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Supporting Information

SUPPORTING INFORMATION FOR:

Allylic Stereocontrol of the Intramolecular Diels–Alder Reaction

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Computational Section

For transition structure identities, refer to Figure 5 and Table 4 of the paper and Figures S1 and S2.
All calculations were carried out with the Gaussian 98 program [Frisch, M. J. et al. *Gaussian 98*, Version A.11; Gaussian, Inc.: Pittsburgh, PA, 2001], using the hybrid B3LYP functional [Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789; Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652] in conjunction with the 6-31G(d) basis set (B3LYP/6-31G(d)) [*The Encyclopedia of Computational Chemistry*; Schleyer, P. v.R.; Allinger, N. L.; Clark, T.; Gasteiger, J.; Kollman, P. A.; Schaefer III, H. F.; Schreiner, P. R., Eds.; John Wiley & Sons. Ltd.: Chichester, 1998], a combination which is known to give acceptable relative energies and geometries for pericyclic reactions [Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378–8388; see also references 4–10 of the paper].

TSs for IMDA reaction of 4f (refer to Figure 5 of the paper)

trans, like-4fTS-(d)

```
b3lyp/6-31G(d) =-1133.6647933

C1  1.3719368148  0.1253696372  -0.7162629422
C2  -1.0373811762  0.1936940071  0.9450901766
C3  -0.6715691064  -0.8790939262  1.7177101985
C4  -0.1439554192  -2.083130183  1.2080523139
C5  0.156150828  -2.2718712767  -0.1505787167
C6  1.6748245544  -1.2382315844  -0.5416895266
C7  0.6808283995  -3.5996725513  -0.6448769603
C8  2.1001488457  -2.0987098315  -1.7443861754
O9  1.5905764425  -3.3543053616  -1.7291058715
C10  0.6303755703  0.5435383952  -1.8904834077
C11  -1.4898379657  1.5144021085  1.5169361968
C12  -0.0078153823  2.3440556421  -3.2753144723
O13  2.882658374  -1.7489232421  -2.5859932161
O14  0.6816982578  1.8874781826  -2.1028146292
O15  -0.0150319941  -0.2125169713  -2.6115461314
O16  -1.5194855524  1.4391766594  2.9426741683
Si17  -2.5233245102  2.3484460974  3.9092147737
C18  -0.604762872  2.683755369  1.0643076845
H19  1.7638472744  0.8773536997  -0.044723685
H20  -1.1775816433  0.0879659497  -0.1247054062
H21  -0.7021662101  -0.7507455913  2.7957393186
H22  0.2311926184  -2.8112236494  1.9267704332
H23  -0.4900444626  -1.7870466846  -0.8828061265
H24  2.3430345175  -1.4392207859  0.2986906942
H25  -0.1135271722  -4.2353630446  -1.0473230811
H26  1.2077562185  -4.1519177334  0.1441669402
H27  -2.5142198869  1.689906011  1.1413836963
H28  0.1500087722  3.4228884711  -3.3056141361
H29  -1.0756545577  2.1139764304  -3.215509004
H30  0.4034059014  1.8711960637  -4.1711288203
H31  -3.925258421  2.2902403769  3.4040920301
H32  -2.1166252103  3.7799276753  3.9765215982
H33  -2.4378040397  1.7535769062  5.2635374139
H34  -1.0296907548  3.6378830113  1.3946746523
H35  -0.498522313  2.7051572334  -0.0237372658
H36  0.3914097447  2.5752913251  1.5042231408
```

trans, like-4fTS-(e)

```
b3lyp/6-31G(d) =-1133.6645022

C1  0.6239667556  -0.8376517474  -0.5754263261
C2  -0.7415530194  1.5887824029  -0.2161291273
C3  0.2304659737  2.3591308673  -0.8099103333
C4  1.6008734914  2.2831601094  -0.4929574561
C5  2.0956827553  1.3099123274  0.3845745689
```

```
C6  1.9461447704  -0.3698315121  -0.5210345947
C7  3.5635468435  1.2006628161  0.7114213244
C8  2.9980352996  -1.0494304721  0.3645823219
O9  3.8717329457  -0.1844512384  0.9409575667
C10  -0.0118212072  -1.3662752335  0.6247137054
C11  -2.1925097646  1.6594364763  -0.6225564274
C12  -1.7828990376  -2.6544029314  1.4937926283
O13  3.1250150562  -2.2378143472  0.4863904463
O14  -1.0728674371  -2.161644037  0.3475529723
O15  0.3449382299  -1.1013755559  1.7676914982
O16  -2.8072816505  0.3761467396  -0.4674950454
Si17  -3.2630184382  -0.5768020861  -1.7537218284
C18  -2.9600680917  2.6517369891  0.261437467
H19  0.1101649397  -0.9363246074  -1.5221405337
H20  -0.5598635575  1.0940252373  0.7315757251
H21  -0.0532529948  2.9833194671  -1.6576447631
H22  2.3027538662  2.8345050251  -1.1172783207
H23  1.460955853  1.0116021576  1.2188430953
H24  2.3804615941  -0.1414487709  -1.4966292475
H25  3.8258714957  1.7282524594  1.6336110199
H26  4.1952902111  1.5799161527  -0.1025131199
H27  -2.2614327854  1.9977369149  -1.6686394925
H28  -2.5486340301  -3.3219781903  1.0977069877
H29  -2.2443775896  -1.8266090241  2.0393699218
H30  -1.1070136762  -3.1941339049  2.1614843673
H31  -2.1140857698  -1.0105207648  -2.5965268747
H32  -4.1956930512  0.1767610882  -2.6436944669
H33  -3.9586495142  -1.7534330768  -1.185803531
H34  -4.0118079822  2.6808890102  -0.0425463713
H35  -2.5381208456  3.6587494955  0.1784916138
H36  -2.9117937949  2.3356474972  1.3086135765
```

***trans, like*-4fTS-(f)**

b3lyp/6-31G(d) =-1133.6626278

```
C1  0.5757021158  -1.2498129315  -0.9397099123
C2  -0.3163562423  1.2634905109  -0.4033563029
C3  0.9207286162  1.8655104884  -0.4259073626
C4  2.0295216959  1.3834185027  0.3021809511
C5  1.9750885262  0.1756304877  1.0017208243
C6  1.8513223769  -1.2209877632  -0.3662995955
C7  3.1628457459  -0.4087766026  1.7181447104
C8  2.3507427312  -2.3088644162  0.5880999742
O9  3.0860819473  -1.8421739995  1.6304517524
C10  -0.557169926  -1.7839197788  -0.192672251
C11  -1.4913788991  1.6112155494  -1.2879469896
C12  -2.8041051139  -2.4928856441  -0.3092732641
O13  2.2091618589  -3.487884519  0.4058785614
O14  -1.6383470411  -1.9951904945  -0.9854503542
O15  -0.5663670404  -1.971276875  1.0172745835
O16  -2.5900626028  2.0934021235  -0.4903371299
Si17  -2.5454338491  3.2920774541  0.6648352361
C18  -1.2004115132  2.5729568836  -2.4381920548
H19  0.4295810575  -0.9882391701  -1.9796505047
H20  -0.5817954957  0.6199276045  0.428102499
H21  1.1076084497  2.6616797617  -1.1433857487
H22  3.0014748455  1.8365149364  0.1114556759
H23  1.0298395225  -0.1107009658  1.4616695693
H24  2.6507869119  -0.9286373948  -1.049475059
H25  3.1630401509  -0.1712578153  2.7866083929
H26  4.1128766202  -0.0715410855  1.2836478284
```

```
H27  -1.8629542893  0.6687072881  -1.7098282926
H28  -3.5569965695  -2.6267486424  -1.0866144617
H29  -3.1503116062  -1.7758915144  0.4402016144
H30  -2.5847579769  -3.4440707081  0.1824975444
H31  -1.8198037245  2.8795763787  1.8980032535
H32  -3.964227574  3.5579031694  1.0009117094
H33  -1.9134118218  4.5476359189  0.1657243341
H34  -2.1169585702  2.7352482621  -3.0123731326
H35  -0.4411284329  2.1580988398  -3.1103362626
H36  -0.8497052667  3.5458491777  -2.0781239345
```

***trans, unlike*-4fTS-(a)**

```
b3lyp/6-31G(d) =-1133.6666156

C1  0.1898702123  -1.1969095061  -0.502975421
C2  -0.1735488762  1.4099033937  0.2208267543
C3  1.0844111474  1.830914412  -0.1323932204
C4  2.2647400592  1.1838162783  0.2936409605
C5  2.2302603832  -0.0159507189  1.0049107028
C6  1.5584402347  -1.3633302954  -0.2741520824
C7  3.4673789808  -0.7794474862  1.3915820442
C8  2.1273145687  -2.5240025434  0.5419596003
O9  3.1677757018  -2.1864384973  1.3480026925
C10  -0.7791307453  -1.5801833102  0.5130716986
C11  -1.4472569996  1.9625051103  -0.3609083849
C12  -3.0534505876  -2.0050240041  0.9743992493
O13  1.776187147  -3.6682276256  0.4311871941
O14  -2.0497556368  -1.6162117396  0.0253245145
O15  -0.5150696419  -1.7935267888  1.6900789183
O16  -1.15711121  2.7165750936  -1.5383920179
Si17  -2.1770677272  2.8335555396  -2.8478567999
C18  -2.1879967654  2.8415664331  0.6602707543
H19  -0.1755714794  -0.8836170643  -1.4721587763
H20  -0.3171590937  0.7957309518  1.1030848862
H21  1.1665243616  2.6007262192  -0.8949721119
H22  3.2071139573  1.5010382922  -0.1516883588
H23  1.4029183246  -0.1850490736  1.6934545267
H24  2.1932389871  -1.1658775243  -1.1396068125
H25  3.7842926041  -0.5726556587  2.4188248983
H26  4.307450779  -0.5688043857  0.7170101094
H27  -2.0920143436  1.1038974673  -0.6115892196
H28  -3.9956967228  -1.9951644129  0.4250642787
H29  -3.090384624  -1.3038773634  1.8132577102
H30  -2.8471585739  -3.0058082424  1.363021332
H31  -1.4055380569  3.5258942688  -3.9064480807
H32  -3.4077991094  3.6179334348  -2.5442304837
H33  -2.5976422381  1.4816159707  -3.3134209936
H34  -2.3997850682  2.2800768264  1.5768775357
H35  -3.1395989399  3.1912584168  0.2458355822
H36  -1.5766431378  3.712394205  0.9166728316
```

***trans, unlike*-4fTS-(b)**

```
b3lyp/6-31G(d) =-1133.6650775

C1  0.4719588214  -1.4890974235  -0.5363939354
C2  -0.4984072321  1.1921204505  -0.8677157873
C3  0.6862560609  1.6902882639  -1.3571115149
C4  1.9546377719  1.4288505638  -0.8029647041
C5  2.1339141599  0.5409348262  0.269717056
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```
C6  1.8400125608  -1.1985492453  -0.3860295922
C7  3.5037813159  0.3016664713  0.8590578832
C8  2.6697476485  -1.8810013142  0.7148998255
O9  3.5712464687  -1.060757925  1.3087455646
C10  -0.3549321993  -1.6794539839  0.6448337394
C11  -1.8177758622  1.3963210454  -1.5726710046
C12  -2.4081734895  -2.4699676118  1.4951230213
O13  2.6133052866  -3.0505439649  0.9815997272
O14  -1.5460946855  -2.2671451138  0.3647767695
O15  -0.0404392534  -1.3175962297  1.7741202914
O16  -2.783343076  1.9306275449  -0.6543262734
Si17  -2.7404838286  3.4896008083  -0.0673252696
C18  -2.4098909408  0.1098904007  -2.1499194511
H19  0.0443580786  -1.6789373878  -1.5115685798
H20  -0.5682526448  0.7970799402  0.1396023262
H21  0.6574145506  2.2384858105  -2.2988168692
H22  2.8306433663  1.7640277597  -1.3568423656
H23  1.346938594  0.4973984745  1.0230894017
H24  2.4023457845  -1.2118942125  -1.3222940846
H25  3.6916200754  0.9259951154  1.7376306379
H26  4.3020995947  0.4754785889  0.1257897033
H27  -1.6679765348  2.1132418866  -2.3959310126
H28  -3.2954392598  -2.9653440681  1.0995417154
H29  -2.6756198676  -1.5141354382  1.9543510027
H30  -1.917916261  -3.098384847  2.2431850889
H31  -2.5067716965  4.4584308979  -1.178089014
H32  -1.6793393959  3.6986628465  0.9564504982
H33  -4.0660629258  3.7301062315  0.549724189
H34  -2.5308758834  -0.6450798239  -1.3685746439
H35  -1.7558283548  -0.2950931009  -2.9293985305
H36  -3.3887332338  0.3268608605  -2.5895775396
```

***trans, unlike*-4fTS-(c)**

b3lyp/6-31G(d) =-1133.6610764

```
C1  0.5421621879  0.4453716768  0.8890992962
C2  -0.8929629416  -1.4976944024  -0.5234079085
C3  -0.0693211811  -2.5561989497  -0.221167828
C4  1.3364459184  -2.514413818  -0.3043403775
C5  2.0327408873  -1.3315633778  -0.5947866753
C6  1.8004780943  -0.1822327914  0.8945272502
C7  3.5418741586  -1.3074591629  -0.6295572354
C8  3.0776751042  0.6247580238  0.6146232971
O9  3.9889010228  -0.0301649715  -0.1470172922
C10  0.2912782904  1.4978388424  -0.0883676745
C11  -2.3852519853  -1.4740337002  -0.2703123257
C12  -0.9670062615  3.4045133668  -0.6556811276
O13  3.3176741645  1.7036158517  1.0861819943
O14  -0.7365938597  2.3135738162  0.2493272637
O15  0.93091746  1.6346631901  -1.1269480819
O16  -2.6894907326  -0.2778228057  0.4661955004
Si17  -3.9049630803  0.7764549018  0.0442551577
C18  -2.9484872574  -2.6739773892  0.4869094996
H19  -0.1976291582  0.2521048817  1.6531479945
H20  -0.528404329  -0.6849688258  -1.1411222009
H21  -0.5044497815  -3.4430061043  0.2335306407
H22  1.8915483652  -3.3585679733  0.1031039994
H23  1.589808142  -0.6418112839  -1.3132529985
H24  1.9662736791  -0.8468559123  1.7448872582
H25  3.9358219458  -1.4070975531  -1.6455666115
H26  3.9782493066  -2.0971130204  -0.0041035576
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H27  -2.8748304992  -1.4277656399  -1.2595344442
H28  -1.7931441702  3.970713237  -0.224445889
H29  -1.2328289807  3.0357058772  -1.6501326782
H30  -0.0734559366  4.0291394838  -0.7365853211
H31  -5.2279563095  0.0867770303  -0.0124043594
H32  -3.6675512295  1.3834244633  -1.2970144225
H33  -3.9429739485  1.8277449864  1.0850557042
H34  -2.4880905966  -2.7545935485  1.4766636206
H35  -2.7832571481  -3.60790331  -0.0610659746
H36  -4.0266607522  -2.5466659696  0.6221228153
```

***cis, like*-4fTS-(j)**

b3lyp/6-31G(d) =-1133.6614512

```
C1  0.7473730142  0.9103784646  -2.3685404743
C2  -0.4788231236  1.168694937  -1.7352951214
C3  -0.5785366003  1.463638371  -0.3629945802
C4  0.4983054092  1.4612110833  0.4875970297
C5  1.2196205495  -1.0459543592  -0.3468956321
C6  1.4889038234  -0.775118556  -1.6966325241
C7  0.8933362033  -1.6331535225  -2.8132610923
O8  0.8323684433  -2.8338347027  -2.7952158315
O9  0.5350438814  -0.9304430783  -3.9188712578
C10  0.753493774  0.488508552  -3.824518711
C11  0.397065357  1.690871016  1.9748557365
C12  -0.0955895073  -1.5361312244  0.0257670713
O13  -1.0650605859  -1.5190689358  -0.7221809098
O14  -0.1542334259  -1.9796086676  1.3106081386
C15  -1.4580065485  -2.3763636007  1.756087402
O16  -0.9542850815  1.5139180917  2.3996417037
Si17  -1.630336974  2.2924981479  3.7066664173
C18  1.3434841807  0.7935308276  2.7811070871
H19  1.5946058492  1.5130955936  -2.0472254345
H20  -1.3983169829  0.9487466265  -2.2723681031
H21  -1.5689929469  1.5348266833  0.0754803933
H22  1.5104086982  1.5092932538  0.0994912445
H23  1.999969439  -0.9983674579  0.4013576519
H24  2.5428380557  -0.5748058163  -1.9068490457
H25  1.7080185518  0.7281471513  -4.3083355541
H26  -0.0519145937  0.954964737  -4.398094618
H27  0.6932738995  2.7430965354  2.1490184603
H28  -2.1244027035  -1.5095292966  1.7998289566
H29  -1.8861992946  -3.1241853634  1.0839916827
H30  -1.313244503  -2.7937082176  2.7535985496
H31  -1.1428982681  1.7610752815  5.0102875754
H32  -1.3193961801  3.7506267926  3.6591030046
H33  -3.0919468693  2.0723274418  3.6064193932
H34  1.3130010583  1.0594768303  3.8430776311
H35  1.0489420387  -0.2526764318  2.6678008772
H36  2.3765473473  0.9142479956  2.4345755997
```

***cis, like*-4fTS-(k)**

b3lyp/6-31G(d) =-1133.6621904

```
C1  0.2100363128  2.4307779229  -1.1899504941
C2  -0.7121124683  2.366063288  -0.1436665165
C3  -0.4644102796  1.6290378403  1.0291883597
C4  0.6694080169  0.8714140469  1.2078589419
C5  0.3468344127  -0.4613717865  -0.9655559098
```

```
C6  0.4527157333  0.5399399904  -1.9326413694
C7  -0.583069058  0.7355199193  -3.0316995178
O8  -1.0548446852  -0.1574339421  -3.6863886586
O9  -0.8673123801  2.0315067065  -3.3243125311
C10  -0.1910876125  3.0195175986  -2.5231072427
C11  0.88481319  -0.0392378683  2.3887246045
C12  -0.9743608915  -0.9272073531  -0.5516189783
O13  -2.0188144914  -0.3349346214  -0.7749761295
O14  -0.9177726001  -2.088778921  0.155904838
C15  -2.1903041907  -2.6117803538  0.5617538487
O16  1.7945615015  -1.0654543074  1.9819758173
Si17  1.853613121  -2.5917803569  2.6444452548
C18  1.4562396104  0.7292842211  3.5904006994
H19  1.2627420083  2.5005227172  -0.9279984675
H20  -1.7337602487  2.6912910292  -0.327869225
H21  -1.2948671334  1.4934141412  1.7201411355
H22  1.5709119562  1.0758061379  0.6400066271
H23  1.2168499764  -1.0037742504  -0.6202846972
H24  1.4614828074  0.6922147051  -2.3222061521
H25  0.68032838  3.3815742113  -3.0812731491
H26  -0.8996434042  3.8458331107  -2.4159129161
H27  -0.0767711132  -0.4905665494  2.675770729
H28  -2.7031740072  -1.9143301359  1.2305742276
H29  -2.8260434079  -2.7943555032  -0.308821977
H30  -1.9717976262  -3.5460771225  1.0801599632
H31  2.6800025049  -2.6315864463  3.8850568445
H32  0.487099192  -3.0721070434  2.9942402948
H33  2.4782699168  -3.4728134044  1.6299022289
H34  1.6189991937  0.0532309627  4.4377364803
H35  2.4160014128  1.1855364264  3.3262028319
H36  0.7680304892  1.5201278981  3.9065964105
```

***cis, like*-4fTS-(l)**

b3lyp/6-31G(d) =-1133.6587056

```
C1  -0.546979181  0.6998711907  -2.1243224579
C2  -1.3241980295  -0.2204349982  -1.4112066669
C3  -1.4487544411  -0.1786958201  -0.0097864559
C4  -0.7646745451  0.7215988418  0.7749021767
C5  1.5635310699  0.1081699183  -0.2661375384
C6  1.3695382689  0.4619205602  -1.606020546
C7  1.6803482237  -0.493975583  -2.7542107445
O8  2.6703561322  -1.1727951241  -2.8274478456
O9  0.7941996871  -0.4390655713  -3.7822616952
C10  -0.2962206855  0.4836263962  -3.6016134905
C11  -0.7186083664  0.7221720963  2.2864692674
C12  1.4063825447  -1.2818492515  0.1428860904
O13  0.8699652949  -2.1432921823  -0.5380371101
O14  1.8887345237  -1.5128456093  1.394487084
C15  1.8105942747  -2.8771995433  1.8307768481
O16  -1.2275857731  1.9700332689  2.7947084324
Si17  -2.6811137383  2.6905709883  2.4221428184
C18  -1.3993334748  -0.4598982835  2.9731747211
H19  -0.5726960965  1.7336953917  -1.7874876603
H20  -1.6671595904  -1.1180730691  -1.9208426391
H21  -1.9570389759  -1.0123330582  0.4667364639
H22  -0.3684647629  1.6310433931  0.3359638701
H23  1.9763763586  0.8155975587  0.442266416
H24  1.7014532649  1.4726618668  -1.854858132
H25  -0.0468170158  1.4231832948  -4.1086531226
H26  -1.153713822  0.0335318358  -4.1091692147
```

```
H27  0.3380055442  0.7193051329  2.5826268762
H28  0.7705537624  -3.212651165  1.8827427244
H29  2.3555031111  -3.5315308698  1.1449242214
H30  2.2669600821  -2.8952955101  2.821269259
H31  -2.712229825  3.2366578352  1.0354735383
H32  -3.8406258668  1.7655277834  2.5690666337
H33  -2.8179105183  3.8102756613  3.3834264798
H34  -1.3020322938  -0.3492463999  4.0568950205
H35  -2.4654018795  -0.5172445595  2.7300137048
H36  -0.9242820102  -1.4012103573  2.6785479563
```

***cis, unlike*-4fTS-(g)**

```
b3lyp/6-31G(d) =-1133.6613624

C1  1.0612362862  0.9886426968  -2.2810914272
C2  0.0113540117  1.5762622922  -1.5657373549
C3  -0.0011672684  1.6534248759  -0.1609367913
C4  0.9803494925  1.0993085366  0.6244231356
C5  0.7780051262  -1.2606029123  -0.5075931284
C6  1.1365606928  -0.9660452245  -1.8269194763
C7  0.2837052651  -1.3905932682  -3.0181840193
O8  -0.2078482987  -2.4807332568  -3.1494027528
O9  0.2128397669  -0.4710011853  -4.0153005589
C10  0.9194552052  0.7597129881  -3.7701344428
C11  0.9210202701  1.0313012678  2.1296287737
C12  -0.6304105086  -1.3414879429  -0.1437992791
O13  -1.5464100051  -0.942721984  -0.8473963038
O14  -0.8184997655  -1.8808238964  1.0916074914
C15  -2.1906313389  -1.9997132078  1.4913967987
O16  -0.3785273266  1.4091222673  2.5760762933
Si17  -1.0303631354  1.0037316636  4.0522929366
C18  1.9964221823  1.9319640494  2.7597724923
H19  2.0704243753  1.1707073559  -1.9187666261
H20  -0.9195193747  1.7855142683  -2.0885117239
H21  -0.9083051487  1.9922063413  0.3289526091
H22  1.9575038948  0.8740865105  0.2106791421
H23  1.5208572173  -1.5760499247  0.2146666557
H24  2.1956671289  -1.1157439627  -2.0497383139
H25  1.8968708136  0.703659913  -4.2639658531
H26  0.330466156  1.5416013948  -4.2574996329
H27  1.1171489622  -0.0108205866  2.429517619
H28  -2.6686036557  -1.0168794753  1.535385774
H29  -2.7434494294  -2.6280680277  0.7875057477
H30  -2.1695899008  -2.4600715851  2.4801220754
H31  -2.487294503  1.2499111635  3.9413104865
H32  -0.4823635146  1.8305100593  5.164248527
H33  -0.7669619197  -0.4279993203  4.3711726496
H34  1.988674433  1.8396872557  3.8513757863
H35  1.8106106511  2.97812207  2.4969624643
H36  2.9951162445  1.653602794  2.4048564606
```

***cis, unlike*-4fTS-(h)**

```
b3lyp/6-31G(d) =-1133.6619021

C1  1.0878167776  -1.9562915311  -0.002448313
C2  0.4040667883  -1.451732521  1.116459897
C3  -0.7755030541  -0.6942378043  0.9937344113
C4  -1.3225905013  -0.3261849114  -0.2125777856
C5  1.0846991995  0.7003413444  -1.025274753
```

```
C6  1.839029791  -0.4839554572  -1.0346234286
C7  3.216343374  -0.5427380781  -0.3694577991
O8  4.0557779897  0.3130297999  -0.4610990609
O9  3.4781094017  -1.7187070649  0.2549858709
C10  2.4068606825  -2.6768875627  0.2003217271
C11  -2.5585485388  0.5319250909  -0.3294859824
C12  1.1487457452  1.5552241578  0.1460635543
O13  1.6119103472  1.1973134093  1.2224881003
O14  0.6081693066  2.7876886612  -0.0548423736
C15  0.663190703  3.6656324999  1.0779697776
O16  -3.6625420419  -0.2938981308  -0.7495342497
Si17  -4.4216647232  -1.4187532182  0.2168822597
C18  -2.432404498  1.6542103879  -1.3546612846
H19  0.4675137554  -2.3293371189  -0.8148498004
H20  0.8906495022  -1.4841836394  2.0879071009
H21  -1.1847704723  -0.2515427606  1.9005632979
H22  -1.0356244377  -0.8288307009  -1.1308834404
H23  0.5575762568  1.0409339255  -1.9067862269
H24  1.8768537562  -0.9761373616  -2.0099005679
H25  2.6091433776  -3.3810819413  -0.6153493472
H26  2.4424833051  -3.2231662805  1.1465266945
H27  -2.7878320192  0.9630191022  0.6569110018
H28  0.0750435402  3.2656787604  1.9094462414
H29  1.6958631964  3.8002840831  1.4105304739
H30  0.2439540061  4.6126089793  0.7357493115
H31  -5.7144853095  -1.7171350642  -0.4438994921
H32  -4.6586759463  -0.8635401743  1.5814240934
H33  -3.6504482214  -2.6845657187  0.3618322075
H34  -3.3783411862  2.2012558088  -1.4176033043
H35  -2.2146702648  1.2377104449  -2.3445479064
H36  -1.6325655537  2.3453276241  -1.0755283968
```

***cis, unlike*-4fTS-(i)**

b3lyp/6-31G(d) =-1133.6619021

```
C1  1.902873177  -1.772059965  0.2258472722
C2  1.3477718193  -1.3783901797  1.4489205104
C3  -0.0322219429  -1.146450059  1.6044364595
C4  -0.9078250156  -1.2217331268  0.5470769387
C5  0.478912501  0.4710045918  -0.9073908248
C6  1.6289129526  -0.2994251377  -1.1164765821
C7  3.0252128947  0.2864242191  -0.9261987757
O8  3.3698393323  1.3620753919  -1.3424350261
O9  3.9205474835  -0.5503233004  -0.3448550827
C10  3.4059706554  -1.8320818054  0.0614469984
C11  -2.3895541359  -0.9378576713  0.5965713861
C12  0.5245091817  1.5187067389  0.1062474635
O13  1.3613158402  1.5704578704  0.9968141995
O14  -0.4759585432  2.4306124395  -0.0226664612
C15  -0.4334414359  3.5105267627  0.9204931739
O16  -2.8153942235  -0.7502822004  -0.7608687185
Si17  -4.3711893734  -0.9964774297  -1.2996440177
C18  -2.7978812045  0.2530645986  1.4637837958
H19  1.3326360162  -2.4848806559  -0.3649091316
H20  2.0118152505  -1.0408962718  2.241160122
H21  -0.368131127  -0.730497449  2.5511213426
H22  -0.6221354577  -1.7561800209  -0.3515011928
H23  -0.3766085904  0.4121468407  -1.567377016
H24  1.5970169392  -0.9269356399  -2.0099172029
H25  3.6991600203  -2.5737488993  -0.6907196521
H26  3.9140926408  -2.0722414605  0.9997211063
```

```
H27  -2.8785685963  -1.8480531128  0.9911263113
H28  -0.570451059  3.1420776525  1.9416005377
H29  0.5240626543  4.0347713423  0.8610927168
H30  -1.2526792376  4.1747218333  0.6420789598
H31  -4.3000133727  -0.9854018098  -2.779372803
H32  -5.3199620918  0.0586813593  -0.8462592439
H33  -4.8837231412  -2.3123748406  -0.8171511448
H34  -2.4571609108  0.124112776  2.4964883599
H35  -3.8880400949  0.3539836294  1.4851112798
H36  -2.3668944086  1.1707033386  1.0562647167
```

TSs for IMDA reaction of 4b (refer to Figure S1)

***trans, like*-4bTS-(d)**

b3lyp/6-31G(d) =-1251.6537877

```
Si1  4.3227769102  -0.2964263355  0.0661321447
O2  2.7858035086  -0.1248730347  -0.5982803126
O3  -5.0238945207  -0.0942464831  -0.7550544367
O4  -4.3567931869  -1.8859533447  0.3970257922
O5  -2.761794936  1.3050548677  1.1632717875
O6  -1.9014871238  2.8071782911  -0.3062573139
C7  5.1856060728  1.3807360936  0.1668890143
C8  5.2261186918  -1.4411943575  -1.1197623379
C9  4.2093933633  -1.0562973716  1.7918978721
C10  1.7367845595  0.6657285779  -0.0526427498
C11  1.4275863115  1.8184999382  -1.0183650704
C12  0.5172553253  -0.1782339271  0.2402098431
C13  0.4128603039  -1.5014627852  -0.1076307466
C14  -4.129686534  -0.8140144333  -0.401265821
C15  -3.1726264937  -2.6374695661  0.7074901047
C16  -2.6730937377  -0.6968848946  -0.8828250781
C17  -1.9719603687  -1.743418051  0.5008147143
C18  -2.2933799033  1.5538168165  0.0552854225
C19  -2.0565938106  0.5659863321  -0.9784225843
C20  -2.1408378478  3.8253195315  0.675096064
C21  -0.7519886068  -2.2784790022  0.0548590989
H22  6.1967873242  1.2735358732  0.5792372718
H23  6.2554717519  -1.6231894091  -0.7876766419
H24  5.2077514712  -1.1842199746  2.2289041941
H25  5.277578038  1.8393375989  -0.8245749274
H26  5.2706197308  -1.0088882512  -2.1257908062
H27  4.6465557803  2.0859876336  0.811310939
H28  4.7238896594  -2.4123214436  -1.1964975031
H29  3.7297965091  -2.0414973411  1.7616552545
H30  3.6314387749  -0.428791516  2.4812421217
H31  2.3032836202  2.4691338499  -1.1124604699
H32  2.0509547413  1.1079276209  0.9094792969
H33  1.1928224643  1.407638853  -2.0052988574
H34  1.2557788935  -1.9463125463  -0.6288110774
H35  0.5747348405  2.4127578672  -0.6778122293
H36  -0.2220084247  0.2857907209  0.8837586182
H37  -3.2764083675  -2.9601073048  1.747767452
H38  -3.1361483087  -3.5269651919  0.0649201643
H39  -3.2060591536  3.8871657206  0.9133063572
H40  -2.5380820252  -1.3218556637  -1.7686643785
H41  -1.9293922992  -0.9361525534  1.2324527875
H42  -1.5868977389  3.6195347911  1.5958913243
```

H43 -1.7957365335 4.7553949295 0.2215898596
H44 -1.4798897916 0.84303941 -1.8505464433
H45 -0.7530115806 -3.2800547546 -0.3746429388

***trans, like*-4bTS-(e)**

b3lyp/6-31G(d) =-1251.6523548

Si1 3.3836278956 -0.2289966812 0.4818004073
O2 -4.6662864024 -0.046284775 0.0617792735
O3 -3.8520136039 -1.9842001702 0.8083704041
O4 -1.5579501265 -1.3775896483 -1.431333031
O5 2.2034192186 0.4169363774 -0.5295380662
O6 0.1430613534 -2.2804526668 -0.2344552689
C7 -4.2912584809 1.3240967069 -0.158091412
C8 -3.679662836 -0.81540672 0.5876641596
C9 -2.7881280719 1.3981243728 -0.2500740438
C10 -2.4128821579 -0.0360613107 0.9637542922
C11 -2.0750149877 2.5061452376 0.2233052696
C12 -1.1373572302 -0.5867673917 0.7660461299
C13 -0.8983490968 -1.4297178387 -0.3985275355
C14 4.7402858168 1.0504457429 0.8044397335
C15 4.0892028013 -1.7004164613 -0.4509207799
C16 2.1375318186 2.5800291894 -1.5847971092
C17 1.6330575858 1.7156678199 -0.4159844717
C18 2.6253805926 -0.7722004354 2.121884119
C19 0.4124670806 -3.1304280951 -1.3592520619
C20 0.1263788734 1.6239376079 -0.4479316309
C21 -0.668724151 2.5620472038 0.1669740853
H22 -4.6827767577 1.9386250187 0.6631487115
H23 -4.7816444394 1.6286223858 -1.0878622041
H24 -2.5508429946 0.4430893385 1.9351921623
H25 -2.5890604432 3.2285185456 0.8563956591
H26 -2.3952642521 0.8751563507 -1.1216201356
H27 5.2275173904 1.3629216644 -0.1267973933
H28 5.5157419805 0.6279392863 1.4558771595
H29 4.527579607 -1.3897941112 -1.4060913516
H30 4.3597787103 1.9516749697 1.3007570889
H31 4.8739588486 -2.1963078319 0.1334813932
H32 3.230466299 2.6449286281 -1.5529881677
H33 3.311995391 -2.4419329856 -0.6631560039
H34 3.3844602377 -1.2012228797 2.7881691457
H35 1.8466688957 2.1257303602 -2.5376357084
H36 1.7223742059 3.5924425363 -1.5368669943
H37 1.9374383365 2.1972249573 0.526397071
H38 1.2102208833 -3.8001296744 -1.0356640213
H39 2.1603366749 0.0663547366 2.6551782844
H40 0.7361249256 -2.5379732149 -2.2195755986
H41 1.856528901 -1.5337966125 1.95086219
H42 -0.1795651962 3.3415423157 0.7521380472
H43 -0.2786830395 0.9346366209 -1.1806172629
H44 -0.4793035556 -3.7001068078 -1.6323561331
H45 -0.3742500009 -0.5164367679 1.5289094023

***trans, like*-4bTS-(f)**

b3lyp/6-31G(d) =-1251.6525174

Si1 -2.9832480648 0.0693119473 -1.8494119755
O2 -2.9147685061 0.1513297243 -0.1702560767
O3 4.5402904115 0.0128878291 0.6948803987

O4 3.8141766803 -1.9158570725 1.5461664862
O5 1.9193917805 -0.1273551615 -1.1445923868
O6 1.2215122123 2.0325410409 -1.0635918859
C7 -1.6656426446 -1.0974594661 -2.5353311233
C8 -2.7818030984 1.7952081703 -2.5927836539
C9 -2.6789797993 1.4938897092 1.7967465309
C10 -4.6970359057 -0.6140798459 -2.2142171141
C11 -1.9426789603 0.8247395395 0.6397439119
C12 -0.8793518915 -0.1757212462 1.0396959955
C13 -0.7413022305 -0.7498525295 2.2799341414
C14 1.3036841424 2.0708229774 -2.4967909747
C15 3.6581035559 -0.60396207 1.2300678954
C16 2.6690848703 -2.5291630702 2.1656927943
C17 2.3468094088 0.0119360442 1.7185228232
C18 1.4434508275 -1.7459699189 1.7824223434
C19 1.6200037676 0.9368920213 0.9638564562
C20 1.6240881683 0.8664881 -0.4918847332
C21 0.3554487171 -1.5651699102 2.6361184436
H22 -0.640167568 -0.7756861786 -2.3163899875
H23 -1.7557863029 -1.1819042357 -3.6262512661
H24 -1.8143471864 2.2484342119 -2.3472576763
H25 -2.8531927853 1.752950451 -3.6869325101
H26 -1.7892684647 -2.1046052603 -2.11900218
H27 -3.3856230567 2.2295120599 1.4018932009
H28 -3.5657844915 2.4739663756 -2.2365542191
H29 -3.2494536417 0.7568487815 2.3709228476
H30 -4.854616231 -0.7343224992 -3.2931113508
H31 -1.9811798695 2.0068787963 2.4678080146
H32 -4.8369255545 -1.5949291834 -1.7455950249
H33 -1.4439142133 1.6071409109 0.0476816537
H34 -5.4791328765 0.0516478234 -1.8321334529
H35 -1.423658864 -0.4597313155 3.0755270956
H36 0.6069910809 1.3600701107 -2.9494838555
H37 -0.3396411234 -0.5987319842 0.1999986815
H38 1.0396948846 3.0915532882 -2.776488066
H39 2.8177284692 -2.5537654078 3.2530873425
H40 2.6427750298 -3.5582910305 1.7935500139
H41 2.4137773479 0.2434660692 2.7827856745
H42 1.2616183865 -1.7505795797 0.7083354129
H43 2.3175332076 1.8317235746 -2.8278098141
H44 0.4566235719 -1.8552098492 3.68144375
H45 1.1733289648 1.8032348978 1.4341286705

***trans, unlike*-4bTS-(a)**

b3lyp/6-31G(d) =-1251.6562161

Si1 3.6043715415 -0.2848569946 -0.6943929002
O2 -4.5841003758 -0.9349047008 -0.3104455868
O3 -4.2408555795 0.9093916362 -1.5161095854
O4 -2.2882335211 1.7785267362 0.886478224
O5 2.5246265355 -0.9075098677 0.4385520808
O6 -0.4308868411 2.5621324168 -0.1614952948
C7 -3.7793409353 -0.0449196356 -0.9492728656
C8 -3.8933246348 -2.0203626492 0.3350825505
C9 -2.3035713908 -0.439344649 -0.9799695991
C10 -2.4836153232 -1.5832496702 0.6236762789
C11 -1.4180985699 1.641634995 0.0359843454
C12 -1.2645227137 0.4824394218 -0.8285945301
C13 -1.3884365734 -2.446203712 0.5825799739
C14 4.835234493 0.8801055769 0.1417633917
C15 4.484108375 -1.7945555032 -1.386945017

```
C16  2.6719109167  0.6458315081  -2.0471471287
C17  2.1153524274  -0.0737579386  2.6728143927
C18  1.6232037753  -0.1293398807  1.2153618838
C19  0.2280304075  -0.6947103509  1.1507083176
C20  -0.0691269776  -1.9821967151  0.7783774145
C21  -0.5352835538  3.7452085022  0.6438303942
H22  -4.4610991045  -2.2361622496  1.2459046211
H23  -3.9249428816  -2.9050036987  -0.3142910605
H24  -2.1333731946  -1.1939629277  -1.7498279856
H25  -2.4415715782  -0.7300259119  1.2994559049
H26  -1.5210373411  -3.4401762987  0.1564074705
H27  -1.479108504  4.2609721861  0.4477973285
H28  5.5603731831  1.2677327645  -0.5849099599
H29  5.3981126961  0.3660495057  0.9297393472
H30  5.2227716742  -1.5096641852  -2.1460271946
H31  4.3386470315  1.7458502414  0.5968667028
H32  5.0110491996  -2.3409763048  -0.5964301334
H33  3.3702063146  1.1050313368  -2.7581709249
H34  3.1006164082  0.4013234259  2.7185188104
H35  3.7749452675  -2.4868786897  -1.8548021704
H36  2.0444911565  1.4481887369  -1.640310778
H37  2.1975924365  -1.0881477653  3.0755505865
H38  2.0206887689  -0.0303364921  -2.6140471021
H39  1.4245484892  0.4983482597  3.3024660614
H40  1.5702174656  0.9032248298  0.8347494507
H41  0.7543872454  -2.6257243843  0.47963108
H42  0.3094280703  4.3720531451  0.3551064226
H43  -0.5233871453  -0.0804295907  1.6360292003
H44  -0.4846475582  3.4989553038  1.7083712894
H45  -0.369629758  0.4071911253  -1.4316138813
```

***trans, unlike*-4bTS-(b)**

b3lyp/6-31G(d) =-1251.6537729

```
Si1  -3.7944782796  -0.319618205  -0.5225005781
O2  -2.6427615909  0.5419258695  0.3530388105
O3  4.8222053628  0.6602098415  -0.1484074568
O4  4.2609136907  -1.3522279059  -0.9338803669
O5  1.8331654838  1.3573151083  -1.2798763262
O6  1.1325759136  2.7963203043  0.3306740611
C7  -4.8476757047  1.0062534577  -1.3398238701
C8  -4.8333876111  -1.3822996125  0.645705472
C9  -2.9890212941  -1.4131466202  -1.8346187955
C10  -1.7632917099  0.0280521809  1.3525921141
C11  -1.4026287003  1.1847221387  2.2903105197
C12  -0.5548086738  -0.6012079732  0.6993135924
C13  -0.0778103176  -1.8408939272  1.0540312515
C14  0.7745143172  3.7161506392  -0.7112131801
C15  4.0513279169  -0.2608301099  -0.1565819947
C16  3.2451567419  -2.3602361653  -0.8099992763
C17  2.8301431464  -0.3812932467  0.769746627
C18  1.9910910224  -1.7103856958  -0.2768160056
C19  1.9917612322  0.7230366027  1.0014914513
C20  1.6738044977  1.6251911549  -0.0928952517
C21  1.1138190763  -2.4122459888  0.5635231925
H22  -5.3436816994  1.6371009783  -0.593607121
H23  -5.6236255079  0.5618411502  -1.9751038626
H24  -5.3080540983  -0.7729643677  1.4239053442
H25  -5.6322093713  -1.8905422777  0.0912361818
H26  -4.2336522074  1.6585194427  -1.9713499747
H27  -4.2423737559  -2.1600131271  1.1443819155
```

```
H28  -3.75202445  -1.9418435831  -2.4202445917
H29  -2.3201361412  1.6139776881  2.7061703348
H30  -2.2779528201  -0.7448441659  1.9452420477
H31  -2.390960549  -0.8163657186  -2.5334981234
H32  -2.32784627  -2.1676422426  -1.39331322
H33  -0.8623698107  1.9647912191  1.747282147
H34  -0.7742571561  0.8302155205  3.1145573173
H35  -0.5982082936  -2.3791401968  1.8465725259
H36  -0.1952192548  -0.0942157031  -0.1892011362
H37  0.0090347242  3.2841710264  -1.3620964794
H38  0.3871701322  4.5985356878  -0.2006735388
H39  3.6095968711  -3.1550519764  -0.1460250901
H40  3.1025504739  -2.7777591244  -1.8112770981
H41  3.1157629886  -0.9214527332  1.6751528895
H42  1.5540570968  -1.008425126  -0.9872717397
H43  1.6493385327  3.9735657523  -1.3140568187
H44  1.4568669311  -3.3409888243  1.0181613904
H45  1.6541350299  0.9696388213  1.9990799406
```

***trans, unlike*-4bTS-(c)**

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b3lyp/6-31G(d) =-1251.6494176

Si1  0.6995658988  0.284405079  3.4095819639
O2  -0.3976804457  0.37744102  2.136296677
O3  -0.0530892538  -2.5153920759  -3.6835497467
O4  -0.3748989208  -0.5146050577  -4.6153399482
O5  1.6898661814  -0.6135873726  -1.6872424474
O6  1.326363691  -1.8892045306  0.1487472525
C7  0.8644205461  -1.5554943527  3.7482419097
C8  0.0499552091  1.1900313275  4.9382858384
C9  2.3465283949  1.0575731239  2.8999425947
C10  -0.9615227203  1.5732543527  1.6003219838
C11  -2.3797812429  1.7526803842  2.1447126541
C12  -0.8548846324  1.5131062438  0.0907350882
C13  -1.8442688295  1.9252509439  -0.7701599225
C14  2.7476209906  -2.0730416472  0.2286846646
C15  -0.422778146  -1.3772565434  -3.5712551545
C16  -0.859808127  0.8028732857  -4.3101934368
C17  -1.0812085915  -0.7979903927  -2.3078388863
C18  -0.8204084888  0.9968319494  -2.8124664975
C19  -0.5423251092  -1.0827234175  -1.0384417232
C20  0.907153349  -1.1548001187  -0.9113912335
C21  -1.8181860443  1.7441917145  -2.1665634953
H22  -0.0514752044  -1.9550266201  4.1988386025
H23  1.6951566004  -1.7708403976  4.4311252931
H24  1.0347931646  -2.0951874313  2.8110841211
H25  -0.8999172324  0.7649590955  5.2833378053
H26  0.7676024976  1.1058342034  5.7644561726
H27  -0.1077547977  2.2600679047  4.7559216381
H28  3.0827237038  0.9807591285  3.7100052588
H29  2.7659939414  0.5592779089  2.0188696164
H30  2.2417265798  2.1226824726  2.6587670294
H31  -0.3596386408  2.4444185411  1.9200723338
H32  -2.3528452461  1.7554672614  3.2377509399
H33  -3.0206305004  0.9267989212  1.8196006797
H34  -2.8248892826  2.6984488434  1.8169957278
H35  0.140482295  1.2961763491  -0.2808032711
H36  -2.7717716902  2.3064667838  -0.350030564
H37  3.2629970012  -1.1124529175  0.3129184751
H38  2.9154779215  -2.6772324413  1.1208440725
H39  3.1156255267  -2.5919867276  -0.6607025553
```

H40 -1.8774124041 0.9063192047 -4.708760823
H41 -0.2039658212 1.502367732 -4.8373135962
H42 -2.1641433215 -0.922685313 -2.3721090195
H43 0.1970537065 1.0626977891 -2.4277681239
H44 -1.1619235375 -1.3779842979 -0.2031772231
H45 -2.7247172055 1.9848459144 -2.7210506846

cis, like-4bTS-(j)

b3lyp/6-31G(d) =-1251.6501024

C1 1.0647461152 1.1826023279 -2.6643357285
C2 -0.2179004907 1.0087018898 -2.1172250836
C3 -0.4638268742 1.0318584995 -0.7322183705
C4 0.5244709325 1.1689515865 0.2097256029
C5 1.9344118859 -0.9058634046 -0.9361510382
C6 2.1884399445 -0.3410420316 -2.1960099028
C7 1.9038581215 -1.1179553081 -3.4821828269
O8 2.1672184147 -2.278368722 -3.655012914
O9 1.4260117278 -0.3501226854 -4.4957259991
C10 1.2524655478 1.0384623811 -4.1619946635
C11 0.2855449344 1.1131804317 1.7000547187
C12 0.7776845973 -1.7661243045 -0.7719969188
O13 -0.1231641125 -1.8590107433 -1.5974456294
O14 0.7717699245 -2.4322635732 0.4143006961
C15 -0.4061542796 -3.2075810878 0.6704822702
O16 -0.988679246 0.55293489 1.9843929771
Si17 -2.1301587263 1.1771447279 3.0524428822
C18 1.3821495847 0.3357117544 2.4399464318
C19 -1.4446075213 1.2379219673 4.8119297263
C20 -2.6412690121 2.9151590797 2.5154637131
C21 -3.5770375147 -0.0173298301 2.9443840392
H22 1.7002037848 1.9211787142 -2.1795246411
H23 -1.0159858052 0.6560080752 -2.7660746479
H24 -1.4569175217 0.765832854 -0.3841836115
H25 1.50715785 1.5353371395 -0.0702857341
H26 2.6334930418 -0.792658668 -0.1179172983
H27 3.161963203 0.1509312789 -2.2713400911
H28 2.1305328591 1.5944574494 -4.5122400726
H29 0.3803143931 1.376838553 -4.72782004
H30 0.3237935083 2.1619641199 2.0520388939
H31 -1.2691993314 -2.5499295065 0.8125557713
H32 -0.6076134278 -3.8923572035 -0.1570428061
H33 -0.1992240991 -3.7621747212 1.5869891267
H34 1.2277576221 0.4042628198 3.5212574253
H35 1.3549324615 -0.7154983703 2.1427253551
H36 2.3726709944 0.746329847 2.2097143813
H37 -0.5762847192 1.9029165162 4.8948472321
H38 -1.1363377926 0.2428852876 5.1534556861
H39 -2.2044964122 1.6083333099 5.5116822317
H40 -3.0615818674 2.9124285276 1.503046852
H41 -1.7981071396 3.6166152437 2.522547673
H42 -3.404632279 3.3205145102 3.191455455
H43 -3.2738796333 -1.0289129624 3.2375419408
H44 -3.9729650379 -0.0712377798 1.9238959342
H45 -4.3964819792 0.2906317381 3.6051697719

cis, like-4bTS-(k)

b3lyp/6-31G(d) =-1251.6507421

```
C1  -0.2755550773  1.3615406184  -2.9637615774
C2  -1.4151315177  1.561148664  -2.1811182199
C3  -1.3489855157  1.6975075357  -0.7819280381
C4  -0.1736382927  1.5804320211  -0.0780387128
C5  0.3823956272  -0.7415632806  -1.0752876656
C6  0.5571657552  -0.4216783617  -2.4239750597
C7  -0.1309223938  -1.1944375659  -3.5419590763
O8  -0.1876719397  -2.3956353202  -3.5996916549
O9  -0.589463881  -0.4314131272  -4.5672635183
C10  -0.4094741038  0.9908109304  -4.4229979281
C11  -0.0880832551  1.5927817218  1.4276005297
C12  -0.8840463485  -1.3223311869  -0.6428094637
O13  -1.9128765096  -1.3037085061  -1.3013700421
O14  -0.8173932353  -1.8706864508  0.6038049167
C15  -2.0270498378  -2.5032215105  1.0454832471
O16  1.1220013403  0.9460119107  1.8000185966
Si17  1.463875747  0.0947753511  3.2121298324
C18  -0.1097681921  3.0355690561  1.9624918102
C19  2.5936966162  1.1466815393  4.2981122006
C20  -0.1242308823  -0.3245615706  4.1458098076
C21  2.3506625365  -1.4755360614  2.6776572812
H22  0.622620827  1.9073421613  -2.6861517672
H23  -2.391515715  1.3807538448  -2.6255658331
H24  -2.2886990549  1.6950898878  -0.2317973204
H25  0.7833496879  1.7178203664  -0.5699747515
H26  1.2048925878  -0.7015603282  -0.3737970701
H27  1.582848421  -0.1717282313  -2.7034131433
H28  0.4772342589  1.2862328421  -4.9961148433
H29  -1.288256324  1.4468611458  -4.8879229719
H30  -0.9515774811  1.0510639792  1.839511219
H31  -2.8426221726  -1.7779371259  1.1192270984
H32  -2.3232171345  -3.2937638615  0.3506938663
H33  -1.7988100164  -2.9224935032  2.0263435979
H34  -0.0449515719  3.0358411243  3.0565732604
H35  0.7433057146  3.597670991  1.5681818784
H36  -1.032585084  3.548131616  1.6701024495
H37  2.0983915599  2.0662059032  4.632194889
H38  3.4996666245  1.438108403  3.7536901876
H39  2.9080737816  0.5951784453  5.1932509299
H40  -0.8027210065  -0.9269772748  3.5314073323
H41  -0.6693704201  0.5673674711  4.4771342704
H42  0.1151007285  -0.9096884831  5.0425979066
H43  3.2553681067  -1.2442773971  2.1028514581
H44  1.6968105193  -2.0861439241  2.0447660143
H45  2.6534257989  -2.0813563137  3.5407324948
```

cis, like-4bTS-(l)

b3lyp/6-31G(d) =-1251.6462234

```
C1  0.1805259224  0.2440054247  -2.4746799478
C2  -1.0403048453  0.3501000806  -1.7960366394
C3  -1.1208286199  0.4584410109  -0.3949448409
C4  -0.0169564352  0.3996615373  0.4246907014
C5  0.835708933  -1.8577000801  -0.6334581362
C6  1.0594307653  -1.4694129923  -1.9597894708
C7  0.4936710588  -2.2517450755  -3.1416557216
O8  0.5091336034  -3.4505483908  -3.2370157475
O9  0.0635602667  -1.4756210963  -4.1703443887
C10  0.187095145  -0.0568267187  -3.9586038762
C11  -0.0332284672  0.3420705158  1.9367751926
C12  -0.4103323607  -2.5222969645  -0.2780566704
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```
O13  -1.3998003098  -2.5604694047  -0.9950419961
O14  -0.3708466392  -3.069293169  0.9682233145
C15  -1.5548470019  -3.779868816  1.3549260203
O16  0.7167233777  1.4267740965  2.4914044134
Si17  0.6891841343  3.0868697566  2.23948024
C18  -1.417627047  0.2390580676  2.576902388
C19  1.4595580201  3.5508920345  0.575158983
C20  -1.0548338864  3.8115374564  2.3243279555
C21  1.747063379  3.7643718556  3.6399226326
H22  1.0041304158  0.8506470134  -2.104755763
H23  -1.9573547943  0.1294855145  -2.3379135783
H24  -2.1102863838  0.3989961421  0.0499330506
H25  0.9698934187  0.5871050294  0.0165204942
H26  1.6273469462  -1.8061012145  0.1036450147
H27  2.087450669  -1.1635466859  -2.1682924679
H28  1.1127125049  0.2878586076  -4.4346581719
H29  -0.6599937931  0.3966003488  -4.4805398635
H30  0.5257603929  -0.5581458193  2.2263083117
H31  -2.4181341625  -3.1089177191  1.3969026383
H32  -1.7703031856  -4.5834467331  0.6454199392
H33  -1.3422507369  -4.1886298154  2.3436373053
H34  -1.3062889932  0.2128195014  3.664672287
H35  -2.054732381  1.0905043788  2.3186637241
H36  -1.9201282717  -0.6813396015  2.2608612164
H37  0.8416303851  3.2262154775  -0.2698184442
H38  2.4560766091  3.1082166869  0.4582330173
H39  1.5731042028  4.6399905665  0.4989006678
H40  -1.5526584213  3.5644437249  3.2690089209
H41  -1.6914159543  3.4586841394  1.504486684
H42  -1.0090013053  4.9059187281  2.2518141644
H43  2.7575093721  3.3409957885  3.6095964902
H44  1.3146629373  3.5193255036  4.6166461541
H45  1.8389628997  4.8556835423  3.5773286637
```

***cis, unlike*-4bTS-(g)**

b3lyp/6-31G(d) =-1251.6500355

```
C1  0.8975896446  1.2200467814  -2.8822061444
C2  -0.3550464449  1.2693587321  -2.2547658901
C3  -0.4979318355  1.4054431025  -0.8610213301
C4  0.5756271697  1.4227004032  -0.0056107457
C5  1.5477182681  -0.8564496641  -1.0093635058
C6  1.856977193  -0.4246151257  -2.3061469492
C7  1.4515586729  -1.2389109638  -3.5332182885
O8  1.5885722388  -2.4305666803  -3.6310627965
O9  1.0276587535  -0.4986049978  -4.5874195228
C10  0.9820150186  0.9231562276  -4.3645679036
C11  0.4725128348  1.4740744051  1.4981486933
C12  0.306771051  -1.5824069312  -0.7979369959
O13  -0.6051896118  -1.6208163442  -1.6131999293
O14  0.2438884056  -2.2071332289  0.4112201141
C15  -0.9326822484  -3.0038749479  0.607069481
O16  -0.8645715675  1.2555252705  1.9097700475
Si17  -1.3898875534  0.5481413818  3.3452386422
C18  0.9877316383  2.831137736  2.0145178246
C19  -3.0752269492  -0.1817027478  2.9394364476
C20  -1.5789544633  1.8523120091  4.6984898827
C21  -0.1693969728  -0.784180456  3.8948410738
H22  1.6649043905  1.8832735325  -2.4888297081
H23  -1.2372047545  0.9985993113  -2.8304595268
H24  -1.4896210056  1.3243364495  -0.4272730204
```

```
H25  1.5727714193  1.623887548  -0.3825107403
H26  2.2685014688  -0.7910401857  -0.2040444216
H27  2.8781494066  -0.0540286741  -2.4241839698
H28  1.8759410294  1.3706212266  -4.814899351
H29  0.1043146376  1.2818020105  -4.9094115344
H30  1.1250616242  0.6847237797  1.9045786552
H31  -1.8337840848  -2.3859488584  0.5625423647
H32  -1.0016989891  -3.7801796959  -0.1601825403
H33  -0.8244592293  -3.4525616109  1.5954396696
H34  0.9826877358  2.8502477759  3.1092398011
H35  0.3443693063  3.6380563931  1.6497783625
H36  2.0131489832  3.0190162577  1.6757557973
H37  -2.9988166206  -0.9715108939  2.1840496132
H38  -3.7501690461  0.5878663787  2.5471175356
H39  -3.5465482031  -0.6132267108  3.8310067109
H40  -2.2424901757  2.6629874965  4.3752126286
H41  -0.6193047757  2.3008264736  4.9813487157
H42  -2.0131162396  1.4104301614  5.604558348
H43  0.7571074446  -0.3596487009  4.3000777852
H44  0.1024630225  -1.4429931358  3.0622089498
H45  -0.6122228066  -1.4032791931  4.6850816825
```

***cis, unlike*-4bTS-(h)**

b3lyp/6-31G(d) =-1251.6502539

```
C1  0.1739355875  0.5678542875  -2.4181547132
C2  -0.9806619298  0.53917306  -1.6177934055
C3  -0.9167136882  0.4630304883  -0.2137053185
C4  0.2577280179  0.3503768781  0.4915558416
C5  0.9886140351  -1.8005539535  -1.0653170693
C6  1.0959805395  -1.1449636811  -2.302629136
C7  0.4494920536  -1.7316896485  -3.5595136635
O8  0.4849750862  -2.8936445852  -3.8668608829
O9  -0.0841147128  -0.8024791912  -4.3922451927
C10  0.0284233862  0.5541841014  -3.9276394287
C11  0.316506319  0.2207809386  1.9955822481
C12  -0.2464814245  -2.4958646362  -0.7552544537
O13  -1.2879667418  -2.342614336  -1.383011019
O14  -0.1492923598  -3.3142951935  0.3279731044
C15  -1.3483862456  -4.0274474178  0.6584922939
O16  0.8410949609  1.4357455798  2.5446877634
Si17  0.042331925  2.894088293  2.8067127671
C18  1.2222117913  -0.9142274545  2.469282403
C19  1.0272640455  3.7332034088  4.1723183381
C20  -1.7385855738  2.5865358329  3.3597130895
C21  0.0562351471  3.9666993341  1.2528409454
H22  1.0098416153  1.1471976667  -2.0315152719
H23  -1.9454352159  0.3834314974  -2.0937937232
H24  -1.8543192684  0.3375189172  0.32580886
H25  1.2102746272  0.5833591031  0.0259411983
H26  1.8356194337  -1.8920416268  -0.39825494
H27  2.107024787  -0.7991467323  -2.5331273124
H28  0.8912718329  1.0201567935  -4.418135486
H29  -0.8782707685  1.0639799044  -4.2640709081
H30  -0.7015611133  0.0502831807  2.3760123115
H31  -2.147183916  -3.3360778091  0.943768983
H32  -1.6879791442  -4.6249330595  -0.1917504824
H33  -1.0847454755  -4.6711910687  1.4986550355
H34  1.2456182764  -0.9299588665  3.563673027
H35  2.2454030219  -0.7519114026  2.1119137786
H36  0.8662716199  -1.8803224516  2.1009387241
```

```
H37  2.07784448  3.8502361408  3.8823973303
H38  1.002183738  3.1468210706  5.0977937246
H39  0.6298176713  4.7311508385  4.3948871722
H40  -1.781767819  1.9397073906  4.2441467449
H41  -2.348981354  2.1234675767  2.5754161767
H42  -2.2197106959  3.5365514102  3.6242698052
H43  -0.4821181933  3.4928040418  0.4245582297
H44  1.0827236473  4.1586132425  0.9180710672
H45  -0.4154109619  4.938820719  1.4453992026
```

***cis, unlike*-4bTS-(i)**

```
b3lyp/6-31G(d) =-1251.6482813

C1  0.9865539425  1.6151169373  -2.335041062
C2  -0.2640452969  2.0960127566  -1.9293105059
C3  -0.7381777225  1.9340045397  -0.6137211572
C4  -0.0331820807  1.2320744082  0.3360030471
C5  0.1570215663  -0.9027170918  -1.1894827254
C6  0.9935818666  -0.3900453509  -2.188471361
C7  0.6938596197  -0.6129486944  -3.6680084013
O8  0.3694771983  -1.6718107035  -4.1403951135
O9  0.9366698532  0.4554940941  -4.4673846385
C10  1.3730424646  1.6529256525  -3.7974128642
C11  -0.4784170258  0.9468608936  1.7522902963
C12  -1.2689986174  -1.0089004468  -1.4746172287
O13  -1.8307181028  -0.4038342211  -2.377467436
O14  -1.9257356714  -1.8381977025  -0.6202263393
C15  -3.3222134625  -2.0084776945  -0.8982196919
O16  0.3276598211  -0.1230718424  2.2489106378
Si17  1.0765364027  -0.1913730111  3.7540040037
C18  -1.9601898  0.5989746294  1.9036444
C19  1.9771576607  -1.8405476208  3.7572262542
C20  -0.191235062  -0.1207701066  5.1531073541
C21  2.2940747796  1.2430490991  3.9384424469
H22  1.8046523029  1.7191771903  -1.6263519916
H23  -0.9739220146  2.4146800391  -2.6890506712
H24  -1.7647962455  2.2283730359  -0.4098758007
H25  1.0260826218  1.0523924317  0.1922937249
H26  0.5499619419  -1.3505831003  -0.2861649152
H27  2.060929887  -0.5153374647  -1.9931647657
H28  2.458393698  1.7401481428  -3.9251134876
H29  0.8954812721  2.4811597854  -4.3287532311
H30  -0.2725666368  1.8635363265  2.3359581531
H31  -3.8620873458  -1.0645458486  -0.7764012716
H32  -3.4698188095  -2.3689384395  -1.9197345394
H33  -3.6768353759  -2.7451720274  -0.1760912245
H34  -2.5997802623  1.3982481078  1.5134296905
H35  -2.2054300627  0.4565897349  2.9603224477
H36  -2.1750522746  -0.3265244375  1.3641909355
H37  2.7139027839  -1.8920166638  2.9475079997
H38  1.2757171579  -2.6714652184  3.6213843392
H39  2.5082127457  -2.0014345839  4.7033299932
H40  -0.9186246019  -0.9368867067  5.0720186884
H41  -0.748419208  0.8239389674  5.1610892702
H42  0.3038982189  -0.2132216493  6.1281278561
H43  1.7992064935  2.2201025402  3.8783561047
H44  3.0659656393  1.2130123476  3.1603325387
H45  2.8015966576  1.1976811861  4.9102344156
```

TSs for IMDA reaction of 4g (refer to Figure S2)

trans, like-4gTS-(d)

b3lyp/6-31G(d) =-1133.6656917

```
C1  0.8047569847  -1.0284018713  -0.6938927058
C2  0.1808430843  1.372162923  0.4061462004
C3  -1.0282523428  1.4497422735  -0.251235929
C4  -1.1622403013  1.3094711897  -1.6438809789
C5  -0.0465437301  1.017723597  -2.4387730066
C6  0.4391783299  -0.8065063497  -2.0280708377
C7  -0.066824771  0.7788499923  -3.9267824666
C8  1.4377227033  -0.8503365062  -3.1631837014
O9  1.0531601982  -0.0817700451  -4.2256664365
C10  -0.1883026129  -1.6740807721  0.1635913394
C11  0.3205254577  1.5003425324  1.9041072996
O12  2.4581502873  -1.4879742795  -3.1960479224
O13  -1.3594327457  -1.8487874017  -0.1403259009
O14  0.3385301909  -2.0908109384  1.3457769693
C15  -0.6013133998  -2.6860898705  2.2508115585
O16  -0.8570288601  1.0039073471  2.5440039167
Si17  -1.4379378234  1.5760648184  3.9958950195
C18  1.5801235873  0.825841418  2.4546873192
H19  1.8346744143  -0.9609275292  -0.364613125
H20  1.1106276145  1.5175805233  -0.1335245092
H21  -1.9313578336  1.4688493551  0.3518075808
H22  -2.1615241986  1.1823785088  -2.0555633787
H23  0.8924641398  1.4722192273  -2.1234937952
H24  -0.516687385  -1.2608940544  -2.2937057209
H25  0.0901894014  1.6902761246  -4.5117024815
H26  -0.9991153963  0.3027735121  -4.2555418564
H27  0.4035037289  2.5854061838  2.1086037577
H28  -1.0944957522  -3.5445686109  1.7874767295
H29  -1.3578661555  -1.9539503682  2.5462244991
H30  -0.0153126186  -3.0018505301  3.1151652283
H31  -0.6096850701  1.1499620355  5.158912799
H32  -1.48162372  3.0671325928  3.985535181
H33  -2.803604024  1.0203772141  4.1411693955
H34  1.5269257825  -0.2544931783  2.3049254639
H35  2.4715491353  1.2139666558  1.9478543801
H36  1.6873969636  1.0320260855  3.5248700238
```

trans, like-4gTS-(e)

b3lyp/6-31G(d) =-1133.6662217

```
C1  -0.1714115568  -0.5543678793  -0.9821764986
C2  0.5076088367  0.9091427198  1.0551135156
C3  -0.1747576233  2.0378502946  0.6546618718
C4  0.00232163  2.6289633576  -0.6116674906
C5  0.8733727193  2.056272579  -1.5368292442
C6  0.0013888597  0.3246821515  -2.0521842841
C7  1.0564736907  2.4689219682  -2.9714182027
C8  1.0299192019  0.1181030119  -3.1354577944
O9  1.4526820993  1.2884574909  -3.7031071213
C10  -1.5272943318  -0.6895544776  -0.444052644
C11  0.2557780804  0.1848277142  2.3536139655
O12  1.4529107383  -0.9408444518  -3.5227007401
O13  -2.4675092287  0.0400495738  -0.7216267261
O14  -1.6463919438  -1.7458838952  0.4066613527
```

```
C15  -2.9775389952  -1.9893661518  0.8845089803
O16  0.9412495788  -1.0639788924  2.2733607654
Si17  0.5636974566  -2.4271480915  3.1481942282
C18  0.7597110963  0.9974595454  3.5576911679
H19  0.5768147645  -1.2903878875  -0.7149774576
H20  1.448771659  0.6347566799  0.5920969668
H21  -1.0132564388  2.3839761098  1.2567783402
H22  -0.7293372255  3.3631131928  -0.9433814597
H23  1.7707553723  1.5899073401  -1.1329715868
H24  -0.9230487689  0.7734867798  -2.4159712861
H25  1.8680307878  3.1899980757  -3.1128984108
H26  0.1370563292  2.8842224876  -3.4030169147
H27  -0.8237676071  0.0069445292  2.4724246797
H28  -3.6512893843  -2.2042318829  0.0503211309
H29  -3.3614824559  -1.123641473  1.431136798
H30  -2.8980228573  -2.8535682422  1.544455535
H31  1.2407957021  -2.4413761782  4.4765361635
H32  -0.9041318712  -2.5147655044  3.392289716
H33  1.0347449616  -3.5923790074  2.363921636
H34  1.8353470972  1.1802655288  3.4679979994
H35  0.2446645148  1.9618706857  3.6179266125
H36  0.5786314288  0.4518744443  4.4910920434

HF=-1133.6662217
```

***trans, like*-4gTS-(f)**

```
b3lyp/6-31G(d) =-1133.6650695

C1  0.9299051454  0.8028875415  -0.6752882965
C2  -0.7521283211  -0.8725595834  0.5503807911
C3  -0.0719296167  -0.8862861177  1.7487618017
C4  1.3062771732  -1.152411739  1.8534493757
C5  2.0819754023  -1.3712461429  0.7113443165
C6  2.1684460009  0.3500709623  -0.2090762458
C7  3.5752937065  -1.5670123516  0.7016908187
C8  3.2424137957  -0.1588957678  -1.14787018
O9  4.0569290286  -1.0904575913  -0.5720456025
C10  0.2945517936  1.9157667184  0.0259141348
C11  -2.1911281536  -0.4527324058  0.3597087046
O12  3.4211171969  0.2040495059  -2.2814641837
O13  0.6637217658  2.3881718878  1.0905925322
O14  -0.7788795999  2.4008241951  -0.6640776483
C15  -1.4000432715  3.5567583794  -0.0853147962
O16  -2.8656645813  -1.5853676932  -0.2200662019
Si17  -4.10783028  -1.4635142127  -1.3205190237
C18  -2.9127506263  -0.0024317308  1.6284129509
H19  0.5582731571  0.5238562567  -1.654549274
H20  -0.3531108407  -1.3958771571  -0.3113781851
H21  -0.5741522715  -0.5246144309  2.6415696095
H22  1.7991375349  -0.9368721693  2.7996787849
H23  1.5967966658  -1.9082845761  -0.1030379722
H24  2.5725071914  0.9396171816  0.6153403469
H25  3.8704948582  -2.6192907859  0.7590456292
H26  4.0680360646  -1.0168105408  1.5131097647
H27  -2.1965065298  0.3785654369  -0.3616692938
H28  -0.681983873  4.3769273834  0.0005127531
H29  -1.7961350462  3.3331127763  0.9094339853
H30  -2.2081314951  3.8272119875  -0.7662561154
H31  -5.3647925363  -0.9393957493  -0.7123505992
H32  -3.7344492096  -0.5572629093  -2.4445720991
H33  -4.3485365952  -2.8354015858  -1.8257871303
```

H34 -2.9516784507 -0.8157579729 2.3599428988
H35 -2.4093336726 0.8590581906 2.0809389901
H36 -3.9398996822 0.2912086334 1.391102819

***trans, unlike*-4gTS-(a)**

b3lyp/6-31G(d) =-1133.6670229

C1 -0.1254483442 0.17442183 -1.4938382278
C2 0.2543657653 0.7897341616 1.0810623467
C3 -0.8953435437 0.1873160947 1.5419012471
C4 -2.1665336958 0.4260879596 0.9884536434
C5 -2.3235288744 1.2805819295 -0.107953155
C6 -1.5038904782 0.3728619088 -1.6259608348
C7 -3.6206950747 1.5344278077 -0.8309979635
C8 -2.0801451877 1.3828305154 -2.5951312547
O9 -3.2853233673 1.8808060461 -2.1911597113
C10 0.3541106107 -1.1808669373 -1.2362660553
C11 1.6370593048 0.4642496406 1.5872976326
O12 -1.5853829165 1.7295577034 -3.6364558233
O13 -0.3513919457 -2.1487077723 -0.9973312266
O14 1.7144063987 -1.2598970366 -1.319491944
C15 2.2501136152 -2.5829511235 -1.1803807201
O16 1.5671299715 -0.6441872136 2.482763244
Si17 2.859754749 -1.5686801629 2.9732273734
C18 2.2613813706 1.6890475436 2.2764115619
H19 0.5870561343 0.9269558761 -1.8118721177
H20 0.2061132367 1.7049134545 0.5022732186
H21 -0.7864419702 -0.6189835064 2.2602225006
H22 -2.9781356254 -0.2464869631 1.260434048
H23 -1.6724512721 2.15445267 -0.1305117128
H24 -2.0853551444 -0.5494423869 -1.580973373
H25 -4.1758956636 2.3892898445 -0.4325421162
H26 -4.2749145814 0.653556324 -0.8236977147
H27 2.2598141316 0.1898771871 0.7214366392
H28 1.8643349491 -3.2376402685 -1.9670330972
H29 1.9891556385 -3.0103996462 -0.2086162921
H30 3.3315029345 -2.4733110867 -1.2721900489
H31 2.2827952889 -2.7784680109 3.6044089341
H32 3.7241438106 -0.8677644383 3.9637494138
H33 3.7117136804 -1.9490597423 1.8104823094
H34 2.2952360113 2.5442389669 1.592282942
H35 3.2871483251 1.4750566209 2.5959591797
H36 1.6734356974 1.9677155853 3.1568184257

***trans, unlike*-4gTS-(b)**

b3lyp/6-31G(d) =-1133.6652121

C1 0.8992119501 -1.3406406753 0.0546057171
C2 -0.7119169689 0.7947800339 0.5291875995
C3 -0.6711178962 1.2016741109 -0.7893582114
C4 0.5198872822 1.4267058843 -1.5017439262
C5 1.7578840725 1.1692185375 -0.8980954736
C6 1.8824849396 -0.7432030754 -0.7474860606
C7 3.1028776843 1.3060189872 -1.56562063
C8 3.335874653 -0.6708610487 -0.3281217286
O9 3.9906328669 0.3806158777 -0.9034339922
C10 -0.1821441231 -2.0353811466 -0.6412171019
C11 -2.0098043362 0.5606195768 1.2686953351
O12 3.9084869221 -1.437284572 0.4014309301

O13 -0.4165392058 -1.9395423222 -1.8377722148
O14 -0.9040579595 -2.8388616012 0.1873008802
C15 -1.9502398643 -3.5858746543 -0.4492064761
O16 -2.3968336261 1.7954918109 1.9085575767
Si17 -3.078152214 3.1064800079 1.1419620424
C18 -1.9092286951 -0.4845971378 2.3721773205
H19 1.0500812687 -1.511484976 1.1136382605
H20 0.1484687798 0.9326976251 1.1762903578
H21 -1.6025299302 1.2109299369 -1.3536335974
H22 0.4626034951 1.5514036878 -2.5810177319
H23 1.8195115162 1.3902243848 0.1670927494
H24 1.7680243302 -0.9722817704 -1.8082833527
H25 3.5472507748 2.2972086168 -1.4347482527
H26 3.0581158609 1.0751112515 -2.6372891333
H27 -2.7900576247 0.2724525119 0.5483118831
H28 -1.5415620088 -4.2286527394 -1.2335051175
H29 -2.6919616041 -2.9165216213 -0.894667162
H30 -2.4030233512 -4.1865708985 0.3404763802
H31 -3.7380299453 3.9057521046 2.2017778095
H32 -4.0849000818 2.6557389303 0.1361849271
H33 -2.0838401141 3.9658296137 0.4417209887
H34 -1.6512619653 -1.4635061181 1.9611136457
H35 -2.8656157532 -0.5542625968 2.8995151742
H36 -1.1432668195 -0.1888979552 3.0979899537

***trans, unlike*-4gTS-(c)**

b3lyp/6-31G(d) =-1133.6623113

C1 -0.2740077776 -0.1829850403 -1.05727548
C2 0.8322915758 0.4577371882 1.2718522936
C3 0.4663154021 1.7863852698 1.2463888082
C4 0.7398980813 2.6335578384 0.1559303242
C5 1.3742833861 2.135800786 -0.9851306299
C6 0.08363728 0.9271967669 -1.8303362571
C7 1.624076473 2.9074319062 -2.2540148424
C8 0.9555159492 0.8060528554 -3.0610566616
O9 1.6577343875 1.9468857336 -3.3300322963
C10 -1.6305218022 -0.2075320539 -0.5032562698
C11 0.5172676899 -0.5138993402 2.3839086178
O12 1.0399382887 -0.1546649146 -3.7812756376
O13 -2.3710632447 0.7614240994 -0.4148469971
O14 -2.0059937989 -1.4590636094 -0.1318692727
C15 -3.3658174536 -1.5852325517 0.3007474149
O16 0.5664316707 -1.8206830263 1.8052271473
Si17 0.7050461312 -3.2487306596 2.6450321473
C18 -0.8022148259 -0.2591603978 3.1144535637
H19 0.2867872973 -1.1087976385 -1.0932878861
H20 1.6201163566 0.0958886027 0.6213580539
H21 -0.1948882219 2.16884798 2.0195551147
H22 0.228636682 3.5932293259 0.1098535293
H23 2.1415500522 1.3808308878 -0.8167167105
H24 -0.7209434828 1.6535060359 -1.9548165402
H25 2.597406205 3.4078416656 -2.2685481097
H26 0.8409102939 3.6520661965 -2.4447331078
H27 1.3390044719 -0.4336910861 3.1202825399
H28 -4.0534240268 -1.2470246268 -0.4796417404
H29 -3.5486736976 -0.9974276272 1.205371235
H30 -3.5104875802 -2.6470070158 0.504273256
H31 1.0453590741 -4.2851144655 1.6434706889
H32 -0.5509957036 -3.6390829243 3.3453288917
H33 1.7857246716 -3.1482386016 3.6703957836

H34 -0.7890015692 0.7147436549 3.614763331
H35 -0.9657523545 -1.0199235309 3.8847568953
H36 -1.6426965997 -0.2817232214 2.4169958749

***cis, like*-4gTS-(j)**

b3lyp/6-31G(d) =-1133.6628273

C1 1.982239341 -1.3100491271 -1.1252584817
C2 1.0393542387 -2.1790211192 -0.5486161571
C3 -0.3112905763 -1.8450893434 -0.3955722454
C4 -0.8616941219 -0.6470795625 -0.8030276586
C5 0.9679155043 0.8443153687 0.5045335764
C6 2.1446218644 0.2348951139 0.043839468
C7 3.0724154615 -0.4813242238 0.9978059656
O8 3.1777282792 -0.2759722297 2.1799088024
O9 3.8408568129 -1.4233013871 0.3761548205
C10 3.4536920864 -1.6533885375 -0.9970570573
C11 -2.337246719 -0.3587554156 -0.6403203826
C12 0.5526493074 2.0850965721 -0.1482526239
O13 0.826213941 2.4010185531 -1.2991718731
O14 -0.1662281099 2.8830066027 0.6836617693
C15 -0.5591636851 4.1474522154 0.1339205509
O16 -2.8629126544 -1.139884668 0.4318116773
Si17 -4.4527189407 -1.6120130016 0.5700795522
C18 -2.668390071 1.1226250587 -0.4571234907
H19 1.6829897813 -0.7445191228 -2.0048873614
H20 1.4108104242 -3.040257694 0.0058559071
H21 -0.9410274904 -2.509950345 0.1884174574
H22 -0.3518464178 -0.0106061185 -1.5190514446
H23 0.5705130418 0.6103142197 1.4843242167
H24 2.6771140986 0.8258773351 -0.7043828361
H25 4.0730975885 -1.0354051894 -1.6573529922
H26 3.6705612129 -2.7062585973 -1.196607031
H27 -2.8057219516 -0.6923823701 -1.5865748485
H28 0.3147474033 4.7068732433 -0.2101013855
H29 -1.2437150935 4.0110768081 -0.7086288952
H30 -1.0581321372 4.6770253671 0.9463618727
H31 -5.355398466 -0.494448088 0.9631522535
H32 -4.9438815791 -2.1678182396 -0.724523349
H33 -4.4817519721 -2.6544122599 1.6224100208
H34 -3.7526943972 1.2753192349 -0.4717347078
H35 -2.2731276677 1.4875991615 0.4932818671
H36 -2.2303531408 1.7131577119 -1.269222828

***cis, like*-4gTS-(k)**

b3lyp/6-31G(d) =-1133.664266

C1 0.9386980272 1.8016996448 -1.7861877933
C2 -0.0180824725 2.5269111721 -1.054430447
C3 -0.3348860258 2.2248892379 0.2743103603
C4 0.2461493488 1.2001611136 0.9975268421
C5 -0.1717138556 -0.6731223833 -0.7954192788
C6 0.2973470615 -0.033344285 -1.9519499204
C7 -0.6353926777 0.3099941846 -3.0876960424
O8 -1.6793321554 -0.2331314677 -3.345112808
O9 -0.1691240172 1.3386016793 -3.8558670026
C10 0.9919464705 1.9882614197 -3.2901114323
C11 -0.1588852076 0.9452597917 2.4331027585
C12 0.7537101747 -1.5782926962 -0.1065995275

O13 1.9730157114 -1.49312207 -0.1660362441
O14 0.1134469202 -2.5412387422 0.5974227614
C15 0.9709510718 -3.4263588644 1.3356183283
O16 -0.3084050976 -0.4531044646 2.6972859324
Si17 -1.8081722836 -1.173654282 2.810428934
C18 0.9050859511 1.4854674588 3.3956277962
H19 1.8667295353 1.5339553833 -1.2857452855
H20 -0.7014363925 3.1751285697 -1.6018558686
H21 -1.1878261257 2.7402098393 0.7153417573
H22 1.2011820787 0.7779190695 0.7034960616
H23 -1.2333119132 -0.7500238525 -0.5968683029
H24 1.2704466368 -0.3958511327 -2.2886160029
H25 1.8995295369 1.5499584485 -3.7208846734
H26 0.9276703623 3.0354961952 -3.597774832
H27 -1.1075626315 1.4699937848 2.6290600177
H28 1.6982638134 -3.8995527361 0.6715210638
H29 1.4988753695 -2.872706572 2.1164998519
H30 0.3093777014 -4.1720294053 1.7770809185
H31 -2.6242555282 -0.4614086389 3.8381194829
H32 -2.5772773837 -1.1399300812 1.5374823474
H33 -1.5783910089 -2.5708244581 3.2423419724
H34 1.8550618299 0.9654923332 3.2332366681
H35 1.0613699889 2.5592320251 3.2474032238
H36 0.5895880103 1.3129069334 4.4298655473

***cis, like*-4gTS-(l)**

b3lyp/6-31G(d) =-1133.6647933

b3lyp/6-31G(d) =-1133.6646789

C1 0.2347492878 1.3067922564 -2.1709248821
C2 -1.1264855849 0.9853129806 -2.1246281278
C3 -1.778205284 0.6002271093 -0.9426797866
C4 -1.1335177687 0.5065890835 0.2740928538
C5 0.7529707221 -1.0502236166 -0.5229987384
C6 1.2383477249 -0.3693442083 -1.6402836186
C7 1.1015153728 -0.939744757 -3.0279563317
O8 1.0307436158 -2.1109395793 -3.3047583928
O9 1.073911312 0.0110835386 -4.0066133139
C10 0.9423068485 1.3622013381 -3.5073093439
C11 -1.7676565569 0.0024305516 1.5541209464
C12 1.4493785071 -0.8776376732 0.7548990668
O13 2.2048677706 0.0434077232 1.028840155
O14 1.1491050423 -1.8731794365 1.6297148736
C15 1.8522914427 -1.8234841409 2.8819195773
O16 -2.031949248 1.1338648931 2.4075075203
Si17 -0.9336225745 1.8278863377 3.4472970784
C18 -3.0780141276 -0.7576392897 1.3872636746
H19 0.6601441239 1.8881414686 -1.3569922697
H20 -1.6369940841 0.7861276955 -3.0664145476
H21 -2.7866798387 0.2058761491 -1.0361846379
H22 -0.2154670345 1.0635345118 0.4301994747
H23 0.0923252031 -1.9007112195 -0.6384504336
H24 2.1622297287 0.1850958387 -1.47082067
H25 1.936509351 1.8146882278 -3.4191481432
H26 0.3782588202 1.9039302306 -4.2718714735
H27 -1.0441489274 -0.6595267331 2.0514955399
H28 2.9324661075 -1.8361918038 2.7147945296
H29 1.590038434 -0.9211239053 3.4408185293
H30 1.5382634838 -2.7143855175 3.42673645
H31 -0.2384149484 0.7814664692 4.2524652831

H32 0.1039400662 2.6317314383 2.7442056867
H33 -1.7171133918 2.7169336599 4.3374161765
H34 -3.8545985712 -0.1094048763 0.9694878995
H35 -2.9478691603 -1.6272086332 0.7342800175
H36 -3.4216847613 -1.1061566439 2.3652050144

***cis, unlike*-4gTS-(g)**

b3lyp/6-31G(d) =-1133.6682491

C1 -0.2249288203 1.001718637 -2.4673234815
C2 -1.3348688931 1.3442263804 -1.6864555163
C3 -1.2644938123 1.5192193554 -0.2962465627
C4 -0.0976050117 1.3746786938 0.425585508
C5 0.4621156914 -0.9897390167 -0.4473893196
C6 0.3876356657 -0.8199417871 -1.8302208408
C7 -0.6693986176 -1.5108662599 -2.6516386473
O8 -1.2024277727 -2.5571821449 -2.3789172025
O9 -0.9909287655 -0.8426948741 -3.7976254981
C10 -0.4330329559 0.4895569674 -3.8758312458
C11 -0.0440024345 1.4703053268 1.9316287875
C12 1.7728887181 -0.9009408676 0.1962156695
O13 2.7812898487 -0.4296496246 -0.3088264272
O14 1.7475467427 -1.3954013109 1.4650684432
C15 3.0143306582 -1.4072032385 2.1416891752
O16 -1.3125458861 1.1912390779 2.523675756
Si17 -1.7082496286 -0.2640119876 3.235179721
C18 0.3828374907 2.8788251925 2.3714592574
H19 0.7321147961 1.4655215251 -2.2422914075
H20 -2.3246259481 1.2292915949 -2.1275660683
H21 -2.1939570111 1.6096678854 0.2595669346
H22 0.866171898 1.4794385985 -0.0627698433
H23 -0.3538083167 -1.444826146 0.1002277051
H24 1.3519930514 -0.7221881691 -2.330655332
H25 0.5081475799 0.4555706533 -4.4363128052
H26 -1.1577976022 1.0774461891 -4.4463054377
H27 0.7074318651 0.7545110011 2.295183375
H28 3.7284648709 -2.0380055385 1.6053982806
H29 3.4254299 -0.3969460946 2.2180913418
H30 2.8122969363 -1.8163214502 3.1320292589
H31 -2.9929448664 -0.0300697476 3.9365414452
H32 -0.6587154913 -0.6706641792 4.2118292825
H33 -1.880042051 -1.3646414558 2.2481699718
H34 1.3489432403 3.1517393028 1.9330173592
H35 0.470272153 2.9155485775 3.4620348517
H36 -0.3662196121 3.6115699927 2.0554577207

***cis, unlike*-4gTS-(h)**

b3lyp/6-31G(d) =-1133.6627244

C1 -1.4771334065 -1.5680186631 0.8988063982
C2 -0.7431817851 -2.1764973804 -0.1342216231
C3 0.4588262221 -1.6469523803 -0.6165338144
C4 1.0639480943 -0.5012389093 -0.1333157281
C5 -1.1436069281 0.9855485284 -0.3962863954
C6 -2.0814511205 0.1582811751 0.2385629271
C7 -3.2300413233 -0.4502010492 -0.5317472109
O8 -3.7144557009 -0.0210015719 -1.5474377393
O9 -3.7138271749 -1.5837272437 0.0558514243
C10 -2.894138481 -2.0448619514 1.153441358

```
C11  2.3884467713  -0.0411265135  -0.7074575996
C12  -0.5968176692  2.1012368377  0.3789869262
O13  -0.5289760514  2.1395925753  1.5995297862
O14  -0.186830088  3.1196377238  -0.4180697899
C15  0.315182998  4.2737771548  0.2711565549
O16  3.4397041923  -0.5434318725  0.1424446344
Si17  3.9828882474  -2.1174439106  0.171623934
C18  2.5773600294  1.4669643048  -0.7811103246
H19  -0.9273995867  -1.1694550757  1.74849456
H20  -1.2378076979  -2.9381653837  -0.7355242357
H21  0.8771277723  -2.0979198409  -1.5163579156
H22  0.8194683524  -0.1044777613  0.8472095336
H23  -1.0764455929  1.017009273  -1.4767373668
H24  -2.3689505147  0.5093809241  1.2317943643
H25  -3.2914999437  -1.650150089  2.0955258999
H26  -2.9886405311  -3.1340086728  1.1613003398
H27  2.5045800021  -0.4730995201  -1.7132042283
H28  -0.4410774589  4.6739911461  0.9515627093
H29  1.2110659228  4.0236436958  0.8464383464
H30  0.5523665559  4.9988968481  -0.5080090382
H31  5.3147857806  -2.0777884122  0.8207344119
H32  4.1040017785  -2.6511038951  -1.2170445683
H33  3.097729227  -3.0348756447  0.9405369923
H34  1.8333421037  1.9297479508  -1.4339653955
H35  3.5785028773  1.6874577984  -1.164149948
H36  2.4891336652  1.9051075984  0.2184251285
```

***cis, unlike*-4gTS-(i)**

```
b3lyp/6-31G(d) =-1133.6650906

C1  2.0904643793  -1.2402066311  -0.950024093
C2  1.7701330952  -2.0460619704  0.1492152757
C3  0.4926096087  -2.0601906512  0.7270625067
C4  -0.5456804456  -1.2683607607  0.2765506059
C5  0.7244170234  0.9711627493  0.3880444997
C6  1.8736643702  0.6773996872  -0.3473479474
C7  3.2321293708  0.6696755432  0.3051898455
O8  3.5525055354  1.3106789251  1.2746701565
O9  4.1306760213  -0.1492370783  -0.3155147647
C10  3.5412775821  -1.0133930537  -1.313741087
C11  -1.9089711003  -1.2473853361  0.9423316455
C12  -0.3924544085  1.6450072051  -0.2873129319
O13  -0.5868711494  1.637207323  -1.4942204776
O14  -1.1856107955  2.2938240464  0.5966060749
C15  -2.3318016913  2.9534301545  0.0386886196
O16  -2.8313845403  -0.4805231875  0.1629436789
Si17  -3.6499721021  -1.089098642  -1.1548380518
C18  -1.9046172531  -0.6729633354  2.3604734958
H19  1.3570947901  -1.136657957  -1.7456505434
H20  2.5866209829  -2.4924195627  0.7159208293
H21  0.3659467363  -2.61250266  1.6574057619
H22  -0.5247445983  -0.8669798156  -0.7298917049
H23  0.7622783689  0.9979573434  1.4701132256
H24  1.8683362867  1.0475091444  -1.3734533211
H25  3.6414207198  -0.5479278193  -2.3008328913
H26  4.1379353176  -1.9300029961  -1.2978156192
H27  -2.2666183846  -2.2911935937  1.000498804
H28  -2.0398061916  3.5928716448  -0.7976309917
H29  -3.058514118  2.2122320733  -0.3022454978
H30  -2.7498161342  3.5486558154  0.8515432232
H31  -4.5667188153  -0.0140266273  -1.5986782714
```

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H32  -4.4269020877  -2.3020946012  -0.7663971517
H33  -2.7420504992  -1.4715813782  -2.271935459
H34  -1.1916920409  -1.2084352937  2.9960999022
H35  -2.9025925321  -0.7670155936  2.7997100785
H36  -1.632112128  0.3847110317  2.3303123981
```

TSs for IMDA reaction of 42–45 (refer to Table 4 of the paper)

***trans*-42aTS**

```
b3lyp/6-31G(d) -767.7260353

C1  -0.2634977977  -0.284219791  -1.2417576125
C2  -0.9916641313  1.8517663822  0.1854654487
C3  0.1451677528  2.587291422  -0.0692687883
C4  1.4527737955  2.0984368612  0.1311875677
C5  1.6847977947  0.7755068249  0.5081219053
C6  1.1224061323  -0.3173915419  -1.0616101037
C7  3.0515257586  0.1581991777  0.6114187848
C8  1.9011991778  -1.5327772676  -0.574718769
O9  2.949560459  -1.2304573601  0.2405263861
C10  -1.2346542545  -1.0861281575  -0.5027030072
C11  -2.3797320213  2.2630041846  -0.2057645549
O12  -2.4001421621  -1.2432479664  -0.8274542585
O13  1.700406591  -2.6670637754  -0.9198986646
O14  -0.7127278135  -1.6043179097  0.648135129
C15  -1.5844157203  -2.4784603431  1.3792568347
C16  -3.2292603835  2.6919432101  1.00698298
H17  -0.6808686506  0.2468559486  -2.0873394734
H18  -0.9348835095  1.0229937501  0.8848226681
H19  0.0378725074  3.5334400338  -0.5992071749
H20  2.2826467116  2.6862691622  -0.2594743994
H21  0.961692134  0.3027486004  1.1702578043
H22  1.6877583389  0.1984603413  -1.8399045054
H23  3.4452130324  0.1638983403  1.6330888965
H24  3.7772024344  0.6563172865  -0.0445867426
H25  -2.3388760787  3.0762854102  -0.9410150382
H26  -2.871356043  1.4079717132  -0.6908472526
H27  -1.0161739475  -2.7940188364  2.2549346494
H28  -1.8549938556  -3.3441650625  0.7691910024
H29  -2.4968005429  -1.9550983106  1.6781130936
H30  -4.2463500801  2.9487714476  0.6915500615
H31  -2.7952442704  3.5644250686  1.5077431985
H32  -3.3014913937  1.8825154316  1.7425403614
```

***trans*-42bTS**

```
b3lyp/6-31G(d) = -767.7239624

C1  -0.5484733186  -0.9463457359  0.3836155742
C2  -0.6139137747  1.6541124443  1.5529684676
C3  -1.5229440237  2.1615672194  0.6517425514
C4  -1.448279971  1.9988393803  -0.7447834141
C5  -0.4657064442  1.2045389398  -1.3570797179
C6  -0.8679217199  -0.6008712561  -0.9427120901
C7  -0.4082447126  1.0400729994  -2.8562248086
C8  -0.0916505911  -1.1699032585  -2.1363257194
O9  0.0850083018  -0.2793443478  -3.1467776764
```

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C10  0.8038605238  -1.2188294151  0.8516680352
C11  -0.808016233  1.7256692024  3.0424098879
O12  1.0978390618  -1.7838196209  1.892702103
O13  0.272241474  -2.3102193225  -2.24169728
O14  1.7516658819  -0.7231068843  -0.0044516404
C15  3.1089497394  -1.0458460779  0.3302078161
C16  -0.9817787944  0.3569310934  3.7300142717
H17  -1.3337778265  -1.1831032362  1.0884573876
H18  0.362446925  1.3314836685  1.2076923262
H19  -2.4229000833  2.6288652532  1.0510334433
H20  -2.3065561854  2.3133087829  -1.3376363567
H21  0.5235911118  1.2039718426  -0.9021967886
H22  -1.9379739514  -0.6442981687  -1.1591802642
H23  0.28893464  1.737743184  -3.3302417835
H24  -1.3962228697  1.1628733666  -3.3186462731
H25  -1.6780481091  2.3563425716  3.2655178133
H26  0.0672296295  2.2270357287  3.4816665112
H27  3.7215327951  -0.5738827933  -0.4389133581
H28  3.2558592098  -2.1290182061  0.3220772001
H29  3.3659366553  -0.659921468  1.3203857997
H30  -1.9097905403  -0.1234929316  3.4012493236
H31  -1.0344941891  0.4858816044  4.8167760858
H32  -0.1550890488  -0.321481007  3.5007497601
```

trans-42cTS

```
b3lyp/6-31G(d) = -767.7251765

C1  -0.5829455551  -0.80494532  -0.6252007441
C2  -1.4698808606  1.3830068308  0.6547767921
C3  -1.0980697177  2.2743435474  -0.327654532
C4  0.2023222094  2.3294271584  -0.872275318
C5  1.1797753896  1.3937300535  -0.5309186144
C6  0.5438880425  -0.3243095058  -1.2999807088
C7  2.5388446856  1.3313012849  -1.170664323
C8  1.9302739639  -0.9518824363  -1.2181845206
O9  2.9496988934  -0.0487956849  -1.2248885297
C10  -0.568730675  -1.5167861768  0.6480517931
C11  -2.8689013087  1.1212751661  1.135374238
O12  -1.5150908076  -2.1303360721  1.1151776995
O13  2.15688124  -2.1327064844  -1.2320820002
O14  0.616659097  -1.3735906616  1.3115521845
C15  0.7334676815  -2.1221097047  2.5299584594
C16  -4.0022286025  1.6858706513  0.2755777191
H17  -1.5469621439  -0.7969776837  -1.1170920449
H18  -0.6941667925  0.9484201117  1.2771447825
H19  -1.8680568026  2.8644132253  -0.8198509117
H20  0.3589809573  2.9518528809  -1.7526398465
H21  1.1794561059  1.0089568458  0.4873603452
H22  0.3466568912  0.0043263163  -2.3221169979
H23  3.3084303312  1.8472503059  -0.5873345833
H24  2.5332295871  1.7477416952  -2.1863776656
H25  -2.954629243  1.5108267869  2.1630410212
H26  -2.9811144185  0.0320437574  1.2424925523
H27  1.7329715241  -1.9088317866  2.9104958561
H28  0.6212167723  -3.1913163718  2.3327423886
H29  -0.028588407  -1.8120371788  3.2503921308
H30  -4.9732380068  1.3997612706  0.6923125342
H31  -3.9534032332  1.3029513701  -0.7503084337
H32  -3.9728620196  2.780520386  0.2285025948
```

trans-43aTS

```
b3lyp/6-31G(d) -1094.3476704

C1  -0.0612906394  -1.1644076144  -0.1151617364
C2  -0.6286300059  1.365238028  0.4361653
C3  -1.1090034154  1.6890530175  -0.8107901475
C4  -0.3885643624  1.4503910655  -1.9998855792
C5  0.8231966676  0.7617683662  -1.9917774582
C6  0.3454415778  -1.1132449982  -1.450341136
C7  1.5679950446  0.3455739522  -3.2286129342
C8  1.6628592546  -1.66272795  -1.9792695671
O9  2.229194926  -0.9067759015  -2.9605634005
C10  0.8264936632  -1.1850202026  1.0437595218
C11  -1.4452304596  1.3901605855  1.6912798923
O12  0.4773405187  -1.4514193945  2.1831302928
O13  2.1548676882  -2.7104958297  -1.6530319824
O14  2.0987015333  -0.8000310635  0.734280378
C15  3.0471346596  -0.8851884588  1.8079802908
O16  -2.8327235718  1.4678700965  1.400269269
Si17  -3.9925970336  1.4624133831  2.5968538258
H18  -1.1017401233  -1.3472452982  0.1205110663
H19  0.4389216069  1.2760893862  0.6068741153
H20  -2.1532223162  1.9789604277  -0.8904892149
H21  -0.9132173023  1.5784905079  -2.9459960819
H22  1.4791106612  0.8958010744  -1.1337341595
H23  -0.4531987443  -1.2956876614  -2.1712895511
H24  2.3633093469  1.0465775034  -3.5025489357
H25  0.8980726713  0.2248912628  -4.0896881897
H26  -1.1342479819  2.254410131  2.3053807674
H27  -1.2099426917  0.4874765618  2.2786673151
H28  3.9968027404  -0.5538344874  1.3867725831
H29  3.1274012266  -1.9154576631  2.1639635549
H30  2.7486364096  -0.2434165524  2.6414979265
H31  -5.2962053145  1.5529007012  1.8991153447
H32  -3.8254235944  2.627309841  3.5126711791
H33  -3.9301587878  0.2161888968  3.4095835869
```

trans-43bTS

```
b3lyp/6-31G(d) -1094.3454311

C1  0.629492809  0.2485446892  1.3266658096
C2  -1.0932901782  -1.3862258505  0.126074189
C3  -0.3124425202  -2.5168660053  0.2028219024
C4  1.0280569066  -2.5674994722  -0.2335353527
C5  1.6853633951  -1.4232301061  -0.6846692012
C6  1.8698362673  -0.2534996437  0.924896959
C7  3.1443088057  -1.3791452937  -1.0439214861
C8  2.9700773339  0.5765195616  0.2735199841
O9  3.6558845713  -0.0759314941  -0.7046490507
C10  -0.0724429254  1.3765154144  0.7168633004
C11  -2.424767215  -1.2408240812  0.8050713967
O12  -1.0520483793  1.9238397223  1.1988404602
O13  3.2959926298  1.6801535428  0.621066034
O14  0.4461812652  1.7178728488  -0.494991279
C15  -0.1423733916  2.8695669291  -1.1206233205
O16  -3.4788144851  -1.1134123129  -0.1518107812
Si17  -4.1632372162  0.3362830355  -0.6051653161
H18  0.1824895299  -0.1046776559  2.2468311651
H19  -0.8637945898  -0.6173405415  -0.6040437388
H20  -0.6900159025  -3.3657676905  0.7718315173
```

H21 1.6170043342 -3.4467328571 0.0240940807
H22 1.0987782801 -0.6804909051 -1.222117893
H23 2.3075409029 -0.9753097412 1.6167041285
H24 3.3186170644 -1.4965346524 -2.1183393781
H25 3.7218840871 -2.1451601776 -0.5107553719
H26 -2.6399258038 -2.1252136444 1.4166366845
H27 -2.3995493672 -0.3661250527 1.4725675405
H28 0.4262596135 3.024652943 -2.0379316279
H29 -0.0587181474 3.7411874845 -0.4669837829
H30 -1.1968580334 2.6891136084 -1.3457026236
H31 -4.5634411234 1.1410530936 0.5805061096
H32 -5.3551634145 -0.0228898338 -1.4106940568
H33 -3.2482669413 1.158957821 -1.4469164781

trans-43cTS

b3lyp/6-31G(d) -1094.3428557

C1 -0.9301752337 -0.440219807 -0.160257888
C2 0.6672786289 1.469859365 -1.1658780463
C3 0.9361415371 0.8620705729 -2.3719663417
C4 1.3452570806 -0.4774136189 -2.5095500358
C5 1.4114079243 -1.3331317335 -1.4033809632
C6 -0.4181448399 -1.579197208 -0.8009703703
C7 1.7339984854 -2.7990957144 -1.5319429433
C8 -0.0916061806 -2.868636837 -0.0478870924
O9 1.0140344141 -3.5116873056 -0.5099365967
C10 -0.6513755636 -0.1137885837 1.2405941172
C11 0.0452007323 2.8406062865 -1.0881355858
O12 -1.3436974319 0.5846016772 1.9583641484
O13 -0.7636906277 -3.3474493101 0.8264465565
O14 0.523593059 -0.667728539 1.6679656281
C15 0.8105282308 -0.4989354943 3.0648552203
O16 -1.1751208414 2.8131399333 -0.355948096
Si17 -1.4520245449 3.7435861187 1.0009877801
H18 -1.7203342122 0.1429080238 -0.6120285646
H19 1.0924864082 1.0831855864 -0.2470248012
H20 0.66897458 1.3982984353 -3.2823400419
H21 1.350499787 -0.908877241 -3.5096041349
H22 1.7541070803 -0.9094497025 -0.461053093
H23 -0.9052644601 -1.816042524 -1.7489168999
H24 2.7934537214 -3.0148773938 -1.3613390446
H25 1.4499504376 -3.1948976206 -2.5154973519
H26 -0.1652982143 3.2142586392 -2.0987322976
H27 0.7678165538 3.5363833672 -0.6289797701
H28 1.7684041447 -0.9935671038 3.2293654261
H29 0.0305934298 -0.9668066487 3.6708066942
H30 0.8734991622 0.5620830882 3.3202272404
H31 -0.3814103108 3.5587275679 2.0197880332
H32 -2.7803406788 3.3644483725 1.5238478814
H33 -1.4608071853 5.1943044813 0.639638257

trans-44aTS

b3lyp/6-31G(d) =-539.8423626

C1 -0.6990386104 -1.3881433168 -0.2825766431
C2 -1.6439728953 0.7335858422 0.1747753928
C3 -1.0393268418 1.5092726291 -0.8059082679
C4 0.3530575754 1.5755936718 -0.9935590039
C5 1.1945821663 0.8356981059 -0.1769323895

```
C6  0.6285351955  -1.1668117201  -0.6171887508
C7  2.6413470902  0.5107696982  -0.4058616685
C8  1.7806110574  -1.609067413  0.2363311886
O9  2.8866611685  -0.801939358  0.1494122405
C10  -3.1413096472  0.5719987287  0.2640113655
O11  1.8029887436  -2.5824895721  0.9492181206
C12  -3.7861020604  1.5710875529  1.2427544575
H13  -0.9444209825  -1.7909328704  0.6955436638
H14  -1.4406060334  -1.5282784603  -1.0592222529
H15  -1.1130732215  0.5656394825  1.1082629566
H16  -1.6724065411  1.9125390002  -1.5964248206
H17  0.7279751988  1.9702110166  -1.9371411633
H18  0.9033443043  0.7226574237  0.8655702286
H19  0.8815593627  -1.0618933561  -1.6705817243
H20  3.3295663916  1.1793566915  0.123591071
H21  2.900912382  0.5208683349  -1.4723767118
H22  -3.3836277489  -0.4479889943  0.5902599651
H23  -3.5859273741  0.6939724421  -0.7322451658
H24  -4.8685804806  1.4114567258  1.3065922975
H25  -3.6113812752  2.6041733905  0.9227066544
H26  -3.3708314574  1.4597479407  2.2513480284

Version=DEC-AXP-OSF/1-G98RevA.7
HF=-539.8423626
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trans-44bTS

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b3lyp/6-31G(d) =-539.8406516

C1  -0.5328569513  -1.3092924109  0.0362272317
C2  -1.7362994671  0.7192406849  -0.4507978959
C3  -0.9770154571  1.1995399924  -1.5097465225
C4  0.4133963212  1.3937001746  -1.4494868764
C5  1.1056938437  1.0813138896  -0.2878951063
C6  0.8110102745  -0.9978442626  -0.1141046689
C7  2.5896374362  0.9243280225  -0.1264065663
C8  1.7835001428  -0.9845344028  1.0303047353
O9  2.8132540103  -0.0916377067  0.8779885919
C10  -3.2147913078  0.4391064415  -0.5972142166
O11  1.7290559597  -1.6764066303  2.0173150515
C12  -3.8089768145  -0.4862132092  0.4718093448
H13  -0.9463162293  -1.4203208839  1.0334165704
H14  -1.0719548796  -1.7951972097  -0.7671904115
H15  -1.4086881488  0.9231292858  0.5652494578
H16  -1.4466378666  1.2421863153  -2.4926464421
H17  0.9585146226  1.5127921784  -2.3851127289
H18  0.6029637283  1.2766192303  0.6576812526
H19  1.2778546193  -1.1999693262  -1.0763366659
H20  3.0858365345  1.8228423912  0.257319029
H21  3.0766432141  0.6344282826  -1.0665763822
H22  -3.4169949672  0.0338821122  -1.597545037
H23  -3.7487579573  1.4023748722  -0.5527027123
H24  -4.8955171072  -0.562275557  0.3555281787
H25  -3.610190781  -0.1047702814  1.4807061744
H26  -3.3950226649  -1.497436234  0.409643816
```

trans-44cTS

```
b3lyp/6-31G(d) =-539.8407369

C1  -0.6352268386  -1.2757981567  0.3331905514
```

```
C2  -1.6759473529  0.8358125949  0.0332869416
C3  -1.0410191443  1.2784551623  -1.1194637256
C4  0.3585122146  1.3456023947  -1.2498735771
C5  1.1745915874  0.9451061832  -0.2025882957
C6  0.7005254681  -1.1097025907  -0.0015956277
C7  2.6428137938  0.6392763402  -0.2531948579
C8  1.8195110357  -1.2066894042  0.9946976785
O9  2.9013415077  -0.4158152178  0.7018395216
C10  -3.1678622372  0.6169153215  0.152484415
O11  1.8353625905  -1.9053381406  1.9784374625
C12  -3.9105285746  0.2998065312  -1.1496534224
H13  -0.9192901161  -1.3501575516  1.3786657393
H14  -1.3285988815  -1.6969218007  -0.3841480622
H15  -1.1816662546  1.0004713307  0.9865222916
H16  -1.6276575277  1.3787990035  -2.0300696596
H17  0.7767115242  1.4365558175  -2.2517138961
H18  0.8307239106  1.1588560489  0.8077644875
H19  1.006103573  -1.3389804088  -1.0208744251
H20  3.2760025574  1.4753709335  0.0644695249
H21  2.9627658289  0.3236955201  -1.25467606
H22  -3.6151668604  1.5116802455  0.6146072916
H23  -3.3419374873  -0.1923364556  0.8741146874
H24  -4.9657626336  0.0896421163  -0.9456319356
H25  -3.4838413172  -0.577445367  -1.6500075575
H26  -3.8742388122  1.1372911762  -1.8549787806
```

***trans*-45aTS**

b3lyp/6-31G(d) -866.4638216

```
C1  0.7120288969  -1.1625822685  -0.0410639451
C2  -0.7646449417  0.4227909918  0.8838467137
C3  -0.9971096839  1.2501010747  -0.2035711772
C4  0.0381404888  1.8677039061  -0.930923146
C5  1.3586460604  1.6560318072  -0.5724090681
C6  1.5751144835  -0.4668572762  -0.8709978971
C7  2.5886384475  1.9140107428  -1.3916705321
C8  3.0319048863  -0.2769097284  -0.5749724573
O9  3.5591331894  0.8953632168  -1.0569855391
C10  -1.865081215  -0.3644599729  1.5445633805
O11  3.7405309482  -1.049775363  0.0228775995
O12  -2.8413513978  -0.7633576174  0.5889128135
Si13  -4.2281284514  -1.5767035169  1.0240109975
H14  1.0681477625  -1.51197275  0.923892892
H15  -0.1524338036  -1.6696912918  -0.4512460801
H16  0.0863592091  0.6059591365  1.5331273311
H17  -1.9885700903  1.2274434041  -0.6489381232
H18  -0.1944087228  2.2598070664  -1.9202474976
H19  1.5798165662  1.5495830263  0.4878458129
H20  1.3227600147  -0.3813982718  -1.9257375328
H21  3.0802042489  2.8649477172  -1.1565449515
H22  2.376470877  1.8915748768  -2.4683574668
H23  -2.3371526141  0.2486309764  2.3324884882
H24  -1.437629455  -1.2472294133  2.0435942741
H25  -5.0468396219  -0.7765708408  1.9795851815
H26  -3.9106587357  -2.8831277292  1.6685092042
H27  -4.9845937699  -1.8009242203  -0.2293757157
```

***trans*-45bTS**

b3lyp/6-31G(d) -866.4629948

```
C1  0.9037152152  -1.6316917597  -0.4148315333
C2  -1.0526660806  -0.3089648341  -0.1656695369
C3  -0.8203869242  0.6984018358  -1.0932058256
C4  0.3509075276  1.4761932244  -1.1130849161
C5  1.3426776102  1.2443317725  -0.1717409233
C6  1.9514119892  -0.7415140515  -0.5981330717
C7  2.7643905369  1.7241214571  -0.20532576
C8  3.0550207169  -0.5523146773  0.4042858282
O9  3.5804775406  0.7137659194  0.4280622757
C10  -2.2431820438  -1.2270369928  -0.2725231768
O11  3.493791536  -1.4003586784  1.1408961913
O12  -3.2616470574  -0.9188152117  0.6831509415
Si13  -4.2051728687  0.4519686899  0.6273332487
H14  0.7825897984  -2.1280876534  0.5432216413
H15  0.44693283  -2.1156843937  -1.2692817171
H16  -0.6476999768  -0.2275149293  0.8385046761
H17  -1.4667508532  0.7418945852  -1.9698102074
H18  0.5824121359  2.0395735912  -2.015812125
H19  1.0205643421  0.9648823579  0.829495238
H20  2.2421877067  -0.4953829069  -1.6177582265
H21  2.9284381859  2.6363536054  0.3789662488
H22  3.1150184924  1.9008963184  -1.2302655842
H23  -1.9501667654  -2.2624636185  -0.0672308401
H24  -2.6538636787  -1.1942389852  -1.2930321029
H25  -4.6785370447  0.7058432539  -0.7656411302
H26  -3.5001159443  1.673910419  1.1038164095
H27  -5.360896505  0.1865646172  1.5166604625
```

***trans*-45cTS**

b3lyp/6-31G(d) -866.4630234

```
C1  0.0726918865  -0.9532503546  -0.686765145
C2  -0.9774571181  0.8821765742  0.3763066011
C3  -0.7356696318  1.9013664539  -0.5321179085
C4  0.5536518706  2.2355420125  -0.9850360702
C5  1.6485548225  1.5229749734  -0.5231685605
C6  1.246533688  -0.4566200353  -1.2320052762
C7  3.0283375237  1.4784695535  -1.1110424042
C8  2.6117356362  -0.8323257328  -0.736030407
O9  3.5568364857  0.1523073645  -0.8875311648
C10  -2.3792991323  0.4828784435  0.7511999637
O11  2.9241579495  -1.8910136299  -0.2493549725
O12  -2.3866401565  -0.8473482738  1.2635896252
Si13  -3.7576735934  -1.5332370756  1.9143250733
H14  0.0994561702  -1.5453038222  0.2212977698
H15  -0.8072134158  -1.0746189361  -1.3058456965
H16  -0.2380880435  0.6436101841  1.1340984369
H17  -1.5823749322  2.313955678  -1.0809576572
H18  0.6423586535  2.8368630826  -1.8887497296
H19  1.6262219382  1.187905741  0.5120274738
H20  1.233628886  -0.1284097946  -2.2696462918
H21  3.7342307309  2.1560537602  -0.617355087
H22  3.0245430998  1.7056149525  -2.1849941996
H23  -3.0466049704  0.5635749265  -0.120284454
H24  -2.7638512827  1.1752661852  1.5206343375
H25  -4.8504536864  -1.6301701945  0.9038961015
H26  -4.2653282632  -0.7305918934  3.0642452589
H27  -3.3684060773  -2.8872658263  2.3694100487
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The structures and relative energies of the 12 diastereomeric TSs resulting from computational modeling of the larger C*–OSi*Me*$_3$ *Z*-dienophile compound **4b** are depicted in Figure S1.

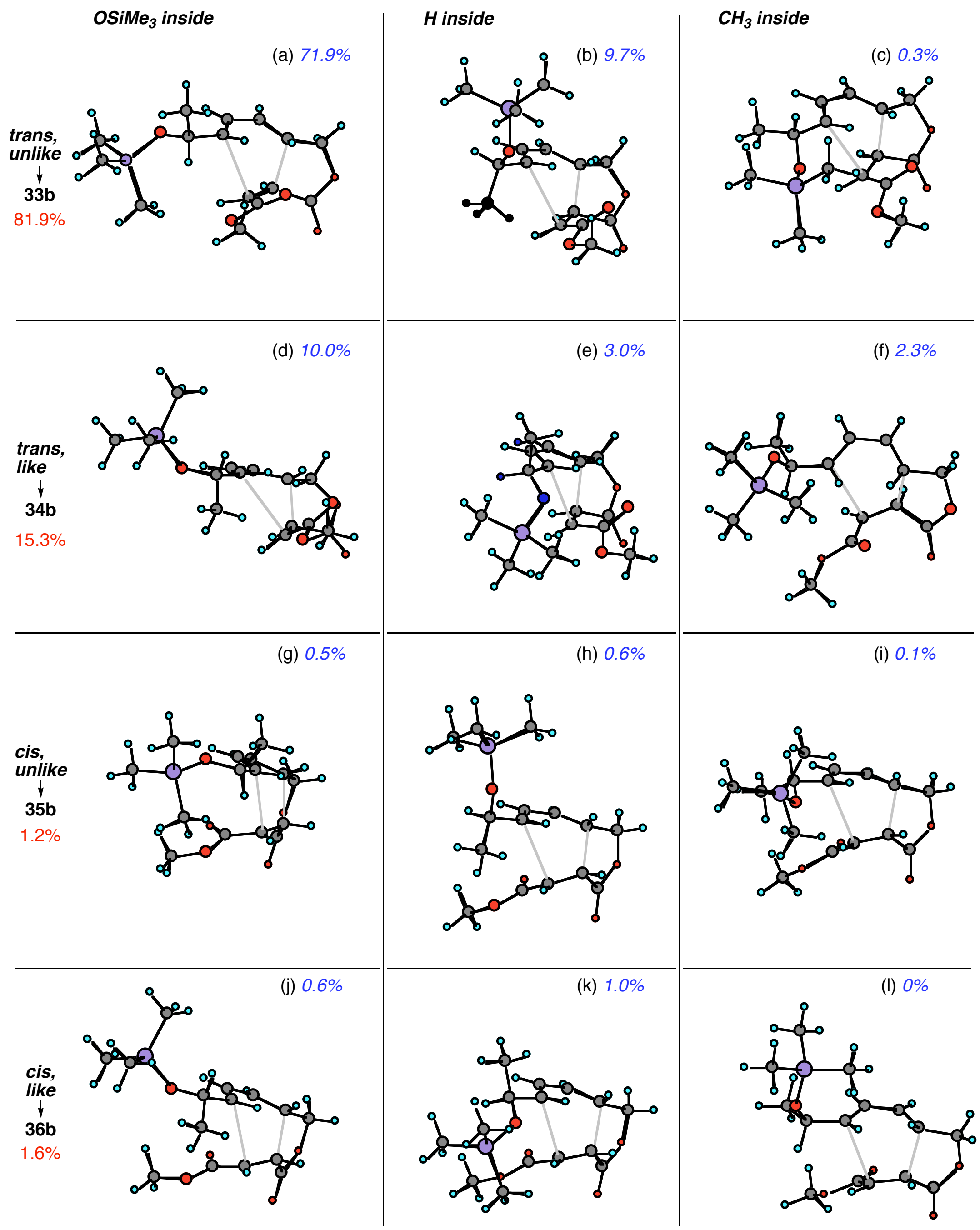

Figure S1. TSs and calculated Boltzmann populations (blue for individual TSs, red is the total for each diastereomeric adduct) at 383K for the IMDA reaction of **4b**. Structures (a)–(c) lead to the *trans, unlike* adduct **33b**; (d)–(f) lead to *trans, like* adduct **34b**; (g)–(i) lead to *cis, unlike* adduct **35b**; and (j)–(l) lead to the *cis, like* adduct **36b**. Structures on the left have the –OSiMe$_3$ group *inside*, those in the center column have the –H *inside*, and those on the right have the –CH$_3$ *inside*. To facilitate comparisons between TSs, dienophile approach from below is depicted throughout, hence the configuration at the allylic stereocenter is inverted in the *unlike* TSs.

The structures and relative energies of the 12 diastereomeric TSs for the IMDA reaction of *E*-dienophile C*–OSiH_3 triene precursor **4g** are shown in Figure S2.

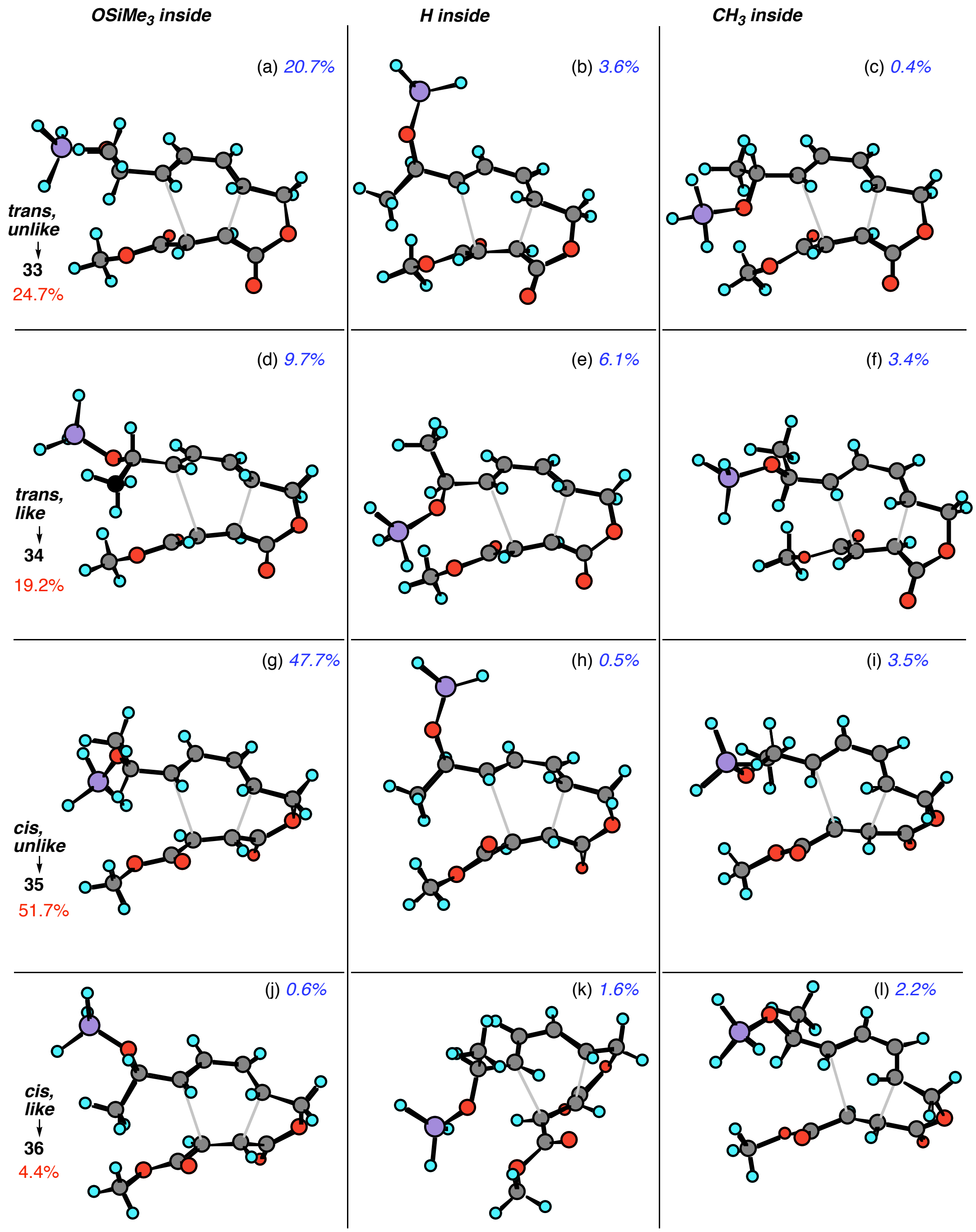

Figure S2. TSs and calculated Boltzmann populations (blue for individual TSs, red is the total for each diastereomeric adduct) at 405K for the IMDA reaction of **4g**. Structures (a)–(c) lead to the *trans, unlike* adduct **33g**; (d)–(f) lead to *trans, like* adduct **34g**; (g)–(i) lead to *cis, unlike* adduct **35g**; and (j)–(l) lead to the *cis, like* adduct **36g**. Structures on the left have the –SiH_3 group *inside*, those in the center column have the –H *inside*, and those on the right have the –CH_3 *inside*. To facilitate comparisons between TSs, dienophile approach from below is depicted throughout, hence the configuration at the allylic stereocenter is inverted in the *unlike* TSs.

Experimental Section

General Methods

NMR spectra were recorded at 298 K using a Varian Unity INOVA 500 MHz, Bruker DPX/DRX 400 Mhz, Varian Unity INOVA 300 MHz spectrometer or a Jeol JNM-GX270W instrument. Residual acetone (δ 2.04 ppm), acetonitrile (δ 1.96 ppm), benzene (δ 7.15 ppm), chloroform (δ 7.26 ppm), and methanol (δ 3.31 ppm) were used as internal references for ^{1}H NMR spectra measured in these solvents. Residual acetone (δ 29.8 ppm, 206.8 ppm), acetonitrile (δ 1.3 ppm, 118.3 ppm), benzene (δ 128.1 ppm), chloroform (δ 77.1 ppm), and methanol (δ 49.0 ppm) were used as internal references for ^{13}C NMR spectra. Assignment of proton signals was assisted by ^{1}H–^{1}H COSY and NOESY experiments when necessary; assignment of carbon signals was assisted by DEPT experiments. IR spectra were recorded on a Perkin–Elmer 1600 FTIR, a Perkin–Elmer Spectrum One spectrometer or a Perkin–Elmer Paragon 1000 FT-IR spectrometer as neat films on NaCl plates for oils or as KBr pellets for solid products. Low resolution mass spectra were recorded on a Finnigan PolarisQ ion trap mass spectrometer using electron impact (EI) ionization mode at 40 or 70 eV. Low resolution electrospray ionization spectra were recorded on a Finnigan LCQ ion trap mass spectrometer. High resolution mass spectra were recorded on a VG Autospec mass spectrometer operating at 70 eV. High resolution electrospray ionization spectra were recorded on a Bruker BioApex FTICR with an Analytica ESI source, operating at 4.7 T. Melting points were measured on a Reichert melting point stage and are uncorrected. Optical rotations were measured with an Optical Activity Polar 2001, Perkin–Elmer 241 optical polarimeter or an Optical Activity Limited AA-100 polarimeter. HPLC was performed using a Shimadzu LC-10ADVP pump with a Shimadzu SIL-10ADVP autoinjector or a Shimadzu LC-8A preparative pump monitored by a Shimadzu SPD-PAVP UV detector at λ = 254 nm and a Shimadzu RID-10A refractive index detector or a Waters 510EF chromatograph pump and Waters U6K injector monitored by an Waters Lambda-Max 481 UV spectrophotometer at λ = 254 nm and an Erma ERC-7512 refractive index detector or a Waters 510EF chromatograph pump and Waters U6K injector monitored by an ISCO 226 UV spectrophotometer at λ = 254 nm and a Waters R403 refractive index detector. GC measurements were recorded on an Agilent 6850 gas chromatograph with a split/splitless capillary inlet and FID detector or

GC measurements were recorded on a Hewlett Packard 5890A gas chromatograph with a split/splitless capillary inlet and FID detector. GC data was processed using Hewlett Packard ChemStation software. Analytical TLC was performed with Merck silica gel plates, precoated with silica gel 60 F254 (0.2 mm). Flash chromatography employed Merck Kiesegel 60 (230–400 mesh) silica gel.

Reactions were conducted under a positive pressure of dry argon or nitrogen. Benzene, diethyl ether, toluene and THF were dried over sodium wire and distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Chlorobenzene was purified by the method of Perrin and Armarego.[1] Commercially available chemicals were purified by standard procedures or used as purchased.

Chiral Dienols

Ethyl (2*R*,3*S*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate (5). Protection of L-ascorbic acid was based on the method of Jung and Shaw.[2] To a stirred solution of L-ascorbic acid (100 g, 0.568 mol) in acetone (400 mL, 5.68 mol, 10 equiv) at RT under a calcium chloride drying-tube was added acetyl chloride (10.0 mL, 1.50 mol, 2.64 equiv). Further acetone (200 mL) was subsequently added to aid stirring, which was continued for 8 h. The mixture was refrigerated overnight and the resulting precipitate rinsed with cold acetone (3 × 100 mL) then dried under vacuum yielding 5,6-*O*-Isopropylidene-L-ascorbic acid (93.6 g, 0.433 mol, 76%) as a white crystalline solid: mp 217–219 °C dec. [lit.[2] 214–218 °C dec.]; $[\alpha]_D^{21}$ +25.7° (*c* = 1.00, water) [lit.[3] $[\alpha]_D^{19}$ +25.3° (*c* = 1.00, water)]; (Found: M^+, 216.0632. $C_9H_{12}O_6$ requires *M*, 216.0633); IR (KBr disc): ν_{max} 3243, 3074, 2992, 1754, 1664 cm^{-1}; ^1H NMR (270 MHz, d_6-DMSO/internal reference 2.50 ppm): δ 1.25 (6H, s, –C(CH_3)$_2$–), 3.17–3.64 (2H, m, –CO*H*=CO*H*–), 3.88 (1H, dd, *J* 6.4, 8.3 Hz, C6-*H*), 4.09 (1H, dd, *J* 7.2, 8.3 Hz, C6-*H'*), 4.26 (1H, m, C5-*H*), 4.70 (1H, d, *J* 2.9 Hz, C4-*H*); ^{13}C NMR (68.1 MHz, d_6-DMSO/internal reference 39.7 ppm): δ 25.7, 26.0, 65.0, 73.6, 74.4, 109.1, 118.2, 152.4, 170.2; EIMS (CI/NH_3, 40 eV) *m/z* (%): 216 (8), 201 (45), 101 (89), 59 (48) and 43 (100).

Oxidative cleavage of 5,6-*O*-isopropylidene-L-ascorbic acid and esterification of the resulting potassium salt was based on the method of Abushanab et al.[4] To a stirred solution of 5,6-*O*-isopropylidene-L-ascorbic acid (93.6 g, 0.433 mol) in water (457 mL) containing potassium carbonate

(119 g, 0.866 mol, 2 equiv), chilled in an ice bath and maintained below 20 °C, was added 30% hydrogen peroxide (95.0 mL, 0.866 mol, 2 equiv). On completion of the addition the solution was warmed to RT and stirring was continued for 24 h. The solvent was evaporated and the moist solid extracted with boiling absolute ethanol (6 × 200 mL). After filtration and evaporation the material was dried under vacuum to give crude potassium (2*R*,3*S*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate salt (107 g) as a white powder. To a stirred solution of the crude salt in acetonitrile (500 mL) at RT under argon was added ethyl iodide (55 mL, 1.5 mol, *ca* 3.5 equiv) and the solution was warmed to reflux. Stirring was continued for 44 h and then the solvent was evaporated. The residue was partitioned between water (100 mL) and dichloromethane (3 × 100 mL). The combined organic layers were then partitioned against water (100 mL), brine (2 × 100 mL), dried, filtered and evaporated to produce the crude product (73.2 g) as an orange oil. Distillation gave ethyl (2*R*,3*S*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate (**5**) (69.0 g, 0.338 mol, 78%) as a yellow oil: bp 84–88 °C/0.5 mmHg; $[\alpha]_D^{21}$ +4.2° (*c* = 1.50, methanol); R_f = 0.20 [hexane:ethyl acetate (5:1)]; (Found: M^+-CH_3, 189.0762. $C_8H_{13}O_5$ requires *M*, 189.0763); IR (thin film): ν_{max} 3489, 2986, 2937, 2906 1743, 1208 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3/D_2O$ shake): δ 1.29 (3H, t, *J* 7.3 Hz, $–OCH_2CH_3$), 1.34, 1.41 [6H, 2 × s, $–C(CH_3)_2–$], 3.99 (1H, dd, *J* 7.0, 8.3 Hz, C4-*H*), 4.08 (1H, dd, *J* 6.6, 8.3 Hz, C4-*H'*), 4.09 (1H, d, *J* = 3.1 Hz, C2-*H*), 4.26 and 4.27 (2H, 2 × q, *J* = 7.3 Hz, $–OCH_2CH_3$), 4.35 (1H, ddd, *J* = 3.1, 6.6, 7.0 Hz, C3-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 14.2, 25.4, 26.1, 61.9, 65.6, 70.4, 76.4, 109.8, 171.8; EIMS (70 eV) *m/z* (%): 189 (73), 131 (28), 101 (100), 60 (54), 42 (84).

(2*R*,3*S*)-3,4-*O*-Isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanal (6). To a stirred solution of ethyl (2*R*,3*S*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate (**5**) (10.2 g, 0.0500 mol) in DMF (10 mL) at 0 °C under argon was added imidazole (4.08 g, 0.0600 mol, 1.2 equiv) and *tert*-butyldimethylsilyl chloride (7.90 g, 0.0525 mol, 1.05 equiv). On completion of the addition the resulting solution was allowed to warm to RT and stirred for 30 min. The reaction mixture was partitioned between water (50 mL) and ethyl acetate (3 × 50 mL) and the combined extracts were dried, filtered and evaporated to give the crude product (15.9 g) as a yellow oil. Distillation gave ethyl (2*R*,3*S*)-3,4-*O*-isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanoate (10.8 g, 0.0340 mol, 68%) as a colorless oil: bp 148–150 °C/14 mmHg; $[\alpha]_D^{20}$ +28.0° (*c* = 4.65, dichloromethane); R_f = 0.63 [hexane:ethyl acetate (5:1)]; (Found: M^+-CH_3, 303.1628. $C_{14}H_{27}O_5Si$ requires *M*, 303.1614); IR (thin film): ν_{max} 2985, 2955, 2932, 2896, 2858, 1735, 1473, 1464, 1380, 1370, 1156cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.08, 0.11 (6H, 2 × s, –Si(CH_3)$_2$–), 0.92 (9H, s, –C(CH_3)$_3$), 1.30 (3H, t, *J* = 7.1 Hz, –OCH$_2$CH_3), 1.35, 1.41 (6H, 2 × s, –C(CH_3)$_2$–), 3.97 (1H, dd, *J* = 6.4, 8.5 Hz, C4-*H*), 4.05 (1H, dd, *J* = 6.4, 8.5 Hz, C4-*H'*), 4.20 (1H, d, *J* = 5.3 Hz, C2-*H*), 4.21, 4.22 (2H, 2 × q, *J* = 7.1 Hz, –OCH_2CH$_3$), 4.33 (1H, td, *J* = 6.4, 5.3 Hz, C3-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –5.17, –4.92, 14.2, 18.4, 25.3, 25.7, 26.3, 60.9, 65.5, 73.3, 77.1, 109.5, 170.8; EIMS (70 eV) *m/z* (%): 303 (22), 261 (52), 203 (35), 101 (54), 75 (100).

To a stirred solution of ethyl (2*R*,3*S*)-3,4-*O*-isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanoate (10.8 g, 0.0338 mol) in dichloromethane (100 mL) at –100 °C under argon was added diisobutylaluminium hydride (1.5 mol/L in toluene, 33.8 mL, 0.0570 mol, 1.5 equiv) using a syringe pump over 1 h. The excess diisobutylaluminium hydride was quenched at –100 °C with 2% aqueous sodium hydroxide (30 mL) then the mixture was allowed to warm to RT. Water (50 mL) and dichloromethane (50 mL) were added resulting in an emulsion, which was eliminated by the stepwise addition of saturated aqueous potassium sodium (+)-tartrate. The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined extracts were partitioned against 50% aqueous potassium sodium (+)-tartrate (50 mL) and brine (50 mL) then dried, filtered and evaporated to give the crude product (11.0 g) as a yellow oil. Distillation gave (2*R*,3*S*)-3,4-*O*-Isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanal (**6**) (7.97 g, 0.0290 mol, 86%) as a colorless oil: bp 96°C/0.01 mmHg; $[\alpha]_D^{21}$ +2.0° (*c* = 4.79, dichloromethane); R_f = 0.46 [hexane:ethyl acetate (5:1)]; (Found: M^++H, 275.1671. $C_{13}H_{27}O_4Si$ requires *M*, 275.1679); IR (thin film): ν_{max} 2986, 2954, 2931, 2888, 2858, 1737, 1472, 1463, 1380, 1371cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.09, 0.11 [6H, 2 × s, –Si(CH_3)$_2$–], 0.94 [9H, s, –C(CH_3)$_3$], 1.35, 1.42 [6H, 2 × s, –C(CH_3)$_2$–], 3.95 (1H, dd, *J* = 6.2, 8.7 Hz, C4-*H*), 4.04 (1H, dd, *J* = 1.4, 4.7 Hz, C2-*H*), 4.07 (1H, dd, *J* = 6.4, 8.7 Hz, C4-*H'*), 4.32 (1H, ddd, *J* = 4.7, 6.2, 6.4 Hz, C3-*H*), 9.70 (1H, d, *J* 1.4 Hz, –C*H*O); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –5.00, –4.68, 18.3, 25.1, 25.7, 26.1, 65.1, 76.4, 77.7, 109.6, 202.0; EIMS (70 eV) *m/z* (%): 275 (3), 131 (25), 117 (31), 101 (100), 75 (69).

(2*S*,3*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (7). To a stirred solution of (2*R*,3*S*)-3,4-*O*-isopropylidene-2-[(*tert*-butyl-dimethylsilyl)oxy]-3,4-dihydroxybutanal (**6**) (5.00 g, 0.0182 mol) in dichloromethane (50 mL) at RT under argon was added ethyl 4-(triphenylphosphoranylidene)-(2*E*)-2-butenoate[5] (**16**) (9.55 g, 0.0255 mol, 1.4 equiv) and the resulting mixture warmed to reflux and heating continued for 1.5 h. (Consumption of the starting material was monitored by proton NMR analysis.) Evaporation gave the crude product (14.5 g) as a yellow oil. This material was adsorbed onto silica (15 g) then loaded onto a silica column (15 g) and eluted with hexane:ethyl acetate (10:1) to give a mixture of *Z*- and *E*-stereoisomers (79:21) of ethyl (4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadienoate (5.24 g, 0.0141 mol, 78%).

To a stirred solution of the *Z*- and *E*-stereoisomers of ethyl (4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadienoate (5.24 g, 0.0141 mol) in benzene (50 mL) at RT under argon was added thiophenol (0.435 mL, 4.23 mmol, 0.3 equiv) and 2,2′-azo-*bis*-isobutyronitrile (0.345 g, 0.213 mmol, 0.15 equiv) in three potions at one hour intervals, during which time the reaction mixture was irradiated with ultraviolet light at reflux for a total of 3 h. (Isomerization was monitored by proton NMR analysis.) The solvent was evaporated to give the crude product (5.65 g) as a yellow oil, which was used without further purification. A small portion of the crude material (103 mg) was purified on silica (10 g) with hexane:ethyl acetate (20:1 then 10:1) to give an analytically pure sample of the ethyl (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadienoate (77.0 mg) as a pale yellow oil: $[\alpha]_D^{20}$ –29.7° (*c* = 1.84, dichloromethane); R_f = 0.26 [hexane:ethyl acetate (10:1)]; (Found: M^+, 370.2174 $C_{19}H_{34}O_5Si$ requires *M*, 370.2176); IR (thin film): ν_{max} 2985, 2956, 2931, 2887, 2858, 1714, 1646, 1620, 1472, 1463, 1380, 1370cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.048, 0.071 [6H, 2 × s, –Si(CH_3)$_2$–], 0.894 [9H, s, –C(CH_3)$_3$], 1.29 (3H, t, *J* = 7.2 Hz, –OCH$_2$CH_3), 1.33, 1.39 [6H, 2 × s, –C(CH_3)$_2$–], 3.77 (1H, dd, *J* = 6.0, 8.6 Hz, C8-*H*), 3.95 (1H, dd, *J* = 6.7, 8.6 Hz, C8-*H′*), 4.07–4.15 (1H, m, C7-*H*), 4.20 (2H, q, *J* = 7.2 Hz, –OCH_2CH$_3$), 4.38 (1H, td, *J* = 5.3, 0.8 Hz, C6-*H*), 5.88 (1H, d, *J* = 15.4 Hz, C2-*H*), 6.13 (1H, dd, *J* = 5.3, 15.3 Hz, C5-*H*), 6.41 (1H, ddd, *J* = 0.8, 11.0, 15.3 Hz, C4-*H*), 7.28 (1H, dd, *J* = 11.0, 15.4 Hz, C3-*H*); ^{13}C NMR (68.1 MHz,

$CDCl_3$): δ –4.76, –4.61, 14.4, 18.3, 25.1, 25.8, 26.4, 60.3, 65.1, 72.8, 78.2, 109.5, 121.5, 129.1, 140.4, 143.4, 166.7; EIMS (70 eV) *m/z* (%): 370 (0.3), 313 (25), 270 (67), 101 (100), 73 (62).

To a stirred solution of the crude ethyl (2*E* ,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadienoate (5.55 g, *ca* 0.0150 mol) in dichloromethane (75 mL) at –78 °C under argon was added dropwise diisobutylaluminium hydride (1.5 mol/L in toluene, 22.0 mL, 0.0330 mol, *ca* 2.2 equiv). The starting material was consumed immediately and the excess diisobutylaluminium hydride was quenched at –60 °C with 2% aqueous sodium hydroxide (20 mL). Saturated aqueous potassium sodium (+)-tartrate (50 mL) was added to disperse the emulsion which formed and the aqueous layer was extracted with further dichloromethane (3 × 50 mL). The combined extracts were partitioned against brine (50 mL) then dried, filtered and evaporated to give the crude product (6.07 g) as a yellow oil. The crude product was adsorbed onto silica (10 g) then loaded onto a silica column (100 g) and eluted with hexane:ethyl acetate (3:1) to give the (2*S*,3*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**7**) [3.50 g, 0.0107 mol, 58% (3 steps)] as a pale yellow oil: $[\alpha]_D^{24}$ –26.0° (*c* = 1.33, dichloromethane); R_f = 0.14 [hexane:ethyl acetate (3:1)]; (Found: M^+, 328.2066. $C_{17}H_{32}O_4Si$ requires *M*, 328.2070); IR (thin film): ν_{max} 3418, 2954, 2929, 2886, 2857, 1661, 1626, 1472, 1462, 1380, 1371 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.02, 0.43 [6H, 2 × s, –Si(CH_3)$_2$–], 0.87 [9H, s, –C(CH_3)$_3$], 1.30, 1.36 [6H, 2 × s, –C(CH_3)$_2$–], 2.37 (1H, s, –O*H*), 3.75 (1H, dd, *J* = 6.2, 8.4 Hz, C1-*H*), 3.90 (1H, dd, *J* = 6.6, 8.4 Hz, C1-*H'*), 4.05 (1H, m, C2-*H*), 4.14 (2H, d, *J* = 5.3 Hz, C8-*H*), 4.24 (1H, t, *J* = 5.7 Hz, C3-*H*), 5.59–5.70 (1H, m, C4-*H*), 5.73–5.88 (1H, m, C7-*H*), 6.15–6.32 (2H, m, C5-*H* and C6-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.75, –4.52, 18.3, 25.2, 25.8, 26.4, 63.0, 65.2, 73.4, 78.6, 109.3, 130.3, 130.9, 131.6, 132.2; EIMS (70 eV) *m/z* (%): 328 (2), 227 (44), 210 (32), 101 (100), 73 (77).

Ethyl (2*R*,3*R*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate (8). Isoascorbic acid was converted into the monoacetonide before oxidative cleavage with potassium carbonate and hydrogen peroxide in water. The resulting potassium carboxylate was treated with ethyl iodide to give ethyl (2*R*, 3*R*)-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate (**8**) following the method of Abushanab et al.[4]

(2*R*,3*R*)-3,4-*O*-Isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanal (9). To a stirred solution of (**8**) (4.5 g, 22.2 mmol, 1.0 equiv) in DMF (5 mL) at 0 °C under argon was added imidazole (1.82 g, 26.7 mmol, 1.2 equiv) and *tert*-butyldimethylsilyl chloride (3.69 g, 24.5 mmol, 1.1 equiv). On completion of the addition the resulting solution was allowed to warm to RT and stirred for 30min. The reaction mixture was partitioned between water (50 mL) and ethyl acetate (3 × 50 mL) and the combined extracts were dried, filtered and evaporated to give the crude product as a yellow oil. Column chromatography gave ethyl (2*R*,3*R*)-3,4-*O*-isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanoate (6.44 g, 20.2 mmol, 91%) as a colorless oil that was used directly in the next step. To a stirred solution of ethyl (2*R*, 3*R*)-3,4-*O*-isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanoate (5.86 g, 18.4 mmol, 1.0 equiv) in dichloromethane (50 mL) at –98 °C under nitrogen was added DIBAL-H (1.0 M in hexanes, 27.6 mmol, 27.6 mL, 1.5 equiv) dropwise over 45 min. The reaction mixture was stirred at this temperature for a further 15 min before being quenched with 2% aqueous sodium hydroxide (15 mL). The reaction mixture was allowed to warm to RT and water (50 mL) and dichloromethane (50 mL) were added resulting in an emulsion, which was eliminated by the stepwise addition of saturated aqueous potassium sodium (+)-tartrate. The aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were dried and concentrated *in vacuo*. Chromatography of the crude product on silica (hexanes/ethyl acetate 95:5) gave (2*R*,3*R*)-3,4-*O*-isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanal (**9**) (2.94 g, 10.7 mmol, 58%) as a colorless oil. $[\alpha]_D^{25}$ +15.79 (*c* = 2.66, chloroform); IR (thin film): ν_{max} 2955, 2931, 2858, 1737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.07, 0.08 [6H, 2 × s, $–Si(CH_3)_2–$], 0.89 [9H, s, $–C(CH_3)_3$], 1.32, 1.41 [6H, 2 × s, $–C(CH_3)_2–$], 3.90 (1H, dd, *J* = 5.8, 8.3 Hz, C4-H′), 4.00 (1H, dd, *J* = 6.3, 8.3 Hz, C4-H), 4.04 (1H, dd, *J* = 1.9, 6.3 Hz, C2-H), 4.22 (1H, dd, *J* = 6.1, 6.1 Hz, C3-H), 9.64 (1H, d, *J* = 1.8 Hz, –CHO); ^{13}C NMR (75 MHz, $CDCl_3$): δ –4.9, –4.5, 18.3, 25.3, 25.7, 26.6, 65.9, 75.9, 78.0, 109.9, 201.5; EIMS (70 eV) *m/z* (%): 259 (10), 217 (40), 159 (80), 101 (95) 75 (100); HRMS: calcd for $C_{12}H_{23}O_4Si$ [M–CH_3]: 259.1366; found: 259.1363.

(2*R*,3*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (10). To a stirred solution of lithium hexamethyldisilazide, prepared from hexamethyldisilazane (3.05 mL, 14.0 mmol, 1.8 equiv) and *n*-butyllithium (6.92 mL of a 1.66 M solution in hexanes, 11.5 mmol, 1.47 equiv) in THF (20 mL) at –78 °C under nitrogen, was added phosphonate **17** (2.58 g, 10.9 mmol, 1.4 equiv) in THF (10 mL). The reaction mixture was warmed to –40 °C and a solution of (2*R*,3*R*)-3,4-*O*-isopropylidene-2-[(*tert*-butyldimethylsilyl)oxy]-3,4-dihydroxybutanal (**9**) (2.14 g, 7.8 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. The reaction mixture was warmed to RT and stirring was continued for 1.5 h. The mixture was concentrated *in vacuo* and the residue was portioned between water (100 mL) and ether (3 × 20 mL). The combined organic layers were washed with 1 M HCl (40 mL), dried and concentrated *in vacuo*. Chromatography of the crude product on silica (hexanes/ethyl acetate 93:7) gave ethyl (2*E* ,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadienoate (1.94 g, 5.4 mmol, 70%) as a colorless oil. $[\alpha]_D^{25}$ –8.13 (*c* = 0.16, chloroform); IR (thin film): ν_{max} 2987, 2954, 2858, 1723, 1649, 1619 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.01, 0.07 [6H, 2 × s, $–Si(CH_3)_2–$], 0.89 [9H, s, $–C(CH_3)_3$], 1.32, 1.40 [6H, 2 × s, $–C(CH_3)_2–$], 3.73 (3H, s, $–OCH_3$), 3.81–4.01 (3H, m, C8-H, C8-H′, C7-H), 4.21 (1H, dt, *J* = 1.1, 5.7 Hz, C6-H), 5.88 (1H, d, *J* = 15.1 Hz, C2-H), 6.11 (1H, dd, *J* = 5.8, 15.1 Hz, C5-H), 6.37 (1H, dd, *J* = 11.3, 14.6 Hz, C4-H), 7.27 (1H, dd, *J* = 11.8, 16.5 Hz, C3-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ –4.7, –4.2, 18.2, 25.4, 26.7, 25.8, 51.6, 66.3, 73.2, 78.8, 109.6, 121.3, 128.8, 142.4, 143.9, 167.4; EIMS (70 eV) *m/z* (%): 356 (5), 341 (50), 299 (10), 241 (35), 101 (100) ; HRMS: calcd for $C_{18}H_{32}O_5Si$ [M^+]: 356.2019; found: 356.2023.

To a stirred solution of ethyl (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadienoate (2.55 g, 7.14 mmol, 1.0 equiv) in diethyl ether (5 mL) at 0 °C under nitrogen was added DIBAL-H (1.0 M solution in hexanes, 15.2 mL, 15.2 mmol, 2.1 equiv). After 1 h 45 min the reaction mixture was added dropwise, *via* cannula, to a stirred solution of sodium potassium tartrate tetrahydrate (7.72 g, 27.4 mmol, 3.7 equiv) in ice/water (50 mL) and dichloromethane (50 mL). The emulsion was stirred at room temperture for 2 h. After separation of the phases the aqueous layer was extracted with ether (3 × 20 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (20 mL), brine (20 mL), dried and concentrated *in vacuo*. Chromatography of the crude product on silica (hexanes/ethyl acetate 80:20) gave (2*R*,3*S*,4*E*,6*E*)-1,2-*O*-isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**10**) (1.88 g, 5.72 mmol, 80%) as a colorless oil. $[\alpha]_D^{25}$ –2.88 (*c* = 3.64, chloroform); IR (thin film): ν_{max} 3436, 2955, 2931, 2858 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$): δ 0.01 (3H, s), 0.06 (3H, s), 0.88 (9 H, s), 1.31 (3 H, s), 1.39 (3H, s), 1.85 (1H, bs), 3.98–3.83 (2H, m), 4.22–4.09 (2H, m), 5.64 (1H, m), 5.81 (1H, m), 6.23–6.16 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.7, –4.1, 18.2, 25.8, 25.9, 26.7, 63.2, 66.2, 73.5, 79.1, 109.4, 130.6, 130.8, 132.4, 133.6; EIMS (70 eV) *m/z* (%): 328 (20), 313 (25), 275 (30), 101 (100), 75 (70), 73 (75); HRMS: calcd for $C_{17}H_{32}O_4Si$ [M^+]: 328.2070; found: 328.2075.

Diethyl-L-malate. To a stirred solution of L-malic acid (13.4 g, 0.100 mol) in ethanol (200 mL) was added concentrated sulfuric acid (17.8 mol/L, 13.4 mL, 0.240 mol, 2.4 equiv) at RT. On completion of the addition the solution was warmed to reflux and stirring was continued for 16 h. The ethanol was partially evaporated then the residue was partitioned between dichloromethane (200 mL) and saturated aqueous sodium bicarbonate (50 mL). Solid sodium bicarbonate was added until effervescence subsided. The extract was partitioned against water (2 × 50 mL) and brine (50 mL) then dried, filtered and evaporated to give the crude product (21.0 g) as a colorless oil. Distillation gave diethyl-L-malate (14.4 g, 0.0757 mol, 76%) as a colorless oil: bp 134–136°C/11 mmHg [lit.[6] 85–86 °C/0.5 mmHg]; $[\alpha]_D^{19}$ –10.2° (neat) [lit.[6] $[\alpha]_D^{22}$ –10.4° (neat)]; R_f = 0.48 [hexane:ethyl acetate (2:1)]; (Found: M^++H, 191.0923. $C_8H_{15}O_5$ requires *M*, 191.0919); IR (thin film): ν_{max} 3490, 2984, 2940, 2908, 1736, 1374, 1271cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.26 (3H, t, J = 7.3 Hz, $–CH_2CO_2CH_2CH_3$), 1.30 (3H, t, J = 7.3 Hz, $–CHOHCO_2CH_2CH_3$), 2.77 (1H, dd, J = 5.9, 16.5 Hz, C3-*H*), 2.82 (1H, dd, J = 4.6, 16.5 Hz, C3-*H'*), 3.27 (1H, d, J = 5.3 Hz, –O*H*), 4.18 (2H, q, J = 7.3 Hz, $–CH_2CO_2CH_2CH_3$), 4.27 (2H, dq, J = 1.1, 7.3 Hz, $–CHOHCO_2CH_2CH_3$), 4.43–4.52 (1H, m, C2-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 14.2 (2 × C), 38.7, 61.0, 62.0, 67.3, 170.3, 173.2; EIMS (70 eV) *m/z* (%): 191 (1), 149 (6), 117 (100), 89 (36), 71 (94), 43 (36).

Ethyl (3*S*)-3,4-*O*-isopropylidene-3,4-dihydroxybutanoate (11). Regiochemical reduction of diethyl L-malate and protection of the resulting diol was based on the method of Saito et al.[7] To a stirred solution of diethyl L-malate (9.00 g, 0.0473 mol) in THF (85 mL) at RT under argon in a 500 mL flask fitted with a short reflux condenser was added dropwise borane-dimethyl sulfide complex (2.0 mol/L in THF, 24.8 mL, 0.0496 mol, 1.05 equiv). On completion of the addition stirring was continued for 30min then the solution was cooled to 10 °C and sodium borohydride (0.0882 g, 2.33 mmol, 0.05 equiv) was added. After effervescence had ceased the solution was warmed to RT and stirring was continued for 30min. Ethanol (16.2 mL, 0.276 mol, 5.84 equiv) and *para*-toluenesulfonic acid monohydrate (0.450 g, 2.33 mmol, 0.05 equiv) were added and the resulting cloudy solution was stirred for 30 min. Benzene:ethanol (1:1, 220 mL) was added and evaporated in two equal portions, followed by benzene (80 mL) to give the crude diol (7.82 g) as a colorless gum. Chromatography of this material on silica (32 g) with ethyl acetate gave ethyl (3*S*)-3,4-dihydroxybutanoate (6.16 g, 0.0416 mol, 88%) as a colorless oil: R_f = 0.39 (ethyl acetate). To a stirred solution of ethyl (3*S*)-3,4-dihydroxybutanoate (6.16 g, 0.0416 mol) in acetone (25 mL) at RT under argon was added 2,2-dimethoxypropane (6.2 mL, 0.050 mol, 1.2 equiv) and *para*-toluenesulfonic acid monohydrate (0.399 g, 2.10 mmol, 0.05 equiv). On completion of the addition the solution was stirred for 30 min then triethylamine (0.291 mL, 2.09 mmol, 0.05 equiv) and diethyl ether (70 mL) were added. The reaction mixture was filtered through a silica plug (50 g) which was rinsed with diethyl ether (250 mL) and the combined extracts were evaporated to give the crude product (7.58 g) as an opaque oil. Distillation of this material gave the ethyl (3*S*)-3,4-*O*-isopropylidene-3,4-dihydroxybutanoate (**11**) (6.16 g, 0.0327 mol, 69%) as a colorless oil. bp 98°C/11 mmHg [lit.[7] bp 110°C/23 mmHg]; $[\alpha]_D^{20}$ +18.5° (*c* = 1.17, chloroform) [lit.[7] $[\alpha]_D^{20}$ +27.0° (*c* = 1.17, chloroform)]; $[\alpha]_D^{20}$ +6.4° (*c* = 1.38, ethanol) [lit.[7] $[\alpha]_D^{20}$ +15.4° (*c* = 1.38, ethanol)]; R_f = 0.70 [hexane:ethyl acetate (2:1)]; (Found: M^+–CH_3, 173.0812. $C_8H_{13}O_4$ requires *M*, 173.0814); IR (thin film): ν_{max} 2986, 2936, 1736, 1371, 1380, 1066cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.27 (3H, t, *J* = 7.3 Hz, –OCH_2CH_3), 1.36, 1.42 [6H, 2 × s, –$C(CH_3)_2$–], 2.52 (1H, dd, *J* = 7.3, 15.8 Hz, C2-*H*), 2.72 (1H, dd, *J* = 6.2, 15.8 Hz, C2-*H'*), 3.66 (1H, dd, *J* = 6.4, 8.3 Hz, C4-*H*), 4.16 (2H, q, *J* = 7.3 Hz, –OCH_2CH_3), 4.17 (1H, dd, *J* = 5.1, 8.3 Hz, C4-*H'*), 4.41–4.53 (1H, m, C3-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 14.2, 25.5, 26.9, 39.0, 60.6, 69.1, 72.0, 109.0, 170.3; EIMS (40 eV) *m/z* (%): 173 (47), 113 (55), 101 (32), 85 (100), 42 (81).

(3*S*)-3,4-*O*-Isopropylidene-3,4-dihydroxybutanal (12). To a stirred solution of ethyl (3*S*)-3,4-*O*-isopropylidene-3,4-dihydroxybutanoate (**11**) (2.16 g, 0.0115 mol) in THF (30 mL) at 0 °C under argon was added lithium aluminium hydride (1.09 g, 0.0287 mol, 2.5 equiv). The solution was stirred at this temperature for 2 h. The reaction mixture was diluted with dichloromethane (25 mL) and the excess lithium aluminium hydride was quenched with THF:water (1:1, 7.5 mL). The reaction mixture was filtered through celite (20 g) which was rinsed with dichloromethane (3 × 100 mL), then the combined extracts were dried, filtered and evaporated to give the crude product (1.70 g) as a colorless oil. Kugelrohr distillation (87.5°C/0.05 mmHg) gave (2*S*)-1,2-*O*-isopropylidene-1,2,4-butanetriol (1.54 g, 0.0105 mol, 91%) as a colorless oil: $[\alpha]_D^{19.5}$ –2.29° (*c* = 9.80, methanol), [lit.[9] $[\alpha]_D$ –2.23° (*c* = 9.80, methanol); R_f = 0.31 [hexane:ethyl acetate (1:1)]; (Found: M^+–CH_3, 131.0709. $C_6H_{11}O_3$ requires *M*, 131.0708); IR (thin film): ν_{max} 3423, 2985, 2937, 2878, 1421, 1380, 1370, 1059 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.37, 1.44 [6H, 2 × d, *J* = 0.7 Hz, –C(CH_3)$_2$–], 1.79–1.87 (2H, m, C3-*H*), 2.20–2.26 (1H, m, –O*H*), 3.61 (1H, dd, *J* = 7.5, 8.1 Hz, C1-*H*), 3.76–3.86 (2H, m, C4-*H*), 4.10 (1H, dd, *J* = 6.2, 8.1 Hz, C1-*H′*), 4.23–4.24 (1H, m, C2-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.6, 26.8, 35.7, 60.1, 69.3, 74.6, 108.8; EIMS (40 eV) *m/z* (%): 131 (57), 71 (78), 60 (36), 42 (100), 31 (21).

To a stirred solution of (2*S*)-1,2-*O*-isopropylidene-1,2,4-butanetriol (1.29 g, 8.83 mmol) in dichloromethane (20 mL) at RT under argon was added Dess–Martin periodinane[8] (6.73 g, 15.9 mmol, 1.8 equiv). Stirring was continued for 16 h then the reaction mixture was filtered through celite (10 g) and evaporated to give the crude product (1.54 g) as a colorless oil. Chromatography of this material on silica (60 g) with hexane:ethyl acetate (2:1) gave (3*S*)-3,4-*O*-isopropylidene-3,4-dihydroxybutanal (**12**) (0.989 g, 6.86 mmol, 78%) as a colorless oil: $[\alpha]_D^{20}$ +15.4° (neat) [lit.[9] $[\alpha]_D^{20}$ +16.5° (neat)]; R_f = 0.64 [hexane:ethyl acetate (2:1)]; (Found: M^++H, 145.0865. $C_7H_{13}O_3$ requires *M*, 145.0865); IR (thin film): ν_{max} 2987, 2937, 2877, 1725, 1372, 1382 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.31, 1.36 [6H, 2 × d, *J* = 0.7 Hz, –C(CH_3)$_2$–], 2.60 (1H, ddd, *J* = 1.3, 6.0, 17.4 Hz, C2-*H*), 2.80 (1H, ddd, *J* = 1.9, 6.6, 17.4 Hz, C2-*H′*), 3.54 (1H, dd, *J* = 6.6, 8.3 Hz, C4-*H*), 4.14 (1H, dd, *J* = 5.9, 8.3 Hz, C4-*H′*), 4.43–4.53 (1H, m C3-*H*), 9.73–9.76 (1H, m, –C*H*O); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.4, 26.8, 47.7, 69.0, 70.5, 109.0, 199.6; EIMS (40 eV) *m/z* (%): 145 (1), 129 (15), 69 (100) 59 (18), 43 (51).

(2*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-4,6-octdadiene-1,2,8-triol (13). To a stirred solution of (3*S*)-3,4-*O*-isopropylidene-3,4-dihydroxybutanal (**12**) (1.02 g, 7.06 mmol) in dichloromethane (10 mL) at RT under argon was added ethyl 4-(triphenylphosphoranylidene)-(2*E*)-2-butenoate[5] (**16**) (3.70 g, 9.89

mmol, 1.4 equiv). On completion of the addition stirring was continued at RT for 1 h. Silica gel (7.5 g) was added and the solvent was evaporated. This material was loaded onto a silica column (75 g) which was eluted with hexane:ethyl acetate (10:1 then 5:1) to give a mixture of *Z*- and *E*-stereoisomers (50:50) of ethyl (4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadienoate (0.598 g, 2.49 mmol, 35%). To a stirred solution of the *Z*- and *E*-stereoisomers of ethyl (4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadienoate (0.598 g, 2.49 mmol) in benzene (5 mL) at RT under argon was added thiophenol (51.0 μL, 0.98 mmol, 0.2 equiv) and 2,2′-azo-bis-isobutyronitrile (40.8 mg, 0.250 mmol, 0.1 equiv) in two potions at one hour intervals, during which time the reaction mixture was irradiated with ultraviolet light at reflux for a total of 2 h. (Isomerization was monitored by proton NMR analysis.) The solvent was evaporated to give the crude product (0.740 g) as a yellow oil. Chromatography of this material on silica (20 g) with hexane:ethyl acetate (10:1 then 5:1) gave ethyl (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadienoate (0.464 g, 1.93 mmol, 78%) as a colorless oil. $[\alpha]_D^{21}$ –4.1° (*c* = 0.40, dichloromethane); R_f = 0.41 [hexane:ethyl acetate (5:1)]; (Found: M^+–CH_3, 225.1116. $C_{12}H_{17}O_4$ requires *M*, 225.1127); IR (thin film): ν_{max} 2984, 2936, 2904, 2875, 1714, 1644, 1618, 1379, 1369, 1262cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.30 (3H, t, *J* = 7.3 Hz, –OCH_2CH_3), 1.36, 1.43 (6H, 2 × s, –$C(CH_3)_2$–), 2.34–2.71 (2H, m, C6-*H*), 3.58 (1H, dd, *J* = 6.8, 8.0 Hz, C8-*H*), 4.04 (1H, dd, *J* = 6.2, 8.0 Hz, C8-*H′*), 4.20 (2H, q, *J* = 7.3 Hz, –OCH_2CH_3), 4.14–4.26 (1H, m, C7-*H*), 5.83 (1H, d, *J* = 15.6 Hz, C2-*H*), 6.03–6.16 (1H, m, C5-*H*), 6.26 (1H, dd, *J* = 10.8, 15.1 Hz, C4-*H*), 7.26 (1H, dd, *J* = 10.8, 15.6 Hz, C3-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 14.4, 25.6, 26.9, 37.2, 60.3, 68.8 74.8, 109.1, 120.4, 130.8, 138.1, 144.1, 166.8; EIMS (CI/NH_3, 40eV) *m/z* (%): 225 (10), 101 (100), 83 (8), 73 (13), 43 (28).

To a stirred solution of ethyl (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadienoate (610 mg, 2.69 mmol, 1.0 equiv) in dichloromethane (26 mL) at –78 °C was added DIBAL-H (1.0 m solution in hexanes, 5.93 mL, 5.93 mmol, 2.2 equiv). Stirring was continued at this temperature for 1.5 h before addition to stirred solution of sodium potassium tartrate tetrahydrate (2.86 g, 10.08 mmol, 3.75 equiv) in ice/water (100 mL) and dichloromethane (100 mL). The emulsion was stirred at RT for 1.5 h. The aqueous layer was extracted with ether (3 × 50 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (50 mL), brine (50 mL), dried and concentrated *in vacuo* to give (2*S*,4*E*,6*E*)-1,2-*O*-isopropylidene-4,6-octdadiene-1,2,8-triol (**13**) (498 mg, mmol, 93%) as a colorless oil. R_f = 0.32

[hexane:ethyl acetate (2:1)]; (Found: M^+, 198.1253. $C_{11}H_{18}O_3$ requires M, 198.1255); IR (thin film): ν_{max} 3418, 2986, 2934, 2873, 1659, 1455, 1371, 1381, 1216 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.36, 1.42 [6H, 2 × s, $–C(CH_3)_2–$], 1.70 (1H, s, –O*H*), 2.23–2.61 (2H, m, C3-*H*), 3.57 (1H, dd, J = 7.0, 7.9 Hz, C1-*H*), 4.02 (1H, dd, J = 5.9, 7.9 Hz, C1-*H'*), 4.09–4.24 (3H, m, C2-*H*, C8-*H*), 5.67 (1H, dt, J = 7.1, 14.5 Hz, C4-*H*) 5.77 (1H, dt, J = 5.9, 14.5 Hz, C7-*H*), 6.06–6.29 (2H, m, C5-*H*, C6-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.7, 26.9, 36.9, 63.3, 68.8, 75.3, 109.0, 129.2, 130.7, 131.1, 132.1; EIMS (70 eV) *m/z* (%): 198 (2), 183 (47), 101 (100), 80 (81), 59 (49).

(*S*)-2-{[*tert*-butyldimethylsilyl]oxy}propanal (14). To a stirred solution of imidazole (10.98 g, 159 mmol, 1.57 equiv) in dichloromethane under N_2 at 0 °C was added DMAP (410 mg, 3.7 mmol, 0.02 equiv) The solution was stirred for 5 min before the addition of (*S*)-ethyl lactate (11.50 mL, 101 mmol, 1.0 equiv). The solution was stirred for a further 5 min before the dropwise addition of a solution of TBS-Cl (15.36 mg, 102 mmol, 1.0 equiv) in dichloromethane (36 mL). The mixture was warmed to RT and stirred for 2.5 h. The reaction mixture was washed with water (100 mL). The aqueous layer was extracted with diethyl ether (2 × 50 mL) and ethyl acetate (50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Distillation of the crude material gave ethyl (*S*)-2-{[*tert*-butyldimethylsilyl]oxy}propanoate (20.02 g, 85 mmol, 85%) as a colorless oil, distilling at 42–50 °C/1–1.5 mmHg. ^1H NMR data for this compound was consistent with that reported in the literature.[10]

To a stirred solution of ethyl (*S*)-2-{[*tert*-butyldimethylsilyl]oxy}propanoate (13.1 g, 57 mmol, 1.0 equiv) in dichloromethane (150 mL) at –78 °C under argon was added a pre-cooled solution of DIBAL-H (1.5 M solution in toluene, 40 mL, 60 mmol, 1.05 equiv) dropwise over 1.5 h. After 1 h the reaction mixture was added dropwise, *via* cannula, to a stirred solution of sodium potassium tartrate tetrahydrate (51.5 g, 182 mmol, 3.2 equiv) in ice/water (500 mL) and dichloromethane (200 mL). The emulsion was stirred at RT for 2 h. After separation of the phases the aqueous layer was extracted with ether (3 × 250 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (250 mL), saturated NaCl (250 mL) and dried ($MgSO_4$). The filtered solution was concentrated *in vacuo*. Distillation of the crude material gave ethyl (*S*)-2-{[*tert*-butyldimethylsilyl]oxy}propanoate (**14**) (6.93 g, 37 mmol, 65%) as a colorless oil distilling at 78 °C/25 mmHg. ^{1}H NMR data for this compound was consistent with that reported in the literature.[10]

Triethyl phosphonocrotonate (17). This product was formed following literature procedure.[11] Methyl 4-bromocrotonate (11.28 g, 63 mmol, 1.0 equiv) was added to triethyl phosphite at such a rate that the temperature remained at 130 °C. The mixture was stirred at this temperature for 1 h 25 min. The mixture was cooled to RT and unreacted triethyl phosphite was removed under reduced pressure to give triethyl phosphonocrotonate (**17**) (14.88 g, 63 mmol, 100%) as a yellow oil. ^{1}H NMR data for this compound was consistent with that reported in the literature.[11]

(2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dien-1-ol (15). To a stirred solution of lithium hexamethyldisilazide, prepared from hexamethyldisilazane (6.55 g, 41 mmol, 1.29 equiv) and *n*-butyllithium (21.4 mL of 1.58 M solution in hexanes, 34 mmol, 1.07 equiv) in THF (56 mL) at –78 °C under argon was added phosphonate **17** (7.51 g, 32 mmol, 1.0 equiv) in THF (9.5 mL). The mixture was warmed to –40 °C and aldehyde **14** (5.94 g, 32 mmol, 1.0 equiv) in THF (6 mL) was added dropwise. The reaction mixture was warmed to RT and concentrated *in vacuo.* The residue was partitioned between water (100 mL) and ether (20 mL). The aqueous phase was extracted with ether (3 × 20 mL). The combined extracts were washed with 1 M HCl (40 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography over silica gel (hexane/ethyl acetate 95:5) gave methyl (2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienoate (2.80 g, 10.2 mmol, 32%) as a colorless oil. R_f = 0.61 (hexanes/ethyl acetate 90:10); $[\alpha]_D$ –1.57 (*c* = 4.35, dichloromethane); IR (thin film): ν_{max} 2954, 2929, 2886, 2857 (C-H), 1723 (C=O), 1649, 1618 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02, 0.04 [6H, 2 × s, –$Si(CH_3)_2$], 0.87 [9H, s, –$SiC(CH_3)_3$], 1.21 (3H, d, *J* = 6.6 Hz, C7-H_3), 3.70 (3H, s, –CO_2CH_3), 4.38 (1H, dq, *J* = 6.11, 12.23 Hz, C6-H), 5.84 (1H, d, *J* = 15.4 Hz, C2-H), 6.08 (1H, ddd, *J* = 0.7, 4.9, 15.2 Hz, C5-H), 6.29 (1H, ddd, *J* = 0.7, 11.0, 15.2 Hz, C4-H), 7.25 (1H, dd, *J* = 11.3, 15.4 Hz, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.8, –4.8, 18.2 (Q), 24.0, 25.8, 51.4, 68.4, 120.4, 125.7, 144.4, 147.1, 167.4 (Q); EIMS (70 eV) *m/z* (%): 213 (35) $[M–C_4H_9]^+$, 131 (100), 75 (95); HRMS: calcd for $C_{10}H_{17}O_3Si$ $[M–C_4H_9]^+$:213.0947; found: 213.0948.

To a stirred solution of DIBAL-H (1.5 M solution in toluene, 10.22 mL, 15.3 mmol, 2.1 equiv) at 0 °C under argon was added a solution of methyl (2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienoate (1.97 g, 7.3 mmol, 1.0 equiv) in dry diethyl ether (3 mL). After 45 min the reaction mixture was added dropwise, *via* cannula, to a stirred solution of sodium potassium tartrate tetrahydrate (7.72 g, 27.4 mmol, 3.75 equiv) in ice/water (50 mL) and dichloromethane (20 mL). The emulsion was stirred at RT for 2 h. After separation of the phases the aqueous layer was extracted with ether (3 × 10 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (15 mL), saturated NaCl (15 mL) and dried ($MgSO_4$). The filtered solution was then concentrated *in vacuo* to give (2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dien-1-ol (**15**) (1.55 g, 6.3 mmol, 88%) as a colorless oil. R_f = 0.48 (hexanes/ethyl acetate 80:20); $[\alpha]_D$ +3.59 (*c* = 0.835, dichloromethane); IR (thin film): ν_{max} 3331 (OH), 2955, 2857 (C–H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.05, 0.06 [6H, 2 × s, $–Si(CH_3)_2$], 0.89 [9H, s, $–SiC(CH_3)_3$], 1.22 (3H, d, *J* = 6.6 Hz, C7-H_3), 4.16 (2H, dd, *J* = 1.2, 5.9 Hz, C1-H_2), 4.34 (1H, dq, *J* = 6.4, 6.4 Hz, C6-H), 5.71 (1H, dd, *J* = 5.6, 14.7 Hz, C5-H), 5.80 (1H, dt, *J* = 5.9, 14.7 Hz, C2-H), 6.16 (1H, ddd, *J* = 1.0, 10.5, 14.4 Hz, C4-H), 6.23 (1H, ddt, *J* = 1.2, 10.5, 14.9 Hz, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ–4.7, –4.5, 18.4 (Q), 24.5, 26.0, 63.5 (CH_2), 68.9, 127.3, 131.3, 131.3, 138.9; EIMS (70 eV) *m/z* (%): 224 (70), 167 (60), 159 (100), 149 (65).

The Ascorbate Series

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl hydrogen maleate (18). To a stirred solution of (2*S*,3*S*,4*E*,6*E*)-1,2-*O*-isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**7**) (0.492 g, 1.50 mmol) in dichloromethane (25 mL) at RT under argon was added triethylamine (0.334 mL, 2.40 mmol, 1.6 equiv), maleic anhydride (0.330 g, 3.37 mmol, 2.25 equiv) and 4-dimethylaminopyridine (0.0180 g, 0.150 mmol, 0.1 equiv). Stirring was continued for 10min and the reaction mixture was diluted with dichloromethane (100 mL) and partitioned against 10% aqueous hydrochloric acid (50 mL), water (50 mL) and brine (50 mL) then dried, filtered and evaporated to give the crude product (0.735 g) as a yellow oil. Chromatography of this material on silica (20 g) with ethyl acetate:hexane:acetic acid (200:50:1) gave (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-

isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl hydrogen maleate (**18**) (0.631 g, 1.48 mmol, 99%) as a pale yellow oil: $[\alpha]_D^{18}$ –39.4° (c = 0.62, dichloromethane); R_f = 0.46 [ethyl acetate:hexane:acetic acid (200:50:1)]; (Found: M^+, 426.2043,. $C_{21}H_{34}O_7Si$ requires M, 426.2074); IR (thin film): ν_{max} 3175, 2986, 2955, 2930, 2889, 2857, 1732, 1714, 1642, 1472, 1462, 1413, 1382, 1372, 1256cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.057, 0.077 [6H, 2 × s, –Si(C*H*$_3$)$_2$–], 0.902 (9H, s, –C(C*H*$_3$)$_3$), 1.34, 1.40 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 3.79 (1H, dd, J = 6.0, 8.6 Hz, C8-*H*), 3.95 (1H, dd, J = 6.6, 8.6 Hz, C8-*H'*), 4.05–4.16 (1H, m, C7-*H*), 4.32 (1H, t, J = 5.6 Hz, C6-*H*), 4.80 (2H, d, J = 7.0 Hz, C1-*H*), 5.71–5.86 (2H, m, C2-*H*, C5-*H*) 6.20–6.52 (2H, m, C3-*H*, C4-*H*), 6.39, 6.46 (2H, 2 × d, B and A of AB, J_{AB} = 12.5 Hz, –C*H*=C*H*CO_2H); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.73, –4.51, 18.3, 25.1, 25.9, 26.4, 65.1, 67.0, 72.9, 78.4, 109.4, 124.1, 129.0, 129.8, 134.4, 135.6, 136.1, 164.1, 167.2; EIMS (70 eV) *m/z* (%): 426 (0.1), 227 (24), 210 (44), 101 (100), 75 (69), 43 (27).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl hydrogen maleate (19). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl hydrogen maleate (**18**) (1.20 g, 2.81 mmol) in THF (15 mL) at RT under argon was added tetrabutylammonium fluoride (1.0 mol/L in THF, 5.62 mL, 5.62 mmol, 2 equiv). On completion of the addition stirring was continued for 16 h then the reaction mixture was diluted with dichloromethane (300 mL) and partitioned against saturated aqueous ammonium chloride solution (150 mL). The ammonium chloride solution was further extracted with chloroform (2 × 150 mL) and the combined extracts were partitioned against brine (150 mL), dried (anhydrous sodium sulfate only), filtered and evaporated to give the crude product (3.35 g) as a yellow oil. The crude product was adsorbed onto silica (7.5 g) then loaded onto a silica column (55 g) and eluted with ethyl acetate:acetic acid (40:1) gave (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl hydrogen maleate (**19**) (0.751 g, 2.41 mmol, 85%) as a colorless oil: $[\alpha]_D^{19.5}$ –16.4° (c = 1.28, dichloromethane); R_f = 0.50 [ethyl acetate:acetic acid (40:1)]; (Found: M^+–H, 311.1130. $C_{15}H_{19}O_7$ requires M, 311.1131); IR (thin film): ν_{max} 3433, 2989, 2937, 2944, 1730, 1713, 1644, 1415, 1383, 1372, 1215cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.37, 1.46 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 3.78 (1H, dd, J = 5.0, 7.8 Hz, C8-*H*), 3.96–4.16 (3H, m, C6-*H*, C7-*H* and C8-*H'*), 4.78 (2H, d, J = 6.4 Hz, C1-*H*), 5.62–5.93 (2H, m, C2-*H* and C5-*H*), 6.16–6.47 (2H, m, C3-*H*, C4-*H*), 6.36, 6.43 (2H, 2 × d, B and A of AB, J_{AB} = 12.5 Hz, –C*H*=C*H*CO_2H); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.3, 26.8, 65.8, 66.6, 73.1, 78.6, 109.9, 125.6, 129.1, 131.1, 133.1, 134.7, 135.2, 164.9, 166.8; *m/z* EIMS (70 eV) *m/z* (%): 311 (2), 113 (17), 101 (100), 59 (14), 43 (25).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (1a). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl hydrogen maleate (**19**) (7.51 g, 2.41 mmol) in diethyl ether (30 mL) at 0 °C was added dropwise an ethereal solution of diazomethane.[12] On completion of the addition the solvent was evaporated to give the crude product (0.800 g) as a yellow oil. Chromatography of this material on silica (25 g) with hexane:ethyl acetate (1:1) gave the (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (**1a**) (0.582 g, 1.78 mol, 74%) as a pale yellow oil. $[\alpha]_D^{20}$ –14.3° (*c* = 1.47, dichloromethane); R_f = 0.34 [hexane:ethyl acetate (1:1)]; (Found: M^+–H, 325.1282. $C_{16}H_{21}O_7$ requires *M*, 325.1287); IR (thin film): ν_{max} 3467, 2987, 2953, 2887, 1731, 1647, 1438, 1372, 1383, 1215 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.31, 1.40 [6H, 2 × s, –C(CH_3)$_2$–], 2.77 (1H, s, –O*H*), 3.70 (1H, dd, *J* = 5.1, 7.7 Hz, C8-*H*), 3.72 (3H, s, –CO_2CH_3), 3.87–4.11 (3H, m, C6-*H*, C7-*H*, C8-*H′*), 4.67 (2H, d, *J* = 6.4 Hz, C1-*H*), 5.64 (1H, dd, *J* = 6.4, 14.3 Hz, C5-*H*), 5.77 (1H, dt, *J* = 14.3, 6.4 Hz, C2-*H*), 6.22 (2H, d, *J* = 0.4 Hz, –C*H*=C*H*CO_2CH_3), 6.15–6.38 (2H, m, C3-*H*, C4-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.2, 26.6, 52.1, 65.1, 65.6, 73.1, 78.5, 109.6, 126.7, 129.3, 129.7, 131.2, 132.3, 133.4, 164.5, 165.3; EIMS (70 eV) *m/z* (%): 325 (0.06), 121 (6), 101 (100), 59 (13), 43 (45).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-[(trimethylsilyl)oxy]-7,8-dihy-droxy-2,4-octadien-1-yl methyl maleate (1b). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (**1a**) (101 mg, 0.311 mmol) in dichloromethane (5 mL) at 0 °C under argon was added triethylamine (94.7 μL, 0.684 mmol, 2.2 equiv), trimethylsilyl trifluoromethanesulfonate (108 μL, 0.559 mmol, 1.8 equiv) and 4-dimethylaminopyridine (crystal). On completion of the addition the solution was warmed to RT and stirring was continued for 2.5 h. The reaction mixture was diluted with diethyl ether (20 mL) and partitioned against saturated aqueous sodium bicarbonate (20 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL) and the combined extracts were partitioned against brine (10 mL) then dried, filtered and evaporated to give the crude product (0.162 g) as a yellow oil. Chromatography of this material on silica (8 g) with hexane:ethyl acetate (10:1 then 5:1) gave (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(trimethylsilyl)oxy]-7,8-dihy-droxy-2,4-octadien-1-yl methyl maleate (**1b**) (63.0 mg, 0.159 mmol, 51%) as a colorless oil. $[\alpha]_D^{20}$ –16.2° (*c* = 0.680, dichloromethane); R_f = 0.28 [hexane:ethyl acetate (5:1)]; (Found: M^+, 398.1755. $C_{19}H_{30}O_7Si$ requires *M*, 398.1761); IR (thin film): ν_{max} 2986, 2955, 2898, 1732, 1645, 1438, 1380, 1371, 1213cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.127 [9H, s, –Si(C*H*$_3$)$_3$], 1.34, 1.40 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 3.75 (1H, dd, *J* = 6.1, 8.4 Hz, C8-*H*), 3.79 (3H, s, –CO_2C*H*$_3$), 3.95 (1H, dd, *J* = 6.5, 8.4 Hz, C8-*H'*), 4.02–4.10 (1H, m, C7-*H*) 4.19–4.26 (1H, m, C6-*H*), 4.73 (2H, d, *J* = 7.0 Hz, C1-*H*), 5.66–5.89 (2H, m, C2-*H*, C5-*H*), 6.20–6.40 (2H, m, C3-*H*, C4-*H*), 6.27 (2H, s, –C*H*=C*H*CO_2CH_3); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 0.252, 25.2, 26.4, 52.1, 65.3 (2 × C), 73.5, 78.6, 109.3, 125.9, 129.4, 129.7, 130.4, 133.2, 133.9, 164.6, 165.3; EIMS (70 eV) *m/z* (%): 398 (0.1), 168 (64), 113 (35), 101 (100), 73 (31).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (1c). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl hydrogen maleate (**18**) (0.503 g, 1.18 mmol) in diethyl ether (10 mL) at RT was added dropwise an ethereal solution of diazomethane.[12] On completion of the addition the solvent was evaporated to give the crude product (0.535 g) as a yellow oil. Chromatography of this material on silica (20 g) with hexane:ethyl acetate (5:1) gave (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**1c**) (0.417 g, 0.946 mmol, 80%) as a pale yellow oil. $[\alpha]_D^{20}$ –27.6° (*c* = 1.89, dichloromethane); R_f = 0.32 [hexane:ethyl acetate (5:1)]; (Found: M^+–CH_3, 425.2022. $C_{21}H_{33}O_7Si$ requires *M*, 425.1996); IR (thin film): ν_{max} 2985, 2954, 2931, 2887, 2857, 1735, 1472, 1462, 1438, 1380, 1371, 1253 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.047, 0.068 [6H, 2 × s, –Si(C*H*$_3$)$_2$–], 0.893 [9H, s, –C(C*H*$_3$)$_3$], 1.33, 1.39 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 3.77 (1H, dd, *J* = 6.3, 8.4 Hz, C8-*H*), 3.78 (3H, s, –CO_2C*H*$_3$), 3.93 (1H, dd, *J* = 6.6, 8.4 Hz, C8-*H'*), 4.04–4.12 (1H, m, C7-*H*), 4.29 (1H, t, *J* = 5.5 Hz, C6-*H*), 4.72 (2H, d, *J* = 6.6 Hz, C1-*H*), 5.67–5.88 (2H, m, C2-*H*, C5-*H*), 6.21–6.39 (2H, m, C3-*H*, C4-*H*), 6.27 (2H, s, –C*H*=C*H*$COCH_3$); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.84, –4.64, 18.2, 25.1, 25.7, 26.3, 52.0, 65.1, 65.2, 73.2, 78.5, 109.2, 125.7, 129.4, 129.6, 130.1, 133.3, 133.9, 164.5, 165.2; EIMS (40 eV) *m/z* (%): 425 (1), 210 (56), 187 (36), 113 (56), 101 (100).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-[(triisopropylsilyl)oxy]-7,8-dihy-droxy-2,4-octadien-1-yl methyl maleate (1d). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (**1a**) (15 mg, 0.05 mmol, 1.0 equiv) in dichloromethane (1 mL) at 0 °C was added 2,6-lutidine (15 μL, 0.14 mmol, 3.0 equiv) and triisopropylsilyl trifluorometanesulphonate (22 μL, 0.08 mmol, 1.8 equiv). The reaction was warmed to RT and stirring was continued for 30 min. The reaction mixture was diluted with diethyl ether (20 mL) and portioned against saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL) and the combined extracts were washed with saturated NaCl (10 mL), dried, filtered and concentrated *in vacuo*. After column chromatography on silica (hexanes/ethyl acetate 85:15) (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(triisopropylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**1d**) (20 mg, 0.05 mmol, 91%) was obtained a colorless oil. $[\alpha]_D^{20}$ –13.8° (*c* = 0.26, dichloromethane); R_f = 0.26 [hexane:ethyl acetate (5:1)]; (Found: M^+, 482.2720. $C_{25}H_{42}O_7Si$ requires *M*, 482.2700); IR (thin film): ν_{max} 2944, 2891, 2867, 1731, 1645, 1462, 1381, 1370 and 1213cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.96–1.13 {21H, m, –Si[C*H*(C*H*$_3$)$_2$]$_3$}, 1.33, 1.37 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 3.78 (3H, s, –CO$_2$C*H*$_3$), 3.82 (1H, dd, *J* = 6.1, 8.6 Hz, C8-*H*), 3.95 (1H, dd, *J* = 6.8, 8.6 Hz, C8-*H′*), 4.14–4.24 (1H, m, C7-*H*), 4.46 (1H, t, *J* = 5.4 Hz, C6-*H*), 4.73 (2H, d, *J* = 6.6 Hz, C1-*H*), 5.68–5.89 (2H, m, C2-*H*, C5-*H*), 6.18–6.40 (2H, m, C3-*H*, C4-*H*), 6.27 (2H, s, –C*H*=C*H*COCH$_3$); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 12.4, 18.1, 25.1, 26.3, 52.2, 65.1, 65.5, 73.3, 78.5, 109.3, 125.7, 129.5, 129.7, 130.5, 133.5, 134.0, 164.6, 165.4; EIMS (40 eV) *m/z* (%): 482 (0.7), 252 (33), 243 (83), 113 (100), 101 (73).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-(4-nitrobenzoyloxy)-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (1e). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (**1a**) (33 mg, 0.10 mmol, 1.0 equiv) in dichloromethane (5 mL) was added pyridine (82 μL, 1.01 mmol, 10.0 equiv), 4-nitrobenzoyl chloride (47 mg, 0.25 mmol, 2.5 equiv) and DMAP (13 mg, 0.10 mmol, 1.0 equiv). The reaction mixture was stirred at RT for 18 h before being diluted with diethyl ether (20 mL) and portioned against 2 M HCl (10 mL), water (10 mL) and brine (10 mL). The organic layer was then dried and concentrated *in vacuo*. After column chromatography (dichloromethane/ethyl acetate) (**1e**) (37 mg, 0.08 mmol, 82%) was obtained as a colorless oil. IR (thin film): ν_{max} 2989, 2953, 1728, 1647, 1608, 1529 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38 (3H, s), 1.47

(3H, s), 3.78 (3H, s), 3.85 (1H, ddd, J = 0.9, 5.7, 8.9 Hz), 4.09 (1H, ddd, J = 1.0, 6.6, 8.7 Hz), 4.38 (1H, q, J = 6.3 Hz), 4.73 (2H, d, J = 6.4 Hz), 5.60 (1H, t, J = 6.8 Hz), 5.76 (1H, dd, J = 7.7, 15.0 Hz), 5.89 (1H, dt, J = 6.8, 15.0 Hz), 6.27 (1H, m), 6.32 (1H, m), 6.47 (1H, dd, J = 10.6, 15.0 Hz), 8.28 (4H, M); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.3, 26.6, 52.3, 65.0, 65.8, 76.4, 76.5, 110.4, 123.6, 127.5, 128.9, 129.6, 130.1, 130.9, 132.8, 134.7, 135.6, 150.7, 163.9, 164.8, 165.7; EIMS (70 eV) *m/z* (%): 460 (40), 417 (15), 245 (35), 150 (100), 101 (75); HRMS: calcd for $C_{22}H_{22}NO_{10}$ [M–CH_3]: 460.1244; found: 460.1238

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (1f). To a stirred solution of (2*S*,3*S*,4*E*,6*E*)-1,2-*O*-isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**7**) (297 mg, 0.903 mmol) in diethyl ether (15 mL) at RT under argon was added methyl hydrogen fumarate[13] (141 mg, 1.08 mmol, 1.2 equiv), 1,3-dicyclohexylcarbodiimide (242 mg, 1.17 mmol, 1.3 equiv) and 4-dimethylaminopyridine (11.0 mg, 0.0900 mmol, 0.1 equiv). Stirring was continued for 19 h then further methyl fumarate (71 mg, 0.59 mmol, 0.60 equiv), 1,3-dicyclohexylcarbodiimide (0.121 mg, 0.585 mmol, 0.65 equiv) and 4-dimethylaminopyridine (5.0 mg, 0.045 mmol, 0.05 equiv) was added and the solution was stirred for a further 3 h. The reaction mixture was filtered and the solvent evaporated to give the crude product (0.621 g) as a yellow oil. Chromatography of this material on silica (4 g) with hexane:ethyl acetate (8:1) gave the (2*E* ,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (**1f**) (0.383 g, 0.869 mmol, 96%) as a colorless oil. $[\alpha]_D^{21}$ –25.6° (c = 8.60, dichloromethane); R_f = 0.20 [hexane:ethyl acetate (8:1)]; (Found: M^+, 440.2240. $C_{22}H_{36}O_7Si$ requires M, 440.2230); IR (thin film): ν_{max} 2986, 2953, 2931, 2857, 1727, 1645, 1472, 1462, 1437, 1380, 1370 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.035, 0.055 [6H, 2 × s, –Si(CH_3)$_2$–], 0.879 [9H, s, –C(CH_3)$_3$], 1.31, 1.37 [6H, 2 × s, –C(CH_3)$_2$–], 3.75 (1H, dd, J = 6.2, 8.5 Hz, C8-*H*), 3.79 (3H, s, –CO_2CH_3), 3.92 (1H, dd, J = 6.6, 8.5 Hz, C8-*H′*), 4.02–4.11 (1H, m, C7-*H*), 4.28 (1H, t, J = 5.6 Hz, C6-*H*), 4.71 (2H, d, J = 6.4 Hz, C1-*H*), 5.67–5.86 (2H, m, C2-*H*, C5-*H*), 6.19–6.38 (2H, m, C3-*H*, C4-*H*), 6.86 (2H, s, –C*H*=C*H*COCH_3); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.77, –4.55, 18.3, 25.2, 25.8, 26.4, 52.3, 65.2, 65.4, 73.1, 78.5, 109.3, 125.6, 130.1, 133.3, 133.4, 133.5, 134.0, 164.4, 165.1; EIMS (40 eV) *m/z* (%): 440 (0.1), 383 (13), 210 (28), 187 (33), 101 (100), 73 (30).

(2*E*,4*E*,6*S*,7*S*)-7,8-*O*-Isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl propiolate (1g). To a stirred solution of (2*S*,3*S*,4*E*,6*E*)-1,2-*O*-isopropylidene-3-[(*tert*-

butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**7**) (0.515 g, 1.57 mmol) in diethyl ether (20 mL) at 0 °C under argon was added propiolic acid (0.174 mL, 2.82 mmol, 1.8 equiv), 1,3-dicyclohexylcarbodiimide (0.647 g, 3.13 mmol, 2 equiv) and 4-dimethylaminopyridine (0.0290 g, 0.235 mmol, 0.15 equiv). Stirring was continued for 30min then a further amount of propiolic acid (0.087 mL, 1.4 mmol, 0.9 equiv) and 1,3-dicyclohexylcarbodiimide (0.323 g, 1.57 mmol, 1 equiv) were added. After 30 min the reaction mixture was warmed to 30 °C and stirring continued for 1 h. The reaction mixture was filtered and the filtrate was rinsed with diethyl ether (20 mL), then the supernatant was partitioned against saturated aqueous sodium bicarbonate (20 mL), water (20 mL) and brine (20 mL) then dried, filtered and evaporated to give the crude product (1.237 g) as a yellow oil. Chromatography of this material on silica (30 g) with hexane:ethyl acetate (10:1, then 5:1, then 2:1) gave (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl propiolate (**1g**) (0.388 g, 1.02 mmol, 65%) as a colorless oil. $[\alpha]_D^{19}$ –26.9° (*c* = 5.4, dichloromethane); R_f = 0.62 [hexane:ethyl acetate (2:1)]; (Found: M^+, 380.2039. $C_{20}H_{32}O_5Si$ requires *M*, 380.2019); IR (thin film): ν_{max} 3256, 2987, 2955, 2931, 2887, 2858, 2120, 1716, 1472, 1462, 1381, 1371, 1222 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.057, 0.077 [6H, 2 × s, –Si(CH_3)$_2$–], 0.90 [9H, s, –C(CH_3)$_3$], 1.34, 1.40 [6H, 2 × s, –C(CH_3)$_2$–], 2.91 (1H, s, –CC*H*), 3.78 (1H, dd, *J* = 6.2, 8.6 Hz, C8-*H*), 3.94 (1H, dd, *J* = 6.6, 8.6 Hz, C8-*H'*), 4.05–4.13 (1H, m, C7-*H*), 4.30 (1H, t, *J* = 5.6 Hz, C6-*H*), 4.73 (2H, d, *J* = 6.8 Hz, C1-*H*), 5.69–5.89 (2H, m, C2-*H*, C5-*H*), 6.22–6.41 (2H, m, C3-*H*, C4-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.70, –4.49, 18.3, 25.2, 25.8, 25.9, 26.4, 65.3, 66.3, 73.3, 74.6, 74.8, 109.4, 125.0, 130.1, 133.9, 134.7, 152.1; EIMS (40 eV) *m/z* (%): 380 (0.1), 323 (11), 210 (34), 101 (100), 73 (34).

IMDA reactions of 1

IMDA reaction of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (1a). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6,7,8-trihydroxy-2,4-octadien-1-yl methyl maleate (**1a**) (0.522 g, 1.60 mmol) in toluene (320 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (71.0 mg, 0.320 mmol, 0.2 equiv). The solution was warmed to reflux and heating was continued for 5 h. Evaporation of the solvent gave the crude product (0.640 g) as a yellow oil. Chromatography of this material on silica (30 g) with hexane:ethyl acetate (1:1) gave a mixture of the 4 IMDA adducts (**20a**, **21a**, **22a** and **23a**) [448 mg, 1.37 mmol, 86%, **20a**:**21a**:**22a**:**23a** (56:32:8:4)].

IMDA reaction of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(trimethyl-silyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (1b). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(trimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**1b**) (45.3 mg, 0.114 mmol) in toluene (27.8 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (6.1 mg, 0.0283 mmol, 0.2 equiv). The solution was warmed to reflux and heating was continued for 12 h. Evaporation of the solvent gave the crude product (65.7 mg) as a yellow oil. Chromatography of this material on silica (5 g) with hexane:ethyl acetate (4:1) gave the IMDA adducts (**20b**, **21b**, **22b** and **23b**) [30.3 g, 0.0760 mmol, 67%, **20b**:**21b**:**22b**:**23b** (80:14:4:2)], *vide infra*.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-{(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(trimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (20b). Colorless oil; $[\alpha]_D^{20}$ –46.3° (*c* = 0.990, dichloromethane); R_f = 0.22 [hexane:ethyl acetate (4:1)]; (Found: M^+–CH_3, 383.1524. $C_{18}H_{27}O_7Si$ requires *M*, 383.1526); IR (thin film): ν_{max} 2985, 2954, 2897, 1789, 1731, 1436, 1379, 1370cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.144 [9H, s, –Si(CH_3)$_3$], 1.33, 1.41 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.77–2.88 (1H, m, C5-*H*), 2.84 (1H, dd, *J* = 3.9, 13.7 Hz, C3a-*H*), 3.03–3.21 (1H, m, C7a-*H*), 3.39 (1H, d, *J* = 3.9 Hz, C4-*H*), 3.57–3.83 [1H, obs, –C*H*H′OC(CH_3)$_2$OCH–], 3.71 (3H, s, –CO_2C*H*$_3$), 3.78 (1H, dd, *J* = 3.9, 5.5 Hz, –C*H*OTMS), 3.85 (1H, dd, *J* = 8.0, 11.3 Hz, C1-*H*), 4.02 [1H, dd, *J* = 6.2, 7.8 Hz, –CH*H′*OC(CH_3)$_2$OCH–], 4.03–4.15 [1H, m, –CHH′OC(CH_3)$_2$OC*H*–], 4.52 (1H, dd, *J* = 7.0, 8.0 Hz, C1-*H′*), 5.63 (1H, dt, *J* = 10.2, 3.1 Hz, C6-*H*), 6.02 (1H, dt, *J* = 10.2, 2.0 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 0.458, 25.8, 26.4, 36.3, 39.2, 42.4, 42.9, 52.2, 66.1, 70.3, 76.3, 109.6, 127.1, 128.1, 172.7, 174.3; (HETCOR demonstrated that δ_C for –*C*HOTMS was completely obscured by the 77.0 ppm peak of the $CDCl_3$ triplet); EIMS (40 eV) *m/z* (%): 383 (10), 297 (21), 268 (99), 237 (72) and 73 (100).

Methyl (3a*S*,4*R*,5*S*,7a*R*)-5-{(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(trimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (21b). Colorless oil; $[\alpha]_D^{19.5}$ +54.5° (*c* = 0.110, dichloromethane); R_f = 0.26 [hexane:ethyl acetate (4:1)]; (Found: M^+–CH_3, 383.1537. $C_{18}H_{27}O_7Si$ requires *M*, 383.1526); IR (thin film): ν_{max} 2986, 2955, 2927, 2855, 1786, 1736, 1437, 1381, 1371 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.101 [9H, s, –Si(C*H*$_3$)$_3$], 1.38, 1.44 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.51–2.57 (1H, m, C5-*H*), 2.71 (1H, dd, *J* = 4.2, 13.8 Hz, C3a-*H*), 3.12–3.30 (1H, m, C7a-*H*), 3.45 (1H, d, *J* = 4.2 Hz, C4-*H*), 3.59 [1H, t, *J* = 8.1 Hz, –C*H*H′OC(CH_3)$_2$OCH–], 3.72 (3H, s, –CO_2C*H*$_3$), 3.74 (1H, dd, *J* = 1.8, 5.0 Hz, –C*H*OTMS), 3.80 (1H, dd, *J* = 8.1, 11.5 Hz, C1-*H*), 4.13 [1H, dd, *J* = 6.4, 8.1 Hz, –CH*H′*OC(CH_3)$_2$OCH–], 4.19–4.29 [1H, m, –CHH′OC(CH_3)$_2$OC*H*–], 4.53 (1H, dd, *J* = 7.2, 8.1 Hz, C1-*H′*), 5.56 (1H, dt, *J* = 10.0, 3.2 Hz, C6-*H*), 6.01 (1H, dt, *J* = 10.0, 2.0 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 0.699, 25.5, 26.8, 35.7, 36.3, 42.2, 42.7, 52.4, 66.2, 70.5, 77.8, 78.0, 109.4, 126.3, 131.9, 172.5, 174.5; EIMS (40 eV) *m/z* (%): 383 (13), 297 (23), 268 (99), 237 (73), 145 (45), 101 (52), 73 (100).

IMDA reaction of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (1c). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**1c**) (0.115 g, 0.261 mmol) in toluene (52.0 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (0.0116 g, 0.0522 mmol, 0.2 equiv). The solution was warmed to reflux and heating was continued for 15 h. Evaporation of the solvent gave the crude product (0.128 g) as a yellow oil. Chromatography of this material on silica (5 g) with hexane:ethyl acetate (4:1) gave the IMDA adducts (**20c**, **21c**, **22c** and **23c**) [0.0922 g, 0.209 mmol, 80%, **20c**:**21c**:**22c**:**23c** (86:9:4:1)], *vide infra*.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-{(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (20c). Yellow oil; $[\alpha]_D^{21}$ –34.3° (*c* = 2.98, dichloromethane); R_f = 0.29 [hexane:ethyl acetate (4:1)]; (Found: M^+–CH_3, 425.1972. $C_{21}H_{33}O_7Si$ requires *M*, 425.1972); IR (thin film): ν_{max} 2985, 2953, 2892, 2857, 1789, 1731, 1472, 1462, 1436, 1472, 1462 1380, 1370 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.114 [6H, s, –Si(C*H*$_3$)$_2$–], 0.903 [9H, s, –C(C*H*$_3$)$_3$], 1.31, 1.42 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.78 (1H, dd, *J* = 4.2, 13.8 Hz, C3a-*H*), 2.91–2.97 (1H, m, C5-*H*), 3.05–3.23 (1H, m, C7a-*H*), 3.58 (1H, d, *J* = 4.2 Hz, C4-*H*), 3.70 (3H, s, –CO_2C*H*$_3$), 3.70–3.82 [2H, m, –C*H*H′OC(CH_3)$_2$OCH–,–C*H*OTBS], 3.84 (1H, dd, *J* = 7.9, 11.4 Hz, C1-*H*), 3.96 [1H, dd, *J* = 6.4, 7.9 Hz, –CH*H*′OC(CH_3)$_2$OCH–], 4.05–4.16 [1H, m, –CHH′OC(CH_3)$_2$OC*H*–], 4.48–4.70 (1H, m, C1-*H*′), 5.66 (1H, dt, *J* = 10.1, 3.1 Hz, C6-*H*), 6.00 (1H, dt, *J* = 10.1, 2.2 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.43, –4.32, 18.2, 25.6, 25.9, 26.4, 36.4, 38.0, 42.6, 43.6, 52.0, 66.1, 70.2, 74.6, 76.6, 109.4, 126.7, 128.7, 172.9, 174.1; EIMS (40 eV) *m/z* (%): 425 (7), 279 (28), 265 (100), 117 (25), 73 (57).

Methyl (3a*S*,4*R*,5*S*,7a*R*)-5-{(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (21c). Colorless oil; $[\alpha]_D^{20}$ +18.0° (*c* = 0.100, dichloromethane); R_f = 0.29 [hexane:ethyl acetate (4:1)]; (Found: M^+–CH_3, 425.1994. $C_{21}H_{33}O_7Si$ requires *M*, 425.1996); IR (thin film): ν_{max} 2925, 2853, 1789, 1737, 1463, 1378, 1368, 1255cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.048, 0.127 [6H, 2 × s, –Si(C*H*$_3$)$_2$–], 0.853 [9H, s, –C(C*H*$_3$)$_3$], 1.38, 1.44 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.52–2.58 (1H, m, C5-*H*), 2.80 (1H, dd, *J* = 4.2, 13.5 Hz, C3a-*H*), 3.10–3.32 (1H, m, C7a-*H*), 3.46 (1H, d, *J* = 4.2 Hz, C4-*H*), 3.57 [1H, t, *J* = 8.1 Hz, –C*H*H′OC(CH_3)$_2$OCH–], 3.72 (3H, s, –CO_2C*H*$_3$), 3.81 (1H, t, *J* = 8.1 Hz, –C*H*OTBS), 3.82 (1H, dd, *J* = 8.0, 13.7 Hz, C1-*H*), 4.13 [1H, dd, *J* = 6.2, 8.1 Hz, –CH*H*′OC(CH_3)$_2$OCH–], 4.20–4.30 [1H, m, –CHH′OC(CH_3)$_2$OC*H*–], 4.54 (1H, dd, *J* = 7.2, 8.0 Hz, C1-*H*′), 5.60 (1H, dt, *J* = 10.0, 3.1 Hz, C6-*H*), 6.01 (1H, dt, *J* = 10.0, 2.2 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.14, –3.97, 18.5, 25.5, 26.2, 26.8, 30.4, 35.7, 36.3, 42.3, 42.9, 52.4, 66.2, 70.4, 77.8, 78.3, 109.4, 126.3, 132.3, 172.5; EIMS (70 eV) *m/z* (%): 425 (4%), 279 (17), 265 (100), 101 (100), 73 (57).

IMDA reaction of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(triisopropylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (1d). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(triisopropylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**1d**) (37.0 mg, 0.0767 mmol) in toluene (15.3 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (3.4 mg, 0.015 mmol, 0.2 equiv). The solution was warmed to reflux and heating was continued for 18 h. Evaporation of the solvent gave the crude product (40.3 mg) as a yellow oil. Chromatography on silica (4 g) with hexane:ethyl acetate (4:1) gave the IMDA adducts (**20d**, **21d**, **23d** and **24d**) [25.1 mg, 0.0520 mmol, 68%, **20d**:**21d**:**22d**:**23d** (92:7:1:0)], *vide infra*.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-{(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(triisopropylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (20d). Colorless oil; $[\alpha]_D^{21}$ –50.0° (*c* = 1.04, dichloromethane); R_f = 0.17 [hexane:ethyl acetate (4:1)]; (Found: M^+–CH_3, 467.2466. $C_{24}H_{39}O_7Si$ requires *M*, 467.2465); IR (thin film): ν_{max} 2945, 2866, 1789, 1731, 1462, 1380, 1370, 1327, 1317, 1215 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.959–1.20 {21H, m, –Si[C*H*(CH_3)$_2$]$_3$}, 1.32, 1.41 [6H, 2 × s, –C(CH_3)$_2$–], 2.77 (1H, dd, *J* = 4.1, 13.7 Hz, C3a-*H*), 2.85–2.92 (1H, m, C5-*H*), 3.00–3.17 (1H, m, C7a-*H*), 3.52 (1H, d, *J* = 4.1 Hz, C4-*H*), 3.68 [1H, t, *J* = 8.0 Hz, –C*H*H′OC(CH_3)$_2$OCH–], 3.70 (3H, s, –CO_2CH_3), 3.84 (1H, dd, *J* = 8.0, 11.4 Hz, C1-*H*), 3.99 [1H, dd, *J* = 6.1, 8.0 Hz, –CH*H′*OC(CH_3)$_2$OCH–], 4.03 (1H, dd, *J* = 3.7, 6.1 Hz, –C*H*OTBS), 4.07–4.18 [1H, m, –CHH′OC(CH_3)$_2$OC*H*–], 4.53 (1H, dd, *J* = 7.2, 8.0 Hz, C1-*H′*), 5.69 (1H, dt, *J* = 10.1, 3.0 Hz, C6-*H*), 6.01 (1H, dt, *J* = 10.1, 2.1 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 13.4, 18.4, 25.5, 26.5, 36.5, 39.1, 42.8, 43.6, 52.2, 66.3, 70.2, 109.4, 126.8, 128.7, 172.8, 173.9; (HETCOR demonstrated that δ_C for –*C*HOTIPS and –CHH′OC(CH_3)$_2$O*C*H– were obscured by the 76.5 and 77.5 ppm peaks of the $CDCl_3$ triplet respectively); EIMS (40 eV) *m/z* (%): 467 (4), 439 (20), 381 (25), 321 (100) and 173 (31).

IMDA reaction (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-(4-nitrobenzoyloxy)-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (1e). To a stirred solution of **1f** (37 mg, 0.078 mmol, 1.0 equiv) in toluene (8 mL) was added 2,6-di-*tert*-butyl-4-methylphenol (3.4 mg, 0.015 mmol, 0.2 equiv), The solution was warmed to reflux and heating was continued for 12 h. Evaporation of the solvent gave the crude product as a yellow oil. Chromatography on silica (4 g) with hexane:ethyl acetate (1:1) gave the IMDA adducts (**20e**, **21e**, **23e** and **24e**) [25.1 mg, 0.0520 mmol, 68%, **20e**:**21e**:**22e**:**23e** (49:39:6:6)].

IMDA reaction of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (1f). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (**1f**) (187 mg, 0.424 mmol, 1.0 equiv) in chlorobenzene (85 mL) was added 2,6-di-*tert*-butyl-4-methylphenol (mg, mmol, 0.1 equiv). The solution was warmed to reflux and heating was continued for 53 h before the reaction mixture was concentrated *in vacuo*. Column chromatography on silica (hexane/ethyl acetate 78:22) gave a mixture of the 4 IMDA adducts (**20f**, **21f**, **22f** and **23f**) [116 mg, 0.26 mmol, 62%, **20f**:**21f**:**22f**:**23f** (12:3:82:3)].

Methyl (3a*S*,4*S*,5*R*,7a*S*)-5-{[(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (22f). Colorless oil; $[\alpha]_D^{21}$ –66.1° (*c* = 1.20, dichloromethane); R_f = 0.50 [hexane:ethyl acetate (2:1)]; (Found: M^+–CH_3, 425.1996. $C_{21}H_{33}O_7Si$ requires *M*, 425.1996); IR (thin film): ν_{max} 2984, 2953, 2930, 2897, 2856, 1787, 1738, 1472, 1462, 1435, 1380, 1370, 1208 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.46, 0.88 [6H, 2 × s, –Si(CH_3)$_2$–], 0.863 [9H, s, –C(CH_3)$_3$], 1.35, 1.40 [6H, 2 × s, –C(CH_3)$_2$–], 2.40–2.50 (1H, m, C5-*H*), 2.91–3.06 (2H, m, C3a-*H*, C4-*H*), 3.07–3.25 (1H, m, C7a-*H*), 3.57 [1H, t, *J* = 8.2 Hz, –C*H*H′OC(CH_3)$_2$OCH–], 3.62 (1H, dd, *J* = 2.8, 7.3 Hz, –C*H*OTBS), 3.77 (3H, s, –CO_2CH_3), 3.91 (1H, t, *J* = 8.8 Hz, C1-*H*), 3.97 [1H, dd, *J* = 6.2, 8.2 Hz, –CH*H′*OC(CH_3)$_2$OCH–], 4.17–4.27 [1H, m, –CHH′OC(CH_3)$_2$OC*H*–], 4.49 (1H, dd, *J* = 8.0, 8.8 Hz, C1-*H′*), 5.70 (1H, dt, *J* = 10.4, 3.3 Hz, C7-*H*), 5.94 (1H, dt, *J* = 10.4, 2.2 Hz, C6-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –5.18, –3.86, 18.5, 25.5, 26.1, 26.6, 35.0, 40.4, 40.5, 40.7, 52.2, 66.0, 71.6, 73.9, 78.0, 109.3, 123.8, 129.2, 173.6, 176, 3; EIMS (40 eV) *m/z* (%): 425 (12), 383 (28), 339 (66), 325 (85), 293 (89), 265 (64), 89 (42), 73 (100).

Methyl (3a*R*,4*R*,5*R*,7a*S*)-5-{(1*S*,2*S*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (20f). Colorless oil; $[\alpha]_D^{19.5}$ –137° (c = 0.190, dichloromethane); R_f = 0.42 [hexane:ethyl acetate (2:1)]; (Found: M^+–CH_3, 425.1999 $C_{21}H_{33}O_7Si$ requires *M*, 425.1996); IR (thin film): ν_{max} 2984, 2952, 2928, 2855, 1789, 1738, 1471, 1462, 1435, 1380, 1370 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.118 [6H, s, $–Si(CH_3)_2–$], 0.878 [9H, s, $–C(CH_3)_3$], 1.35, 1.41 [6H, 2 × s, $–C(CH_3)_2–$], 2.54–2.62 (1H, m, C5-*H*), 2.70–2.86 (1H, m, C7a-*H*), 2.96 (1H, dd, *J* = 7.2, 11.6 Hz, C4-*H*), 3.16 (1H, dd, *J* = 11.6, 13.4 Hz, C3a-*H*), 3.56 [1H, t, *J* = 8.1 Hz, $–CHH'OC(CH_3)_2OCH–$], 3.79 (1H, dd, *J* = 2.0, 7.5 Hz, –C*H*OTBS), 3.80 (3H, s, $–CO_2CH_3$), 3.90 (1H, dd, *J* = 8.0, 11.4 Hz, C1-*H*), 3.99 [1H, dd, *J* = 6.4, 8.1 Hz, $–CHH'OC(CH_3)_2OCH–$], 4.08–4.19 [1H, m, $–CHH'OC(CH_3)_2OCH–$], 4.45 (1H, dd, *J* = 6.6, 8.0 Hz, C1-*H′*), 5.74 (1H, dt, *J* = 9.9, 3.5 Hz, C6-*H*), 5.96 (1H, dt, *J* = 9.9, 2.0 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.53, –3.64, 18.6, 25.5, 26.3, 26.6, 40.7, 41.1, 41.4, 44.1, 51.9, 66.2, 70.1, 74.9, 78.3, 109.6, 124.7, 129.1, 170.7, 173.7; EIMS (70 eV) *m/z* (%): 425 (9), 383 (19), 339 (65), 325 (61), 293 (55), 265 (49), 89 (36), 75 (100).

IMDA reaction of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl propiolate (1g). To a stirred solution of (2*E*,4*E*,6*S*,7*S*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl propiolate (**1g**) (13 mg, 0.03 mmol) in toluene (3 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (0.5 mg, mmol). The solution was warmed to reflux and heating was continued for 43 h. Evaporation of the solvent gave the crude product as a yellow oil. Chromatography of this material on silica (1 g) with hexane:ethyl acetate (80:20) gave the IMDA adducts (**24** and **25**) [12 mg, 0.03 mmol, 92%, **24**:**25** (64:36)], *vide infra*.

(5*R*,7a*S*)-5-{(1*S*,2*S*)-2,3-*O*-Isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,5,7a-tetrahydroisobenzofuran (24). Colorless oil; $[\alpha]_D^{20}$ –13.5° (*c* = 1.12, dichloromethane); R_f = 0.30 [hexane:ethyl acetate (3:1)]; (Found: M^+, 380.2030. $C_{20}H_{32}O_5Si$ requires *M*, 380.2019); IR (thin film): ν_{max} 2984, 2954, 2929, 2897, 2856, 1769, 1482, 1471, 1380, 1370 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.080, 0.112 [6H, 2 × s, $–Si(CH_3)_2–$], 0.871 [9H, s, $–C(CH_3)_3$], 1.33, 1.41 [6H, 2 × s, $–C(CH_3)_2–$], 3.05–3.16 (1H, m, C5-*H*), 3.46–3.59 (1H, m, C7a-*H*), 3.58 [1H, t, *J* = 8.1 Hz, $–CHH'OC(CH_3)_2OCH–$], 3.82 (1H, t, *J* = 8.6 Hz, C1-*H*), 3.85 [1H, dd, *J* = 4.4, 8.1 Hz, $–CHH'OC(CH_3)_2OCH–$], 3.92 (1H, dd, *J* = 3.7, 6.6 Hz, –C*H*OTBS), 4.00–4.10 [1H, m, CHH′OC(CH_3)$_2$OC*H*–], 4.64 (1H, dd, *J* = 8.2, 8.6 Hz, C1-*H′*), 5.76–5.93 (2H, m, C6-*H*, C7-*H*), 6.96–7.01 (1H, m, C4-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.74, –4.18, 18.3, 25.7, 25.9, 26.6, 37.8, 42.8, 65.9, 70.4, 75.2, 77.9, 108.9, 123.8, 127.5, 128.0, 135.1, 168.9; EIMS (40 eV) *m/z* (%): 380 (0.3), 187 (35), 131 (59), 101 (39), 91 (42), 73 (100).

(5*S*,7a*R*)-5-{(1*S*,2*S*)-2,3-*O*-Isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,5,7a-tetrahydroisobenzofuran (25). Colorless oil; $[\alpha]_D^{20}$ +51.8° (*c* = 0.36, dichloromethane); R_f = 0.39 [hexane:ethyl acetate (3:1)]; (Found: M^+, 380.1999 $C_{20}H_{32}O_5Si$ requires *M*, 380.2019); IR (thin film): ν_{max} 2984, 2953, 2929, 2897, 2856, 1770, 1697, 1471, 1462, 1380, 1370, 1206 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.052, 0.098 [6H, 2 × s, –Si(C*H*$_3$)$_2$–], 0.841 [9H, s, –C(C*H*$_3$)$_3$], 1.35, 1.41 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.95–3.05 (1H, m, C5-*H*), 3.46–3.63 (1H, m, C7a-*H*), 3.61 [1H, t, *J* = 8.1 Hz, –C*H*H′OC(CH_3)$_2$OCH–], 3.82 (1H, dd, *J* = 8.3, 10.4 Hz, C1-*H*), 3.87–3.95 [2H, m, –CH*H′*OC(CH_3)$_2$OC*H*–], 4.13–4.22 (1H, m, –C*H*OTBS), 4.65 (1H, t, *J* = 8.3 Hz, C1-*H′*), 5.82–5.99 (2H, m, C6-*H*, C7-*H*), 6.86–6.90 (1H, m, C4-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ –4.74, –4.10, 18.3, 25.6, 25.9, 26.6, 37.8, 42.0, 65.8, 70.4, 75.7, 78.1, 109.2, 123.2, 128.8, 130.4, 133.3, 168.9; EIMS (40 eV) *m/z* (%): 380 (0.1), 265 (25), 187 (36), 131 (69), 91 (50), 73 (100).

Isoascorbate and Malate series

(2*E*,4*E*,6*S*,7*R*)-7,8-*O*-Isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (2a). To a stirred solution of (2*R*,3*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**10**) (234 mg, 0.71 mmol, 1.0 equiv) in dichloromethane (5 mL) at 0 °C was added triethylamine (159 µL, 1.14 mmol, 1.6 equiv), maleic anhydride (181 mg, 1.85 mmol, 2.6 equiv) and DMAP (10 mg, 0.08 mmol, 0.12 equiv). The reaction was stirred at this temperature for 15 min before being diluted with diethyl ether (50 mL), washed with 2 M HCl (25 ml), water (25 mL), dried and concentrated *in vacuo*. Chromatography of the crude product on silica (hexane/ethyl acetate/acetic acid 49:50:1) gave (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-

[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl hydrogen maleate (302 mg, 0.71 mmol, 100%) as a colorless oil. To a stirred solution of (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl hydrogen maleate (215 mg, 0.50 mmol) in dichloromethane (5 mL) at –78 °C was added an ethereal solution of diazomethane. After 15 min the reaction mixture was concentrated *in vacuo*. After column chromatography on silica (hexane/ethyl acetate 5:1) (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**2a**) (165 mg, 0.39 mmol, 74%) was obtained as a colorless oil. $[\alpha]_D^{25}$ –5.88 (c = 0.26, chloroform); IR (thin film): ν_{max} 2931, 2858, 1734, 1647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.02, 0.07 [6H, 2 × s, $–Si(CH_3)_2$], 0.88 [9H, s, $–C(CH_3)_3$], 1.40, 1.32 [6H, 2 × s, $–C(CH_3)_2–$], 3.77 (3H, s, $–OCH_3$), 3.84–3.99 (3H, m, C7-H, C8-H, C8-H′), 4.15 (1H, t, J = 5.7 Hz, C6-H), 4.71 (2H, d, J = 6.7 Hz, C1-H), 5.74 (2H, m, C2-H, C5-H), 6.26 (2H, m, C3-H, C4-H), 6.26 (2H, s, $–CH{=}CHCOCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.7, –4.1, 18.2, 25.4, 25.9, 26.8, 52.3, 65.5, 66.2, 73.3, 79.1, 109.5, 126.0, 129.7, 129.9, 130.1, 134.3, 135.3, 165.0, 165.7; EIMS (70 eV) *m/z* (%): 425 (30), 409 (10), 101 (100); HRMS: calcd for $C_{21}H_{33}O_7$ [M–CH_3]: 425.1996; found: 425.1992.

(2*E*,4*E*,6*S*,7*R*)-7,8-*O*-Isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (2b). To a stirred solution of (2*R*,3*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-3-[(*tert*-butyldimethylsilyl)oxy]-4,6-octadien-1,2,8-triol (**10**) (239.4 mg, 0.73 mmol, 1.0 equiv) in diethyl ether (15 mL) at RT under nitrogen was added monomethyl fumarate (170.7 mg, 1.31 mmol, 1.8 equiv), DCC (300.0 mg, 1.45 mmol, 2.0 equiv) and DMAP (13.4 mg, 0.1 mmol, 0.15 equiv). Stirring was continued for 3 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Chromatography of the crude product on silica (hexanes/ethyl acetate 89:11) gave (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (**2b**) (199.8 mg, 0.45 mmol, 62%) as a colorless oil. $[\alpha]_D^{25}$ –10.52° (c = 0.32, chloroform); IR (thin film): ν_{max} 2954, 2858, 1727 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.00, 0.04 [6H, 2 × s, $–Si(CH_3)_2–$], 0.86 [9H, s, $–C(CH_3)_3$], 1.29, 1.37 [6H, 2 × s, $–C(CH_3)_2–$], 3.77 (3H, s, $–OCH_3$), 3.79–3.97 (3H, m, C7-H, C8-H, C8-H′), 4.13 (1H, t, J = 5.2 Hz, C6-H), 4.69 (1H, d, J = 5.2 Hz, C1-H), 5.67–5.80 (2H, m, C2-H, C5-H), 6.25 (2H, m, C3-H, C4-H), 6.84 (2H, s, $–CH{=}CHCOCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.7, –4.2, 18.4, 25.4, 25.8, 26.7, 52.3, 65.4, 66.1, 73.2, 78.9, 109.4, 125.9, 129.9, 133.5, 133.6, 134.1, 135.3, 164.6, 165.3; EIMS (70 eV) *m/z* (%): 425 (35), 383 (55), 101 (100); HRMS: calcd for $C_{21}H_{33}O_7Si$ [M–CH_3]: 425.1996; found: 425.1991.

(2*E*,4*E*,7*S*)-7,8-*O*-Isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (3x). To a stirred solution of (2*S*,4*E*,6*E*)-1,2-*O*-Isopropylidene-4,6-octdadiene-1,2,8-triol (**13**) (258 mg, 1.3 mmol, 1.0 equiv) in dichloromethane (10 mL) at 0 °C was added triethylamine (210 μL, 2.08 mmol, 1.6 equiv), maleic anhydride (331 mg, 3.39 mmol, 2.6 equiv) and DMAP (19 mg, 0.16 mmol, 0.12 equiv). The reaction was stirred at this temperature for 15 min before being diluted with diethyl ether (50 mL), washed with 2 M HCl (25 mL), water (25 mL), dried and concentrated *in vacuo*. To a stirred solution of the crude product in dichloromethane (10 mL) at –78 °C was added an ethereal solution of diazomethane. After 15 min the reaction mixture was concentrated *in vacuo*. Column chromatography on silica (hexane/ethyl acetate 2:1) gave (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**3a**) (226 mg, 0.73 mmol, 56%) as a colorless oil. $[\alpha]_D^{21}$ +5.6° (*c* = 0.290, dichloromethane); R_f = 0.56 [hexane:ethyl acetate (2:1)]; (Found: M^+, 310.1416. $C_{16}H_{22}O_6$ requires *M*, 310.1416); IR (thin film): ν_{max} 2986, 2921, 2851, 1731, 1644, 1437, 1380, 1370, 1212 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.36, 1.43 [6H, 2 × s, –C(CH_3)$_2$–], 2.27–2.57 (2H, m, C6-*H*), 3.58 (1H, dd, *J* = 6.8, 7.9 Hz, C8-*H*), 3.79 (3H, s, –CO_2CH_3), 4.03 (1H, dd, *J* = 5.9, 7.9 Hz, C8-*H'*), 4.11–4.21 (1H, m, C7-*H*), 4.71 (2H, d, *J* = 6.6 Hz, C1-*H*), 5.66–5.80 (2H, m, C2-*H*, C5-*H*), 6.07–6.36 (2H, m, C3-*H*, C4-*H*), 6.27 (2H, s, –C*H*=C*H*CO_2CH_3); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.7, 27.0, 37.0, 52.2, 65.6, 68.9, 75.2, 109.0, 124.5, 129.6, 129.7, 130.9, 131.6, 134.8, 164.7, 165.5; EIMS (CI/NH_3, 40 eV) *m/z* (%): 310 (3), 295 (55), 113 (100), 101 (94), 73 (47).

(2*E*,4*E*,7*S*)-7,8-*O*-Isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (3y). To a stirred solution of (2*S*,4*E*,6*E*)-1,2-*O*-isopropylidene-4,6-octdadiene-1,2,8-triol (**13**) (210 mg, 1.06 mmol, 1.0 equiv) in diethyl ether (15 mL) was added monomethyl fumarate (248 mg, 1.91 mmol, 1.8 equiv), DCC (437 mg, 2.11 mmol, 2.0 equiv) and DMAP (19.4 mg, 0.16 mmol, 0.15 equiv). The reaction mixture was stirred for 16 h before being filtered. The filtrate was concentrated *in vacuo*.

Chromatography of the crude product on silica (hexanes/ethyl acetate 75:25) gave (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (**3b**) (243 mg, mmol, 74%) as a colorless oil. $[\alpha]_D^{25}$ +2.97 (*c* = 1.62, chloroform); IR (thin film): ν_{max} 2987, 2952, 2877, 1725, 1645 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (3H, s), 1.39 (3H, s), 2.32 (1H, m), 2.39 (1H, m), 3.53 (1H, dd, *J* = 7.0, 8.2 Hz), 3.78 (3H, s), 4.01 (1H, dd, *J* = 6.1, 8.1 Hz), 4.12 (1H, dq, *J* = 6.3, 6.3 Hz), 4.68 (2H, d, *J* = 6.9 Hz), 5.68 (1H, m), 5.69 (1H, m), 6.10 (1H, dd, *J* = 10.3, 15.0 Hz), 6.25 (1H, dd, *J* = 10.3, 15.0 Hz), 6.83 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.6, 26.9, 36.9, 52.4, 65.6, 68.8, 75.2, 109.1, 124.5, 131.2, 131.7, 133.5, 133.6, 134.9, 164.6, 165.4; EIMS (70 eV) *m/z* (%): 310 (2), 295 (30), 221 (10), 113 (40), 101 (100); HRMS: calcd for $C_{16}H_{22}O_6$ [M]: 310.1416; found: 310.1419

IMDA Reactions of 2 and 3

IMDA reaction of (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (2a). A solution of **2a** (165 mg, 0.37 mmol, 1.0 equiv) and BHT (8 mg, 0.04 mmol, 0.1 equiv) in toluene (37 mL) was heated at reflux for 9.5 h. The solution was then cooled to RT and concentrated *in vacuo*. After column chromatography on silica (hexanes/ethyl acetate 85:15) a mixture of 4 products **26a**:**27a**:**28a**:**29a** (141 mg, 0.32 mmol, 86%) in a ratio of 78:16:4:2 was obtained. Normal phase HPLC (hexanes/ethyl acetate 85:15) yielded compounds **26a** and **27a**.

Methyl (3a*S*,4*R*,5*S*,7a*R*)-5-{(1*S*,2*R*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (27a). $[\alpha]_D^{25}$ +60.34 (*c* = 0.29, chloroform); IR (thin film): ν_{max} 2955, 2931, 2893, 2858, 1788, 1736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.07, 0.11 (6H, 2 × s), 0.87 (9H, s), 1.30, 1.39 (6H, 2 × s), 2.61 (1H, dd, *J* = 4.4, 13.4 Hz), 2.95 (1H, m), 3.27 (1H, m), 3.38 (1H, dd, *J* = 1.5, 4.4 Hz), 3.72 (3H, s), 3.76–3.82 (2H, m), 3.85 (1H, dd, *J* = 11.7, 8.3 Hz), 4.00–4.08 (2H, m), 4.55 (1H, t, *J* = 7.6 Hz), 5.81 (1H, dt, *J* = 2.9, 9.8 Hz), 6.04 (1H, dt, *J* = 2.4, 10.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.6, –3.5, 18.0, 25.5, 25.8, 26.8, 36.2, 37.0, 43.0, 43.9, 52.2, 67.9, 76.4, 76.6, 109.6, 126.8, 130.1, 173.3, 174.8; EIMS (70 eV) *m/z* (%): 425

(10), 383 (15), 339 (10), 325 (20), 310 (55), 265 (100), 101 (40); HRMS: calcd for $C_{21}H_{33}O_7Si$ $[M^+–CH_3]$: 425.1996; found: 425.1996.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-{(1*S*,2*R*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (26a). $[\alpha]_D^{25}$ –23.44 (*c* = 0.32, chloroform); IR (thin film): ν_{max} 2986, 2892, 2858, 1788, 1735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.10, 0.11 (6H, 2 × s), 0.87 (9H, s), 1.29, 1.37 (6H, s), 2.57 (1H, dd, *J* = 4.7, 13.5 Hz), 3.02 (1H, m), 3.20 (1H, m), 3.32 (1H, d, *J* = 4.5 Hz), 3.70 (3H, s), 3.80–3.87 (2H, m), 3.99–4.06 (2H, m), 4.53 (1H, dd, *J* = 7.4, 7.4 Hz), 5.76 (1H, dt, *J* = 2.6, 9.8 Hz), 5.88 (1H, dm, *J* = 9.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.3, –3.9, 18.1, 25.8, 26.7, 27.5, 36.5, 37.5, 42.8, 43.9, 52.2, 67.4, 70.6, 75.6, 76.6, 109.3, 124.6, 129.9, 172.9, 174.7; EIMS (70 eV) *m/z* (%): 425 (20), 383 (50), 339 (10), 310 (55), 187 (60), 101 (50), 73 (100); HRMS: calcd for $C_{21}H_{33}O_7Si$ $[M^+–CH_3]$: 425.1996; found:425.1991

IMDA reaction of (2*E*,4*E*,6*S*,7*R*)-7,8-*O*-isopropylidene-6-[(*tert*-butyldimethylsilyl)oxy]-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (2b). A solution of **2b** (330 mg, 0.75 mmol, 1.0 equiv) and BHT (17 mg, 0.08 mmol, 0.1 equiv) in chlorobenzene (75 ml) was heated at reflux for 72 h. The reaction mixture was cooled to RT and concentrated *in vacuo*. After column chromatography on silica (hexanes/ethyl acetate 80:20) a mixture of 5 products (295 mg, 0.67 mmol, 89%) was obtained. Normal phase HPLC (hexanes/ethyl acetate 85:15) yielded compounds **26b**, **27b**, **28b** and **29b** in a ratio of 9:6:66:19.

Methyl (3a*R*,4*R*,5*S*,7a*R*)-5-{(1*S*,2*R*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (29b). $[\alpha]_D^{25}$ –149.59 (*c* = 0.903, chloroform); IR (thin film): ν_{max} 2954, 2931, 2896, 2857, 1790, 1742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.09, 0.13 (6H, 2 × s), 0.86 (9H, s), 1.31 (3H, s), 1.38 (3H, s), 2.78 (1H, m), 3.01 (2H, m), 3.09 (1H, m), 3.72 (1H, dd, *J* = 2.2, 5.9 Hz), 3.77 (1H, dd, *J* = 5.2, 8.3 Hz), 3.77 (3H, s), 3.88 (1H, dd, *J* = 7.9, 11.5 Hz), 4.03 (1H, dd, *J* = 5.8, 7.0 Hz), 4.09 (1H, q, *J* = 5.8 Hz), 4.44 (1H, dd, *J* = 7.0, 8.2 Hz), 5.90 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.2, –3.5, 18.6, 25.1, 26.1, 26.7, 40.5, 41.5, 41.5, 43.5, 51.9, 67.3, 70.4, 74.3, 77.8, 109.4, 123.7, 130.5, 171.5, 174.2; EIMS (70 eV) *m/z* (%): 425 (15), 383 (100), 339 (85), 325 (50), 73 (95); HRMS: calcd for $C_{21}H_{33}O_7Si$ [M–CH_3]: 425.1996; found: 425.1997

Methyl (3a*R*,4*R*,5*R*,7a*S*)-5-{(1*S*,2*R*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (26b). $[\alpha]_D^{25}$ +75.73 (*c* = 0.780, chloroform); IR (thin film): ν_{max} 2954, 2930, 2858, 1782, 1736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.08, 0.10 (6H, 2 × s), 0.88 (9H, s), 1.30, 1.35 (6H, 2 × s), 2.78 (1H, m), 2.86 (1H, dd, *J* = 7.4, 10.8 Hz), 3.12 (1H, dd, *J* = 10.8 Hz), 3.18 (1H, m), 3.70 (1H, dd, *J* = 3.6, 6.5 Hz), 3.75 (1H, dd, *J* = 12.6, 7.1 Hz), 3.75 (3H, s), 3.93 (1H, dd, *J* = 8.3, 8.3 Hz), 3.96–4.02 (2H, m), 4.49 (1H, dd, *J* = 8.3, 8.3 Hz), 5.76 (1H, dt, *J* = 3.2, 9.9 Hz), 6.04 (1H, dt, *J* = 2.0, 10.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.7, –4.3, 18.0, 25.8, 26.4, 29.8, 36.2, 39.0, 41.3, 43.5, 52.2, 67.8, 71.8, 73.1, 76.0, 109.5, 123.6, 128.7, 174.1, 176.6; EIMS (70 eV) *m/z* (%): 425 (10), 383 (15), 339 (40), 325 (40), 105 (100); HRMS: calcd for $C_{21}H_{33}O_7Si$ [M–CH_3]: 425.1996; found: 425.1997.

Methyl (3a*S*,4*S*,5*R*,7a*S*)-5-{(1*S*,2*R*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (28b). $[\alpha]_D^{25}$ –49.06 (*c* = 1.27, chloroform); IR (thin film): ν_{max} 2954, 2931, 2897, 2858, 1780, 1741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.06, 0.07 (6H, 2 × s), 0.85 (9H, s), 1.32, 1.38 (6H, 2 × s), 2.83 (2H, m), 3.07 (1H, m), 3.18 (1H, m), 3.69 (1H, dd, *J* = 2.1, 6.0 Hz), 3.75 (3H, s), 3.84 (1H, dd, *J* = 6.3, 8.2 Hz), 3.91 (1H, dd, *J* = 8.5, 8.5 Hz), 4.05 (1H, dd, *J* = 6.2, 8.0 Hz), 4.14 (1H, q, *J* = 5.9 Hz), 4.48 (1H, dd, *J* = 7.8, 8.8 Hz), 5.66 (1H, ddd, *J* = 2.1, 3.8, 10.4 Hz), 5.96 (1H, dt, *J* = 2.0, 11.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.2, –4.0, 18.3, 25.3, 26.0, 26.7, 34.9, 40.3, 40.5, 40.6, 52.3, 66.9, 71.7, 73.6, 76.9, 109.3, 123.2, 129.6, 173.6, 176.8; EIMS (70 eV) *m/z* (%): 425 (10), 409 (5), 383 (15), 339 (85), 73 (100); HRMS: calcd for $C_{21}H_{33}O_7Si$ [M–CH_3]: 425.1996; found: 425.1996.

Methyl (3a*S*,4*S*,5*S*,7a*R*)-5-{(1*S*,2*R*)-2,3-*O*-isopropylidene-1-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydroxypropyl}-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (27b). $[\alpha]_D^{25}$ +157.09 (c = 1.24, chloroform); IR (thin film): ν_{max} 2986, 2954, 2929, 2857, 1790, 1743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.09, 0.14 (6H, 2 × s), 0.93 (9H, s), 1.35, 1.42 (6H, 2 × s), 1.88 (1H, m), 2.37 (1H, dd, J = 12.2, 13.2 Hz), 2.71 (1H, dd, J = 9.4, 12.0 Hz), 2.75 (1H, m), 2.95 (1H, dd, J = 8.5, 12.0 Hz), 3.46 (3H, s), 3.56 (1H, dd, J = 6.9, 8.3 Hz), 3.80–3.88 (2H, m), 4.00 (1H, t, J = 3.0 Hz), 4.30 (1H, ddd, J = 2.5, 6.3, 8.3 Hz), 5.12 (1H, dt, J = 2.0, 10.3 Hz), 5.64 (1H, dt, J = 3.1, 10.0 Hz); ^{13}C NMR (125 MHz, C_6D_6): δ –4.9, –4.3, 18.3, 26.1, 26.1, 26.9, 40.5, 41.9, 42.1, 43.3, 51.6, 65.0, 69.4, 73.3, 77.5, 107.8, 125.1, 129.0, 170.8, 173.1; EIMS (70 eV) *m/z* (%): 425 (5), 383 (10), 325 (25), 310 (15), 105 (100); HRMS: calcd for $C_{21}H_{33}O_7Si$ [M–CH_3]: 425.1996; found: 425.1991.

(3a*S*,5a*R*,6*S*,7*R*,9a*S*,9b*S*)-3,3a,6,7-tetrahydro-6-[(*tert*-butyldimethylsilyl)oxy]-7-(hydroxymethyl)-5a*H*-furo[3,4-*h*]isochromene-1,9(9a*H*,9b*H*)-dione (30). To a stirred solution of **28b** (22 mg, 0.05 mmol, 1.0 equiv) in wet dichloromethane (500 μL) was added trifluoroacetic acid (195 μL, 2.5 mmol, 50 equiv). Stirring was continued for 4 h 40 min. Evaporation of the solvent gave the crude product as a colorless oil. Chromatography of this material on silica (hexane/ethyl acetate 70:30) gave **30** (10 mg, 0.03 mmol, 56%) as a colorless solid. $[\alpha]_D^{25}$ +4.18 (c = 0.335, chloroform); IR (thin film): ν_{max} 3468, 2957, 2918, 2851, 1769, 1647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.15 (3H, s), 0.17 (3H, s), 0.92 (9H, s), 1.63 (1H, bs), 2.38 (1H, ddd, J = 2.3, 2.3, 10.1 Hz), 2.61 (1H, dd, J = 7.4, 12.8 Hz), 3.07 (1H, m), 3.57 (1H, dd, J = 7.3, 8.3 Hz), 3.80 (1H, dd, J = 3.5, 12.6 Hz), 3.95 (1H, dd, J = 2.4, 12.3 Hz), 4.05 (1H, dd, J = 6.5, 10.4 Hz), 4.25 (1H, dd, J = 3.1, 9.2 Hz), 4.28 (1H, ddd, J = 3.2, 6.4, 9.8 Hz), 4.49 (dd, J = 7.0, 9.3 Hz), 5.85 (1H, dt, J = 2.7, 9.7 Hz), 6.12 (1H, dt, J = 2.4, 9.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ –3.9, –3.9, 18.1, 25.8, 35.4, 38.8, 39.3, 39.4, 62.3, 69.7, 71.8, 86.3, 129.6, 130.8, 171.5, 177.8; EIMS (70 eV) *m/z* (%): 368 (30), 311 (30), 293 (35), 219 (45), 75 (100); HRMS: calcd for $C_{18}H_{28}O_6Si$ [M]: 368.1655; found: 368.1656.

IMDA reaction of (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (3a). To a stirred solution of (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl maleate (**3a**) (0.9 mg, 2.9 mmol) in toluene (0.6 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (0.1 mg, 0.6 mmol, 0.2 equiv). The solution was warmed to reflux and heating was continued for 18 h. Evaporation of the solvent gave the crude product (1.0 mg) as a yellow oil. Chromatography of this material on silica (1 g) with hexane:ethyl acetate (2:1) gave the IMDA adducts (**26x** and **27x**) (0.8 mg, 2.6 mmol, 89%).

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (26x) and methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (27x) (as a mixture). Colorless oil; R_f = 0.24 [hexane:ethyl acetate (2:1)]; (Found: M^+, 310.1418. $C_{16}H_{22}O_6$ requires *M*, 310.1416); IR (thin film): ν_{max} 2985. 2933, 1788, 1731, 1436, 1380, 1371, 1217 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.35, 1.37, 1.42, 1.43 [12H, 4 × s, 2 × –C(C*H*$_3$)$_2$–], 1.57–1.86 (4H, m, 2 × –C5-C*H*$_2$–), 2.34, 2.39 (2H, 2 × dd, *J* = 3.5, 13.6 Hz and *J* = 3.9, 13.6 Hz, 2 × C3a-*H*), 2.92–3.08 (2H, m, 2 × C5-*H*), 3.14–3.34 (2H, m, 2 × C7a-*H*), 3.18, 3.31 (2H, 2 × d, *J* = 3.9, Hz and *J* = 3.5 Hz, 2 × C4-*H*), 3.50–3.58 [2H, m, 2 × –C*H*H′OC(CH$_3$)$_2$OCH–], 3.72 (6H, s, 2 × –CO$_2$C*H*$_3$), 3.87 (2H, dd, *J* = 8.1, 11.4 Hz, 2 × C1-*H*), 4.04–4.14 [2H, m, 2 × –CH*H′*OC(CH$_3$)$_2$OCH–], 4.15–4.30 [2H, m, 2 × –CHH′OC(CH$_3$)$_2$OC*H*–], 4.53, 4.56 (2H, 2 × dd, *J* = 1.5, 6.8 Hz and *J* = 1.8, 6.6 Hz, 2 × C1-*H′*), 5.71, 5.75 (2H, 2 × dt, *J* = 3.1, 9.9 Hz and *J* = 3.3, 10.3 Hz, 2 × C6-*H*), 5.86, 5.88 (2H, 2 × dt, *J* = 1.8, 10.3 Hz and *J* = 2.0, 9.9 Hz, 2 × C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 25.8 (2 × C), 27.0, 27.1, 29.7, 36.3, 36.6, 36.7, 37.0, 39.4, 39.8, 40.7, 40.9, 41.7, 41.9, 52.3, 69.4, 69.7, 70.6 (2 × C), 73.5, 74.3, 109.2, 109.3, 124.2, 124.3, 132.6, 133.0, 172.0, 172.2, 174.4, 174.5; (a Pure Inverse Gated Decoupling NMR experiment was used to confirm that δ_C at 25.8 ppm and 70.6 ppm each contained two overlapping peaks.); EIMS (40 eV) *m/z* (%): 310 (1), 295 (100), 252 (23), 221 (28), 175 (45), 131 (50), 91 (64), 72 (32), 59 (26), 43 (71).

IMDA reaction of (2*E*,4*E*,7*S*)-7,8-*O*-isopropylidene-7,8-dihydroxy-2,4-octadien-1-yl methyl fumarate (3b). To a stirred solution of (**3b**) (179 mg, 0.58 mmol, 1.0 equiv) in toluene (65 mL) at RT under argon was added 2,6-di-*tert*-butyl-4-methylphenol (13 mg, 0.06 mmol, 0.1 equiv). The solution was warmed to reflux and heating was continued for 43 h. Evaporation of the solvent gave the crude product as a yellow oil. Chromatography of this material on silica with hexane:ethyl acetate (60:40) gave the IMDA adducts (**26y**, **27y**, **28y** and **29y**) [160 mg, 0.52 mmol, 89%, **26y**:**27y**:**28y**:**29y** (32:33:18:17)] as a mixture.

Methyl (3a*S*,4*S*,5*R*,7a*S*)-5-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (28y). $[\alpha]_D^{25}$ –148.8 (*c* = 0.73, chloroform); IR (thin film): ν_{max} 2925, 1769, 1734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (3H, s), 1.40 (3H, s), 1.61 (2H, m), 2.79 (1H, m), 3.08 (1H, t, *J* = 4.3 Hz), 3.19 (1H, dd, *J* = 4.3, 8.3 Hz), 3.22 (1H, m), 3.50 (1H, t, *J* = 7.9 Hz), 3.76 (3H, s), 4.07 (2H, m), 4.24 (1H, dq, *J* = 5.3, 7.2 Hz), 4.45 (1H, dd, *J* = 7.2, 9.0 Hz), 5.62 (1H, dt, *J* = 2.6, 10.1 Hz), 5.94 (1H, ddd, *J* = 1.8, 3.9, 10.1 Hz); ^{13}C NMR (125 MHz, C_6D_6): δ 26.0, 27.3, 33.8, 33.9, 38.8, 39.3, 41.1, 51.9, 69.8, 71.1, 74.5, 109.2, 124.5, 132.6, 173.9, 176.8; EIMS (70 eV) *m/z* (%): 295 (80), 279 (5), 105 (100); HRMS: calcd for $C_{15}H_{19}O_6$ [M–CH_3]: 295.1182; found: 295.1182.

Methyl (3a*R*,4*R*,5*S*,7a*R*)-5-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (29y). $[\alpha]_D^{25}$ –48.75 (*c* = 0.08, chloroform); IR (thin film): ν_{max} 2923, 1772, 1734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (3H, s), 1.42 (3H, s), 1.54 (1H, m), 1.79 (1H, m), 2.87 (1H, m), 3.01 (1H, t, *J* = 4.1 Hz), 3.22 (2H, m), 3.52 (1H, t, *J* = 6.7 Hz), 3.75 (3H, s), 4.04 (1H, dd, *J* = 5.7, 8.0 Hz), 4.08 (1H, dd, *J* = 3.0, 9.0 Hz), 4.19 (1H, m), 4.45 (1H, dd, *J* = 6.9, 9.0 Hz), 5.67 (1H, dt, *J* = 2.2, 10.4 Hz), 5.97 (1H, ddd, *J* = 1.7, 4.2, 10.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.9, 27.1, 32.6, 33.9, 39.2, 39.4, 42.6, 52.5, 69.6, 71.7, 73.5, 109.2, 124.9, 131.3, 173.9, 177.4; EIMS (70 eV) *m/z* (%): 310 (1), 295 (100); HRMS: calcd for $C_{16}H_{22}O_6$ [M]: 310.1416; found: 310.1414.

Methyl (3a*R*,4*R*,5*R*,7a*S*)-5-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (26y). $[\alpha]_D^{25}$ +130.37 (*c* = 0.135, chloroform); IR (thin film): ν_{max} 2925, 1785, 1735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (3H, s), 1.39 (3H, s), 1.64 (2H, m), 2.56 (1H, dd, *J* = 11.6, 14.2 Hz), 2.81 (2H, m), 2.99 (1H, dd, *J* = 7.3, 12.4 Hz), 3.45 (1H, m), 3.77 (3H, s), 3.94 (1H, dd, J = 8.7, 11.9 Hz), 4.02 (2H, m), 4.46 (1H, dd, J = 6.8, 8.2 Hz), 5.86 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.9, 27.1, 35.9, 36.1, 41.1, 41.7, 43.2, 52.0, 69.6, 70.3, 74.7, 109.3, 123.0, 134.1, 171.7, 174.1; EIMS (70 eV) *m/z* (%): 310 (1), 295 (95), 43 (100); HRMS: calcd for $C_{16}H_{22}O_6$ [M]: 310.1416; found: 310.1414.

Methyl (3a*S*,4*S*,5*S*,7a*R*)-5-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (27y). $[\alpha]_D^{25}$ +78.4 (c = 0.31, chloroform); IR (thin film): ν_{max} 2925, 1785, 1734 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (3H, s), 1.39 (3H, s), 1.51 (2H, m), 2.56 (1H, dd, J = 11.3, 13.4 Hz), 2.84 (1H, m), 3.01 (2H, m), 3.51 (1H, dd, J = 6.3, 7.8 Hz), 3.79 (3H, s), 3.93 (1H, dd, J = 8.0, 11.2 Hz), 4.04 (1H, dd, J = 6.0, 8.0 Hz), 4.18 (1H, m), 4.46 (1H, dd, J = 6.6, 8.0 Hz), 5.87 (1H, d, J = 9.8 Hz), 5.96 (1H, dt, J = 3.3, 10.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.6, 27.2, 34.4, 36.6, 41.3, 41.5, 43.5, 52.0, 69.9, 70.3, 73.1, 109.4, 123.7, 132.5, 171.5, 174.1; EIMS (70 eV) *m/z* (%): 295 (80), 279 (15), 105 (100); HRMS: calcd for $C_{15}H_{19}O_6$ [M–CH_3]: 295.1182; found: 295.1178.

Lactate series

(2*Z*)-4-{[(2*E*,4*E*,6*S*)-6-[(*tert*-Butyldimethylsilyl)oxy]hepta-2,4-dienyl]oxy}-4-oxobut-2-enoic acid (31). To a stirred solution of **15** (1.11 g, 4.58 mmol, 1.0 equiv) in dichloromethane (30 mL) at 0 °C under argon was added triethylamine (1.02 mL, 7.33 mmol, 1.6 equiv), maleic anhydride (1.26 g, 12.82 mmol, 2.8 equiv) and DMAP (61 mg, 0.5 mmol, 0.1 equiv). The reaction mixture was stirred at this temperature for 15 min before being diluted with diethyl ether (110 mL), washed with 2 M HCl (55 mL), water (55 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography of the crude product on silica (hexane/ethyl acetate/methanol/acetic acid 20:20:1:1) gave **31** (1.16 g, 3.4 mmol, 75%). R_f = 0.41 (hexanes/ethyl acetate/ methanol/acetic acid 20:20:1:1); $[\alpha]_D$ +4.54 (c = 0.573, dichloromethane); IR (thin film): ν_{max} 2955, 2929, 2886, 2857 (C-H), 1769, 1738, 1732, 1713, 1682, 1651, 1633 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.05, 0.06 [6H, 2 × s, –$Si(CH_3)_2$], 0.89 [9H, s, –$SiC(CH_3)_3$], 1.22 (3H, d, J

= 6.6 Hz, C7-H_3), 4.35 (1H, dq, J = 5.5, 11.7 Hz, C6-H), 4.78 (2H, d, J = 7.0 Hz, C1-H_2), 5.73 (1H, dt, J = 6.6, 15.0 Hz, C2-H), 5.80 (1H, dd, J = 5.5, 15.0 Hz, C5-H), 6.17 (1H, ddd, J = 1.5, 10.6, 15.0 Hz, C4-H), 6.28–6.47 (3H, m, C2′-H, C3′-H, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.7, –4.6, 18.3 (Q), 24.3, 25.9, 67.3 (CH_2), 68.6, 123.6, 126.5, 129.5, 135.8, 136.2, 141.2, 165.2 (Q), 167.3 (Q); ESIMS (positive ion) *m/z* (%): 341 (100). HRMS: calcd for $C_{17}H_{29}SiO_5$ $[M + H]^+$: 341.1786; found 341.1782

(2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*Z*)-but-2-enedioate (4c). To a stirred solution of dienol **15** (307 mg, 1.26 mmol, 1.0 equiv) in dichloromethane (8.5 mL) at 0 °C was added triethylamine (281 μL, 2.02 mmol, 1.6 equiv), maleic anhydride (347 mg, 3.54 mmol, 2.8 equiv) and DMAP (15 mg, 0.12 mmol, 0.1 equiv). The reaction mixture was stirred at this temperature for 20 min. The mixture was diluted with diethyl ether (30 mL) and washed with 2 M HCl (15 mL), water (15 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in dichloromethane (15 mL) and an ethereal solution of diazomethane was added dropwise at –78 °C. The reaction mixture was concentrated *in vacuo.* After column chromatography on silica (hexane/ethyl acetate 88:12) the triene **4c** (384 mg, 1.10 mmol, 87%) was obtained as a colorless oil. R_f = 0.34 (hexanes/ethyl acetate 88:12); $[\alpha]_D$ +2.21 (c = 1.27, dichloromethane); IR (thin film): ν_{max} 2954, 2886, 2856 (C-H), 1732 (C=O), 1644 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04, 0.05 [6H, 2 × s, –$Si(CH_3)_2$], 0.89 [9H, s, –$SiC(CH_3)_3$], 1.20 (3H, d, J = 6.4 Hz, C7-H_3), 3.77 (3H, s, –OCH_3), 4.34 (1H, dq, J = 5.6, 12.2 Hz, C6-H), 4.70 (2H, dd, J = 1.0, 6.6 Hz, C1-H_2), 5.73 (1H, dt, J = 6.6, 14.9 Hz, C2-H), 5.76 (1H, dd, J = 5.4, 15.2 Hz, C5-H), 6.16 (1H, ddd, J = 1.2, 10.8, 15.2 Hz, C4-H), 6.25 (2H, m, C3′-H, C2′-H), 6.29 (1H, dd, J = 10.8, 14.9 Hz, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.7, –4.6, 18.3 (Q), 24.4, 25.9, 52.3, 65.7 (CH_2), 68.7, 125.0, 126.8, 129.7, 129.9, 134.9, 140.3, 165.0 (Q), 165.7 (Q); ESIMS (positive ion) *m/z* (%): 377 (100) HRMS: calcd for $C_{18}H_{30}O_5SiNa$ $[M + Na]^+$: 377.1755; found 377.1756

(2*E*,4*E*,6*S*)-6-hydroxyhepta-2,4-dienyl methyl (2*Z*)-but-2-enedioate (4a). To a stirred solution of **34** (53.7 mg, 0.16 mmol, 1.0 equiv) in THF (2 mL) under argon at 0 °C was added TBAF (0.50 mL, 0.50 mmol, 3.1 equiv) The reaction mixture was warmed to RT and stirring was continued for 23 h. The reaction mixture was diluted with diethyl ether (20 mL) and partitioned against saturated NH_4Cl (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was then diluted in dichloromethane (3 mL) and an ethereal solution of diazomethane was added dropwise at –78 °C. The mixture was then concentrated *in vacuo.* Chromatography of the crude product on silica (hexane/ethyl acetate 60:40) gave **1a** (16.7 mg, 0.07 mmol, 44%) as a colorless oil. R_f = 0.29 (hexanes/ethyl acetate 60:40) $[\alpha]_D$ +5.82 (*c* = 0.75, dichloromethane); IR (thin film): ν_{max} 3437 (OH), 2971, 2875 (C–C), 1738, 1731, 1720 (C=O), 1660, 1651, 1633 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (3H, d, *J* = 6.36 Hz, C7-H_3), 1.80 (1H, s, –OH), 3.79 (3H, d, *J* = 0.5 Hz, –OCH_3), 4.37 (1H, dq, *J* = 6.6, 12.7 Hz, C6-H), 4.72 (2H, d, *J* = 6.6 Hz, C1-H_2), 5.79 (1H, dt, *J* = 6.6, 14.0 Hz, C2-H), 5.81 (1H, dd, *J* = 6.6, 13.7 Hz, C5-H), 6.22 (1H, dd, *J* = 10.5, 14.9 Hz, C4-H), 6.27 (2H, m, C3′-H, C2′-H), 6.31 (1H, dd, *J* = 10.5, 15.2 Hz, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 52.3, 65.5 (CH_2), 68.3, 126.0, 128.1, 129.7, 130.0, 134.3, 139.2, 164.9 (Q), 165.8 (Q); ESIMS (positive ion) *m/z* (%): 263 (100). HRMS: calcd for $C_{15}H_{16}O_5Na$ $[M+Na]^+$: 263.0896; found 263.0899

(2*E*,4*E*,6*S*)-6-[(trimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*Z*)-but-2-enedioate (4b). To a stirred solution of **4a** (24.8 mg, 0.10 mmol, 1.0 equiv) in dichloromethane (2 mL) at 0 °C under argon was added 2,6-lutidine (36 µL, 0.31 mmol, 3.0 equiv) and trimethylsilyl trifluoromethanesulfonate (35 µL, 0.18 mmol, 1.8 equiv). On completion of addition the solution was warmed to RT and stirred for 15 min. The reaction mixture was diluted with diethyl ether (10 mL) and partitioned against saturated $NaHCO_3$ (10 mL). The aqueous layer was extracted with diethyl ether (2 × 5 mL). The combined organic layers were washed with NaCl (5 mL), dried ($MgSO_4$) and concentrated *in vacuo*. After column chromatography on silica (hexane/ethyl acetate 90:10) **4b** (27.5 mg, 0.09 mmol, 88%) was obtained as a colorless oil. R_f = 0.24 (hexanes/ethyl acetate 90:10); $[\alpha]_D$ +8.24 (*c* = 0.17, dichloromethane); IR (thin film): ν_{max} 2955 (C-H), 1732, 1644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.11 [9H, s, –$Si(CH_3)_3$], 1.23 (3H, d, *J* = 6.4 Hz, C7-H_3), 3.77 (3H, s, –OCH_3), 4.33 (1H, dq, *J* = 5.9, 12.2 Hz, C6-H), 4.70 (2H, d, *J* = 6.4 Hz, C1-H_2), 5.75 (2H, dt, *J* = 5.9, 15.2 Hz, C2-H, C5-H), 6.14 (1H, ddd, *J* = 1.0, 10.8, 15.2 Hz, C4-H), 6.25 (2H, m, C3′-H, C2′-H), 6.29 (1H, dd, *J* = 10.8, 15.2 Hz, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.2, 24.3, 52.3, 65.6 (CH_2), 68.6, 120.0, 125.3, 127.2, 127.7, 129.7, 130.0, 134.7, 140.0, 165.0 (Q), 165.7 (Q); ESIMS (positive ion) *m/z* (%): 647 (14), 335 (100), 263 (24). HRMS: calcd for $C_{14}H_{21}O_5Si$ [M–CH_3]: 297.1158; found 297.1166.

(2*E*,4*E*,6*S*)-6-[(trimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*Z*)-but-2-enedioate (4d). To a stirred solution of **1a** (41 mg, 0.17 mmol, 1.0 equiv) in dichloromethane (5 mL) at 0 °C under argon was added 2,6-lutidine (56 μL, 0.51 mmol, 3.0 equiv) and triisopropylsilyl trifluoromethanesulphonate (83 μL, 0.31 mmol, 1.8 equiv). On completion of addition the solution was warmed to RT and the stirring was continued for 1.5 h. The reaction mixture was diluted with diethyl ether (20 mL) and partitioned against saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL) and the combined extracts were washed with NaCl (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. After column chromatography on silica (hexanes/ethyl acetate 85:15) **4d** (53 mg, 0.13 mmol, 78%) was obtained as a colorless oil. R_f = 0.48 (hexanes/ethyl acetate 80:20); $[\alpha]_D$ +5.96 (*c* = 0.94, dichloromethane); IR (thin film): ν_{max} 2944, 2866, 1732, 1645, 1463, 1437, 1396, 1368 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.99–1.12 {21H, m, –Si[$CH(CH_3)_2$]$_3$}, 1.24 (3H, d, *J* = 6.2 Hz, C7-H_3), 3.77 (3H, s, –OCH_3), 4.44 (1H, dq, *J* = 6.2, 6.2 Hz, C6-H), 4.71 (2H, d, *J* = 6.6 Hz, C1-H_2), 5.73 (1H, dt, *J* = 6.6, 15.2 Hz, C2-H), 5.79 (1H, dd, *J* = 5.6, 14.9 Hz, C5-H), 6.18 (1H, dd, *J* = 10.8, 15.2 Hz, C4-H), 6.26 (2H, m, C3′-H, C2′-H), 6.30 (1H, dd, *J* = 10.3, 14.9 Hz, C3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 18.1, 24.9, 52.3, 65.8 (CH_2), 68.8, 124.9, 126.7, 129.8, 139.9, 135.0, 140.8, 165.0 (Q), 165.8 (Q); ESIMS (positive ion) *m/z* (%): 419 (100), 815 (10). HRMS: calcd for $C_{21}H_{36}NaSiO_5$ $[M + Na]^+$: 419.2230; found 419.2228.

(2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*E*)-but-2-enedioate (4e). To a stirred solution of **15** (162.1 mg, 0.60 mmol, 1.0 equiv) in diethyl ether (5 mL) at RT under nitrogen was added monomethyl fumarate (140.4 mg, 1.08 mmol, 1.8 equiv), DCC (247.3 mg, 1.20 mmol, 2.0 equiv) and DMAP (11.0 mg, 0.09 mmol, 0.15 equiv). Stirring was continued for 3 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Chromatography of the crude product on silica (hexanes/ethyl acetate 97:3) gave (2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*E*)-but-2-enedioate (**4e**) (182.2 mg, 0.53 mmol, 89%) as a colorless oil. $[\alpha]_D^{25}$ +21.47 (*c* =

0.340, chloroform); IR (thin film): ν_{max} 2955, 2930, 2887, 2857, 1727, 1662 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.03, 0.04 [6H, 2 × s, –$Si(CH_3)_2$–], 0.88 [9H, s, –$C(CH_3)_3$], 1.19 (3H, d, *J* = 7.4 Hz, C7-H_3), 3.79 (3H, s, –OCH_3), 4.09 (2H, d, *J* = 7.0 Hz, C1-H_2), 4.33 (1H, dq, *J* = 6.0, 11.3 Hz, C6-H), 5.70 (1H, dd, *J* = 6.6, 14.9 Hz, C5-H), 5.75 (1H, dd, *J* = 5.1, 15.0 Hz, C2-H), 6.14 (1H, ddd, *J* = 1.4, 10.5, 14.8 Hz, C4-H), 6.28 (1H, dd, *J* = 10.4, 15.5 Hz, C3-H), 6.85 (2H, s, C3′-H, C2′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.8, –4.7, 18.3, 24.3, 25.9, 52.3, 65.6, 68.6, 124.9, 126.7, 133.5, 133.7, 134.8, 140.3, 164.7, 165.4; EIMS (70 eV) *m/z* (%): 339 (2), 297 (30), 224 (35), 187 (100), 113 (50), 75 (65); HRMS: calcd for $C_{17}H_{27}O_5Si$ [M^+–CH_3]:339.1628; found: 339.1624.

IMDA reactions of 4

Thermal IMDA reaction of (2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*Z*)-but-2-enedioate (4c). A solution of **4c** (238.4 mg, 0.67 mmol, 1.0 equiv) and BHT (15 mg, 0.07 mmol, 0.1 equiv) in toluene (85 mL) was heated at reflux for 7 h and 25 min. The reaction mixture was concentrated *in vacuo*. After column chromatography on silica (hexanes/ethyl acetate 80:20) a mixture of 4 products (229.7 mg, 0.65 mmol, 96%) was obtained. Normal phase HPLC (hexanes/ethyl acetate 85:15) yielded compounds **35c** as a white solid and **36c** as a colorless oil, as well as a mixture of compounds **33c** and **34c**. Reverse phase HPLC (methanol/water 80:20) of this mixture yielded compound **33c** as a white solid and **34**c as a colorless oil.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (34c). R_f = 0.33 (hexanes/ethyl acetate 60:40); $[\alpha]_D$ +53.90 (*c* = 0.590, dichloromethane); IR (thin film): ν_{max} 2953 (C-H), 1790, 1731 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, MeOD): δ 0.07, 0.10 [6H, 2 × s, –$Si(CH_3)_2$], 0.89 [9H, s, –$SiC(CH_3)_3$], 1.28 (3H, d, *J* = 6.1 Hz, C2′-H_3), 2.63 (1H, m, C5-H), 2.67 (1H, dd, *J* = 3.9, 13.5 Hz, C3a-H), 3.2 (1H, m, C7a-H), 3.35 (1H, d, *J* = 3.7 Hz, C4-H), 3.69 (3H, s, –OCH_3), 3.84 (1H, dd, *J* = 8.1, 11.5 Hz, C1-Hβ), 4.04 (1H, dq, *J* = 3.9, 6.1 Hz, C1′-H), 4.56 (1H, dd, *J* = 7.1, 8.1 Hz, C1-Hα), 5.74 (1H, ddd, *J* = 3.2, 3.2, 10.0 Hz, C6-H/C7-

H), 6.01 (1H, ddd, *J* = 2.2, 2.2, 10.0, Hz, C6-H/C7-H); ^{13}C NMR (100 MHz, MeOD): δ –4.5, –4.3, 18.8 (Q), 22.2, 26.3, 37.2, 37.5, 44.0, 48.0, 52.5, 72.3 (CH_2), 72.3, 127.0, 132.6, 174.6 (Q), 177.6 (Q); EIMS (70 eV) *m/z* (%): 339 (7), 323 (15), 310 (55), 297 (100), 159 (85), 73 (85) HRMS: calcd for $C_{17}H_{27}O_5Si$ $[M – CH_3]^+$: 339.1628; found 339.1629.

Methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (33c). R_f = 0.33 (hexanes/ethyl acetate 60:40); mp 54–56 °C; $[\alpha]_D$ +84.0 (*c* = 0.300, dichloromethane); IR (KBr disc): ν_{max} 2950, 2929, 2857, 2350 (C-H), 1780, 1731 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.06, 0.07 [6H, 2 × s, $–Si(CH_3)_2$], 0.87 [9H, s, $–SiC(CH_3)_3$], 1.16 (3H, d, *J* = 6.4, C2′-H_3), 2.50 (1H, dd, *J* = 4.2, 13.5, Hz, C3a-H), 2.78 (1H, m, C5-H), 3.24 (1H, m, C7a-H), 3.31 (1H, d, *J* = 3.9 Hz, C4-H), 3.68 (3H, s, $–OCH_3$), 3.83 (1H, dd, *J* = 7.8, 11.5 Hz, C1-Hβ), 4.00 (1H, dq, *J* = 4.7, 6.4, Hz C1′-H), 4.52 (1H, dd, *J* = 7.8, 7.8 Hz, C1-Hα), 5.74 (1H, ddd, *J* = 3.0, 3.0, 10.0 Hz, C6-H/C7-H), 5.96 (1H, ddd, *J* = 2.2, 2.2, 10.0 Hz, C6-H/C7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.4, –4.9, 18.1 (Q), 20.9, 25.8, 36.4, 38.0, 43.1, 46.1, 52.1, 70.6 (CH_2), 71.3, 125.9, 129.4, 173.2 (Q), 174.6 (Q); EIMS (70 eV) *m/z* (%): 339 (30), 310 (30), 297 (100), 159 (65), 73 (70); HRMS: calcd for $C_{17}H_{27}O_5Si$ $[M–CH_3]^+$: 339.1628; found 339.1626.

Methyl (3a*S*,4*R*,5*R*,7a*S*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (36c). R_f = 0.24 (hexanes/ethyl acetate 60:40); $[\alpha]_D$ +23.53 (*c* = 0.136, dichloromethane); IR (thin film): ν_{max} 2958, 2856, 2358 (C-H), 1770, 1731 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.08, 0.09 [6H, 2 × s, $–Si(CH_3)_2$], 0.89 [9H, s, $–SiC(CH_3)_3$], 1.29 (3H, d, *J* = 5.9 Hz, C2′-H), 2.24 (1H, m, C5-H), 2.95 (1H, dd, *J* = 6.1, 11.3 Hz, C3a-H), 3.21 (1H, m, C7a-H), 3.36 (1H, dd, *J* = 4.2, 5.6 Hz, C4-H), 3.64 (3H, s, $–OCH_3$), 3.84 (1H, dq, *J* = 5.9, 9.8 Hz, C1′-H), 4.09 (1H, dd, *J* = 8.1, 9.8 Hz, C1-Hβ), 4.53 (1H, dd, *J* = 8.3, 9.5 Hz, C1-Hα), 5.68 (1H, ddd, *J* = 2.7, 2.7, 10.0 Hz, C6-H/C7-H), 5.96 (1H, ddd, *J* = 2.5, 2.5, 10.0 Hz, C6-H/C7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.6, –3.8, 18.2 (Q), 22.1, 25.9, 34.0, 40.5, 41.3, 46.7, 51.9, 69.4, 72.0 (CH_2), 125.0, 129.1, 172.3 (Q), 177.9 (Q); EIMS (70 eV) *m/z* (%): 355 (5), 339 (35), 297 (100), 159 (30), 73 (80); HRMS: calcd for $C_{17}H_{27}O_5Si$ $[M–CH_3]^+$: 339.1628; found 339.1629.

Methyl (3a*R*,4*S*,5*S*,7a*R*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (35c). R_f = 0.33 (hexanes/ethyl acetate 60:40); mp 95–98 °C; $[\alpha]_D$ –20.44 (*c* = 0.450, dichloromethane); IR (KBr disc): ν_{max} 2931, 2857 (C-H), 1760, 1737 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.03, 0.07 [6H, 2 × s, $–Si(CH_3)_2$], 0.87 [9H, s, $–SiC(CH_3)_3$], 1.24 (3H, d, *J* = 5.9 Hz), 2.24 (1H, m, C3a-H), 2.95 (1H, dd, *J* = 6.4, 10.8 Hz, C5-H), 3.20 (1H, m, C7a-H), 3.60 (1H, dd, *J* = 3.9, 6.1 Hz, C4-H), 3.62 (3H, s, $–OCH_3$), 4.00 (1H, dd, *J* = 8.3, 10.3 Hz, C1-Hβ), 4.06 (1H, dq, *J* = 6.1, 9.3 Hz, C1′-H), 4.50 (1H, dd, *J* = 8.1, 9.5 Hz, C1-Hα), 5.67 (2H, m, C6-H, C7-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –4.9, –3.9, 18.1 (Q), 22.3, 26.0, 34.6, 39.5, 41.6, 47.0, 51.6, 68.6, 71.6 (CH_2), 125.7, 128.2, 172.3 (Q), 177.6 (Q); EIMS (70 eV) *m/z* (%): 339 (40), 297 (100), 159 (30), 89 (80), 73 (85); HRMS calcd for $C_{17}H_{27}O_5Si$ $[M–CH_3]^+$: 339.1628; found 339.1627.

Thermal IMDA reaction of (2*E*,4*E*,6*S*)-6-hydroxyhepta-2,4-dienyl methyl (2*Z*)-but-2-enedioate (4a). A solution of **4a** (35 mg, 0.15 mmol, 1.0 equiv) and BHT (4.4 mg, 0.02 mmol, 0.1 equiv) in toluene (15 mL) was heated at reflux for 4.5 h. The reaction mixture was concentrated *in vacuo.* After column chromatography on silica (hexanes/ethyl acetate 40:60) a mixture of 4 products (30.8 mg, 0.13 mmol, 88%) was obtained.

Thermal IMDA reaction of (2*E*,4*E*,6*S*)-6-[(trimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*Z*)-but-2-enedioate (4b). A solution of **4b** (98.5 mg, 0.32 mmol, 1.0 equiv) and BHT (6.6 mg, 0.03 mmol, 0.1 equiv) in toluene (32 mL) was heated at reflux for 6.5 h. The reaction mixture was concentrated *in vacuo.* After column chromatography on silica (hexanes/ethyl acetate 60:40) a mixture of 4 products (81.6 mg, 0.27 mmol, 83%) was obtained.

Thermal IMDA reaction of (2*E*,4*E*,6*S*)-6-[(trimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*Z*)-but-2-enedioate (4d). A solution of **4d** (53 mg, 0.13 mmol, 1.0 equiv) and BHT (3 mg, 0.01 mmol, 0.1 equiv) in toluene (13 mL) was heated at reflux for 8.25 h. The reaction mixture was concentrated *in* *vacuo*. After column chromatography on silica (hexanes/ethyl acetate 85:15) a mixture of 4 products (45 mg, 0.11 mmol, 85%) was obtained.

IMDA reaction of (2*E*,4*E*,6*S*)-6-[(*tert*-butyldimethylsilyl)oxy]hepta-2,4-dienyl methyl-(2*E*)-but-2-enedioate (4e). A solution of **4e** (173 mg, 0.51 mmol, 1.0 equiv) and BHT (11 mg, 0.051 mmol, 0.1 equiv) in chlorobenzene (102 mL) was heated at reflux for 43 h. The solution was cooled to RT and concentrated *in vacuo*. After column chromatography on silica (hexanes/ethyl acetate 80:20) a mixture of 4 products (129.8 mg, 0.38 mmol, 75%) was obtained. Normal phase HPLC of the mixture yielded compounds **33e**, **34e**, **35e** and **36e** in a ratio of 8:28:40:24.

Methyl (3a*S*,4*S*,5*S*,7a*R*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (33e). $[\alpha]_D^{25}$ –164.52 (*c* = 0.420, chloroform); IR (thin film): ν_{max} 3032, 2954, 2930, 1788, 1735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.04, 0.04 (6H, 2 × s), 0.86 (9H, s), 1.10 (3H, d, *J* = 6.4 Hz), 2.57 (1H, t, *J* = 12.7 Hz), 2.93 (1H, m), 3.03 (1H, dd, *J* = 9.0, 12.3 Hz), 3.68 (1H, m), 3.77 (3H, s), 3.95 (1H, dd, *J* = 8.4, 11.5 Hz), 4.46 (1H, t, *J* = 7.4 Hz), 6.00 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ –5.0, –4.7, 18.1, 20.7, 25.8, 41.2, 41.5, 41.7, 44.7, 51.8, 68.9, 70.5, 124.5, 129.9, 171.3, 174.2; EIMS (70 eV) *m/z* (%): 339 (4), 310 (20), 297 (90), 159 (55), 73 (100); HRMS: calcd for $C_{17}H_{27}O_5Si$ $[M^+–CH_3]$:339.1628; found: 339.1625.

Methyl (3a*S*,4*S*,5*R*,7a*S*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (36e). $[\alpha]_D^{25}$ +191.98 (*c* = 0.424, chloroform); IR (thin film): ν_{max} 3015, 2951, 2929, 2904, 2882, 1783, 1748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.04, 0.07 (6H, 2 × s), 0.90 (9H, s), 1.24 (3H, d, *J* = 6.4 Hz), 2.64 (1H, m), 2.78 (1H, m), 2.95 (1H, dd, 7.4, 11.1 Hz), 3.14 (1H, dd, *J* = 12.0, 14.4 Hz), 3.77 (3H, s), 3.88 (1H, dd, *J* = 7.8, 11.3 Hz), 3.90 (1H, dq, *J* = 2.7, 6.6 Hz), 4.43 (1H, dd, *J* = 6.7, 8.0 Hz), 5.87 (1H, ddd, *J* = 3.3, 3.3, 9.9 Hz), 5.94 (1H, ddd, *J* = 1.9, 1.9, 10.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.8, –3.7, 18.2, 23.0, 26.0, 41.3, 41.6, 43.8, 45.4, 51.8, 69.4, 70.3, 124.5, 129.5, 171.5, 174.3; EIMS (70 eV) *m/z* (%): 310 (15), 297 (100), 159 (35), 75 (65); HRMS: calcd for $C_{14}H_{21}O_5Si$ [M^+–C_4H_9]: 297.1158; found: 297.1157.

Methyl (3a*R*,4*R*,5*R*,7a*S*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (34e). $[\alpha]_D^{25}$ –44.88 (*c* = 0.205, chloroform); IR (thin film): ν_{max} 2930, 2847, 1778, 1735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.06, 0.10 (6H, 2 × s), 0.90 (9H, s), 1.09 (3H, d, *J* = 6.5 Hz), 2.58 (1H, m), 2.99 (1H, dd, *J* = 6.6, 6.6 Hz), 3.10 (1H, dd, *J* = 7.7, 7.7 Hz), 3.20 (1H, m), 3.75 (3H, s), 3.75 (1H, dq, *J* = 6.3, 12.3 Hz), 3.98 (1H, dd, *J* = 6.0, 8.8 Hz), 4.45 (1H, dd, *J* = 7.5, 8.9 Hz), 5.70 (1H, ddd, *J* = 2.9, 2.9, 10.4 Hz), 5.94 (1H, ddd, *J* = 2.3, 2.3, 10.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –4.8, –4.3, 18.1, 20.2, 25.9, 34.7, 39.0, 39.9, 44.6, 52.4, 69.0, 71.7, 125.0, 129.3, 174.4, 177.0; EIMS (70 eV) *m/z* (%): 339 (5), 297 (100), 159 (55), 73 (75); HRMS: calcd for $C_{14}H_{21}O_5Si$ [M^+–C_4H_9]:297.1158; found: 297.1158.

Methyl (3a*R*,4*R*,5*S*,7a*R*)-5-[(1*S*)-1-(*tert*-butyldimethylsilyl)oxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (35e). $[\alpha]_D^{25}$ +92.86 (*c* = 0.868); IR (thin film): ν_{max} 2929, 2856, 1788, 1735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.00, 0.02 (6H, 2 × s), 0.87 (9H, s), 1.25 (3H, d, *J* = 6.4 Hz), 2.52 (1H, m), 2.93 (1H, dd, *J* = 6.1, 7.5 Hz), 3.07 (1H, dd, *J* = 8.0, 8.0 Hz), 3.20 (1H, m), 3.73 (3H, s), 3.76 (1H, dq, *J* = 6.0, 11.9 Hz), 3.97, (1H, dd, *J* = 6.5, 9.3 Hz), 4.45 (1H, dd, *J* = 7.5, 8.9 Hz), 5.66 (1H, ddd, *J* = 2.6, 3.3, 10.4 Hz), 5.96 (1H, ddd, *J* = 2.1, 3.2, 10.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ –5.1, –4.2, 18.1, 21.6, 25.9, 34.6, 39.3, 40.0, 44.4, 52.3, 69.8, 71.9, 123.9, 130.3, 174.3, 177.3; EIMS (70 eV) *m/z* (%): 339 (4), 310 (15), 297 (100), 159 (50), 73 (70); HRMS: calcd for $C_{17}H_{27}O_5Si$ [M^+–CH_3]: 339.1628; found: 339.1629.

Methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(1*S*)-1-hydroxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (33a). To a stirred solution of **33c** (40 mg, 0.11 mmol, 1.0 equiv) in $CDCl_3$ (500 μL) was added trifluoroacetic acid (348 μL, 4.5 mmol, 40 equiv). After 2.5 h the mixture was concentrated *in vacuo*. Chromatography of the crude product on silica (hexane/ethyl acetate 50:50) gave **33a** (26 mg, 0.11 mmol, 95%) as a colorless oil. $[\alpha]_D^{25}$ +3.20 (*c* = 0.625, chloroform); IR (thin film): ν_{max} 3462, 2962, 2902, 1781, 1730 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (3H, d, *J* = 6.4 Hz), 1.97 (1H, bs), 2.64 (1H, dd, *J* = 4.3, 13.6 Hz), 2.80 (1H, m), 3.24 (1H, m), 3.31 (1H, d, *J* = 4.3 Hz), 3.73 (3H, s), 3.89 (1H, dd, *J* = 8.2, 11.5 Hz), 4.05 (1H, dq, *J* = 4.2, 6.5 Hz), 4.55 (1H, t, *J* = 8.3 Hz), 5.82 (1H, dt, *J* = 3.1, 10.1 Hz), 6.06 (1H, dt, *J* = 2.1, 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 36.4, 39.4, 42.8, 45.4, 52.3, 70.6, 71.4, 127.1, 128.0, 172.9, 174.8; EIMS (70 eV) *m/z* (%): 209 (15), 196 (35), 136 (70), 119 (75), 91 (100); HRMS: calcd for $C_{11}H_{13}O_4$ [M–OMe]: 209.0814; found: 209.0815.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*)-1-hydroxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (34a). To a stirred solution of **34c** (15 mg, 0.04 mmol, 1.0 equiv) in $CDCl_3$ (300 μL) was added trifluoroacetic acid (132 μL, 1.8 mmol, 40 equiv). After 5 h the mixture was concentrated *in vacuo*. Chromatography of the crude product on silica (hexane/ethyl acetate 50:50) gave **34a** (10 mg, 0.04 mmol, 98%) as colorless crystals. $[\alpha]_D^{25}$ –20.57 (*c* = 0.125, chloroform); mp 128 °C; IR (thin film): ν_{max} 3469, 2917, 1780, 1730 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (3H, d, *J* = 6.2 Hz), 1.56 (1H, bs), 2.49 (1H, dd, *J* = 4.1, 13.6 Hz), 2.67 (1H, m), 3.28 (1H, m), 3.49 (1H, d, *J* = 4.3 Hz), 3.71 (3H, s), 3.87 (1H, dd, *J* = 8.1, 11.4 Hz), 3.94 (1H, dq, *J* = 4.8, 6.4 Hz), 4.55 (1H, t, *J* = 7.9 Hz), 5.72 (1H, dt, *J* = 3.1, 9.8 Hz), 6.03 (1H, dt, *J* = 1.8, 10.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.5, 36.2, 36.3, 42.8, 46.5, 52.4, 70.2, 70.6, 126.8, 130.9, 173.0, 174.8; EIMS (70 eV) *m/z* (%): 209 (20), 196 (35), 150 (45), 136 (70), 119 (70), 91 (100); HRMS: calcd for $C_{11}H_{13}O_4$ [M–OMe]: 209.0814; found: 209.0814.

(3*S*,3a*R*,5a*S*,8a*S*,8b*R*)-3-methyl-3,3a,5a,6,8a,8b-hexahydrofuro[3,4-e][2]benzofuran-1,8-dione (37). To a stirred solution of **36c** (30.8 mg, 0.09 mmol, 1.0 equiv) in $CDCl_3$ (300 μL) was added trifluoroacetic acid (250 μL, 3.2 mmol, 36 equiv). The mixture was stirred at RT for 2.25 h before being concentrated *in vacuo*. After column chromatography on silica (hexane/ethyl acetate 15:85) **37** (13 mg, 0.6 mmol, 66%) was obtained as a colorless crystalline solid. R_f = 0.31 (hexanes/ethyl acetate 15:85); mp 90 °C; IR (KBr disc): ν_{max} 2989, 2878, 2359, 2339, 1764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (3H, d, *J* = 6.4 Hz), 2.68 (1H, m), 3.11–3.19 (2H, m), 3.24 (1H, dd, *J* = 6.9, 6.9 Hz), 4.13 (1H, dd, *J* = 2.9, 9.3 Hz), 4.24 (1H, dq, *J* = 6.4, 8.3 Hz), 4.37 (1H, dd, *J* = 6.4, 9.3 Hz), 5.80 (1H, ddd, *J* = 2.0, 2.0, 10.3 Hz), 5.89 (1H, ddd, J = 2.0, 3.4, 10.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.4, 35.6, 37.2, 37.4, 41.7, 71.4 (CH_2), 80.4, 126.9, 127.9, 175.7 (Q), 175.8 (Q); EIMS (70 eV) *m/z* (%): 209 (30), 164 (47), 149 (20), 136 (70), 92 (100). HRMS: calcd for $C_{11}H_{13}O_4$ $[M + H]^+$: 209.0814; found 209.0813.

(3*S*,3a*S*,5a*R*,8a*R*,8b*S*)-3-methyl-3,3a,5a,6,8a,8b-hexahydrofuro[3,4-e][2]benzofuran-1,8-dione (38). To a stirred solution of **35c** (10.2 mg, 0.03 mmol, 1.0 equiv) in $CDCl_3$ (300 μL) at RT was added trifluoroacteic acid (89 μL, 1.15 mmol, 40 equiv). The mixture was stirred at RT for 3 h before being concentrated *in vacuo*. Recrystallization from TBME gave (3*S*,3a*S*,5a*R*,8a*R*,8b*S*)-3-methyl-3,3a,5a,6,8a,8b-hexahydrofuro[3,4-e][2]benzofuran-1,8-dione (**38**) (5 mg, 0.02 mmol, 85%) as a colorless crystalline solid. $[\alpha]_D^{25}$ –1.19 (c = 0.23, chloroform); mp 139 °C; IR (thin film): ν_{max} 3749, 2916, 1768 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (3H, d, J = 6.4 Hz), 2.97 (1H, dd, J = 6.8, 9.5 Hz), 3.06 (1H, m), 3.20 (1H, m), 3.39 (1H, t, J = 6.6 Hz), 3.90 (1H, dd, J = 8.5, 10.2 Hz), 4.51 (1H, t, J = 8.6 Hz), 4.71 (1H, dq, J = 5.3, 6.4 Hz), 5.91 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.0, 29.8, 34.6, 35.9, 39.3, 39.9, 71.6, 124.0, 127.8, 147.8, 175.3, 179.8; EIMS (70 eV) *m/z* (%): 208 (10), 164 (40), 149 (15), 136 (75), 91 (100); HRMS: calcd for $C_{11}H_{12}O_4$ $[M]^+$: 208.0736; found 208.0730.

(3*S*,3a*S*,5a*R*,8a*S*,8b*S*)-3-methyl-3,3a,5a,6,8a,8b-hexahydrofuro[3,4-e][2]benzofuran-1,8-dione (39). To a stirred solution of **34e** (6 mg, 0.02 mmol, 1.0 equiv) in $CDCl_3$ (300 μL) at RT was added trifluoroacteic acid (55 μL, 0.32 mmol, 16 equiv). The mixture was stirred at RT for 3 h before being concentrated *in vacuo*. Recrystallization from TBME gave (**39**) (3 mg, 0.01 mmol, 81%) as a colorless crystalline solid. $[\alpha]_D^{25}$ –59.13 (c = 0.12, chloroform); mp 170 °C; IR (thin film): ν_{max} 3749, 2973, 2917, 2851, 1788 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.51 (3H, d, J = 6.3 Hz), 2.43 (1H, t, J = 13.2 Hz), 2.79–2.99 (2H, m), 3.13 (1H, dd, J = 8.8, 12.2 Hz), 4.00 (1H, dd, J = 7.7, 10.5 Hz), 4.34 (1H, dq, J = 6.1, 8.6 Hz), 4.55 (1H, dd, J = 7.1, 8.4 Hz), 5.80 (1H, dt, J = 3.3, 9.8 Hz), 6.05 (1H, dt, J = 2.1, 9.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.0, 39.7, 40.4, 40.7, 45.2, 70.0, 79.9, 126.6, 127.7, 172.4, 173.5; EIMS (70 eV) *m/z* (%): 208 (10), 164 (35), 149 (20), 136 (80), 91 (100); HRMS: calcd for $C_{11}H_{12}O_4$ $[M]^+$: 208.0736; found 208.0730.

Methyl (3a*R*,4*R*,5*S*,7a*R*)-5-[(1*S*)-1-hydroxyethyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (40). To a stirred solution of **35e** (21 mg, 0.06 mmol, 1.0 equiv) in dichloromethane (1 mL) was added trifluoroacetic acid (183 μL, 2.4 mmol, 40 equiv). After 5 h the mixture was concentrated *in vacuo*. Chromatography of the crude product on silica (hexane/ethyl acetate 50:50) gave **40** (12 mg, 0.06 mmol, 85%) as colorless crystals. $[\alpha]_D^{25}$ +83.85 (c = 0.390, chloroform); mp 90 °C; IR (thin film): ν_{max} 3503, 2956, 2917, 1770, 1733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.33 (3H, d, J = 6.3 Hz), 1.66 (1H, bs), 2.62 (1H, m), 3.04 (1H, t, J = 6.0 Hz), 3.18 (1H, t, J = 6.4 Hz), 3.77 (3H, s), 3.24 (1H, m), 3.90 (1H, dq, J = 6.0, 11.8 Hz), 4.08 (1H, dd, J = 5.0, 8.7 Hz), 4.50 (1H, dd, J = 7.5, 8.7 Hz), 5.78 (1H, dt, J = 2.8, 10.2 Hz), 5.99 (1H, ddd, J = 1.9, 3.1, 10.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 34.3, 39.7, 40.2, 43.4, 52.6, 69.8, 71.8, 126.1, 128.2, 174.3, 177.7; EIMS (70 eV) *m/z* (%): 209 (4), 196 (80), 164 (35), 136 (65), 105 (40), 92 (100); HRMS: calcd for $C_{11}H_{13}O_4$ [M–OMe]: 209.0814; found: 209.0817.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (48) and methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (49) (66:34). To a stirred solution of methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(2*S*,3*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxy-3-propyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**20a**) and methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(2*S*,3*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxy-3-propyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**21a**) [**20a**:**21a** (66:34)] (36.0 mg, 0.110 mmol) in acetone (2 mL) at RT under argon was added Amberlyst IR-118 resin (36 mg). Stirring was continued for 21 h then the reaction mixture was filtered and evaporated to give the crude product (36.0 mg) as a yellow oil. Chromatography of this material on silica (5 g) with ethyl acetate:hexane (1.5:1) gave methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**48**) and methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexa-hydro-4-isobenzofurancarboxylate (**49**) [34.5 mg, 0.106 mmol, 96%, **48**:**49** (66:34)], *vide infra*.

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-tri-hydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (48). Colorless oil; $[\alpha]_D^{21}$ –96.8° (*c* = 0.440, dichloromethane); R_f = 0.33 [ethyl acetate:hexane (1.5:1)]; (Found: M^+–CH_3, 311.1139. $C_{15}H_{19}O_7$ requires *M*, 311.1131); IR (thin film): ν_{max} 3468, 2986, 2932, 1783, 1732, 1437, 1381, 1371, 1218 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.39, 1.41 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.06 (1H, t, *J* = 6.0 Hz, –O*H*), 2.66 (1H, dd, *J* = 3.8, 13.5 Hz, C3a-*H*), 2.98–3.05 (1H, m, C5-*H*), 3.11–3.28 (1H, m, C7a-*H*), 3.26 (1H, d, *J* = 3.8 Hz, C4-*H*), 3.64–3.77 (1H, m, –C*H*H′OH), 3.73 (3H, s, –CO$_2$C*H*$_3$), 3.78–3.95 (1H, m, –CH*H′*OH), 3.88 (1H, dd, *J* = 7.9, 11.4 Hz, C1-*H*), 3.98–4.06 [2H, m, –C*H*OC(CH$_3$)$_2$OC*H*–], 4.53 (1H, dd, *J* = 7.3, 7.9 Hz, C1-*H′*), 5.82 (1H, dt, *J* = 10.1, 3.3 Hz, C6-*H*), 6.03 (1H, dt, *J* = 10.1, 2.2 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 27.3, 27.4, 36.6, 40.1, 40.5, 42.3, 52.5, 62.5, 70.4, 78.7, 80.6, 109.4, 126.7, 127.8, 171.9, 174.2; EIMS (70 eV) *m/z* (%): 311 (12), 196 (19), 131 (76), 91 (19), 59 (100), 43 (29).

Methyl (3a*S*,4*R*,5*S*,7a*R*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-tri-hydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (49). Colorless oil; $[\alpha]_D^{21}$ +20.0° (*c* = 0.460, dichloromethane); R_f = 0.25 [ethyl acetate:hexane (1.5:1)]; (Found: M^+–CH_3, 311.1138. $C_{15}H_{19}O_7$ requires *M*, 311.1131); IR (thin film): ν_{max} 3458, 2984, 2923, 1782, 1731, 1437, 1380, 1370, 1215cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 1.42, 1.44 [6H, 2 × s, –C(C*H*$_3$)$_2$–], 2.57 (1H, dd, *J* = 3.7, 13.6 Hz, C3a-*H*), 2.89–2.96 (1H, m, C5-*H*), 3.11–3.30 (1H, m, C7a-*H*), 3.45 (1H, m, C4-*H*), 3.49–3.89 (1H, m, –C*H*H′OH), 3.73 (3H, s, –CO$_2$C*H*$_3$), 3.81–3.93 (1H, m, –CH*H′*OH), 3.91 (1H, dd, *J* = 8.1, 11.4 Hz, C1-*H*), 4.00–4.06 [2H, m, –C*H*OC(CH$_3$)$_2$OC*H*–], 4.49–4.59 (1H, m, C1-*H′*), 5.67 (1H, dt, *J* = 3.1, 9.9 Hz, C6-*H*), 6.03 (1H, dt, *J* = 2.0, 9.9 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 27.2, 27.3, 36.2, 37.0, 41.2, 42.5, 52.5, 62.1, 70.3, 78.9, 79.1, 109.5, 126.8, 130.0, 172.2, 174.1; EIMS (70 eV) *m/z* (%): 311 (12), 196 (19), 131 (75), 59 (100), 43 (26).

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*R*)-3-iodo-1,2-*O*-isopropylidene-1,2-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (50). To methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*S*)-1,2-*O*-isopropylidene-1,2,3-trihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-

isobenzofurancarboxylate (**48**) (18.0 mg, 0.0552 mmol) at RT under argon was added chloroform (1 mL) containing imidazole (7.1 mg, 0.11 mmol 1.9 equiv), triphenyphosphine (23.2 mg, 0.0880 mmol, 1.6 equiv) and iodine (21.0 mg, 0.0827 mmol, 1.5 equiv) and the solution was stirred for 8 h. An additional volume of the chloroform solution (1 mL) was added and stirring was continued for 12 h. The reaction mixture was diluted with heaxane:ethyl acetate (20:1, 5 mL), silica (0.1 g) was added and then rapid vacuum filtration through a silica plug (0.5 g) was carried out with hexane:ethyl acetate (20:1 then 5:1) to give methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*R*)-3-iodo-1,2-*O*-isopropylidene-1,2-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**50**) (15.9 mg, 0.0364 mmol, 67%) as a yellow oil: $[\alpha]_D^{21}$ –76.3° (*c* = 0.79, dichloromethane); R_f = 0.09 [hexane:ethyl acetate (5:1)]; (Found: M^+–CH_3, 421.0149. $C_{15}H_{18}O_6I$ requires *M*, 421.0148); ν_{max} (film) 2987, 2932, 1789, 1731, 1435, 1381, 1371, 1218cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.38, 1.45 [6H, 2 × s, –C(CH_3)$_2$–], 2.46 (1H, dd, *J* = 4.0, 13.4 Hz, C3a-*H*), 3.09–3.15 (1H, m, C5-*H*), 3.16–3.29 (1H, m, C7a-*H*), 3.27 (1H, d, *J* = 4.0 Hz, C4-*H*), 3.29–3.35 (2H, m, –CH_2I), 3.74 (3H, s, –CO_2CH_3), 3.89 (1H, dd, *J* = 8.1, 11.4 Hz, C1-*H*), 3.95 [1H, dd, *J* = 4.6, 6.4 Hz, –C*H*OC(CH_3)$_2$OCHCH_2I], 4.01–4.10 [1H, m, –CHOC(CH_3)$_2$OC*H*CH_2I], 4.55 (1H, dd, *J* = 7.0, 8.1 Hz, C1-*H'*), 5.82 (1H, dt, *J* = 10.1, 3.1 Hz, C6-*H*), 6.06 (1H, dt, *J* = 2.0, 10.1 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 6.26, 27.8, 27.9, 36.5, 40.4, 41.0, 42.2, 52.5, 70.4, 77.6, 85.0, 110.1, 127.1, 127.3, 171.8, 174.0; EIMS (70 eV) *m/z* (%): 421 (10), 241 (100), 183 (49), 91 (35), 43 (44).

Methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*R*)-1,2-dihydroxy-3-iodopropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (51). To a stirred solution of methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*R*)-3-iodo-1,2-*O*-isopropylidene-1,2-dihydroxypropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**50**) (13.8 mg, 0.0316 mmol) in methanol:water (5:1, 1 mL) at RT under argon was added Amberlite IR 118 ion exchange resin (16.0 mg). On completion of the addition the solution was warmed to 50 °C and stirred for 30 min. The solution was then warmed to reflux and stirring was continued for 18 h. The solution was filtered through cotton wool and evaporated to give the crude product (13.8 mg) as a yellow oil. Chromatography of this material on silica (0.5 g) with benzene then hexane:ethyl acetate (1:1 then 1:2) gave recovered starting material (**50**) (5.8 mg, 0.0133 mmol, 42%) followed by the methyl

(3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*R*)-1,2-dihydroxy-3-iodopropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**51**) (5.8 mg, 0.015 mmol, 82% based on 58% conversion) as a yellow oil. $[\alpha]_D^{21}$ –28.0° (c = 0.054, dichloromethane); R_f = 0.36 [hexane:ethyl acetate (1:2)]; (Found: M^++H, 397.0138. $C_{13}H_{18}O_6I$ requires M, 397.0148); IR (thin film): ν_{max} 3444, 2919, 2850, 1777, 1731, 1435, 1378cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.60–2.76 (1H, m, –C*H*H′I), 2.71 (1H, dd, *J* = 4.2, 13.6 Hz, C3a-*H*), 2.95–3.05 (1H, m, C5-*H*), 3.12–3.32 (1H, m, C7a-*H*), 3.32–3.45 (2H, m, C4-*H*, –CH*H*′I), 3.74 (3H, s, –CO_2CH_3), 3.79–3.90 (2H, m, –C*H*OH-C*H*OH–), 3.92 (1H, dd, *J* = 8.1, 11.4 Hz, C1-*H*), 4.56 (1H, dd, *J* = 7.3, 8.1 Hz, C1-*H*′), 5.81 (1H, dt, *J* = 3.1, 10.1 Hz, C6-*H*), 6.08 (1H, dt, *J* = 2.2, 10.1 Hz, C7-*H*); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 10.5, 36.4, 39.2, 42.5, 42.8, 52.5, 70.4, 71.6, 75.5, 127.4, 127.7, 172.3, 174.4; EIMS (70 eV) *m/z* (%): 397 (2), 196 (46), 136 (44), 91 (100), 77 (34).

Methyl 2-oxa-3-oxo-(4*R*,5*S*,6*R*,7*S*,8*S*,10*S*,12*S*)-7,8-dihydroxytricyclo-[7.3.0.0^{6,10}]-5-dodecanecarboxylate (52). To a stirred solution of methyl (3a*R*,4*S*,5*R*,7a*S*)-5-[(1*S*,2*R*)-1,2-dihydroxy-3-iodopropyl]-3-oxo-1,3,3a,4,5,7a-hexahydro-4-isobenzofurancarboxylate (**51**) (5.8 mg, 0.015 mmol) in benzene (0.6 mL) at RT under argon was added *tris*-trimethylsilylsilane (5.2 µL, 0.016 mmol, 1.1 equiv) and 2,2′-azo-bis-isobutyronitrile (crystal). On completion of the addition the solution was warmed to reflux and stirring was continued for 45 min. The solvent was evaporated to give the crude product (9.7 mg) as a yellow oil. Chromatography of this material on silica (0.5 g) with ethyl acetate gave methyl 2-oxa-3-oxo-(4*R*,5*S*,6*R*,7*S*,8*S*,10*S*,12*S*)-7,8-dihydroxytricyclo-[7.3.0.0^{6,10}]-5-dodecanecarboxylate (**52**) (2.6 mg, 0.0096 mmol, 64%) as a colorless oil: $[\alpha]_D^{21}$ –6.0° (c = 0.100, dichloromethane); R_f = 0.40 (ethyl acetate); (Found: M^++H, 271.1196. $C_{13}H_{19}O_6$ requires M, 271.1181); IR (thin film): ν_{max} 3440, 2920, 2851, 1731, 1426cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.21–1.41 (1H, m, C11-*H*), 1.84 (1H, ddd, *J* = 4.0, 8.2, 14.3 Hz, C9-*H*), 1.95 (1H, ddd, *J* = 2.4, 6.3, 12.0 Hz, C11-*H*′), 2.03 (1H, ddd, *J* = 2.4, 6.8, 14.3 Hz, C9-*H*′), 2.18–2.37 (1H, m, C10-*H*), 2.67 (1H, dd, *J* = 5.8, 7.6 Hz, C6-*H*), 2.72–2.89 (2H, m, C4-*H* and C12-*H*), 3.40 (1H, d, *J* = 4.2 Hz, C5-*H*), 3.72 (3H, s, –CO_2CH_3), 3.81 (1H, dd, *J* = 8.3, 11.1 Hz, C1-*H*), 4.13–4.25 (2H, m, C7-*H* and C8-*H*), 4.42 (1H, dd, *J* = 6.4, 8.3 Hz, C1-*H*′); ^{13}C NMR (68.1 MHz, $CDCl_3$): δ 29.8, 34.6, 35.4, 37.5, 37.9, 42.4, 44.2, 52.2, 72.1, 79.4, 83.0, 173.4, 176.4; EIMS (70 eV) *m/z* (%): 271 (3), 192 (48), 91 (100), 105 (46), 77 (70).

Crystallography: The identities of the four sets of products from each of the reactions of **4a**, **4b** and **4d** were correlated with the four derived from **4c** by interconversions. Thus, crude reaction mixtures obtained by heating **4b** and **4c** were treated with trifluoroacetic acid. NMR and GC analyses of these reaction mixtures linked the TMS and TBS cycloadducts with those derived from the alcohol precursor **4a**. Attempts to deprotect TIPS-protected cycloadducts were unsuccessful, so two *trans*-alcohols **33a** and **34a** were converted to TIPS ethers **33d** and **34d**, respectively. *Cis*-adducts **35a** and **36a** in this series rapidly form tricyclic *bis*-lactones **37** and **38** respectively (Figure S3) under the reaction conditions. Crystal structures were obtained of compounds **34a**, **37**, **38** (Figure S3). Treatment of compound **34e** with trifluoroacetic acid generated the alcohol which spontaneously lactonized to bislactone **39**. Similar treatment of **35e** with TFA gave alcohol **40**. The structures of **39** and **40** were also confirmed by single crystal X-ray analyses (Figure S3).

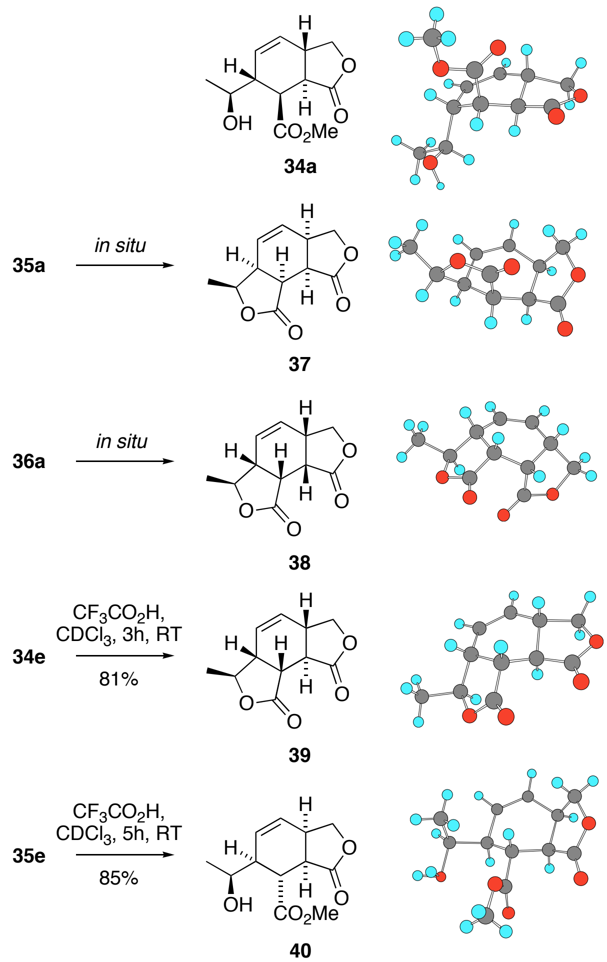

Figure S3. Molecular structures from single crystal X-ray analysis of **34a**, **37**, **38**, **39** and **40**.

Table S1. X-ray crystallographic data for compounds **34a**, **37**, **38**, **39** and **40**:

	34a	**37**	**38**	**39**	**40**
CCDC No.	243538	243536	244532	243539	243537
Formula	$C_{12}H_{16}O_5$	$C_{11}H_{12}O_4$	$C_{11}H_{12}O_4$	$C_{11}H_{12}O_4$	$C_{12}H_{16}O_5$
FW	240.25	208.21	208.21	208.21	240.25
Crystal system	monoclinic	orthorhombic	triclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P1$	$P2_12_12_1$	$P2_1$
a/Å	6.7425(2)	6.2705(2)	10.230(3)	7.4420(1)	8.4510(3)
b/Å	7.5101(3)	7.9808(2)	10.228(3)	8.1357(1)	6.2019(2)
c/Å	12.0271(4)	19.4486(4)	10.682(4)	16.2950(3)	11.6509(3)
α/°	–	–	69.720(5)	–	–
β/°	103.131(2)	–	69.678(5)	–	105.488(2)
γ/°	–	–	78.536(5)	–	–
V/Å^3	593.09(4)	973.28(4)	979.2(6)	986.60(3)	588.48(3)
Z/Z'	2/1	4/1	4/4	4/1	2/1
T/K	200	200	150(2)	200	200
μ/mm^{-1}	0.10	0.108	0.108	0.107	0.106
Reflections:					
Measured	10262	16128	9255	27651	10040
Unique	1450	2219	4497	1680	1467
Observed	1263 (3σ)	851 (3σ)	4497	1186 (2σ)	1160 (3σ)
no. refined parameters	154	136	546	172	161
$R(F)$	0.035	0.032	0.036 (F^2)	0.029	0.033
Rw(F)	0.024	0.036	0.065 (F^2, 2σ)	0.034	0.040
S	1.038	1.046	1.020	1.072	1.141

Structure Determinations

Compounds 34a, 37, 39 and 40:

All crystals were mounted on fine drawn glass capillaries in a coating of Paratone oil. Data were collected using standard methods by means of a Nonius Kappa CCD Diffractometer[14] (MoKα radiation, graphite monochromated) at 200K. Data were extracted from frames via Denzo[15] and an analytical absorption correction[16] was applied. Structures were solved by direct methods (SIR97[17]: **34a**, **37** and **40**, or SIR92[18]: **39**) and refined using the CRYSTALS[19] suite of programs. Least-squares refinements were on *F*. All non-hydrogen atoms were included in the refinement with positional and anisotropic displacement parameters, H-atoms were treated variously. H atoms bonded to C were assigned an isotropic displacement parameter of 1.2 x U_{eq} of the C: for **34a**, the OH hydrogen was refined positionally, all other H atoms ride on the atom of attachment; for **37** all H-atoms ride on atom of attachment; for **39** H atom positions were included in refinement and for **40** the H atom of the OH appeared to be distributed over two sites (both of which gave rise to reasonable hydrogen bond geometry) and both sites were included in the refinement with a common isotropic displacement parameter, positional and occupancy (restrained to sum to unity) parameters. All structures are chiral, but due to the absence of heavy atoms, no determination of absolute stereochemistry based on anomalous dispersion data was possible. The absolute stereochemistry reported is chosen to correspond to the known stereochemistry of synthetic precursors. Complete details for all structures have been deposited with the CCDC (see table).

Compound 38:

A colorless blade like crystal was attached with Exxon Paratone N, to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. A Bruker SMART 1000 CCD diffractometer employing graphite monochromated MoKα radiation generated from a sealed tube was used for the data collection. Cell constants were obtained from a least squares refinement against 908 reflections located between 5 and 49º 2θ. Data were collected at 150(2) Kelvin with ω scans to 56.7º 2θ.

The data integration and reduction were undertaken with SAINT and XPREP[20], and subsequent computations were carried out with the teXsan,[21] WinGX[22] and XTAL[23] graphical user interfaces.

The structure was solved in the space group *P*1(#1) by direct methods with SIR97,[17] and extended and refined with SHELXL-97.[24] The crystal symmetry is triclinic and the unit cell contains four crystallographically independent molecules. The crystal is twinned by a two fold rotation about the *b* axis of a C-centred monoclinic super cell; the twin rotation is about the –1 1 0 axis of the triclinic cell. The non-hydrogen atoms were modelled with anisotropic displacement parameters, and a riding atom model with group displacement parameters was used for the hydrogen atoms. The bond angles of the independent molecules were constrained to be equal, without reducing the geometry uncertainties. The absolute structure could not be determined, and Friedel pairs were accordingly merged.

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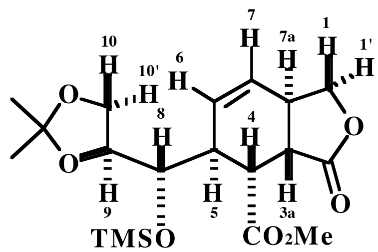
COSY spectrum of 20b



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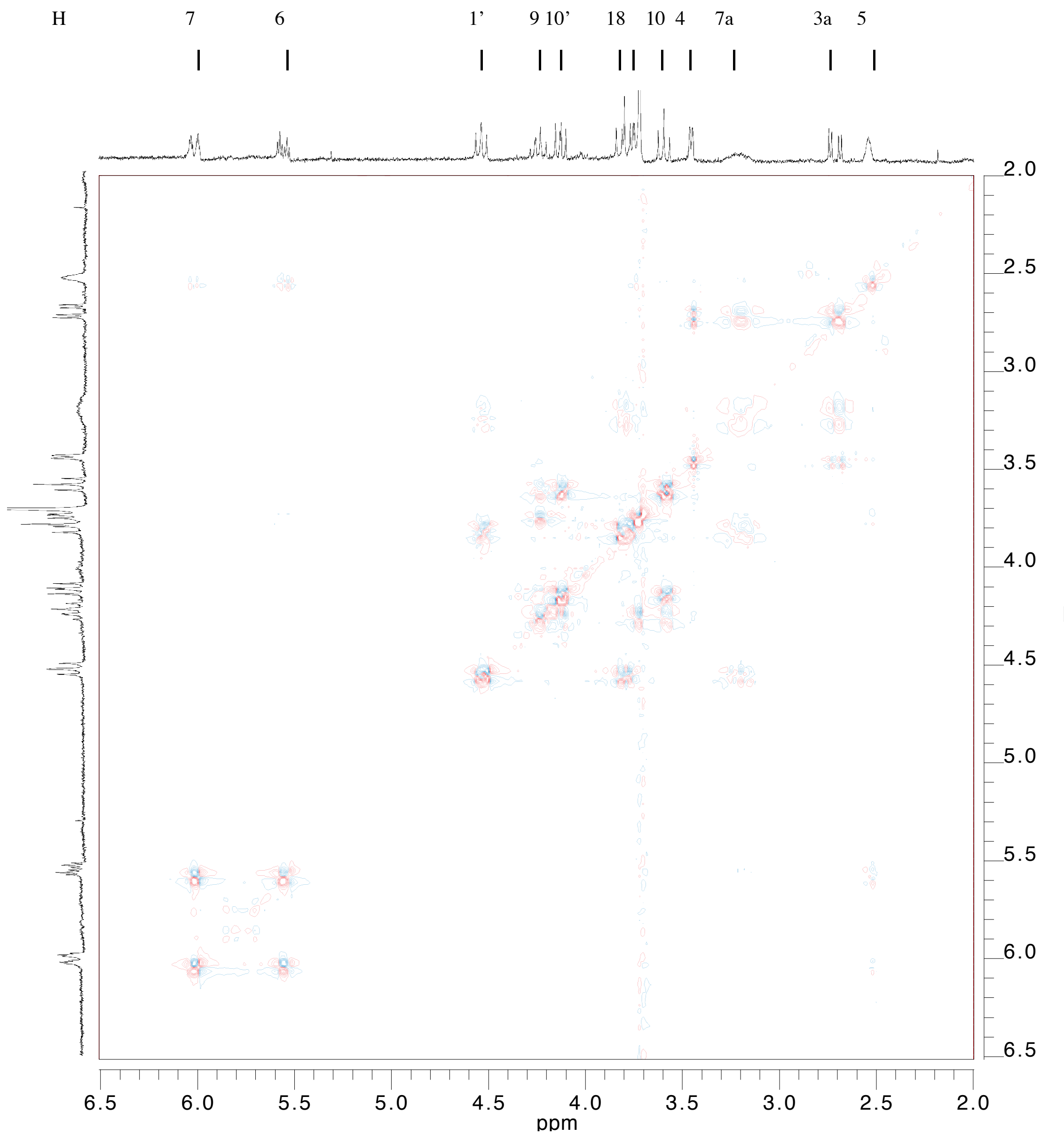

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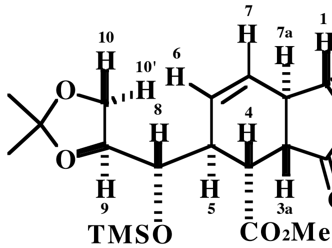

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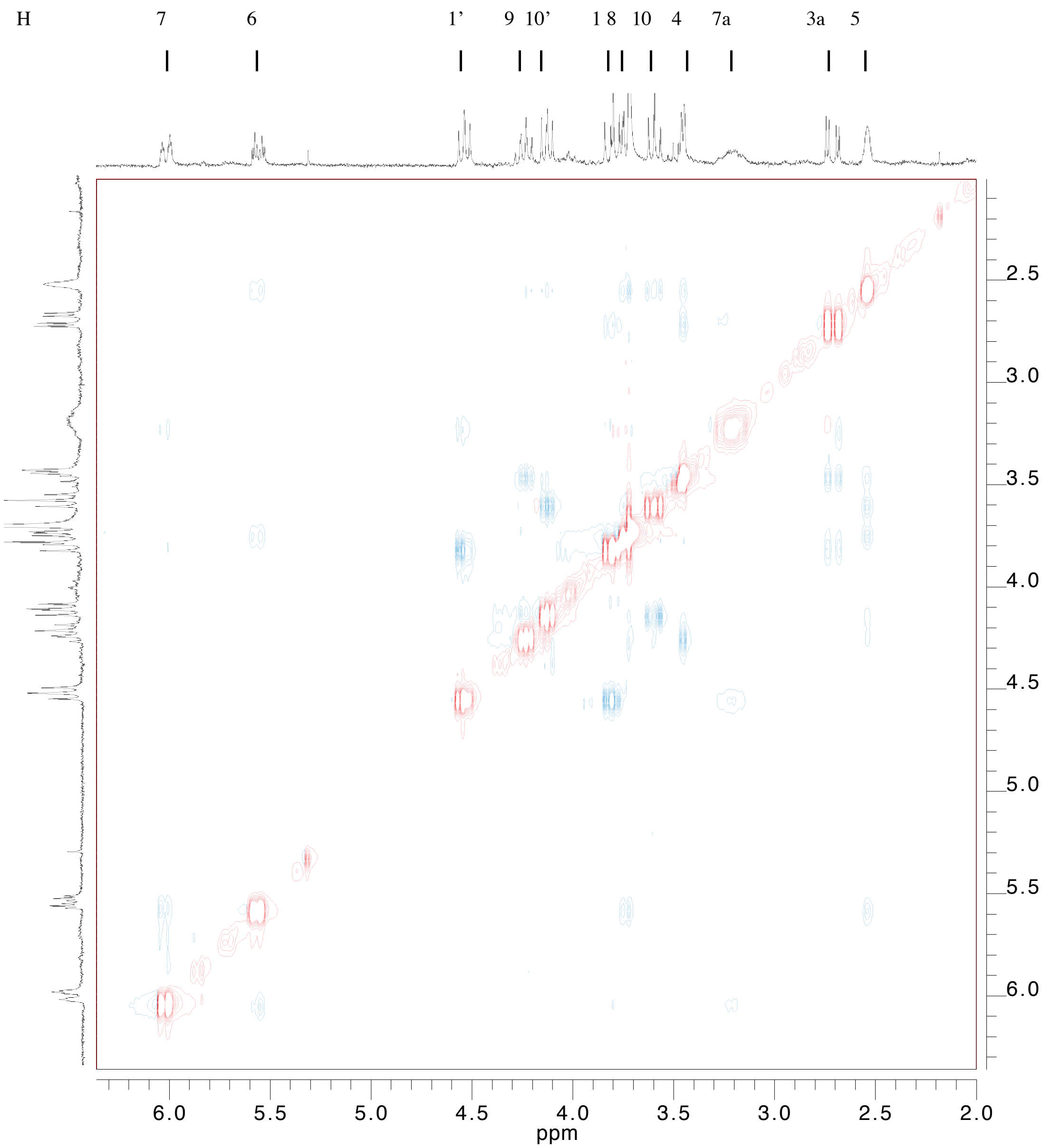

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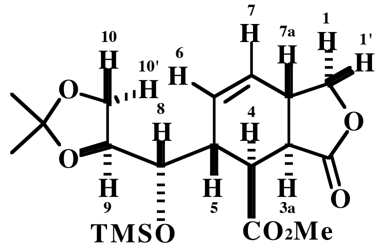

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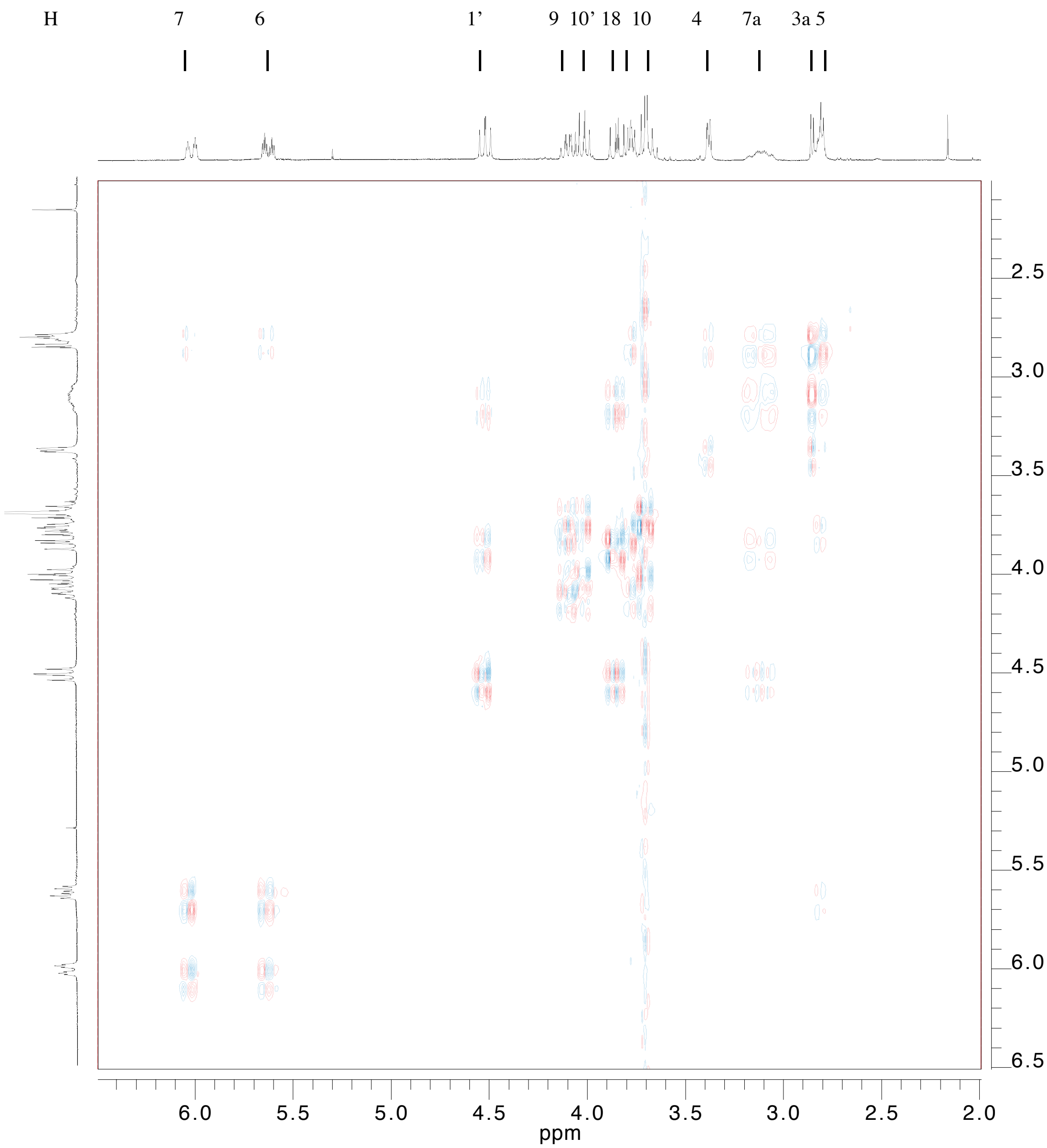

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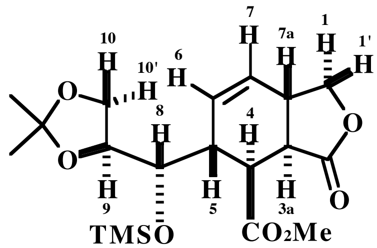

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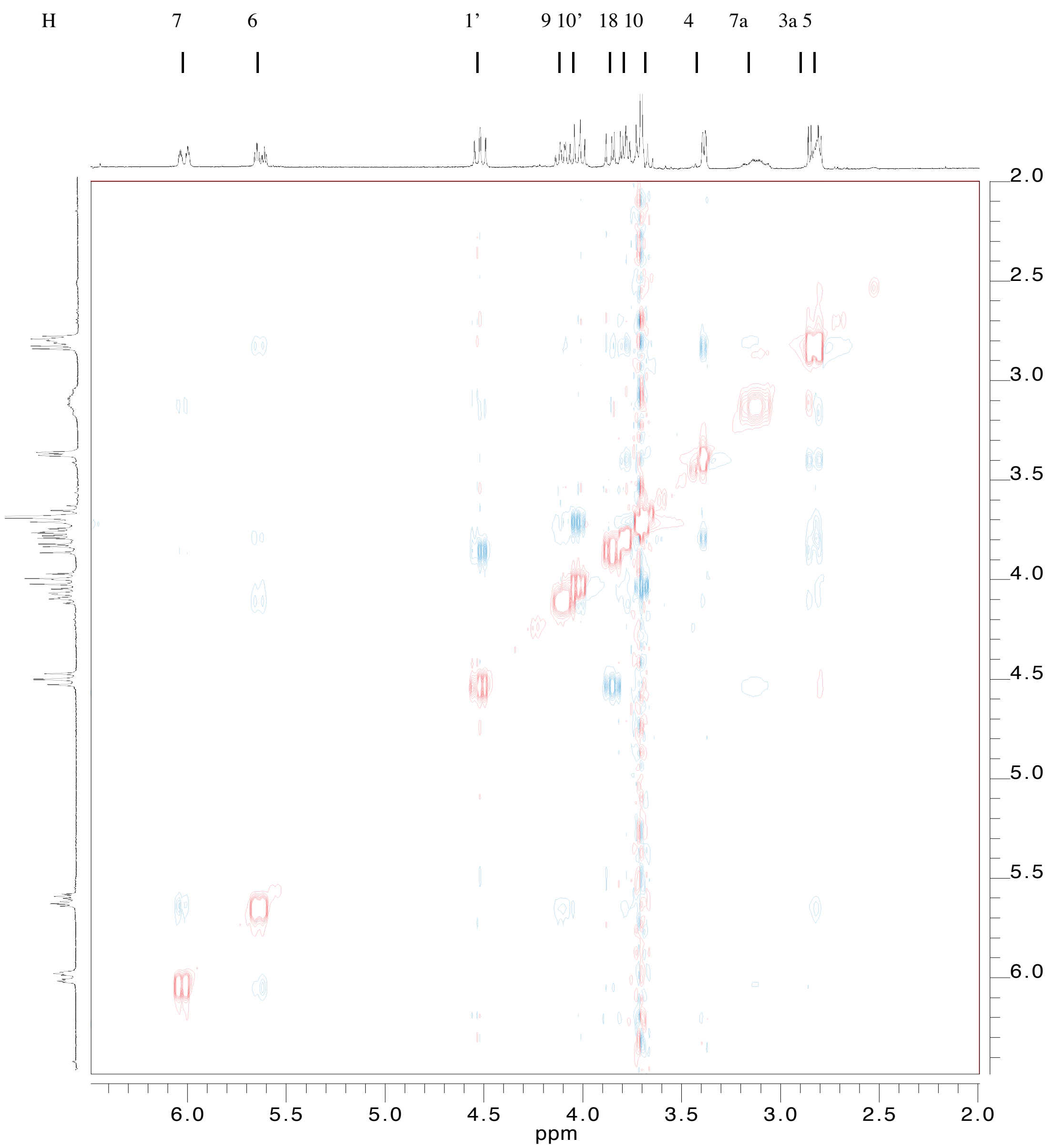

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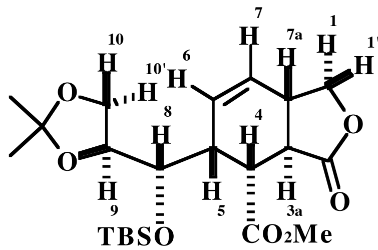

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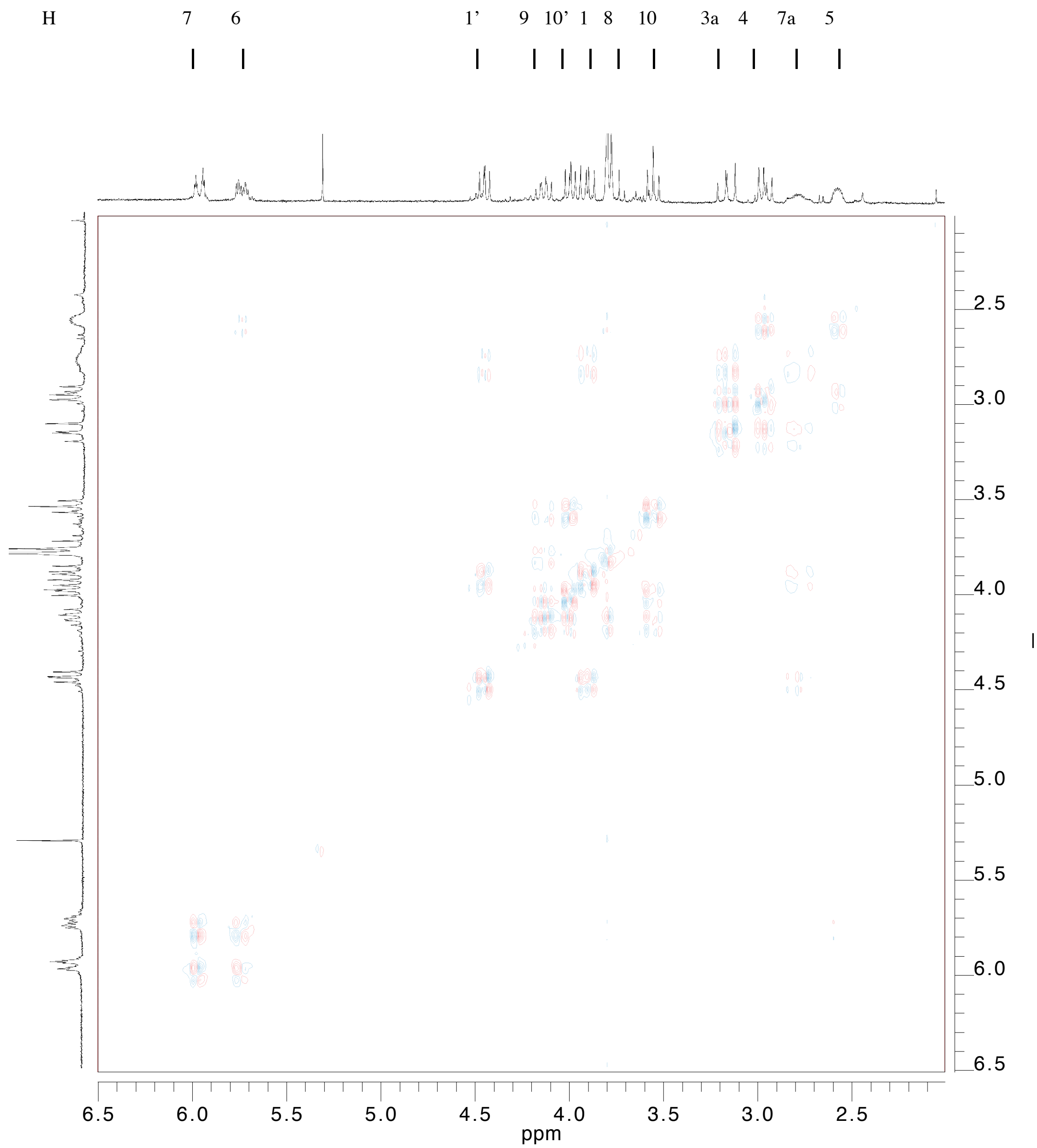

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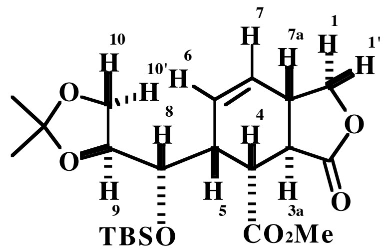

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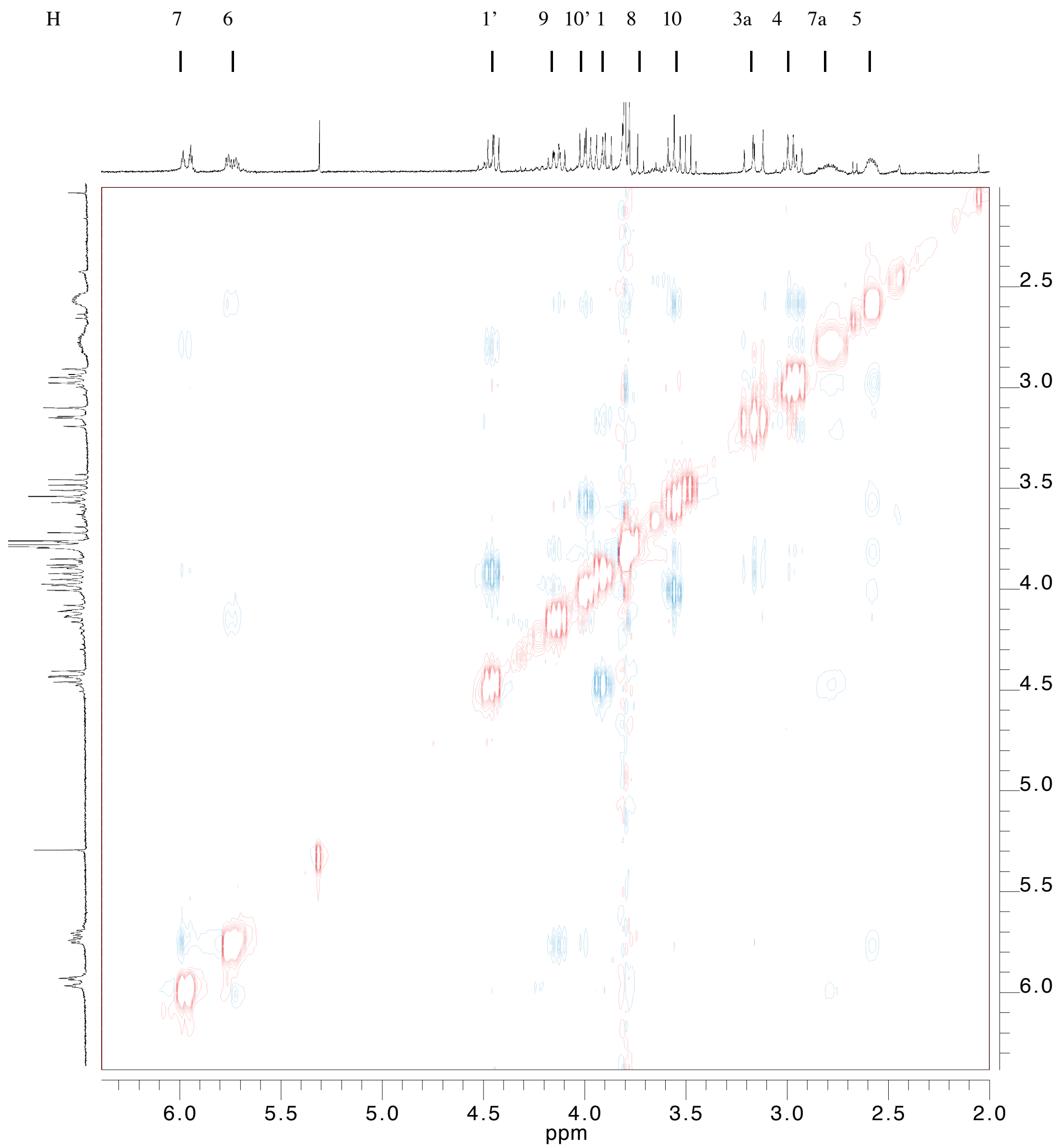
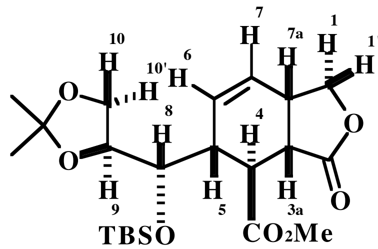
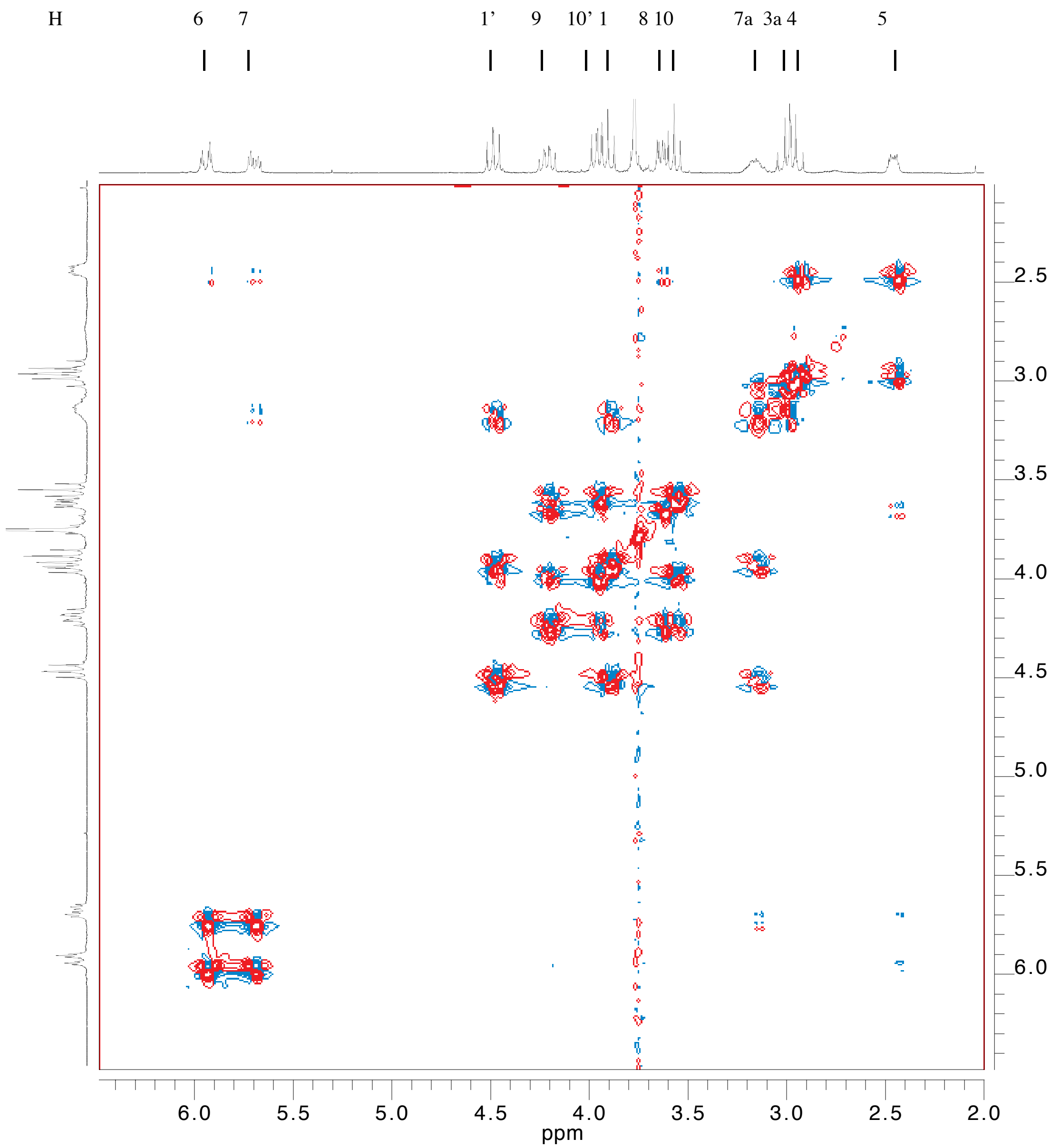


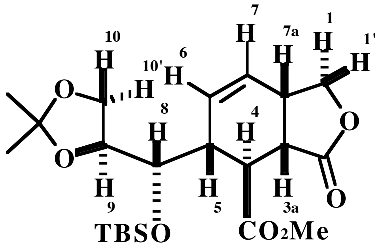
COSY spectrum of 22f



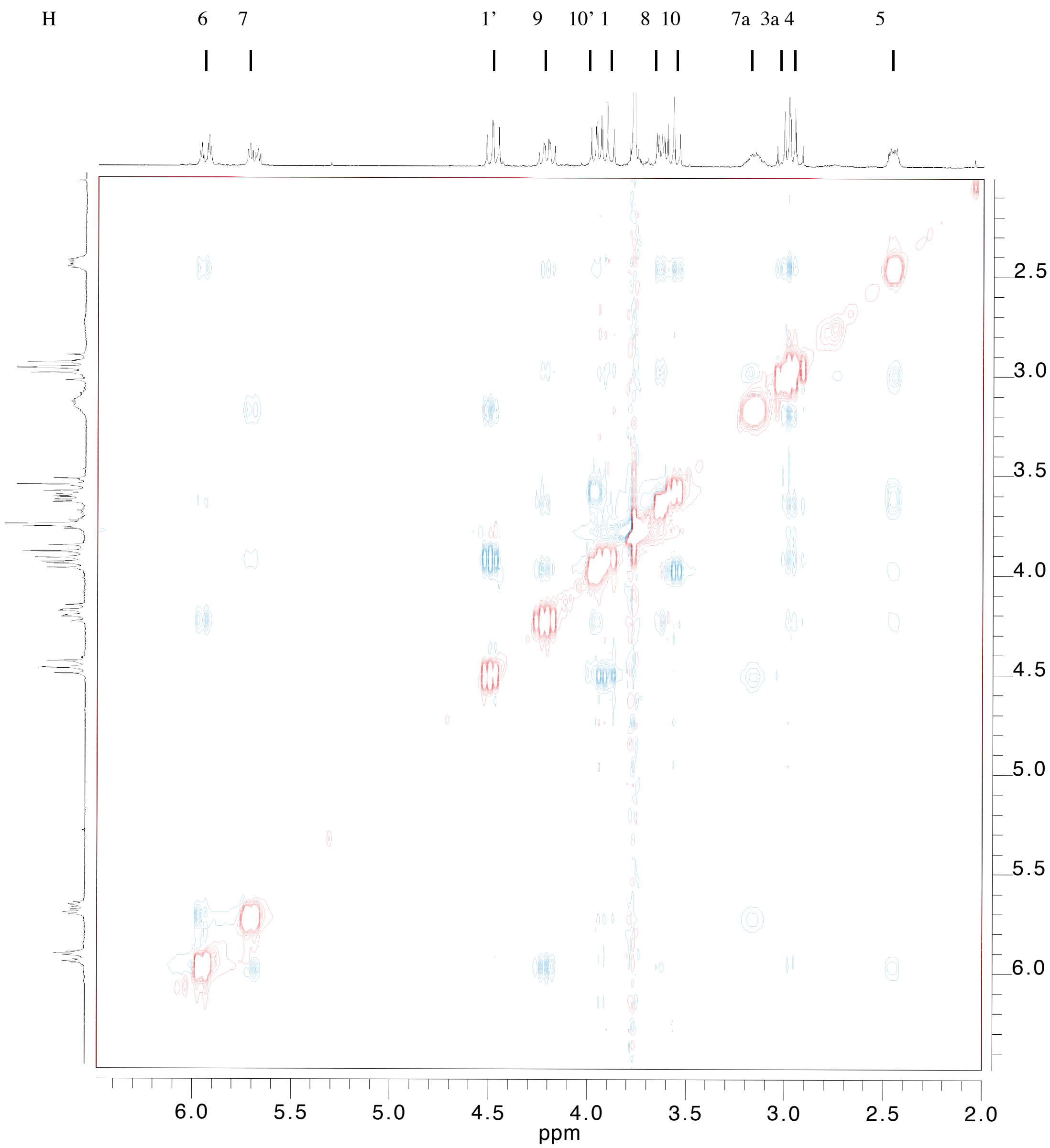
22f



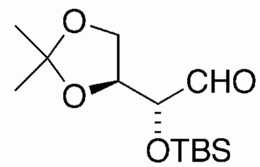
NOESY spectrum of 22f



22f



270 MHz ^{1}H NMR spectrum in $CDCl_3$



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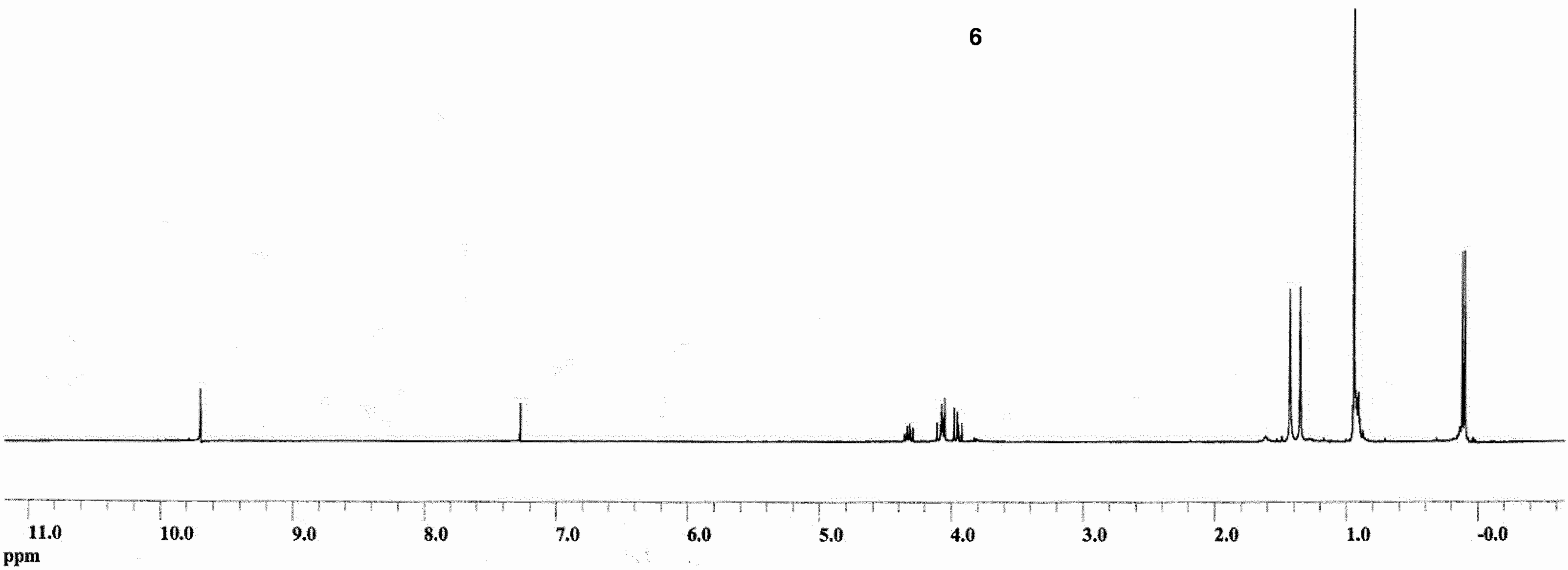
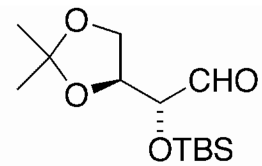


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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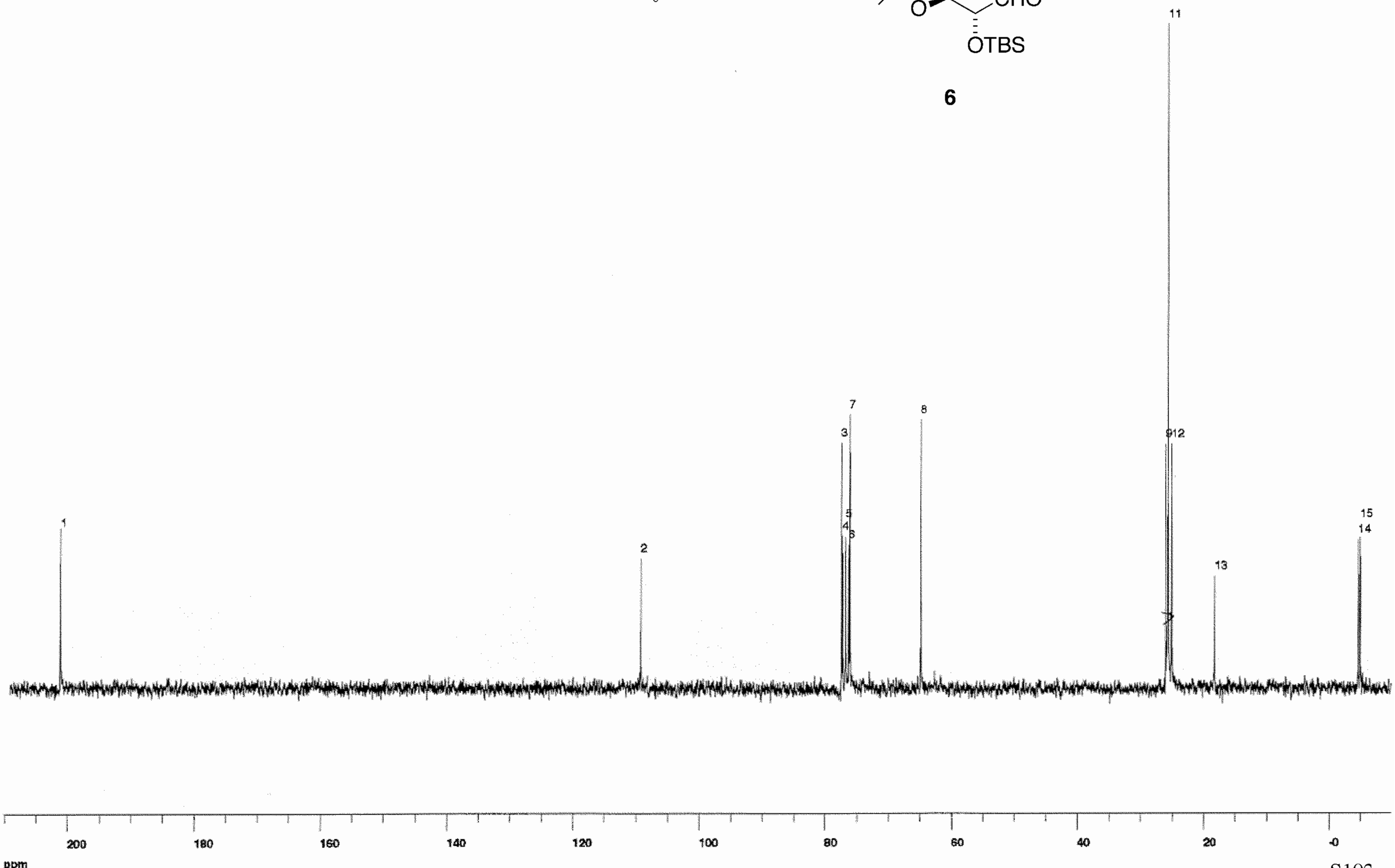
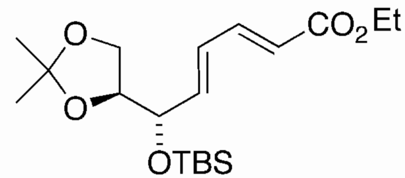
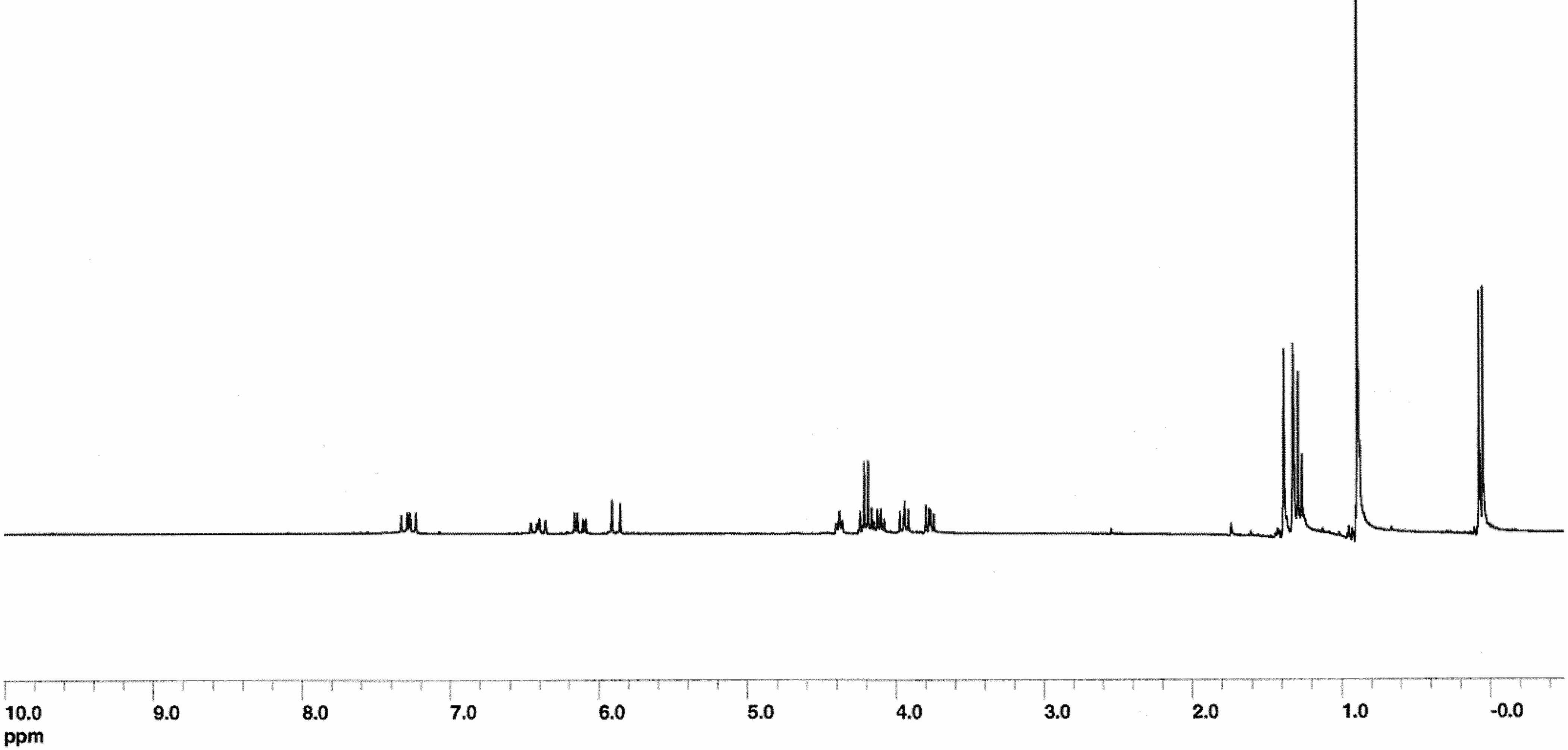
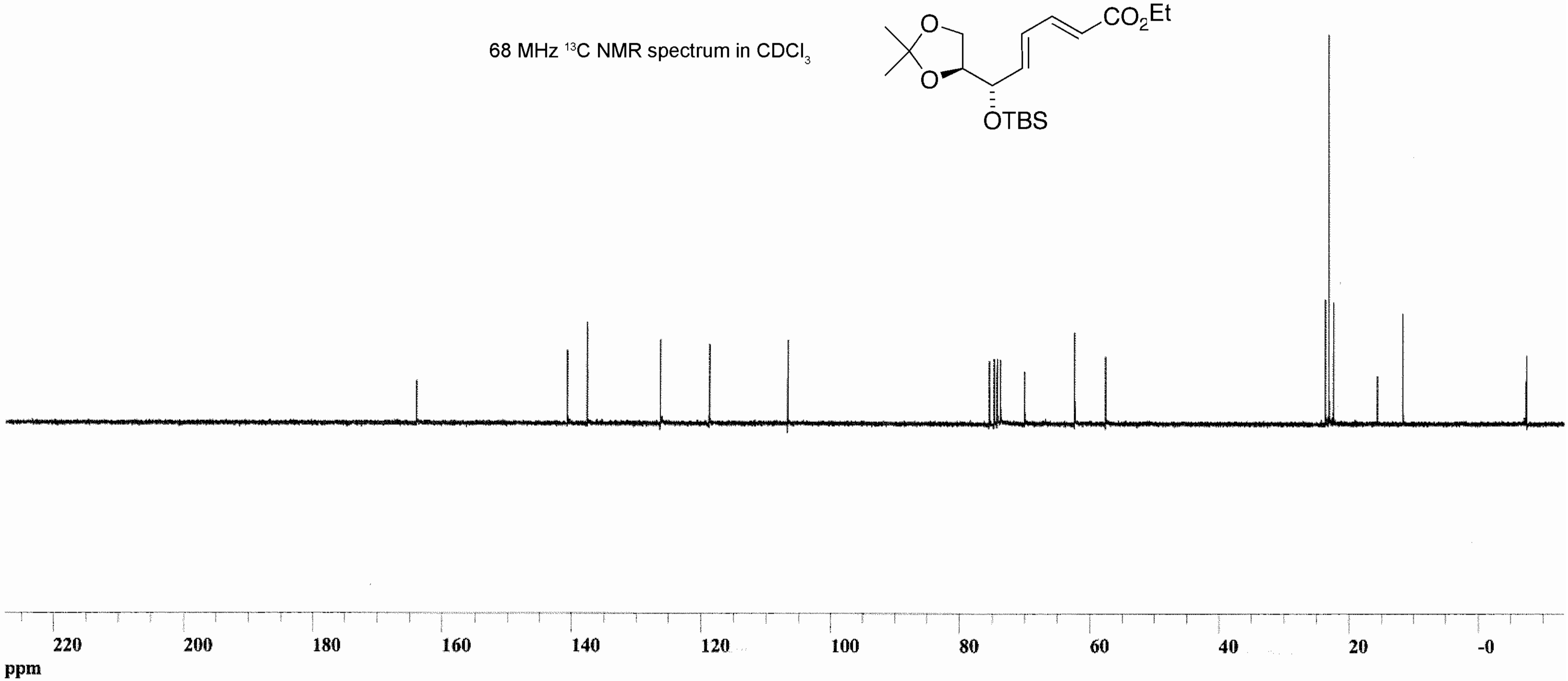


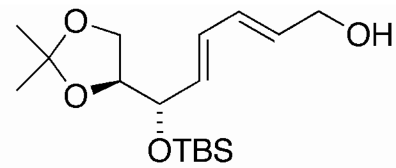
270 MHz ^{1}H NMR spectrum in $CDCl_3$






68 MHz ^{13}C NMR spectrum in $CDCl_3$
O
O
CO_2Et
OTBS
220
200
180
160
140
120
100
80
60
40
20
-0
ppm

270 MHz ^1H NMR spectrum in $CDCl_3$



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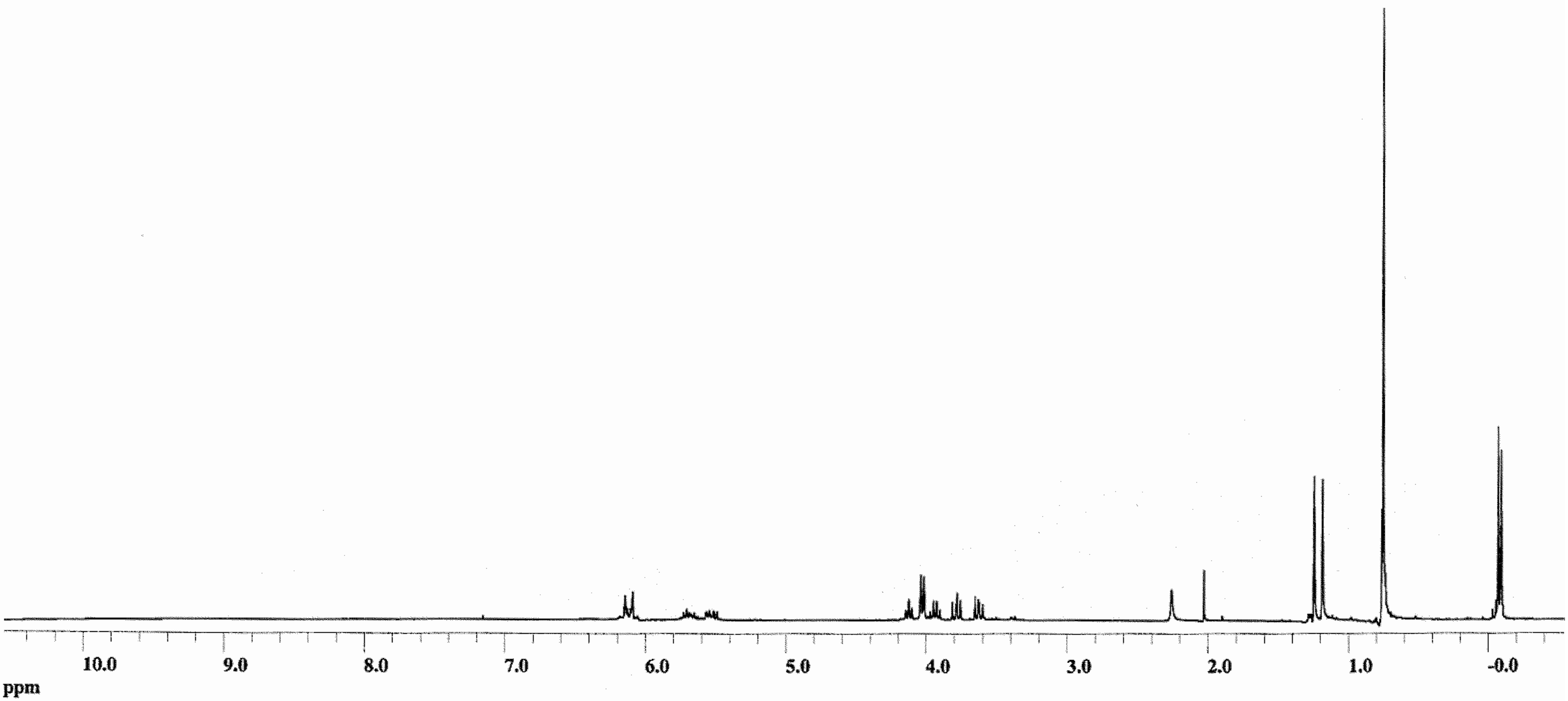
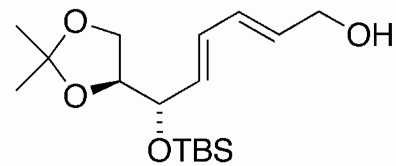


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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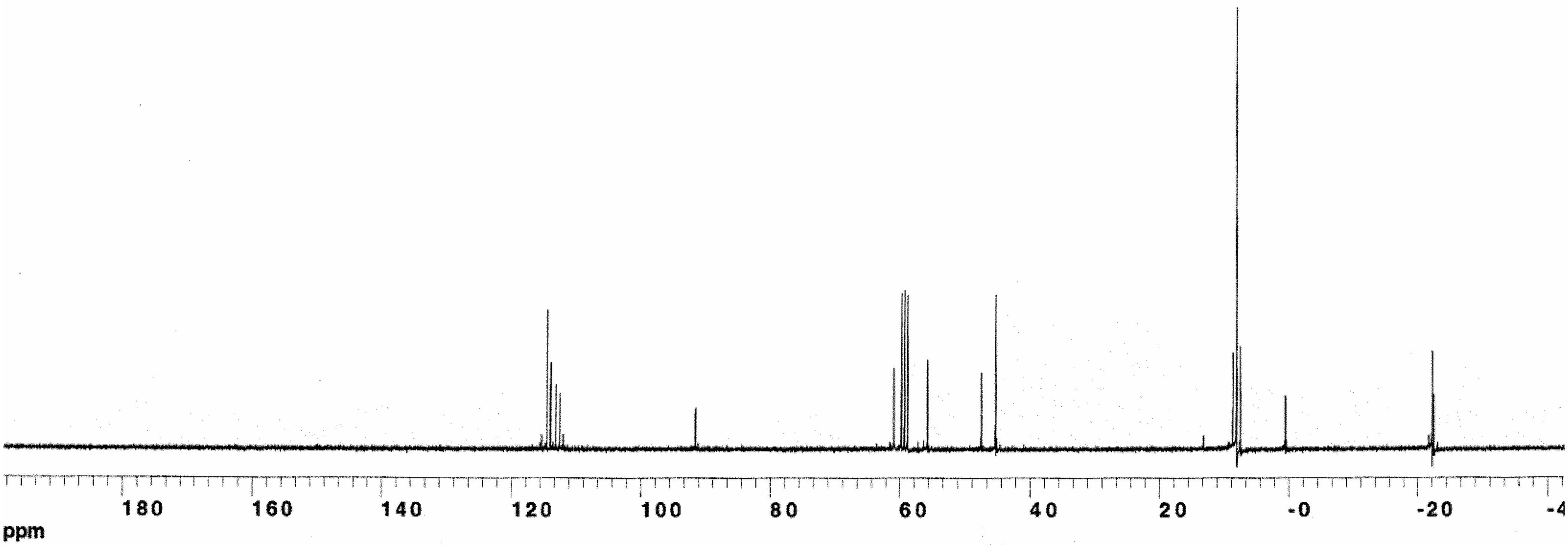
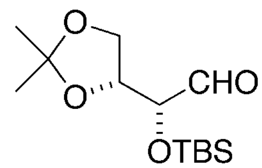


300 MHz ^{1}H NMR spectrum in $CDCl_3$



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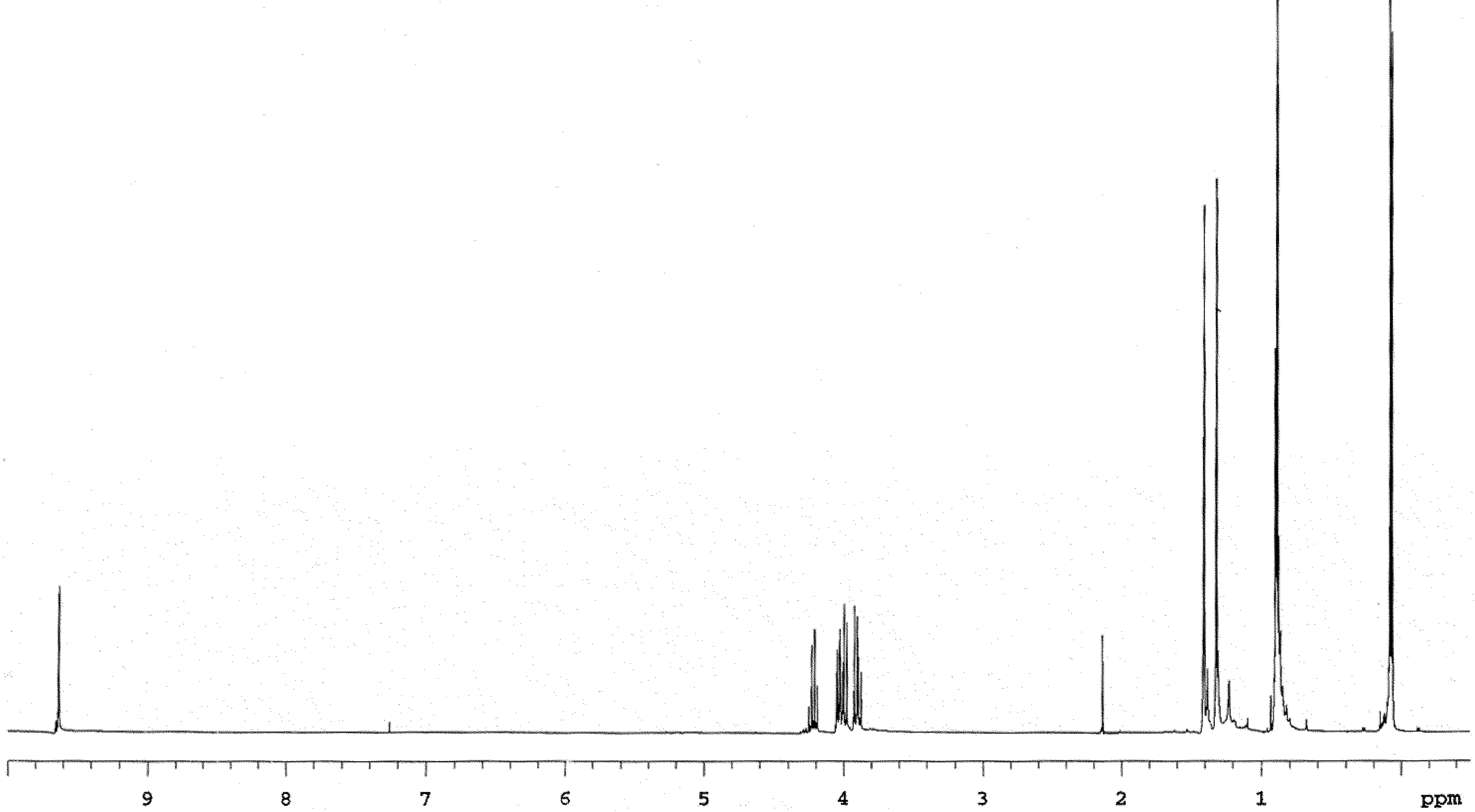
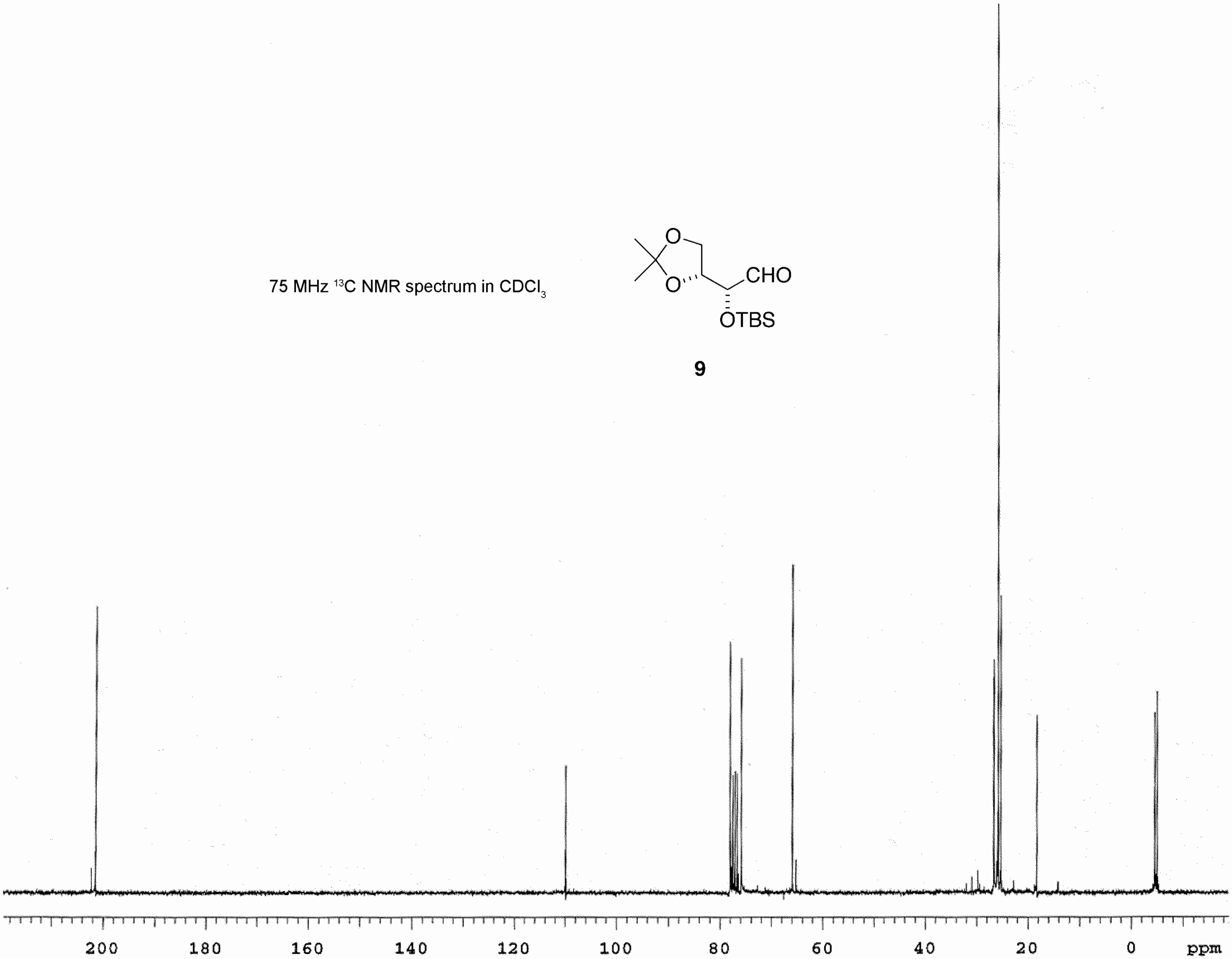
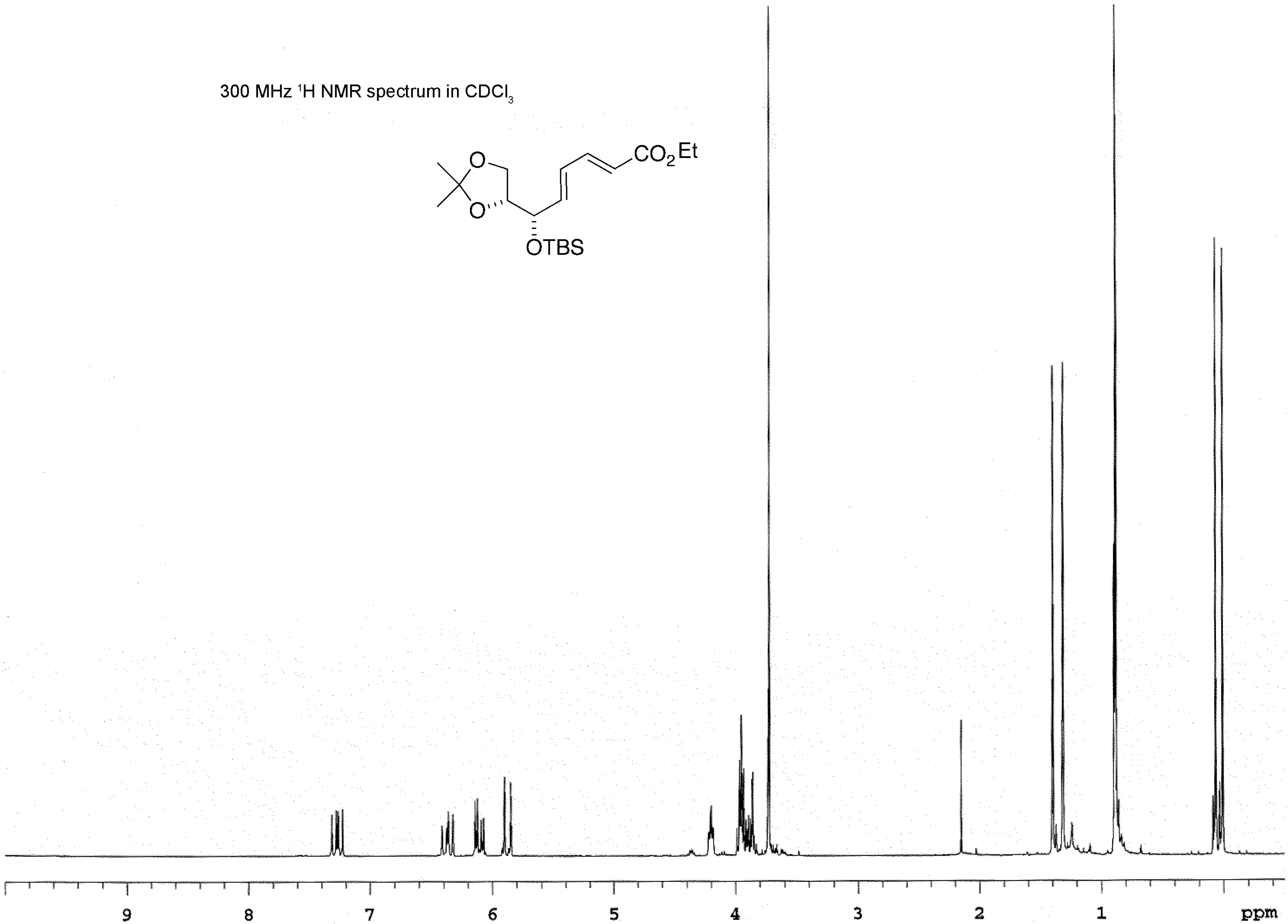


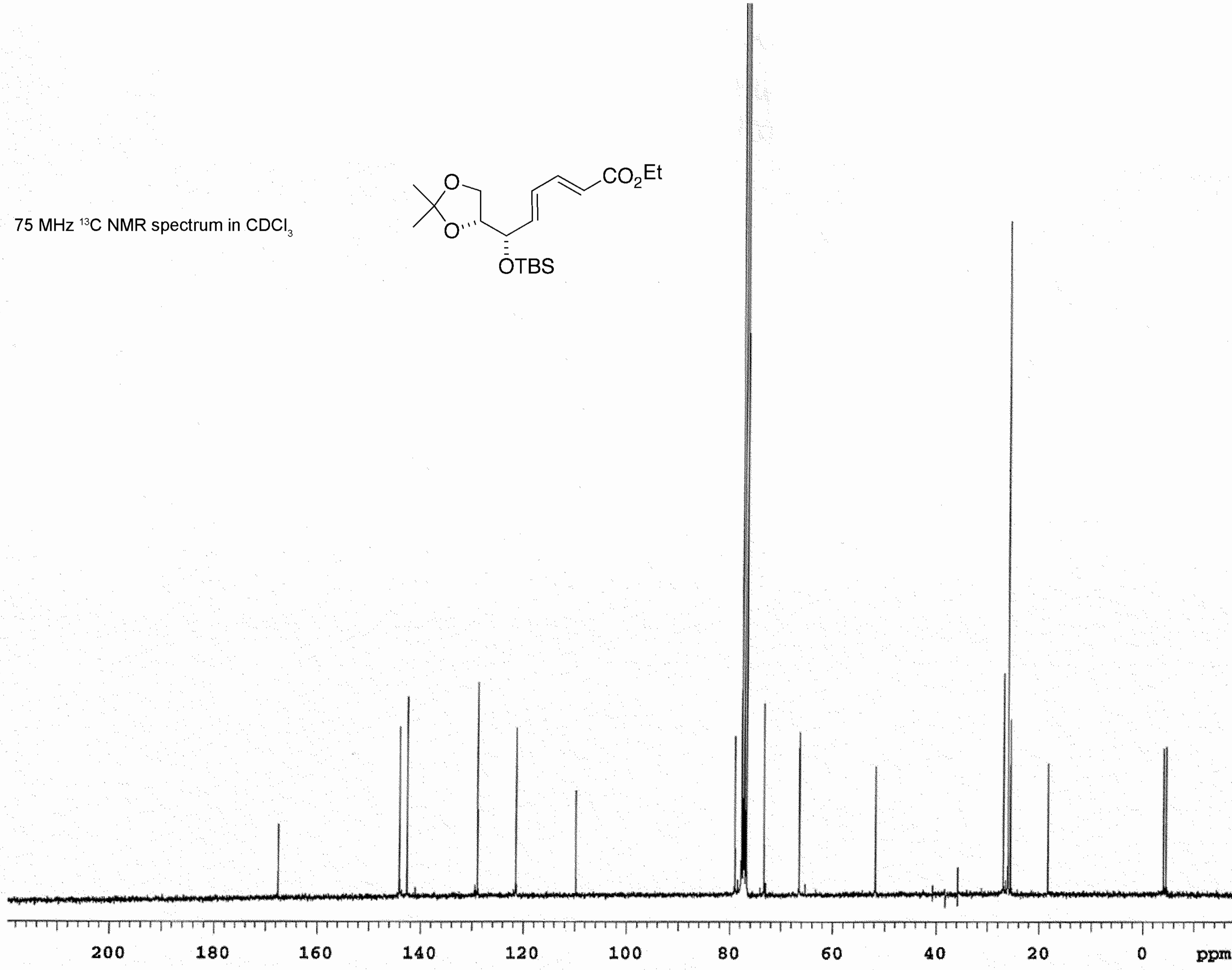
75 MHz ^{13}C NMR spectrum in $CDCl_3$



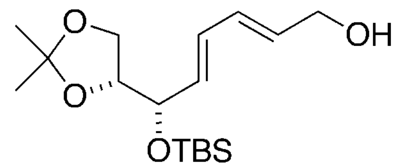
300 MHz ^{1}H NMR spectrum in $CDCl_3$



75 MHz ^{13}C NMR spectrum in $CDCl_3$



300 MHz ^{1}H NMR spectrum in $CDCl_3$



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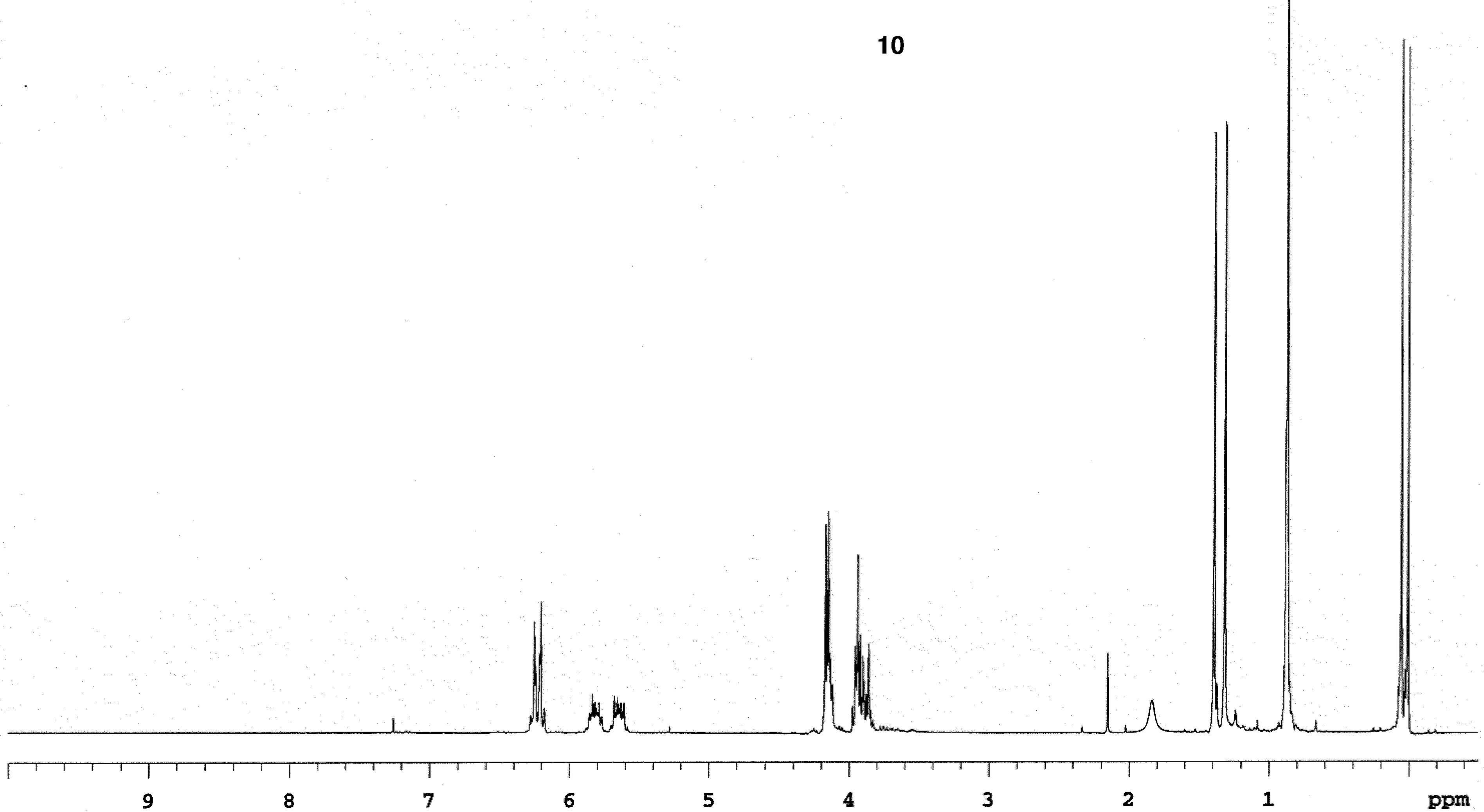
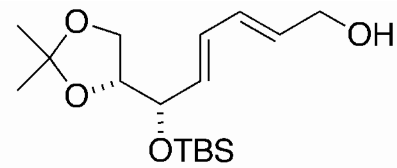


75 MHz ^{13}C NMR spectrum in $CDCl_3$



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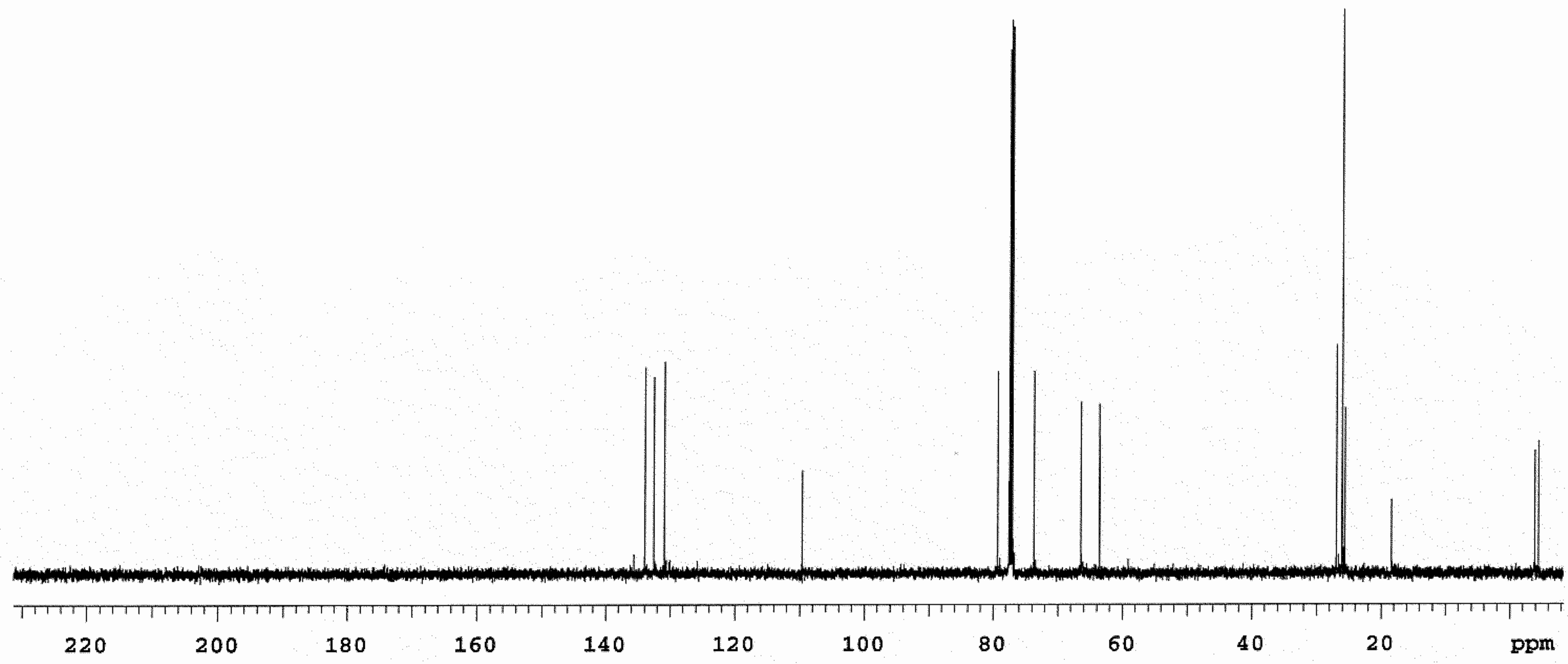
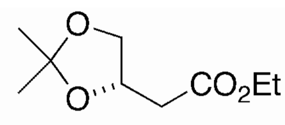


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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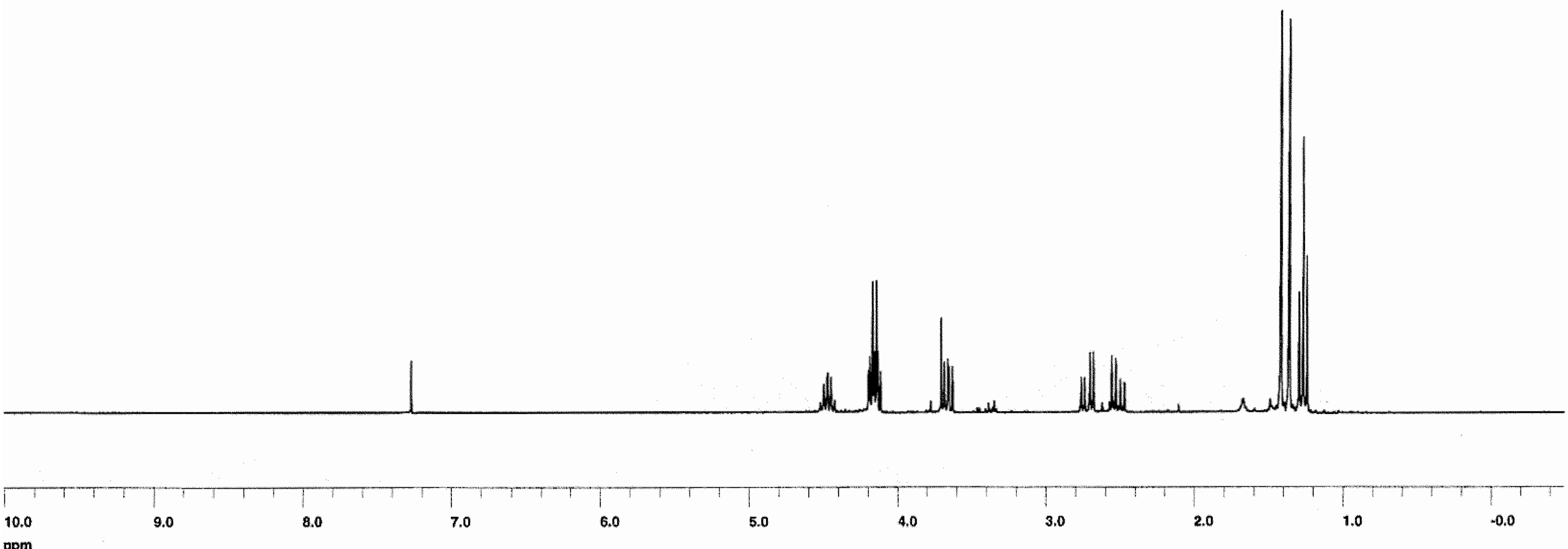
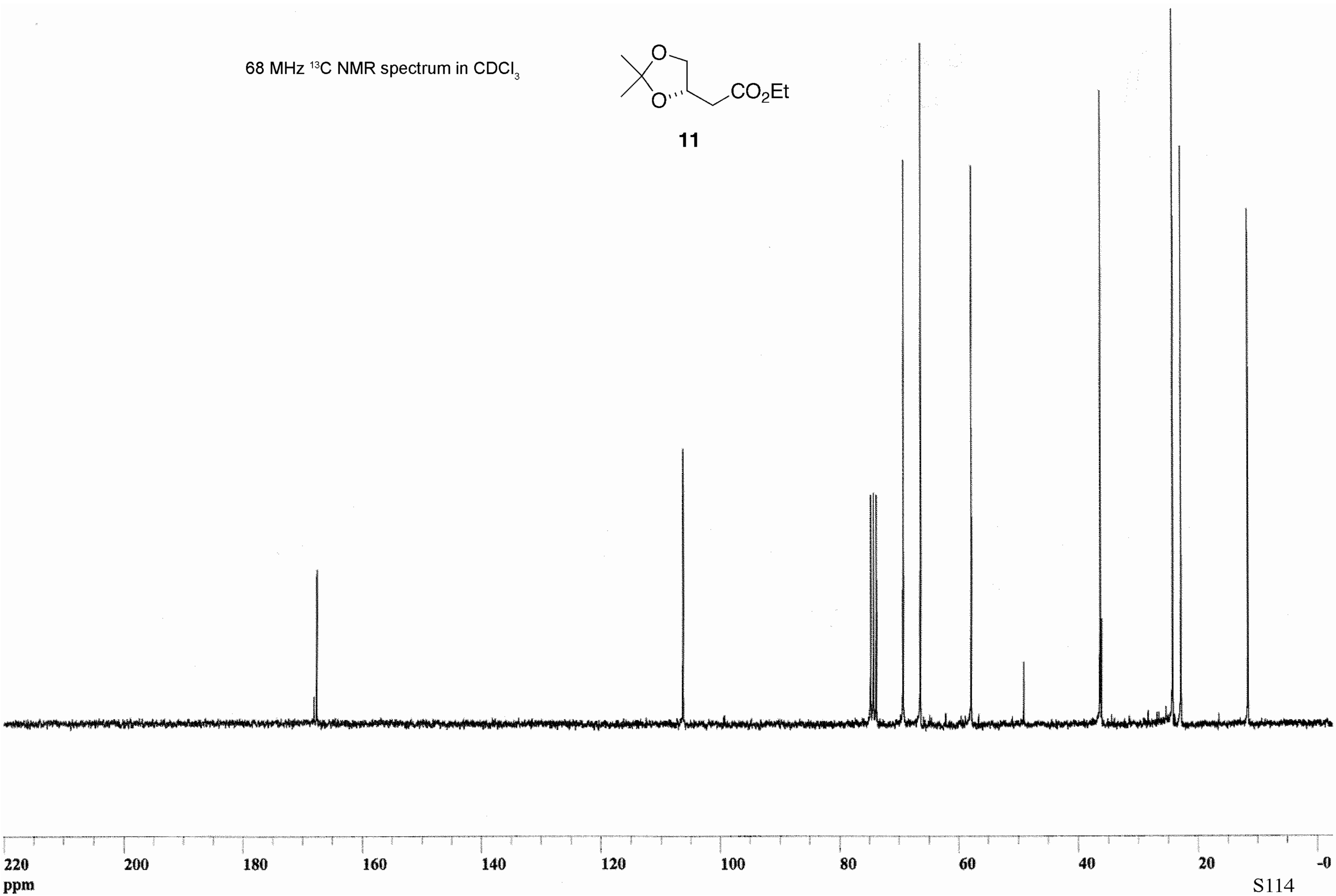
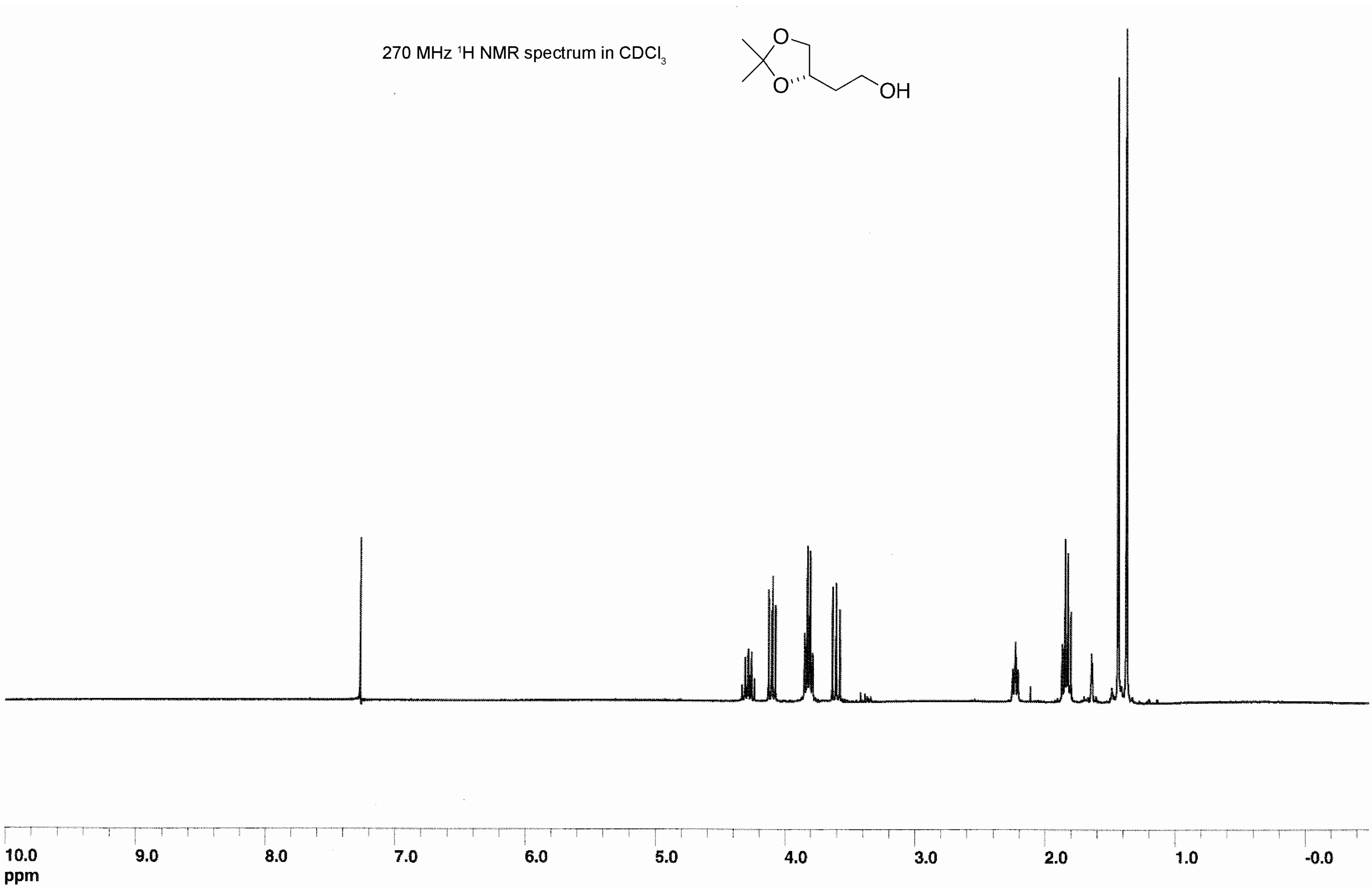
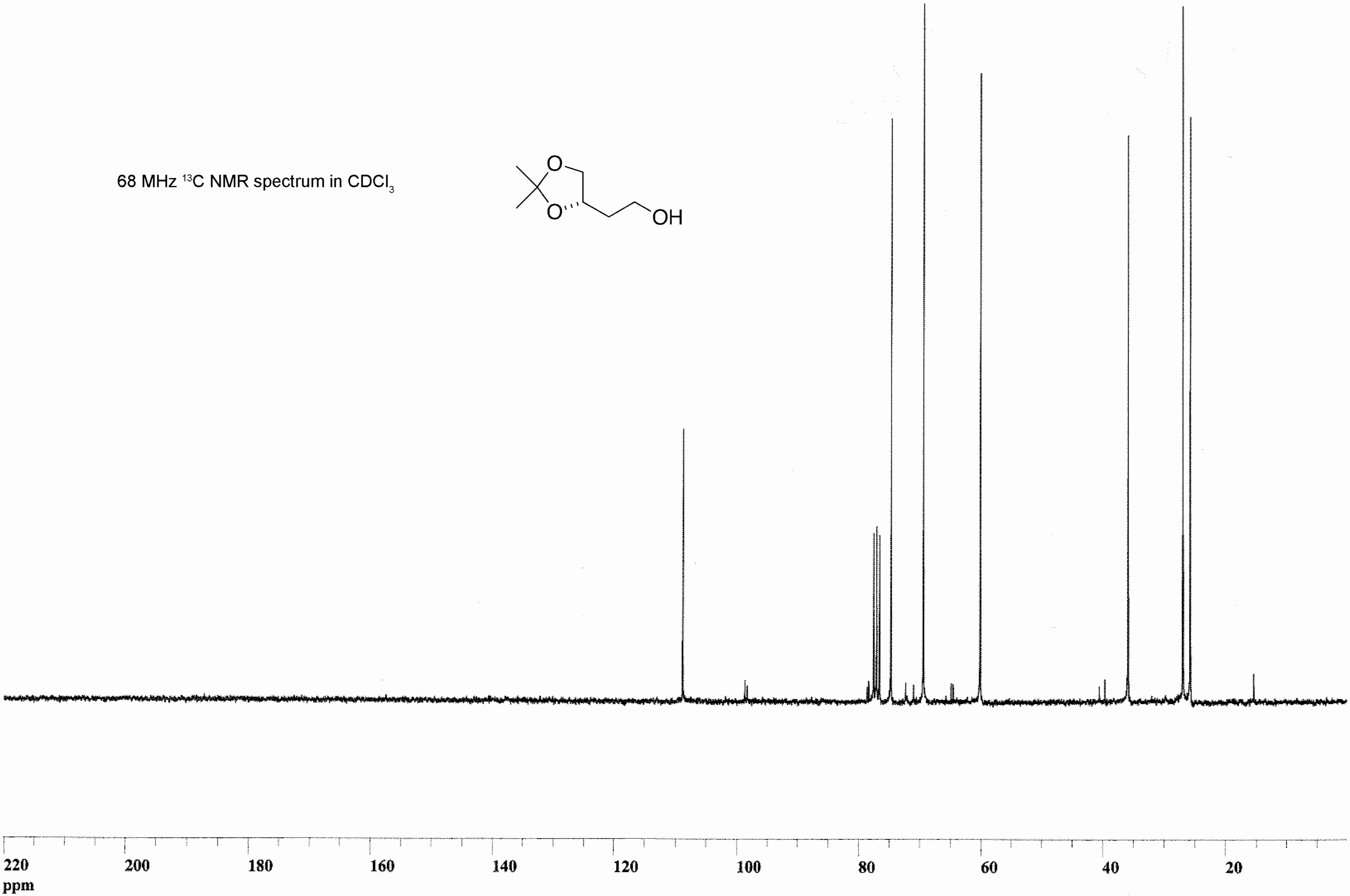


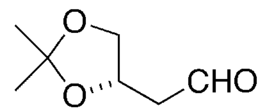

68 MHz ¹³C NMR spectrum in $CDCl_3$
O
O
CO_2Et
11
220
200
180
160
140
120
100
80
60
40
20
-0
ppm


270 MHz ¹H NMR spectrum in CDCl₃
OH
O
O
10.0
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
-0.0

68 MHz ^{13}C NMR spectrum in $CDCl_3$



270 MHz [1]H NMR spectrum in $CDCl_3$



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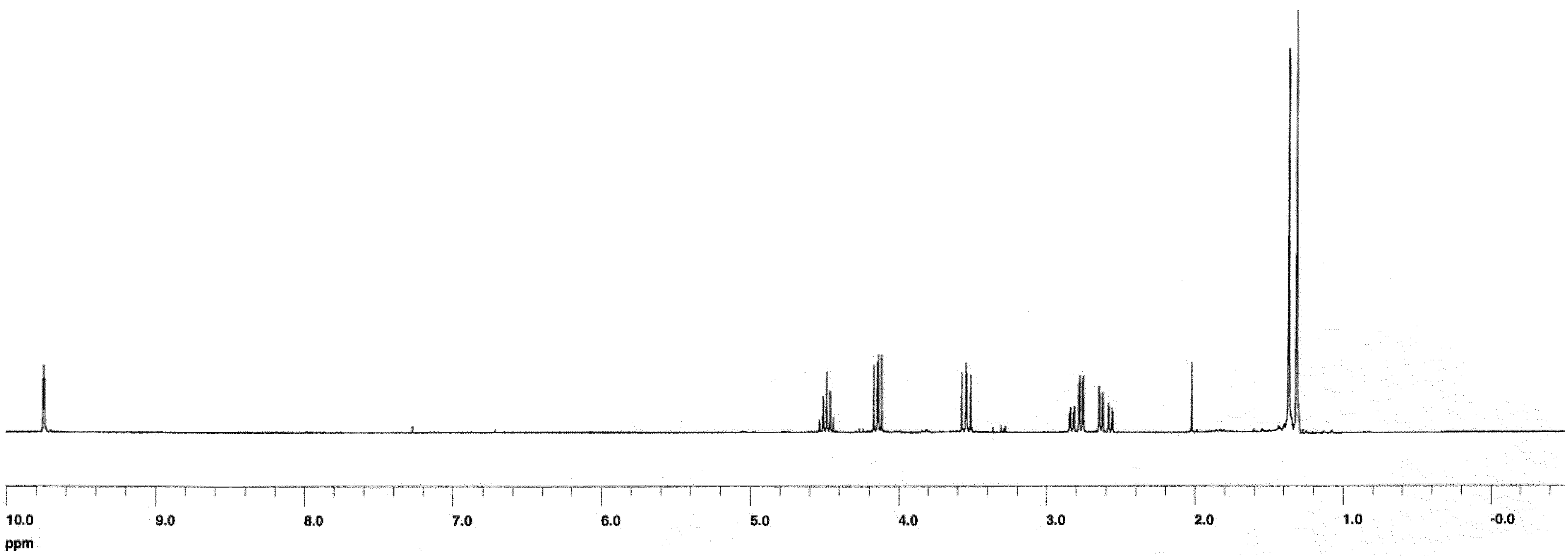
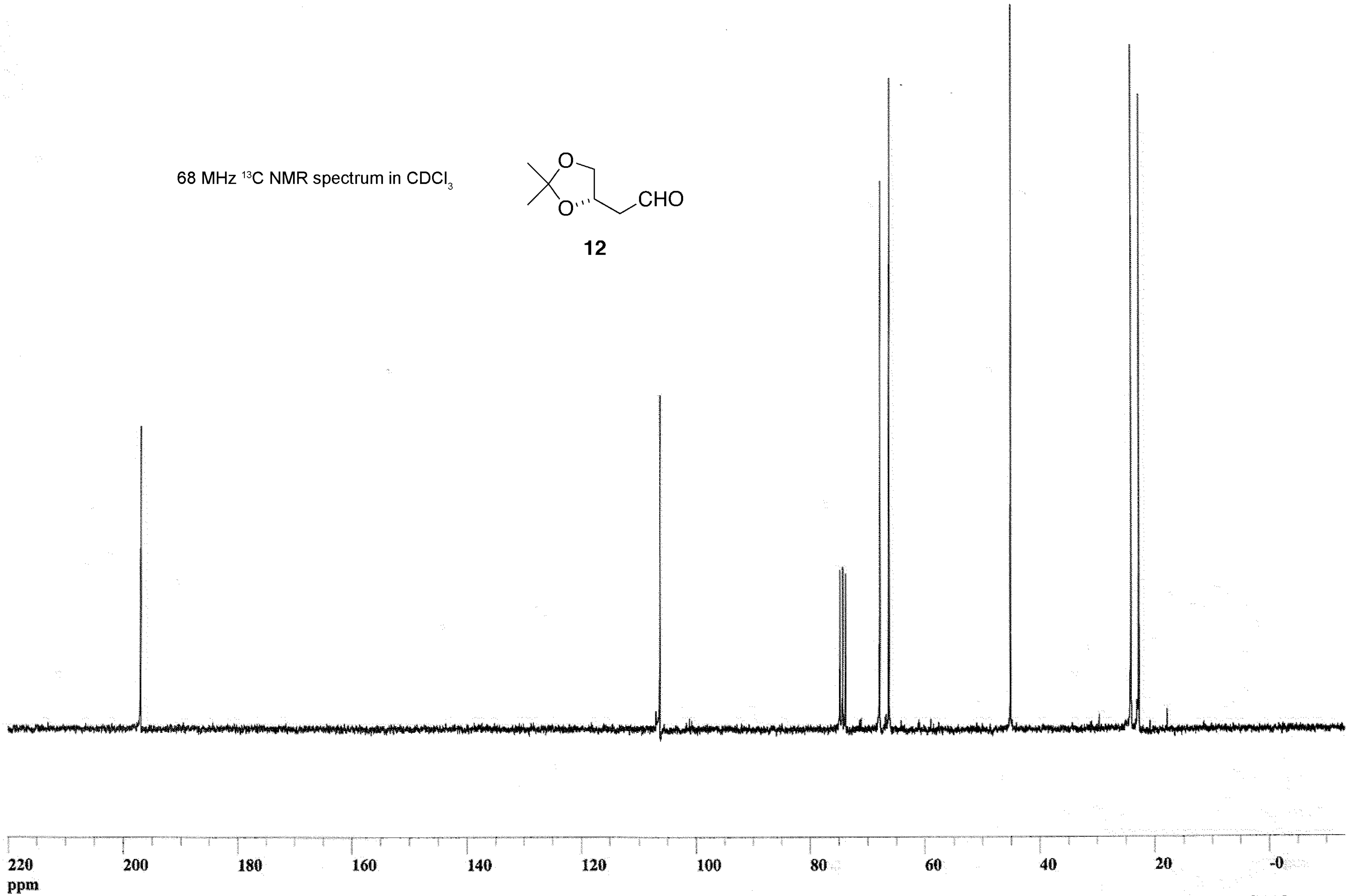


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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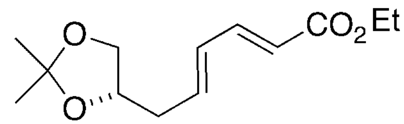
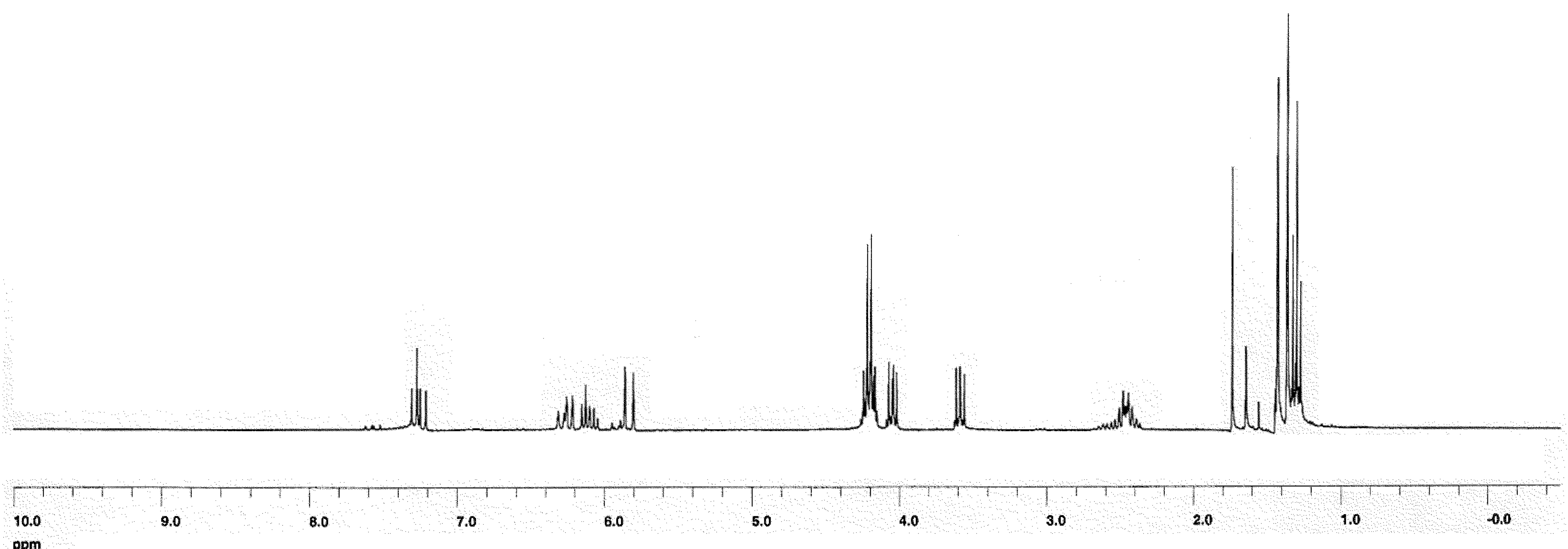
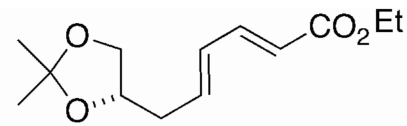
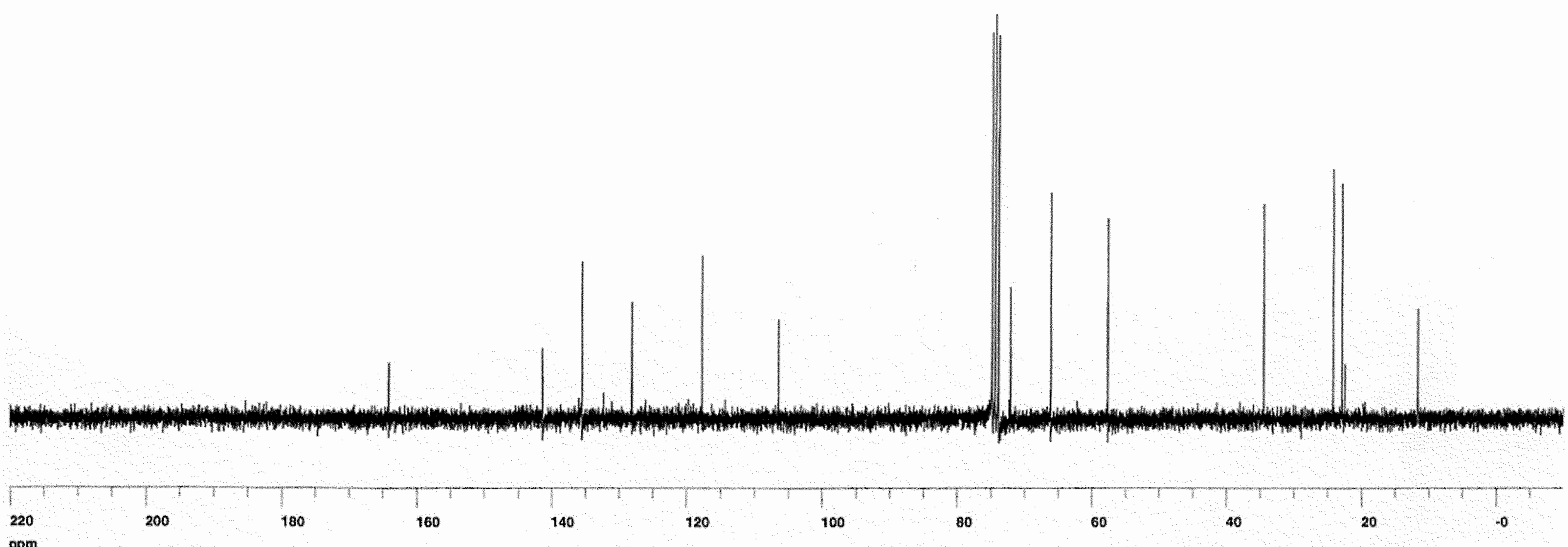
270 MHz ¹H NMR spectrum in $CDCl_3$



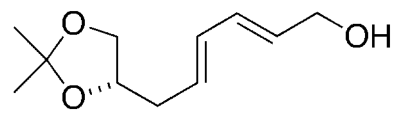


68 MHz ^{13}C NMR spectrum in $CDCl_3$





270 MHz ^{1}H NMR spectrum in $CDCl_3$



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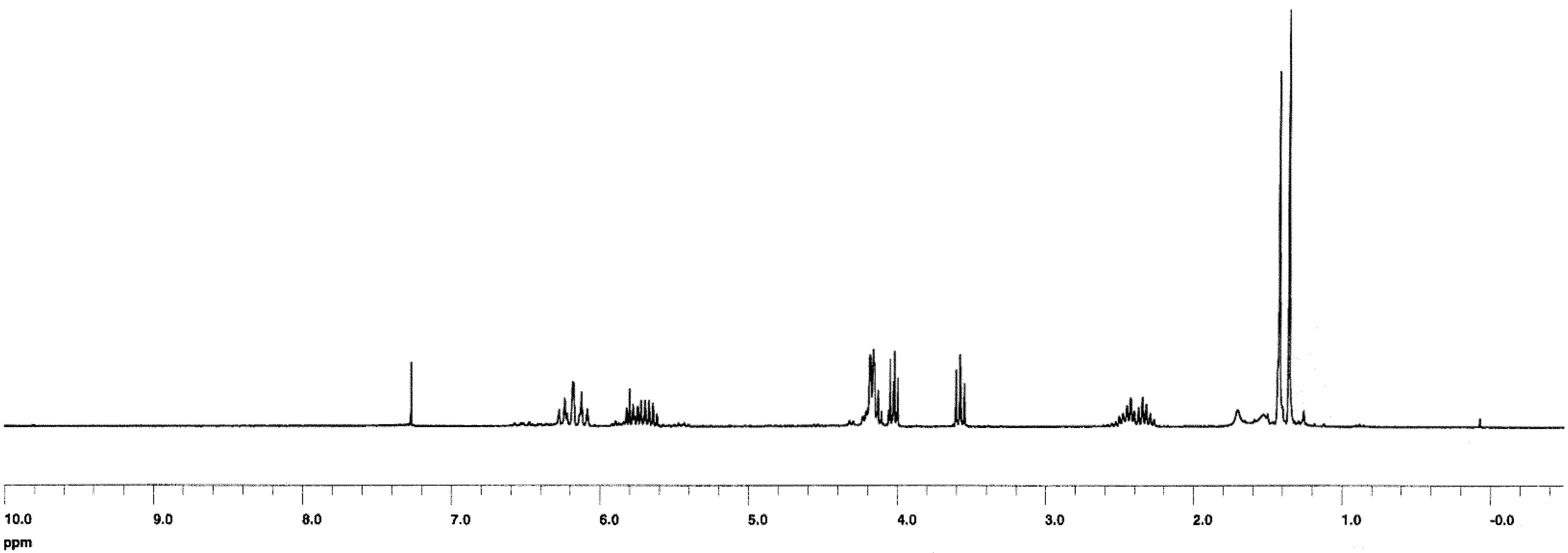
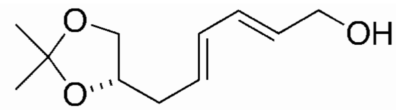


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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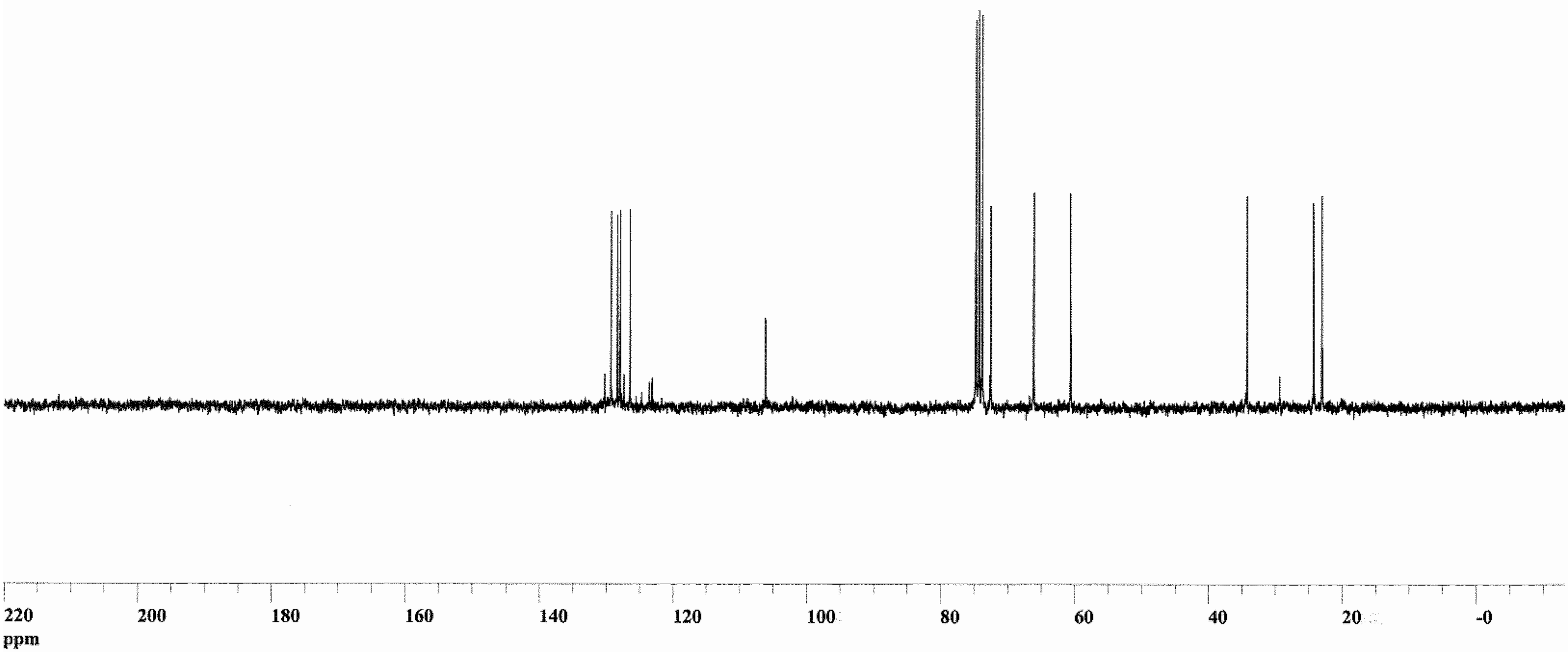
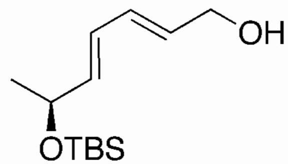


400 MHz ^{1}H NMR spectrum in $CDCl_3$



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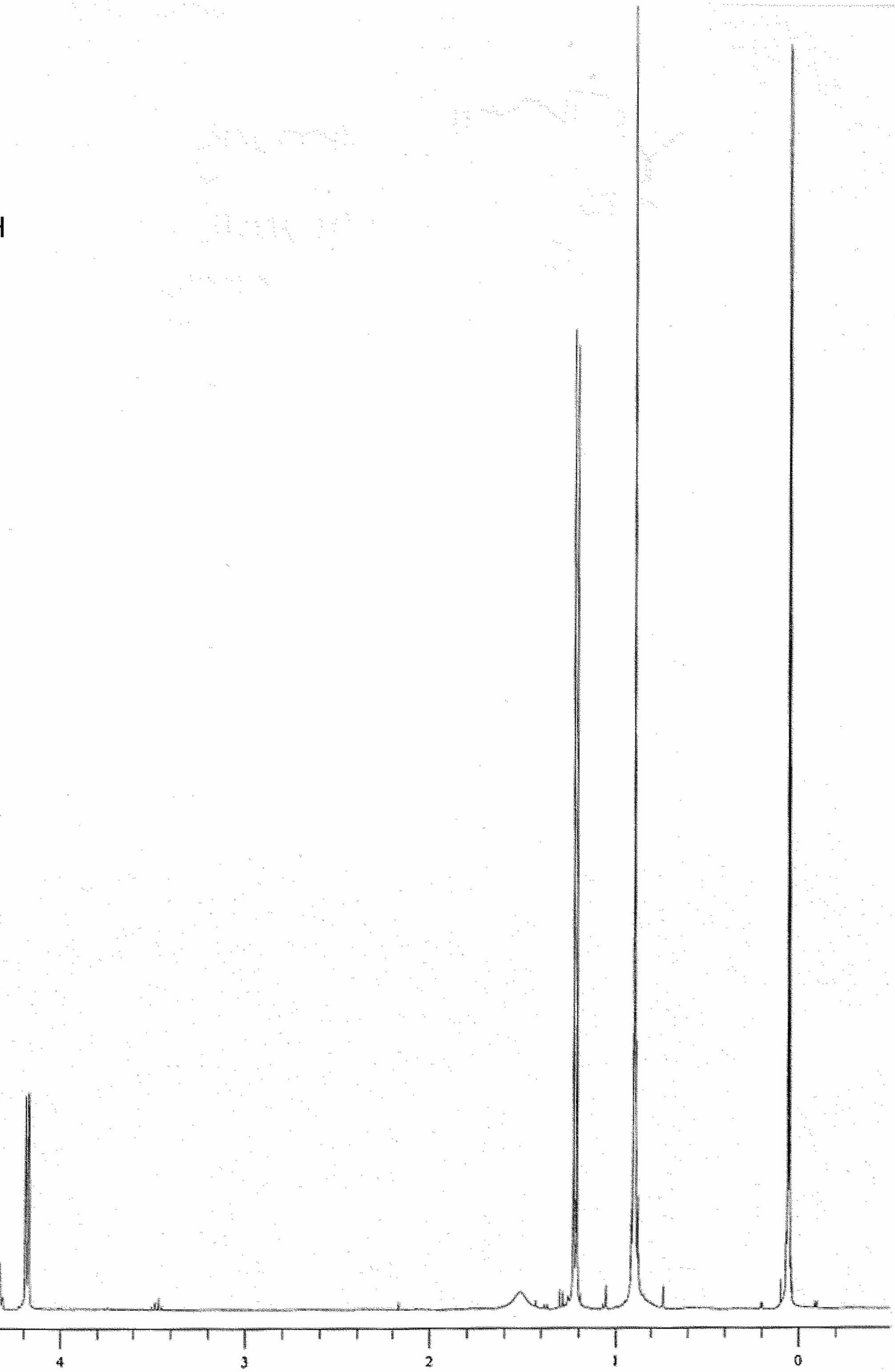
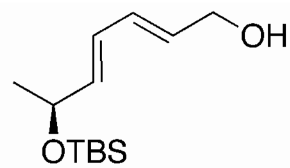


75 MHz ^{13}C NMR spectrum in $CDCl_3$



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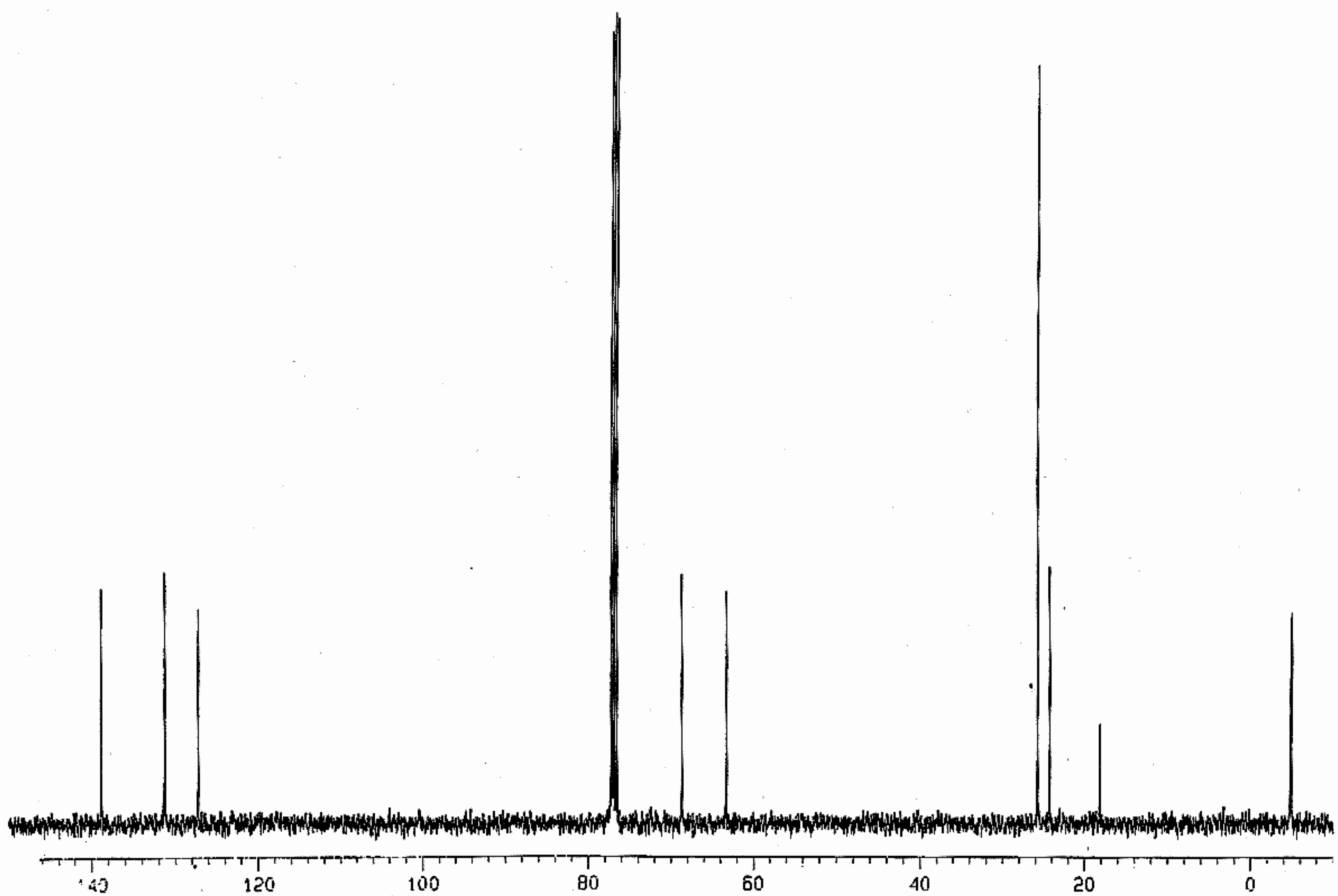
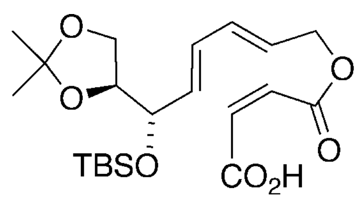


270 MHz ^1H NMR spectrum in $CDCl_3$



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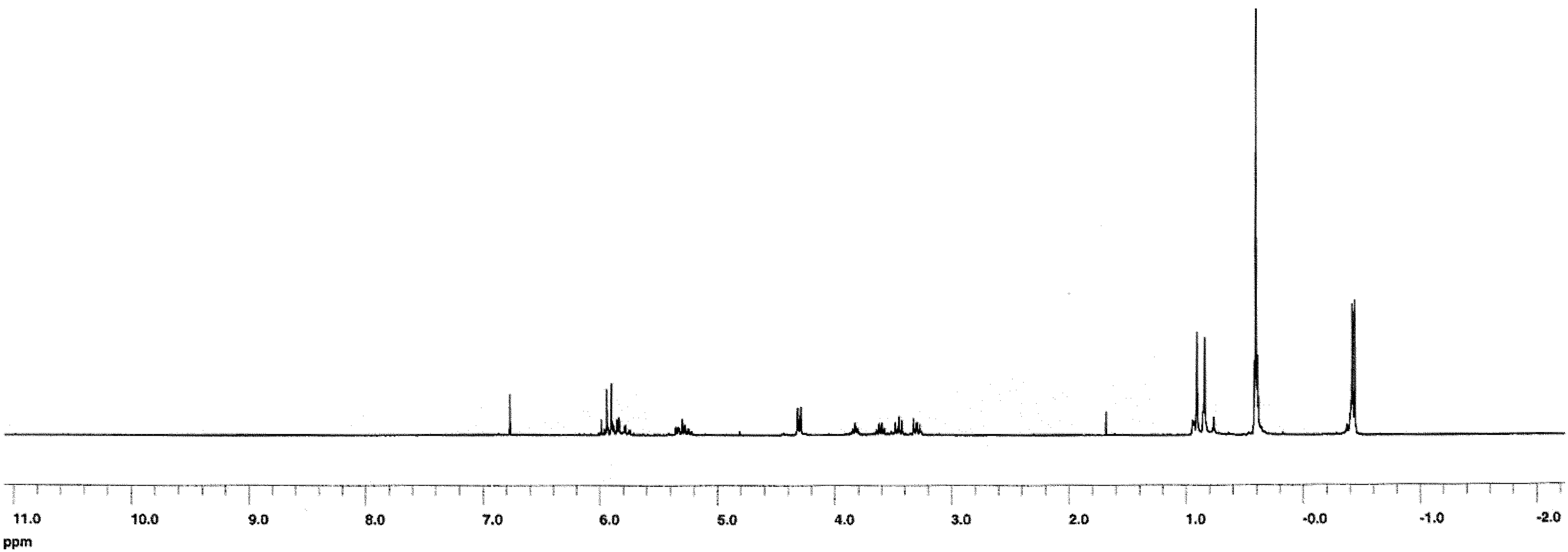
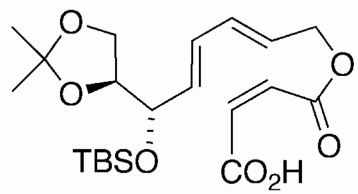


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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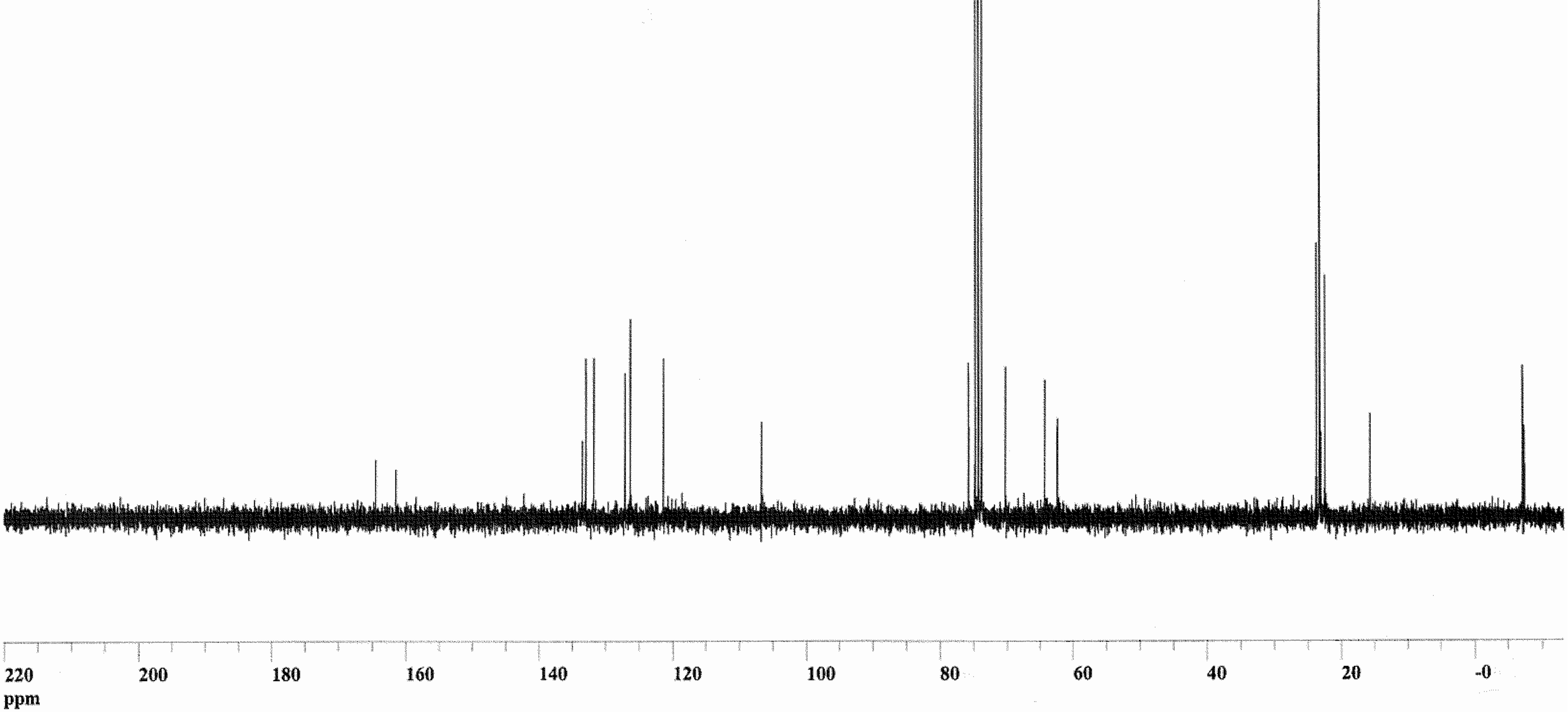
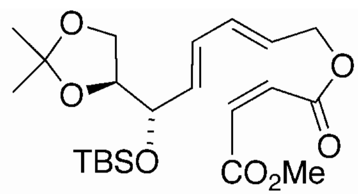


270 MHz ^1H NMR spectrum in $CDCl_3$



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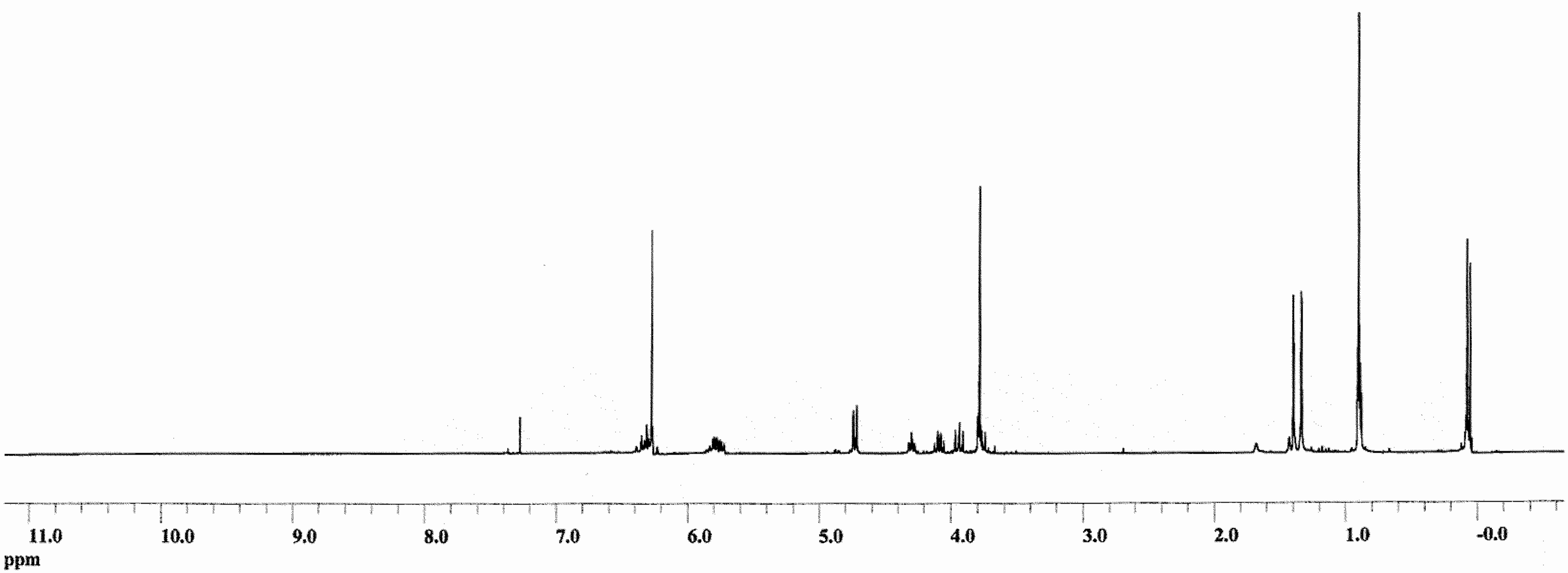
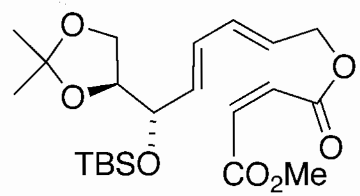


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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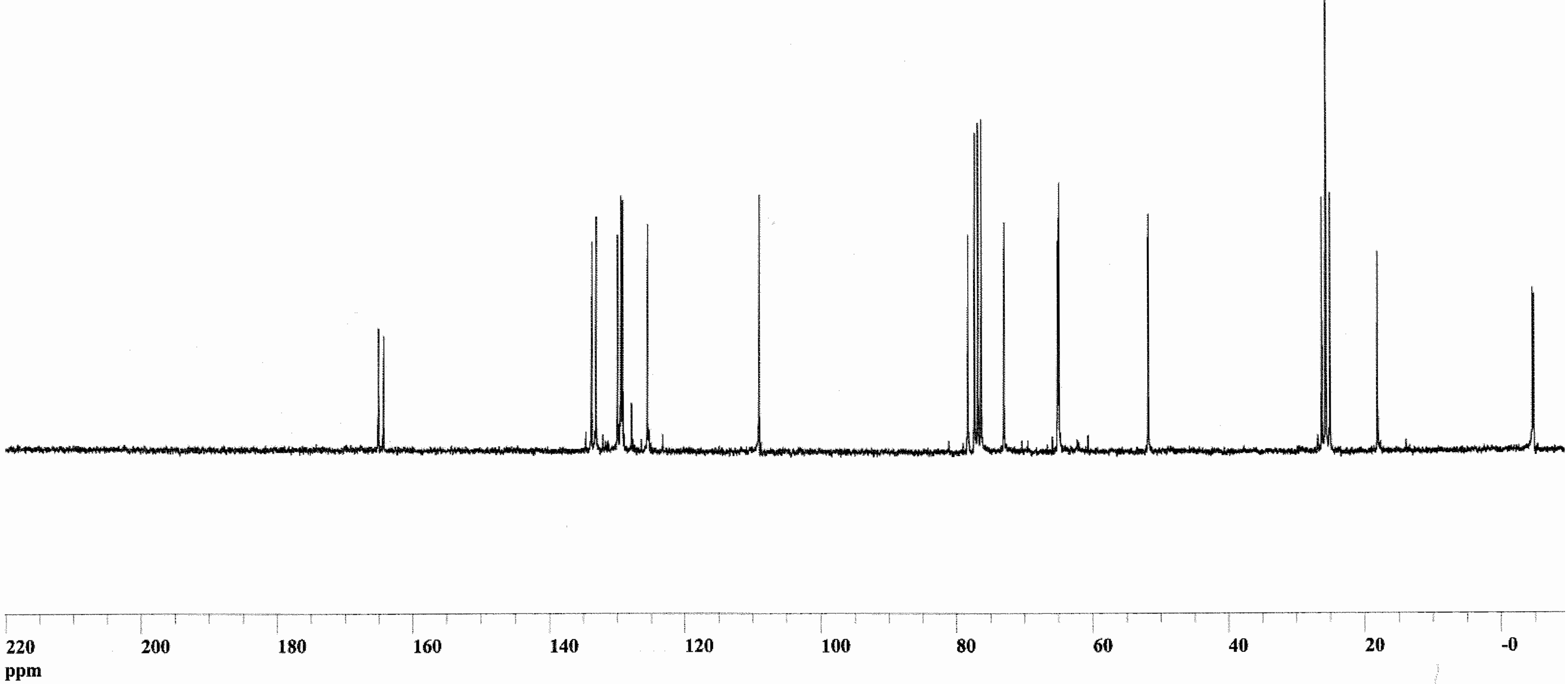
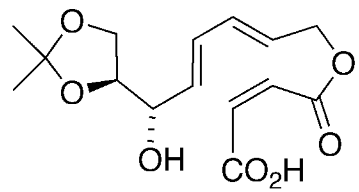


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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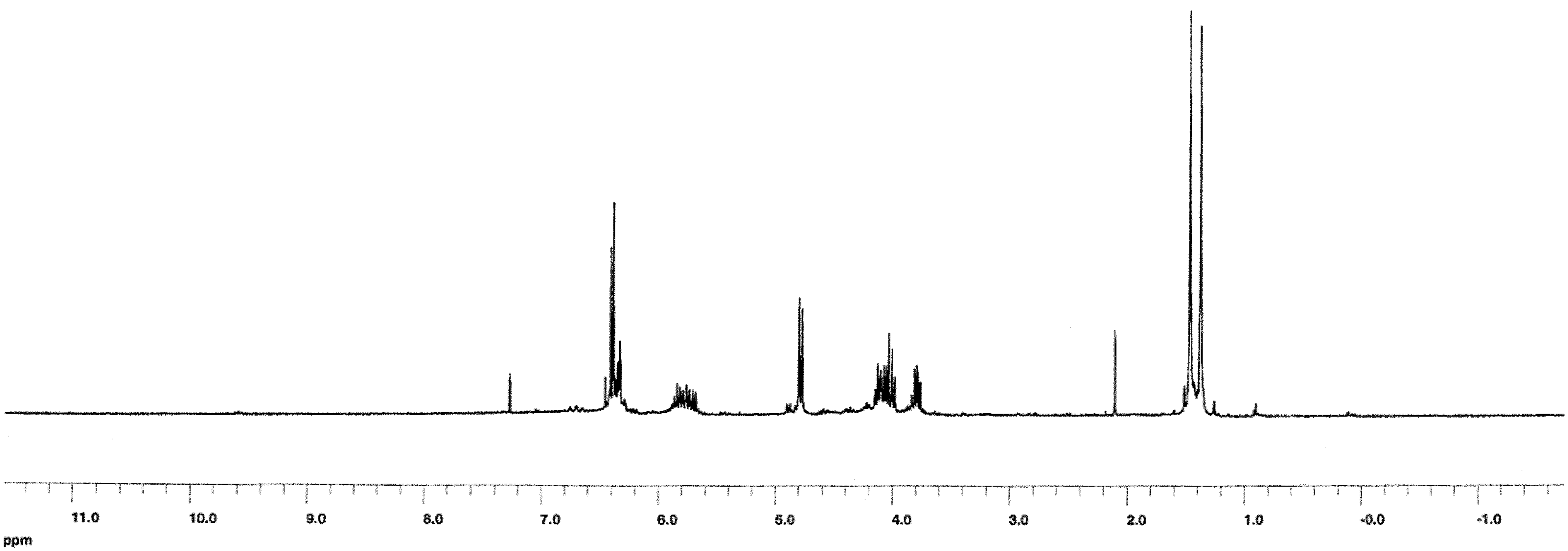
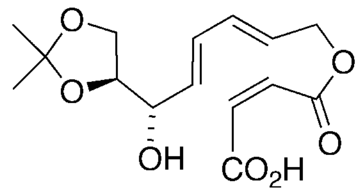


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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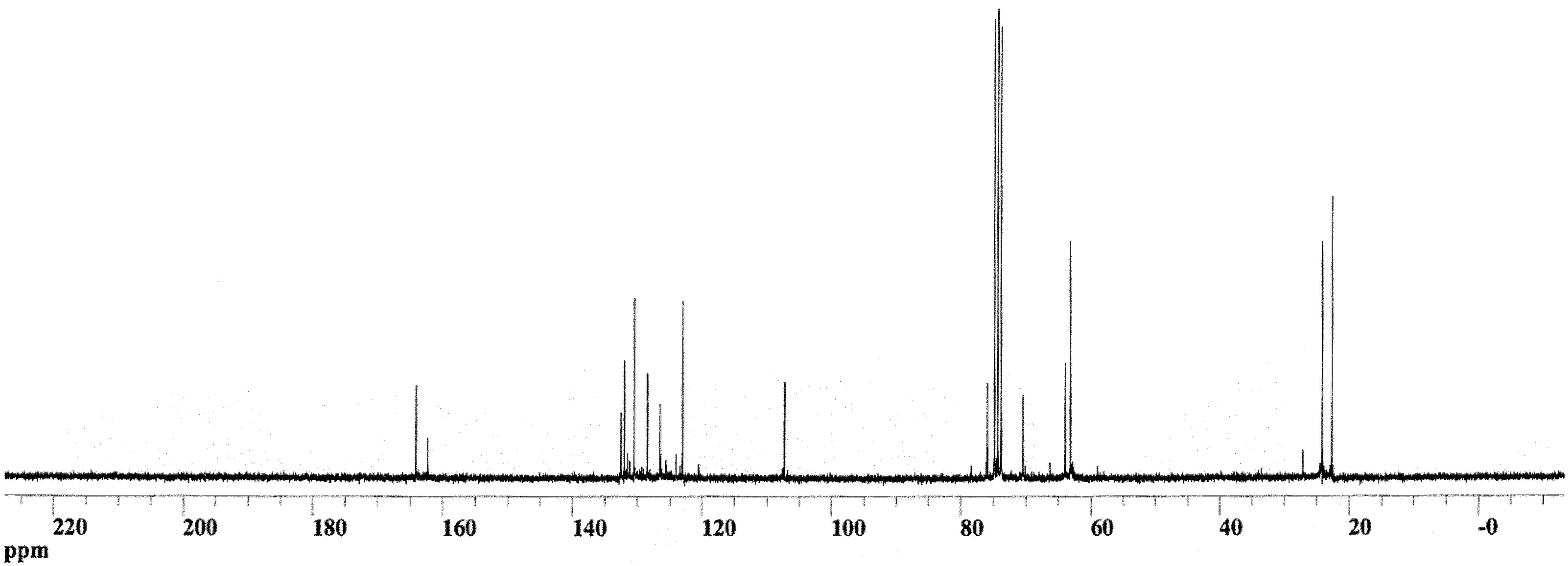
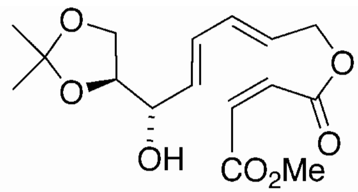


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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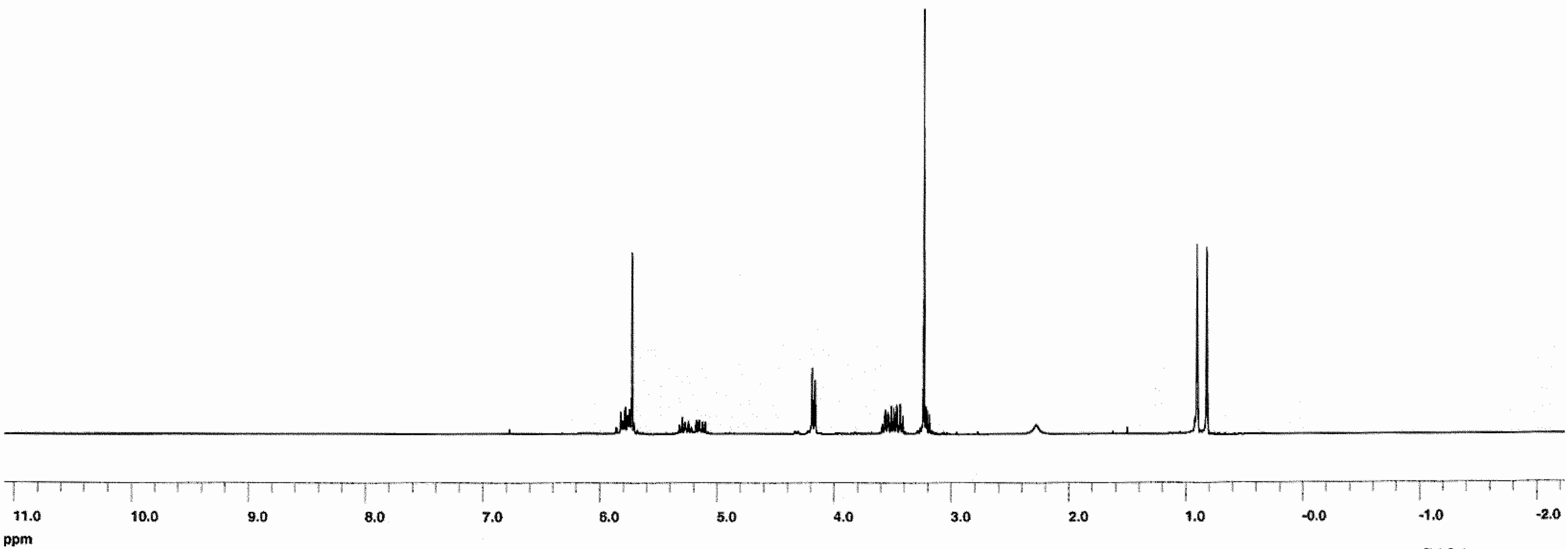
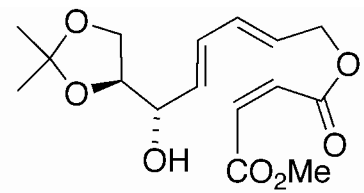


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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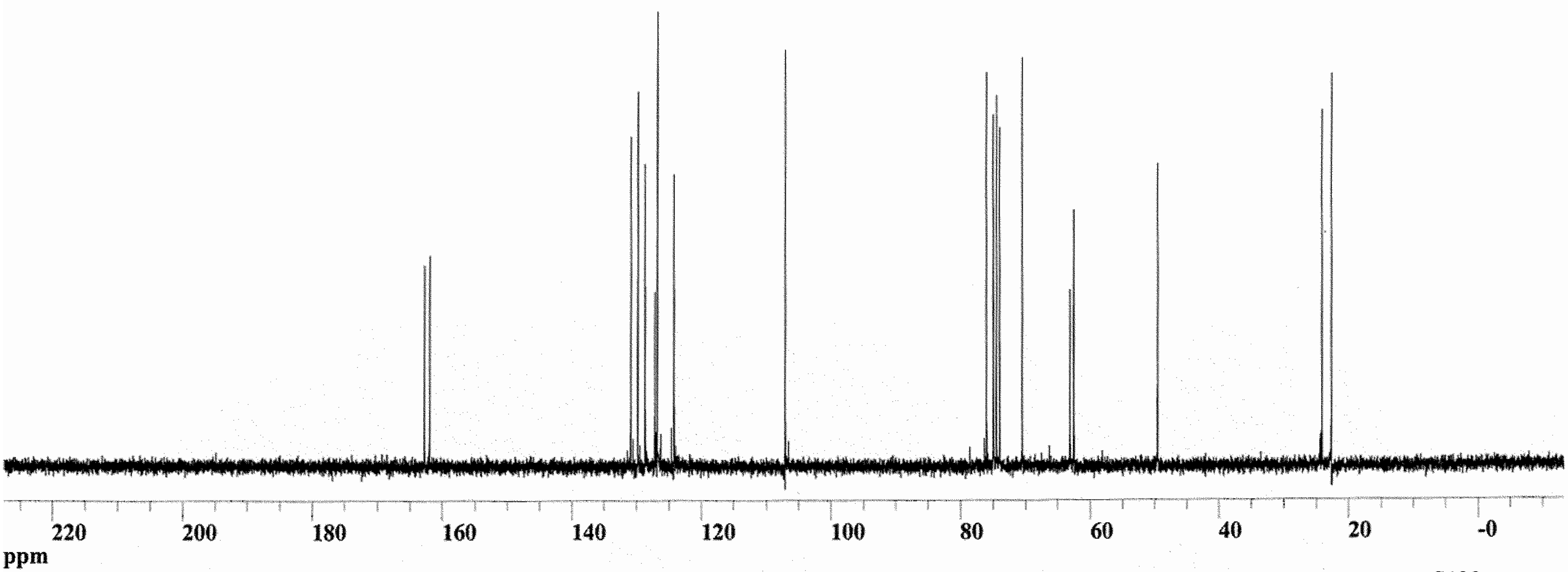
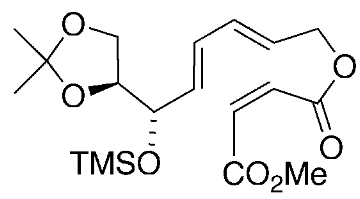


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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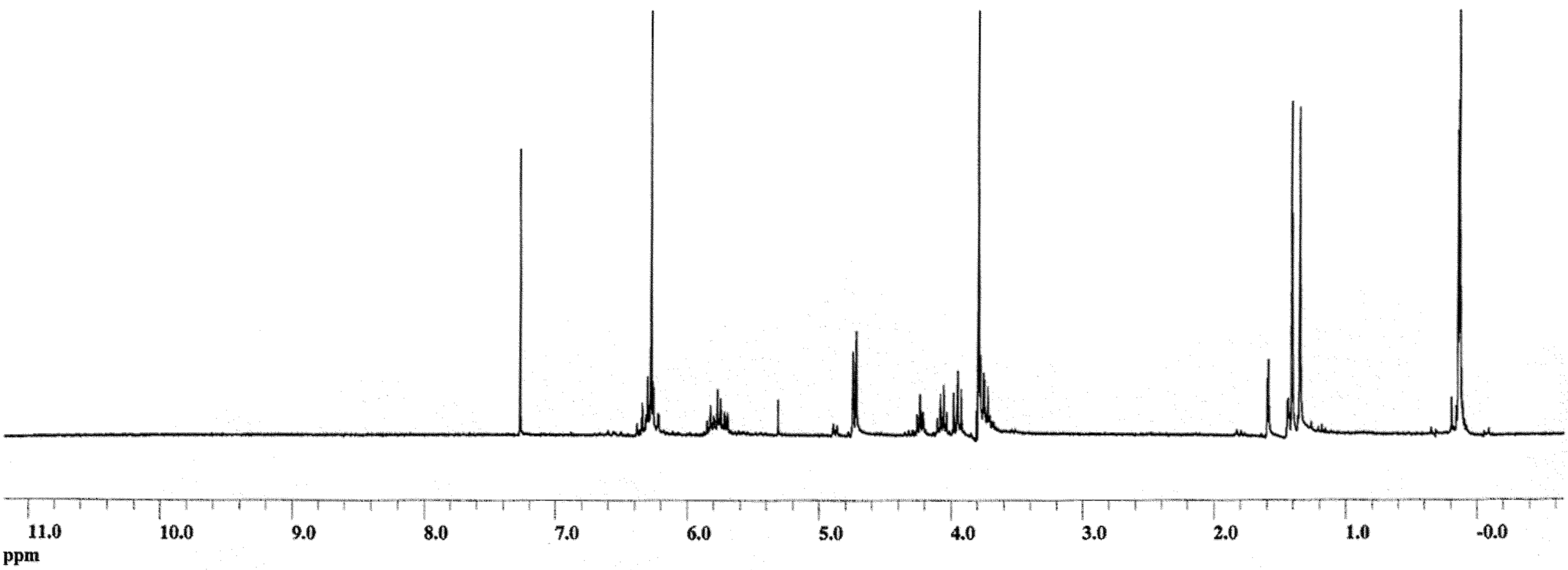
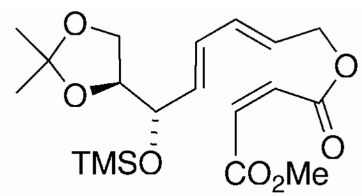


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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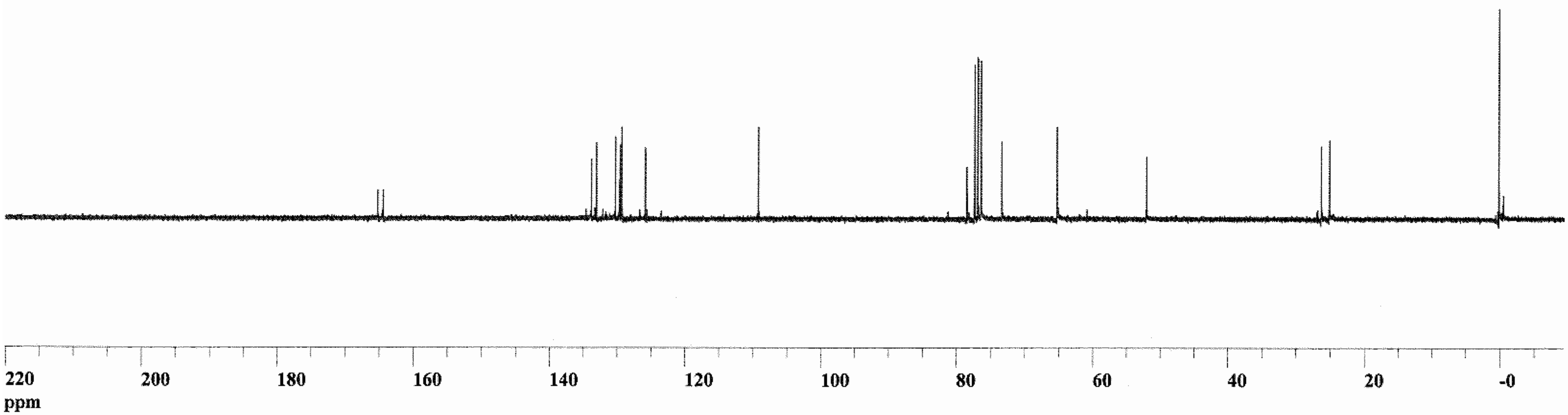
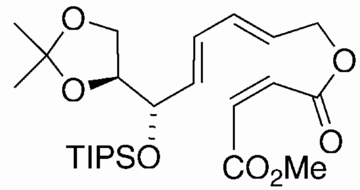


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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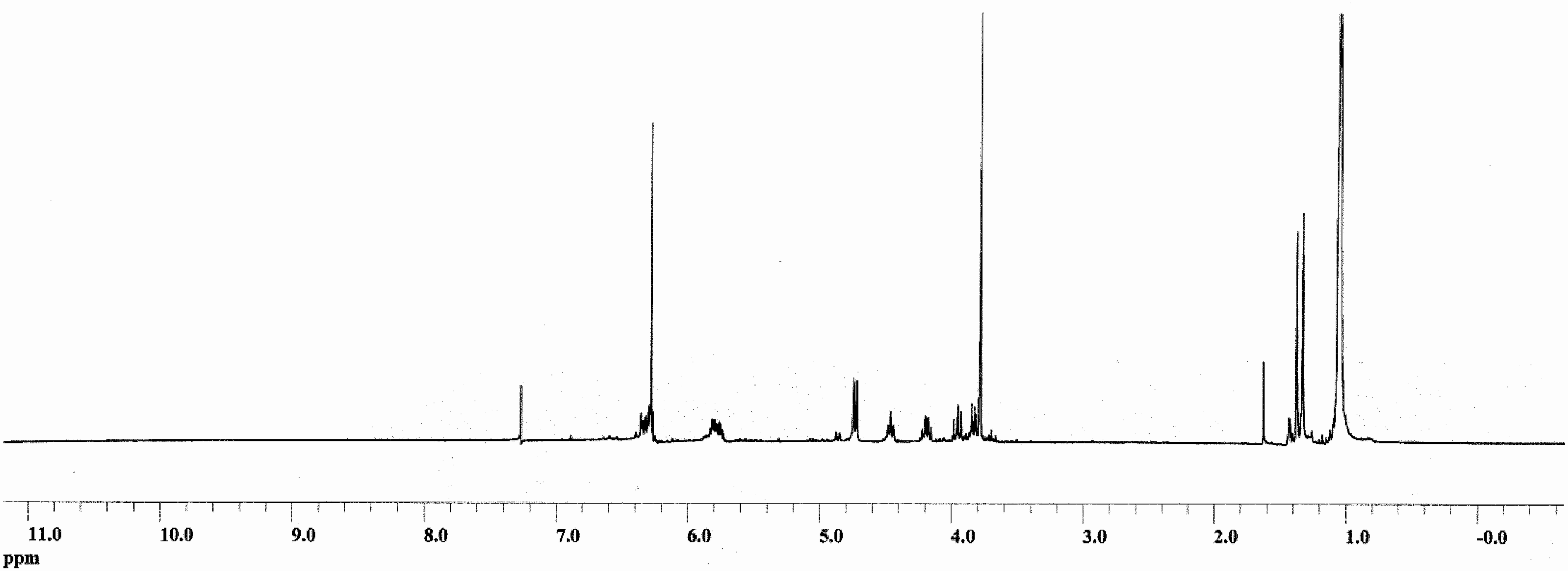
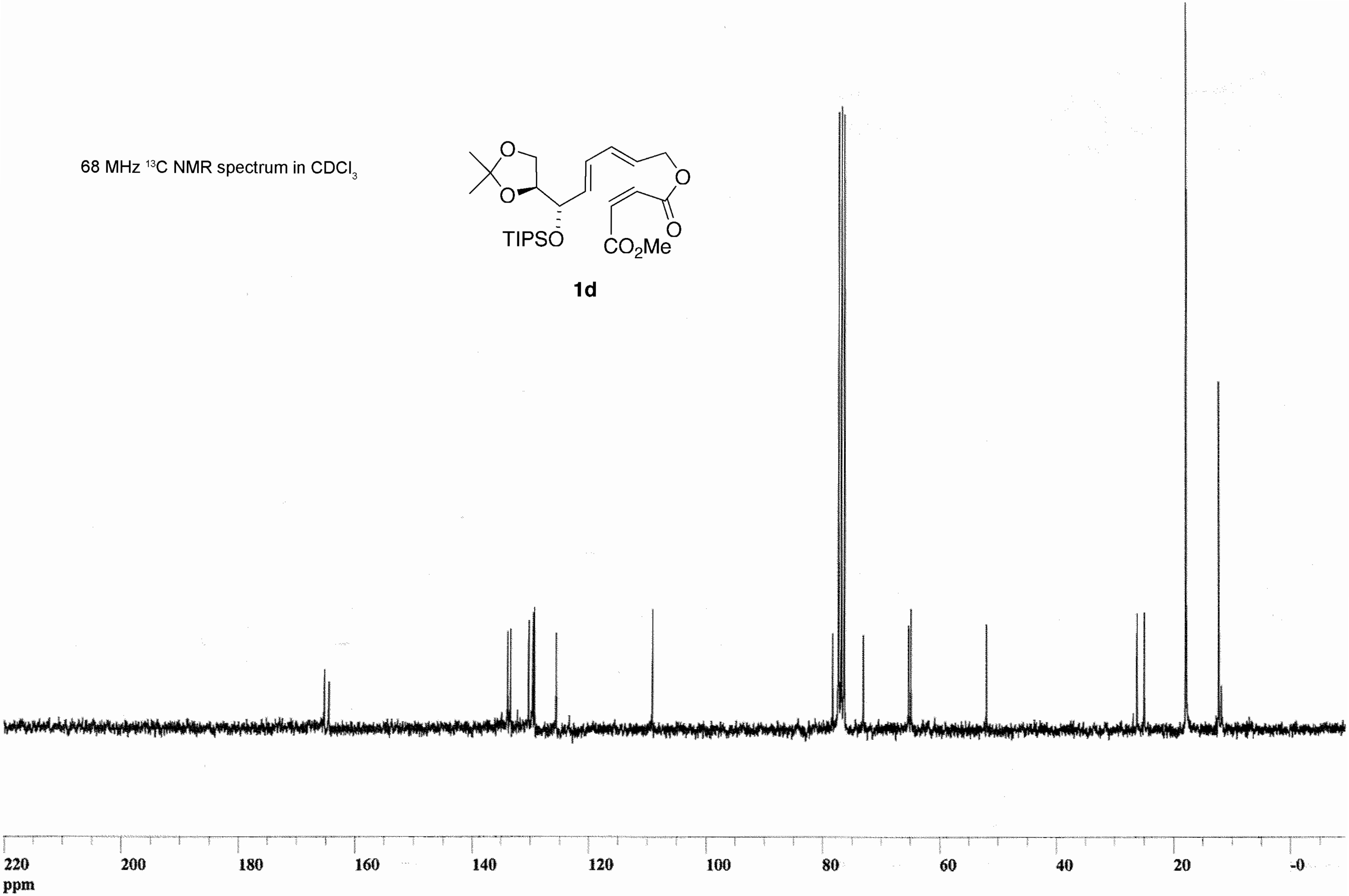
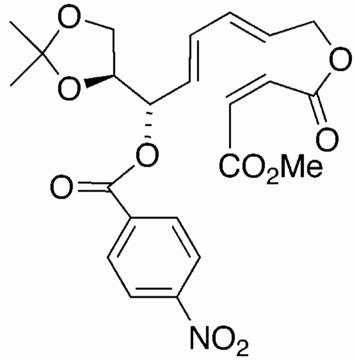


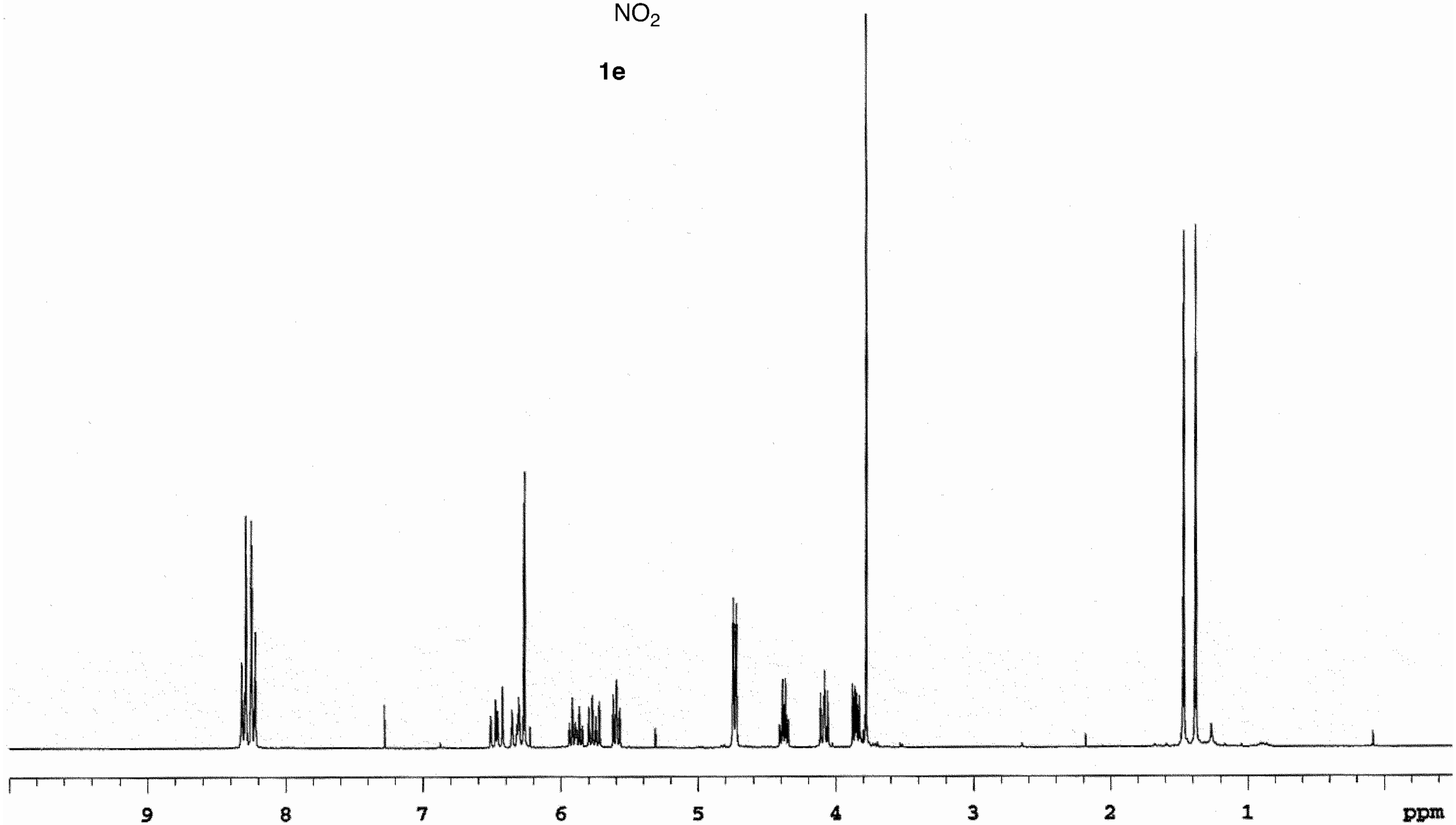
68 MHz ^{13}C NMR spectrum in $CDCl_3$



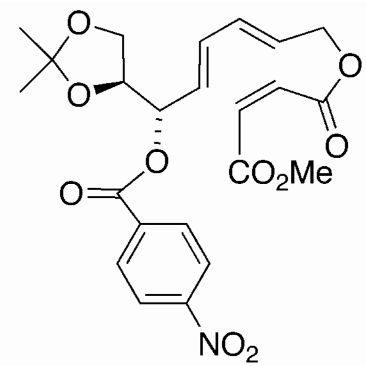
500 MHz ^1H NMR spectrum in $CDCl_3$



1e



125 MHz ^{13}C NMR spectrum in $CDCl_3$



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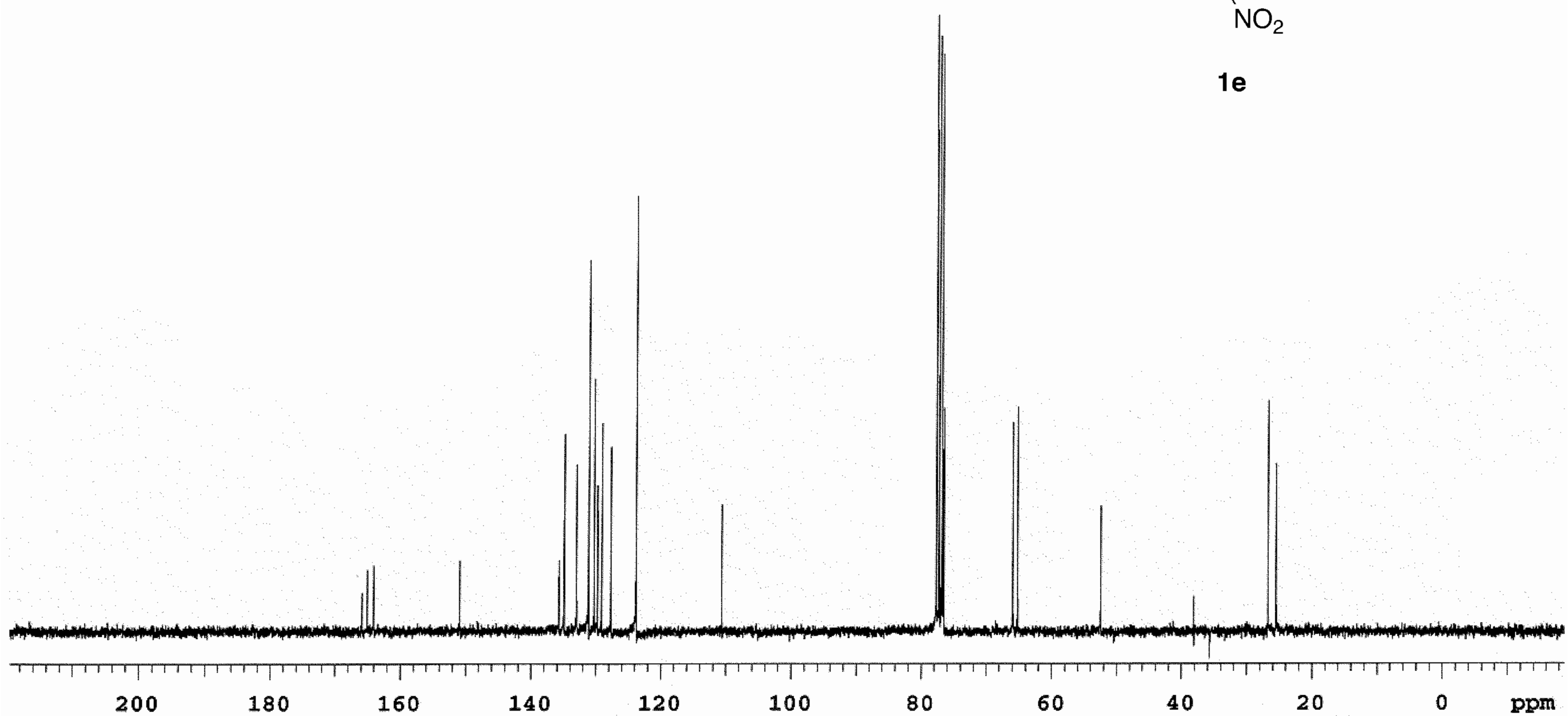
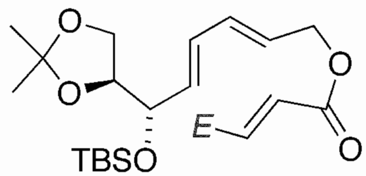


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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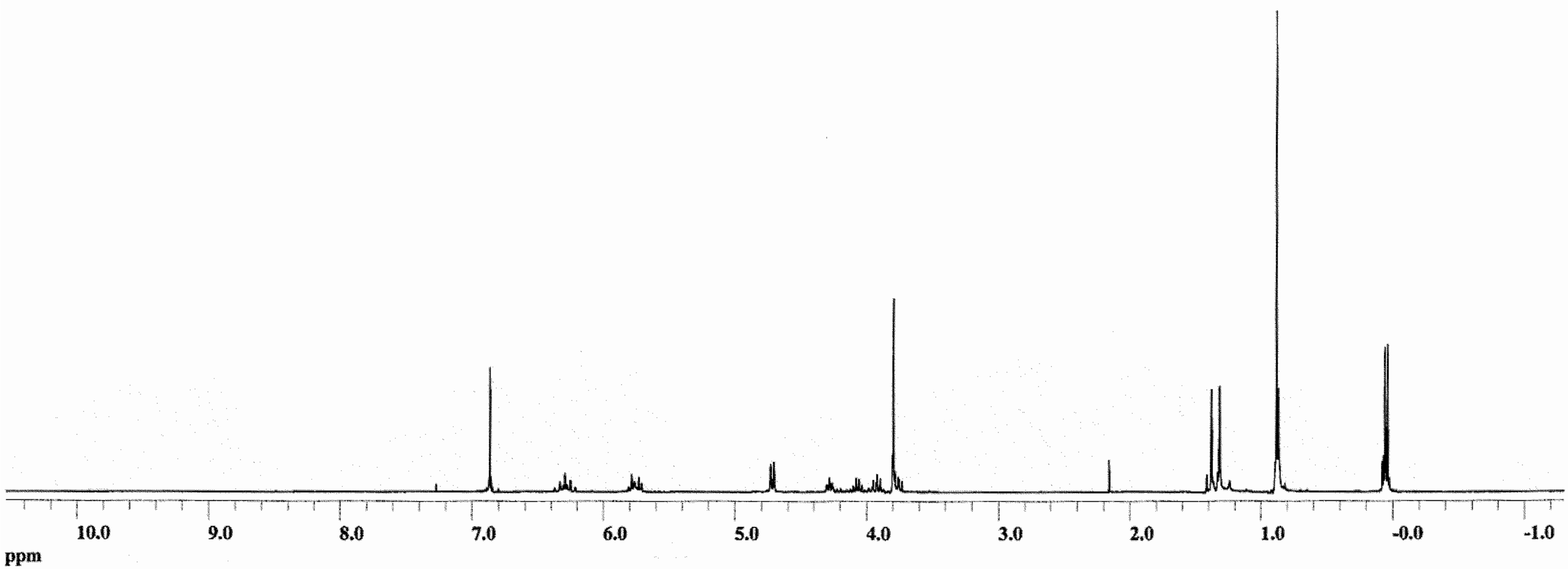
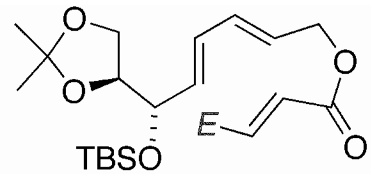
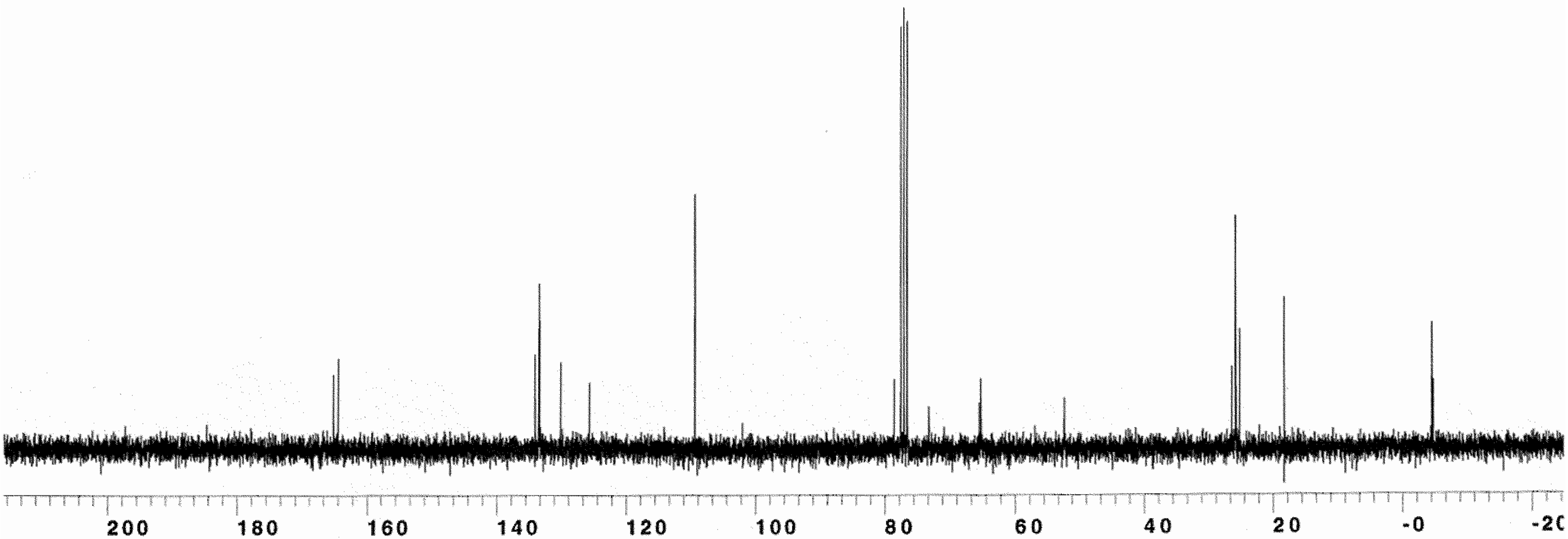


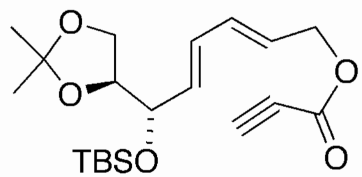
68 MHz ^{13}C NMR spectrum in $CDCl_3$



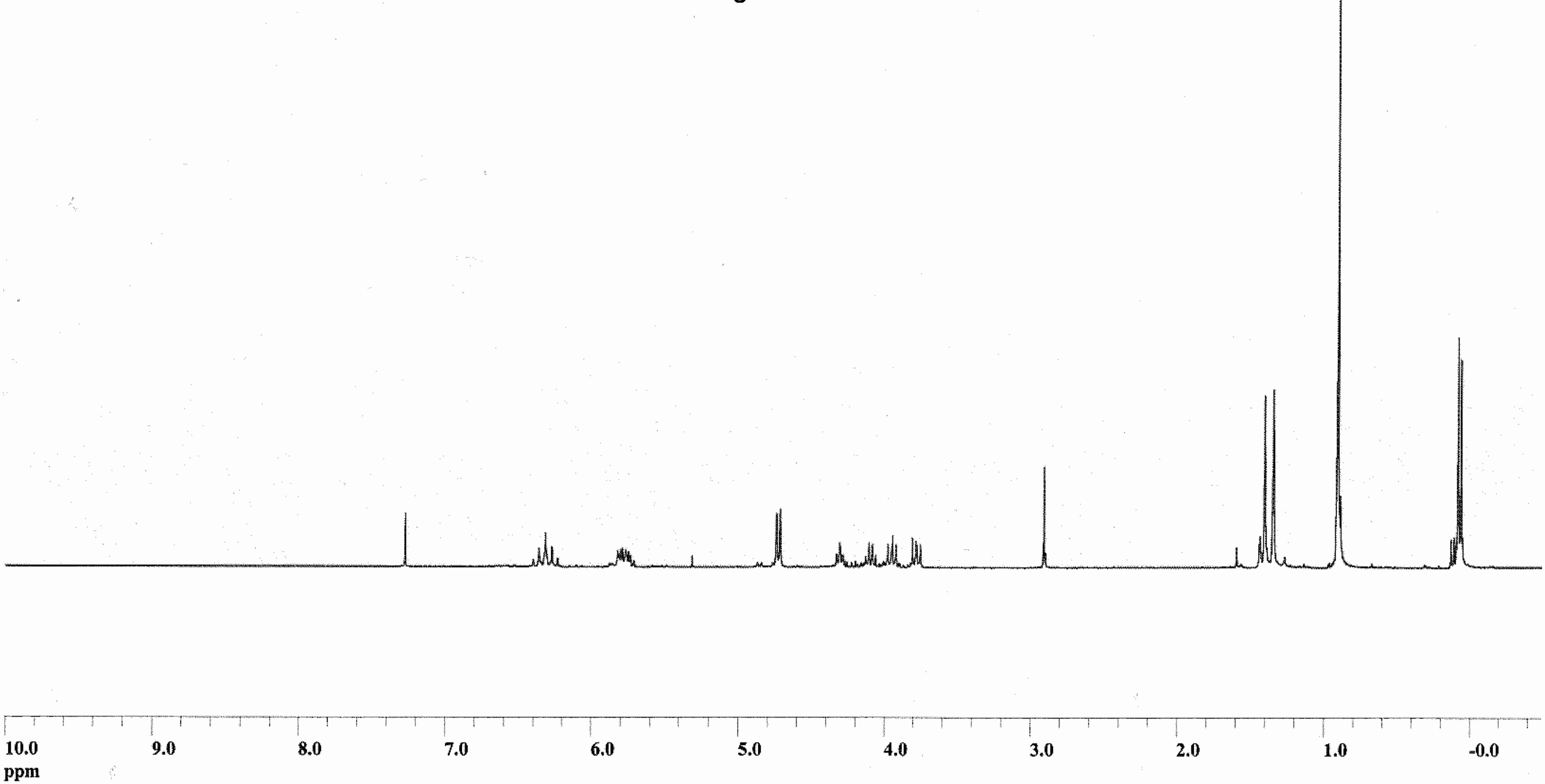
1f *E* = CO_2Me



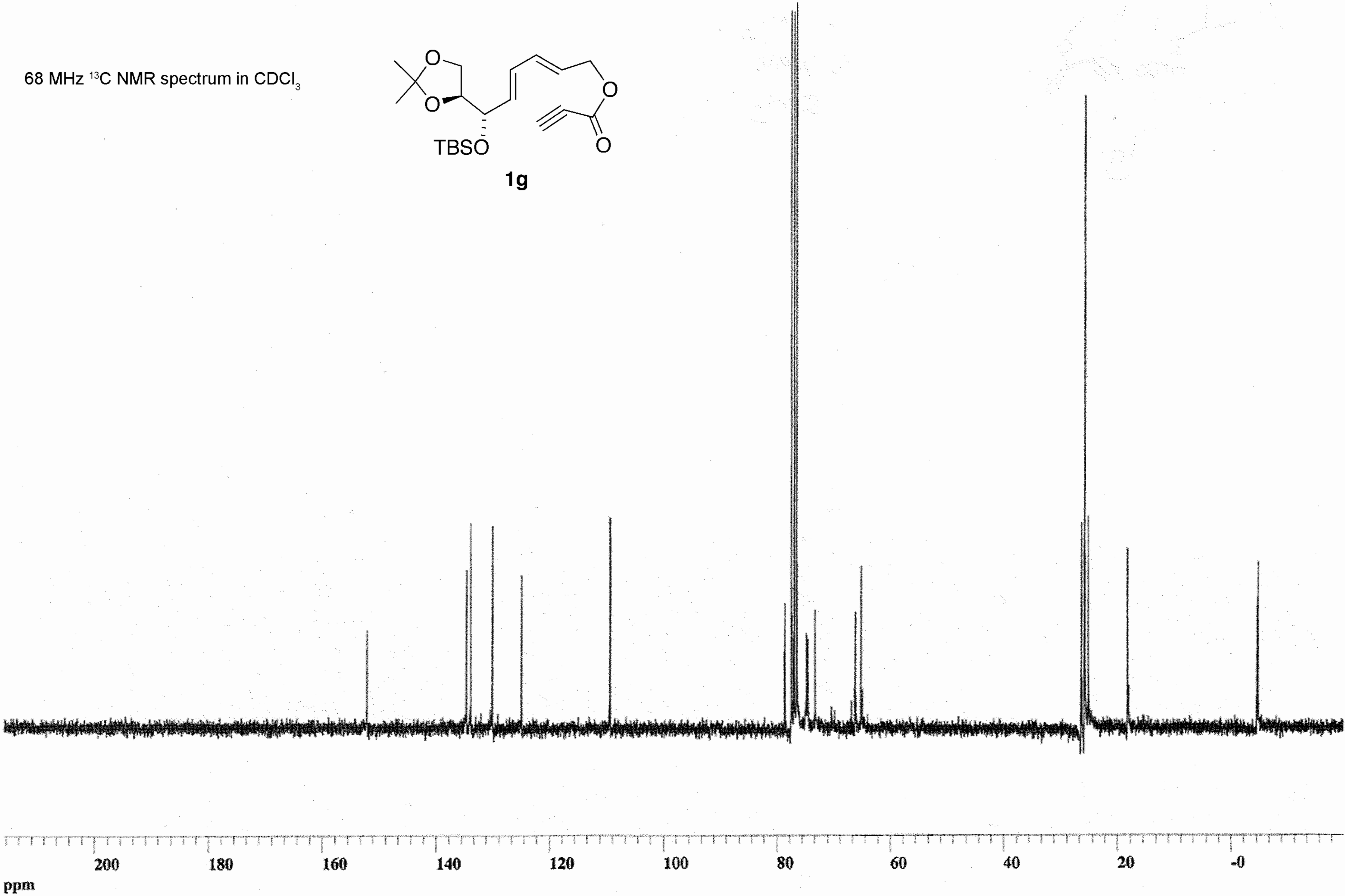
270 MHz ^{1}H NMR spectrum in $CDCl_3$



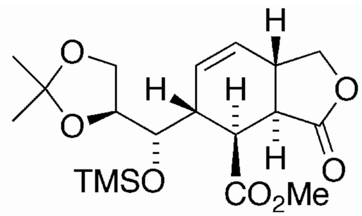
1g



68 MHz ^{13}C NMR spectrum in $CDCl_3$



270 MHz ^{1}H NMR spectrum in $CDCl_3$



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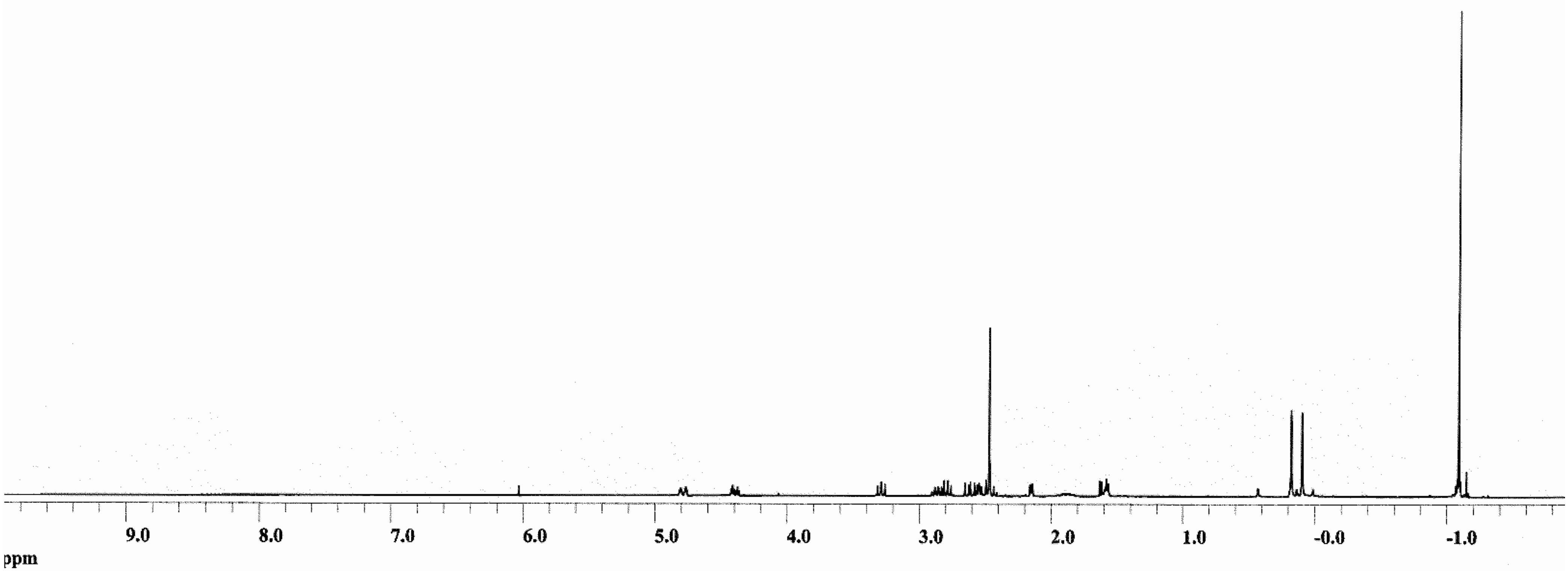
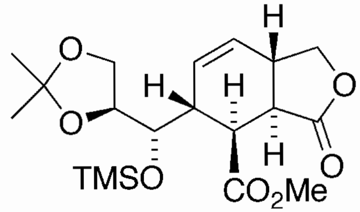


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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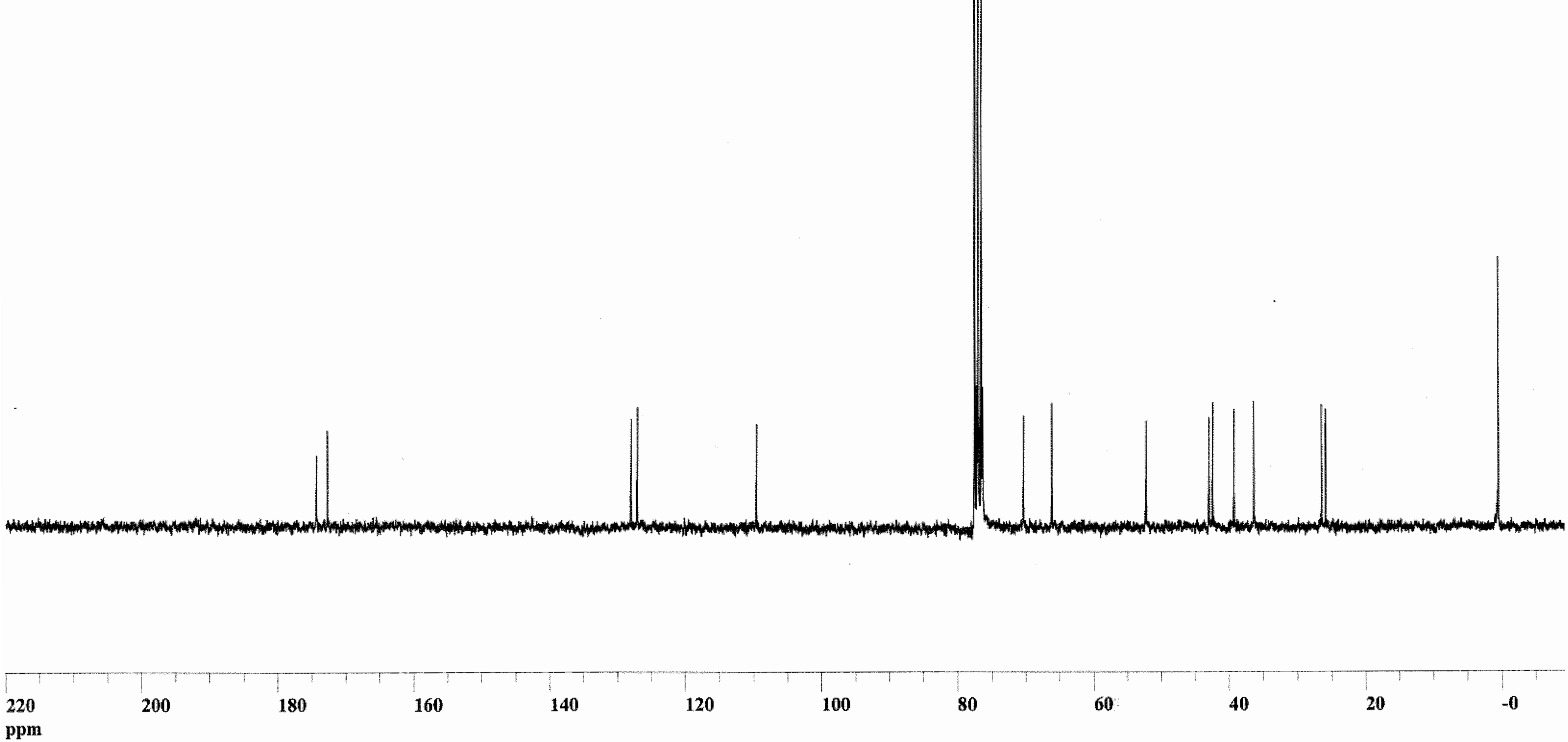
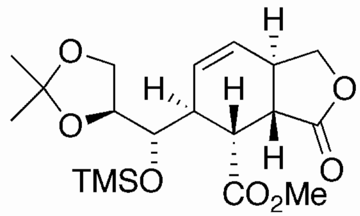


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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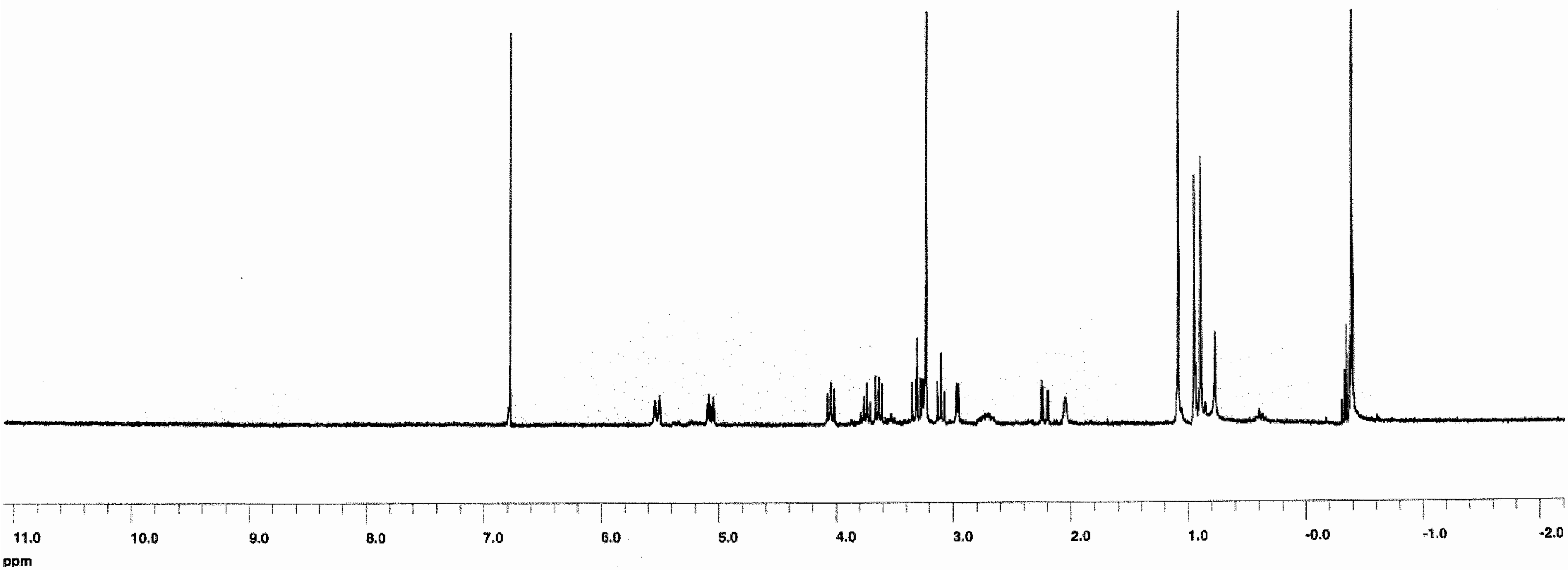
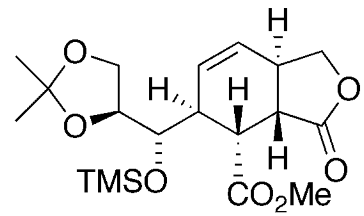


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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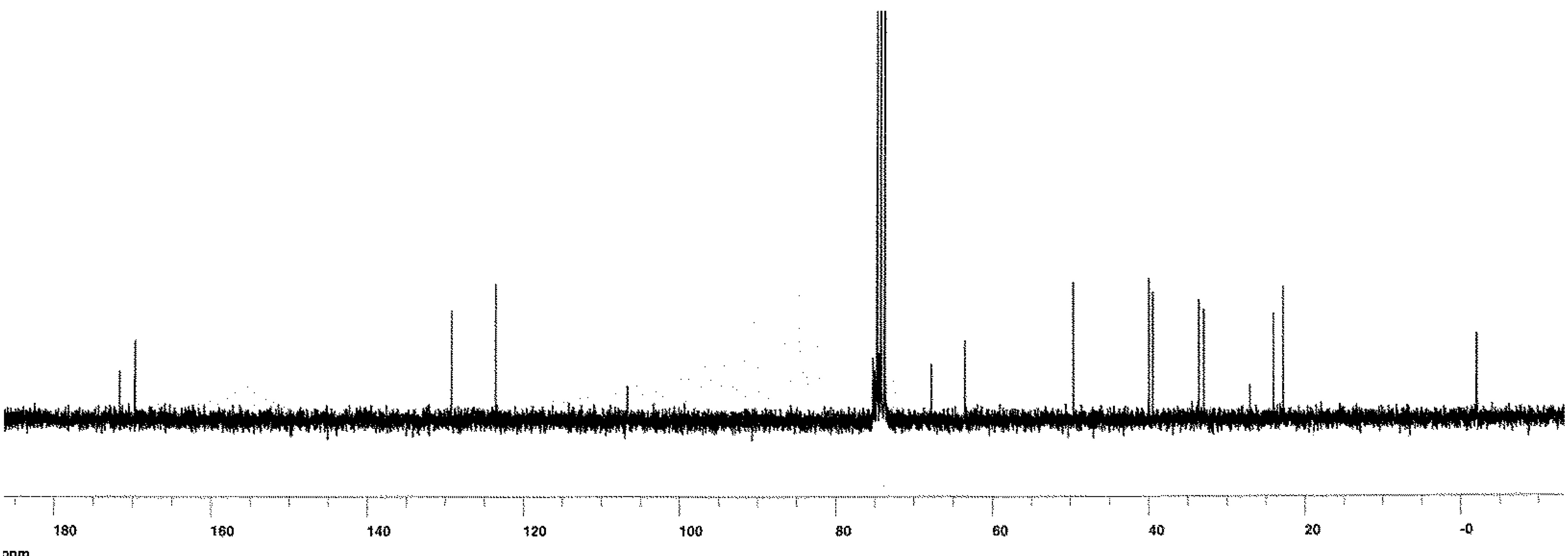
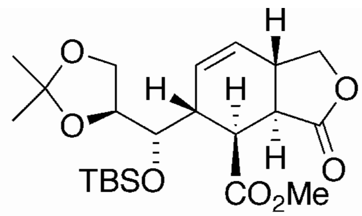


270 MHz ^1H NMR spectrum in $CDCl_3$



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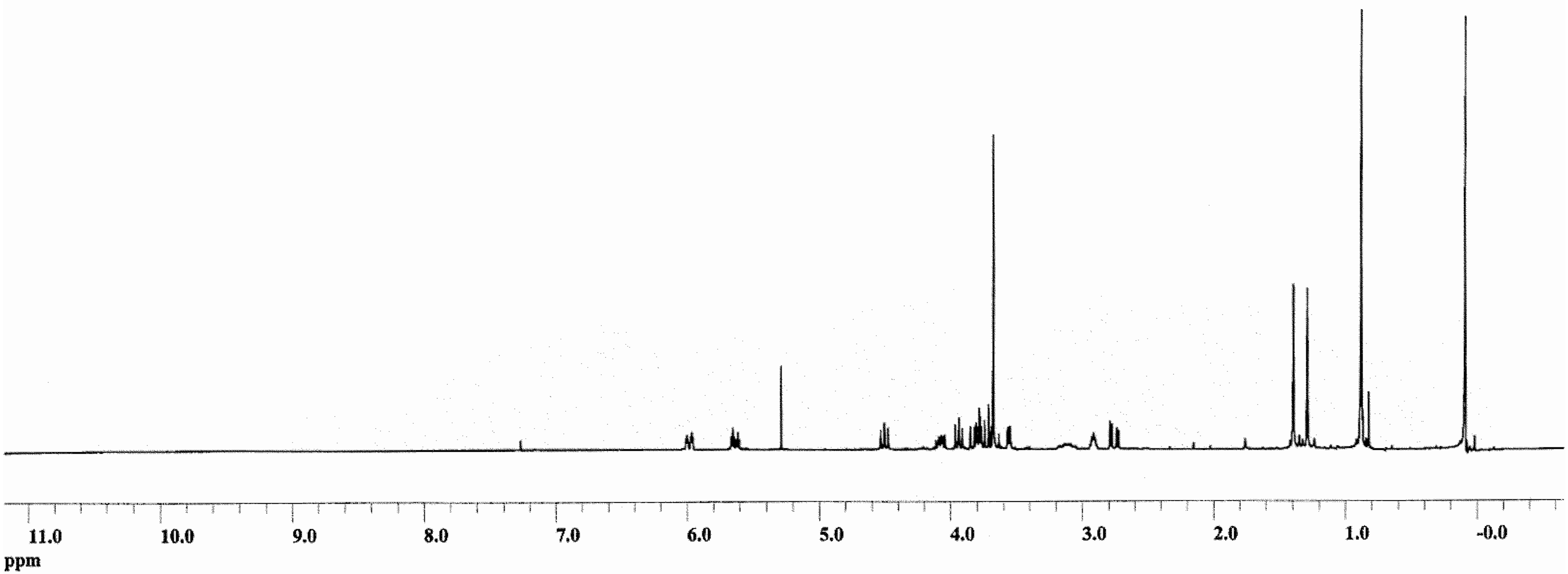
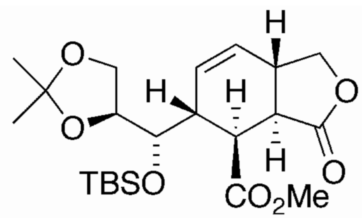


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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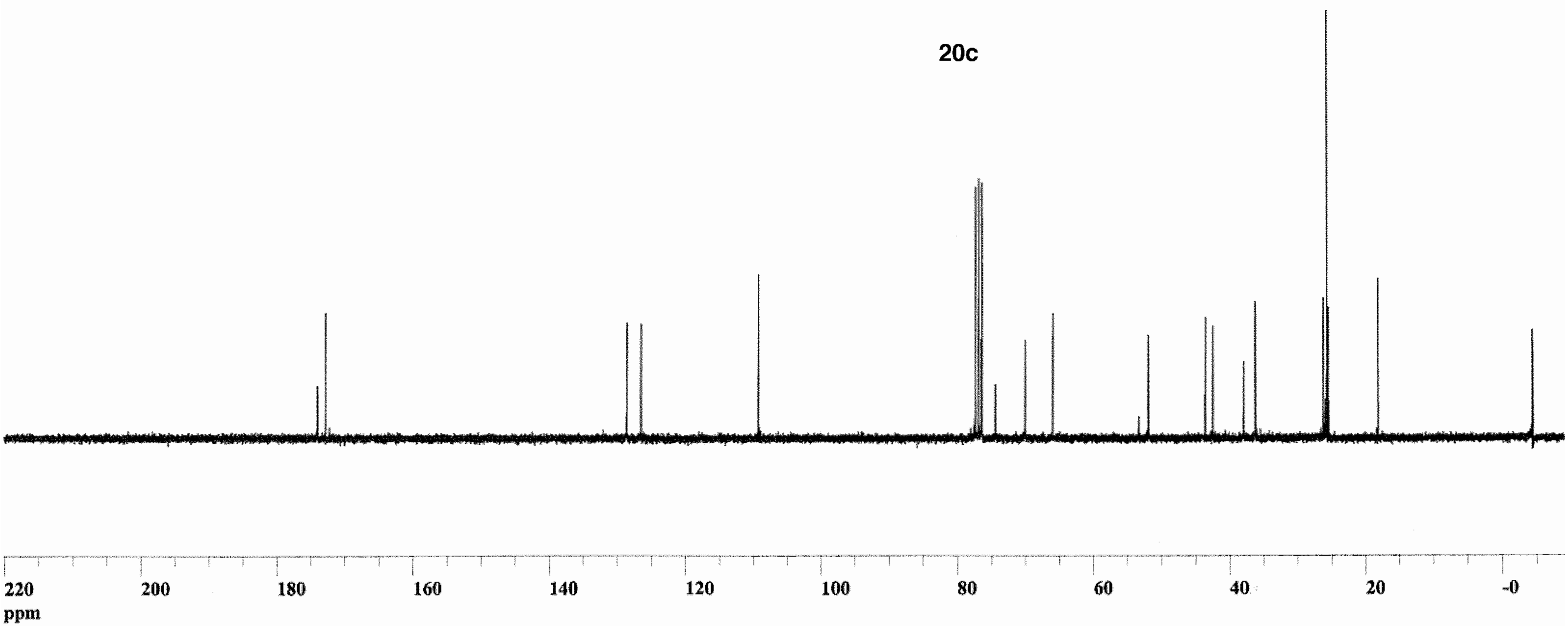
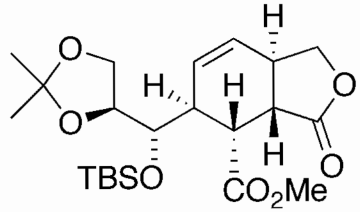


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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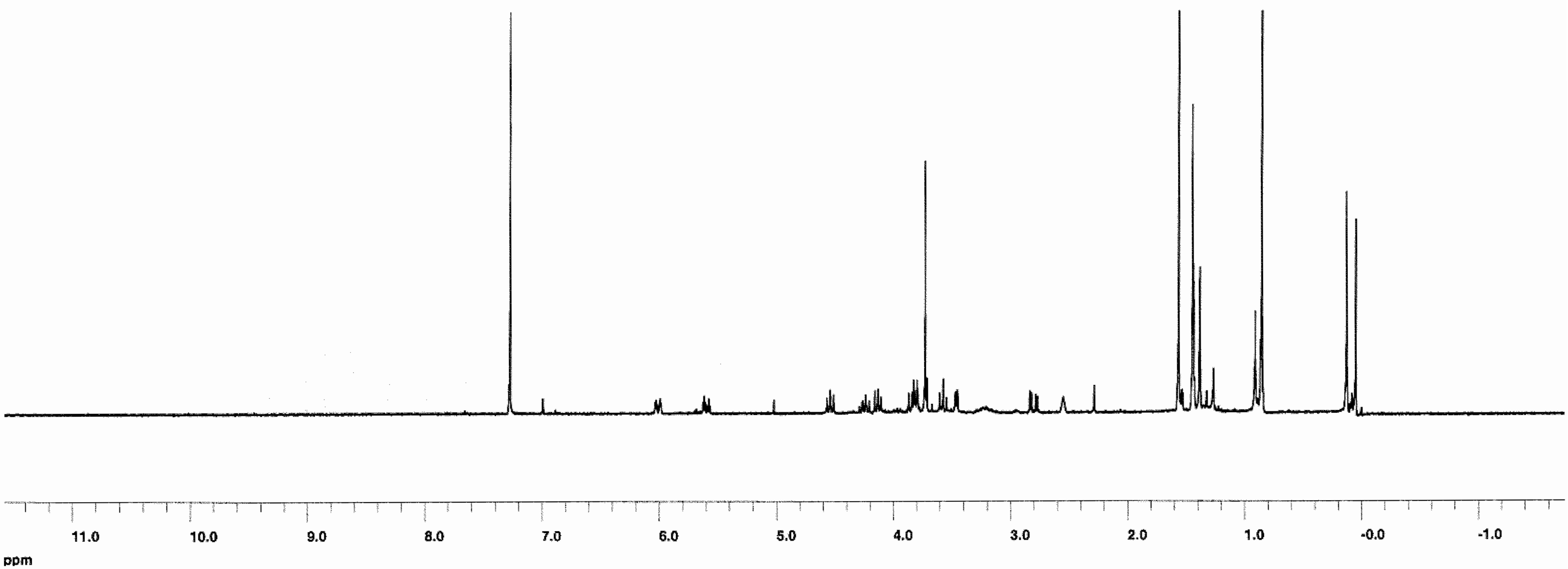
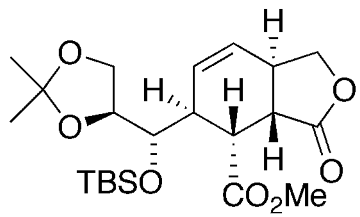


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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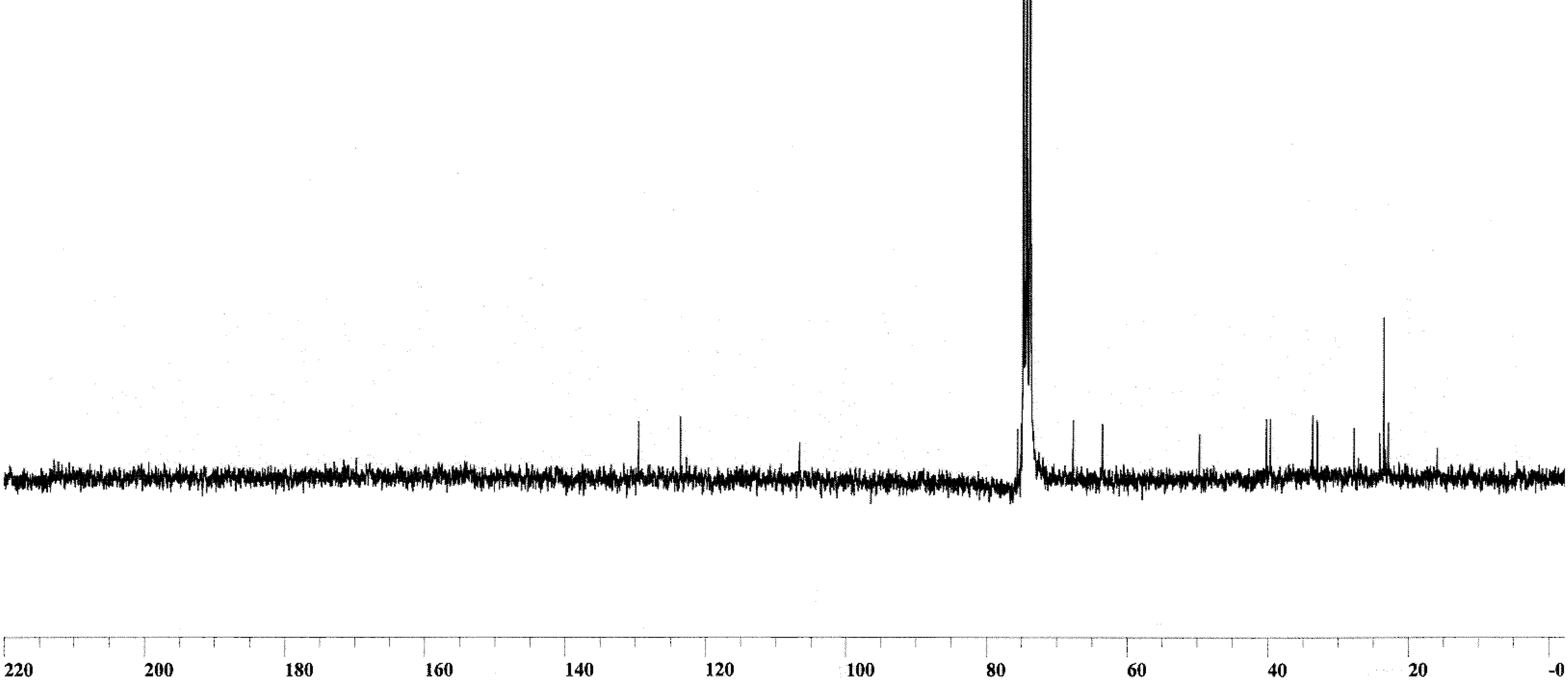
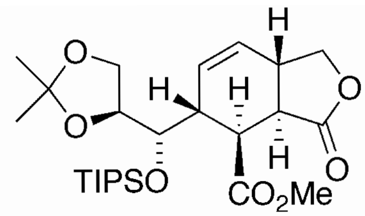


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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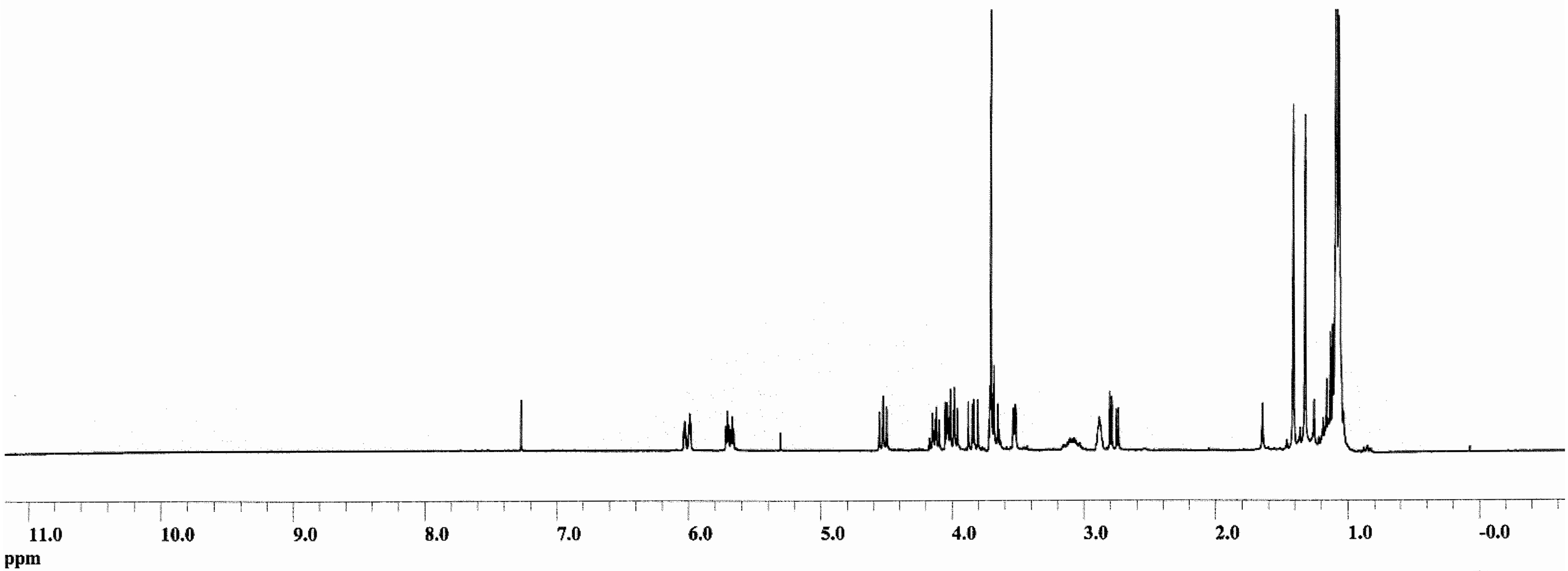
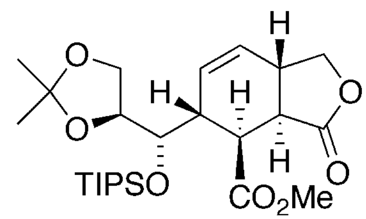


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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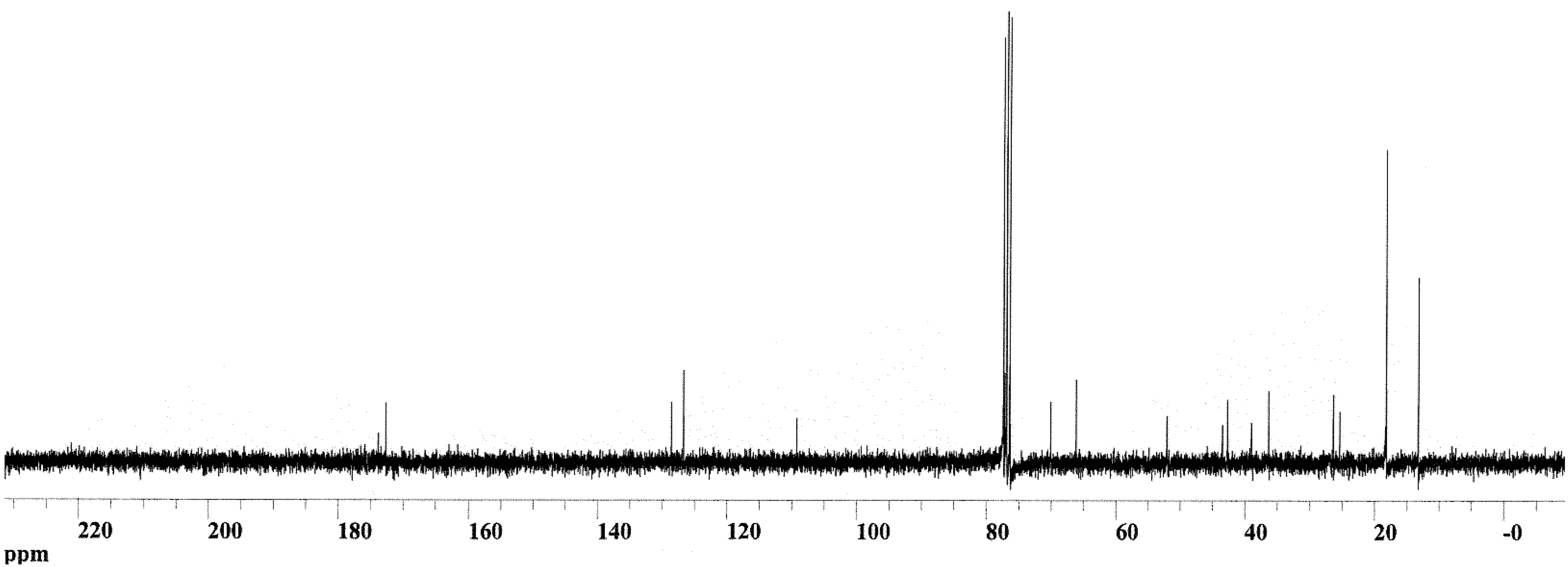
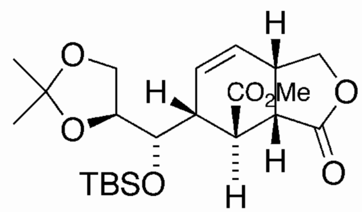


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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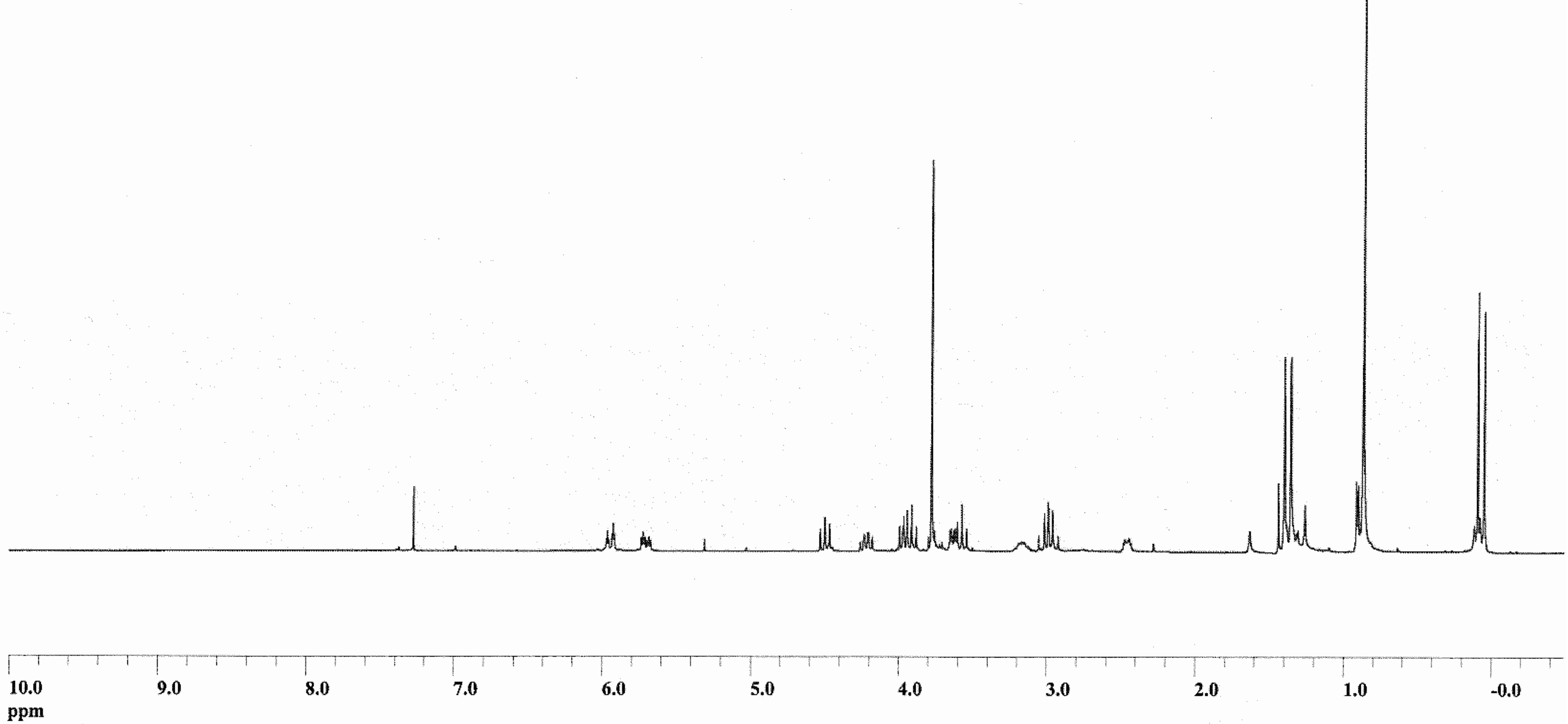
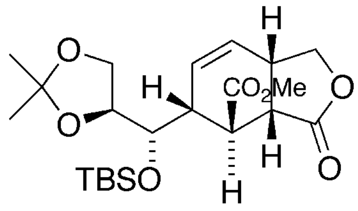


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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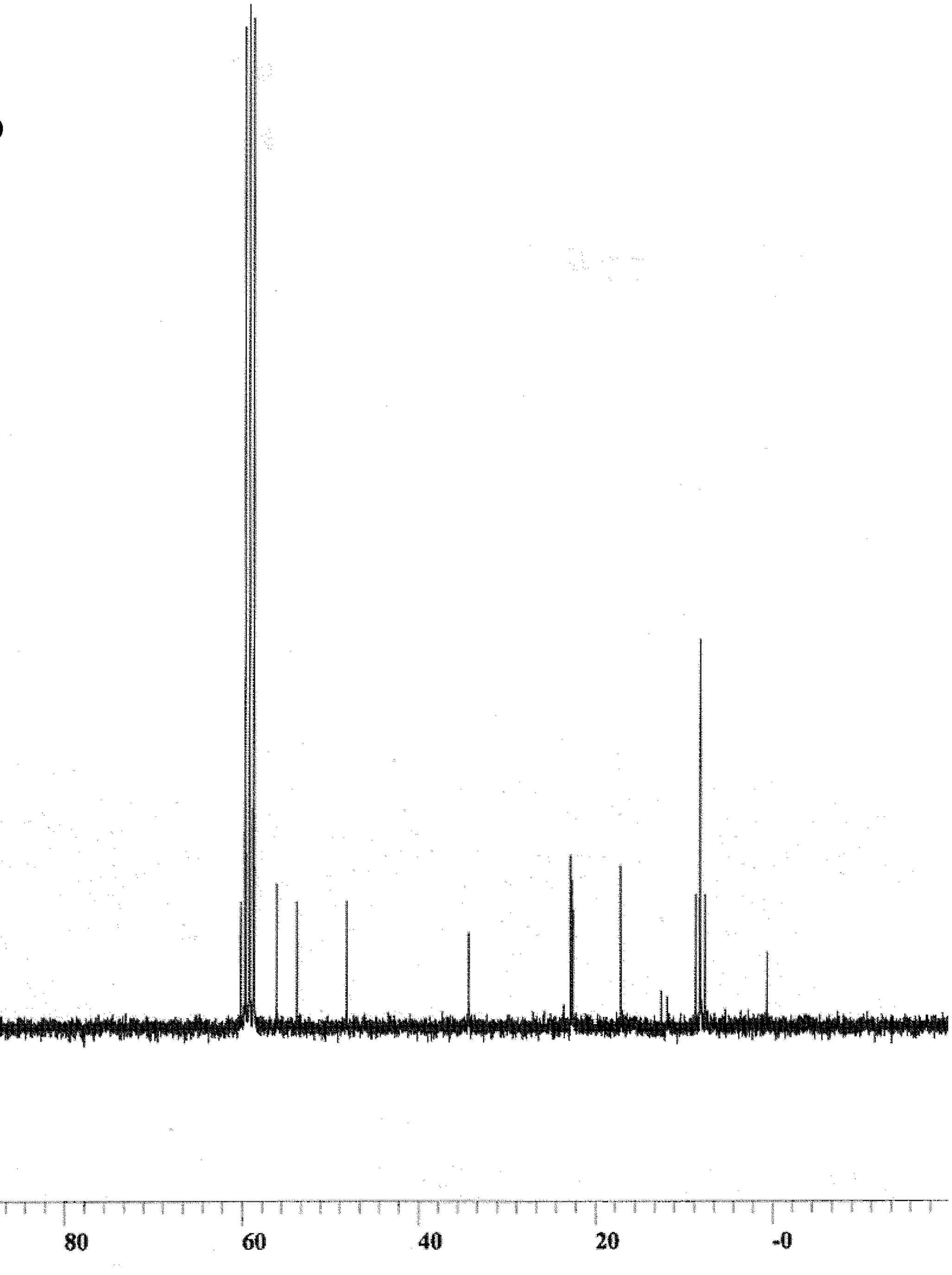
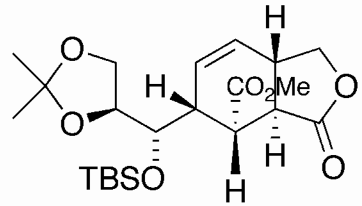


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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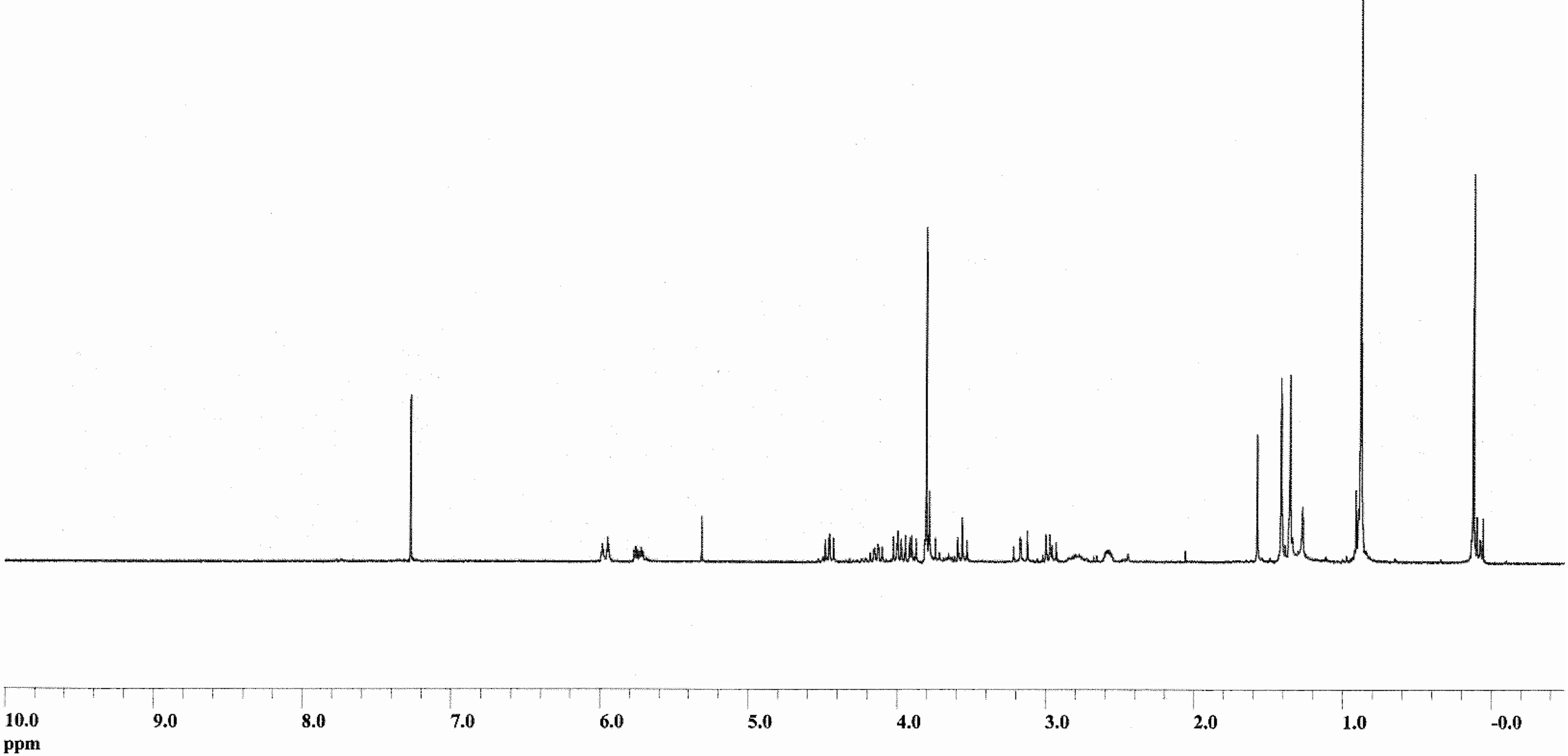
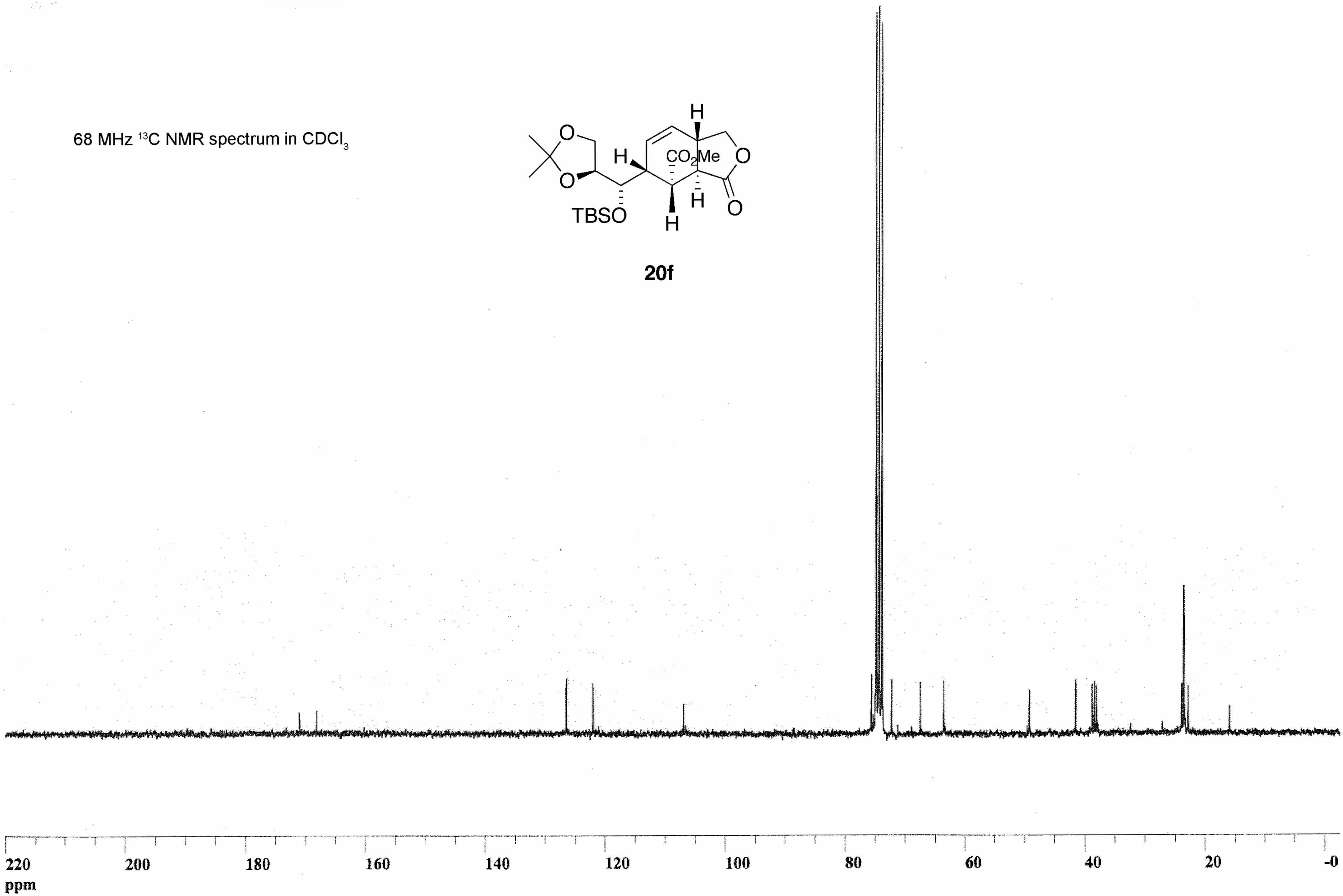
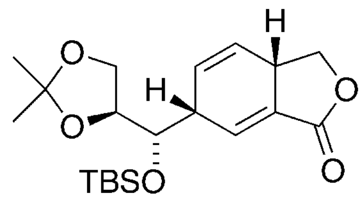
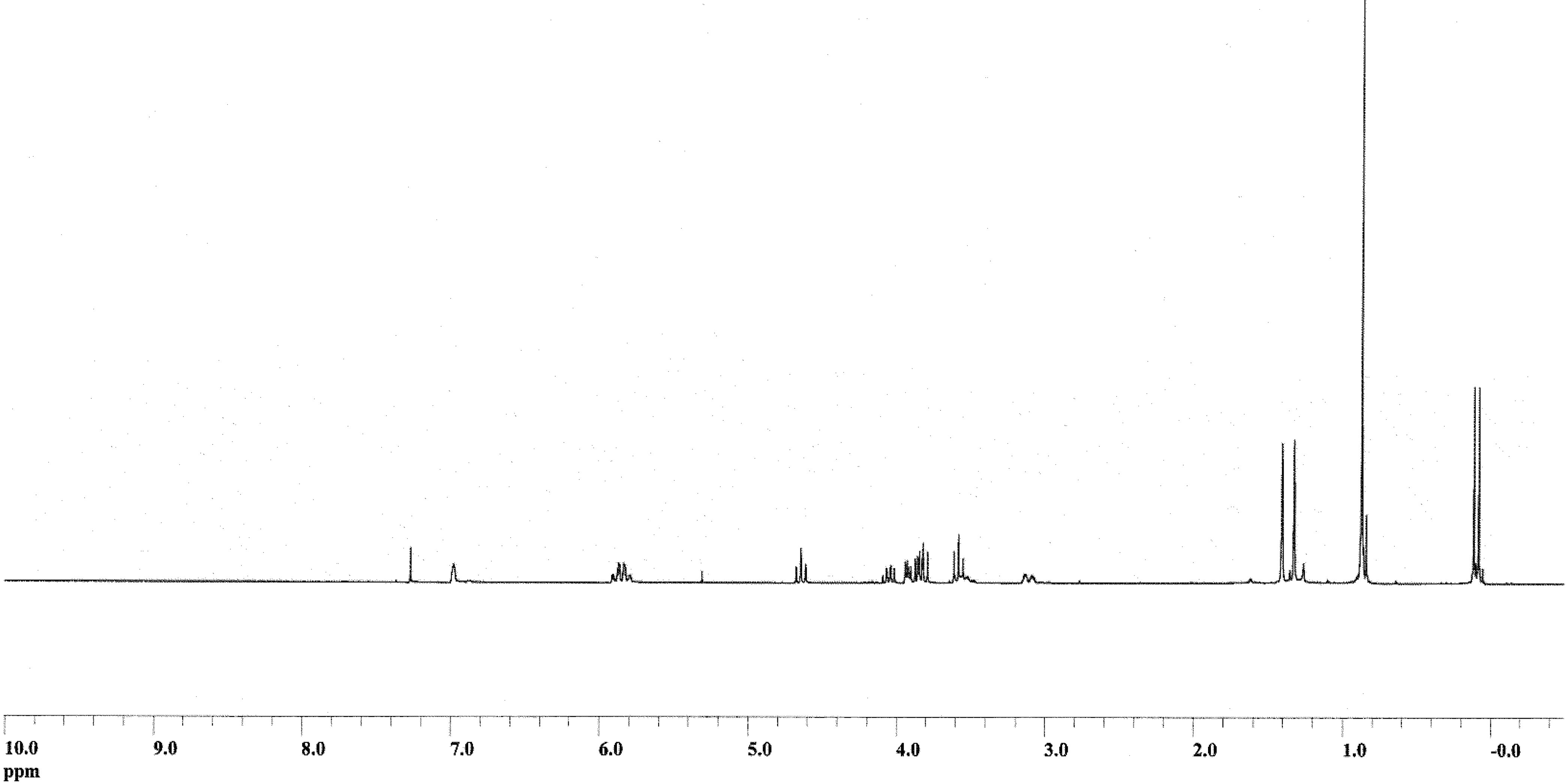



68 MHz 13C NMR spectrum in CDCl3
H
O
O
H
CO2Me
O
TBSO
H
H
O
20f
220
200
180
160
140
120
100
80
60
40
20
-0
ppm

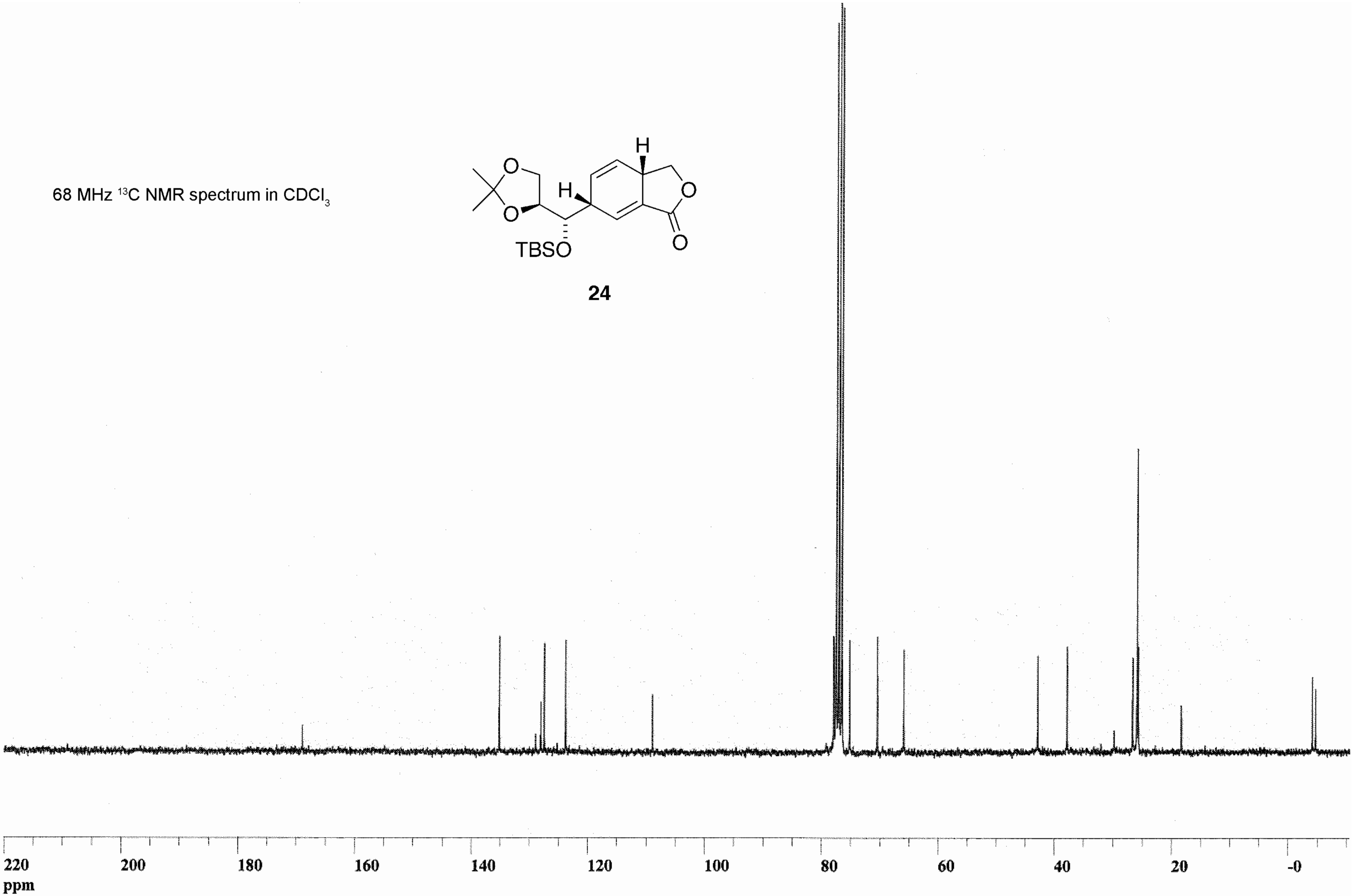
270 MHz ^{1}H NMR spectrum in $CDCl_3$



24

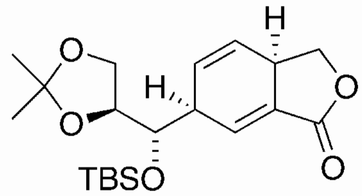


68 MHz ^{13}C NMR spectrum in $CDCl_3$



24

270 MHz ^{1}H NMR spectrum in $CDCl_3$



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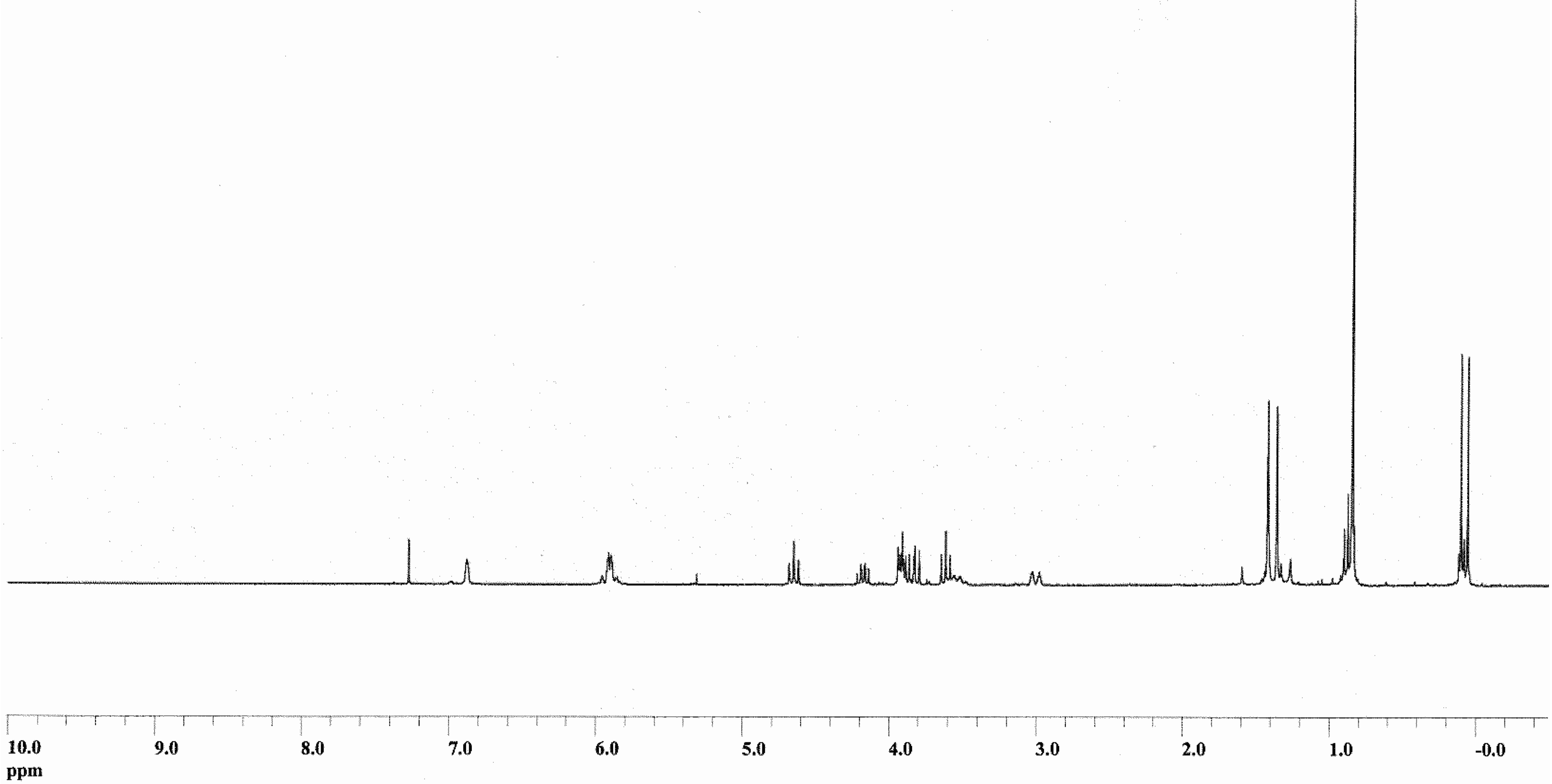
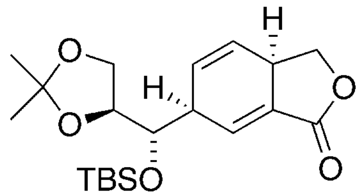
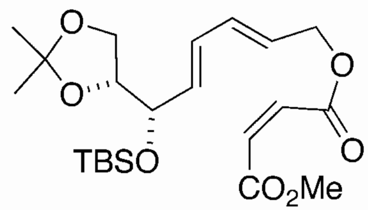


68 MHz ^{13}C NMR spectrum in $CDCl_3$

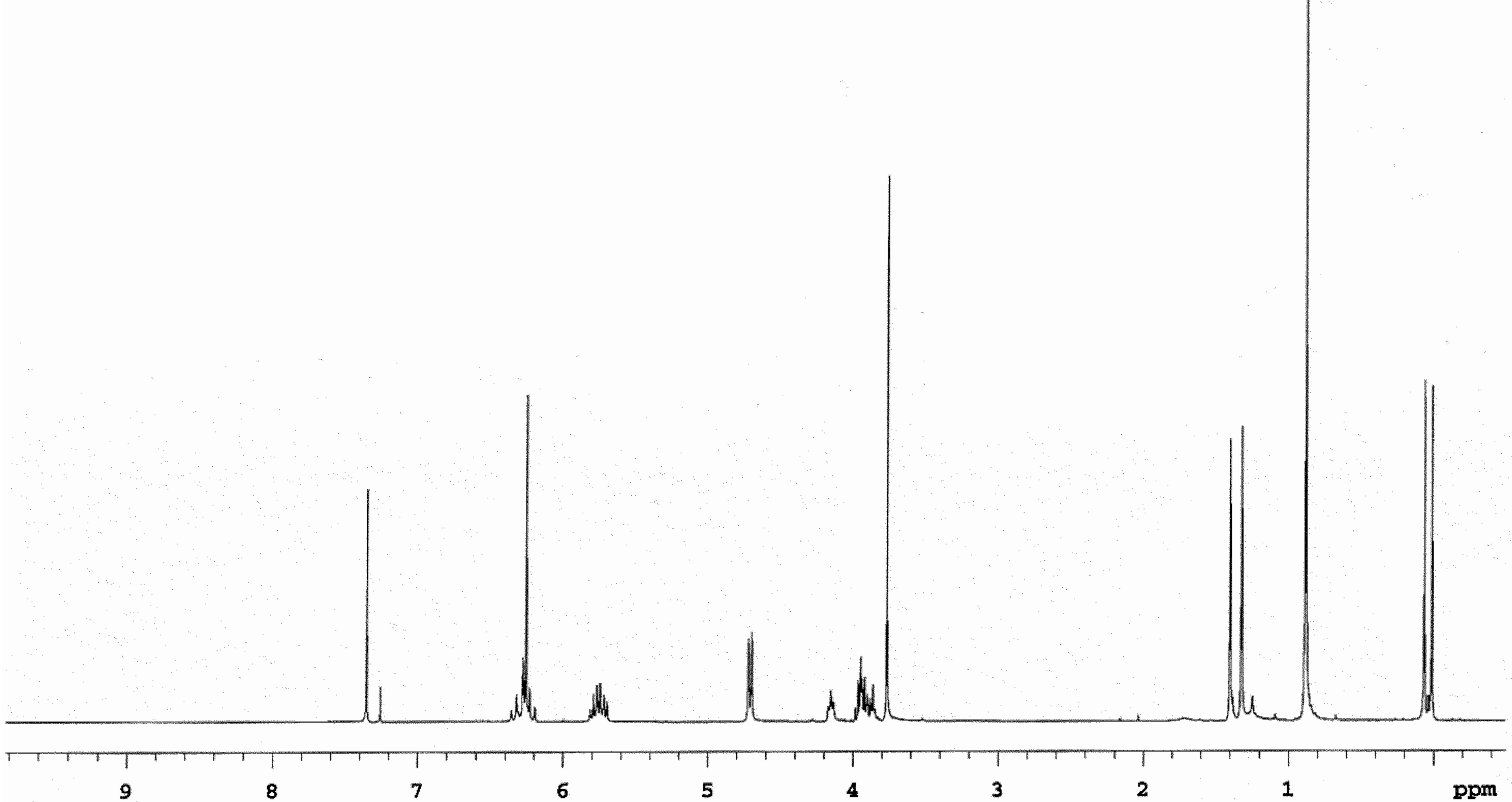


25

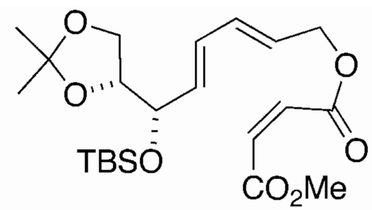
500 MHz ¹H NMR spectrum in $CDCl_3$



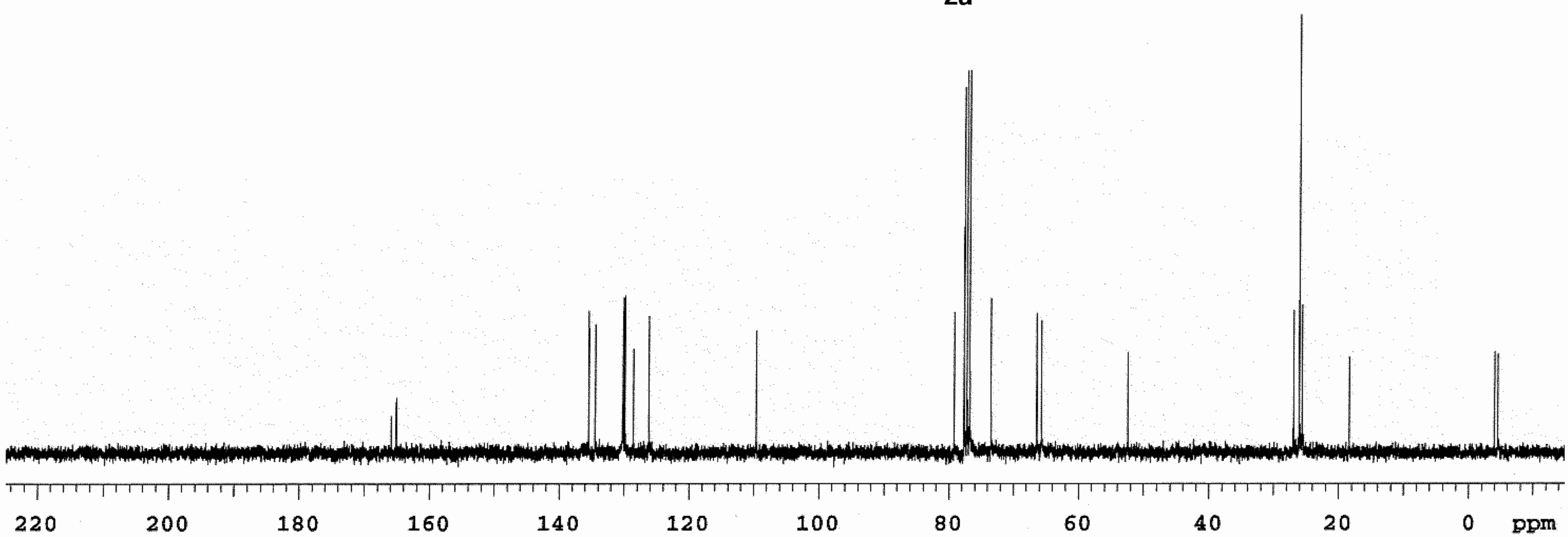
2a



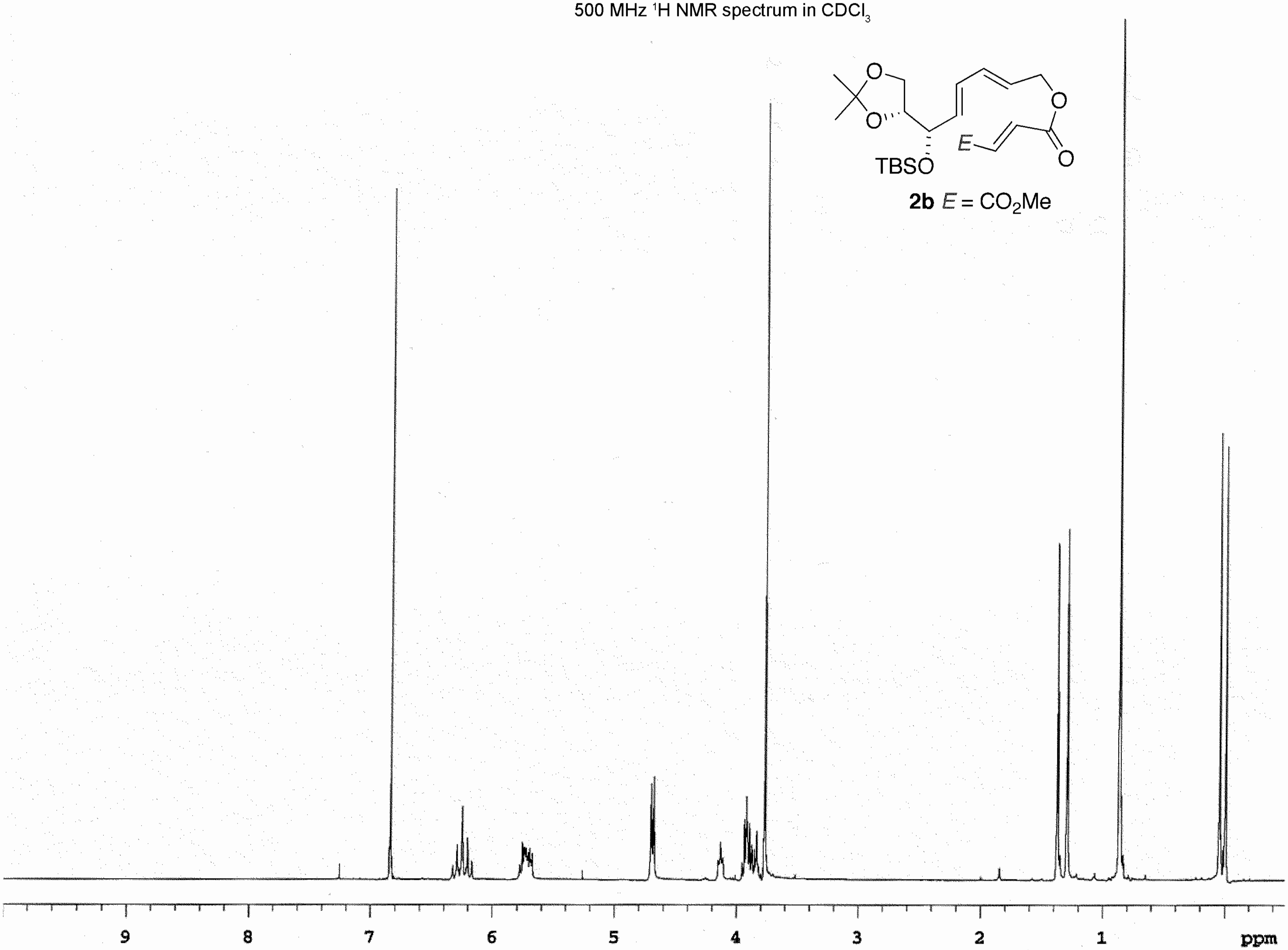
125 MHz ^{13}C NMR spectrum in $CDCl_3$



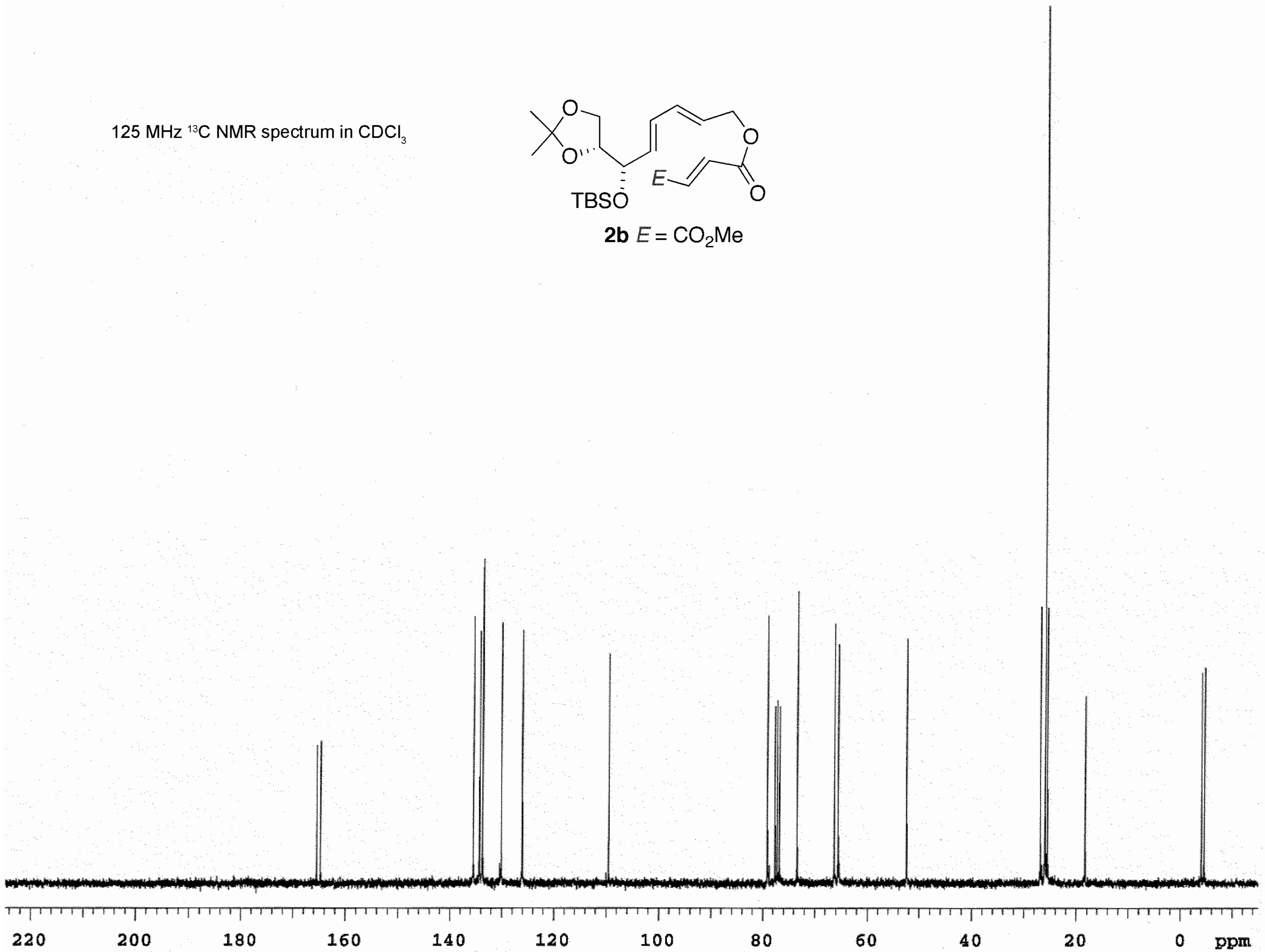
2a



500 MHz ^{1}H NMR spectrum in $CDCl_3$

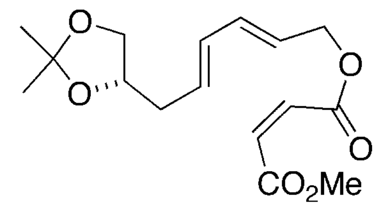


125 MHz ^{13}C NMR spectrum in $CDCl_3$

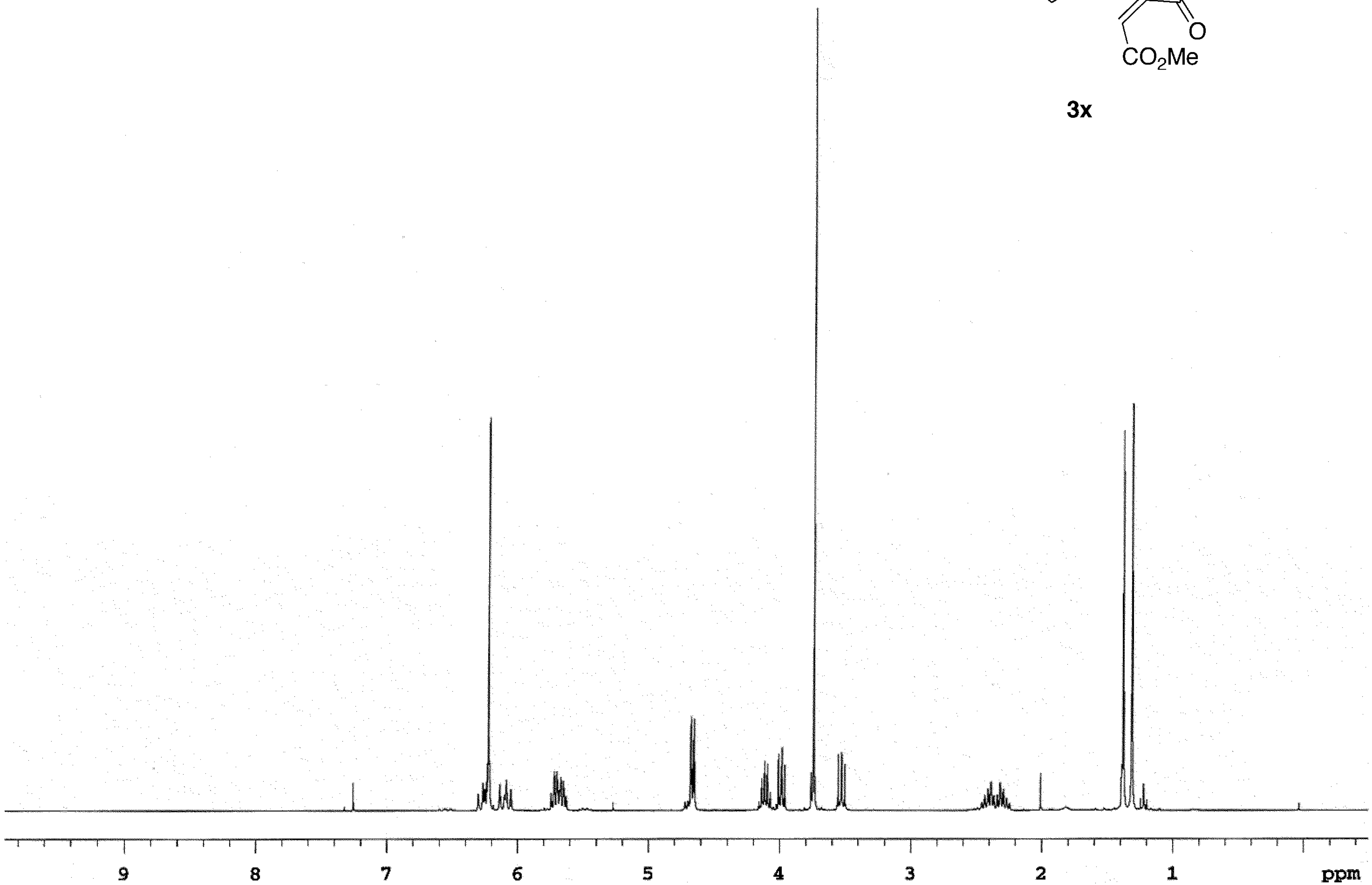


2b *E* = CO_2Me

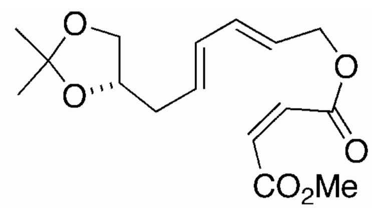
500 MHz ^1H NMR spectrum in $CDCl_3$



3x



125 MHz ^{13}C NMR spectrum in $CDCl_3$



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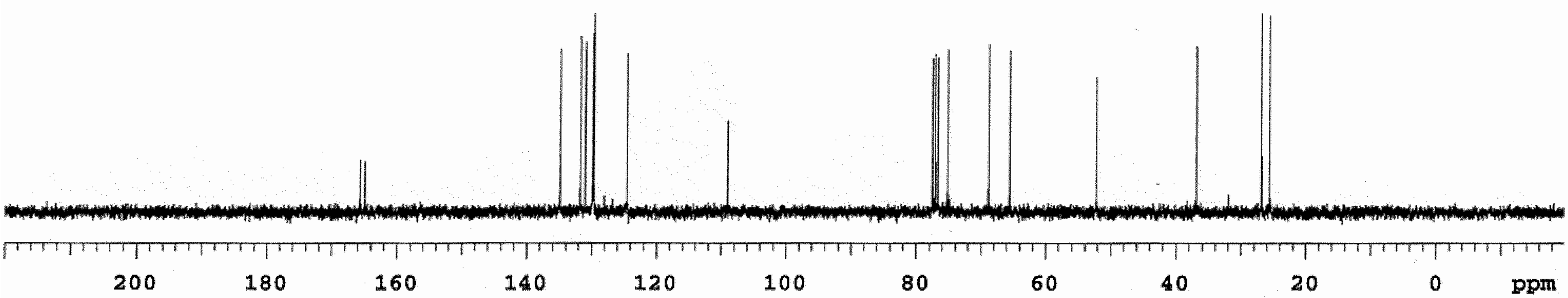
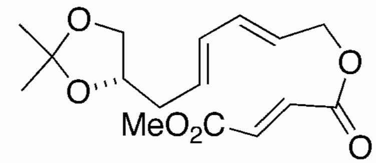
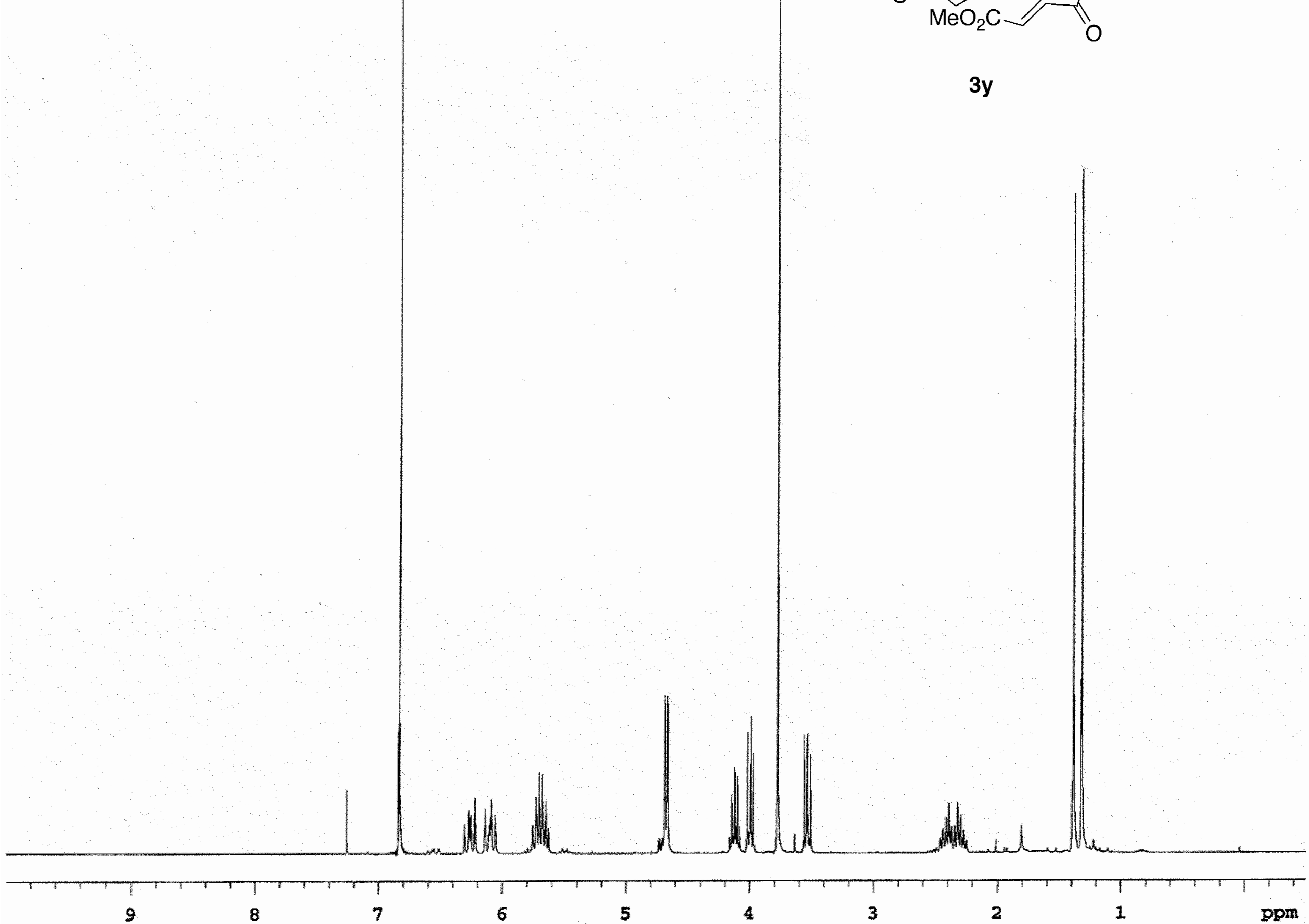


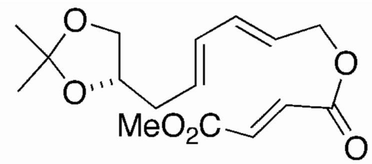
500 MHz ^{1}H NMR spectrum in $CDCl_3$



3y



125 MHz ^{13}C NMR spectrum in $CDCl_3$



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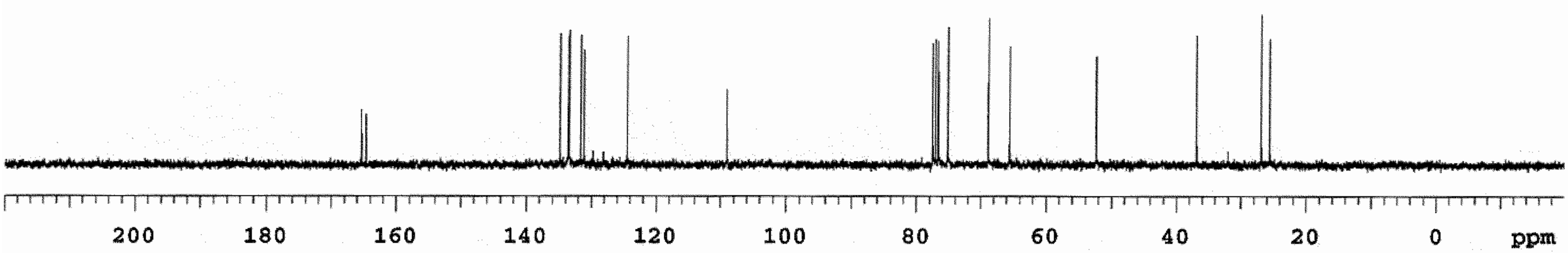
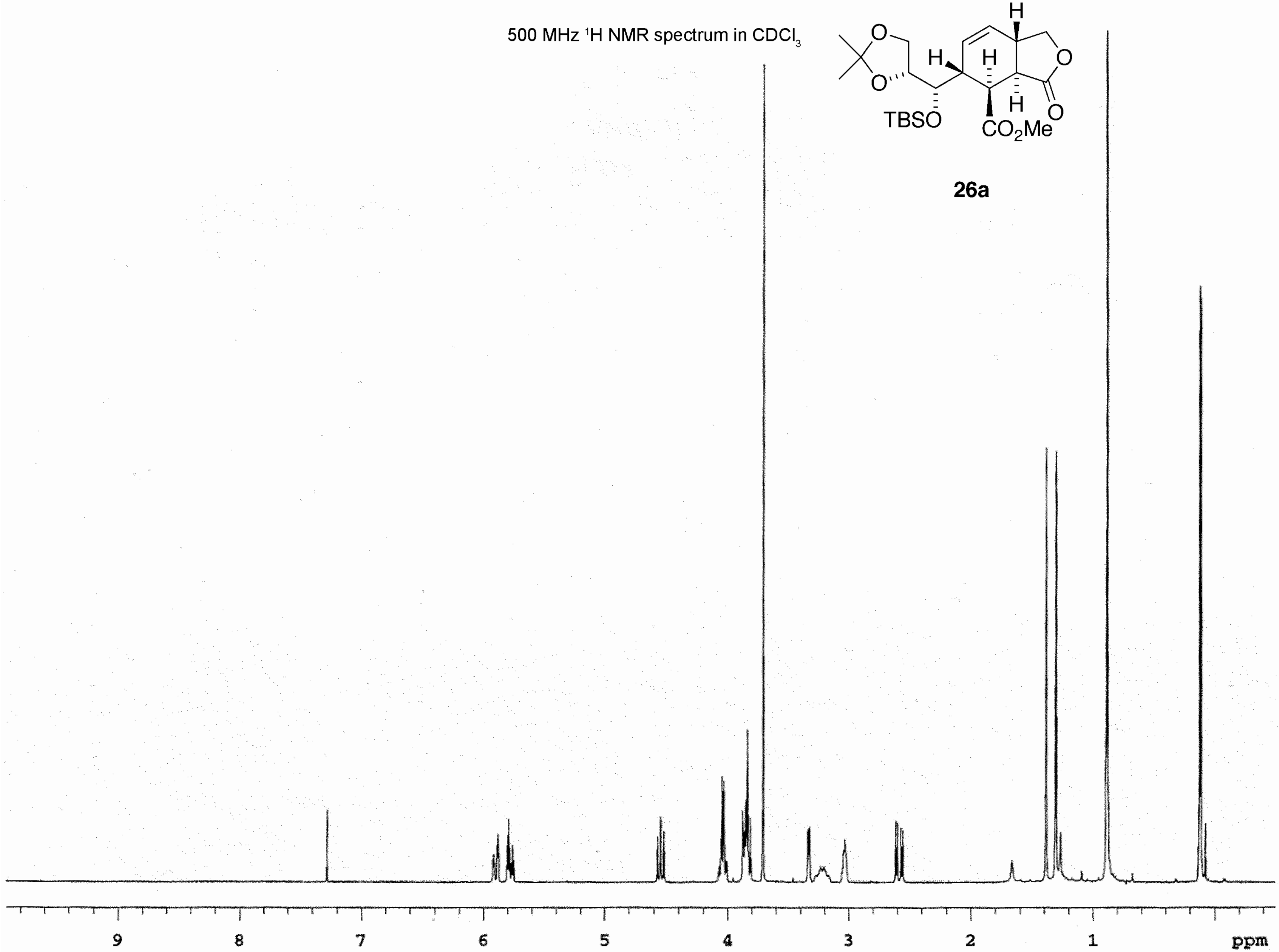
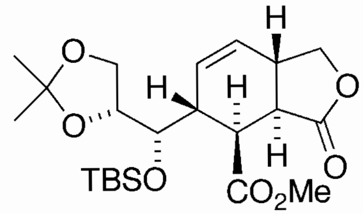


500 MHz ^{1}H NMR spectrum in $CDCl_3$

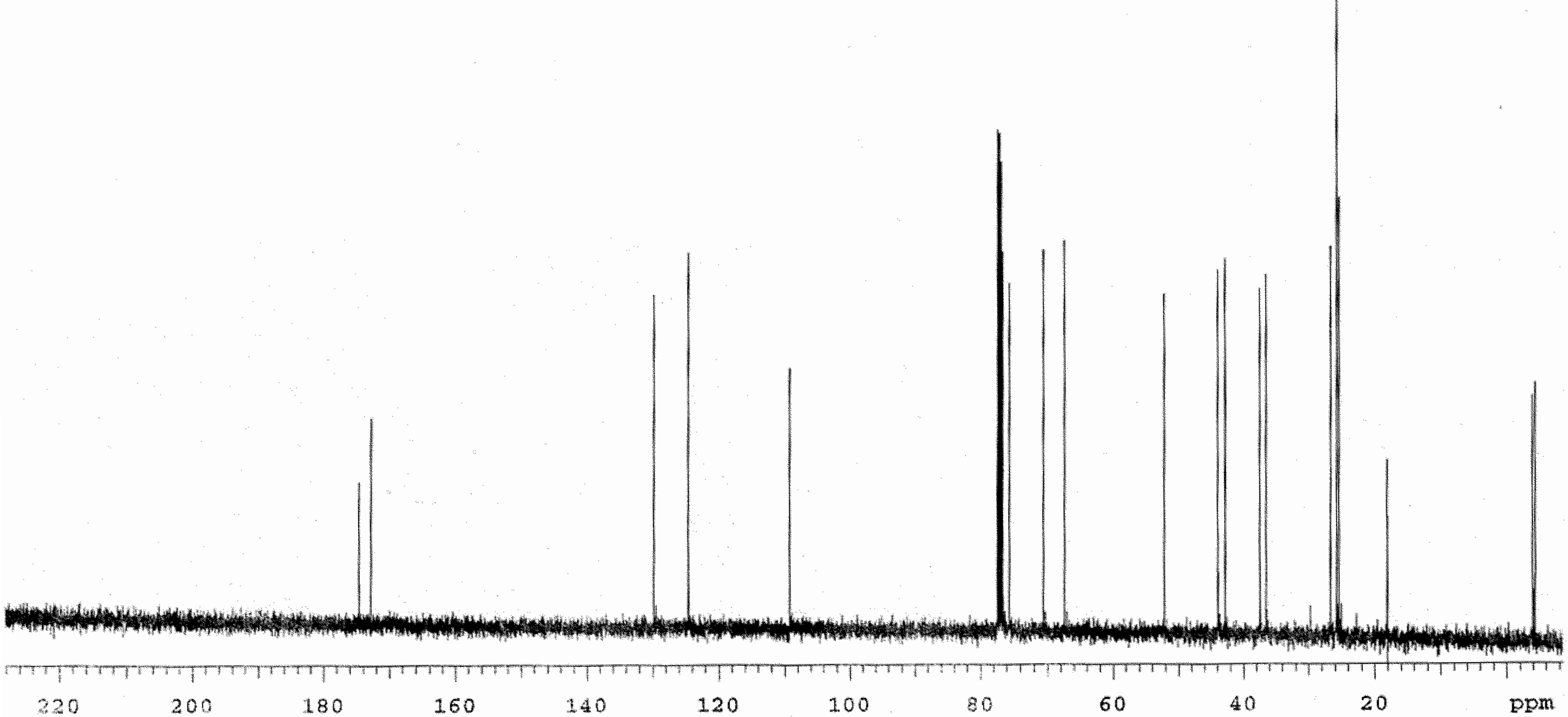


26a

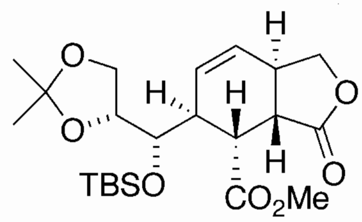
125 MHz ^{13}C NMR spectrum in $CDCl_3$



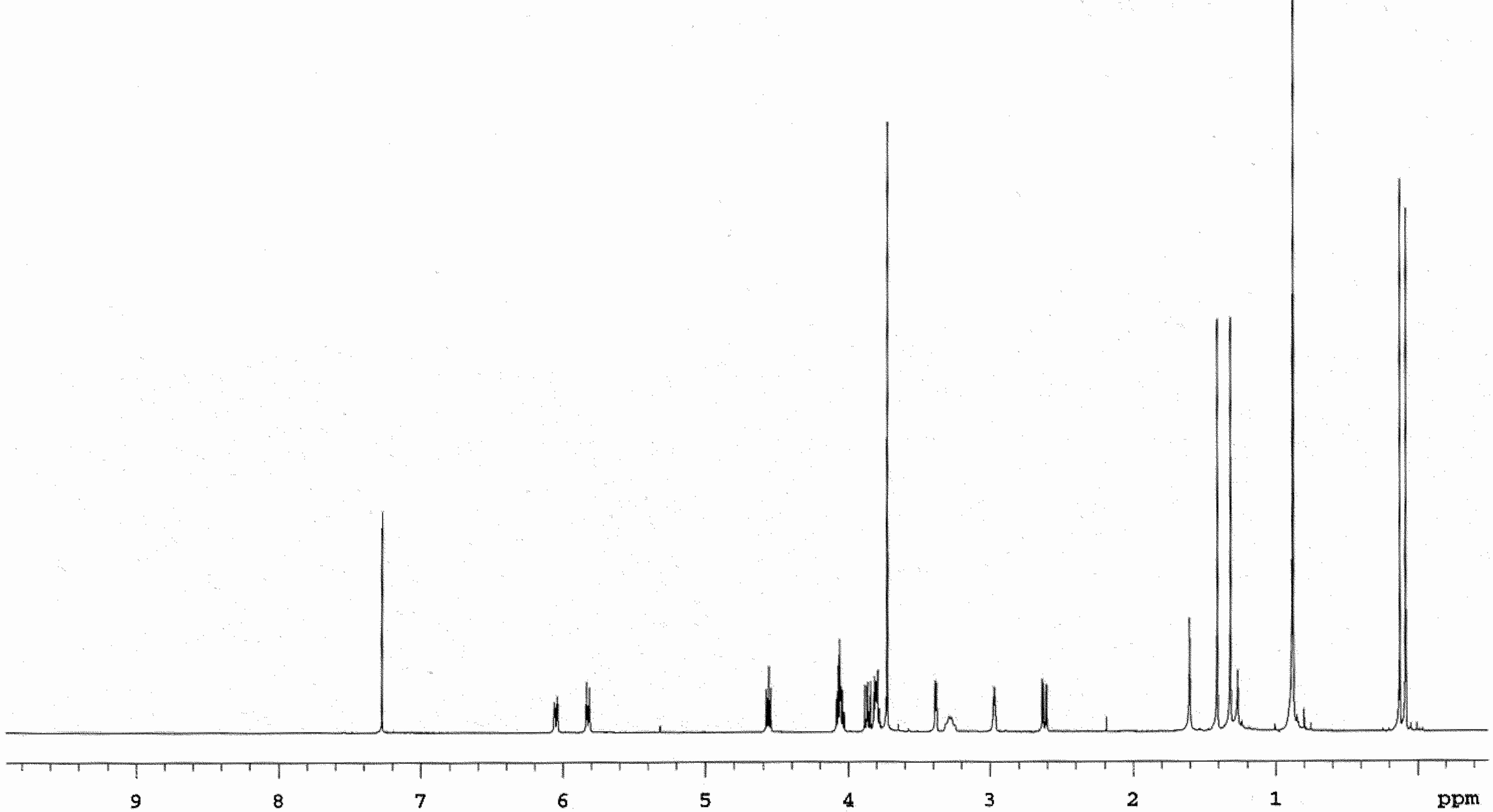
26a



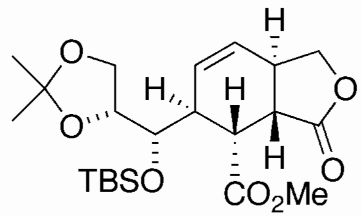
500 MHz ^1H NMR spectrum in $CDCl_3$



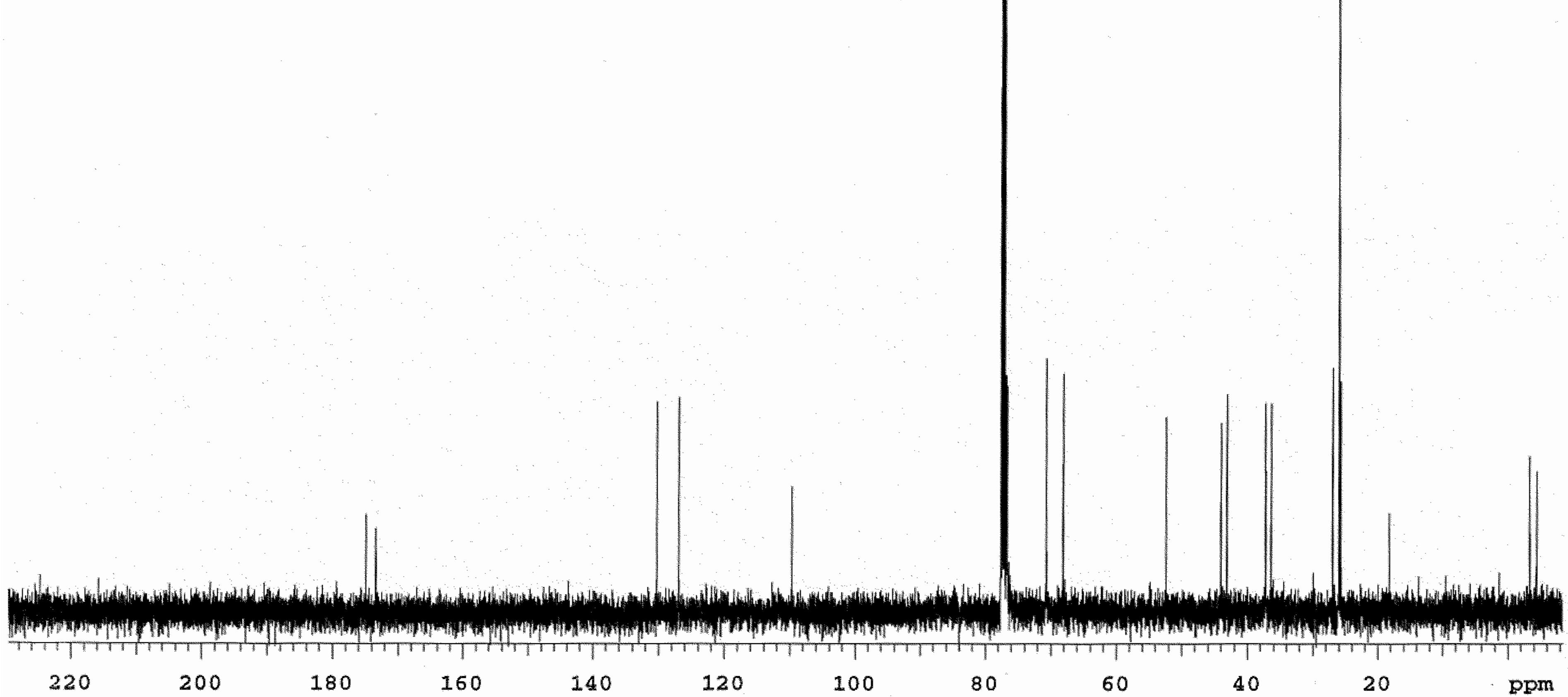
27a



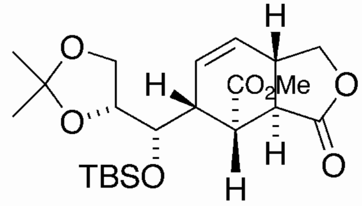
125 MHz ^{13}C NMR spectrum in $CDCl_3$



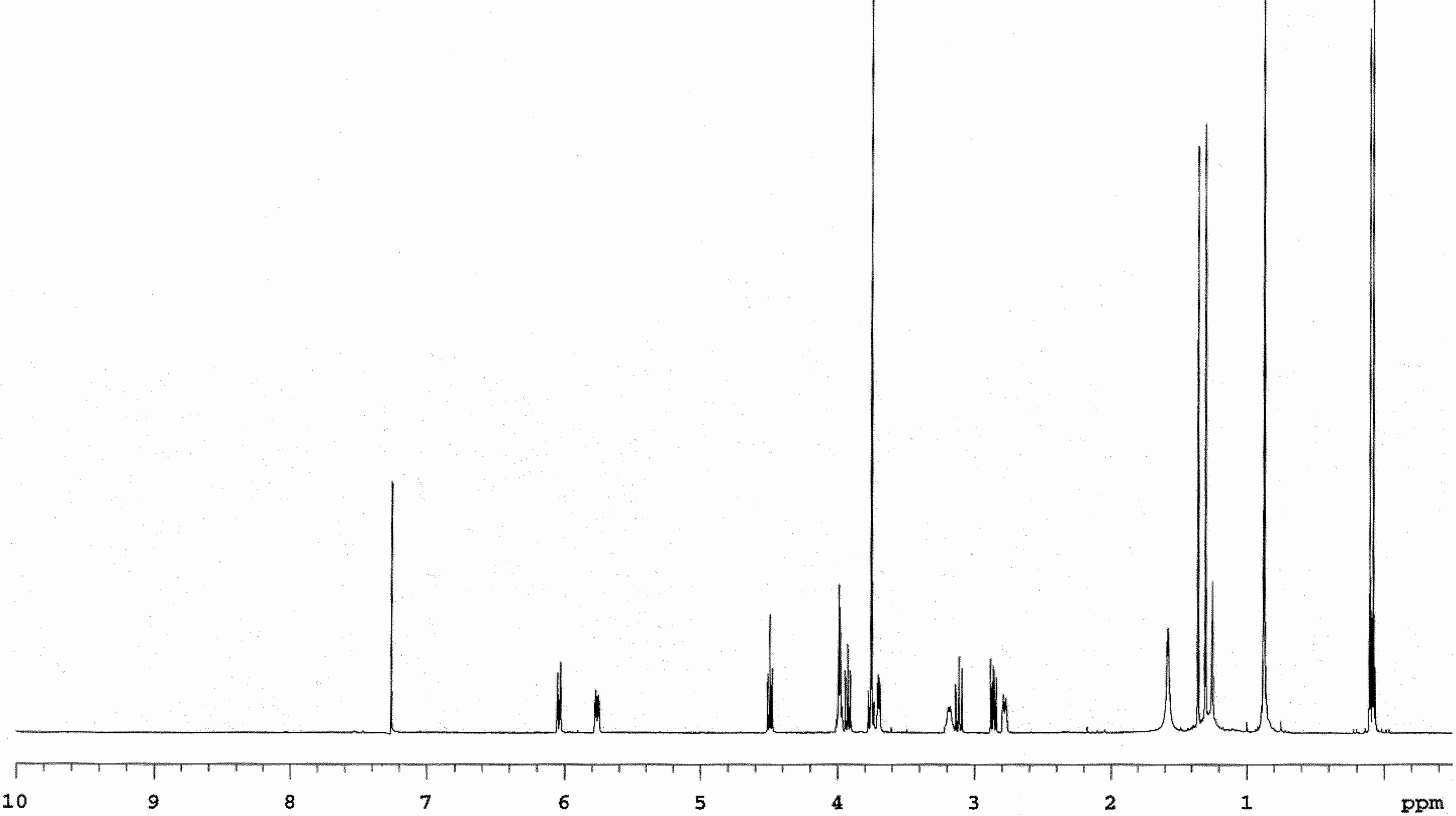
27a



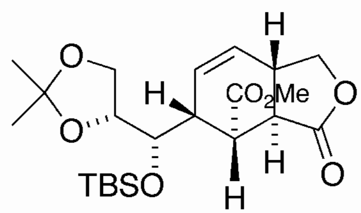
500 MHz ¹H NMR spectrum in $CDCl_3$



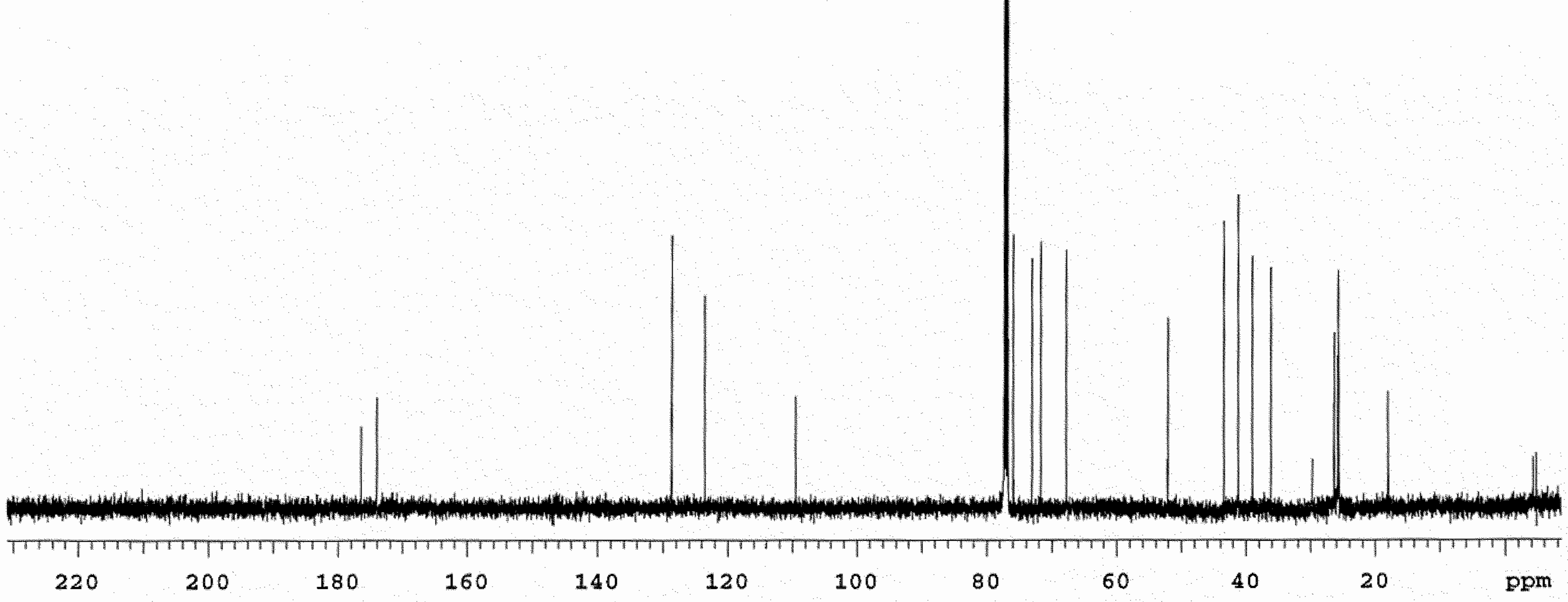
26b



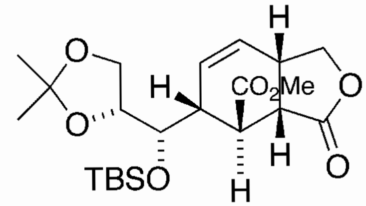
125 MHz ^{13}C NMR spectrum in $CDCl_3$



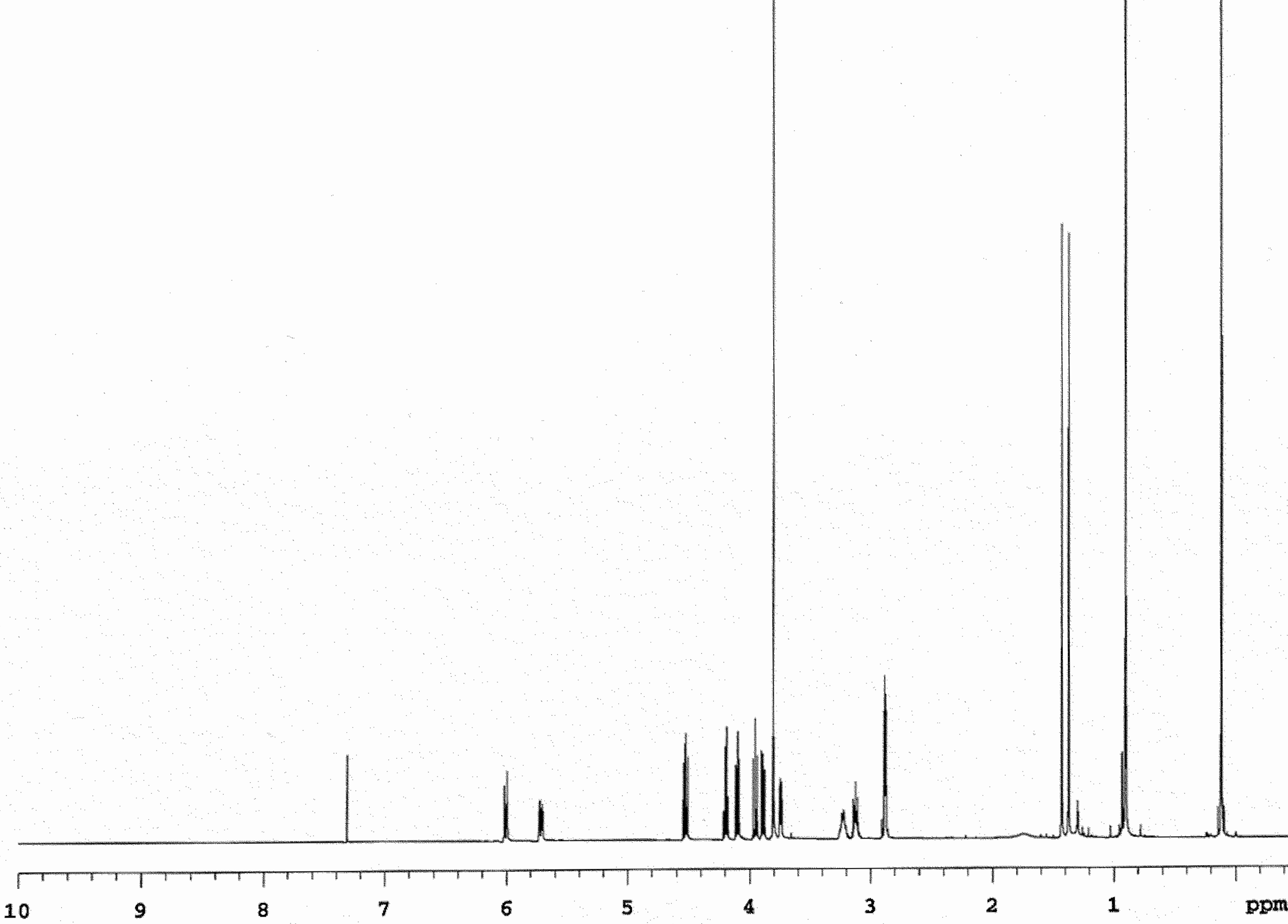
26b



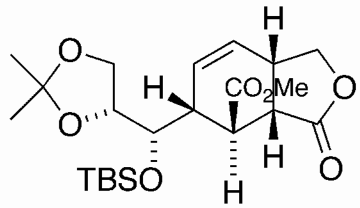
500 MHz ^1H NMR spectrum in $CDCl_3$



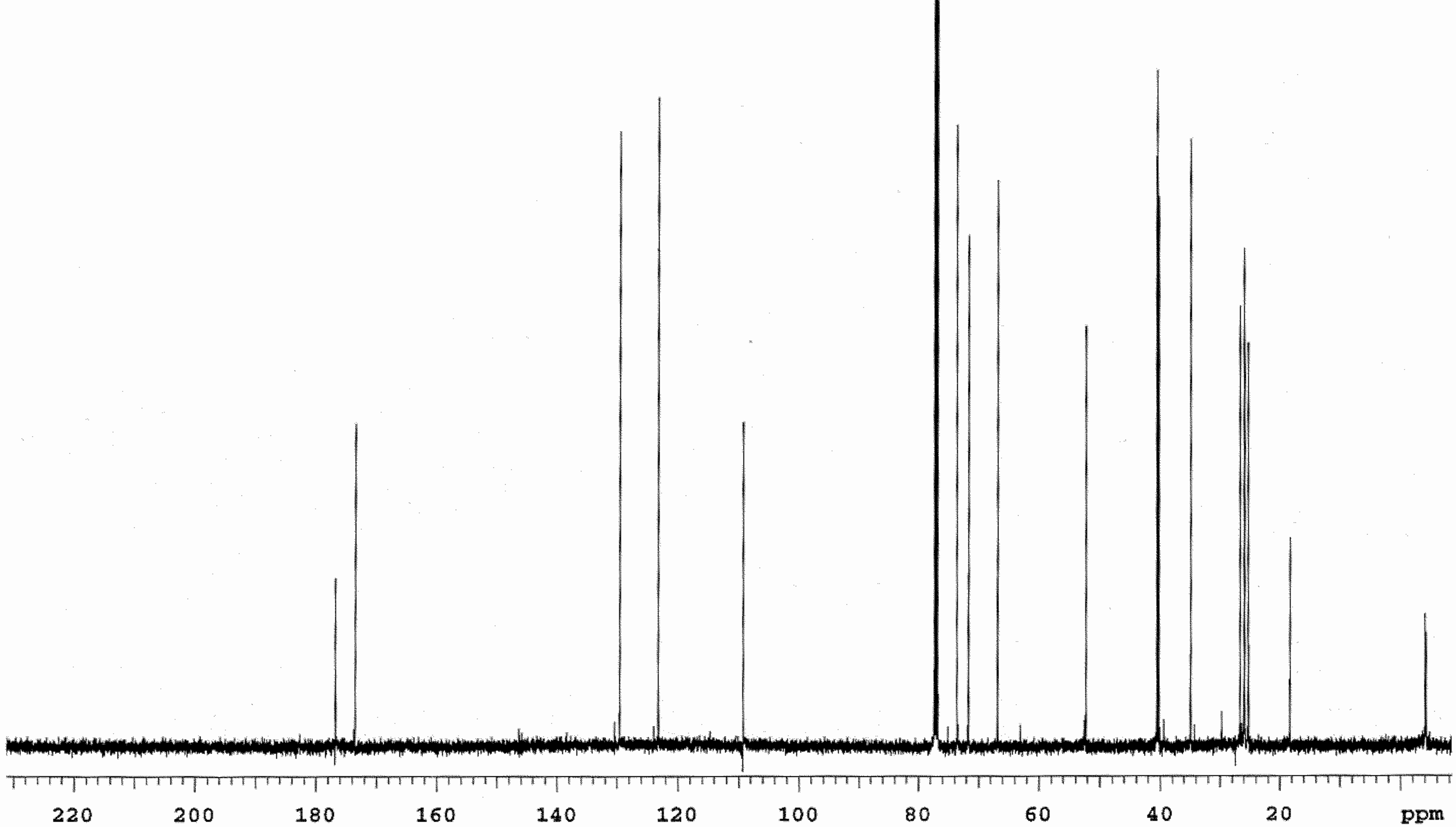
28b



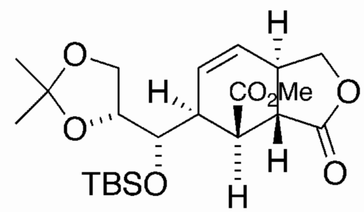
125 MHz ^{13}C NMR spectrum in $CDCl_3$



28b



500 MHz ¹H NMR spectrum in C_6D_6



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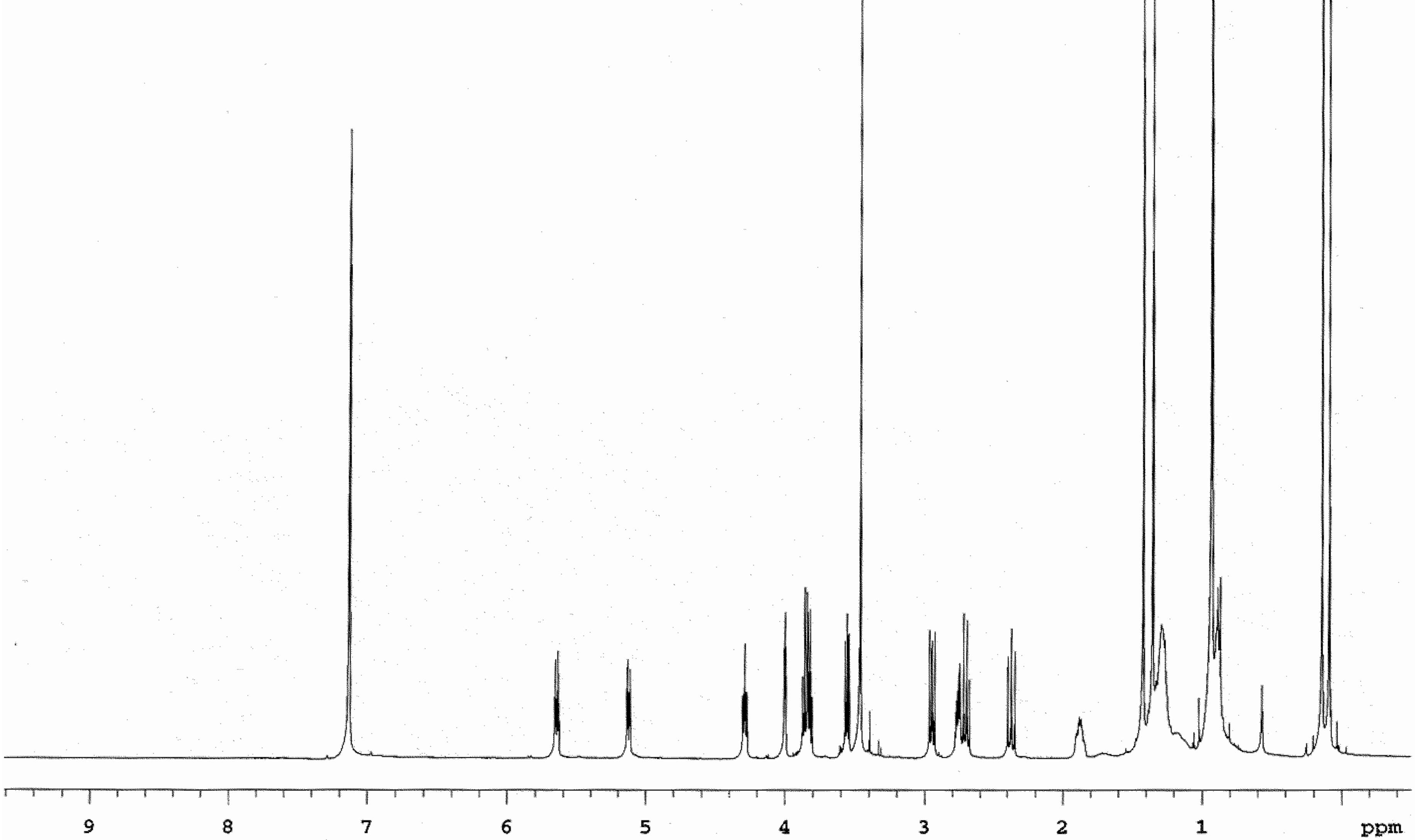
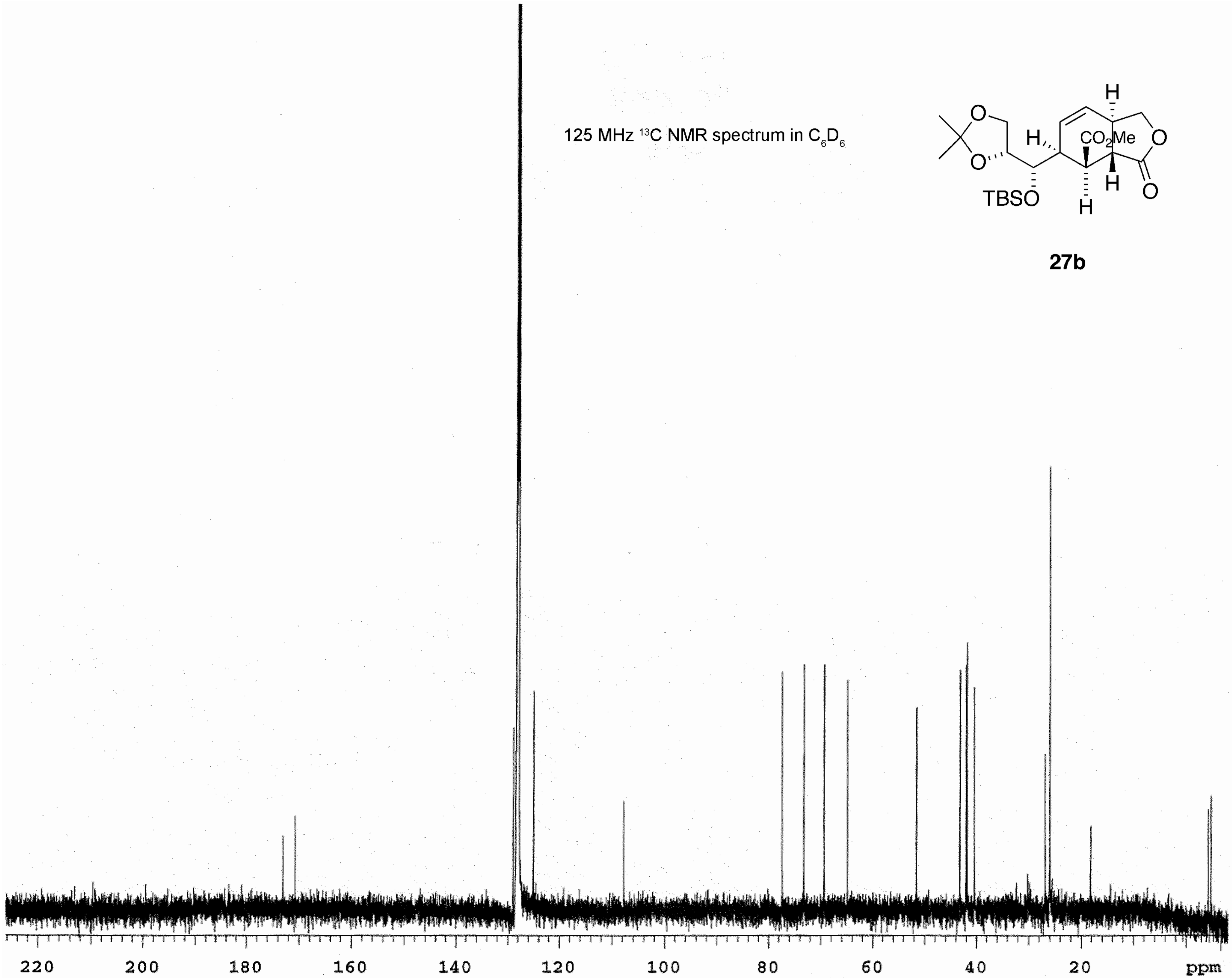
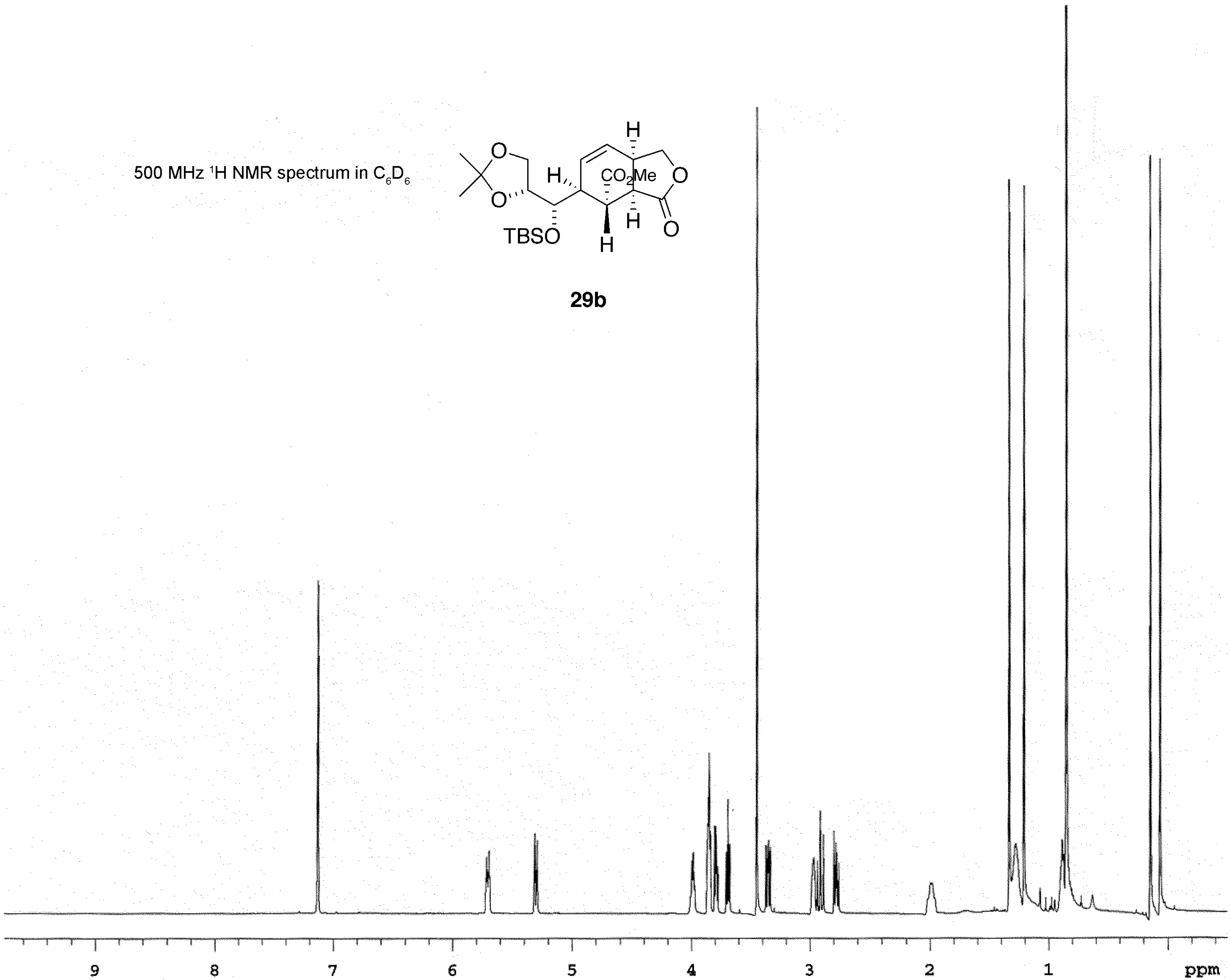
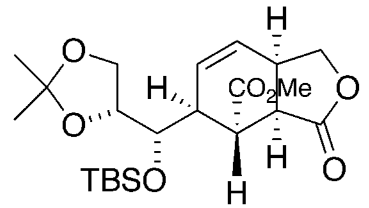



125 MHz ¹³C NMR spectrum in C₆D₆
TBSO
CO₂Me
H
O
27b
220
200
180
160
140
120
100
80
60
40
20
ppm

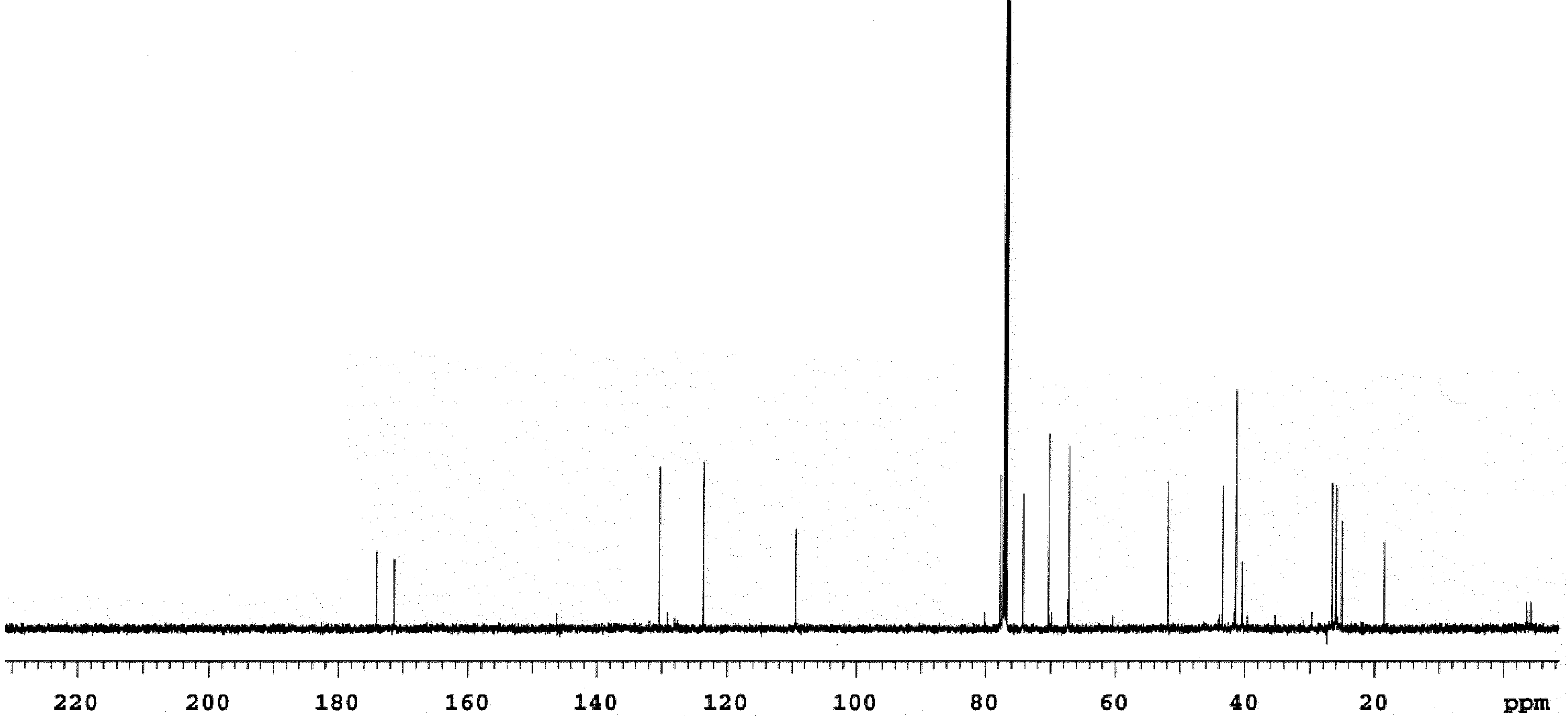
500 MHz ^{1}H NMR spectrum in C_6D_6



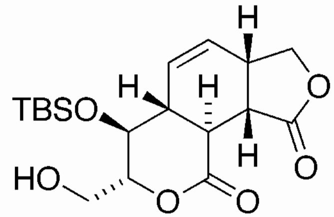
125 MHz ^{13}C NMR spectrum in $CDCl_3$



29b



500 MHz ^{1}H NMR spectrum in $CDCl_3$



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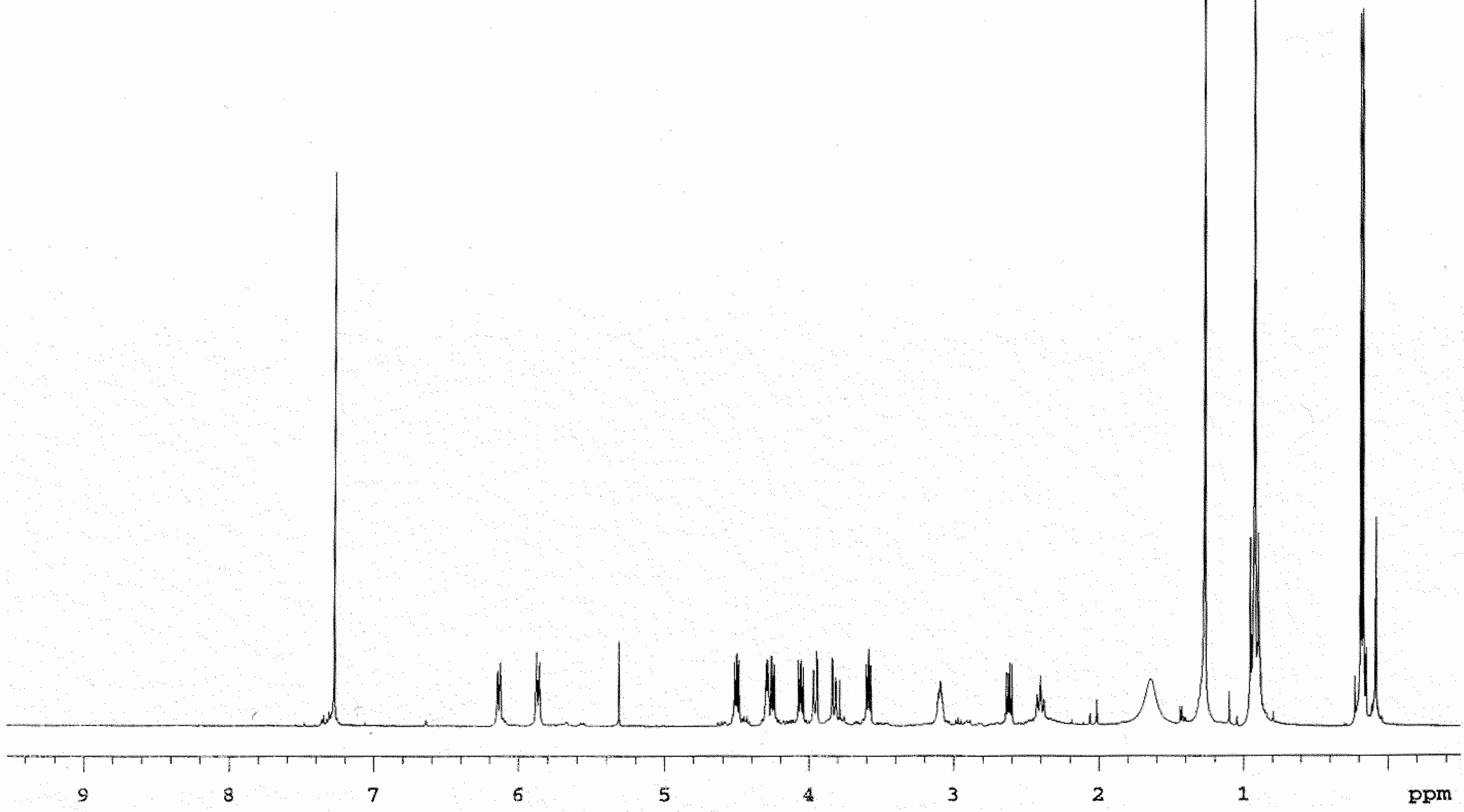
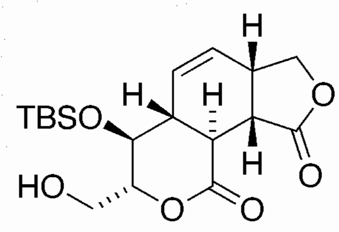


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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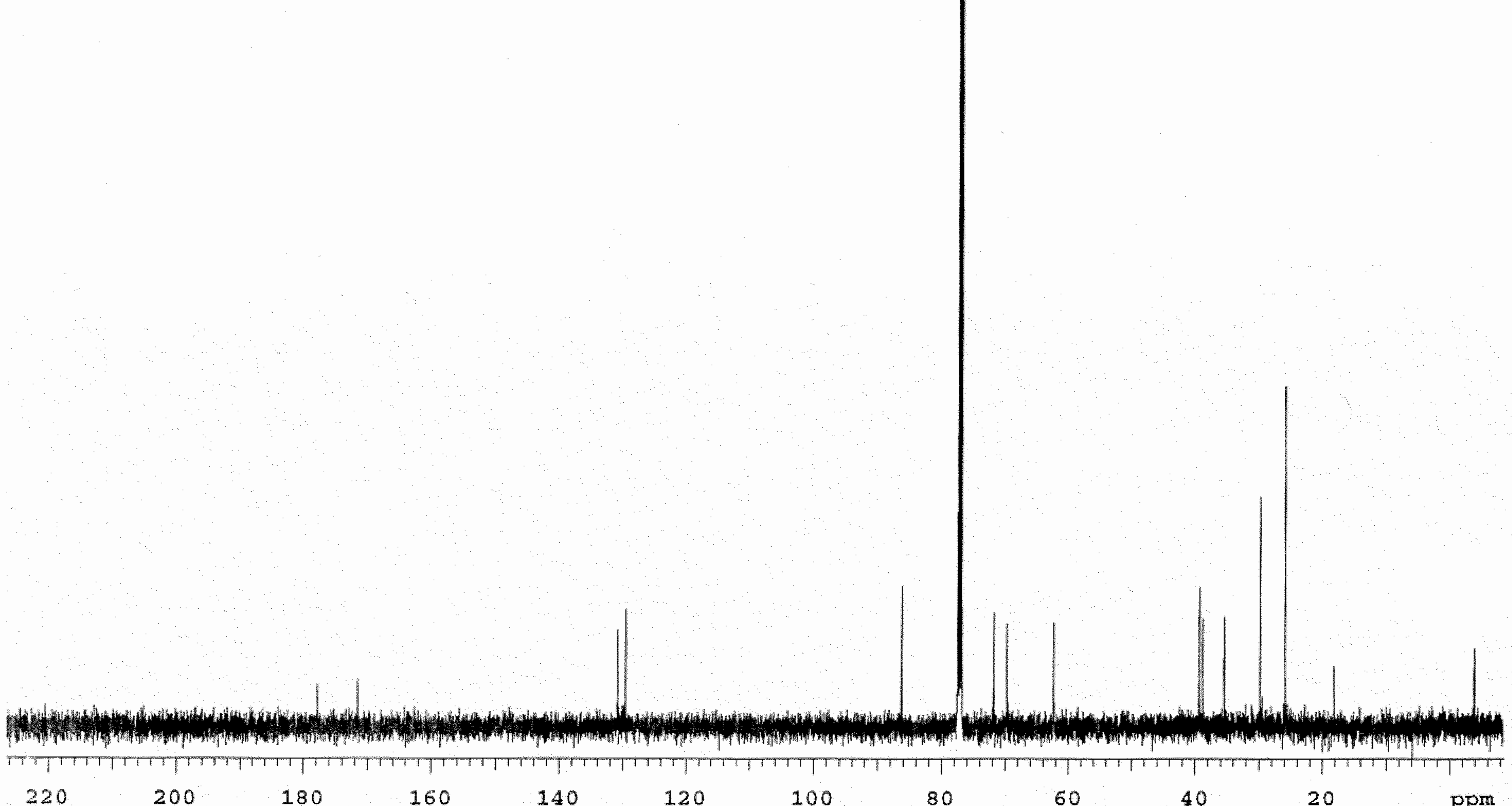
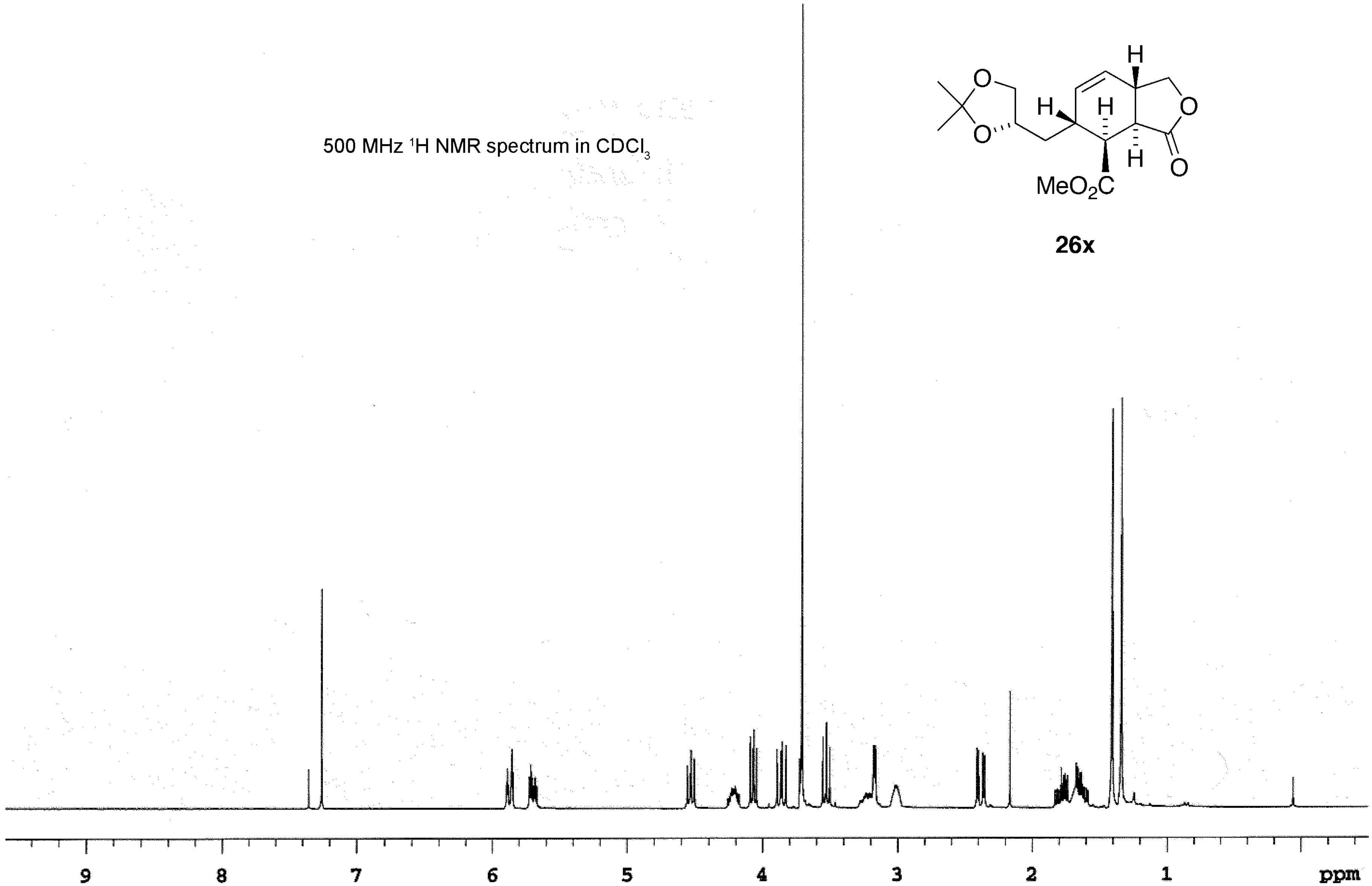
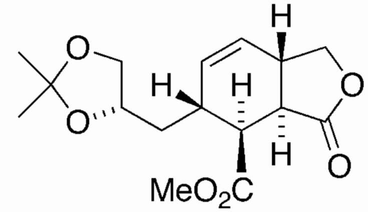


500 MHz ^{1}H NMR spectrum in $CDCl_3$

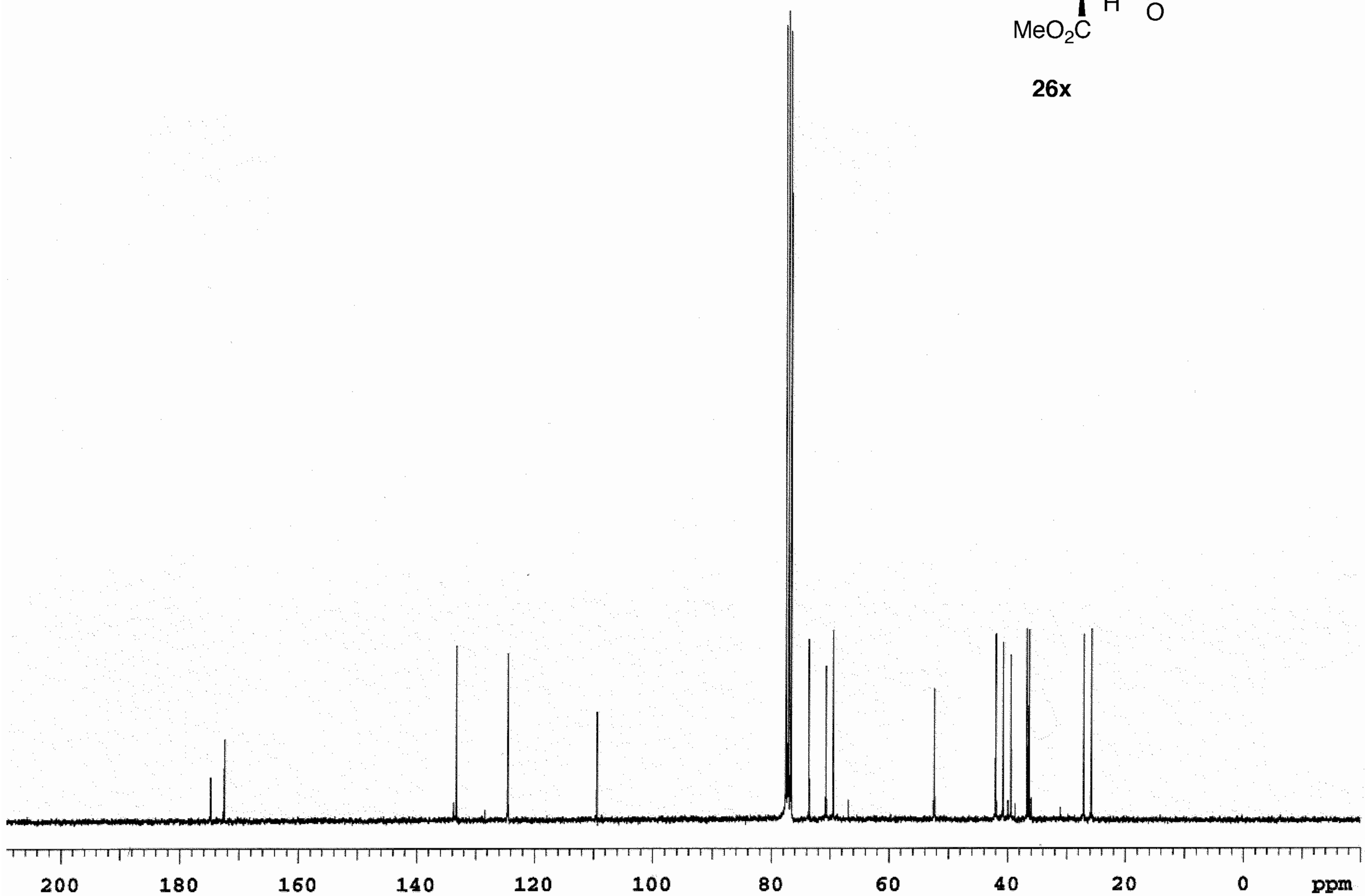


26x

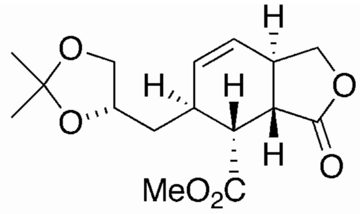
125 MHz ^{13}C NMR spectrum in $CDCl_3$



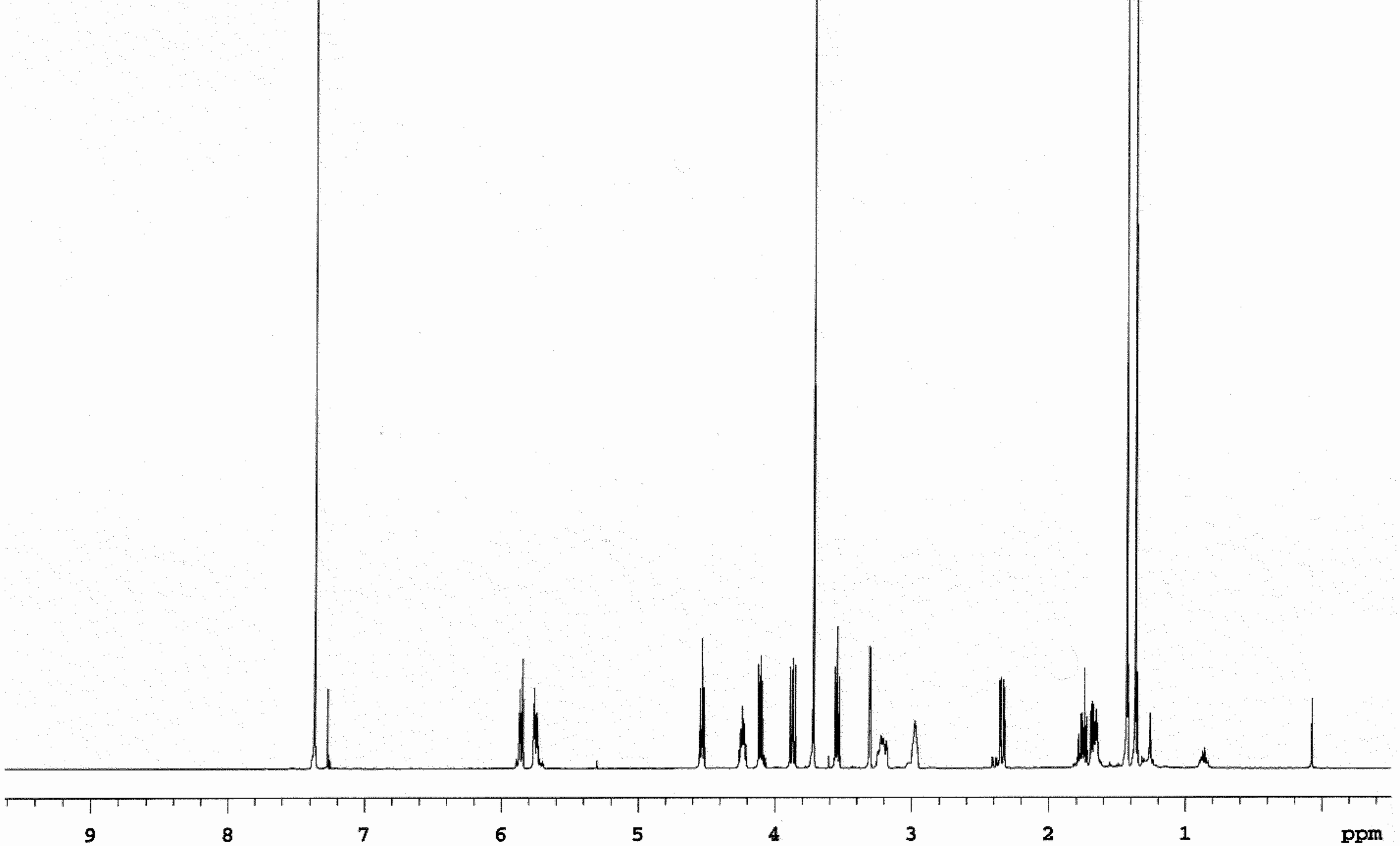
26x



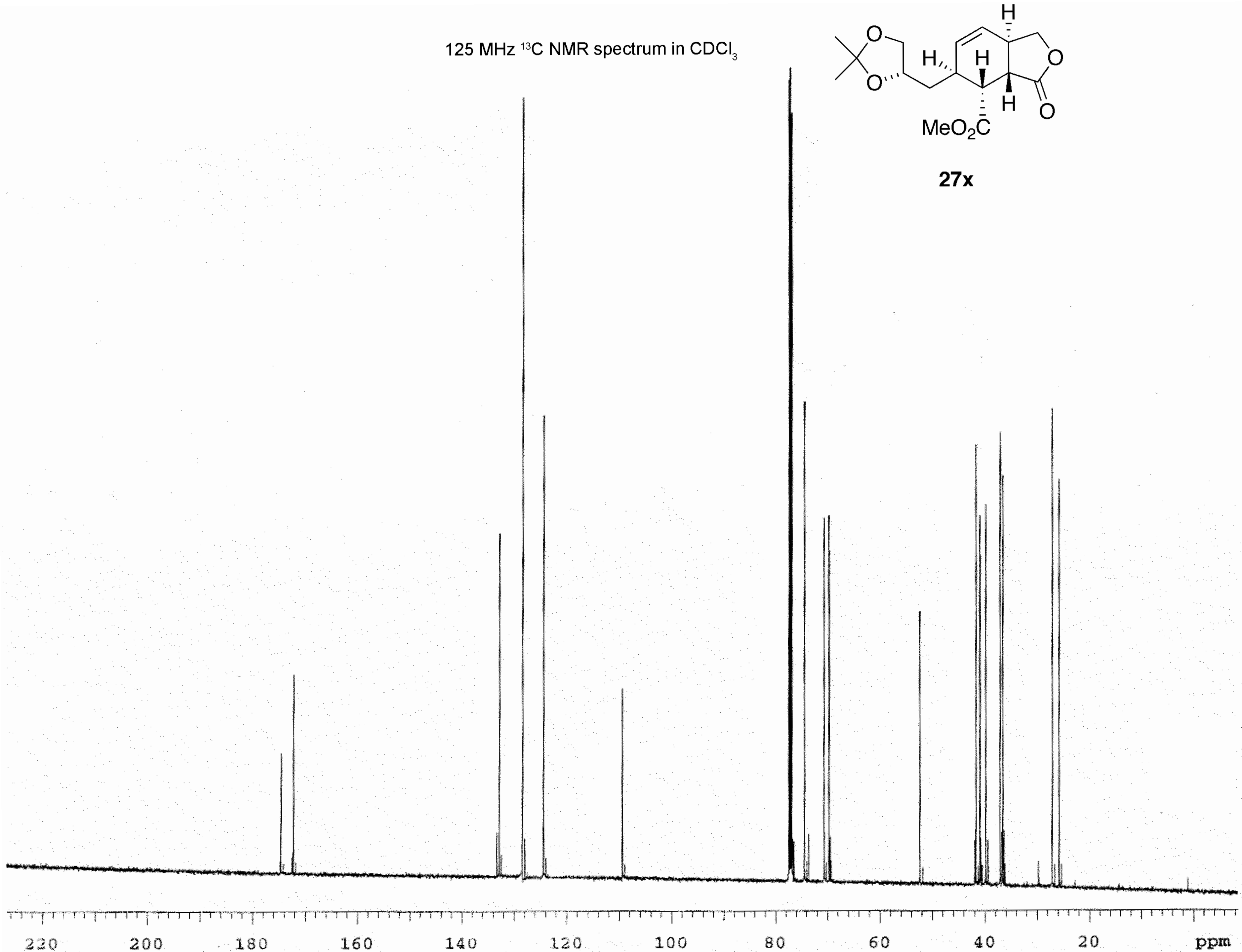
500 MHz ^1H NMR spectrum in $CDCl_3$



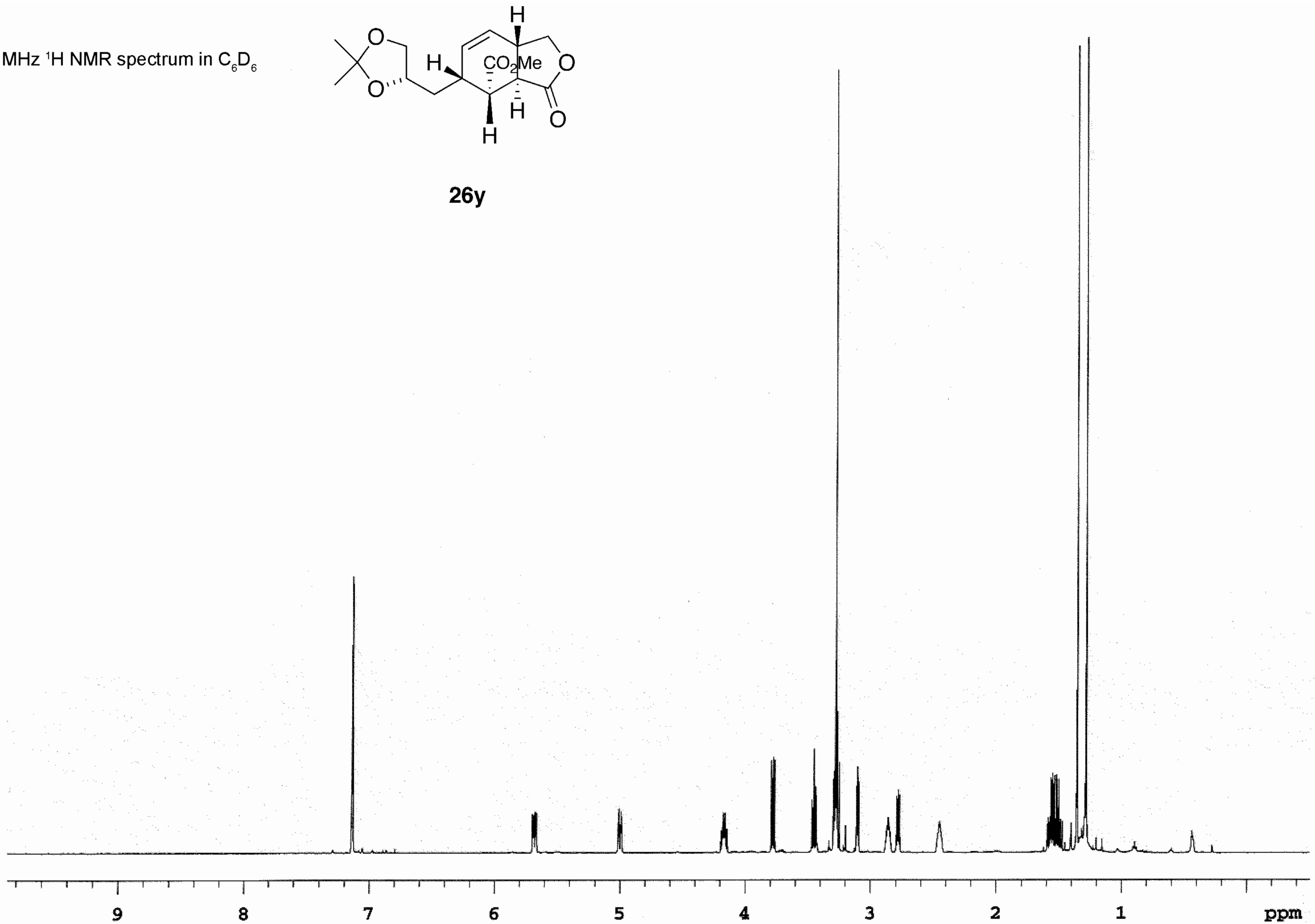
27x



125 MHz ^{13}C NMR spectrum in $CDCl_3$

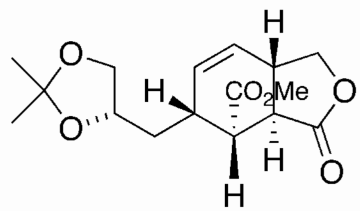


500 MHz ^{1}H NMR spectrum in C_6D_6

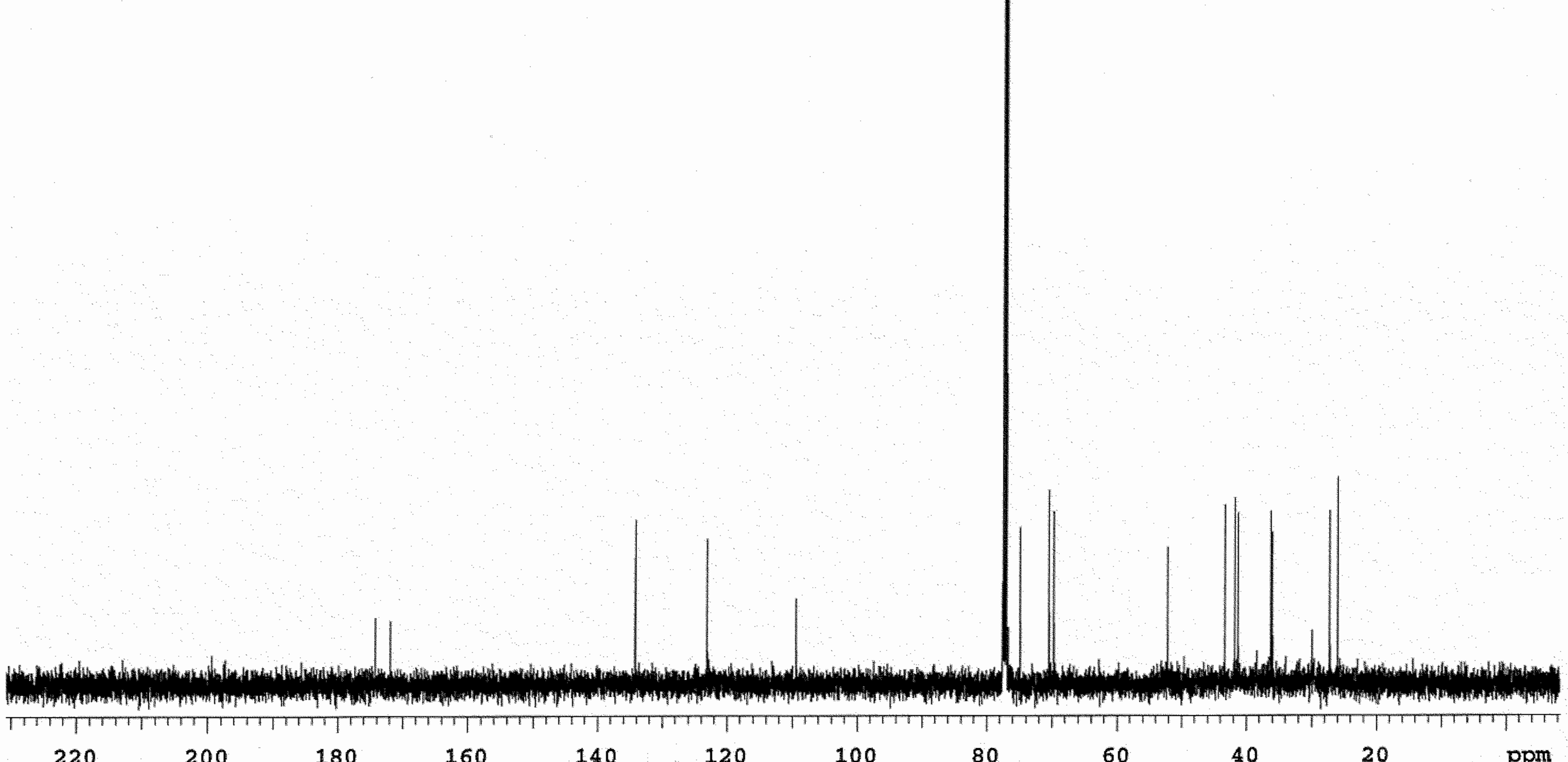


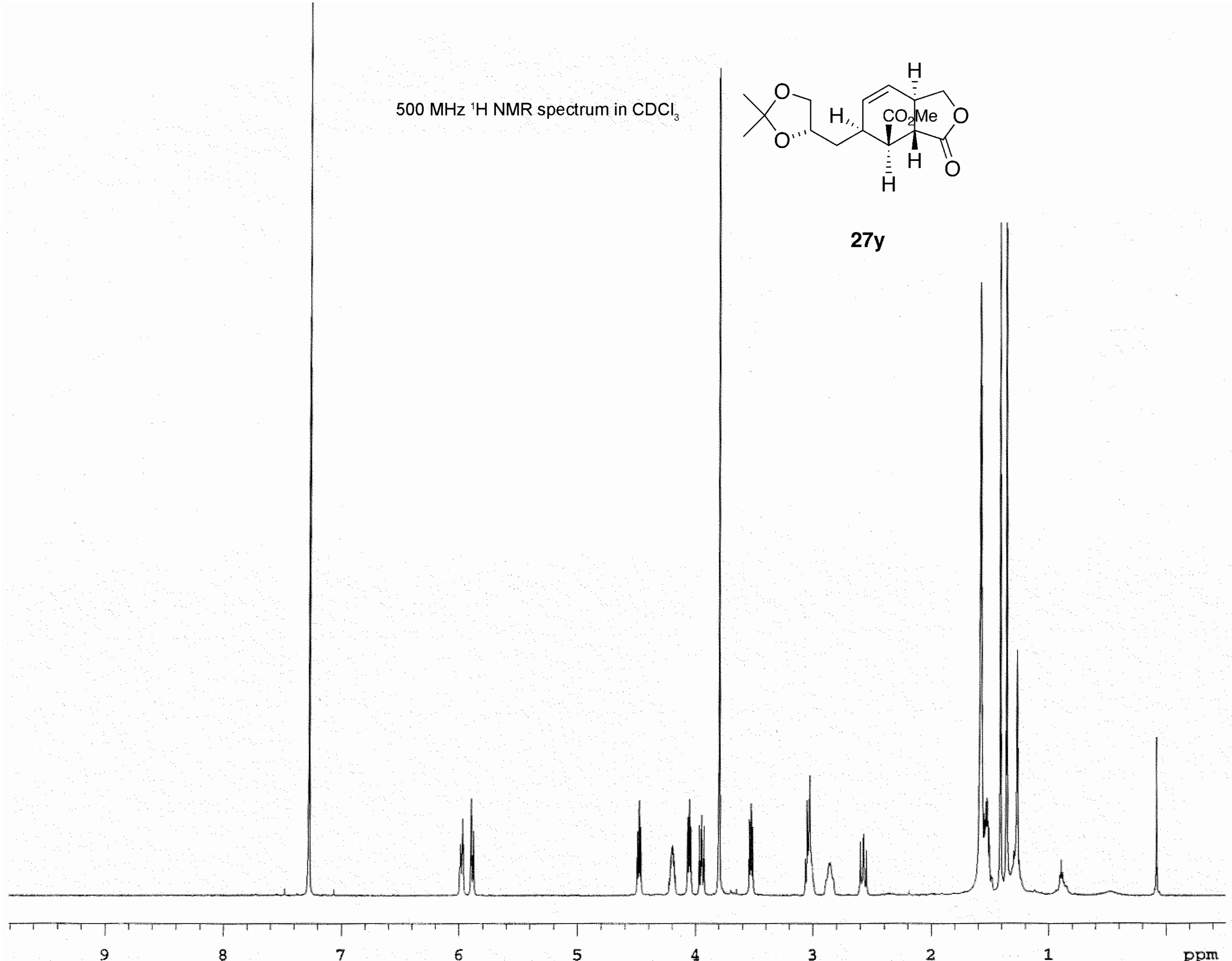
26y

125 MHz ^{13}C NMR spectrum in $CDCl_3$

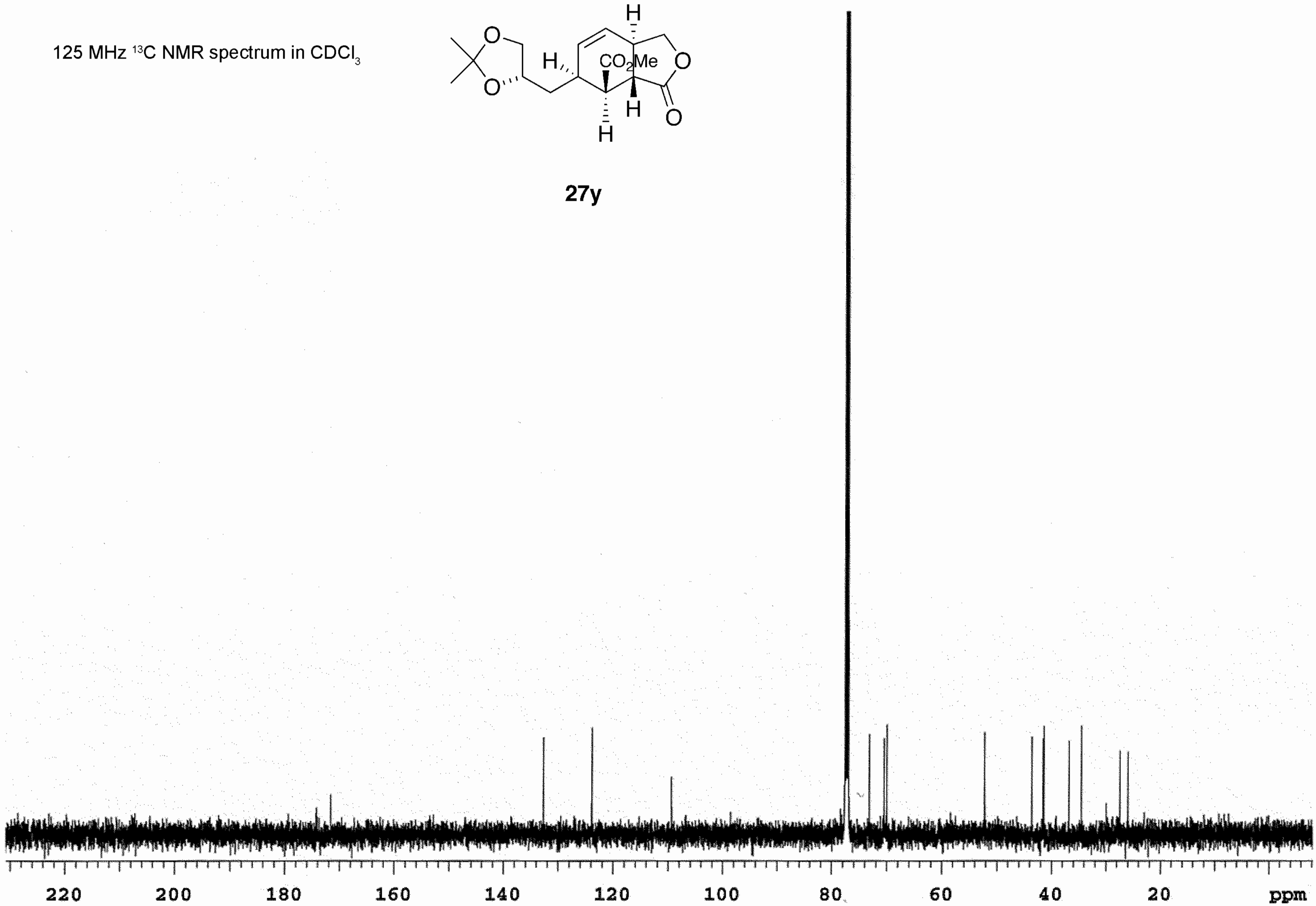


26y



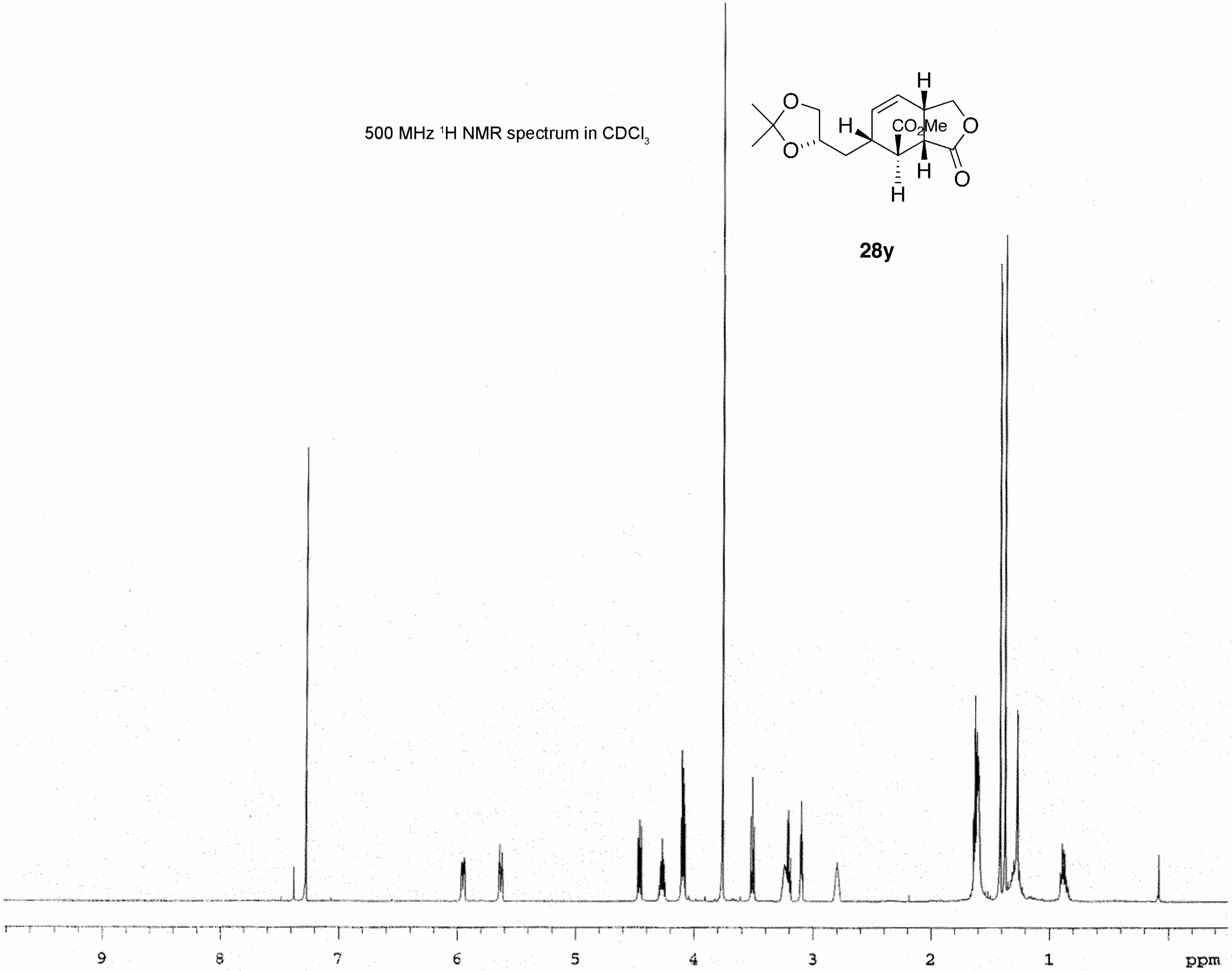

500 MHz ^{1}H NMR spectrum in $CDCl_3$
H
CO_2Me
O
O
O
O
H
H
H
27y
9
8
7
6
5
4
3
2
1
ppm

125 MHz ^{13}C NMR spectrum in $CDCl_3$



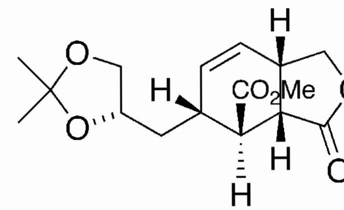
27y

500 MHz ¹H NMR spectrum in $CDCl_3$

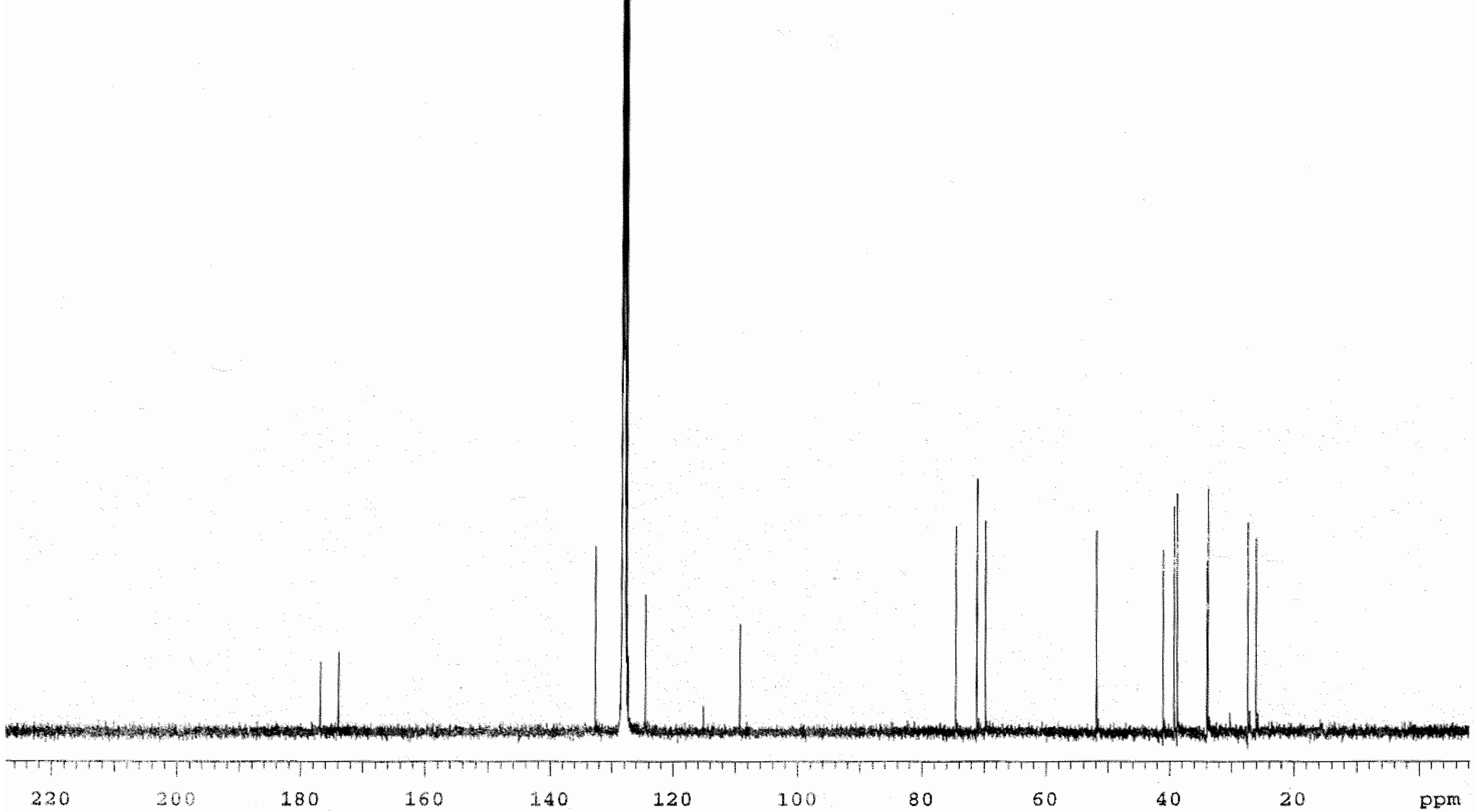


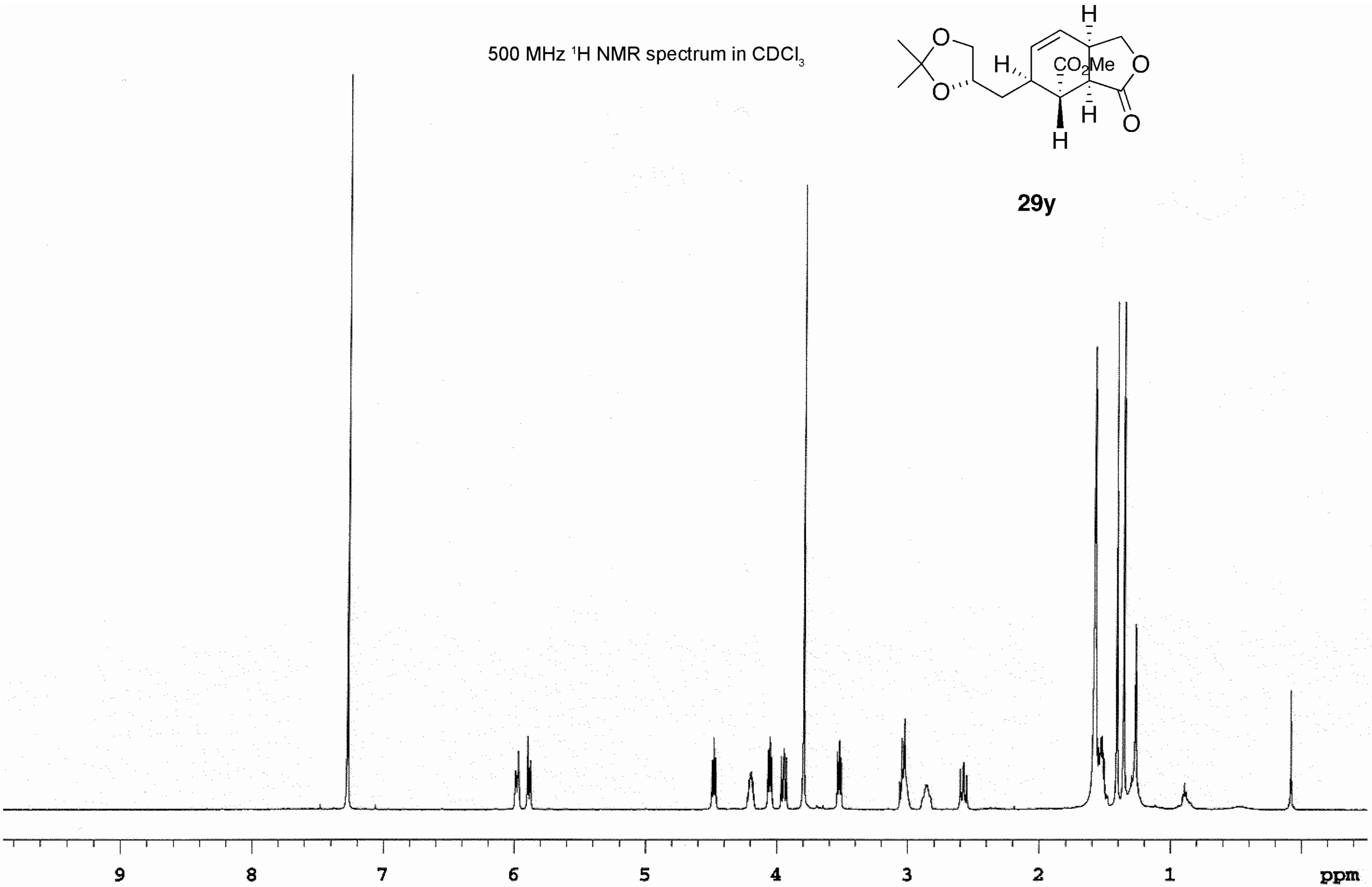
28y

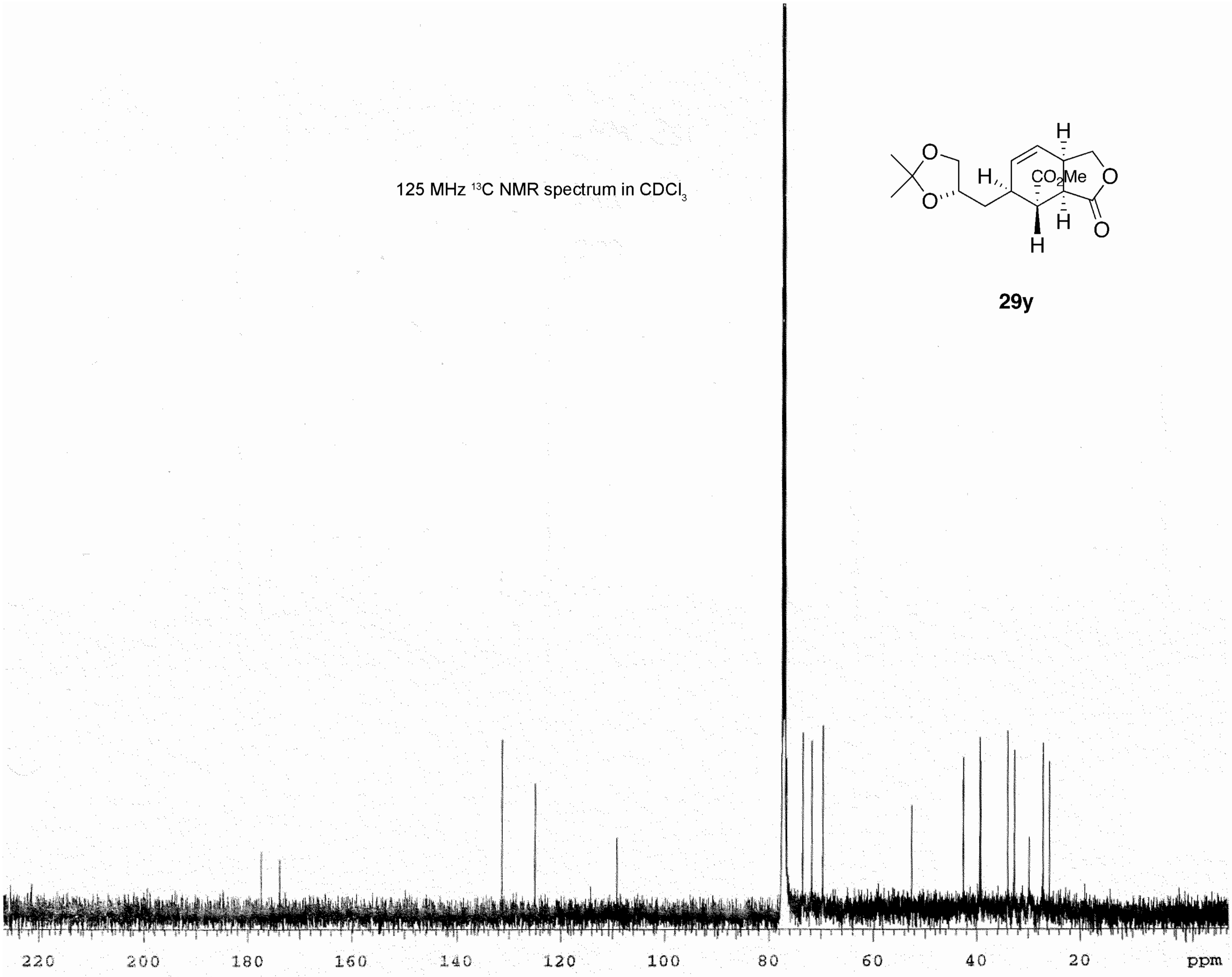
125 MHz ^{13}C NMR spectrum in C_6D_6



28y

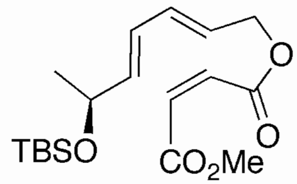



500 MHz ¹H NMR spectrum in CDCl₃
29y
9
8
7
6
5
4
3
2
1
ppm

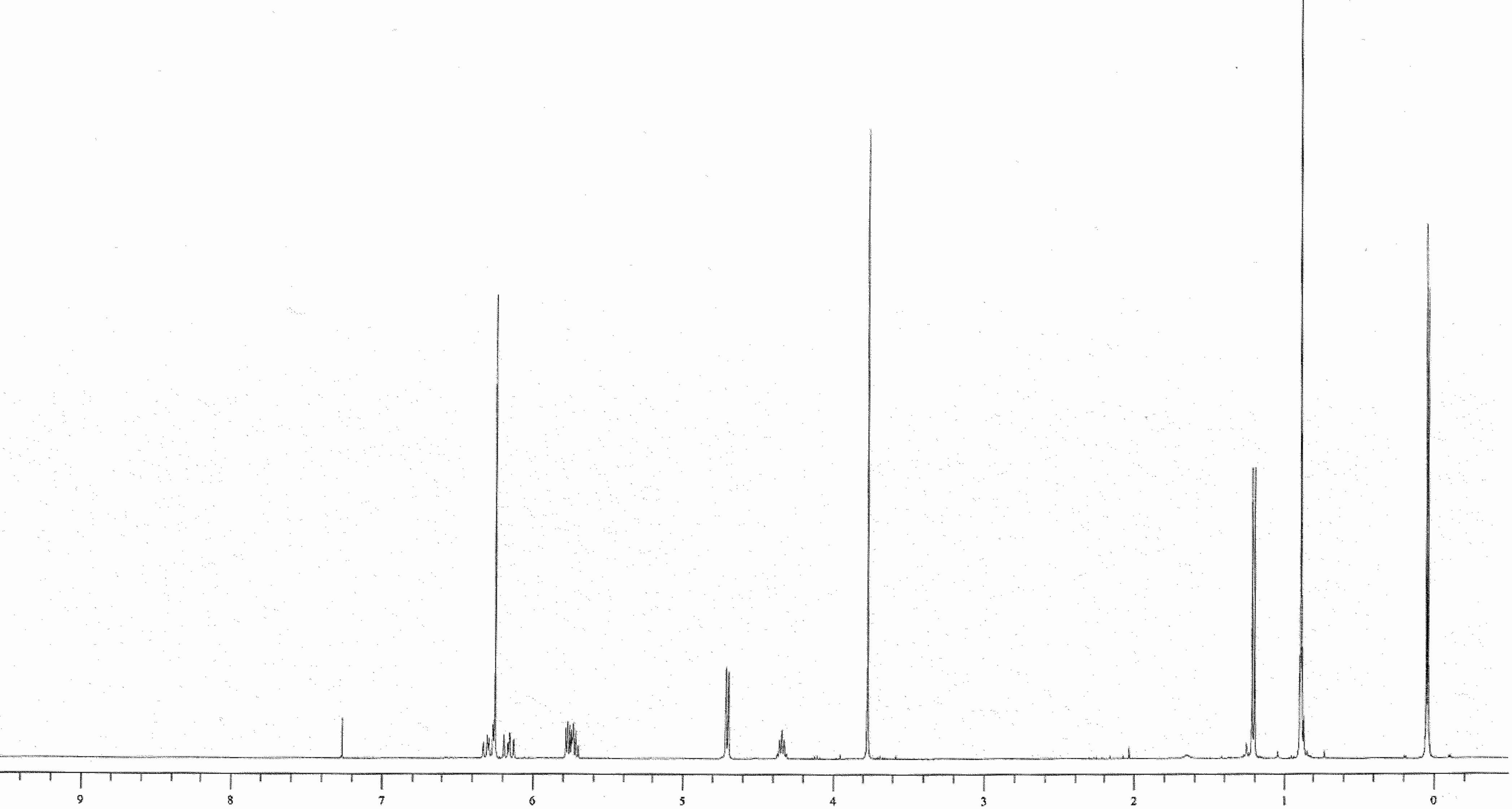

125 MHz ^{13}C NMR spectrum in $CDCl_3$
O
O
H
H
H
H
CO_2Me
O
O
220
200
180
160
140
120
100
80
60
40
20
ppm

29y

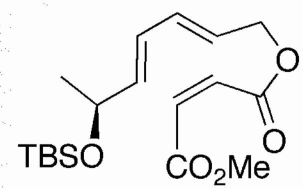
400 MHz ^{1}H NMR spectrum in $CDCl_3$



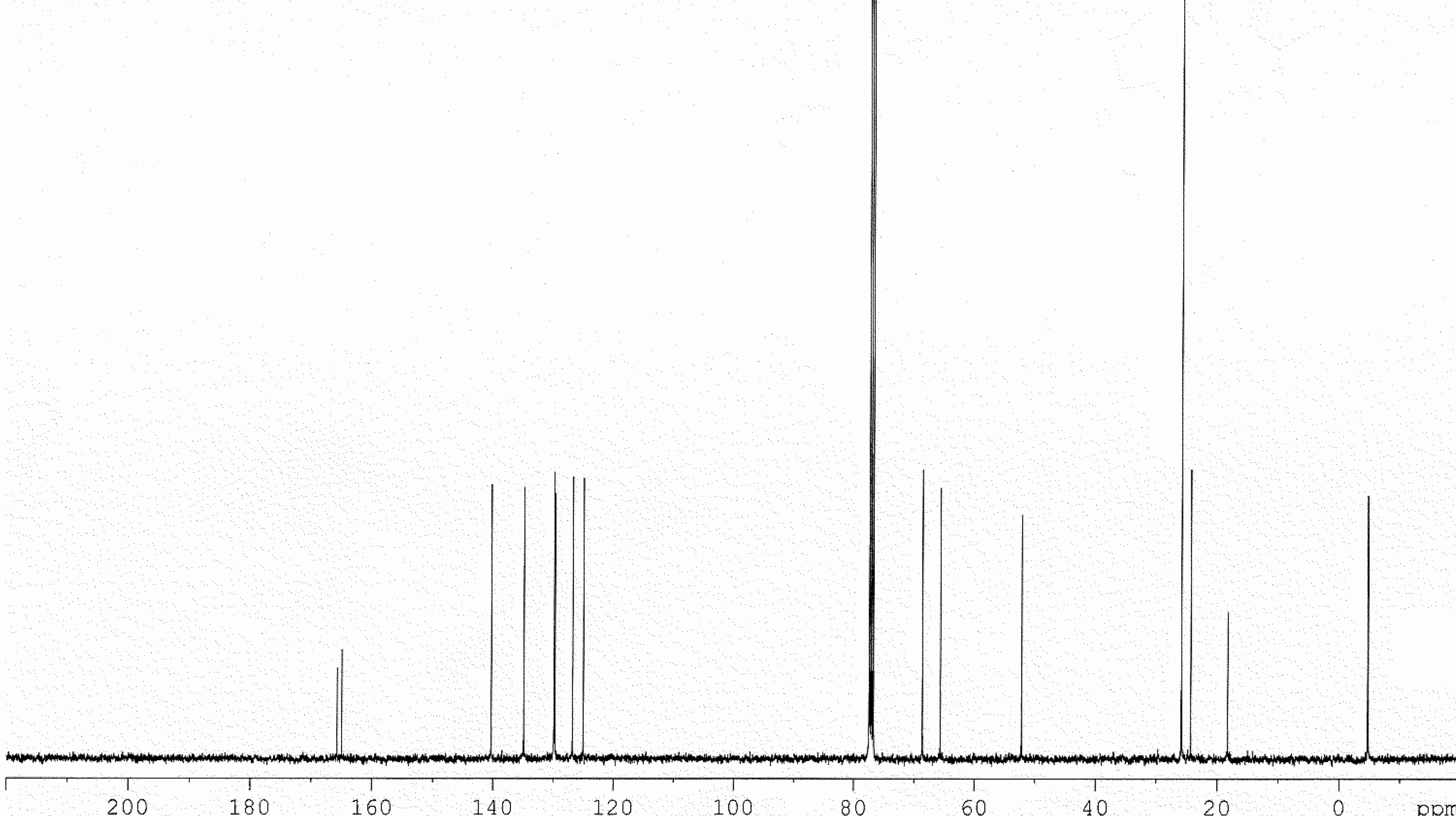
4c



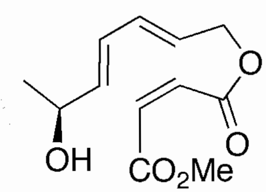
100 MHz ^{13}C NMR spectrum in $CDCl_3$



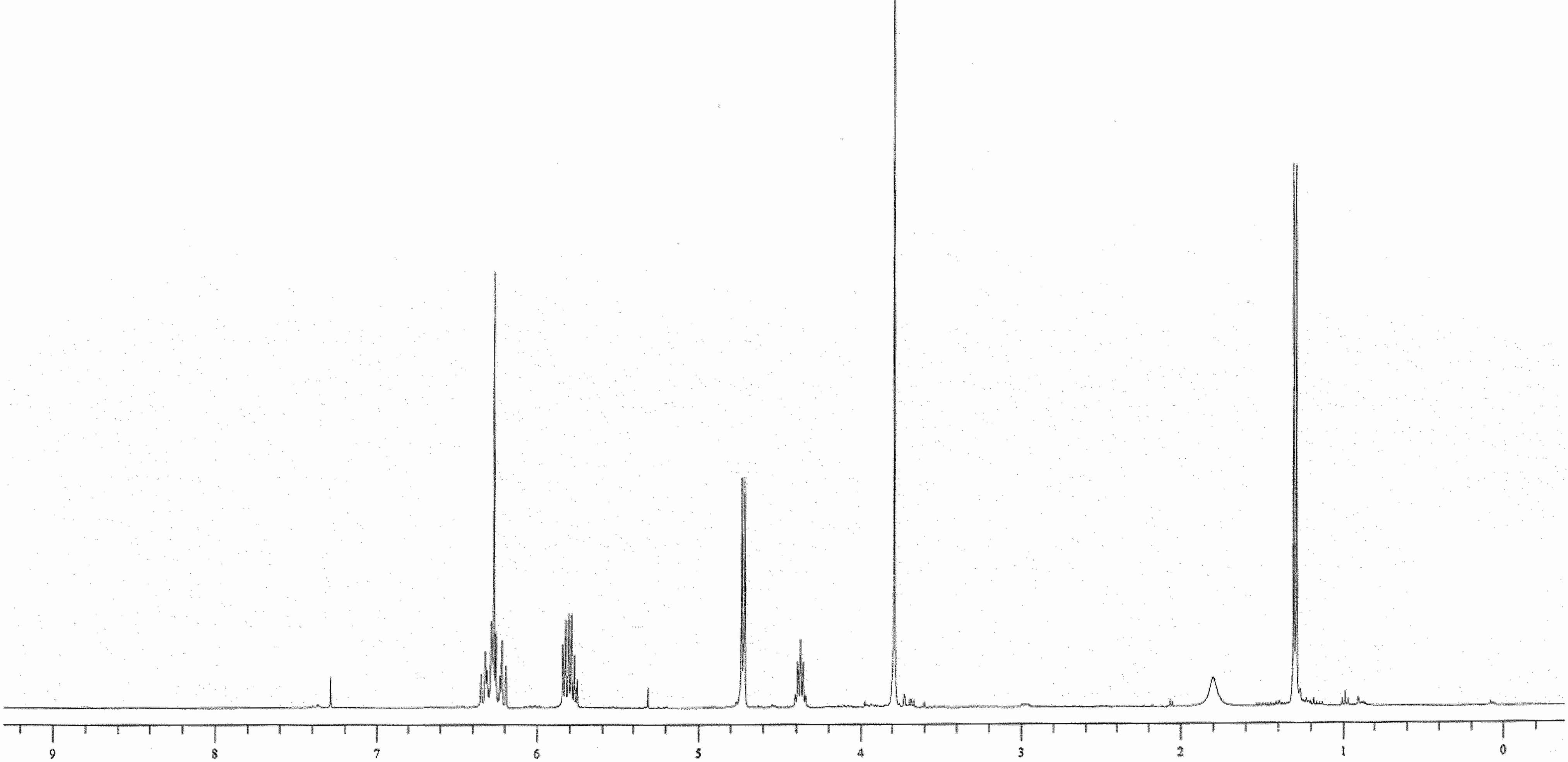
4c



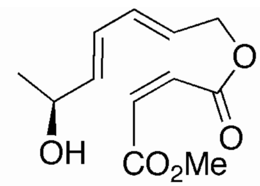
400 MHz ^{1}H NMR spectrum in $CDCl_3$



4a



100 MHz ^{13}C NMR spectrum in $CDCl_3$



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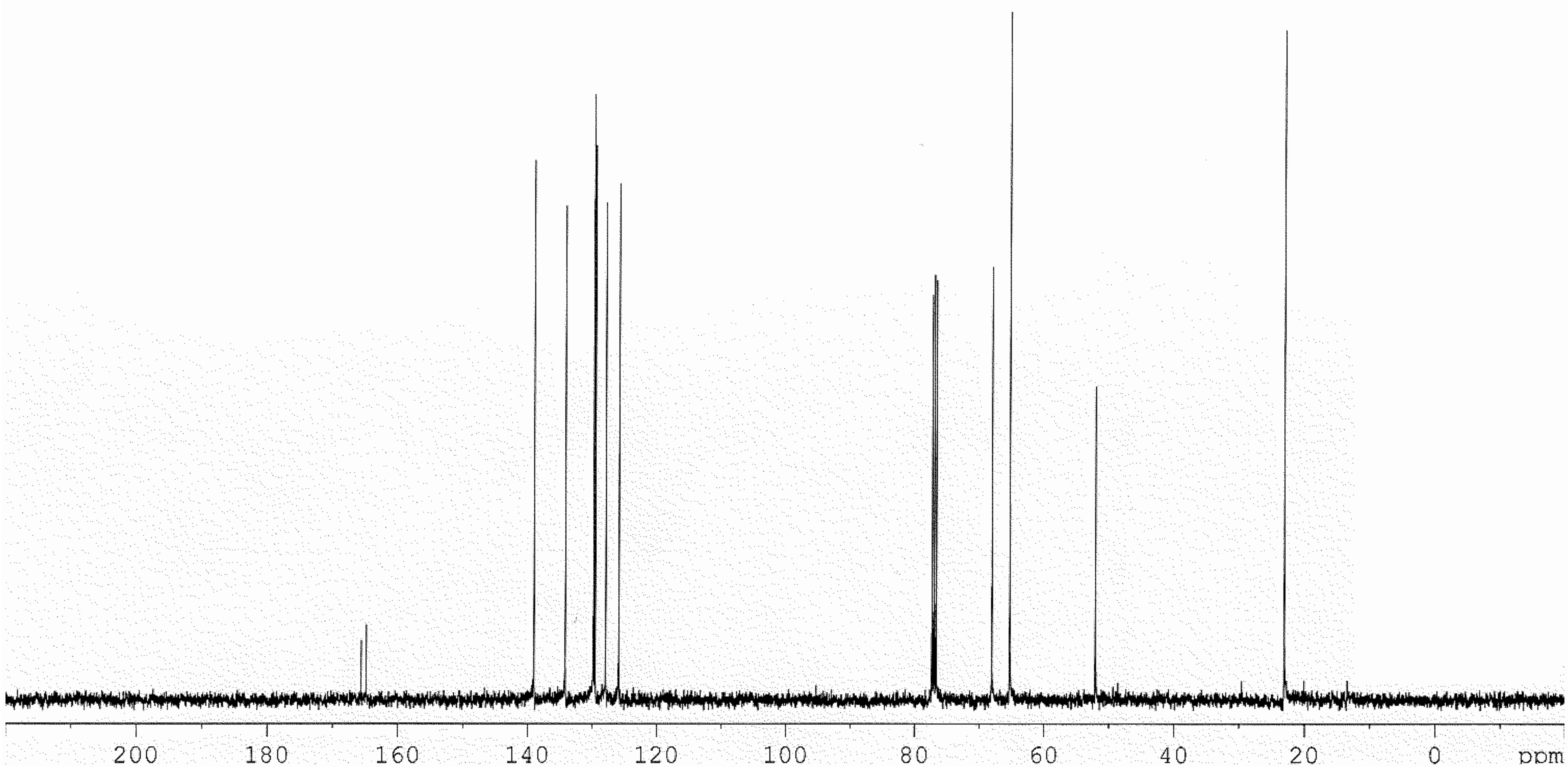
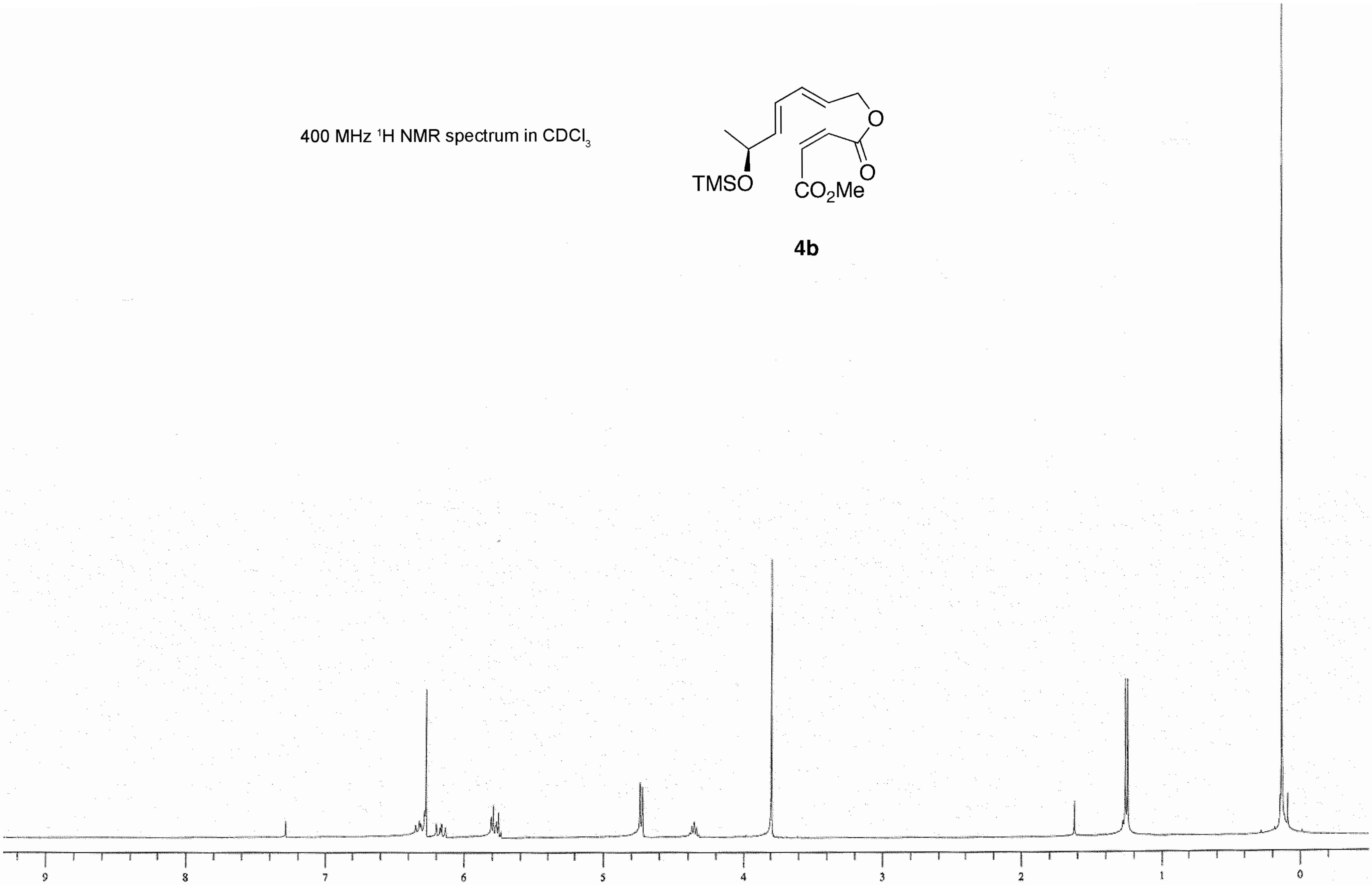
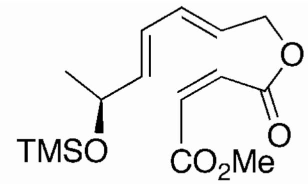


400 MHz ^1H NMR spectrum in $CDCl_3$

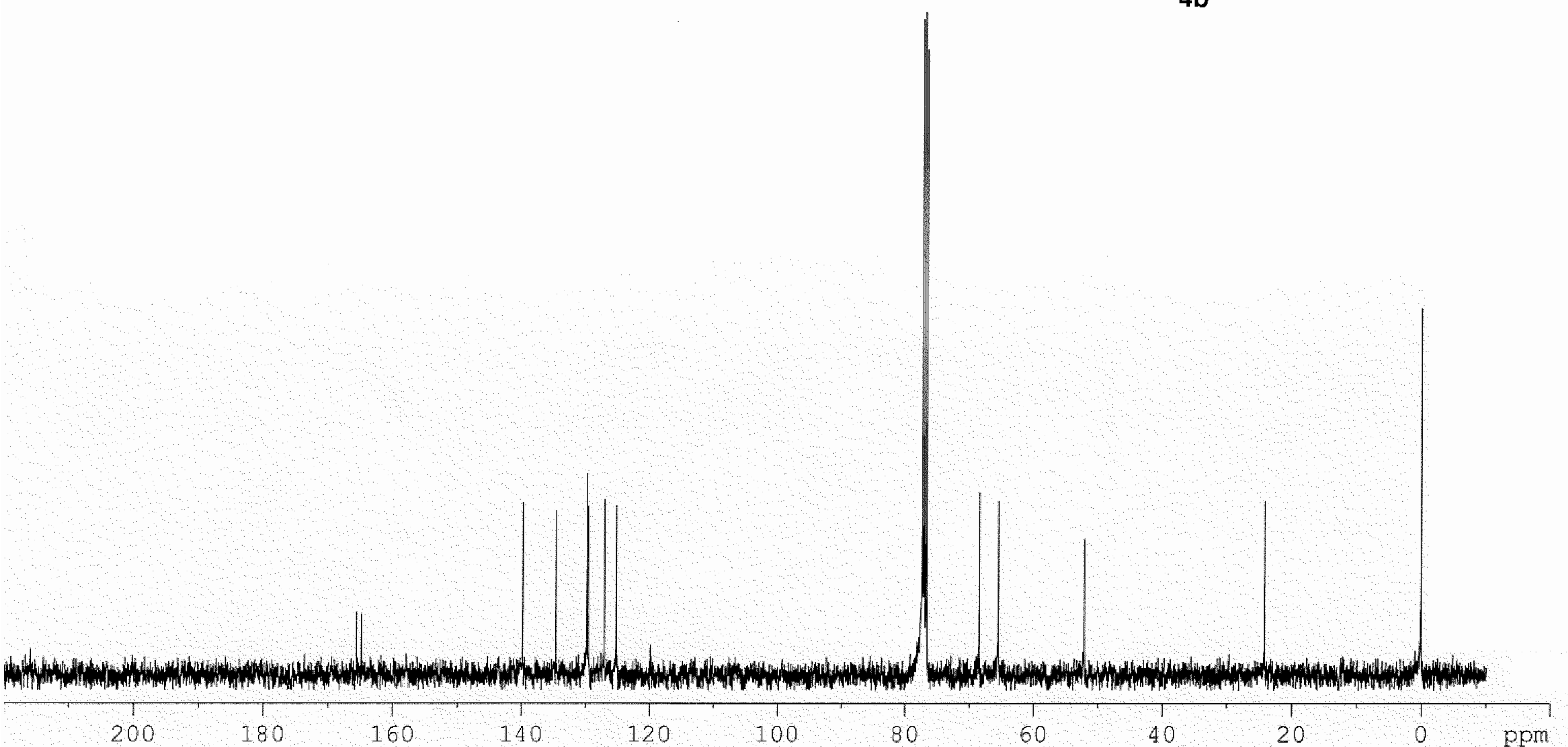


4b

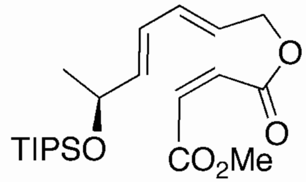
100 MHz ^{13}C NMR spectrum in $CDCl_3$



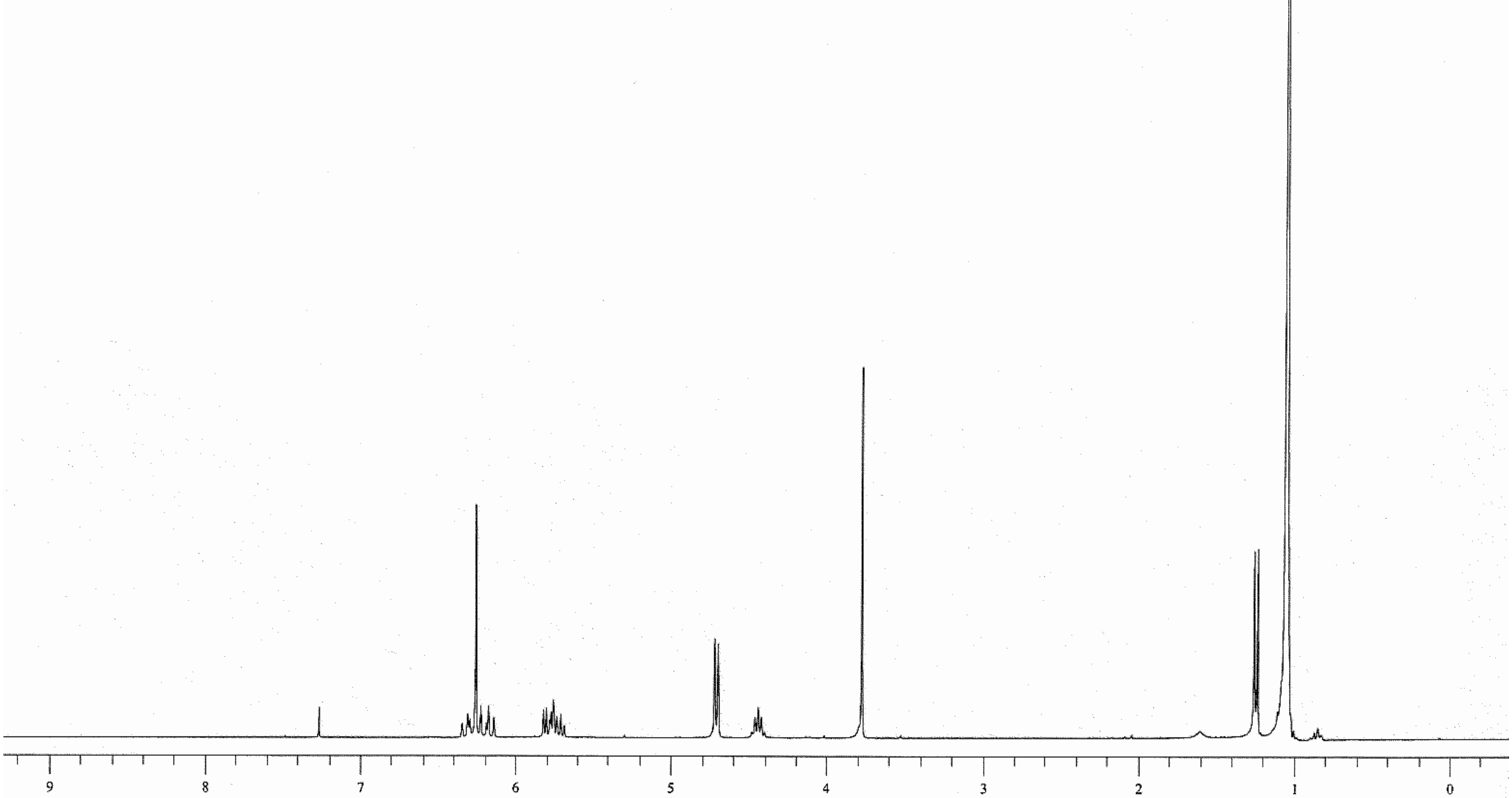
4b



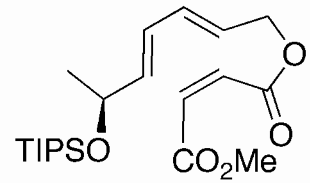
400 MHz ^1H NMR spectrum in $CDCl_3$



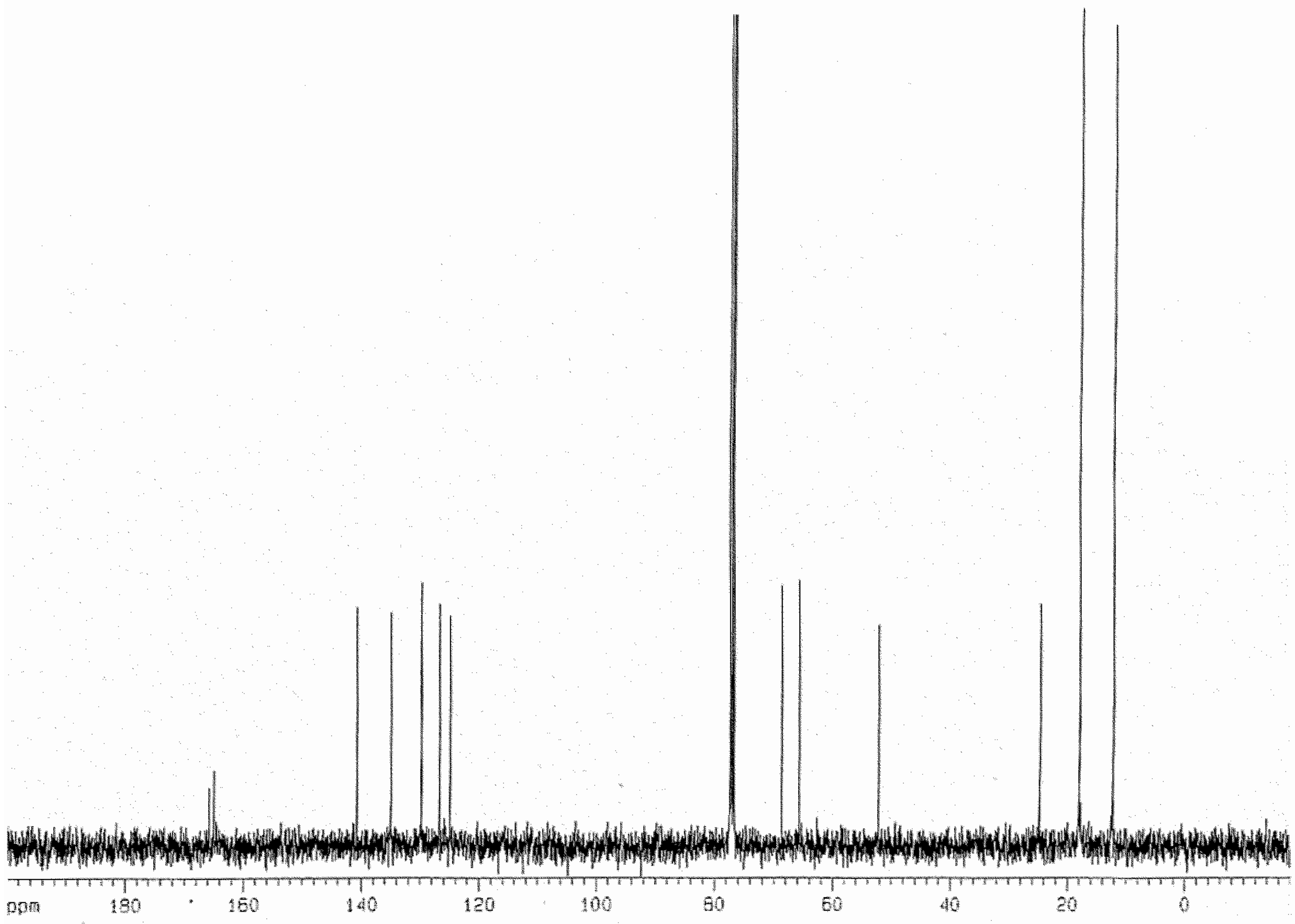
4d

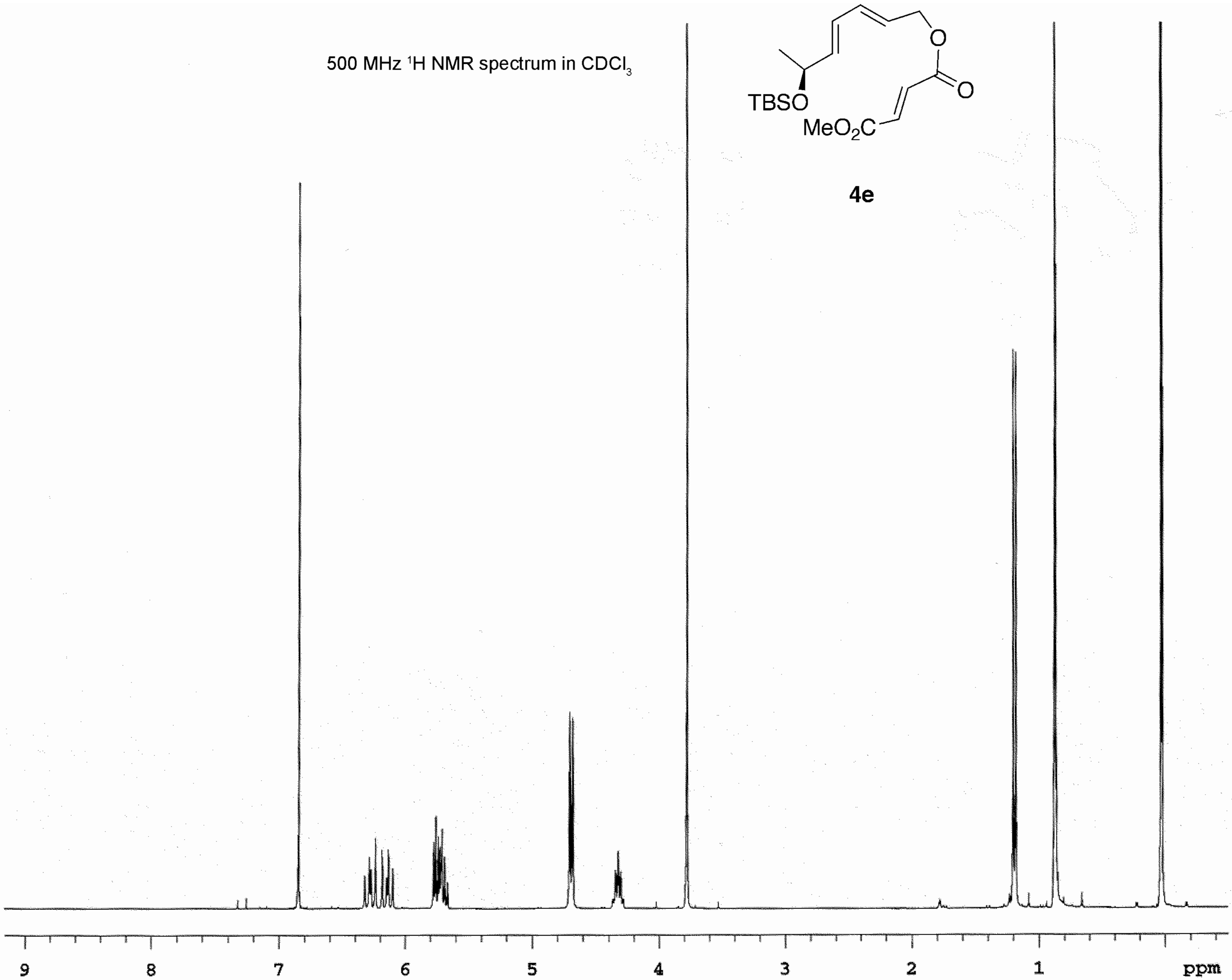


100 MHz ^{13}C NMR spectrum in $CDCl_3$

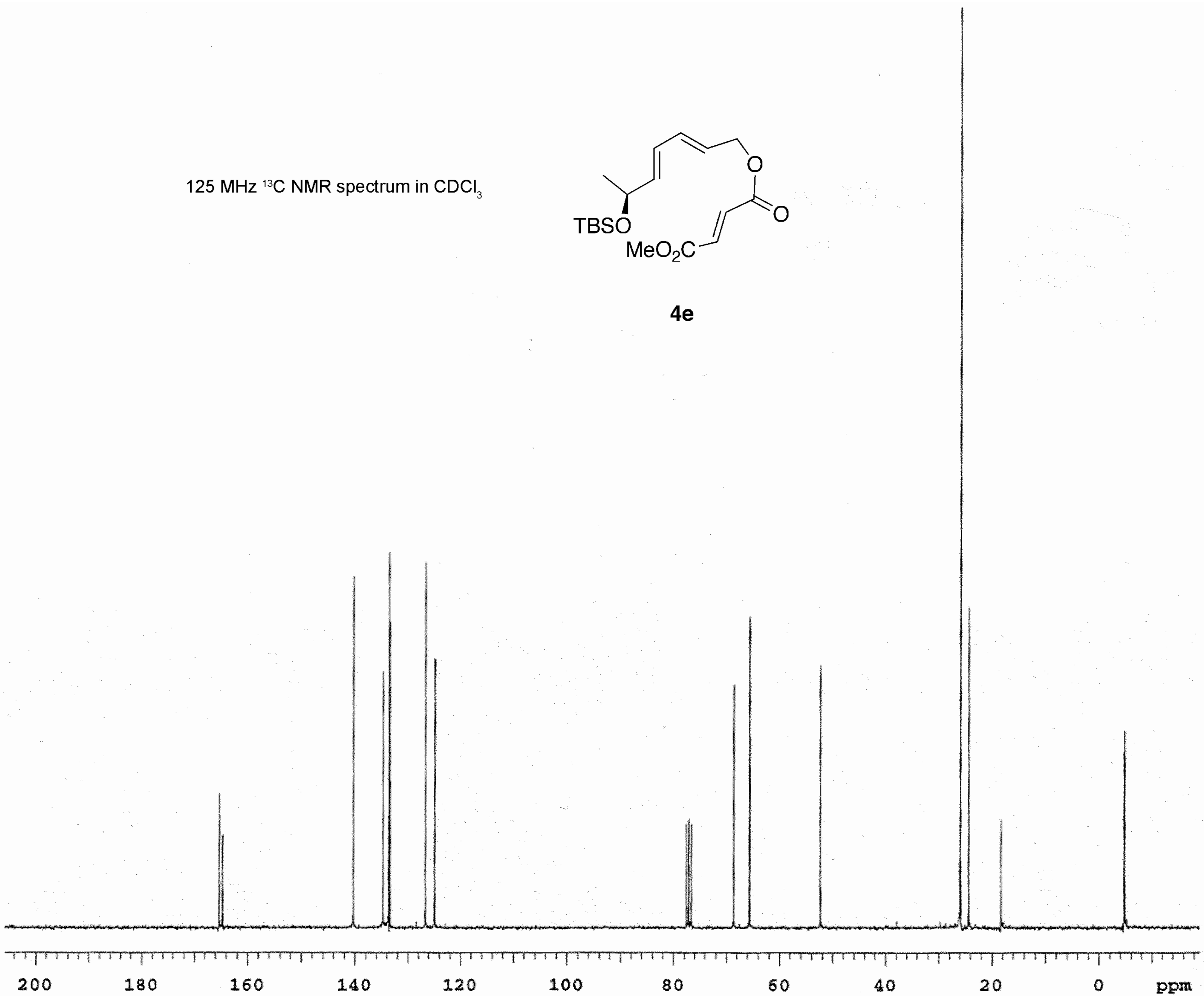


4d



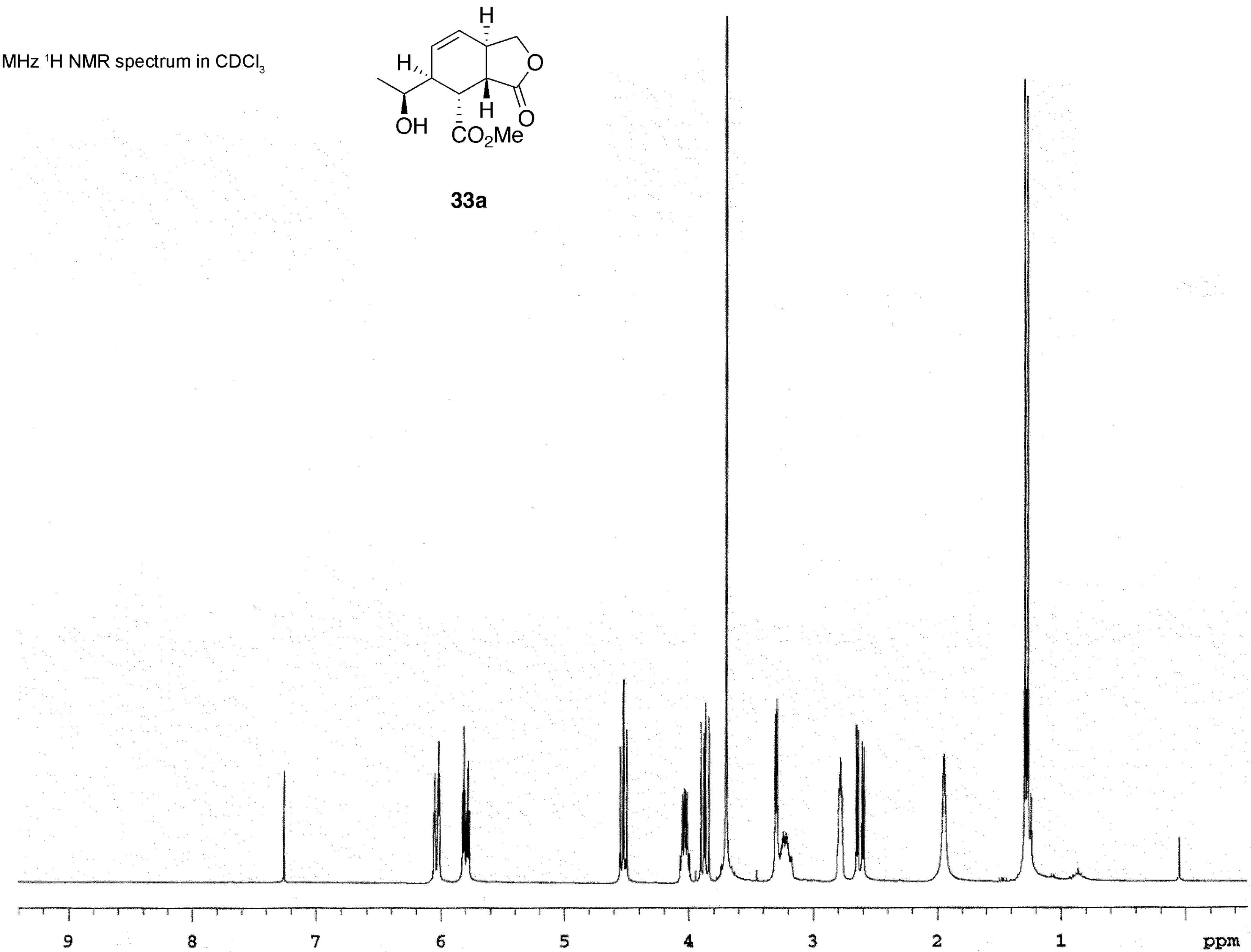

500 MHz ¹H NMR spectrum in CDCl3
TBSO
MeO2C
O
O
4e
9
8
7
6
5
4
3
2
1
ppm

125 MHz ^{13}C NMR spectrum in $CDCl_3$

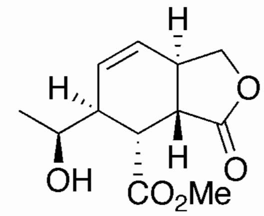


4e

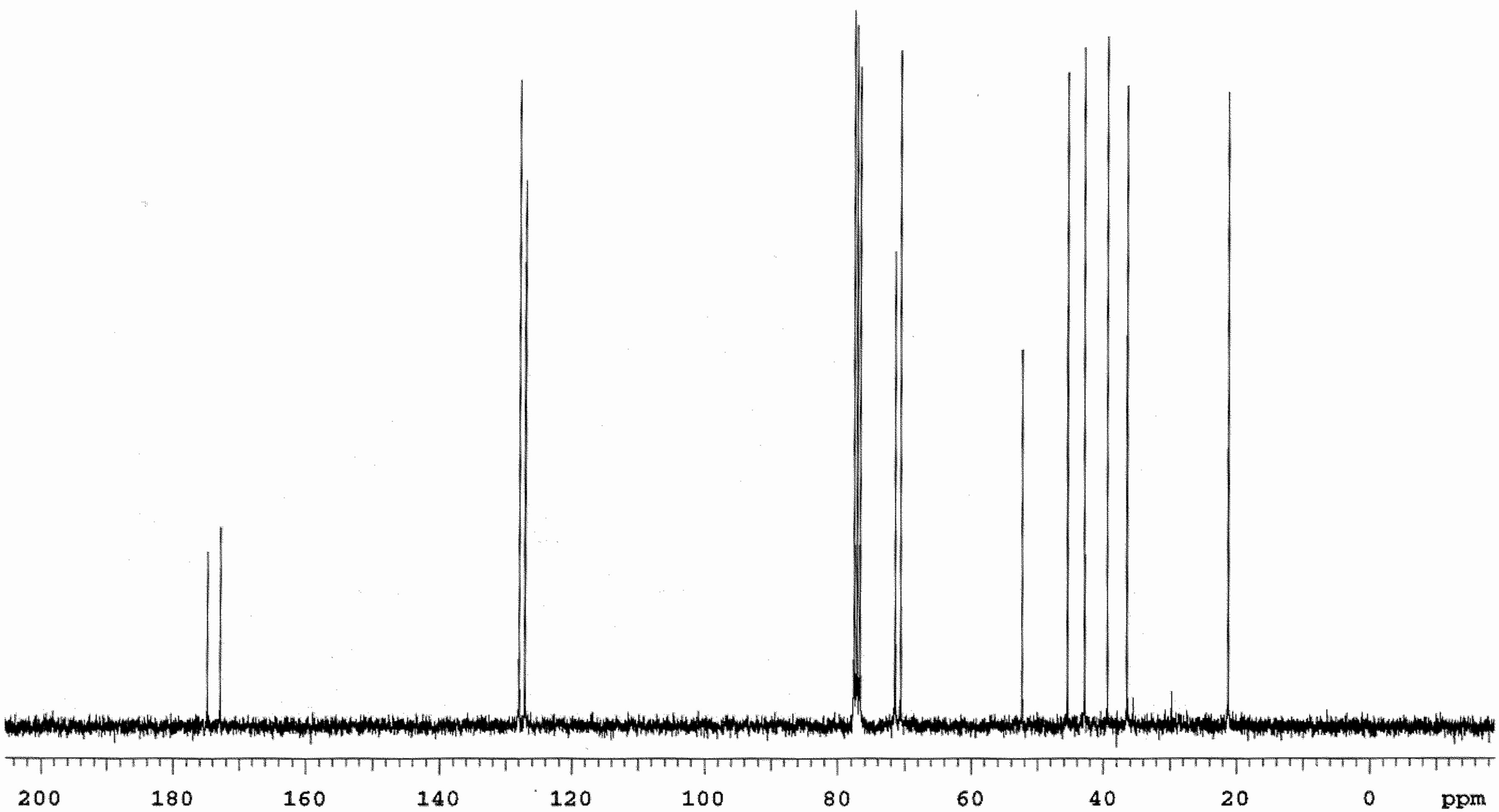
500 MHz ^{1}H NMR spectrum in $CDCl_3$



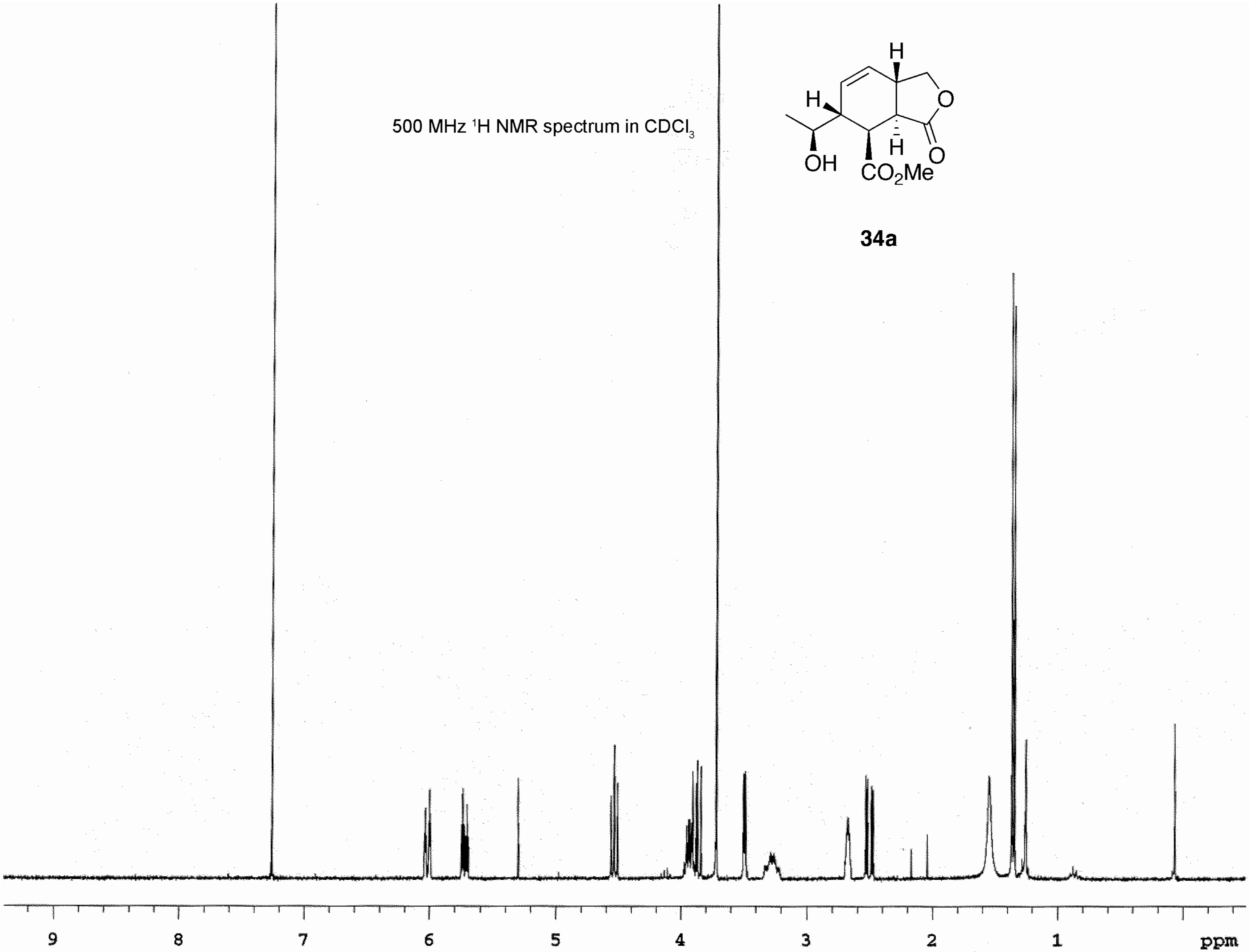
125 MHz ^{13}C NMR spectrum in $CDCl_3$



33a

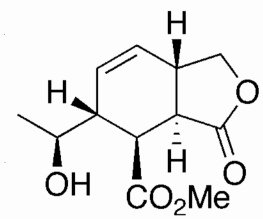


500 MHz [1]H NMR spectrum in CDCl$_3$

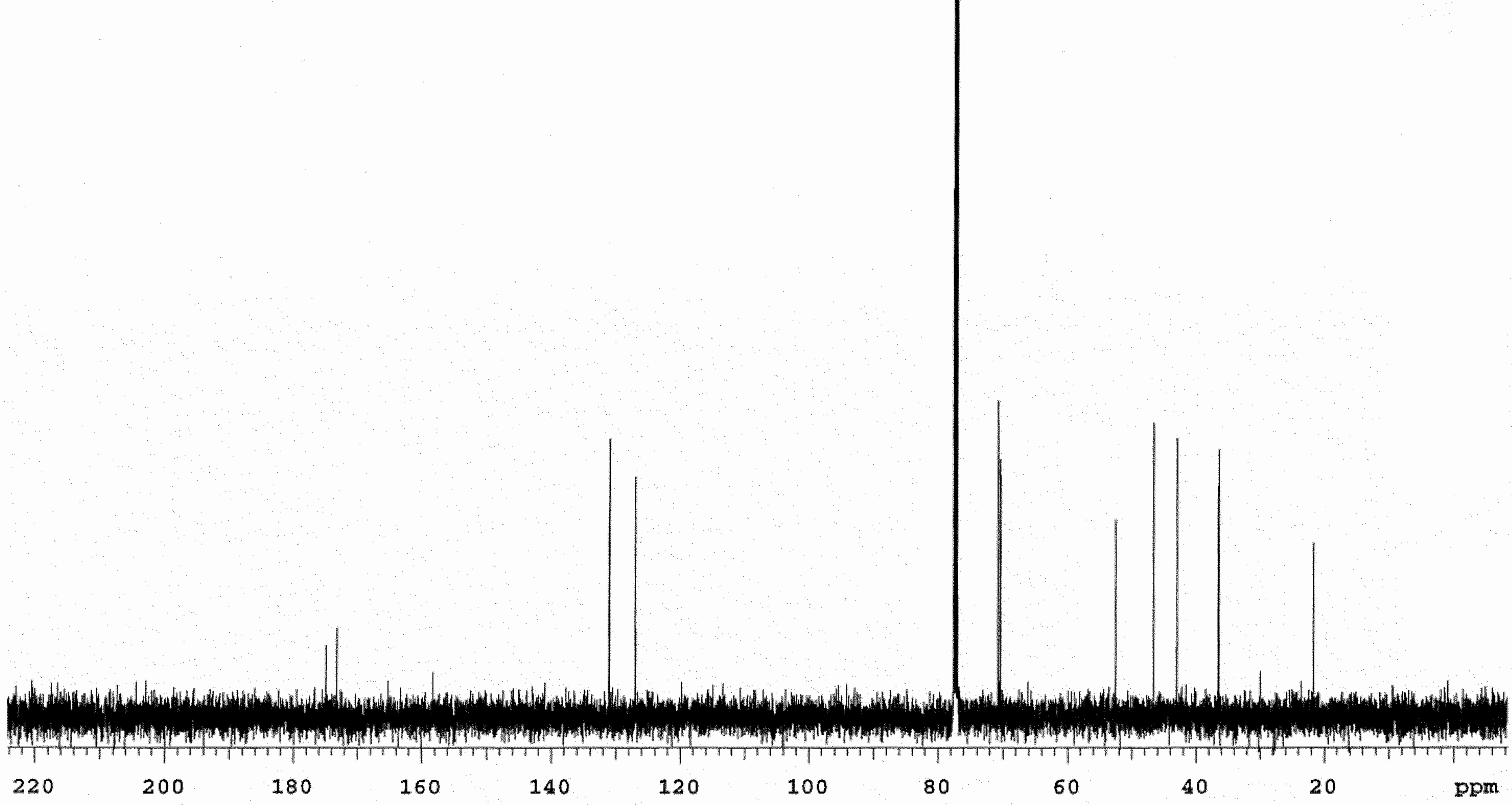


34a

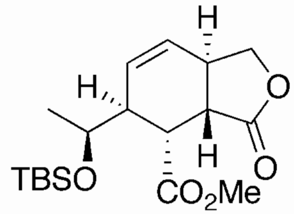
125 MHz ^{13}C NMR spectrum in $CDCl_3$



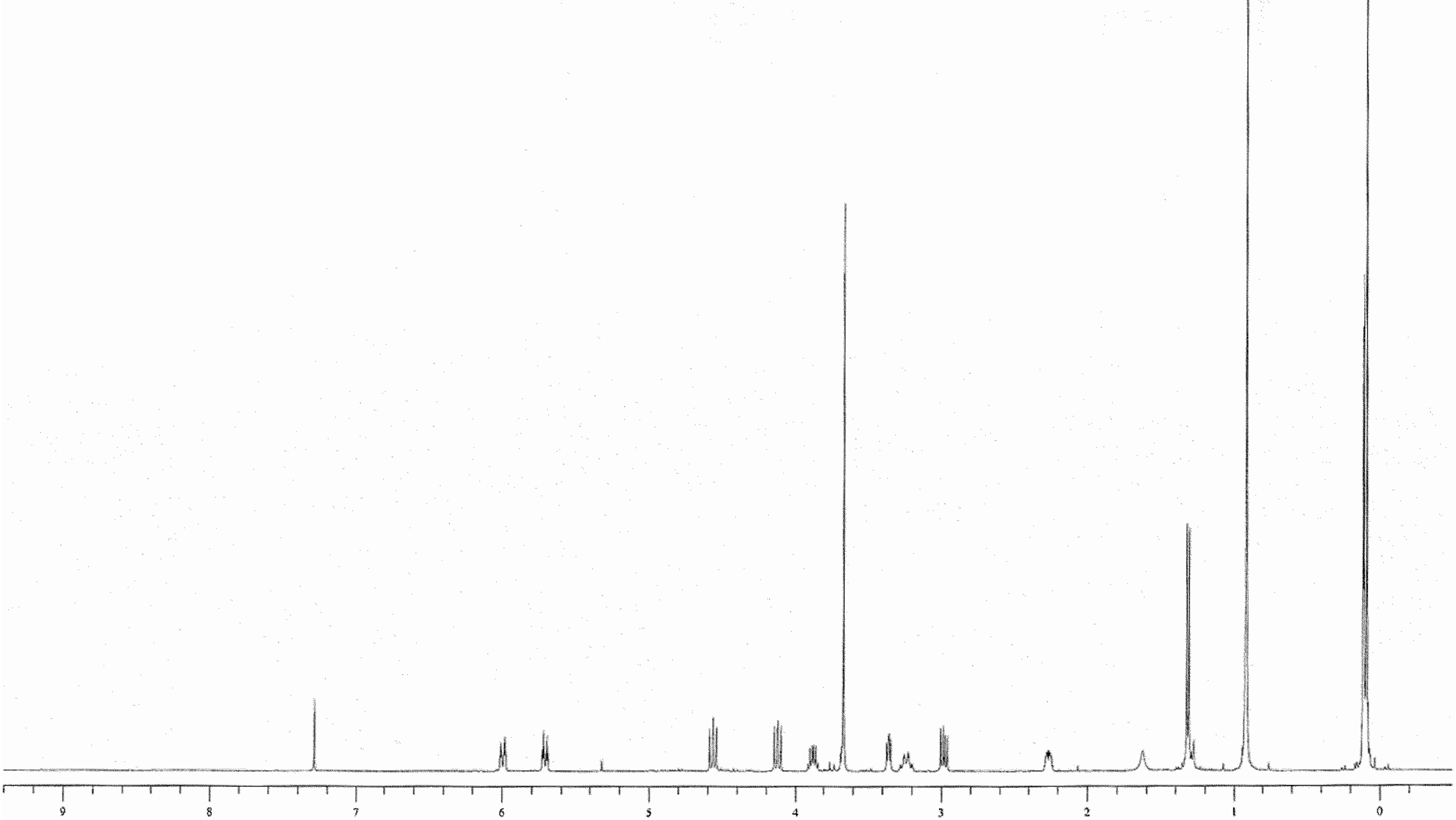
34a



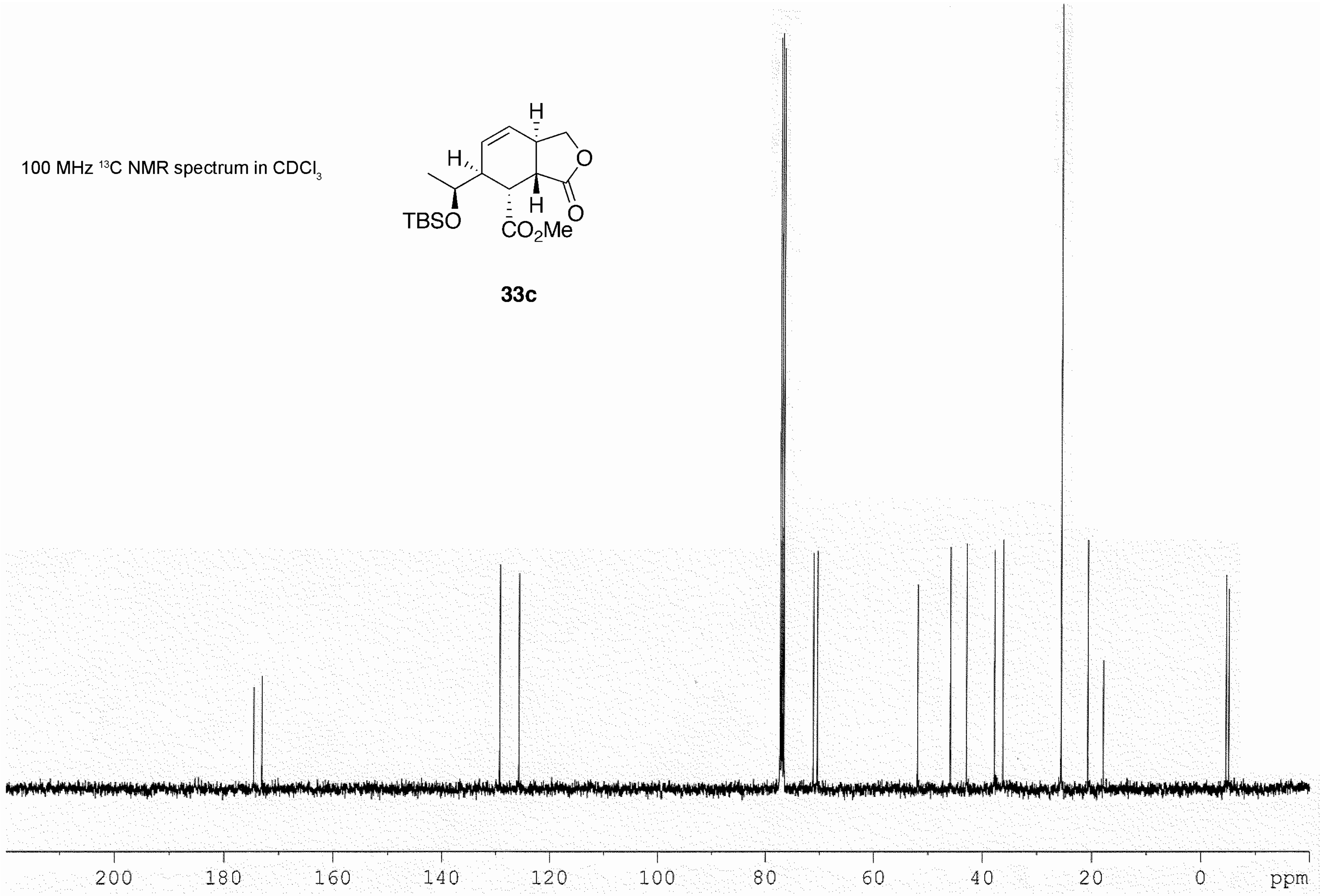
400 MHz ^{1}H NMR spectrum in $CDCl_3$



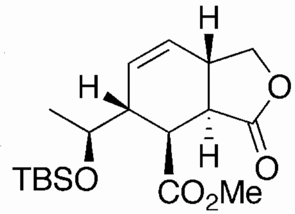
33c



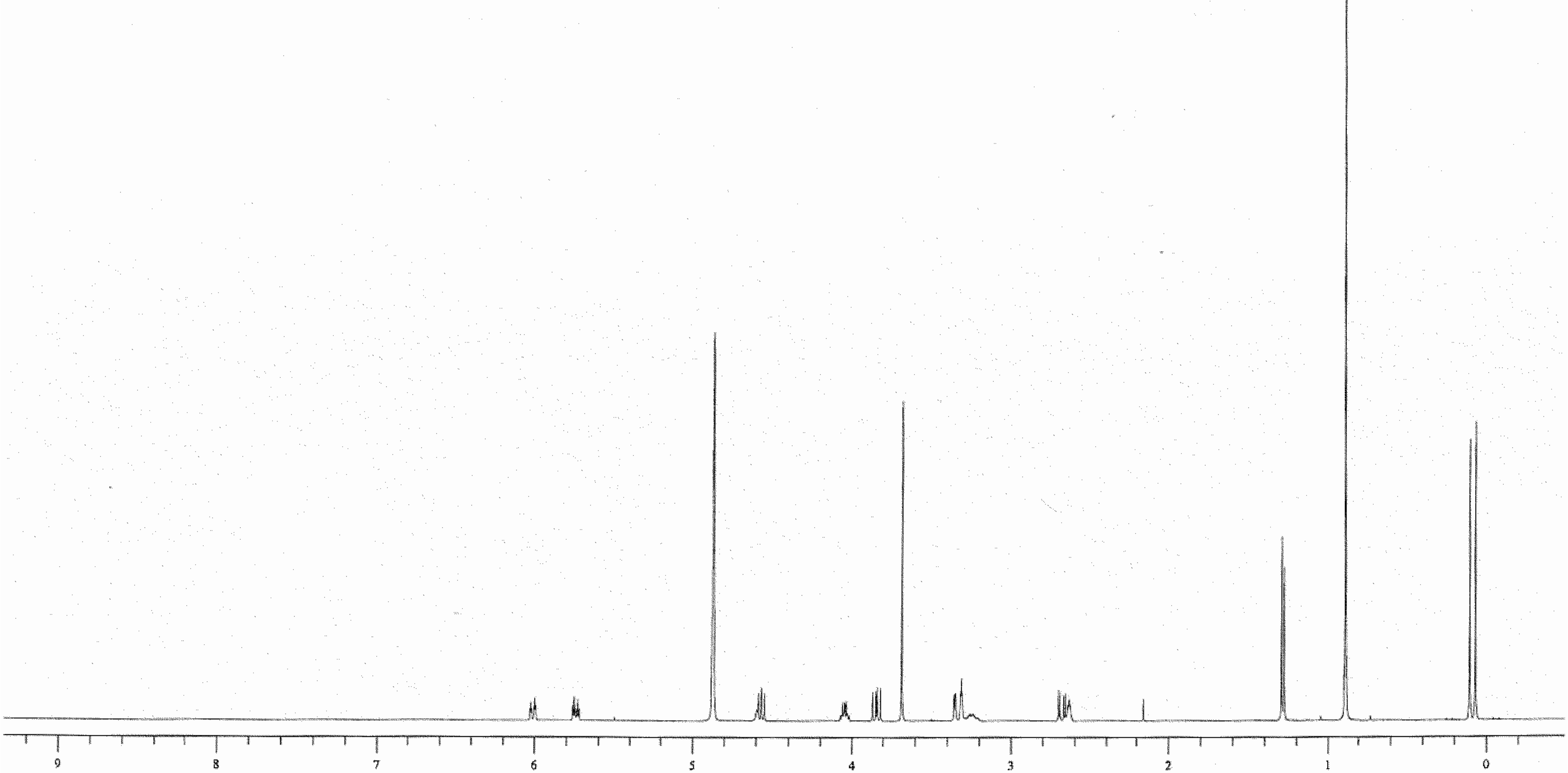
100 MHz ^{13}C NMR spectrum in $CDCl_3$



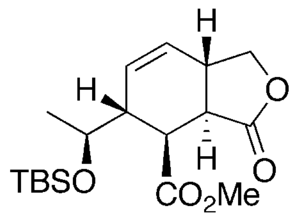
400 MHz ¹H NMR spectrum in CD_3OD



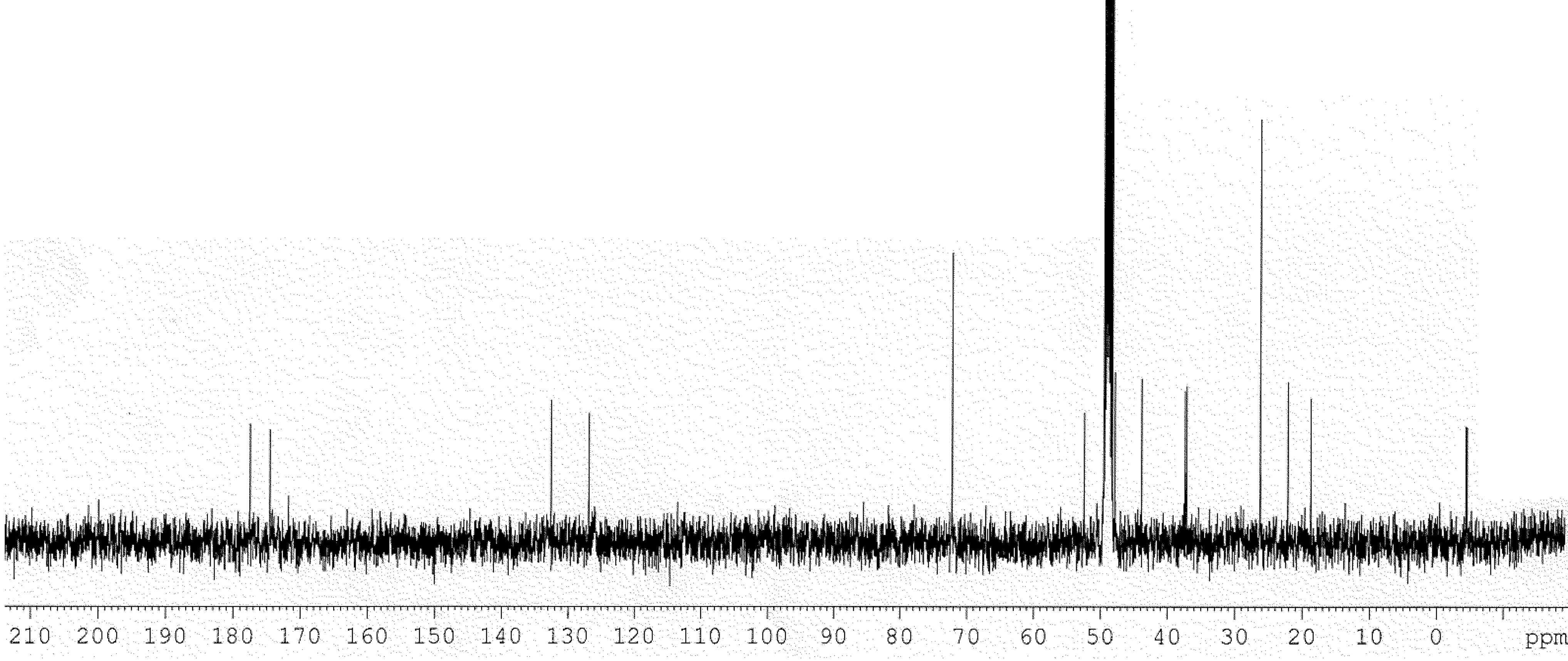
34c



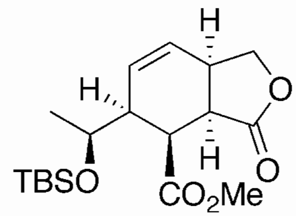
100 MHz ^{13}C NMR spectrum in CD_3OD



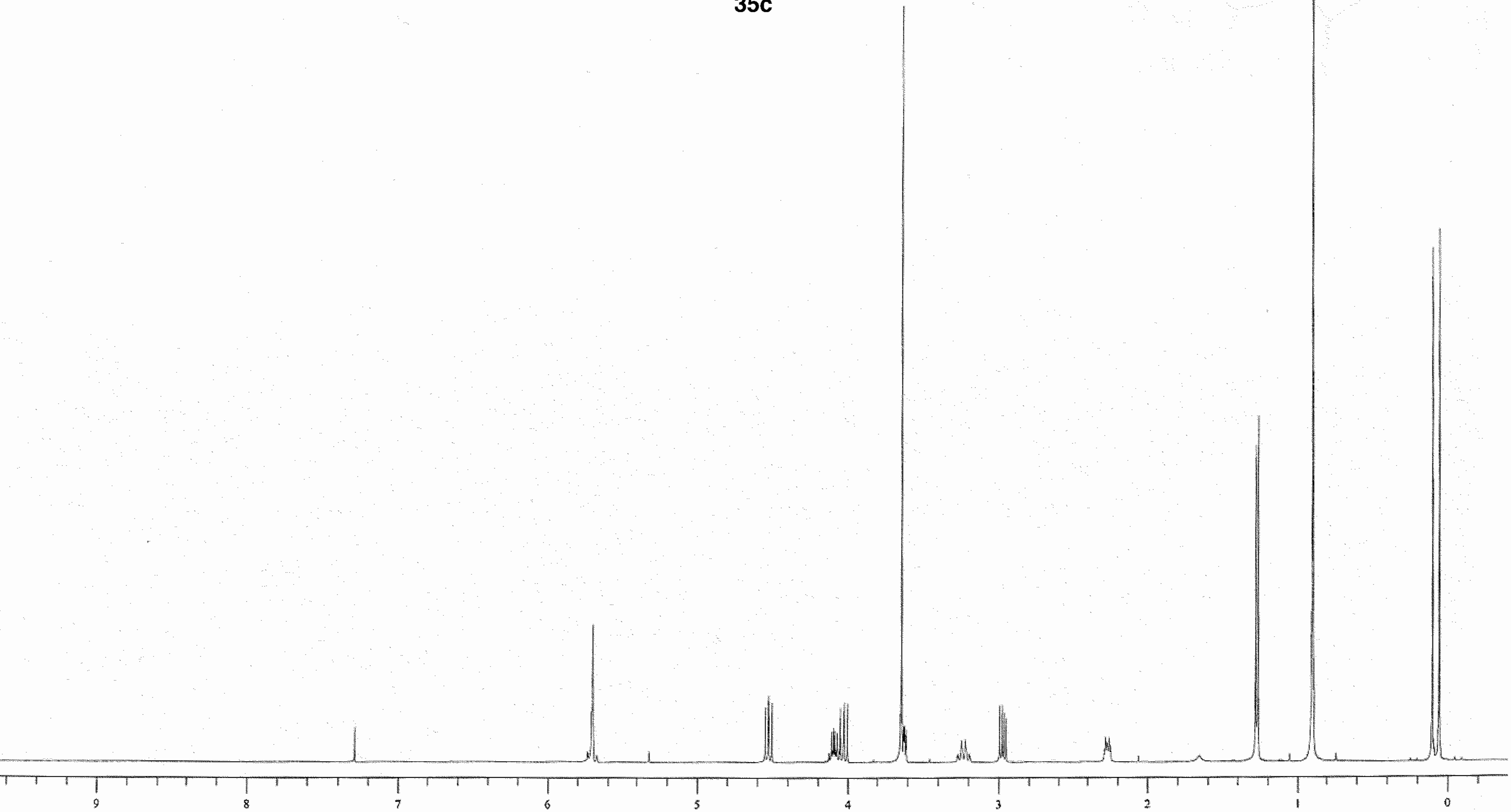
34c



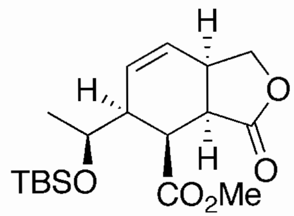
400 MHz ^{1}H NMR spectrum in $CDCl_3$



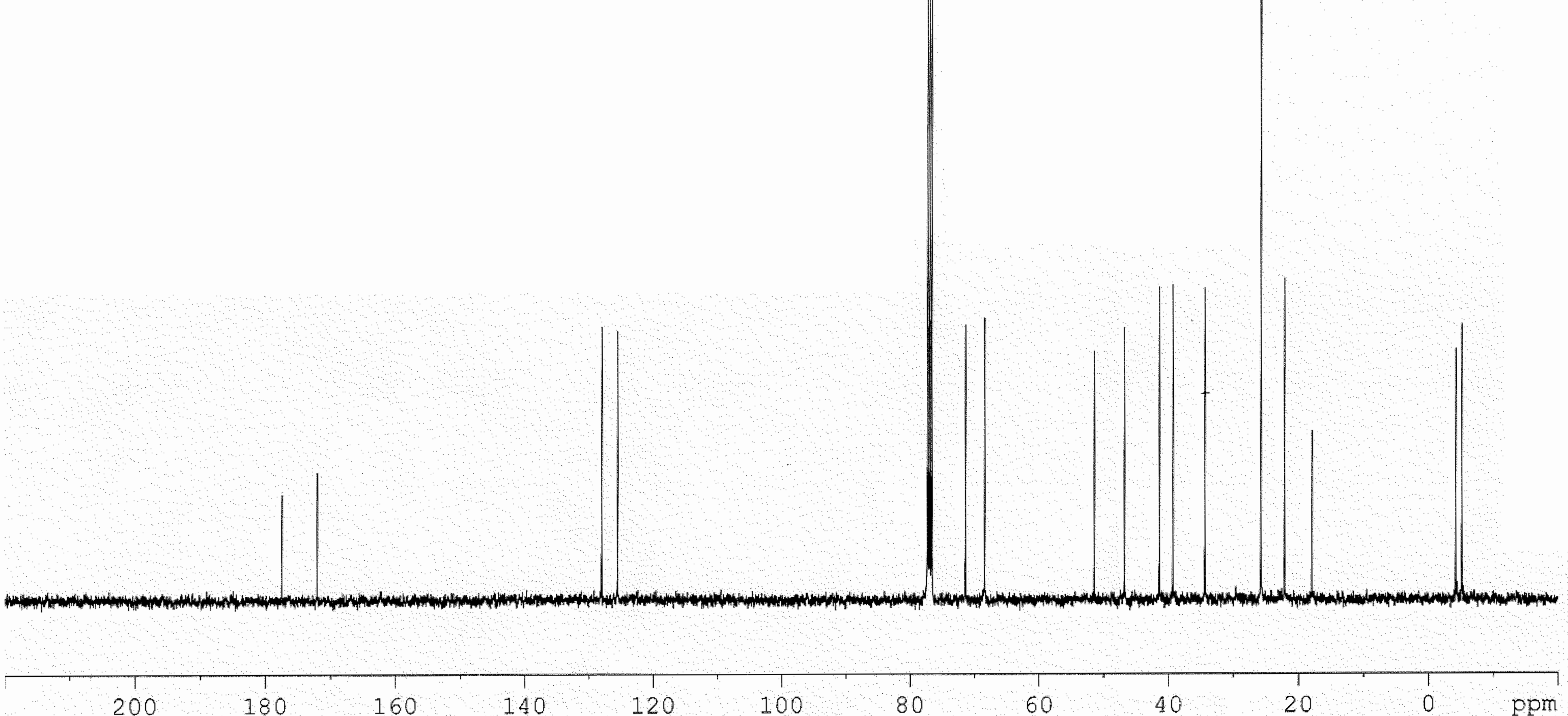
35c



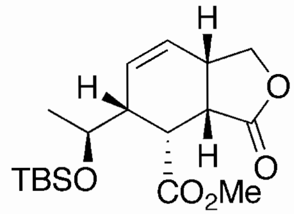
100 MHz ^{13}C NMR spectrum in $CDCl_3$



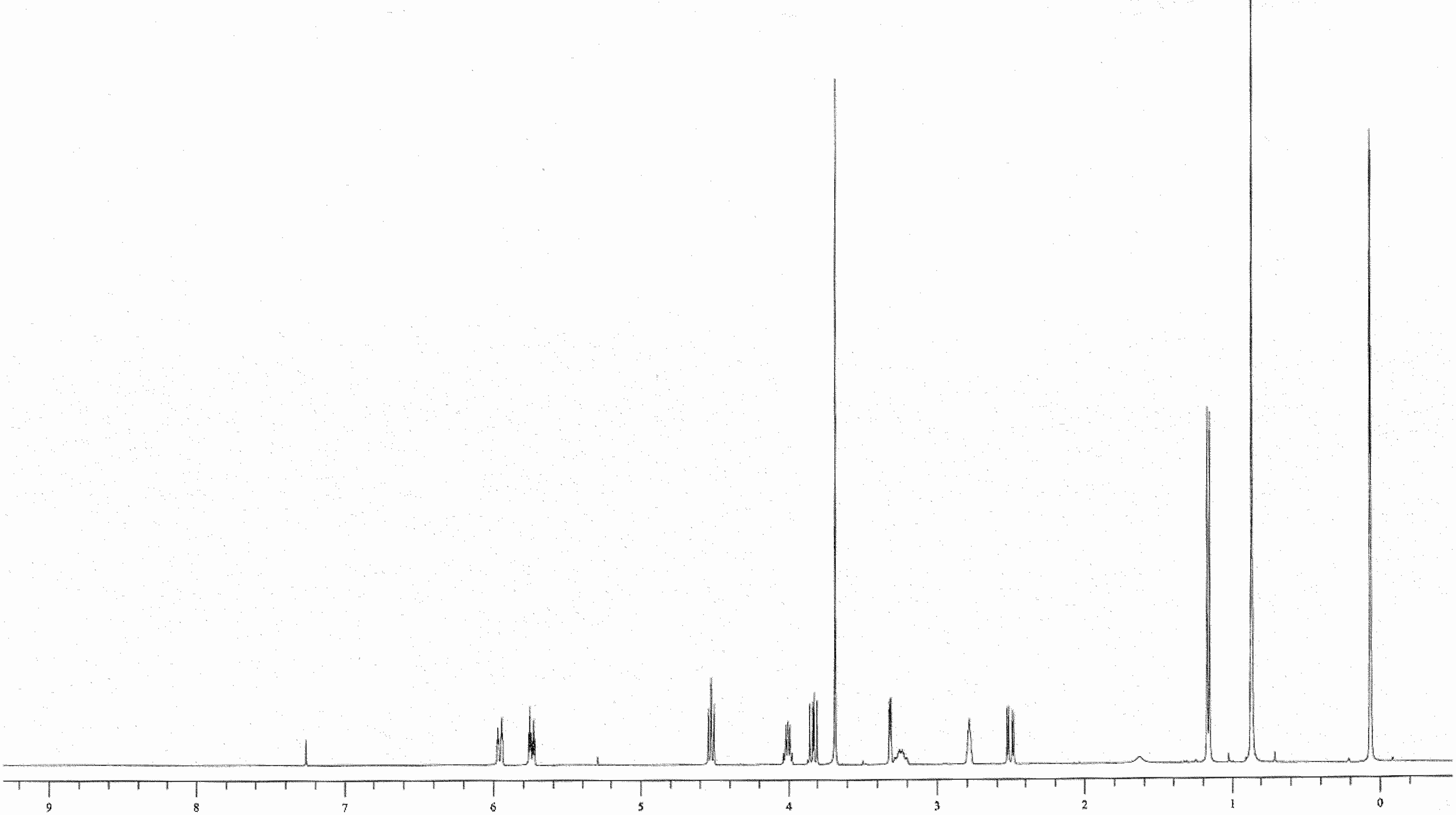
35c



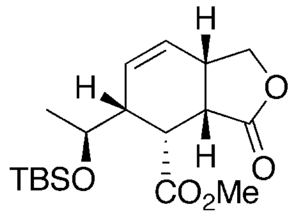
400 MHz ¹H NMR spectrum in $CDCl_3$



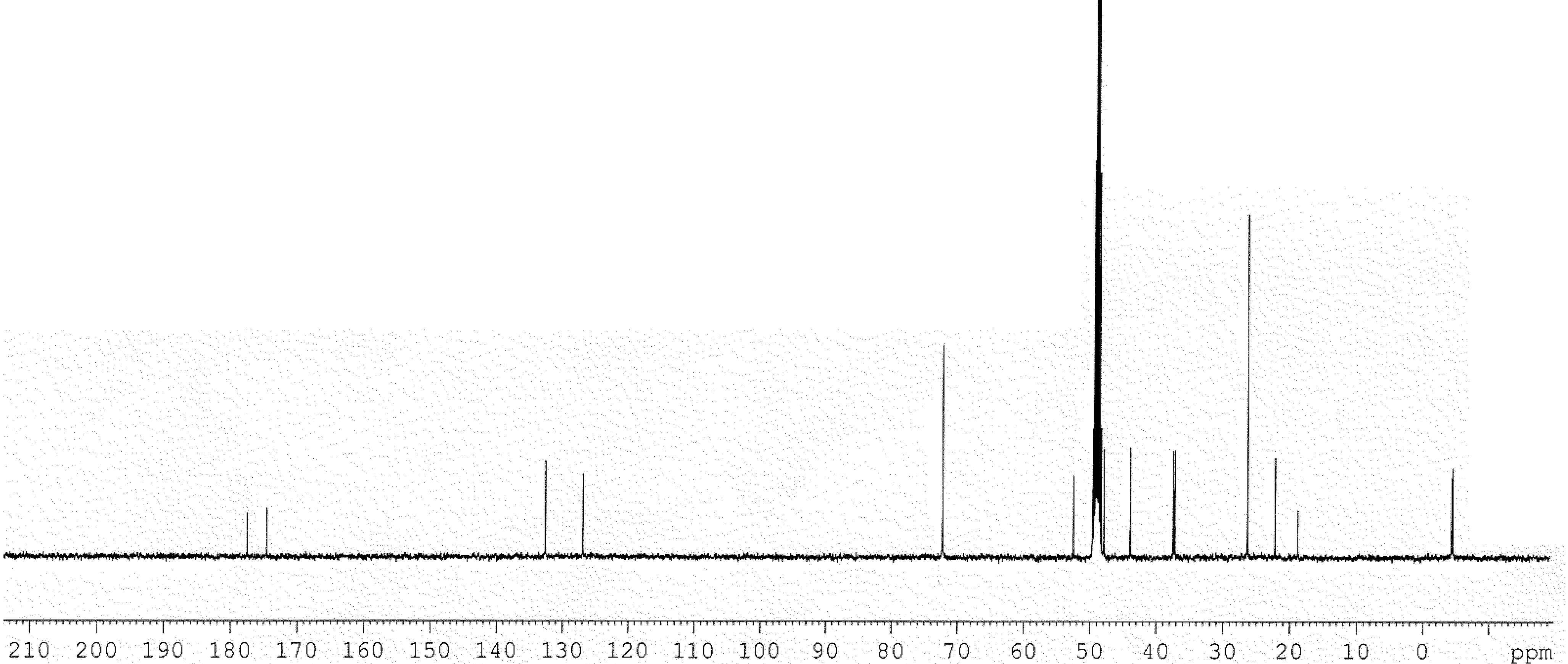
36c



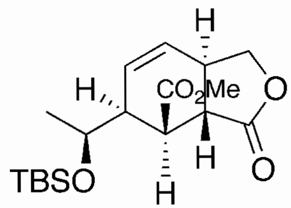
100 MHz ^{13}C NMR spectrum in CD_3OD



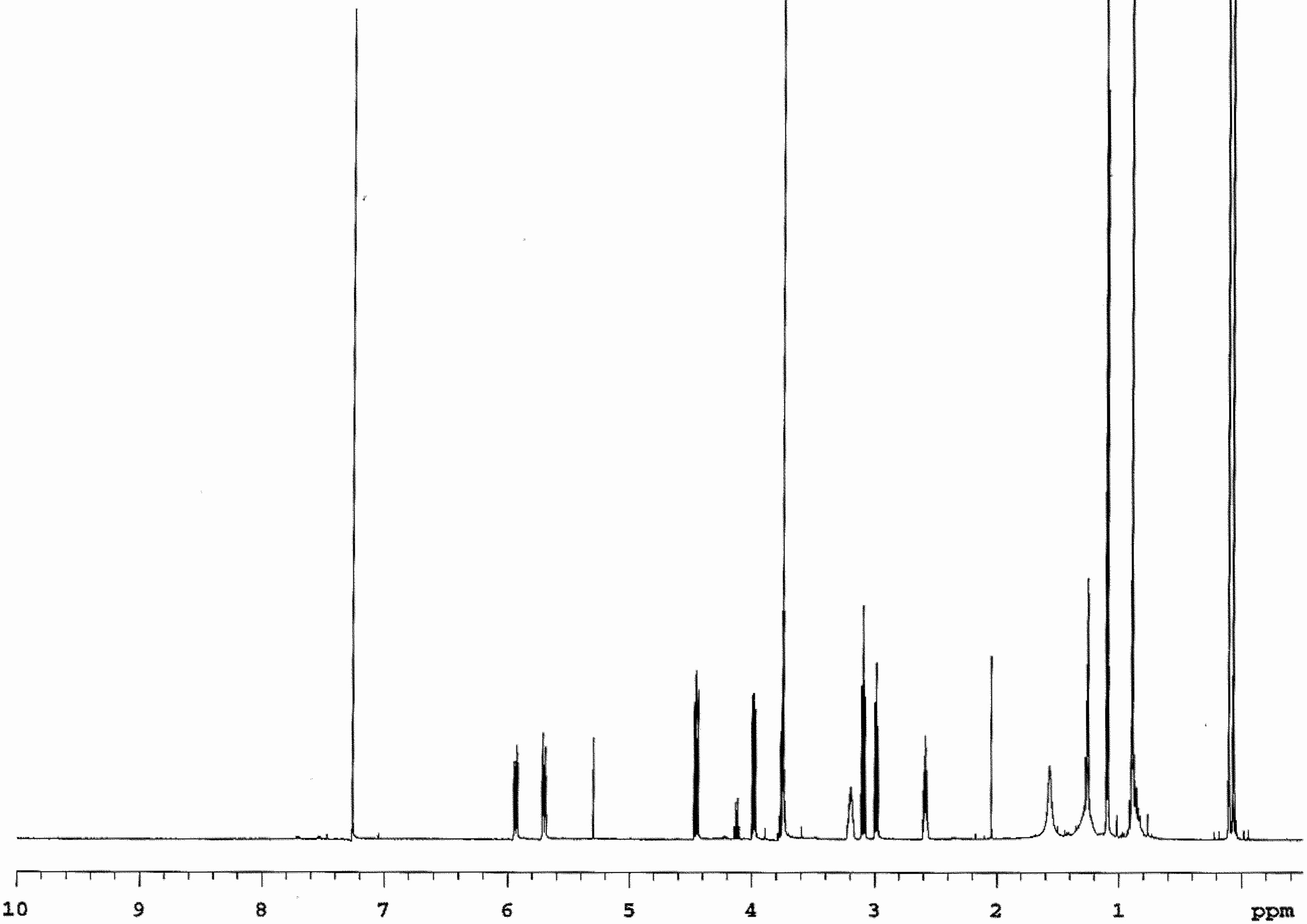
36c



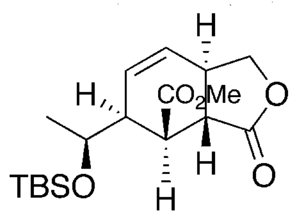
500 MHz ^{1}H NMR spectrum in $CDCl_3$



33e



125 MHz ^{13}C NMR spectrum in $CDCl_3$



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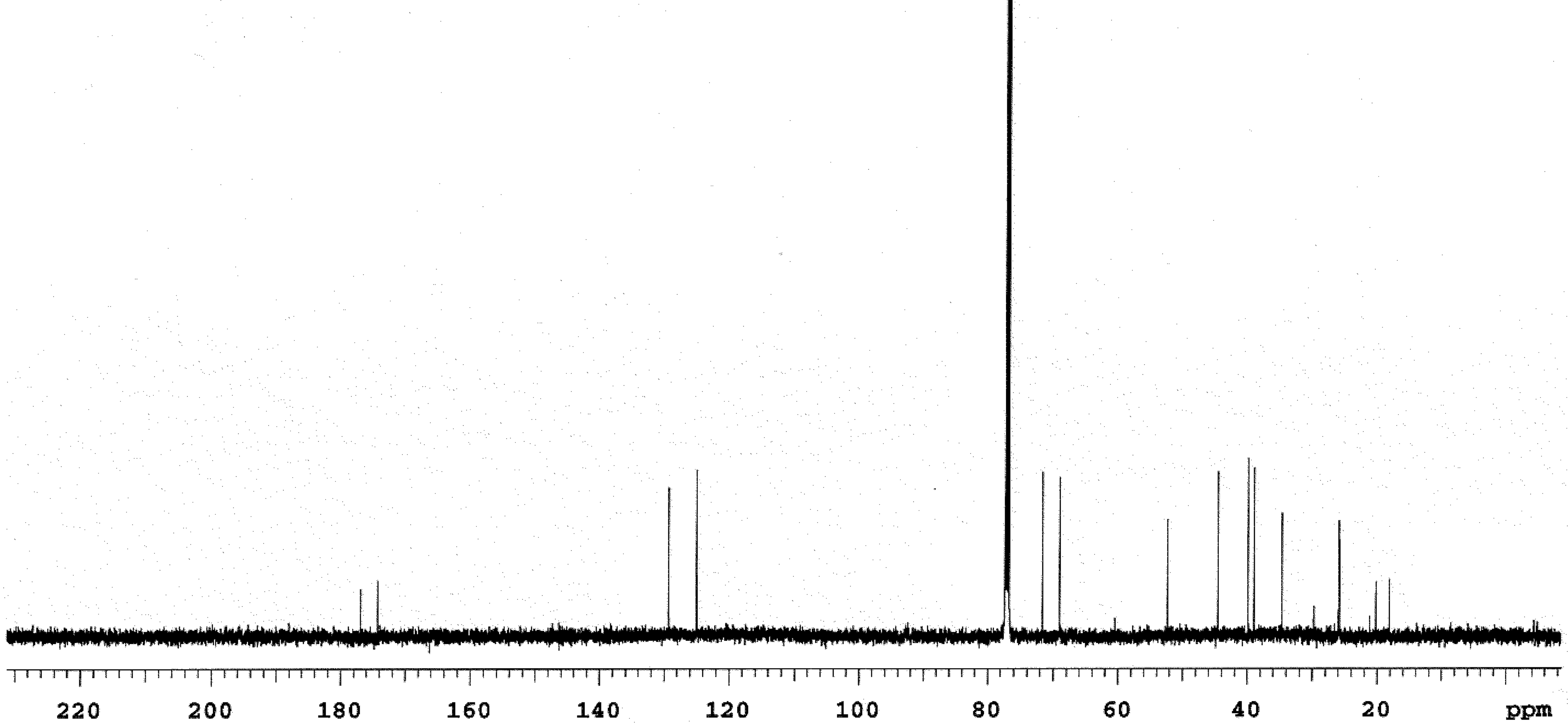
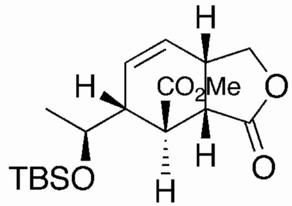


500 MHz ^{1}H NMR spectrum in $CDCl_3$



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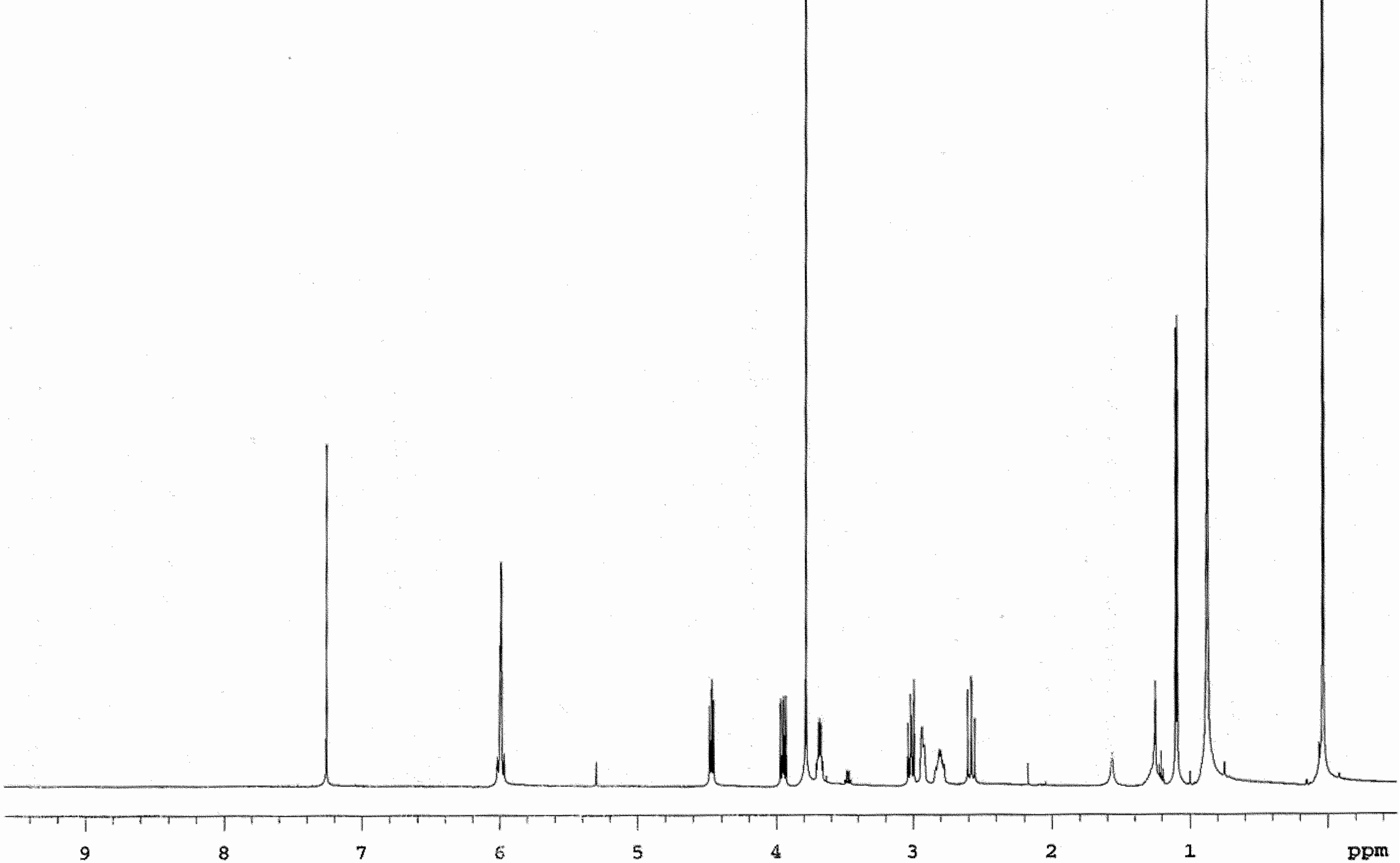
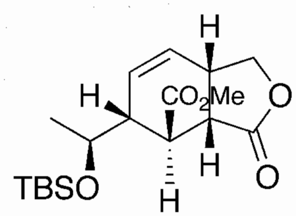


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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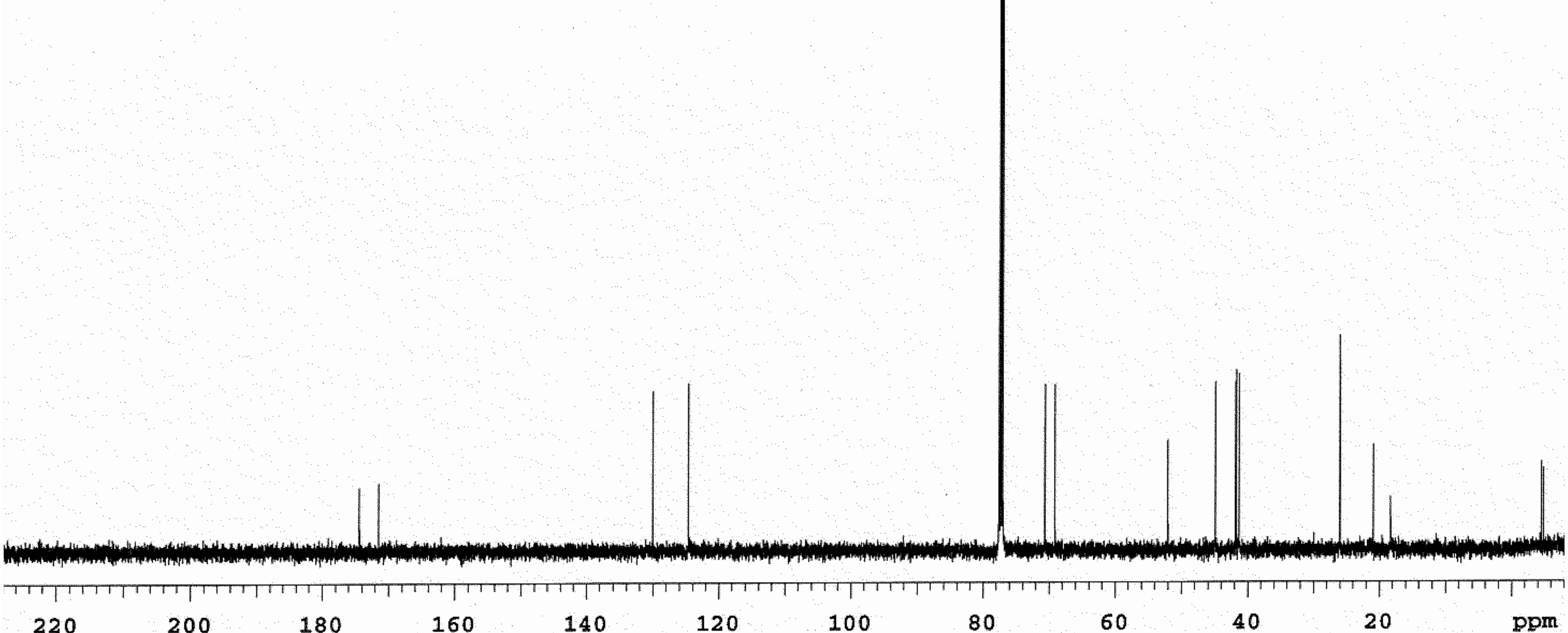
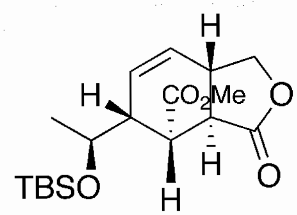


500 MHz ^{1}H NMR spectrum in $CDCl_3$



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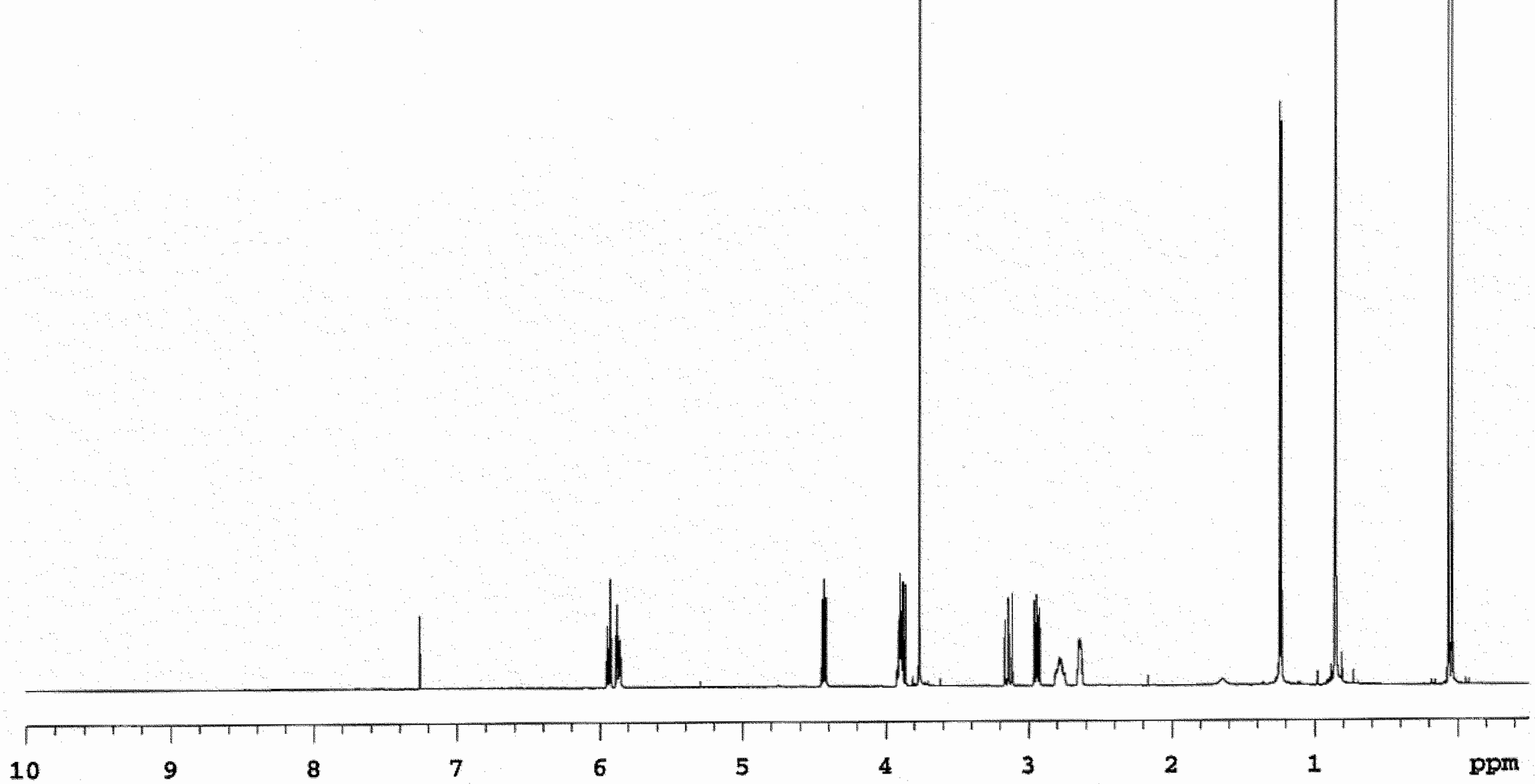
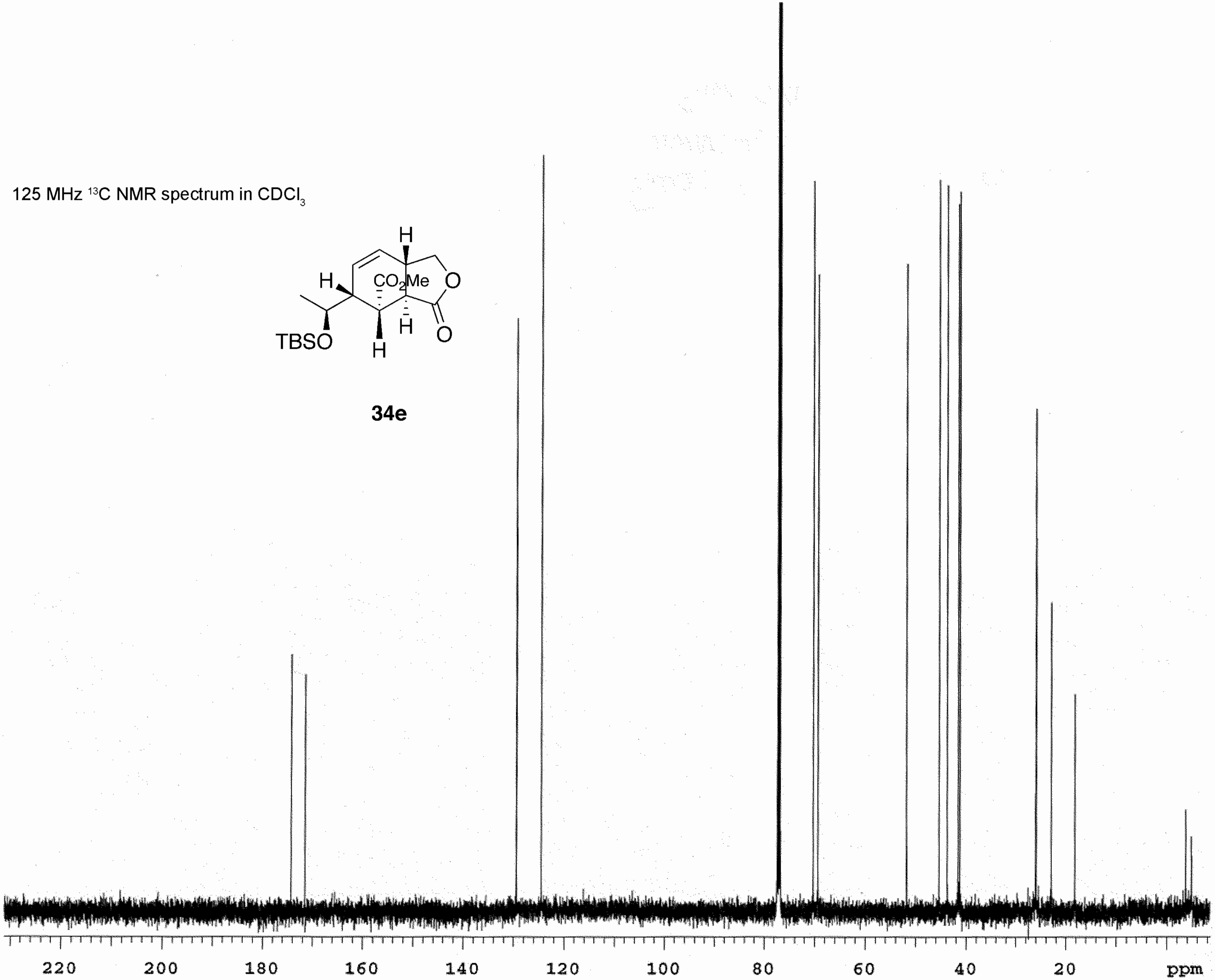


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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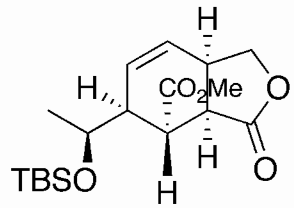
500 MHz ^{1}H NMR spectrum in $CDCl_3$



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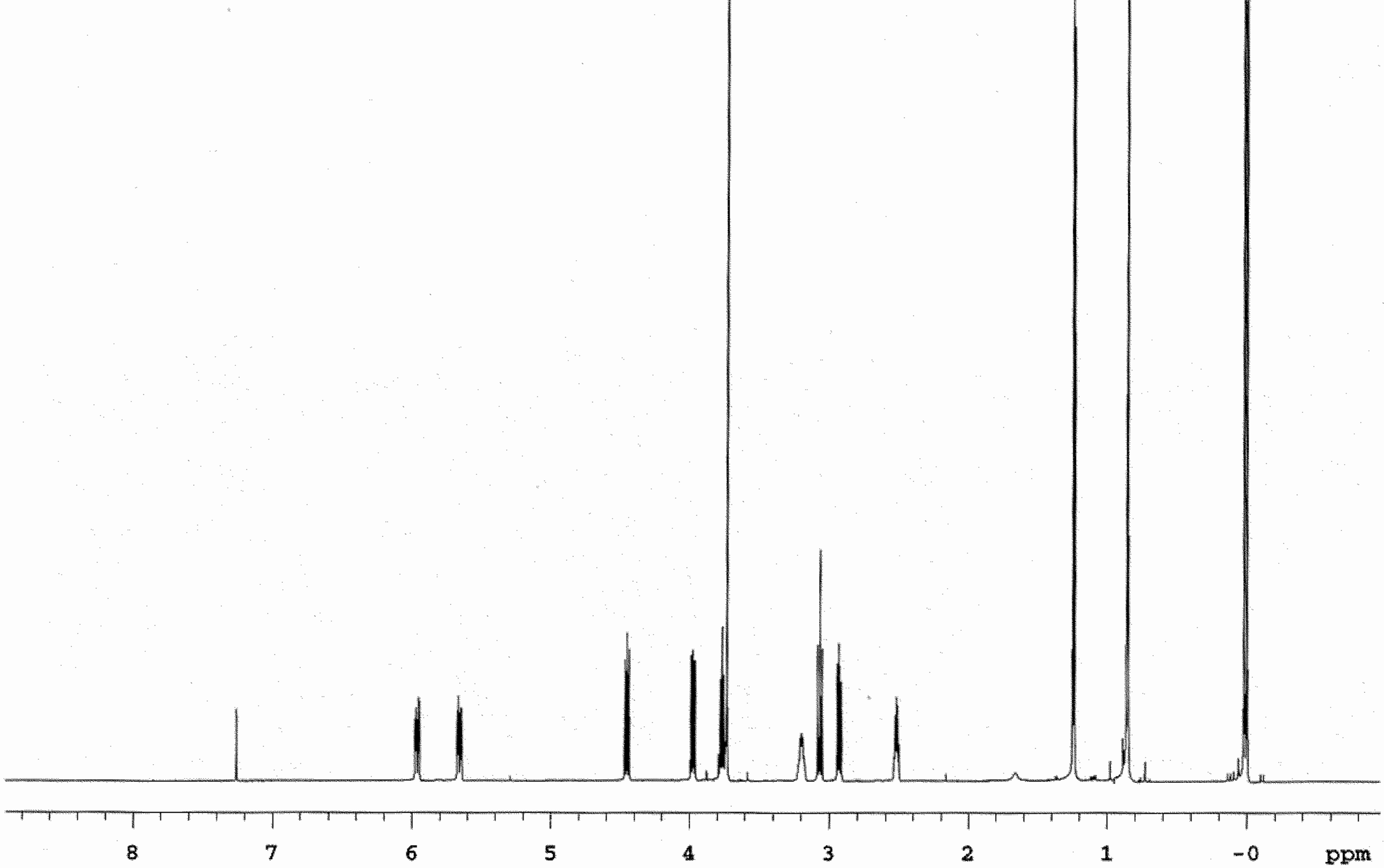
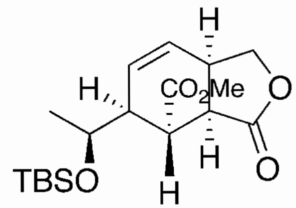


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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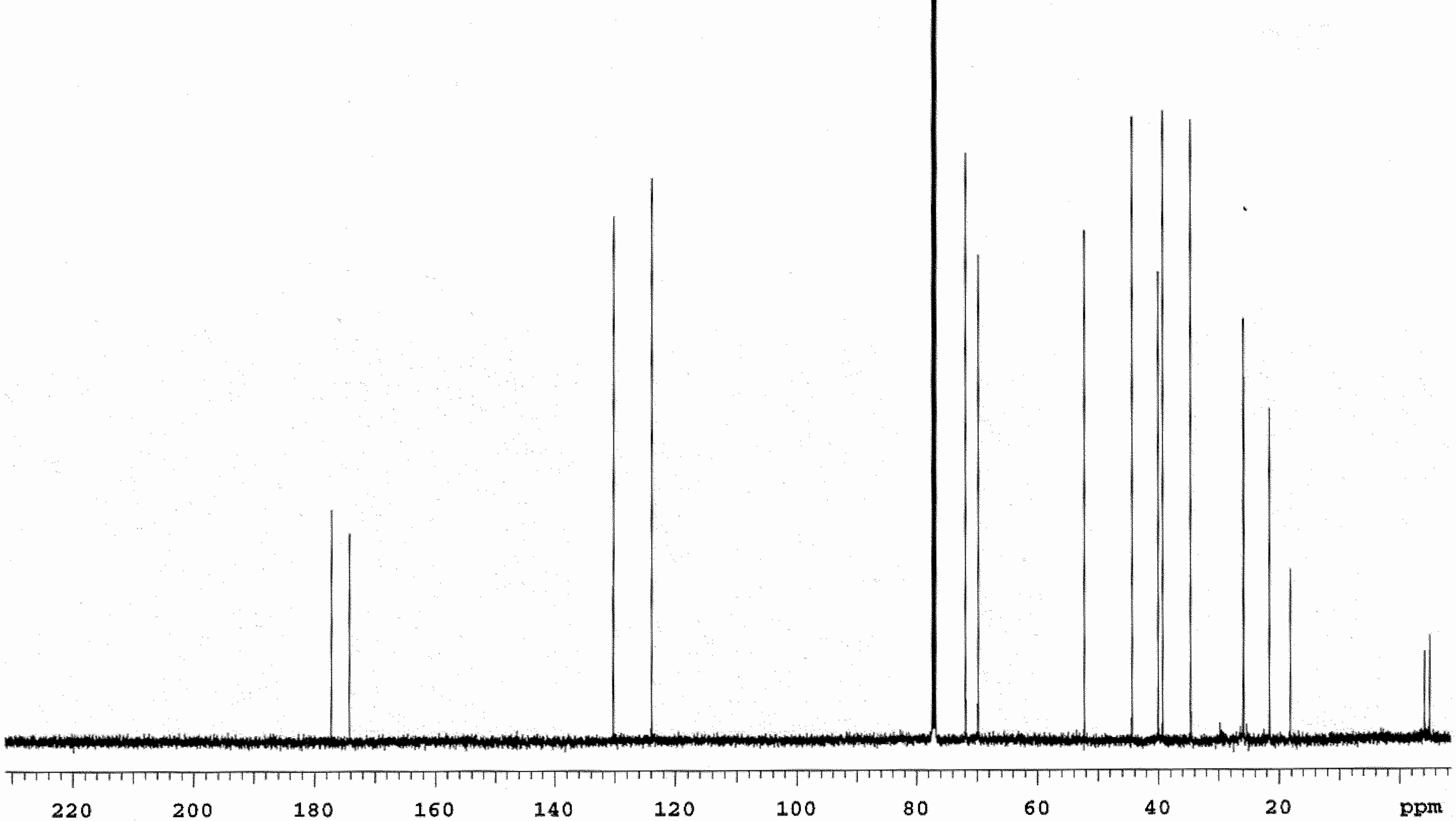
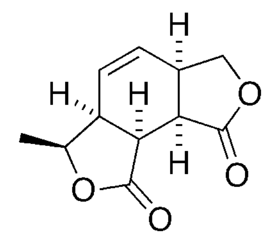


300 MHz ^{1}H NMR spectrum in $CDCl_3$



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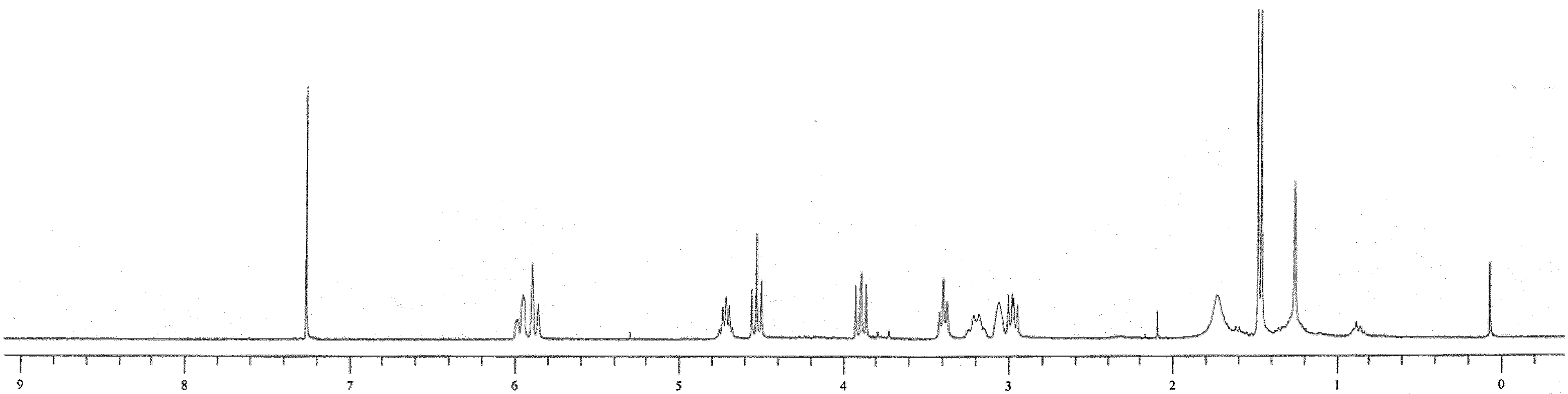
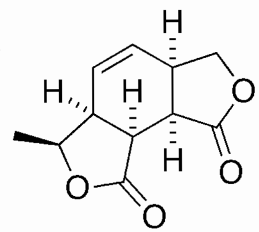


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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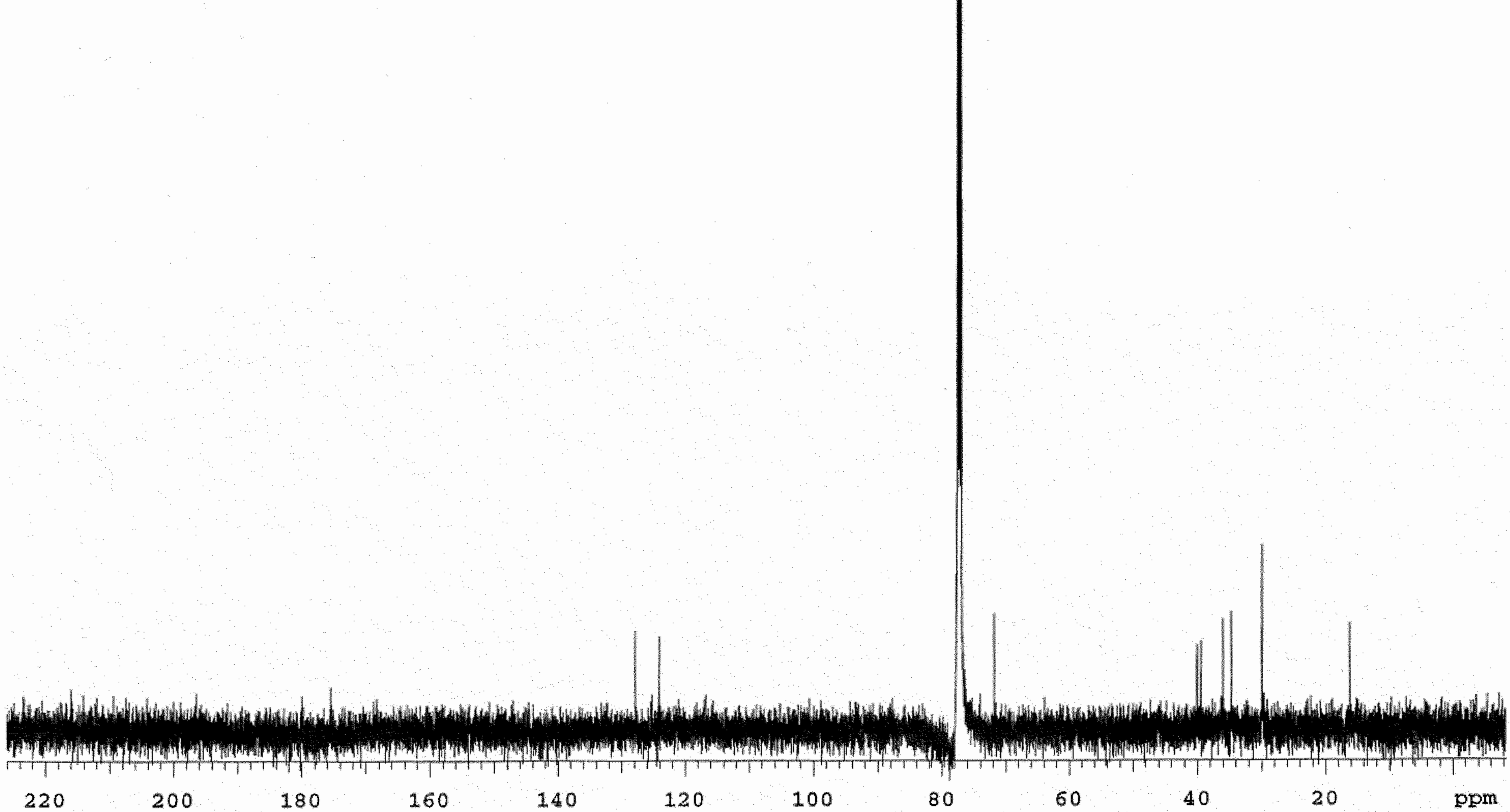
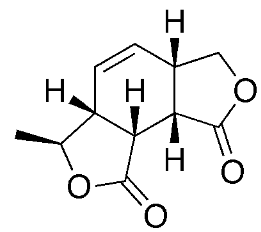


400 MHz [1]H NMR spectrum in $CDCl_3$



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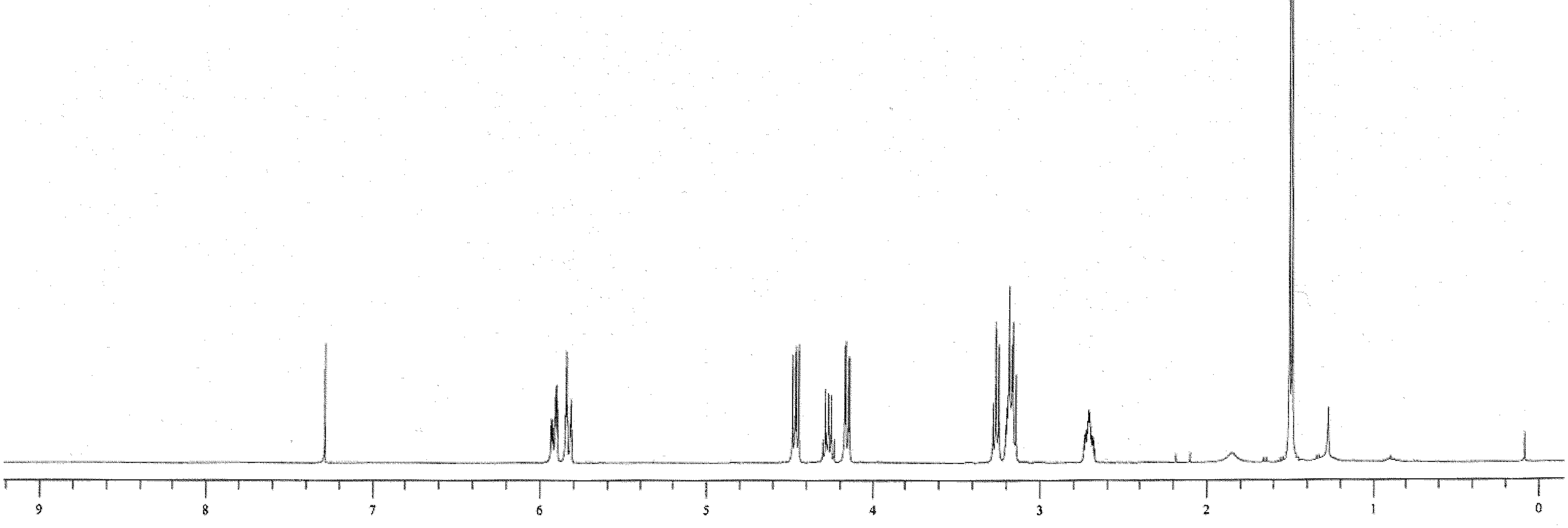
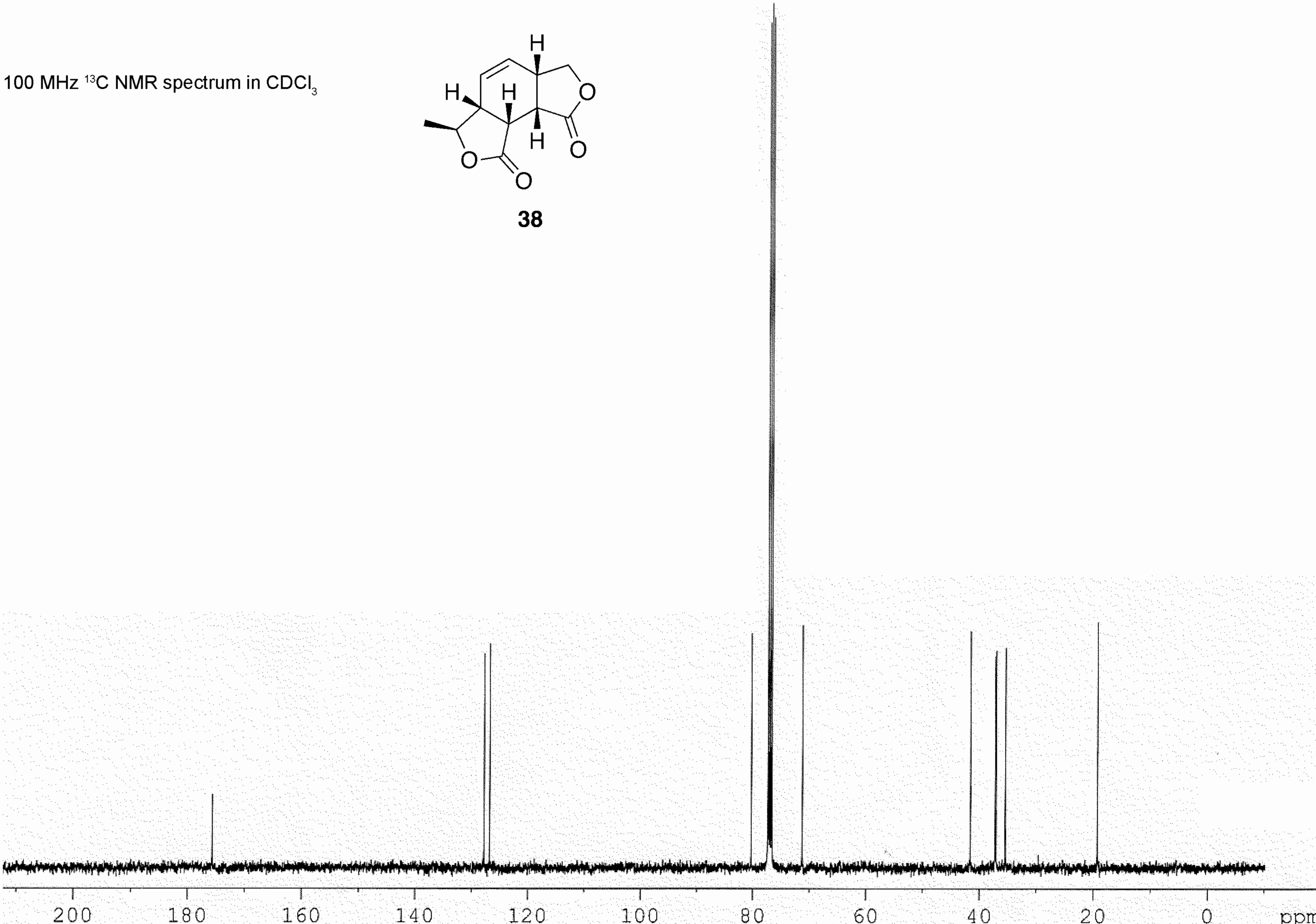
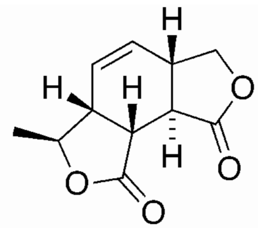


100 MHz ^{13}C NMR spectrum in $CDCl_3$



500 MHz ^{1}H NMR spectrum in $CDCl_3$



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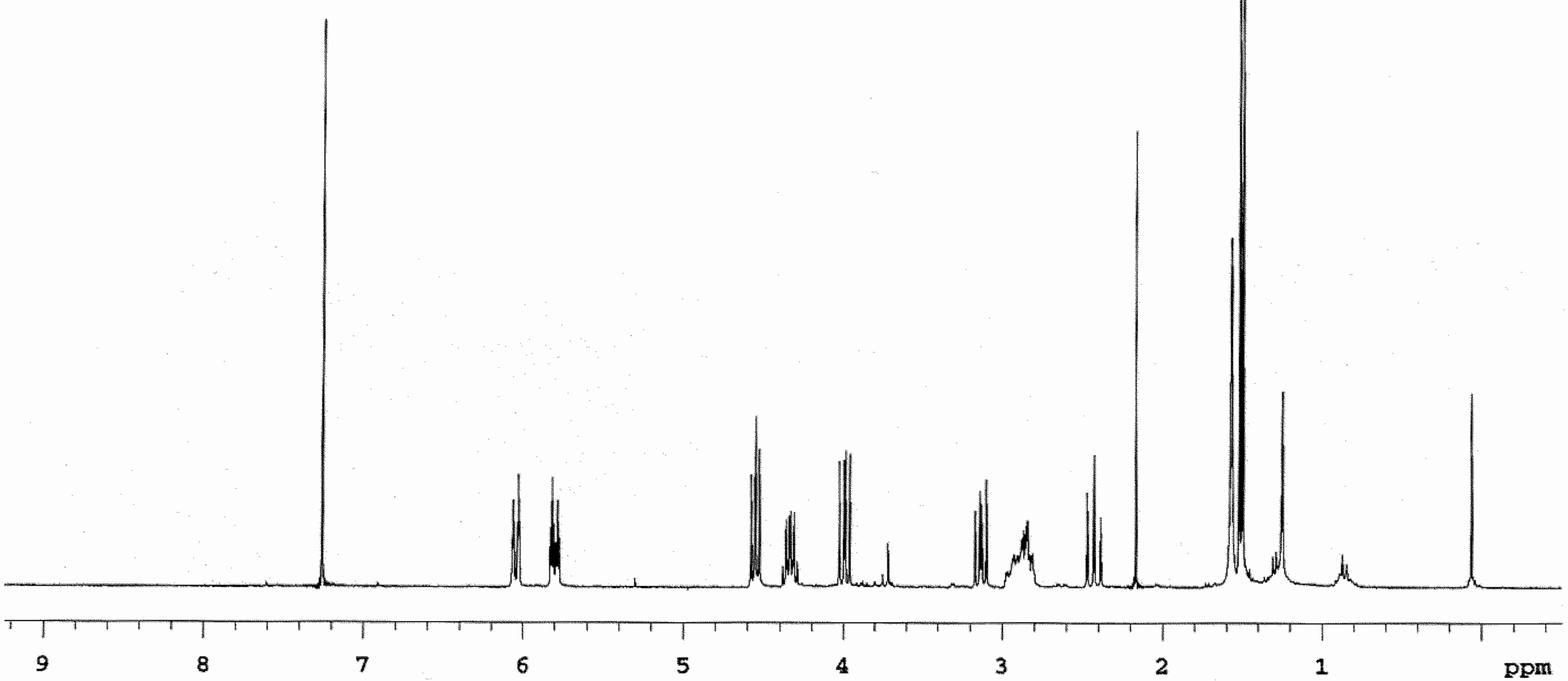
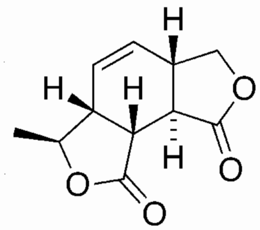


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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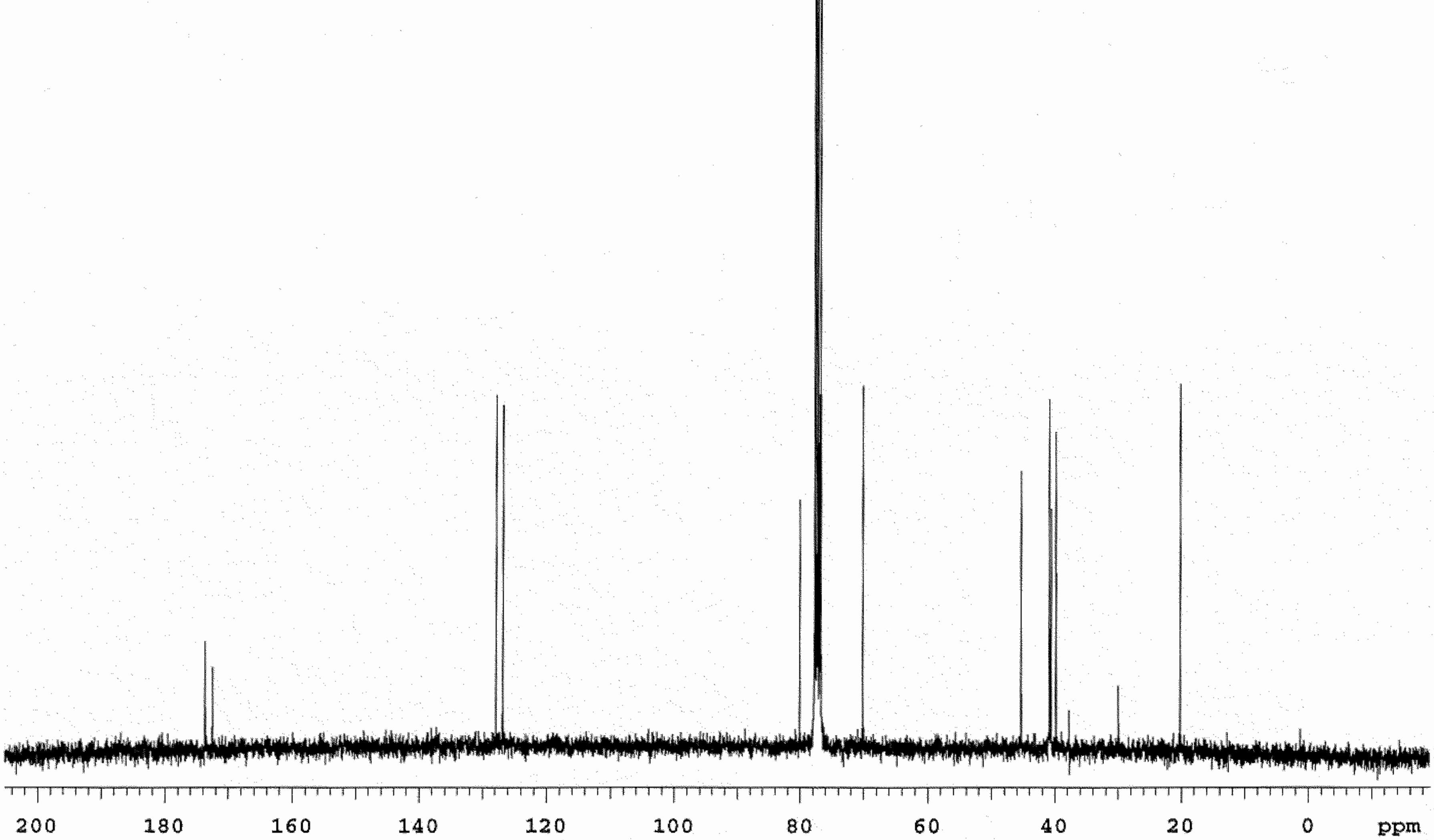
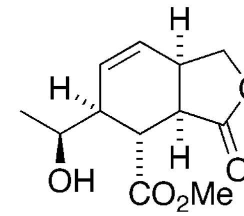


500 MHz ^{1}H NMR spectrum in $CDCl_3$



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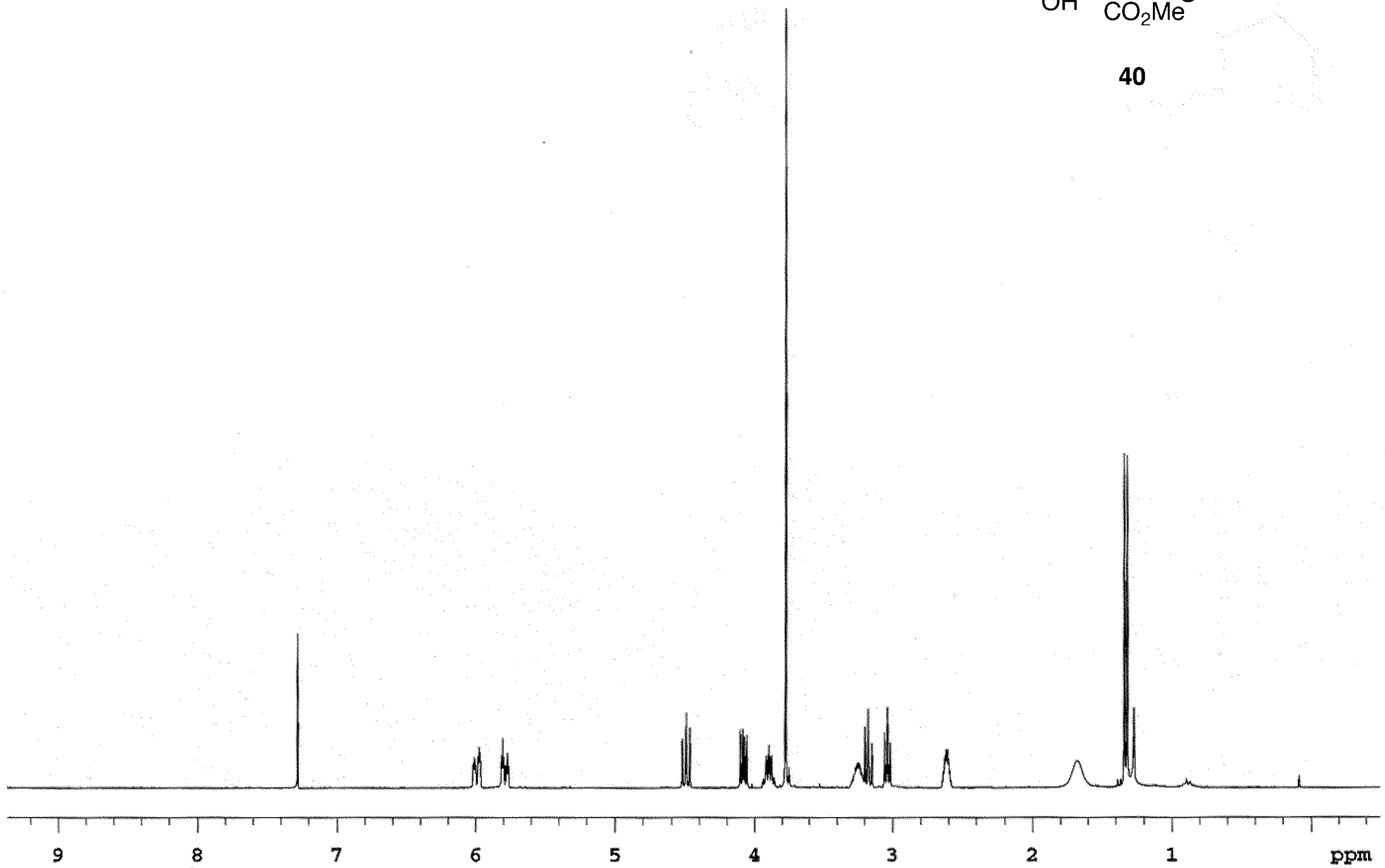
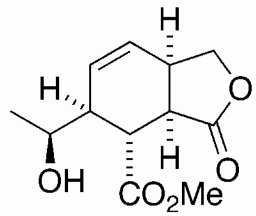


125 MHz ^{13}C NMR spectrum in $CDCl_3$



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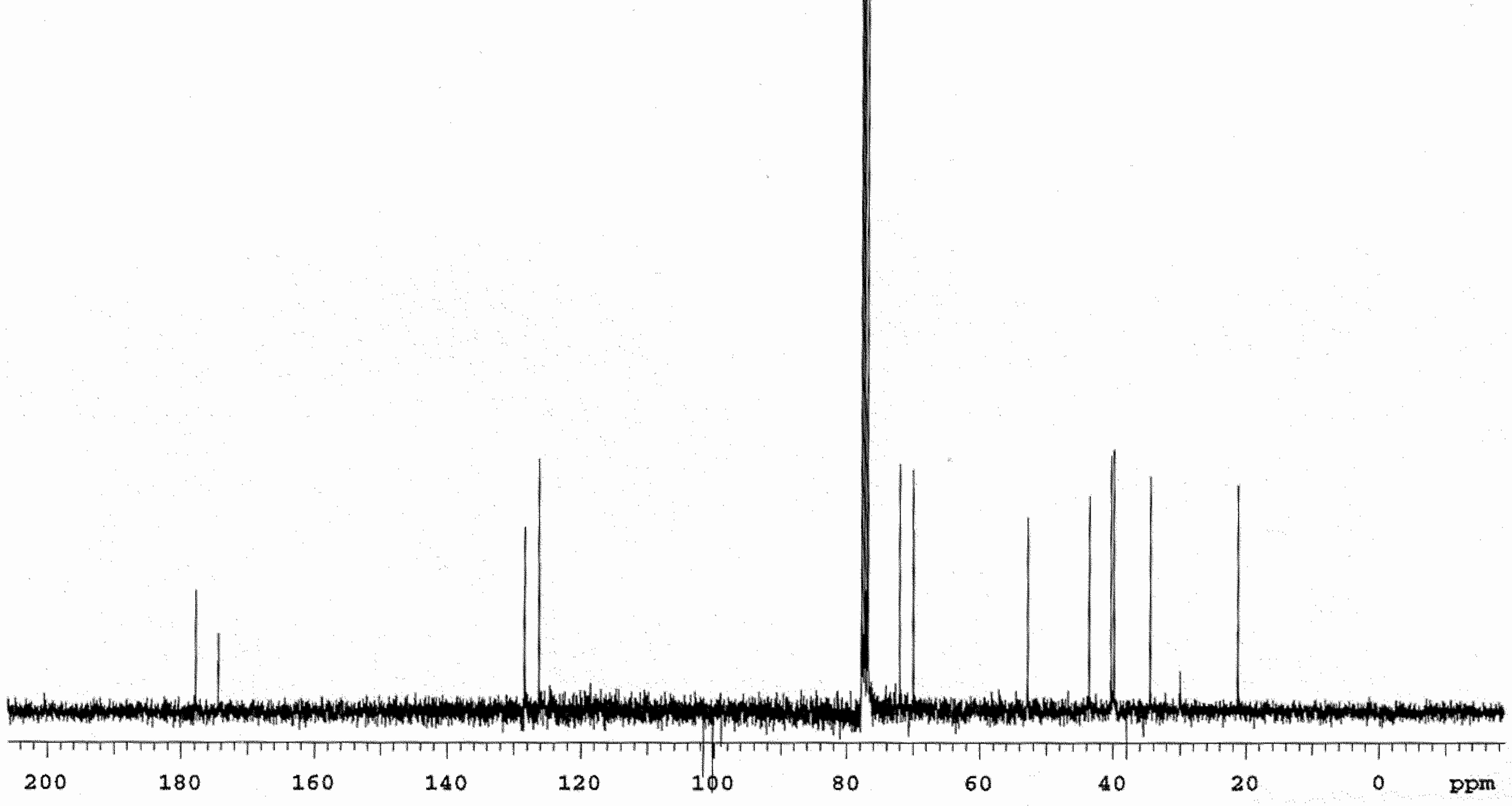
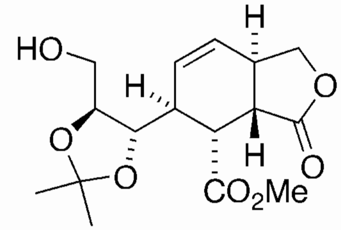


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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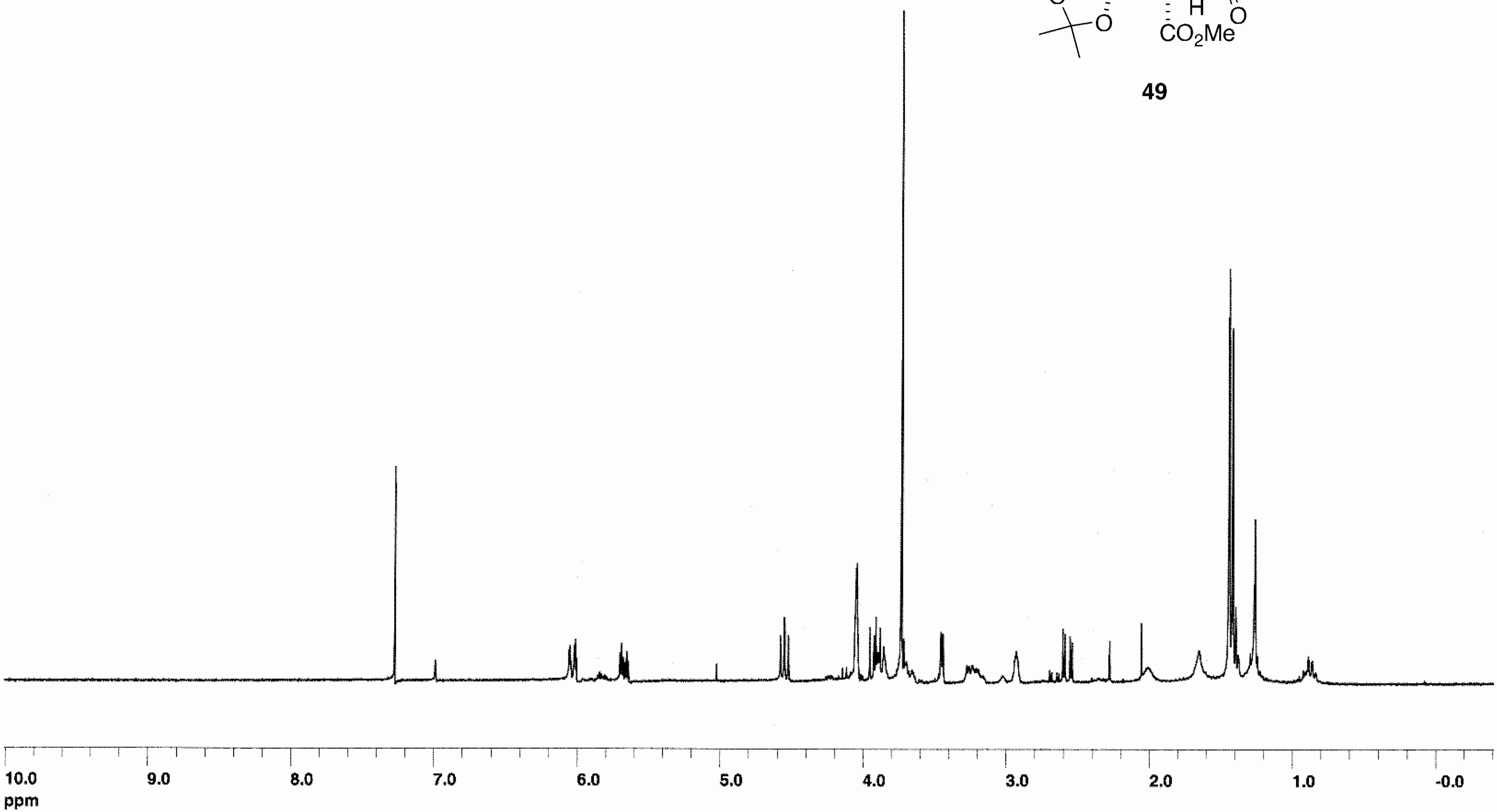
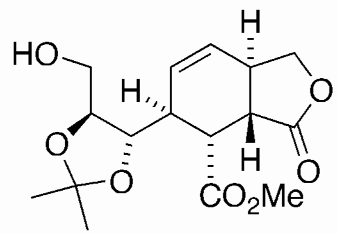


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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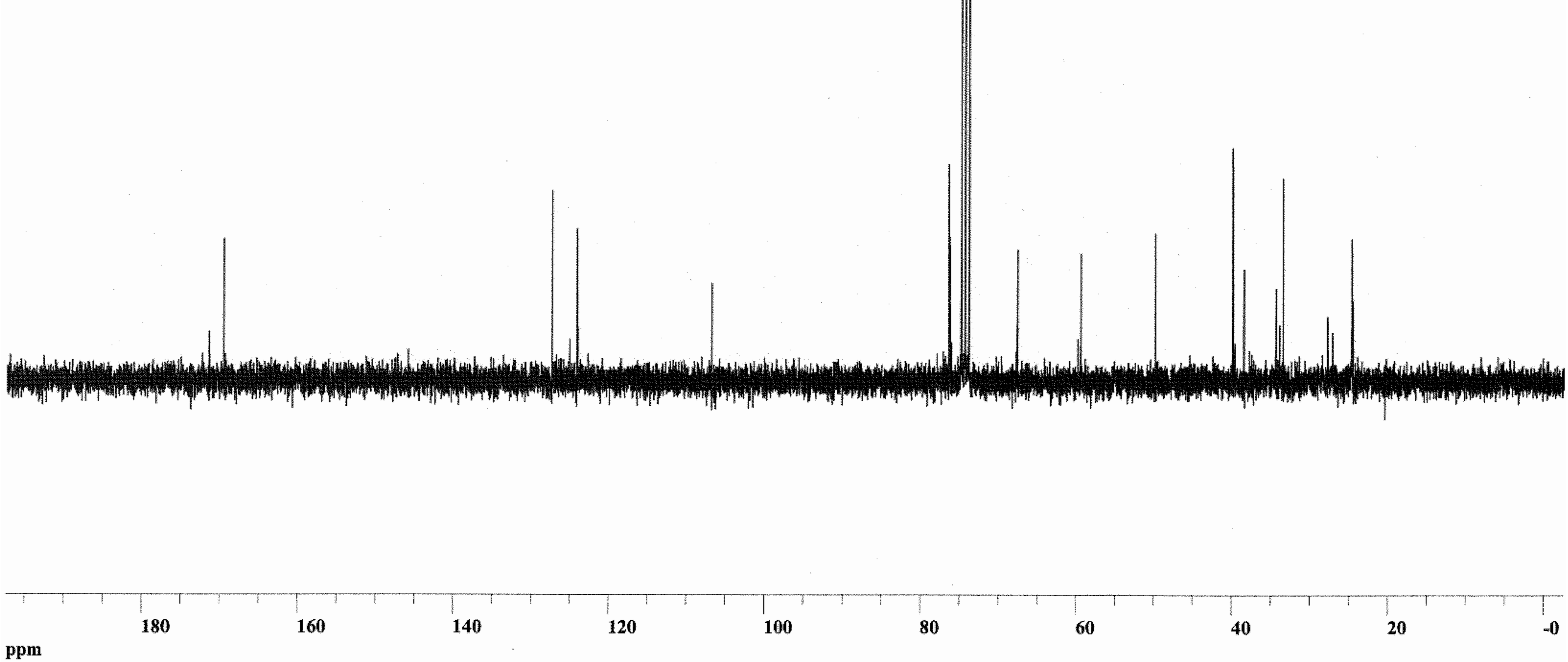
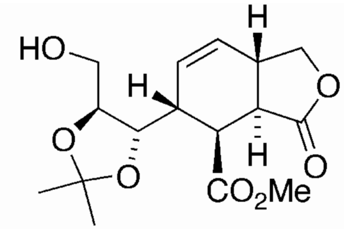


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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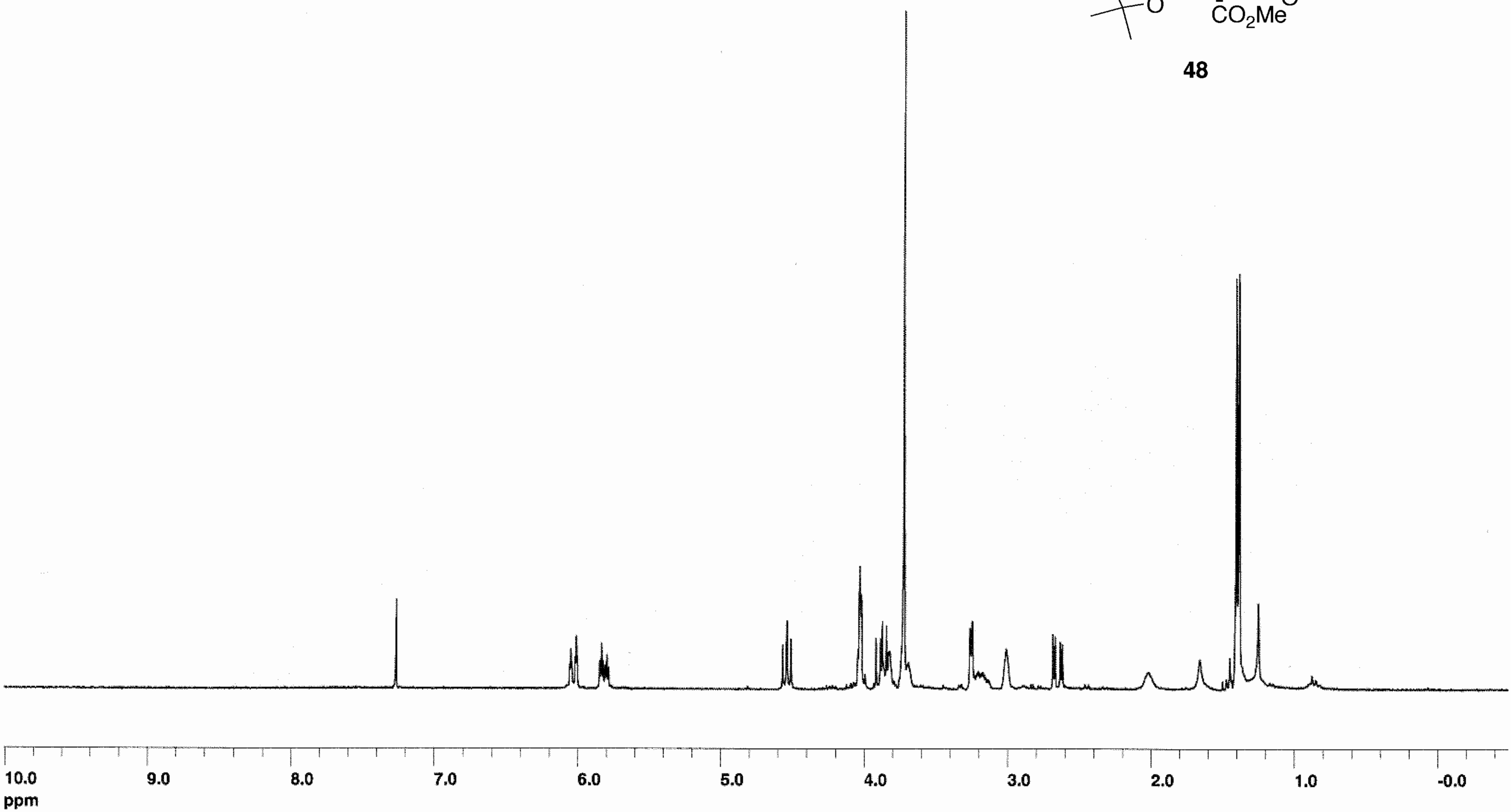
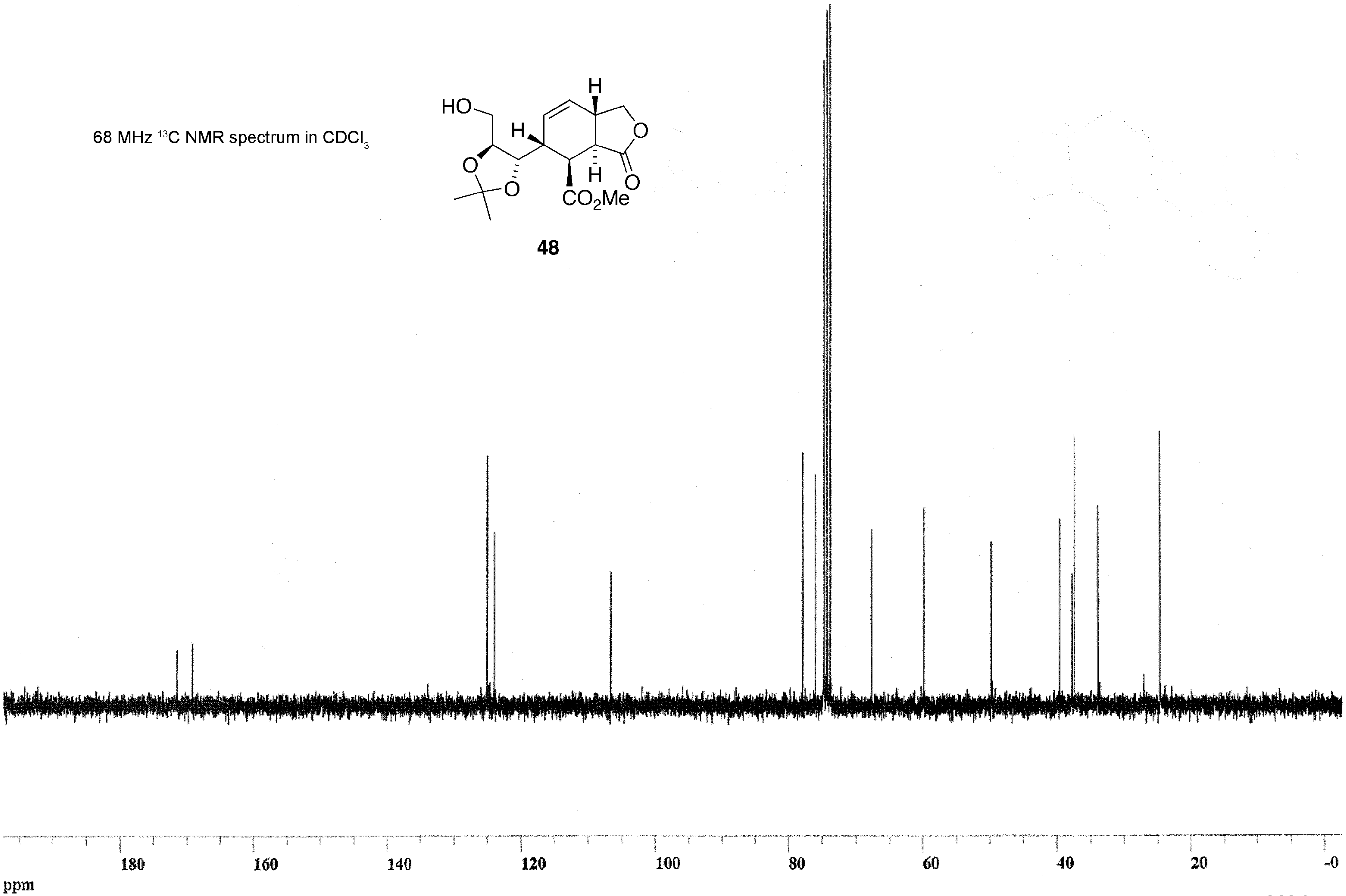
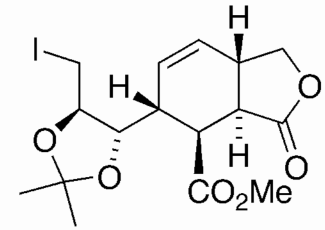


68 MHz ^{13}C NMR spectrum in $CDCl_3$



270 MHz ^{1}H NMR spectrum in $CDCl_3$



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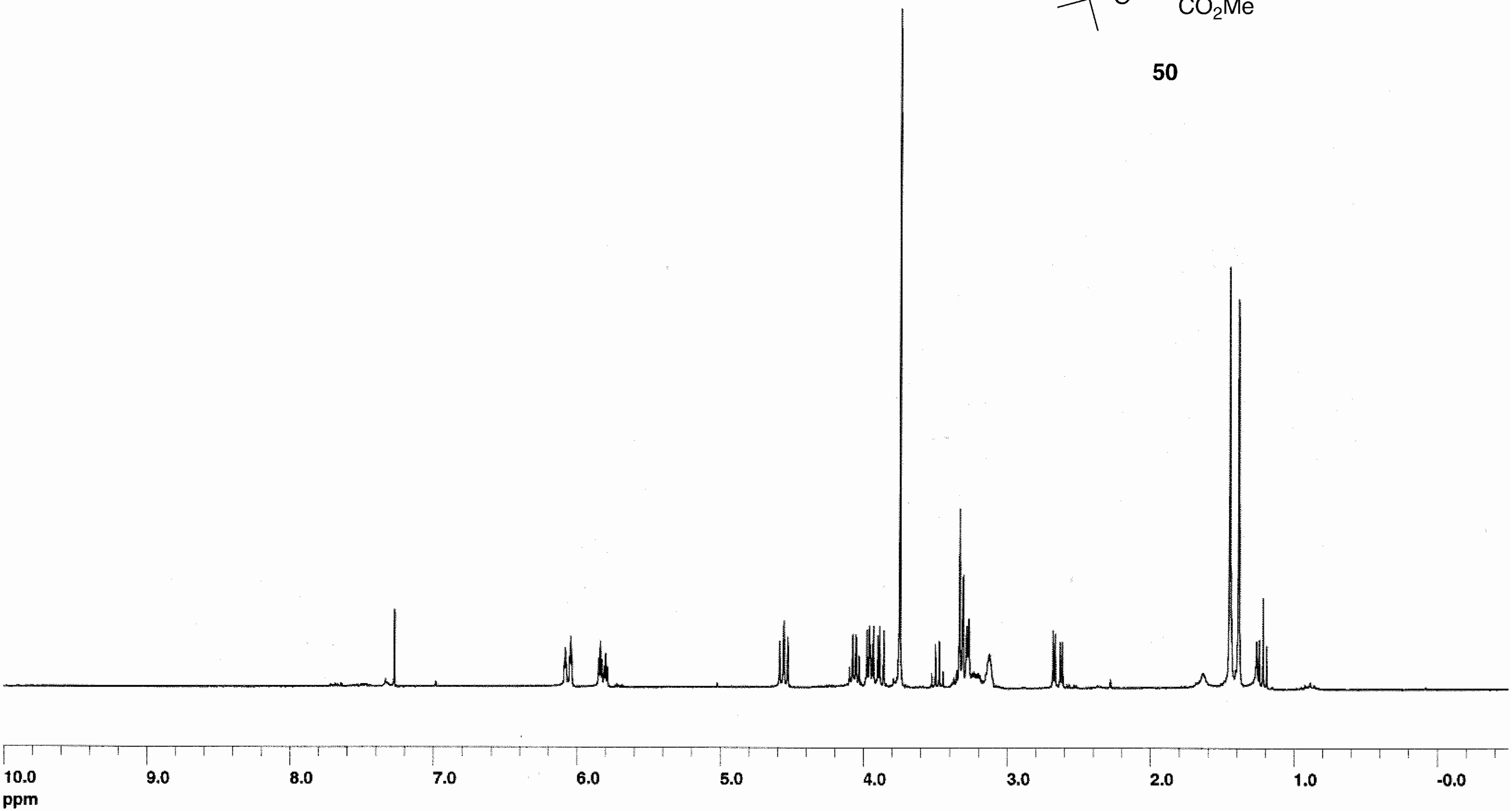
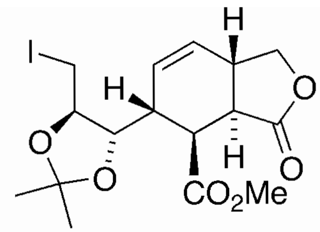


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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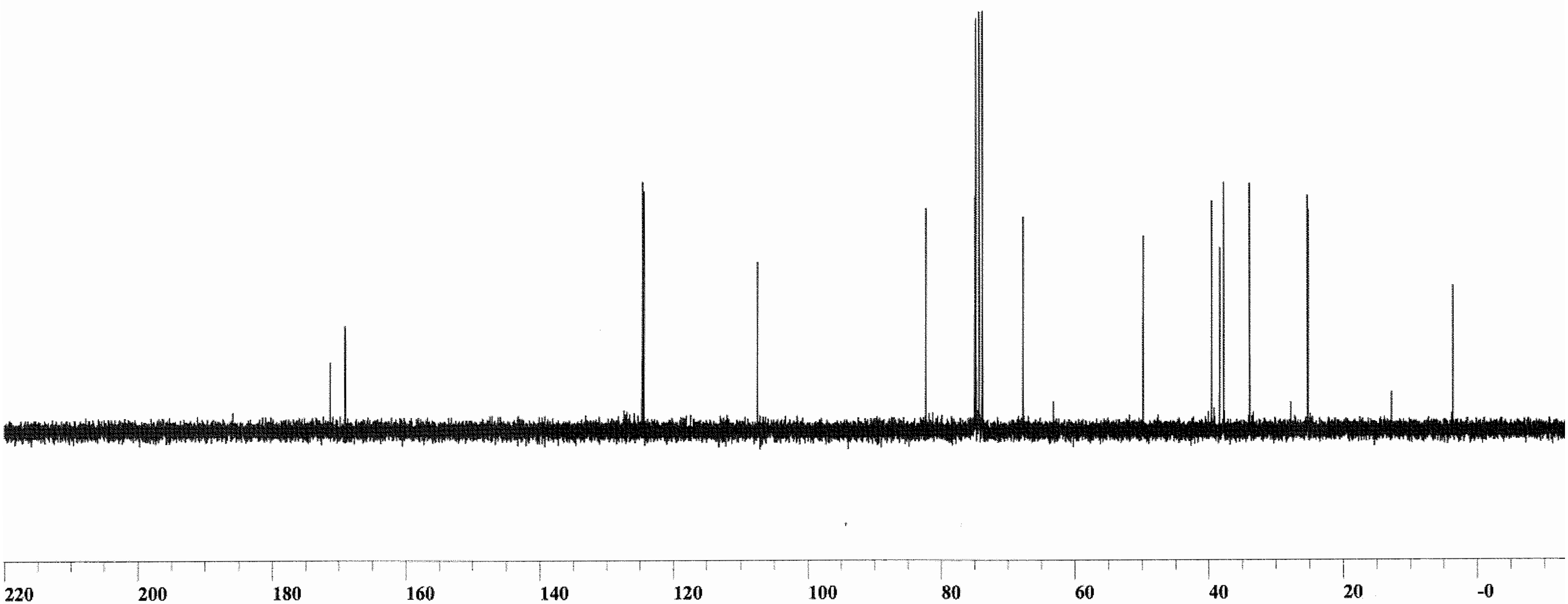
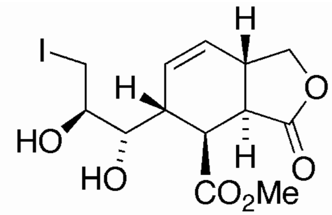


270 MHz ^{1}H NMR spectrum in $CDCl_3$



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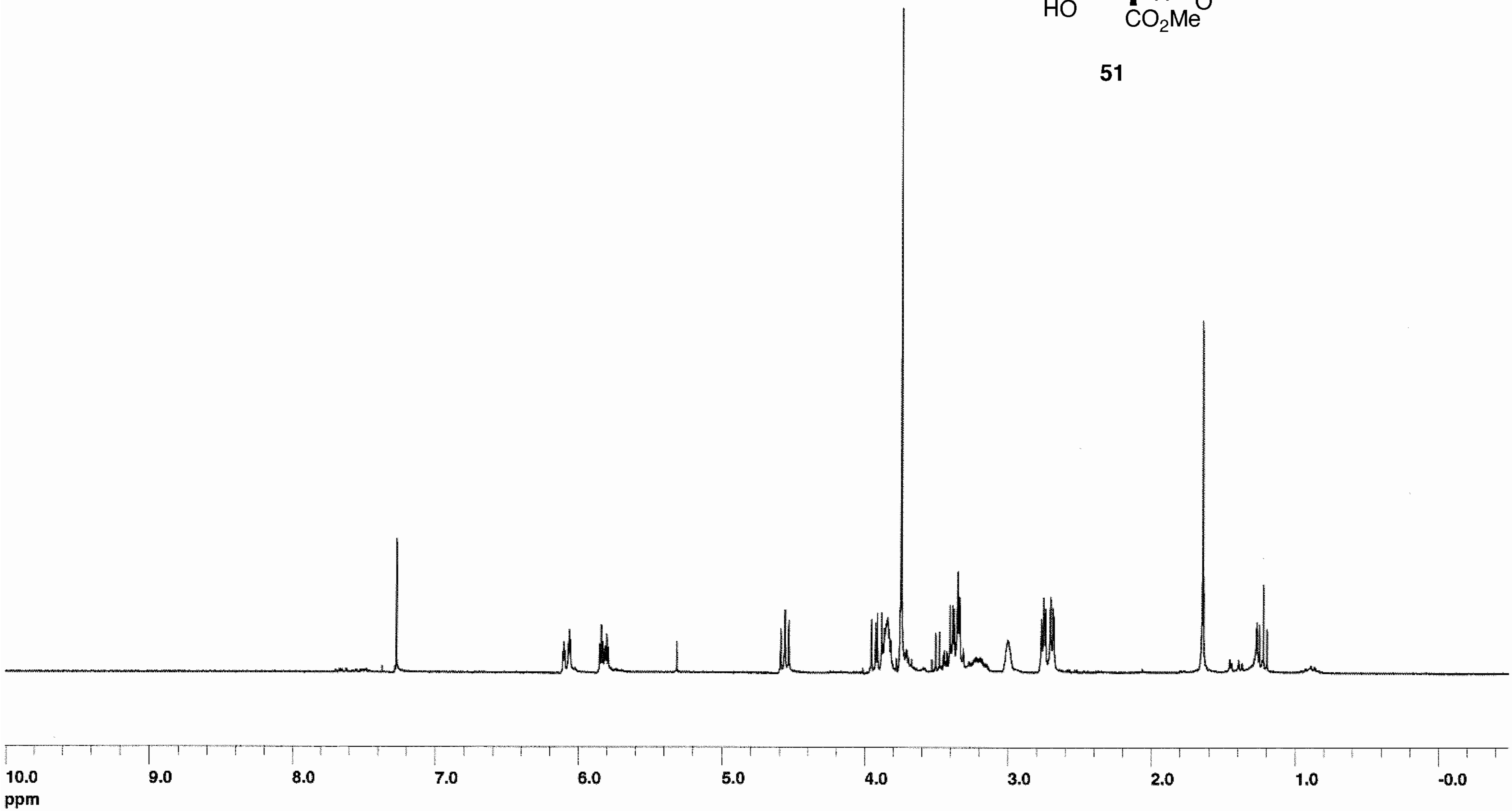
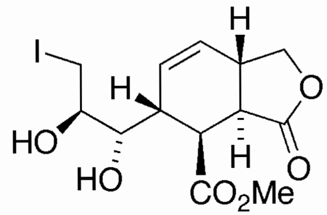


68 MHz ^{13}C NMR spectrum in $CDCl_3$



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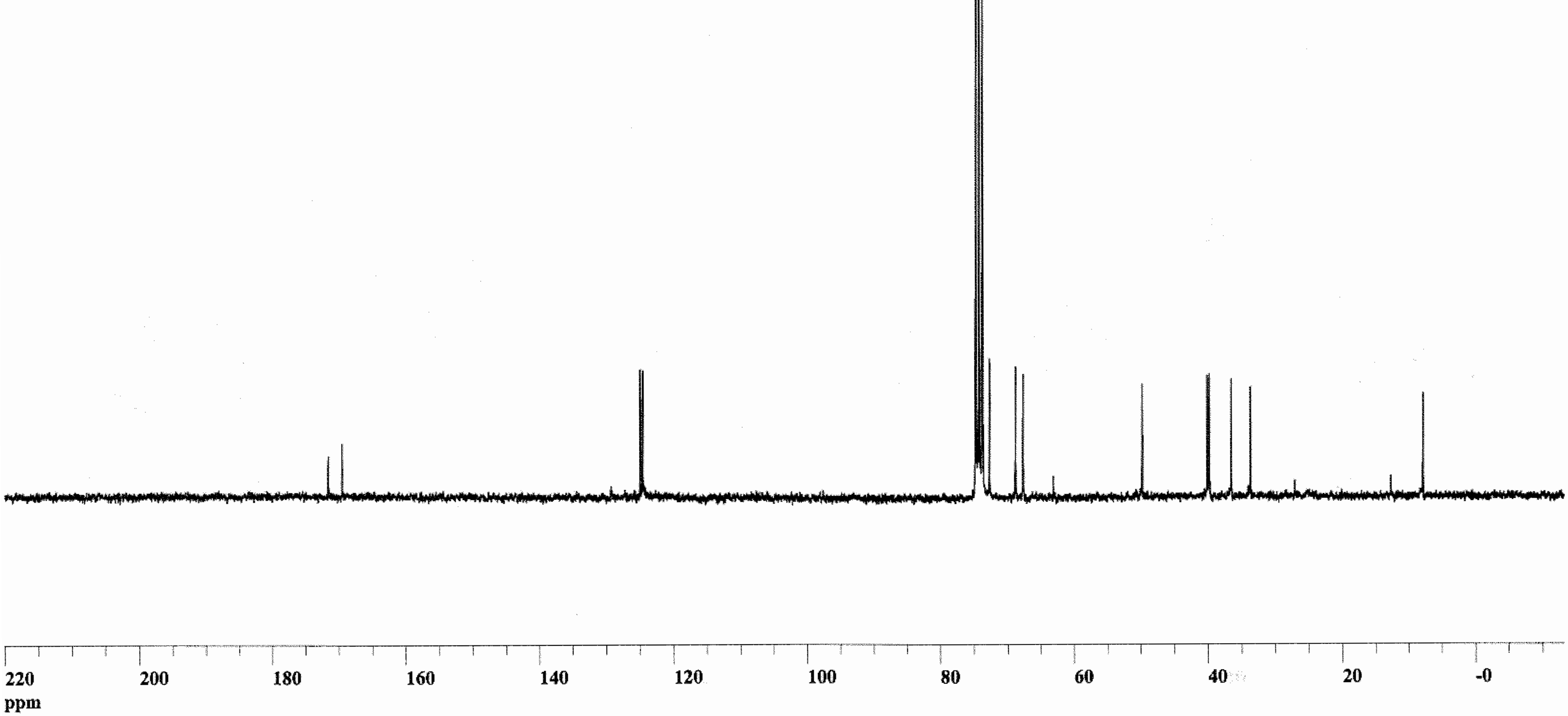
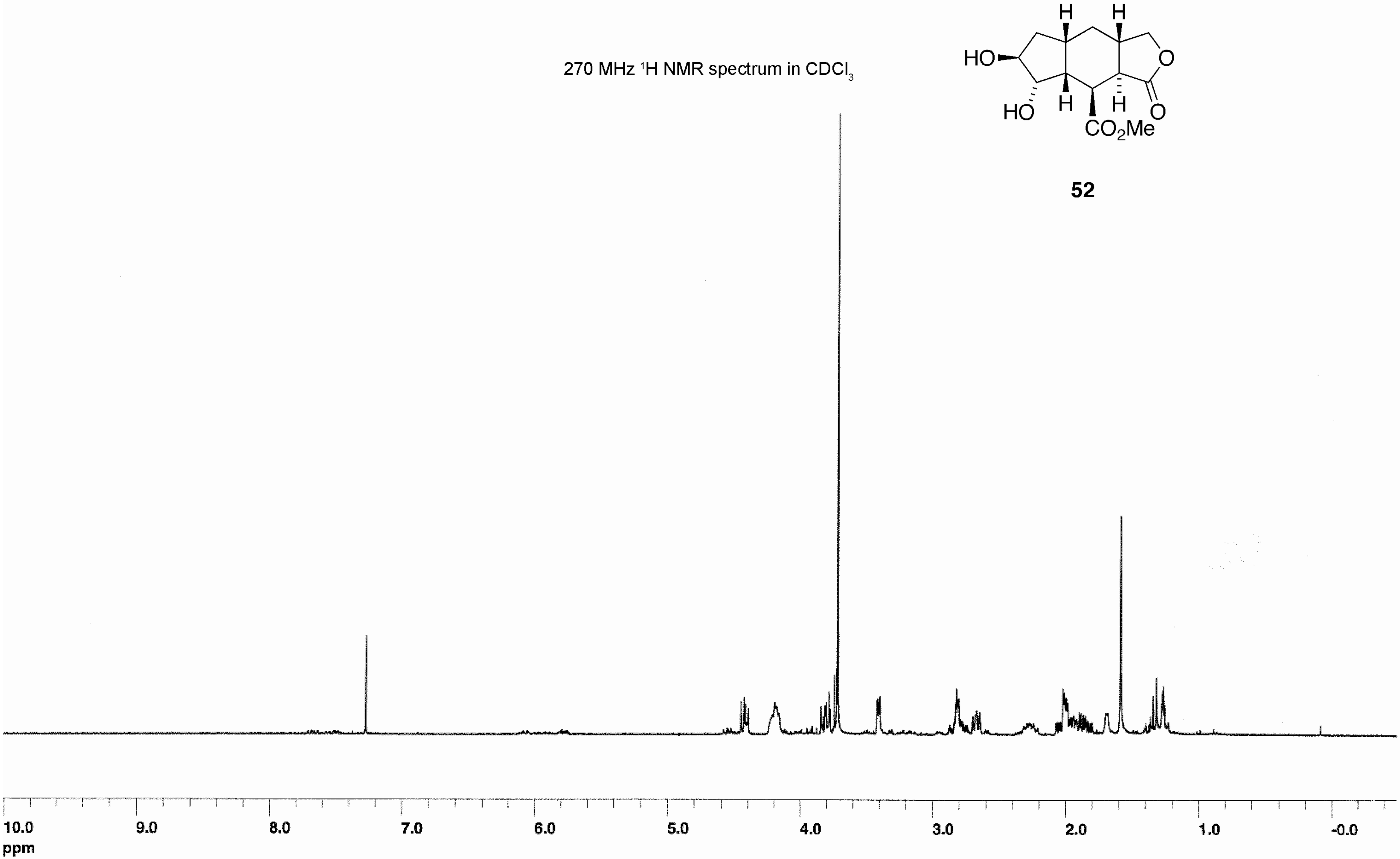
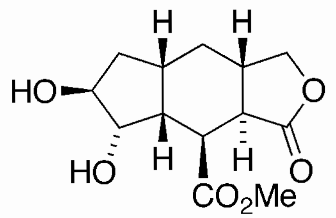



270 MHz ¹H NMR spectrum in CDCl3
HO
HO
H
H
H
H
O
O
CO2Me
52
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
-0.0
ppm

68 MHz ^{13}C NMR spectrum in $CDCl_3$



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