Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Straightforward Synthesis of Functionalized 6*H*-Benzo[*c*]chromenes from 3-Alkenyl Chromenes by Intermolecular Diels-Alder/Aromatization Sequence

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Kinetic analysis approach to the Diels-Alder cycloadditions of dienes with methyl propiolate

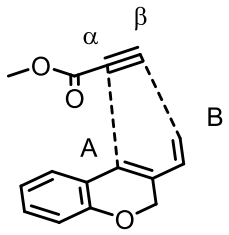
Assuming that the Diels-Alder reaction is under kinetic control, the Eyring equation has been used to calculate the relative reaction rates by knowing the relative energy differences between the 4 transition states. The *ortho* and *meta* nomenclature is referred to the relative position of the methyl propiolate carbonyl group and aromatic ring of the 2*H*-chromene core.

$$k_{rel} = e^{\frac{\Delta\Delta G}{RT}}$$

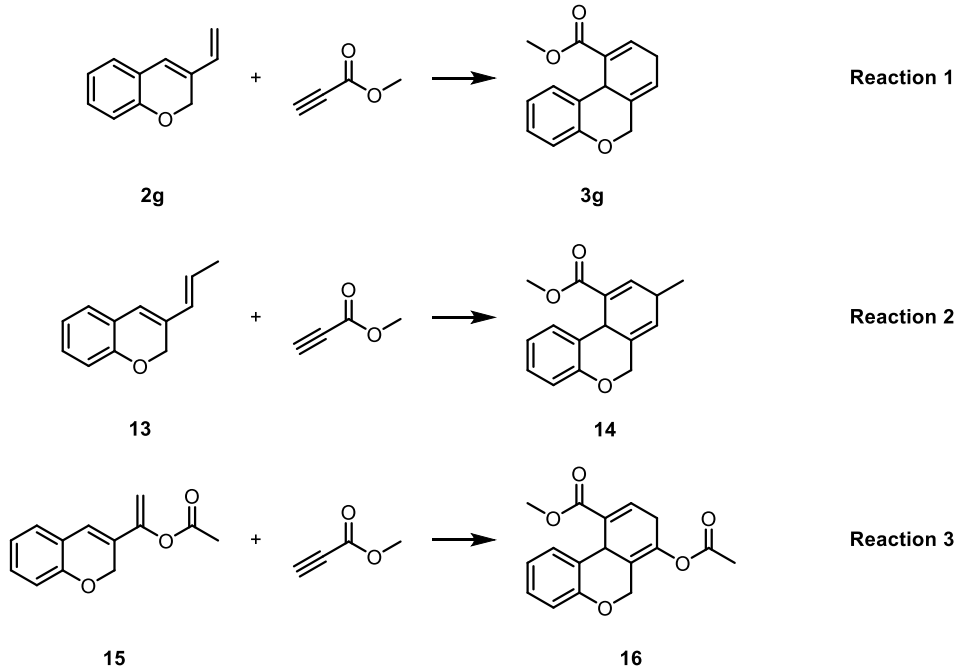
Using the found relative reaction rates, the regioisomeric ratio was calculated as:

$$Product\ ratio_{ortho-para} = \frac{k_{ortho-endo} + k_{ortho-exo}}{k_{meta-endo} + k_{meta-exo}}$$

The Activation Gibbs free energies are calculated by subtracting the energy of the optimized reactants from the energy of the most stable Transition State.



Scheme S1: Naming scheme of the atoms involved in the Diels-Alder cycloaddition



Scheme S2: Representative reactions used for the computational analyses.

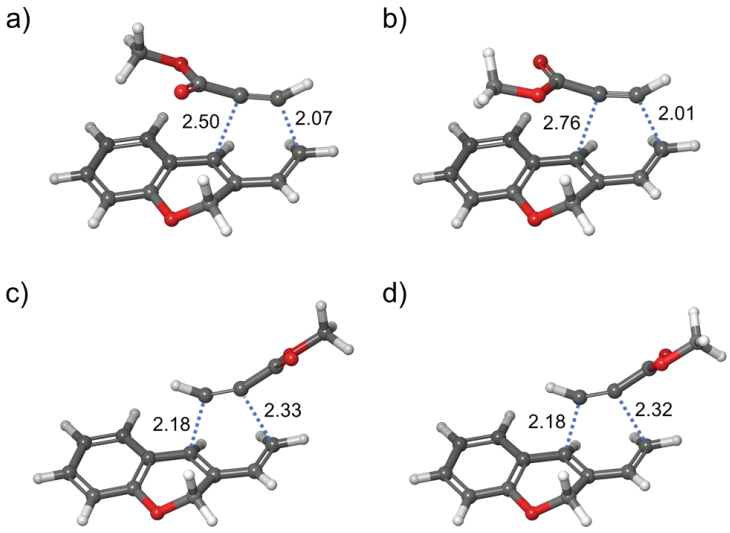


Figure S1: Balls-and-sticks representations of the found TSs for the Reaction 1. Carbons, hydrogens and oxygen atoms are coloured in grey, white and red respectively. Atom distances are shown as dashed lines and reported in Å. a) Ortho-endo TS. b) Ortho-exo TS. c) Meta-endo TS. d) Meta-exo TS.

Table S1: M06-2X-D3/6-31+G ZPE-corrected gas phase energies of the located Transition States and relative reaction rates for Reaction 1.**

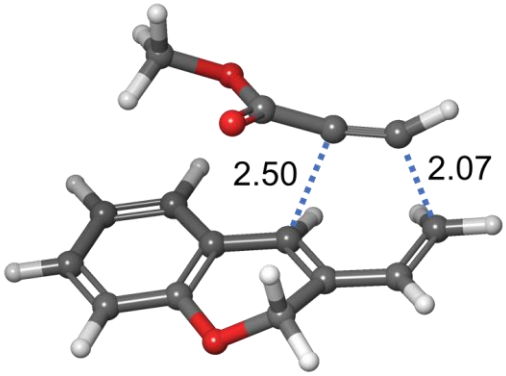
Transition State	Total Gibbs Free Energy (Hartree)	Relative Energy (kcal/mol)	Relative reaction rate (k_{rel})	Predicted product ratio	Experimental product ratio
TS_{2g}-ortho-endo	-805.045295	0.6237	12.4	95	100
TS_{2g}-ortho-exo	-805.046289	0.0000	26.3		
TS_{2g}-meta-endo	-805.042004	2.6888	1.0	5	Not detected
TS_{2g}-meta-exo	-805.041957	2.7183	1.0		

Table S2: Bond lengths and negative frequencies of the located TSs for Reaction 1.

Transition State	Bond lengths (Å)	Negative frequency
TS_{2g}-ortho-endo	α-A = 2.50 β-B = 2.07	-487.96 cm^{-1}
TS_{2g}-ortho-exo	α-A = 2.76 β-B = 2.01	-470.80 cm^{-1}
TS_{2g}-meta-endo	α-B = 2.33 β-A = 2.18	-487.67 cm^{-1}
TS_{2g}-meta-exo	α-B = 2.32 β-A = 2.18	-491.42 cm^{-1}

Optimized geometries and Z-Matrices of the located transition states for Reaction 1 at the B3LYP-D3/6-31+G level of theory**

Figure S2: TS_{2g}-ortho-endo optimized geometry



0 1

C	0.0000000000000	0.0000000000000	0.0000000000000
C	0.0000000000000	0.0000000000000	1.3937071926200
C	1.1981248900999	0.0000000000000	2.1007451995348
C	2.4005362259450	0.0113091216926	1.4046977910545
C	2.4229998849387	-0.0046363202607	0.0006399513773
C	1.2076610677366	-0.0114137507147	-0.6871007835501
O	3.5599928500642	-0.0413614287376	2.1194316735201
C	4.6976205894664	0.5402593888899	1.4967748197581
C	4.8449819678458	0.1558386681334	0.0426011281664
C	3.7237561082645	-0.0842126215676	-0.6545160262851
C	6.1963385059680	0.1150207020363	-0.5268655612490
C	6.5043008237074	0.4446075712856	-1.7829147751278
H	-0.9369918851825	0.0012680427787	-0.5459465432779
H	-0.9396914538204	0.0013754959401	1.9365073024923
H	1.2234579866793	-0.0062491518613	3.1847642462648
H	1.2215718271080	-0.0312717968124	-1.7735245946928
H	3.7667845361242	-0.3780092857976	-1.7002233167587
H	7.5196720130254	0.3635700914698	-2.1539329022027
H	5.7498661328298	0.8125970868196	-2.4717796176037
H	6.9922638646675	-0.1974231626866	0.1489554857379

H	5.5575131165564	0.2003564453942	2.0799904940125
H	4.6414382047085	1.6369486529485	1.5890308513002
C	4.8815965146491	3.5457203557836	-2.0109305559582
C	3.7613035413231	3.4932238029681	-1.5235819073656
C	2.3415846422565	3.4742055881784	-0.8447659809223
O	2.1636829575245	3.7086127884656	0.3510678872002
O	1.3727258230722	3.1748554722119	-1.7322197350095
C	0.0122790979482	3.1330299521537	-1.3205395221471
H	-0.6252978975773	2.8617158770356	-2.1618846033229
H	-0.1435330720737	2.3954750071705	-0.5299314574672
H	-0.3138877020821	4.1063526331568	-0.9491707032484
H	5.8640321895173	3.5980048076843	-2.4253148248615

Zero Point Energy: 160.333 kcal/mol

Total internal energy: -804.988215 Hartrees

Total enthalpy: -804.987271 Hartrees

Total Gibbs free energy: -805.045295 Hartrees

Number of negative frequencies: 1

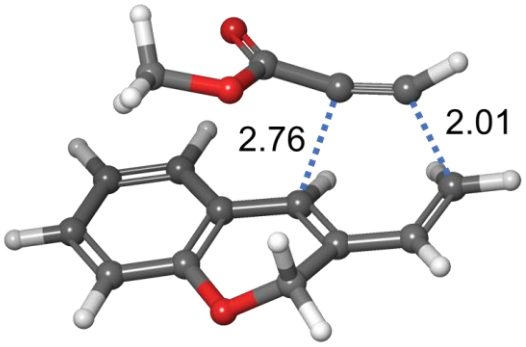
Frequency: -487.96

Red. Masses: 3.14

Frc. const.: 0.44

IR inten.: 16.62

Figure S3: TS_{2g}-ortho-exo optimized geometry



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C	-3.7569480000000	3.0381790000000	-1.6850680000000
C	-3.0519880000000	3.7670710000000	-0.7182560000000
C	-2.0671060000000	3.1528380000000	0.0596500000000
C	-1.7768200000000	1.8045630000000	-0.1429660000000
C	-2.4806940000000	1.0465330000000	-1.1096490000000
C	-3.4778280000000	1.6863740000000	-1.8704640000000
O	-0.8583330000000	1.2119000000000	0.6768210000000
C	-0.1787790000000	0.0714610000000	0.1263500000000
C	-1.1080470000000	-0.9090040000000	-0.5578980000000
C	-2.1854930000000	-0.3641720000000	-1.2291170000000
C	-0.7011720000000	-2.2496360000000	-0.7021330000000
C	-1.2614510000000	-3.1175620000000	-1.6431590000000
H	-4.5192150000000	3.5222360000000	-2.2870110000000
H	-3.2700660000000	4.8202470000000	-0.5663640000000
H	-1.5198050000000	3.6982800000000	0.8211790000000
H	-4.0072930000000	1.1132750000000	-2.6240900000000
H	-2.9098380000000	-0.9888120000000	-1.7386900000000
H	-0.8590140000000	-4.1253010000000	-1.7074970000000

H	-2.3199210000000	-3.0576010000000	-1.8770410000000
H	0.2337060000000	-2.5439920000000	-0.2275360000000
H	0.3460710000000	-0.3869540000000	0.9670850000000
H	0.5662840000000	0.4302700000000	-0.6019630000000
C	-0.7515620000000	-2.3100670000000	-3.4114850000000
C	-1.0277670000000	-1.1109280000000	-3.6182070000000
C	-1.3116500000000	0.2375280000000	-3.9780120000000
O	-2.3468800000000	0.6201380000000	-4.5091570000000
O	-0.2874910000000	1.0707060000000	-3.6499570000000
C	-0.5008610000000	2.4622410000000	-3.9651900000000
H	0.4169540000000	2.9663380000000	-3.6629840000000
H	-0.6764600000000	2.5897560000000	-5.0364460000000
H	-1.3555180000000	2.8526600000000	-3.4084190000000
H	-0.2957280000000	-3.1650780000000	-3.8813930000000

Zero Point Energy: 159.631 kcal/mol

Total internal energy: -804.989090 Hartrees

Total enthalpy: -804.988146 Hartrees

Total Gibbs free energy: --805.046289 Hartrees

Number of negative frequencies: 1

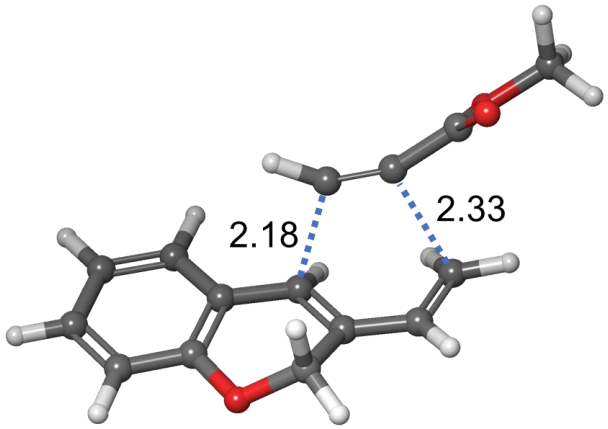
Frequency: -470.80

Red. Masses: 3.92

Frc. const.: 0.51

IR inten.: 57.77

Figure S4: TS_{2g}-meta-endo optimized geometry



0 1

C	-0.1282350000000	-1.5678890000000	-3.3477790000000
C	-0.6238130000000	-0.4393560000000	-3.1604460000000
C	0.6647740000000	-2.5713160000000	-4.0188020000000
O	1.8796850000000	-2.6458390000000	-3.9754570000000
O	-0.1193410000000	-3.4505830000000	-4.6930470000000
C	0.5858370000000	-4.5026090000000	-5.3820160000000
H	-0.1885970000000	-5.1035530000000	-5.8584770000000
H	1.2650670000000	-4.0836380000000	-6.1289210000000
H	1.1623510000000	-5.1042030000000	-4.6737300000000
H	-0.7672650000000	0.5793130000000	-3.4686180000000
C	-3.5514020000000	3.0498590000000	-1.9067840000000
C	-3.1977830000000	3.7135130000000	-0.7250650000000
C	-2.3841930000000	3.0885130000000	0.2200540000000
C	-1.9138530000000	1.7959550000000	-0.0216440000000
C	-2.2734600000000	1.1014190000000	-1.1954930000000
C	-3.0948590000000	1.7519290000000	-2.1302170000000
O	-1.1606270000000	1.1975990000000	0.9514620000000
C	-0.2664970000000	0.1735390000000	0.4883320000000
C	-0.9384440000000	-0.8209140000000	-0.4269880000000
C	-1.8373020000000	-0.2925950000000	-1.3559410000000

C	-0.4219030000000	-2.1233680000000	-0.5380440000000
C	-0.7486400000000	-2.9636740000000	-1.5827680000000
H	-4.1840260000000	3.5387640000000	-2.6407990000000
H	-3.5545010000000	4.7222930000000	-0.5396500000000
H	-2.1028980000000	3.5810880000000	1.1449130000000
H	-3.3835280000000	1.2192910000000	-3.0334620000000
H	-2.5292620000000	-0.9504040000000	-1.8710520000000
H	-0.2072220000000	-3.8943820000000	-1.7193210000000
H	-1.7003090000000	-2.9060330000000	-2.0976890000000
H	0.4217810000000	-2.3899460000000	0.0966130000000
H	0.1214550000000	-0.3075320000000	1.3882650000000
H	0.5734740000000	0.6578050000000	-0.0377530000000

Zero Point Energy: 159.578 kcal/mol

Total internal energy: -804.984600 Hartrees

Total enthalpy: -804.983656 Hartrees

Total Gibbs free energy: -805.042004 Hartrees

Number of negative frequencies: 1

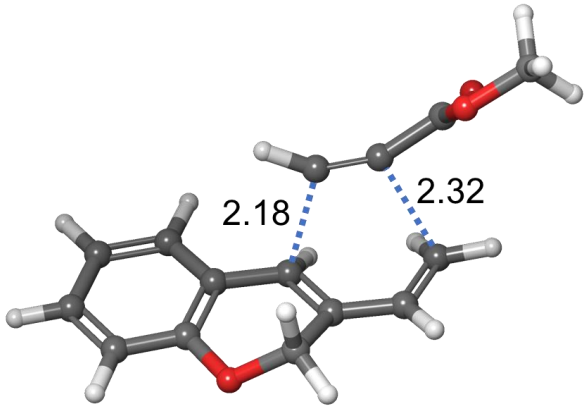
Frequency: -487.67

Red. Masses: 2.41

Frc. const.: 0.34

IR inten.: 3.85

Figure S5: TS_{2g}-meta-exo optimized geometry



0 1

C	-3.5626020000000	3.0704270000000	-1.9402720000000
C	-3.2252880000000	3.7385390000000	-0.7562100000000
C	-2.4246040000000	3.1167440000000	0.2021170000000
C	-1.9512030000000	1.8234080000000	-0.0288590000000
C	-2.2939730000000	1.1246920000000	-1.2051120000000
C	-3.1030220000000	1.7716030000000	-2.1529050000000
O	-1.2127340000000	1.2280440000000	0.9576650000000
C	-0.3127100000000	0.2023140000000	0.5117750000000
C	-0.9689930000000	-0.7946450000000	-0.4123660000000
C	-1.8543580000000	-0.2689770000000	-1.3557340000000
C	-0.4473090000000	-2.0952920000000	-0.5125300000000
C	-0.7490690000000	-2.9369520000000	-1.5648840000000
H	-4.1857780000000	3.5563310000000	-2.6843470000000
H	-3.5849640000000	4.7478240000000	-0.5790110000000
H	-2.1566390000000	3.6122980000000	1.1294070000000
H	-3.3800320000000	1.2356370000000	-3.0577640000000
H	-2.5358840000000	-0.9283800000000	-1.8825540000000
H	-0.2038730000000	-3.8669950000000	-1.6917570000000
H	-1.6928500000000	-2.8889800000000	-2.0951610000000
H	0.3843890000000	-2.3585500000000	0.1393690000000

H	0.0601560000000	-0.2766560000000	1.4192390000000
H	0.5361070000000	0.6848820000000	-0.0017890000000
C	-0.1215440000000	-1.5544120000000	-3.3211790000000
C	-0.6129090000000	-0.4221540000000	-3.1446910000000
C	0.5941290000000	-2.5943730000000	-4.0236830000000
O	0.0719600000000	-3.4638370000000	-4.7002990000000
O	1.9297700000000	-2.5045460000000	-3.8135980000000
C	2.7218410000000	-3.5264290000000	-4.4521770000000
H	3.7519170000000	-3.3077540000000	-4.1714990000000
H	2.4249270000000	-4.5173130000000	-4.0974700000000
H	2.5982860000000	-3.4845170000000	-5.5373690000000
H	-0.7689100000000	0.5894130000000	-3.4687900000000

Zero Point Energy: 159.598 kcal/mol

Total internal energy: -804.984618 Hartrees

Total enthalpy: -804.983674 Hartrees

Total Gibbs free energy: -805.041957 Hartrees

Number of negative frequencies: 1

Frequency: -491.42

Red. Masses: 2.40

Frc. const.: 0.34

IR inten.: 4.43

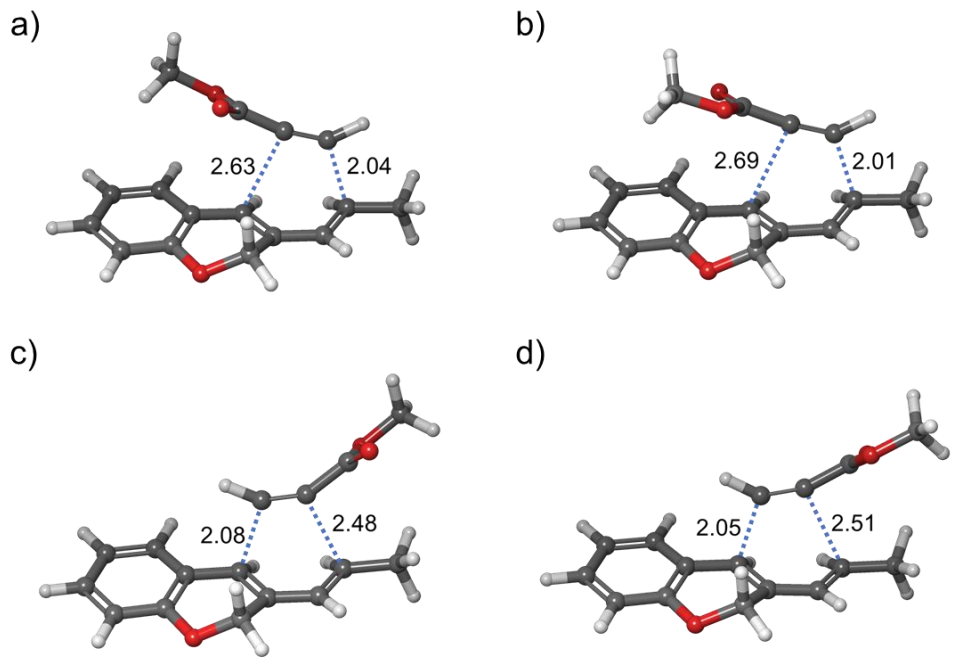


Figure S6: Balls-and-sticks representations of the found TSs for Reaction 2. Carbons, hydrogens and oxygen atoms are coloured in grey, white and red respectively; Atom distances are shown as dashed lines and reported in Å. a) Ortho-endo TS. b) Ortho-exo TS. c) Meta-endo TS. d) Meta-exo TS.

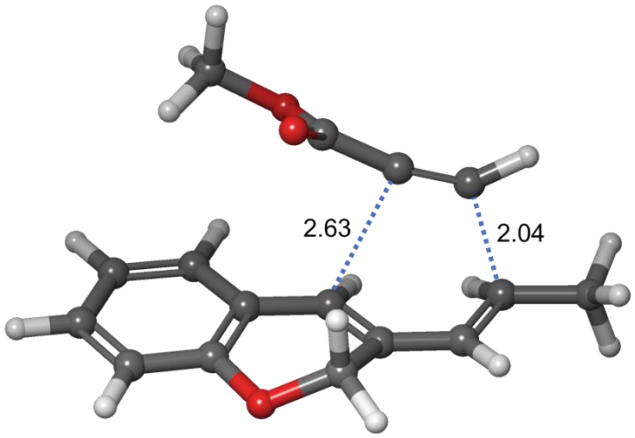
Table S3: M06-2X-D3/6-31+G ZPE-corrected gas phase energies and relative reaction rates of the located Transition States for Reaction 2.**

Transition State	Total Gibbs Free Energy (Hartree)	Relative Energy (kcal/mol)	Relative reaction rate (k_{rel})	Predicted product ratio	Experimental product ratio
TS_{13}-ortho-endo	-844.317539	1.1897	1.54	80	87
TS_{13}-ortho-exo	-844.319435	0.0000	6.43		
TS_{13}-meta-endo	-844.316971	1.5462	1.00	20	13
TS_{13}-meta-exo	-844.316972	1.5455	1.00		

Table S4: Bond lengths and negative frequencies of the located TSs for Reaction 2.

Transition State	Bond lengths (Å)	Negative frequency
TS_{13}-ortho-endo	α-A = 2.63 β-B = 2.04	-471.63 cm^{-1}
TS_{13}-ortho-exo	α-A = 2.69 β-B = 2.01	-475.35cm^{-1}
TS_{13}-meta-endo	α-B = 2.48 β-A = 2.08	-484.42 cm^{-1}
TS_{13}-meta-exo	α-B = 2.51 β-A =2.05	-491.69 cm^{-1}

Figure S7: TS_{13}-ortho-endo optimized geometry



0 1

C	-3.7591806166979	3.0301611695148	-1.6922169025453
C	-3.0770235817827	3.7507297391290	-0.7018324200448
C	-2.1042596336982	3.1315414763046	0.0839455216974
C	-1.7980833285164	1.7878066178677	-0.1336718958768
C	-2.4774697794267	1.0392668714589	-1.1229881639777
C	-3.4648567299081	1.6843183752873	-1.8897999841694
O	-0.8953795669935	1.1914291337439	0.6989647215618
C	-0.2112647368973	0.0516156720024	0.1500254542278
C	-1.1459361692721	-0.9316241985753	-0.5210612986758
C	-2.1932487983084	-0.3772718424288	-1.2362719893691
C	-0.7716617525937	-2.2822301873407	-0.6198431329023
C	-1.3394060836386	-3.1728858972836	-1.5381186191963
H	-4.5193511318694	3.5165215868484	-2.2954348808383
H	-3.3048491039463	4.8000920664294	-0.5394395417414
H	-1.5737473655830	3.6690052976561	0.8627104282915
H	-3.9880921615779	1.1098956657599	-2.6479768823571
H	-2.9370387518205	-0.9978953950318	-1.7211448628152
H	-2.3888629957899	-3.0363183547608	-1.7888716666138
H	0.1484900537822	-2.5874512486153	-0.1208782556478
H	0.3201897339025	-0.4000507679196	0.9898129612354

H	0.5254509967101	0.4117780236628	-0.5848902049929
C	-0.7901366765800	-2.3131696545508	-3.3084950601286
C	-1.0199712663126	-1.0982060386972	-3.4820394422892
C	-1.0537156938914	0.2560243039426	-3.9358252688254
O	-0.1467698875343	1.0618992651350	-3.7809433496600
O	-2.2225094549910	0.5570885670334	-4.5635429846701
C	-2.3076133513744	1.8993509901020	-5.0837481727452
H	-3.3116785804785	1.9807756241446	-5.5010126752807
H	-2.1601361349240	2.6303358387541	-4.2859353563290
H	-1.5547521987414	2.0521754193127	-5.8615932783020
H	-0.3472802303663	-3.1774927242398	-3.7758665656434
C	-0.8744485568794	-4.6099424737203	-1.6006350352072
H	-1.1324720705621	-5.0730794416758	-2.5589174147952
H	0.2094971243854	-4.6867941810907	-1.4638614067306
H	-1.3567976644441	-5.2030210858750	-0.8142385506823

Zero Point Energy: 177.165 kcal/mol

Total internal energy: -844.257124 Hartrees

Total enthalpy: -844.256180 Hartrees

Total Gibbs free energy: -844.317539 Hartrees

Number of negative frequencies: 1

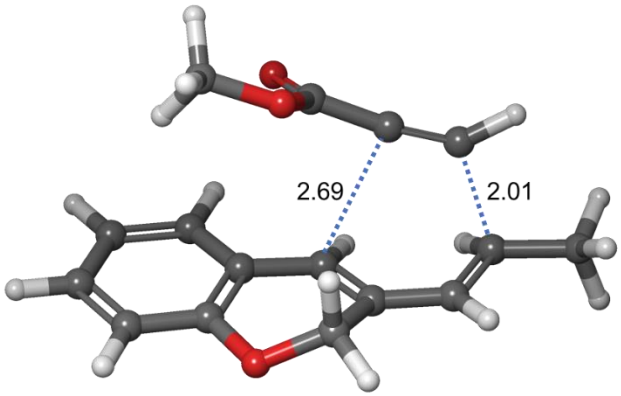
Frequency: -471.63

Red. Masses: 3.17

Frc. const.: 0.42

IR inten.: 44.66

Figure S8: TS_{13}-ortho-exo optimized geometry



0 1

C	-3.7608890000000	3.0291120000000	-1.6898040000000
C	-3.0778340000000	3.7502510000000	-0.7017580000000
C	-2.1021080000000	3.1319870000000	0.0841390000000
C	-1.7996620000000	1.7884000000000	-0.1313110000000
C	-2.4816120000000	1.0377840000000	-1.1188030000000
C	-3.4698870000000	1.6813610000000	-1.8876210000000
O	-0.8909860000000	1.1922400000000	0.6976760000000
C	-0.1953240000000	0.0645080000000	0.1426400000000
C	-1.1093310000000	-0.9178910000000	-0.5586810000000
C	-2.1792270000000	-0.3725260000000	-1.2465380000000
C	-0.6917470000000	-2.2515210000000	-0.7000570000000
C	-1.2315830000000	-3.1372670000000	-1.6431570000000
H	-4.5170180000000	3.5153440000000	-2.2976340000000
H	-3.3059170000000	4.7996700000000	-0.5394050000000
H	-1.5713900000000	3.6701680000000	0.8624190000000
H	-3.9849900000000	1.1144510000000	-2.6556380000000
H	-2.9059250000000	-0.9981980000000	-1.7505430000000
H	-2.2884040000000	-3.0319410000000	-1.8780210000000
H	0.2379410000000	-2.5415520000000	-0.2095960000000
H	0.3256750000000	-0.3974430000000	0.9836630000000

H	0.5533370000000	0.4377220000000	-0.5744180000000
C	-0.7166670000000	-2.2673320000000	-3.3783870000000
C	-1.0206050000000	-1.0715830000000	-3.5770540000000
C	-1.3085470000000	0.2640530000000	-3.9823650000000
O	-2.3374410000000	0.6258780000000	-4.5398830000000
O	-0.2978000000000	1.1123670000000	-3.6526640000000
C	-0.5183120000000	2.4969040000000	-3.9912160000000
H	0.3908570000000	3.0129440000000	-3.6823060000000
H	-0.6785800000000	2.6078010000000	-5.0669590000000
H	-1.3848350000000	2.8870150000000	-3.4522430000000
H	-0.2285030000000	-3.1012860000000	-3.8572650000000
C	-0.7287970000000	-4.5623860000000	-1.7165580000000
H	-0.9831320000000	-5.0283460000000	-2.6741780000000
H	0.3581510000000	-4.6099940000000	-1.5900590000000
H	-1.1872430000000	-5.1700410000000	-0.9274230000000

Zero Point Energy: 177.185 kcal/mol

Total internal energy: -844.259093 Hartrees

Total enthalpy: -844.258149 Hartrees

Total Gibbs free energy: -844.319435 Hartrees

Number of negative frequencies: 1

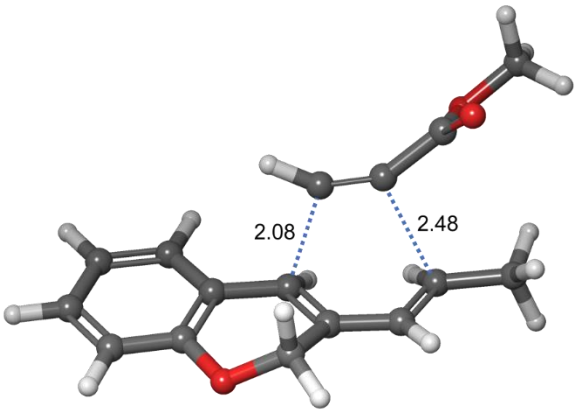
Frequency: -475.35

Red. Masses: 3.44

Frc. const.: 0.46

IR inten.: 52.21

Figure S9: TS_{13}-meta-endo optimized geometry



0 1

C	-3.3430910000000	3.1527950000000	-1.9075890000000
C	-3.0249200000000	3.7743780000000	-0.7090570000000
C	-2.3268820000000	3.0914330000000	0.2696590000000
C	-1.9397600000000	1.7808480000000	0.0468990000000
C	-2.2550360000000	1.1343900000000	-1.1459350000000
C	-2.9614690000000	1.8405190000000	-2.1144750000000
O	-1.3014450000000	1.1274810000000	1.0434280000000
C	-0.4373520000000	0.0866370000000	0.6562710000000
C	-1.0773160000000	-0.8589150000000	-0.3299690000000
C	-1.8733370000000	-0.2859140000000	-1.3095690000000
C	-0.6367830000000	-2.1758810000000	-0.4055130000000
C	-0.9546410000000	-2.9978320000000	-1.4594000000000
H	-3.8873270000000	3.6835190000000	-2.6674340000000
H	-3.3210480000000	4.7934800000000	-0.5355840000000
H	-2.0790090000000	3.5527980000000	1.2074870000000
H	-3.2221930000000	1.3461150000000	-3.0348420000000
H	-2.5813990000000	-0.8932710000000	-1.8395630000000
H	-1.8736550000000	-2.8376310000000	-1.9883710000000
H	0.1345760000000	-2.4950410000000	0.2770520000000
H	-0.1648410000000	-0.4271860000000	1.5662550000000

H	0.4651560000000	0.5169460000000	0.2248740000000
C	-0.3763190000000	-4.3816120000000	-1.5924350000000
H	-0.4774380000000	-4.7538640000000	-2.6037590000000
H	0.6707150000000	-4.4062230000000	-1.3166890000000
H	-0.9174500000000	-5.0658890000000	-0.9425150000000
C	-0.1606370000000	-1.6074250000000	-3.1379430000000
C	-0.5872360000000	-0.4672590000000	-2.9612080000000
C	0.6550810000000	-2.5242850000000	-3.9102260000000
O	1.8203140000000	-2.7006830000000	-3.7454600000000
O	-0.0630900000000	-3.1742240000000	-4.8189740000000
C	0.6431460000000	-4.0760070000000	-5.6531970000000
H	-0.0986430000000	-4.5174630000000	-6.3004060000000
H	1.3840650000000	-3.5491600000000	-6.2369260000000
H	1.1327610000000	-4.8387930000000	-5.0655300000000
H	-0.6460350000000	0.5537340000000	-3.2529870000000

Zero Point Energy: 177.095 kcal/mol

Total internal energy: -844.256132 Hartrees

Total enthalpy: -844.255188 Hartrees

Total Gibbs free energy: -844.316971 Hartrees

Number of negative frequencies: 1

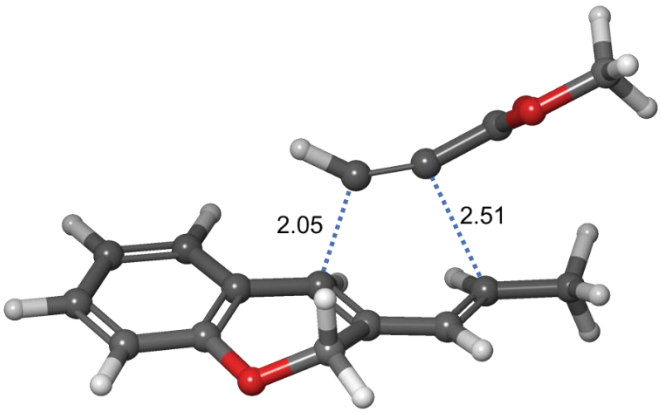
Frequency: -484.42

Red. Masses: 2.60

Frc. const.: 0.36

IR inten.: 10.94

Figure S10: TS_{13}-meta-exo optimized geometry



0 1

C	-3.7549496152460	3.0327188896168	-1.6943593848551
C	-3.0799061606308	3.7517519742984	-0.7001932740198
C	-2.1087030793699	3.1294038566444	0.0838443101857
C	-1.8053338455079	1.7831561444475	-0.1323680086461
C	-2.4849937194851	1.0352967461764	-1.1145756076546
C	-3.4582717604933	1.6843834145646	-1.8901132307020
O	-0.8801794738508	1.1987856253979	0.6907018084068
C	-0.2088147643944	0.0569769479387	0.1375691280478
C	-1.1586591804673	-0.9427167085925	-0.4715202968976
C	-2.2023785860336	-0.4086026990026	-1.2447781034908
C	-0.8043774376793	-2.3000094085733	-0.5138929212414
C	-1.4503737136642	-3.2365025877279	-1.2964507908515
H	-4.5107407494324	3.5179472142052	-2.3038115024684
H	-3.3082209927083	4.8006745448527	-0.5364562902889
H	-1.5765814761523	3.6646017222471	0.8632698650743
H	-3.9944121271231	1.1120478675489	-2.6436786850318
H	-3.0708112251830	-1.0281711912903	-1.4493091956731
H	-2.4635143977070	-3.0450322812717	-1.6363268394866
H	0.1256792104369	-2.5956387821910	-0.0281798109444
H	0.3598427302739	-0.3784522463093	0.9616269494530

H	0.5028372881723	0.4096475461594	-0.6282768736923
C	-0.9894996728139	-4.6563164571386	-1.4239854729906
H	-1.1559254356202	-5.0357971054496	-2.4374870933040
H	0.0687887508906	-4.7661435835377	-1.1695749833228
H	-1.5735177345099	-5.3002183296145	-0.7518991065853
C	-1.1606312610683	-1.9301287526645	-3.4152646514668
C	-1.5194397018336	-0.7626908046701	-3.1484221193746
C	-0.7377939725667	-3.0870779731546	-4.1410603386694
O	-1.4863587433592	-3.9182191447664	-4.6364194200811
O	0.6170610977679	-3.1876335363275	-4.1825059002022
C	1.1259715339479	-4.3361663800906	-4.8873738868737
H	0.8033356921631	-4.3201724759080	-5.9317379104391
H	2.2109902607517	-4.2575089586677	-4.8181648459302
H	0.7753248280180	-5.2609386828792	-4.4210805363993
H	-1.6548725654586	0.2288813878757	-3.5462795348970

Zero Point Energy: 177.202 kcal/mol

Total internal energy: -844.256522 Hartrees

Total enthalpy: -844.255578 Hartrees

Total Gibbs free energy: -844.316972 Hartrees

Number of negative frequencies: 1

Frequency: -491.69

Red. Masses: 2.70

Frc. const.: 0.38

IR inten.: 13.17

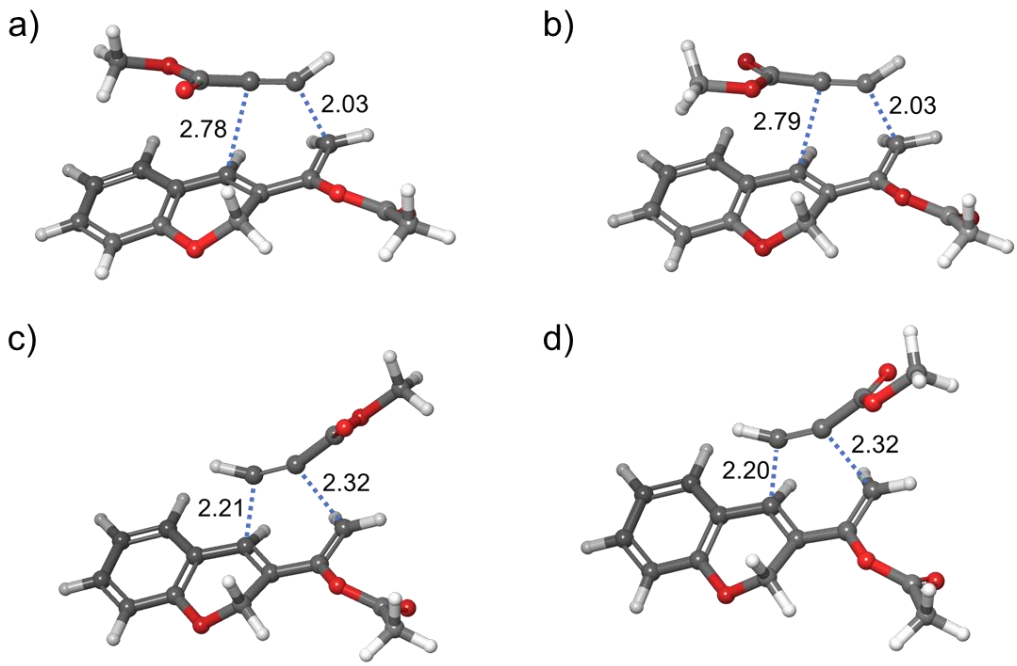


Figure S11: Balls-and-sticks representations of the found TSs for Reaction 3. Carbons, hydrogens and oxygen atoms are coloured in grey, white and red respectively; Atom distances are shown as dashed lines and reported in Å. a) Ortho-endo TS. b) Ortho-exo TS. c) Meta-endo TS. d) Meta-exo TS.

Table S5: M06-2X-D3/6-31+G ZPE-corrected gas phase energies and relative reaction rate of the located Transition States (TSs) for Reaction 3.**

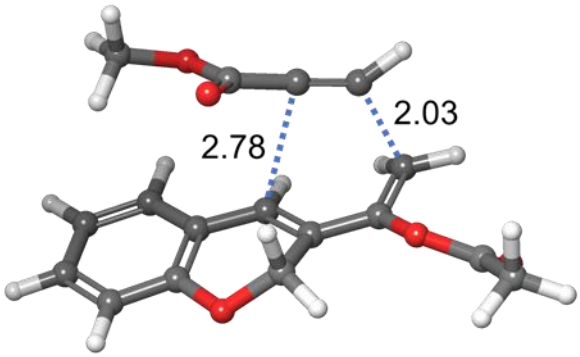
Transition State	Total Gibbs Free Energy (Hartree)	Relative Energy (kcal/mol)	Relative reaction rate (k_{rel})	Predicted product ratio	Experimental product ratio
TS_{15}-ortho-endo	-1032.810080	1.3899	19.03	98	100
TS_{15}-ortho-exo	-1032.812295	0.0000	101.35		
TS_{15}-meta-endo	-1032.806602	3.5724	1.38	2	Not detected
TS_{15}-meta-exo	-1032.806179	3.8378	1.00		

Table S6: Bond lengths and negative frequencies of the located TSs for Reaction 3.

Transition State	Bond lengths (Å)	Negative frequency
TS_{15}-ortho-endo	α-A = 2.03 β-B = 2.78	-444.03 cm^{-1}
TS_{15}-ortho-exo	α-A = 2.03 β-B = 2.79	-438.18 cm^{-1}
TS_{15}-meta-endo	α-B = 2.32 β-A = 2.21	-481.22 cm^{-1}

TS_{15}-meta-exo	α-B = 2.32 β-A = 2.20	-483.62 cm^{-1}

Figure S12: TS_{15}-ortho-endo optimized geometry



0 1

C	-3.7043850000000	3.0649130000000	-1.7958070000000
C	-2.9644200000000	3.7777740000000	-0.8409490000000
C	-2.0648540000000	3.1207560000000	-0.0007880000000
C	-1.8922470000000	1.7417540000000	-0.1257350000000
C	-2.6348390000000	1.0016880000000	-1.0747010000000
C	-3.5433220000000	1.6874230000000	-1.9025760000000
O	-1.0618580000000	1.1148350000000	0.7537110000000
C	-0.4942040000000	-0.1328440000000	0.3162800000000
C	-1.5151070000000	-1.0443030000000	-0.3330140000000
C	-2.4900310000000	-0.4352700000000	-1.0932550000000
C	-1.3084220000000	-2.4415310000000	-0.3653930000000
C	-1.9618930000000	-3.2979360000000	-1.2478530000000
H	-4.4028940000000	3.5843830000000	-2.4440210000000
H	-3.0892760000000	4.8528010000000	-0.7506760000000
H	-1.4911850000000	3.6545480000000	0.7492050000000
H	-4.1079090000000	1.1195870000000	-2.6358960000000
H	-3.2499240000000	-1.0080450000000	-1.6097900000000
H	-1.7092010000000	-4.3507690000000	-1.2145350000000

H	-2.9989340000000	-3.0949340000000	-1.4866330000000
H	-0.0550220000000	-0.5771040000000	1.2076910000000
H	0.3061020000000	0.0796030000000	-0.4093250000000
O	-0.1312890000000	-2.8533090000000	0.2665400000000
C	1.2890660000000	-4.1929370000000	1.5855510000000
C	-0.0956370000000	-4.0011340000000	1.0265490000000
O	-1.0460840000000	-4.7225600000000	1.2066840000000
H	1.3190630000000	-5.1137190000000	2.1671540000000
H	2.0174800000000	-4.2341810000000	0.7701810000000
H	1.5548270000000	-3.3405520000000	2.2184400000000
C	-1.2589260000000	-2.7102300000000	-3.0557770000000
C	-1.2560900000000	-1.4976460000000	-3.3507570000000
C	-1.0158050000000	-0.1312570000000	-3.6720450000000
O	0.0054830000000	0.4751580000000	-3.3711490000000
O	-2.0389480000000	0.4316740000000	-4.3701640000000
C	-1.8128010000000	1.7924620000000	-4.7903150000000
H	-2.7309950000000	2.0914620000000	-5.2964150000000
H	-1.6221390000000	2.4359810000000	-3.9291580000000
H	-0.9627090000000	1.8400100000000	-5.4762510000000
H	-0.9669460000000	-3.6730810000000	-3.4402200000000

Zero Point Energy:186.141 kcal/mol

Total internal energy: -1032.743181 Hartrees

Total enthalpy: -1032.742236 Hartrees

Total Gibbs free energy: -1032.810080 Hartrees

Number of negative frequencies: 1

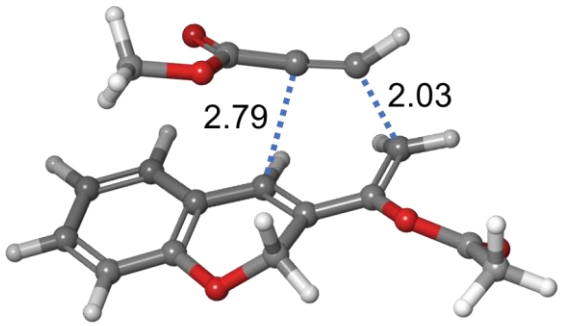
Frequency: -444.03

Red. Masses: 3.99

Frc. const.: 0.46

IR inten.: 74.99

Figure S13: TS_{15}-ortho-exo optimized geometry



0 1

C	-1.3095730000000	-2.6935420000000	-3.0949100000000
C	-1.4175410000000	-1.4897880000000	-3.4004230000000
C	-1.5167580000000	-0.1418900000000	-3.8476850000000
O	-2.4750290000000	0.3326430000000	-4.4455580000000
O	-0.4087430000000	0.5766690000000	-3.5204800000000
C	-0.4319800000000	1.9622720000000	-3.9208570000000
H	0.5288440000000	2.3662050000000	-3.6015500000000
H	-0.5444480000000	2.0464130000000	-5.0051010000000
H	-1.2536350000000	2.4878390000000	-3.4287230000000
H	-0.9663680000000	-3.6420070000000	-3.4714730000000
C	-3.6779930000000	3.0714100000000	-1.8315570000000
C	-2.9345240000000	3.7838160000000	-0.8814550000000
C	-2.0608580000000	3.1203290000000	-0.0160440000000
C	-1.9228740000000	1.7369730000000	-0.1138970000000
C	-2.6699650000000	0.9964420000000	-1.0593380000000
C	-3.5517990000000	1.6868240000000	-1.9120660000000
O	-1.1167990000000	1.1034650000000	0.7882610000000
C	-0.5482070000000	-0.1467720000000	0.3685740000000
C	-1.5492280000000	-1.0513250000000	-0.3209410000000
C	-2.5311510000000	-0.4425020000000	-1.0721180000000

C	-1.3094860000000	-2.4420250000000	-0.3837370000000
C	-1.9512840000000	-3.3048580000000	-1.2666060000000
H	-4.3519280000000	3.5940360000000	-2.5024210000000
H	-3.0351330000000	4.8629710000000	-0.8115850000000
H	-1.4860580000000	3.6535820000000	0.7336430000000
H	-4.1120480000000	1.1247440000000	-2.6513740000000
H	-3.2902960000000	-1.0161110000000	-1.5890080000000
H	-1.6712780000000	-4.3511660000000	-1.2449560000000
H	-2.9955660000000	-3.1259610000000	-1.4925250000000
H	-0.1492750000000	-0.5997690000000	1.2749570000000
H	0.2893180000000	0.0564340000000	-0.3172360000000
O	-0.1155930000000	-2.8357240000000	0.2318970000000
C	1.3398060000000	-4.1520690000000	1.5378300000000
C	-0.0539220000000	-3.9816530000000	0.9942680000000
O	-0.9911740000000	-4.7165350000000	1.1870860000000
H	1.3883540000000	-5.0685090000000	2.1250300000000
H	2.0589980000000	-4.1904420000000	0.7141470000000
H	1.6025840000000	-3.2923390000000	2.1619580000000

Zero Point Energy: 186.170 kcal/mol

Total internal energy: -1032.745458 Hartrees

Total enthalpy: -1032.744514 Hartrees

Total Gibbs free energy: -1032.812295 Hartrees

Number of negative frequencies: 1

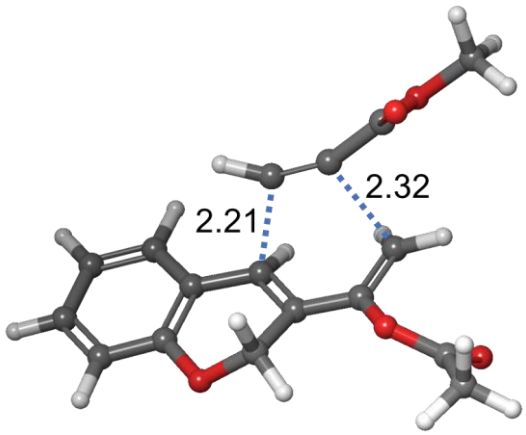
Frequency: -438.18

Red. Masses: 3.97

Frc. const.: 0.45

IR inten.: 69.06

Figure S14: TS_{15}-meta-endo optimized geometry



0 1

C	-1.2824710000000	-1.8122180000000	-3.6828870000000
C	-1.5976520000000	-0.6376140000000	-3.4127550000000
C	-0.7588970000000	-2.8857390000000	-4.4998850000000
O	0.4159290000000	-3.0381730000000	-4.7802020000000
O	-1.7444920000000	-3.7277080000000	-4.8975610000000
C	-1.3161590000000	-4.8503870000000	-5.6948970000000
H	-2.2258790000000	-5.4070750000000	-5.9189280000000
H	-0.8356680000000	-4.5065370000000	-6.6143330000000
H	-0.6116790000000	-5.4701970000000	-5.1332960000000
H	-1.7419040000000	0.3892140000000	-3.6896140000000
C	-3.8444950000000	3.0631130000000	-1.4990170000000
C	-3.1418820000000	3.7030820000000	-0.4699360000000
C	-2.1587160000000	3.0201500000000	0.2461640000000
C	-1.8696600000000	1.6921340000000	-0.0748050000000
C	-2.5760700000000	1.0236300000000	-1.0953190000000
C	-3.5634140000000	1.7315500000000	-1.7994310000000
O	-0.9418880000000	1.0378840000000	0.6869730000000
C	-0.2790240000000	-0.0687450000000	0.0572110000000
C	-1.2382650000000	-0.9935270000000	-0.6540050000000
C	-2.3008840000000	-0.3973780000000	-1.3326440000000

C	-0.8894960000000	-2.3344530000000	-0.8915920000000
C	-1.5360210000000	-3.1393290000000	-1.8023280000000
H	-4.6095460000000	3.5969130000000	-2.0536610000000
H	-3.3591020000000	4.7384770000000	-0.2251180000000
H	-1.6080900000000	3.4935760000000	1.0522270000000
H	-4.1187600000000	1.2182420000000	-2.5810000000000
H	-3.1423770000000	-0.9966420000000	-1.6604890000000
H	-1.1233080000000	-4.1085150000000	-2.0501870000000
H	-2.5901970000000	-3.0102030000000	-2.0027980000000
H	0.2569710000000	-0.5816560000000	0.8542600000000
H	0.4615250000000	0.3231690000000	-0.6593810000000
O	0.3776210000000	-2.7009350000000	-0.4092270000000
C	1.9892610000000	-4.0623270000000	0.6398140000000
C	0.5511540000000	-3.9118670000000	0.2189960000000
O	-0.3313170000000	-4.7174750000000	0.3929150000000
H	2.1166680000000	-5.0125460000000	1.1574430000000
H	2.6356560000000	-4.0230600000000	-0.2424450000000
H	2.2774140000000	-3.2341400000000	1.2942310000000

Zero Point Energy: 186.120 kcal/mol

Total internal energy: -1032.739691 Hartrees

Total enthalpy: -1032.738747 Hartrees

Total Gibbs free energy: -1032.806602 Hartrees

Number of negative frequencies: 1

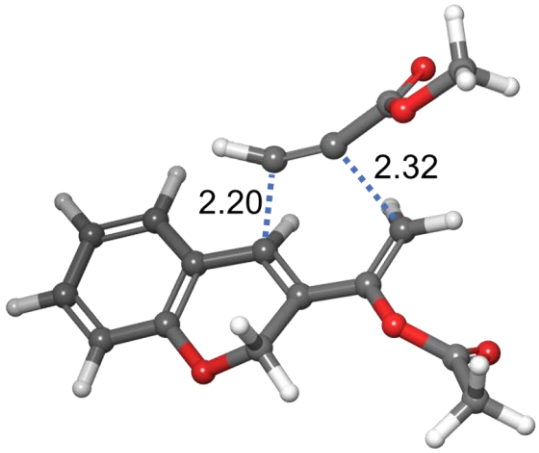
Frequency: -481.22

Red. Masses: 2.43

Frc. const.: 0.33

IR inten.: 2.99

Figure S15: TS_{15}-meta-exo optimized geometry



0 1

C	-3.7071950000000	3.0541160000000	-1.8051930000000
C	-3.0772530000000	3.7429910000000	-0.7603970000000
C	-2.2222540000000	3.0726380000000	0.1145640000000
C	-1.9879100000000	1.7072040000000	-0.0618230000000
C	-2.6260320000000	0.9904120000000	-1.0944430000000
C	-3.4841290000000	1.6870340000000	-1.9607610000000
O	-1.1901800000000	1.0729560000000	0.8501440000000
C	-0.5411670000000	-0.1229210000000	0.3928000000000
C	-1.4818470000000	-1.0518910000000	-0.3372840000000
C	-2.4259400000000	-0.4608170000000	-1.1773020000000
C	-1.2069480000000	-2.4272650000000	-0.4146260000000
C	-1.8159080000000	-3.2808070000000	-1.3057760000000
H	-4.3723270000000	3.5783150000000	-2.4839290000000
H	-3.2515080000000	4.8064940000000	-0.6268600000000
H	-1.7307660000000	3.5844350000000	0.9353470000000
H	-3.9863000000000	1.1375490000000	-2.7536480000000
H	-3.2733680000000	-1.0366500000000	-1.5316120000000
H	-1.4474320000000	-4.2927160000000	-1.4175920000000
H	-2.8345430000000	-3.1143240000000	-1.6276890000000

H	-0.1272380000000	-0.5908470000000	1.2849700000000
H	0.2949650000000	0.1588810000000	-0.2683980000000
O	-0.0206690000000	-2.8263380000000	0.2273790000000
C	1.3389160000000	-4.1557320000000	1.6227570000000
C	-0.0349750000000	-3.9299850000000	1.0486470000000
O	-1.0154470000000	-4.6000550000000	1.2629000000000
H	1.3198990000000	-5.0324330000000	2.2697810000000
H	2.0601660000000	-4.2985690000000	0.8122190000000
H	1.6549320000000	-3.2756060000000	2.1912730000000
C	-1.3155120000000	-2.1610130000000	-3.2756000000000
C	-1.5631040000000	-0.9474210000000	-3.1414560000000
C	-0.9813080000000	-3.3798570000000	-3.9791770000000
O	-1.7980280000000	-4.1409590000000	-4.4675010000000
O	0.3553290000000	-3.5913320000000	-4.0052180000000
C	0.7710480000000	-4.8078490000000	-4.6602040000000
H	1.8582230000000	-4.8130680000000	-4.5914100000000
H	0.3458100000000	-5.6783790000000	-4.1533360000000
H	0.4478480000000	-4.8108850000000	-5.7039670000000
H	-1.6070390000000	0.0524850000000	-3.5292010000000

Zero Point Energy: 186.121 kcal/mol

Total internal energy: -1032.739305 Hartrees

Total enthalpy: -1032.738361 Hartrees

Total Gibbs free energy: -1032.806179 Hartrees

Number of negative frequencies: 1

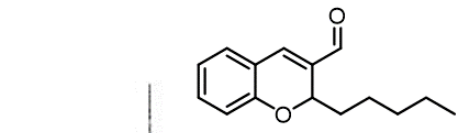
Frequency: -483.62

Red. Masses: 2.43

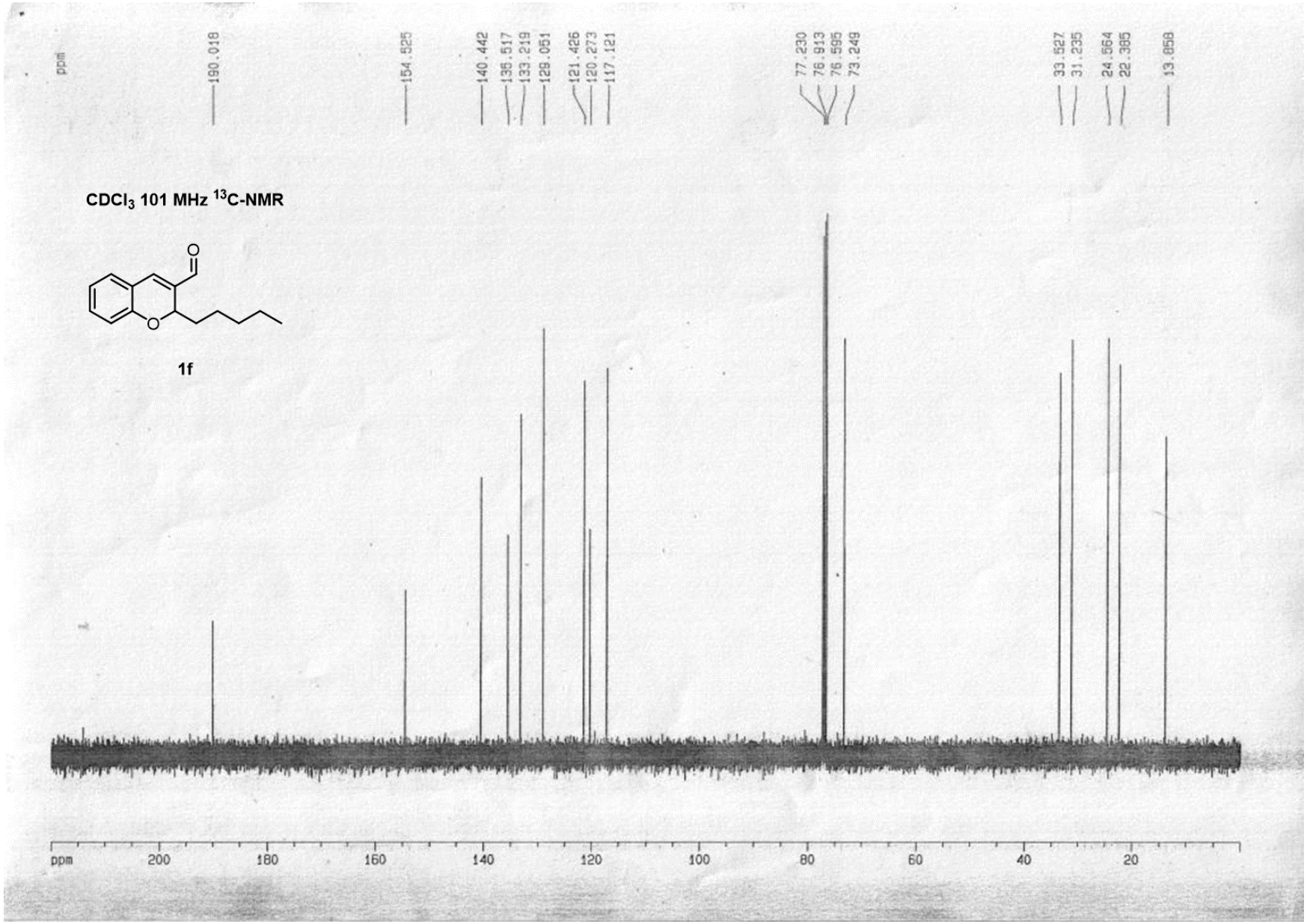
Frc. const.: 0.33

IR inten.: 3.68

$CDCl_3$ 400 MHz ^{1}H-NMR



1f


ppm
190.018
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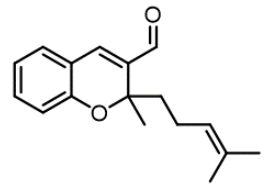
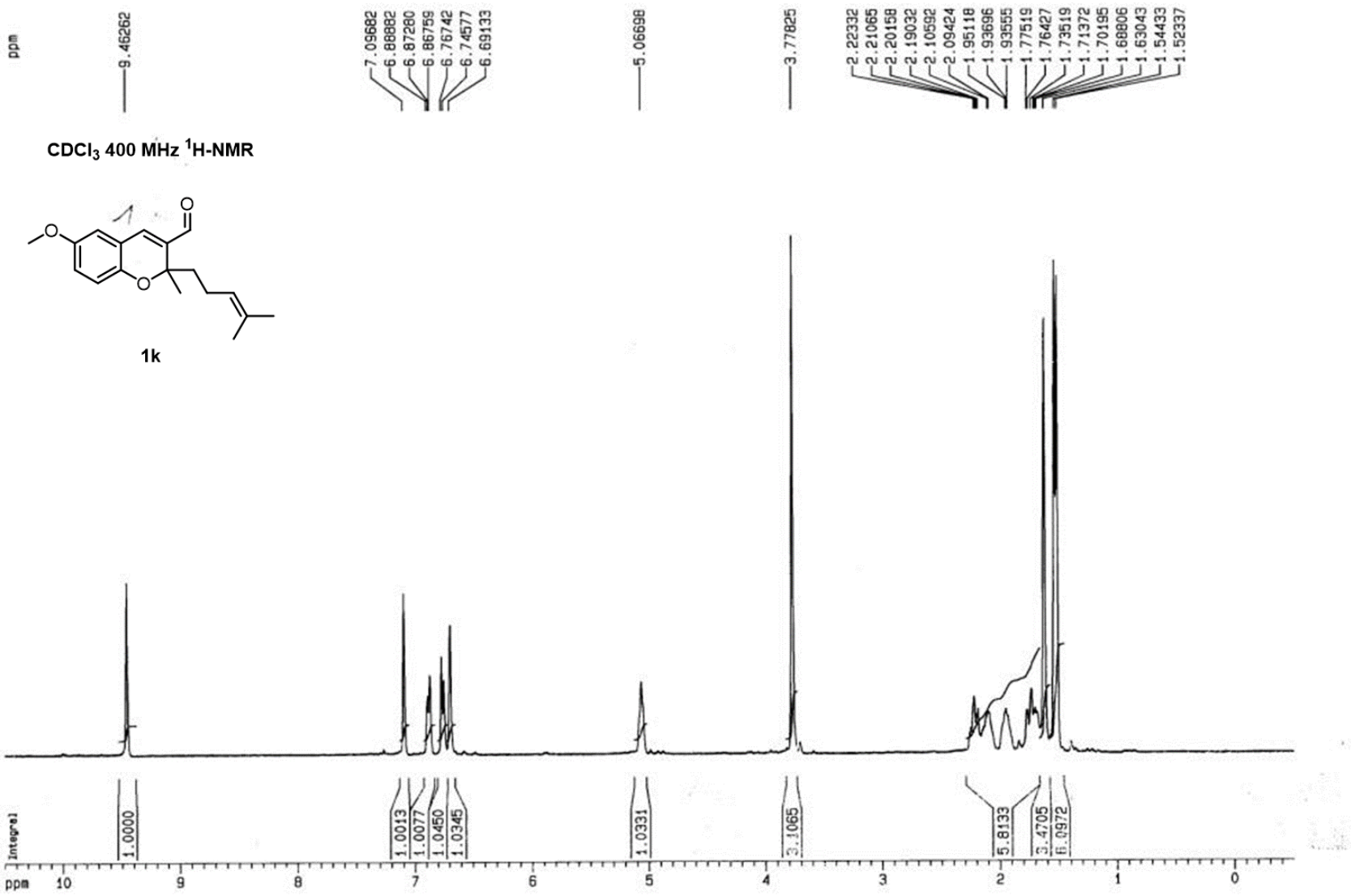
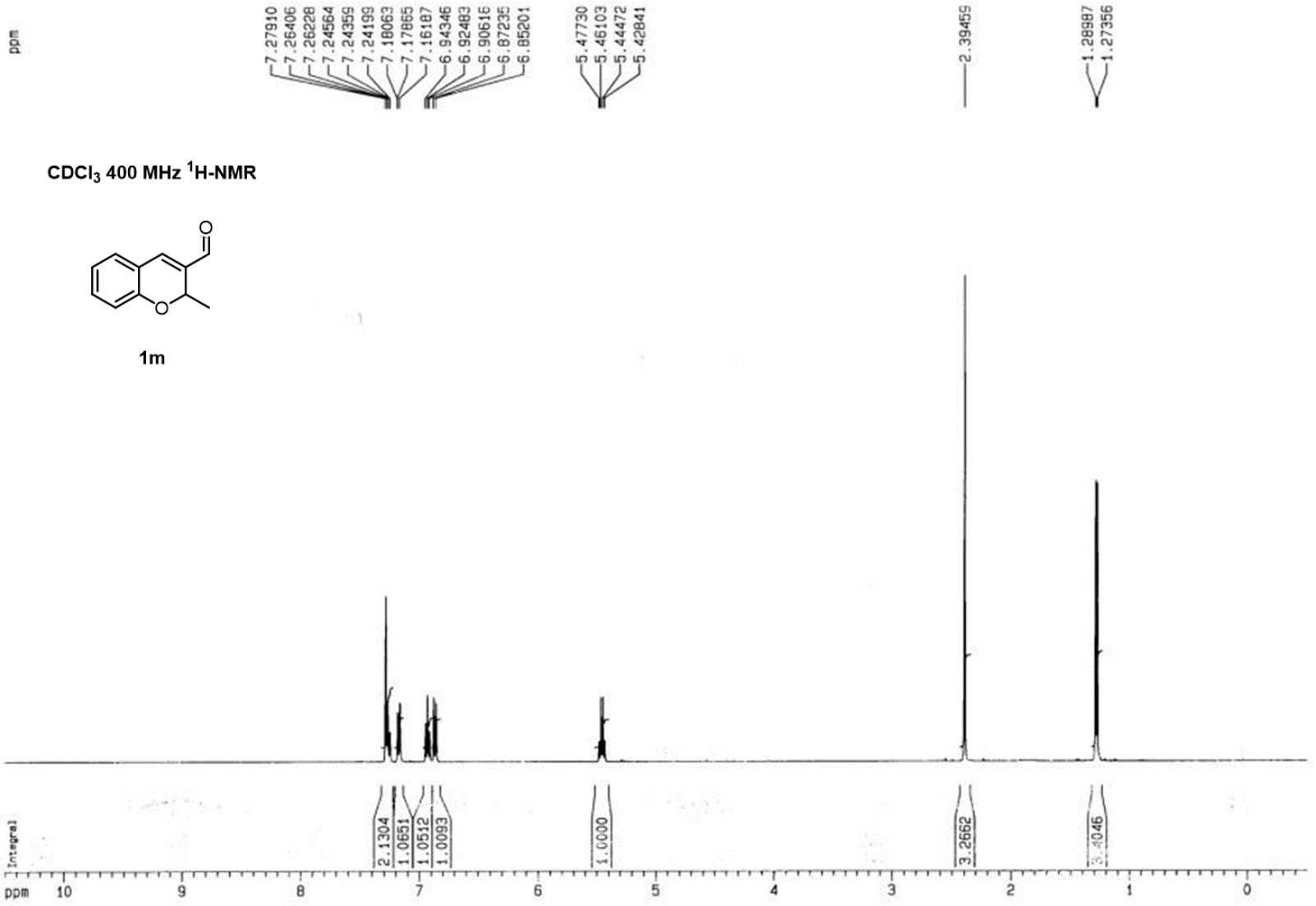
140.442
136.517
133.219
129.051
121.426
120.273
117.121
77.230
76.913
76.595
73.249
33.527
31.235
24.564
22.385
13.858
CDCl3 101 MHz 13C-NMR
O
O
1f
ppm
200
180
160
140
120
100
80
60
40
20

$CDCl_3$ 400 MHz ^{1}H-NMR



1j


ppm
9.46262
7.09682
6.88882
6.87280
6.86759
6.76742
6.74577
6.69133
5.06698
3.77825
2.22332
2.21065
2.20158
2.19032
2.10592
2.09424
1.95118
1.93696
1.93555
1.77519
1.76427
1.73619
1.71372
1.70195
1.68806
1.63043
1.54433
1.52337
CDCl3 400 MHz 1H-NMR
O
O
O
1k
integral
1.0000
1.0013
1.0077
1.0460
1.0345
1.0331
3.1065
5.8133
3.4705
6.0972
ppm
10
9
8
7
6
5
4
3
2
1
0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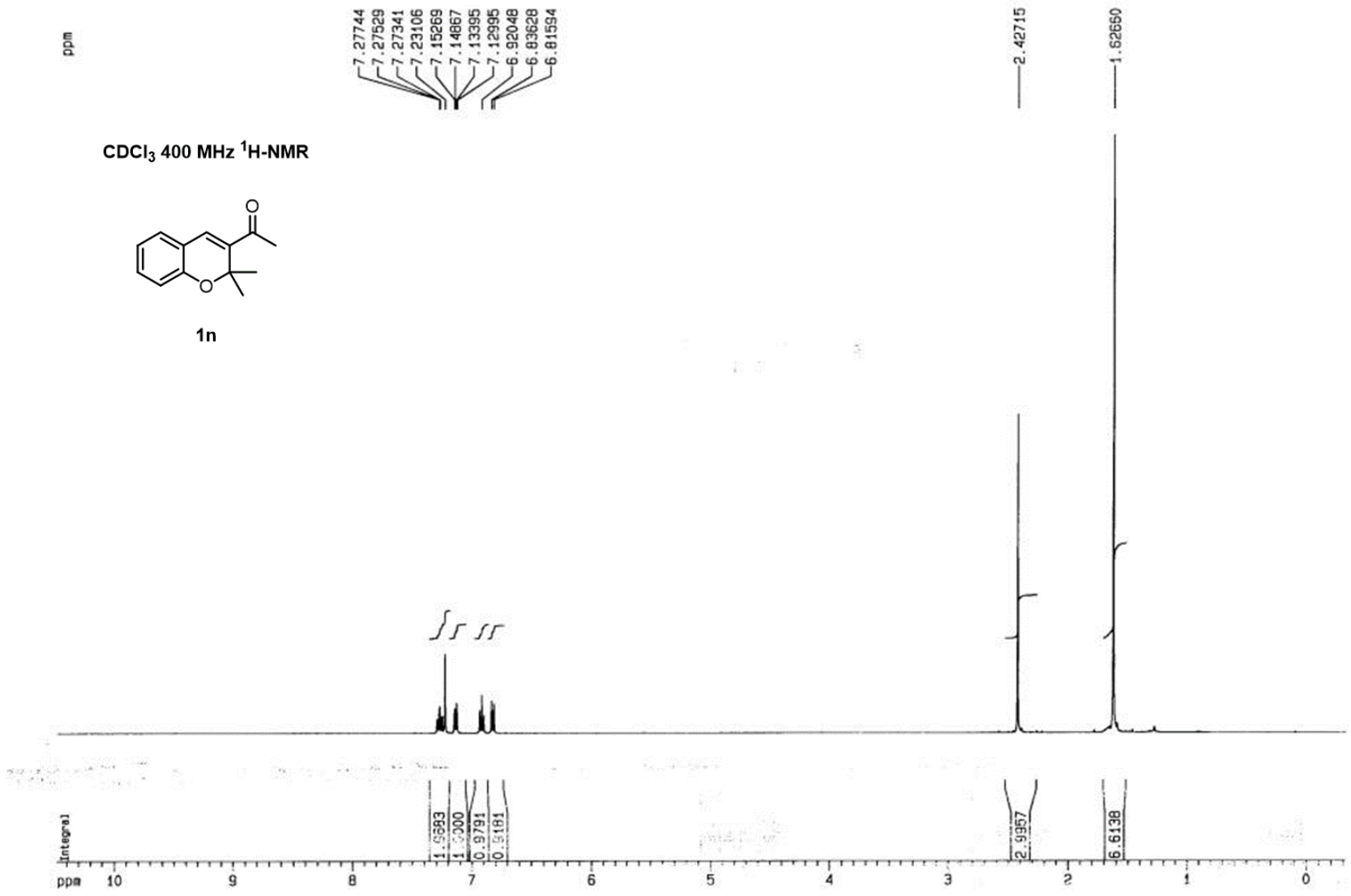
7.26406
7.26228
7.24564
7.24359
7.24199
7.18063
7.17865
7.16187
6.94346
6.92483
6.90616
6.87235
6.85201
5.47730
5.46103
5.44472
5.42841
2.39459
1.28987
1.27356
CDCl3 400 MHz 1H-NMR
O
O
1m
Integral
2.1304
1.0651
1.0512
1.0093
1.0000
3.2662
3.4046
ppm
10
9
8
7
6
5
4
3
2
1
0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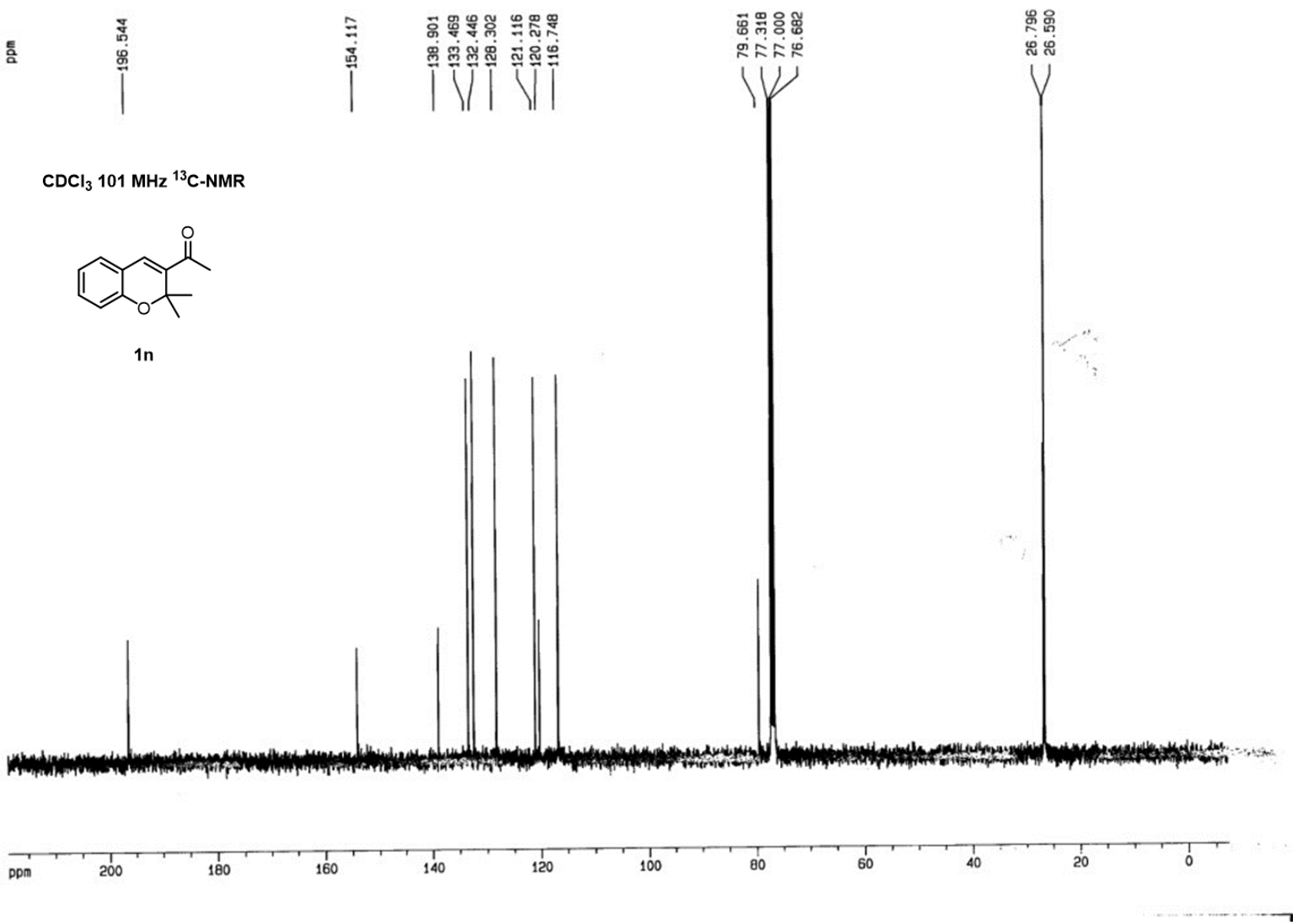
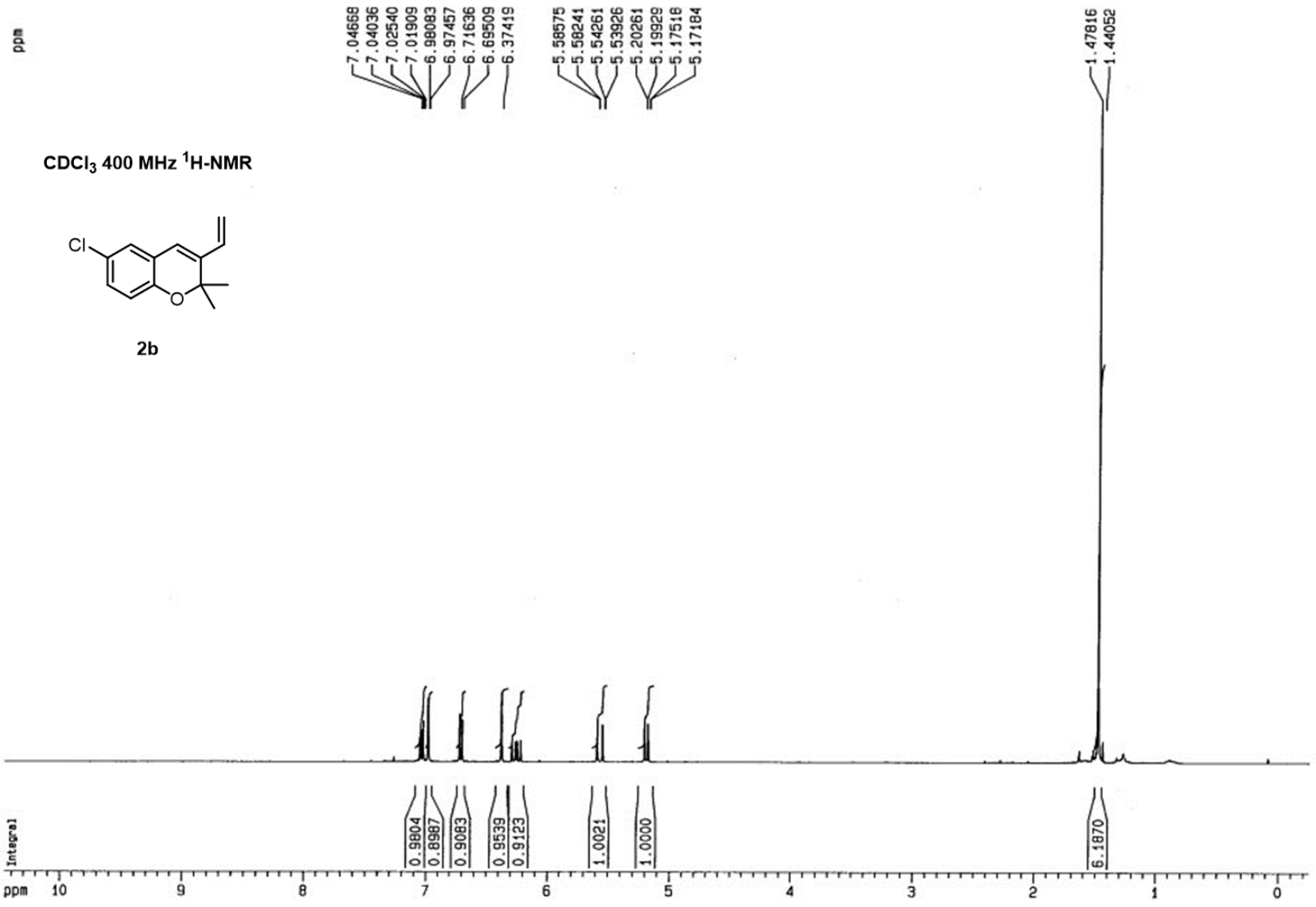
7.27744
7.27529
7.27341
7.23106
7.15269
7.14867
7.13395
7.12995
6.92048
6.83628
6.81594
2.42715
1.62650
CDCl3 400 MHz 1H-NMR
O
O
1n
Integral
1.6383
1.0000
0.9791
0.9181
2.9357
6.6138
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
196.544
154.117
138.901
133.469
132.446
128.302
121.116
120.278
116.748
79.661
77.318
77.000
76.682
26.796
26.590
CDCl3 101 MHz 13C-NMR
1n
ppm
200
180
160
140
120
100
80
60
40
20
0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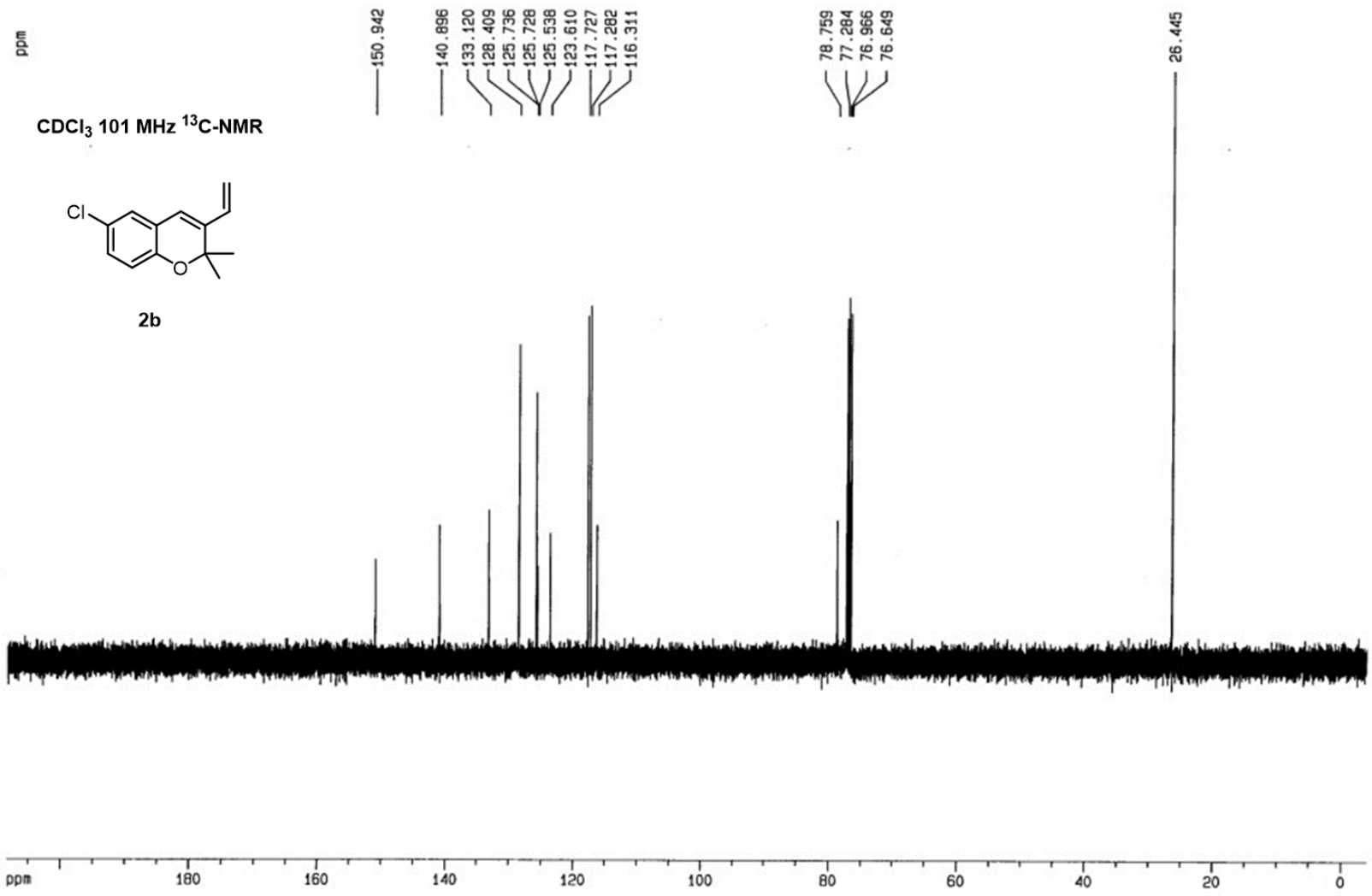
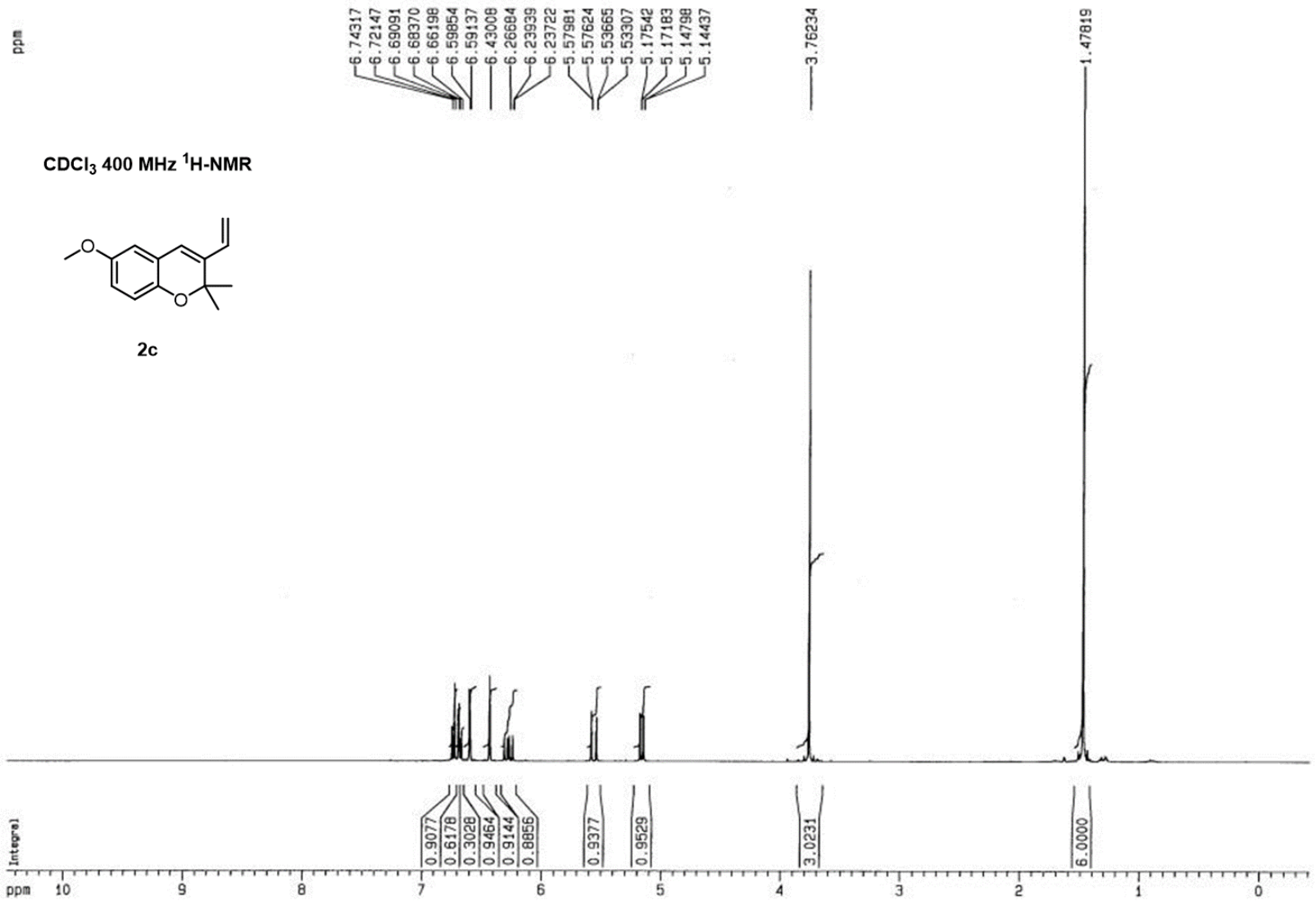
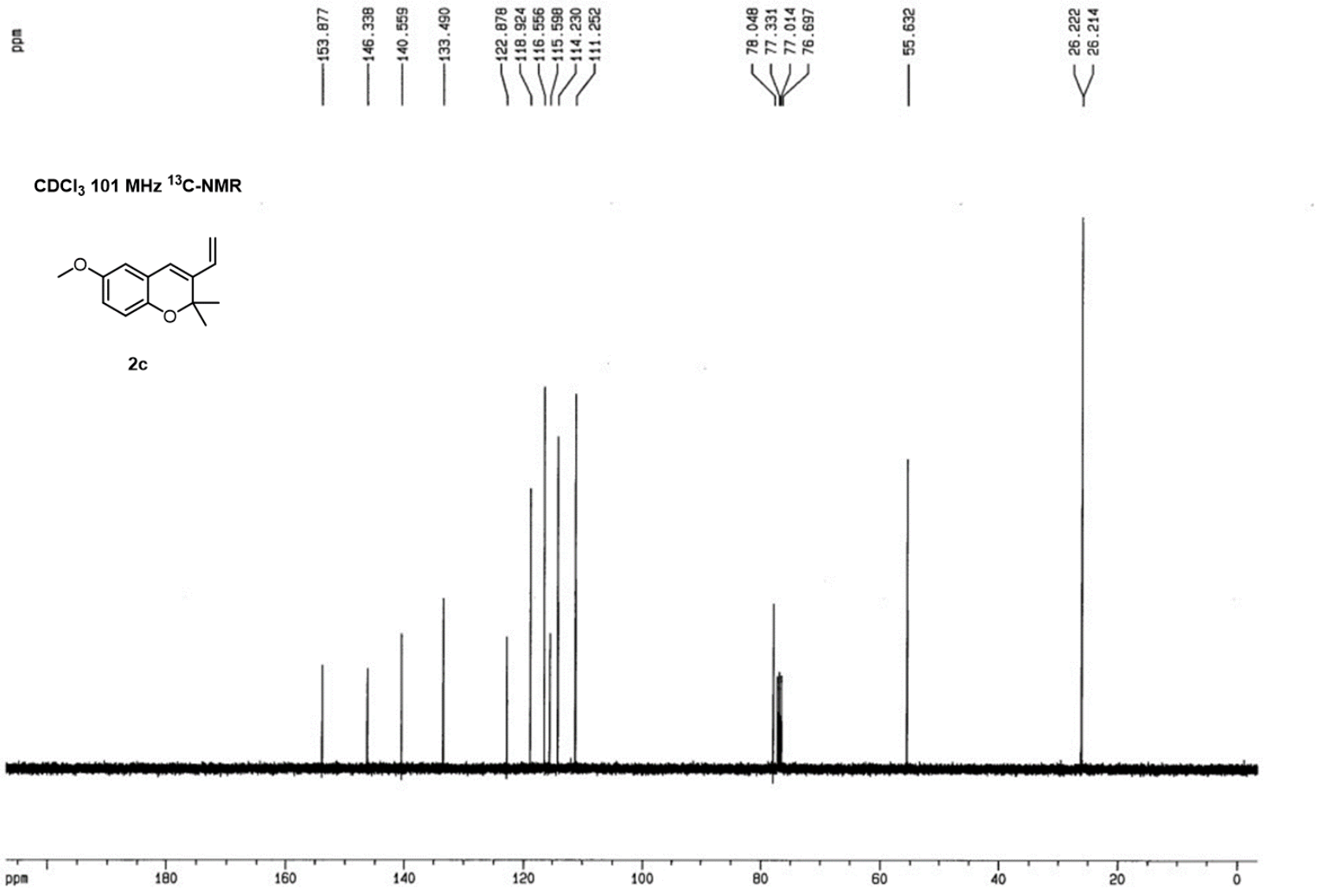
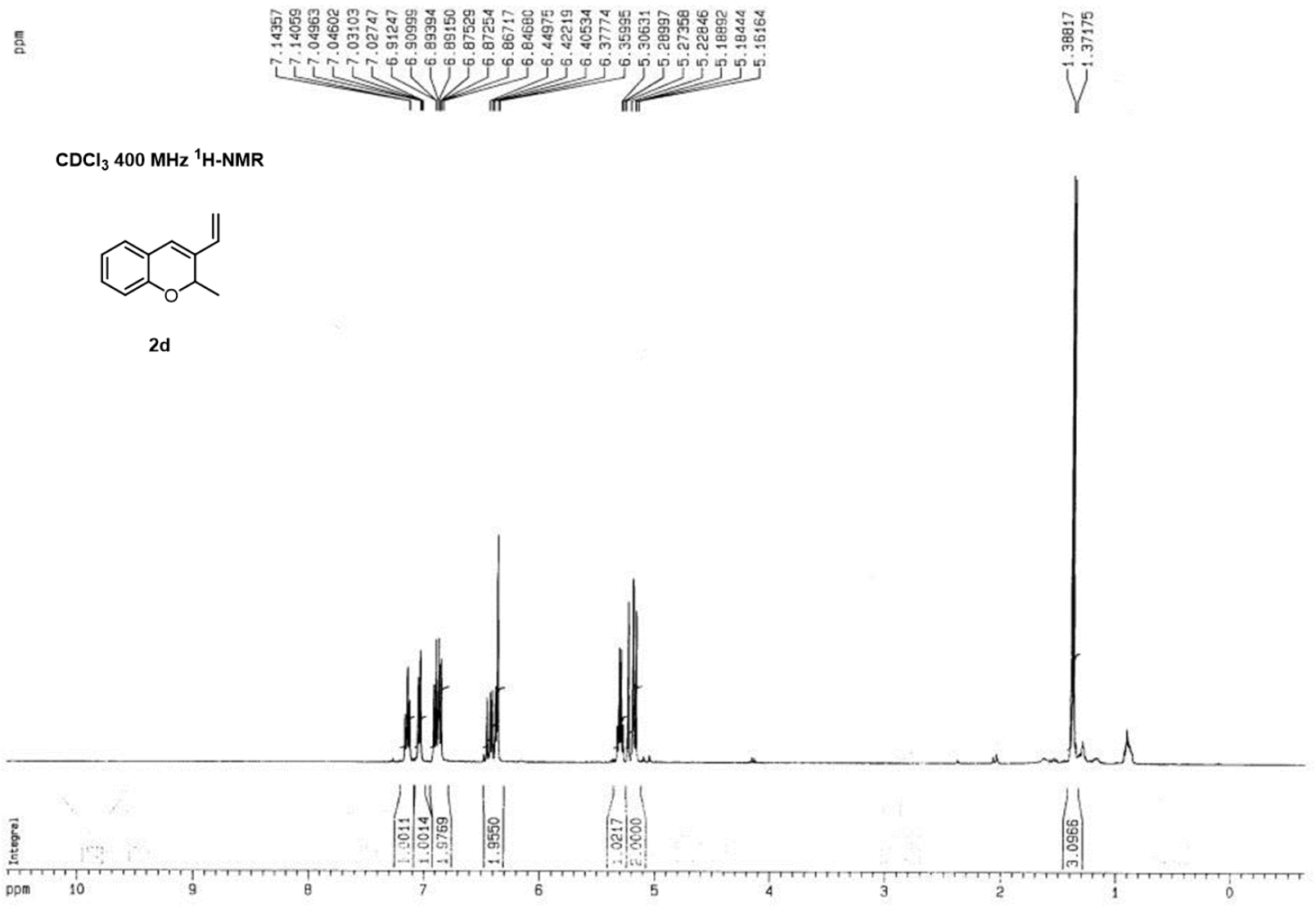
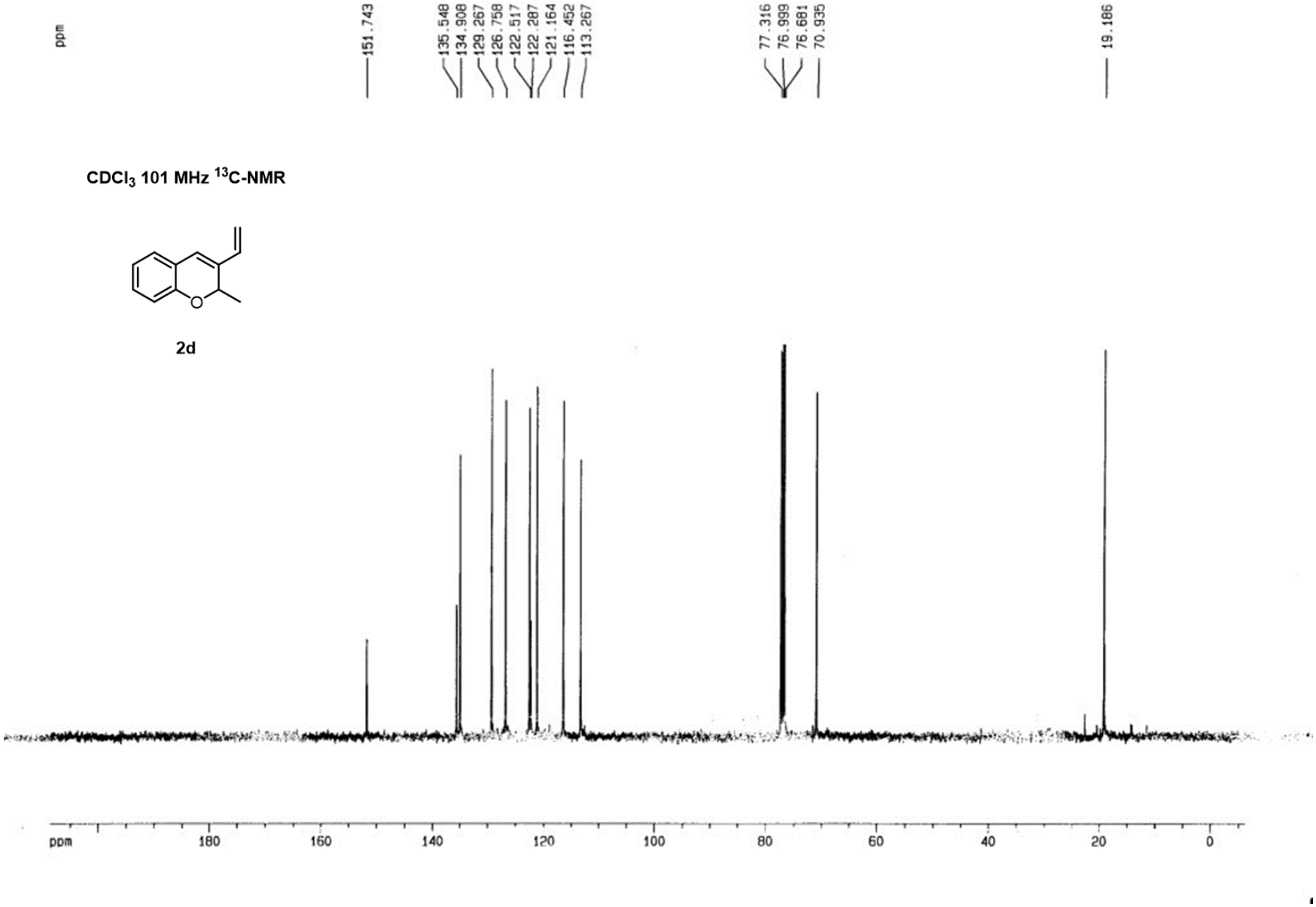
7.04036
7.02540
7.01909
6.98083
6.97457
6.71636
6.69509
6.37419
5.58575
5.58241
5.54261
5.53926
5.20261
5.19929
5.17518
5.17184
1.47816
1.44052
CDCl3 400 MHz 1H-NMR
Cl
O
2b
Integral
0.9804
0.8987
0.9083
0.9539
0.9123
1.0021
1.0000
6.1870
ppm 10 9 8 7 6 5 4 3 2 1 0


ppm
150.942
140.896
133.120
128.409
125.736
125.728
125.538
123.610
117.727
117.282
116.311
78.759
77.284
76.966
76.649
26.445
CDCl3 101 MHz 13C-NMR
Cl
O
2b
ppm
180
160
140
120
100
80
60
40
20
0


ppm
6.74317
6.72147
6.69091
6.68370
6.66198
6.59854
6.59137
6.43008
6.26684
6.23939
6.23722
5.57981
5.57624
5.53665
5.53307
5.17542
5.17183
5.14798
5.14437
3.76234
1.47819
CDCl3 400 MHz 1H-NMR
2c
Integral
0.9077
0.6178
0.3028
0.9464
0.9144
0.8856
0.9377
0.9529
3.0231
6.0000
ppm 10 9 8 7 6 5 4 3 2 1 0


ppm
153.877
146.338
140.559
133.490
122.878
118.924
116.556
115.598
114.230
111.252
78.048
77.331
77.014
76.697
55.632
26.222
26.214
CDCl3 101 MHz 13C-NMR
2c
ppm
180
160
140
120
100
80
60
40
20
0

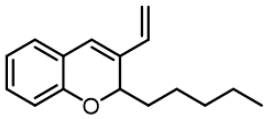

ppm
7.14357
7.14059
7.04963
7.04602
7.03103
7.02747
6.91247
6.90999
6.89394
6.89150
6.87529
6.87254
6.86717
6.84680
6.44975
6.42219
6.40534
6.37774
6.35995
5.30631
5.28997
5.27358
5.22846
5.18892
5.18444
5.16164
1.38817
1.37175
CDCl3 400 MHz 1H-NMR
2d
Integral
1.0011
1.0014
1.9769
1.9550
1.0217
2.0000
3.0966
ppm
10
9
8
7
6
5
4
3
2
1
0



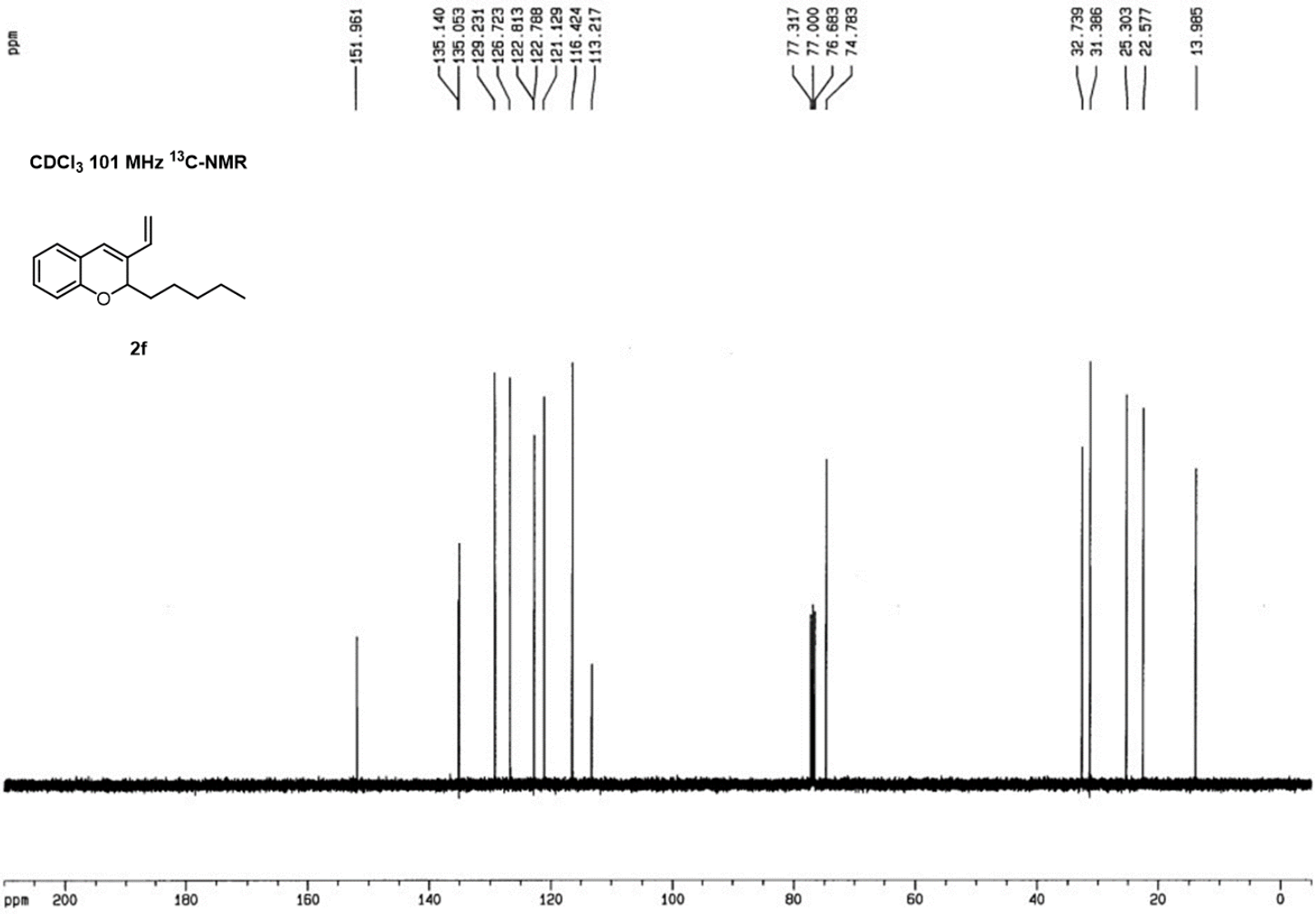
$CDCl_3$ 101 MHz ^{13}C-NMR

2d

$CDCl_3$ 400 MHz ^{1}H-NMR

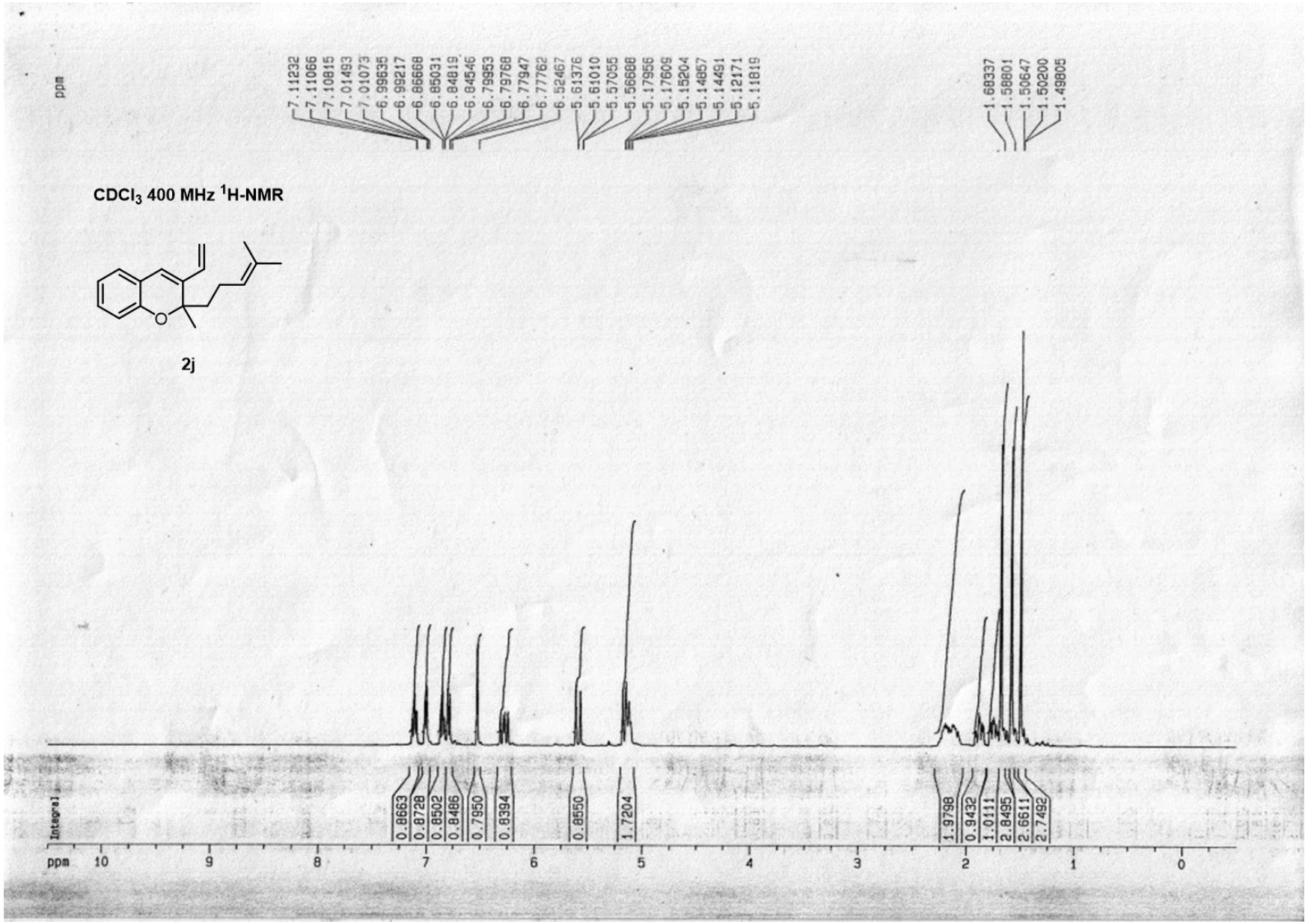


2f



$CDCl_3$ 101 MHz ^{13}C-NMR

2f


ppm
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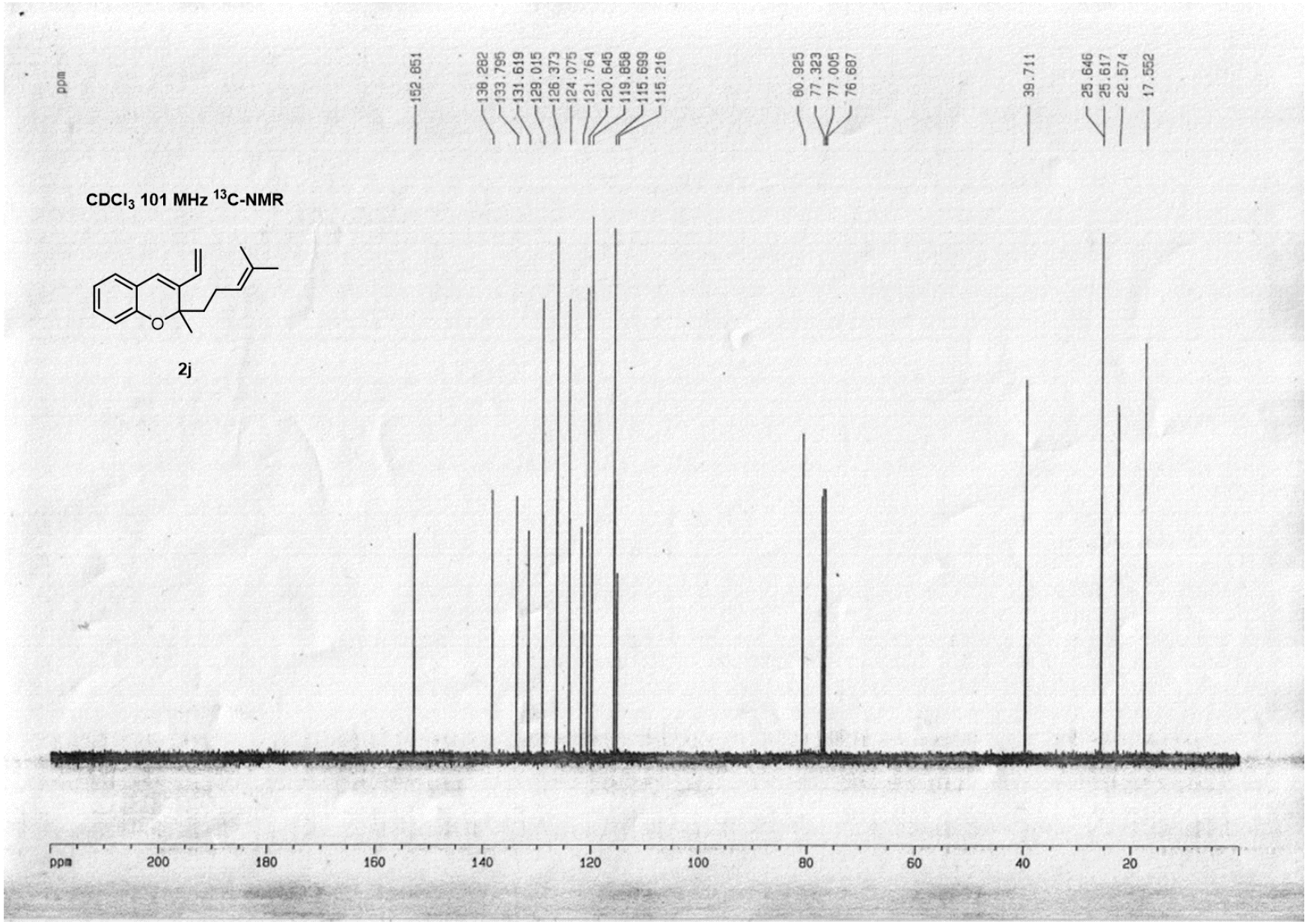
7.11066
7.10815
7.01493
7.01073
6.99635
6.99217
6.86668
6.85031
6.84819
6.84546
6.79953
6.79768
6.77947
6.77762
6.52467
5.61376
5.61010
5.57055
5.56668
5.17956
5.17609
5.15204
5.14857
5.14491
5.12171
5.11819
1.68337
1.58801
1.50647
1.50200
1.49805
CDCl3 400 MHz 1H-NMR
O
2j
Integral
0.8663
0.8728
0.8502
0.8486
0.7950
0.8394
0.8550
1.7204
1.9798
0.9432
1.0111
2.8495
2.6611
2.7492
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
152.851
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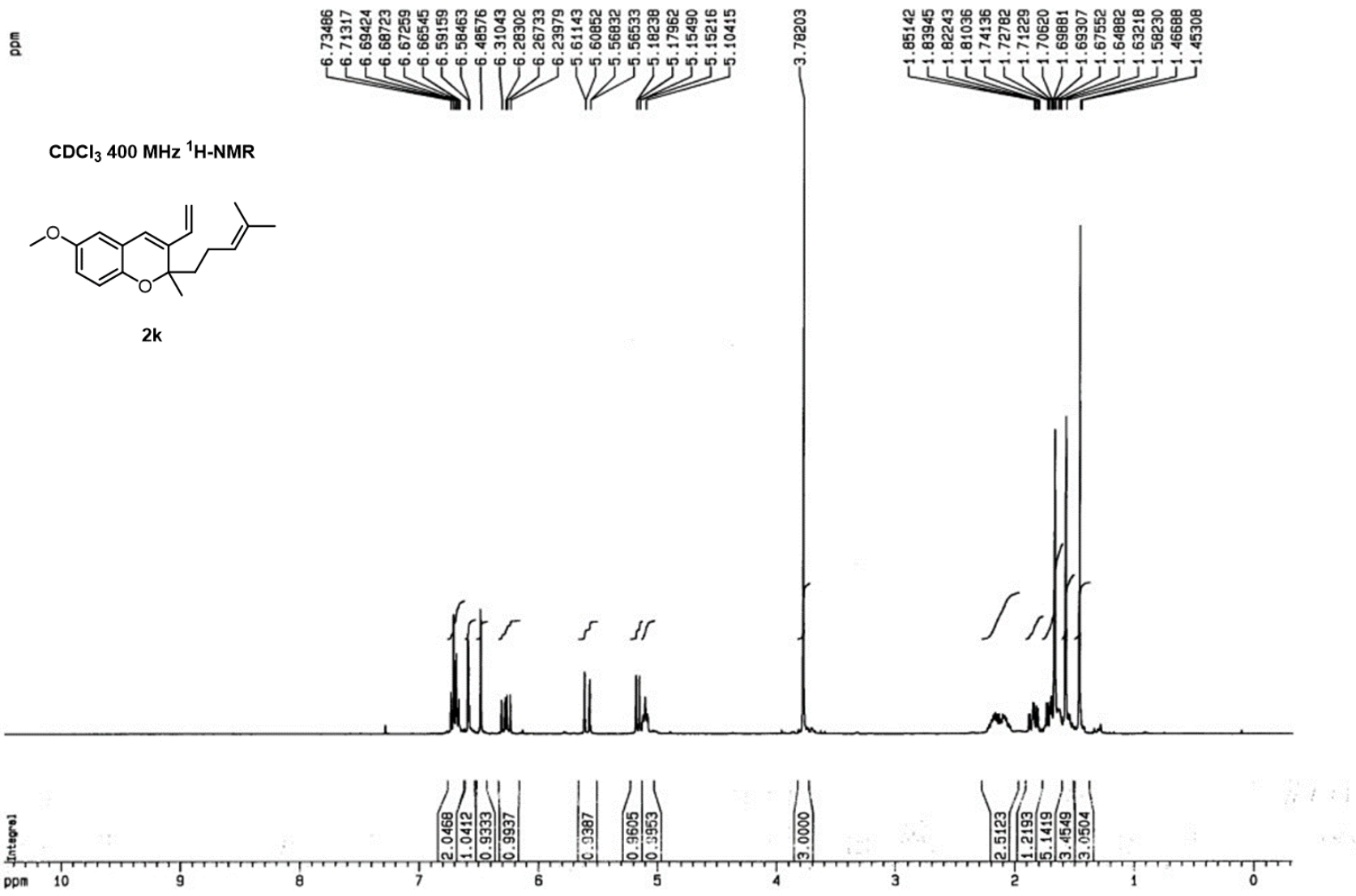
133.795
131.619
129.015
126.373
124.075
121.764
120.645
119.858
115.699
115.216
80.925
77.323
77.005
76.687
39.711
25.646
25.617
22.574
17.552
CDCl3 101 MHz 13C-NMR
2j
ppm
200
180
160
140
120
100
80
60
40
20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6.67259
6.66545
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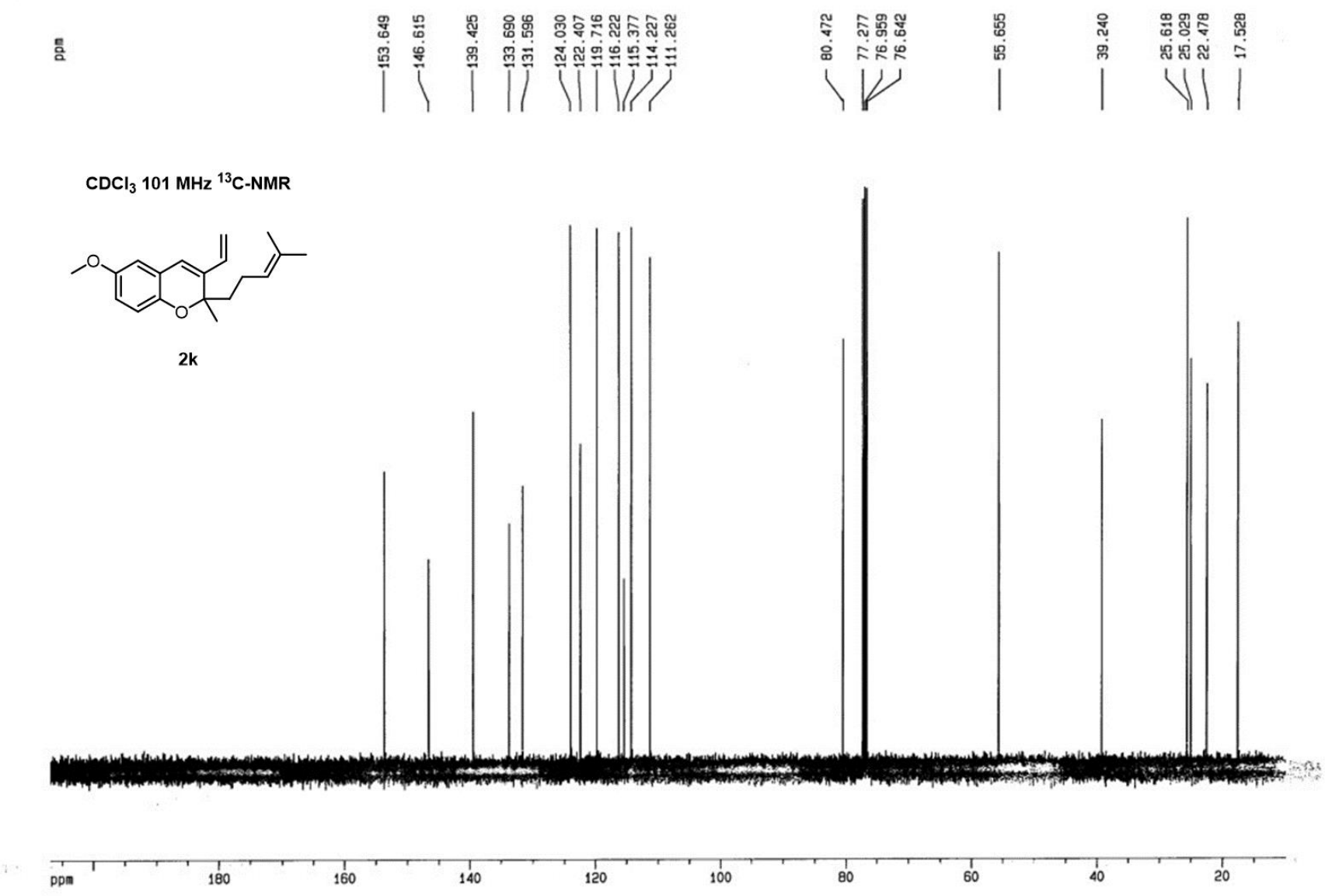
6.58463
6.48576
6.31043
6.28302
6.26733
6.23979
5.61143
5.60852
5.56832
5.56533
5.18238
5.17962
5.15490
5.15216
5.10415
3.78203
1.85142
1.83945
1.82243
1.81036
1.74136
1.72782
1.71229
1.70620
1.69881
1.69307
1.67552
1.64882
1.63218
1.58230
1.46688
1.45308
CDCl3 400 MHz 1H-NMR
O
O
2k
Integral
2.0468
1.0412
0.9333
0.9937
0.3387
0.9605
0.3953
3.0000
2.5123
1.2193
5.1419
3.4549
3.0504
ppm
10
9
8
7
6
5
4
3
2
1
0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153.649
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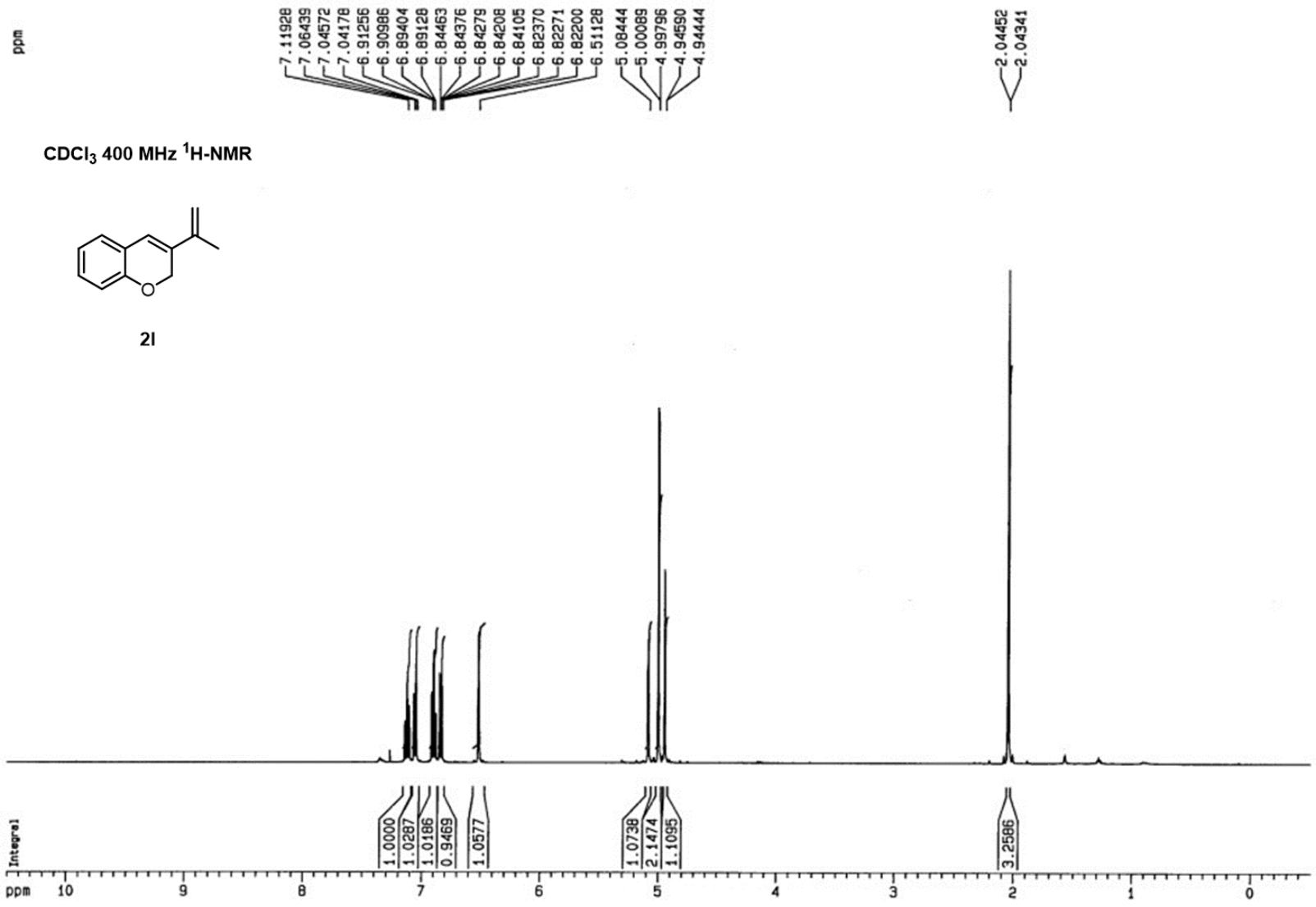
139.425
133.690
131.596
124.030
122.407
119.716
116.222
115.377
114.227
111.262
80.472
77.277
76.959
76.642
55.655
39.240
25.618
25.029
22.478
17.528
CDCl3 101 MHz 13C-NMR
2k
ppm
180
160
140
120
100
80
60
40
20


ppm
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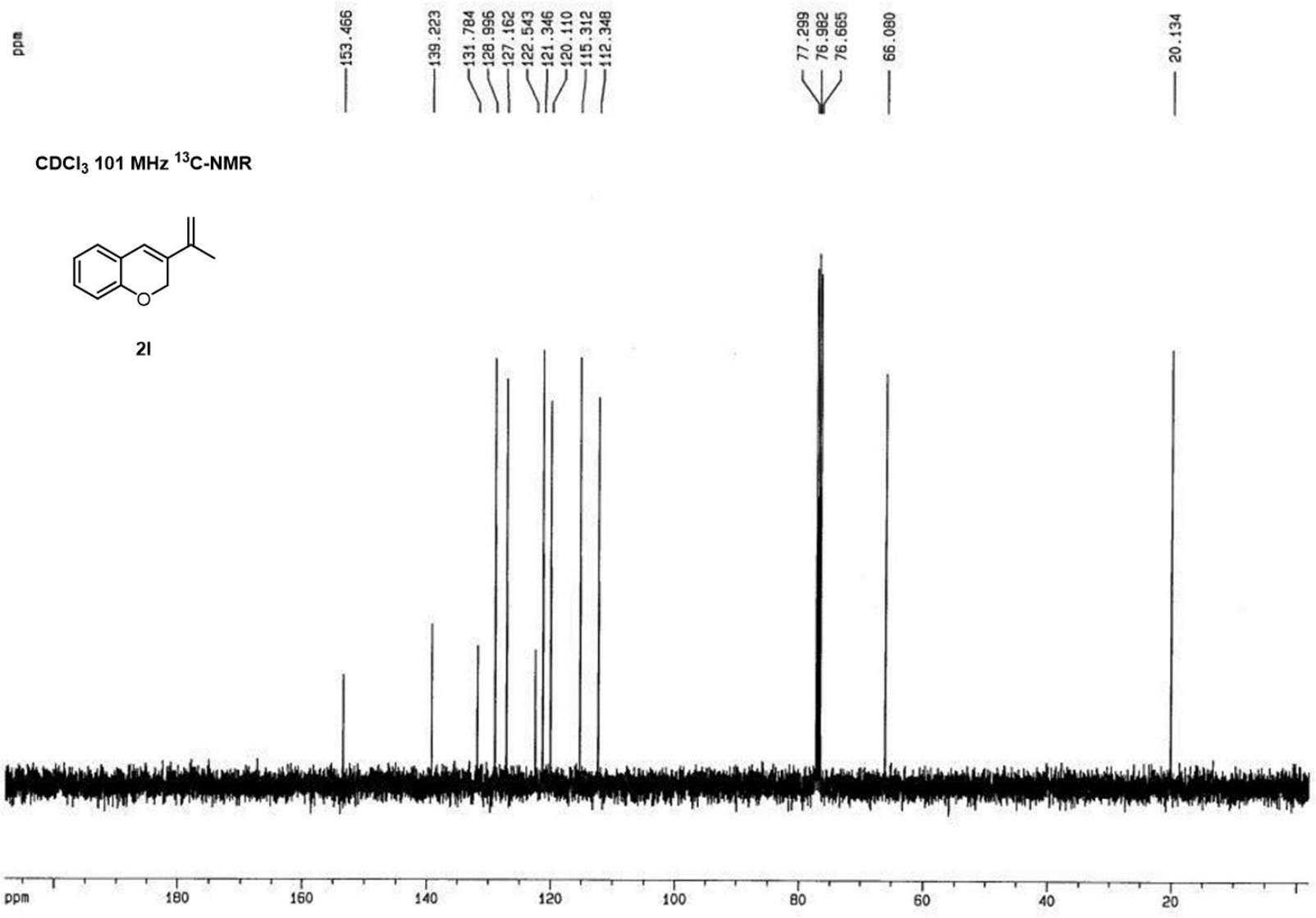
7.06439
7.04572
7.04178
6.91256
6.90986
6.89404
6.89128
6.84463
6.84376
6.84279
6.84208
6.84105
6.82370
6.82271
6.82200
6.51128
5.08444
5.00089
4.99796
4.94590
4.94444
2.04452
2.04341
CDCl3 400 MHz 1H-NMR
2l
Integral
1.0000
1.0287
1.0186
0.9469
1.0577
1.0738
2.1474
1.1095
3.2586
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
153.466
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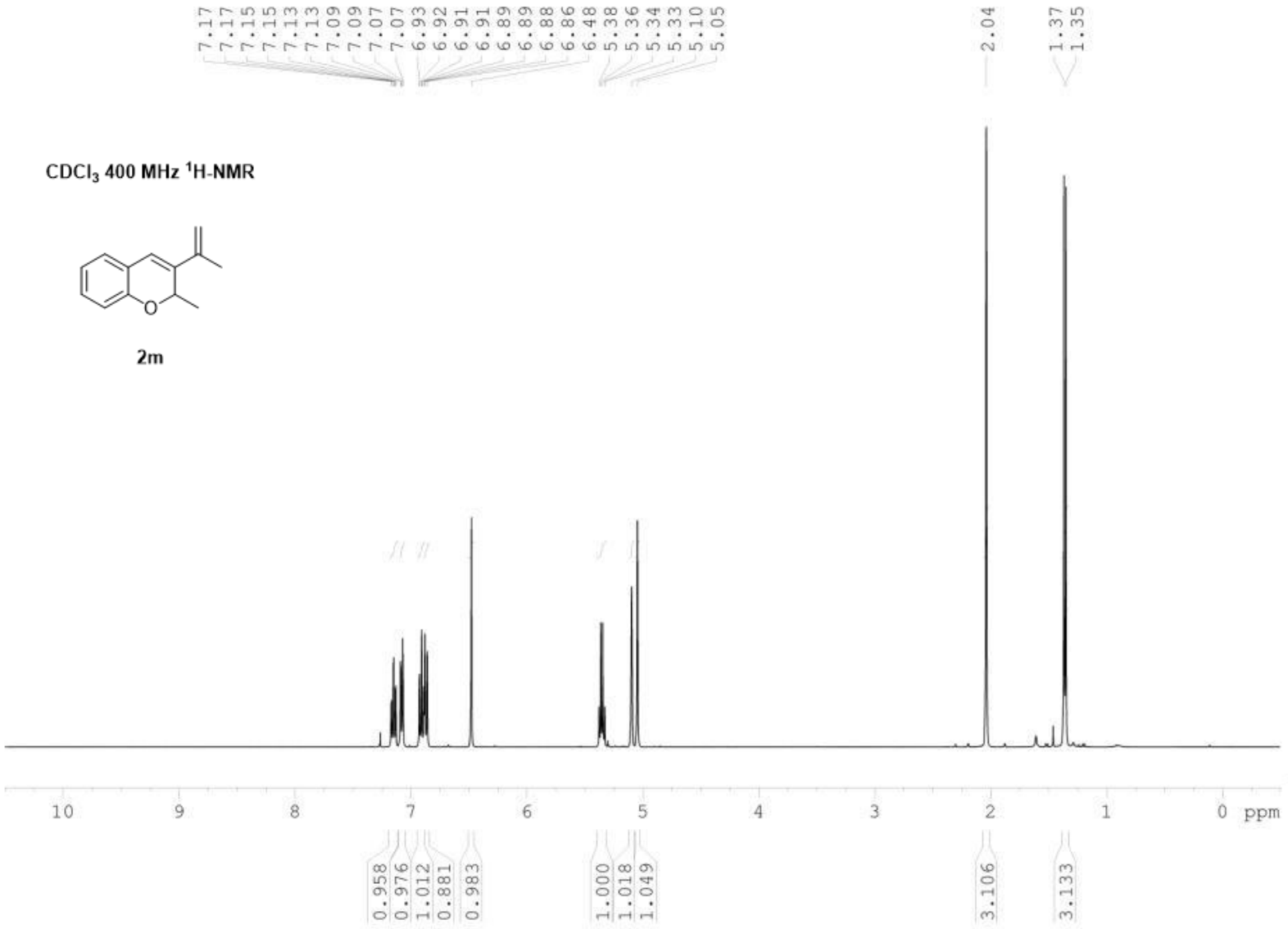
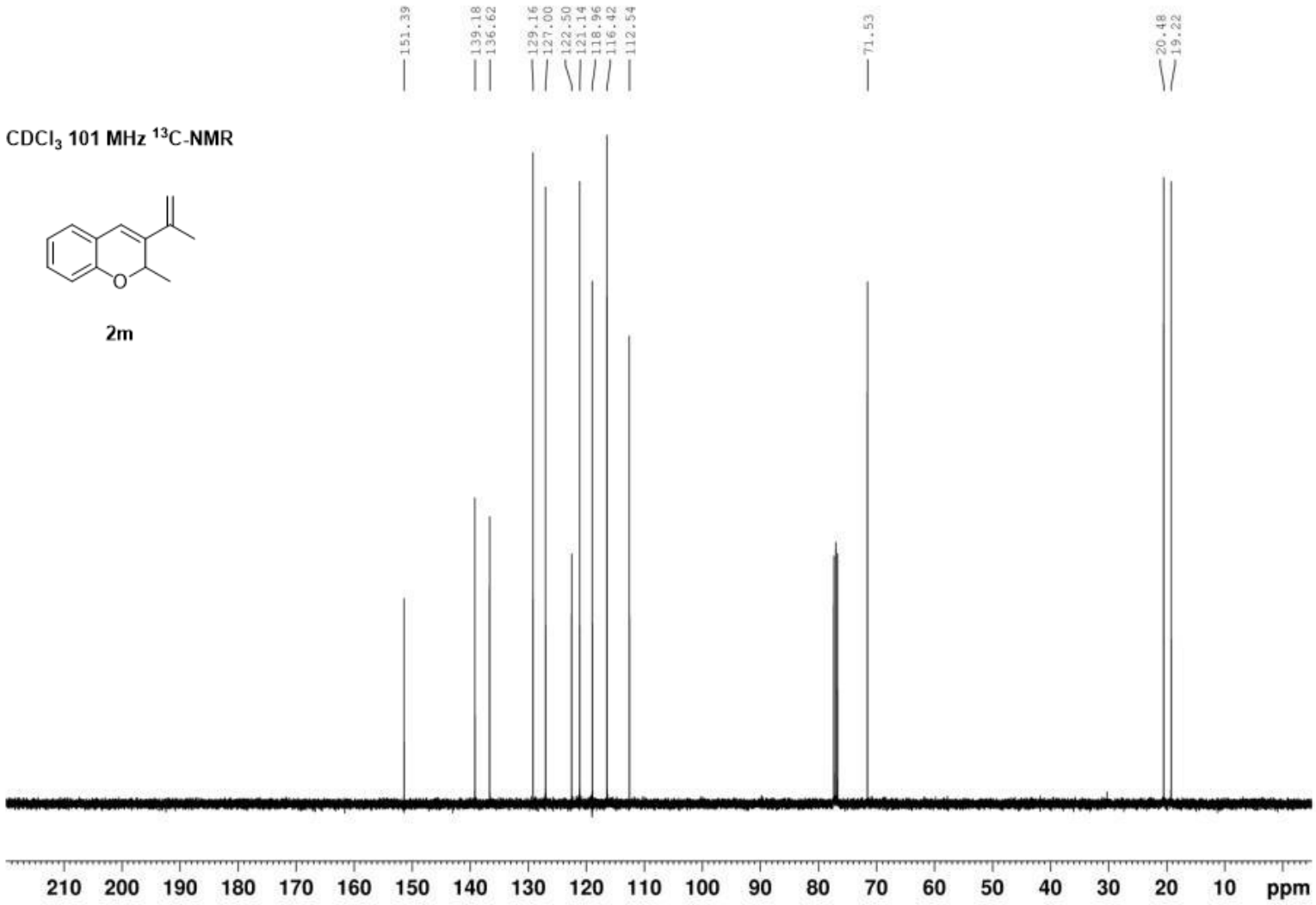
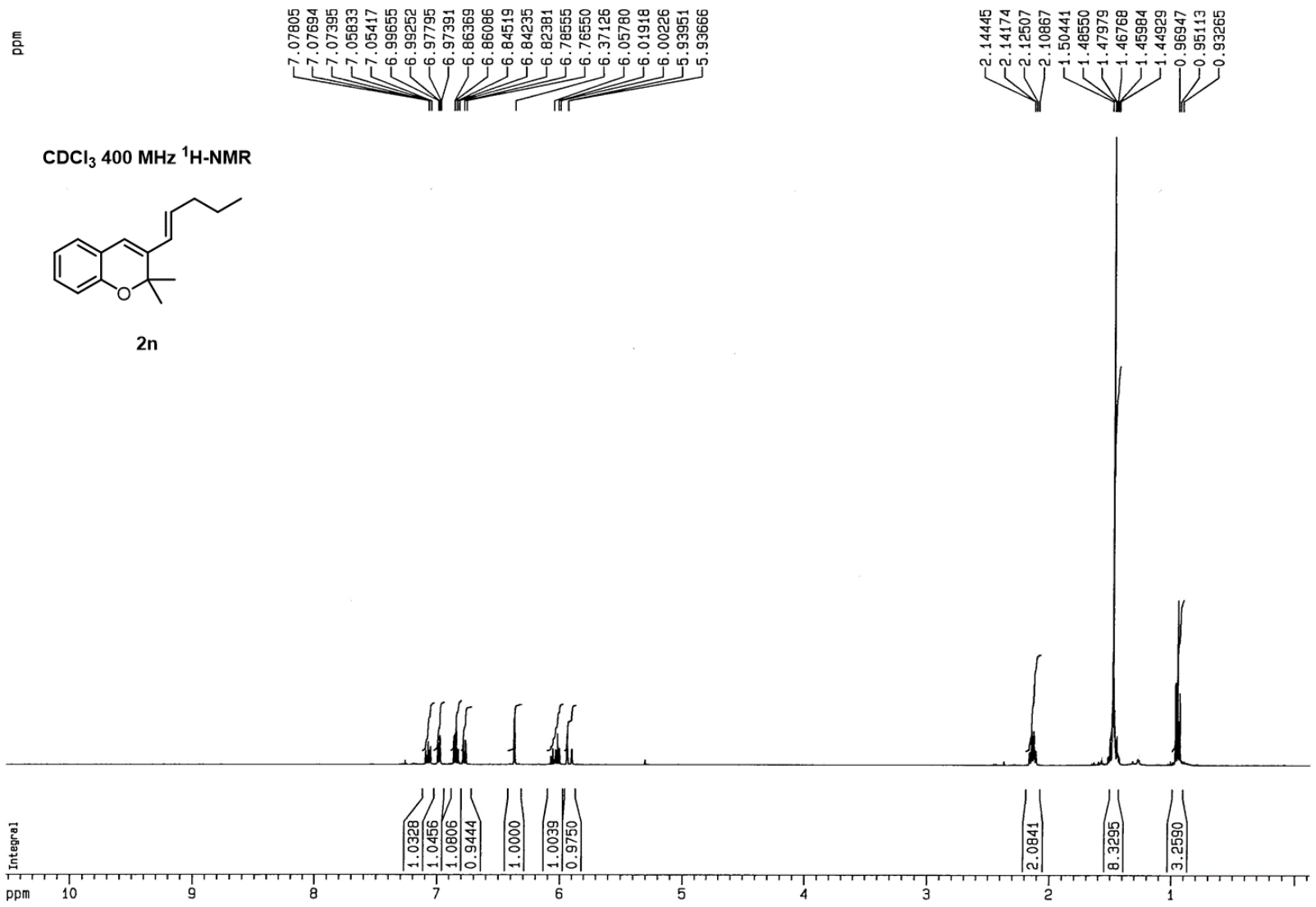
131.784
128.996
127.162
122.543
121.346
120.110
115.312
112.348
77.299
76.982
76.665
66.080
20.134
CDCl3 101 MHz 13C-NMR
2l
ppm
180
160
140
120
100
80
60
40
20


7.17
7.17
7.15
7.15
7.13
7.13
7.09
7.09
7.07
7.07
6.93
6.92
6.91
6.89
6.89
6.88
6.86
6.48
5.38
5.36
5.34
5.33
5.10
5.05
2.04
1.37
1.35
CDCl3 400 MHz 1H-NMR
O
2m
10
9
8
7
6
5
4
3
2
1
0 ppm
0.958
0.976
1.012
0.881
0.983
1.000
1.018
1.049
3.106
3.133


151.39
139.18
136.62
129.16
127.00
122.50
121.14
118.96
116.42
112.54
71.53
20.48
19.22
CDCl3 101 MHz 13C-NMR
O
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


ppm
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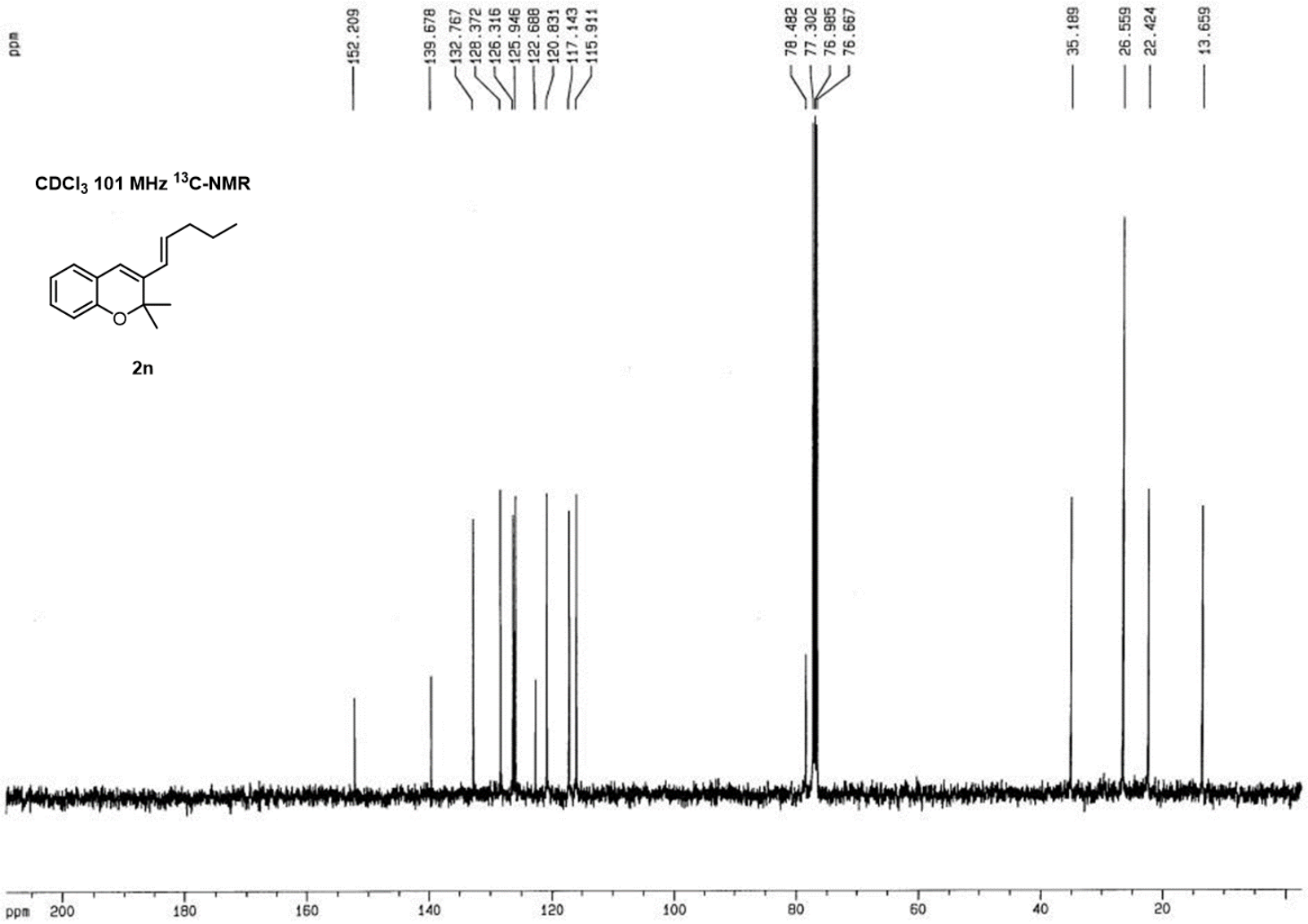
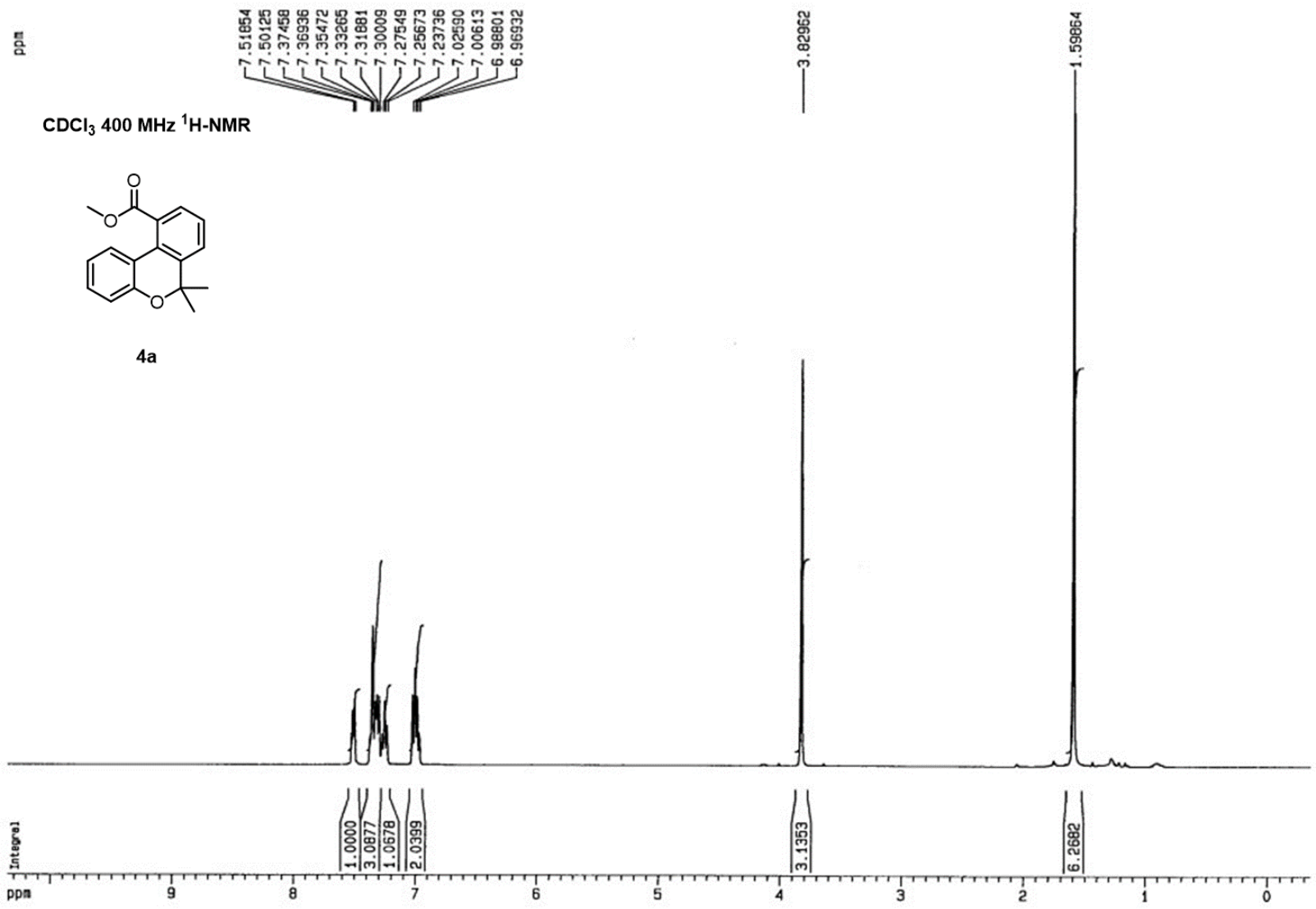
7.07694
7.07395
7.05833
7.05417
6.99655
6.99252
6.97795
6.97391
6.86369
6.86086
6.84519
6.84235
6.82381
6.78555
6.76550
6.37126
6.05780
6.01918
6.00226
5.93951
5.93666
2.14445
2.14174
2.12507
2.10867
1.50441
1.48550
1.47979
1.46768
1.45984
1.44929
0.96947
0.95113
0.93265
CDCl3 400 MHz 1H-NMR
2n
Integral
1.0328
1.0456
1.0806
0.9444
1.0000
1.0039
0.9750
2.0841
8.3295
3.2590
ppm
10
9
8
7
6
5
4
3
2
1


ppm
152.209
139.678
132.767
128.372
126.316
125.946
122.688
120.831
117.143
115.911
78.482
77.302
76.985
76.667
35.189
26.559
22.424
13.659
CDCl3 101 MHz 13C-NMR
2n
ppm 200
180
160
140
120
100
80
60
40
20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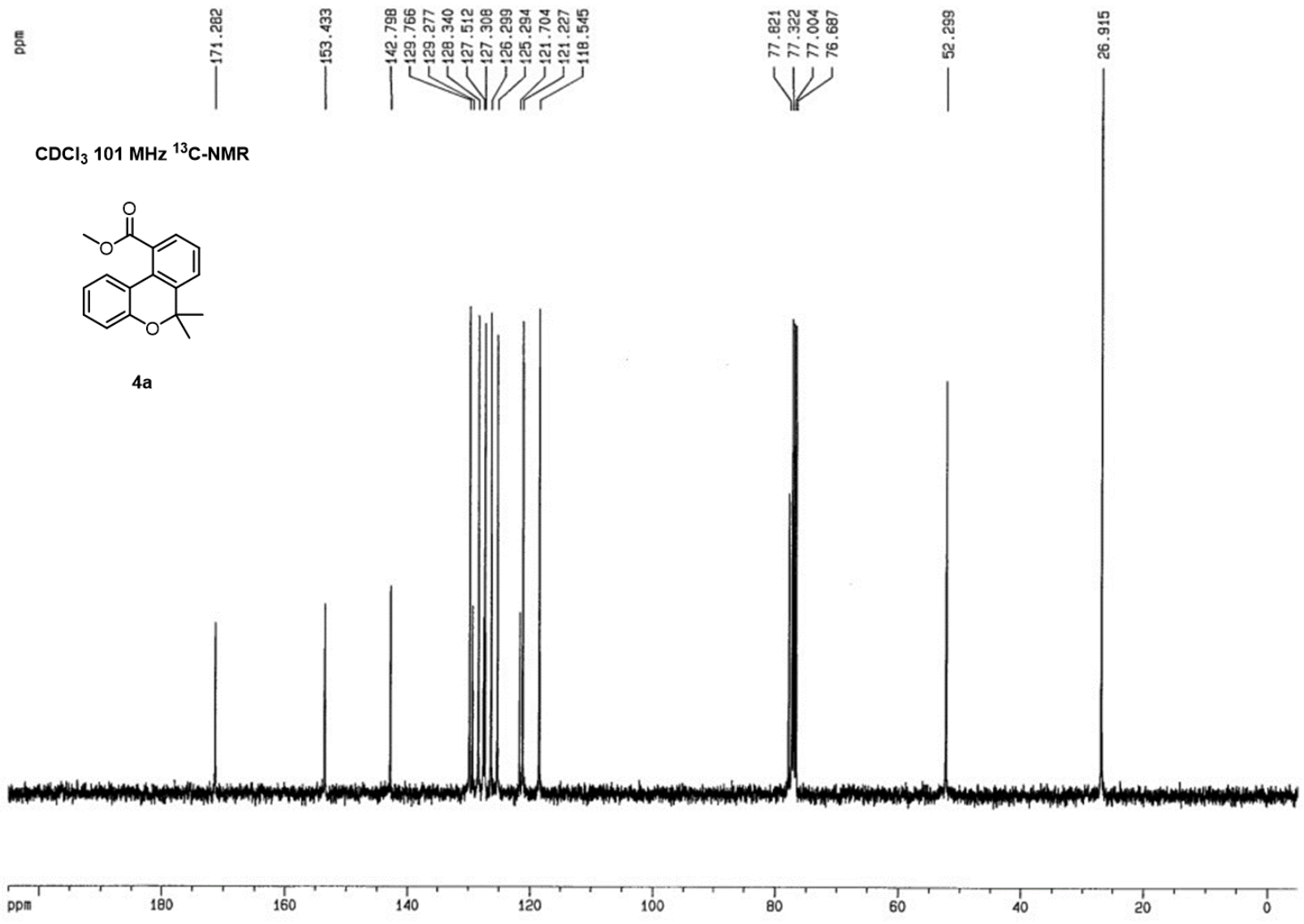
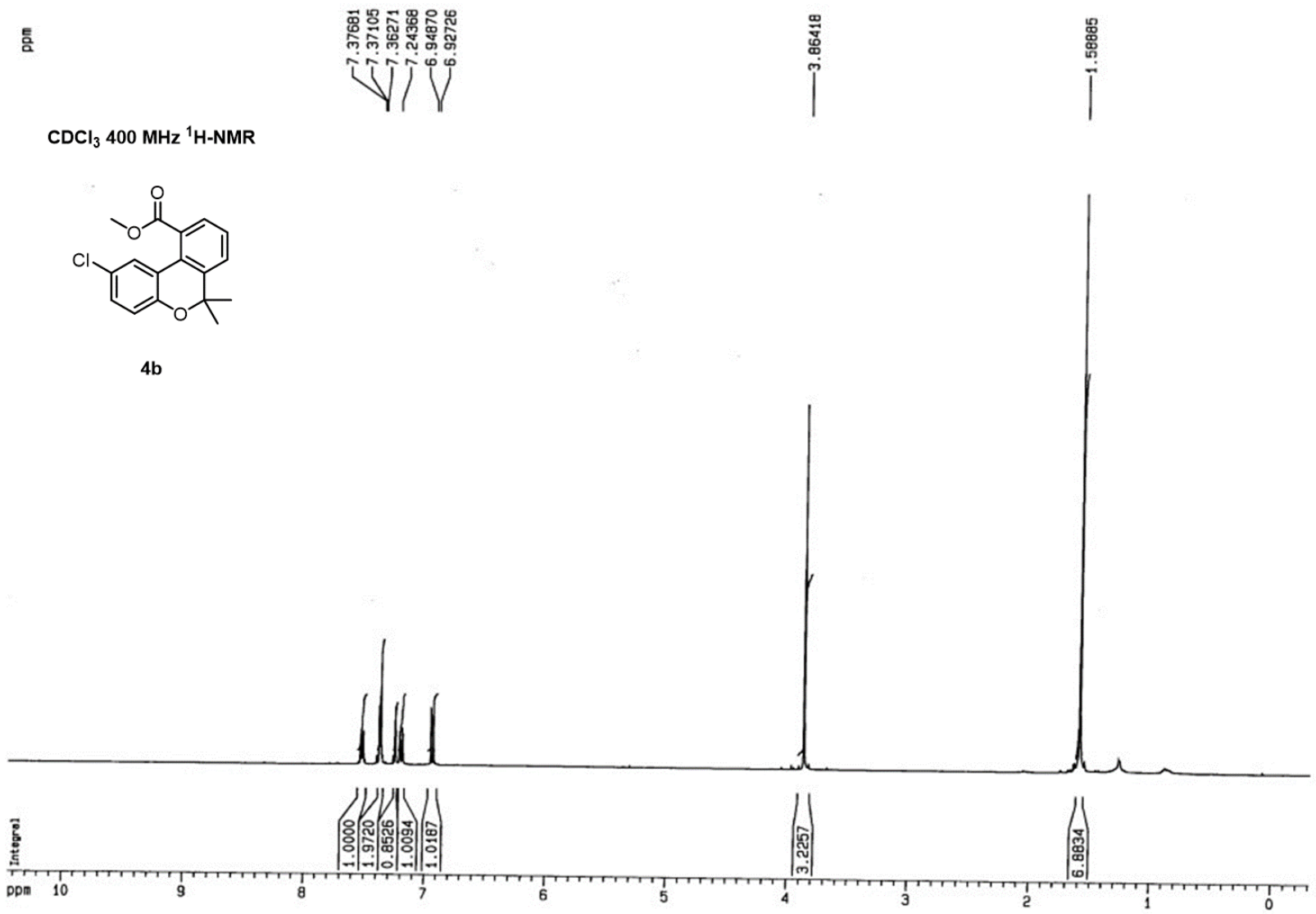
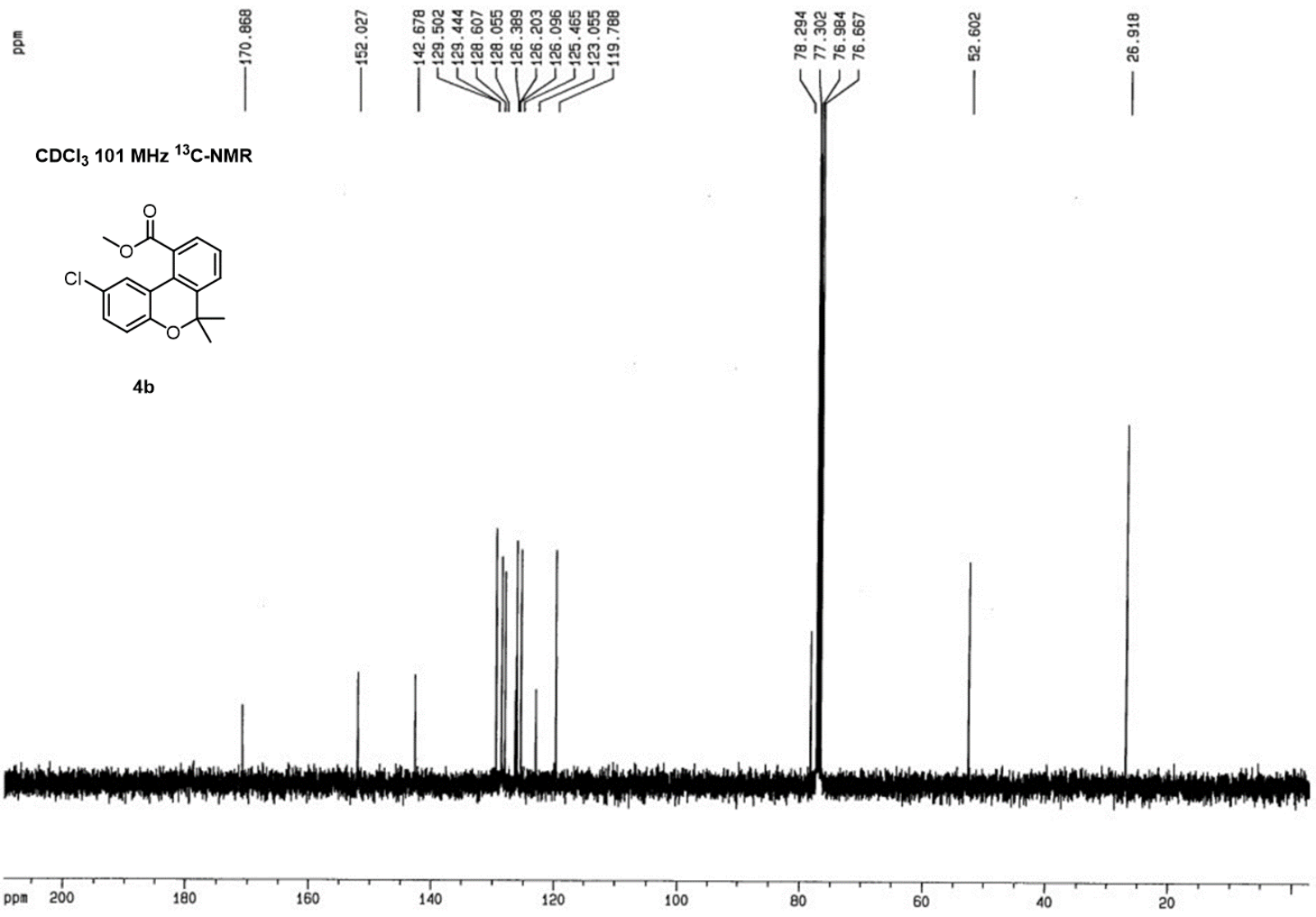
7.51654
7.50125
7.37458
7.36936
7.35472
7.33265
7.31881
7.30009
7.27549
7.25673
7.23736
7.02590
7.00613
6.98801
6.96932
3.82962
1.59864
CDCl3 400 MHz 1H-NMR
4a
Integral
1.0000
3.0877
1.0678
2.0399
3.1353
6.2682
ppm
9
8
7
6
5
4
3
2
1
0


ppm
171.282
153.433
142.798
129.766
129.277
128.340
127.512
127.308
126.299
125.294
121.704
121.227
118.545
77.821
77.322
77.004
76.687
52.299
26.915
CDCl3 101 MHz 13C-NMR
4a
ppm
180
160
140
120
100
80
60
40
20
0


ppm
7.37681
7.37105
7.36271
7.24368
6.94870
6.92726
3.86418
1.58885
CDCl3 400 MHz 1H-NMR
Cl
O
O
O
4b
Integral
1.0000
1.9720
0.8526
1.0094
1.0187
3.2257
6.8834
ppm
10
9
8
7
6
5
4
3
2
1
0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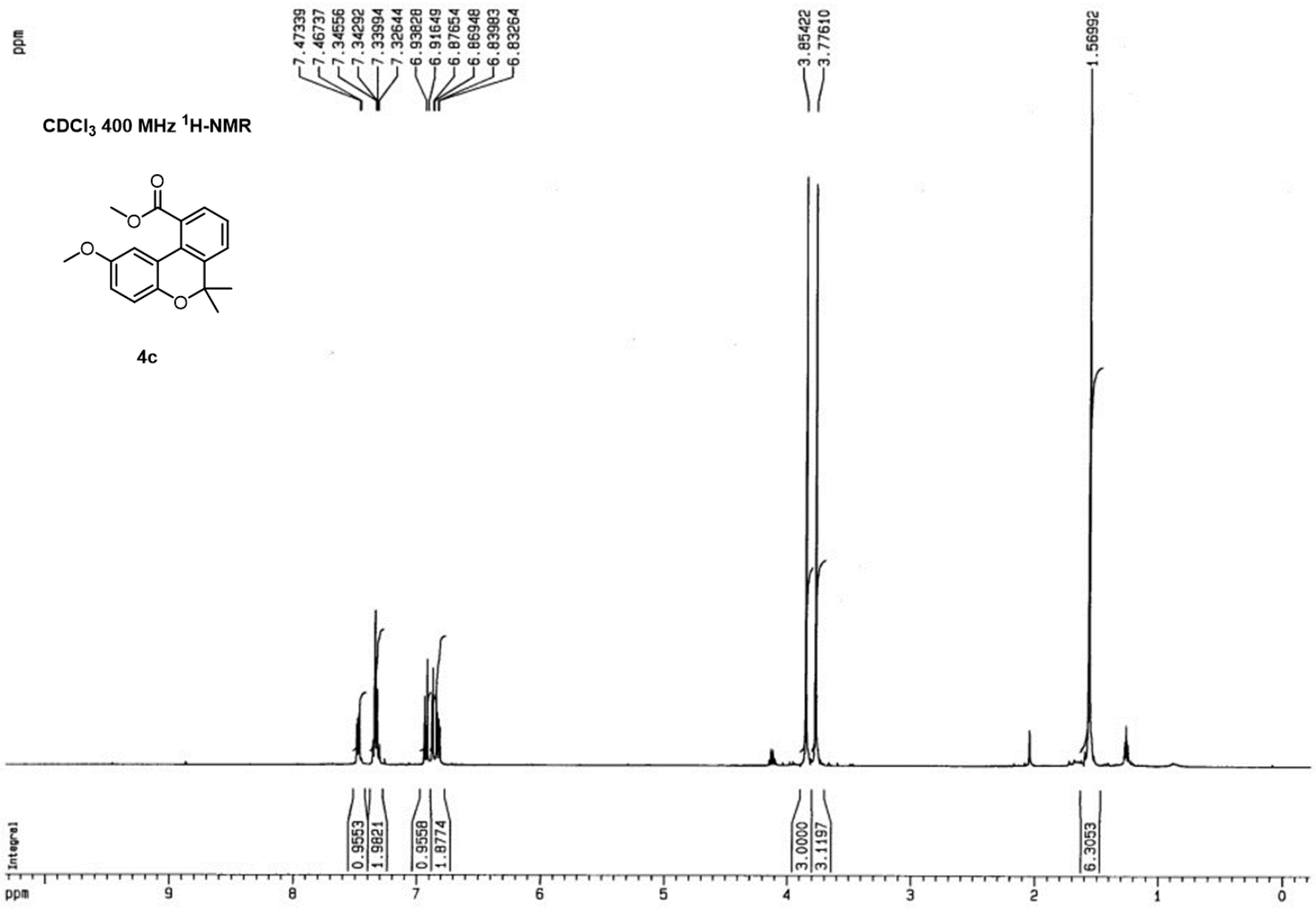
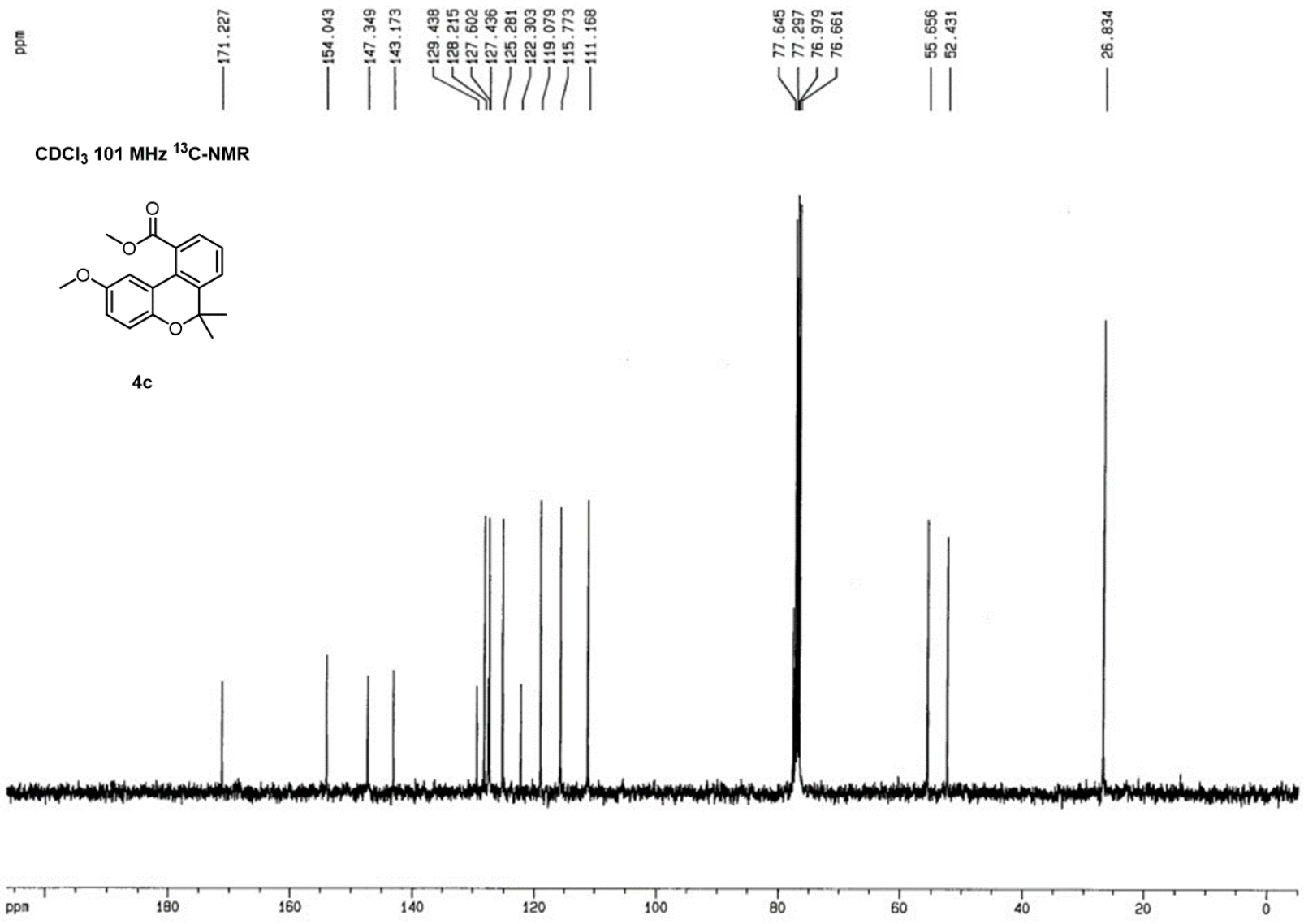
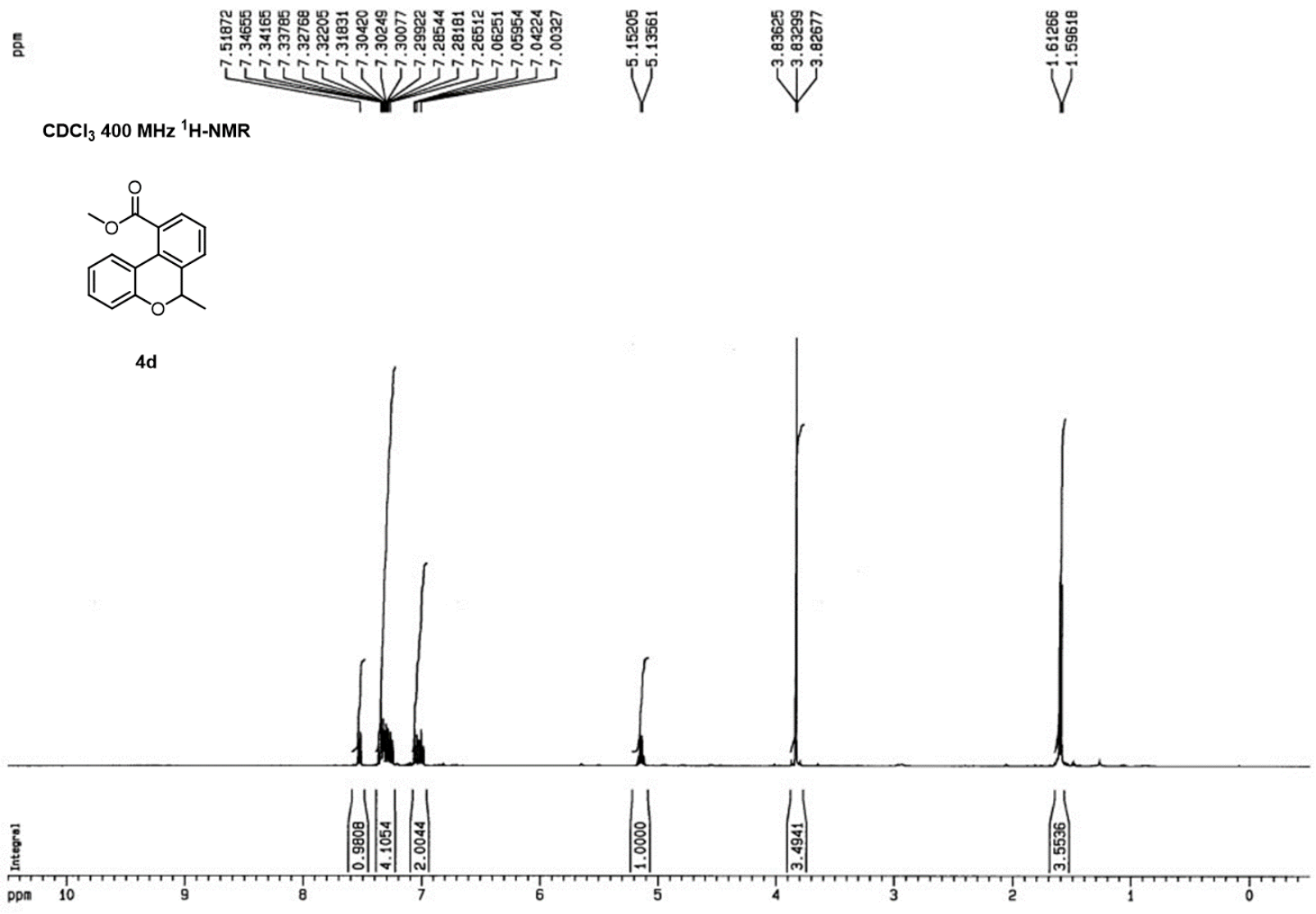
129.502
129.444
128.607
128.055
126.389
126.203
126.096
125.465
123.055
119.788
78.294
77.302
76.984
76.667
52.602
26.918
CDCl3 101 MHz 13C-NMR
Cl
O
O
O
4b
ppm 200 180 160 140 120 100 80 60 40 20

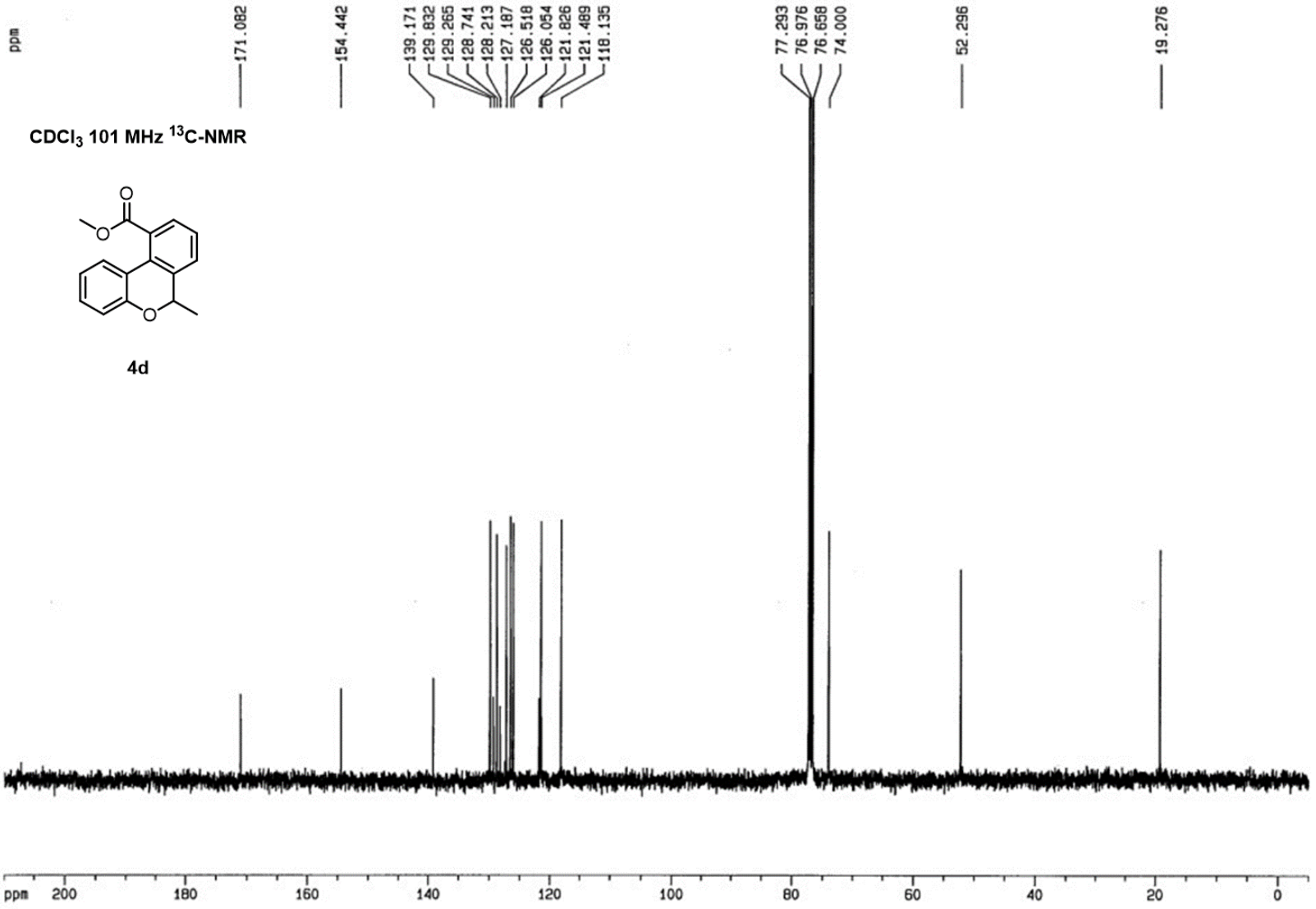

ppm
7.47339
7.46737
7.34556
7.34292
7.33994
7.32644
6.93828
6.91649
6.87654
6.86948
6.83983
6.83264
3.85422
3.77610
1.56992
CDCl3 400 MHz 1H-NMR
4c
Integral
0.9553
1.9821
0.9558
1.8774
3.0000
3.1197
6.3053
ppm
9
8
7
6
5
4
3
2
1
0

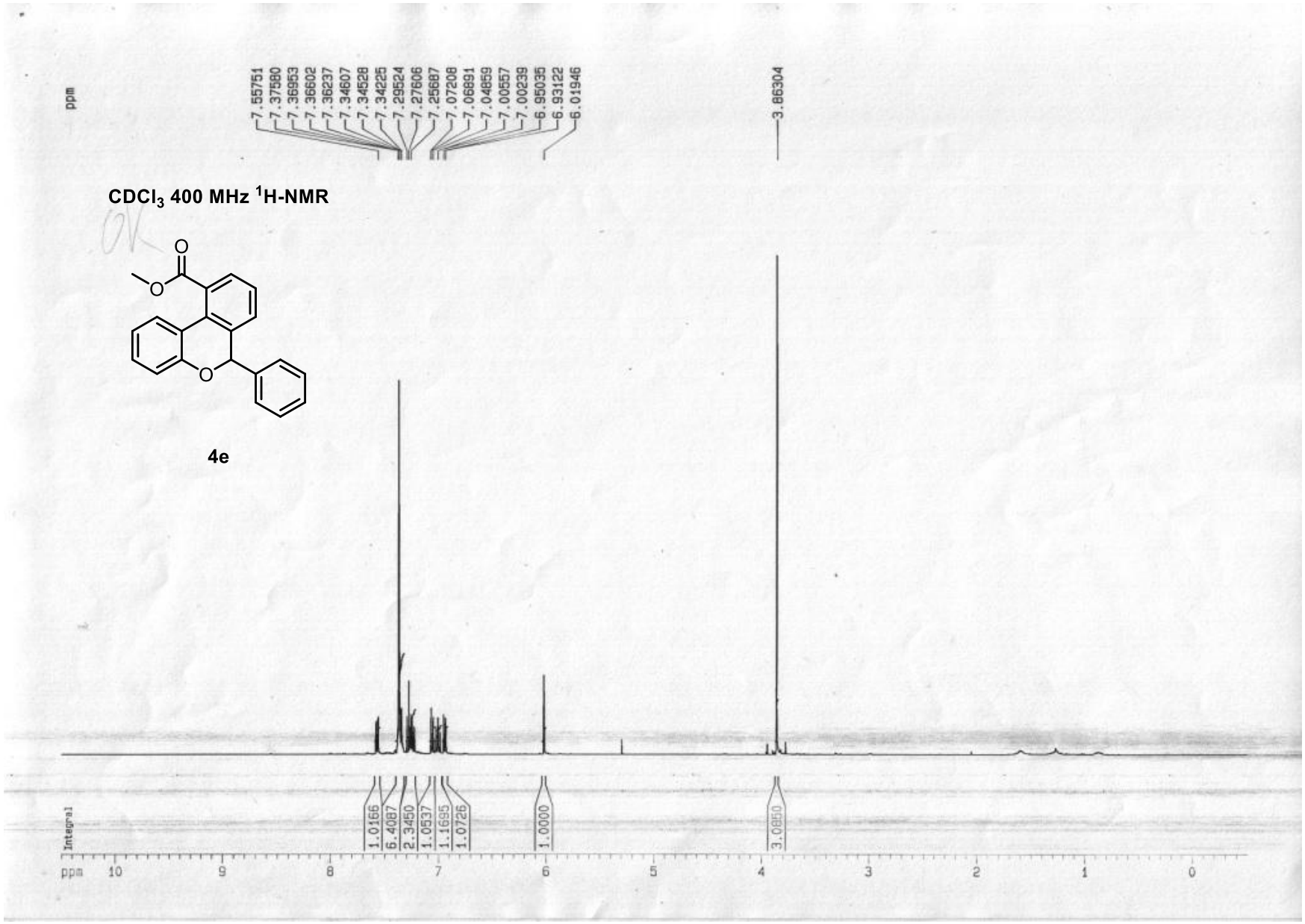


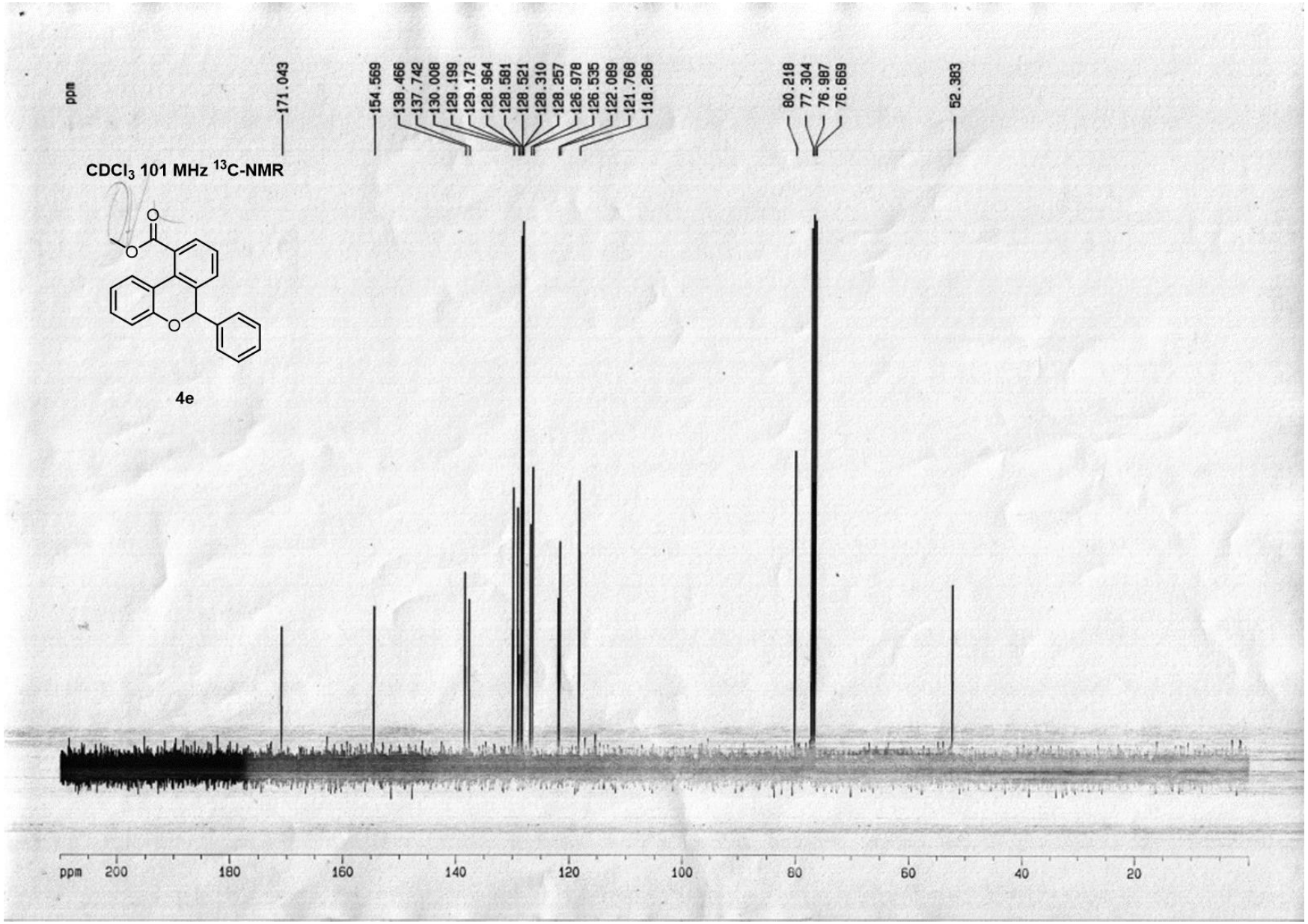
$CDCl_3$ 101 MHz ^{13}C-NMR

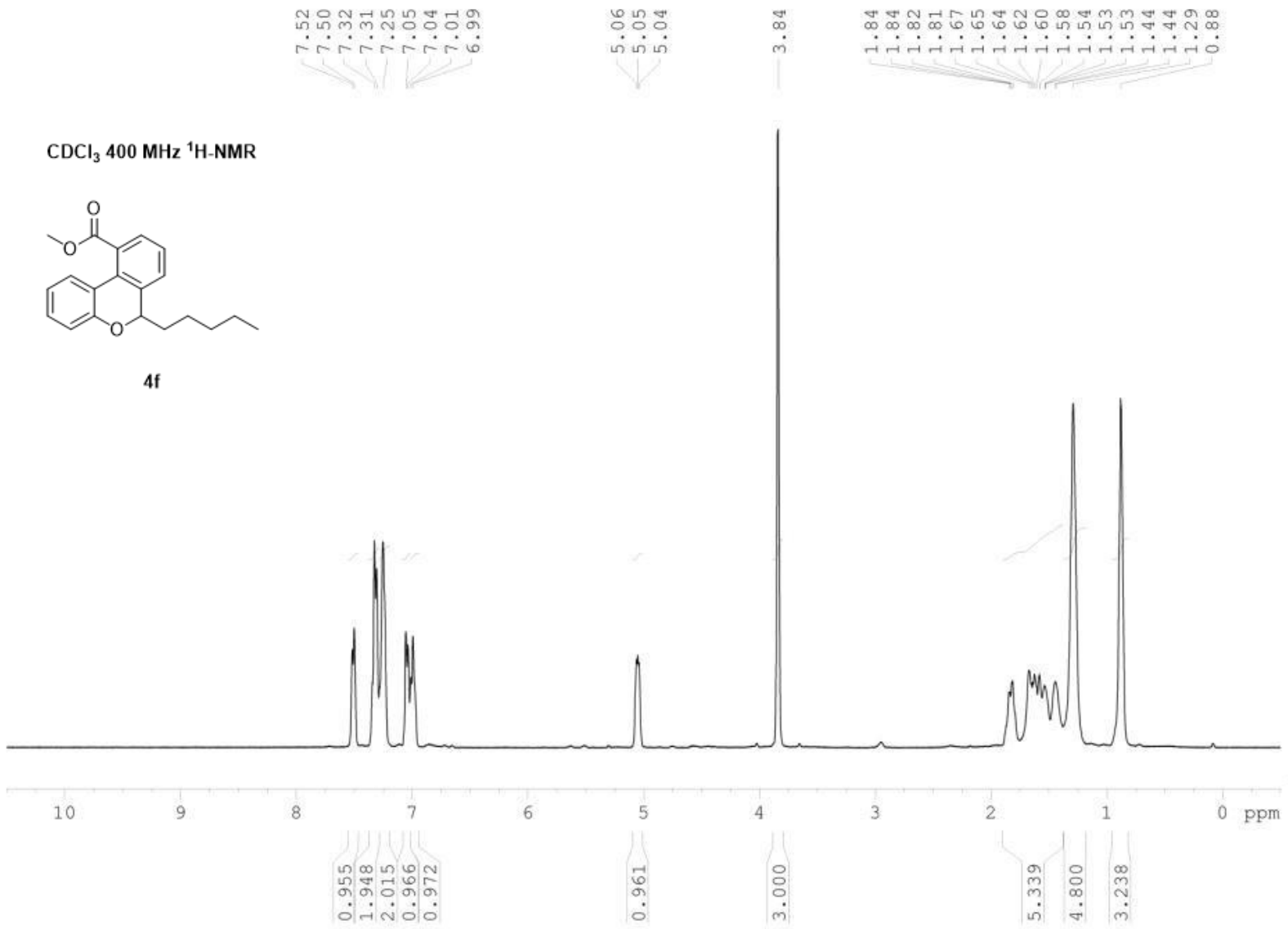
4c

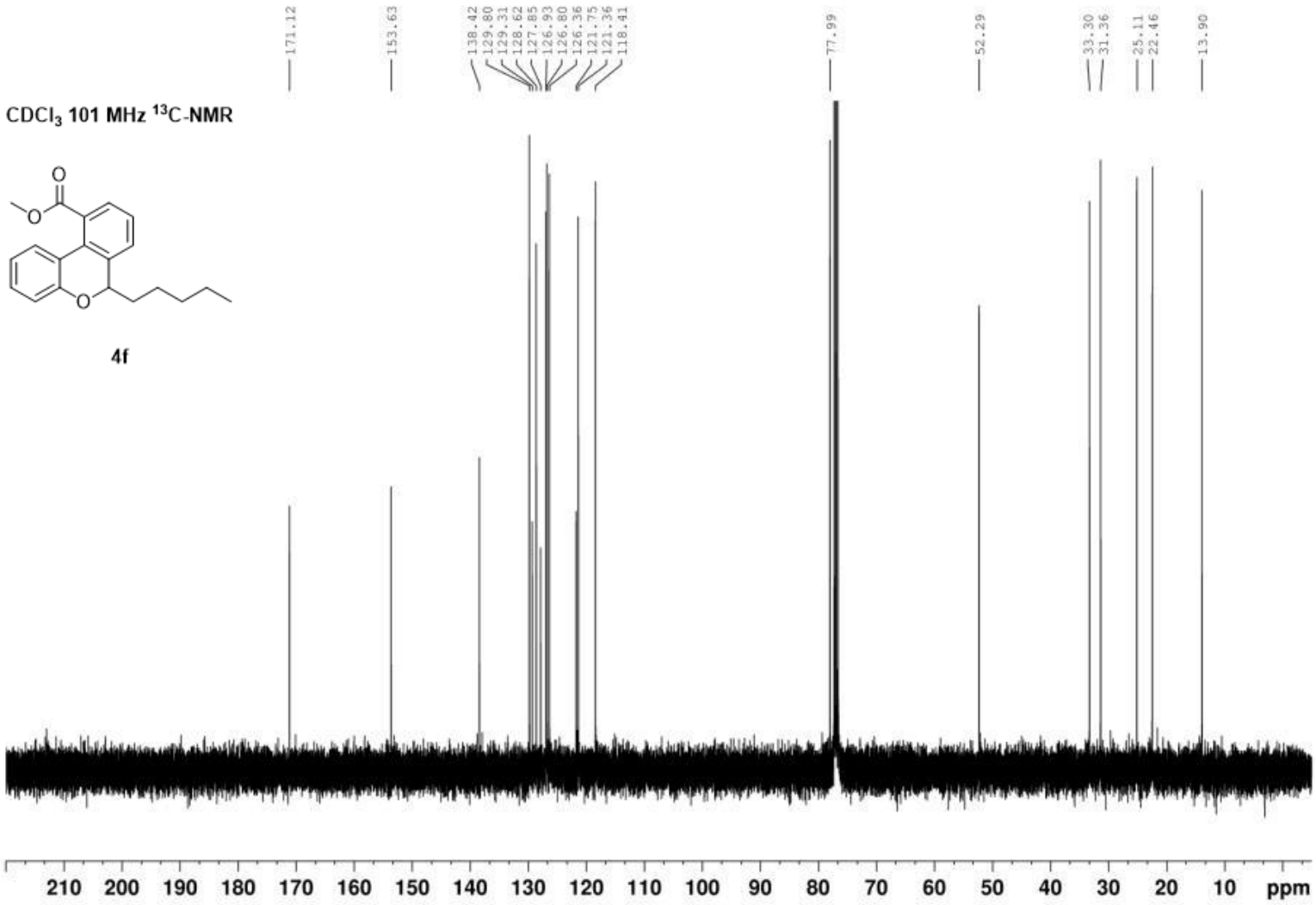

ppm
7.51872
7.34655
7.34165
7.33785
7.32768
7.32205
7.31831
7.30420
7.30249
7.30077
7.29922
7.28544
7.28181
7.26512
7.06251
7.05954
7.04224
7.00327
5.15205
5.13561
3.83625
3.83299
3.82677
1.61266
1.59618
CDCl3 400 MHz 1H-NMR
4d
Integral
0.9808
4.1054
2.0044
1.0000
3.4941
3.5536
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
171.082
154.442
139.171
129.832
129.265
128.741
128.213
127.187
126.518
126.054
121.826
121.489
118.135
77.293
76.976
76.658
74.000
52.296
19.276
CDCl3 101 MHz 13C-NMR
4d
ppm 200 180 160 140 120 100 80 60 40 20 0


ppm
7.55751
7.37580
7.36953
7.36602
7.36237
7.34607
7.34528
7.34225
7.29524
7.27606
7.25687
7.07206
7.06891
7.04859
7.00557
7.00239
6.95035
6.93122
6.01946
3.86304
CDCl3 400 MHz 1H-NMR
O
O
O
4e
Integral
1.0166
6.4087
2.3450
1.0537
1.1695
1.0726
1.0000
3.0850
ppm
10
9
8
7
6
5
4
3
2
1
0


ppm
171.043
154.569
138.466
137.742
130.008
129.199
129.172
128.964
128.581
128.521
128.310
128.257
126.978
126.535
122.089
121.768
118.286
80.218
77.304
76.987
76.669
52.383
CDCl3 101 MHz 13C-NMR
4e
ppm 200 180 160 140 120 100 80 60 40 20


7.52
7.50
7.32
7.31
7.25
7.05
7.04
7.01
6.99
5.06
5.05
5.04
3.84
1.84
1.84
1.82
1.81
1.67
1.65
1.64
1.62
1.60
1.58
1.54
1.53
1.53
1.44
1.44
1.29
0.88
CDCl3 400 MHz 1H-NMR
O
O
O
4f
10
9
8
7
6
5
4
3
2
1
0 ppm
0.955
1.948
2.015
0.966
0.972
0.961
3.000
5.339
4.800
3.238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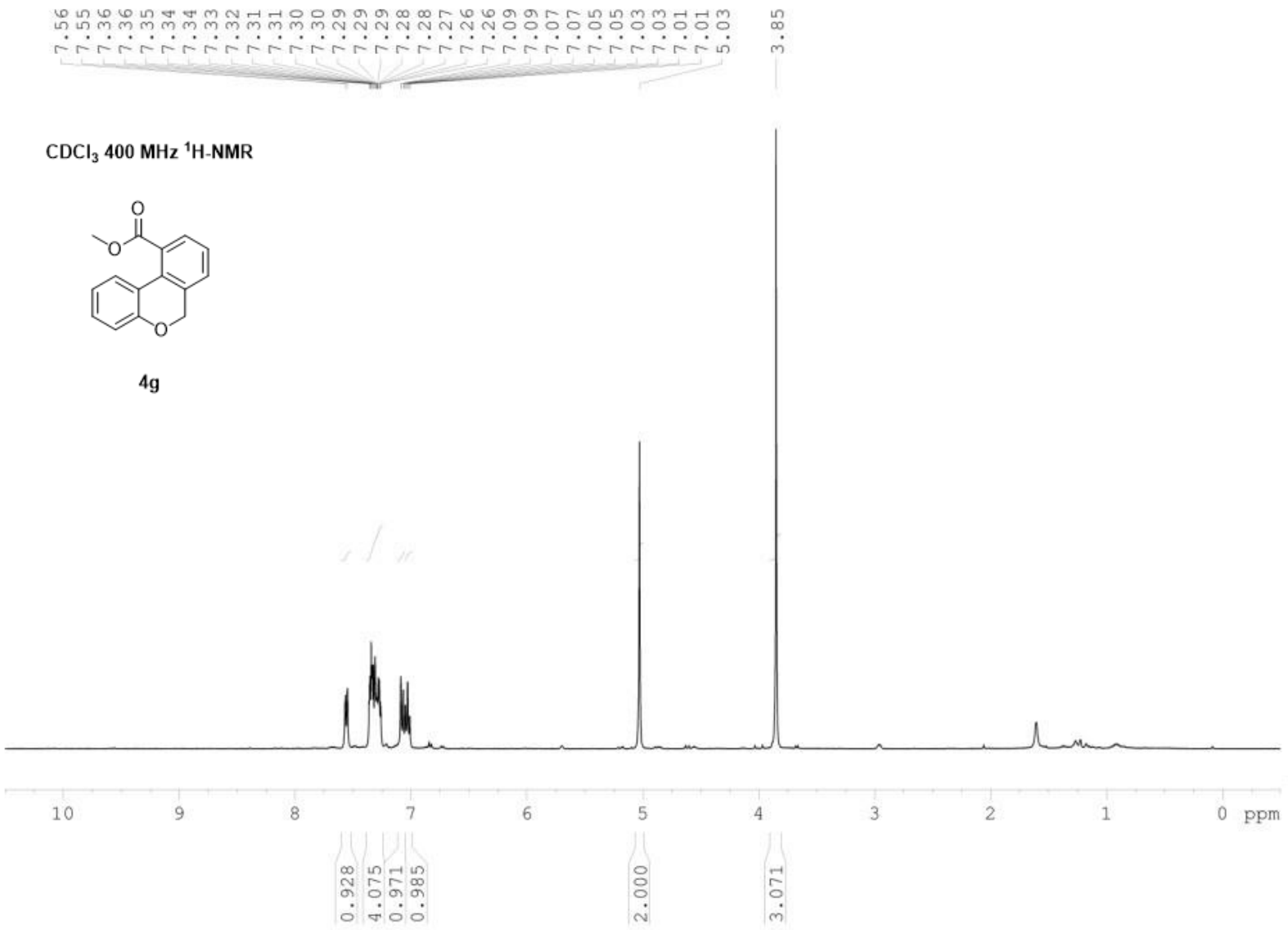
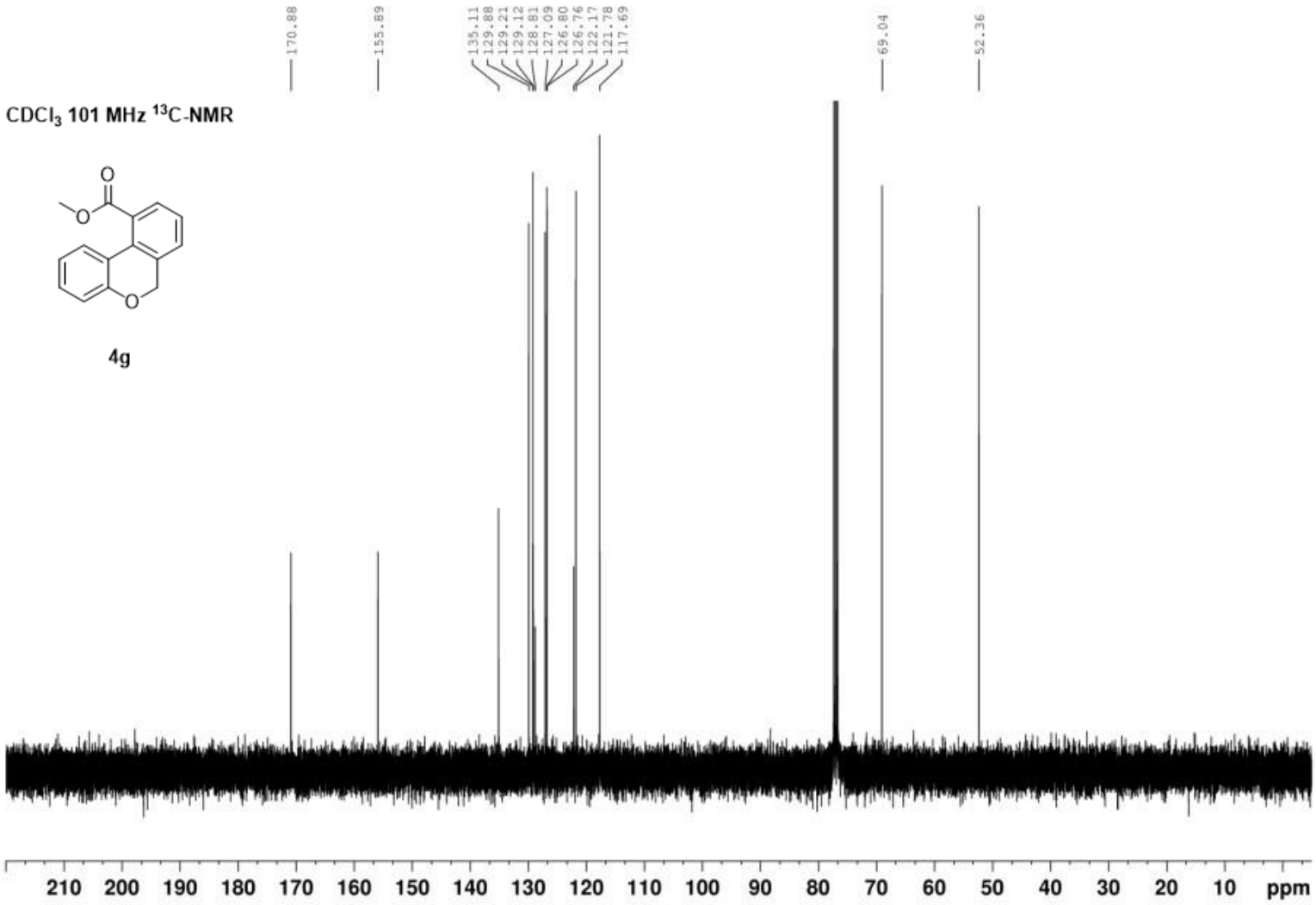
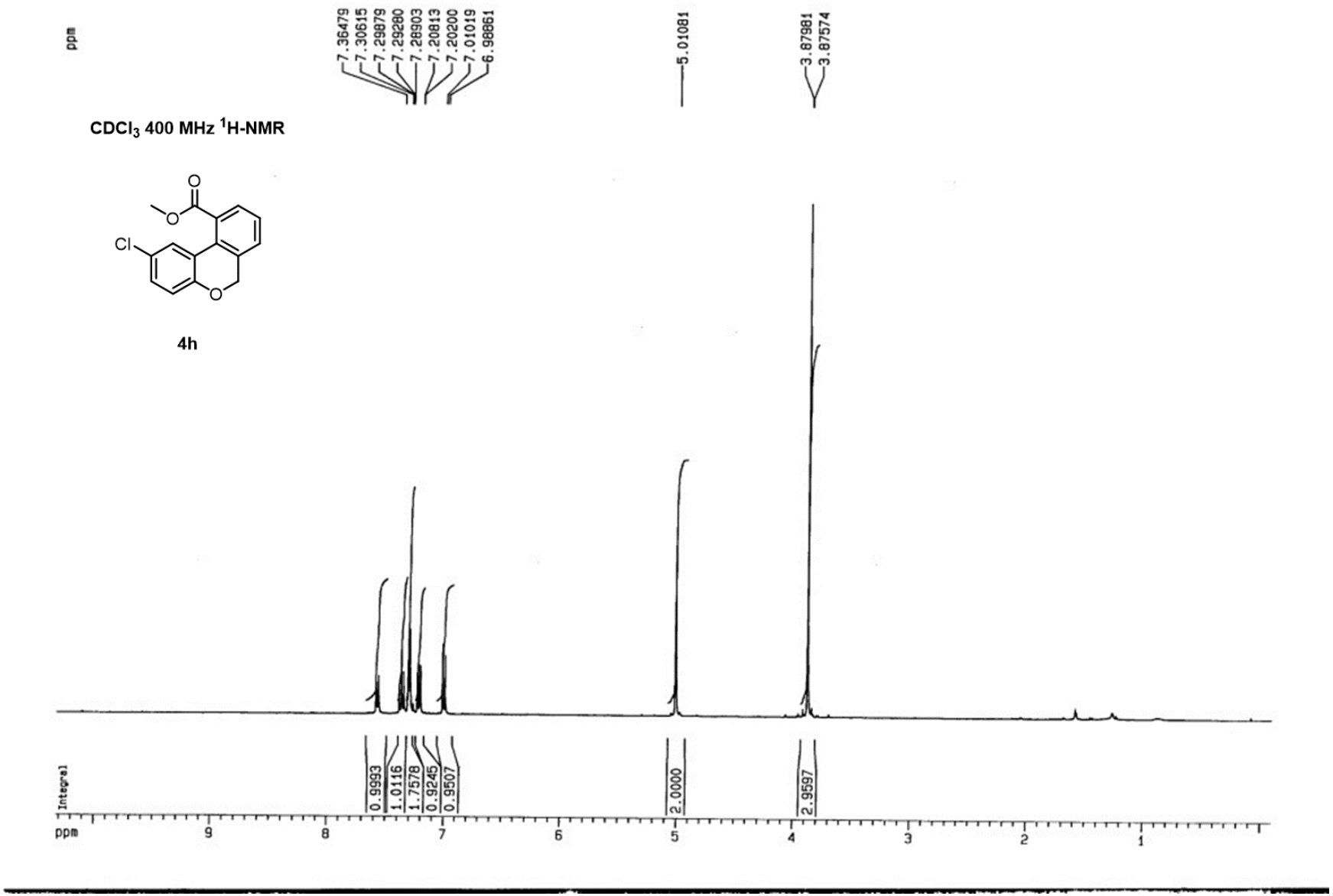
153.63
138.42
129.80
129.31
128.62
127.85
126.93
126.80
126.36
121.75
121.36
118.41
77.99
52.29
33.30
31.36
25.11
22.46
13.90
CDCl3 101 MHz 13C-NMR
O
O
O
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.56
7.55
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.09
7.09
7.07
7.07
7.05
7.05
7.03
7.03
7.01
7.01
5.03
3.85
CDCl3 400 MHz 1H-NMR
O
O
O
4g
10
9
8
7
6
5
4
3
2
1
0 ppm
0.928
4.075
0.971
0.985
2.000
3.071


170.88
155.89
135.11
129.88
129.21
129.12
128.81
127.09
126.80
126.76
122.17
121.78
117.69
69.04
52.36
CDCl3 101 MHz 13C-NMR
O
O
O
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


ppm
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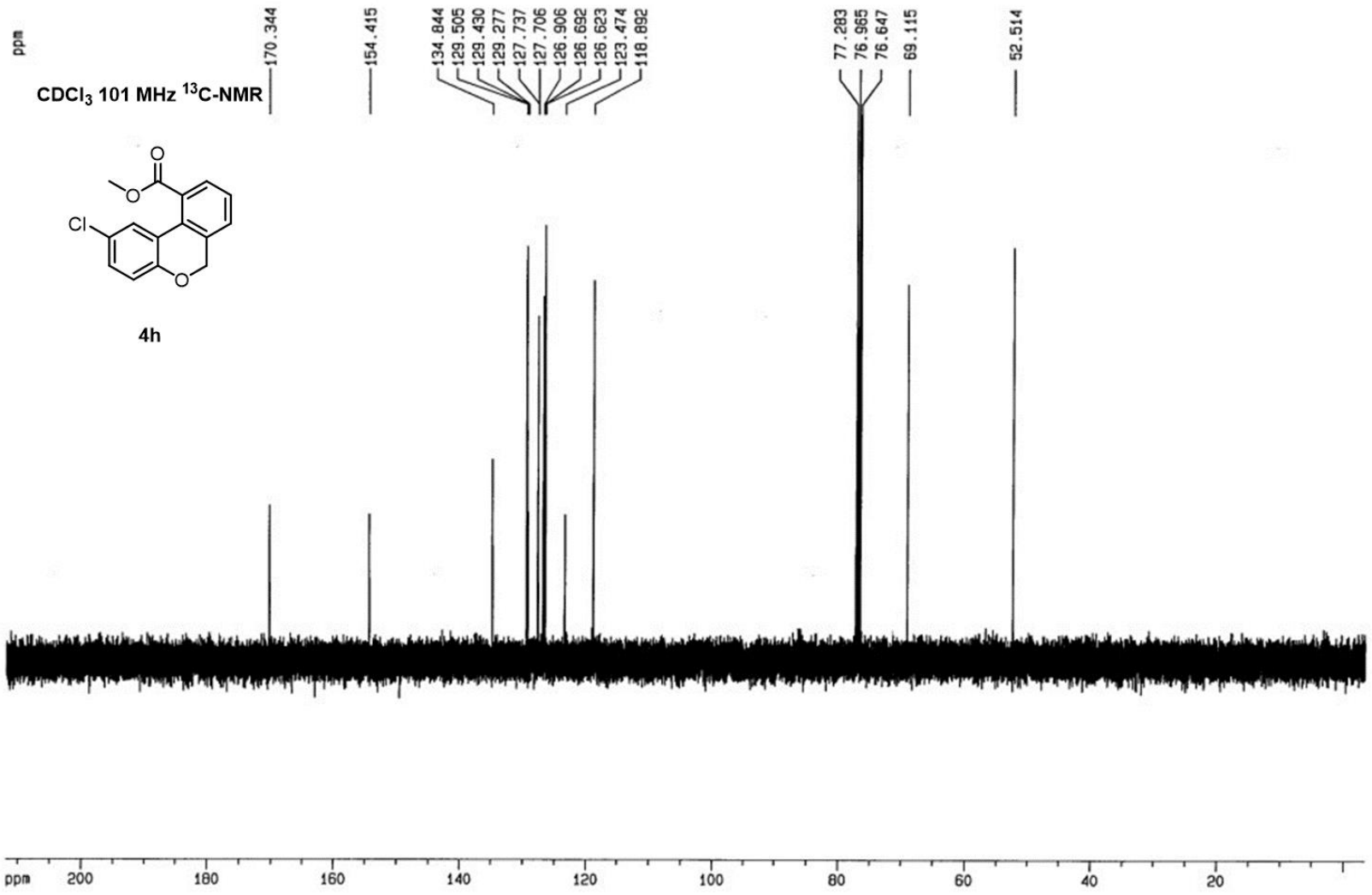
7.29879
7.29280
7.28903
7.20813
7.20200
7.01019
6.98861
5.01081
3.87981
3.87574
CDCl3 400 MHz 1H-NMR
Cl
O
O
O
4h
Integral
0.9993
1.0116
1.7578
0.9245
0.9507
2.0000
2.9597
ppm
9
8
7
6
5
4
3
2
1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134.844
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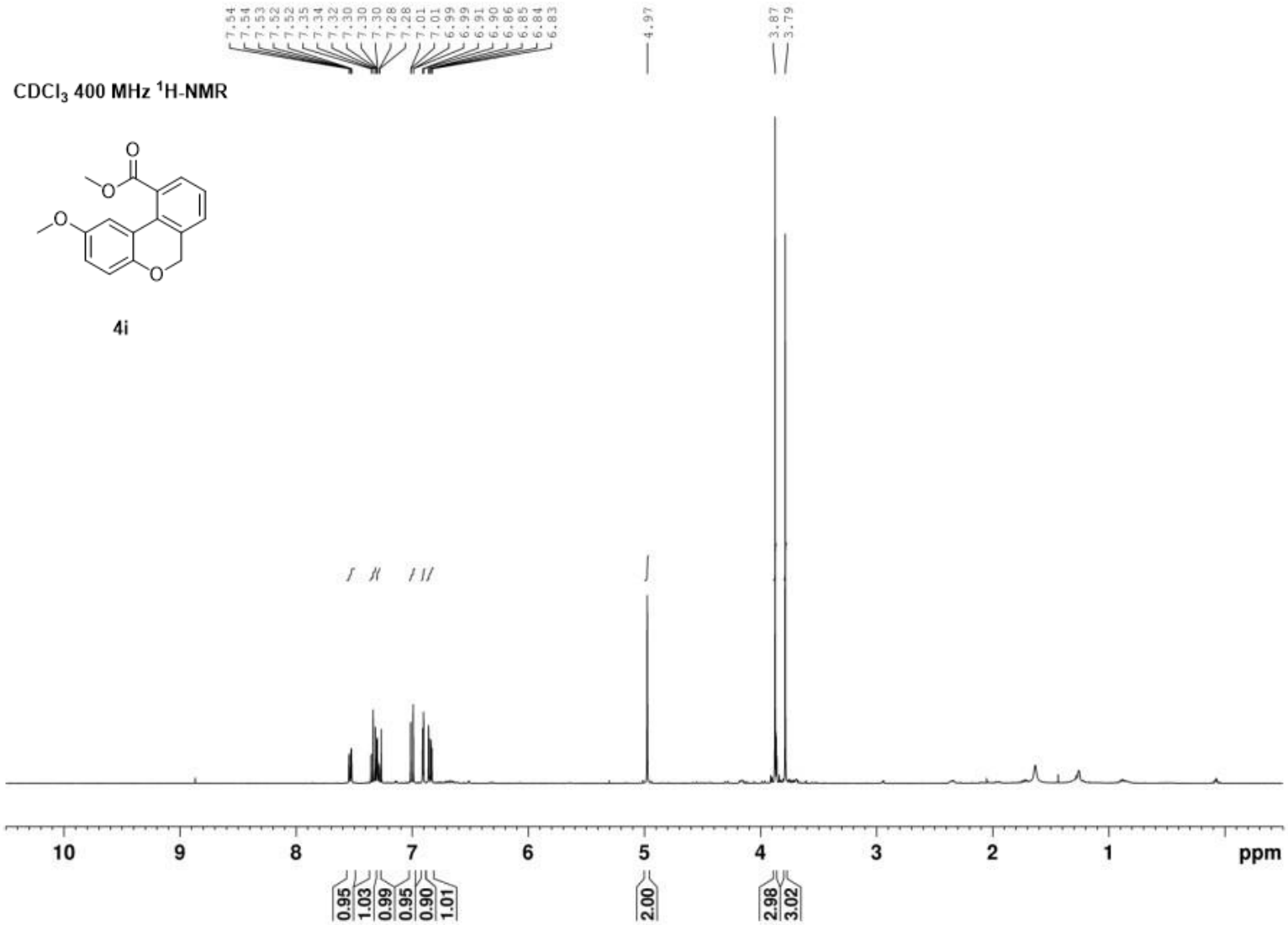
129.430
129.277
127.737
127.706
126.906
126.692
126.623
123.474
118.892
77.283
76.965
76.647
69.115
52.514
CDCl3 101 MHz 13C-NMR
Cl
O
O
O
4h
ppm
200
180
160
140
120
100
80
60
40
20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7.54
7.53
7.52
7.52
7.35
7.34
7.32
7.30
7.30
7.30
7.28
7.01
7.01
6.99
6.99
6.91
6.90
6.86
6.85
6.84
6.83
4.97
3.87
3.79
CDCl3 400 MHz 1H-NMR
O
O
O
O
4i
10
9
8
7
6
5
4
3
2
1
ppm
0.95
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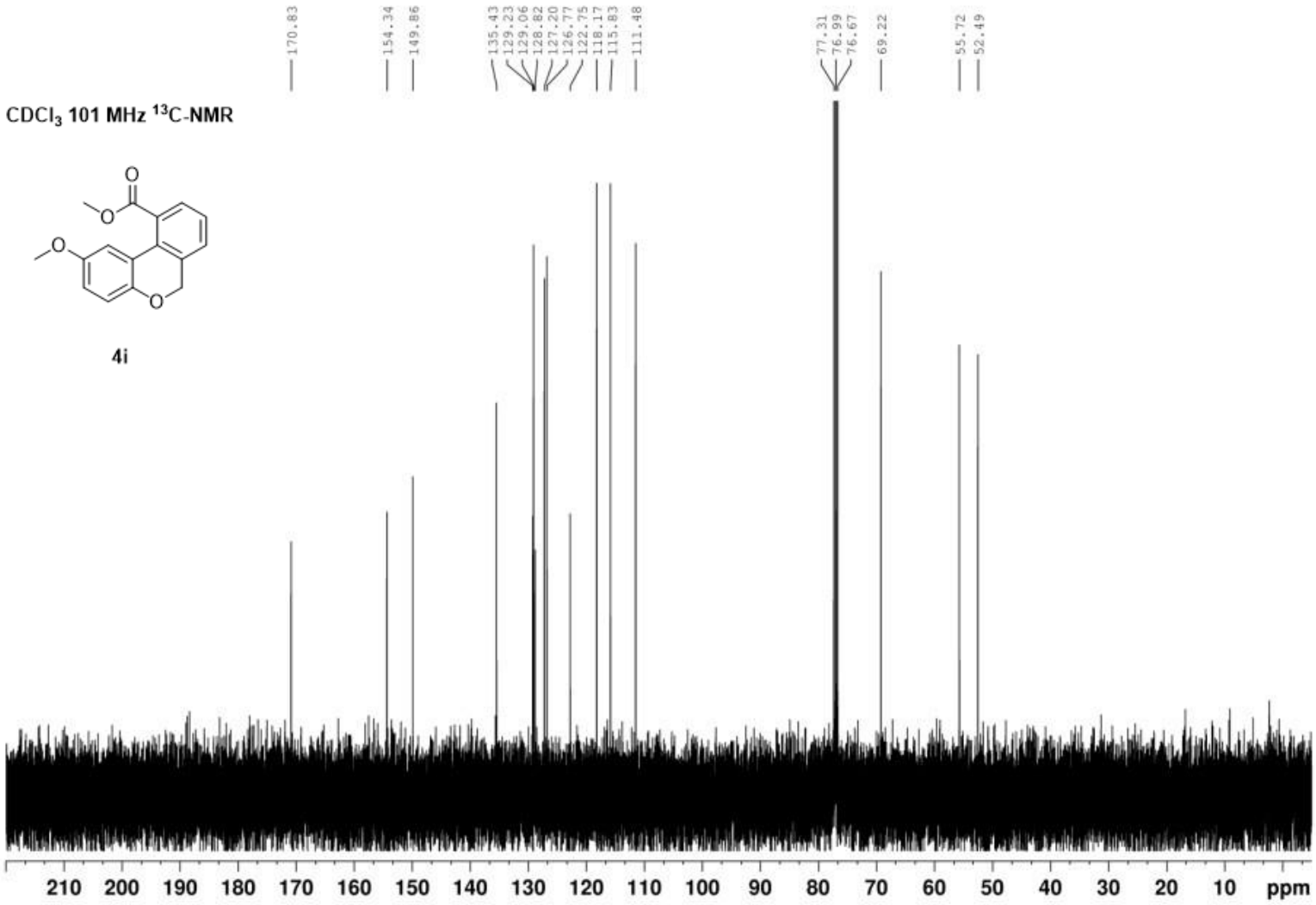
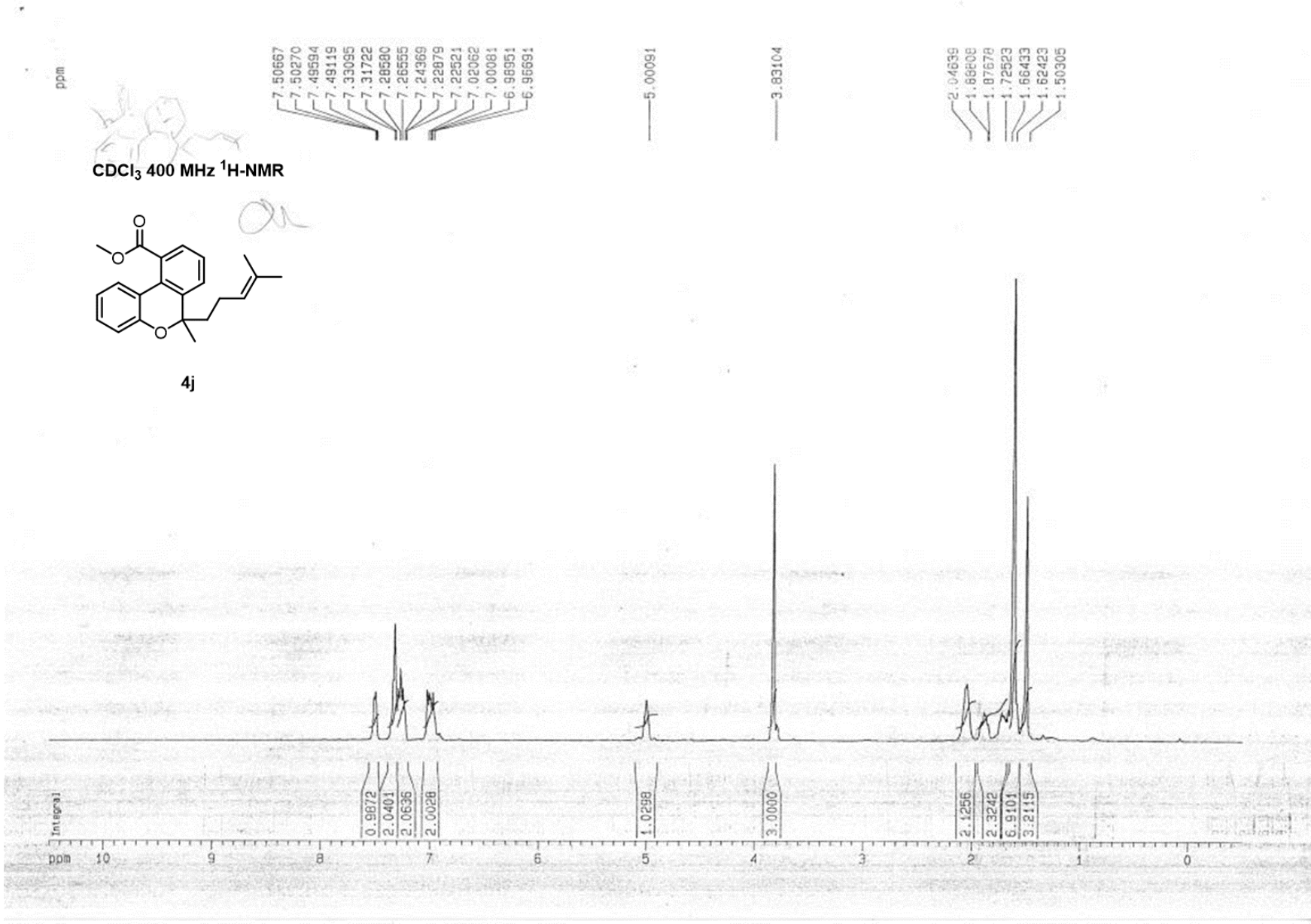
0.99
0.95
0.90
1.01
2.00
2.98
3.02


170.83
154.34
149.86
135.43
129.23
129.06
128.82
127.20
126.77
122.75
118.17
115.83
111.48
77.31
76.99
76.67
69.22
55.72
52.49
CDCl3 101 MHz 13C-NMR
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


ppm
7.50667
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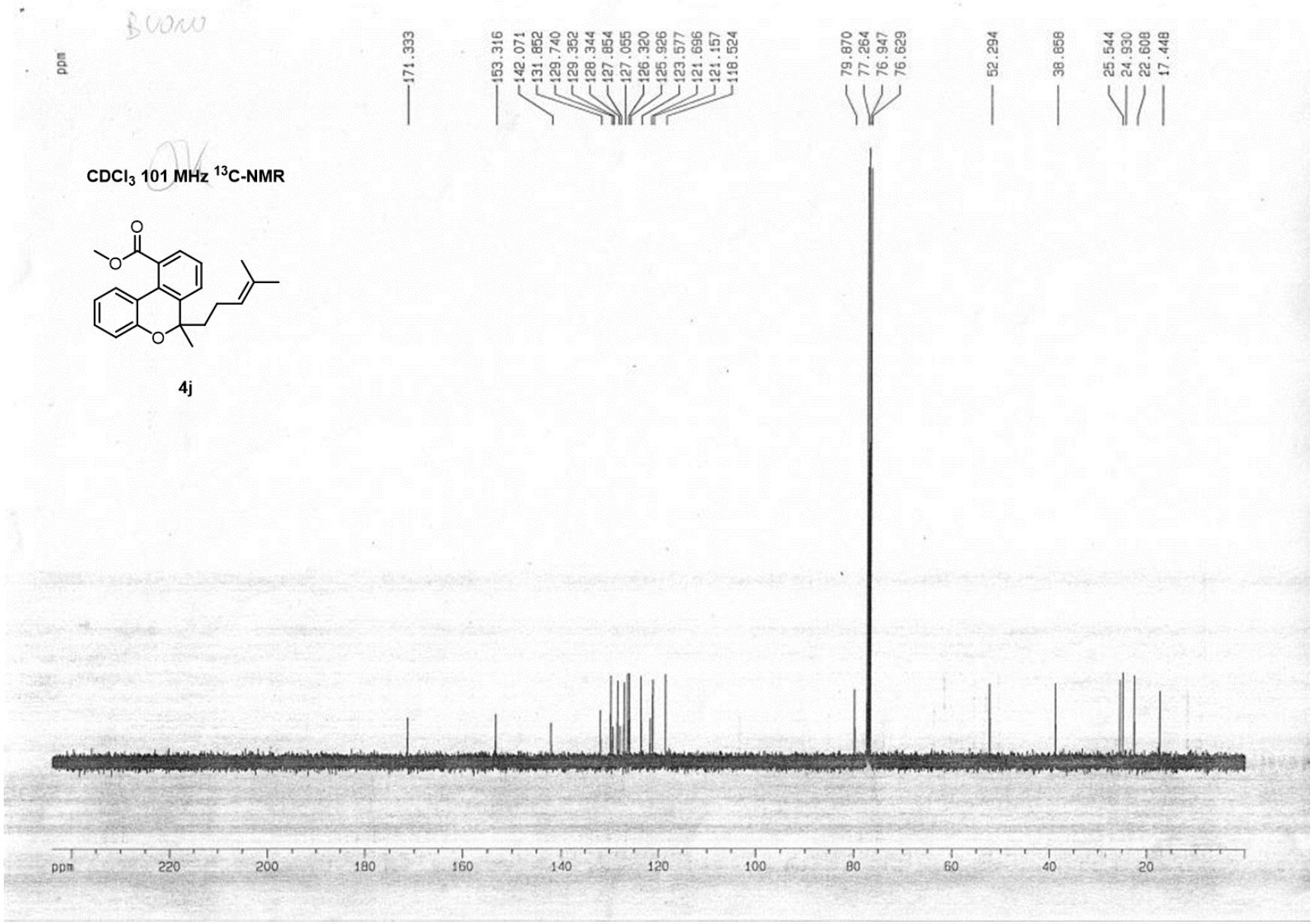
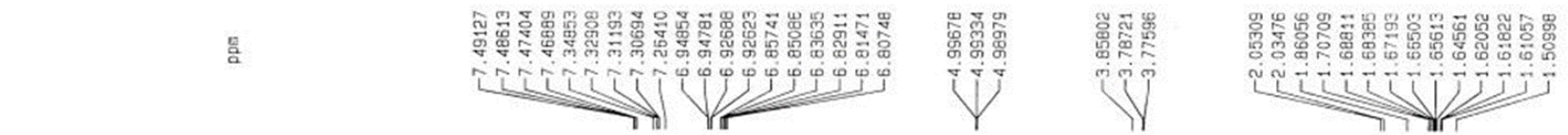
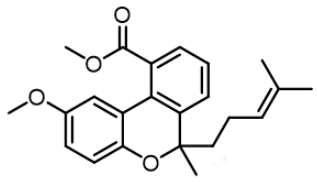
7.49594
7.49119
7.33095
7.31722
7.28580
7.26555
7.24369
7.22879
7.22521
7.02062
7.00081
6.98951
6.96691
5.00091
3.83104
2.04639
1.88808
1.87670
1.72523
1.66433
1.62423
1.50305
CDCl3 400 MHz 1H-NMR
O
O
O
4j
Integral
0.9672
2.0401
2.0636
2.0028
1.0298
3.0000
2.1256
2.3242
6.9101
3.2115
ppm
10
9
8
7
6
5
4
3
2
1
0

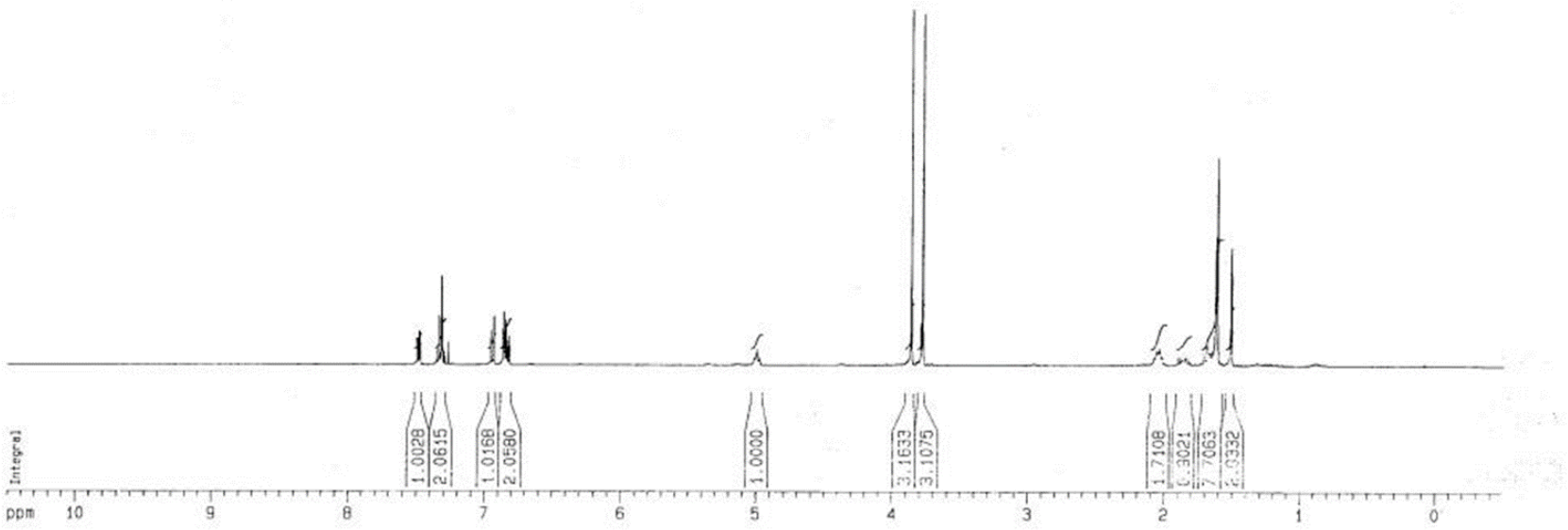

ppm
171.333
153.316
142.071
131.852
129.740
129.352
128.344
127.854
127.055
126.320
125.926
123.577
121.696
121.157
118.524
79.870
77.264
76.947
76.629
52.294
38.656
25.544
24.930
22.608
17.448
CDCl3 101 MHz 13C-NMR
4j
ppm
220
200
180
160
140
120
100
80
60
40
20

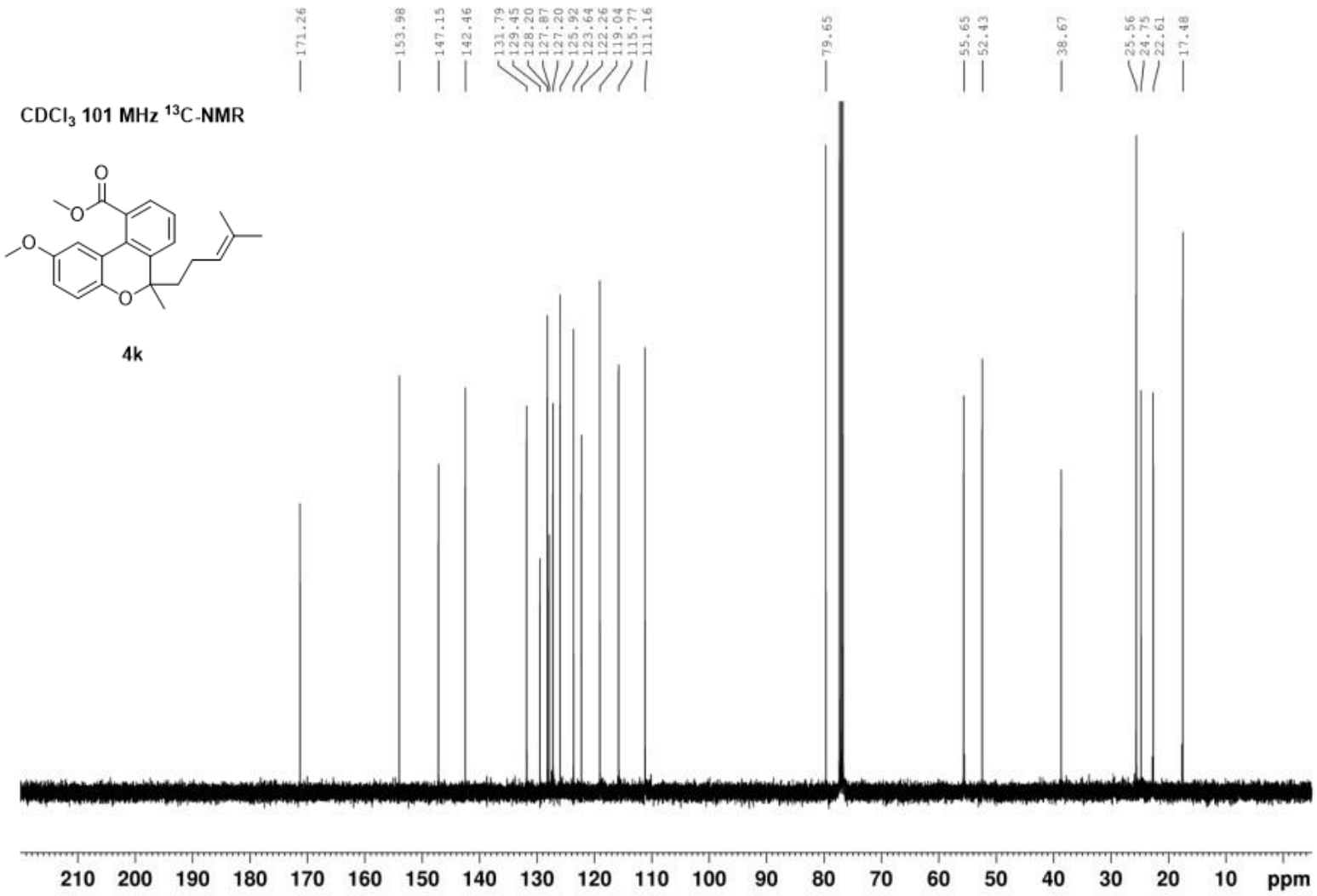


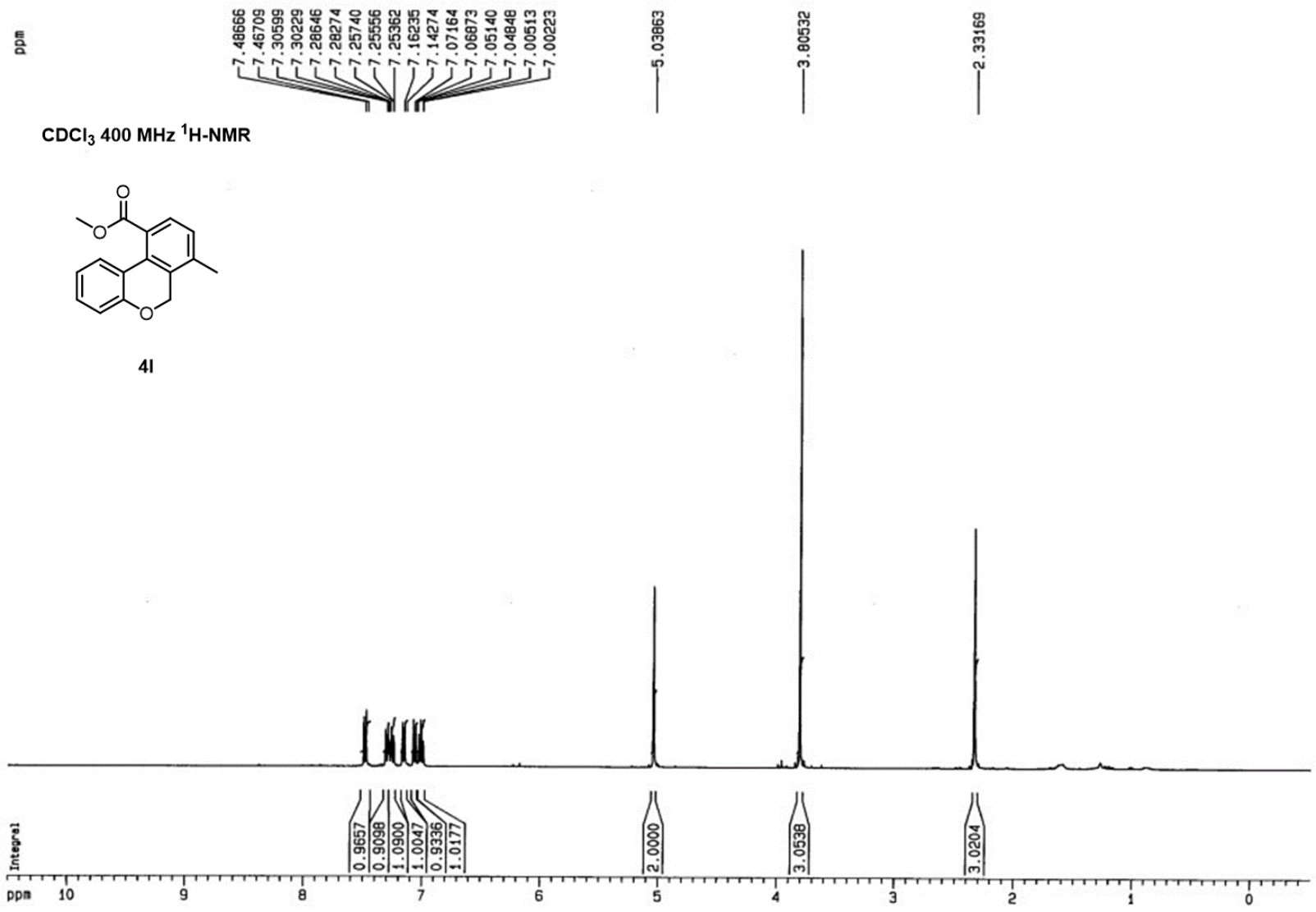
$CDCl_3$ 400 MHz ^{1}H-NMR

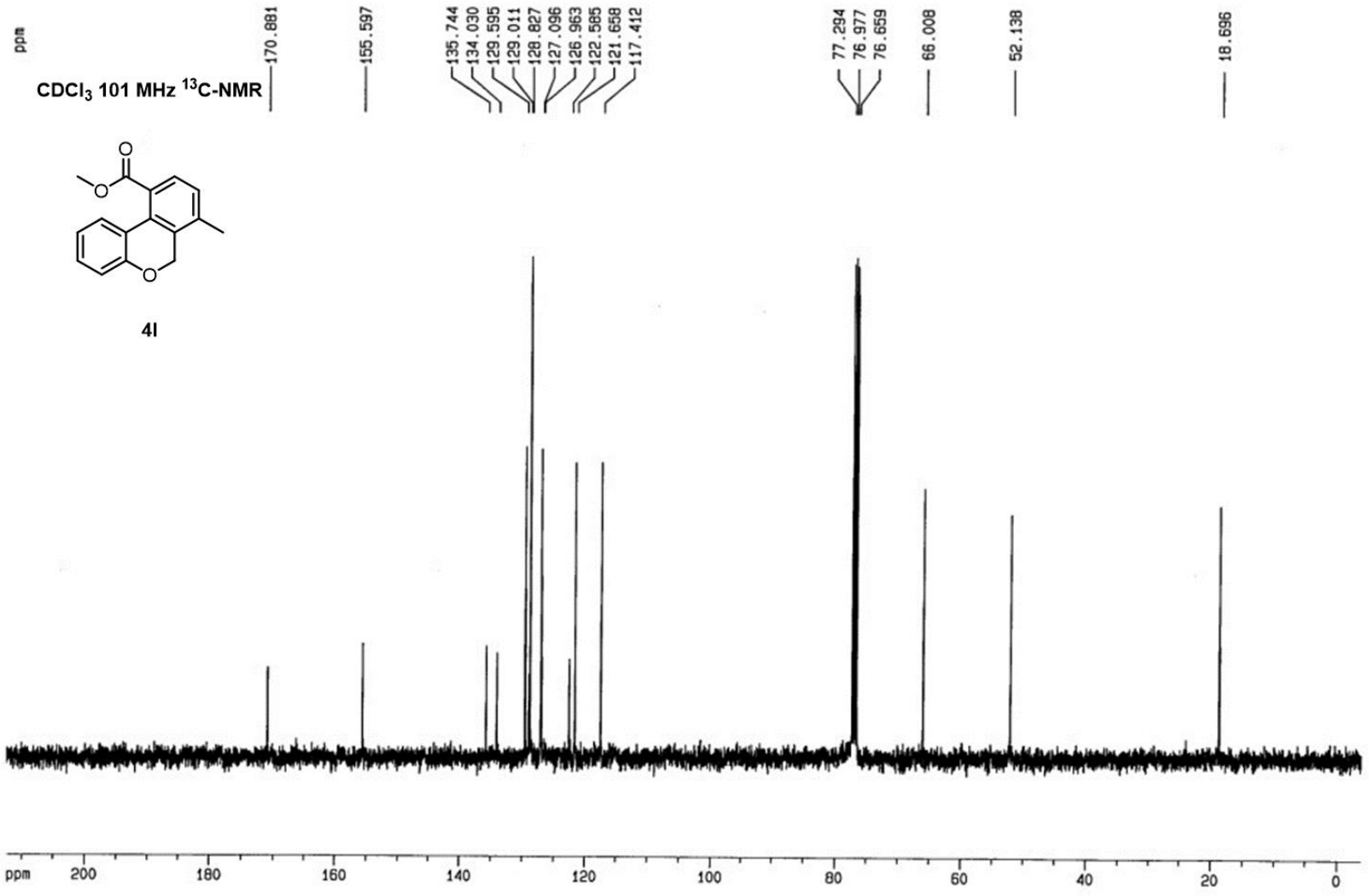


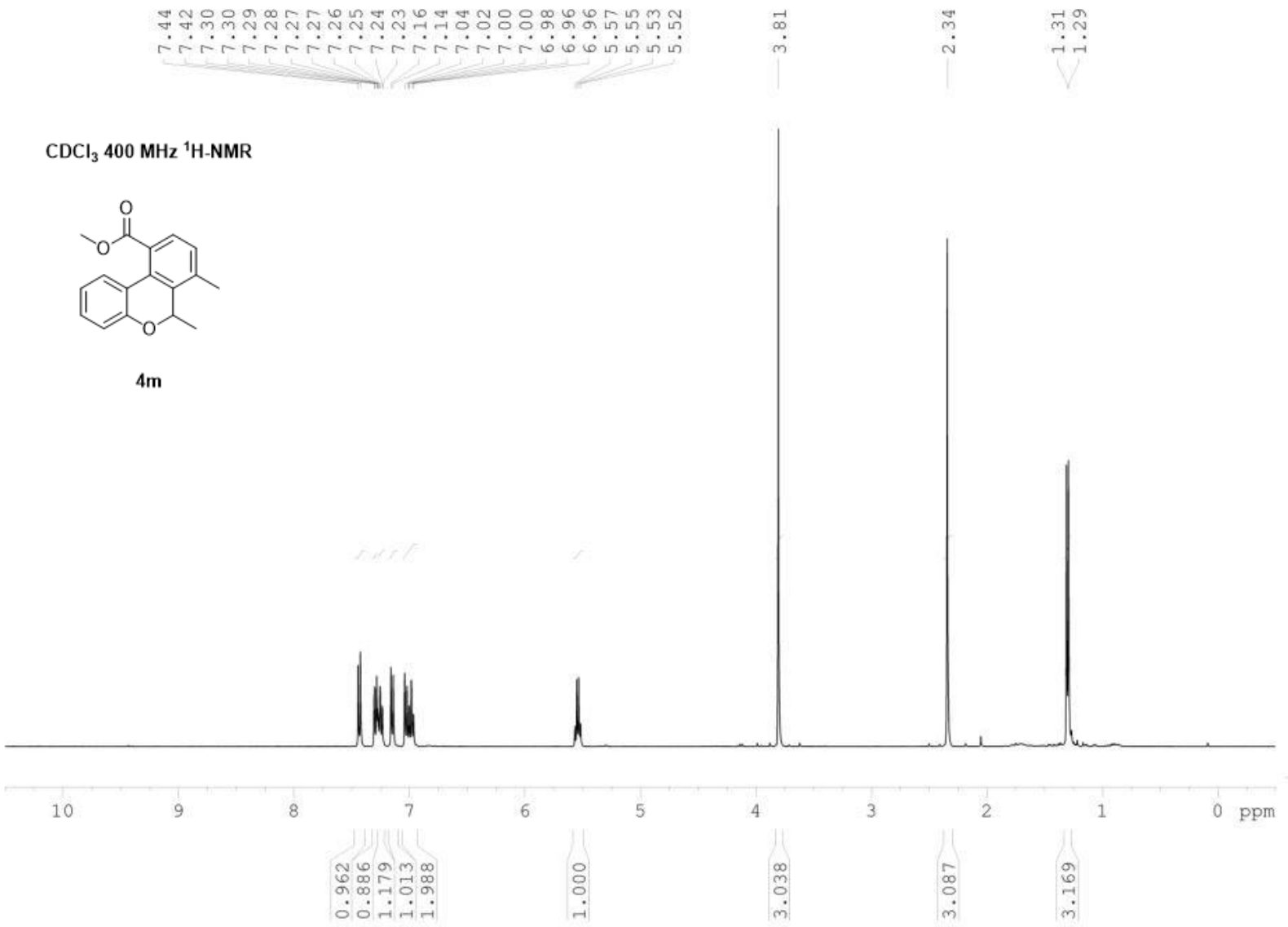
4k

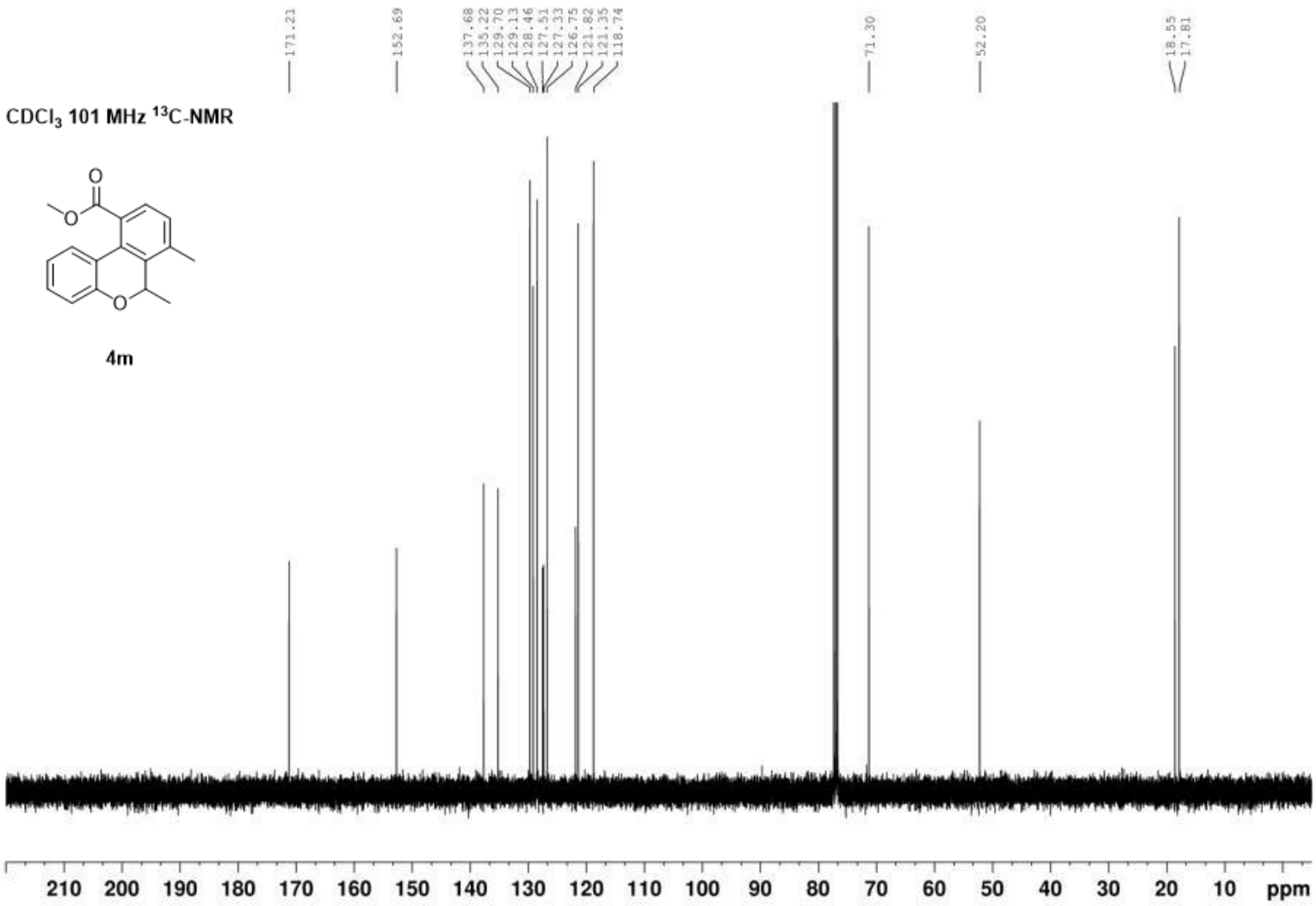


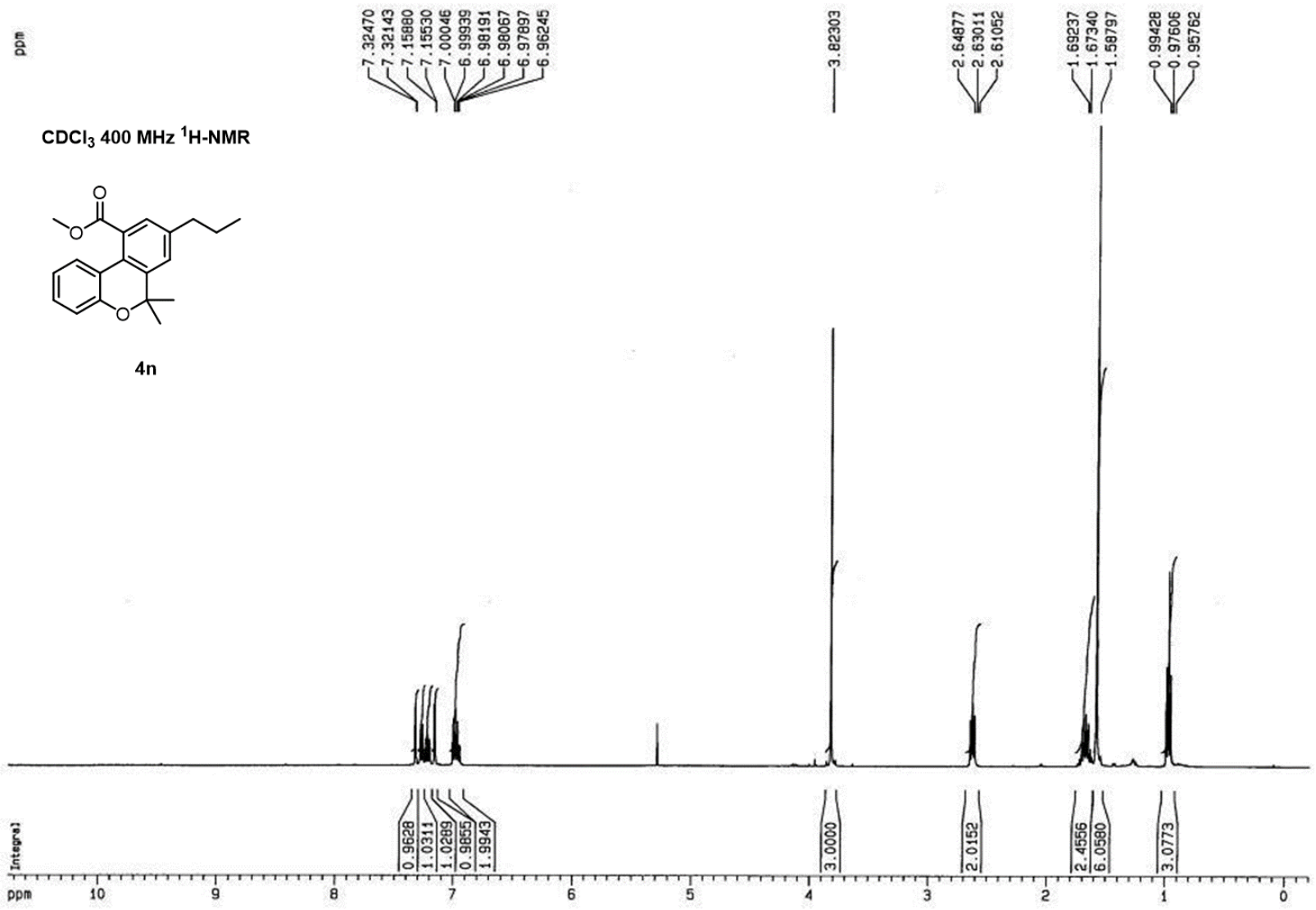

171.26
153.98
147.15
142.46
131.79
129.45
128.20
127.87
127.20
125.92
123.64
122.26
119.04
115.77
111.16
79.65
55.65
52.43
38.67
25.56
24.75
22.61
17.48
CDCl3 101 MHz 13C-NMR
4k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

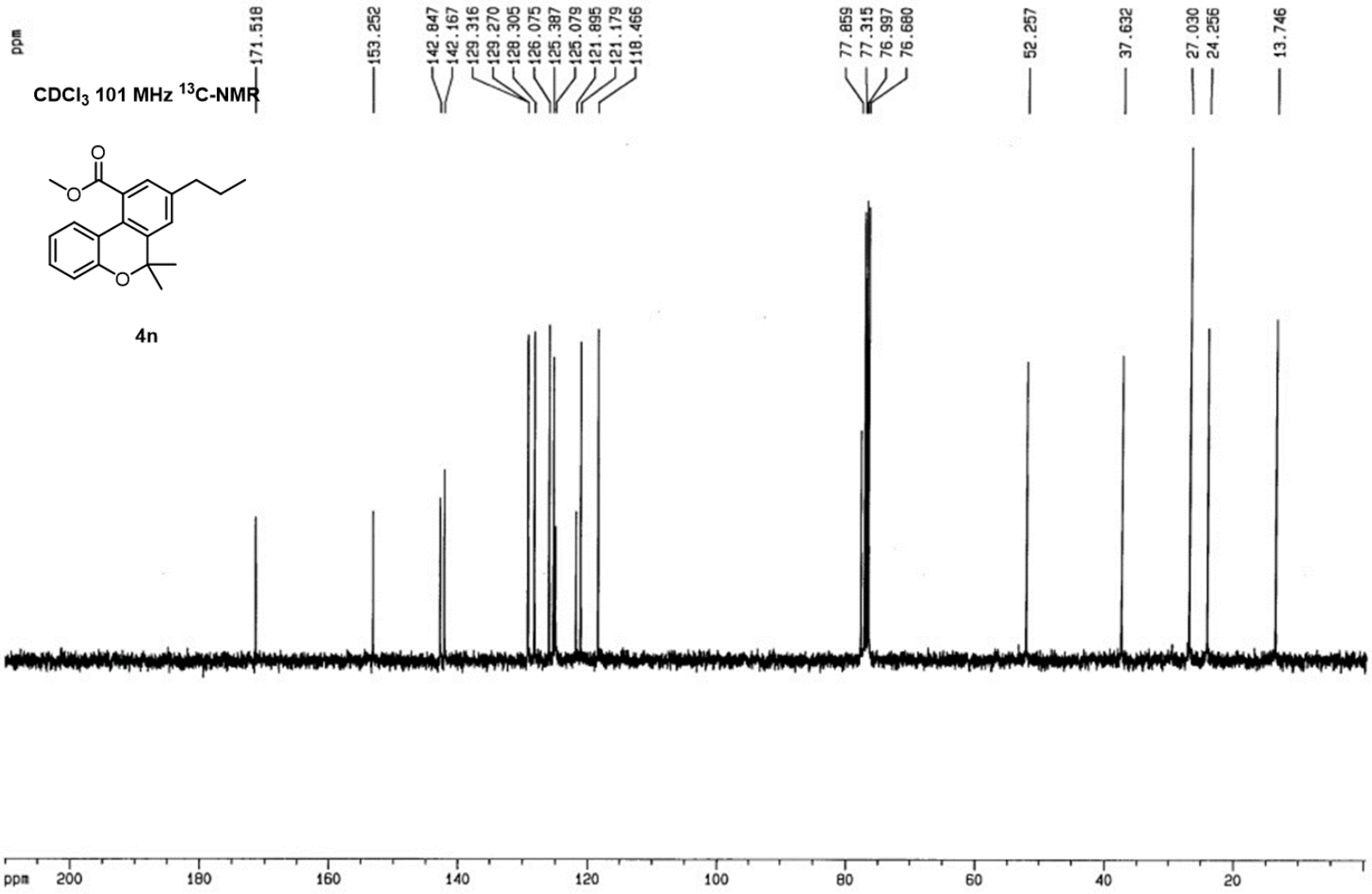

ppm
7.48666
7.46709
7.30599
7.30229
7.28646
7.28274
7.25740
7.25556
7.25362
7.16235
7.14274
7.07164
7.06873
7.05140
7.04848
7.00513
7.00223
5.03863
3.80532
2.33169
CDCl3 400 MHz 1H-NMR
4l
Integral
0.9657
0.9098
1.0900
1.0047
0.9336
1.0177
2.0000
3.0538
3.0204
ppm
10
9
8
7
6
5
4
3
2
1
0

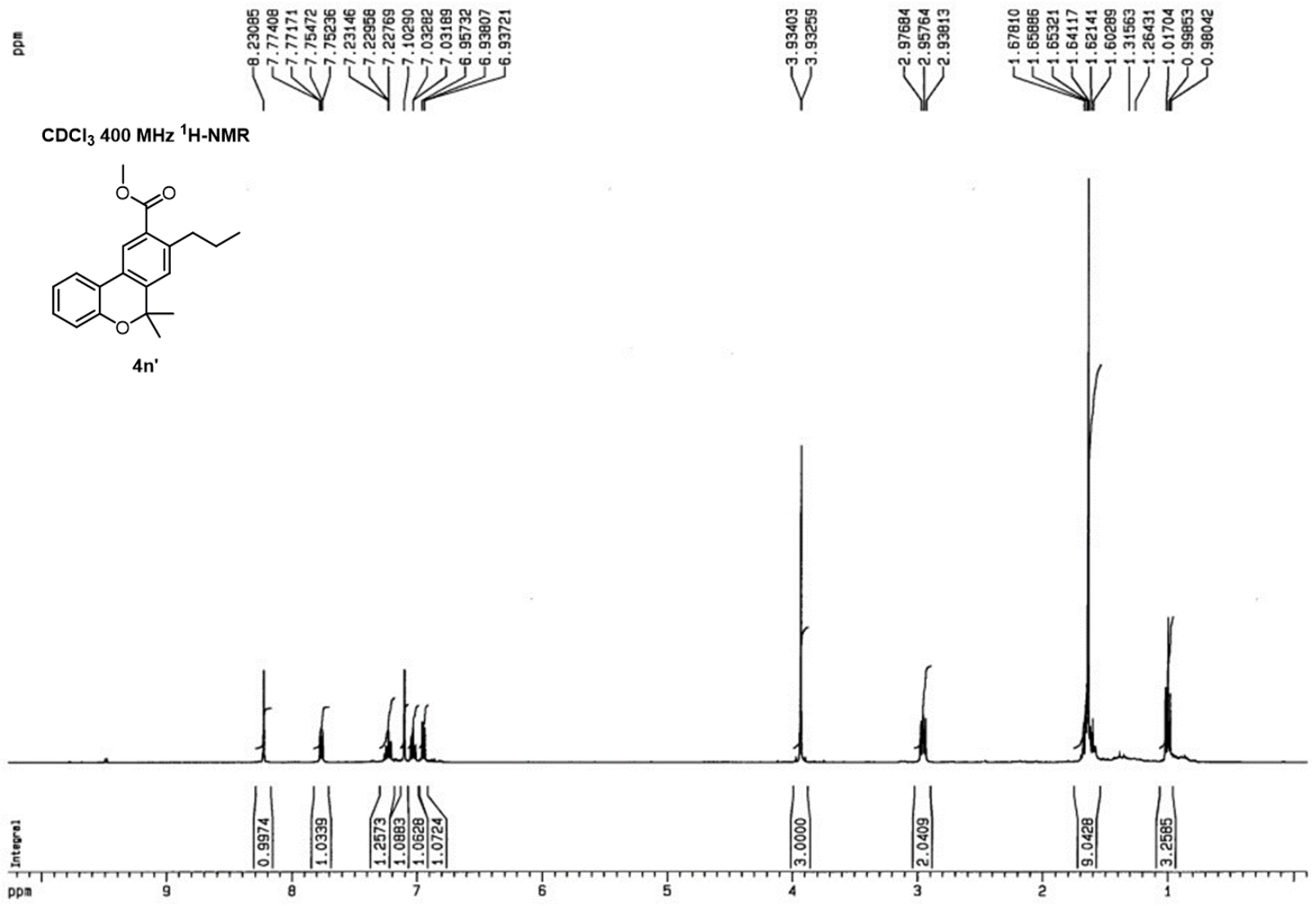

ppm
CDCl3 101 MHz 13C-NMR
170.881
155.597
135.744
134.030
129.595
129.011
128.827
127.096
126.963
122.585
121.658
117.412
77.294
76.977
76.659
66.008
52.138
18.696
4l
ppm
200
180
160
140
120
100
80
60
40
20
0

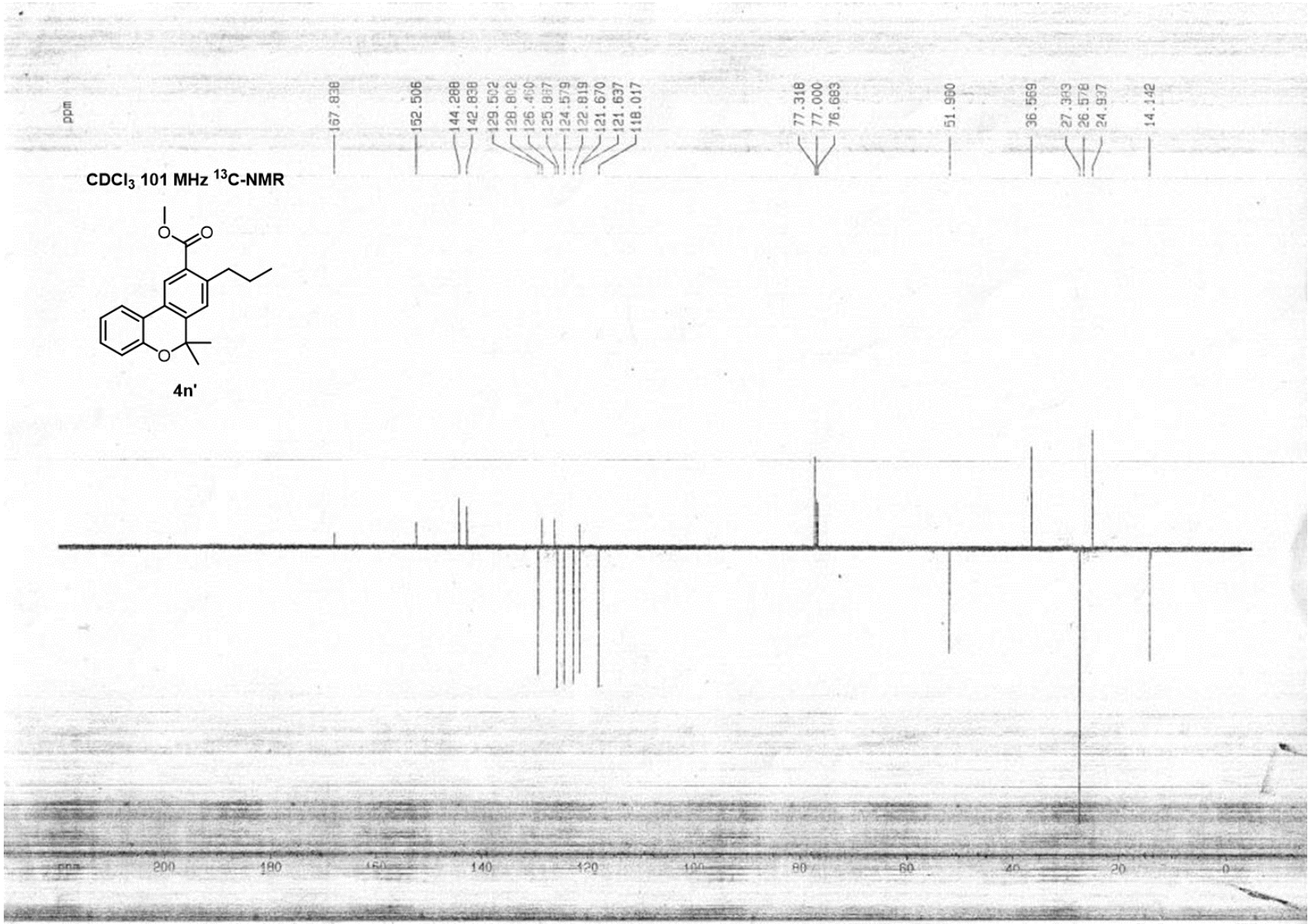

7.44
7.42
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.16
7.14
7.04
7.02
7.00
7.00
6.98
6.96
6.96
5.57
5.55
5.53
5.52
3.81
2.34
1.31
1.29
CDCl3 400 MHz 1H-NMR
4m
10
9
8
7
6
5
4
3
2
1
0 ppm
0.962
0.886
1.179
1.013
1.988
1.000
3.038
3.087
3.169

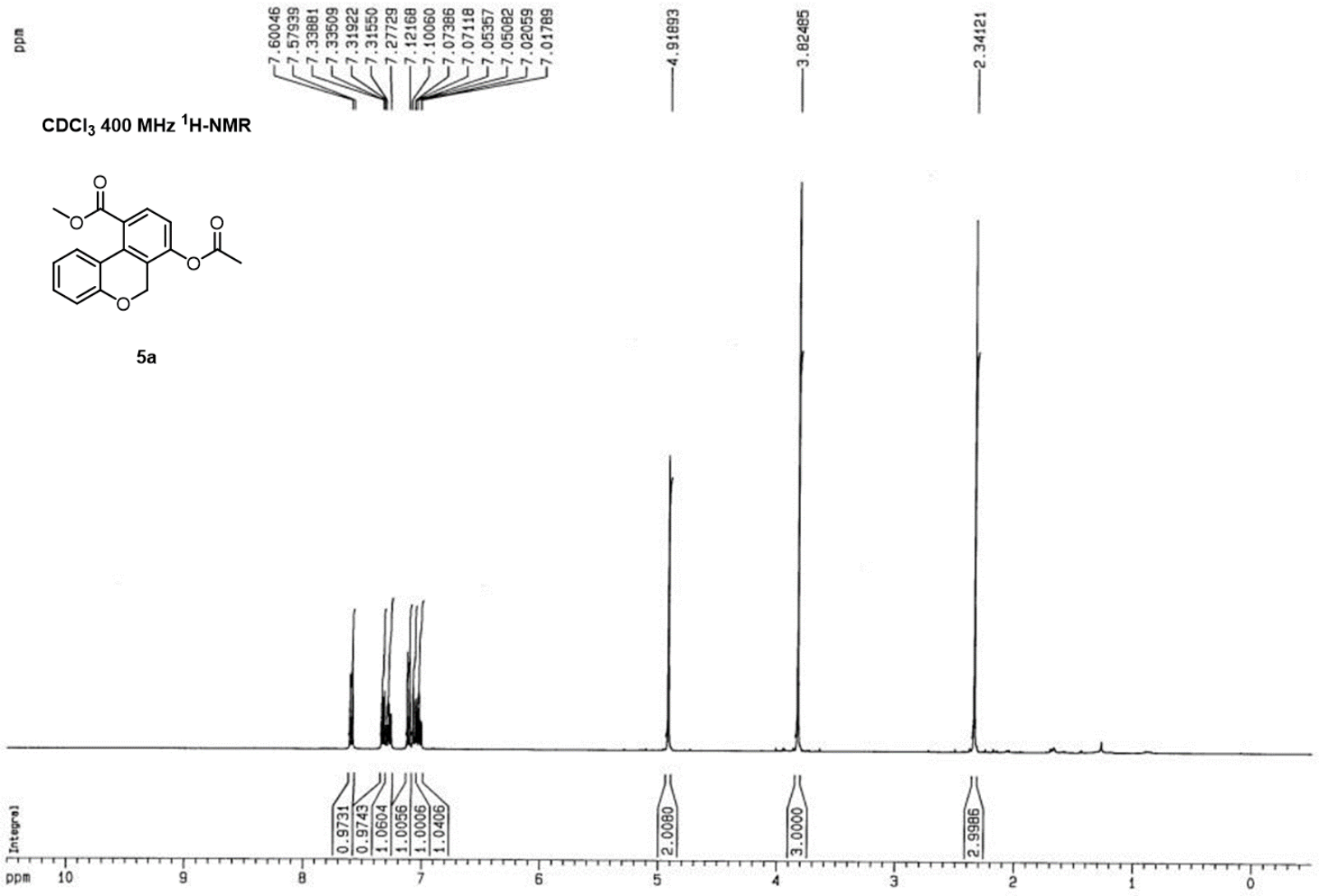

171.21
152.69
137.68
135.22
129.70
129.13
128.46
127.51
127.33
126.75
121.82
121.35
118.74
71.30
52.20
18.55
17.81
CDCl3 101 MHz 13C-NMR
O
O
O
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

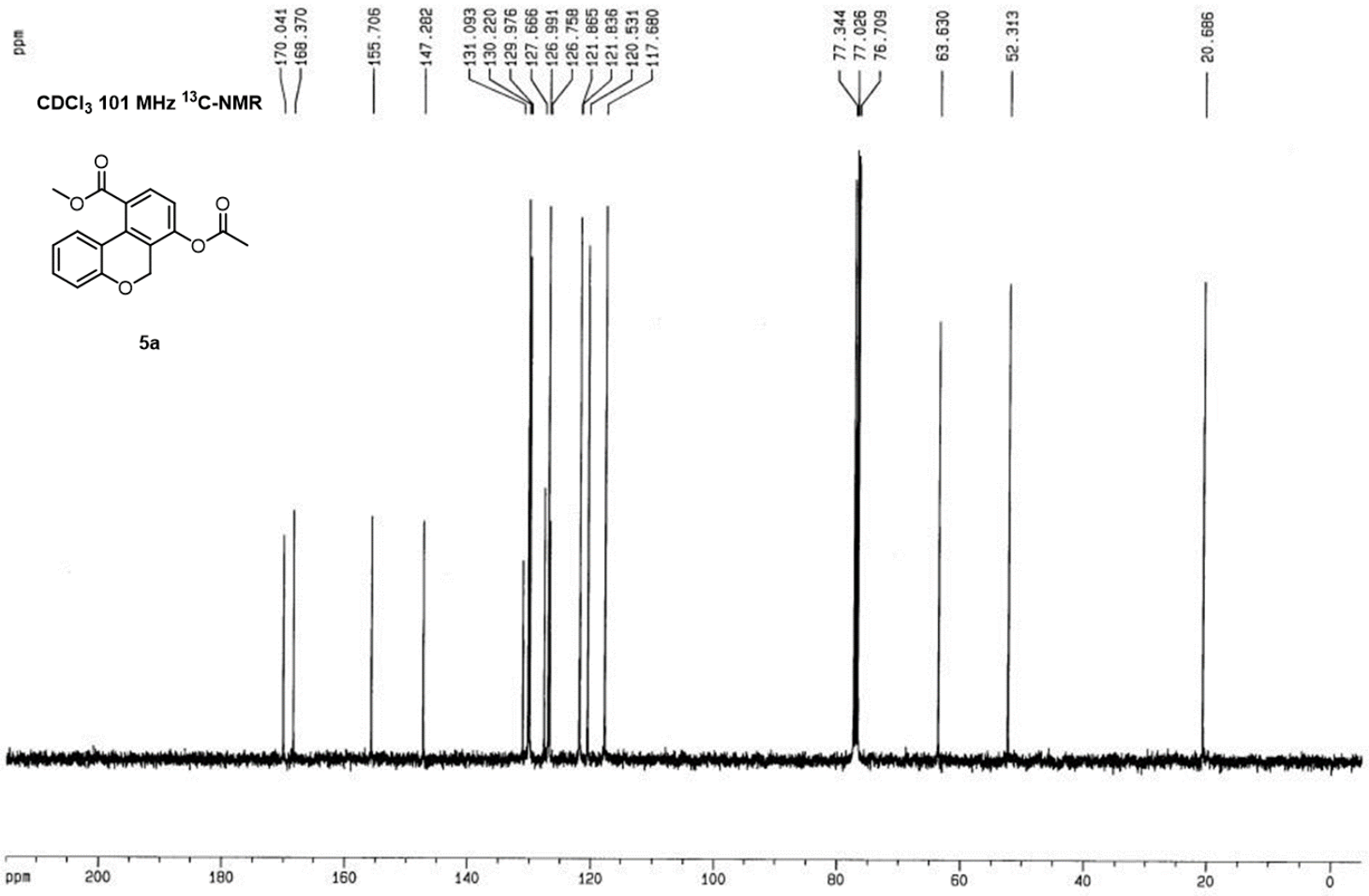

CDCl3 400 MHz 1H-NMR
4n
ppm
7.32470
7.32143
7.15880
7.15530
7.00046
6.99939
6.98191
6.98067
6.97897
6.96245
3.82303
2.64877
2.63011
2.61052
1.69237
1.67340
1.58797
0.99428
0.97606
0.95762
Integral
0.9628
1.0311
1.0289
0.9855
1.9943
3.0000
2.0152
2.4556
6.0580
3.0773
ppm
10
9
8
7
6
5
4
3
2
1
0

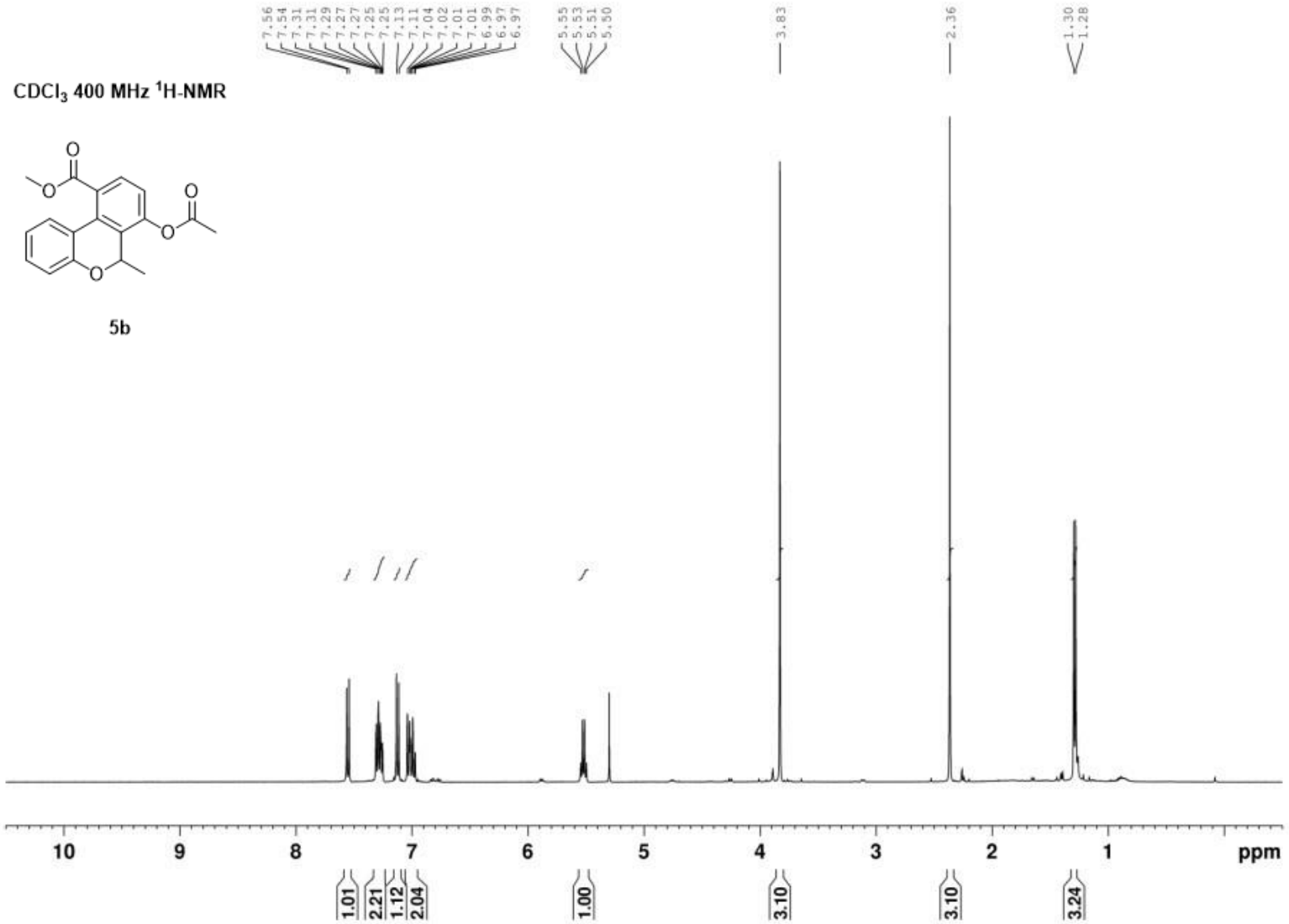

ppm
171.518
153.252
142.847
142.167
129.316
129.270
128.305
126.075
125.387
125.079
121.895
121.179
118.466
77.859
77.315
76.997
76.680
52.257
37.632
27.030
24.256
13.746
CDCl3 101 MHz 13C-NMR
4n
ppm 200 180 160 140 120 100 80 60 40 20

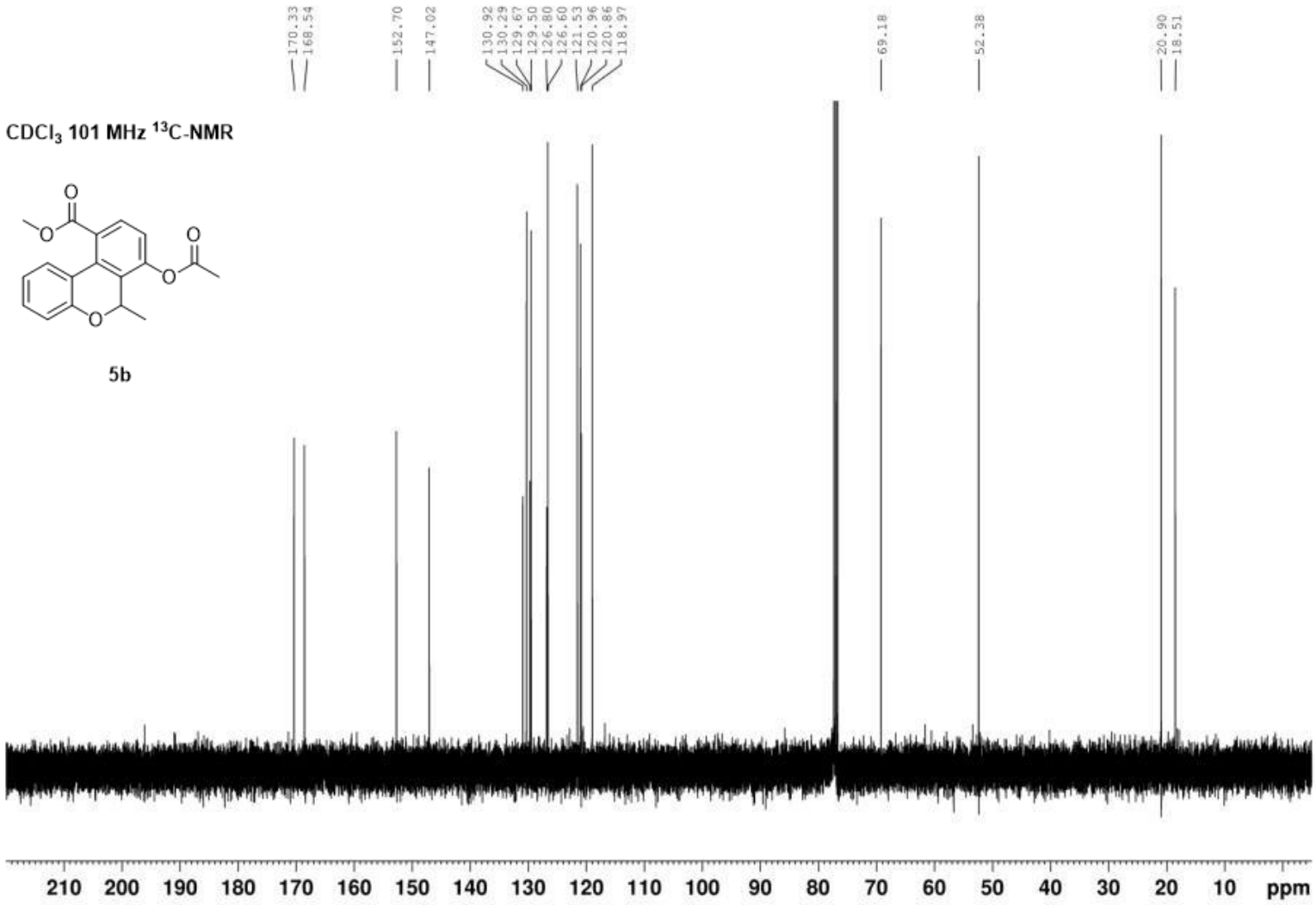

ppm
8.23085
7.77408
7.77171
7.75472
7.75236
7.23146
7.22958
7.22769
7.10290
7.03282
7.03189
6.95732
6.93807
6.93721
3.93403
3.93259
2.97684
2.95764
2.93813
1.67810
1.65886
1.65321
1.64117
1.62141
1.60289
1.31563
1.26431
1.01704
0.99853
0.98042
CDCl3 400 MHz 1H-NMR
4n'
Integral
0.9974
1.0339
1.2573
1.0883
1.0628
1.0724
3.0000
2.0409
9.0428
3.2585
ppm
9
8
7
6
5
4
3
2
1

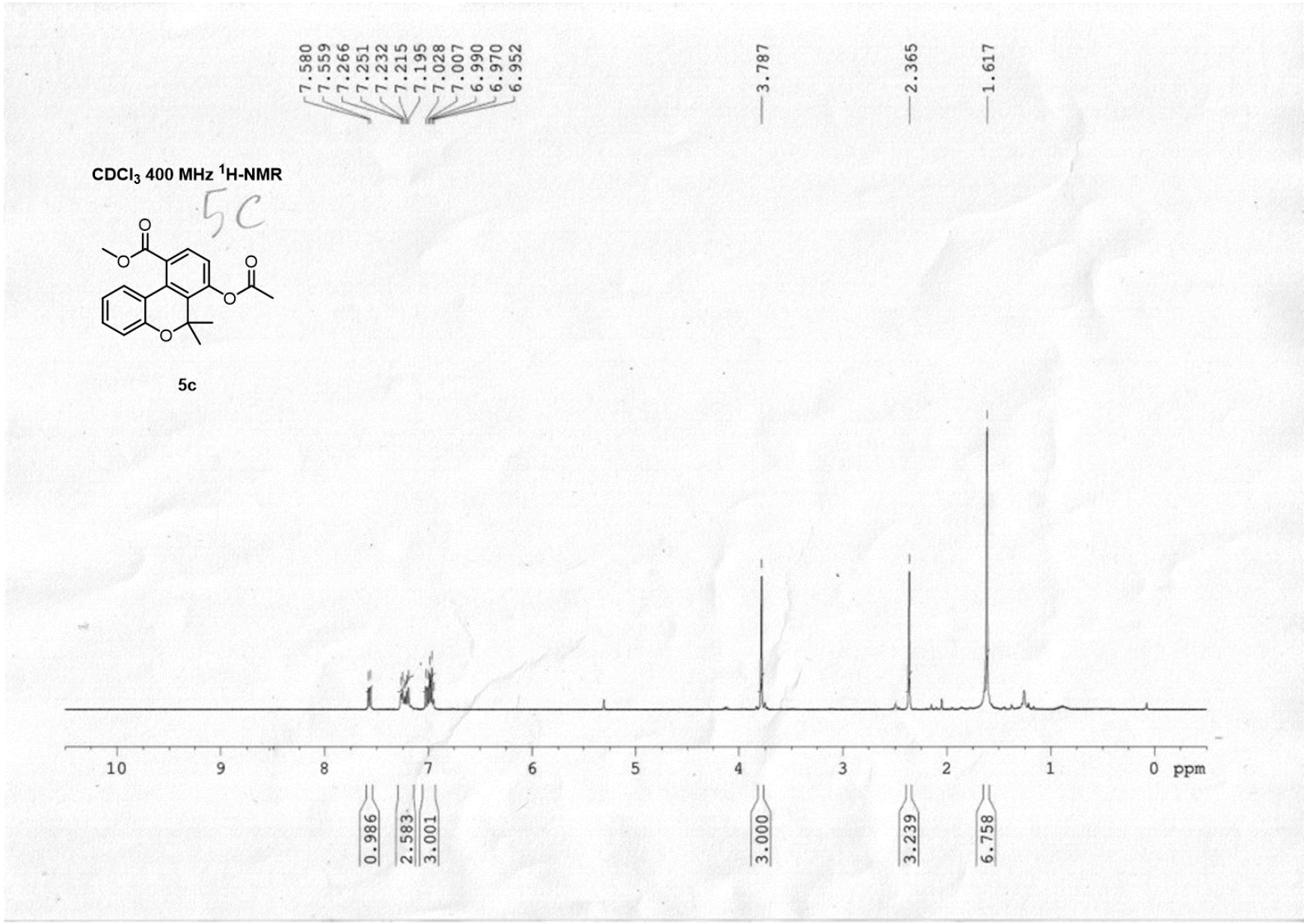

ppm
167.838
152.506
144.288
142.838
129.502
128.802
126.460
125.887
124.579
122.819
121.670
121.637
118.017
77.318
77.000
76.683
51.960
36.569
27.393
26.578
24.937
14.142
CDCl3 101 MHz 13C-NMR
4n'
ppm
200
180
160
140
120
100
80
60
40
20
0

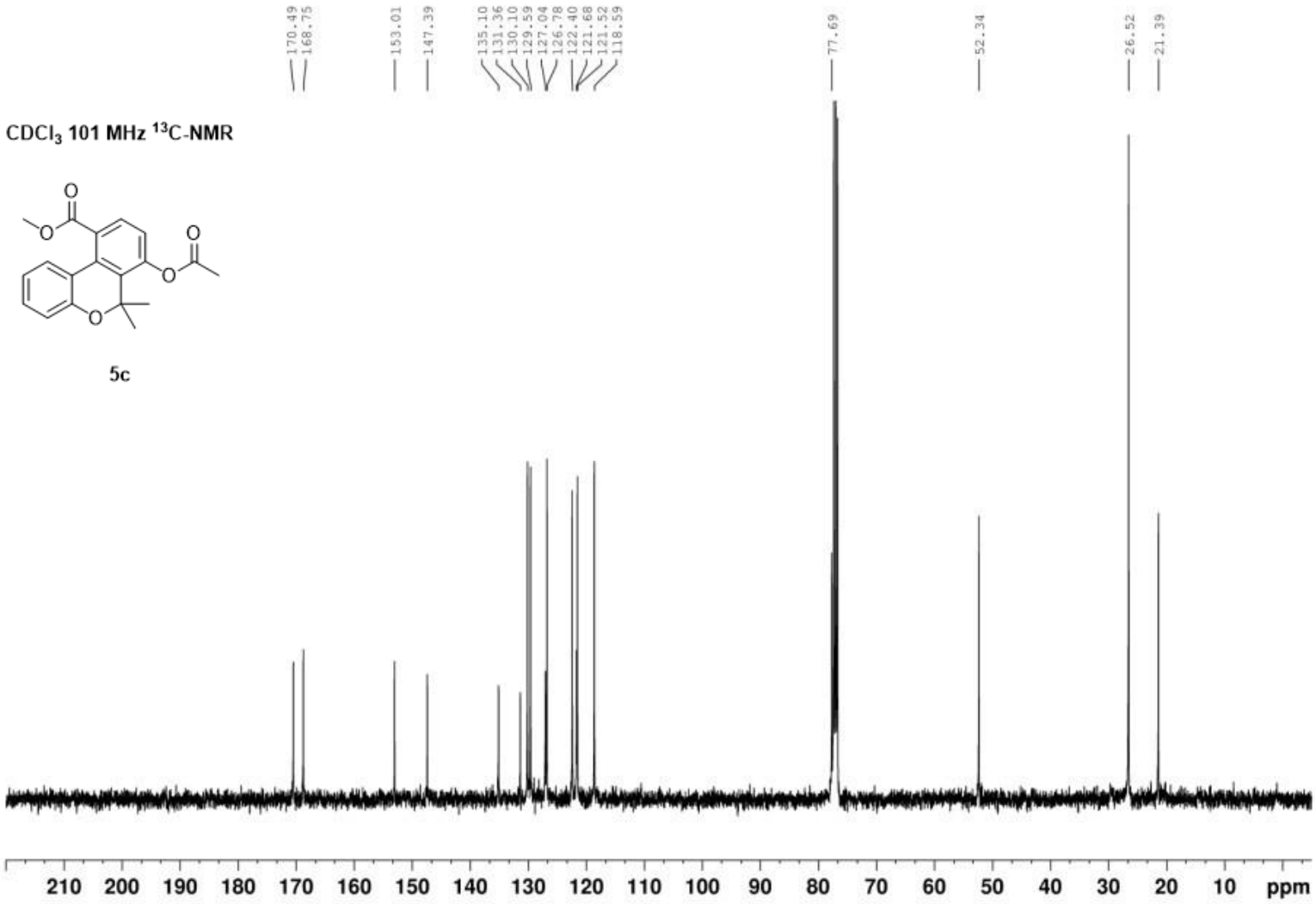

ppm
7.60046
7.57939
7.33881
7.33509
7.31922
7.31550
7.27729
7.12168
7.10060
7.07386
7.07118
7.05357
7.05082
7.02059
7.01769
4.91893
3.82485
2.34121
CDCl3 400 MHz 1H-NMR
5a
Integral
0.9731
0.9743
1.0604
1.0056
1.0006
1.0406
2.0080
3.0000
2.9986
ppm
10
9
8
7
6
5
4
3
2
1
0

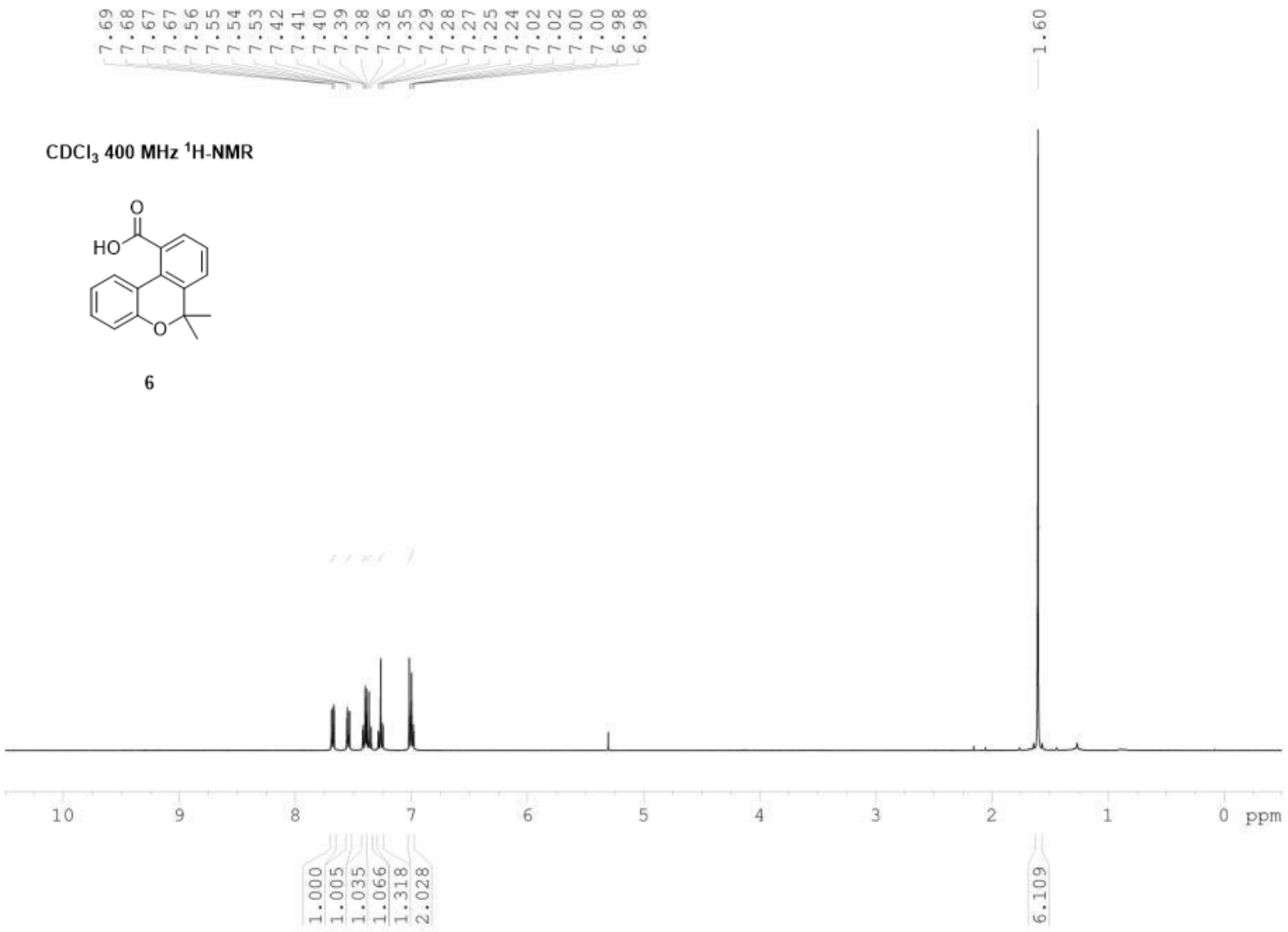

ppm
170.041
168.370
155.706
147.282
131.093
130.220
129.976
127.666
126.991
126.758
121.865
121.836
120.531
117.680
77.344
77.026
76.709
63.630
52.313
20.686
CDCl3 101 MHz 13C-NMR
5a
ppm
200
180
160
140
120
100
80
60
40
20
0

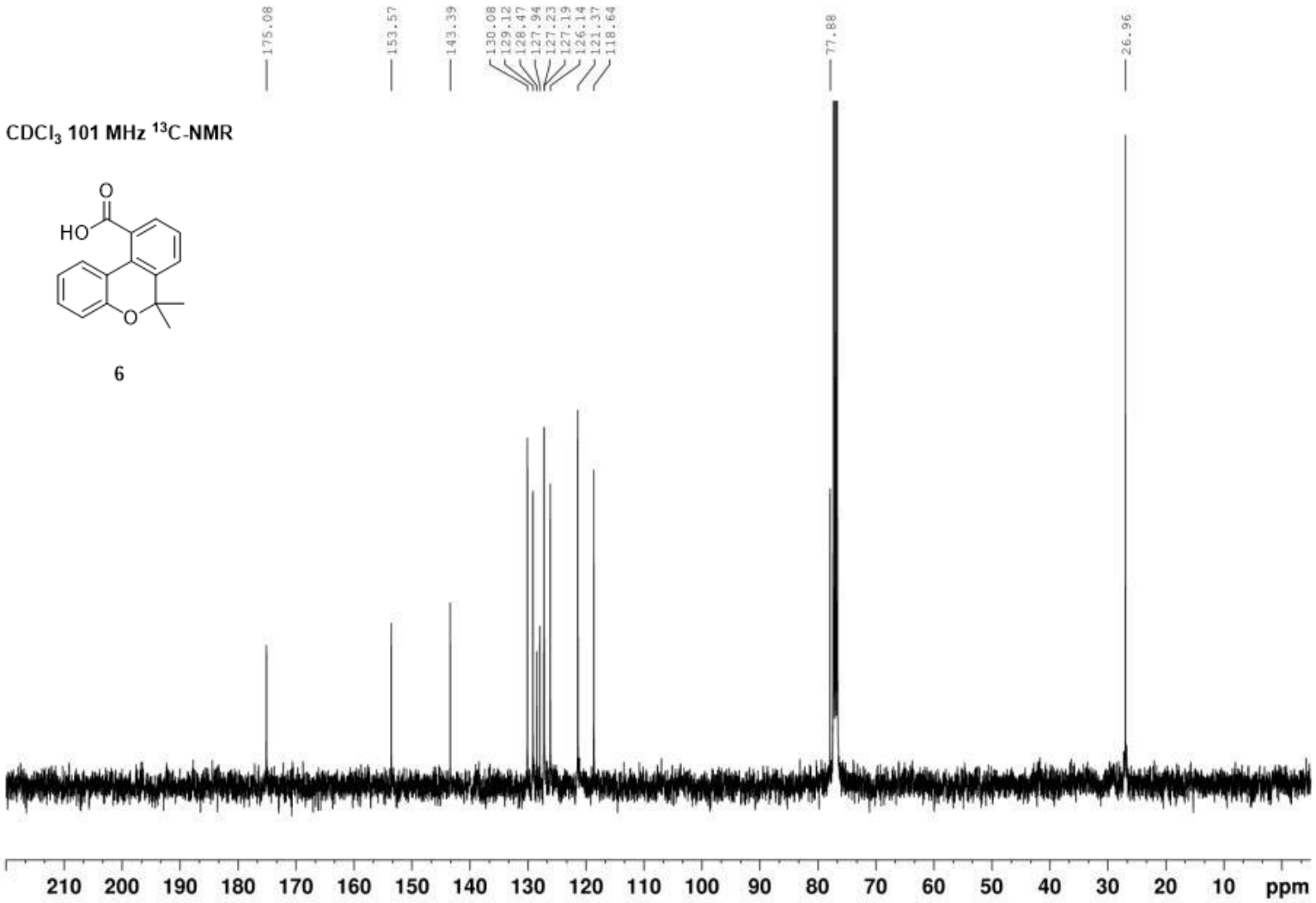

CDCl3 400 MHz 1H-NMR
7.56
7.54
7.31
7.31
7.29
7.27
7.27
7.25
7.25
7.13
7.11
7.04
7.02
7.01
7.01
6.99
6.97
6.97
5.55
5.53
5.51
5.50
3.83
2.36
1.30
1.28
5b
10
9
8
7
6
5
4
3
2
1
ppm
1.01
2.21
1.12
2.04
1.00
3.10
3.10
3.24

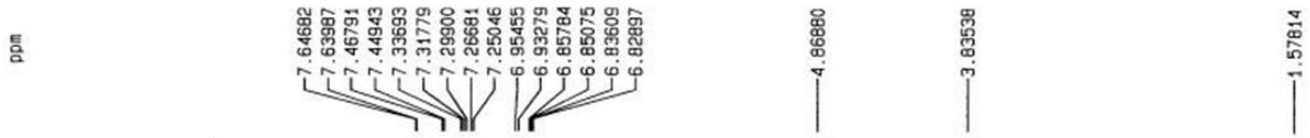

170.33
168.54
152.70
147.02
130.92
130.29
129.67
129.50
126.80
126.60
121.53
120.96
120.86
118.97
69.18
52.38
20.90
18.51
CDCl3 101 MHz 13C-NMR
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.580
7.559
7.266
7.251
7.232
7.215
7.195
7.028
7.007
6.990
6.970
6.952
3.787
2.365
1.617
CDCl3 400 MHz 1H-NMR
5c
5c
10
9
8
7
6
5
4
3
2
1
0 ppm
0.986
2.583
3.001
3.000
3.239
6.758

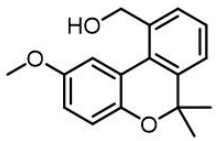

170.49
168.75
153.01
147.39
135.10
131.36
130.10
129.59
127.04
126.78
122.40
121.68
121.52
118.59
77.69
52.34
26.52
21.39
CDCl3 101 MHz 13C-NMR
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.69
7.68
7.67
7.67
7.56
7.55
7.54
7.53
7.42
7.41
7.40
7.39
7.38
7.36
7.35
7.29
7.28
7.27
7.25
7.24
7.02
7.02
7.00
7.00
6.98
6.98
1.60
CDCl3 400 MHz 1H-NMR
HO
O
O
6
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.005
1.035
1.066
1.318
2.028
6.109


175.08
153.57
143.39
130.08
129.12
128.47
127.94
127.23
127.19
126.14
121.37
118.64
77.88
26.96
CDCl3 101 MHz 13C-NMR
HO
O
O
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



$CDCl_3$ 400 MHz ^{1}H-NMR



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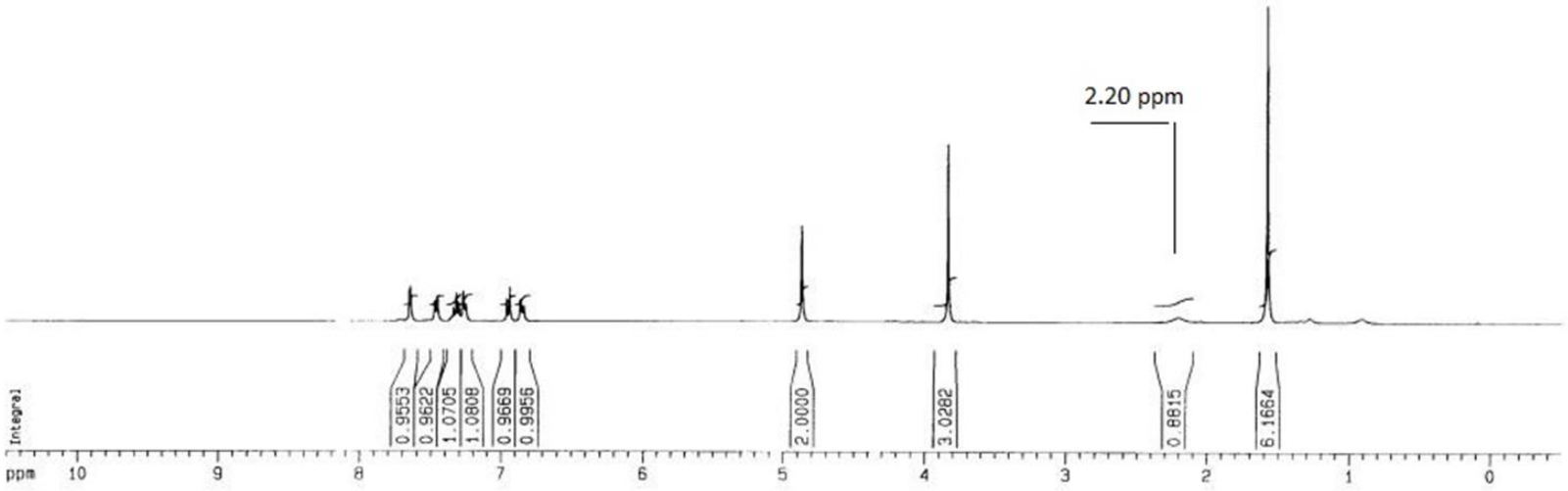
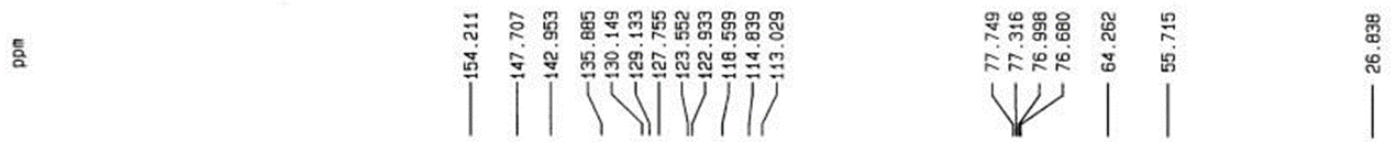
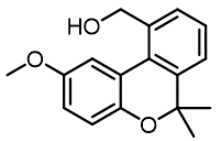




$CDCl_3$ 101 MHz ^{13}C-NMR



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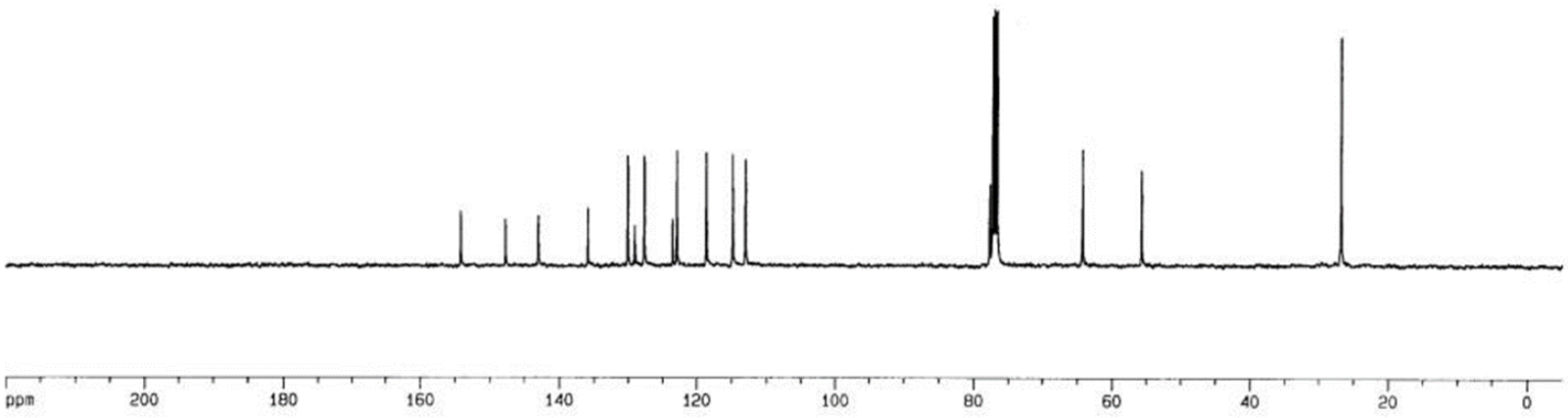
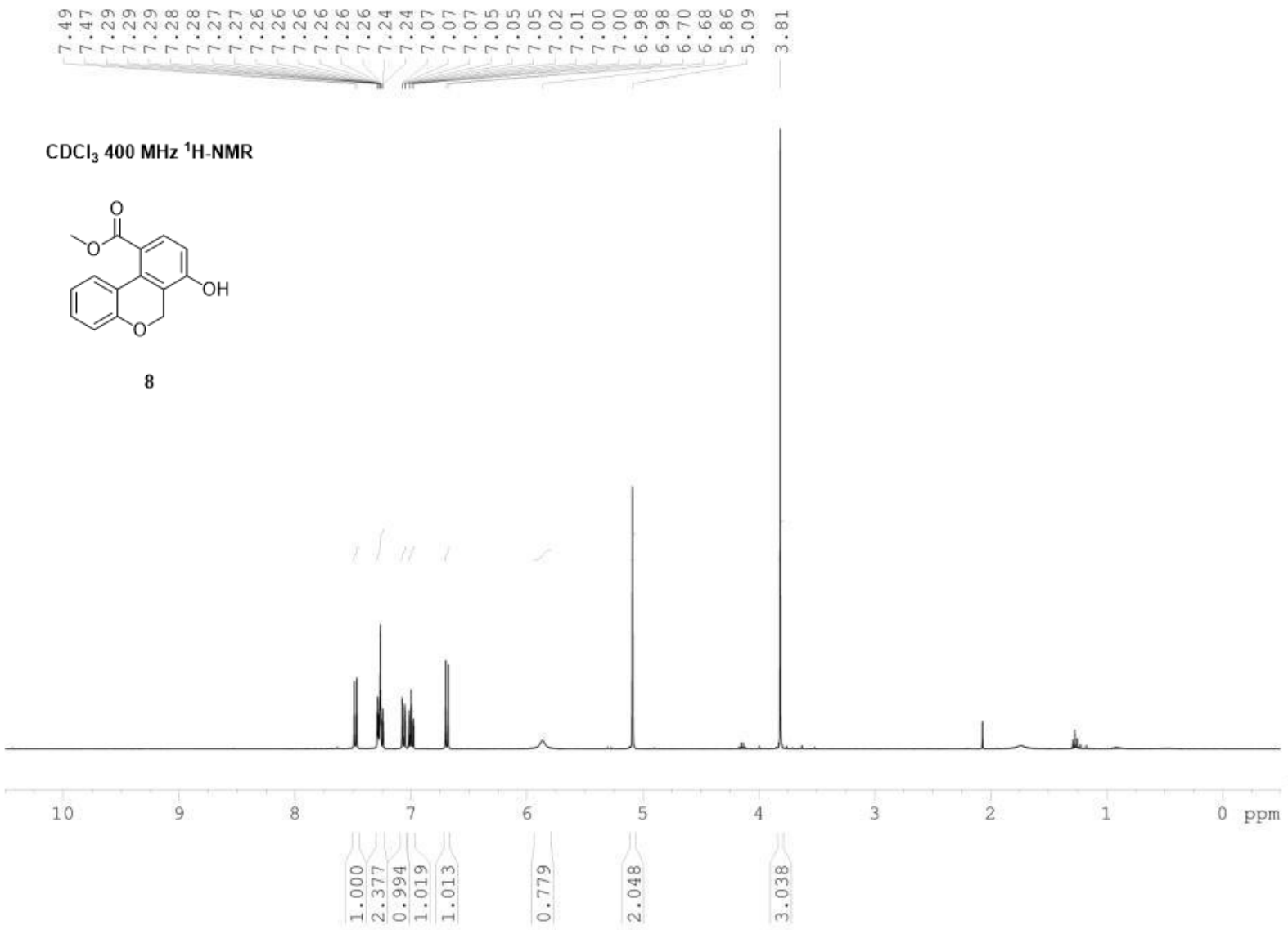
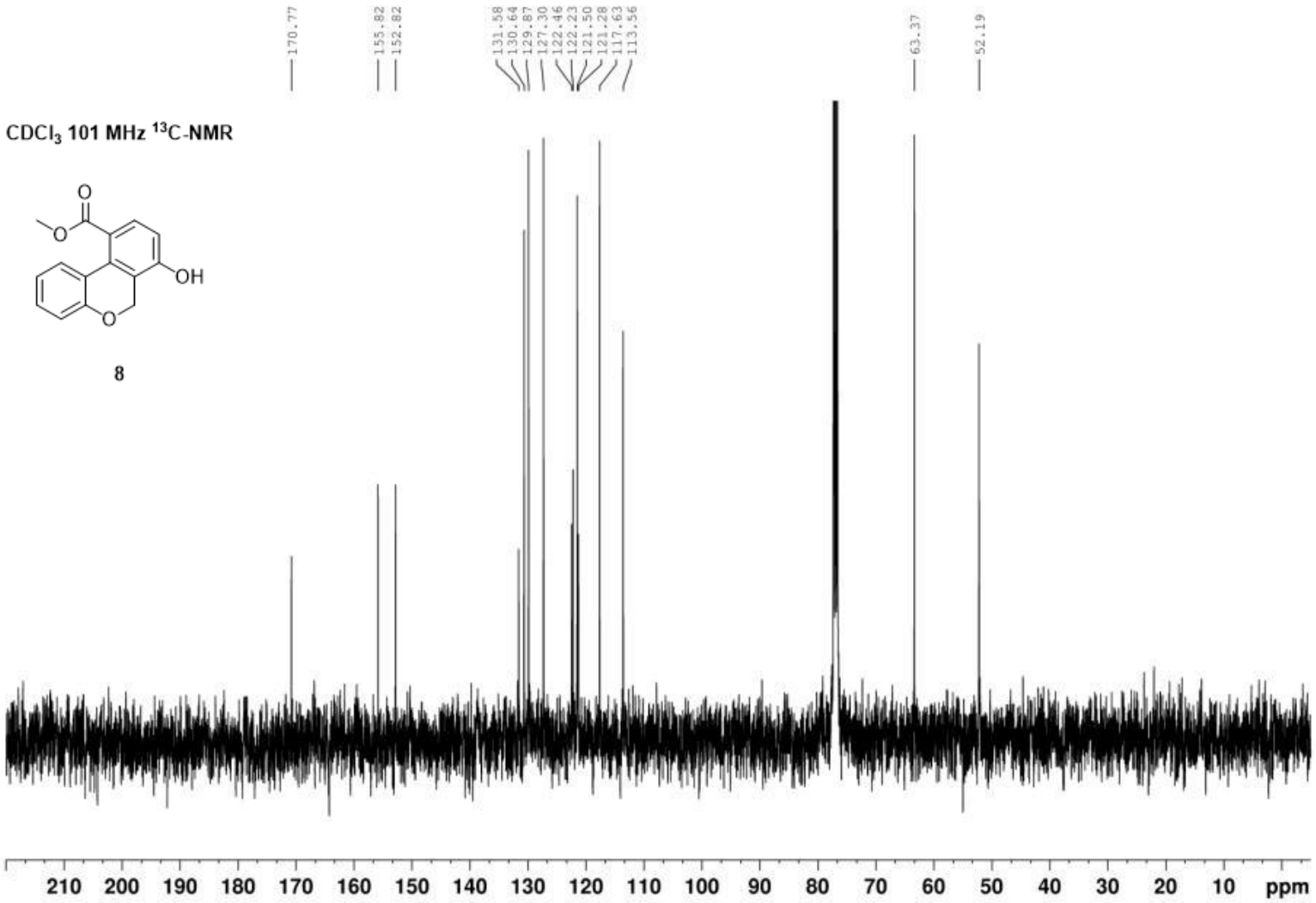
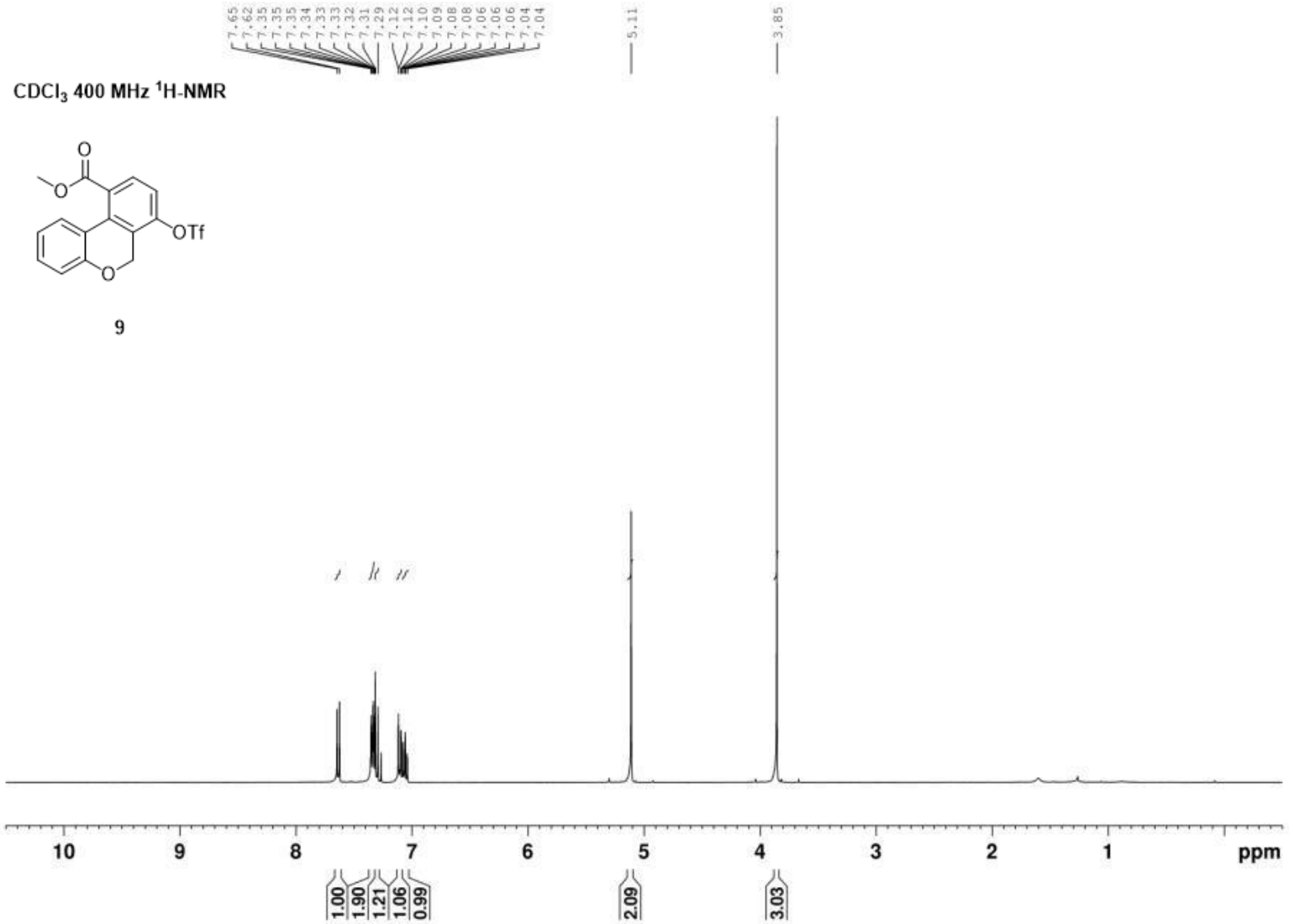
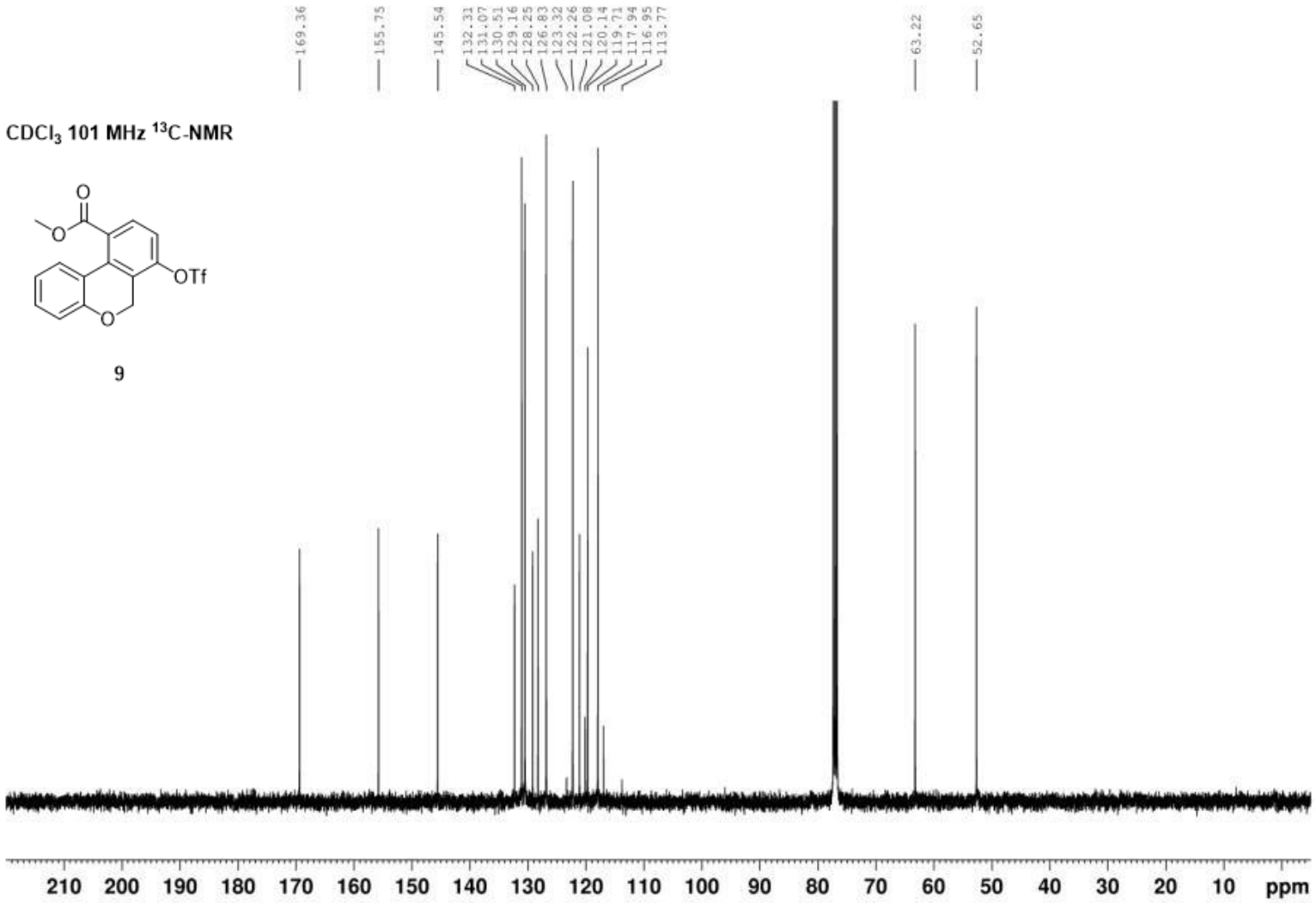
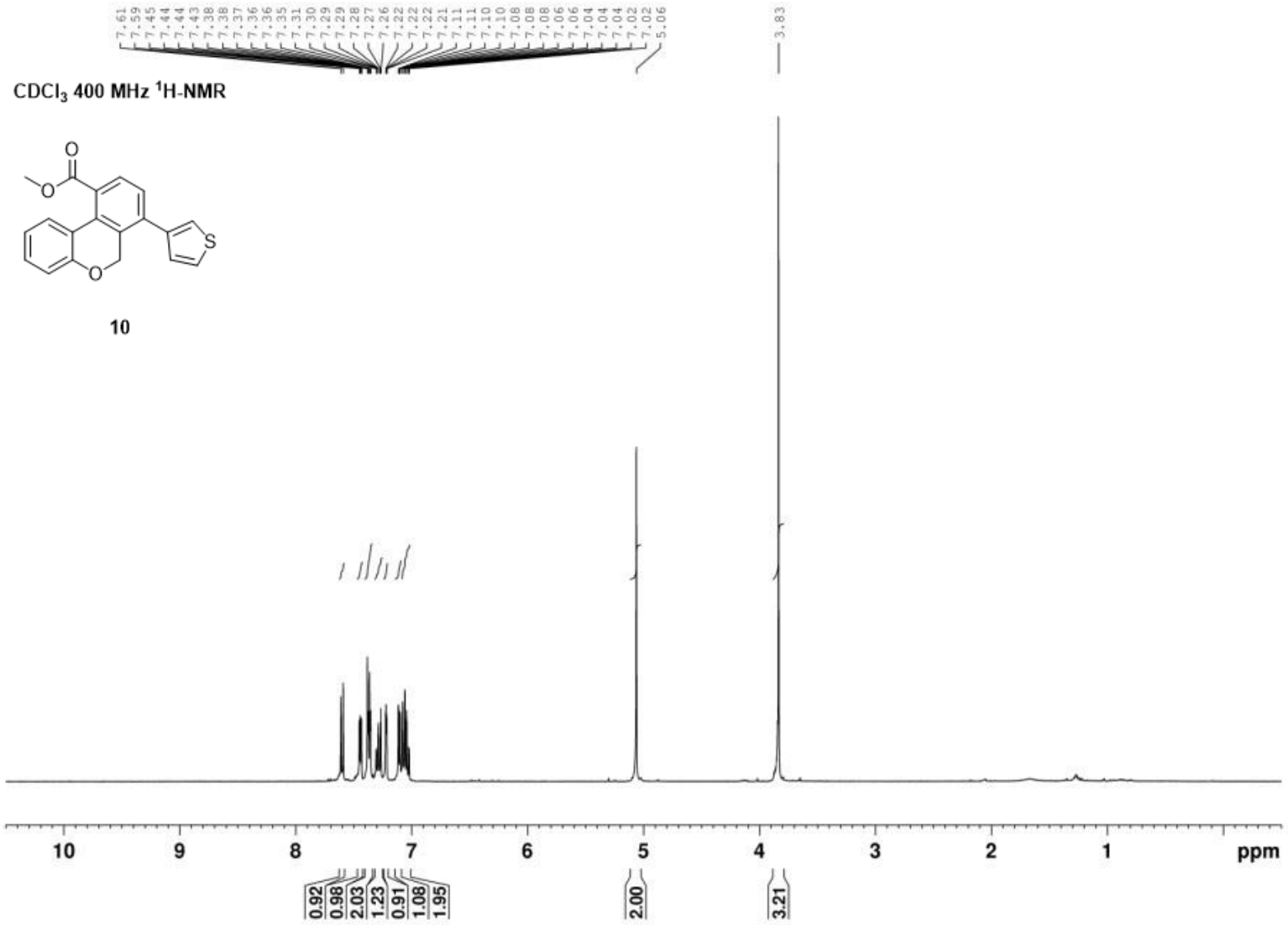


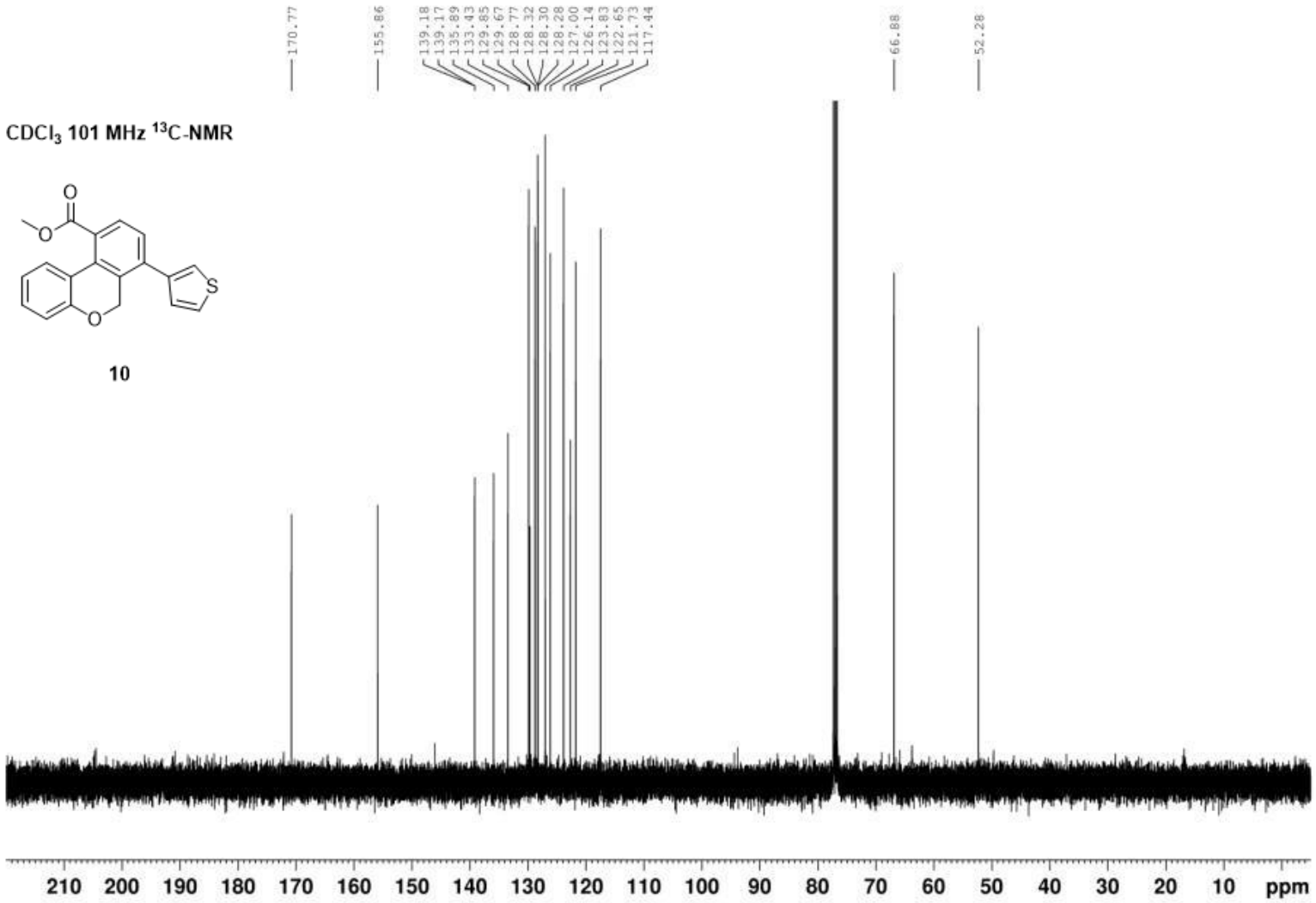

7.49
7.47
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.26
7.26
7.26
7.24
7.24
7.07
7.07
7.07
7.05
7.05
7.05
7.02
7.01
7.00
7.00
6.98
6.98
6.70
6.68
5.86
5.09
3.81
CDCl3 400 MHz 1H-NMR
O
O
OH
O
8
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
2.377
0.994
1.019
1.013
0.779
2.048
3.038

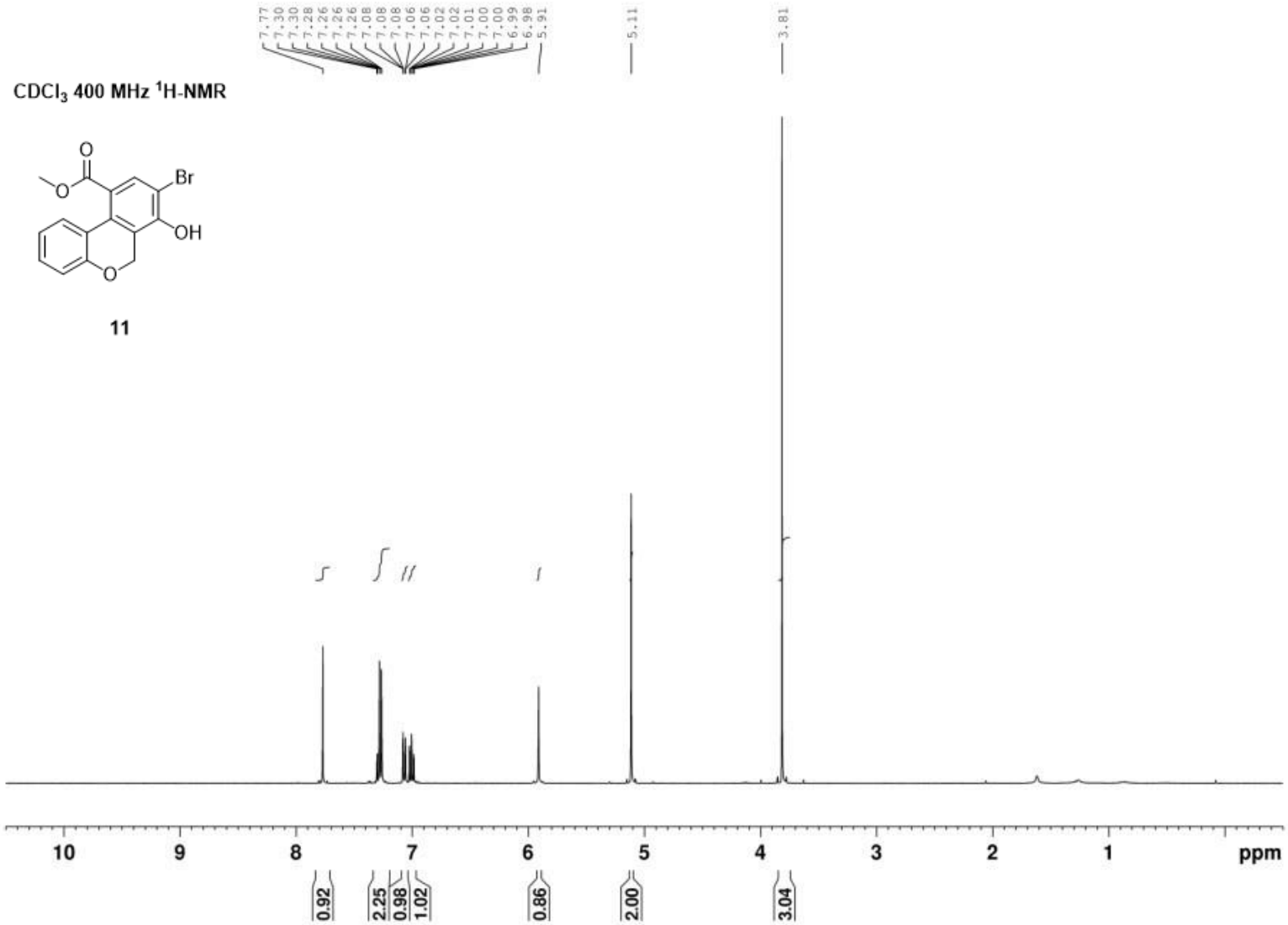

170.77
155.82
152.82
131.58
130.64
129.87
127.30
122.46
122.23
121.50
121.28
117.63
113.56
63.37
52.19
CDCl3 101 MHz 13C-NMR
O
O
OH
O
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

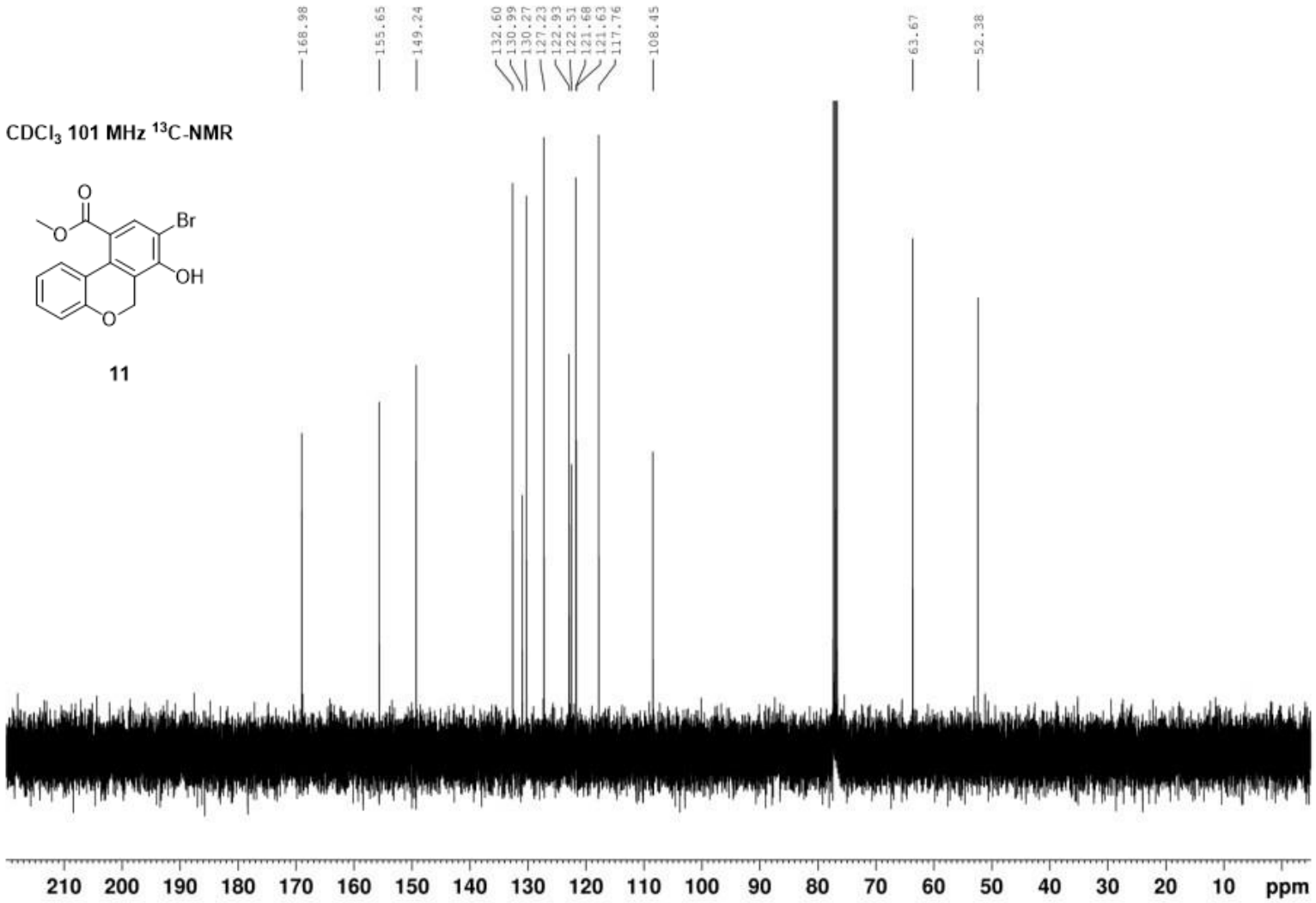

7.65
7.62
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.29
7.12
7.12
7.10
7.09
7.08
7.08
7.06
7.06
7.06
7.04
7.04
5.11
3.85
CDCl3 400 MHz 1H-NMR
O
O
OTf
O
9
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.90
1.21
1.06
0.99
2.09
3.03

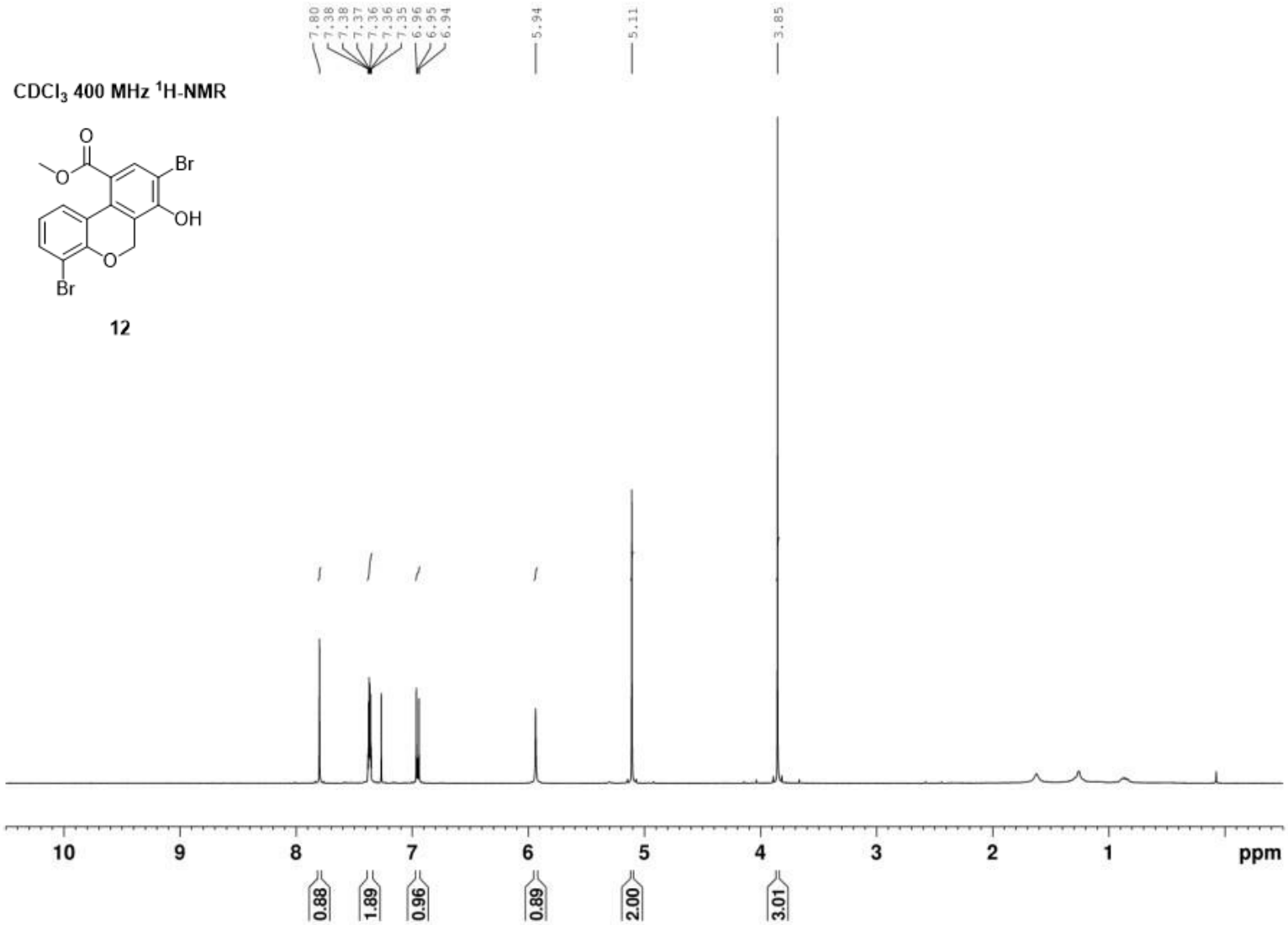

169.36
155.75
145.54
132.31
131.07
130.51
129.16
128.25
126.83
123.32
122.26
121.08
120.14
119.71
117.94
116.95
113.77
63.22
52.65
CDCl3 101 MHz 13C-NMR
O
O
OTf
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

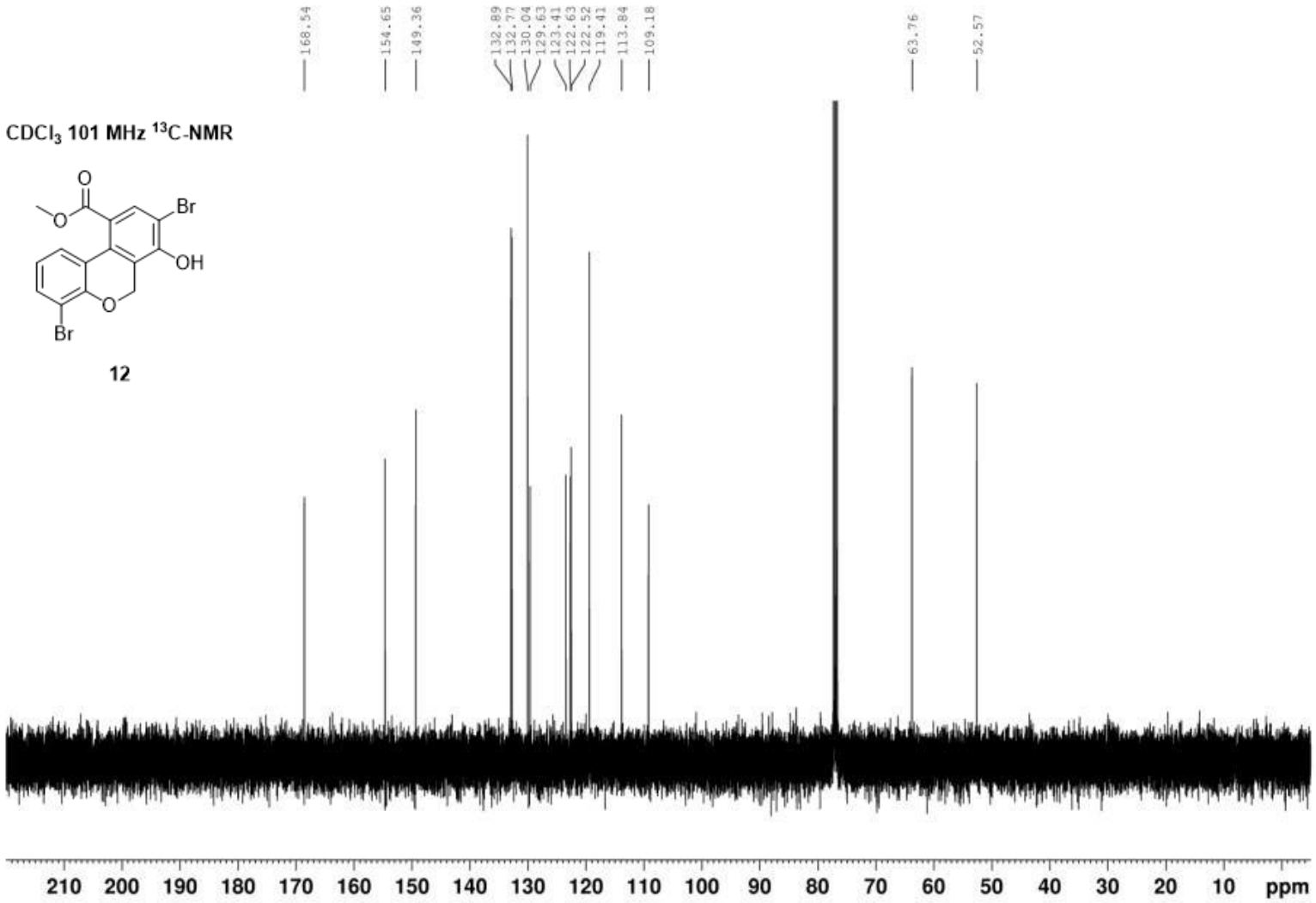

7.61
7.59
7.45
7.44
7.44
7.43
7.38
7.38
7.37
7.36
7.36
7.35
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.22
7.22
7.22
7.21
7.11
7.11
7.10
7.10
7.08
7.08
7.08
7.06
7.06
7.04
7.04
7.04
7.02
7.02
5.06
3.83
CDCl3 400 MHz 1H-NMR
O
O
O
S
10
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.98
2.03
1.23
0.91
1.08
1.95
2.00
3.21


170.77
155.86
139.18
139.17
135.89
133.43
129.85
129.67
128.77
128.32
128.30
128.28
127.00
126.14
123.83
122.65
121.73
117.44
66.88
52.28
CDCl3 101 MHz 13C-NMR
O
O
S
O
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.77
7.30
7.30
7.28
7.26
7.26
7.26
7.08
7.08
7.08
7.06
7.06
7.02
7.02
7.01
7.00
7.00
6.99
6.98
5.91
5.11
3.81
CDCl3 400 MHz 1H-NMR
O
O
Br
OH
O
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
2.25
0.98
1.02
0.86
2.00
3.04


168.98
155.65
149.24
132.60
130.99
130.27
127.23
122.93
122.51
121.68
121.63
117.76
108.45
63.67
52.38
CDCl3 101 MHz 13C-NMR
O
O
Br
OH
O
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


CDCl3 400 MHz 1H-NMR
O
O
Br
OH
O
Br
12
7.80
7.38
7.38
7.37
7.36
7.36
7.35
6.96
6.95
6.94
5.94
5.11
3.85
10
9
8
7
6
5
4
3
2
1
ppm
0.88
1.89
0.96
0.89
2.00
3.01


168.54
154.65
149.36
132.89
132.77
130.04
129.63
123.41
122.63
122.52
119.41
113.84
109.18
63.76
52.57
CDCl3 101 MHz 13C-NMR
O
O
Br
OH
O
Br
12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm