrum of compound **12a**

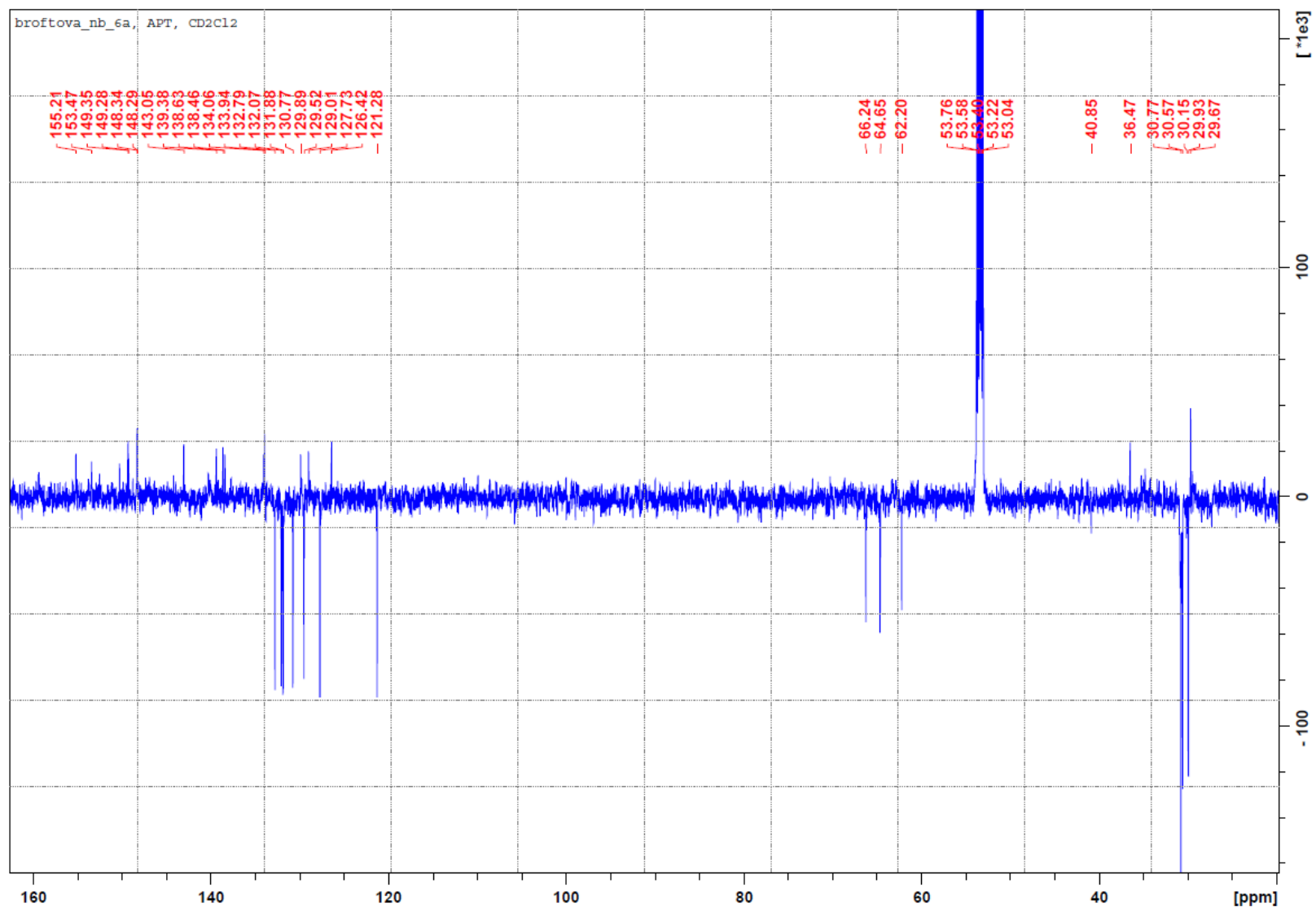


Figure 24: ^{13}C NMR (APT, 150 MHz, CD_2Cl_2 , 298 K) spectrum of compound **12a**

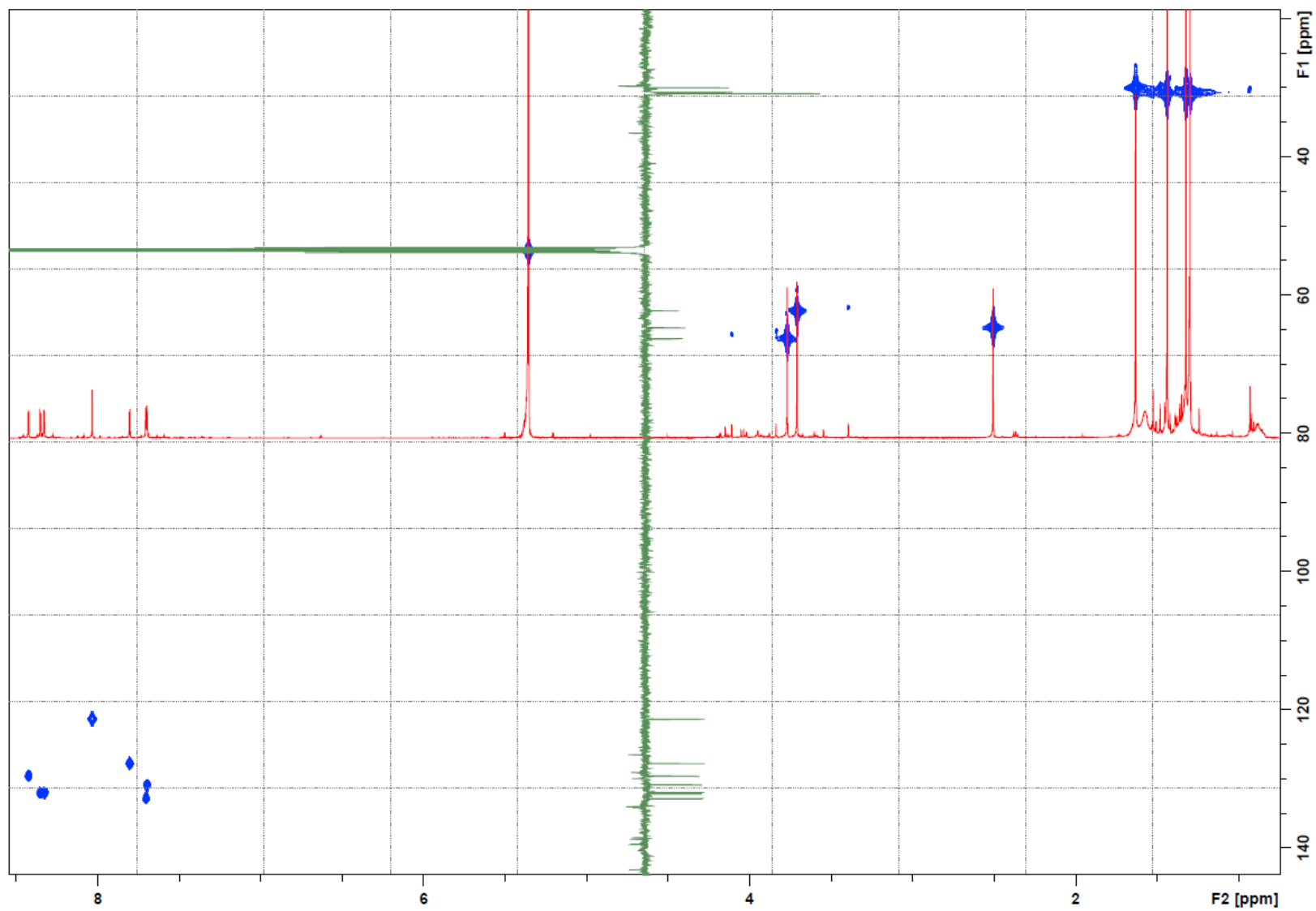


Figure 25: HMQC spectrum of compound 12a

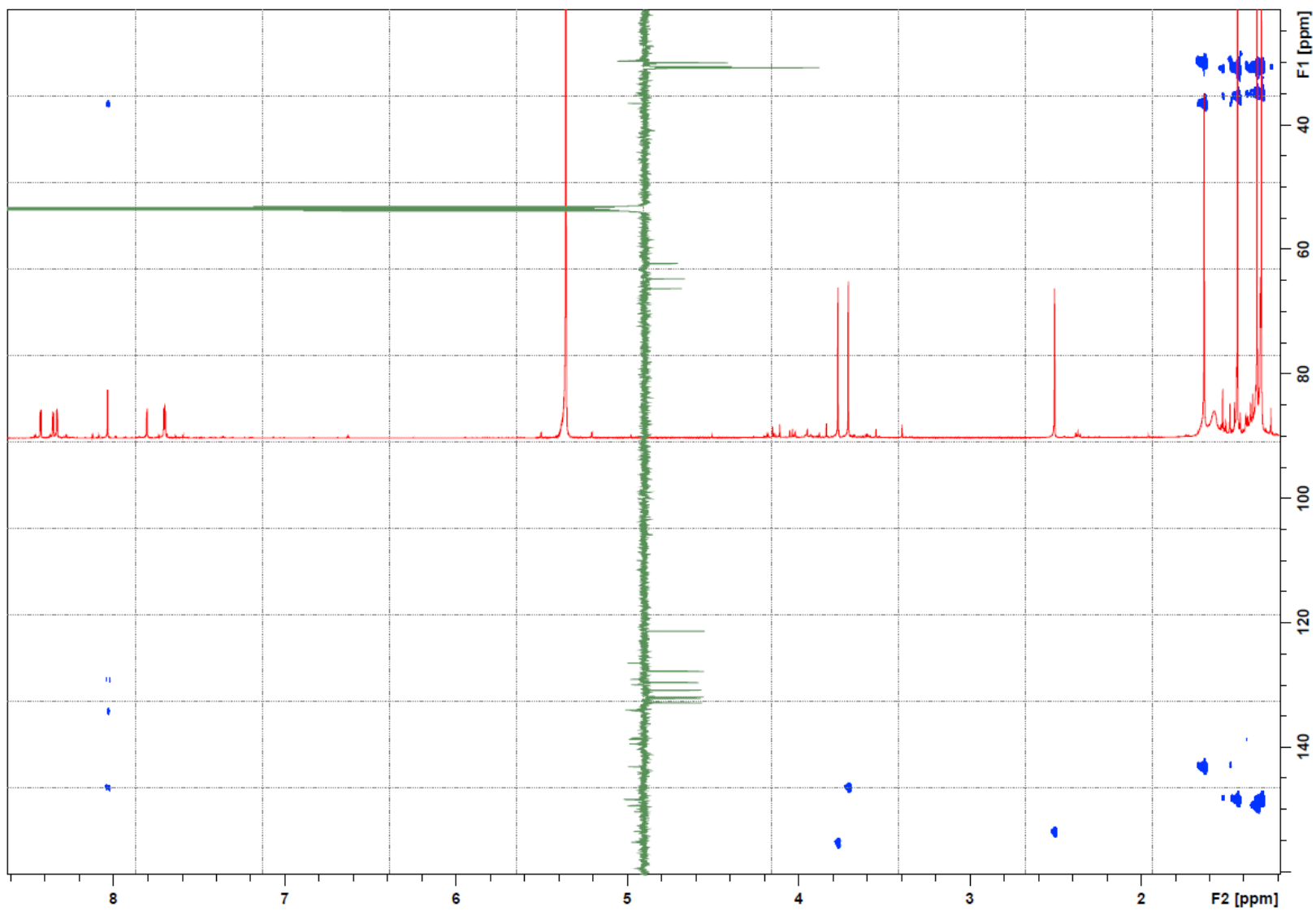


Figure 26: HMBC spectrum of compound 12a

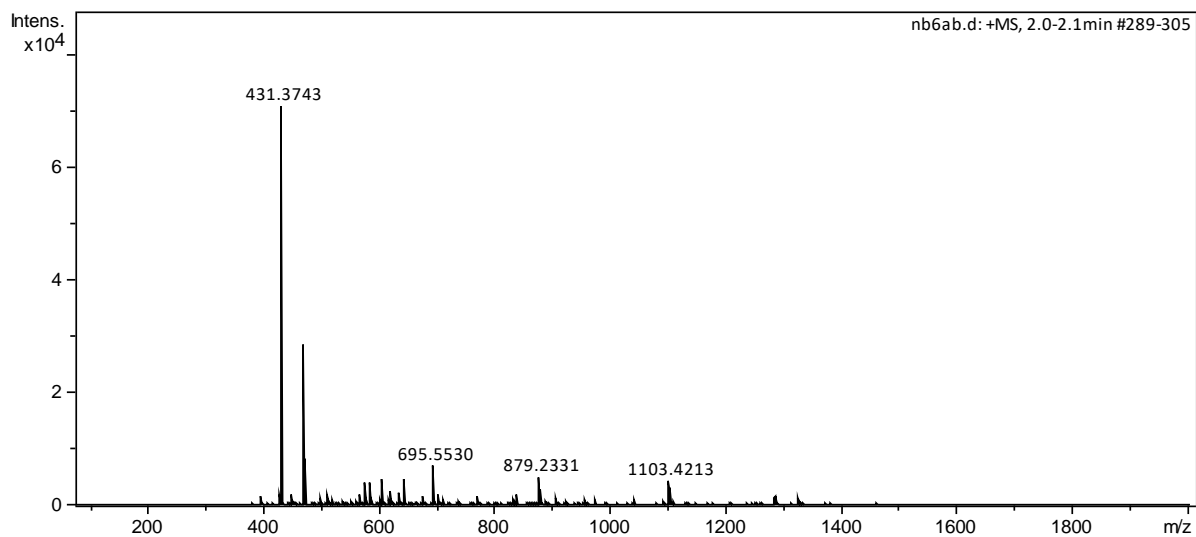


Figure 27: HRMS ESI+ spectrum of compound **12a**

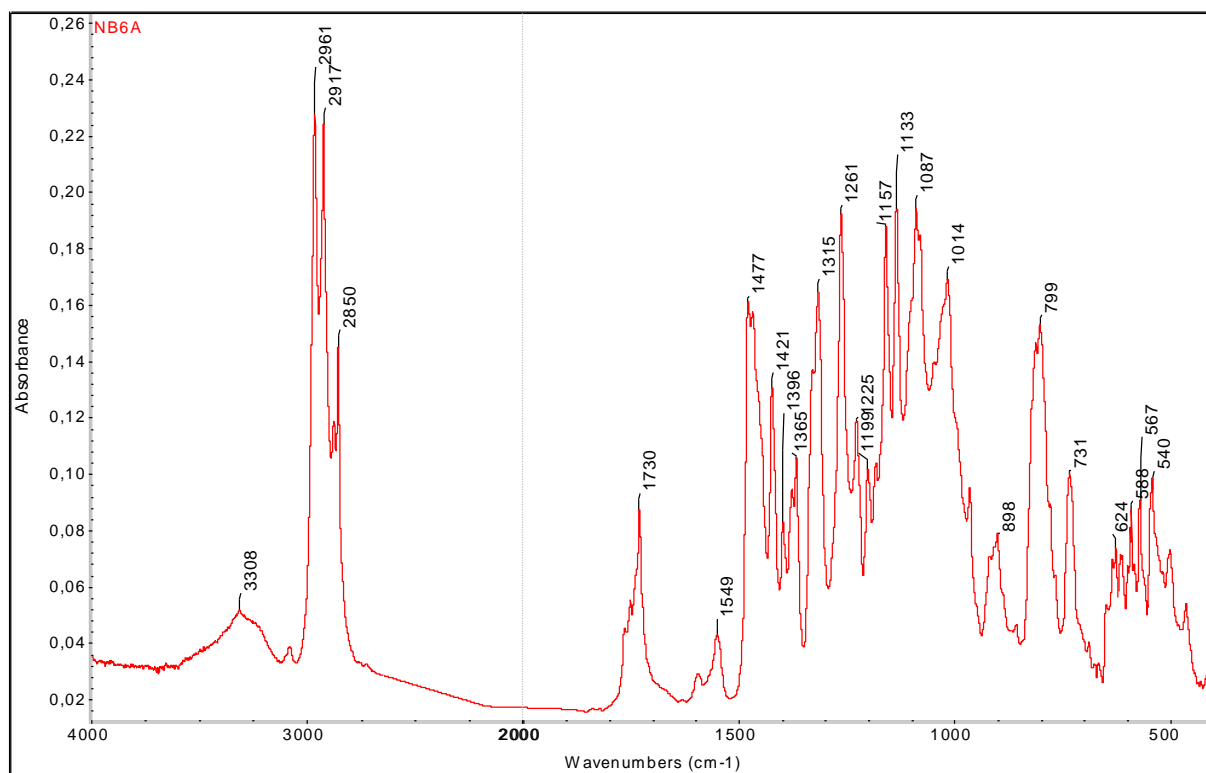


Figure 28: IR spectrum of compound **12a**

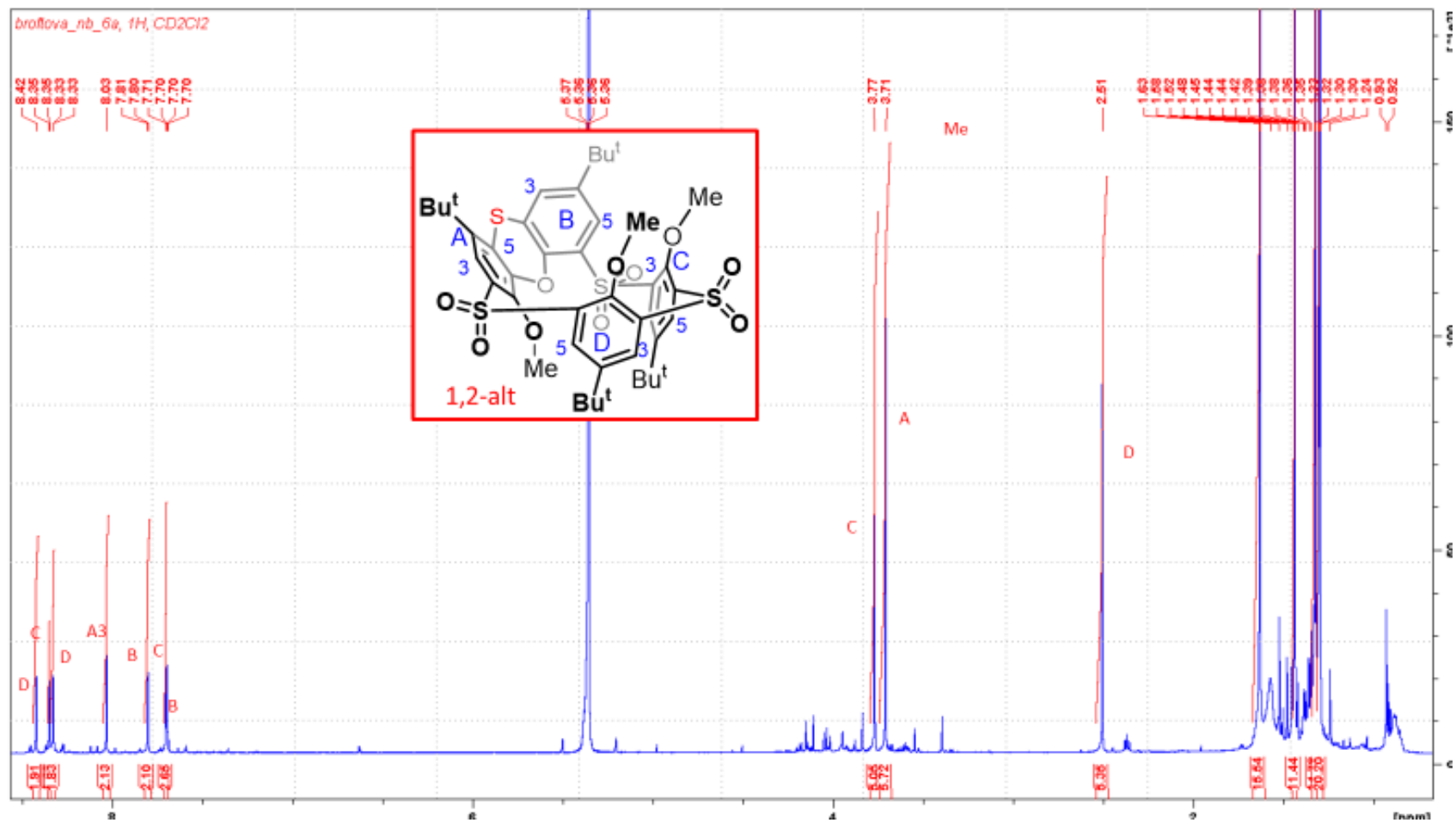


Figure 29: ^1H NMR (600 MHz, CD_2Cl_2 , 298 K) spectrum of compound 12b

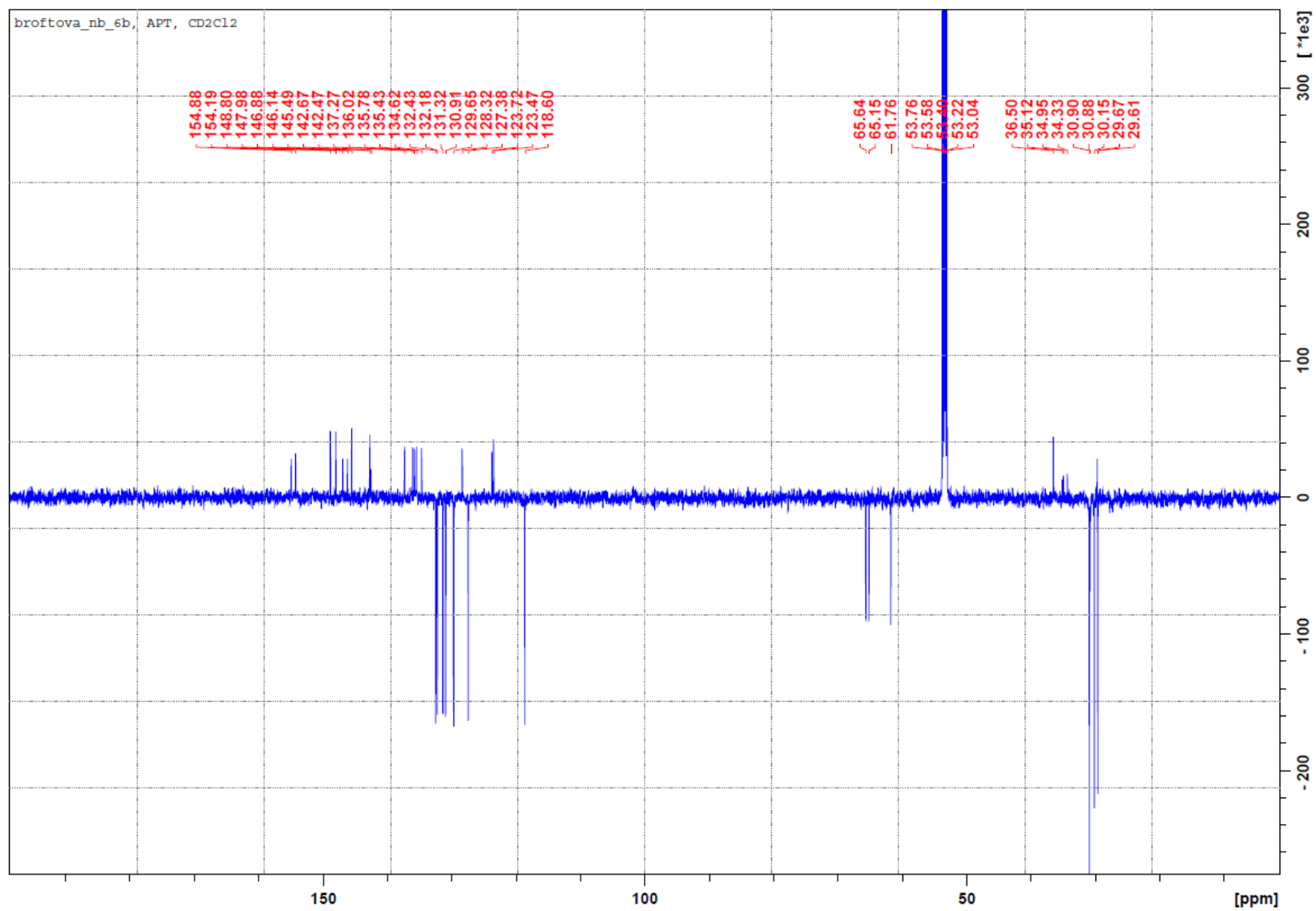


Figure 30: ¹³C NMR (APT, 150 MHz, CD₂Cl₂, 298 K) spectrum of compound **12b**

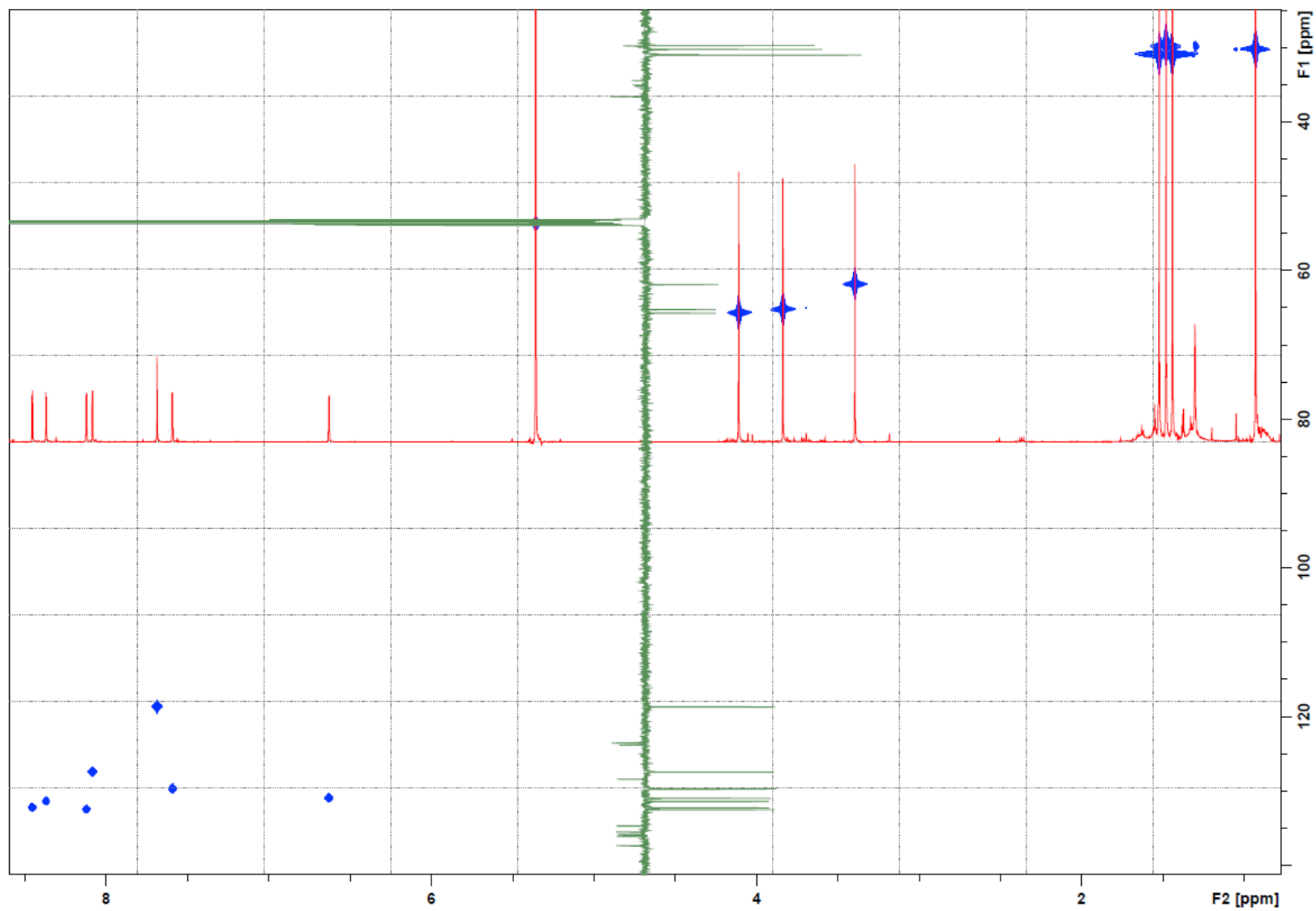


Figure 31: HMQC spectrum of compound **12a**

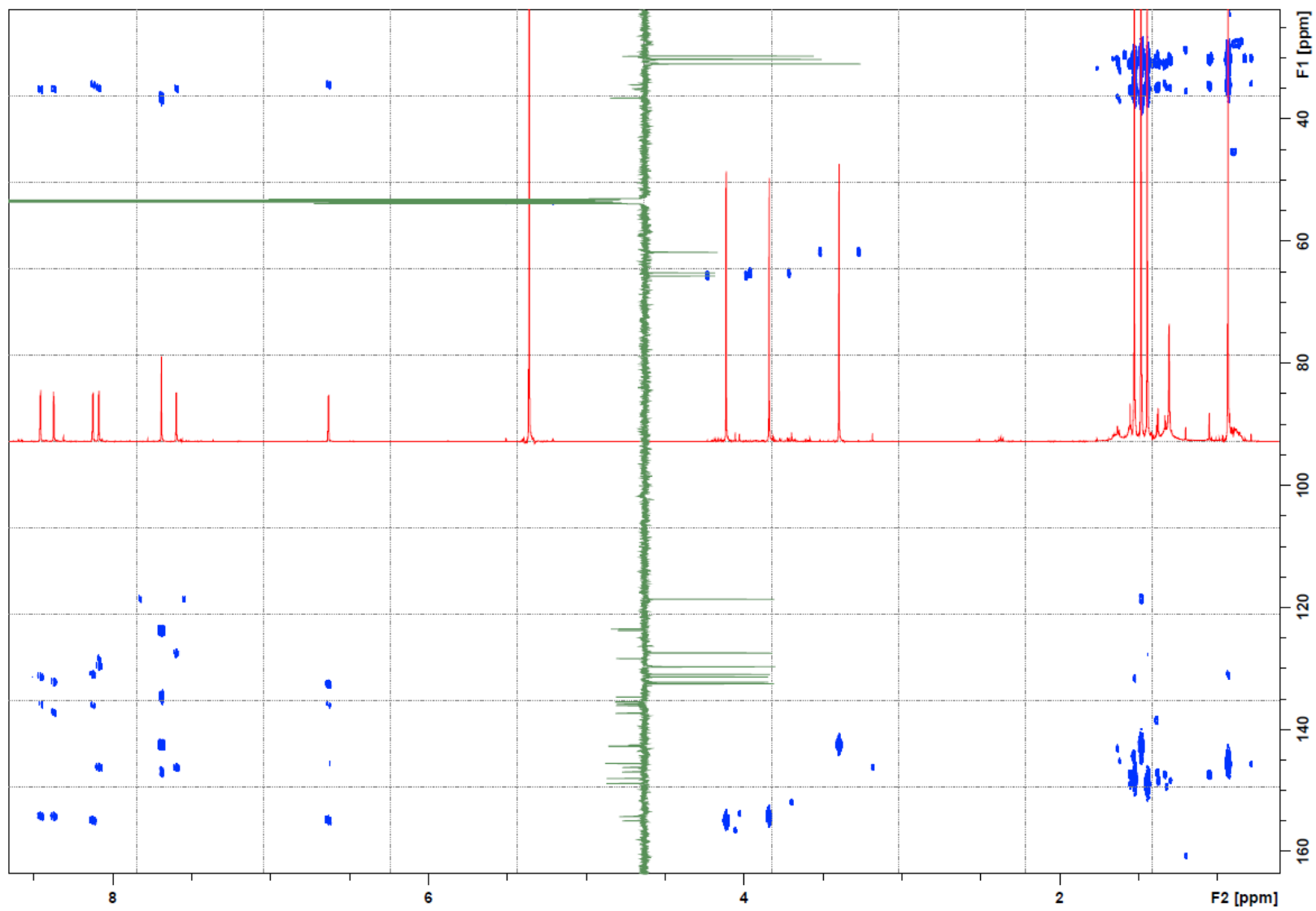


Figure 32: HMBC spectrum of compound **12a**

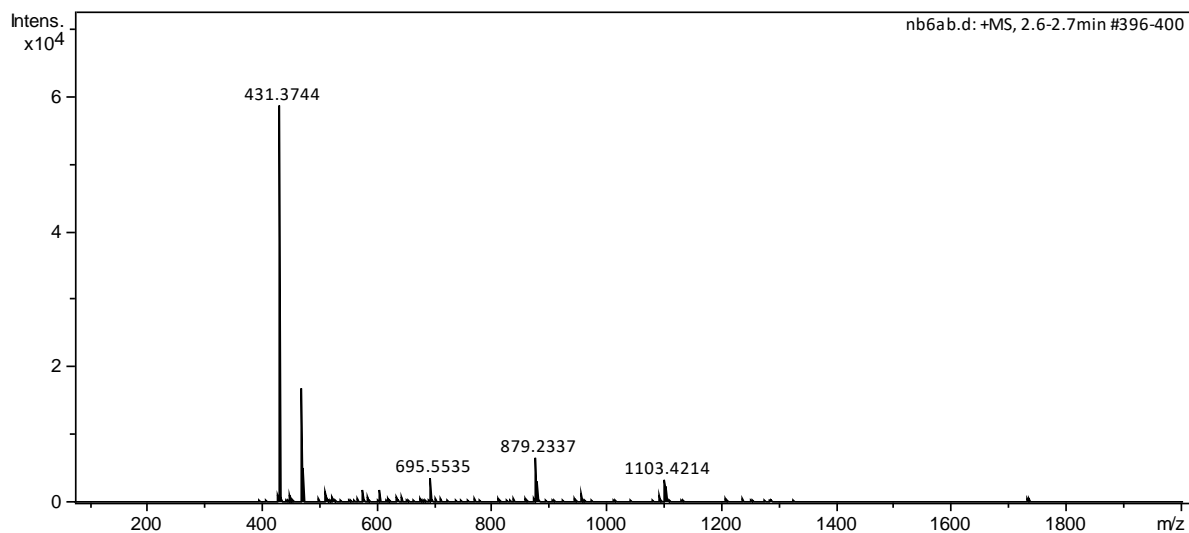


Figure 33: HRMS ESI+ spectrum of compound **12b**

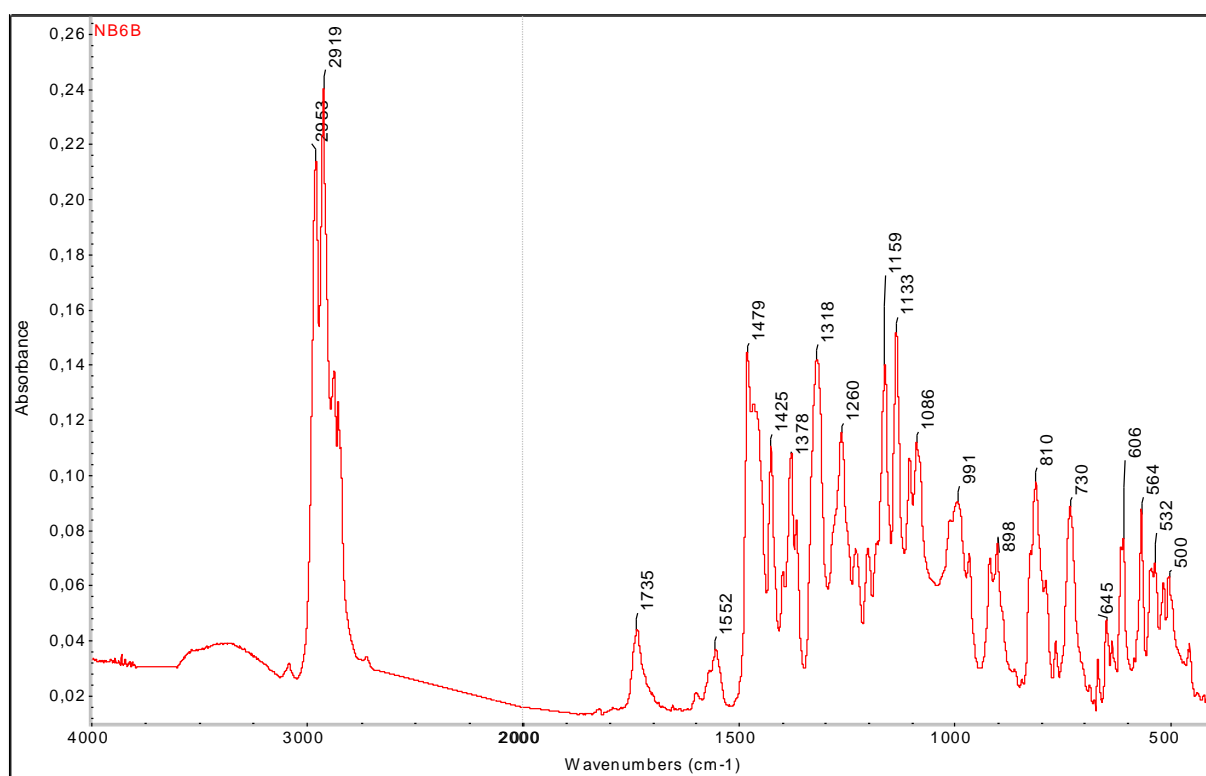


Figure 34: IR spectrum of compound **12b**

2. Variable temperature NMR spectra

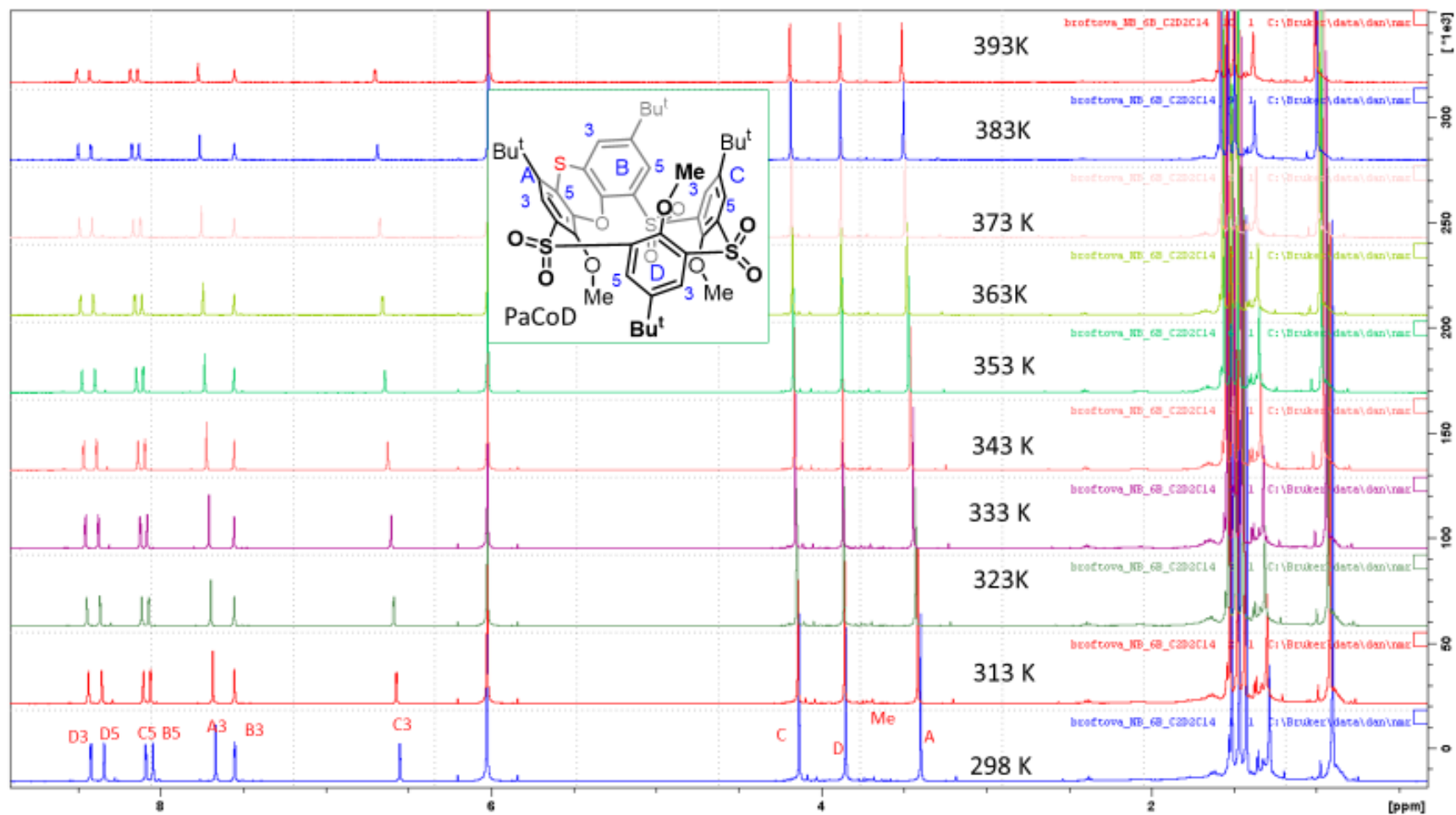


Figure 35: VT NMR spectrum (heating) of compound of 12a (600 MHz, CD₂Cl₂)

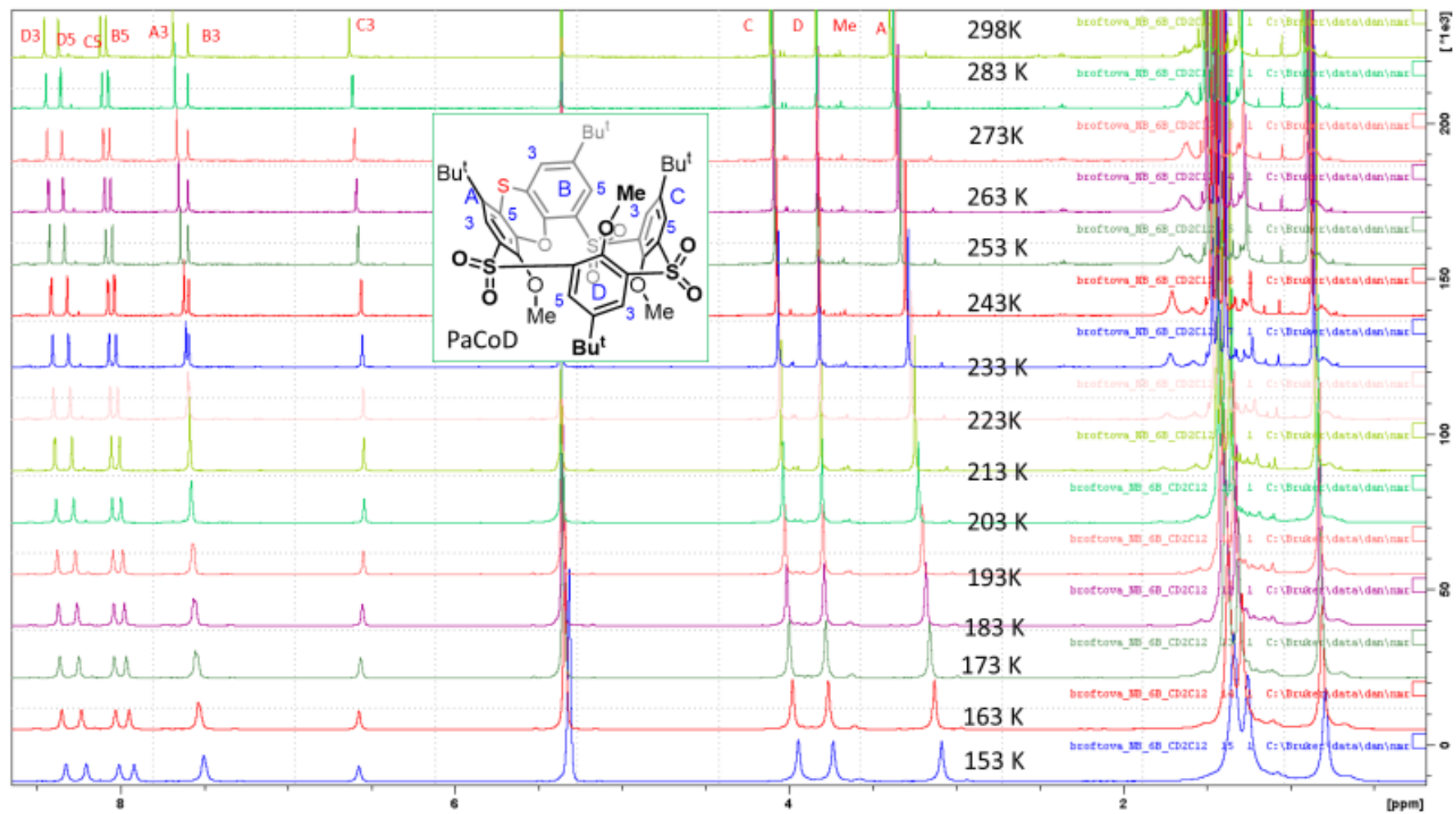


Figure 36: VT NMR spectrum (cooling) of compound 12a (600 MHz, CD₂Cl₂)

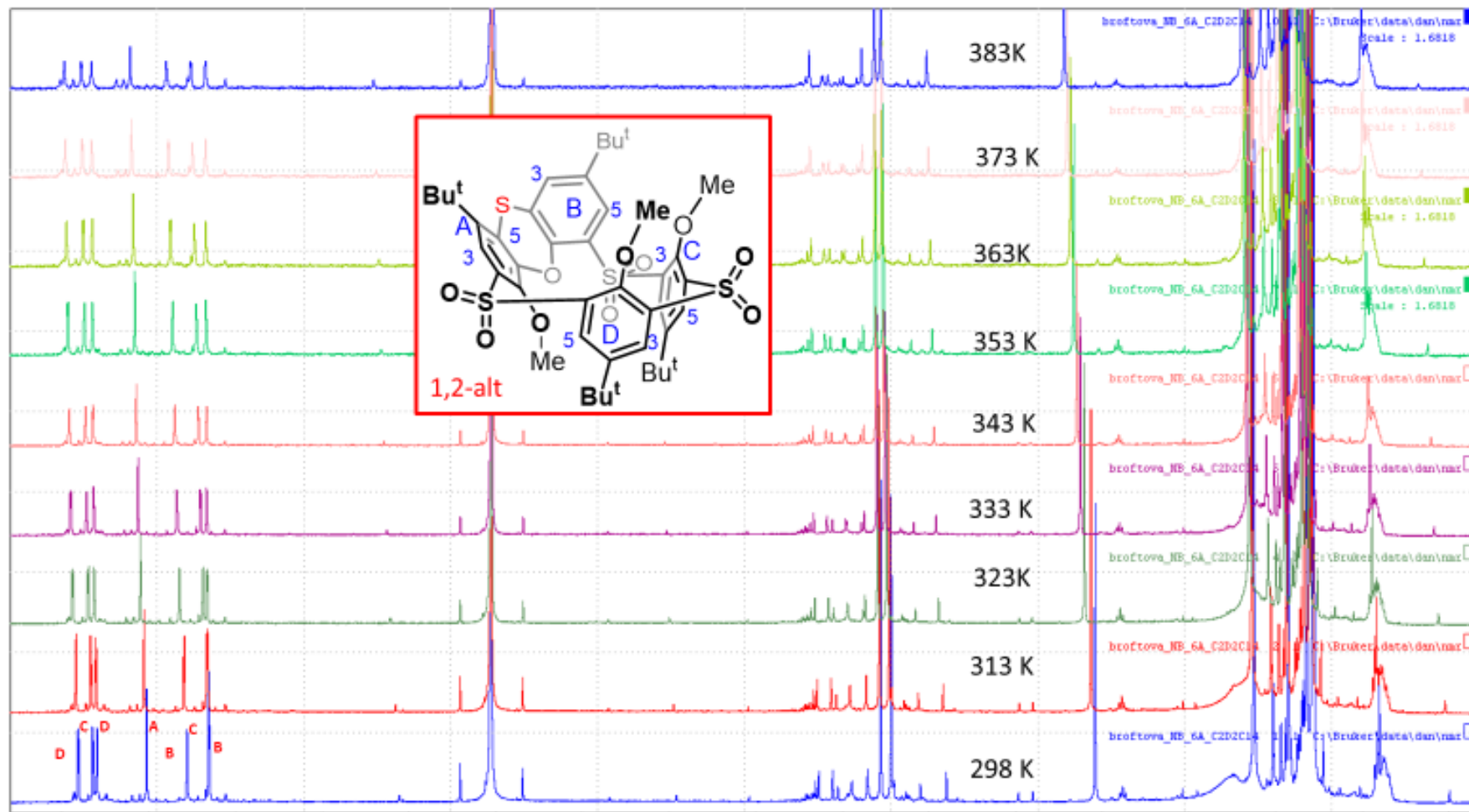


Figure 37: VT NMR spectrum (heating) of compound **12b** (600 MHz, CD₂Cl₂)

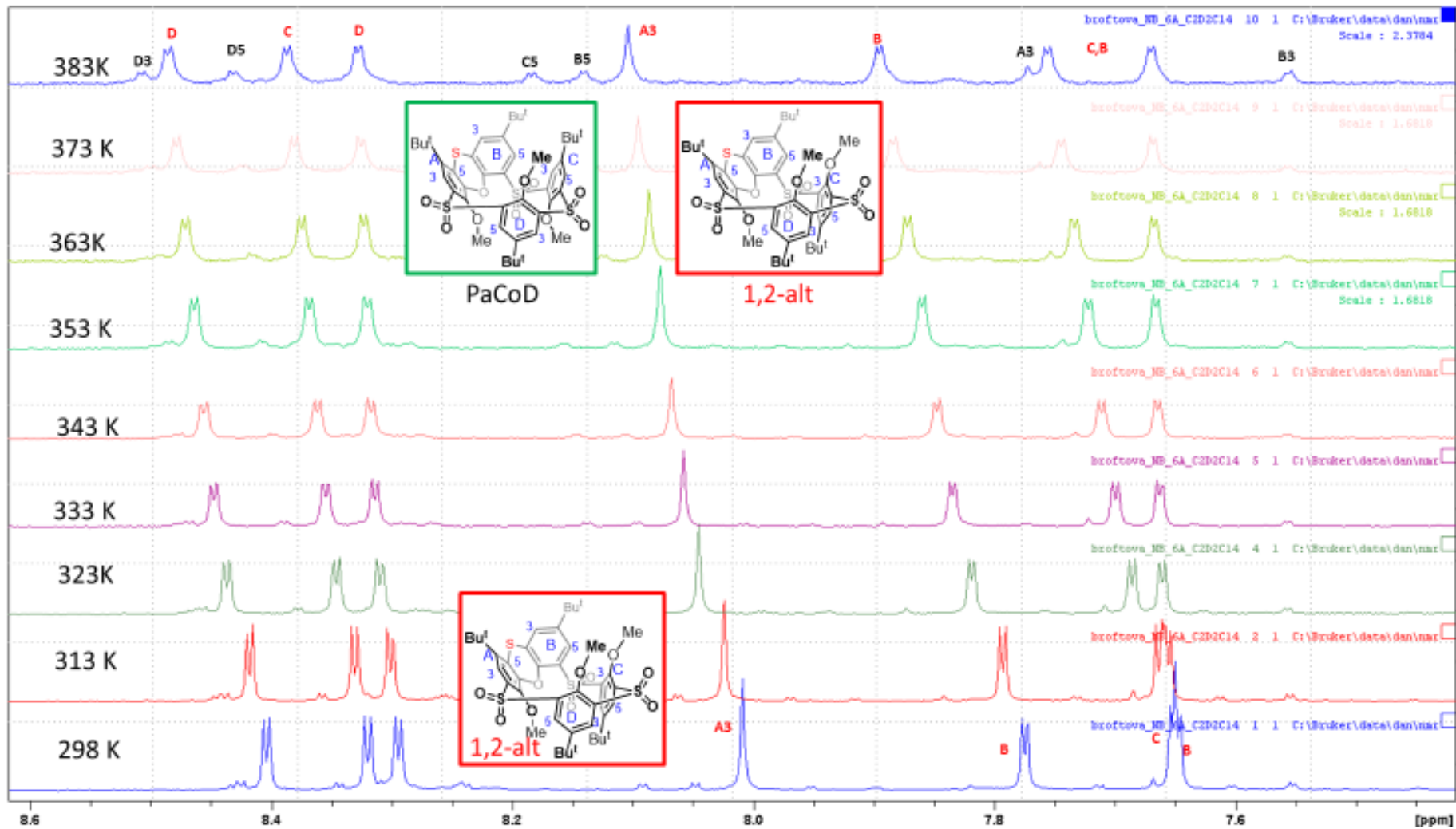


Figure 38: VT NMR spectrum – aromatic region (heating) of compound **12b** (600 MHz, CD₂Cl₂)

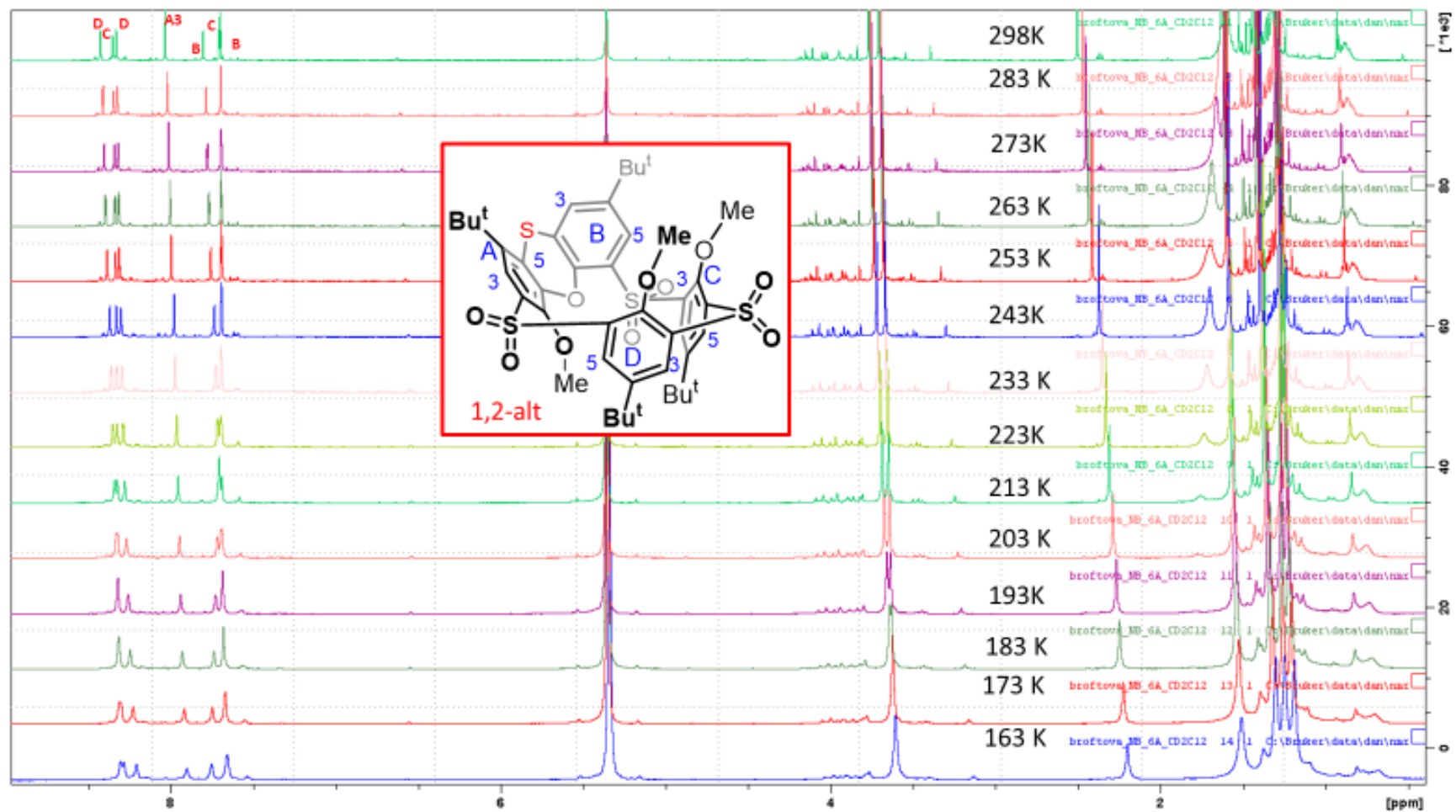


Figure 39: VT NMR spectrum (cooling) of compound **12b** (600 MHz, CD₂Cl₂)

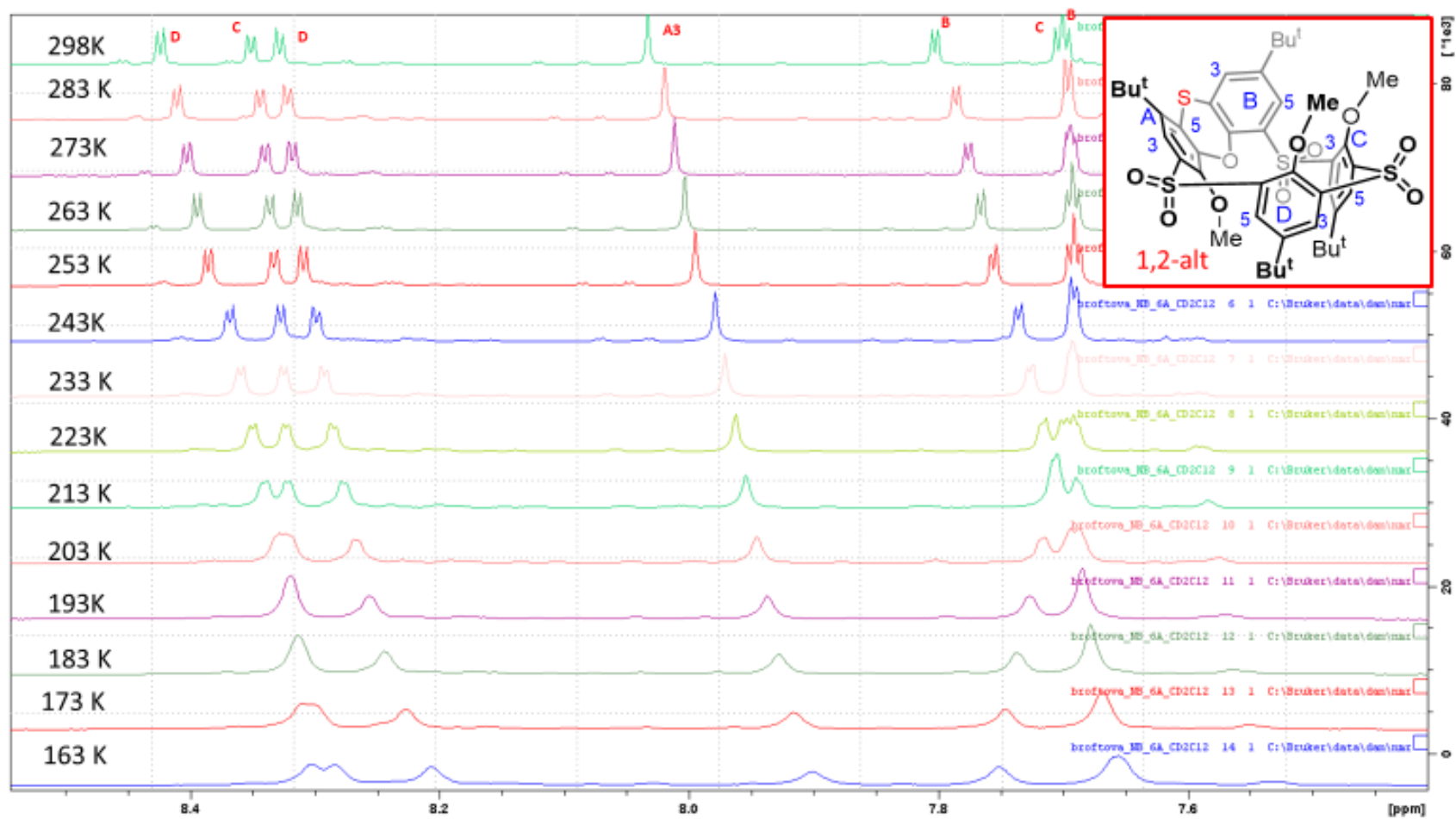


Figure 40: VT NMR spectrum – aromatic region (cooling) of compound **12b** (600 MHz, CD₂Cl₂)

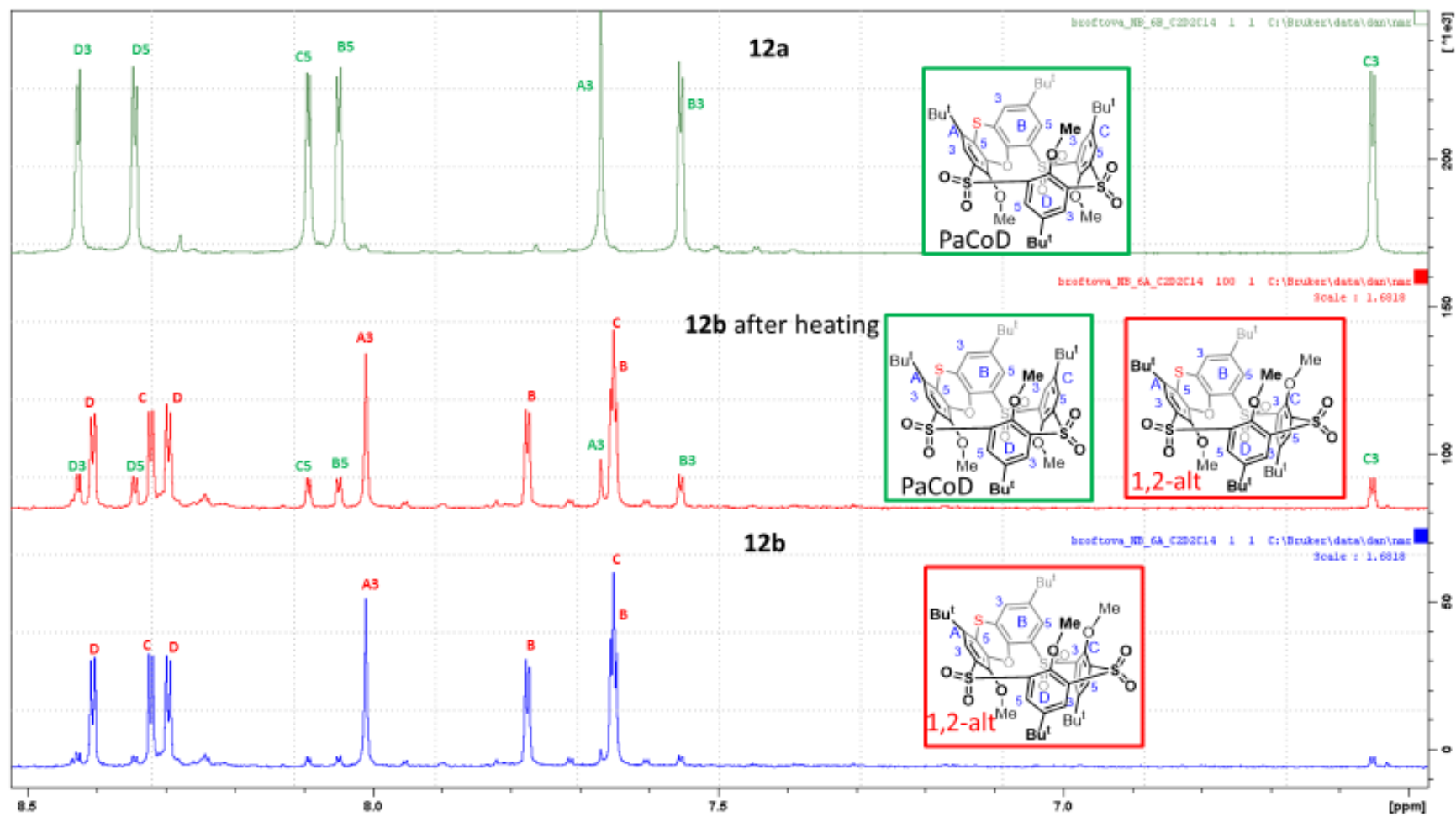


Figure 41: The change of conformation of **12b** (heating 15 min at 140 °C)

3. UV/VIS spectra

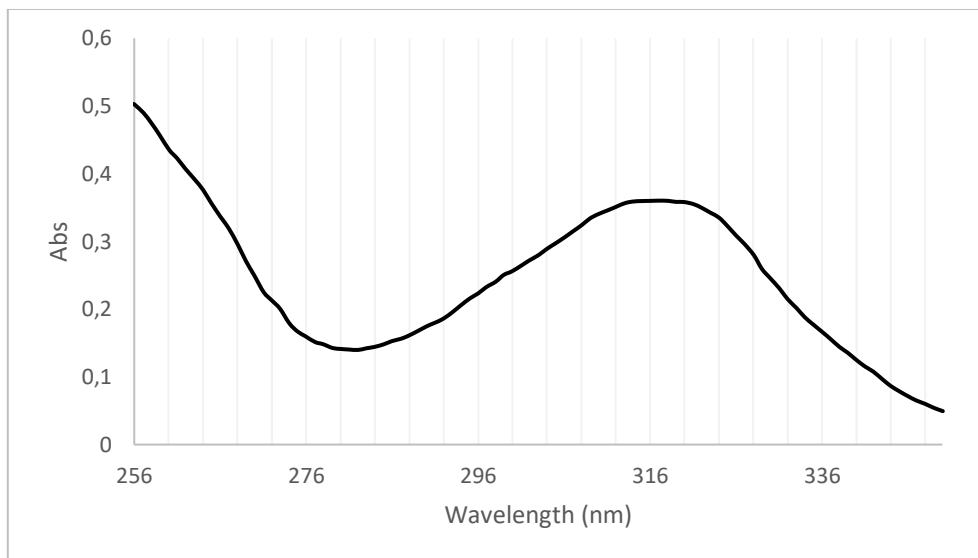


Figure 42: UV/VIS spectrum of compound **8**

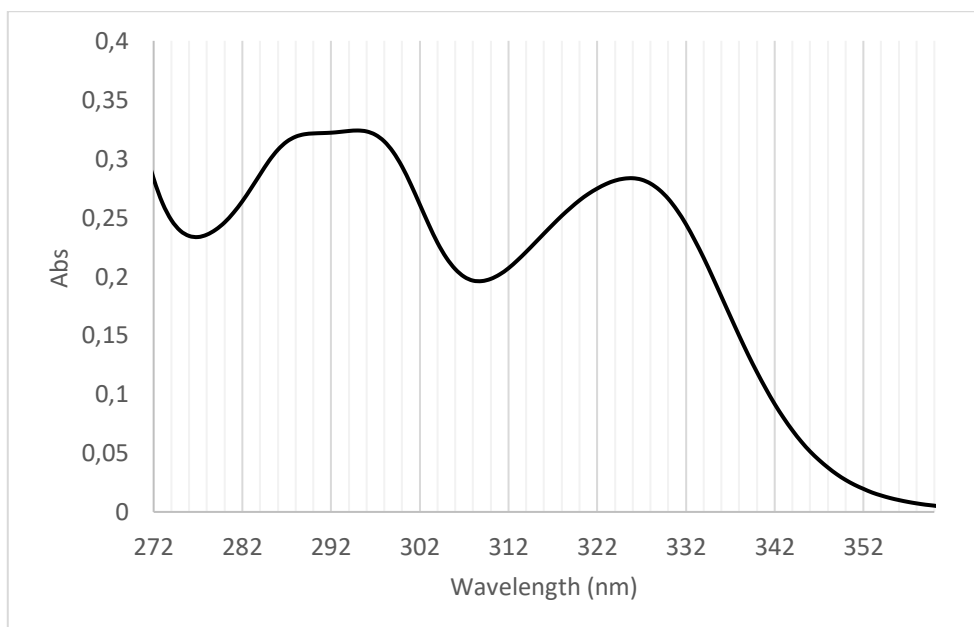


Figure 43: UV/VIS spectrum of compound **9a**

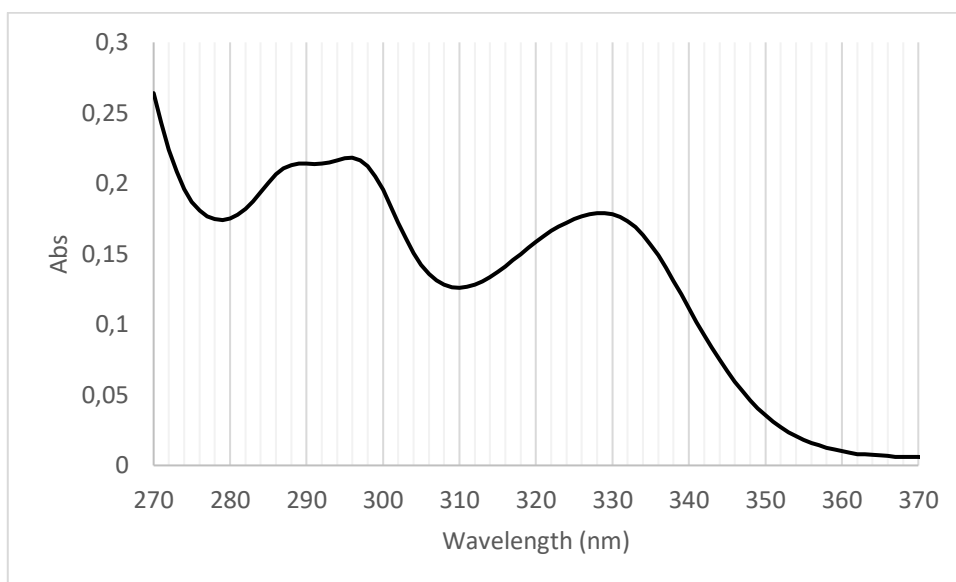


Figure 44: UV/VIS spectrum of compound **9b**

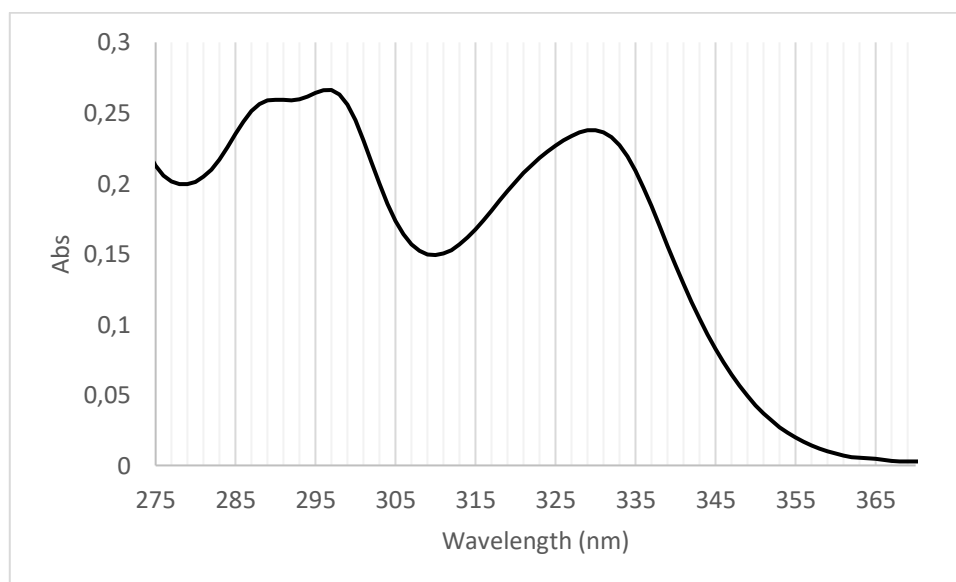


Figure 45: UV/VIS spectrum of compound **9c**

4. Theoretical calculations

Structure sulphide **12a** (Phenoxathiin – S as sulphide)

109

C	0.83198511563584	1.55942344053399	-1.26772123336555
O	1.35042881019171	0.49660975509166	-1.96668572551576
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H	-7.06599254854445	0.35483989074805	-2.30175725166751

H	-5.71788881191040	0.13188648593948	-3.44790695817618
H	-7.14613515396052	-0.91873009576074	-3.54570297805455
H	-7.62112994918665	-2.67449490724599	-1.89396420203036
H	-7.58572656894829	-1.48719135847039	-0.56257247261956
H	-6.57315858642567	-2.94883947997859	-0.48658642779297
H	0.12741356797969	6.27996823067208	0.67929315783097
H	0.35740812250615	5.29127689415667	2.14892604607687
H	1.48538923112816	6.61198930624931	1.77422902593998
H	3.00646971833924	6.53275039573001	-0.15056065732557
H	3.18125951211665	5.09781508767140	-1.17527261447249
H	1.69481130385908	6.06703641823122	-1.26774197605344
H	2.38865415504861	3.83102924085396	2.39401694466813
H	3.43839901298817	5.19872328099131	1.94885670401589
H	3.58255354818536	3.65008557222264	1.08677332332768

Structure 9a (Phenoxathiin – S as sulfoxide, oxygen out)

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C	0.80723576181126	1.51281593446400	-0.89253544595081
O	1.22843746852186	0.48604071183256	-1.68439334254513
C	2.47548416559911	-0.01164126670247	-1.60837386857684
C	3.57311433092587	0.74153477403074	-1.21028673546198
C	4.83276916607011	0.13420687615754	-1.09061188120478
C	5.01480044201063	-1.23230760363458	-1.33950524722415
C	3.87360676889190	-1.98706372923897	-1.68111923839450
C	2.62612863169721	-1.39183058137302	-1.80174364498865
S	1.15603219834203	-2.44318212428805	-1.76696017500968
C	0.57462794429469	-2.10590763407680	-0.07183022909809
C	1.48292508523372	-1.60670783557878	0.87304601952706
C	1.10323192983872	-1.28908455746323	2.17908144681122
C	-0.22126968814034	-1.56122749426673	2.53938853704034
C	-1.11870211717032	-2.08423698899971	1.61857396453946
S	-2.82241211105875	-2.26735367397944	2.17622813016782
C	-3.60741042506489	-1.00445609809893	1.17695111514402
C	-4.45179424797695	-1.42027238731821	0.15347789817528
C	-4.93316491010230	-0.52048707282843	-0.80991351297345
C	-4.49241214924956	0.80580365737080	-0.71971844583469
C	-3.63361175092062	1.20994726897027	0.30701458640526
S	-2.88369479239873	2.83733255886610	0.18669418092522
C	-1.10309235021261	2.53022399468100	0.10715118746854
C	-0.26477848021215	3.42519974234463	0.77448068919378
C	1.12658007801596	3.41296508251361	0.61240866402652
C	1.65982255801666	2.42790125143064	-0.26551382848176
S	3.39190896888520	2.51498254913035	-0.88018270514391
C	-0.76396495411435	-2.35287681001875	0.28142527293771
C	-3.19356855671168	0.33159880677583	1.29909926646655
C	-0.59040100669098	1.53609291786851	-0.71920749842821
O	-1.69876741649526	-2.76398143241624	-0.60007913317041
C	-1.71733411097402	-4.15618938359602	-0.94747184226960
O	-2.29024716151371	0.72856812275632	2.23086214945074
C	-2.83274990475359	1.23676113431778	3.46247589792749

O	-1.36204838806819	0.55798516458013	-1.23234574787599
C	-1.59691085011251	0.52787832422665	-2.64513625435563
O	0.16722261189782	-2.00160307509900	-2.75188703913218
O	1.63760673578914	-3.83488221848651	-1.80177295384053
O	-2.85708322241475	-1.88631531644509	3.59724675517676
O	-3.35252202366964	-3.57160343765023	1.75828911787647
O	-3.27474658766487	3.37649247473571	-1.12527825868836
O	-3.13565218971746	3.62134248898826	1.40538642046192
C	6.35423228080319	-1.95648874970874	-1.14162637530500
C	7.50549113948345	-0.98236445703178	-0.85429021906801
C	6.69821891499368	-2.76485579746061	-2.41004504540080
C	6.20871513216223	-2.90844575890736	0.06614667411280
C	2.04250441196337	-0.60933214409527	3.18261672024143
C	2.29256734341803	-1.55718675463687	4.37244534699923
C	1.35788296844090	0.68529058244293	3.67882481810221
C	3.39153108787889	-0.23963551236942	2.54298305615464
C	-5.79968235787005	-1.04754044842704	-1.96332364264724
C	-7.02697958873271	-1.79156722884068	-1.39582925339889
C	-4.95026601322106	-2.02544478716172	-2.80569566427632
C	-6.29206522197850	0.08482660313031	-2.87468275463929
C	1.99555287592230	4.45797515673801	1.34523276710737
C	1.15359318958635	5.31542484876504	2.30874418996161
C	2.63443872144688	5.42397391774060	0.32173956844578
C	3.06944520580516	3.75186049431551	2.19980147628706
H	5.67033446815305	0.75444486309989	-0.76900902070706
H	3.91933443730954	-3.07242470651271	-1.78528850276941
H	2.51091886034074	-1.43189696278127	0.57390905253090
H	-0.59895472605987	-1.34584955044156	3.53781543751410
H	-4.68491614489736	-2.48386402716135	0.10197942686140
H	-4.74710941583132	1.54867466852970	-1.47387733875530
H	-0.74795132979482	4.15537496671885	1.41826164906407
H	-0.72490317906623	-4.49441094636233	-1.28167741764581
H	-2.06557893628076	-4.74474655721109	-0.08489812612707
H	-2.42965192105039	-4.25471301580727	-1.77562574523900
H	-1.97240980854808	1.57501472000036	4.05318882130451
H	-3.35885066524762	0.43061000439531	3.99368207624695
H	-3.48947259895926	2.09386764701700	3.25732372955122
H	-2.32702623275711	1.30987841744960	-2.90704775177806
H	-1.98639361308960	-0.47274661376891	-2.86050487607858
H	-0.66366300637978	0.66610680259917	-3.20671600302487
H	7.34904427052017	-0.42219088974859	0.08106604692308
H	7.64890681538908	-0.25892190781385	-1.67208904436742
H	8.44263695643291	-1.54929765042306	-0.74199269018159
H	5.92093330722065	-3.50529434596431	-2.64996752900673
H	6.81233111696540	-2.10001114890982	-3.28046736416248
H	7.64506949416261	-3.31022718330771	-2.26944774468617
H	7.15345834365507	-3.44385925753195	0.25356659212005
H	5.95034918755366	-2.34129813798098	0.97548716757682
H	5.42496274913234	-3.66319573895122	-0.09655204574933
H	2.80099591285169	-2.47580783359601	4.03931131657359
H	2.92782328474977	-1.06801805775305	5.12896789938367

H	1.35094594220055	-1.85153325460166	4.86146386260727
H	2.02261288952328	1.23058476953895	4.36772172782481
H	1.10507610033169	1.34627724633955	2.83596707309645
H	0.42718835071239	0.46888677849754	4.22377132320147
H	4.02591482286116	0.27556252961078	3.28056675568006
H	3.26005524797995	0.43667287201316	1.68533266296629
H	3.94117246004653	-1.12862386226224	2.19519998976002
H	-7.64443934499181	-2.18288265321814	-2.22045673096968
H	-7.65212356393465	-1.11783582683881	-0.78895479836921
H	-6.73651348649161	-2.64348566388254	-0.76268736632227
H	-4.08085513577764	-1.51271101571668	-3.24446019066891
H	-4.57221717468545	-2.86103081236078	-2.19819723676444
H	-5.55329820538488	-2.44727314924764	-3.62613709159420
H	-6.88535809447698	0.82571768584250	-2.31605571135898
H	-6.93276921806674	-0.33111027563054	-3.66785442824492
H	-5.45899787618239	0.61060811889095	-3.36562434072783
H	1.81776163354314	6.01707726020500	2.83674103291289
H	0.39822428100132	5.91275114263784	1.77758907928983
H	0.64310824091224	4.70384789945007	3.06856084516971
H	1.84997260386287	5.97380859677427	-0.22216089663380
H	3.26614562025971	6.15621951959525	0.85011204465303
H	3.25119673365175	4.92796886048081	-0.43832002468253
H	3.67998330193546	4.50142884586715	2.72855221202405
H	3.75128168612712	3.13370519550905	1.60042904251124
H	2.59145352643999	3.10833045739452	2.95229461017321
O	3.30960357939263	3.23538788175369	-2.20318942205452

Structure 10a (Phenoxathiin – S as sulfoxide, oxygen in)

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C	-0.71964553315057	-1.63727758336196	-1.21805853632555
O	-1.14718302099428	-0.68335508255730	-2.11394479663374
C	-2.38662759849035	-0.15018470075437	-2.01093631570837
C	-3.47272030398726	-0.91451333381283	-1.62056321951517
C	-4.72707299624676	-0.33879963558664	-1.40473107979604
C	-4.92717866265201	1.03452563741995	-1.59774371643489
C	-3.81343126286216	1.80711991650773	-1.97996855153105
C	-2.55816895037251	1.23160355743166	-2.15768370524207
S	-1.11289587705256	2.30908959570873	-2.08270221892688
C	-0.60727454749293	2.00108023549210	-0.35826294430034
C	-1.51715128513871	1.41546764468850	0.53230182867533
C	-1.18806152296068	1.13212230447186	1.85887601939174
C	0.07988952715233	1.52633276473408	2.29857046482621
C	0.97958270146306	2.12846120022136	1.42816659526276
S	2.64342371963192	2.40577155296562	2.06238372919320
C	3.51465389839162	1.17041444384514	1.09796224081083
C	4.35104623246190	1.62112498183648	0.08366144194882
C	4.87431629977216	0.74566025669854	-0.87961991409036
C	4.49756793335978	-0.60057955377038	-0.79002712939162
C	3.64559512095675	-1.04172552598560	0.22823687630446

S	2.99228135433335	-2.71170450116914	0.12945298051867
C	1.20052404114360	-2.50719629443164	-0.09001112054807
C	0.38510538320895	-3.45956341488801	0.51587349364025
C	-0.99446560445240	-3.56043156031370	0.27513892030455
C	-1.55037557334793	-2.60085938580763	-0.62147577604584
S	-3.28669119220771	-2.68827542862226	-1.30819494182161
C	0.68088773711482	2.36239842782523	0.07114640066436
C	3.15091232113219	-0.18215689613997	1.21149454816552
C	0.66444120889779	-1.55973894190279	-0.95865712105891
O	1.62201272012678	2.84320541285137	-0.76859506668246
C	1.58919991408164	4.24797582028179	-1.06404149408328
O	2.24584636739733	-0.61819085000926	2.12204192883258
C	2.76872637025781	-1.06796564043617	3.38508426212937
O	1.39651289480862	-0.54034178840719	-1.44850929841795
C	1.72851688807431	-0.53115845395149	-2.84158415692761
O	-0.08056769106819	1.86779637657231	-3.02107325701975
O	-1.60961094406905	3.69359559206887	-2.15806136094660
O	2.63946883566977	2.03712444990527	3.48652306539800
O	3.13359710747761	3.72904122132450	1.65491864391778
O	3.51641451413406	-3.29613071308224	-1.11494985828880
O	3.19021495287008	-3.42510193005189	1.40107638248374
C	-6.26177703193883	1.72848178262596	-1.29238538739521
C	-6.04216003250589	2.68131630619757	-0.09662925795336
C	-7.35988720964444	0.72361354710562	-0.91519885143388
C	-6.72187101123563	2.52942170753869	-2.52701431082356
C	-2.12429166052573	0.36056759228483	2.79491452707917
C	-2.56343315454864	1.28346470154994	3.94887336398850
C	-1.34853912621555	-0.85145993275746	3.35819511655625
C	-3.37315112823598	-0.15369306521470	2.05962784846866
C	5.70772581097195	1.32162815434180	-2.03406334126377
C	6.88359566322826	2.14536773124755	-1.46930923418165
C	4.79745484161464	2.24111383881934	-2.88078369721029
C	6.26963907312457	0.21956377651070	-2.94119060134739
C	-1.77784473890309	-4.69814840605579	0.97409598763933
C	-2.73480650103755	-4.10507367159244	2.03105074245901
C	-0.82487367318303	-5.65656595772229	1.71593405801257
C	-2.54398184198325	-5.55631367607833	-0.05715380376896
H	-5.51511073737615	-0.99063630359665	-1.02971263128240
H	-3.87461526810887	2.89383383445455	-2.05728616977211
H	-2.50698388175364	1.15030433720955	0.18217781648773
H	0.41542491937805	1.34375180361439	3.31826799131396
H	4.53799177198267	2.69391057005175	0.03449730056745
H	4.80090117033336	-1.33418358003772	-1.53522948688887
H	0.87945022608276	-4.15619337002552	1.18696155013084
H	2.35204971272955	4.41381296798644	-1.83422948569423
H	0.60439492725660	4.54174278363739	-1.45755636534918
H	1.84534988554103	4.82156997814007	-0.16076925912499
H	3.47513681633491	-1.89386488455892	3.22329065627593
H	1.90472697801240	-1.43805653771596	3.95084822783326
H	3.23180571118854	-0.22351142022299	3.91489099199757
H	2.50408282379309	-1.28923987627357	-3.03778668399907

H	2.09321482344184	0.47937992328484	-3.05155127647730
H	0.84247641937639	-0.71439270439293	-3.46321763960961
H	-5.69409062293975	2.11924349642272	0.78494590128009
H	-6.98308307825988	3.18804395791764	0.17177706069713
H	-5.29518784877762	3.45715050384406	-0.31988501356032
H	-7.56151283763553	0.00869799877574	-1.72812142640702
H	-7.10311571344368	0.15019658882891	-0.01094605088001
H	-8.29528594731878	1.26500995599335	-0.70617370580814
H	-6.88948731890939	1.86284602201973	-3.38726345318579
H	-7.66581632917066	3.05528080453622	-2.31180111704422
H	-5.98023981705822	3.28570209158394	-2.82415219473229
H	-3.14168573946388	2.13936384513859	3.56592050638709
H	-3.19763173446574	0.73182247511207	4.66202707700519
H	-1.69664498674383	1.67858420504144	4.50110139539992
H	-0.94228201032225	-1.46924682867544	2.54386973425651
H	-0.50741190609966	-0.53549802453156	3.99214390907192
H	-2.01189234773400	-1.47754247164631	3.97562592654768
H	-4.02323519258935	-0.69674526512216	2.76164221953749
H	-3.12370518632712	-0.85101396164996	1.24732720885411
H	-3.96654584548886	0.67046820635645	1.63214554767960
H	7.48055576938815	2.56528371963212	-2.29491560185520
H	7.54543830133224	1.51927262468709	-0.85040378336549
H	6.53669994574020	2.98568054651768	-0.84916784230951
H	4.34834297029514	3.03979855182877	-2.27263171446340
H	5.37722381077304	2.71250880868283	-3.69078249435235
H	3.97483900796017	1.66745611131440	-3.33327631172674
H	6.88347978526306	0.67192016334296	-3.73577160012466
H	5.46977895736623	-0.35691484127377	-3.43093091364400
H	6.90658288132502	-0.48223715187041	-2.37990513864030
H	-3.47521812516179	-3.43756024775573	1.57576327035901
H	-3.27489877273649	-4.92094992636357	2.53864741398041
H	-2.16283043255802	-3.55334845048719	2.79131071953357
H	-0.10097115187152	-6.13587261313977	1.03839229717203
H	-0.26979458247402	-5.15179937125578	2.52083924053378
H	-1.42415333804826	-6.45156953970861	2.18358022826627
H	-3.38204700877824	-5.02542807471114	-0.52271670601869
H	-2.98243233375030	-6.42758548403932	0.45427081705236
H	-1.86430564470567	-5.92839764738579	-0.83988624122647
O	-4.34934332187708	-2.96054854092460	-0.26405818763517

Structure 11a (Phenoxathiin – S as sulfone)

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C	0.82702356456189	1.44225960384646	-1.28754943633756
O	1.29392467199445	0.36321331739279	-1.98703630399314
C	2.50997012882132	-0.17403305789957	-1.77201256662140
C	3.59254709531552	0.57942000475548	-1.34286112043496
C	4.80632748215554	-0.02547831751242	-0.99304086203969
C	4.96686714036563	-1.41253657308174	-1.08499791315118
C	3.85749823141786	-2.16820565044609	-1.51656142536457
C	2.64270158384757	-1.56841621740247	-1.82509061264834
S	1.15619917918537	-2.58575842922741	-1.71690511014692
C	0.62039064808742	-2.11075911515033	-0.03727103738268
C	1.53808182602801	-1.52942446853752	0.85249381578326
C	1.17353024493968	-1.09581602294227	2.13056999594498
C	-0.14499133500743	-1.34157216672916	2.53000477143995
C	-1.04687194728572	-1.94693294741401	1.66696968382139
S	-2.74360046964087	-2.09681096558238	2.23531841962204
C	-3.56223112074915	-0.96936087777034	1.10487796240742
C	-4.52287249709640	-1.50487491919838	0.25830114729204
C	-5.09635223547170	-0.74573120688597	-0.77107973097666
C	-4.61208159152532	0.55584240846310	-0.95530133920524
C	-3.63969592538228	1.08372259129230	-0.10178522402712
S	-2.96381786159144	2.70591328986510	-0.49973573867719
C	-1.16209785023379	2.50035077440890	-0.50041390676455
C	-0.38579978690120	3.49966282153292	0.08132447239023
C	1.01660191962929	3.52197749224267	0.00938523373173
C	1.62810187141965	2.44590306348954	-0.70469890278522
S	3.39520031494732	2.34412143660225	-1.17581660616624
C	-0.71157317731694	-2.32666161919385	0.35423356105217
C	-3.12249574550884	0.35810512521485	0.97440093082246
C	-0.57859057184265	1.43720423890109	-1.17755008587692
O	-1.66363548469265	-2.80067637080863	-0.47397805903192
C	-1.70937818738879	-4.21712810710924	-0.69806929406524
O	-2.14219795533341	0.87796598176068	1.75418890388319
C	-2.57108376964838	1.56744995757368	2.94237062336783
O	-1.30156369447800	0.38156575317901	-1.59610484087346
C	-1.59727280419589	0.24345343533026	-2.99240577453833
O	0.16029432012471	-2.18519137787859	-2.71056303303185
O	1.60558705746857	-3.98753847118011	-1.66478674856207
O	-2.80011274949367	-1.55990235101243	3.60326548502741
O	-3.23905966624969	-3.45549088175949	1.96872234269454
O	-3.36357407603002	2.99358453549589	-1.88736091776735
O	-3.29057955513984	3.67151183868147	0.56140364946395
C	6.22549752743611	-2.14238672580643	-0.59888375169164
C	5.83465605083637	-3.01560697822702	0.61580542198188
C	7.32334260489559	-1.16168009863548	-0.16359195178491
C	6.77366467989098	-3.03954825690750	-1.72500291145928
C	2.12111863381510	-0.32001059486205	3.05651069554603
C	2.45514291772745	-1.18524843016127	4.28847023315465
C	1.40547614287737	0.97549106907988	3.50413791487853

C	3.42649899466097	0.07074051074439	2.34614824350299
C	-6.13930434712602	-1.40191111530797	-1.68149081302726
C	-6.73216745134450	-0.40470113394696	-2.68493108959358
C	-7.28259901843978	-1.97308574891333	-0.81722211956469
C	-5.45433190581632	-2.54733633894146	-2.45806150912501
C	1.76714821702682	4.69762035321149	0.68112395205728
C	0.77794700189428	5.74420358004233	1.22836187444913
C	2.65972286162412	5.43592347234734	-0.34000196233229
C	2.58225298084174	4.18948599828111	1.89167139283685
H	5.58929819871839	0.61781066838168	-0.59467530189631
H	3.88070444408166	-3.25943686178649	-1.51063261489343
H	2.56352793294172	-1.38420924593999	0.53354331405760
H	-0.51385515329216	-1.03875026737715	3.50884188178777
H	-4.78320746869957	-2.55416259452629	0.40109678970460
H	-4.94480262892222	1.17840471670046	-1.78478959302426
H	-0.92488370870233	4.28720762948237	0.60022023551365
H	-2.46533134929177	-4.37534925705792	-1.47690324454667
H	-0.73748817365359	-4.59347435841160	-1.05116710532998
H	-2.01858317723848	-4.72603737941544	0.22737797766405
H	-1.65950280679456	1.97010020211887	3.40279820467472
H	-3.05563218991168	0.85719527905319	3.62794452375234
H	-3.24128964355319	2.39690608375308	2.67463588203752
H	-2.14755527406418	-0.69989717195770	-3.08097270996171
H	-0.67430894177428	0.16859432408696	-3.58188797579427
H	-2.21698448558727	1.09198882518888	-3.32111003257637
H	5.08486472162070	-3.77641775957912	0.35217130629272
H	5.41567757933205	-2.39558123069813	1.42353354829548
H	6.71981451568287	-3.53770457138902	1.01222565761324
H	8.20488982805908	-1.72482476069960	0.17878830213984
H	7.64110619564711	-0.51192152493168	-0.99393802760407
H	6.99913757359005	-0.52107989020324	0.67111444028618
H	6.03186794365762	-3.78194234410539	-2.05586447648600
H	7.06723053894378	-2.44033828732325	-2.60079047764427
H	7.65980109637950	-3.59043078726972	-1.37177660845650
H	1.54428091683199	-1.49591829922761	4.82408002256243
H	3.00021279163922	-2.09528557099231	3.99214123295982
H	3.08790319956117	-0.62198944779442	4.99359918450345
H	1.05385530069175	1.54777552159209	2.63283383368632
H	0.53537019396747	0.76079178300932	4.14222784507135
H	2.09195552877397	1.61247147902272	4.08371910265077
H	3.99137630677183	-0.80911801842153	2.00235944676756
H	4.07621469647102	0.62999121764094	3.03606502317653
H	3.24521079258149	0.71914160873584	1.47853911108242
H	-7.21877988417650	0.44102142785677	-2.17425297783709
H	-7.49192984082483	-0.90963334434165	-3.30144037143753
H	-5.96676502182384	-0.00137847980977	-3.36631061800225
H	-7.78949546324035	-1.17266856105334	-0.25524666591293
H	-8.03067462817792	-2.46965408025572	-1.45541279094001
H	-6.92062094742719	-2.71668774940926	-0.09089362439506
H	-5.01165529583842	-3.28957706032278	-1.77677179794865
H	-4.64739683917408	-2.15790196032658	-3.09824996685732

H	-6.18350104680032	-3.06994505491585	-3.09899683938527
H	1.35382402778651	6.55791746913924	1.69305818274268
H	0.15524527585053	6.18620485503804	0.43564261810390
H	0.11676871721398	5.32893871204253	2.00406036815443
H	3.49200431144038	4.83613619239532	-0.71762747124586
H	2.06152941535084	5.77398343915238	-1.20016608557148
H	3.09815260223854	6.32408365367459	0.14147520439387
H	1.91179417089867	3.75054973627173	2.64450932422000
H	3.10514150503573	5.03901023064633	2.35981674028547
H	3.33292521479089	3.44758829574599	1.60603604088219
O	4.32856989200539	2.73681042135263	-0.10708868584256
O	3.51476992310683	2.97601090415741	-2.49294647087656

Transition state for oxidation of sulfide **12a** to sulfoxide from **9a** (Transition state for oxidation of sulfide to sulfoxide from outside)

118

C	1.01134803549236	0.46322914847080	0.58902991358694
O	1.33622776664129	-0.08036130239285	-0.62027597116009
C	2.39300554954174	-0.89241142446387	-0.80366431517942
C	3.52235910877183	-0.88442741365943	0.01199705791638
C	4.58358118254319	-1.76955045988690	-0.22956744074214
C	4.54024955013951	-2.68779000846608	-1.28556528647133
C	3.37011268718930	-2.71916787626677	-2.06868903376361
C	2.31499183341710	-1.85096654836443	-1.82188862305488
S	0.76189477718552	-2.08648882252705	-2.71530339485513
C	-0.34891762945379	-2.52011764938498	-1.35243336937063
C	0.20471450898410	-3.17820238135612	-0.25292485988678
C	-0.54710978298554	-3.50018811077395	0.88419055454315
C	-1.91487817158844	-3.21691298243203	0.84126453883702
C	-2.47863752883234	-2.59979997084745	-0.27299710118076
S	-4.24433026542330	-2.24744382893572	-0.21525554000209
C	-4.24637378398692	-0.45935212189796	-0.07449776452205
C	-4.78216945192310	0.28384864369556	-1.12136811735523
C	-4.68886297730013	1.68430308823265	-1.14352452477942
C	-3.98346011356112	2.29547400538884	-0.10013061193266
C	-3.43643151318917	1.53801434103971	0.93640208261832
S	-2.29972879916838	2.36283042039122	2.05197061975436
C	-0.73327372507624	1.47617141262122	1.86385451544174
C	0.10131531686434	1.48459745001886	2.97983306709394
C	1.43202857542397	1.04881188765713	2.93186428786550
C	1.88352651900343	0.55000795043675	1.68451430812459
S	3.62273013391258	0.27817629489829	1.33654714380114
C	-1.72016017554693	-2.20043543389095	-1.38524489667392
C	-3.58258650801286	0.15012571545906	1.00034818449885
C	-0.30408356261162	0.95589634747215	0.64183364354948
O	-2.29837935001874	-1.49080343604184	-2.37363855901033
C	-2.54123430596223	-2.15083539124661	-3.62169672870321
O	-2.95635404822572	-0.57383334358709	1.96052367218722
C	-3.68394945280738	-0.80540061547405	3.17868450008450
O	-1.12009896995878	0.81954076686331	-0.41844542843312

C	-0.86984083639558	1.58334156982986	-1.61103033235636
O	0.35210218208331	-0.82287010619801	-3.33014414974800
O	0.94035200247313	-3.28626177966697	-3.54942554390152
O	-4.76614985336231	-2.83456981227188	1.02872737871794
O	-4.85680366845158	-2.60670946892992	-1.50214487722822
O	-2.09311843942933	3.71635599919376	1.51817052102530
O	-2.72088743257057	2.18733962542297	3.45165323984502
C	5.67735520686346	-3.67386502393284	-1.58417827558066
C	5.14136638443277	-5.11416203527379	-1.43038369506188
C	6.86616303837929	-3.48656131280125	-0.62964261923876
C	6.16670569557692	-3.45507922171447	-3.03170519990092
C	0.15642485643974	-4.04206454217392	2.13452674045082
C	1.05102728417389	-2.91154871532454	2.69364383324139
C	1.02574289594114	-5.26314524451979	1.77439636486053
C	-0.85109943285165	-4.45265385937699	3.21878173983793
C	-5.25413979889643	2.46877212294246	-2.33378071237653
C	-5.11831907964951	3.98581913467209	-2.13273548181143
C	-6.74710778871939	2.12522161963914	-2.51418200207011
C	-4.46825665831308	2.06407578322284	-3.60049683255867
C	2.33305064615583	1.18583436578014	4.17666208310495
C	2.92829809773513	-0.18530169097711	4.56441647151542
C	1.53446553563287	1.69383841743734	5.39120469407447
C	3.44521425349693	2.22528755620194	3.90336853973870
H	5.44681897386665	-1.72715833084246	0.43397413391974
H	3.23410850380465	-3.45502756968720	-2.86265698806363
H	1.26913485963044	-3.40700876748030	-0.26324708244211
H	-2.57924926751069	-3.44883655770259	1.67071968659665
H	-5.24262436718932	-0.27011953260019	-1.94015875445240
H	-3.78631903657156	3.36627832550209	-0.09136634413703
H	-0.31733269625012	1.88373416814643	3.90025039564822
H	-3.38281622937569	-2.84981874636555	-3.50243544791648
H	-2.80197395708039	-1.36273776942257	-4.33886822356901
H	-1.64306038747635	-2.67825449304288	-3.97647395888144
H	-3.92243963270185	0.15225921819185	3.66256872690951
H	-3.00838860385659	-1.38220090145091	3.82417286677725
H	-4.58628518721267	-1.39620131869461	2.96525603997421
H	0.20558341767380	1.73504626748927	-1.77004566267380
H	-1.37478526313407	2.55625902271182	-1.52163798283770
H	-1.27887385244020	0.99326844486942	-2.43753628169749
H	4.31809187751582	-5.32123640804431	-2.13058587629014
H	4.76964334473138	-5.28939567146831	-0.40802144210763
H	5.94235826159201	-5.84281389985078	-1.63334322515911
H	7.29573749903718	-2.47513756847589	-0.70380186314724
H	6.58415703155980	-3.66850665254980	0.41949714293822
H	7.66192694521217	-4.20272597847826	-0.88475690543690
H	5.36085967862947	-3.61393194147389	-3.76406926230375
H	6.55077013388921	-2.43202850107390	-3.16809880974832
H	6.97789297811037	-4.16166045386807	-3.26913835888577
H	1.55250021041384	-3.23710194434231	3.61935162537463
H	1.83153364288416	-2.61911472804321	1.97382086040580
H	0.45573514598191	-2.01285235433688	2.91793875215102

H	0.41294964244901	-6.07283358184499	1.34829316745962
H	1.80946118935920	-5.01091357486877	1.04314760851816
H	1.52907783095466	-5.65104627438414	2.67434757029399
H	-1.45280871556725	-3.59694978114905	3.56120026967192
H	-0.31506269062540	-4.85019004967775	4.09417826128735
H	-1.54004550464954	-5.23380061455543	2.86170835086178
H	-5.64258899739855	4.32416671284621	-1.22535273651832
H	-5.55929951589290	4.51433444287295	-2.99176756035371
H	-4.06557439417830	4.29900777423689	-2.05831117996031
H	-7.32466223932806	2.39253541724225	-1.61517861741098
H	-7.16525886345226	2.68198578227801	-3.36801622966383
H	-6.90126668375187	1.05295157635160	-2.70823809059301
H	-3.39801607692091	2.29557221791517	-3.48613116127792
H	-4.84774996757514	2.61042491998995	-4.47899659746763
H	-4.55775101201991	0.98652849269190	-3.80775192682517
H	3.52666609172858	-0.63290234745203	3.75923591044344
H	3.58306167060793	-0.07294018758019	5.44305427480312
H	2.12728207037882	-0.89462816168508	4.82315644969357
H	2.20245098512807	1.74135314858718	6.26434521143868
H	1.13326823726589	2.70480726556986	5.22771077506316
H	0.69966225841161	1.02370906692383	5.64671003840337
H	4.17591180505876	1.88996360662679	3.15320390648754
H	4.00971657025766	2.41787789695655	4.82933300165857
H	3.01254380739496	3.17169286428597	3.54780193854713
O	3.41338692672283	2.02004124775617	-0.02700641879806
H	3.25521554461124	2.59159279492998	0.76955195261852
O	2.62790626770829	3.36054410877330	-0.96980615931256
C	2.07541168826738	4.06942960501236	-0.05288530728563
O	2.22475553038450	3.95342901664000	1.15728869046765
C	1.07463948749259	5.12137447476843	-0.60487182792375
F	0.97433452222463	6.15526712687502	0.22456764514825
F	1.43717650580982	5.57415140950112	-1.80798492093506
F	-0.13558499992242	4.54962747211876	-0.71974764049242

Transition state for oxidation of sulfide **12a** to sulfoxide from **10a** (Transition state for oxidation of sulfide to sulfoxide from inside)

118

C	-0.08236606436745	-1.45817256051745	1.12394134294492
O	0.31963045886231	-0.27019284588866	1.64233325862651
C	1.60557910712727	0.06252300558941	1.88811188430678
C	2.64591810748071	-0.85261773813133	1.96899853271402
C	3.94932406219434	-0.41831718307069	2.24545849734077
C	4.24640996666793	0.93700861704627	2.41073610680075
C	3.18779851943562	1.85544223956755	2.28429041504312
C	1.89492680222971	1.42481157720487	2.02156749749563
S	0.58259335102321	2.64510251602114	1.79972795570607
C	-0.02285314134025	2.28935835173345	0.12860487810849
C	0.89267173914386	1.82581449220858	-0.82075526511086
C	0.49958504669189	1.51496789492194	-2.13385837178785

C	-0.83826198123812	1.73078048170845	-2.47060143472139
C	-1.74554799324922	2.20666117745371	-1.52842038764623
S	-3.45688737420750	2.38287473065556	-2.05669250828656
C	-4.28006594729181	1.07347583263194	-1.13907902602626
C	-5.26481126357630	1.43904277423203	-0.21907056773794
C	-5.86861024842202	0.48997224778459	0.61356555420551
C	-5.40478021262394	-0.83283669371698	0.52012513279695
C	-4.41806616234685	-1.18458757800681	-0.39539177603262
S	-3.71079553057531	-2.82622464747662	-0.25854338939827
C	-1.96246159904949	-2.58631110333078	0.16184617012630
C	-1.15456055695158	-3.70719530831356	-0.05007176535371
C	0.17796343932865	-3.77664397113416	0.36722751989623
C	0.72377913341791	-2.59629299253896	0.95892932597808
S	2.42243180544671	-2.54980401848039	1.50733757859701
C	-1.37910227192133	2.48647135577139	-0.20434954286672
C	-3.85154383869847	-0.25111174491270	-1.27571903038057
C	-1.45120281691682	-1.45009552984680	0.77983736259927
O	-2.32487889360377	2.85404867671492	0.68644322776074
C	-2.35880019453826	4.23014194931487	1.08304329126776
O	-2.81730217008563	-0.59856207298993	-2.07623717434180
C	-3.13390943299620	-1.05771309530790	-3.40280055910970
O	-2.17215984930048	-0.32942849276042	0.96693268440261
C	-2.56842068603891	0.01336847773183	2.30255526968427
O	-0.46642325975314	2.37573026065926	2.79024966554529
O	1.23074178354882	3.96580240991601	1.77369775806888
O	-3.50785267796235	2.05762107406086	-3.49133403330985
O	-3.99525245186427	3.66669422669460	-1.58429920690384
O	-4.33650410478066	-3.46599783657301	0.90901531399978
O	-3.73477184790353	-3.51891762049974	-1.55585257284718
C	5.67376592580719	1.44532224515067	2.65368204047816
C	5.77358710785527	1.94041157871322	4.11237444670074
C	5.98268785587090	2.60846303889990	1.68559499315300
C	6.71868482465727	0.34145970541404	2.42282281168512
C	1.49290651567971	0.87878873475877	-3.11233047953698
C	0.89030727692666	0.71314848338145	-4.51621998959891
C	1.84651150399434	-0.52127134347013	-2.56214789440635
C	2.75619730973280	1.75543719180941	-3.22903911106585
C	-6.94080843529997	0.85259003179499	1.64953640118409
C	-8.22363225373622	0.04934012451206	1.34951624380132
C	-7.27712095423966	2.35126309536362	1.61874472585244
C	-6.42307959342207	0.49469334796419	3.05927117702057
C	0.93669892117128	-5.12055799409673	0.23941288404807
C	0.08928190770353	-6.17162342235561	-0.50387750254684
C	1.21747176120228	-5.67439822444966	1.65532657159347
C	2.25834567621564	-4.97926314555945	-0.55338255841640
H	4.74504404970959	-1.16096774971187	2.25281068558340
H	3.35503345879168	2.93086559811620	2.34612437012030
H	1.93066425036786	1.66046845476255	-0.52280648444186
H	-1.21908104743706	1.51929719583226	-3.46699038464530
H	-5.51287867347011	2.49742906305860	-0.15867256380944
H	-5.76551523673794	-1.61127211961905	1.19344557015858

H	-1.61834665327756	-4.55618476096432	-0.54522355816806
H	-3.01454197157121	4.28236262327467	1.96109569297418
H	-1.35672939482445	4.58867369663592	1.36194302768083
H	-2.77380863652537	4.83334436015844	0.26133502120991
H	-2.16818599608429	-1.26501495248598	-3.88187536989088
H	-3.65921845333625	-0.26516785615862	-3.95377603105660
H	-3.72249823349409	-1.98409633395066	-3.34817390327506
H	-3.22581431974566	-0.77361531062233	2.70692957684463
H	-3.10944585609857	0.96003391446193	2.20756580378793
H	-1.69267566024878	0.17478533227057	2.94419516859449
H	5.57598816584950	1.12162969916080	4.82263459568288
H	5.04664589985720	2.74305683025137	4.31230695667197
H	6.78165551226162	2.33692251267794	4.31556123455775
H	5.34797288744426	3.48636211814750	1.87749667820637
H	7.02869540731801	2.92956795856538	1.81162657813056
H	5.82928005899010	2.30071319353605	0.64156304108386
H	7.72732436162703	0.74924409491530	2.58898061596090
H	6.59221328384820	-0.50442143079363	3.11673439307466
H	6.68108708170878	-0.04182402894794	1.39130000194253
H	0.58031207525690	1.67838419238080	-4.94624317271852
H	1.64396061549895	0.27405446529289	-5.18770459626796
H	0.01775088798194	0.04131516722077	-4.51626701179307
H	2.59115601610547	-1.01402268074942	-3.20788140847679
H	2.26956053765964	-0.47008502151709	-1.55161182406151
H	0.94527823777609	-1.15515295940815	-2.52033534733916
H	3.49615359901837	1.26833221759264	-3.88410906412065
H	3.23886339051198	1.92551012919480	-2.25880122246750
H	2.50685656934201	2.73507352336921	-3.66650517886383
H	-8.61054793931116	0.28863748050097	0.34660882893137
H	-9.00679207678512	0.29024535500192	2.08634280212719
H	-8.04478522055581	-1.03600166239843	1.39315724542592
H	-7.66500015397343	2.66306524354312	0.63669079185026
H	-8.05167240301899	2.57269691262759	2.36895088366681
H	-6.39920543614728	2.97282809895913	1.85400938209806
H	-7.17554219852630	0.75753105518227	3.81992619225956
H	-5.49741758378784	1.04497371521109	3.28985845340092
H	-6.21117071645349	-0.58078215375666	3.15889725298948
H	-0.85423942724587	-6.39102102814414	0.01618153716374
H	-0.14418693054301	-5.86082177796924	-1.53374613896664
H	0.65731123257233	-7.11201600003445	-0.55949349881832
H	0.27413208028846	-5.84546108790458	2.19601692471679
H	1.75146869439934	-6.63548489054769	1.58503426338533
H	1.83425459140385	-4.99410231868268	2.25965566479680
H	2.11334934325716	-4.37868399299540	-1.46578408107823
H	2.61178461454771	-5.97497355838733	-0.86087416803615
H	3.06796979891482	-4.54229884812626	0.04609262768253
O	3.73025376274788	-2.01822923227885	-0.19669617732453
H	3.65684608340469	-2.83212230391831	-0.72746127483314
O	4.91369057263233	-1.41033405093709	-1.43291443851862
C	4.97704940125474	-0.13534249999093	-1.27797228757357
O	4.32464993392140	0.60651948692018	-0.57359784962277

C	6.11999811465112	0.45155410915651	-2.16691097991080
F	5.98049826959048	0.08463090618094	-3.44833248986421
F	6.12144217740129	1.78411567462147	-2.11479483809580
F	7.31152534487661	0.01537614286141	-1.72955395821887

Transition state for oxidation of sulfoxide **9a** (from inside) (Transition state for oxidation of sulfoxide with oxygen out (from inside))

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C	0.04907876701546	1.01385307369976	-0.86049162574037
O	0.21001408046357	-0.14160127395400	-1.55802989956316
C	1.32857219718538	-0.89714263447084	-1.48707419574613
C	2.58709461298429	-0.38323081338770	-1.15767944948189
C	3.70267795105890	-1.22128257953483	-1.02717548066795
C	3.57907801489878	-2.60788286168133	-1.22827850962161
C	2.30665244012124	-3.11186783579461	-1.54708904589265
C	1.19848197689556	-2.27678946158948	-1.65942062666785
S	-0.44519605580700	-3.02461300016705	-1.72258682564423
C	-1.05859699996121	-2.57083440830975	-0.07701693274167
C	-0.10772233579528	-2.39345129431302	0.93560841967567
C	-0.45284265676478	-1.95927648620391	2.21654127329914
C	-1.81925558045106	-1.80721508505016	2.48882529182405
C	-2.76995594324544	-2.03174802474966	1.50086918916275
S	-4.49847409539076	-1.78329081350167	1.94507782380638
C	-4.89569800370368	-0.30776831970930	1.00335715064661
C	-5.85478476522329	-0.40052417157277	-0.00690500495569
C	-6.09957825618785	0.67102116827310	-0.87410038724250
C	-5.29705824151027	1.81456426023975	-0.72371015225371
C	-4.34079212336549	1.89100128626925	0.28350026661490
S	-3.19216133219605	3.26441045686224	0.25100003545330
C	-1.54311583294755	2.52149325159886	0.09064426044850
C	-0.49798776636150	3.26297314846646	0.64711965018624
C	0.84615767422422	2.94470805283755	0.43608352019561
C	1.10293625009691	1.79261762563224	-0.35734878031594
S	2.72913769221971	1.39248021291769	-1.08266711881966
C	-2.42668713999204	-2.38076565456192	0.18072705096122
C	-4.14072039220615	0.85257448949570	1.20088284731619
C	-1.30212103321210	1.37188991754810	-0.65702160612796
O	-3.38632342758772	-2.44658416317080	-0.76308196555742
C	-3.76276405927140	-3.74214269974140	-1.24679901302425
O	-3.14554977265991	0.92686957579079	2.11777015295435
C	-3.49170212741053	1.47548191925493	3.40297845861387
O	-2.29286772475920	0.56211863635339	-1.07058561167667
C	-2.58688189624501	0.47125759596118	-2.47242338564582
O	-1.24845121421426	-2.38160524377381	-2.76494636654678
O	-0.24551792198206	-4.48211675179334	-1.74901240820126
O	-4.54006367136213	-1.46912250430345	3.38179274578547
O	-5.30598315114087	-2.89183800254744	1.41844852934823
O	-3.44171059014807	3.99693651664953	-0.99920997361649
O	-3.20559455467418	3.98531764788293	1.53318438249933

C	4.79093227255179	-3.53028352591025	-1.03600970713690
C	4.45480444524046	-4.98664410003433	-1.39358630216413
C	5.22234878930780	-3.47041720016383	0.44698689031490
C	5.95100007015652	-3.05390197426117	-1.93598833341176
C	0.60330096465005	-1.54433927847666	3.24767457109698
C	0.52732848720707	-0.00536864623811	3.37707878721706
C	2.02477417140308	-1.92708262992415	2.80313105616211
C	0.31227271851210	-2.20220937126986	4.60995726616850
C	-7.13820289634219	0.60943182122196	-2.00165823322765
C	-7.88998118395936	-0.73055054723850	-2.01115435443303
C	-6.42198681263165	0.78020436858323	-3.35867198629350
C	-8.15979788038391	1.74992036986902	-1.80806881950729
C	1.95093575109776	3.80879715823506	1.07288381874836
C	1.36369361968773	4.96895730038491	1.89831880800823
C	2.82780599551536	4.45731263715875	-0.02540766680551
C	2.76953471669218	2.93614187624533	2.05196547049574
H	4.66580791468319	-0.78780233541329	-0.74192660467464
H	2.12850786766189	-4.18057921373681	-1.65726274570079
H	0.93932145468005	-2.55747735047610	0.70113392711797
H	-2.17685322069002	-1.49174230245243	3.46861449287635
H	-6.37440502326723	-1.35179706181860	-0.10886758944399
H	-5.36436489292702	2.65228349378741	-1.41887573493982
H	-0.77485881268901	4.12371265734301	1.25115674978271
H	-4.34537080512825	-4.26221434746447	-0.47127551794219
H	-4.38461130490207	-3.56919164524174	-2.13384870902227
H	-2.88069587637862	-4.33369485169055	-1.53396575647372
H	-3.83495720457990	2.51308776795936	3.28737326500874
H	-2.56573609501723	1.46049447492366	3.99225818784098
H	-4.24860891537112	0.84078474372044	3.88457205341098
H	-1.72018633471899	0.10199851149109	-3.03521918863283
H	-2.92003651939078	1.45450497858404	-2.84159932444813
H	-3.39462132559035	-0.26398117790591	-2.54736355408583
H	3.67193702628024	-5.40460049984980	-0.74132569882456
H	5.35276647369254	-5.60959813090421	-1.26584626267165
H	4.12406063131015	-5.08936061579423	-2.43935668474485
H	6.06691518991358	-4.15726298754013	0.61759426683413
H	5.55133272374420	-2.46183481425230	0.73091508669371
H	4.39559653544168	-3.77733953423092	1.10838126293878
H	6.81063694178871	-3.73355242167824	-1.82328424939496
H	5.65247782549665	-3.05537263390673	-2.99659831005882
H	6.29123519200912	-2.04623381232848	-1.66202108055926
H	1.26842193571515	0.35928842754922	4.10664740111135
H	0.72934789597414	0.47772487621288	2.40839762781859
H	-0.47048999951136	0.32209836564973	3.70531568589958
H	2.32148394926743	-1.41399150077779	1.87514535913417
H	2.74840850471719	-1.63643375582374	3.57948029307452
H	2.12579252462147	-3.01218132795133	2.64309995780958
H	1.06097424254369	-1.88605864311352	5.35343796937692
H	0.34861325388597	-3.30018693497467	4.53259230022859
H	-0.67822905512880	-1.92237748492074	4.99875981978689
H	-8.43102346480706	-0.90281677330942	-1.06785549423194

H	-7.20997655770186	-1.58041639819753	-2.17742693873927
H	-8.63007148632568	-0.73357257516971	-2.82586676852471
H	-5.88761858595633	1.74010172735227	-3.42447193632685
H	-5.68982322433673	-0.02623317918203	-3.52150307664240
H	-7.15334637458433	0.74834149614252	-4.18195241661037
H	-8.68480951391957	1.64797825827979	-0.84530509392037
H	-8.91141154190180	1.72807329383631	-2.61335484323708
H	-7.67646029060731	2.73871993933822	-1.82726600720619
H	0.74361521500363	4.60820201831129	2.73237348589648
H	2.19084710443005	5.55256572862556	2.32971613916839
H	0.75985551580923	5.65361301618872	1.28414619981408
H	3.18135516678818	3.76913998164225	-0.80451616597672
H	2.25064859162972	5.22470768150715	-0.56389067531992
H	3.70259105055348	4.94921246785258	0.42876364578711
H	2.12374171743553	2.58983333925985	2.87258244037187
H	3.58790816048451	3.52934887374363	2.49029062266587
H	3.22017025647169	2.05567844931217	1.58177338744824
O	4.63308378761937	1.53642633616839	-0.11419417588641
H	4.62585129847562	2.51000928875755	-0.15753939276743
O	6.30989382835161	1.79119831124818	0.58090860692412
C	6.91312454315998	0.66027619589110	0.55261352223489
O	2.73355991389203	1.95360347261026	-2.46569827662759
O	6.53965088871599	-0.41642751750294	0.13118127914129
C	8.36064174321570	0.76399568519125	1.13548610113545
F	9.23678574328548	0.82478431153606	0.12377239113196
F	8.53618639842241	1.84110000490637	1.90450723647799
F	8.63507907196262	-0.32043159663586	1.86421175614538

Transition state for oxidation of sulfoxide **9a** (from outside) (Transition state for oxidation of sulfoxide with oxygen out (from outside))

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C	0.04907876701546	1.01385307369976	-0.86049162574037
O	0.21001408046357	-0.14160127395400	-1.55802989956316
C	1.32857219718538	-0.89714263447084	-1.48707419574613
C	2.58709461298429	-0.38323081338770	-1.15767944948189
C	3.70267795105890	-1.22128257953483	-1.02717548066795
C	3.57907801489878	-2.60788286168133	-1.22827850962161
C	2.30665244012124	-3.11186783579461	-1.54708904589265
C	1.19848197689556	-2.27678946158948	-1.65942062666785
S	-0.44519605580700	-3.02461300016705	-1.72258682564423
C	-1.05859699996121	-2.57083440830975	-0.07701693274167
C	-0.10772233579528	-2.39345129431302	0.93560841967567
C	-0.45284265676478	-1.95927648620391	2.21654127329914
C	-1.81925558045106	-1.80721508505016	2.48882529182405
C	-2.76995594324544	-2.03174802474966	1.50086918916275
S	-4.49847409539076	-1.78329081350167	1.94507782380638
C	-4.89569800370368	-0.30776831970930	1.00335715064661
C	-5.85478476522329	-0.40052417157277	-0.00690500495569
C	-6.09957825618785	0.67102116827310	-0.87410038724250
C	-5.29705824151027	1.81456426023975	-0.72371015225371

C	-4.34079212336549	1.89100128626925	0.28350026661490
S	-3.19216133219605	3.26441045686224	0.25100003545330
C	-1.54311583294755	2.52149325159886	0.09064426044850
C	-0.49798776636150	3.26297314846646	0.64711965018624
C	0.84615767422422	2.94470805283755	0.43608352019561
C	1.10293625009691	1.79261762563224	-0.35734878031594
S	2.72913769221971	1.39248021291769	-1.08266711881966
C	-2.42668713999204	-2.38076565456192	0.18072705096122
C	-4.14072039220615	0.85257448949570	1.20088284731619
C	-1.30212103321210	1.37188991754810	-0.65702160612796
O	-3.38632342758772	-2.44658416317080	-0.76308196555742
C	-3.76276405927140	-3.74214269974140	-1.24679901302425
O	-3.14554977265991	0.92686957579079	2.11777015295435
C	-3.49170212741053	1.47548191925493	3.40297845861387
O	-2.29286772475920	0.56211863635339	-1.07058561167667
C	-2.58688189624501	0.47125759596118	-2.47242338564582
O	-1.24845121421426	-2.38160524377381	-2.76494636654678
O	-0.24551792198206	-4.48211675179334	-1.74901240820126
O	-4.54006367136213	-1.46912250430345	3.38179274578547
O	-5.30598315114087	-2.89183800254744	1.41844852934823
O	-3.44171059014807	3.99693651664953	-0.99920997361649
O	-3.20559455467418	3.98531764788293	1.53318438249933
C	4.79093227255179	-3.53028352591025	-1.03600970713690
C	4.45480444524046	-4.98664410003433	-1.39358630216413
C	5.22234878930780	-3.47041720016383	0.44698689031490
C	5.95100007015652	-3.05390197426117	-1.93598833341176
C	0.60330096465005	-1.54433927847666	3.24767457109698
C	0.52732848720707	-0.00536864623811	3.37707878721706
C	2.02477417140308	-1.92708262992415	2.80313105616211
C	0.31227271851210	-2.20220937126986	4.60995726616850
C	-7.13820289634219	0.60943182122196	-2.00165823322765
C	-7.88998118395936	-0.73055054723850	-2.01115435443303
C	-6.42198681263165	0.78020436858323	-3.35867198629350
C	-8.15979788038391	1.74992036986902	-1.80806881950729
C	1.95093575109776	3.80879715823506	1.07288381874836
C	1.36369361968773	4.96895730038491	1.89831880800823
C	2.82780599551536	4.45731263715875	-0.02540766680551
C	2.76953471669218	2.93614187624533	2.05196547049574
H	4.66580791468319	-0.78780233541329	-0.74192660467464
H	2.12850786766189	-4.18057921373681	-1.65726274570079
H	0.93932145468005	-2.55747735047610	0.70113392711797
H	-2.17685322069002	-1.49174230245243	3.46861449287635
H	-6.37440502326723	-1.35179706181860	-0.10886758944399
H	-5.36436489292702	2.65228349378741	-1.41887573493982
H	-0.77485881268901	4.12371265734301	1.25115674978271
H	-4.34537080512825	-4.26221434746447	-0.47127551794219
H	-4.38461130490207	-3.56919164524174	-2.13384870902227
H	-2.88069587637862	-4.33369485169055	-1.53396575647372
H	-3.83495720457990	2.51308776795936	3.28737326500874
H	-2.56573609501723	1.46049447492366	3.99225818784098
H	-4.24860891537112	0.84078474372044	3.88457205341098

H	-1.72018633471899	0.10199851149109	-3.03521918863283
H	-2.92003651939078	1.45450497858404	-2.84159932444813
H	-3.39462132559035	-0.26398117790591	-2.54736355408583
H	3.67193702628024	-5.40460049984980	-0.74132569882456
H	5.35276647369254	-5.60959813090421	-1.26584626267165
H	4.12406063131015	-5.08936061579423	-2.43935668474485
H	6.06691518991358	-4.15726298754013	0.61759426683413
H	5.55133272374420	-2.46183481425230	0.73091508669371
H	4.39559653544168	-3.77733953423092	1.10838126293878
H	6.81063694178871	-3.73355242167824	-1.82328424939496
H	5.65247782549665	-3.05537263390673	-2.99659831005882
H	6.29123519200912	-2.04623381232848	-1.66202108055926
H	1.26842193571515	0.35928842754922	4.10664740111135
H	0.72934789597414	0.47772487621288	2.40839762781859
H	-0.47048999951136	0.32209836564973	3.70531568589958
H	2.32148394926743	-1.41399150077779	1.87514535913417
H	2.74840850471719	-1.63643375582374	3.57948029307452
H	2.12579252462147	-3.01218132795133	2.64309995780958
H	1.06097424254369	-1.88605864311352	5.35343796937692
H	0.34861325388597	-3.30018693497467	4.53259230022859
H	-0.67822905512880	-1.92237748492074	4.99875981978689
H	-8.43102346480706	-0.90281677330942	-1.06785549423194
H	-7.20997655770186	-1.58041639819753	-2.17742693873927
H	-8.63007148632568	-0.73357257516971	-2.82586676852471
H	-5.88761858595633	1.74010172735227	-3.42447193632685
H	-5.68982322433673	-0.02623317918203	-3.52150307664240
H	-7.15334637458433	0.74834149614252	-4.18195241661037
H	-8.68480951391957	1.64797825827979	-0.84530509392037
H	-8.91141154190180	1.72807329383631	-2.61335484323708
H	-7.67646029060731	2.73871993933822	-1.82726600720619
H	0.74361521500363	4.60820201831129	2.73237348589648
H	2.19084710443005	5.55256572862556	2.32971613916839
H	0.75985551580923	5.65361301618872	1.28414619981408
H	3.18135516678818	3.76913998164225	-0.80451616597672
H	2.25064859162972	5.22470768150715	-0.56389067531992
H	3.70259105055348	4.94921246785258	0.42876364578711
H	2.12374171743553	2.58983333925985	2.87258244037187
H	3.58790816048451	3.52934887374363	2.49029062266587
H	3.22017025647169	2.05567844931217	1.58177338744824
O	4.63308378761937	1.53642633616839	-0.11419417588641
H	4.62585129847562	2.51000928875755	-0.15753939276743
O	6.30989382835161	1.79119831124818	0.58090860692412
C	6.91312454315998	0.66027619589110	0.55261352223489
O	2.73355991389203	1.95360347261026	-2.46569827662759
O	6.53965088871599	-0.41642751750294	0.13118127914129
C	8.36064174321570	0.76399568519125	1.13548610113545
F	9.23678574328548	0.82478431153606	0.12377239113196
F	8.53618639842241	1.84110000490637	1.90450723647799
F	8.63507907196262	-0.32043159663586	1.86421175614538

Trifluoroperoxoacetic acid

9

C	0.56459126943917	-0.35773085655753	0.00034459342686
O	0.96574909205356	-1.49055956594137	0.00305544004151
O	1.34645909186742	0.72173035489177	-0.00133487175621
C	-0.92261047138325	0.06475886708013	-0.00006326076901
F	-1.19644979509997	0.79024171717619	-1.08654568433336
F	-1.68816119836450	-1.01775820379571	0.00229213421873
F	-1.19596552397786	0.79467097026576	1.08354158821554
O	2.72842255581843	0.36930658915133	-0.00081666562443
H	2.67418335874701	-0.61664657667056	0.00058920818037

Trifluoroacetic acid

8

C	0.99430540600664	0.10738518305573	0.00005802846824
O	1.59595520401027	1.14205703487140	0.00002592152197
O	1.52764634365881	-1.11531039837685	0.00005435191263
H	2.49617085132030	-1.01686296984980	0.00001121103050
C	-0.54825681991050	0.00957585301401	-0.00002023231498
F	-0.96841518276934	-0.64916664626090	-1.08652008567263
F	-0.96850129594955	-0.65095441637048	1.08534650716807
F	-1.08615357146664	1.22258376891689	0.00094736268620

Energies of structures

	GFN-xTB2	B3LYP/def2- SVP D3BJ	HF/def2- QZVPP	DLPNO- MP2/def2- QZVPP	DLPNO- CCSD(T)/def2- QZVPP
Phenoxathiin – S as sulfide	-172.28373	-4011.0459	-3998.21029	-4009.14651	-4009.73259
Phenoxathiin – S as sulfoxide, oxygen out	-176.32979	-4086.1219	-4073.05154	-4084.25825	-4084.84581
Phenoxathiin – S as sulfoxide, oxygen in	-176.32865	-4086.121	-4073.04048	-4084.25277	-4084.84049
Phenoxathiin – S as sulfone	-180.39608	-4161.2347	-4147.94278	-4159.41383	-4160.00152
Transition state for oxidation of sulfide to sulfoxide from outside	-203.37656	-4612.2734	-4597.54277	-4610.44335	-4611.07957
Transition state for oxidation of sulfide to sulfoxide from inside	-203.38147	-4612.2762	-4597.53563	-4610.44235	-4611.0762
Transition state for oxidation of sulfoxide with oxygen out (attack from inside)	-207.4314	-4687.3467	-4672.38728	-4685.55212	-4686.18818
Transition state for oxidation of sulfoxide with oxygen out (attack from outside)	-207.4295	-4687.3453	-4672.38809	-4685.54762	-4686.18456
Trifluoroperoxoacetic acid	-31.09291	-601.22606	-599.408559	-601.309435	-601.367085
Trifluoroacetic acid	-27.11498	-526.19473	-524.628914	-526.27129	-526.319247